Construction of Terminal Conjugated Enynes: Cu-Mediated Cross-Coupling Reaction of Alkenyldialkylborane with (Trimethylsilyl)ethynyl Bromide

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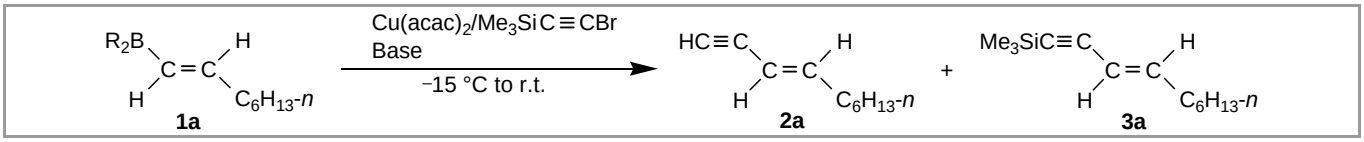
Abstract: The cross-coupling reaction of (*E*)- and (*Z*)-alk-1-enyldialkylborane with (trimethylsilyl)ethynyl bromide proceeds in the presence of a catalytic amount of $Cu(acac)_2$ and a base under extremely mild conditions to provide conjugated enynes whose carbon-carbon triple bond is in distal position. The use of 1M NaOMe as the base results in not only cross-coupling but also desilylation affording both (*E*)- and (*Z*)-alk-3-en-1-ynes exclusively, while the use of $LiOH•H_2O$ instead of 1M NaOMe preferentially gives both (*E*)- and (*Z*)-1-(trimethylsilyl)alk-3-en-1-ynes with high regio- and stereoselectivity. On the other hand, the cross-coupling reaction of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane with (trimethylsilyl)ethynyl bromide proceeds in the presence of a small amount of CuI and aqueous NaOH under extremely mild conditions to afford (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne with high regio- and stereoselectivity. In addition, treatment of the resultant product with 1M NaOMe leads to the stereoselective formation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-yne in a one-pot manner.

Key words: alkenyldialkylborane, (trimethylsilyl)ethynyl bromide, cross-coupling, alk-3-en-1-yne, 1,3-bis(trimethylsilyl)alk-3-en-1-yne

Conjugated enynes are valuable precursors to a variety of functionalized compounds such as stereodefined conjugated dienes via stereospecific reduction of their triple bond[1] and polysubstituted benzenes via benzannulation reactions.[2] Enyne systems are also found in a number of natural products such as neocarzinostatin chromophore.[3] Among conjugated enynes, there has been a lively interest in terminal conjugated enyne, alk-3-en-1-yne, due to its synthetic utility in which the acetylenic hydrogen can be converted into various functionalities including carbon-carbon bond formation. Furthermore, the terminal conjugated enyne is a useful building block for the synthesis of natural products in organic synthesis, because the terminal conjugated enyne unit occurs in natural products such as Laurencin,[4] Dactylyne,[5] Quinolizidine,[6] and Histrionicotoxin.[7] Although a large number of methods have been developed for constructing conjugated enynes, cross-coupling reactions appear to be the most reliable and straightforward methodology due to their high regio- and stereoselectivity and high product yields.[8] There have been several reports on the synthesis of terminal conjugated enynes employing cross-coupling reactions with (trimethylsilyl)ethynyl halide as an ethynyl unit so far;[8c,9-11] however, to the best of our knowledge, the Suzuki-Miyaura cross-coupling reaction[12] with (trimethylsilyl)ethynyl halide has not been demonstrated. The cross-coupling reaction using organoboranes requires base together with catalyst, while sp-hybridized carbon-silicon bond can be readily cleaved by basic methanolysis. If cleavage of the carbon-silicon bond is controlled during the cross-coupling reaction between alkenylborane and (trimethylsilyl)ethynyl halide, terminal conjugated enynes with trimethylsilyl group as well as without it are selectively furnished and are of great significance for further transformation.[13] Thus we are interested in applying Cu-mediated cross-coupling reaction of alkenylborane in the presence of base to (trimethylsilyl)ethynyl halide in an effort to obtain the sole product in a selective fashion.[14] Herein, we report the successful syntheses of not only (*E*)- and (*Z*)-alk-3-en-1-ynes with or without trimethylsilyl group at the 1-position but also (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes with or without it at the terminal position via the present Cu-mediated cross-coupling reaction.

We initially focused our attention on the use of (trimethylsilyl)ethynyl bromide in the cross-coupling reaction. This substrate was easily prepared from (trimethylsilyl)ethyne using a known procedure.[15] (*E*)-Oct-1-enyldialkylborane (**1a**) was chosen as a coupling partner. The cross-coupling reaction of **1a** with (trimethylsilyl)ethynyl bromide was optimized by using $Cu(acac)_2$ (0.05 equiv) as catalyst, THF as solvent, and a variety of bases. It was found that the reaction proceeded under very mild conditions (–15 °C to r.t.) to yield two products, (*E*)-dec-3-en-1-yne (**2a**) and (*E*)-1-(trimethylsilyl)dec-3-en-1-yne (**3a**) (Scheme 1). The results are summarized in Table 1. The ratio of product **2a** to product **3a** was dependent on base employed. Thus, the reaction using 1M NaOMe gave product **2a** exclusively (entries 1, 8 and 9), while the reaction using $LiOH•H_2O$ gave product **3a** preferentially (entries 6 and 7). In addition, making use of a certain excess amount of **1a** (1.5 equiv) increased the yield of the products (entries 7 and 9). It was also observed that the ratio and the yield of the products were affected by changing the dialkylboryl group of **1a** (entry 6 vs. 10 and entry 1 vs. 8). In coupling reactions using organoboron compounds such as the Suzuki-Miyaura reaction, the substituent on the boron atom influences the reactivity of the boron compounds.[12] The reaction using (*E*)-oct-1-enyldisiamylborane (1.5 equiv) and 1M NaOMe provided the best results for the synthesis of **2a** (desilylated cross-coupling product) (entry 9). In marked contrast, using (*E*)-oct-1-enyldicyclohexylborane (1.5 equiv) and $LiOH•H_2O$ proved to be the best conditions for the synthesis of **3a** (silyl-retained cross-coupling product) (entry 7).



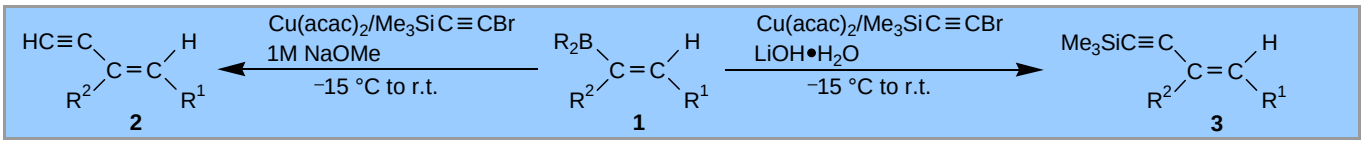
Scheme 1

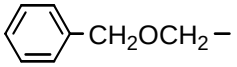
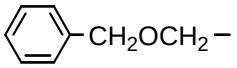
Table 1 Effect of Base and Dialkylborane for Cross-Coupling Reaction of **1a** with (Trimethylsilyl)ethynyl Bromide[a]

Entry	R	Base	Yield of Products (%)[b]	
			2a	**3a**
1		1M NaOMe	66	trace
2		2M NaOH	56	2
3		*n*-BuLi	39	12
4		*t*-BuOK	15	14
5		CsF	21	1
6		LiOH·H_2O	2	50
7[c]			1	78
8	$(CH_3)_2CHCH(CH_3)$	1M NaOMe	71	0
9[c]			75	0
10		LiOH·H_2O	17	53

[a] Unless otherwise specified, the reaction of **1a** (1 mmol) with (trimethylsilyl)ethynyl bromide (1 mmol) was carried out using $Cu(acac)_2$ (0.05 mmol) and base (1 mmol) at –15 ˚C to room temperature for overnight.
[b] The yields were estimated by GC and based on (trimethylsilyl)ethynyl bromide employed.
[c] A certain excess amount of **1a** (1.5 mmol) was used.

Table 2 Cross-coupling Reaction of (*E*)-Alk-1-enyldialkylborane with (Trimethylsilyl)ethynyl Bromide[a]

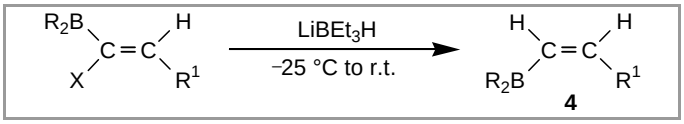


Entry	R	Base	R^1	R^2	Product	Yield(%)[b]
1	$(CH_3)_2CHCH(CH_3)$	1M NaOMe	*n*-C_6H_{13}	H	**2a**	70
2					**2b**	70
3					**2c**	63
4			$Cl(CH_2)_3$–		**2d**	67
5					**2e**	74
6			*n*-C_3H_7	*n*-C_3H_7	**2f**	70
7		LiOH·H_2O	*n*-C_6H_{13}	H	**3a**	72[c]
8					**3b**	73[c]
9					**3c**	62[c]
10			$Cl(CH_2)_3$–		**3d**	72
11					**3e**	63[c]
12			*n*-C_3H_7	*n*-C_3H_7	**3f**	65

[a] The reaction of **1** (4 mmol) with (trimethylsilyl)ethynyl bromide (2.68 mmol) was carried out using $Cu(acac)_2$ (0.2 mmol) and base (4 mmol) at –15 ˚C to r.t. for overnight.
[b] Isolated yields based on (trimethylsilyl)ethynyl bromide employed.
[c] A slight amount of **2** (1 to 4 %) was formed.

The optimized conditions were applied to the cross-coupling reaction of different types of **1** with (trimethylsilyl)ethynyl bromide. As shown in Table 2, the reactions proceeded with satisfactory yields and high product selectivity. The present reaction was tolerant of functional groups including conjugated alkenyl, chloro and ether. The cross-coupling reactions using alkenyldisiamylborane and 1M NaOMe provided the corresponding products **2** with complete product selectivity (entries 1–6), while the cross-coupling reactions using alkenyldicyclohexylborane and LiOH•H_2O afforded the corresponding products **3**, exclusively (entries 10 and 12) or together with slight amounts of **2** (entries 7–9 and 11). It should be noted that the present reaction can be also applied to internal alkenyldialkylborane derived from symmetrically internal alkyne (entries 6 and 12).

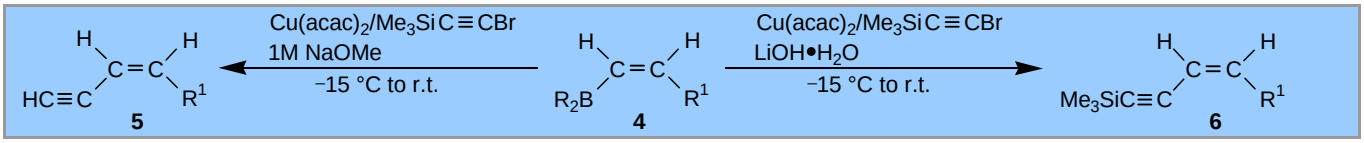
To synthesize terminal conjugated enynes with the opposite geometry, we next examined the reaction employing (*Z*)-alk-1-enyldialkylborane (**4**) which was prepared by treatment of (*Z*)-1-haloalk-1-enyldialkylborane with $LiBEt_3H$ (Scheme 2).[16]

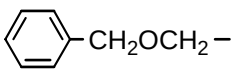
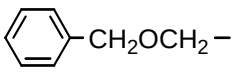


Scheme 2

Thus, **4** was subjected to the reaction with (trimethylsilyl)ethynyl bromide under the same conditions as described above, and the results are summarized in Table 3. The reactions using (*Z*)-alk-1-enyldisiamylborane and 1M NaOMe led to the selective formation of (*Z*)-alk-3-en-1-yne (**5**) in satisfactory yields (entries 1–5) and tolerated the same functional groups as shown in Table 2. It is important to note that Et_3B, liberated from $LiBEt_3H$, has to be removed from the reaction mixture to give the favorable results. In the presence of Et_3B, for example, the cross-coupling reaction of (*Z*)-oct-1-enyldisiamylborane decreased the yield of (*Z*)-dec-3-en-1-yne (**5a**) substantially, probably due to consumption of NaOMe by forming $NaBEt_3OMe$. In fact, further addition of NaOMe (2 equiv in total) restored the formation of product **5a** to nearly the same yield. On the other hand, the reaction using (*Z*)-alk-1-enyldicyclohexylboran and LiOH•H_2O, however, was applicable to only limited substrates (entries 6 and 7). Whereas the cross-coupling reaction of (*Z*)-oct-1-enyldicyclohexylborane, prepared from (*Z*)-1-iodooct-1-enyldicyclohexylborane, gave (*Z*)-1-(trimethylsilyl)dec-3-en-1-yne (**6a**) in only 14% yield, use of DMF as co-solvent increased the yield of product **6a** to 49% (entry 6). Removing Et_3B gave rise to the concomitant formation of desilylated product **5a**, although removal of Et_3B is a critical process for the synthesis of **5**. The cross-coupling reaction of (*Z*)-3-benzyloxyprop-1-enyldicyclohexylborane, prepared from (*Z*)-1-bromo-3-benzyloxylprop-1-enyldicyclohexylborane, by contrast, produced (*Z*)-3-benzyloxy-1-(trimethylsilyl)pent-3-en-1-yne (**6e**) in 66% yield without using DMF (entry 7). However, the cross-coupling reaction of (*Z*)-2-(cyclohex-1-enyl)ethenyldicyclohexylborane or (*Z*)-5-chloropent-1-enyldicyclohexylborane gave low yields of the corresponding products, despite prepared from (*Z*)-1-bromoalk-1-enyldicyclohexylborane. In the case of (*Z*)-2-phenylethenyldicyclohexylborane derived from (*Z*)-1-iodo-2-phenylethenyldicyclohexylborane, the addition of DMF was not very useful to gain a practical yield. The reason why this method lacks generality for the synthesis of **6** is unclear at present.

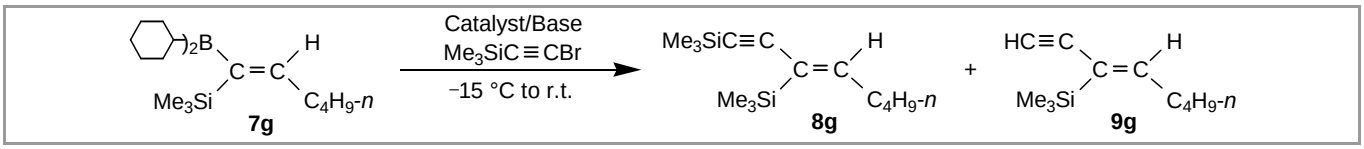
Table 3 Cross-Coupling Reaction of (*Z*)-Alk-1-enyldialkylborane[a] with (Trimethylsilyl)ethynyl Bromide[b]



Entry	R	Base	R^1	Product	Yield (%)[c]
1	$(CH_3)_2CHCH(CH_3)$	1M NaOMe	*n*-C_6H_{13}	**5a**	75
2				**5b**	66
3				**5c**	57
4			$Cl(CH_2)_3$	**5d**	70
5				**5e**	60
6		LiOH·H_2O	*n*-C_6H_{13}	**6a**	14 (49)[d,e]
7				**6e**	66

[a] Compound **4** was prepared by the reaction of (*Z*)-1-haloalk-1-enyldialkylborane (4 mmol) with $LiBEt_3H$ (4 mmol) at –25 ˚C to r.t. over 1 h.
[b] The reaction of **4** (4 mmol) with (trimethylsilyl)ethynyl bromide (2.68 mmol) was carried out using $Cu(acac)_2$ (0.2 mmol) and base (4 mmol) at –15 ˚C to r.t. for overnight.

[c]Isolated yields based on (trimethylsilyl)ethynyl bromide employed.
[d] A slight amount of **5a** (3 %) was formed.
e DMF was used as co-solvent in the cross-coupling step.



Scheme 3

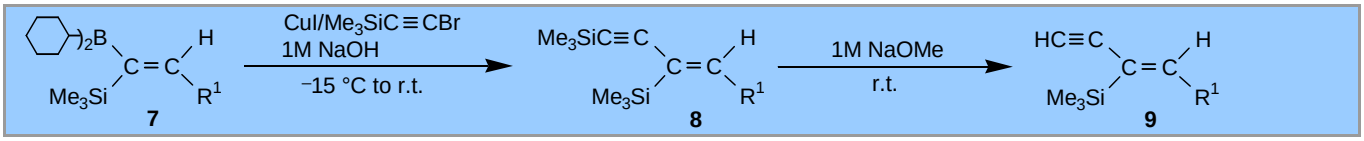
Table 4 Effect of Catalyst and Base for Cross-Coupling Reaction of **7g** with (Trimethylsilyl)ethynyl Bromide[a]

Entry	Catalyst	(mol %)	Base	Yield of Products (%)[b] **8g**	**9g**
1	$Cu(acac)_2$	5	1M NaOMe	10	43
2		10		30	18
3		5	$LiOH·H_2O$	43	trace
4		5	1M NaOH	83	7
5		5	2M NaOH	78	10
6	CuI	5	1M NaOMe	28	25
7		10		63	4
8		10	$LiOH·H_2O$	22	trace
9		10	1M NaOH	93	0
10		10	2M NaOH	73	trace

[a] The reaction of **7g** (1 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was carried out using copper catalyst and base (0.75 mmol) at –15 ˚C to r.t. for overnight.
[b] The yields were estimated by GC and based on (trimethylsilyl)ethynyl bromide employed.

Continuing with our investigation, we explored the cross-coupling reaction of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane with (trimethylsilyl)ethynyl bromide. To determine the optimized reaction conditions, (*Z*)-1-(trimethylsilyl)hex-1-enyldicyclohexylborane (**7g**) was chosen as a coupling partner and allowed to react with (trimethylsilyl)ethynyl bromide under various conditions, and the results are shown in Table 4. It was found that the reaction proceeded under very mild conditions (–15 °C to r.t.) to yield two products, (*Z*)-1,3-bis(trimethylsilyl)oct-3-en-1-yne (**8g**) (silyl-retained cross-coupling product) and (*Z*)-3-(trimethylsilyl)oct-3-en-1-yne (**9g**) (desilylated cross-coupling product) (Scheme 3). In the presence of $Cu(acac)_2$ as a catalyst, use of 1M NaOMe resulted in the formation of a mixture of products **8g** and **9g** (entries 1 and 2), while using $LiOH•H_2O$ gave product **8g** exclusively, albeit in low yield (entry 3). When aq. NaOH was used, the reaction afforded product **8g** preferentially in higher yields (entries 4 and 5). Changing the catalyst to CuI proved to be advantageous for this cross-coupling. Thus, the reaction was conducted in the presence of CuI (0.1 equiv) and 1M NaOH (0.75 equiv), leading to the exclusive formation of **8g** and that in high yield (entry 9). Unfortunately, selective formation of **9g** was not performed during the cross-coupling reaction. It is useful to note that subsequent treatment of **8g** with 1M NaOMe gave product **9g** exclusively in a one-pot manner. The configurations of the products **8g** and **9g** were assigned on the basis of $^3J_{CH}$ values of the alkynyl carbon to the alkenyl proton. It is well known that $^3J_{CH(cis)}$ values are smaller than $^3J_{CH(trans)}$ values in alkenes. The ^{13}C NMR spectrum of product **8g** showed that two sp carbons appeared at δ 93.6 and 109.0 in the broadband-decoupled spectrum, the later of which appeared as a doublet ($^3J_{CH}$ = 11.6 Hz) in the coupled spectrum. Also, the internal sp carbon of product **9g** appeared at δ 87.2 in the broadband-decoupled spectrum, and the coupled spectrum of it appeared as a double doublet ($^2J_{CH}$ = 48.5 Hz, $^3J_{CH}$ = 11.2 Hz). On the other hand, the $^3J_{CH}$ values of *E*-isomer revealed larger values ($^3J_{CH}$ = 15.8 Hz).[17] These $^3J_{CH}$ values are larger than those in 1,2-disubstituted alkenes without trimethylsilyl group on the alkenyl carbons. To our knowledge, 1-(trimethylsilyl)alk-1-enes have larger $^3J_{HH}$ values of the alkenyl protons,[18] implying that the $^3J_{CH}$ values of the alkynyl carbon to the alkenyl proton in **8g** and **9g** would indicate larger values relative to the $^3J_{HH}$ values.

Table 5 Cross-Coupling Reaction of **7** with (Trimethylsilyl)ethynyl Bromide[a] and Desilylation of **8**[b]



Entry	R^1	Product	Yield (%)[c]
1	*n*-C_4H_9	**8g**	85
2	*t*-C_4H_9	**8h**	90
3		**8b**	65 (75)[d]
4		**8c**	73
5	$Cl(CH_2)_3$–	**8d**	72
6	Me_3Si–	**8i**	64
7	*n*-C_4H_9	**9g**	77
8	*t*-C_4H_9	**9h**	70
9		**9b**	40[d]
10		**9c**	75
11	$Cl(CH_2)_3$–	**9d**	71
12	Me_3Si–	**9i**	65

[a] The reaction of **7** (4 mmol) with (trimethylsilyl)ethynyl bromide (2.68 mmol) was carried out using CuI (0.4 mmol) and base (3 mmol) at –15 °C to r.t. for overnight.
[b] The reaction mixture containing **8** was treated with 1M NaOMe (8 mmol) at r.t. for overnight.
[c] Isolated yields based on (trimethylsilyl)ethynyl bromide employed.
[d] 2M NaOH (3 mmol) was used instead of 1M NaOH.

Under optimized conditions (0.1 equiv of CuI, 0.67 equiv of $Me_3SiC{\equiv}CBr$, 0.75 equiv of 1M NaOH, –15 °C to r.t.) good to high yields of (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne (**8**) could be obtained from the cross-coupling reaction between different types of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane (**7**) and (trimethylsilyl)ethynyl bromide. In addition, the cross-coupling−desilylation sequence afforded (*Z*)-3-(trimethylsilyl)alk-3-en-1-yne (**9**) in moderate to good yields. These results are summarized in Table 5. Both the cross-coupling and desilylation reactions were not only tolerant of functional groups including conjugated alkenyl and chloro (entries 4, 5, 10 and 11) but also applicable to bulky *tert*-butyl and trimethylsilyl group (entries 2, 6, 8 and 12). It is noteworthy that three trimethylsilyl groups of (*Z*)-1,2,4-tris(trimethylsilyl)but-1-en-3-yne (**8i**) are on respective unsaturated carbons in a conjugated system (entry 6). For the reaction of (*Z*)-2-phenyl-1-(trimethylsilyl)ethenyldicyclohexylborane (**7b**) the use of 2M NaOH gave a better yield of (*Z*)-4-phenyl-1,3-bis(trimethylsilyl)but-3-en-1-yne (**8b**) (entry 3).

In summary, we have developed a highly flexible protocol for the synthesis of terminal conjugated enynes using (trimethylsilyl)ethynyl bromide as an ethynyl unit. This protocol allows the stereoselective synthesis of (*E*)- and (*Z*)-alk-3-en-1-yne as well as (*E*)- and (*Z*)-1-(trimethylsilyl)alk-3-en-1-yne. Moreover, the synthesis of (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne and (*Z*)-3-(trimethylsilyl)alk-3-en-1-yne has successfully been achieved. Taking also into account mild reaction conditions, ready availability of the starting materials and simple experimental operations, this protocol provides a convenient route to several types of terminal conjugated enynes that are useful intermediates for organic synthesis. Studies on synthetic application of this protocol are ongoing in our laboratory.

NMR spectra were recorded on a JEOL JNM-A-500 spectrometer with TMS, $CHCl_3$ (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 spectrometer, and only the strongest/structurally most important absorption peaks are listed. Mass spectra determinations 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), a flame ionization detector, and a Shimadzu C-R8A digital integrator-recorder. TLC analyses were carried out using aluminum sheets pre-coated with silica gel 60 F_{254} or glass plates pre-coated aluminum oxide 60 F_{254} purchased from Merck. Purification of product was performed by flash chromatography using Merck silica gel (Silica gel 60, 40-63 μm) or column chromatography using Merck aluminium oxide (aluminium oxide 60 active basic, 70-230 μm). All reactions were carried out under an argon atmosphere. Alk-1-yne, oct-4-yne, 2-methylbut-2-ene, cyclohexene and DMF were used after distillation over CaH_2 under argon. THF was distilled from sodium benzophenone ketyl under argon before use. A solution of $LiBEt_3H$ in THF, 1-(trimethylsilyl)hex-1-ene, 1-phenyl-2-(trimethylsilyl)ethyne and bis(trimethylsilyl)ethyne were purchased from Aldrich. (Trimethylsilyl)ethynyl bromide,[19] 1-iodoalk-1-yne (from hex-1-yne and phenylethyne),[20] 1-bromoalk-1-yne (from cyclohex-1-enylethyne, 5-chloropent-1-yne and 3-benzyloxyprop-1-yne),[19,21] 1-(trimethylsilyl)alk-1-yne [from 3,3-dimethylbut-1-yne, (cyclohex-1-enyl)ethyne and 5-chloropent-1-yne][22] and a solution of BH_3 in THF[23] were prepared according to the literature procedures.

General Procedure for the Synthesis of (*E*) -Alk-3-en-1-yne (2)

To a solution of BH_3 (4 mmol) in THF (0.33 M solution) was added 2-methylbut-2-ene (0.56 g, 8 mmol) dropwise at – 15 ºC under argon, and the reaction mixture was stirred for 2 h at 0 ºC to form a solution of disiamylborane in THF. To this solution was added alkyne (4 mmol) dropwise at – 15 ºC and the mixture was stirred for 2 h at 0 ºC. The solution of alkenyldisiamylborane in THF, thus prepared, was cooled to – 15 ºC, and $Cu(acac)_2$ (0.052 g, 0.2 mmol) was added to the solution under an argon flow, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) and 1M-NaOMe (4 mL, 4 mmol). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. The reaction mixture was treated with aq 3M NaOH (4 mL) and H_2O_2 (30 wt% solution in H_2O) (2 mL) at 0 ºC and stirred for 1 h at the same temperature to decompose the residual organoboron compound. The resultant mixture was extracted with pentane, washed with brine, dried (Na_2SO_4), and concentrated under vacuo. Purification by flash chromatography on silica gel provided product **2**.

General Procedure for the Synthesis of (*E*)-1-(Trimethylsilyl)alk-3-en-1-yne (3)

To a solution of BH_3 (4 mmol) in THF (0.33 M solution) was added cyclohexene (0.66 g, 8 mmol) dropwise at 0 ºC under argon, and the reaction mixture was stirred for 2 h at this temperature to form a white suspension of dicyclohexylborane in THF. To this suspension was added alkyne (4 mmol) dropwise at 0 ºC and the mixture was stirred for 2 h at this temperature. The solution of alkenyldicyclohexylborane in THF, thus prepared, was cooled to – 15 ºC, and $Cu(acac)_2$ (0.052 g, 0.2 mmol) was added to the solution under an argon flow, followed by addition of (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) dropwise and $LiOH·H_2O$ (0.168 g, 4 mmol) under argon flow. The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. After the reaction mixture was neutralized with sat. NH_4Cl, the resultant mixture was treated with $NaBO_3·4H_2O$ (1.846 g, 12 mmol) and H_2O (4 mL) at r.t. with vigorous stirring for 2 h to decompose the residual organoboron compound. Work-up procedure was the same as described above. Purification by flash chromatography on silica gel provided product **3**.

General Procedure for the Synthesis of (*Z*)-Alk-3-en-1-yne (5)

To a solution of disiamylborane (4 mmol) in THF (12 mL) was added 1-haloalk-1-yne (4 mmol) dropwise at – 15 ºC under argon, and the reaction mixture was stirred for 2 h at 0 ºC to form a solution of (*Z*)-1-haloalk-1-enyldisiamylborane in THF. To this solution was added 1M $LiBEt_3H$ (4 mL, 4 mmol) in THF dropwise at – 25 ºC, and the mixture was allowed to warm gradually to r.t. over 1 h. Triethylborane, liberated from $LiBEt_3H$, was removed under reduced pressure, accompanied by the solvent. After addition of THF (12 mL) to the residue under argon, the resulting solution of (*Z*)-alk-1-enyldisiamylborane in THF was subjected to the cross-coupling as described in the general procedure for the synthesis of **2**.

General Procedure for the Synthesis of (*Z*)-1-(Trimethylsilyl)alk-3-en-1-yne (6)

To a suspension of dicyclohexylborane (4 mmol) in THF (12 mL) was added 1-haloalk-1-yne (4 mmol) dropwise at 0 ºC under argon, and the reaction mixture was stirred for 2 h at this temperature to form a solution of (*Z*)-1-haloalk-1-enyldicyclohexylborane in THF. To this solution was added 1M $LiBEt_3H$ (4 mL, 4 mmol) in THF dropwise at – 25 ºC, and the mixture was allowed to warm gradually to r.t. over 1 h. The solution of (*Z*)-alk-1-enyldicyclohexylborane in THF, thus prepared, was subjected to the cross-coupling as described in the general procedure for the synthesis of **3**. [For the synthesis of **6a**, DMF (16 mL) was added to the reaction mixture after treatment with $LiBEt_3H$.]

General Procedure for the Synthesis of (*Z*)-1,3-Bis(trimethylsilyl)alk-3-en-1-yne (8)

To a suspension of dicyclohexylborane (4 mmol) in THF (12 mL) was added 1-(trimethylsilyl)alk-1-yne (4 mmol) dropwise at 0 ºC under argon, and the reaction mixture was stirred for 2 h at this temperature to form a solution of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane in THF. The solution was cooled to – 15 ºC, and CuI (0.076 g, 0.4 mmol) was added under an argon flow, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) and 1M NaOH (3 mL, 3 mmol) or 2M NaOH (1.5 mL, 3mmol) (for **8b**). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. Work-up procedure was the same as that described in the general procedure for the synthesis of **2**, except for elimination of washing with brine. Purification by column chromatography on aluminum oxide (basic) provided product **8**.

General Procedure for the Synthesis of (*Z*)-3-(Trimethylsilyl)alk-3-en-1-yne (9)

The cross-coupling reaction of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane (4 mmol) in THF (12 mL) with (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) was carried out as described in the general procedure for the synthesis of **8**. To the reaction mixture containing (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne was added 1M NaOMe (8 mL, 8 mmol) dropwise at 0 ºC under argon, and the mixture was stirred at r.t. for overnight. The resulting mixture was treated as described in the general procedure for the synthesis of **8**.

(*E*)-Dec-3-en-1-yne (2a)

Eluent: pentane.

IR (neat): 3315, 3024, 2956, 2927, 2856, 2104, 1629, 1465, 1436, 954 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.28–1.44 (m, 8H), 2.12–2.18 (m, 2H), 2.76 (dd, *J* = 2.2, 0.4 Hz, 1H), 5.47 (ddt, *J* = 16.0, 2.2, 1.5 Hz, 1H), 6.22 (dtd, *J* = 16.0, 6.8, 0.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 28.5 (CH_2), 28.7 (CH_2), 31.6 (CH_2), 33.0 (CH_2), 75.4 (≡CH), 82.6 (≡C), 108.5 (=CH), 146.9 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{16}$ [M^+]: 136.1252; found: 136.1254.

(*E*)-1-Phenylbut-1-en-3-yne (2b)

Eluent: pentane.

IR (neat): 3292, 3058, 3031, 2923, 2852, 2098, 1490, 1448, 954, 748, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.04 (d, *J* = 2.4 Hz, 1H), 6.11 (dd, *J* = 16.2, 2.4 Hz, 1H), 7.04 (d, *J* = 16.2 Hz, 1H), 7.23–7.38 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 79.2 (≡CH), 82.9 (≡C), 107.1 (=CH), 126.3 (=CH × 2), 128.7 (=CH × 2), 128.9 (=CH), 135.9 (=C), 143.1 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_8$ [M^+]: 128.0626; found: 128.0623.

(*E*)-1-(Cyclohex-1-enyl)but-1-en-3-yne (2c)

Eluent: pentane.

IR (neat): 3305, 3031, 2931, 2860, 2829, 2098, 1625, 954 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55–1.70 (m, 4H), 2.14–2.18 (m, 2H), 2.58–2.62 (m, 2H), 2.92 (d, *J* = 2.2 Hz, 1H), 5.44 (ddd, *J* = 16.0, 2.2, 0.9 Hz, 1H), 5.85–5.87 (m, 1H), 6.67 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.2 (CH_2 × 2), 23.8 (CH_2), 26.1 (CH_2), 77.8 (≡CH), 83.7 (≡C), 102.9 (=CH), 133.1 (=CH), 135.3 (=C), 146.7 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{12}$ [M^+]: 132.0939; found: 132.0948.

(*E*)-7-Chlorohept-3-en-1-yne (2d)

Eluent: pentane–CH_2Cl_2 (9: 1).

IR (neat): 3296, 3026, 2958, 2848, 2104, 1629, 1444, 958, 731, 651 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.83–1.89 (m, 2H), 2.22–2.28 (m, 2H), 2.79 (dd, *J* = 2.2, 0.4 Hz, 1H), 3.53 (t, *J* = 6.4 Hz, 2H), 5.48–5.54 (m, 1H), 6.19 (dt, *J* = 16.0, 6.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 30.0 (CH_2), 31.3 (CH_2), 43.9 (CH_2), 76.2 (≡CH), 82.0 (≡C), 110.1 (=CH), 144.3 (=CH).

HRMS (EI): *m/z* calcd for $C_7H_9{}^{37}Cl$ [M^+]: 130.0364; found: 130.0347.

HRMS (EI): *m/z* calcd for $C_7H_9{}^{35}Cl$ [M^+]: 128.0393; found: 128.0376.

(*E*)-5-Benzyloxypent-3-en-1-yne (2e)

Eluent: pentane–CH_2Cl_2 (7: 3).

IR (neat): 3292, 3031, 2852, 1496, 1454, 1359, 1116, 1076, 1028, 954, 738, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.88 (dd, *J* = 2.2, 0.4 Hz, 1H), 4.06 (ddd, *J* = 5.0, 1.7, 0.4 Hz, 2H), 4.51 (s, 2H), 5.76 (dt, *J* = 16.0, 1.7 Hz, 1H), 6.30 (dt, *J* = 16.0 Hz, 5.0 Hz, 1H), 7.25–7.40 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 69.5 (CH_2), 72.4 (CH_2), 77.8 (≡CH), 81.6 (≡C), 110.4 (=CH), 127.7 (=CH × 3), 128.4 (=CH × 2), 138.0 (=C), 141.4 (=CH).

EI-MS: *m/z* (%) = 172 (1, [M^+]), 92 (14), 91 (100), 65 (13).

(*E*)-3-Propylhept-3-en-1-yne (2f)

Eluent: pentane.

IR (neat): 3313, 2960, 2931, 2871, 1458, 1379, 896 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H), 1.25 (br s, 1H), 1.40 (sext, *J* = 7.3 Hz, 2H), 1.54 (sext, *J* = 7.3 Hz, 2H), 2.08 (q, *J* = 7.3 Hz, 2H), 2.11 (t, *J* = 7.3 Hz, 2H), 5.96 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6 (CH_3), 13.8 (CH_3), 21.4 (CH_2), 22.4 (CH_2), 30.2 (CH_2), 32.4 (CH_2), 73.9 (≡CH), 86.1 (≡C), 122.0 (=C), 139.9 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{16}$ [M^+]: 136.1252; found: 136.1268.

(*E*)-1-(Trimethylsilyl)dec-3-en-1-yne (3a)

Eluent: pentane.

IR (neat): 2958, 2927, 2856, 2175, 2133, 1249, 1085, 952, 842, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.28–1.44 (m, 8H), 2.12–2.18 (m, 2H), 5.52 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 14.0 (CH_3), 22.5 (CH_2), 28.5 (CH_2), 28.7 (CH_2), 31.6 (CH_2), 33.0 (CH_2), 92.4 (≡C), 104.2 (≡C), 109.6 (=CH), 146.2 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{24}Si$ [M^+]: 208.1647; found: 208.1664.

(*E*)-1-Phenyl-4-(trimethylsilyl)but-1-en-3-yne (3b)

Eluent: pentane.

IR (neat): 3060, 3028, 2958, 2927, 2898, 2852, 2167, 2119, 1492, 1448, 1249, 1082, 1068, 952, 842, 746, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.28 (s, 9H), 6.22 (d, *J* = 16.2 Hz, 1H), 7.05 (d, *J* = 16.2 Hz, 1H), 7.23–7.38 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 96.8 (≡C), 104.4 (≡C), 108.1 (=CH), 126.3 (=CH × 2), 128.7 (=CH × 3), 136.2 (=C), 142.3 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{16}Si$ [M^+]: 200.1021; found: 200.1012.

(*E*)-1-(Cyclohex-1-enyl)-4-(trimethylsilyl)but-1-en-3-yne (3c)

Eluent: pentane.

IR (neat): 3028, 2956, 2933, 2860, 2165, 2121, 1625, 1448, 1247, 1089, 1072, 952, 842, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.18 (s, 9H), 1.55–1.70 (m, 4H), 2.15–2.20 (m, 2H), 2.58–2.62 (m, 2H), 5.49 (dd, *J* = 16.0, 0.6 Hz, 1H), 5.83–5.85 (m, 1H), 6.80 (d, *J* = 16.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 22.2 (CH_2 × 2), 23.8 (CH_2), 26.1 (CH_2), 95.2 (≡C), 103.9 (=CH), 105.3 (≡C), 132.9 (=CH), 135.5 (=C), 146.1 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{20}Si$ [M^+]: 204.1334; found: 204.1359.

(*E*)-7-Chloro-1-(trimethylsilyl)het-3-en-1-yne (3d)

Eluent: pentane–CH_2Cl_2 (9: 1).

IR (neat): 2958, 2900, 2177, 2135, 1444, 1249, 1085, 956, 844, 759, 655 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (s, 9H), 1.83–1.89 (m, 2H), 2.22–2.28 (m, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 5.57 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.13 (dt, *J* = 15.8, 6.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 30.0 (CH_2), 31.3 (CH_2), 43.9 (CH_2), 93.3 (≡C), 103.6 (≡C), 111.2 (=CH), 143.5 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{17}{}^{37}ClSi$ [M^+]: 202.0761; found: 202.0759.

HRMS (EI): *m/z* calcd for $C_{10}H_{17}{}^{35}ClSi$ [M^+]: 200.0788; found: 200.0811.

(*E*)-5-Benzyloxy-1-(trimethylsilyl)pent-3-en-1-yne (3e)

Eluent: pentane–CH_2Cl_2 (7: 3).

IR (neat): 3064, 3031, 2958, 2898, 2852, 2177, 2133, 1496, 1454, 1359, 1249, 1116, 1085, 954, 854, 759 698 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.24 (s, 9H), 4.11 (dd, *J* = 5.0, 1.5 Hz, 2H), 4.56 (s, 2H), 5.86 (dt, *J* = 16.0, 1.5 Hz, 1H), 6.30 (dt, *J* = 16.0 Hz, 5.2 Hz, 1H), 7.25–7.40 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (CH_3 × 3), 69.6 (CH_2), 72.2 (CH_2), 95.1 (≡C), 103.1 (≡C), 111.6 (=CH), 127.6 (=CH × 3), 128.3 (=CH × 2), 138.0 (=C), 140.6 (=CH).

EI-MS: *m/z* (%) = 229 (5, [M^+]–15), 158 (8), 109 (7), 92 (11), 91 (100), 83 (5), 77 (6), 75 (8), 73 (15), 65 (5).

(*E*)-3-Propyl-1-(trimethylsilyl)hept-3-en-1-yne (3f)

Eluent: pentane.

IR (neat): 2960, 2931, 2900, 2873, 2142, 1458, 1249, 840, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (s, 9H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H), 1.39 (sext, *J* = 7.3 Hz, 2H), 1.53 (sext, *J* = 7.3 Hz, 2H), 2.06 (q, *J* = 7.3 Hz, 2H), 2.09 (t, *J* = 7.3 Hz, 2H), 5.93 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.1 (CH_3 × 3), 13.7 (CH_3), 13.8 (CH_3), 21.4 (CH_2), 22.4 (CH_2), 30.3 (CH_2), 32.4 (CH_2), 90.4 (≡C), 107.8 (≡C), 123.1 (=C), 139.3 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{24}Si$ [M^+]: 208.1647; found: 208.1668.

(*Z*)-Dec-3-en-1-yne (5a)

Eluent: pentane.

IR (neat): 3313, 3024, 2956, 2927, 2856, 1465, 738 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.28–1.45 (m, 8H), 2.32–2.38 (m, 2H), 3.05 (d, *J* = 2.2, Hz, 1H), 5.45 (ddt, *J* = 11.0, 1.3, 0.9 Hz, 1H), 5.98 (dtd, *J* = 11.0, 7.3, 0.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.6 (CH_2), 28.7 (CH_2), 28.8 (CH_2), 30.2 (CH_2), 31.6 (CH_2), 80.6 (≡CH), 81.1 (≡CH), 108.0 (=CH), 146.2 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{16}$ [M^+]: 136.1252; found: 136.1253.

(*Z*)-1-Phenylbut-1-en-3-yne (5b)

Eluent: pentane.

IR (neat): 3290, 3084, 3062, 3024, 2958, 2931, 2088, 1492, 1446, 779, 690 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.33 (dd, *J* = 2.6, 0.9 Hz, 1H), 5.67 (dd, *J* = 12.1, 2.6 Hz, 1H), 6.70 (d, *J* = 12.1 Hz, 1H), 7.30–7.37 (m, 3H), 7.80–7.90 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 81.9 (≡C), 84.0 (≡CH), 106.3 (=CH), 128.2 (=CH × 2), 128.7 (=CH × 3), 136.1 (=C), 140.6 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_8$ [M^+]: 128.0626; found: 128.0617.

(*Z*)-1-(Cyclohex-1-enyl)but-1-en-3-yne (5c)

Eluent: pentane.

IR (neat): 3303, 3014, 2931, 2858, 2829, 2088, 1622, 1433, 848, 798 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.55–1.70 (m, 4H), 2.14–2.18 (m, 2H), 2.58–2.62 (m, 2H), 3.31 (d, *J* = 2.9

Hz, 1H), 5.28 (dd, *J* = 12.2, 2.4 Hz, 1H), 5.96–5.99 (m, 1H), 6.19 (d, *J* = 12.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.8 (CH_2), 22.4 (CH_2), 26.1 (CH_2), 26.8 (CH_2), 82.2 (≡CH), 82.8 (≡C), 102.3 (=CH), 133.7 (=CH), 136.9 (=C), 144.3 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{12}$ [M^+]: 132.0939; found: 132.0945.

(*Z*)-7-Chlorohept-3-en-1-yne (5d)

Eluent: pentane–CH_2Cl_2 (9: 1).

IR (neat): 3294, 3026, 2958, 2869, 2088, 1444, 731, 650 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.88–1.94 (m, 2H), 2.45–2.52 (m, 2H), 3.11 (d, *J* = 2.1 Hz, 1H), 3.55 (t, *J* = 6.7 Hz, 2H), 5.50–5.55 (m, 1H), 5.98 (dt, *J* = 11.0, 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.6 (CH_2), 31.6 (CH_2), 44.2 (CH_2), 80.0 (≡C), 82.0 (≡CH), 109.5 (=CH), 143.6 (=CH).

HRMS (EI): *m/z* calcd for $C_7H_9{}^{37}Cl$ [M^+]: 130.0364; found: 130.0353.

HRMS (EI): *m/z* calcd for $C_7H_9{}^{35}Cl$ [M^+]: 128.0393; found: 128.0382.

(*Z*)-5-Benzyloxypent-3-en-1-yne (5e)

Eluent: pentane–CH_2Cl_2 (7: 3).

IR (neat): 3288, 3031, 2858, 1496, 1454, 1336, 1099, 1076, 1028, 736, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.13 (dd, *J* = 2.2, 0.4 Hz, 1H), 4.32 (ddd, *J* = 6.3, 1.5, 0.4 Hz, 2H), 4.52 (s, 2H), 5.60–5.65 (m, 1H), 6.15 (dtd, *J* = 11.0, 6.4, 0.9 Hz, 1H), 7.20–7.32 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 67.9 (CH_2), 72.5 (CH_2), 79.3 (≡C), 83.1 (≡CH), 110.4 (=CH), 127.7 (=CH), 127.8 (=CH × 2), 128.3 (=CH × 2), 138.1 (=C), 141.6 (=CH).

EI-MS: *m/z* (%) = 172 (1, [M^+]), 129 (10), 92 (14), 91 (100), 65 (15).

(*Z*)-1-(Trimethylsilyl)dec-3-en-1-yne (6a)

Eluent: pentane.

IR (neat): 3020, 2958, 2927, 2856, 2148, 1249, 842, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.19 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.28–1.45 (m, 8H), 2.32–2.38 (m, 2H), 5.48 (dt, *J* = 11.0, 1.3 Hz, 1H), 5.94 (dt, *J* = 11.0, 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 14.0 (CH_3), 22.5 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 30.2 (CH_2), 31.5 (CH_2), 98.4 (≡C), 102.2 (≡CH), 109.1 (=CH), 145.5 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{24}Si$ [M^+]: 208.1647; found: 208.1671.

(*Z*)-5-Benzyloxy-1-(trimethylsilyl)pent-3-en-1-yne (6e)

Eluent: pentane–CH_2Cl_2 (7: 3).

IR (neat): 3031, 2958, 2852, 2150, 1496, 1454, 1336, 1249, 1090, 852, 759 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.23 (s, 9H), 4.36 (dd, *J* = 6.3, 1.5 Hz, 2H), 4.58 (s, 2H), 5.71 (dt, *J* = 11.0, 1.5 Hz, 1H), 6.15 (dt, *J* = 11.0, 6.3 Hz, 1H), 7.32–7.43 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (CH_3 × 3), 67.8 (CH_2), 72.3 (CH_2), 100.6 (≡C), 100.7 (≡C), 111.6 (=CH), 127.6 (=CH), 127.8 (=CH × 2), 128.3 (=CH × 2), 138.0 (=C), 140.5 (=CH).

EI-MS: *m/z* (%) = 244 (1, [M^+]), 92 (11), 91 (100), 73 (31).

(*Z*)-1,3-Bis(trimethylsilyl)oct-3-en-1-yne (8g)

Eluent: pentane.

IR (neat): 2956, 2923, 2856, 2119, 1579, 1456, 1247, 840, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.16 (s, 9H), 0.21 (s, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 1.30–1.47 (m, 4H), 2.16–2.23 (m, 2H), 6.70 (t, *J* = 7.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (CH_3 × 3), 0.2 (CH_3 × 3), 13.8 (CH_3), 22.3 (CH_2), 31.5 (CH_2), 32.2 (CH_2), 93.6 (≡C), 109.0 (≡C), 123.3 (=C), 155.8 (=CH).

HRMS (EI): *m/z* calcd for $C_{14}H_{28}Si_2$ [M^+]: 252.1730; found: 252.1687.

(*Z*)-5,5-Dimethyl-1,3-bis(trimethylsilyl)hex-3-en-1-yne (8h)

Eluent: pentane.

IR (neat): 2958, 2900, 2131, 2110, 1249, 840, 759 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.16 (s, 9H), 0.28 (s, 9H), 1.11 (s, 9H), 6.92 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.1 (CH_3 × 3), 1.9 (CH_3 × 3), 30.6 (CH_3 × 3), 35.0 (C), 92.5 (≡C), 111.3 (≡C), 120.8 (=C), 167.4 (=CH).

HRMS (EI): *m/z* calcd for $C_{14}H_{28}Si_2$ [M^+]: 252.1730; found: 252.1731.

(*Z*)-4-Phenyl-1,3-bis(trimethylsilyl)but-3-en-1-yne (8b)

Eluent: pentane.

IR (neat): 3058, 3026, 2958, 2898, 2854, 2117, 1249, 866, 839, 758, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.13 (s, 9H), 0.26 (s, 9H), 7.25–7.42 (m, 5H), 7.79 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 0.1 (CH_3 × 3), 96.8 (≡C), 109.2 (≡C), 127.9 (=C), 127.9 (=CH × 2), 128.3 (=CH × 2), 128.7 (=CH), 138.5 (=C), 152.3 (=CH).

HRMS (EI): *m/z* calcd for $C_{16}H_{24}Si_2$ [M^+]: 272.1417; found: 272.1396.

(*Z*)-4-(Cyclohex-1-enyl)-1,3-bis(trimethylsilyl)but-3-en-1-yne (8c)

Eluent: pentane.

IR (neat): 2956, 2935, 2896, 2858, 2833, 2117, 1247, 842, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (s, 9H), 0.18 (s, 9H), 1.53–1.65 (m, 4H), 1.93–2.10 (m, 4H), 5.60–5.64 (m, 1H), 7.00 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.1 (CH_3 × 3), 0.2 (CH_3 × 3), 21.8 (CH_2), 22.3 (CH_2), 25.3 (CH_2), 27.9 (CH_2), 95.2 (≡C), 109.6 (≡C), 123.0 (=C), 126.8 (=CH), 137.1 (=C), 155.5 (=CH).

HRMS (EI): *m/z* calcd for $C_{16}H_{28}Si_2$ [M^+]: 276.1730; found: 276.1733.

(*Z*)-7-Chloro-1,3-bis(trimethylsilyl)hept-3-en-1-yne (8d)

Eluent: pentane–CH_2Cl_2 (9: 1).

IR (neat): 2958, 2898, 2121, 1249, 848, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (s, 9H), 0.24 (s, 9H), 1.84–1.90 (m, 2H), 2.34–2.39 (m, 2H), 3.55 (t, *J* = 6.3 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.2 (CH_3 × 3), 0.1 (CH_3 × 3), 29.6 (CH_2), 32.0 (CH_2), 44.3 (CH_2), 94.6 (≡C), 108.4 (≡C), 125.1 (=C), 153.0 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{25}{}^{37}ClSi_2$ [M^+]: 274.1158; found: 274.1156.

HRMS (EI): *m/z* calcd for $C_{13}H_{25}{}^{35}ClSi_2$ [M^+]: 272.1183; found: 272.1183.

(*Z*)-1,2,4-Tris(trimethylsilyl)but-1-en-3-yne (8i)

Eluent: pentane.

IR (neat): 2956, 2900, 2104, 1249, 840, 758 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.15 (s, 9H), 0.17 (s, 9H), 0.23 (s, 9H), 7.12 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 0.1 (CH_3 × 3), 0.5 (CH_3 × 3), 96.5 (≡C), 110.7 (≡C), 143.4 (=C), 158.1 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{28}Si_3$ [M^+]: 268.1499; found: 268.1452.

(*Z*)-3-(Trimethylsilyl)oct-3-en-1-yne (9g)

Eluent: pentane.

IR (neat): 3315, 2958, 2929, 2873, 2860, 1249, 840, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.22 (s, 9H), 0.90 (t, *J* = 7.0 Hz, 3H), 1.30–1.47 (m, 4H), 2.16–2.23 (m, 2H), 2.91 (s, 1H), 6.74 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.2 (CH_3 × 3), 13.8 (CH_3), 22.3 (CH_2), 31.4 (CH_2), 32.2 (CH_2), 76.6 (≡CH), 87.2 (≡C), 122.1 (=C), 156.8 (=CH).

HRMS (EI): *m/z* calcd for $C_{11}H_{20}Si$ [M^+]:180.1334; found: 180.1335.

(*Z*)-5,5-Dimethyl-3-(trimethylsilyl)hex-3-en-1-yne (9h)

Eluent: pentane.

IR (neat): 3313, 2956, 2925, 2866, 1560, 1458, 1375, 1363, 1249, 842, 761 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 0.83 (s, 9H), 2.58 (s, 1H), 6.67 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 1.8 (CH_3 × 3), 30.6 (CH_3 × 3), 35.0 (C), 75.8 (≡CH), 89.5 (≡C), 119.6 (=C), 168.4 (=CH).

HRMS (EI): *m/z* calcd for $C_{11}H_{20}Si$ [M^+]: 180.1334; found: 180.1326.

(*Z*)-4-Phenyl-3-(trimethylsilyl)but-3-en-1-yne (9b)

Eluent: pentane.

IR (neat): 3307, 3057, 3026, 2956, 2896, 1249, 840, 752, 698 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.13 (s, 9H), 3.19 (s, 1H), 7.25–7.38 (m, 5H), 7.84 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.1 (CH_3 × 3), 79.3(≡CH), 87.5 (≡C), 125.9 (=C), 127.9 (=CH × 2), 127.9 (=CH), 128.3 (=CH × 2), 138.4 (=C), 153.4 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{16}Si$ [M^+]: 200.1021; found: 200.1029.

(*Z*)-1-(Cyclohex-1-enyl)-2-(trimethylsilyl)but-1-en-3-yne (9c)

Eluent: pentane.

IR (neat): 3313, 2925, 2856, 1247, 842, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.19 (s, 9H), 1.53–1.65 (m, 4H), 1.93–2.10 (m, 4H), 2.99 (s, 1H), 5.61–5.65 (m, 1H), 7.05 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.2 (CH_3 × 3), 21.8 (CH_2), 22.3 (CH_2), 25.3 (CH_2), 28.0 (CH_2), 77.9 (≡CH), 87.8 (≡C), 122.1 (=C), 126.9 (=CH), 137.1 (=C), 156.4 (=CH).

HRMS (EI): *m/z* calcd for $C_{13}H_{20}Si$ [M^+]: 204.1334; found: 204.1349.

(*Z*)-7-Chloro-3-(trimethylsilyl)hept-3-en-1-yne (9d)

Eluent: pentane–CH_2Cl_2 (9: 1).

IR (neat): 3305, 2956, 2898, 1583, 1249, 842, 759 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.24 (s, 9H), 1.84–1.90 (m, 2H), 2.35–2.40 (m, 2H), 2.96 (s, 1H), 3.55 (t, *J* = 6.3 Hz, 2H), 6.68 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.2 (CH_3 × 3), 29.6 (CH_2), 32.0 (CH_2), 44.2 (CH_2), 77.5(≡CH), 86.7(≡C), 124.0 (=C), 154.1 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{17}{}^{37}ClSi$ [M^+]: 202.0761; found: 202.0751.

HRMS (EI): *m/z* calcd for $C_{10}H_{17}{}^{35}ClSi$ [M^+]: 200.0788; found: 200.0787.

(*Z*)-1,2-Bis(trimethylsilyl)but-1-en-3-yne (9i)

Eluent: pentane.

IR (neat): 3313, 2956, 2902, 1249, 867, 837, 754 cm $^{-1}$.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.17 (s, 9H), 0.24 (s, 9H), 3.18 (s, 1H), 7.17 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.0 (CH_3 × 3), 0.5 (CH_3 × 3), 79.3 (≡CH), 89.1 (≡C), 142.4 (=C), 159.5 (=CH).

HRMS (EI): *m/z* calcd for $C_{10}H_{20}Si_2$ [M^+]: 196.1104; found: 196.1119.

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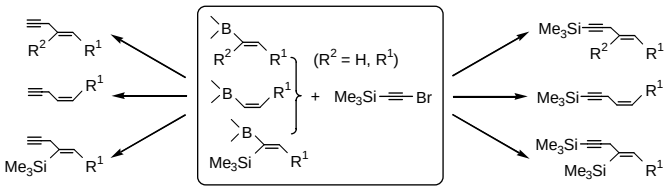

Construction of Terminal Conjugated Enynes.

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