One-Pot Synthesis of Internal Conjugated (*Z*)-Enynyltrimethylsilanes Possessing Aryl, Cycloalkenyl, (*E*)- or (*Z*)-Alk-1-enyl Moieties on the sp Carbon Atom via Two Types of Cross-Coupling Reaction

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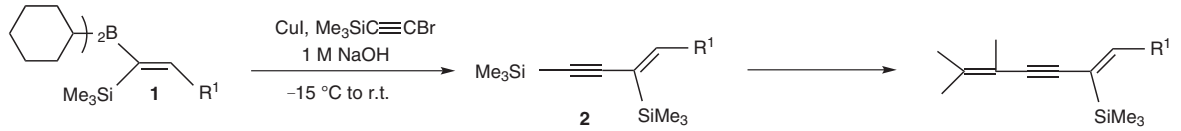
Abstract: Described herein is an operationally simple and mild method for the stereospecific synthesis of internal conjugated (*Z*)-enynyltrimethylsilanes whose conjugation is extended away from the distal alkynyl carbon atom. This protocol involves two types of cross-coupling reaction, a Suzuki-type reaction and a sila-Sonogashira reaction, and the desired synthesis can be performed in a one-pot manner. Thus, the copper-mediated cross-coupling reaction of dicyclohexyl[(*Z*)-1-(trimethylsilyl)alk-1-enyl]boranes with (trimethylsilyl)ethynyl bromide is carried out in the presence of aqueous lithium hydroxide at –15 °C to room temperature, resulting in the stereospecific formation of (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes. Subsequent reaction is allowed to proceed without isolation of the enynes. Thus, palladium/copper-catalyzed cross-coupling reactions with aryl iodides, cycloalk-1-enyl triflates, and (*E*)- and (*Z*)-alk-1-enyl iodides can be accomplished in the presence of either 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or tetrabutylammonium fluoride (TBAF) at ambient temperature to provide the corresponding internal conjugated (*Z*)-enynyltrimethylsilanes possessing one more sp–sp^2 carbon bond.

Key words: (*Z*)-enynyltrimethylsilane, (trimethylsilyl)ethynyl bromide, (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne, Suzuki-type reaction, sila-Sonogashira reaction

Alkenylsilanes are significant intermediates for a variety of synthetic processes including electrophilic substitutions[1] and palladium-catalyzed cross-couplings.[2] 1,4-Disilylbut-1-en-3-ynes are regarded as alkenylsilanes possessing a conjugated C≡C bond and useful building blocks for a conjugated four-carbon homologation. The synthesis of 1,4-bis(trimethylsilyl)but-1-en-3-yne and substituted derivatives thereof has been performed by carbometalation of 1,4-bis(trimethylsilyl)butadiyne with trimethylaluminum,[3] titanation of 1,4-bis(trimethylsilyl)butadiyne,[4] and nickel-catalyzed dimerization of silylethyne.[5] On the other hand, (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes **2**, in which one of the trimethylsilyl groups is located on the internal alkenyl carbon atom, have been synthesized by cross-coupling of dicyclohexyl[(*Z*)-1-(trimethylsilyl)alk-1-enyl]boranes **1** with (trimethylsilyl)ethynyl bromide, as reported by our group.[6] The cross-coupling reaction proceeded in the presence of a catalytic amount of copper(I) iodide and a stoichiometric amount of aqueous sodium hydroxide under very mild conditions, giving products **2** stereospecifically in good to high yield. Compound **2** has two trimethylsilyl groups, one on an sp^2 carbon atom and the other on an sp carbon atom, the latter, in particular, can be utilized for C–C bond formation. Thus, it is feasible to assemble π-extended conjugation taking advantage of the desilylative Sonogashira–Hagihara reaction (sila-Sonogashira reaction)[7–9] (Scheme 1). Herein, we report a one-pot synthesis of internal conjugated (*Z*)-enynyltrimethylsilanes, in which aryl, cycloalkenyl, (*E*)- or (*Z*)-alk-1-enyl moieties are installed on the distal alkynyl carbon atom, via a Suzuki-type reaction/sila-Sonogashira reaction sequence.

Initially, the sila-Sonogashira reaction with an aryl iodide was explored. (*Z*)-1,3-Bis(trimethylsilyl)oct-3-en-1-yne (**2a**) and iodobenzene were selected as substrates to optimize the reaction conditions. Thus, the cross-coupling reaction of dicyclohexyl[(*Z*)-1-(trimethylsilyl)hex-1-enyl]borane (**1a**) (1 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was conducted in the presence of copper(I) iodide (0.1 mmol) and 1 M sodium hydroxide (0.75 mmol) at –15 °C to room temperature overnight to generate compound **2a** (ca. 0.6 mmol).[10] On the basis of the conditions reported by Brisbois and Grieco,[8e] compound **2a** was subjected to reaction with iodobenzene (0.5 mmol) in a one-pot manner at room temperature overnight.[11] The typical results are shown in Table 1. Use of 1,8-diazabicyclo[5.4.0]undec-7-ene (6 mmol) and dichlorobis(triphenylphosphine)palladium (0.02 mmol) gave



Scheme 1

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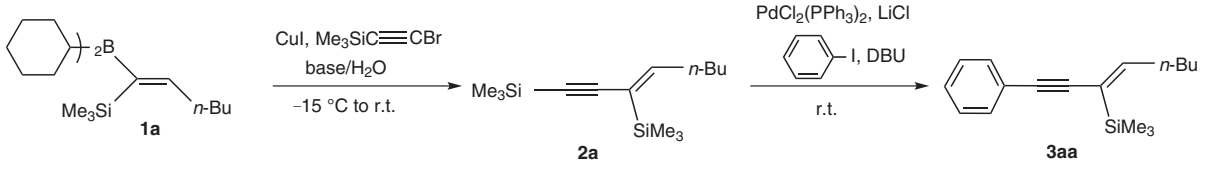
the desired product, (*Z*)-1-phenyl-3-(trimethylsilyl)oct-3-en-1-yne (**3aa**), albeit in moderate yield (Table 1, entry 1). We previously observed that the Sonogashira reaction of terminal conjugated enynes was occasionally promoted by the addition of a lithium salt.[12] This prompted us to examine the reaction with iodobenzene in the presence of lithium chloride (0.75 mmol), but otherwise under identical conditions. To our delight, the yield of product **3aa** improved considerably (Table 1, entry 2). This observation would give us some insight into modification of the process. Reducing the loading of dichlorobis(triphenylphosphine)palladium, by contrast, gave a lower yield (Table 1, entry 3). Considering the mechanism of the Suzuki–Miyaura reaction, the metal cation of an inorganic base, such as sodium hydroxide, is held by a halide anion liberated from organic halide.[13] In the cross-coupling reaction with (trimethylsilyl)ethynyl bromide, changing the base from sodium hydroxide to lithium hydroxide will lead to the formation of lithium bromide, and hence the addition of a lithium salt will not be necessary for the sila-Sonogashira coupling step. We thus examined a sequence of reactions using lithium hydroxide monohydrate instead of 1 M sodium hydroxide solution. The use of lithium hydroxide monohydrate (0.75 mmol) and water (0.375 mL) gave an unsatisfactory result (Table 1, entry 4); however, on increasing the amount of water (0.75 mL), the yield of product **3aa** improved dramatically (Table 1, entry 5). In the cross-coupling reaction of **1a** with (trimethylsilyl)ethynyl bromide using aqueous lithium hydroxide, the yield of compound **2a** was nearly constant regardless of the amount of water.[14] Thus it is clear that the sila-Sonogashira reaction is affected by water, but the reason is unclear at present.

Having established the optimal conditions for the sequential coupling reaction, we explored the scope of the one-pot synthesis of (*Z*)-1-aryl-3-(trimethylsilyl)alk-3-en-1-ynes **3**. The results are summarized in Table 2. Typically compounds **2** underwent smooth coupling with various aryl iodides to afford products **3** in moderate to good yields. This sila-Sonogashira reaction was successfully applied to compound **2** with a structurally and electronically diverse substituent (R^1) (Table 2, entries 1–4). Electron-donating as well as electron-withdrawing aryl iodides could be used as coupling partners (Table 2, entries 5–9). In the reaction with sterically hindered 2-iodotoluene, the desired product **3ad** was obtained in good yield (Table 2, entry 7). Interestingly, the reactions with 1-chloro- and 1-bromo-4-iodobenzene provided products **3ae** and **3af**, leaving the chloro and bromo moieties untouched under the reaction conditions (Table 2, entries 8 and 9). It should be noted that heteroaromatic iodides such as 2-iodothiophene and 3-iodopyridine were also good substrates for this sila-Sonogashira reaction (Table 2, entries 10 and 11).

Next we investigated the one-pot synthesis of both (1*Z*,5*E*)-2-(trimethylsilyl)alka-1,5-dien-3-ynes **4** and (1*Z*,5*Z*)-2-(trimethylsilyl)alka-1,5-dien-3-ynes **5** via a sila-Sonogashira reaction with (*E*)- and (*Z*)-alk-1-enyl iodides. The cross-coupling reaction of **2a**, generated by the reaction between **1a** and (trimethylsilyl)ethynyl bromide, with (*E*)-1-iodohex-1-ene, the selected substrate, was carried out under several conditions based on the optimal conditions for the synthesis of **3** mentioned above. It was found that only the amount of 1,8-diazabicyclo[5.4.0]undec-7-ene was reduced to half to give the best result. Thus, the reaction with (*E*)-1-iodohex-1-ene (2 mmol) was run in the presence of dichlorobis(triphenylphosphine)palladium (0.08 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (12 mmol) at room temperature under argon. Table 3 summarizes the results of the synthesis of **4** and **5** using representative substrates. Most of the reactions proceeded under the conditions described above to furnish the desired cross-coupling products **4** and **5** with retention of configuration at both double bonds in moderate to good yields. Phenylvinyl group as well as hex-1-enyl group participated in the sila-Sonogashira reaction, although the

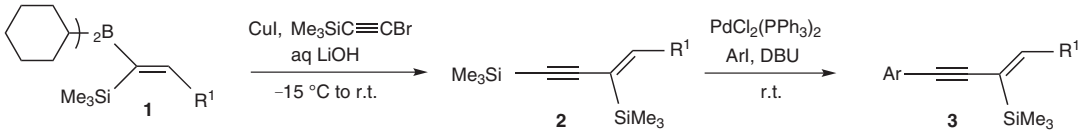
Table 1 Optimization of Reaction Conditions for the (*Z*)-1-Aryl-3-(trimethylsilyl)alk-3-en-1-yne Synthesis[a]



Entry	Base	H_2O (mL)	LiCl (mmol)	$PdCl_2(PPh_3)_2$ (mmol)	Yield[b] (%) of **3aa**
1	1 M NaOH	0	0	0.02	55
2	1 M NaOH	0	0.75	0.02	72
3	1 M NaOH	0	0.75	0.01	54
4	$LiOH·H_2O$	0.375	0	0.02	48
5	$LiOH·H_2O$	0.75	0	0.02	84

[a] Reagents and conditions: (1) **1a** (1 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), CuI (0.1 mmol), base (0.75 mmol), –15 °C to r.t., overnight; (2) PhI (0.5 mmol), $PdCl_2(PPh_3)_2$, DBU (6 mmol), r.t., overnight.
[b] Yields were estimated by GC and based on the amount of PhI employed.

Table 2 Synthesis of (*Z*)-1-Aryl-3-(trimethylsilyl)alk-3-en-1-ynes[a]



2a R^1 = *n*-Bu
2b R^1 = *t*-Bu
2c R^1 = cyclohex-1-enyl
2d R^1 = Ph

Entry	R^1	Ar	Product	Yield[b] (%)
1	*n*-Bu	Ph	**3aa**	80
2	*t*-Bu	Ph	**3ba**	86
3	cyclohex-1-enyl	Ph	**3ca**	80
4	Ph	Ph	**3da**	59
5	*n*-Bu	4-Tol	**3ab**	72
6	*n*-Bu	4-$MeOC_6H_4$	**3ac**	74
7	*n*-Bu	2-Tol	**3ad**	84
8	*n*-Bu	4-ClC_6H_4	**3ae**	61
9	*n*-Bu	4-BrC_6H_4	**3af**	54
10	*n*-Bu	2-thienyl	**3ag**	80
11	*n*-Bu	3-pyridyl	**3ah**	74

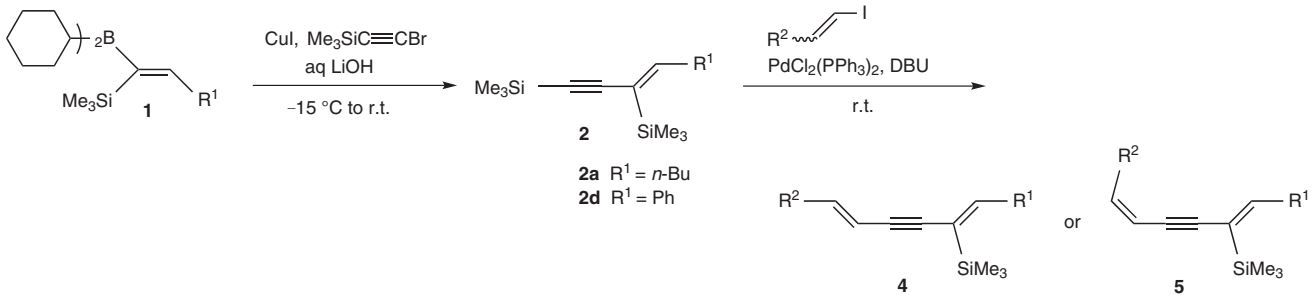
[a] Reagents and conditions: (1) **1** (4 mmol), $Me_3SiC{\equiv}CBr$ (2.68 mmol), CuI (0.4 mmol), $LiOH{\cdot}H_2O$ (3 mmol), H_2O (3 mL), –15 °C to r.t., overnight; (2) ArI (2 mmol), $PdCl_2(PPh_3)_2$ (0.08 mmol), DBU (24 mmol), r.t., overnight.
[b] Isolated yields based on the amount of ArI employed.

yields of products incorporating the phenylvinyl group were lower than those incorporating hex-1-enyl group (Table 3, entries 2, 4, and 6 vs entries 1, 3, 5, and 7). In the cross-coupling reaction of **2a** with (*Z*)-1-iodo-2-phenylethene, reducing the amount of 1,8-diazabicyclo[5.4.0]undec-7-ene gave a better result (Table 3, entry 6). Unfortunately, the reaction of (*Z*)-2,4-bis(trimethylsilyl)-1-phenylbut-1-en-3-yne (**2d**) with (*Z*)-1-iodo-2-phenylethene failed to provide the desired product. It is noteworthy that this protocol can stereospecifically install the alk-1-enyl moiety in the distal sp carbon atom of **2**.

Continuing with the investigation, the scope of the reaction with regard to alk-1-enyl triflate was examined. 4-*tert*-Butylcyclohex-1-enyl triflate was chosen as a model substrate, and the cross-coupling reaction with **2a**, derived from **1a**, was carried out under the same conditions as those described for the reaction with aryl iodide. After stirring for four hours at room temperature, 4-*tert*-butylcyclohex-1-enyl triflate was consumed, whereas the desired product, 1-(4-*tert*-butylcyclohex-1-enyl)-3-(trimethylsilyl)oct-3-en-1-yne (**6aa**), was formed in only moderate yield. Pale and co-workers have reported that tetrabutylammonium fluoride promotes the sila-Sonogashira reaction with alkenyl triflates.[9b,c] The report led us to examine the cross-coupling reaction using tetrabutylammonium fluoride in place of 1,8-diazabicyclo[5.4.0]undec-7-ene. Thus, the reaction with 4-*tert*-butylcyclohex-1-enyl triflate (0.5 mmol) was conducted in the presence of dichlorobis(triphenylphosphine)palladium and tetrabutylammonium fluoride (1 M solution in THF) at room temperature for four hours under argon. Table 4 shows the results of the reaction varying the amounts of dichlorobis(triphenylphosphine)palladium and tetrabutylammonium fluoride. When increasing the amount of tetrabutylammonium fluoride in the presence of a fixed amount of dichlorobis(triphenylphosphine)palladium (0.02 mmol), the yield of product **6aa** improved considerably (Table 4, entries 1 and 2). Further increasing the amount of tetrabutylammonium fluoride led to no improvement in the yield (Table 4, entry 3). On the other hand, reducing the amount of dichlorobis(triphenylphosphine)palladium to half, the yield increased slightly (Table 4, entry 4). Further reducing the amount of dichlorobis(triphenylphosphine)palladium caused a decrease in the yield (Table 4, entry 5). Thus it is appropriate to employ 2 mol% of dichlorobis(triphenylphosphine)palladium (0.01 mmol) and three equivalents of tetrabutylammonium fluoride (1.5 mmol).

The one-pot synthesis of (*Z*)-1-(cycloalk-1-enyl)-3-(trimethylsilyl)alk-3-en-1-ynes **6** was conducted under the optimized conditions, and the results are summarized in Table 5. Representative compounds **2** underwent cou-

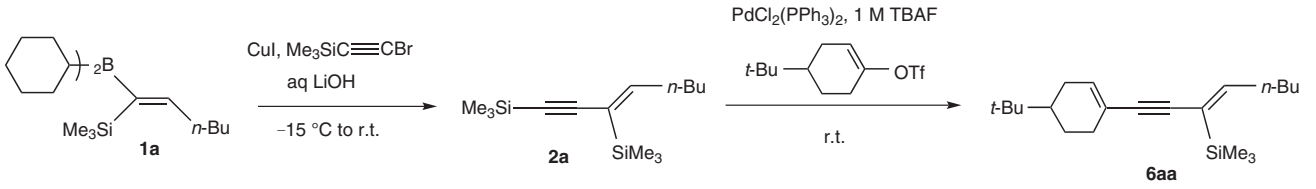
Table 3 Synthesis of (1*Z*,5*E*)-2-(Trimethylsilyl)alka-1,5-dien-3-ynes **4** and (1*Z*,5*Z*)-2-(Trimethylsilyl)alka-1,5-dien-3-ynes **5**[a]



Entry	Alk-1-enyl iodide	R^1	R^2	Product	Yield[b] (%)
1	(*E*)-BuCH=CHI	*n*-Bu	*n*-Bu	**4aa**	70
2	(*E*)-PhCH=CHI	*n*-Bu	Ph	**4ab**	58
3	(*E*)-BuCH=CHI	Ph	*n*-Bu	**4da**	60
4	(*E*)-PhCH=CHI	Ph	Ph	**4db**	44
5	(*Z*)-BuCH=CHI	*n*-Bu	*n*-Bu	**5aa**	74
6	(*Z*)-PhCH=CHI	*n*-Bu	Ph	**5ab**	38 (44)[c]
7	(*Z*)-BuCH=CHI	Ph	*n*-Bu	**5da**	72
8	(*Z*)-PhCH=CHI	Ph	Ph	**5db**	–[d]

[a] Reagents and conditions: **1** (4 mmol), $Me_3SiC{\equiv}CBr$ (2.68 mmol), CuI (0.4 mmol), $LiOH{\cdot}H_2O$ (3 mmol), H_2O (3 mL), –15 °C to r.t., overnight; (2) $R^2CH{=}CHI$ (2 mmol), $PdCl_2(PPh_3)_2$ (0.08 mmol), DBU (12 mmol), r.t., overnight, unless otherwise stated.
[b] Isolated yields based on the amount of $R^2CH{=}CHI$ employed.
[c] A reduced amount of DBU (8 mmol) was used.
[d] No **5db** could be isolated due to a co-eluting impurity.

Table 4 Optimization of Reaction Conditions for the (*Z*)-1-(Cycloalk-1-enyl)-3-(trimethylsilyl)alk-3-en-1-yne Synthesis[a]



Entry	$PdCl_2(PPh_3)_2$ (mmol)	TBAF (mmol)	Yield[b] (%) of **6aa**
1	0.02	1.0	48
2	0.02	1.5	71
3	0.02	2.0	69
4	0.01	1.5	76
5	0.005	1.5	68

[a] Reagents and conditions: **1a** (1 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), CuI (0.1 mmol), $LiOH{\cdot}H_2O$ (0.75 mmol), H_2O (0.75 mL), –15 °C to r.t., overnight; (2) 4-*tert*-butylcyclohex-1-enyl triflate (0.5 mmol), $PdCl_2(PPh_3)_2$, 1 M TBAF, r.t., for 4 h.
[b] Yields were estimated by GC and based on the amount of 4-*tert*-butylcyclohex-1-enyl triflate employed.

pling with some different types of cycloalk-1-enyl triflate to afford products **6** in moderate to good yields. Sterically hindered 6-methylcyclohex-1-enyl triflate reacted with **2a** and **2d** smoothly in analogy with 4-*tert*-butylcyclohex-1-enyl triflate (Table 5, entries 2 and 6). Conjugated cycloalkenyl triflate derived from α-tetralone underwent smooth coupling with **2a** (Table 5, entry 3), while the reaction with **2d** gave a low yield of product **6dc** (Table 5, entry 7). The cyclooct-1-enyl group took part in the sila-

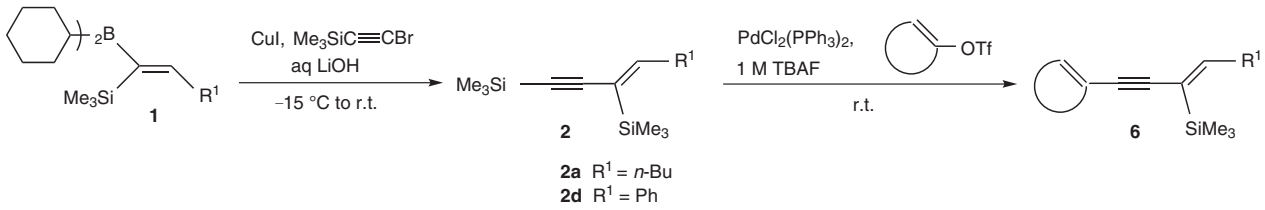
Sonogashira reaction without any difficulties (Table 5, entries 4 and 8).

To our knowledge, there is only one report on stereoselective synthesis of (*Z*)-1,3-enynyltrimethylsilanes via titanium-catalyzed hydromagnesiation of 1-(trimethylsilyl)alk-1-yne followed by palladium-catalyzed cross-coupling with 1-iodoalk-1-yne.[15] The present protocol has the advantage of introducing a variety of unsaturated substituents into the distal sp carbon atom.

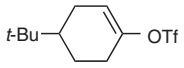
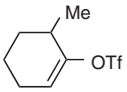
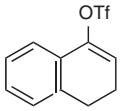
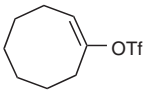
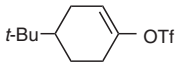
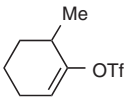
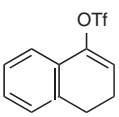
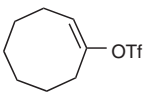
In summary, we have developed a one-pot procedure for the synthesis of internal conjugated (*Z*)-enynyltrimethylsilanes such as (*Z*)-1-aryl-3-(trimethylsilyl)alk-3-en-1-ynes **3**, (1*Z*,5*E*)-2-(trimethylsilyl)alka-1,5-dien-3-ynes **4**, (1*Z*,5*Z*)-2-(trimethylsilyl)alka-1,5-dien-3-ynes **5**, and (*Z*)-1-(cycloalk-1-enyl)-3-(trimethylsilyl)alk-3-en-1-ynes **6** from easily available starting materials via a Suzuki-type reaction/sila-Sonogashira reaction sequence. The present method has demonstrated that (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes **2** serves as a useful precursor for constructing internal conjugated (*Z*)-enynyltrimethylsilanes. Some features, such as simple operation, mild reaction conditions, overall stereospecificity, and good functional compatibility, make this strategy a useful and environmentally benign process for the construction of various internal conjugated (*Z*)-enynyltrimethylsilanes.

NMR spectra were recorded on a Jeol JNM-A-500 spectrometer with $CHCl_3$ (δ = 7.26 and 77.0) or CH_2Cl_2 (δ = 5.32 and 53.1) as internal standard. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrophotometer, and only the strongest/structurally most important absorption peaks are listed. MS were performed on a Jeol JMS-SX102A spectrometer (EI, 70 eV). GC analyses were performed with a Shimadzu GC-14B gas chromatograph equipped with a glass column (5% FFAP on Uniport B, 1 m or 5% SE-30 on Uniport B, 1 m), a flame ionization detector, and a Shimadzu C-R8A digital integrator-recorder. TLC analyses were carried out using glass plates pre-coated aluminum oxide 60 F_{254} purchased from Merck. Product purification was performed by column chromatog-

Table 5 Synthesis of (*Z*)-1-(Cycloalk-1-enyl)-3-(trimethylsilyl)alk-3-en-1-ynes **6**[a]



2a R^1 = *n*-Bu
2d R^1 = Ph

Entry	R^1	Cycloalk-1-enyl triflate	Product	Yield[b] (%)
1	Bu		**6aa**	70
2	Bu		**6ab**	74
3	Bu		**6ac**	65
4	Bu		**6ad**	62
5	Ph		**6da**	70
6	Ph		**6db**	75
7	Ph		**6dc**	40
8	Ph		**6dd**	70

[a] Reagents and conditions: (1) **1** (4 mmol), $Me_3SiC{\equiv}CBr$ (2.68 mmol), CuI (0.4 mmol), $LiOH{\cdot}H_2O$ (3 mmol), H_2O (3 mL), –15 °C to r.t., overnight; (2) cycloalk-1-enyl triflate (2 mmol), $PdCl_2(PPh_3)_2$ (0.04 mmol), 1 M TBAF(6 mmol), r.t., 4 h.
[b] Isolated yields based on the amount of cycloalk-1-enyl triflate employed.

raphy using Merck aluminum oxide (aluminum oxide 60 active basic, 70–230 μm). All reactions were carried out under an argon atmosphere. Unless otherwise noted, commercially available materials were used without any purification. Cyclohexene was used after distillation over CaH_2 under argon. THF was distilled from Na benzophenone ketyl under argon before use. 1-(Trimethylsilyl)hex-1-ene and 1-phenyl-2-(trimethylsilyl)ethyne were purchased from Aldrich and distilled under argon. (Trimethylsilyl)ethynyl bromide,[16] 1-(trimethylsilyl)alk-1-yne [from 3,3-dimethylbut-1-yne and (cyclohex-1-enyl)ethyne],[17] (*E*)-alk-1-enyl iodide,[18] (*Z*)-alk-1-enyl iodide,[19] cycloalk-1-enyl triflate[20] and a solution of BH_3 in THF[21] were prepared according to the literature procedures.

(*Z*)-1-Aryl-3-(trimethylsilyl)alk-3-en-1-ynes 3, (1*Z*,5*E*)-2-(Trimethylsilyl)alka-1,5-dien-3-ynes 4, and (1*Z*,5*Z*)-2-(Trimethylsilyl)alka-1,5-dien-3-ynes 5; General Procedure

To a 0.33 M soln of BH_3 in THF (4 mmol) was added cyclohexene (0.66 g, 8 mmol) dropwise at 0 °C under argon, and the mixture was stirred for 2 h at this temperature to form a white suspension of dicyclohexylborane in THF. To this suspension was added 1-(trimethylsilyl)alk-1-yne (4 mmol) dropwise at 0 °C and the mixture was stirred for 2 h at this temperature. The soln of dicyclohexyl[(*Z*)-1-(trimethylsilyl)alk-1-enyl]borane **1**, thus prepared, was cooled to –15 °C, and CuI (0.076 g, 0.4 mmol) and $LiOH·H_2O$ (0.126 g, 3 mmol) were added under a flow of argon, followed by dropwise addition of $Me_3SiC{\equiv}CBr$ (0.474 g, 2.68 mmol) and H_2O (3 mL). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. The mixture was then cooled to 0 °C, $PdCl_2(PPh_3)_2$ (0.056 g, 0.08 mmol) was added to the cooled mixture under a flow of argon followed by dropwise addition of DBU [3.65 g, 24 mmol for the synthesis of **3**, 1.83 g, 12 mmol for the synthesis of **4** and **5** except **5ab** (1.22 g, 8 mmol)] and aryl or alk-1-enyl iodide (2 mmol), and the resultant mixture was stirred at r.t. overnight. The mixture was treated by bubbling air through the soln with tube pump at r.t. for 2 h to oxidize the residual organoboron compound. The resulting mixture was extracted with pentane, washed with H_2O, dried (K_2CO_3), and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (aluminum oxide, basic) to provide product **3**, **4** or **5**.

(*Z*)-1-(Cycloalk-1-enyl)-3-(trimethylsilyl)alk-3-en-1-ynes 6; General Procedure

The cross-coupling reaction of dicyclohexyl[(*Z*)-1-(trimethylsilyl)alk-1-enyl]borane (4 mmol) in THF (12 mL) with $Me_3SiC{\equiv}CBr$ (0.474 g, 2.68 mmol) was carried out as described in the general procedure for the synthesis of **3**, **4**, and **5**. To the mixture containing (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne was added $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol) under a flow of argon, followed by dropwise addition of cycloalkenyl triflate (2 mmol) and 1 M TBAF (6 mL, 6 mmol) at 0 °C; the mixture was stirred at r.t. for 4 h. The workup procedure was the same as described in the general procedure for the synthesis of **3**, **4**, and **5**, except for extracting with Et_2O and washing with brine.

(*Z*)-1-Phenyl-3-(trimethylsilyl)oct-3-en-1-yne (3aa)

Eluent: pentane.

IR (neat): 2956, 2927, 2871, 2858, 2187, 1577, 1488, 1249, 840, 754, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.33 (s, 9 H), 0.97 (t, *J* = 7.0 Hz, 3 H), 1.37–1.50 (m, 4 H), 2.26–2.33 (m, 2 H), 6.78 (t, *J* = 7.7 Hz, 1 H), 7.26–7.36 (m, 3 H), 7.42–7.48 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.3 (CH_2), 89.7 (≡C), 93.0 (≡C), 122.8 (=C), 124.4 (=C), 127.3 (=CH), 128.1 (2 =CH), 131.2 (2 =CH), 154.7 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{24}Si$: 256.1647; found: 256.1686.

(*Z*)-5,5-Dimethyl-1-phenyl-3-(trimethylsilyl)hex-3-en-1-yne (3ba)

Eluent: pentane.

IR (neat): 2956, 2925, 2860, 1560, 1489, 1363, 1249, 842, 760, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.29 (s, 9 H), 1.12 (s, 9 H), 6.93 (s, 1 H), 7.27–7.33 (m, 3 H), 7.41–7.45 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.9 (3 CH_3), 30.6 (3 CH_3), 35.0 (C), 90.0 (≡C), 93.0 (≡C), 122.8 (=C), 124.4 (=C), 127.4 (=CH), 128.2 (2 =CH), 131.3 (2 =CH), 154.5 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{24}Si$: 256.1647; found: 256.1667.

(*Z*)-1-(Cyclohex-1-enyl)-4-phenyl-2-(trimethylsilyl)but-1-en-3-yne (3ca)

Eluent: pentane.

IR (neat): 2933, 2858, 2831, 2185, 1596, 1490, 1442, 1434, 1245, 925, 842, 754, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.30 (s, 9 H), 1.61–1.72 (m, 4 H), 2.04–2.18 (m, 4 H), 5.72–5.75 (m, 1 H), 7.08 (br s, 1 H), 7.28–7.36 (m, 3 H), 7.44–7.47 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.4 (3 CH_3), 21.8 (CH_2), 22.4 (CH_2), 25.4 (CH_2), 28.1 (CH_2), 91.1 (≡C), 93.7 (≡C), 122.7 (=C), 124.3 (=C), 126.8 (=CH), 127.4 (=CH), 128.1 (2 =CH), 131.2 (2 =CH), 137.3 (=C), 154.4 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{24}Si$: 280.1647; found: 280.1630.

(*Z*)-1,4-Diphenyl-2-(trimethylsilyl)but-1-en-3-yne (3da)

Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 3078, 3055, 3024, 2956, 2896, 1596, 1488, 1442, 1247, 866, 840, 752, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 7.32–7.42 (m, 8 H), 7.51–7.54 (m, 2 H), 7.85 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.1 (3 CH_3), 92.4 (≡C), 93.6 (≡C), 124.1 (=C), 126.6 (=C), 127.7 (=CH), 127.8 (=CH), 127.9 (2 =CH), 128.2 (2 =CH), 128.4 (2 =CH), 131.3 (2 =CH), 138.7 (=C), 151.2 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}Si$: 276.1334; found: 276.1364.

(*Z*)-1-(4-Methylphenyl)-3-(trimethylsilyl)oct-3-en-1-yne (3ab)

Eluent: pentane.

IR (neat): 2956, 2925, 2871, 2858, 2187, 1577, 1508, 1456, 1247, 840, 815, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.29 (s, 9 H), 0.93 (t, *J* = 7.0 Hz, 3 H), 1.34–1.46 (m, 4 H), 2.23–2.28 (m, 2 H), 2.34 (s, 3 H), 6.72 (t, *J* = 7.8 Hz, 1 H), 7.08–7.12 (m, 2 H), 7.29–7.32 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 21.4 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.3 (CH_2), 89.9 (≡C), 92.2 (≡C), 121.3 (=C), 122.9 (=C), 128.9 (2 =CH), 131.1 (2 =CH), 137.3 (=C), 154.3 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{26}Si$: 270.1804; found: 270.1790.

(*Z*)-1-(4-Methoxyphenyl)-3-(trimethylsilyl)oct-3-en-1-yne (3ac)

Eluent: pentane–CH_2Cl_2 (8:2).

IR (neat): 2956, 2929, 2871, 2856, 2835, 1606, 1508, 1463, 1440, 1290, 1247, 1170, 1031, 839, 806, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.32 (s, 9 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 1.37–1.49 (m, 4 H), 2.26–2.31 (m, 2 H), 3.83 (s, 3 H), 6.73 (t, *J* = 7.8 Hz, 1 H), 6.84–6.89 (m, 2 H), 7.36–7.41 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.3 (CH_2), 55.1 (CH_3), 89.6 (≡C), 91.5 (≡C), 113.8 (2 =CH), 116.6 (=C), 122.9 (=C), 132.5 (2 =CH), 153.9 (=CH), 158.9 (=C).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{26}OSi$: 286.1753; found: 286.1747.

(*Z*)-1-(2-Methylphenyl)-3-(trimethylsilyl)oct-3-en-1-yne (3ad)
Eluent: pentane.

IR (neat): 3058, 3020, 2956, 2925, 2871, 2858, 2183, 1577, 1485, 1458, 1377, 1247, 840, 754, 715, 692 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.30 (s, 9 H), 0.94 (t, *J* = 7.0 Hz, 3 H), 1.34–1.47 (m, 4 H), 2.25–2.30 (m, 2 H), 2.45 (s, 3 H), 6.75 (t, *J* = 7.8 Hz, 1 H), 7.10–7.20 (m, 3 H), 7.38–7.41 (m, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 13.9 (CH_3), 20.9 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.3 (CH_2), 88.3 (≡C), 96.9 (≡C), 123.0 (=C), 124.2 (=C), 125.3 (=CH), 127.3 (=CH), 129.2 (=CH), 131.8 (=CH), 139.4 (=C), 154.7 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{26}Si$: 270.1804; found: 270.1835.

(*Z*)-1-(4-Chlorophenyl)-3-(trimethylsilyl)oct-3-en-1-yne (3ae)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 2956, 2927, 2871, 2860, 2188, 1488, 1249, 1091, 1014, 840, 827, 758, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.32 (s, 9 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 1.37–1.50 (m, 4 H), 2.26–2.33 (m, 2 H), 6.79 (t, *J* = 7.8 Hz, 1 H), 7.24–7.28 (m, 2 H), 7.31–7.35 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (3 CH_3), 14.0 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.4 (CH_2), 88.7 (≡C), 94.0 (≡C), 122.6 (=C), 123.0 (=C), 128.4 (2 =CH), 132.4 (2 =CH), 133.6 (=C), 155.2 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{23}ClSi$: 290.1258; found: 290.1272.

(*Z*)-1-(4-Bromophenyl)-3-(trimethylsilyl)oct-3-en-1-yne (3af)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 2956, 2927, 2871, 2858, 2187, 1589, 1575, 1485, 1465, 1392, 1249, 1070, 1010, 840, 823, 758, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.32 (s, 9 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 1.37–1.50 (m, 4 H), 2.27–2.32 (m, 2 H), 6.78 (t, *J* = 7.8 Hz, 1 H), 7.28–7.31 (m, 2 H), 7.44–7.47 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 31.5 (CH_2), 32.4 (CH_2), 88.6 (≡C), 94.2 (≡C), 121.3 (=C), 122.6 (=C), 123.4 (=C), 131.3 (2 =CH), 132.6 (2 =CH), 155.3 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{23}BrSi$: 334.0753; found: 334.0764.

(*Z*)-1-(2-Thienyl)-3-(trimethylsilyl)oct-3-en-1-yne (3ag)
Eluent: pentane.

IR (neat): 2956, 2927, 2871, 2858, 2185, 1579, 1465, 1425, 1249, 1197, 840, 758, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.31 (s, 9 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 1.37–1.49 (m, 4 H), 2.27–2.32 (m, 2 H), 6.75 (t, *J* = 7.8 Hz, 1 H), 6.98 (dd, *J* = 5.4, 3.4 Hz, 1 H), 7.14 (dd, *J* = 3.4, 1.0 Hz, 1 H), 7.22 (dd, *J* = 5.4, 1.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 31.5 (CH_2), 32.4 (CH_2), 82.8 (≡C), 96.8 (≡C), 122.6 (=C), 124.7 (=C), 126.1 (=CH), 126.9 (=CH), 130.5 (=CH), 154.7 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{22}SSi$: 262.1212; found: 262.1214.

(*Z*)-1-(3-Pyridyl)-3-(trimethylsilyl)oct-3-en-1-yne (3ah)
Eluent: pentane–Et_2O (1:1).

IR (neat): 2956, 2927, 2871, 2858, 2189, 1587, 1573, 1558, 1475, 1406, 1249, 1020, 840, 802, 758, 704 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.32 (s, 9 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 1.37–1.50 (m, 4 H), 2.27–2.33 (m, 2 H), 6.81 (t, *J* = 7.8 Hz, 1 H), 7.26 (ddd, *J* = 7.8, 4.9, 1.0 Hz, 1 H), 7.71 (dt, *J* = 7.8, 2.0 Hz, 1 H), 8.50 (dd, *J* = 4.9, 1.5 Hz, 1 H), 8.66 (d, *J* = 1.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (3 CH_3), 13.9 (CH_3), 22.3 (CH_2), 31.4 (CH_2), 32.4 (CH_2), 86.0 (≡C), 96.5 (≡C), 121.6 (=C), 122.3 (=C), 122.9 (=CH), 138.1 (=CH), 147.3 (=CH), 151.6 (=CH), 156.1 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}NSi$: 257.1600; found: 257.1590.

(5*Z*,9*E*)-6-(Trimethylsilyl)tetradeca-5,9-dien-7-yne (4aa)[22]
Eluent: pentane.

IR (neat): 2956, 2927, 2871, 2858, 1465, 1249, 952, 840, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 0.88 (t, *J* = 7.0 Hz, 3 H), 1.26–1.40 (m, 8 H), 2.06–2.12 (m, 2 H), 2.16–2.22 (m, 2 H), 5.60 (d, *J* = 15.6 Hz, 1 H), 6.03 (dt, *J* = 15.6, 7.3 Hz, 1 H), 6.58 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (3 CH_3), 13.8 (CH_3), 13.9 (CH_3), 22.1 (CH_2), 22.3 (CH_2), 31.0 (CH_2), 31.6 (CH_2), 32.2 (CH_2), 32.7 (CH_2), 88.6 (≡C), 91.3 (≡C), 110.2 (=CH), 123.0 (=C), 142.9 (=CH), 153.8 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{30}Si$: 262.2117; found: 262.2105.

(1*E*,5*Z*)-1-Phenyl-5-(trimethylsilyl)deca-1,5-dien-3-yne (4ab)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 3060, 3026, 2956, 2925, 2871, 2856, 2167, 1596, 1569, 1492, 1465, 1448, 1247, 948, 840, 758, 746, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.30 (s, 9 H), 0.96 (t, *J* = 7.0 Hz, 3 H), 1.36–1.48 (m, 4 H), 2.25–2.30 (m, 2 H), 6.38 (d, *J* = 16.1 Hz, 1 H), 6.72 (t, *J* = 7.8 Hz, 1 H), 6.89 (d, *J* = 16.1 Hz, 1 H), 7.27–7.31 (m, 1 H), 7.33–7.37 (m, 2 H), 7.40–7.43 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.3 (CH_2), 89.2 (≡C), 95.7 (≡C), 109.2 (=CH), 123.0 (=C), 126.0 (2 =CH), 128.1 (=CH), 128.6 (2 =CH), 136.7 (=C), 139.4 (=CH), 154.8 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}Si$: 282.1804; found: 282.1791.

(1*Z*,5*E*)-1-Phenyl-2-(trimethylsilyl)deca-1,5-dien-3-yne (4da)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 2956, 2925, 2871, 2854, 1488, 1444, 1247, 952, 840, 752, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.13 (s, 9 H), 0.96 (t, *J* = 7.3 Hz, 3 H), 1.34–1.48 (m, 4 H), 2.16–2.22 (m, 2 H), 5.76 (br d, *J* = 15.6 Hz, 1 H), 6.17 (dt, *J* = 15.6, 7.3 Hz, 1 H), 7.25–7.38 (m, 5 H), 7.69 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 13.8 (CH_3), 22.1 (CH_2), 30.9 (CH_2), 32.8 (CH_2), 91.4 (≡C), 92.0 (≡C), 110.1 (=CH), 127.0 (=C), 127.6 (=CH), 127.8 (2 =CH), 128.3 (2 =CH), 138.8 (=C), 144.0 (=CH), 150.5 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}Si$: 282.1804; found: 282.1805.

(1*Z*,5*E*)-1,6-Diphenyl-2-(trimethylsilyl)hexa-1,5-dien-3-yne (4db)
Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 3024, 2954, 1490, 1446, 1247, 948, 840, 750, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.19 (s, 9 H), 6.46 (d, *J* = 16.1 Hz, 1 H), 6.98 (d, *J* = 16.1 Hz, 1 H), 7.28–7.50 (m, 10 H), 7.77 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 91.9 (≡C), 96.2 (≡C), 108.9 (=CH), 126.1 (2 =CH), 126.9 (=C), 127.8 (=CH), 127.9 (2 =CH), 128.3 (=CH), 128.4 (2 =CH), 128.6 (2 =CH), 136.5 (=C), 138.7 (=C), 140.1 (=CH), 151.1 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{22}Si$: 302.1491; found: 302.1479.

(5*Z*,9*Z*)-6-(Trimethylsilyl)tetradeca-5,9-dien-7-yne (5aa)[22]
Eluent: pentane.

IR (neat): 2956, 2927, 2871, 2858, 1465, 1249, 840, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 1.30–1.43 (m, 8 H), 2.18–2.24 (m, 2 H), 2.28–2.34 (m, 2 H), 5.60 (d, *J* = 10.7 Hz, 1 H), 5.79 (dt, *J* = 10.7, 7.3 Hz, 1 H), 6.62 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 13.9 (CH_3), 22.3 (CH_2), 22.4 (CH_2), 30.0 (CH_2), 31.1 (CH_2), 31.6 (CH_2), 32.2 (CH_2), 86.5 (≡C), 97.0 (≡C), 109.6 (=CH), 123.1 (=C), 142.1 (=CH), 154.2 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{30}Si$: 262.2117; found: 262.2107.

(1*Z*,5*Z*)-1-Phenyl-5-(trimethylsilyl)deca-1,5-dien-3-yne (5ab)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 2956, 2927, 2871, 2856, 2167, 1448, 1249, 840, 785, 758, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.30 (s, 9 H), 0.97 (t, *J* = 7.0 Hz, 3 H), 1.36–1.49 (m, 4 H), 2.27–2.33 (m, 2 H), 5.91 (d, *J* = 11.7 Hz, 1 H), 6.58 (d, *J* = 11.7 Hz, 1 H), 6.75 (t, *J* = 7.8 Hz, 1 H), 7.28–7.33 (m, 1 H), 7.36–7.41 (m, 2 H), 7.90–7.93 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 31.6 (CH_2), 32.4 (CH_2), 88.0 (≡C), 100.2 (≡C), 108.4 (=CH), 123.2 (=C), 127.9 (=CH), 128.1 (2 =CH), 128.6 (2 =CH), 136.3 (=CH), 136.8 (=C), 155.4 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}Si$: 282.1804; found: 282.1795.

(1*Z*,5*Z*)-1-Phenyl-2-(trimethylsilyl)deca-1,5-dien-3-yne (5da)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 3020, 2956, 2925, 2871, 2854, 1488, 1444, 1247, 840, 752, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 0.97 (t, *J* = 7.0 Hz, 3 H), 1.38–1.51 (m, 4 H), 2.38–2.43 (m, 2 H), 5.71 (br d, *J* = 10.7 Hz, 1 H), 5.92 (dt, *J* = 10.7, 7.3 Hz, 1 H), 7.26–7.37 (m, 5 H), 7.72 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 13.9 (CH_3), 22.3 (CH_2), 30.1 (CH_2), 31.1 (CH_2), 89.2 (≡C), 97.5 (≡C), 109.5 (=CH), 127.1 (=C), 127.7 (=CH), 127.8 (2 =CH), 128.4 (2 =CH), 138.8 (=C), 142.9 (=CH), 150.7 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}Si$: 282.1804; found: 282.1789.

(*Z*)-1-(4-*tert*-Butylcyclohex-1-enyl)-3-(trimethylsilyl)oct-3-en-1-yne (6aa)[22]
Eluent: pentane.

IR (neat): 2956, 2871, 1465, 1365, 1249, 840, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 0.86 (s, 9 H), 0.89 (t, *J* = 7.0 Hz, 3 H), 1.17–1.29 (m, 2 H), 1.29–1.31 (m, 4 H), 1.78–1.90 (m, 2 H), 2.08–2.25 (m, 5 H), 5.99–6.03 (m, 1 H), 6.58 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 23.8 (CH_2), 27.1 (3 CH_3), 27.4 (CH_2), 31.0 (CH_2), 31.6 (CH_2), 32.1 (C), 32.2 (CH_2), 43.2 (CH), 90.5 (≡C), 91.4 (≡C), 121.2 (=C), 123.0 (=C), 133.3 (=CH), 153.4 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{36}Si$: 316.2586; found: 316.2620.

(*Z*)-1-(6-Methylcyclohex-1-enyl)-3-(trimethylsilyl)oct-3-en-1-yne (6ab)[22]
Eluent: pentane.

IR (neat): 2954, 2923, 2854, 1456, 1377, 1247, 840, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 0.90 (t, *J* = 7.0 Hz, 3 H), 1.14 (d, *J* = 7.3 Hz, 3 H), 1.28–1.41 (m, 5 H), 1.48–1.56 (m, 1 H), 1.62–1.70 (m, 1 H), 1.75–1.82 (m, 1 H), 2.05–2.10 (m, 2 H), 2.17–2.28 (m, 3 H), 6.02 (dt, *J* = 3.9, 1.9 Hz, 1 H), 6.60 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0 (3 CH_3), 13.9 (CH_3), 19.6 (CH_2), 20.5 (CH_3), 22.4 (CH_2), 26.0 (CH_2), 30.7 (CH_2), 31.7 (CH_2), 32.2 (CH_2), 32.8 (CH), 90.7 (≡C), 91.1 (≡C), 123.0 (=C), 126.9 (=C), 133.4 (=CH), 153.6 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{30}Si$: 274.2117; found: 274.2135.

(*Z*)-1-(3,4-Dihydro-1-naphthyl)-3-(trimethylsilyl)oct-3-en-1-yne (6ac)
Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 2956, 2929, 2871, 2858, 2829, 1577, 1487, 1450, 1425, 1247, 840, 763, 734 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.33 (s, 9 H), 0.97 (t, *J* = 7.3 Hz, 3 H), 1.37–1.50 (m, 4 H), 2.28–2.33 (m, 2 H), 2.43 (dt, *J* = 8.0, 4.9 Hz, 2 H), 2.84 (t, *J* = 8.0 Hz, 2 H), 6.43 (t, *J* = 4.9 Hz, 1 H), 6.78 (t, *J* = 7.8 Hz, 1 H), 7.14 (br d, *J* = 6.8 Hz, 1 H), 7.20 (dt, *J* = 7.3, 1.5 Hz, 1 H), 7.25–7.30 (m, 1 H), 7.63 (br d, *J* = 7.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 23.7 (CH_2), 27.2 (CH_2), 31.6 (CH_2), 32.3 (CH_2), 87.2 (≡C), 93.8 (≡C), 122.4 (=C), 122.8 (=C), 125.1 (=CH), 126.4 (=CH), 127.2 (=CH), 127.3 (=CH), 133.1 (=C), 133.9 (=CH), 135.1 (=C), 154.7 (=CH).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{28}Si$: 308.1960; found: 308.1938.

(*Z*)-1-(Cyclooct-1-enyl)-3-(trimethylsilyl)oct-3-en-1-yne (6ad)[22]
Eluent: pentane.

IR (neat): 2954, 2925, 2852, 1575, 1465, 1448, 1247, 840, 758, 692 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (s, 9 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 1.29–1.41 (m, 4 H), 1.45–1.55 (m, 6 H), 1.55–1.65 (m, 2 H), 2.13–2.23 (m, 4 H), 2.27–2.33 (m, 2 H), 6.00 (t, *J* = 8.3 Hz, 1 H), 6.58 (t, *J* = 7.8 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.0 (3 CH_3), 13.9 (CH_3), 22.4 (CH_2), 25.8 (CH_2), 26.4 (CH_2), 27.0 (CH_2), 28.4 (CH_2), 29.8 (CH_2),

30.2 (CH_2), 31.6 (CH_2), 32.2 (CH_2), 89.8 (≡C), 92.5 (≡C), 123.1 (=C), 124.5 (=C), 136.0 (=CH), 153.3 (=CH).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{32}Si$: 288.2273; found: 288.2303.

(*Z*)-4-(4-*tert*-Butylcyclohex-1-enyl)-1-phenyl-2-(trimethylsilyl)but-1-en-3-yne (6da)

Eluent: pentane.

IR (neat): 2958, 2922, 2898, 2868, 2841, 1488, 1477, 1365, 1247, 916, 858, 840, 752, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.13 (s, 9 H), 0.92 (s, 9 H), 1.21–1.37 (m, 2 H), 1.86–1.99 (m, 2 H), 2.17–2.36 (m, 3 H), 6.14–6.17 (m, 1 H), 7.25–7.37 (m, 5 H), 7.69 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 23.8 (CH_2), 27.1 (3 CH_3), 27.5 (CH_2), 30.9 (CH_2), 32.1 (C), 43.2 (CH), 91.1 (≡C), 94.2 (≡C), 121.1 (=C), 127.0 (=C), 127.6 (=CH), 127.8 (2 =CH), 128.3 (2 =CH), 134.3 (=CH), 138.9 (=C), 150.1 (=CH).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{23}H_{32}Si$: 336.2273; found: 336.2279.

(*Z*)-4-(6-Methylcyclohex-1-enyl)-1-phenyl-2-(trimethylsilyl)but-1-en-3-yne (6db)

Eluent: pentane.

IR (neat): 3022, 2956, 2929, 2868, 2829, 1488, 1454, 1442, 1338, 1247, 862, 840, 752, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 1.24 (d, *J* = 6.8 Hz, 3 H), 1.38–1.45 (m, 1 H), 1.55–1.64 (m, 1 H), 1.69–1.77 (m, 1 H), 1.82–1.89 (m, 1 H), 2.12–2.18 (m, 2 H), 2.31–2.39 (m, 1 H), 6.15 (dt, *J* = 3.9, 1.9 Hz, 1 H), 7.26–7.37 (m, 5 H), 7.70 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 19.6 (CH_2), 20.5 (CH_3), 26.1 (CH_2), 30.7 (CH_2), 32.7 (CH), 91.8 (≡C), 93.6 (≡C), 126.9 (=C), 127.1 (=C), 127.5 (=CH), 127.8 (2 =CH), 128.3 (2 =CH), 134.2 (=CH), 138.9 (=C), 150.1 (=CH).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{20}H_{26}Si$: 294.1804; found: 294.1799.

(*Z*)-4-(3,4-Dihydro-1-naphthyl)-1-phenyl-2-(trimethylsilyl)but-1-en-3-yne (6dc)

Eluent: pentane–CH_2Cl_2 (95:5).

IR (neat): 3053, 2952, 2933, 2895, 2829, 1487, 1450, 1357, 1334, 1247, 993, 918, 840, 763, 752, 734, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.21 (s, 9 H), 2.48 (dt, *J* = 8.0, 4.9 Hz, 2 H), 2.88 (t, *J* = 8.0 Hz, 2 H), 6.53 (t, *J* = 4.9, Hz, 1 H), 7.18 (br d, *J* = 7.3 Hz, 1 H), 7.24 (dt, *J* = 7.3, 1.5 Hz, 1 H), 7.28–7.42 (m, 6 H), 7.71 (br d, *J* = 7.3 Hz, 1 H), 7.86 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.1 (3 CH_3), 23.7 (CH_2), 27.2 (CH_2), 90.0 (≡C), 94.4 (≡C), 122.4 (=C), 125.1 (=CH), 126.5 (=CH), 126.8 (=C), 127.3 (=CH), 127.5 (=CH), 127.7 (=CH), 127.9 (2 =CH), 128.4 (2 =CH), 132.9 (=C), 134.7 (=CH), 135.1 (=C), 138.7 (=C), 151.1 (=CH).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{23}H_{24}Si$: 328.1647; found: 328.1629.

(*Z*)-4-(Cyclooct-1-enyl)-1-phenyl-2-(trimethylsilyl)but-1-en-3-yne (6dd)

Eluent: pentane.

IR (neat): 2925, 2850, 1488, 1465, 1444, 1247, 840, 752, 696 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9 H), 1.52–1.64 (m, 6 H), 1.64–1.74 (m, 2 H), 2.21–2.28 (m, 2 H), 2.38–2.43 (m, 2 H), 6.15 (t, *J* = 8.3 Hz, 1 H), 7.26–7.38 (m, 5 H), 7.70 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (3 CH_3), 25.8 (CH_2), 26.4 (CH_2), 27.1 (CH_2), 28.5 (CH_2), 29.8 (CH_2), 30.1 (CH_2), 90.5 (≡C), 95.3 (≡C), 124.4 (=C), 127.1 (=C), 127.5 (=CH), 127.8 (2 =CH), 128.3 (2 =CH), 136.9 (=CH), 138.9 (=C), 150.0 (=CH).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{21}H_{28}Si$: 308.1960; found: 308.1935.

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(10) Compound **2a** was formed in about 90% GC yield based on $Me_3SiC{\equiv}CBr$ employed; see ref. 6.

(11) Addition of CuI was not necessary because CuI had already been used for the cross-coupling reaction of **1a** with $Me_3SiC{\equiv}CBr$.

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