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One-Pot Synthesis of Quinoline Derivatives Directly from Terminal Alkynes *via* Sequential Ruthenium(II) and Acid Catalysis

Min Zhang,[a,b,*] Thierry Roisnel,[c] and Pierre H. Dixneuf[c,*]

[a] School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi, Jiangsu Province 214122, People's Republic of China
E-mail: zm31289@yahoo.com.cn
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
[c] Institut Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes1, Campus de Beaulieu, 35042 Rennes, France
Fax: (+33)-22-2323-6939; e-mail: pierre.dixneuf@univ-rennes1.fr

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Abstract: A convenient one-pot synthesis of 2,3-disubstituted, 2,3,6-trisubstituted, and 2,3,6,7-tetrasubstituted quinoline analogues from terminal alkynes *via* sequential ruthenium(II) and *para*-toluenesulfonic acid (*p*-TSA) co-catalyzed reactions is described. The catalytic process is shown to take place first *via* intermediate formation of an allyl ketone and then addition of an aniline derivative to the allyl ketone. The *p*-TSA is a catalyst for both allyl ketone and quinoline synthetic steps. The method allowed us to synthesize a wide range of quinoline derivatives and introduce different substituents by employing various simple starting materials. The reaction allows the synthesis of halogen-containing products.

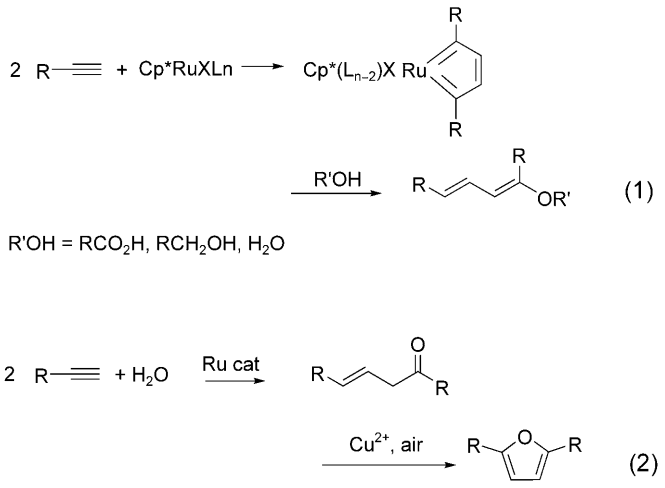
Keywords: alkynes; allyl ketones; anilines; quinolines; ruthenium; sequential catalysis

Quinolines and their analogues represent a very important class of nitrogen-containing heterocycles, as the quinoline scaffold is present in both various biologically active compounds and useful functionalized molecular materials. Applications of quinolines in medicinal chemistry include their use as antimalarial,[1] antileishmanial,[2] anti-inflammatory,[3] antiasthmatic,[4] antibacterial,[5] antihypertensive,[6] tyrosine kinase inhibitory agents,[7] histamine H_3 receptor inverse agonists[8] and for the treatment of estrogen-dependent diseases.[9] Quinoline-based polymers have been produced for applications as thermally stable transparent materials in the fields of electronics, optoelectronics and non-linear optics.[10] Sugar-quinoline fluorescent chemosensors can be used for selective detection of Hg^{2+} ions in water.[11]

The conventional synthetic methods for quinoline derivatives such as the Skraup,[12] Friedlander,[13] and Combes reactions[14] were reported as early as the end of the 19th century. In the past decade, remarkable new protocols have brought about a new access to functional quinolines. They involve, for example, the cyclization of *ortho*-alkynylanilines,[15] *ortho*-propargylanilines[16] or *ortho*-azido-containing derivatives,[17] multicomponent coupling reactions[18], imine Diels–Alder reactions[19], the condensation-cyclization from *ortho*-haloacetophenones[20] and sequential cyclization *via* Baylis–Hillman adduct intermediates.[21] These recent methods are not always satisfactory due to the not readily available starting materials or the requirement of multiple steps. However, there is still a continuous interest to discover direct quinoline syntheses from readily available starting materials under mild conditions.

Previous work on head-to-head oxidative coupling of alkynes at a Cp*Ru(II) moiety have led to the catalytic formation of dienes *via* proton and oxygen nucleophile addition at the 1,4-positions of the resulting biscarbene intermediate [Eq. (1)], by addition of carboxylic acids generating dienyl esters,[22] alcohols leading to dienyl ethers[23] and water to generate allylic ketones.[24].

The latter allylic ketones are the precursors of the Cu(II)-catalyzed formation of furans [Eq. (2)].[23] This

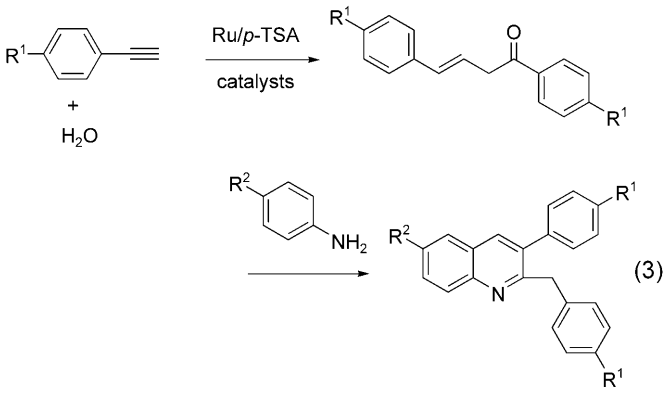


(1)

(2)

catalytic transformation of allyl ketones into furans led us to study the formation of nitrogen-containing heterocycles from alkynes *via* their sequential catalytic transformations.

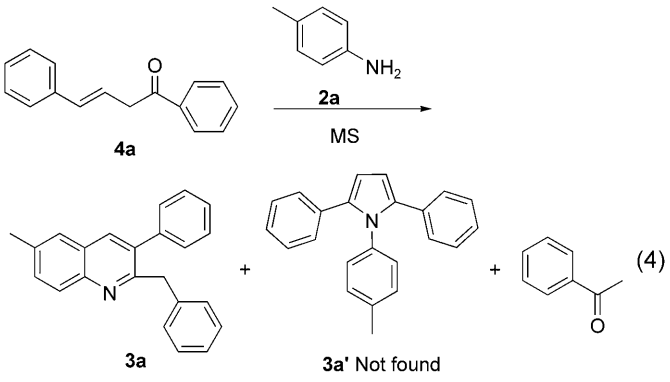
Herein, we now wish to report the new one-pot sequential ruthenium $Cp^*Ru(NCMe)_3^+BF_4^-$ and *para*-toluenesulfonic acid (*p*-TSA) catalyzed synthesis of 2-substituted 3-arylquinolines directly from terminal alkynes and aniline derivatives [Eq. (3)].



(3)

The reaction of an allyl ketone **4a** with *p*-toluidine in the presence of molecular sieves to generate the imine and of Cu^{2+} salt with air to afford the 2,5-disubstituted pyrrole, an analogue of furan, was studied first. In that case, a mixture of the corresponding furan, pyrrole **3a′** and quinoline **3a** was formed, each of them in a small amount. However, when the same reaction was performed in the presence of molecular sieves (MS) but without Cu^{2+} salt, the pyrrole was no longer formed and the 2-benzyl-3-phenylquinoline product **3a** and acetophenone were obtained [Eq. (4)].

We then evaluated the influence of *p*-TSA acid and $Cp^*Ru(MeCN)_3^+PF_6^-$ catalysts and temperature on this reaction in the absence of Cu(II) salt, by using the allylic ketone **4a** and *p*-toluidine **2a** with molecular sieves. The results leading to the formation of **3a** are reported in Table 1.



(4)

Table 1. Influence of *p*-TSA, ruthenium catalyst and temperature on the formation of quinoline **3a** from allyl ketone **4a**.[a]

Entry	Catalyst	*T* [°C]	Yield [%] of **3a**[b]
1	*p*-TSA (30 mol%)	120	65
2	*p*-TSA (30 mol%)	100	83
3	*p*-TSA (30 mol%)	90	31
4	$Cp^*Ru(MeCN)_3^+PF_6^-$ (8 mol%)	100	–
5	*p*-TSA (30 mol%) and $Cp^*Ru(MeCN)_3^+PF_6^-$ (8 mol%)	100	81

[a] Reaction performed in a closed Schlenk tube: the mixture of 1 mmol of **4a**, 0.6 mmol of *p*-toluidine **2a** with molecular sieves in 2 mL of dioxane was stirred at 90–120 °C for 6 h.

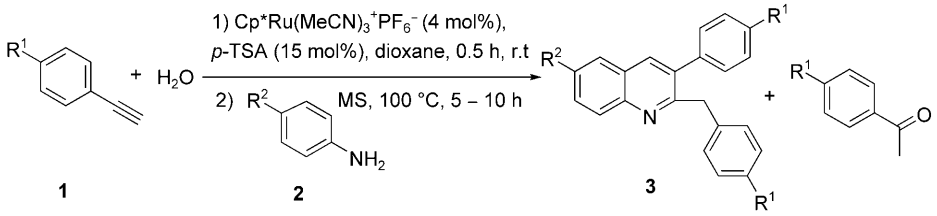
[b] GC yields based on **4a**.

When the reaction mixture was stirred at 120 °C, 100 °C, 90 °C for 5 h in the presence of 30 mol% of *p*-TSA catalyst alone in dioxane, the quinoline **3a** was formed in 65%, 83%, 31% GC yields, respectively. Thus, a temperature of 100 °C was more suitable for this transformation (Table 1, entries 1, 2 and 3). The utilization of 8 mol% of $Cp^*Ru(MeCN)_3^+PF_6^-$ catalyst alone in the absence of acid at 100 °C for 5 h did not produce the desired product (Table 1, entry 4). The combination of 8 mol% $Cp^*Ru(MeCN)_3^+PF_6^-$ and 30 mol% *para*-toluenesulfonic acid (*p*-TSA) catalysts resulted in similar result as with the use of 30 mol% *para*-toluenesulfonic acid (*p*-TSA) catalyst alone at 100 °C for 5 h (Table 3, entries 2 and 5). This observation proved that the real catalyst for the transformation of allyl ketones into quinoline was *para*-toluenesulfonic acid itself and not the ruthenium catalyst.

After having found the best conditions for the formation of **3a** without any negative influence of $Cp^*Ru(MeCN)_3^+PF_6^-$, we have attempted the synthesis of quinolines directly from alkynes by sequential catalytic reactions, *via* the formation of *in situ* generated allyl ketones. Thus, after the co-catalyzed formation of allyl ketone **4a** from terminal alkyne **1a** (1 mmol) and water in the presence of $Cp^*Ru(NCMe)_3^+PF_6^-$ (4 mol%) and *p*-TSA (15 mol%), aniline derivative **2a** (0.3 mmol) and molecular sieves were added and the catalytic mixture was heated at 100 °C for 6 h. The quinoline **3a** was isolated in 39% yield with respect to the alkyne, and 78% yield with respect to the aniline, as the formation of methyl aryl ketone was also observed (Table 2, entry 1). It is noteworthy that the initially introduced *p*-TSA (15 mol% with respect to alkyne and 30 mol% with respect to the *in situ* formed allyl ketone) promotes the formation of both allyl ketone and then quinoline.

The scope of this reaction was then investigated. A series of commercially available terminal arylacetylenes **1** and the aromatic primary amines **2** were employed to evaluate the substrate scope (Table 2). 1 mmol of arylacetylene **1** was used to give the allyl ketone, after completion of the reaction after 0.5 h, the aromatic primary amine **2** (0.3 mmol) was then added with molecular sieves and the mixture was heated at 100 °C for 5–24 h. All the reactions proceeded smoothly in a closed Schlenk tube and provided the 2,3-disubstituted and 2,3,6-trisubstituted quinoline

Table 2. Sequential ruthenium and acid co-catalyzed synthesis of substituted quinolines directly from terminal alkynes.[a]



2a: $R^2 = CH_3$; **2b**: $R^2 = OCH_3$; **2c**: $R^2 = H$;
2d: $R^2 = Cl$; **2e**: $R^2 = Br$;

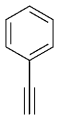
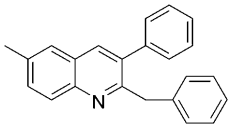
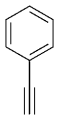
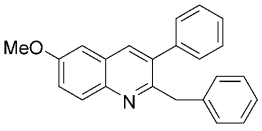
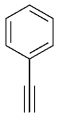
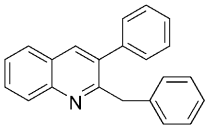
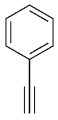
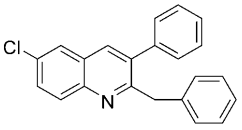
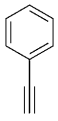
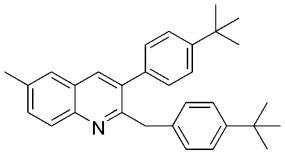
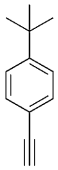
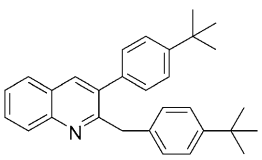
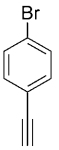
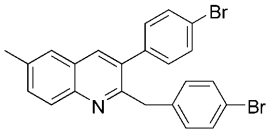
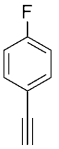
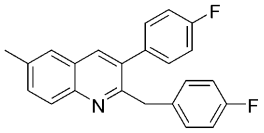
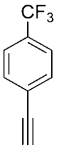
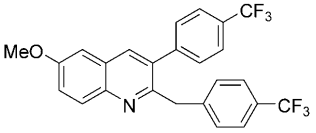
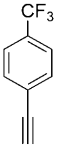
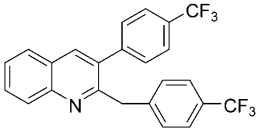
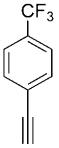
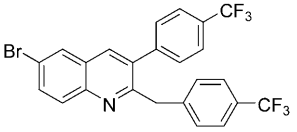
Entry	1		2	Time [h][b]	Quinoline 3		Yield [%]
1	**1a**		**2a**	6	**3a**		78,[b] 39[c]
2	**1a**		**2b**	5	**3b**		84[b]
3	**1a**		**2c**	10	**3c**		72[b]
4	**1a**		**2d**	24	**3d**		54[b]
5	**1b**		**2a**	6	**3e**		78[b]
6	**1b**		**2c**	10	**3f**		62[b]

Table 2. (Continued)

Entry	1	2	Time [h][b]	Quinoline 3	Yield [%]
7	**1c** 	**2a**	6	**3g** 	72[b]
8	**1d** 	**2a**	5	**3h** 	82[b]
9	**1e** 	**2b**	5	**3i** 	86[b]
10	**1e** 	**2c**	5	**3j** 	86[b]
11	**1e** 	**2e**	10	**3k** 	60[b]

[a] Reaction performed in a closed Schlenk tube: the mixture of 1 mmol of **1** and 1 mmol of H_2O with 0.04 mmol of RuCp*-$(NCMe)_3^+PF_6^-$ catalyst (4 mol% based on alkyne and 13 mol% on aniline) and 0.15 mmol *p*-TSA.H_2O (15 mol% based on alkyne and 50 mol% on aniline) in 2 mL of dioxane was stirred at room temperature for 0.5 h, then molecular sieves and 0.3 mmol aniline derivatives were added, the resulting mixture was stirred at 100 °C for 5–24 h.

[b] Isolated yields based on anilines.

[c] Isolated yields based on alkynes.

derivatives (Table 2, entries 1–11). We observed that the electronic influence of substituents on the arylacetylenes **1** did not affect too much the formation of quinolines. However, the influence of substituents on the aromatic primary amines **2** is quite effective for the transformation. The aromatic amines bearing electron-donating substituents such as CH_3, OCH_3 groups favored the reaction (Table 2, entries 1, 2, 5, 7, 8 and 9), for example, the *p*-toluidine **2a** and anisidine **2b** needed relatively shorter reaction times and provided relatively higher yields, while the use of 4-chlorobenzenamine **2d** and 4-bromobenzenamine **2e** afforded relatively lower yields of **3d** and **3k** (Table 2, entries 4 and 11). As the products tolerate aryl halides (Table 2, entries 4, 7, 8 and 11), the method has the potential to provide access for further functionalization *via* classical cross-coupling reactions.

The nature of the 2,3-disubstituted quinolines **3**, with the benzyl group linked to carbon 2, was established by NMR experiments, and then confirmed by the X-ray crystal diffraction of derivative **3g**. (Figure 1).[25]

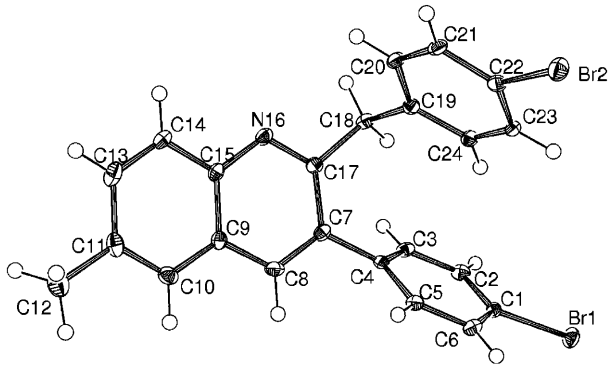
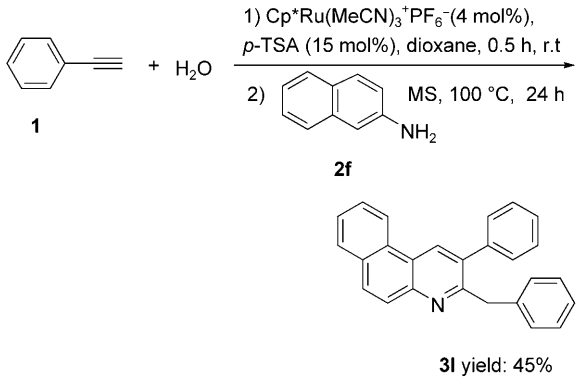


Figure 1. The X-ray structure of quinoline **3g**.

The reaction of 2-naphylamine **2f** with phenylacetylene led only to one regioisomer **3l** isolated in 45% yield with respect to the alkyne, corresponding at the expected selective reactivity of the α-carbon [Eq. (5)].

The substrate scope of aniline derivative **2g** was then investigated to evaluate the regioselectivity of

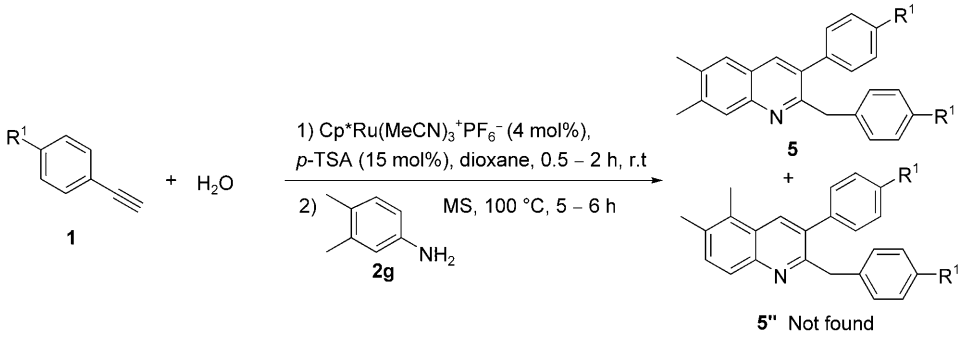


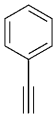
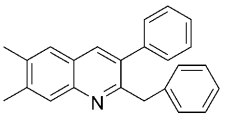
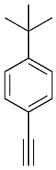
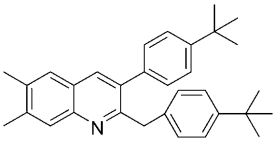
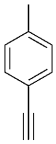
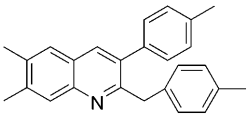
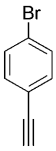
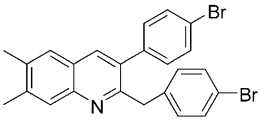
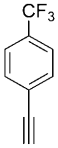
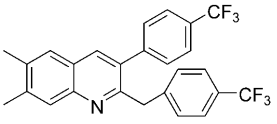
(5)

the reaction which can lead to two possible regioisomers **5** and **5″**. The results showed that only one regioisomer **5** was formed, the 2,3,6,7-tetrasubstituted quinoline derivatives **5a–5e** (Table 3, entries 1–5).

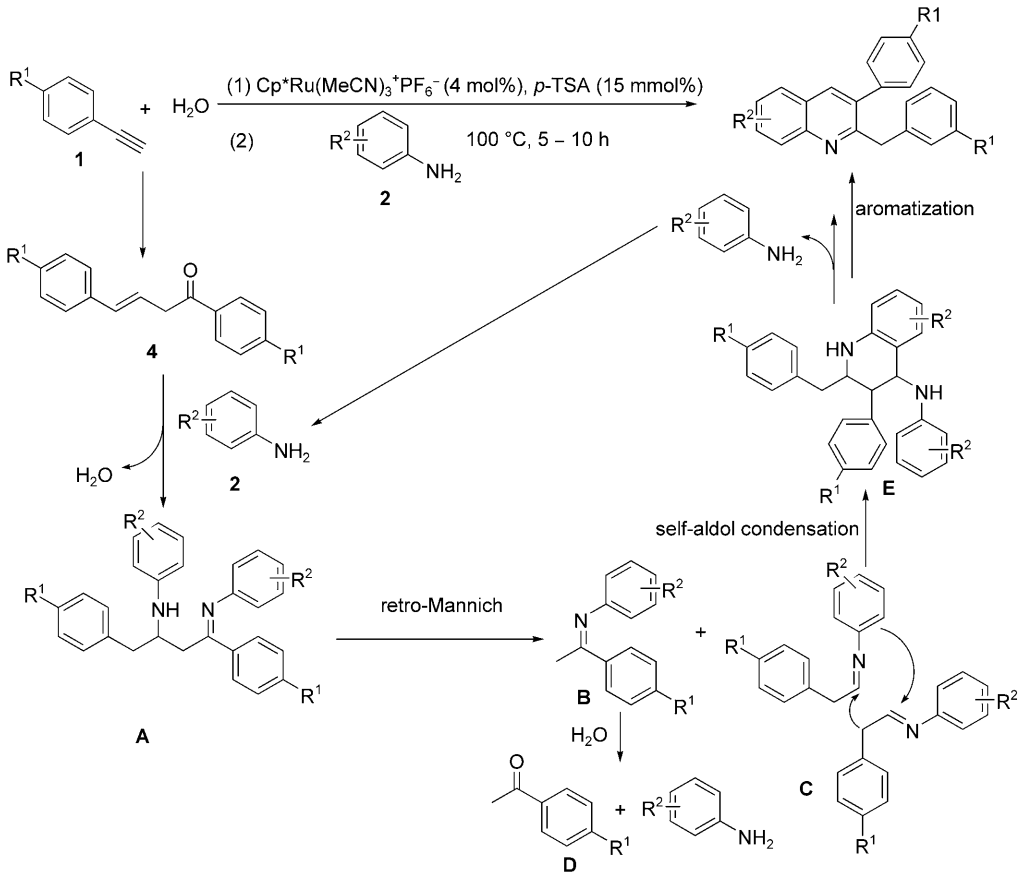
It is to be noted that the quinoline yield never exceed 50% with respect to the alkyne and, besides the formation of the quinoline **3**, that the formation of the aryl ketone, arising from water addition to the arylacetylene, is always observed. This indicates that all the alkyne is not incorporated into the quinoline and that the allyl ketone is fragmented [Eq. (4)]. Thus the mechanism of the quinoline formation is

Table 3. Regioselective synthesis of quinolines directly from terminal alkynes.[a]



Entry	**1**		Time [h]	Quinoline **5**		Yield [%]
1	**1a**		6	**5a**		80%,[b] 40[c]
2	**1b**		5	**5b**		68[b]
3	**1f**		5	**5c**		62[b]
4	**1c**		5	**5d**		74[b]
5	**1e**		5	**5e**		78[b]

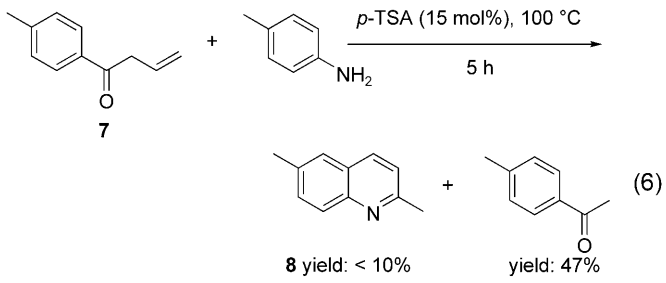
[a] Reaction performed in closed Schlenk tube: The mixture of 1 mmol of **1** and 1 mmol of H_2O with 0.04 mmol of RuCp*-$(NCMe)_3^+PF_6^-$ catalyst and 0.15 mmol *p*-TSA.H_2O in 2 mL of dioxane was stirred at room temperature for 0.5; then molecular sieves and 0.3 mmol 3,4-dimethylbenzenamine was added, the resulting mixture was stirred at 100 °C for 5–6 h.
[b] Isolated yields based on anilines.
[c] Isolated yields based on alkynes.



Scheme 1. Proposed mechanism for quinoline derivative formation directly from terminal alkynes.

likely to take place as shown in Scheme 1. The allyl ketone **4** is first generated starting from arylacetylene and water with the cooperative action of Cp*Ru-$(MeCN)_3^+PF_6^-$ and *p*-TSA catalysts.[23,24] The condensation and aza-Michael addition of the aniline derivative with the allyl ketone **4** result in the formation of ketimine **A**. The *p*-TSA-catalyzed retro-Mannich type fragmentation is expected to produce the ketimine **B** (giving the methyl aryl ketone **D** on hydrolysis) and the imine **C**. The more reactive imine **C** should undergo a self-aldol condensation and *o*-carbon nucleophilic addition to the imine moiety to generate tetrahydroquinoline intermediate **E**, and the quinoline is finally formed by aniline elimination and aromatization.

To support this mechanism the 1-*para*-tolylbut-3-en-1-one **7** which contains differently substituted carbons 1 and 4, was reacted with *p*-toluidine in the presence of *p*-TSA. The 2,6-dimethylquinoline **8** and 1-*p*-tolylethanone were produced and this formation is consistent with a retro-Mannich fragmentation [Eq. (6)].[26,27]



This experiment and mechanism explain that, in the formation of quinoline **3** from terminal alkyne **1**, water and *p*-TSA, only one molecule of alkyne is transformed into quinoline. This sequential ruthenium and *p*-TSA-catalyzed formation of quinoline from terminal alkynes is a new method to produce quinolines *via* allyl ketone intermediates, but does not constitute an atom-economic reaction as the loss of one alkyne skeleton is observed.

In conclusion, we have established a convenient one-pot synthesis of 2,3-disubstituted, 2,3,6-trisubstituted, and 2,3,6,7-tetrasubstituted quinoline analogues simply from terminal alkynes *via* sequential a ruthenium(II) and *p*-TSA co-catalyzed processes. The reaction is shown to take place *via* intermediate formation

of allyl ketones. The acid *p*-TSA is a catalyst for both allyl ketone and quinoline synthetic steps. The method allowed us to synthesize a wide range of quinoline derivatives and introduce different substituents by simply changing the starting materials, the alkyne and aniline derivatives. The obtained products with a halide substituent have the potential for further functionalization.

Experimental Section

Typical Procedure

In a Schlenk tube equipped with a magnetic stirring bar, the catalyst $RuCp^*(NCMe)_3^+PF_6^-$ (0.04 mmol, 20 mg), and *para*-toluenesulfonic acid monohydrate (*p*-TSA·H_2O) (0.15 mmol, 28.5 mg) were introduced and then dissolved in 2 mL of dioxane. Water (1 mmol, 18 mg) and phenylacetylene (1 mmol, 102 mg) were added successively and the resulting mixture was stirred under argon protection at room temperature for 0.5 hour. TLC indicated the completion of the reaction. Then activated molecular sieves (200 mg) and *p*-toluidine (0.3 mmol, 32 mg) were added, the resulting mixture was put in an oil bath at 100 °C for 6 h. After cooling down to room temperature, the resulting mixture was directly filtered through a pad of silica, washed with 20 mL of a mixture of ethyl acetate and petroleum ether (1:20), the combined solvents were evaporated to afford the crude product. This was purified by flash column chromatography on silica, eluting with petroleum ether: ethyl acetate (20: 1) to give 4-benzyl-6-methyl-2-phenylquinoline **3a** as a light yellow oil; yield: 60.3 mg (78%).

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References

[1] a) L. Roberts, T. J. Egan, K. A. Joiner, H. C. Hoppe. *Antimicrob. Agent. Chem.* **2008**, 1840.
[2] N. C. Vieira, C. Herrenknecht, J. Vacus, A. Fournet, C. Bories, B. Figadère, L. S. Espindola, P. M. Loiseau, *Biomed. & Pharmacother.* **2008**, 684.
[3] G. Roma, M. Di Braccio, G. Grossi, F. Mattioli, M. Ghia, *Eur. J. Med. Chem.* **2000**, *35*, 1021.
[4] D. Dube, M. Blouin, C. Brideau, C. C. Chan, S. Desmarais, D. Ethier, J. P. Falgueyret, R. W. Friesen, M. Girard, Y. Girard, J. Guay, D. Riendeau, P. Tagari, R. N. Young, *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1255.
[5] Y. L. Chen, K. C. Fang, J. Y. Sheu, S. L. Hsu, C. C. Tzeng, *J. Med. Chem.* **2001**, *44*, 2374.
[6] H. Ebisu, M. Nishikawa, M. Tanaka, T. Okazoe, Y. Morizawa, H. Shinyama, N. Nakamura, *J. Cardiovasc. Pharmacol.* **1999**, *34*, 526.
[7] M. P. Maguire, K. R. Sheets, K. McVety, A. P. Spada, A. Zilberstein, *J. Med. Chem.* **1994**, *37*, 2129.
[8] R. J. Altenbach, H. Liu, P. N. Banfor, K. E. Browman, G. B. Fox, R. M. Fryer, V. A. Komater, K. M. Krueger, K. Marsh, T. R. Miller, J. Pan, L. Pan, M. Sun, C. Thiffault, J. Wetter, C. Zhao, D. Zhou, T. A. Esbenshade, A. A. Hancock, M D. Cowart, *J. Med. Chem.* **2007**, *50*, 5439.
[9] M. Frotscher, E. Ziegler, S. Marchais-Oberwinkler, P. Kruchten, A. Neugebauer, L. Fetzer, C. Scherer, U. Müller-Vieira, J. Messinger, H. Thole, R. W. Hartmann, *J. Med. Chem.* **2008**, *51*, 2158.
[10] a) S. Concilio, P. M. Pfister, N. Tirelli, C. Kocher, U. W. Suter, *Macromolecules* **2001**, *34*, 3607; b) L. M. Espinosa, J. C. Ronda, M. Galia, V. Cadiz. *J. Polym. Sci. Polym. Chem.* **2010**, 869–878.
[11] S. Ou, Z. Lin, C. Duan, H. Zhang, Z. Bai, *Chem. Commun.* **2006**, 4392.
[12] Z. H. Skaup, *Ber. Dtsch. Chem. Ges.* **1880**, *13*, 2086.
[13] a) P. Friedlander, *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 2572; b) C. S. Cho, W. X. Ren, N. S. Yoon, *J. Mol. Catal. A: Chem.* **2009**, *299*, 117–120; c) B. Jiang, J. J. Dong, Y. Jin, X. L. Du, M. Xu, *Eur. J. Org. Chem.* **2008**, 2693–2696; d) H. V. Mierde, P. V. D. Voort, D. D. Vos, F. Verpoort, *Eur. J. Org. Chem.* **2008**, 1625–1631; e) D. Q. Yang, K. L. Jiang, J. N. Li, F. Xu, *Tetrahedron* **2007**, *63*, 7654–7658; f) S. Atechian, N. Nock, R. D. Norcross, H. Ratni, A. W. Thomas, J. Verron, R. Masciadri, *Tetrahedron* **2007**, *63*, 2811–2323.
[14] A. Combes, *Bull. Soc. Chim. Fr.* **1888**, *49*, 89.
[15] a) C. Praveen, S. Jegatheesan, P. T. Perumal, *Synlett* **2009**, *17*, 2795–2800; b) L. Y. Liu, Y. Wang, H. G. Wang, C. L. Peng, J. J. Zhao, Q. Zhu, *Tetrahedron Lett.* **2009**, *50*, 6715–6719; c) N. Sakai, K. Annaka, T. Konakahara, *J. Org. Chem.* **2006**, *71*, 3653; d) C. L. Peng, Y. Wang, L. Y. Liu, H. G. Wang, J. J. Zhao, Q. Zhu, *Eur. J. Org. Chem.* **2010**, 818–822; e) X. X. Zhang, T. L. Yao, M. A. Campo, R. C. Larock, *Tetrahedron* **2010**, *66*, 1177–1187.
[16] B. Gabriele, R. Mancuso, E. Lupinacci, R. Spina, G. Salerno, L. Veltri, A. Dibenedetto, *Tetrahedron* **2009**, *65*, 8507–8512.
[17] a) C. G. Han, H. J. Kim, K. J. Lee, *Tetrahedron* **2009**, *65*, 9616–9625; b) Z. B. Huo, I. D. Gridnev, Y. Yamamoto, *J. Org. Chem.* **2010**, *75*, 1266–1270.
[18] a) S. Majumder, K. R. Gipson, A. L. Odom, *Org. Lett.* **2009**, *11*, 4720–4723; b) F. P. Xiao, Y. L. Chen, Y. Liu, J. B. Wang, *Tetrahedron* **2008**, *64*, 2755–2761; c) S. K. Guchhait, K. Jadeja, C. Madaan, *Tetrahedron Lett.* **2009**, *50*, 6861–6865; d) O. D. Paolis, L. Teixeira, B. Torok, *Tetrahedron Lett.* **2009**, *50*, 2939–2942.
[19] a) G. Bhargava, C. Mohan, M. P. Mahajan, *Tetrahedron* **2008**, *64*, 3017–3024; b) P. H. Dobbelaar, C. H. Marzabadi, *Tetrahedron Lett.* **2010**, *51*, 201–204.
[20] C. M. Qi, Q. W. Zheng, R. M. Hua, *Tetrahedron* **2009**, *65*, 1316–1320.
[21] O. B. Familoni, P. J. Klaas, K. A. Lobb, V. E. Pakade, P. T. Kaye, *Org. Biomol. Chem.* **2006**, *4*, 3960.
[22] J. Le Paih, F. Monnier, S. Derien, P. H. Dixneuf, E. Clot, O. Eisenstein, *J. Am. Chem. Soc.* **2003**, *125*, 11964–11975.

[23] M. Zhang, H.-F. Jiang, H. Neumann, M. Beller, P. H. Dixneuf, *Angew. Chem.* **2009**, *121*, 1709–1712; *Angew. Chem. Int. Ed.* **2009**, *48*, 1681–1684.
[24] M. Zhang, H. F. Jiang, P. H. Dixneuf, *Adv. Synth. Catal.* **2009**, *351*, 1488–1494.
[25] CCDC 780497 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.
[26] J. J. Eisch, T. Dluzniewski, *J. Org. Chem.* **1989**, *54*, 1269.
[27] S. E. Denmark, S. Venkatraman, *J. Org. Chem.* **2006**, *71*, 1668.

