HETEROCYCLES, Vol. 98, No. 11, 2019, pp. 1536 - 1545. © 2019 The Japan Institute of Heterocyclic Chemistry
Received, 17th October, 2019, Accepted, 15th November, 2019, Published online, 25th November, 2019
DOI: 10.3987/COM-19-14172

SUGAR BASED γ-AMINO ALCOHOL ORGANOCATALYST FOR ASYMMETRIC MICHAEL ADDITION OF β-KETO ESTERS WITH NITROOLEFINS

Divakar Ganesan,[a] Madhu Chennapuram,[a] Zubeda Begum,[a] Chigusa Seki,[a] Yuko Okuyama,[b] Eunsang Kwon,[c] Koji Uwai,[a] Michio Tokiwa,[d] Suguru Tokiwa,[d] Mitsuhiro Takeshita,[d] and Hiroto Nakano[a]*

[a]Division of Sustainable and Environmental Engineering, Graduate School of Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran 050-8585, E-mail: catanaka@mmm.muroran-it.ac.jp

[b]Tohoku Medical and Pharmaceutical University, 4-4-1 Komatsushima, Aoba-Ku, Sendai 981-8558, Japan, E-mail: yoku@tohoku-mpu.ac.jp

[c]Research and Analytical Center for Giant Molecules, Graduate School of Sciences, Tohoku University, 6-3 Aoba, Aramaki, Aoba-Ku, Sendai 980-8578, Japan, E-mail: ekwon@tohoku.ac.jp

[d]Tokiwakai Group, 62 Numajiri Tsuduri-Chou Uchigo Iwaki 973-8053, Japan, E-mail: hisyo@tokiwa.or.jp

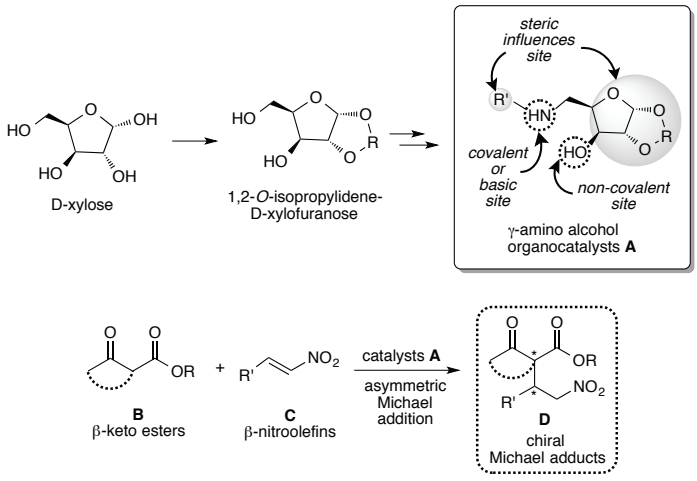
Abstract - Sugar based γ-amino alcohol was used in asymmetric Michael addition of β-keto esters with nitroolefins for the first time affording the corresponding several chiral Michael adducts bearing quaternary chiral carbon center in moderate to good chemical yields and stereoselectivities (up to 98%, up to *dr*. 95:5, up to 84% ee).

INTRODUCTION

The development of highly functionalized small chiral molecules and its application as organocatalyst towards the asymmetric synthesis has considerably attracted immense interest in the scientific community.[1] In the last two decades, several efficient chiral organocatalysts have been developed and utilized in various asymmetric reactions.[2] Our research group has been also continuously and extensively exploring a series of novel amino alcohol and amino amide type organocatalysts for asymmetric reactions.[3]

*Dedicated to Prof. Kaoru Fuji on the occasion of his 80th birth anniversary

In continuation of our interest in developing new type of amino alcohol organocatalyst, we focused γ-amino alcohol as an organocatalyst. In contrast to β-amino alcohol as an organocatalyst, the utility of γ-amino alcohol was not much explored even though it is expected to have a high potential functionality as an organocatalyst similar to β-amino alcohol. As a compound, we selected a sugar based γ-amino alcohol **A** fixing 1,2-*O*-isopropylidene-D-xylofuranose structure as a backbone (Scheme 1). We have already reported that γ-amino alcohol **A** with sugar backbone is efficient as chiral ligand of Pd-catalyzed asymmetric allylation.[4] Besides, there are a few reports for the use of γ-amino alcohol **A** as an organocatalyst, although its efficient steric and/or electronic influences is expected in an asymmetric reaction.[5] Proposed xylofuranose-based γ-amino alcohol organocatalyst **A** contains an amino group acting as covalent or basic site and hydroxy group acting as a non-covalent hydrogen bonding site and also sugar backbone acting as steric influence site for controlling stereoselective reaction course. Furthermore, this compound **A** can be easily prepared from commercially available D-xylose by few steps.[6] As a model reaction for providing the utility of the catalyst **A**, asymmetric Michael addition of β-keto esters **B** with nitroolefins **C** to afford the chiral Michael adducts **D** bearing both quaternary and tertiary chiral carbon centers was selected.[7] To the best of our knowledge, the successful use of γ-amino alcohol organocatalyst for this addition has not been reported until now. Herein, we describe the first use of chiral sugar based γ-amino alcohol organocatalysts **A** in asymmetric Michael addition of β-keto esters **B** with various nitroolefins **C** to afford the corresponding chiral Michael adducts **D** in moderate to good chemical yields and stereoselectivities (up to 97%, up to *dr*. 95:5, up to 84% *ee*).

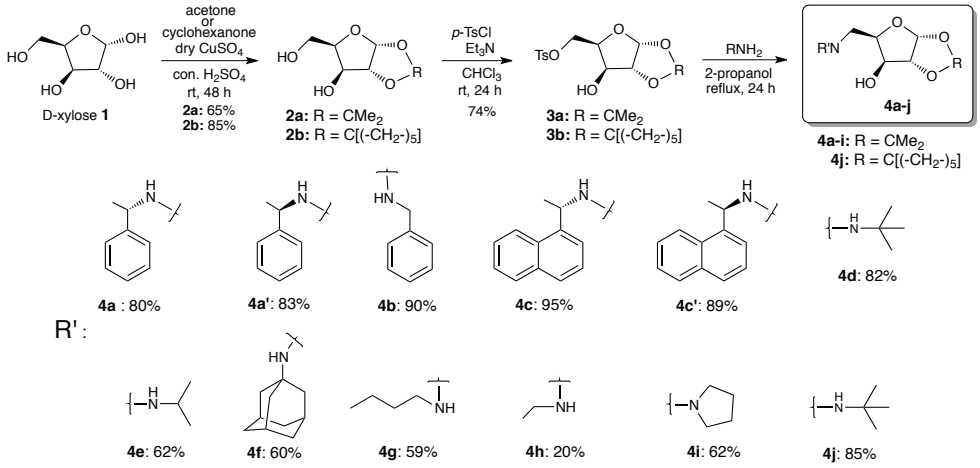


Scheme 1. Concept of xylofuranose-based γ-amino alcohol

RESULTS AND DISCUSSION

Xylofuranose-based γ-amino alcohol organocatalysts **4a-j** were prepared from D-xylose *via* three steps (Scheme 2). 1,2-*O*-Isopropylidene-α-D-xylofuranoses **2a,b** were prepared by the reactions of D-xylose **1**

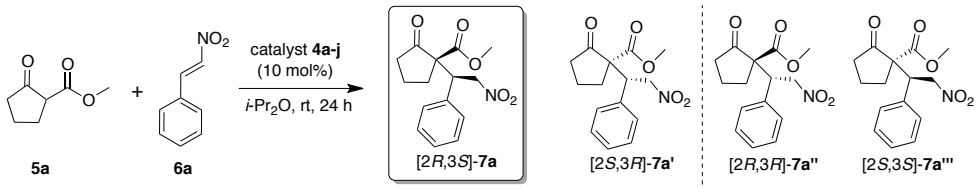
with acetone or cyclohexanone, followed by the tosylation of hydroxy group on **2a,b** afforded the tosylate **3a,b**. Furthermore, the substitution reactions of the obtained **3a,b** with several amines afforded the desired γ-amino alcohols **4a-j**.[6]



Scheme 2. Preparation of catalysts **4a-j**

First, the catalytic activities of obtained γ-amino alcohols **4a-j** as an organocatalyst were examined in the Michael addition of methyl 2-oxocyclopentanecarboxylate **5a** with nitrostyrene **6a** (Table 1). The reactions were carried out in the presence of 10 mol% of catalysts **4a-j** in *i*-Pr_2O at room temperature, respectively.

Table 1. Michael addition of **5a** with **6a** using **4a-j**



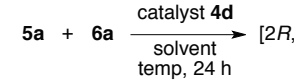
entry	catalyst **4**	yield (%)[a]	*dr*[b] (**7a,a'/7a'',a'''**)	*ee* (%)[c] **7a**
1	**a**	98	81:19	12
2	**a'**	53	77:23	52
3	**b**	65	59:41	27
4	**c**	71	71:29	52
5	**c'**	57	88:12	28
6	**d**	69	89:11	64
7	**e**	61	63:37	23
8	**f**	74	75:25	13
9	**g**	76	82:18	33
10	**h**	79	83:17	25
11	**i**	53	77:23	39
12	**j**	70	85:15	58

[a]Isolated yield. [b]Determined by ^{1}H NMR of crude reaction mixture. [c]The *ee* was determined by HPLC using CHIRALCEL OD-H column.

As a result, all catalysts **4a-j** showed catalytic activities to afford the desired chiral Michael adduct [2*R*,3*S*]-**7a**, as a main product with moderate to excellent chemical yields (53-98%) and moderate to good diastereoselectivities (59:41-89:11), although satisfactory enantioselectivities (13-58% ee) were not conformed in this reaction condition. In these catalysts **4a-j**, catalyst **4d** with *t*-butyl group on nitrogen atom showed good catalytic activity in this reaction conditions to afford the Michael adduct **7a** with comparatively good chemical yield, diastereoselectivity and moderate enantioselectivity (73%, *dr*. 89:11, 64% ee) (entry 6). The determination of absolute stereochemistry of **7a** was conformed on comparison with previous report.[3a]

In order to optimize the reaction conditions using superior catalyst **4d**, the effect of solvent, the molar ratio of catalyst, and the reaction temperature were examined (Table 2). First, the effects of solvents were examined in the presence of 10 mol% of superior catalyst **4d** at room temperature for 24 h (entries 1-12). Chemical yields and stereoselectivities were mostly depended on the nature of solvents and the utilization of *i*-Pr_2O as a solvent afforded the Michael adduct **7a** in better chemical yield, diastereoselectivity and moderate enantioselectivity (73%, *dr*. 89:11, 64% ee) (entry 6, Table 1 and entry 1, Table 2) than other solvents (entry 2-12, Table 2). Next, we examined the molar ratios of catalyst **4d** in superior *i*-Pr_2O solvent at room temperature (entries 13-15). As a result, best enantioselectivity (84% ee) was obtained when the reaction was carried out in the presence of 20 mol% of catalyst **4d** to afford **7a** with moderate chemical yield and good diastereoselectivity (65%, *dr*. 87:13) (entry 15). Furthermore, reaction temperature was also screened at 0 °C, -10 °C, -20 °C and 40 °C, respectively (entries 16-19). Chemical

Table 2. Screening of the reaction condition using catalyst **4d**



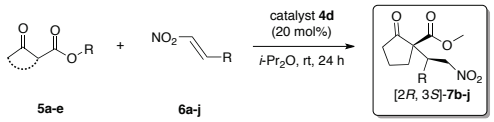
entry	solvent	mole (%)	temp (°C)	yield (%)[a]	*dr*[b] (**7a,a'/7a'',a'''**)	*ee* (%)[c] **7a**
1	*i*-Pr_2O	10	rt	69	89:11	64
2	Et_2O	10	rt	50	84:16	24
3	toluene	10	rt	50	89:11	43
4	benzene	10	rt	71	88:12	21
5	hexane	10	rt	63	86:14	28
6	$CHCl_3$	10	rt	53	90:10	10
7	CH_2Cl_2	10	rt	92	80:20	46
8	THF	10	rt	53	90:10	54
9	MeCN	10	rt	61	85:15	64
10	acetone	10	rt	85	83:17	35
11	DMF	10	rt	90	73:27	18
12	MeOH	10	rt	43	78:22	13
13	*i*-Pr_2O	1	rt	43	87:13	34
14	*i*-Pr_2O	5	rt	55	88:12	53
15	*i*-Pr_2O	20	rt	65	87:13	84
16	*i*-Pr_2O	20	0	66	90:10	60
17	*i*-Pr_2O	20	-10	65	90:10	32
18	*i*-Pr_2O	20	-20	64	92:08	23
19	*i*-Pr_2O	20	40	71	87:13	75

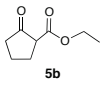
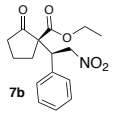
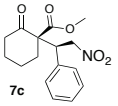
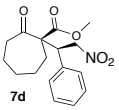
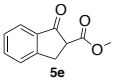
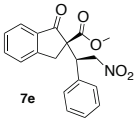
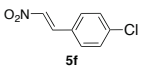
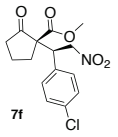
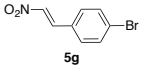
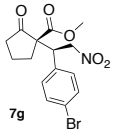
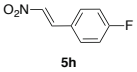
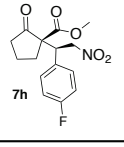
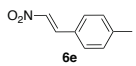
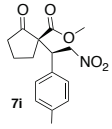
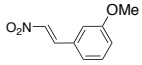
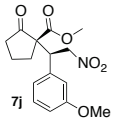
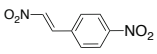
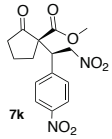
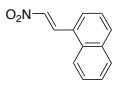
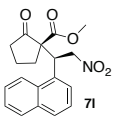
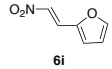
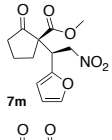
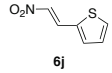
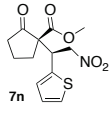
[a]Isolated yield. [b]Determined by ^{1}H NMR of crude reaction mixture. [c]The *ee* was determined by HPLC using CHIRALCEL OD-H column.

yield and diastereoselectivity were did not change at different reaction temperature at 0 °C, -10 °C and -20 °C (entries 16-18). However, satisfactory enantioselectivity was not observed in those temperatures. On the other hand, chemical yield improved to 75% at 40 °C, but enantioselectivity was reduced to 75% ee (entry 19). Considering of these results, it was assumed that the use of 20 mol% of catalyst **4d**, *i*-Pr_2O as a solvent, and the reaction at room temperature is the superior reaction condition to deliver the chiral Michael adduct **7a** with comparatively good satisfactory chemical yield and stereoselectivities (65%, 87:13, 84% ee) (entry 15).

After optimization of the reaction conditions, the ability of superior catalyst **4d** was extended to the addition using various β-keto esters **5a-e** and nitroolefins **6a-j** (Table 3). As a result, catalyst **4d** showed moderate to comparatively good catalytic activities to afford the corresponding Michael adducts **7b-n** for chemical yields (65-97%) and diastereoselectivities (75:25-95:5). However, those enantioselectivities were low to moderate (7-63% ee) in all of cases, although the reason is not clear. The results might be

Table 3. Substrate scope for Michael addition of **5a-e** with **6a-j** using catalyst **4d**

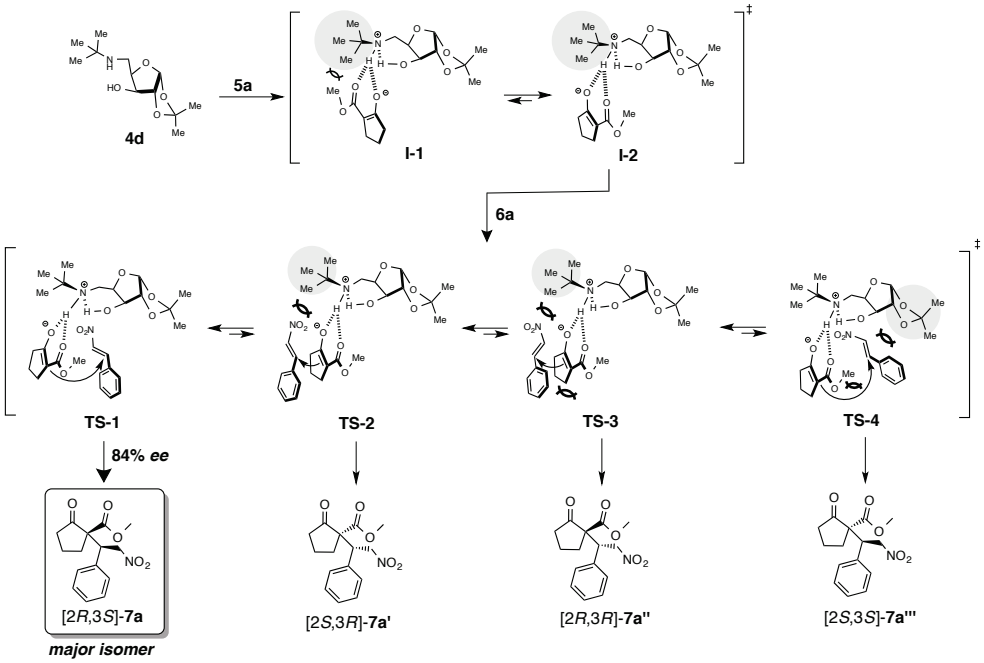


entry	substrate 5 or 6	adduct 7	yield (%)[a]	dr[b]	ee (%)[c] 7b-h
1	 5b	 7b	73	75:25	42[8]
2	 5c	 7c	69	92:8	38[9a]
3	 5d	 7d	70	78:22	7[9a]
4	 5e	 7e	80	90:10	8[9b]
5	 5f	 7f	75	90:10	34[8,9a]
6	 5g	 7g	77	89:11	29[8,9a]
7	 5h	 7h	84	86:14	35[3a,8]
8	 6e	 7i	80	87:13	12[3a,8]
9	 6f	 7j	65	87:13	35[8,9a]
10	 6g	 7k	72	80:20	36[8]
11	 6h	 7l	78	95:5	63[8,9a]
12	 6i	 7m	70	89:11	55[8,9a]
13	 6j	 7n	97	89:11	55[3a,8]

[a]Isolated yield. [b]Determined by ^{1}H NMR of crude reaction mixture. [c]*ee* was calculated by HPLC using CHIRALCEL OD-H or IC columns.

depended on each electric and/or steric properties of both β-keto esters **5b-e** having 5-7 membered carbocyclic rings structures or indanone structure and nitroolefins **6b-g** having the electron-withdrawing or electron-donating substituents on phenyl group (**6b**: Cl, **6c**: Br, **6d**: F, **6e**: Me, **6f**: OMe and **6g**: NO_2 groups) or the nature of aromatic rings (**6h**: naphthyl, **6i**: furanyl and **6j**: thiophenyl groups). The reactions of **5b-e** with **6a** were carried out in the presence of catalyst **4d** (entries 1-4). The reaction using ethyl 2-oxocyclopentanecarboxylate **5b** and **6a** did not afford better result than the same reaction using **5a** (entry 15, Table 2). The uses of β-keto esters **5c,d** having 6 or 7 membered carbocyclic rings afforded the corresponding Michael adducts **7c-d**. The enantioselectivities were decreased as with expansion of ring size, although moderate to good chemical yields and diastereoselectivities were afforded (**7c**: 62%, *dr*. 92:8, 38% ee, **7d**: 70%, *dr*. 78:22, 7% ee) (entries 2-3). On the other hand, the reaction of bulkier indanone **5e** with **6a** afforded adduct **7e** at good chemical yield and diastereoselctivity, but unfortunately enantioselectivity was drastically decreased (8% ee) (entry 4). The reactions of **5a** with **6b-g** afforded the corresponding Michael adducts **7f-k** with good chemical yields and diastereoselectivities (65-84%, *dr*. 80:20-90:10) (entries 5-10). However, those enantioselectivities were also low (12-36% ee) in this reaction condition. Moderate enantioselectivities (55-63% ee) were conformed when nitroolefins with bulky naphthyl group **6h**, heterocyclic furanyl **6i** and thiophenyl **6j** groups were used to afford the Michael adducts **7l-n** with good chemical yields and diastereoselectivities (70-97%, *dr*. 89:11-95:5) (entries 11-13). The determination of absolute stereochemistries of **7b-n** were confirmed on comparison with previous reports.[3a,b,8,9]

Based on good enantiopurity of the obtained Michael adduct [2*R*,3*S*]-**7a** (84% ee) in the reaction of **5a** with **6a** using catalyst **4d** (entry 15, Table 2) and the generation rate of the adducts **7a-a'''** based on HPLC data,[7a,b,k] the model of enantioselective reaction course was proposed as shown in Scheme 4. Initially, catalyst **4d** acts as a base to β-keto ester **5a** and the generated possible enolate is fixed with the ammonium hydrogen atom on catalyst species by hydrogen bonding interactions to generate stable intermediate **I-2** that has less steric interaction between *t*-butyl substituent on amino group of catalyst and enolate than that of intermediate **I-1**. Then, the enantioselective reaction might proceed through **TS-1** for affording major product **7a** that has a less steric interactions between substrate **6a** and *t*-butyl group on amino substituent of the ammonium catalyst species than that of **TS-2** for affording minor enantiomer **7a',** and also **TS-3** and **TS-4** for affording minor diastereomers **7a'', a'''** that have more steric interactions both between substrate **6a** and *t*-butyl group on amino substituent of the ammonium catalyst species and between **6a** and xylofuranose backbone of the catalyst species that those of **7a**.



Scheme 4. Plausible reaction course

In conclusion, xylofuranose based γ-amino alcohol **4** as an organocatalysts was used in asymmetric Michael addition of β-keto esters **5a-e** with nitroolefins **6a-j** for the first time and the corresponding several Michael adducts **7** bearing quaternary chiral carbon center were obtained (up to 98%, up to *dr*. 95:5, up to 84% ee). Although, catalyst **4** did not show remarkable catalytic activity in this reaction, the results might be useful for development of more effective sugar based amino alcohol organocatalyst to this reaction and others. The modification of xylofuranose based γ-amino alcohol organocatalysts, their applications to other substrates and the detailed mechanistic studies are in progress.

EXPERIMENTAL

Reagents and analytical grade solvents were obtained from commercial suppliers and used without further purification. All reactions were carried out under an argon atmosphere in flame-dried glassware. The reactions were monitored by thin layer chromatography (TLC). TLC was performed on Merck pre-coated silica gel 60 F-254 plates. Spots were visualized by exposure to UV light, by immersion into a solution of *p*-anisaldehyde followed by heating at ca. 200 °C. Column chromatography was performed on silica gel 60 N (Kanto Chemical Co., Inc., spherical, neutral, 40–50 μm). Melting points are uncorrected. IR spectra were recorded on JASCO FT/IR-4100. High-resolution mass spectra (HRMS) were measured on EI and FAB using sector instruments [Hitachi RMG-GMG and JEOL JNK- DX303]. NMR spectra were recorded on a JEOL JNM-ECA500 spectrometer, operating at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported downfield from TMS (δ = 0 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported downfield from TMS (δ = 0 ppm) or in the scale relative to the solvent signal [$CHCl_3$ (77.0 ppm)] as an internal reference. Coupling constants (*J*) are reported as hertz

(Hz). Splitting patterns are indicated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The enantiomeric excess (*ee*) was determined by HPLC analysis.

General procedure for the Michael addition of β-keto esters 5a-e to *trans*-β-nitroolefins 6a-j

To a stirred solution of *trans*-β-nitroolefins **6a-j** (0.34 mmol) and organocatalysts **4a-j** (0.03 mmol, 20 mol%) in *i*-Pr_2O (0.5 mL) were added β-keto esters **5a-e** (0.67 mmol) at room temperature. After the reaction completion was monitored by TLC, the mixture was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under a reduced pressure. The residue was purified by flash column chromatography on SiO_2 (*n*-hexane/EtOAc = 9:1) to afford the corresponding chiral Michael adducts **7a-n**. The ee were determined by HPLC using DAICEL CHIRALCEL OD-H (**7a-c,e-m**) or CHIRALPAK IC (**7d**) columns. DAICEL CHIRALCEL OD-H, (*n*-hexane/2-propanol = 90/10, flow rate 1.0 mL/min, λ= 220 nm) were used: (2*R*,3*S*)-**7a**[8,9a] [t_R (major): 14.01 min, t_R (minor): 10.03 min], (2*R*,3*S*)-**7b**[8] [t_R (major): 16.31 min, t_R(minor): 11.55 min], (2*R*,3*S*)-**7f**[8,9a] [t_R (major): 32.96 min, t_R(minor): 20.29 min], (2*R*,3*S*)-**7g**[8,9a] [t_R (major): 35.31 min, t_R (minor): 24.11 min], (2*R*,3*S*)-**7h**[3a,8] [t_R (major): 35.78 min, t_R(minor): 17.45 min], (2*R*,3*S*)-**7i**[3a,8] [t_R (major): 20.98 min, t_R (minor): 15.84 min], (2*R*,3*S*)-**7j**[8,9a] [t_R (major): 23.76 min, t_R(minor): 31.33 min], (2*R*,3*S*)-**7k**[3a,8] [t_R (major): 27.43 min, t_R (minor): 18.27 min], (2*R*,3*S*)-**7l**[8,9a] [(*n*-hexane/2-propanol:70/30, flow rate 1.0 mL/min, λ= 254 nm): t_R (major): 12.52 min, t_R(minor): 10.75 min], (2*R*,3*S*)-**7m**[8,9a] [t_R (major): 13.23 min, t_R(minor): 11.56 min], (2*R*,3*S*)-**7n**[3a,8] [t_R (major: 28.56 min, t_R(minor): 17.36 min), CHIRALCEL OD-H (*n*-hexane/2-propanol: 90/10, flow rate 0.5 mL/min, λ= 254 nm) was used: (2*R*,3*S*)-**7e**[9b] [t_R (major): 35.01 min, t_R(minor): 68.47 min], DAICEL CHIRALPAK IC (*n*-hexane/2-propanol:90/10, flow rate 1.0 mL/min, λ= 220 nm) was used: (2*R*,3*S*)-**7c**[9a] [t_R (major): 39.9 61 min, t_R(minor): 24.40 min], DAICEL CHIRALPAK IC (*n*-hexane/2-propanol:90/10, flow rate 1.0 mL/min, λ= 210 nm) was used: (2*R*,3*S*)-**7d**[9a] [t_R (major): 38.56 min, t_R(minor): 23.96 min].

General procedure for the preparations of γ-amino alcohol organocatalysts 4a-j

To a stirred solution of compounds **3a,b** (0.20 g, 0.58 mmol) in 2-propanol (15 mL) was added corresponding amines (2.40 mmol) and heated to reflux condition for 24 h. After completion of reaction, solvents were evaporated under reduced pressure. Neutralized with solid $NaHCO_3$ and organic layer was extracted using Et_2O as three portions (3 × 10 mL). The obtained combined organic layers were dried on Na_2SO_4, concentrated and recrystallized using hexane to give the compounds **4a-j**. Compounds **4a-i** are known compounds and were identified by spectroscopic data, which were in good agreement with those reports.

1,2-Cyclohexylidene-5-*O*-(*t*-butylamino)-α-D-xylofuranose 4j: Yellow solid; mp 76.7 °C; IR (neat): 3294, 2936, 1391, 1298, 1109 cm^{-1}; $[\alpha]_D^{20}$ +23.52 (c 0.51, CH_2Cl_2); ^{1}H-NMR (DMSO-D_6) δ 5.82 (d, *J* = 4.0 Hz, 1H), 4.35 (d, *J* = 4.0 Hz, 1H), 3.98 (m, 2H), 2.82 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.73 (q, *J* = 5.7 Hz, 1H), 1.58-1.45 (m, 8H), 1.32 (m, 2H), 1.01 (s, 9H); ^{13}C-NMR (DMSO-D_6) δ 111.3, 104.4, 85.4, 79.9, 75.4, 50.5, 41.1, 36.5, 35.8, 28.9, 25.0, 24.1, 23.8; MS (EI): *m/z* = 285 $[M]^+$, HRMS *m/z*: [EI] calculated for $C_{15}H_{27}NO_4$: 285.1940; found: 285.1945.

REFERENCES

1. (a) K. W. Quasdorf and L. E. Overman, *Nature*, 2014, **516**, 181; (b) J. G. Hernandez and E. Juaristi, *Chem. Commun*., 2012, **48**, 5396; (c) H. Pellissier, 'Recent advances in asymmetric organocatalysis,' RSC Publishing, 2010, pp. 1-220; (d) E. Marques-Lopez, R. P. Herrera, and M. Christmann, *Nat. Prod. Rep*., 2010, **27**, 1138; (e) S. Bertelsen and K. A. Jorgensen, *Chem. Soc. Rev*., 2009, **38**, 2178; (f) D. W. C. MacMillan, *Nature*, 2008, **455**, 304; (g) M. Gruttadauria, F. Giacalone, and R. Noto, *Chem. Soc. Rev*., 2008, **37**, 1666; (h) M. J. Gaunt, C. C. C. Johansson, A. McNally, and N. T. Vo, *Drug Discov. Today*, 2007, **12**, 8; (i) B. List, *Chem. Rev*., 2007, **107**, 5413; (j) P. I. Dalko, 'Enantioselective organocatalysis: reaction and experimental procedure', WILEY-VCH, 2007; (k) J. Seayad and B. List, *Org. Biomol. Chem*., 2005, **3**, 719; (l) W. Notz, F. Tanaka, and C. F. Barbas, *Acc. Chem. Res*., 2004, **37**, 580.
2. (a) K. Jain, S. Chaudhuri, K. Pal, and K. Das, *New J. Chem*., 2019, **43**, 1299; (b) O. Illa, O. Porcar-Tost, C. Robledillo, C. Elvira, P. Nolis, O. Reiser, V. Branchadell, and R. M. Ortuno, *J. Org. Chem*., 2018, **83**, 350; (c) S. Umemiya, D. Sakamoto, G. Kawauchi, and Y. Hayashi, *Org. Lett*., 2017, **19**, 1112; (d) Y. Fan and S. R. Kass, *J. Org. Chem*., 2017, **82**, 13288; (e) M. Chennapuram, U. V. Subba Reddy, C. Seki, Y. Okuyama, E. Kwon, K. Uwai, M. Tokiwa, M. Takeshita, and H. Nakano, *Eur. J. Org. Chem*., 2017, 4633; (f) J. M. Andres, J. Losada, A. Maestro, P. R. Ferrer, and R. Pedrosa, *J. Org. Chem*., 2017, **82**, 8444; (g) F. E. Held and S. B. Tsogoeva, *Catal. Sci. Technol*., 2016, **6**, 645; (h) A. Ruiz-Olalla, M. G. Retamosa, and F. P. Cossio, *J. Org. Chem*., 2015, **80**, 5588; (i) P. Chauhan, S. Mahajan, U. Kaya, D. Hack, and D. Enders, *Adv. Synth. Catal*., 2015, **357**, 253; (j) C. H. Muller, C. Rosner, and U. Hennecke, *Chem. Asian J*., 2014, **9**, 2162; (k) O. V. Serdyuk, C. M. Heckel, and S. B. Tsogoeva, *Org. Biomol. Chem*., 2013, **11**, 7051; (l) H. W. Moon and D. Y. Kim, *Tetrahedron Lett*., 2012, **53**, 6569; (m) W. Yang and D.-M. Du, *Org. Lett*., 2010, **12**, 5450; (n) Vishnumaya and V. K. Singh, *Org. Lett*., 2007, **9**, 1117; (o) J. Wang, H. Li, X. Yu, L. Zu, and W. Wang, *Org. Lett*., 2005, **71**, 4293; (p) J. F. Austin and D. W. C. MacMillan, *J. Am. Chem. Soc*., 2002, **124**, 1172.
3. (a) R. Togashi, M. Chennapuram, C. Seki, Y. Okuyama, E. Kwon, K. Uwai, M. Tokiwa, M. Takeshita, and H. Nakano, *Eur. J. Org. Chem*., 2019, 3882; (b) I. A. Owolabi, M. Chennapuram, C. Seki, Y. Okuyama, E. Kwon, K. Uwai, M. Tokiwa, M. Takeshita, and H. Nakano, *Bull. Chem. Soc.*

Jpn., 2019, **92**, 696; (c) M. Chennapuram, I. A. Owolabi, C. Seki, Y. Okuyama, E. Kwon, K. Uwai, M. Tokiwa, M. Takeshita, and H. Nakano, *ACS Omega*, 2018, **39**, 11718; (d) I. A. Owalabi, U. V. S. Reddy, C. Seki, Y. Okuyama, K. Uwai, M. Tokiwa, M. Takeshita, and H. Nakano, *Tetrahedron*, 2018, **74**, 4705; (e) U. V. Subba Reddy, M. Chennapuram, K. Seki, C. Seki, B. Anusha, E. Kwon, Y. Okuyama, K. Uwai, M. Tokiwa, M. Takeshita, and H. Nakano, *Eur. J. Org. Chem*., 2017, 3874.

4. (a) H. Nakano, J. Yokoyama, Y. Okuyama, R. Fujita, and H. Hongo, *Tetrahedron: Asymmetry*, 2003, **14**, 2361; (b) M. Dieguez, A. Ruiz, and C. Claver, *Tetrahedron: Asymmetry*, 2001, **12**, 2861.
5. (a) X. Gel, C. Qian, and X. Chen, *J. Mater. Sci. Chem. Eng*., 2015, **3**, 48; (b) X. Gel, C. Qian, Y. Chen, and X. Chen, *Tetrahedron: Asymmetry*, 2014, **25**, 596.
6. (a) B. T. Cho and N. Kim, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2901; (b) B. T. Cho and N. Kim, *Synth. Commun*., 1995, **25**, 167; (c) M. Popsavin, V. Popsavin, N. Vukojevic, and D. Miljkovic, *Chem. Commun*., 1994, **59**, 1884.
7. (a) S. A. Chhanda and S. Itsuno, *J. Catal*., 2019, **377**, 543; (b) P. Chauhan and S. S. Chimni, *Asian J. Org. Chem*., 2012, **1**, 138; (c) Y. F. Wang, R. X. Chen, K. Wang, B. B. Zhang, Z. B. Lib, and D. Q. Xu, *Green Chem*., 2012, **14**, 893; (d) A. Lattanzi, C. D. Fusco, A. Russo, A. Poaterb, and L. Cavallo, *Chem. Commun*., 2012, **48**, 1650; (e) T. Nemoto, K. Obuchi, S. Tamura, T. Fukuyama, and Y. Hamada, *Tetrahedron Lett*., 2011, **52**, 987; (f) A. M. Flock, A. Krebs, and C. Bolm, *Synlett*, 2010, 1219; (g) X. Jiang, Y. Zhang, X. Liu, G. Zhang, L. Lai, L. Wu, J. Zhang, and R. Wang, *J. Org. Chem*., 2009, **74**, 5562; (h) Z. Zhang, X. Dong, D. Chen, and C. Wang, *Chem. Eur. J*., 2008, **14**, 8780; (i) F. Z. Peng, Z. H. Shao, B. M. Fan, H. Song, G. P. Li, and H. B. Zhang, *J. Org. Chem*., 2008, **73**, 5202; (j) J. Wang, H. Li, W. Duan, L. Zu, and W. Wang, *Org. Lett*., 2005, **7**, 4713; (k) J. Deutsch and H. J. Niclas, *J. Prakt. Chem*., 1995, **337**, 23.
8. (a) M. S. Ullah and S. Itsuno, *Mol. Catal*., 2017, **438**, 239; (b) B. T. Kumpuga and S. Itsuno, *Catal. Commun*., 2019, **118**, 5; (c) M. S. Ullah and S. Itsuno, *ACS Omega*, 2018, **3**, 4573; (d) K. Murai, S. Fukushima, S. Hayashi, Y. Takahara, and H. Fujioka, *Org. Lett*., 2010, **12**, 964.
9. (a) D. F. Chen, P. Y. Wu, and L. Z. Gong, *Org. Lett*., 2013, **15**, 3958; (b) J. Luo, L. Xu, R. A. S. Hay, and Y. Lu, *Org. Lett*., 2009, **11**, 437.