Catalytic Alcohol Conversion

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Synthesis of *meta*-Functionalized Pyridines by Selective Dehydrogenative Heterocondensation of β- and γ-Amino Alcohols

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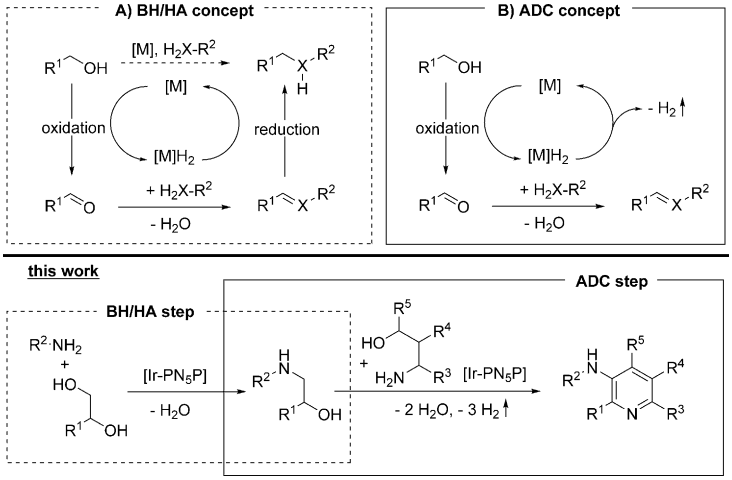
Abstract: *New reactions that convert alcohols into important classes of compounds are becoming increasingly important as their development contributes to the conservation of our fossil carbon feedstock and the reduction of CO_2 emissions. Two key catalytic alcohol conversion concepts are borrowing hydrogen or hydrogen autotransfer and acceptorless dehydrogenative condensation. Herein, we combined both concepts to synthesize meta-functionalized pyridines. First, diols and amines were linked to β-amino alcohols, which can then undergo a selective dehydrogenative heterocondensation with γ-amino alcohols. Iridium catalysts stabilized by PN_5P pincer ligands that were developed in our laboratory mediate the reactions most efficiently. All of the 3-aminopyridines that we describe in this paper have been synthesized for the first time, emphasizing the degree of innovation of this method and the problems associated with the synthesis of such meta-functionalized pyridines.*



Scheme 1. Top: A) Borrowing hydrogen (BH/HA) concept and B) acceptorless dehydrogenative condensation (ADC). X = CH, N; [M] = transition-metal catalyst. Bottom: Synthesis of *meta*-functionalized pyridines described in this work.

The development of novel reactions that convert alcohols into important organic compounds can be viewed as a contribution to a new approach to sustainable chemistry in which finite fossil resources are saved for future generations and CO_2 emissions are reduced.[1] Such novel reactions are especially appealing if existing synthetic methods are significantly extended. An elegant concept is the borrowing hydrogen (BH) or hydrogen autotransfer (HA) approach (Scheme 1 A), which permits the conversion of alcohols into amines and has been intensively studied.[2,3] Related to this is the combination of catalytic dehydrogenation and condensation in acceptorless dehydrogenative condensation (ADC), which enables the synthesis of aromatic N-heterocyclic compounds from alcohols.[1,3–5]

We have contributed to the development of both concepts[1,4,6] and herein report on the synthesis of 3-aminopyridines by combining BH/HA and ADC. Diols are catalytically reacted with amines to form β-amino alcohols, which then underwent a highly selective dehydrogenative heterocondensation with γ-amino alcohols. The key to success is the selective heterocondensation to avoid the homocoupling of the two amino alcohol building blocks. Iridium catalysts stabilized by PN_5P pincer ligands that were developed in our laboratory mediate this reaction selectively and most efficiently.[4] The problems associated with the synthesis of 3-aminopyridines[7] and the degree of novelty of the catalytic synthesis discussed here are also expressed by the fact that all examples that we have catalytically synthesized are novel compounds. The privileged pyridine motif is found in many natural products, bioactive molecules, agrochemicals, pharmaceuticals, and functional materials.[8] Consequently, the synthesis of pyridine derivatives is of high interest.[9]

First, we were interested in the synthesis of different β-amino alcohols by alkylation of amines with 1,2-diols (Scheme 1, BH/HA step). The selective alkylation of amines with 1,2-diols is a challenging reaction itself, and only a few methods have been described thus far.[1,10] To optimize the reaction conditions, we investigated the reaction of aniline with butane-1,2-diol (Table 1). Solvent screening revealed that diglyme is the optimal solvent. Adjusting the aniline/butane-1,2-diol ratio to 1:3 led to the best yield of the desired amino alcohol **1a**. Furthermore, we observed that a reaction temperature of at least 130 °C was required. A catalyst screening with 0.2 mol % of the complexes shown in Table 1 in the presence of KO^{t}Bu (2 equiv) was carried out next. Complexes **D** (93 % yield) and **E** (86 % yield) were found to be the most active precatalysts in the test reaction. With optimized reaction conditions for the amino alcohol synthesis in hand, we used this method to synthesize seven β-amino alcohols (see the Supporting Information, Table S8, **1a**–**g**).

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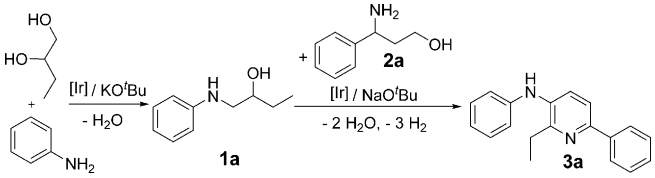
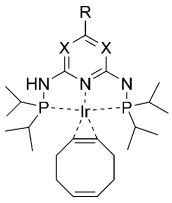
Table 1: Model reactions and precatalyst screening for the synthesis of β-amino alcohols[a] and 3-aminopyridines.[b]



	Precat.	Yield **1a** [%][c]	Yield **3a** [%][c]
1	**A**	78	61
2	**B**	85	58
3	**C**	78	47
4	**D**	93	76
5	**E**	86	90

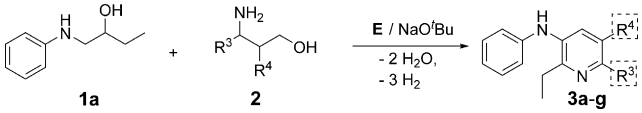
[a] Reaction conditions: Aniline (100.0 mmol, 1.0 equiv), butane-1,2-diol (3.0 equiv), KO^{t}Bu (2.0 equiv), [Ir] (0.2 mol%), diglyme (3 mL), 20 h, 130°C. [b] Reaction conditions: **1a** (4.0 equiv), **2a** (3.0 mmol, 1.0 equiv), NaO^{t}Bu (1.0 equiv), [Ir] (3.0 mol%), THF (15.0 mL), 24 h/90°C, 24 h/130°C. [c] Yield determined by GC analysis with dodecane as the internal standard.

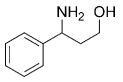
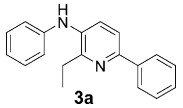
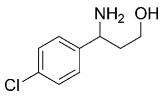
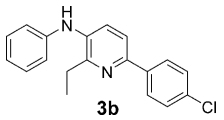
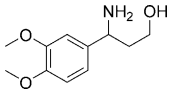
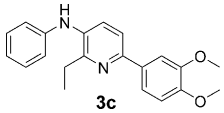
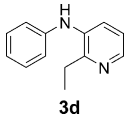
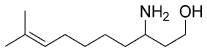
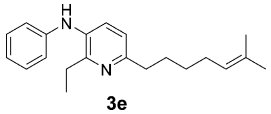
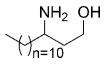
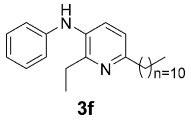
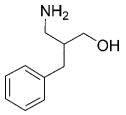
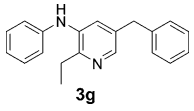


A: X=CH, R=H
B: X=CH, R=CH_3
C: X=N, R=CH_3
D: X=N, R=C_6H_5
E: X=N, R=C_6H_4-*p*-CF_3

Next, we investigated the reaction of the resultant N-substituted β-amino alcohols **1** with γ-amino alcohols (Scheme 1, ADC step). The synthesis of 3-aminopyridine **3a** from 1-(phenylamino)butan-2-ol (**1a**) and 3-amino-3-phenylpropan-1-ol (**2a**) was chosen as the model reaction (Table 1). Screening tridentate $PN_{3-5}P$ ligand stabilized iridium complexes (Table 1) as precatalysts indicated good conversions for **D**, the complex that was identified as the most efficient precatalyst in the BH/HA step for the synthesis of β-amino alcohols. However, the highest yield of **3a** was achieved using precatalyst **E** (Table 1, entry 5). Both precatalysts are based on a triazine motif and an aryl substituent at the triazine. In the case of **E**, the additional electron-withdrawing group (-CF_3) in *para* position seems to be beneficial. The optimal precatalyst loading was found to be 3.0 mol%.Adjusting the **1a**/**2a** ratio to 4:1, the nature and the amount of the base (NaO^{t}Bu, 1.0 equiv), the solvent (THF), and the reaction temperature (24 h at 90°C followed by an additional 24 h at 130°C) gave rise to nearly quantitative formation of 3-aminopyridine **3a**. The two-step procedure is needed to complete the dehydrogenation. A noticed side reaction was the deamination of the products, which takes place at higher base loadings. An increase in the amount of base can thus lead to complete deamination, giving rise to the corresponding pyridine motif (2-ethyl-6-phenylpyridine) and aniline (see Figure S6).Finally, we examined the scope of our new 3-aminopyridine synthesis. Varying the substituents in 2- and 3-position of the γ-amino alcohol led to compounds **3a–g** (Table 2, entries 1–7). Phenyl, chlorophenyl, and dimethoxyphenyl substituents were well tolerated. Compounds **3a**, **c**, **d**, and **g** were isolated in very good yields, and **3b** (entry 2) was

Table 2: Synthesis of 3-aminopyridines **3a–g** through variation of the γ-amino alcohol.[a]



	γ-Amino alcohol	Product	Yield [%][b]
1		 **3a**	84
2		 **3b**	69
3		 **3c**	85
4		 **3d**	91
5		 **3e**	32[c]
6		 **3f**	21[c]
7		 **3g**	97[d]

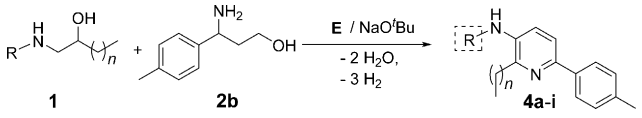
[a] Reaction conditions: **1a** (4.0 equiv), γ-amino alcohol (3.0 mmol, 1.0 equiv), NaO^{t}Bu (1.0 equiv), **E** (3.0 mol%), THF (15 mL), 24 h/90°C, 24 h/130°C. [b] Yield of isolated product. [c] Yield determined by GC analysis with dodecane as the internal standard. [d] **E** (5.0 mol%).

isolated in slightly lower yield owing to dehalogenation. Commercially available 3-aminopropan-1-ol reacted smoothly to the corresponding 3-aminopyridine **3d** (entry 4). Furthermore, unsaturated 3-alkyl-substituted γ-amino alcohols are suitable substrates (entry 5), but provide the corresponding products in only moderate yields. When a 2-substituted γ-amino alcohol (entry 7) is used, 2,5-substituted 3-aminopyridines can be obtained, as exemplarily demonstrated for **3g**, which was isolated in almost quantitative yield. For this reaction, 5 mol% of **E** were required.After variation of the γ-amino alcohol, we turned our attention to the reaction of 3-amino-3-(*para*-tolyl)propan-1-ol with a variety of differently N-substituted β-amino alcohols under the same reaction conditions. As shown in Table 3, different aryl and alkyl groups can be introduced, giving rise to the 3-aminopyridines **4a–i** in good to very good yields. We prepared 3-aminopyridines with heteroaromatic substituents (**4c**,**d**) and a chlorophenyl moiety (**4e**). Only the yields of **4f** (84%) and **4b** (78%) were slightly lower, which might be due to the bulky biphenyl substituent next to the amino group (**4f**) and

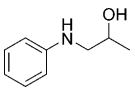
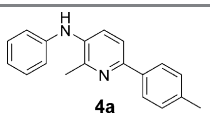
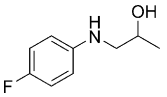
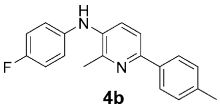
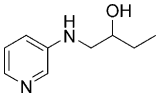
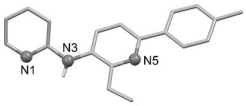
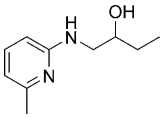
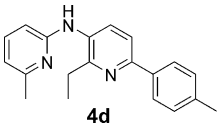
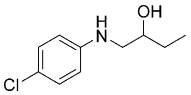
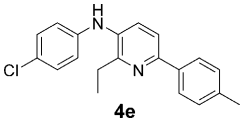
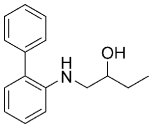
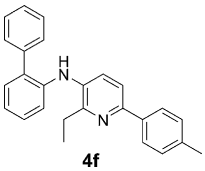
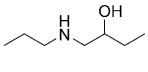
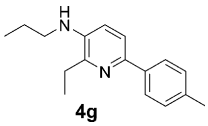
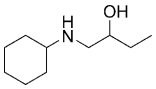
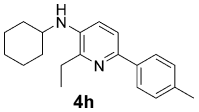
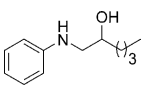
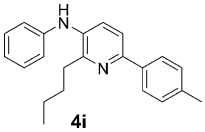
the electron-withdrawing effect of the fluorine atom (**4b**). When comparing the yields of products **4a–i**, and especially those of **4a** and **4i**, no dependence of the yield on the length of the alkyl chain in the 2-position of the 3-aminopyridine was observed. It was necessary to decrease the amount of base (NaO^{t}Bu) to 0.9 equiv for reactions with N-alkyl/cycloalkyl-substituted β-amino alcohols (**4g**,**h**), otherwise the yield was reduced by deamination. X-ray crystal-structure analysis of **4c**[11] was performed to determine the molecular structure of one of the novel 3-aminopyridines (Table 3, entry 3). The amino hydrogen atoms form strong intermolecular hydrogen bonds to adjacent pyridine N atoms (d(N3H···N6$_{pyridine}$) = 2.248 Å; d(N2H···N1$_{pyridine}$) = 2.077 Å). These similar intermolecular hydrogen bonds lead to the formation of a dimeric structure in the solid state.Finally, we varied both amino alcohol components (Table 4). All products were isolated in very good to excellent yields. Interestingly, with piperidin-3-ol as a building block, a polycyclic product, 6-phenyl-1,2,3,4-tetrahydro-1,5-naphthyridine (**5e**), was obtained in very good yield (isolated in 78%).

In summary, we have described a new catalytic method for the synthesis of 3-aminopyridines. γ-Amino alcohols and β-amino alcohols can be selectively linked in dehydrogenation and condensation steps. In combination with the selective alkylation of amines with diols according to the BH/HA concept, the final products are formed in a consecutive three-component reaction from a diol, an amine, and a γ-amino alcohol. A strength of this method is the introduction of aryl and alkyl substituents at various positions of the 3-aminopyridine moiety. One third of the compounds synthesized could be isolated in yields greater than 90%. Functional groups such as olefins are tolerated despite the liberation of H_2 (3 equiv per pyridine unit) during the reaction. The liberated hydrogen can be collected. All of the 20 3-amino-

Table 3: Synthesis of 3-aminopyridines **4a–i** through variation of β-amino alcohol **1**.[a]

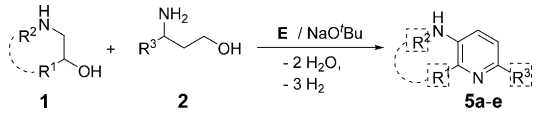


1 **2b** **4a-i**

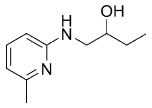
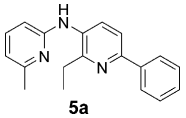
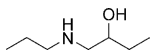
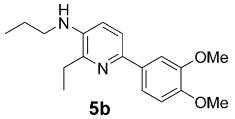
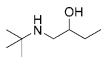
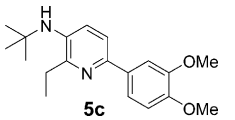
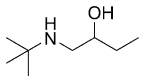
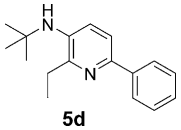
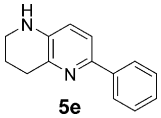
	1	Product	Yield [%][b]
1		 **4a**	89
2		 **4b**	78
3		 **4c**	92
4		 **4d**	92
5		 **4e**	90
6		 **4f**	84
7		 **4g**	93[c]
8		 **4h**	87[c]
9		 **4i**	89

[a] Reaction conditions: β-amino alcohol (4.0 equiv), 3-amino-3-*para*-tolylpropan-1-ol (3.0 mmol, 1.0 equiv), NaO^{t}Bu (1.0 equiv), **E** (3.0 mol%), THF (15 mL), 24 h/90°C, 24 h/130°C. [b] Yield of isolated product. [c] NaO^{t}Bu (0.9 equiv).

Table 4: Synthesis of 3-aminopyridines **5a–d** and 1,2,3,4-tetrahydro-1,5-naphthyridine **5e** through variation of β-amino alcohol **1** and γ-amino alcohol **2**.[a]



1 **2** **5a-e**

	1	2	Product	Yield [%][b]
1		R^3 = Ph	 **5a**	90
2		R^3 = 3,4-(MeO)$_2$C$_6$H$_3$	 **5b**	91[c]
3		R^3 = 3,4-(MeO)$_2$C$_6$H$_3$	 **5c**	94[c]
4		R^3 = Ph	 **5d**	88[c]
5		R^3 = Ph	 **5e**	78

[a] Reaction conditions: β-amino alcohol (4.0 equiv), γ-amino alcohol (3.0 mmol, 1.0 equiv), NaO^{t}Bu (1.0 equiv), **E** (3.0 mol%), THF (15 mL), 24 h/90°C, 24 h/130°C. [b] Yield of isolated product. [c] NaO^{t}Bu (0.9 equiv).

pyridines and the 1,5-naphthyridine reported in this paper have been synthesized for the first time, emphasizing the degree of innovation of this approach and the problems associated with the synthesis of such *meta*-functionalized pyridines.

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Keywords: amino alcohols · dehydrogenative heterocondensation · iridium · PNP ligands · pyridines

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[11] CCDC 1514538 (**4c**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Communications

Catalytic Alcohol Conversion

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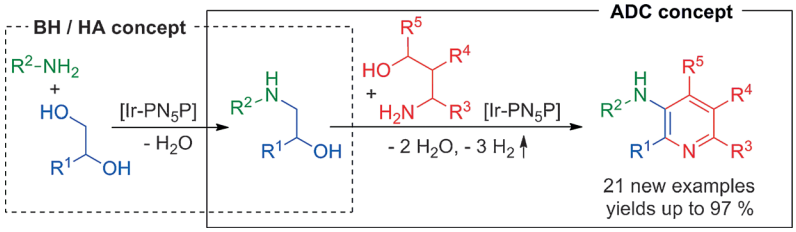
Synthesis of *meta*-Functionalized Pyridines by Selective Dehydrogenative Heterocondensation of β- and γ-Amino Alcohols



Diols and amines were linked to β-amino alcohols according to the borrowing hydrogen (BH) or hydrogen autotransfer (HA) concept, which then underwent a selective dehydrogenative heterocondensation with γ-amino alcohols in an Ir/PN_5P complex catalyzed synthesis of 3-aminopyridines (ADC = acceptorless dehydrogenative condensation). With this method, aryl and alkyl substituents can be introduced at various positions of the 3-aminopyridine moiety.