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# α-Alkylation of arylacetonitriles with primary alcohols catalyzed by backbone modified N-heterocyclic carbene iridium(I) complexes†

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A series of backbone-modified N-heterocyclic carbene (NHC) complexes of iridium(I) (**1d–f**) have been synthesized and characterized. The electronic properties of the NHC ligands have been assessed by comparison of the IR carbonyl stretching frequencies of the *in situ* prepared [IrCl(CO)$_2$(NHC)] complexes in $CH_2Cl_2$. These new complexes (**1d–f**), together with previously prepared **1a–c**, were applied as catalysts for the α-alkylation of arylacetonitriles with an equimolar amount of primary alcohols or 2-aminobenzyl alcohol. The catalytic activities of these complexes could be controlled by modifying the N-substituents and backbone of the NHC ligands. The NHC–Ir$^{I}$ complex **1f** bearing 4-methoxybenzyl substituents on the N-atoms and 4-methoxyphenyl groups at the 4,5-positions of imidazole exhibited the highest catalytic activity in the α-alkylation of arylacetonitriles with primary alcohols. Various α-alkylated nitriles and aminoquinolines were obtained in high yields through a borrowing hydrogen pathway by using 0.1 mol% **1f** and a catalytic amount of KOH (5 mol%) under an air atmosphere within significantly short reaction times.

## Introduction

The transition-metal (TM) catalyzed borrowing hydrogen (BH) strategy, also called hydrogen autotransfer, has become an important alternative for alkylation reactions in which inexpensive and environmentally friendly alcohols are used as alkylating agents.[1] This highly valuable process has emerged as a powerful approach to construct C–C and C–N bonds for the one-step synthesis of highly complicated molecules including α-alkylated ketones,[1c–g] β-alkylated alcohols,[1d–g,2] α-alkylated nitriles,[1c,d,e,g] quinolines,[1d,e,3] and amines.[1e–g] Among these valuable molecules, α-alkylated nitriles are versatile building blocks in organic synthesis because they can easily be converted to carboxylic acids, ketones, amines, amides, and various biologically active compounds.[4] In the traditional synthesis of α-alkylated nitriles, toxic alkyl halides are employed as alkylating reagents with a stoichiometric or excess amount of a strong base. Alternatively, the α-alkylation of nitriles with alcohols as green alkylating reagents through a BH strategy was first explored by Grigg *et al.*[5] Subsequently, heterogeneous Ru[6] or Pd[7] catalysts were employed for the α-alkylation of nitriles with alcohols; however, these systems require very high temperatures (180 °C), prolonged reaction times, or an excess amount of alkylating alcohols for the selective formation of the desired alkylnitrile product over the undesired olefinic nitrile intermediate. Homogeneous TM complexes, including Ru,[8] Os,[9] Ir,[10] Rh,[11] Mn,[12] Fe,[13] and Ni,[14] have also been developed for this transformation; however, most of these catalysts suffer from high catalyst loadings, the necessity of using an excess amount of alkylating alcohols, or inert reaction conditions. There exist only two reports wherein equimolar amounts of arylacetonitrile and alkylating alcohol were used for this transformation.[9,11] In the first report, Yus *et al.* discussed the alkylation of arylacetonitriles with primary alcohols catalyzed by an N-heterocyclic carbene (NHC)–osmium(II) complex (1.0 mol%, giving TONs up to 98), which required the removal of the *in situ* formed water molecule during the reaction.[9] In the second report, Wang and coworkers discussed the α-alkylation or olefination of nitriles with primary alcohols by using 0.5 equivalent of NaOH and a 0.5 mol% rhodium complex at 110 °C and the total TON for the α-alkylation reaction was reported to be up to 198.[11] Recently, the Kundu group reported the first example of the TM-free base-catalyzed α-alkylation of nitriles by using primary alcohols; however, the main limitation of this system is that it requires 0.8 equivalent of KO$^t$Bu as the base and an excess of alkylating alcohol (3.0 equivalents).[15]

However, the electronic and steric properties of the NHC ligand are important for homogeneous TM catalysis. For classical NHCs, N-substituents and backbone modifications primarily change their electronic and steric properties.[16] NHC–Ir

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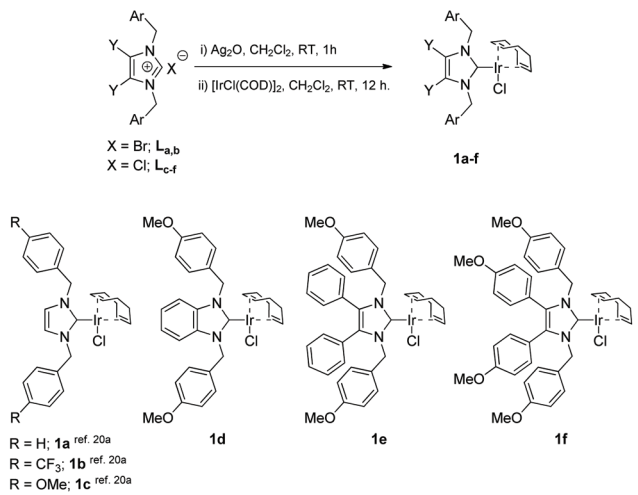
complexes have been utilized in various catalytic reactions including transfer hydrogenation, (de)hydrogenation, and BH reactions.[16c,17] Our group recently demonstrated that the N-substituents and backbone modifications on the NHC ligand play a critical role in the catalytic activity of the related NHC–Ir complexes in the transfer hydrogenation of carbonyls[18] and acceptorless dehydrogenation of alcohols.[19] Inspired by these studies, we subsequently prepared a set of [IrCl(cod)(NHC)] (cod = 1,5-cyclooctadiene) complexes and reported their superior catalytic activities for the alkylation of secondary alcohols or ketones with primary alcohols to give α-alkylated ketones,[20a] β-alkylated alcohols,[20b] quinoline derivatives,[20b] α,α-disubstituted ketones,[20c] and β,β-disubstituted alcohols.[20c] Encouraged by these results, we herein describe the synthesis of a set of [IrCl(cod)(NHC)] complexes (Scheme 1) with different NHC skeletons and explore the catalytic activities of these complexes in the α-alkylation of nitriles with primary alcohols.

## Results and discussion

Scheme 1 shows the route to the synthesis of NHC–Ir$^{I}$ complexes (**1a–f**). The NHC precursors $\mathbf{L_{a-d}}$[19] and $\mathbf{L_{e,f}}$[21] and complexes **1a–c**[20a] were synthesized according to the published procedures. The new complexes **1d–f** were obtained in 71–83% yields as air- and moisture-stable yellow solids by a two-step process that involved transmetalation from the *in situ* formed NHC–Ag species.[22] The formation of **1d–f** was confirmed by NMR spectroscopy, HRMS, and elemental analysis. Complexes **1d–f** exhibited characteristic Ir–$C_{carbene}$ signals at $\delta$ = 192.4, 180.9, and 180.3 ppm, respectively. Meanwhile, the characteristic downfield signals for the NC*H*N$^{+}$ protons of NHC precursors $\mathbf{L_{d-f}}$ disappeared from the $^{1}$H NMR spectrum.

Measuring the carbonyl stretching frequencies of the [IrCl(CO)$_2$(NHC)] complexes by infrared spectroscopy allows us to understand the electronic effects of the NHC ligands, which are important for homogeneous catalysis.[23] Thus, the corresponding [IrCl(CO)$_2$($\mathbf{NHC_{a-f}}$)] complexes were prepared *in situ* by passing carbon monoxide gas through a dichloromethane solution (0.01 M) of complexes **1a–f** at room temperature for 1 h to compare the electronic properties of the NHC ligands with one another. However, these [IrCl(CO)$_2$($\mathbf{NHC_{a-f}}$)] species were not isolated. Subsequently, these solutions were analyzed by IR spectroscopy. The IR spectra showed two strong $\nu_{CO}$ bands for each complex. The average carbonyl stretching frequencies $\nu_{CO}^{av}$ in the IR spectra were then used to calculate the Tolman electronic parameters (TEP)[24] by using the linear regression equation described by Crabtree[23a] and Nolan[23b] (see Table 1). The results revealed that both the benzylic wingtip substituents on the N-atoms and backbone modifications played important roles in the electron-donating properties of the NHC ligands. $\mathbf{NHC_f}$ bearing 4-methoxybenzyl groups at the 1,3-positions and 4-methoxyphenyl groups at the 4,5-positions appeared as the most strongly electron-donating ligand assessed in this study.

To probe the potential of NHC–Ir$^{I}$ catalysts **1a–f** for the α-alkylation of arylacetonitriles with primary alcohols, benzyl cyanide (**2a**) and benzyl alcohol (**3a**) were selected as model substrates (see Table 2). The yields are based on the $^{1}$H NMR analysis of the crude reaction mixtures by using 1,3,5-trimethoxybenzene as an internal standard. In the presence of **1a–f** as the catalyst (0.1 mol%), respectively, and KOH (10 mol%), the reaction was performed in toluene (1 mL) at 135 °C (oil-bath temperature) open to the air for 1 h (entries 1–6). In the presence of complexes **1a–e**, poor to moderate conversions were observed; additionally, 30–77% yield of the desired product **4a** and 5–14% yield of the unsaturated olefin intermediate **4′a** along with unreacted starting materials were obtained (entries 1–5). To our delight, NHC–Ir$^{I}$ complex **1f** with a strongly electron donating NHC ligand demonstrated the highest catalytic activity to give **4a** in 93% NMR yield as the sole product where the unsaturated olefin intermediate **4′a** could not be detected (entry 6). Considering complexes **1a–f** bearing NHC ligands, the significant differences in the catalytic ability among these iridium complexes could be attributed to the different electron densities at the iridium centers.[16a]



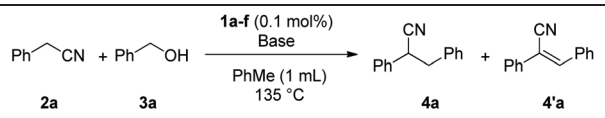

**Scheme 1** Synthesis route to the NHC–Ir$^{I}$ complexes used in this study.

**Table 1** $\nu_{CO}$, $\nu_{CO}^{av}$, and TEP values for [IrCl(CO)$_2$($\mathbf{NHC_{a-f}}$)] complexes derived from **1a–f**[a]

| NHC | $\nu_{CO}$ (cm$^{-1}$) | $\nu_{CO}^{av}$ (cm$^{-1}$) | TEP[b] (cm$^{-1}$) | TEP[c] (cm$^{-1}$) |
|---|---|---|---|---|
| $\mathbf{NHC_a}$ | 1985.4; 2068.9 | 2027.2 | 2056.6 | 2053.0 |
| $\mathbf{NHC_b}$ | 1987.7; 2071.4 | 2029.6 | 2058.4 | 2055.1 |
| $\mathbf{NHC_c}$ | 1984.6; 2068.1 | 2026.4 | 2056.1 | 2052.4 |
| $\mathbf{NHC_d}$ | 1988.7; 2071.6 | 2030.2 | 2058.8 | 2055.6 |
| $\mathbf{NHC_e}$ | 1984.2; 2067.3 | 2025.8 | 2055.6 | 2051.9 |
| $\mathbf{NHC_f}$ | 1983.5; 2066.5 | 2025.0 | 2055.1 | 2051.2 |

[a] The IR spectra of the *in situ* prepared [IrCl(CO)$_2$($\mathbf{NHC_{a-f}}$)] complexes were recorded in a $CH_2Cl_2$ solution as the film using NaCl plates. [b] Calculated using Crabtree's equation: 0.722 × $\nu_{CO}^{av}$ + 593 cm$^{-1}$. [c] Calculated using Nolan's equation: 0.847 × $\nu_{CO}^{av}$ + 336 cm$^{-1}$.

Table 2 Optimization of the reaction conditions[a]

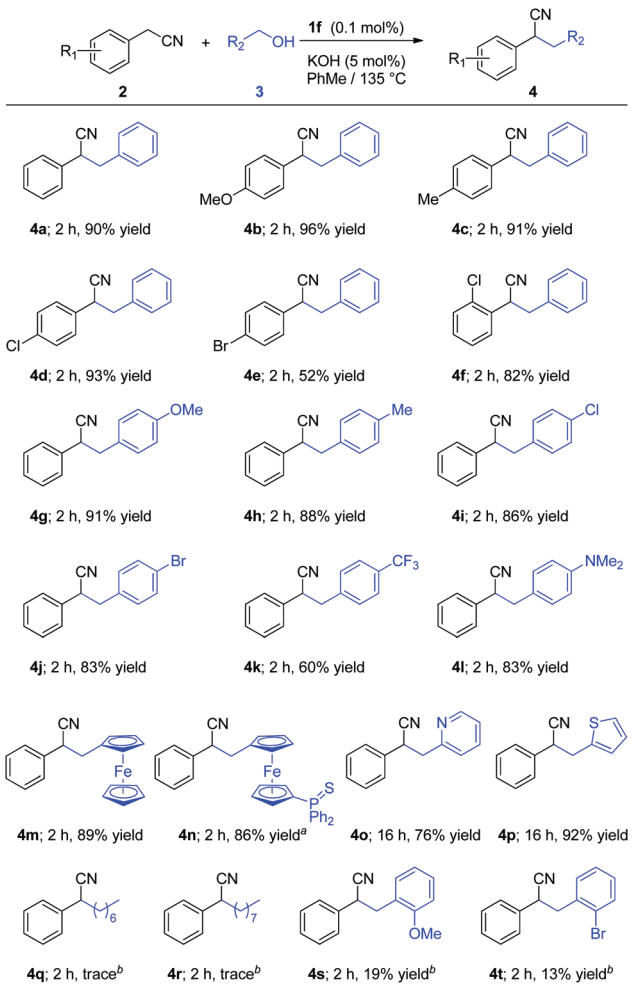



| Entry | Cat. | Base (mol%) | Time (h) | Yield 4a[b] (%) | Yield 4′a[b] (%) |
|---|---|---|---|---|---|
| 1 | **1a** | KOH (10) | 1 | 38 | 6 |
| 2 | **1b** | KOH (10) | 1 | 29 | 4 |
| 3 | **1c** | KOH (10) | 1 | 56 | 8 |
| 4 | **1d** | KOH (10) | 1 | 53 | 9 |
| 5 | **1e** | KOH (10) | 1 | 77 | 5 |
| 6 | **1f** | KOH (10) | 1 | 93 | — |
| 7 | **1f** | KOH (5) | 2 | 95 | — |
| 8[c] | **1f** | KOH (5) | 2 | 94 | — |
| 9[d] | **1f** | KOH (5) | 2 | 91 | — |
| 10 | **1f** | KO$^t$Bu (5) | 2 | 87 | 4 |
| 11 | **1f** | NaOH (5) | 2 | 78 | 20 |
| 12 | **1f** | NaO$^t$Bu (5) | 2 | 65 | 17 |
| 13 | **1f** | — | 2 | — | — |
| 14 | — | KOH (5) | 2 | — | — |
| 15 | **[IrCl(cod)(IMe)]** | KOH (5) | 2 | 26 | 3 |

[a] Reaction conditions: **2a** (1.0 mmol), **3a** (1.0 mmol), **1a–f** (0.1 mol%), base (5–10 mol%), toluene (1.0 mL), 135 °C (oil bath temperature), open to the air. [b] Yields were determined by the $^1$H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] A drop of mercury was added to the reaction mixture. [d] The reaction was performed under an argon atmosphere.

Pleasingly, decreasing the KOH loading to 5 mol% resulted in 95% NMR yield with complete chemoselectivity in 2 h (entry 7), and **4a** was isolated in 90% yield. A similar yield was observed upon adding a drop of mercury to the reaction mixture, indicating the homogeneous nature of the catalytic system (entry 8). Noteworthily, an inert atmosphere seemed to be unnecessary (entry 9). The use of other strong bases including KO$^t$Bu, NaOH, and NaO$^t$Bu resulted in a decrease in the yield and selectivity (entries 10–12). Control experiments showed no activity in the absence of KOH or complex **1f** (entries 13 and 14). In addition, the catalytic performance of the [IrCl(cod)(IMe)] complex was evaluated in the present reaction and only 26% yield of the desired product was observed (entry 15). Considering the TEP value of the [IrCl(CO)$_2$(IMe)] complex (2051 cm$^{-1}$, Nolan's equation),[25] which is very close to that of [IrCl(CO)$_2$(**NHC$_f$**)], the significant differences in the catalytic abilities (entry 15 compared to entry 7) among these iridium complexes could be related to the different wingtip and backbone substituents on the NHC ligands.

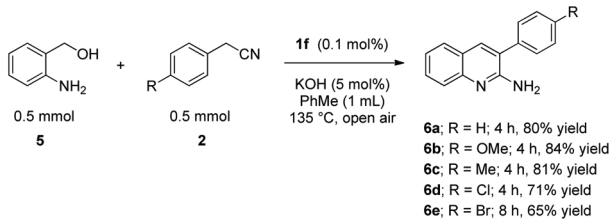
Under the optimized conditions (Table 2, entry 7) in hand, we next explored the scope of the reaction (Scheme 2). Pleasingly, all the reactions resulted in the selective formation of the desired α-alkylated nitrile products **4a–p**. The reaction of substituted arylacetonitriles bearing 4-Me, 4-OMe, 4-Cl, 4-Br, and 2-Cl substituents with benzyl alcohols gave the desired products **4b–4f** in 52–96% isolated yields. We also explored the reactions with respect to primary alcohols. For instance, the reactions with various benzyl alcohols bearing substituents with different electronic properties at the *para*-position of the phenyl ring gave the corresponding products **4g–4l** in 60–91% isolated yields. Furthermore, the reaction of benzyl cyanide with ferrocenemethanol derivatives afforded the desired products **4m** and **4n** in 89% and 86% isolated yields, respectively. In the case of heterocycles containing primary alcohols 2-pyridinemethanol and 2-thiophenemethanol, long reaction time (16) was required for obtaining high yields, and the corresponding alcohols **4o** and **4p** were isolated in 76% and 92% yields, respectively. However, applications of long-chain alcohols such as 1-heptanol and 1-octanol and *ortho*-substituted benzyl alcohols were not successful in conversion to the desired product, and we observed only a trace amount of conversions to the desired products under the standard conditions.




**Scheme 2** Scope of the α-alkylation of arylacetonitriles with primary alcohols catalyzed by complex **1f**. Reaction conditions: arylacetonitrile (1.0 mmol), primary alcohol (1.0 mmol), **1f** (0.1 mol%), KOH (5 mol%), toluene (1.0 mL), 135 °C (oil bath temperature), open to the air. Isolated yields. [a]The reaction was performed on a 0.5 mmol scale. [b]Determined by $^1$H NMR analysis.

Thereafter, the α-alkylation of electronically different aryl acetonitriles (**2a–e**) with 2-aminobenzyl alcohol (**5**) to give 2-aminoquinolines[8c,26] was investigated to extends the poten-




**Scheme 3** Synthesis of 2-aminoquinolines catalyzed by complex **1f** (isolated yields).

tial of complex **1f** (Scheme 3). The reaction of equimolar amounts of arylacetonitriles (**2a–e**), respectively, with 2-aminobenzyl alcohol (**5**) in the presence of complex **1f** (0.1 mol%) and KOH (5 mol%) at 135 °C in toluene for 4–8 h gave moderate to high isolated yields (65%–84%) of the desired 2-aminoquinoline derivatives **6a–e**.

Then, we monitored the progress of the model reaction of benzyl cyanide (**2a**) and benzyl alcohol (**3a**) as a function of time under the reaction conditions as in Table 2, entry 7 by performing individual experiments over different reaction times (Fig. 1). $^1$H NMR monitoring of the reaction progress confirmed the complete conversion of the starting materials in 120 min. The formation of the desired product **4a** and the unsaturated intermediate **4′a** was also observed. After 1 h, **4a** was formed with 79% yield, accompanied by 8% of unsaturated intermediate **4′a**. During this time, the amount of unsaturated intermediate **4′a** was almost constant (*ca.* 10%). Further completion of the reaction by the consumption of benzyl cyanide and benzyl alcohol occurred at a slow rate over a 2 h period. From these observations, it can be suggested that the dehydrogenation of benzyl alcohol is most likely the rate-limiting step.

Several control experiments were performed to elucidate the reaction mechanism (Scheme 4). First, we investigated the

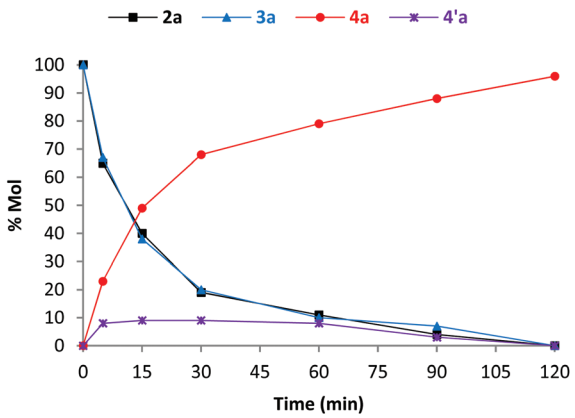
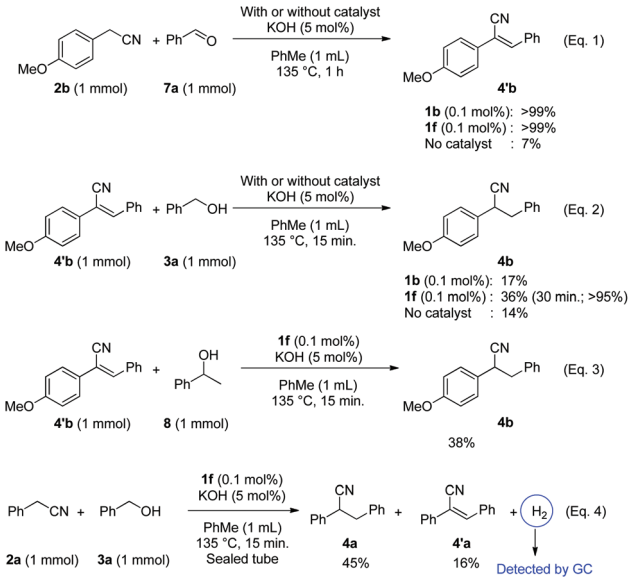


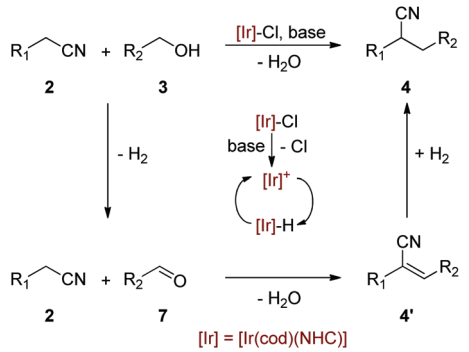

**Fig. 1** Monitoring of the reaction progress. Reaction conditions: **2a** (1 mmol), **3a** (1 mmol), **1f** (0.1 mol%), KOH (5 mol%), toluene (1 mL), 135 °C (oil bath temperature), open to the air. % Mol values were determined by $^1$H NMR analyses of the independent reaction mixtures using 1,3,5-trimethoxybenzene as the internal standard.




**Scheme 4** Control experiments.

effect of the catalyst on the formation of olefinic nitrile intermediate **4′b** by the aldol condensation of 4-methoxybenzyl nitrile (**2b**) with benzaldehyde (**7**) (Scheme 4, eqn (1)). The reaction with both the most active catalyst **1f** and the least active catalyst **1b** resulted in a complete conversion, whereas the reaction without any catalyst was inefficient (7% yield in comparison with >99% yield with **1b** or **1f**). This indicates that the NHC–Ir complex was involved in this step of the reaction. The reduction of olefinic nitrile intermediate **4′b** to **4b** using benzyl alcohol as a hydrogen source was also studied (Scheme 4, eqn (2)). However, the conversion to **4b** varies with the nature of the catalyst. Thus, **4b** was obtained in 36% yield with 0.1 mol% of **1f** in 15 min, whereas **4b** was obtained in 17% yield in the presence of 0.1 mol% of **1b** under the same conditions. The electronic nature of the NHC ligand in the corresponding NHC–Ir complex seems to be highly important in the transfer hydrogenation of the olefinic nitrile intermediate. Increasing the reaction time to 30 min in the presence of **1f** resulted in >95% conversion to **4b**. Without an NHC–Ir catalyst, **4′b** could also be reduced by benzyl alcohol to give **4b** only in 14% conversion under the conditions employed. Upon replacing benzyl alcohol with 1-phenylethanol (**8**), **4′b** was reduced to **4b** in 38% yield in the presence of 0.1 mol% **1f** within 15 min (Scheme 4, eqn (3)). Notably, the reaction of benzyl cyanide (**2a**) and benzyl alcohol (**3a**) was carried out in a sealed reaction tube for 15 min, resulting in the formation of **4a** (45%) together with unsaturated olefin intermediate **4′a** (16%) and the presence of free hydrogen in the gas phase of the reaction was detected by GC analysis (Fig. S30, see the ESI†) (Scheme 4, eqn (4)).

On the basis of relevant studies involving similar catalysts in our earlier work[20] and experimental evidence obtained in this study, a plausible mechanism for this transformation can be proposed as shown in Scheme 5. The mechanism involves




Scheme 5 Plausible reaction mechanism.

the decoordination of Cl in the presence of KOH to generate an $[Ir(COD)(NHC)]^+$ intermediate. Thereafter, the dehydrogenation of primary alcohol (**3**) to the corresponding aldehyde (**7**) generates transient iridium hydride.[20a] Next, an NHC–Ir-catalyzed condensation of **2** and **7** gives the olefinic nitrile intermediate **4′**. Finally, **4′** is reduced to afford **4** using iridium hydride.

# Experimental

### General considerations

Experiments that involved air- or moisture-sensitive reagents were performed under an atmosphere of dry argon by using standard Schlenk techniques. Unless otherwise specified, all the reagents and solvents were commercially obtained and used without further purification. Imidazolium salts $\mathbf{L_{a–d}}$[19] and $\mathbf{L_{d,f}}$[21] and complexes **1a–c**[20a] were synthesized according to the published procedures, and the physical properties and spectroscopic data of the obtained compounds were in accordance with previous reports. The NMR spectra were recorded on a Varian AS 400 Mercury NMR spectrometer and reported in the unit of parts per million (ppm) relative to $CDCl_3$ ($\delta$ = 7.26 ppm for $^1$H and $\delta$ = 77.0 ppm for $^{13}$C NMR). The elemental analyses were performed using a PerkinElmer PE 2400 elemental analyzer. FTIR spectra were recorded using a PerkinElmer Spectrum 100 series system. HRMS was performed using an Agilent 6530 Accurate-Mass Q-TOF mass spectrometer at the East Anatolia High Technology Application and Research Center, Atatürk University. GC analysis for the $H_2$ evolution experiment was performed using an Agilent 7890A GC instrument, and gas products were identified according to the standard gas mixture (Agilent P/N 5190-0519).

### Synthesis of the NHC–Ir$^{I}$ complexes used in this study

A mixture of $\mathbf{L_{a–f}}$ (0.5 mmol) and $Ag_2O$ (60 mg, 0.26 mmol) was suspended in $CH_2Cl_2$ (10 mL) under an argon atmosphere and stirred at ambient temperature for 1 h shielded from light. $[IrCl(COD)]_2$ (168 mg, 0.25 mmol) was then added to the suspension, and the reaction mixture was stirred at ambient temperature for an additional 12 h. The resulting suspension was filtered through Celite®. The remaining solid was washed with $CH_2Cl_2$ (2 × 5 mL), and the solvent of the filtrate was evaporated. The residue was purified by silica gel column chromatography using a $CH_2Cl_2$ and hexane (9 : 1) mixture as an eluent to give a pure complex as a yellow solid. Complexes **1d–f** are new compounds and their spectroscopic data are given in the following text.

**Complex 1d.** Yield: 74%, 257 mg. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.37 (d, $J$ = 7.6 Hz, 4H), 6.98–7.03 (m, 4H), 6.88 (d, $J$ = 8.8 Hz, 4H), 6.18 (d, $J$ = 15.2 Hz, 2H), 5.89 (d, $J$ = 15.6 Hz, 2H), 4.77 (t, $J$ = 3.0 Hz, 2H), 3.78 (s, 6H), 2.96 (t, $J$ = 2.8 Hz, 2H), 2.27–2.05 (m, 4H), 1.81–1.73 (m, 2H), 1.62–1.57 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 192.4, 159.2, 135.0, 128.6, 127.9, 122.5, 114.2, 111.2, 87.1, 55.3, 52.9, 52.2, 33.5, 29.3. Anal. Calcd for $C_{31}H_{34}ClIrN_2O_2$: C, 53.63; H, 4.94; N, 4.03. Found: C, 53.72; H, 4.88; N, 3.96. HRMS (ESI) $m/z$: $[M - Cl]^+$ Calcd for $C_{31}H_{34}IrN_2O_2$ 659.2250; Found: 659.2291.

**Complex 1e.** Yield: 71%, 283 mg. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.18–7.08 (m, 6H), 6.97 (d, $J$ = 8.8 Hz, 4H), 6.92 (d, $J$ = 8.8 Hz, 4H), 6.66 (d, $J$ = 8.8 Hz, 4H), 5.99 (d, $J$ = 14.8 Hz, 2H), 5.53 (d, $J$ = 14.8 Hz, 2H), 4.66 (t, $J$ = 2.8 Hz, 2H), 3.72 (s, 6H), 2.95 (t, $J$ = 2.8 Hz, 2H), 2.22–2.00 (m, 4H), 1.73–1.65 (m, 2H), 1.54–1.49 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 180.9, 158.7, 132.1, 130.5, 129.1, 129.0, 128.7, 128.3, 128.1, 113.5, 84.5, 55.2, 52.7, 52.1, 33.5, 29.4. Anal. Calcd for $C_{39}H_{40}ClIrN_2O_2$: C, 58.82; H, 5.06; N, 3.52. Found: C, 58.75; H, 5.02; N, 3.57. HRMS (ESI) $m/z$: $[M - Cl]^+$ Calcd for $C_{39}H_{40}IrN_2O_2$ 761.2719; Found: 761.2735.

**Complex 1f.** Yield: 83%, 355 mg. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.00 (d, $J$ = 8.4 Hz, 4H), 6.82 (d, $J$ = 8.0 Hz, 4H), 6.69 (d, $J$ = 8.0 Hz, 4H), 6.63 (d, $J$ = 8.0 Hz, 4H), 5.92 (d, $J$ = 15.2 Hz, 2H), 5.50 (d, $J$ = 14.8 Hz, 2H), 4.64 (t, $J$ = 3.2 Hz, 2H), 3.73 (s, 6H), 3.71 (s, 6H), 2.91 (t, $J$ = 3.0 Hz, 2H), 2.16–2.02 (m, 4H), 1.70–1.63 (m, 2H), 1.53–1.46 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 180.3, 159.4, 158.6, 131.8, 131.8, 129.4, 128.9, 121.0, 113.6, 113.5, 84.2, 55.2, 55.1, 52.6, 52.0, 33.5, 29.3. Anal. Calcd for $C_{41}H_{44}ClIrN_2O_4$: C, 57.50; H, 5.18; N, 3.27. Found: C, 57.39; H, 5.25; N, 3.30. HRMS (ESI) $m/z$: $[M - Cl]^+$ Calcd for $C_{41}H_{44}IrN_2O_4$ 821.2930; Found: 821.2967.

### General procedure for the α-alkylation of arylacetonitriles with primary alcohols

To a 20 mL reaction tube (1 cm × 20 cm) with a condenser, were added KOH (2.8 mg, 0.05 mmol, 5 mol%), arylacetonitrile (1.0 mmol), primary alcohol (1.0 mmol), and a solution of complex **1f** (0.001 mmol, 0.1 mol%) in toluene (1.0 mL) under open air conditions. The reaction mixture was then vigorously stirred (1200 rpm) in a preheated oil bath at 135 °C for 2–16 h. Thereafter, the reaction mixture was cooled down to ambient temperature, and $CH_2Cl_2$ (5.0 mL) was added to the reaction mixture. After filtration, the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel

column chromatography using a hexane and ethyl acetate (9 : 1) mixture as an eluent to afford the desired product.

**2,3-Diphenylpropanenitrile (4a).**[8c,d,12b,14] White solid. Yield: 187 mg, 90%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.40–7.26 (m, 8H), 7.16 (d, $J$ = 7.6 Hz, 2H), 4.02 (t, $J$ = 7.2 Hz, 1H), 3.24–3.12 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 136.2, 135.2, 129.1, 128.9, 128.5, 128.1, 127.4, 127.3, 120.3, 42.1, 39.7.

**2-(4-Methoxyphenyl)-3-phenylpropanenitrile (4b).**[8c,d,15] White solid. Yield: 228 mg, 96%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.33–7.14 (m, 7H), 6.90–6.87 (m, 2H), 3.96 (t, $J$ = 7.2 Hz, 1H), 3.81 (s, 3H), 3.21–3.08 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 159.3, 136.3, 129.2, 128.5, 128.5, 127.2, 127.1, 120.6, 114.3, 55.2, 42.2, 38.9.

**3-Phenyl-2-(*p*-tolyl)propanenitrile (4c).**[8c,d,14,15] Yellow solid. Yield: 201 mg, 91%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.35–7.16 (m, 9H), 3.98 (t, $J$ = 7.4 Hz, 1H), 3.22–3.10 (m, 2H), 2.37 (s, 3H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 137.9, 136.4, 132.2, 129.6, 129.1, 128.5, 127.3, 127.2, 120.5, 42.1, 39.3, 21.0.

**2-(4-Chlorophenyl)-3-phenylpropanenitrile (4d).**[8d,14] White solid. Yield: 225 mg, 93%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.34–7.26 (m, 5H), 7.19–7.10 (m, 4H), 3.99 (t, $J$ = 7.2 Hz, 1H), 3.22–3.09 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 135.7, 134.2, 133.6, 129.2, 129.1, 128.8, 128.5, 127.5, 119.9, 41.9, 39.0.

**2-(4-Bromophenyl)-3-phenylpropanenitrile (4e).**[8c,14,15] White solid. Yield: 149 mg, 52%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.48 (d, $J$ = 8.4 Hz, 2H), 7.33–7.11 (m, 7H), 3.98 (t, $J$ = 7.2 Hz, 1H), 3.21–3.08 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 135.7, 134.1, 132.0, 129.1, 128.6, 127.4, 122.2, 119.8, 41.8, 39.1.

**2-(2-Chlorophenyl)-3-phenylpropanenitrile (4f).**[15] Yellow solid. Yield: 198 mg, 82%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.53–7.24 (m, 9H), 4.54 (q, $J$ = 4.6 Hz, 1H), 3.26–3.06 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 136.0, 132.9, 132.5, 129.9, 129.6, 129.1, 129.1, 128.6, 127.5, 127.4, 119.6, 40.0, 37.2.

**3-(4-Methoxyphenyl)-2-phenylpropanenitrile (4g).**[14,15] White solid. Yield: 216 mg, 91%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.43–7.26 (m, 7H), 7.03–6.94 (m, 2H), 4.48 (t, $J$ = 7.0 Hz, 1H), 3.87 (s, 3H), 3.22–3.14 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 155.8, 136.9, 129.3, 128.9, 128.2, 128.2, 126.9, 123.4, 120.6, 120.4, 110.6, 55.3, 39.7, 33.9.

**2-Phenyl-3-(*p*-tolyl)propanenitrile (4h).**[8c,12b,14,15] Yellow solid. Yield: 195 mg, 88%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.42–7.30 (m, 5H), 7.15 (d, $J$ = 8.0 Hz, 2H), 7.08 (d, $J$ = 8.0 Hz, 2H), 4.01 (t, $J$ = 7.4 Hz, 1H), 3.18–3.14 (m, 2H), 2.37 (s, 3H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 136.8, 135.2, 133.1, 129.1, 128.9, 128.8, 128.0, 127.3, 120.3, 41.6, 39.7, 20.9.

**3-(4-Chlorophenyl)-2-phenylpropanenitrile (4i).**[8d,14,15] White solid. Yield: 208 mg, 86%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.39–7.23 (m, 7H), 7.05 (d, $J$ = 12.4 Hz, 2H), 3.99 (t, $J$ = 7.2 Hz, 1H), 3.19–3.09 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 134.7, 134.5, 133.3, 130.6, 129.0, 128.7, 128.3, 127.4, 120.0, 41.3, 39.5.

**3-(4-Bromophenyl)-2-phenylpropanenitrile (4j).**[8d,15] White solid. Yield: 238 mg, 83%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.42–7.22 (m, 7H), 6.98 (dd, $J_1$ = 5.6 Hz, $J_2$ = 1.6 Hz, 2H), 3.99 (t, $J$ = 7.2 Hz, 1H), 3.18–3.07 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 135.0, 134.7, 131.7, 130.9, 129.0, 128.3, 127.4, 121.4, 120.0, 41.4, 39.4.

**2-Phenyl-3-(4-(trifluoromethyl)phenyl)propanenitrile (4k).**[8d,14] White solid. Yield: 165 mg, 60%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.56 (d, $J$ = 8.0 Hz, 2H), 7.40–7.24 (m, 2H), 4.05 (t, $J$ = 7.4 Hz, 1H), 3.28–3.18 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 140.1, 134.5, 129.9, 129.6, 129.1, 128.4, 127.4, 125.5, 125.5, 125.4, 125.4, 122.7, 119.8, 41.7, 39.3. $^{19}$F NMR (376 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = −62.6.

**3-(4-(Dimethylamino)phenyl)-2-phenylpropanenitrile (4l).**[27] Yellow solid. Yield: 208 mg, 83%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.40–7.26 (m, 5H), 7.03 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz, 2H), 6.68 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz, 2H), 3.95 (dd, $J_1$ = 8.4 Hz, $J_2$ = 6.4 Hz, 1H), 3.15–3.03 (m, 2H), 2.94 (s, 6H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 149.8, 135.6, 129.8, 128.9, 127.9, 127.5, 124.0, 120.7, 112.6, 41.4, 40.5, 40.2.

**2-Phenyl-3-(ferrocene-1-yl)propanenitrile (4m).** Yellow solid. Yield: 281 mg, 89%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.38–7.23 (m, 5H), 4.11 (s, 8H), 4.04–4.03 (m, 1H), 3.82 (dd, $J_1$ = 8.0 Hz, $J_2$ = 6.0 Hz, 1H), 3.04–2.89 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 135.5, 128.8, 128.0, 127.3, 120.7, 82.7, 69.2, 68.9, 68.6, 68.0, 68.0, 39.9, 37.2. HRMS (ESI) $m/z$: $[M]^+$ Calcd for $C_{19}H_{17}FeN$ 315.0710; Found: 315.0711.

**2-Phenyl-3-([1′-(diphenylphosphorothioyl)]ferrocene-1-yl)propanenitrile (4n).** Dark yellow solid. Yield: 228 mg, 86%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.74–7.66 (m, 4H), 7.44–7.19 (m, 11H), 4.47–4.43 (m, 2H), 4.36–4.33 (m, 2H), 4.16–4.15 (m, 2H), 4.03–4.00 (m, 2H), 3.79 (t, $J$ = 7.0 Hz, 1H), 2.73 (d, $J$ = 7.2 Hz, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 135.2, 134.9, 134.8, 133.9, 131.6, 131.5, 128.8, 128.2, 128.1, 128.0, 127.4, 120.5, 84.4, 75.9, 75.0, 71.4, 71.2, 69.8, 39.5, 36.1. HRMS (ESI) $m/z$: $[M + H]^+$ Calcd for $C_{31}H_{27}FeNPS$ 532.0951; Found: 532.0961.

**2-Phenyl-3-(pyridin-2-yl)propanenitrile (4o).**[12b,14] Yellow liquid. Yield: 158 mg, 76%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 8.60 (d, $J$ = 4,8 Hz, 1H), 7.62–7.38 (m, 1H), 7.36–7.26 (m, 5H), 7.18 (dd, $J_1$ = 7.6 Hz, $J_2$ = 4.8 Hz, 1H), 7.11 (d, $J$ = 7.6 Hz, 1H), 4.48 (dd, $J_1$ = 9.2 Hz, $J_2$ = 6.4 Hz, 1H), 3.39–3.25 (m, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 156.0, 149.6, 136.6, 135.4, 129.0, 128.0, 127.3, 123.8, 122.2, 120.5, 44.0, 37.1.

**2-Phenyl-3-(thiophen-2-yl)propanenitrile (4p).**[12b,15] Yellow liquid. Yield: 196 mg, 92%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.41–7.30 (m, 6H), 7.19 (dd, $J_1$ = 5.2 Hz, $J_2$ = 1.2 Hz, 1H), 6.95 (dd, $J_1$ = 5.2 Hz, $J_2$ = 3.6 Hz, 1H), 4.06 (dd, $J_1$ = 8.4 Hz, $J_2$ = 6.4 Hz, 1H), 3.48–3.33 (m, 2H). $^{13}$C {$^1$H} NMR

(100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 137.9, 134.7, 129.0, 128.3, 127.4, 127.0, 126.9, 124.8, 120.0, 40.0, 36.1.

### General procedure for the synthesis of 2-aminoquinolines

To a 20 mL reaction tube with a condenser, were added KOH (1.4 mg, 0.025 mmol, 5 mol%), arylacetonitrile (0.5 mmol), 2-aminobenzy alcohol (0.5 mmol), and a solution of complex **1f** (0.0005 mmol, 0.1 mol%) in toluene (1.0 mL) under open air conditions. The reaction mixture was then vigorously stirred (1200 rpm) in a preheated oil bath at 135 °C for 4–8 h. Thereafter, the reaction mixture was cooled to ambient temperature, and ethyl acetate (5.0 mL) was added to the reaction mixture. After filtration, the filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using a hexane : ethyl-acetate : triethyl-amine (7 : 3 : 0.1) mixture as an eluent to afford the desired 2-aminoquinolines.

**3-Phenylquinolin-2-amine (6a).**[8c,26c,28] Yellow solid. Yield: 88 mg, 80%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.77 (s, 1H), 7.69 (d, $J$ = 8.4 Hz, 1H), 7.63 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 7.56–7.41 (m, 6H), 7.26 (td, $J_1$ = 7.2 Hz, $J_2$ = 0.8 Hz, 1H), 5.12 (s, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 155.2, 147.2, 137.6, 137.1, 129.5, 129.1, 128.9, 128.1, 127.4, 125.6, 125.0, 124.2, 122.7.

**3-(4-Methoxyphenyl)quinolin-2-amine (6b).**[28] Yellow solid. Yield: 105 mg, 84%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.73 (s, 1H), 7.67 (d, $J$ = 8.4 Hz, 1H), 7.61 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 7.54 (td, $J_1$ = 6.8 Hz, $J_2$ = 1.2 Hz, 1H), 7.43 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.0 Hz, 2H), 7.24 (td, $J_1$ = 6.8 Hz, $J_2$ = 0.8 Hz, 1H), 7.00 (dd, $J_1$ = 6.8 Hz, $J_2$ = 2.0 Hz, 2H), 5.16 (s, 2H), 3.85 (s, 3H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 159.5, 155.6, 147.0, 136.9, 130.0, 129.7, 129.3, 127.3, 125.5, 124.2, 122.6, 114.5, 55.3.

**3-(*p*-Tolyl)quinolin-2-amine (6c).**[26c,28] Yellow solid. Yield: 95 mg, 81%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.75 (s, 1H), 7.68 (dd, $J_1$ = 8.6 Hz, $J_2$ = 0.8 Hz, 1H), 7.62 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 7.55 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.2 Hz, 1H), 7.41 (dd, $J_1$ = 6.0 Hz, $J_2$ = 2.0 Hz, 2H), 7.30–7.23 (m, 3H), 5.17 (s, 2H), 2.42 (s, 3H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 155.4, 147.1, 138.0, 136.9, 134.6, 129.7, 129.4, 128.7, 127.5, 125.5, 125.0, 124.2, 122.6, 21.2.

**3-(4-Chlorophenyl)quinolin-2-amine (6d).**[26c] Yellow solid. Yield: 90 mg, 71%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.76 (s, 1H), 7.69 (dd, $J_1$ = 8.2 Hz, $J_2$ = 0.8 Hz, 1H), 7.64 (dd, $J_1$ = 8.0 Hz, $J_2$ = 1.2 Hz, 1H), 7.57 (td, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz, 1H), 7.47 (s, 4H), 7.27 (td, $J_1$ = 7.6 Hz, $J_2$ = 2.0 Hz, 1H), 4.93 (s, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 154.8, 147.3, 137.3, 136.0, 134.3, 130.3, 129.9, 129.4, 127.5, 125.7, 124.1, 123.7, 122.9.

**3-(4-Bromophenyl)quinolin-2-amine (6e).**[26c,28] Yellow solid. Yield: 97 mg, 65%. $^1$H NMR (400 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 7.77 (s, 1H), 7.70 (d, $J$ = 8.4 Hz, 1H), 7.64 (d, $J$ = 8.0 Hz, 1H), 7.60–7.53 (m, 2H), 7.38 (td, $J_1$ = 7.6 Hz, $J_2$ = 6.0 Hz, 3H), 7.28 (t, $J$ = 7.0 Hz, 1H), 4.88 (s, 2H). $^{13}$C {$^1$H} NMR (100.6 MHz, $CDCl_3$, TMS, 25 °C, ppm): $\delta$ = 155.2, 147.2, 137.6, 137.1, 129.5, 129.1, 128.9, 128.1, 127.4, 125.6, 125.0, 124.2, 122.7.

### Procedure for the time profile of the reaction

Six identical reactions were performed in different reaction tubes at different time intervals (5, 15, 30, 60, 90, and 120 min). To a 20 mL reaction tube (1 cm × 20 cm) with a condenser, were added KOH (2.8 mg, 0.05 mmol, 5 mol%), arylacetonitrile (1.0 mmol), primary alcohol (1.0 mmol), and a solution of complex **1f** (0.001 mmol, 0.1 mol%) in toluene (1.0 mL) under open air conditions. The reaction mixture was then vigorously stirred (1200 rpm) in a preheated oil bath at 135 °C for 5–120 min. After completion of the reactions, conversions and yields were determined by $^1$H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

## Conclusions

We have successfully synthesized and characterized a series of backbone-modified [IrCl(cod)(NHC)] complexes. The variation of the benzyl groups at the 1,3-positions and aryl groups at the 4,5-positions of imidazole affects the electronic nature of the NHC ligands, as confirmed by the comparison of the IR carbonyl stretching frequencies of the *in situ* prepared [IrCl$(CO)_2$(NHC)] complexes. The electronic nature of the NHC ligands seemed to play an important role in determining the reaction efficiency of the NHC–Ir-catalyzed α-alkylation of nitriles with primary alcohols. Complex **1f** with an NHC ligand bearing 4-methoxybenzyl groups at the 1,3-positions and 4-methoxyphenyl groups at the 4,5-positions proved that it is a general and highly productive catalyst for this transformation under an air atmosphere requiring significantly short reaction times. To the best of our knowledge, one of the highest turnover numbers (TONs up to 960) is reported for the α-alkylation of nitriles with primary alcohols among all the reported TM complexes as catalysts for these transformations.

## Conflicts of interest

There are no conflicts to declare.

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