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Preparation of new β-D-xyloside- and β-D-xylobioside-based ionic liquids through chemical and/or enzymatic reactions

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ABSTRACT

Several tetraalkylphosphonium and tetraalkylammonium salts containing xyloside- and xylobioside-based anionic moieties have been prepared. Two stereoselective routes have been developed: i) a chemical pathway in four steps from D-xylose, and ii) a chemoenzymatic pathway directly from biomass-derived xylans. These salts displayed interesting properties as ionic liquids. Their structures have been correlated to their thermal properties (melting, glass transition and decomposition temperatures).

1. Introduction

Ionic Liquids (ILs) are compounds of importance due to their potential applications in various fields such as catalysis [1,2], synthetic chemistry [3–6], electrochemistry [7,8], solubilization and transformation of biopolymers [9,10], etc … The wide variety of combinations of cations and anions allows refining their physico-chemical properties (melting temperature, viscosity, density, hydrophobicity, solubility …) for well-chosen applications. For example, their low volatility makes them compounds of choice for greener solvents as alternatives to common organic solvents. Their development is therefore part of a sustainable development strategy.

In this context, one approach to produce greener ILs is to use renewable resources such as D-glucose or D-xylose the most abundant carbohydrates in the plant kingdom [11,12]. Some examples of ILs based on fructose, glucose derivatives, isomannide or isosorbide were recently reported for their uses as solvents for chiral discrimination or asymmetric organic reactions [12].

Lignocellulosic biomass represents an abundant source of valuable molecules in a biorefinery context [13]. Among these molecules, xylans, mainly constituted of xylose residues, generate a growing interest for processing into various molecules of interest [14], such as xylitol, ethanol, and might be building blocks of choice for more complex molecules [15]. Xylans could represent 25–35% of dry matter in graminaceous plants and in hardwoods and this level could reach up to 50% in some tissues of cereal grains [16,17]. In this paper, following previous works on valorization of pentoses into surfactants [18–20], glycodendrimers [21,22] or as ionic liquids [23], we will describe the synthesis of xyloside- and xylobioside-based ILs from D-xylose or directly from xylans.

Our work is also part of an approach to assess how the physicochemical properties of ILs vary with different anion/cation associations. For this purpose, we designed a general structure of β-D-xyloside- and β-D-xylobioside-based ILs with a modular amphiphilic anionic structure that can be divided into three blocks (Scheme 1): i) a polar head containing one or two xylose units, ii) a modular linker on the anomeric position of the sugar (methylene, pentyl, benzyl or triazolyl), and iii) a carboxylate anion type, which makes these ILs very attractive for various applications [24–27]. As counter cations, we chose tetralkylammonium ($^{+}NBu_4$, $^{+}NHex_4$) or

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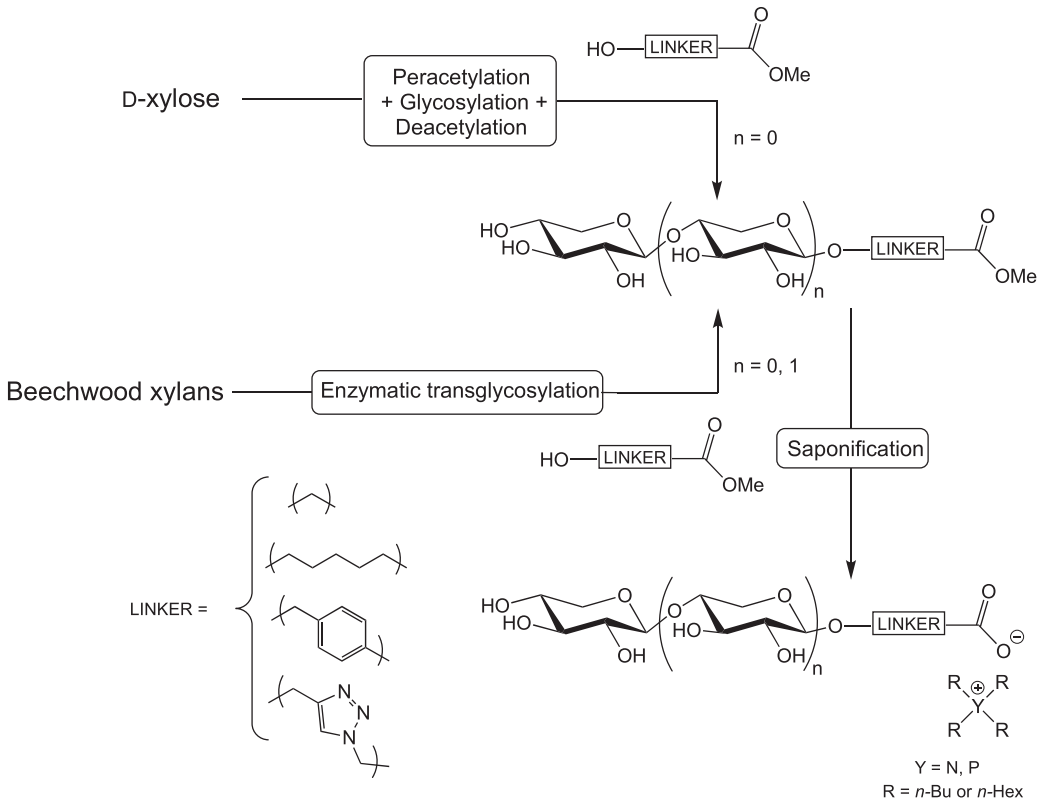


Scheme 1. Chemical and chemo-enzymatic pathways to access to the β-D-xyloside- and β-D-xylobioside-based ILs.

-phosphonium ($^{+}PBu_4$), which are large cations and generate salts with lower melting points than imidazolium- or pyridinium-based ILs [3].

To access to these salts, two stereoselective routes have been developed. In a chemical pathway from D-xylose, peracetylated β-D-xylopyranose was first glycosylated with a hydroxyester in the presence of a Lewis acid. After deacetylation, a subsequent saponification reaction was carried out to form the β-D-xyloside-based ILs. In a chemo-enzymatic strategy from xylans, an enzymatic transglycosylation catalyzed by a xylanase followed by a saponification step led to both β-D-xyloside- and β-D-xylobioside-based ILs. The range of ILs has also been expanded by introducing a triazolyl linker through a copper-catalyzed azide-alkyne cycloaddition (CuAAC), which appeared as an increasingly popular tool to synthesize ionic liquids [23,28–30]. The melting, glass transition and decomposition temperatures of all the β-D-xyloside- and β-D-xylobioside-based ILs were then measured in order to determine their liquidus range.

2. Experimental section

2.1. Materials

Methyl 6-hydroxyhexanoate [31] and compounds **1** [32] and **15** [33] were synthesized as previously described in the literature. A recombinant thermophilic family 10 *endo*-xylanase (Tx-xylanase) from *Thermobacillus xylanilyticus* was produced by *E. coli* BL21 (DE3) using a previously established protocol [34]. All other reagents were commercially available and used as received. CH_2Cl_2 was dried using a Pure Solv solvent drying system over aluminum oxide under an argon atmosphere before use.

2.2. Analysis

^{1}H (500.1 MHz, 600.2 MHz), ^{13}C (125.0 MHz, 150.0 MHz) and ^{31}P-NMR (202.4 MHz) spectra were recorded on an AC 500 and AC 600 Bruker instruments in D_2O or DMSO-*d6*. Chemical shifts are expressed in parts per million (ppm), coupling constants $|J|$ are given in Hertz (Hz) and pattern abbreviations are s for singlet, d for doublet, dd for doublet of doublet, t for triplet, q for quartet, quint for quintuplet, sext for sextuplet and m for multiplet. IR spectra were recorded on a Perkin Elmer spectrometer (UATR Two). C and H analyses were performed on a Perkin Elmer 2400 CHN equipment. Chromatographies were carried out on MN Silica 60 (40–63 μm) or Silica 60 F254 (TLC plates). ESI-HRMS spectra were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive and negative mode. The electrospray potential was set to 3 kV in positive ion mode (flow of injection 5 μL min^{-1}) and the extraction cone voltage was usually varied between 30 and 90 V. Optical rotations were measured on a Perkin Elmer 241 polarimeter. The DSC experiments were carried out on a Q100 TA instruments heat flux differential calorimeter at a heating rate of 5 K min^{-1} under a constant flow of dry nitrogen (50 mL min^{-1}). Aluminum crucibles were loaded with around 2 mg of sample. The decomposition temperatures of the ILs were measured using a Q500 TA instruments, with the mass of TGA samples varying between 10 and 20 mg (protocol followed: flow of dry nitrogen at 60 mL min^{-1} on sample; isotherm for 5 min at 50 °C to stabilize the apparatus and purge the oven; heating from 50 °C to 400 °C at a rate of 10 K min^{-1}; isotherm for 15 min at 400 °C; for liquid or viscous samples, an aluminum capsule was used to avoid fouling the measurement platform).

2.3. Synthesis

2.3.1. General procedure for the glycosylation and deacetylation reactions

To a solution of 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose **1** (1.0 equiv) and the corresponding alcohol (1.2 equiv, ethyl glycolate, methyl 6-hydroxyhexanoate or methyl 4-(hydroxymethyl)benzoate) in CH_2Cl_2 was added $BF_3.Et_2O$ (1.5 equiv) at 0 °C under Ar. After stirring for 2 h, at room temperature, the organic mixture was washed with a saturated solution of $NaHCO_3$ and water, dried over Na_2SO_4 and concentrated to dryness under reduced pressure.

To a solution of the previously xyloside obtained in MeOH was added Na (10.0 mol %) under Ar. After stirring for 1 h at room temperature, the mixture was neutralized with DOWEX (H^+), filtered and concentrated to dryness under reduced pressure. Xyloside **2** was obtained as a white solid and was characterized without any further purification. The xyloside **3** was purified by flash chromatography over silica gel with eluting mixture CH_2Cl_2/MeOH: 8:2 to afford a white solid. In the case of xyloside **4**, the residue was washed with CH_2Cl_2 (3 × 50 mL) to afford a pure compound.

Xyloside 2. Yield 72%, white solid, m.p. 95 °C; ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 3.29 (1H, dd, $^3J_{5,4}$ 10.6, $^2J_{5,5}$ 11.6, 5-H), 3.34 (1H, dd, $^3J_{2,1}$ 7.8, $^3J_{2,3}$ 9.3, 2-H), 3.44 (t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.60–3.62 (1H, m, 4-H), 3.78 (3H, s, OC*H*$_3$), 3.95 (1H, dd, $^3J_{5,4}$ 5.5, $^2J_{5,5}$ 11.6, 5-H), 4.43 (2H, s, OC*H*$_2$), 4.44 (1H, d, $^3J_{1,2}$ 7.8, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 52.5 (O*C*H$_3$), 65.2 (C-5), 66.2 (O*C*H$_2$), 69.1 (C-4), 72.7 (C-2), 75.5 (C-3), 102.9 (C-1), 172.3 (*C*=O); IR (ATR, neat): 1748 cm^{-1} (C=O); ESI-HRMS: *m/z* calcd for $C_8H_{14}NaO_7$: $[M+Na]^+$: 245.0637; found: 245.0627; elemental analysis: calcd for $C_8H_{14}O_7$+0.25 H_2O: C 42.38, H 6.44; found: C 42.12, H 6.24.

Xyloside 3. Yield 26%, white solid, m.p. 92 °C; ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 1.33–1.39 (2H, m, OCH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$), 1.52–1.58 (2H, m, OCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.61 (2H, quint, ^3J 7.6, OCH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$), 2.41 (2H, t, ^3J 7.4, OCH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$), 3.23 (1H, dd, $^3J_{2,1}$ 7.9, $^3J_{2,3}$ 9.3, 2-H), 3,31 (1H, t, $^3J_{5,4} = {}^2J_{5,5}$ 11.7, 5-H), 3.42 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.59 (2H, t, ^3J 6.5, OC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 3.69 (3H, s, OC*H*$_3$), 3.83–3.88 (1H, m, 4-H), 3.86 (1H, dd, $^3J_{5,4}$ 5.4, $^2J_{5,5}$ 11.7, 5-H), 4.38 (1H, d, $^3J_{1,2}$ 7.9, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 24.5 (OCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$), 28.4 (OCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$), 30.8 (OCH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 33.5 (OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 48.8 (O*C*H$_3$), 61.5 (OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 65.0 (C-5), 70.3 (C-4), 72.9 (C-2), 75.7 (C-3), 102.9 (C-1), 177.5 (*C*=O); IR (ATR, neat): 1728 cm^{-1} (C=O); ESI-HRMS: *m/z* calcd for $C_{12}H_{22}NaO_7$: $[M+Na]^+$: 301.1263; found: 301.1259.

Xyloside 4. Yield 70%, white solid, m.p. 148 °C; ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 3.32–3.36 (2H, m, 2-H, 5-H), 3.45 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.63–3.67 (1H, m, 4-H), 3.96 (3H, s, OC*H*$_3$), 3.99 (1H, dd, $^3J_{5,4}$ 5.4, $^2J_{5,5}$ 11.3, 5-H), 4.52 (1H, d, $^3J_{1,2}$ 7.8, 1-H), 4.84 (1H, d, ^3J 13.3, OC*H*$_2$), 4.97 (1H, d, ^3J 13.3, OC*H*$_2$), 7.58 (1H, d, ^3J 8.1, C*H*$_{Ar}$), 8.06 (1H, d, ^3J 8.1, C*H*$_{Ar}$); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 52.7 (O*C*H$_3$), 65.2 (C-5), 69.2 (C-4), 70.8 (O*C*H$_2$), 73.0 (C-2), 75.7 (C-3), 102.4 (C-1), 128.2 (*C*H$_{Ar}$), 129.2 (*C*$_{qAr}$), 129.7 (*C*H$_{Ar}$), 142.5 (*C*$_{qAr}$), 169.2 (*C*=O); IR (ATR, neat): 1713 cm^{-1} (C=O); ESI-HRMS: *m/z* calcd for $C_{14}H_{18}NaO_7$: $[M+Na]^+$: 321.0950; found: 321.0952.

2.3.2. General procedure for the saponification reactions

Compounds **2**–**4** and **16** (1.0 equiv) were dissolved in distilled water. An aqueous solution of NBu_4OH (1 equiv) or PBu_4OH (1 equiv) or $NHex_4OH$ (1 equiv) was then added, and the mixture was stirred at 50 °C for 1 h. After lyophilization, compounds **5**–**13** and **19**–**21** were isolated and characterized without further purification.

IL 5. Yield 98%, white solid, $[\alpha]_D^{20} = -25.7$ (c = 0.40 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.99 (12H, t, ^3J 7.3, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.40 (8H, sext, ^3J 7.4, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.65–1.73 (8H, m, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.20–3.26 (8H, m, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.32–3.40 (2H, m, 2-H, 5-H), 3.49 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.63–3.69 (1H, m, 4-H), 3.98 (1H, dd, $^3J_{5,4}$ 5.4, $^2J_{5,5}$ 11.6, 5-H), 4.10 (1H, d, ^3J 15.5, OC*H*$_2$), 4.27 (1H, d, ^3J 15.5, OC*H*$_2$), 4.45 (1H, d, $^3J_{1,2}$ 7.7, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 12.8 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 19.2 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 23.2 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 58.2 (NCH$_2$CH$_2$CH$_2$CH$_3$), 65.2 (C-5), 68.5 (O*C*H$_2$), 69.2 (C-4), 73.0 (C-2), 75.5 (C-3), 103.1 (C-1), 177.2 (*C*=O); IR (ATR, neat): 1590 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{23}H_{47}NO_7$: C 61.44, H 10.53, N 3.11; found: C 61.50, H 10.54, N 3.11.

IL 6. Yield 77%, white solid, m.p. 72 °C; $[\alpha]_D^{20} = -15.1$ (c=0.40 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.88 (12H, t, ^3J 7.4, NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.30–1.37 (24H, m, NCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.63–1.67 (8H, m, NCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.15–3.20 (8H, m, NC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.28–3.35 (2H, m, 2-H, 5-H), 3.44 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.0, 3-H), 3.58–3.65 (1H, m, 4-H), 3.93 (1H, dd, $^3J_{5,4}$ 5.4, $^2J_{5,5}$ 11.6, 5-H), 4.04 (1H, d, ^2J 15.5, OC*H*$_2$), 4.22 (1H, d, ^2J 15.5, OC*H*$_2$), 4.39 (1H, d, $^3J_{1,2}$ 7.7, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 13.2 (NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_3$), 20.9 (NCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 21.7 (NCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_3$), 25.2 (NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 30.4 (NCH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 58.1 (N*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 65.2 (C-5), 68.5 (O*C*H$_2$), 69.1 (C-4), 73.0 (C-2), 75.5 (C-3), 103.1 (C-1), 177.0 (*C*=O); IR (ATR, neat): 1602 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{31}H_{63}NO_7$: C 66.27, H 11.30, N 2.49; found: C 66.67, H 11.51, N 2.94.

IL 7. Yield 96%, oily, $[\alpha]_D^{20} = -25.3$ (c = 0.40 in H_2O); ^{1}H NMR (500 MHz, D_2O, 25 °C): δ = 0.92 (12H, t, ^3J 7.4, PCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.46 (8H, sext, ^3J 7.4, PCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.49–1.59 (8H, m, PCH$_2$CH$_2$C*H*$_2$CH$_3$), 2.11–2.19 (8H, m, PC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.28–3.35 (2H, m, 2-H, 5-H), 3.34 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.58–3.65 (1H, m, 4-H), 3.94 (1H, dd, $^3J_{5,4}$ 5.4, $^2J_{5,5}$ 11.6, 5-H), 4.04 (1H, d, ^3J 15.5, OC*H*$_2$), 4.23 (1H, d, ^3J 5.5, OC*H*$_2$), 4.40 (1H, d, $^3J_{1,2}$ 7.7, 1-H); ^{13}C NMR (125 MHz, D_2O, 25 °C): δ = 12.5 (PCH$_2$CH$_2$CH$_2$*C*H$_3$), 17.6 (d, J 48.2, PCH$_2$CH$_2$CH$_2$CH$_3$), 22.6 (d, J 4.5, PCH$_2$CH$_2$CH$_2$CH$_3$), 23.2 (d, J 15.3, PCH$_2$CH$_2$CH$_2$CH$_3$), 65.2 (C-5), 68.5 (O*C*H$_2$), 69.2 (C-4), 73.0 (C-2) 75.5 (C-3), 103.1 (C-1), 177.0 (*C*=O); ^{31}P NMR (202.4 MHz, D_2O, 25 °C, TMS): δ = 33.25 (s, *P*Bu$_4$); IR (ATR, neat): 1594 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{23}H_{47}O_7P$: C 59.21, H 10.15; found: C 59.35, H 10.42.

IL 8. Yield 99%, oily, $[\alpha]_D^{20} = -22.6$ (c = 0.18 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.93 (12H, t, ^3J 7.6, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.31–1.39 (10H, m, OCH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.56 (2H, quint, ^3J 7.6, OCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.60–1.67 (10H, m, OCH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.16 (2H, t, ^3J 7.5, OCH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$), 3.15–3.20 (8H, m, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.21 (1H, dd, $^3J_{2,1}$ 7.9, $^3J_{2,3}$ 9.3, 2-H), 3.27 (1H, t, $^3J_{5,4} = {}^2J_{5,5}$ 11.7, 5-H), 3.40 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.56–3.60 (1H, m, 4-H), 3.63–3.67 (1H, m, OC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 3.82–3.87 (1H, m, OC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 3.91 (1H, dd, $^3J_{5,4}$ 5.7, $^2J_{5,5}$ 11.7, 5-H), 4.37 (1H, d, $^3J_{1,2}$ 7.9, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 12.8 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 19.1 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 23.1 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 25.0 (OCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$), 25.6 (OCH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$), 28.5 (OCH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 37.5 (OCH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 58.1 (NCH$_2$CH$_2$CH$_2$CH$_3$), 65.1 (C-5), 69.2 (C-4), 70.5 (OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 73.0 (C-2), 75.7 (C-3), 102.9 (C-1), 183.8 (*C*=O); IR (ATR, neat): 1563 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{27}H_{55}NO_7$+0.75 H_2O: C 62.45, H 10.97, N 2.69; found: C 62.28, H 11.10, N 2.80.

IL 9. Yield 94%, oily, $[\alpha]_D^{20} = -15.1$ (c = 0.13 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.88 (12H, t, ^3J 7.0, NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$), 1.30–1.37 (26H, m, OCH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$, NCH$_2$CH$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.57 (2H, quint, ^3J 7.6, OCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.61–1.67 (10H, m, OCH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$,

$NCH_2CH_2CH_2CH_2CH_2CH_3$), 2.17 (2H, t, ^3J 7.4, $OCH_2CH_2CH_2CH_2CH_2$), 3.17–3.19 (8H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.21 (1H, dd, $^3J_{2,1}$ 7.9, $^3J_{2,3}$ 9.3, 2-H), 3.28 (1H, t, $^3J_{5,4} = {}^2J_{5,5}$ 11.7, 5-H), 3.40 (t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.57–3.62 (1H, m, 4-H), 3.64–3.68 (1H, m, $OCH_2CH_2CH_2CH_2CH_2$), 3.85 (1H, m, $OCH_2CH_2CH_2CH_2CH_2$), 3.91 (1H, dd, $^3J_{5,4}$ 5.7, $^2J_{5,5}$ 11.7, 5-H), 4.38 (1H, d, $^3J_{1,2}$ 7.9, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 13.2 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 20.9 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 21.7 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 25.0 ($OCH_2CH_2CH_2CH_2CH_2$), 25.1 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 25.6 ($OCH_2CH_2CH_2CH_2CH_2$), 28.6 ($OCH_2CH_2CH_2CH_2CH_2$), 30.4 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 37.5 ($OCH_2CH_2CH_2CH_2CH_2$), 58.1 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 65.1 (C-5), 69.2 (C-4), 70.5 ($OCH_2CH_2CH_2CH_2CH_2$), 73.0 (C-2), 75.8 (C-3), 102.9 (C-1), 183.7 (*C*=O); IR (ATR, neat): 1566 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{35}H_{71}NO_7$+H_2O: C 66.10, H 11.56, N 2.20; found: C 66.40, H 11.39, N 2.42.

IL 10. Yield 96%, oily, $[\alpha]_D^{20} = -20.1$ (c = 0.15 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.91 (12H, t, ^3J 7.3, $PCH_2CH_2CH_2CH_3$), 1.34 (2H, quint, ^3J 7.2, $OCH_2CH_2CH_2CH_2CH_2$), 1.44 (8H, sext, ^3J 7.3, $PCH_2CH_2CH_2CH_3$), 1.50–1.55 (10H, m, $OCH_2CH_2CH_2CH_2CH_2$, $PCH_2CH_2CH_2CH_3$), 1.57–1.63 (2H, m, $OCH_2CH_2CH_2CH_2CH_2$), 2.12–2.17 (10H, m, $OCH_2CH_2CH_2CH_2CH_2$, $PCH_2CH_2CH_2CH_3$), 3.21 (1H, dd, $^3J_{2,1}$ 7.9, $^3J_{2,3}$ 9.3, 2-H), 3.29 (1H, t, $^3J_{5,4} = {}^2J_{5,5}$ 11.6, 5-H), 3.40 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.56–3.60 (1H, m, 4-H), 3.62–3.66 (1H, m, $OCH_2CH_2CH_2CH_2CH_2$), 3.82–3.86 (1H, m, $OCH_2CH_2CH_2CH_2CH_2$), 3.91 (1H, dd, $^3J_{5,4}$ 5.5, $^2J_{5,5}$ 11.6, 5-H), 4.37 (1H, d, $^3J_{1,2}$ 7.9, 1-H); ^{13}C NMR (150 MHz, D_2O, 25 °C, TMS): δ = 12.5 ($PCH_2CH_2CH_2CH_3$), 17.6 (d, *J* 48.2, $PCH_2CH_2CH_2CH_3$), 22.6 (d, *J* 4.5, $PCH_2CH_2CH_2CH_3$), 23.2 (d, *J* 15.3, $PCH_2CH_2CH_2CH_3$), 25.0 ($OCH_2CH_2CH_2CH_2CH_2$), 25.6 ($OCH_2CH_2CH_2CH_2CH_2$), 28.5 ($OCH_2CH_2CH_2CH_2CH_2$), 37.5 ($OCH_2CH_2CH_2CH_2CH_2$), 65.1 (C-5), 69.2 (C-4), 70.5 ($OCH_2CH_2CH_2CH_2CH_2$), 73.0 (C-2), 75.8 (C-3), 102.9 (C-1), 183.7 (*C*=O); ^{31}P NMR (202.4 MHz, D_2O, 25 °C): δ = 33.23 (s, *P*Bu_4); IR (ATR, neat): 1565 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{27}H_{55}O_7P$+0.5 H_2O: C 60.99, H 10.62; found: C 60.80, H 10.51.

IL 11. Yield 88%, white solid, $[\alpha]_D^{20} = -24.3$ (c = 0.40 in H_2O); ^{1}H NMR (500 MHz, D_2O, 25 °C): δ = 0.92 (12H, t, ^3J 7.4, $NCH_2CH_2CH_2CH_3$), 1.32 (8H, sext, ^3J 7.4, $NCH_2CH_2CH_2CH_3$), 1.55–1.64 (8H, m, $NCH_2CH_2CH_2CH_3$), 3.11–3.14 (8H, m, $NCH_2CH_2CH_2CH_3$), 3.27–3.32 (2H, m, 2-H, 5-H), 3.41 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.57–3.64 (1H, m, 4-H), 3.94 (1H, dd, $^3J_{5,4}$ 5.4, $^2J_{5,5}$ 11.6, H-5), 4.47 (1H, d, $^3J_{1,2}$ 7.8, 1-H), 4.75 (1H, d, ^2J 12.0, OCH_2), 4.90 (1H, d, ^2J 12.0, OCH_2), 7.47 (2H, d, ^3J 8.3, CH_{Ar}), 7.87 (2H, d, ^3J 8.3, CH_{Ar}); ^{13}C NMR (125 MHz, D_2O, 25 °C): δ = 12.8 ($NCH_2CH_2CH_2CH_3$), 19.1 ($NCH_2CH_2CH_2CH_3$), 23.1 ($NCH_2CH_2CH_2CH_3$), 58.0 ($NCH_2CH_2CH_2CH_3$), 65.1 (C-5), 69.2 (C-4), 71.0 (OCH_2), 73.0 (C-2), 75.7 (C-3), 102.3 (C-1), 128.0 (CH_{Ar}), 129.1 (CH_{Ar}), 136.3 (C_{qAr}), 139.6 (C_{qAr}), 175.0 (*C*=O); IR (ATR, neat): 1598 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{29}H_{51}NO_7$+0.75 H_2O: C 64.59, H 9.81, N 2.60; found: C 64.48, H 10.32, N 2.89.

IL 12. Yield 99%, white solid, $[\alpha]_D^{20} = -24.5$ (c = 0.38 in DMSO); ^{1}H NMR (500 MHz, DMSO-*d6*, 25 °C): δ = 0.84–0.89 (12H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.26–1.30 (24H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.52–1.57 (8H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.01–3.08 (2H, m, 2-H, 5-H), 3.12–3.20 (9H, m, 3-H, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.29–3.36 (1H, m, 4-H), 3.44 (3H, br s, O*H*), 3.73 (1H, dd, $^3J_{5,4}$ 5.3, $^2J_{5,5}$ 11.2, 5-H), 4.21 (1H, d, $^3J_{1,2}$ 7.6, 1-H), 4.53 (1H, d, ^2J 12.3, OCH_2), 4.75 (1H, d, ^2J 12.3, OCH_2), 7.25 (1H, d, ^3J 8.1, CH_{Ar}), 7.80 (1H, d, ^3J 8.1, CH_{Ar}); ^{13}C NMR (125 MHz, DMSO-*d6*, 25 °C): δ = 13.8 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 21.0 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 21.9 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 25.5 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 30.6 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 57.7 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 65.9 (C-5), 69.0 ($OCH_2$), 69.8 (C-4), 73.5 (C-2), 76.8 (C-3), 103.3 (C-1), 126.2 (CH_{Ar}), 128.9 (CH_{Ar}), 138.3 (C_{qAr}), 139.7 (C_{qAr}), 169.2 (*C*=O); IR (ATR, neat): 1599 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{37}H_{67}NO_7$+0.1 H_2O: C 69.46, H 10.58, N 2.18; found: C 69.01, H 10.75, N 2.23.

IL 13. Yield 99%, oily, $[\alpha]_D^{20} = -28.6$ (c = 0.12 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.91 (12H, t, ^3J 7.3, $PCH_2CH_2CH_2CH_3$), 1.43 (8H, sext, ^3J 7.2, $PCH_2CH_2CH_2CH_3$), 1.47–1.54 (8H, m, $PCH_2CH_2CH_2CH_3$), 2.07–2.14 (8H, m, $PCH_2CH_2CH_2CH_3$), 3.24–3.39 (2H, m, 2-H, 5-H), 3.41 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.58–3.65 (1H, m, 4-H), 3.95 (1H, dd, $^3J_{5,4}$ 5.5, $^2J_{5,5}$ 11.6, 5-H), 4.47 (1H, d, $^3J_{1,2}$ 7.9, 1-H), 4.75 (1H, d, ^2J 12.0, OCH_2), 4.90 (1H, d, ^2J 12.0, OCH_2), 7.44 (2H, d, ^3J 8.0, CH_{Ar}), 7.83 (2H, d, ^3J 8.0, CH_{Ar}); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 12.5 ($PCH_2CH_2CH_2CH_3$), 17.6 (d, *J* 48.2, $PCH_2CH_2CH_2CH_3$), 22.6 (d, *J* 4.6, $PCH_2CH_2CH_2CH_3$), 23.2 (d, *J* 15.3, $PCH_2CH_2CH_2CH_3$), 65.1 (C-5), 69.2 (C-4), 71.0 (OCH_2), 73.0 (C-2), 75.7 (C-3), 102.2 (C-1), 128.0 (CH_{Ar}), 129.0 (CH_{Ar}), 136.2 (C_{qAr}), 139.5 (C_{qAr}), 175.0 (*C*=O); ^{31}P NMR (202.4 MHz, D_2O, 25 °C, TMS): = δ33.21 (s, *P*Bu_4); IR (ATR, neat): 1597 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{29}H_{51}O_7P$+1.25 H_2O: C 61.62, H 9.54; found: C 61.71, H 9.48.

IL 14. Yield 95%, oily, $[\alpha]_D^{20} = -23.9$ (c 4.10 in H_2O); ^{1}H NMR (500 MHz, D_2O, 25 °C): δ = 0.92 (12H, t, ^3J 7.2, $NCH_2CH_2CH_2CH_3$), 1.35 (8H, sext, ^3J 7.2, $NCH_2CH_2CH_2CH_3$), 1.58–1.66 (8H, m, $NCH_2CH_2CH_2CH_3$), 3.13–3.17 (8H, m, $NCH_2CH_2CH_2CH_3$), 3.27 (1H, dd, $^3J_{2,1}$ 8.0, $^3J_{2,3}$ 9.0, 2-H), 3.34 (1H, t, $^3J_{5,4} = {}^2J_{5,5}$ 11.3, 5-H), 3.42 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ = 9.0, 3-H), 3.58–3.65 (1H, m, 4-H), 3.97 (1H, dd, $^3J_{5,4}$ 5.5, $^2J_{5,5}$ 11.3, 5-H), 4.52 (1H, d, $^3J_{1,2}$ 8.0, 1-H), 4.87 (1H, d, ^2J 12.5, OCH_2), 4.97 (1H, d, ^2J 12.5, OCH_2), 5.10 (2H, s, triazolyl-CH_2), 8.00 (1H, s, *H*-triazolyl); ^{13}C NMR (125 MHz, D_2O, 25 °C): δ = 13.3 ($NCH_2CH_2CH_2CH_3$), 19.6 ($NCH_2CH_2CH_2CH_3$), 23.6 ($NCH_2CH_2CH_2CH_3$), 53.6 (OCH_2), 58.5 ($NCH_2CH_2CH_2CH_3$), 62.4 (triazolyl-CH_2), 63.4 (C-5), 69.6 (C-4), 74.1 (C-2), 76.0 (C-3), 102.3 (C-1), 126.7 (*C*-H triazolyl), 143.8 (*C*-triazolyl), 173.4 (*C*=O); IR (cm^{-1}): 1620, 2784, 2957, 3445, 2957, 2784; elemental analysis: calcd (%) for $C_{26}H_{50}N_4O_7$: C 58.84, H 9.49, N 10.54; found: C 58.47, H 9.70, N 10.33.

IL 19. Yield, 95%, white solid, $[\alpha]_D^{20} = -39.0$ (c = 0.34 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.93 (12H, t, ^3J 7.6, $NCH_2CH_2CH_2CH_3$), 1.34 (8H, sext, ^3J 7.4, $NCH_2CH_2CH_2CH_3$), 1.60–1.67 (8H, m, $NCH_2CH_2CH_2CH_3$), 3.13–3.22 (8H, m, $NCH_2CH_2CH_2CH_3$), 3.24 (1H, dd, $^3J_{2',1'}$ 7.8, $^3J_{2',3'}$ 9.1, 2′-H), 3.29 (1H, t, $^3J_{5',4'} = {}^2J_{5',5'}$ 11.6, 5′-H), 3.34–3.38 (2H, m, 2-H, 5-H), 3.41 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.56 (1H, t, $^3J_{3',2'} = {}^3J_{3',4'}$ 9.1, 3′-H), 3.58–3.63 (1H, m, 4′-H), 3.74–3.80 (1H, m, 4-H), 3.95 (1H, dd, $^3J_{5',4'}$ 5.5, $^2J_{5',5'}$ 11.6, 5′-H), 4.05 (1H, d, ^2J 15.6, OCH_2), 4.06 (1H, dd, $^3J_{5,4}$ 5.3, $^2J_{5,5}$ 11.7, 5-H), 4.22 (1H, d, ^2J 15.6, OCH_2), 4.42 (1H, d, $^3J_{1,2}$ 7.7, 1-H), 4.44 (1H, d, $^3J_{1',2'}$ 7.8, 1′-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 12.8 ($NCH_2CH_2CH_2CH_3$), 19.1 ($NCH_2CH_2CH_2CH_3$), 23.1 ($NCH_2CH_2CH_2CH_3$), 58.0 ($NCH_2CH_2CH_2CH_3$), 62.9 (C-5), 65.2 (C-5′), 68.4 (OCH_2), 69.1 (C-4′), 72.7 (C-2′), 72.8 (C-2), 73.5 (C-3′), 75.5 (C-3), 76.3 (C-4), 101.8 (C-1′), 102.9 (C-1), 177.0 (*C*=O); IR (ATR, neat): 1599 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{28}H_{55}NO_{11}$: C 57.81, H 9.53, N 2.41; found: C 57.56, H 9.61, N 3.04.

IL 20. Yield 91%, white solid, m.p. 93 °C, $[\alpha]_D^{20} = -35.7$ (c = 0.34 in H_2O); ^{1}H NMR (600 MHz, D_2O, 25 °C): δ = 0.88 (12H, t, ^3J 7.0, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.30–1.35 (24H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.63–1.67 (8H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.15–3.20 (8H, m, $NCH_2CH_2CH_2CH_2CH_2CH_3$), 3.25 (1H, dd, $^3J_{2',1'}$ 7.8, $^3J_{2',3'}$ 9.1, 2′-H), 3.30 (1H, t, $^3J_{5',4'} = {}^2J_{5',5'}$ 11.6, 5′-H), 3.34–3.39 (2H, m, 2-H, 5-H), 3.41 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3 Hz, 3-H), 3.57 (1H, t, $^3J_{3',2'} = {}^3J_{3',4'}$ 9.1, 3′-H), 3.60–3.65 (1H, m, 4′-H), 3.75–3.81 (1H, m, 4-H), 3.96 (1H, dd, $^3J_{5',4'}$ 5.4, $^2J_{5',5'}$ 11.6, 5′-H), 4.05 (1H, d, ^2J 15.6, OCH_2), 4.07 (1H, dd, $^3J_{5,4}$ 5.2, $^2J_{5,5}$ 11.6, 5-H), 4.22 (1H, d, ^2J 15.6, OCH_2), 4.42 (1H, d, $^3J_{1,2}$ 7.7, 1-H), 4.44 (1H, d, $^3J_{1',2'}$ 7.8, 1′-H); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 13.2 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 20.9 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 21.7 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 25.1 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 30.3 ($NCH_2CH_2CH_2CH_2CH_2CH_3$), 58.1

($NCH_2CH_2CH_2CH_2CH_2CH_3$), 62.9 (C-5), 65.2 (C-5′), 68.4 (OCH_2), 69.1 (C-4′), 72.7 (C-2′), 72.8 (C-2), 73.5 (C-3′), 75.5 (C-3), 76.3 (C-4), 101.8 (C-1′), 102.9 (C-1), 177.0 (*C*=O); IR (ATR, neat): 1598 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{36}H_{71}NO_{11}$: C 62.31, H 10.31, N 2.02; found: C 61.97, H 10.41, N, 2.32.

IL 21. Yield 99%, oily, $[\alpha]_D^{20} = -40.5$ ($c = 0.35$ in H_2O); ^1H NMR (500 MHz, D_2O, 25 °C): δ = 0.92 (12H, t, ^3J 7.3, $PCH_2CH_2CH_2CH_3$), 1.44 (8H, sext, ^3J 7.2, $PCH_2CH_2CH_2CH_3$), 1.49–1.57 (8H, m, $PCH_2CH_2CH_2CH_3$), 2.12–2.18 (8H, m, $PCH_2CH_2CH_2CH_3$), 3.25 (1H, dd, $^3J_{2',1'}$ 7.8, $^3J_{2',3'}$ 9.1, 2′-H), 3.30 (1H, t, $^3J_{5',4'} = {}^2J_{5',5'}$ 11.6, 5′-H), 3.35–3.40 (2H, m, 2-H, 5-H), 3.40 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.3, 3-H), 3.57 (1H, t, $^3J_{3',2'} = {}^3J_{3',4'}$ 9.1, 3′-H), 3.60–3.64 (1H, m, 4′-H), 3.75–3.81 (1H, m, 4-H), 3.95 (1H, dd, $^3J_{5',4'}$ 5.4, $^2J_{5',5'}$ 11.6, 5′-H), 4.04 (1H, d, ^2J 15.6, OCH_2), 4.06 (1H, dd, $^3J_{5,4}$ 5.3, $^2J_{5,5}$ 11.7, 5-H), 4.22 (1H, d, ^2J 15.6, OCH_2), 4.42 (1H, d, $^3J_{1,2}$ 7.7, 1-H), 4.44 (1H, d, $^3J_{1',2'}$ 7.8, 1′-H); ^{13}C NMR (125 MHz, D_2O, 25 °C): δ = 12.5 ($PCH_2CH_2CH_2CH_3$), 17.6 (d, *J* 48.2, $PCH_2CH_2CH_2CH_3$), 22.7 (d, *J* 4.6, $PCH_2CH_2CH_2CH_3$), 23.2 (d, *J* 15.3, $PCH_2CH_2CH_2CH_3$), 62.9 (C-5), 65.2 (C-5′), 68.4 (OCH_2), 69.1 (C-4′), 72.7 (C-2′), 72.8 (C-2), 73.5 (C-3′), 75.5 (C-3), 76.3 (C-4), 101.8 (C-1′), 102.9 (C-1), 177.0 (*C*=O); ^{31}P NMR (202.4 MHz, D_2O, 25 °C, TMS): δ = 33.23 (s; *P*Bu_4); IR (ATR, neat): 1601 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{28}H_{55}O_{11}P$+0.25 H_2O: C 55.75, H 9.27; found: C 55.37, H 9.15.

2.3.3. "Click" reaction

Propargyl-β-D-xyloside 15 (470 mg, 2.5 mmol) and ethyl 2-azidoacetate (387 mg, 3 mmol) were dissolved in a mixture *t*-butanol/water: 1/1 (4 mL). $CuSO_4.5H_2O$ (45 mg, 0,18 mmol) and sodium ascorbate (100 mg, 0.5 mmol) were then added. After 12 h stirring at room temperature, the reaction mixture was purified by flash chromatography over silica gel (EtOAc/MeOH: 9/1). After evaporation to dryness, compound 16 was obtained as a white solid.

Xyloside 16. Yield 86%, white solid, m.p. 103 °C, $[\alpha]_D^{20} = -43.4$ ($c = 0.35$ in H_2O); ^1H NMR (500 MHz, D_2O, 25 °C): δ = 1.28 (3H, t, ^3J 7.1, $C(O)OCH_2CH_3$), 3.26–3.35 (2H, m, 2-H, 5-H), 3.43 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.59–3.64 (1H, m, 4-H), 3.97 (1H, dd, $^3J_{5,4}$ 5.5, $^2J_{5,5}$ 11.6, 5-H), 4.28 (2H, q, ^3J 7.1, $C(O)OCH_2CH_3$), 4.50 (1H, d, $^3J_{1,2}$ 7.8, 1-H), 4.88 (1H, d, ^2J 12.6, OCH_2), 4.97 (1H, d, ^2J 12.6, OCH_2), 5.40 (2H, s, triazolyl-CH_2), 8.12 (1H, s, *H*-triazolyl); ^{13}C NMR (125 MHz, D_2O, 25 °C): δ = 13.4 ($C(O)OCH_2CH_3$), 28.5 ($C(O)OCH_2CH_3$), 51.6 (OCH_2), 62.4 (triazolyl-CH_2), 63.4 (C-5), 69.6 (C-4), 74.1 (C-2), 76.0 (C-3), 102.3 (C-1), 127.0 (*C*-H triazolyl), 143.2 (*C*-triazolyl), 169.2 (*C*=O); IR (ATR, neat): 1737 cm^{-1} (C=O); elemental analysis: calcd (%) for $C_{12}H_{19}N_3O_7$: C 45.42, H 6.03, N 13.24; found: C 44.99, H 5.97, N 13.16.

2.3.4. Enzymatic transglycosylation reaction

Xylans (14 g, 10% p/v), ethyl glycolate (14 mL, 10% v/v), xylanase 10 IU/mL (50 mL) and water (76 mL) were introduced in a closed glass vessel with a magnetic stirring. The reaction was incubated in a thermostated oil bath for 24 h at 60 °C and stopped by incubating during 10 min at 100 °C. Then, the reaction mixture was centrifuged for 10 min in order to pellet the residual xylans. The surnageant was concentrated to dryness under reduced pressure and the residue, extracted with a mixture EtOAc/MeOH (1:1) (3 × 140 mL). The combined extracts were concentrated to dryness under reduced pressure and the crude product was purified by flash chromatography over silica gel (EtOAc/MeOH: 9:1) in order to isolate compounds **17** and **18** in a pure form.

Xyloside 17. 815 mg, oily; ^1H NMR (500 MHz, D_2O, 25 °C): δ = 1.30 (3H, t, ^3J 7.2, $C(O)OCH_2CH_3$), 3.34 (1H, dd, $^3J_{5,4}$ 10.4, $^2J_{5,5}$ 11.6, 5-H), 3.39 (1H, dd, $^3J_{2,1}$ 7.7, $^3J_{2,3}$ 9.2, 2-H), 3.48 (1H, t, $^3J_{3,2} = {}^3J_{3,4}$ 9.2, 3-H), 3.65–3.70 (1H, m, 4-H), 4.00 (1H, dd, $^3J_{5,4}$ 5.5, $^2J_{5,5}$ 11.6, 5-H), 4.29 (2H, q, ^3J 7.2, $C(O)OCH_2CH_3$), 4.45 (2H, s, OCH_2), 4.49 (1H, d, $^3J_{1,2}$ 7.7, 1-H); ^{13}C NMR (125 MHz, D_2O, 25 °C): δ = 14.6 ($C(O)OCH_2CH_3$), 62.1 ($C(O)OCH_2CH_3$), 65.2 (C-5), 66.3 (OCH_2), 68.7 (C-4), 73.4 (C-2), 75.2 (C-3), 103.6 (C-1), 173.9 (*C*=O); IR (ATR, neat): 1745 cm^{-1} (C=O); ESI-HRMS: *m/z* calcd for $C_9H_{16}NaO_7$: $[M+Na]^+$: 259.0794; found: 259.0797.

Xyloside 18. 1.136 g, oily; ^1H NMR (600 MHz, D_2O, 25 °C): δ = 1.31 (3H, t, ^3J 7.2, $C(O)OCH_2CH_3$), 3.24–3.29 (2H, m, 2′-H, 5′-H), 3.32–3.38 (3H, m, 2-H, 3-H, 5-H), 3.50–3.56 (2H, m, 3′-H, 4′-H), 3.66–3.72 (1H, m, 4-H), 3.93 (1H, dd, $^3J_{5',4'}$ 5.4, $^2J_{5',5'}$ 11.6, 5′-H), 4.04 (1H, dd, $^3J_{5,4}$ 5.2, $^2J_{5,5}$ 11.7, 5-H), 4.24 (2H, q, ^3J 7.2, $C(O)OCH_2CH_3$), 4.29 (1H, d, ^2J 12.6, OCH_2), 4.35–4.38 (3H, m, 1-H, 1′-H, OCH_2); ^{13}C NMR (150 MHz, D_2O, 25 °C): δ = 13.1 ($C(O)OCH_2CH_3$), 60.9 ($C(O)OCH_2CH_3$), 63.1 (C-5), 65.4 (C-1′), 65.7 (C-5), 69.6 (C-4′), 72.9 (C-2′), 73.0 (C-2), 74.0 (C-3′), 76.2 (C-3), 76.6 (C-4), 102.5 (C-1′), 103.2 (C-1), 170.7 (*C*=O); IR (ATR, neat): 1736 cm^{-1} (C=O); ESI-HRMS: *m/z* calcd for $C_{14}H_{24}NaO_{11}$: $[M+Na]^+$: 391.1216; found: 391.1219.

3. Results and discussion

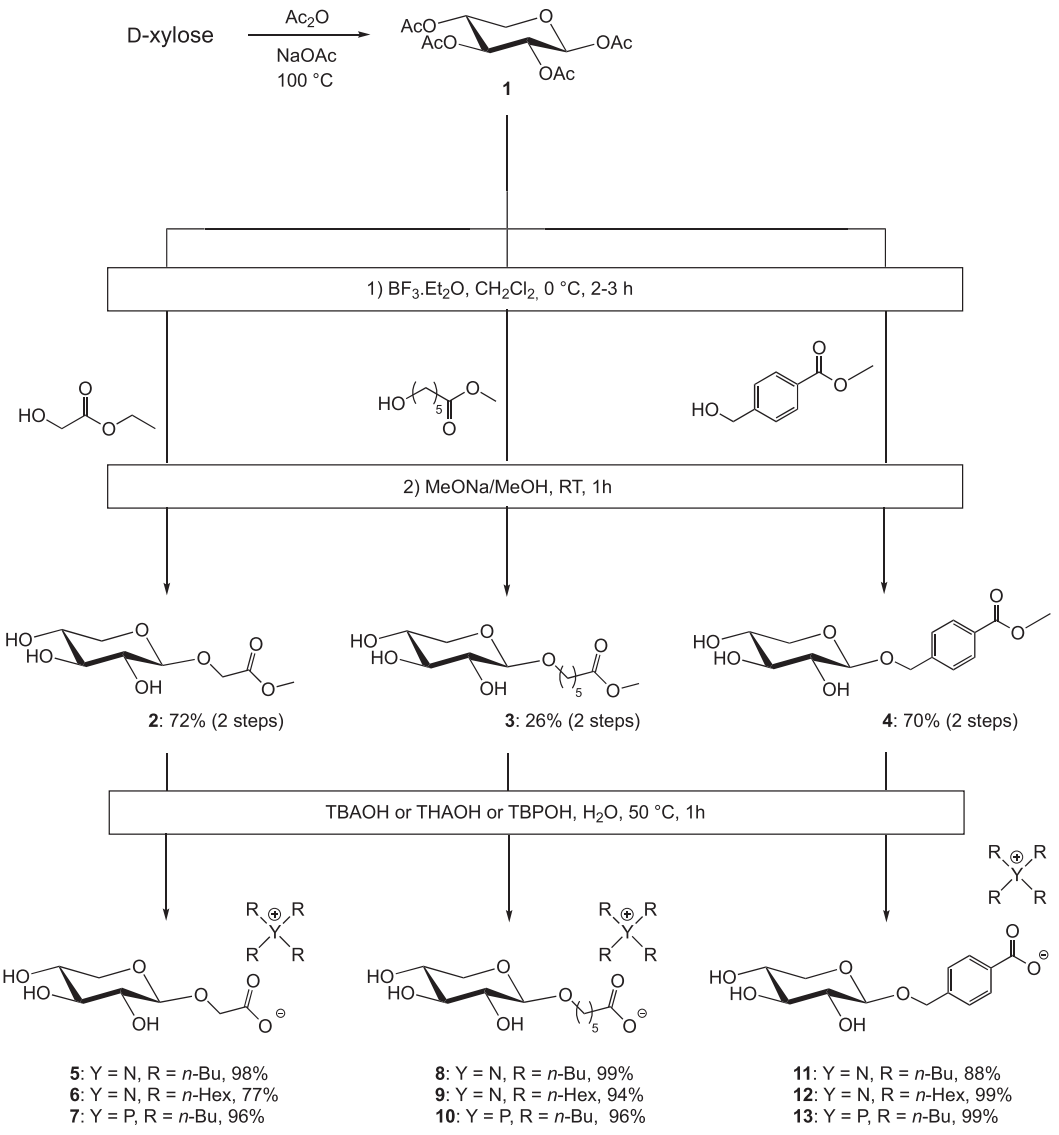
3.1. Synthesis

The β-D-xyloside-based salts **5**–**13** were synthesized in four steps from D-xylose (Scheme 2). First, 1,2,3,4-tetra-*O*-acetyl-β-D-xylopyranose **1** was selectively prepared under kinetic control from D-xylose and sodium acetate in acetic anhydride at 100 °C [32]. Freshly prepared peracetylated xylopyranose **1** was then treated with either ethyl glycolate, methyl 6-hydroxyhexanoate [31] or methyl 4-(hydroxymethyl)benzoate in the presence of $BF_3.Et_2O$. The prepared β-D-xylosides were then deacetylated without further purification under Zemplén conditions [35] to give the β-D-xylopyranosides **2**–**4** with free hydroxyl groups. Compounds **2** and **4** were isolated in a pure form with good overall yields over two steps, respectively 72% and 70%, while **3** was obtained with a low yield (26%) probably due to a lack of reactivity of the methyl 6-hydroxyhexanoate towards the peracetylated xylopyranose **1** during the glycosylation step. Alternative reaction conditions using 4 equiv. of $BF_3.Et_2O$ and 6-methylhexanoate or longer reaction times didn't improve the yield.

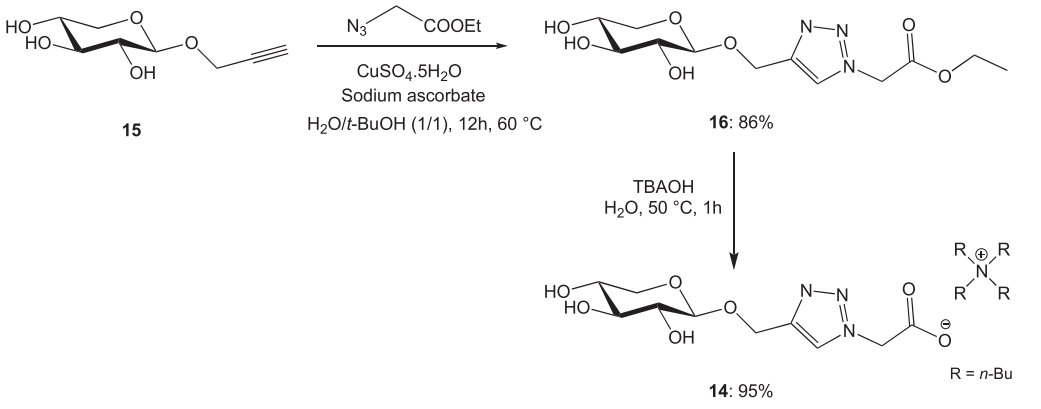
Compounds **2**–**4** were then mixed with either tetrabutylammonium hydroxide (TBAOH), tetrahexylammonium hydroxide (THAOH) or tetrabutylphosphonium hydroxide (TBPOH) in a 1:1 stoichiometry in water for 1 h at 50 °C to yield the corresponding salts **5**–**13**. Saponification reactions occurred in high yields in all cases (77–99%). ^1H and ^{13}C NMR spectra showed the total disappearance of the signals of the methyl group of the ester function. Furthermore, theoretical and experimental proportions in elemental analyses appear to be consistent with an acceptable error of less than 0.4% by taking into account in some cases the hydrophilic nature of these molecules.

The β-D-xyloside-based IL **14** containing a triazolyl linker was synthesized from propargyl-β-D-xyloside **15** (Scheme 3), as previously described [33]. First, a Huisgen-type 1,3 dipolar reaction [36,37] catalyzed by Cu(I) species (CuAAC) [38–40] was applied in the presence of ethyl 2-azidoacetate in a mixture t-BuOH/H_2O (1/1) to give the "click" compound **16** [41]. Direct purification by flash chromatography (eluting mixture EtOAc/MeOH: 7/3) provided compound **16** in a pure form with a good yield (86%). The presence of the 1,2,3-triazolyl linkage was confirmed in ^1H NMR spectra by the signal at 8.12 ppm. FTIR spectrum shows the disappearance of the band around 2110 cm^{-1} suggesting that the excess of azide was removed during the purification. The ^{13}C NMR spectrum confirmed the 1,4-substitution of the triazole moiety by the large $\Delta(\delta_{C\text{-}H\ triazolyl} - \delta_{C\text{-}triazolyl})$ value of 16.2 ppm.

Compound **16** was then mixed with tetrabutylammonium hydroxide (TBAOH) in a 1:1 stoichiometry in water for 1 h at 50 °C to



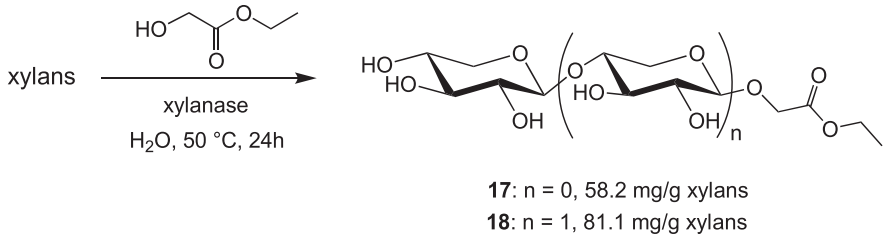
Scheme 2. Synthesis of the β-D-xyloside-based ILs **5**–**13**.



Scheme 3. "Click" synthesis of the β-D-xyloside-based IL **14**.

form the corresponding salt **14** in high yield (Scheme 3). ESI-HRMS indicates the presence of the corresponding anion, with a signal at 288.0826 (m/z) for **14** (corresponding chemical formula $C_{10}H_{14}N_3O_7$).

Using enzymatic transglycosylation with glycoside hydrolases to perform glycosylation reactions: i) avoids to proceed *via* chemical route such as the well-known Fischer glycosidation [42] or the Koenigs-Knorr reaction [43] that require organic solvents and acid



Scheme 4. Xylanase-catalyzed transglycosylation of xylans with ethyl glycolate.

catalysts, ii) minimizes waste, iii) favors the anomeric stereoselectivity and iv) can lead in the same time to oligoxylosides with a degree of polymerization greater than one. Previous studies demonstrated the ability of xylanases to produce xylosides and oligoxylosides from xylans [18,32,33,44–48]. From beechwood xylans and ethyl glycolate, the xylanase from *Thermobacillus xylanilyticus*, selectively produced β-D-xyloside **17** (58.2 mg per g of xylans) and β-D-xylobioside **18** (81.1 mg per g of xylans) in aqueous media (Scheme 4).

To study the influence of the polar head on the physico-chemical properties of the corresponding salts, β-D-xylobioside-based ILs **19**–**21** were synthesized from β-D-xylobioside **18** *via* a saponification reaction in the presence of either tetrabutylammonium hydroxide (TBAOH), tetrahexylammonium hydroxide (THAOH) or tetrabutylphosphonium hydroxide (TBPOH) in a 1:1 stoichiometry (Scheme 5). These salts were isolated in high yields (91–99%) and characterized by ^{1}H and ^{13}C NMR spectra, and elemental analyses.

All the prepared ILs are highly soluble in water and methanol and very poorly soluble in classical organic solvents such as dichloromethane, chloroform, diethyl ether or ethyl acetate.

3.2. Physicochemical properties

Table 1 gives some of their physicochemical properties. Glass transition (T_g) and decomposition (T_{dec}) temperatures were evaluated by differential scanning calorimetry (DSC) and thermal gravimetric analysis (ATG) experiments.

All the phosphonium salts **7**, **10**, **13** and **21** are extremely viscous liquids at room temperature whereas most of the corresponding ammonium salts **5**, **6**, **11**, **12**, **19** and **20** are solids. A few studies have previously described that the replacement of the nitrogen atom by the phosphorus one, lowers the melting points of the phosphonium salts in comparison to their ammonium analogs [49–51]. This decrease might be attributed to a larger radius of the phosphorus atom compared to the nitrogen atom, which decreases the lattice energy and gives more flexibility to the cation structure.

Surprisingly, for a same linker, changing the size of the alkyl chain from butyl to hexyl in the ammonium series brings a slight increase to the melting temperatures measured for these ILs [3]. Thus, the melting points for **5** and **6** are respectively 59 °C and 74 °C and for **11** and **12**, respectively 98 °C and 112 °C.

In addition to the nature of the cation, the hydrophilic lipophilic balance (HLB) of the anionic part seems to partially influence the physical properties at room temperature of the β-D-xyloside- and β-D-xylobioside-based ILs. Indeed, β-D-xyloside-based ILs **8** and **9** bearing a pentyl linker and **14** with a triazolyl linker are very viscous liquids whereas **5** and **6** containing a methylene linker or **11** and **12** with a benzyl linker are solid compounds.

Incorporating a benzyl linker instead of a methylene on the anomeric position of the sugar leads to an increase of the solid-liquid transitions, respectively at 98 °C for **11** and 112 °C for **12**, probably due to the presence of aromatic rings which allows π-π stacking between ions and results in an increase of the lattice energy.

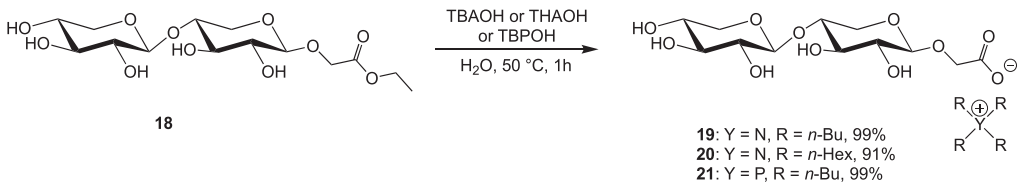
However, increasing the number of xylose units from 1 to 2 does not result in a significant change in the physical state, since compounds **19**, **20**, **21** and their parent compounds **5**, **6**, **7** follow the same trend. Only a slight increase of the melting temperature from 72 °C to 93 °C in the tetrahexylammonium series (**6** → **20**) by increasing the number of xylose units from 1 to 2 is observed.

The thermogravimetric analyses show that the decomposition temperatures of the β-D-xyloside- and β-D-xylobioside-based ILs are included between 140 °C and 260 °C. The thermal stability of these ILs seems to be limited likely due to the strength of heteroatom-carbon and heteroatom-hydrogen bonds [53]. As expected, the phosphonium derivatives have higher thermal stability than their ammonium analogs [54]. Likewise, increasing the number of xylose units from 1 to 2 enhances the decomposition temperature. However, no trend was observed for a same linker, changing the size of the alkyl chain from butyl to hexyl in the ammonium series.

The glass transition temperatures, which indicate the lower limit for the salts **7**, **8**, **9**, **10**, **13**, **14** and **21** in which they can be used as liquid if no melting point is determined, are generally included between −35 °C and 2 °C. Negative T_g values are classical for ionic liquids [51].

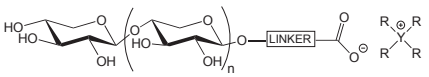
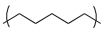
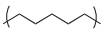
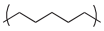
4. Conclusions

In conclusion, a chemical and a chemo-enzymatic route enabled the easy preparation of β-D-xyloside- and β-D-xylobioside-based ILs containing either tetraalkylphosphonium or tetraalkylammonium cations with a modular amphiphilic anionic structure. The HLB of each IL anion is designed by introducing one or two xylose



Scheme 5. Synthesis of the β-D-xylobioside-based ILs **19**–**21**.

Table 1
Properties of β-D-xyloside- and β-D-xylobioside-based ILs.

Compound				mp[a] (°C) [52]	T_g[b] (°C)	$[\alpha]_D^{20}$	Physical aspect
	n	Linker	Y, R				
5	0		N, *n*-Bu	59	–	−25.7	Solid
6	0		N, *n*-Hex	74	−4	−15.1	Solid
7	0		P, *n*-Bu	–	–	−25.3	Oil
8	0		N, *n*-Bu	–	−35	−22.6	Oil
9	0		N, *n*-Hex	–	−30	−15.1	Oil
10	0		P, *n*-Bu	–	0	−20.1	Oil
11	0		N, *n*-Bu	98	−32	−24.3	Solid
12	0		N, *n*-Hex	112	−4	−24.5	Solid
13	0		P, *n*-Bu	–	−19	−28.9	Oil
14	0		N, *n*-Bu	–	−26	−23.9	Oil
19	1		N, *n*-Bu	–	−32	−39.0	Solid
20	1		N, *n*-Hex	93	16	−35.7	Solid
21	1		P, *n*-Bu	–	2	−40.5	Oil

[a] Determined on a Stuart™ melting point apparatus SMP3.
[b] Determined by DSC.

units and various hydrophobic moieties (methylene, pentyl, benzyl or triazolyl) into the anomeric position bearing a carboxylate group. ILs containing phosphonium cations and a pentyl moiety are generally liquids while those containing ammonium cations and a small alkyl or benzyl moiety are solids. The glass transition temperatures for the liquids are between −35 and 0 °C, and the transition melting temperatures for the solids are generally lower than 100 °C. In addition, the thermal stability of the phosphonium ILs is higher than their ammoniums analogs. These results illustrate the impact of the various anion/cation combinations on the thermal properties of these biomass-derived ILs.

Acknowledgements

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