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One-pot sequential diprop-2-ynylation and cycloaddition: An efficient synthesis of novel *N,N*-bis(1,2,3-triazol-4-yl) methylarylamines starting from primary amines

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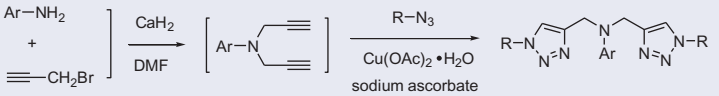
ABSTRACT

A facile, one-pot synthesis strategy for the tertiary arylamines bearing *N,N*-bis(1,2,3-triazol-4-yl)methyl structure has been developed by sequential diprop-2-ynylation of primary amines with propargyl bromide in the presence of calcium hydride in DMF and [3 + 2] "click" cycloaddition with organic azides promoted by cupric acetate in the mixed DMF-H_2O media. This protocol provides some features, such as high efficiency and regioselectivity, easy operation, and moderate to good product yield (56–84%) with a wide substrate scope under mild conditions.

GRAPHICAL ABSTARCT



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Cycloaddition; diprop-2-ynylation; *N,N*-bis(1,2,3-triazol-4-yl) methylarylamines; one-pot procedure

Introduction

Aromatic amines and 1,2,3-triazoles are all nitrogen-containing compounds. Aromatic amines are widely used as versatile building blocks for organic synthesis, natural products, agrochemicals, pharmaceuticals, and material science.[1] The formation of C–N bond through cross-coupling reaction of primary amines and organic halides has been applied as the major method to prepare secondary and tertiary amines.[2] 1,2,3-Triazoles have displayed an ample range of application in synthetic, pharmaceutical, agrochemical, medicinal and material chemistry.[3] Introduction of triazole scaffold into amines is meaningful research to explore biologically active compounds and pharmaceutical agents. As far as we know, some synthetic methods have been developed for the construction of triazolyl-containing amines.[4] However, arylamines with *N,N*-bis(1,2,3-triazol-4-yl)methyl groups have been reported only rarely.[5] It is well known that

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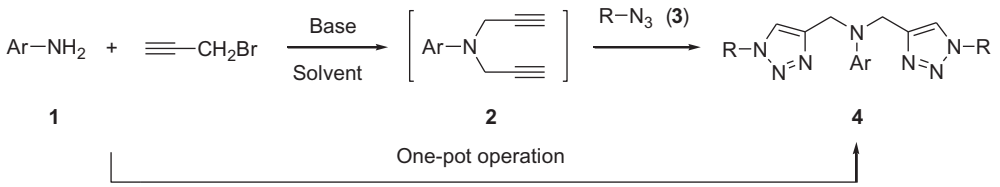
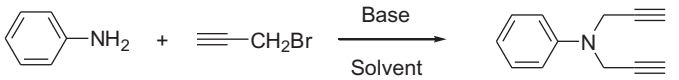


Scheme 1. Access to *N,N-bis*(1,2,3-triazol-4-yl)methylarylamines (**4**) by a diprop-2-ynylation and CuAAC sequence.



1a **2a**

Scheme 2. Formation of *N,N*-di(prop-2-yn-1-yl)aniline (**2a**).

copper-catalyzed alkyne-azide cycloaddition (CuAAC), a click chemistry reaction, is one of the most attractive methods for the regioselective synthesis of 1,4-disubstituted 1,2,3-triazole derivatives for a different purpose.[6] Although there are numerous methods for the preparation of 1,4-disubstituted 1,2,3-triazoles, the starting materials are mainly terminal alkynes that need to be prepared and isolated separately. Obviously, the generation of terminal alkynes *in situ* from suitable precursors, followed by the reaction with azides in a one-pot process to form the corresponding 1,2,3-triazoles would avoid the difficulties associated with the volatile nature of terminal alkynes. Recently, our group has been engaged in the development of new multi-component and one-pot reactions for the preparation of 1,2,3-triazole derivatives under various conditions.[7] Herein, we would like to report our recent efforts to a facile and one-pot synthesis of *N,N*-bis(1,2,3-triazol-4-yl)methylarylamines, involving *in situ* generations of terminal alkynes, *N,N*-di(prop-2-yn-1-yl)arylamines through diprop-2-ynylation of primary amines with propargyl bromide, followed by CuAAC reaction with organic azides, as outlined in Scheme 1.

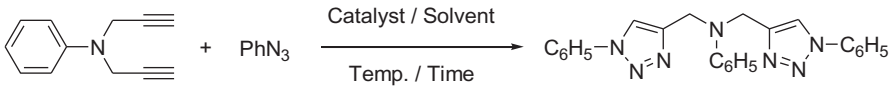
In order to find the most suitable reaction conditions for our purpose, aniline (**1a**), propargyl bromide and phenyl azide (**3a**) were chosen as model substrates for the preparation of *N,N*-bis[(1-phenyl-1*H*-1,2,3-triazol-4-yl)methyl]aniline (**4a**). Initially, the diprop-2-ynylation conditions of **1a** with propargyl bromide, the key to the success of this protocol were investigated (Scheme 2).

It was reported N,N-di(prop-2-yn-1-yl)aniline (**2a**) could be obtained in 80% yield by reaction of **1a** with propargyl bromide in *N,N*-dimethylformamide (DMF) at room temperature in the presence of potassium carbonate.[8] Encouraged by this positive result, other polar solvents and bases were further screened (Table 1, entries 2–8). Clearly, good yield of **2a** in the model reaction was obtained in DMF and dimethylsulfoxide (DMSO) in the presence of different bases such as potassium carbonate, *N,N*-diisopropylethylamine (DIPEA) and calcium hydride (CaH_2) (Table 1, entries 1, 2, 7, and 8). Among them, the presence of CaH_2 was shown to be very effective for the reaction to occur (Table 1, entry 8). After a considerable number of experiments, **2a** was produced

Table 1. Optimization of the diprop-2-ynylation conditions of **1a**[a].

Entry	Solvent	Base (mol %)	Time (h)	Yield (%)[b]
1	DMF	K_2CO_3[c]	6	80
2	DMSO	K_2CO_3 (20)	6	78
3	Dioxane	K_2CO_3 (20)	6	65
4	MeCN	K_2CO_3 (20)	6	68
5	THF	K_2CO_3 (20)	6	60
6	DMF	Et_3N (20)	6	72
7	DMF	DIPEA (20)	6	82
8	DMF	CaH_2 (20)	6	85
9	DMF	CaH_2 (30)	6	90
10	DMF	CaH_2 (40)	6	92
11	DMF	CaH_2 (40)	8	95
12	DMF	CaH_2 (50)	8	96

[a]Unless otherwise noted, all reaction was performed with 1.0 mmol of aniline (**1a**), 4.0 mmol of propargyl bromide, 5 mL of solvent at room temperature. [b]Isolated yield after column chromatography, based on **1a**. [c]The data are cited from the work of Ji et al.[8]



2a **3a** **4a**

Scheme 3. [3 + 2]-Cycloaddition of **2a** with phenyl azide (**3a**).

Table 2. Optimization for the click process between **2a** and **3a**[a].

Entry	Catalyst/Time/Temp	Yield of **4a** (%)[b]
1	$CuCl_2$, sodium ascorbate, DMF, rt, 6 h	44
2	$Cu(OAc)_2$, sodium ascorbate, DMF, rt, 6 h	55
3	$CuSO_4$, sodium ascorbate, DMF, rt, 6 h	51
4	$CuCl_2 \cdot 2H_2O$, sodium ascorbate, DMF, rt, 6 h	50
5	$CuSO_4 \cdot 5H_2O$, sodium ascorbate, DMF, rt, 6 h	63
6	$Cu(OAc)_2 \cdot H_2O$, sodium ascorbate, DMF, rt, 6 h	72
7	$Cu(OAc)_2 \cdot H_2O$, sodium ascorbate, DMF, 60 °C, 4 h	78
8	$Cu(OAc)_2 \cdot H_2O$, sodium ascorbate, DMF-H_2O (5:1), 60 °C, 2 h	83

[a]Copper(II) salt (0.2 mmol), sodium ascorbate (0.1 mmol), and phenyl azide (1.0 mmol) were used. [b]Isolated yield based on aniline after column chromatography.

in 95% yield when the reaction was carried out in DMF at room temperature in the presence of 40 mol.% CaH_2 for 8 h (Table 1, entry 11).

After the completion of the diprop-2-ynylation, the excess propargyl bromide was removed by vacuum distillation. Without further isolation and purification of the intermediate **2a**, the subsequent [3 + 2] cycloaddition reaction with **3a** for the target molecule **4a**, as shown in Scheme 3, was studied, and the corresponding results are summarized in Table 2.

As mentioned earlier, CuAAC reaction has been used to prepare 1,4-disubstituted-1*H*-1,2,3-triazoles exclusively. Although copper(I) salts can be directly used, practically, Cu(I) salts generated *in situ* by reduction of copper(II) salts was less costly and was reported to give more pure material than some Cu(I) salts that were commercially available. Moreover, by this method, the reaction can be smoothly performed under milder conditions avoiding the use of inert atmospheres. Therefore, copper(II) salts such as

Table 3. Sequential transformation of different arylamines and azides into *N,N*-bis(1,2,3-triazol-4-yl) methylarylamines (**4**).

Entry	Ar	R	Product	Yield (%)[a]
1	C_6H_5	C_6H_5	**4a**	83
2	C_6H_5	2-$CH_3C_6H_4$	**4b**	64
3	C_6H_5	2-$CH_3OC_6H_4$	**4c**	66
4	C_6H_5	2-ClC_6H_4	**4d**	59
5	C_6H_5	$C_6H_5CH_2$	**4e**	83
6	3-$CH_3C_6H_4$	C_6H_5	**4f**	81
7	3-$CH_3C_6H_4$	2-$CH_3C_6H_4$	**4g**	63
8	3-$CH_3C_6H_4$	2-$CH_3OC_6H_4$	**4h**	70
9	3-$CH_3C_6H_4$	2-ClC_6H_4	**4i**	61
10	3-$CH_3C_6H_4$	$C_6H_5CH_2$	**4j**	84
11	2-$CH_3C_6H_4$	2-$CH_3C_6H_4$	**4k**	58
12	2-$CH_3C_6H_4$	2-$CH_3OC_6H_4$	**4l**	61
13	2-$CH_3C_6H_4$	2-ClC_6H_4	**4m**	56
14	2-$CH_3C_6H_4$	3-$CH_3C_6H_4$	**4n**	81
15	4-ClC_6H_4	2-$CH_3OC_6H_4$	**4o**	66
16	4-ClC_6H_4	$C_6H_5CH_2$	**4p**	80
17	C_6H_5	2-$NO_2C_6H_4$	**4q**	0
18	C_6H_5	2-pyridyl	**4r**	0

[a]Isolated yield based on the corresponding arylamine after column chromatography.

copper sulfate and cupric acetate, together with a reducing reagent like sodium ascorbate were employed in the ring formation between **2a** with **3a**. After preliminary screening of several copper salts (Table 2, entries 1–6), $Cu(OAc)_2 \cdot H_2O$ was be found to be the most effective (Table 2, entry 6). In addition, when the reaction was heated to an elevated temperature of 60 °C for 4 h, **4a** with 78% yield as an exclusive product was isolated (Table 2, entry 7). To our delight, the addition of a small amount of water into the reaction system resulted in a good yield of 83% and shorter reaction time at 60 °C for 2 h (Table 2, entry 8), which may be due to the increased solubility of sodium ascorbate and copper salt in the solvent.

The structure of **4a** was characterized by NMR spectroscopic and mass spectrometric data. In the ^{1}H NMR spectrum of **4a**, a characteristic singlet appeared at $\delta = 8.76$ ppm due to the triazolyl C5–H proton and a singlet at $\delta = 4.82$ for $ArNCH_2$ along with other protons. In its ^{13}C NMR spectrum the $ArNCH_2$ carbon appeared at $\delta = 46.2$, C4 of the triazole ring appeared at $\delta = 146.3$ and C5 at $\delta = 121.8$ along with other carbons. Besides, the mass spectrum data of this compound were in agreement with the calculated values.

Finally, the optimized reaction conditions were extended to a variety of primary aromatic amines and organic azides with different substituents. As shown in Table 3, for most of the examined substrates, experiments were performed smoothly and the corresponding tertiary arylamines containing *N,N*-bis(1,2,3-triazol-4-yl)methyl groups were obtained. In general, no significant difference in reactivity was observed for the examined arylamines substituted by 3-Me, 2-Me, 4-Cl on the benzene rings (Table 3, entries 6–16). It is noteworthy that a variety of functional groups such as chloro, methyl, and methoxy were tolerated on aromatic azides that could be successfully converted to the desired product in moderate to good yields (Table 3, entries 2–4, entries 7–9, and entries 11–15). Moreover, benzyl azide also reacted satisfactorily in all reactions (Table 3, entries 5, 10, and 16). However, low yields were found when the organic azides were hindered (Table 3, entries 2–4, entries 7–9, entries 11–13 and 15), and

sensitive functional groups like 2-nitrophenyl azide and heterocyclic azide rendered the cycloaddition unresponsive (Table 3, entries 17 and 18). In addition, alkyl azide like *n*-butylazide instead of aryl azide tested in the similar procedure did not afford the corresponding product.

In summary, a facile and efficient, one-pot method for the preparation of *N,N*-bis(1,2,3-triazol-4-yl)methylarylamines from primary amines, propargyl bromide and organic azides has been developed. The procedure does not require isolation of the *N,N*-dipropargylated arylamine intermediates, and has considerable advantages in terms of its use of easily available substrates, its mild reaction conditions, its simple operation, and the moderate-to-good yields.

Experimental

Melting points were measured with a Beijing-Taike X-4 apparatus (Beijing, China) without corrections. ^{1}H NMR and ^{13}C NMR spectra were recorded on an Avance-Bruker 400 MHz NMR spectrometer (Billerica, MA), operating at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to TMS or the deuterated solvent as an internal reference. IR analyses were performed with a Perkin-Elmer SP One FT-IR spectrophotometer (Waltham, MA). Microanalyses were performed with a Carlo Erba 1106 Elemental Analyzer (CE Elantech, Lakewood, NJ). Mass spectra were recorded on a Thermofisher scientific LCQ FLEET mass spectrometer. All organic azides are known compounds and were prepared from primary amine using sodium nitrite and hydrazine hydrate at room temperature through the reported method.[9] Other reagents and solvents were purchased from commercial suppliers and were used as received without further purification. All experiments were carried out in air. Analytical TLC was carried out on Merck 0.2-mm silica gel 60 F254 analytical aluminum plates, and the products were visualized by UV detection. Column chromatography was performed on Merck silica gel 60 (250–400 mesh).

General procedure for the preparation of N,N-Bis(1,2,3-triazol-4-yl) methylarylamines

To a stirred solution of primary amine (**1**) (1.0 mmol) in DMF (5 mL) was added calcium hydride (20 mg, 0.4 mmol) and propargyl bromide (480 mg, 4.0 mmol). The mixture was stirred at room temperature until the complete conversion of amine to *N,N*-di(prop-2-yn-1-yl)arylamine (**2**) (as monitored by TLC). The excess of propargyl bromide was then removed under reduced pressure. After this, water (1 mL), $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol), sodium ascorbate (20 mg, 0.1 mmol), and organic azide (**3**) (1.0 mmol) were added to the reaction mixture and stirred for 30 min. Then the reaction mixture was warmed up to 60 °C and stirred until the completion of the reaction (by TLC). The resulting solution was filtered through a short pad of Celite 545, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using (petroleum ether/EtOAc = 10:1) to afford the target compound **4**.

Characterization data of all target compounds, copies of ^{1}H NMR and ^{13}C NMR spectra of all compounds can be found through the "Supplementary Content" section of this article's webpage.

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