

## Supplementary data

# Alkoxy carbonylation of Ethylene with Cellulose in Ionic Liquids

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**Materials and General Considerations.** Unless noted otherwise, all manipulations were carried out under an inert gas atmosphere using standard glovebox or Schlenk techniques. Microgranular cellulose was purchased from Sigma Aldrich. 1-*n*-butyl-3-methylimidazolium methanesulfonate ( $\geq 95\%$ ) and 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene were obtained from Sigma Aldrich and used as purchased. Carbonmonoxide (3.7 grade) supplied by Air Liquide and ethylene (4.0) supplied by Gerling Holz + Co were used as received. NMR spectra were recorded on a Varian Unity INOVA 400 instrument.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were referenced to the solvent signal. High-temperature NMR measurements of cellulose propionates were performed in  $\text{DMSO-}d_6$  at  $100\text{ }^\circ\text{C}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR assignments are supported by COSY and phase sensitive HSQC experiments.  $^{13}\text{C}$  NMR spectra of cellulose propionate were recorded with power-gated proton decoupling, a relaxation delay of 1 s, and 20000 scans. The IR spectra were recorded on a Perkin-Elmer Spectrum 100 instrument with an attenuated total reflection (ATR) sampling accessory. Optical microscopy images were recorded on a Leica DM4000M microscope. For annealing studies cellulose propionate was annealed with desired temperature program in a Linkam hotstage (THMS 600) equipped with liquid  $\text{N}_2$  cooling.

**DOSY NMR Experiments.** Spectra were recorded on a Bruker Avance DRX 600 or a Bruker Avance III 400 MHz instrument with a QXI or BBO Bruker 5 mm gradient probe, respectively, which allows to use field gradients up to about  $50\text{ G}\cdot\text{cm}^{-1}$ . The temperature was kept at 393.5 K, and the NMR tube was not spun. The diffusion NMR experiments were performed with a pulsed-gradient stimulated echo (LED-PFGSTE) sequence, using a bipolar gradient. Samples were prepared by dissolving the solid samples in  $\text{DMSO-}d_6$  at  $130\text{ }^\circ\text{C}$ . Sequence delays were  $\Delta = 100\text{ ms}$  (diffusion delay),  $\delta = 2\text{ ms}$ ,  $\tau = 200\text{ }\mu\text{s}$  (gradient recovery delay), and  $T_e = 5\text{ ms}$  (LED recovery delay). The number of scans was 16, the number of dummy scans was 16 before the first experiment in the 2D series, the number of sampled points in the gradient strength dimension was 64-128 (with a linear gradient ramp) and 4096 in the spectral dimension (frequency resolution was not a critical factor), and the relaxation delay was 1 s. Diffusion coefficients were not calibrated. Spectrum processing was performed with Bruker TOPSPIN 2.1 software.

**Alkoxy carbonylations** were carried out in a 22 mL stainless steel magnetic stirred pressure reactor with an aluminium heating jacket controlled by a thermocouple connected to the heating jacket.

The reactor was charged with 3 g 1-*n*-butyl-3-methylimidazolium methanesulfonate, 150 mg cellulose, 5 mol %  $\text{Pd}(\text{OAc})_2$  and phosphine ligand (Pd:P = 1:10). The reactor was evacuated for several hours and purged with nitrogen. After this procedure the reactor was charged with 250-750  $\mu\text{mol}$  methanesulfonic acid against a nitrogen flow.

The reactor was pressurised with carbon monoxide and ethylene ( $p = 50\text{ bar}$ ), and heated to the desired reaction temperature ( $T = 90 - 100\text{ }^\circ\text{C}$ ). After the desired reaction time the reactor was cooled to room temperature, and vented. The reaction mixture was poured into 100 mL

dest. water and the precipitated cellulose propionate was isolated by filtration, washed several times with water, and dried in vacuum at 50 °C.

### **Non-catalytic propionylation of cellulose for preparation of comparative samples.<sup>1</sup>**

To a solution of 0.3 g (9.3 mmol OH) of cellulose in 7 g of [bmim][Cl], 15 mL (117 mmol) of propionic anhydride and 15 mL of pyridine were added. The solution was stirred for 24 h at 80 °C. To isolate the product, the solution was precipitated into 200 mL of dest. water. The product was separated and washed twice with water and finally dried at 50 °C in vacuum.

### **NMR and IR analysis cellulose propionate**

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, 100 °C): δ/ppm = 0.97 (m, 9H, H-9), 2.2-2.3 (m, 8H, H-8), 3.4-5.1 (cellulose backbone).

<sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz, 100 °C): δ/ppm = 8.2 (C-9), 26.3 (C-8), 62.0 (C-6'), 59.1 (C-6), 71.3-74.9 (C-2, C-3, C-5), 79.5 (C-4), 99.1 (C-1'), 101.8 (C-1), 171.6 (CO), 172.2 (CO), 172.8 (CO).

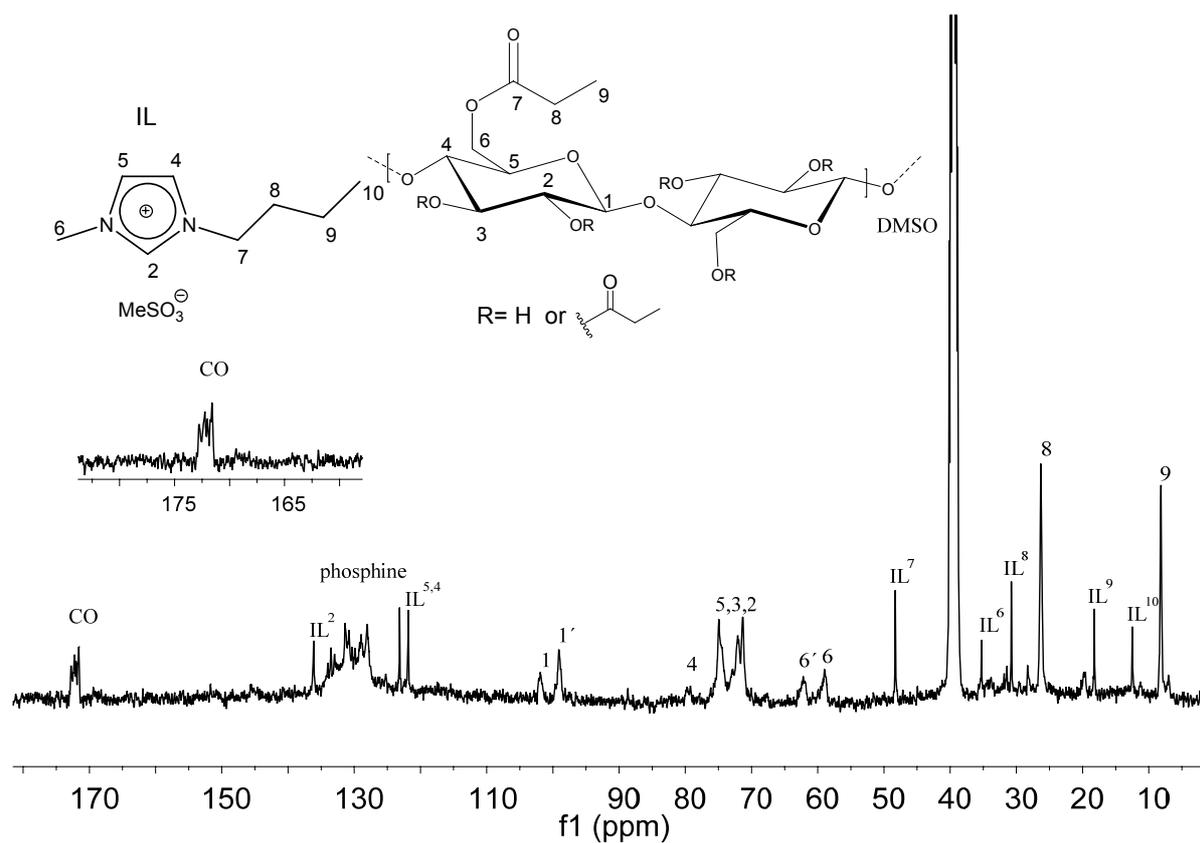
FT-IR: 3340 ν(OH), 2963 and 2940 ν(CH), 2877 ν(CH<sub>2</sub>), 1738 ν(C=O ester), 1163 ν(C-O-C).

### **9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene-2,7-bissulfonic acid (1a)<sup>2</sup>**

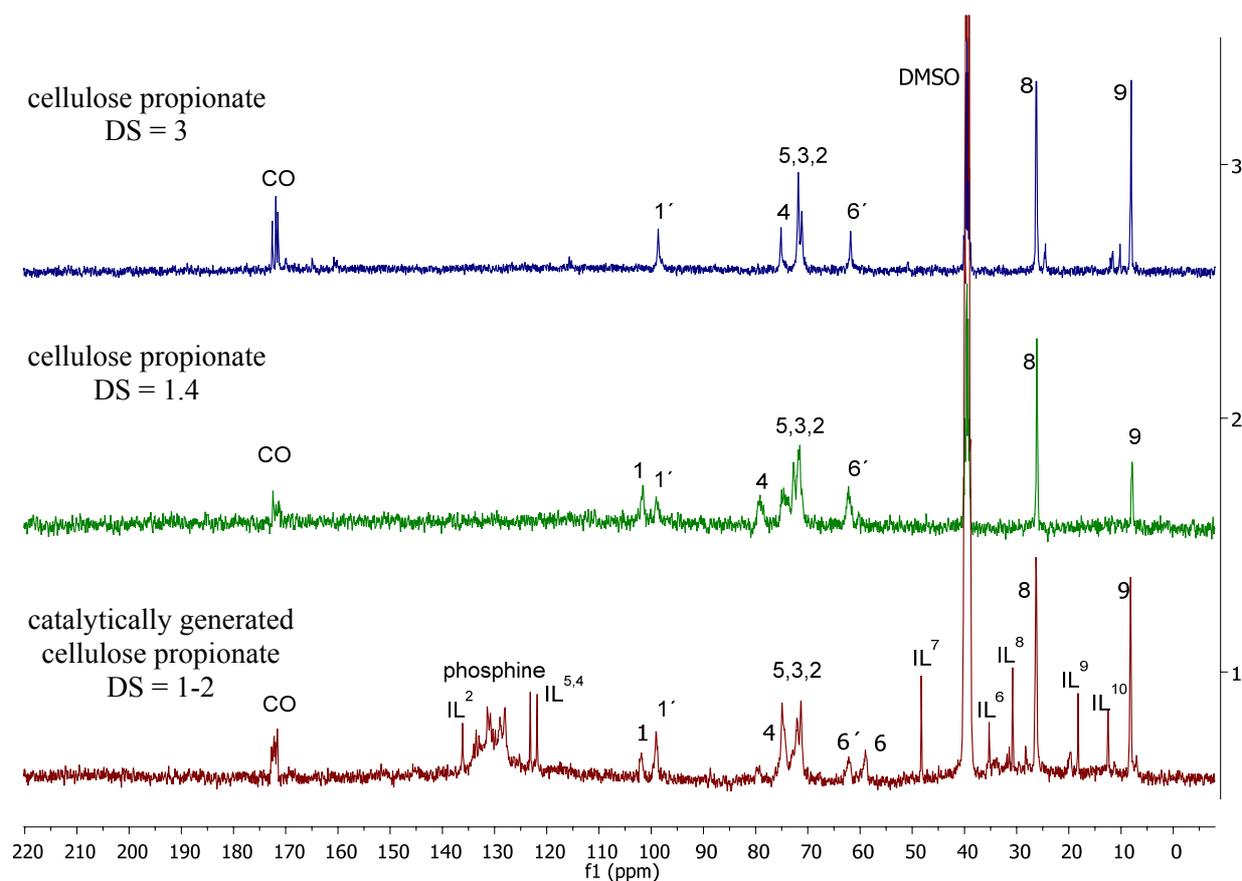
A solution of 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (0.7 g, 1.21 mmol) in dry dichloromethane (2 mL) was cooled to 0 °C and concentrated sulfuric acid (1.03 mL) was added. Dichloromethane was removed by evaporation under vacuum, and after 9,9-dimethyl-4,5-bis(diphenylphosphine) xanthene was completely dissolved in the concentrated sulphuric acid, oleum (1.03 mL) was added to the cooled solution. Subsequently the mixture was warmed to room temperature and stirred for 24 h. After cooling the reaction mixture to -10 °C, degassed ice/water (5.5 mL) was added slowly to the solution, which resulted in a white precipitate. After filtration, the white solid was used without further purification. After drying at 50 °C under vacuum crude **1a** was obtained; yield: 1.0 g; <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400MHz, 25 °C): δ/ppm = 1.71 (s, 6H), 7.23 - 7.38 (m, 22H), 8.06 (s, 2H); <sup>31</sup>P NMR (CD<sub>3</sub>OD, 161MHz, 25 °C): δ/ppm = -16 (s).

### **9,9-Dimethyl-2,7-bissulfonato-4,5-bis(diphenylphosphino)xanthene Sodium Salt (1b)<sup>2</sup>**

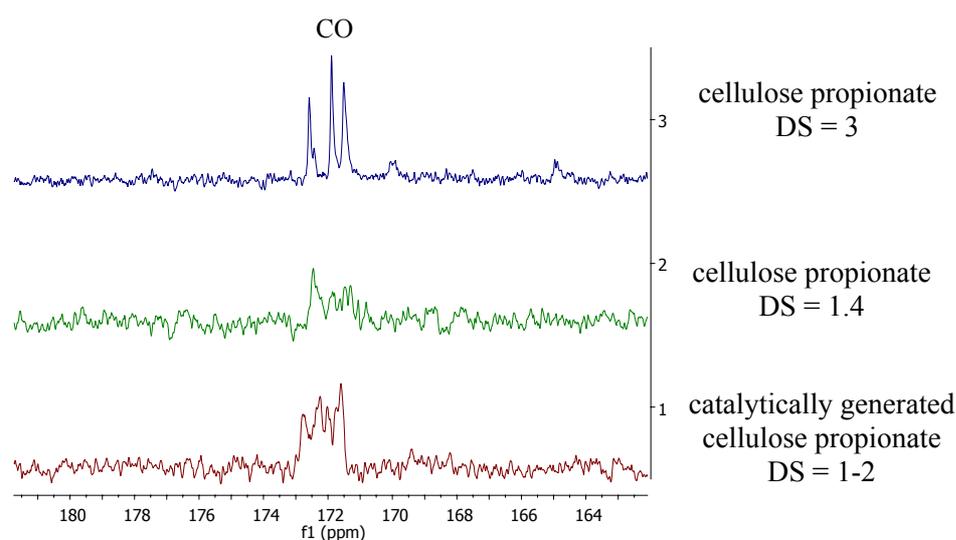
Compound **1a** (1.0 g) was neutralized with a 0.5 M NaOH solution (6 mL) in water and the water was removed by freeze-drying. The product was washed with EtOH (10 mL) and a white powder was obtained; yield: 0.9 g (95 %); <sup>1</sup>H NMR (CD<sub>3</sub>OD, 400MHz, 25 °C): δ/ppm = 1.69 (s, 6H), 7.18 ± 7.28 (m, 22H), 8.00 (s, 2H); <sup>31</sup>P NMR (CD<sub>3</sub>OD, 161MHz, 25 °C): δ/ppm = -17.7 (s).



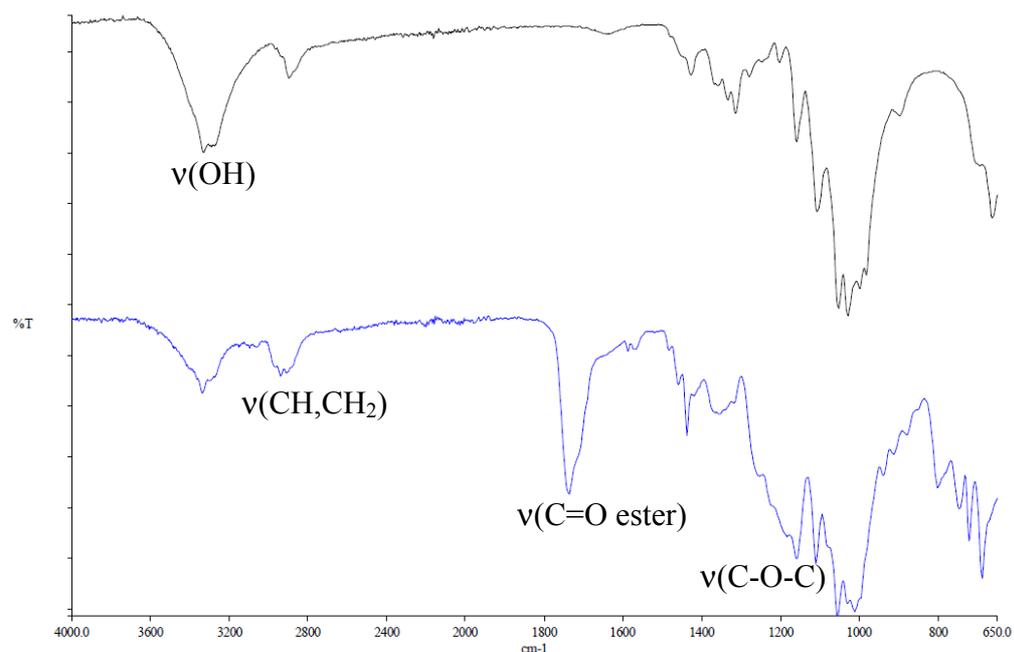
**Figure S1.**  $^{13}\text{C}$  NMR spectrum of a cellulose propionate (DS = 1 - 2) from catalytic alkoxyacylation,  $\text{DMSO-}d_6$ , 100 MHz, 100 °C (carbon signals for positions C-1 and C-6 of substituted cellulose are indexed by ').



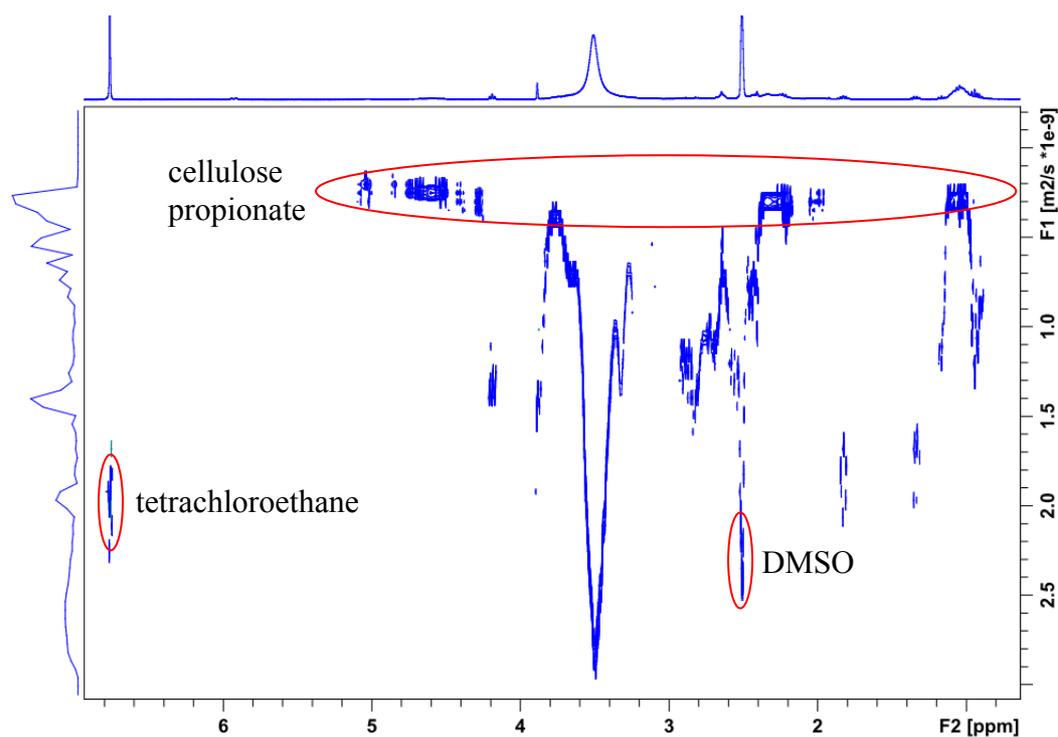
**Figure S2.**  $^{13}\text{C}$  NMR spectra of a non-catalytically generated cellulose propionate (DS = 3 and 1.4) (top and center) and cellulose propionate (DS = 1-2) from catalytic alkoxylation (bottom);  $\text{DMSO-}d_6$ ; 100 MHz; 100 °C; carbon signals for positions C-1 and C-6 of substituted cellulose are indexed by '.



**Figure S3.** Enlarged section of the above  $^{13}\text{C}$  NMR spectra of a non-catalytically generated cellulose propionate (DS = 3 and 1.4) (top and center) and cellulose propionate (DS = 1 - 2) from catalytic alkoxylation (bottom);  $\text{DMSO-}d_6$ ; 100 MHz; 100 °C.



**Figure S4.** FT-IR spectra of cellulose (top) and cellulose propionate (DS = 1 - 2) (bottom).



**Figure S5.** DOSY spectrum of a cellulose propionate (DS = 1-2) from catalytic alkoxylation and tetrachloroethane, DMSO- $d_6$ , 400 MHz, 120 °C.

## References

- (1) K. Schlüter, H.-P. Schmauder, S. Dorn, T. Heinze, *Macromol. Rapid Commun.*, 2006, **27**, 1670-1676.
- (2) P. M. Wilhelmus, K. Ramkisoensing, P. C. J. Kamer, J. N. H. Reek, A. J. van der Linden, A. Marson, P. W. N. M. van Leeuwen, *Adv. Synth. Catal.*, 2002, **344**, 293-298.