

Synergistic Effect of Pd(II) and Acid Catalysts on Tandem Annulation Reaction for the Regioselective Synthesis of Ring-Fused Quinolines[†]

Su Kyung Ock[‡] and So Won Youn^{*}

Department of Chemistry, Hanyang University, Seoul 133-791, Korea. *E-mail: sowony73@hanyang.ac.kr

[‡]Department of Chemistry, Pukyong National University, Busan 608-737, Korea

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Transition-metal-catalyzed tandem annulations are powerful methods for the synthesis of a wide range of carbocycles and heterocycles in a convergent way.¹ Molecules having two or more different unsaturated bonds are particularly interesting substrates for the construction of a variety of cyclic compounds not only involving multiple C-C or C-X bond formations with a single catalyst in one operation but also allowing for multiple mechanistic possibilities, which in turn may lead to different products.

In 2004, Yamamoto and co-workers reported a Cu-catalyzed tandem reaction between 2-alkynyl-*N*-arylideneanilines and alcohols to afford *N*-(alkoxybenzyl)indoles.² In contrast, Zhu *et al.* demonstrated that the regioselective synthesis of 4-alkoxy-2-arylquinolines has been achieved by acid-catalyzed reaction of 2-(2-(trimethylsilyl)ethynyl)aniline, arylaldehydes, and alcohols.³ In Yamamoto's work, CuCl acts as a transition-metal catalyst which activates the alkyne moiety to first promote the intramolecular addition of the nitrogen atom of the imine to the activated alkynes, allowing the synthesis of indoles (Scheme 1, path a). On the other hand, acid catalyst activates the imine moiety which first undergoes the intramolecular attack of the alkyne, leading to quinolines (Scheme 1, path b).

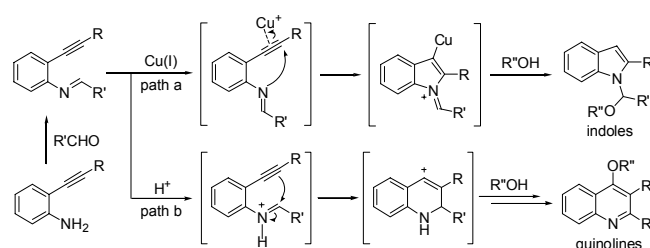
The corresponding intramolecular version of these reactions could provide the ring-fused *N*-heterocycles. It has been shown that carbophilic Au(III) salts can catalyze the tandem reaction of *N*-(*o*-alkynylphenyl)imine (**A**) which has a tethered nucleophile, OH group, in the molecule, to give ring-fused indoles (Scheme 2, path a).⁴ Interestingly, iodonium-mediated reaction of the same substrates provided either ring-fused indoles or quinolines depending on the reaction conditions (Scheme 2, path a or b).⁵

Since the reactivity of the same substrates could be modulated to afford different outcomes through an alternative reaction pathway by tuning metal catalysts and/or reaction conditions, we envisioned that *N*-(*o*-alkynylphenyl)imine (**A**) might be cyclized to give ring-fused quinoline derivatives through the following mechanism; either *via* the intramolecular attack of the alkyne moiety to iminium ion, followed by trapping the vinyl cationic intermediate with a tethered nucleophile in a stepwise mechanism or by a concerted mechanism in which intramolecular addition of a tethered nucleophile to the activated alkyne upon coordination to a metal catalyst is followed by subsequent

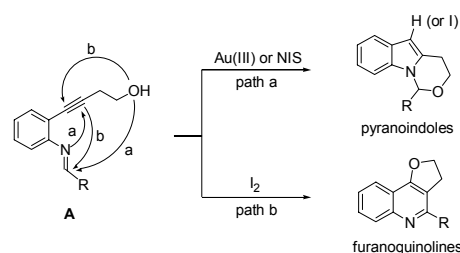
nucleophilic attack to the iminium ion. Quinolines are found to possess a wide range of biological activities.⁶ In parallel with our efforts to develop a catalytic system for heterocyclic synthesis,⁷ we were interested in developing a one-pot synthesis of quinolines. Herein we report a new tandem reaction of *o*-alkynylanilines bearing OH moiety placed at an appropriate position with aldehydes catalyzed by the combination of Pd(OAc)₂ and *p*-TsOH for the regioselective synthesis of ring-fused quinolines.

We focused our initial efforts on establishing optimal conditions for the tandem cyclization reactions between **1a** and benzaldehyde, which were selected as the first substrates for screening of several metal salts and complexes, additives, and solvents. Based on the mechanisms established for the related tandem reactions,^{3,5} the success of a tandem cyclization triggered by the intramolecular attack of the alkyne to the iminium ion could be achieved by choosing the more Lewis acidic metal salts which have the more bias to activate the imine moiety than the alkyne functionality, resulting in both the enhancement of the electrophilicity of the imine and the decreased nucleophilicity of the nitrogen atom of the imine, while suppressing or preventing the intramolecular attack of imine to alkyne.

In accord with this hypothesis, Lewis acids such as Fe(III) and Sc(III) promoted the tandem reaction to give the desired

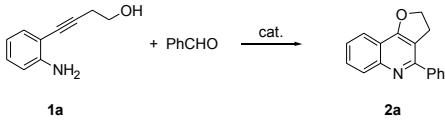


Scheme 1



Scheme 2

[†]This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

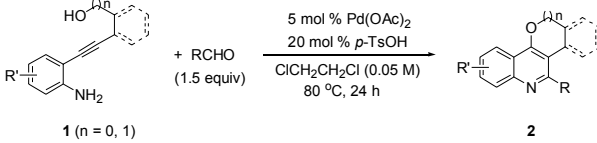
Table 1. Selected data from a systematic screening for the optimizations of reaction conditions for the synthesis of furanoquinoline **2a**^a


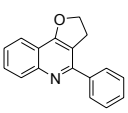
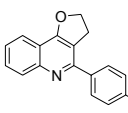
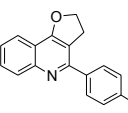
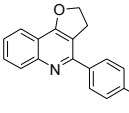
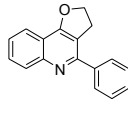
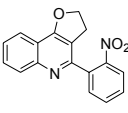
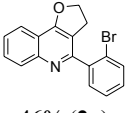
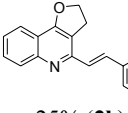
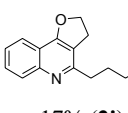
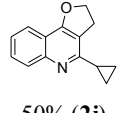
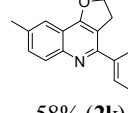
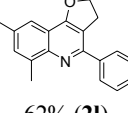
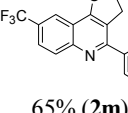
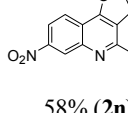
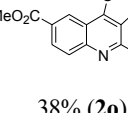
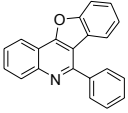
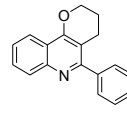
entry	catalyst	additive	yield (%) ^b
1	FeCl ₃ /AgOTf	-	35
2 ^c	Sc(OTf) ₃	-	25
3 ^c	RhCl(PPh ₃) ₃ /AgOTf	-	35
4	PtCl ₂ /AgOTf	-	30
5 ^c	Ph ₃ PAuCl/AgOTf	-	35
6 ^c	AuCl ₃ /AgOTf	-	15
7 ^c	AgOTf	-	-
8 ^d	Pd(OAc) ₂	-	10
9	FeCl ₃ /AgOTf	CF ₃ CO ₂ H	50
10 ^c	RhCl(PPh ₃) ₃ /AgOTf	CF ₃ CO ₂ H	55 (50) ^d
11	PtCl ₂ /AgOTf	CF ₃ CO ₂ H	30
12 ^c	Ph ₃ PAuCl/AgOTf	CF ₃ CO ₂ H	30
13 ^c	AuCl ₃ /AgOTf	CF ₃ CO ₂ H	15
14 ^d	Pd(OAc) ₂	CF ₃ CO ₂ H	85
15 ^{d,e}	Pd(OAc) ₂	AcOH	-
16 ^{d,e}	Pd(OAc) ₂	MsOH	75
17 ^d	Pd(OAc) ₂	<i>p</i> -TsOH	90
18	-	CF ₃ CO ₂ H	35
19	-	<i>p</i> -TsOH	30

^aReaction conditions: **1a** (1 equiv), PhCHO (1 equiv), catalyst (5 mol %), and additive (20 mol %) in ClCH₂CH₂Cl (0.05 M) at 80 °C for 24 h, unless otherwise noted. ^bDetermined by ¹H NMR using trichloroethylene as an internal standard. ^cPerformed with 4 mol % of catalyst. ^dPerformed with 1.5 equiv of PhCHO. ^ePerformed for 12 hours.

furanoquinoline **2a**, albeit only in 25 ~ 35% yields (Table 1, entries 1-2). Interestingly, however, Rh(I), Pt(II), and Au(I) also afforded the similar results (Table 1, entries 3-5), whereas Au(III) gave the poorer yield as expected due to its high carbo-philicity (Table 1, entry 6).⁸ In contrast, other Lewis acids such as Cu(II), Ag(I), Pd(II), Zn(II), and In(III) were not effective. To boost the reactivity by increasing the electrophilicity of imine more efficiently, acid additives including organic and inorganic acids such as AcOH, CF₃CO₂H, *p*-TsOH, MsOH, HCl, H₂SO₄, *etc.* as well as Lewis acids such as AlCl₃, ZnCl₂, In(OTf)₃, YbCl₃, *etc.* were added to the reaction mixture. With the exception of Au(I), Au(III), and Pt(II), most of the metal salts examined provided **2a** in substantially improved yields upon the addition of catalytic amount (20 mol %) of acids (Table 1, entries 9-14). Among various acids examined, CF₃CO₂H, MsOH, and *p*-TsOH showed outstanding effects (Table 1, entries 14 & 16-17), and control experiments employing only these acids as the sole catalyst gave lower yields (~30%) (Table 1, entries 18-19). These results indicate that there is a remarkable synergistic effect of metal and acid catalysts which can obviously increase the reactivity of the substrate for this tandem cyclization reaction, whereas either catalyst alone is not active enough under the same conditions.

Finally, we were delighted to identify an exciting lead, which unambiguously stood out in the array of experiments. The com-

Table 2. Pd(OAc)₂/*p*-TsOH-catalyzed synthesis of a variety of quinolines^a


 88% (2a)	 51% (2b)	 55% (2c)
 38% (2d)	 49% (2e)	 49% (2f)
 46% (2g)	 25% (2h)	 17% (2i)
 50% (2j)	 58% (2k)	 62% (2l)
 65% (2m)	 58% (2n)	 38% (2o)
 52% (2p)	 11%, 30% ^b (2q)	

^aIsolated yields. ^bPerformed with 5 mol % FeCl₃/AgOTf for 29 hours.

bination of 5 mol % Pd(OAc)₂ and 20 mol % *p*-TsOH was optimal in this reaction system to produce **2a** as a sole product in 90% yield (Table 1, entry 17). Increasing the amount of either metal catalyst or acid catalyst and reaction temperature caused slightly lower yields or marginal effect. Various solvents were examined, and dichloroethane appeared preferable.

With the establishment of these optimized conditions, we set out to explore the scope of this tandem process (Table 2). No successful results have not been reported employing either highly electron-deficient arylaldehydes, such as 4-nitrobenzaldehyde, or alkylaldehydes in the previously reported related tandem cyclization reactions.³⁻⁵ In contrast, in our reaction system both electron-rich and electron-deficient arylaldehydes as well as sterically hindered arylaldehydes underwent tandem cyclization reaction to form the corresponding quinolines (Table 2, **2a-2g**). Moreover, cyclopropanecarboxaldehyde was also suitable substrate (Table 2, **2j**), whereas cinnamaldehyde and

hexanal were not successful to give the corresponding products in good yields (Table 2, **2h-2i**).

We proceeded to examine the effects of substituent R' on the aniline ring. A variety of aniline derivatives with electron-donating or -withdrawing substituents at various positions were found to be good substrates in this reaction (Table 2, **2k-2o**).

Next, we tried to change the substituent at the end of the alkyne moiety. The reaction of 2-hydroxyphenyl-substituted aniline derivative proceeded smoothly to give the corresponding benzofuranoquinoline **2p** in 52% yield. Unfortunately, however, this transformation could not be successfully extended to the substrate with a longer carbon tether for the synthesis of the corresponding pyranoquinoline **2q**, although replacing Pd(II) by Fe(III) provided slightly improved yield.

In most reactions, analysis of the crude reaction mixture by ¹H NMR showed the remainder of the material to be either 2-(4,5-dihydrofuran-2-yl)anilines or *N*-benzylidene-2-(4,5-dihydrofuran-2-yl)anilines which could be both formed *via* only intramolecular addition of hydroxyl group to alkyne moiety. It should be noted that the corresponding indole products were not observed. Increasing either catalyst loadings or reaction temperature could not improve yields of products but only resulted in shorter reaction time.

In summary, we have developed tandem cyclization reaction of *o*-alkynylanilines and aldehydes to afford ring-fused quinolines. The combination of Pd(II) and protic acid catalysts exhibited synergistic effect to improve the efficiency of this tandem cyclization. Rational design of catalytic system and exquisite tune of catalysts and reaction conditions could modulate the reaction propensity and reaction pathway for the regioselective synthesis of quinoline derivatives. In no case were the corresponding indole products formed as a byproduct of this reaction. Although more detailed investigations are needed to clarify the mechanism for the present reaction, it is likely that this tandem reaction proceeds *via* a reaction pathway involving alkyne activation by coordination to Pd(II) as well as imine activation by acid alone or by acid and Pd(II) together. Noteworthy is the fact that this process can tolerate various functional groups such as methoxy, amino, bromo, CF₃, alkene, cyclopropyl, nitro, and ester groups. In comparison with other related tandem reactions,^{4,5} imine preparation prior to tandem annulation is not required, and thus anilines and aldehydes can be used directly as substrates, obviating the need for pregeneration of imine in an additional step. Therefore, this regioselective one-pot reaction offers considerable advantages with regard to simplicity and high efficiency.

Experimental Section

General procedure for Pd(OAc)₂/*p*-TsOH-catalyzed tandem cyclization reaction of *o*-alkynylanilines and aldehydes for the synthesis of ring-fused quinolines. To a solution of the substrate **1** in 1,2-dichloroethane (0.05 M) were added Pd(OAc)₂ (5 mol %), *p*-TsOH (20 mol %), and aldehyde (1.5 equiv). The resulting mixture was stirred at the 80 °C for 24 hours. After the reaction was completed, the reaction mixture was quenched with distilled water, extracted with CH₂Cl₂ (three times), washed with brine, dried over MgSO₄, and concentrated

in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:10 ~ 1:20) to give the corresponding product **2**.

Spectral data for **2a-2c** and **2q** were consistent with data reported in the literature.⁵

4-(2,3-Dihydrofuro[3,2-*c*]quinolin-4-yl)-*N,N*-dimethylbenzenamine (2d): ¹H NMR (400 MHz, in CDCl₃) δ 3.03 (s, 6H), 3.61 (t, *J* = 8.9 Hz, 2H), 4.86 (t, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.87-7.92 (m, 3H), 8.08 (d, *J* = 8.9 Hz, 1H); ¹³C NMR (100 MHz, in CDCl₃) δ 30.6, 40.3, 72.9, 112.0, 114.3, 115.7, 121.2, 124.6, 127.7, 128.8, 129.4, 149.1, 149.2, 150.9, 155.5, 164.1; IR (NaCl) 2919, 1607, 1590, 1501, 1363, 1196, 1085, 764, 694, 550 cm⁻¹; EIMS *m/z* 290 (74, M⁺), 289 (100, M⁺-H), 273 (28), 246 (13), 144 (15), 130 (11), 123 (10), 95 (4), 77 (3).

2,3-Dihydro-4-(4-nitrophenyl)furo[3,2-*c*]quinoline (2e): ¹H NMR (400 MHz, in CDCl₃) δ 3.61 (t, *J* = 8.9 Hz, 2H), 4.94 (t, *J* = 8.9 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 3H), 8.37 (d, *J* = 8.9 Hz, 2H); ¹³C NMR (100 MHz, in CDCl₃) δ 30.0, 73.2, 115.2, 116.2, 121.5, 123.8, 126.2, 129.2, 129.4, 130.2, 146.0, 147.8, 149.2, 152.7, 164.9; IR (NaCl) 2923, 1556, 1519, 1344, 1089, 854, 766, 704 cm⁻¹; EIMS *m/z* 292 (89, M⁺), 291 (84, M⁺-H), 246 (28), 245 (100), 217 (25), 189 (8), 122 (5), 108 (25), 94 (12), 82 (7).

2,3-Dihydro-4-(2-nitrophenyl)furo[3,2-*c*]quinoline (2f): ¹H NMR (400 MHz, in CDCl₃) δ 3.23 (t, *J* = 8.9 Hz, 2H), 4.89 (t, *J* = 8.9 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.58-7.62 (m, 2H), 7.65-7.75 (m, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, in CDCl₃) δ 28.4, 73.2, 116.0, 116.2, 121.5, 124.6, 125.9, 129.2, 129.4, 129.9, 131.2, 133.2, 135.2, 148.4, 148.9, 153.4, 164.0; IR (NaCl) 2922, 2364, 1555, 1528, 1407, 1350, 1083, 915, 854, 766, 718, 694 cm⁻¹; EIMS *m/z* 293 (18, M⁺), 292 (71, M⁺-H), 262 (100), 245 (32), 234 (24), 217 (98), 108 (29), 76 (20).

4-(2-Bromophenyl)-2,3-dihydrofuro[3,2-*c*]quinoline (2g): ¹H NMR (400 MHz, in CDCl₃) δ 3.29 (t, *J* = 8.9 Hz, 2H), 4.89 (t, *J* = 8.9 Hz, 2H), 7.28-7.32 (m, 1H), 7.42-7.46 (m, 2H), 7.48-7.52 (m, 1H), 7.66-7.70 (m, 2H), 7.99 (d, *J* = 8.2 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H); ¹³C NMR (100 MHz, in CDCl₃) δ 28.7, 73.3, 116.2, 116.8, 121.4, 121.7, 125.7, 127.6, 129.3, 129.7, 129.9, 130.4, 132.8, 141.0, 148.9, 156.3, 163.6; IR (NaCl) 2923, 1633, 1596, 1554, 1508, 1406, 1261, 1088, 1054, 1024, 914, 800, 762, 694, 644 cm⁻¹; EIMS *m/z* 326 (60, M⁺), 325 (74, M⁺-H), 246 (100), 217 (62), 123 (20), 115 (18), 109 (52), 94 (22), 76 (12).

2,3-Dihydro-4-styrylfuro[3,2-*c*]quinoline (2h): ¹H NMR (400 MHz, in CDCl₃) δ 3.59 (t, *J* = 8.9 Hz, 2H), 4.95 (t, *J* = 9.0 Hz, 2H), 7.30-7.35 (m, 2H), 7.38-7.45 (m, 3H), 7.64-7.68 (m, 3H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.90 (dd, *J* = 0.7, 8.2 Hz, 1H), 8.12 (d, *J* = 4.8 Hz, 1H); ¹³C NMR (100 MHz, in CDCl₃) δ 28.8, 73.1, 115.5, 116.1, 121.3, 125.1, 126.2, 127.3, 128.6, 128.7, 129.8, 135.2, 136.7, 149.1, 152.3, 164.0; IR (NaCl) 2923, 2369, 2343, 1594, 1505, 1259, 1069, 969, 917, 756, 698 cm⁻¹; EIMS *m/z* 273 (86, M⁺), 272 (100, M⁺-H), 245 (31), 217 (12), 196 (63), 167 (10), 120 (10), 115 (25), 77 (10).

2,3-Dihydro-4-pentylfuro[3,2-*c*]quinoline (2i): ¹H NMR (400 MHz, in CDCl₃) δ 0.91 (t, *J* = 8.0 Hz, 3H), 1.33-1.45 (m, 4H), 1.74-1.81 (m, 2H), 2.88 (t, *J* = 7.9 Hz, 2H), 3.38 (t, *J* = 9.1 Hz,

2H), 4.88 (t, $J = 8.9$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.89 (dd, $J = 0.7, 8.2$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 14.0, 22.5, 28.1, 28.6, 31.9, 36.7, 73.2, 115.6, 115.8, 121.3, 125.0, 127.8, 129.7, 159.6 cm^{-1} ; EIMS m/z 242 (2, M^+), 241 (4, M^+-H), 226 (1), 212 (12), 198 (25), 185 (100), 167 (4), 130 (8), 102 (5).

4-Cyclopropyl-2,3-dihydrofuro[3,2-*c*]quinoline (2j): ^1H NMR (400 MHz, in CDCl_3) δ 1.01-1.05 (m, 2H), 1.30 (s, 2H), 2.01-2.07 (m, 1H), 3.46 (t, $J = 9.0$ Hz, 2H), 4.88 (t, $J = 9.0$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 9.3, 15.3, 28.1, 29.7, 73.0, 115.6, 115.8, 121.2, 124.2, 128.3, 129.1, 148.6, 159.8, 162.6; IR (NaCl) 2919, 2352, 1595, 1557, 1505, 1257, 1079, 1051, 913, 803, 756, 641 cm^{-1} ; EIMS m/z 211 (63, M^+), 210 (93, M^+-H), 196 (100), 184 (12), 167 (33), 154 (12), 115 (11), 83 (12), 77 (15), 63 (11).

2,3-Dihydro-8-methyl-4-phenylfuro[3,2-*c*]quinoline (2k): ^1H NMR (400 MHz, in CDCl_3) δ 2.53 (s, 3H), 3.57 (t, $J = 8.9$ Hz, 2H), 4.87 (t, $J = 8.9$ Hz, 2H), 7.41-7.45 (m, 1H), 7.48-7.52 (m, 3H), 7.71 (s, 1H), 7.89 (dd, $J = 3.2, 5.3$ Hz, 2H), 8.03 (d, $J = 8.9$ Hz, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 21.6, 30.1, 73.0, 115.0, 115.9, 120.0, 128.3, 128.5, 128.7, 128.9, 132.0, 135.3, 139.9, 147.7, 154.6, 163.8; IR (NaCl) 2923, 1636, 1599, 1555, 1494, 1402, 1332, 1197, 1086, 1040, 944, 824, 768, 700, 659 cm^{-1} ; EIMS m/z 261 (64, M^+), 260 (100, M^+-H), 230 (4), 217 (9), 189 (1), 130 (11), 115 (18), 89 (5), 77 (5).

2,3-Dihydro-6,8-dimethyl-4-phenylfuro[3,2-*c*]quinoline (2l): ^1H NMR (400 MHz, in CDCl_3) δ 2.48 (s, 3H), 2.82 (s, 3H), 3.62 (t, $J = 8.9$ Hz, 2H), 4.85 (t, $J = 8.9$ Hz, 2H), 7.37 (s, 1H), 7.41-7.45 (m, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.57 (s, 1H), 8.03 (dd, $J = 1.3, 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, in CDCl_3) δ 18.4, 21.6, 30.5, 72.8, 114.6, 115.8, 117.8, 128.4, 128.5, 132.0, 134.8, 137.0, 140.4, 146.8, 152.5, 164.0; IR (NaCl) 2919, 2374, 1599, 1492, 1399, 1336, 1209, 998, 926, 856, 770, 699 cm^{-1} ; EIMS m/z 275 (100, M^+), 274 (97, M^+-H), 259 (19), 230 (11), 137 (14), 130 (15), 115 (21), 77 (6).

8-(Trifluoromethyl)-2,3-dihydro-4-phenylfuro[3,2-*c*]quinoline (2m): ^1H NMR (400 MHz, in CDCl_3) δ 3.63 (t, $J = 8.9$ Hz, 2H), 4.94 (t, $J = 8.9$ Hz, 2H), 7.46-7.55 (m, 3H), 7.82 (dd, $J = 1.9, 9.1$ Hz, 1H), 7.92 (dd, $J = 1.3, 7.2$ Hz, 2H), 8.23 (d, $J = 8.9$ Hz, 1H), 8.29 (s, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 30.1, 73.5, 114.9, 116.4, 119.9, 119.9, 125.3, 128.3, 128.7, 129.4, 130.3, 139.2, 149.9, 157.4, 165.1; IR (NaCl) 2926, 2363, 1601, 1561, 1343, 1306, 1267, 1157, 1105, 840, 697 cm^{-1} ; EIMS m/z 315 (52, M^+), 314 (100, M^+-H), 285 (7), 245 (9), 217 (12), 158 (6), 133 (8), 108 (6), 77 (4).

2,3-Dihydro-7-nitro-4-phenylfuro[3,2-*c*]quinoline (2n): ^1H NMR (400 MHz, in CDCl_3) δ 3.66 (t, $J = 9.0$ Hz, 2H), 4.96 (t, $J = 9.0$ Hz, 2H), 7.48-7.57 (m, 3H), 7.94 (d, $J = 7.5$ Hz, 2H), 8.08 (d, $J = 8.9$ Hz, 1H), 8.22 (dd, $J = 2.2, 9.1$ Hz, 1H), 9.03 (s, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 30.3, 73.6, 118.3, 118.6, 119.0, 123.3, 125.5, 127.4, 128.3, 128.7, 129.1, 129.6, 138.9, 148.0, 148.5, 157.9, 164.3; IR (NaCl) 2927, 2369, 1639, 1524, 1332, 1246, 1066, 738, 696 cm^{-1} ; EIMS m/z 292 (87, M^+), 291

(100, M^+-H), 245 (99), 233 (22), 217 (33), 203 (11), 189 (19), 108 (27), 94 (34), 82 (15), 77 (20), 63 (18).

Methyl 2,3-dihydro-4-phenylfuro[3,2-*c*]quinoline-8-carboxylate (2o): ^1H NMR (400 MHz, in CDCl_3) δ 3.62 (t, $J = 8.9$ Hz, 2H), 3.98 (s, 3H), 4.95 (t, $J = 9.1$ Hz, 2H), 7.46-7.55 (m, 3H), 7.93 (dd, $J = 1.4, 8.2$ Hz, 2H), 8.18 (s, 1H), 8.25 (dd, $J = 1.7, 8.9$ Hz, 1H), 8.74 (d, $J = 2.4$ Hz, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 29.7, 30.0, 52.3, 73.5, 115.1, 116.0, 125.0, 126.7, 128.4, 128.6, 129.3, 129.4, 139.1, 139.2, 150.6, 157.4, 165.7, 166.6; IR (NaCl) 2927, 2374, 1706, 1635, 1263, 1115, 1077, 773, 694 cm^{-1} ; EIMS m/z 305 (77, M^+), 304 (100, M^+-H), 245 (25), 217 (15), 189 (5), 152 (4), 123 (9), 108 (25), 94 (8), 77 (3).

6-Phenylbenzofuro[3,2-*c*]quinoline (2p): ^1H NMR (400 MHz, in CDCl_3) δ 7.29 (t, $J = 7.6$ Hz, 1H), 7.51 (dt, $J = 1.1, 7.8$ Hz, 1H), 7.57-7.68 (m, 3H), 7.74 (d, $J = 7.5$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.82 (dt, $J = 1.4, 7.7$ Hz, 1H), 7.96 (dd, $J = 1.4, 8.9$ Hz, 2H), 8.37 (d, $J = 8.2$ Hz, 1H), 8.46 (dd, $J = 0.7, 8.2$ Hz, 1H); ^{13}C NMR (100 MHz, in CDCl_3) δ 111.9, 114.5, 116.2, 120.7, 122.2, 122.8, 123.6, 126.7, 127.0, 128.7, 129.0, 129.4, 129.6, 129.7, 139.5, 146.8, 155.8, 156.0, 158.3 cm^{-1} ; EIMS m/z 295 (71, M^+), 294 (100, M^+-H), 265 (16), 239 (6), 147 (16), 132 (22), 119 (14), 94 (3).

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- In general, the use of AgOTf along with metal salts such as FeCl_3 , $\text{RhCl}(\text{PPh}_3)_3$, PtCl_2 , Ph_3PAuCl , and AuCl_3 afforded the better yields of the product **2a** than use of only these metal salts.