Selective Anomeric Deacetylation of Per-Acetylated Carbohydrates Using \((i-Pr)_3Sn(OEt)\) and Synthesis of New Derivatives

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Abstract

In this study natural carbohydrates such as glucose, galactose, xylose, fructose and lactose, are acetylated by acetic anhydride and sodium acetate catalyst. Anomeric configuration is deacetylated by \((i-Pr)_3Sn(OEt)\) as a catalyst, an easy synthetic regioselective deacetylation of fully acetylated carbohydrates using \((i-Pr)_3Sn(OEt)\) is described. The acetylated carbohydrates reacted with HBr (solution in AcOH, 32 wt.%) for the bromination of anomeric position. The synthesis oxazaphosphorine, and bromo hexa alkyl Methylsulfonate derivatives from anomeric position of carbohydrates was reacted. FT IR, \(^1H\), \(^13C\) NMR, \(^31P\)NMR spectroscopy techniques were employed to examine the synthesized compounds.

Keywords: Carbohydrates, Deacetylation, Anomeric Deacetylation, \((iPr)_3Sn(OEt)\)

1. Introduction

Carbohydrates are a large class of organic compounds which can be found in the structure of living organisms. They are major energy source for both plants, and animals that play an important role in feeding the living organisms. Likewise, these compounds are quintessential reactions of ATP, RNA and DNA. Carbohydrates are polyhydroxy ketone or aldehydes that can be found in nature. Carbohydrates can be divided into three major classes: monosaccharides, disaccharides and polysaccharides. Monosaccharides can be classified into classes, aldose and ketose. The presence of the heteroatom in-ring has an appreciable effect on both formation and reactivity of carbohydrates. The existence of an electron-withdrawing substituent (as halogens) onto C1 in axial position is more stable due to the anomeric effect. This tendency not only is not limited to carbohydrates but also observes in annular systems like substitutability of 2-tetrahydropyrans. This phenomenon is known as the anomeric effect. (Sorg, Hull, Kliem, Mier, & Wiessler, 2005) The hydroxyl groups in carbohydrates are esterified easily. Acetylation is the most common reaction for esterification. Selective anomeric acetylation is considered as an important stage in synthesis of glycoside. Acetylated-1-hydroxy of carbohydrates contains valuable structures for diverse reactions of glycosides.

There are various procedures to release anomeric configuration of acetylated carbohydrates, such as butylamine, (Pawar & Edgar, 2013) ammonia, (Li, Li, Zhaiyg, & Guan, 2004) bis (tributyltin) oxide, (Li, Li, Zhaiyg, & Guan, 2004) HgO/HgCl, (Sambaiah, Fanwick, & Cushman, 2001) piperidine, (Zhang & Kovač, 1999) hydrazine acetate, (Excoffier, Gagnaire, & Utille, 1975) zinc chloride, (Hanessian & Kagotani, 1990) Zn–NH₂Cl–EtOH, (Zhang, Fu, Si, Wang, Wang, & Tang, 2011) HClO₄–SiO₂, (Tiwari & Misra, 2006) Nd(OTf)₃, (Tran, Deydier, Bonnaffé, & Le Narvor, 2008) FeCl₃/6H₂O,\(^{12}\) MgO/MeOH, (Herzig & Nudelman, 2009) zinc acetate, (Kaya, Sonmez, Kucukislamoglu, & Nebioglu, 2012) AlCl₃, (Wang, Mo, Chiuo, & Liu, 2010) enzyme, (Moriyoshi, Yamanaka, Ohmoto, Ohe, & Sakai, 2005) silica-supported boron sulfonic, (Bhat, Naikoo, Tomar, Ahmad Bhat, Malla, Kumar, & Tiwari, 2017), MgO/MeOH (Jabbari & Noroozi, 2018), Potassium carbonate, (Calvaresi & Hergenrother, 2013) Many reactions can be created by carbohydrate invertebrates that often have pharmaceutical application. Oxazaphosphorin compounds are used as DNA alkylating agents in malignant chemotherapy (Park, Lee, Cho, & Park, 2007).

Carbohydrates are used in medicine usages such as heparin of anticoagulant, antibiotics, vaccines, anticancer medicines, antibacterial and antifungal (Liang, Huang, & Duan, 2007). carbohydrates hasn’t been extended for cellular biology improvements in drug receiving (Mazur, Opydo-Chanek, & Stojak, 2011). Hence, carbohydrates performance hasn’t been studied widespread in biology because of the complicated structures of
oligosaccharids, non existence of synthesis methods and analysis of structure.

In this paper, a sample of carbohydrates consisting of glucose, galactose, xylose, fructose and lactose is acetylated using Ac₂O/AcONa under the 50-60°C and anomic configuration of acetylated carbohydrates using \((\text{Pr})_3\text{Sn(OEt)}\) as a new catalyst has been released. Then, it is reacted with HBr (AcOH solution), new derivatives of oxazaphosphorine, and alkyl sulfonate from anomeric position reacted. All of these compounds are identified by FT-IR, \(^1\text{H}, \(^{13}\text{C}\) and \(^{31}\text{P}\)NMR spectroscopy techniques.

2. Experiment

All materials were obtained from Merck Co. \(^1\text{H}, \(^{13}\text{C}\) and \(^{31}\text{P}\) NMR spectra of in CDCl₃ and/or DMSO-d₆ were measured using Brucker 400 AC spectrometer as a solvent at room temperature (University of Tabriz, Tabriz, Iran and Shahid Beheshti University, Tehran, Iran).

2.1 Typical Procedure for Preparation of D-Glucose Pentaacetate (2a)

A mixture of D-glucose (15.0g), acetic anhydride (70mL), sodium acetate (15.0g) and butyl acetate (150mL) was refluxed with stirring for one-half hours. Then the reaction mixture was added to water (100mL), the mixture was stirred and produced a neutral solution with a 3% sodium hydroxide After the concentration of the organic layer it give 62.0g (yield 95%) of pentaacetyl-\(\beta\)-D-glucopyranose as crude crystals. The crude crystals contained 13% of pentaacetyl-\(\alpha\)-D-glucopyranose, but recrystallization from ethanol gave 49.7g of pure pentaacetyl-\(\beta\)-D-glucopyranose (M. p. 132°C, yield 77%).

\[\delta (\text{ppm}) 6.6 (\text{d}, 1\text{H}, J = 3.6\text{Hz}), 5.80 (\text{t}, 1\text{H}, J = 9.8\text{Hz}), 5.33 (\text{t}, 1\text{H}, J = 9.8\text{Hz}), 5.24 (\text{dd}, 1\text{H}, J = 10.5, 3.7\text{Hz}), 4.29 (\text{dd}, J = 12.2, 4.3\text{Hz}), 4.08-4.15 (\text{m}, 1\text{H}), 4.0 (\text{dd}, J = 12.3, 2.2\text{Hz}), 1.50-1.70 (3\text{s}, 5\text{CH}_3).\]

2.2 General Procedure for Selective Anomericdeacetylation of D-Glucose Pentaacetate (3a)

\((\text{Pr})_3\text{Sn(OEt)}\) (1mmol) was added to solution pentaacetyl-\(\alpha\)-D-glucopyranose (1mmol) in methanol (20mL). A drop of ammonium acetate solution was added to the reaction mixture. The reaction mixture was refluxed for 4-5 hours and controlled by TLC. then the solvent was separated, Solid matter is white. The compound was washed with hexane (3 times), and was crystallized by Ethyl acetate. and identified by NMR spectroscopy techniques.

\[\text{H-NMR (CDCl}_3\text{)}: \delta (\text{ppm}) 6.35 (\text{d}, 1\text{H}, J = 3.8\text{Hz}, \text{H}-1), 5.33 (\text{dd}, 1\text{H}, J = 10.1\text{Hz}, \text{J}_10.1 = 6\text{Hz}), 4.98 (\text{dd}, 1\text{H}, J = 10\text{Hz}, \text{J}_10 = 3.9\text{Hz}), 4.98 (\text{dd}, 1\text{H}, J = 10.1\text{Hz}, \text{J}_10.1 = 4.0\text{Hz}), 4.38-5.1 (\text{m}, 2\text{H}), 4.77 (\text{d}, 1\text{H}, J = 10.8\text{Hz}), 2.45 (\text{s}, 3\text{H}), 2.66 (\text{s}, 3\text{H}), 2.2 (\text{s}, 3\text{H}), 2.11 (\text{s}, 3\text{H}); \text{C-NMR (CDCl}_3\text{)}: \delta (\text{ppm}) 175.19, 170.5, 166.35, 90.00, 72.51, 72.29, 69.31, 66.20, 59.01.\]

2.3 The Deacetylation of \(\alpha\)-D-Lactose Octaacetate

\((\text{Pr})_3\text{SnOEt} (1\text{mmol})\) was added by stirring to D-lactoseoctaacetate (1mmol) an appropriate solvent (20ml). under reflux, stirring and boiling were continued for 4-5h (hexane/EtOAc=3:1).

\[\text{H-NMR (CDCl}_3\text{)}: \delta (\text{ppm}) 5.97 (\text{d}, 1\text{H}, J = 4.1\text{Hz}), 5.52 (\text{d}, 1\text{H}, J = 3.0\text{Hz}), 5.42 (\text{dd}, 1\text{H}, J = 10.7\text{Hz}, \text{J}_10.7 = 3.10\text{Hz}), 4.98 (\text{dd}, 1\text{H}, J = 10\text{Hz}, \text{J}_10 = 3.3\text{Hz}), 4.98 (\text{dd}, 1\text{H}, J = 10.1\text{Hz}, \text{J}_10.1 = 4.0\text{Hz}), 4.38-5.1 (\text{m}, 2\text{H}), 4.77 (\text{d}, 1\text{H}, J = 10.8\text{Hz}), 2.45 (\text{s}, 3\text{H}), 2.66 (\text{s}, 3\text{H}), 2.2 (\text{s}, 3\text{H}), 2.11 (\text{s}, 3\text{H}); \text{C-NMR (CDCl}_3\text{)}: \delta (\text{ppm}) 170.32, 170.12, 169.92, 1369.78, 91.17, 70.22, 66.77, 66.30, 68.19, 59.00.\]

2.4 Preparation of 2,3,4,6-Tetra-O-Acetyl-\(\beta\)-D-Galactopyranosyl Bromide with HBr/AcOH\(\alpha\)

HBr solution in acetic acid (4.5ml) was mixed with galactosepentaacetate. The reaction mixture was stirred until it became a homogeneous mixture and was stirred for 30 min. The obtained precipitate became smooth and rinsed with water. Then it was dissolved in ether and separated by separatory funnel. Organic phase was transferred into another container and dried. Solvent, was extracted without heating in vacuum and during two steps at 5 minutes interval, insignificant amount of petroleum ether was added. After a milky precipitate was formed, it kept in freezer for 24h. After that time, 2.5ml of petroleum ether was mixed with 2.5ml of ether and added to it. Precipitate was smoothed and washed with mixture of ether and petroleum ether, a white precipitate yielded with 59% efficiency.

2.5 Preparation of 5e, 6e and 7e as New Oxazaphosphorines as a Representative

Solution of compound 3a (0.01mol) in dry DMF (20mL), NaOH (0.01mol), pyridine (0.01mol), POCl₃(0.01mol) under N₂ atmosphere was reacted in 0°C. The mixture could be detected (by TLC). After purification by column chromatography (petroleum ether: EtOAc: 4:1), 5a was obtained as a yellowish-white oil.

In order to prepare 6a, a compound 5a (0.01mol) and ethanol amine(0.015mol) in 30mL of dry DMF, and 0.01mol pyridine were cooled at 0°C were cooled to 0°C in N₂ atmosphere the solvent was removed in vacuum pump. After removing solvent, 6a was obtained as a red oil.
In order to prepare 7a SOCl₂ was reacted for 1h and finally, the deprotection process of acetyl group was occurred.

2.6 Preparation 1-(2,3,4,6-Tetra-o-Acetyl-β-D-Galactopyranosile)-6-(Methyl Oxy Sulfonile) Hexane

Compound 2b obtained from previous stage (1.4mmol). NaOH(1mmol), is dissolved in pyridine (0.4mL) and solution is cooled to 0°C, and added to bromo hexa alkyl Methylsulfonate (2mmol). After 6h water (4mL) added. After gathering sediment, it dissolved in dichloromethane (12mL) and organic phase was extracted by salt water (2*6mL), then dried by using sodium sulphate, and solution was filtered. Finally it was crystallized by ethanol with 53% efficiency (scheme4).

FT-IR(KBr,υcm⁻¹): 2942, 2867, 1751, 1434, 1369, 1226, 1174, 1069, 953 cm⁻¹, ¹H NMR(300MHz,CDCl₃)δ(ppm)1.23(m, 2H), 1.44(m, 2H, -O(CH₂)₂(CH₂)₂(OCH₂)(CH₂)₂S(=O) ), 1.56(m, 2H, -OCH₂CH₂CH₂-OCH₂CH₂O-S(=O)-), 1.72(m, 2H, -OCH₂CH₂CH₂-OCH₂CH₂O-S(=O)-), 1.96 -1.97(2s, 3H₂), 1.98 -1.97(2s, 3H₂), 2.14-2.17(2s, 3H₂), 2.14-2.17(2s, 3H₂), 3.02(2d, 1H, J=3.6Hz).

3. Results and Discussion

This paper aimed to describe the full acetylation of some carbohydrates such as D-glucose (1a), D-galactose (1b), D-xylose (1c), D-fructose (1d) and D-lactose (1e) in the presence of Ac₂O/AcONa as well as selective deacetylation of anomeric position using (iPr)₃Sn(OEt) as a new catalyst (Scheme 1, Tables 1 and 2). Anomeric configuration is deacetylated by (iPr)₃Sn(OEt) as a catalyst, A convenient synthetic approach to regioselective deacetylation of full acetylated carbohydrates using (Pr)₃Sn(OEt) is described. The acetylated carbohydrates are reacted with HBr (solution in AcOH, 32 wt.%) for the bromination of anomeric position. As a representative bromination of 2a is yielded 4a (Scheme 1, Table 3).

Representatively, the ¹H NMR spectrum of glucose pentaacetate 2a is shown in Figure 1. Its structure was characterized by ¹H, ¹³C NMR and FT-IR spectra. The ¹H NMR spectrum of 2a showed doublets at δ 6.6ppm (J = 3.6Hz) for H-1, a double of doublet at δ 5.24ppm (J = 10.5Hz) for H-2, a triplet at δ 5.80ppm (J = 9.9Hz) for H-3, a triplet at δ 5.33ppm (J = 9.9Hz) for H-4, a double of doublet at δ 4.29ppm (J = 12.2Hz) for H-5, a double doublet at δ 4.0ppm (J = 12.3Hz) for H-6. Methyl groups show three singlets at δ 1.50-1.70ppm. The FT-IR spectrum showed a strong absorption at 1741cm⁻¹ due to carbonyl stretching frequency (See supporting information).

Figure 1. ¹H NMR spectrum of D-glucose pentaacetate 2a of a representative
Scheme 1. Full acetylation and anomeric deacetylation of carbohydrates
The acetyl ester plays an important role for protection of the hydroxyl group in organic synthesis. Methodologies that are widely used have been put forth for the esterification. The deprotection of the acetyl esters is much less studied despite its practical significance in synthetic processes. A convenient methodology has been developed for the selective removal of the anomeric acyl group of carbohydrate derivatives using (iPr)₃SnOEt conditions. Representatively, the proposed mechanism of the formation of 3b is shown in Scheme 2.

Scheme 2. Representatively, proposed mechanism of the formation of 3b

In IR spectrums the existence of 1730cm⁻¹ peaks shows a Carbonyl group and peaks 1000cm⁻¹ are related to aliphatic group. absorption vibrat e of esters are appeared in 1000-1300cm⁻¹ acetylation of galactos while organizing Carbonyle in position 2 which shows the effect of neighbor group so the existing quitter group easily take apart from number one carbon and organize stable Carbocation. In this mode there is a possibility of attacking carbon anomeric by nucleofilic agent. Absorption band in 1379cm⁻¹ location is related to symmetrical
Curvature of methyl CO-CH$_3$ and seen absorption in 1221 cm$^{-1}$ is related to neighbor C-O vibration of ester Carbonyl group and absorption band in 1100 cm$^{-1}$ is related to ester tension of alcoholic section of ester.

In order to synthesize the new oxazaphosphorine derivatives, the anomeric hydroxyl group should be deprotected. For this purpose, we used (iPr)$_3$SnOEt for the selectively deacetylation of the anomeric position. Therefore, as a representative, 2a was selectively converted to 3a in good yield (Scheme 1). The reaction of compound 3a with POCl$_3$ yielded 5a. The reaction of this compound with 2-eyhanolamine gave 6a, then in the presence of thionyl chloride yielded 7a. The deprotection of acetyl groups of later compound (7a) in the presence of trimethylsilane yielded 8a.

![Figure 2. Representatively, $^{31}$P NMR spectrum of 7a](image)

The $^{31}$P NMR spectrum of 7a is shown in Figure 2. A singlet peak at $\delta$ -12.82 ppm corresponded to a unique phosphorous atom connected to oxygen, nitrogen and halogen atoms.

| Table 1. Reaction conditions and conversions of carbohydrate to per acetate with Ac$_2$O/AcONa |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Entry  | Sugar | Product | Reaction Temperature(°C) | Reaction time (min) | Conversion (%) |
|--------|-------|---------|---------------------------|---------------------|----------------|
| 1      | 1a    | 2a      | 30-40                      | 180                 | 77             |
| 2      | 1b    | 2b      | 50-60                      | 180                 | 79             |
| 3      | 1c    | 2c      | 60                         | 240                 | 72             |
| 4      | 1d    | 2d      | 60-70                      | 240                 | 75             |
| 5      | 1e    | 2e      | 70-80                      | 300                 | 65             |

| Table 2. Selective anomeric-deacetylation of carbohydrates |
|---------------------------------|-----------------|-----------------|-----------------|
| Entry  | Sugar | Product | Reaction Temperature(°C) | Reaction time (min) | Conversion (%) |
|--------|-------|---------|---------------------------|---------------------|----------------|
| 1      | 2a    | 3a      | 70                         | 240                 | 79             |
| 2      | 2b    | 3b      | 80                         | 240                 | 77             |
| 3      | 2c    | 3c      | 80                         | 240                 | 70             |
| 4      | 2d    | 3d      | 80                         | 260                 | 70             |
| 5      | 2e    | 3e      | 90                         | 300                 | 61             |
Table 3. Bromination of some carbohydrates in anomeric position, reaction times and yields

| Entry | Sugar | Reaction Temperature (°C) | Reaction time (h) | Conversion (%) |
|-------|-------|---------------------------|------------------|---------------|
| 1     | 2a    | 65                        | 12               | 65            |
| 2     | 2b    | 61                        | 12               | 61            |
| 3     | 2c    | 60                        | 18               | 60            |
| 4     | 2d    | 62                        | 18               | 62            |
| 5     | 2e    | 59                        | 30               | 59            |

As a representative, FTIR spectrum of 2b showed vibration bands of carbonyl (C=O), C-O groups are appeared in 1746 and 1224 cm⁻¹, respectively, and vibration band at 1371 cm⁻¹ is related to bending vibration of methyl group. No hydroxyl group stretching frequency was observed at 3500-3600 cm⁻¹. These observations demonstrated the full acetylation of 1b the acetylation of D-galactose within formation of aceethoxy group in position 2 demonstrates neighboring group participation (NGP). In this manner, charging of nucleophilic agent to anomeric carbon is only possible from one side. The selective deacetylation of 2b was carried out in the presence of (iPr)₃Sn(OEt) and yielded 3b.

Table 4. Conjugated POCl₃ and ethanol amine in anomeric position, reaction times and yields

| Entry | Reactant | Products (T) | Yield% |
|-------|----------|--------------|--------|
| 1     | 3a       | ![Image]     | 77     |
| 2     | 3b       | ![Image]     | 72     |
| 3     | 3c       | ![Image]     | 67     |
| 4     | 3d       | ![Image]     | 62     |
| 5     | 3e       | ![Image]     | 52     |

Carbohydrate is one of the natural materials with the biggest organic compounds classification which exist in a high level biomolecule such as lipids or glycoproteins. Carbohydrates play an important role in different kinds of biological processes. Mutual and specific performances of protein-carbohydrate in processes such as cell breakdown, cell adhesion, safety reaction, congestion and tumor cell.
Metamorphosis, glycolipid, glycoprotein and Polysaccharide creation in lektins and proteins, are the biological responsibilities of carbohydrates.

The FT-IR spectrum in combination with it, showed that there was no penetration with the OH absorption range. All compounds synthesized in Table 4 are confirmed by $^{31}$PNMR spectroscopy.

In order to prepare (1F), compound $3b$ obtained from previous stage (1.4mmol) was dissolved in pyridine (0.4mL) and deprotonated by NaOH. A mixture is cooled at $0^\circ$C in an ice water bath, then bromohexaalkylsulfonate is added (2mmol, 0.2mL), and then the reaction mixture is stirred for 6 h at room temperature. After gathering sediment, it is dissolved in dichloromethane (12mL) and organic phase is extracted by salt water (2*6mL) and then dried by using sodium sulphate, the solution is filtered and removed by rotary, and crystallized by ethanol with 53% efficiency (scheme 4).

Under base conditions, Compound 1F is reacted in bromo hexaalkyl Methylsulfonate reaction in presence of pyridine. In FT-IR spectrum (Figure 4), peak 1226, and 1751 cm$^{-1}$ is related to ester carbonyl strength groups and peak located at 2942, and 2867 cm$^{-1}$ is related to CH aliphatic group. Also, 1173 cm$^{-1}$ peak is related to ($S=O$) group and 1374 cm$^{-1}$ peak is related to methyl absorption group, 1069 cm$^{-1}$ peak is related to (-CH$_2$-O-CH$_2$-) absorption group. Removal of OH peak showed product formation.

![Scheme 4. Reaction process and synthesis of 1F](image)

**Figure 4. FT-IR spectrum of compound of 1F**
In **1H NMR spectrum of 1f**, (-O(CH$_2$)$_2$-(CH$_2$)$_2$-(CH$_2$)$_2$-S(=O)-) is a quintet peak at $\delta = 1.23$ and $\delta = 1.38$ppm is for 4 protons and $\delta = 1.56$ppm is for two protons. One peak at $\delta = 1.72$ppm is for two protons (Figure 5). All of peaks corresponded to the equilibrium mixture of $\alpha$ and $\beta$ isomers. A peak at $\delta = 1.96$, 1.97, 2.02, 2.09, 2.14, 2.17ppm is related to 12 methyl’s protons. Two singlet peaks are related to (S(=O)$_2$-CH$_3$) in chemical shift with $\delta = 2.99$ and $\delta = 3.02$ppm and they equal with 3 protons of $\alpha$ and $\beta$ isomers. Two doublet of doublets peaks relate to (-O-CH$_2$-(CH$_2$)$_2$-CH$_2$-O-S(=O)-) at $\delta = 3.42$-4.02ppm. Multiplet peaks at $\delta=4.02$-4.42ppm corresponded to (C4, C5 and C6-H). A doublet of doublet peak for (C2 and C3-H) at $\delta = 4.97$ -5.47 ppm has 4 protons relate to $\alpha$ and $\beta$ isomers.

In **$^{13}$C NMR spectrum of 1f**, four peaks observed at $\delta = 20.9$, 20.7, 20.63, 20.56ppm are related to four methyis of OAc groups. Four peaks observed at $\delta = 29.6$, 29.2, 29.0, 26.5, 25.3, 25.1 and 24.9ppm are related to six carbons (-CH$_2$)$_n$- of $\alpha$ and $\beta$ isomers. Two peaks observed at $\delta = 37.3$ and 32.4ppm related to (S(=O)$_2$-CH$_3$) are equal with two carbons in $\alpha$ and $\beta$ isomers. Observed peak at $\delta = 61$ppm is related to methylene carbon (C6). Also, Observed peak at $\delta = 101.3$ppm corresponded to anomeric carbon atom. Eight peaks in carbonyl region at $\delta = 169.9$,
170.07, 170.13, 170.3, 170.3, 168.9, 169.3 and 170.4ppm corresponded to α and β isomers (Figure 6).

4. Conclusion

The present study investigated a productive manner for deacetylation of anomeric position. This method has several advantages such as the good-natured reaction conditions, experimental simplicity, good yield. Then the basic reagents are unfavorable for anomeric deacetylation this approach can be very effective. In all cases, the yields were good to excellent. However, in this paper carbohydrates such as glucos, xylose, fructose, galactose, lactose by acetic anhydride in the presence of sodium acetate were acetylated. Then the deacetylation of anomeric position by (iPr)3Sn(OEt) was reacted. In order to prepare derivatives such as oxazaphosphorine and bromoheptyl methanesulfonate, deporptonation of the hydroxyl group was reacted with carbohydrates to supply new compounds.

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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