EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Addition of organozinc reagent to glycopyranosyl cyanides: Access to ketoester-C-glycosides or unsaturated acyl-C-glycosides

Authors: Idriss Ella obame, Prathap Irredy, Nicolas Guisot, arnaud Nourry, Christine Saluzzo, Gilles Dujardin, Didier Dubreuil, Muriel Pipelier, and Stéphane Guillarme

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201800090

Link to VoR: http://dx.doi.org/10.1002/ejoc.201800090

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

10.1002/ejoc.201800090

WILEY-VCH

Addition of organozinc reagents to glycopyranosyl cyanides: Access to ketoester-*C*-glycosides or unsaturated acyl-*C*-glycosides

Idriss Ella Obame,[a] Prathap Ireddy,[a] Nicolas E.S. Guisot,[a] Arnaud Nourry,[a] Christine Saluzzo,[a] Gilles Dujardin,[a] Didier Dubreuil,[b] Muriel Pipelier[b] and Stéphane Guillarme*[a]

Abstract: Addition of Reformatsky-type or allylic zinc reagents to 2,3,4,6-tetra-*O*-benzylglycopyranosyl cyanides led to ketoester-*C*-glycosides or unsaturated acyl-*C*-glycosides in moderate to excellent yields in galactose, glucose and mannose series.

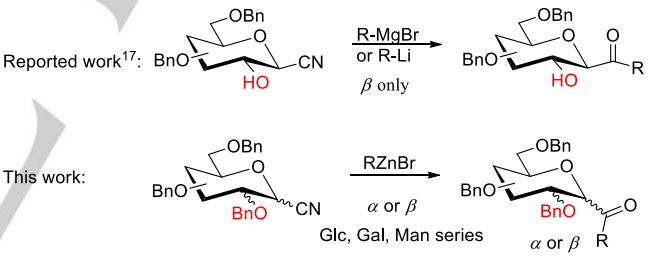
Introduction

Carbohydrates play an essential role in intra or intercellular processes such as cell-cell, cell-virus or cell-bacterium adhesion and cellular transport.[1] It is well established that the use of carbohydrate-derived molecules as drugs has been limited due to the hydrolytic lability of the glycosidic bond. To overcome this limitation, replacing the anomeric oxygen (or nitrogen) atom of the glycosidic bond by a methylene group is the usual strategy used in medicinal chemistry to access stable mimics. Although numerous methods have been developed for the synthesis of *C*-glycosides,[2] glycopyranosyl cyanides have proven to be interesting building blocks to prepare *C*-glycoconjugates. For example, the reduction of glycopyranosyl cyanides into the corresponding aminomethyl-*C*-glycosides which could be incorporated in a peptide sequence to lead to a *C*-glycopeptide [3] or used as a precursor in the preparation of an aza-*C*-disaccharide[4] have been reported. Glycopyranosyl cyanides are also great precursors of important classes of molecules such as 1-formamide-,[5] 1-formyl-[6] and 1-carboxylic acid-*C*-glycosides[7]. The access to *C*-glycosyl *β*-amino acids from glycosyl cyanide has also been described by Dondoni *et al*.[8] As part of a program aiming to synthesize new carbohydrate-based glycogen phosphorylase inhibitors, Vidal *et al.* have published aminocyclopropyl-substituted glucopyranoses[9] which were prepared by a titanium-mediated cyclopropanation of glucopyranosyl cyanide.[10] For the same purpose, numerous heteroaryl-*C*-glucopyranoses have been produced using a protected glucopyranosyl cyanide as starting material. Regarding the heterocycle synthesis, 1,2,4-thiadiazole,[11] 1,2,4-oxadiazole,[12] 1,3,4-oxa- and 1,3,4-thia- diazole,[13] 1,2,4-triazole,[14] dihydropyridine,[15] benzo-thiazole and -imidazole[16] were formed from the nitrile group.

[a] IMMM, Le Mans Université and CNRS UMR 6283
Faculté des Sciences Avenue O. Messiaen, 72085 Le Mans cedex 9, France
E-mail: stephane.guillarme@univ-lemans.fr
http://immm.univ-lemans.fr
[b] CEISAM, Université de Nantes and CNRS UMR 6220
Faculté des Sciences et des Techniques, 2, rue de la Houssinière, 44322 Nantes cedex 3, France

Supporting information for this article is given via a link at the end of the document.

We have recently reported the reactivity of glycopyranosyl cyanide towards organomagnesium and organolithium reagents leading to original acyl-*C*-glycosides.[17] In this study, we have shown that glycal formation was avoided by using a glycopyranosyl cyanide bearing a hydroxyl group in position 2, which was deprotonated during the process (Scheme 1), contrary to the reaction of 2,3,4,6-tetra-*O*-benzylgalactopyranosyl cyanide with Grignard reagents which led to a mixture of the acyl-*C*-galactopyranose and the corresponding acyl-*C*-galactal.
Herein, we report the possibility to use these 2,3,4,6-tetra-*O*-benzylglycopyranosyl cyanides with less basic organometallic reagents such as activated organozinc species affording ketoester-*C*-glycosides or unsaturated acyl-*C*-glycosides (Scheme 1).

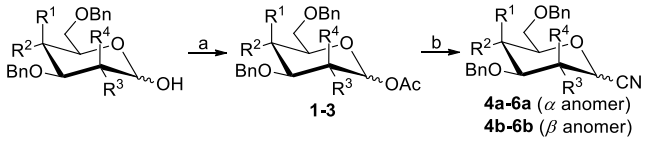


Scheme 1. Access to acyl-*C*-glycoside from glycopyranosyl cyanide.

Results and Discussion

The synthesis of glycopyranosyl cyanides **4-6** was carried out starting from 2,3,4,6-tetra-*O*-benzyl-D-galactose, D-glucose and D-mannose (Scheme 2). Acetylation of the anomeric position with acetic anhydride in the presence of triethylamine in dichloromethane at room temperature led to the corresponding acetates **1**-**3** in 83 to 95% yields.[18] Treatment of galactoside derivative **1** with TMSCN in the presence of boron trifluoride diethylether complex in nitromethane under the conditions described by de las Heras and Fernández-Resa[19a] was unsuccessful in our hands whereas the use of scandium (III) triflate (5 mol-%) as Lewis acid afforded galactopyranosyl cyanide in 90% yield as a separable mixture of *α* and *β* anomers (**4a** and **4b**). However, this reaction proved to be of low reproducibility depending on the quality of nitromethane and, in some case no formation of the expected glycosyl cyanide was detected. When nitromethane was replaced by acetonitrile,[19b] a separable mixture of anomers **4a** and **4b** was obtained in 96% yield in a 43:57 ratio. Finally, optimized conditions using zinc

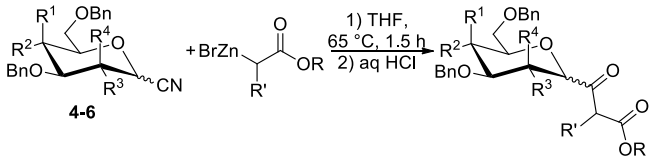
triflate as Lewis acid in acetonitrile led to the two anomers (**4a**/**4b**, 1:1) in quantitative yield. [20]

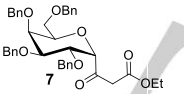
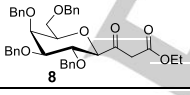
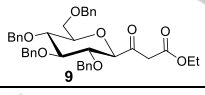
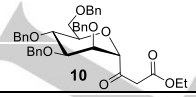
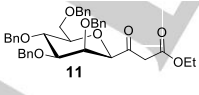
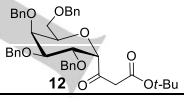
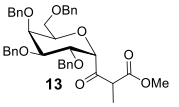


Gal series, **1** and **4** : R^1 = OBn, R^2 = H, R^3 = OBn, R^4 = H
Glc series, **2** and **5** : R^1 = H, R^2 = OBn, R^3 = OBn, R^4 = H
Man series, **3** and **6** : R^1 = H, R^2 = OBn, R^3 = H, R^4 = OBn

Scheme 2. Synthesis of glycopyranosyl cyanides. Reagents and conditions: (a) Ac_2O, Et_3N, CH_2Cl_2, r.t.; (b) TMSCN, $Zn(OTf)_2$, CH_3CN, r.t..

Table 1. Addition of Reformatsky-type reagents to glycopyranosyl cyanides.

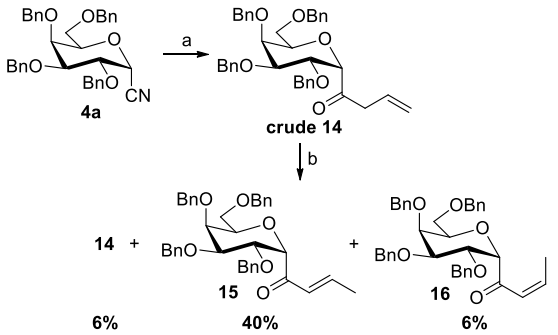


Entry	Glycopyranosyl cyanide	R, R'	Product	Yield (%)
1	**4a**	Et, H	 **7**	82
2	**4b**	Et, H	 **8**	87
3	**5b**	Et, H	 **9**	85
4	**6a**	Et, H	 **10**	73
5	**6b**	Et, H	 **11**	10
6	**4a**	*t*-Bu, H	 **12**	65
7	**4a**	Me, Me	 **13**	-

In glucose series, the yield reached 79%, but the separation of the two anomers by silica gel column chromatography was very challenging and only 15% and 8% of pure *β* (**5b**) and *α* (**5a**) anomers were isolated respectively. In mannose series, *α* (**6a)** and *β* (**6b**) anomers were easily obtained in 56 and 33% yield respectively.

With the glycopyranosyl cyanides in hand, their reactivity towards Reformatsky-type reagents was first examined following Dondoni's procedure.[21] Addition of the ethyl 2-bromoacetate-derived organozinc derivative to galactonitrile **4a** under modified Blaise conditions[22] led to ketoester **7** in 82% yield (entry 1, Table 1). Under the same conditions, glycopyranosyl cyanides **4b** and **5b** afforded the corresponding ketoesters **8** and **9** in high 87 and 85% yields (entries 2 and 3). In mannose series, *α*-anomer **6a** furnished the corresponding *α*-ketoester **10** in 73% yield (entry 4) while reaction from *β*-anomer **6b** was not complete, and only 10% of pure ketoester **11** was isolated along with starting material in a 1:1 ratio (entry 5). The reaction between the *α*-galactopyranosyl cyanide **4a** and the organozinc reagent prepared from *tert*-butyl 2-bromoacetate provided the corresponding *α*-ketoester **12** in 65% yield (entry 6).[23] Finally, the addition of a more hindered organozinc reagent to galactopyranosyl cyanide **4a** did not allow to access the corresponding ketoester (entry 7).

The reactivity of galactopyranosyl **4a** with allylzinc bromide was then evaluated. Addition of substrate **4a** to a freshly prepared allylzinc bromide solution, followed by acidic hydrolysis afforded *α*-ketone **14** (Scheme 3). ^{1}H NMR spectrum of the crude product confirmed the formation of **14** as the sole compound of the reaction with the presence of olefinic proton signals at 5.90, 5.14 and 5.06 ppm respectively and allylic proton signals at 3.36 and 3.48 ppm. Partial isomerization of the allyl group was detected after purification of the compound **14** by column chromatography on silica gel. Although the separation was difficult, three keto-*C*-glycosides were isolated, the allyl ketone **14** in 6% yield along with the two *α*,*β*-unsaturated ketones **15** and **16** in 40 and 6% yield respectively (Scheme 3).

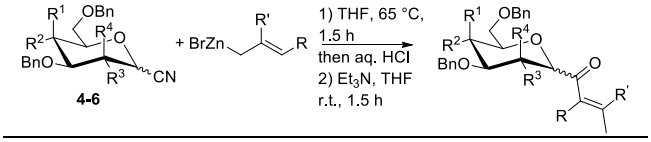


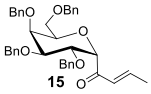
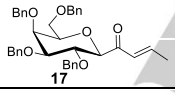
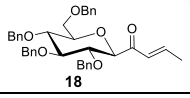
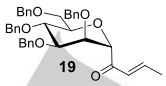
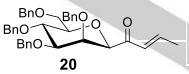
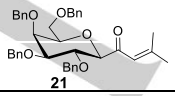
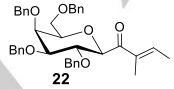
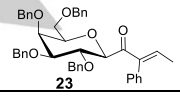
Scheme 3. Addition of allylzinc bromide to galactopyranosyl cyanides **4a**. Reagents and conditions: (a) allylzinc bromide, THF, 65 °C, 1.5 h then aq. HCl. (b) purification on silica.

Considering the difficult separation of these three ketones, and our great interest in such a building block as **15**, we opted to develop a strategy which could exclusively afford this ketone. In a first attempt, the crude allyl ketone **14** was treated with *p*-toluenesulfonic acid but a mixture of keto-*C*-glycosides **15** and

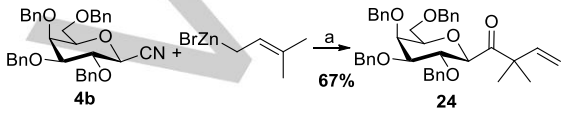
16 was still obtained in a 5:1 ratio. Nevertheless, treatment of the crude compound **14** with triethylamine in THF provided exclusively the isomerized *α*-keto-*C*-galactoside **15** in 72% yield (entry 1, Table 2). It is noteworthy that when the addition step was carried out under Barbier conditions the yield of the two-step sequence was slightly lower (55%). This reaction sequence was also performed on *β* anomer of galacto- and gluco-pyranosyl cyanides **4b** and **5b** and the corresponding *α*,*β*-unsaturated ketones **17** and **18** were isolated in 61 and 58% yield respectively (entries 2 and 3). In mannose series, *α*-anomer **6a** led to the corresponding unsaturated acyl-*C*-mannoside **19** in the same range of yield (57%, entry 4). The yield was lower when *β*-anomer **6b** was involved in the same reaction process (entry 5). The *E* configuration of the double bond of compounds **15** and **17-20** was confirmed by the ^{1}H NMR spectra which presented two olefinic signals with a coupling constant ^3J > 15 Hz.

Table 2. Two-step sequence to access unsaturated acyl-*C*-glycoside.



Entry	Glycopyranosyl cyanide	R, R'	Product	Yield (%)
1	**4a**	H, H	 **15**	72
2	**4b**	H, H	 **17**	61
3	**5b**	H, H	 **18**	58
4	**6a**	H, H	 **19**	57
5	**6b**	H, H	 **20**	48
6	**4b**	H, Me	 **21**	53
7	**4b**	Me, H	 **22**	64
8	**4b**	Ph, H	 **23**	-

Reactivity of galactopyranosyl cyanide **4b** towards substituted allylzinc bromide was then evaluated. Following the two-step sequence described above, reaction with the organozinc reagent prepared from 3-bromo-2-methylprop-1-ene afforded the corresponding the *β*-keto-*C*-galactoside **21** in 53% yield (entry 6). Similarly, the reaction with the crotyl bromide-derived organozinc reagent led to the *β*-ketone **22** in 64% yield (entry 7). It is noteworthy that, in that case, the addition step proceeded with complete allylic transposition. With cinnamyl bromide, the starting material was not consumed after 6 h of reaction, and some Wurtz-type coupling products can be detected in the crude mixture by ^{1}H NMR, even though the organozinc reagent was prepared at -15 °C to avoid such side reaction. Finally, complete allylic transposition with 4-bromo-2-methylbut-2-ene-derived organozinc reagent was also observed delivering *β*-ketone **24** in 67% yield (Scheme 4).



Scheme 4. Synthesis of ketone **24**. Reagents and conditions: (a) THF, 65 °C, 1.5 h.

In addition, the reactivity of benzylic organozinc reagent was evaluated with *β*-galactopyranosyl cyanide **4b**, but no formation of the corresponding ketone was observed. The same outcome was observed with propargyl organozinc reagent although the starting material was totally consumed.
Furthermore, addition of a large excess of allylic organozinc reagents to glycopyranosyl cyanides did not provide the formation of the corresponding carbinamine contrary to the addition with the organomagnesium analogs.[24]

Conclusions

We have described the addition of Reformatsky-type or allylic zinc reagents to 2,3,4,6 tetra-*O*-benzylgalacto-, gluco- and mannopyranosyl cyanides affording ketoester-*C*-glycosides or unsaturated acyl-*C*-glycosides in moderate to excellent yields. These compounds are prepared in only three or four steps from the corresponding 2,3,4,6 tetra-*O*-benzylglycopyranoses involving simple process since Blaise or Barbier conditions could be implemented. Furthermore, the substrates used are highly stable and could be stored for a long time even at room temperature. The reactivity and the behavior of these acyl-*C*-glycosides make them very interesting precursors to access new various original biologically relevant C-glycoconjugates.

Experimental Section

Typical Procedure for Reformatsky addition. A stirred suspension of activated zinc (7 eq) in THF (1 mL/0.1 mmol of glycopyranosyl cyanide) was heated at 70°C for 15 minutes. To this stirred suspension, 25 µL of ethyl bromoacetate was added and refluxed for 20 minutes.

Glycopyranosyl cyanide (1 eq) in THF (1 mL/0.2 mmol of glycopyranosyl cyanide) was added in one portion followed by slow addition of ethyl bromoacetate (5 eq) over 45 minutes and stirred for another 15 minutes. The reaction mixture was cooled to room temperature, quenched with slow addition of a 3N aqueous HCl solution, stirred for 1 hour, diluted with ether and the layers were separated. The organic layer was washed with a saturated aqueous solution of $NaHCO_3$, brine, dried over $MgSO_4$ and concentrated to afford crude product. The crude residue was purified by column chromatography to afford the desired compound.

Typical Procedure for the two step sequence addition/isomerisation. *1- addition of organozinc reagents*: To a stirred suspension of activated zinc (5 eq.) in dry THF (1 mL/0.18-0.2 mmol of glycopyranosyl cyanide) was added dropwise allyl bromide (4.95 eq) and the solution was heated at 70 °C for 1.5 h. The glycopyranosyl cyanide (1 eq.) in dry THF (1 mL/0.18-0.2 mmol of glycopyranosyl cyanide) was then added and the solution was stirred for 1.5 h at this temperature. After complete conversion (TLC), the solution was cooled to room temperature before quenching with an aqueous 3N HCl solution. The solution was stirred for 30 minutes and diluted with diethyl ether. The aqueous phase was extracted twice with diethyl ether and the combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude residue.

2- isomerisation step: The crude residue was taken up with THF (1 mL/0.1 mmol) and triethylamine (1 mL/0.6 mmol) was added at room temperature. The solution was stirred for 1.5 h and the solvents were removed. Further purification by column chromatography afforded the desired product.

Supporting Information: General methods, experimental procedures, characterization data, and copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgements

The authors thank the Ministère de l'Enseignement Supérieur of Gabon for a PhD fellowship (I. E. O.), the ANR (ANR PCV Galcerdeo, ANR-08-PCVI-0024-02) (N.E.S.G), and the Région des Pays de la Loire through the CIMATH program (P.I.) for post-doctoral fellowships. The authors are grateful to the Ministère de l'Enseignement Supérieur et de la Recherche of France and CNRS for financial support. We also thank Frédéric Legros for technical support, Amélie Durand and Corentin Jacquemoz for the NMR analyses, Patricia Gangnery and Emmanuelle Mebold for the HRMS analyses.

Keywords: Glycopyranosyl cyanide • Acyl-*C*-glycoside • Organozinc reagents • *C*-glycosides • *β*-Ketoester

[1] R. A. Dwek, *Chem. Rev.* **1996**, *96*, 683-720.

[2] a) M. H. D. Postema, *Tetrahedron* **1992**, *48*, 8545-8599; b) M. H. D.Postema, in *C-Glycoside Synthesis*; CRC Press: Boca Raton, **1995**; c) D. E. Levy, C. Tang, in *The Chemistry of C-Glycosides*; Pergamon: Tarrytown, NY, **1995**; d) H. Togo, W. He, Y. Waki, M. Yokoyama, *Synlett* **1998**, 700-717; e) I. P. Smoliakova, *Curr. Org. Chem.* **2000**, *4*, 589-608; f) Y. Du, R. J. Linhardt, I. R. Vlahov, *Tetrahedron* **1998**, *54*, 9913-9959; g) É. Bokor, S. Kun, D. Goyard, M. Tóth, J.-P. Praly, S. Vidal, L. Somsák *Chem. Rev.* **2017**, *117*, 1687–1764; h) Y. Yang, B. Yu, *Chem. Rev.* **2017**, *117*, 12281–12356; i) K. Kitamura, Y. Ando, T. Matsumoto, K. Suzuki, *Chem. Rev.* DOI:10.1021/acs.chemrev.7b00380.

[3] a) F. Schweizer, O. Hindsgaul, *Carbohydrate Res.* **2006**, *341*, 1730–1736; b) R. F. Barghash, A. Massi, A. Dondoni, *Org. Biomol. Chem.* **2009**, *7*, 3319–3330.

[4] a) D.H. Lenz, G. E. Norris, C. M. Taylor, G. C. Slim, *Tetrahedron Lett.* **2001**, *42*, 4589-4591; b) P. Phiasivongsa, J. Gallagher, C.-N. Chen, P. R. Jones, V. V. Samoshin, P. H. Gross, *Org. Lett.* **2002**, *4*, 4587-4590.

[5] See for example: A. K. Misra, É. Bokor, S. Kun, E. Bolyog-Nagy, Á. Kathó, F. Joó, L. Somsák, *Tetrahedron Lett.* **2015**, *56*, 5995- 5998 and references therein.

[6] See for example: S. Sipos, I. Jablonkai, *Carbohydrate Res.* **2011**, *346*, 1503-1510 and references therein.

[7] See for example: G. J. L. Bernardes, L. Linderoth, K. J. Doores, O. Boutureira, B. G. Davis, *ChemBioChem* **2011**, *12*, 1383-1386.

[8] A. Dondoni, A. Massi, E. Minghini, *Synlett* **2006**, 539-542.

[9] P. Bertus, J. Szymoniak, E. Jeanneau, T. Docsa, P. Gergely, J.-P. Praly, S. Vidal, *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4774-4778.

[10] See for example: C. Laroche, J.-B. Behr, J. Szymoniak P. Bertus, R. Plantier-Royon, *Eur. J. Org. Chem.* **2005**, 5084-5088.

[11] E. Ősz, K. Czifrák, T. Deim, L. Szilágyi, A. Bényei, L. Somsák, *Tetrahedron* **2001**, *57*, 5429-5434.

[12] (a) M. Benltifa, S. Vidal, B. Fenet, M. Msaddek, P. G. Goekjian, J.-P. Praly, A. Brunyánszki, T. Docsa, P. Gergely, *Eur. J. Org. Chem.* **2006**, 4242–4256. (b) M. Benltifa, S. Vidal, D. Gueyrard, P. G. Goekjian, M. Msaddek, J.-P. Praly, *Tetrahedron Lett.* **2006**, 47, 6143-6147. (c) M. Tóth, S. Kun, É. Bokor, M. Benltifa, G. Tallec, S. Vidal, T. Docsa, P. Gergely, L. Somsák, J.-P. Praly, *Bioorg. Med. Chem.* **2009**, 17, 4773–4785. (d) Glucal series: É. Bokor, E. Szennyes, T. Csupász, N. Tóth, T. Docsa, P. Gergely, L. Somsák, *Carbohydrate Res.* **2015**, *412*, 71-79 .

[13] (a) S. Kun, G. Z. Nagy, M. Tóth, L. Czecze, A. Nguyen Van Nhien, T. Docsa, P. Gergely, M.-D. Charavgi, P. V. Skourti, E. D. Chrysina, T. Patonay, L. Somsák, *Carbohydrate Res.* **2011**, *346*, 1427-1438. (b) B. Szőcs, M. Tóth, T. Docsa, P. Gergely, L. Somsák, *Carbohydrate Res.* **2013**, *381*, 187-195.

[14] (a) É. Bokor, T. Docsa, P. Gergely, L. Somsák, *ACS Med. Chem. Lett.* **2013**, *4*, 612-615. (b) É. Bokor, A. Fekete, G. Varga, B. Szőcs, K. Czifrák, I. Komáromi L. Somsák, *Tetrahedron* **2013**, *69*, 10391-10404. (c) S. Kun, É. Bokor, G. Varga, B. Szőcs, A. Páhi, K. Czifrák, M. Tóth, L. Juhász, T. Docsa, P. Gergely, L. Somsák, *Eur. J. Med. Chem.* **2014**, *76*, 567-579. (d) B. Szőcs, K. E. Szabó, A. Kiss-Szikszai, M. Tóth, L. Somsák, *RSC Adv.* **2015**, *5*, 43620-43629.

[15] A. Dondoni, A. Massi, E. Minghini, V. Bertolasi, *Helv. Chim. Acta* **2002**, *85*, 3331-3348.

[16] (a) Z. Hadady, M. Tóth, L. Somsák, *Arkivoc* **2004**, (*vii*), 140-149. (b) É. Bokor, E. Szilágyi, T. Docsa, P. Gergely, L. Somsák, *Carbohydrate Res.* **2013**, *381*, 179-186.

[17] N. E. S. Guisot, I. Ella Obame, P. Ireddy, A. Nourry, C. Saluzzo, G. Dujardin, D. Dubreuil, M.Pipelier, S. Guillarme *J. Org. Chem.* **2016**, *81*, 2364-2371 and see references therein for main synthetic methods to prepare acyl-*C*-glycosides.

[18] S. S. Kulkarni, J. Gervay-Hague, *Org. Lett.* **2006**, *8*, 5765-5768.

[19] a) F. G. de las Heras, P. Fernández-Resa, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 903-907. b) M.-T. García López, F. G. De las Heras, A. San Félix, *J. Carbohydr. Chem.* **1987**, *6,* 273-279.

[20] Y. Igarashi, T. Shiozawa, Y. Ichikawa, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 613-616.

[21] a) A. Dondoni, A. Massi, E. Minghini, *Synlett*, **2006**, 539-542. b) As first example of Reformatsky-type addition to ribofuranosyl cyanide, see: A.C. Veronese, C. F. Morelli, *Tetrahedron Lett.* **1998**, *39*, 3853-3856

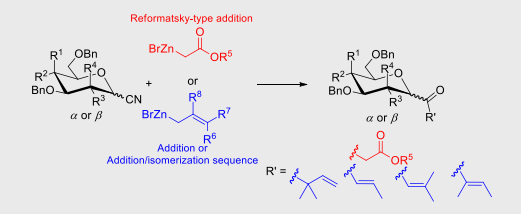
[22] S. M. Hannick, Y. J. Kishi, *J. Org. Chem.* **1983**, *48*, 3833-3835.

[23] It is noteworthy that for all isolated ketoesters **7**-**12**, few signals of the enol tautomer could be observed on the ^{1}H and ^{13}C NMR spectra. Characteristic signals located at 5.5 and 12 ppm were assigned to enol tautomer.

[24] a) T. Hill, M. B. Tropak, D. Mahuran, S. G. Withers, *ChemBioChem* **2011**, *12*, 2151-2154. b) M. S. M. Pearson-Long, F. Boeda, P. Bertus, *Adv. Synth. Catal.* **2017**, *359*, 179-201.

Entry for the Table of Contents (Please choose one layout)

COMMUNICATION



Original ketoester-*C*-glycosides or unsaturated acyl-*C*-glycosides have been prepared in moderate to excellent yields in galactose, glucose and mannose series involving addition of Reformatsky-type or allylic zinc reagents to 2,3,4,6-tetra-*O*-benzylglycopyranosyl cyanides.

Key Topic*

*Idriss Ella Obame, Prathap Ireddy, Nicolas E.S. Guisot, Arnaud Nourry, Christine Saluzzo, Gilles Dujardin, Didier Dubreuil, Muriel Pipelier, Stéphane Guillarme**

Page No. – Page No.

Addition of organozinc reagents to glycopyranosyl cyanides: Access to *β*-ketoester-*C*-glycosides or unsaturated acyl-*C*-glycosides