Synthesis of Quinolines Through Acceptorless Dehydrogenative Coupling Catalyzed by Rhenium PN(H)P Complexes

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Synthesis of quinolines via acceptorless dehydrogenative coupling catalyzed by rhenium PN(H)P complexes

Duo Wei,[a,b] Vincent Dorcet,[a] Christophe Darcel,[a] and Jean-Baptiste Sortais [b,c]*

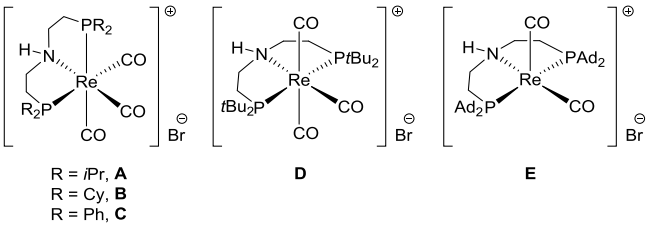
Abstract: A practical and sustainable synthesis of substituted quinolines was achieved *via* the annulation of 2-aminobenzyl alcohol with various secondary alcohols, ketones, aldehyde or nitriles, under hydrogen borrowing conditions. Under the catalysis of well-defined rhenium complexes bearing tridentate diphosphinoamino ligands, the reaction proceeds efficiently (31 examples with isolated yields up to 96%) affording a diversity of quinoline derivatives.

N-heterocycles are ubiquitous skeleton in natural products and biologically active molecules.[1] Among this family, substituted quinolines are extensively used in pharmaceuticals, medicinal chemistry,[2] agrochemicals, and functional materials.[3] Accordingly, new synthetic protocols are continuously needed to access a large diversity of functionalized quinolines. Conventional routes for the preparation of quinolines,[1] such as Skraup[4], Camps[5] and Knorr[6] synthesis, have been reported over a century ago. However most of these methods suffer from multiple steps synthesis, harsh conditions (high temperature, excess of bases or acids) and low chemoselectivity leading to overall low yields and poor atom economy.[7] Among those synthetic approaches, the Friedländer reaction has been proven to be one of the simplest and most efficient methods.[8] Although the Friedländer method is quite versatile, the primary limitation of this approach is the preparation and stability of the starting materials, i.e. 2-aminobenzaldehyde derivatives, since these compounds undergo easily self-condensation.

To overcome these limitations, the indirect Friedländer reaction, involving the oxidative annulation of stable 2-aminobenzylalcohols with either readily available secondary alcohols or ketones, via hydrogen auto-transfer reactions, is a powerful and sustainable way to access quinolines.[9] Several catalytic systems based on group 8 to 10 transition metals (Ru,[10], Rh,[11] Pd,[12] Ir,[13], Au[14], Cu,[15], Co[16]) have been developed. In particular, our group reported the first non-noble metal catalyzed Friedländer annulation reaction using iron Knölker-type complexes.[17] It is also worth noting that stoichiometric amount of bases are also able to promote metal-free indirect Frieländer reactions.[18]

By contrast, group 7 transition metal based catalysts have just emerged very recently as suitable metals for promoting hydrogen borrowing reactions.[19] Manganese catalysis for (de)-hydrogenation reactions has grown exponentially over the last two years.[20] Nevertheless, to date, only three catalytic systems are reported for the synthesis of quinolines, two of which are using over-stoichiometric amount of bases.[21] On the opposite, hydrogen auto-transfer reactions catalyzed by rhenium are still quite rare.[22] Recently, we have developed a series of rhenium complexes with the tridentate PN(H)P ligands (Scheme 1, **A**-**E**), which are efficiently employed in the hydrogenation of carbonyl derivatives[23] and mono *N*-methylation of anilines with methanol as C1 source.[24] In the meantime, Beller's group independently reported hydrogen auto-transfer and related dehydrogenative coupling reactions to form α-alkylated ketones and substituted pyrroles, using the same rhenium PN(H)P pincer complex **A**.[25]

Inspired by these recent developments in the area of synthesis of *N*-heterocycles and following our interest in hydrogenation[20m, 26] and hydrogenation borrowing reactions[27] based on group 7 transition metal complexes, we described hereafter the first example of synthesis of quinolines *via* acceptorless dehydrogenative coupling catalyzed by rhenium catalysts in the presence of a catalytic amount of base.



R = *i*Pr, **A**
R = Cy, **B**
R = Ph, **C**

D **E**

Scheme 1. Rhenium PN(H)P complexes involved in this study.

Initially, we selected 2-aminobenzyl alcohol (**1a**, 1.0 equiv.) and 1-phenylethanol (**2a**, 1.0 equiv.) as a benchmark system for the dehydrogenative cross-coupling formation of 2-phenylquinoline. It is worth noting that all the reactions were performed with a stoichiometric ratio between the two coupling partners. To our delight, complexes **A**, **B** and **C** showed excellent reactivity (Table 1, entries 1-3) at a catalyst loading of 5 mol% in toluene at 140 °C for 24 h in the presence of catalytic amount of *t*-BuOK (10 mol%), giving respectively 88%, 87% and, 90% yields. Not surprisingly, complexes **D** and **E,** bearing the more steric hindered PNP ligands, and the precursor $Re(CO)_5Br$ were not active, (Table 1, entries 4-6) which is in line with the reactivity already observed for the mono *N*-methylation of anilines.[24] The conditions of the reaction were further optimized with catalyst **C** (1 mol%) at 150 °C: various bases were tested (Table 1, entries 7-10), showing that *t*-BuOK was the best candidate, giving 87% yield. Further decreasing of the amount of base to 5 or 2 mol% led to lower yields, 74% and 50% respectively (Table 1, entries 13 and 14). Two blank reactions, in

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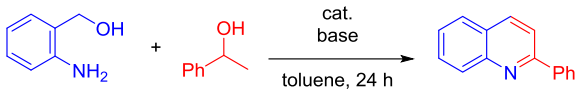
the absence of catalyst or base, gave no detectable conversion, demonstrating that the presence of both components is important in this protocol (Table 1, entries 11 and 12).

Table 1. Optimization of the parameters of the reaction.[a]



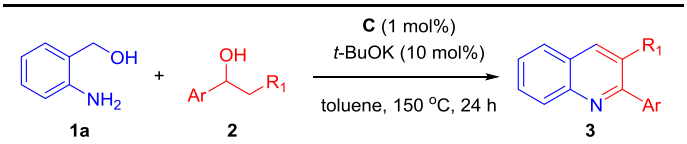
1a **2a** **3a**

Entry	Cat.(mol%)	Base (mol%)	Temp. (°C)	Yield (%)
1	**A** (5)	*t*-BuOK (10)	140	88
2	**B** (5)	*t*-BuOK (10)	140	87
3	**C** (5)	*t*-BuOK (10)	140	90
4	**D** (5)	*t*-BuOK (10)	140	7
5	**E** (5)	*t*-BuOK (10)	140	5
6	$Re(CO)_5Br$ (5)	*t*-BuOK (10)	140	0
7	**C** (1)	*t*-BuOK (10)	150	87
8	**C** (1)	KOH (10)	150	70
9	**C** (1)	Cs_2CO_3 (10)	150	58
10	**C** (1)	K_2CO_3 (10)	150	3
11	**C** (1)	None	150	0
12	No catalyst	*t*-BuOK (10)	150	3
13	**C** (1)	*t*-BuOK (5)	150	74
14	**C** (1)	*t*-BuOK (2)	150	50

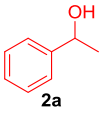
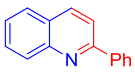
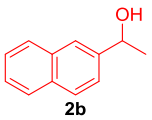
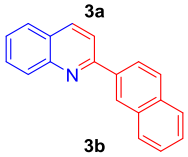
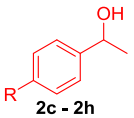
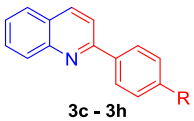
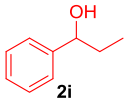
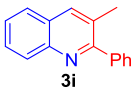
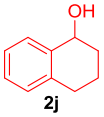
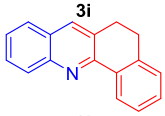
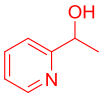
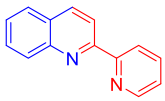
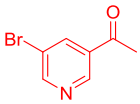
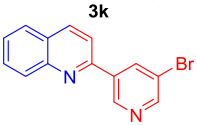
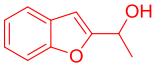
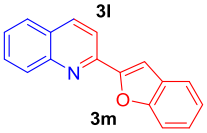
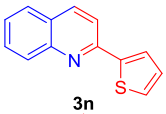
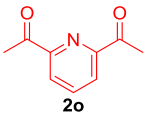
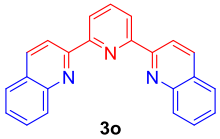
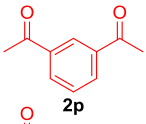
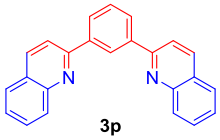
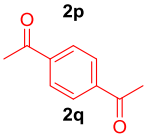
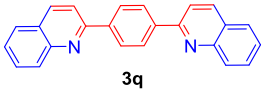
[a] General conditions: in an argon-filled glovebox, a Schlenk tube was charged with rhenium catalyst, **1a** (0.5 mmol), **2a (0.5 mmol)**, base and toluene (2 mL), in that order. The reaction was heated in an oil bath with argon stream. The yield of **3a** was determined by ^1H NMR.

With our optimized conditions in hands, we then explored the substrates amenable for this transformation (Tables 2, 3 and 4). First, with 2-aminobenzyl alcohol **1a**, a series of secondary aromatic alcohols or ketones were engaged as coupling partners (Table 2). The reaction proceeded well for various substituted 1-phenylethanol derivatives. (Table 2, 1-9). 1-(naphthalen-2-yl)ethanol (**2b**) gave full conversion and an excellent isolated yield (93%). Halide substituents, such as fluoro, chloro, bromo and even iodo groups at the *para*-position of the phenyl ring were well-tolerated (**3c**-**3f,** 75-92% isolated yields).

Table 2. Synthesis of quinolines *via* the annulation of 2-aminobenzyl alcohol with aromatic alcohols and ketones under the catalysis of rhenium complex **C**.



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

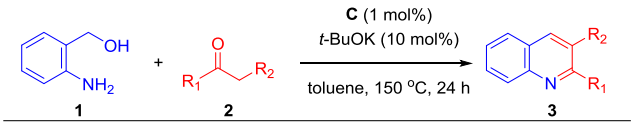
Entry	2	3	Conv./% (Yield /%)
1	 **2a**	 **3a**	90 (87)
2[b]			>98 (91)
3	 **2b**	 **3b**	>98 (93)
4	 **2c - 2h**	 **3c - 3h**	**3c** R = F 95 (80)
5			**3d** R = Cl 97 (92)
6			**3e** R = Br 93 (89)
7			**3f** R = I 81 (75)
8			**3g** R = OMe 85 (79)
9			**3h** R = CF_3 90 (85)
10	 **2i**	 **3i**	87 (79)
11	 **2j**	 **3j**	86 (80)
12	 **2k**	 **3k**	96 (91)
13[c]	 **2l**	 **3l**	93 (91)
14	 **2m**	 **3m**	>98 (92)
15	 **2n**	 **3n**	>98 (95)
16[d]	 **2o**	 **3o**	>98 (95)
17[d]	 **2p**	 **3p**	97 (86)
18[d]	 **2q**	 **3q**	>98 (96)

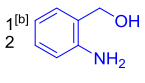
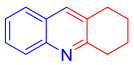
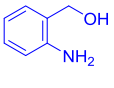
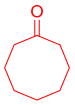
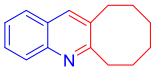
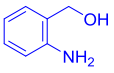
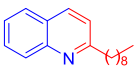
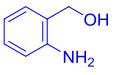
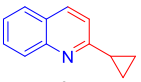
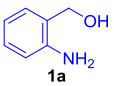
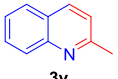
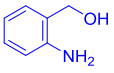
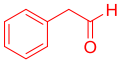
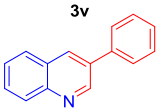
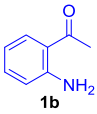
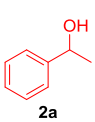
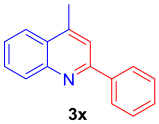
[a] General reaction conditions: **1a** (0.5 mmol), **2** (0.5 mmol), catalyst **C** (1 mol%), toluene (2 mL), *t*-BuOK (10 mol%) at 150 °C with argon stream for 24 h; conversion determined by ^{1}H NMR (based on substrate **2**); isolated yield in parenthesis. [b] Acetophenone was used instead of 1-phenylethanol. [c] Yield of isolated product with 7% of starting material **2l**. [d] 1.0 mmol of **1a** was used.

Substrates bearing electron-donating and electron-withdrawing groups, such as *p*-methoxy-(**2g**), *p*-trifluoromethyl-1-phenylethanol (**2h**), were well tolerated, affording the products **3g** and **3h** in 79% and 85% isolated yields, respectively. It should be noted that starting from the ketone instead of the alcohol (Table 2, entry 1*vs* entry 2) slightly higher conversions and isolated yields were obtained (>98 *vs* 90% conversion), as the sole dehydrogenation of **1a** is needed when starting from ketones. 1-Phenylpropanol (**2i**) and 1-tetralol (**2j**) gave corresponding 2,3-disubstituted quinolines **3i** and **3j** in good isolated yields (entries 10 and 11). Interestingly, heteroaromatic alcohols or ketones **2k**-**2n**, based on pyridine, benzofuran and thiophene core, were smoothly converted into corresponding 2-heteroaryl quinolines. 1,2 and 1,3-diketones, such **2o**, **2p** and **2q**, gave di-quinolinyl (hetero)-arene products in quantitative yields, which could be further employed in coordination chemistry as polydentate ligands.

Then, aliphatic and cyclic alcohols were engaged in this acceptorless dehydrogenative coupling. Disappointingly, the coupling of cyclohexanol, used as model aliphatic secondary alcohol, did not proceed (4% yield, Table 3, entry 1), even if **1a** was fully consumed yielding mostly 2-aminobenzaldehyde. It is likely that the dehydrogenative oxidation of aliphatic alcohol is more difficult than the one of 1-phenylethanol derivatives leading to relatively stable arylketone intermediates. Therefore, we continued to explore the scope with aliphatic ketones. Under our standard conditions, cyclic substrates and aliphatic ones **2r**-**2v** gave all good isolated yields (up to 96%). Notably, cyclopropylethan-1-one **2u** furnished **3u** in good yield, which indicated that the reaction did not proceed *via* radical intermediates. The reaction of phenylacetaldehyde (**2w**) with **1a** led to 3-phenylquinoline (**3w**) in moderate yield (63%). Finally, 2-aminoacetophenone (**1b**) can be converted smoothly into 2-phenyl-4-methylquinoline (**3x**) by coupling with **2a**.

Table 3. Scope of the synthesis of quinoline derivatives with aliphatic ketones and aldehydes.



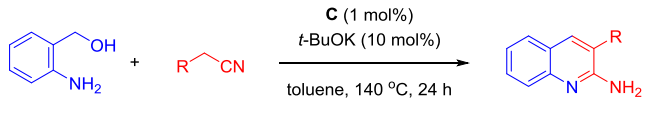
Entry	1	2	3	Conv./% (Yield /%)
1[b]				>98 (4)
2	**1a**	**2r**	**3r**	>98 (86)
3[c]	 **1a**	 **2s**	 **3s**	>98 (88)
4	 **1a**	 **2t**	 **3t**	80 (76)
5	 **1a**	 **2u**	 **3u**	92 (89)
6[d]	 **1a**	 **2v**	 **3v**	>98 (96)
7[e]	 **1a**	 **2w**	 **3w**	95 (63)
8	 **1b**	 **2a**	 **3x**	>98 (89)

[a] General reaction conditions: catalyst **C** (1 mol%), **1** (0.5 mmol), **2** (0.5 mmol), toluene (2 mL), *t*-BuOK (10 mol%) at 150 °C with argon stream for 24 h; conversion determined by ^{1}H NMR; isolated yield in parenthesis. [b] Cyclohexanol was used instead of cyclohexanone and NMR yield is shown in parentheses. [c] Yield of isolated product with 8% of starting material **1a**. [d] 1 mL of acetone was used. [e] 130 °C.

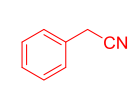
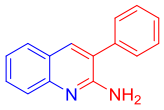
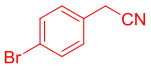
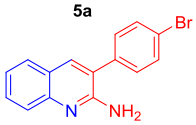
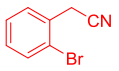
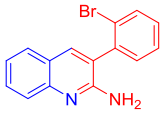
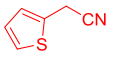
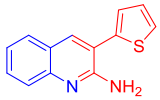
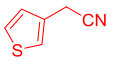
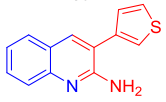
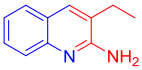
Interestingly, 2-phenylacetonitrile **4a** has been recently proven to be an effective annulation partner in the synthesis of 2-alkylaminoquinolines.[28] To our delight, **4a** could also be smoothly converted to 2-amino-3-phenylquinoline **5a** with our catalytic system at 140 °C. The molecular structure of **5a** (as well as **5b**) were confirmed by X-Ray diffraction studies (Figure 1). As shown in Table 4, all the reactions proceeded smoothly and gave the desired products in moderate to good isolated yields. In particular, bromo-substituted 2-phenylacetonitriles **4b** and **4c** gave the corresponding products **5b** and **5c**, in 67% and 33% yield, respectively (Table 4, entries 2 and 3). Interestingly, halogen-containing products, such as **3e**, **3l, 5b** and **5c,** can be further converted into more complex molecules via cross-coupling reactions. 2-(2-thiophenyl)acetonitrile **4d** afforded the corresponding product in high yield (90%, entry 4) while, unexpectedly, parent 2-(3-thiophenyl)acetonitrile **4e** led to

moderate conversion (42%) (Table 4, entries 4 and 5). Eventually, aliphatic butyronitrile **4f** gave 2-amino-3-ethylquinoline **5f** in good yield (80%).

Table 4. Scope of the synthesis of 2-amino-quinoline derivatives with nitriles.



1a **4** **5**

Entry	4	5	Conv./% (Yield /%)
1	 **4a**	 **5a**	70 (67)
2	 **4b**	 **5b**	67 (52)
3	 **4c**	 **5c**	33
4	 **4d**	 **5d**	95 (90)
5	 **4e**	 **5e**	42
6[b]	 **4f**	 **5f**	93 (80)

[a] General reaction conditions: catalyst **C** (1 mol%), **1a** (0.5 mmol), **4** (0.5 mmol), *t*-BuOK (10 mol%), toluene (2 mL) at 140 °C for 24 h; conversion determined by ^{1}H NMR (based on substrate **4**); isolated yield in parenthesis. [b] 2.0 equiv. of **4f** was used.

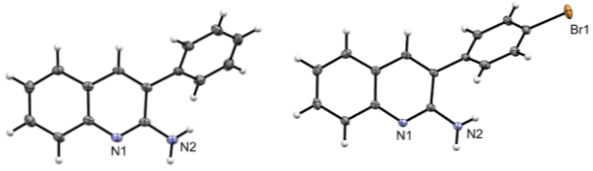


Figure 1. Perspective view of the products **5a** (left) and **5b** (right) (thermal ellipsoids drawn at the 50% probability level.

In summary, a practical and sustainable synthesis of substituted quinolines was achieved *via* the annulation of 2-aminobenzyl alcohol with a variety of secondary alcohols, ketones, aldehyde or nitriles. The reaction proceeds with a high atom efficiency *via* a sequence of dehydrogenation and condensation steps that give rise to selective C−C and C−N bond formations. The key to develop this first rhenium catalyzed acceptorless dehydrogenative coupling was the use of a well-defined complex bearing a tridentate diphosphinoamino ligand as the catalyst (1 mol%) in the presence of *t*-BuOK (10 mol%) at 150 °C.

Experimental Section

Typical procedure for catalytic synthesis of quinolines

In an argon-filled glovebox, a 20 mL Schlenk tube was charged with the rhenium catalyst **C** (1 mol%), **1** (0.5 mmol), **2** (0.5 mmol), toluene (2 mL) and *t*-BuOK (10 mol%), in that order. The reaction was heated in an oil bath with argon stream at 150 °C for 24 h. After cooling to room temperature, the solution was diluted with ethyl acetate (2 mL) and filtered through a small pad of silica (2 cm in a Pasteur pipette). The silica was washed with ethyl acetate. The filtrate was evaporated and the crude residue was purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate as eluent).

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Keywords: quinoline • rhenium • hydrogen borrowing • acceptorless dehydrogenative coupling

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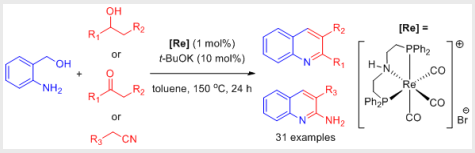

A sustainable rhenium catalyzed synthesis of substituted quinolines was achieved *via* the annulation of 2-aminobenzyl alcohol with various secondary alcohols, ketones, aldehyde or nitriles, under hydrogen borrowing conditions.

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Synthesis of quinolines via acceptorless dehydrogenative coupling catalyzed by rhenium PN(H)P complexes