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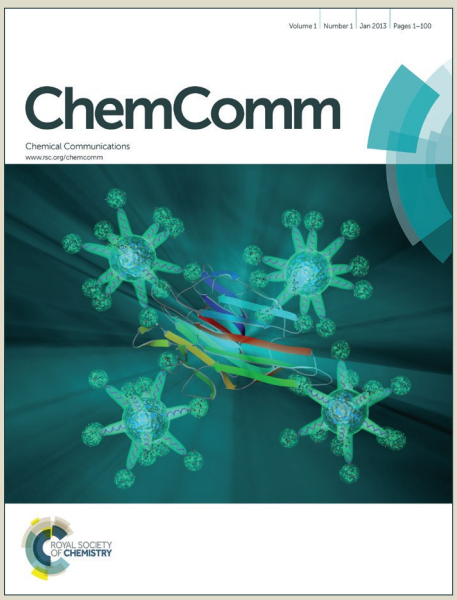

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Synthesis of 2,3-allenylamides utilizing [1,2]-phospha-Brook rearrangement and their application to gold-catalyzed cycloisomerization providing 2-aminofuran derivatives

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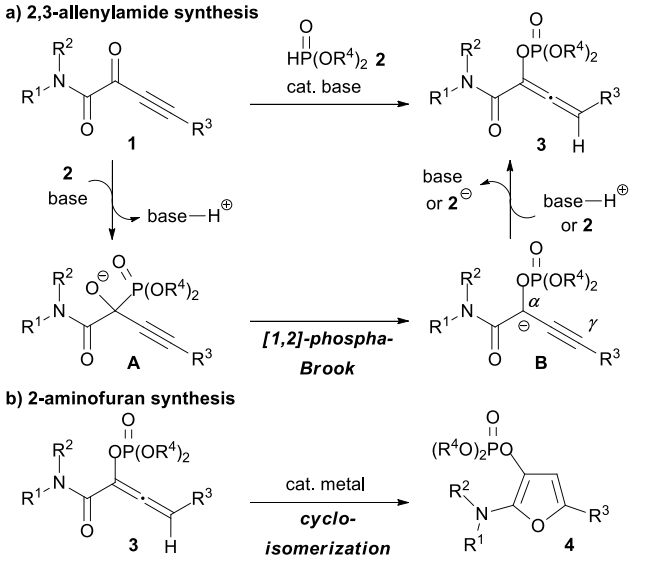
An efficient synthetic method for 2,3-allenylamides having an oxygen functionality at the 2-position, which are difficult to access by conventional methods, was newly developed by utilizing the [1,2]-phospha-Brook rearrangement under Brønsted base catalysis. Further manipulation of the 2,3-allenylamides via gold-catalyzed cycloisomerization enables the formation of 2-aminofuran derivatives.

2,3-Allenylcarbonyl compounds are one of the privileged classes of compounds used as building blocks in organic synthesis.[1] A variety of transformations have been developed on the basis of their versatile reactivities, including nucleophilic cyclization catalyzed by transition metals,[2] cycloaddition under nucleophilic catalysis,[3] and others.[4] A new synthesis of 2,3-allenylcarbonyl compounds also has received considerable attention in recent years.[5,6] Particularly, the synthesis of 2,3-allenylcarbonyl compounds having a functional group on a specific sp^2-carbon is attractive because it paves the way for the synthesis of highly functionalized complex molecules through the transformation of 2,3-allenylcarbonyl compounds. In this context, we have developed an efficient synthesis of 2,3-allenylcarbonyl compounds having an oxygen-functionality at the 2-position,[7] which are difficult to access by conventional methods, by utilizing the [1,2]-phospha-Brook rearrangement under Brønsted base catalysis.[8,9] Our reaction design is shown in Scheme 1. α-Alkynylketoamide **1** is employed as the substrate and is treated with phosphite **2** in the presence of a catalytic amount of Brønsted base (Scheme 1a). The deprotonation of phosphite **2** by the Brønsted base and the following 1,2-selective addition of the resulting anion of **2** provide alkoxide **A**. The migration of the dialkoxyphosphoryl moiety from carbon



Scheme 1 Synthesis of 2,3-allenylamides utilizing [1,2]-phospha-Brook rearrangement and their application to metal-catalyzed cycloisomerization

to oxygen, i.e., the [1,2]-phospha-Brook rearrangement, proceeds to form enolate **B**. Finally, the regioselective protonation at the γ-position by the conjugated acid of the Brønsted base catalyst or **2** provides desired 2,3-allenylamide **3**. Our methodology is characterized by the catalytic generation of enolate (propargyl anion) having an oxygen-functionality under mild reaction conditions. Generally, the synthesis of related funtionalized allenes involves the stoichiometric generation of allenyl or propargyl anions under highly basic conditions.[7] As an application of newly synthesized **3**, we also have developed a cycloisomerization reaction catalyzed by π-acidic transition metals,[2] which provides 2-aminofuran derivative **4** having an oxygen-functionality at the 3-position, in hopes that **4** would be a useful building block for the construction of six-membered cyclic frameworks through the Diels-Alder reaction (Scheme 1b).[10] Herein we report an efficient synthesis of 2,3-allenylamides utilizing the [1,2]-phospha-Brook rearrangement catalyzed by a phosphazene

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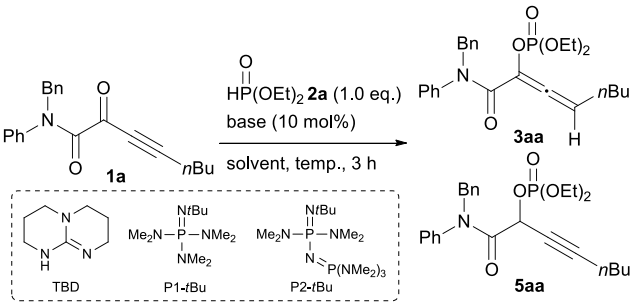
base, and the cycloisomerization of the 2,3-allenylamides catalyzed by a cationic Au(I) complex.

At the outset of our study, *N*-benzyl-2-oxo-*N*-phenyloct-3-ynamide (**1a**) was employed as the initial substrate. **1a** was treated with 1.0 equivalent of diethyl phosphite (**2a**) in the presence of 10 mol% Brønsted base in toluene at room temperature. The use of a tertiary amine, such as *N*,*N*-diisopropylethylamine, provided no adduct, and 72% of starting **1a** was recovered (Table 1, entry 1). The use of DBU and TBD accelerated the consumption of **1a**, and desired 2,3-allenylamide **3aa** was obtained along with propargylic amide **5aa**, albeit in low yield (entries 2 and 3). A dramatic improvement of the yield of **3aa** was achieved by employing phosphazene bases, such as P1-*t*Bu and P2-*t*Bu (entries 4 and 5). In particular, P1-*t*Bu facilitated the regioselective protonation and desired **3aa** was obtained in 63% yield along with 2% of **5aa** (entry 4). The use of *t*BuOK resulted in an almost 1:1 mixture of **3aa** and **5aa** in moderate combined yield (entry 6). Whereas the solvents screened did not increase the yield of **3aa** so much (entries 7-11), the decrease of the reaction temperature was beneficial as it improved the mass balance of the reaction and increased the yield of **3aa**. The optimum reaction temperature was − 40 °C; at that temperature, **3aa** was obtained in 82% yield, and **5aa** was not detected (entry 13). Finally, the yield of **3aa** was improved to 92% by employing 1.5 equivalents of **2a** (entry 14). In order to clarify whether or not **3aa** was formed by the isomerization of **5aa**, **5aa** was treated with a catalytic amount of P1-*t*Bu in the presence or absence of **2a**. This resulted in the recovery of **5aa** and the formation of only a trace amount of **3aa**, thus clearly suggesting that **3aa** was formed through the regioselective protonation of the enolate intermediate (**B** in Scheme 1) at the *γ*-position.[11] Considering the acidity of diethyl phosphite (dimethyl phosphite, pK_a = 18.4 in DMSO, estimated)[12] and the conjugated acid of P1-*t*Bu (*p*K_{BH+} = 15.7 in DMSO),[13] the latter would preferentially serve as the proton source, and its bulkiness would contribute to the regioselective protonation at the less hindered *γ*-position to provide 2,3-allenylamide **3aa**. With the optimum reaction conditions in hand, the scope of α-alkynylketoamide **1** and phosphite **2** was investigated (Table 2). At first, different phosphites were tested (entries 1-3). Dimethyl phosphite (**2b**) gave a similar result to **2a** (entry 1). Sterically hindered diisopropyl phosphite (**2c**) provided only a trace amount of the desired product and a substantial amount of recovered **1a** (entry 2). The reaction of diphenyl phosphite (**2d**) proceeded to provide **3ad** in 76% yield along with propargylic amide **5ad** in 16% NMR yield (entry 3). Then the effect of substituents on the nitrogen of α-alkynylketoamide **1** was examined. Both diphenylamide **1b** and dibenzylamide **1c** were applicable to the reaction, affording corresponding products **3ba** and **3ca** in good yields, respectively (entries 4

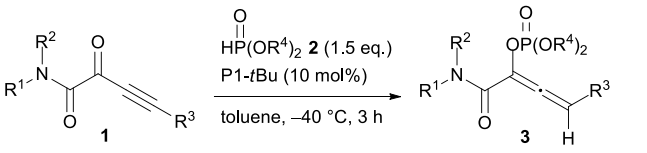
Table 1 Optimization of reaction conditions[a]



entry	base	solvent	temp. (°C)	yield[b] (%) 3aa	5aa	1a
1	*i*Pr$_2$NEt	toluene	rt	0	0	72
2	DBU	toluene	rt	15	12	6
3	TBD	toluene	rt	28	18	0
4	P1-*t*Bu	toluene	rt	63	2	0
5	P2-*t*Bu	toluene	rt	63	28	0
6	*t*BuOK	toluene	rt	32	34	0
7	P1-*t*Bu	CH_2Cl_2	rt	55	2	0
8	P1-*t*Bu	Et_2O	rt	59	3	0
9	P1-*t*Bu	THF	rt	66	<1	0
10	P1-*t*Bu	DMF	rt	26	<1	20
11	P1-*t*Bu	EtOH	rt	70	7	3
12	P1-*t*Bu	toluene	−20	79	1	0
13	P1-*t*Bu	toluene	−40	82	<1	0
14[c]	P1-*t*Bu	toluene	−40	92 (91)	<1	0

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), base (0.025 mmol), solvent (1.0 mL). [b]Yields were determined by ^{1}H and ^{31}P NMR analyses of the crude mixture. Trimethyl phosphate was used as the internal standard. Isolated yield is shown in parentheses. [c]0.38 mmol **2a** (1.5 eq.) was used.

Table 2 Scope of ketoamides **1** and phosphites **2**[a]



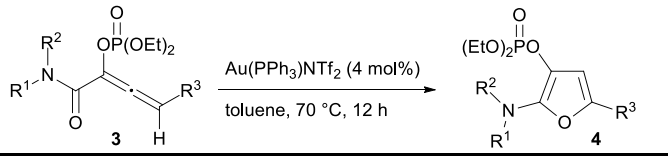
entry	1	R^1	R^2	R^3	2	R^4	3	yield (%)[b]
1	**1a**	Ph	Bn	*n*Bu	**2b**	Me	**3ab**	94
2	**1a**	Ph	Bn	*n*Bu	**2c**	*i*Pr	**3ac**	<5[c]
3	**1a**	Ph	Bn	*n*Bu	**2d**	Ph	**3ad**	76[d]
4	**1b**	Ph	Ph	*n*Bu	**2a**	Et	**3ba**	79
5	**1c**	Bn	Bn	*n*Bu	**2a**	Et	**3ca**	83
6	**1d**	Me	Me	*n*Bu	**2a**	Et	**3da**	80[e]
7	**1e**	$(CH_2)_2O(CH_2)_2$		*n*Bu	**2a**	Et	**3ea**	69[f]
8	**1f**	Ph	Bn	*c*Hex	**2a**	Et	**3fa**	92
9[g]	**1g**	Ph	Bn	*t*Bu	**2a**	Et	**3ga**	56[h]
10	**1h**	Ph	Bn	Ph	**2a**	Et	**3ha**	96[i]
11	**1i**	Bn	Bn	Ph	**2a**	Et	**3ia**	90[i]
12	**1j**	Ph	Bn	$(CH_2)_4Cl$	**2a**	Et	**3ja**	80
13	**1k**	Ph	Bn	$(CH_2)_4Br$	**2a**	Et	**3ka**	71
14	**1l**	Ph	Bn	$(CH_2)_4OAc$	**2a**	Et	**3la**	86
15	**1m**	Ph	Bn	$(CH_2)_4OTHP$	**2a**	Et	**3ma**	87
16	**1n**	Ph	Bn	$(CH_2)_4OTBS$	**2a**	Et	**3na**	89
17	**1o**	Ph	Bn	$(CH_2)_4OH$	**2a**	Et	**3oa**	80
18	**1p**	Ph	Bn	TIPS	**2a**	Et	**3pa**	<1[j]
19	**1q**	Ph	Bn	H	**2a**	Et	**3qa**	80

[a]Reaction conditions: **1** (0.25 mmol), **2** (0.38 mmol), P1-*t*Bu (0.025 mmol), toluene (1.0 mL), −40°C, 3 h. [b]Isolated yields unless otherwise noted. [c]60% of **1a** was recovered. [d]**5ad** (16% NMR yield) was formed. [e]**5da** (13% NMR yield) was formed. [f]**5ea** (20% NMR yield) was formed. [g]The reaction was conducted for 3.5 h. [h]**5ga** (29% NMR yield) was formed. [i]NMR yields. [j]**5pa** (95% NMR yield) was formed.

and 5). Less sterically hindered dialkyl amides, such as dimethyl amide **1d** and morpholine amide **1e**, provided corresponding allenylamides **3da** and **3ea** in moderate yields along with propargylic amides, indicating that the size of the amide moiety influenced the regioselectivity of the enolate protonation (entries 6 and 7). Next, the substituents on the alkyne terminus of **1** were screened. Cyclohexyl-substituted **1f** underwent the reaction smoothly and **3fa** was obtained in good yield (entry 8). The reaction of *tert*-butyl- substituted **1g** resulted in the formation of a mixture of **3ga** and **5ga** (entry 9). The reactions of **1h** and **1i** having a phenyl group proceeded to provide allenylamides **3ha** and **3ia**, which were incompatible with silica-gel column purification (entries 10 and 11). A variety of functional groups including chloro, bromo, and even unprotected hydroxy groups, were tolerated under the reaction conditions, and the corresponding products were obtained in good yields (entries 12-17). The reaction of triisopropylsilyl-substituted **1p** provided only alkynylamide **5pa** (entry 18). The results of the reactions of **1g** and **1p** (entries 9 and 18) suggested that the bulky substituents on the alkyne terminus prevented regioselective protonation at the *γ*-position. **1q** having a terminal alkyne moiety underwent the reaction without any problems to afford **3qa** in good yield (entry 19).

Next, we investigated the cycloisomerization of 2,3-allenylamides **3** into 2-aminofuran derivatives **4** as an application of newly synthesized 2,3-allenylamides **3**. Screening for π-acidic transition metals as catalyst revealed that the cationic Au(I) complex efficiently catalyzed the cycloisomerization of **3aa** in toluene at 70 °C, providing **4aa** in 85% yield (Table 3, entry 1).[11] It is noteworthy that heating **3aa** in the absence of Au(I) catalyst accelerated the intramolecular Diels-Alder reaction of the phenyl group on the nitrogen with

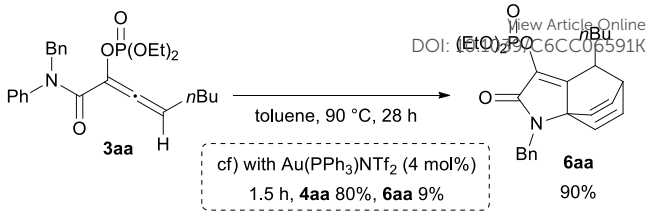
Table 3 Cycloisomerization of 2,3-allenylamides **3** into 2-aminofuran derivatives **4**[a]



3 4

entry	3	R^1	R^2	R^3	4	yield (%)[b]
1	**3aa**	Ph	Bn	*n*Bu	**4aa**	85
2	**3ba**	Ph	Ph	*n*Bu	**4ba**	80
3	**3ca**	Bn	Bn	*n*Bu	**4ca**	<1
4	**3fa**	Ph	Bn	*c*Hex	**4fa**	78
5	**3ga**	Ph	Bn	*t*Bu	**4ga**	83
6	**3ha**	Ph	Bn	Ph	**4ha**	15[c]
7	**3ia**	Bn	Bn	Ph	**4ia**	64
8	**3ja**	Ph	Bn	$(CH_2)_4Cl$	**4ja**	83
9	**3ka**	Ph	Bn	$(CH_2)_4Br$	**4ka**	69
10	**3la**	Ph	Bn	$(CH_2)_4OAc$	**4la**	50
11	**3ma**	Ph	Bn	$(CH_2)_4OTHP$	**4ma**	60
12	**3na**	Ph	Bn	$(CH_2)_4OTBS$	**4na**	79
13	**3oa**	Ph	Bn	$(CH_2)_4OH$	**4oa**	42
14	**3qa**	Ph	Bn	H	**4qa**	12[d]

[a]Reaction conditions: **3**, $Au(PPh_3)NTf_2$ (4 mol%), toluene (0.125 *M*), 70 °C, 12 h. [b]Isolated yields. [c]**6ha** (68% NMR yield) was formed. [d]**6qa** (52% NMR yield) was formed.

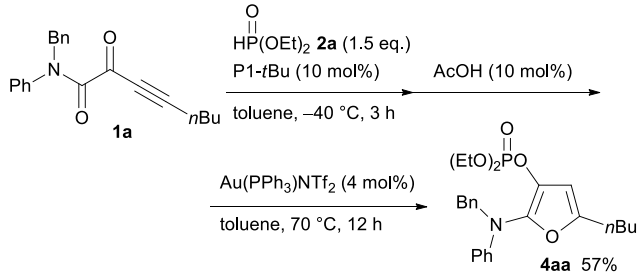


Scheme 2 Intramolecular Diels-Alder reaction of **3aa**

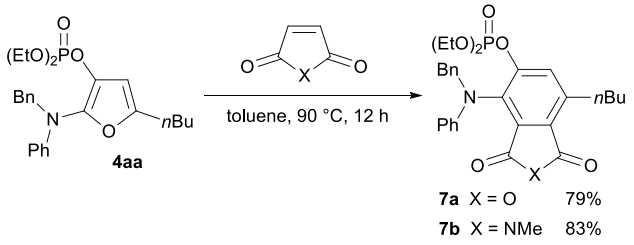
an allene moiety to provide **6aa**,[14] which indicated the potential of the newly synthesized allenylamide for diverse applications (Scheme 2). Then, investigation of the substrate scope for the cycloisomerization was carried out (Table 3). The reaction of diphenylamide **3ba** proceeded smoothly to provide **4ba** in good yield; in contrast, the reaction of dibenzylamide **3ca** did not take place (entries 2 and 3). Then, substrates having various substituents on the allene moiety were examined. The reaction of cyclohexyl- and *tert*-butyl-substituted **3fa** and **3ga** proceeded without any problems to afford **4fa** and **4ga** in good yields, respectively (entries 4 and 5). When the reaction was performed with **3ha**, which had a phenyl group on the allene moiety, the intramolecular Diels-Alder reaction proceeded in preference to the cycloisomerization even in the presence of Au(I) catalyst (entry 6). In contrast, the reaction of dibenzylamide **3ia** having a phenyl group on the allene moiety proceeded to afford **4ia** in good yield (entry 7). 2,3-Allenylamides **3** possessing a variety of functional groups were applicable to the cycloisomerization, and corresponding 2-aminofuran derivatives **4** were obtained in moderate to good yields (entries 8-13). The reaction of **3qa** provided Diels-Alder product **6qa** as the major product (entry 14).

The investigation was further extended to the one-pot synthesis of 2-aminofuran derivative **4aa** from α-alkynylketoamide **1a** (Scheme 3). **1a** was treated with **2a** in the presence of 10 mol% P1-*t*Bu in toluene at −40 °C for 3 h. After adding 10 mol% AcOH to deactivate P1-*t*Bu, 4 mol% $Au(PPh_3)NTf_2$ was added, and the resulting mixture was stirred at 70 °C for 12 h to furnish desired product **4aa** in 57% yield.

Finally, the transformation of 2-aminofuran derivatives was attempted.[15] **4aa** was found to participate in the Diels-Alder reaction with maleic anhydride and *N*-methylmaleimide and subsequent dehydrative aromatization to furnish 2-aminophenol derivatives **7a** and **7b** in high yields (Scheme 4).[10c]



Scheme 3 One-pot synthesis of 2-aminofuran derivative **4aa** from **1a**



Scheme 4 Transformation of **4aa**

In conclusion, we have newly developed an efficient synthesis of 2,3-allenylamides by utilizing the [1,2]-phospha-Brook rearrangement under Brønsted base catalysis. The reaction involves the generation of an amide enolate by treatment of α-alkynylketoamide with phosphite through the [1,2]-phospha-Brook rearrangement, followed by the regioselective protonation at the γ-position to provide 2,3-allenylamides having an oxygen functionality at the 2-position, which are difficult to access by conventional methods. Thus synthesized 2,3-allenylamides were subsequently applied to the gold-catalyzed cycloisomerization to afford 2-aminofuran derivatives. The one-pot synthesis of 2-aminofuran derivatives as well as their further transformation into 2-aminophenol derivatives was also achieved.

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