Supporting information

Dirhodium complex immobilization on modified cellulose for highly selective heterogeneous cyclopropanation reactions

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1. Solution state-NMR analyses

Fmoc-TTDS (3)

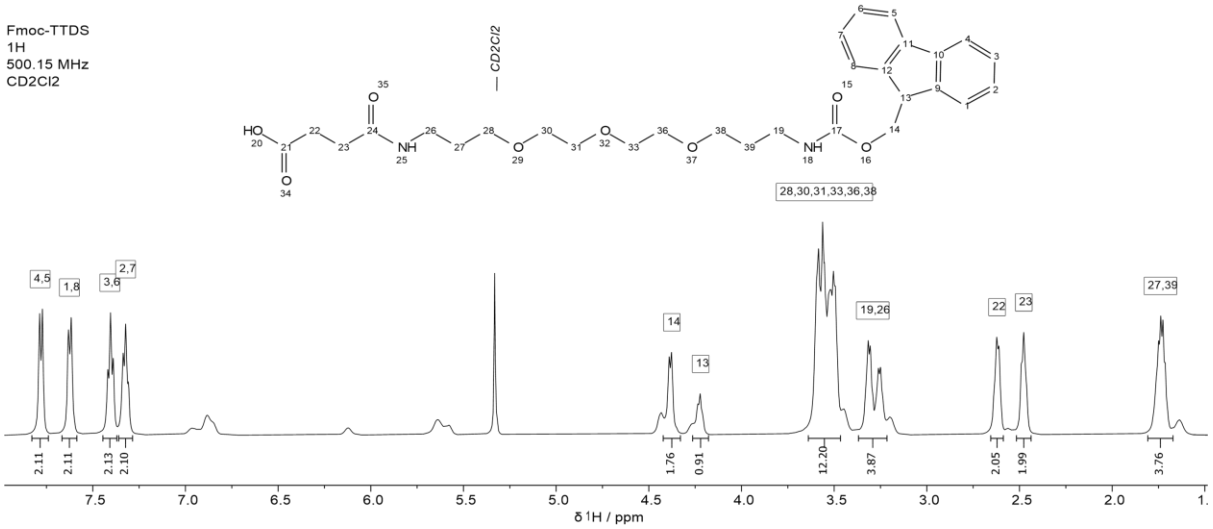

Figure S1: ^{1}H NMR spectrum of Fmoc-TTDS (**3**).

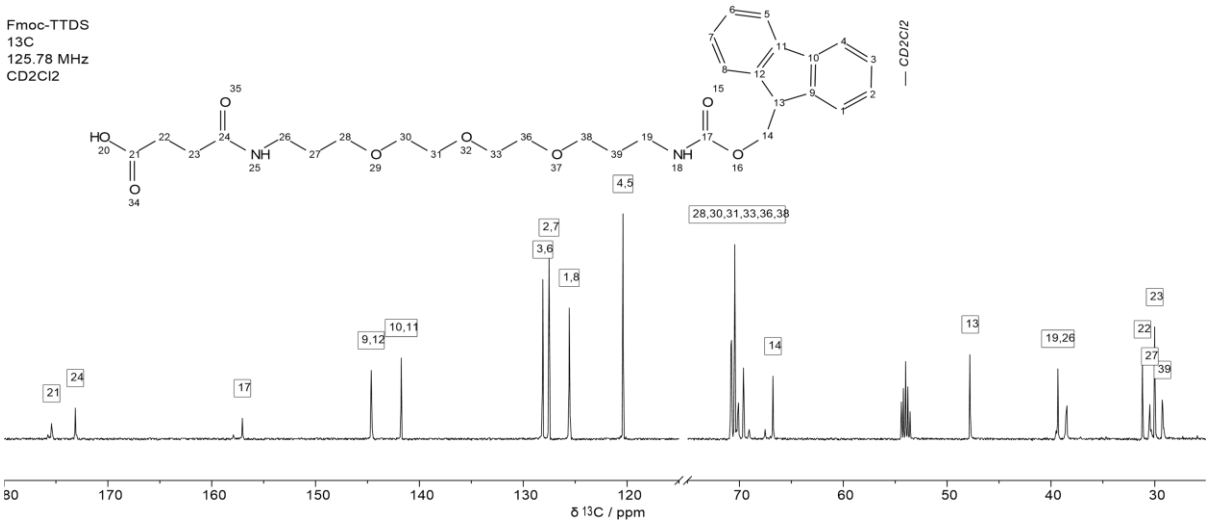

Figure S2: ^{13}C NMR spectrum of Fmoc-TTDS (**3**).

Methyl (3*E*)-2-diazo-4-phenyl-3-butenoate (4)

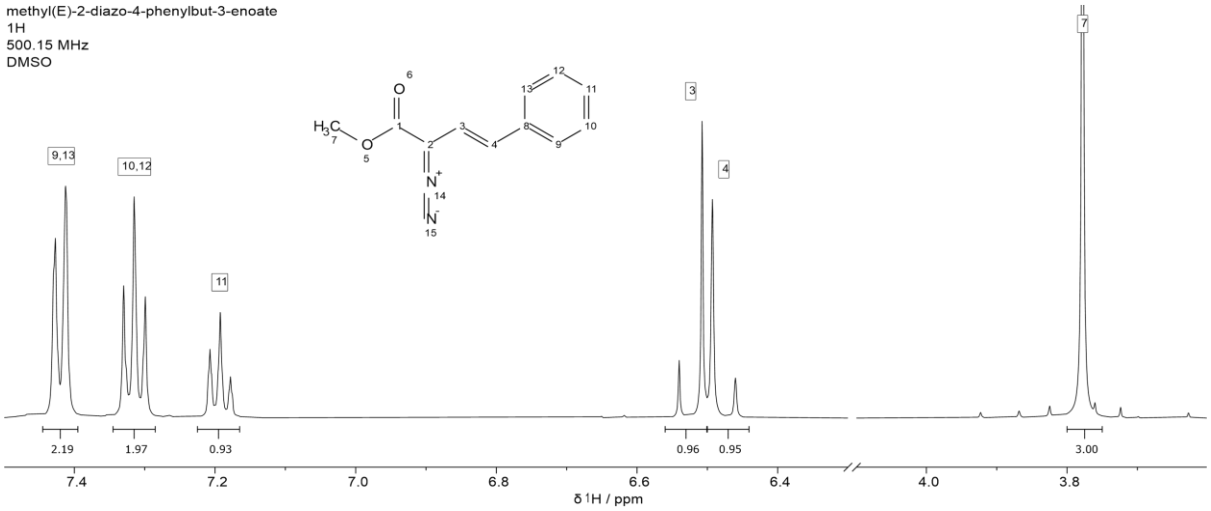

Figure S3: ^{1}H NMR spectrum of methyl (3*E*)-2-diazo-4-phenyl-3-butenoate (**4**).

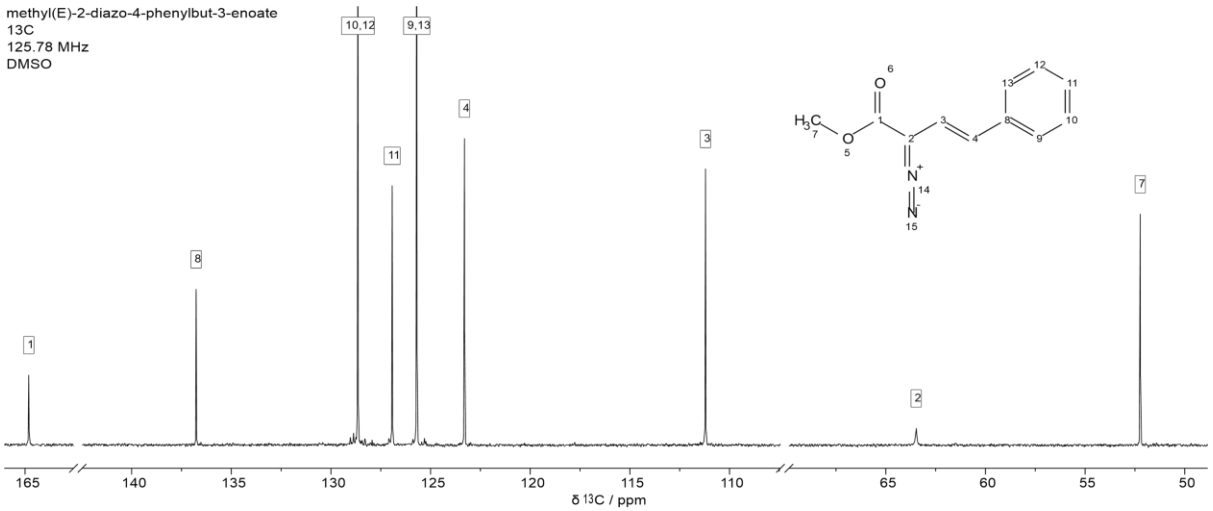

Figure S4: ^{13}C NMR spectrum of methyl (3*E*)-2-diazo-4-phenyl-3-butenoate (**4**).

2. Solid state NMR analyses

Analysis of the crystallinity of the modified celluloses

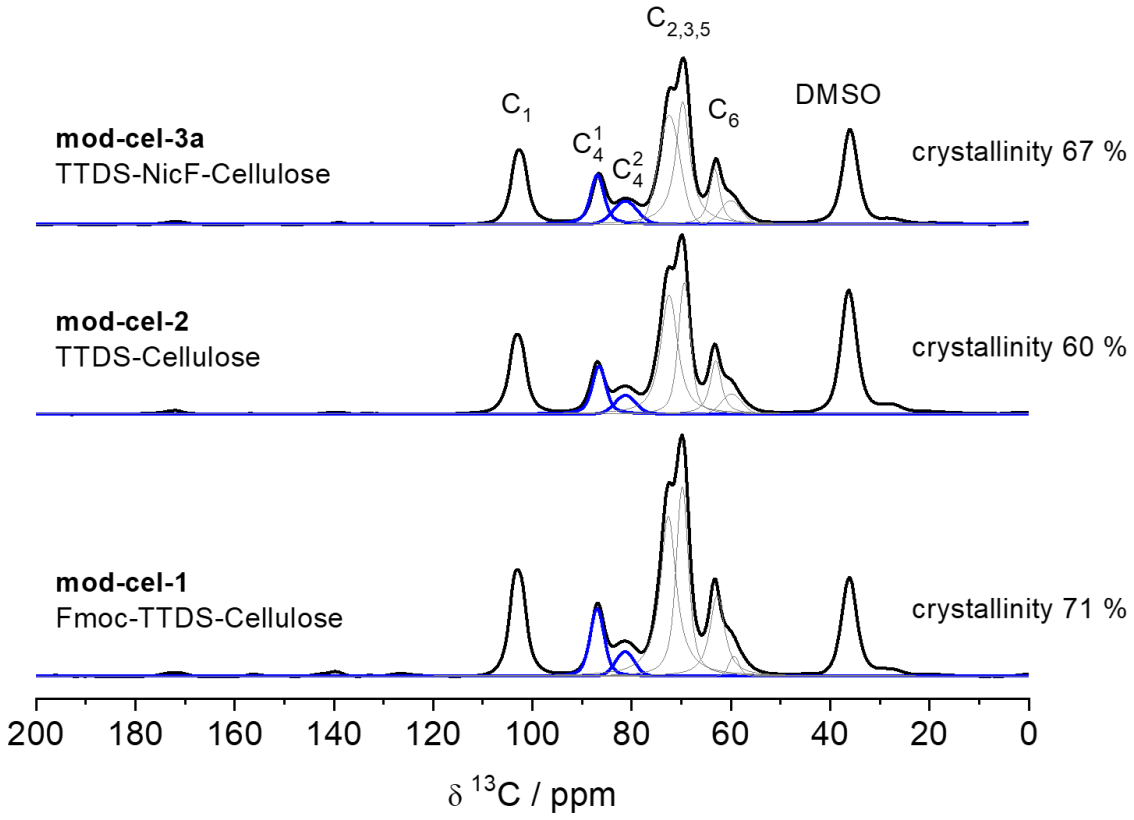

Figure S5: Comparison of the DNP enhanced ^{13}C CP MAS NMR spectra of the modified celluloses **mod-cel-1**, **mod-cel-2**, and **mod-cel-3a** with deconvolution to calculate the amount of crystallinity.

To determine the amount of crystallinity in the modified celluloses **mod-cel-1**, **mod-cel-2**, and **mod-cel-3a**, DNP enhanced ^{13}C CP MAS NMR spectra of the samples were analyzed by deconvolution of the peaks of the C_4 carbon of the cellulose material. The signal of C_4^1

represents the part of crystalline cellulose in the sample, the signal of C_4[2] the proportion of amorphous regions in the sample. The crystallinity percentage in Figure S5 was approximated by comparing the areas of the deconvoluted peaks (blue).

Determination of spinning side bands in DNP enhanced $^{1}H \rightarrow ^{13}C$ CP MAS NMR spectra

To inspect which signals in the DNP enhanced $^{1}H \rightarrow ^{13}C$ CP MAS NMR are isotropic and which ones originate from spinning sidebands, the experiments were repeated with different spinning rates. This enables to distinguish between isotropic signals which do not change their position at various spinning rates and spinning sidebands which are located with a distance of a multiple of the spinning rate with respect to the appropriate isotropic signal. In this work, every spectrum was recorded using a spinning rate of 10.5 kHz and additionally with a spinning rate of 8 kHz. In Figure S6, the method for identifying spinning side bands is shown exemplary on the DNP enhanced $^{1}H \rightarrow ^{13}C$ CP MAS NMR spectra of **mod-cel-2.**

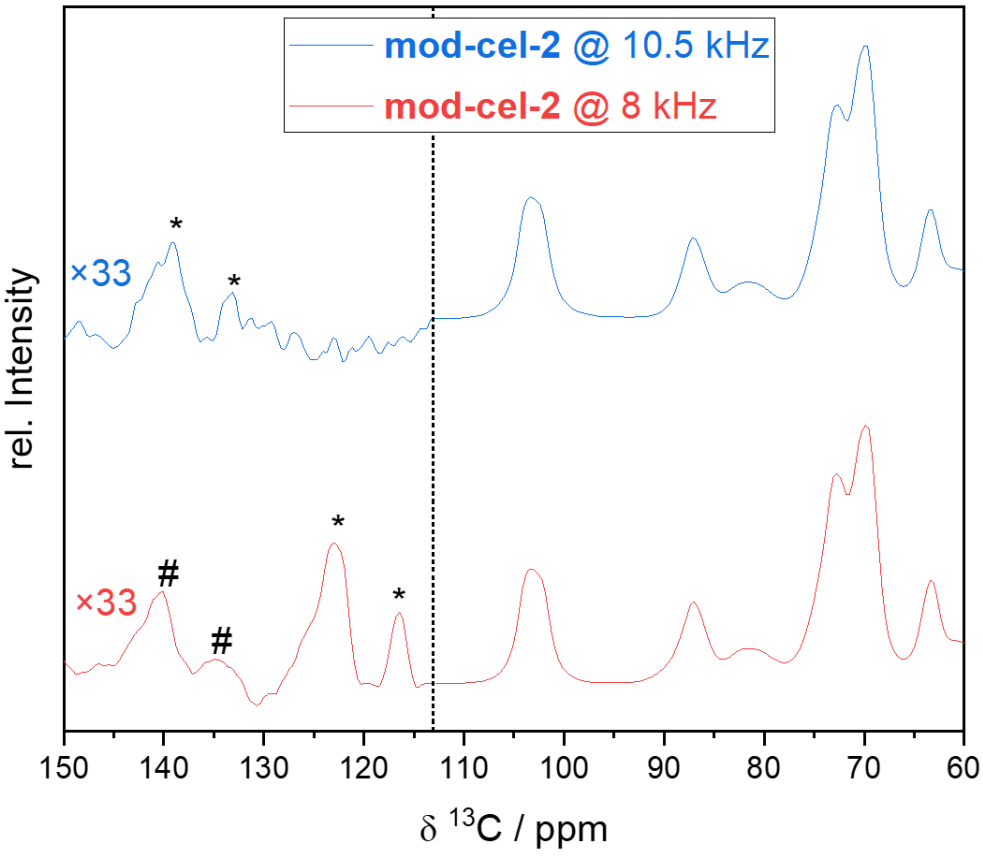

Figure S6: Comparison of the $^{1}H \rightarrow ^{13}C$ CP MAS NMR spectra of **mod-cel-2** with 10.5 kHz (top/blue) and 8 kHz (bottom/red) spinning rate. The noise level in the 10.5 kHz spectrum is higher since it was recorded with ¼ number of scans before normalizing on the signal with the highest intensity. The spectral range between 113 and 150 ppm of both spectra is magnified by a factor of 33. Spinning side bands are denoted with * and #, respectively.

The spinning sidebands denoted with an asterisk in the 10.5 kHz spectrum have an offset of 10.5 kHz to the isotropic signals around 70 ppm (overlapped signals of cellulose and the glycerol used in the measurements as a matrix). These signals also appear in the 8 kHz spectrum but moved to an offset of 8 kHz with respect to the isotropic signal. The signals denoted with # in this spectrum have an offset of 8 kHz to the signals around 85 ppm and can therefore also be identified as spinning sidebands. The signal at around 140 ppm which is obtained in both spectra is thus assigned to a spinning sideband which may however overlap with a signal referring to residual aromatics in the sample whose chemical shift is expected at a similar chemical shift. To resolve this quest, DNP measurements at higher spinning frequencies may help, which are beyond the scope of the present work.

1. Quantitative ^{19}F MAS NMR

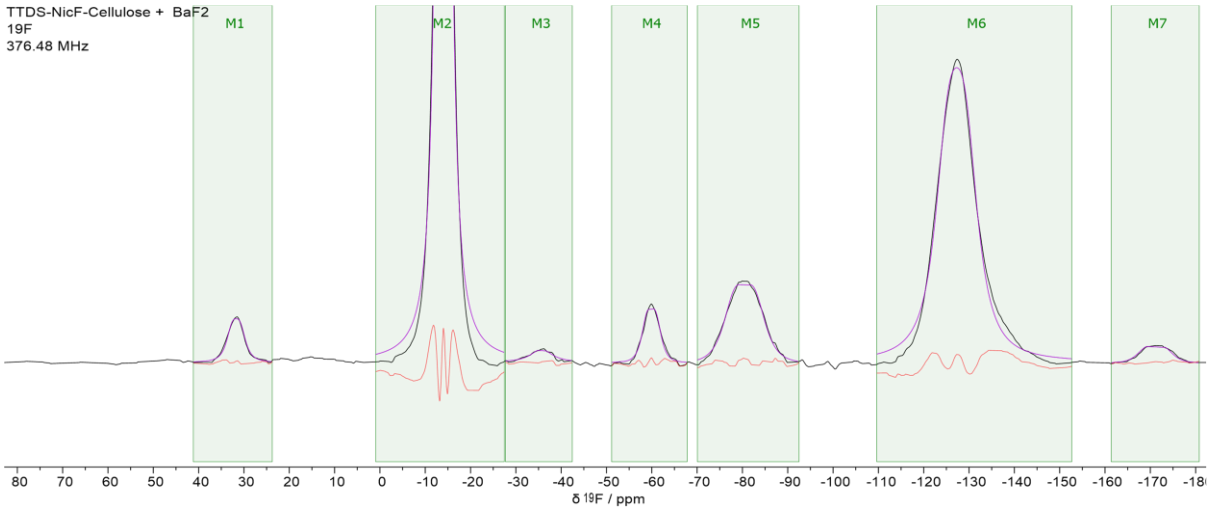

Figure S7: ^{19}F MAS NMR of TTDS-NicF-cellulose (**mod-cel-3a**) with areas of Integration marked in green.

Table S1: Results of the integration of the fitted Peaks in the ^{19}F MAS NMR spectrum of **mod-cel-3a** with barium fluoride.

INTEGRALS		
	Range /ppm	**Integral**
M1	37.82 .. 25.61	12277.90
M2	-2.35 .. -24.28	303665.54
M3	-28.80 .. -40.77	4730.59
M4	-54.99 .. -66.96	14912.86
M5	-70.98 .. -90.40	45217.55
M6	-113.83 .. -149.57	189521.71
M7	-164.22 .. -178.95	8049.01

For this measurement 12.7 mg BaF_2 were mixed with 238 mg of **mod-cel-3a** and 160.2 mg of that mixture were packed into a 3.2 mm ZrO_2 rotor. The ^{19}F spectrum was measured using a

one-pulse sequence with 809 scans and a recycle delay of 300 s. The acquisition time was set to 82 ms and a π/9 pulse with a length of 0.46 µs was used.

The acquired integrals M1, M2 and M4 can be assigned to barium fluoride with its central signal M2 and the spinning side bands M1 and M4. The signal of **mod-cel-3a** M6 is accompanied by its spinning sidebands M3, M5 and M7.

To determine the amount of fluorine in **mod-cel-3a**, the sum of the integrals M3, M5, M6 and M7 was compared with the sum of the integrals M1, M2 and M4, which is assigned to the known amount of fluorine nuclei in barium fluoride as follows:

The mass of the prepared sample mixture m_{mix} is calculated from the sum of the masses of the BaF_2 standard ($m_{BaF_2,mix}$) and the analyte ($m_{\boldsymbol{mod-cel-3a},mix}$).

$$m_{mix} = m_{BaF_2,mix} + m_{\boldsymbol{mod-cel-3a},mix} = 12.7\ mg + 238\ mg = 250.7\ mg$$

After filling an aliquot of the sample ($m_{rotor-filling}$) into the MAS rotor, the mass of BaF_2 inside the rotor ($m_{BaF_2,rotor}$) can be calculated.

$$m_{BaF_2,rotor} = \frac{m_{BaF_2,mix}}{m_{mix}} \cdot m_{rotor-filling} = \frac{12.7\ mg}{250.7\ mg} \cdot 160.2\ mg = 8.1\ mg$$

Also, the amount of BaF_2 ($n_{BaF_2,rotor}$) can then be calculated using the molar mass of it (M_{BaF_2}).

$$n_{Ba_{F_2},rotor} = \frac{m_{BaF_2,rotor}}{M_{BaF_2}} = \frac{8.1\ mg}{175.32\ \frac{g}{mol}} = 46\ \mu mol$$

The amount of fluorine atoms, originating from the standard BaF_2, inside the rotor ($n_{F_{standard},rotor}$) is then given by:

$$n_{F_{standard},rotor} = 2 \cdot n_{BaF_2,rotor} = 92\ \mu mol$$

The sum of the integrals of the signals originating from BaF_2 (A_{BaF_2}) is then calculated by adding up the integrals of sections M1, M2 and M4 (A_{M1}, A_{M2} and A_{M4}) in the spectrum shown in Figure S7.

$$A_{BaF_2} = A_{M1} + A_{M2} + A_{M4} = 330856.3$$

The response factor for fluorine in the present experiment (f_F) can then be calculated according to:

$$f_F = \frac{A_{BaF_2}}{n_{F_{standard},rotor}} = \frac{330856.3}{92\ \mu mol} = 3596\ \mu mol^{-1}$$

To determine the amount of fluorine in the analyte ($n_{F,\boldsymbol{mod-cel-3a}}$), the sum of the integrals ($A_{\boldsymbol{mod-cel-3a}}$) of sections M3, M5, M6 and M7 (A_{M3}, A_{M5}, A_{M_6} and A_{M7}), which cover the signals originating from **mod-cel-3a**, is calculated and divided by f_F, calculated above.

$$A_{\boldsymbol{mod-cel-3a}} = A_{M3} + A_{M5} + A_{M6} + A_{M7} = 247518.9$$

$$n_{F,\boldsymbol{mod-cel-3a}} = \frac{A_{\boldsymbol{mod-cel-3a}}}{f_F} = \frac{247518.9}{3596\ \mu mol^{-1}} = 69\ \mu mol$$

In order to determine the amount of fluorine per gram of **mod-cel-3a** ($q_{linker\ head,\boldsymbol{mod-cel-3a}}$), the mass of the analyte **mod-cel-3a** in the MAS rotor ($m_{\boldsymbol{mod-cel-3a},rotor}$) is determined.

$$m_{\boldsymbol{mod-cel-3a},rotor} = \frac{m_{\boldsymbol{mod-cel-3a},mix}}{m_{mix}} \cdot m_{rotor-filling} = \frac{238\ mg}{250.7\ mg} \cdot 160.2\ mg = 152.1\ mg$$

$$q_{linker\ head,\boldsymbol{mod-cel-3a}} = \frac{n_{F,\boldsymbol{mod-cel-3a}}}{m_{\boldsymbol{mod-cel-3a},rotor}} = \frac{69\ \mu mol}{152.1\ mg} \approx 0.5\ \frac{mmol}{g}$$

The calculated amount of fluorine in the sample is directly related to the amount of fluorinated linker head in the sample, since the linker head contains one fluorine atom per molecule. Thus, the loading of **mod-cel-3a** is calculated to 0.5 mmol/g of coordinating linker head (NicF) with respect to the weight of the material.

This value can be converted to a degree of functionalization for the linker head ($DF_{linker\ head}$) with respect to the primary hydroxy groups of the cellulose, assuming that the DF of the linker in the material is preserved as follows:

$DF = 6.8\ \%$ determined by UV/Vis spectroscopy (see below).

The molar mass of a single glucose unit of cellulose ($M_{glucose\ unit}$), of a glucose unit, modified with one TTDS-Linker molecule, ($M_{TTDS-modified\ glucose\ unit}$) and of a glucose unit, modified with one TTDS-Linker and a linker head molecule, ($M_{(TTDS+NicF)-modified\ glucose\ unit}$) are given as:

$$M_{glucose\ unit} = 162.141\ \frac{g}{mol}$$

$$M_{TTDS-modified\ glucose\ unit} = 464.512\ \frac{g}{mol}$$

$$M_{(TTDS+NicF)-modified\ glucose\ unit} = 587.5984\ \frac{g}{mol}$$

The amount of fluorine per gram of **mod-cel-3a** (see above) is given as:

$$q_{linker\ head,\boldsymbol{mod-cel-3a}} \approx 0.5\ \frac{mmol}{g}$$

From the molar masses shown above, the molar weight gain by the modification of a glucose unit – or a TTDS-modified glucose unit – by functionalization with one mole of the linker head ($M_{\Delta_{linker\ head}}$) can be calculated.

$$M_{\Delta_{linker\ head}} = M_{(TTDS+NicF)-modified\ glucose\ unit} - M_{TTDS-modified\ glucose\ unit} = 123.0864\ \frac{g}{mol}$$

The relative mass gain of linker head by modification of **mod-cel-2** with the linker head ($\omega_{linker\ head,\boldsymbol{mod-cel-3a}}$) can then be determined.

$$\omega_{linker\ head,\boldsymbol{mod-cel-3a}} = q_{linker\ head,\boldsymbol{mod-cel-3a}} \cdot M_{\Delta_{linker\ head}}$$

$$\omega_{linker\ head,\boldsymbol{mod-cel-3a}} = 0.5\ \frac{mmol}{g} \cdot 123.0864\ \frac{g}{mol} = 61.5\ \frac{mg}{g}$$

This means, that the mass fraction of the starting material **mod-cel-2** in 1 g of the modified material **mod-cel-3a** ($\omega_{\boldsymbol{mod-cel-2,mod-cel-3a}}$) results to:

$$\omega_{\boldsymbol{mod-cel-2,mod-cel-3a}} = 1000\ \frac{mg}{g} - \omega_{linker\ head,\boldsymbol{mod-cel-3a}} = (1000 - 61.5)\ \frac{mg}{g} = 938.5\ \frac{mg}{g}$$

With the DF of 6.8 % obtained for **mod-cel-2**, the averaged molar mass of **mod-cel-2** ($M_{\boldsymbol{mod-cel-2}}$) can be calculated.

$$M_{\boldsymbol{mod-cel-2}} = 6.8\ \% \cdot M_{TTDS-modified\ glucose\ unit} + (1 - 6.8\ \%) \cdot M_{glucose\ unit}$$

$$M_{\boldsymbol{mod-cel-2}} = 182.702\ \frac{g}{mol}$$

With this, the amount of **mod-cel-2** per gram of **mod-cel-3a** ($q_{\boldsymbol{mod-cel-2,mod-cel-3a}}$), which is also the amount of glucose units in **mod-cel-3a** is then given by:

$$q_{\boldsymbol{mod-cel-2,mod-cel-3a}} = \frac{\omega_{\boldsymbol{mod-cel-2,mod-cel-3a}}}{M_{\boldsymbol{mod-cel-2}}} = \frac{938.5\ \frac{mg}{g}}{182.702\ \frac{g}{mol}} = 5.14\ \frac{mmol}{g}$$

This leads to a degree of functionalization for the linker head ($DF_{linker\ head}$) with respect to the primary hydroxy groups of the cellulose of:

$$DF_{linker\ head} = \frac{q_{\boldsymbol{linker\ head,mod-cel-3a}}}{q_{\boldsymbol{mod-cel-2,mod-cel-3a}}} \approx 9.7\ \%$$

Determination of the degree of complexation in cel-cat

ICP-OES analysis of **cel-cat** showed a rhodium content of 4.4 wt.-% or 44 mg rhodium per gram of **cel-cat**, as shown in Table S2.

Table S2: Results and method of the ICP-OES measurements of **cel-cat**

RHODIUM CONTENT	DETECTION LIMIT	METHOD
4.35 WT.-%	0.0125 wt.-%	DIN EN ISO 11885:2009-09

With 0.5 mmol/g of coordinating linker head in **mod-cel-3**, as determined by ^{19}F MAS NMR (see above), the degree of complexation in **cel-cat** can be calculated as follows:

The amount of Rh$_2$(*S*-DOSP)$_4$ per gram of **cel-cat** ($q_{Rh_2(S-DOSP)_4,\boldsymbol{cel-cat}}$) is half of the amount of rhodium per gram of **cel-cat** $\left(\frac{\omega_{Rh,\boldsymbol{cel-cat}}}{M_{Rh}}\right)$, which is calculated using the mass fraction of rhodium in **cel-cat** ($\omega_{Rh,\boldsymbol{cel-cat}}$), determined by ICP-OES.

$$q_{Rh_2(S-DOSP)_4,\boldsymbol{cel-cat}} = \frac{\left(\frac{\omega_{Rh,\boldsymbol{cel-cat}}}{M_{Rh}}\right)}{2} = \frac{44\ \frac{mg}{g}}{102.905\ \frac{g}{mol}\cdot 2} = 0.2138\ \frac{mmol}{g}$$

With a molar mass of $M_{Rh_2(S-DOSP)_4} = 1896.22\ \frac{g}{mol}$, the mass fraction of Rh$_2$(*S*-DOSP)$_4$ in **cel-cat** ($\omega_{Rh_2(S-DOSP)_4,\boldsymbol{cel-cat}}$) can be determined.

$$\omega_{Rh_2(S-DOSP)_4,\boldsymbol{cel-cat}} = q_{Rh_2(S-DOSP)_4,\boldsymbol{cel-cat}} \cdot M_{Rh_2(S-DOSP)_4}$$
$$= 0.2138\ \frac{mmol}{g}\cdot 1896.22\ \frac{g}{mol} = 405.4\ \frac{mg}{g}$$

The mass of **mod-cel-3a** in 1 g of **cel-cat** ($\omega_{\boldsymbol{mod-cel-3},\boldsymbol{cel-cat}}$) is therefore calculated by:

$$\omega_{\boldsymbol{mod-cel-3},\boldsymbol{cel-cat}} = 1000\ \frac{mg}{g} - \omega_{Rh_2(S-DOSP)_4,\boldsymbol{cel-cat}} = (1000 - 405.4)\ \frac{mg}{g}$$
$$= 594.6\ \frac{mg}{g}$$

With this value and the amount of coordinating linker head in 1 g of **mod-cel-3** ($q_{linker\ head,\boldsymbol{mod-cel-3}}$), determined via ^{19}F MAS NMR above, the amount of linker head per gram of **cel-cat** ($q_{linker\ head,\boldsymbol{cel-cat}}$) can be calculated:

$$q_{linker\ head,\boldsymbol{cel-cat}} = q_{linker\ head,\boldsymbol{mod-cel-3}} \cdot \omega_{\boldsymbol{mod-cel-3},\boldsymbol{cel-cat}} = 0.5\ \frac{mmol}{g}\cdot 594.6\ \frac{mg}{g}$$
$$= 0.297\ \frac{mmol}{g}$$

The degree of complexation in **cel-cat** ($\eta_{complexation}$) is then given as the ratio of coordinated Rh$_2$(*S*-DOSP)$_4$ in **cel-cat** ($q_{Rh_2(S-DOSP)_4,\boldsymbol{cel-kat}}$) to available coordination sites, namely linker head, in **cel-cat** ($q_{linker\ head,\boldsymbol{cel-cat}}$).

$$\eta_{complexation} = \frac{q_{Rh_2(S-DOSP)_4,\boldsymbol{cel-kat}}}{q_{linker\ head,\boldsymbol{cel-cat}}} = \frac{0.2138\ \frac{mmol}{g}}{0.297\ \frac{mmol}{g}} = 72\ \%$$

UV/Vis Analyses

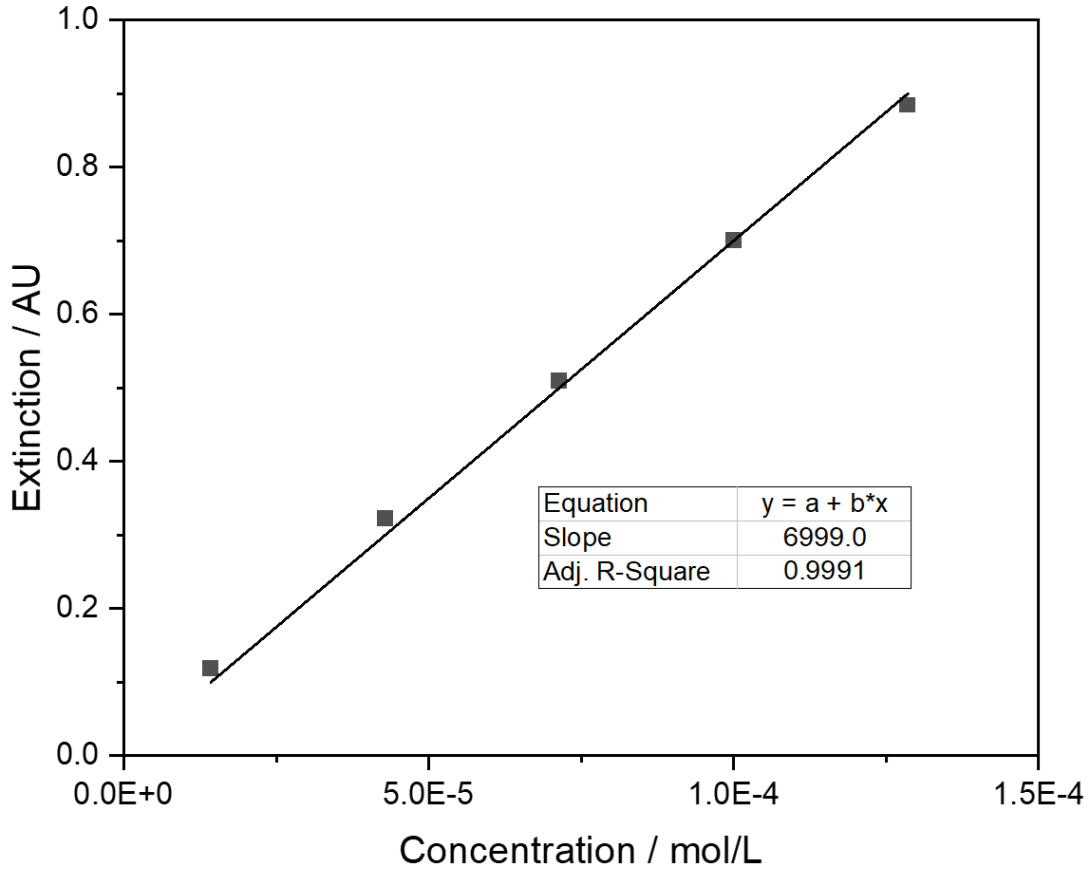

Figure S8: External standard for the quantification of dibenzolfulvene-piperidine adduct in DMF/piperidine.

For the quantification of the concentration of dibenzofulvene-piperidine adduct in the reaction solution of the deprotection of **mod-cel-1**, an external standard was used.

For the calibration, a set of 5 different concentrations of Fmoc-alanine was prepared in a solution of 20 % piperidine in DMF. The solutions were shaken for 20 minutes to ensure complete deprotection of the amino group of alanine. The absorption of the resulting solutions was then measured at 301 nm (Figure S8).

ICP-OES analyses

The sample for the ICP-OES measurements to determine the leaching characteristics of **cel-cat** was prepared from the reaction mixture of the first recycling experiment. Most of the solvent of the mixture was removed under reduced pressure. The resulting solution was then diluted with a nitric acid / alcoholic (i-PrOH & EtOH) solution to accurately 20 mL.

Table S3: Results and method of the ICP-OES measurements

RHODIUM CONTENT	DETECTION LIMIT	METHOD
1.77 mg/L	0.1 mg/L	DIN EN ISO 11885:2009-09

HPLC measurements

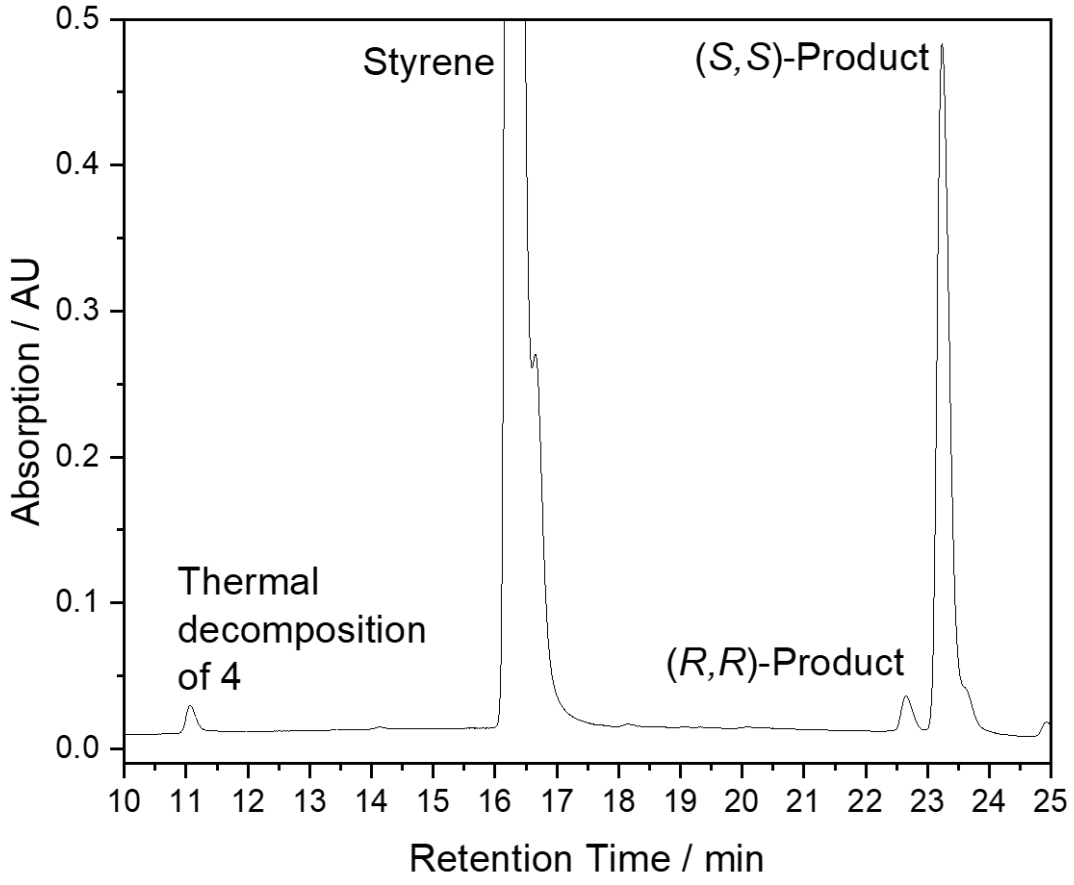

Figure S9: Sample chromatogram of the reaction mixture in a catalytic test reaction at 214 nm.

The enantiomeric excess of the (*S*,*S*)-product was calculated by integrating the peaks of both products and comparing the areas directly. The chromatograms were recorded using a gradient from 30 % to 80 % of acetonitrile in water over the course of 25 minutes with a flow of 1 mL/min. The column used was a Reprosil Chiral OM-R 5µ 250x4.6 mm column.