Support Information for:

Detailed understanding of the DBU/CO₂ switchable solvent system for cellulose solubilization and derivatization

Kelechukwu N. Onwukamike,[a,b] Thierry Tassaing,[c] Stéphane Grelier,[b] Etienne Grau,[b] Henri Cramail,[b] Michael A.R. Meier[a*]*

[a] Institute of Organic Chemistry (IOC), Materialwissenschaftliches Zentrum (MZE), Karlsruhe Institute of Technology (KIT), Straße am Forum 7, 76131 Karlsruhe, Germany; Email: m.a.r.meier@kit.edu; web: www.meier-michael.com

[b] Laboratoire de Chimie des Polymères Organiques, Université de Bordeaux, UMR5629, CNRS - Bordeaux INP - ENSCBP, 16 Avenue Pey-Berland, 33607 Pessac Cedex France

[c] Institut des Sciences Moléculaires, U.M.R. 5255 CNRS - Université de Bordeaux, 351, Cours de la Libération 33405 Talence-France

I: FT-IR monitoring of stability of in-situ carbonate of octanol with temperature using DBU, MTBD and TMG as super bases

II: FT-IR monitoring of cellulose solubilization for pressure and temperature optimization

III: Concentration study of cellulose solubilization at various temperature

IV: Concentration study of octanol

V: Characterization of synthesized model octanol carbonate

VI; Characterization of synthesized cellulose carbonate

I: FT-IR monitoring of stability of *in-situ* carbonate of octanol with temperature using DBU, MTBD and TMG as super bases
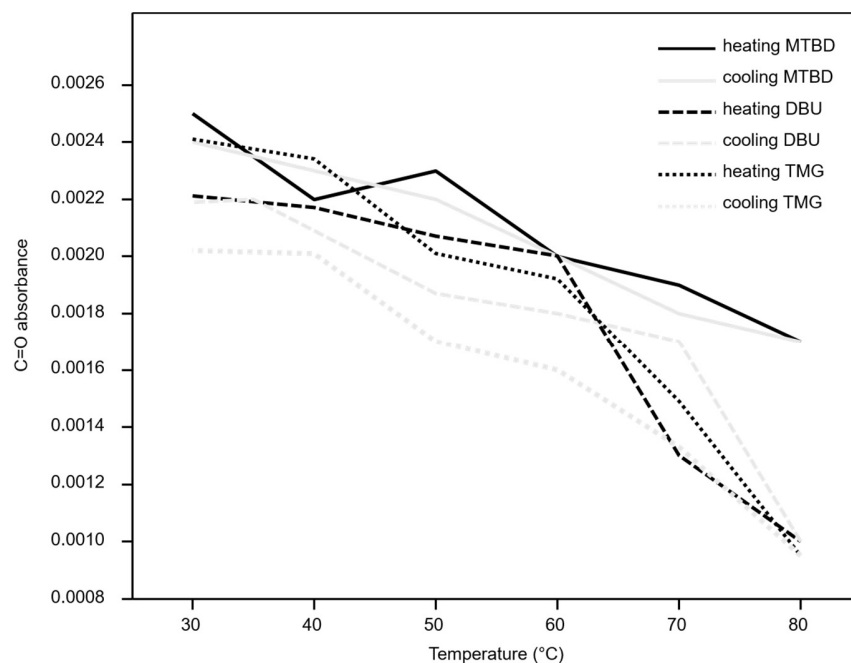

Figure S1: *FT-IR C=O absorbance at 1665 cm^{-1} during stability study of in-situ formed carbonate of octanol at different temperatures using DBU, MTBD and TMG as super bases (conditions: 20 bar CO$_2$, 30 °C).*

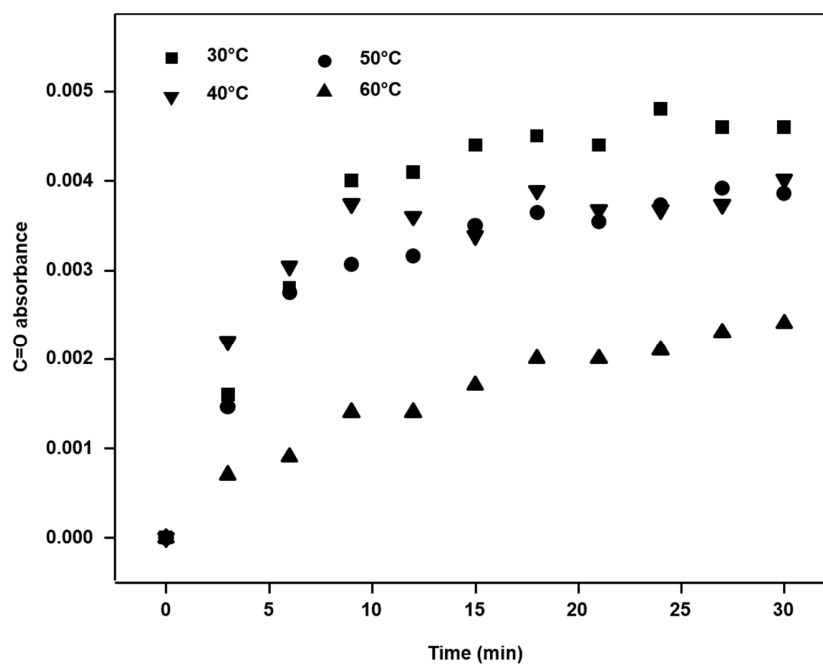**II: FT-IR monitoring of cellulose solubilization for pressure and temperature optimization**

Figure S2: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose (3 % (w/w)) solubilization with DBU as super base and 10 bar CO_2 at different temperatures observed over time.*
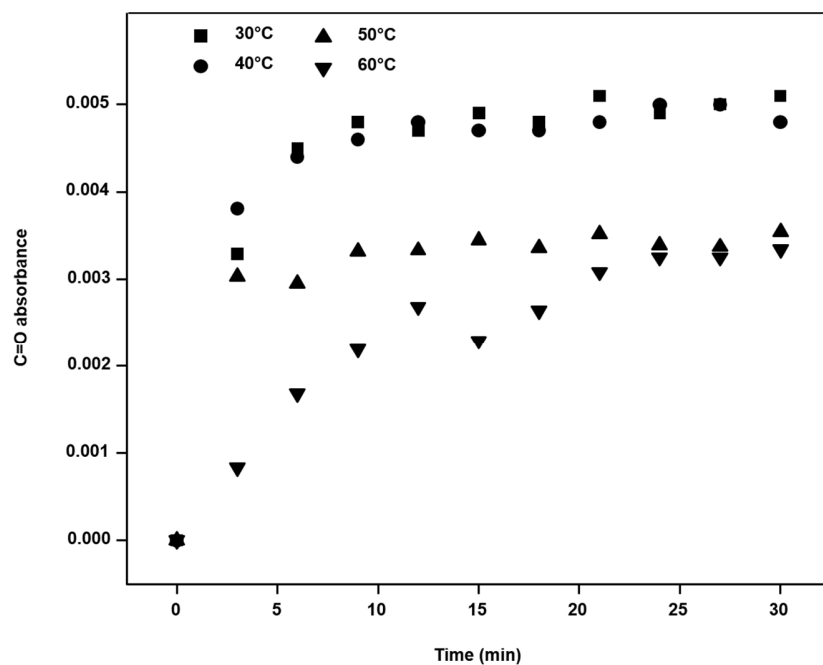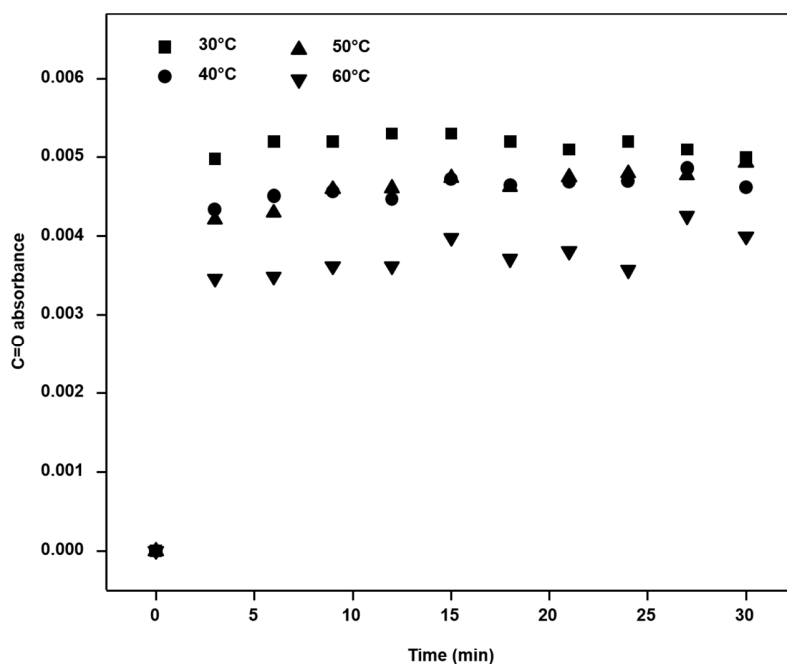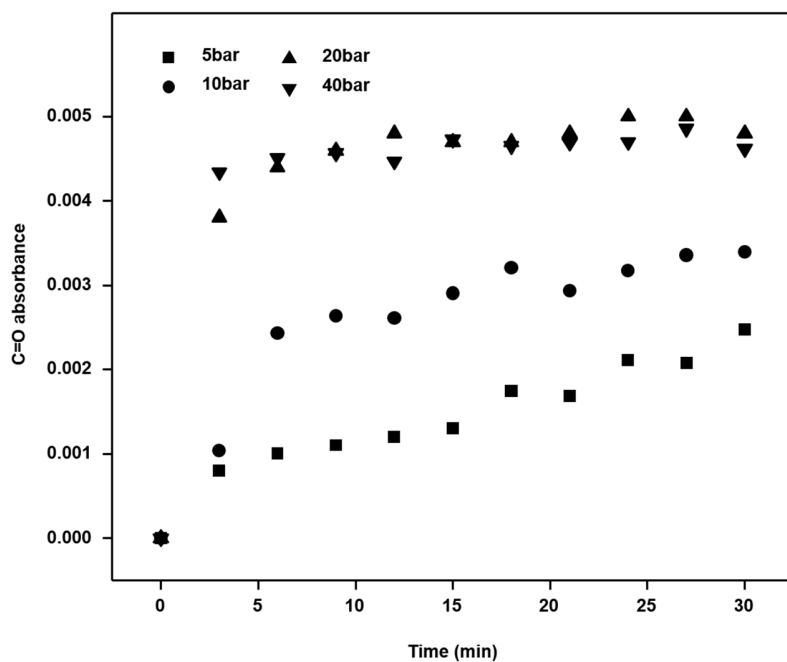

Figure S3: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose (3 % (w/w)) solubilization with DBU as super base and 20 bar CO_2 at different temperatures observed over time.*

Figure S4: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose (3 % (w/w)) solubilization with DBU as super base and 40 bar CO$_2$ at different temperatures observed over time.*

Figure S5: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose (3 % (w/w)) solubilization with DBU as super base at 40 °C at different CO$_2$ pressures (in bar) observed over time.*
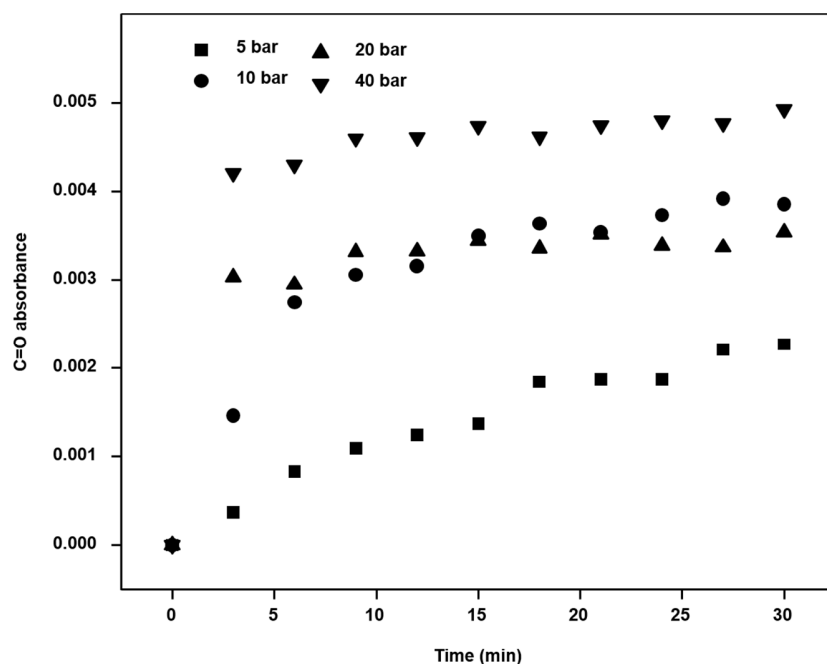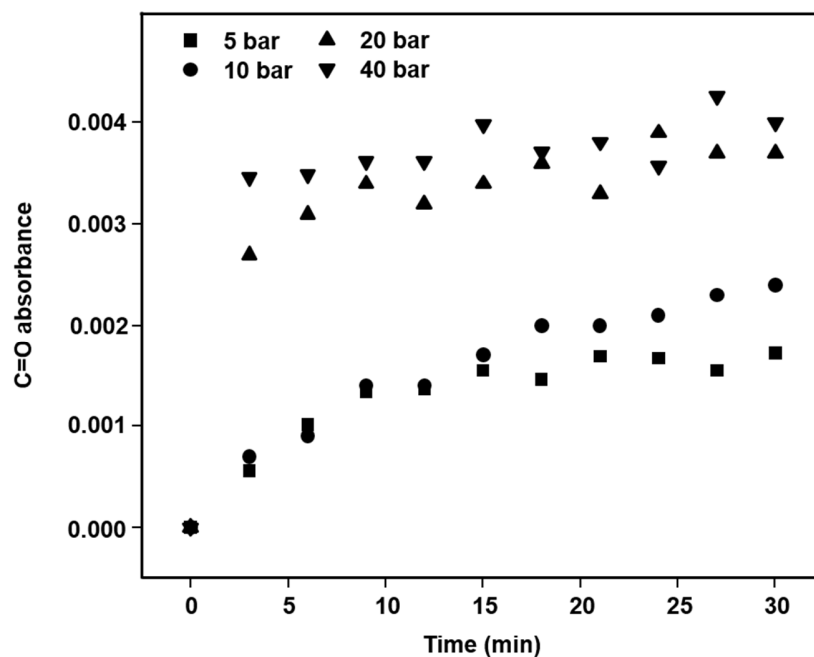
Figure S6: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose (3 % (w/w)) solubilization with DBU as super base at 50 °C at different CO_2 pressures (in bar) observed over time.*

Figure S7: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose (3 % (w/w)) solubilization with DBU as super base at 60 °C at different CO_2 pressures (in bar) observed over time.*
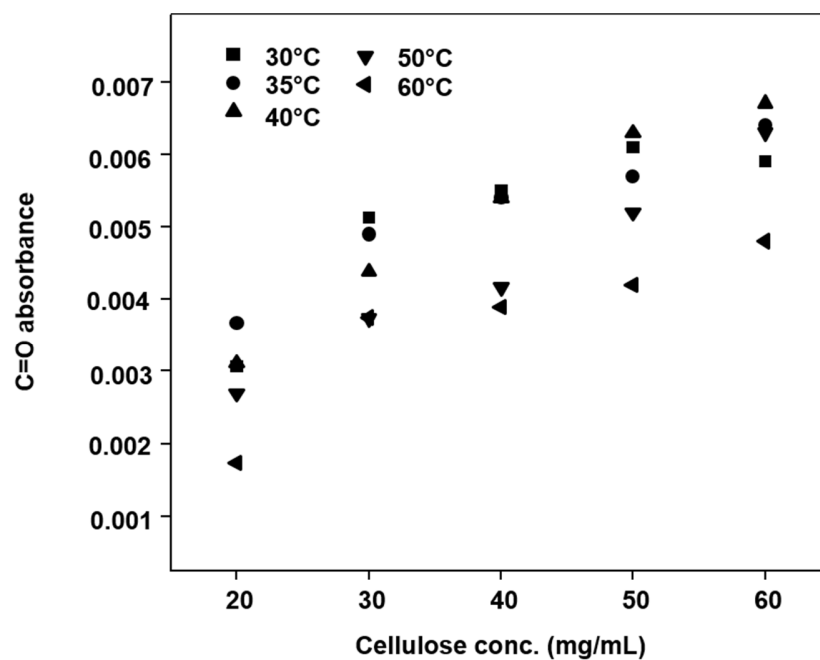
III: Concentration study of cellulose solubilization

Figure S8: *FT-IR C=O absorbance at 1665 cm^{-1} during cellulose solubilization using DBU as super base after 20 bar of CO_2 applied for 15 minutes at various temperatures (30, 35, 40, 50, 60 °C) and varying cellulose concentration.*
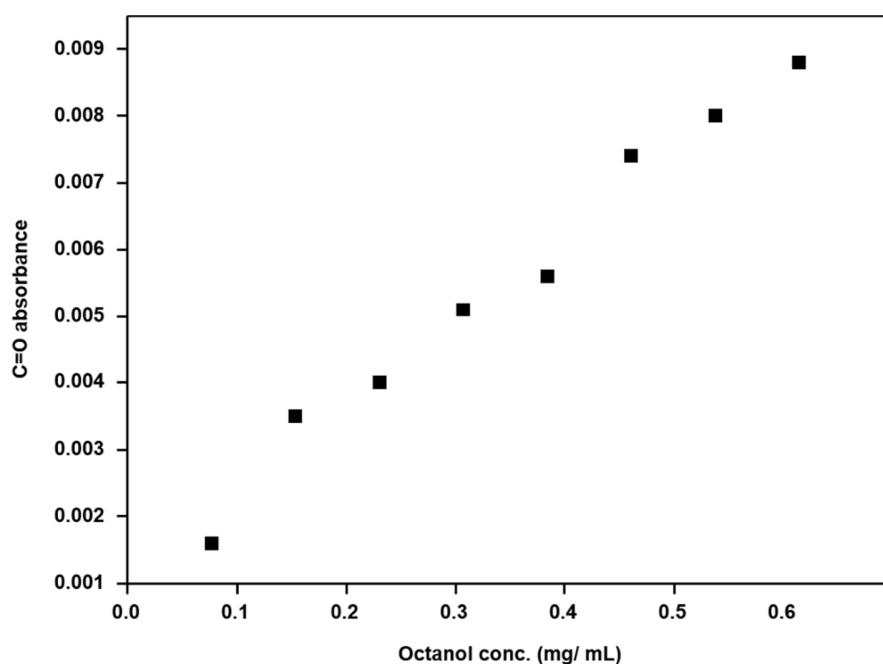
IV: Concentration study of octanol

Figure S9: *FT-IR C=O absorbance at 1665 cm^{-1} during variation in octanol concentration using DBU as super base after 20 bar of CO$_2$ applied for 15 minutes at 30 °C.*

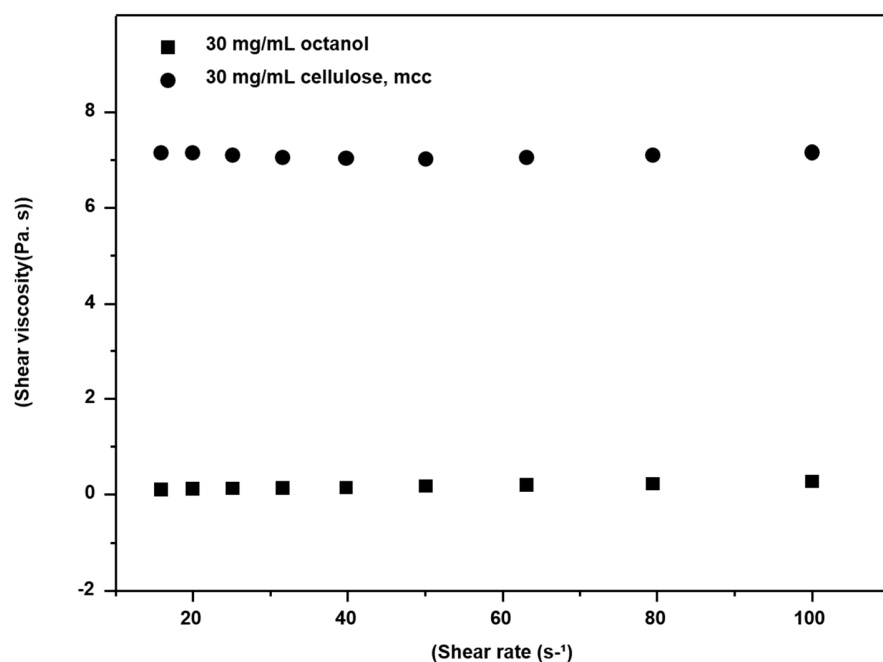**Figure S10:** *Viscosity measurement comparison between octanol and cellulose in a DBU-DMSO-CO$_2$ solvent mixture at concentration of 30 mg/mL.*

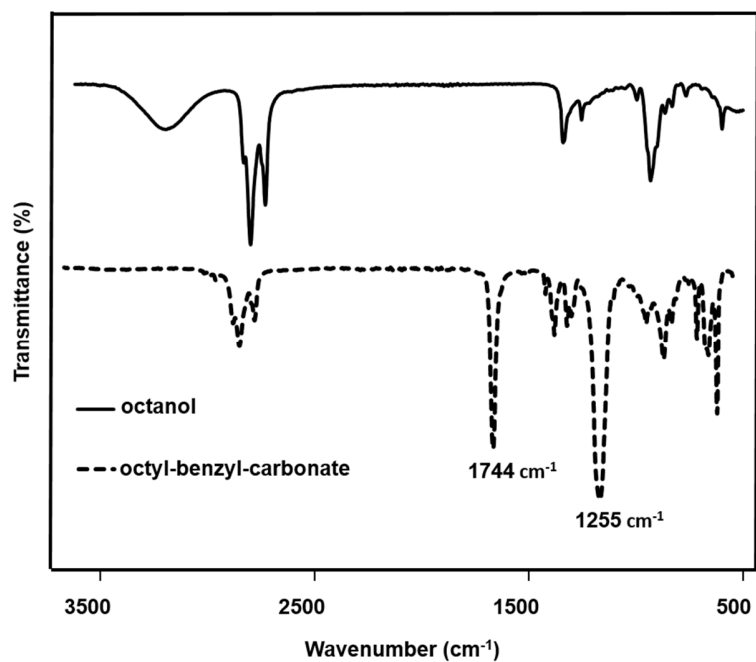## V: Characterization of synthesized model octanol carbonate

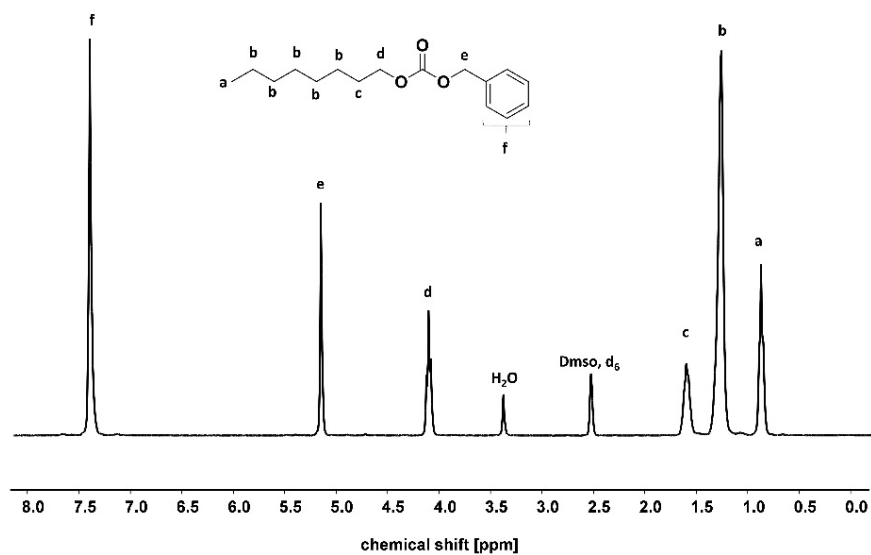**Figure S11:** *FT-IR spectra of octanol and octyl-benzyl-carbonate.*

Figure S12: *^{1}H NMR spectrum of octyl-benzyl-carbonate.*
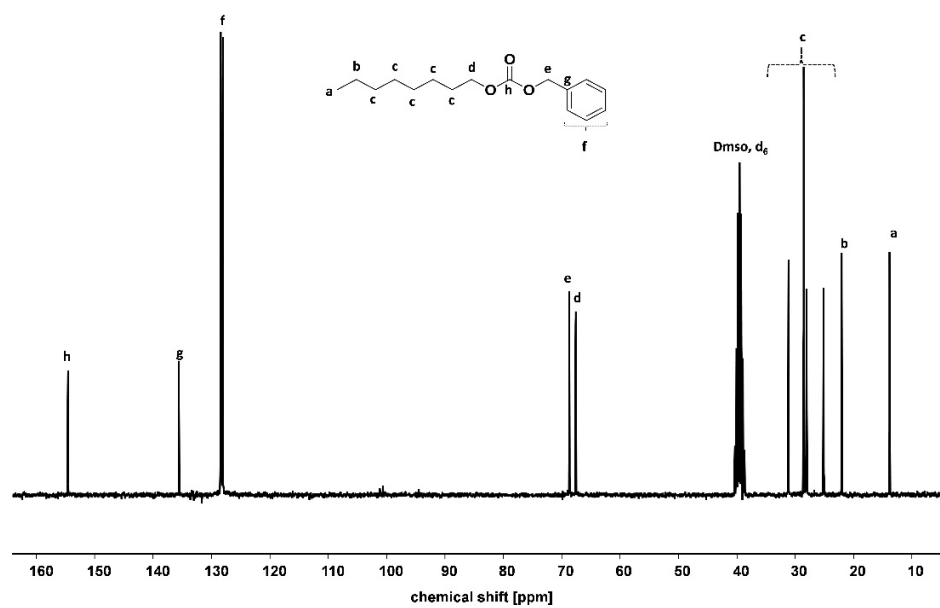
Figure S13: ^{13}C NMR spectrum of octyl-benzyl-carbonate.
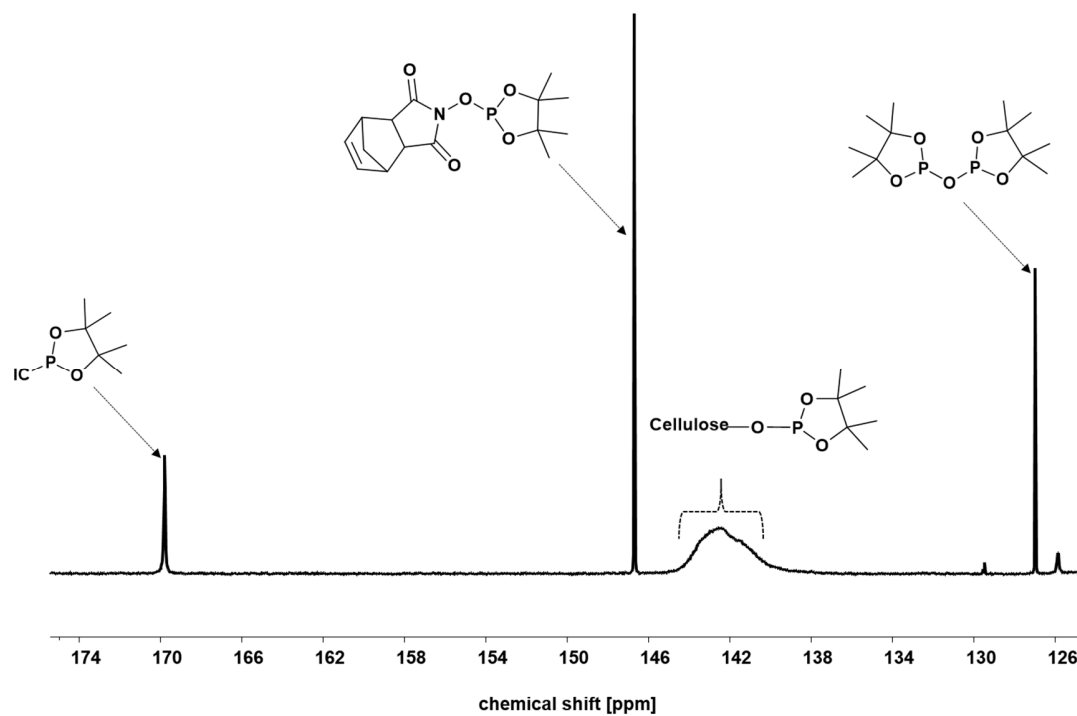
VI: Characterization of synthesized cellulose carbonate

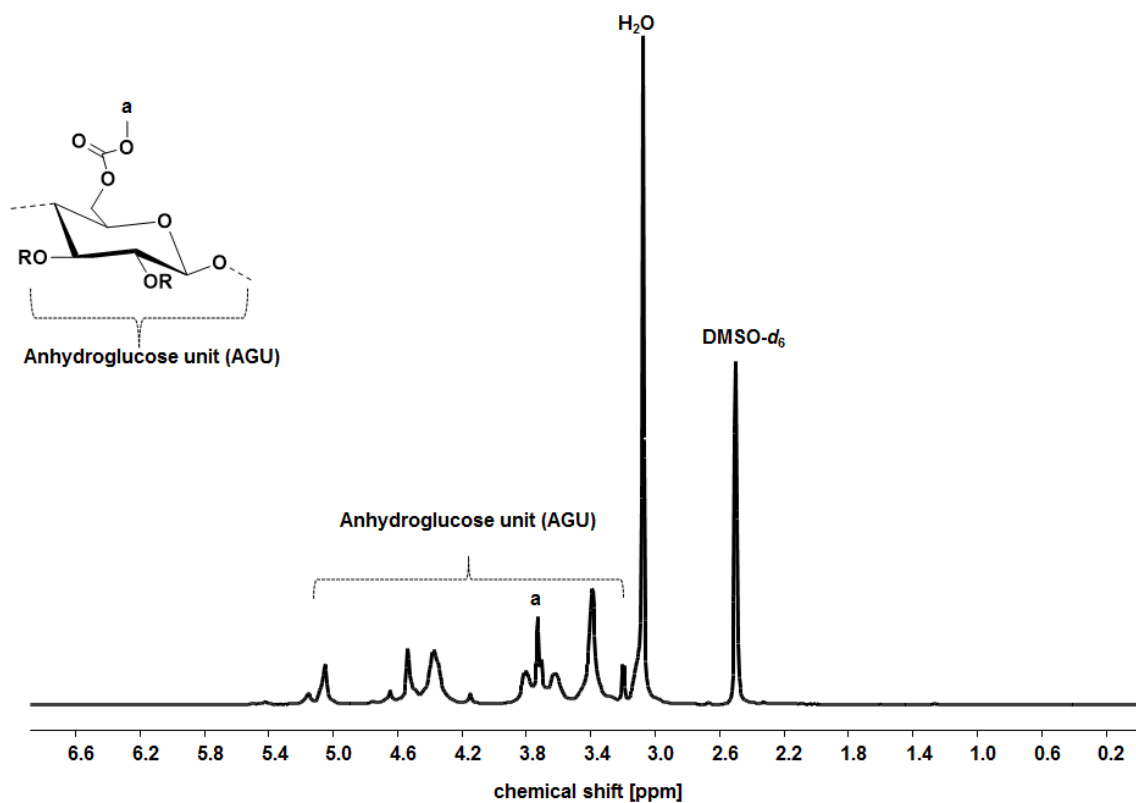**Figure S14:** ^{31}P NMR of cellulose-benzyl-carbonate for DS determination.

Figure S15: ^{1}H NMR spectrum of cellulose-methyl-carbonate measured in DMSO (d_6) at 80 °C.
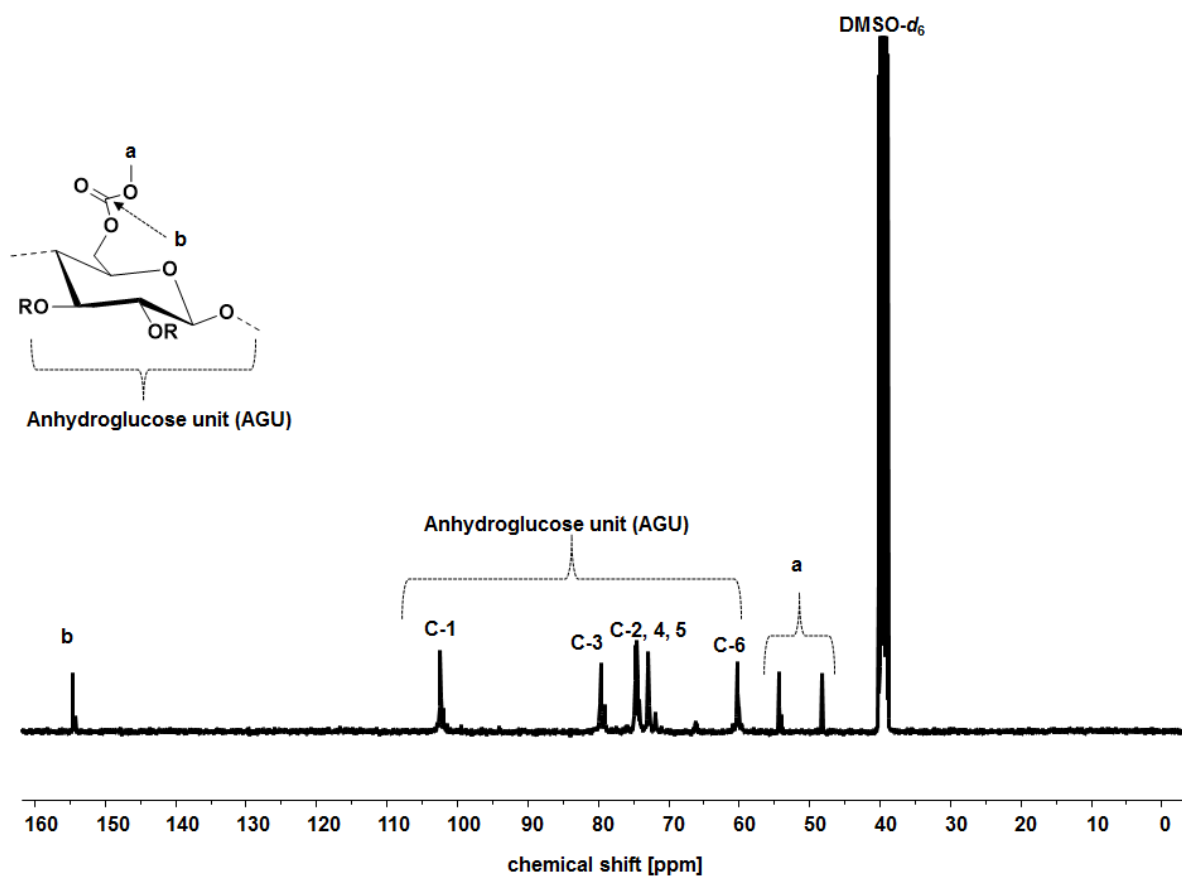
Figure S16: ^{13}C NMR of cellulose-methyl-carbonate measured in DMSO (d$_6$) at 80 °C.