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Redox-neutral processes involving hydrogen transfers known as “hydrogen borrowing”, “hydrogen autotransfer” or “hydrogen shuttling” represent eco-friendly approaches for the development of benign and atom-efficient protocols, allowing the formation of carbon-heteroatom or carbon-carbon bonds.[1] In these reactions, the cascade transformation involves the activation of alcohols or amines *via* dehydrogenation followed by condensation then reduction of the resulting unsaturated intermediates with the *in situ* generated metal hydride species. Since the seminal results of Laine and coworkers on dealkylation/alkylation of tertiary amines involving iminium intermediates[2] in the presence of $Ru_3(CO)_{12}$ followed by the work of Watanabe[3] and Griggs[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 the transformation.[8] By suppressing the final hydrogenation step, Acceptorless Dehydrogenative Condensation (ADC) represents another elegant sustainable approach for the preparation of pyrroles, pyridines and more recently quinolines through dual or multicomponent cascades.[9-13]

Due to their strong electron releasing and fluorescent properties, julolidine derivatives have found broad applications as photosensitizer in material sciences such as OLEDs and solar cells (Figure 1).[14] Surprisingly, traditional approaches to julolidines usually involve reaction of anilines or tetrahydroquinolines with 1,3-dihalogenated propanes such as harmful 3-chloro-1-bromopropane followed by functionalization of the C(9) atom through bromination with NBS (*N*-bromosuccinimide) or Vilsmeier-Haack formylation to allow the introduction of the electron acceptor.[14,15]

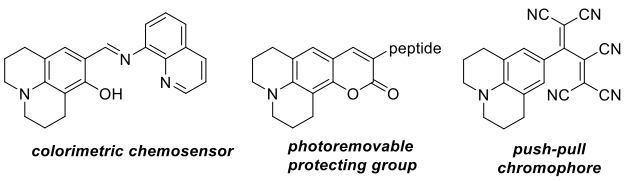
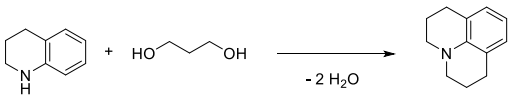


Figure 1. Some examples and applications of julolidines

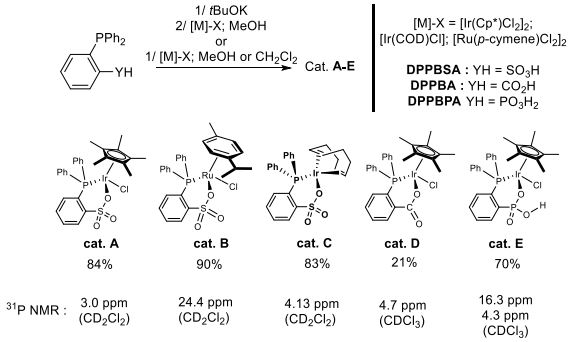
In 1985 Watanabe and coworkers pioneered the preparation of quinoline *via* dehydrogenative condensation from 1,3-propanediol and aniline in the presence of a ruthenium trichloride/tributylphosphine catalytic system along with a stoichiometric amount of nitrobenzene acting as a hydrogen acceptor.[16] Since, several reports deal with N-,C(sp^2)-cyclization *via* either acceptor mediated dehydrogenative coupling or more recently through acceptorless dehydrogenative coupling in the presence of base.[10,16] However, a catalytic system allowing the reduction of the final unsaturated intermediates through hydrogen autotransfer is so far unknown. The development of such transformation is highly desirable and could afford ecofriendly halogenated reagent free syntheses of functionalized julolidines, generating water as the only side product, which could open new insights for immobilization, matrix incorporation and cell permeation enhancement (Scheme 1).



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

Herein, we report the development of a straightforward methodology for the preparation of julolidines *via* 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 to tackle the influence of acidic moiety on the chelating ligands towards the competitive side dehydration/reduction. The diversity–oriented syntheses of functionalized julolidines is achieved through selective β-alkylation involving hydrogen borrowing processes on the resulting challenging substrates.

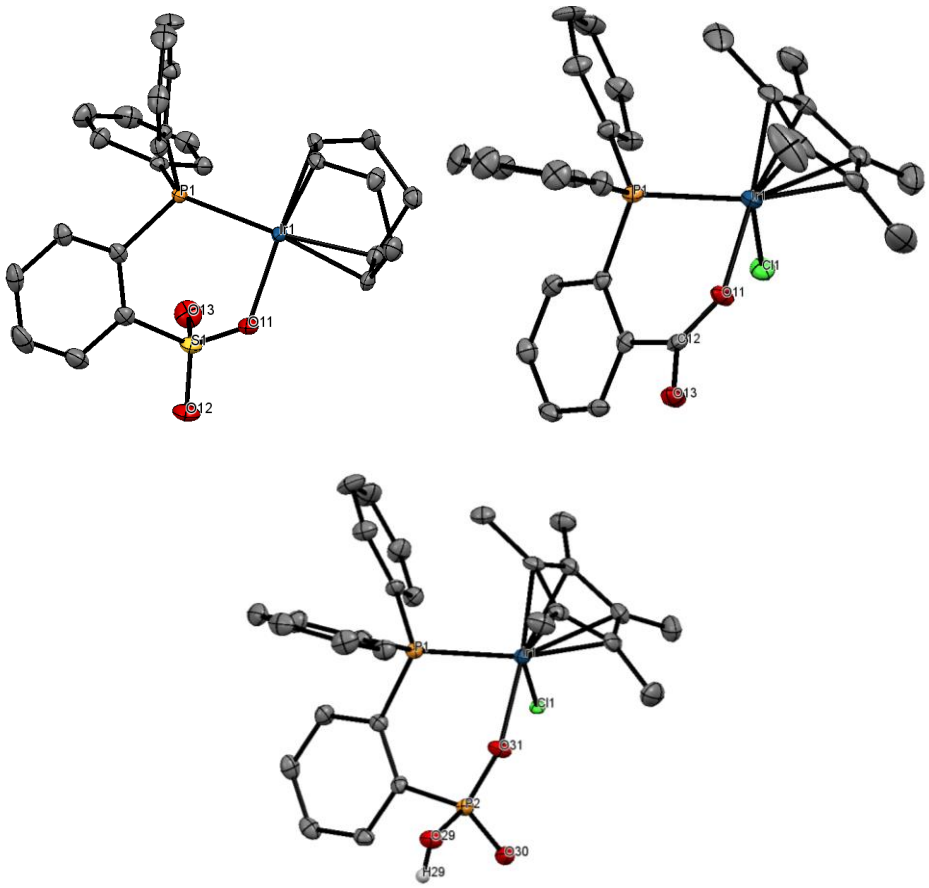
With this idea in mind, we first focused our attention on the preparation of various ruthenium and iridium complexes containing an acidic chelating ligand to further evaluate the impact of the carboxylate, sulfonate and phosphonate moieties toward the targeted cyclization. The phosphinosulfonate-containing either Cp*-iridium(III) 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] The new square planar iridium(I)



Scheme 2. Preparation of the iridium and ruthenium complexes

complex cat. **C** was similarly synthesized starting from $[Ir(COD)Cl]_2$ in 83% yield, characterized by NMR analyses and confirmed by X-ray crystallography (Figure 2).[18,19] We next investigated the use of the less acidic DiPhenylPhosphinoBenzoic Acid (DPPBA). Using similar methodology as for the preparation of cat. **A**, reaction revealed the formation of the expected but surprisingly sensitive complex cat. **D** located at 4.7 ppm in ^{31}P NMR spectroscopy along with two distinct undesired species. Therefore slight modifications of the reaction conditions by performing the reaction with DPPBA gave after crystallization with solvent diffusion technique (CH_2Cl_2/*n*-hexane) the expected complex cat. **D** along with $2(H_3O^+;Cl^-);1H_2O$ molecules with a 9.5 ppm chemical shift in ^{31}P NMR (Figure 2).[20] Further neutralization by a careful water treatment finally afforded cat.**D** in 21% yield (Scheme 2). Recently, Rieger and coworkers reported the synthesis of phosphinophosphonic prochelates from diethylphosphonates for the preparation of various palladium(II) complexes.[21] Following this methodology, we thus decided to prepare the corresponding new Ir(III) complex cat. **E**. Treatment of this phosphonic acid with one equivalent of potassium *tert*-butoxide followed by the addition of $[Cp^*IrCl_2]_2$ gave two complexes. ^{31}P NMR analyses confirmed the formation of one major species at 16.3 ppm and 4.3 ppm corresponding the phosphonate and the phosphine, respectively which gave after purification, the 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 reacted with 1,3-propanediol **2a** during 20 h at 130 °C using toluene as a solvent without any basic or acidic additive. The [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

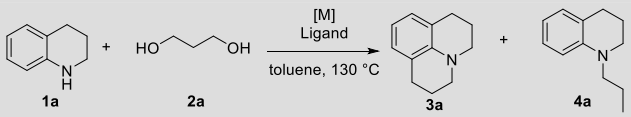


	cat. **A**	cat. **B**	cat. **C**	cat. **D**	cat. **E**
M-Cl (Å)	2.4042(9)	2.4138(8)	-	2.387(1)	2.408(2)
M-P (Å)	2.328(1)	2.3601(9)	2.2841(8)	2.287(1)	2.301(1)
M-O (Å)	2.140(2)	2.122(2)	2.093(2)	2.165(2)	2.150(4)

Figure 2. X-ray structures of the new complexes cat. **C**, cat. **D**, cat. **E** and relevant bond lengths comparison. Hydrogens, solvents have been removed for clarity

attempts (entry 1). Analysis of the reaction mixture highlighted the side formation of the *N*-propyltetrahydroquinoline **4a**, reaching a 61/39 ratio of **3a**/**4a**.[16,24] Modification of the reaction 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 the *N*-alkylated product **4a** and afforded julolidine **3a** in 72% yield with a **3a**/**4a** ratio of 87/13 (entry 2). As expected, the corresponding *in situ* generated

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

complex obtained by treatment of $[Ir(Cp^*)Cl_2]_2$ in the presence of **DPPBSA** afforded similar conversion, ratio and yield (entry 7 compared to 2). Lowering the concentration of **2a** resulted in higher conversion but the **3a**/**4a** ratio decreased (entries 7-9). We next investigated the influence of the chelate toward selectivity and yield. The new complex **D** featuring the softer phosphinocarboxylate chelate diminished the side reductive dehydration process affording similar conversion but with an improved 92/08 ratio in 77% yield of **3a** (entry 3). In contrast, the new Ir(III) complex **E** even with a 2:1 **1a**/**2a** ratio which favored the formation of the expected julolidine with **A** and **D**, enhanced the formation of the *N*-propyltetrahydroquinoline with a complete conversion and a 60/40 ratio demonstrating the influence of the second acidic dissociation constant (P-OH) on this complex toward the side dehydration/reduction (entry 4 compared to 2 and 3).

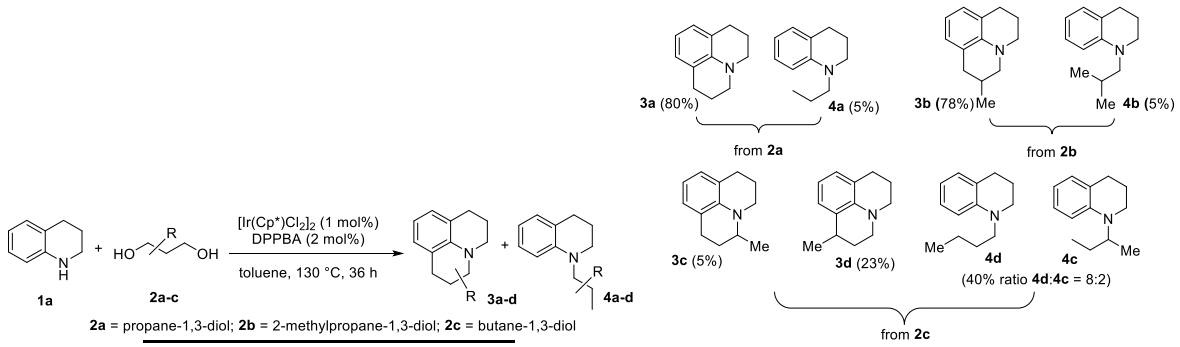


Chart 1. Isolated yields of julolidines **3a**-**d** and product distribution with propanediol derivatives **2**.

The use of the arene ruthenium(II) complex **B** afforded similar ratio as **A** but with a modest 53% conversion (entry 5). Low conversion was also observed in the presence of the new iridium(I) precatalyst **C** but with an equimolar ratio of **3a**/**4a** (entry 6). Optimization of the promising result obtained with **D** led us to use **DPPBA** as proligand for further investigations. Similar result and conversion was obtained by mixing **DPPBA** in the presence of $[Ir(Cp^*)Cl_2]_2$ (entry 10 compared to 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 (entry 11). The tedious separation of the remaining **1a** with the formed **3a** along with traces of **4a** by column chromatography over silica gel led to isolation of pure **3a** in 80% yield (entry 11). It is noteworthy that the reactions have been also achieved on gram scale affording similar ratio and yield.[25]

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

Rationalization of the formation of **3** and **4** was next undertaken (Figure 3). In the presence of the catalytic species, activation of the substrate propane-1,3-diol *via* dehydrogenation followed by condensation in the presence of amine **1a** gave the iminium intermediate **I**. Deprotonation would afford the key enaminoalcohol intermediate **II**. According to path **I** and depending on the acidity of the ligand held by the iridium, this latter can undergo protonation in the presence of acidic catalytic species to form the α,β-unsaturated *exo* cyclic iminium **IV** after a loss of a molecule of water. Then, consecutive reduction with the generated metal hydride species and protonation gave the 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 the enaminoiminium **V** as a formal Povarov key intermediate.[26-28] Therefore, consecutive electrocyclization followed by protonation and the release of the amine **1a** might lead to the α,β-unsaturated *endo* cyclic iminium **VI**. Finally, consecutive reduction/protonation/reduction affords the 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 autotransfers (path III). The formation of **4a** could also arise from prior dehydration/isomerization processes of the starting diol **1a** to afford propanal which might also

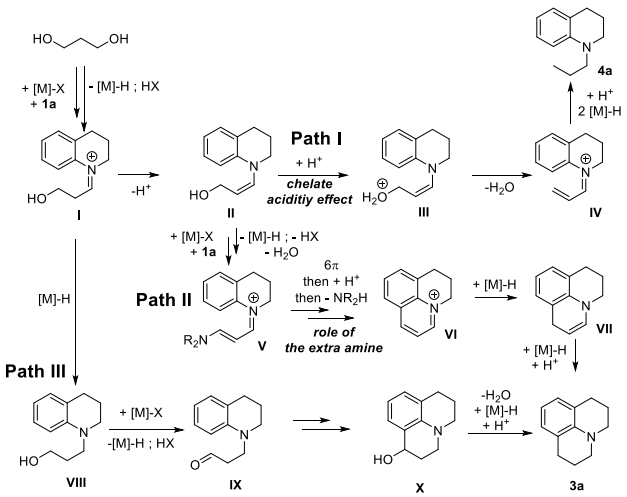
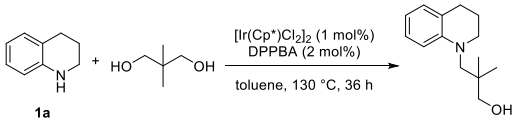


Figure 3. Proposed intermediates accounting for **3a** and **4a**.

account on **4a**.[29] To distinguish between the postulated pathways, we decided to perform the reaction of 2,2-dimethylpropane-1,3-diol which cannot lead to the key enaminoalcohol of type **II**. In this case, the corresponding uncyclized aminoalcohol product was predominantly formed whereas the 2,2-dimethyljulolidine was only detected during GC/MS analysis *i.e* < 1% (Scheme 3). This result tends to suggest the requirement of enaminoiminium intermediate **V** to ensure cyclization and might explain that the path **II** mainly accounts for the formation of julolidine **3**. This overall transformation complements traditional Povarov cyclizations that require specific dienophiles.[27]



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

At this first stage, considering the importance of the susbstitution patterns to ensure selective cyclization and the limited number of commercially available propane-1,3-diol derivatives, the diversity of julolidines arising from hydrogen autotransfers could appear quite limited. However, we considered that the prepared julolidines would be suitable candidates for postfunctionalization through hydrogen autotransfers in the presence of electrophiles

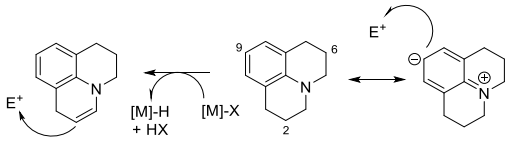


Figure 4. Competitive alkylation pathways

such as aldehydes to access β-alkylated julolidines. Noteworthy, the chromophoric properties of julolidine is inherent to their strong electron donating properties. Therefore, the highly nucleophilic site at C(9) adds another challenge to the target transformation (Figure 4).

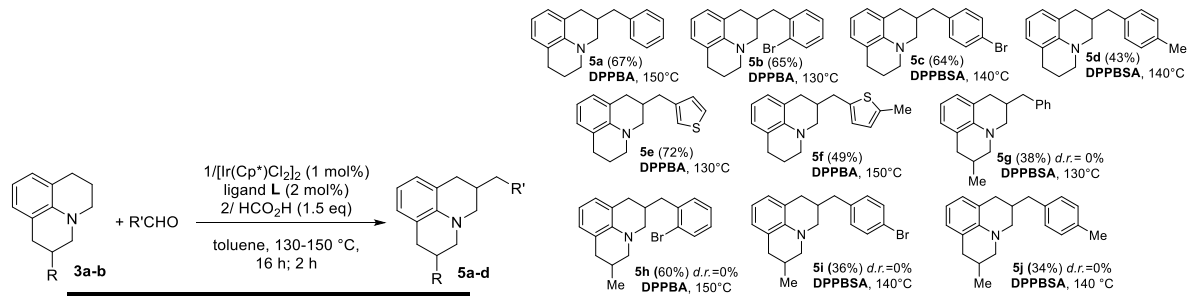
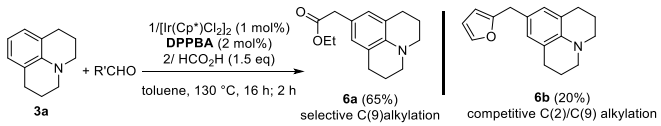


Chart 2. Isolated yields during β-alkylation of julolidines **3**

To our delight, the use of phosphinocarboxylate **DPPBA** or phoshinosulfonate **DPPBSA** chelates allowed the formation of the expected Cβ-functionalized julolidines from various aldehydes acting as electrophiles (Chart 2). Under conditions that we previously used for Cβ-alkylation[8b], e.g. in the presence of formic acid to achieve final reduction, reaction of benzaldehyde and **3a** afforded **5a** in 67% yield. Similarly, *p*-methylbenzaldehyde reacted cleanly to yield **5d** in 43%. Bromobenzaldehydes either at the *ortho*- or *para*- position gave the halogenated julolidines **5b** and **5c** in 65 and 64% yields, respectively, opening new perspectives of transformation of julolidines *via* catalyzed cross coupling reactions. Thiophene carboxaldehydes were compatible with the transformation yielding **5e**-**f** in up to 72%. In each case, the use of the Me-substituted julolidine **3b** led to the formation of two isomers without diastereoselectivity, affording the disubstituted products in 34-60% yields. It is important to note that with the aldehydes employed above, no C(9)-alkylated 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 the C(9)-alkylated julolidine **6b** in 20% isolated yield (Scheme 4). The use of ethyl glyoxylate completely suppressed the β-alkylation and only **6a** was formed during the reaction highlighting that aldehyde featuring a coordinating oxygen atom at the α-position favored Friedel-Crafts type products. Taken together, these results open new insights for the access to julolidines *via* hydrogen borrowing processes, keeping intact the C(9)-position for the introduction of an electron-acceptor.



Scheme 4. C(9)-alkylation of julolidine **3a**.

In conclusion we have demonstrated that the preparation of various julolidines can be easily achieved through hydrogen autotransfers involving consecutive N,C-dialkylation of tetrahydroquinoline and β-alkylation under green conditions with formation of water as the sole byproduct. Phosphino-sulfonate and -carboxylate were found to be efficient ligands for these transformations whereas more acidic phosphine-phosphonate favored dehydration/reduction pathway. 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.

Experimental Section

General Procedure for preparation of the julolidines **3**

To a 25 mL flame dried Schlenk, 1,3-propanediol **2** (0.67 mmol, 1.0 eq.), 1,2,3,4-tetrahydroquinoline **1a** (2.0 eq.), 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%) were successively added. The reaction mixture was evacuated by vacuum-argon cycles 5 times and stirred at 130 °C (Oil bath temperature) for 20-36 hours. After cooling the reaction at room temperature, the crude was suspended on silica and by column chromatography (Et_2O/PE) to isolate the expected julolidine **3**.

Acknowledgements

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