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## Accepted Article

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# Intramolecular and Ferrier Rearrangement Strategy for the Construction of C1-*β*-D-xylopyranosides: Synthesis, Mechanism and Biological Activity Study

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**Abstract.** A stereoselective synthesis of C1-*β*-D-xylopyranoside derivatives had been developed via intramolecular 1,3-acyloxy migration/Ferrier rearrangement stategy from readily available propargylic carboxylates and D-xylal. A combined catalytic system of chloro(triphenylphosphine)gold(I) ($Ph_3PAuCl$) and silver hexafluoroantimonate ($AgSbF_6$) was found to possess the most effective of the reaction, and 20 examples tested the wide functional compatibility for these transformation. Nuclear magnetic resonance (NMR), infrared spectrum (IR), high resolution electrospray ionization mass spectroscopy (HRESIMS) and isotopic labelling experiments were utilized to investigate the C1-glycosylation process. The relative configuration for the products was determined by two-dimensional (2D) NMR NMR and electronic circular dichroism spectroscopy. 3-(4,5)-Dimethylthiahiazo(-z-y1)-3,5-diphenytetrazoliumro-mide (MTT) cell viability assays indicated that three of them showed strong anti-proliferative activities against human gastric cancer HGC-27 cells with $IC_{50}$ values of 17.09-38.88 μM. This method opened up new horizons for the synthesis of bioactive C-glycosylated molecules.

**Keywords:** C1-glycosylation; 1,3-acyloxy migration; Ferrier rearrangement; gold (I) catalysis; cytotoxicity

Compared to O- and N-glycoside, the C-glycoside comprises a carbohydrate unit attached to an aglycone or another carbohydrate unit through a C-C bond linkage. Due to the stability toward hydrolysis of C-glycosides, the mimics of O-glycosides have been widely reported with potent biologically activities in natural products and synthetic drugs in recent years, such as (-)-Dysiherbaine[1], (-)-Neodysiherbaine A[2], Deoxyfrenolicin[3], Pro-Xylane™[4],(-)-Kendomycin[5], Lactoquinomycin A[6] and (+)-Ambruticin S[7] (Figure 1). Because of the potential bioactivity as well as the synthetic challenges, these carbohydrate moieties have attracted considerable interest in the total synthesis and glycosylation methodologies[8].

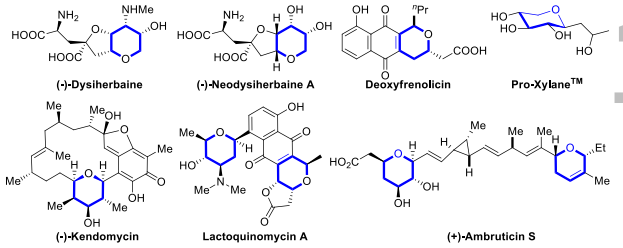


**Figure 1.** Some natural products and drugs containing C-glycosides.

Generally, C-glycosylation reactions can involve glycosyl electrophilic/cationic species, anionic species, radical species, or transition-metal complexes. Therefore, the synthesis of C-glycosylation usually involves the metal reagents as glycosyl donors or catalysts, and the process is much more sluggish due to the air and moisture sensitivities[9]. Although lots of transitional metal-catalyzed cross coupling including Heck, Suzuki, Stille and Negishi-type reactions have been developed for the synthesis of C-glycosides using glycals, the functional regioselectivity and *α*/*β* stereoselectivity at the anomeric carbon constitute are still one of the most challenging issues in carbohydrate chemistry[10]. For example, Ernest's group utilized $Pd^0$-mediated cyclo-etherification of 1-acetoxy-2,3-dideoxy-oct-2-enitols to produce C-vinyl *α*- and *β*-glycopyranosides with high stereoselectivity

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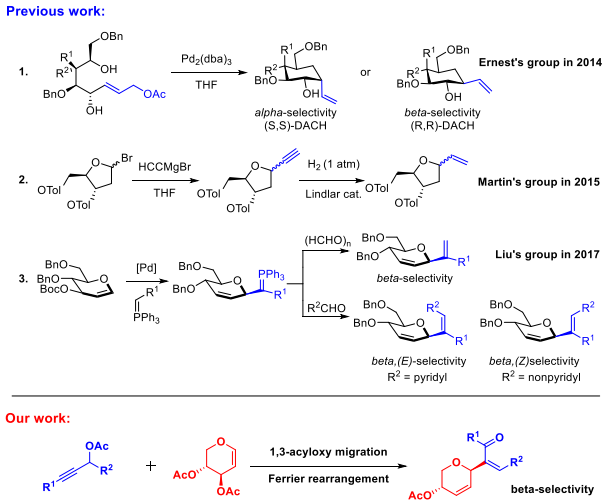
using (*S*,*S*) or (*R*,*R*)-DACH ligands in 2014[11], and then Martin's group produced epimeric mixture of C-vinyl deoxyriboside by the Lindlar hydrogenation of the epimeric mixture of C-ethynyl deoxyriboside[12]. Liu's group reported a palladium-catalyzed one-pot Tsuji-Trost type decarboxylative allylation/Wittig reaction to synthesize *β*,(*E*)-selective C-vinyl glycosides with pyridyl group containing aldehydes and *β*,(*Z*)-selective C-vinyl glycosides with nonpyridyl aldehydes in 2017, which had potential to be applied in synthesizing C-vinyl glycosides in high efficiency with controlled diastereoselectivity[13].

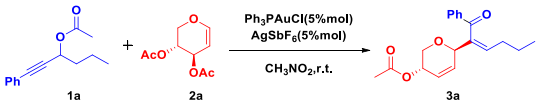



**Scheme 1.** The synthesis of C-vinyl glycosides

For facial construction of synthetically valuable complex C-glycosides, the intramolecular rearrangements including Claisen rearrangement, Ramberg-Bäcklund rearrangement, and 1,2-Wittig rearrangement have become powerful tools for the C-glycosylations[14]. The homogeneous gold catalysis, an exciting new synthetic tool to build synthetically valuable complex molecules, has become a hot spot in organometallic chemistry since 2005[15], which could activate alkenyl, allenyl and alkynyl p-bonds based on the strong *p*-acidic character of complexes of Au(I) and Au(III)[16]. Among them, cationic phosphine-gold (I) complexes are especially versatile and selective catalysts for a growing number of synthetic transformations[17]. Recently, *β*-xylopyranosides have attracted renewed interest due to the development of interesting biological activities and material usage[18]. As continuation of previous studies on the C-glycosylation reaction using homogeneous gold catalysis by Ferrier rearrangement[19], the one-pot intramolecular cross coupling reactions of propargylic acetates and diacetyl-D-xylal via 1,3-acyloxy migration and Ferrier rearrangement was investigated in this work.

In order to screen the proper conditions for C1-glycosylation from propargylic acetate (**1a**) and diacetyl-D-xylal (**2a**), seven transitional metals were evaluated the abilities of inducing the Ferrier rearrangement of **2a** to give the C1-alkylation products, however, gold (III) chloride was found to be the effective catalyst to transform the propargylic ester to the nucleophillic allene intermediate and give the final Ferrier rearrangement C1-glycosylation product **3a** in 24% isolated yields (Table 1, entries 1-7). This positive result promoted us to further search more appropriate catalyst to improve the efficiency of the reaction, and then the gold (I) complex and silver (I) salts could catalyze the reaction in comparative yields (entries 8-10). To our surprise, we found that the combined catalytic system exhibited superior to the single catalyst (entries 11-14). Therefore, $Ph_3PAuCl$ and $AgSbF_6$ system was selected as the best catalyst for the high yield of 58% yields, and further optimization of solvent contributed to improve the yield of **3a** in 75% yields (Table 1, entries 14-20). Finally, the C1-glycoside could be smoothly prepared from propargylic acetate and diacetyl-D-xylal under the catalytic $Ph_3PAuCl/AgSbF_6$ in nitromethane at ambient temperature.

**Table 1.** Optimization of C1-glycosylation[a]




| Entry | Catalyst | Solvent | Yield[b] |
|---|---|---|---|
| 1 | $AgNO_3$ | $CH_2Cl_2$ | N.D. |
| 2 | $Pd(OAc)_2$ | $CH_2Cl_2$ | N.D. |
| 3 | $Cr(OAc)_3$ | $CH_2Cl_2$ | N.D. |
| 4 | $Cu(OAc)_2$ | $CH_2Cl_2$ | N.D. |
| 5 | $PdCl_2$ | $CH_2Cl_2$ | N.D. |
| 6 | $SrCl_2$ | $CH_2Cl_2$ | N.D. |
| 7 | $AuCl_3$ | $CH_2Cl_2$ | 24% |
| 8 | $Ph_3PAuCl$ | $CH_2Cl_2$ | 45% |
| 9 | $AgSbF_6$ | $CH_2Cl_2$ | 35% |
| 10 | AgOTf | $CH_2Cl_2$ | 20% |
| 11 | $Ph_3PAuCl$+ AgOTf | $CH_2Cl_2$ | 50% |
| 12 | $AuCl_3$+ AgOTf | $CH_2Cl_2$ | 42% |
| 13 | $AuCl_3$+ $AgSbF_6$ | $CH_2Cl_2$ | 38% |
| 14 | $Ph_3PAuCl$ + $AgSbF_6$ | $CH_2Cl_2$ | 58% |
| 15 | $Ph_3PAuCl$ + $AgSbF_6$ | $CH_3NO_2$ | 75% |
| 16 | $Ph_3PAuCl$ + $AgSbF_6$ | $CHCl_3$ | 37% |
| 17 | $Ph_3PAuCl$ + $AgSbF_6$ | Toluene | 43% |
| 18 | $Ph_3PAuCl$ + $AgSbF_6$ | EtOAc | N.D. |
| 19 | $Ph_3PAuCl$ + $AgSbF_6$ | $CH_3CN$ | N.D. |
| 20 | $Ph_3PAuCl$ + $AgSbF_6$ | $HCON(CH_3)_2$ | N.D. |

[a] General conditions: propargylic carboxylate (**1a**, 1.0 equiv.), diacetyl-D-xylal (**2a**, 1.0 equiv.), $Ph_3PAuCl$ and $AgSbF_6$ (5 mol %). Solvent: 2 mL. [b] Isolated yield. N.D. = not detected.

Under the optimized reaction condition, the substrate scope of the C1-glycosylation reaction was examined (Scheme 2). The electron-donating groups connected on the phenyl group ($R^1$) of propargylic acetate resulted in poor *β*-stereoselectivity at the anomeric carbon and lower yields (62%-70%) for the C1-*β*-D-xylopyranoside derivatives (compounds **3k**-

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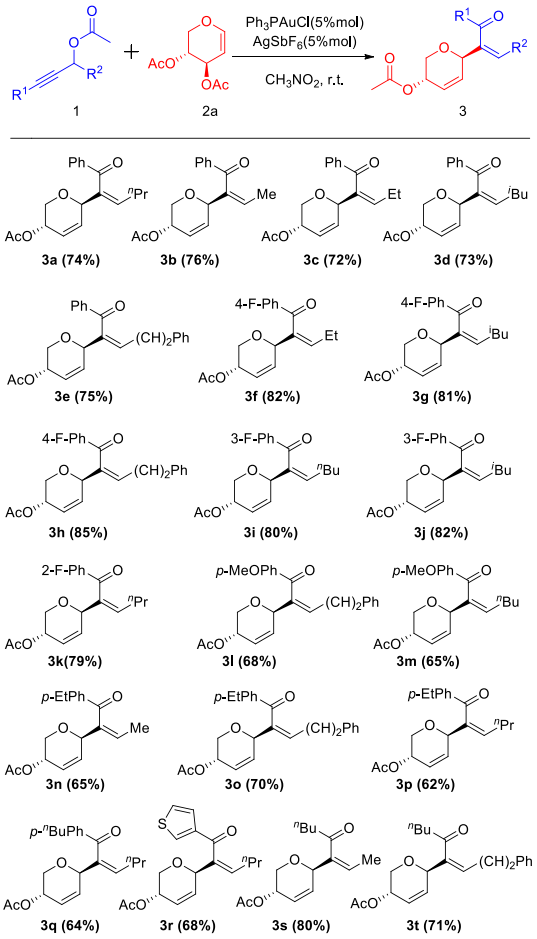
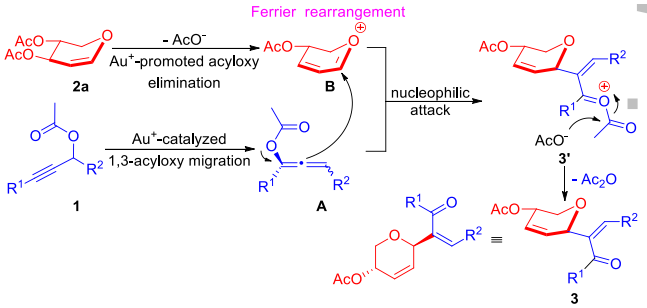
**3q**), while the electron-withdrawing groups usually resulted in better stereoselectivity and yields (79%-85%, compounds **3f**-**3k**). Further exploration of the substrate scope was focused on the aliphatic substituted group or heterocyclic group ($R^1$) on the triple bond of propargylic acetate, which also gave moderate yields (68%~80%) for compounds **3r**-**3t**. It was worth noticing that the Boc-protecting-D-xylal failed to give the C1-*β*-D-xylopyranosides (**3**) under the same reaction condition.

The relative *β*-configuration for **3d** was confirmed by NMR and electronic circular dichroism spectroscopy. In NOESY, the correlation between H-1 (5.32 ppm) and H-7 (6.38 ppm) could be observed, and its relative *β*-configuration could be defined as trans-isomer for the anomeric carbon with the observed coupling constants of 5-H$^a$ (4.27 ppm, dd, $J$ = 10.8, 5.2 Hz, 1H) and 5-H$^b$ (3.59 ppm, dd, $J$ = 10.8, 7.6 Hz, 1H), which were consistent with previuos reported[20]. Furthermore, the absolute configuration of the C1-glycoside was also tested by experimental electronic circular dichroism spectroscopy, and its possible configurations were calculated by DFT B3LYP method of gaussian software[21]. The result was found to be consistent with the *β*-anomer's calculations and the product configuration was inferred to be the *β*-configuration.




**Scheme 2.** Substrate scope for C1-*β*-D-xylopyranoside derivatives

Based on the experimental results and related literatures[22], the following mechanistic pathways were proposed. At first, the formation of allylic oxocarbenium ion (**B**) from diacetyl-D-xylal (**2a**) via a Ferrier rearrangement was promoted by gold catalyst, then transformation of the propargylic carboxylate (**1**) into the nucleophilic allenic intermediate (**A**) through a 1,3-acyloxymigration which subsequently attacked intermediate (**B**) to give the oxocar benium ion (**3'**). Finally, the hydrolysis of oxocarbenium ion (**3'**) delivered the target C1-*β*-D-xylopyranosides (**3**). Owing to the stability of the equatorial conformation for large substituents, the stereo-structure for the C1-*β*-D-xylopyranosides was finally obtained (Scheme 3).




**Scheme 3.** Proposed mechanism for C1-*β*-D-xylopyranosyl ation reaction

In order to confirm this reaction mechanism, $^{31}P$ NMR experiment, infrared detection experiment, $^1H$ NMR detection experiments and isotopic labeling experiments were carried out to monitor the catalyst combination way and reaction process more clearly. Considering the proposed mechanism for the synthesis of the C1-*β*-D-xylopyranosides (Scheme 3) and the prerequisite for the generation of nucleophillic allene intermediate (**A**) from propargylic acetate (**1**), the monitored infrared spectrum experiment was also carried out to observe the spectrum properties of intermediate and the synchronous monitoring results were shown in Figure 2. Notably, a peak signal at the wavelength of 2435 $cm^{-1}$ could be observed when the catalyst was added, which disappeared after quenching. This signal might be attributed to the allene intermediate (**A**) from propargylic carboxylate (**1**) (Figure 2a). Furthermore, allene experiment in the same condition further confirmed this result (Figure 2b).

To assess the product more clearly, $^1H$ NMR detection experiment was carried out in $CDCl_3$ solution[23]. As shown in Figure 3, before adding the catalyst, the multiplet $^1H$ NMR peaks appeared 6.52 ppm which be longed to 1-H signal of the diacetyl-D-xylal. With the catalyst added in, this proton signal

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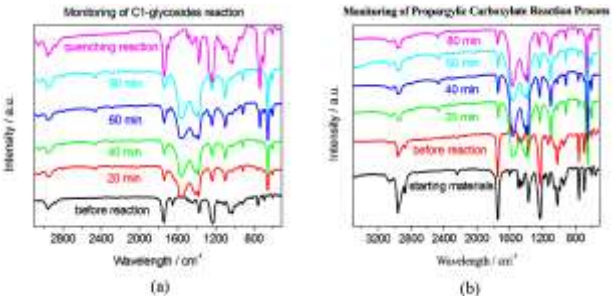



**Figure 2.** IR monitoring of the reaction progress.
[a] propargylic carboxylates (**1a**, 0.05 mol), diacetyl-D-xylal (**2a**, 0.05 mol) and $(Ph_3P)AuSbF_6$ (5% mol). [b] allenic intermediate (0.05 mol), D-xylal (0.05 mol) and $(Ph_3P)AuSbF_6$ (5% mol).

disappeared because of Ferrier rearrangement. Two minutes later, a new doublet appeared at 6.38 ppm when the catalyst was added, which might attribute as the olefinic proton of H-7 in the enone skeleton.

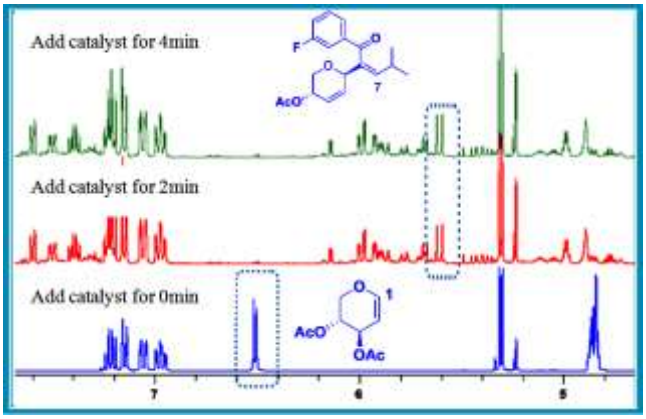
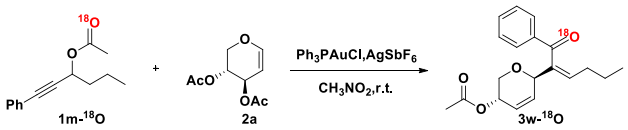



**Figure 3.** $^1$H NMR monitoring of the reaction progress.

The mechanism was further confirmed through isotopic labeling experiments by performing the reaction with $^{18}$O-labeled propargylic carboxylate **1m**-$^{18}$O according to related literatures[24]. The $^{18}$O-labeled ketone's carbon signal at 197.2 ppm could be clearly found in the $^{13}$C NMR of **3w**-$^{18}$O, where ESI-HR-MS analysis also showed the presence of $^{18}$O in the product, which indicated the success of the 1,3-acyloxy rearrangement and nucleophilic C1-glycosylation process (Scheme 4).

As our continuous interest in search of the biological antitumor agents[25], all the target




**Scheme 4.** Isotopic labeling experiment

compounds were also evaluated for *in vitro* anti-proliferative activities against two human cancer cell lines (HGC-27 and Caski) for 48 h at 37 ˚C by MTT assays[26]. Unfortunately, just three of them (**3c**, **3f**, **3l**) were found to possess the better anti-cytotoxic activities against HGC-27 cells with $IC_{50}$ values of 17.09~38.88 μM (Table 2). Compound **3l** also showed cytotoxic activities against Caski cells with $IC_{50}$ 63.63 μM. These results indicated the introduction of phenyl resulted in increasing cytostatic effect while unsubstituted phenyl group shows better inhibition rate than substituted. Notably, these C1-*β*-D-xylopyranosides exhibited low toxicity against to the normal human hepatic LO2 cells ($IC_{50}$ > 500 μM). The further structural exploration and anti-tumor mechanism study for these C1-*β*-D-xylopyranosides are under way in our research group.

**Table 2.** Calculated antiproliferative $IC_{50}$ values for some cytotoxic compounds

| Compounds | $IC_{50}$ values (μM) | | |
|---|---|---|---|
| | HGC-27 | Caski | $LO_2$ |
| **3c** | 17.09 | >100 | >500 |
| **3f** | 30.12 | >100 | >500 |
| **3l** | 38.88 | 63.63 | >500 |

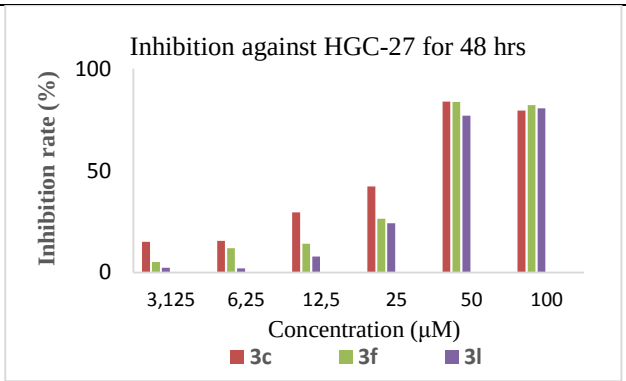



**Figure 4.** Inhibition against HGC-27 cells for 48 hours

In conclusion, a highly stereoselective synthesis of bioactive C1-*β*-D-xylopyranosides was developed based on strategy of intramolecular 1,3-acyloxy migration/Ferrier rearrangement process. The versatility and flexibility of this method was evident from its extensive substrate scope. Remarkably, high yields and exclusive regioselectivity and diasteroselectivity were obtained, demonstrating that the reaction tolerates a wide range of substituents. In addition, the potential of employing this method to construct synthetically valuable complex molecules will be their increasing applications in synthesizing of structurally diverse and functional natural products.

## Experimental Section

**Typical procedure for the synthesis of 1-phenylhept-1-yn-3-yl acetate (1a)**

Phenylacetylene (0.91 g, 7.0 mmol) was added to the reaction flask and then nitrogen protection, after that, added in re-steamed THF (6 mL) to stir for 5 minutes. *n*-BuLi (2.4 mol/L, 2.9 mL, 7mmol) was injected at a low temperature (-78℃), after the mixture was stirred for 5 min under the dewar, added the 1-butyraldehyde (0.435 g) and stirred at room temperature until the starting material was completely consumed. The mixture was concentrated in vacuo. Purification of the residue by flash chromatography on silica gel (petroleum ether / ethyl acetate = 100:1, V/V) and afforded the propargylic carboxylate (**1a**) as colorless oil.

**Typical procedure for the synthesis of (3*R*,6*S*)-6-((*Z*)-1-oxo-1-phenylhex-2-en-2-yl)-3,6-dihydro-2H-pyran-3-yl acetate (3a)**

A solution of diacetyl-D-xylal (**2a**, 0.2 mmol) and 1-phenylhex-1-yn-3-yl acetate (**1a**, 0.2 mmol) in anhydrous $CH_3NO_2$ (2.0 mL) was stirred at room temperature for 10 min. $Ph_3PAuCl$ (4.9 mg, 5.0 mol %) and $AgSbF_6$ (2.6 mg, 5 mol %) was added sequentially. The reaction was stirred at room temperature until the starting material was completely consumed. The mixture was filtered through a plug of silica and concentrated in vacuo. Purification of the residue by flash chromatography on silica gel (petroleum ether / ethyl acetate = 100:1, V/V) and afforded the C-xylopyranoside (**3a**).

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## References

[1] a) R. Sakai, H. Kamiya, M. Murata, K. Shimamoto, *J. Am. Chem. Soc.* **1997**, *119*, 4112-4116. b) H. Masak, J. J. Maeyama, Kazuko Kamada, T. Esumi, Y. Iwabuchi, S. Hatakeyama, *J. Am. Chem. Soc.* **2000**, *122*, 5216-5217. c) L. V. Flórez, P. H. W. Biedermann, T. Engla, M. Kaltenpoth, *Nat. Prod. Rep.* **2015**, *32*, 904-936.

[2] a) R. Sakai, T. Koike, M. Sasaki, K. Shimamoto, C. Oiwa, A. Yano, K. Suzuki, K. Tachibana, H. Kamiya, *Org. Lett.* **2001**, *3*, 1479-1482. b) P. Escavabaja, J. Viala, Y. Coquerel, J. Rodriguez, *Adv. Synth. Catal.* **2012**, *354*, 3200-3204. c) R. Sakai, G. T. Swansonb, *Nat. Prod. Rep*. **2014**, *31*, 273-309.

[3] a) L. D. Foland, O. H. W. Decker, H. W. Moore, *J. Am. Chem. Soc.* **1989**, *111*, 989-995. b) Briar J. Naysmith, Paul A. Hume, Jonathan Sperry and Margaret A. Brimble, *Nat. Prod. Rep*. **2017**, *34*, 25-61.

[4] A. Cavezza, C. Boulle, A. Gueguiniat, P. Pichaud, S. Trouille, L. Ricard and M. Dalko-Csiba, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 845-849. N. Pineau, D. A. Carrino, A. I. Caplan, L. Breton, *Eur. J. Dermatol.* **2011**, *21*, 359-370.

[5] a) Y. Yuan, H. Men, C. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 14720-14721. b) K. C. Nicolaou, S. P. Ellery, J. S. Chen, *Angew.Chem. Int. Ed.* **2009**, *48*, 7140-7165. c) T. Sengoku, S. Xu, K. Ogura, Y. Emori, K. Kitada, D. Uemura, H. Arimoto, *Angew. Chem. Int. Ed.* **2014**, *53*, 4213-4216.

[6] a) P. M. Léo, C. Morin, C. Philouze, *Org. Lett.* **2002**, *4*, 2711-2714. b) R. T. Williamson, L. A. McDonald, L. R. Barbieri, G. T. Carter, *Org. Lett.* **2002**, *4*, 4659-4662. c) H. Sun, Z. Liu, H. Zhao, E. L. Ang, *Drug Des. Devel. Ther.* **2015**, *9*, 823-833.

[7] a) T. A. Kirkland, J. Colucci, L. S. Geraci, M. A. Marx, M. Schneider, D. E. Kaelin, S. F. Martin, *J. Am. Chem. Soc.* **2001**, *123*, 12432-12433. b) E. Lee, S. J. Choi, H. Kim, H. O. Han, Y. K. Kim, S. J. Min, S. H. Son, S. M. Lim, W. S. Jang, *Angew. Chem. Int. Ed.* **2002**, *41*, 176-178. c) S. F. Martin, *J. Org. Chem.* **2017**, *82*, 10757-10794.

[8] a) C. Taillefumier, Y. Chapleur, *Chem. Rev.* **2004**, *104*, 263-292. b) K. Lalitha, K. Muthusamy, Y. S. Prasad, P. K. Vemula, S. Nagarajan, *Carbohydr. Res.* **2015**, *402*, 158-171. c) M. M. Wei, Y. S. Wang, X. S. Ye, *Med. Res. Rev.* **2018**, *38*, 1003-1026. d) S. Tang, Q. Zheng, D. C. Xiong, S. Jiang, Q. Li, X. S. Ye, *Org. Lett.* **2018**, *20*, 3079-3082.

[9] For selected reviews on chemical synthesis of C-glycosides, see: a) Y. Yang, B. Yu, *Chem. Rev.* **2017**, *117*, 12281-12356. b) H. Liao, J. Ma, H. Yao, X. W. Liu, *Org. Biomol. Chem.* **2018**, *16*, 1791-1806. c) W. L. Leng, H. Yao, J. X. He, X. W. Liu, *Acc. Chem. Res.* **2018**, *51*, 628-639.

[10] M. J. Mckay, H. M. Nguyen, *ACS. Catal.* **2012**, *2*, 1563-1595.

[11] E. G. Nolen, V. C. Ezeh, M. J. Feeney, *Carbohydr. Res.* **2014**, *396*, 43-47.

[12] I. Snajdr, K. Parkan, F. Hessler, M. Kotora, *Beilstein. J. Org. Chem.* **2015**, *11*, 1392-1397.

[13] W. L. Leng, H. Liao, H. Yao, Z. E. Ang, S. Xiang, X. W. Liu, *Org. Lett.* **2017**, *19*, 416-419.

[14] Y. Yang, B. Yu, *Chem. Rev.* **2017**, *117*, 12281-12356. b) B. Yu, *Acc. Chem. Res.* **2018**, *51*, 507-516.

[15] For reviews on gold-catalyzed reactions, see: a) A. Stephen K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180-3211 b) D. Qian, J. Zhang, *Chem. Soc. Rev.* **2015**, *44*, 677-698. c) D. Pflästerer, A. S. K. Hashmi, *Chem. Soc. Rev.* **2016**, *45*, 1331-1367. d) G. J. Hutchings. *ACS Cent Sci.* **2018**, *4*, 1095-1101.

[16] a) D. P. Day, P. W. H. Chan, *Adv. Synth. Catal.* **2016**, *358*, 1368-1384. b) Y. Yu, W. B. Yang, F. Rominger, A. Stephen, K. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 7586-7589. c) C. Obradors, A. M. Echavarren, *Acc. Chem. Res.* **2013**, *47*, 902-912. d) D. H. Zhang, X.Y. Tang, M. Shi, *Acc. Chem. Res.* **2013**, *47*, 913-924.

[17] D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395-403.

[18] a) C. H. Yao, J. S. Song, C. T. Chen, T. K. Yeh, M. S. Hung, *J. Med. Chem.* **2011**, *54*, 166-178. b) A. Siegbahn, K. Thorsheim, J. Stahle, S. Manner, C. Hamark, *Org. Biomol. Chem.* **2015**, *13*, 3351-3362. c) C. Brusa, M. Muzard, C. Rémond, R. Plantier-Royon, *RSC Adv.* **2015**, *5*, 91026-91055.

[19] a) N. Y. Huang, H. Liao, H. Yao, T. P. Xie, S. Zhang, K. Zou, X. W. Liu, *Org. Lett.* **2018**, *20*, 16-19. b) H. Liao, W. L. Leng, K. L. M. Hoang, H. Yao, J. He, A. Y. H. Voo, X. W. Liu, *Chem. Sci.* **2017**, *8*, 6656-6661.

[20] a) R. F.N. Pradilla, M. Tortosa, *Org. Lett.* **2004**, *6*, 2157-2160. b) R. F. N. Pradilla, N. Lwoff, M. N.Guila, M. Tortosa, A.Viso, *J. Org. Chem*. **2008**, *73*, 8929-8941.

[21] a) M. B.Arapinis, V. Gandon, E. Prost, L. Micouin, T. Lecourt, *Adv. Synth. Catal.* **2014**, *356*, 2493-2505. b) M. Khajehzadeh, M. Moghadam, *S. Acta A. Mol. Biomol. Spectrosc.* **2017**, *180*, 51-66.

[22] a) Meng Yu, G. T. Li, S. Z. Wang, L. M. Zhang, *Adv. Synth. Catal.* **2007**, *349*, 871-875. b) P. Nun, S. Gaillard, A. M. Slawin, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 9113-9115. c) L. M. Zhang, S. Z. Wang, *J. Am. Chem. Soc.* **2006**, *128*, 1442-1443.

[23] a) N. Conde, R. Sanmartin, M. T. Herrero, E. Domínguez, *Adv. Synth. Catal.* **2016**, *358*, 3283-3292. b) S. P. Swain, Y. L. Chou, D. R. Hou, *Adv. Synth. Catal.* **2015**, *357*, 2644-2650.

[24] a) H. Aruri, U. Singh, S. Kumar, M. Kushwaha, A. P. Gupta, R. A. Vishwakarma, P. P. Singh, *Org. Lett.* **2016**, *18*, 3638-3641. b) C. Veryser, G. Steurs, L. V. Meervelt, W. M. Borggraeve, *Adv. Synth. Catal.* **2017**, *359*, 1271-1276.

[25] a) X. Y. Li, B. F. He, H. J. Luo, N. Y. Huang, W. Q. Deng, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 4617-4621. b) X. F. Lu, Z. Yang, N. Y. Huang, H. B. He, W. Q. Deng, K. Zou, *Bioorg. Med. Chem. Lett*. **2015**, *25*, 3726-3729. c) L. Wang, Y. B. Xie, N. Y. Huang, J. Y. Yan, W. M. Hu, M. G. Liu, M. W. Ding, *ACS Catal.* **2016**, *6*, 4010-4016. d) N. Y. Huang, W. B. Wang, L. Chen, H. J. Luo, J. Z. Wang, W. Q. Deng, K. Zou, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 2268-2272

[26] Q. Xiao, F. Zheng, Q. Tang, J. J. Wu, J. Xie, H. D. Huang, X. B. Yang, S. S. Hann, *Cell Physiol. Biochem.* **2018**, *49*, 1615-1632.

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# Intramolecular and Ferrier Rearrangement Strategy for the Construction of C1-$\beta$-D-xylopyranosides: Synthesis, Mechanism and Biological Activity Study

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