Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information for:

Sustainable succinylation of cellulose in a CO_2-based switchable solvent and subsequent Passerini 3-CR and Ugi 4-CR modification

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1) Calculation of DS and conversion values of modified cellulose samples

- **Calculation method of DS values of succinylated cellulose samples**

The DS values of succinylated cellulose samples were calculated by **Eq. (1)**:

$$\textbf{EQ. (1):}\ DS = \frac{7 \times (I_{\text{-COOH}})}{1 \times (I_{\text{H, AGU}})}$$

Where $I_{\text{-COOH}}$ is the integral of peak of the carboxylic acid protons and I_{AGU} is the peak of the integral of the anhydroglucose unit, both obtained by ^{1}H NMR.

- **Calculation method of DS of Passerini products of cellulose**

As mentioned in the manuscript, since full conversions were obtained for all Passerini products (i.e. no peak was detected from phosphorylated cellulose referring to the carboxylic acid at around 134 ppm in ^{31}P NMR), the DS could be directly calculated as follows:

^{31}P NMR analysis was carried out as follows:

MW_S: molecular weight (g mol^{-1}) of the substituent without including the oxygen atom between cellulose and the substituent (succinylation + Passerini components);
IS_{vol}: amount of internal standard used in volume, mL;
IS_{mol}: amount of internal standard used in mole, mmol;
I_R: integration ratio of remaining phosphorylated cellulose hydroxyl groups against internal standard;
W_S: sample weight, mg;
DS_{max}: maximum DS value of 3 for unsubstituted cellulose;
OH_C: free hydroxyl groups per weight unit of cellulose = DS_{max}/MW_{AGU} = 3/162.16 = 0.01852 mol g^{-1}

Eq. (2) for the calculation of the number of free hydroxyl groups per weight unit of substrate (**OH_S**, mol g^{-1}):

$$\textbf{EQ. (2):}\ OH_S = \frac{IS_{mol} \times IS_{vol} \times I_R}{1\,000\,000 \times W_S}$$

The final **Eq. (3)** for the calculation of the DS from ^{31}P NMR analysis (**DS_{31P}**):

$$\textbf{EQ. (3):}\ DS_{31P} = DS_{max} = \frac{\frac{1}{OH_S} - \frac{1}{OH_C}}{MW_S + \frac{1}{OH_S} - 1}$$

- **Calculation method of conversion of Ugi products of cellulose**

DS values calculated from Passerini products, which correspond to the DS of succinylation (see aboveand manuscript), were taken as reference, since the same batch of succinylated cellulose was used in all cases. For the calculation of conversions of carboxylic acid moieties in Ugi products were carried out as follows:

MW_S: molecular weight (g mol^{-1}) of the substituent, molecular weight of the Ugi components without including linking oxygen atom of the carboxylic acid from succinylation;

IS_{vol}: amount of internal standard used in volume, mL;
IS_{mol}: amount of internal standard used in mole, mmol;
I_R: integration ratio of remaining phosphorylated carboxyl moieties against internal standard;
W_S: sample weight, mg;
$DS_{Passerini}$: DS value of 2.64 for Passerini product of cellulose;
MW_{SFP}: calculated molecular weight of the succinylated cellulose from the DS value of 2.64 = 426 g mol^{-1} ;
$COOH_C$: free carboxylic acid groups per weight unit of cellulose = $DS_{Passerini}/MW_{SFP}$ = 2.64/426 = 0.0062 mol g^{-1}

Eq. (4) for calculation of the number of free carboxylic acid groups per weight unit of substrate (**$COOH_S$**, mol g^{-1}):

$$\textbf{EQ. (4):}\ COOH_S = \frac{IS_{mol} \times IS_{vol} \times I_R}{1\,000\,000 \times W_S}$$

Eq. (5) and **Eq. (6)** for the calculation of the conversion and conversion in percentage from ^{31}P NMR analysis, respectively (**$Conversion_{31P}$ and $\%_{Conversion}$**):

$$\textbf{EQ. (5):}\ Conversion_{31P} = DS_{Passerini} = \frac{\frac{1}{COOH_S} - \frac{1}{COOH_C}}{MW_S + \frac{1}{COOH_S} - 1}$$

$$\textbf{EQ. (6):}\ \%_{Conversion} = \frac{Conversion_{31P}}{DS_{Passerini}} \times 100$$

2) IR-Spectra of modified cellulose (including optimization studies)

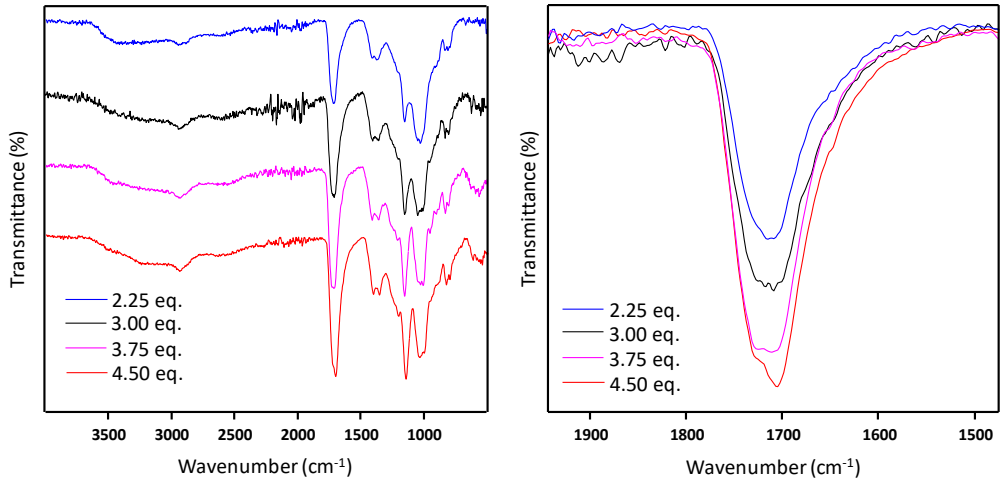
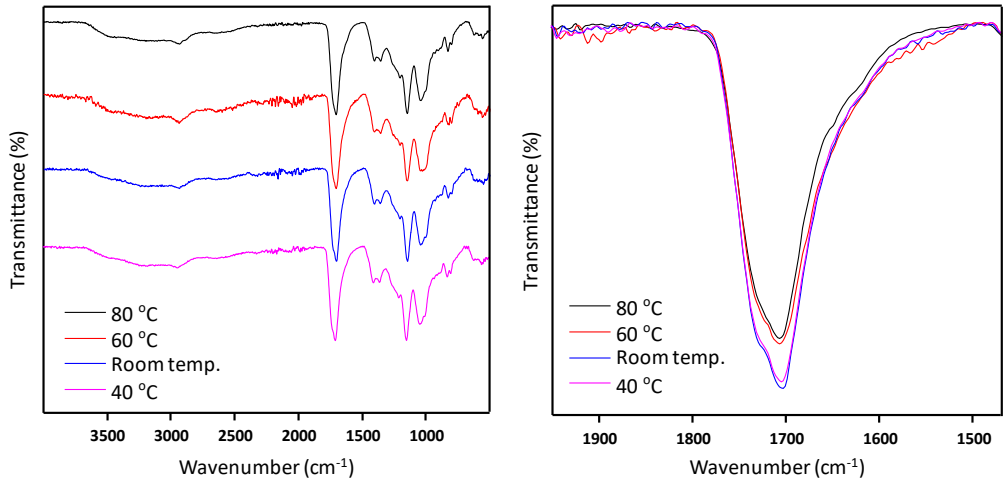


Fig. S1 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with different equivalents (per AGU) of succinic anhydride in CO_2-based switchable solvent (30 min., room temperature, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

Fig. S2 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at different reaction temperatures



in CO_2-based switchable solvent (10 min for. reactions at 60 °C and 80 °C, 30 min for. reaction at room temp), 4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

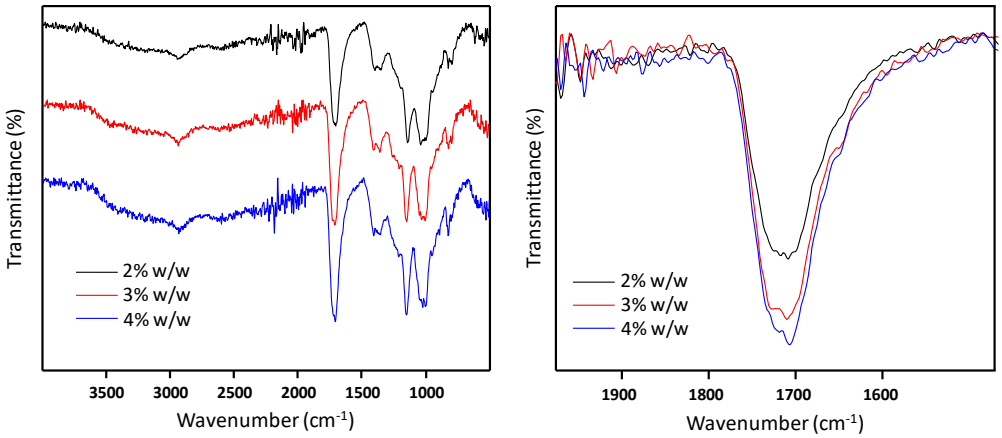


Fig. S3 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at different cellulose concentrations in CO_2-based switchable solvent (30 min., room temperature, 4.5 eq. per AGU succinic anhydride). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

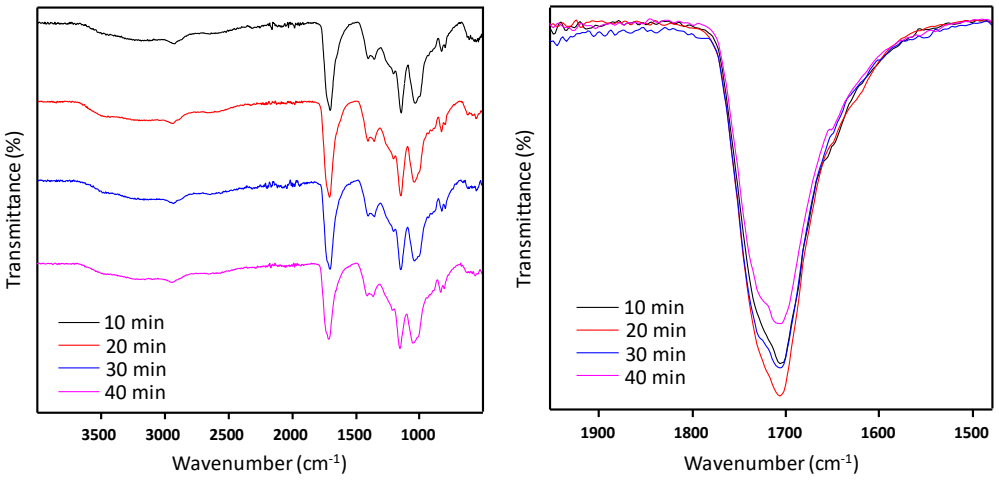


Fig. S4 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at 60 °C in CO_2-based switchable solvent (4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

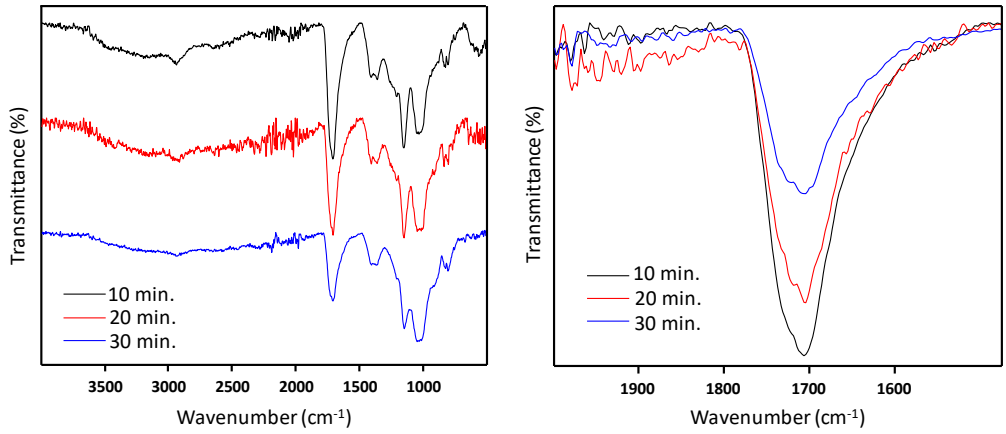


Fig. S5 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at 80 °C in CO_2-based switchable solvent (4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

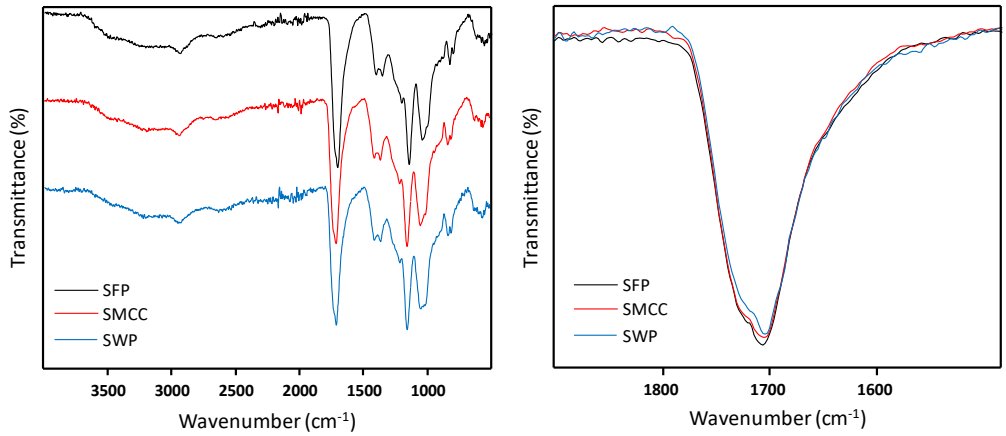


Fig. S6 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper (SFP), microcrystalline cellulose (SMCC), and organosolv wood pulp (SWP) with succinic anhydride in CO_2-based switchable solvent (30 min, 4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

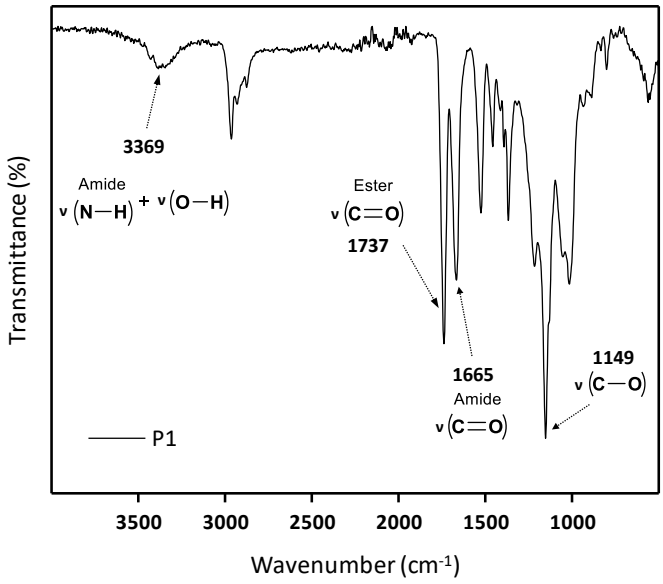


Fig. S7 ATR-IR spectra of Passerini product (**P1**) of succinylated filter paper. (24 h, isobutyraldehyde (2 eq.), tertbutyl isocyanide (2 eq.), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

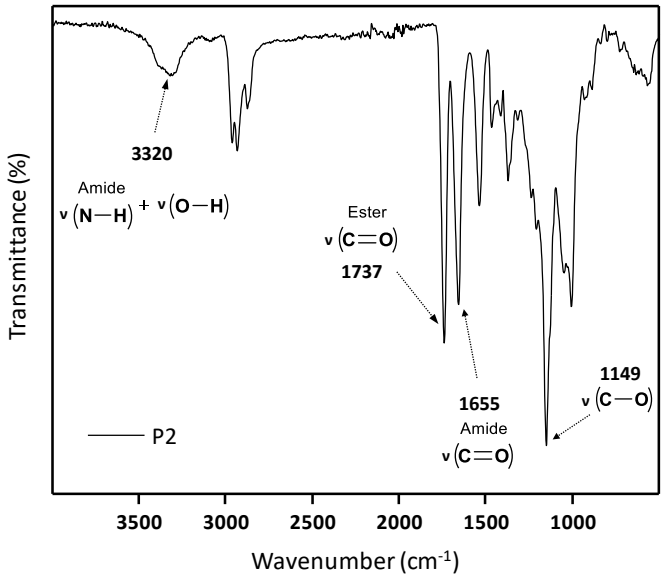


Fig. S8 ATR-IR spectra of Passerini product (**P2**) of succinylated filter paper. (24 h, isobutyraldehyde (2 eq.), 1-pentyl isocyanide (2 eq.), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

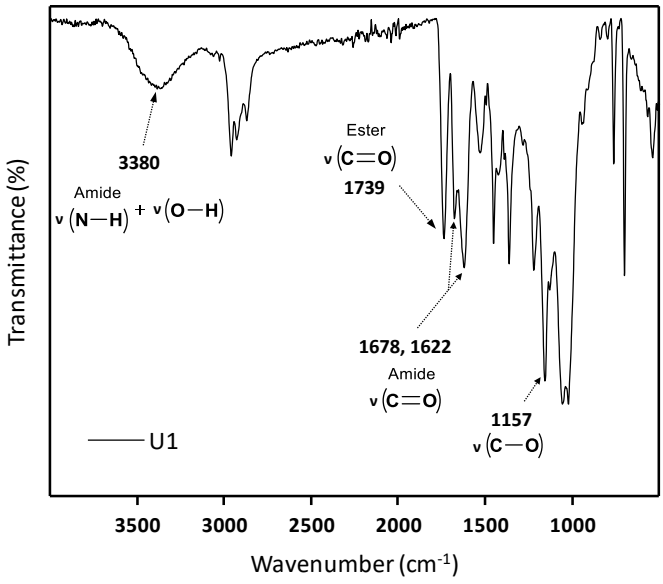


Fig. S9 ATR-IR spectra of Ugi product (**U1**) of succinylated filter paper. (48 h, 2-phenylpropionaldehyde (2 eq.), butylamine (2 eq.), tertbutyl isocyanide (2 eq), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

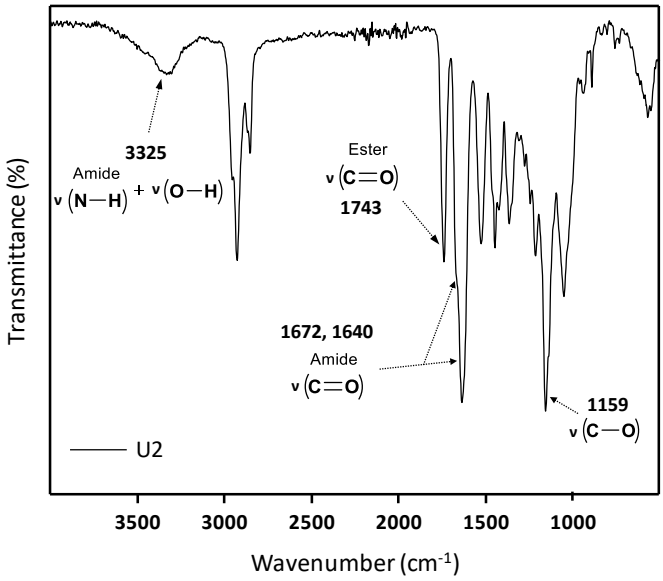


Fig. S10 ATR-IR spectra of Ugi product (**U2**) of succinylated filter paper. (48 h, isobutyraldehyde (2 eq.), butylamine (2 eq.), cyclohexyl isocyanide (2 eq), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

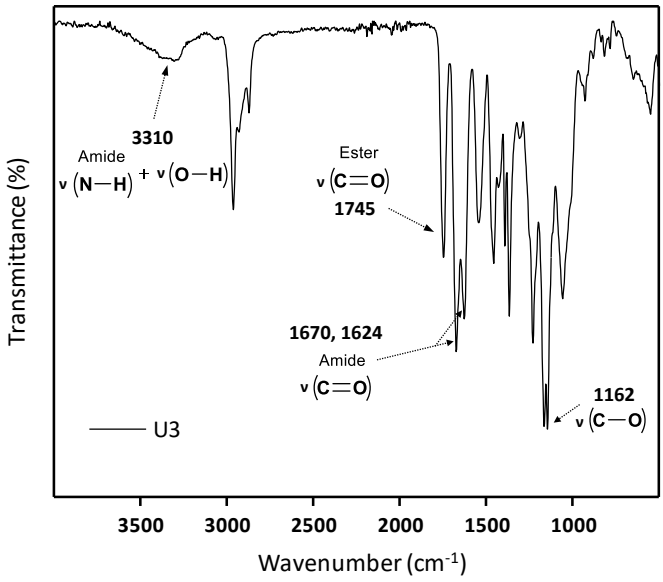


Fig. S11 ATR-IR spectra of Ugi product (**U3**) of succinylated filter paper. (48 h, isobutyraldehyde (2 eq.), butylamine (2 eq.), tertbutyl isocyanide (2 eq), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

3) NMR data of modified cellulose

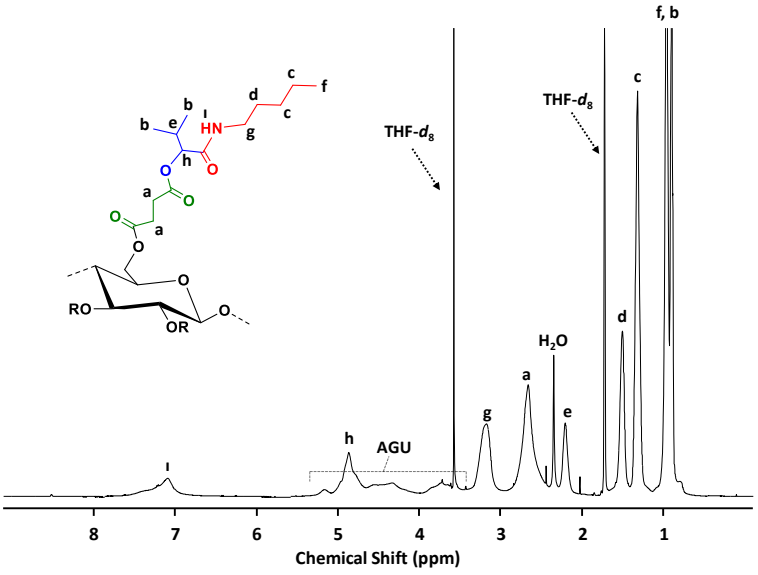


Fig. S12 ^{1}H NMR of Passerini product (**P2**).

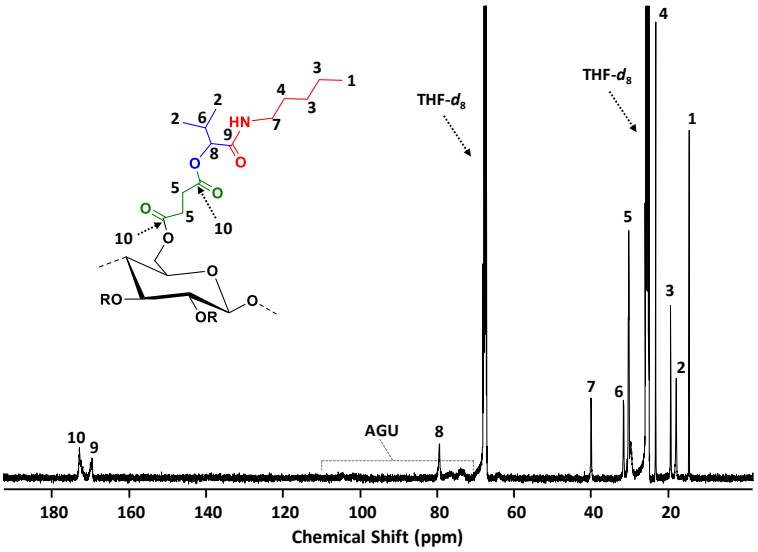


Fig. S13 ^{13}C NMR of Passerini product (**P2**).

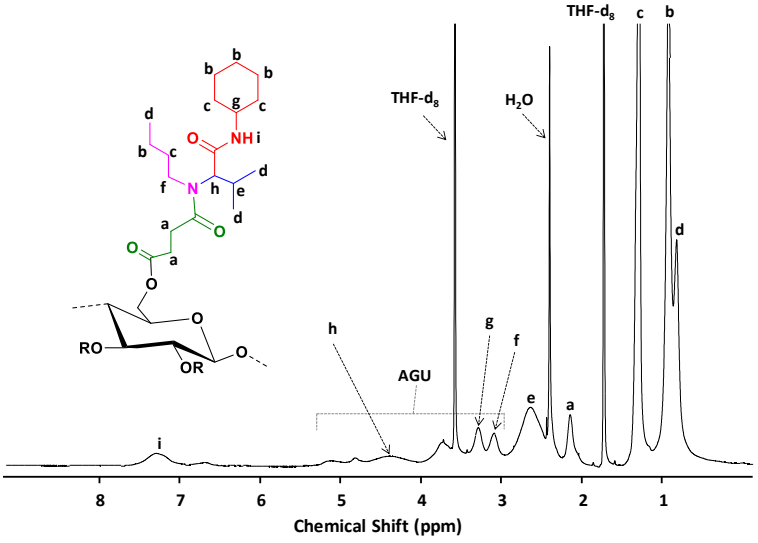


Fig. S14 ^{1}H NMR of Ugi product (**U2**).

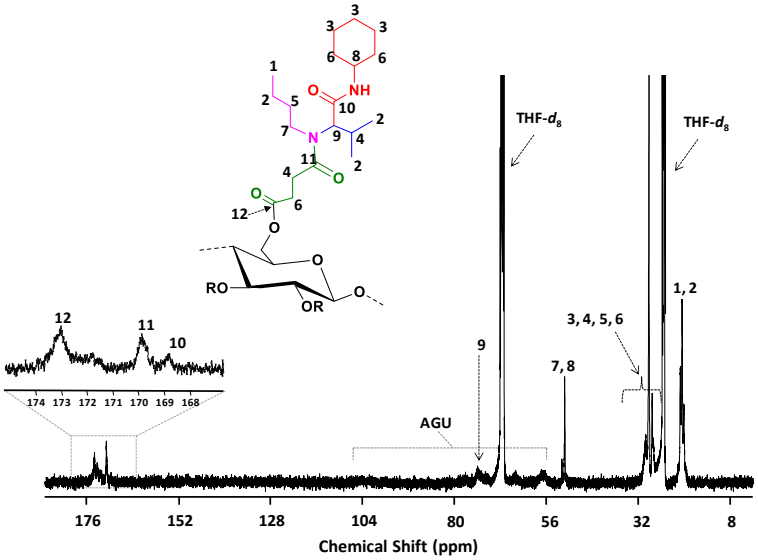


Fig. S15 ^{13}C NMR of Ugi product (**U2**).

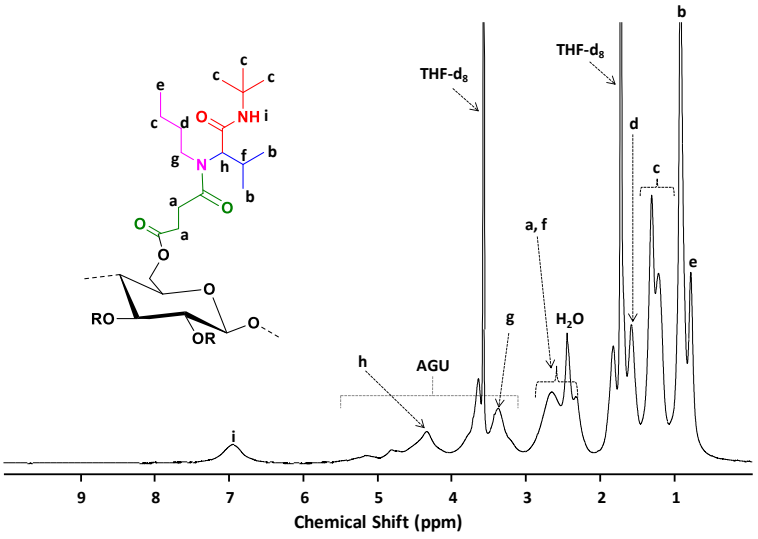


Fig. S16 ^{1}H NMR of Ugi product (**U3**).

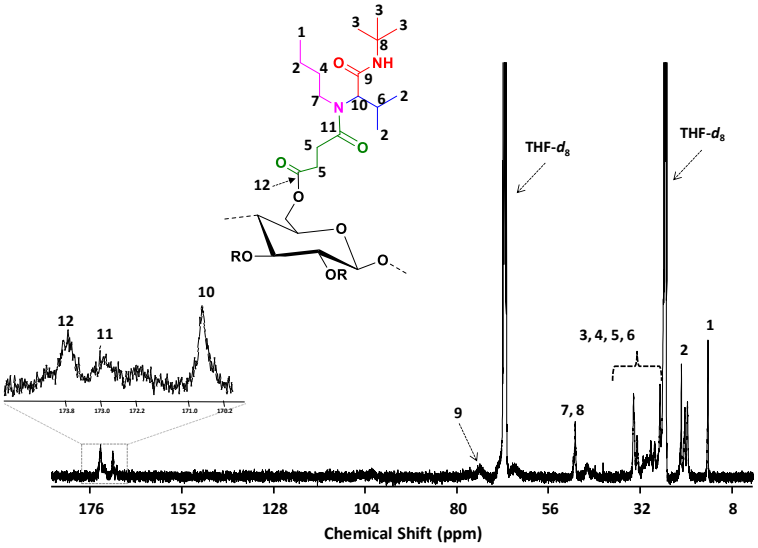
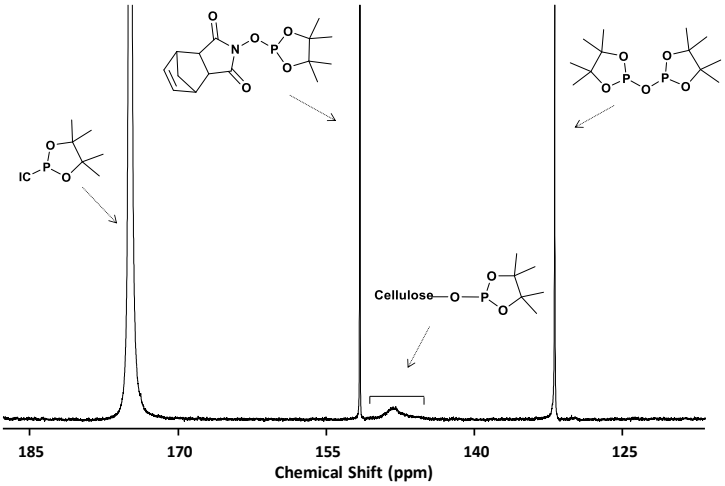


Fig. S17 ^{13}C NMR of Ugi product (**U3**).

4) NMR data of phosphorylated, modified cellulose

Fig. S18 ^{31}P NMR of phosphorylated Passerini product (**P1**).



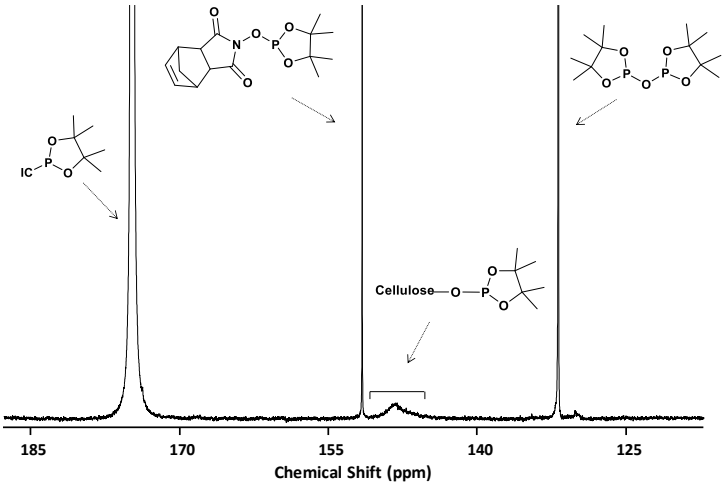


Fig. S19 ^{31}P NMR of phosphorylated Passerini product (**P2**).

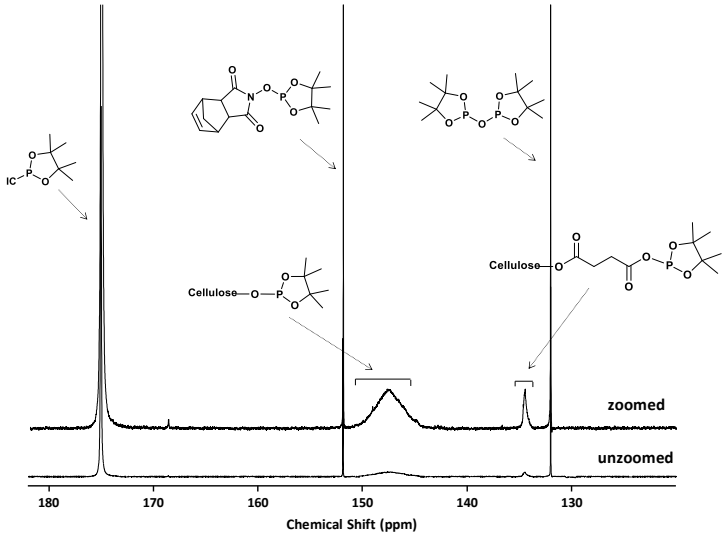


Fig. S20 ^{31}P NMR of phosphorylated Ugi product (**U1**).

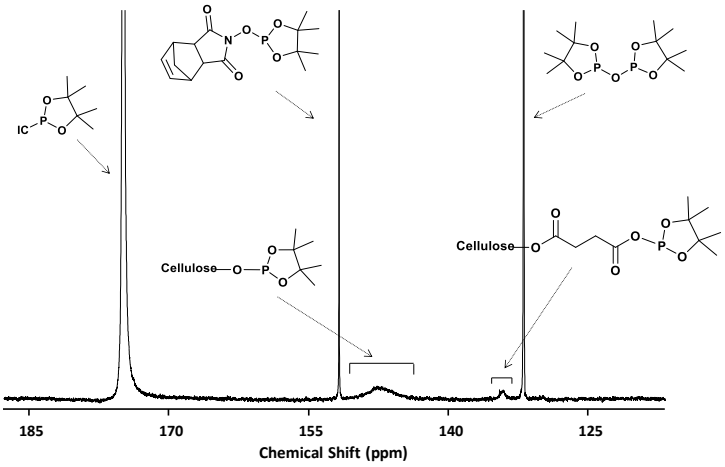


Fig. S21 ^{31}P NMR of phosphorylated Ugi product (**U2**).

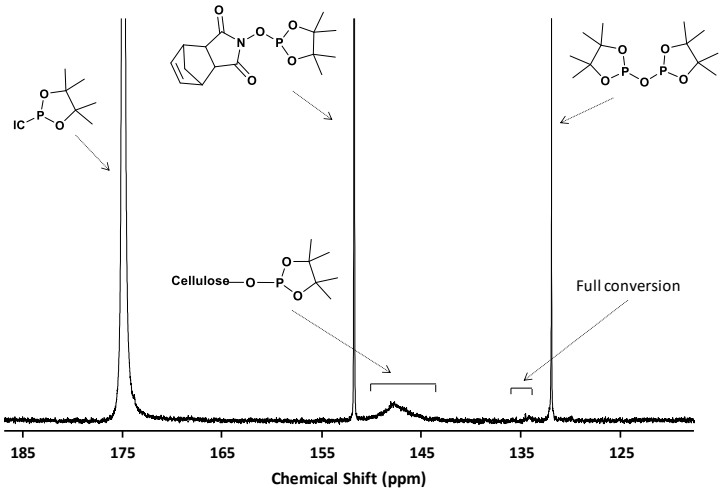
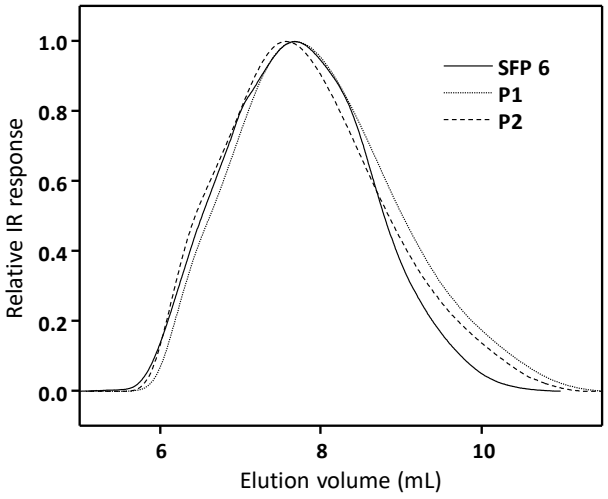


Fig. S22 ^{31}P NMR of phosphorylated Ugi product (**U3**).

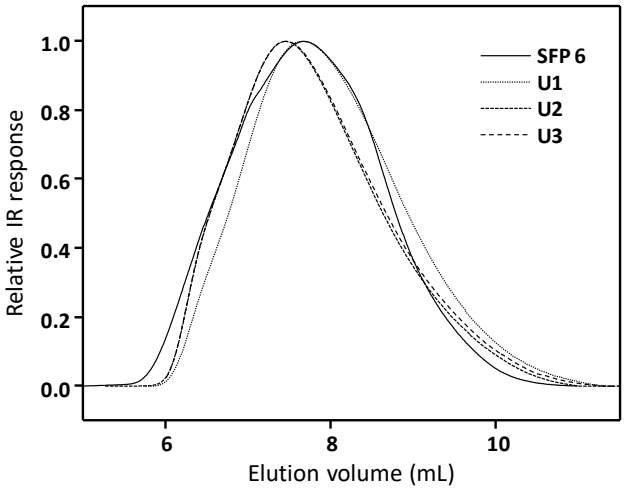
5) SEC data of modified cellulose



Product	M_n [kDa][b]	M_w [kDa][b]	Đ
SFP	271	714	2.6
P1	177	587	3.3
P2	212	690	3.2

[b]Data obtained from the GPC performed in DMAc/LiBr (1%, w/w) relative to PMMA calibration.

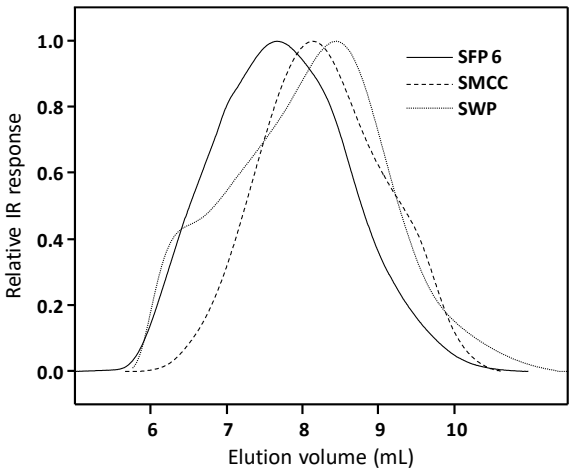
Fig. S23 SEC traces of succinylated filter paper (**SFP 6**) and Passerini products of succinylated filter paper (**P1, P2**).



Product	M_n [kDa][b]	M_w [kDa][b]	Đ
SFP	271	714	2.6
U1	193	533	2.7
U2	242	656	2.7
U3	225	647	2.8

[b]Data obtained from the GPC performed in DMAc/LiBr (1%, w/w) relative to PMMA calibration.

Fig. S24 SEC traces of succinylated filter paper (**SFP 6**) and Ugi products of succinylated filter paper (**U1, U2, U3**).

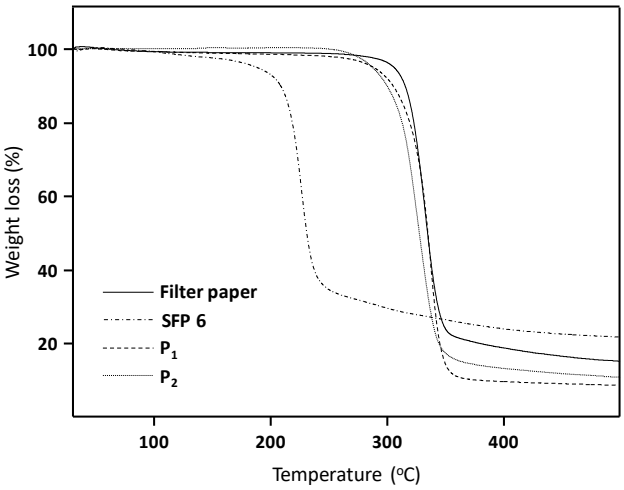


Product	M_n [kDa][a]	M_w [kDa][a]	Đ	DS[b]
SFP	271	714	2.6	2.64
SMCC	166	353	2.1	2.51
SWP	167	593	3.5	2.57

[a]Data obtained from the GPC performed in DMAc/LiBr (1%, w/w) relative to PMMA calibration. [b]Data obtained from ^{1}H NMR.

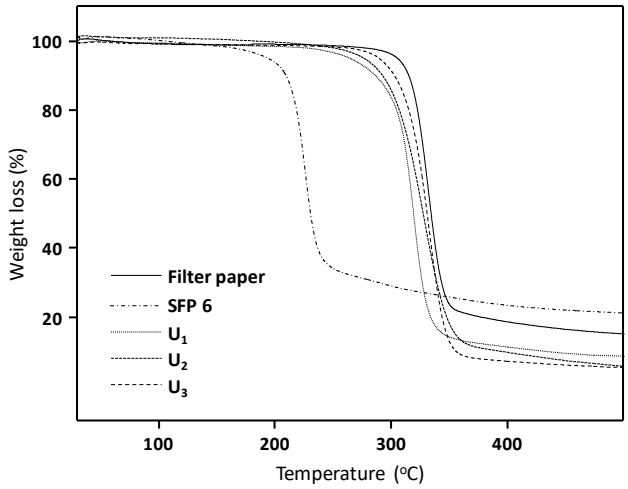
Fig. S25 SEC traces of succinylated filter paper (**SFP 6**), succinylated microcrystalline cellulose (**SMCC**), and succinylated organosolv wood pulp (**SWP**).

6) TGA data of modified cellulose



Product	T_d [°C]
Filter paper	305
SFP 6	202
P_1	289
P_2	278

Fig. S26 TGA data of filter paper, succinylated filter paper (**SFP 6**), and Passerini products of succinylated filter paper (**P1, P2**).



Product	T_d [°C]
Filter Paper	305
SFP 6	202
U_1	263
U_2	276
U_3	290

Fig. S27 TGA data of filter paper, succinylated filter paper (**SFP 6**), and Ugi products of succinylated filter paper (**U1, U2, U3**).

7) DSC data of modified cellulose

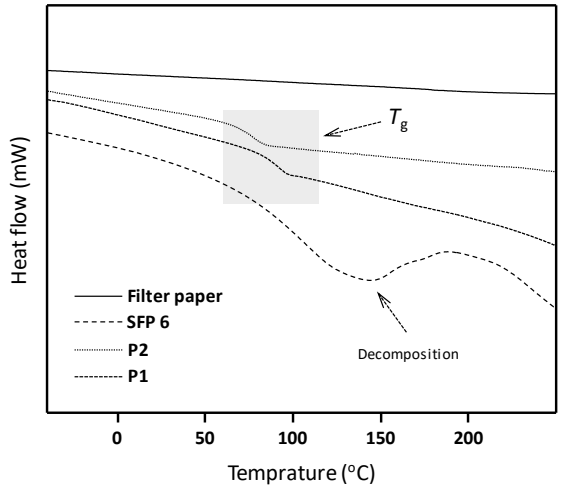


Fig. S28 DSC data of filter paper, succinylated filter paper (**SFP 6**), and Passerini products of succinylated filter paper (**P1, P2**).

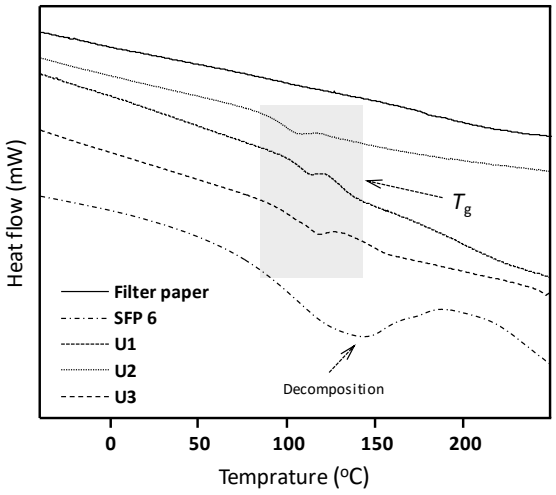


Fig. S29 DSC data of filter paper, succinylated filter paper (**SFP 6**), and Ugi products of succinylated filter paper (**U1, U2, U3**).

8) NMR data of recovered DBU

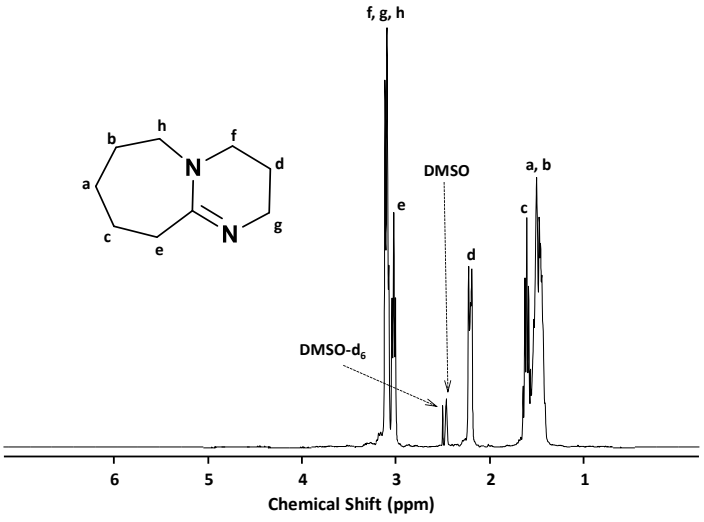


Fig. S30 ^{1}H NMR of recovered 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

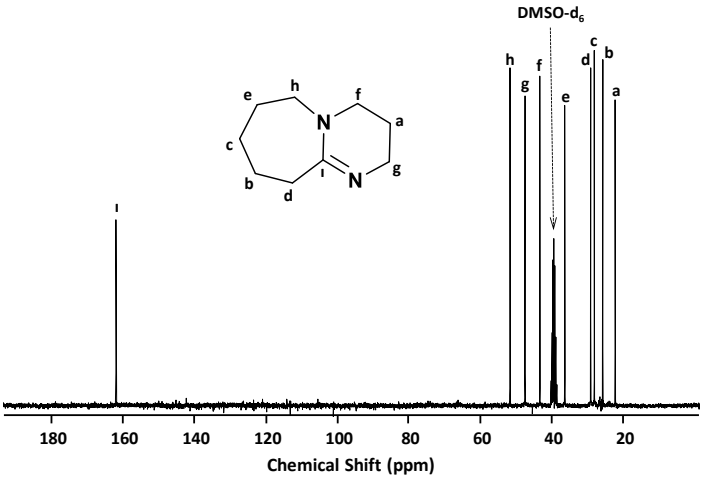


Fig. S31 ^{13}C NMR of recovered 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

9) Elemental analysis results of modified cellulose

Table S1 Elemental analysis of the Passerini and Ugi products of cellulose.

Product	C %	N %	H %	S %
P1	57.89	4.30	8.15	0
P2	56.99	4.22	8.12	0
U1	62.16	6.63	8.91	0
U2	60.80	7.33	9.02	0
U3	63.13	7.30	8.94	0