Stereoselective Syntheses of (*E*)- and (*Z*)-1-Arylalk-3-en-1-ynes and (*E*,*E*)-, (*Z*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-Alka-1,5-dien-3-ynes via a One-pot Multicomponent Coupling Reaction

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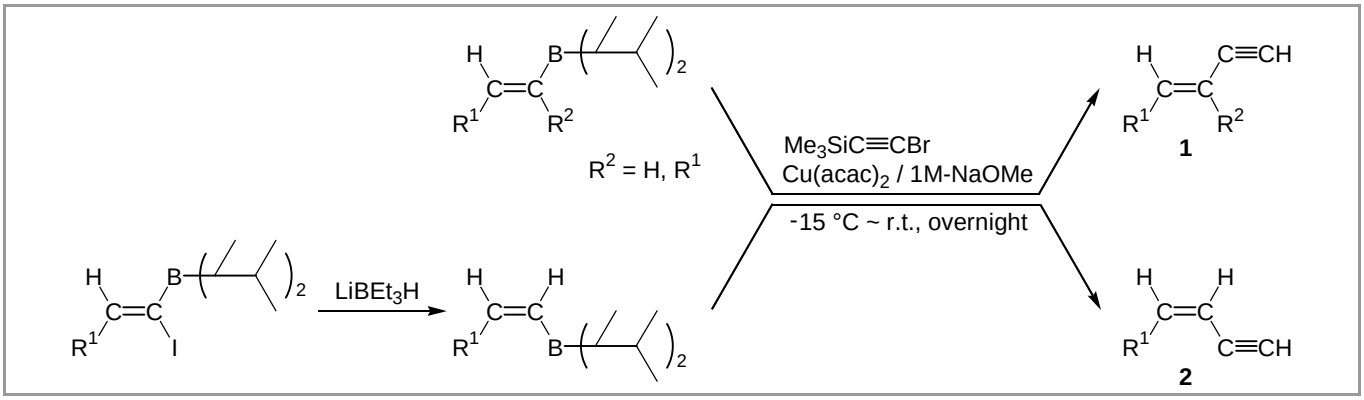
Abstract: Both 1-arylalk-3-en-1-yne and alka-1,5-dien-3-yne have been synthesized under extremely mild reaction conditions in good to high yields via a sequential Suzuki-type and Sonogashira reaction in a one-pot manner. Thus, the protocol involves Cu-mediated cross-coupling reaction of (*E*)- or (*Z*)-alkenyldisiamylborane with (trimethylsilyl)ethynyl bromide in the presence of 1M-NaOMe and Pd/Cu-catalyzed cross-coupling reaction with aryl or alkenyl iodide in the presence of aqueous *n*-Bu_4NOH. The reaction with aryl iodide is tolerant of a wide variety of functional groups on the aromatic ring and leads to the stereoselective formation of (*E*)- and (*Z*)-1-arylalk-3-en-1-ynes. In addition, the reactions with (*E*)- and (*Z*)-1-iodoalk-1-enes have accomplished the construction of all possible combinations of geometrical isomers, (*E*,*E*)-, (*Z*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)- alka-1,5-dien-3-ynes.

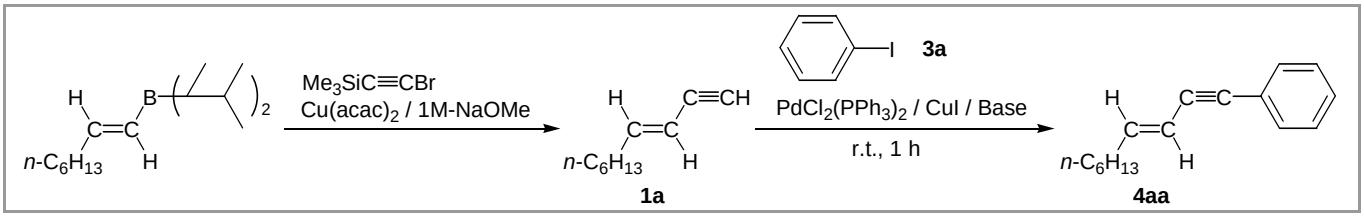
Key words: alkenylborane, (trimethylsilyl)ethynyl bromide, cross-coupling, 1-arylalk-3-en-1-yne, alka-1,5-dien-3-yne

Construction of conjugated compounds bearing alkynyl moieties is of great significance due to the fact that they are found in diverse areas ranging from natural products[1] and pharmaceuticals[2] to functional materials.[3] Among the conjugated systems, the system having sp^2 carbon atoms at both ends of ethynyl unit, unexpectedly, is found in bioactive natural products including phytotoxin[4] and mitotic inhibitor.[5] Furthermore, the conjugated dienyne system is employed for forming soluble polymers by anionic polymerization[6] and chrysene derivatives by tandem cyclizations.[7] For the formation of sp-sp^2 carbon bond, transition metal-catalyzed cross-coupling reaction is the key step.[8] Suzuki-Miyaura reaction[9] and Sonogashira-Hagihara reaction[10] are used complementarily in such construction. Thus, the former can perform the desired coupling upon reaction of alkenyl- or arylborane with alk-1-ynyl halide, and the latter can perform the same one upon reaction of alk-1-yne with alkenyl or aryl halide. In the former alkenyl group functions as nucleophile, while in the latter alkenyl and aryl groups function as electrophiles. If sp^2 carbon atom is introduced into each end of ethynyl unit in a different manner with each other, the protocol will provide an intriguing access to conjugated dienyne and arylenyne.

We have recently reported the stereoselective synthesis of (*E*)- and (*Z*)-alk-3-en-1-ynes (**1** and **2**) from (*E*)- and (*Z*)-alk-1-enyldisiamylboranes and (trimethylsilyl)ethynyl bromide through a Suzuki-type reaction (Scheme 1).[11] Thus, the cross-coupling reaction proceeds in the presence of a catalytic amount of $Cu(acac)_2$ and an excess amount of 1M-NaOMe at –15 ºC to room temperature to afford products **1** and **2**, desilylated during the reaction, respectively. The terminal conjugated enyne, where an alkenyl group has already been introduced into one end of ethynyl unit, has the feasibility of assembling π-extended conjugation taking advantage of Sonogashira reaction. We now report the stereoselective synthesis of conjugated enynes tethering aryl or alkenyl substituent to the alkynyl carbon, in which a sequential three-component cross-coupling reaction of (trimethylsilyl)ethynyl bromide as an ethynyl unit can be achieved under extremely mild conditions.[12]



Scheme 1



Scheme 2

Table 1 Effect of Base for Cross-coupling Reaction of **1a**[a] with **3a**[b]

Entry	Base	Yield of **4aa** (%)[c]
1	Et_3N	54
2	Pyrrolidine	86
3	*n*-Bu_4NF (1M solution in THF)	43
4	NH_4OH (1M solution in H_2O)	32
5	*n*-Bu_4NOH (40 wt% in H_2O)	90
6	*n*-Bu_4NOH (40 wt% in H_2O)	68[d]
7	*n*-Bu_4NOH (40 wt% in H_2O)	60[e]

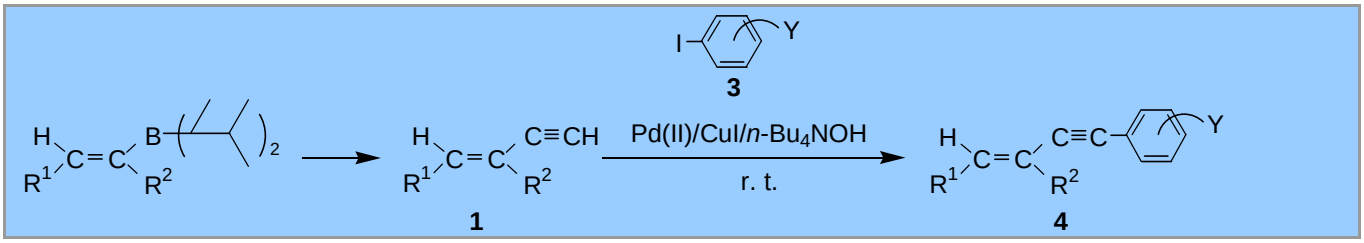
[a] The preparation of **1a** was conducted by the reaction of (*E*)-oct-1-enyldisiamylborane (1 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) in the presence of $Cu(acac)_2$ (0.05 mmol) and 1M-NaOMe (0.75 mmol) at –15 °C to room temperature for overnight. [b] Unless otherwise stated, the reaction with **3a** (0.5 mmol) was carried out using $PdCl_2(PPh_3)_2$ (0.01 mmol), CuI (0.02 mmol) and base (1.0 mmol) at room temperature for 1h. [c] The yields were estimated by GLC and based on **3a**. [d] *n*-Bu_4NOH (0.5 mmol) was used. [e] $PdCl_2(PPh_3)_2$ (0.005 mmol) and CuI (0.01 mmol) were used.

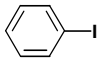
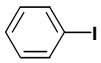
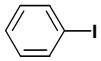
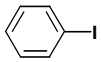
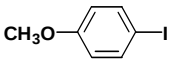
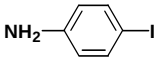
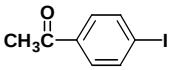
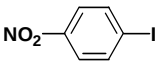
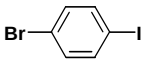
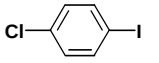
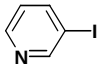
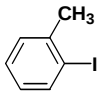
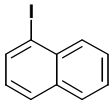
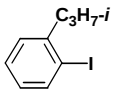
On the basis of our synthetic route to (*E*)- and (*Z*)-alk-3-en-1-ynes (**1** and **2**), we investigated the one-pot synthesis of 1-arylalk-3-en-1-yne by means of Sonogashira coupling with aryl halide. (*E*)-dec-3-en-1-yne (**1a**) and iodobenzene (**3a**) were chosen as model substrates for that coupling. The choice of iodide was to make feasible the room temperature cross-coupling reaction. Thus, the reaction of (*E*)-oct-1-enyldisiamylborane with (trimethylsilyl)ethynyl bromide was conducted in the same manner as previously reported,[11] except for the amount of 1M-NaOMe,[13] to generate **1a**, which was subjected to the reaction with **3a** (1 equiv) under $PdCl_2(PPh_3)_2$/CuI catalyst conditions, a typical combination of catalysts for the Sonogashira reaction (Scheme 2). We initially examined the effect of base, one of important experimental variables. The cross-coupling reaction was carried out in the presence of $PdCl_2(PPh_3)_2$ (0.02 equiv), CuI (0.04 equiv) and base (2 equiv) at room temperature for 1 h under argon to afford the corresponding conjugated arylenyne, (*E*)-1-phenyldec-3-en-1-yne (**4aa**), with retention of configuration at the double bond. Some bases were employed, and the results are shown in Table 1. Use of Et_3N, an amine base for the Sonogashira reaction, gave a 54 % yield of **4aa** along with a significant amount of unreacted **3a** (entry 1). Using pyrrolidine instead of Et_3N, the yield of **4aa** was increased to 86 %; however, undefined by-products were observed in the reaction mixture (entry 2). Mori and co-workers reported that quaternary ammonium compounds such as *n*-Bu_4NF, *n*-Bu_4NOH and NH_4OH promoted the Sonogashira reaction in the absence of amine base.[14] Although the reactions using *n*-Bu_4NF and NH_4OH led to the formation of **4aa**, whose yields were far inferior to those of amine bases under the stated conditions (entries 3 and 4). When *n*-Bu_4NOH was used, the reaction was completed within 1 h to afford **4aa** in 90 % yield with good purity compared with pyrrolidine (entry 5). It is noteworthy that the synthesis of **4aa** was achieved in high yield without isolation of **1a**. The reduced amount of either *n*-Bu_4NOH or $PdCl_2(PPh_3)_2$/CuI catalyst gave rise to retardation of the reaction (entries 6 and 7).

With our optimized reaction conditions in hand (Table 1, entry 5), we then carried out the coupling reaction of different types of **1** with a wide range of **3**. Table 2 shows that this method is applicable to a diversity of substrates and compatible with a variety of functional groups. This coupling reaction was successfully applied to **1** bearing alkyl substituent(s) as well as unsaturated one, affording the corresponding phenylated enynes (**4ba-ea**) in good to excellent yields with high stereoselectivity (= 99 %) (entries 2-5). Although a plenty of methods have been developed for preparing conjugated enynes, the transition metal-catalyzed dimerization of terminal alkynes is a practical and straightforward method for the synthesis of them. There are many reports on the preparation of conjugated enynes with the same two aryl groups[15] or a phenyl group[16] using the dimerization reaction. It should be noted that the present reaction regio- and stereoselectively furnishes products **4aa**, **4ba** and **4da** (entries 1, 2, and 4) as if a stereospecific head-to-head cross-dimerization were realized. The other methods, including cross-coupling reaction, were also reported for the synthesis of conjugated enynes with phenyl group(s).[17] We continued to examine the cross-coupling reaction of (*E*)-oct-3-en-1-yne (**1f**), bearing an alkyl substituent, with a range of aryl iodides at room temperature. The reactions with electron-donating aryl iodides proceeded without any trouble in good yields (entries 6 and 7). Electron-deficient aryl iodides also coupled with **1f** in good to high yields (entries 8-11). A free aniline, a ketone, and a nitro group all proved to be compatible with our reaction conditions. It is well-known that the relative reactivity of aryl halide is Ar-I >> Ar-Br > Ar-Cl. Indeed, the reactions with 1-bromo-4-iodobenzene (**3g**) and 1-chloro-4-iodobenzene (**3h**) afforded (*E*)-1-(4-bromophenyl)oct-3-en-1-yne (**4fg**) and (*E*)-1-(4-chlorophenyl)oct-3-en-1-yne (**4fh**), respectively, suitable for further functionalization (entries 10 and 11). Heteroaromatic compounds such as 2-iodothiophene (**3i**) and 3-iodopyridine (**3j**) reacted with **1f** as well to give the corresponding products **4fi** and **4fj** in good yields, respectively (entries 12 and 13). In contrast, sterically demanding 2-iodotoluene (**3k**) and 1-iodonaphthalene (**3l**) coupled with **1f** in rather moderate yields (entries 14 and 16), and more sterically hindered 2-iodocumene (**3m**) gave only 7 % yield of product **4fm** under the same

reaction conditions (entry 18). It is interesting to note that the ligand on palladium center played a crucial role in the present reaction. Thus, changing the palladium catalyst from $PdCl_2(PPh_3)_2$ to $PdCl_2(dppf)\cdot CH_2Cl_2$ improved the yield of product **4fk** significantly. Moreover, addition of $AsPh_3$ (0.02 equiv) was found to make the reaction clean[18] with being the same yield (entry 15) as the reaction in the absence of $AsPh_3$. The use of $PdCl_2(dppf)\cdot CH_2Cl_2$ together with $AsPh_3$ improved the yield of product **4fl** likewise (entry 17) and resulted in a dramatic increase of the yield of product **4fm** (entry 19). The effectiveness of $PdCl_2(dppf)\cdot CH_2Cl_2$ superior to that of $PdCl_2(PPh_3)_2$ would be attributable to its structure.[19]

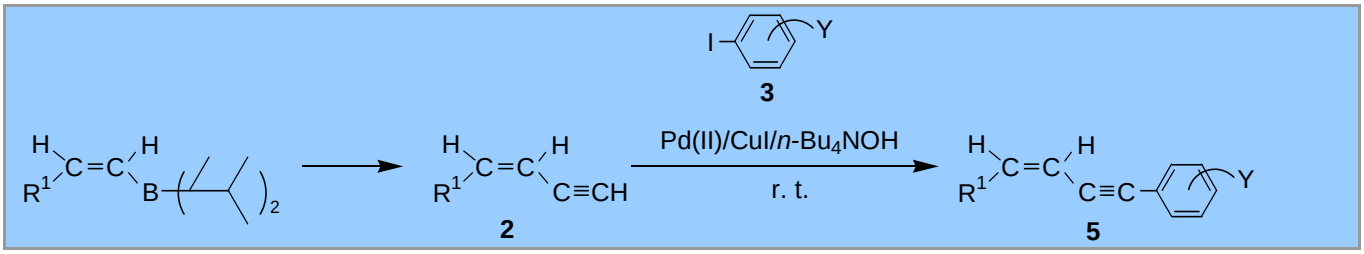
Table 2 Cross-coupling Reaction of (*E*)-Alk-3-en-1-yne with Aryl Iodide[a]

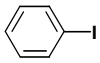
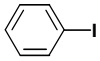
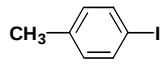
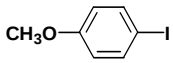
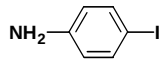
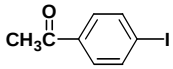
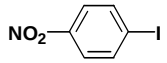
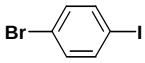
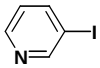
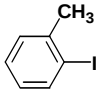
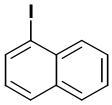
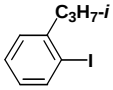


Entry	R^1	R^2	Aryl iodide (R^3)	Product	Yield (%)[b]
1	*n*-C_6H_{13}	H		**4aa**	83
2	*t*-C_4H_9	H		**4ba**	95
3		H		**4ca**	82
4		H		**4da**	75
5	*n*-C_3H_7	*n*-C_3H_7		**4ea**	77
6	*n*-C_4H_9	H		**4fc**	80
7	*n*-C_4H_9	H		**4fd**	67
8	*n*-C_4H_9	H		**4fe**	72
9	*n*-C_4H_9	H		**4ff**	77
10	*n*-C_4H_9	H		**4fg**	85
11	*n*-C_4H_9	H		**4fh**	82
12	*n*-C_4H_9	H		**4fi**	75
13	*n*-C_4H_9	H		**4fj**	82
14	*n*-C_4H_9	H		**4fk**	60
15					80[c]
16	*n*-C_4H_9	H		**4fl**	52
17					78[c]
18	*n*-C_4H_9	H		**4fm**	7
19					70[c]

[a] The reaction was carried out using $PdCl_2(PPh_3)_2$ (0.04 mmol), CuI (0.08 mmol), **3** (2.0 mmol), and *n*-Bu_4NOH (4.0 mmol) at room temperature for 1 to 4 h, unless otherwise noted. [b] Isolated yields based on **3**. [c] $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.04 mmol) and $AsPh_3$ (0.08 mmol) were used instead of $PdCl_2(PPh_3)_2$.

Table 3 Cross-coupling Reaction of (*Z*)-Alk-3-en-1-yne with Aryl Iodide[a]

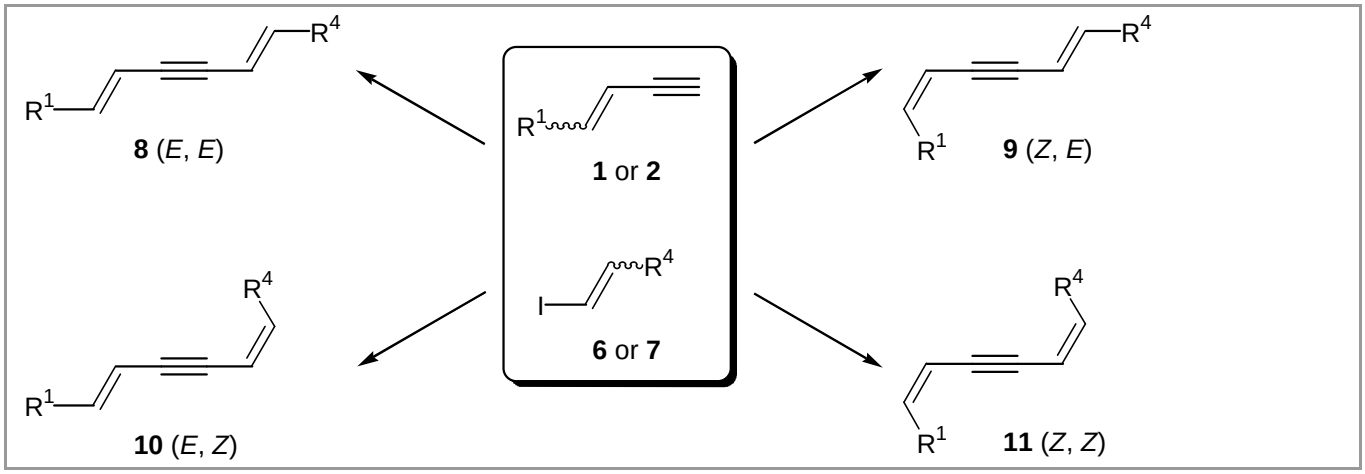


Entry	R^1	Aryl iodide (R^3)	Product	Yield (%)[b]
1	*n*-C_6H_{13}		**5aa**	85
2			**5ca**	52
3				72[c]
4	*n*-C_4H_9		**5fb**	85
5	*n*-C_4H_9		**5fc**	82
6	*n*-C_4H_9		**5fd**	91
7	*n*-C_4H_9		**5fe**	80
8	*n*-C_4H_9		**5ff**	82
9	*n*-C_4H_9		**5fg**	86
10	*n*-C_4H_9		**5fi**	75
11	*n*-C_4H_9		**5fj**	84
12	*n*-C_4H_9		**5fk**	86[c]
13	*n*-C_4H_9		**5fl**	89[c]
14	*n*-C_4H_9		**5fm**	58[c,d]

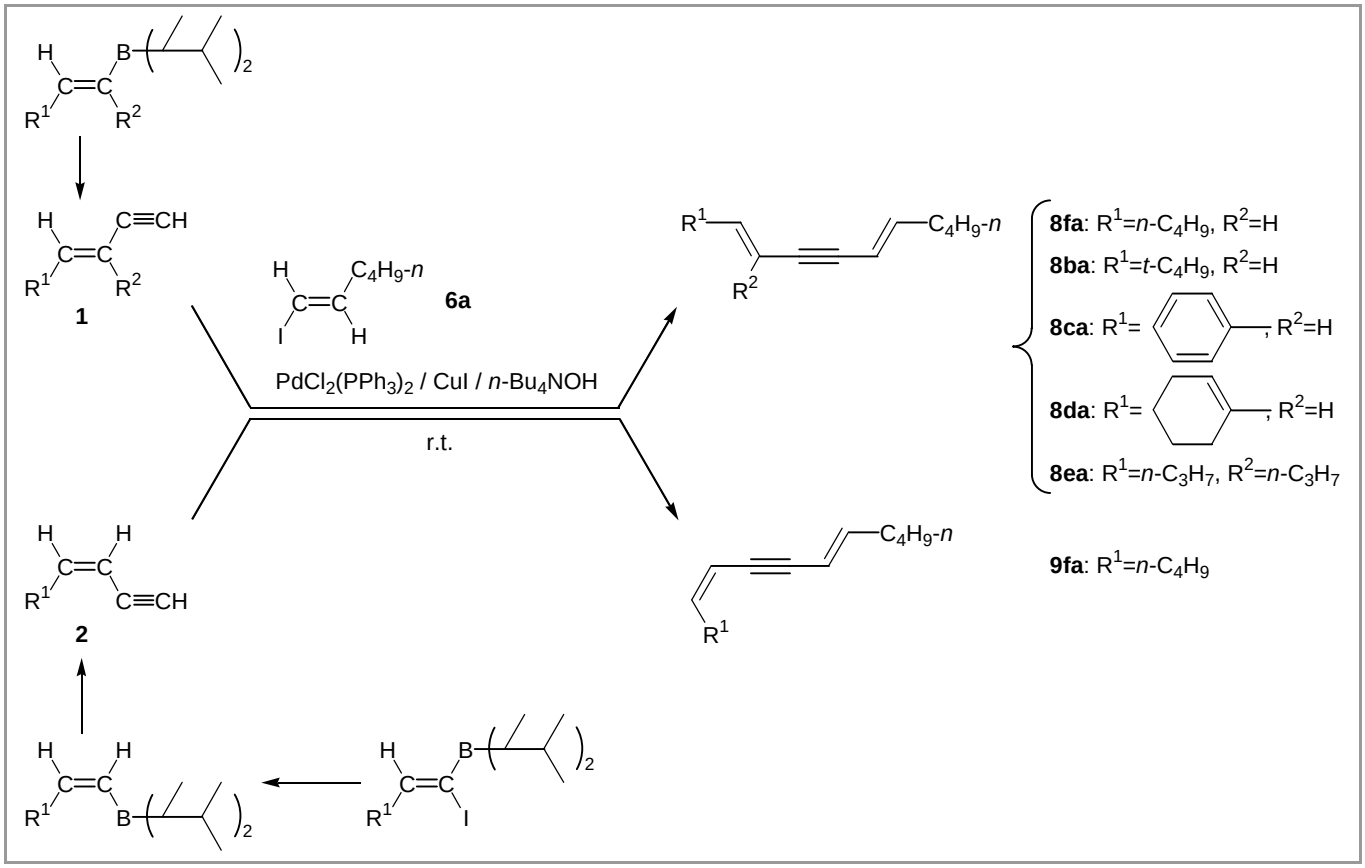
[a] The reaction was carried out using $PdCl_2(PPh_3)_2$ (0.04 mmol), CuI (0.08 mmol), **3** (2.0 mmol), and *n*-Bu_4NOH (4.0 mmol) at room temperature for 1 to 4 h, unless otherwise noted. [b] Isolated yields based on **3**. [c] $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.04 mmol) and $AsPh_3$ (0.08 mmol) were used instead of $PdCl_2(PPh_3)_2$. [d] The reaction time was prolonged to 8 h.

Next we examined the cross-coupling reaction of (*Z*)-alk-3-en-1-yne (**2**), which was generated by treatment of (*Z*)-1-iodoalk-1-enyldisiamylborane with $LiBEt_3H$[20] followed by cross-coupling reaction with (trimethylsilyl)ethynyl bromide as illustrated in Scheme 1, with aryl iodide (**3**) and the results are summarized in Table 3. The reaction of (*Z*)-dec-3-en-1-yne (**2a**) with iodobenzene (**3a**) was carried out under the same conditions as described for the reaction of (*E*)-dec-3-en-1-yne (**1a**). It was found that the cross-coupling reaction proceeded to completion in 1 h and afforded the desired product, (*Z*)-1-phenyldec-3-en-1-yne (**5aa**), in 85 % yield with high stereoselectivity (= 98 %) (entry 1). The identical conditions were applied to the reaction of (*Z*)-1-phenylbut-1-en-3-yne (**2c**) with **3a**, giving a moderate yield of product **5ca** (entry 2); however, switching the palladium catalyst from $PdCl_2(PPh_3)_2$ to $PdCl_2(dppf)\cdot CH_2Cl_2$ and adding $AsPh_3$ resulted in a significant increase of the yield (entry 3). In this case, why the reaction using $PdCl_2(dppf)\cdot CH_2Cl_2$ together with $AsPh_3$ gave a better yield than $PdCl_2(PPh_3)_2$ remains unclear at present. We also explored the *n*-Bu_4NOH-promoted reaction of a

variety of functionalized aryl iodides (**3**). Electron-donating, electron-deficient, and heteroaromatic aryl iodides could undergo the cross-coupling reaction with (*Z*)-oct-3-en-1-yne (**2f**) under $PdCl_2(PPh_3)_2$/CuI catalyst conditions, leading to the formation of (*Z*)-1-aryloct-3-en-1-ynes, products **5fb-fj**, in good to high yields (entries 4-11). On the other hand, the cross-coupling reaction of sterically demanding aryl iodides with **2f** could be performed under $PdCl_2(dppf)\cdot CH_2Cl_2/AsPh_3$/CuI catalyst conditions, affording the corresponding products **5fk-fm** in moderate to high yields (entries 12-14). Therefore, the present reaction provides not only (*E*)- but also (*Z*)-1-arylalk-3-en-1-yne that is the same product as if a stereoselective head-to-head cross-dimerization of terminal alkynes were realized.



Scheme 3

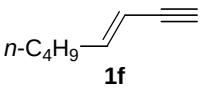
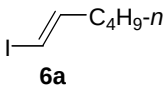
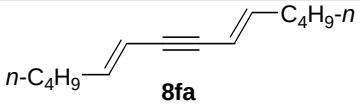
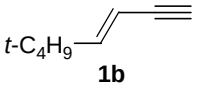
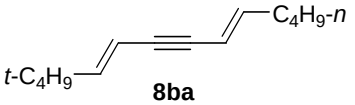
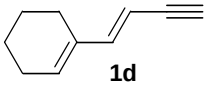
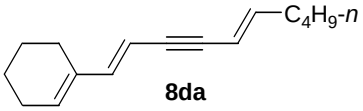
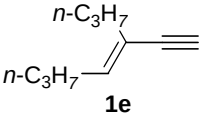
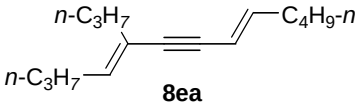
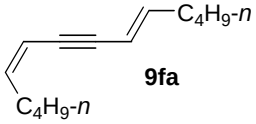
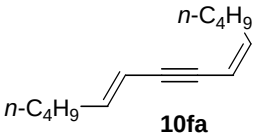
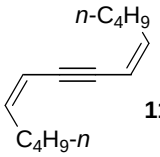
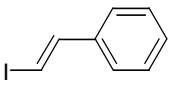
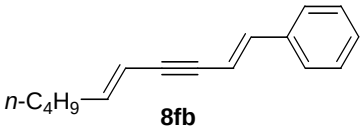
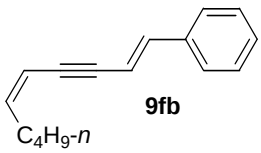
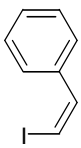
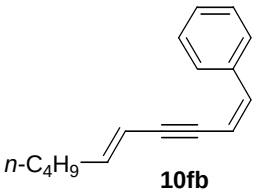


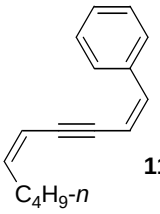
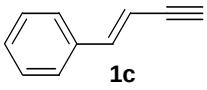
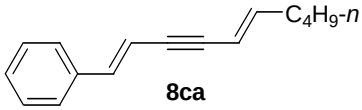
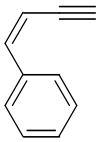
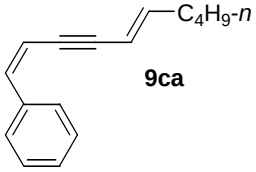
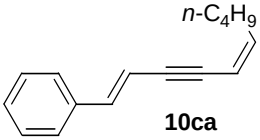
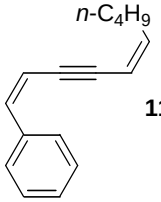
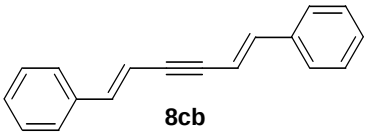
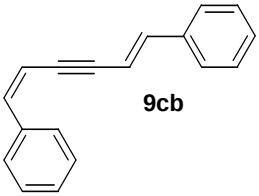
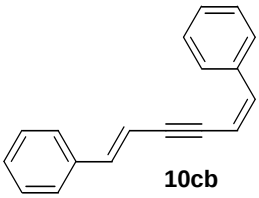
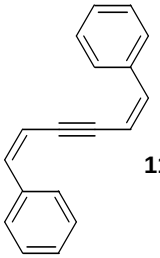
Scheme 4

Our attention then turned to the cross-coupling reaction of (*E*)- and (*Z*)-alk-3-en-1-ynes (**1** and **2**) with alkenyl iodide for the stereoselective synthesis of alka-1,5-dien-3-ynes. We applied the optimized conditions for the synthesis of 1-arylalk-3-en-1-ynes to the cross-coupling reactions with (*E*)- and (*Z*)-1-iodoalk-1-enes (**6** and **7**). It was found that most of the reactions proceeded smoothly to furnish the desired cross-coupling products (Scheme

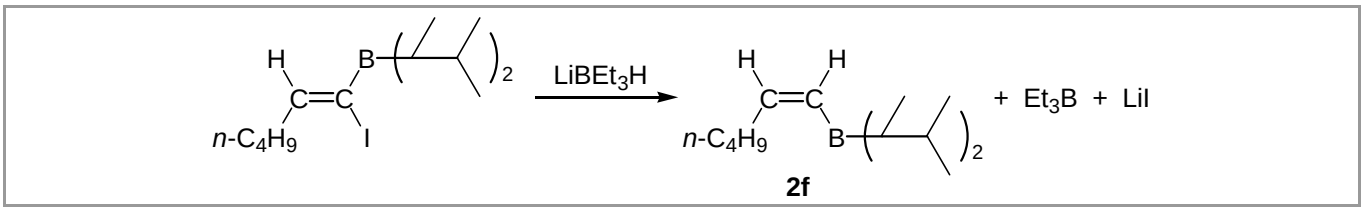
3). The reaction between (*E*)-oct-3-en-1-yne (**1f**), generated by the reaction of (*E*)-hex-1-enyldisiamylborane with (trimethylsilyl)ethynyl bromide, and (*E*)-1-iodohex-1-ene (**6a**) (1 equiv) was carried out in the presence of $PdCl_2(PPh_3)_2$ (0.02 equiv), CuI (0.04 equiv) and *n*-Bu_4NOH (2 equiv) at room temperature under argon. Thus the reaction was completed within 1 h to afford the corresponding conjugated dienyne, (5*E*,9*E*)-tetradeca-5,9-dien-7-yne (**8fa**), in 80 % yield with retention of configuration at both double bonds (Scheme 4) (Table 4, entry **1**). Reducing the catalyst loading showed retardation of the reaction, analogous to the aforementioned reaction of (*E*)-dec-3-en-1-yne (**1a**) with iodobenzene (**3a**). Different types of **1** could coupled with **6a** to give the corresponding conjugated *E*,*E*-dienynes in good yields (Scheme 4) (entries 2-4 and 15). The above conditions could be also applied to the cross-coupling reaction of (*Z*)-oct-3-en-1-yne (**2f**), affording the desired product, (5*Z*,9*E*)-tetradeca-5,9-dien-7-yne (**9fa**), in 78 % yield with high stereoselectivity (= 98 %) (Scheme 4) (entry 5).

Table 4 Cross-coupling Reaction of (*E*)- and (*Z*)-Alk-3-en-1-yne (**1** and **2**) with (*E*)- and (*Z*)-1-Iodoalk-1-ene (**6** and **7**)[a]

Entry	Alk-3-en-1-yne	1-Iodoalk-1-ene (R^4)	Product	Yield (%)[b]
1	 **1f**	 **6a**	 **8fa**	80
2	 **1b**	**6a**	 **8ba**	79
3	 **1d**	**6a**	 **8da**	66
4	 **1e**	**6a**	 **8ea**	65
5	 **2f**	**6a**	 **9fa**	78
6	**1f**	 **7a**	 **10fa**	77
7	**2f**	**7a**	 **11fa**	85
8	**1f**	 **6b**	 **8fb**	80
9	**2f**	**6b**	 **9fb**	76
10				5
11	**1f**	 **7b**	 **10fb**	64[c]
12				72[d]

13	**2f**	**7b**	 **11fb**	45
14				77[e]
15	 **1c**	**6a**	 **8ca**	78
16	 **2c**	**6a**	 **9ca**	63
17	**1c**	**7a**	 **10ca**	69
18	**2c**	**7a**	 **11ca**	57
19	**1c**	**6b**	 **8cb**	53
20	**2c**	**6b**	 **9cb**	57
21				4
22	**1c**	**7b**		21[c]
23			**10cb**	59[d]
24				24
	2c	**7b**	 **11cb**	
25				60[e]

[a] The reaction was carried out using $PdCl_2(PPh_3)_2$ (0.04 mmol), CuI (0.08 mmol), **6** or **7** (2.0 mmol), and *n*-Bu_4NOH (4.0 mmol) at room temperature for 1 to 4 h, unless otherwise noted. [b] Isolated yields based on **6** or **7**. [c] Before the reaction with **7b**, LiI (4 mmol) was added to the reaction mixture containing (*E*)-alk-3-en-1-yne, and the mixture was stirred for 0.5 h at room temperature. [d] In the presence of LiI (4 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.04 mmol) and $AsPh_3$ (0.08 mmol) were used instead of $PdCl_2(PPh_3)_2$. [e] $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.04 mmol) and $AsPh_3$ (0.08 mmol) were used instead of $PdCl_2(PPh_3)_2$.



Scheme 5

Having achieved the one-pot synthesis of **9fa** as well as **8fa**, we made an effort to construct all possible combinations of geometrical isomers of alka-1,5-dien-3-ynes (**8**, **9**, **10**, **11**) using representative substrates (Scheme 3), and the results are summarized in Table 4. (*Z*)-1-iodohex-1-ene (**7a**) produced high yields of (5*E*, 9*Z*)-tetradeca-5,9-dien-7-yne (**10fa**) and (5*Z*, 9*Z*)-tetradeca-5,9-dien-7-yne (**11fa**) in the reactions with **1f** and **2f** (entries 6 and 7), except that **10fa** is the same product as **9fa**. On the other hand, use of (*Z*)-1-bromohex-1-ene instead of **7a** yielded no product and resulted in the recovery of the bromide under the same reaction conditions. The reactions of (*E*)-1-iodo-2-phenylethene (**6b**) also proceeded with high yields and stereoselectivity (entries 8 and 9), while the reaction of (*Z*)-1-iodo-2-phenylethene (**7b**) gave only 5 % yield of product **10fb** (entry 10). In contrast, the cross-coupling of **2f** with **7b** gave a higher yield (45 %) of product **11fb** under the identical conditions (entry 13). We were aware that the difference between the two reactions was the presence or absence of LiI, which was formed in the step of the generation of **2f** as shown in Scheme 5.

This prompted us to carry out the coupling of **1f** with **7b** in the presence of LiI (2 equiv) otherwise under the same conditions, thereby leading to a marked increase in the yield of **10fb** (from 5 to 64 %) (entry 11). Moreover, using $PdCl_2(dppf)\cdot CH_2Cl_2$ together with $AsPh_3$ in place of $PdCl_2(PPh_3)_2$, combined with LiI, led to 72 % yield (entry 12). When the cross-coupling of **2f** with **7b** was carried out under $PdCl_2(dppf)\cdot CH_2Cl_2/AsPh_3$/CuI catalyst conditions, the yield of **11fb** increased to 77 % in a similar manner as described above (entry 14). Amatore and Jutand have reported that the oxidative addition to Pd(0) is faster in the presence of a lithium cation due to the generation of a more active Pd(0) complex.[21] Although we have no clear evidence for the remarkable effect on LiI in the present reaction, the in situ generation of such a reactive Pd catalyst[22] possibly plays a critical role in the reaction mechanism. It is interesting to note that addition of LiCl instead of LiI led to the same result. The reactions of (*E*)- and (*Z*)-4-phenylbut-3-en-1-yne (**1c** and **2c**) with 1-iodoalk-1-ene, except for **7b**, under $PdCl_2(PPh_3)_2$/CuI catalyst conditions afforded the corresponding conjugated dienynes in good to high yields (entries 15-20). In the reactions with **7b** (entries 21-25), we observed similar results to those described above. Consequently, LiI as well as $PdCl_2(dppf)\cdot CH_2Cl_2$ is necessary to accomplish the cross-coupling reaction with **7b** in good yields. The catalysis of $PdCl_2(dppf)\cdot CH_2Cl_2$ superior to that of $PdCl_2(PPh_3)_2$ would be attributable to its structure.[19] The present protocol allowed us to synthesize all the four geometrical isomers of conjugated alka-1,5-dien-3-ynes in good to high yields with high stereoselectivity.

To the best of our knowledge, there have been a few reports on the synthesis of conjugated alka-1,5-dien-3-ynes. Hiyama and co-workers reported that trimethylsilyl(trimethylstannyl)ethyne could couple sequentially with two different alkenyl iodides in the presence of the same palladium catalyst, where the reaction required a wide temperature (from –78 to 50 ºC) and a large excess amount of expensive tris(dimethylamino)sulfur (trimethylsilyl)difluoride.[23] Rossi and co-workers converted trimethylsilylethynylzinc chloride into alka-1,5-dien-3-yne upon the stepwise procedure, coupling with alkenyl halide, desilylation, and coupling with another alkenyl halide.[24] Tellier and co-workers also reported that butenynylzinc bromide derived from 1,1-difluoroethene was coupled with alkenyl iodide to give terminal 1,5-dien-3-yne, where the reaction required a very low temperature (–100 ºC).[25] The present protocol has some advantageous properties over other methods: advantages such as low toxicity, inexpensive reagents, operational simplicity, and easy operating conditions (from –15 ºC to room temperature).

In summary, we have successfully developed a one-pot method for the stereoselective syntheses of 1-arylalk-3-en-1-yne and alka-1,5-dien-3-yne via a three-component coupling in which (trimethylsilyl)ethynyl bromide reacts with alkenyldisiamylborane and aryl or alkenyl iodide in turn. The first cross-coupling forms (*E*)- and (*Z*)-alk-3-en-1-ynes whose alkenyl group is introduced as nucleophile into the sp carbon atom attached to bromine atom. In the second cross-coupling, aryl or alkenyl group is introduced as electrophile into the other sp carbon atom. Thus, (trimethylsilyl)ethynyl bromide is used as an ethynyl unit, and sp^2 carbon atom can be introduced into each end of the ethynyl unit by employing a Suzuki-type reaction and the Sonogashira reaction. The second cross-coupling with aryl iodide is tolerant of a wide variety of functional groups on the aromatic ring under the present conditions and leads to the stereoselective and efficient formation of (*E*)- and (*Z*)-1-arylalk-3-en-1-ynes. Moreover, the reactions with (*E*)- and (*Z*)-1-iodoalk-1-enes effect the assembly of (*E*,*E*)-, (*Z*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-alka-1,5-dien-3-ynes, in good yields with high stereoselectivity. Synthetic application of this protocol is currently under investigation.

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 determinations were performed on a JEOL JMS-SX102A spectrometer (EI, 70 eV). GLC analyses were performed with a Shimadzu GC-14B gas chromatograph equipped with a glass column (5% FFAP on Uniport B, 1 m or 5% Silicone 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 pre-coated with silica gel 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 Ar atmosphere. Unless otherwise noted, commercially available materials were used without any purification. Alkyne and 2-methylbut-2-ene were used after distillation over calcium hydride under argon. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon before use. (Trimethylsilyl)ethynyl bromide,[26] 1-iodoalk-1-yne,[27] (*E*)-1-iodoalk-1-ene,[28] (*Z*)-1-iodoalk-1-ene,[29] and a solution of BH_3 in THF[30] were prepared according to the literature procedures.

General Procedure for the Syntheses of (*E*)-1-Aryl-3-alken-1-yne (4), (*E*,*E*)-Alka-1,5-dien-3-yne (8) and (*E*,*Z*)-Alka-1,5-dien-3-yne (10)

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 the solution was added alkyne (4 mmol) dropwise at – 15 ºC and the mixture was stirred for 2 h at 0 ºC. To the solution of alkenyldisiamylborane in THF was added $Cu(acac)_2$ (0.052 g, 0.2 mmol) under an argon flow, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.474 g, 2.68 mmol) and 1M-NaOMe (3 mL, 3 mmol), and the resulting mixture was allowed to warm gradually to room temperature and to stir overnight. After the reaction mixture was cooled to 0 ºC, $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol) and CuI (0.015 g, 0.08 mmol) were added to the cooled mixture under an argon flow followed by dropwise addition of *n*-Bu_4NOH (40 wt.% solution in water) (2.66 mL, 4 mmol) and aryl or alkenyl iodide (2 mmol). [In the cases of synthesis of **4fk**, **4fl**, and **4fm**, $PdCl_2(dppf)\cdot CH_2Cl_2$ (0.033 g, 0.04 mmol) and $AsPh_3$ (0.027 g, 0.08 mmol) were employed instead of $PdCl_2(PPh_3)_2$. In the cases of synthesis of **10fb** and **10cb**, the procedure is as follows. After the reaction mixture was cooled to 0 ºC, LiI (0.535 g, 4 mmol) was added under an argon flow, and then the mixture was stirred for 0.5 h at room temperature. Except for the use of $PdCl_2(dppf)\cdot CH_2Cl_2$ and $AsPh_3$ in place of $PdCl_2(PPh_3)_2$, subsequent operations were the same as described above.] After being stirred for 1 to 4 h at room temperature, the mixture was treated with 3M-NaOH (4 mL) and H_2O_2 (30 wt.% solution in water) (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 or ether (for **4fe** and **4ff**), washed with brine, dried over anhydrous Na_2SO_4, and concentrated under vacuo. Purification by flash chromatography on silica gel or column chromatography on aluminiumu oxide (basic) (for **4fd**, **8cb**, and **10cb**[31]) provided product **4**, **8**, or **10**.

General Procedure for the Syntheses of (*Z*)-1-Arylalk-3-en-1-yne (5), (*Z*,*E*)-Alka-1,5-dien-3-yne (9) and (*Z*,*Z*)-Alka-1,5-dien-3-yne (11)

To a solution of disiamylborane (4 mmol) in THF (12 mL) was added 1-iodoalk-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-iodoalk-1-enyldisiamylborane in THF. After the solution was cooled to – 25 ºC, 1M-$LiBEt_3H$ (4 mL, 4 mmol) in THF was added dropwise to the cooled solution, and the reaction mixture was allowed to warm gradually to room temperature 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 was treated as described above General Procedure. In the cases of synthesis of **5ca**, **5fk**, **5fl**, **5fm**, **11fb**, and **11cb**, $PdCl_2(dppf)\cdot CH_2Cl_2$ and $AsPh_3$ in stead of $PdCl_2(PPh_3)_2$ were employed. Work-up procedure was the same as described above, except for extracting with ether for **5fe** and **5ff** and purifying by column chromatography on aluminiumu oxide (basic) for **5fd**, **5fm**, **9cb**,[31] and **11cb**.[31]

(*E*)-1-Phenyldec-3-en-1-yne (**4aa**)

Pentane as eluent.

IR (neat): 3020, 2954, 2927, 2854, 1596, 1488, 952, 754, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 3H), 1.25–1.45 m, 8H), 2.1–2.2 (m, 2H), 5.70 (dt, *J* = 16.0, 1.5 Hz, 1H), 6.22 (dt, *J* = 16.0, 7.0 Hz, 1H), 7.25–7.3 (m, 3H), 7.4–7.45 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (Me), 22.6 (CH_2), 28.7 (CH_2 × 2), 31.6 (CH_2), 33.2 (CH_2), 87.9 (=C), 88.4 (=C), 109.5 (=CH), 123.7 (=C), 127.8 (=CH), 128.2 (=CH × 2), 131.4 (=CH × 2), 145.1 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{20}$: 212.1565; found: 212.1541.

EI-MS: *m/z* (%) = 212 (50) [M^+], 155 (23), 142 (17), 141 (78), 129 (16), 128 (100), 115 (40), 91 (12).

(*E*)-5,5-Dimethyl-1-phenylhex-3-en-1-yne (4ba)

Pentane as eluent.

IR (neat): 3020, 2960, 2902, 2866, 1595, 1490, 1363, 1255, 960, 754, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (s, 9H), 5.63 (d, *J* = 16.1 Hz, 1H), 6.29 (d, *J* = 16.1 Hz, 1H), 7.27–7.32 (m, 3H), 7.4–7.44 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.0 (Me × 3), 34.1 (C), 88.2 (=C), 88.4 (=C), 105.0 (=CH), 123.6 (=C), 127.8 (=CH), 128.2 (=CH × 2), 131.3 (=CH × 2), 155.3 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{16}$: 184.1252; found: 184.1277.

EI-MS: *m/z* (%) = 184 (87) [M^+], 170 (14), 169 (100), 167 (12), 155 (13), 154 (63), 153 (32), 152 (25), 141 (25), 129 (12), 128 (17), 115 (22), 91 (34).

(*E*)-1,4-Diphenylbut-1-en-3-yne (4ca)

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 3053, 3031, 1487, 1446, 1070, 950, 750, 688 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.39 (d, *J* = 16.1 Hz, 1H), 7.04 (d, *J* = 16.1 Hz, 1H), 7.27–7.37 (m, 6H), 7.42–7.5 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 88.8 (=C), 91.7 (=C), 108.1 (=CH), 123.4 (=C), 126.3 (=CH × 2), 128.1 (=CH), 128.3 (=CH × 2), 128.6 (=CH), 128.7 (=CH × 2), 131.5 (=CH × 2), 136.3 (=C), 141.2 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{12}$: 204.0939; found: 204.0868.

EI-MS: *m/z* (%) = 204 (100) [M^+], 203 (79), 202 (77), 201 (10), 101 (14).

(*E*)-1-(Cyclohex-1-enyl)-4-phenylbut-1-en-3-yne (4da)

Pentane as eluent.

IR (neat): 3020, 2929, 2858, 1624, 1587, 1488, 1440, 950, 754, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.57–1.72 (m, 4H), 2.12–2.2 (m, 2H), 5.69 (d, *J* = 16.1 Hz, 1H), 5.87–5.9 (m, 1H), 6.68 (d, *J* = 16.1 Hz, 1H), 7.27–7.32 (m, 3H), 7.4–7.44 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.2 (CH_2 × 2), 23.8 (CH_2), 26.1 (CH_2), 89.6 (=C), 90.4 (=C), 103.9 (=CH), 123.7 (=C), 127.7 (=CH), 128.2 (=CH × 2), 131.3 (=CH × 2), 132.8 (=CH), 135.6 (=C), 145.0 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{16}$: 208.1252; found: 208.1267.

EI-MS: *m/z* (%) = 208 (100) [M^+], 207 (17), 193 (12), 181 (14), 180 (90), 179 (64), 178 (60), 167 (65), 166 (21), 165 (80), 153 (13), 152 (32), 151 (10), 139 (11), 131 (11), 128 (16), 126 (10), 117 (23), 115 (36), 91 (28), 89 (13), 77 (15).

(*E*)-1-Phenyl-3-propylhept-3-en-1-yne (4ea)

Pentane as eluent.

IR (neat): 3018, 2958, 2929, 2869, 1595, 1488, 1458, 1442, 754, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 1.43 (sext *J* = 7.3 Hz, 2H), 1.61 (sext, *J* = 7.3 Hz, 2H), 2.12 (q *J* = 7.3 Hz, 2H), 2.20 (t, *J* = 7.3 Hz, 2H), 5.98 (t, *J* = 7.3 Hz, 1H), 7.23–7.32 (m, 3H), 7.4–7.44 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7 (Me), 13.9 (Me), 21.7 (CH_2), 22.5 (CH_2), 30.4 (CH_2), 32.6 (CH_2), 86.5 (=C), 91.8 (=C), 123.0 (=C), 123.9 (=C), 127.6 (=CH), 128.2 (=CH × 2), 131.4 (=CH × 2), 138.5 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{20}$: 212.1565; found: 212.1550.

EI-MS: *m/z* (%) = 212 (100) [M^+], 184 (14), 183 (77), 170 (10), 169 (28), 168 (11), 167 (14), 165 (18), 156 (10), 155 (46), 154 (25), 153 (30), 152 (31), 143 (10), 142 (55), 141 (79), 139 (18), 129 (21), 128 (29), 127 (17), 126 (11), 115 (66), 91 (38), 77 (18).

(*E*)-1-(4-Methoxyphenyl)oct-3-en-1-yne (4fc)

Pentane/CH_2Cl_2 8:2 as eluent.

IR (neat): 3001, 2956, 2927, 2869, 2856, 2837, 1604, 1508, 1463, 1440, 1288, 1247, 1172, 1105, 1035, 954, 831 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3H), 1.3–1.44 (m, 4H), 2.12–2.18 (m, 2H), 3.78 (s, 3H), 5.67 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.19 (dt, *J* = 15.8, 7.3 Hz, 1H), 6.8–6.85 (m, 2H), 7.33–7.38 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.9 (CH_2), 32.8 (CH_2), 55.2 (Me), 86.9 (=C), 87.7 (=C), 109.6 (=CH), 113.9 (=CH × 2), 115.7 (=C), 132.8 (=CH × 2), 144.4 (=CH), 159.3 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{18}O$: 214.1358; found: 214.1357.

EI-MS: *m/z* (%) = 214 (73) [M^+], 185 (43), 172 (16), 171 (100), 158 (24), 141 (11), 128 (38), 121 (12), 115 (17).

(*E*)-1-(4-Aminophenyl)oct-3-en-1-yne (4fd)

Pentane/ether 7:3 as eluent.

IR (neat): 3471, 3381, 3030, 2956, 2925, 2869, 2856, 2192, 1618, 1604, 1512, 1290, 1176, 954, 827 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.1 Hz, 3H), 1.3–1.42 (m, 4H), 2.1–2.18 (m, 2H), 3.75 (broad s, 2H), 5.67 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.15 (dt, *J* = 15.8, 7.1 Hz, 1H), 6.61–6.65 (m, 2H), 7.2–7.24 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.9 (CH_2), 32.8 (CH_2), 86.2 (=C), 88.4 (=C), 109.7 (=CH), 113.0 (=C), 114.7 (=CH × 2), 132.7 (=CH × 2), 143.7 (=CH), 146.3 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{17}N$: 199.1361; found: 199.1376.

EI-MS: *m/z* (%) = 199 (92) [M^+], 170 (58), 157 (17), 156 (100), 154 (16), 143 (14), 142 (10), 141 (14), 130 (22), 128 (18), 117 (12), 106 (12).

(*E*)-1-(4-Acetoxyphenyl)oct-3-en-1-yne (4fe)

CH_2Cl_2 as eluent.

IR (neat): 2956, 2927, 2871, 2858, 2198, 1685, 1598, 1402, 1357, 1263, 1178, 956, 839 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H), 1.31–1.47 (m 4H), 2.16–2.22 (m, 2H), 2.58 (s, 3H), 5.71 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.30 (dt, *J* = 15.8, 7.3 Hz, 1H), 7.46–7.5 (m, 2H), 7.86–7.9 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 26.5 (Me), 30.7 (CH_2), 33.0 (CH_2), 87.1 (=C), 91.9 (=C), 109.1 (=CH), 128.2 (=CH × 2), 128.6 (=C), 131.4 (=CH × 2), 135.8 (=C), 146.6 (=CH), 197.3 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1372.

EI-MS: *m/z* (%) = 226 (100) [M^+], 211 (33), 184 (10), 183 (64), 170 (38), 156 (10), 155 (82), 152 (10), 141 (13), 140 (24), 139 (32), 127 (11).

(*E*)-1-(4-Nitrophenyl)oct-3-en-1-yne (4ff)

Pentane/CH_2Cl_2 8:2 as eluent.

IR (neat): 2958, 2929, 2871, 2858, 2200, 1591, 1517, 1490, 1342, 1107, 956, 854, 750, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3H), 1.32–1.44 (m, 4H), 2.17–2.23 (m, 2H), 5.72 (dt, *J* = 16.1, 1.5 Hz, 1H), 6.35 (dt, *J* = 16.1, 7.3 Hz, 1H), 7.52–7.56 (m, 2H), 8.14–8.19 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.7 (CH_2), 33.0 (CH_2), 86.2 (=C), 94.0 (=C), 108.8 (=CH), 123.5 (=CH × 2), 130.7 (=C), 132.0 (=CH × 2), 146.6 (=C), 147.8 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}NO_2$: 229.1103; found: 229.1096.

EI-MS: *m/z* (%) = 229 (52) [M^+], 186 (26), 174 (11), 173 (100), 154 (10), 143 (10), 140 (20), 139 (33), 127 (10), 115 (10).

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(*E*)-1-(4-Bromophenyl)oct-3-en-1-yne (4fg)

Pentane as eluent.

IR (neat): 2956, 2927, 2869, 2860, 1485, 1465, 1070, 1010, 956, 823 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.0 Hz, 3H), 1.3–1.45 (m, 4H), 2.15–2.21 (m, 2H), 5.66 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.8, 7.0 Hz, 1H), 7.25–7.3 (m, 2H), 7.4–7.45 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.8 (CH_2), 32.9 (CH_2), 86.7 (=C), 89.5 (=C), 109.2 (=CH), 121.9 (=C), 122.6 (=C), 131.5 (=CH × 2), 132.8 (=CH × 2), 145.8 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}{}^{81}Br$: 264.0338; found: 264.0368.

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}{}^{79}Br$: 262.0357; found: 262.0394.

EI-MS: *m/z* (%) = 264 (72) [M^+], 262 (75) [M^+], 222 (10), 221 (64), 220 (11), 219 (67), 208 (85), 207 (10), 206 (85), 195 (14), 193 (14), 168 (15), 155 (22), 154 (86), 153 (34), 152 (28), 141 (35), 140 (100), 139 (94), 128 (11), 127 (38), 126 (15), 115 (16), 114 (27), 113 (23), 87 (12), 75 (14), 63 (18).

(*E*)-1-(4-Chlorophenyl)oct-3-en-1-yne (4fh)

Pentane as eluent.

IR (neat): 2956, 2927, 2871, 2860, 1488, 1465, 1091, 1014, 956, 827 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 3H), 1.3–1.5 (m, 4H), 2.1–2.2 (m, 2H), 5.67 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.8, 7.0 Hz, 1H), 7.24–7.28 (m, 2H), 7.31–7.35 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.8 (CH_2), 32.9 (CH_2), 86.7 (=C), 89.3 (=C), 109.2 (=CH), 122.1 (=C), 128.5 (=CH × 2), 132.5 (=CH × 2), 133.7 (=C), 145.7 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}{}^{37}Cl$: 220.0836; found: 220.0808.

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}{}^{35}Cl$: 218.0862; found: 218.0893.

EI-MS: *m/z* (%) = 220 (22) [M^+], 218 (69) [M^+], 189 (18), 177 (29), 176 (13), 175 (86), 164 (33), 163 (12), 162 (100), 154 (22), 153 (27), 152 (19), 151 (16), 149 (37), 141 (18), 140 (29), 139 (48), 127 (19), 125 (15), 114 (10), 113 (13), 63 (10).

(*E*)-1-(2-Thienyl)oct-3-en-1-yne (4fi)

Pentane as eluent.

IR (neat): 3018, 2956, 2927, 2869, 2858, 1197, 954, 848, 827, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 3H), 1.3–1.44 (m, 4H), 2.13–2.19 (m, 2H), 5.68 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.23 (dt, *J* = 15.8, 7.3 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.15 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.21 (dd, *J* = 5.1, 1.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.8 (CH_2), 32.9 (CH_2), 80.9 (=C), 92.1 (=C), 109.2 (=CH), 123.7 (=C), 126.7 (=CH), 126.9 (=CH), 131.3 (=CH), 145.4 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{12}H_{14}S$: 190.0816; found: 190.0818.

EI-MS: *m/z* (%) = 190 (69) [M^+], 161 (37), 148 (13), 147 (100), 134 (51), 128 (13), 121 (19), 115 (13), 103 (12), 77 (10).

(*E*)-1-(3-Pyridyl)oct-3-en-1-yne (4fj)

Pentane/ether 7:3 as eluent.

IR (neat): 3026, 2956, 2927, 2871, 2858, 1475, 1406, 956, 804, 704 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H), 1.32–1.46 (m, 4H), 2.16–2.21 (m, 2H), 5.69 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.30 (dt, *J* = 15.8, 7.3 Hz, 1H), 7.23 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 7.69 (dt, *J* = 7.9, 1.8 Hz, 1H), 8.49 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.65 (d, *J* = 1.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.7 (CH_2), 32.9 (CH_2), 84.3 (=C), 91.7 (=C), 108.9 (=CH), 120.9 (=C), 123.0 (=CH), 138.2 (=CH), 146.5 (=CH), 148.0 (=CH), 151.9 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{13}H_{15}N$: 185.1204; found: 185.1190.

EI-MS: *m/z* (%) = 185 (74) [M^+], 156 (25), 143 (13), 142 (64), 141 (22), 130 (14), 129 (100), 128 (12), 116 (15), 115 (18).

(*E*)-1-(2-Methylphenyl)oct-3-en-1-yne (4fk)

Pentane as eluent.

IR (neat): 3020, 2956, 2927, 2871, 2858, 1483, 1456, 954, 756 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.0 Hz, 3H), 1.32–1.45 (m, 4H), 2.15–2.2 (m, 2H), 2.42 (s, 3H), 5.73 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.23 (dt, *J* = 15.8, 7.0 Hz, 1H), 7.08–7.13 (m, 1H), 7.15–7.18 (m, 2H), 7.37–7.39 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 20.6 (Me), 22.2 (CH_2), 30.9 (CH_2), 32.9 (CH_2), 86.7 (=C), 92.2 (=C), 109.6 (=CH), 123.4 (=C), 125.4 (=CH), 127.8 (=CH), 129.3 (=CH), 131.7 (=CH), 139.9 (=C), 144.8 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{18}$: 198.1409; found: 198.1364.

EI-MS: *m/z* (%) = 198 (100) [M^+], 169 (37), 156 (12), 155 (86), 154 (41), 153 (50), 152 (30), 143 (12), 142 (77), 141 (66), 139 (12), 129 (38), 128 (55), 127 (30), 116 (13), 115 (57), 91 (10), 77 (18).

(*E*)-1-(1-Naphthyl)oct-3-en-1-yne (4fl)

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 3057, 2956, 2927, 2869, 2856, 1396, 954, 798, 773; cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.0 Hz, 3H), 1.35–1.49 (m, 4H), 2.18–2.23 (m, 2H), 5.84 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.36 (dt, *J* = 15.8, 7.0 Hz, 1H), 7.38–7.42 (m, 1H), 7.48–7.57 (m, 2H), 7.63–7.65 (m, 1H), 7.76–7.79 (m, 1H), 7.81–7.84 (m, 1H), 8.32–8.35 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 30.9 (CH_2), 32.9 (CH_2), 85.9 (=C), 93.3 (=C), 109.6 (=CH), 121.3 (=CH), 125.2 (=C), 126.2 (=CH), 126.3 (=C), 126.5 (=CH), 128.2 (=CH), 128.3 (=CH), 130.0 (=CH), 133.1 (=CH), 133.2 (=C), 145.4 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{18}H_{18}$: 234.1409; found: 234.1410.

EI-MS: *m/z* (%) = 234 (100) [M^+], 205 (42), 203 (18), 202 (17), 192 (16), 191 (84), 190 (64), 189 (79), 179 (13), 178 (54), 176 (14), 165 (28), 164 (11), 163 (17), 152 (24).

(*E*)-1-(2-Isopropylphenyl)oct-3-en-1-yne (4fm)

Pentane as eluent.

IR (neat): 3022, 2958, 2927, 2869, 1483, 1463, 1444, 954, 756 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.32–1.46 (m, 4H), 2.14–2.2 (m, 2H), 3.44 (hept, *J* = 6.8 Hz, 1H), 5.73 (dt, *J* = 15.6, 1.4 Hz, 1H), 6.22 (dt, *J* = 15.6, 7.3 Hz, 1H), 7.09–7.13 (m, 1H), 7.24–7.26 (m, 2H), 7.38–7.41 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 23.1 (Me × 2), 30.9 (CH_2), 31.5 (CH_2), 32.9 (CH), 86.5 (=C), 91.9 (=C), 109.7 (=CH), 122.3 (=C), 124.8 (=CH), 125.4 (=CH), 128.2 (=CH), 132.1 (=CH), 144.6 (=CH), 150.2 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{17}H_{22}$: 226.1722; found: 226.1699.

EI-MS: *m/z* (%) = 226 (100) [M^+], 184 (13), 183 (82), 170 (10), 169 (27), 168 (30), 167 (24), 166 (10), 165 (25), 156 (22), 155 (80), 154 (14), 153 (34), 152 (25), 144 (12), 143 (48), 142 (24), 141 (58), 129 (39), 128 (30), 127 (10), 115 (28), 91 (11), 55 (17), 42 (14).

(*Z*)-1-Phenyldec-3-en-1-yne (5aa)

Pentane as eluent.

IR (neat): 3020, 2956, 2927, 2856, 1488, 754, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.25–1.45 (m, 8H), 2.35–2.45 (m, 2H), 5.68 (dt, *J* = 10.7, 1.5 Hz, 1H), 5.96 (dt, *J* = 10.7, 7.0 Hz, 1H), 7.25–7.3 (m, 3H), 7.4–7.45 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (Me), 22.6 (CH_2), 28.8 (CH_2 × 2), 30.4 (CH_2), 31.7 (CH_2), 86.5 (=C), 93.4 (=C), 109.0 (=CH), 123.8 (=C), 127.9 (=CH), 128.2 (=CH × 2), 131.4 (=CH × 2), 144.3 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{20}$: 212.1565; found: 212.1559.

EI-MS: *m/z* (%) = 212 (48) [M^+], 155 (32), 142 (15), 141 (59), 129 (16), 128 (100), 115 (40), 91 (13).

(*Z*)-1,4-Diphenylbut-1-en-3-yne (5ca)

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 3060, 3020, 1488, 1446, 783, 754, 688 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.91 (d, *J* = 11.9 Hz, 1H), 6.69 (d, *J* = 11.9 Hz, 1H), 7.27–7.4 (m, 8H), 7.47–7.52 (m, 1H), 7.9–7.95 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 88.2 (=C), 95.8 (=C), 107.3 (=CH), 123.4 (=C), 128.2 (=CH × 2), 128.3 (=CH), 128.4 (=CH × 2), 128.5 (=CH), 128.7 (=CH × 2), 131.4 (=CH × 2), 136.5 (=C), 138.6 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{12}$: 204.0939; found: 204.0941.

EI-MS: *m/z* (%) = 204 (100) [M^+], 203 (84), 202 (79), 201 (11), 200 (10), 101 (16).

(*Z*)-1-(2-Methylphenyl)oct-3-en-1-yne (5fb)

Pentane as eluent.

IR (neat): 3026, 2956, 2927, 2869, 2860, 2187, 1508, 1465, 1458, 815 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3H), 1.34–1.5 (m, 4H), 2.33 (s, 3H), 2.37–2.42 (m, 2H), 5.66 (d, *J* = 10.6 Hz, 1H), 5.94 (dt, *J* = 10.6, 7.3 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 21.4 (Me), 22.2 (CH_2), 30.0 (CH_2), 31.0 (CH_2), 85.8 (=C), 93.5 (=C), 109.0 (=CH), 120.6 (=C), 129.0 (=CH), 131.2 (=CH), 138.0 (=C), 143.9 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{18}$: 198.1409; found: 198.1452.

EI-MS: *m/z* (%) = 198 (79) [M^+], 170 (11), 169 (55), 156 (19), 155 (100), 154 (33), 153 (31), 152 (23), 143 (11), 142 (67), 141 (35), 139 (18), 129 (28), 128 (33), 127 (19), 116 (10), 115 (32), 105 (14), 91 (10), 77 (12).

(*Z*)-1-(4-Methoxyphenyl)oct-3-en-1-yne (5fc)

Pentane/CH_2Cl_2 8:2 as eluent.

IR (neat): 3018, 2956, 2929, 2871, 2858, 2837, 1602, 1508, 1463, 1440, 1290, 1247, 1172, 1035, 831 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3H), 1.34–1.47 (m, 4H), 2.37–2.42 (m, 2H), 3.79 (s, 3H), 5.65 (d, *J* = 10.6 Hz, 1H), 5.92 (dt, *J* = 10.6, 7.3 Hz, 1H), 6.81–6.86 (m, 2H), 7.35–7.40 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 30.0 (CH_2), 31.0 (CH_2), 55.2 (Me), 85.1 (=C), 93.3 (=C), 109.1 (=CH), 113.9 (=CH × 2), 115.8 (=C), 132.7 (=CH × 2), 143.5 (=CH), 159.3 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{18}O$: 214.1358; found: 214.1359.

EI-MS: *m/z* (%) = 214 (84) [M^+], 186 (11), 185 (64), 172 (20), 171 (100), 170 (16), 158 (28), 153 (12), 145 (10), 141 (14), 128 (44), 127 (12), 121 (18), 115 (22), 102 (12).

(*Z*)-1-(Aminophenyl)oct-3-en-1-yne (5fd).

Pentane/ether 7:3 as eluent.

IR (neat): 3473, 3382, 3016, 2956, 2927, 2869, 2856, 2185, 1622, 1602, 1512, 1292, 1176, 827 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3H), 1.35–1.48 (m, 4H), 2.36–2.41 (m, 2H), 3.77 (broad s, 2H), 5.65 (d, *J* = 10.7 Hz, 1H), 5.88 (dt, *J* = 10.7, 7.3 Hz, 1H), 6.57–6.61 (m, 2H), 7.22–7.26 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 29.9 (CH_2), 31.0 (CH_2), 84.4 (=C), 94.0 (=C), 109.2 (=CH), 113.1 (=C), 114.7 (=CH × 2), 132.6 (=CH × 2), 142.8 (=CH), 146.3 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{17}N$: 199.1361; found: 199.1389.

EI-MS: *m/z* (%) = 199 (73) [M^+], 171 (11), 170 (76), 157 (23), 156 (100), 154 (13), 143 (20), 141 (12), 130 (20), 128 (19), 117 (13), 115 (13), 106 (14).

(*Z*)-1-(4-Acetoxyphenyl)oct-3-en-1-yne (5fe)

CH_2Cl_2 as eluent.

IR (neat): 3020, 2958, 2929, 2871, 2858, 2194, 1685, 1596, 1404, 1357, 1263, 839 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.3 Hz, 3H), 1.36–1.49 (m, 4H), 2.38–2.43 (m, 2H), 5.69 (dt, *J* = 10.6, 1.5 Hz, 1H), 6.04 (dt, *J* = 10.6, 7.3 Hz, 1H), 7.48–7.51 (m, 2H), 7.88–7.91 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 26.6 (Me), 30.2 (CH_2), 30.9 (CH_2), 89.9 (=C), 92.6 (=C), 108.6 (=CH), 128.2 (=CH × 2), 128.6 (=C), 131.4 (=CH × 2), 135.9 (=C), 145.7 (=CH), 197.2 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{18}O$: 226.1358; found: 226.1386.

EI-MS: *m/z* (%) = 226 (100) [M^+], 211 (31), 183 (49), 170 (44), 169 (11), 156 (11), 155 (91), 153 (13), 152 (13), 141 (16), 140 (24), 139 (35), 127 (11), 115 (12).

(*Z*)-1-(4-Nitrophenyl)oct-3-en-1-yne (5ff)

Pentane/CH_2Cl_2 8:2 as eluent.

IR (neat): 2958, 2929, 2869, 2858, 2194, 1589, 1517, 1340, 1107, 852, 748 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.3 Hz, 3H), 1.35–1.5 (m, 4H), 2.39–2.44 (m, 2H), 5.70 (dt, *J* = 10.7, 1.5 Hz, 1H), 6.10 (dt, *J* = 10.7, 7.3 Hz, 1H), 7.53–7.57 (m, 2H), 8.16– (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 30.3 (CH_2), 30.8 (CH_2), 91.6 (=C), 91.9 (=C), 108.3 (=CH), 123.6 (=CH × 2), 130.7 (=C), 132.0 (=CH × 2), 146.7 (=C), 146.8 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}NO_2$: 229.1103; found: 229.1084.

EI-MS: *m/z* (%) = 229 (49) [M^+], 186 (17), 174 (11), 173 (100), 154 (13), 153 (12), 143 (12), 140 (17), 139 (28), 127 (13), 115 (12).

(*Z*)-1-(4-Bromophenyl)oct-3-en-1-yne (5fg)

Pentane as eluent.

IR (neat): 3020, 2956, 2927, 2869, 2858, 1485, 1465, 1394, 1070, 1010, 823 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3H), 1.35–1.47 (m, 4H), 2.35–2.41 (m, 2H), 5.64 (dt, *J* = 10.6,

1.5 Hz, 1H), 5.99 (dt, *J* = 10.6, 7.3 Hz, 1H), 7.26–7.31 (m, 2H), 7.41–7.46 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 30.1 (CH_2), 30.9 (CH_2), 87.6 (=C), 92.2 (=C), 108.7 (=CH), 122.1 (=C), 122.6 (=C), 131.5 (=CH × 2), 132.7 (=CH × 2), 144.9 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}{}^{81}Br$: 264.0338; found: 264.0259.

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{15}{}^{79}Br$: 262.0357; found: 262.0344.

EI-MS: *m/z* (%) = 264 (51) [M^+], 262 (53) [M^+], 221 (38), 219 (39), 208 (64), 206 (67), 195 (10), 193 (11), 168 (15), 155 (22), 154 (100), 153 (34), 152 (24), 141 (32), 140 (70), 139 (74), 128 (11), 127 (34), 126 (13), 115 (15), 114 (21), 113 (18), 87 (10), 77 (10), 75 (12), 63 (16).

(*Z*)-1-(2-Thienyl)oct-3-en-1-yne (5fi)

Pentane as eluent.

IR (neat): 3018, 2956, 2927, 2869, 2858, 1186, 848, 827, 731, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3H), 1.33–1.47 (m, 4H), 2.35–2.4 (m, 2H), 5.66 (dt, *J* = 10.7, 1.2 Hz, 1H), 5.97 (dt, *J* = 10.7, 7.3 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.17 (dd, *J* = 3.6, 0.9 Hz, 1H), 7.23 (dd, *J* = 5.1, 1.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 30.1 (CH_2), 30.9 (CH_2), 86.3 (=C), 90.3 (=C), 108.7 (=CH), 123.7 (=C), 126.8 (=CH), 127.0 (=CH), 131.2 (=CH), 144.5 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{12}H_{14}S$: 190.0816; found: 190.0813.

EI-MS: *m/z* (%) = 190 (78) [M^+], 162 (11), 161 (60), 148 (16), 147 (100), 135 (10), 134 (62), 128 (22), 121 (21), 115 (19), 103 (14), 97 (13), 77 (13).

(*Z*)-1-(3-Pyridyl)oct-3-en-1-yne (5fj)

Pentane/ether 7:3 as eluent.

IR (neat): 3024, 2956, 2927, 2871, 2858, 1475, 1407, 1022, 802, 732, 704 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.0 Hz, 3H), 1.35–1.48 (m, 4H), 2.38–2.43 (m, 2H), 5.68 (dt, *J* = 10.7, 1.5 Hz, 1H), 6.04 (dt, *J* = 10.7, 7.6 Hz, 1H), 7.24 (ddd, *J* = 7.9, 4.9, 0.6 Hz, 1H), 7.71 (dt, *J* = 7.9, 1.8 Hz, 1H), 8.50 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.67 (d, *J* = 1.2 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.2 (CH_2), 30.2 (CH_2), 30.9 (CH_2), 89.7 (=C), 89.8 (=C), 108.4 (=CH), 120.8 (=C), 122.9 (=CH), 138.2 (=CH), 145.6 (=CH), 148.2 (=CH), 150.2 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{13}H_{15}N$: 185.1204; found: 185.1202.

EI-MS: *m/z* (%) = 185 (58) [M^+], 156 (30), 143 (10), 142 (40), 141 (17), 130 (13), 129 (100), 128 (11), 116 (12), 115 (13).

(*Z*)-1-(2-Methylphenyl)oct-3-en-1-yne (5fk)

Pentane as eluent.

IR (neat): 3020, 2956, 2927, 2871, 2858, 1485, 1456, 756, 715 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3H), 1.36–1.49 (m, 4H), 2.39–2.46 (m, 2H), 2.45 (s, 3H), 5.72 (dt, *J* = 10.7, 1.5 Hz, 1H), 5.97 (dt, *J* = 10.7, 7.3 Hz, 1H), 7.11–7.17 (m, 1H), 7.18–7.21 (m, 2H), 7.39–7.42 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 20.8 (Me), 22.3 (CH_2), 30.1 (CH_2), 31.0 (CH_2), 90.4 (=C), 92.3 (=C), 109.2 (=CH), 123.5 (=C), 125.5 (=CH), 127.9 (=CH), 129.3 (=CH), 131.7 (=CH), 139.8 (=C), 143.9 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{15}H_{18}$:198.1409; found: 198.1429.

EI-MS: *m/z* (%) = 198 (100) [M^+], 169 (47), 156 (12), 155 (68), 154 (41), 153 (43), 152 (28), 143 (13), 142 (69), 141 (66), 139 (12), 129 (34), 128 (51), 127 (24), 116 (12), 115 (53), 105 (10), 91 (10), 77 (16).

(*Z*)-1-(1-Naphthyl)oct-3-en-1-yne (5fl)

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 2956, 2927, 2869, 2858, 1404, 798, 773, 732 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.3 Hz, 3H), 1.4–1.54 (m, 4H), 2.49–2.55 (m, 2H), 5.82 (dt, *J* = 10.7, 1.5 Hz, 1H), 6.04 (dt, *J* = 10.7, 7.3 Hz, 1H), 7.41–7.44 (m, 1H), 7.48–7.58 (m, 2H), 7.65–7.68 (m, 1H), 7.78–7.81 (m, 1H), 7.82–7.85 (m, 1H), 8.34–8.38 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.3 (CH_2), 30.3 (CH_2), 31.0 (CH_2), 91.4 (=C), 91.5 (=C), 109.2 (=CH), 121.4 (=CH), 125.2 (=C), 126.2 (=CH), 126.3 (=C), 126.6 (=CH), 128.2 (=CH), 128.4 (=CH), 130.1 (=CH), 133.1 (=C), 133.1 (=CH), 144.4 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{18}H_{18}$: 234.1409; found: 234.1422.

EI-MS: *m/z* (%) = 234 (100) [M^+], 206 (11), 205 (57), 203 (20), 202 (18), 192 (16), 191 (80), 190 (64), 189 (78), 179 (15), 178 (54), 176 (16), 165 (34), 164 (10), 163 (18), 152 (29).

(*Z*)-1-(2-Isopropylphenyl)oct-3-en-1-yne (5fm)

Pentane as eluent.

IR (neat): 3022, 2958, 2927, 2869, 1483, 1463, 1444, 756, 732 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.34–1.48 (m, 4H), 2.38–2.45 (m, 2H), 3.49 (hept, *J* = 6.8 Hz, 1H), 5.71 (d, *J* = 10.7

Hz, 1H), 5.97 (dt, *J* = 10.7, 7.3 Hz, 1H), 7.1–7.15 (m, 1H), 7.25–7.28 (m, 2H), 7.4–7.43 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.4 (CH_2), 23.1 (Me × 2), 30.2 (CH_2), 31.1 (CH_2), 31.5 (CH), 90.1 (=C), 92.1 (=C), 109.3 (=CH), 122.4 (=C), 124.8 (=CH), 125.5 (=CH), 128.3 (=CH), 132.2 (=CH), 143.8 (=CH), 150.0 (=C).

HRMS (EI): *m/z* [M^+] calcd for $C_{17}H_{22}$: 226.1722; found: 226.1698.

EI-MS: *m/z* (%) = 226 (100) [M^+], 184 (11), 183 (77), 170 (10), 169 (28), 168 (25), 167 (22), 166 (10), 165 (26), 156 (25), 155 (83), 154 (14), 153 (31), 152 (26), 144 (14), 143 (50), 142 (24), 141 (53), 129 (43), 128 (34), 127 (11), 115 (31), 91 (15), 55 (16), 42 (15).

(*5E,9E*)-Tetradeca-5,9-dien-7-yne (8fa)

Pentane as eluent.

IR (neat): 3020, 2956, 2927, 2871, 2860, 1465, 954 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 6H), 1.25–1.4 (m, 8H), 2.05–2.15 (m, 4H), 5.56 (d, *J* = 15.3 Hz, 2H), 6.10 (dt, *J* = 15.3, 7.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me × 2), 22.1 (CH_2 × 2), 30.8 (CH_2 × 2), 32.8 (CH_2 × 2), 86.7 (=C × 2), 109.6 (=CH × 2), 144.3 (=CH × 2).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{22}$: 190.1722; found: 190.1680.

EI-MS: *m/z* (%) = 190 (76) [M^+], 147 (26), 134 (19), 119 (21), 105 (50), 103 (11), 93 (10), 92 (13), 91 (100), 79 (25), 78 (67), 77 (17), 67 (12), 65 (14).

(*3E,7E*)-2,2-Dimethyldodeca-3,7-dien-5-yne (8ba)

Pentane as eluent.

IR (neat): 3024,2960, 2929, 2869, 1475, 1463, 1363, 1265, 956 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3H), 1.02 (s, 9H), 1.28–1.41 (m, 4H), 2.08–2.13 (m, 2H), 5.51 (dd, *J* = 16.1, 2.1 Hz, 1H), 5.55–5.6 (m, 1H), 6.10 (dt, *J* = 15.8, 7.3 Hz, 1H), 6.15 (d, *J* = 16.1 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 29.0 (Me × 3), 30.9 (CH_2), 32.8 (CH_2), 33.9 (C), 86.9 (=C), 87.2 (=C), 105.1 (=CH), 109.6 (=CH), 144.2 (=CH), 154.4 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{22}$: 190.1722; found: 190.1727.

EI-MS: *m/z* (%) = 190 (77) [M^+], 175 (16), 147 (46), 133 (22), 119 (64), 117 (19), 115 (14), 107 (11), 106 (10), 105 (100), 93 (13), 91 (52), 79 (13), 77 (16), 55 (13).

(*1E,5E*)-1-(Cyclohex-1-enyl)deca-1,5-dien-3-yne (8da)

Pentane as eluent.

IR (neat): 3024, 2954, 2927, 2858, 2837, 1624, 1448, 1434, 1201, 950, 790 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3H), 1.28–1.42 (m, 4H), 1.55–1.7 (m, 4H), 2.07–2.18 (m, 6H), 5.5–5.63 (m, 1H), 5.82 (s, 1H), 6.11 (dt, *J* = 15.6, 7.3 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 22.2 (CH_2), 22.3 (CH_2), 23.8 (CH_2), 26.1 (CH_2), 30.9 (CH_2), 32.8 (CH_2), 88.0 (=C), 89.5 (=C), 104.2 (=CH), 109.8 (=CH), 132.2 (=CH), 135.6 (=C), 144.2 (=CH), 144.3 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{22}$: 214.1722; found: 214.1703.

EI-MS: *m/z* (%) = 214 (72) [M^+], 185 (18), 171 (20), 157 (16), 144 (13), 143 (38), 142 (15), 141 (21), 131 (20), 129 (100), 128 (48), 127 (13), 117 (38), 116 (13), 115 (48), 105 (15), 95 (35), 92 (10), 91 (55), 79 (16), 77 (19), 67 (14), 65 (13).

(*4E,8E*)-5-Propyltrideca-4,8-dien-6-yne (8ea)

Pentane as eluent.

IR (neat): 3018, 2958, 2929, 2871, 1458, 1377, 952, 894 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H), 1.28–1.43 (m, 4H), 1.5–1.57 (m, 2H), 2.05–2.14 (m, 4H), 5.58 (d, *J* = 15.6 Hz, 1H), 5.84 (t, *J* = 7.3 Hz, 1H), 6.09 (dt, *J* = 15.6, 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7 (Me), 13.8 (Me), 13.8 (Me), 21.6 (CH_2), 22.1 (CH_2), 22.5 (CH_2), 30.4 (CH_2), 30.9 (CH_2), 32.7 (CH_2), 32.8 (CH_2), 85.3 (=C), 90.2 (=C), 109.8 (=CH), 123.2 (=C), 137.7 (=CH), 143.7 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{26}$: 218.2035; found: 218.2035.

EI-MS: *m/z* (%) = 218 (74) [M^+], 190 (13), 189 (68), 175 (28), 161 (12), 148 (13), 147 (17), 133 (38), 131 (14), 128 (11), 120 (10), 119 (46), 117 (29), 116 (10), 115 (27), 106 (10), 105 (70), 103 (14), 95 (10), 93 (18), 92 (24), 91 (100), 81 (14), 79 (29), 78 (11), 77 (26), 69 (10), 67 (14), 65 (14), 55 (20).

(*5Z,9E*)-Tetradeca-5,9-dien-7-yne (9fa) (10fa)

Pentane as eluent.

IR (neat): 3020, 2956, 2929, 2871, 2860, 1465, 954, 731 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H), 1.3–1.5 (m, 8H), 2.1–2.15 (m, 2H), 2.3–2.35 (m, 2H), 5.55 (d, *J* = 10.7 Hz, 1H), 5.62 (d, *J* = 15.8 Hz, 1H), 5.86 (dt, *J* = 10.7, 7.3 Hz, 1H), 6.12 (dt, *J* = 15.8, 7.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 13.9 (Me), 22.1 (CH_2), 22.2 (CH_2), 29.9 (CH_2), 30.9 (CH_2), 31.0 (CH_2), 32.8 (CH_2), 84.9 (=C), 92.4 (=C), 109.1 (=CH), 109.7 (=CH), 143.3 (=CH), 144.3 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{22}$: 190.1722; found: 190.1726.

EI-MS: *m/z* (%) = 190 (77) [M^+], 147 (17), 134 (20), 133 (11), 119 (22), 117 (11), 105 (57), 103 (12), 93 (11), 92 (13), 91 (100), 79 (27), 78 (66), 77 (20), 67 (13), 65 (15).

(*5Z,9Z*)-Tetradeca-5,9-dien-7-yne (11fa)

Pentane as eluent.

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

^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 6H), 1.3–1.45 (m, 8H), 2.3–2.4 (m, 4H), 5.60 (d, *J* = 10.0 Hz, 2H), 5.89 (dt, *J* = 10.0, 7.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me × 2), 22.3 (CH_2 × 2), 30.0 (CH_2 × 2), 31.0 (CH_2 × 2), 90.5 (=C × 2), 109.2 (=CH × 2), 143.4 (=CH × 2).

HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{22}$: 190.1722; found: 190.1741.

EI-MS: *m/z* (%) = 190 (75) [M^+], 147 (13), 134 (21), 133 (13), 119 (32), 117 (13), 115 (10), 106 (13), 105 (70), 103 (12), 93 (12), 92 (14), 91 (100), 79 (32), 78 (62), 77 (20), 67 (12), 65 (14).

(*1E,5E*)-1-Phenyldeca-1,5-dien-3-yne (8fb) (8ca)

Pentane as eluent.

IR (neat): 3026, 2954, 2923, 2854, 1456, 950, 746, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 3H), 1.27–1.42 (m, 4H), 2.12–2.17 (m, 2H), 5.65 (d, *J* = 15.8 Hz, 1H), 6.18 (dt, *J* = 15.8, 7.0 Hz, 1H), 6.27 (dd, *J* = 16.1, 2.1 Hz, 1H), 6.90 (d, *J* = 16.1 Hz, 1H), 7.23–7.38 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.1 (CH_2), 30.8 (CH_2), 32.9 (CH_2), 87.4 (=C), 90.9 (=C), 108.4 (=CH), 109.6 (=CH), 126.1 (=CH × 2), 128.4 (=CH), 128.6 (=CH × 2), 136.4 (=C), 140.4 (=CH), 145.1 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{18}$: 210.1409; found: 210.1378.

EI-MS: *m/z* (%) = 210 (85) [M^+], 181 (22), 168 (13), 167 (76), 166 (50), 165 (100), 154 (24), 153 (57), 152 (72), 151 (11), 141 (17), 139 (21), 128 (23), 116 (10), 115 (48), 95 (38), 91 (11), 89 (10).

(*1E,5Z*)-1-Phenyldeca-1,5-dien-3-yne (9fb) (10ca)

Pentane as eluent.

IR (neat): 3024, 2956, 2925, 2869, 2856, 1448, 948, 746, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.3 Hz, 3H), 1.32–1.47 (m, 4H), 2.35–2.4 (m, 2H), 5.63 (d, *J* = 10.6 Hz, 1H), 5.93 (dt, *J* = 10.6, 7.3 Hz, 1H), 6.33 (dd, *J* = 16.1, 2.1 Hz, 1H), 6.92 (d, *J* = 16.1 Hz, 1H), 7.23–7.43 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.3 (CH_2), 30.1 (CH_2), 31.0 (CH_2), 89.0 (=C), 92.9 (=C), 108.5 (=CH), 109.0 (=CH), 126.2 (=CH × 2), 128.4 (=CH), 128.6 (=CH × 2), 136.4 (=C), 140.4 (=CH), 144.2 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{18}$: 210.1409; found: 210.1458.

EI-MS: *m/z* (%) = 210 (69) [M^+], 181 (28), 179 (10), 168 (15), 167 (72), 166 (52), 165 (100), 154 (24), 153 (57), 152 (69), 151 (10), 141 (17), 139 (21), 128 (24), 116 (11), 115 (46), 95 (38), 91 (12), 77 (11).

(*1Z,5E*)-1-Phenyldeca-1,5-dien-3-yne (10fb) (9ca)

Pentane as eluent.

IR (neat): 3018, 2954, 2925, 2869, 2854, 1448, 954, 785, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.0 Hz, 3H), 1.3–1.45 (m, 4H), 2.14–2.19 (m, 2H), 5.71 (dt, *J* = 15.8, 1.2 Hz, 1H), 5.80 (dd, *J* = 11.9, 2.4 Hz, 1H), 6.20 (dt, *J* = 15.8, 7.0 Hz, 1H), 6.58 (d, *J* = 11.9 Hz, 1H), 7.23–7.37 (m, 3H), 7.83–7.87 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (Me), 22.2 (CH_2), 30.8 (CH_2), 32.9 (CH_2), 86.7 (=C), 95.3 (=C), 107.6 (=CH), 109.8 (=CH), 128.2 (=CH × 2), 128.2 (=CH), 128.5 (=CH × 2), 136.6 (=C), 137.6 (=CH), 145.5 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{18}$: 210.1409; found: 210.1419.

EI-MS: *m/z* (%) = 210 (60) [M^+], 181 (29), 179 (10), 168 (18), 167 (75), 166 (49), 165 (100), 154 (22), 153 (53), 152 (65), 151 (10), 141 (17), 139 (19), 128 (23), 116 (13), 115 (45), 95 (60), 91 (11).

(*1Z,5Z*)-1-Phenyldeca-1,5-dien-3-yne (11fb) (11ca)

Pentane as eluent.

IR (neat): 3020, 2956, 2925, 2869, 2856, 1448, 783, 731, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.3 Hz, 3H), 1.3–1.47 (m, 4H), 2.36–2.42 (m, 2H), 5.68 (dt, *J* = 10.6, 1.2 Hz, 1H), 5.86 (dd, *J* = 11.9, 2.7 Hz, 1H), 5.95 (dt, *J* = 10.6, 7.3 Hz, 1H), 6.60 (d, J = 11.9 Hz, 1H), 7.23–7.37 (m, 3H), 7.85–7.9 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (Me), 22.3 (CH_2), 30.3 (CH_2), 31.1 (CH_2), 92.0 (=C), 93.5 (=C), 107.7 (=CH), 109.1 (=CH), 128.2 (=CH × 2), 128.3 (=CH), 128.5 (=CH × 2), 136.5 (=C), 137.6 (=CH), 144.5 (=CH).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{18}$: 210.1409; found: 210.1452.

EI-MS: *m/z* (%) = 210 (64) [M^+], 181 (24), 168 (16), 167 (76), 166 (47), 165 (100), 154 (21), 153 (56), 152 (72), 141 (15), 139 (21), 128 (25), 116 (13), 115 (44), 95 (54), 89 (10).

(*1E,5E*)-1,6-Diphenylhexa-1,5-dien-3-yne (8cb)

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 954, 792, 746, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.34 (dd, *J* = 15.8, 1.8 Hz, 2H), 6.97 (d, *J* = 15.8 Hz, 2H), 7.23–7.42 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 91.5 (=C × 2), 108.2 (=CH × 2), 126.2 (=CH × 4), 128.6 (=CH × 2), 128.7 (=CH × 4), 136.3 (=C × 2), 141.1 (=CH × 2).

EI-MS: *m/z* (%) = 230 (51) [M^+], 229 (34), 228 (30), 227 (10), 226 (16), 215 (14), 202 (10), 115 (100).

(*1Z,5E*)-1,6-Diphenylhexa-1,5-dien-3-yne (9cb) (10cb)[31]

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 950, 790, 761, 690 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.88 (dd, *J* = 11.9, 2.7 Hz, 1H), 6.40 (dd, *J* = 16.1, 2.7 Hz, 1H), 6.65 (d, *J* = 11.9 Hz, 1H), 6.98 (d, *J* = 16.1 Hz, 1H), 7.23–7.42 (m, 8H), 7.83–7.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 90.6 (=C), 95.6 (=C), 107.5 (=CH), 108.2 (=CH), 126.2 (=CH × 2), 128.3 (=CH × 2), 128.3 (=CH), 128.4 (=CH × 2), 128.6 (=CH), 128.7 (=CH × 2), 136.2 (=C), 136.5 (=C), 138.3 (=CH), 141.4 (=CH).

EI-MS: *m/z* (%) = 230 (52) [M^+], 229 (42), 228 (32), 227 (11), 226 (17), 215 (16), 202 (10), 116 (12), 115 (100).

(*1Z,5Z*)-1,6-Diphenylhexa-1,5-dien-3-yne (11cb)[31]

Pentane/CH_2Cl_2 9:1 as eluent.

IR (neat): 783, 746, 688 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.82–5.96 (m, 2H), 6.64–6.82 (m, 2H), 7.23–7.41 (m, 6H), 7.82–7.85 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 94.6 (=C × 2), 107.5 (=CH × 2), 128.3 (=CH × 2), 128.4 (=CH × 4), 128.5 (=CH × 4), 136.4 (=C × 2), 138.5 (=CH × 2).

EI-MS: *m/z* (%) = 230 (46) [M^+], 229 (37), 228 (32), 227 (10), 226 (17), 215 (17), 202 (11), 116 (10), 115 (100).

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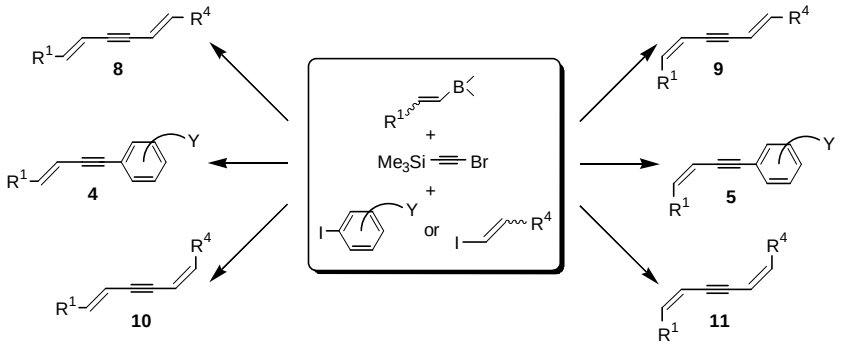

Stereoselective Synthesis of 1-Arylalk-3-en-1-yne and Alka-1,5-dien-3-yne.