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Cu(I)-Catalyzed Coupling of Bis(trimethylsilyl)diazomethane with Terminal Alkynes: A Synthesis of 1,1-Disilyl Allenes

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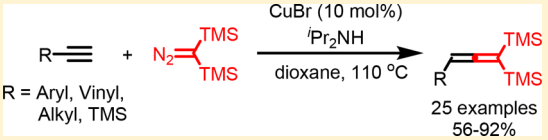
Supporting Information

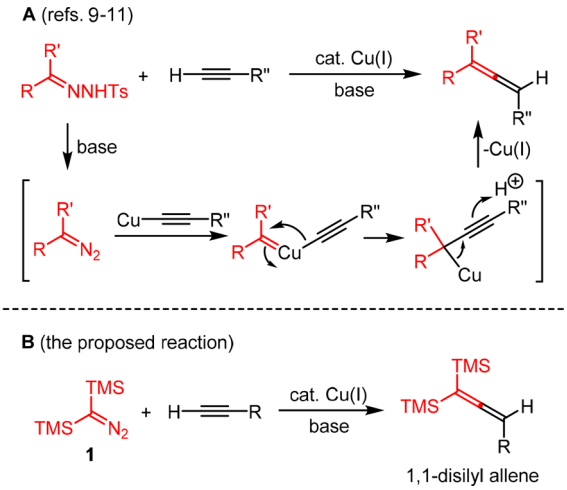
ABSTRACT: A Cu(I)-catalyzed cross-coupling reaction of terminal alkynes and bis(trimethylsilyl)diazomethane is reported. Mechanistically, the reaction is based on the recently developed cross-coupling reactions through metal-carbene migratory insertion. This reaction provides an efficient synthetic method for 1,1-disilyl allenes. Subsequent transformations of 1,1-disilyl allenes are investigated, which show diverse reactivities of these allenes.



Geminal disilyl compounds are a special kind of organosilicon compounds, which can take part in many synthetically useful transformations.[1] For example, they have great potential for bifunctional transformations and the construction of C=C bonds in modified Peterson reaction. Traditional methods to construct this type of bimetallic compounds include substitution reactions under strong basic conditions, Kumada cross-coupling reactions,[2] carbene insertion reaction of Si−H or Si−Si bonds,[3,4] hydrosilylation of internal alkynes,[5] and rearrangement reactions.[6] However, most of these methods can only construct sp^3-geminal disilyl compounds. The methods that are applicable for the synthesis of sp^2-geminal disilyl compounds are rare.[5] To the best of our knowledge, the methods for the synthesis of 1,1-disilyl allenes have few documents in the literature.[7] Moreover, the synthetic application of this type of allene compounds has not been explored.

On the other hand, transition-metal catalyzed cross-coupling of diazo compounds has emerged as an efficient method for the construction of carbon−carbon bonds.[8] In particular, we have previously developed an efficient method for the synthesis of allenes through Cu(I)-catalyzed cross-coupling of terminal alkynes with *N*-tosylhydrazones or diazo compounds (Scheme 1A).[9−11] Allenes have diverse reactivities and have attracted considerable attention in recent years.[12] While many synthetic methods toward allenes have been developed,[13] the direct coupling with terminal alkynes and diazo compounds represents a useful alternative approach. The allene formation through Cu(I)-catalyzed coupling is proposed to involve a Cu(I) carbene migratory insertion process. To further expand the scope of this coupling reaction, we have conceived to use bis(trimethylsilyl)diazomethane **1** to access *gem*-disilyl allene compounds (Scheme 1B). Bis(trimethylsilyl)diazomethane **1** has been previously synthesized;[14] however, their application in organic synthesis has not been explored. Due to the significant steric and electron-withdrawing effect of the two trimethylsilyl groups, compound **1** shows higher stability and different reactivity as compared with the corresponding (trimethylsilyl)diazomethane ($TMSCHN_2$). For example, compound **1** usually undergoes an isomerization process rather than metal carbene formation.[14b,15] Herein, we demonstrate that bis(trimethylsilyl)diazomethane **1** undergoes efficient coupling in the presence of Cu(I) catalyst, affording 1,1-disilyl allenes in moderate to excellent yields.

Scheme 1. Allene Synthesis through Cu(I)-Catalyzed Cross-Coupling Reaction



First, we have examined the reactivity of bis(trimethylsilyl)diazomethane **1** in the presence of various transition-metal catalysts. Upon testing the reaction with transition-metal catalysts such as Cu(I), Pd(II), Rh(II), we found the Cu(I) catalyst could decompose compound **1** at high temperature,

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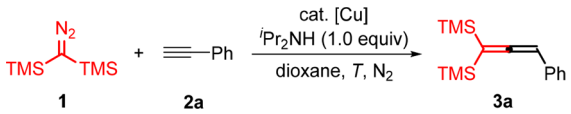
while **1** remained inert with other transition metals. Subsequently, we began to optimize the reaction conditions for the Cu(I)-catalyzed coupling of **1** with terminal alkyne **2a** (Table 1). Copper iodide was evaluated as the Cu(I) catalyst.

Table 1. Optimization of the Reaction Conditions[a]



1 **2a** **3a**

entry	[Cu] (mol %)	T (°C)	yield (%)[b]
1	CuI (20)	60	*trace*
2	CuI (20)	90	11
3	CuI (20)	110	32
4	CuI/1,10-Phen (20)	110	0
5	$Cu(MeCN)_4PF_6$ (20)	110	0
6	CuCl (20)	110	60
7	CuCl (20)	100	62
8	CuCl (20)	120	58
9	CuCl (10)	110	65
10	$CuCl_2$ (10)	110	46
11	CuBr (10)	110	80[c]

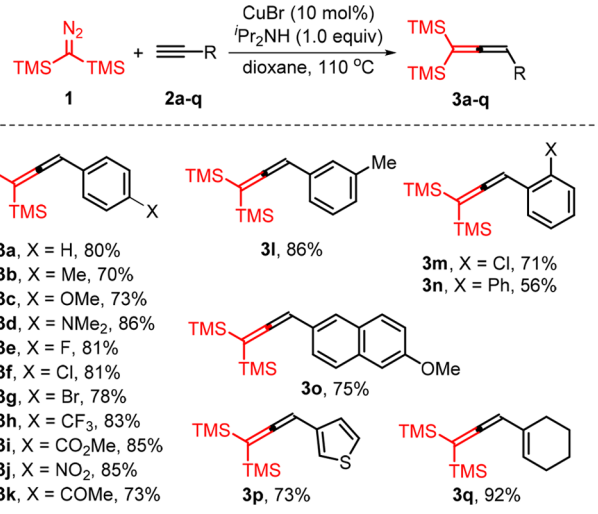
[a]Reaction conditions: bis(trimethylsilyl)diazomethane **1** (0.10 mmol), **2a** (1.0 equiv), $^iPr_2NH$ (0.10 mmol, 1.0 equiv), dioxane (1.0 mL) for 6 h. [b]If not otherwise noted, the yields were determined by the ^1H NMR using CH_3NO_2 as the internal standard. [c]Isolated yield.

The diazo compound **1** was found stable below 60 °C, and a trace amount of the allene **1** could be observed (entry 1). When elevating the reaction temperature, the yield of the desired allene product increased (entries 2 and 3). At 110 °C, the ligand 1,10-phenanthroline (1,10-phen) was added, but the reaction failed to give allene product (entry 4). When $Cu(MeCN)_4PF_6$ was used as the catalyst, no allene product could be observed (entry 5). With CuCl as the catalyst, the allene product was formed in moderate yields at the reaction temperature ranging from 100 to 120 °C (entries 6–9). When $CuCl_2$ was the catalyst, the allene product was formed in slightly lower yield (entry 10). Finally, it was found that, with 10 mol % CuBr, the reaction gave allene product in 80% isolated yield (entry 11).

With the optimized reaction conditions in hand (Scheme 2), we explored the substrate scope of this reaction. As for aryl acetylenes, both electron-donating (**2b–d**) and electron-withdrawing groups (**2e–k**) are tolerated. An ester group that is sensitive to basic condition is also tolerated in this reaction, affording the desired product **3i** in good yield. Substituents on *meta* (**2l**) or *ortho* (**2m**, **2n**) positions are found not to affect the reaction, indicating that this reaction is not sensitive to steric effect. Besides, naphthyl (**2o**) and thienyl (**2p**) acetylenes also take part in this transformation effectively. Apart from aryl acetylenes, alkenyl acetylene (**2q**) is also a good substrate for the reaction.

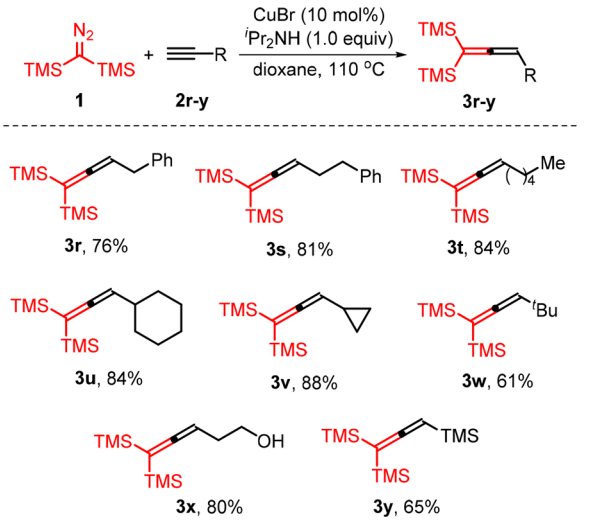
Next, we explored the scope of alkyl acetylenes (Scheme 3). Gratifyingly, the reaction also works with a broad scope of alkyl terminal alkynes. Not only simple alkyl groups with different substituted types (**2r–w**) are suitable substrates, the alkynes with some sensitive functional group such as a hydroxyl group (**2x**) can also take part in this reaction, affording the corresponding allene products in good yields. Notably, when using trimethylsilylethyne (**2y**) as the substrate, we can also obtain the allene product **3y** with good chemoselectivity. This

Scheme 2. Scope of Aryl Acetylenes and Alkenyl Acetylene[a]



[a]Reaction conditions: bis(trimethylsilyl)diazomethane **1** (0.10 mmol), **2a–q** (0.10 mmol, 1.0 equiv), CuBr (10 mol %), $^iPr_2NH$ (0.10 mmol, 1.0 equiv), dioxane (1.0 mL), 110 °C, 6 h.

Scheme 3. Scope of Alkyl Acetylenes[a]



[a]Reaction conditions: bis(trimethylsilyl)diazomethane **1** (0.10 mmol), **2r–y** (0.10 mmol, 1.0 equiv), CuBr (10 mol %), $^iPr_2NH$ (0.10 mmol, 1.0 equiv), dioxane (1.0 mL), 110 °C, 6 h.

result is different from the Cu(I)-catalyzed cross-coupling reaction of *N*-tosylhydrazones and trimethylsilylethyne, in which case C(sp)–C(sp^3) bond formation occurs to afford alkyne products.[16] We have reasoned that this chemoselectivity derives from the steric effect of the trimethylsilyl groups of the diazo substrate **1**.

Since the allene moiety is reactive under Cu(I) catalysis, it is possible to develop tandem reactions following the generation of an allene moiety through the cross-coupling reactions. Thus, with *o*-amino or *o*-hydroxyl aromatic acetylenes as the substrates, it was possible to obtain the annulation products in good yields. Mechanistically, these reactions are proposed to proceed through intramolecular nucleophilic attack of the NH_2, NHAc, or OH groups to the Cu(I)-activated allene moiety (Scheme 4).

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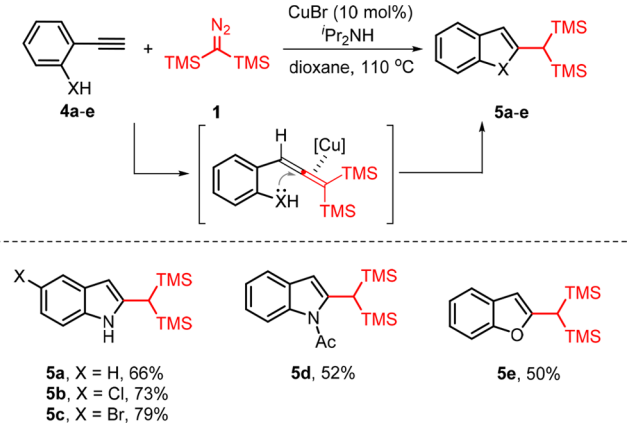
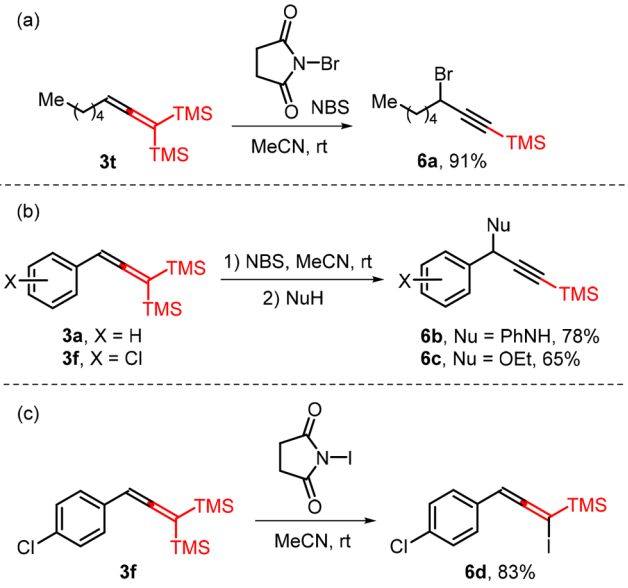
Scheme 4. CuBr-Catalyzed Tandem Reaction[a]



[a]Reaction conditions: bis(trimethylsilyl)diazomethane **1** (0.10 mmol), **4a**–**e** (0.10 mmol, 1.0 equiv), CuBr (10 mol %), $^{i}Pr_2NH$ (0.10 mmol, 1.0 equiv), dioxane (1.0 mL), 110 °C, 6 h.

The 1,1-disilyl allenes obtained from simple Cu(I)-catalyzed cross-coupling between terminal alkynes and diazo compound **1** open up the possibility to explore their synthetic applications. However, to the best of our knowledge, the reactivity of 1,1-disilyl allenes has few reports in the literature. Thus, we proceeded to investigate the reaction of 1,1-disilyl allenes (Scheme 5). Preliminary studies indicated that aryl allenes (**3a**, **3f**) and alkyl allene (**3t**) can react with NBS, yielding propargyl bromide derivatives (Scheme 5a). The propargyl bromides can further react with nucleophiles such as aniline or alcohol to give the corresponding products **6b** and **6c** (Scheme 5b).[17] Interestingly, when the aryl allene **3f** was treated with NIS, the expected propargyl iodide was not obtained. Instead, allenic iodide **6d** was formed in good yield and excellent chemoselectivity.

Scheme 5. Reaction of 1,1-Disilyl Allenes



In summary, we have developed a Cu(I)-catalyzed cross-coupling reaction of bis(trimethylsilyl)diazomethane **1** with terminal alkynes *via* a metal carbene migratory insertion process. With this coupling reaction, a series of 1,1-disilyl allenes can be obtained from easily available starting materials. Preliminary investigation on the reactivity of 1,1-disilyl allenes shows that this type of allene compounds may find useful applications in organic synthesis.

EXPERIMENTAL SECTION

General Methods. All the reactions were performed under a nitrogen atmosphere in oven-dried reaction flasks. All solvents were freshly distilled and degassed according to the handbook *Purification of Laboratory Chemicals* (Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, U.K., 1996). The boiling point of petroleum ether (PE) was between 60 and 90 °C. Commercially available reagents were used as received. For chromatography, 200–300 mesh silica gel (Qingdao, China) was used. ^{1}H NMR spectra were recorded on a Bruker ARX 400 (400 MHz); ^{13}C {^{1}H} NMR spectra were recorded on a Bruker ARX 400 (101 MHz). The data for NMR spectra were reported as follows: chemical shifts (δ) were reported in ppm; coupling constants (J) were in hertz (Hz). IR spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and were reported in wavenumbers (cm^{-1}). HRMS data were obtained on a VG ZAB-HS mass spectrometer, Bruker Apex IV FTMS spectrometer, and ThermoFisher Q Exactive hybrid quadrupole-orbitrap GC–MS/MS system. PE: petroleum ether; EA: ethyl acetate.

Preparation of Bis(trimethylsilyl)diazomethane 1.[14b] A solution of trimethylsilyldiazomethane (9.6 mmol, 2.0 M solution in hexane, 4.8 mL) in *n*-hexane (15 mL) was cooled to −100 °C; then *n*-BuLi (9.6 mmol, 1.6 M solution in hexane, 6.0 mL) was added dropwise over a period of 1 h. The resulting reddish solution was stirred for 15 min at −100 °C. Trimethylsilyl chloride TMSCl (9.6 mmol, 0.82 mL) was added dropwise by syringe at −80 °C, which was slowly warmed to ambient temperature over 2 h. After a further 3 h at room temperature, the suspension was filtered and the solvent was removed in vacuo. The resulting red colored liquid was purified by column chromatography saturated with Et_3N, which yielded 0.864 g of bis(trimethylsilyl)diazomethane **1** as a yellow liquid (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 16.6, −0.29; ^{29}Si NMR (101 MHz, $CDCl_3$) δ 1.27; GC–MS (EI, m/z, relative intensity) 186 (M^+, 40), 171 (15), 143 (80), 83 (40), 73 (100); IR (film): 2955, 2046, 1252, 840 cm^{-1}.

General Procedure for Cu(I)-Catalyzed Coupling of Bis(trimethylsilyl)diazomethane 1 with Terminal Alkynes. CuBr (10 mol %, 0.01 mmol, 1.4 mg), terminal alkyne (1.0 equiv, 0.10 mmol), and 1.0 mL of dioxane were mixed in an oven-dried reaction flask. Then bis(trimethylsilyl)diazomethane **1** (1.0 equiv, 0.10 mmol, 18.6 mg) and $^{i}Pr_2NH$ (1.0 equiv, 0.10 mmol, 10.1 mg, 14.0 μL) were added to the mixture. The mixture was stirred at 110 °C under a nitrogen atmosphere for about 6 h. Then the crude mixture was cooled to room temperature. Petroleum ether was added to the mixture. The mixture was filtered through Celite. Solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel.

(3-Phenylpropa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3a.*** Yield 80% (20.8 mg); colorless oil; TLC R_f = 0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 7.1 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 5.51 (s, 1H), 0.18 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.0, 136.6, 128.6, 125.1, 124.8, 94.0, 81.2, 0.4. GC–MS (EI, m/z, relative intensity) 260 (M^+, 40), 245 (10), 172 (100), 73 (80); HRMS (ESI-FTICR) calcd for: $C_{15}H_{24}Si_2$ $[M]^+$ 260.1416, found: 260.1412; IR (film): 1907, 1597, 1250, 841 cm^{-1}.

(3-(p-Tolyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3b.*** Yield 70% (19.2 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17–6.84 (m, 4H), 5.49 (s, 1H), 2.30 (s, 3H), 0.17 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.9, 134.4 133.4, 129.4, 125.0, 94.0, 90.0, 21.1, 0.4. GC–MS (EI, m/z, relative intensity) 274 (M^+, 40), 259 (5), 186 (100), 73 (60); HRMS (ESI-FTICR) calcd for: $C_{16}H_{26}Si_2$ $[M]^+$ 274.1573, found: 274.1568; IR (film): 1907, 1512, 1249, 840 cm^{-1}.

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(3-(4-Methoxyphenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3c***. Yield 73% (21.2 mg); colorless oil; TLC R_f = 0.80 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 5.49 (s, 1H), 3.78 (s, 3H), 0.17 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.2, 157.3, 128.6, 126.0, 114.3, 94.2, 80.6, 55.4, 0.4. GC−MS (EI, m/z, relative intensity) 290 (M^+, 70), 275 (90), 218 (20), 202 (80), 73 (80); HRMS (ESI-FTICR) calcd for: $C_{16}H_{26}OSi_2$ $[M]^+$ 290.1522, found: 290.1516; IR (film): 1908, 1606, 1247, 839 cm^{-1}.

4-(3,3-Bis(trimethylsilyl)propa-1,2-dien-1-yl)-N,N-dimethylaniline ***3d***. Yield 91% (27.6 mg); colorless oil; TLC R_f = 0.80 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 5.48 (s, 1H), 2.91 (s, 6H), 0.16 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.0, 148.6, 125.8, 124.3, 113.5, 94.1, 80.8, 41.0, 0.4. GC−MS (EI, m/z, relative intensity) 303 (M^+, 90), 288 (10), 230 (100), 215 (40), 73 (10); HRMS (ESI-FTICR) calcd for: $C_{17}H_{29}NSi_2$ $[M]^+$ 303.1838, found: 303.1831; IR (film): 1906, 1519, 1249, 892, 820 cm^{-1}.

(3-(4-Fluorophenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3e***. Yield 81% (22.5 mg); colorless oil; TLC R_f = 0.75 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11−7.03 (m, 2H), 6.99−6.83 (m, 2H), 5.48 (s, 1H), 0.17 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.5, 160.7 (d, J_F = 242.9 Hz), 132.4 (d, J_F = 3.0 Hz), 126.1 (d, J_F = 7.8 Hz), 115,5 (d, J_F = 21.7 Hz), 94.4, 80.3, 0.3. GC−MS (EI, m/z, relative intensity) 278 (M^+, 60), 263 (5), 190 (100), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{15}H_{23}FSi_2$ $[M]^+$ 278.1322, found: 278.1314; IR (film): 1909, 1606, 1250, 887, 834 cm^{-1}.

(3-(4-Chlorophenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3f***. Yield 81% (23.8 mg); colorless oil; TLC R_f = 0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 5.47 (s, 1H), 0.18 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.1, 135.3, 130.0, 128.7, 126.1, 94.5, 80.4, 0.3. GC−MS (EI, m/z, relative intensity) 294 (M^+, 45), 279 (10), 206 (80), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{15}H_{23}ClSi_2$ $[M]^+$ 294.1026, found: 294.1020; IR (film): 1906, 1590, 1250, 841 cm^{-1}.

(3-(4-Bromophenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3g***. Yield 78% (26.4 mg); colorless oil; TLC R_f = 0.85 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.32 (m, 2H), 7.00−6.98(m, 2H), 5.45 (s, 1H), 0.17 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.0, 135.8, 131.6, 126.5, 117.9, 94.6, 80.5, 0.3. GC−MS (EI, m/z, relative intensity) 338 (M^+, 20), 250 (60), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{15}H_{23}BrSi_2$ $[M]^+$ 338.0521, found: 338.0516; IR (film): 1907, 1251, 845, 759 cm^{-1}.

(3-(4-(Trifluoromethyl)phenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3h***. Yield 80% (26.2 mg); colorless oil; TLC R_f = 0.85 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 5.52 (s, 1H), 0.19 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.5, 141.2, 126.6 (q, J_F = 32.3 Hz), 125.6(q, J_F = 3.8 Hz), 124.8, 124.6(q, J_F = 271.2 Hz), 94.5, 80.6, 0.3. GC−MS (EI, m/z, relative intensity) 328 (M^+, 20), 313 (10), 221 (60), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{16}H_{23}F_3Si_2$ $[M]^+$ 328.1290, found: 328.1285; IR (film): 1905, 1618, 1251, 841 cm^{-1}.

Methyl 4-(3,3-Bis(trimethylsilyl)propa-1,2-dien-1-yl)benzoate ***3i***. Yield 85% (27.0 mg); colorless oil; TLC R_f = 0.80 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 5.53 (s, 1H), 3.88 (s, 3H), 0.19 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.6, 167.2, 142.6, 130.1, 126.3, 124.6, 94.2, 80.5, 51.9, 0.4. GC−MS (EI, m/z, relative intensity) 318 (M^+, 30), 303 (10), 214 (100), 73 (50); HRMS (ESI-FTICR) calcd for: $C_{17}H_{26}O_2Si_2$ $[M]^+$ 318.1471, found: 318.1464; IR (film): 1902, 1720, 1604, 1250, 843 cm^{-1}.

(3-(4-Nitrophenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3j***. Yield 85% (26.0 mg); colorless oil; TLC R_f = 0.85 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H), 5.56 (s, 1H), 0.21 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 207.7, 145.5, 144.8, 124.8, 124.3, 94.6, 80.7, 0.3. HRMS (ESI-FTICR) calcd for: $C_{15}H_{24}NO_2Si_2$ $[M + H]^+$ 306.1340, found: 306.1341; IR (film): 1918, 1655, 1594, 1250, 845 cm^{-1}.

1-(4-(3,3-Bis(trimethylsilyl)propa-1,2-dien-1-yl)phenyl)ethanone ***3k***. Yield 73% (22.0 mg); colorless oil; TLC R_f = 0.30 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 5.54 (s, 1H), 2.55 (s, 3H), 0.20 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.6, 197.4, 143.0, 133.8, 129.0, 124.7, 94.2, 81.0, 26.5, 0.4. GC−MS (EI, m/z, relative intensity) 302 (M^+, 100), 287 (10), 214 (50), 73 (80); HRMS (ESI-FTICR) calcd for: $C_{17}H_{27}OSi_2$ $[M + H]^+$ 303.1595, found: 303.1598; IR (film): 1902, 1680, 1597, 1269, 1250, 842 cm^{-1}.

(3-(m-Tolyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3l***. Yield 86% (23.6 mg); colorless oil; TLC R_f = 0.60 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, J = 7.5 Hz, 1H), 7.00−6.92 (m, 2H), 6.88 (d, J = 7.5 Hz, 1H), 5.48 (s, 1H), 2.30 (s, 3H), 0.18 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.7, 138.1, 136.5, 128.5, 125.7, 122.1, 93.9, 81.2, 21.5, 0.4. GC−MS (EI, m/z, relative intensity) 274 (M^+, 30), 259 (5), 186 (100), 73 (50); HRMS (ESI-FTICR) calcd for: $C_{16}H_{26}Si_2$ $[M]^+$ 274.1573, found: 274.1568; IR (film): 1907, 1600, 1250, 841 cm^{-1}.

(3-(2-Chlorophenyl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3m***. Yield 71% (20.9 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.01−6.93 (m, 1H), 5.95 (s, 1H), 0.19 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.9, 134.5, 130.1, 129.7, 126.8, 126.2, 125.6, 93.7, 77.5, 0.4. GC−MS (EI, m/z, relative intensity) 294 (M^+, 45), 279 (10), 206 (50), 73 (100); HRMS (EI-hybrid quadrupole-orbitrap) calcd for: $C_{15}H_{23}ClSi_2$ $[M]^+$ 294.1022, found: 274.1021; IR (film): 1906, 1588, 1250, 841 cm^{-1}.

(3-([1,1′-Biphenyl]-2-yl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3n***. Yield 56% (18.8 mg); colorless oil; TLC R_f = 0.45 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−6.91 (m, 9H), 5.56 (s, 1H), 0.18 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.9, 141.5, 138.6, 134.0, 130.2, 129.8, 128.2, 127.5, 126.8, 125.6, 124.7, 93.3, 79.1, 0.4. GC−MS (EI, m/z, relative intensity) 336 (M^+, 80), 321 (5), 248 (80), 233 (100), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{21}H_{28}Si_2$ $[M]^+$ 336.1729, found: 336.1723; IR (film): 1905, 1594, 1247, 842 cm^{-1}.

(3-(6-Methoxynaphthalen-2-yl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3o***. Yield 85% (28.9 mg); colorless oil; TLC R_f = 0.30 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.5 Hz, 2H), 7.43 (s, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.11−7.05 (m, 2H), 5.67 (s, 1H), 3.89 (s, 3H), 0.20 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.2, 156.9, 132.7, 131.7, 129.6, 128.7, 127.1, 124.5, 122.6, 118.7, 106.1, 94.3, 81.6, 55.4, 0.4. GC−MS (EI, m/z, relative intensity) 340 (M^+, 80), 325 (100), 252 (90), 73 (80); HRMS (ESI-FTICR) calcd for: $C_{20}H_{28}OSi_2$ $[M]^+$ 340.1678, found: 340.1673; IR (film): 1907, 1600, 1501, 1247, 840 cm^{-1}.

(3-(Thiophen-3-yl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3p***. Yield 73% (19.4 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J = 5.0, 2.9 Hz, 1H), 6.91 (dd, J = 5.0, 0.9 Hz, 1H), 6.82 (dd, J = 2.8, 0.9 Hz, 1H), 5.61 (s, 1H), 0.17 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.8, 136.9, 125.8, 125.5, 116.2, 93.5, 76.3, 0.3. GC−MS (EI, m/z, relative intensity) 266 (M^+, 50), 251 (5), 178 (100), 73 (80); HRMS (ESI-FTICR) calcd for: $C_{13}H_{22}SSi_2$ $[M]^+$ 266.0980, found: 266.0975; IR (film): 1909, 1251, 1121, 840 cm^{-1}.

(3-(Cyclohex-1-en-1-yl)propa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3q***. Yield 92% (24.3 mg); colorless oil; TLC R_f = 0.80 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (t, J = 3.8 Hz, 1H), 5.27 (s, 1H), 5.48 (s, 1H), 2.91 (s, 6H), 0.16 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.8, 132.0, 119.8, 92.6, 84.6, 26.1, 25.9, 22.9, 22.8, 0.2. GC−MS (EI, m/z, relative intensity) 264 (M^+, 40), 249 (10), 190 (10), 176 (100), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{15}H_{28}Si_2$ $[M]^+$ 264.1729, found: 264.1723; IR (film): 2151, 1714, 1448, 1249, 843 cm^{-1}.

(4-Phenylbuta-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3r***. Yield 76% (20.8 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.02 (m, 5H), 4.67 (t, J = 6.8 Hz, 1H), 3.35 (d, J = 6.8 Hz, 2H), 0.15 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.5, 141.7, 128.7, 128.2, 125.9, 89.4, 76.0, 34.1, 0.2. GC−MS (EI, m/z, relative intensity) 274 (M^+, 60), 259 (5), 186 (100), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{16}H_{26}Si_2$ $[M]^+$ 274.1573, found: 274.1568; IR (film): 2176, 1604, 1492, 1250, 841, cm^{-1}.

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(5-Phenylpenta-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3s***. Yield 81% (23.3 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.30 (m, 2H), 7.27−7.18 (m, 3H), 4.48 (t, J = 6.7 Hz, 1H), 2.82−2.61 (m, 2H), 2.44−2.22 (m, 2H), 0.15 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.4, 142.3, 128.5, 128.4, 125.8, 89.1, 75.4, 36.9, 29.5, 0.2. GC−MS (EI, m/z, relative intensity) 288 (M^+, 5), 273 (5), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{17}H_{28}Si_2$ $[M]^+$ 288.1729, found: 288.1723; IR (film): 1921, 1248, 840, 759 cm^{-1}.

Nona-1,2-diene-1,1-diylbis(trimethylsilane) ***3t***. Yield 84% (21.3 mg); colorless oil; TLC R_f = 0.95 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (t, J = 6.8 Hz, 1H), 1.91 (q, J = 6.8 Hz, 1H), 1.43−1.19 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H), 0.10 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.9, 88.5, 76.0, 31.6, 30.1, 27.4, 22.6, 14.2, 0.2. GC−MS (EI, m/z, relative intensity) 254 (M^+, 20), 239 (15), 109 (20), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{14}H_{30}Si_2$ $[M]^+$ 254.1886, found: 254.1881; IR (film): 1909, 1461, 1254, 1046, 851 cm^{-1}.

(3-Cyclohexylpropa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3u***. Yield 84% (22.3 mg); colorless oil; TLC R_f = 0.90 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (d, J = 5.9 Hz, 1H), 2.01−1.81 (m, 1H), 1.72−1.69 (m, 4H), 1.44−0.86 (m, 6H), 0.11 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 209.8, 89.5, 82.4, 36.1, 34.2, 26.5, 26.4, 0.2. GC−MS (EI, m/z, relative intensity) 266 (M^+, 50), 251 (15), 192 (10), 178 (70), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{15}H_{30}Si_2$ $[M]^+$ 266.1886, found: 266.1881; IR (film): 2095, 2846, 2172, 1728, 1448, 1250, 1031, 892, 841, 759 cm^{-1}.

(3-Cyclopropylpropa-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3v***. Yield 88% (19.7 mg); colorless oil; TLC R_f = 0.95 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (d, J = 5.7 Hz, 2H), 1.13−1.01 (m, 1H), 0.65−0.52 (m, 2H), 0.30−0.18 (m, 2H), 0.10 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.7, 91.2, 79.7, 29.8, 7.5, 6.5, 0.2. GC−MS (EI, m/z, relative intensity) 224 (M^+, 20), 209 (30), 181 (20), 151 (20), 97 (60), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{12}H_{24}Si_2$ $[M]^+$ 224.1416, found: 224.1410; IR (film): 3085, 2955, 2927, 2896, 2175, 1912, 1714, 1250, 1031, 842, 760 cm^{-1}.

(4,4-Dimethylpenta-1,2-diene-1,1-diyl)bis(trimethylsilane) ***3w***. Yield 61% (14.6 mg); colorless oil; TLC R_f = 0.90 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.42 (s, 1H), 1.01 (s, 1H), 0.11 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.7, 90.8, 88.7, 31.1, 30.7, 0.2. GC−MS (EI, m/z, relative intensity) 240 (M^+, 30), 225 (50), 152 (15), 137 (100); HRMS (ESI-FTICR) calcd for: $C_{13}H_{28}Si_2$ $[M]^+$ 240.1729, found: 240.1725; IR (film): 1919, 1665, 1457, 1248, 840 cm^{-1}.

5,5-Bis(trimethylsilyl)penta-3,4-dien-1-ol ***3x***. Yield 91% (20.7 mg); colorless oil; TLC R_f = 0.30 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (t, J = 7.0 Hz, 1H), 3.63 (t, J = 6.4 Hz, 2H), 2.20 (q, J = 6.6 Hz, 2H), 1.54 (brs, 1H), 0.13 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 210.3, 88.9, 71.4, 63.1, 31.1, 0.2. GC−MS (EI, m/z, relative intensity) 228 (M^+, 10), 213 (5), 147 (50), 123 (100), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{11}H_{25}OSi_2$ $[M + H]^+$ 229.1438, found: 229.1443; IR (film): 3357, 1920, 1248, 840 cm^{-1}.

Propa-1,2-diene-1,1,3-triyltris(trimethylsilane) ***3y***. Yield 65% (16.6 mg); colorless oil; TLC R_f = 0.95 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 1H), 0.11 (s, 18H), 0.06 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.4, 75.5, 62.3, 0.3, −0.2. GC−MS (EI, m/z, relative intensity) 256 (M^+, 50), 241 (60), 168 (100), 153 (60), 73 (80); HRMS (ESI-FTICR) calcd for: $C_{12}H_{28}Si_3$ $[M]^+$ 256.1498, found: 256.1492; IR (film): 1895, 1405, 1248, 1090, 837 cm^{-1}.

2-(Bis(trimethylsilyl)methyl)-1H-indole ***5a***. Yield 66% (18.2 mg); colorless oil; TLC R_f = 0.30 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.47−7.41 (m, 1H), 7.25−7.21 (m, 1H), 7.06−6.99 (m, 2H), 5.99 (d, J = 1.5 Hz, 1H), 1.54 (s, 1H), 0.08 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.2, 135.4, 130.1, 119.8, 119.4, 118.8, 109.7, 98.6, 22.2, 0.2. GC−MS (EI, m/z, relative intensity) 275 (M^+, 100), 260 (20), 202 (30), 172 (20), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{15}H_{26}NSi_2$ $[M]^+$ 276.1598, found: 276.1600; IR (film): 1711, 1526, 1458, 1414, 1369, 1250, 1220, 841 cm^{-1}.

2-(Bis(trimethylsilyl)methyl)-5-chloro-1H-indole ***5b***. Yield 73% (22.6 mg); colorless oil; TLC R_f = 0.50 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.12 ((d, J = 8.5 Hz, 1H), 6.98 (dd, J = 8.5, 2.0 Hz, 1H), 5.93 (d, J = 1.5 Hz, 1H), 1.53 (s, 1H), 0.07 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 133.7, 131.2, 125.1, 119.9, 118.2, 110.6, 98.2, 22.5, 0.1. GC−MS (EI, m/z, relative intensity) 309 (M^+, 45), 294 (5), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{15}H_{25}ClNSi_2$ $[M + H]^+$ 310.1209, found: 310.1211; IR (film): 2345, 1727, 1575, 1523, 1464, 1402, 1340, 1250, 1056, 1022 cm^{-1}.

2-(Bis(trimethylsilyl)methyl)-5-bromo-1H-indole ***5c***. Yield 79% (27.9 mg); colorless oil; TLC R_f = 0.50 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.15−6.93 (m, 2H), 5.93 (d, J = 1.9 Hz, 1H), 1.53 (s, 1H), 0.07 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 133.9, 131.8, 122.5, 121.3, 112.8, 110.0, 98.1, 22.5, 0.1. GC−MS (EI, m/z, relative intensity) 353 (M^+, 30), 274 (100), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{15}H_{25}BrNSi_2$ $[M + H]^+$ 354.0703, found: 354.0711; IR (film): 1727, 1566, 1523, 1460, 1303, 1250, 1023, 841, 769 cm^{-1}.

1-(2-(Bis(trimethylsilyl)methyl)-1H-indol-1-yl)ethanone ***5d***. Yield 52% (16.5 mg); colorless oil; TLC R_f = 0.75 (PE:EA = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.49 (m, 1H), 7.47−7.37 (m, 1H), 7.20−7.13 (m, 2H), 6.18 (d, J = 0.5 Hz, 1H), 3.16 (s, 1H), 2.76 (s, 3H), 0.06 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.7, 144.2, 135.2, 130.7, 122.7, 121.9, 119.5, 113.7, 106.0, 28.2, 19.1, 0.2. GC−MS (EI, m/z, relative intensity) 317 (M^+, 60), 302 (50), 244 (50), 229 (10), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{17}H_{28}NOSi_2$ $[M + H]^+$ 318.1709, found: 318,1720; IR (film): 1705, 1547, 1458, 1295, 1249, 1105, 841 cm^{-1}.

(Benzofuran-2-ylmethylene)bis(trimethylsilane) ***5e***. Yield 50% (13.8 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.37 (m, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.17−7.04 (m, 2H), 6.09 (s, 1H), 1.78 (s, 1H), 0.09 (s, 18H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.2, 154.3, 130.2, 122.2, 121.7, 119.2, 110.3, 99.8, 22.6, 0.1. GC−MS (EI, m/z, relative intensity) 276 (M^+, 50), 261 (10), 203 (10), 188 (50), 73 (100); HRMS (ESI-FTICR) calcd for: $C_{15}H_{25}OSi_2$ $[M + H]^+$ 277.1438, found: 277.1446; IR (film): 1566, 1455, 1252, 1161, 1022, 849 cm^{-1}.

Experimental Procedure for the Reaction of 1,1-Disilyl Allenes with NBS or NIS. 1,1-Disilyl allene (1.0 equiv, 0.10 mmol), NBS (1.0 equiv, 0.10 mmol, 17.8 mg) or NIS (1.0 equiv, 0.10 mmol, 22.5 mg), and 1.0 mL of CH_3CN were mixed in an oven-dried reaction flask. The mixture was stirred at room temperature under a nitrogen atmosphere for about 1 h. Petroleum ether was added to the mixture. The mixture was filtered through Celite. The solvents were evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel.

Experimental Procedure for Three-Component Reaction of 1,1-Disilyl Allenes, NBS, Aniline.[17] 1,1-Disilyl allene (1.0 equiv, 0.10 mmol), NBS (1.0 equiv, 0.10 mmol, 17.8 mg), and 1.0 mL of CH_3CN were mixed in an oven-dried reaction flask. The mixture was stirred at room temperature under a nitrogen atmosphere for about 1 h. The solvents were evaporated under reduced pressure. Then the mixture, aniline (1.5 equiv, 0.15 mmol), *i*-Pr_2NEt (1.2 equiv, 0.12 mmol, 12.1 mg, 16.8 μL), and 1.0 mL of toluene were mixed in an oven-dried reaction flask. The mixture was stirred at 90 °C under a nitrogen atmosphere for about 20 h. Then the crude mixture was cooled to room temperature. Diethyl ether was added to the mixture. The mixture was filtered through Celite. The solvents were evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel.

Experimental Procedure for Three-Component Reaction of 1,1-Disilyl Allenes, NBS, Ethanol. 1,1-Disilyl allene (1.0 equiv, 0.10 mmol), NBS (1.0 equiv, 0.10 mmol, 17.8 mg), and 1.0 mL of CH_3CN were mixed in an oven-dried reaction flask. The mixture was stirred at room temperature under a nitrogen atmosphere for about 1 h. The solvents were evaporated under reduced pressure. Then the mixture and 1.0 mL of ethanol were mixed in an oven-dried reaction flask. The solution was stirred at room temperature for about 1 h. Diethyl ether was added to the mixture. The mixture was filtered through Celite. The solvents were evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel.

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(3-Bromooct-1-yn-1-yl)trimethylsilane **6a**. Yield 91% (23.7 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (t, J = 6.8 Hz, 1H), 2.01−1.96 (m, 2H), 1.59−1.46 (m, 2H), 1.37−1.26 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H), 0.18 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 104.1, 92.0, 39.7, 37.5, 30.9, 27.1, 22.5, 14.0, −0.2. GC−MS (EI, m/z, relative intensity) 260 (M^+, 2), 245 (2), 165 (5), 139 (10), 109 (10), 73 (100); HRMS (EI-hybrid quadrupole-orbitrap) calcd for: $C_{11}H_{21}BrSi$ $[M]^+$ 260.0590, found: 260.0591.

N-(1-Phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)aniline **6b**. Yield 78% (21.8 mg); colorless oil; TLC R_f = 0.50 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.56 (m, 2H), 7.42−7.28 (m, 3H), 7.22−7.15 (m, 2H), 6.80−6.74 (m, 1H), 6.72−6.70 (m, 2H), 5.27 (s, 1H), 4.05 (s, 1H), 0.15 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.6, 139.7, 129.2, 128.8, 128.1, 127.3, 118.6, 114.2, 104.9, 89.8, 50.9, 0.0. GC−MS (EI, m/z, relative intensity) 279 (M^+, 50), 206 (30), 187 (80), 159 (100), 145 (10); HRMS (ESI-FTICR) calcd for: $C_{18}H_{20}NSi$ $[M - H]^+$ 278.1360, found: 278.1352; IR (film): 2175, 1601, 1502, 1250, 844 cm^{-1}.

(3-(4-Chlorophenyl)-3-ethoxyprop-1-yn-1-yl)trimethylsilane **6c**. Yield 65% (17.2 mg); colorless oil; TLC R_f = 0.80 (PE:EA = 20:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.39−7.29 (m, 2H), 5.12 (s, 1H), 3.72 (dq, J = 9.0, 7.0 Hz, 1H), 3.54 (dq, J = 9.1, 7.0 Hz, 1H), 1.25 (t, J = 7.0 Hz, 3H), 0.20 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.4, 134.2, 128.9, 128.7, 102.9, 92.8, 71.1, 64.0, 15.2, −0.1. GC−MS (EI, m/z, relative intensity) 266 (M^+, 60), 237 (90), 231 (80), 193 (100), 73 (90); HRMS (ESI-FTICR) calcd for: $C_{14}H_{18}ClOSi$ $[M - H]^+$ 265.0810, found: 265.0818; IR (film): 2169, 1488, 1408, 1250, 1089, 1015, 843 cm^{-1}.

(3-(4-Chlorophenyl)-1-iodopropa-1,2-dien-1-yl)trimethylsilane **6d**. Yield 83% (28.9 mg); colorless oil; TLC R_f = 0.70 (PE); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.27 (m, 2H), 7.22−7.17 (m, 2H), 5.75 (s, 1H), 0.24 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 206.6, 133.2, 131.4, 129.2, 128.4, 92.3, 60.7, −1.2; HRMS (EI-hybrid quadrupole-orbitrap) calcd for: $C_{12}H_{14}ClSi$ $[M - I]^+$ 221.0548, found: 221.0546.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00651.

Copies of ^{1}H and ^{13}C spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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