Synthesis Q. Wang et al. Paper

Synthesis of Quinolines via Iron-Catalyzed Redox Condensation of Alcohols with 2-Nitrobenzyl Methyl Ether/2-Nitrobenzyl Alcohols

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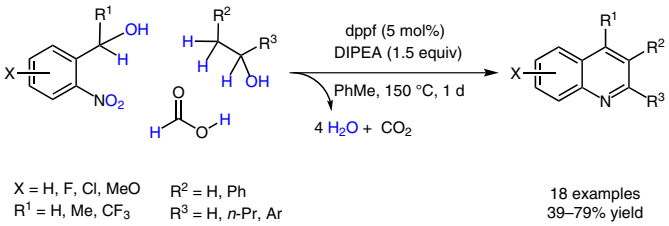

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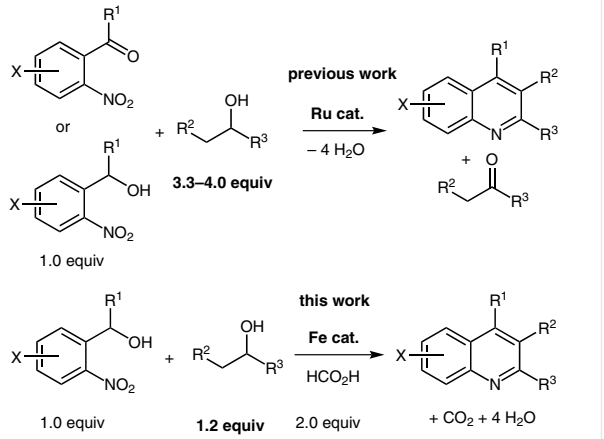
Abstract An iron-catalyzed redox condensation of 2-nitrobenzyl alcohols, formic acid, and alcohols has been developed, which affords substituted quinolines with carbon dioxide and water as the only side products. With the use of formic acid as a redox moderator to fill the electron gap of the global redox condensation process, the reaction goes smoothly with a smaller amount of alcohol in comparison to previous reports (i.e. 1.2 equiv versus 3.3–4 equiv). The reaction goes equally well when 2-nitrobenzyl methyl ether was used instead of 2-nitrobenzyl alcohol under otherwise identical conditions, shedding a new light on the study of this quinoline synthetic method.

Key words quinolines, 2-nitrobenzyl alcohols, iron catalysis, redox condensation, Friedländer annulation

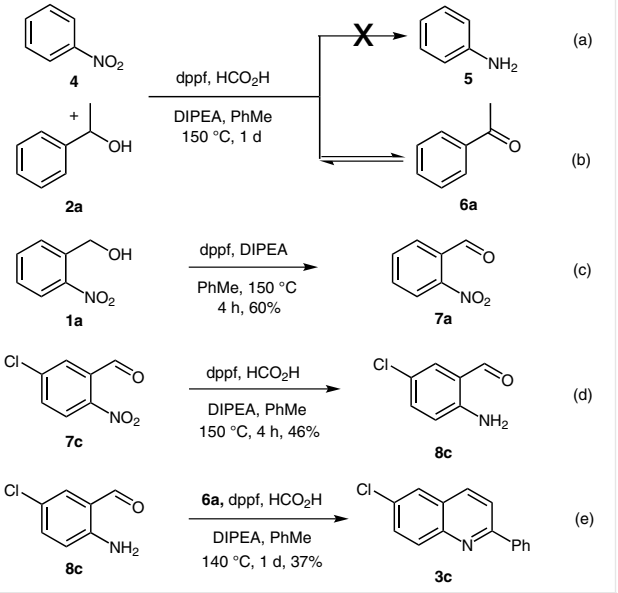
Quinolines are important building blocks for the construction of a large number of pharmaceuticals,[1] natural products,[2] and functional materials.[3] Accordingly, various synthetic methods have been developed for the construction of quinolines,[4–6] amongst which the Friedländer quinoline synthesis is still one of the simplest and most straightforward methods.[6,7] 2-Aminobenzaldehydes, as the typical starting materials for a Friedländer annulation, can readily undergo self-condensation reactions and this, thereby, limits the scope and generality of the quinoline synthesis.[6] To overcome this inherent problem, 2-aminobenzyl alcohols were used instead of 2-aminobenzaldehydes in some modified Friedländer quinoline syntheses, which underwent oxidation to produce reactive 2-aminobenzaldehydes and the latter were condensed with aldehydes/ketones for conversion in situ into quinolines.[8] This approach indeed provided a shortcut for quinoline synthesis, but still has some drawbacks, such as the potential formation of oxazines from 2-aminobenzyl alcohols and aldehydes,[9] and potential nucleophilic substitution of the benzyl alcohol moiety with the amino moiety of 2-aminobenzyl alcohols in the presence of various Lewis acids.[10] Another solution is the redox condensation of 2-nitrobenzaldehydes with alcohols in the presence of $Ru(PPh_3)_3Cl_2$, which offered an alternative access to quinolines using easily available and stable starting materials (Scheme 1).[11a] However, no less than three equivalents of alcohol were required in this reaction, and the formation of side products, aldehydes/ketones, is obviously unavoidable.[11a] This is because the oxidation of an alcohol to an aldehyde/ketone can transfer only two electrons while the reduction of a 2-nitrobenzaldehyde to the corresponding 2-aminobenzaldehyde requires six electrons.[12] A large amount of alcohol (3.3–4 equiv) was still required when 2-nitrobenzyl alcohols were used instead of 2-nitrobenzaldehydes (Scheme 1),[11] which is not in agreement with the principles of green and sustainable chemistry. Considering the dehydrogenation of formic acid and its salts is substantially irreversible due to the evolution of CO_2,[13] we envisioned that they might be better suited hydrogen donors than alcohols to fill the electron gap for this unbalanced electron-transfer process. Notably, formic acid as the hydrogen donor is abundant, inexpensive, and easy to handle.[13] In this context, we wish to describe here a new quinoline synthesis via iron-catalyzed redox condensation of 2-nitrobenzyl alcohols, formic acid, and alcohols (Scheme 1).[14]

Initially, the reaction of 2-nitrobenzyl alcohol (**1a**) with 1-phenylethanol (**2a**) was used as a probe for evaluating the reaction conditions, and representative results are summarized in Table 1. Reaction of **1a** (1.0 equiv) with **2a** (3.3 equiv) in the presence of $Ru(PPh_3)_3Cl_2$ (5 mol%) and K_2CO_3



Scheme 1 Synthesis of quinolines via redox condensation of alcohols with 2-nitrobenzaldehydes/2-nitrobenzyl alcohols

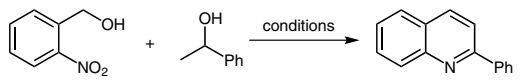
(1.0 equiv) at 150 °C for 1 day afforded quinoline **3a** in only 25% yield (entry 1), in which $Ru(PPh_3)_3Cl_2$ appeared to serve the role of not only a Friedländer annulation catalyst but also a hydrogen-transfer catalyst.[11a] Accordingly, a series of other hydrogen-transfer catalysts were investigated, in which dppf was found to be a relatively effective catalyst.[15] By treating **1a** (1.0 equiv) with **2a** (2.0 equiv) in the presence of dppf (5 mol%) at 150 °C for 1 day, quinoline **3a** was obtained in 37% yield (entry 2). Subsequently, various iron salts were tested for this reaction, in which dppf showed the best efficiency (entries 2–8). Quinoline **3a** was not obtained at all when ferrocene was used instead of dppf under otherwise the same conditions, reflecting the phosphine moiety of dppf effect on this reaction (entries 2 and 8).



Scheme 2 Verification experiments

Thus, the ferrocene/Ph_3P catalytic system was investigated for this reaction, which afforded quinoline **3a** in 17% yield (entries 8 and 9). Quinoline **3a** was not obtained in the absence of ferrocene under otherwise identical conditions (entries 9 and 10). An increased yield was also observed with the use of $FeSO_4/Ph_3P$ in comparison to $FeSO_4$ (entries 5 and 11). These results indicated that the iron/phosphine couple might be responsible for transfer reduction of the nitro group with an alcohol group, which agrees well with Beller's observation that the in situ combination of $Fe(BF_4)_2{\cdot}6H_2O$ and $P(CH_2CH_2PPh_2)_3$ is an excellent catalytic system for the transfer reduction of nitroarenes.[16] Solvent played an important role in this transformation. The reaction did not work in *tert*-amyl alcohol or DMF (entries 12 and 13). With the use of 1-methylpyrrolidin-2-one (NMP) in comparison to PhCl, a lower yield was observed (entries 2 and 14). To our delight, the yield of quinoline **3a** increased to 55% when this reaction was performed in toluene (entries 2 and 15). The reaction went equally well when the loading of dppf was greater than 5 mol% (entries 15–17). Further parameter optimization identified 150 °C as the most effective reaction temperature (entries 15, 18, and 19). The choice of base was also important for this reaction, and an inappropriate base might promote the conversion of an in situ generated 2-aminobenzaldehyde intermediate into the corresponding 2-aminobenzoic acid via a Cannizzaro reaction.[17] With the addition of Li_2CO_3 or Na_2CO_3 under otherwise identical conditions, quinoline **3a** was obtained in 61% and 62% yields, respectively (entries 20 and 21). However, quinoline **3a** was obtained in relatively lower yields when K_2CO_3, Cs_2CO_3, KOH, K_3PO_4, *t*-BuOK, $NaHCO_3$, or NaOH was used as the base (entries 15 and 22–28). With the use of $Pd(PPh_3)_3Cl_2$, $Ir(PPh_3)_2(CO)Cl$, $CuH(PPh_3)$, and $Ru(PPh_3)_3Cl_2$ in comparison to dppf, there was no improvement in the results obtained (entries 28–32). Two equivalents of alcohol **2a** were used in these transformations (entries 2–31), in which one equivalent of **2a** served as a reducing agent (hydrogen donor). Considering HCO_2Na could serve a dual role as the base and hydrogen donor, it was used instead of Na_2CO_3 to save nearly one equivalent of alcohol **2a** (entry 33). However, the reaction afforded quinoline **3a** in only a moderate yield even with excess HCO_2Na. Thus, the combination of HCO_2H with an organic base was next investigated. Fortuitously, the combination of HCO_2H (2.0 equiv) with DIPEA (1.5 equiv) was found to be a good choice in the formation of quinoline **3a** (entry 34). Addition of NiCl (5 mol%), $CoCl_2$ (5 mol%), $PtCl_2$ (5 mol%), $PdCl_2$ (5 mol%), or $RuCl_3$ (5 mol%) to the above reaction system did not provide any better results (entries 34–39). Unsurprisingly, the reaction did not work in the absence of dppf (entry 40). Decreased yields of quinoline **3a** were observed in the absence of either DIPEA or HCO_2H (cf. entries 34 with 41 and 42). Furthermore, scaling up **1a** to 1.53 g the reaction provided the yield at an excellent level (entry 43).

Table 1 Survey of Conditions for the Synthesis of Quinoline **3a** from 2-Nitrobenzyl Alcohol (**1a**) with 1-Phenylethanol (**2a**)[a]



1a **2a** **3a**

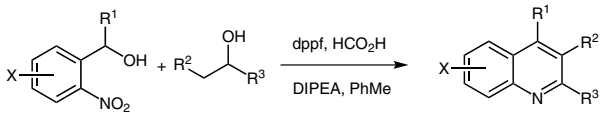
Entry	Catalyst	Base	Solvent	Temp (°C)	Yield (%)
1[b]	$Ru(PPh_3)_3Cl_2$	K_2CO_3	PhCl	150	25
2	dppf	–	PhCl	150	37
3	$Fe(NO_3)_3$	–	PhCl	150	13
4	$FeCl_3$	–	PhCl	150	10
5	$FeSO_4$	–	PhCl	150	9
6	$Fe(OTf)_3$	–	PhCl	150	0
7	$Fe(OH)_3$	–	PhCl	150	0
8	ferrocene	–	PhCl	150	0
9	ferrocene/Ph_3P	–	PhCl	150	17
10	Ph_3P	–	PhCl	150	0
11	$FeSO_4$/Ph_3P	–	PhCl	150	11
12	dppf	–	Me_2EtCOH	150	0
13	dppf	–	DMF	150	0
14	dppf	–	NMP	150	10
15	dppf	–	PhMe	150	55
16[c]	dppf	–	PhMe	150	33
17[d]	dppf	–	PhMe	150	55
18	dppf	–	PhMe	140	48
19	dppf	–	PhMe	160	29
20	dppf	Li_2CO_3	PhMe	150	61
21	dppf	Na_2CO_3	PhMe	150	62
22	dppf	K_2CO_3	PhMe	150	33
23	dppf	Cs_2CO_3	PhMe	150	33
24	dppf	KOH	PhMe	150	10
25	dppf	K_3PO_4	PhMe	150	27
26	dppf	*t*-BuOK	PhMe	150	22
27	dppf	$NaHCO_3$	PhMe	150	51
28	dppf	NaOH	PhMe	150	29
29	$Pd(PPh_3)Cl_2$	Na_2CO_3	PhMe	150	0
30	$Ir(PPh_3)_2(CO)Cl$	Na_2CO_3	PhMe	150	21
31	$CuH(PPh_3)$	Na_2CO_3	PhMe	150	10
32	$Ru(PPh_3)_3Cl_2$	Na_2CO_3	PhMe	150	22
33[e]	dppf	HCO_2Na	PhMe	150	43
34[e,f]	dppf	DIPEA	PhMe	150	73
35[e,f]	dppf/NiCl	DIPEA	PhMe	150	28
36[e,f]	dppf/$CoCl_2$	DIPEA	PhMe	150	18
37[e,f]	dppf/$PtCl_2$	DIPEA	PhMe	150	24
38[e,f]	dppf/$PdCl_2$	DIPEA	PhMe	150	15
39[e,f]	dppf/$RuCl_3$	DIPEA	PhMe	150	8
40[e,f]	–	DIPEA	PhMe	150	0
41[e,g]	dppf	–	PhMe	150	52
42[e,h]	dppf	DIPEA	PhMe	150	23
43[e,f,i]	dppf	DIPEA	PhMe	150	72

[a] General conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (5 mol%), base (0. 5 mmol), solvent (1.0 mL), under argon, 1 d.
[b] 1.65 mmol of **2a** was used.
[c] 3 mol% of dppf was used.
[d] 10 mol% of dppf was used.
[e] 0.6 mmol of **2a** was used.
[f] 1.0 mmol of HCO_2H and 0.75 mmol of DIPEA were used.
[g] 1.0 mmol of HCO_2H was used.
[h] 0.75 mmol of DIPEA was used.
[i] 1.53 g of **1a** was used.

With the optimized reaction conditions in hand, the scope of the reaction was subsequently investigated (Table 2). With the aromatic rings of 2-nitrobenzyl alcohols bearing hydrogen atoms (entry 1), electron-withdrawing groups (entries 2 and 3), and electron-donating groups (entry 4), 2-nitrobenzyl alcohols **1a**–**d** reacted smoothly with 1-phenylethanol (**2a**) and formic acid in the presence of DIPEA at 150 °C to afford quinolines **3a**–**d** in 53–73% yields within 1 day. 1-(2-Nitrophenyl)ethanol (**1e**) reacted with alcohol **2a** and formic acid uneventfully to afford 2,4-substituted quinoline **3e** under standard conditions, albeit at a relatively higher reaction temperature (entry 5). An obvious increase yield was observed with 2,2,2-trifluoro-1-(2-nitrophenyl)ethanol (**1f**) in comparison to 2-nitrobenzyl alcohol **1e** (entries 5 and 6). 1-(4-Fluorophenyl)ethanol (**2b**) and 1-(4-methoxyphenyl)ethanol (**2c**) reacted equally well with 2-nitrobenzyl alcohol **1f** and formic acid under standard conditions to give quinolines **3g**,**h** in 79% and 67% yields, respectively (entries 7 and 8). With the *para* position of the aromatic rings bearing electron-withdrawing groups such as fluoro, chloro, and bromo, benzyl alcohols **2b**,**d**,**e** reacted smoothly with 2-nitrobenzyl alcohol **1a** and formic acid to afford quinolines **3i**–**k** in good yields (entries 9–11). With an electron-donating group such as a methoxy group at the *para* position of the aromatic ring, benzyl alcohol **2c** reacted with 2-nitrobenzyl alcohol **1a** and formic acid to afford quinoline **3l** with decreased yield (cf. entries 1 and 12). *ortho*-Substituted benzyl alcohols **2f**,**g** and a *meta*-substituted benzyl alcohol **2h** were also investigated, which reacted with 2-nitrobenzyl alcohol (**1a**) and formic acid under standard conditions to afford quinolines **3m**–**o** in moderate yields (entries 13–15). By treatment of 1-(4-tolyl)propan-1-ol (**2i**) with 2-nitrobenzyl alcohol (**1a**) and formic acid under standard conditions, 2-substituted quinoline **3p** was obtained in 60% yield (entry 16). Primary aliphatic alcohol

2j reacted smoothly with 2-nitrobenzyl alcohol **1a** and formic acid under standard conditions to afford 3-substituted quinoline **3q** in 68% yield (entry 17). Only one quinoline regioisomer **3r** was obtained (62% yield) when a non-symmetric secondary aliphatic alcohol (**2j**) was used (entry 18), demonstrating excellent regioselectivity.

Table 2 Synthesis of Various Quinolines [a]



1 2 3

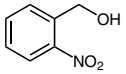
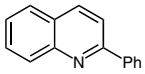
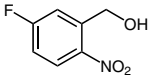
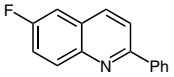
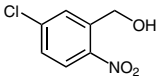
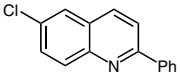
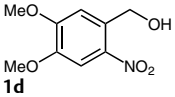
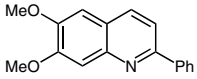
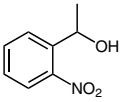
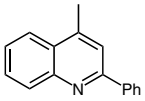
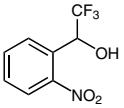
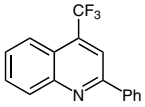
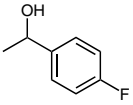
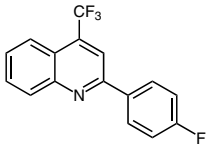
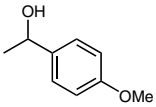
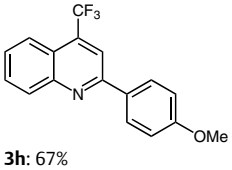
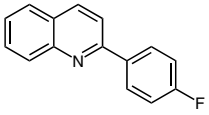
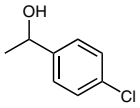
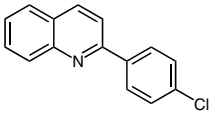
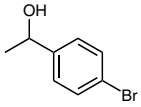
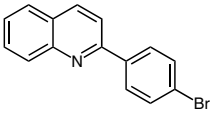
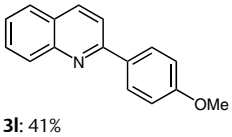
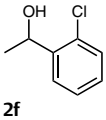
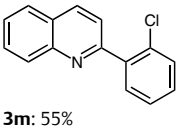
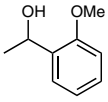
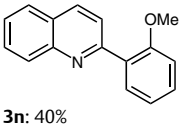
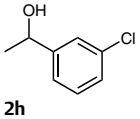
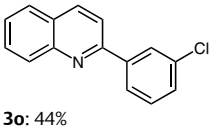
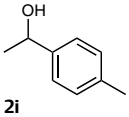
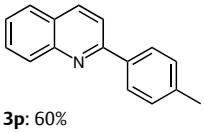
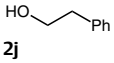
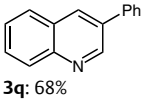
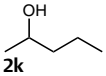
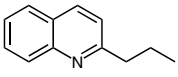
Entry	1	2	Product **3**: yield
1	 **1a**	 **2a**	 **3a**: 73%
2	 **1b**	**2a**	 **3b**: 61%
3	 **1c**	**2a**	 **3c**: 53%
4	 **1d**	**2a**	 **3d**: 70%
5[b]	 **1e**	**2a**	 **3e**: 39%
6	 **1f**	**2a**	 **3f**: 73%
7	**1f**	 **2b**	 **3g**: 79%
8	**1f**	 **2c**	 **3h**: 67%

Table 2 (continued)

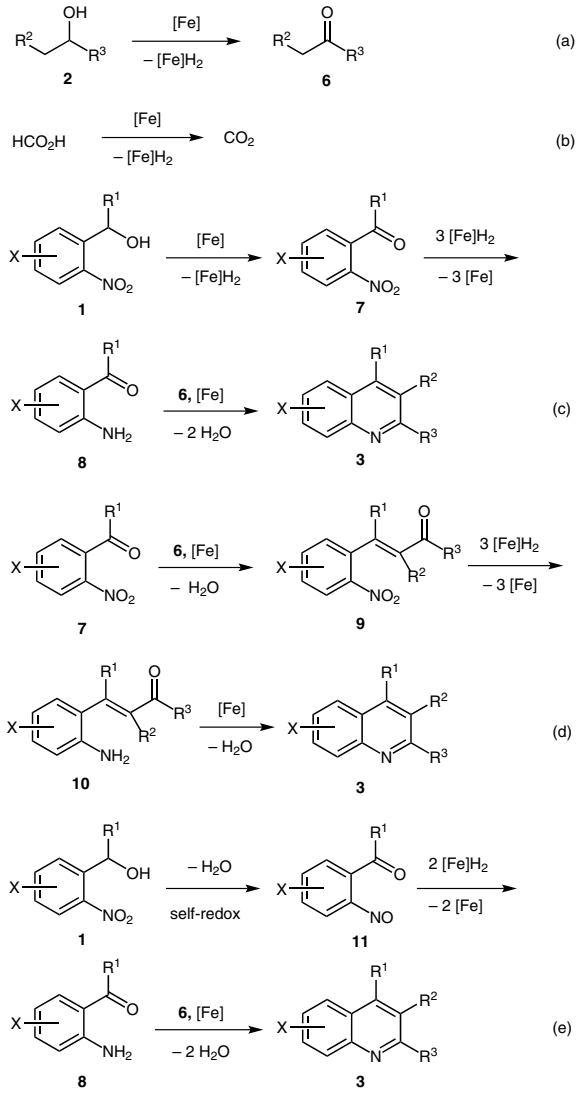
Entry	1	2	Product 3: yield
9	1a	2b	 **3i**: 66%
10	1a	 **2d**	 **3j**: 59%
11	1a	 **2e**	 **3k**: 70%
12	1a	**2c**	 **3l**: 41%
13	1a	 **2f**	 **3m**: 55%
14	1a	 **2g**	 **3n**: 40%
15	1a	 **2h**	 **3o**: 44%
16	1a	 **2i**	 **3p**: 60%
17	1a	 **2j**	 **3q**: 68%
18	1a	 **2k**	 **3r**: 62%

[a] General conditions: **1** (0.5 mmol), **2** (0.6 mmol), HCO_2H (1.0 mmol), DIPEA (0.75 mmol), dppf (5 mol%), toluene (1.0 mL), under argon, 150 °C, 1 d.
[b] The reaction was performed at 170 °C for 1 d.

The reaction mechanism of this quinoline synthetic method was next studied, and representative results are illustrated in Scheme 2. Reduction of nitrobenzene (**4a**) to aniline (**5a**) with 1-phenylethanol (**2a**, 1.2 equiv) and formic acid (2 equiv) did not take place in the presence of dppf (5 mol%) and DIPEA (1.5 equiv) in toluene at 150 °C, and nitrobenzene (**4a**) was recovered [Scheme 2 (a)], indicating that reduction of simple nitrobenzenes is a difficult process under these conditions. Instead, acetophenone (**6a**) could be detected in this reaction, even in the absence of nitrobenzene **4a** [Scheme 2 (b)], indicating that dehydrogenation of benzyl alcohols is a relatively easy process compared to the reduction of simple nitrobenzenes under these conditions. By treating 2-nitrobenzyl alcohol (**1a**) in the presence of dppf (5 mol%) and DIPEA (1.5 equiv) in toluene at 150 °C for 4 hours, 2-nitrobenzaldehyde (**7a**) was obtained in 60% yield [Scheme 2 (c)]. As the redox reaction of 2-nitrobenzaldehyde with alcohols could take place to afford quinolines,[11a] reduction of 2-nitrobenzaldehyde (**7a**) to the potential 2-aminobenzaldehyde intermediate should take place. Considering the 2-aminobenzaldehyde intermediate might be unstable and degraded under the above conditions and thus was not isolated, various 2-nitrobenzaldehyde substrates were next screened to obtain a relatively stable 2-aminobenzaldehyde. In one case, for example, 2-amino-5-chlorobenzaldehyde (**8c**) was obtained in 46% yield by treating 2-nitro-5-chlorobenzaldehyde (**7c**) with formic acid (6 equiv) in the presence of dppf (5 mol%) and DIPEA (4.5 equiv) in toluene at 150 °C for 4 hours [Scheme 2 (d)].

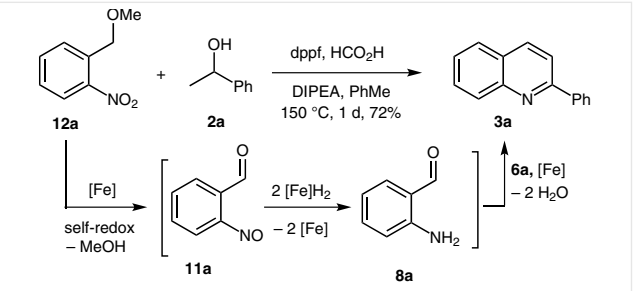
2-Amino-5-chlorobenzaldehyde (**8c**) reacted with acetophenone (**6a**) at 140 °C for 1 day under otherwise the same conditions to afford quinoline **3c** in 37% yield [Scheme 2 (e)]. There was a decrease in the yield with the direct use of unstable 2-amino-5-chlorobenzaldehyde (**8c**) in comparison to the use of in situ generated **8c** [Scheme 2 (e), and Table 2, entry 3], reflecting the importance of the in situ generated 2-aminobenzaldehyde strategy to this reaction.

Based on the above results, a possible reaction mechanism is illustrated in Scheme 3. Dehydrogenation of alcohols **2** [Scheme 3 (a)] and formic acid [Scheme 3 (b)] in the presence of the [Fe] catalyst, dppf, provides carbonyl compounds **6** and two equivalents of $[Fe]H_2$. Dehydrogenation of the alcohol moiety of 2-nitrobenzyl alcohols **1** gives another equivalent of $[Fe]H_2$ [Scheme 3 (c)]. The above three equivalents of $[Fe]H_2$ together facilitate the reduction of the nitro moiety of 2-nitrobenzyl alcohols **1** and thereby form 2-aminobenzaldehydes **8**, in which $[Fe]H_2$ is converted back into [Fe] [Scheme 3 (c)]. Finally, annulation of 2-aminobenzaldehydes **8** with compounds **6** in the presence of the [Fe] catalyst affords quinolines **3** [Scheme 3 (c)]. On the other hand, the aldol reaction between compounds **7** and carbonyl compounds **6** might also take place to give compounds **9**, which undergo nitro reduction and subsequent annulation to afford quinolines **3** [Scheme 3 (d)]. It was reported that 2-nitrobenzyl alcohols **1** could be converted into 2-nitrosobenzaldehydes **11** via a dehydrating self-redox rearrangement under photochemical or non-photochemical reaction conditions [Scheme 3 (e)].[18] Reduction of 2-nitrosobenzaldehydes **11** to 2-aminobenzaldehydes **8** with two equivalents of $[Fe]H_2$, which are generated from the dehydrogenation of alcohols **2** [Scheme 3 (a)] and formic acid [Scheme 3 (b)], followed by Friedländer annulation with carbonyl compounds **6** might be also possible to afford quinolines **3** [Scheme 3 (e)]. The failure detection of the potential 2-nitrosobenzaldehyde intermediates **11** might be due to their much slower formation than their conversion into 2-aminobenzaldehydes **8**. It was reported that 2-nitrobenzyl methyl ethers could also be converted into 2-nitrosobenzaldehydes via a methanol-releasing self-redox rearrangement.[19] If 2-nitrosobenzaldehydes **11** were indeed in-



Scheme 3 Proposed mechanism

volved the intermediates, quinolines **3** could be also formed when 2-nitrobenzyl methyl ethers **12** were used instead of 2-nitrobenzyl alcohols **1** under otherwise identical conditions. Accordingly, the condensation of 2-nitrobenzyl methyl ether (**12a**), formic acid and 1-phenylethanol (**2a**) was performed under standard conditions as shown in Table 2, which afford quinoline **3a** in 72% yield (Scheme 4).



Scheme 4 An additional verification experiment

In conclusion, we have developed an iron-catalyzed redox condensation of alcohols with 2-nitrobenzyl methyl ether/2-nitrobenzyl alcohols, which provides a shortcut to quinolines from stable and easily available starting materials. Obviously, this reaction goes smoothly with a smaller amount of alcohols in comparison to the previous reports (i.e., 1.2 equiv versus 3.3–4 equiv, Scheme 1),[11] and carbon dioxide and water are the only side products. These characteristics agree well with the principles of green and sustainable chemistry. Moreover, the reaction does not require an expensive ruthenium catalyst, and thus would facilitate its practical applications. Further mechanistic investigations as well as applications of this method are in progress in our laboratory.

Common reagents and materials were purchased from commercial sources and were used without further purification. Organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. All experiments were carried out under an argon atmosphere in flame-dried glassware using standard inert techniques for introducing reagents and solvents unless otherwise noted. TLC plates were visualized by exposure to UV light. IR spectra were recorded by using an Electrothemal Nicolet 380 spectrophotometer. HRMS were recorded by using an Electrothemal LTQ-Orbitrap mass spectrometer. Elemental analyses were performed on Vario EL III elementary analyzer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained by using a Bruker Avance III 400 MHz NMR spectrometer referenced to solvent or residual solvent [$CHCl_3$: δ = 7.26 (^{1}H) and $CDCl_3$: δ = 77.0 (^{13}C)].

Quinolines 3; General Procedure

The mixture of 2-nitrobenzyl alcohol **1a**–**f** (0.5 mmol), alcohol **2a**–**k** (0.6 mmol), HCO_2H (53 μL, 1.0 mmol), DIPEA (125 μL, 0.75 mmol), and dppf (14.1 mg, 0.025 mmol) in toluene (1.0 mL) was stirred at 150 °C (screw-capped vial) for 1 d under argon, cooled to r.t., then water (5 mL) was added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford the desired quinoline **3a**–**r**.

2-Phenylquinoline (3a)

White solid; yield: 74.9 mg (73%); mp 82–84 °C (Lit.[5b] 81.9–83.6 °C).

FTIR (film): 2922, 2851, 1598, 1554, 1493, 1446, 1423, 1320, 1285, 1256, 1177, 1028, 831, 813, 773 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26–8.16 (m, 4 H), 7.88 (d, *J* = 8.6 Hz, 1 H), 7.83 (d, *J* = 8.1 Hz, 1 H), 7.74 (t, *J* = 7.8 Hz, 1 H), 7.58–7.44 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 148.1, 139.4, 136.9, 129.7, 129.6, 129.4, 128.8, 127.6, 127.4, 127.2, 126.3, 119.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{11}NNa$: 228.0784; found: 228.0761.

6-Fluoro-2-phenylquinoline (3b)

Pale yellow solid; yield: 68.1 mg (61%); mp 128–130 °C (Lit.[20] 128–131 °C).

FTIR (film): 2921, 2851, 1606, 1555, 1510, 1493, 1447, 1342, 1280, 1238, 1143, 1114, 1075, 963, 920, 871, 836, 780, 758, 693 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.13 (m, 4 H), 7.89 (d, *J* = 8.6 Hz, 1 H), 7.58–7.41 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (d, $^1J_{C-F}$ = 246.7 Hz, 1 C), 156.7 (d, $^4J_{C-F}$ = 2.7 Hz, 1 C), 145.1, 139.1, 136.3 (d, $^4J_{C-F}$ = 5.0 Hz, 1 C), 132.0 (d, $^3J_{C-F}$ = 9.0 Hz, 1 C), 129.5, 128.9, 127.7 (d, $^3J_{C-F}$ = 10.0 Hz, 1 C), 127.5, 119.9 (d, $^2J_{C-F}$ = 25.6 Hz, 1 C), 119.7, 110.5 (d, $^2J_{C-F}$ = 21.6 Hz, 1 C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}FNNa$: 246.0689; found: 246.0679.

6-Chloro-2-phenylquinoline (3c)

Pale yellow solid; yield: 63.5 mg (53%); mp 133–135 °C (Lit.[20] 134–137 °C).

FTIR (film): 2920, 2849, 1646, 1596, 1548, 1485, 1469, 1445, 1420, 1319, 1280, 1130, 1076, 970, 876, 833, 783, 755, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19–8.11 (m, 4 H), 7.90 (d, *J* = 8.6 Hz, 1 H), 7.81 (s, 1 H), 7.67 (d, *J* = 8.6 Hz, 1 H), 7.58–7.45 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 146.3, 138.9, 136.1, 132.1, 131.1, 130.7, 129.7, 128.9, 127.7, 127.6, 126.1, 119.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}ClNNa$: 262.0394; found: 262.0379.

6,7-Dimethoxy-2-phenylquinoline (3d)

Pale yellow solid; yield: 92.8 mg (70%); mp 132–134 °C (Lit.[11a] 132–134 °C).

FTIR (film): 2923, 1623, 1597, 1496, 1463, 1435, 1409, 1390, 1340, 1241, 1211, 1162, 1131, 1054, 1026, 1006, 858, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17–8.09 (m, 3 H), 7.77–7.42 (m, 5 H), 7.08 (s, 1 H), 4.09 (s, 3 H), 4.37 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 152.4, 149.5, 145.1, 139.8, 134.6, 128.61, 128.55, 127.0, 122.5, 116.9, 108.2, 104.8, 55.9, 55.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{16}NO_2$: 266.1176; found: 266.1172.

4-Methyl-2-phenylquinoline (3e)

Pale yellow solid; yield: 42.7 mg (39%); mp 65–67 °C (Lit.[21] 65–67 °C).

FTIR (film): 2922, 2851, 1597, 1551, 1509, 1495, 1451, 1348, 1079, 1029, 861, 769, 694 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 1 H), 8.19 (d, *J* = 7.2 Hz, 2 H), 7.97 (d, *J* = 8.1 Hz, 1 H), 7.77–7.46 (m, 6 H), 2.73 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 148.1, 144.7, 139.8, 130.3, 129.2, 129.1, 128.7, 127.5, 127.2, 125.9, 123.5, 119.6, 18.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}N$: 220.1121; found: 220.1120.

2-Phenyl-4-(trifluoromethyl)quinoline (3f)

Pale yellow form; yield: 99.7 mg (73%).

FTIR (film): 2926, 2854, 1609, 1439, 1371, 1359, 1137, 1125, 865, 768, 695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.36–8.17 (m, 5 H), 7.85–7.81 (m, 1 H), 7.68–7.51 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 148.8, 138.0, 135.1 (q, $^2J_{C-F}$ = 30.8 Hz, 1 C), 130.7, 130.4, 130.0, 129.1, 129.0, 127.9, 127.3, 123.9, 123.2 (q, $^1J_{C-F}$ = 273.6 Hz, 1 C), 115.9 (q, $^3J_{C-F}$ = 7.3 Hz, 1 C).

Anal. Calcd for $C_{16}H_{10}F_3N$: C, 70.33; H, 3.69; N, 5.13. Found: C, 70.49; H, 3.52; N, 5.30.

2-(4-Fluorophenyl)-4-(trifluoromethyl)quinoline (3g)

Pale yellow form; yield: 115.0 mg (79%).

FTIR (film): 2924, 2853, 1601, 1506, 1431, 1373, 1358, 1229, 1136, 1112, 872, 841, 761 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.17–8.02 (m, 5 H), 7.74–7.70 (m, 1 H), 7.58–7.54 (m, 1 H), 7.16–7.12 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2 (d, $^1J_{C-F}$ = 248.9 Hz, 1 C), 155.4, 149.0, 135.2 (q, $^2J_{C-F}$ = 31.3 Hz, 1 C), 134.5 (d, $^3J_{C-F}$ = 3.2 Hz, 1 C), 130.5, 129.5, 129.4, 127.9, 123.85, 123.83, 123.5 (q, $^1J_{C-F}$ = 273.2 Hz, 1 C), 116.0 (d, $^2J_{C-F}$ = 21.7 Hz, 1 C), 115.5 (q, $^3J_{C-F}$ = 5.3 Hz, 1 C).

Anal. Calcd for $C_{16}H_9F_4N$: C, 65.98; H, 3.11; N, 4.81. Found: C, 66.10; H, 3.07; N, 4.93.

2-(4-Methoxyphenyl)-4-(trifluoromethyl)quinoline (3h)

Pale yellow form; yield: 101.5 mg (67%).

FTIR (film): 2928, 2839, 1604, 1551, 1509, 1463, 1432, 1376, 1357, 1268, 1252, 1176, 1135, 1115, 1033, 870, 833, 760 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.11 (m, 5 H), 7.81–7.77 (m, 1 H), 7.64–7.60 (m, 1 H), 7.07 (d, *J* = 8.8 Hz, 2 H), 3.90 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 156.1, 149.1, 134.8 (q, $^2J_{C-F}$ = 31.0 Hz, 1 C), 130.9, 130.4, 130.3, 128.9, 127.4, 123.8, 123.6 (q, $^1J_{C-F}$ = 272.9 Hz, 1 C), 115.5 (q, $^3J_{C-F}$ = 5.2 Hz, 1 C), 114.4, 113.6, 55.4.

Anal. Calcd for $C_{17}H_{12}F_3NO$: C, 67.32; H, 3.99; N, 4.62. Found: C, 67.41; H, 3.84; N, 4.81.

2-(4-Fluorophenyl)quinoline (3i)

Pale yellow solid; yield: 73.6 mg (66%); mp 93–95 °C (Lit.[22] 94–95 °C).

FTIR (film): 2920, 2849, 1592, 1497, 1431, 1124, 1097, 852, 820, 788, 757, 719 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.13 (m, 4 H), 7.83–7.69 (m, 3 H), 7.52 (t, *J* = 7.3 Hz, 1 H), 7.25–7.17 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8 (d, $^1J_{C-F}$ = 247.4 Hz, 1 C), 156.1, 148.1, 136.9, 135.7 (d, $^4J_{C-F}$ = 2.8 Hz, 1 C), 129.8, 129.5, 129.4 (d, $^3J_{C-F}$ = 8.3 Hz, 1 C), 127.4, 127.0, 126.3, 118.5, 115.4 (d, $^2J_{C-F}$ = 22.2 Hz, 1 C).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}FNNa$: 246.0689; found: 246.0673.

2-(4-Chlorophenyl)quinoline (3j)

White solid; yield: 70.7 mg (59%); mp 113–115 °C (Lit.[5b] 114.8–116.2 °C).

FTIR (film): 2919, 2849, 1659, 1631, 1593, 1469, 1429, 816, 788, 752, 715 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.14 (m, 2 H), 8.06 (d, *J* = 8.1 Hz, 2 H), 7.85–7.79 (m, 2 H), 7.74 (t, *J* = 7.2 Hz, 1 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 148.2, 138.4, 137.0, 131.9, 129.8, 129.7, 129.1, 127.5, 127.2, 126.5, 123.9, 118.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}ClNNa$: 262.0394; found: 262.0377.

2-(4-Bromophenyl)quinoline (3k)

White solid; yield: 99.4 mg (70%); mp 121–123 °C (Lit.[23] 121–122 °C).

FTIR (film): 2920, 2850, 1632, 1594, 1572, 1469, 1429, 1317, 1126, 1073, 1006, 817, 788, 752, 716 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.4 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 1 H), 8.06 (d, *J* = 7.1 Hz, 2 H), 7.87–7.81 (m, 2 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 7.66 (d, *J* = 7.1 Hz, 2 H), 7.54 (t, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 148.2, 138.4, 137.0, 132.0, 129.9, 129.7, 129.1, 127.5, 127.3, 126.5, 124.0, 118.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}BrNNa$: 305.9889; found: 305.9875.

2-(4-Methoxyphenyl)quinoline (3l)

White solid; yield: 48.2 mg (41%); mp 123–125 °C (Lit.[5b] 123.7–125.6 °C).

FTIR (film): 2920, 2850, 1645, 1597, 1499, 1431, 1289, 1252, 1176, 1031, 819, 790, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.13 (m, 4 H), 7.86–7.77 (m, 2 H), 7.72 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.4 Hz, 1 H), 7.05 (d, *J* = 8.2 Hz, 2 H), 3.89 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 156.8, 147.9, 147.2, 136.9, 129.7, 129.3, 129.0, 127.4, 126.9, 126.0, 118.6, 114.3, 55.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO$: 236.1070; found: 236.1072.

2-(2-Chlorophenyl)quinoline (3m)

White solid; yield: 65.9 mg (55%); mp 71–72°C (Lit.[24] 74–78°C).

FTIR (film): 2923, 2851, 1618, 1596, 1553, 1505, 1431, 1315, 1283, 1240, 1077, 879, 827, 780, 753 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.25–8.17 (m, 3 H), 8.05–8.02 (m, 1 H), 7.84–7.72 (m, 3 H), 7.57–7.52 (m, 1 H), 7.45–7.43 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6, 148.1, 141.2, 137.1, 134.9, 130.0, 129.9, 129.7, 129.3, 127.7, 127.4, 127.3, 126.6, 125.6, 118.6.

Anal. Calcd for $C_{15}H_{10}ClN$: C, 75.16; H, 4.21; N, 5.84. Found: C, 75.29; H, 4.08; N, 5.96.

2-(2-Methoxyphenyl)quinoline (3n)

Pale yellow solid; yield: 47.0 mg (40%); mp 57–59 °C (Lit.[25] 59 °C).

FTIR (film): 2920, 2850, 1599, 1581, 1554, 1504, 1491, 1461, 1437, 1421, 1315, 1259, 1232, 1181, 1127, 1063, 1023, 833, 790, 756, 681 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.5 Hz, 1 H), 8.18 (d, *J* = 8.0 Hz, 1 H), 7.93–7.82 (m, 3 H), 7.73 (t, *J* = 7.3 Hz, 1 H), 7.55 (t, *J* = 7.0 Hz, 1 H), 7.44 (t, *J* = 7.3 Hz, 1 H), 7.14 (t, *J* = 7.0 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 3.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3, 156.8, 135.7, 131.6, 130.6, 129.5, 129.1, 127.4, 127.0, 126.4, 123.5, 121.3, 111.5, 55.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}NO$: 236.1070; found: 236.1066.

2-(3-Chlorophenyl)quinoline (3o)

Pale yellow solid; yield: 52.7 mg (44%); mp 66–68 °C (Lit.[23] 67–69 °C).

FTIR (film): 2922, 2851, 1659, 1597, 1554, 1506, 1481, 1433, 1315, 1284, 1241, 1078, 875, 828, 796, 781, 755, 694 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.32–8.18 (m, 3 H), 8.10–7.54 (m, 4 H), 7.61–7.44 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6, 148.1, 141.3, 136.9, 134.9, 130.0, 129.8, 129.7, 129.2, 127.6, 127.4, 127.3, 126.6, 125.5, 118.6.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{10}ClNNa$: 262.0394; found: 262.0382.

2-(4-Tolyl)quinoline (3p)

Pale yellow oil; yield: 69.9 mg (60%).

FTIR (film): 2922, 2851, 1659, 1614, 1598, 1489, 1441, 1410, 1373, 1271, 1006, 902, 833, 808, 787, 755, 730, 616 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.0 Hz, 1 H), 8.04 (s, 1 H), 7.78 (d, *J* = 7.8 Hz, 1 H), 7.67 (t, *J* = 7.4 Hz, 1 H), 7.54–7.48 (m, 3 H), 7.31 (d, *J* = 7.0 Hz, 2 H), 2.48 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 146.2, 138.1, 137.5, 136.9, 129.2 (2 C), 128.9 (2 C), 128.8, 127.4, 126.6, 126.3, 21.2, 20.5.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{15}NNa$: 256.1097. Found: 256.1085.

3-Phenylquinoline (3q)

Pale yellow solid; yield: 69.7 mg (68%); mp 49–51 °C (Lit.[26] 49–50 °C).

FTIR (film): 2922, 2851, 1659, 1633, 1493, 1469, 1449, 1412, 1363, 1341, 1125, 1077, 1026, 954, 787, 762, 697 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.07 (s, 1 H), 8.18 (s, 1 H), 8.06 (d, *J* = 7.7 Hz, 1 H), 7.75 (d, *J* = 7.3 Hz, 1 H), 7.61–7.30 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.5, 146.9, 137.6, 133.8, 133.4, 129.4, 129.1, 128.9, 128.1, 128.0, 127.9, 127.3, 127.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{11}NNa$: 228.0784; found: 228.0776.

2-Propylquinoline (3r)

Colorless oil; yield: 53.0 mg (62%).

FTIR (film): 2960, 2929, 2871, 1618, 1601, 1561, 1508, 1464, 1426, 1310, 1116, 825, 755 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.3 Hz, 1 H), 8.06 (d, *J* = 8.2 Hz, 1 H), 7.78–7.46 (m, 3 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 2.96 (t, *J* = 7.8 Hz, 2 H), 1.90–1.79 (m, 2 H), 1.02 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 147.5, 136.4, 129.4, 128.5, 127.4, 126.7, 125.7, 121.3, 41.0, 23.2, 13.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{14}N$: 172.1121; found: 172.1113.

2-Nitrobenzaldehyde (7a)

A mixture of 2-nitrobenzyl alcohol (**1a**, 78.1 mg, 0.5 mmol), DIPEA (125 μL, 0.75 mmol), and dppf (14.1 mg, 5 mol%) in toluene (1.0 mL) was stirred at 150 °C (screw-capped vial) for 4 h under argon, cooled to r.t., then water (5 mL) was added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography (silica gel, 100–200 mesh) to afford **7a** (45.8 mg, 60%) as a bright yellow solid; mp 43–44 °C.

FTIR (film): 3104, 2923, 1697, 1605, 1572, 1524, 1446, 1397, 1344, 1270, 1182, 1141, 1080, 871, 856, 819, 788, 737, 693 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.34 (s, 1 H), 8.06 (d, *J* = 7.6 Hz, 1 H), 7.89 (d, *J* = 7.6 Hz, 1 H), 7.80–7.72 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.0, 149.4, 134.0, 133.6, 131.1, 129.5, 124.3.

Anal. Calcd for $C_7H_5NO_3$: C, 55.63; H, 3.33; N, 9.27. Found: C, 55.75; H, 3.19; N, 9.48.

2-Amino-5-chlorobenzaldehyde (8c)

A mixture of 5-chloro-2-nitrobenzaldehyde (**7c**, 95.6 mg, 0.5 mmol), HCO_2H (159 μL, 3.0 mmol), DIPEA (374 μL, 2.25 mmol), and dppf (14.1 mg, 0.025 mmol) in toluene (1.0 mL) was stirred at 150 °C (screw-capped vial) for 4 h under argon, cooled to r.t., then water (5 mL) was added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography (silica gel, 100–200 mesh) to afford **8c** (35.8 mg, 46%) as a yellow solid; mp 72–73 °C.

FTIR (film): 3465, 3352, 1689, 1660, 1617, 1590, 1551, 1474, 1388, 1311, 1186, 1157, 904, 819, 728, 642 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1 H), 7.42 (s, 1 H), 7.23 (d, *J* = 8.8 Hz, 1 H), 6.60 (d, *J* = 8.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 148.3, 135.2, 134.2, 120.7, 119.2, 117.6.

Anal. Calcd for C_7H_6ClNO: C, 54.04; H, 3.89; N, 9.00. Found: C, 54.26; H, 3.71; N, 9.15.

6-Chloro-2-phenylquinoline (3c) from 2-Amino-5-chlorobenzaldehyde (8c)

A mixture of 2-aminobenzaldehyde **8c** (77.8 mg, 0.5 mmol), acetophenone (**6a**, 71 μL, 0.6 mmol), HCO_2H (53 μL, 1.0 mmol), DIPEA (125 μL, 0.75 mmol), and dppf (14.1 mg, 0.025 mmol) in toluene (1.0 mL) was stirred at 140 °C (screw-capped vial) for 1 d under argon, cooled to r.t., then water (5 mL) was added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography (silica gel, 100–200 mesh) to afford quinoline **3c** (44.3 mg, 37%).

2-Phenylquinoline (3a) from 2-Nitrobenzyl Methyl Ether (12a)

The mixture of 2-nitrobenzyl methyl ether (**12a**, 83.6 mg, 0.5 mmol), 1-phenylethanol (**2a**, 75 μL, 0.6 mmol), HCO_2H (53 μL, 1.0 mmol), DIPEA (125 μL, 0.75 mmol), and dppf (14.1 mg, 0.025 mmol) in toluene (1.0 mL) was stirred at 150 °C (screw-capped vial) for 1 d under argon, cooled to r.t., then water (5 mL) was added. The two layers were separated, and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed by brine, dried (Na_2SO_4), filtered, and concentrated. The residue was purified by flash chromatography (silica gel, 100–200 mesh) to afford quinoline **3a** (73.9 mg, 72%).

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Supporting Information

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