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Iridium-Catalyzed Sustainable Access to Functionalized Julolidines through Hydrogen Autotransfer

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The straightforward and ecofriendly preparation of functionalized julolidines starting from tetrahydroquinoline, diols, and aldehydes, for which water is produced as the only side product was investigated. To achieve this task, several well-defined ruthenium and iridium complexes including three new complexes were prepared from the corresponding phosphine–sulfonates, phosphine–carboxylates, and phosphine–phosphonates. The first transformation involved in situ generation of enaminoiminium intermediates, which allowed the formation of the julolidines through formal N,C(sp^2)-cyclization of tetrahydroquinoline and the propane-1,3-diols. The influence of the chelate acidity points out that [Cp*Ir^{III}]-based catalysts (Cp* = C_5Me_5) featuring phosphine–carboxylate and phosphine–sulfonate ligands were suitable for the cyclization, whereas the acidic phosphinophosphonate-containing complex favored the formation of reduced N-alkylated tetrahydroquinoline. We found that substitution of the propane-1,3-diols was crucial for the generation of enaminoiminium ions, which accounts for the efficiency and selectivity of the reaction. Applying another hydrogen autotransfer process, the prepared julolidines were easily functionalized at the C2 position.

Redox-neutral processes involving hydrogen transfers known as "borrowing hydrogen", "hydrogen autotransfer", and "hydrogen shuttling" represent ecofriendly approaches for the development of benign and atom-efficient protocols that allow the formation of carbon–heteroatom and carbon–carbon bonds.[1] In these reactions, the cascade transformation involves the activation of the alcohols or amines through dehydrogenation followed by condensation then reduction of the resulting unsaturated intermediates with the in situ generated metal hydride species. Since the seminal results of Shvo and Laine on the dealkylation/alkylation of tertiary amines involving iminium intermediates[2] in the presence of $Ru_3(CO)_{12}$ followed by the works of Griggs[3] and Watanabe[4], who independently developed ruthenium complexes to achieve N-alkylation with alcohols, recent examples adopting these strategies have been documented to allow more selective and milder reaction conditions,[5] water-soluble or reusable/immobilized catalysts,[6] and asymmetric approaches.[7] Recently, α- and β-alkylation of cyclic amines broadened the scope of this transformation.[8] By suppressing the final hydrogenation step, acceptorless dehydrogenative condensation represents another elegant sustainable approach for the preparation of pyrroles, pyridines, and, more recently, quinolines through dual or multicomponent cascades.[9–13]

Owing to their strong electron-releasing and fluorescent properties, julolidine derivatives have found broad applications as photosensitizers in material sciences, including in organic light-emitting diodes and solar cells (Figure 1).[14] Surprisingly, traditional approaches to julolidines usually involve the reaction of anilines or tetrahydroquinolines with 1,3-dihalogenated

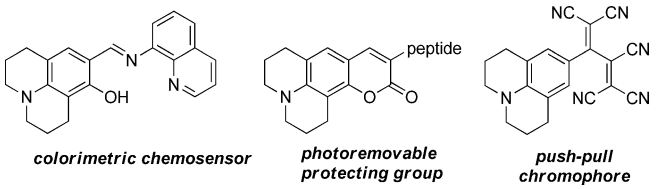

Figure 1. Some examples and applications of julolidines.

propanes such as harmful 3-chloro-1-bromopropane followed by functionalization of the C9 atom through bromination with *N*-bromosuccinimide (NBS) or Vilsmeier–Haack formylation to allow the introduction of the electron acceptor.[14,15]

In 1985, Watanabe and co-workers pioneered the preparation of quinoline through dehydrogenative condensation from 1,3-propanediol and aniline in the presence of a ruthenium trichloride/tributylphosphine catalytic system along with a stoichiometric amount of nitrobenzene acting as a hydrogen acceptor.[16] Since then, several reports have dealt with N,C(sp^2)-cyclization through either acceptor-mediated dehydrogenative coupling or, more recently, acceptorless dehydrogenative coupling in the presence of a base.[10,16] However, a catalytic system allowing the reduction of the final unsaturated inter-

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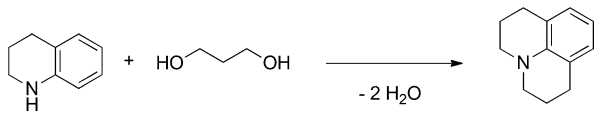
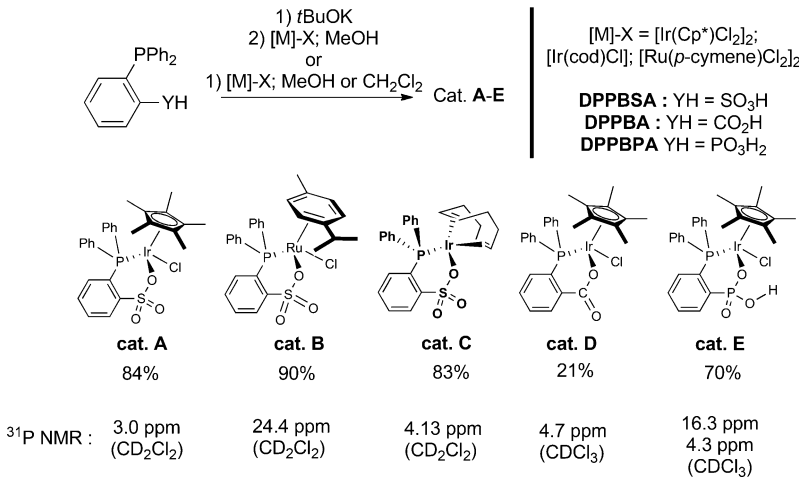
mediates through hydrogen autotransfer is so far unknown. The development of such a transformation is highly desirable and could lead to ecofriendly, halogenated reagent-free syntheses of functionalized julolidines with the generation of water as the only side product; this could provide new insight into immobilization, matrix incorporation, and cell-permeation enhancement (Scheme 1).

Herein, we report the development of a straightforward method for the preparation of julolidines by cyclization of 1,3-propanediols with tetrahydroquinoline involving borrowing-hydrogen processes. Particularly, the preparations of various ruthenium and iridium complexes featuring phosphine–sulfonate/carboxylate/phosphonate chelates allow the influence of the acidic moiety on the chelating ligands towards the competitive side dehydration/reduction to be tackled. The diversity-oriented synthesis of functionalized julolidines is achieved through selective β-alkylation involving borrowing-hydrogen processes on the resulting challenging substrates.



Scheme 1. Direct access to julolidines from tetrahydroquinoline and propane-1,3-diol.

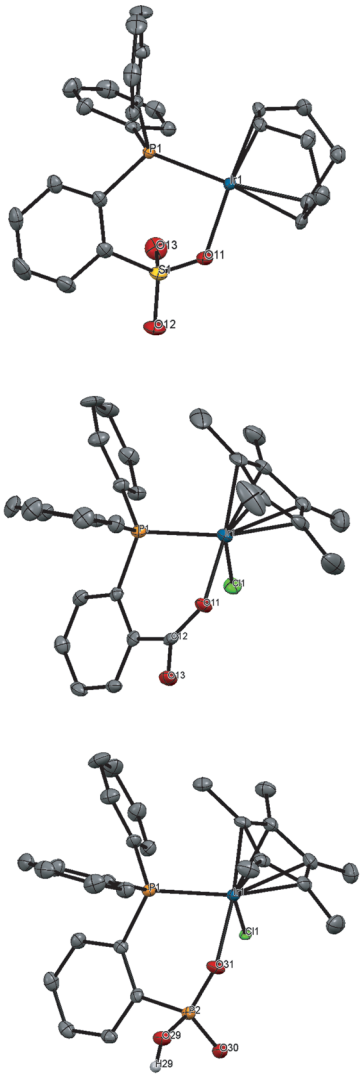
With this idea in mind, we first focused our attention on the preparation of various ruthenium and iridium complexes containing an acidic chelating ligand to further evaluate the impact of the carboxylate, sulfonate, and phosphonate moieties toward the targeted cyclization. The phosphinosulfonate-containing either Cp*-iridium(III) (Cp* = C_5Me_5) cat. **A** or arene ruthenium(II) cat. **B** complexes were prepared from deprotonated diphenylphosphinobenzenesulfonic acid (DPPBSA) and the $[Cp^*IrCl_2]_2$ and $[Ru(p\text{-cymene})Cl_2]_2$ metal precursors, respectively (Scheme 2).[17] New square-planar iridium(I) complex cat. **C** was similarly synthesized starting from $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) in 83% yield; it was characterized by NMR spectroscopy and its structure was confirmed by X-ray crystallography (Figure 2).[18,19] We next investigated the use of the less acidic diphenylphosphinobenzoic acid (DPPBA). By using methodology similar to that used for the preparation of cat. **A**, the reaction led to the formation of the expected, but surprisingly sensitive, complex cat. **D** characterized by a resonance at $\delta = 4.7$ ppm in its ^{31}P NMR spectrum along with two distinct undesired species. Therefore, slight modification to the reaction conditions by performing the reaction with DPPBA gave,



Scheme 2. Preparation of the iridium and ruthenium complexes.

after crystallization with solvent-diffusion techniques (CH_2Cl_2/*n*-hexane), expected complex cat. **D** along with 2 (H_3O^+; Cl^-); 1 H_2O molecules with a signal at $\delta = 9.5$ ppm in the ^{31}P NMR spectrum (Figure 2).[20] Further neutralization by careful treatment with water finally afforded cat. **D** in 21% yield (Scheme 2). Recently, Rieger and co-workers reported the synthesis of phosphinophosphonic prochelates from diethyl phosphonates for the preparation of various palladium(II) complexes.[21] Following this methodology, we thus decided to prepare corresponding new Ir^{III} complex cat. **E**. Treatment of this phosphonic acid with 1 equivalent of potassium *tert*-butoxide followed by the addition of $[Cp^*IrCl_2]_2$ gave two complexes. Analysis by ^{31}P NMR spectroscopy confirmed the formation of one major species with resonances at $\delta = 16.3$ and 4.3 ppm corresponding to the phosphonate and phosphine groups, respectively, which after purification gave expected iridium(III) cat. **E** in 70% yield (Scheme 2).[22,23]

Having prepared the well-defined complexes, we next investigated the target transformation to access to the corresponding julolidines (Table 1). Thus, tetrahydroquinoline (**1a**) was first treated with 1,3-propanediol (**2a**) for 20 h at 130 °C by using toluene as the solvent without any base or acid additive. $[Ir^{III}(Cp^*)]$-based catalyst **A** was found to be active in this novel N,C(sp^2)-dialkylation of **1a** with **2a** to give **3a**. However, a modest yield of 43% was obtained during our initial attempts (Table 1, entry 1). Analysis of the reaction mixture highlighted the side formation of *N*-propyltetrahydroquinoline (**4a**); a 61:39 ratio of **3a**/**4a** was reached.[16,24] Modification of the temperature and concentration had only a limited impact on this ratio. Gratifyingly, increasing the amine **1a**/diol **2a** ratio from 1:1.2 to 2:1 minimized the formation of N-alkylated product **4a** and afforded julolidine **3a** in 72% yield with a **3a**/**4a** ratio of 87:13 (Table 1, entry 2). As expected, the corresponding in situ generated complex obtained by treatment of $[Ir(Cp^*)Cl_2]_2$ with DPPBSA afforded a similar conversion, ratio, and yield (Table 1, compare entries 7 and 2). Lowering the concentration of **2a** resulted in a higher conversion, but the ratio of **3a**/**4a** decreased (Table 1, entries 7–9). We next investigated the influence of the chelate toward selectivity and yield. Com-



	cat. **A**	cat. **B**	cat. **C**	cat. **D**	cat. **E**
M-Cl [Å]	2.4042(9)	2.4138(8)	-	2.387(1)	2.408(2)
M-P [Å]	2.328(1)	2.3601(9)	2.2841(8)	2.287(1)	2.301(1)
M-O [Å]	2.140(2)	2.122(2)	2.093(2)	2.165(2)	2.150(4)

Figure 2. X-ray structures of new complexes cat. **C** (top), cat. **D** (middle), and cat. **E** (bottom), and comparison of the relevant bond lengths. Hydrogen atoms and solvents are omitted for clarity.

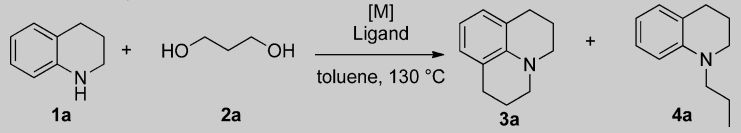
plex **D** featuring the softer phosphinocarboxylate chelate diminished the side reductive dehydration process to afford a similar conversion but an improved 92:08 ratio of **3a**/**4a** and **3a** was obtained in 77% yield (Table 1, entry 3). In contrast, Ir^{III} complex **E** even with a 2:1 ratio of **1a**/**2a**, which favored the formation of expected julolidine with **A** and **D**, enhanced the formation of *N*-propyltetrahydroquinoline with complete conversion with a 60:40 ratio of **3a**/**4a**, which demonstrates the influence of the second acidic dissociation constant (P-OH) on this complex toward the side dehydration/reduction reaction (Table 1, entry 4 vs. entries 2 and 3).

The use of arene ruthenium(II) complex **B** afforded a ratio of products similar to that provided by **A** but with a modest 53% conversion (Table 1, entry 5). Low conversion was also observed in the presence of iridium(I) precatalyst **C**, but an equimolar ratio of **3a**/**4a** was obtained (Table 1, entry 6). Optimization of the promising result obtained with **D** led us to use DPPBA as a proligand for further investigations. A similar result and a similar conversion were obtained by mixing DPPBA with $[Ir(Cp^*)Cl_2]_2$ (Table 1, entry 10 vs. 3); therefore, in situ generation of the active species was next used for convenience. Increasing the reaction time to 36 h led to complete conversion and 91% yield (Table 1, entry 11). The tedious separation of remaining **1a** with formed **3a** along with trace amounts of **4a** by column chromatography over silica gel led to isolation of pure **3a** in 80% yield (Table 1, entry 11). Notably, the reactions were also performed on gram scale, and similar ratios and yields were observed.[25]

With our best reaction conditions in hand, we next investigated the scope of the transformation with substituted 1,3-propanediols (Table 2) The reaction of 2-methylpropane-1,3-diol (**2b**) with $[Ir(Cp^*)Cl_2]_2$ in the presence of DPPBA cleanly afforded expected julolidine **3b** in 78% yield with 5% yield of *N*-isobutyltetrahydroquinoline. Butane-1,3-diol (**2c**) was a more challenging substrate. In this case, competitive formation of the iminium and ketiminium ions resulting from condensation of the in situ generated aldehyde and ketone, respectively, led to julolidines **3c** and **3d** in yields of 5 and 23%, respectively. However, dehydration processes became the major pathway, and undesired N-alkylation products were obtained in 40% yield. The favored formation of **3d**+**4d** relative to that of **3c**+**4c** revealed the selective formation of the iminium ion.

Rationalization of the formation of **3** and **4** was next undertaken (Figure 3). In the presence of the catalytic species, activation of the propane-1,3-diol substrate through dehydrogenation followed by condensation in the presence of amine **1a** gives iminium intermediate **I**. Deprotonation affords key enamino alcohol intermediate **II**. According to path I and depending on the acidity of the ligand held by iridium, intermediate **II** can undergo protonation in the presence of an acidic catalytic species to form α,β-unsaturated exocyclic iminium ion **IV** after loss of a molecule of water. Then, reduction with the generated metal hydride species followed by protonation gives side product **4a**. On the other hand, in the presence of the required extra amount of amine **1a** and with the less acidic softer species arising from cat. **A** and cat. **D** following path II, key intermediate **II** after dehydrogenation and condensation could afford enaminoiminium ion **V** as a formal Povarov key intermediate.[26–28] Therefore, electrocyclization followed by protonation and the release of amine **1a** might lead to α,β-unsaturated endocyclic iminium ion **VI**. Finally, reduction/protonation/reduction affords expected julolidine **3a**. This pathway tends to explain the competitive formation of **3c** and **3d** during the reaction with **2c**. However, we cannot totally exclude the formation of **3a** from sequential alkylations through hydrogen autotransfer (path III). The formation of **4a** could also arise from prior dehydration/isomerization processes of starting diol **1a** to afford propanal, which might also account for the formation of **4a**.[29] To distinguish between the postulated pathways, we decided to perform the reaction with 2,2-dimethylpropane-1,3-diol, which cannot lead to key enamino

Table 1. Reaction of tetrahydroquinoline (**1a**) with propan-1,3-diol (**2a**).[a]



Entry	Catalyst ([mol%])	Ligand ([mol%])	*t* [h]	Ratio **1a**/**2a**	[**2a**] [M]	Ratio **3a**/**4a**	Conv. [%][b]	Yield of **3a** [%][c]
1	**A** (2.5)	–	20	1:1.2	1.3	61:39	87	43
2	**A** (2)	–	20	2:1	1.3	87:13	84	72
3	**D** (2)	–	20	2:1	1.3	92:08	85	77
4	**E** (2)	–	20	2:1	1.3	60:40	99	52
5	**B** (2.5)	–	20	2:1	1.3	85:15	53	25
6	**C** (2)	–	20	2:1	1.3	50:50	25	15
7	$[Cp^*IrCl_2]_2$ (1)	DPPBSA (2)	20	2:1	1.3	85:15	82	67
8	$[Cp^*IrCl_2]_2$ (1)	DPPBSA (2)	20	2:1	0.8	85:15	95	80
9	$[Cp^*IrCl_2]_2$ (1)	DPPBSA (2)	20	2:1	0.4	75:25	99	70
10	$[Cp^*IrCl_2]_2$ (1)	DPPBA (2)	20	2:1	1.3	91:9	82	71
11	$[Cp^*IrCl_2]_2$ (1)	DPPBA (2)	36	2:1	1.3	95:5	99	91 (80)

[a] All reactions were performed in dry and degassed toluene under an inert atmosphere of argon. [b] Conversion was calculated based on GC analysis of the limiting substrate. [c] Yield of **3a** was determined by GC analysis by using dodecane as an internal standard, and the number in parentheses is the yield of the isolated product after purification by column chromatography on SiO_2.

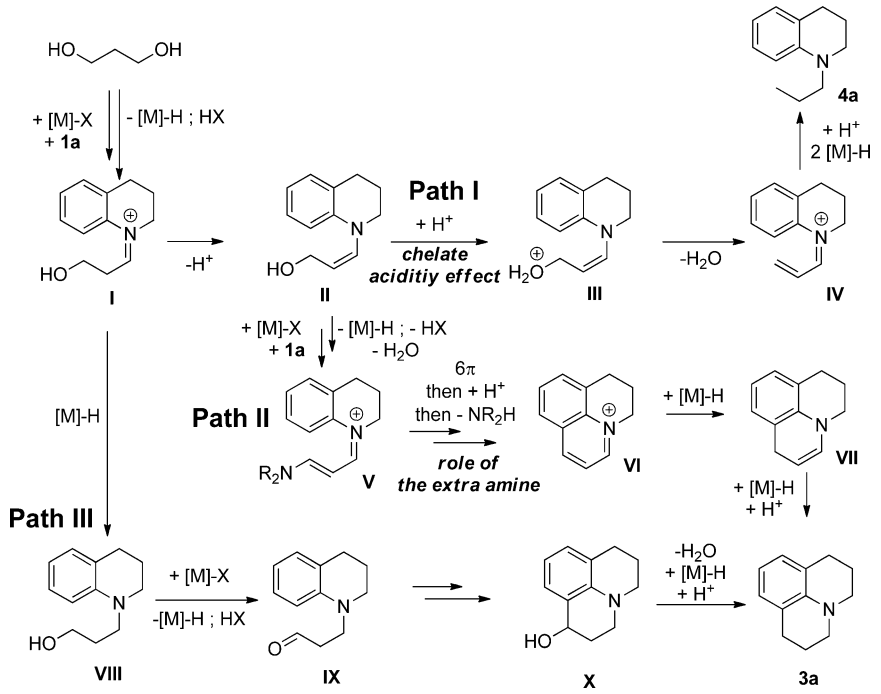
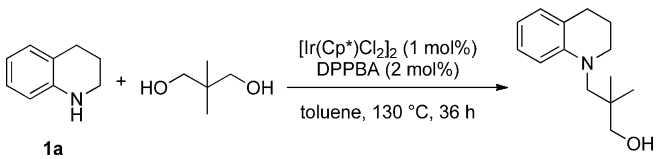


Figure 3. Proposed intermediates accounting for the formation of **3a** and **4a**.

alcohol of type **II**. In this case, the corresponding uncyclized amino alcohol product was predominantly formed, whereas 2,2-dimethyljulolidine was only detected by GC–MS analysis, that is, it was formed in $<1\%$ (Scheme 3). This result tends to suggest the requirement of enaminoiminium intermediate **V** to ensure cyclization and might confirm that path II mainly accounts for the formation of julolidine **3**. This overall transformation complements traditional Povarov cyclizations that require specific dienophiles.[27]

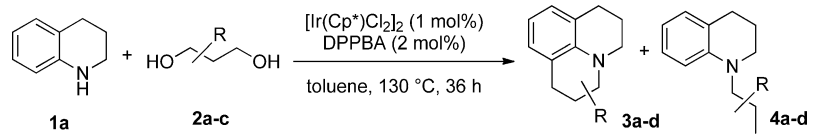
At this first stage, considering the importance of the substitution patterns to ensure selective cyclization and the limited number of commercially available propane-1,3-diol derivatives, the diversity of julolidines arising from hydrogen autotransfer could appear quite limited. However, we considered that the prepared julolidines would be suitable candidates for post-functionalization through hydrogen autotransfer in the presence of electrophiles such as aldehydes to access β-alkylated julolidines. Noteworthy, the chromophoric properties of julolidines are inherent to their strong electron-donating properties. Therefore, the highly nucleophilic site at C9 adds another challenge to the target transformation (Figure 4).

To our delight, the use of phosphinocarboxylate DPPBA and phosphinosulfonate DPPBSA chelates allowed the formation of the expected Cβ-functionalized julolidines from various aldehydes acting as electrophiles (Table 3). Under conditions that we previously used for Cβ-alkylation,[8b] for example, in the presence of formic acid to achieve final reduction, reaction of benzaldehyde with **3a** afforded **5a** in 67% yield. Similarly, *p*-methylbenzaldehyde reacted cleanly to give **5d** in 43% yield. *ortho*- and *para*-Bromobenzaldehyde gave halogenated julolidines **5b** and **5c** in yields of 65 and 64%, respectively; this opens new perspectives of transformations of julolidines through catalyzed cross-coupling reactions. Thiophene carboxaldehydes were compatible with the transforma-



Scheme 3. Importance of α,β-unsaturated intermediates **II** to ensure julolidine formation.

Table 2. Yields of isolated julolidines **3a–d**, and product distributions from propanediol derivatives **2**.



2a = propane-1,3-diol; **2b** = 2-methylpropane-1,3-diol; **2c** = butane-1,3-diol

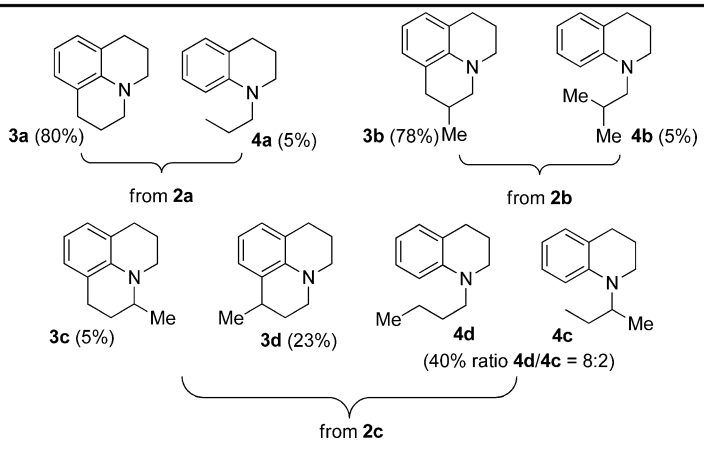
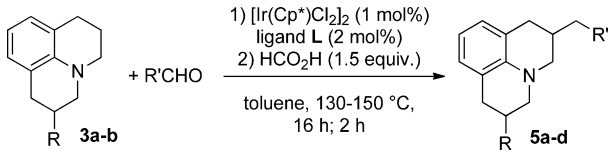
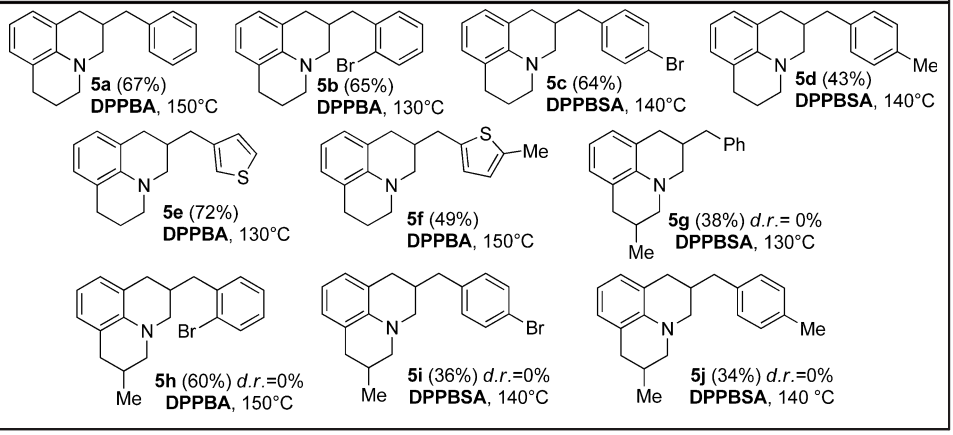


Table 3. Yields of isolated products from the β-alkylation of julolidines **3**.





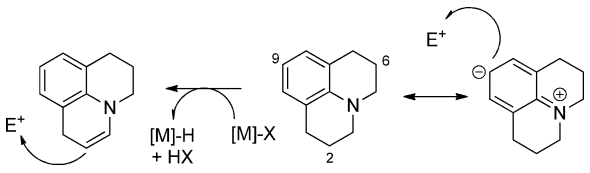
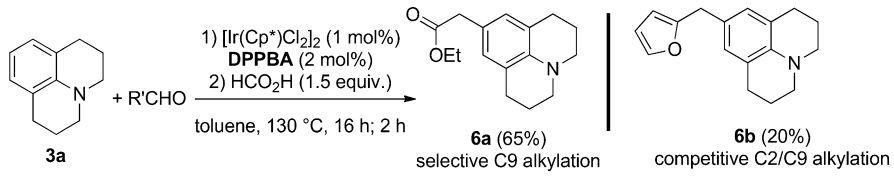


Figure 4. Competitive alkylation pathways.

tion, as they yielded products **5e** and **5f** in up to 72% yield. In each case, the use of methyl-substituted julolidine **3b** led to the formation of two isomers without diastereoselectivity, which afforded the disubstituted products in 34–60% yields. Notably, with the aldehydes employed above, no C9-alkylation products were detected during the transformation. However, during our attempts to react 2-furfural with julolidine **3a**, a temperature-dependent mixture of products was observed. Analyses revealed the formation of C9-alkylated julolidine **6b** in 20% yield (Scheme 4). The use of ethyl glyoxylate completely suppressed the β-alkylation and only **6a** was formed during the reaction, which highlights that aldehydes featuring a coordinating oxygen atom in the α-position favor Friedel–Crafts-type products. Taken together, these results provide new insight into accessing julolidines through borrowing-hydrogen processes and the C9 position is kept intact for the introduction of an electron acceptor.

In conclusion we have demonstrated that the preparation of various julolidines can be easily achieved through hydrogen autotransfer involving consecutive N,C-dialkylation of tetrahydroquinoline and β-alkylation under green conditions with formation of water as the sole byproduct. Phosphinosulfonate and phosphinocarboxylate were found to be efficient ligands for these transformations, whereas more acidic phosphinophosphonate favored dehydration/reduction pathways. The efficiency of the same iridium catalysts in both synthesis and functionalization reactions suggests that a tandem protocol might be possible for the overall transformation. Modification of the optical properties during β-alkylation of the julolidines by suppressing the final reduction with formic acid would afford interesting results. Extension of this methodology to N-substituted anilines is currently underway.



Scheme 4. C9-Alkylation of julolidine **3a**.

Experimental Section

General Procedure for the preparation of the julolidines 3

A 25 mL, flame-dried Schlenk tube was charged with 1,3-propanediol (**2**; 0.67 mmol, 1.0 equiv.), 1,2,3,4-tetrahydroquinoline (**1a**, 2.0 equiv.), toluene (0.5 mL), well-defined cat. **D** (2.5 mol%) or in situ $[Ir(C_5Me_5)Cl_2]_2$ (1 mol%), and 2-(diphenylphosphino)benzoic acid (DPPBA, 2 mol%). The mixture was evacuated by vacuum–argon cycles (5×) and stirred at 130 °C (oil bath temperature) for 20–36 h. After cooling the mixture to room temperature, the crude material was suspended on silica and purified by column chromatography (Et_2O/petroleum ether) to isolate expected julolidine **3**.

Acknowledgements

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Keywords: borrowing hydrogen · chelates · cyclization · green chemistry · iridium

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