# Supporting Information

## Unveiling the role of choline chloride on furfural synthesis from highly concentrated feeds of xylose

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## FIGURE CAPTIONS

Figure S1. Conversion of xylose (33 wt. %) at 120 °C and pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20, without any salt, and either with ChCl or NaCl.

Figure S2. Thermal profiles of different system (furfural/water, xylose/water with or without ChCl) in the presence of HCl (A) and in the absence of HCl (B)

Figure S3. (A) $^1$H NMR and (B) $^{13}$C NMR spectra at initial time of xylose/HCl/$D_2O$/ChCl and xylose/HCl/$D_2O$.

Figure S4. (A) $^1$H NMR and (B) $^{13}$C NMR spectra of the synthesized choline xyloside.

Figure S5. Conversion of xylose (33 wt%) and choline xyloside (same molar content as xylose) at 120 °C and pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20.

Figure S6. Conversion of xylose (33 wt%) in the presence of ChCl and BzTEACl at 120 °C, pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20.

Figure S7. $^1$H NMR spectra of (A) commercial ChCl and (B) recovered ChCl.

Figure S8. $^{13}$C NMR *spectra of (A) commercial ChCl and* (B) *recovered ChCl.*

Figure S9. Conversion of xylose (50 wt%) in the presence of variable ChCl concentration relative to water at 120 °C, pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20.

Figure S10. Conversion of xylose (33 wt%) to furfural at 120 °C, pH = 0.86 and a $H_2O$/MIBK weight ratio of 1/20.

## TABLE CAPTIONS

Table S1. Results from TG analysis.

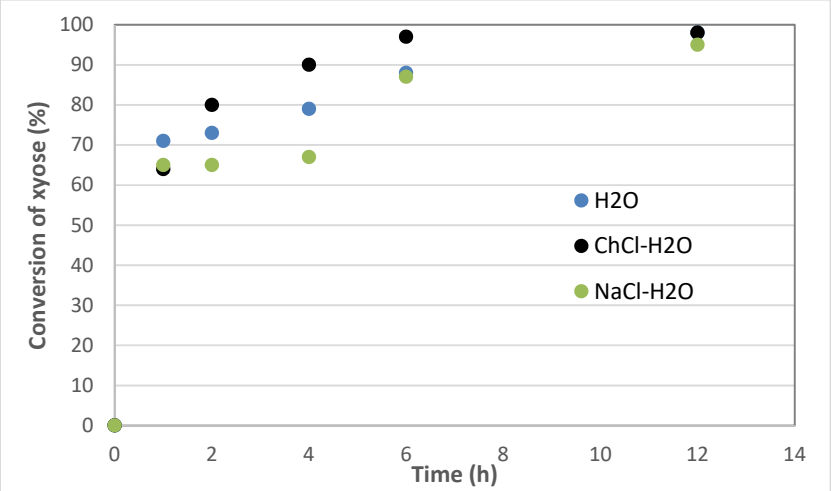



Figure S1. Conversion of xylose (33 wt%) at 120 °C and pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20, without any salt, and either with ChCl or NaCl.

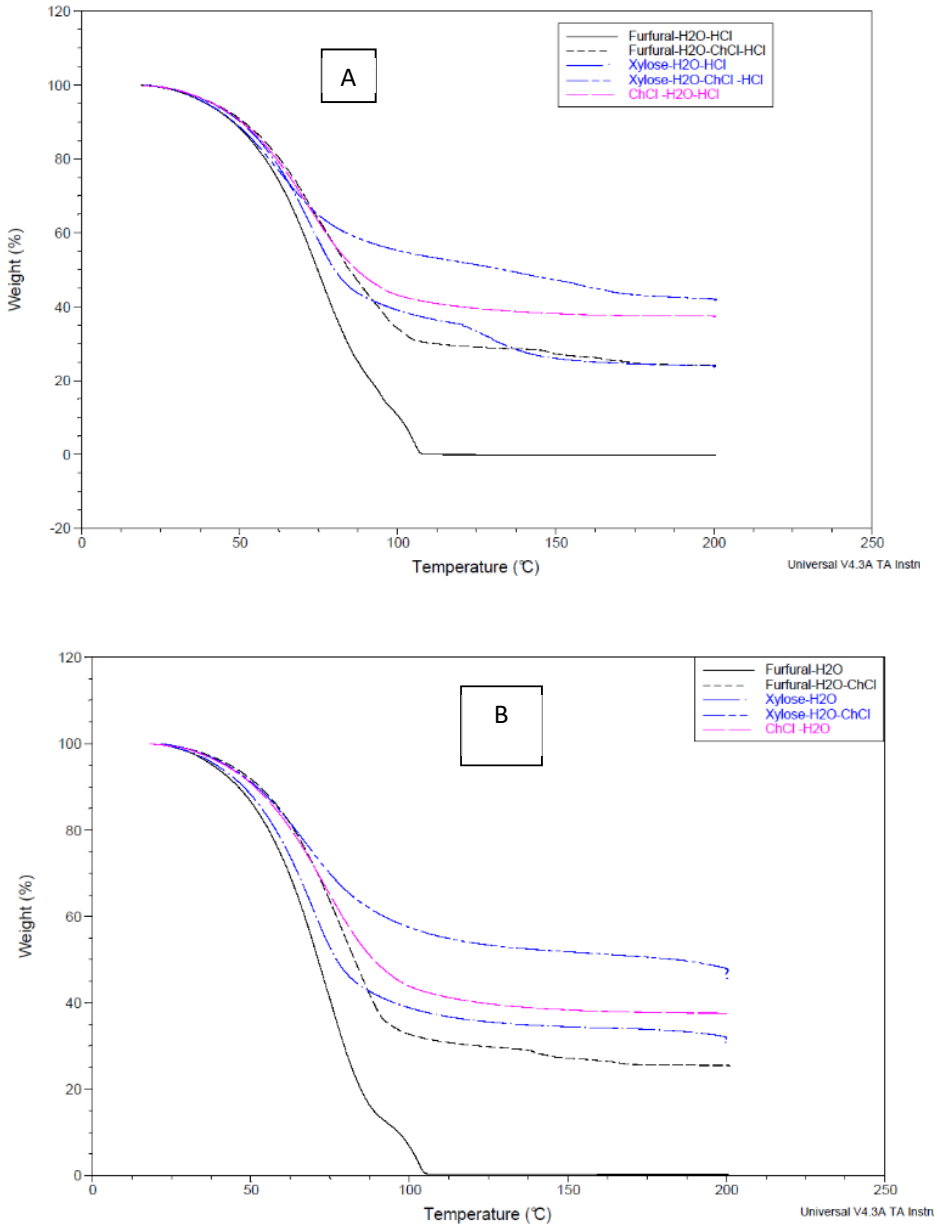



Figure S2. Thermal profiles of different system (furfural/water, xylose/water with or without ChCl) in the presence of HCl (A) and in the absence of HCl (B)

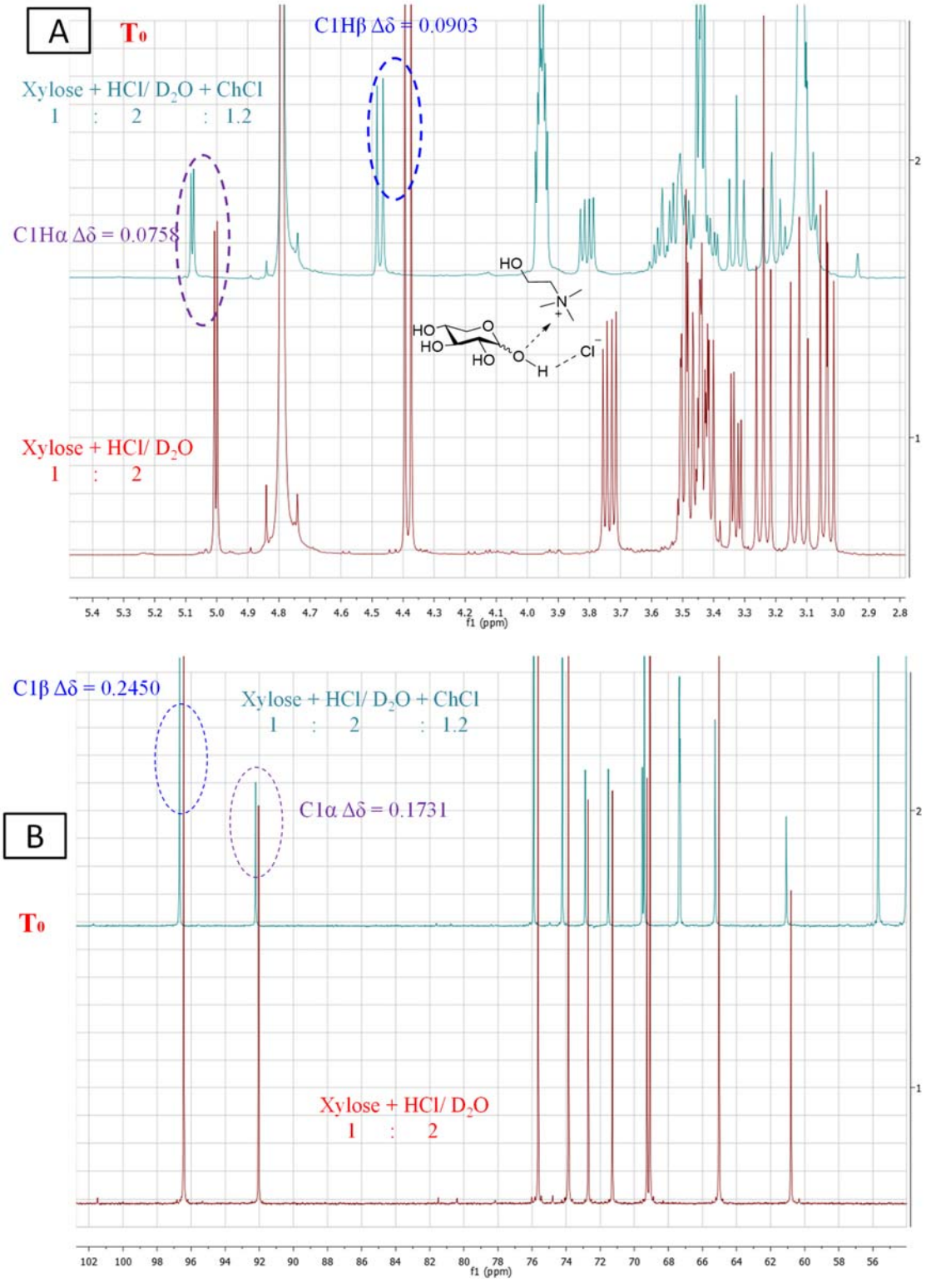



Figure S3. (A) $^{1}H$ NMR and (B) $^{13}C$ NMR spectra at initial time of xylose/HCl/$D_2O$/ChCl and xylose/HCl/$D_2O$.

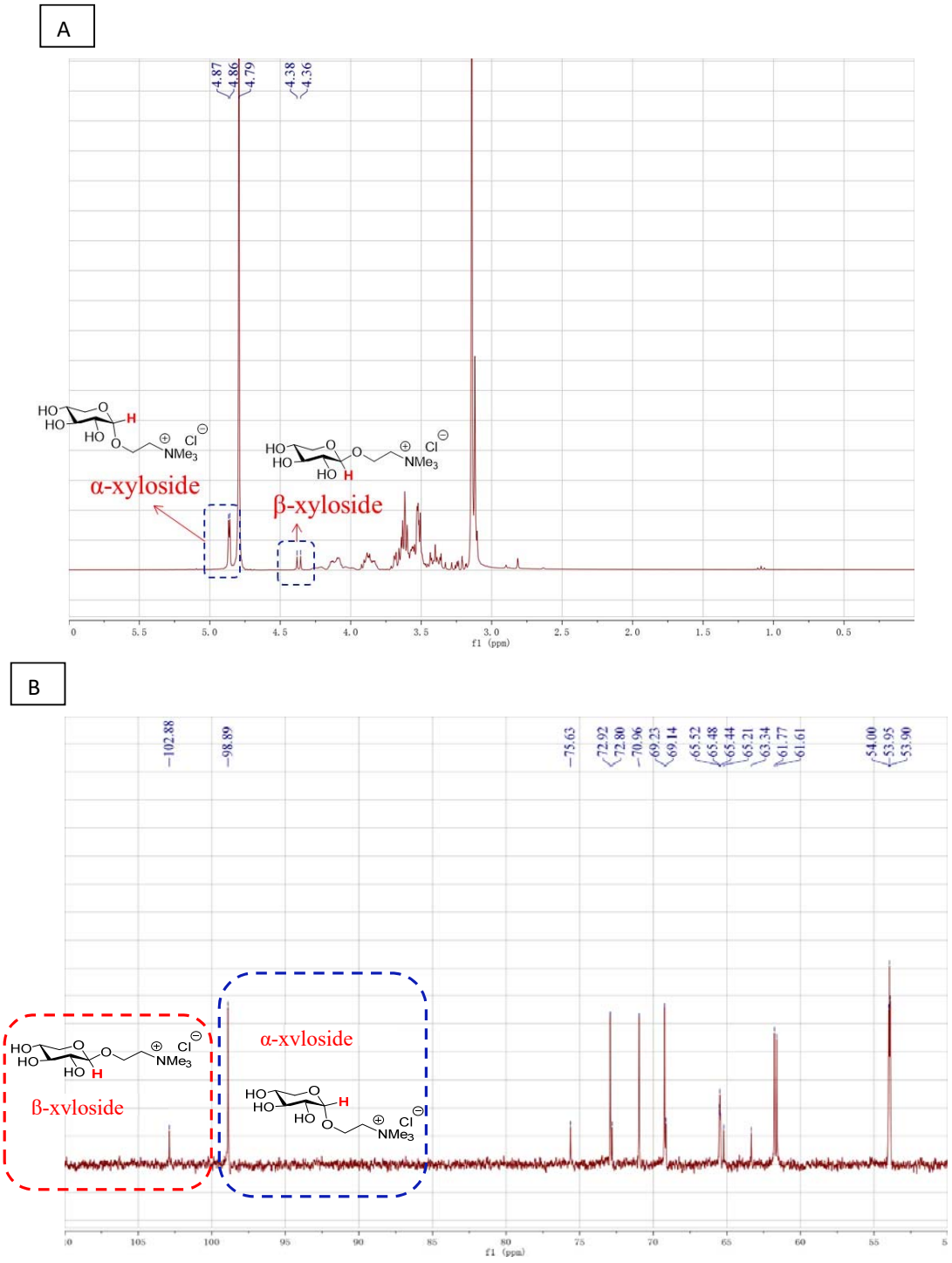



Figure S4. (A) $^{1}H$ NMR and (B) $^{13}C$ NMR spectra of the synthesized choline xyloside.

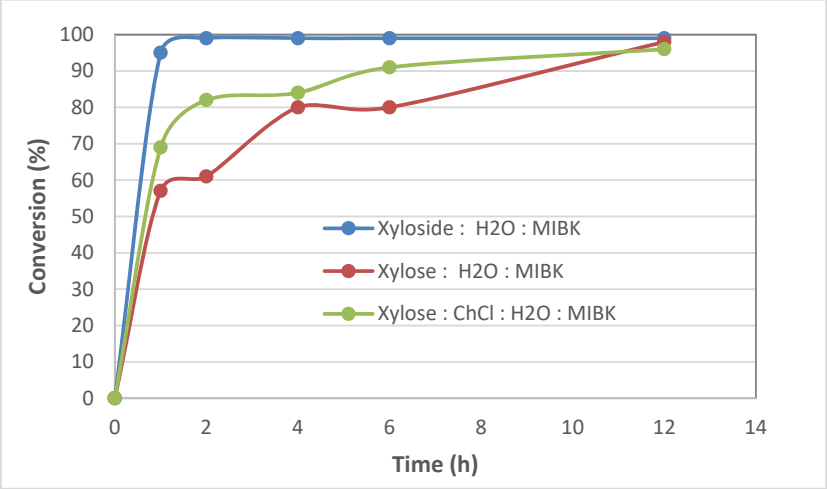



Figure S5. Conversion of xylose (33 wt%) and choline xyloside (same molar content as xylose) at 120 °C and pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20.

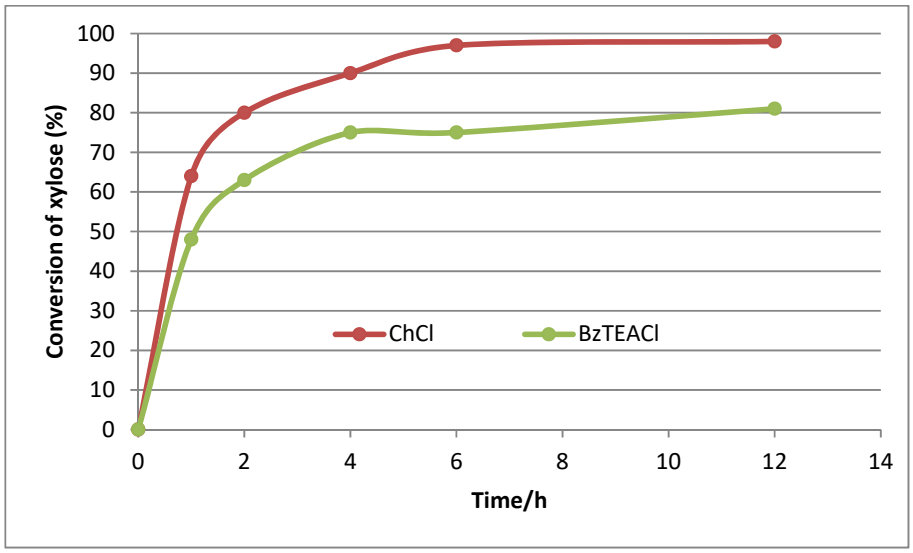
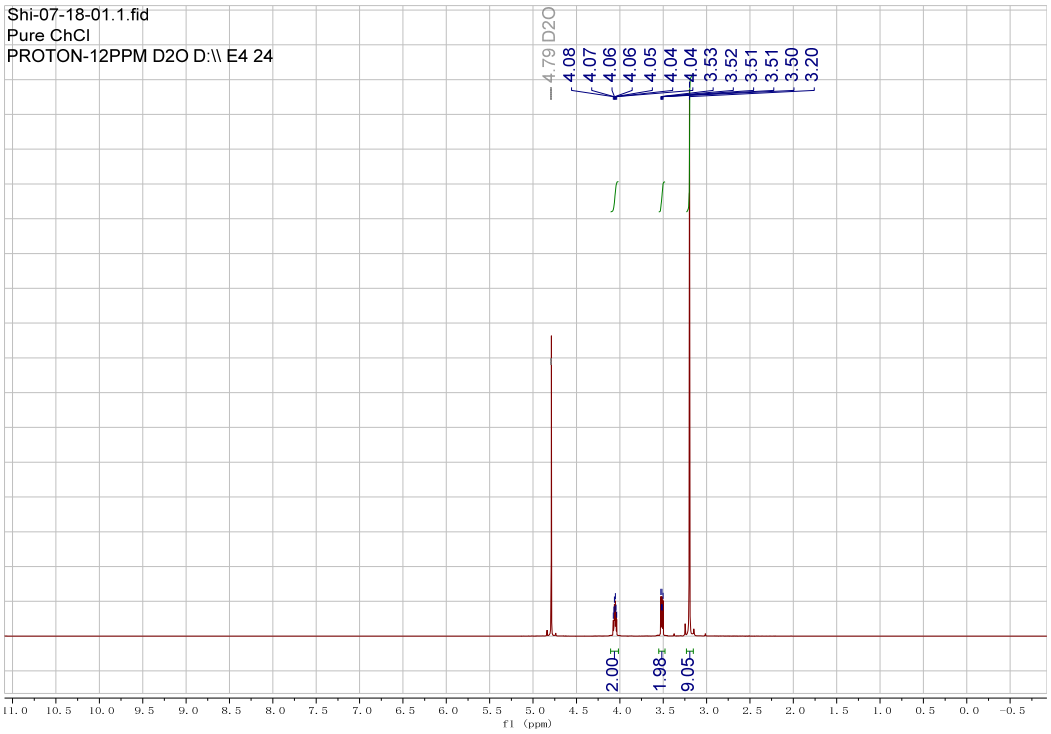



Figure S6. Conversion of xylose (33 wt.) in the presence of ChCl and BzTEACl at 120 °C, pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20.

A. $^{1}$H NMR of commercial ChCl




B. $^{1}$H NMR of recovered ChCl

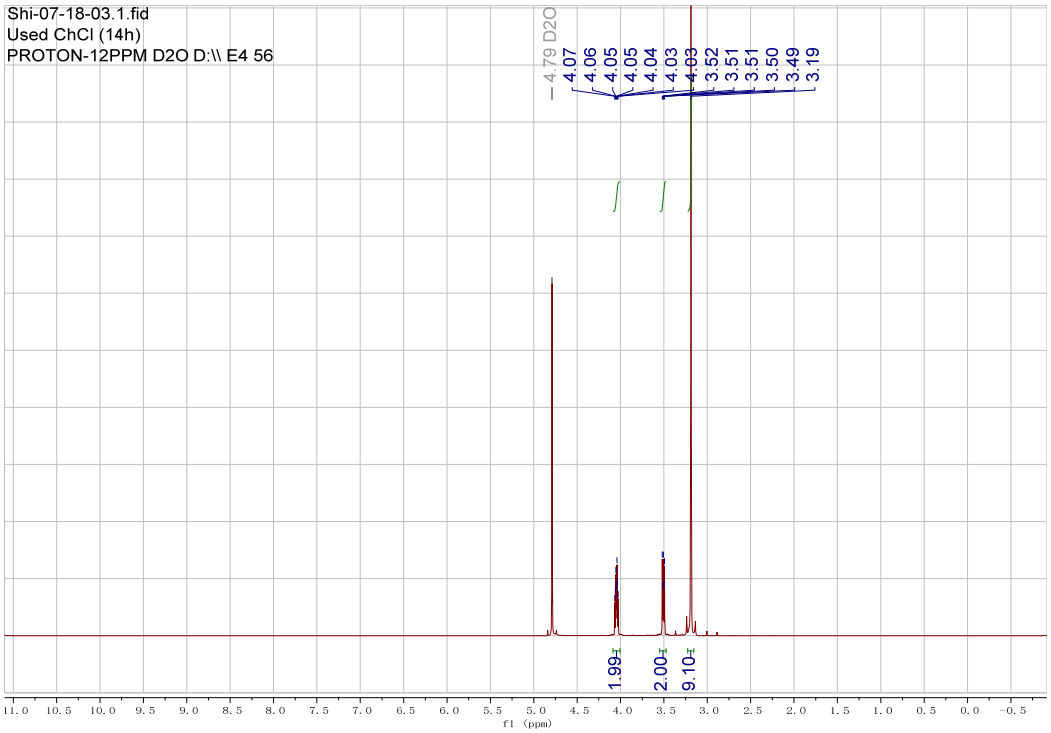
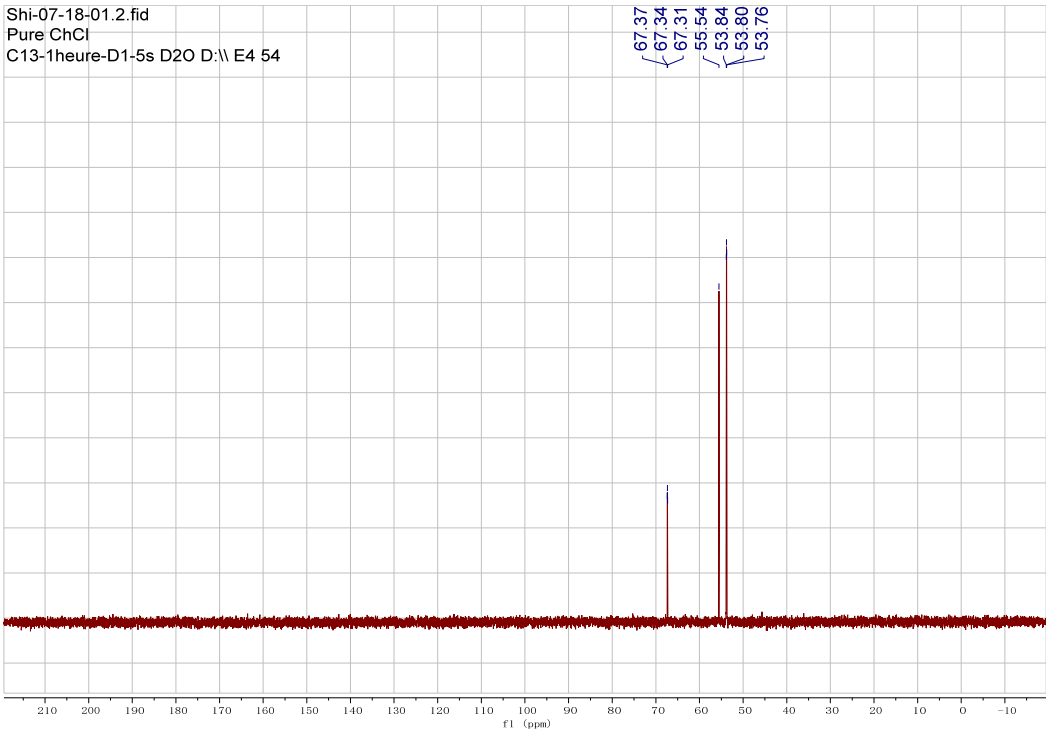



Figure S7. $^{1}$H NMR spectra of (A) commercial ChCl and (B) recovered ChCl.

A. $^{13}C$ NMR of commercial ChCl




B. $^{13}C$ NMR of recoveredChCl

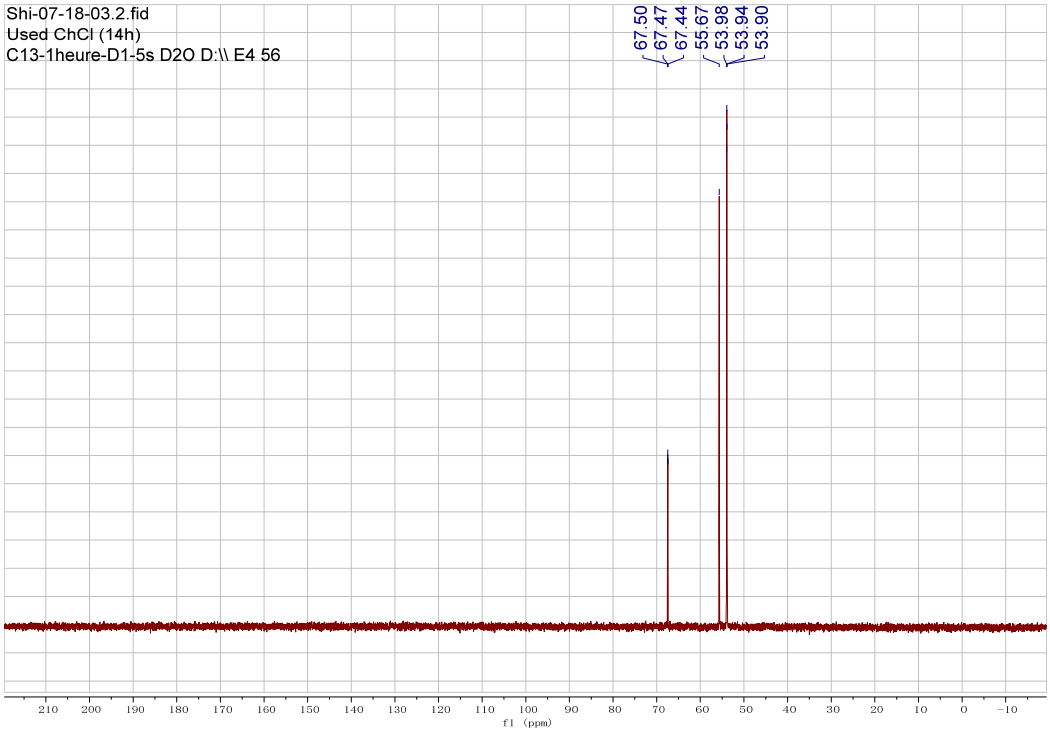



Figure S8. $^{13}C$ NMR *spectra of (A) commercial ChCl and* (B) *recovered ChCl.*

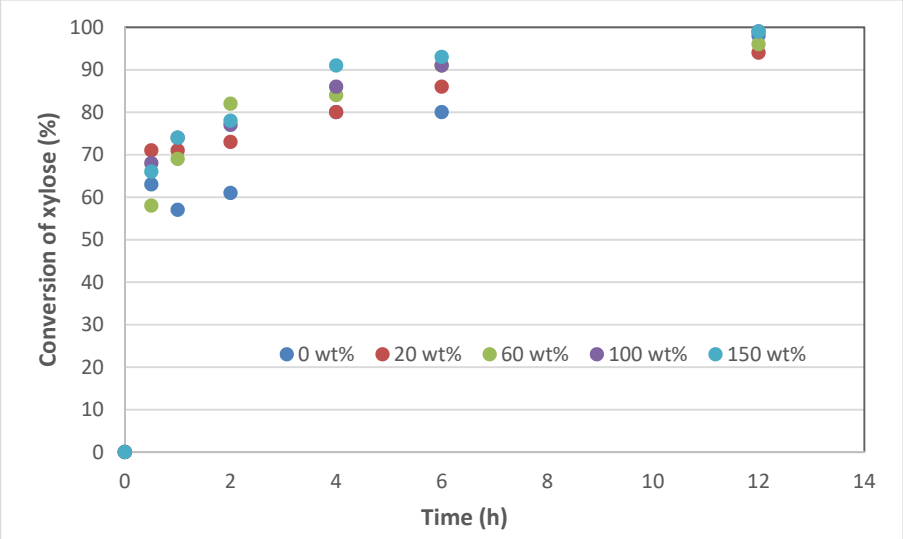



Figure S9. Conversion of xylose (50 wt%) in the presence of variable ChCl concentration relative to water at 120 °C, pH = 1.28 and a $H_2O$/MIBK weight ratio of 1/20.

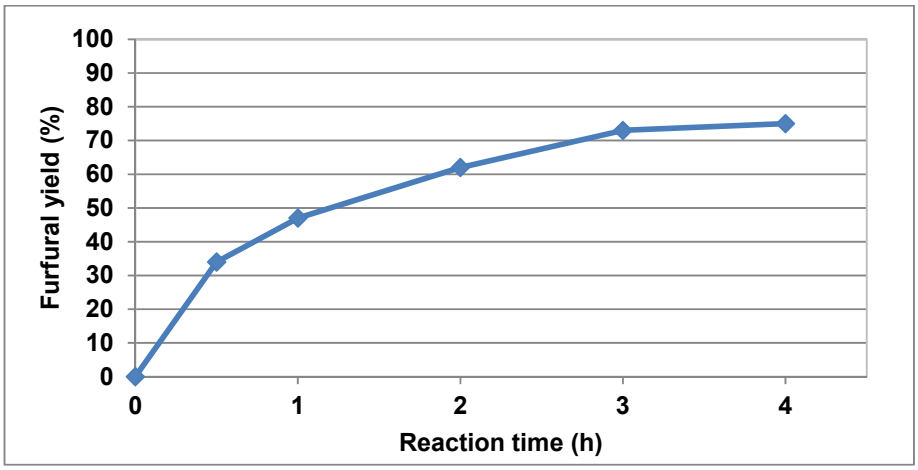


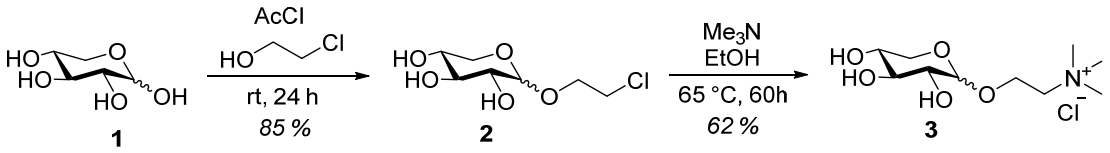

Figure S10. Conversion of xylose (33 wt%) to furfural at 120 °C, pH = 0.86 and a $H_2O$/MIBK weight ratio of 1/20.

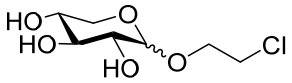
Table S1. Results from TG analysis

| Entry | System | 1st weight loss (°C/weight loss %) | 2nd weight loss (°C/weight loss %) | 3rd weight loss (°C/weight loss %) |
|---|---|---|---|---|
| 1 | Xylose/water | 74/66 | - | - |
| 2 | ChCl/water | 79/62 | - | - |
| 3 | Furfural/water | 80/88 | 104/12 | - |
| 4 | Xylose/water/ChCl | 72/48 | - | - |
| 5 | Furfural/water/ChCl | 84/70 | 140/4 | - |
| 7 | Xylose/water/HCl | 78/64 | 130/11 | - |
| 9 | Furfural/water/HCl | 80/78 | 96/9 | 107/13 |

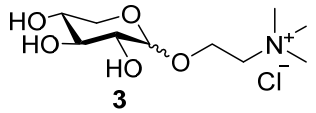
***Procedure for the préparation of choline xylosides :***

Choline xyloside **3** was prepared in two steps from xylose **1** by glycosylation with chloroethanol followed by SN2 reaction with trimethylamine and precipitation.



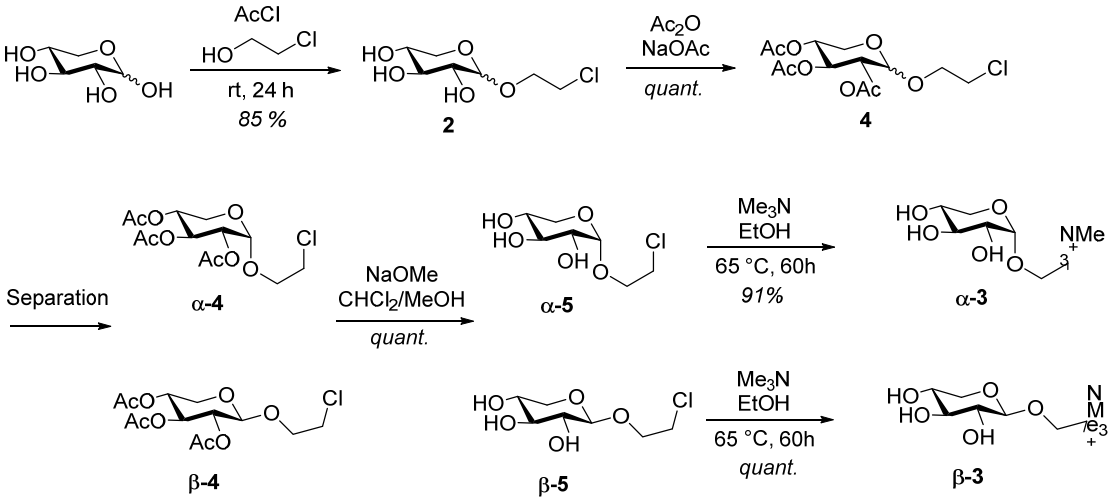

***2-Chloroethyl D-xylopyranoside 2*** **(α/β 70 to 30)**. To a solution of D-xylose (8g, 53.33 mmol, 1 equiv.) in chloroehanol (24 mL, 9 equiv.) was added acetyl chloride (3 mL, 42 mmol, 0.8 equiv.) at 0 °C. The reaction was stirred at room temperature for 24 h under nitrogen atmosphere. After the completion of the reaction, $NaHCO_3$ solid was added until no more bubbling was observed, the mixture was filtered and the solid was washed with ethanol. After concentration of the filtrate, the crude reaction mixture was purified by column chromatography (DCM : MeOH (9 : 1)) to give chloroehtyl xylopyranoside $\alpha$ and $\beta$, without separation (9.6 g, 85 %, α/β 70 to 30). The ratio of $\alpha$ and $\beta$ isomers is determined by NMR analysis related to H1$\alpha$ and H1$\beta$ chemical shifts. $^1$H NMR ($CD_3OD$, 300 MHz): anomer α: δ 4.73 (1H, d, *J* 6.0 Hz, H-1), 3.8-3.9 (1H, m, H-1'), 3.38-3.75 (4H, m, H-1', H-2, H-3, H-4, H-5e), 3.33 (1H, dd, *J* 12.0 Hz, *J* 9.0 Hz, H-5a), 3.26 (2H, m, H-2'). anomer β: δ 4.23 (1H, d, *J* 7.3 Hz, H-1), 3.96 (1H, dt, *J* 9.0 Hz, *J* 6.0 Hz, H-1'), 3.74-3.86 (2H, m, H-2, H-1', H-5e), 3.63-3.70 (2H, m, H-3, H-4), 3.23-3.30 (2H, m, H-2', H-3), 3.12-3.20 (2H, m, H-2, H-5a). $^{13}$C NMR ($CD_3OD$, 76 MHz): anomer α: δ 100.7 (C-1), 75.1 (C-3), 73.5 (C-2), 71.4 (C-4), 69.7 (C-1'), 63.2 (C-5), 43.8 (C-2'). anomer β: δ 105.2 (C-1), 77.7 (C-3), 74.7 (C-2), 71.1 (C-4), 70.9 (C-1'), 66.9 (C-5), 43.6 (C-2'). HRMS : calcd for [M+Na] , 235.0349, found 235.0338.



**3**

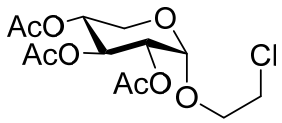
***N-[2-(D-Xylopyranosyl)ethyl]-N,N,N-trimethylammonium chloride 3 (α/β 80 to 20).*** In a 25 mL sealable round bottom flask equipped with a magnetic stirrer was placed a solution of 2- chloroethyl xylopyranoside **2** (2.87 g, 13.5 mmol) in anhydrous ethanol (7 mL). A 33 %solution of trimethylamine in EtOH (13 mL, 54.8 mmol, 4 equiv) was then added, the tube sealed and placed at 65 °C for 60h. The formation of a white precipitate was observed and the reaction cooled to room temperature. The product was collected by filtration and washed with cold absolute ethanol. The resulting highly hygroscopic white powder was rapidly placed under vacuum to remove the volatiles, yielding compound **3** (2.26 g, 8.3 mmol, 62 % yield) as a mixture of anomers (α/β 80 to 20). $^{1}$H NMR ($CD_3OD$, 300 MHz): anomer α: 4.79 (1H, d, *J* 6.0 Hz, H-1), 4.04-4.15 (1H, m, H-1'), 3.84-3.94 (1H, m, H-1'), 3.61-3.68 (2H, m, H-2'), 3.35-3.61 (4H, m, H-2, H-3, H-4, H-5e), 3.15-3.30 (10H, H-5ª, 3x$CH_3$). anomer β: 4.25 (1H, d, *J* 6.0 Hz, H-1), 4.20 (1H, m, H-1'), 3.97 (1H, m, H-1'), 3.84 (1H, dd, *J* 6.0 Hz, *J* 11.5 Hz, H-5e), 3.59 (2H, m, H-2'), 3.38-3.46 (2H, m, H-2, H-3), 3.17-3.75 (10H, H-4, 3x$CH_3$), 3.13 (1H, dd, *J* 11.5 Hz, *J* 9.0 Hz). $^{13}$C NMR ($CD_3OD$, 76 MHz): anomer α: 100.9 (C-1), 74.9 (C-2), 73.1 (C-3), 71.3 (C-4), 66.7 (t, C-2'), 63.6, 63.1 (C-1', C-5), 54.9 (t, 3x$CH_3$). anomer β: 104.8 (C-1), 77.9 (C-2), 74.7 (C-3), 71.1 (C-4), 67.1 (C-5), 66.9 (t, C-2'), 64.2 (C-1'), 54.8 (t, 3x$CH_3$). HRMS : calcd for $[C_{10}H_{22}NO_5]^+$: 236.1492, found : 236.1490.

The structural attribution of each anomer xylosides was ascertained thanks to the preparation of each of them as pure anomers, thanks to their possible separation at the peracetylated stage by silica gel chromatography, and further deprotection by reaction with trimethylamine.



*Procedure for the acetylation of chloroethyl xyloside **2:***

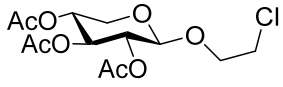
The crude mixture of **α-2** and **β-2** was acetylated by adding $Ac_2O$ (10 mL) and anhydrous NaOAc (1.6 equiv). The resulting mixture was stirred for 2 h at 45 °C. Diethylether (80 mL) was added and the organic phase was washed carefully with saturated $Na_2CO_3$ (5 x 50 mL). After drying over $Na_2SO_4$ and concentration under reduced pressure, α- and β-xylosides were separated by chromatography on silica gel (9:1 the 8:2 petroleum ether–EtOAc).




**α-4**

***2-Chloroethyl 2,3,4-tri-O-acetyl-α-D-xylopyranoside***.

$[\alpha]_D$ = +84.2 (*c* 0.8, $CHCl_3$). $^1$H NMR ($CDCl_3$): δ 5.49 (1H, dd, *J* 9.0 Hz, H-3), 5.08 (1H, d, *J* 6.0 Hz, H-1), 4.96 (1H, ddd, *J* 9.0 Hz, *J* 6.0 Hz, *J* 3.0 Hz, H-4), 4.79 (1H, dd, *J* 9.0 Hz, *J* 3.0 Hz, H-2), 3.95 (1H, dt, *J* = 11.0, 5.6 Hz, 1 H, OC*H*$HCH_2$-Cl), 3.83-3.64 (m, 5 H, OCH*HCH*$_2$Cl, H-5), 2.07, 2.05, 2.04 (9H, 3xs, COC*H3*). $^{13}$C NMR (CDCl3): δ 170.3, 170.0, 169.9 (3C=O), 96.1 (C-1), 71.0 (C-2), 69.4 (C-3), 69.3 (C-4), 68.6 (C-6), 58.6 (C-5), 42.6 (C-7), 20.7 ($3CH_3$). HRMS: calcd for [M+Na] 361.0665, found 361.0656.



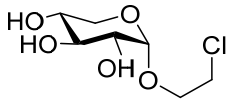

**β-4**

***2-Chloroethyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside***.

$[\alpha]_D$ = -23.6 (*c* 1.4, $CHCl_3$). $^1$H NMR ($CDCl_3$): δ 5.17 (1H, dd, *J* 9.0 Hz, H-3), 4.90-5.00 (2H, m, H-4, H-2), 4.55 (1H, d, *J* 6.6 Hz, H-1), 4.14 (1H,dd, *J* 5.1 Hz, *J* 11.8 Hz, H-5e), 4.04 (1H, dt, *J* 12.0 Hz, *J* 6.0Hz, H-1'), 3.73 (1H, dt, *J* 12.0 Hz, *J* 6.0 Hz, H-1'), 3.62 (2H, t, *J* 6.0 Hz, H-2'), 3.38 (1H, dd, *J* 12.0 Hz, *J* 9.0 Hz, H-5a). $^{13}$C NMR (CDCl3): δ 170.1, 169.9, 169.5 (C=O), 100.92 ((C-1), 71.2 (C-2), 70.5 (C-3), 69.5 (C-1'), 68.8 (C-4), 62.1, (C-5), 42.7 (C-2'), 20.8 ($3CH_3$). HRMS: calcd for [M+Na] 361.0665, found 361.0658.

*Procedure for the deprotection of acetylated chloroethyl xylosides **α-4 and β-4** :*

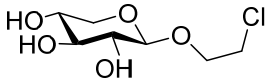
The acetylated compound was dissolved in 1:1 MeOH–$CH_2Cl_2$, and a 0.5 M soln of NaOMe (1.5 equiv) was then added. After stirring for 24 h at room temperature, the mixture was neutralized with Amberlite IR120, filtered and evaporated to give almost quantitatively the unprotected corresponding compound.




**α-5**

***2-Chloroethyl α–D-xylopyranoside* (α-5)**.

$[\alpha]_D$ = +114 (*c* 1.8, MeOH). $^1$H NMR (MeOD): δ 4.73 (1H, d, *J* 6.0 Hz, H-1), 3.8-3.9 (1H, m, H-1'), 3.38-3.75 (4H, m, H-1', H-2, H-3, H-4, H-5e), 3.33 (1H, dd, *J* 12.0 Hz, *J* 9.0 Hz, H-5a), 3.26 (2H, m, H-2'). $^{13}$C NMR (MeOD): δ 100.7 (C-1), 75.1 (C-3), 73.5 (C-2), 71.4 (C-4), 69.7 (C-1'), 63.2 (C-5), 43.8 (C-2'). HRMS: calcd for [M+Na] , 235.0349, found 235.0338.

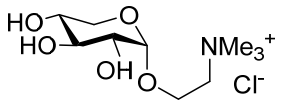



**β-5**

***2-Chloroethyl β–D-xylopyranoside* (β-5 )**.

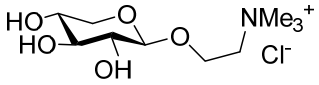
$[\alpha]_D$ = -11 (*c* 1.2, MeOH). $^1$H NMR (MeOD): δ 4.23 (1H, d, *J* 7.3 Hz, H-1), 3.96 (1H, dt, *J* 9.0 Hz, *J* 6.0 Hz, H-1'), 3.74-3.86 (2H, m, H-2, H-1', H-5e), 3.63-3.70 (2H, m, H-3, H-4), 3.23-3.30 (2H, m, H-2', H-3), 3.12-3.20 (2H, m, H-2, H-5a). $^{13}$C NMR (MeOD): δ 105.2 (C-1), 77.7 (C-3), 74.7 (C-2), 71.1 (C-4), 70.9 (C-1'), 66.9 (C-5), 43.6 (C-2'). HRMS: calcd for [M+Na] 235.0349, found 235.0341.

*Procedure for the preparation of choline xylosides **α-3 and β-3 :***



**α-3**

***N-[2-(α-D-Xylopyranosyl)ethyl]-N,N,N-trimethylammonium chloride***. To a 25 ml microwave adapted round-bottom flask equipped with a magnetic stirrer, an ethanolic solution of trimethylamine (12 mmol) and 10 ml of methanol were added and the flask was closed under $N_2$ gas atmosphere. The contents of the flask were cooled to 0 °C in an ice bath, and the chloroalcohol (0.8 g, 3.76 mmol) was added. The reaction was stirred at 65–68 °C for 24 h, and the solvent was subsequently evaporated. The product was washed five times with 10 ml of diethyl ether and with 10 ml of acetone until the solid was precipitated. After drying under vacuum, the choline xyloside ***α-3*** was obtained as solid (0.86 g, 91 %). $[\alpha]_D$ = +104 (*c* 0.5, MeOH). $^1$H NMR (MeOD): δ 4.79 (1H, d, *J* 6.0 Hz, H-1), 4.04-4.15 (1H, m, H-1'), 3.84-3.94 (1H, m, H-1'), 3.61-3.68 (2H, m, H-2'), 3.35-3.61 (4H, m, H-2, H-3, H-4, H-5e), 3.15-3.30 (10H, H-5ª, 3x$CH_3$). $^{13}$C NMR ($CDCl_3$): δ 100.9 (C-1), 74.9 (C-2), 73.1 (C-3), 71.3 (C-4), 66.7 (t, C-2'), 63.6, 63.1 (C-1', C-5), 54.9 (t, 3x$CH_3$). ESI-MS [M+] calcd for [$C_{10}H_{22}NO_5^+$]: 236.1492, found: 236.1486.



**β-3**

***N-[2-(β-D-Xylopyranosyl)ethyl]-N,N,N-trimethylammonium chloride***. Following the same procedure as for the α-isomer with 0.4 g (1.18 mmol) scale, the reaction gave the desired ammonium chloride in quantitative yield (0,475 g, 1.18 mmol). $[\alpha]_D$ = -20 (*c* 0.5, MeOH). $^1$H NMR (MeOD): δ 4.25 (1H, d, *J* 6.0 Hz, H-1), 4.20 (1H, m, H-1'), 3.97 (1H, m, H-1'), 3.84 (1H, dd, *J* 6.0 Hz, *J* 11.5 Hz, H-5e), 3.59 (2H, m, H-2'), 3.38-3.46 (2H, m, H-2, H-3), 3.17-3.25 (10H, H-4, 3x$CH_3$), 3.13 (1H, dd, *J* 11.5 Hz, *J* 9.0 Hz) . $^{13}$C NMR (MeOD): δ 104.8 (C-1), 77.9 (C-2), 74.7 (C-3), 71.1 (C-4), 67.1 (C-5), 66.9 (t, C-2'), 64.2 (C-1'), 54.8 (t, 3x$CH_3$). ESI-MS [M+] calcd for [$C_{10}H_{22}NO_5^+$]: 236.1492, found : 236.1490.