

Supporting Information

Synthesis of polystyrene-grafted cellulose acetate copolymers via nitroxide-mediated polymerization

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Synthesis of alkoxyamine (1)

Figure S1 ¹H liquid NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-β-*D*-glucose

Figure S2 ¹³C liquid NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-β-*D*-glucose

Figure S3 ¹³C liquid NMR spectrum of 1,2,3,4-tetra-*O*-acetyl-6-*O*-acryloyl-β-*D*-glucose

Figure S4 ³¹P liquid NMR spectrum of alkoxyamine 1

Synthesis of alkoxyamine (2)

Figure S5 ¹³C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-*D*-glucose

Figure S6 Zoom 1 of ¹³C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-*D*-glucose (60-96 ppm)

Figure S7 Zoom 2 of ¹³C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-*D*-glucose (on the left: 169-171 ppm, on the right: 19-21 ppm)

Figure S8 ¹³C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl-*D*-glucose

Figure S9 Zoom 1 of ¹³C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl-*D*-glucose (60-140 ppm).

Figure S10 Zoom 2 of ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl- D -glucose performed in CDCl_3 (on the left: 163-171 ppm, on the right: 19-21 ppm)

Figure S11 ^{31}P liquid NMR spectrum of alkoxyamine 2

Synthesis of alkoxyamine (3)

Figure S12 ^{13}C liquid NMR spectrum of product of route b

Figure S13 ^{13}C liquid NMR spectrum of 2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl- D -cellobiose

Figure S14 Zoom 1 of ^{13}C liquid NMR spectrum of 2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl- D -cellobiose (61-77 ppm).

Figure S15 Zoom 2 of ^{13}C liquid NMR spectrum of 2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl- D -cellobiose (on the left: 163-172 ppm, on the right: 19-22 ppm).

Figure S16 ^{31}P liquid NMR spectrum of alkoxyamine 3

Synthesis of alkoxyamine (4)

Figure S17 ^{31}P liquid NMR spectrum of alkoxyamine 4

Figure S18 solid-state NMR; CPMAS ^{13}C NMR of acroylated cellulose acetate, DS = 0.03

Figure S19 HRMAS ^{13}C NMR of CA-BB; the signals were assigned thanks to ^1H - ^{13}C HSQC experiment

Figure S20 Solid-state NMR; CPMAS ^{13}C NMR of CA-BB, DS = 0.03

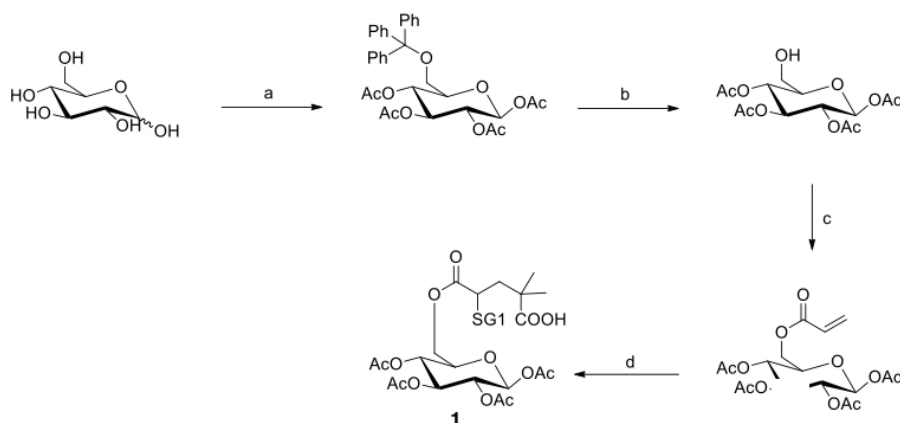
Figure S21 Solid-state NMR; CPMAS ^{31}P NMR of CA-BB, DS = 0.03. Side product due to the decomposition of SG1 is recorded at 0 ppm

Figure S22 HRMAS DOSY NMR characterization. A) Cellulose acetate functionalized with BlocBuilder[®]; B) Physical mixture of cellulose acetate and BlocBuilder[®]

Figure S23 CPMAS ^{13}C NMR of the PS chains obtained after the basic hydrolysis of the CA-*g*-PS

Figure S24 HRMAS DOSY NMR of CA-*g*-PS graft copolymers with a 20% grafting ratio

Synthesis of alkoxyamine 1



Reagents and conditions: (a) ClC(Ph)₃, Ac₂O, Pyridine, (b) HBr, AcOH, (c) CH₂=CHC(O)Cl, Et₃N, THF, (d) BlocBuilder[®], EtOH

1,2,3,4-tetra-O-acetyl-β-D-glucose (routes a + b)

D-glucose (6 g, 33.3 mmol) and trityl chloride (9.7g, 34.8 mmol) dissolved in pyridine (25 mL) at 95 °C, acetic anhydride (159 mmol, 15 mL) was added in one shot and the solution stirred overnight at room temperature. After precipitation in an iced water/acetic acid solution (475 mL/25 mL), the precipitate was isolated by filtration. To remove residual pyridine, the white solid was poured into iced water (500 mL) under stirring for 20 min. The solid was then filtrated and washed carefully with water. After dissolving at 70 °C in glacial acetic acid (100 mL), the mixture was cooled down to 10 °C and a solution of hydrogen bromide in glacial acetic acid solution (33 %, 41.1 mmol, 7.2 mL) was added. After 3 min, trityl bromide was removed by filtration and the filtrate was poured in iced water (400 mL). The aqueous layer was extracted three times with CHCl₃ and after separation, the organic layer was washed three times with iced water, dried over MgSO₄ and solvents were evaporated under reduced pressure to give a viscous oil. Et₂O (250 mL) and pentane (250 mL) were successively added under stirring to give a white solid after filtration (2.15 g, 19 %). ¹H NMR (400 MHz, CDCl₃) δ 5.70 (d, *J* = 8.3 Hz, 1H, C₁-H), 5.28 (t, *J* = 9.4 Hz, 1H), 5.00-5.15 (m, 2H), 3.68-3.79 (m, 1H), 3.49-3.67 (m, 2H), 2.34-2.44 (m, 1H), 2.08 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 2.00 (s, 3H, CH₃), 1.99 (s, 3H, CH₃). ¹³C NMR (400 MHz, CDCl₃) δ 170.3 (C=O), 170.2 (C=O), 169.4 (C=O), 169.2 (C=O), 91.8 (C₁), 75.0, 72.7, 70.5, 68.3 (4C), 60.9 (C₆), 20.9 (2 CH₃), 20.7 (2 CH₃).

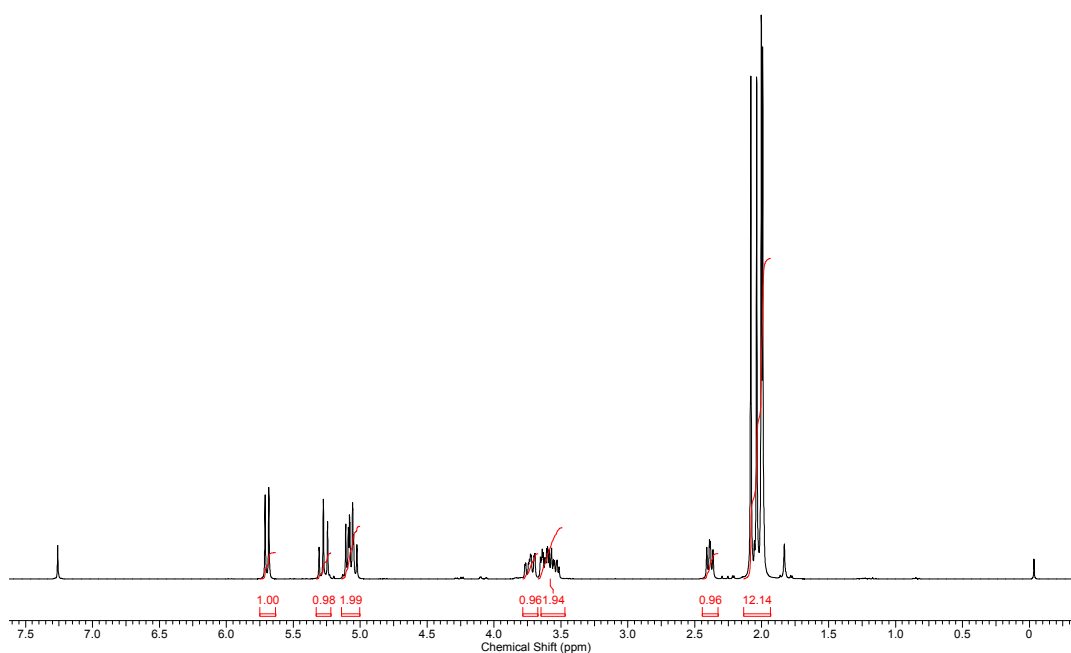


Figure S1 ^1H liquid NMR spectrum of 1,2,3,4-tetra-*O*-acetyl- β -D-glucose performed in CDCl_3

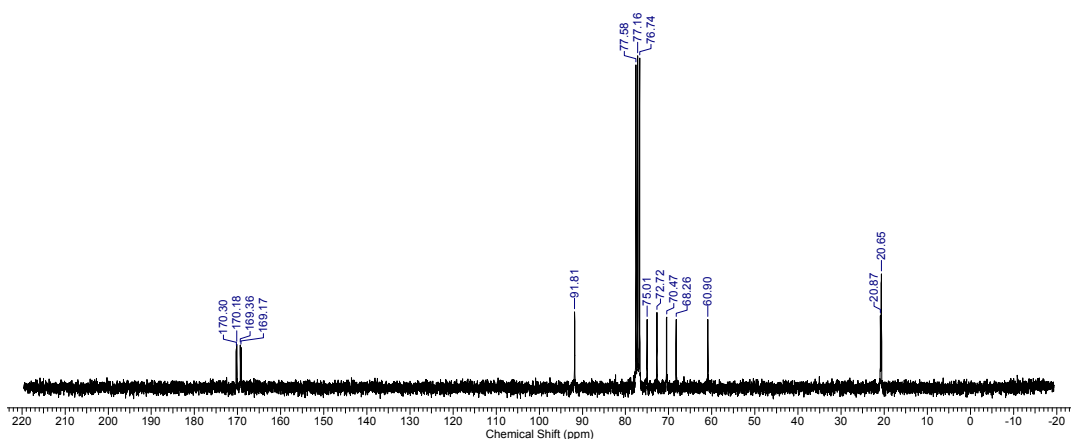


Figure S2 ^{13}C liquid NMR spectrum of 1,2,3,4-tetra-*O*-acetyl- β -D-glucose performed in CDCl_3

1,2,3,4-tetra-*O*-acetyl-6-*O*-acryloyl- β -D-glucose (route c)

Et_3N (1.9 mL, 13.3 mmol) was added to 1,2,3,4-tetra-*O*-acetyl- β -D-glucose (1.5 g, 4.3 mmol) in solution in anhydrous THF (30 mL) at room temperature under argon. At 0 °C, acryloyl chloride (1.05 mL, 12.9 mmol) in solution in anhydrous THF (10 mL) was introduced dropwise. The mixture was then stirred overnight under argon at room temperature. Triethylammonium chloride was removed by filtration and the solvent was evaporated under reduced pressure. The yellow residue was recrystallized in EtOH

to give a white powder (1,2,3,4-tetra-*O*-acetyl-6-*O*-acryloyl- β -D-glucose) (0.8 g, 46 %). ^{13}C NMR (400 MHz, CDCl_3) δ 170.3 (C=O), 169.5 (C=O), 169.4 (C=O), 169.1 (C=O), 165.7 ((-CO-(CH=CH₂))), 132.0 (CH=CH₂), 127.7 (CH=CH₂), 91.7 (C₁), 72.9, 72.7, 70.3, 68.0 (4C), 61.8 (C₆), 20.8 (CH₃), 20.6 (3CH₃).

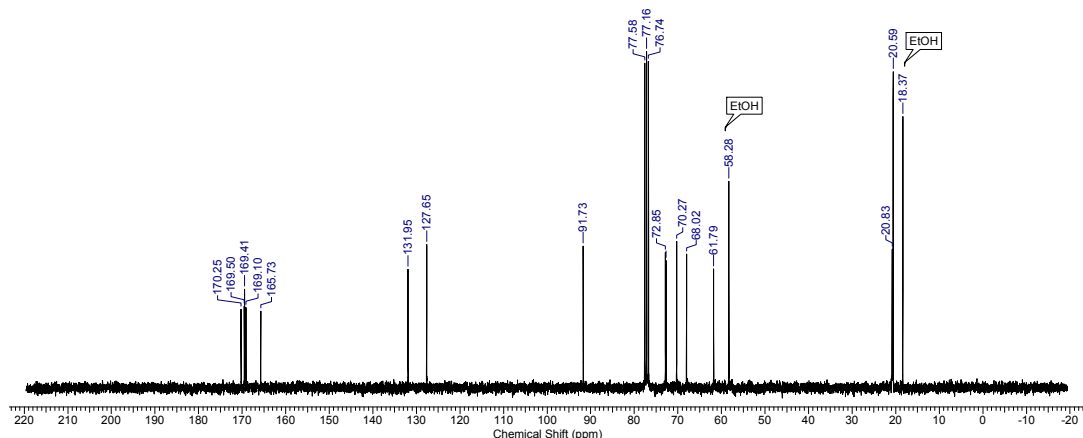


Figure S3 ^{13}C liquid NMR spectrum of product of 1,2,3,4-tetra-*O*-acetyl-6-*O*-acryloyl- β -D-glucose performed in CDCl_3

TOF HR-MS (ESI⁺) calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_{11}^+$, $[\text{M}+\text{NH}_4]^+$, 420.1500; found, 420.1510.

Alkoxyamine 1 (route d)

1,2,3,4-tetra-*O*-acetyl-6-*O*-acryloyl- β -D-glucose (0.22 g, 0.55 mmol) and BlocBuilder[®] (0.29 g, 0.77 mmol) in solution in absolute EtOH (3 mL) was deoxygenated by argon bubbling for 30 minutes at room temperature. The solution was then heated under reflux for 5 h. After cooling, the solvent was evaporated under reduced pressure and the solid residue was poured in a large excess of pentane. After filtration, a yellow solid was obtained (0.24 g, 56 %). ^{31}P NMR (400 MHz, CDCl_3 , major diastereoisomers) δ 25.16, 25.07.

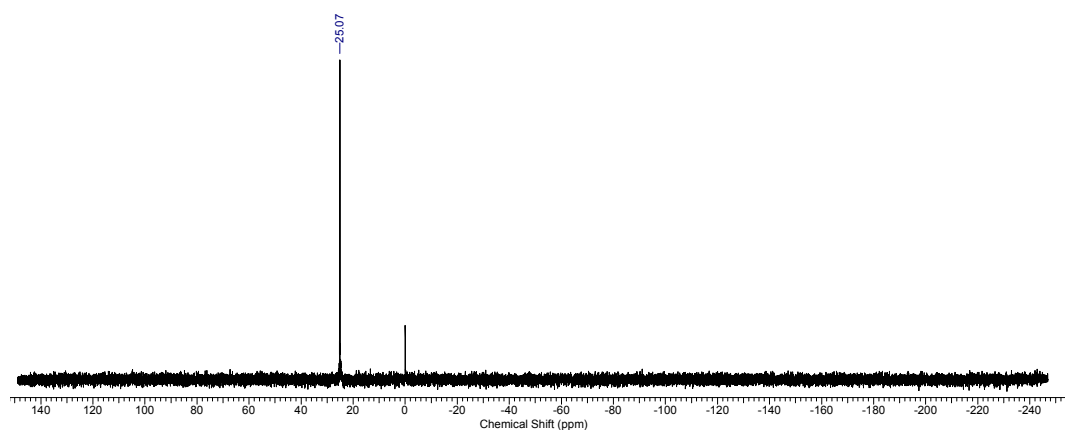
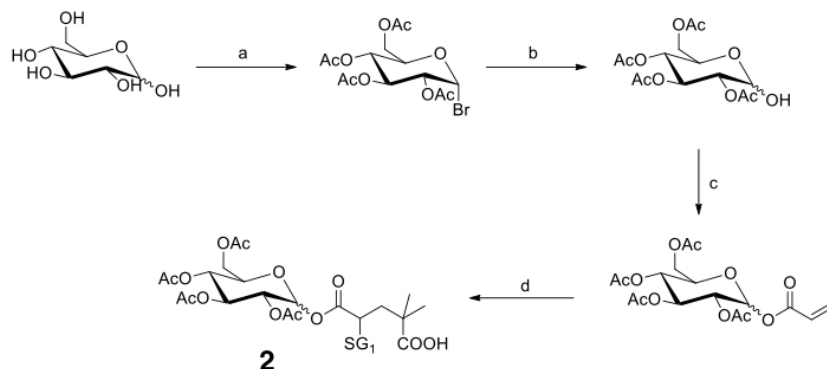


Figure S 4 ^{31}P liquid NMR spectrum of alkoxyamine 1 (product of route d) performed in CDCl_3

The little non assigned peak in region of 0 ppm probably corresponds to byproducts of degradation of SG1 (from BlocBuilder[®]).

TOF HR-MS (ESI^+) calculated for $\text{C}_{34}\text{H}_{59}\text{NO}_{17}\text{P}^+$, $[\text{M}+\text{H}]^+$, 784.3515; found, 784.3497. ESR: $E_{a,d}$ (tBuPh) = 123.8 kJ/mol ; $E_{a,d}$ (DMF) = 121.5 kJ/mol.

Synthesis of alkoxyamine 2



Reagents and conditions (a) 1. Ac₂O, HClO₄, AcOH and AcBr, MeOH, (b) Ag₂CO₃, acetone/H₂O, (c) CH₂=CHC(O)Cl, Et₃N, THF, (d) BlocBuilder®, EtOH

2,3,4,6-tetra-O-acetyl-D-glucose (route a + b)

To a solution of D-glucose (10 g, 55.5 mmol) in AcOH (100 mL) were added acetic anhydride (33 mL, 346.4 mmol) and perchloric acid (20 drops) at room temperature under argon. After 1 h, acetyl bromide (12.5 mL, 168.8 mmol) and MeOH (9 mL, 221.9 mmol) were added and the suspension was stirred for 7 h (protected from light). The resulting solution was poured into ice-water (600 mL) and the white solid that precipitated was filtered off. The solid was next added to silver carbonate (15.8 g, 57.16 mmol) in acetone/H₂O (120 mL/110 mL). The resulting mixture was stirred overnight at room temperature in the absence of light. After filtration through a layer of silica gel (EtOAc), organic solvents were evaporated. The aqueous layer was extracted three times with CH₂Cl₂ and after separation, the organic layer was dried over MgSO₄ and solvent was evaporated under reduced pressure to give a viscous oil (14.0 g, 72 % of desired product, 9 % of peracetate based on ¹H NMR spectrum). Only ¹³C NMR is shown, ¹H NMR spectrum being of high complexity because of the presence of two diastereoisomers α , β and peracetate. ¹³C NMR (400 MHz, CDCl₃) δ 170.90 (anomer α , C=O), 170.81 (anomer β , C=O), 170.34 (anomer β , C=O), 170.26 (anomer $\alpha+\beta$, 2 C=O), 170.23 (anomer α , C=O), 169.73 (anomer α , C=O), 169.56 (anomer β , C=O), 95.37 (anomer β , C₁), 90.02 (anomer α , C₁), 73.03, 72.57, 71.94 (anomer β , 3C), 71.26, 70.02, 68.63 (anomer α , 3C), 68.49 (anomer β , 1C), 66.93 (anomer α , 1C), 62.10 (2 C₆), 20.70 (3 CH₃), 20.67 (2 CH₃), 20.61 (2 CH₃), 20.57 (1 CH₃).

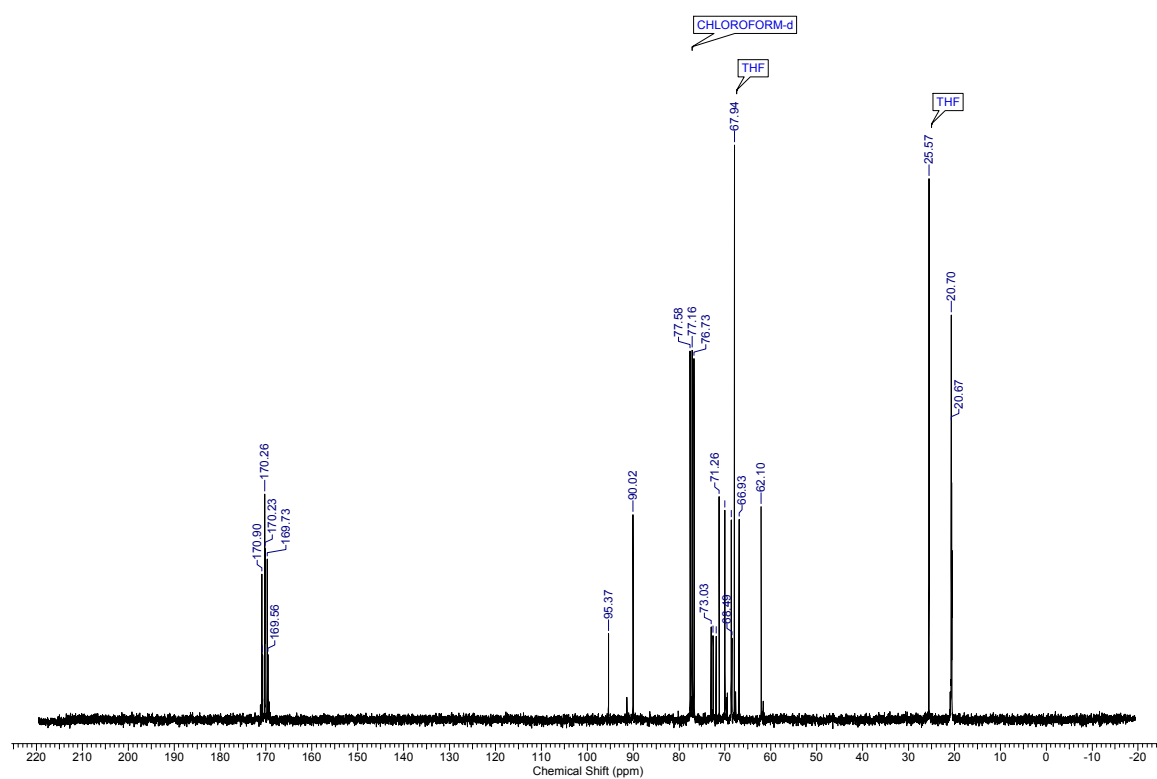


Figure S5 ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-D-glucose performed in CDCl_3

The little non-assigned peaks correspond at peracetate product.

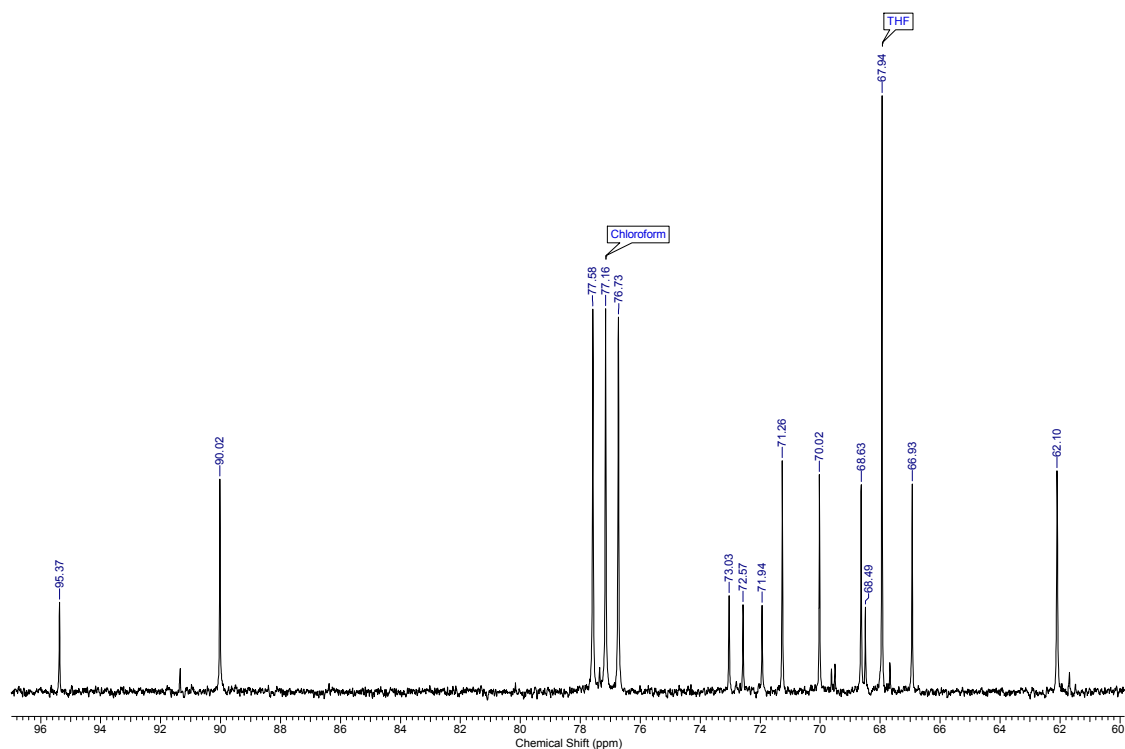


Figure S6 Zoom 1 of ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-D-glucose performed in CDCl_3 (60-96 ppm)

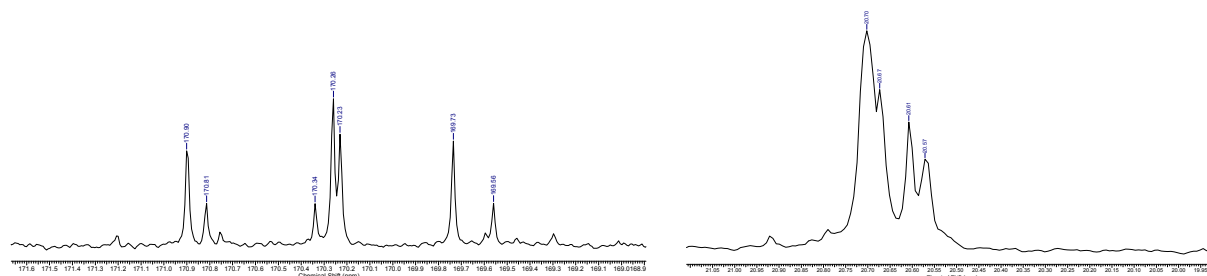


Figure S7 Zoom 2 of ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-D-glucose performed in CDCl_3 (on the left: 169-171 ppm, on the right : 19-21 ppm)

1.1. a) 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl-D-glucose (route c)

Et_3N (4.2 mL, 30.2 mmol) was added to 2,3,4,6-tetra-*O*-acetyl-D-glucose (2.5 g, 7.2 mmol) in solution in anhydrous THF (70 mL) at room temperature under argon. At 0 °C, acryloyl chloride (2.3 mL, 28.7 mmol) was introduced dropwise. The mixture was then stirred for 9 h 30 under argon at room temperature. Triethylammonium chloride was removed by filtration and the solvent was evaporated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 and the organic media was successively washed twice with saturated NaHCO_3 and with H_2O . After drying over MgSO_4 , CH_2Cl_2

was evaporated and the crude product was purified by column chromatography on silica gel (CH₂Cl₂/EtOAc : 100/0 and 95/5) to give 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl- β -D-glucose (1.4 g, 48 %). ¹³C NMR (400 MHz, CDCl₃, anomer α + β) δ 170.30 (2 C=O), 169.83 (C=O), 169.71 (C=O), 169.41 (C=O), 169.17 (C=O), 169.15 (C=O), 168.98 (C=O), 163.44 ((-CO-(CH=CH₂)), 163.41 ((-CO-(CH=CH₂)), 133.04 (CH=CH₂), 132.70 (CH=CH₂), 126.82 (CH=CH₂), 126.63 (CH=CH₂), 91.50 (C₁), 88.86 (C₁), 72.22, 72.13, 69.88 (3C), 69.46 (2C), 68.92 (1C), 67.49 (2C), 61.09 (2 C₆), 20.00 (2 CH₃), 19.97 (CH₃), 19.90 (3 CH₃), 19.83 (CH₃), 19.73 (CH₃).

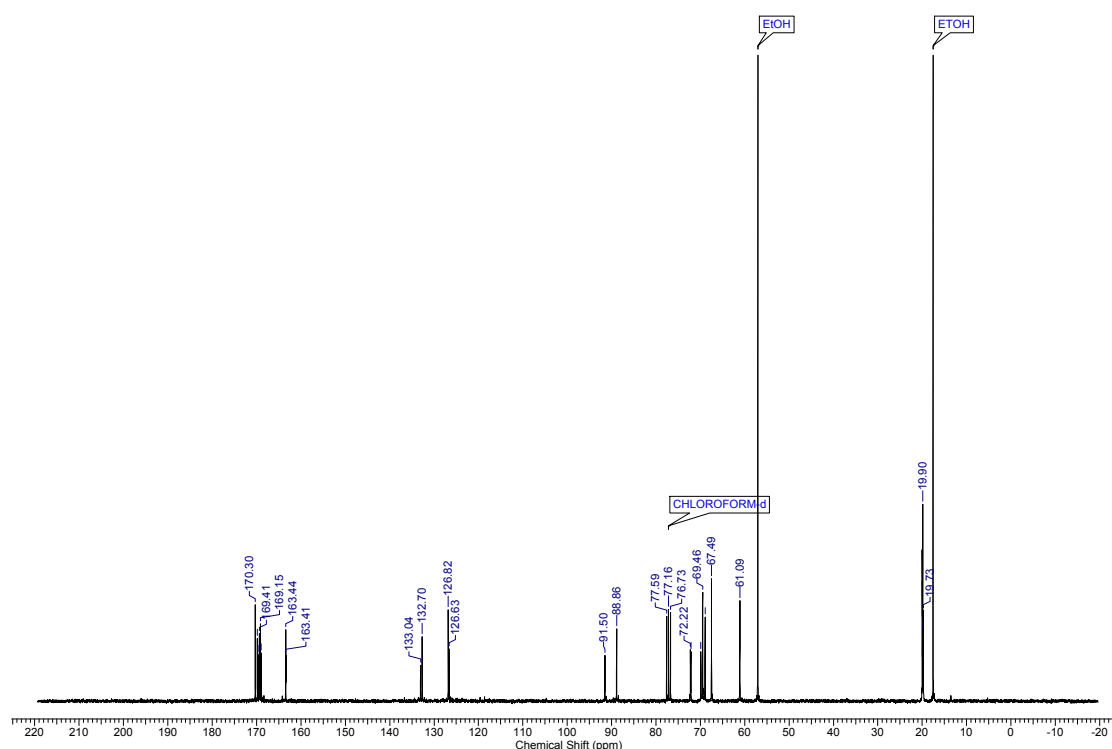


Figure S8 ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl-D-glucose performed in CDCl_3

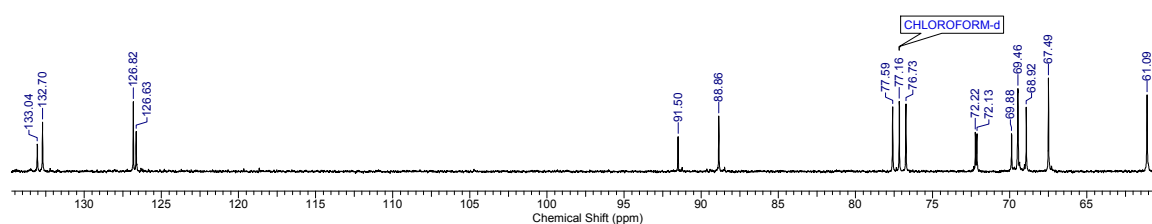


Figure S9 Zoom 1 of ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl-D-glucose performed in CDCl_3 (60-140 ppm)

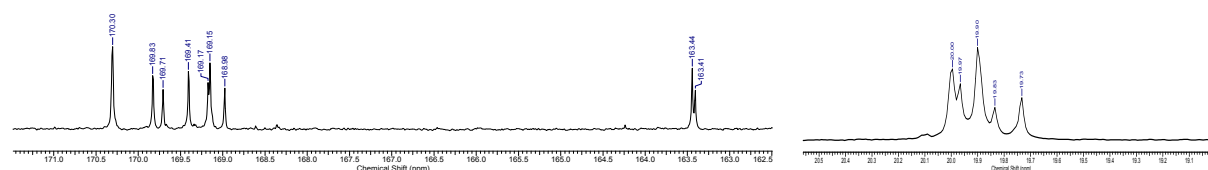


Figure S10 Zoom 2 of ^{13}C liquid NMR spectrum of 2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl-D-glucose performed in CDCl_3 (on the left: 163-171 ppm, on the right: 19-21 ppm)

TOF HR-MS (ESI⁺) calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_{11}^+$, $[\text{M}+\text{NH}_4]^+$, 420.1500; found, 420.1506.

Alkoxyamine 2 (route d)

2,3,4,6-tetra-*O*-acetyl-6-*O*-acryloyl- β -D-glucose (0.50 g, 1.24 mmol) and BlocBuilder[®] (0.62 g, 1.62 mmol) in solution in absolute EtOH (7 mL) was deoxygenated by argon bubbling for 20 minutes at room temperature. The solution was then heated under reflux for 4 h 30. After cooling, the solvent was evaporated under reduced pressure and the solid residue was poured in a large excess of pentane. After filtration, a white solid was obtained (0.66 g, 68 %). ³¹P NMR (400 MHz, CDCl₃, major diastereoisomers) δ 23.96, 23.92, 23.60.

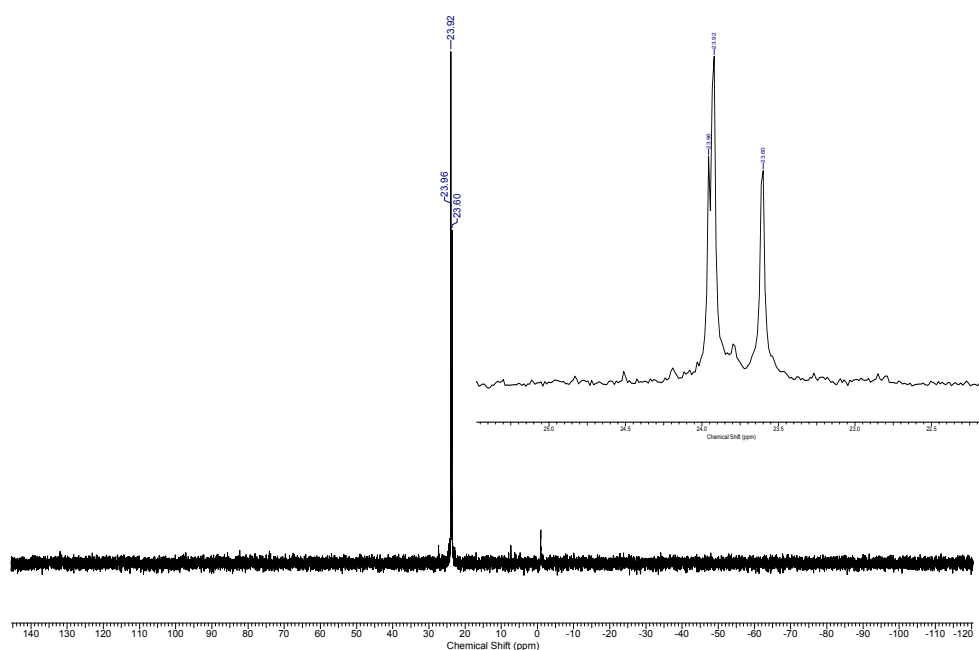
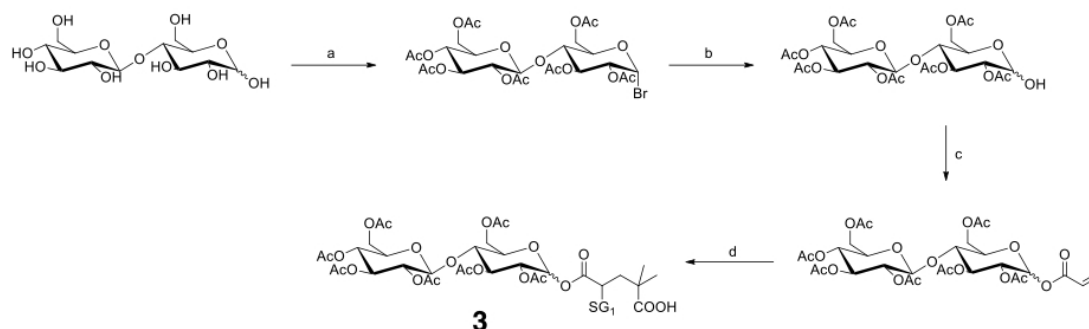


Figure S11 ³¹P liquid NMR spectrum of alkoxyamine 2 (route d) performed in CDCl₃

The little non-assigned peaks in region of 0 ppm probably corresponds to byproducts of degradation of SG1 (from BlocBuilder[®]).

TOF HR-MS (ESI⁺) calculated for C₃₄H₆₂N₂O₁₇P⁺, [M+NH₄]⁺, 801.3781; found, 801.3794. ESR: $E_{a,d}$ (tBuPh) = 122.7 kJ/mol ; $E_{a,d}$ (DMF) = 122.1 kJ/mol. ³¹P NMR: $E_{a,d}$ (DMA) = 120.4 kJ/mol.

Synthesis of alkoxyamine 3



Reagents and conditions (a) 1. Ac₂O, HClO₄, AcOH and AcBr, MeOH, (b) Ag₂CO₃, Acétone/H₂O, (c) CH₂=CHC(O)Cl, Et₃N, THF, (d) BlocBuilder®, EtOH

2,3,6,2',3',4',6'-hepta-O-acetyl-α-D-cellobiosyl bromide (route a)

To a solution of D-cellobiose (20.0 g, 58.5 mmol) in AcOH (200 mL) were added acetic anhydride (53 mL, 556.3 mmol) and perchloric acid (40 drops) at room temperature under argon. After 2 h, acetyl bromide (13 mL, 175.5 mmol) and MeOH (9.6 mL, 236.7 mmol) were added and the suspension was stirred overnight (protected from light). The resulting solution was poured into ice-water (1 L) and the white solid that precipitated was filtered off. The resulting solid was dissolved in CH₂Cl₂ and the organic media was washed once with H₂O. After drying over MgSO₄, CH₂Cl₂ was evaporated to give 2,3,6,2',3',4',6'-hepta-O-acetyl-α-D-cellobiosyl bromide (36.4 g, 89 %).

2,3,6,2',3',4',6'-hepta-O-acetyl-6-O-acryloyl-D-cellobiose (route b + c)

2,3,6,2',3',4',6'-hepta-O-acetyl-α-D-cellobiosyl bromide (18.1 g, 25.9 mmol) was added to silver carbonate (8.3 g, 30.1 mmol) in acetone/H₂O (70 mL/70 mL). The resulting mixture was stirred overnight at room temperature in the absence of light. After filtration through a layer of silica gel (EtOAc), organic solvents were evaporated. The aqueous layer was extracted three times with CH₂Cl₂ and after separation, the organic layer was dried over MgSO₄ and solvent was evaporated under reduced pressure to give the product of route b (white solid, 16.35 g, 99 %). Two diastereoisomers α and β can be observed on the ¹³C NRM spectrum.

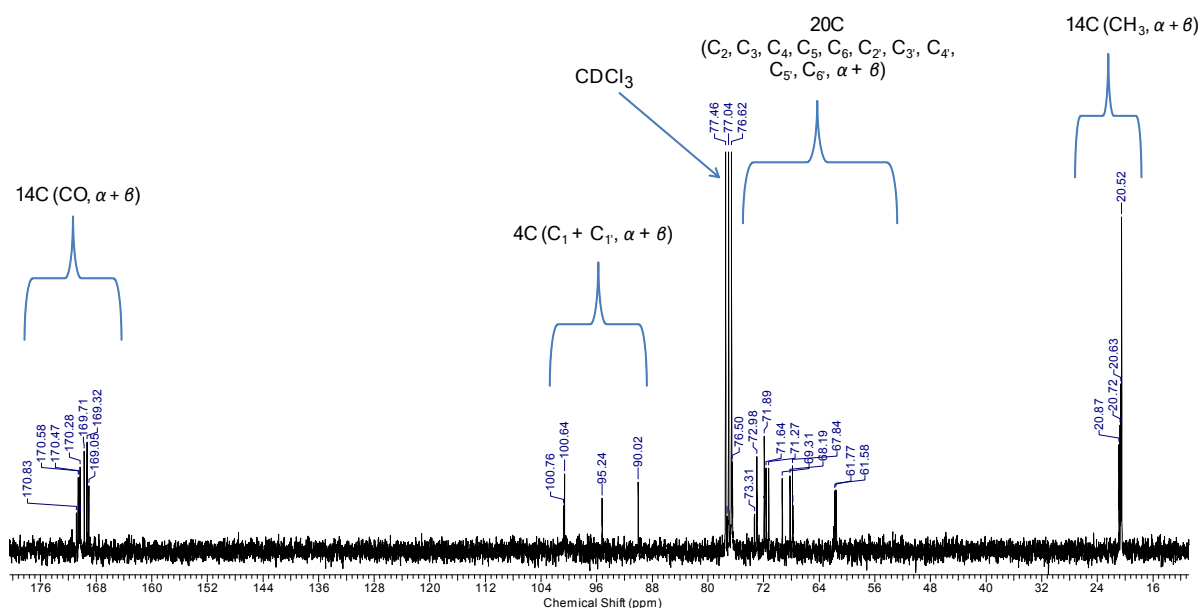


Figure S12 ^{13}C liquid NMR spectrum of product of route b performed in CDCl_3

Then, Et_3N (5.5 mL, 39.5 mmol) was added to the product of route b (6 g, 9.4 mmol) in solution in anhydrous THF (84 mL) at room temperature under argon. At 0°C , acryloyl chloride (3.1 mL, 37.7 mmol) was introduced dropwise. The mixture was then stirred for 6 h 30 under argon at room temperature. Triethylammonium chloride was removed by filtration and the solvent was evaporated under reduced pressure. The yellow residue was recrystallized in EtOH to give a white solid (2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl- D -cellobiose, diastereoisomers $\alpha+\beta$, 2.8 g, 43 %). According to recrystallization conditions (quantity of EtOH added), anomer α can be favored. ^{13}C NMR (400 MHz, CDCl_3 , anomer α shown) δ 170.6 (C=O), 170.3 (2 C=O), 170.1, 169.8, 169.4, 169.2 (4 C=O), 164.1 ((-CO-(CH=CH₂))), 133.3 (CH=CH₂), 127.4 (CH=CH₂), 101.1 (C_{1'}), 89.3 (C₁), 76.2, 73.1, 72.1, 71.8, 70.9, 69.49, 69.47, 67.9 (8C), 61.7, 61.4 (C_{6'} + C₆), 20.9 (CH₃), 20.8 (CH₃), 20.71 (2 CH₃), 20.66 (2 CH₃), 20.6 (CH₃).

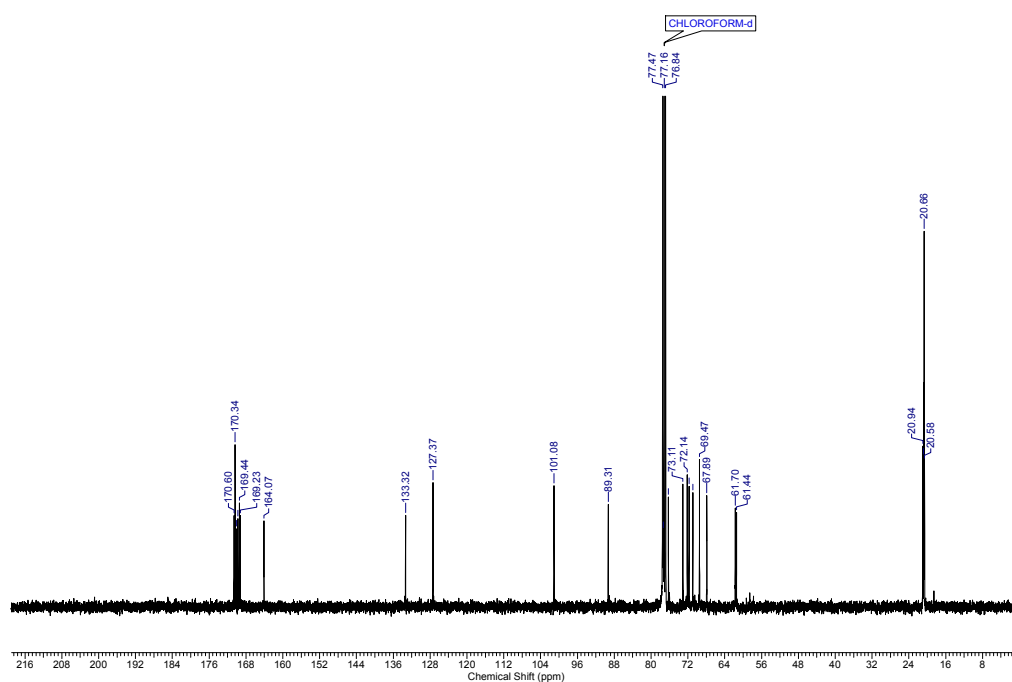


Figure S13 ^{13}C liquid NMR spectrum of 2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl-*D*-cellobiose performed in CDCl_3

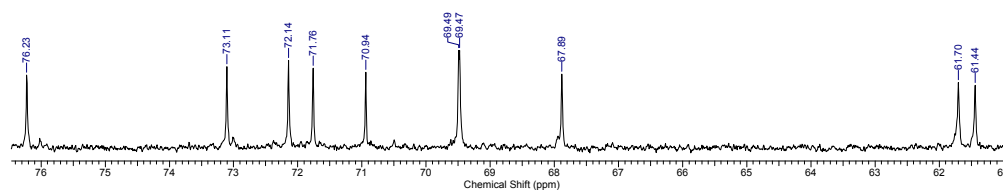


Figure S14 Zoom 1 of ^{13}C liquid NMR spectrum of 2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl-*D*-cellobiose performed in CDCl_3 (61-77 ppm)

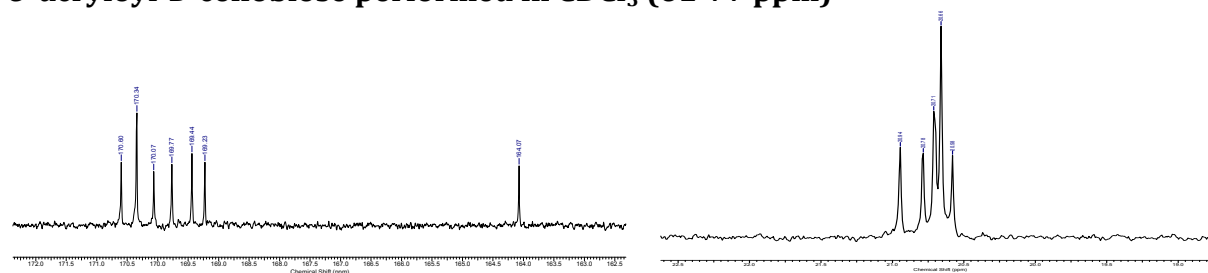


Figure S15 Zoom 2 of ^{13}C liquid NMR spectrum of product of route c performed in CDCl_3 (on the left: 163-172 ppm, on the right: 19-22 ppm)

TOF HR-MS (ESI⁺) calculated for $\text{C}_{29}\text{H}_{42}\text{NO}_{19}^+$, $[\text{M}+\text{NH}_4]^+$, 708.2346; found, 708.2345.

Alkoxyamine 3 (route d)

2,3,6,2',3',4',6'-hepta-*O*-acetyl-6-*O*-acryloyl- β -cellobiose (0.50 g, 0.72 mmol) and BlocBuilder[®] (0.39 g, 1.01 mmol) in solution in absolute EtOH (2.4 mL) was deoxygenated by argon bubbling for 30 minutes at room temperature. The solution was then heated under reflux for 5 h. After cooling, the solvent was evaporated under reduced pressure and the solid residue was poured in a large excess of pentane. After filtration, a white solid was obtained (0.57 g, 73 %). ³¹P NMR (400 MHz, CDCl₃, major diastereoisomers) δ 24.56, 24.01, 23.97, 23.87, 23.59.

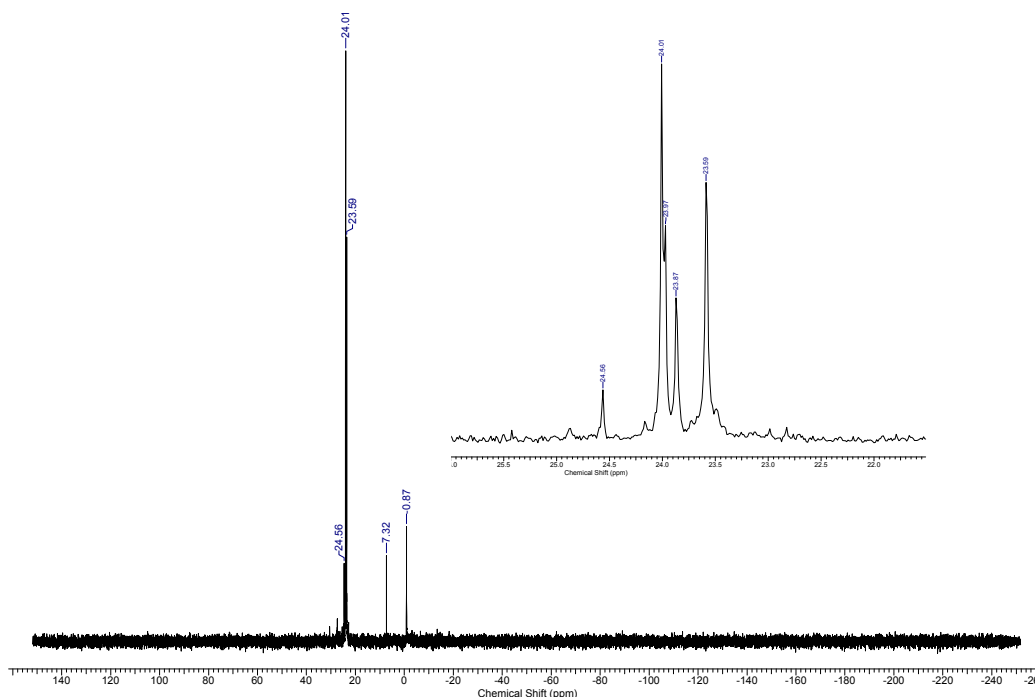
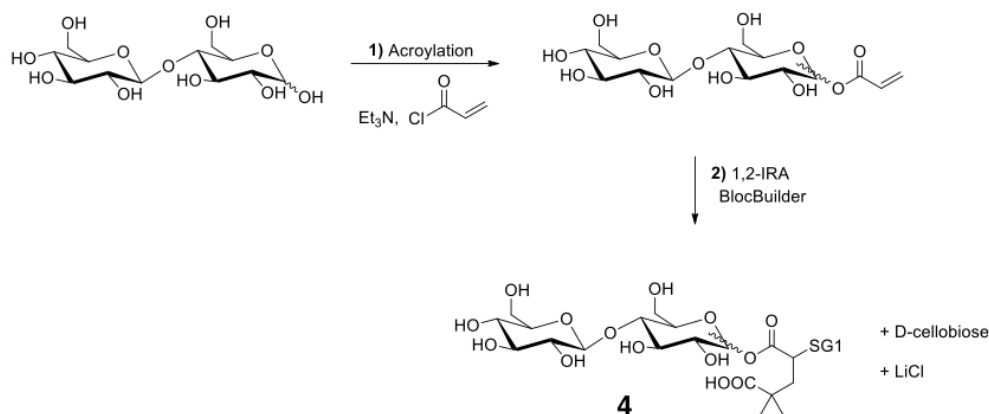


Figure S 16 ³¹P liquid NMR spectrum of alkoxyamine 3 performed in CDCl₃

The little non assigned peaks in regions of 0 and 10 ppm probably correspond to byproducts of degradation of SG1 (from BlocBuilder[®]).

TOF HR-MS (ESI⁺) calculated for C₄₆H₇₈N₂O₂₅P⁺, [M+NH₄]⁺, 1089.4626; found, 1089.4629. ESR: $E_{a,d}$ (tBuPh) = 123.3 kJ/mol.

Synthesis of alkoxyamine **4**



Reagents and conditions (1) $\text{CH}_2=\text{CHC}(\text{O})\text{Cl}$, Et_3N , DMA/LiCl ; (2) BlocBuilder[®], DMA/LiCl .

D-cellobiose (10 g, 29 mmol) was dissolved in a solution of DMA/LiCl (94 mL/1.5 g) at 100 °C for 20 min under argon atmosphere. After cooling, Et_3N (4.5 mL, 32 mmol) was added at room temperature, and acryloyl chloride (2.4 mL, 29 mmol) was introduced dropwise at 0 °C for 10 min (0.24 mL/min). The temperature was kept at 0 °C for 20 min. The mixture was then heated at 40 °C for 2 h. Triethylammonium chloride was removed by filtration at room temperature and the filtrate (98 mL) was kept for the next step. ESI-MS analyses proved the presence of a mixture of cellobiose mono, di- and tri-acroylated, acrylic acid (resulting from the hydrolysis of acryloyl chloride), and free cellobiose. It is noteworthy that this reaction is not regioselective, so that several regioisomers are formed, which are very difficult to separate and quantify. BlocBuilder[®] (4.8 g, 12.6 mmol) was added to the previous filtrate (50 mL). After deoxygenation by argon bubbling for 20 min at room temperature, the solution was heated at 80 °C for 3 h. After cooling, EtOAc was added to the media and the product was recovered by precipitation. The obtained white solid was dried under reduced pressure to give the cellobiose-based alkoxyamine **4** (two steps yield reaction: 13 %, measured by ^{31}P NMR with $\text{P}(\text{O})(\text{OEt})_3$ as an internal reference). The protonated molecule ($\text{C}_{32}\text{H}_{61}\text{NO}_{18}\text{P}^+$, m/z_{theo} 778.3621) was accurately mass measured with a relative error of ± 0.3 ppm by using two reference ions from a poly(propylene glycol) as internal standards. ^{31}P NMR (400 MHz, $\text{DMSO}-d_6$, regioisomers) δ 23.5-24.5 ppm.

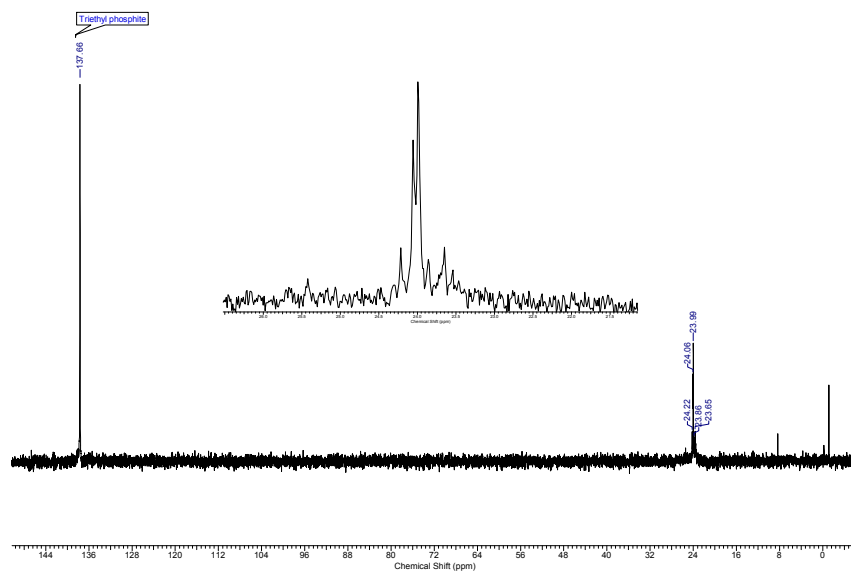


Figure S17 ^{31}P liquid NMR spectrum of alokxyamine 4 performed in $\text{DMSO-}d_6$
 The little non assigned peaks in regions of 0 and 10 ppm probably correspond to byproducts of degradation of SG1 (from BlocBuilder[®]).

^{31}P NMR: $E_{a,d}$ (DMA) = 121.9 kJ/mol.

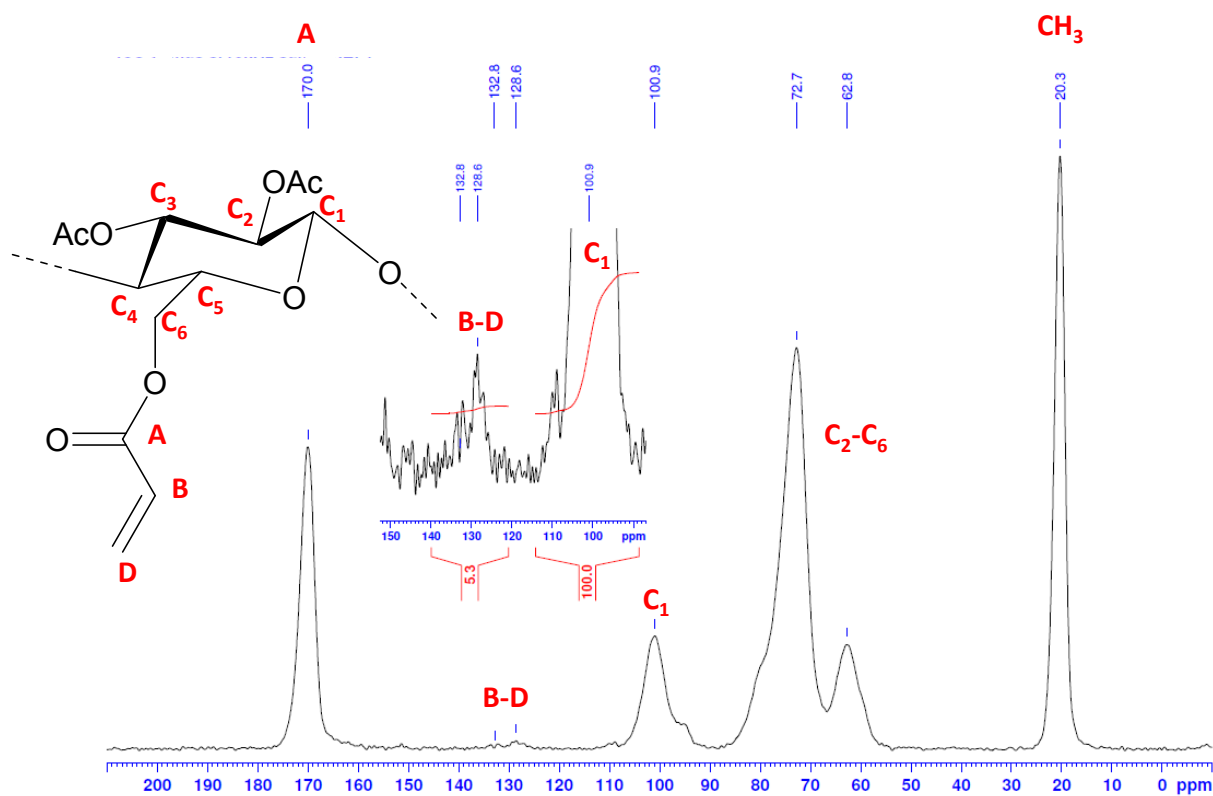


Figure S18 Solid -state NMR; CPMAS ^{13}C NMR of acroylated cellulose acetate (CA=), DS = 0.03

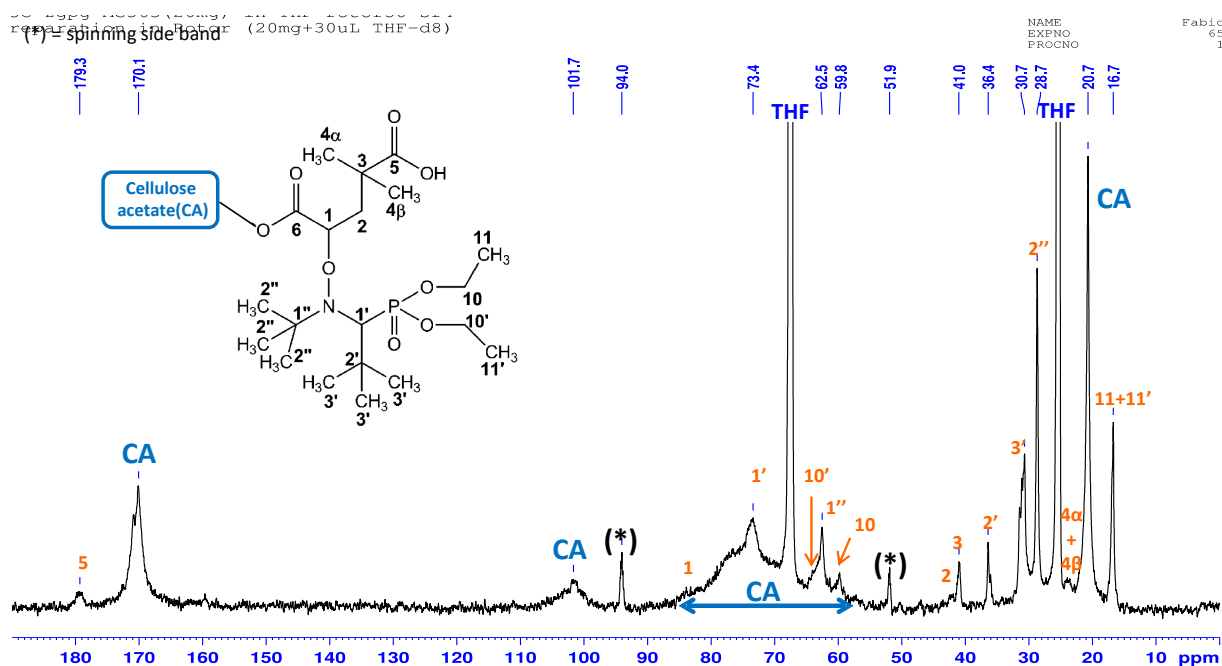


Figure S19 HRMAS ^{13}C NMR of CA-BB; the signals where assigned thanks to ^1H - ^{13}C HSQC experiment

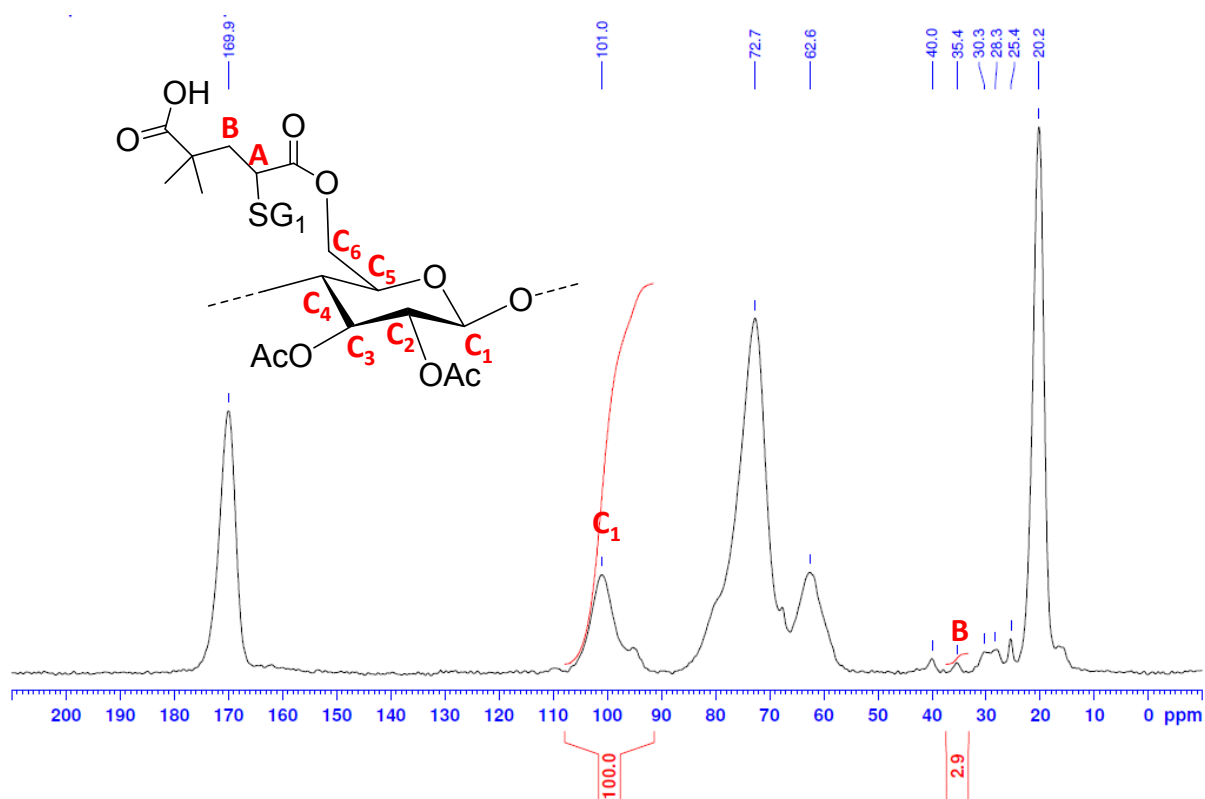


Figure S20 Solid -state NMR; CPMAS ^{13}C NMR of CA-BB, DS = 0.03

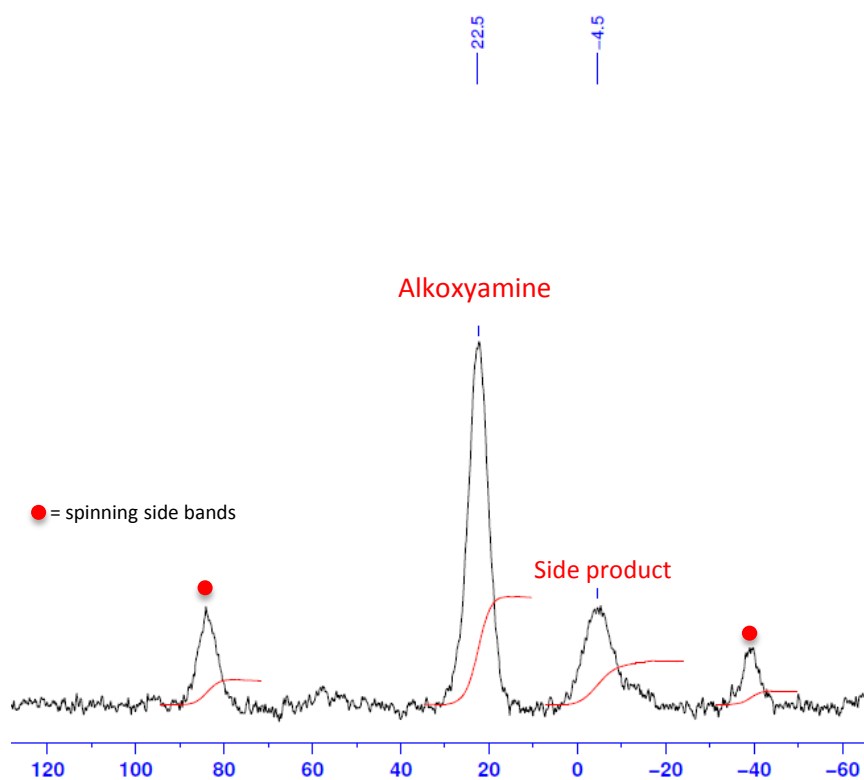


Figure S21 Solid -state NMR; CPMAS ^{31}P NMR of CA-BB, DS = 0.03. Side product due to the decomposition of SG1 is recorded at 0 ppm

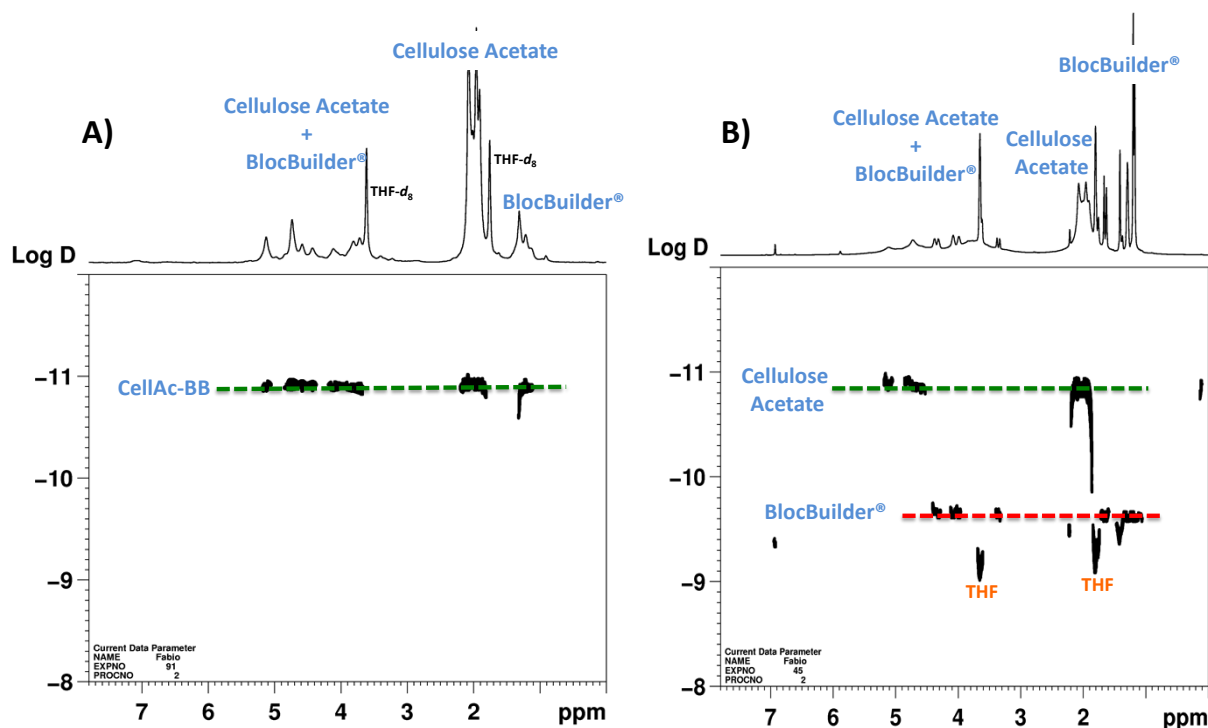


Figure S22 HRMAS DOSY NMR characterization. A) Cellulose acetate functionalized with BlocBuilder®; B) Physical mixture of cellulose acetate and BlocBuilder®

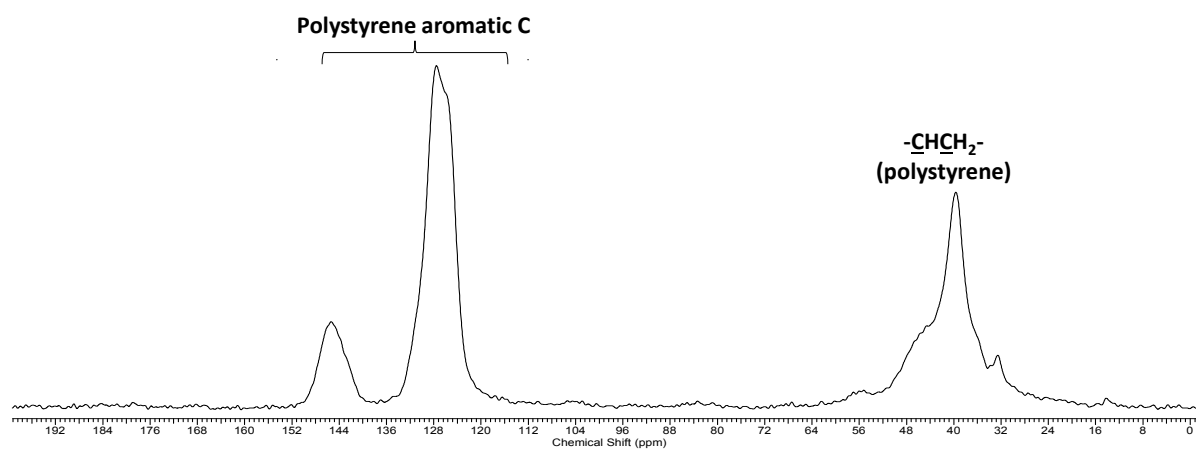


Figure S23 CPMAS ^{13}C NMR of the PS chains obtained after the basic hydrolysis of the CA-g-PS

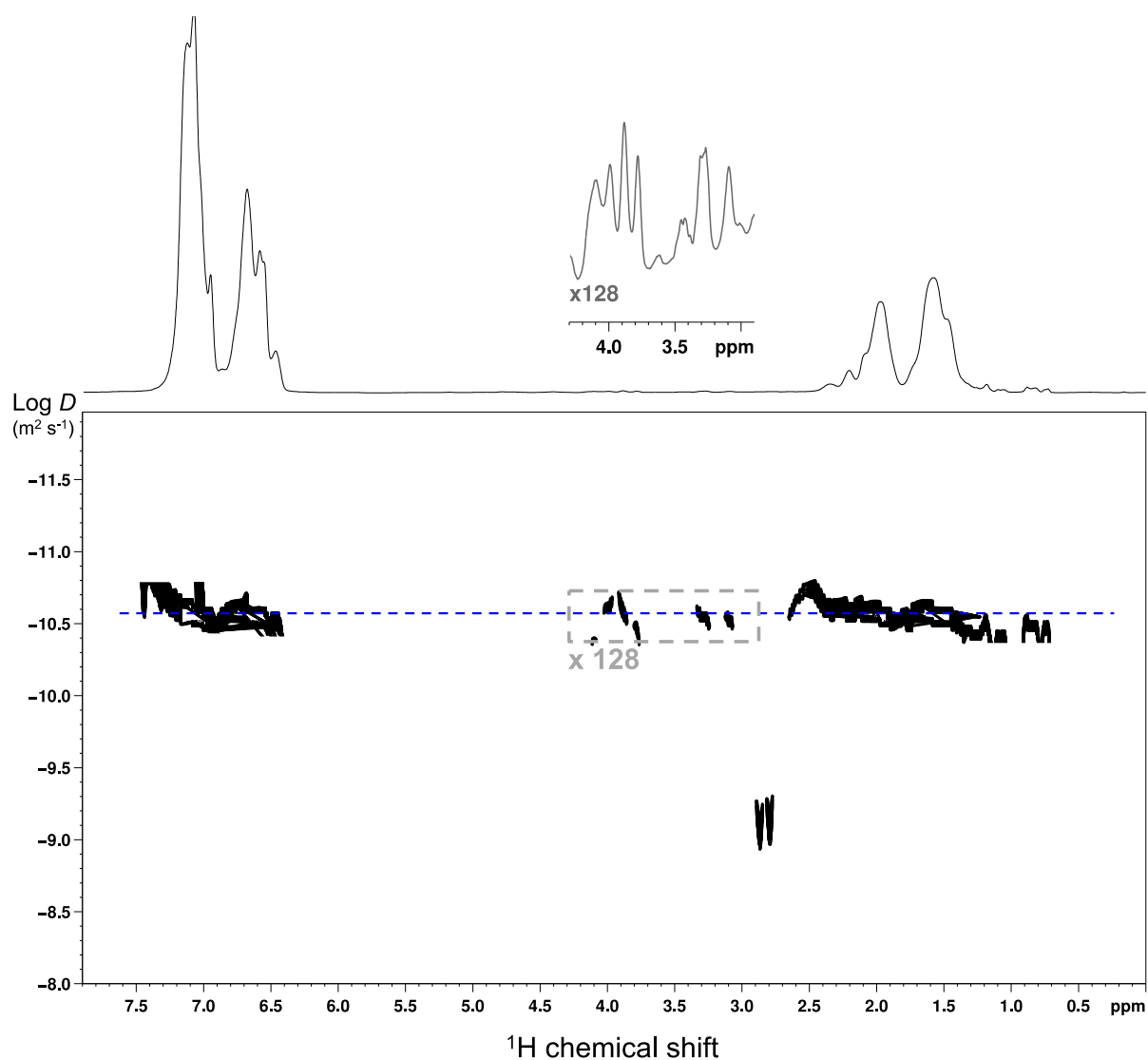


Figure S24 ^1H HRMAS DOSY spectrum recorded on a CA-*g*-PS_{20%} sample (5 mg) in THF-*d*₈ (20 μL) at 300 K with a 4 kHz sample spinning rate. The horizontal and vertical axes show the ^1H chemical shift (expressed in ppm) and the diffusion coefficients D (expressed in $\text{m}^2 \text{s}^{-1}$) on a logarithmic scale, respectively. The corresponding ^1H spectrum is reported in the top projection. The dashed blue horizontal line in the DOSY spectrum emphasizes the average diffusion coefficient for the CA-*g*-PS_{20%} macromolecules, showing that all the correlations due to the AC and the PS blocks are aligned on the same horizontal trace. This indicates that they belong to the same macromolecular species, hereby confirming the success of the grafting procedure). Note that the intensity of the correlations due to the AC blocks in the DOSY spectrum (in the 4.3–2.9 ppm region) have been increased by a factor of 128 in order to be observable.