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Asymmetric Michael addition using sugar derived organocatalysts

P.B. Lalthanpuii[1,2], C. Lalhriatpuia[1], K. Vanlaldinpuia[1*]

[1]Department of Chemistry, [2]Department of Zoology, Pachhunga University College, Aizawl 796001, Mizoram

Sugars are low-molecular-weight carbohydrates which consist of polyhydroxyl and carbonyl (aldehyde or ketone) functional groups. Different types of compounds derived from sugars have been used extensively as powerful and effective catalysts for asymmetric synthesis. They are readily available at a reasonable price, easily prepared, no metal contamination and are inert towards moisture and air. They are highly functionalized and have well defined stereogenic centres. Most of them are employed as chiral ligands in metal based asymmetric catalysis and are used for various asymmetric transformations. Different compounds derived from sugars have also been used recently as organocatalysts for asymmetric synthesis. The present article provides some of the organocatalysts used for asymmetric synthesis.

Key words: Asymmetric Michael addition, organocatalysts, sugar.

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*For correspondence ✉:
mapuiakhiangte@gmail.com

Contact us ✉:
sciencevision@outlook.com

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Introduction

The word 'sugar' is often signified as a synonym for carbohydrates in general, but in everyday usage it means the table sugar, sucrose.[1] The carbohydrates (saccharides) are a group of organic compounds which consists of polyhydroxyl and carbonyl (aldehyde or ketone) functional groups with the capability of forming an intramolecular hemiacetal or hemiketal.[2,3] They are divided into three groups namely: monosaccharides, oligosaccharides, and polysaccharides. The nomenclature suffix "-ose" is used to denote carbohydrates. The name carbohydrate originates from "carbon hydrate" (hydrate of carbon), as they were originally believed to consist solely of carbon and water and thus were commonly designated by the generalised formula $C_x(H_2O)_y$.[4] Nowadays, the definition of carbohydrates has been much expanded to include substances derived from reduction or oxidation of monosaccharides and also those containing other elements (nitrogen, sulphur and halogens).[5]

Generally, among the carbohydrates mentioned above, monosaccharides and oligosaccharides (usually disaccharides and trisaccharides) having lower molecular weight are commonly referred to as sugars.[6]

Monosaccharides (**Fig. 1**) are divided into two main groups depending on which carbonyl functionalities they contain: "aldoses" for those containing aldehyde and "ketoses" for those having ketone functional group.[4] They can further be classified according to the number of carbon atoms in the monomeric chain into triose (n = 3), tetrose (n = 4), pentose (n = 5), hexose (n = 6),

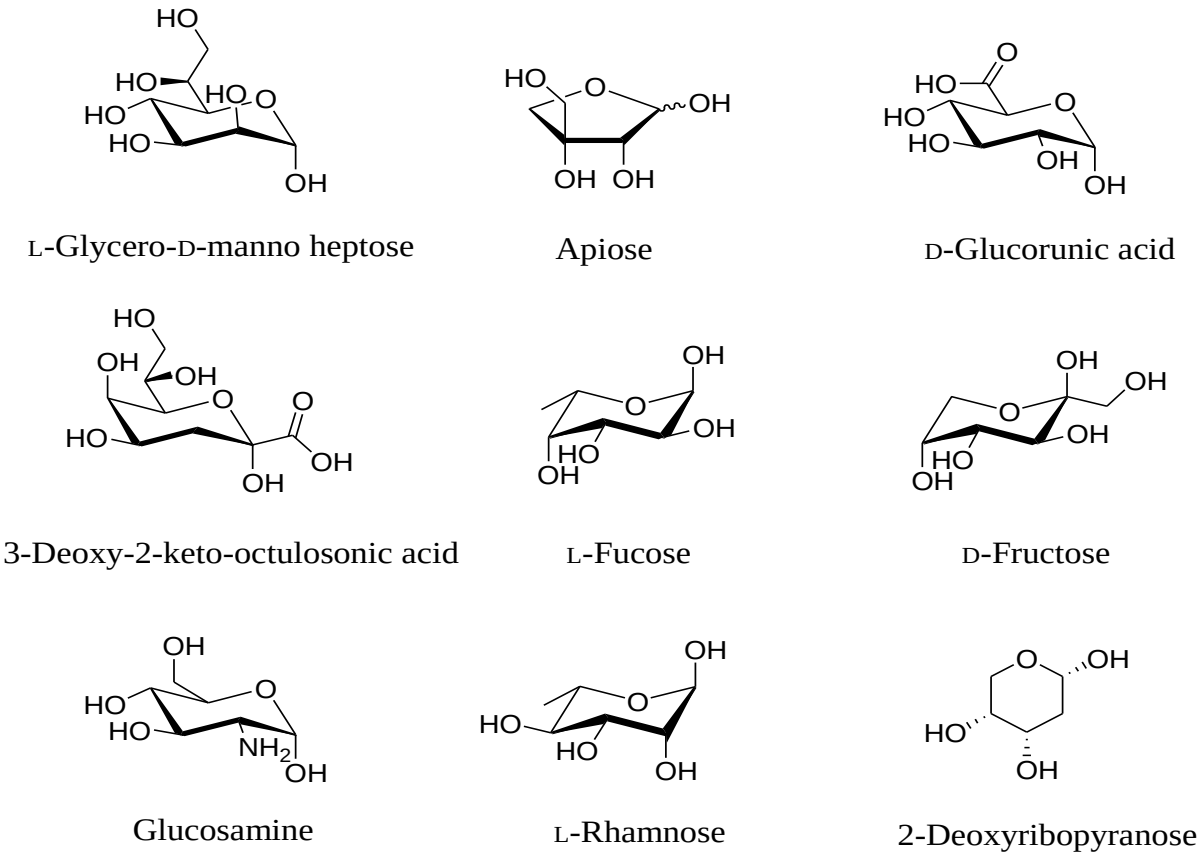


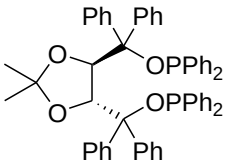
Fig. 1 | Some naturally occurring monosaccharides.

heptose (n = 7), etc. and the types of functional groups that are present.

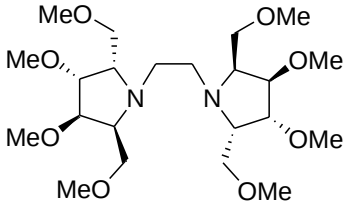
(+)-D-glucose, also known as grape sugar, is the most abundant monosaccharide found in nature followed by (+)-D-mannose and (+)-D-galactose.[3] On the other hand, (+)-D-fructose is the sweetest of all naturally occurring carbohydrates and regarded as 1.73 times sweeter than sucrose.[7] It is also the most abundant ketose.[4]

Carbohydrates are the most abundant biomolecule and play an important role in a number of biological reactions.[4,5] They are the main source of energy in most cells. For example, polysaccharides such as starch and glycogen serve as the storage of energy. Cellulose and chitin are important structural components in plants and arthropods respectively.[4,8] The 5-carbon monosaccharide ribose is an important component of co-enzymes (e.g. ATP, FAD, and NAD) and the backbone of the genetic molecule known as RNA. Likewise, the related deoxyribose is a component of DNA.[8] Carbohydrates and their derivatives include many important biomolecules that play key roles in the cell-cell recognition, immune system, embryogenesis, hormonal activities, fertilization, preventing pathogenesis, blood clotting, neuronal development, viral and bacterial infections, proliferation of cells and tumour cell metastasis.[4,8]

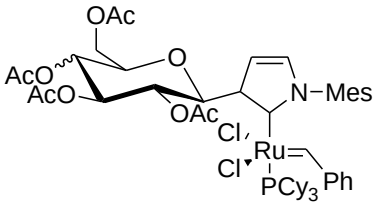
In recent years, different types of compounds derived from sugars have emerged as powerful and effective catalysts for asymmetric synthesis. They are readily available at a reasonable price, are highly functionalized, and have several well



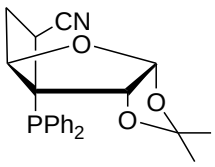
Pd-allylic alkylation 76% *ee*



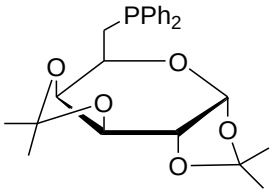
Zn- 1,2-addition 82% *ee*



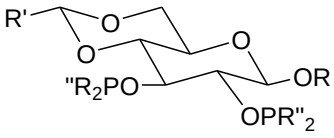
Ru-olefin metathesis 88% *ee*



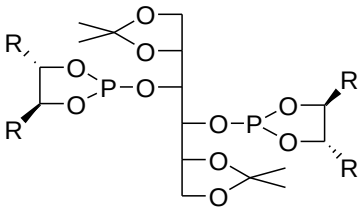
Rh-hydrogenation 92% *ee*



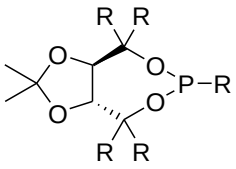
Ni-Cross-coupling 100% *ee*



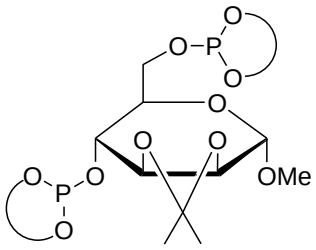
Ni-hydrocyanation 91% *ee*



Rh-hydrogenation < 34% *ee*



Rh-hydroboration 23% *ee*



Rh-hydroformylation 64% *ee*

Fig. 2 | Some chiral catalysts used for various asymmetric transformation.

defined stereogenic centres. Most of them are employed as chiral ligands (**Fig. 2**) in metal based asymmetric catalysis and are used for various asymmetric transformations.[9-15]

Recently, different compounds derived from sugars are also used as organocatalyst for asymmetric synthesis. In continuation with our efforts to explored different types of organocatalysts used for asymmetric Michael addition,[16] here we will highlight a short historical review on the synthesis and applications of sugar derived chiral organocatalysts for the said reaction.

Michael addition using sugar derived organocatalysts

Though asymmetric Michael addition using organocatalysts has been well documented, there are only few reports of sugar derived organocatalysts used for enantioselective Michael addition. In 2007, Liu *et al.*[17] reported a highly enantioselective Michael addition of aromatic ketones to nitro olefins promoted by bifunctional thiourea catalyst (**2**) readily prepared from commercially available β-D-glucopyranose (**1**) *via* acetylation, bromination, substitution reac-

tion and subsequent addition of chiral 1, 2-cyclohexyldiamines (**Scheme 1**). The other two thiourea catalyst **2c** and **2d** were synthesised from maltose and lactose, respectively. With catalyst **2b**, Michael addition adducts was obtained in good yields (up to 99%) and high enantioselectivity (up to 98%) (**Scheme 2**). The origin of enantioselectivity seems to arise from the attack of the enamine to the *si*-face of the nitro olefins as the *re*-face attack was block by cyclohexyl group of the catalyst (**Fig. 4**).

In 2008, Gao *et al.*[18] employed bifunctional thiourea organocatalysts **3a**, **3b** and **3c** (**Fig. 5**) synthesised from α-D-glucopyranose, galactose and lactose, respectively for asymmetric Michael addition of acetyl acetone to nitro olefins. Using β-nitrostyrene as a test substrate, thiourea **3a** gave the best result in terms of enantioselectivity. The reaction was done at -40 °C using exactly 10 mol% catalyst and β-nitrostyrene concentration of 0.4 M in toluene to get the best possible result. Under the optimized condition, the versatility of the reaction was investigated using various nitro olefins. The reactions gave up to >99% yield and up to 96% enantioselectivity (**Scheme 3**).

In the same year Li *et al.*[19] also reported enantioselective Michael addition of malonates to nitroolefins catalyzed by chiral bifunctional tertiary amine-thioureas based on saccharides (**Fig. 6**). Using **4a** and **4b** as catalysts in the presence of toluene as a solvent and at -20°C, the reaction gave up to 99% yield and 99% *ee* (**Scheme 4**).

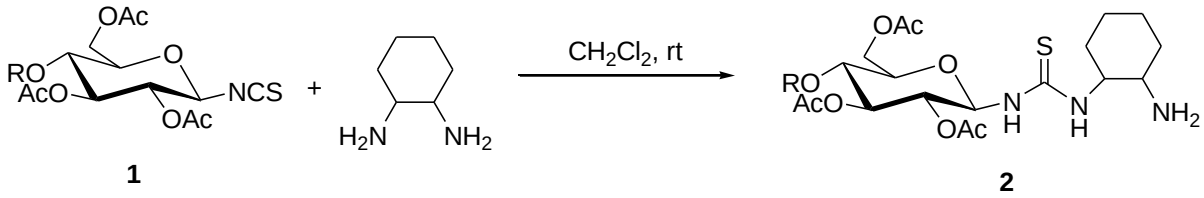
Pu *et al.*[20] developed a series of new organocatalysts (**7**) from both α-amino acids and carbohydrates (**Figure 7**) which were consequently used for asymmetric Michael addition of acetylacetone to nitroolefins. The catalysts were readily prepared by coupling amines (**5**) derived from α-amino acids and isothiocyanate (**6**) derived from D-glucopyranose (**Scheme 5**). They also described the "matched" and "mismatch" effect of two different chiral units in a chiral organocatalysts, in which both the enantiomers of the product was obtained in almost the same enantioselectivity with "matched" and "mismatched" organocatalysts simply by changing the solvent system from THF to toluene. With **7a** (derived from L-valine and D-glucopyranose), addition of acetylacetone to β-nitrostyrene gave 88% yield and 85% enantiomeric excess having (*S*)-configuration when THF was used as a solvent.

On the other hand, the use of **7a'** (derived from D-valine and D-glucopyranose) in THF gave the opposite enantiomer with lower enantioselectivity (76% ee) which suggest that L- configuration of valine matched the D-glucopyranose, whereas D- configuration of valine mismatched the D-glucopyrano se. But, by changing the solvent from THF to toluene, **7a'** gave the product with the opposite absolute configuration in almost the same enantiomeric excess (86%).

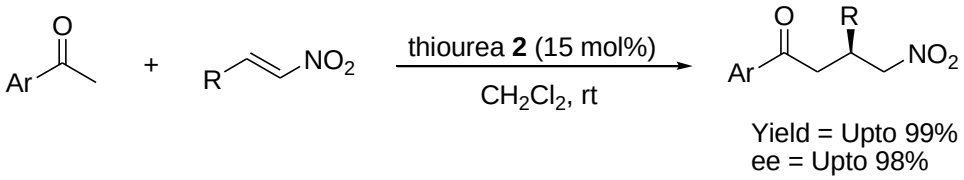
Doubly stereo controlled catalytic conjugate addition of acetylacetone to nitroolefins was also achieved with thiourea catalyst **7e** and **7e'** in the same solvent (i.e. toluene). Addition of acetylacetone to a variety of nitroolefins in the presence of **7e** and **7e'** gave the desire products with (*S*) or (*R*) configuration (**Scheme 6 & 7**) in high yields (up to 90%) and good enantioselectivity (up to 91%).

Lu *et al.*[21] also reported a newly designed pyrrolidine thioureas for asymmetric Michael addition of cyclohexanone to nitro olefins. (*S*)- or (*R*)-*tert*-butyl 2-(amino-methyl)pyrrolidine-1-carboxylate (**8**) coupled with glucosyl isothiocyanate (**6**) to give the catalysts (**Scheme 8**). With **9a**, the reactions gave γ–nitroketones with good yields (up to >99%) and excellent diastereo- (up to >99/1 *dr*) and enantioselectivity (up to 97% *ee*) (Scheme 9). They proposed a transition state in which nucleophilic attack of the enamine to the nitroolefin from *re*-face resulted in the formation of the desired product (**Figure 8**).

Another new class of carbohydrate-based bifunctional organocatalysts for nucleophilic Michael addition to nitroolefins and imines was reported by Puglisi *et al.*[22] They prepared the catalysts from readily available D-glucosamine to prepare **11a-d**, which were subsequently converted to the desired thiourea catalysts as shown in the Scheme 9 and 10. With **12b**, addition of acetylacetone to nitroolefins gave up to 93% yield and up to 83% enantioselectivity (**Scheme 12**). Asymmetric addition of diethyl malonate to *N*-Boc imine of benzaldehyde was



Scheme 1 | Synthesis of primary amine-thiourea catalyst.



Scheme 2 | Enantioselective Michael addition using thiourea catalyst **2.**

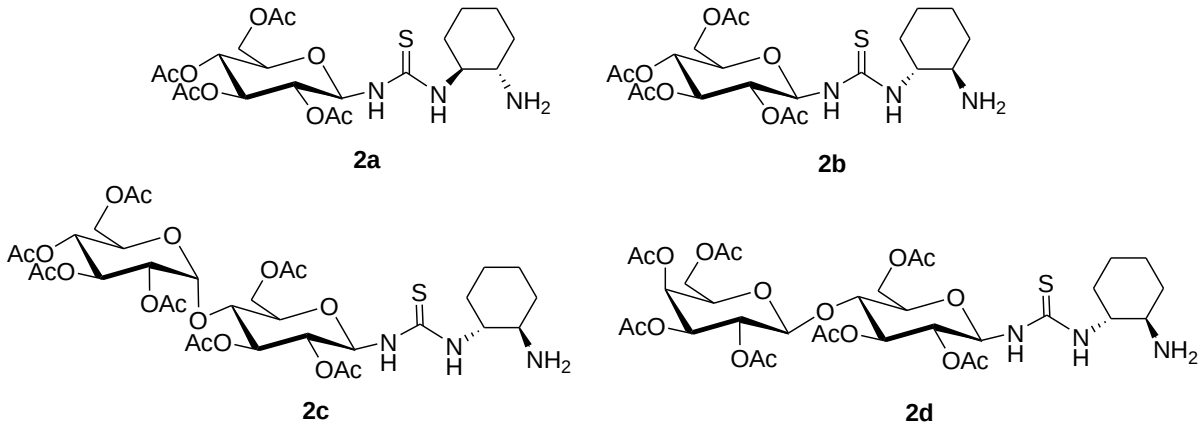


Fig. 3 | Sugar derived organocatalyst used for asymmetric Michael addition.

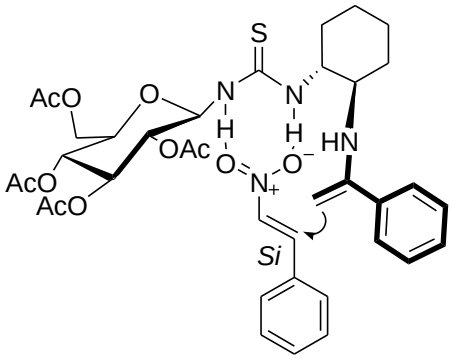


Fig. 4 | Transition sate model.

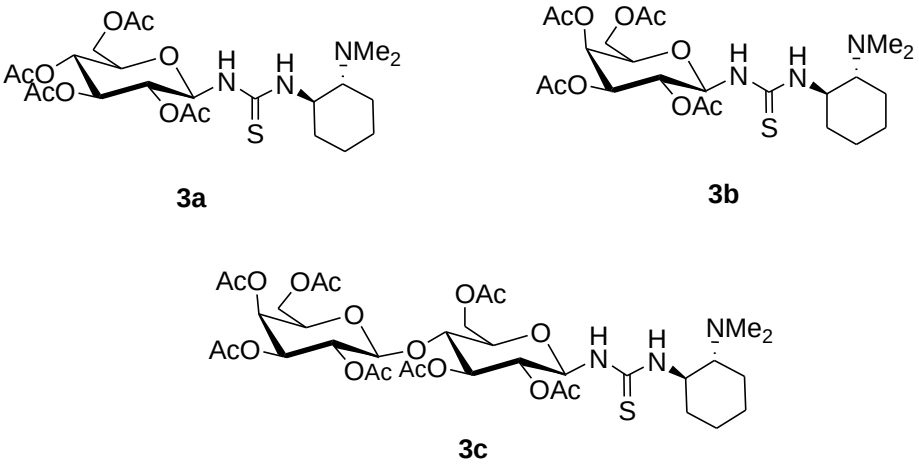
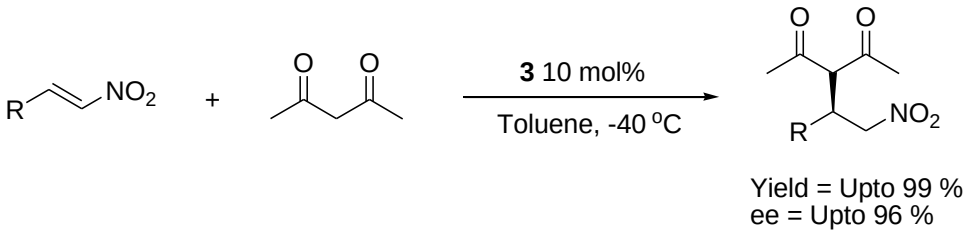


Fig. 5 | Bifunctional thiourea catalysts from sugars.



Scheme 3 | Asymmetric Michael addition of acetylacetone to nitroolefins using 3.

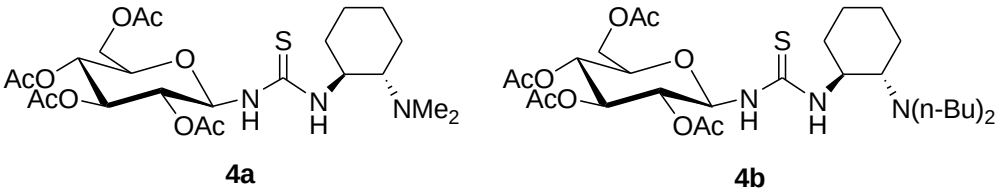
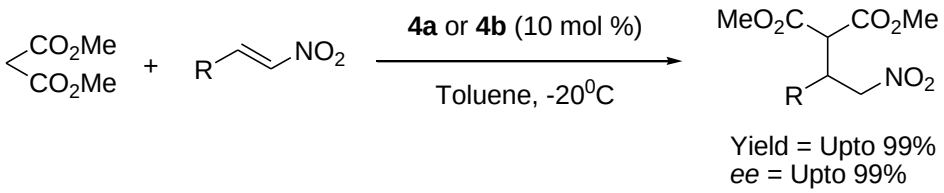
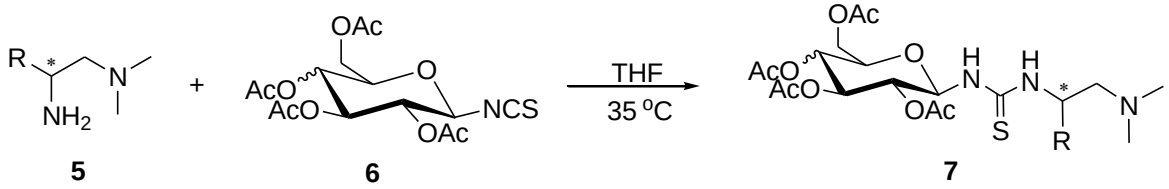


Fig. 6 | Saccharides based bifunctional tertiary amine-thioureas catalysts.



Scheme 4 | Enantioselective Michael addition of malonates to nitro olefins.



Scheme 5 | Synthesis of thioureacatalyst 7.

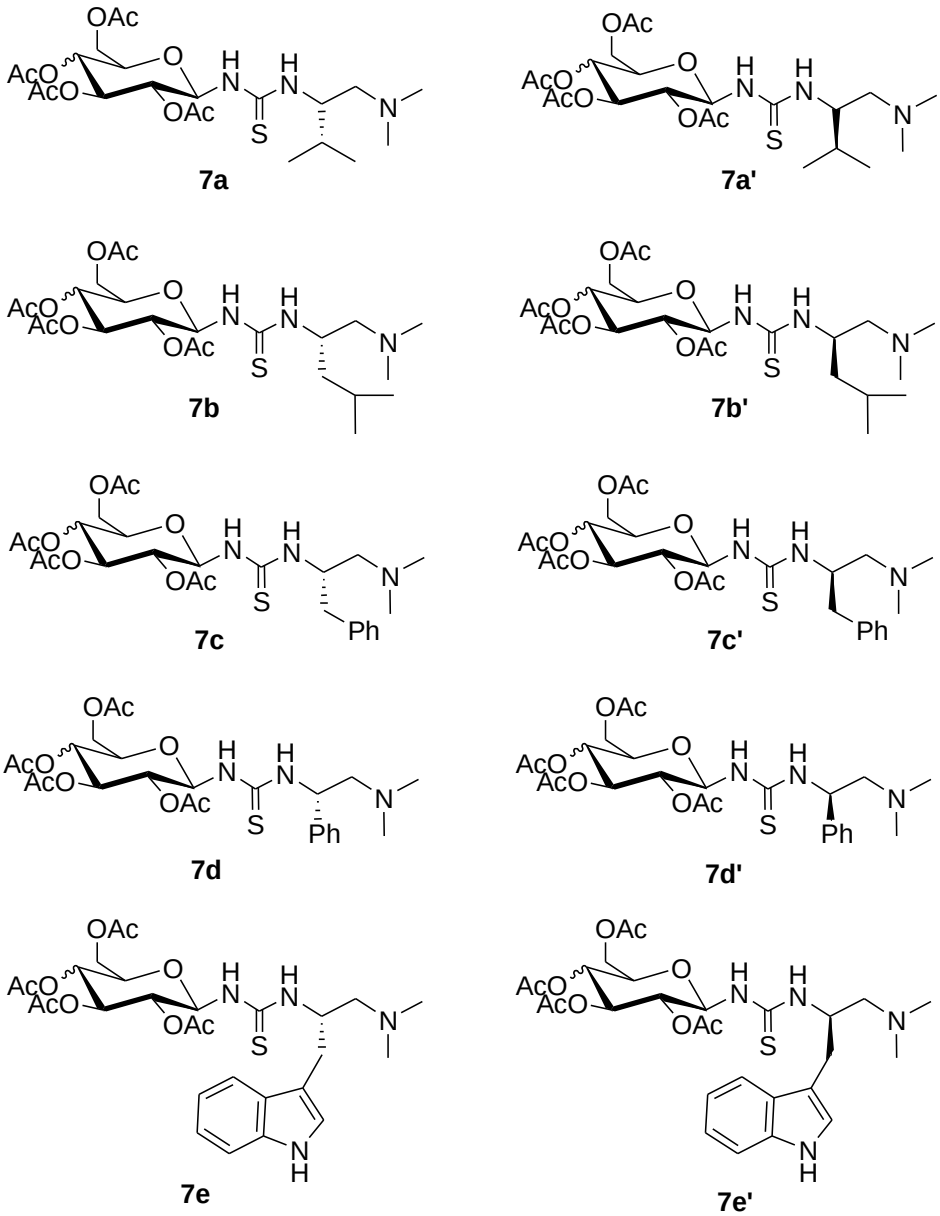
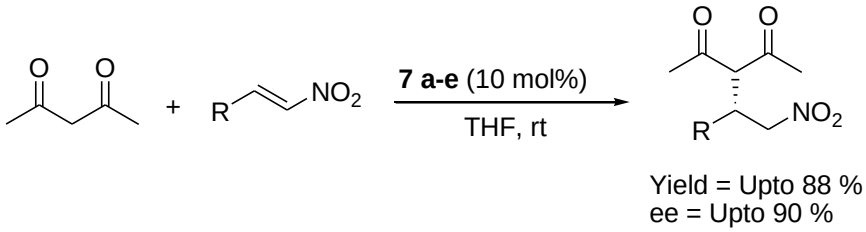
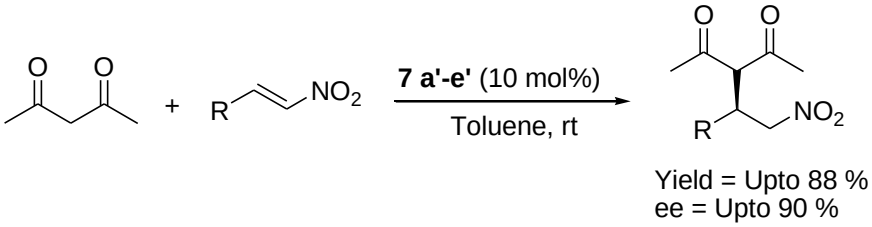


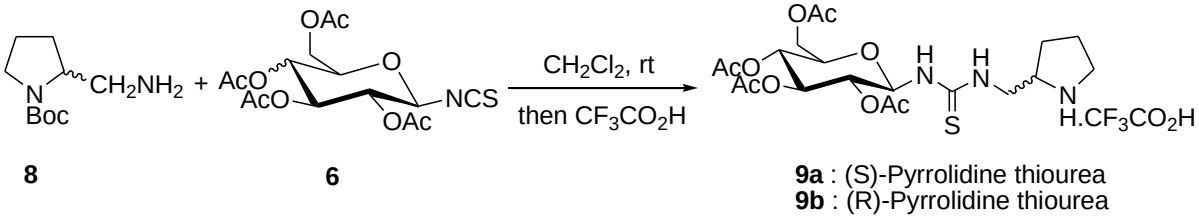
Fig. 7 | Different thiourea catalyst derived from amino acids and carbohydrates.



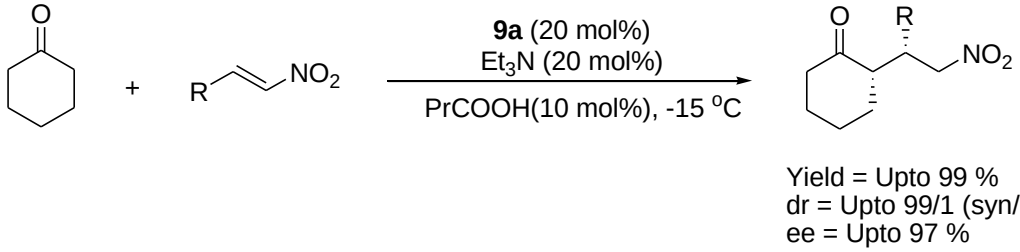
Scheme 6 | Asymmetric addition of acetylacetone to nitroolefins giving (S) configuration.



Scheme 7 | Asymmetric addition of acetylacetone to nitroolefins giving (R) configuration.



Scheme 8 | Synthesis of pyrrolidine thiourea catalyst.



Scheme 9 | Asymmetric addition of cyclohexanone to nitro olefins.

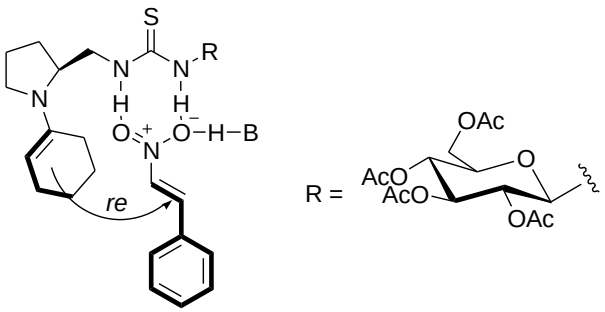
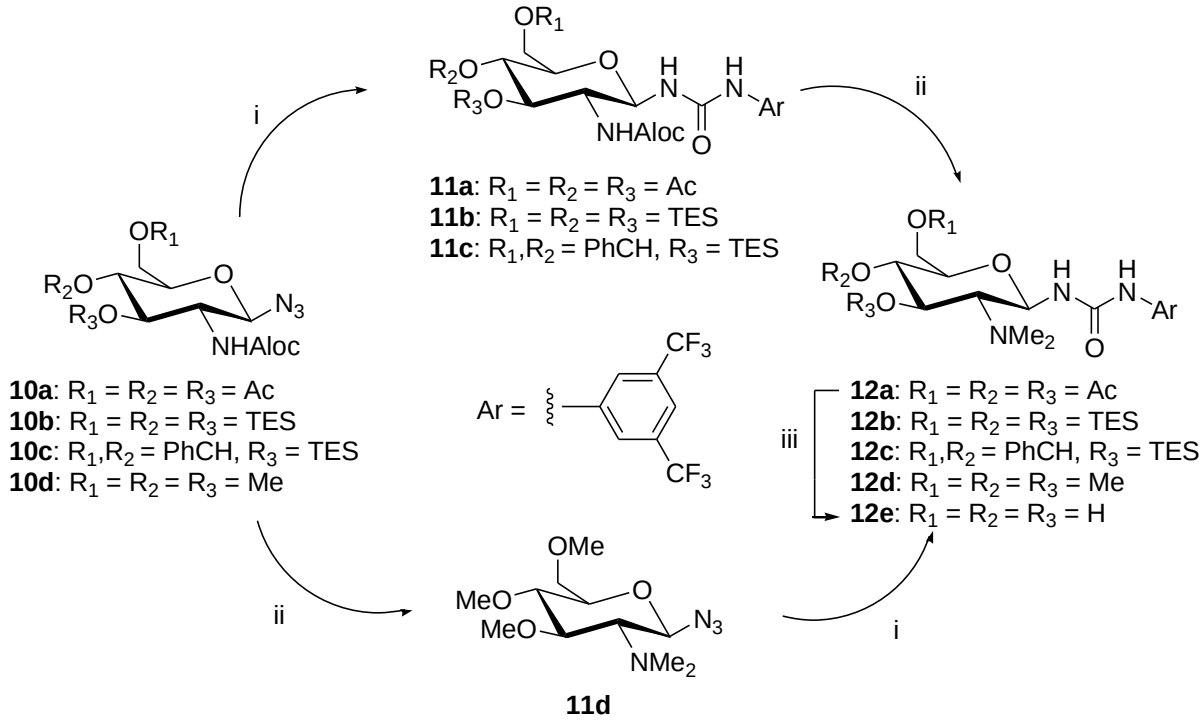
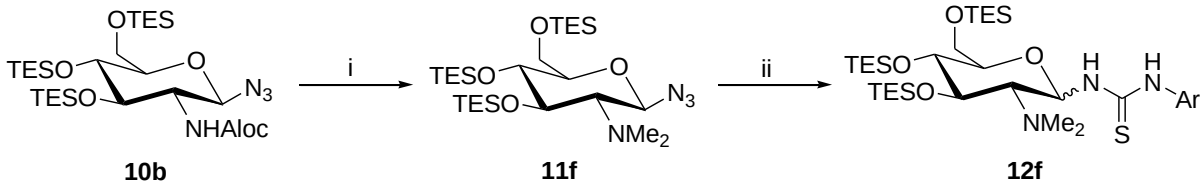


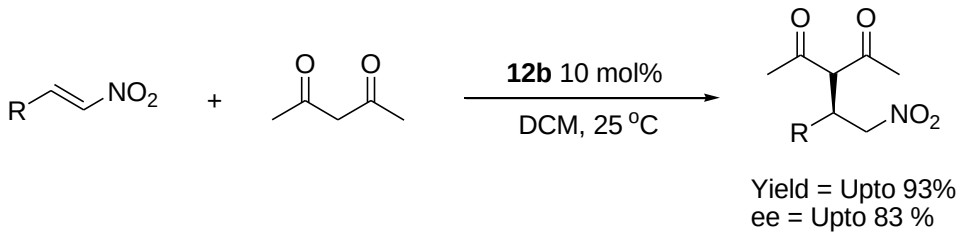
Fig. 8 | Proposed transition model.



Scheme 10 | Synthesis of glucosaminylurea-based organocatalyst. i) . i) PPh_3, ArNCS, THF; ii) $Pd(PPh_3)_4$, Bu_3SnH, AcOH, CH_2Cl_2, then HCHO, $NaCNBH_3$, THF; iii) NaOMe, MeOH, (qu).



Scheme 11 | Synthesis of glucosaminylurea-based organocatalyst **12f**. i) $Pd(PPh_3)_4$, Bu_3SnH, AcOH, CH_2Cl_2, then HCHO, $NaCNBH_3$, THF (57%); ii) H_2, Pd/C, ArNCS, THF (46%).



Scheme 12 | Asymmetric Michael addition of acetylacetone to nitroolefins with **12b**.

Scheme 13 | Asymmteric Michael addition of diethyl malonate to *N*-Boc imine.

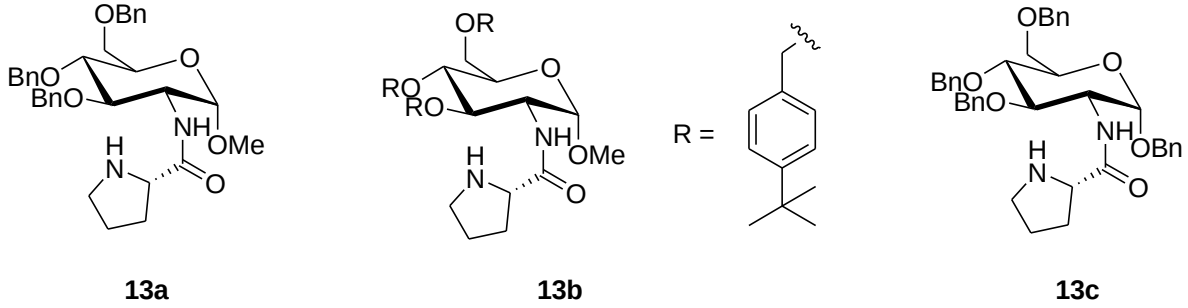
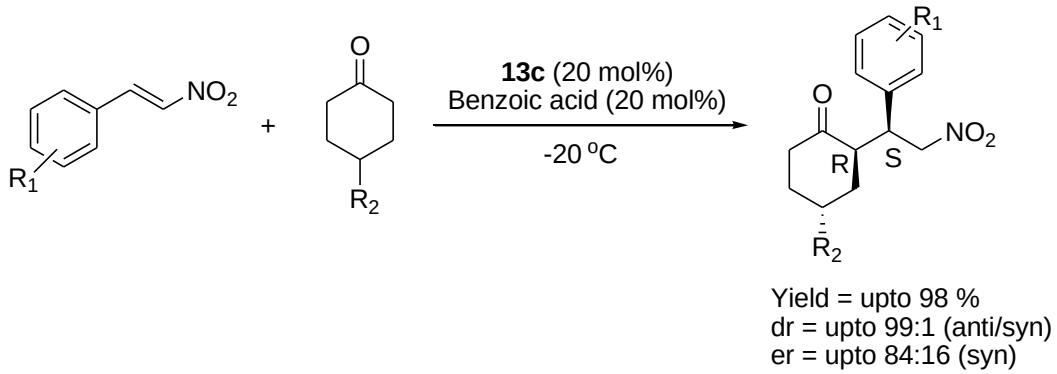
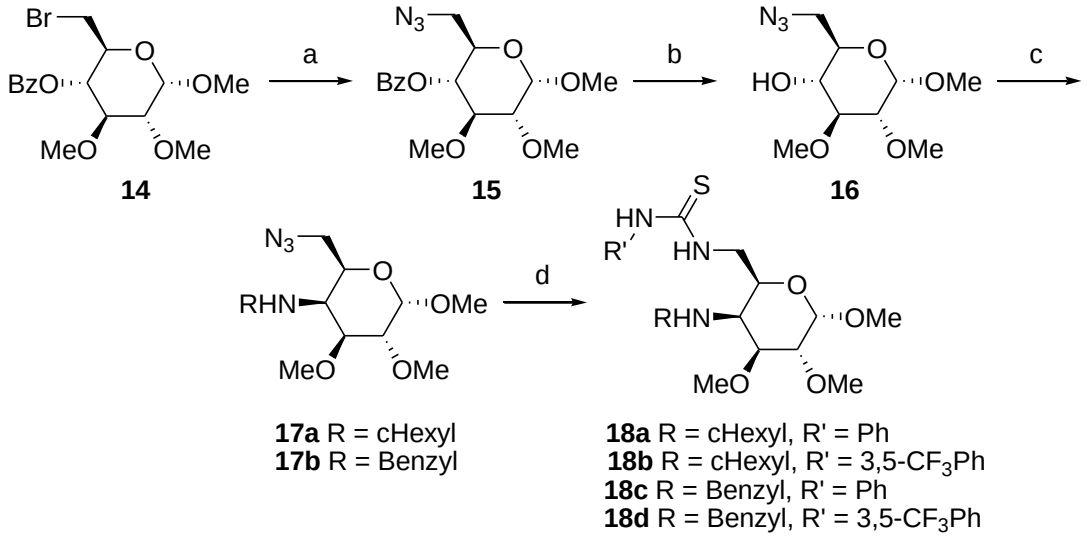


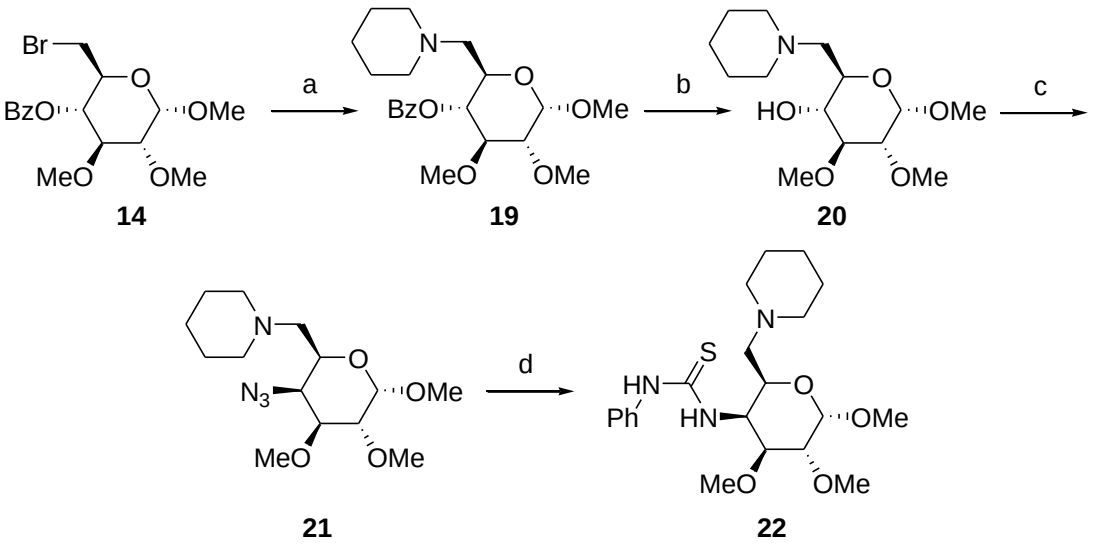
Fig. 9 | Sugar based prolinamides from L-proline and D-glucosamine.



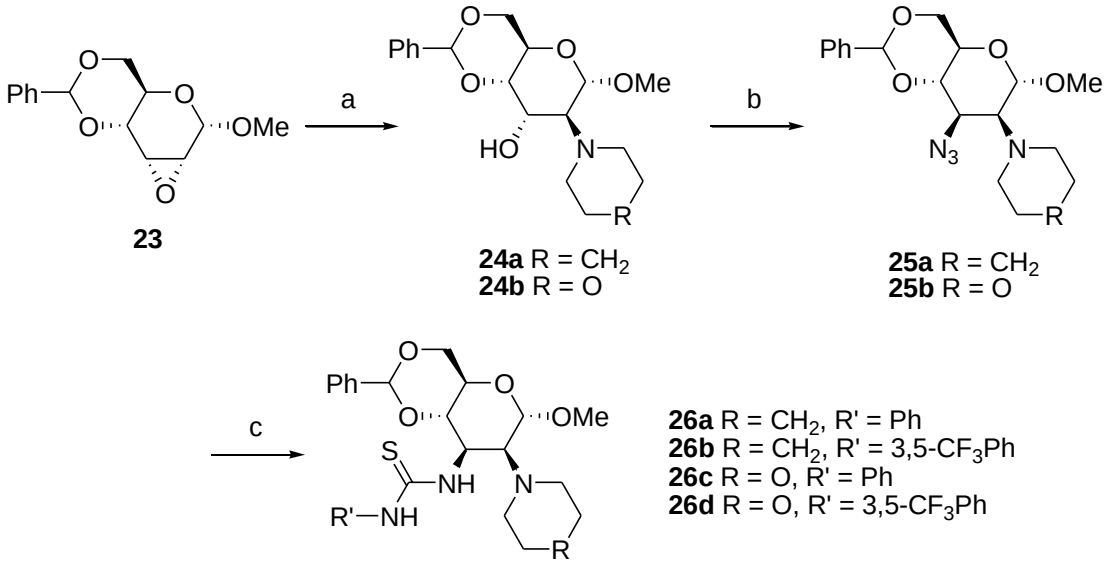
Scheme 14 | Asymmetric addition of cyclohexanone to nitroolefins with **13c**.



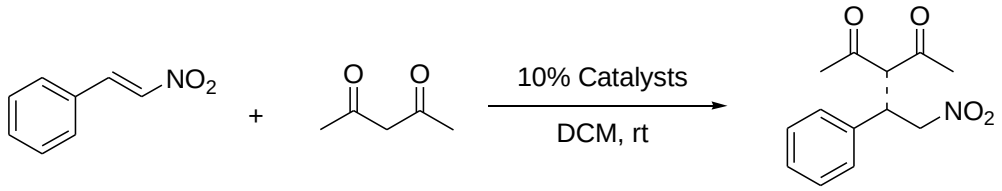
Scheme 15 | Synthesis of the catalysts; (a) NaN_3, DMF, 70°C, 6 h, 94%; (b) NaOMe, MeOH, rt, 1h, 80%; (c) (i) Tf_2O, pyridine, CH_2Cl_2, 0oC, 2 h, (ii) amine, DMF, 45°C, 10 h, 50-70%; (d) (i) propanedithiol, MeOH, rt, 48 h (**18a** and **18b**), or PPh_3, H_2O, THF, 80°C, (**18c** and **18d**), (ii) isothiocyanate, MeOH, rt, 4 h, 30-50%.



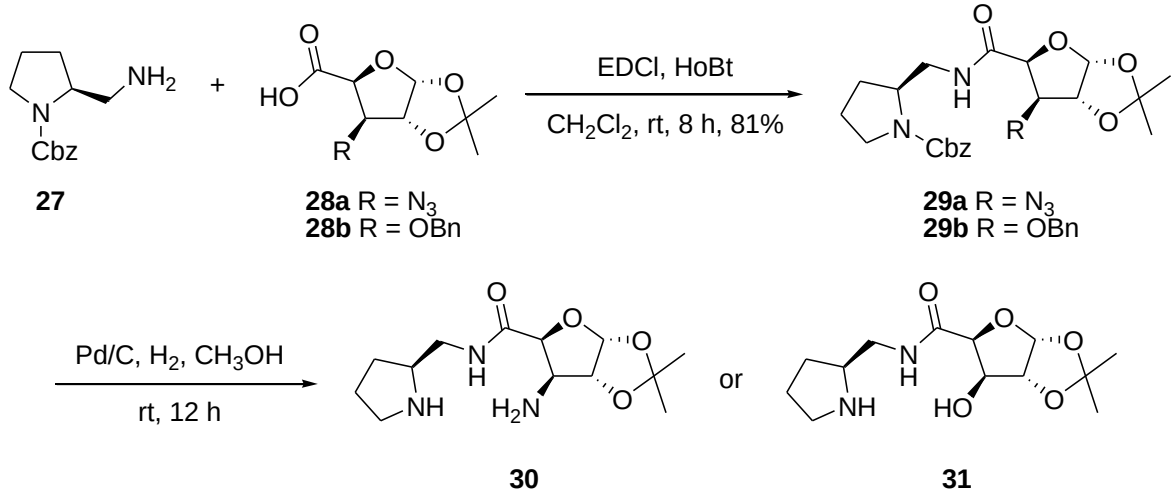
Scheme 16 | Synthesis of organocatalysts; (a) piperidine, DMF, 70°C, 50 h, 90%; (b) NaOMe, MeOH, reflux, 2 h, 85%; (c) Tf_2O, pyridine, DCM, 0°C, 2 h, (ii) NaN_3, DMF, 45°C, 72 h, 40%; (d) (i) propanedithiol, MeOH, rt, 48 h, (ii) phenyl isothiocyanate, MeOH, rt, 8 h, 69%.



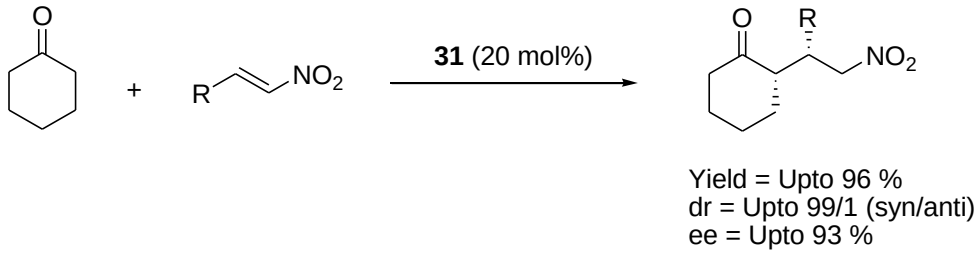
Scheme 17 | Synthesis of catalysts **26**; (a) piperidine or morpholine, $LiClO_4$, MeCN, 90°C, 24 h, 80-90%; (b) (i) PPh_3, DIAD, THF, 0°C, (ii) DPPA, THF, rt, 24 h, 60-80%; (c) (i) PPh_3, THF, H_2O, 80°C, (ii) isothiocyanate, MeOH, rt, 8 h, 60-80%.



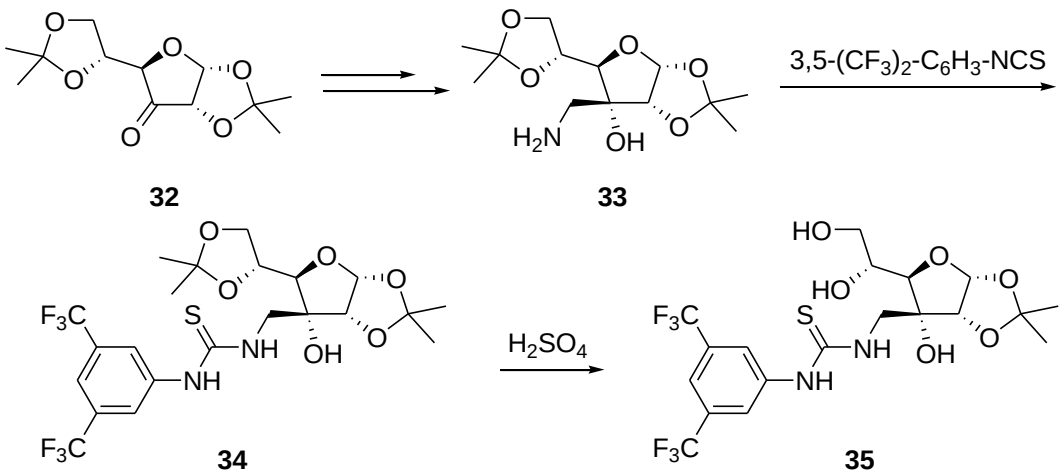
Scheme 18 | Michael addition of acetylacetone to β-nitrostyrene using **18**, **22** and **26**.



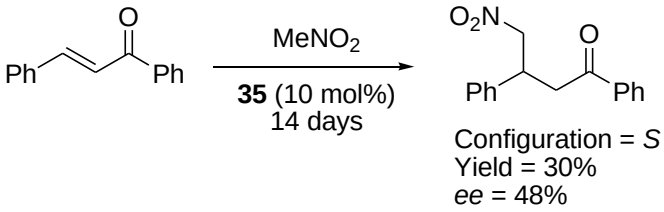
Scheme 19 | Sugar amide-pyrrolidine catalyst for the asymmetric Michael addition.



Scheme 20 | Asymmetric Michael addition of ketones to nitroolefins using catalyst **31**.



Scheme 21 | Synthesis of thiourea derived 3-*C*-aminomethyl-hexafuranose (**35**).



Scheme 22 | Organocatalyst **35** catalyzed Michael addition of nitromethane to *trans*-chalcone.

also investigated using **12b**, **12c**, **12d** and **12f**. In terms of enantioselectivity, **12b** gave the best result (81% *ee*) but the yield was low (25% only) (**Scheme 14**).

Agarwal and Peddinti[23] also describe a sugar-based prolinamides organocatalysts for asymmetric Michael addition in solvent-free condition. The catalysts (**13a**-**13c**, **Fig. 9**) were prepared from commercially available L-proline and D-glucosamine. The reaction condition was found to be optimum at -20°C in the absence of solvent with 20 mol% catalysts and another 20 mol% organic acid additive (benzoic acid). The Michael adducts were obtained in excellent yields (up to 98%), high diastereoselectivity (up to 99/1) and moderate enantioselectivity (*er* up to 84/16 for *syn*) (**Scheme 14**). The catalytic system was found to provide (1R,2S)-*syn* adducts as a major antipodes.

In 2014, Agoston and Fugedi[24] designed and prepared a group of new-bifunctional-thiourea-amine catalysts starting from D-glucose. The

two catalytic centres in those molecules synthesised were connected by a carbohydrate residue. The catalysts were designed in such a way that the catalytic centers were placed at various positions of the carbohydrate scaffold to see the possible effect arising from carbohydrate chirality. So, they synthesized molecules having the amino and thioureido groups in positions 4 and 6, or in positions 2 and 3 of the carbohydrate scaffold. Methyl 4-O-benzoyl-6-bromo-6-deoxy-2,3-di-O-methyl-α–D-glucopyranoside (**14**) which was prepared from methyl α–D-glucopyranoside was used as a starting material for the preparation of catalysts having the catalytic groups in the 4 and 6 position (**Scheme 15 & 16**).

The synthesis of 2-amino-3-thioureido derivatives (**26a-d**) started from *allo*-epoxide (**23**) as starting material which was further prepared from commercially available methyl α–D-glucopyranoside (**Scheme 17**).

The catalysts synthesised were used for Michael addition of acetylacetone to β–nitrostyrene (**Scheme 18**). It was found that only those compounds having secondary amine groups were able to promote the reaction (up to 78% yield). The active catalysts favoured the formation of Michael adduct having *S*-configuration, but enantioselectivity is very low (up to 18.7% only).

Recently, Kumar and Balaji[25] developed new sugar based pyrrolidine-amide catalysts (**30** and **31**) derived from L-proline and the furanose form of D-glucose and used it for asymmetric Michael addition of ketones to nitroolefins (**Scheme 19**).

Catalyst **30** gave good yields and diastereoselectivities but low enantioselectivities (up to 21% only). The best results were observed with catalyst **31** in which 20 mol% of the catalyst was used under solvent free condition. Up to 96% yield, 99:1 (*syn*/*anti*) diastereoselectivity and up to 93% *ee* were obtained (**Scheme 20**).

More recently, Turks *et al.*[26] also reported the synthesis of thiourea derived 3-C-aminomethyl-hexafuranose (**35**) which was employed for the asymmetric addition of nitromethane to *trans*-chalcone (**Scheme 21**). The reaction took place over 14 days and gave the product in 30% yield and 48% ee.

Conclusion

Different types of compounds derived from sugars are used recently as organocatalyst for asymmetric synthesis. These are due to their commercial availability, low cost and inertness towards moisture and air. The catalysts described in this paper mainly showed high yield and enantioselectivity leading to huge demand and widespread utility. The highest yield and enantioselectivity (both 99%) were seen in Michael addition of malonates to nitroolefins catalyzed by chiral bifunctional tertiary amine-thioureas based on saccharides in the presence of toluene as a solvent and at -20°C. However, the lowest yield and enantioselectivity, 30% and 48% respectively were seen in the synthesis of thiourea derived 3-C-aminomethyl-hexafuranose which was employed for the asymmetric addition of nitromethane to *trans*-chalcone. As organic catalysts are easily available, cheap, easily prepared and are useful in complex steric reactions, they may be used as an alternative to the present transition metals catalysis.

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