

Silica Gel-Promoted Tandem Addition–Cyclization Reactions of 2-Alkynylbenzenamines with Isothiocyanates

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Tandem addition–cyclization reactions of 2-alkynylbenzenamines with isothiocyanates promoted by silica gel are described. This reaction proceeds smoothly at 80 °C under metal- and solvent-free conditions, which provides an efficient and practical route for the generation of 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazines. The recovered silica gel could be reused for several times.

Introduction

In the combinatorial chemistry field, tandem reactions have been regarded as a powerful approach for construction of small molecule libraries. Usually, tandem reactions involve multiple chemical transformations in one synthetic operation, and their importance stems from the intermediates not needing to be stable enough for isolation and the tandem processes with minimal work up and less waste generation.¹ Meanwhile, the formation of C–S bond is one of the most important processes in the synthesis of many molecules that are of biological, pharmaceutical, and materials interest.² Among the strategies utilized, transition-metal-catalyzed cross-coupling reactions of thiols with aryl halides to achieve aryl C–S bond formation are well developed.³ Tandem reaction is another powerful method for the synthesis of structurally complex molecules containing the C–S bonds from relatively simple starting materials in a convergent way.

Synthesis of 3,1-benzothiazines is a continuing hot topic because the 3,1-benzothiazines moieties are privileged pharmacophores, as well as valuable reactive intermediates.⁴ While 3,1-benzothiazines are well studied and are known for their biological activities, for example, anti-inflammatory activity, the constitutional isomers 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazines have attracted much less attention. On the other hand, transition metal- or Lewis acid-catalyzed tandem addition–cyclization reactions of alkynes possessing a nucleophile in proximity to the triple bond are important processes in organic synthesis, which can construct various heterocycles in an efficient and atom-economic way.^{5–10} As part of a continuing effort in our laboratory toward the development of new methods for the expeditious synthesis of biologically relevant heterocyclic compounds,¹¹ we became interested in the possibility of developing a novel and efficient method to construct the 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazine scaffold.

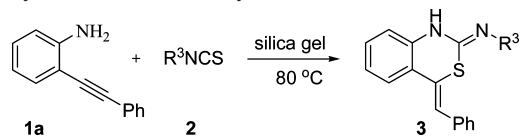
Although several methods have been described for the synthesis of benzo[*d*][1,3]thiazines, most of them suffered

from harsh reaction conditions, high temperature, and low yields.¹² Recently, two alternative approaches have been developed: one was the use of Lawesson's reagent,¹³ and the other involved isothiocyanates.¹⁴ However, in these systems the presence of metal is essential for reaction development. It is well-known that metal-free conditions are crucial in drug discovery process. In addition, from the environmental point of view, design and implementation of new organic-chemical synthetic methodologies is an important process. An alternative potential process was devised based on the adsorptive nature of silica gel.¹⁵ Herein, we would like to report our preliminary results for the synthesis of 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazines starting from 2-alkynylbenzenamines with isothiocyanates in the presence of silica gel under metal- and solvent-free conditions.

Result and Discussion

Generally, the synthetic procedure involves impregnating the mixture of silica gel, 2-alkynylbenzenamine, and isothiocyanate and heating the mixture in oil bath. When a mixture of 2-alkynylbenzenamine **1a** and the phenyl isothiocyanate **2a** was adsorbed on silica gel at 80 °C, the reaction completed overnight. The result was very excellent in terms of yield (Table 1, entries 1). Blank experiment showed that silica gel was necessary in the reaction to obtain the respectable yield. Only 15% of the corresponding product was generated in the absence of silica gel. The structure of **3a** was verified by ¹H and ¹³C NMR, mass spectroscopy, and also by comparison with our previously result,^{14h} which was characterized, as well as with X-ray diffraction analysis. The aryl isothiocyanates substituted with an electron-donating (**2b**) or electron-withdrawing group (**2c**) were suitable substrates in this process because of the high electrophilicity of isothiocyanate, and they afforded the desired products, **3b** or **3c**, in high yields (Table 1, entries 2–3). In addition to aryl isothiocyanates, the reactions of alkyl isothiocyanates also proceeded smoothly. For example, the reaction of alkyl isothiocyanate **2d** with 2-alkynylbenzenamine **1a** gave the corresponding 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazines **3d** in good yield with prolonged reaction times (Table 1, entry 4).

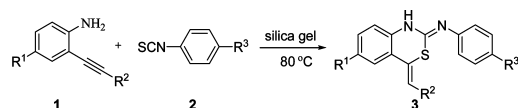
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Table 1. Reactions of 2-Alkynylbenzenamine **1a** with Various Isothiocyanates **2** Promoted by Silica Gel^a

Entry	Isothiocyanate 2	Time (h)	Product 3	Yield (%) ^b
1	2a	12	3a	97
2	2b	12	3b	88
3	2c	12	3c	92
4	2d	48 ^c	3d	79

^a Reaction conditions: 2-alkynylbenzenamine **1a** (0.20 mmol), phenyl isothiocyanate **2a** (0.3 mmol, 1.5 equiv), silica gel 200 mg, $80\text{ }^\circ\text{C}$. ^b Isolated yield based on 2-alkynylbenzenamine **1a**. ^c Stirred at r.t. for 1 h, then at $80\text{ }^\circ\text{C}$ for another 47 h.

In a similar fashion, various 2,4-dihydro-1H-benzo-[d][1,3]thiazines **3** were prepared (Table 2) using different

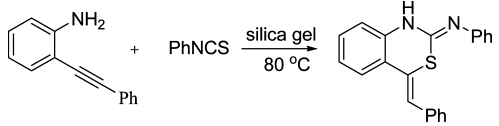
Table 2. Reaction of 2-Alkynylbenzenamine **1** with Isothiocyanate **2** Promoted by Silica Gel^a

Entry	1/R ¹	R ²	2/R ³	Time (h)	Product 3	Yield (%) ^b
1	1b /CH ₃	Ph	2a /H	15	3e	87
2	1b /CH ₃	Ph	2b /OCH ₃	36	3f	82
3	1b /CH ₃	Ph	2c /NO ₂	15	3g	98
4	1c /H	<i>n</i> -Bu	2a /H	48	3h	27
5	1d /CF ₃	Ph	2a /H	8	3i	77
6	1d /CF ₃	Ph	2b /OCH ₃	8	3j	66
7	1d /CF ₃	Ph	2c /NO ₂	24	3k	92
8	1e /F	Ph	2a /OCH ₃	48	3l	63
9	1e /Cl	Ph	2b /H	24	3m	88
10	1e /Cl	Ph	2c /OCH ₃	24	3n	89
11	1f /Cl	Ph	2b /NO ₂	24	3o	92
12	1g /Br	Ph	2c /NO ₂	24	3p	68

^a Reaction conditions: 2-alkynylbenzenamine **1a** (0.20 mmol), phenyl isothiocyanate **2a** (0.3 mmol, 1.5 equiv), silica gel 200 mg, $80\text{ }^\circ\text{C}$. ^b Isolated yield based on 2-alkynylbenzenamine **1a**.

substituted 2-alkynylbenzenamines **1** and isothiocyanates **2**. The reactions proceeded efficiently with in mediate to excellent yields at $80\text{ }^\circ\text{C}$ under solvent free conditions. As expected, both electron-rich and -poor aryl 2-alkynylbenzenamines **1** are suitable partners in this process. For instance, 2-alkynylbenzenamine **1b** reacted with phenyl isothiocyanate **2a** leading to the desired product **3e** in 87% yield (Table 2, entry 1), and the reaction of 2-alkynylbenzenamine **1d** with **2c** afforded the product **3k** in 92% yield (Table 2, entry 7). Other 2-alkynylbenzenamines, **1e–g** with substituents (F, Cl, and Br) on aromatic ring were also tried, and similar results were obtained (Table 2, entries 8–12). However, low yields (27%) were obtained when 2-alkynylbenzenamine **1c** ($\text{R}^2 = n\text{-Bu}$) was reacted with phenyl isothiocyanate **2a** (Table 2, entries 4) because of the complicated reaction. However, in the case of substrate **1h** ($\text{R}^1 = \text{CF}_3$, $\text{R}^2 = 4\text{-(CH}_3)_2\text{NC}_6\text{H}_4$) only indole derivatives was generated. All new products were characterized by ^1H NMR, ^{13}C NMR, and elemental analysis. The advantage of the use of heterogeneous system for this transformation is that ease of promoter/substrate separation provided by a heterogeneous system.

To check the recyclability of silica gel (Table 3), the silica gel used in the conversion of **1a** to **3a**, and the remainder, after leaching out of the products, was thoroughly washed with ethyl acetate and dried in the air at $80\text{ }^\circ\text{C}$ for 2 h. The dried silica gel was then reused directly in the next reaction, and the expected product **3a** was obtained in excellent yield.

Table 3. Efficiency of the Recovered Catalyst


no. of cycles	cycle I	cycle II	cycle III	cycle IV
yield (%)	98	95	92	89

The same procedure was repeated for all further cycles. The recovered silica gel could be reused for several times with just slight loss of catalytic activity.

It is well-known that silica gel has mild Lewis acidity with many reactive hydroxyl groups on the surface and has been used as promoter in organic synthesis. We reasoned that silica gel would be effective as promoter in the reaction process because it may involve the formation of complex via coordination of alkynyl moiety of **1** to hydrogen of silica gel. The proposed tandem cyclization mechanism was generally explained by generation of intermediate thiourea at first via addition of amine **1** to isothiocyanate **2**, and then the sulfur atom in thiourea was regioselectively nucleophilic attacked on the activated triple bond, giving rise to the corresponding product.

In summary, we described herein the silica gel promoted highly efficient, one-pot, tandem addition-cyclization reactions of a series of 2-alkynylbenzenamines with isothiocyanates for the synthesis of 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazines. The silica gel could be used several times. The silica gel showed its important role in this tandem addition-cyclization reaction. Easy work up, inexpensive, ready availability of the promoter, metal- and solvent-free conditions, and combinatorial format makes the procedure an attractive alternative to the existing methods for the synthesis of 2,4-dihydro-1*H*-benzo[*d*][1,3]thiazines.

Experimental Section

General Procedure for Preparation of 4-Benzylidene-1*H*-benzo[*d*][1,3]thiazin-2(4*H*)-ylidene)benzenamine (3a**).** A mixture of 2-alkynylbenzenamine **1a** (0.20 mmol), isothiocyanate **2a** (0.3 mmol, 1.5 equiv), and silica gel (200 mg, surface area = 200–300 m²/g, and pore size = 50–75 μm) was stirred at 80 °C. After completion of reaction as indicated by TLC, the silica gel was filtered by EtOAc. Evaporation of the solvent followed by purification on silica gel provided the corresponding product **3a**. Yield: 97%. ¹H NMR (400 MHz, CDCl₃): δ 7.06 (t, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.29–7.36 (m, 4H), 7.40–7.44 (m, 4H), 7.54 (d, *J* = 8.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 120.2, 121.6, 123.5, 124.8, 124.9, 125.9, 126.7, 127.2, 127.7, 128.2, 128.9, 129.3, 129.6, 135.6, 139.9, 143.2, 147.6. MS (EI): *m/z* 328 (M⁺).

Compounds **3b–3p** were prepared in the same manner. For details, please see the Supporting Information.

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Supporting Information Available. Experimental procedures, characterization data, and ¹H and ¹³C NMR spectra of compound **3**. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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