Homo- and Heterocoupling of Terminal Conjugated Enynes: One-Pot Synthesis of Alka-1,7-diene-3,5-diynes and Alk-1-ene-3,5-diynes via Two Types of Coupling Reaction

Masayuki Hoshi,* Mitsuhiro Okimoto, Shingo Nakamura, Shinya Takahashi

Department of Biotechnology and Environmental Chemistry, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507, Japan
Fax +81(157)247719; E-mail: hoshi-m@chem.kitami-it.ac.jp
Received 1 August 2011; revised 4 September 2011

Abstract: Conjugated dienediynes and enediynes with definite geometry have been prepared in a one-pot manner. This protocol involves two types of coupling reaction, a Suzuki-type coupling and either a Hay coupling or a Cadiot–Chodkiewicz coupling. Thus, the copper-mediated cross-coupling reaction of (*E*)-alk-1-enyldisiamylborane with (trimethylsilyl)ethynyl bromide is carried out in the presence of 1 M NaOMe to generate (*E*)-alk-3-en-1-yne, which is subjected to either palladium/copper-catalyzed homocoupling in the presence of DABCO or copper-catalyzed heterocoupling with 1-iodoalk-1-yne in the presence of TBD or pyrrolidine in a single reaction pot without isolating (*E*)-alk-3-en-1-yne. The homocoupling has realized the stereoselective construction of (1*E*,7*E*)-alka-1,7-diene-3,5-diynes, and the heterocoupling has achieved the formation of (*E*)-alk-1-ene-3,5-diynes. In addition, starting from (*Z*)-alk-1-enyldisiamylborane instead of the *E*-isomer, this series of reactions has led to the formation of (1*Z*,7*Z*)-alka-1,7-diene-3,5-diynes and (*Z*)-alk-1-ene-3,5-diynes, albeit limiting the scope of the substrate.

Key words: alkenylborane, (trimethylsilyl)ethynyl bromide, alk-1-en-3-yne, Suzuki-type reaction, acetylenic coupling

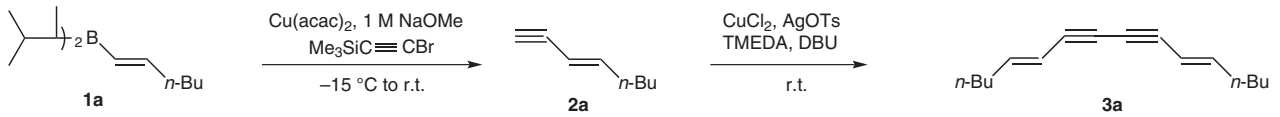
Conjugated diyne and polyyne units are found in natural products and materials science. A huge number of metal-catalyzed homo- and heterocoupling reactions have been reported for the formation of diynes,[1] and these reactions have been applied to the synthesis of natural products[2] and the construction of π-conjugated oligomers and polymers.[3] Hay coupling has particular importance from the viewpoint of copper-catalyzed oxidative homocoupling reaction of terminal alkyne.[4] A large number of methods for the synthesis of symmetrical diynes have been developed so far using terminal alkynes,[5] 1-haloalk-1-ynes,[6] and alk-1-ynyl metals.[7] On the other hand, Cadiot–Chodkiewicz coupling is a powerful copper-catalyzed heterocoupling protocol involving terminal alkyne and 1-haloalk-1-yne.[8] A number of variations have thus been developed, including palladium-catalyzed coupling reaction.[9] In parallel with the development, other methods have also been reported for preparing unsymmetrical diynes and polyynes.[10–12] Consequently, both of the homo- and heterocoupling reactions are among the most important strategies for the synthesis of π-extended compounds.

We have investigated the assembly of π-extended conjugation utilizing terminal conjugated enynes,[13] which can be generated by copper-mediated cross-coupling reaction of alk-1-enyldisiamylborane with (trimethylsilyl)ethynyl bromide.[14] As part of our research directed toward synthesizing π-extended compounds, we describe herein a one-pot synthesis of alka-1,7-diene-3,5-diynes and alk-1-ene-3,5-diynes employing homo- and heterocoupling of terminal conjugated enynes.

Oxidative homocoupling using O_2 as an oxidant is significant for the environmental concerns, and homocoupling under aerobic conditions makes it an easy and environmentally benign process. We first employed a palladium-free protocol where homocoupling could be performed in the presence of a catalytic system of AgOTs-$CuCl_2$-TMEDA at room temperature under O_2 atmosphere.[5d] (*E*)-Oct-3-en-1-yne (**2a**) was chosen as a test substrate for the homocoupling reaction. Thus, the cross-coupling reaction of (*E*)-hex-1-enyldisiamylborane (**1a**) (1 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was carried out in the presence of $Cu(acac)_2$ (0.05 mmol) and 1 M NaOMe (0.75 mmol) at –15 °C to room temperature overnight to generate compound **2a** (ca. 0.5 mmol).[15] Without isolation of **2a**, the homocoupling was conducted in the presence of $CuCl_2$ (0.05 mmol), AgOTs (0.05 mmol), TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) (0.05 mL), and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (0.25 mL) in THF at room temperature under air. After stirring overnight, the desired product, (5*E*,11*E*)-hexadeca-5,11-diene-7,9-diyne (**3a**), was formed in 52% yield estimated by GC analysis (Scheme 1). The reaction conditions including use of various Ag salts were examined; however, all attempts failed to improve the yield of **3a**. Accordingly, we next applied a palladium-catalyzed protocol to the homocoupling.

On the basis of the reaction conditions reported by Zhang et al.,[5b] homocoupling of in situ prepared compound **2a** (ca. 0.5 mmol) was examined using $PdCl_2(PPh_3)_2$ (0.01 mmol), CuI (0.01 mmol), and DABCO (1,4-diazabicyclo[2.2.2]octane) (0.6 mmol). It was found that the homocoupling reaction proceeded even under air[16] to give the desired product **3a**, after three hours at room temperature, in 76% yield estimated by GC analysis. We then checked

SYNTHESIS 2011, No. x, pp 0001–0009
Advanced online publication: xx.xx.2011
DOI: 10.1055/s-0031-xxxxx; Art ID: F75711SS

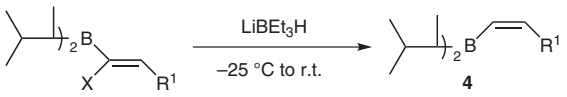


Scheme 1

the effect of combinations of $PdCl_2(PPh_3)_2$, CuI, and DABCO on the homocoupling of **2a** under air, and the results are shown in Table 1. The homocoupling in the absence of $PdCl_2(PPh_3)_2$ could hardly proceed (Table 1, entry 1), and the homocoupling in the absence of DABCO gave product **3a** in only low yield (entry 2). In contrast to the above two cases, CuI had little effect on the formation of **3a** (entry 3). This result can be attributed to using $Cu(acac)_2$ to generate compound **2a**. It should be noted that at least both $PdCl_2(PPh_3)_2$ and DABCO were required for the homocoupling of in situ prepared compound **2a**.

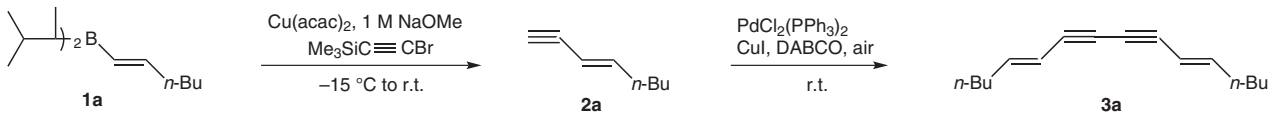
To optimize the reaction conditions, oxidative homocoupling of **2a** was carried out using various Pd catalysts and bases in the presence of CuI at room temperature under air, and the results are summarized in Table 2. Several Pd catalysts, such as $PdCl_2(PPh_3)_2$, $PdCl_2$, $Pd_2(dba)_3{\cdot}CHCl_3$, $PdCl_2$(dppf), and $Pd(OAc)_2$, were screened for this homocoupling reaction, and thus $PdCl_2(PPh_3)_2$ proved to be the best Pd catalyst (Table 2, entries 1–6). DBU is a non-nucleophilic and strong base in marked contrast to DABCO. Nevertheless, DBU was substantially effective for the homocoupling, albeit being inferior to DABCO (entry 7). Common tertiary amine bases, such as Et_3N and *i*-Pr_2NEt, were less effective and gave low yields even after prolonging to 24 hours (entries 8 and 9). These results confirmed that using $PdCl_2(PPh_3)_2$ as the catalyst and DABCO as the base in combination with CuI as the cocatalyst was the optimal catalyst/base combination.

The optimal conditions were applied to the homocoupling of a variety of (*E*)-alk-3-en-1-ynes **2**. As shown in Table 3, in situ prepared compounds **2** underwent smooth homocoupling to afford (1*E*,7*E*)-alka-1,7-diene-3,5-diynes **3** in moderate to high yields in a one-pot manner. (*E*)-(Cyclohex-1-enyl)but-3-en-1-yne (**2c**), bearing a conjugated C=C bond besides a conjugated enyne, gave higher yield compared with compound **2a**, which had no conjugation other than a conjugated enyne (Table 3, entry 1 vs. entry 3). (*E*)-4-Phenylbut-3-en-1-yne (**2b**), possessing a conjugated phenyl group, also afforded the corresponding product in high yield (entry 2). (*E*)-4-(4-Methylphenyl)but-3-en-1-yne (**2d**) and (*E*)-4-(4-trifluoromethylphenyl)but-3-en-1-yne (**2e**), having an electron-donating or an electron-withdrawing substituent on phenyl ring, did not influence the progress of the homocoupling, while both compounds **2d** and **2e** gave lower yields compared to compound **2b** (entries 4 and 5 vs. entry 2). It is noteworthy that the homocoupling of compound **2** bearing a phenyl ring, such as **2b**, **2d**, and **2e**, provides π-conjugated molecules. To synthesize conjugated dienediynes with the opposite geometry, (*Z*)-alk-3-en-1-ynes **5** were subjected to the homocoupling reaction under the same conditions as those used for compounds **2**. Compounds **5** were generated by copper-mediated cross-coupling reaction between (trimethylsilyl)ethynyl bromide and (*Z*)-alk-1-enyldisiamylboranes **4**, which were prepared by treatment of (*Z*)-1-haloalk-1-enyldisiamylboranes with $LiBEt_3H$ (Scheme 2).[17] The homocoupling reactions of (*Z*)-oct-3-en-1-yne (**5a**) and (*Z*)-4-phenylbut-3-en-1-yne (**5b**) gave the corresponding products, (1*Z*,7*Z*)-alka-1,7-diene-3,5-diynes **6**, in good yields (entries 6 and 7). Unfortunately, the homocoupling reactions of (*Z*)-(cyclohex-1-enyl)but-3-en-1-yne (**5c**) and (*Z*)-4-(4-methylphenyl)but-3-en-1-yne (**5d**) caused isomerization to form the corresponding (1*E*,7*E*)-alka-1,7-diene-3,5-diynes **3** (entries 8 and 9). The reason why the synthesis of **6** depends on substrate is unclear at present.



Scheme 2

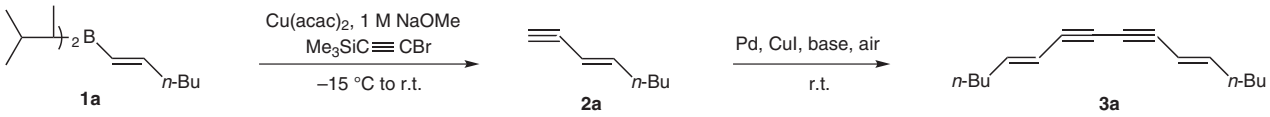
Table 1 Effect of Combinations of $PdCl_2(PPh_3)_2$, CuI, and DABCO on Oxidative Homocoupling of **2a** under Air[a]



Entry	Combination	Yield (%)[b] of **3a**
1	CuI/DABCO	3
2	$PdCl_2(PPh_3)_2$/CuI	15
3	$PdCl_2(PPh_3)_2$/DABCO	62
4	$PdCl_2(PPh_3)_2$/CuI/DABCO	76

[a] Reaction conditions: (1) **1a** (1.0 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), $Cu(acac)_2$ (0.05 mmol), 1 M NaOMe (0.75 mmol), –15 °C to r.t., overnight; (2) $PdCl_2(PPh_3)_2$ (0.01 mmol), CuI (0.01 mmol), DABCO (0.6 mmol), r.t., 3 h.
[b] Yields were estimated by GC on the basis of **2a** (0.5 mmol) formed.

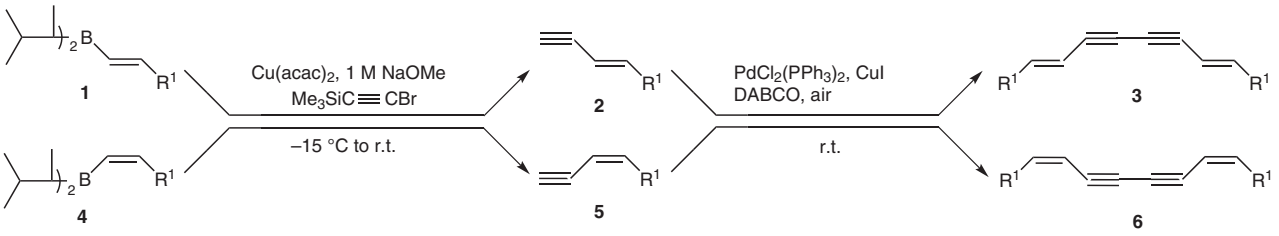
Table 2 Pd Catalyst and Base Screening for Oxidative Homocoupling of **2a**[a]



Entry	Pd catalyst	Base	Yield (%)[b] of **3a**
1	$PdCl_2(PPh_3)_2$	DABCO	76
2	$PdCl_2$	DABCO	70
3	$Pd_2(dba)_3{\cdot}CHCl_3$[c]	DABCO	26
4	$Pd_2(dba)_3{\cdot}CHCl_3/Ph_3P$[c,d]	DABCO	70
5	$PdCl_2$(dppf)	DABCO	23
6	$Pd(OAc)_2$	DABCO	13
7	$PdCl_2(PPh_3)_2$	DBU	62
8	$PdCl_2(PPh_3)_2$	Et_3N[e]	38
9	$PdCl_2(PPh_3)_2$	*i*-Pr_2NEt[e]	33

[a] Reaction conditions: (1) **1a** (1.0 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), $Cu(acac)_2$ (0.05 mmol), 1 M NaOMe (0.75 mmol), –15 °C to r.t., overnight; (2) Pd catalyst (0.01 mmol), CuI (0.01 mmol), base (0.6 mmol), r.t., 3 h, unless otherwise stated.
[b] Yields were estimated by GC on the basis of **2a** (0.5 mmol) formed.
[c] Reagent: $Pd_2(dba)_3{\cdot}CHCl_3$ (0.005 mmol).
[d] Reagent: Ph_3P (0.02 mmol).
[e] Reaction time: 24 h.

Table 3 Homocoupling Reaction of Terminal Conjugated Enyne Prepared in situ[a]



Entry	R^1	Product	Yield (%)[b]
1	*n*-Bu	**3a**	(76)[c]
2	Ph	**3b**	93
3	cyclohex-1-enyl	**3c**	89
4	4-MeC_6H_4	**3d**	63
5	4-$CF_3C_6H_4$	**3e**	60
6	*n*-Bu	**6a**	(74)[c]
7	Ph	**6b**	81
8	cyclohex-1-enyl	**6c**	–[d]
9	4-MeC_6H_4	**6d**	–[d]

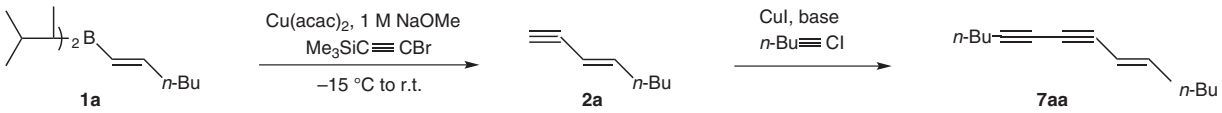
[a] Reaction conditions: (1) **1** or **4** (4.0 mmol), $Me_3SiC{\equiv}CBr$ (2.68 mmol), $Cu(acac)_2$ (0.2 mmol), 1 M NaOMe (3.0 mmol), –15 °C to r.t., overnight; (2) $PdCl_2(PPh_3)_2$ (0.04 mmol), CuI (0.04 mmol), DABCO (2.4 mmol), r.t., 3–4 h.
[b] Isolated yields on the basis of **2** or **5**[18] (2 mmol) formed.
[c] Yields were estimated by GC. Isolated yields by column chromatography could not be estimated due to a co-eluting impurity.
[d] No desired product could be isolated due to isomerization to the corresponding compound **3**.

The one-pot synthesis of conjugated enediynes via a Suzuki-type reaction/heterocoupling reaction sequence was investigated next. On the basis of the reaction conditions reported by Alami et al.,[9c] heterocoupling of in situ prepared (*E*)-oct-3-en-1-yne (**2a**) (ca. 0.5 mmol) with 1-iodohex-1-yne (0.5 mmol) was carried out in the presence of CuI (0.05 mmol) and base (1 mmol) under different conditions in order to optimize the reaction conditions, and the results are listed in Table 4. Some bases, such as pyrrolidine, piperidine, DBU, and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene), were screened, and thus TBD was found to be the best base at any reaction temperature employed. In particular, when conducted at –15 °C to room temperature, the desired product, (*E*)-tetradec-5-ene-7,9-diyne (**7aa**), was formed in 81% yield estimated by GC analysis. We further examined the effect of the amount of CuI on the yield of **7aa**. It was revealed that the yield was directly proportional to the amount of CuI. Increasing the amount of CuI from 10 to 20 mol% afforded an 88% yield, while decreasing it to 5 mol% gave a 76% yield estimated by GC analysis. Thus, it is appropriate to carry out the heterocoupling in the presence of 20 mol% of CuI (0.1 mmol) and two equivalents of TBD (1 mmol) at –15 °C to room temperature (Method A).

Heterocoupling reaction of different types of in situ prepared (*E*)-alk-3-en-1-ynes (**2**) with 1-iodohex-1-yne or 1-iodo-2-phenylethyne was conducted according to Method A, and the results are summarized in Table 5. (*E*)-Oct-3-en-1-yne (**2a**) and (*E*)-5,5-dimethylhex-3-en-1-yne (**2f**) underwent smooth heterocoupling to afford the corresponding (*E*)-alk-1-ene-3,5-diynes **7** in moderate to good yields (Table 5, entries 1, 2, 8, and 9). However, the heterocoupling reactions of (*E*)-4-phenylbut-3-en-1-yne (**2b**) and (*E*)-4-(cyclohex-1-enyl)but-3-en-1-yne (**2c**) with 1-iodohex-1-yne gave unsatisfactory results (entries 3 and 6), and the heterocoupling of **2b** with 1-iodo-2-phenylethyne resulted in failure (entry 5). Considering the mechanism proposed for the Cadiot–Chodkiewicz heterocoupling reaction, the formation of copper(I) acetylide is crucial to subsequent oxidative addition to 1-haloalk-1-yne to generate an intermediate copper(III) species.[8] Hence, solvent should play a critical role for the formation of copper(I) acetylide. This led us to examine the heterocoupling of **2b** with 1-iodohex-1-yne using aprotic polar solvent such as DMF and MeCN. It was found that use of DMF together with pyrrolidine as the base improved the yield of (*E*)-1-phenyldec-1-ene-3,5-diyne (**7ba**) considerably. Moreover, the reaction could be performed in the presence of only 5 mol% of CuI (entry 4, Method B). The heterocoupling of **2c** with 1-iodohex-1-yne by Method B also showed a substantial improvement in the yield of (*E*)-1-(cyclohex-1-enyl)dec-1-ene-3,5-diyne (**7ca**) (entry 7). However, no improvement to the formation of (*E*)-1,6-diphenylhex-1-ene-3,5-diyne (**7bb**) was observed under the same reaction conditions. Next we explored the heterocoupling reactions of (*Z*)-oct-3-en-1-yne (**5a**) and (*Z*)-4-phenylbut-3-en-1-yne (**5b**), selected as typical substrates, with 1-iodohex-1-yne or 1-iodo-2-phenylethyne. The heterocoupling of **5a** with 1-iodohex-1-yne based on Method A proceeded smoothly to furnish the desired product, (*Z*)-tetradec-5-ene-7,9-diyne (**8aa**), in moderate yield (entry 10); however, the other three heterocoupling reactions gave low or no products (entries 11, 13, and 16). Although Method B showed no improvement in the yield of (*Z*)-1-phenyldec-1-ene-3,5-diyne (**8ba**) (entry 14), by addition of 2 mol% of $PdCl_2(PPh_3)_2$ as a co-catalyst the yield of **8ba** was improved dramatically (entry 15).

In conclusion, we have developed a one-pot method for the syntheses of (1*E*,7*E*)- and (1*Z*,7*Z*)-alka-1,7-diene-3,5-diynes via a Suzuki-type cross-coupling reaction/homocoupling reaction sequence and of (*E*)- and (*Z*)-alk-1-ene-3,5-diynes via a Suzuki-type cross-coupling reaction/heterocoupling reaction sequence. The two one-pot multistep procedures developed herein have the advantage of using reduced number of workup and purification steps. The Suzuki-type cross-coupling reaction can be carried out under mild conditions to form terminal conjugated enynes with definite geometry. The homocoupling reaction of in situ prepared terminal conjugated enyne has been achieved in the presence of $PdCl_2(PPh_3)_2$-CuI-DABCO catalytic system at room temperature under aerobic

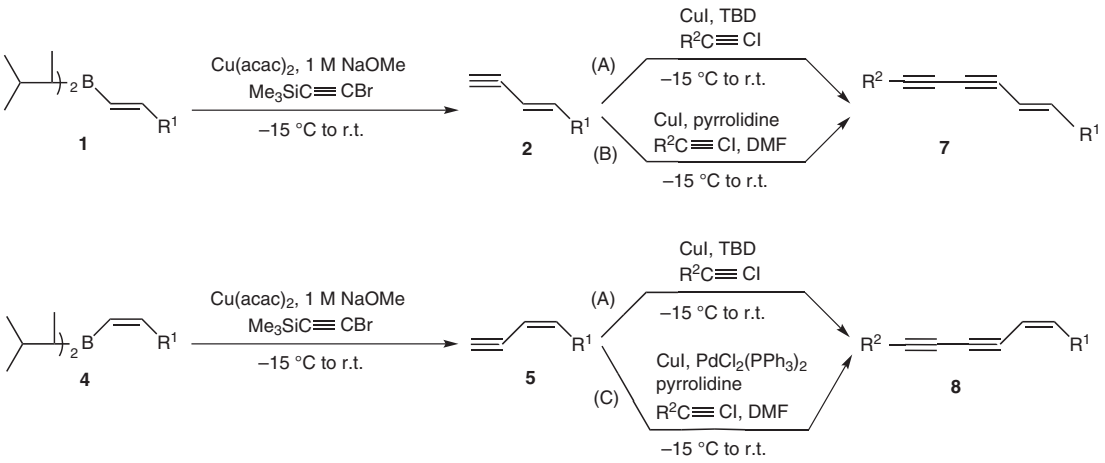
Table 4 Effect of Base and Reaction Temperature on Heterocoupling of **2a** with 1-Iodohex-1-yne[a]



Base	Yield (%)[b] of **7aa**		
	r.t.	0 °C to r.t.	15 °C to r.t.
pyrrolidine	31	59	60
piperidine	37	40	59
DBU	30	56	58
TBD	57	72	81

[a] Reaction conditions: (1) **1a** (1.0 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), $Cu(acac)_2$ (0.05 mmol), 1 M NaOMe (0.75 mmol), –15 °C to r.t., overnight; (2) CuI (0.05 mmol), base (1.0 mmol), *n*-BuC≡CI (0.5 mmol), overnight.
[b] Yields were estimated by GC based on the amount of *n*-BuC≡CI used.

Table 5 Heterocoupling Reaction of in situ Prepared Terminal Conjugated Enyne with 1-Iodoalk-1-yne[a]



Entry	R^1	R^2	Product	Yield (%)[b]
1	*n*-Bu	*n*-Bu	**7aa**	83
2	*n*-Bu	Ph	**7ab**	60
3	Ph	*n*-Bu	**7ba**	(35)
4				55[c]
5	Ph	Ph	**7bb**	–[d]
6	cyclohex-1-enyl	*n*-Bu	**7ca**	(28)
7				66[c]
8	*t*-Bu	*n*-Bu	**7fa**	78
9	*t*-Bu	Ph	**7fb**	77
10	*n*-Bu	*n*-Bu	**8aa**	62
11	*n*-Bu	Ph	**8ab**	26
12				(9)[e]
13	Ph	*n*-Bu	**8ba**	(6)
14				(4)
15				69[e]
16	Ph	Ph	**8bb**	0

[a] Reaction conditions: (1) **1** or **4** (4.0 mmol), $Me_3SiC{\equiv}CBr$ (2.68 mmol), $Cu(acac)_2$ (0.2 mmol), 1 M NaOMe (3.0 mmol), –15 °C to r.t., overnight; (2) Method A: CuI (0.4 mmol), TBD (4.0 mmol), $R^2C{\equiv}CI$ (2.0 mmol), –15 °C to r.t., overnight, unless otherwise stated.
[b] Isolated yields based on $R^2C{\equiv}CI$ employed. GC yields are shown in parentheses.
[c] Reaction conditions: (2) Method B: CuI (0.1 mmol), pyrrolidine (4.0 mmol), *n*-BuC≡CI (2.0 mmol), DMF (16 mL), –15 °C to r.t., overnight.
[d] No desired product could be isolated due to very low yield.
[e] Reaction conditions: (2) Method C: CuI (0.1 mmol), $PdCl_2(PPh_3)_2$ (0.04 mmol), pyrrolidine (4.0 mmol), $R^2C{\equiv}CI$ (2.0 mmol), DMF (16 mL), –15 °C to r.t., overnight.

conditions. In the heterocoupling reaction with 1-iodoalk-1-yne, two methods have been employed. For in situ prepared aliphatic terminal conjugated enynes the reaction has been realized in the presence of CuI and TBD at –15 °C to room temperature, while for in situ prepared terminal conjugated enynes having a phenyl group or an additional conjugated C=C bond the reaction has been accomplished in the presence of CuI [or CuI and $PdCl_2(PPh_3)_2$] and pyrrolidine in DMF at –15 °C to room temperature. The present study extends synthetic applications of terminal conjugated enynes as intermediates in a one-pot manner.

NMR spectra were recorded on a JEOL JNM-A-500 spectrometer with TMS 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 were performed on a JEOL JMS-SX102A spectrometer (EI, 70 eV) or JEOL JMS-T100GCV 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 aluminum sheets precoated with silica gel 60 F_{254} or glass plates pre-coated Al_2O_3 60 F_{254} purchased from Merck. Product purification was performed by flash chromatography using Merck silica gel (silica gel 60, 40–63 μm) or column chromatography using Merck

Al_2O_3 (Al_2O_3 60 active basic, 70–230 μm). All reactions except oxidative homocoupling reaction were carried out under an argon atmosphere. Unless otherwise noted, commercially available materials were used without any purification. Alk-1-yne, 2-methylbut-2-ene, and DMF were used after distillation over CaH_2 under argon. THF was distilled from Na-benzophenone ketyl under argon before use. A solution of $LiBEt_3H$ in THF was 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 and 4-ethynyltoluene),[19,21]and a solution of BH_3 in THF[22] were prepared according to the literature procedures.

(1*E*,7*E*)-Alka-1,7-diene-3,5-diynes 3; General Procedure
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 °C under argon, and the reaction mixture was stirred for 2 h at 0 °C to form a solution of disiamylborane in THF. To this solution was added alk-1-yne (4 mmol) dropwise at –15 °C and the mixture was stirred for 2 h at 0 °C. A solution of (*E*)-alk-1-enyldisiamylborane **1** in THF, thus prepared, was cooled to –15 °C, and $Cu(acac)_2$ (0.052 g, 0.2 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) and 1 M NaOMe in **????** (3 mL, 3 mmol). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. The mixture was then cooled to 0 °C, $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol), CuI (0.008 g, 0.04 mmol), and DABCO (0.269 g, 2.4 mmol) were added to the cooled mixture under air, and the resultant mixture was stirred at r.t. for 3–4 h. The reaction mixture was treated with aq 3 M NaOH (4 mL) and 30% H_2O_2 (2 mL) at 0 °C and stirred for 1 h at the same temperature to decompose the residual organoboron compound. The resulting mixture was extracted with Et_2O (**?** × **??** mL), the combined Et_2O extracts were washed with brine (**??** mL), dried (Na_2SO_4), and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to provide product **3**.

(5*E*,11*E*)-Hexadeca-5,11-diene-7,9-diyne (3a)
Eluent: pentane.

IR (neat): 3020, 2956, 2927, 2871, 2858, 1465, 1379, 1301, 952 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 6 H), 1.27–1.42 (m, 8 H), 2.10–2.16 (m, 4 H), 5.54 (d, *J* = 15.6 Hz, 2 H), 6.29 (dt, *J* = 15.6, 7.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (2 CH_3), 22.1 (2 CH_2), 30.6 (2 CH_2), 33.0 (2 CH_2), 72.5 (2 × ≡C), 79.8 (2 × ≡C), 108.6 (2 × =CH), 148.5 (2 × =CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{22}$: 214.1722; found: 214.1728.

(1*E*,7*E*)-1,8-Diphenylocta-1,7-diene-3,5-diyne (3b)
Eluent: pentane–CH_2Cl_2 (9:1); mp 119–121 °C.

IR (neat): 1446, 956, 746, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.26 (d, *J* = 15.6 Hz, 2 H), 7.10 (d, *J* = 15.6 Hz, 2 H), 7.28–7.37 (m, 6 H), 7.38–7.43 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 76.3 (2 × ≡C), 82.0 (2 × ≡C), 106.8 (2 × =CH), 126.4 (4 × CH_{arom}), 128.8 (4 × CH_{arom}), 129.2 (2 × CH_{arom}), 135.7 (2 × C_{arom}), 144.4 (2 × =CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{14}$: 254.1095; found: 254.1086.

(1*E*,7*E*)-1,8-Di(cyclohex-1-enyl)octa-1,7-diene-3,5-diyne (3c)
Eluent: pentane–CH_2Cl_2 (9:1); mp 102–104 °C.

IR (neat): 3020, 2947, 2929, 950 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.56–1.63 (m, 4 H), 1.64–1.70 (m, 4 H), 2.06–2.12 (m, 4 H), 2.14–2.20 (m, 4 H), 5.54 (d, *J* = 15.6 Hz, 2 H), 5.89 (m, 2 H), 6.70 (d, *J* = 15.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.1 (2 CH_2), 22.1 (2 CH_2), 23.7 (2 CH_2), 26.2 (2 CH_2), 75.3 (2 × ≡C), 82.2 (2 × ≡C), 102.8 (2 × =CH), 134.2 (2 × =$CH_{cyclohexenyl}$), 135.6 (2 × =$C_{cyclohexenyl}$), 147.8 (2 × =CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{20}H_{22}$: 262.1721; found: 262.1713.

(1*E*,7*E*)-1,8-Bis(4-methylphenyl)octa-1,7-diene-3,5-diyne (3d)
Eluent: pentane–CH_2Cl_2 (9:1); mp 163–165 °C.

IR (neat): 956, 798 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 6 H), 6.20 (d, *J* = 16.1 Hz, 2 H), 7.06 (d, *J* = 16.1 Hz, 2 H), 7.14 (d, *J* = 8.3 Hz, 4 H), 7.29 (d, *J* = 8.3 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.3 (2 CH_3), 76.1 (2 × ≡C), 82.1 (2 × ≡C), 105.7 (2 × =CH), 126.3 (4 × CH_{arom}), 129.5 (4 × CH_{arom}), 133.1 (2 × C_{arom}), 139.4 (2 × C_{arom}), 144.3 (2 × =CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{22}H_{18}$: 282.1408; found: 282.1397.

(1*E*,7*E*)-1,8-Bis[4-(trifluoromethyl)phenyl]octa-1,7-diene-3,5-diyne (3e)
Eluent: pentane–CH_2Cl_2 (9:1); mp 192–194 °C.

IR (neat): 1323, 1176, 1126, 1110, 1068, 1014, 943, 813 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.35 (d, *J* = 16.1 Hz, 2 H), 7.12 (d, *J* = 16.1 Hz, 2 H), 7.50 (d, *J* = 8.3 Hz, 4 H), 7.60 (d, *J* = 8.3 Hz, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 77.4 (2 × ≡C), 81.9 (2 × ≡C), 109.4 (2 × =CH), 123.9 (q, $J_{C,F}$ = 272 Hz, 2 CF_3), 125.8 (4 × CH_{arom}), 126.6 (4 × CH_{arom}), 128.7 (2 × C_{arom}), 130.8 (q, $J_{C,F}$ = 33 Hz, 2 × C_{arom}), 142.9 (2 × =CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{22}H_{12}F_6$: 390.0843; found: 390.0901.

(1*Z*,7*Z*)-Alka-1,7-diene-3,5-diynes 6; General Procedure
To a solution of disiamylborane (4 mmol) in THF (12 mL) was added 1-haloalk-1-yne (4 mmol) dropwise at –15 °C under argon, and the reaction mixture was stirred for 2 h at 0 °C to form a solution of (*Z*)-1-haloalk-1-enyldisiamylborane in THF. To this solution was added a THF solution of 1 M $LiBEt_3H$ (4 mL, 4 mmol) dropwise at –25 °C, and the mixture was allowed to warm gradually to r.t. over 1 h. Et_3B, liberated from $LiBEt_3H$, was removed under reduced pressure, accompanied by the solvent. After the addition of THF (12 mL) to the residue under argon, the resulting solution of (*Z*)-alk-1-enyldisiamylborane **4** was treated in the same manner as described in the general procedure for the synthesis of **3**.

(5*Z*,11*Z*)-Hexadeca-5,11-diene-7,9-diyne (6a)
Eluent: pentane.

IR (neat): 3020, 2956, 2929, 2871, 2858, 1465, 1436, 1388, 1379, 732 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 6 H), 1.30–1.44 (m, 8 H), 2.32–2.38 (m, 4 H), 5.54 (d, *J* = 10.2 Hz, 2 H), 6.06 (dt, *J* = 10.2, 7.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (2 CH_3), 22.2 (2 CH_2), 30.5 (2 CH_2), 33.9 (2 CH_2), 77.7 (2 × ≡C), 79.0 (2 × ≡C), 108.1 (2 × =CH), 148.1 (2 × =CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{22}$: 214.1722; found: 214.1710.

(1*Z*,7*Z*)-1,8-Diphenylocta-1,7-diene-3,5-diyne (6b)
Eluent: pentane–CH_2Cl_2 (9:1); mp 48–50 °C.

IR (neat): 3060, 3026, 1492, 1446, 950, 781, 688 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.83 (d, *J* = 11.7 Hz, 2 H), 6.79 (d, *J* = 11.7 Hz, 2 H), 7.28–7.44 (m, 6 H), 7.82–7.89 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 80.5 (2 × ≡C), 82.2 (2 × ≡C), 105.9 (2 × =CH), 128.4 (4 × CH_{arom}), 128.6 (4 × CH_{arom}), 129.2 (2 × CH_{arom}), 136.0 (2 × C_{arom}), 142.4 (2 × =CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{20}H_{14}$: 254.1095; found: 254.1080.

(*E*)-Alk-1-ene-3,5-diynes 7; General Procedure

The cross-coupling reaction of (*E*)-alk-1-enyldisiamylborane **1** (4 mmol) in THF (12 mL) with (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) was carried out in the same manner as described in the general procedure for the synthesis of **3**.

Method A: To the reaction mixture was added CuI (0.076 g, 0.4 mmol) and TBD (0.557 g, 4 mmol) at –15 °C under a flow of argon, followed by dropwise addition of 1-iodoalk-1-yne (2 mmol). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. The reaction mixture was treated by bubbling air through the solution with a tube pump for 2 h at r.t. to oxidize the residual organoborane compound. The resulting mixture was extracted with pentane (?? mL), the combined pentane layers were washed with H_2O (?? mL), dried (K_2CO_3), and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on Al_2O_3 (basic) to provide product **7**.

Method B: After removal of solvent under reduced pressure, DMF (16 mL) was added to the residue containing (*E*)-alk-3-en-1-yne **2** under argon. The mixture was then cooled to –15 °C, CuI (0.019 g, 0.1 mmol) was added to the cooled mixture under a flow of argon, followed by dropwise addition of pyrrolidine (0.284 g, 4 mmol) and 1-iodoalk-1-yne (2 mmol). The resulting mixture was allowed to warm gradually to r.t. and stirred overnight. The workup was the same as that described in Method A.

(*E*)-Tetradec-5-ene-7,9-diyne (7aa)

Eluent: pentane.

IR (neat): 3020, 2956, 2929, 2871, 2860, 1465, 1427, 1379, 1301, 954 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H), 1.27–1.47 (m, 6 H), 1.49–1.56 (m, 2 H), 2.09–2.14 (m, 2 H), 2.31 (t, *J* = 7.3 Hz, 2 H), 5.48 (d, *J* = 15.9 Hz, 1 H), 6.27 (dt, *J* = 15.9, 7.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 13.8 (CH_3), 19.2 (CH_2), 21.9 (CH_2), 22.1 (CH_2), 30.3 (CH_2), 30.6 (CH_2), 32.9 (CH_2), 65.2 (≡C), 72.8 (≡C), 74.0 (≡C), 83.6 (≡C), 108.6 (=CH), 148.2 (=CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_{20}$: 188.1565; found: 188.1568.

(*E*)-1-Phenyldec-5-ene-1,3-diyne (7ab)

Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 3020, 2956, 2927, 2871, 2858, 1620, 1595, 1488, 1465, 1456, 1442, 1026, 954, 754, 688 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3 H), 1.28–1.43 (m, 4 H), 2.13–2.18 (m, 2 H), 5.58 (dt, *J* = 15.9, 1.5 Hz, 1 H), 6.35 (dt, *J* = 15.9, 7.3 Hz, 1 H), 7.27–7.38 (m, 3 H), 7.45–7.51 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (CH_3), 22.1 (CH_2), 30.6 (CH_2), 33.0 (CH_2), 72.3 (≡C), 77.8 (≡C), 77.9 (≡C), 80.9 (≡C), 108.4 (=CH), 122.0 (C_{arom}), 128.4 (2 × CH_{arom}), 128.9 (CH_{arom}), 132.4 (2 × CH_{arom}), 149.1 (=CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{16}$: 208.1252; found: 208.1257.

(*E*)-1-Phenyldec-1-ene-3,5-diyne (7ba)

Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 3028, 2958, 2931, 2871, 2229, 1490, 1465, 1448, 1425, 1296, 950, 746, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3 H), 1.40–1.48 (m, 2 H), 1.51–1.58 (m, 2 H), 2.35 (t, *J* = 7.3 Hz, 2 H), 6.16 (d, *J* = 16.1 Hz, 1 H), 7.04 (d, *J* = 16.1 Hz, 1 H), 7.27–7.34 (m, 3 H), 7.35–7.39 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 19.3 (CH_2), 21.9 (CH_2), 30.2 (CH_2), 65.3 (≡C), 74.3 (≡C), 76.6 (≡C), 85.5 (≡C), 107.0 (=CH), 126.3 (2× CH_{arom}), 128.7 (2 × CH_{arom}), 129.0 (CH_{arom}), 135.8 (C_{arom}), 143.9 (=CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{16}$: 208.1252; found: 208.1244.

(*E*)-1-(Cyclohex-1-enyl)dec-1-ene-3,5-diyne (7ca)

Eluent: pentane.

IR (neat): 3028, 2956, 2931, 2860, 2827, 1622, 1589, 1456, 1434, 1350, 1330, 1292, 1238, 1136, 950, 790 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3 H), 1.38–1.47 (m, 2 H), 1.49–1.63 (m, 4 H), 1.64–1.70 (m, 2 H), 2.05–2.10 (m, 2 H), 2.14–2.19 (m, 2 H), 2.33 (t, *J* = 7.3 Hz, 2 H), 5.46 (d, *J* = 16.1 Hz, 1 H), 5.87 (br s, 1 H), 6.68 (d, *J* = 16.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 19.3 (CH_2), 21.9 (CH_2), 22.1 (CH_2), 22.2 (CH_2), 23.7 (CH_2), 26.1 (CH_2), 30.3 (CH_2), 65.4 (≡C), 75.2 (≡C), 75.2 (≡C), 84.6 (≡C), 102.8 (=CH), 133.8 (=$CH_{cyclohexenyl}$), 135.5 (=$C_{cyclohexenyl}$), 147.7 (=CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{20}$: 212.1565; found: 212.1564.

(*E*)-2,2-Dimethyldodec-3-ene-5,7-diyne (7fa)

Eluent: pentane.

IR (neat): 2958, 2927, 2864, 1463, 1363, 958 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3 H), 1.02 (s, 9 H), 1.38–1.46 (m, 2 H), 1.48–1.56 (m, 2 H), 2.31 (t, *J* = 7.3 Hz, 2 H), 5.40 (d, *J* = 16.1 Hz, 1 H), 6.30 (d, *J* = 16.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 19.2 (CH_2), 21.9 (CH_2), 28.8 (3 CH_3), 30.3 (CH_2), 34.2 (C), 65.2 (≡C), 73.1 (≡C), 74.2 (≡C), 83.4 (≡C), 104.1 (=CH), 158.1 (=CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_{20}$: 188.1565; found: 188.1555.

(*E*)-2,2-Dimethyl-7-phenyloct-3-ene-5,7-diyne (7fb)

Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 2960, 2902, 2864, 1616, 1488, 1475, 1463, 1440, 1363, 1278, 1263, 1024, 960, 916, 754, 688 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (s, 9 H), 5.51 (d, *J* = 16.1 Hz, 1 H), 6.39 (d, *J* = 16.1 Hz, 1 H), 7.28–7.34 (m, 3 H), 7.46–7.49 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = [illegible] (3 CH_3), 34.4 (C), 72.7 (≡C), 74.[illegible]C), 80.3 (≡[illegible]1.2 (≡C), [illegible] (=CH), 122.0 (C_{arom}), 128.3 (CH_{arom}), 128.9 (=CH), 132.4 (CH_{arom}), 159.0 (=CH).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{16}$: 208.1252; found: 208.1189.

(*Z*)-Alk-1-ene-3,5-diynes 8; General Procedure

The cross-coupling reaction of respective (*Z*)-alk-1-enyldisiamylborane **4** (4 mmol) in THF (12 mL) with (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) was carried out in the same manner as described in the general procedure for the synthesis of **3**. The resulting (*Z*)-alk-3-en-1-yne **5** was treated according to Method A in the general procedure for the synthesis of **7**.

Method C: Procedure was the same as that described in the Method B, except that $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol) was added after the addition of CuI.

(*Z*)-Tetradec-5-ene-7,9-diyne (8aa)
Eluent: pentane.

IR (neat): 2958, 2929, 2871, 2860, 1465, 731 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3 H), 0.92 (t, *J* = 7.[illegible], 3 H), 1.30–1.47 (m, 6 H), 1.50–1.57 (m, 2 H), 2.30–2.36 (m, 2 H), 5.46 (d, *J* = 10.7 Hz, 1 H), 6.03 (dt, *J* = 10.7, 7.3 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 13.9 (CH_3), 19.3 (CH_2), 21.9 (CH_2), 22.2 (CH_2), 30.3 (CH_2), 30.4 (CH_2), 30.9 (CH_2), 65.1 (≡C), 72.0 (≡C), 78.1 (≡C), 84.8 (≡C), 108.1 (=CH), 147.7 (=CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{20}$: 188.1565; found: 188.1559.

(*Z*)-1-Phenyldec-5-ene-1,3-diyne (8ab)
Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 3020, 2956, 2927, 2858, 1488, 1463, 1442, 1398, 1026, 914, 754, 732, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3 H), 1.32–1.45 (m, 4 H), 2.34–2.41 (m, 2 H), 5.56 (d, *J* = 10.7 Hz, 1 H), 6.09 (dt, *J* = 10.7, 7.3 Hz, 1 H), 7.27–7.37 (m, 3 H), 7.46–7.51 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = [illegible] (CH_3), 22.2 (CH_2), 30.6 ([illegible]), 30.9 (CH_2), 74.1 (≡C), 77.6 ([illegible]), 79.0 (≡C), 81.6 (≡C), [illegible] (=CH), 121.9 (C_{arom}), 128.3 (CH_{arom}), 129.0 (CH_{arom}), 132.3 (CH_{arom}), 148.6 (=CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{16}$: 208.1252; found: 208.1245.

(*Z*)-1-Phenyldec-1-ene-3,5-diyne (8ba)
Eluent: pentane–CH_2Cl_2 (9:1).

IR (neat): 2958, 2931, 2871, 2225, 1492, 1448, 781, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3 H), 1.39–1.48 (m, 2 H), 1.50–1.59 (m, 2 H), 2.37 (t, *J* = 7.3 Hz, 2 H), 5.71 (dd, *J* = 12.2, 1.0 Hz, 1 H), 6.70 (d, *J* = 12.2 Hz, 1 H), 7.34–7.49 (m, 3 H), 7.77–7.85 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5 (CH_3), 19.4 (CH_2), 21.9 (CH_2), 30.2 (CH_2), 6[illegible]C), 73.2 ([illegible]), 81.1 (≡C), 86.9 (≡C), 106.2 (=CH), 128.3 (CH_{arom}), 128.4 (CH_{arom}), 128.9 (CH_{arom}), 136.1 (C_{arom}), 141.6 (=CH).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{16}$: 208.1252; found: 208.1253.

References

(1) (a) Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem. Int. Ed.* **2000**, *39*, 2632; and references cited therein. (b) *Metal-Catalyzed Cross-Coupling Reactions*, Vol. 1; de Meijere, A.; Diederich, F., Eds.; Wiley-VCH: Weinheim, **2004**.

(2) Shi Shun, A. L. K.; Tykwinski, R. R. *Angew. Chem. Int. Ed.* **2006**, *45*, 1034; and references cited therein.

(3) (a) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791. (b) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (c) Gholami, M.; Tykwinski, R. R. *Chem. Rev.* **2006**, *106*, 4997.

(4) Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320.

(5) (a) Kabalka, G. W.; Wang, L.; Pagni, R. M. *Synlett* **2001**, 108. (b) Lei, A.; Srivastava, M.; Zhang, X. *J. Org. Chem.* **2002**, *67*, 1969. (c) Fairlamb, I. J. S.; Bäuerlein, P. S.; Marrison, L. R.; Dickinson, J. M. *Chem. Commun.* **2003**, 632. (d) Liao, Y.; Fathi, R.; Yang, Z. *Org. Lett.* **2003**, *5*, 909. (e) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Gayathri, K. U.; Prasad, A. R. *Tetrahedron Lett.* **2003**, *44*, 6493. (f) Batsanov, A. S.; Collings, J. C.; Fairlamb, I. J. S.; Holland, J. P.; Howard, J. A. K.; Lin, Z.; Marder, T. B.; Parsons, A. C.; Ward, R. M.; Zhu, J. *J. Org. Chem.* **2005**, *70*, 703. (g) Li, J.-H.; Liang, Y.; Zhang, X.-D. *Tetrahedron* **2005**, *61*, 1903. (h) Li, J.-H.; Liang, Y.; Xie, Y.-X. *J. Org. Chem.* **2005**, *70*, 4393. (i) Jiang, H.-F.; Tang, J.-Y.; Wang, A.-Z.; Deng, G.-H.; Yang, S.-R. *Synthesis* **2006**, 1155. (j) Shi, M.; Qian, H.-X. *Appl. Organomet. Chem.* **2006**, *20*, 771. (k) Zhu, B. C.; Jiang, X. Z. *Appl. Organomet. Chem.* **2007**, *21*, 345. (l) Yan, J.; Lin, F.; Yang, Z. *Synthesis* **2007**, 1301. (m) Yan, F.; Cui, X.; Li, Y.-N.; Zhang, J.; Ren, G.-R.; Wu, Y. *Tetrahedron* **2007**, *63*, 1963. (n) Kurita, T.; Abe, M.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Synlett* **2007**, 2521. (o) Yan, J.; Wu, J.; Jin, H. *J. Organomet. Chem.* **2007**, *692*, 3636. (p) Kamata, K.; Yamaguchi, S.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Angew. Chem. Int. Ed.* **2008**, *47*, 2407. (q) Li, D.; Yin, K.; Li, J.; Jia, X. *Tetrahedron Lett.* **2008**, *49*, 5918. (r) Chen, S.-N.; Wu, W.-Y.; Tsai, F.-Y. *Green Chem.* **2009**, *11*, 269. (s) Kuhn, P.; Alix, A.; Kumarraja, M.; Louis, B.; Pale, P.; Sommer, J. *Eur. J. Org. Chem.* **2009**, 423. (t) Hilt, G.; Hengst, C.; Arndt, M. *Synthesis* **2009**, 395. (u) Li, L.; Wang, J.; Zhang, G.; Liu, Q. *Tetrahedron Lett.* **2009**, *50*, 4033. (v) Oishi, T.; Katayama, T.; Yamaguchi, K.; Mizuno, N. *Chem. Eur. J.* **2009**, *15*, 7539. (w) Adimurthy, S.; Malakar, C. C.; Beifuss, U. *J. Org. Chem.* **2009**, *74*, 5648. (x) Chassaaing, S.; Alix, A.; Boningari, T.; Sani Souna Sido, K.; Keller, M.; Kuhn, P.; Louis, B.; Sommer, J.; Pale, P. *Synthesis* **2010**, 1557. (y) Balaraman, K.; Kesavan, V. *Synthesis* **2010**, 3461.

(6) (a) Damle, S. V.; Seomoon, D.; Lee, P. H. *J. Org. Chem.* **2003**, *68*, 7085. (b) Chen, Z.; Jiang, H.; Wang, A.; Yang, S. *J. Org. Chem.* **2010**, *75*, 6700.

(7) (a) Ikegashira, K.; Nishihara, Y.; Hirabayashi, K.; Mori, A.; Hiyama, T. *Chem. Commun.* **1997**, 1039. (b) Ishikawa, T.; Ogawa, A.; Hirao, T. *Organometallics* **1998**, *17*, 5713. (c) Nishihara, Y.; Ikegashira, K.; Hirabayashi, K.; Ando, J.; Mori, A.; Hiyama, T. *J. Org. Chem.* **2000**, *65*, 1780. (d) Bharathi, P.; Periasamy, M. *Organometallics* **2000**, *19*, 5511. (e) Shirakawa, E.; Nakao, Y.; Murota, Y.; Hiyama, T. *J. Organomet. Chem.* **2003**, *670*, 132. (f) Yoshida, H.; Yamaryo, Y.; Ohshita, J.; Kunai, A. *Chem. Commun.* **2003**, 1510. (g) Oh, C. H.; Reddy, V. R. *Tetrahedron Lett.* **2004**, *45*, 5221. (h) Nishihara, Y.; Okamoto, M.; Inoue, Y.; Miyazaki, M.; Miyasaka, M.; Takagi, K. *Tetrahedron Lett.* **2005**, *46*, 8661. (i) Krasovskiy, A.; Tishkov, A.; del Amo, V.; Mayr, H.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 5010. (j) Cahiez, G.; Moyeux, A.; Buendia, J.; Duplais, C. *J. Am. Chem. Soc.* **2007**, *129*, 13788. (k) Paixão, M. W.; Weber, M.; Braga, A. L.; de Azeredo, J. B.; Deobald, A. M.; Stefani, H. A. *Tetrahedron Lett.* **2008**, *49*, 2366. (l) Maji, M. S.; Pfeifer, T.; Studer, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 9547. (m) Singh, F. V.; Amaral, M. F. Z. J.; Stefani, H. A. *Tetrahedron Lett.* **2009**, *50*, 2636.

(8) Cadiot, P.; Chodkiewicz, W. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Dekker: New York, **1969**, 597.

(9) (a) Wityak, J.; Chan, J. B. *Synth. Commun.* **1991**, *21*, 977. (b) Cai, C.; Vasella, A. *Helv. Chim. Acta* **1995**, *78*, 2053. (c) Alami, M.; Ferri, F. *Tetrahedron Lett.* **1996**, *37*, 2763. (d) Barbu, E.; Tsibouklis, J. *Tetrahedron Lett.* **1996**, *37*, 5023. (e) Montierth, J. M.; DeMario, D. R.; Kurth, M. J.; Schore, N. E. *Tetrahedron* **1998**, *54*, 11741. (f) Marino, J. P.; Nguyen, H. N. *J. Org. Chem.* **2002**, *67*, 6841. (g) Jiang, H.-F.; Wang, A.-Z. *Synthesis* **2007**, 1649.

(10) (a) Nye, S. A.; Potts, K. T. *Synthesis* **1988**, 375. (b) Balova, I. A.; Morozkina, S. N.; Knight, D. W.; Vasilevsky, S. F. *Tetrahedron Lett.* **2003**, *44*, 107. (c) Fiandanese, V.; Bottalico, D.; Marchese, G.; Punzi, A. *Tetrahedron Lett.* **2003**, *44*, 9087. (d) Liang, Y.; Tao, L.-M.; Zhang, Y.-H.; Li, J.-H. *Synthesis* **2008**, 3988.

(11) (a) Kwon, J. H.; Lee, S. T.; Shim, S. C.; Hoshino, M. *J. Org. Chem.* **1994**, *59*, 1108. (b) Alami, M.; Crousse, B.;

Linstrumelle, G. *Tetrahedron Lett.* **1995**, *36*, 3687. (c) Negishi, E.; Hata, M.; Xu, C. *Org. Lett.* **2000**, *2*, 3687.

(12) (a) Ziegler, C. B. Jr.; Harris, S. M.; Baldwin, J. E. *J. Org. Chem.* **1987**, *52*, 443. (b) Nishihara, Y.; Ikegashira, K.; Mori, A.; Hiyama, T. *Tetrahedron Lett.* **1998**, *39*, 4075. (c) Shen, W.; Thomas, S. A. *Org. Lett.* **2000**, *2*, 2857. (d) Shin Shun, A. L. K.; Chernick, E. T.; Eisler, S.; Tykwinski, R. R. *J. Org. Chem.* **2003**, *68*, 1339. (e) Yin, W.; He, C.; Chen, M.; Zhang, H.; Lei, A. *Org. Lett.* **2009**, *11*, 709. (f) Coste, A.; Couty, F.; Evano, G. *Synthesis* **2010**, 1500.

(13) (a) Hoshi, M.; Nakayabu, H.; Shirakawa, K. *Synthesis* **2005**, 1991. (b) Hoshi, M.; Suzuki, S.; Saitoh, S.; Okimoto, M.; Shirakawa, K. *Tetrahedron Lett.* **2007**, *48*, 119. (c) Hoshi, M.; Iizawa, T.; Okimoto, M.; Shirakawa, K. *Synthesis* **2008**, 3591. (d) Hoshi, M.; Yamazaki, H.; Okimoto, M. *Synlett* **2010**, 2461.

(14) (a) Hoshi, M.; Shirakawa, K. *Synlett* **2002**, 1101. (b) Hoshi, M.; Kawamura, N.; Shirakawa, K. *Synthesis* **2006**, 1961.

(15) Compound **2a** was formed in about 75% GC yield based on $Me_3SiC{\equiv}CBr$ used; unpublished results.

(16) In the original procedure ethyl bromoacetate was used as the oxidant.

(17) Negishi, E.; Williams, R. M.; Lew, G.; Yoshida, T. *J. Organomet. Chem.* **1975**, *92*, C4.

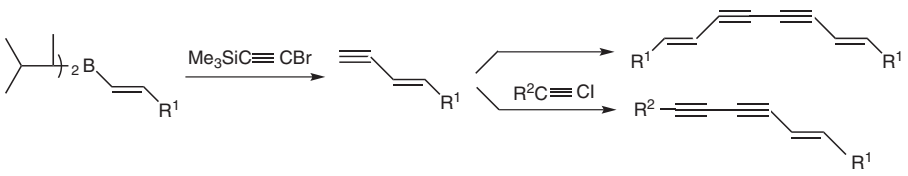
(18) Compounds **5a** and **5b** were formed in 72–75% GC yield based on $Me_3SiC{\equiv}CBr$ used; unpublished results.

(19) Hofmeister, H.; Annen, K.; Laurent, H.; Wiechert, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 727.

(20) Southwick, P. L.; Kirchiner, J. R. *J. Org. Chem.* **1962**, *27*, 3305.

(21) Schulte, K. E.; Goes, M. *Arch. Pharm. (Weinheim, Ger.)* **1959**, *290*, 118.

(22) (a) Zweifel, G.; Brown, H. C. *Org. React.* **1963**, *13*, 1. (b) Brown, H. C. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, **1975**.



graphical abstract