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Synthesis of internal alkynes via one-pot palladium-catalyzed and dehydrobromination reactions of 1,1-dibromo-1-alkenes

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ABSTRACT

Tandem palladium-catalyzed cross-coupling of alkyl, alkenyl, alkynyl, aryl, and heteroaryl 2-substituted 1,1-dibromo-1-alkenes with aryl or heteroaryl boronic acids or borate esters and dehydrobromination of the intermediate coupled products afforded internal alkynes in moderate to good yields (up to 89%). The synthesis has been carried out in a one-pot process and in a two-step sequence according to the nature of the starting 1,1-dibromoalkenes. The reported protocol is compatible with the presence in the 1,1-dibromo-1-alkene molecule of additional reactive halogen–carbon bonds, thus allowing to build up more complex alkyne derivatives.

1. Introduction

Alkynes are among the most important compounds in organic chemistry, since they are useful and versatile intermediates en route to complex systems including natural products.[1] Among the several approaches described in the literature to obtain such compounds, some of them use 1,1-dibromoalkenes as starting points. Thus, the treatment of *gem*-dibromoalkenes with a strong base such as NaHMDS,[2] *t*-BuOK,[3] DBU,[4] or NaOH/phase-transfer agents[5] yields 1-bromoalkynes, whereas the use of 2 equiv of *n*-BuLi (more rarely MeLi or *t*-BuLi) produces the related lithium-acetylides, that can be quenched with MeOH to give terminal alkynes or trapped with various electrophiles to furnish the corresponding internal alkynes.[6] 1,1-Dibromoalkenes are precursors of intermediate alkylidene carbenes that can generate, by a 1,2-migration process, terminal or internal alkynes according to whether the group bonded to the alkene of the alkylidene carbene is a hydrogen or an alkyl, alkenyl, or aryl group, respectively.[7] Finally, internal alkynes have been directly obtained by coupling of 2-alkyl and 2-aryl-1,1-dibromoalkenes with organostannanes under Stille coupling conditions (Pd_2dba_3, TFP, DIPEA, DMF, 80 °C).[8] This method is very effective for the synthesis of internal alkynes, but organostannanes generally suffer from toxicity and environmental concerns, as well as issues associated to the purification of the final products.

Organoboron compounds used in the Suzuki–Miyaura cross-coupling[9] represent a valuable alternative to the use of organostananes utilized in the Stille coupling.[10] Moreover, a variety of organoboron compounds are now commercially available or readily prepared from a variety of starting points via transmetallation or hydroboration reactions.[9]

Since the Suzuki–Miyaura reaction of 1,1-dibromoalkenes with alkyl,[11] alkenyl,[11,12] alkynyl,[13] aryl,[14] and heteroaryl[14b] boronic acids and organotrifluoroborates[11] has proven to be successful for the synthesis of tri- and tetrasubstituted olefins and also the stereoselective formation of (*Z*)-1-aryl- or (*Z*)-alkenyl-1-bromo-1-alkenes,[11–14] it was of interest to explore the feasibility to obtain internal alkynes from 1,1-dibromoalkenes exploiting this reaction.

Herein we report the one-pot conversion of 1,1-dibromoalkenes into internal alkynes by sequential Suzuki and dehydrobromination reactions.[15]

2. Results and discussion

As a model substrate for our studies we prepared (*Z*)-1-[1-bromo-2-(4-methoxyphenyl)vinyl]benzene **2a** (Scheme 1) starting from dibromide 1-(2,2-dibromovinyl)-4-methoxybenzene **1a** and phenylboronic acid under the optimized reaction conditions established by Shen for the Suzuki–Miyaura coupling of 1,1-dibromoalkenes with arylboronic acids [Pd_2dba_3, TFP, Na_2CO_3, 1,4-dioxane, H_2O, 65 °C, 4–6 h].[14a]

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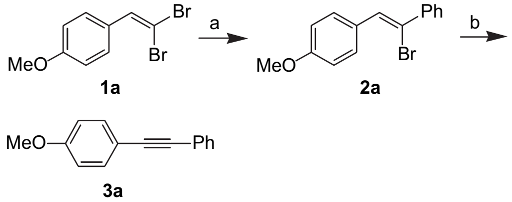


Scheme 1. (a) $PhB(OH)_2$, Pd_2dba_3 (2.5%), TFP (15%), Na_2CO_3 (2.0 equiv), 1,4-dioxane, H_2O, 65 °C, 4 h; (b) Table 1.

With bromoalkene **2a** in hand, we devoted our attention to find a method for its dehydrobromination that should have been compatible with the aqueous conditions of the Suzuki–Miyaura reaction. When 10 equiv of NaOH was added to a mixture of **2a** in 1,4-dioxane and aqueous Na_2CO_3, no reaction occurred at room temperature (Table 1, entry 1), whereas partial conversion of the starting material was obtained at 65 °C (entry 2). The addition of the phase-transfer catalyst $Bu_4N(HSO_4)$ greatly improved the reaction, but the yield was moderate (entry 3). Finally, nearly quantitative yield was obtained when $Bu_4N(OH)\cdot 30H_2O$ was added to the mixture and stirring was continued at 65 °C for 1 h (entry 4).

Based on these results, a sequential one-pot process was next examined. Thus, the Suzuki–Miyaura coupling of **1a** with phenylboronic acid (1.05 equiv) was accomplished using tri(2-furyl)phosphine (TFP, 15 mol %) and tris(dibenzylideneacetone)dipalladium (Pd_2dba_3, 2.5 mol %) in 1,4-dioxane and aqueous cesium carbonate (2.0 equiv)[16] at 65 °C and once all the dibromides have been converted (6 h, TLC monitoring), $Bu_4N(OH)\cdot 30H_2O$ was added. After stirring for further 1 h, the related terminal alkyne **3a** was obtained in 56% yield.

With a suitable protocol in hand, the scope of this methodology was examined by first using various 1,1-dibromoalkenes (Table 2) and phenylboronic acid as a prototype of boronic acids. Under the optimized reaction conditions, the corresponding alkynes were obtained in moderate to good yields with both electron rich (Table 2, entries 1 and 2) and electron deficient 1,1-dibromoalkenes (entries 3 and 4). These results did not change substantially when both π-excessive (entry 5) and π-deficient heteroaromatic substituents (entries 6 and 7) were used.

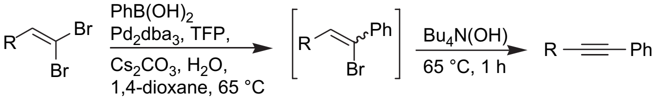
The scope of the method was next extended to functionalized boron reagents. Thus, a number of 1,1-dibromoalkenes were cross-reacted with the electron deficient boronate esters **4b** and **4c** and electron rich boronate ester **4d**. Also in this instance moderate to good results were obtained (Table 3) indicating that this procedure allows the synthesis of aryl–aryl, aryl–heteroaryl, and heteroaryl–heteroaryl substituted internal alkynes by a proper choice of the *gem*-dibromide or boron reagent.

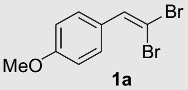
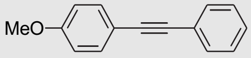
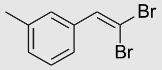
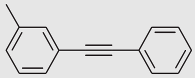
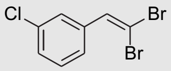
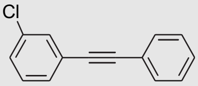
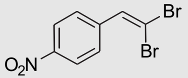
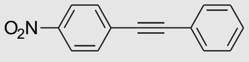
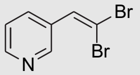
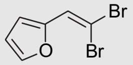
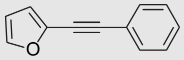
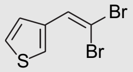
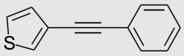
Table 1
Dehydrobromination of **2a**[a]

Entry	Base (equiv)	Time /temperature (°C/h)	Conversion[b] (%)	Yield[c] (%)
1	NaOH (10.0)	25/24	0	—
2	NaOH (10.0)	65/15	65	—
3	NaOH (10.0)/$Bu_4N(HSO_4)$ (1.0)	65/4	100	72
4	$Bu_4N(OH)\cdot 30H_2O$ (5.0)	65/1	100	>95

[a] The reaction was carried out at 1.0 mmol scale with Na_2CO_3 (2.0 equiv) in a mixture of 1,4-dioxane (5.0 ml) and H_2O (2.0 ml).
[b] Determined by ^1H NMR spectroscopy.
[c] Isolated yields after flash chromatography.

Table 2
Synthesis of alkynes from 1,1-dibromoalkenes[a]



Entry	Dibromide	Coupling time (h)	Product	Yield[b] (%)
1	 **1a**	6	 **3a**	56
2	 **1b**	14	 **3b**	76
3	 **1c**	14	 **3c**	94
4	 **1d**	6	 **3d**	82
5	 **1e**	17	 **3e**	67
6	 **1f**	17	 **3f**	79
7	 **1g**	4	 **3g**	72

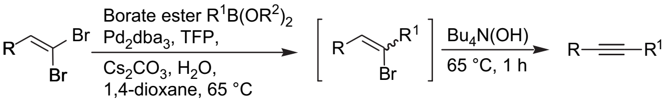
[a] Reaction conditions: 1,1-dibromoalkene (1.0 mmol), boronic acid or ester (1.05 equiv), Pd_2dba_3 (2.5 mol %), TFP (15.0 mol %), Cs_2CO_3 (1.0 M in H_2O, 2.0 ml, 2.0 equiv), 1,4-dioxane (5.0 ml), 65 °C, 4–17 h; then $Bu_4N(OH)\cdot 30H_2O$ (4 g, 5.0 equiv), 65 °C, 1 h.
[b] Isolated yields after flash chromatography.

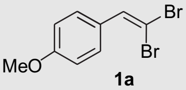
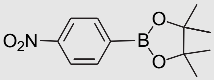
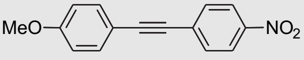
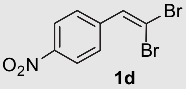
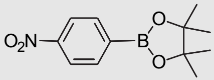
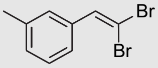
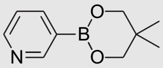
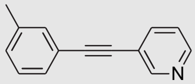
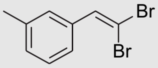
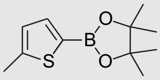
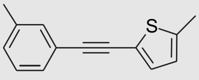
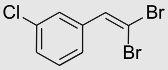
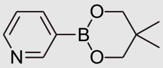
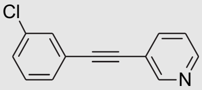
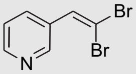
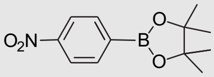
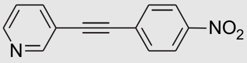
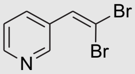
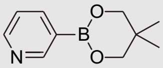
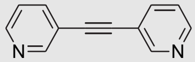
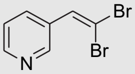
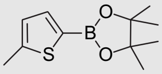
Next, the conversion of some examples of alkyl, alkenyl, and alkynyl-1,1-dibromo-1-alkenes into internal alkynes was examined using phenylboronic acid as the coupling partner (Table 4). In this case, however, in order to determine the best conditions for both coupling and dehydrobromination reactions, a two-step protocol was initially followed. Coupling of alkyl 2-substituted 1,1-dibromo-1-alkenes **1h**–**j** afforded the related (*Z*)-1-bromo-1-phenyl-1-alkenes **2b**–**d** in moderate yields (50–56%). However, while the coupling of **1h** and **1i** was carried out at 65 °C, that of **1j** gave a better yield when the reaction was performed at room temperature, though a longer reaction time was required.

The coupling of alkenyl and alkynyl *gem*-dibromides **1k** and **1l** occurred smoothly to give the phenyl derivatives **1e** and **1f** in satisfactory yields (77 and 62%, respectively). These compounds were isolated as single stereoisomers, although the exact geometry of the double bond was not determined. When the dehydrobromination of bromoalkenes **2b**–**f** was carried out using $Bu_4N(OH)\cdot 30H_2O$ at 65 °C, no reaction occurred, so the reaction temperature was gradually increased. A right compromise between yield and reaction time was found carrying out the reaction at 100 °C. Under these conditions, the related alkynes were obtained in high yields (81–95%), except alkyne **3q** that was formed in 50% yield. Having determined the proper conditions for each starting point, the one-pot process was pursued. The data reported in Table 4 show that the alkyne products were isolated in yields that are very close to that obtained in the two-step protocol.

It was also of interest to determine the compatibility of this method by using 1,1-dibromo-1-alkene bearing additional reactive halogen–carbon bonds. The successful implementation of this process should allow for further elaboration of the remaining halogen in order to build up more complex derivatives. With the aim of demonstrating this opportunity 2-bromo-3-(2,2-

Table 3
Synthesis of alkynes from 1,1-dibromoalkenes[a]



Entry	Dibromide	Borate ester	Coupling time (h)	Product	Yield[b] (%)
1	 **1a**	 **4b**	16	 **3h**	30
2	 **1d**	 **4b**	16	 **3i**	50
3	 **1b**	 **4c**	17	 **3j**	48
4	 **1b**	 **4d**	14	 **3k**	64
5	 **1c**	 **4c**	15	 **3l**	63
6	 **1e**	 **4b**	5	 **3m**	61
7	 **1e**	 **4c**	16	 **3n**	82
8	 **1e**	 **4d**	20	 **3o**	67

[a] Reaction conditions: 1,1-dibromoalkene (1.0 mmol), boronic acid or ester (1.05 equiv), Pd_2dba_3 (2.5 mol %), TFP (15.0 mol %), Cs_2CO_3 (1.0 M in H_2O, 2.0 ml, 2.0 equiv), 1,4-dioxane (5.0 ml), 65 °C, 5–20 h; then $Bu_4N(OH)\cdot 30H_2O$ (4 g, 5.0 equiv), 65 °C, 1 h.

[b] Isolated yields after flash chromatography.

dibromovinyl)pyridine **1m** was submitted, under the usual reaction conditions, to tandem coupling with phenylboronic acid and dehydrobromination (Scheme 2). Interestingly, alkyne **3u** was obtained in 84% yield that was even higher than that obtained with pyridine **1e** without the bromide in the pyridine ring (67%). This interesting result demonstrates clearly that in tribromide **1m** the insertion of the Pd(0) complex into the (*E*)- and/or (*Z*)-bromoalkene bonds is faster than that of the Br–pyridine bond. Next, to complete the demonstration, alkyne **3u** was cross-coupled with 4-methoxy-3-methylphenylboronic acid under standard Suzuki-type conditions [$Pd(PPh_3)_4$, $PhB(OH)_2$ in MeOH, aqueous Na_2CO_3, toluene, 80–85 °C, 5 h] to give phenylpyridine **5** in 86% yield. On the basis of these findings, the synthetic scope of the Pd-catalyzed synthesis of alkynes from a variety of polybrominated alkene derivatives was examined. The results, summarized in Table 5, show that satisfactory yields (53–84%) were obtained with benzene derivatives (**1n** and **1o**) and π-deficient heteroaromatic systems (**1m** and **1r**), whereas lower yields (32–66%) were found with π-excessive structures (**1p** and **1q**).

3. Conclusion

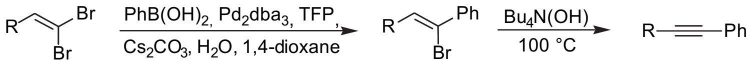
In summary, one-pot palladium-catalyzed Suzuki–Miyaura coupling of alkyl, alkenyl, alkynyl, aryl, and heteroaryl 2-substituted 1,1-dibromo-1-alkenes with aryl or heteroaryl boronic acids or borate esters and subsequent dehydrobromination of the intermediate cross-coupled products afford internal alkynes in moderate to good yields. Interestingly, this procedure is compatible with the presence in the 1,1-dibromo-1-alkene molecule of additional reactive halogen–carbon bonds, thus facilitating the assembly of more complex alkyne derivatives. Given the easy availability of a variety of organoboron compounds, this protocol represents a valuable alternative to the Stille reaction to prepare this important class of compounds. Notably, 1,1-dibromoalkenes are easily obtainable in high yields from the related aldehydes[6,17] and so the complete process offers a convenient and simple route for aldehydes to internal alkynes (Scheme 3).

4. Experimental

4.1. General methods

TLC was performed on Merck silica gel 60 TLC plates F_{254} and visualized using UV or phosphomolibdic acid. Flash chromatography was carried out on silica gel (230–400 mesh). All reagents and solvents were purchased from Aldrich and used as received. Melting points were determined on a Büchi 510 capillary apparatus and are uncorrected. The NMR spectra were obtained with a Varian VXR-300 spectrometer at 300 MHz for ^1H and 75.4 MHz for ^{13}C.

Table 4
Synthesis of alkynes from 2-alkyl-, 2-alkenyl-, and 2-alkynyl-1,1-dibromoalkenes



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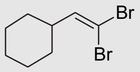
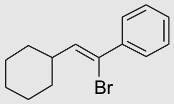
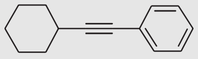
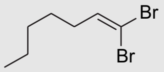
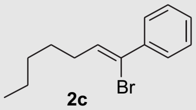
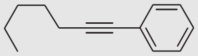
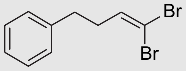
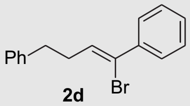
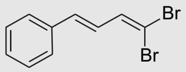
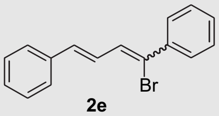
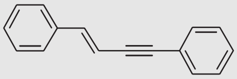
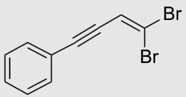
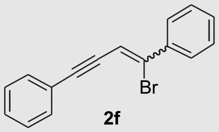
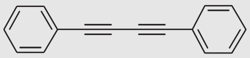
1	 **1h**	 **2b**	2/50	 **3p**	2/81	43
2	 **1i**	 **2c**	2/53	 **3q**	2/50	23
3	 **1j**	 **2d**	24/56[e]	 **3r**	2/82	52
4	 **1k**	 **2e**	2/77	 **3s**	2/95	69
5	 **1l**	 **2f**	4/62	 **3t**	1/93	55

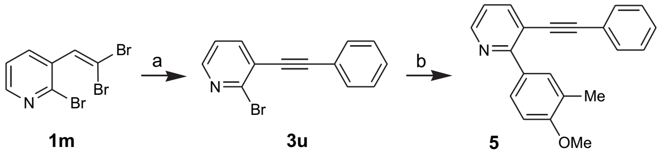
[a] Reaction conditions: 1,1-dibromoalkene (1.0 mmol), boronic acid or ester (1.05 equiv), Pd_2dba_3 (2.5 mol %), TFP (15.0 mol %), Cs_2CO_3 (1.0 M in H_2O, 2.0 ml, 2.0 equiv), 1,4-dioxane (5.0 ml), 65 °C, 2–24 h.

[b] Reaction conditions: 1-dibromoalkene (1.0 mmol), Cs_2CO_3 (1.0 M in H_2O, 2.0 ml, 2.0 equiv), 1,4-dioxane (5.0 ml), $Bu_4N(OH)\cdot 30H_2O$ (4.0 g, 5.0 equiv), 100 °C, 1-2 h.

[c] Reaction conditions: 1,1-dibromoalkene (1.0 mmol), boronic acid or ester (1.05 equiv), Pd_2dba_3 (2.5 mol %), TFP (15.0 mol %), Cs_2CO_3 (1.0 M in H_2O, 2.0 ml, 2.0 equiv), 1,4-dioxane (5.0 ml), 65 °C, 2–24 h; then $Bu_4N(OH)\cdot 30H_2O$ (4.0 g, 5.0 equiv), 100 °C, 1-2 h.

[d] Isolated yields after flash chromatography.

[e] Reactions run at 25 °C.



Scheme 2. (a) $PhB(OH)_2$, Pd_2dba_3 (2.5%), TFP (15%), Na_2CO_3 (2.0 equiv), 1,4-dioxane, H_2O, 65 °C, 20 h; then $Bu_4N(OH)$, 65 °C, 1 h, 84%; (b) 4-MeO-3-$MeC_6H_4B(OH)_2$, $Pd(PPh_3)_4$, MeOH, aqueous Na_2CO_3, toluene, 80–85 °C, 5 h, 86%.

Chemical shifts are reported in parts per million downfield from internal Me_4Si in $CDCl_3$. Elemental analyses were performed on a Perkin–Elmer 240 B analyser. All aldehydes, starting material for the synthesis 1,1-dibromo-1-alkenes were purchased from Aldrich.

4.2. General procedure for the preparation of 1,1-dibromo-1-alkenes

To a solution of PPh_3 (0.516 g, 19.8 mmol) in CH_2Cl_2 (110 ml) in an ice bath was added a solution of CBr_4 (0.329 g, 9.92 mmol) in CH_2Cl_2 (4 ml) at a rate to maintain the reaction temperature below 15 °C under nitrogen. The mixture was cooled at 0 °C and a solution of the aldehyde (7.36 mmol) and triethylamine (106 ml, 0.763 mol) in CH_2Cl_2 (100 ml) was added dropwise. After stirring at 0 °C for 30 min, the reaction mixture was warmed to room temperature. The mixture was poured in petroleum ether (1.0 l). The mixture was filtered through Celite and the solid was washed with ether (2×200 ml). The filtrate was concentrated under reduced pressure. Petroleum ether (800 ml) was added. The mixture was filtered and the filtrate was concentrated to give the crude 1,1-dibromo-1-alkene that was purified by flash chromatography.

4.2.1. *1-Chloro-3-(2,2-dibromovinyl)benzene (**1c**)*

Compound **1c** was obtained from 3-chlorobenzaldehyde and purified by flash chromatography using petroleum ether; yield 90%; oil; ^1H NMR: δ 7.51 (s, 1H), 7.41–7.33 (m, 2H), 7.31–7.25 (m, 2H). ^{13}C NMR: δ 136.8, 135.4, 134.3, 129.6, 128.5, 128.2, 126.5, 91.3. Anal. Calcd for $C_8H_5Br_2Cl$: C, 32.42; H, 1.70. Found: C, 32.23; H, 1.72.

4.2.2. *2-Bromo-3-(2,2-dibromovinyl)pyridine (**1m**)*

Compound **1m** was obtained from 2-bromonicotinaldehyde and purified by flash chromatography using petroleum ether/ethyl acetate=8:2; yield 85%; mp 44–45 °C; ^1H NMR: δ 8.34 (dd, 1H, J=4.8, 1.8 Hz), 7.94 (dd, 1H, J=7.8, 1.8 Hz), 7.47 (s, 1H), 7.33 (dd, 1H, J=7.8, 4.8 Hz). ^{13}C NMR: δ 149.2, 142.0, 138.2, 134.1, 133.0, 122.3, 94.6. Anal. Calcd for $C_7H_4Br_3N$: C, 24.60; H, 1.18; N, 4.10. Found: C, 24.45; H, 1.14; N, 4.11.

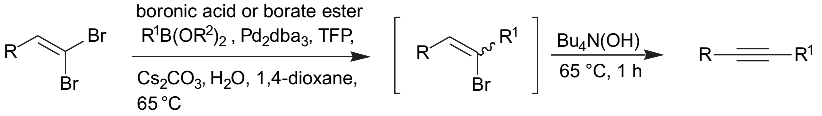
4.2.3. *2-Bromo-5-(2,2-dibromovinyl)furan (**1p**)*

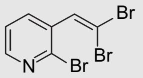
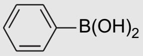
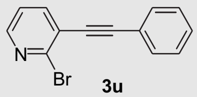
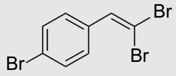
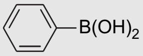
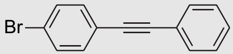
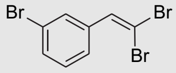
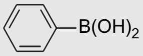
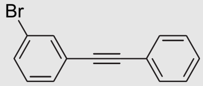
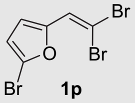
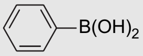
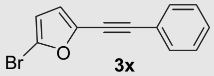
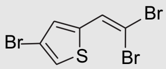
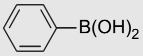
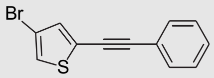
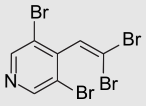
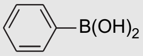
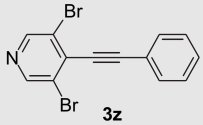
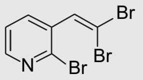
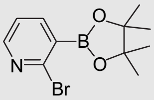
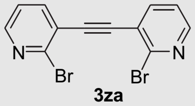
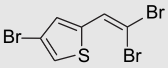
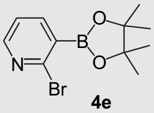
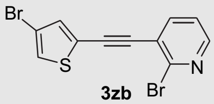
Compound **1p** was obtained from 5-bromofuran-2-carbaldehyde and purified by flash chromatography using petroleum ether; yield 90%; low melting solid; ^1H NMR: δ 7.29 (s, 1H), 6.87 (d, 1H, J=3.3 Hz), 6.35 (d, 1H, J=3.3 Hz). ^{13}C NMR: δ 151.7, 125.3, 122.6, 113.6, 113.3, 87.9. Anal. Calcd for $C_6H_3Br_3O$: C, 21.78; H, 0.91. Found: C, 21.66; H, 0.93.

4.2.4. *4-Bromo-2-(2,2-dibromovinyl)thiophene (**1q**)*

Compound **1q** was obtained from 4-bromothiophene-2-carbaldehyde and purified by flash chromatography using petroleum

Table 5
Synthesis of alkynes from 1,1-dibromoalkenes[a]



Entry	Dibromide	Boronic acid or borate ester	Coupling time (h)	Product	Yield[b] (%)
1	 **1m**	 **4a**	20	 **3u**	84
2	 **1n**	 **4a**	3	 **3v**	57
3	 **1o**	 **4a**	2	 **3w**	63
4	 **1p**	 **4a**	3	 **3x**	32
5	 **1q**	 **4a**	5	 **3y**	66
6	 **1r**	 **4a**	9	 **3z**	53
7	 **1m**	 **4e**	12	 **3za**	81
8	 **1q**	 **4e**	32	 **3zb**	46

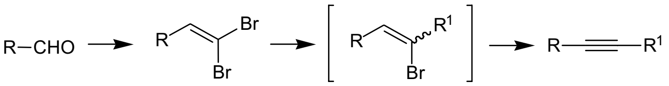
[a] Reaction conditions: 1,1-dibromoalkene (1.0 mmol), boronic acid or ester (1.05 equiv), Pd_2dba_3 (2.5 mol %), TFP (15.0 mol %), Cs_2CO_3 (1.0 M in H_2O, 2.0 ml, 2.0 equiv), 1,4-dioxane (5 ml), 65 °C, 2–32 h; then $Bu_4N(OH)\cdot 30H_2O$ (4 g, 5.0 equiv), 65 °C, 1 h.

[b] Isolated yields after flash chromatography.

ether; yield 86%; mp 77–78 °C; ^{1}H NMR: δ 7.53 (s, 1H), 7.26 (d, 1H, J=0.6 Hz), 7.14 (d, 1H, J=0.6 Hz). ^{13}C NMR: δ 139.0, 131.6, 129.4, 124.0, 110.1, 89.1. Anal. Calcd for $C_6H_3Br_3S$: C, 20.78; H, 0.87. Found: C, 20.67; H, 0.86.

4.2.5. *3,5-Dibromo-4-(2,2-dibromovinyl)pyridine (**1r**)*

Compound **1r** was obtained from 3,5-dibromoisonicotinaldehyde and purified by flash chromatography using petroleum ether/ethyl acetate=8:2; yield 80%; mp 84–85 °C; ^{1}H NMR: δ 8.67 (s, 2H), 7.25 (s, 1H). ^{13}C NMR: δ 150.3, 145.0, 133.7, 121.1, 97.9. Anal. Calcd for $C_7H_3Br_4N$: C, 19.98; H, 0.72; N, 3.33. Found: C, 19.77; H, 0.71; N, 3.35.



Scheme 3.

4.2.6. *1-(2,2-Dibromovinyl)-4-methoxybenzene (**1a**), 1-(2,2-dibromovinyl)-3-methylbenzene (**1b**), 1-chloro-3-(2,2-dibromovinyl)benzene (**1d**), 1-(2,2-dibromovinyl)-4-nitrobenzene (**1e**), 3-(2,2-dibromovinyl)pyridine 2-(2,2-dibromovinyl)furan (**1f**), 3-(2,2-dibromovinyl)thiophene (**1g**), (2,2-dibromovinyl)-cyclohexane (**1h**), 1,1-dibromohept-1-ene (**1i**), 1-(4,4-dibromobut-3-enyl)benzene (**1j**), (E)-1-(4,4-dibromobuta-1,3-dienyl)benzene (**1k**), 1-(4,4-dibromobut-3-en-1-ynyl)benzene (**1l**), 1-bromo-4-(2,2-dibromovinyl)benzene (**1n**), and 1-bromo-3-(2,2-dibromovinyl)benzene (**1o**)*

Compounds **1a**,[18] **1b**,[19] **1d**,[20] **1e**,[21] **1f**,[22] **1g**,[23] **1h**,[24] **1i**,[25] **1j**,[26] **1k**,[27] **1l**,[28] **1n**,[29] and **1o**[30] showed satisfactory spectroscopic and analytical data that were consistent with those reported in the literature.

4.3. General procedure for the preparation of alkenes 2

A mixture of the 1,1-dibromo-1-alkene (1.0 mmol), organoboronic acid or borate ester (1.05 mmol), and Cs_2CO_3 (0.706 g, 2.0 mmol) in 1,4-dioxane (5.0 ml) and H_2O (2.0 ml) was degassed by bubbling nitrogen for few minutes. Then, $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and tri(2-furyl)phosphine (TFP) (35 mg, 0.15 mmol) were added and the resulting mixture was heated at 65 °C under nitrogen for the appropriate time (Table 4). The mixture was diluted with ethyl acetate (50 ml) and washed with brine (2×15 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated, and the residue was purified by flash chromatography.

4.3.1. *(Z)-1-Bromo-1,4-diphenylbut-1-ene (**2d**)*

Compound **2d** was obtained from **1j** and purified by flash chromatography using petroleum ether; yield 56%; oil; ^1H NMR: δ 7.48 (dd, 2H, J=8.4, 1.8 Hz), 7.36–7.18 (m, 8H), 6.20 (t, 1H, J=6.9 Hz), 2.86–2.76 (m, 2H), 2.68 (t, 2H, J=6.9 Hz). ^{13}C NMR: δ 141.2, 139.9, 130.5, 128.4 (3×C), 128.3, 128.2, 127.5, 126.0, 34.4, 34.1. Anal. Calcd for $C_{16}H_{15}Br$: C, 66.91; H, 5.26. Found: C, 66.73; H, 5.24.

4.3.2. *(E)-1-Bromo-1,4-diphenylbuta-1,3-diene (**2e**)*

Compound **2e** was obtained from **1k** and purified by flash chromatography using petroleum ether; yield 77%; oil; ^1H NMR: δ 7.64 (dd, 2H, J=8.4, 1.8 Hz), 7.51 (dd, 2H, J=8.4, 1.8 Hz), 7.41–7.21 (m, 7H), 7.18 (d, 1H, J=7.8 Hz), 6.84 (d, 1H, J=15.6 Hz). ^{13}C NMR: δ 139.4, 136.9, 136.3, 129.4, 128.7, 128.6, 128.3, 128.2, 127.4, 127.3, 126.8, 125.7. Anal. Calcd for $C_{16}H_{13}Br$: C, 67.39; H, 4.59. Found: C, 67.23; H, 4.57.

4.3.3. *1-Bromo-1,4-diphenylbut-1-en-3-yne (**2f**)*

Compound **2f** was obtained from **1l** and purified by flash chromatography using petroleum ether; yield 69%; low melting solid; ^1H NMR: δ 7.65–7.59 (m, 2H), 7.57–7.49 (m, 2H), 7.40–7.28 (m, 6H), 6.65 (s, 1H). Anal. Calcd for $C_{16}H_{11}Br$: C, 67.87; H, 3.92. Found: C, 67.68; H, 3.90.

4.3.4. *(Z)-1-(1-Bromo-2-(4-methoxyphenyl)vinyl)benzene (**2a**), (Z)-1-(1-bromo-2-cyclohexylvinyl)benzene (**2b**), and (Z)-1-(1-bromohept-1-enyl)benzene (**2c**)*

Compounds **2a**,[31] **2b**,[32] and **2c**[33] showed satisfactory spectroscopic and analytical data that were consistent with those reported in the literature.

4.4. General procedure for the dehydrobromination of alkenes 2

$Bu_4N(OH)\cdot30H_2O$ (4.0 g, 5.0 mmol) was added to a solution of alkenes **2a–f** and Cs_2CO_3 (0.706 g, 2.0 mmol) in 1,4-dioxane (5.0 ml) and H_2O (2.0 ml). The resulting mixture was heated at 65 or 100 °C for 1–2 h (Tables 1 and 4) and then, after cooling, diluted with ethyl acetate (50 ml), and washed with brine (2×15 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated, and the residue was purified by flash chromatography.

4.5. General procedure for the one-pot preparation of alkynes 3 from 1,1-dibromo-1-alkenes

A mixture of the 1,1-dibromo-1-alkene (1.0 mmol), boronic acid or borate ester (1.05 mmol), and Cs_2CO_3 (0.706 g, 2.0 mmol) in 1,4-dioxane (5.0 ml) and H_2O (2.0 ml) was degassed by bubbling nitrogen for few minutes. Then, $Pd_2(dba)_3$ (23 mg, 0.025 mmol) and tris(2-furyl)phosphine (TFP) (35.0 mg, 0.15 mmol) were added and the resulting mixture was stirred under nitrogen at proper temperature and time (Tables 2–5). Then, $Bu_4N(OH)\cdot30H_2O$ (4.0 g, 5.0 mmol) was added and stirring was continued at 65 °C for further 1 h (Table 2,4 and 5) or 100 °C for 1–2 h (Table 3). The mixture was diluted with ethyl acetate (50 ml) and washed with brine (2×15 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated, and the residue was purified by flash chromatography.

4.5.1. *1-Chloro-3-(2-phenylethynyl)benzene (**3c**)*

Compound **3c** was obtained from **1c** and purified by flash chromatography using petroleum ether/ethyl acetate=9:1; yield 94%; oil; ^1H NMR: δ 7.58–7.46 (m, 3H), 7.42–7.14 (m, 6H). ^{13}C NMR: δ 134.1, 131.6, 131.4, 129.6, 129.5, 128.5, 128.4, 128.3, 124.9, 122.7, 90.5, 87.9. Anal. Calcd for $C_{14}H_9Cl$: C, 79.06; H, 4.27. Found: C, 79.22; H, 4.29.

4.5.2. *3-(2-m-Tolylethynyl)pyridine (**3j**)*

Compound **3j** was obtained from **1b** and purified by flash chromatography using petroleum ether/ethyl acetate=9:1; yield 48%; oil; ^1H NMR: δ 8.76 (d, 1H, J=1.8 Hz), 8.53 (dd, 1H, J=4.8, 1.8 Hz), 7.78 (td, 1H, J=7.8, 1.8 Hz), 7.35 (d, 2H, J=7.8 Hz), 7.29–7.19 (m, 2H), 7.16 (d, 1H, J=7.2 Hz), 2.34 (s, 3H). ^{13}C NMR: δ 152.1, 148.3, 138.3, 138.0, 132.1, 129.6, 128.7, 128.2, 122.9, 122.2, 120.5, 92.8, 85.5, 21.1. Anal. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 87.23; H, 5.77; N, 7.23.

4.5.3. *2-Methyl-5-(2-m-tolylethynyl)thiophene (**3k**)*

Compound **3k** was obtained from **1b** and purified by flash chromatography using petroleum ether/ethyl acetate=99.5:0.5; yield 64%; oil; ^1H NMR: δ 7.35–7.27 (m, 2H), 7.26–7.18 (m, 1H), 7.13 (d, 1H, J=7.8 Hz), 7.07 (d, 1H, J=3.6 Hz), 6.68–6.62 (m, 1H), 2.48 (s, 3H), 2.34 (s, 3H). ^{13}C NMR: δ 142.0, 138.0, 132.0, 131.8, 129.1, 128.4, 128.2, 125.3, 122.9, 120.9, 92.4, 82.7, 21.2, 15.4. Anal. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70. Found: C, 79.31; H, 5.68.

4.5.4. *3-(2-(3-Chlorophenyl)ethynyl)-3,4-dihydropyridine (**3l**)*

Compound **3l** was obtained from **1c** and purified by flash chromatography using petroleum ether/ethyl acetate=8:2: yield 63%; mp 41–42 °C; ^1H NMR: δ 8.76 (d, 1H, J=1.8 Hz), 8.56 (dd, 1H, J=4.8, 1.8 Hz), 7.79 (td, 1H, J=7.8, 1.8 Hz), 7.52 (d, 1H, J=1.8 Hz), 7.41 (td, 1H, J=7.8, 1.8 Hz), 7.37–7.22 (m, 3H). ^{13}C NMR: δ 152.1, 148.7, 138.4, 134.1, 131.4, 129.7, 129.5, 128.9, 124.1, 122.9, 119.8, 91.0, 86.9. Anal. Calcd for $C_{13}H_8ClN$: C, 73.08; H, 3.77; N, 6.56. Found: C, 73.32; H, 3.75; N, 6.54.

4.5.5. *3-(2-(4-Nitrophenyl)ethynyl)pyridine (**3m**)*

Compound **3m** was obtained from **1e** and purified by flash chromatography using petroleum ether/ethyl acetate=7:3; yield 61%; mp 134–135 °C; ^1H NMR: δ 8.80 (d, 1H, J=1.8 Hz), 8.60 (dd, 1H, J=4.8, 1.8 Hz), 8.25 (d, 2H, J=9.0 Hz), 7.85 (td, 1H, J=7.8, 1.8 Hz), 7.70 (d, 2H, J=9 Hz), 7.34 (dd, 1H, J=7.8, 1.8 Hz). ^{13}C NMR: δ 152.3, 149.4, 147.2, 138.6, 132.4, 129.3, 123.6, 123.1, 119.3, 90.9, 90.5. Anal. Calcd for $C_{13}H_8N_2O_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.44; H, 3.62; N, 12.51.

4.5.6. *3-(2-(5-Methylthiophen-2-yl)ethynyl)-3,4-dihydropyridine (**3o**)*

Compound **3o** was obtained from **1e** and purified by flash chromatography using petroleum ether/ethyl acetate 7:3; yield 67%; mp 45–46 °C; ^1H NMR: δ 8.72 (s, 1H), 8.51 (dd, 1H, J=4.8, 1.8 Hz), 7.75 (td, 1H, J=7.8, 1.8 Hz), 7.35–7.18 (m, 1H), 7.12 (d, 1H, J=3.3 Hz), 6.71–6.61 (m, 1H), 2.48 (s, 3H). ^{13}C NMR: δ 151.6, 148.1, 142.8, 137.9, 132.7, 125.4, 122.8, 120.2, 119.7, 88.7, 86.3, 15.2. Anal. Calcd for $C_{12}H_9NS$: C, 72.33; H, 4.55; N, 7.03. Found: C, 72.42; H, 4.53; N, 7.05.

4.5.7. *2-Bromo-3-(2-phenylethynyl)pyridine (**3u**)*

Compound **3u** was obtained from **1m** and purified by flash chromatography using petroleum ether/ethyl acetate=8:2; yield 84%; mp 73–74 °C; ^1H NMR: δ 8.29 (dd, 1H, J=4.8, 1.8 Hz), 7.79 (dd, 1H, J=7.8, 1.8 Hz), 7.62–7.54 (m, 2H), 7.42–7.34 (m, 3H), 7.25 (dd, 1H, J=7.8, 4.8). ^{13}C NMR: δ 148.3, 144.4, 140.6, 131.6, 129.1, 128.4, 123.5, 122.1, 96.5, 85.8. Anal. Calcd for $C_{13}H_8BrN$: C, 60.49; H, 3.12; N, 5.43. Found: C, 60.61; H, 3.11; N, 5.41.

*4.5.8. 1-Bromo-3-(2-phenylethynyl)benzene (**3w**)*

Compound **3w** was obtained from **1o** and purified by flash chromatography using petroleum ether; yield 63%; mp 84 °C; ^{1}H NMR: δ 7.67 (s, 1H), 7.55–7.48 (m, 1H), 7.44 (dd, 2H, J=7.8, 1.2 Hz), 7.36–7.29 (m, 3H), 7.18 (d, 1H, J=7.8 Hz). ^{13}C NMR: δ 134.3, 131.6, 131.3, 130.1, 129.7, 128.6, 128.4, 125.3, 122.7, 122.1, 90.7, 87.8. Anal. Calcd for $C_{14}H_9Br$: C, 65.40; H, 3.53. Found: C, 65.31; H, 3.52.

*4.5.9. 2-Bromo-5-(2-phenylethynyl)furan (**3x**)*

Compound **3x** was obtained from **1p** and purified by flash chromatography using petroleum ether; yield 32%; low melting solid; ^{1}H NMR: δ 7.54–7.45 (m, 2H), 7.39–7.29 (m, 3H), 6.59 (d, 1H, J=3.3 Hz), 6.34 (d, 1H, J=3.3 Hz). ^{13}C NMR: δ 139.1, 131.4, 128.9, 128.4, 122.5, 121.9, 117.5, 112.9, 94.5, 78.4. Anal. Calcd for $C_{12}H_7BrO$: C, 58.33; H, 2.86. Found: C, 58.13; H, 2.88.

*4.5.10. 4-Bromo-2-(2-phenylethynyl)thiophene (**3y**)*

Compound **3y** was obtained from **1q** and purified by flash chromatography using petroleum ether; yield 66%; mp 32–33 °C; ^{1}H NMR: δ 7.53–7.45 (m, 2H), 7.37–7.29 (m, 3H), 7.15 (s, 1H), 7.14 (s, 1H). ^{13}C NMR: δ 133.7, 131.5, 128.8, 128.4, 124.8, 124.3, 122.3, 109.6, 94.4, 81.2. Anal. Calcd for $C_{12}H_7BrS$: C, 54.77; H, 2.68. Found: C, 54.88; H, 2.69.

*4.5.11. 3,5-Dibromo-4-(2-phenylethynyl)pyridine (**3z**)*

Compound **3z** was obtained from **1r** and purified by flash chromatography using petroleum ether; yield 53%; mp 108–109 °C; ^{1}H NMR: δ 8.66 (s, 2H), 7.70–7.60 (m, 2H), 7.45–7.25 (m, 3H). ^{13}C NMR: δ 149.7, 134.5, 132.1, 130.0, 128.6, 123.1, 121.5, 103.3, 85.3. Anal. Calcd for $C_{13}H_7Br_2N$: C, 46.33; H, 2.09; N, 4.16. Found: C, 46.44; H, 2.07; N, 4.12.

*4.5.12. 2-Bromo-3-(2-(2-bromopyridin-3-yl)ethynyl)pyridine (**3za**)*

Compound **3za** was obtained from **1m** and purified by flash chromatography using petroleum ether/ethyl acetate 7:3; yield 81%; mp 180–182 °C; ^{1}H NMR: δ 8.37 (dd, 1H, J=4.8, 1.8 Hz), 7.89 (dd, 1H, J=7.8, 1.8 Hz), 7.32 (dd, 1H, J=7.8, 4.8 Hz). ^{13}C NMR: δ 149.3, 144.4, 141.2, 122.8, 122.2, 92.3. Anal. Calcd for $C_{12}H_6Br_2N_2$: C, 42.64; H, 1.79; N, 8.29. Found: C, 42.43; H, 1.81; Br, 47.28; N, 8.26.

*4.5.13. 2-Bromo-3-(2-(4-bromothiophen-2-yl)ethynyl)-pyridine (**3zb**)*

Compound **3zb** was obtained from **1p** and purified by flash chromatography using petroleum ether/ethyl acetate=8:2; yield 46%; mp 100 °C; ^{1}H NMR: δ 8.31 (dd, 2H, J=4.8, 1.8 Hz), 7.77 (dd, 2H, J=7.8, 2.1 Hz), 7.28 (dd, 2H, J=7.8, 4.8 Hz), 7.26 (s, 2H). ^{13}C NMR: δ 148.8, 144.1, 140.5, 134.7, 125.6, 123.5, 122.8, 122.1, 109.9, 90.6, 88.1. Anal. Calcd for $C_{11}H_5Br_2NS$: C, 38.51; H, 1.47; N, 4.08. Found: C, 38.44; H, 1.44; N, 4.09.

*4.5.14. 1-(2-(4-Methoxyphenyl)ethynyl)benzene (**3a**), 1-methyl-3-(2-phenylethynyl)benzene (**3b**), 1-chloro-3-(2-phenylethynyl)-benzene (**3c**), 1-nitro-4-(2-phenylethynyl)benzene (**3d**), 3-(2-phenylethynyl)pyridine3-(2-phenylethynyl)pyridine (**3e**), 2-(2-phenylethynyl)furan (**3f**), 3-(2-phenylethynyl)thiophene (**3g**), 1-(2-(4-methoxyphenyl)ethynyl)-4-nitrobenzene (**3h**), 3-(2-(pyridin-3-yl)ethynyl)pyridine (**3n**), 1-(2-cyclohexyl-ethynyl)benzene (**3p**), 1-(hept-1-ynyl)benzene (**3q**), 1,4-diphenylbut-1-yne (**3r**), (E)-1,4-diphenylbut-1-en-3-yne (**3s**), 2-bromo-3-(2-phenylethynyl)pyridine (**3u**), 1-bromo-4-(2-phenylethynyl)benzene (**3v**), and 1-bromo-3-(2-phenylethynyl)benzene (**3w**)*

Compounds **3a**,[34] **3b**,[35] **3c**,[36] **3d**,[37] **3e**,[35] **3f**,[38] **3g**,[39] **3h**,[40] **3i**,[41] **3n**,[42] **3p**,[43] **3q**,[44] **3r**,[45] **3s**,[46] **3t**,[47] **3v**,[48] and **3w**[49] showed satisfactory spectroscopic and analytical data that were consistent with those reported in the literature.

4.6. 2-(4-Methoxy-3-methylphenyl)-3-(2-phenylethynyl)pyridine (5)

A solution of 2-bromo-3-(2-phenylethynyl)pyridine (124 mg, 0.48 mmol) and tetrakis(triphenylphosphane)palladium(0) (16.0 mg, 0.014 mmol) in toluene (1.0 ml) was treated with a solution of Na_2CO_3 (0.10 g, 0.95 mmol) in H_2O (0.48 ml) followed by a solution of 4-methoxy-3-methylphenylboronic acid (0.07 g, 0.57 mmol) in methanol (0.24 ml). The mixture was heated at 80–85 °C under argon for 5 h. After cooling at room temperature, a solution of concentrated aqueous NH_3 (0.24 ml) in saturated aqueous Na_2CO_3 (2.4 ml) was added and the mixture was extracted with CH_2Cl_2 (3×10 ml). The combined organic layers were washed with brine (5 ml) and dried over anhydrous Na_2SO_4 and then filtered. Removal of the solvent under reduced pressure gave a residue, which was purified by flash chromatography (petroleum ether/ethyl acetate=7:3) to give compound **5**; 123.6 mg (86%); oil; ^{1}H NMR: δ 8.58 (dd, 1H, J=4.8, 0.9 Hz), 7.97–7.82 (m, 3H), 7.46–7-38 (m, 2H), 7.35–7.26 (m, 3H), 7.13 (dd, 1H, J=7.8, 4.8 Hz), 6.90 (d, 1H, J=8.4 Hz), 3.85 (s, 3H), 2.31 (s, 3H). ^{13}C NMR: δ 159.1, 158.4, 148.3, 140.8, 131.6, 131.3, 128.4, 128.3, 128.1, 125.8, 122.9, 120.6, 117.1, 109.1, 94.2, 87.9, 55.2, 16.3. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 84.14; H, 5.74; N, 4.66.

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