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Proton-Promoted Hydroamination of 3-Dialkylthiomethylene-1,4-pentadiynes with *o*-Phenylenediamines: A Facile Route to Benzo[*b*][1,4]diazepines

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Abstract: The first proton-promoted intermolecular hydroamination reaction of the enynes, α,α-dialkynylketene *S,S*-acetals **2**, is described. A series of benzo[*b*][1,4]diazepines, with the structures of **3** and **5**, were prepared chemo- and regioselectively in good to high yields by reacting the readily available 1,4-diynes **2** with both terminal and internal alkyne functions with *o*-phenylenediamines under very mild conditions.

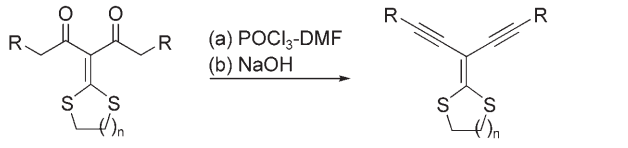
Keywords: alkynes; amines; benzo[*b*][1,4]diazepines; hydroamination; proton catalysis

Introduction

The generation of C–N bonds is of tremendous current interest. From the atom economic point of view, catalytic hydroamination is one of the most efficient approaches for the synthesis of nitrogen-containing products, which are important bulk and fine chemicals or building blocks in organic chemistry.[1] The catalyzed hydroamination of alkynes has been attracting increasing interest in recent years with the aim to develop economic and efficient catalysts and to control the regioselectivity.[1,2] However, most of the catalysts have some disadvantages with respect to their extreme air- and water-sensitivity, high costs and/or toxicity. Therefore, the development of new protocols for the hydroamination reactions of alkynes remains an important goal in organic chemistry.

Acid-promoted hydroamination is generally unsuccessful mainly due to the buffering effect of the amine substrate. However, some proton-catalyzed hydroamination reactions of alkenes were recently carried out in the presence of Brønsted acids.[3] In contrast to many examples of proton-catalyzed hydroamination of alkenes, the proton-catalyzed hydroamination of alkynes is scarcely reported, although selected metal-catalyzed hydroaminations of alkynes did use acids as co-catalysts.[4] To the best of our knowledge, only two examples of proton-catalyzed hydroamination of alkynes have been reported by Fensterbank and co-workers[5a] and Cossy and co-workers,[5b] but these reactions were limited to intramolecular hydroaminations. Herein, we report the first proton-promoted intermolecular hydroamination reaction of alkylthio-activated enynes under mild conditions.

Over the past decades, the potential of α-oxoketene *S,S*-acetals as versatile intermediates in organic synthesis has been recognized.[6] During the course of our studies on the chemistry of functionalized ketene dithioacetals,[7] a series of α,α-dialkynylketene *S,S*-acetals **2** (Scheme 1) and analogues were prepared in high yields *via* a consecutive Vilsmeier–Haack and dehydrochlorination reaction starting from easily available α-oxoketene dithioacetals under mild conditions.[8] As synthetic applications of these electron-rich enynes, we have described the self-coupling reactions of the α-ethynylketene cyclic dithioacetals to the corresponding heteroatom-substituted expanded 1,3-dithiolan[5]radialene[9a] and alkyne-spaced TTFs[9b] and the aza-Diels–Alder reaction of α-ethynylketene dithioacetals with *N*-arylimines to afford 4-functionalized quinolines.[10] Recently, the addition reaction of



1a: R = H; n = 2
1b: R = H; n = 1
1c: R = Me; n = 2

2a: R = H; n = 2 yield = 83%
2b: R = H; n = 1 yield = 86%
2c: R = Me; n = 2 yield = 90%

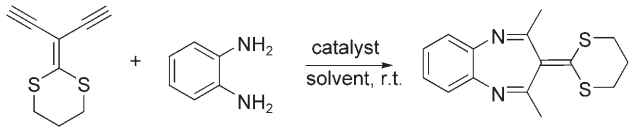
Scheme 1. Synthesis of α,α-dialkynylketene *S,S*-acetals **2**.

carboxylic acids to α-ethynylketene *S,S*-acetals at the carbon-carbon triple bond was also performed successively in the absence of catalysts.[11] These studies and our continued interest in the development of new general methods for biologically important heterocycles[12] promoted us to explore the feasibility of the hydroamination reaction of α-alkynylketene *S,S*-acetals with amines. In this paper we describe the results of the hydroamination reaction of α,α-dialkynylketene *S,S*-acetals with amines.

Results and Discussion

In the initial experiment, the hydroamination reaction of the 1,4-diyne **2a** (1.0 equiv.) with *o*-phenylenediamine (1.0 equiv.) was examined under various reaction conditions (Table 1). With ethanol as the solvent, when $Cu(OAc)_2$ (2.0 equiv.) or $FeCl_3$ (2.0 equiv.) was used as a promoter, no reaction was observed at room temperature for 24 h (Table 1, entries 1 and 2). To our delight, under essentially identical conditions as above, the hydroamination reaction of **2a** with *o*-phenylenediamine can easily proceed in the presence of $BF_3{\cdot}OEt_2$ (2.0 equiv.) at room temperature for 0.5 h to give benzo[*b*][1,4]diazepine **3a1** in 75% yield (Table 1, entry 3). Meanwhile, it was found that catalytic amounts of $BF_3{\cdot}OEt_2$ (1.0 or 0.5 equiv.) led to lower yields of **3a** (Table 1, entries 4 and 5). Among the solvents tested, ethanol seemed to be the best choice although comparable results were obtained with acetonitrile as the solvent (Table 1, entry 6). Other solvents examined, such as dichloromethane and diethyl ether, gave lower yields (Table 1, entries 7 and 8). When the reaction was carried out in benzene or toluene, only a trace amount of **3a1** was observed (TLC) (Table 1, entries 9 and 10). In addition, it was found that the protic acid, CF_3COOH (2.0 equiv.), was as efficient as $BF_3{\cdot}OEt_2$ for the above hydroamination reaction and **3a1** was obtained in 73% yield under essentially identical conditions as above (Table 1, entry 11). Similarly, a catalytic amount of CF_3COOH (1.0 or 0.5 equiv.) led to lower yields of **3a1** (Table 1, entries 12 and 13). The structure of **3a1** was determined based on its spectroscopic and analytical data and confirmed by X-ray crystal structure analysis (Figure 1).[13] The above experimental results showed that the hydroamination reaction is chemo- and regioselective since the two amino groups of *o*-phenylenediamine were added to the two triple bonds of **2a** in the Markovnikov fashion.

Table 1. Hydroamination of diyne **2a** with *o*-phenylenediamine under various reaction conditions.



2a **3a1**

Entry	Catalyst (equiv.)	Solvent	Time [h]	**3a1** Yield [%][a]
1	$Cu(OAc)_2$ (2.0)	C_2H_5OH	24	-
2	$FeCl_3$ (2.0)	C_2H_5OH	24	-
3	$BF_3{\cdot}OEt_2$ (2.0)	C_2H_5OH	0.5	75
4	$BF_3{\cdot}OEt_2$ (1.0)	C_2H_5OH	24	30
5	$BF_3{\cdot}OEt_2$ (0.5)	C_2H_5OH	24	13
6	$BF_3{\cdot}OEt_2$ (2.0)	CH_3CN	0.5	70
7	$BF_3{\cdot}OEt_2$ (2.0)	CH_2Cl_2	2	35
8	$BF_3{\cdot}OEt_2$ (2.0)	$(C_2H_5)_2O$	2	28
9	$BF_3{\cdot}OEt_2$ (2.0)	benzene	24	trace
10	$BF_3{\cdot}OEt_2$ (2.0)	toluene	24	trace
11	CF_3COOH (2.0)	C_2H_5OH	0.5	73
12	CF_3COOH (1.0)	C_2H_5OH	24	32
13	CF_3COOH (0.5)	C_2H_5OH	24	15

[a] Isolated yields.

Benzo[1,4]diazepines constitute an important class of heterocyclic compounds because of their wide range of therapeutic and pharmacological properties.[14] Obviously, the above results provide an efficient route to benzo[1,4]diazepine derivatives from readily available starting materials. Therefore, the scope of this novel and efficient hydroamination reaction was extended by the use of **2a** or **2b** and some typical *o*-phenylenediamines in the presence of CF_3COOH or $BF_3{\cdot}OEt_2$ (Table 1, entries 3 and 11) and the results are described in Table 2. It was found that, with either CF_3COOH or $BF_3{\cdot}OEt_2$ as a promoter, all of the selected *o*-phenylenediamines with either electron-withdrawing or electron-donating groups on the aryl ring could efficiently react with 1,4-diynes **2a** or **2b** to give the corresponding benzo-[1,4]diazepines **3a** or **3b** in good to high yields, respectively (Table 2, entries 1–16). It was obvious that the *o*-phenylenediamine bearing an electron-donating group on the aryl ring, such as 4-methyl-*o*-phenylenediamine led to higher yields of **3** (Table 2, entries 3, 4, 11 and 12). In comparison, *o*-phenylenediamines with an electron-withdrawing group on the aryl ring, for

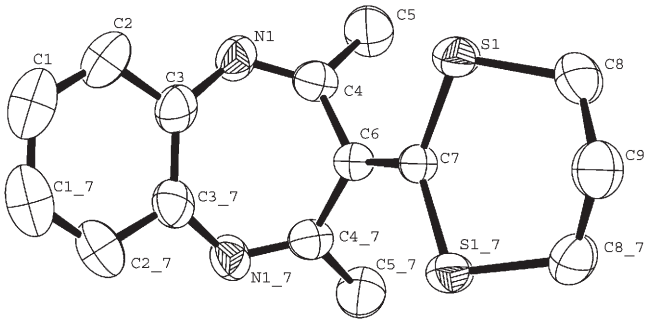
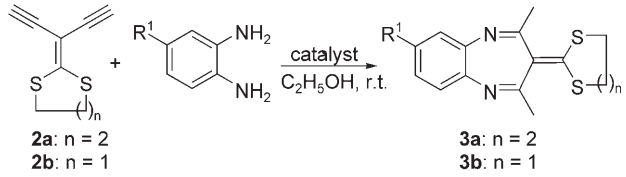


Figure 1. ORTEP drawing of **3a1**.

Table 2. Hydroamination of diynes **2a** and **2b** with *o*-phenylenediamines.



2a: n = 2
2b: n = 1

3a: n = 2
3b: n = 1

Entry	n	R^1	Catalyst	Time [h]	Product	Yield [%][a]
1	2	H	CF_3COOH	0.5	**3a1**	77
2	2	H	$BF_3{\cdot}OEt_2$	0.5	**3a1**	75
3	2	CH_3	CF_3COOH	0.5	**3a2**	80
4	2	CH_3	$BF_3{\cdot}OEt_2$	0.5	**3a2**	82
5	2	Cl	CF_3COOH	0.5	**3a3**	61
6	2	Cl	$BF_3{\cdot}OEt_2$	0.5	**3a3**	66
7	2	PhCO	CF_3COOH	0.5	**3a4**	66
8	2	PhCO	$BF_3{\cdot}OEt_2$	0.5	**3a4**	60
9	1	H	CF_3COOH	0.5	**3b1**	76
10	1	H	$BF_3{\cdot}OEt_2$	0.5	**3b1**	71
11	1	CH_3	CF_3COOH	0.5	**3b2**	83
12	1	CH_3	$BF_3{\cdot}OEt_2$	0.5	**3b2**	80
13	1	Cl	CF_3COOH	0.5	**3b3**	60
14	1	Cl	$BF_3{\cdot}OEt_2$	0.5	**3b3**	63
15	1	PhCO	CF_3COOH	0.5	**3b4**	55
16	1	PhCO	$BF_3{\cdot}OEt_2$	0.5	**3b4**	58
17	2	NO_2	CF_3COOH	1	**3a5**	65
18	1	NO_2	CF_3COOH	1	**3b5**	40

[a] Isolated yields.

example, 4-chloro-*o*-phenylenediamine and 4-benzoyl-*o*-phenylenediamine, gave relatively lower yields of **3** (Table 2, entries 5–8 and 13–16). In the above cases, the effects of both the dialkylthio moiety of 1,4-diynes **2a** or **2b** and promoters (CF_3COOH and $BF_3{\cdot}OEt_2$) on the hydroamination reaction were not significant.

However, it was noticed that when the *o*-phenylenediamine bears a very strong electron-withdrawing group on the aryl ring, for example, 4-nitro-*o*-phenylenediamine, the orientation of the reaction was found to be strongly influenced by both the structure of the dialkylthio moiety in 1,4-diynes **2a** or **2b** and the promoters. As a result, when CF_3COOH was used as a promoter, the hydroamination reactions of **2a** and **2b** with 4-nitro-*o*-phenylenediamine produced the corresponding benzo[1,4]diazepines **3a5** and **3b5** in 65% and 40% yields, respectively (Table 2, entries 17 and 18). However, with $BF_3{\cdot}OEt_2$ as the promoter, the reaction of **2b** with 4-nitro-*o*-phenylenediamine gave imine **4** in 72% yield and the benzo[*b*][1,4]diazepine **5** was obtained in 55% yield by reacting **2a** with 4-nitro-*o*-phenylenediamine (Scheme 2). The molecular structures of both imine **4** and diazepine **5** were confirmed by X-ray analysis (Figure 2 and Figure 3).[15]

In addition, the hydroamination of internal 1,4-diyne **2c** was also investigated in the presence of CF_3COOH (2.0 equiv.) under essentially identical conditions as above. As expected, the hydroamination reactions of **2c** with *o*-phenylenediamine and 4-chloro-*o*-phenylenediamine could also proceed smoothly at room temperature for 5–6 h to give the

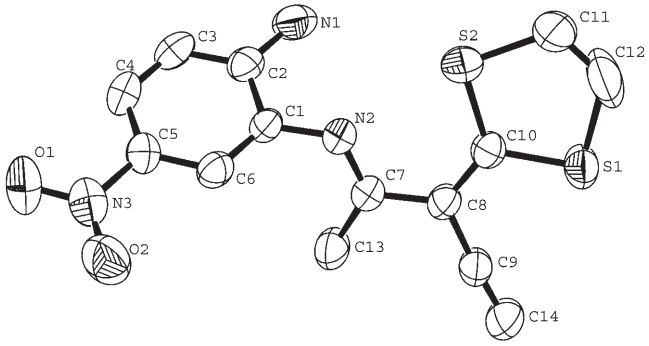


Figure 2. ORTEP drawing of **4**.

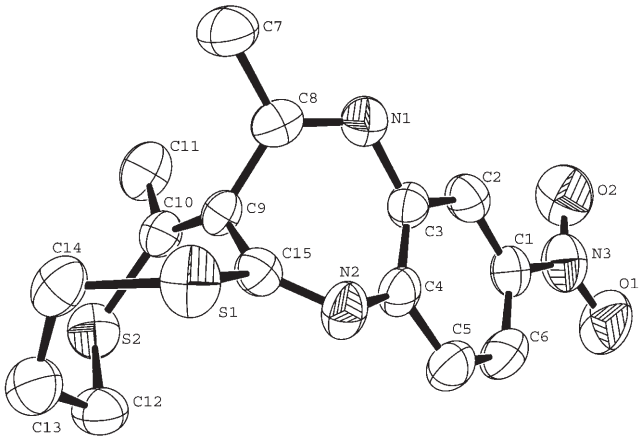
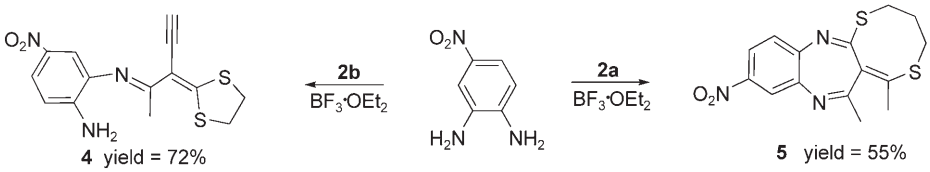
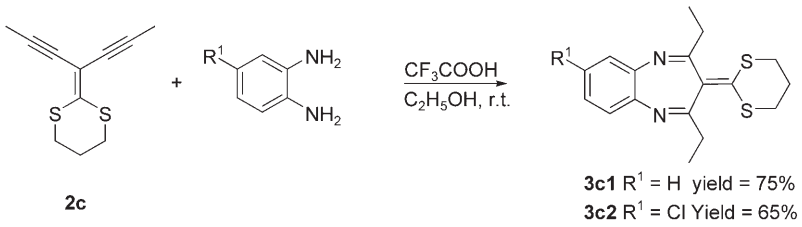


Figure 3. ORTEP drawing of **5**.



Scheme 2. Reaction of 4-nitro-*o*-phenylenediamine with 1,4-diynes **2a** and **2b** in the presence of $BF_3{\cdot}OEt_2$.

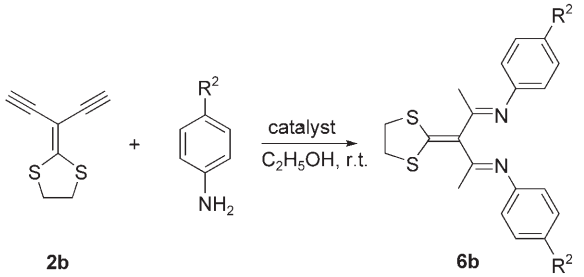


Scheme 3. Hydroamination of **2c** with *o*-phenylenediamines.

corresponding benzo[1,4]diazepines **3c1** and **3c2** in 75% and 65% yields, respectively (Scheme 3).

In the next studies, the hydroamination reaction of diyne **2b** with some typical anilines with either electron-withdrawing or electron-donating groups on the aryl ring was investigated in the presence of CF_3COOH or $BF_3{\cdot}OEt_2$ and the results are described in Table 3. Under identical conditions as above for 2 h, it was found that both aniline and 4-nitroaniline readily underwent the hydroamination reaction with **2b** to give the corresponding imine products **6b1** (the *Z*/*E* isomer ratio of 85/15) and **6b2** (the *Z*/*E* isomer ratio of 75/25) in good to high yields, respectively (Table 3, entries 1–4). However, in the case of the reaction of 4-methylaniline with **2b**, although diyne **2b** was exhausted completely, no hydroamination product **6b3** was observed (Table 3, entries 5 and 6). Similarly, with either CF_3COOH or $BF_3{\cdot}OEt_2$ as a promoter, the reaction of diyne **2b** with ethylenediamine (1.0 equiv.) also did not produce the corresponding [1,4]diazepine product under identical conditions as above and only a polymer was formed. Additionally, the polymerization of diyne **2b** was also observed when **2b** was treated with $BF_3{\cdot}OEt_2$ (2.0 equiv.) in ethanol solvent in the absence of ethylenediamine or *o*-phenylenediamine.[16] In the present research, the reaction of α,α-diacetylketene *S,S*-acetal **1b** with *o*-phenylenediamine (1.0 equiv.) was also examined and the results indicated that **1b** was intact under the identical conditions (solvent: ethanol; $BF_3{\cdot}OEt_2$ or CF_3COOH: 2.0 equiv.).

Table 3. Hydroamination of diyne **2b** with anilines.

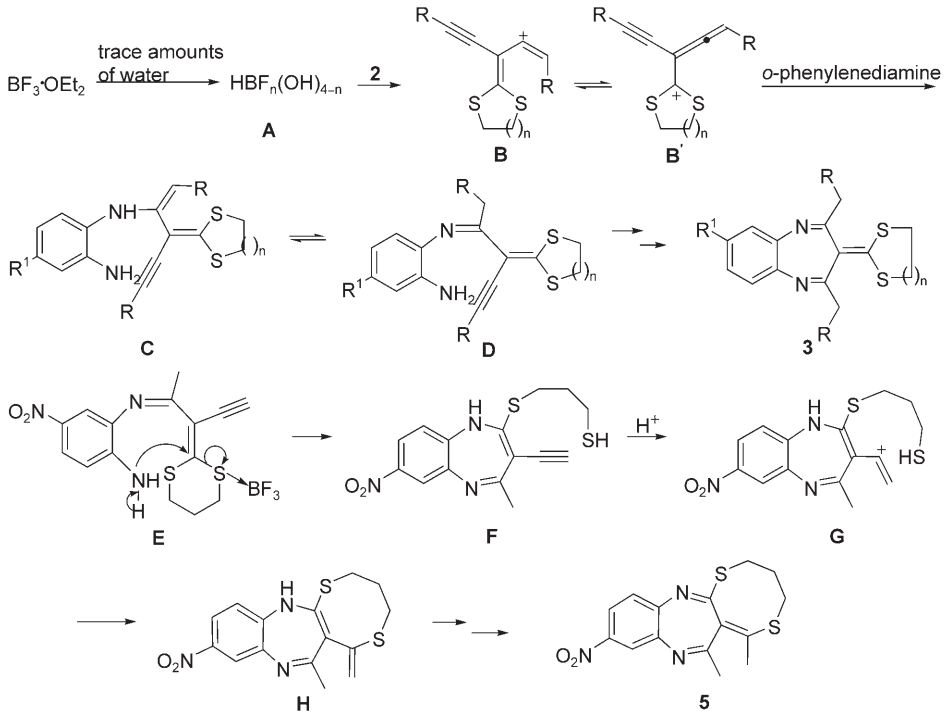


Entry	n	R^2	Catalyst	Time [h]	Product	Yield [%][a]
1	1	H	CF_3COOH	2	**6b1**	70
2	1	H	$BF_3{\cdot}OEt_2$	2	**6b1**	65
3	1	NO_2	CF_3COOH	2	**6b2**	60
4	1	NO_2	$BF_3{\cdot}OEt_2$	2	**6b2**	62
5	1	CH_3	CF_3COOH	12	**6b3**	-
6	1	CH_3	$BF_3{\cdot}OEt_2$	12	**6b3**	-

[a] Isolated yields.

The above results reveal that: 1) diynes **2** are sensitive to $BF_3{\cdot}OEt_2$ or CF_3COOH and both the hydroamination of a diyne **2** with a suitable aniline and the polymerization of diynes **2** could be initiated in the presence of $BF_3{\cdot}OEt_2$ or CF_3COOH; 2) the hydroamination of diynes **2** is amine-dependent due to the formation of a complex or salt between amine and $BF_3{\cdot}OEt_2$ or CF_3COOH. Strong basic amines, such as aliphatic ethylenediamine and aromatic 4-methylbenzeneamine could not give the hydroamination products due to the preferential formation of the complex or salt between the strongly basic amines and $BF_3{\cdot}OEt_2$ or CF_3COOH. However, in the case of the hydroamination of diynes **2** and *o*-phenylenediamines, although the basicity of some *o*-phenylenediamines, such as *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine, is higher than that of 4-methylbenzeneamine and aniline and thus a complex or salt may be created preferentially by the interaction of these amines with boron trifluoride etherate or CF_3COOH, nevertheless, there should be only one of the two amino groups with relatively strong basicity involved and a free amino group left as a nucleophilic center. According to the above analysis and the regioselectivity of the hydroamination reaction of diynes **2**, a possible mechanism is proposed in Scheme 4 (with $BF_3{\cdot}OEt_2$ as a promoter).

As depicted in Scheme 4, initially, the reaction of $BF_3{\cdot}OEt_2$ with trace amounts of water in the system generates the Brønsted acid catalyst **A**.[17] On the other hand, owing to the strong electron-donating effect of the alkylthio groups (S–C sp^2-conjugation), the carbon atom adjacent to R group of diyne **2** is believed to be more electron-rich, which favors the protonation occurring at the carbon atom adjacent to the R group of the carbon-carbon triple bond and leads to the formation of intermediate **B** (Scheme 4).[11] Then, the nucleophilic attacking of the free or higher basic amino group of an *o*-phenylenediamine could occur at either carbon cation of intermediate **B** or the



Scheme 4. Proposed mechanism for proton-catalyzed hydroamination reaction of diynes **2**.

carbon cation of intermediate **B'** and the attacking at the carbon cation of intermediate **B** (Scheme 4, **B** to **D**) would be preferred at this stage for reasons of steric hindrance. Subsequently, intramolecular hydroamination followed by an ene-amine to imine tautomer will finally lead to the formation of benzo[*b*][1,4]diazepines (Scheme 4, **C**/**D** to **3**). For intermediate **E**, generated by the intermolecular hydroamination of diyne **2a** with 4-nitro-*o*-phenylenediamine, the nucleophilicity of the amino group would be largely reduced due to the existence of two strong EWGs (imine and nitro group at 2- and 4-positions of the aryl ring of intermediate **E**) and the further transformation of the imine intermediate **E** may be directed by the relative electrophilicity of the carbon cation and the methylene carbon atom of the 1,3-dithiane moiety of intermediate **E**.

In the previous research, we have found that the methylene carbon atom at the 2-position of the 1,3-dithiane moiety of an α-oxoketene dithioacetal compound was more prone to be attacked by a tethered nucleophilic group than that of 1,3-dithiolane catalyzed by a Lewis acid.[7e,18] This might be the reason why benzo[*b*][1,4]diazepine **5** was formed *via* a sequential intramolecular S_NV[7a,f,i] (Scheme 4, **E** to **F**), thiolation process (Scheme 4, **G** to **H**) and tautomerization (Scheme 4, **H** to **5**). According to the above analysis, the formation of the imine **4** is not difficult to understand. For the CF_3COOH-promoted hydroamination reaction of **2** with 4-nitro-*o*-phenylenediamine, the methylene carbon atom of the dithiane/dithiolane methylene moiety of intermediate **C** was not activated as in the formation of the complex of $BF_3{\cdot}OEt_2$ with the sulfur atoms of **2**, as a result, benzo[1,4]diazepines **3a5** and **3b5** were finally produced *via* a consecutive intramolecular hydroamination and rearrangement from **C** to **3** (Scheme 4).

Conclusions

In conclusion, we have documented the first proton-catalyzed intermolecular hydroamination reaction of electron-rich alkynes, α,α-dialkynylketene *S,S*-acetals **2**, with various aromatic amines. The hydroamination reaction can proceed in a highly chemo- and regioselective manner under very mild conditions in the open air and no metal-based catalyst is required. The synthesis of benzo[*b*][1,4]diazepines **3** and **5** provides a new and facile route to these biologically important molecules. Further research on the synthetic applications of the alkylthio activated enynes **2** is in progress.

Experimental Section

Typical Procedure for the Preparation of 3–5 (3a1 as Example)

To a solution of **2a** (1.0 mmol, 180 mg) and *o*-phenylenediamine (1.0 mmol, 108 mg) in C_2H_5OH (10 mL) was cooled to 0 °C in an ice bath, and $BF_3{\cdot}OEt_2$ (2.0 mmol, 0.25 mL)

was added dropwise by syringe within 3 min. The reaction mixture was stirred for 0.5 h at room temperature. After **2a** had been consumed (monitored by TLC), the reaction mixture was poured into water (30 mL). The solid crude product **3a1** was filtered off, then purified by silica gel chromatography (diethyl ether/hexane = 1/1, v/v) to give **3a1**; yield: 216 mg (75%).

Physical Data of Typical Compounds Isolated

3a1: white crystals; mp 200–202 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.03–2.24 (m, 2H), 2.76 (s, 6H), 2.78–2.82 (m, 2H), 2.94–2.99 (m, 2H), 7.20 (dt, J = 6.0, 3.5 Hz, 2H), 7.38 (dt, J = 6.0, 3.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 23.4, 25.4 (2C), 28.5 (2C), 124.8 (2C), 127.6 (2C), 129.9 (2C), 135.2 (2C), 140.1, 160.1; IR (KBr): ν = 762, 790, 1213, 1272, 1365, 1426, 1460, 1559, 1620, 2916, 2956, 3442 cm^{-1}; MS (EI): m/z = 289 $[(M+1)]^+$; anal. calcd. (found) for $C_{15}H_{16}N_2S_2$: C 62.46 (62.59), H 5.59 (5.64), N 9.71 (9.76).

4: red crystals; mp 183–185 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.26 (s, 3H), 3.40–3.44 (m, 4H), 3.72 (s, 1H), 4.65 (s, 2H), 6.68 (d, J = 9.0 Hz, 1H), 7.52 (s, 1H), 7.89 (q, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.3, 35.7, 40.7, 82.3, 86.5, 107.9, 112.9, 115.9, 122.1, 134.9, 138.9, 145.9, 165.1, 166.0; IR (KBr): ν = 740, 830, 1212, 1264, 1309, 1460, 1484, 1500, 1592,1613, 3261, 3351, 3462 cm^{-1}; MS (EI): m/z = 320 $[(M+1)]^+$; anal. calcd. (found) for $C_{14}H_{13}N_3O_2S_2$: C 52.65 (52.70), H 4.10 (4.05), N 13.16 (13.24).

5: white crystals; mp 220–222 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.88 (s, 3H), 2.36 (s, 3H), 2.38–2.41 (m, 2H), 2.58 (d, J = 16.0 Hz, 1H), 3.06 (d, J = 16.0 Hz, 1H), 3.75–3.81 (m, 1H), 3.93–3.99 (m, 1H), 7.56 (d, J = 9.0 Hz, 1H), 8.03 (d, J = 9.0 Hz, 1H), 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.9, 26.0, 27.4, 30.2, 36.2, 119.6, 123.3, 125.8, 128.5, 134.7, 139.9, 143.9, 145.0, 161.9, 163.2; IR (KBr): ν = 884, 1085, 1168, 1211, 1248, 1343, 1450, 1511, 1623, 2962, 3433 cm^{-1}; MS (EI): m/z = 334 $[(M+1)]^+$; anal. calcd. (found) for $C_{15}H_{15}N_3O_2S_2$: C 54.03 (54.13), H 4.53 (4.55), N 12.60 (12.66).

6b1: yellow crystals; mp 112–114 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.04 (s, 6H), 3.31 (s, 4H), 6.86 (d, J = 7.5 Hz, 4H), 7.08 (q, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.1 (2C), 37.5 (2C), 119.8, 119.9 (2C), 120.3, 123.8 (2C), 124.5, 128.2, 128.8, 129.0, 129.3 (2C), 150.2 (2C), 153.8, 166.5; IR (KBr): ν = 3378, 3060, 1618, 1592, 1483, 1364, 1212, 1159, 802, 701 cm^{-1}; MS (EI): m/z = 353 $[(M+1)]^+$.

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[13] Crystal data for **3a1**: $C_{15}H_{16}N_2S_2$, white crystal, $M=$ 288.44, orthorhombic, *Pnma*, $a=9.4232(19)$ Å, $b=$ 12.307(3) Å, $c=12.476(3)$ Å, $\alpha=90.00°$, $\beta=90.00°$, $\gamma=$ 90.00°, $V=1446.9(5)$ Å^3, $Z=4$, $T=293(2)$, $F_{000}=608$, $R_1=0.0390$, $wR_2=0.1750$. CCDC 667660 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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[15] a) Crystal data for **4**: $C_{14}H_{13}N_3O_2S_2$, red crystal, $M=$ 319.05, hexagonal, p_32_2_1, $a=8.5536(12)$ Å, $b=$ 8.5536(12) Å, $c=35.520(11)$ Å, $\alpha=90.00°$, $\beta=90.00°$, $\gamma=120.00°$, $V=2250.6(8)$ Å^3, $Z=6$, $T=293(2)$, $F_{000}=$ 984, $R_1=0.0487$, $wR_2=0.0942$, CCDC 667661 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif; b) Crystal data for **5**: $C_{15}H_{15}N_3O_2S_2$, white crystals, $M=333.44$, triclinic, P-1, $a=6.2670(17)$ Å, $b=11.174(3)$ Å, $c=11.537(3)$ Å, $\alpha=86.475(5)°$, $\beta=76.678(6)°$, $\gamma=83.499(5)°$, $V=$ 780.6(4) Å^3, $Z=2$, $T=293(2)$, $F_{000}=348$, $R_1=0.0484$, $wR_2=0.0546$, CCDC 667662 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[16] In additional experiments, the reaction of diyne **2b** with CF_3COOH was also attempted in ethanol solvent in the absence of ethylenediamine or *o*-phenylenediamine. We found that, when the diyne **2b** (1.0 equiv.) was treated with CF_3COOH (2.0 equiv.) at room temperature for 2–3 h, the addition reaction of CF_3COOH to diyne **2b** could proceed to give the corresponding enol ester compound in 50% yield along with a certain amount of polymer (See Supporting Information).

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