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Protonated DBU as catalyst for cascade addition–cyclization of 2-alkynylaniline and carbon disulfide

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ABSTRACT

Protonated 1,8-diazabicyclo[5,4,0]undec-7-ene as catalyst for cascade addition/cyclization of 2-alkynylaniline and carbon disulfide has been described. This process provides a convenient route for synthesis of a variety of benzo[*d*][1,3]thiazine-2(4*H*)-thiones in high yields with high regio- and stereoselectivity at room temperature without metal.

Heterocyclic compounds are ubiquitous in natural products, pharmaceuticals, and organic materials.[1] As a consequence, the ongoing interest for developing new versatile and efficient syntheses of heterocycles has always been a thread in the synthetic community. Among them, cascade reaction is one of the most powerful strategic tools for the rapid assembly of heterocyclic compounds.[2] This process enables multiple bond-forming to occur in one sequence, which greatly enhances the synthetic efficiency, while producing less waste and minimizing handling. Recently, the metallic Lewis acid-catalyzed cascade reaction provided a straightforward method for the construction of heterocyclic compounds.[3] For example, Pd- or Cu-catalyzed amination/cyclization of *o*-haloalkynylarenes or haloenynes afforded indoles, pyrroles, or quinoline[3h,i,4] and Ag-catalyzed addition/cyclization of 2-alkynylbenzenamines gave benzo[*d*][1,3]thiazine derivatives.[3v,w] Nonetheless, all reactions required metallic reagents such as palladium, silver, and copper and in many cases the corresponding ligands were used as co-catalyst, which made these reactions more expensive. Lately, great progress has been made in the development of metal-free transformation in organic synthesis.[5–7] In this respect, Brønsted acid-catalyzed cascade reaction has attracted considerable attention.[8] In contrast to the metallic Lewis acid-catalyzed reaction, Brønsted acid-catalyzed reaction is more economic and has environmental benefits. With a point of these views, herein we would like to report protonated 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as a catalyst for cascade addition/cyclization of 2-alkynylaniline and carbon disulfide, in which $DBUH^+$ is a catalyst for both activation of CS_2 and carbon–carbon triple bond. This process provided a convenient synthetic route to benzo[*d*][1,3]thiazine-2(4*H*)-thione for a variety of substrates at room temperature without metal.

To optimize the reaction condition, several experiments were performed using the reaction of *p*-methyl-2-(phenylethynyl)aniline **1a** and carbon disulfide to obtain (*Z*)-4-benzylidene-6-methyl-4*H*-benzo[*d*][1,3]thiazine-2-thiol **2a** as model substrates under different solvents and catalytic conditions (Table 1). Initially we chose DBU as a catalyst for this reaction, based on our previous work regarding DBU-promoted tandem reaction of *o*-haloanilines and carbon disulfide.[9a,b] The reaction occurred and product **2a** was obtained in 40% yield (entry 1). We next changed the reaction temperatures and the amounts of DBU, respectively, the yield of product **2a** did not improve (entries 2–5). It is known that Brønsted acid or conjugated acid as a catalyst could activate carbon–carbon triple bonds to make them much more electrophilic.[10] Therefore, 5 mol % of H_2SO_4 was added into the reaction mixture. Gratifyingly, the reaction proceeded smoothly and the yield of **2a** increased to 80% (entry 6). It is noteworthy that H_2SO_4 was added as a single catalyst and the reaction did not proceed (entry 7). When amount and ratio of DBU/H_2SO_4 and solvents were screened (entries 8–16), 20 mol % DBU/10 mol % H_2SO_4 was found to be the best catalyst system in acetonitrile as medium at room temperature (entry 9). When other Brønstead acids such as *p*-toluenesulfonic acid (*p*-TsOH), trifluoromethanesulfonic acid (CF_3SO_3H), trifluoroacetic acid (CF_3CO_2H), and acetic acid (CH_3CO_2H) were employed, the reaction performed smoothly and product **2a** was also obtained

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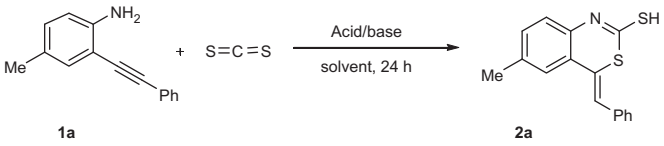
Table 1
Optimization between *p*-methyl-2-(phenylethynyl)-aniline **1a** and carbon disulfide[a]



1a **2a**

Entry	Acid/base (mol %/mol %)	*T* (°C)	Solvent	Yield of **2a**[b] (%)
1	DBU/— (20/0)	25	CH_3CN	40
2	DBU/— (20/0)	50	CH3CN	48
3	DBU/— (20/0)	80	CH_3CN	27
4	DBU/— (50/0)	25	CH_3CN	33
5	DBU/— (100/0)	25	CH_3CN	25
6	DBU/H_2S0_4 (20/5)	25	CH3CN	80
7	—/H_2SO_4 (0/5)	25	CH_3CN	NR[c]
8	DBU/H_2SO_4 (10/5)	25	CH_3CN	53
9	DBU/H_2SO_4 (20/10)	25	CH_3CN	94
10	DBU/H_2SO_4 (50/25)	25	CH_3CN	91
11	DBU/H_2SO_4 (100/50)	25	CH_3CN	73
12	DBU/H_2SO_4 (100/100)	25	CH_3CN	NR[c]
13	DBU/H_2SO_4 (20/10)	25	*p*-Toluene	79
14	DBU/H_2SO_4 (20/10)	25	THF	21
15	DBU/H_2SO_4 (20/10)	25	CH2CI2	NR[c]
16	DBU/H_2SO_4 (20/10)	25	CH3OH	NR[c]
17	DBU/*p*-TsOH (20/10)	25	CH_3CN	85
18	DBU/CF_3SO_3H (20/10)	25	CH_3CN	87
19	DBU/CF_3C0_2H (20/10)	25	CH_3CN	87
20	DBU/CH_3C0_2H (20/10)	25	CH_3CN	91
21	Et_3N/H_2S0_4 (20/10)	25	CH_3CN	22
22	DABCO/H_2S0_4 (20/10)	25	CH_3CN	25
23	Pyridine/H_2S0_4 (20/10)	25	CH_3CN	NR[c]

[a] Unless otherwise noted the reactions were performed in a sealed tube with 4-methyl-2-(phenylethynyl)aniline **1a** (1 mmol), carbon disulfide (1.5 mmol) in solvent (1.5 mL) for 24 h.
[b] The yield were evaluated by ^{1}H NMR with CH_2Br_2 as internal standard.
[c] NR means no reaction.

in high yield (entries 17–20). Out of concern of the cost, H_2SO_4 was chosen as a Brønstead acid. Furthermore, we used other protonated organic bases such as triethylamine (Et_3N) and 1,4-diazabicyclo[2.2.2]octane (DABCO), the reaction proceeded in lower yields (entries 21 and 22). When a protonated pyridine was used as a catalyst the reaction did not proceed (entry 23). On the basis of these results, the optimal condition involved the following parameters: DBU 20 mol %/H_2SO_4 10 mol % as catalyst, acetonitrile as a solvent, and reaction temperature at 25 °C.

Under the optimized conditions, a study on the substrate scope was carried out, and the results are summarized in Table 2. Firstly, treatment of (phenylethynyl)aniline **1b** and carbon disulfide afforded product **2b** in 82% yield (entry 2). To our delight, crystals of **2b** were suitable for single crystal analysis, and its structure was fully characterized by X-ray diffraction analysis.[11] The structure of **2b** clearly shows the formation of (*Z*)-4-benzylidene-4*H*-benzo[*d*][1,3]thiazine-2-thiol, in which the substituent on double bond is on the same side with the carbamodithioic group. Then we used other 2-alkynylbenzenamine derivatives **1** to react with carbon disulfide. Both electron-donating groups (such as methyl and methoxyl group) and electron-withdrawing groups (such as chloro and fluoro atom) on the benzene ring showed good performance (entries 1, 3–5). It is noteworthy that 2-alkynylbenzenamine with stronger electron-withdrawing groups, such as CO_2Et or CN group, on the *para*-position of 2-alkynylbenzenamine failed to generate any product and starting materials remained (entries 6 and 7). When 2,4-dimethyl-6-(phenylethynyl)aniline **1h** was used as a substrate, the desired product **2h** was also formed in 71% yield (entry 8). Notably, in all cases, only one product was observed in situ by ^{1}H NMR, it is different from Ag-catalyzed reaction.[3v] Next, different N-substituted 2-alkynylbenzenamine derivatives were applied under the optimized conditions. For example, when *N*-methyl-2-bromobenzamide **1i** or *N*-ethyl-2-bromobenzamide **1j** was treated with carbon disulfide, the desired product **2i** or **2j** was obtained in 72% or 54% isolated yield (entries 9 and 10), respectively. Benzyl substituted 2-alkynylbenzenamine **1k** with carbon disulfide proceeded in 26% yield of product **2k**

Table 2
Reaction of various 2-alkynylbenzenamine **1** with carbon disulfide[a]

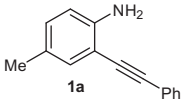
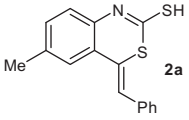
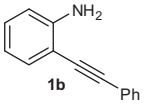
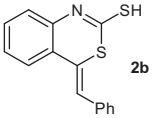
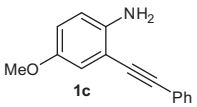
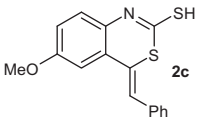
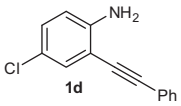
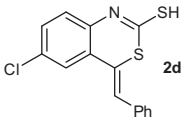
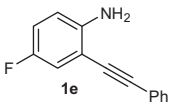
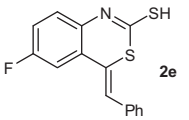
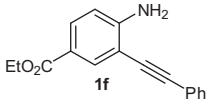
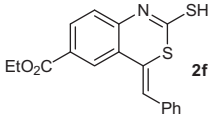
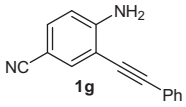
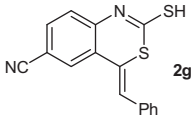
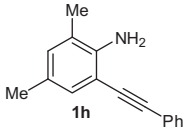
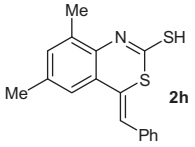
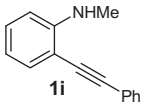
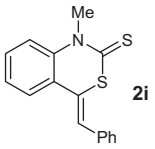
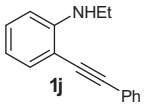
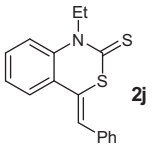
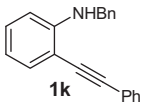
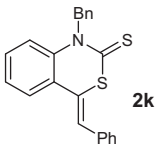
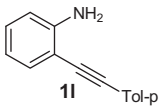
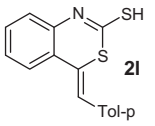
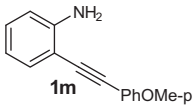
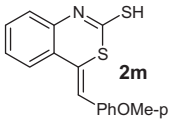
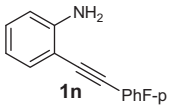
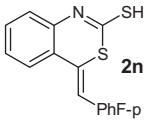
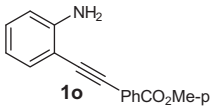
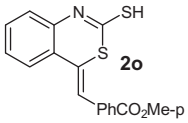
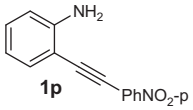
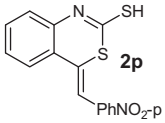
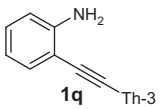
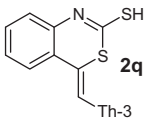
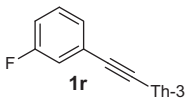
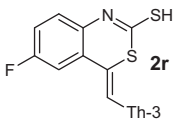
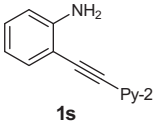
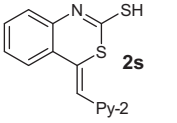
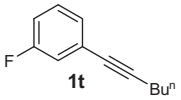
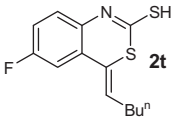
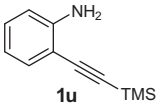
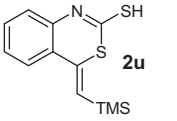
Entry	Substrate	Time (h)	Product	Yield[b] (%)
1	 **1a**	24	 **2a**	82
2	 **1b**	24	 **2b**	80
3	 **1c**	24	 **2c**	84
4	 **1d**	32	 **2d**	74
5	 **1e**	24	 **2e**	86

Table 2 (*continued*)

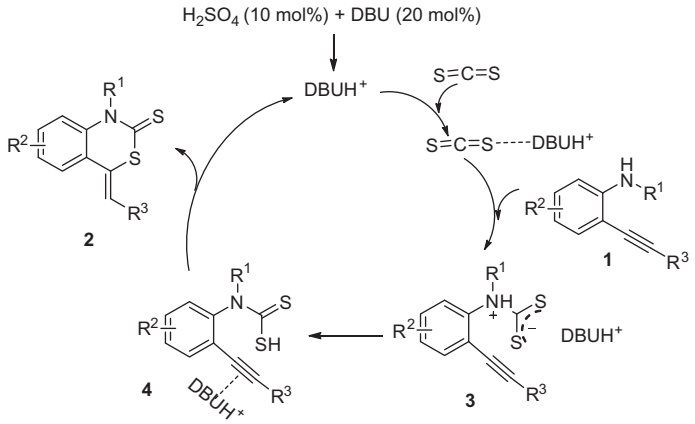
Entry	Substrate	Time (h)	Product	Yield[b] (%)
6	 **1f**	36	 **2f**	0
7	 **1g**	36	 **2g**	0
8	 **1h**	24	 **2h**	71
9	 **1i**	24	 **2i**	72
10	 **1j**	24	 **2j**	54
11	 **1k**	48	 **2k**	26
12	 **1l**	24	 **2l**	78
13	 **1m**	24	 **2m**	71[c]
14	 **1n**	24	 **2n**	75
15	 **1o**	24	 **2o**	67
16	 **1p**	24	 **2p**	50
17	 **1q**	24	 **2q**	73
18	 **1r**	24	 **2r**	81

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Time (h)	Product	Yield[b] (%)
19	 **1s**	48	 **2s**	68
20	 **1t**	24	 **2t**	0
21	 **1u**	48	 **2u**	0

[a] Unless otherwise noted the reactions were performed in a sealed tube with **1** (1.0 mmol), carbon disulfide (1.5 mmol), DBU (20 mol %)–H_2SO_4 (10 mol %) (0.134 M in CH_3CN, 1.5 mL).
[b] Isolated yields.
[c] Reaction temperature: 50 °C.



Scheme 1. Proposed route for $DBUH^+$-catalyzed reaction of 2-alkynylaniline with carbon disulfide.

(entry 11). In addition, different substituent groups on the alkynes of 2-alkynylbenzenamine were employed. Aromatic substituents were on the end of alkynes, the reaction proceeded smoothly. For instance, the aryl group attached on the triple bond with electron-donating groups (such as Me or OMe) (entries 12 and 13) and electron-withdrawing groups (such as F, CO_2Me, and NO_2) (entries 14–16). Both proceeded well and the desired products were obtained in satisfying yields. Furthermore, thienyl and pyridyl were on the end of alkynes, the desired products were formed in 73%, 81%, and 68% isolated yields, respectively (entries 17–19). When alkyl and TMS groups were on the end of alkynes, the desired product could not be observed and starting materials remained (entries 20 and 21).

Based on the above results, the mechanism of this reaction is proposed as shown in Scheme 1. First, the nucleophilic nitrogen of 2-alkynylbenzenamine **1** attacks the carbon atom of carbon disulfide,[12,13] which might be activated by $DBUH^+$ to form intermediate **3** and release $DBUH^+$.[9a,13] The intermediate **3** undergoes proton-transfer and complexation of carbon–carbon triple bond with $DBUH^+$ to form intermediate **4**, which goes through intramolecular nucleophilic addition to afford product **2** and release $DBUH^+$ again.[10] A single $DBUH^+$ catalyst mediates both activities for CS_2 molecule and alkyne species.

In summary, we have developed a simple and practical method for the synthesis of benzo[*d*][1,3]thiazine-2(4*H*)-thione derivatives via protonated DBU as a dual functionalized catalyst in the reaction of 2-alkynylaniline with carbon disulfide. The presented cascade addition/cyclization represents a facile route for generation of heterocycles and avoids utilization of any metal under mild reaction. Further reactions and mechanism of these small molecules are under investigation in our laboratory, and the results will be reported in due course.

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Supplementary data

Supplementary data (experimental procedures and full characterization including ^1H NMR, and ^{13}C NMR data, and NMR spectra for compounds compound **2a–2e** and **2h–2s**) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.02.074.

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