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One-Pot Synthesis of Triazolothiadiazepine 1,1-Dioxide Derivatives *via* Copper-Catalyzed Tandem [3+2] Cycloaddition/*N*-Arylation

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Abstract: A practical and efficient synthesis of triazolothiadiazepine-1,1-dioxide derivatives *via* copper-catalyzed [3+2]cycloaddition, followed by *N*-arylation is described. The method is also applicable to the synthesis of indoline- and thiophene-fused triazolothiadiazepine 1,1-dioxide derivatives.

Keywords: copper(I) iodide; fused triazoles; one-pot porcess; sultams; triazolothiadiazepine 1,1-dioxides

The sultam moiety is a backbone scaffold of many heterocyclic compounds of synthetic and pharmaceutical importance.[1] Among the sultam derivatives, benzothiadiazepine 1,1-oxides are a pivotal structural entity and possess a remarkable range of biological properties such as antiblastic, antitumor, apoptotic and antihypertensive activities.[2] On the other hand, the 1,2,3-triazole moiety has its own importance in synthetic, medicinal and materials chemistry.[3] Especially, fused triazole derivatives have gained much attention due to their wide range of biological activities.[4] Hence, one can expect upon fusion of benzothiadiazepine 1,1-dioxides with 1,2,3-triazoles the products may display an interesting range of biological properties. Examples of a few bioactive molecules consisting of sultam and triazole rings can be seen in the Figure 1.

A number of approaches are available for the synthesis of 1,2,3-triazoles[3,5] as well as benzothiadiazepine 1,1-oxide derivatives.[2] In addition, the synthesis of several fused triazoles has been reported in the literature.[6a–i] However, to the best of our knowledge,

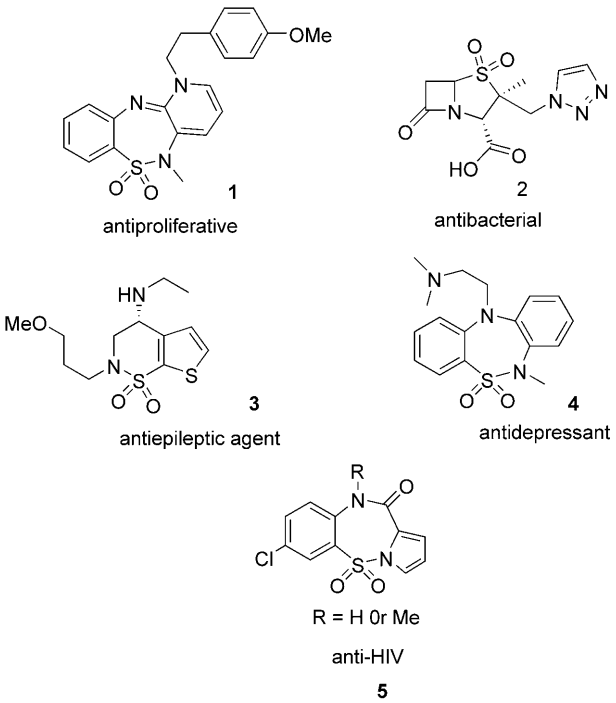
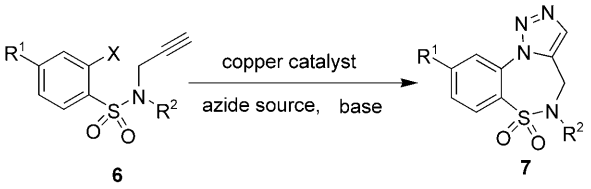


Figure 1. Biologically active heterocycles containing a sultam moiety.

the synthesis of a 1,2,3-triazole fused with benzothiadiazepine 1,1-oxides by using this strategy, has not yet been reported.[6j] The Cu(I)-catalyzed 1,3-diploar cycloaddition is frequently employed for the synthesis of 1,2,3-triazoles.[5] Moreover, Cu(I) salts are known to be efficient catalysts for the formation of C–N bonds.[7] It is noteworthy that they also play a vital role in the construction of certain types of bioactive N-heterocycles through the formation of multiple bonds.[8] We wish to report herein on a one-pot strat-



Scheme 1. One-pot strategy for the synthesis of **7**.

egy for the synthesis of a 1,2,3-triazole fused with benzothiadiazepine 1,1-oxides **7** (Scheme 1).

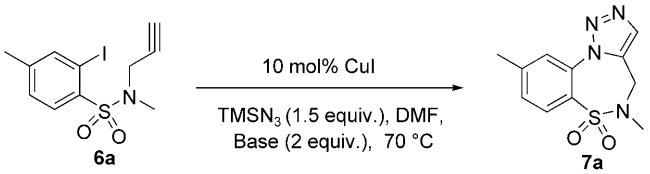
We initially examined various reaction conditions using **6a** as a model precursor. Unfortunately, our initial results, which involved the reaction of sodium azide as well as tosyl azide in the presence of an inorganic or organic base with copper(I) catalyst failed to yield the desired product. However, a trace amount of the desired product was detected using the procedure of Yamamoto et al.[9] employing $TMSN_3$. A series of bases was screened in an attempt to improve the product yield. A slight improvement in product yield was observed when inorganic bases (*t*-BuOK, NaOMe, K_2CO_3 and Cs_2CO_3) were used and an organic base (Et_3N) gave a slightly better yield than the inorganic bases. On the other hand, the yield of the desired product was further increased when Hunig's base (DIPEA) was used in the reaction. The results of these experiments are summarized in Table 1.

We next increased the amount of catalyst loading to 20 mol%. Under these conditions, the conversion was increased to 80% for a 12 h reaction period. However, the use of 30 mol% of CuI resulted in a considerable acceleration of the reaction. No significant improvement was observed when an additional amount of catalyst was used. Moreover, the use of other Cu(I) salts, such as CuBr and CuCl were less efficient for the reaction but did afford the products albeit in low yield. Furthermore, the effect of solvent on the reaction was examined for a range of solvents. Non-polar solvents were ineffective and no product was detected. A poor yield was obtained when DMSO was used as a solvent, and DMF was found to be the best solvent for the reaction (Table 2).

After optimizing the reaction conditions, we further pursued the scope of the reaction with respect to other 2-iodo-*N*,4-disubstituted-*N*-(prop-2-ynyl)benzenesulfonamide derivatives.

The present protocol could be successfully applied to the *in situ* [3+2]cycloaddition/*N*-arylation of various 2-iodo-*N*,4-disubstituted-*N*-(prop-2-ynyl)-benzenesulfonamide derivatives and the results are summarized in Table 3. As shown in Table 3, the formation of a cyclized product was efficient in most cases, affording the corresponding triazolobenzothiadiazepine 1,1-dioxide derivatives in moderate to good yields. The functional group on benzene in the *o*-iodobenzenesulfonamide derivatives had no significant effect on the course of the reaction (Table 3, entries 1–3). The substituent on the nitrogen, however, had a considerable effect on the reaction. The product yields were drastically decreased when the *N*-methyl group was replaced with an *N*-ethyl group or an *N*-butyl group (Table 3, entries 4 and 5). This one-pot cyclization re-

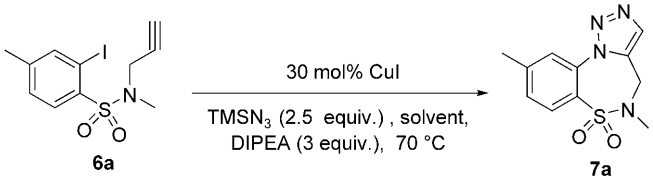
Table 1. Effect of base in presence of CuI, $TMSN_3$ in DMF.



Entry	Base	Time [h]	Yields [%][a,b]
1	*t*-BuOK	12	5
2	NaOMe	12	10
3	K_2CO_3	12	21
4	Cs_2CO_3	12	23
5	Et_3N	12	35
6	**DIPEA**	**12**	**60**

[a] All reactions were carried out on a 0.5-mmol scale.
[b] Isolated yields.

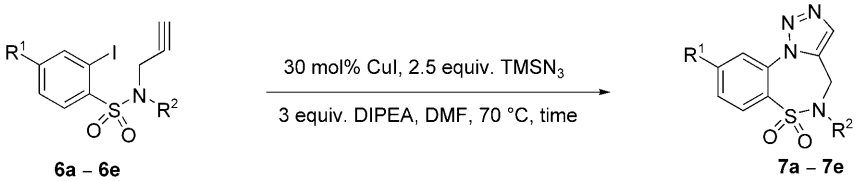
Table 2. Effect of solvent in the presence of 30 mol% CuI, and $TMSN_3$.



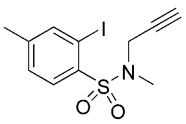
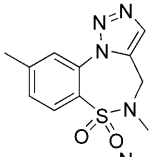
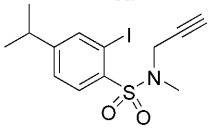
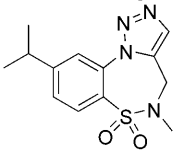
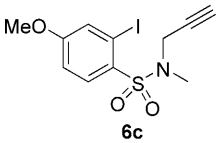
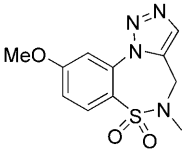
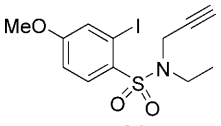
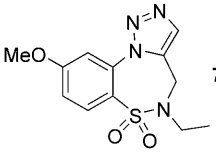
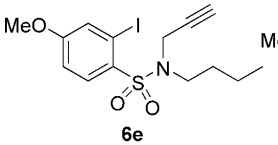
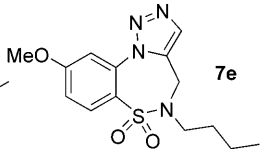
Entry	Solvent	Time [h]	Yields [%][a,b]
1	**DMF**	**2**	**80**
2	DMSO	2	42
3[c]	MeOH	4	0
4[c]	MeCN	4	0
5	Dioxane	12	trace
6	THF	12	trace
7	Toulene	12	trace

[a] All reactions were carried out on 0.5-mmol scale.
[b] Isolated yields.
[c] Substrate decomposed.

Table 3. One-pot synthesis of triazolobenzothiadiazepine 1,1-dioxide from 2-iodo-*N*,4-disubstituted-*N*-(prop-2-ynyl)-benzenesulfonamides.



6a – 6e **7a – 7e**

Entry	Substrate [10]	Product	Time [h]	Yield [%][a,b]
1	 **6a**	 **7a**	2	80
2	 **6b**	 **7b**	2	78
3	 **6c**	 **7c**	2	75
4	 **6d**	 **7d**	3	60
5	 **6e**	 **7e**	4	50

[a] All reactions were carried out on a 1-mmol scale.
[b] Isolated yields.

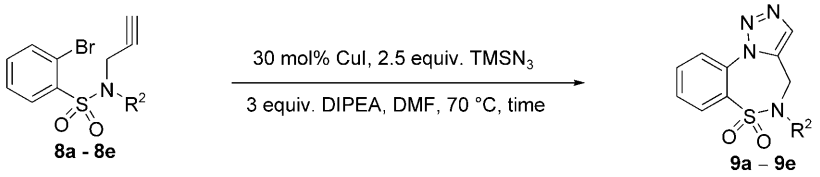
action of *N*-methyl derivatives proceeds much faster than reactions using *N*-ethyl and *N*-butyl derivatives.

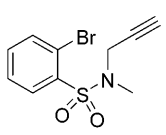
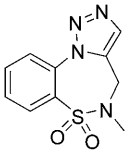
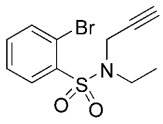
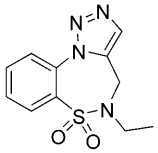
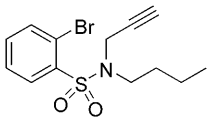
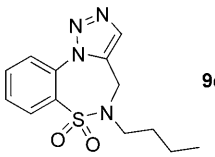
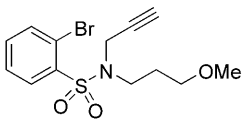
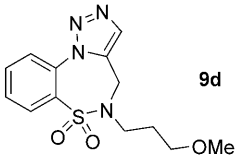
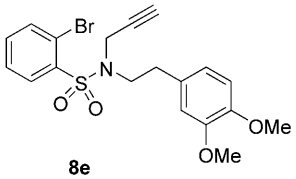
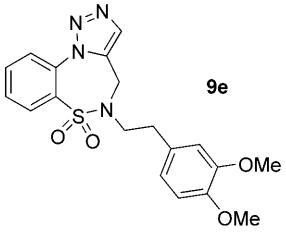
Using the optimized reaction conditions we next examined various 2-bromo-*N*-substituted-*N*-(prop-2-ynyl)benzenesulfonamide derivatives. As summarized in Table 4, a number of 2-bromo-*N*-substituted-*N*-(prop-2-ynyl)benzenesulfonamide derivatives were used in the present reaction conditions and triazolobenzothiadiazepine 1,1-dioxide derivatives were isolated in moderate to good yields. Despite the comparable yields of the products, reactions using bromo precursors required a slightly longer time for completion than those of iodo precursors. This may be due to differences in the reactivities of iodide and bromide groups. Unlike the reactions of iodo precursors, the substituent on the nitrogen had no effect on the reaction in the case of the bromo compounds. Moreover, the 2-bromo-*N*-substituted-*N*-(prop-2-ynyl)benzenesulfonamides, derived from the amine, which contain an electron-releasing group also afforded the corresponding products (Table 4, entries 4 and 5).

Indoline is an important motif that is found in many natural products and pharmaceuticals. Hence, we attempted to incorporate an indoline motif into the cycloaddition precursor. The precursor (**15**) was prepared in 5 steps by following known literature procedures.[11] Using the present reaction conditions, the precursor (**15**) was converted into the corresponding indoline-fused 1,2,3-triazolobenzothiadiazepine 1,1-oxide (**16**) in moderate yield (Scheme 2).

The diversity of the present methodology was additionally demonstrated by the synthesis of thiophene-fused 1,2,3-triazolothiadiazepine 1,1-oxides (Scheme 3). It is known that the thiophene-fused

Table 4. One-pot synthesis of triazolobenzothiadiazepine-1,1-dioxides from 2-bromo-*N*-substituted-*N*-(prop-2-ynyl)benzenesulfonamides.



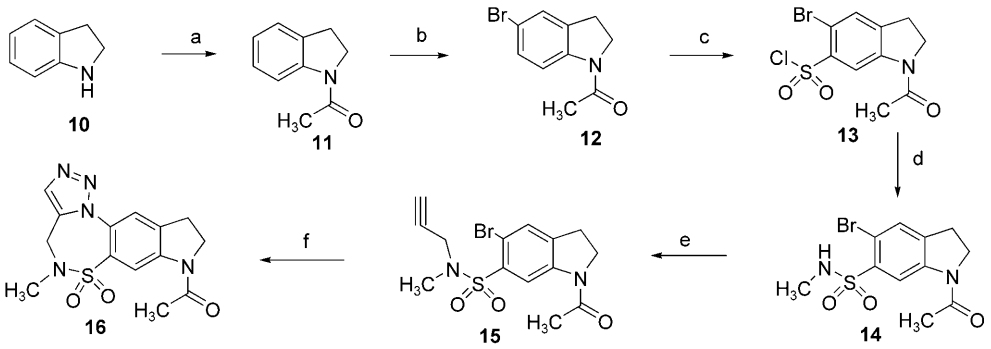
Entry	Substrate	Product		Time [h]	Yields [%][a,b]
1	 **8a**		**9a**	4	65
2	 **8b**		**9b**	4	63
3	 **8c**		**9c**	5	60
4	 **8d**		**9d**	6	60
5	 **8e**		**9e**	5	61

[a] All reactions were carried on a 1-mmol scale.
[b] Isolated yield.

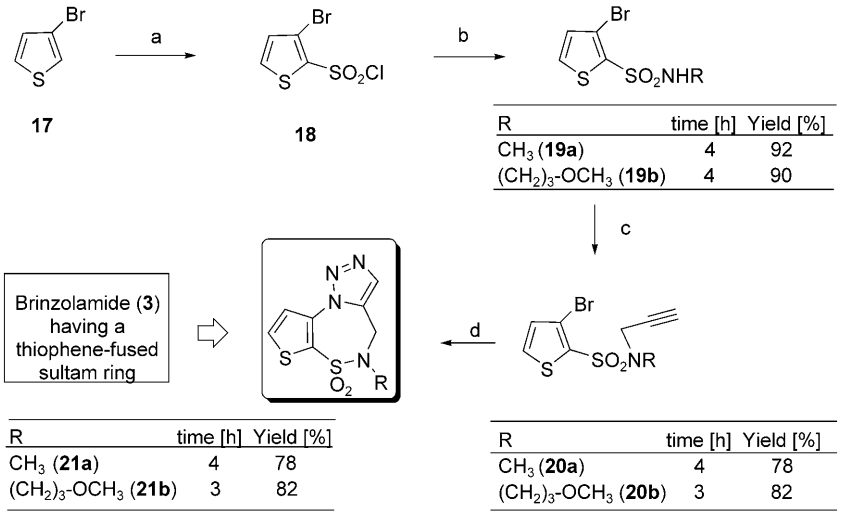
sultam brinzolamide (**3**) has a potent antiepileptic activity.[12]

To propose a mechanism for this reaction, we considered two literature reports, the first of which reported on the direct catalytic transformation of aryl and vinyl halides into azides, in the presence of Cu(I) or Cu(II).[13] The other study reports on the formation of a 1,2,3-triazole from its corresponding *N*-methyl-*N*-(prop-2-ynyl)benzenesulfonamide.[9] Based on these two reports we envisage two mechanistic pathways for the formation of **7a** from **6a**.

Among them the first route involves the Cu(I)-oxidative addition to the aryl halide, followed by the transmetallation with $TMSN_3$, and then reductive elimination to provide intermediate aryl azide **I.** Furthermore, this intermediate could serve for activation of the triple bond through a copper-coordinated intermediate to afford the cyclized compound **7a**. The second pathway goes *via* the generation of copper acetylide. The copper acetylide generated was reacted with azide to furnish the six-membered copper(III) metallacycle intermediate. This six-membered intermediate undergoes ring contraction to produce a five-membered triazolyl-copper intermediate (**IV**). Protonation of this intermediate by terminal alkyne or HI generates the triazole compound (**V**), which will un-



Scheme 2. Synthesis of indoline-fused triazole sultams. *Reagents and conditions:* a) $(CH_3CO)_2O$, CH_2Cl_2, room temperature, 30 min, 79%; b) Br_2, AcOH, room temperature, 10 min, 71%; c) $ClSO_3H$, neat, 80 °C, 12 h, 35%; d) CH_3NH_2, Et_3N, reflux, 2 h, 87%; e) propargyl bromide, K_2CO_3, acetone, reflux, 12 h, 81%; f) 30 mol% CuI, 2.5 equiv. $TMSN_3$, 3 equiv. DIPEA, DMF, 70 °C, 12 h, 40%. $TMSN_3$ = trimethylsilyl azide, DIPEA = *N*,*N*-diisopropylethylamine (Hunig's base).



R	time [h]	Yield [%]
CH_3 (**19a**)	4	92
$(CH_2)_3$-OCH_3 (**19b**)	4	90

R	time [h]	Yield [%]
CH_3 (**21a**)	4	78
$(CH_2)_3$-OCH_3 (**21b**)	3	82

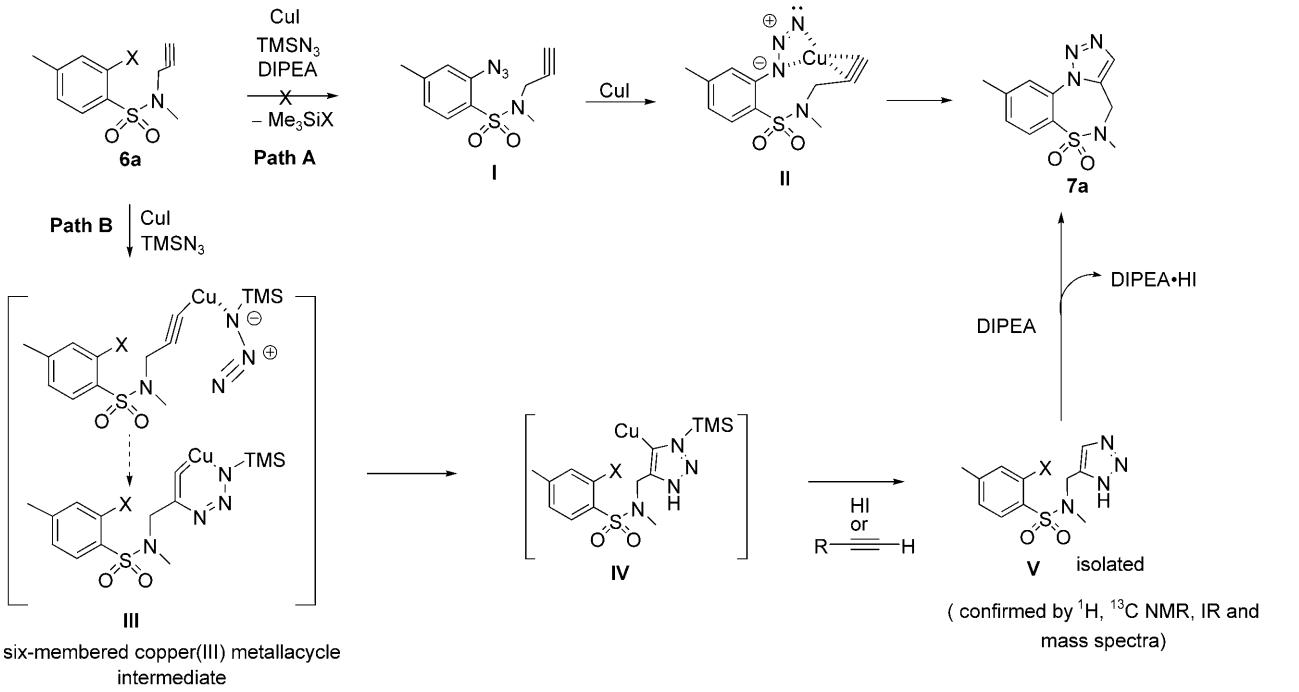
R	time [h]	Yield [%]
CH_3 (**20a**)	4	78
$(CH_2)_3$-OCH_3 (**20b**)	3	82

Scheme 3. Synthesis of thiophene-fused 1,2,3-triazolo-thiadiazepine 1,1-oxides. *Reagents and conditions:* a) $ClSO_3H$, −78 °C, 3 h, 82%; b) RNH_2, CH_2Cl_2, room temperature; c) propargyl bromide, K_2CO_3, acetone, reflux; d) 30 mol% CuI, 2.5 equiv. $TMSN_3$, 3 equiv. DIPEA, DMF, 70 °C.

dergo *N*-arylation to afford **7a**. (Scheme 4). The Cu(I) species catalyst regenerated during the process facilitates the progrees of the catalytic cycle. The structure of the representative compound **7a** was confirmed unambiguously by single crystal X-ray analysis as shown in Figure 2.[16]

In the proposed mechanisms, the crucial steps are azidination (Path A) and copper-acetylide formation (Path B). Hence, in order to verify which mechanism is operative in this reaction, it is necessary to have information on the intermediate involved in the reaction.To determine this, we carried out the reaction in the absence of base. To our delight, 30% of the expected cyclized product, triazolobenzothiadiazepine 1,1-dioxide (**7a**) along with trace amounts of intermediate was observed under the base-free conditions.[15] The intermediate was isolated and characterized by ^1H, ^{13}C NMR and mass spectroscopic techniques which indicated the formation of triazole (**V**).

Although we could obtain the intermediate compound (**V**), this cannot rule out the other possibility. If we look into the literature, the copper-catalyzed azidination of aryl halides using NaN_3 (Ma et al.)[13b] is faster than the copper-catalyzed azide alkyne cycloaddition reported by Yamamoto et al.[9] using $TMSN_3$.[9] Therefore, in order to compare the azidination and cycloaddition reactions, we carried out the reaction of *N*,4-dimethyl-*N*-(prop-2-ynyl)benzenesulfonamide (**22**) and iodobenzene (**23**) under similar reaction conditions of the present protocol. Under the optmized reaction condition, we could isolate the *N*-[(1*H*-1,2,3-triazol-4-yl)methyl]-*N*,4 dimethylbenzenesulfonamide (**24**) as a sole product. There was no trace amount of phenyl azide that could be isolated



Scheme 4. Plausible mechanism for the formation of **7a**.

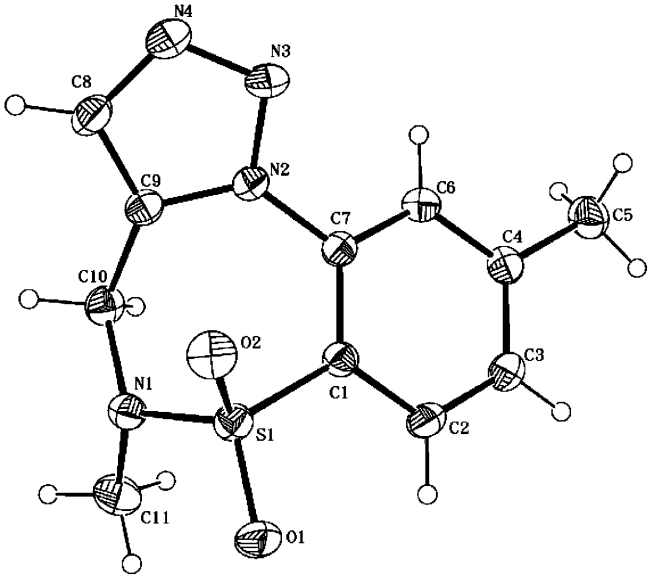
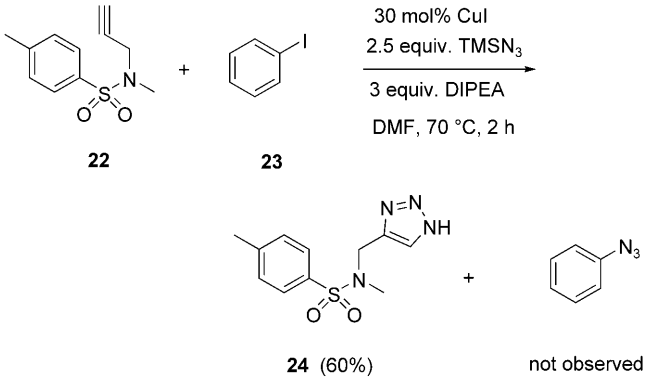


Figure 2. X-ray crystal structure of 5,9-dimethyl-4,5-dihydrobenzo[*f*][1,2,3]triazolo[5,1-*d*][1,2,5]thiadiazepine 1,1-dioxide (**7a**) (ORTEP view).[16]



Scheme 5. Reaction of *N*,4-dimethyl-*N*-(prop-2-ynyl)benzenesulfonamide and iodobenzene under optimized conditions.

from the reaction mixture (Scheme 5). A recent report of Chen et al. has also shown the triazole product as an intermediate in a similar tandem process.[14] Based on these facts we predict that Path B is reasonable mechanistic route for the formation of **7a**.

In conclusion, we report on a practical and efficient synthesis of triazole-fused sultams *via* copper catalyzed [3+2]cycloaddition followed by C–N bond formation. This method has been applied to the synthesis of indoline- and thiophene-fused triazole sultams, which are synthetically valuable as novel heterocycles. Biological studies of these compounds are currently underway.

Experimental Section

General Procedure for Preparation of 5,9-Dimethyl-4,5-dihydrobenzo[*f*][1,2,3]triazolo[5,1-*d*][1,2,5]thiadiazepine 1,1-Dioxides

To a stirred solution of the *N*-propargylated benzenesulfonamide (1 mmol) in DMF (3 mL), copper iodide

(30 mol%), azidotrimethylsilane (2.5 equiv.) and DIPEA (3 equiv.) were added and the whole reaction mixture was heated at 70 °C for 2–6 h under a nitrogen atmosphere. After consumption of starting material, the mixture was cooled to room temperature then methanol and ethyl acetate were added, the inorganic solid that separated out was filtered through a short celite pad. The filtrate was concentrated under reduced pressure. The residue was purified with silica gel column chromatography to afford the cyclized compound in moderate to good yields (40–82%).

Physical and Spectral data of Representative Compound (7a)

5,9-Dimethyl-4,5-dihydrobenzo[*f*][1,2,3]triazolo[5,1-*d*]-[1,2,5]thiadiazepine 1,1-dioxide (7):[16] Yield: 80%; white solid, mp 183–184 °C; FT-IR (KBr): $\nu = 2930$, 1346, 1160 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.06$ (s, 1H), 7.95 (d, $J = 7.9$ Hz, 1H), 7.76 (s, 1H), 7.42 (d, $J = 7.9$ Hz, 1H), 4.40 (s, 2H), 2.86 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 146.1$, 134.0, 133.1, 132.7, 130.0, 128.8, 127.3, 125.5, 44.1, 38.0, 21.7; LR-MS (EI): *m/z* (relative intensity) = 264 (M^+,100), 171 (98), 118 (18), 68 (19); HR-MS: *m/z* = 264.0681, calcd. for $C_{11}H_{12}N_4O_2S$ (M^+): 264.0681.

Supporting Information

Experimental details, characterization, ^1H and ^{13}C NMR spectra of products **1**–**36** are provided in the Supporting Information.

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[15] DMF is a weak Lewis base, which may be responsible for formation of the desired product.

[16] Crystallographic data for the structure reported in this publication have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 777830 (**7a**).These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

