Iron-Based Imidazolium Salts as Versatile Catalysts for the Synthesis of Quinolines and 2- and 4-Allylanilines by Allylic Substitution of Alcohols

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Abstract: Readily available iron(III)-based imidazolium salts have proven to be very versatile catalysts for the allylic substitution reaction of alcohols with anilines, allowing the synthesis of quinolines, 2-allylanilines and 4-allylanilines just by modulating the reaction conditions. Noteworthy, the formation of quinoline derivatives proceeds by *ortho*-allylation of the corresponding aniline and subsequent oxidative

Introduction

The search for and development of new strategies towards the design of green and sustainable transformations, which minimize waste production and avoid the use of toxic or expensive reagents or catalysts, is a current challenge for the organic chemical community. Indeed, sustainability is the main goal of green chemistry.^[1] In this sense, and in the particular case of allylic substitution reactions, the replacement of the most commonly used 'big' leaving groups (e.g., carbonates and acetates) with the direct use of a hydroxy group, is an attractive strategy from both practical and environmental points of view, as water would be the only by-product. However, this approach has two main limitations, the poor ability of the hydroxy group as leaving group and the formation of stoichiometric amounts of water, which could deactivate the catalyst.

Remarkable efforts have been made in the last years in the design of new catalytic systems which can carry out this reaction and overcome these limitations.^[2] Recently, iron-based catalysts have emerged as an interesting alternative to other more expensive and toxic metallic catalysts.^[3] These iron catalysts cover a good range of transformations, but there is still room for improvement and new discoveries in the area. Being aware of that, our group, interested in the cyclization mediated by atmospheric oxygen. The reaction using anilines as nucleophiles is selective to the C-alkylation versus the N-alkylation, under any reaction conditions studied.

Keywords: C-alkylation; allylic alcohols; imidazolium salts; iron(III) catalysts; quinolines

development and study of efficient, cost-effective and environmentally friendly processes, envisioned the design of different iron(III)-based Lewis acidic ionic liquids (IBLAILs) (Figure 1). This type of metal-ioncontaining ionic liquids has received attention in the last years.^[4] Indeed, imidazolium-based ionic liquids (ILs) containing anionic iron(III) has been reported for extractive desulfurization of fuel oils,^[5] being also effective in the extraction coupled with oxidative desulfurization.^[6] Moreover, the 1-butyl-3-methylimidazolium tetrachloroferrate has been employed as an efficient catalyst in the coupling between aryl Grignard reagents and alkyl halides^[7] and in the dimerization of norbornadiene,^[8] recyclability of the catalyst also



$$\begin{split} \mathbf{I} &: \mathbf{R}^1 = \mathbf{Me}, \, \mathbf{R}^2 = \mathbf{CH}_2\mathbf{CO}_2\mathbf{Me}, \, \mathbf{R}^3 = \mathbf{H} \\ \mathbf{II} &: \mathbf{R}^1 = \mathbf{Me}, \, \mathbf{R}^2 = (\mathbf{CH}_2)_3\mathbf{CO}_2\mathbf{E}t, \, \mathbf{R}^3 = \mathbf{H} \\ \mathbf{III} &: \mathbf{R}^1 = \mathbf{Me}, \, \mathbf{R}^2 = (\mathbf{CH}_2)_5\mathbf{CO}_2\mathbf{Me}, \, \mathbf{R}^3 = \mathbf{H} \\ \mathbf{IV} &: \mathbf{R}^1 = \mathbf{Me}, \, \mathbf{R}^2 = (\mathbf{CH}_2)_3\mathbf{CO}_2\mathbf{E}t, \, \mathbf{R}^3 = \mathbf{Me} \\ \mathbf{V} &: \mathbf{R}^1 = n\text{-Bu}, \, \mathbf{R}^2 = \mathbf{CH}_2\mathbf{CO}_2\mathbf{Me}, \, \mathbf{R}^3 = \mathbf{H} \\ \mathbf{V} &: \mathbf{R}^1 = \mathbf{Me}, \, \mathbf{R}^2 = \mathbf{CH}_2\mathbf{CO}_2\mathbf{Me}, \, \mathbf{R}^3 = \mathbf{H} \end{split}$$

Figure 1. Iron(III)-based Lewis acidic ionic liquids (IBLAILs).

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being possible. The three-component reaction between an aldehyde, a β -keto ester and urea (Biginelli reaction) has been performed successfully in the presence of an iron-containing ionic liquid as solvent and catalyst.^[9]

The main advantages of these transition metalbased ILs are their easy preparation and the fact that they can be used as catalysts in green chemical protocols. Inspired by previous works of Powel and Dyson,^[4b,10] we have designed different IBLAILs by changing \mathbb{R}^1 , \mathbb{R}^2 and \mathbb{R}^3 groups (Figure 1), which have been analysed by ICP-MS (*ca.* 15% of iron, see the Supporting Information). The combination of the imidazolium chloride and iron(III) chloride in a 1:1 ratio provided the corresponding ionic liquid with the anion [FeCl₄]⁻, as described by different groups.^[8,11] Next, we studied the catalytic activity of these IBLAILs **I–V** in the allylic substitution reaction with allylic alcohols. Herein, we report the results obtained from this study.

Results and Discussion

Catalytic Activity of the Iron(III)-Based Lewis Acidic Imidazolium Salts

The reaction between (E)-1,3-diphenylprop-2-en-1-ol (1a) and N-methylaniline (2a) was chosen as model reaction to optimize the reaction conditions (Scheme 1, Table 1). First, the reaction was carried out with 5 mol% of Fe(III)-based Lewis acidic ionic liquid I (Figure 1) at 25°C under solvent-free conditions. Unexpectedly, a 1:1 mixture of the para and ortho alkylation products (3aa and 4aa, respectively) was obtained, instead of the amination product, although the conversion was low (Table 1, entry 1). Previous protocols in the literature reveal that anilines as nucleophiles provide the corresponding N-allylanilines as predominant product regardless of the catalyst employed [including iron(III) catalysts] and independent of the aniline derivative.^[12] In addition, the reaction between activated alcohols and aromatic compounds to produce C-alkylation products (Frie-



Scheme 1. Model reaction for optimization of the reaction conditions.

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Table 1. Optimization of the reaction conditions.^[a]

Entry	IBLAIL (mol%)	<i>T</i> [°C]	Conversion [%] ^[b]	
-			3aa	4 aa
1	I (5)	25	7	7
2	II (5)	25	18	14
3	III (5)	25	25	16
4	IV (5)	25	30	16
5	$\mathbf{V}(5)$	25	15	11
6	VI (5)	25	21	10
7	I (5)	50	32	34
8	I (5)	70	24	32
9	I (5)	100	61	21
10	I (10)	50	40	43
11	I (10)	70	42	32
12	I (10)	100	73	27
13 ^[c]	I (10)	50	9	6
14 ^[c]	I (10)	70	40	25
15 ^[c]	I (10)	100	37	17
16 ^[d]	I (10)	100	28	17
17	II (10)	70	18	14
18	III (10)	70	35	23
19	IV (10)	70	68	32
20	IV (10)	100	84	16
21	V (10)	70	63	37
22	V (10)	100	90	-
23	VI (10)	70	65	33
24	VI (10)	100	75	15
25 ^[c]	V (10)	70	22	12
26 ^[c]	V (10)	100	47	23
27 ^[e]	V (10)	100	25	12
28 ^[f]	V (10)	100	36	10
29 ^[g]	V (10)	100	12	3

^[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (0.5 mmol). Reaction performed in an open vessel.

- ^[b] Conversion determined by GC analysis.
- [c] Microwave irradiation was employed to heat the reaction. Microwaves conditions: 40 W (initial potency), 36 psi and 60 min.
- ^[d] Microwave irradiation conditions: 40 W (initial potency), 36 psi and 30 min.
- ^[e] Reaction performed with toluene (0.2 mL) as solvent.
- ^[f] Reaction performed with 1,2-dichloroethane (0.2 mL) as solvent.
- ^[g] Reaction performed with dioxane (0.2 mL) as solvent.

del–Crafts reaction) has been reported by means of different metal-based catalysts,^[13] albeit there are only few examples for the formation of C-alkylation products with anilines.^[14]

Rising the temperature to 50 °C and using IBLAIL I, the same mixture of products **3aa** and **4aa** was obtained in 32% and 34% conversion, respectively (Table 1, entry 7). An increase of the catalyst loading to 10 mol% or of the temperature to 70 °C did not produce a significant improvement in the results (Table 1, entries 8, 10 and 11), although a slight selectivity towards compound **3aa** was observed at 70 °C. Next, we performed the reaction at 100 °C, obtaining

full conversion with 10 mol% of IBLAIL I, and *ca.* 3:1 selectivity ratio for the *para*-alkylated product **3aa** (Table 1, entry 12). Other reaction conditions such as microwave irradiation at 50, 70 or 100 °C were also tested, but lower conversions to the desired products were observed (Table 1, compare entries 13–16 with entries 9–12).

The properties of ionic liquids (such as imidazolium salts) vary depending on the size of the different components (i.e., cation and anion),^[15] so different substituents in the imidazole nitrogens can modulate the catalytic activity of the salts. Consequently, other Fe(III)-based Lewis acidic ionic liquids, such as **II-VI** (Figure 1), were evaluated as catalysts in the reaction between 1a and 2a. The reactions were performed with 10 mol% of IBLAIL (II-VI) at 25 and 70°C, in order to detect differences in the conversion and/or in the selectivity of the reaction. The use of IBLAILs **II-VI** provided comparable conversions and similar regioselectivities in our model reaction than catalyst IBLAIL I at 25°C (Table 1, entries 2-6), but a different catalytic activity was observed in all cases at 70°C (Table 1, entries 11, 17–19, 21 and 23). While catalysts II and III provided lower conversions than I at 70°C (Table 1, entries 17 and 18), catalysts IV, V and VI proved to be superior at that temperature (Table 1, entries 19, 21 and 23). Gratifyingly, when the reaction was performed at 100 °C for 24 h under solvent-free conditions, using IBLAIL V as catalyst, 90% of conversion was obtained with complete regioselectivity towards the *para*-alkylation product **3aa** (Table 1, entry 22). Salts IV and VI were also tested at 100°C (Table 1, entries 20 and 24), but the selectivity was lower than with V. Using IBLAIL V, the reaction was performed under microwave irradiation (Table 1, entries 25 and 26), but no improvement was observed. Furthermore, different solvents were evaluated, such as toluene, 1,2-dichloroethane and dioxane (Table 1, entries 27-29), all providing, in general, lower conversions and regioselectivities than 'neat' reaction conditions (in the absence of solvent).

Quinoline Synthesis by Allylic Substitution and Oxidative Cyclization

Next, we decided to explore *para* substituted anilines as nucleophiles. To our surprise, the reaction of *p*-toluidine (**2b**) with allylic alcohol **1a** at 100 °C in the presence of **V** (10 mol%) in the absence of solvent (Table 2) provided a mixture of the *ortho* alkylation product **4ab** and the quinoline **5ab** (Table 2, entry 1). The formation of the quinoline can be explained by an oxidative cyclization process^[16] after the allylic substitution reaction. In an attempt to improve the selectivity of the process and favor the quinoline formation, we evaluated different solvents (see the Support**Table 2.** Optimization of the reaction conditions for quino-line synthesis $^{[a]}$



Entry	Catalyst (x mol%)	Conv. [%] ^[b]	
-		4ab	5ab
1	V (10)	27	35
2 ^[c]	V (10)	32	62
3 ^[c]	V (20)	8	92
4 ^[c]	no catalyst	_[d]	_[d]
5 ^[c]	imidazolium chloride ^[e] (20)	20	_
6 ^[c]	$FeCl_3 \cdot 6H_2O$ (20)	7	30
7	$\{(Me)_2[HO(CH_2)_2]NBn\}FeCl_4$ (20)	26	66
8	$[(Et)_3NBn]FeCl_4$ (20)	38	50

^[a] *Reaction conditions:* **1a** (0.5 mmol), **2a** (0.5 mmol), 100 °C. Reaction performed in an open vessel.

^[b] Conversion was determined by GC analysis.

^[c] Reaction time: 48 h.

^[d] Less than 10% of the *N*-allylaniline was observed in the reaction crude together with the starting materials, but neither **4ab** nor **5ab** were observed.

 [e] 1-(Methoxycarbonylmethyl)-3-butylimidazolium chloride (20 mol%) was used as catalyst.

ing Information) without any success. Only the use of 1,2-dichloroethane provided the corresponding orthoalkylation product 4ab exclusively in 97% conversion (see the Supporting Information). Working under 'neat' reaction conditions and extending the reaction time to 48 h, the conversion to the desired quinoline 5ab increased to 62% (Table 2, entry 2). Raising the catalyst loading of IBLAIL V to 20 mol%, provided 92% of quinoline 5ab after 48 h (Table 2, entry 3). It is worth noting that in the absence of catalyst, no reaction was observed (Table 2, entry 4 and footnote [d]). When the imidazolium salt precursor of **V**, without iron [i.e., 1-(methoxycarbonylmethyl)-3-butylimidazolium chloride] was tested as catalyst, only the ortho alkylation product 4ab with low conversion (20%) was obtained after 48 h of heating at 100°C (Table 2, entry 5). Furthermore, a mixture of both products 4ab and 5ab was obtained when 20 mol% of FeCl₃·6H₂O was used as catalyst under the same reaction conditions (Table 2, entry 6), although with very low conversion. Other ammonium tetrachloroferrate salts [i.e., benzyl(2-hydroxyethyl)dimethylammonium tetrachloroferrate and benzyl(triethyl)ammonium tetrachloroferrate] in the absence of an imidazolium cation, were also tested in the reaction. These ammonium salts catalyzed the reaction between 1a and 2b with high conversion but giving a mixture of both

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compounds **4ab** and **5ab** (Table 2, entries 7 and 8). From these experiments, we concluded that the combination of an iron(III) source with the imidazolium salt constitutes a better catalytic system in terms of activity and selectivity. IBLAIL **V** was highlighted as the optimal catalyst for the process, at a loading of 20 mol%. It is remarkable that the amount of iron(III) employed is about 3 mol% (20 mol% of **V**, which contains *ca.* 15% of iron as measured by ICP).

With the optimized reaction conditions for the preparation of quinolines in hand, we examined the scope of the present reaction with different anilines and allylic alcohol **1a** (Table 3). As mentioned before, p-toluidine was transformed into the corresponding quinoline **5ab** with excellent conversion (>90%), being isolated in 70% yield. The electron-rich substituted p-methoxyaniline provided quinoline **5ac** in high yield (Table 3), however, the presence of two methoxy groups in the aniline caused lower yields (product **5ad**, Table 3). Anilines provided with halo-

Table 3. Quinoline synthesis: scope.^[a]



[a] Reaction conditions: 1a (0.5 mmol), 2 (0.5 mmol), V (20 mol%), 100 °C for 48 h. Reaction performed in an open vessel. In parentheses: isolated yield after flash chromatography.

^[b] PMP=para-methoxyphenyl.

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gen groups, such as chloro and bromo, were also compatible with the present reaction conditions, affording the corresponding quinolines **5ae** and **5af**, respectively, in good yields (Table 3).

To broaden the scope to other allylic alcohols we carried out the reaction with cinnamyl alcohol (1b), (E)-4-phenylbut-3-en-2-ol (1c) and its isomeric allylic alcohol (*E*)-1-phenylbut-2-en-1-ol (1c'). Using *p*-toluidine (2b) as nucleophile, quinolines 5bb (76% from alcohol 1b) and 5cb (65% from alcohol 1c and 60% from 1c') were obtained as exclusive regioisomers (Table 3). This fact can be explained by the stability of the double bond instead of the intermediate formed in the reaction media.^[12] Besides, (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (1d) produced a mixture of both possible regioisomers 5db and 5db' (in a 2:1 ratio, Table 3), the difference, in this case, being lower in terms of stability between both intermediates.

Mechanistic Considerations in the Formation of Quinoline Derivatives

Several tests were performed in order to get a better insight into the reaction mechanism for the formation of the quinoline derivatives. First, the reaction flask was flushed with a stream of air, to understand if atmospheric oxygen was the oxidant agent. Indeed, both yield and conversion of the corresponding quinoline **5ab** increased (full conversion and 79% isolated yield). On the contrary, only product **4ab** was observed when the reaction was carried out under argon inert atmosphere (Scheme 2).

To reinsure that the atmospheric oxygen is the true oxidant in the process, the reaction, under an inert atmosphere, was attempted on the *ortho*-alkylated product **4ab**. After 48 h, unaltered product **4ab** was obtained as main product, together with a small amount of quinoline **5ab** (less than 5%, Scheme 3). In a parallel experiment, **4ab** was treated with catalyst **V** under the optimized standard reaction conditions (air atmosphere), and quinoline **5ab** was quantitatively obtained (Scheme 3). These experiments prove the



Scheme 2. Experiments under an (a) air stream and (b) argon atmosphere. Isolated yields.





Scheme 3. Experiments for oxidative cyclization under an (a) air stream and (b) argon atmosphere. Isolated yields.

importance of the atmospheric oxygen in our reaction. Consequently, it can be postulated that first the ortho-alkylated intermediate 4ab is formed in the reaction media followed by an oxidative cyclization that leads to the formation of the corresponding quinoline.^[16] To corroborate this point, the product distribution profiles were obtained for the reaction between 1a and 2b (Figure 2), under the optimal reaction conditions (Table 2, entry 4). From this study, different conclusions can be drawn: (i) the corresponding product of ortho-alkylation (4ab) is formed in more than 90% in the first 5 min of the reaction (Figure 2); (ii) this intermediate undergoes oxidative cyclization to form the corresponding quinoline during the rest of the reaction time (Figure 2). Moreover, the formation of the amination intermediate can be ruled out since it is not detected in the reaction profile.

Previous work by others,^[12b,17] demonstrates that the allylic alcohol (*E*)-1,3-diphenylprop-2-en-1-ol (**1a**) could be oxidized to chalcone in the presence of



Figure 2. Product distribution profiles (by GC analysis) in the reaction media *vs.* reaction time (minutes): (•) starting allylic alcohol **1a**; (•) *ortho*-alkylation product **4ab**; (×) quinoline **5ab**. Error bars represent standard deviation from three experiments.

FeCl₃·6H₂O as catalyst at high temperatures. With this in mind, we decided to test whether this intermediate was involved in our catalytic system, with the reaction going through a Doebner–Miller (or Skraup) synthesis.^[18] Thus, allylic alcohol **1a** was stirred in the presence of IBLAIL **V** without aniline at 100 °C, and after 48 h, chalcone (**6**) was observed as the main product (Scheme 4). Next, the reaction of chalcone (**6**) with *p*-toluidine, under the optimized conditions, was attempted, however, only starting materials were recovered after 48 h (Scheme 4). Therefore, the formation of the imine intermediate can be discarded from our mechanistic pathway.



Scheme 4. Oxidation of allylic alcohol to the chalcone under the optimized reaction conditions.

Based on these experiments and on similar transformations previously reported,^[16] we speculate that the mechanism for the formation of the corresponding quinolines involves an ortho-allylation process and a subsequent oxidation, as represented in Scheme 5. The iron(III) salt assists in the formation of an incipient allylic carbocation (intermediate A),^[19] which reacts with the aniline to produce the 2-allylaniline derivative 4 and a molecule of water via a Friedel-Crafts reaction.^[13] Compound 4 could be in equilibrium with the cyclized tetrahydroquinoline **B**, although we believe this equilibrium must be shifted towards 4, since the tetrahydroquinoline **B** has never been observed. Next, the dehydrogenation with molecular oxygen (from air) promoted by iron generates quinoline 5 and two molecules of water (Scheme 5).^[20] The oxidation mediated by iron has been described before via a radical pathway.^[21] At this point, a control experiment between 1a and 2b in the presence of a radical scavenger (i.e., cumene)^[22] under the standard conditions, was performed. After the reaction time (48 h), quinoline 5ab was only obtained in 9%, whereas 2-allylaniline 4ab was produced in 89% conversion. Accordingly, it has been proved that the first step of the mechanism of the reaction is anionic (the formation of **4ab** not being affected), but the second step (oxidation to **5ab**) involves radicals (a process that has been inhibited in the presence of the radical scavenger).

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Scheme 5. Possible mechanism for the allylation and subsequent oxidation.

ortho-Allylation of Aniline Derivatives

Our optimization studies (vide supra) showed that milder reaction conditions favor the formation of ortho-alkylation products. For this reason, we decided to study the scope of the reaction between allylic alcohol 1a and different anilines, at 50°C for 2 h (Table 5). Under these conditions, the corresponding 2-allylanilines were selectively obtained in good to high yields, without detecting, in any case, the formation of the quinoline via oxidative cyclization. Thus, 4-substituted anilines with electron-donating groups, such as methyl, methoxy and phenoxy, provided the corresponding anilines 4ab, 4ac and 4ah, respectively, in good yields (Table 4). Surprisingly and, to our delight, anilines with electron-withdrawing groups (e.g., Br, Cl), which give no reaction or poor results with previously described catalytic systems,^[14,23] allowed the formation of products 4ae and 4af in high yields (Table 4). Furthermore, this methodology could be successfully extended to anilines bearing a strong electron-withdrawing group (e.g., NO₂), providing 4aj in high yield (Table 4). Additionally, when the reaction was performed with 4-ethynylaniline, the product 4ai was obtained with good yield (Table 4) due to a triple bond hydration during the reaction.

Finally, a mixture of both 2-allyl- and 4-allylaniline was obtained, when the *N*-methylaniline was employed as nucleophile. Compound **4aa** was isolated in 43% yield under the reaction conditions detailed in Table 4, although the corresponding regioisomer **3aa** was observed in 20% yield. Similarly, the aniline nu-

Ph $rac{r}{r}$ $rac{r}{r}$

Table 4. 2-Allylanilines synthesis: scope.^[a]



 [[]a] Reaction conditions: 1 (0.5 mmol), 2 (0.5 mmol), V (20 mol%), 50 °C for 2 h. Reaction performed in an open vessel. In parentheses: isolated yield after flash chromatography.

cleophile containing two methoxy groups at the 2 and 5 positions gave a mixture of *ortho-* and *para-*alkylation products with a preference for the *ortho-*alkylation product in a 2:1 ratio (compound **4ag** in Table 4 and compound **3ag** in Table 5).

para-Allylation of Aniline Derivatives

Lastly, we extended our study on the catalytic activity of IBLAIL V to anilines without *para* substituents. As far as we know, this class of substrates has been scarcely studied in protocols involving the synthesis of C-allylanilines.^[14] As detailed in Table 5, with our catalytic system, if the *para* and one or both *ortho* positions are available on the aniline ring, *para*-alkylation was preferentially observed instead of *ortho*-alkyla-

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Table 5. 4-Allylanilines synthesis: scope^[a]

[a] Reaction conditions: 1 (0.5 mmol), 2 (0.5 mmol), V (20 mol%), 100°C for 24 h. Reaction performed in an open vessel. In parentheses: isolated yield after flash chromatography.

tion. In general, the corresponding 4-allylanilines were obtained in good to excellent yields (65–80%) when performing the reaction at 100 °C as previously optimized (*vide supra*). Only the 2,5-dimethoxy-substituted aniline provided lower results (50% yield).

Scale-Up and Recycling

The catalytic activity of IBLAIL V was also examined on a larger scale, under neat conditions. Thus, when the *ortho*-alkylation reaction between **1a** and **2b** was scaled up to 10 mmol, 1.90 g of compound **4ab** were obtained (64% isolated yield, Scheme 6).

Moreover, IBLAIL V could be recovered from the reaction mixture by simple washes with ethyl acetate and centrifugation of the reaction crude. The recovered IBLAIL V showed catalytic activity for the next three cycles, although a slight decrease in activity was observed (range 80–70% conversion, see the Supporting Information). This fact maybe due to the reaction being carried out on a 10 mmol scale.



Scheme 6. Scaled-up synthesis of 2-allylaniline 3ab.

Conclusions

To conclude, we have demonstrated the efficacy of Fe(III)-based Lewis acidic ionic liquids, which are easy to prepare, as catalysts for the allylic substitution reactions of alcohols with anilines. In contrast with previously reported iron-catalyzed procedures with allylic alcohol and anilines, IBLAIL catalysts did not promote N-allylations, but C-allylation reactions. About 3 mol% of iron is employed in the different transformations, given that 20 mol% of the IBLAIL are used as catalyst, which contains *ca.* 15% of iron.

The catalytic system proved versatile. Modulating the reaction conditions (temperature, reaction time), the catalytic system can be employed selectively in the preparation of quinoline derivatives, 2-allylanilines and 4-allylanilines. The synthesis of quinolines, in a one-pot reaction, involved an allylic substitution reaction in the *ortho*-position of the aniline and a subsequent oxidative cyclization promoted by atmospheric oxygen.

Experimental Section

General

All reagents and solvents were used as supplied commercially. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated Science silica gel (EM 60-F254) plates purchased from Merck, Germany. Visualization was achieved by UV light (254 nm). Flash column chromatography was performed using silica gel and a gradient solvent system (hexane-ethyl acetate as eluent). ¹H and ¹³C NMR spectra were measured on 300 and 400 MHz spectrometers and the residual solvent peak was used as an internal reference: proton (chloroform $\delta = 7.26$ ppm) and carbon (chloroform $\delta = 77$ ppm). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), brs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The number of protons (n) for a given resonance is indicated by nH and coupling constants are reported as J values in Hz. The conversions of the reactions and purity of the products were determinate by GC analysis using a Younglin 6100GC, equipped with a flame ionization detector and a Phenomenex ZB-5 MS column (5% PH-ME siloxane): 30 m (length), 0.25 mm (inner diameter) and 0.25 µm (film).

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General Procedure for Ouinoline Synthesis

To a 10-mL tube, IBLAIL (20 mol%), the corresponding allylic alcohol (0.5 mmol) and aniline (0.5 mmol) were sequentially added. The resultant reaction mixture was stirred at 100 °C for 48 h in an open vessel. After this time, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with water $(3 \times 10 \text{ mL})$. The organic extract was dried over anhydrous MgSO4. The solvent was removed under reduced pressure to provide the crude product, which was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent.

6-Methyl-2,4-diphenylquinoline (5ab):^[24] Orange oil; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.18 - 8.13$ (m, 3 H), 7.77 (s, 1H), 7.64 (s, 1H), 7.56–7.22 (m, 9H), 2.46 (s, 3H); ¹³C NMR: $\delta = 155.9$, 148.4, 147.4, 139.7, 138.6, 136.2, 131.7, 129.8, 129.5, 129.1, 128.8, 128.6, 128.3, 127.5, 125.7, 124.4, 119.4, 21.8; MS: m/z (%)=295 (100) [M⁺], 294 (83), 281 (14), 280 (59), 189 (12), 140 (11), 139 (13).

6-Methoxy-2,4-diphenylquinoline (5ac):^[25] Brown oil; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.13 - 8.18$ (m, 3H), 7.78 (s, 1 H), 7.26–7.58 (m, 9 H), 7.20 (d, J = 3 Hz, 2 H), 3.81 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 131.6$, 129.3, 128.9, 128.8, 128.7, 128.3, 127.3, 126.3, 121.8, 119.7, 103.7, 55.5, 29.7; MS: m/z (%)=311 (100) [M⁺], 310 (34), 296 (41), 267 (10), 148 (10).

6,7-Dimethoxy-2,4-diphenylquinoline (5ad):^[26] Brown oil; ¹H NMR (300 MHz, CDCl₃): $\delta = 8.14$ (d, J = 8.1 Hz, 2H), 7.67 (s, 1H), 7.59-7.43 (m, 8H), 7.17 (s, 2H), 4.08 (s, 3H), 3.86 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 155.1$, 152.4, 149.7, 147.5, 145.9, 138.9, 129.3, 128.9, 128.8, 128.7, 128.3, 127.3, 121.0, 117.9, 108.7, 103.3, 56.2, 55.9; MS: m/z (%) = 341 (100) [M⁺], 340 (11), 326 (16), 311 (33), 254 (14).

6-Chloro-2,4-diphenylquinoline (5ae):^[27] Brown oil: ¹H NMR (400 MHz, CDCl₃): $\delta = 7.21 - 7.34$ (m, 2H), 7.48– 7.57 (m, 6H), 7.67 (dd, J=2.2, 8.9 Hz, 1H), 7.84 (s, 1H), 7.86 (d, J=2.2 Hz, 1 H), 8.16–8.19 (m, 3 H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 120.1, 124.5, 126.3, 126.5, 127.5,$ 128.7, 128.8, 128.9, 129.4, 129.6, 130.4, 131.7, 132.2, 137.7, 139.2, 147.2, 148.5, 157.1; MS: m/z (%)=315 (92) [M⁺], 314 (100), 280 (30), 278 (16), 201 (13), 176 (11), 140 (17), 139 (20).

6-Bromo-2,4-diphenylquinoline (5af):^[28] Yellow oil: ¹H NMR (300 MHz, CDCl₃): $\delta = 7.49 - 7.57$ (m, 8H), 7.79 (d, J=8.9 Hz, 1 H), 7.83 (s, 1 H), 8.09 (s, 1 H), 8.12 (s, 1 H), 8.16–8.20 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 119.4$, 120.1, 127.6, 127.6, 127.8, 128.6, 128.7, 128.9, 129.4, 129.6, 131.9, 133.0, 137.8, 139.1, 147.6, 148.3, 157.2; MS: m/z (%) = 359 (100) [M⁺], 358 (85), 282 (10), 281 (17), 280 (59), 279 (16), 278 (38), 277 (15), 203 (12), 202 (22), 201 (20), 176 (18), 139 (39), 138 (35).

6-Methyl-2-phenylquinoline (5bb):^[29] Brown oil; ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 8.16 - 8.12 \text{ (m, 3H)}, 8.07 \text{ (d, } J = 3.16 - 8.12 \text{ (m, 3H)}, 8.07 \text{ (d, } J = 3.16 - 8.12 \text{ (m, 3H)}, 8.07 \text{ (d, } J = 3.16 - 8.12 \text{ (m, 3H)}, 8.07 \text{ (m, 3H)}, 8.0$ 8.5 Hz, 1H), 7.84 (d, J = 8.6 Hz, 1H), 7.63–7.38 (m, 5H), 2.55 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 156.5$, 146.9, 139.8, 136.1, 129.4, 129.1, 128.8, 127.5, 127.127.2, 126.3, 118.9, 21.6; MS: m/z (%)=220 (17) [M⁺+1], 219 (100) [M⁺], 218 (47), 217 (12), 204 (15), 109 (11).

(5cb):^[30] 4,6-Dimethyl-2-phenylquinoline ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3): \delta = 2.57 \text{ (s, 3H)}, 2.74 \text{ (s, 3H)}, 7.14 \text{ (s, })$ 1H), 7.41-7.59 (m, 5H), 7.68-7.85 (m, 2H), 8.05-8.16 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 140.0$, 136.1, 135.9, 131.9, 131.5, 129.9, 128.8, 128.3, 127.4, 126.3, 122.6, 119.8, 118.9, 21.9, 19.0; MS: m/z (%)=233 (100) [M⁺], 232 (27), 218 (41), 217 (12).

2-(4-Methoxyphenyl)-6-methyl-4-phenylquinoline (5db) and 4-(4-Methoxyphenyl)-6-methyl-2-phenylquinoline (5db'):^{[31] 1}H NMR (300 MHz, CDCl₃): $\delta = 8.18 - 8.08$ (m, 6H), 7.75 (s, 1H), 7.73 (s, 1H), 7.62 (s, 1H), 7.56-7.49 (m, 14H), 7.09 (d, J=8.8 Hz, 1H), 7.09 (d, J=8.9 Hz, 2H), 3.92 (s, 3H), **3.88** (s, 3H), 2.48 (s, 3H), **2.46** (s, 3H); ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3): \delta = 160.7, 155.6, 148.3, 147.4, 138.8, 136.1,$ 135.8, 132.4, 131.6, 130.9, 130.8, 129.9, 129.6, 129.5, 129.1, 128.8, 128.5, 128.2, 127.5, 126.3, 125.4, 124.4, 124.3, 119.4, 118.9, 114.2, 114.1, 113.9, 55.4, 55.38, 21.8, 21.77; MS (5db): m/z (%) = 325 (100) [M⁺], 324 (46), 310 (30), 281 (12); MS $(5db'): m/z (\%) = 325 (100) [M^+], 324 (43), 311 (14), 310$ (46), 294 (21), 281 (19), 280 (12), 267 (14), 207 (14).

General Procedure for 2-Allylanilines Synthesis

To a 10-mL tube were successively added IBLAIL (20 mol%), allylic alcohol (0.5 mmol) and aniline (0.5 mmol). The resultant reaction mixture was stirred at 50°C for 2 h. After this time, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (3 \times 10 mL). The organic extract was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to provide the crude product which was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent.

(E)-2-(1,3-Diphenylallyl)-N-methylaniline (4aa): Amber oil; FT-IR (neat): $\nu = 3058$, 3024, 2921, 2814, 1601, 1509, 1491, 1459, 1448, 1377, 1307, 1263, 1222, 1158 cm^{-1} ; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.38 - 7.17$ (m, 11 H), 7.07 (dd, J=7.6, 1.4 Hz, 1 H), 6.75 (td, J=7.5, 1.1 Hz, 1 H), 6.76-6.69 (m, 2H), 6.24 (dd, J=15.9, 1.1 Hz, 1H), 4.84 (d, J=6.8 Hz, 1 H), 2.74 (s, 3 H); 13 C NMR (75 MHz, CDCl₃): $\delta =$ 146.7, 141.8, 137.1, 131.7, 131.4, 128.9, 128.8, 128.5, 127.8, 127.6, 127.3, 127.1, 126.8, 126.3, 117.1, 110.5, 49.2, 30.8; MS: m/z (%)=299 (12) [M⁺], 209 (17), 208 (100), 206 (16), 194 (13), 193 (23); HR-MS (ESI): m/z = 299.1664, calcd. for C₂₂H₂₁N (M⁺): 299.1674.

(E)-2-(1,3-Diphenylallyl)-4-methylaniline (4ab):^[14] Orange oil; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.38-7.21$ (m, 10 H), 6.90 (s, 1 H), 6.68 (dd, J=15.9, 7.1 Hz, 1 H), 6.60 (d, J=8.5 Hz, 1H), 6.28 (d, J=15.9 Hz, 1H), 4.87 (d, J=7.1 Hz, 1H), 3.41 (brs, 2H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 141.9, 141.7, 137.2, 131.6, 131.5, 129.7, 128.8, 128.7, 128.5,$ 128.1, 127.3, 126.7, 126.4, 116.7, 49.62, 29.7; MS: m/z (%)= 299 (27) [M⁺], 209 (18), 208 (100), 207 (36), 206 (11), 194 (12), 193 (19), 191 (11).

(E)-4-Methoxy-2-(1,3-diphenylallyl)aniline (4ac):^[14] Brown oil; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.38-7.21$ (m, 10 H), 6.71–6.62 (m, 4 H), 6.30 (d, J = 15.9 Hz, 1 H), 4.90 (d, J = 6.9 Hz, 1 H), 3.71 (s, 3 H), 3.30 (s, 2 H); ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3): \delta = 152.9, 141.6, 137.9, 131.6, 131.1, 128.8,$ 128.7, 128.5, 127.9, 127.4, 126.8, 126.5, 117.5, 115.8, 112.1,55.6, 49.6; MS: m/z (%) = 315 (69) [M⁺], 225 (18), 224 (100), 223 (28), 210 (14), 209 (23), 207 (12), 193 (12), 191 (14), 180 (12), 178 (10), 167 (14), 165 (11), 115 (13), 91 (18).

(E)-4-Chloro-2-(1,3-diphenylallyl)aniline (4ae):^[12c] Orange oil; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.40-7.18$ (m, 9H), 7.1 (d, J = 8.9 Hz, 2H) 6.60–6.49 (m, 3H), 6.34 (dd, J = 15.9, 6.1 Hz, 1 H), 5.01 (d, J = 6.1 Hz, 1 H), 4.10 (brs, 2 H);

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¹³C NMR (75 MHz, CDCl₃): δ =145.7, 141.6, 136.4, 131.3, 130.2, 128.9, 128.8, 128.7, 128.5, 127.8, 127.6, 127.1, 126.5, 122.3, 114.7, 60.7; MS: *m*/*z* (%)=319 (5) [M⁺], 194 (21), 193 (100), 192 (12), 191 (13), 178 (19), 127 (23), 115 (59), 91 (16).

(*E*)-4-Bromo-2-(1,3-diphenylallyl)aniline (4af):^[16] Yellow oil; ¹H NMR (300 MHz, CDCl₃): δ =7.17–7.34 (m, 12H), 6.59 (dd, *J*=15.9, 7.0 Hz, 1H), 6.52 (d, *J*=8.95 Hz, 1H), 6.26 (dd, *J*=15.9, 1.1 Hz, 1H), 4.80 (d, *J*=6.8 Hz, 1H), 3.51 (brs, 2H); ¹³C NMR (75 MHz, CDCl₃): δ =143.3, 140.9, 136.8, 132.1, 131.9, 131.7, 130.3, 130.3, 130.1, 128.9, 128.7, 128.5, 127.6, 127.1, 126.4, 117.9, 116.6, 110.7, 49.5; MS: *m/z* (%)=363 (18) [M⁺], 284 (22), 274 (28), 273 (42), 272 (29), 271 (39), 206 (26), 193 (100), 191 (21), 165 (15), 102 (12), 91 (18).

(*E*)-2-(1,3-Diphenylallyl)-3,5-dimethoxyaniline (4ag): Pale yellow oil; FT-IR (neat): $\nu = 3371$, 3023, 2934, 2837, 1597, 1491, 1448, 1202, 1153, 1120, 1078 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.39$ (dd, J = 8.3 Hz, 1.2 Hz, 1H), 7.09–7.32 (m, 8H), 6.94 (dd, J = 15.9, 8.5 Hz, 1H), 6.48 (d, J = 15.8 Hz, 1H), 5.92 (s, 2H), 5.39 (d, J = 8.5 Hz, 1H), 3.66 (s, 6H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 158.9$, 146.5, 144.9, 128.2, 132.4, 130.2, 128.3, 127.6, 127.4, 126.6, 126.2, 125.1, 110.6, 92.5, 55.7, 42.9; MS: m/z (%) = 345 (100) [M⁺], 315 (26), 314 (87), 268 (19), 254 (20), 239 (15), 207 (11), 167 (11), 166 (82), 164 (11), 153 (27), 152 (13), 124 (12), 115 (16), 91 (19); HR-MS (ESI): m/z = 345.1722, calcd for C₂₃H₂₃NO₂ (M⁺): 345.1729.

(E)-2-(1,3-Diphenylallyl)-4-phenoxyaniline(4ah):Brown oil; ¹H NMR (300 MHz, CDCl₃): δ =7.35–722 (m,11H), 7.02–6.89 (m, 5H), 6.79 (dd, J=8.5, 2.74 Hz, 1H),6.67 (d, J=8.5 Hz, 1H), 6.62 (dd, J=15.9, 7.0 Hz, 1H), 6.29 (dd, J=15.9, 1.1 Hz, 1H), 4.88 (d, J=7.0 Hz, 1H), 3.47 (brs,2H); ¹³C NMR (75 MHz, CDCl₃): δ =158.8, 148.6, 141.3,140.5, 136.9, 131.8, 130.9, 129.9, 129.5, 128.8, 128.7, 128.5,127.5, 127.3, 126.9, 126.4, 121.9, 121.3, 119.1, 117.4, 117.1,49.6; MS: m/z (%)=370 (31) [M⁺-77], 299 (100), 207 (12).(E)-1-[4-Amino-3-(1,3-diphenylallyl)phenyl]ethanone

(4a): Orange oil; FT-IR (neat): $\nu = 3349$, 3058, 3027, 1654, 1591, 1522, 1491, 1449, 1420, 1357, 1271, 1177 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.78$ (d, J = 8.8 Hz, 2H), 7.19–7.48 (m, 9H), 6.57–6.62 (m, 3H), 6.37 (dd, J = 15.9, 6.0 Hz, 1H), 5.18 (t, J = 5.4 Hz, 1H), 4.70 (brs, 2H), 2.46 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 196.3$, 150.9, 131.7, 130.6, 129.4, 128.9, 128.6, 127.8, 127.1, 126.5, 112.4, 59.9, 25.9; MS: m/z (%) = 327 (5) [M⁺], 207 (12), 194 (21), 193 (100), 178 (20), 135 (20), 120 (37), 115 (52), 92 (19), 91 (16); HR-MS (ESI): m/z = 327.1616, calcd. for C₂₃H₂₁NO (M⁺): 327.1623.

(*E*)-2-(1,3-Diphenylallyl)-4-nitroaniline (4aj):^[16] Yellow solid; mp 128.3 °C; ¹H NMR (300 MHz, CDCl₃): δ = 8.02 (d, J = 9.2 Hz, 2 H), 7.13–7.51 (m, 9 H), 6.50–6.66 (m, 3 H), 6.36 (dd, J = 15.9, 6.1 Hz, 1 H), 5.19 (t, J = 4.8 Hz, 1 H), 4.99 (d, J = 4.1 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ = 152.1, 140.2, 132.2, 129.1, 128.6, 128.5, 128.1, 127.1, 126.5, 126.2, 112.1, 59.9; MS: m/z (%) = 330 (2) [M⁺], 194 (27), 193 (100), 178 (19), 116 (11), 115 (18), 108 (11), 91 (13).

General Procedure for ortho-Alkylation Products

To a 10-mL tube were successively added IBLAIL (20 mol%), allylic alcohol (0.5 mmol) and aniline

(0.5 mmol). The resultant reaction mixture was stirred at 100 °C for 24 h. After this time, the reaction mixture was diluted with ethyl acetate (5 mL) and washed with water (3×10 mL). The organic extract was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to provide the crude product which was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent.

(*E*)-4-(1,3-Diphenylally)-*N*-methylaniline (3aa): Amber oil; FT-IR (neat): ν =3058, 3024, 2929, 2881, 1613, 1491, 1448, 1317, 1265, 1183 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ =7.36 (d, *J*=8.2 Hz, 2H), 7.33–7.15 (m, 8H), 7.05 (d, *J*=8.3 Hz, 2H), 6.65 (dd, *J*=15.8, 7.5 Hz, 1H), 6.57 (d, *J*=8.3 Hz, 2H), 6.32 (d, *J*=15.8 Hz, 1H), 4.79 (d, *J*=7.5 Hz, 1H), 2.82 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =147.8, 144.2, 137.4, 133.3, 132.0, 130.7, 129.3, 128.7, 128.6, 128.4, 128.3, 127.0, 126.2, 126.1, 112.4, 53.3, 30.7; MS: *m/z* (%)=299 (100) [M⁺], 298 (50), 222 (17), 191 (14), 165 (12), 120 (19); HR-MS (ESI): *m/z*=299.1666, calcd. for C₂₂H₂₁N (M⁺): 299.1674.

(E)-4-(1,3-Diphenylallyl)-3,5-dimethoxyaniline (3ag): Yellow solid; mp 144.2 °C; FT-IR (neat): $\nu = 3420, 3341,$ 3058, 3025, 2936, 2835, 1607, 1594, 1491, 1466, 1449, 1428, 1238, 1216, 1203, 1153, 1090 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.14-7.43$ (m, 10H), 6.84 (dd, J = 15.9, 7.5 Hz, 1 H), 6.47 (dd, J = 15.9, 1 Hz, 1 H), 6.02 (d, J = 2.4 Hz, 1 H), 5.82 (d, J=2.4 Hz, 1H), 5.54 (d, J=7.4 Hz, 1H), 3.74 (s, 3H), 3.72 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 159.8$, 159.1, 146.4, 142.7, 137.5, 131.5, 128.5, 128.4, 128.38, 128.3, 127.6, 127.5, 127.0, 126.2, 126.1, 108.3, 94.4, 89.7, 55.8, 54.9, 42.5; MS: m/z (%)=345 (70) [M⁺], 315 (14), 314 (54), 255 (17), 254 (100), 253 (46), 240 (15), 239 (15), 224 (10), 223 (13), 192 (18), 191 (28), 178 (13), 167 (11), 166 (28), 165 (10), 153 (15), 115 (14), 91 (15); HR-MS (ESI): m/z =345.1730, calcd. for C₂₃H₂₃NO₂ (M⁺): 345.1729.

(*E*)-4-(1,3-Diphenylallyl)-*N*,*N*-dimethylaniline (3ak):^[32] Red oil; ¹H NMR (300 MHz, CDCl₃): δ =7.38–7.19 (m, 10 H), 7,10 (d, *J*=8.6 Hz, 2 H), 6.72–6.62 (m, 3 H), 6.33 (d, *J*=15.9 Hz, 1 H), 4.81 (d, *J*=7.6 Hz, 1 H), 2.92 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ =149.2, 144.2, 136.3, 133.3, 130.8, 129.2, 128.6, 128.4, 128.3, 127.6, 127.1, 126.3, 126.2, 112.8, 53.3, 40.8; MS: *m*/*z* (%)=313 (100) [M⁺], 312 (44), 236 (21), 210 (10), 191 (22), 165 (18), 134 (21), 117 (11).

(*E*)-4-(1,3-Diphenylallyl)-2-methylaniline (3al):^[14] Pale yellow oil; ¹H NMR (300 MHz, CDCl₃): δ =7.38–7.19 (m, 10H), 6.91 (s, 1H), 6.88 (s, 1H), 6.65 (dd, *J*=15.4, 7.5 Hz, 1H), 6.32 (d, *J*=15.4 Hz, 1H), 4.77 (d, *J*=7.5 Hz, 1H), 3.59 (s, 2H), 2.08 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ =144.1, 142.9, 137.4, 133.6, 133.3, 130.8, 130.7, 128.6, 128.4, 128.3, 127.1, 127.0, 126.3, 126.2, 122.4, 115.0, 53.4, 17.5; MS: *m/z* (%)=299 (100) [M⁺], 298 (31), 285 (15), 284 (64), 222 (17), 208 (12), 207 (14), 206 (19), 193 (14), 192 (14), 191 (23), 180 (16), 165 (11), 120 (24), 115 (15).

(*E*)-4-(1,3-Diphenylallyl)-2,5-dimethylaniline (3am): Orange oil; FT-IR (neat): $\nu = 3023$, 2923, 2854, 1624, 1598, 1572, 1491, 1461, 1447, 1290, 1204, 1028 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.39-7.12$ (m, 10H), 6.83 (s, 1H), 6.64 (dd, J = 15.9, 6.9 Hz, 1H), 6.50 (s, 1H), 6.19 (d, J = 15.9, 1H), 4.95 (d, J = 6.9 Hz, 1H), 3.49 (brs, 2H), 2.16 (s, 3H), 2.09 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 143.5$, 142.8, 137.6, 134.8, 133.3, 131.6, 130.7, 130.6, 128.8, 128.4, 128.2, 127.1, 126.3, 126.0, 119.8, 117.3, 49.8, 19.32, 17.0; MS: m/z

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(%)=313 (92) [M⁺], 298 (100), 236 (15), 221 (13), 220 (16), 207 (13), 206 (14), 193 (12), 192 (11), 191 (25), 165 (10), 134 (33), 115 (14), 91 (11); HR-MS (ESI): m/z=313.1826, calcd. for C₂₃H₂₃N (M⁺): 313.1833.

(*E*)-2-Chloro-6-(1,3-diphenylallyl)aniline (3an):^[14] Yellow oil; ¹H NMR (300 MHz, CDCl₃): δ =7.38–7.20 (m, 10H), 7.11 (d, *J*=2.0 Hz, 1H), 6.92 (dd, *J*=8.2, 2.0 Hz, 1H), 6.71 (d, *J*=8.2 Hz, 1H), 6.60 (dd, *J*=15.8, 7.4 Hz, 1H), 6.32 (d, *J*=15.8 Hz, 1H), 4.76 (d, *J*=7.4 Hz, 1H), 3.97 (brs, 2H); ¹³C NMR (75 MHz, CDCl₃): δ =143.4, 141.3, 137.2, 134.5, 132.4, 131.4, 129.3, 128.6, 128.5, 128.4, 127.9, 127.3, 126.5, 126.3, 119.3, 115.9; MS: *m/z* (%)=319 (100) [M⁺], 318 (26), 284 (61), 242 (15), 241 (14), 206 (41), 193 (28), 192 (31), 191 (31), 180 (25), 178 (15), 165 (15), 152 (13), 140 (23), 115 (19), 91 (14).

(*E*)-2-Bromo-6-(1,3-diphenylallyl)aniline (3ao):^[14] Yellow oil; ¹H NMR (300 MHz, CDCl₃): δ =7.38–7.20 (m, 10H), 6.98–6.97 (m, 1H), 6.70 (d, *J*=8.2 Hz, 1H), 6.59 (dd, *J*=15.8, 7.4 Hz, 1H), 6.32 (d, *J*=15.8 Hz, 1H), 4.76 (d, *J*=7.4 Hz, 1H), 4.01 (brs, 2H); ¹³C NMR (75 MHz, CDCl₃): δ =143.4, 142.5, 137.2, 134.8, 132.4, 132.4, 131.4, 128.7, 128.54, 128.5, 128.4, 127.5, 127.3, 126.5, 126.3, 115.8, 109.4, 53.0, 29.7; MS: *m*/*z* (%)=365 (99) [M⁺], 364 (46), 363 (99), 362 (25),285 (28), 284 (100), 283 (21), 208 (20), 207 (66), 206 (86), 204 (16), 193 (42), 192 (45), 191 (49), 185 (21), 180 (44), 178 (25), 165 (30), 152 (25), 103 (30), 91 (24), 78 (13).

Acknowledgements

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FULL PAPERS

12 Iron-Based Imidazolium Salts as Versatile Catalysts for the Synthesis of Quinolines and 2- and 4-Allylanilines by Allylic Substitution of Alcohols

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