Green Chemistry

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ROYAL SOCIETY OF CHEMISTRY
View Article Online
DOI: 10.1039/C9GC01195A

Journal Name

ARTICLE

Direct hydroxyethylation of amines by carbohydrates *via* ruthenium catalysis

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An efficient and halogen-free catalytic methodology for the synthesis of β-amino alcohols from aromatic amines and biomass-derived carbohydrates is demonstrated for the first time. The activation of C5/C6 sugars by ruthenium catalyst selectively generates the C2 alkylating reagent glycolaldehyde. The transformation involves metal catalyzed hydrogen borrowing for the reduction of imine intermediate. A series of arylamines bearing various substituents were successfully transformed to the desired products in good to excellent yields.

Introduction

The utilization of biomass and renewable resources has attracted significant amounts of interests owing to the depletion of fossil fuels and environmental protection concerns. In this regard, biomass-derived carbohydrates such as glucose and xylose produced from chemical or enzymatic hydrolysis of biomass (*i.e.* hemicellulose and cellulose) are emerging as promising building blocks for value-added chemicals.[1] The development of cost effective methods to access valuable chemicals from carbohydrates is not only highly desirable but also challenging. More recently, some promising advances have been made in this area.[2] Importantly, biomass-derived sugars conversion into valuable nitrogenous compounds represents a major advance in the sustainable synthesis of biologically active amines.[3-7] β-Amino alcohols for instance are commonly encountered moieties in many bioactive natural products and synthetic pharmaceutical intermediates.[8-11] Representative examples include reactive oxygen species (ROS)-activated agent against acute myeloid leukemia (AML), Efonidipine and Thiazolidinedione derivatives used in the treatment of hypertension and diabetes (Figure 1).

Conventional methods of the synthesis of β-amino alcohols use epoxides or haloalkanols that are toxic, carcinogenic and/or flammable.[12,13] Improved methods use radical initiator

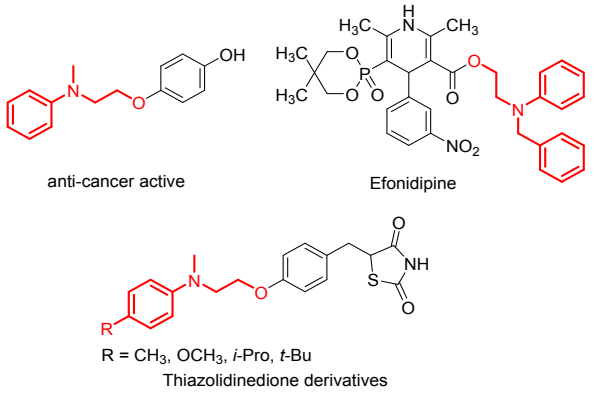

Figure 1 Examples of biologically active compounds featuring β-amino alcohol building blocks.

peroxide and ethylene carbonate based epoxide (Scheme 1A).[14] In the other hand, the process of sugar and sugar alcohol hydrogenolysis has been explored as a potential means to make various polyols; glycerol, ethylene glycol and propylene glycol from renewable biomass resources.[15] This usually requires high temperature and high hydrogen pressure for C-C bonds cleavage. Catalytic methods were devised for preparing β-amino alcohols utilizing hydrogen borrowing (HB) strategy. This approach overcomes alcohol's low reactivity by involving dehydrogenative generation of aldehyde intermediate. The aldehyde and amine forms imine intermediate, which is hydrogenated to β-amino alcohols (Scheme 1B).[16] The transformation of polyol/carbohydrates usually involves the formation of aldehyde intermediates from C-C bond cleavage *via* retro-aldol reaction.[17] For example, hydrogenolysis of biomass-derived sugars to ethylene glycol requires cleavage of specific C-C and C-O bonds, and generally involves the formation of glycoaldehyde intermediate.[18] In addition, sugars have been used as C1 source to generate acyl anion intermediate as one-carbon nucleophile in Stetter reaction.[19] Due to our continuous interest in catalytic dehydrogenations,[20]

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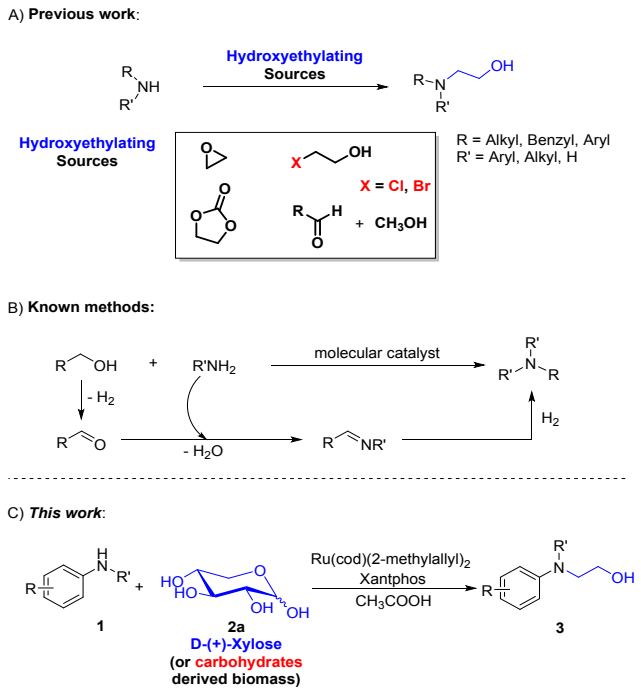


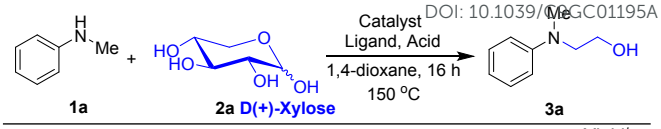
Scheme 1 A) Selected strategies for conventional syntheses of β-amino alcohols; B) Hydrogen borrowing (HB) process methodology; C) Ruthenium-catalyzed direct hydroxyethylation of amines with carbohydrates.

we examined biomass-derived sugars for the hydroxyethylation of amines using ruthenium catalysts based on phosphine ligands. Herein, we report the first example of ruthenium-catalyzed hydroxyethylation of aromatic amines using carbohydrates for the preparation of β-amino alcohols (Scheme 1C).

Results and discussion

Initially, we started our investigation of Ru-catalyzed hydroxyethylation using N-methylaniline (**1a**) as model substrate with different carbohydrates to screen C5, C6 sugars and higher oligomeric carbohydrates. To our delight, we found that most C5 and C6 sugars tested are suitable N-hydroxyethylating reagents providing the desired β-amino alcohol product in 51% to 87% yields in the presence of acid additives. Polysaccharides were less effective for this transformation under similar reaction conditions, understandably due to solubility constraints. We then used xylose saccharide to further optimize the reaction conditions. We examined several ruthenium complexes and phosphine ligands using 1,4-dioxane as solvent (Table 1). When the reaction was performed in the presence of $RuCl_2(PPh_3)_3$ (2.0 mol%), Xantphos (2.0 mol%) and acetic acid (30 mol%), product **3a** was formed in 37% yield (Table 1, entry 1). Other ruthenium precursors, such as $Ru(acac)_3$, $Ru_3(CO)_{12}$ and Ru(cod)(2-methylallyl)$_2$ were also screened and all showed reasonable catalytic activity (56-87% yields; Table 1, entries 2-4). Interestingly, Ru(cod)(2-methylallyl)$_2$ with

Table 1 Optimization of the reaction conditions[a]



1a 2a D(+)-Xylose 3a

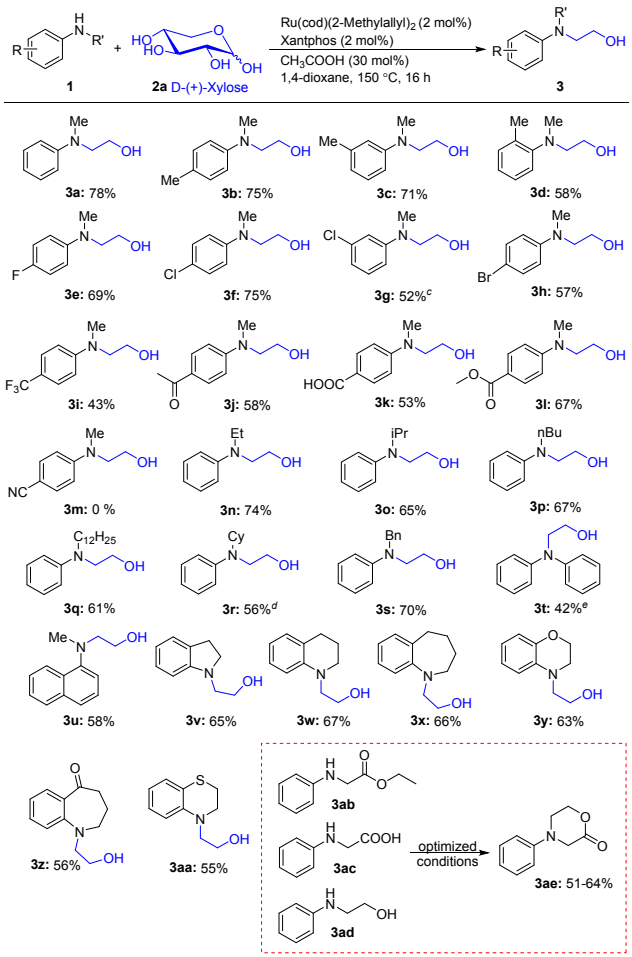
Entry	Catalyst	Ligand	Acid	Yield[b] **3a** (%)
1	$RuCl_2(PPh_3)_3$	Xantphos	CH_3COOH	37
2	$Ru(acac)_3$	Xantphos	CH_3COOH	56
3	$Ru_3(CO)_{12}$	Xantphos	CH_3COOH	60
4	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	**87**
5	Ru(cod)(2-methylallyl)$_2$	-	CH_3COOH	24
6	-	Xantphos	CH_3COOH	n.d.
7	Ru(cod)(2-methylallyl)$_2$	DPPM	CH_3COOH	16
8	Ru(cod)(2-methylallyl)$_2$	DPPE	CH_3COOH	23
9	Ru(cod)(2-methylallyl)$_2$	Xantphos	-	29
10	Ru(cod)(2-methylallyl)$_2$	Xantphos	H_3PO_4	n.d.
11	Ru(cod)(2-methylallyl)$_2$	Xantphos	$(CH_3)_3CCOOH$	15
12[c]	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	74
13[d]	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	46
14[e]	Ru(cod)(2-methylallyl)$_2$	Xantphos	CH_3COOH	44

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst (2 mol%), ligand (2 mol%), 1,4-dioxane (2 mL), at 150 °C under N_2 atmosphere for 16 h. [b]Yields were determined by GC using n-docecane as an internal standard. [c] 1 mol% Ru(cod)(2-Methylallyl)$_2$, 1 mol% Xantphos. [d] Ethylene glycol (1.5 mmol) instead of **2a** (1.5 mmol). [e] Glycerol (1.5 mmol) instead of **2a** (1.5 mmol). Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; Ru(cod)(2-methylallyl)$_2$ = Bis(2-methylallyl)(1,5-cyclooctadiene)ruthenium(II).

Xantphos generated the desired product **3a** in 87% yield. We then tested the effect of phosphine ligand using Ru(cod)(2-methylallyl)$_2$. When the reaction was performed in the absence of Xantphos, the yield of **3a** declined to 24% (Table 1, entry 5). Substituting Xantphos with other bi-dentate phosphine ligands (DPPM or DPPE) showed no improvement on the catalytic activity (Table1, entries 7-8). We further investigated the reaction in the absence of acetic acid and observed lowered yield of 29%, too (Table1, entry 9). Hence, we investigated the effect of inorganic acids on the reaction affording lower yields or no reaction compared to acetic acid (Table1, entries 10-11). The catalyst loading was also considered and found product yield is slightly lowered by decreasing the amount of catalyst (Table1, entry 12). Alternatively, we tested other N-hydroxyethylating agents under similar reaction conditions by substituting xylose with either ethylene glycol or glycerin affording β-amino alcohols **3a** in lower yields, 46% and 44%, respectively.

Under the optimized reaction conditions, we explored the substrate scope of various N-alkyl-anilines for this ruthenium-catalyzed N-hydroxyethylation reaction (Table 2). In general, we observed that substrates bearing electron-donating substituents on the phenyl ring proved more reactive with yields ranging from 58%-75% (**3b-d**). Fluoro-, chloro- and bromo-substituted aromatic amines

Table 2 Scope of amine substrates[a, b]



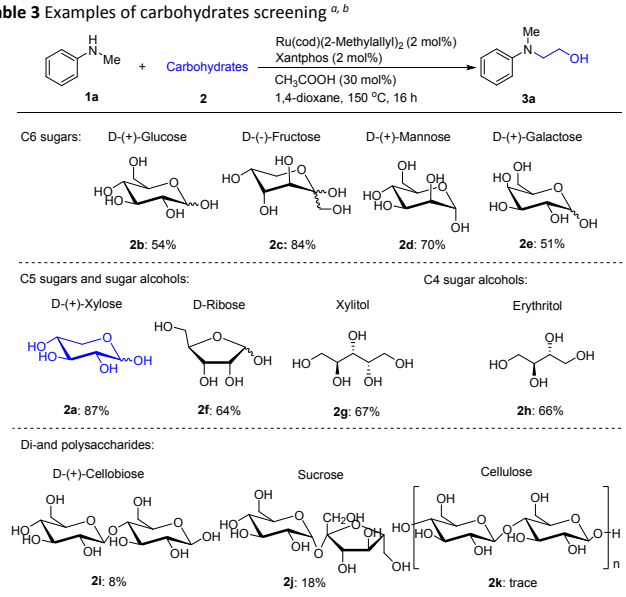
[a] Reaction conditions: **1** (0.5 mmol), **2a** D-(+)-xylose (1.5 mmol), Ru(cod)(2-methylallyl)$_2$ (2 mol%), Xantphos (2 mol%), CH_3COOH (0.15 mmol), 1,4-dioxane (2 mL), at 150 °C in the nitrogen atmosphere for 16 h; [b] isolated yields. [c] 170 °C. [d] 48 h. [e] 180 °C.

also underwent smooth reaction to furnish the corresponding products in yields 52%-75% (**3e-h**). However, aromatic amines bearing other electron-withdrawing substituents such as trifluoromethyl and acetyl groups afforded the corresponding products **3i** and **3g** in slightly lower yields (43-58%); while the presence of carboxylic acid and ester substituents afforded product **3k** and **3l** in 53% and 67%, respectively. In addition, aniline substrates bearing various alkyl groups (Et, *i*Pr, *n*Bu, $C_{12}H_{25}$, Cy and benzyl) at the amine were smoothly transformed to the corresponding hydroxyethylated products in moderate to good yields (**3n-3s**; 56-74%). N-Substituted anilines with bulkier groups required prolonged reaction times (48 h) or elevated temperatures to achieve moderate yields (**3r** and **3t**; 56% and 42%). N-Benzyl substitution provided the benzyl product **3s** in 70% isolated yield. Notably, **3s** is a key building block for the synthesis of the calcium channel blocker Efonidipine which is conventionally prepared using excess amounts of 2-chloroethanol.[10] Moreover, transformation of aromatic amino compounds with pento- and benzo-fused cyclic motifs were well tolerated giving **3u-3x** hydroxyethylated products in 58% to 67% yields. Heterocyclic compounds, benzomorpholine, benzothiazine and 5*H*-1-benzazepin-5-one can also be successfully transformed to the desired corresponding products **3y**, **3aa** and **3z** in good to moderate yields (63%, 55% and 56%, respectively). The *dehydrogenative lactonization* of N-substituted diethanolamine with this catalytic system generates N-substituted 2-morpholinone **3ae** from 2-(phenylamino)ethanol **3ad**. Interestingly, N-substituted 2-morpholinone can also be obtained with D-(+)-xylose from aniline derivatives **3ab** or **3ac** in good yields under the optimized reaction conditions.

To further demonstrate the generality of this strategy with carbohydrates as hydroxyethylating reagent, we studied a set of commercially available natural saccharides (Table 3). The examined C6-sugars (**2b-e**) were effective giving β-amino alcohols product **3a** in 51-84% yields. Testing several C5-sugars and sugar alcohols (**2f**, **2g-h**) also showed good reactivity giving β-amino alcohol product **3a** in excellent yields (64-87%). C5-sugar, D-(+)-xylose (**2a**) gave near complete conversion with *N*-methylaniline substrate. The reaction was efficient and produced **3a** with high purity after a simple workup. Remarkably, both disaccharides (**2i**, **2j**) and polysaccharide cellulose (**2k**) could be used equally as hydroxyethylating reagent, albeit with diminished yields (8-18%). This is due to slow hydrolysis and further studies needed to develop more practical protocols especially for cellulose and other polysaccharides.

Interestingly, pre-treatment of α-cellulose (particle size of ca. 25 μm) with inorganic acids H_2SO_4/H_3PO_4 at ambient temperature and further hydrolysis with water

Table 3 Examples of carbohydrates screening [a, b]



[a] Reaction conditions: **1a** (0.5 mmol), **2** (1.5 mmol), Ru(cod)(2-methylallyl)$_2$ (2 mol%), Xantphos (2 mol%), CH_3COOH (0.15 mmol), 1,4-dioxane (2 mL), N_2 atmosphere. [b] Yields were determined by GC using n-docecane as internal standard.

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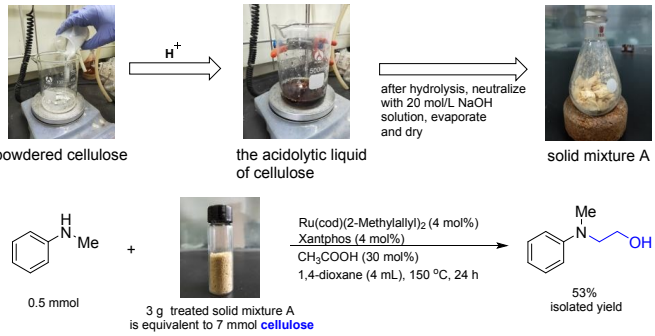
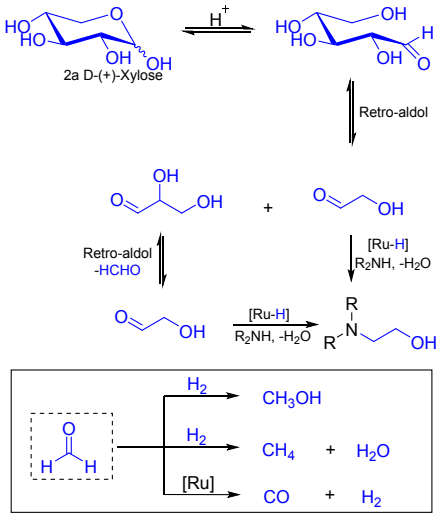


Scheme 2 Cellulose pre-treatment experiment.

followed by neutralization afforded a degradation mixture A suitable for this reaction.[21] Although the degradation of cellulose in the pre-treatment gives a complex mixture of oligosaccharides, the reaction performance was not undermined and the desired product was obtained in an appreciable yield (See Supporting information). Specifically, N-methyl aniline reacted with solid mixture A smoothly giving hydroxyethylated product in 53% yield (Scheme 2).

Regarding the mechanism, it has been proposed that polyols are dehydrogenated to the corresponding carbonyl intermediates over metal catalysts, and their subsequent C-C bond cleavage is likely *via* the retro-aldol reaction.[17] Based on the current understanding of the mechanism, we further carried additional experiments and we propose the reaction pathway according to the conditions employed in this work (Scheme 3). Initially, xylose is in equilibrium between its cyclic acetal and acyclic aldehyde forms promoted under acidic conditions. The initial step involves a C-C bond cleavage through retro-aldol reaction to generate the aldehyde intermediate. Upon condensation with the amine substrate, the formed imine intermediate is hydrogenated to β-amino alcohols in the presence of Ru-based catalyst. We achieved evidence of the presence of



Scheme 3 Proposed reaction pathways

metal hydrides from in-situ ^{1}H NMR experiments as described in Figure 2. Further evidence of the reaction pathway through control experiments for this Ru-catalyzed N-hydroxyethylation of N-methyl aniline with D-(+)-xylose were obtained in support of the mechanism.

Components in the gas phase of the reaction mixture were analyzed by Gas Chromatography. The results showed that CO, CH_4 and H_2 were generated during the reaction, presumably as decomposition products of the cleaved formaldehyde in the presence of excess amounts of sugar substrates (Figure 2b). In order to get further insights into the mechanism of this ruthenium catalyzed hydroxyethylation of arylamines, we conducted in-situ NMR to detect hydride species generally involved the hydrogen borrowing process. The phosphorus ^{31}P NMR showed the presence of two phosphorus environments for the Ru-Xantphos complexes at 33.7 ppm and 35.2 ppm. Moreover, in-situ ^{1}H NMR showed a high field multiplet chemical shift at around -15.6 ppm consistent with hydride hydrogens and in line with ruthenium-Xantphos catalyst dehydrogenative mode of action (Figure 2c).

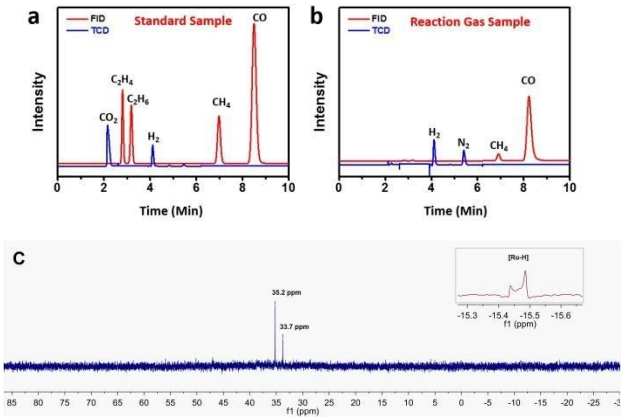
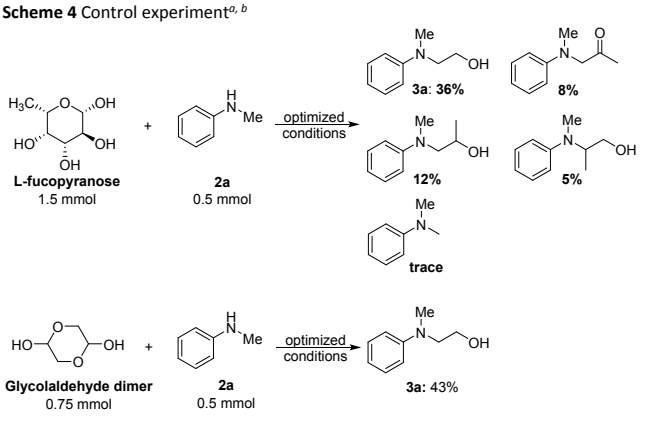


Figure 2 GC analysis of gas samples (a) GC spectrum of reference gas sample, (b) GC spectrum of gas sample taken from gas phase of the reaction and (c) ^{31}P NMR of Ru-Xantphos catalyst with D-(+)-xylose (inset ^{1}H NMR of Ru-H species).

Control experiments with glycerol or with cyclic form of glycoaldehyde afforded β-amino alcohols in good moderate yield (Scheme 4). Under the optimized reaction conditions, the desired N-hydroxyethylated product was smoothly generated in moderate yield (43%). This is further evidence of the involvement of glycoadehyde in the reaction pathway. Moreover, we conducted experiment with methyl group-containing L-fucopyranose instead of D-(+)-xylose using the same reaction conditions. We found that the reaction gave a mixture of products with the majority include 2-(methyl(phenyl)amino)ethan-1-ol obtained in 36% and 1-(methyl(phenylamino)propan-2-ol in 12%. This result clearly shows the presence of retro-aldol reaction preferring the C-C bond cleavage to generate C2 intermediates and the potential of this

methodology as a mean to generate a wide variety of molecules by using different polyol substrates (Scheme 4).

Scheme 4 Control experiment[a, b]



[a] Reaction conditions: Ru(cod)(2-Methylallyl)$_2$ (2 mol%), Xantphos (2 mol%), CH_3COOH (0.15 mmol), 1,4-dioxane (2 mL), 150 °C, N_2 atmosphere. [b] Yields were determined by ^1H NMR using dibromomethane as an internal standard.

Experimental

Reactions were carried out in moisture and oxygen exclusion under nitrogen atmosphere and inert atmosphere techniques in glovebox. All solvents were dried and degassed before use by standard methods and stored under nitrogen atmosphere. All reactions were monitored with silica gel-coated plates (TLC). NMR spectra were recorded on a Bruker 400 MHz spectrometer. The NMR chemical shift values are referenced to $CDCl_3$ (δ (^1H), 7.26 ppm; δ ($^{13}C\{^1H\}$), 77.00 ppm). GC-MS data were obtained from Shimadzu GCMS-QP2010 SE, GC data were obtained from Shimadzu GC-2010 Plus. HRMS data were obtained on an Agilent 6530 spectrometer at Suzhou Research Institute of LICP.

General procedure for synthesis of β-amino alcohols:

The reaction of N-methylaniline and D-(+)-xylose as representative example: Ru(cod)(2-methylallyl)$_2$ (3.2 mg, 0.01 mmol), Xantphos (5.8 mg, 0.01 mmol) added to anhydrous 1,4-dioxane (0.5 mL) in 15 mL pressure-resistant tube containing magnetic stir bar. Then the mixture was allowed to stir under nitrogen atmosphere in the pressure-resistant tube at room temperature for 10 minutes. To the pressure-resistant tube containing pre-prepared catalyst, representative aryl amine and saccharide were added, N-methylaniline (53.6 mg, 0.5 mmol), D-(+)-xylose (225.0 mg, 1.5 mmol) with CH_3COOH (9.0 mg, 0.15 mmol) in anhydrous 1,4-dioxane (1.5 mL). The reaction mixture is heated to 150 °C and allowed to stir under a nitrogen atmosphere in the closed pressure-resistant tube for 16 h. After the reaction finished, the reaction tube was cooled to room temperature and the pressure was carefully released. The reactions yield determined by GC using n-dodecane as internal standard. The crude reaction mixture was concentrated *in vacuo* and purified by column chromatography [petroleum ether /ethyl acetate = 5:1] to give the corresponding β-amino alcohols (2-(methyl(phenyl)amino)ethan-1-ol) in good yields. All the prepared β-amino alcohols and related characterisation data are available in the supporting information. 2-(methyl(phenyl)amino)ethan-1-ol (**3a**): Yield: 78% (59 mg), light yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24 (t, J = 7.2 Hz, 2H), 6.81-6.73 (m, 3H), 3.80 (t, J = 4.8 Hz, 2H), 3.46 (t, J = 4.8 Hz, 2H), 2.95 (s, 3H), 1.87 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.1, 129.2 (2C), 117.2, 113.0 (2C), 60.0, 55.4, 38.7.

Conclusions

In summary, this work describes the first protocol for utilising mono- and oligosaccharides as alkylating reagents of arylamines. In the presence of ruthenium complexes based on Xantphos ligand under acidic conditions, this methodology is chemo-selective and general producing a wide variety of β-amino alcohols with good yields. This process is also practical to access important heterocyclic compounds and has the advantage of minimizing chemical waste and reducing costs. These findings extend the scope of the use of carbohydrates for the synthesis of valuable amines from renewable resources, as shown by the use of cellulose as source of hydroxyethyl group. This approach opened up new line of enquiries for other type of reactions of polyols we are currently pursuing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the financial supports from NSFC (21633013, 21101109, 21602228).

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