Regioselective Synthesis of Annulated Quinoline and Pyridine Derivatives by Silver-Catalyzed 6-*endo*-dig Cycloisomerization

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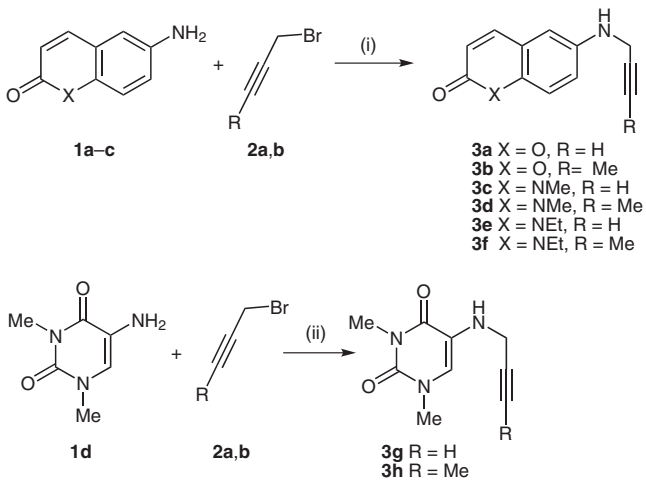
Abstract: 3*H*-pyrano[3,2-*f*]quinoline-3-one, 4-methyl-4,7-phenanthrolin-3(4*H*)-one, and 1,3-dimethylpyrido[3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-dione derivatives have been synthesized by hitherto unreported silver-catalyzed 6-*endo*-dig mode of cycloisomerization from various N-propargylated heterocyclic compounds. The silver-catalyzed reaction provides the synthesis of potential bioactive compounds in excellent yields.

Key words: 3*H*-pyrano[3,2-*f*]quinoline-3-one, 4-methyl-4,7-phenanthrolin-3(4*H*)-one, 1,3-dimethylpyrido[3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-dione, $AgSbF_6$, cycloisomerization, 6-*endo*-dig

There is flurry of activities on the synthesis of quinoline and its annulated derivatives due to their broad spectrum of biological profiles, which includes antialergic, antidiabetic, antimicrobial, analgesic, insecticidal, antifungal, antipyretic, tyrosine kinase inhibition, and also cytotoxic properties.[1] Due to these bioactivities quinoline derivatives are widely used in pharmaceutical and agrochemical sectors, besides these derivatives are also used as functional materials.[2] The quinoline derivatives have gained considerable attention due to their central role as building blocks in the synthesis of natural products.[3] On the other hand natural products possessing coumarin, quinolone, and uracil subunits show wide range of bioactivity.[4] There are many alkaloids which contain pyrido-coumarin, pyrido-quinolone skeleton, due to the presence of these cores the alkaloids are also bioactive.[5] Some examples of natural products are dutadrupine, helietidine, geibalansine, and amphimedine.[6] Moreover bioactivity of pyrido-pyrimidines are well known,[7] besides their antibacterial and antiallergic properties they also inhibit enzyme adenosine kinase (AK) and dihydrofolate reductase (DHFR).[8] Recently, it has been found that substituted pyridines efficiently inhibit HMG-CoA reductase and cholesterol transport proteins.[9]

Traditional approaches[10] have frequently been employed for the synthesis of quinoline ring system in the total synthesis of quinoline based alkaloids. However, all these reactions usually require harsh conditions, tedious reaction procedure, or give poor yield. Over the last two decades, there has been growing interest for the development of syntheses of quinoline derivatives, which include radical reaction,[11] iodine-mediated cyclization,[12] and metal-catalyzed reaction.[13] Nevertheless, these are improvements over traditional methods. However, these methods also have some limitations. Some methods are not environmentally benign in terms of toxicity,[11,12] some are time consuming processes or having different byproducts.[13] A thorough search of literature reveals that there are a few examples of activated gold- and copper-catalyzed cycloisomerization reactions to afford substituted pyridine and quinoline derivatives.[14] To our knowledge, there is no such report for the synthesis of bioactive pyridocoumarin or pyridoquinolone or pyridopyrimidine solely by silver-catalyzed reaction. This prompted us to undertake a study to develop a methodology for the synthesis of these heterocycles. We report here the results of our investigation.

The required precursors **3a–f** were prepared in high yields by the reaction of **1a–c** with propargyl bromides **2a**,**b** in the presence of anhydrous potassium carbonate in refluxing acetone for five hours and the precursors **3g**,**h** were prepared by the reaction of 5-amino-1,3-dimethyl uracil **1d** and **2a**,**b** in dry acetonitrile at room temperature for seven hours (Scheme 1).



Scheme 1 *Reagents and conditions*: (i) anhyd K_2CO_3, dry acetone, reflux for 5 h; (ii) anhyd K_2CO_3 (1 equiv), dry MeCN, r.t., stirred for 7 h.

The substrate **3a**, when subjected to cycloisomerization in the presence of $AgSbF_6$ (0.1 equiv) in DMSO at 110 °C[15] for 45 minutes, gave the product **4a**[16] in 98% yield. The optimized conditions for this cycloisomerization were established through a series of experiments, in which sequential changes were made in catalyst, amount of cat-

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alyst, and also solvent used for the reaction of the substrate **3a** (Table 1).

To optimize the reaction conditions we have used various metal catalysts. Among the catalysts used, the $AuCl_3$ in DMSO (entry 4) gave very poor yield of the product. However, when the reaction was carried out with equal mol% of $AuCl_3$ and $AgSbF_6$ (10 mol% of each catalyst) gave excellent yield (96%) both in DMSO and acetic acid as a solvent (entries 5 and 6). There are reports[14a,b,d] where this high yield has been explained by the activation of gold catalyst in the presence of the silver salt, but whenever the reaction was carried out solely in the presence of $AgSbF_6$ in DMSO, we observed a reasonably good yield (entry 1) compared to the mixed catalyst.[17]

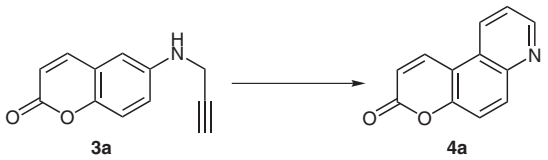
Among different solvents used DMSO and acetic acid both gave better results but we have chosen DMSO as an optimized solvent as it is milder than acetic acid. We have also carried out this reaction with another coinage metal-based (copper) catalyst (entries 13–15). In the case of Cu(I) we obtained very poor yield, but Cu(II) gave a comparatively good result. A series of Lewis acid catalysts were investigated (entries 17–20) but none of them provided a good result. It is also noticeable that another silver species $AgNO_3$ (entry 16) gave a better result under the same conditions. Toste reported[18] that over 80 °C coinage metal catalyst are not that stable and produce related Brønsted acid. We have carried out the reaction at room temperature for five hours to give 60% yield of the product (entry 2). The same reaction has also been conducted at 80 °C for one hour to give 75% yield (entry 3). Moreover, the reaction in DMSO at 110 °C for four hours with catalytic amount of HCl, H_2SO_4, and TfOH (entries 21–23) failed to give any product, only the starting material was recovered. Variation of the catalyst and solvent showed that in DMSO solvent 10 mol% $AgSbF_6$ at 110 °C provides best result. The optimized reaction conditions were used to examine the cycloisomerization of the other N-propargyl amines (**3b**–**h**). The results are summarized in Table 2.

Treatment of **3b** with 10 mol% $AgSbF_6$ in DMSO at 110 °C for 45 minutes afforded the product **4b** in 97% yield. Similarly, compound **3c** furnished product **4c** in 98% yield. When the same reactions were carried out with **3d** and **3e** products **4d**[19] and **4e** were obtained in 96% and 93% yields, respectively, after 45 minutes. Similarly, the product **4f** was obtained in 96% yield when the reaction was carried out with **3f** for 45 minutes. Under the similar reaction conditions substrates **3g** and **3h** afforded products **4g** and **4h** in 89% and 94% yields, respectively, after one hour. The products were characterized from their spectroscopic data.

Using the optimized conditions, we next explored the scope and generality of the silver-catalyzed cycloisomerization reaction by carrying out this reaction with N-propargylated aniline (Scheme 2).

The precursors **6a**,**b** were prepared by the reaction of aniline (**5**) with propargyl bromides **2a**,**b** in the presence of anhydrous potassium carbonate and dry acetonitrile at room temperature for seven hours. When the substrate **6a** was subjected to cycloisomerization in the presence of 10 mol% $AgSbF_6$ in DMSO at 110 °C for one hour the product **7a**[20a] was obtained in 84% yield. Similarly, substrate **6b** afforded the product **7b**[20b] in 88% yield.

Table 1 Optimization of Cycloisomerization of Compound **3a**

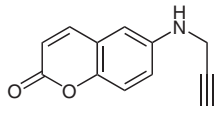
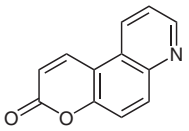
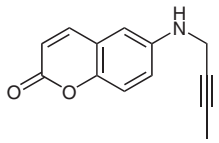
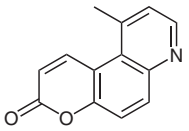
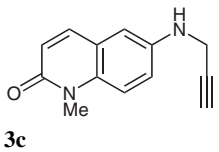
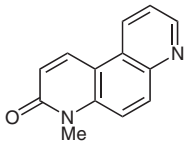
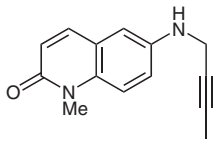
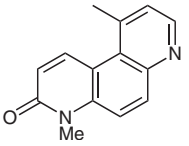
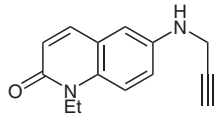
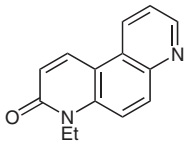
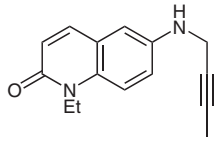
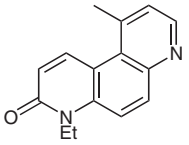
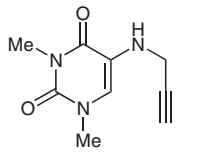
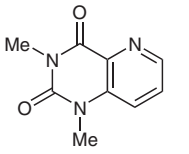
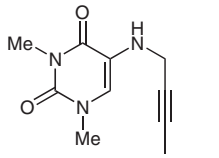
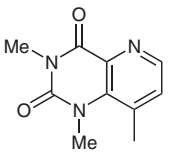


3a **4a**

Entry	Catalyst[a]	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	$AgSbF_6$	DMSO	110	0.75	98
2	$AgSbF_6$	DMSO	r.t.	5	60
3	$AgSbF_6$	DMSO	80	1	75
4	$AuCl_3$	DMSO	110	4	5
5	$AuCl_3$·$AgSbF_6$[c]	DMSO	110	1	96
6	$AuCl_3$·$AgSbF_6$[c]	AcOH	100	1	96
7	$AgSbF_6$	AcOH	100	1	96
8	$AuCl_3$	AcOH	100	5	–
9	$AgSbF_6$	MeCN	reflux	4	98
10	$AgSbF_6$	MeOH	reflux	4	72
11	$AgSbF_6$	toluene	110	7	68
12	$AgSbF_6$	CH_2Cl_2	reflux	6	45
13	CuI	DMSO	110	6	15
14	$Cu(OAc)_2$	DMSO	110	3.5	82
15	$CuSO_4$·$5H_2O$	DMSO	110	4	68
16	$AgNO_3$	DMSO	110	5	64
17	$ZnCl_2$	DMSO	110	12	21
18	$NiCl_2$·$2H_2O$	DMSO	110	14	18
19	$FeCl_3$	DMSO	110	12	7
20	$AlCl_3$	DMSO	110	12	15
21	HCl	DMSO	110	4	–
22	H_2SO_4	DMSO	110	4	–
23	TfOH	DMSO	110	4	–

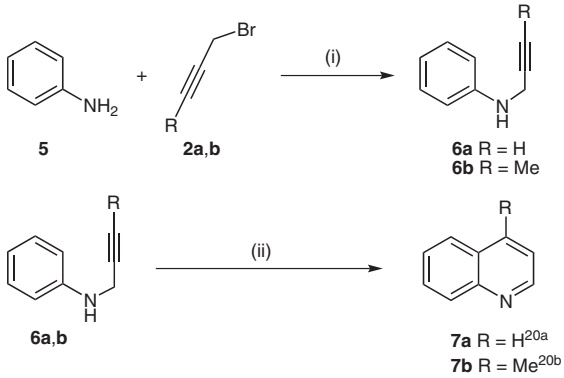
[a] Reactions (enries 1–20) were carried out with **3a** (1 equiv) and catalyst (0.1 equiv). Reactions (entries 21–23) were carried out in the presence of a catalytic amount of the Brønsted acid.
[b] Isolated yield,
[c] Conditions: 0.1 equiv each of both catalyst were used.

Table 2 Cycloisomerization of **3a–h**

Entry	Starting material **3**	Products **4**	Time (min)	Yield (%)[a]
1	 **3a**	 **4a**[16]	45	98
2	 **3b**	 **4b**	45	97
3	 **3c**	 **4c**	45	98
4	 **3d**	 **4d**[19]	45	96
5	 **3e**	 **4e**	45	93
6	 **3f**	 **4f**	45	96
7	 **3g**[13c]	 **4g**[13c]	60	89
8	 **3h**	 **4h**	60	94

[a] Isolated yields.

Recently, Kuninobu et al.[14b] have reported the synthesis of quinoline derivatives from various N-propynyl anilines by the treatment of catalytic amount of silver triflate and copper(I) chloride or gold (I) chloride in dichloroethane at 80 °C for 24 hours. In this respect, our reaction is interesting as we have achieved quinoline derivatives in the absence of any co-catalyst like CuCl or AuCl and the reaction time is also shorter. There are also reports of metal-catalyzed synthesis of quinoline and pyridine derivatives where costly gold catalyst is used as catalyst.[14] It is pertinent to mention that Hon et al.[16] have recently reported the synthesis of 3*H*-pyrano[3,2-*f*]quinoline-3-one (**4a**) in low yield through a multistep process.

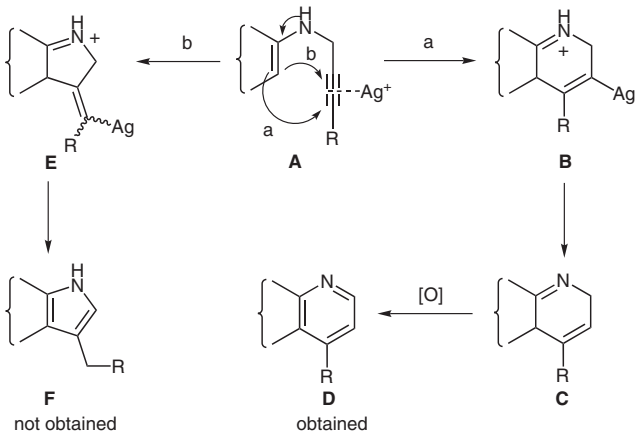


Scheme 2 *Reagents and conditions*: (i) K_2CO_3, dry MeCN, r.t. (ii) $AgSbF_6$ (10 mol%), DMSO, 110 °C.

From the results shown in Table 2 and Scheme 2 it is observed that the reaction shows high regioselectivity, only six-membered quinoline derivatives are obtained (Scheme 3). Therefore, the reaction proceeds via 6-*endo*-dig mode of cyclization (i.e., path a) and not via 5-*exo*-dig cyclization (i.e., path b). On the basis of the above results, the formation of the products can be rationalized (path a). Initially a π-complex **A** may be formed between the alkyne moiety and silver cation. The lone pair of the nitrogen atom assists the conjugated double bond to attack regioselectively at the complex segment via 6-*endo*-dig mode of cyclization leading to the intermediate **B**. The cyclized intermediate **B** then may lose H^+ and silver ion to give the intermediate **C**, which on aromatization may afford the pyridine (quinoline) skeleton **D**. We have also carried out the reaction by protecting the NH of the substrate **3a** with tosyl/methyl group, but in these cases the reactions did not occur. Regioselective formation of the angular pyridocoumarins and pyridoquinolones **4a–f** instead of the linear pyridocoumarins and pyridoquinolones may be rationalized by the greater reactivity of the 5-position than that of the 7-position of the respective heterocyclic system.

Here we have developed a new straightforward methodology for the regioselective synthesis of bioactive molecules exclusively by 6-*endo*-dig cyclization followed by aromatization with the use of a silver catalyst. Silver catalyst is usually applied to activate the gold catalyst for this type of cycloisomerization,[14a,b] To our knowledge the efficacy of the $AgSbF_6$ individually as a catalyst for this type of cycloisomerization has not been examined.[14a,b,d] Moreover, the silver-catalyzed reaction has received less attention.[17,21]

In conclusion, we have developed a novel and efficient method for the regioselective synthesis of 3*H*-pyrano[3,2-



Scheme 3 Proposed mechanism of cycloisomerization

f]quinoline-3-one, 4-methyl-4,7-phenanthrolin-3(4*H*)-one, and 1,3-dimethylpyrido[3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-dione derivatives from various N-propargylated heterocyclic substrates by solely silver-catalyzed 6-*endo*-dig mode of cycloisomerization followed by aromatization. The reaction proceeds smoothly and provides excellent yield of the product.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(19) **Synthesis of 4,10-Dimethyl-4,7-phenanthrolin-3 (4*H*)-one (4d)**
To a stirred solution of $AgSbF_6$ (7.6 mg, 0.022 mmol) in DMSO (5 mL), 6-(but-2-ynylamino)-1-methylquinolin-2 (1*H*)-one (**3d**, 50 mg, 0.22 mmol) was added at r.t. and stirred at 110 °C for 45 min to complete the reaction (as monitored by TLC). The light green colored reaction mixture was cooled and neutralized with sat. $NaHCO_3$ solution. This was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extract was washed with brine and dried over (Na_2SO_4). The solvent was distilled off. The resulting crude product was purified by column chromatography over silica gel (60–120 mesh) using PE–EtOAc mixture (3:2) as an eluent to give the product **4d**. Yield 96%, yellow solid, mp 172 °C. IR (KBr): 1646, 1561 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (s, 3 H, CH_3), 3.88 (s, 3 H, NCH_3), 6.81 (d, 1 H, *J* = 10.0 Hz, C_3H of quinolone), 7.34 (d, 1 H, *J* = 4.4 Hz, ArH), 7.77 (d, 1 H, *J* = 9.6 Hz, ArH), 8.22 (d, 1 H, *J* = 9.2 Hz, ArH), 8.72 (d, 2 H, *J* = 10.0 Hz, C_4H of quinolone and ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4, 30.6, 115.6, 117.9, 119.7, 125.8, 126.5, 134.2, 136.9, 140.4, 143.3, 145.4, 148.6, 161.5. HRMS: *m/z* calcd for $C_{14}H_{12}N_2O$ [M + H]: 225.1016; found: 225.1022.

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