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An Efficient Approach to Fused Indolines via a Copper(I)-Catalyzed Reaction of Sulfonyl Azide with 2-Ethynylaryl Methylenecyclopropane

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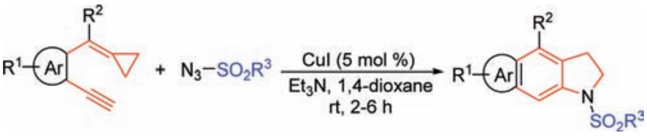
ABSTRACT



A cascade reaction of 2-ethynylaryl methylenecyclopropane with sulfonyl azide catalyzed by copper(I) iodide under mild conditions is described, which provides a novel and efficient route for the generation of fused indolines.

The indoline framework which is embedded in a wide range of natural products and designed compounds with varied biological activities is regarded as a privileged scaffold.[1,2] So far, intensive research has been involved for the synthesis of this type of heterocycle.[3] In parallel with our efforts to develop efficient synthetic methods for heterocyclic synthesis,[4] the diverse biological activities of indolines inspired us to undertake preparation of indoline-based small molecule libraries.

The pursuit of concise methods for rapid build-up of molecular complexity is a major focus of the synthetic

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(1) Indoline derivatives constitute a structural class of heterocycles from which several drugs have emerged, including antineoplastic sulfonamides, 5-hydroxytryptamine receptor antagonists (5-HT3), and muscarine receptor agonists and antagonists. See, for example: (a) Bermudez, J.; Dabbs, S.; Joiner, K. A.; King, F. D. *J. Med. Chem.* **1990**, *33*, 1929. (b) Adachi, S.; Koike, K.; Takayanagi, I. *Pharmacology* **1996**, *53*, 250. (c) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893.

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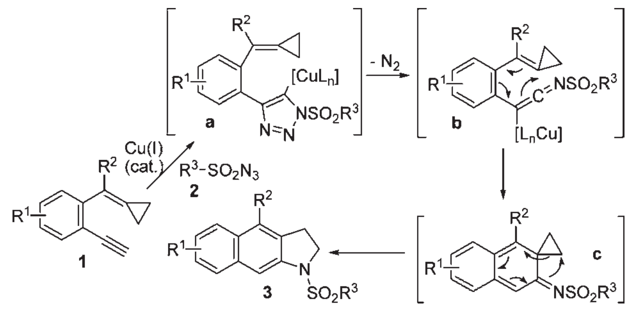
organic chemical community. Cascade reactions that allow multiple transformations in a single-pot process are especially attractive.[5] Recently, Chang, Wang, and others made a great contribution in ketenimine chemistry, which involves a Cu-catalyzed azide−alkyne cycloaddition.[6−8] Various heterocycles have been constructed based on this strategy. For example, the 1,2-dihydroisoquinolin-3(4*H*)-imine scaffold could be produced via a copper(I)-catalyzed reaction of (*E*)-2-ethynylphenylchalcone, sulfonyl azide, and amine.[4f] In the meantime, reactions of methylenecyclopropanes are particularly appealing due to their diverse reactivity driven by the relief of ring strain.[9]Over the past decades, the ring-opening reactions of methylenecyclopropanes to form a variety of carbocycles and heterocycles have been extensively explored.[10−12] Prompted by the advancement of ketenimine chemistry and the attractiveness of methylenecyclopropanes, we envisaged that the combination might be applied to the preparation of fused indoline derivatives based on our recent efforts for *N*-heterocycles generation.

Our strategy is illustrated in Scheme 1. We reasoned that 2-ethynylaryl methylenecyclopropane **1** would react with sulfonyl azide **2** catalyzed by a copper salt affording the triazole intermediate **a**, which then transferred to the reactive ketenimine **b** via a ring-opening rearrangement. A consecutive 6π-electrocyclization would occur to form an intermediate **c**, which subsequently underwent a rearrangement to produce the fused indolines **3**. To demonstrate the feasibility of this proposed synthetic route, we started to explore the possibility of this transformation.

Scheme 1. Proposed Synthetic Route for the Generation of Fused Indoline Derivatives



The preliminary screening was performed for the reaction of 1-(cyclopropylidenemethyl)-2-ethynylbenzene **1a** with 4-methylbenzenesulfonyl azide **2a** catalyzed by copper(I) iodide (5 mol %) in the presence of triethylamine in 1,4-dioxane at room temperature (Table 1). Gratifyingly, the desired product **3a** was isolated in 67% yield (Table 1, entry 1). The corresponding structure of indoline **3a** was confirmed by X-ray diffraction analysis (see the Supporting Information). With this promising result in hand, we started to optimize the reaction conditions. Lower yields were obtained when copper(I) bromide or copper(I) chloride was used as a replacement (Table 1, entries 2 and 3). Further screening of organic and inorganic bases indicated that triethylamine was the best choice. Inferior yields were displayed when other bases were employed in the model reaction (Table 1, entries 4−11). No better results were generated when the reaction occurred in other solvents (Table 1, entries 12−15). The yield was decreased dramatically when the catalytic amount of copper(I) iodide was reduced to 2 mol % (Table 1, entry 16). The result could not be improved when the reaction was performed at 70 °C (Table 1, entry 17).

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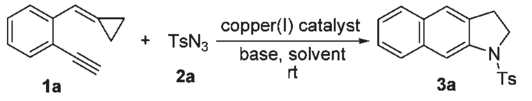
Table 1. Initial Studies for the Copper(I)-Catalyzed Reaction of 1-(Cyclopropylidenemethyl)-2-ethynylbenzene **1a** with Sulfonyl Azide **2a**



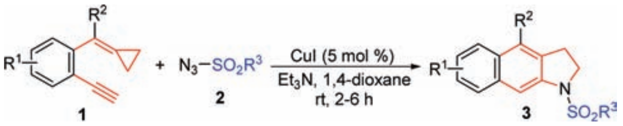
entry	[Cu]	base	solvent	time (h)	yield[a] (%)
1	CuI	Et_3N	1,4-dioxane	3	67
2	CuBr	Et_3N	1,4-dioxane	6	40
3	CuCl	Et_3N	1,4-dioxane	12	31
4	CuI	pyridine	1,4-dioxane	3	47
5	CuI	DIPEA	1,4-dioxane	12	54
6	CuI	DABCO	1,4-dioxane	12	N.R.
7	CuI	DBU	1,4-dioxane	3	N.D.
8	CuI	K_2CO_3	1,4-dioxane	3	53
9	CuI	NaOAc	1,4-dioxane	24	10
10	CuI	K_3PO_4	1,4-dioxane	3	33
11	CuI	Cs_2CO_3	1,4-dioxane	3	43
12	CuI	Et_3N	THF	5	41
13	CuI	Et_3N	MeCN	5	53
14	CuI	Et_3N	DCE	5	38
15	CuI	Et_3N	toluene	5	48
16[b]	CuI	Et_3N	1,4-dioxane	12	35
17[c]	CuI	Et_3N	1,4-dioxane	2	46

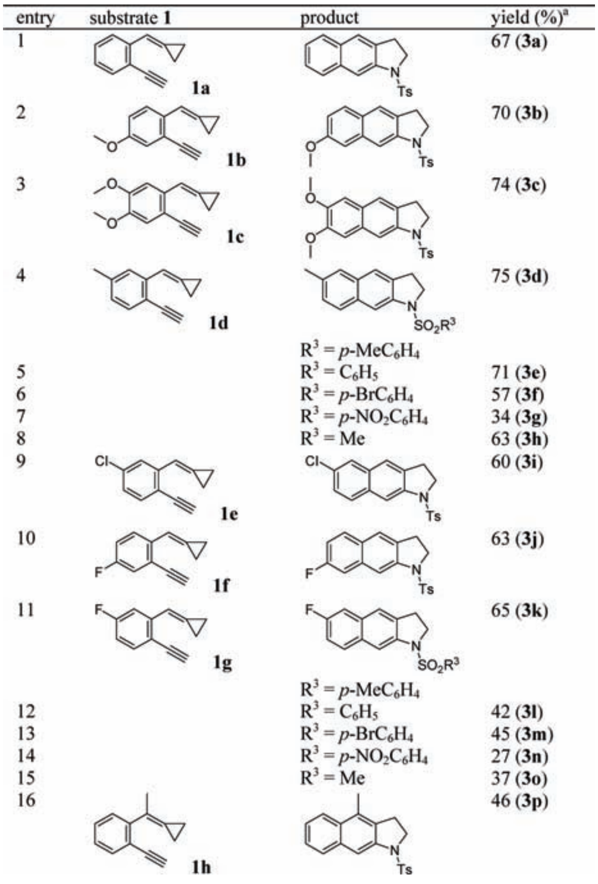
[a] Isolated yield based on 1-(cyclopropylidenemethyl)-2-ethynylbenzene **1a**. [b] In the presence of CuI (2 mol %). [c] The reaction was performed at 70 °C.

Under the optimized conditions highlighted in Table 1 [CuI (5 mol %), Et_3N (1.4 equiv), 1,4-dioxane, room temperature], the cascade reaction of 1-(cyclopropylidenemethyl)-2-ethynylbenzene **1** with sulfonyl azide **2** was then carried out to define the protocol generality (Table 2). The reaction proceeded smoothly when methoxy-substituted compound **1b** reacted with 4-methylbenzenesulfonyl azide **2a** under the standard conditions, which gave rise to the expected product **3b** in 70% yield (Table 2, entry 2). A similar outcome was generated when substrate **1c** or **1d** was employed in the reaction of sulfonyl azide **2a** (Table 2, entries 3 and 4). The reaction also worked well to afford the desired product **3e** in 71% yield when sulfonyl azide was replaced by compound **2b** (Table 2, entry 5). However, the yield decreased when benzenesulfonyl azides with electron-withdrawing groups attached to the aromatic ring were utilized. For instance, 2-(cyclopropylidenemethyl)-1-ethynyl-4-methylbenzene **1d** reacted with 4-bromobenzenesulfonyl azide **2c**, leading to the corresponding product **3f** in 57% yield (Table 2, entry 6). A low yield was observed when 4-nitrobenzenesulfonyl azide **2d** was used in the reaction (34% yield, Table 2, entry 7). Interestingly, a moderate yield was obtained when methylsulfonyl azide **2e** was employed as a partner in the reaction of substrate q**1d** (63% yield, Table 2, entry 8). Reactions of 1-(cyclopropylidenemethyl)-2-ethynylbenzene **1** with electron-withdrawing group substitutions gave rise to the expected products in slightly lower yields (Table 2, entries 9−15).

The reaction of 1-(1-cyclopropylideneethyl)-2-ethynylbenzene **1h** with 4-methylbenzenesulfonyl azide **2a** was examined subsequently, which furnished the indoline product **3p** in 46% yield (Table 2, entry 16).

Table 2. Copper(I)-Catalyzed Reaction of 1-(Cyclopropylidenemethyl)-2-ethynylbenzene **1** with Sulfonyl Azide **2**



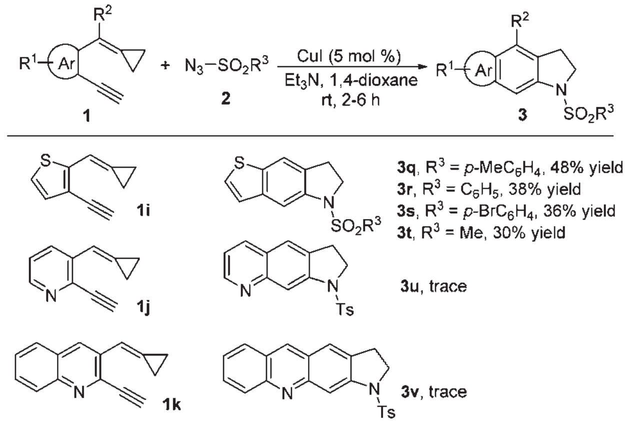


entry	substrate **1**	product	yield (%)[a]
1	**1a**	N Ts	67 (**3a**)
2	**1b**	N Ts	70 (**3b**)
3	**1c**	N Ts	74 (**3c**)
4	**1d**	R^3 = *p*-MeC_6H_4	75 (**3d**)
5		R^3 = C_6H_5	71 (**3e**)
6		R^3 = *p*-BrC_6H_4	57 (**3f**)
7		R^3 = *p*-$NO_2C_6H_4$	34 (**3g**)
8		R^3 = Me	63 (**3h**)
9	**1e**	N Ts	60 (**3i**)
10	**1f**	N Ts	63 (**3j**)
11	**1g**	R^3 = *p*-MeC_6H_4	65 (**3k**)
12		R^3 = C_6H_5	42 (**3l**)
13		R^3 = *p*-BrC_6H_4	45 (**3m**)
14		R^3 = *p*-$NO_2C_6H_4$	27 (**3n**)
15		R^3 = Me	37 (**3o**)
16	**1h**	N Ts	46 (**3p**)

[a] Isolated yield based on 1-(cyclopropylidenemethyl)-2-ethynylbenzene **1**.

We next investigated the reactions of 1-(cyclopropylidenemethyl)-2-ethynylheteroarenes with different sulfonyl azides. The results are displayed in Scheme 2. It seemed that 2-(cyclopropylidenemethyl)-3-ethynylthiophene **1i** was a suitable reactant as well, although the yields obtained were not as expected. It is noteworthy that the thiophene-incorporated indoline derivatives has been found applications as 5-$HT_{2C/2B}$ receptor antagonists.[2] However, the construction of such scaffold suffered from multisteps (up to eight steps), harsh conditions, and low yields.[2] Recently, Hashmi and co-workers reported the synthesis of structurally related thiophene-fused indolines through a gold-catalyzed reaction.[13] Using the method described herein, the thiophene-incorporated indoline skeleton could be easily produced under mild conditions. We subsequently explored the reactions of 3-(cyclopropylidenemethyl)-2-ethynylpyridine **1j** and 3-(cyclopropylidenemethyl)-2-ethynylquinoline **1k** with 4-methylbenzenesulfonyl azide **2a** under the standard conditions. However, only trace amounts of products were detected after 24 h.

Scheme 2. Copper(I)-Catalyzed Reaction of 1-(Cyclopropylidenemethyl)-2-ethynylheteroarene **1** with Sulfonyl Azide **2**



In summary, we have discovered a novel cascade reaction of 2-ethynylaryl methylenecyclopropane with sulfonyl azide catalyzed by copper(I) iodide under mild conditions. The reaction works efficiently to generate fused indolines. A ketenimine species and 6π-electrocyclization are believed to be involved in the transformation. Application of 2-ethynylaryl methylenecyclopropanes for the formation of other heterocycles is currently ongoing.

Acknowledgment. Financial support from National Natural Science Foundation of China (No. 21032007) is gratefully acknowledged.

Supporting Information Available. Experimental procedures, characterization data, ^{1}H and ^{13}C NMR spectra of compounds **3**, and X-ray data for compound **3a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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