Doctoral Thesis

Study on organic synthesis using arylboronic acids

（アリールボロン酸を用いる有機合成に関する研究）

March, 2017

Asuka Oikawa

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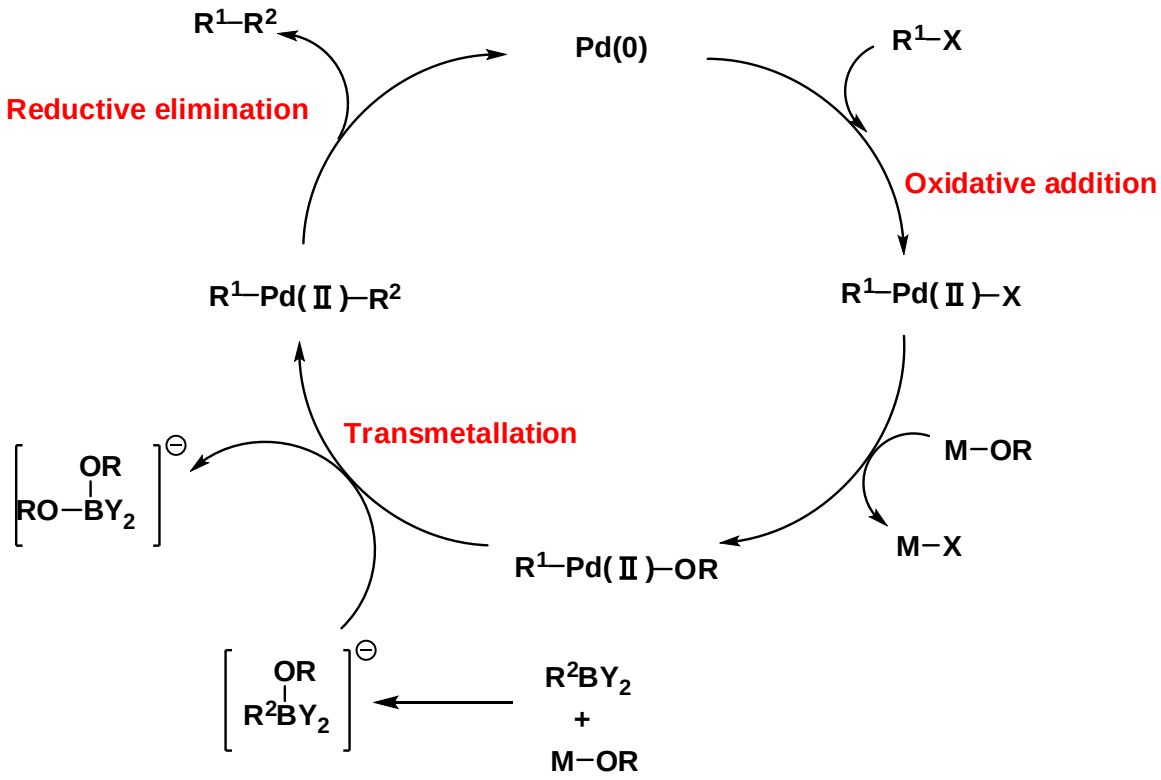
Chapter IV

Chapter I

Introduction

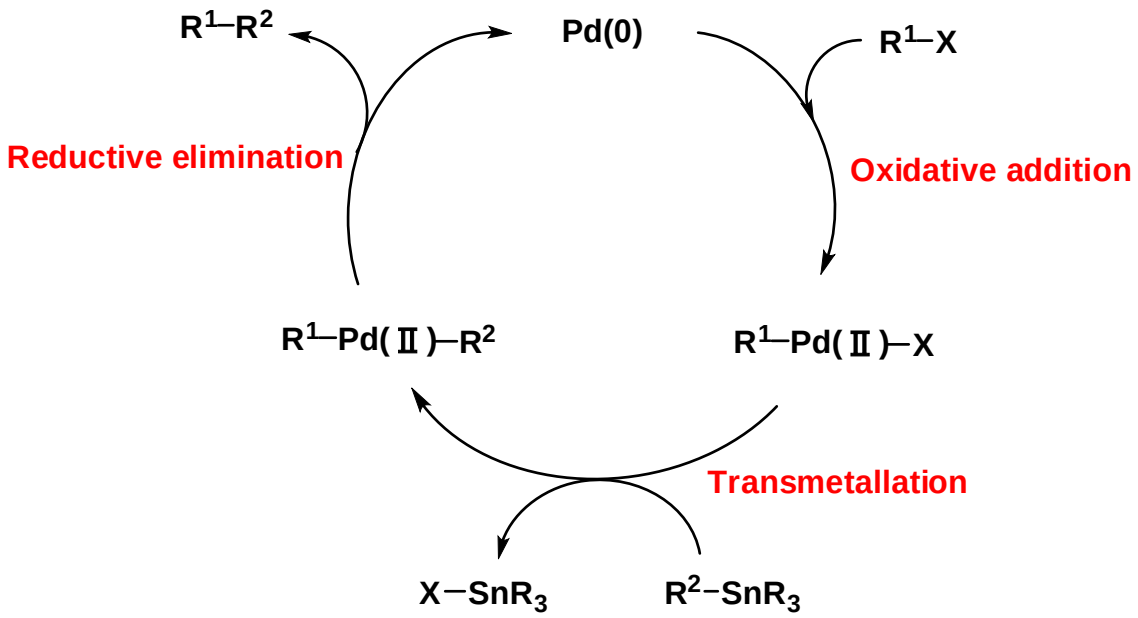
The first preparation and isolation of organoboronic acids was reported by Flankland in 1860.[1] Organoboronic acids can be obtained by the substitution reaction of trialkyl borates with Grignard reagents or lithium reagents, followed by acidic hydrolysis. Arylboronic and alkenylboronic acids, which are stable under air and commercially available, have been employed in a wide variety of synthetic processes. Among them, Suzuki-Miyaura cross-coupling reaction of arylboronic acids proceeds even in the presence of water, tolerates a wide range of functional groups, and yields nontoxic wastes.[2] Therefore, the palladium-catalyzed cross-coupling reaction is one of the most important strategies for carbon-carbon bond formation not only in laboratories but also in industry.

The mechanism of the cross-coupling reaction is illustrated in the following scheme. At the outset, oxidative addition of organic halide to palladium(0) forms organopalladium(II) halide, which undergoes ligand exchange with base to yield (alkoxo)palladium(II) intermediate. The nucleophilicity of organic group on boron atom is enhanced by quarternization of the boron with base, and thus organoboron compounds readily transfer their organic groups to (alkoxo)palladium(II) to furnish diorganopalladium(II). Finally, reductive elimination of organic partners from diorganopalladium(II) releases the cross-coupling product and regenerates palladium(0) to complete the catalytic cycle.



On the other hand, the palladium-catalyzed cross-coupling reaction between organotin compounds and electrophiles is also a significant strategy in synthetic organic chemistry. The cross-coupling reaction was reported by Migita and Kosugi[3] as well as Stille[4] in the latter half of 1970. Extensive investigation by Stille made it versatile carbon-carbon bond forming reaction,[5] which proceeds with broad functional group tolerance under neutral conditions.

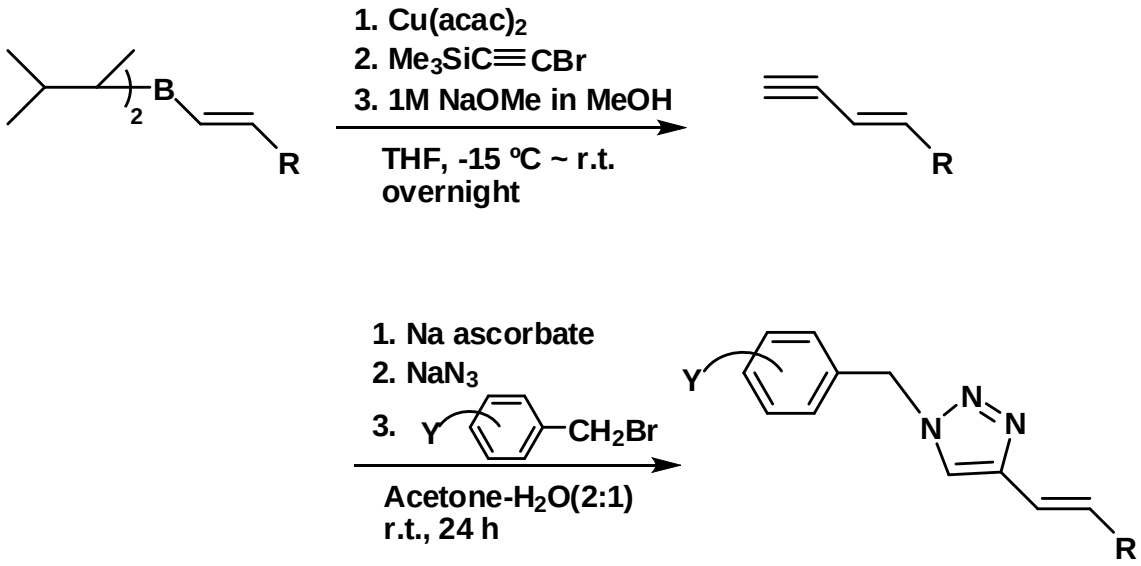
The reaction mechanism of the cross-coupling process is shown in the following scheme. In a similar manner as described in the mechanism of Suzuki-Miyaura cross-coupling reaction, the catalytic cycle starts from oxidative addition of organic halide to palladium(0) to form organopalladium(II) halide. Next transmetallation of organotin compounds with organopalladium(II) halide takes place to generate diorganopalladium(II), which undergoes reductive elimination to afford the cross-coupling product and to regenerate palladium(0).



In chapter 2, the 1,3-dipolar cycloaddition of arylazides with conjugated enynes, prepared by the copper-mediated cross-coupling reaction between alkenyldialkylboranes and (trimethylsilyl)ethynyl bromide, is described. In this study arylazides were prepared by the copper-mediated reaction of arylboronic acids with NaN_3. Meldal and Sharpless independently reported that in the presence of copper(I) compound the 1,3-dipolar cycloaddition between organic azide and alkyne proceeded with high regioselectivity to afford 1,4-disubstituted 1,2,3-triazoles.[6] The copper(I)-catalyzed azide-alkyne cycloaddition is a representative of click chemistry, the so-called click reaction, which has notable features, such as easy operation, high yielding, and potential use of various solvents including water.

In our laboratory, a one-pot method has been realized for the synthesis of 1-arylmethyl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles in good to exellent yields.[7] This one-pot reaction includes three chemical transformations: the cross-coupling reaction between (*E*)-alk-1-enyldisiamylboranes and (trimethylsilyl)ethynylbromide to form terminal conjugated (*E*)-enynes, the nucleophilic substitution reaction of functionalized benzyl bromides with sodium azide to generate funtionalized benzyl azides, and the 1,3-dipolar cycloaddition reaction. The present protocol can, therefor, proceed without the need for isolation of both terminal conjugated (*E*)-enynes and benzyl azides. Moreover, the inherent advantage of this method is that copper species formed during

the cross-coupling reaction using $Cu(acac)_2$ as catalyst can be utilized in combination with sodium ascorbate for the subsequent 1,3-dipolar cycloaddition reaction. Some features, such as tandem catalyst, mild reaction conditions, overall regio- and stereoselectivity, and good functional compatibility, make this strategy a practical and environmentally benign process for the construction of various 1-arylmethyl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles.

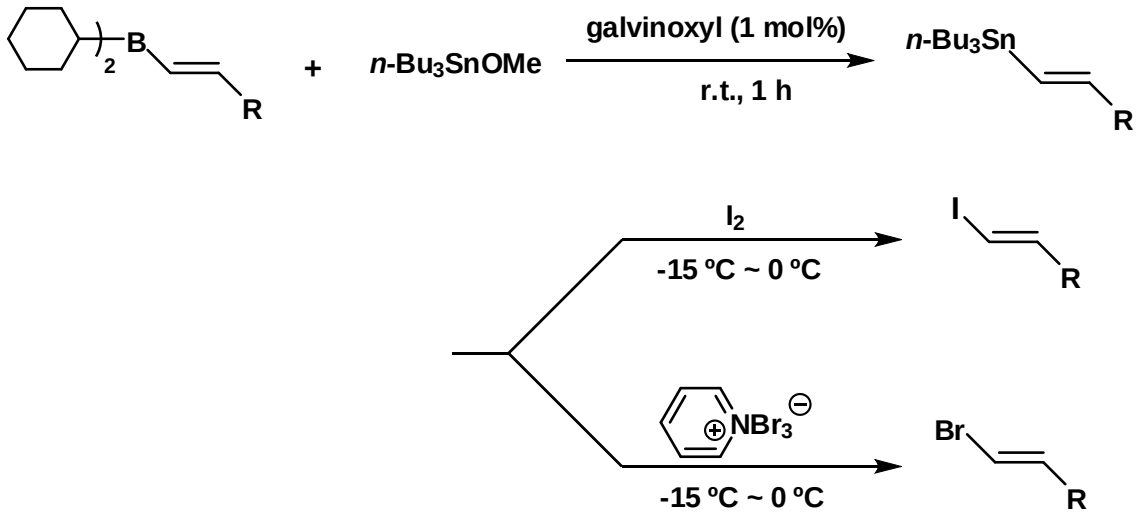


I investigate the synthesis of 4-alkenyl-1-aryl-1,2,3-triazoles, π-extended 1,2,3-triazoles, as a part of synthetic organic chemistry utilizing conjugated enynes.

In chapter 3, the preparation of aryltributylstannane through transfer of aryl group from boron to tin and its application to the synthesis of diaryl ketones via Stile cross-coupling reaction are described. Arylstannanes are useful intermediates for organic synthesis due to their stability to water as well as air and high functional group tolerance. In general, arylstannanes can be prepared by halogen-metal exchange reaction of aryl halides with lithium reagents followed by transmetallation with triorganyltin chloride.[8] Palladium-catalyzed cross-coupling reaction between aryl halides and hexaalkyldistannnane can be also used.[9] These methods have disadvantages such as the use of unstable lithium reagents and expensive hexaalkyldistannane, and thus an easy

and low cost alternative protocol is highly desirable.

In our laboratory, the preparation of (*E*)-alk-1-enyltributylstannanes has been achieved via transfer of (*E*)-alk-1-enyl group from boron to tin under neutral and mild reaction conditions.[10] In addition, it has been demonstrated that the resulting (*E*)-alk-1-enyltributylstannanes can undergo iodo- and bromodestannylation in a one-pot manner to provide the corresponding (*E*)-1-iodoalk-1-enes and (*E*)-1-bromoalk-1-enes in good to high yields, respectively. The synthetic advantages, including applicability to various substrates and compatibility to functional groups, would make it an alternative to currently available methods.



I investigate the preparation of aryltributylstannanes from arylboronic acids as a part of transmetallation of organyl group from boron to tin.

References

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Chapter II

First synthesis of both 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles and 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles: Assembly of π-extended 1,2,3-triazoles using a cross-coupling/click reaction sequence

Abstract

A practical and general synthetic approach to a series of π-extended 1,2,3-triazoles with both aryl and alkenyl moieties on the triazole ring is described. Synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles can be achieved by the click reaction between terminal conjugated (*E*)-enynes, prepared by copper-mediated cross-coupling reaction of (*E*)-alk-1-enyldisiamylboranes with (trimethylsilyl)ethynyl bromide, and aryl azides, prepared from arylboronic acids and sodium azide in another flask and employed for the following click reaction without any purification. 1-Aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles can be also synthesized by a sequential three-step reaction, which involves copper-mediated cross-coupling reaction of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylboranes with (trimethylsilyl)ethynyl bromide to form (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes, deprotection of the trimethylsilyl group on the alkynyl carbon atom to generate (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes and click reaction with aryl azides prepared in the same manner as described above. Both synthetic routes are tolerant of a wide range of functional groups with moderate to good yields.

1. Introduction

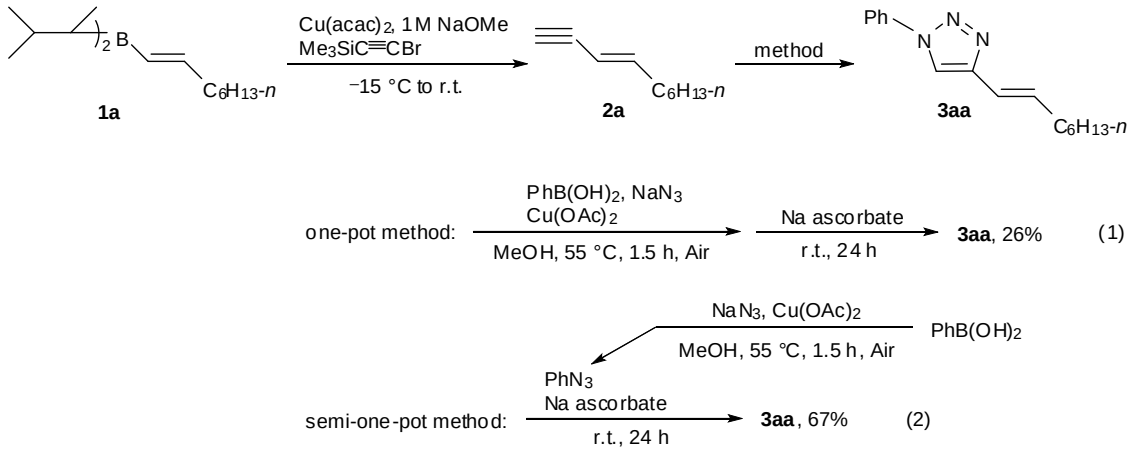
Since Sharpless and Meldal independently pioneered the copper(I)-catalyzed 1,3-dipolar cycloaddition reaction between organic azides and terminal alkynes to give 1,4-disubstituted 1,2,3-triazoles exclusively,[1] a wide variety of strategies have been developed for the cycloaddition reaction, the so-called click reaction.[2] As well as showing biological activities,[3] compounds bearing 1,2,3-triazole moiety have found a large number of applications in different fields such as bioconjugation[4] and materials science.[5] The 1,2,3-triazole scaffold is stable not only under acidic and basic conditions but also under oxidative and reductive conditions. The chemically robust properties can be attributed to the heterocyclic aromatic system. Assembling further π-extended 1,2,3-triazoles can be performed by introduction of substituents such as aryl and alkenyl groups into 1-, 4-, and 5-positions of the triazole ring. The extension of conjugated system on 1,2,3-triazole ring, in fact, has been realized in the click reaction by making a choice from the substrates. Thus, use of arylethynes as terminal alkynes gives 4- or 5-aryl 1,2,3-triazoles upon choosing the reaction conditions[2,6] and use of aryl and alkenyl azides furnishes 1-aryl[7-9] and 1-alkenyl[7a,h,8a,10] 1,2,3-triazoles, respectively. Although there are several reports on the formation of 4- or 5-alkenyl 1,2,3-triazoles,[6a,h,7a,c,11] the precursor of the alkenyl group is limited to only a few conjugated enynes such as 1-ethynylcyclohexene. The click reaction using terminal conjugated (*E*)-enynes (**2**), to our knowledge, is the only our previous report,[12] in which the reaction with *in situ* generated various benzyl azides proceeded at room temperature to afford a wide range of 1-arylmethyl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles in high yields. As our continued interest in assembling π-extended compounds utilizing *in situ* generated terminal conjugated enynes,[13] I focused my attention on the copper(I)-catalyzed click reaction with aryl azides to extend π-conjugation at the 1-position as well as at the 4-position of 1,2,3-triazole. Herein, I report the first synthesis of both 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles (**3**) through a sequential two-step reaction and 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles (**6**)

through a sequential three-step reaction. The present protocol provides a practical and general way to access π-extended 1,2,3-triazoles **3** and **6**, respectively, and is applicable to a wide range of starting materials.

2. Results and discussion

At first, our attention was turned to one-pot synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles (**3**) through a sequence of copper-mediated cross-coupling reaction of (*E*)-alk-1-enyldisiamylborane (**1**) with (trimethylsilyl)ethynyl bromide followed by click reaction with *in situ* generated aryl azides. Although a lot of methods have been reported for the synthesis of 1-aryl 1,2,3-triazoles employing *in situ* generation of aryl azides,[7-9] most of these methods suffer from limitations such as prolonged heating, use of expensive ligand, substrate or solvent, use of modified copper catalyst or unstable substrate, troublesome preparation of substrate, and low yield. Accordingly, I chose a method where the preparation of aryl azides could be performed by the reaction of sodium azide with arylboronic acids, which are stable under air and commercially readily available, in the presence of a small amount of $Cu(OAc)_2$ in methanol under an air atmosphere at 55 ºC for 1-3 h.[8b] Thus, the cross-coupling reaction of (*E*)-oct-1-enyldisiamylborane (**1a**) (1.0 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was carried out in the presence of $Cu(acac)_2$ (0.05 mmol) and NaOMe (1M, 0.75 mmol) at temperatures gradually rising from –15 ºC to room temperature overnight to form (*E*)-dec-3-en-1-yne (**2a**). To the resulting solution of **2a**, phenylboronic acid (1 mmol), NaN_3 (1.5 mmol), $Cu(OAc)_2$ (0.1 mmol), and MeOH (5 mL) were added, and the reaction mixture was stirred at 55 ºC in open air for 1.5 h in order to generate phenyl azide. After cooled to ambient temperature, sodium ascorbate (0.1 mmol) for reduction of $Cu(OAc)_2$ was added to the resultant mixture, which was stirred at room temperature for 24 h (Scheme 1, eq 1). The desired product, 1-phenyl-4-[(*E*)-oct-1-enyl]-1*H*-1,2,3-triazole (**3a**), was isolated in 26% yield based on (trimethylsilyl)ethynyl bromide, indicating that the yield of the click reaction between **2a** and phenyl azide was estimated to be less than 40%.[14] It has been recognized that the

click chemistry using copper(I)-catalyzed azide-alkyne cycloaddition furnishes 1,4-disubstituted 1,2,3-triazoles in very high yields.[2] I surmised that incomplete formation of phenyl azide may be responsible for the low yield of **3a**. This guess led us to prepare phenyl azide in another flask from phenylboronic acid in the same manner as described above. After phenyl azide, thus prepared, was transferred to the flask containing **2a**, sodium ascorbate (0.1 mmol) was added to the mixture, which was stirred at room temperature for 24 h (Scheme 1, eq 2). To our delight, the click reaction could be improved to afford **3a** in 67% overall yield, indicating that the yield of the click reaction between **2a** and phenyl azide increased up to 90%. This result ensured sufficient potential of our protocol. While all the steps could not be carried out in a one-pot manner, each step could be performed without operation such as exchange of solvent and filtration.



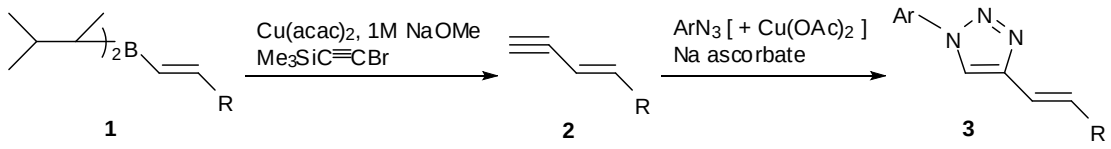
Scheme 1 Choice of the step for the preparation of phenyl azide.

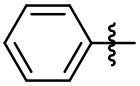
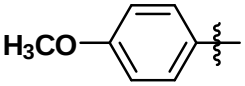
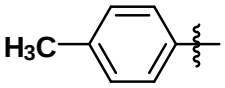
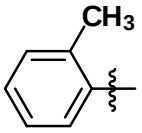
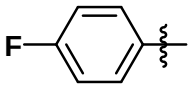
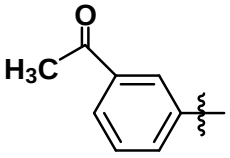
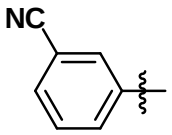
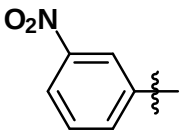
Having identified the separate preparation of aryl azides from arylboronic acids as the key step, I then explored the substrate scope of this semi-one-pot transformation using various combinations of terminal conjugated (*E*)-enynes (**2**) and aryl azides. The results are shown in Table 1. The semi-one-pot process mostly afforded products **3** in moderate to good yields with excellent regio- and stereoselectivities. It should be noted that aryl azides, prepared in another flask, could be directly used for the following click reaction without any purification. Different compounds **2** were suitable in this transformation. In particular, pre-chlorinated (*E*)-enyne, (*E*)-7-chlorohept-3-en-1-yne (**2b**), was tolerated

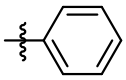
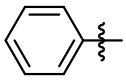
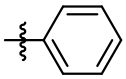
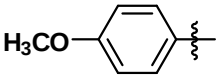
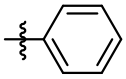
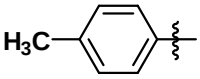
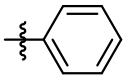
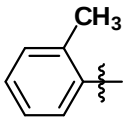
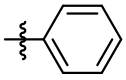
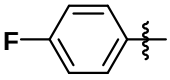
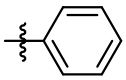
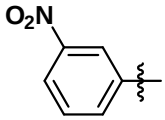
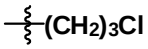
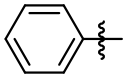
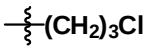
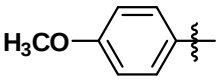
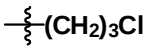
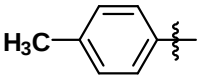
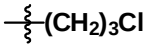
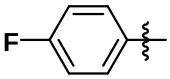
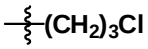
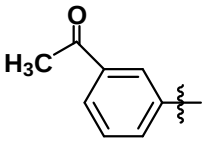
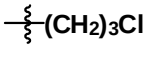
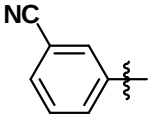
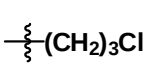
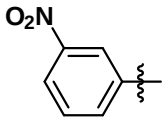
well (entries 15-21). A variety of aryl azides, bearing electron-donating groups such as methoxy (entries 2, 10 and 16) and methyl (entries 3, 11, 12 and 17), and electron-withdrawing groups such as fluoro (entries 5 and 18), acetyl (entries 6 and 19), cyano (entriea 7 and 20) and nitro (entries 8, 14 and 21), worked well under the same reaction conditions. The electronic effect on the phenyl ring had little influence on the reactivity of aryl azide substrates. Unfortunately, a combination of substrates resulted in a complex mixture which could not be separated (entries 4 and 13).

Table 1

Synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles via a sequence of cross-coupling[a] followed by click reaction[b]



Entry	R	Ar	Product	Yield (%)[c]
1	C_6H_{13}-*n*		3aa	67
2	C_6H_{13}-*n*		3ab	69
3	C_6H_{13}-*n*		3ac	66
4	C_6H_{13}-*n*		3ad	messy
5	C_6H_{13}-*n*		3ae	65
6	C_6H_{13}-*n*		3af	64
7	C_6H_{13}-*n*		3ag	58
8	C_6H_{13}-*n*		3ah	65

Entry	R	Ar	Product	Yield (%)[c]
9			3ba	74
10			3bb	69
11			3bc	59
12			3bd	41
13			3be	messy
14			3bh	46
15			3ca	73
16			3cb	65
17			3cc	71
18			3ce	73
19			3cf	68
20			3cg	58
21			3ch	63

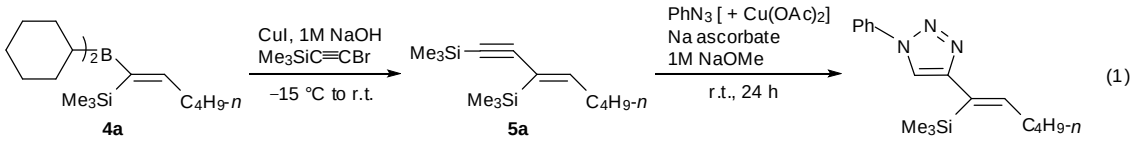
[a] Reaction conditions: **1** (1 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), $Cu(acac)_2$ (0.05 mmol), 1M NaOMe (0.75 mmol), – 15 ºC to room temperature overnight under argon.

[b] Reaction conditions: ArN_3 prepared from arylboronic acid (1 mmol) and NaN_3 (1.5 mmol) in the presence of $Cu(OAc)_2$ (0.1 mmol) under air, Na ascorbate (0.1 mmol), room temperature for 24 h under argon.

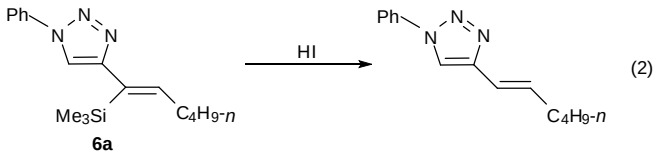
[c] Isolated yields after silica gel column chromatography.

I next focused on broadening the scope of enynes for the π-conjugated 1,2,3-triazole synthesis. In our previous report on the synthesis of conjugated enynes,[15] it was demonstrated that not only terminal conjugated (*E*)-enynes (**2**) but also trimethylsilyl-protected terminal conjugated enynes, (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes (**5**), could be prepared by copper-mediated cross-coupling reaction with (trimethylsilyl)ethynyl bromide under extremely mild conditions. Provided deprotection of the trimethylsilyl group attached to the alkyne moiety of **5** is performed, the deprotected compounds, (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes, can participate in click reaction. It has been reported that click reaction involving a deprotection step can be also carried out in a one-pot fashion,[16] where tetrabutylammonium fluoride (TBAF) was frequently employed as the desilylating reagent. Alternatively, it was found that a solution of NaOMe in MeOH was an efficient reagent for the deprotection of the trimethylsilyl group from **5**.[15] Our previous results as well as literature reports prompted us to examine a two-step process involving the deprotection of **5** followed by click reaction with aryl azide. Thus, the cross-coupling reaction of (*Z*)-1-(trimethylsilyl)hex-1-enyldicyclhexylborane (**4a**) (1.0 mmol) with (trimethylsilyl)ethynyl bromide (0.67 mmol) was performed in the presence of CuI (0.1 mmol) and NaOH (1M, 0.75 mmol) at temperatures gradually rising from –15 ºC to room temperature overnight to form (*Z*)-1,3-bis(trimethylsilyl)oct-3-en-1-yne (**5a**). To the resulting solution of **5a**, phenyl azide, prepared from phenylboronic acid (1 mmol), NaN_3 (1.5 mmol), and $Cu(OAc)_2$ (0.1 mmol) in MeOH (5 mL) at 55 ºC in open air for 1.5 h, was added, followed by addition of sodium ascorbate (0.1 mmol) and NaOMe (1

M, 1 mmol). The reaction mixture was stirred at room temperature for 24 h (Eq. 1). I was pleased to find that the two steps proceeded smoothly at the same time to afford the desired product, 1-phenyl-4-[(*Z*)-1-(trimethylsilyl)hex-1-enyl]-1*H*-1,2,3-triazole (**6a**), in 60% isolated yield based on (trimethylsilyl)ethynyl bromide. The geometry of **6a** was assigned by using desilylation of alkenylsilanes with retention of the double bond.[17] Protodesilylation of **6a** with HI gave 1-phenyl-4-[(*E*)-hex-1-enyl]-1*H*-1,2,3-triazole[18] as the sole product, thus demonstrating *Z*-configuration of **6a** (Eq. 2).



(1)

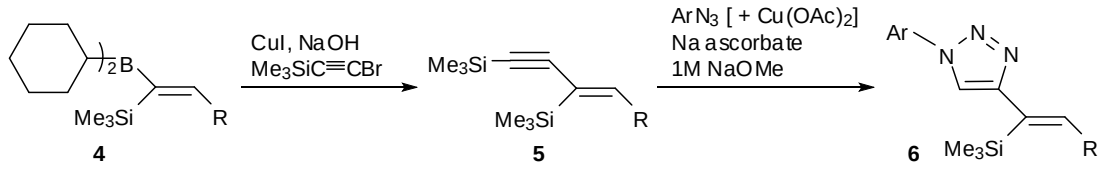


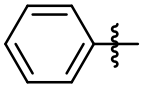
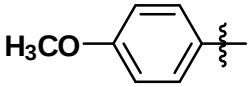
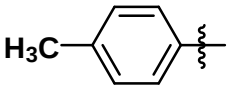
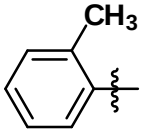
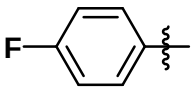
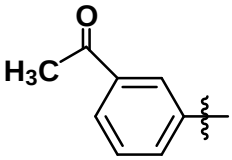
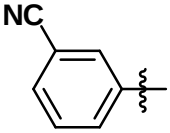
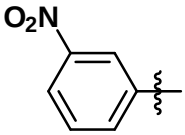
(2)

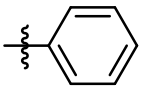
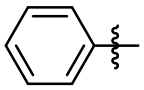
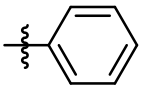
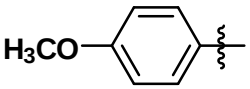
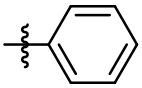
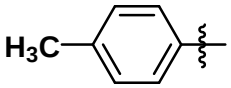
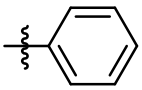
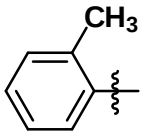
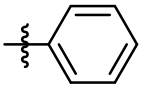
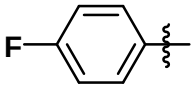
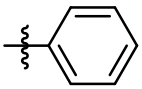
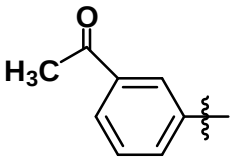
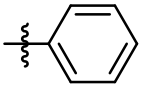
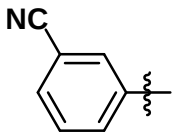
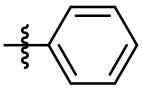
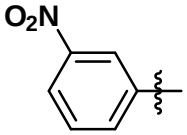
To evaluate the scope of this semi-one-pot transformation, various combinations of (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes (**5**) and aryl azides were used. The reactions were conducted under the conditions described above, and the results are shown in Table 2. The semi-one-pot process afforded 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles (**6**) exclusively in moderate to good yields. In this process, aryl azides, prepared in another flask, could be also used without any purification. It is noteworthy that such functional groups as acetyl, cyano, and nitro on the phenyl ring of aryl azides were tolerated under basic conditions. However, the products bearing cyano group (entries 7 and 15) were obtained in lower yields compared with those bearing the other two functional groups (entries 6, 8, 14 and 16). The reaction with 2-methylphenyl azide resulted in low product yields (entries 4 and 12), probably due to steric hindrance. It is interesting to note that the use of NaOMe as the desilylating reagent afforded products **6** in higher yields than that of TBAF (entries 1, 8 and 9).

Table 2

Synthesis of 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles via a sequence of cross-coupling[a] followed by desilylation/click reaction[b]



Entry	R	Ar	Product	Yield (%)[c]
1	C_4H_9-*n*		6aa	60 (45)[d]
2	C_4H_9-*n*		6ab	63
3	C_4H_9-*n*		6ac	68
4	C_4H_9-*n*		6ad	32
5	C_4H_9-*n*		6ae	65
6	C_4H_9-*n*		6af	62
7	C_4H_9-*n*		6ag	30
8	C_4H_9-*n*		6ah	58 (42)[d]

Entry	R	Ar	Product	Yield (%)[c]
9			6ba	54 (44)[d]
10			6bb	61
11			6bc	53
12			6bd	40
13			6be	52
14			6bf	58
15			6bg	39
16			6bh	55

[a] Reaction conditions: **4** (1 mmol), $Me_3SiC{\equiv}CBr$ (0.67 mmol), CuI (0.1 mmol), 1M or 2M NaOH (0.75 mmol), – 15 ºC to room temperature overnight under argon.

[b] Reaction conditions: ArN_3 prepared from arylboronic acid (1 mmol) and NaN_3 (1.5 mmol) in the presence of $Cu(OAc)_2$ (0.1 mmol) under air, Na ascorbate (0.1 mmol), 1M NaOMe (1 mmol), room temperature for 24 h under argon.

[c] Isolated yields after silica gel column chromatography.

[d] 1M TBAF (2 mmol) was used instead of 1M NaOMe (1 mmol).

3. Conclusion

In conclusion, I have reported a practical and general method for the synthesis of not only 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles but also 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles through a cross-coupling/click reaction sequence. To the best of our knowledge, the present protocol represents the first example of constructing a series of π-extended 1,2,3-triazoles with both an aryl moiety at the 1-position and a geometricaldefined alkenyl moiety at the 4-position on the triazole ring. This approach uses simple and readily available starting materials and shows good functional compatibility. The procedure can be successfully performed without isolation and purification of any compounds during the process, albeit in a semi-one-pot manner. These features make this protocol potentially attractive for the synthesis of the π-extended 1,2,3-triazoles.

4. Experimental

4.1. General information

NMR spectra were recorded on JEOL JNM-A-500 or JEOL JNM-ECA-600 spectrometer. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Coupling constants *J* are quoted in Hz. IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer, and only the strongest/structurally most important absorption peaks are listed. Electrospray ionization (ESI) HRMS analyses were measured on a Thermo Scientific Exactive instrument. Melting points were determined on a Yamato MP-21 and are uncorrected. TLC analyses were carried out using aluminum sheets pre-coated with silica gel 60 F_{254} purchased from Merck. Product purification was performed by column chromatography using silica gel 60 (Kanto Chemical, 63-210 μm). Unless otherwise noted, commercially available materials were used without any purification. Alk-1-yne, 2-methylbut-2-ene, and cyclohexene were used after distillation over CaH_2 under argon. 1-(Trimethylsilyl)alk-1-ynes were used after distillation under argon. THF was distilled

from Na-benzophenone ketyl under argon before use. Borane dimethyl sulfide complex ($BH_3 \cdot SMe_2$) was purchased from Aldrich. (Trimethylsilyl)ethynyl bromide was prepared according to the literature procedure.[19]

4.2. General procedure for the synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles

A 25 mL round-bottomed flask was charged with a solution of $BH_3 \cdot SMe_2$ (1 mmol) in THF (3 mL) under an argon atmosphere. To the solution was added 2-methylbut-2-ene (0.14 g, 2 mmol) dropwise at – 15 ºC, and the reaction mixture was stirred for 2 h at room temperature to form a solution of disiamylborane in THF.[20] To this solution was added alk-1-yne (1 mmol) dropwise at – 15 ºC, and the mixture was stirred for 2 h at 0 ºC. A solution of (*E*)-alk-1-enyldisiamylborane **1** (1 mmol) in THF, thus prepared, was cooled to – 15 ºC, and $Cu(acac)_2$ (0.013 g, 0.05 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.119 g, 0.67 mmol) and NaOMe (1M, 0.75 mL, 0.75 mmol). The resulting mixture was allowed to warm gradually to room temperature and stirred overnight to form (*E*)-alk-3-en-1-yne **2**. In another 25 mL round-bottomed flask, aryl azide was prepared by using arylboronic acid (1 mmol), NaN_3 (0.098 g, 1.5 mmol), $Cu(OAc)_2$ (0.018 g, 0.1 mmol) and MeOH (5 mL). Thus, the mixture was stirred at 55 ºC for 1.5-3.0 h under aerobic condition.[8b] To the flask containing (*E*)-alk-3-en-1-yne **2** was transferred a dark brown suspension of aryl azide in MeOH, and (+)-sodium L-ascorbate (0.02 g, 0.1 mmol) was added to the mixture under a flow of argon. The resulting mixture was stirred at room temperature for 24 h and then treated by bubbling air through the solution with tube pump at room temperature for 2 h to oxidize the residual organoboron compound. The mixture was extracted with EtOAc (3 × 10 mL), washed with brine (10 mL), dried (Na_2SO_4), and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to give product **3**.

4.3. General procedure for the synthesis of 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles

A 25 mL round-bottomed flask was charged with a solution of $BH_3 \cdot SMe_2$ (1 mmol) in THF (3 mL) under an argon atmosphere. To the solution was added cyclohexene (0.164 g, 2 mmol) dropwise at 0 ºC, and the reaction mixture was stirred for 2 h at this temperature to form a white suspension of dicyclohexylborane in THF.[20] To this suspension was added 1-(trimethylsilyl)alk-1-yne (1 mmol) dropwise at 0 ºC, and the mixture was stirred for 2 h at this temperature to produce a clear solution of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylborane **4** in THF. This solution was cooled to – 15 ºC, and CuI (0.019 g, 0.1 mmol) was added to the solution under a flow of argon, followed by dropwise addition of (trimethylsilyl)ethynyl bromide (0.119 g, 0.67 mmol) and NaOH (1M, 0.75 mL for **4a** or 2M, 0.375 mL for **4b**, 0.75 mmol). The resulting mixture was allowed to warm gradually to room temperature and stirred overnight to form (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne **5**. In another 25 mL round-bottomed flask, aryl azide was prepared as described in general procedure for the synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles. To the flask containing (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-yne **5** was transferred a dark brown suspension of aryl azide in MeOH, and (+)-sodium L-ascorbate (0.02 g, 0.1 mmol) was added to the mixture under a flow of argon, followed by addition of NaOMe (1M, 1.0 mL, 1.0 mmol). The resulting mixture was stirred at room temperature for 24 h and worked up as described in a typical experimental procedure for the synthesis of 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles. Product **6** was isolated by column chromatography on silica gel.

4.4. Characterization of the products

4.4.1. 4-[(E)-Oct-1-enyl]-1-phenyl-1H-1,2,3-triazole (3aa).

Light-brown solid, hexane-EtOAc (7:3) as eluent, mp. 58-59 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.26-1.40 (m, 6H), 1.45-1.53 (m, 2H), 2.21-2.27 (m, 2H), 6.45 (d, *J* = 16.1 Hz, 1H), 6.52 (dt, *J* = 16.1 and 6.8 Hz, 1H), 7.40-7.45 (m, 1H), 7.49-7.54 (m, 2H), 7.70-7.75 (m, 2H), 7.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 32.9 (CH_2), 117.4 (=CH), 117.8 (=CH), 120.4 (2 × CH_{arom}), 128.5 (CH_{arom}), 129.7 (2 × CH_{arom}), 134.6 (=CH), 137.0 (C_{arom}), 147.1 (=C). IR (KBr): ν = 3132, 2923, 2854, 1598, 1504, 1465, 1234, 1217, 1045, 977, 756, 684 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{21}N_3Na$: 278.1626; found 278.1630.

4.4.2. 1-(4-Methoxyphenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3ab).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 57-58 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.26-1.39 (m, 6H), 1.45-1.51 (m, 2H), 2.20-2.25 (m, 2H), 6.43 (d, *J* = 16.1 Hz, 1H), 6.48 (dt, *J* = 16.1 and 6.8 Hz, 1H), 6.97-7.02 (m, 2H), 7.58-7.63 (m, 2H), 7.77 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 31.7 (CH_2), 32.9 (CH_2), 55.6 (CH_3), 114.7 (2 × CH_{arom}), 117.5 (=CH), 118.0 (=CH), 122.0 (2 × CH_{arom}), 130.5 (C_{arom}), 134.2 (=CH), 146.9 (=C), 159.6 (C_{arom}). IR (KBr): ν = 3122, 2923, 2856, 1519, 1251, 1232, 1043, 970, 833 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{23}ON_3Na$: 308.1731; found 308.1732.

4.4.3. 1-(4-Methylphenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3ac).

White solid, hexane-EtOAc (7:3) as eluent, mp. 77-78 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.25-1.40 (m, 6H), 1.45-1.53 (m, 2H), 2.19-2.27 (m, 2H), 2.41 (s, 3H), 6.44 (d, *J* = 16.1 Hz, 1H), 6.50 (dt, *J* = 16.1 and 6.3 Hz, 1H), 7.27-7.32 (m, 2H), 7.57-7.62 (m, 2H), 7.82 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3),

21.0 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 32.9 (CH_2), 117.3 (=CH), 117.8 (=CH), 120.2 (2 × CH_{arom}), 130.1 (2 × CH_{arom}), 134.4 (=CH), 134.7 (C_{arom}), 138.6 (C_{arom}), 146.9 (=C). IR (KBr): ν = 3122, 2923, 2854, 1519, 1232, 1217, 1041, 975, 817, 738 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{23}N_3Na$: 292.1782; found 292.1781.

4.4.4. 1-(4-Fluorophenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3ae).

Light-brown solid, hexane-EtOAc (7:3) as eluent, mp. 71-73 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.23-1.42 (m, 6H), 1.44-1.53 (m, 2H), 2.18-2.28 (m, 2H), 6.43 (d, *J* = 16.1 Hz, 1H), 6.51 (dt, *J* = 16.1 and 6.3 Hz, 1H), 7.15-7.25 (m, 2H), 7.65-7.75 (m, 2H), 7.82 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 32.9 (CH_2), 116.6 (d, *J* = 23.7 Hz, 2 × CH_{arom}), 117.5 (=CH), 117.7 (=CH), 122.3 (d, *J* = 8.2 Hz, 2 × CH_{arom}), 133.3 (CH_{arom}), 134.6 (=CH), 147.2 (=C), 162.2 (d, *J* = 248.3 Hz, C_{arom}). IR (KBr): ν = 3124, 2925, 2856, 1519, 1224, 1041, 977, 839, 742 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{20}N_3FNa$: 296.1532; found 296.1531.

4.4.5. 1-(3-Acetoxyphenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3af).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 56-57 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.25-1.40 (m, 6H), 1.44-1.53 (m, 2H), 2.20-2.27 (m, 2H), 2.66 (s, 3H), 6.44 (d, *J* = 16.1 Hz, 1H), 6.53 (dt, *J* = 16.1 and 8.3 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.96-8.02 (m, 2H), 8.01 (s, 1H), 8.25-8.28 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.4 (CH_2), 26.5 (CH_3), 28.6 (CH_2), 28.7 (CH_2), 31.5 (CH_2), 32.7 (CH_2), 117.1 (=CH), 117.4 (=CH), 119.1 (CH_{arom}), 124.2 (CH_{arom}), 128.0 (CH_{arom}), 129.9 (CH_{arom}), 134.8 (=CH), 137.1 (C_{arom}), 138.1 (C_{arom}), 147.1 (=C), 196.5 (C=O). IR (KBr): ν = 3134, 2925, 2854, 1674, 1593, 1504, 1454, 1267, 1215, 1043, 968, 893, 806, 682 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{23}ON_3Na$: 320.1731; found 320.1730.

4.4.6. 1-(3-Cyanophenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3ag).

White solid, hexane-EtOAc (7:3) as eluent, mp. 52-53 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.26-1.40 (m, 6H), 1.46-1.53 (m, 2H), 2.22-2.28 (m, 2H), 6.44 (dt, *J* = 16.1 and 1.4 Hz, 1H), 6.56 (dt, *J* = 16.1 and 6.8 Hz, 1H), 7.64-7.74 (m, 2H), 7.89 (s, 1H), 8.01-8.07 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5 (CH_2), 28.8 (CH_2), 28.8 (CH_2), 31.6 (CH_2), 32.9 (CH_2), 114.0 (C_{arom}), 116.8 (=CH), 117.2 (=CH), 117.4 (≡C), 123.2 (CH_{arom}), 124.1 (CH_{arom}), 130.8 (CH_{arom}), 131.7 (CH_{arom}), 135.5 (=CH), 137.5 (C_{arom}), 147.6 (=C). IR (KBr): ν = 3130, 2925, 2854, 2235, 1587, 1487, 1217, 1043, 972, 893, 804, 680, 667 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{20}N_4Na$: 303.1580; found 303.1579.

4.4.7. 1-(3-Nitrophenyl)-4-[(E)-oct-1-enyl]-1H-1,2,3-triazole (3ah).

Light-yellow solid, hexane-EtOAc (7:3) as eluent, mp. 80-81 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.8 Hz, 3H), 1.27-1.44 (m, 6H), 1.46-1.53 (m, 2H), 2.22-2.28 (m, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.57 (dt, *J* = 15.8 and 6.8 Hz, 1H), 7.74 (t, *J* = 8.2 Hz, 1H), 7.98 (s, 1H), 8.17-8.21 (m, 1H), 8.26-8.30 (m, 1H), 8.57 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.6 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 33.0 (CH_2), 114.9 (CH_{arom}), 117.0 (=CH), 117.3 (=CH), 122.9 (CH_{arom}), 125.7 (CH_{arom}), 130.9 (CH_{arom}), 135.6 (=CH), 137.8 (C_{arom}), 147.8 (=C), 148.9 (C_{arom}). IR (KBr): ν = 3143, 2920, 2852, 1541, 1348, 1265, 1043, 966, 885, 800, 734, 704 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{20}O_2N_4Na$: 323.1478; found 323.1479.

4.4.8. 1-Phenyl-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (3ba).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 149-150 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 16.5 Hz, 1H), 7.26-7.31 (m, 1H), 7.34-7.40 (m, 2H), 7.42 (d, *J* = 16.5 Hz, 1H), 7.42-7.47 (m, 1H), 7.50-7.56 (m, 4H), 7.73-7.78 (m, 2H), 8.01 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 116.2 (=CH), 118.2 (=CH), 120.4 (2 × CH_{arom}), 126.5 (2 × CH_{arom}), 128.1 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.7 (2 × CH_{arom}), 131.3 (=CH), 136.6 (C_{arom}), 136.9 (C_{arom}), 146.8 (=C). IR (KBr): ν = 3130, 1504, 1232, 1043, 964,

756, 688 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{13}N_3Na$: 270.1001; found 270.1001.

4.4.9. 1-(4-Methoxyphenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (3bb).

White solid, hexane-EtOAc (7:3) as eluent, mp. 153-154 ºC. ^1H NMR (600 MHz, DMSO-d_6): δ = 3.84 (s, 3H), 7.14-7.18 (m, 2H), 7.26 (d, *J* = 16.5 Hz, 1H), 7.28-7.32 (m, 1H), 7.37 (d, *J* = 16.5 Hz, 1H), 7.38-7.42 (m, 2H), 7.60-7.64 (m, 2H), 7.81-7.85 (m, 2H), 8.87 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 55.5 (CH_3), 114.8 (2 × CH_{arom}), 117.0 (=CH), 119.9 (=CH), 121.5 (2 × CH_{arom}), 126.3 (2 × CH_{arom}), 127.8 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.9 (C_{arom}), 130.0 (=CH), 136.4 (C_{arom}), 145.9 (=C), 159.2 (C_{arom}). IR (KBr): ν = 3118, 1515, 1245, 1232, 1035, 1026, 962, 833, 815, 750, 704, 692 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{15}ON_3Na$: 300.1107; found 300.1106.

4.4.10. 1-(4-Methylphenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (3bc).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 156-157 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.14 (d, *J* = 16.6 Hz, 1H), 7.25-7.40 (m, 5H), 7.41 (d, *J* = 16.6 Hz, 1H), 7.49-7.54 (m, 2H), 7.60-7.65 (m, 2H), 7.98 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.1 (CH_3), 116.2 (=CH), 118.3 (=CH), 120.3 (2 × CH_{arom}), 126.5 (2 × CH_{arom}), 128.0 (CH_{arom}), 128.7 (2 × CH_{arom}), 130.2 (2 × CH_{arom}), 131.3 (=CH), 134.6 (C_{arom}), 136.6 (C_{arom}), 138.9 (C_{arom}), 146.5 (=C). IR (KBr): ν = 3120, 1517, 1215, 962, 839, 767, 750, 694 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{15}N_3Na$: 284.1158; found 284.1157.

4.4.11. 1-(2-Methylphenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (3bd).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 106-107 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 7.17 (d. *J* = 16.1 Hz, 1H), 7.26-7.31 (m, 1H), 7.32-7.48 (m, 7H), 7.51-7.55 (m, 2H), 7.76 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 17.9 (CH_3), 116.3 (=CH), 121.9 (=CH), 125.9 (CH_{arom}), 126.5 (2 × CH_{arom}), 126.8 (CH_{arom}), 128.0 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.8 (CH_{arom}), 131.0 (CH_{arom}), 131.5 (=CH), 133.6

(C_{arom}), 136.4 (C_{arom}), 136.7 (C_{arom}), 145.9 (=C). IR (KBr): ν = 3134, 1504, 1041, 966, 761, 707, 692 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{15}N_3Na$: 284.1158; found 284.1158.

4.4.12. 1-(3-Nitrophenyl)-4-[(E)-2-phenylethenyl]-1H-1,2,3-triazole (3bh).

Yellow solid, hexane-EtOAc (7:3) as eluent, mp. 124-125 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 16.5 Hz, 1H), 7.30-7.34 (m, 1H), 7.37-7.42 (m, 2H), 7.48 (d, *J* = 16.5 Hz, 1H), 7.53-7.57 (m, 2H), 7.77 (t, *J* = 8.2 Hz, 1H), 8.12 (s, 1H), 8.22-8.25 (m, 1H), 8.30-8.33 (m, 1H), 8.62 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 114.4 (CH_{arom}), 116.5 (=CH), 120.3 (=CH), 122.9 (CH_{arom}), 125.8 (CH_{arom}), 126.4 (2 × CH_{arom}), 128.0 (CH_{arom}), 128.7 (2 × CH_{arom}), 130.7 (=CH), 131.5 (CH_{arom}), 136.1 (C_{arom}), 137.0 (C_{arom}), 146.4 (=C), 148.4 (C_{arom}). IR (KBr): ν = 3139, 3085, 1537, 1494, 1346, 1217, 1045, 968, 883, 871, 798, 748, 734, 702, 686, 669 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{16}H_{12}O_2N_4Na$: 315.0854; found 315.0855.

4.4.13. 4-[(E)-5-Chloropent-1-enyl]-1-phenyl-1H-1,2,3-triazole (3ca).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 69-70 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.92-2.00 (m, 2H), 2.37-2.44 (m, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 6.84-6.51 (m, 2H), 7.40-7.44 (m, 1H), 7.48-7.53 (m, 2H), 7.70-7.74 (m, 2H), 7.88 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9 (CH_2), 31.6 (CH_2), 44.2 (CH_2), 117.7 (=CH), 119.2 (=CH), 120.3 (2 × CH_{arom}), 128.6 (CH_{arom}), 129.7 (2 × CH_{arom}), 131.8 (=CH), 136.9 (C_{arom}), 146.5 (=C). IR (KBr): ν = 3122, 2956, 1598, 1504, 1230, 1045, 970, 759, 688 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{14}N_3ClNa$: 270.0768; found 270.0768.

4.4.14. 4-[(E)-5-Chloropent-1-enyl]-1-(4-methoxyphenyl)-1H-1,2,3-triazole (3cb).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 76-77 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.94-2.00 (m, 2H), 2.38-2.44 (m, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.86 (s, 3H), 6.44-6.52 (m, 2H), 6.99-7.03 (m, 2H), 7.59-7.63 (m, 2H), 7.78 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 29.9 (CH_2), 31.7 (CH_2), 44.2 (CH_2), 55.6 (CH_3), 114.7 (2 × CH_{arom}),

117.9 (=CH), 119.3 (=CH), 122.0 (2 × CH_{arom}), 130.4 (C_{arom}), 131.7 (=CH), 146.3 (=C), 159.7 (C_{arom}). IR (KBr): ν = 3132, 2958, 2839, 1519, 1257, 1218, 1110, 1028, 970, 837, 815 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{16}ON_3ClNa$: 300.0874; found 300.0872.

4.4.15. 4-[(E)-5-Chloropent-1-enyl]-1-(4-methylphenyl)-1H-1,2,3-triazole (3cc).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 80-81 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.92-1.99 (m, 2H), 2.36-2.43 (m, 2H), 2.40 (s, 3H), 3.58 (t, *J* = 6.8 Hz, 2H), 6.47-6.50 (m, 2H), 7.26-7.31 (m, 2H), 7.56-7.61 (m, 2H), 7.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9 (CH_3), 29.8 (CH_2), 31.5 (CH_2), 44.1 (CH_2), 117.6 (=CH), 119.0 (=CH), 120.1 (2 × CH_{arom}), 130.0 (2 × CH_{arom}), 131.7 (=CH), 134.5 (C_{arom}), 138.6 (C_{arom}), 146.1 (=C). IR (KBr): ν = 3149, 3049, 2925, 1515, 1444, 1265, 1230, 1045, 968, 817, 746 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{16}N_3ClNa$: 284.0924; found 284.0923.

4.4.16. 4-[(E)-5-Chloropent-1-enyl]-1-(4-fluorophenyl)-1H-1,2,3-triazole (3ce).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 80-82 ºC. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.91-2.00 (m, 2H), 2.36-2.44 (m, 2H), 3.59 (t, *J* = 6.3 Hz, 2H), 6.46-6.50 (m, 2H), 7.16-7.23 (m, 2H), 7.66-7.73 (m, 2H), 7.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.9 (CH_2), 31.6 (CH_2), 44.3 (CH_2), 116.6 (d, *J* = 22.7 Hz, 2 × CH_{arom}), 117.9 (=CH), 119.1 (=CH), 122.3 (d, *J* = 9.3 Hz, 2 × CH_{arom}), 132.0 (=CH), 133.2 (d, *J* = 2.0 Hz, C_{arom}), 146.6 (=C), 162.2 (d, *J* = 249.3 Hz, C_{arom}). IR (KBr): ν = 3126, 1504, 1444, 1230, 1197, 1047, 972, 833, 744 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{13}N_3FClNa$: 288.0674; found 288.0673.

4.4.17. 1-(3-Acetoxyphenyl)-4-[(E)-5-chloropent-1-enyl]-1H-1,2,3-triazole (3cf).

Off-white solid, hexane-EtOAc (7:3) as eluent, mp. 90-91 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.95-2.02 (m, 2H), 2.40-2.47 (m, 2H), 2.68 (s, 3H), 3.61 (t, *J* = 6.8 Hz, 2H), 6.52 (d, *J* = 16.5 Hz, 1H), 6.54 (dt, *J* = 16.5 and 6.2 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H),

7.97 (s, 1H), 7.99-8.04 (m, 2H), 8.27 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.7 (CH_3), 29.9 (CH_2), 31.6 (CH_2), 44.2 (CH_2), 117.6 (=CH), 118.9 (=CH), 119.4 (CH_{arom}), 124.6 (CH_{arom}), 128.3 (CH_{arom}), 130.2 (CH_{arom}), 132.5 (=CH), 137.3 (C_{arom}), 138.4 (C_{arom}), 146.8 (=C), 196.7 (C=O). IR (KBr): ν = 3128, 2937, 1681, 1591, 1494, 1450, 1359, 1265, 1045, 999, 966, 792, 686 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{15}H_{16}ON_3ClNa$: 312.0874; found 312.0875.

4.4.18. 4-[(E)-5-Chloropent-1-enyl]-1-(3-cyanophenyl)-1H-1,2,3-triazole (3cg).

Light-brown solid, hexane-EtOAc (7:3) as eluent, mp. 62-63 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.95-2.02 (m, 2H), 2.41-2.47 (m, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 6.50 (d, *J* = 16.5 Hz, 1H), 6.55 (dt, *J* = 16.5 and 6.8 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.71-7.75 (m, 1H), 7.90 (s, 1H), 8.01-8.05 (m, 1H), 8.05-8.07 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 29.9 (CH_2), 31.5 (CH_2), 44.2 (CH_2), 114.1 (C_{arom}), 117.2 (=CH), 117.4 (≡C), 118.7 (=CH), 123.3 (CH_{arom}), 124.2 (CH_{arom}), 130.9 (CH_{arom}), 131.9 (CH_{arom}), 132.9 (=CH), 137.5 (C_{arom}), 147.1 (=C). IR (KBr): ν = 3134, 2233, 1587, 1487, 1444, 1043, 999, 966, 794, 680 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{14}H_{13}N_4ClNa$: 295.0722; found 295.0723.

4.4.19. 4-[(E)-5-Chloropent-1-enyl]-1-(3-nitrophenyl)-1H-1,2,3-triazole (3ch).

Light-yellow solid, hexane-EtOAc (7:3) as eluent, mp. 100-101 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.96-2.02 (m, 2H), 2.42-2.48 (m, 2H), 3.61 (t, *J* = 6.8 Hz, 2H), 6.51 (d, *J* = 16.4 Hz, 1H), 6.57 (dt, *J* = 16.4 and 6.8 Hz, 1H), 7.75 (t, *J* = 8.2 Hz, 1H), 8.00 (s, 1H), 8.18-8.21 (m, 1H), 8.28-8.31 (m, 1H), 8.58 (t, *J* = 2.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 29.9 (CH_2), 31.6 (CH_2), 44.2 (CH_2), 114.9 (CH_{arom}), 117.3 (=CH), 118.6 (=CH), 123.0 (CH_{arom}), 125.7 (CH_{arom}), 131.0 (=CH), 133.0 (CH_{arom}), 137.6 (C_{arom}), 147.2 (=C), 148.9 (C_{arom}). IR (KBr): ν = 3151, 3093, 1537, 1494, 1346, 1224, 1047, 964, 883, 871, 798, 734, 669 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{13}H_{13}O_2N_4ClNa$: 315.0620; found 315.0621.

4.4.20. 1-Phenyl-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6aa).

Yellow liquid, hexane-EtOAc (95:5) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.36-1.51 (m, 4H), 2.31-2.37 (m, 2H), 6.63 (t, *J* = 7.4 Hz, 1H), 7.39-7.43 (m, 1H), 7.48-7.54 (m, 2H), 7.71 (s, 1H), 7.72-7.77 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 13.9 (CH_3), 22.3 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 117.1 (=CH), 120.0 (2 × CH_{arom}), 128.2 (CH_{arom}), 129.5 (2 × CH_{arom}), 137.0 (C_{arom}), 149.3 (=CH), 152.4 (=C). IR (KBr): ν = 2954, 2925, 2856, 1514, 1247, 1222, 1045, 877, 839 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{25}N_3NaSi$: 322.1707; found 322.1706.

4.4.21.

1-(4-Methoxyphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6ab).

Yellow liquid, hexane-EtOAc (9:1) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.36-1.50 (m, 4H), 2.30-2.37 (m, 2H), 3.84 (s, 3H), 6.62 (br s, 1H), 6.97-7.02 (m, 2H), 7.58-7.70 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.9 (Me_3Si), 14.0 (CH_3), 22.4 (CH_2), 31.9 (2 × CH_2), 55.5 (CH_3), 114.6 (2 × CH_{arom}), 117.5 (=CH), 121.8 (2 × CH_{arom}), 129.8 (=C), 130.7 (C_{arom}), 149.1 (=CH), 152.4 (=C), 159.5 (C_{arom}). IR (KBr): ν = 2956, 2929, 2856, 1595, 1514, 1463, 1253, 1222, 1039, 987, 877, 833, 759 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{27}ON_3NaSi$: 352.1810; found 352.1811.

4.4.22. 1-(4-Methylphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6ac).

Yellowish liquid, hexane-EtOAc (95:5) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.28 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.35-1.49 (m, 4H), 2.30-2.36 (m, 2H), 2.37 (s, 3H), 6.61 (t, *J* = 7.6 Hz, 1H), 7.24-7.28 (m, 2H), 7.58-7.62 (m, 2H), 7.70 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 13.8 (CH_3), 20.8 (CH_3), 22.2 (CH_2), 31.7 (CH_2), 31.7 (CH_2), 117.0 (=CH), 119.8 (2 × CH_{arom}), 129.6 (=C), 129.9 (2 × CH_{arom}), 134.7 (C_{arom}), 138.0 (C_{arom}), 148.9 (=CH), 152.3 (=C). IR (KBr): ν = 2954, 2925, 2856, 1515, 1247, 1222, 1045, 1028, 987, 877, 839, 758 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd

for $C_{18}H_{27}N_3NaSi$: 336.1861; found 336.1862.

4.4.23.

1-(2-Methylphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6ad).

Yellowish liquid, hexane-EtOAc (95:5) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.93 (t, *J* = 7.2 Hz, 3H), 1.36-1.51 (m, 4H), 2.23 (s, 3H), 2.32-2.37 (m, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 7.29-7.41 (m, 4H), 7.46 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.8 (Me_3Si), 14.0 (CH_3), 17.9 (CH_3), 22.5 (CH_2), 31.9 (CH_2), 31.9 (CH_2), 120.9 (=CH), 125.9 (CH_{arom}), 126.7 (CH_{arom}), 129.4 (=C), 129.5 (CH_{arom}), 131.3 (CH_{arom}), 133.6 (C_{arom}), 136.7 (C_{arom}), 149.3 (=CH), 151.4 (=C). IR (KBr): ν = 2954, 2927, 2856, 1500, 1463, 1247, 1043, 877, 840, 761 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{27}N_3NaSi$: 336.1861; found 336.1861.

4.4.24. 1-(4-Fluorophenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6ae).

Yellowish liquid, hexane-EtOAc (9:1) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.35-1.49 (m, 4H), 2.30-2.36 (m, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 7.15-7.21 (m, 2H), 7.69-7.74 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 13.8 (CH_3), 22.3 (CH_2), 31.7 (2 × CH_2), 116.4 (d, *J* = 23.1 Hz, 2 × CH_{arom}), 117.2 (=CH), 122.0 (d, *J* = 8.7 Hz, 2 × CH_{arom}), 129.5 (=C), 133.3 (C_{arom}), 149.3 (=CH), 152.7 (=C), 161.9 (d, *J* = 248.5 Hz, C_{arom}). IR (KBr): ν = 2956, 2927, 2856, 1514, 1245, 1222, 1045, 877, 839 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{24}N_3FNaSi$: 340.1611; found 340.1612.

4.4.25.

1-(3-Acetoxyphenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6af).

Yellowish liquid, hexane-EtOAc (8:2) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.29 (s, 9H), 0.93 (t, *J* = 6.8 Hz, 3H), 1.36-1.50 (m, 4H), 2.31-2.38 (m, 2H), 2.66 (s, 3H), 6.62 (t, *J* = 7.5 Hz, 1H), 7.58-7.65 (m, 1H), 7.89 (s, 1H), 7.94-7.99 (m, 1H), 8.00-8.05 (m, 1H), 8.29 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.8 (Me_3Si), 14.0 (CH_3), 22.4

(CH_3), 26.7 (CH_2), 31.8 (CH_2), 31.8 (CH_2), 117.2 (=CH), 119.3 (CH_{arom}), 124.3 (CH_{arom}), 127.9 (CH_{arom}), 129.6 (=C), 130.1 (CH_{arom}), 137.5 (C_{arom}), 138.3 (C_{arom}), 149.6 (=CH), 153.1 (=C), 196.7 (C=O). IR (KBr): ν = 2956, 2927, 2858, 1693, 1591, 1448, 1357, 1259, 1224, 1045, 877, 840, 792, 686 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{27}ON_3NaSi$: 364.1810; found 364.1811.

4.4.26. 1-(3-Cyanophenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6ag). White solid, hexane-EtOAc (9:1) as eluent, mp. 98-99 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.27 (s, 9H), 0.94 (t, *J* = 6.8 Hz, 3H), 1.35-1.51 (m, 4H), 2.31-2.38 (m, 2H), 6.62 (t, *J* = 7.5 Hz, 1H), 7.63-7.72 (m, 2H), 7.75 (s, 1H), 8.03-8.08 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.8 (Me_3Si), 14.0 (CH_3), 22.4 (CH_3), 31.8 (CH_2), 31.9 (CH_2), 114.0 (CH_{arom}), 116.8 (=CH), 117.5 (≡C), 123.1 (CH_{arom}), 124.1 (CH_{arom}), 129.4 (=C), 130.8 (CH_{arom}), 131.5 (CH_{arom}), 137.7 (C_{arom}), 150.1 (=CH), 153.4 (=C). IR (KBr): ν = 3149, 2954, 2929, 2233, 1732, 1589, 1487, 1247, 1226, 1051, 1004, 883, 839, 758, 682 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{18}H_{24}N_4NaSi$: 347.1662; found 347.1661.

4.4.27. 1-(3-Nitrophenyl)-4-[(Z)-1-(trimethylsilyl)hex-1-enyl]-1H-1,2,3-triazole (6ah). Yellow solid, hexane-EtOAc (9:1) as eluent, mp. 100-101 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.28 (s, 9H), 0.94 (t, *J* = 6.8 Hz, 3H), 1.36-1.51 (m, 4H), 2.32-2.38 (m, 2H), 6.62 (t, *J* = 7.6 Hz, 1H), 7.72-7.76 (m, 1H), 7.84 (s, 1H), 8.19-8.23 (m, 1H), 8.25-8.29 (m, 1H), 8.57-8.59 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.8 (Me_3Si), 14.0 (CH_3), 22.4 (CH_3), 31.8 (CH_2), 31.9 (CH_2), 114.8 (CH_{arom}), 116.9 (=CH), 122.7 (CH_{arom}), 125.7 (CH_{arom}), 129.4 (=C), 130.8 (CH_{arom}), 137.9 (C_{arom}), 148.9 (C_{arom}), 150.1 (=CH), 153.6 (=C). IR (KBr): ν = 3139, 3101, 2952, 2925, 2860, 1539, 1350, 1244, 1228, 1043, 879, 839, 808, 736, 669 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{17}H_{24}O_2N_4NaSi$: 367.1560; found 367.1560.

4.4.28. 1-Phenyl-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6ba). Off-white solid, hexane-EtOAc (9:1) as eluent, mp. 111-112 ºC. ^1H NMR (600 MHz,

$CDCl_3$): δ = 0.07 (s, 9H), 7.28-7.37 (m, 5H), 7.40-7.45 (m, 1H), 7.50-7.55 (m, 2H), 7.76-7.80 (m, 2H), 7.84 (s, 1H), 7.90 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 117.5 (=CH), 120.3 (2 × CH_{arom}), 127.4 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.4 (CH_{arom}), 128.5 (2 × CH_{arom}), 129.7 (2 × CH_{arom}), 133.8 (C_{arom}), 137.1 (C_{arom}), 139.4 (=C), 146.1 (=CH), 152.4 (=C). IR (KBr): ν = 2952, 1598, 1500, 1417, 1247, 1224, 1047, 1035, 840, 756, 690 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{21}N_3NaSi$: 342.1393; found 342.1394.

4.4.29.

1-(4-Methoxyphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bb).

White solid, hexane-EtOAc (9:1) as eluent, mp. 100-102 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 3.86 (s, 3H), 7.00-7.04 (m, 2H), 7.28-7.37 (m, 5H), 7.65-7.69 (m, 2H), 7.81 (s, 1H), 7.83 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.8 (Me_3Si), 55.6 (CH_3), 114.7 (2 × CH_{arom}), 117.7 (=CH), 121.9 (2 × CH_{arom}), 127.4 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.6 (C_{arom}), 133.9 (C_{arom}), 139.5 (=C), 145.9 (=CH), 152.2 (=C), 159.6 (C_{arom}). IR (KBr): ν = 2956, 1515, 1255, 1226, 1043, 839, 754, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{20}ON_3NaSi$: 369.1264; found 369.1265.

4.4.30.

1-(4-Methylphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bc).

White solid, hexane-EtOAc (9:1) as eluent, mp. 112-113 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 2.46 (s, 3H), 7.27-7.37 (m, 7H), 7.62-7.67 (m, 2H), 7.81-7.87 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.8 (Me_3Si), 21.1 (CH_3), 117.5 (=CH), 120.2 (2 × CH_{arom}), 127.4 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.2 (2 × CH_{arom}), 133.9 (C_{arom}), 134.9 (C_{arom}), 138.5 (C_{arom}), 139.5 (=C), 145.9 (=CH), 152.3 (=C). IR (KBr): ν = 2954, 1519, 1247, 1224, 1031, 989, 840, 817, 754, 698, 667 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{20}N_3NaSi$: 353.1315; found

353.1316.

4.4.31.

1-(2-Methylphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bd). Yellowish liquid, hexane-EtOAc (95:5) as eluent. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 2.24 (s, 3H), 7.25-7.41 (m, 9H), 7.65 (s, 1H), 7.89 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.6 (Me_3Si), 17.7 (CH_3), 121.1 (=CH), 125.7 (CH_{arom}), 126.6 (CH_{arom}), 127.3 (CH_{arom}), 127.7 (2 × CH_{arom}), 128.3 (2 × CH_{arom}), 129.5 (CH_{arom}), 131.2 (CH_{arom}), 133.5 (C_{arom}), 133.5 (C_{arom}), 136.4 (C_{arom}), 139.3 (=C), 145.8 (=CH), 151.1 (=C). IR (KBr): ν = 2952, 1498, 1247, 1045, 840, 761, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{20}N_3NaSi$: 353.1315; found 353.1314.

4.4.32.

1-(4-Fluorophenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6be). White solid, hexane-EtOAc (9:1) as eluent, mp. 123-124 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 7.18-7.24 (m, 2H), 7.28-7.37 (m, 5H), 7.72-7.77 (m, 2H), 7.82 (s, 1H), 7.86 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 116.6 (d, *J* = 23.1 Hz, 2 × CH_{arom}), 117.6 (=CH), 122.2 (d, *J* = 8.6 Hz, 2 × CH_{arom}), 127.5 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 133.4 (C_{arom}), 133.7 (C_{arom}), 139.3 (=C), 146.2 (=CH), 152.6 (=C), 162.2 (d, *J* = 248.5 Hz, C_{arom}). IR (KBr): ν = 3112, 1514, 1228, 1053, 835, 761 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{20}N_3FNaSi$: 360.1299; found 360.1300.

4.4.33.

1-(3-Acetoxyphenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bf). White solid, hexane-EtOAc (8:2) as eluent, mp. 112-113 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.08 (s, 9H), 2.69 (s, 3H), 7.29-7.38 (m, 5H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.83 (s, 1H), 7.99 (s, 1H), 7.99-8.03 (m, 1H), 8.06-8.09 (m, 1H), 8.32 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 26.7 (CH_3), 117.3 (=CH), 119.3 (CH_{arom}), 124.5

(CH_{arom}), 127.5 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.1 (CH_{arom}), 128.5 (2 × CH_{arom}), 130.1 (CH_{arom}), 133.7 (C_{arom}), 137.5 (C_{arom}), 138.4 (C_{arom}), 139.3 (=C), 146.3 (=CH), 152.9 (=C), 196.7 (C=O). IR (KBr): ν = 2954, 1693, 1591, 1488, 1448, 1357, 1259, 1226, 1047, 842, 792, 756, 698 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{21}H_{23}ON_3NaSi$: 384.1498; found 384.1499.

4.4.34.

1-(3-Cyanophenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bg). White solid, hexane-EtOAc (9:1) as eluent, mp. 182-184 ºC. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 7.29-7.39 (m, 5H), 7.66-7.74 (m, 2H), 7.82 (s, 1H), 7.94 (s, 1H), 8.07-8.12 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 114.1 (C_{arom}), 117.0 (=CH), 117.5 (≡C), 123.3 (CH_{arom}), 124.2 (CH_{arom}), 127.6 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.8 (CH_{arom}), 131.7 (CH_{arom}), 133.5 (C_{arom}), 137.6 (C_{arom}), 139.1 (=C), 146.7 (=CH), 153.3 (=C). IR (KBr): ν = 3138, 2235, 1589, 1498, 1444, 1245, 1228, 1047, 842, 802, 754, 696, 677 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{20}H_{20}N_4NaSi$: 367.1350; found 367.1349.

4.4.35.

1-(3-Nitrophenyl)-4-[(Z)-2-phenyl-1-(trimethylsilyl)ethenyl]-1H-1,2,3-triazole (6bh). Light-brown solid, hexane-EtOAc (8:2) as eluent, mp. 200 ºC (dec). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.08 (s, 9H), 7.30-7.39 (m, 5H), 7.74-7.79 (m, 1H), 7.83 (s, 1H), 8.01 (s, 1H), 8.22-8.27 (m, 1H), 8.29-8.34 (m, 1H), 8.61-8.64 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 0.7 (Me_3Si), 114.9 (CH_{arom}), 117.1 (=CH), 122.8 (CH_{arom}), 125.7 (CH_{arom}), 127.7 (CH_{arom}), 127.9 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 130.9 (CH_{arom}), 133.5 (C_{arom}), 137.8 (C_{arom}), 139.1 (C_{arom}), 146.8 (=CH), 148.9 (C_{arom}), 153.4 (=C). IR (KBr): ν = 3138, 1535, 1488, 1350, 1245, 1226, 1043, 889, 844, 806, 756, 734, 711, 696 cm^{-1}. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{19}H_{20}O_2N_4NaSi$: 387.1248; found 387.1247.

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18 The ^{1}H NMR spectrum of 1-phenyl-4-[(*E*)-hex-1-enyl]-1*H*-1,2,3-triazole exhibits the alkenyl protons at δ = 6.46 (d, *J* = 15.8 Hz, 1H) and 5.52 (dt, *J* = 15.8 and 6.8 Hz, 1H) ppm.

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Chapter III

Simple preparation of aryltributylstannanes and its application to one-pot synthesis of diaryl ketones

Abstract

Transfer of aryl group from boron to tin can be achieved by simple treatment of arylboronic acids with tributyltin methoxide at 100 ºC for 1 h under neat conditions. The resulting aryltributylstannanes are applicable to one-pot synthesis of diaryl ketones. Thus, Pd-catalyzed cross-coupling reaction with aroyl chlorides is allowed to proceed without isolation step to produce the corresponding diaryl ketones in good to high yields.

1. Introduction

Arylstannanes are versatile building blocks in synthetic organic chemistry, especially for Stille coupling reaction,[1] due to their air and moisture stability and tolerance for various functional groups. A variety of synthetic methods have been developed for preparation of arylstannanes. The methodology for preparing arylstannanes can be divided into four categories: (1) stannylation of aryl halides via a halogen-metal exchange/transmetallation sequence,[2] (2) stannylation of aryl halides via Pd-catalyzed coupling with hexaorganyl distannane,[3] (3) stannylation of aryne intermediates,[4] (4) stannylation of aryl halides or aryl ammonium salts via radical nucleophilic substitution of triorganostannyl anions.[5] These strategies involve the use of air and moisture sensitive organometallic compounds, expensive reagents, or intractable materials. Thus, it is desirable to make the procedure as simple as possible, as well as to reduce the cost as low as possible. In particular, the development of a straightforward route from readily available materials would allow for reduction of energy consumption and waste

production and be applicable to one-pot synthesis via arylstannane. We recently reported the preparation of (*E*)-alk-1-enyltributylstannanes via a hydroboration/transmetallation one-pot sequence, in which (*E*)-alk-1-enyl group transferred from boron to tin with retention of the double bond geometry upon inhibition of radical species.[6] Prompted by our continuous interest in transfer of organyl group from boron to tin, I envisaged preparing arylstannanes from arylboronic acids which are stable under air and commercially available. Herein, I disclose a straightforward procedure for the preparation of aryltributylstannanes under solvent-free conditions at 100 ºC for 1 h. The subsequent Pd-catalyzed cross-coupling reaction with aroyl chlorides has been successfully performed in a one-pot manner to demonstrate the synthetic utility of the present procedure.

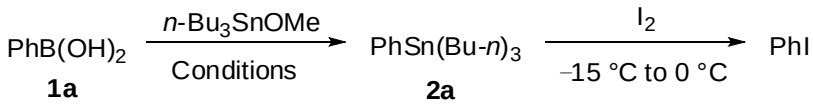
2. Results and discussion

Our study was initiated by the model reaction between phenylboronic acid (**1a**) and tributyltin methoxide (*n*-Bu_3SnOMe) to optimize the reaction conditions under argon atmosphere. Formation of phenyltributylstannane (**2a**) was ascertained by treatment of the reaction mixture with iodine. Thus, product **2a** undergoes iododestannylation to give iodobenzene; by comparison, starting material **1a** does not undergo iododeboronation in the absence of base.[7] The amount of **2a** can be estimated by the determination of iodobenzene employing GC analysis. Various conditions were screened, and the results are summarized in Table 1. Initially, the reaction of **1a** with an equimolar amount of *n*-Bu_3SnOMe was carried out in THF at room temperature for 2 h. The reaction mixture was then treated with a solution of iodine in THF to give iodobenzene in only 3% yield, indicating that the desired reaction scarcely proceeded under the conditions described above (Table 1, entry 1). Raising the temperature to 60 ºC, iodobenzene was formed in 39% yield for 2 h and 58% yield for 4 h, respectively (Table 1, entries 2 and 3). These results led us to examine the reaction in other solvents at different temperature. When the reaction was carried out in 1,2-dichloroethane (DCE) at 80 ºC for 3 h, the yield was dramatically increased to 86% (Table 1, entry 6). Moreover, conducting the reaction in

toluene at 100 ºC for 3 h led to an improved yield of 99% (Table 1, entry 10). Under similar conditions, iodobenzene was formed in 63% yield at 60 ºC, 84% yield at 80 ºC, and 92% yield at 100 ºC, respectively (Table 1, entries 7-9). The reaction appeared to be sensitive to temperature rather than solvent. I was pleased to find that in the absence of solvent the reaction proceeded at 100 ºC to give iodobenzene in 99% yield after only 1 h (Table 1, entry 13). Meanwhile, lowering the reaction temperature to 80 ºC led to a reduced yield of 93% even after 3 h (Table 1, entry 14).

Table 1

Optimization of reaction conditions for preparation of phenyltributylstannane from phenylboronic acid[a]

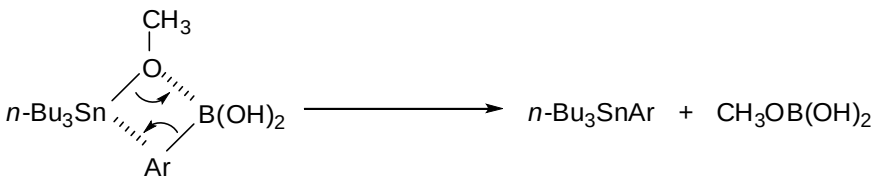


Entry	Conditions			Yield (%)[b]
	Solvent	Temp (ºC)	Time (h)	
1	THF	rt	2	3
2	THF	60	2	39
3	THF	60	4	58
4	DCE	60	2	43
5	DCE	80	2	81
6	DCE	80	3	86
7	Toluene	60	2	63
8	Toluene	80	2	84
9	Toluene	100	2	92
10	Toluene	100	3	99
11	None	100	3	99
12	None	100	2	99
13	None	100	1	99
14	None	80	3	93

[a] Reaction conditions: **1a** (1 mmol), *n*-Bu_3SnOMe (1 mmol), solvent (4 mL), under argon.

[b] Determined by GC analysis.

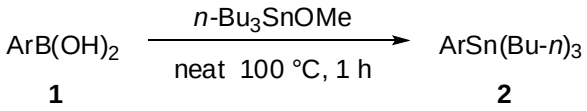
I next extended the scope of the substrate to various arylboronic acids **1** bearing electron-donating and electron-withdrawing groups under the optimized conditions, and the products **2** were isolated by column chromatography on silica gel (Table 2, entries 1-8). The model reaction of **1a** led to the isolation of product **2a** in 85% yield (Table 2, entry 1). Similarly, 4-methoxy-, 4-methyl-, 2-methyl- and 4-fluorophenylboronic acid (**1b**-**e**) were converted into the corresponding products **2b-e** in yields ranging from 60% to 82% (Table 2, entries 2-5). The present reaction tolerated functional groups such as bromo, acyl and nitro groups on the phenyl ring, leading to the desired products **2f-h** in moderate yields (Table 2, entries 6-8). It was strange that the yield of **2c** was lower than those of **2b** and **2e**, despite the para-position of methyl substituent on the phenyl ring. I experienced that organotributylstannane was sometimes unstable for column chromatography on silica gel. To our delight, using column chromatography on aluminium oxide (basic) improved the isolated yields of products **2a-e** up to 81-92% (Table 2, entries 9-13). The yield of **2f** was also increased to 64% (Table 2, entry 14), whereas the same isolation did not give products **2g** and **2h** at all due to their base-sensitive functionalities (Table 2, entries 15 and 16). The reactions of 1- and 2-naphthylboronic acid (**1i** and **1j**) proceeded efficiently to afford the corresponding products **2i** and **2j** in good isolated yields (Table 2, entries 17 and 18). Although ortho-methyl substituent on the phenyl ring showed no steric hindrance in the reaction, sterically more hindered 2,6-dimethlphenylboronic acid failed to generate the expected product. Boron generally acts as a Lewis acid and has a strong affinity of oxygen, while *n*-Bu_3SnOMe tends to give a five-coordinate complex.[1c] Accordingly, transfer of aryl group from boron to tin might proceed via a four-centre transition state as shown in Scheme 1.



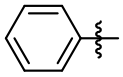
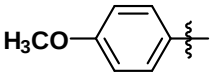
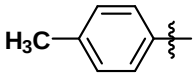
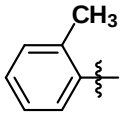
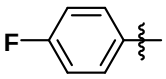
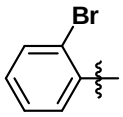
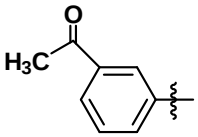
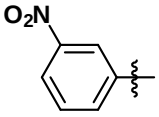
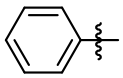
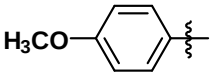
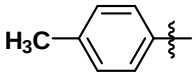
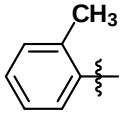
Scheme 1 Proposed mechanism for the formation of aryltributylstannane

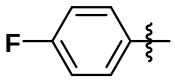
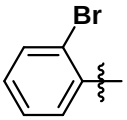
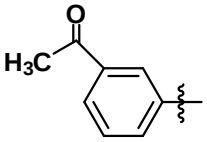
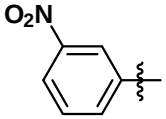
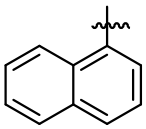
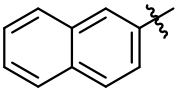
Table 2

Preparation of aryltributylstannanes from arylboronic acids[a]



1 **2**

Entry	Ar	Product	Yield (%)[b]
1		2a	85[c]
2		2b	73[c]
3		2c	60[c]
4		2d	61[c]
5		2e	82[c]
6		2f	50[c]
7		2g	72[c]
8		2h	60[c]
9		2a	92[d]
10		2b	91[d]
11		2c	81[d]
12		2d	92[d]

Entry	Ar	Product	Yield (%)[b]
13		2e	90[d]
14		2f	64[d]
15		2g	0[d]
16		2h	0[d]
17		2i	85[d]
18		2j	87[d]

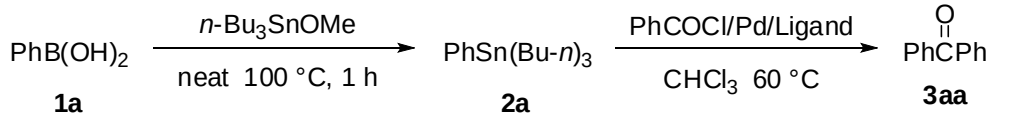
[a] Reaction conditions: **1** (1 mmol), *n*-Bu_3SnOMe (1 mmol), under argon.
[b] Isolated yields.
[c] Isolated by column chromatography on silica gel.
[d] Isolated by column chromatography on basic aluminium oxide.

In an effort to demonstrate the synthetic utility of the present method for preparing aryltributylstannanes **2**, I investigated one-pot synthesis of diaryl ketones which are significant building blocks in the synthesis of biologically active compounds.[8] Among synthetic methodologies for the formation of diaryl ketones, one of the most important and efficient methods is the transition-metal-catalyzed cross-coupling reaction of organometallic reagents.[9-11] An important characteristic of the Stille coupling is that the cross-coupling reaction proceeds without any base. Meanwhile, use of base is essential for Suzuki-Miyaura type coupling and the cross-coupling reaction of arylboronic acid with acid chloride requires harsh conditions[12] unless Pd catalyst with a unique ligand is employed.[9y] Based on the reaction conditions in the literature,[10c] the cross-coupling

reaction of phenyltributylstannane (**2a**) with benzoyl chloride was examined as a model reaction. Thus, the reaction between phenylboronic acid (**1a**) and *n*-Bu_3SnOMe was carried out at 100 ºC for 1 h after which the cross-coupling reaction with benzoyl chloride was conducted under Pd catalytic system in $CHCl_3$ as solvent at 60 ºC for 4 h under argon atmosphere. Different Pd sources and ligands were screened, and the results are summarized in Table 3. Among the Pd sources tested, $Pd(OAc)_2$ proved to be the best Pd precursor for the one-pot, two-step reaction (Table 3, entry 4).[13] It was also found that the same reaction proceeded to completion in 2 h (Table 3, entry 5). Alternatively, use of a combination of $PdCl_2$ and tri(2-furyl)phosphine as the catalytic system gave a far superior result to other combinations employed (Table 3, entry 8).

Table 3

Optimization of reaction conditions for one-pot synthesis of diphenylmethanone via transmetallation[a] followed by Stille coupling[b]



Entry	Pd source	Ligand	Yield (%)[c]
1	$PdCl_2(PPh_3)_2$	—	73
2	$PdCl_2$(dppf)	—	44
3	$Pd_2(dba)_3$	—	27[d]
4	$Pd(OAc)_2$	—	93
5	$Pd(OAc)_2$	—	94[e]
6	$PdCl_2$	—	29
7	$PdCl_2$	Ph_3P	1
8	$PdCl_2$	$(2\text{-Furyl})_3P$	84
9	$PdCl_2$	$(4\text{-}CH_3OC_6H_4)_3P$	51
10	$Pd(OAc)_2$	Ph_3P	5
11	$Pd(OAc)_2$	$(2\text{-Furyl})_3P$	46
12	$Pd(OAc)_2$	$(4\text{-}CH_3OC_6H_4)_3P$	26

[a] Reaction conditions: **1a** (1 mmol), *n*-Bu_3SnOMe (1 mmol), under argon.

[b] Reaction conditions: PhCOCl (1 mmol), Pd source (0.01 mmol), ligand (0.02 mmol), $CHCl_3$ (4 mL), 4 h, under argon.

[c] Determined by GC analysis.

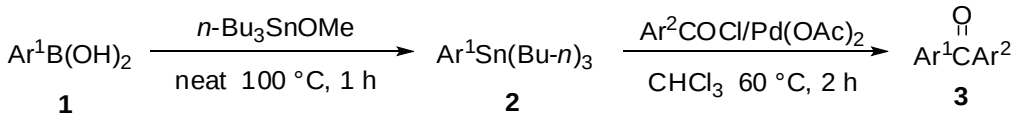
[d] $Pd_2(dba)_3$ (0.005 mmol).
[e] For 2 h.

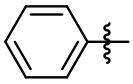
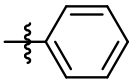
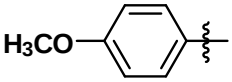
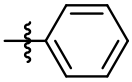
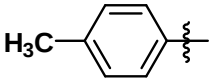
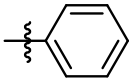
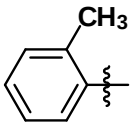
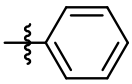
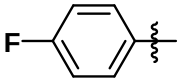
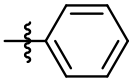
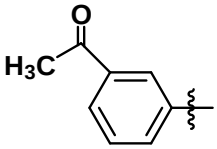
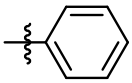
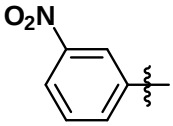
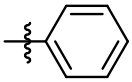
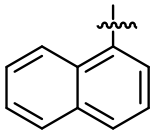
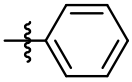
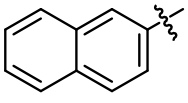
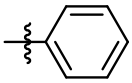
With optimized reaction conditions in hand (Table 3, entry 4), I evaluated a range of aryltributylstannanes **2**, prepared from arylboronic acids **1**, for their performance in the cross-coupling reaction with benzoyl chloride. Compounds **2** bearing both electron-donating and electron-withdrawing groups on the phenyl ring were good coupling partners in this transformation. A sterically hindered 2-methylphenyltributylstannane (**2d**) could react efficiently, giving (2-methylphenyl)(phenyl)methanone (**3da**) in 87% yield (Table 4, entry 4). Both 1-naphthyltributylstannane (**2i**) and 2-naphthyltributylstannane (**2j**) also participated in the cross-coupling reaction to afford the corresponding products **3i** and **j** in 89% and 85% yields, respectively (Table 4, entries 8 and 9). To understand the scope and generality of the one-pot synthesis of diaryl ketones, I examined the cross-coupling with other aroyl chlorides. The reaction of phenyltributylstannane (**2a**) with 4-methybenzoyl chloride proceeded smoothly to produce (4-methylphenyl)(phenyl)methanone (**3ac**) in 82% yield (Table 4, entry 10), whereas under the same conditions the reaction with 4-chlorobenzoyl chloride resulted in a 66% yield of (4-chlorophenyl)(phenyl)methanone (**3ak**) (Table 4, entry 11). Using $PdCl_2$ and tri(2-furyl)phosphine as the catalytic system instead of $Pd(OAc)_2$ was found to increase the yield of product **3ak** to 81% (Table 4, entry 12). Similar results were obtained with regard to 2-furoyl chloride and 2-thiophenecarbonyl chloride (Table 4, entries 13-16). In case of the reaction between 4-methylphenyltributylstannane (**2c**) and 4-methylbenzoyl chloride, however, no improvement in yield was observed (Table 4, entries 17 and 18). It is worth noting that a combination of **2** and aroyl chloride to furnish the same product affected the yield of product. For example, the cross-coupling reaction of **2c** with 2-methylbenzoyl chloride gave a higher yield of (2-methylphenyl)(4-methylphenyl)methanone (**3cd**) compared with that of **3d** with 4-methylbenzoyl chloride (Table 4, entries 19 and 21). In the cross-coupling reaction of **2** with aroyl chloride both of which consist of any one of 4-methylphenyl, 2-methylphenyl, or 4-fluorophenyl group, the corresponding diaryl

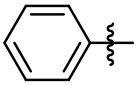
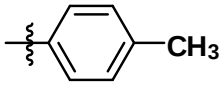
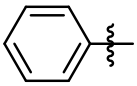
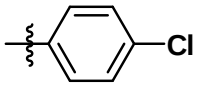
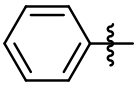
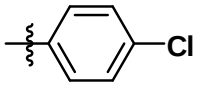
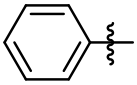
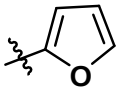
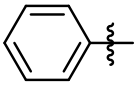
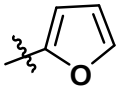
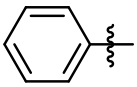
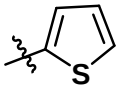
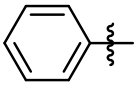
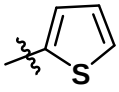
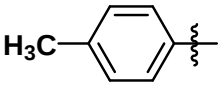
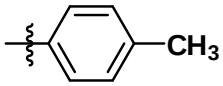
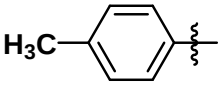
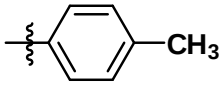
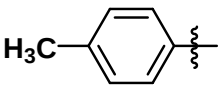
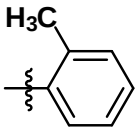
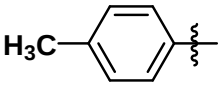
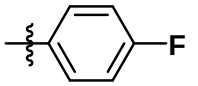
ketones were obtained in good to high yields (Table 4, entries 19, 20, and 22-26), except for two cases (Table 4, entries 17 and 21).

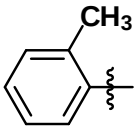
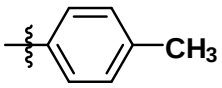
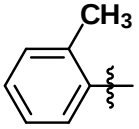
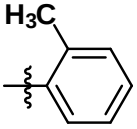
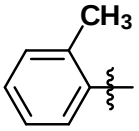
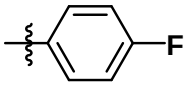
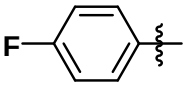
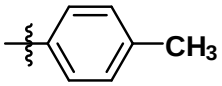
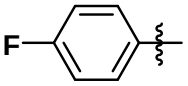
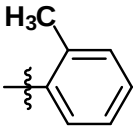
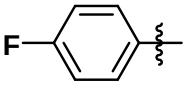
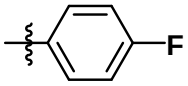
Table 4

One-pot synthesis of diarylmethanones via transmetallation[a] followed by Stille coupling[b]



Entry	Ar^1	Ar^2	Product	Yield (%)[c]
1			3aa	90
2			3ba	78
3			3ca (3ac)	80
4			3da	87
5			3ea	83
6			3ga	73
7			3ha	62
8			3ia	89
9			3ja	85

Entry	Ar^1	Ar^2	Product	Yield (%)[c]
10			3ac (3ca)	82
11			3ak	66
12			3ak	81[d]
13			3am	41
14			3am	60[d]
15			3an	59
16			3an	85[d]
17			3cc	52
18			3cc	50[d]
19			3cd (3dc)	90
20			3ce (3ec)	72

Entry	Ar^1	Ar^2	Product	Yield (%)[c]
21			3dc (3cd)	53
22			3dd	93
23			3de (3ed)	92
24			3ec (3ce)	89
25			3ed (3de)	86
26			3ee	70

[a] Reaction conditions: **1** (1 mmol), *n*-Bu_3SnOMe (1 mmol), under argon.

[b] Reaction conditions: Ar^2COCl (1 mmol), $Pd(OAc)_2$ (0.01 mmol), $CHCl_3$ (4 mL), under argon.

[c] Isolated yields after silica gel column chromatography.

[d] $PdCl_2$ (0.01 mmol) and $(2\text{-Furyl})_3P$ (0.02 mmol) were used instead of $Pd(OAc)_2$.

3. Conclusion

I have developed a straightforward method for the preparation of aryltributylstannanes from bench-stable arylbononic acids via transfer of aryl group from boron to tin under solvent-free conditions. The reactions use a 1:1 stoichiometric ratio of the reaction partners, arylboronic acid and *n*-Bu_3SnOMe, are easy to conduct, and furnish the desired products in good to high yields. The synthetic utility of the present method has been demonstrated by the cross-coupling reaction with various aroyl

chlorides. The reactions provide moderate to high yields of a wide variety of diaryl ketones and can be performed in a one-pot manner. This method has several advantages including convenient operation, inexpensive and commercially available materials, safe handling, and one-pot viability, which make it useful.

4. Experimental

4.1. General information

NMR spectra were recorded on JEOL JNM-A-500 or JEOL JNM-ECA-600 spectrometer. Chemical shifts are quoted in parts per million (ppm) downfield of TMS. Coupling constants *J* are quoted in hertz (Hz). 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-T100GCV spectrometer (EI, 70 eV). GC analyses using the internal standard method were performed with a Shimadzu GC-14B gas chromatograph equipped with a glass column (5% FFAP on Uniport B, 1 m), a flame ionization detector, and a Shimadzu C-R8A digital integrator-recorder. Melting points were determined on a Yamato MP-21 and are uncorrected. TLC analyses were carried out using aluminium sheets pre-coated with silica gel 60 F_{254} or glass plates pre-coated aluminium oxide 60 F_{254} purchased from Merck. Product purification was performed by column chromatography using silica gel 60 (Kanto Chemical, 63-210 μm) or aluminium oxide 60 (Merck, active basic, 70-230 μm). All reactions were carried out under argon atmosphere. Unless otherwise noted, commercially available materials were used without any purification. Chloroform and 1,2-dichloroethane were used after distillation over P_2O_5 under argon. Toluene was used after distillation over CaH_2 under argon. THF was distilled from Na/benzophenone ketyl under argon before use.

4.2. General procedure for iododestannylation of phenyltributylstannane with iodine

Into a 25 mL round-bottomed flask was added phenylboronic acid (0.122 g, 1 mmol), and the flask was purged with argon. Either solvent (3 mL) and tributyltin methoxide (0.321 g, 1 mmol) or tributyltin methoxide (0.321 g, 1 mmol) alone was then added at room temperature and the mixture was stirred at different reaction temperatures and times. The reaction mixture was cooled to −15 ºC, and a solution of I_2 (0.279 g, 1.1 mmol) in THF (1 mL) was added dropwise. The resulting mixture was allowed to warm to 0 ºC, stirred for 0.5 h, and treated with aqueous $Na_2O_3S_2$ to remove excess I_2. The organic phase was analyzed by GC.

4.3. General procedure for reaction of arylboronic acid with tributyltin methoxide

Into a 25 mL round-bottomed flask was added arylboronic acid (1 mmol), and the flask was purged with argon. Tributyltin methoxide (0.321 g, 1 mmol) was then added at room temperature and the mixture was heated in a heating block with stirring at 100 ºC for 1 h. The resulting mixture was cooled to room temperature and purified by column chromatography to give pure aryltributylstannane.

4.4. General procedure for reaction of aryltributylstannane with aroyl chloride

After the reaction of arylboronic acid (1 mmol) with tributyltin methoxide (0.321 g, 1 mmol) at 100 ºC for 1h under solvent-free conditions, chloroform (4 mL) was added to the reaction mixture at room temperature. Either $Pd(OAc)_2$ (0.0022 g, 0.01 mmol) or $PdCl_2$ (0.0017 g, 0.01 mmol) and tri(2-furyl)phosphine (0.0046 g, 0.02 mmol) were added under an argon gas stream, followed by addition of aroyl chloride (1 mmol) at room temperature. The resulting mixture was heated in a heating block with stirring at 60 ºC for 2 h. The reaction mixture was filtered through a Celite pad, and the solvent was removed under reduced pressure. After addition of THF (5 mL) and 3M NaOH (1 mL) to the residue, the mixture was stirred for 0.5 h at room temperature and then

diluted with H_2O (4 mL). The aqueous phase was extracted with EtOAc (3 × 5 mL) and organic layers were washed with brine (5 mL) dried over Na_2SO_4, filtered, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel to give pure diaryl ketone.

4.5. Characterization of the compounds

4.5.1. Phenyltributylstannane (2a).[2l]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3 Hz, 9H), 0.98-1.13 (m, 6H), 1.29-1.38 (m, 6H), 1.46-1.63 (m, 6H), 7.24-7.34 (m, 3H), 7.40-7.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.5 (3 × CH_2), 13.6 (3 × CH_3), 27.4 (3 × CH_2), 29.1 (3 × CH_2), 127.9 (2 × CH_{arom}), 136.5 (2 × CH_{arom}), 141.9 (CH_{arom}). IR (neat): 3062, 2956, 2925, 2869, 2852, 1458, 1427, 1074, 725, 698 cm^{-1}.

4.5.2. 4-Methoxyphenyltributylstannane (2b).[2n]

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.5 Hz, 9H), 0.97-1.09 (m, 6H), 1.29-1.36 (m, 6H), 1.46-1.61 (m, 6H), 3.77 (s, 3H), 6.87-6.92 (m, 2H), 7.32-7.42 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 9.6 (3 × CH_2), 13.7 (3 × CH_3), 27.4 (3 × CH_2), 29.1 (3 × CH_2), 54.8 (CH_3), 113.9 (2 × CH_{arom}), 131.9(C_{arom}), 137.4 (2 × CH_{arom}), 159.7 (C_{arom}). IR (neat): 2954, 2925, 2869, 2852, 1587, 1494, 1458, 1276, 1242, 1180, 1074, 1035, 806 cm^{-1}.

4.5.3. 4-Methylphenyltributylstannane (2c).[14]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3 Hz, 9H), 0.97-1.12 (m, 6H), 1.28-1.39 (m, 6H), 1.44-1.63 (m, 6H), 2.31 (s, 3H), 7.10-7.17 (m, 2H), 7.30-7.41 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.5 (3 × CH_2), 13.6 (3 × CH_3), 21.3 (CH_3), 27.4 (3 × CH_2), 29.1 (3 × CH_2), 128.8 (2 × CH_{arom}), 136.4 (2 × CH_{arom}), 137.5 (C_{arom}), 137.7 (C_{arom}). IR (neat): 2956, 2923, 2869, 2852, 1456, 1068, 790 cm^{-1}.

4.5.4. 2-Methylphenyltributylstannane (2d).[15]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3 Hz, 9H), 1.01-1.16 (m, 6H), 1.29-1.38 (m, 6H), 1.45-1.62 (m, 6H), 2.38 (s, 3H), 7.06-7.22 (m, 3H), 7.32-7.44 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.0 (3 × CH_2), 13.6 (3 × CH_3), 24.9 (CH_3), 27.4 (3 × CH_2), 29.2 (3 × CH_2), 124.8 (CH_{arom}), 128.2 (CH_{arom}), 128.8 (CH_{arom}), 136.4 (CH_{arom}), 141.7 (C_{arom}), 144.4 (C_{arom}). IR (neat): 2956, 2925, 2869, 2852, 1458, 1375, 740 cm^{-1}.

4.5.5. 4-Fluorophenyltributylstannane (2e).[2n]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3 Hz, 9H), 0.98-1.14 (m, 6H), 1.28-1.38 (m, 6H), 1.46-1.63 (m, 6H), 6.95-7.03 (m, 2H), 7.34-7.46 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.6 (3 × CH_2), 13.6 (3 × CH_3), 27.4 (3 × CH_2), 29.1 (3 × CH_2), 115.1 (d, *J* = 18.6 Hz, 2 × CH_{arom}), 136.5 (d, *J* = 4.1 Hz, C_{arom}), 137.8 (d, *J* = 7.2 Hz, 2 × CH_{arom}), 163.3 (d, *J* = 247.2 Hz, C_{arom}). IR (neat): 2956, 2925, 2871, 2852, 1581, 1490, 1463, 1228, 1163, 1062, 815 cm^{-1}.

4.5.6. 2-Bromophenyltributylstannane (2f).[16]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3 Hz, 9H), 1.09-1.24 (m, 6H), 1.29-1.38 (m, 6H), 1.47-1.65 (m, 6H), 7.06-7.12 (m, 1H), 7.16-7.22 (m, 1H), 7.25-7.36 (m, 1H), 7.42-7.48 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.8 (3 × CH_2), 13.6 (3 × CH_3), 27.3 (3 × CH_2), 29.0 (3 × CH_2), 126.2 (CH_{arom}), 129.8 (CH_{arom}), 131.6 (CH_{arom}), 133.3 (C_{arom}), 137.9 (CH_{arom}), 146.5 (C_{arom}). IR (neat): 2954, 2922, 2869, 2852, 1463, 1413, 1245, 1085, 1006, 746 cm^{-1}.

4.5.7. 3-Acetylphenyltributylstannane (2g).[15]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3 Hz, 9H), 1.04-1.20 (m, 6H), 1.30-1.40 (m, 6H), 1.47-1.66 (m, 6H), 2.56 (s, 3H), 7.32-7.42 (m, 1H), 7.60-7.71 (m, 1H), 7.79-7.88 (m, 1H), 8.09 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.3 (3 × CH_2), 13.3 (3 × CH_3), 26.1 (CH_3), 27.0 (3 × CH_2), 28.8 (3 × CH_2), 127.6 (CH_{arom}), 127.7 (CH_{arom}), 135.6 (CH_{arom}), 136.0 (C_{arom}), 140.8 (CH_{arom}), 142.4 (C_{arom}), 198.0 (C=O). IR (neat): 2956, 2925, 2869, 2852, 1685, 1463, 1355, 1255, 790, 696 cm^{-1}.

4.5.8. 3-Nitrophenyltributylstannane (2h).[3d]

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.5 Hz, 9H), 1.07-1.20 (m, 6H), 1.30-1.38 (m, 6H), 1.47-1.62 (m, 6H), 7.45-7.51 (m, 1H), 7.73-7.82 (m, 1H), 8.10-8.15 (m, 1H), 8.26-8.34 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 9.8 (3 × CH_2), 13.6 (3 × CH_3), 27.3 (3 × CH_2), 28.9 (3 × CH_2), 122.9 (CH_{arom}), 128.4 (CH_{arom}), 130.4 (CH_{arom}), 142.5 (CH_{arom}), 144.9 (C_{arom}), 147.7 (C_{arom}). IR (neat): 2956, 2925, 2871, 2852, 1523, 1463, 1344, 864, 727, 680 cm^{-1}.

4.5.9. 1-Naphthyltributylstannane (2i).[17]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.85 (t, *J* = 7.3 Hz, 9H), 1.13-1.28 (m, 6H), 1.29-1.38 (m, 6H), 1.49-1.66 (m, 6H), 7.30-7.38 (m, 2H), 7.40-7.45 (m, 1H), 7.61-7.65 (m, 1H), 7.67-7.75 (m, 2H), 7.78-7.82 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.4 (3 × CH_2), 13.6 (3 × CH_3), 27.4 (3 × CH_2), 29.2 (3 × CH_2), 125.3 (CH_{arom}), 125.3 (CH_{arom}), 125.6 (CH_{arom}), 128.5 (CH_{arom}), 128.9 (CH_{arom}), 130.1 (CH_{arom}), 133.8 (C_{arom}), 135.1 (CH_{arom}), 139.1 (C_{arom}), 142.7 (C_{arom}). IR (neat): 3049, 2954, 2925, 2869, 2852, 1500, 1463, 1375, 790, 773 cm^{-1}.

4.5.10. 2-Naphthyltributylstannane (2j).[18]

^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3 Hz, 9H), 1.06-1.22 (m, 6H), 1.31-1.41 (m, 6H), 1.51-1.68 (m, 6H), 7.30-7.39 (m, 2H), 7.50-7.60 (m, 1H), 7.66-7.77 (m, 3H), 7.90-8.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 9.6 (3 × CH_2), 13.7 (3 × CH_3), 27.4 (3 × CH_2), 29.2 (3 × CH_2), 125.6 (CH_{arom}), 125.6 (CH_{arom}), 126.8 (CH_{arom}), 127.5 (CH_{arom}), 127.7 (CH_{arom}), 133.0 (CH_{arom}), 133.4 (C_{arom}), 133.4 (C_{arom}), 136.5 (CH_{arom}), 139.3 (C_{arom}). IR (neat): 2954, 2925, 2869, 2850, 1463, 812, 736 cm^{-1}.

4.5.11. (4-Methoxyphenyl)(phenyl)methanone (3ba).[9b]

Mp 42-43 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.86 (s, 3H), 6.91-6.98 (m, 2H), 7.42-7.48 (m, 2H), 7.52-7.57 (m, 1H), 7.72-7.77 (m, 2H), 7.79-7.85 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.4 (CH_3), 113.5 (2 × CH_{arom}), 128.1 (2 × CH_{arom}), 129.7 (2 × CH_{arom}),

130.1(C_{arom}), 131.8 (CH_{arom}), 132.5 (2 × CH_{arom}), 138.2 (C_{arom}), 163.2 (C_{arom}), 195.4 (C=O). IR (neat): 1651, 1598, 1573, 1504, 1446, 1417, 1280, 1257, 1172, 1149, 1029, 937, 921, 844, 792, 740, 702, 599 cm^{-1}.

4.5.12. (4-Methylphenyl)(phenyl)methanone (3ca).[19]

Mp 47-48 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.20-7.24 (m, 2H), 7.39-7.43 (m, 2H), 7.49-7.53 (m, 1H), 7.67-7.70 (m, 2H), 7.73-7.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3 (CH_3), 127.9 (2 × CH_{arom}), 128.6 (2 × CH_{arom}), 129.5 (2 × CH_{arom}), 129.9 (2 × CH_{arom}), 131.8 (CH_{arom}), 134.5 (C_{arom}), 137.5 (C_{arom}), 142.8 (C_{arom}), 195.9 (C=O). IR (neat): 1645, 1604, 1448, 1319, 1276, 937, 920, 839, 788, 738, 700, 599 cm^{-1}.

4.5.13. (2-Methylphenyl)(phenyl)methanone (3da).[9h]

^{1}H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H), 7.15-7.20 (m, 1H), 7.21-7.27 (m, 2H), 7.30-7.34 (m, 1H), 7.35-7.40 (m, 2H), 7.47-7.51 (m, 1H), 7.76-7.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.6 (CH_3), 124.8 (CH_{arom}), 128.0 (2 × CH_{arom}), 128.1 (CH_{arom}), 129.6 (2 × CH_{arom}), 129.8 (CH_{arom}), 130.6 (CH_{arom}), 132.7 (CH_{arom}), 136.3 (C_{arom}), 137.3 (C_{arom}), 138.2 (C_{arom}), 197.9 (C=O). IR (neat): 1666, 1596, 1579, 1448, 1315, 1290, 1267, 1153, 923, 763, 732, 709, 698, 640 cm^{-1}.

4.5.14. (4-Fluorophenyl)(phenyl)methanone (3ea).[9n]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.05-7.12 (m, 2H), 7.39-7.45 (m, 2H), 7.49-7.55 (m, 1H), 7.70-7.75 (m, 2H), 7.76-7.81 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 112.9 (d. J = 22.1 Hz, 2 × CH_{arom}), 125.9 (2 × CH_{arom}), 127.4 (2 × CH_{arom}), 130.0(CH_{arom}), 130.2 (d, J = 9.6 Hz, 2 × CH_{arom}), 131.3 (d, J = 2.8 Hz, C_{arom}), 135.0 (C_{arom}), 162.8 (d, J = 254.0 Hz, C_{arom}), 192.4 (C=O). IR (neat): 1660, 1598, 1504, 1301, 1276, 1228, 1155, 923, 850, 736, 700, 599 cm^{-1}.

4.5.15. (3-Acetylphenyl)(phenyl)methanone (3ga).[9n]

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.69 (s, 3H), 7.46-7.51 (m, 2H), 7.56-7.62 (m, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 7.6 Hz, 1H), 8.36 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.6 (CH_3), 128.4 (2 × CH_{arom}), 128.7 (CH_{arom}), 129.5 (CH_{arom}), 129.9 (2 × CH_{arom}), 131.7 (CH_{arom}), 132.8 (CH_{arom}), 134.1 (CH_{arom}), 136.9 (C_{arom}), 137.0 (C_{arom}), 137.9(C_{arom}), 195.6 (C=O), 197.1 (C=O). IR (neat): 1681, 1660, 1598, 1446, 1427, 1357, 1286, 1242, 1145, 968, 779, 719, 700, 646, 594 cm^{-1}.

4.5.16. (3-Nitrophenyl)(phenyl)methanone (3ha).[9a]

Mp 94-95 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 8.14 (d, *J* = 6.8 Hz, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 8.61 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 124.6 (CH_{arom}), 126.7 (CH_{arom}), 128.7 (2 × CH_{arom}), 129.6 (CH_{arom}), 130.0 (2 × CH_{arom}), 133.3 (CH_{arom}), 135.4 (CH_{arom}), 136.2 (C_{arom}), 139.0 (C_{arom}), 148.0 (C_{arom}), 194.1 (C=O).

4.5.17. (1-Naphthyl)(phenyl)methanone (3ia).[20]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.51 (m, 7H), 7.79-7.84 (m, 3H), 7.88-7.91 (m, 1H), 8.08-8.12 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 124.2 (CH_{arom}), 125.5 (CH_{arom}), 126.3 (CH_{arom}), 127.1 (CH_{arom}), 127.6 (CH_{arom}), 128.2 (CH_{arom}), 128.3 (2 × CH_{arom}), 130.2 (2 × CH_{arom}), 130.8 (C_{arom}), 131.1 (CH_{arom}), 133.1 (CH_{arom}), 133.6 (C_{arom}), 136.2 (C_{arom}), 138.2 (C_{arom}), 197.7 (C=O). IR (neat): 1722, 1660, 1596, 1508, 1448, 1315, 1280, 1249, 912, 798, 775, 713, 696, 624 cm^{-1}.

4.5.18. (2-Naphthyl)(phenyl)methanone (3ja).[20]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.56 (m, 5H), 7.79-7.93 (m, 6H), 8.20 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 125.6 (CH_{arom}), 126.7 (CH_{arom}), 127.7 (CH_{arom}), 128.2 (CH_{arom}), 128.2 (2 × CH_{arom}), 129.3 (CH_{arom}), 129.9 (2 × CH_{arom}), 131.7 (CH_{arom}), 132.1 (C_{arom}), 132.2 (CH_{arom}), 134.7 (C_{arom}), 135.1 (C_{arom}), 137.7 (C_{arom}), 196.4 (C=O). IR (neat): 1651, 1625, 1596, 1446, 1353, 1288, 1236, 794, 750, 715, 698 cm^{-1}.

4.5.19. (4-Chlorophenyl)(phenyl)methanone (3ak).[9s]

Mp 72-74 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.51 (m, 4H), 7.58-7.62 (m, 1H), 7.74-7.79 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.3 (2 × CH_{arom}), 128.5 (2 × CH_{arom}), 129.8 (2 × CH_{arom}), 131.4 (2 × CH_{arom}), 132.5 (CH_{arom}), 135.7 (C_{arom}), 137.1 (C_{arom}), 138.8 (C_{arom}), 195.4 (C=O). IR (neat): 1649, 1585, 1301, 1284, 1089, 844, 788, 729, 694, 663 cm^{-1}.

4.5.20. (Furan-2-yl)(phenyl)methanone (3am).[9a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56-6.59 (m, 1H), 7.20-7.22 (m, 1H), 7.45-7.50 (m, 2H), 7.55-7.59 (m, 1H), 7.68-7.70 (m, 1H), 7.94-7.97 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 112.0 (CH_{arom}), 120.4 (CH_{arom}), 128.2 (2 × CH_{arom}), 129.0 (2 × CH_{arom}), 132.3 (CH_{arom}), 136.9 (C_{arom}), 146.9 (C_{arom}), 151.9 (C_{arom}), 182.3 (C=O). IR (neat): 1647, 1598, 1560, 1463, 1390, 1317, 1299, 1022, 956, 887, 869, 763, 727, 696, 677 cm^{-1}.

4.5.21. (Phenyl)(thien-2-yl)methanone (3an).[9u]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09-7.12 (m, 1H), 7.42-7.47 (m, 2H), 7.51-7.56 (m, 1H), 7.57-7.59 (m, 1H), 7.65-7.67 (m, 1H), 7.81-7.84 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.7 (CH_{arom}), 128.0 (2 × CH_{arom}), 128.7 (2 × CH_{arom}), 131.9 (CH_{arom}), 133.9 (CH_{arom}), 134.6 (CH_{arom}), 137.6 (C_{arom}), 143.1 (C_{arom}), 187.7 (C=O). IR (neat): 1637, 1598, 1577, 1514, 1446, 1411, 1353, 1288, 1232, 1053, 881, 842, 715, 700, 648 cm^{-1}.

4.5.22. Di(4-methylphenyl)methanone (3cc).[19]

Mp 78-79 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.39 (s, 6H), 7.23 (d, *J* = 7.6 Hz, 4H), 7.68 (d, *J* = 7.6 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.5 (2 × CH_3), 128.8 (4 × CH_{arom}), 130.1 (4 × CH_{arom}), 135.1 (2 × C_{arom}), 142.8 (2 × C_{arom}), 196.1 (C=O). IR (neat): 1651, 1606, 1315, 1278, 1178, 927, 842, 821, 748 cm^{-1}.

4.5.23. (2-Methylphenyl)(4-methylphenyl)methanone (3cd).[19]

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.38 (s, 3H), 7.18-7.29 (m, 5H), 7.32-7.36 (m, 1H), 7.69 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.8 (CH_3), 21.6 (CH_3), 125.1 (CH_{arom}), 128.2 (CH_{arom}), 129.1 (2 × CH_{arom}), 129.9 (CH_{arom}), 130.2 (2 × CH_{arom}), 130.8 (CH_{arom}), 135.1 (C_{arom}), 136.3 (C_{arom}), 138.9 (C_{arom}), 144.0 (C_{arom}), 198.1 (C=O). IR (neat): 1660, 1606, 1311, 1296, 1269, 1182, 1151, 925, 839, 773, 742, 607 cm^{-1}.

4.5.24. Di(2-Methylphenyl)methanone (3dd). [20]

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.42 (s, 6H), 7.12-7.16 (m, 2H), 7.21-7.24 (m, 2H), 7.26-7.29 (m, 2H), 7.30-7.34 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.6 (2 × CH_3), 125.3 (2 × CH_{arom}), 130.2 (2 × CH_{arom}), 131.0 (2 × CH_{arom}), 131.3 (2 × CH_{arom}), 138.0 (C_{arom}), 138.9 (C_{arom}), 200.5 (C=O). IR (neat): 1662, 1454, 1301, 1257, 923, 763, 738, 640 cm^{-1}.

4.5.25. (4-Fluorophenyl)(2-methylphenyl)methanone (3de).

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.31 (s, 3H), 7.06-7.11 (m, 2H), 7.20-7.24 (m, 1H), 7.25-7.29 (m, 2H), 7.34-7.38 (m, 1H), 7.79-7.84 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.8 (CH_3), 115.6 (d, *J* = 21.7 Hz, 2 × CH_{arom}), 125.2 (CH_{arom}), 128.3 (CH_{arom}), 130.3 (CH_{arom}), 131.0 (CH_{arom}), 132.7 (d, *J* = 10.1 Hz, 2 × CH_{arom}), 134.1 (d, *J* = 2.9 Hz, C_{arom}), 136.6 (C_{arom}), 138.3 (C_{arom}), 165.7 (d, *J* = 254.4 Hz, C_{arom}), 196.8 (C=O). IR (neat): 1664, 1596, 1504, 1294, 1267, 1230, 1149, 927, 852, 748, 605 cm^{-1}. MS (EI, 70eV), *m/z* (%): 214 (63, M^+), 213 (100), 123 (38), 119 (40), 95 (38), 91 (35), 69 (38). HRMS (EI): *m/z* [M^+] calcd for $C_{14}H_{11}FO$, 214.0794; found, 214.0801.

4.5.26. (4-Fluorophenyl)(4-methylphenyl)methanone (3ec).[19]

Mp 95-96 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.10-7.15 (m, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.78-7.83 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.6 (CH_3), 115.3 (d, *J* = 21.7 Hz, CH_{arom}), 129.0 (2 × CH_{arom}), 130.1 (2 ×

CH_{arom}), 132.5 (d, *J* = 8.7 Hz, CH_{arom}), 134.1 (d, *J* = 2.9 Hz, C_{arom}), 134.7 (C_{arom}), 143.3 (C_{arom}), 165.2 (d, *J* = 254.4 Hz, C_{arom}), 194.9 (C=O). IR (neat): 1651, 1596, 1296, 850, 831, 752, 677 cm^{-1}.

4.5.27. Di(4-Fluorophenyl)methanone (3ee).[9x]

Mp 103-105 ºC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13-7.18 (m, 4H), 7.79-7.84 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 115.6 (d, *J* = 21.6 Hz, 4 × CH_{arom}), 132.5 (d, *J* = 8.7 Hz, 4 × CH_{arom}), 133.7 (d, *J* = 2.9 Hz, 2 × C_{arom}), 165.4 (d, *J* = 254.3 Hz, 2 × C_{arom}), 193.7 (C=O). IR (neat): 1651, 1600, 1504, 1298, 1282, 1230, 1155, 908, 846, 767, 732, 675, 580 cm^{-1}.

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Chapter IV

conclusion

In Chapter 2, it has been demonstrated that the synthesis of both 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles and 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles can be achieved by a cross-coupling/click reaction sequence in a semi-one-pot manner.[1] Thus, the $Cu(acac)_2$-mediated cross-coupling reaction of (*E*)-alk-1-enyldisiamylboranes with (trimethylsilyl)ethynyl bromide is carried out in the presence of 1M-NaOMe to form (*E*)-alk-3-en-1-ynes, which undergo click reaction with various arylazides, prepared by the $Cu(OAc)_2$-catalyzed reaction of arylboronic acids with NaN_3 in another flask, in a small amount of sodium ascorbate as the reductant for Cu(II) species, affording 1-aryl-4-[(*E*)-alk-1-enyl]-1*H*-1,2,3-triazoles in moderate to good yields. Similarly, the CuI-mediated cross-coupling reaction of (*Z*)-1-(trimethylsilyl)alk-1-enyldicyclohexylboranes with (trimethylsilyl)ethynyl bromide is conducted in the presence of aq. NaOH to form (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes, which are subjected to click reaction with arylazides in the presence of small amount of sodium ascorbate and 1M NaOMe as the deprotecting agent for trimethylsilyl group furnishes 1-aryl-4-[(*Z*)-1-(trimethylsilyl)alk-1-enyl]-1*H*-1,2,3-triazoles exclusively. The present protocol can be successfully performed without isolation and purification of any compounds during the process. The construction of a series of π-extended 1,2,3-triazoles with both an aryl moiety at the 1-position and a geometricaldefined alkenyl moiety at the 4-positin on the triazole ring. This approach uses simple and readily available starting materials and shows good functional compatibility. These features make this protocol potentially attractive for the synthesis of the π-extended 1,2,3-triazoles.

In Chapter 3, it has been demonstrated that the preparation of aryltributylstannanes is

easily performed by the reaction of arylboronic acids with tributyltin methoxide at 100℃ for 1 h under solvent-free conditions. Furthermore, the application to the synthesis of diaryl ketones has been described in this chapter. Thus, transmetalation of arylboronic acids with tributyltin methoxide followed by palladium-catalyzed cross-coupling reaction with aroyl chlorides proceeds successfully in a one-pot manner to afford the corresponding diaryl ketones in good to high yields. This approach to aryltributylstannanes has such advantages as the ready availability of the starting materials, the experimental simplicity of the reaction, and the compatibility of functional groups. These advantages should make this approach a potential synthetic protocol.

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