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Review

Sustainable Amination of Bio-Based Alcohols by Hydrogen Borrowing Catalysis

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Abstract: In this review, we aim to give an overview of the use of the Borrowing Hydrogen (BH) methodology with bio-based alcohols. This methodology only forms water as a by-product, thus providing a sustainable way to amines, which have a large range of applications. This process is of particular interest when related to biomass due to the high abundance of alcohol functions in natural compounds. However, natural compounds often comprise multiple chemical functions that can change the reactivity of the substrate. This comprehensive review, comprising both homogeneous and heterogeneous catalysts, aims at summarizing the recent advancements in biomass amination for every class of substrate, highlighting the key parameters governing their reactivity and the remaining scientific hurdles. Even though most substrates have successfully been converted into the corresponding amines, reaction selectivity and functional group tolerance still need to be improved.

Keywords: bio-based alcohol; amination; hydrogen borrowing

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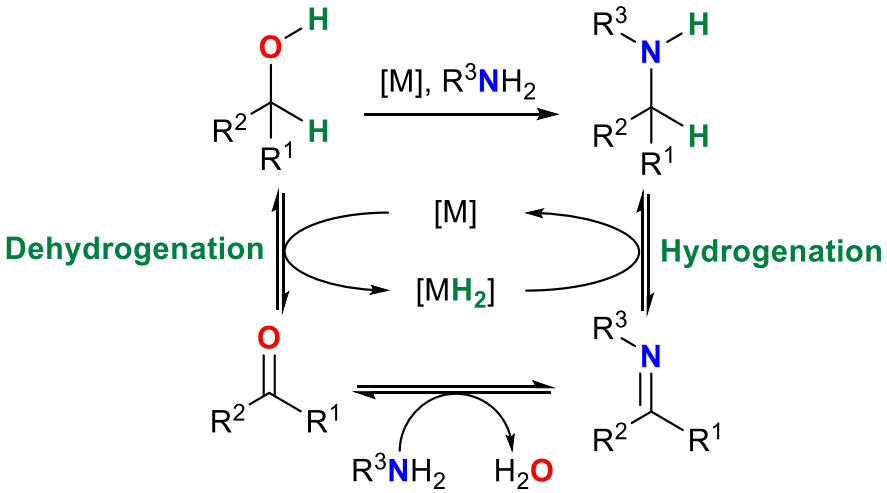
1. Introduction

Replacing fossil fuels used in the production of energy or as industrial feedstocks with renewable sources has become the paramount objective in combating climate change and environmental pollution. In this context, biorefining, which aims to use biomass as a raw material, stands out as a relevant solution towards sustainable development [1]. Because of the inherent differences between hydrocarbons—simple molecules composed of C and H atoms—and the complex entities that make up biomass feedstocks, new approaches are required to achieve efficient conversion. Lignocellulosic biomass represents 90% of all plants and presents the advantage of being abundant and available from non-edible resources. Lignocellulose is composed of lignin, cellulose, and hemicellulose and is easily available from waste residue. Cellulose and hemicellulose are carbohydrate polymers and thus contain large amounts of oxygen atoms, often in the form of hydroxyl functions, which are also found in a large number of natural compounds [2]. Hydroxyl groups have two reactive bonds: the C-O and the O-H bonds, each of which displays a particular reactivity. Aside from the well-known redox and elimination reactions, substitution pathways are a possibility, and mastering them could pave the way to a large variety of compounds. On the one hand, substitution of the hydroxyl hydrogen proved to be relatively easy due to its acid nature. On the other hand, nucleophilic substitution of the hydroxyl moiety can be problematic due to the poor leaving group ability of the OH group. To circumvent its low reactivity, acids can be added, but the main drawback of this strategy lies in the stoichiometric amounts often required along with the formation of side products. Transforming the alcohol functional groups into more reactive entities via treatment with $SOCl_2$ or PBr_3 is another possible approach with the inconvenience of adding an extra step to the synthesis.

A particular interest is devoted to the formation of amines as they are essential building blocks used to yield pharmaceutical compounds, solvents, food additives, polymer

materials, personal care products, detergents, or agrochemicals. On a general basis, amines can be obtained by various methods such as the Hofmann N-alkylation reaction, the Gabriel method, reduction of nitro compounds, Ullmann/Buchwald-Hartwig coupling, reductive amination, and hydroamination [3]. These approaches involve multiple steps and/or generate a stoichiometric amount of waste. Alternatives are thus in high demand.

The conversion of oxygen-rich biomass into amines usually involves C=O bond transformations since they are easily reactive and can undergo reductive amination reactions [4]. However, when these bonds are not present in the initial substrate, an extra step involving a stoichiometric amount of oxidant must be added to form the C=O moiety. Alternatively, the borrowing hydrogen methodology (BH) can be used when alcohol functions are found in the substrate. This reaction is also referred to as transfer hydrogenation or hydrogen autotransfer (Scheme 1) [5–7].

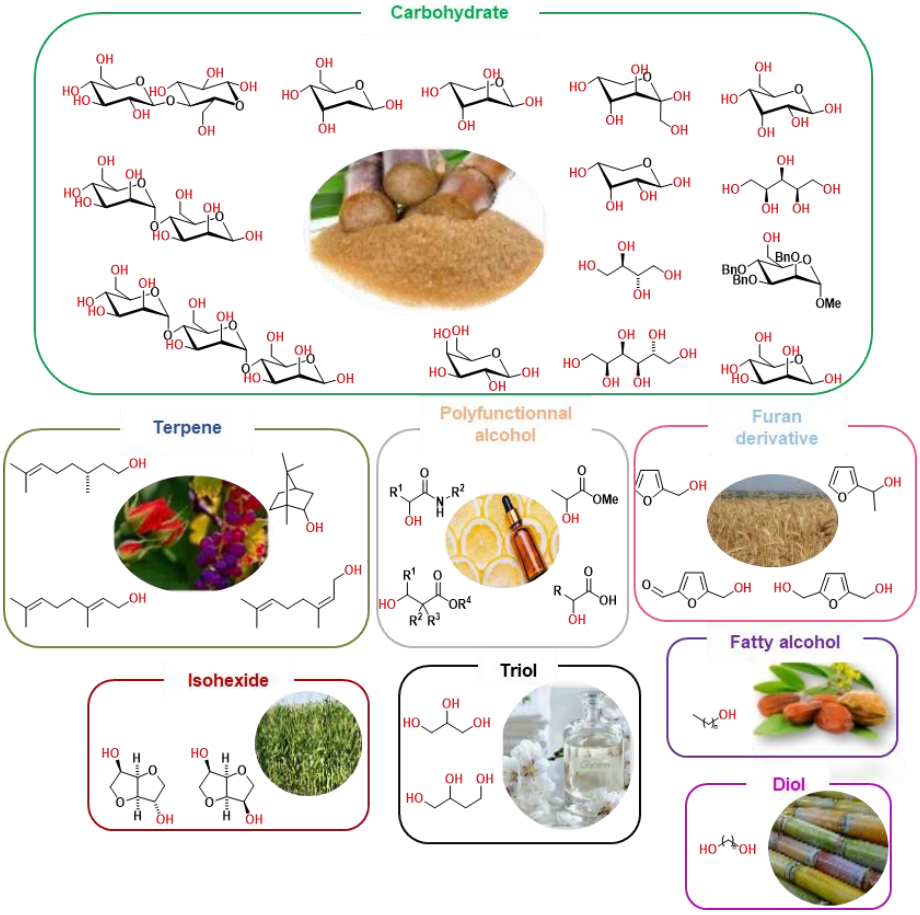


Scheme 1. Alcohol amination via hydrogen borrowing.

Complex structures can be catalytically obtained in only one step, thus suppressing multistep sequences. The key step of this methodology involves dehydrogenation of the substrate and its storage on the catalyst for later use in the last step of the catalytic cycle. Within only one step, oxidation/dehydrogenation and reduction/hydrogenation reactions are coupled, thus allowing the coupling of exothermic with endothermic reactions, which presents various advantages [8]. When this methodology is applied to an alcohol, the transformation starts with the dehydrogenation of the alcohol, forming a carbonyl moiety in concomitance with the catalyst hydrogenation. This step is followed by the classical amine/carbonyl condensation to form the corresponding imine. Finally, hydrogenation of the imine occurs, leading to the targeted amine such as the regeneration of the catalyst to complete the catalytic cycle. The H_2 used for this transformation arises from the catalyst (from the first dehydrogenation). The need for a stoichiometric amount of oxidant/reductant is thus removed. It is important to note that in some cases, extra H_2 was required to perform the reaction. An imbalance between the hydrogen borrowed from the substrate and consumed during the reaction can thus be observed. This extra hydrogen can be needed to prevent the catalyst deactivation, to reduce the amount of catalyst used, to control the selectivity of the reaction or to help to perform the last hydrogenation step [9].

Alcohol amination was first mentioned in 1932 by Winans and Adkins [10]. Hydrogen borrowing using homogeneous catalysts was first reported by Grigg [11] and Watanabe [12] and is gaining increasing attention due to the ease of the synthesis and the low amount of by-products formed. The term "borrowing hydrogen" was first used in 2004 [13] and was followed by extensive research on the topic. This has become an appealing methodology since functionalization of a large variety of alcohols is possible, with water being the only by-product formed in contrast with classical amine synthesis methods.

Due to the high presence of alcohol functions in natural substrates, this methodology was applied to a large variety of compounds arising from biomass, such as terpenes, furan derivatives, isohexides, fatty alcohols, diols, triols, polyfunctional alcohols, and carbohydrates (Scheme 2). Herein, we review these reactions and identify the key parameters for the amination of natural substrates. As an example, the use of fatty alcohols involves the presence of long aliphatic chains. The impact of these chains on the reaction conditions will be examined. The presence of multiple chemical functions will also be evaluated (double bonds, heterocycles, amides, carboxylic acids, and esters). Finally, the impact of the presence of multiple alcohol functions will be investigated. A large alcohol structural diversity can indeed be produced from biomass, and each class of natural substances will present some particular specificities. We have decided to classify the substrates used, to give a general trend for the BH amination. The latest studies on biomass amination via BH methodology will be summarized and discussed in this comprehensive review with an emphasis on the structure/functionalization-reactivity relationship.



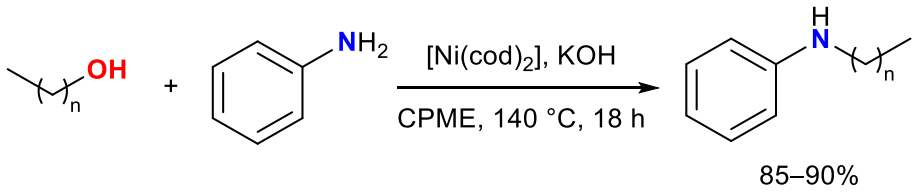
Scheme 2. Substrate aminated with a borrowing hydrogen strategy.

2. Amination of Bio-Based Alcohols by Hydrogen Borrowing Catalysis

2.1. Fatty Alcohols

Fatty alcohols are derived from natural fats and oils and correspond to long-straight-chain primary alcohols. The amination of small-chain alcohols has been extensively studied and is well documented in the literature [5,6]. We will only discuss long-chain fatty alcohols with carbon chains containing at least 14 carbon atoms. To the best of our knowledge, only two examples are reported in the literature [14]. The fatty alcohols were aminated in methoxycyclopentane using $[Ni(cod)_2]$ as catalyst, in the presence of 30 mol% of KOH with an 85–90% yield (Scheme 3). KOH is used to stabilize the in situ formed Ni nanoparticles. This methodology is well suited for the amination of alcohols with aniline, but the use

of aliphatic amines, leads to catalyst poisoning due to the increased basicity of aliphatic amines thus providing a stronger coordination ability. Shorter aliphatic chains could also be aminated and give similar yields. The length of the aliphatic chain has no impact on the reactivity of the catalytic system. In 2021, Ding et al. reported a homogeneous catalyst that was efficient in the presence of a base as an additive with slightly increased yields (90–99%) [15].

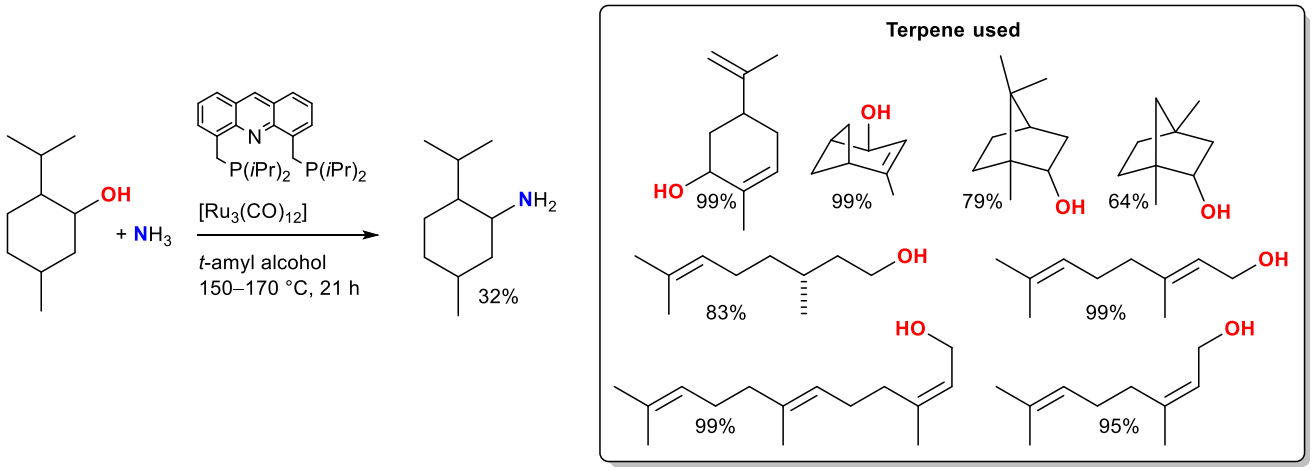


Scheme 3. Amination of fatty alcohols.

2.2. Terpenoids

Terpenoids are natural compounds arising from isoprene units that can be found in plants and are often used for their aromatic properties. They present a large structural and functional variety, and some display alcohol functions that were used in hydrogen borrowing reactions.

Vogt et al. described in 2013 the amination of various alcohols belonging to the terpene family (Scheme 4) [16]. Satisfactory conversion ranging from 32 to 99% was achieved depending on the substrate used. Selectivity varied from 44 to 98% due to the high functionality of the targeted terpenoids. As an example, since unsaturations are commonly found in terpenoids, the intermediate formation of enals is observed. They could easily isomerize to a mixture of compounds (such as the corresponding saturated amines or alcohols). Additionally, the formation of secondary amines from the primary alcohols was also observed, i.e., the dialkylation of ammonia instead of the desired monoalkylation. Moreover, in the case of bulky terpenoids, the reaction is hardly completed. The corresponding ketone is thus the main product obtained with these substrates. This highlights some of the difficulties encountered with natural substrates.



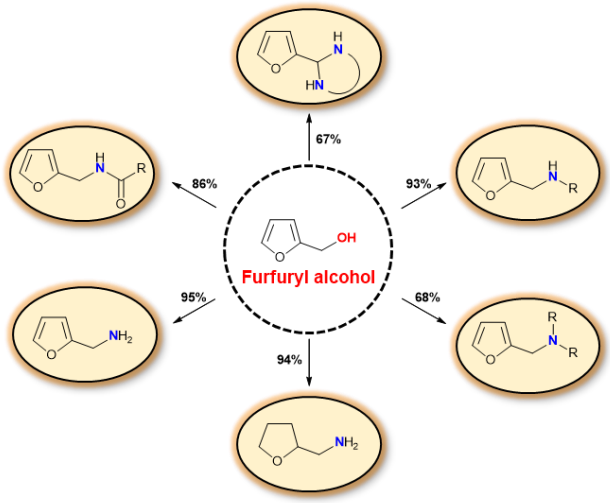
Scheme 4. Terpene amination.

2.3. Furan Derivatives

Furan derivatives can be obtained via the dehydration of carbohydrate monomers under acid conditions. The amination of several furan derivatives is reported in the literature: mainly 5-(hydroxymethyl)furfural (5-HMF), 2,5-bis(hydroxymethyl)furan (BHMF), and furfuryl alcohol. In addition, rare examples of 1-(2-furyl)ethanol, 5-methylfurfuryl alcohol or tetrahydrofurfuryl alcohol were also mentioned in the literature. This section will be ordered according to the alcohol substrate used.

2.3.1. Furfuryl Alcohol

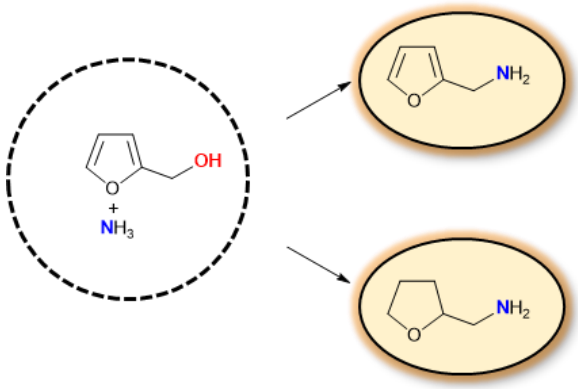
Furfuryl alcohol was aminated under various reaction conditions. Interestingly, a large structural variety of products was obtained, such as various primary, secondary, or tertiary amines, depending on the amine substrates and the reaction conditions (Scheme 5).



Scheme 5. Furfuryl alcohol amination.

Ammonia as a Nitrogen Source

Only two different structures are accessible from furfuryl alcohol and ammonia: furfuryl amine and its hydrogenated counterpart, tetrahydrofurfurylamine (Scheme 6).



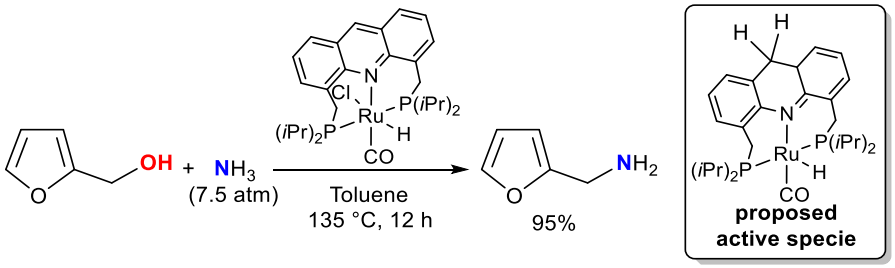
Scheme 6. Furfuryl alcohol amination using ammonia as a nitrogen source.

The catalytic systems used to provide furfuryl amine from furfuryl alcohol and ammonia are summarized in Table 1.

Table 1. Catalytic synthesis of furfuryl amine.

Entry	Catalyst	T (°C)	t (h)	Solvent	Additive	Yield (%)	Ref
1	Ru-PNP complex	135	12	Toluene	—	95	[17]
2	$[Ru_3CO_{12}]$/ CataCXium® PCy	150	20	Neat	—	71	[18]
3	Ru nanoparticles	180	20	Neat	H_2 (2 bar)	38	[19]
4	Ru/Al_2O_3	180	20	Neat	H_2 (2 bar)	10	[19]
5	$Ru–MgO/TiO_2$	110	20	Toluene	—	94	[20]
6	RANEY® Ni	180	24	THF	—	82	[21]
7	Ni/Al_2O_3-SiO_2	160	18	*t*-amyl alcohol	—	52	[22]

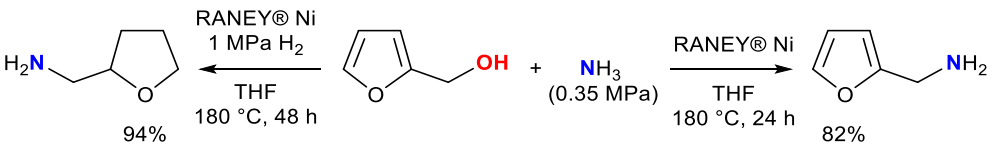
This reaction was first reported in 2008 by Milstein et al. with the synthesis and catalytic activity of an acridine-based Ru complex for the production of primary amines (Scheme 7, Table 1 Entry 1) [17]. This catalyst provided 95% of furfurylamine after 12 h. This particular catalyst is believed to operate via metal-ligand cooperation. Indeed, the acridine moiety is known to dearomatize and thus activate the alcohol in concomitance with the metallic center to perform the oxidation of the alcohol to a carbonyl [23]. In 2010, Beller also described the synthesis of the primary amine in 71% yield using $[Ru_3CO_{12}]$/CataCXium® PCy as a catalyst (Table 1 Entry 2) [18]. Even though a lower yield was obtained compared to the previous report by Milstein, the catalytic system is commercially available.



Scheme 7. Furfuryl alcohol amination to the corresponding primary amine.

Additionally, for these homogeneous systems, several heterogeneous catalysts were reported (Table 1 Entry 3–7). To the best of our knowledge, only Ru- and Ni-based catalysts have been described. Although the non-supported Ru nanoparticles proved to have superior catalytic activity, the primary amine yield was quite low: 38 and 10% for Ru NP and Ru/Al_2O_3, respectively (Table 1 Entry 3 and 4) [19]. The yield of the reaction was drastically increased in 2020 with the work of Hara (Table 1 Entry 5) [20]. In the presence of $Ru\text{-}MgO/TiO_2$, 94% of the desired furfurylamine was obtained. The main advantage of this catalyst, besides its high yield, is that no external H_2 was needed for the reaction to proceed at excellent yields.

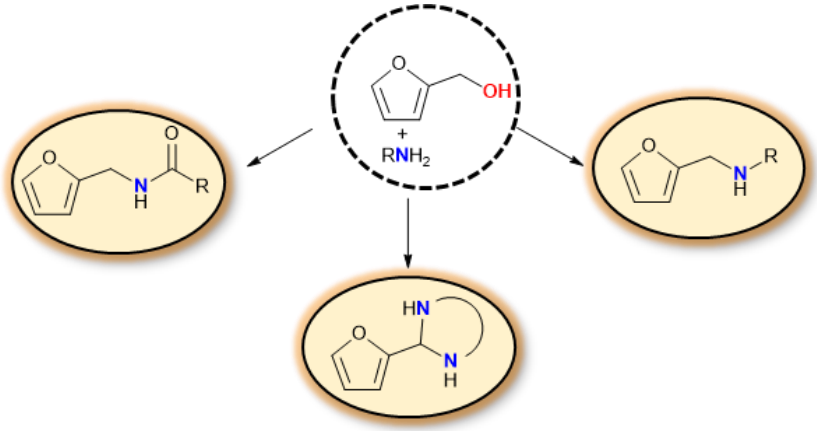
Earth abundant based catalysts were also efficient in furfuryl alcohol amination with ammonia. The most efficient system consists of the use of RANEY® Ni (Table 1, Entry 6) [21,24]. When this catalyst was used, furfuryl alcohol could be transformed into either furfurylamine or tetrahydrofurfurylamine depending on the reaction conditions (Scheme 8) [21,24]. Indeed, the selectivity of the reaction was driven by the presence of H_2. Although the alcohol amination does not require the use of external H_2 since it is "borrowed" from the alcohol dehydrogenation, it is mandatory for the hydrogenation of the furan ring. Indeed, 1 MPa of H_2 led to the hydrogenation of the furan ring in addition to the amination reaction, thus forming tetrahydrofurfurylamine. Whereas the catalyst could be reused at least five times in the case of the tetrahydrofurfurylamine, the absence of H_2 pressure for the furfurylamine formation catalysis led to catalyst deactivation after one run [21]. The remarkable catalytic activity of RANEY® Ni was ascribed to the small absorption energy difference between NH_3 and H_2. Thanks to this small difference, some of the active sites of the catalyst are available to perform the dehydrogenation/hydrogenation reactions that are required for the amination to occur and thus improve the overall catalytic activity of the catalyst [21].



Scheme 8. Furfuryl alcohol amination over RANEY® Ni.

Primary Amines as a Nitrogen Source

Furfuryl amination using a primary amine as a nitrogen source led to the expected furfuryl amine and to more unexpected structures. Indeed, cyclic aminated compounds can be obtained from the use of diamine as a nitrogen source, and one example of amidation has been reported (Scheme 9).



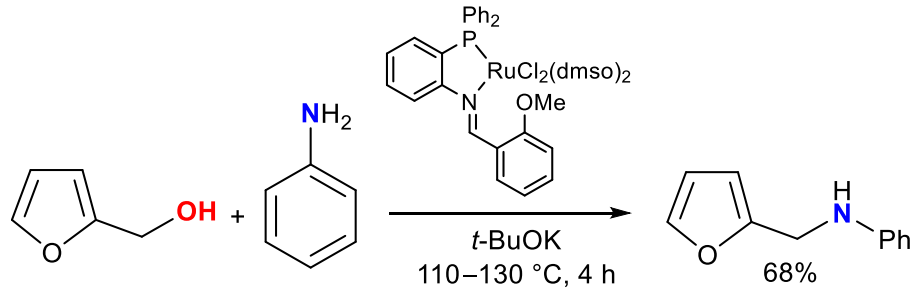
Scheme 9. Furfuryl alcohol amination/amidation using a primary amine as a nitrogen source.

If a primary amine was used instead of ammonia, secondary amines were obtained under various conditions. The catalytic activity of various homogeneous catalysts was assessed and resulted in yields ranging from 66 to 93% (Table 2 Entry 1–6). The first report in 2007 described the use of $[Ru_3CO_{12}]$/CataCXium® PCy, which allowed the isolation of 66% of products (Table 2 Entry 1) [25]. Only a moderate yield was obtained for this reaction due to the occurrence of side reactions (mainly difuryl side products). More and more well-defined catalysts were designed, synthesized, and investigated on natural alcohol, such as a complex containing a tridentate P,N,O ligand which efficiently catalyzed the amination of furfuryl alcohol with aniline with a 68% yield in only 4 h (Scheme 10, Table 2 Entry 2) [26]. It is worth mentioning that the presence of a base as an additive was used for this reaction. The base was assumed to deprotonate the alcohol, thus facilitating the coordination of the formed alcoholate to the Ru center.

Table 2. Catalytic furfuryl alcohol amination with a primary amine as a nitrogen source.

Entry	Catalyst	T (°C)	t (h)	Solvent	Additive	Yield (%)	Ref
1	$[Ru_3CO_{12}]$/ CataCXiumPCy®	110	24	Neat	—	66	[25]
2	Ru-PNO complex	110–130	4	Neat	*t*-BuOK	68	[26]
3	Ru-NHC	120	24	Toluene	*t*-BuOK	93	[27]
4	$[IrI_2Cp^*]_2$	115	10	H_2O	—	86	[28]
5	Cyclometalated Iridium complex	80	24	H_2O	KOH	91	[29]
6	Mn-NNS complex	140	72	Toluene	KOH	67 [1]	[30]
7	$Ti^{III}_{0.2}Ti^{IV}_{0.8}(NTf_2)_2(O)_x(OH)_y(H_2O)_z \cdot 2.5H_2O$	100	2	Toluene	Bipyridine or terpyridine	98 [2]	[31]
8	Nanosized zeolite beta	135	4	Neat	—	52	[32]
9	$PdZn/Al_2O_3$	110	4	*p*-xylene	—	85	[33]
10	$[Ni(COD)_2]$	140	18	CPME	KOH	51	[14]

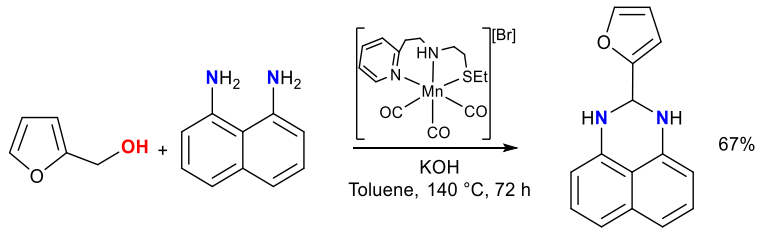
[1] A diamine was used as a nitrogen source. [2] The reaction was performed under microwave irradiation. Cp* is the classical aabbreviation for pentamethylcyclopentadiene.



Scheme 10. Amination of furfuryl alcohol with aniline.

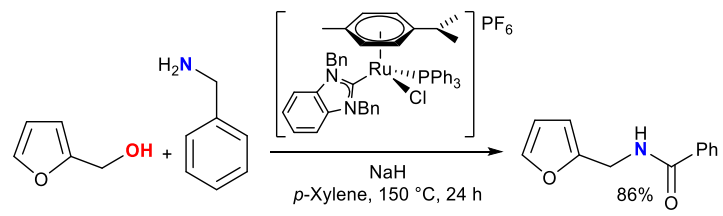
In addition to the homogeneous systems already described, heterogeneous catalysts were used to perform this reaction (Table 2 Entry 7–10). The most efficient catalyst is the complex $Ti^{III}_{0.2}Ti^{IV}_{0.8}(NTf_2)_2(O)_x(OH)_y(H_2O)_z \cdot 2.5H_2O$ (Table 2 Entry 7) [31]. Indeed, only 2 h were required at 100 °C in the presence of bipyridine or terpyridine as ligands under microwave irradiations to reach a 98% yield of the targeted amines. Interestingly, the authors are proposing an SN-type mechanism rather than the classical borrowing hydrogen one, which is classically encountered in alcohol amination. The ligand may help to solubilize the catalyst, avoiding its deactivation and increasing its activity by forming cationic species. Zeolites were also used as catalysts and their catalytic activity was ascribed to the acidity of the catalyst (Table 2 Entry 8) [32]. The first step of the mechanism is assumed to be the adsorption of the alcohol on the acid sites of the zeolite for further reaction with the amine, thus increasing its reactivity. Oxophilic catalysts such as $PdZn/Al_2O_3$ were effective for this transformation (Table 2 Entry 9) [33]. The alcohol is believed to be alkylated on the surface of the PdZn catalyst. Indeed, the oxophilic nature of Zn atoms played a crucial role in the reaction, whereas Pd atoms are azophilic. This may explain the high catalytic activity of the intermetallic $PdZn/Al_2O_3$ catalyst.

When a diamine was used as a substrate, the corresponding 2,3-dihydro-1*H*-perimidine derivative was formed (Scheme 11, Table 2 Entry 6) [30]. This sustainable system, comprising a nontoxic earth-abundant manganese complex and an air- and moisture-stable ligand scaffold, could afford a 67% yield of the desired compound.



Scheme 11. Amination of furfuryl alcohol with 1,8-diaminonaphthalene.

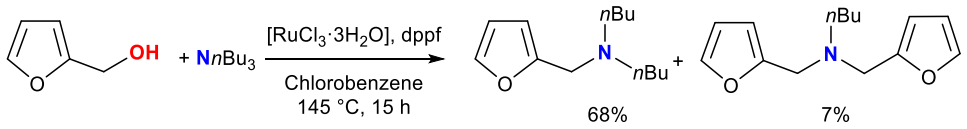
Note that Huynh et al. used a cationic Ru-NHC catalyst [RuCl(*p*-cymene)(NHC)(PPh_3)][PF_6] to perform the amidation of furfuryl alcohol in the presence of NaH as a base (Scheme 12) [34]. Interestingly, the nature of the base influences the nature of the product formed. The amidation reaction was effective only in the presence of a strong base otherwise, the formation of the expected amine was observed.



Scheme 12. Furfuryl alcohol amidation.

Tertiary Amines as Nitrogen Sources

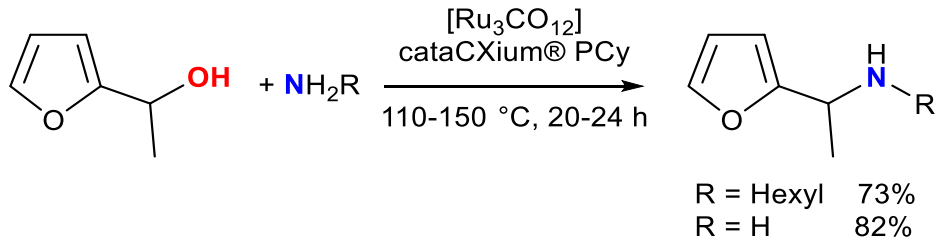
There is only one example of tertiary amines synthesized from furfuryl alcohol reported in the literature [35]. The use of [$RuCl_3 \cdot 3H_2O$] and 1,10-bis(diphenylphosphino)ferrocene (dppf) allowed for the alkylation of a tertiary amine at a good yield (Scheme 13). Interestingly, the amination agent was a tertiary amine. The reaction afforded a mixture of mono- and bis-substituted products with a preference for the mono-substituted product.



Scheme 13. Tertiary amines synthesis from furfuryl alcohol.

2.3.2. 1-(2-Furyl)ethanol

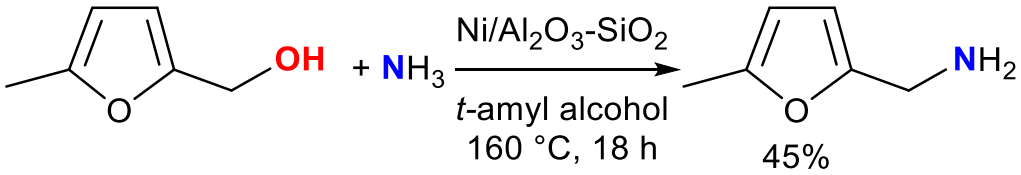
Under the same conditions used for furfuryl alcohol, the amination of 1-(2-furyl)ethanol was investigated. The reaction was performed with a primary amine or with ammonia as nitrogen sources, leading to the formation of a secondary or primary amine respectively. Both reactions proceeded using [Ru_3CO_{12}] in combination with CataCXium® PCy as catalyst (Scheme 14) [18,25].



Scheme 14. 1-(2-furyl)ethanol amination.

2.3.3. 5-Methylfurfuryl Alcohol

Similar to that which was reported with furfuryl alcohol, in 2019, Barta et al. performed the amination of 5-methylfurfuryl alcohol using Ni/Al_2O_3-SiO_2 as a catalyst to provide 45% of the desired primary amine (Scheme 15) [22].



Scheme 15. 5-methylfurfuryl alcohol amination.

2.3.4. 5-(Hydroxymethyl)furfural

The compound 2,5-bisaminomethylfuran (2,5-BAMF) can be formed starting with either 5-(hydroxymethyl)furfural (5-HMF) [21,36,37] or 2,5-bis(hydroxymethyl)furan (BHMF) (see below) [20,36].

When 5-HMF was used as a substrate, the reaction combined a reductive amination of the carbonyl moiety and the borrowing hydrogen methodology on the alcohol function. Whereas it was possible to perform selectively the reductive amination of the carbonyl function, selective transformation of the alcohol function has never been observed. This is presumably due to the increased reactivity of the carbonyl group compared to the alcohol and to the similar reaction conditions needed to undergo both reductive amination and hydrogen borrowing reactions. This shows the selectivity limit of the use of natural substrates with hydrogen borrowing methodology. As an example, a stepwise amination of 5-HMF was described in 2017 by Hara [38]. The reductive amination of the aldehyde

function was performed by Ru/Nb_2O_5 using ammonia as a nitrogen source. No amination of the alcohol function was observed. It was necessary to perform the amination of this amino alcohol with [Ru(CO)ClH(PPh3)3]/Xantphos to yield the desired diamine at a yield of 93%.

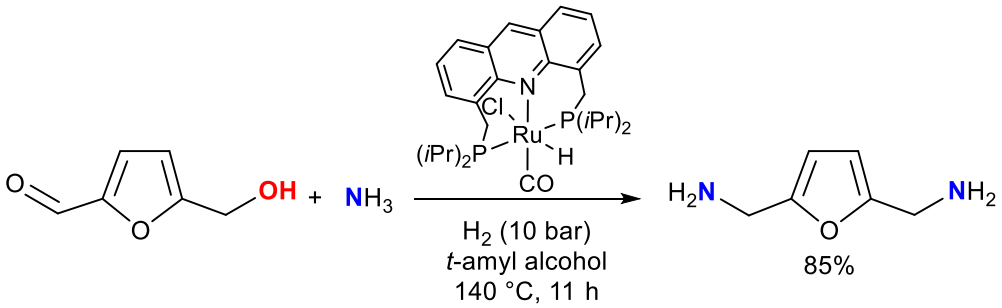
However, the formation of 2,5-BAMF starting from 5-HMF can be performed using either homogeneous (Table 3 Entry 1) or heterogeneous catalysts (Table 3 Entry 2–3). All systems required the use of external H_2 as an additive.

Table 3. Catalytic amination of 5-HMF with ammonia as a nitrogen source to produce 2,5-BAMF.

Entry	Catalyst	T (°C)	t (h)	Solvent	Additive	Yield (%)	Refs
1	Ru-PNP complex	140	11	*t*-amyl alcohol	H_2 (10 bar)	85	[36]
2	RANEY® Ni	160	12	THF	H_2 (10 bar)	61	[21]
3	$CuNiAlO_x$	210 [1]	27	Dioxane	Na_2CO_3 H_2 (45 bar)	86	[37,39,40]

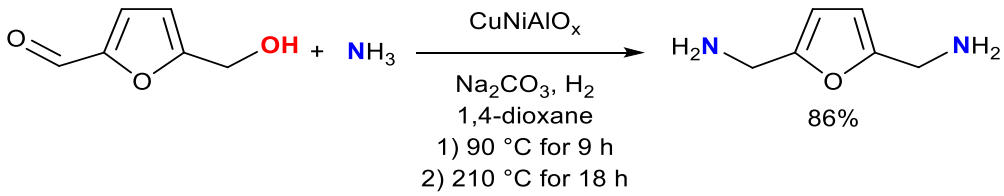
[1] 9 h at 90 °C, followed by 18 h at 210 °C.

Homogeneous catalysts proved to be efficient with complete conversion in the reaction of 5-HMF with ammonia using 10 bar H_2 and *t*-amyl alcohol as solvent at 140 °C for 11 h (Scheme 16, Table 3 Entry 1) [36].



Scheme 16. Homogeneous amination of 5-HMF.

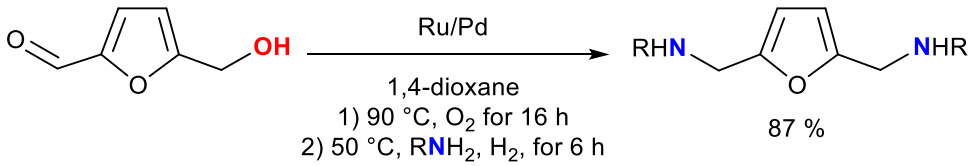
Several heterogeneous catalysts were also tested for this reaction: RANEY® Ni, RANEY® Co, $CuNiAlO_x$ Pd/C, Pt/C, and Ru/C [21,37,39,40]. Whereas Pd/C, Pt/C, and Ru/C were only efficient for reductive amination of the carbonyl moiety, RANEY® Ni was effective for 5-HMF diamination with a 61% yield (Table 3 Entry 2) [21]. The catalytic activity could be increased to 86% with the use of the bifunctional $CuNiAlO_x$ catalyst (Scheme 17, Table 3 Entry 3) [37,39,40]. This catalyst combined the hydrogenation ability of Ni with the dehydrogenation ability of Cu. A base was used as an additive to promote the hydrogen transfer reaction. A gradual heating of the reaction was necessary to achieve high selectivity. Indeed, the reductive amination of the aldehyde only required 90 °C heating for 9 h, whereas the hydrogen borrowing of the alcohol required 210 °C for 18 h.



Scheme 17. Heterogeneous amination of 5-HMF.

Only one example of 5-HMF amination using primary amines as nitrogen sources was described by Pera-Titus et al. [41]. A mechanical mixture of 5%Ru/C + 5%Pd/C catalysts or a bifunctional (Ru + Pd)/C were required to afford more than an 87% yield of

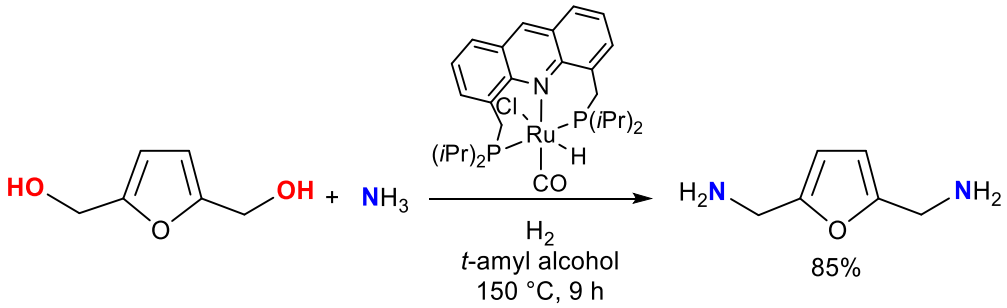
diamines (Scheme 18). The reaction consists of two consecutive steps: the aerobic oxidation of HMF to 2,5-diformylfuran, followed by reductive amination of 2,5-diformylfuran to the corresponding diamines in the presence of H_2. Even though the reaction cannot be categorized as a hydrogen borrowing reaction, the overall chemical equation is a reductive amination of the carbonyl and the amination of the alcohol of HMF in a one-step process and shall therefore be mentioned here.



Scheme 18. Tandem oxidation-amination reaction of 5-HMF.

2.3.5. 2,5-Bis(hydroxymethym)furan

The compound 2,5-bis(hydroxymethyl)furan (BHMF) was used as a substrate in amination reactions with ammonia as a nitrogen source to produce 2,5-bis(aminomethyl)furan (BAMF) using either homogeneous or heterogeneous catalysts [20,36]. For homogeneous reaction, the amination of the alcohol moieties was observed with an 85% yield after 9 h (Scheme 19) [36]. The heterogeneous system provided a similar yield since 86% of BAMF was obtained when Ru–MgO/TiO_2 was used as a catalyst [20].



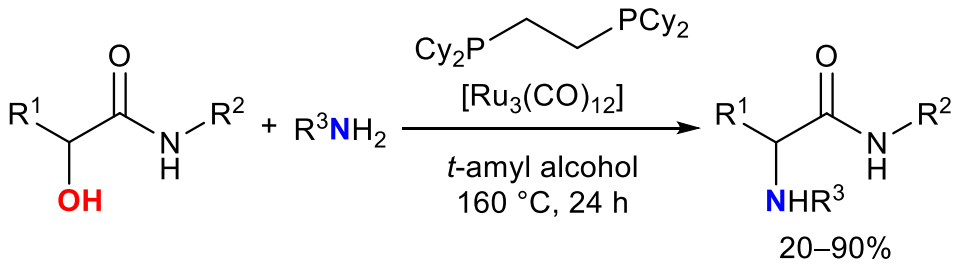
Scheme 19. Homogeneous amination of BHMF.

2.4. Polyfunctional Alcohols

Alcohols found in nature are often bearing multiple functionalities, for this reason, the reaction conditions should be adapted to the specificities of other groups that may also be reactive. The amination is complex due to the functional group, which may hinder the coordination sites of the catalyst. In some cases, the functional groups can also be reactive, as shown with the aldehyde function of 5-HMF, which is more reactive than the alcohol function. We will here take α-hydroxy amides, α-hydroxy acids, and α-/β-hydroxy esters as examples of bifunctional molecules.

2.4.1. α-hydroxy Amides

The first amination of α-hydroxy amides was reported in 2011 by Beller et al. [42]. The reaction went well when [$Ru_3(CO)_{12}$] was used as a metallic precursor with 1,2-bis(dicyclohexylphosphino)ethane as a ligand in *t*-amyl alcohol at 160 °C for 24 h, yielding 91% (Scheme 20). The reaction was quite tolerant to the substituent borne by the amine and by the α-hydroxy amides, even though the yields decreased to 20% when both alcohol and nitrogen sources were sterically hindered. Alternatively, [$TiCl_4$] could be used stoichiometricaly at only 100 °C, instead of the Ru based catalyst, to provide the desired α-amino amides with moderate to good yields [43].

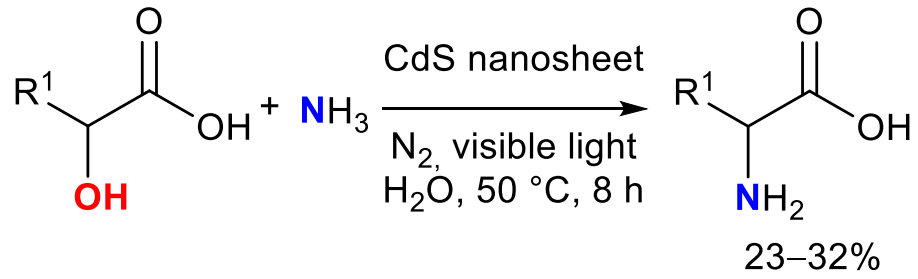


Scheme 20. α-hydroxy amides amination.

2.4.2. α-hydroxy Acids

α-hydroxy acids can be transformed into α-amino acids in one step with high yields using ruthenium nanoparticles supported on carbon nanotubes or on nitrogen-doped carbon nanotubes as catalysts [44–46]. This methodology provides an alternative to the classical microbial cultivation process used for α-amino acids production. It seems, however, limited to the transformation of α-hydroxy acids since the use of β-hydroxy acids only led to poor yields (below 4%). Doping the carbon nanotubes with nitrogen led to an increase in catalytic activity. This enhancement is believed to be due to the improvement of the Ru nanoparticle dispersion on the support and to their strong interaction with the support. Additionally, the absorption of the substrate is believed to be facilitated when a N-dopant is used.

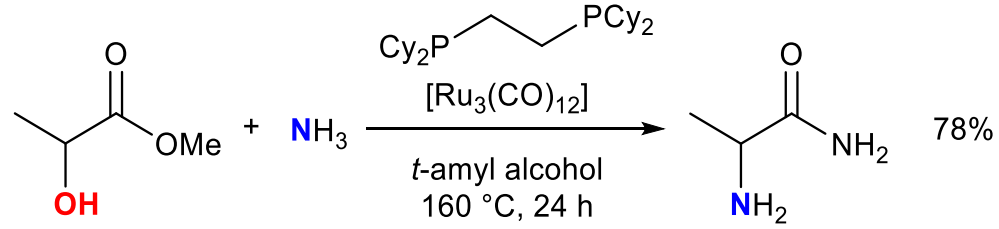
Changing the catalyst to an ultrathin CdS nanosheet using NH_3 under visible light irradiation provides the formation of the desired α-amino acids at only 50 °C with relatively low yields (Scheme 21) [47]. The formation of oxygen-centered radicals under these conditions is considered to be responsible for the activity of the catalytic system. Unfortunately, once again low activity was detected with β-hydroxy acids (yields below 6%).



Scheme 21. α-hydroxy acid amination.

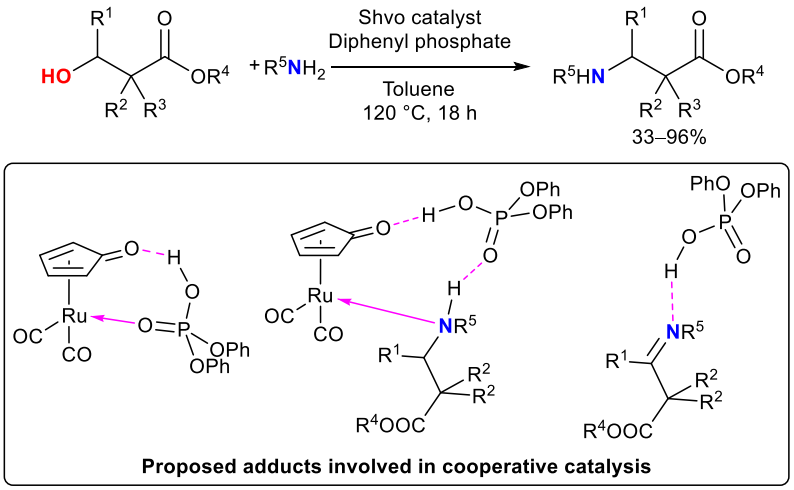
2.4.3. α-and β-hydroxy Esters

The use of α-hydroxy esters as substrates under reaction conditions which are known to be effective for non-functional alcohols provided a rather unexpected reaction [42]. Indeed, the reaction was selectively performed on the alcohol but also on the ester moiety, with 78% of alanamide observed (Scheme 22). This indicates a low ester tolerance under these conditions.



Scheme 22. α-hydroxy ester amination.

However, the reaction of ammonia and α-hydroxy esters in the presence of [RuHCl(PPh_3)$_3$(CO)] and Xantphos resulted in the formation of the desired primary amine in good yields [48]. In the particular case of β-hydroxyl acid esters, the use of a Brønsted acid as an additive was an efficient methodology for their amination with various aniline derivatives [49]. The catalyst and the additive are believed to form adducts which are presumably more active than the catalyst alone (Scheme 23).



Scheme 23. β-hydroxy esters amination.

2.5. Polyols

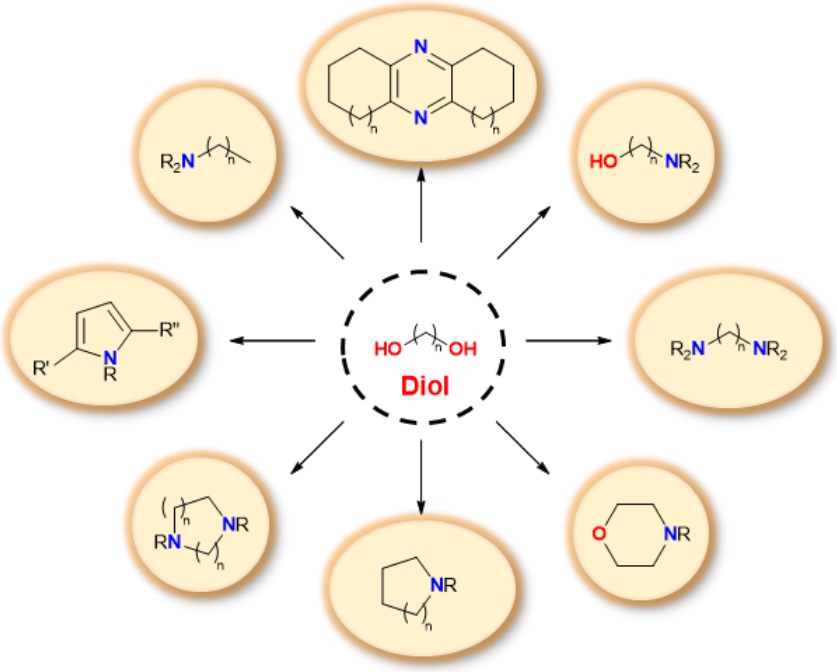
2.5.1. Diols

A large number of publications on the amination of diols can be found in the literature. For this reason, we have selected examples to give a general trend to understand the remaining barriers with this type of substrate. Isohexides will be treated separately as they are complex compounds due to the difference in reactivity between the two hydroxyl groups.

As shown in Scheme 24, amination of diols can lead to a broad structural variety depending on: (i) the substrates used (nitrogen source and/or diol), (ii) the catalysts used, and (iii) the reaction conditions. The main products encountered in this section are the expected diamines, formed by the double amination of the two alcohol functions, and the amino alcohols, arising from the amination of only one alcohol, in line with the cyclization products. This cyclization can be inter- or intra-molecular. On the one hand, a diamine reacts with a diol, thus forming a cycle, and on the other hand, an amino alcohol is formed, and the amine function reacts with the remaining alcohol, thus providing cyclization of the product. Finally, aromatic heterocycles or dehydrated/aminated products can sometimes be obtained. In these reactions, oligomer formation (or at least dimerization) was one of the side reactions often encountered [50–57].

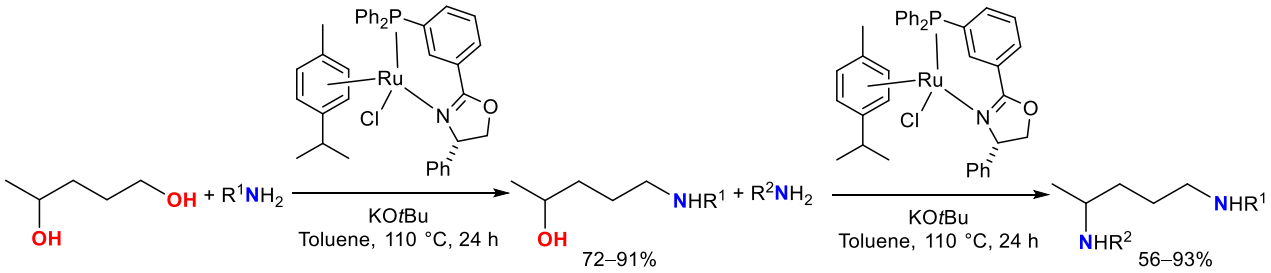
Diamines and Amino Alcohol Synthesis

The main products of diol amination are diamines. However when the reaction does not go to completion, the formation of amino alcohols was observed. Homogeneous and heterogeneous catalysts leading to diamination and/or monoamination of diols are reported in Table 4. Several factors influence the reactivity of the catalytic system, and the important parameters will be reviewed herein with selected examples. Note that the reaction could also provide the formation of an amino ketone when the reaction proceeds further than amino alcohol formation without going to completion [58].



Scheme 24. Diol amination.

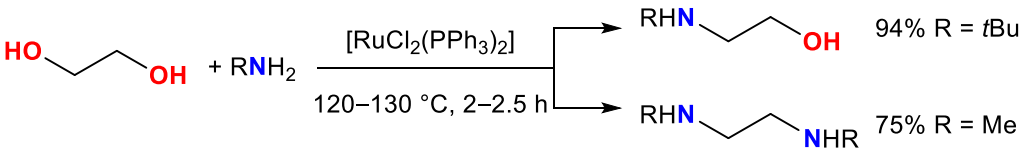
Nature of the alcohols: primary alcohols were found to be much more reactive than secondary ones. When primary and secondary alcohol diols were combined, amino-alcohols were formed instead of the corresponding diamines [59,60]. This shows the increased activity of primary alcohols toward secondary ones and the importance of the steric hindrance of alcoholic substrates [59]. However, under certain conditions, the reactivity of secondary alcohols can be pushed to complete the reaction. Stepwise amination of primary and secondary diols was also performed and was significantly faster with primary alcohols compared to secondary ones (Scheme 25) [61].



Scheme 25. Stepwise amination of diol.

The selectivity of the reaction was also driven by the length/nature of the spacer between the two alcohol functions [62] and its steric hindrance [63]. For example, the use of an *O*-tethered spacer led to the formation of amino-alcohols, whereas the use of a simple aliphatic chain gave diamines [62].

Nature of the nitrogen sources: in addition to the nature of the alcohol substrates, the selectivity of the reaction strongly depends on the steric hindrance of the nitrogen sources (Scheme 26) [64]. It was demonstrated that, within a homogeneous process catalyzed by $[RuCl_2(PPh_3)_2]$, highly sterically hindered amines preferentially provided the formation of amino alcohols, while the use of small nitrogen sources allowed access to diaminated compounds.



Scheme 26. Effect of the steric parameter on selectivity.

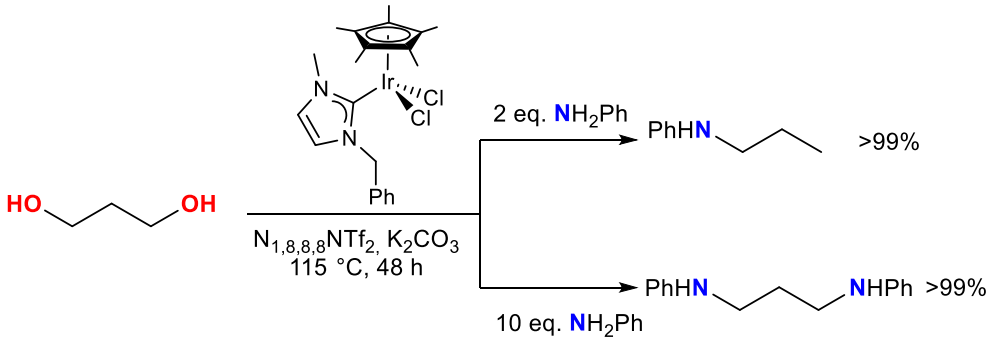
Table 4. Typical catalysts used for diol amination.

	Diamination		Monoamination	
Heterogeneous Catalysts	zeolite	[65]	zeolites	[65,66]
	$Ni\text{-}Cu\text{-}Cr_2O_3$	[63]	$Ni\text{-}Cu\text{-}Cr_2O_3$	[63]
	$Ru/Co/Al_2O_3$	[63]	$Ru/Co/Al_2O_3$	[67]
	Ru-Co-Sn	[68]	Ru-Co-Sn	[68]
	$CuNiAlO_x$	[69]	$CuNiAlO_x$	[69]
	Re-Ru-Co	[67]	Re-Ru-Co	[70]
	Co-Fe	[52]	Co-Fe	[52]
	Cu-Zn-Zr oxide	[71]	Cu-Zn-Zr oxide	[71]
	Cu/Al_2O_3	[64,72]	Cu/Al_2O_3	[72,73]
	Cu-Ni-Ca-Ba	[74]	Ni nanoparticles	[14]
	$Pt\text{-}Sn/\gamma\text{-}Al_2O_3$	[62]	CuCrO	[75]
	Ru/Al_2O_3	[51]	RhIn/C	[76,77]
	Ru/C	[78]	$Co/\gamma\text{-}Al_2O_3$	[79]
	Re-Ru-Co	[70]		
	RANEY® Ni	[22]		
	Co-Fe	[53]		
Homogeneous Catalysts	$[RuCl_3{\cdot}xH_20]$	[80]	$[RuCl_3{\cdot}xH_20]/PPh_3$	[80]
	$[RuCl_2(PPh_3)_3]$	[64]	$[RuCl_2(PPh_3)_3]$	[64,80]
	$[Ru_3(CO)_{12}]$/ CataCXium PCy	[59]	$[Ru_3(CO)_{12}]$/ CataCXium PCy	[59]
	[RuCl(*p*-cymene)(P,N)][Cl]	[61]	[RuCl(*p*-cymene)(P,N)][Cl]	[61]
	$[IrCl_2Cp^*(NHC)]$	[50]	$[IrCl_2Cp^*(NHC)]$	[50,81]
	$[Ru_3(CO)_{12}]$/ PNP	[16,36,82–86]	$[Ru_3(CO)_{12}]$/ PNP	[16,83,85,86]
	$[IrCl_3{\cdot}xH_20]/PPh_3$	[80,87]	$[RuHCl(PPh_3)_3]$	[80]
	$[RuHCl(CO)(PPh_3)_3]$/ Xantphos	[48]	$[RuHCl(CO)(PPh_3)_3]$/ Triphos	[84]
			$[RuCl_2(p\text{-cymene})]_2$/ DPEphos	[54,60]
			$[RuCl_2(p\text{-cymene})]_2$/ Josiphos	[88]
			$[IrH_2Cl\{(iPr_2PC_2H_4)_2NH\}]$	[87]
			$[Fe(CO)_4$ (cyclopentadienone)]	[89]

Reaction conditions: the reaction temperature was found to be a critical parameter [72,90]. For example, in 1987, the amination of 1,6-hexanediol was performed at temperatures ranging from 165 to 230 °C. A mixture of diamines and aminols was always obtained. However, selectivity toward amino-alcohols is increased at low temperatures (up to 90% at 180 °C) and selectivity toward diaminated products increases with temperature (up to 65% at 230 °C) [72]. This temperature dependence is commonly observed [67,83]. The selectivity also strongly depends on the catalyst loading [69]. In the case of a heterogeneous process, the nature of the support, is also of capital importance. Li et al. showed that basic (Ru/MgO) and neutral (Ru/Al_2O_3) supported catalysts were efficient for monoamination reactions, whereas acidic supported catalysts (Ru/Nb_2O_5) provided mainly diaminated products (in line with by-products formation) [51].

Stoichiometry: in addition to the amination of one of the alcohol moiety, a dehydration of the second alcohol and subsequent hydrogenation can sometimes be observed [16,50,81].

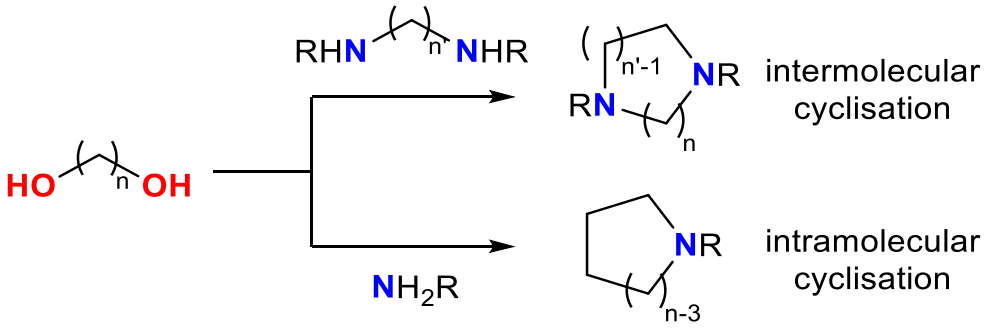
The quantity of amines plays a crucial role in the latter transformation. Hence, the use of an excess of amines led to the formation of the expected diamines, preventing the dehydration reaction (Scheme 27). Similar dehydration reactions were observed in the absence of amine [50].



Scheme 27. Dehydration reaction.

Cyclization Reactions

Cyclized compounds could also be obtained as products owing to the presence of two alcohol functions on the same molecule. Cyclization could either be inter- or intramolecular depending on the nitrogen sources used (Scheme 28). The homogeneous and heterogeneous catalysts leading to the cyclization of diols are reported in Table 5.



Scheme 28. Cyclization reactions.

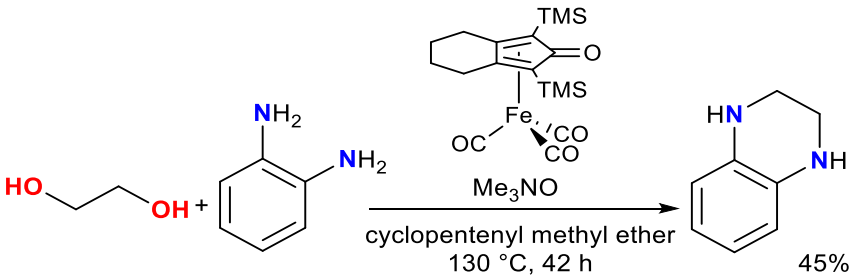
Table 5. Typical catalysts used for diol cyclization.

	Intermolecular Cyclization		Intramolecular Cyclization	
Heterogeneous Catalysts	Pt-Sn/γ-Al_2O_3	[62]	Pt-Sn/γ-Al_2O_3	[62,91]
	Pd/MgO	[92]	zeolites	[65,66,93–95]
			Re-Ru-Co	[70]
			$NiCuFeO_x$	[96]
			$CuNiAlO_x$	[69]
			$(Ni_{0.5}Cu_{0.5})Fe_2O_4$	[97]
			Cu-Zn-Zr oxide	[71]
			CuCrO	[75]
			Ru/Co/Al_2O_3	[67]
			Ru-Co-Sn	[68]
			Ni/Co/Cu/Sn/Al_2O_3	[98]
			Ru/C	[78]

Table 5. *Cont.*

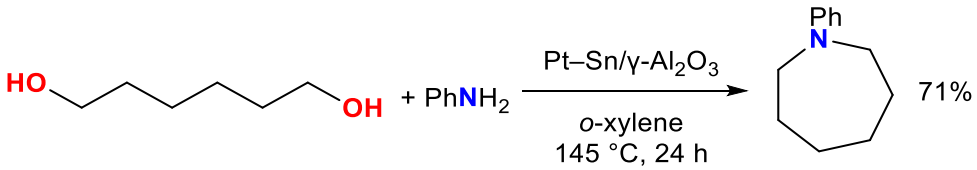
	Intermolecular Cyclization		Intramolecular Cyclization	
Homogeneous Catalysts	[Fe(CO)$_4$ (cyclopentadienone)]	[89]	[Fe(CO)$_4$ (cyclopentadienone)]	[89]
	[IrCl$_2$Cp*]$_2$	[55,90]	[IrCl$_2$Cp*]$_2$	[55,99,100]
	[RuCl(*p*-cymene)(P,N)][Cl]	[61]	[RuCl(*p*-cymene)(P,N)][Cl]	[61]
	[RuCl$_2$(*p*-cymene)]$_2$/DPEphos	[60,101]	[RuCl$_3$·xH$_2$0]/PPh$_3$	[102]
	[Pd(OAc)$_2$]/PPh$_3$	[103]	[RuCl$_2$(PPh$_3$)$_3$]	[104]
			[RuCl(*p*-cymene)(NHC)(PPh$_3$)][PF$_6$]	[105]
			[RuCl$_2$(PPh$_3$)(C$_5$H$_3$N-2,6-(CH$_2$NMe$_2$)$_2$]	[106]
			Ru-PNP complex	[83,85,86]
			[RuHCl(CO)(PPh$_3$)$_3$]/Triphos	[84]
			[Ru(acac)$_3$]/Triphos	[107]
			cyclometalated Ir catalyst	[108]
			[CuBr$_2$]	[109]
			1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-hexachloride (TAPC)	[110]

On the one hand, diols can react with diamines to promote the cyclization process, thus providing an intermolecular reaction. In this case, two nitrogen atoms are comprised in the newly formed cycle when [Fe(CO)$_4$(cyclopentadienone)] is used as a catalyst (Scheme 29).



Scheme 29. Intermolecular cyclization.

On the other hand, cyclization occurred by reaction of the newly formed amine with the second alcohol function of the starting diols, thus providing a heterocycle with only one nitrogen atom. A critical parameter in the cyclization is the stability of the cycle formed. Cycles comprising of five or six atoms are the most common, even though seven-atom rings were also reported (Scheme 30) [62].



Scheme 30. Intramolecular cyclization.

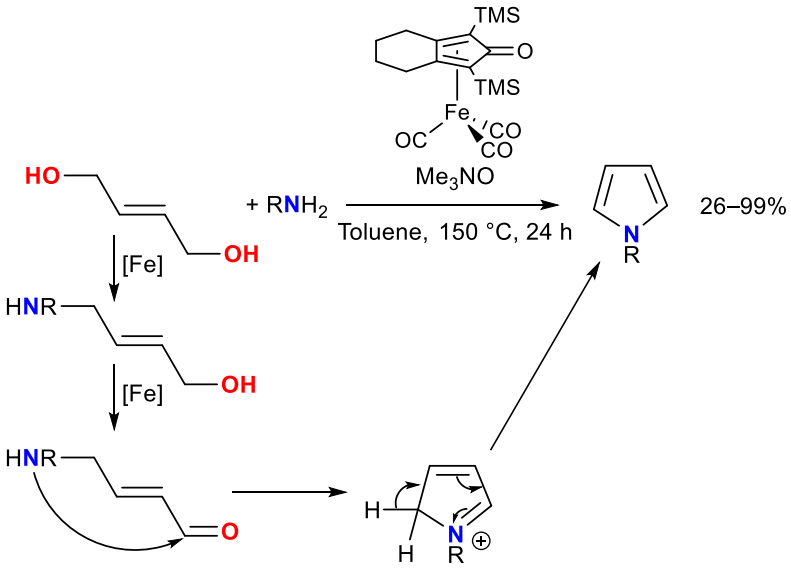
Nature of the amines: the nature of the amines used was of prime importance for the cyclization. As an example, the use of unsubstituted benzylamine led to the formation of an amino alcohol, whereas the chloro-substituted one led to a high yield of cycle products [89], highlighting the importance of electronic density on the nitrogen sources.

Nature of the alcohols: the cyclization reaction also seems to be sensitive to steric hindrance of the alcohol substrates used, as shown by Madsen et al. [55]. Although $[IrCl_2Cp^*]_2$, can efficiently convert ethylene glycol into the corresponding piperazine in the presence of a catalytic amount of base (isolated yields from 35 to 86%), no dimerization was observed when phenylethylene glycol and cyclohexane-1,2-diol were used as substrates.

One example of morpholine derivatives formation was reported from the intermolecular amination of ethanolamine. A 75% yield was obtained from the reaction of ethyleneglycol and NH_3 in the presence of a $NiO/CuO/TiO_2/Cr_2O_3$ catalyst under an H_2 atmosphere [111].

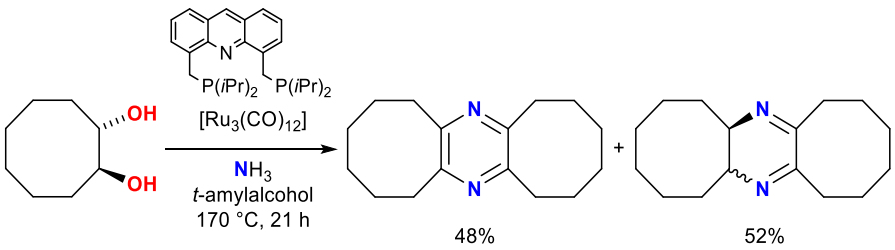
Aromatic Heterocycles Formation

Pyrrole: coupling amines with unsaturated 1,4-diols led to the formation of pyrrole using [Fe(CO)$_3$(cyclopentadienone)] as a catalyst (Scheme 31) [56,112]. Trimethylamine N-oxide (Me_3NO) was used as an additive to generate the catalytically active species. Alternatively, $[RuH_2(CO)(PPh_3)_3]$/Xantphos could be used to provide pyrroles without the use of additives [113]. The reaction is believed to proceed via preliminary isomerization of the 1,4-alkylediol into a 1,4-diketone followed by a Paal–Knorr cyclization. Similar reactivity was observed with the reaction of ketones, vicinal diols, and amines in the presence of $[Ru_3(CO)_{12}]$/Xantphos or $[Ru(p\text{-cymene})Cl_2]_2$/Xantphos as catalysts [114,115].



Scheme 31. Pyrrole formation.

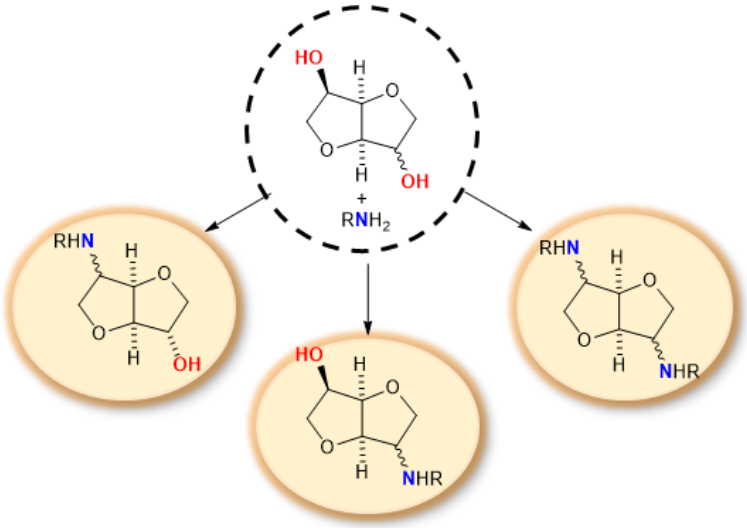
Pyrazine and phenazine: amination of 1,2-cyclooctanediol led to the formation of a mixture of dicycloocta[*b*,*e*]pyrazine and dicycloocta[*b*,*e*]-2,3-dihydropyrazine [16]. A similar behavior was observed with 1,2-cyclohexanediol, yielding octahydrophenazine upon reaction with $[Ru_3(CO)_{12}]$/acridine-based diphosphine (Scheme 32).



Scheme 32. 1,2-cyclohexanediol amination.

2.5.2. Isohexides

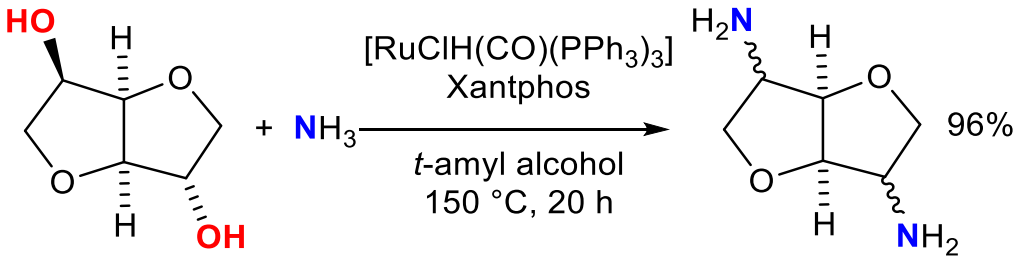
Isohexides are obtained from sorbitol dehydration. For this biogenic diol, three isomers can be found. To the best of our knowledge, only examples of isosorbide and isomannide aminations have been reported in the literature. Either one or the two alcohols can be aminated (Scheme 33). Amination often leads to isomerization of the aminated position due to the carbonyl/imine intermediates which comprise a sp^2 carbon atom, thus leading to a loss of the chiral information. Isosorbide isomerization to isoidide or isomannide instead of amination was often observed, highlighting the particular and challenging nature of this substrate. Note that isosorbide isomerization is also known to occur in the presence of a Ru catalyst and under H_2 pressure [116].



Scheme 33. Isohexide amination products.

Ammonia as a Nitrogen Source

The first report on isohexide amination was published by Beller in 2011 [48]. They reported the amination of isosorbide with ammonia to provide the corresponding primary diamine (Scheme 34, Table 6 Entry 1). No details were given on the stereoselectivity of the reaction.

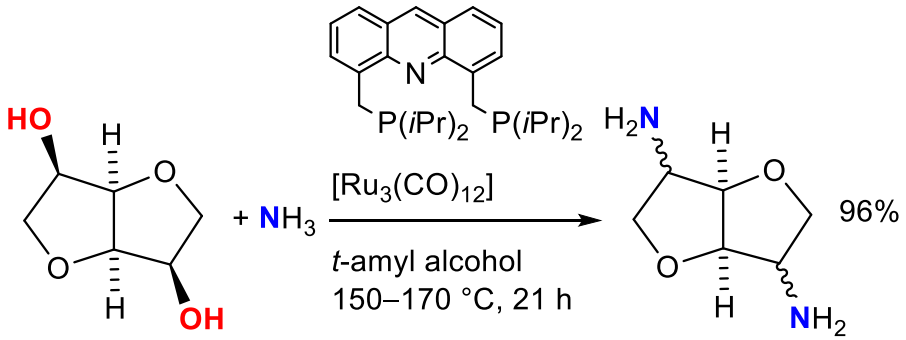


Scheme 34. Isosorbide amination.

Table 6. Catalytic isohexides diamination using ammonia as a nitrogen source.

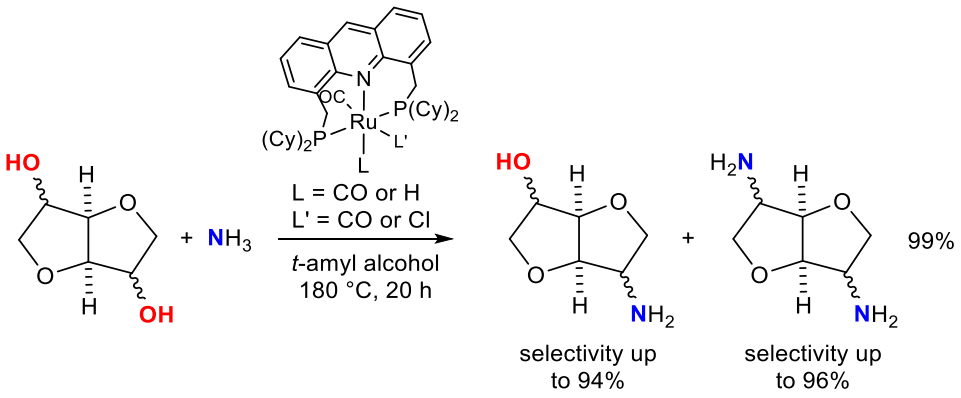
Entry	Catalyst	T (°C)	t (h)	Solvent	Additive	Yield (%)	Refs
1	$[RuHCl(CO)(PPh_3)_3]$/ Xantphos	150	20	*t*-amyl alcohol	—	96	[48]
2	[RuHCl(CO)(POP)]	170	48	*t*-amyl alcohol	—	90	[117]
3	$[Ru_3(CO)_{12}]$/PNP	170–200	21	*t*-amyl alcohol	—	96	[16,118]
4	[RuHCl(CO)(PNP)]	170	48	*t*-amyl alcohol	—	90	[119]

Excellent yields were obtained by Vogt with isomannide by using a mixture of $[Ru_3(CO)_{12}]$ and the acridine-based diphosphine developed by Milstein as a catalyst at 170 °C (Scheme 35, Table 6 Entry 3) [16]. In this case, a mixture of diamino-isosorbide/diamino-isomannide/ diaminoisoidide in a 45, 15, and 35% yield was obtained, respectively (total conversion = 96%). This isomer distribution corresponds to the thermodynamic equilbrium expected at this temperature. The authors highlighted the importance of using an excess of ammonia for the reaction to proceed to an acceptable yield with correct kinetics.



Scheme 35. Isomannide amination.

In 2014, the amination of isosorbide and isomannide was patented by Schelwies et al. using a homogeneous Ru-based catalyst (Scheme 36, Table 6 Entry 3 and Table 7 Entry 1) [118]. Excellent conversions of 99% were obtained, and the selectivity of the reaction toward mono- or di-amination was tuned according to the nature of the catalysts and to the reaction conditions (concentration, stoichiometry, and pressure). Selectivity of up to 94% for mono-amination and up to 96% for di-amination was achieved.



Scheme 36. Isosorbide and isomannide mono- and di-amination.

Table 7. Catalytic isohexides mono-amination using ammonia as a nitrogen source.

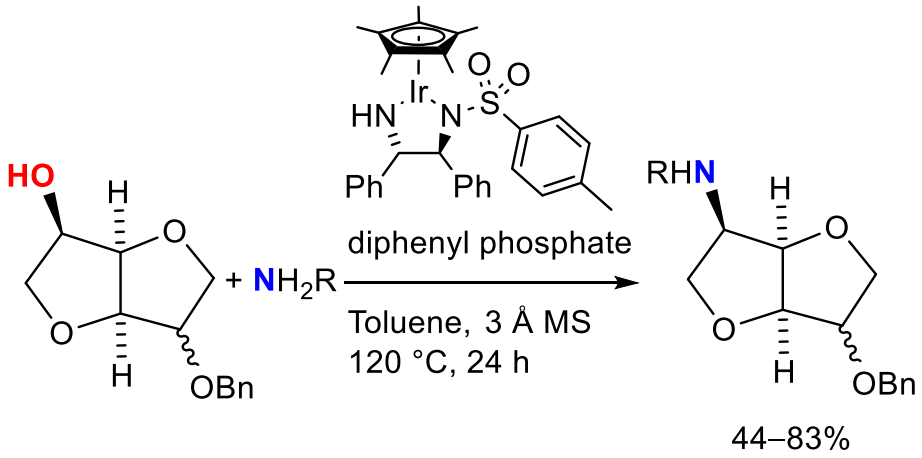
Entry	Catalyst	T (°C)	t (h)	Solvent	Additive	Yield (%)	Refs
1	[RuHCl(CO)(PNP)]	180	20	*t*-amyl alcohol	—	94	[118]
2	[RuHCl(CO)$(PPh_3)_3$]	150	20	Neat	—	50	[48]
3	Ru/C	170	24	H_2O	H_2 (10 bar)	50	[78,120,121]
4	RANEY® Ni	160	18	*t*-amyl alcohol	—	32	[22]
5	$Ni/Al_2O_3-SiO_2$	160	18	*t*-amyl alcohol	—	51	[22]

The catalytic activity of several heterogeneous catalysts was assessed in isohexide amination but only resulted in mono-aminations (Table 7 Entry 3–5). As an exemple, Rose et al. described the synthesis of aminoalcohol or isomerization reactions using Ru/C

as a catalyst [78,120,121]. The moderate conversion of the reaction highlights the complexity of the catalytic system. No diastereoselectivity was observed in this case since a mixture of the *endo* and *exo* amino alcohols were obtained. Both isosorbide and isomannide were used as substrates in the course of this study [120,121]. Both substrates gave rise to different reactivities, presumably due to the configuration of the hydroxyl groups in both isomers. It was found that the *endo*-configured alcohols were more reactive due to the lower activation barrier on the Ru/C catalyst and to their higher accessibility. Slight hydrogen pressure was beneficial for the reaction, even though increasing the pressure led to an increase in the isomerization. To the best of our knowledge, only one other report regarding the use of heterogeneous catalysts was published using RANEY® Ni or Ni/Al_2O_3-SiO_2 to obtain moderate yields of the mono aminated product (32 and 51% respectively) [22]. No details were given concerning the regioselectivity of the reaction.

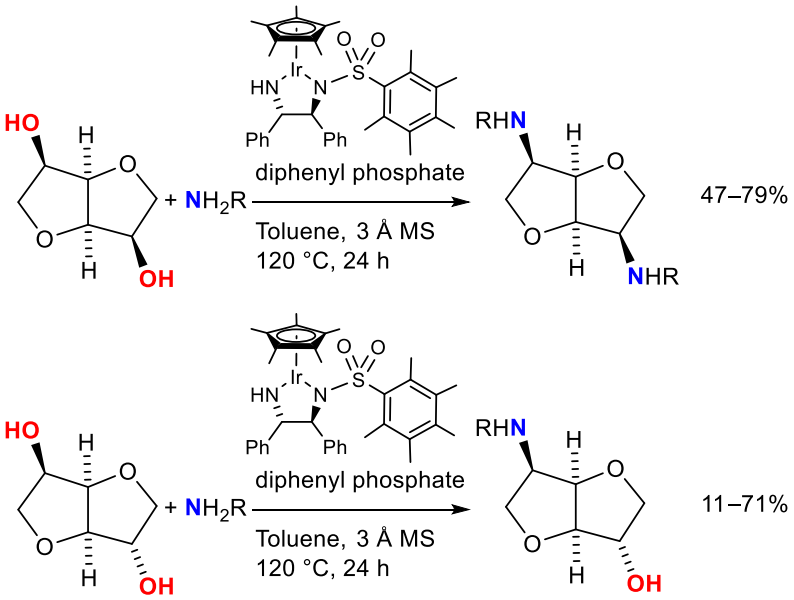
Primary Amines as Nitrogen Sources

With the aim of reducing the number of by-products formed and to gain a better understanding of the selectivity of the reaction, partially protected isohexides were used as substrates. In 2018, Popowycz and collaborators studied the stereoselective amination of an *exo*-monobenzylated isosorbide, which will reduce the number of by-products due to the reduced number of alcohol functions available for the BH reaction [122]. The activity of classical Ru-based homogeneous catalysts was limited even when a base was used as an additive. The catalytic activity was drastically increased using [$IrCl_2Cp^*$]$_2$. The best results were finally obtained by using the well-defined Ir catalyst depicted in Scheme 37, along with diphenyl phosphate as an additive. Less nucleophilic or hindered amines led to a lower yield of the aminated product. Interestingly, the reaction gave similar results, independently of the orientation of the benzyloxy group, i.e., with excellent diastereoselectivity, highlighting the spectator role of the C6 position. This was the first report concerning the controlled stereochemistry of the product formed. When *endo*-benzyloxy-isosorbide, which comprises the alcohol function at the *exo* configuration, was used as substrate, no reaction was observed, thus pointing to the disfavored reaction at *exo* positions.



Scheme 37. Monobenzylated isosorbide amination.

When unprotected isosorbide was used as a substrate under similar conditions, only one isomer was formed with yields ranging from 11 to 71% (Scheme 38) [123]. The reaction of isomannide with various amines led to the formation of the desired diamine in a stereoselective fashion with a 47–79% yield (Scheme 38).

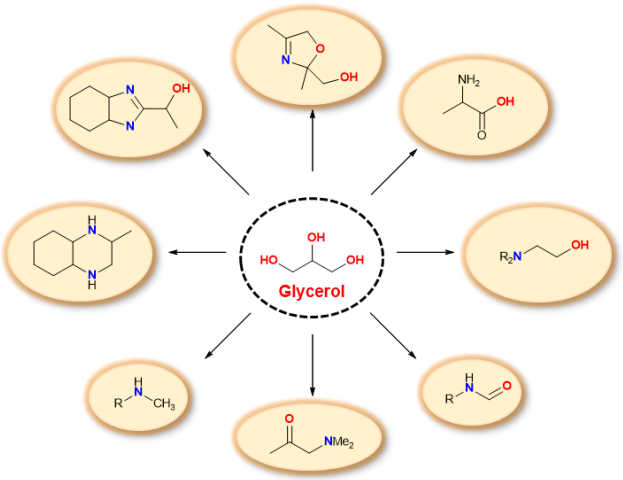


Scheme 38. Isosorbide and isomannide amination over a homogeneous Ir catalyst.

The use of isohexide as a substrate is a challenging task in hydrogen borrowing reactions. Indeed, as shown before, the presence of two alcohol functions on the same substrate can lead to unexpected reactions and to uncompleted amination. Even though side reactions were not observed, amination selectivity is challenging. The main hurdle here is to succeed in the amination of both alcohol functions. Whereas monoaminated and diaminated products can now be obtained depending on reaction conditions with both isomannide and isosorbide, further research is still required to achieve stereoselective reactions.

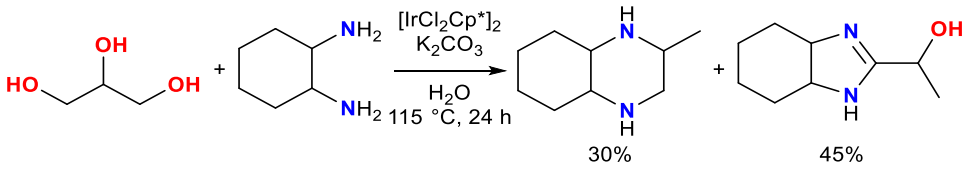
2.5.3. Triols

The most available biobased triol is glycerol since it is a by-product of biodiesel production. As shown in Scheme 39, a large structural variety of products were achieved via dehydration reactions, partial aminations, amine formylations, condensations, cyclizations, and C-C bond cleavages.



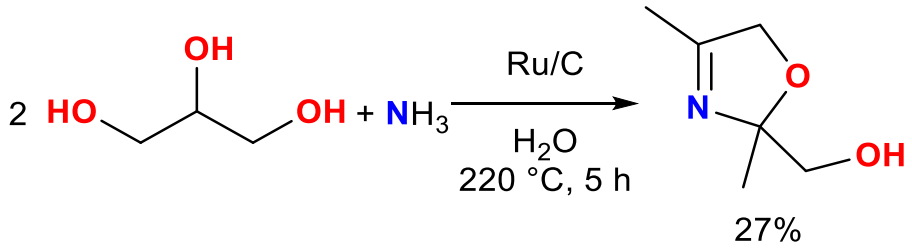
Scheme 39. Glycerol amination.

The first amination of glycerol was reported in 2014 by Crotti et al. [124]. They reacted glycerol with a diamine to perform an intermolecular cyclization reaction. Due to the high number of alcohol functions on the substrate, the reaction provided a mixture of *N*-heterocyclic compounds (Scheme 40).



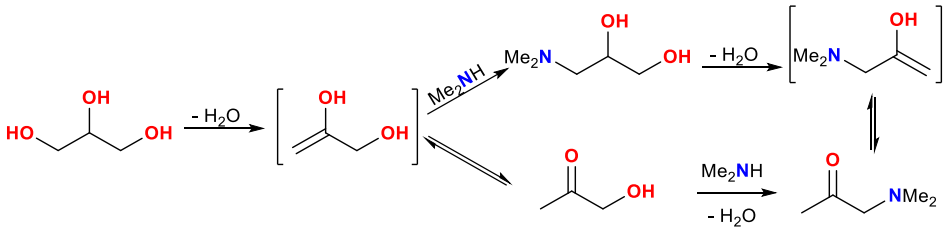
Scheme 40. Glycerol intermolecular cyclization.

The other cyclic compound that can be formed by glycerol amination is oxazoline (Scheme 41) [125]. Indeed, Ru/C was able to achieve 95% selectivity to oxazoline (27% conversion). A mechanism was proposed involving the preliminary formation of acetol by glycerol dehydration followed by imine formation and finally a reaction of the imine with a second acetol molecule to achieve the formation of oxazoline.



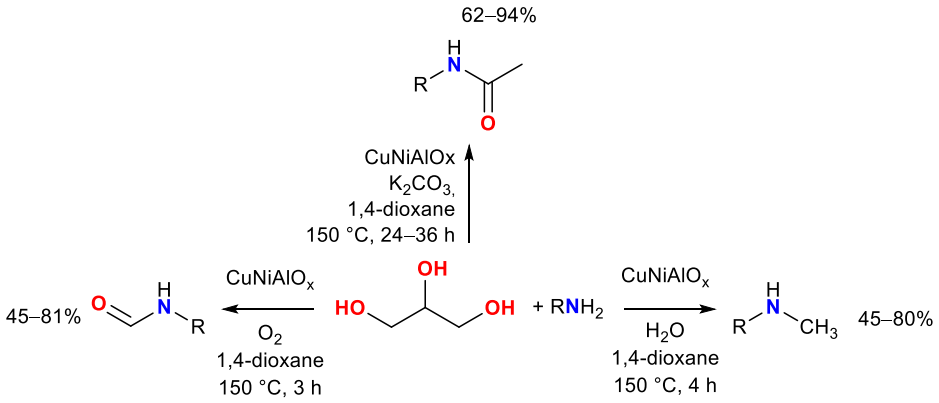
Scheme 41. Oxazoline formation from glycerol and ammonia.

Glycerol amination was then reported by Katryniok et al. in 2016 [126]. They used salts of phosphomolybdic acid as catalysts to yield (dimethylamino)acetone by the N-acetonylation reaction of dimethylamine with glycerol. The conversion can be increased by up to 33% by supporting the catalyst on silica, which leads to an increase in the catalyst acidity. A mechanism was proposed for the formation of (dimethylamino)acetone from glycerol as depicted in Scheme 42. A similar reactivity was reported the same year with improved yields (up to 94%) [127]. A homogeneous Ru catalyst could also be used to perform this reaction under acid conditions with yields of up to 81% [128].



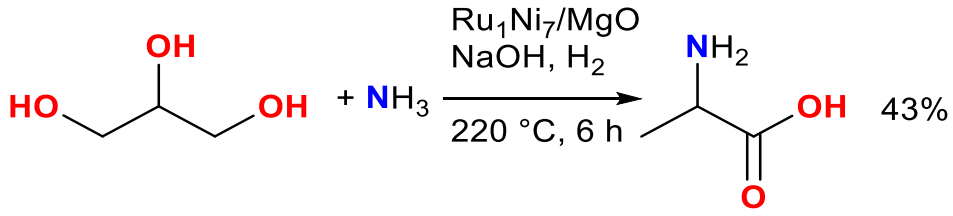
Scheme 42. (dimethylamino)acetone synthesis.

In addition to the formation of *N*-Acetonyl amine over the $CuNiAlO_x$ catalyst, glycerol could also be used as a methylation agent for various amines (Scheme 43) [127]. The reactivity was driven by the solvent, i.e., use of pure 1,4-dioxane led to the formation of *N*-Acetonyl amines, whereas a mixture of water and 1,4-dioxane provided methylated amines. Finally, performing the reaction under 5 bar of O_2 led to the formation of amides through a formylation reaction (Scheme 43) [127]. This highlights the versatility of glycerol as a substrate and the importance of the reaction conditions in this type of reaction. Indeed, small changes lead to the formation of different products.



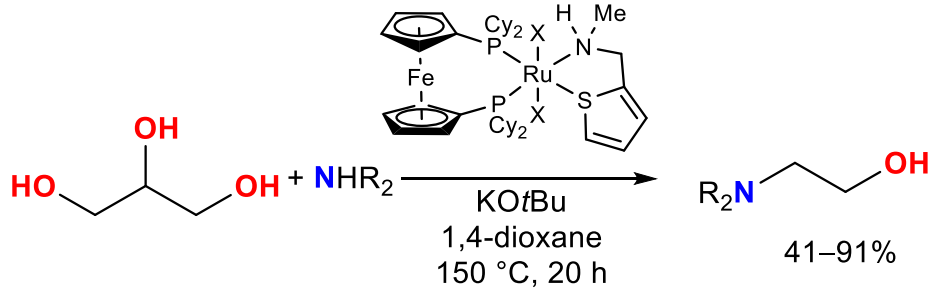
Scheme 43. Glycerol reactivity over a $CuNiAlO_x$ catalyst.

Alanine production was also possible in a 43% yield, starting from glycerol over a RuNi/MgO catalyst in aqueous ammonia (Scheme 44) [129]. The glycerol was believed to be first transformed into lactic acid, which then was aminated to alanine.



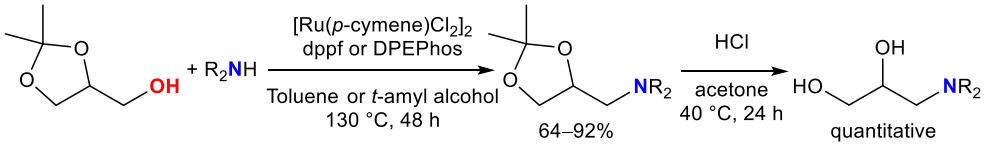
Scheme 44. Alanine formation from glycerol.

C-C bond cleavages were also observed upon glycerol amination. Glycerol was transformed into a mixture of methyl amine, ethyl amine, and propylamine by reaction with aqueous ammonia under H_2 pressure over Ru/C [130]. Other chemicals such as 2,6-dimethylpiperazine, piperazine, 2-methypiperazine, and various alcoholic products were observed as by-products. However, a selectivity of 51% in alkyl amines could be obtained after optimization of the reaction conditions. Finally, glycerol was used to perform N-hydroxyethylation of amines in basic media (Scheme 45) [128,131]. The proposed mechanism for this reaction involves C-C bond cleavage via dehydrogenation and retroaldol/decarbonylation sequences.



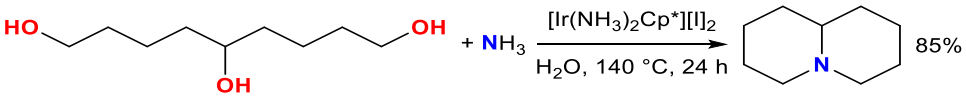
Scheme 45. Glycerol as an N-hydroxyethylation agent.

As shown here, the expected product in which all alcohol functions are aminated has not been observed yet. To perform the amination only at one position, it is necessary to protect glycerol by forming solketal (Scheme 46) [132]. The product could easily be deprotected afterward.



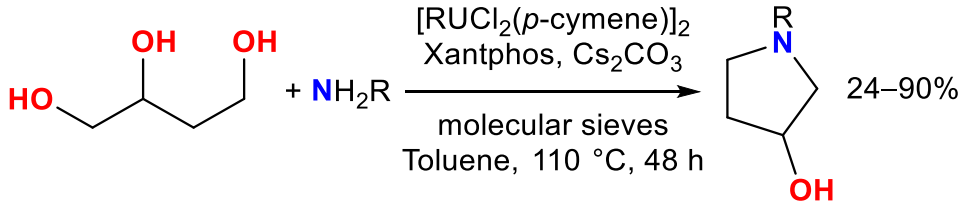
Scheme 46. Solketal amination.

Only two examples of amination of other triols than glycerol have been reported, both led to cyclization reactions. When 1,5,9-nonanetriol was used as substrate in the presence of $[Ir(NH_3)_3Cp^*][I]_2$, the formation of quinolizidine was observed (Scheme 47) [133]. The cyclization occurred with an 85% yield in a very selective fashion, highlighting the efficiency of the reaction.



Scheme 47. 1,5,9-nonantriol amination.

The amination of 1,2,4-butanetriol has also been studied in detail [134]. Again, cyclization was observed with $[RuCl_2(p\text{-cymene})]_2$/Xantphos in the presence of a base (Scheme 48). One of the hydroxyl groups remained intact after the reaction. The extension of this methodology to 1,3,4-hexanetriol and 1,2,5-pentanetriol led to the formation of 2-ethyl pyrrolidinol and an equimolar mixture of pyrrolidine/piperidine respectively.



Scheme 48. 1,2,4-butanetriol amination.

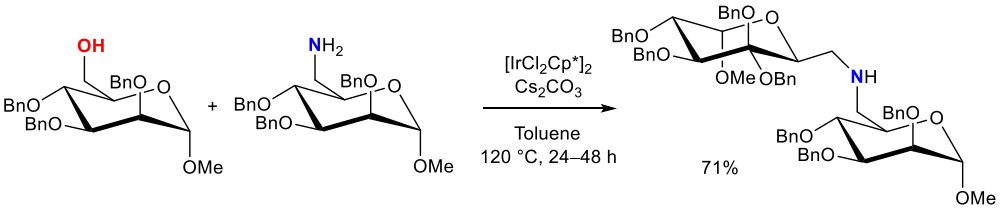
2.5.4. Carbohydrates

Carbohydrates can be obtained from cellulose/hemicellulose depolymerization under acid conditions. Carbohydrates often comprise a reactive aldehyde or ketone function that can be masked in their closed ring form. This function is prone to reductive amination and can be protected to facilitate the reactivity of the less reactive alcohol functions in amination reactions. Additionally, protection steps can be added to trigger the reactivity of a particular alcohol function. In this section, we will thus differentiate between protected and unprotected carbohydrates.

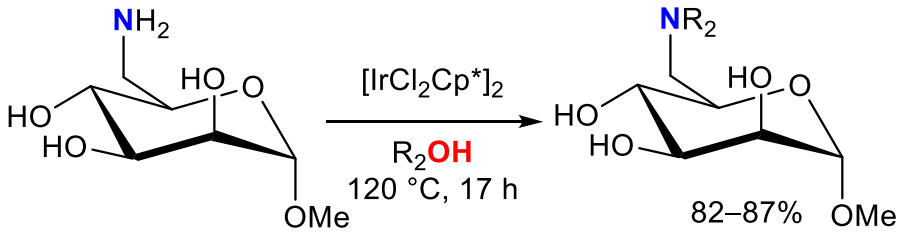
Protected Carbohydrates

The first report of carbohydrate amination was published in 2011 by Cumpstey and Martín-Matute [135]. As shown in Scheme 49, the amination of protected α-mannose was achieved using $[IrCl_2Cp^*]_2$ as a catalyst. Interestingly, the amination agent was a carbohydrate amine, thus providing pseudodisaccharide in the presence of a base. All the products were isolated as only one diastereoisomer. A good selectivity toward the primary C6 alcohol was achieved (71% of product).

The carbohydrate amine could also be used in combination with other alcohols with good yields. Note that the unprotected amino sugar could also react with various alcohols to provide alkylated amines with no oligomer formation (Scheme 50). This highlights the lower reactivity of the alcohols borne by secondary carbons on the carbohydrate. In this case, toluene could not be used as a solvent due to solubility issues. The reaction was thus performed using the alcohol as a solvent. These reactions could also be performed using glucose derivatives instead of mannose, producing a yield of 44–78%.



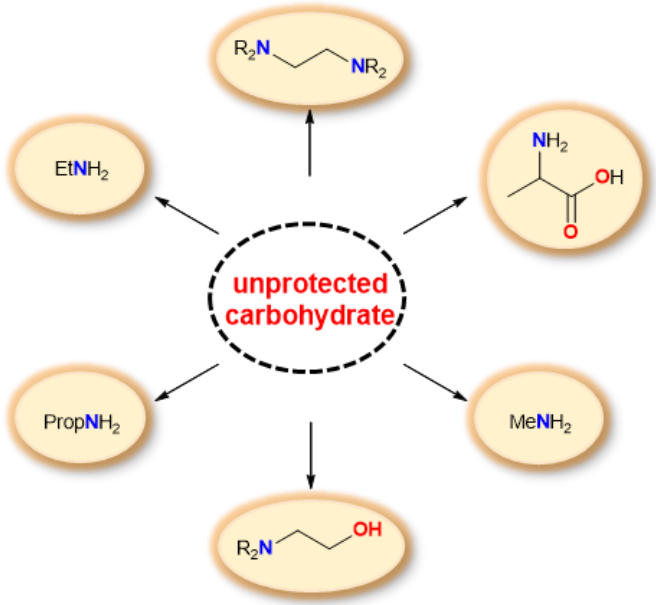
Scheme 49. Amination of protected carbohydrates.



Scheme 50. An amino sugar is used as a nitrogen source in a hydrogen borrowing strategy.

Unprotected Carbohydrates

The use of protected carbohydrates led to the selective formation of the desired products. However, several synthesis steps were added to perform the synthesis of the alcoholic substrates. As shown in Scheme 51, the use of unprotected carbohydrates only led to C-C bond cleavages in line with the results obtained with glycerol. However, even when C-C bond cleavages were observed, good selectivities and conversions in various amines and amino alcohols were obtained.

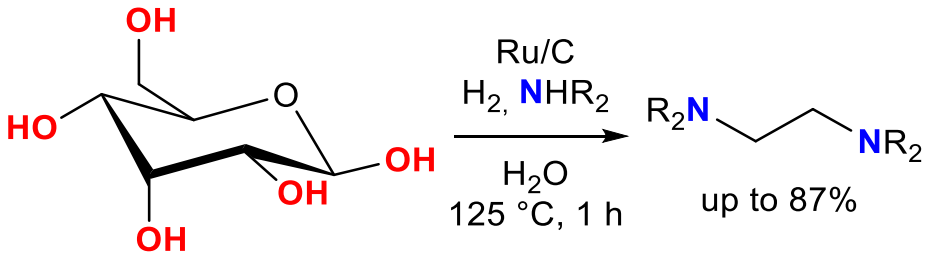


Scheme 51. Unprotected carbohydrate amination.

Note that N-heterocyclic chemical formation from unprotected carbohydrates amination is well described, these reactions are not considered borrowing hydrogen because the amination usually occurs on carbonyl functions, and thus will not be reported here [136–141].

The authors of [142,143] describe the use of a series of monosaccharides such as glucose, fructose, 2-deoxy-D-glucose, and xylose in combination with Ru/C as a catalyst to provide C2-diamines (Scheme 52, Table 8 Entry 1). In the course of these reactions, the presence of H_2 pressure was mandatory to avoid decomposition of the starting materials

and to obtain complete reactions (i.e., the formation of diaminated products instead of monoaminated). The proposed mechanism involved a hemiaminal formation followed by an iminium formation by dehydration. A C-C cleavage on the latter, followed by a hydrogenation reaction thus formed the amine. Supported Ni catalysts also allowed the reaction to perform nicely (up to a 92% yield, Table 8 Entry 2). A large series of monomeric substrates were used under these conditions, such as mannose, galactose, or arabinose. Interestingly, trimeric carbohydrates and disaccharides could also be used (cellobiose, maltose, and maltotriose), with a decrease in the yield indicating poor hydrolysis of the glycosidic linkages.

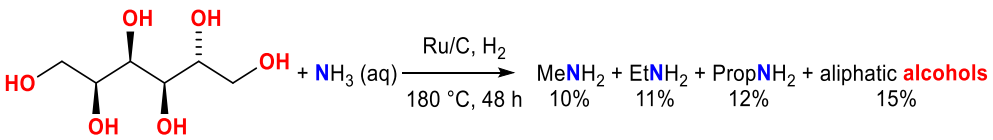


Scheme 52. C2-diamine formation from glucose amination over Ru/C.

Table 8. Catalytic amination of unprotected carbohydrates.

Entry	Catalyst	T (°C)	t (h)	Solvent	Additive	Products	Refs
1	Ru/C	125	1	H_2O	H_2 (70 bar)	Ethan-diamines	[142,143]
2	Supported Ni	125	1	H_2O	H_2 (70 bar)	Ethan-diamines	[142,143]
3	[Ru(2-methylallyl)$_2$(cod)$_2$]/Xantphos	150	16	Dioxane	Acetic acid	Ethanol-amines	[131]
4	[RuCl$_2$(*p*-cymene)]/DCyPF/*N*-MeTMA	150	20	Dioxane	*t*-BuOK	Ethanol-amines	[128]
5	CdS nanosheet	50	8	H_2O	NaOH, hν	Alanine	[47]

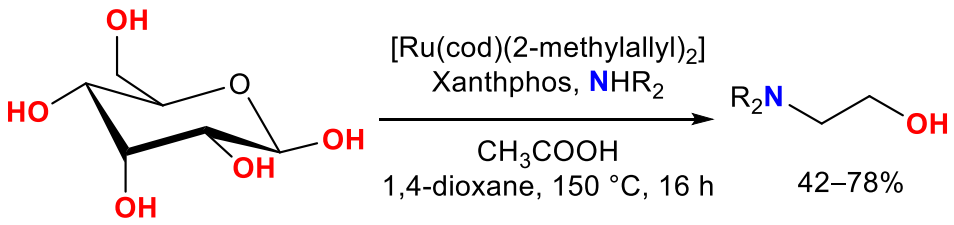
Chaudhari described in 2018 the amination of sorbitol (a compound obtained via the hydrogenation of glucose) using a similar Ru/C catalyst under H_2 pressure and observed the formation of a complex mixture of aliphatic amines (10% methylamine, 11% ethylamine, 12% propylamine, and 15% other alcoholic products) with excellent conversion. These results highlight the C-C cleavages occurring during the course of the reaction, thus forming smaller carbon chains similar to that which was observed with glycerol (Scheme 53) [130].



Scheme 53. Sorbitol amination.

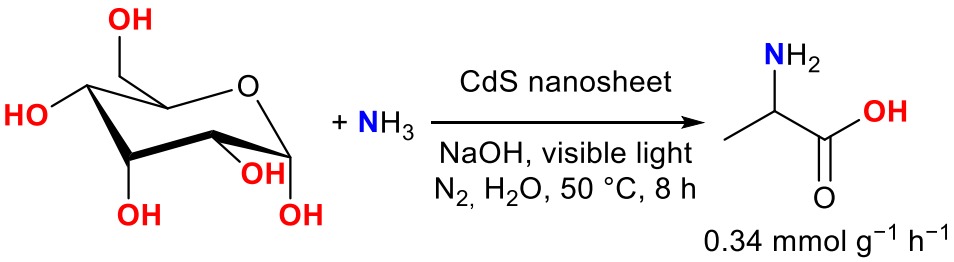
Carbohydrates were used to perform hydroxyethylation of amines [128,131]. The skeleton of the carbohydrate was cleaved similar to work by Sels et al. [142,143]. Two homogeneous systems enabling the formation of β-amino alcohols from amines and carbohydrates were described in the literature. The use of [Ru(2-methylallyl)$_2$(cod)$_2$] and Xantphos allow the transformation of various C5 and C6 sugars, as well as oligomeric carbohydrates, in the presence of acid derivatives, even though lower yields were obtained with oligosaccharides (Scheme 54). Only traces of product were obtained when cellulose was used as a substrate. Interestingly, pre-treatment of α-cellulose with inorganic acids for further hydroxyethylation reaction led to the formation of the desired β-amino alcohols.

The second system enabling the reaction was described in 2020, and allowed the reaction to be performed in basic media instead of under acidic conditions as reported in 2019 (Table 8 Entry 4) [128].



Scheme 54. Hydroxyethylation of amines from glucose.

Finally, a photocatalytic conversion of glucose into alanine was performed over an ultrathin CdS nanosheet (Scheme 55) [47]. Even though low amounts of alanine were isolated, conversion to the key intermediate, namely lactic acid, was observed.



Scheme 55. Alanine formation.

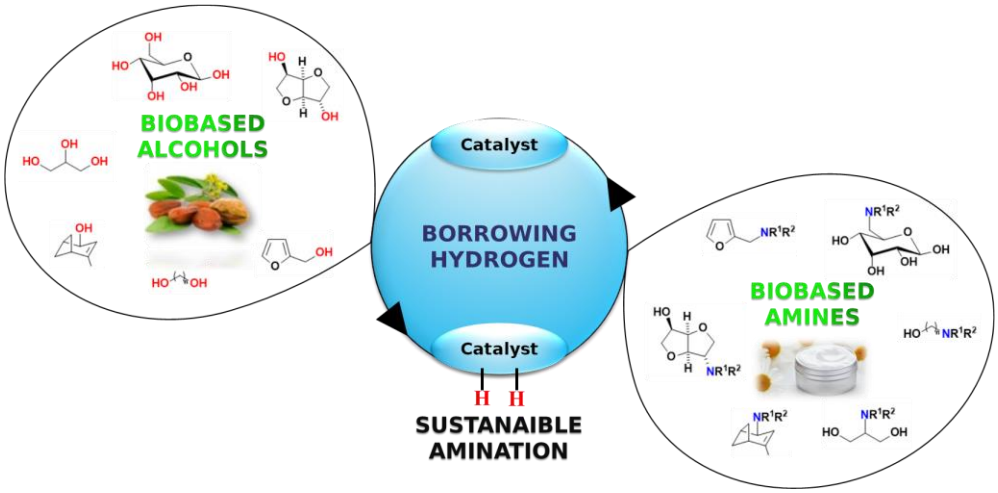
As shown in this section, the alcohol protection of carbohydrates to deactivate several positions for amination reactions or the use of aminated carbohydrates as amination agents were the only routes to access more complex structures. Indeed, without these strategies, C-C bond cleavages were always observed even though selective reactions could occur under specific conditions (Table 8). Carbohydrate amination has not yet been achieved under acceptable conditions since tremendous protection steps are required to avoid C-C bond cleavages of the carbohydrate structure. Research in this field is still limited, and more effort could be devoted to uncovering new reaction conditions that could alleviate the protection procedure and achieve carbohydrate amination instead of decomposition.

3. Conclusions: Challenges and Future Directions

In this review, we provide an overview of the most significant advances in the use of bio-based alcohols with the hydrogen borrowing approach (Scheme 56). We discussed the versatility of the available catalysts and demonstrated the most recent advancements in the use of biobased substrates. Despite its incontestable success, highlighted by the increased number of publications in the last decade, several hurdles remain.

Some of the bio-based substrates, such as the fatty alcohols, are successfully converted to the corresponding amines. It appears that the presence of a long aliphatic chain has no impact on the efficiency of the reaction. When terpenoids are used as substrates, selectivity issues are observed due to the presence of C=C double bonds, which leads to the formation of enals, which can then isomerize. Additionally, when bulky terpenoids are used, the reaction does not go to completion and the formation of the intermediate ketone as the main product is observed instead of the expected amines. In the case of furan derivatives, despite efficient conditions reported for the formation of the desired amines, several by-products are obtained. Reduction of the furan cycle is indeed observed, such as amidation reactions. The selectivity toward furan cycle reduction is driven by the presence of external H_2 pressure, whereas the selectivity toward an amidation reaction (instead of amination) is driven by the presence of a strong base. This highlights the importance of the reaction

conditions. Interestingly, the use of 5-HMF only leads to di-amination reactions since it is not possible to selectively aminate the alcohol functions without affecting the carbonyl moiety. However, 2,5-BAMF is selectively obtained from 5-HMF or BHMF even though H_2 pressure is required. For polyfunctional alcohols, ester functions are compatible with hydrogen borrowing methodology even though, under certain conditions, α-amino acid amides are obtained by di-amination of the corresponding α-hydroxy esters. Additionally, whereas amination of α-hydroxy acids is efficient, β-hydroxy acids only leads to poor yields.



Scheme 56. Overview of the use of bio-based alcohol with the hydrogen borrowing approach.

A large number of publications are dealing with polyols since they are one of the predominant classes of alcoholic compounds found in nature or that can be obtained from biomass. A broad structural diversity is achieved when polyols are used as substrates in amination reactions. Indeed, aside from the expected diamines, incomplete reactions are observed with the formation of the corresponding amino alcohols, such as cyclization reactions or even the formation of aromatic heterocycles or dehydrated/aminated products. The selectivity of the reaction is driven by the substrates used (nitrogen sources and/or diols), the catalytic systems, or the reaction conditions. The selectivity of these reactions can be considered as the main hurdle for the expansion of the use of this methodology with bio-based substrates. The most striking example of this lack of selectivity is the use of carbohydrate, which only leads to C-C bond cleavages of the carbohydrate backbone unless the alcohol functions are all protected.

Additionally, to pursue efforts for milder reaction conditions and lower catalyst loading, efforts targeting the special needs for bio-based substrates still need to be made. Various catalysts have been used for this purpose, either homogeneous or heterogeneous. However, most of them comprise noble metallic centers, which are expensive and environmentally harmful. We are thus anticipating the breakthrough of an earth-abundant based catalyst, which is still limited when it comes to natural substrates. Additionally, within this review, we have highlighted the strong dependence between the selectivity of the reaction and either the catalyst structure/nature or the reaction conditions. We have indeed identified selectivity as one of the main issues to circumvent for the amination of bio-based alcohols. We strongly believe that the tuning of the catalyst structure and the adaptation of the reaction conditions to the pre-requisite of the use of natural substrates is the way to overcome this hurdle. The design of a more active catalyst will also allow milder reaction conditions such as the decrease of the reaction temperature or the use of additives, which are critical parameters for the reaction selectivity. Even though hydrogen borrowing is a powerful strategy to provide C-N bond formation, only a few examples of stereo controlled reactions have been described [144], and the reports concerning the asymmetric amination of bio-based substrates are still scarce. This is critical in order to apply this methodology to higher-value product formation, such as pharmaceutical drug

precursors. Additionally, several catalytic systems still require the use of an external H_2 source, which is not mandatory when a borrowing hydrogen mechanism is involved. More active catalysts which are less prone to oxidation are thus required.

In conclusion, with this overview, bio-based alcohols can be aminated in only one step to provide highly desirable products. A high atom economy is achieved within this reaction since water is the only by-product formed. However, we find that selectivity and functional group tolerance are the main issues to circumvent. We hope that further research on sustainable catalysis will promote bio-based alcohol amination as a new route for biomass valorization.

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