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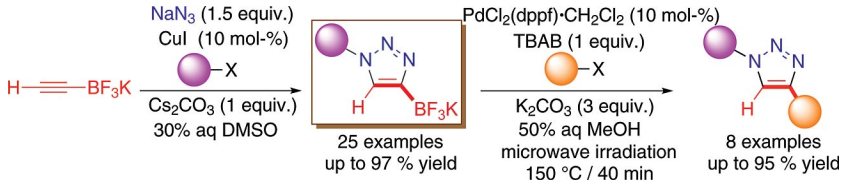
SHORT COMMUNICATION

Click Chemistry



The preparation of potassium (1-organo-1*H*-1,2,3-triazol-4-yl)trifluoroborates from potassium ethynyltrifluoroborate and alkyl or aryl halides by employing a regioselective one-pot Cu-catalyzed azide–alkyne cycloaddition (CuAAC) is elaborated. This strategy allows unrestricted access to an infinite variety of 1,4-disubstituted 1,2,3-triazoles.

Keywords: Copper / Click chemistry / Boron / Nitrogen heterocycles / Cross-coupling

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Potassium (1-Organo-1*H*-1,2,3-triazol-4-yl)trifluoroborates from Ethynyltrifluoroborate through a Regioselective One-Pot Cu-Catalyzed Azide–Alkyne Cycloaddition Reaction

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Keywords: Copper / Click chemistry / Boron / Nitrogen heterocycles / Cross-coupling

A novel series of 1,4-disubstituted 1,2,3-triazole-containing potassium trifluoroborates were prepared in good to excellent yields from the corresponding organohalides and potassium ethynyltrifluoroborate through a regioselective one-pot Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction. Further Suzuki–Miyaura cross-coupling of these (organo-1,2,3-triazol-4-yl)trifluoroborates with aryl and alkenyl bromides by using a $PdCl_2$(dppf)·CH_2Cl_2/TBAB [dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, TBAB = tetrabutylammonium bromide] system under microwave irradiation was explored.

Introduction

Being one of the most important structural motifs for the development of potentially bioactive molecules and new materials, 1,4-disubstituted 1,2,3-triazoles are widely used in various fields such as organic synthesis, medicinal chemistry, and materials science.[1] Ever since the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) reaction was reported by Sharpless[2] and Meldal,[3] a number of mild and efficient methods for the preparation of various 1,2,3-triazole compounds have been disclosed. However, despite significant recent improvements, the diversity of 1,2,3-triazoles that can be obtained through the CuAAC reaction is limited by the availability and high price of the terminal alkyne derivatives from commercial sources. Moreover, some low-molecular-weight alkynes are difficult to handle because of their low boiling points. Therefore, new facile and efficient methods to obtain multifariously C4-functionalized triazole compounds are still of synthetic interest.

In 2009, Harrity's group reported the thermal [3+2] cycloaddition reactions of various alkyl azides and alkynylboronates[4] in the first literature report of the construction of a library of triazole compounds through a Pd-catalyzed cross-coupling reaction. However, they could not perfectly control the regioselectivity for 1,4- and 1,5-disubstituted products containing pinacol boronate moieties unless a trimethylsilyl-substituted alkynyl boronate was used as the starting material. More recently, Grob's group at Novartis Institutes published a report disclosing a regioselective method for the CuAAC reaction by using *N*-methyl iminodiacetic acid (MIDA)-masked ethynylboronic acid and cross-coupling reactions.[5] However, these previous methods for the preparation of the target triazole compounds require long reaction times, high reaction temperatures, and purification by column chromatography to obtain the boron reagents in satisfactory yields.

Over the past decade, potassium organotrifluoroborates have become powerful synthetic building blocks for the formation of new carbon–carbon bonds through Suzuki–Miyaura cross-coupling, because these compounds are easy to prepare and purify. They are also convenient to handle because they are air- and moisture-stable crystalline solids. Furthermore, the inertness of the trifluoroborate ($-BF_3$) group under reaction conditions for direct transformation by using palladium or copper catalysts allows the preparation of hightly functionalized organotrifluoroborates.[6] Recently, we demonstrated an efficient and rapid method to prepare potassium (organo-1,2,3-triazol-1-aryl)trifluoroborates through a regioselective one-pot CuAAC reaction from (azidoaryl)trifluoroborates generated in situ.[7] Surprisingly, click reactions with potassium ethynyltrifluoroborate and cross-coupling reactions of these (1,2,3-triazol-4-yl)trifluoroborates have yet to be reported, to the best our knowledge (Scheme 1).

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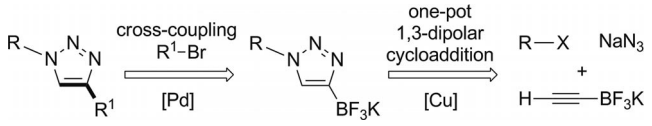


Scheme 1. Reaction strategy for the development of various 1,4-disubstituted 1,2,3-triazoles through potassium (1-organo-1*H*-1,2,3-triazol-4-yl)trifluoroborates.

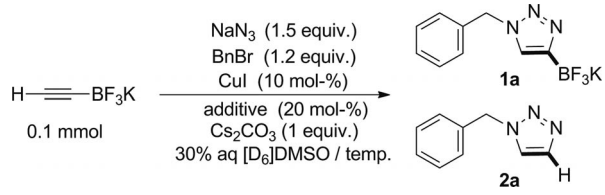
In continuation of our studies on the development of synthetic strategies for the direct functionalization of organotrifluoroborates, we found that potassium ethynyltrifluoroborate could be used as a starting material in the CuAAC reaction instead of commercially available terminal alkynes. Also, the resulting triazole compounds containing trifluoroborate moieties could be utilized as coupling partners in the Suzuki–Miyaura reaction. Herein, we report the first one-pot preparation of potassium (1-organo-1*H*-1,2,3-triazol-4-yl)trifluoroborates from potassium ethynyltrifluoroborate through a regioselective one-pot CuAAC reaction and subsequent Suzuki–Miyaura cross-coupling reaction of the trifluoroborates thus generated.

Results and Discussion

Initially, we attempted to find optimized reaction conditions for the formation of potassium (1-benzyl-1*H*-1,2,3-triazol-4-yl)trifluoroborate (**1a**) through a regioselective one-pot CuAAC reaction with potassium ethynyltrifluoroborate (Table 1). In tests aimed at studying the effects of solvent and base on reactivity (Table 1, entries 1–3), we found that desired **1a** could not be obtained if CuI was used as the catalyst and NaN_3 was used as the azide source at 80 °C; instead, protodeboronated product **2a** was easily generated (Table 1, entries 1 and 2). However, if the reaction was performed with 30% aqueous [D_6]DMSO and Cs_2CO_3 (1 equiv.) at the same temperature for 5 h, **1a** was obtained in 51% isolated yield along with side product **2a** in 40% yield (Table 1, entry 3). Further optimization of the temperature revealed that if the reaction was performed at 30 °C, only **1a** was obtained in 55% yield (Table 1, entry 4). Although a detailed reaction mechanism has yet to be determined, we propose the following mechanism for the desired and undesired reaction cycles on the basis of literature precedence.[8] As shown in Scheme 2, the two reaction cycles are probably initiated by nucleophilic attack of the acetylide, generated with base, onto the copper catalyst (catalytic cycle A) and boron–copper transmetalation under heating conditions (catalytic cycle B). In the next step, R–N_3 is then activated by coordination to the C–CuL_x complex, which provides intermediates **A1** and **B1**. These intermediates subsequently undergo formation of copper metallacycles **A3** and **B3**. Finally, 1,2,3-triazoles **A5** and **B5** are generated by protonation of copper–triazolide intermediates **A4** and **B4**, and the copper catalyst is regenerated.

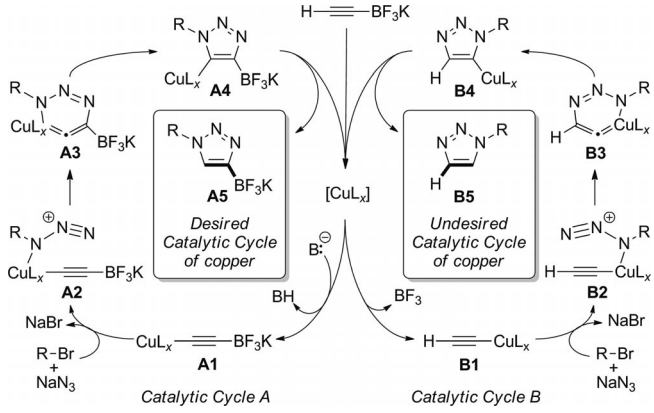
Dramatically, when 20 mol-% of sodium ascorbate was used as an additive[9] and *N*,*N*′-dimethylethylenediamine (DMEDA) was used as a ligand[10] (Table 1, entry 6), these

Table 1. Survey of one-pot CuAAC reaction conditions.[a]



Entry	Temp. [°C]	Additive	Time [h]	Isolated yield [%] **1a**	**2a**
1[b,c]	80	none	12	none	67
2[c]	80	none	2	none	87
3	80	none	5	51	40
4	30	none	7	55	none
5	30	Na-ascorbate	2.5	95	none
6[d]	30	Na-ascorbate	0.5	96	none
7[d,e]	30	Na-ascorbate	2	93[f]	–[g]

[a] All reactions were performed on a 0.1 mmol scale in 0.5 mL of 30% aqueous [D_6]DMSO in an NMR tube and then directly monitored by ^{1}H NMR spectroscopy. [b] Without H_2O. [c] Without Cs_2CO_3. [d] 20 mol-% of DMEDA was used as a ligand. [e] Reaction was carried out by using 4-iodobenzene as a starting material instead of benzyl bromide. [f] Isolated product was potassium (1-phenyl-1*H*-1,2,3-triazol-4-yl)trifluoroborate (**3a**). [g] Other side products were not observed.



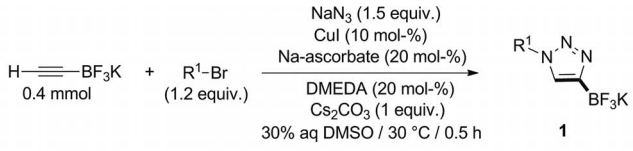
Scheme 2. Proposed catalytic cycle for 1,2,3-triazole formation from potassium ethynyltrifluoroborate with R–N_3 in the presence of copper.

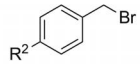
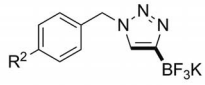
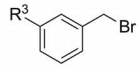
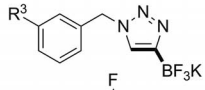
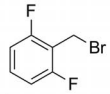
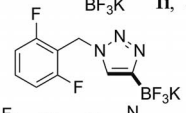
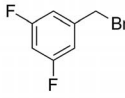
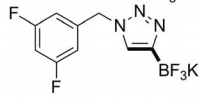
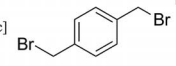
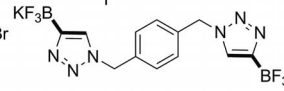
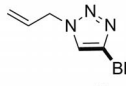
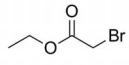
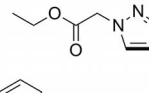
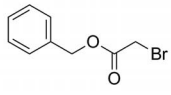
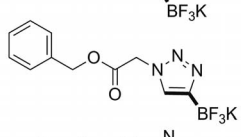
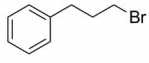
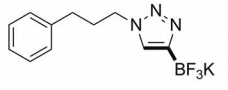
one-pot CuAAC reaction conditions not only curtailed the reaction time to 0.5 h, but also increased the yield of **1a** to 96% without contamination of side product **2a**. Interestingly, an attempt to prepare potassium (1-phenyl-1*H*-1,2,3-triazol-4-yl)trifluoroborate (**3a**) from iodobenzene was also successful under the same reaction conditions. However, the reaction time was slightly extended to 2 h (Table 1, entry 7). These CuAAC conditions served as the basis for all of our other studies.

With the optimized conditions in hand, we examined reactions of various alkyl bromides with potassium ethynyltrifluoroborate, and the results are shown in Table 2. This method tolerates various functional groups attached to the benzyl bromide. The reactions with benzyl bromides that contained either electron-donating groups or electron-withdrawing groups afforded the desired products in 79–96%

yields (Table 2, entries 1–11). Interestingly, when 4-bromomethylbenzyl bromide was used as the starting material, the reaction gave the desired dipotassium bis[(1,2,3-triazol-4-yl)trifluoroborate] product[11] in 83% yield (Table 2, entry 12). Also, the regioselective one-pot CuAAC reactions of allyl bromide, α-bromo esters, and alkyl bromide proceeded easily to give the desired products in good yields (Table 2, entries 13–16).

Table 2. Regioselective one-pot CuAAC reactions with various alkyl bromides and potassium ethynyltrifluoroborate.[a]

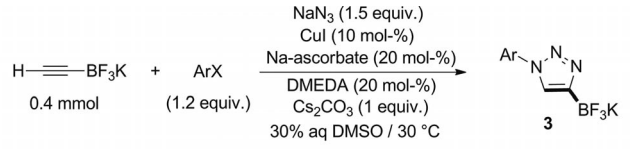


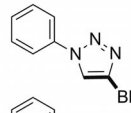
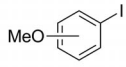
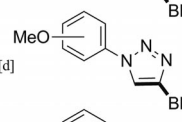
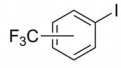
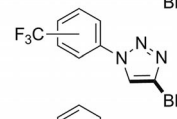
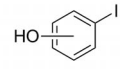
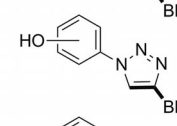
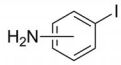
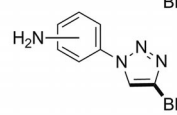
Entry	R^1-Br	Product	Yield [%][b]
1		 **1a**, R^2 = H	96
2		**1b**, R^2 = Me	87
3		**1c**, R^2 = OMe	96
4		**1d**, R^2 = CN	96
5		**1e**, R^2 = NO_2	84
6		**1f**, R^2 = CF_3	84
7		**1g**, R^2 = Br	88
8		 **1h**, R^3 = CF_3	83
9		**1i**, R^3 = CO_2Me	81
10		 **1j**	79
11		 **1k**	81
12[c]		 **1l**	83
13		 **1m**	88
14		 **1n**	86
15		 **1o**	89
16		 **1p**	83

[a] All reactions were performed on a 0.4 mmol scale in 2.0 mL of 30% aqueous DMSO and monitored by ^{1}H NMR spectroscopy in D_2O. [b] Isolated yield. [c] Reaction was performed with potassium ethynyltrifluoroborate (2 equiv.), NaN_3 (3 equiv.), CuI (20 mol-%), Na-ascorbate and DMEDA (40 mol-%), and Cs_2CO_3 (2 equiv.) based on 1,4-bis(bromomethyl)benzene.

Next, having obtained the optimal reaction conditions (Table 1, entry 7), we examined the regioselective one-pot CuAAC reaction of aryl halides with potassium ethynyltrifluoroborate (Table 3). In a test of the different reactivities of *o*-, *m*-, and *p*-iodoanisole, the yields of the corresponding products increased in the order *ortho* < *meta* < *para* (Table 3, entries 2–4). The use of bromobenzene and 4-bromoanisole instead of iodobenzene and 4-iodoanisole resulted in a slight decrease in the yield to 87% in both cases (Table 3, entries 1 and 4). Encouraged by these results, we proceeded with further screening, which revealed that the use of trifluoromethyl-functionalized iodobenzene also provided good yields of the desired products with *m*- and *p*-iodobenzotrifluoride (Table 3, entries 6 and 7). Notably, the reactions also tolerate free hydroxy groups (Table 3, entries 9 and 10) and amino groups (Table 3, entry 13); the corresponding desired products were observed in all cases. Unfortunately, the regioselective one-pot CuAAC reaction in some cases of *o*- or *m*-substituted aryl halides did not proceed because of steric hindrance or because of the low reactivity of the aryl azides (Table 3, entries 5, 8, 11, and 12).

Table 3. Regioselective one-pot CuAAC reactions with various aryl halides and potassium ethynyltrifluoroborate.[a]



Entry	ArI	Time [h]	Product	Yield [%][b]
1		2 (6)[c]	 **3a**	96 (87)[c]
2		*o*- 4	 **3b**	83
3		*m*- 2		**3c**	88
4		*p*- 2 (6)[d]		**3d**	91 (87)[d]
5		*o*- –	 –	–
6		*m*- 2		**3e**	88
7		*p*- 2		**3f**	92
8		*o*- –	 –	–
9		*m*- 6		**3g**	88
10		*p*- 4		**3h**	88
11		*o*- –	 –	–
12		*m*- –		–	–
13		*p*- 4		**3i**	87

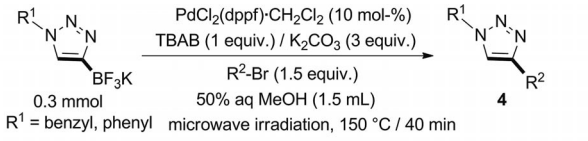
[a] All reactions were performed on a 0.4 mmol scale in 2.0 mL of 30% aqueous DMSO and monitored by ^{1}H NMR spectroscopy in D_2O. [b] Isolated yield. [c] Bromobenzene was used. [d] 4-Bromoanisole was used.

With the synthesis of 1,4-disubstituted 1,2,3-triazoles ultimately in mind, the scope of the Suzuki–Miyaura cross-coupling reaction of **1a** was investigated with respect to coupling conditions. We found that if the reaction was performed at 150 °C for 40 min in the presence of $PdCl_2$(dppf)·CH_2Cl_2 [10 mol-%, dppf = 1,1′-bis(diphenylphosphanyl)-ferrocene] and tetrabutylammonium bromide (TBAB) as an additive[12] under microwave irradiation of 80 W, the best isolated yield was obtained under the optimized reaction conditions (see the Supporting Information).

Finally, we examined the Suzuki–Miyaura cross-coupling reactions of **1a** and **3a** with different aryl and alkenyl brom-

ides under the optimized coupling conditions, and the reaction results are summarized in Table 4. As expected, the coupling reactions with various functionalized aryl bromides gave the desired products in good yields (Table 4, entries 1–5). In the reaction with 1,2,2-triphenylvinyl bromide as a sterically bulky coupling partner alkene, the product was isolated in a reasonable yield of 57% (Table 4, entry 6). Moderate yields were also obtained for the coupling reactions of **3a** to yield **4g** and **4h** (Table 4, entries 7 and 8).

Table 4. Microwave-assisted C–C bond-forming cross-coupling.[a]



Entry	Product	Yield [%][b]
1	**4a**, $R^3 = R^4 = H$	90
2	**4b**, $R^3 = OMe$, $R^4 = H$	89
3	**4c**, $R^3 = CF_3$, $R^4 = H$	85
4	**4d**, $R^3 = CH_2OH$, $R^4 = OMe$	81
5	**4e**, $R^3 = R^4 = -OCH_2O-$	88
6	**4f**	57
7	**4g**, $R^5 = H$	81
8	**4h**, $R^5 = CF_3$	88

[a] All reactions were performed on a 0.3 mmol scale by using a microwave reactor for 40 min at 150 °C. [b] Isolated yield.

Conclusions

We have successfully prepared potassium (1-organo-1*H*-1,2,3-triazol-4-yl)trifluoroborates from ethynyltrifluoroborate through a perfectly regioselective one-pot CuAAC reaction and have shown that these products can be cross-coupled under Pd-catalyzed Suzuki–Miyaura cross-coupling reaction conditions. This method allows convenient access to versatile triazole-containing trifluoroborate reagents, a class that can be difficult to obtain by other means. Further development of these 1,2,3-triazoletrifluoroborates and their applications are currently under investigation by our group.

Experimental Section

General Procedure for the Synthesis of Potassium (1-Organo-1*H*-1,2,3-triazol-4-yl)trifluoroborates: To a solution of potassium ethynyltrifluoroborate (0.4 mmol), sodium azide (0.6 mmol, 1.5 equiv.), CuI (0.04 mmol, 10 mol-%), sodium ascorbate (0.08 mmol, 20 mol-%), *N*,*N*′-dimethylethylenediamine (0.08 mmol, 20 mol-%), and Cs_2CO_3 (0.4 mmol, 1 equiv.) in 30% aq. DMSO (2.0 mL) was added the corresponding alkyl or aryl halide (0.48 mmol, 1.2 equiv.) under atmospheric conditions. The reaction mixture was stirred in an oil bath at 30 °C. Upon completion of the reaction, the solvent was removed in vacuo at 60–70 °C. The residual product was dissolved in dry acetone (3 × 3 mL), and the insoluble salts were removed by filtration through Celite. The solvent was concentrated on a rotary evaporator. The addition of Et_2O led to the precipitation of the product. The product was filtered and dried in vacuo to afford the desired pure product.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and analytical and spectroscopic data for new compounds.

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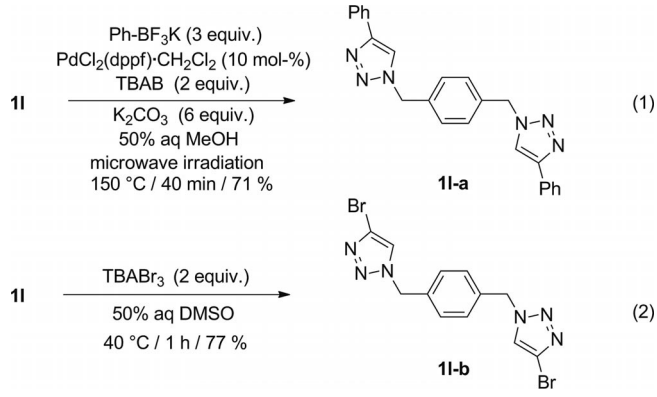
[11] For determination of the dipotassium bis[(1,2,3-triazol-4-yl)trifluoroborate] **1l**, we performed a Pd-catalyzed Suzuki–Miyaura cross-coupling reaction under the optimized conditions (Table 4) [Eq. (1)] and bromodeboronation by using tetrabutylammonium tribromide ($TBABr_3$) [Eq. (2)][13] as shown below. The structures of reaction products **1l-a** and **1l-b** were determined by ^1H NMR, ^{13}C NMR, and IR spectroscopy and mass spectrometry (see the Supporting Information).



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