

Sc(OTf)₃-Catalyzed Bicyclization of *o*-Alkynylanilines with Aldehydes: Ring-Fused 1,2-Dihydroquinolines**

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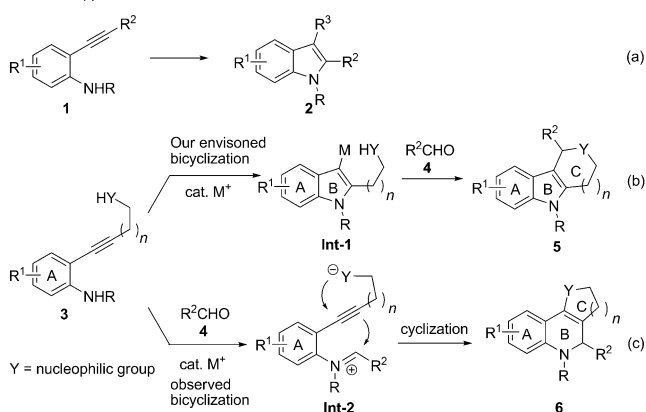
Dedicated to Professor Lixin Dai on the occasion of his 90th birthday

Abstract: A Sc(OTf)₃-catalyzed cascade Prins-type cyclization reaction of *o*-alkynylanilines, bearing a hydroxy or amine functionality, with aldehydes affords 1,2-dihydroquinoline derivatives having an extra fused ring efficiently under mild reaction conditions. It is interesting to observe the reversed reactivity in the highly selective formation of 1,2-dihydroquinoline derivatives instead of the formation of the usually favored indole derivatives.

Polycyclic structures are often important structural motifs which exist in nature and display significant pharmacological and biological activities.^[1] Thus, much attention has been paid to the development of new approaches to such skeletons. Tandem reactions,^[2,3] in which multistep reactions are combined into one synthetic operation, have shown high efficiency for the construction of complex skeletons. In contrast, ring-fused indoles are a class of important heterocyclic structural motifs found in many natural products, as well as in bioactive substances.^[4] An efficient coupling/cyclization approach to the indole skeletons **2** by the cyclization of the *o*-alkynylanilines **1** starting from 2-haloanilines and alkynes has been well developed (Scheme 1a).^[5] On this basis, we envisioned that the *o*-alkynylaryl amines **3**, having an extra nucleophilic functionality, may undergo poly-heteroannulation under the metal catalysis to provide the indolyl intermediate **Int-1**,^[6] which would sequentially react with the aldehydes **4**^[6a,7] and the pre-installed nucleophilic unit (YH) to afford ring-fused indole skeletons **5** (Scheme 1b).^[8]

Our initial attempt began with the cyclization reaction of the *o*-alkynylaniline **3a** in the presence of 4-bromobenzaldehyde (**4a**) under the catalysis of Fe(OTf)₃ (10 mol %). Inspiringly, the reaction in dichloromethane (CH₂Cl₂) at

Common approach to indoles:



Scheme 1. Possibilities for forming different fused tricyclic skeletons.

room temperature for 10 hours unexpectedly afforded the furanoquinoline **6a**, albeit in only 23% yield (Table 1, entry 1). It is surprising to observe that instead of undergoing the most favored 5-*endo* cyclization mode between the NH group of **3a** with the triple bond, **3a** first reacted with **4a** to produce **Int-2** (Scheme 1c). Subsequent bicyclization triggered the double *endo*-cyclization mode to afford **6a**, thus exhibiting reversed selectivity. Because of the importance of 1,2-dihydroquinoline derivatives,^[9–11] we then turned to optimizing the reaction conditions for the efficient formation of **6a**. FeCl₃ failed to execute such a transformation (Table 1, entry 2). Further catalyst screening showed that Sc(OTf)₃ was the best: the yield of **6a** was improved to 72% at 45°C with 5% recovery of **4a** (entries 3–10). The reaction at a higher concentration improved the yield further to 87% with a reaction time of 6.5 hours (entry 11). The yield of **6a** decreased dramatically when using 5 mol% of Sc(OTf)₃ (entry 12). Other solvents, such as THF, 1,4-dioxane, toluene, and 1,2-dichloroethane (DCE) did not deliver better results than CH₂Cl₂ (entries 13–16). An additive, such as 4 Å M.S. (M.S. = molecular sieves), did not improve the yield (entry 17). Thus, Sc(OTf)₃ (10 mol %) in CH₂Cl₂ at 45°C was defined as the optimal reaction conditions for further study.

The scope of the reaction was then investigated by using the optimal reaction conditions (Table 2). We first studied the bicyclization reaction of **3a** with different aldehydes (**4**). The groups *p*-Br, *p*-MeO, *m*-MeO, and *o*-I may be introduced to benzene ring of aldehydes, thus giving the corresponding products in decent yields (entries 1–4). The reaction worked

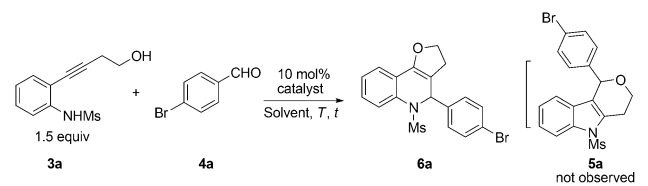
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Table 1: Optimization of the reaction conditions for the bicyclization of **3a** in the presence of **4a**.^[a]

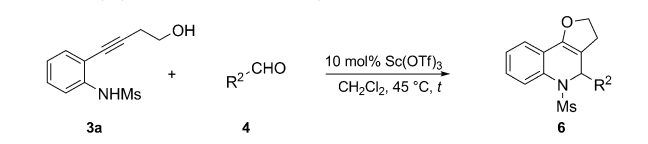


Entry	Catalyst	Solvent	T [°C]	t [h]	6a Yield [%] ^[b]	4a Recovery [%] ^[b]
1	Fe(OTf) ₃	CH ₂ Cl ₂	RT	10	23	45
2	FeCl ₃	CH ₂ Cl ₂	RT	10	—	71
3	In(OTf) ₃	CH ₂ Cl ₂	RT	10	19	59
4	Zn(OTf) ₃	CH ₂ Cl ₂	RT	10	—	91
5	Cu(OTf) ₂	CH ₂ Cl ₂	RT	10	—	92
6	Yb(OTf) ₃	CH ₂ Cl ₂	RT	10	—	93
7	Er(OTf) ₃	CH ₂ Cl ₂	RT	10	—	85
8	Pd(OAc) ₂	CH ₂ Cl ₂	RT	10	—	92
9	CuI	CH ₂ Cl ₂	RT	10	—	86
10	Sc(OTf) ₃	CH ₂ Cl ₂	45	10	72	5
11 ^[c]	Sc(OTf) ₃	CH ₂ Cl ₂	45	6.5	87	—
12 ^[c,d]	Sc(OTf) ₃	CH ₂ Cl ₂	45	6.5	30	55
13 ^[c]	Sc(OTf) ₃	THF	45	6.5	3	82
14 ^[c]	Sc(OTf) ₃	1,4-dioxane	45	6.5	12	57
15 ^[c]	Sc(OTf) ₃	toluene	45	6.5	20	41
16 ^[c]	Sc(OTf) ₃	DCE	45	6.5	39	25
17 ^[c,e]	Sc(OTf) ₃	CH ₂ Cl ₂	45	6.5	46	13

[a] The reaction was conducted at 45 °C CH₂Cl₂ with **4a** (*c* = 0.1 M) and **3a** (1.5 equiv) in the presence of Sc(OTf)₃ (10 mol %). [b] Determined by ¹H NMR analysis with CH₃NO₂ as the internal standard. [c] *c* = 0.2 M. [d] Sc(OTf)₃ (5 mol %) was used. [e] 4 Å molecular sieves (25.0 mg mL⁻¹) were added to the reaction. DCE = 1,2-dichloroethane, Ms = methanesulfonyl, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

equally well using benzaldehyde itself, thus producing **6e** in 70 % yield (entry 5). Heteroaryl-substituted aldehydes seem to be compatible under the reaction conditions: 2-thiophenecarboxaldehyde produced **6f** in 50 % yield (entry 6). It is

Table 2: Sc(OTf)₃-catalyzed one-pot synthesis of furanoquinolines **6** from *o*-alkynylaniline **3a** and aldehydes **4**.^[a]



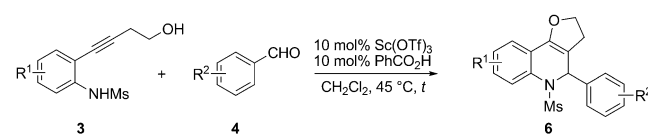
Entry	R ² (4)	t [h]	6 Yield [%] ^[b]
1	4-BrC ₆ H ₄ (4a)	6.5	80 (6a)
2	4-MeOC ₆ H ₄ (4b)	10	72 (6b)
3	3-MeOC ₆ H ₄ (4c)	4	53 (6c)
4 ^[c]	2-IC ₆ H ₄ (4d)	3.5	52 (6d)
5	Ph (4e)	4.5	70 (6e)
6	2-thienyl (4f)	16	50 (6f)
7	<i>t</i> Bu (4k)	18	64 (6r)
8	<i>c</i> Pr (4l)	14.5	30 (6s)

[a] The reaction was conducted at 45 °C in CH₂Cl₂ with the aldehyde **4** (*c* = 0.2 M) and **3a** (1.5 equiv) in the presence of Sc(OTf)₃ (10 mol %). [b] Yield of isolated product. [c] Yield of product isolated after chromatography on silica gel and then recrystallized from dichloromethane and petroleum ether.

observed that aliphatic aldehydes could also react with **3a** to give the corresponding products **6r** and **6s** in 64 and 30 % yield, respectively (entries 7 and 8).

Furthermore, for a class of aromatic aldehydes with electron-withdrawing groups such as *p*-NC, *p*-MeO₂C, *p*-Cl, and *m*-Br on the phenyl ring, PhCO₂H (10 mol %) together with Sc(OTf)₃ (10 mol %) was required to accelerate the reaction rate, thus affording **6g** (61 %), **6h** (60 %), **6i** (70 %), and **6j** (69 %), respectively (Table 3, entries 1–4). PhCO₂H probably helps to enhance the electrophilic capability of aldehydes, thus favoring the formation of the imine intermediates **Int-2** (Scheme 1 c).^[12] It is noteworthy that different substituents on the benzene ring of the *o*-alkynylanilines (**3**), such as fluoro and methoxy at the 4-position, turned out to be compatible under the reaction conditions, thus leading to the corresponding dihydroquinoline derivatives **6k** and **6l** in good yields (Table 3, entries 5 and 6).

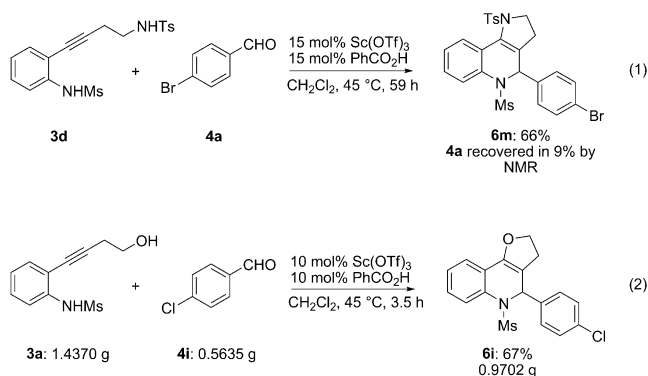
Table 3: Sc(OTf)₃/PhCO₂H cocatalyzed one-pot synthesis of furanoquinolines (**6**) from *o*-alkynylanilines (**3**) and aldehydes (**4**).^[a]



Entry	R ¹ (3)	R ² (4)	t [h]	6 Yield [%] ^[b]
1 ^[c,d]	H (3a)	4-NC (4g)	5.5	61 (6g)
2	H (3a)	4-MeO ₂ C (4h)	4	60 (6h)
3	H (3a)	4-Cl (4i)	3	70 (6i)
4	H (3a)	3-Br (4j)	2.5	69 (6j)
5 ^[e]	4-MeO (3b)	4-Br (4a)	34	80 (6k)
6	4-F (3c)	4-Br (4a)	7.5	73 (6l)

[a] The reaction was conducted at 45 °C in CH₂Cl₂ with the aldehyde **4** (*c* = 0.2 M) and **3** (1.5 equiv) in the presence of Sc(OTf)₃ (10 mol %) and PhCO₂H (10 mol %). [b] Yield of isolated product. [c] Yield of product isolated after chromatography on silica gel and then recrystallized from dichloromethane and petroleum ether. [d] Only 32 % yield of **6g** was obtained without the addition of PhCO₂H, while **4g** was recovered in 28 % yield. [e] The reaction was carried out without PhCO₂H.

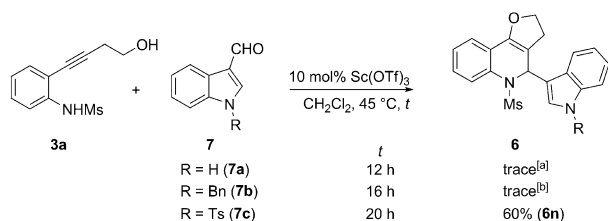
Further studies showed that the reaction worked equally well using NHTs as the nucleophilic unit (YH = NHTs), and the corresponding tricyclic dihydroquinoline derivative **6m** was obtained in 66 % yield [Eq. (1)]. Finally, it is easy to



conduct the reaction on a one gram scale to afford **6i** in 67 % yield [Eq. (2)].

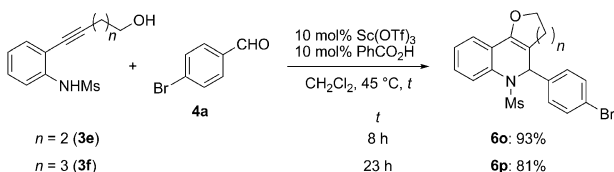
The ring-fused 1,2-dihydroquinoline structure of the products **6a–m** has been determined by the an X-ray single-crystal diffraction study of **6i** (see the Supporting Information).^[13]

Further studies showed that this bicyclization reaction of **3a** may also proceed with the *N*-Ts-substituted indole-3-carbaldehyde **7c**, while trace amounts of the corresponding products were formed from the non-protected **7a** and the *N*-Bn-substituted indole-3-carbaldehyde **7b** (Scheme 2).



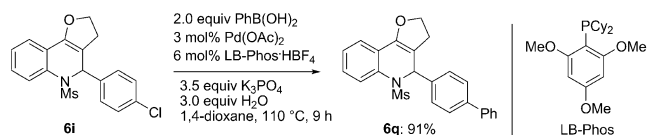
Scheme 2. Bicyclization reaction of the *o*-alkynylaniline **3a** with indole-3-carbaldehyde. [a] **7a** was recovered in 35 % as determined by ¹H NMR analysis. [b] **7b** was recovered in 84 % as determined by ¹H NMR analysis.

Six- and seven-membered oxacyclo-fused products may also be easily obtained under the standard reaction conditions, thus producing **6o** and **6p** in 93 and 81 % yield, respectively (Scheme 3).



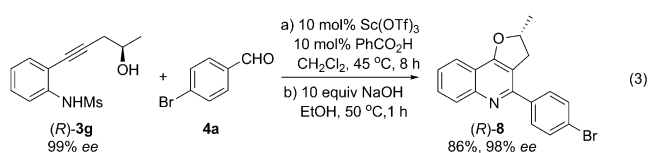
Scheme 3. Synthesis of six- and seven-membered ring-fused 1,2-dihydroquinolines.

The Suzuki coupling reaction of the 1,2-dihydroquinoline derivative **6i** with phenylboronic acid was realized using LB-Phos as the ligand, thus affording the cross-coupled product **6q** in excellent yield (Scheme 4).^[14]



Scheme 4. Synthetic application of **6i**.

Finally, when the optically active *o*-alkynylaniline (*R*)-**3g**, having a central chirality (99 % *ee*), was subjected to the standard reaction conditions followed by subsequent treatment with NaOH, the quinoline derivative (*R*)-**8** was obtained directly (86 % yield, 98 % *ee*) [Eq. (3)].^[15]



In conclusion, we have developed a Sc(OTf)₃-catalyzed tandem aza-Prins cyclization^[16] reaction of *o*-alkynylanilines (**3**) with aldehydes (**4**) to construct fused tricyclic derivatives with a potentially useful 1,2-dihydroquinoline unit under mild reaction conditions. Considering the common knowledge that nucleophilicity of the NH group is stronger than that of the OH group in the substrates of the type **3**, the formation of indole-containing derivatives (**5**) should be, in principle, much more favorable. However, the reversed selectivity on the highly chemoselective formation of the 1,2-dihydroquinoline derivatives **6** was observed. In view of the mild reaction conditions and decent functional-group tolerance, this type of transformation may be useful in organic synthesis and medicinal chemistry. Further studies, including mechanistic studies and asymmetric variants of such cyclization reactions, are currently under way in our laboratory.

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