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# ***N*-Alkylation of aromatic amines with alcohols by using a commercially available Ru complex under mild conditions†**

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An *N*-alkylation procedure has been developed under very mild conditions using a known commercially available Ru-based catalyst. As a result, a wide range of aromatic primary amines has been selectively alkylated with several primary alcohols, yielding the corresponding secondary amines in high yields. The methodology also enables the methylation of anilines in refluxing methanol and the preparation of a set of heterocycles in a straightforward way.

## Introduction

The straightforward functionalization of amines is a crucial transformation for the pharmaceutical and fine chemical industries.<sup>1,2</sup> Among various methods enabling the synthesis of a new C–N bond, the so-called borrowing hydrogen (BH) strategy stands out for its intrinsic atom efficiency and selectivity traits.<sup>3–7</sup> In a typical BH or hydrogen autotransfer (HT) reaction, alcohol is temporarily dehydrogenated in the presence of a suitable metal catalyst, resulting in a carbonylic compound available to condense with an appropriate amine. Lastly, the imine is reduced by the resulting metal hydride [M]H<sub>2</sub> to give the alkylated secondary amine without the formation of waste other than water (Scheme 1). As well as avoiding alkyl halides, the catalytic system allows the *in situ* generation of the carbonyl source directly from alcohols, accessible from renewable feedstock.<sup>8</sup>

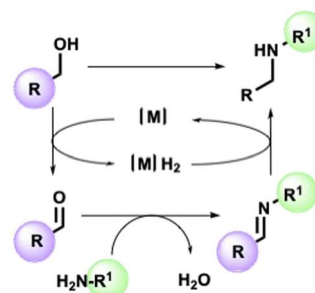
The extraordinary utility of this reaction is demonstrated by the plethora of examples reported in the literature. Since the pioneering studies<sup>9,10</sup> involving homogenous catalysts based on triphenylphosphine complexes of Rh, Ru, and Ir, introducing new ligands allowed the development of innovative catalytic platforms to realize more efficient processes under milder conditions.<sup>11–13</sup>

In this framework, some of these catalytic systems are represented by metal complexes requiring complex preparation

and appropriate expertise. A few of the most representative ones follow: [(η<sup>6</sup>-arene)RuCl<sub>2</sub>]X or [(η<sup>6</sup>-arene)RuCl<sub>2</sub>L] where L = PR<sub>3</sub>, NHC, Py, SR<sub>2</sub>, SeR<sub>2</sub> and X = Cl, PF<sub>6</sub>, OTf, and PNN, PNO/PNS, PNP, and NNC pincer complexes.<sup>14</sup> Recently, some remarkable examples of BH reactions catalyzed by non-noble metals such as Fe,<sup>15</sup> Mn,<sup>16,17</sup> and Co<sup>18,19</sup> have also been reported. However, Ru and Ir-based catalysts are still the most represented in this scenario.<sup>4</sup>

To this day, most *N*-alkylation reactions of amines with alcohols are mainly conducted at high temperatures (>100 °C).<sup>20,21</sup> Very few examples of room-temperature BH *N*-alkylation are reported in the literature.<sup>16,22–25</sup>

Finding an accessible methodology to perform such a significant transformation under very mild conditions remains highly demanded and challenging. We envisioned fetching from a library of pincer Ru (and Os) complexes and bidentate amino derivatives to achieve this goal. These catalysts were selected based on their notable efficacy in facilitating both the acceptorless dehydrogenation of alcohols to ketones and the transfer hydrogenation of carbonyl compounds. Prior investigations demonstrated the proficient catalytic abilities of these ruthenium


 Scheme 1 *N*-alkylation BH mediated general mechanism.

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(Ru) and osmium (Os) complexes in promoting carbonyl compound/alcohol interconversion reactions, highlighting in certain instances a superior activity of Os complexes in terms of turn over frequency. Consequently, we postulated that these attributes could be harnessed for amine alkylation.<sup>26–31</sup>

## Results and discussion

We started screening a set of 12 ruthenium and osmium-based catalysts by using 4-methoxy-anisidine and 1-octanol as model substrates in toluene and in the presence of 1 equivalent of *t*BuOK as a base (Fig. 1 and Table 1).<sup>4</sup> Since we aimed to perform the *N*-alkylation under mild conditions, we tested the catalytic process only by switching the reaction temperature from 25 °C to 70 °C (Table 1). The Ru complexes performed best among the twelve catalysts examined (Table 1, entries 1–8). Regarding the Ru bidentate amino derivatives, we observe complete conversion as early as room temperature in the presence of a dpfp ligand on the metal center (see entries 1 and 4 for comparison).

*Trans* and *cis* isomers of RuCl<sub>2</sub>(AMPY)(DPPF) displayed a sharp gap in catalytic activity ([Ru]-2 and [Ru]-3); the *cis* isomer proved efficient already at 25 °C after 24 hours, while the *trans* isomer (see ESI, Table S1† and entries 2 and 3 in Table 1) provided complete conversion into amine only at 70 °C.<sup>29</sup> At the same time, when dpfp diphosphine complexed the metal in the presence of other diamino derivatives (1,2-cyclohexanediamine and 1,2-ethylenediamine, [Ru]-4 and [Ru]-5), we obtained the quantitative formation of the desired alkylated amine **3a** in 36 and 24 hours (Table 1, entries 4 and 5).

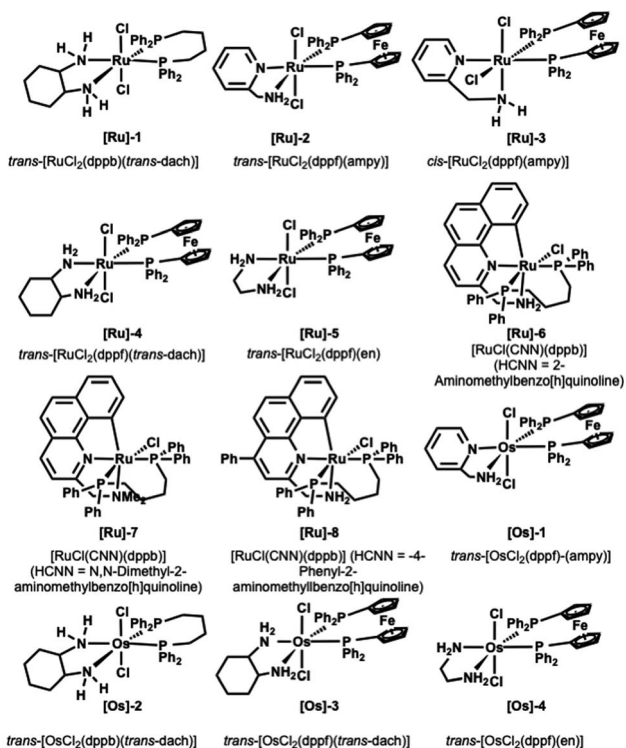


Fig. 1 Ru and Os catalysts tested.<sup>21–25</sup>

Table 1 Screening of catalysts under mild conditions<sup>a</sup>

| Entry          | Catalyst | Time (h) | Temperature | Yield of <b>3b</b> |
|----------------|----------|----------|-------------|--------------------|
| 1              | [Ru]-1   | 36       | 70 °C       | —                  |
| 2              | [Ru]-2   | 12       | 70 °C       | 99                 |
| 3              | [Ru]-3   | 24       | 25 °C       | 99                 |
| 4              | [Ru]-4   | 36       | 25 °C       | 97                 |
| 5              | [Ru]-5   | 24       | 25 °C       | 99                 |
| 6              | [Ru]-6   | 12       | 25 °C       | 99                 |
| 7              | [Ru]-7   | 36       | 70 °C       | —                  |
| 8              | [Ru]-8   | 2.5      | 25 °C       | 99                 |
| 9 <sup>c</sup> | [Ru]-3   | 24       | 25 °C       | 99                 |
| 10             | [Os]-1   | 36       | 70 °C       | —                  |
| 11             | [Os]-2   | 24       | 50 °C       | 99%                |
| 12             | [Os]-3   | 36       | 70 °C       | Traces             |
| 13             | [Os]-4   | 36       | 70 °C       | —                  |

<sup>a</sup> Reaction conditions: anisidine (1.0 mmol), octanol (1.0 mmol), potassium *tert*-butoxide (1.0 mmol), catalyst (2.5 mol%), in toluene (1.0 mL) for the given time and given temperature. <sup>b</sup> Determined by GC-MS analysis. <sup>c</sup> Catalyst loading 2 mol%.

The benzo[*h*]quinoline derivatives ligands confer a marked increase of activity to the catalyst. Indeed, the reaction proceeds smoothly in the presence of the catalysts [Ru]-6 and [Ru]-8 (Table 1, entries 6 and 8). Conversely, the absence of a free NH<sub>2</sub> moiety in the analogue [Ru]-7 results in diminished performance (see Table 1, entry 7).

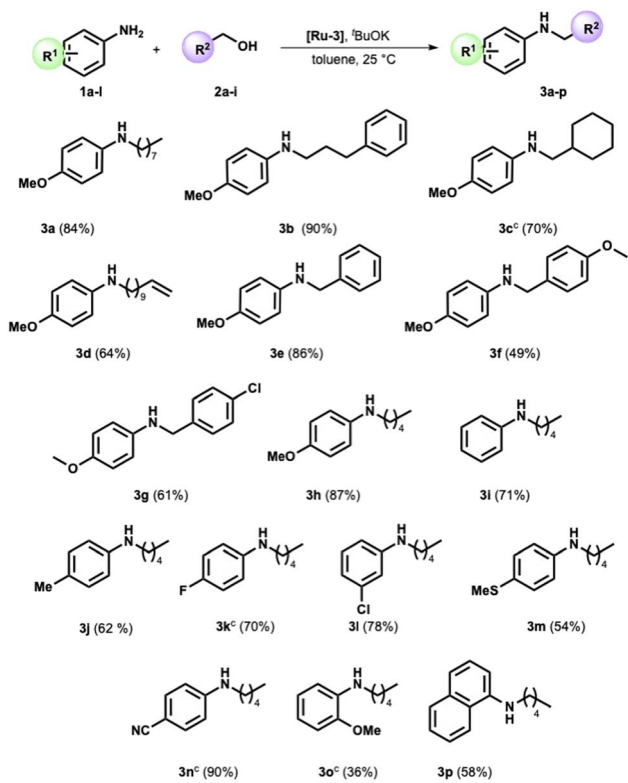
This behavior agrees with studies on analogous pincer CNN ruthenium(II) complexes made by Baratta *et al.*, in which the influence of NH<sub>2</sub> on the TH and HY catalytic activity was established.<sup>32</sup> Conversely, Martin-Matute observed an opposite trend, finding the NMe<sub>2</sub> pincer catalyst more active in forming secondary amine concerning the NH<sub>2</sub> analogous.<sup>31</sup> Finally, we tested the Os complexes shown in Fig. 1 (Table 1, entries 10–13). Even though none showed catalytic activity under room temperature conditions, we were pleased to observe the formation of the targeted *N*-alkylamine using [Os]-2 at only 50 °C (Table 1, entry 11). This result is noteworthy because, in a previous report, the BH osmium-mediated amine alkylation occurred at 200 °C.<sup>33</sup>

With this data in hand, we expanded the scope of our findings. We synthesized an array of secondary amines in high yield using catalysts [Ru]-6 and [Ru]-8 (see ESI, Table S3† for further details). Moreover, we were more intrigued by the potential feasibility of the catalyst [Ru]-3, which is commercially available.

We completed the reaction conditions tuning by reducing the catalyst loading to 2 mol% (see ESI† for further details and entry 9, Table 1). We applied the optimized conditions to an array of amines and alcohols (see Scheme 2).

Variations in the steric and electronic character of aliphatic alcohols provided the targeted compounds with high yields at a satisfactory reaction rate. Indeed, the 3-phenyl-1-propanol and





**Scheme 2** Scope of the *N*-alkylation reaction of aromatic amines with alcohols.<sup>a,b</sup> <sup>a</sup>Reaction conditions: amine (1 mmol), alcohol (1 mmol), potassium *tert*-butoxide (1 mmol), [Ru]-3 (2 mol%), in toluene (1 mL) for 24 h. <sup>b</sup>Isolated yields. <sup>c</sup>36 h.

cyclohexylmethanol were reacted with *p*-anisidine, providing the corresponding secondary amine in 90% and 70% yield, respectively (Scheme 2, compounds **3b** and **3c**). The reaction displayed good selectivity in the presence of the alkene moiety. The alkylamine **3d** was obtained in high yield (64%), while the product of double bond hydrogenation was not detected by GC-MS analysis.

Benzyl alcohol, the archetypal starting material for the BH-mediated *N*-alkylation, reacted with anisidine under optimized conditions. Pleasingly, *N*-benzyl *p*-anisidine **3e** was isolated in 85% yield. Compounds **3f** and **3g** were then successfully prepared with a yield of 49% and 61%, respectively (Scheme 2). *p*-Anisidine was then reacted with amyl alcohol, providing the corresponding secondary amine in high yield (Scheme 2, compound **3h**).

At this stage, we verified the effect of several substituents on the aromatic ring in the amine moiety. In detail, the less nucleophilic aniline and 4-methyl aniline showed good reactivity toward the pentyl alcohol, forming products **3i** and **3j** in satisfying yields (71% and 62%, respectively). A halide substituent such as F or Cl is well tolerated (Scheme 2). Indeed, products **3k** and **3l** were selectively synthesized in high yields (Scheme 2), while the product of hydrodehalogenation was not detected. The reaction proved suitable for an aniline bearing a sulfide group, as witnessed by the formation of **3m** in satisfactory yield (54%).

To our delight, when the 4-amino benzonitrile was reacted under the optimized conditions with 1-pentyl alcohol, the formation of the secondary amine **3n** was almost quantitative (Scheme 2). Furthermore, the presence of the methoxy substituent in the *ortho* position slightly affects the outcome of the reaction (Scheme 2, compare amines **3h** and **3o**). Lastly, 1-naphthylamine is effectively functionalized with a yield of 58% (Scheme 2, compound **3p**).

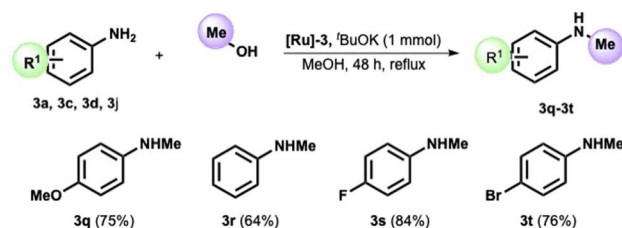
Shifting the focus to aliphatic amines yielded unfavorable outcomes. Specifically, attempts to react *N*-phenylethylamine with either heptanol or benzyl alcohol under the established optimized conditions proved inadequate for attaining the intended product.

Despite its value, applying BH reaction to the *N*-methylation is rather challenging. High temperatures are needed for the reaction, often requiring an appropriate pressure tube. However, the chance to perform this transformation, avoiding using formaldehyde or other toxic reagents such as methyl iodide or diazomethane, is of remarkable appeal.<sup>34–38</sup>

We then decided to test our catalyst in the reaction of *p*-anisidine and methanol. After tuning the reaction parameters (see ESI, Table S1†), we obtained the formation of the *N*-methyl-*p*-anisidine **3q** in 75% yield in refluxing methanol after 48 h. The method was then extended to various anilines, providing the corresponding *N*-methyl functionalized product in high yield (see Scheme 3). The reaction proceeds smoothly without substituents on the aryl ring (Scheme 3, amine **3r**) and with an electron-withdrawing group, such as the fluoro substituent in position 4. The 4-bromo-aniline also provided the methylated analogue in high isolated yields (see product **3t**).

At last, the borrowing hydrogen and acceptorless dehydrogenation catalysis provide access to the straightforward and elegant synthesis of various relevant heterocycles.<sup>39–41</sup> Elevated temperatures in the 100–140 °C range are typically necessary for this process to occur. This section evaluated our catalytic system for the acceptorless dehydrogenative synthesis of indole, benzimidazole, and quinoxaline.

Indole ring is perhaps the most preeminent *N*-heterocycle in nature and a worthy structural component in many pharmaceutical ingredients,<sup>42,43</sup> arousing strong interest through its synthesis.<sup>44</sup> The intramolecular cyclization of 2-amino-phenethyl alcohol is an elegant strategy for this target. However, despite sporadic examples,<sup>23</sup> operating temperatures hover



**Scheme 3** Scope of the *N*-methylation of aromatic amines with methanol.<sup>a,b</sup> <sup>a</sup>Reaction conditions: amine (1 mmol), potassium *tert*-butoxide (1 mmol), [Ru]-3 (2 mol%), in refluxing methanol (2 mL) for 48 h. <sup>b</sup>Isolated yields.



around 100 °C or above. For example, in 2016, Beller reported this cyclization in the presence of an Mn pincer complex at 100 °C.<sup>16</sup> Other examples are those written by Banerjee<sup>45</sup> and Adhikari,<sup>46</sup> which employ Ni catalysts for synthesizing indoles starting from aminoalcohols at 130 °C and 110 °C.

In our first trial, we tested the cyclization of 2-amino-phenethyl alcohol using commercially available [Ru]-3, potassium *tert*-butoxide in toluene at room temperature.

Under these conditions, only 50% conversion was observed after 48 hours. However, when the temperature was increased to 70 °C for 24 hours, complete conversion of indole was achieved, as confirmed by GC-MS analysis. Indole **5a** was subsequently isolated with a yield of 61%, as shown in Scheme 4.

Benzimidazole derivatives synthesis has attracted significant interest due to their important biological and pharmacological properties.<sup>47,48</sup> In this scenario, their practical, direct synthesis from primary alcohol and *o*-phenylenediamine has gained much attention.<sup>49–51</sup> However, operating temperatures over 100 °C are required. We then decided to test the *o*-phenylenediamine in the presence of benzyl alcohol and 1-pentanol (Scheme 4). While the benzyl alcohol provided the 1,2-disubstituted benzimidazoles in satisfying yield (Scheme 4, compound **7a**), the formation of the monoalkylated *o*-phenylenediamine was preferred to the ring closure when the diamine was coupled with 1-pentanol.

Finally, we focused on synthesizing the quinoxaline ring, a pharmaceutical occurring and key starting material nitrogen-containing heterocycle. Same here; most methods involve high temperatures up to 160 °C.<sup>52–56</sup> The catalyst proved suitable as product **9a** was obtained after 48 h at 90 °C in satisfying yield (Scheme 4).

Finally, an array of experiments for qualitative hydrogen detection were performed. For these experiments, three case substrates were reacted under an N<sub>2</sub> atmosphere in anhydrous toluene in the presence of catalyst [Ru]-3 and <sup>t</sup>BuOK. No significant hydrogen evolution was observed during **3a**, **3e**, and **5a** formation at room temperature after 12 hours. Conversely, indole formation from aminophenyl alcohol (see Scheme 4) at 70 °C was complemented by a consistent hydrogen

evolution after only 8 hours. As a comparison, the benzylic alcohol was similarly reacted at 70 °C in the presence of anisidine, and consistent hydrogen formation was observed in this case as well.

## Conclusion

In summary, we reported using a commercially available and robust [Ru]-3 catalyst for the mild *N*-alkylation reaction of aromatic amines with several alcohols, including methanol. The catalyst displayed good versatility when applied to the acceptorless dehydrogenative synthesis of a set of relevant heterocycles.

## Conflicts of interest

There are no conflicts to declare.

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Scheme 4 Application of the catalytic system to synthesize heterocycles.



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