Iron-Promoted Tandem Reaction of Anilines with Styrene Oxides via C—C Cleavage for the Synthesis of Quinolines
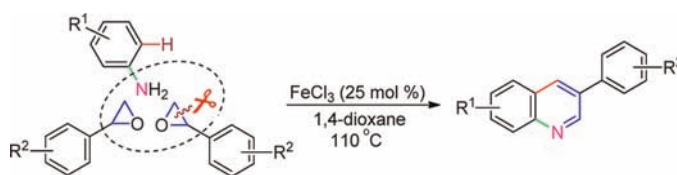
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ABSTRACT

A novel iron-promoted tandem reaction of anilines with styrene oxides via C—C cleavage and C—H activation has been developed. The reaction utilizes an inexpensive FeCl$_3$ as promoter and is suitable for forming a variety of 3-arylquinolines from the simple and readily available starting materials.

Transition-metal-catalyzed selective cleavage of C—C bonds and their applications as versatile tools in modern organic synthesis have attracted much attention.[1] Several modes of the catalytic process have been reported to activate inert C—C bonds, such as the relief of ring strain,[2]

the formation of a stable complex by chelation,[1a,c,3] and other means.[4] In general, the transition metals used in the cleavage of C—C reactions are Rh, Ru, Pd,[1–4] and Cu.[5] In comparison with the catalytic selective C—C cleavage of tertiary[1g,i,5b] and secondary alcohols[1f,j] via β-carbon elimination, transition-metal-catalyzed C—C bond cleavage of epoxides has not been described.

Quinolines have received considerable interest because they are widely found in natural products with biological activity.[6] They have also played an important role in medicinal chemistry due to their pharmacological properties.[7] In addition, quinolines as building blocks have been used for preparing functional materials with enhanced electronic and photonic properties.[8] Recently, a

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(1) For selected reviews, see: (a) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222. (b) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (c) Jun, C.-H.; Moon, C. W.; Lee, D.-Y. *Chem.—Eur. J.* **2002**, *8*, 2422. (d) Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610. For selected examples, see: (e) Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 11010. (f) Jun, C.-H.; Lee, D.-Y.; Kim, Y.-H.; Lee, H. *Organometallics* **2001**, *20*, 2928. (g) Zhao, P.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 3124. (h) Iwasaki, M.; Hayashi, S.; Hirano, K.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4463. (i) Niwa, T.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 2643. (j) Li, H.; Li, Y.; Zhang, X.-S.; Chen, K.; Wang, X.; Shi, Z.-J. *J. Am. Chem. Soc.* **2011**, *133*, 15244 and references cited therein.

(2) For selected examples, see: (a) Seiser, T.; Cramer, N. *J. Am. Chem. Soc.* **2010**, *132*, 5340. (b) Winter, C.; Krause, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 2460. (c) Matsumura, S.; Maeda, Y.; Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **2003**, *125*, 8862. (d) Bart, S. C.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 886.

(3) For selected examples, see: (a) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1999**, *121*, 8645. (b) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687.

(4) For selected examples, see: (a) Sugiishi, T.; Kimura, A.; Nakamura, H. *J. Am. Chem. Soc.* **2010**, *132*, 5332. (b) Chiba, S.; Xu, Y.-J.; Wang, Y.-F. *J. Am. Chem. Soc.* **2009**, *131*, 12886. (c) Takahashi, T.; Song, Z.; Hsieh, Y.-F.; Nakajima, K.; Kanno, K.-i. *J. Am. Chem. Soc.* **2008**, *130*, 15236. (d) Gunay, A.; Jones, W. D. *J. Am. Chem. Soc.* **2007**, *129*, 872. (e) Najera, C.; Sansano, J. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 2452.

(5) For selected examples, see: (a) He, C.; Guo, S.; Huang, L.; Lei, A. *J. Am. Chem. Soc.* **2010**, *132*, 8273. (b) Sai, M.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 3294.

(6) (a) Habermehl, G.; Hammann, P. E. *Naturstoffchemie*; Springer: Berlin, 1992; p 192. (b) Michael, J. P. *Nat. Prod. Rep.* **2001**, *18*, 543. (c) Funayama, S.; Murata, K.; Noshita, T. *Heterocycles* **2001**, *54*, 1139.
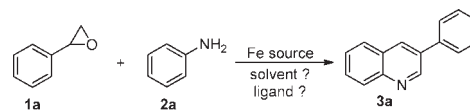
(7) (a) Balasubramanian, M.; Keay, J. G. Isoquinoline Synthesis. In *Comprehensive Heterocyclic Chemistry II*; McKillop, A. E., Katrizky, A. R., Rees, C. W., Scrivem, E. F. V., Eds.; Elsevier: Oxford, UK, 1996; Vol. 5, p 245. (b) Claret, P. A.; Osborne, A. G. In *The Chemistry of Heterocyclic Compounds, Quinolines*; Jones, G., Ed.; John Wiley and Sons: Chichester, 1982, Vol. 32, Part 2, p 31. (c) Sawada, Y.; Kayakiri, H.; Abe, Y.; Imai, K.; Katayama, A.; Oku, T.; Tanaka, H. *J. Med. Chem.* **2004**, *47*, 1617.

(8) (a) Zhang, X.; Shetty, A. S.; S. Jenekhe, A. *Macromolecules* **1999**, *32*, 7422. (b) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315.

number of modifications for preparing quinolines have been reported, including Skraup, Combes, Miller, Friedländer, Conrad−Limpach, and Pfitzinger syntheses,[9] and transition-metal-catalyzed synthetic methodologies.[10] However, the existing methods suffer from limited availability of substrates, complicated multistep procedures, and low regioselectivity in most cases. Compared to the traditional stepwise synthesis, the tandem (domino) reaction is the most facile and economic synthetic approach. It enhances the reaction efficiency and avoids the tedious step-by-step separations and purifications of intermediates.[11] An example of preparing 2,3-disubstituted quinolines through a rhodium-catalyzed tandem amination of aromatic olefins with anilines was developed.[12]

Over the past decade, iron-based catalysts have significantly risen to promote a broad range of organic transformations, such as cross-couplings, allylations, hydrogenations, and direct C−H bond functionalizations owing to their abundance, affordability, and environmental friendliness.[13] Most recently, an $FeCl_3$-catalyzed A^3-reaction of aldehydes, alkynes, and amines via a tandem process in one-pot for preparing 2,4-disubstituted quinolines was reported.[14] As part of our continuing effort for accessing natural-product-like compounds and the development of iron-catalyzed organic transformations,[15] we report herein a novel $FeCl_3$-promoted tandem reaction of anilines with styrene oxides via C−C cleavage and C−H activation for

(9) (a) Jones, G. In *Comprehensive Heterocyclic Chemistry*, Katritzky, A. R., Rees, A. R., Eds.; Pergamon, New York, 1984; Vol. 2, Part 2A, p 395. (b) Chan, B. K.; Ciufolini, M. A. *J. Org. Chem.* **2007**, *72*, 8489. (c) Zong, R.; Zhou, H.; Thummel, R. P. *J. Org. Chem.* **2008**, *73*, 4334. (d) Powell, D. A.; Batey, R. A. *Org. Lett.* **2002**, *4*, 2913. (e) Cho, I. S.; Gong, L.; Muchowski, J. M. *J. Org. Chem.* **1991**, *56*, 7288. (f) Riesgo, E. C.; Jin, X.; Thummel, R. P. *J. Org. Chem.* **1996**, *61*, 3017. (g) Wu, Y.; Liu, L.; Li, H.; Wang, D.; Chen, Y. *J. Org. Chem.* **2006**, *71*, 6592. (h) Denmark, S. E.; Venkatraman, S. *J. Org. Chem.* **2006**, *71*, 1668. (i) Akbari, J.; Heydari, A.; Kalhor, H. R.; Kohan, S. A. *J. Comb. Chem.* **2010**, *12*, 137.

(10) (a) Liang, Z.; Wu, J. *Adv. Synth. Catal.* **2007**, *349*, 1047. (b) Tokunaga, M.; Eckert, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3222. (c) Korivi, R. P.; Cheng, C. *J. Org. Chem.* **2006**, *71*, 7079. (d) McNaughton, B. R.; Miller, B. L. *Org. Lett.* **2003**, *5*, 4257. (e) Zhang, Z.; Tan, J.; Wang, Z. *Org. Lett.* **2008**, *10*, 173. (f) Wu, J. L.; Cui, X. L.; Chen, L. M.; Jiang, G. J.; Wu, Y. J. *J. Am. Chem. Soc.* **2009**, *131*, 13888. (g) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (h) Cho, C. S.; Kim, B. T.; Kim, T. J.; Shim, S. C. *Chem. Commun.* **2001**, 2576.

(11) Tietze, L. F.; Brasche, G.; Gericke, K. *Domino Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, 2006.

(12) Beller, M.; Thiel, O.; Trauthwein, H.; Hartung, C. G. *Chem.—Eur. J.* **2000**, *6*, 2513.

(13) For selected reviews, see: (a) Enthaler, S.; Junge, K.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3317. (b) Correa, A.; García Mancheno, O.; Bolm, C. *Chem. Soc. Rev.* **2008**, *37*, 1108. (c) Sherry, B. D.; Fürstner, A. *Acc. Chem. Res.* **2008**, *41*, 1500. (d) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293. (e) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* **2004**, *104*, 6217. For selected examples, see: (f) Fürstner, A.; Majima, K.; Martin, R.; Krause, H.; Kattnig, E.; Goddard, R.; Christian, W. L. *J. Am. Chem. Soc.* **2008**, *130*, 1992. (g) Chen, M. S.; White, M. C. *Science* **2007**, *318*, 783. (h) Fürstner, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 1364. (i) Buchwald, S. L.; Bolm, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 5586. (j) Fan, J.; Gao, L.; Wang, Z. *Chem. Commun.* **2009**, 5021. (k) Fan, J.; Wang, Z. *Chem. Commun.* **2008**, 5381.

(14) (a) Cao, K.; Zhang, F.-M.; Tu, Y.-Q.; Zhou, X.-T.; Fan, C.-A. *Chem.—Eur. J.* **2009**, *15*, 6332. (b) Zhang, Y.; Li, P.; Wang., L. *J. Heterocycl. Chem.* **2011**, *48*, 153.

(15) (a) Li, P.; Zhang, Y.; Wang, L. *Chem.—Eur. J.* **2009**, *15*, 2045. (b) Liu, J.; He, T.; Wang, L. *Tetrahedron* **2011**, *67*, 3420. (c) Wang, B.; Wu, H.; Li, P.; Wang, L. *Chem. Commun.* **2010**, *46*, 5891. (d) Wang, M.; Ren, K.; Wang, L. *Adv. Synth. Catal.* **2009**, *351*, 1586.

Table 1. Optimization of the Reaction Parameters[a]

entry	Fe (mol %)	solvent/T (°C)	ligand[b]	yield[c] (%)
1	FeCl$_3$ (10)	dioxane/110		38
2	FeCl$_3$ (10)	CH$_3$CN/80		26
3	FeCl$_3$ (10)	C$_2$H$_5$OH/80		18
4	FeCl$_3$ (10)	CH$_3$NO$_2$/100		20
5	FeCl$_3$ (10)	toluene/110		17
6	FeCl$_3$ (10)	(CH$_2$Cl)$_2$/80		25
7	FeCl$_3$ (10)	(CH$_2$Br)$_2$/110		13
8	FeCl$_3$ (10)	PEG-400/110		23
9	FeCl$_3$ (10)	DMSO/110		0
10	FeCl$_3$ (10)	DMF/110		0
11	FeCl$_3$ (10)	dioxane/110		15[d]
12	FeCl$_3$ (10)	dioxane/110		38[e]
13	FeCl$_3$ (10)	−/110		22[f]
14	FeCl$_2$ (10)	dioxane/110		16
15	FeBr$_3$ (10)	dioxane/110		29
16	FeBr$_2$ (10)	dioxane/110		15
17	Fe(OTf)$_3$ (10)	dioxane/110		10
18	Fe(ClO$_4$)$_3$·xH$_2$O (10)	dioxane/110		8
19	Fe$_2$O$_3$ (10)	dioxane/110		0
20	Fe$_2$(acac)$_3$ (10)	dioxane/110		0
21	FeCl$_3$ (10)	dioxane/110	PPh$_3$	34
22	FeCl$_3$ (10)	dioxane/110	PCy$_3$	37
23	FeCl$_3$ (10)	dioxane/110	Dppf	36
24	FeCl$_3$ (10)	dioxane/110	DMEDA	33
25	FeCl$_3$ (10)	dioxane/110	TMEDA	35
26	FeCl$_3$ (10)	dioxane/110	Phen	35
27	FeCl$_3$ (10)	dioxane/110	L-proline	33
28	FeCl$_3$ (10)	dioxane/110	TMHD	45
29	FeCl$_3$ (10)	dioxane/110	2-acetylcyclohexanone	49
30	FeCl$_3$ (20)	dioxane/110		70
31	FeCl$_3$ (25)	dioxane/110		81
32	FeCl$_3$ (35)	dioxane/110		80

[a] Reaction conditions: styrene oxide (**1a**, 2.0 mmol), aniline (**2a**, 1.0 mmol), Fe source (10−35 mol %), ligand (20 mol %) if necessary, solvent (2.0 mL) at the temperature indicated in Table 1 for 12 h. [b] PCy$_3$ = tricyclohexylphosphine, Dppf = 1,1′-bis(diphenylphosphino)ferrocene, DMEDA = N,N'-dimethylethylenediamine, TMEDA = N,N,N',N'-tetramethylethylenediamine, Phen = 1,10-phenanthroline, TMHD = 2,2,6,6-tetramethyl-3,5-heptanedione. [c] Isolated yield. [d] **1a** (1.0 mmol), **2a** (1.0 mmol). [e] **1a** (3.0 mmol), **2a** (1.0 mmol). [f] **1a** (5.0 mmol), **2a** (1.0 mmol) without additional solvent. Cu(OAc)$_2$ was used instead of FeCl$_3$; no **3a** was detected.

the preparation of quinolines. It is important to note that this is an inexpensive, regioselective, alternative, and efficient approach to 3-arylquinolines from the simple and readily available starting materials.

This novel tandem reaction of styrene oxide with aniline was observed during our investigation on the preparation of a 2-phenylindole framework via $FeCl_3$-catalyzed ring opening of styrene oxide (**1a**) with aniline (**2a**).[16] Instead of the anticipated 2-phenylindole product, 3-phenyquinoline (**3a**) was isolated in 38% yield when the reaction was

(16) Cho, C. S.; Kim, J. H.; Choi, H.-J.; Kim, T.-J.; Kim, T.-J.; Shim, S. C. *Tetrahedron Lett.* **2003**, *44*, 2975.
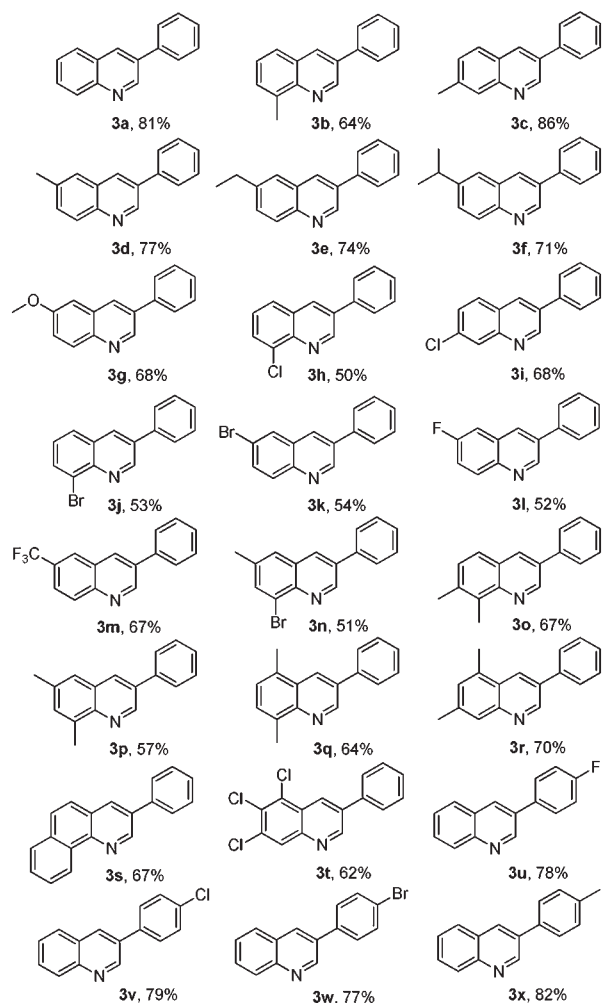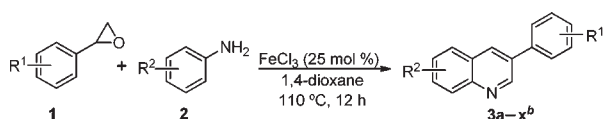
^{a} Reaction conditions: **1** (2.0 mmol), **2** (1.0 mmol), FeCl$_3$ (0.25 mmol), 1,4-dioxane (2.0 mL) at 110 °C for 12 h. ^{b} Isolated yields.

performed in 1,4-dioxane at 110 °C for 12 h. This preliminary finding prompted us to develop a facile, practical, and economic approach to 3-aryl-quinolines.

To improve the yield of **3a**, a variety of reaction parameters were optimized. At first, the effect of solvent on the model reaction of styrene oxide (**1a**) with aniline (**2a**) in the presence of FeCl$_3$ (10 mol %) was examined. Among the solvents tested, 1,4-dioxane was found to be the most suitable one, although only 38% yield of **3a** was obtained (Table 1, entry 1). Lower yields of **3a** were observed when using other solvents, such as CH$_3$CN, C$_2$H$_5$OH, CH$_3$NO$_2$, toluene, 1,2-dichloroethane, 1,2-dibromoethane, and PEG-400 (Table 1, entries 2−8). However, no desired **3a** was detected when the reaction was performed in DMSO or DMF (Table 1, entries 9 and 10). The product yield was

considerably affected by the molar ratio of **1a** to **2a**. The optimal ratio of **1a** to **2a** was found to be 2:1. As expected, two molecules of **1a** reacted with one molecule of **2a** to form a quinoline skeleton. The product yield of **3a** did not improve when increasing the molar ratio of **1a** to **2a**. Conversely, reaction of **2a** (1.0 equiv) with **1a** (5.0 equiv), without additional solvent, led to a lower yield of **3a** (Table 1, entries 11−13).

The effect of the Fe source on the model reaction was examined. Various iron salts were tested; FeCl$_3$ was found to be the best one. FeCl$_2$, FeBr$_3$, FeBr$_2$, Fe(OTf)$_3$, and Fe(ClO$_4$)$_3$·xH$_2$O were less effective, while Fe$_2$O$_3$ and Fe$_2$(acac)$_3$ were inactive (Table 1, entries 14−20). Furthermore, when a Cu source, such as CuI, CuO, or Cu(OAc)$_2$ was used instead of FeCl$_3$, no **3a** was detected.

Next, the ligand was added to improve the product yield. When *P*-ligands, such as triphenylphosphine, tricyclohexylphosphine, and 1,1′-bis(diphenylphosphino)ferrocene, *N*-ligands, such as *N,N*′-dimethylethylenediamine, *N,N, N*′,*N*′-tetramethylethylenediamine, and 1,10-phenanthroline, and an *N,O*-ligand, i.e., L-proline, were used (20 mol %) in the model reaction, the reaction afforded **3a** in slightly lower yields than obtained under ligand-free conditions (Table 1, entries 21−27). When bidentate *O*-ligands 2,2, 6,6-tetramethyl-3,5-heptanedione and 2-acetylcyclohexanone were employed, **3a** was obtained in 45 and 49% yields, respectively (Table 1, entries 28 and 29).

To further improve the product yield, we added up to 35 mol % of FeCl$_3$, considering its low cost. To our surprise, 81% yield of **3a** was isolated when the model reaction was performed in the presence of FeCl$_3$ (25 mol %) without ligand. Thus, the optimal amount of FeCl$_3$ used in the reaction was 25 mol % (Table 1, entries 30−32).

Under the optimized reaction conditions, the reaction scope of various styrene oxides with a variety of anilines was investigated. As shown in Scheme 1, for the monosubstituted arylamines, a series of substituents on anilines, including *o*-Me, *m*-Me, *p*-Me, *p*-Et, *p*-(*i*-Pr), *p*-MeO, *o*-Cl, *m*-Cl, *o*-Br, *p*-Br, *p*-F, and *p*-CF$_3$ groups were tolerated, and the corresponding quinolines were obtained in 50−86% yields (Scheme 1, **3b−m**). Anilines with an electron-donating group on their *ortho*-, *meta*-, or *para*-position (**3b−g**) gave yields superior to that of the anilines with an electron-withdrawing group on their corresponding position (**3h−m**). The *ortho*-position effect was obviously observed in the formation of **3b**, **3h**, and **3j**. It should be noted that only 7-methyl-3-phenylquinoline (**3c**) or 7-chloro-3-phenylquinoline (**3i**) as sole regioisomer was isolated when *m*-methylaniline or *m*-chloroaniline reacted with styrene oxide. Further investigation revealed that disubstituted arylamines bearing electron-rich or electron-poor functional groups could react with styrene oxide to form the corresponding products in moderate to good yields (**3n−r**). The *ortho*-position effect was also observed (**3n−q** vs **3r**). A more bulky aniline substrate, 1-naphthylamine, reacted with styrene oxide to generate **3s** in 67% yield. Trisubstituted arylamine, such as 3,4,5-trichloroaniline, reacted with styrene oxide to form **3t** in 62% yield. On the other hand, a variety of styrene oxides bearing substituents on the benzene rings were

Scheme 2. Proposed Reaction Mechanism
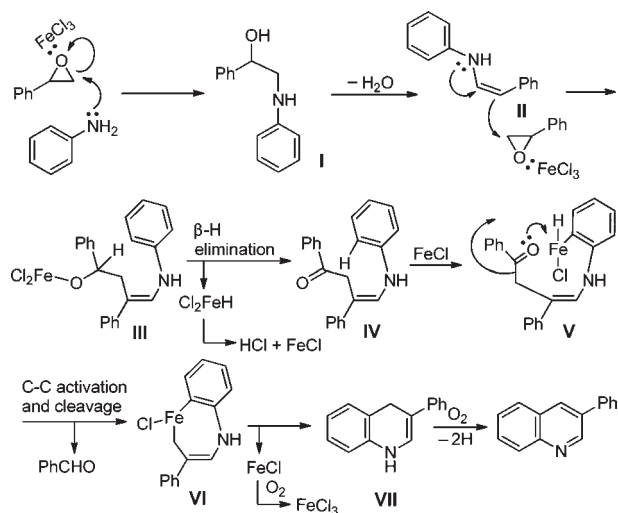
examined, and the results in Scheme 1 indicated that electron-withdrawing groups (*p*-F, *p*-Cl, *p*-Br) and electron-donating one (*p*-Me) were tolerated, and the corresponding products (**3u**−**x**) were obtained in high yields (77−82%). It is obvious that the electronic effect of substituted groups on the benzene rings in styrene oxides had little impact on the yields of the products. It is worth noting that no desired product was isolated when 2-methyl styrene oxide reacted with aniline under the present reaction conditions. However, aliphatic epoxides, such as 3-chloro-1,2-epoxypropene and 1,2-epoxybutane, did not react with aniline. It is important to note that quinolines with halo groups on the benzene rings (**3h**−**k**, **3n**, **3t**, **3v**, and **3w**) could be utilized in the further transition-metal-catalyzed organic transformations.[17]

Although the reaction mechanism has not been clear up to now, a possible process was proposed in Scheme 2. First, aniline reacted with styrene oxide in the presence of FeCl$_3$ as Lewis acid, to form β-amino alcohol (**I**),[16,18] which

(17) Nolt, M. B.; Zhao, Z. J.; Wolkenberg, S. E. *Tetrahedron Lett.* **2008**, *49*, 3137.

(18) Onaka, M.; Kawai, M.; Izumi, Y. *Chem. Lett.* **1985**, 779.

(19) Garcia-Cuadrado, D.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066.

(20) (a) Echavarren, A. M.; Gómez-Lor, B.; González, J. J.; de Frutos, Ó. *Synlett* **2003**, 585. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.

underwent dehydration to generate enamine (**II**). Subsequently, the obtained **II** reacted with another styrene oxide assisted by FeCl$_3$ to form **III**, which could undergo β-H elimination from iron alkoxide linkage, leading to the formation of a ketone intermediate (**IV**) and iron hydride species (which might eliminate HCl to reach Fe^{I} oxidation state). The ketone intermediate (**IV**) could then undergo Fe^{I}-mediated, directed C−H bond activation at the *ortho*-position of aniline moiety to generate (**V**),[19] followed by chelation-assisted C−C bond activation and cleavage to form the 7-membered cyclometalate (**VI**) and eliminate PhCHO. After reductive elimination of FeCl from **VI**, **VII** was obtained.[20] Finally, the desired quinoline was generated through dehydrogenation of **VII** in the presence of oxygen.[14] It should be noted that benzaldehyde and intermediate (**I**) was detected by HPLC during the reaction of **1a** with **2a** by controlling the reaction conditions. Moreover, the structure of **3w** was further confirmed by X-ray crystallography.[21]

In summary, we have developed a novel iron-promoted tandem reaction for the synthesis of quinoline derivatives. The reactions of anilines and styrene oxides via C−C cleavage and C−H activation in the presence of FeCl$_3$ generated 3-substituted quinolines with good yields. This is an inexpensive and convenient approach to 3-arylquinolines from simple and readily available starting materials and reagents. Detailed mechanistic study and further investigation are currently underway.

Supporting Information Available. Analytical data and spectra (¹H and ¹³C NMR) for all products, CIF of **3w**, typical procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

(21) X-ray crystal structure of 3-(4-bromophenyl)quinoline (**3w**):
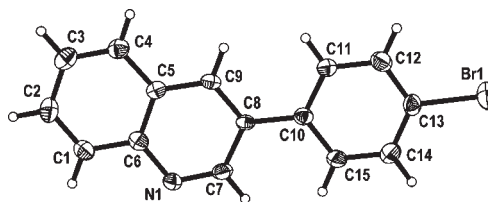
The authors declare no competing financial interest.