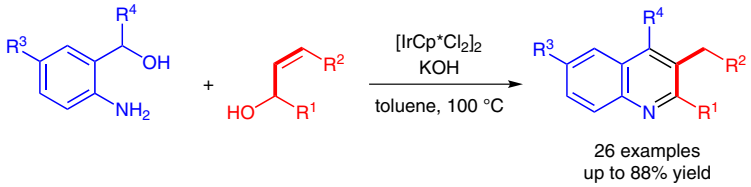
Synthesis S.-j. Chen et al. Paper

Synthesis of Quinolines from Allylic Alcohols via Iridium-Catalyzed Tandem Isomerization/Cyclization Combined with Potassium Hydroxide

Shu-jie Chen
Guo-ping Lu
Chun Cai*

Chemical Engineering College, Nanjing University of Science & Technology, 200 Xiaolingwei, Nanjing, Jiangsu 210094, P. R. of China
c.cai@mail.njust.edu.cn



Received: 23.10.2014
Accepted after revision: 19.12.2014
Published online: 28.01.2015
DOI: 10.1055/s-0034-1380110; Art ID: ss-2014-h0646-op

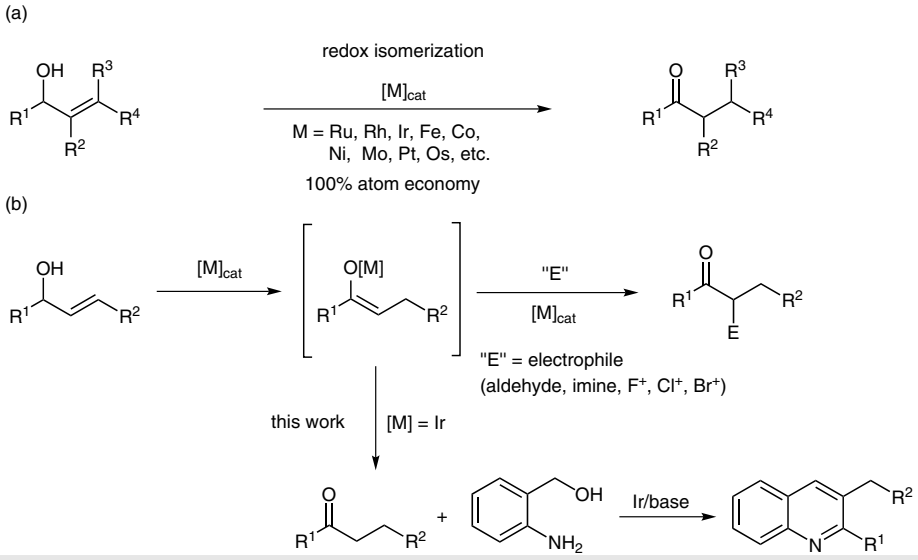
Abstract A new tandem catalytic process has been established for the synthesis of quinolines. This process utilizes the $[IrCp^*Cl_2]_2$/KOH catalyzed isomerization/cyclization of allylic alcohols with 2-aminobenzyl alcohol. Both the secondary and primary allylic alcohols were investigated in this catalytic system to afford different substituted quinoline derivatives in moderate to good yields. A mechanism study showed the reaction following a tandem process integrating isomerization of allylic alcohols and oxidative cyclization of 2-aminobenzyl alcohol.

Key words iridium, quinolines, allylic alcohol, isomerization, cyclization

Ketones and aldehydes, as one of the most important building blocks in organic chemistry, are widely used in the synthesis of natural products, drugs, and functional materials. Oxidation of the corresponding alcohols to ketones or aldehydes is a practical and efficient synthetic route, but it usually requires stoichiometric amount of oxidant or liberates hydrogen as a waste product, which is not consistent with the demands of green chemistry and atom economy. In this regard, the internal redox isomerization of allylic alcohols is an atom-economic and environmentally friendly alternative that avoids the use of costly and/or toxic oxidants and maintains 100% atom economy. Transition-metal complexes derived from molybdenum and group 8, 9, and 10 metals have been predominantly employed for this transposition, with ruthenium and rhodium species showing the best performance [Scheme 1 (a)].[1] Reports on the iridium-catalyzed transposition of allylic alcohols are relatively rare.[2]

The tandem approach is an appealing strategy that utilizes two or more transformations of an organic substrate in a single procedure.[3] Furthermore, enolates are key intermediates in the isomerization process of allylic alcohols catalyzed by transition-metal complexes. In recent years there has been significant use of allylic alcohols as synthetic enolate equivalents in tandem isomerization/C–X bond formation reactions. The Grée,[4] Martín-Matute,[5] and Li groups[6] have performed much excellent work in this field. A series of electrophiles, including aldehydes, imines, F^+, Cl^+, and Br^+, have been used in the isomerization processes [Scheme 1 (b)].[4–6] In addition, allylic alcohols have also been developed as ketone equivalents in tandem isomerization/C–H activation and tandem isomerization/amination.[7,8]

Quinolines and their derivatives are heterocycles that play an important role in pharmaceutical and agricultural chemistry, as well as in the total synthesis of natural products.[9] A great many synthetic routes are documented for the formation of quinoline, such as Combes, Conrad–Limpach, Doebner–Miller, Friedländer, Skraup, Povarov, and Camps quinoline syntheses. Among them, the Friedländer annulation is one of the most simple and straightforward approaches for the synthesis of quinoline derivatives, but the existing drawback is that 2-aminobenzaldehyde is both expensive and unstable. In 2001, Shim and co-workers proposed a modified Friedländer quinoline synthesis that uses 2-aminobenzyl alcohol instead of 2-aminobenzaldehyde as the substrate. In their approach, 2-aminobenzyl alcohol is oxidatively cyclized with ketones via hydrogen-transfer processes by a ruthenium/potassium hydroxide catalytic system.[10] Since then, different transition-metal complexes derived from ruthenium,[11] palladium,[12] iridium,[13] rhodium,[14] and copper[15] have been synthesized and applied for the catalysis of this indirect Friedlander reaction.[16] In our previous work, we reported an iridium-catalyzed allylation of indoles utilizing allylic alcohols as the allylating agents.[17] Continuing our work of utilizing allylic alcohols as building blocks in organic synthesis, here, we wish to disclose an iridium/base catalytic system for indirect Friedländer quinoline synthesis that uses readily accessible allylic alcohols

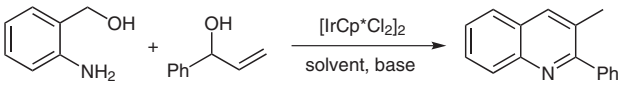


Scheme 1 Transformation of allylic alcohols

as the ketone precursors via iridium-catalyzed tandem isomerization/cyclization with 2-aminobenzyl alcohols to assemble the valuable substituted quinolines.

We began our studies by utilizing 2-aminobenzyl alcohol (**1a**) and allylic alcohol (**2a**) as the model substrates. Dichloro(pentamethylcyclopentadienyl)iridium dimer $[IrCp^*Cl_2]_2$,[18] introduced by Martín-Matute and co-workers in an iridium-catalyzed 1,3-hydrogen shift/fluorination of allylic alcohols,[5b] was chosen as the precatalyst. The results are summarized in Table 1. Treatment of **1a** with two equivalents of **2a** in the presence of catalytic amounts of $[IrCp^*Cl_2]_2$ (1 mol%) in toluene at 80 °C for 20 hours did not afford the desired product, but only the isomerization of allylic alcohol was observed (entry 1). When one equivalent of sodium hydroxide was added, 3-methyl-2-phenylquinoline (**3a**) was obtained in 23% yield (entry 2). Then screening of bases was carried out (entries 3–6); among the tested bases, potassium hydroxide was the most effective giving the product **3a** in 83% yield (entry 3). Organic base triethylamine and weak base sodium carbonate were totally ineffective in this transformation, and only the isomerization of allylic alcohol was observed (entries 5 and 6). A higher yield (93%) was obtained in a shorter period of time by elevating the temperature to 100 °C (entry 7). Dioxane, which was a superior solvent in the previous report, resulted in a low yield,[11a] while tetrahydrofuran afforded a moderate yield (entries 8 and 9). Attempts to decrease the reaction temperature and reduce the amount of potassium hydroxide resulted in low yields of product **3a** (entries 10 and 11). It should be noted that the yield of product **3a** dramatically reduced when the reaction was carried out under an atmosphere of air (entry 12). In addition, two equivalents of allylic alcohol **2a** were necessary to give satisfactory yields, using only one equivalent of **2a** resulted in a moderate yield (entry 13). In the absence of the iridium catalyst, **3a** was formed in a low yield (entry 14).

Table 1 Optimization of Reaction Conditions[a]



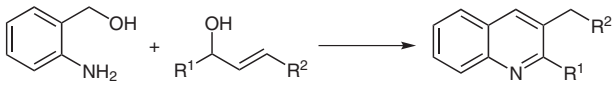
1a **2a** **3a**

Entry	Solvent	Base (mol%)	Temp (°C)	Time (h)	GC yield[b] (%) of **3a**
1	toluene	none	80	20	–[c]
2	toluene	NaOH (100)	80	20	23
3	toluene	KOH (100)	80	20	83
4	toluene	*t*-BuOK (100)	80	20	78
5	toluene	Et_3N (100)	80	20	–[c]
6	toluene	Na_2CO_3 (100)	80	20	–[c]
7	toluene	KOH (100)	100	12	93
8	dioxane	KOH (100)	100	12	37
9	THF	KOH (100)	100	12	53
10	toluene	KOH (10)	100	12	50
11	toluene	KOH (100)	60	12	6
12[d]	toluene	KOH (100)	100	12	10
13[e]	toluene	KOH (100)	100	12	62
14	toluene	KOH (100)	100	12	28

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[IrCp^*Cl_2]_2$ (1 mol% based on **1a**), base (1 equiv), solvent (1 mL), N_2.
[b] GC yield of **3a** based on **1a**.
[c] Not found.
[d] **2a** (0.2 mmol).
[e] Reaction was performed under an atmosphere of air.

To evaluate the scope of the reaction, a variety of secondary allylic alcohols **2a**–**o**, including α-aryl- and α-alkyl-substituted allylic alcohols substrates, were subjected to the optimized reaction conditions (Table 1, entry 7), as summarized in Table 2. The reactions of 2-aminobenzyl alcohol (**1a**) with electron-rich and electron-deficient α-aryl allylic alcohols **2c**–**h** containing *para*, *meta*, and *ortho* substitution occurred in 69–82% yield (entries 3–8). Disubstituted α-aryl allylic alcohols **2i** and **2j** reacted with **1a** smoothly to give the desired product **3i** and **3j** in 73% and 76% yields, respectively (entries 9 and 10). Heterocyclic substituted allylic alcohols **2k**–**m** also proved to be suitable substrates giving the corresponding products **3k**–**m** in good yields (entries 11–13). Among them, **3m** is a key building block of an efficient potent PI3K inhibitor.[19] The α-alkyl allylic alcohol pent-1-en-3-ol (**2n**) reacted with **1a** to give a moderate yield of the desired quinoline **3n** (entry 14), while reactions of cyclic allylic alcohol cyclohex-2-en-1-ol (**2o**) occurred in high yield (entry 15). In addition, substitution of the terminal position of the double bond by a phenyl group did not affect the transformation (entry 16). In the case of 5-phenylpent-1-en-3-ol (**2q**), the corresponding quinoline was obtained as a regioisomeric mixture of **3q**/**3q′**, favoring cyclization at the less-hindered α-methylene position [Scheme 2 (a)]. A starting material bearing two allylic alcohol functional groups **2r** was also investigated, it gave the corresponding product **3r** in 51% yield [Scheme 2 (b)]. Quinoline **3r** contains a bisquinolines structure that could act as a latent (N,C,N)-type pincer ligand in the metal catalytic and light-emitting materials.[20] It was noteworthy that α-aryl allylic alcohols, prepared from the corresponding aldehyde and vinylmagnesium bromide, are more diverse when compared with the corresponding α-aryl ketones.

Table 2 Iridium-Catalyzed Tandem Isomerization/Cyclization of Secondary Allylic Alcohols with 2-Aminobenzyl Alcohol (**1a**)[a]

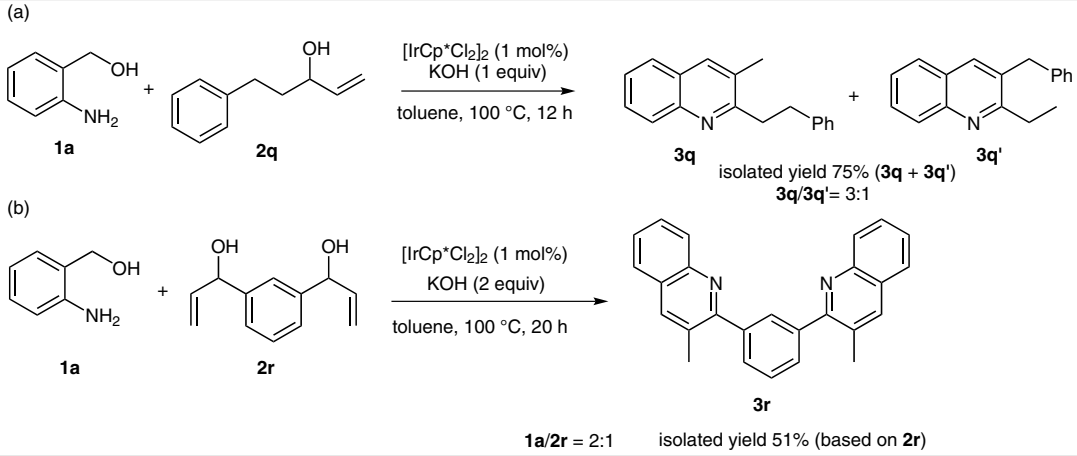


1a **2a–p** **3a–p**

Entry	**2**	R^1	R^2	Yield[b] (%) of **3**
1	**2a**	Ph	H	81 (**3a**)
2	**2b**	1-naphthyl	H	84 (**3b**)
3	**2c**	2-$MeOC_6H_4$	H	77 (**3c**)
4	**2d**	2-$F_3CC_6H_4$	H	82 (**3d**)
5	**2e**	3-$MeOC_6H_4$	H	78 (**3e**)
6	**2f**	3-$F_3CC_6H_4$	H	81 (**3f**)
7	**2g**	4-MeC_6H_4	H	75 (**3g**)
8	**2h**	4-ClC_6H_4	H	69 (**3h**)
9	**2i**	2,4-$Cl_2C_6H_3$	H	73 (**3i**)
10	**2j**	3,5-$(MeO)_2C_6H_3$	H	76 (**3j**)
11	**2k**	2-furyl	H	80 (**3k**)
12	**2l**	2-thienyl	H	75 (**3l**)
13	**2m**	2-pyridyl	H	78 (**3m**)
14	**2n**	Et	H	37 (**3n**)[c]
15	**2o**	$(CH_2)_3$		84 (**3o**)
16	**2p**	Ph	Ph	82 (**3p**)

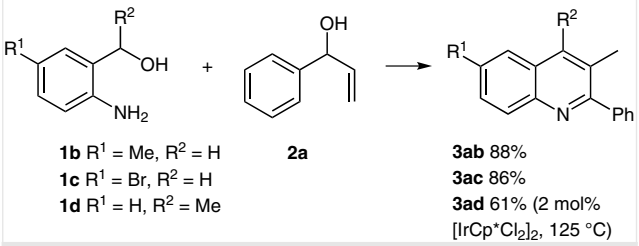
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $[IrCp^*Cl_2]_2$ (1 mol% based on **1a**), KOH (0.2 mmol), toluene (1 mL), 100 °C, 12 h, N_2.
[b] Isolated yield based on **1a**.
[c] **2n** (0.8 mmol) was used.

Several substituted 2-aminobenzyl alcohols were then examined, as summarized in Scheme 3. The substitution of the aromatic ring was studied, and quinolines **3ab** and **3ac** were obtained in good yields from the corresponding substituted 2-aminobenzyl alcohol **1b** and **1c** possessing elec-



Scheme 2 Transformation of allylic alcohols **2q** and **2r**

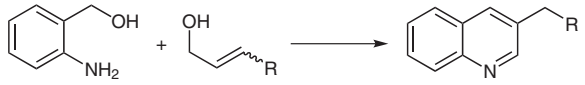
tron-donating and electron-withdrawing groups on the aromatic ring. The 1-(2-aminophenyl)ethanol **1d** also gave the desired quinoline **3ad** in 61% yield under a higher catalyst loading and temperature.



Scheme 3 Transformation of substituted 2-aminobenzyl alcohols

Next, the reactions of various primary allylic alcohols with 2-aminobenzyl alcohol **1a** were investigated (Table 3). Compared to the secondary allylic alcohols, the primary allylic alcohols needed a longer reaction time to achieve a satisfactory result (22 h vs. 12 h). Moreover, an aldol-type side reaction was observed in the reaction, which resulted in a slightly lower yield.[21]

Table 3 Iridium-Catalyzed Tandem Isomerization/Cyclization of Primary Allylic Alcohol with 2-Aminobenzyl Alcohol (**1a**)[a]

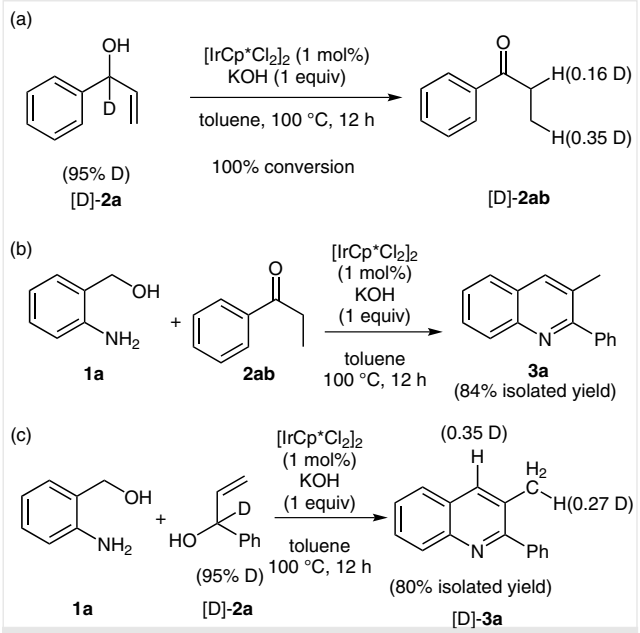


1a **2s–w** **3s–w**

Entry	2s–w	R	Quinoline	Yield[b] (%)
1	**2s**	H	**3s**	67
2	**2t**	Ph	**3t**	79
3	**2u**	3-MeOC$_6$H$_4$	**3u**	72
4	**2v**	4-MeC$_6$H$_4$	**3v**	65
5	**2w**	4-ClC$_6$H$_4$	**3w**	70

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), [IrCp*Cl$_2$]$_2$ (1 mol% based on **1a**), KOH (0.2 mmol), toluene (1 mL), 100 °C, N$_2$, 22 h.
[b] Isolated yield based on **1a**.

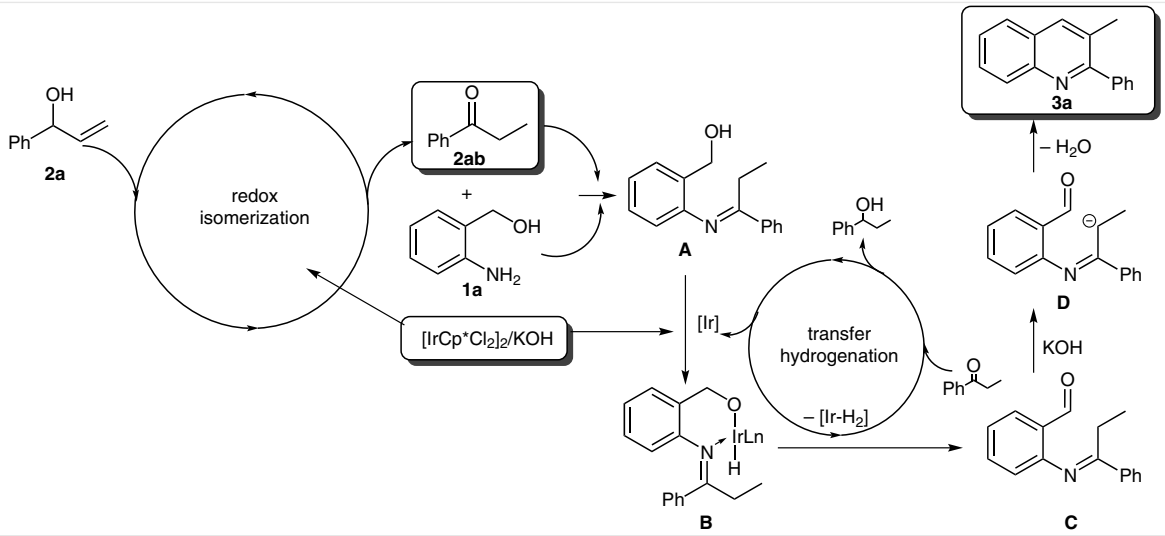
In order to obtain more information about the mechanism of this tandem isomerization–cyclization process. Three sets of experiments with deuterium-labeled allylic alcohol [D]-**2a** and propiophenone (**2ab**) were carried out. Firstly, in the absence of 2-aminobenzyl alcohol, the deuterium-labeled allylic alcohol [D]-**2a** isomerized to the corresponding ketone [D]-**2ab** under the reaction conditions. The location of 0.35 of one deuterium in the methyl group of propiophenone was easily deduced by a combination of mass and NMR spectra. Moreover, 16% D-incorporation was observed at one H of the methylene position. This indicated that the mechanism is not a strict intramolecular 1,3-hydrogen shift under this catalytic system [Scheme 4 (a)]. Then, a second experiment was performed starting from propiophenone (**2ab**) with the addition of 2-aminobenzyl alcohol which gave the corresponding quinoline **3a** in 84% yield [Scheme 4 (b)]. These results were consistent with our proposal that the reaction proceeded via a tandem isomerization/cyclization process. Finally, the third experiment was performed with the deuterated allylic alcohol [D]-**2a** and 2-aminobenzyl alcohol (**1a**); the corresponding quinoline [D]-**3a** was obtained in 80% yield and 0.37 of one deuterium in the methyl group of quinoline was easily deduced [Scheme 4 (c)]. Beyond this, approximately 35% D-incorporation in the 4-position of [D]-**3a** was also observed. This result indicated that the oxidation of the benzyl alcohol was reversible, and the Ir–H(D) species took part in this process. This is also a powerful evidence that [Ir] played an importance role in the oxidation of the benzyl alcohol, although transition-metal-free approaches have been developed for this transformation.[16,22]



Scheme 4 Transformation of substituted 2-aminobenzyl alcohols

Based on the results shown above and according to literature data,[13] we propose the mechanism shown in Scheme 5.

The reaction is initiated by the formation of propiophenone (**2ab**) from allylic alcohol **2a** via the iridium-catalyzed redox isomerization process.[1b] Then the propiophenone (**2ab**) reacted with the 2-aminobenzyl alcohol (**1a**) to form the ketimine **A**, which is then oxidized by the [Ir] species with another equivalent of **2ab** as hydrogen acceptor to give the corresponding aldehyde **C**.[13] Eventually, **C** converted into **3a** through a potassium hydroxide mediated intramolecular aldol-type condensation.



Scheme 5 A possible reaction pathway for the iridium-catalyzed tandem isomerization/cyclization of allylic alcohol **2a** with **1a**

In conclusion, we have reported the first synthesis of substituted quinolines from allylic alcohols and 2-aminobenzyl alcohols. A wide range of substrates include secondary and primary allylic alcohols were investigated using this catalytic system to afford different substituted quinoline derivatives in moderate to good yields. A mechanism studies revealed that the reaction proceed by an iridium-catalyzed tandem process. Firstly, the iridium-catalyzed isomerization of the allylic alcohols to the corresponding ketones that reacted with the 2-aminobenzyl alcohol to form ketimines. The ketimines were then oxidized to the corresponding aldehydes through a transfer hydrogenation process. Finally, a potassium hydroxide mediated intramolecular aldol-type condensation yielded the desired quinolines.

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a N_2 atmosphere. THF and toluene were freshly distilled from sodium benzophenone ketyl under N_2. TLC were performed on glass plates precoated with silica gel and visualization with UV light (254 nm). All melting points are uncorrected. Mass spectra were taken on a Finnigan TSQ Quantum-MS instrument. IR spectra were recorded on Thermo Scientific Nicolet iS10. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on an Avance 500 Bruker spectrometer operating at 500, 125, and 470 MHz in $CDCl_3$, respectively, with respect to internal TMS. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. GC analysis were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: N_2, FID detector. $[IrCp^*Cl_2]_2$[23] and deuterated allylic alcohol ([D]-**2a**)[24] were synthesized according to previous reports.

Quinolines 3; General Procedure

A mixture of 2-aminobenzyl alcohol **1** (0.2 mmol), allylic alcohol **2** (0.4 mmol), $[IrCp^*Cl_2]_2$ (0.0020 mmol, 1.0 mol%), and KOH (0.2 mmol) were dissolved in anhyd toluene (1 mL) in a 25-mL Schlenk tube. The system was flushed with N_2 and allowed to react at the specified temperature and for the specified time. The mixture was allowed to cool to r.t. and filtered through a short silica gel column (washed with EtOAc). Removal of the solvent left an oil that was separated by column chromatography (silica gel, EtOAc–hexane) to give the quinoline.

Secondary Allylic Alcohols; General Procedure[25]

In an oven-dried round-bottom flask, a solution of the aldehyde (10 mmol, 1 equiv) in anhyd THF (10 mL) was stirred for 10 min under N_2 at 0 °C. To the mixture, 1 M vinylmagnesium bromide in THF (12 mmol, 1.2 equiv) was added slowly. After 15 min the mixture was allowed to warm to r.t. and stirred for an additional 1–3 h. The reaction was quenched with sat. aq NH_4Cl solution and extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and evaporated to give the crude allylic alcohols **2a**–**n**,**q**–**r**, which were used in the next step without further purification.

1-Phenylprop-2-en-1-ol (2a)

Colorless oil; yield: 1313 mg (98%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.37 (m, 4 H), 7.34–7.30 (m, 1 H), 6.07 (ddd, *J* = 17.0, 10.2, 6.1 Hz, 1 H), 5.37 (d, *J* = 17.1 Hz, 1 H), 5.22 (d, *J* = 10.3 Hz, 2 H), 2.33 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.74, 140.37, 128.66, 127.84, 126.47, 115.21, 75.41.

(*E*)-3-(4-Chlorophenyl)prop-2-en-1-ol (2w); Typical Procedure[26]

To a solution of secondary allylic alcohol **2h** (1.0 mmol) in THF–H_2O (4:1, 5 mL), methanesulfonic acid (2.0 mmol) was added dropwise over 5 min at r.t. and stirring was continued at this temperature for 12 h (TLC monitoring). After complete conversion, the mixture was quenched with sat. $NaHCO_3$ solution (10 mL). The resulting mixture was extracted with Et_2O (3 × 10 mL). The combined organic layers

were washed with water, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (silica gel, EtOAc–hexane) to afforded **2w** (141 mg, 84%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.23 (m, 4 H), 6.55 (d, *J* = 15.9 Hz, 1 H), 6.32 (dtd, *J* = 15.8, 5.6, 2.2 Hz, 1 H), 4.30 (d, *J* = 5.6 Hz, 2 H), 2.04 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.22, 132.30, 128.74, 128.22, 127.76, 126.67, 62.46.

1,3-Diphenylprop-2-en-1-ol (2p)[27]

In an oven-dried round-bottom flask, a solution of chalcone (2 mmol, 1 equiv) in THF–MeOH (1:1, 10 mL) was stirred for 5 min at 0 °C. Then $NaBH_4$ (2.59 g, 2 mmol, 1.0 equiv) was added in one portion and the mixture is maintained at this temperature for 30 min. Then the solvent was removed under vacuum and the residue was dissolved in Et_2O (15 mL) and treated with 0.6 M HCl (1 mL). The organic layer was separated, washed with sat. $NaHCO_3$ until the aqueous phase had neutral pH and then sat. NaCl, and dried (anhyd $MgSO_4$). The solvent was removed under vacuum to afford **2p** (403 mg, 96%) as a colorless oil which was used without further purification.

3-Methyl-2-phenylquinoline (3a)[16a]

Colorless oil; yield: 35 mg (81%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 1 H), 8.04 (s, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.71–7.64 (m, 1 H), 7.64–7.58 (m, 2 H), 7.57–7.48 (m, 3 H), 7.48–7.43 (m, 1 H), 2.48 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.54, 145.60, 139.84, 135.81, 128.29, 127.88, 127.80, 127.33, 127.23, 126.63, 125.72, 125.45, 19.64.

3-Methyl-2-(naphthalen-1-yl)quinoline (3b)[28]

Colorless oil; yield: 45 mg (84%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 1 H), 8.10 (s, 1 H), 7.94 (t, *J* = 8.4 Hz, 2 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 7.74–7.67 (m, 1 H), 7.59 (dt, *J* = 10.4, 7.1 Hz, 2 H), 7.49 (ddd, *J* = 8.8, 8.1, 4.4 Hz, 2 H), 7.42–7.33 (m, 2 H), 2.21 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.46, 145.66, 137.50, 135.11, 132.75, 130.50, 129.78, 128.43, 127.83, 127.49, 127.39, 126.93, 125.87, 125.63, 125.40, 125.21, 124.94, 124.49, 124.44, 18.73.

2-(2-Methoxyphenyl)-3-methylquinoline (3c)[28]

Colorless oil; yield: 38 mg (77%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 8.4 Hz, 1 H), 7.91 (s, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.41–7.32 (m, 1 H), 7.31–7.24 (m, 1 H), 7.04 (t, *J* = 7.4 Hz, 1 H), 6.94 (d, *J* = 8.3 Hz, 1 H), 3.71 (s, 3 H), 2.25 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.34, 155.74, 145.62, 134.33, 130.04, 129.29, 128.70, 128.35, 127.38, 126.86, 125.76, 125.27, 120.03, 109.89, 54.44, 18.26.

3-Methyl-2-[2-(trifluoromethyl)phenyl]quinoline (3d)

White solid; yield: 47 mg (82%); mp 58–59 °C.

IR (neat): 751, 1107, 1121, 1312, 1736, 3062 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.4 Hz, 1 H), 8.02 (s, 1 H), 7.81 (dd, *J* = 7.9, 3.2 Hz, 2 H), 7.66 (dt, *J* = 15.4, 7.7 Hz, 2 H), 7.56 (dd, *J* = 14.3, 7.1 Hz, 2 H), 7.38 (d, *J* = 7.5 Hz, 1 H), 2.22 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.90, 144.95, 138.45, 134.96, 130.77, 129.22, 128.69, 128.32, 127.90, 127.35 (q, *J* = 32.5 Hz), 127.34, 126.93, 125.83, 125.79, 125.60, 123.02 (q, *J* = 272.6 Hz), 18.59.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –58.90.

MS (EI): *m*/*z* = 287 (M^+).

Anal. Calcd for $C_{17}H_{12}F_3N$: C, 71.07; H, 4.21; N, 4.88. Found: C, 71.25; H, 4.13; N, 5.11.

2-(3-Methoxyphenyl)-3-methylquinoline (3e)

Colorless oil; yield: 39 mg (78%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.4 Hz, 1 H), 8.04 (s, 1 H), 7.80 (d, *J* = 8.1 Hz, 1 H), 7.68 (dd, *J* = 11.3, 4.0 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.42 (t, *J* = 7.9 Hz, 1 H), 7.16 (dd, *J* = 10.6, 4.9 Hz, 2 H), 7.01 (dd, *J* = 8.1, 2.2 Hz, 1 H), 3.88 (s, 3 H), 2.48 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.34, 158.59, 145.45, 141.06, 135.86, 128.36, 128.23, 127.85, 126.66, 125.72, 125.51, 120.29, 113.36, 113.17, 54.37, 19.56.

MS (EI): *m*/*z* = 249 (M^+).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.06; H, 6.27; N, 5.28.

3-Methyl-2-[3-(trifluoromethyl)phenyl]quinoline (3f)

White solid; yield: 46 mg (81%); mp 86–87 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.5 Hz, 1 H), 8.06 (s, 1 H), 7.89 (s, 1 H), 7.80 (d, *J* = 8.0 Hz, 2 H), 7.74–7.66 (m, 2 H), 7.62 (t, *J* = 7.7 Hz, 1 H), 7.55 (dd, *J* = 11.1, 3.9 Hz, 1 H), 2.47 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.83, 145.69, 140.60, 136.16, 131.30, 129.81 (q, *J* = 32.5 Hz), 128.34, 128.08, 127.83, 126.78, 125.85, 125.79, 124.92, 124.02, 123.14 (q, *J* = 270.6 Hz), 19.44.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.53.

MS (EI): *m*/*z* = 287 (M^+).

Anal. Calcd for $C_{17}H_{12}F_3N$: C, 71.07; H, 4.21; N, 4.88. Found: C, 70.95; H, 4.44; N, 4.98.

3-Methyl-2-(*p*-tolyl)quinoline (3g)[28]

Colorless oil; yield: 35 mg (75%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.4 Hz, 1 H), 8.03 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.68 (dd, *J* = 11.2, 4.1 Hz, 1 H), 7.53 (t, *J* = 8.0 Hz, 3 H), 7.32 (d, *J* = 7.8 Hz, 2 H), 2.49 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.50, 145.50, 137.10, 136.79, 135.86, 128.34, 128.14, 127.99, 127.84, 126.55, 125.68, 125.36, 20.34, 19.69.

2-(4-Chlorophenyl)-3-methylquinoline (3h)

White solid; yield: 35 mg (69%); mp 93–94 °C.

IR (neat): 725, 748, 837, 1086, 1483, 1597, 2979, 3051 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.4 Hz, 1 H), 8.02 (s, 1 H), 7.78 (d, *J* = 8.1 Hz, 1 H), 7.67 (t, *J* = 7.5 Hz, 1 H), 7.54 (dd, *J* = 15.6, 7.9 Hz, 3 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 2.46 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.23, 145.68, 138.32, 135.99, 133.36, 129.36, 128.29, 127.94, 127.54, 126.67, 125.75, 125.64, 19.57.

MS (EI): *m*/*z* = 253 (M^+).

Anal. Calcd for $C_{16}H_{12}ClN$: C, 75.74; H, 4.77; N, 5.52. Found: C, 75.46; H, 4.97; N, 5.36.

2-(2,4-Dichlorophenyl)-3-methylquinoline (3i)

Colorless oil; yield: 42 mg (73%).

IR (neat): 754, 780, 835, 1000, 1099, 1586, 2926 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.5 Hz, 1 H), 8.03 (s, 1 H), 7.81 (d, *J* = 8.1 Hz, 1 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.58–7.50 (m, 2 H), 7.39 (dd, *J* = 8.2, 1.8 Hz, 1 H), 7.33 (d, *J* = 8.2 Hz, 1 H), 2.30 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.85, 145.41, 137.38, 135.30, 133.82, 132.63, 130.15, 128.98, 128.46, 128.30, 128.00, 127.07, 126.50, 125.92, 18.17.

MS (EI): *m*/*z* = 287 (M^+).

Anal. Calcd for $C_{16}H_{11}Cl_2N$: C, 66.69; H, 3.85; N, 4.86. Found: C, 66.92; H, 3.93; N, 4.69.

2-(3,5-Dimethoxyphenyl)-3-methylquinoline (3j)

Colorless oil; yield: 42 mg (76%).

IR (neat): 723, 1024, 1159, 1583, 2962 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.4 Hz, 1 H), 8.01 (s, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H), 7.71–7.61 (m, 1 H), 7.52 (dd, *J* = 11.1, 3.9 Hz, 1 H), 6.71 (d, *J* = 2.3 Hz, 2 H), 6.55 (t, *J* = 2.3 Hz, 1 H), 3.84 (s, 6 H), 2.46 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.73, 159.44, 145.47, 141.79, 135.71, 128.32, 128.20, 127.78, 126.69, 125.72, 125.49, 105.99, 99.56, 54.48, 19.50.

MS (EI): *m*/*z* = 279 (M^+).

Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.52; H, 6.29; N, 4.95.

2-(2-Furyl)-3-methylquinoline (3k)

Colorless oil; yield: 33 mg (80%).

IR (neat): 736, 1003, 1494, 1722, 2928 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.5 Hz, 1 H), 7.97 (s, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.66 (dd, *J* = 14.0, 5.8 Hz, 2 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 7.12 (d, *J* = 3.4 Hz, 1 H), 6.60 (dd, *J* = 3.3, 1.7 Hz, 1 H), 2.72 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.65, 147.98, 145.56, 142.70, 136.62, 128.20, 127.95, 127.30, 126.27, 125.62, 125.42, 111.47, 110.64, 20.30.

MS (EI): *m*/*z* = 209 (M^+).

Anal. Calcd for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69. Found: C, 80.51; H, 5.16; N, 6.82.

3-Methyl-2-(2-thienyl)quinoline (3l)[29]

Colorless oil; yield: 34 mg (75%).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 8.5 Hz, 1 H), 7.95 (s, 1 H), 7.70 (d, *J* = 8.1 Hz, 1 H), 7.66–7.57 (m, 2 H), 7.45 (t, *J* = 6.4 Hz, 2 H), 7.20–7.09 (m, 1 H), 2.70 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.68, 145.58, 144.18, 136.58, 128.04, 127.93, 127.32, 127.14, 126.75, 126.63, 126.23, 125.56, 125.35, 20.83.

3-Methyl-2-(2-pyridyl)quinoline (3m)[30]

Colorless oil; yield: 34 mg (78%).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.72 (d, *J* = 4.7 Hz, 1 H), 8.13 (d, *J* = 8.4 Hz, 1 H), 8.04 (s, 1 H), 7.92–7.82 (m, 2 H), 7.79 (d, *J* = 8.1 Hz, 1 H), 7.71–7.62 (m, 1 H), 7.57–7.48 (m, 1 H), 7.35 (ddd, *J* = 6.8, 4.9, 1.9 Hz, 1 H), 2.61 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.12, 156.99, 147.58, 145.44, 136.38, 135.78, 129.08, 128.40, 127.73, 127.08, 125.78, 123.37, 121.97, 19.39.

2-Ethyl-3-methylquinoline (3n)[16a]

White solid; yield: 13 mg (37%); mp 50–51 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.4 Hz, 1 H), 7.80 (s, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 7.58 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1 H), 7.45–7.38 (m, 1 H), 2.97 (q, *J* = 7.6 Hz, 2 H), 2.45 (d, *J* = 0.4 Hz, 3 H), 1.35 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.43, 146.77, 135.86, 129.52, 128.61, 128.40, 127.43, 126.79, 125.70, 29.63, 19.23, 12.98.

1,2,3,4-Tetrahydroacridine (3o)[16a]

Colorless oil; yield: 31 mg (84%).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.5 Hz, 1 H), 7.78 (s, 1 H), 7.67 (d, *J* = 8.1 Hz, 1 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 3.12 (t, *J* = 6.6 Hz, 2 H), 2.95 (t, *J* = 6.4 Hz, 2 H), 2.01–1.94 (m, 2 H), 1.90–1.84 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.26, 145.40, 134.17, 130.00, 127.60, 127.11, 126.21, 125.90, 124.61, 2.46, 28.23, 22.19, 21.89.

3-Benzyl-2-phenylquinoline (3p)[12c]

Yellow solid; yield: 48 mg (82%); mp 94–95 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 8.5 Hz, 1 H), 7.94 (s, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.70 (t, *J* = 7.4 Hz, 1 H), 7.58–7.48 (m, 3 H), 7.48–7.39 (m, 3 H), 7.26 (t, *J* = 7.3 Hz, 2 H), 7.21 (t, *J* = 7.2 Hz, 1 H), 7.02 (d, *J* = 7.3 Hz, 2 H), 4.15 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.78, 145.69, 139.69, 139.00, 136.06, 131.56, 128.34, 128.20, 128.05, 127.91, 127.53, 127.33, 127.24, 126.58, 126.16, 125.54, 125.31, 38.15.

3-Methyl-2-phenethylquinoline (3q)[31] **and 3-Benzyl-2-ethylquinoline (3q')**[32]

Colorless oil; yield: 37 mg (75%).

^1H NMR (500 MHz, $CDCl_3$): δ = 8.09 (t, *J* = 7.8 Hz, 1 H), 7.84 (s, 1 H), 7.77 (s, 1 H), 7.71 (t, *J* = 8.9 Hz, 1 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.47 (dd, *J* = 15.0, 7.4 Hz, 1 H), 7.37–7.27 (m, 5 H), 7.25–7.20 (m, 1 H), 7.18 (d, *J* = 7.4 Hz, 1 H), 4.19 (s, 1 H), 3.28 (dd, *J* = 10.2, 5.6 Hz, 2 H), 3.19 (dd, *J* = 10.5, 5.9 Hz, 2 H), 2.98 (q, *J* = 7.5 Hz, 1 H), 2.42 (s, 3 H), 1.34 (t, *J* = 7.5 Hz, 1 H).

1,3-Bis(3-methylquinolin-2-yl)benzene (3r)

Pale yellow solid; yield: 39 mg (51%); mp 170–171 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.5 Hz, 1 H), 8.01 (s, 1 H), 7.86 (s, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.71–7.66 (m, 1 H), 7.66–7.57 (m, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 2.52 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.17, 145.71, 139.88, 135.89, 128.81, 128.34, 127.86, 127.77, 127.29, 126.66, 125.73, 125.47, 28.72, 19.79.

MS (EI): *m*/*z* = 360 (M^+).

Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.86; H, 5.70; N, 7.96.

3,6-Dimethyl-2-phenylquinoline (3ab)[28]

Colorless oil; yield: 41 mg (88%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.6 Hz, 1 H), 7.92 (s, 1 H), 7.59 (d, *J* = 7.2 Hz, 2 H), 7.53 (s, 1 H), 7.48 (t, *J* = 7.5 Hz, 3 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 2.54 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.72, 145.37, 141.12, 136.31, 136.19, 131.14, 129.21, 129.09, 128.99, 128.36, 128.15, 127.74, 125.63, 21.74, 20.72.

6-Bromo-3-methyl-2-phenylquinoline (3ac)

Pale yellow solid; yield: 51 mg (86%); mp 91–92 °C.

IR (neat): 685, 816, 903, 1472, 1590, 2922 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.9 Hz, 1 H), 7.95–7.88 (m, 2 H), 7.71 (dd, *J* = 8.9, 2.1 Hz, 1 H), 7.62–7.54 (m, 2 H), 7.49 (t, *J* = 7.3 Hz, 2 H), 7.47–7.41 (m, 1 H), 2.46 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.04, 145.30, 140.58, 135.77, 132.29, 131.18, 130.44, 128.89, 128.83, 128.47, 120.32, 20.78.

MS (EI): *m*/*z* = 297 (M^+).

Anal. Calcd for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.20; H, 4.14; N, 4.84.

3,4-Dimethyl-2-phenylquinoline (3ad)[33]

Colorless oil; yield: 28 mg (61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.3 Hz, 1 H), 8.05 (d, *J* = 8.4 Hz, 1 H), 7.66 (t, *J* = 7.3 Hz, 1 H), 7.60–7.52 (m, 3 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 2.70 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.60, 144.98, 141.23, 140.89, 129.17, 127.95, 127.26, 126.92, 126.24, 126.11, 125.13, 122.37, 16.55, 13.80.

3-Methylquinoline (3s)[34]

Colorless oil; yield: 19 mg (67%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 1.2 Hz, 1 H), 8.10 (d, *J* = 8.4 Hz, 1 H), 7.95 (s, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.67 (dd, *J* = 11.2, 4.0 Hz, 1 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 2.54 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.18, 145.30, 133.96, 129.52, 127.97, 127.60, 127.18, 126.15, 125.67, 17.75.

3-Benzylquinoline (3t)[21a]

Colorless oil; yield: 35 mg (79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.81 (d, *J* = 1.8 Hz, 1 H), 8.07 (d, *J* = 8.5 Hz, 1 H), 7.87 (s, 1 H), 7.73 (d, *J* = 8.2 Hz, 1 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.31 (t, *J* = 7.5 Hz, 2 H), 7.23 (t, *J* = 7.7 Hz, 3 H), 4.16 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 151.14, 145.94, 138.71, 133.85, 132.86, 128.22, 127.98, 127.85, 127.77, 127.15, 126.46, 125.69, 125.59, 38.28.

3-(3-Methoxybenzyl)quinoline (3u)

Yellow oil; yield: 36 mg (72%).

IR (neat): 751, 1046, 1257, 1489, 1582, 1736, 2927 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.76 (d, *J* = 1.6 Hz, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.83 (s, 1 H), 7.68 (d, *J* = 8.1 Hz, 1 H), 7.61 (t, *J* = 7.6 Hz, 1 H), 7.46 (t, *J* = 7.4 Hz, 1 H), 7.19 (dd, *J* = 12.7, 4.7 Hz, 1 H), 6.77 (d, *J* = 7.5 Hz, 1 H), 6.75–6.70 (m, 2 H), 4.08 (s, 2 H), 3.72 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.96, 151.07, 145.95, 140.26, 133.86, 132.70, 128.75, 128.20, 127.86, 127.15, 126.48, 125.68, 120.38, 113.89, 110.81, 54.20, 38.29.

MS (EI): *m*/*z* = 249 (M^+).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.14; H, 6.17; N, 5.41.

3-(4-Methylbenzyl)quinoline (3v)[35]

Colorless oil; yield: 30 mg (65%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.83 (s, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 7.91 (s, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.72–7.63 (m, 1 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.20–7.06 (m, 4 H), 4.15 (s, 2 H), 2.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.89, 145.61, 135.56, 135.18, 134.04, 133.20, 128.46, 127.95, 127.85, 127.20, 126.46, 125.75, 37.85, 20.02.

3-(4-Chlorobenzyl)quinoline (3w)

Colorless oil; yield: 35 mg (70%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.78 (d, *J* = 1.9 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.85 (s, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.70–7.62 (m, 1 H), 7.52 (dd, *J* = 11.1, 3.9 Hz, 1 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.3 Hz, 2 H), 4.12 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.88, 145.99, 137.15, 133.87, 132.29, 131.49, 129.30, 128.22, 128.03, 127.90, 127.08, 126.45, 125.83, 37.57.

MS (EI): *m*/*z* = 253 (M^+).

Anal. Calcd for $C_{16}H_{12}ClN$: C, 75.74; H, 4.77; N, 5.52. Found: C, 75.70; H, 4.89; N, 5.44.

1-Deuterio-1-phenylprop-2-en-1-ol ([D]-2a)[24]

Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39 (dd, *J* = 6.7, 3.4 Hz, 4 H), 7.35–7.29 (m, 1 H), 6.07 (dd, *J* = 17.1, 10.3 Hz, 1 H), 5.36 (dd, *J* = 17.1, 1.3 Hz, 1 H), 5.22 (dd, *J* = 10.3, 1.3 Hz, 1.05 H), 2.33 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.68, 140.31, 128.67, 127.85, 126.45, 115.24, 75.02 (t, *J* = 22.5 Hz).

Compound [D]-2ab

Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.9 Hz, 2 H), 7.55 (t, *J* = 7.3 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 3.01 (q, *J* = 7.2 Hz, 1.84 H), 1.23 (q, *J* = 7.7 Hz, 2.65 H).

Compound [D]-3a

Colorless oil; yield: 35 mg (80%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.13 (d, *J* = 8.4 Hz, 1 H), 8.01 (s, 0.65 H), 7.78 (d, *J* = 8.1 Hz, 1 H), 7.66 (t, *J* = 7.6 Hz, 1 H), 7.59 (d, *J* = 7.3 Hz, 2 H), 7.50 (dt, *J* = 13.1, 7.5 Hz, 3 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 2.46 (s, 1.84 H), 2.45 (s, 0.89 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.57, 145.68, 139.93, 135.73, 135.58, 135.38, 135.19, 128.34, 128.22, 127.87, 127.75, 127.31, 127.19, 126.63, 126.57, 125.71, 125.41, 76.30, 76.04, 75.79, 19.62, 19.56, 19.35, 19.19.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380110.

References

(1) For reviews, see: (a) van der Drift, R. C.; Bouwman, E.; Drent, E. *J. Organomet. Chem.* **2002**, *650*, 1. (b) Uma, R.; Crevisy, C.; Grée, R. *Chem. Rev.* **2003**, *103*, 27. (c) Lorenzo-Luis, P.; Romerosa, A.; Serrano-Ruiz, M. *ACS Catal.* **2012**, *2*, 1079. (d) Ahlsten, N.; Bartoszewicz, A.; Martín-Matute, B. *Dalton Trans.* **2012**, *41*, 1660.

(2) For a recent example, see: Nelson, D. J.; Fernandez-Salas, J. A.; Truscott, B. J.; Nolan, S. P. *Org. Biomol. Chem.* **2014**, *12*, 6672.

(3) (a) Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev.* **2004**, *248*, 2365. (b) Wasilke, J. C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001.

(4) (a) Crévisy, C.; Wietrich, M.; Le Boulaire, V.; Uma, R.; Grée, R. *Tetrahedron Lett.* **2001**, *42*, 395. (b) Uma, R.; Davies, M.; Crévisy, C.; Grée, R. *Tetrahedron Lett.* **2001**, *42*, 3069. (c) Grée, R.; Cuperly, D.; Crévisy, C. *Synlett* **2004**, 93. (d) Cuperly, D.; Petrignet, J.; Crevisy, C.; Grée, R. *Chem. Eur. J.* **2006**, *12*, 3261. (e) Petrignet, J.; Prathap, I.; Chandrasekhar, S.; Yadav, J. S.; Grée, R. *Angew. Chem. Int. Ed.* **2007**, *46*, 6297. (f) Cao, H. T.; Roisnel, T.; Valleix, A.; Grée, R. *Eur. J. Org. Chem.* **2011**, 3430.

(5) (a) Bartoszewicz, A.; Jeżowska, M. M.; Laymand, K.; Möbus, J.; Martín-Matute, B. *Eur. J. Org. Chem.* **2012**, 1517. (b) Ahlsten, N.; Martín-Matute, B. *Chem. Commun.* **2011**, *47*, 8331. (c) Martín-Matute, B.; Ahlsten, N.; Bartoszewicz, A.; Agrawal, S. *Synthesis* **2011**, 2600. (d) Ahlsten, N.; Bermejo Gomez, A.; Martín-Matute, B. *Angew. Chem. Int. Ed.* **2013**, *52*, 6273. (e) Gomez, A. B.; Erbing, E.; Batuecas, M.; Vazquez-Romero, A.; Martín-Matute, B. *Chem. Eur. J.* **2014**, *20*, 10703.

(6) (a) Wang, M.; Li, C.-J. *Tetrahedron Lett.* **2002**, *43*, 3589. (b) Wang, M.; Yang, X.-F.; Li, C.-J. *Eur. J. Org. Chem.* **2003**, 998. (c) Yang, X.-F.; Wang, M.; Varma, R. S.; Li, C.-J. *Org. Lett.* **2003**, *5*, 657.

(7) Bartoszewicz, A.; Martín-Matute, B. *Org. Lett.* **2009**, *11*, 1749.

(8) Sahli, Z.; Sundararaju, B.; Achard, M.; Bruneau, C. *Org. Lett.* **2011**, *13*, 3964.

(9) (a) Sundbelg, R. J. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Vol. 14; Kroschwitz, J. I.; Howe-Grand, M., Eds.; Wiley: New York, **1995**, 161. (b) Katritzky, A. R.; Rachwal, S.; Rachwal, B. *Tetrahedron* **1996**, *52*, 15031. (c) Wang, T.; Zhuo, L.-G.; Li, Z.; Chen, F.; Ding, Z.; He, Y.; Fan, Q.-H.; Xiang, J.; Yu, Z.-X.; Chan, A. S. C. *J. Am. Chem. Soc.* **2011**, *133*, 9878; and references therein.

(10) Cho, C. S.; Kim, B. T.; Kim, T.-J.; Shim, S. C. *Chem. Commun.* **2001**, 2576.

(11) (a) Cho, C. S.; Kim, B. T.; Choi, H.-J.; Kim, T.-J.; Shim, S. C. *Tetrahedron* **2003**, *59*, 7997. (b) Motokura, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2004**, *45*, 6029. (c) Martínez, R.; Brand, G. J.; Ramón, D. J.; Yus, M. *Tetrahedron Lett.* **2005**, *46*, 3683. (d) Vander Mierde, H.; Ledoux, N.; Allaert, B.; Van Der Voort, P.; Drozdzak, R.; De Vos, D.; Verpoort, F. *New J. Chem.* **2007**, *31*, 1572.

(12) (a) Cho, C. S.; Ren, W. X.; Shim, S. C. *Bull. Korean Chem. Soc.* **2005**, *26*, 1286. (b) Cho, C. S.; Ren, W. X. *J. Organomet. Chem.* **2007**, *692*, 4182. (c) Chen, B. W. J.; Chng, L. L.; Yang, J.; Wei, Y. F.; Yang, J. H.; Ying, J. Y. *ChemCatChem* **2013**, *5*, 277.

(13) Taguchi, K.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **2005**, *46*, 4539.

(14) Cho, C. S.; Seok, H. J.; Shim, S. O. *J. Heterocycl. Chem.* **2005**, *42*, 1219.

(15) (a) Cho, C. S.; Ren, W. X.; Shim, S. C. *Tetrahedron Lett.* **2006**, *47*, 6781. (b) Cho, C. S.; Ren, W. X.; Yoon, N. S. *J. Mol. Catal. A: Chem.* **2009**, *299*, 117. (c) Phan, N. T. S.; Nguyen, T. T.; Nguyen, K. D.; Vo, A. X. T. *Appl. Catal., A* **2013**, *464*, 128.

(16) For transition-metal-free indirect Friedländer quinoline synthesis, see: (a) Martinez, R.; Ramon, D. J.; Yus, M. *J. Org. Chem.* **2008**, *73*, 9778. (b) Mierde, H. V.; Van Der Voort, P.; Verpoort, F. *Tetrahedron Lett.* **2008**, *49*, 6893.

(17) Chen, S.-J.; Lu, G.-P.; Cai, C. *Synthesis* **2014**, *46*, 1717.

(18) $\{[IrCp^*Cl_2]_2\}$ was also used as an efficient catalyst for the hydrogen autotransfer (or hydrogen-borrowing) process, see: (a) Fujita, K.; Asai, C.; Yamaguchi, T.; Hanasaka, F.; Yamaguchi, R. *Org. Lett.* **2005**, *7*, 4017. (b) Whitney, S.; Grigg, R.; Derrick, A.; Keep, A. *Org. Lett.* **2007**, *9*, 3299. (c) Bhat, S.; Sridharan, V. *Chem. Commun.* **2012**, *48*, 4701. (d) Ogawa, S.; Obora, Y. *Chem. Commun.* **2014**, *50*, 2491.

(19) Gonzalez-Lopez de Turiso, F.; Shin, Y.; Brown, M.; Cardozo, M.; Chen, Y.; Fong, D.; Hao, X.; He, X.; Henne, K.; Hu, Y. L.; Johnson, M. G.; Kohn, T.; Lohman, J.; McBride, H. J.; McGee, L. R.; Medina, J. C.; Metz, D.; Miner, K.; Mohn, D.; Pattaropong, V.; Seganish, J.; Simard, J. L.; Wannberg, S.; Whittington, D. A.; Yu, G.; Cushing, T. D. *J. Med. Chem.* **2012**, *55*, 7667.

(20) (a) Soro, B.; Stoccoro, S.; Minghetti, G.; Zucca, A.; Cinellu, M. A.; Gladiali, S.; Manassero, M.; Sansoni, M. *Organometallics* **2005**, *24*, 53. (b) Rausch, A. F.; Murphy, L.; Williams, J. A.; Yersin, H. *Inorg. Chem.* **2012**, *51*, 312.

(21) (a) Mierde, H. V.; Voort, P. V. D.; Verpoort, F. *Tetrahedron Lett.* **2009**, *50*, 201. (b) Cho, C. S.; Ren, W. X.; Shim, S. C. *Bull. Korean Chem. Soc.* **2005**, *26*, 2038. (c) Isomerization/aldol-type reaction, see: Esteruelas, M. A.; Hernández, Y. A.; López, A. M.; Oliván, M.; Rubio, L. *Organometallics* **2010**, *27*, 799.

(22) Liang, Y.-F.; Zhou, X.-F.; Tang, S.-Y.; Huang, Y.-B.; Feng, Y.-S.; Xu, H.-J. *RSC Adv.* **2013**, *3*, 7739.

(23) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.

(24) Bartoszewicz, A.; Livendahl, M.; Martín-Matute, B. *Chem. Eur. J.* **2008**, *14*, 10547.

(25) Logan, A. W.; Parker, J. S.; Hallside, M. S.; Burton, J. W. *Org. Lett.* **2012**, *14*, 2940.

(26) Leleti, R. R.; Hu, B.; Prashad, M.; Repič, O. *Tetrahedron Lett.* **2007**, *48*, 8505.

(27) (a) Xu, W.; Zhou, Y.; Wang, R.; Wu, G.; Chen, P. *Org. Biomol. Chem.* **2012**, *10*, 367. (b) Aramini, A.; Brinchi, L.; Germani, R.; Savelli, G. *Eur. J. Org. Chem.* **2000**, 1793.

(28) Jacob, J.; Jones, W. D. *J. Org. Chem.* **2003**, *68*, 3563.

(29) Jacob, J.; Cavalier, C. M.; Jones, W. D.; Godleski, S. A.; Valente, R. R. *J. Mol. Catal. A: Chem.* **2002**, *182*, 565.

(30) Sakashita, S.; Takizawa, M.; Sugai, J.; Ito, H.; Yamamoto, Y. *Org. Lett.* **2013**, *15*, 4308.

(31) Wang, D. W.; Wang, X. B.; Wang, D. S.; Lu, S. M.; Zhou, Y. G.; Li, Y. X. *J. Org. Chem.* **2009**, *74*, 2780.

(32) Kim, S. C.; Gowrisankar, S.; Kim, J. N. *Bull. Korean Chem. Soc.* **2005**, *26*, 1001.

(33) Kiss, Á.; Potor, A.; Hell, Z. *Catal. Lett.* **2008**, *125*, 250.

(34) Huiban, M.; Huet, A.; Barre, L.; Sobrio, F.; Fouquet, E.; Perrio, C. *Chem. Commun.* **2006**, 97.

(35) Krasovskaya, V.; Krasovskiy, A.; Lipshutz, B. H. *Chem. Asian J.* **2011**, *6*, 1974.