Electronic Supplementary Material (ESI) for Green Chemistry.

# HMF-glycerol acetals as additives for the debonding of polyurethane adhesives

## Supporting Information

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## Contents

## S1. Methods

$^1$H-NMR and $^{13}$C-NMR spectra were recorded at room temperature on 300 MHz spectrometers (Avance 300 or Fourier 300) or a 400 MHz spectrometer (Avance 400) from Bruker. The chemical shifts δ are given in ppm and referenced to the residual proton signal of the particular solvent.

GC-measurements were carried out on a Agilent 7890B-GC-System equipped with a 30 m x 320 µm x 0.25 µm poly-methylsiloxane column and a flame ionization detector.

ESI mass spectrometry was performed on an Agilent 1260/6130 Quadrupol LC-MS equipped with a time-of-flight detector.

Diffraction data were collected on a Bruker Kappa APEX II Duo diffractometer. The structure was solved by direct methods (SHELXS-97: Sheldrick, G. M. Acta Cryst. 2008, A64, 112.) and refined by full-matrix least-squares procedures on $F^2$ (SHELXL-2018: Sheldrick, G. M. Acta Cryst. 2015, C71, 3.). XP (Bruker AXS) was used for graphical representation.

CCDC 2022131 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures

For the quantification of CHN, a microanalyzer-TruSpec CHNS from the company Leco was used. The samples were catalytically combusted with pure oxygen in a helium stream. For the analysis of C and H contents an IR-detector was used.

DSC was measured on a DSC Q2000 (TA Instruments) at a heating rate of 10 K/min under a nitrogen atmosphere in open aluminium pans. The samples were cooled to – 60 °C and heated to 120 °C. This cycle was repeated. Each sample was measured in duplicate.

TGA was measured on a TGA Q5000 (TA Instruments) at a heating rate of 10 K/min under a nitrogen atmosphere in open aluminium pans. The samples were heated from rt to 500 °C. Each sample was measured in duplicate.

ATR-IR was measured on a Bruker IR alpha.

APC-GPC was measured on a Waters Acquity Advanced Polymer Chromatography system equipped with a Waters Acquity APC RI dectector. The columns used were Waters APC XT Columns 450 A, 125 A and 45 A. The samples were measured at 40 °C, the eluent was unstabilised THF. Results were calibrated against polystyrene standards in the range of 682 to 552000 Da.

## S2. Additional NMR data of other acetal isomers

### *cis*-2-(5-(hydroxymethyl)furan-2-yl)-1,3-dioxan-5-ol (cis-dioxane isomer)

$^1$H NMR (300 MHz, DMSO-d6) δ 6.35 (d, J = 0.6 Hz, 1H), 6.25 (d, J = 0.7 Hz, 1H), 5.57 (s, 1H), 5.24 (t, J = 5.8 Hz, 2H), 4.99 (d, J = 4.2 Hz, 2H), 4.36 (d, J = 5.7 Hz, 2H), 4.03 – 3.85 (m, 4H), 3.49 (dt, J = 3.9, 1.9 Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO) δ 155.1, 150.3, 107.9, 107.3, 94.8, 71.1, 62.3, 55.6.

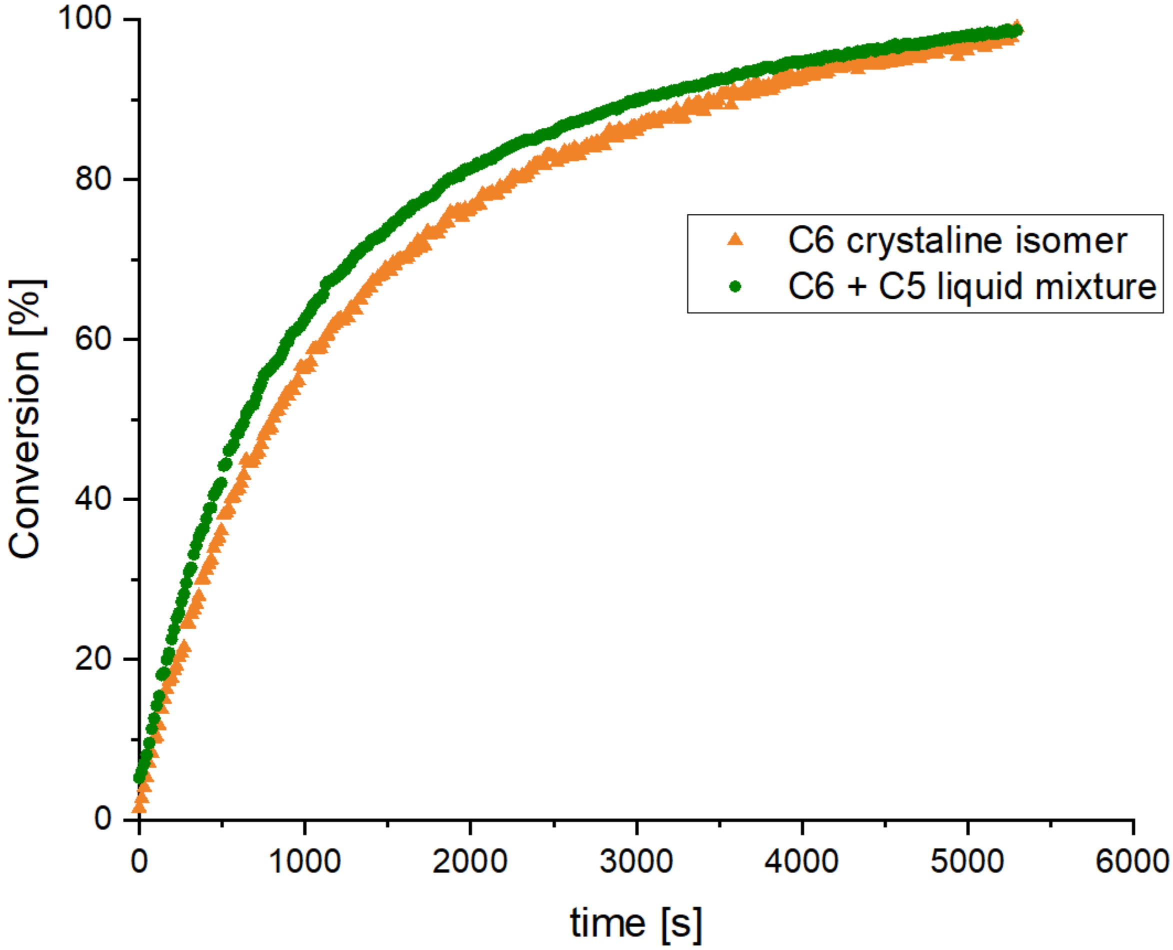
### (5-(4-(hydroxymethyl)-1,3-dioxolan-2-yl)furan-2-yl)methanol (*cis* and *trans* dioxolane isomers)

$^1$H-NMR (400 MHz, DMSO-d6) δ 6.48 (d, J = 3.2 Hz, 1H), 6.44 (dd, J = 3.2, 0.4 Hz, 1H), 6.25 (ddd, J = 3.9, 2.3, 1.6 Hz, 2H), 5.90 (s, 0.54H), 5.79 (s, 0.46H), 5.25 (t, J = 5.8 Hz, 1H), 4.92 (td, J = 5.7, 3.7 Hz, 1H), 4.36 (d, J = 6.0 Hz, 2H), 4.26 – 4.18 (m, 0.54H), 4.15 – 4.08 (m, 1H), 3.98 (dd, J = 8.0, 6.7 Hz, 0.46H), 3.77 (dd, J = 8.0, 6.0 Hz, 0.46H), 3.71 (dd, J = 8.0, 6.3 Hz, 0.54H), 3.58 – 3.46 (m, 2H).

$^{13}$C-NMR (101 MHz, DMSO) δ 156.1, 156.0, 150.1, 149.7, 109.9, 109.6, 107.4, 107.3, 97.2, 97.0, 77.0, 76.3, 66.8, 66.4, 61.7, 61.4, 55.7.

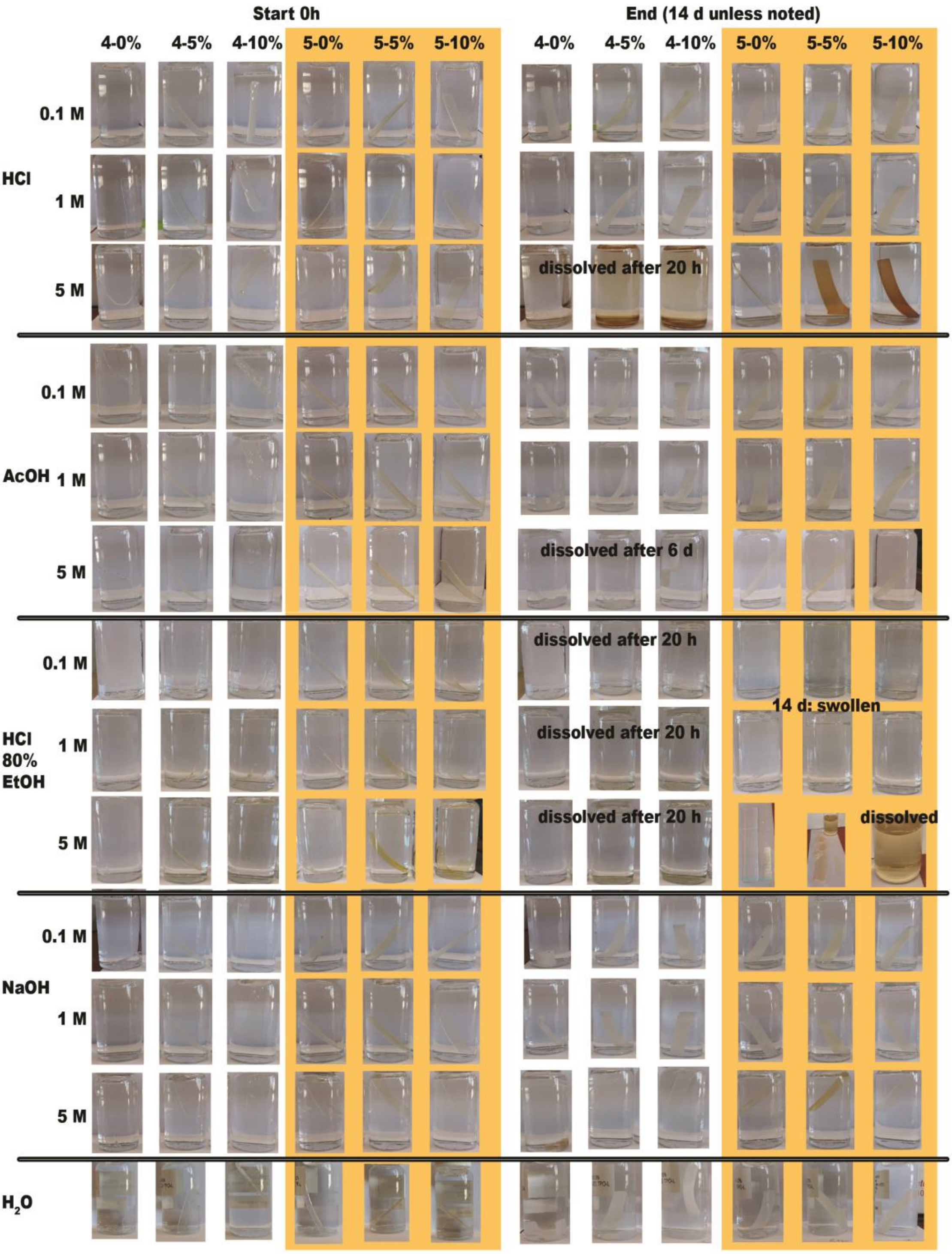
## S3. Kinetics of reaction with isocyanate for dioxane isomer and mixture of isomers

Reaction kinetics were measured on a Magritek Spinsolve 60 MHz benchtop NMR. A solution of phenyl isocyanate (35 mg, 0.30 mmol, 2 eq) and 1,2,3,4-Tetrahydronaphthalene (19 mg, 0.15 mmol, 1 eq) in DMSO (0.3 mL) was added to a solution of the acetal (29 mg, 0.15 mmol, 1 eq) in DMSO (0.2 mL) in an oven-dried Young NMR tube under argon atmosphere. The tube was placed in the NMR machine and the reaction was continuously monitored (one spectrum every 15 s; acquisition time 6.4 s; repetition time 7 s; pulse angle 90 °). The data were processed with MNova, monitoring the ratio between the NH of the product and the aliphatic $CH_2$ of the standard using the integral data analysis function of the software. Each kinetic curve is obtained from the average values between two different experiments.

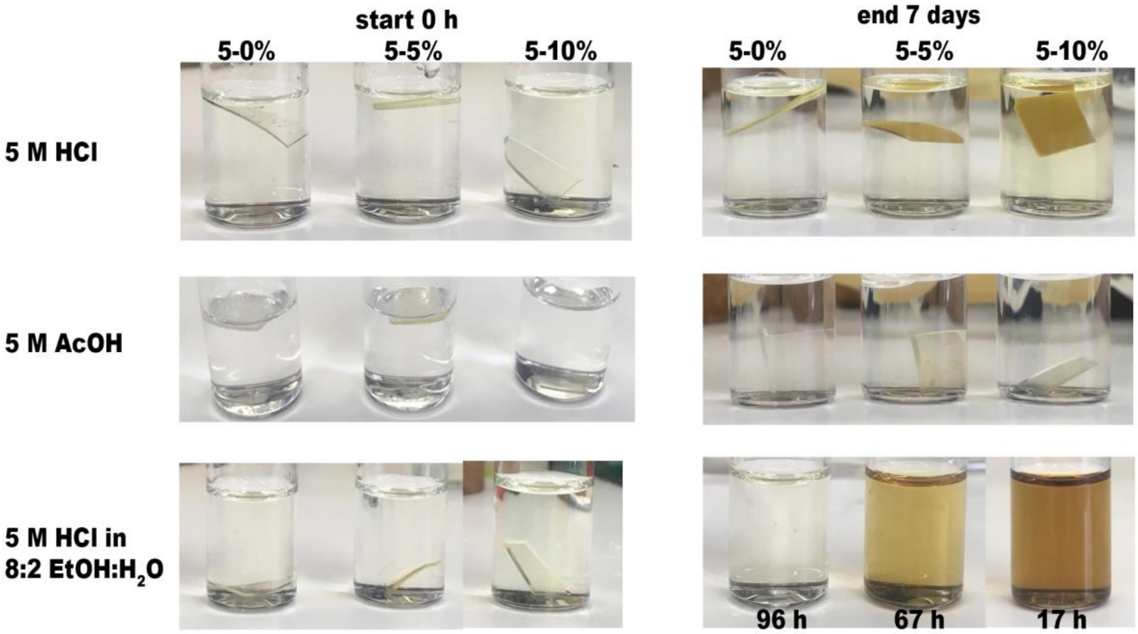


## S4. Degradation studies

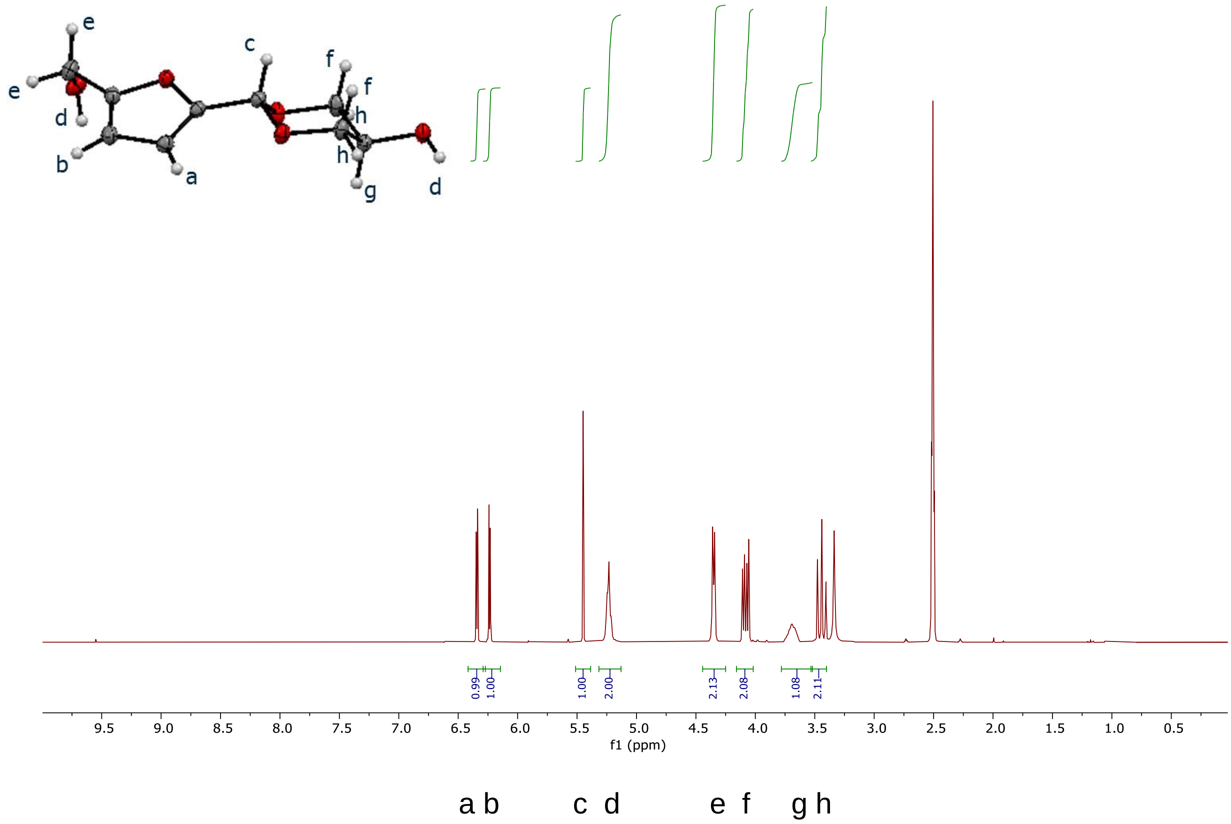
### S4.1 Degradation study of films 4 and 5 at room temperature



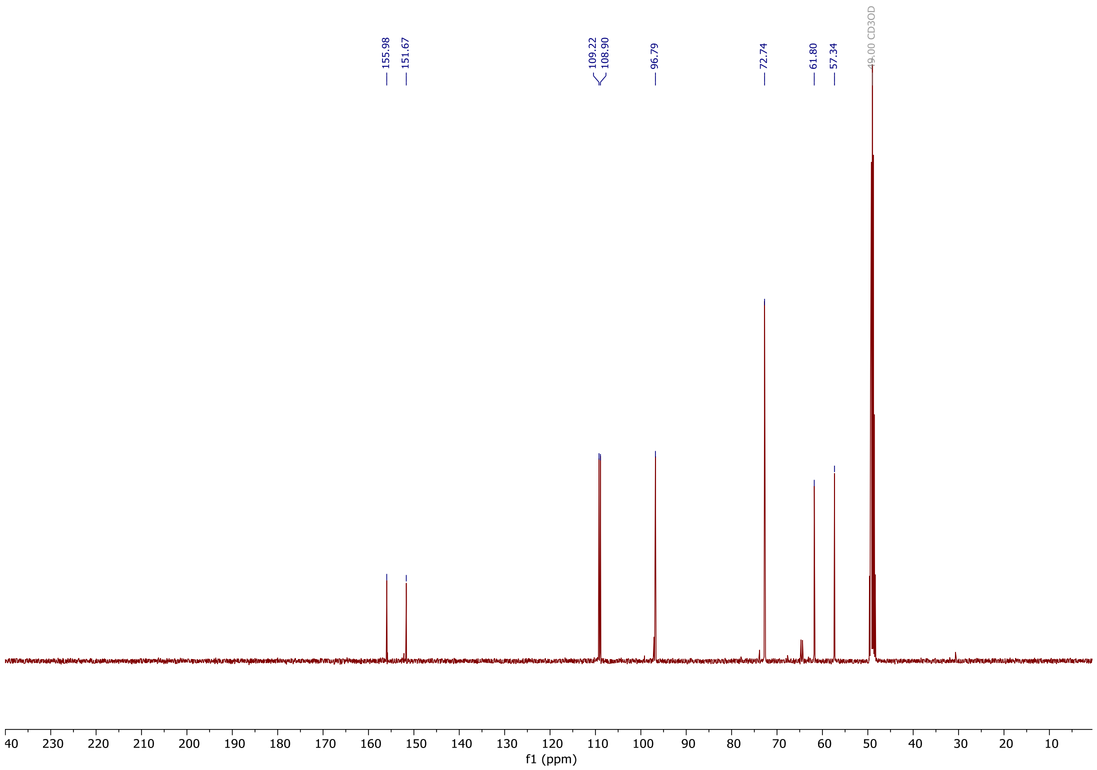
## S4.2 Degradation study of films 5 at 50 °C (repeat experiment)



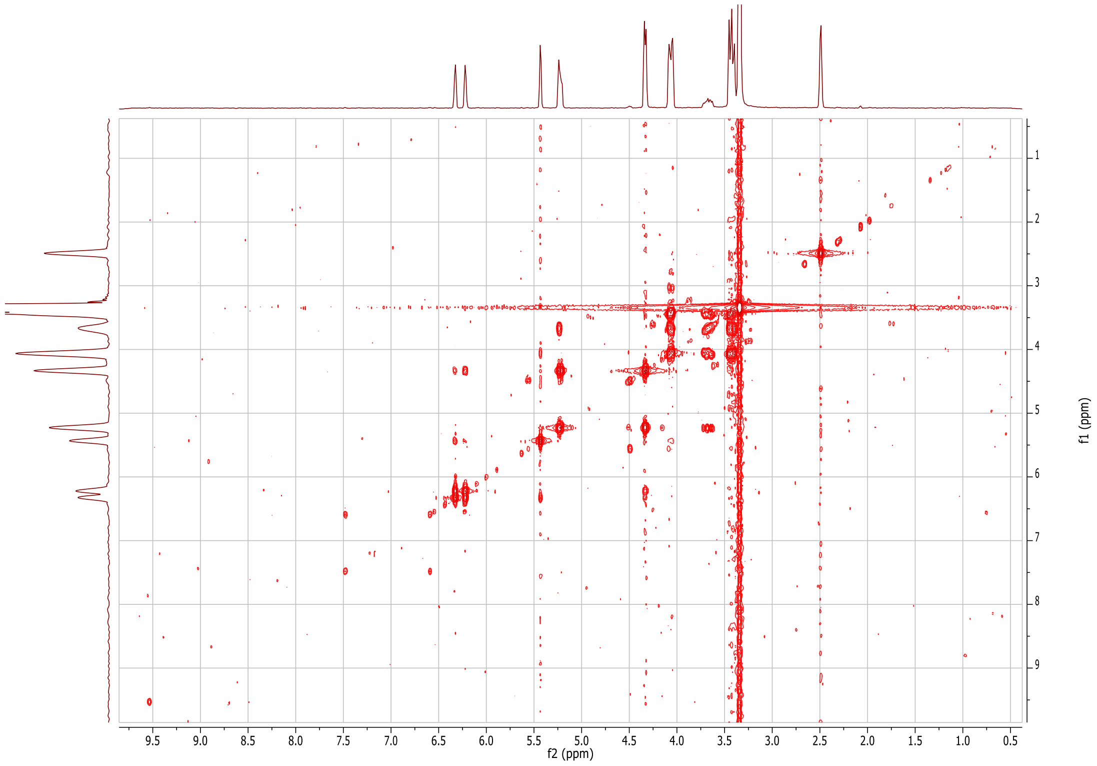
## S5. Spectroscopic data for acetal diols



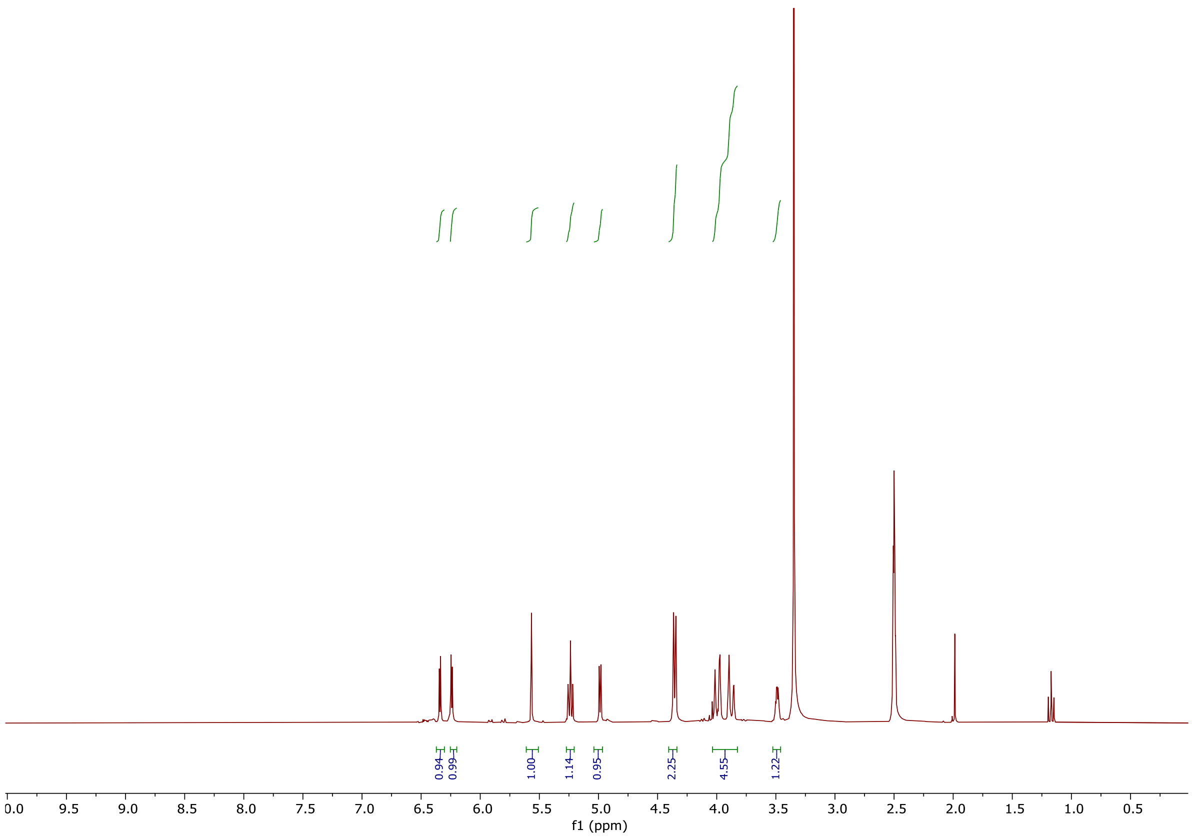
$^1$H-NMR spectrum of crystalline isomer 1 in DMSO-d$_6$



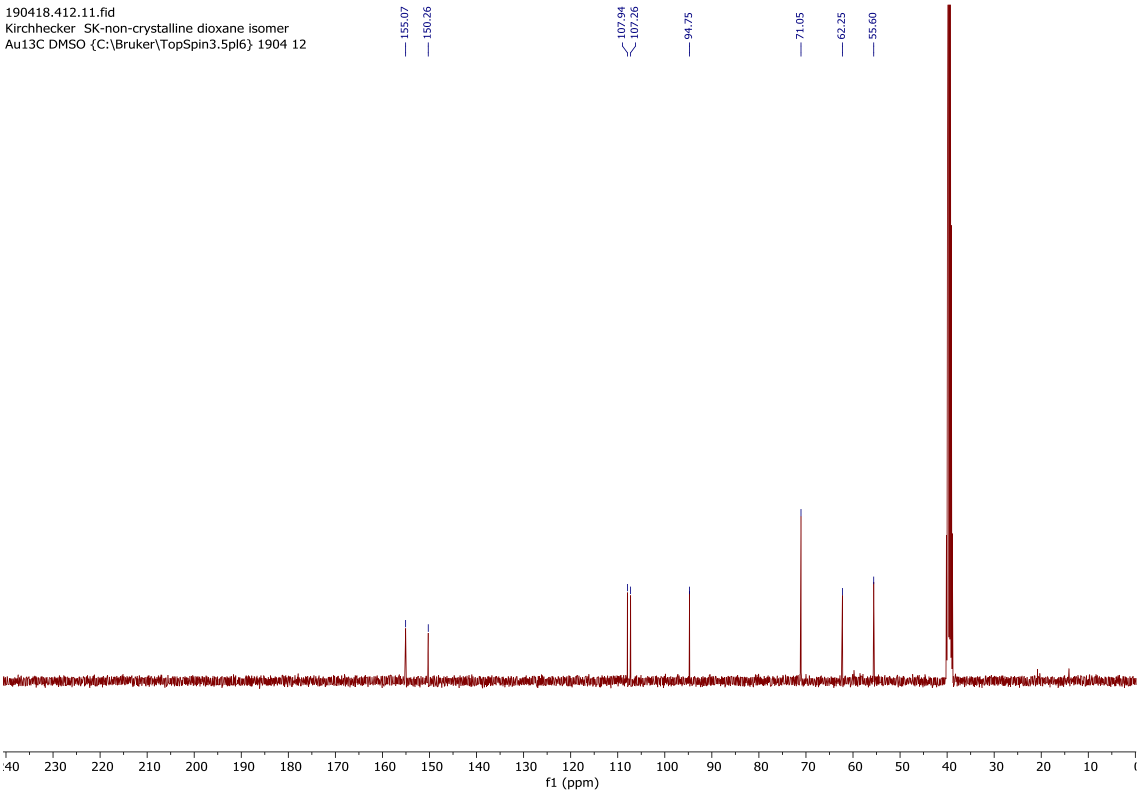
**$^{13}$C-NMR spectrum of crystalline isomer 1 in MeOH-$d_4$**



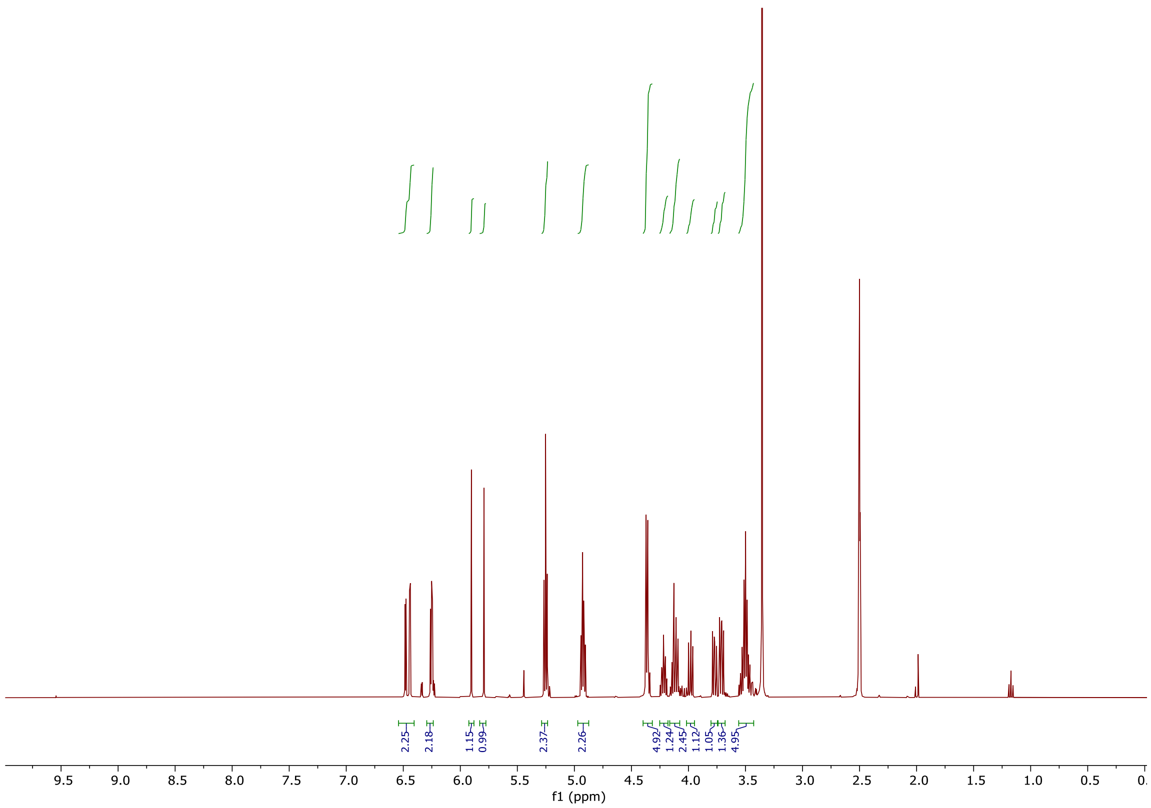
**COSY-NMR of crystalline isomer 1**



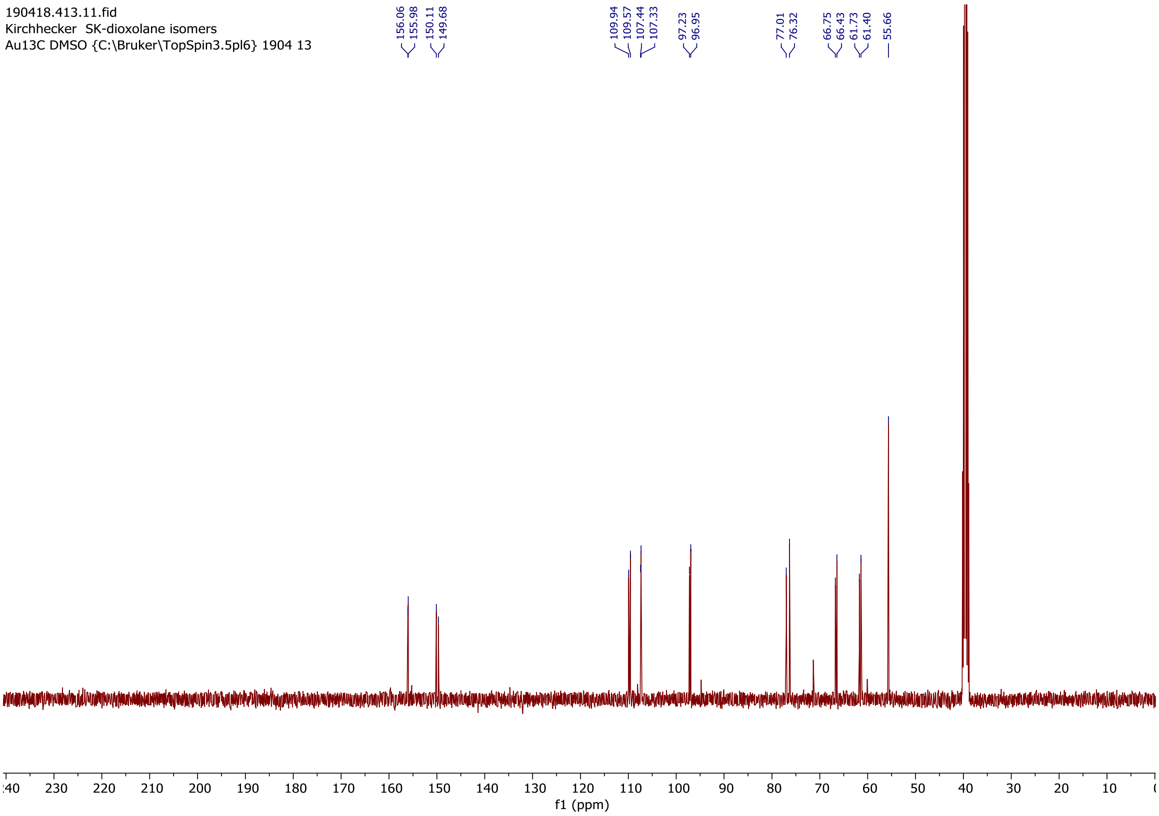
## $^1$H-NMR of cis-dioxane isomer



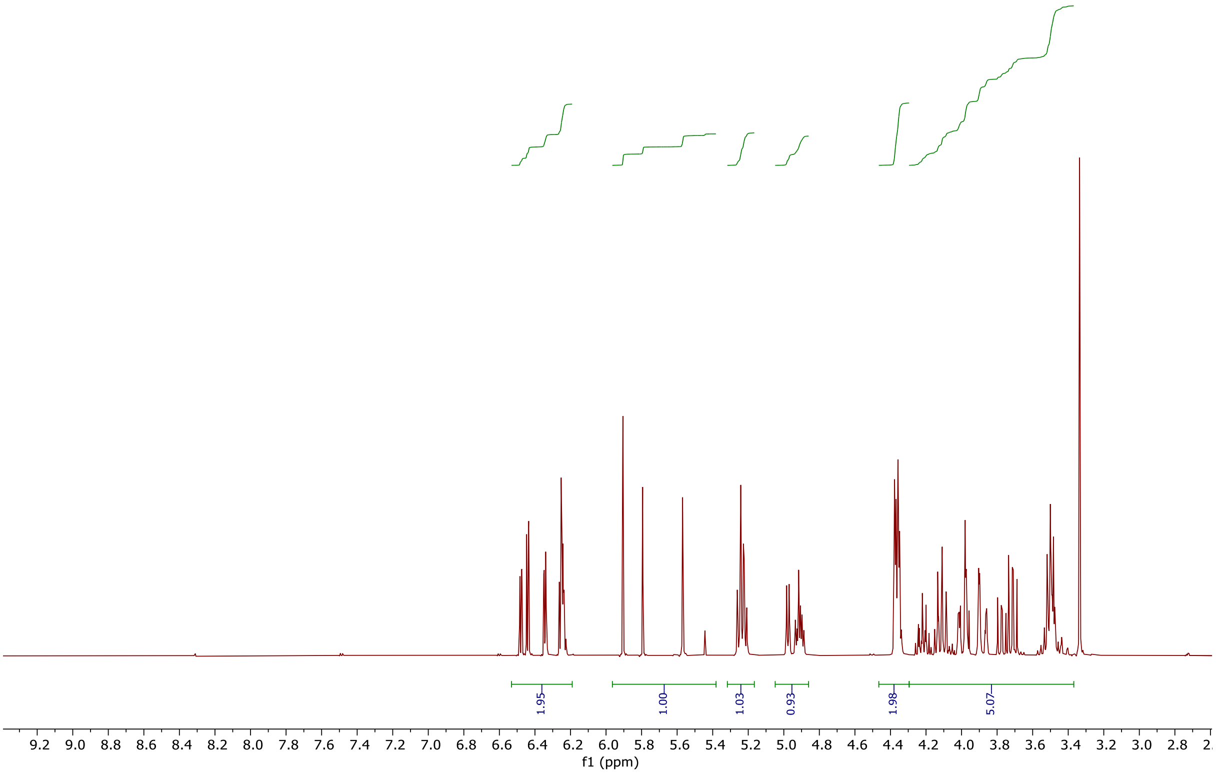
## $^{13}$C-NMR of cis-dioxane isomer



$^{1}$H-NMR of dioxolane isomers

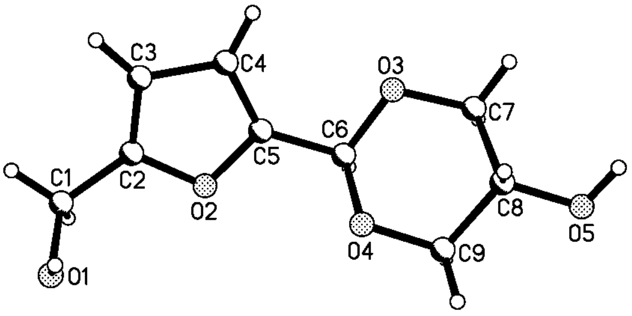


$^{13}$C-NMR of dioxolane isomers



**$^1$H-NMR spectrum of the mixture of acetals** after most of **1** crystallised out (used in kinetics experiment)

## S6. Crystallographic data for crystalline isomer 1

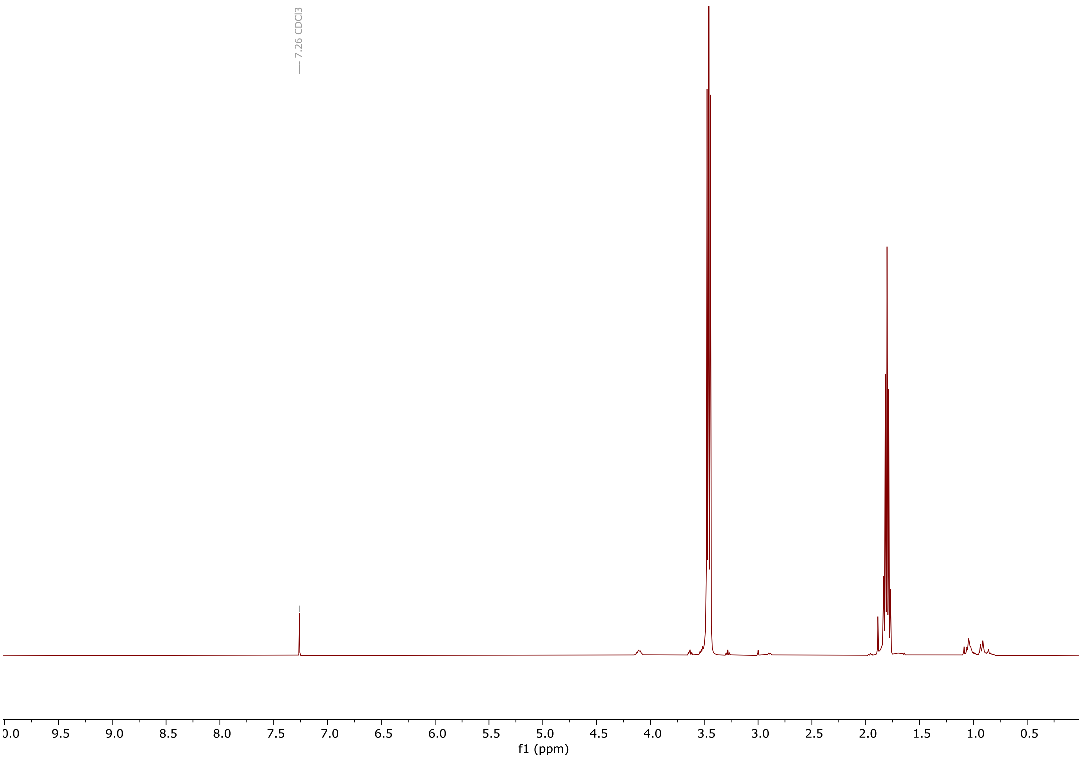


| | |
|---|---|
| Chemical formula | $C_9H_{12}O_5$ |
| Formula weight | 200.19 g/mol |
| Color | colorless |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| a, b, c | 10.7742(5) Å |
| | 7.0350(3) Å |
| | 12.0329(6) Å |
| α, β, γ | 90° |
| | 101.6189(17)° |
| | 90° |
| Volume | 893.36(7) Å$^3$ |
| $Z$ | 4 |
| Temperature | 150(2)K |
| Wavelength | 0.71073 |
| Reflections collected | 16827 |
| Independent reflections | 2151 |
| Observed reflections ($I > 2\sigma(I)$) | 1993 |
| Parameters | 135 |
| GOF on $F^2$ | 1.048 |
| $R_1(I > 2\sigma(I))$ | 0.0331 |
| $wR_2$ (all data) | 0.0920 |

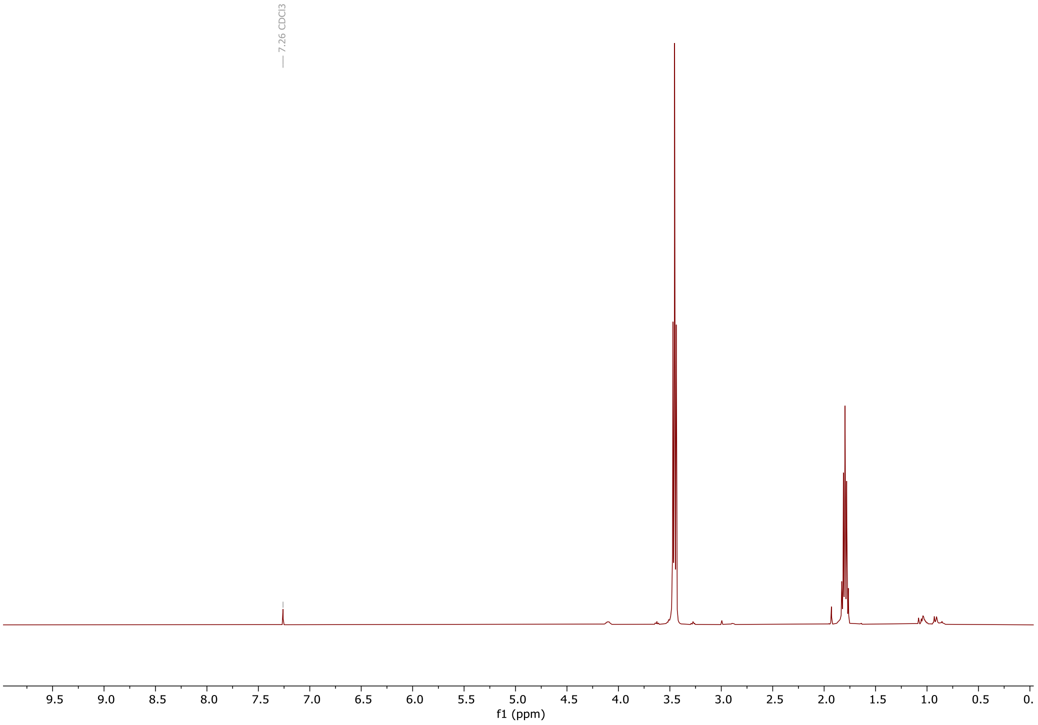
# S7. Spectroscopic data for the polyurethanes

## S7.1 NMR spectra

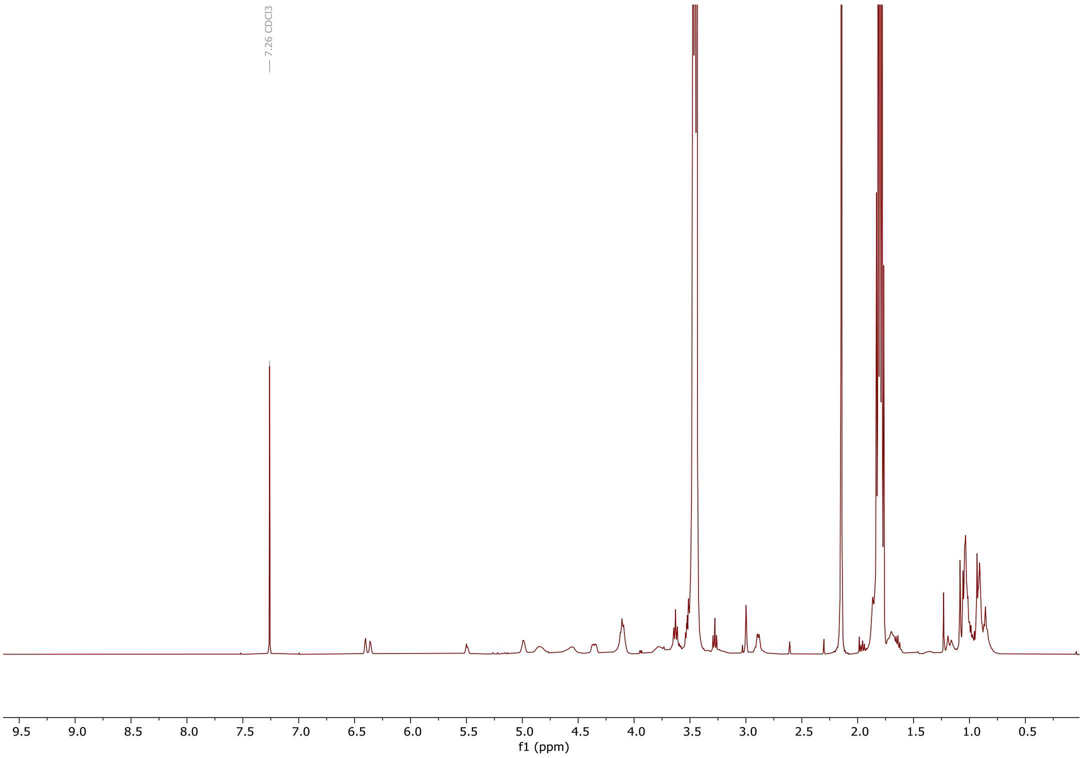
### $^1$H-NMR spectrum of polyurethane 2-0% (before cure)



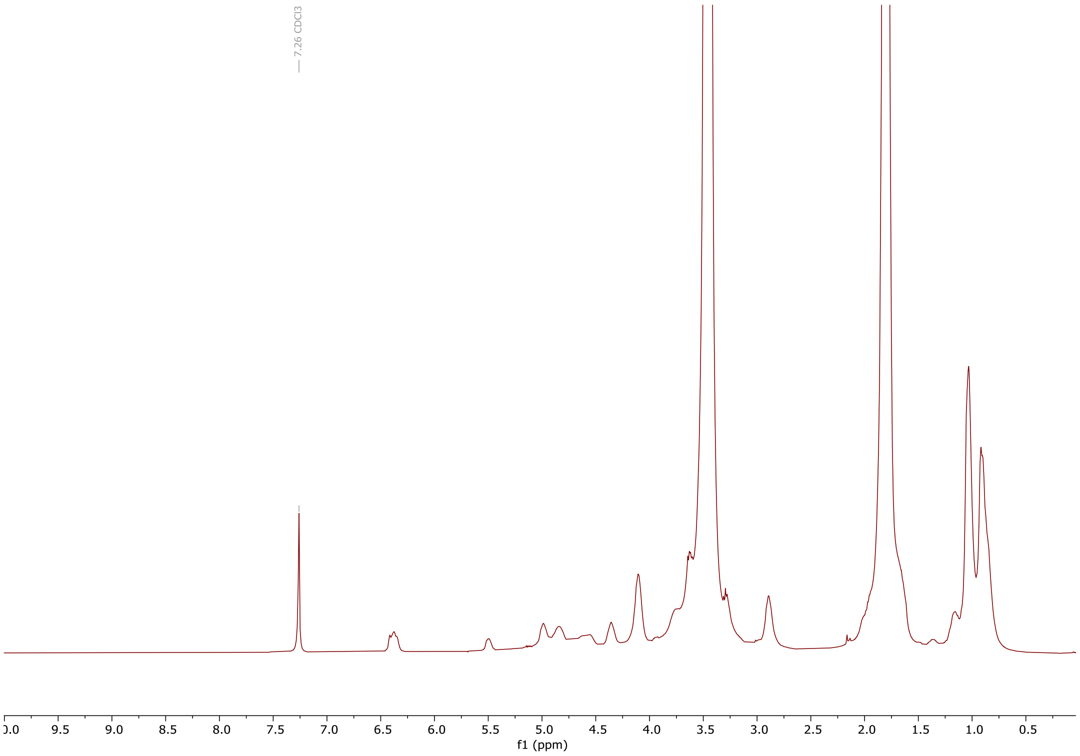
### $^1$H-NMR spectrum of polyurethane film 4-0% (after cure)



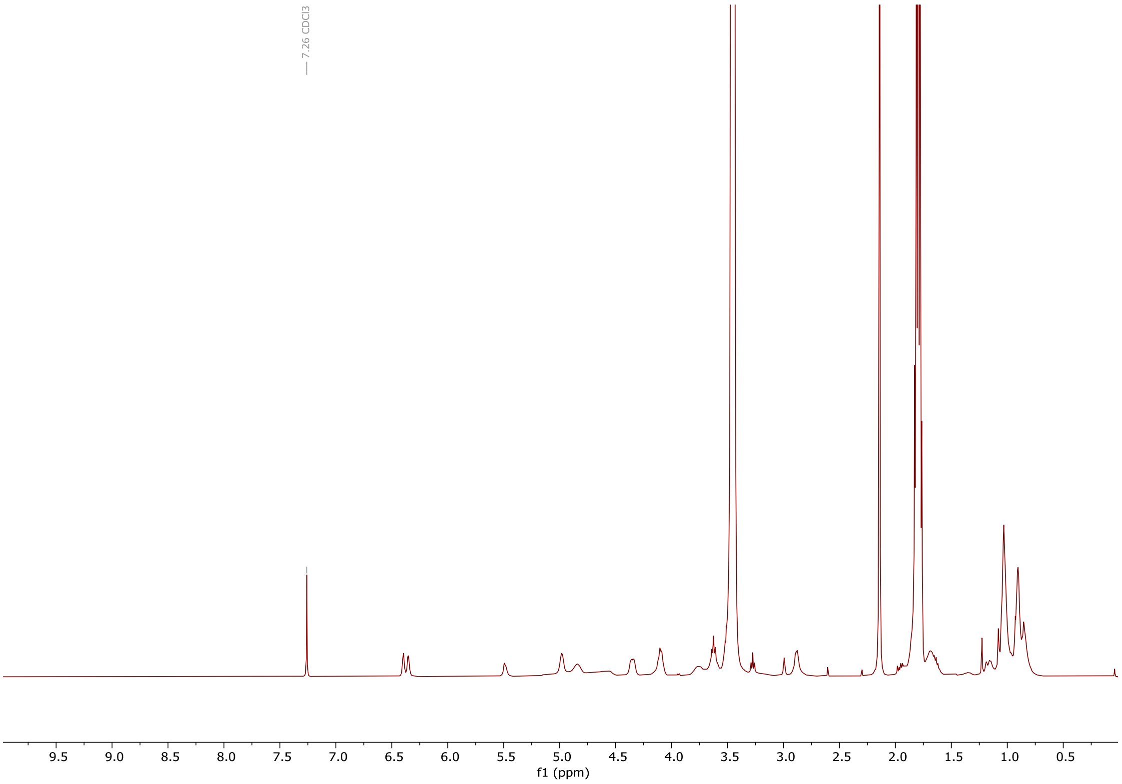
## $^1$H-NMR spectrum of polyurethane 2-5% (before cure)



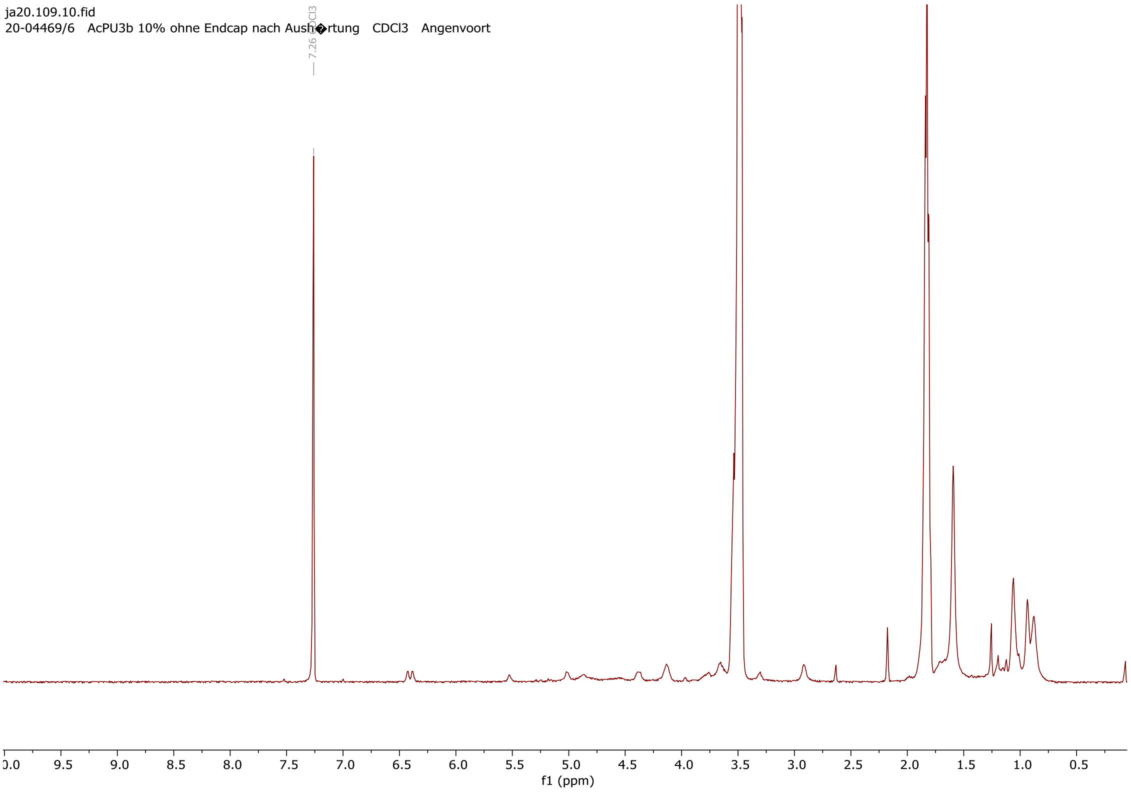
## $^1$H-NMR spectrum of polyurethane film 4-5% (after cure)



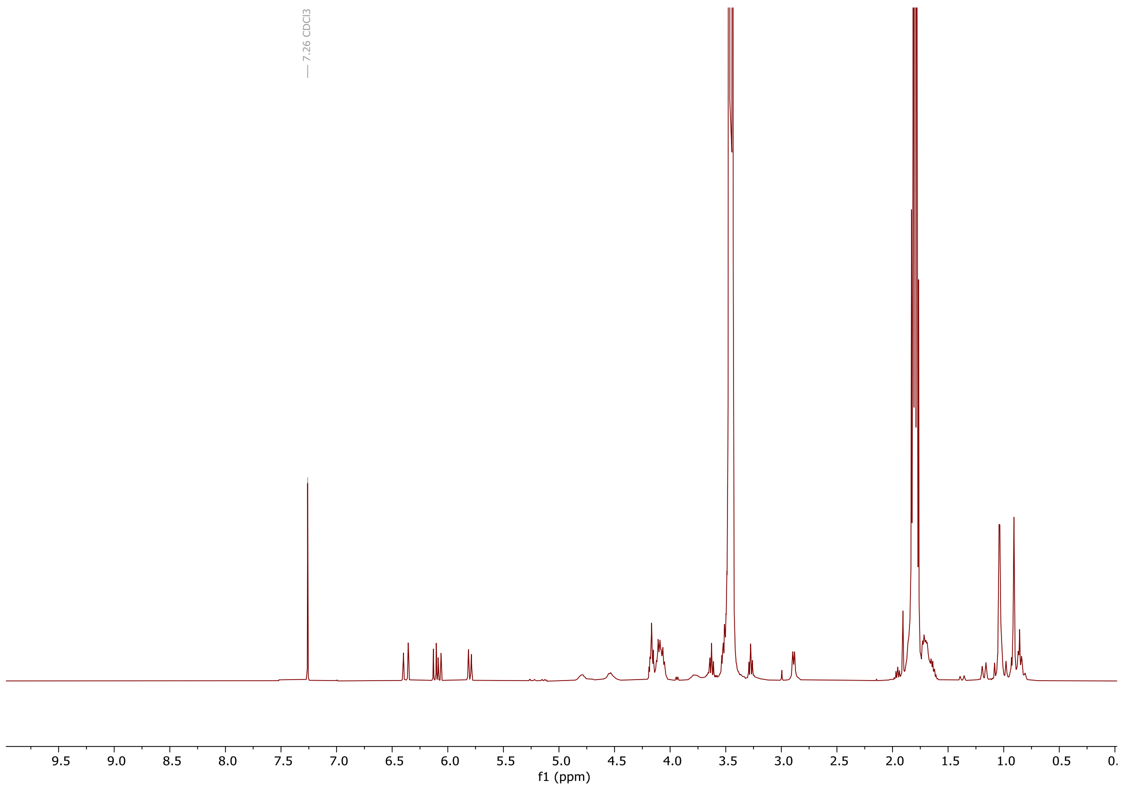
## $^1$H-NMR spectrum of polyurethane 2-10% (before cure)



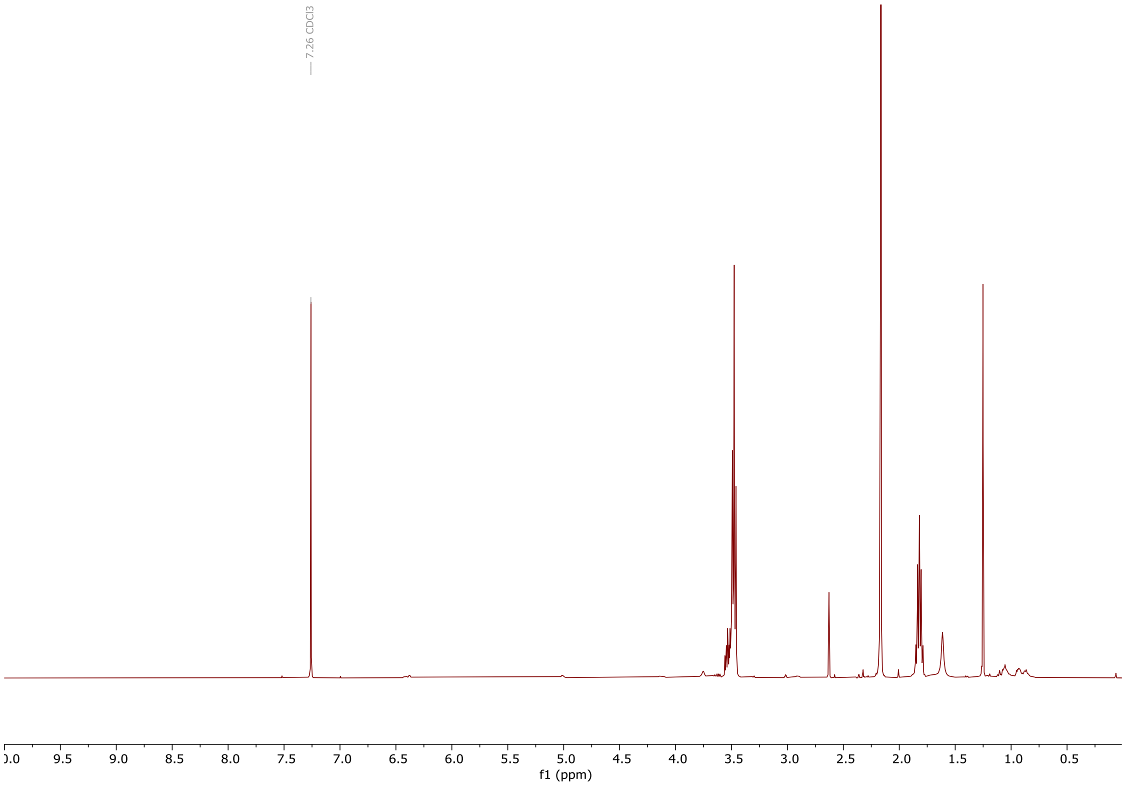
## $^1$H-NMR spectrum of polyurethane film 4-10% (after cure)



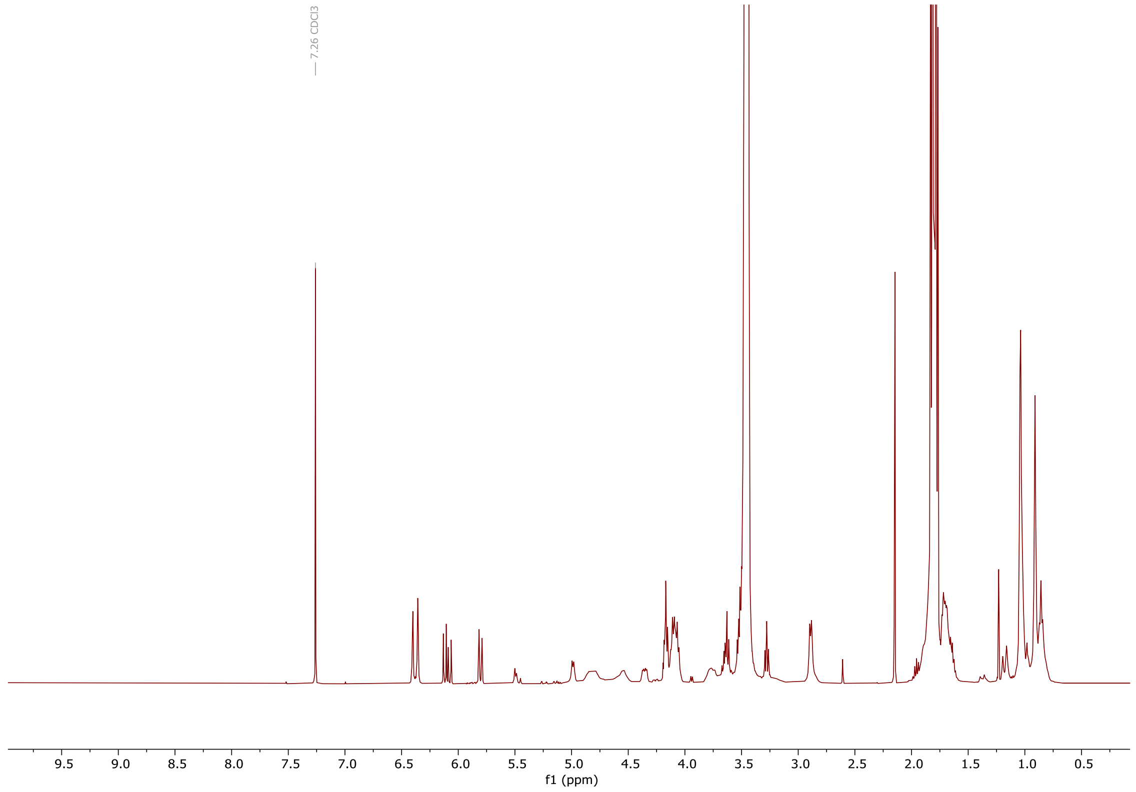
## $^1$H-NMR spectrum of polyurethane 3-0%



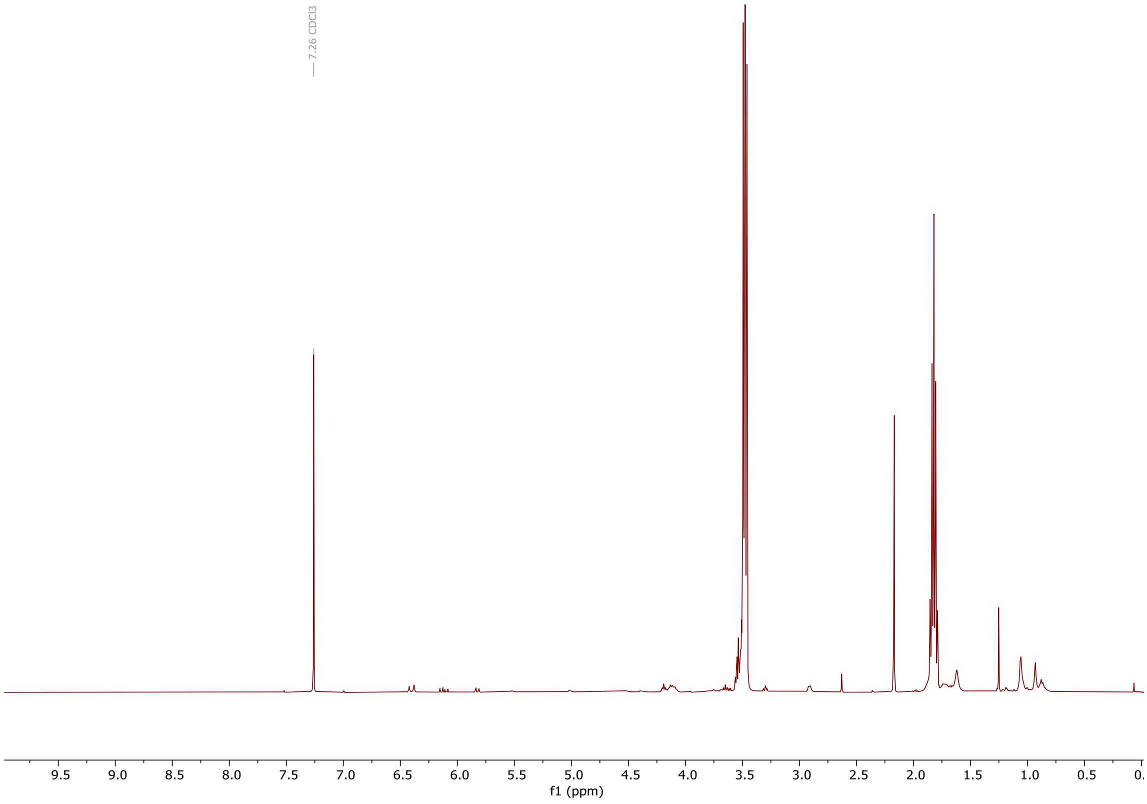
## $^1$H-NMR spectrum of polyurethane film 5-0%



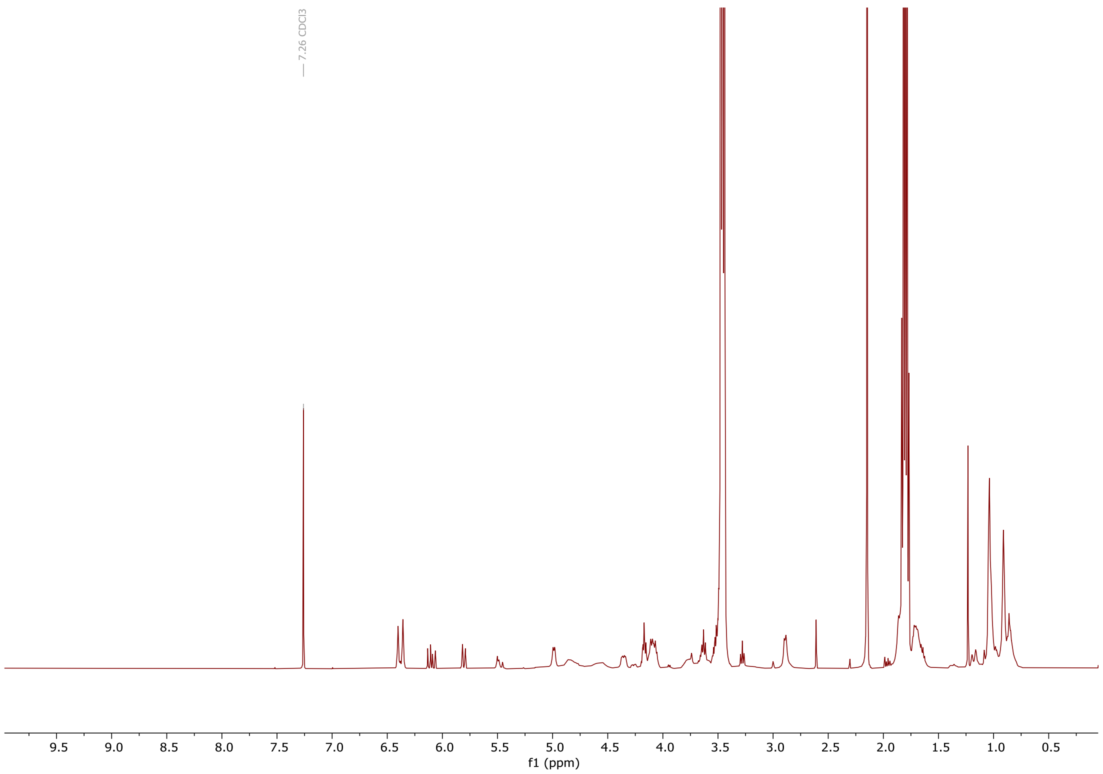
## $^1$H-NMR spectrum of polyurethane 3-5%



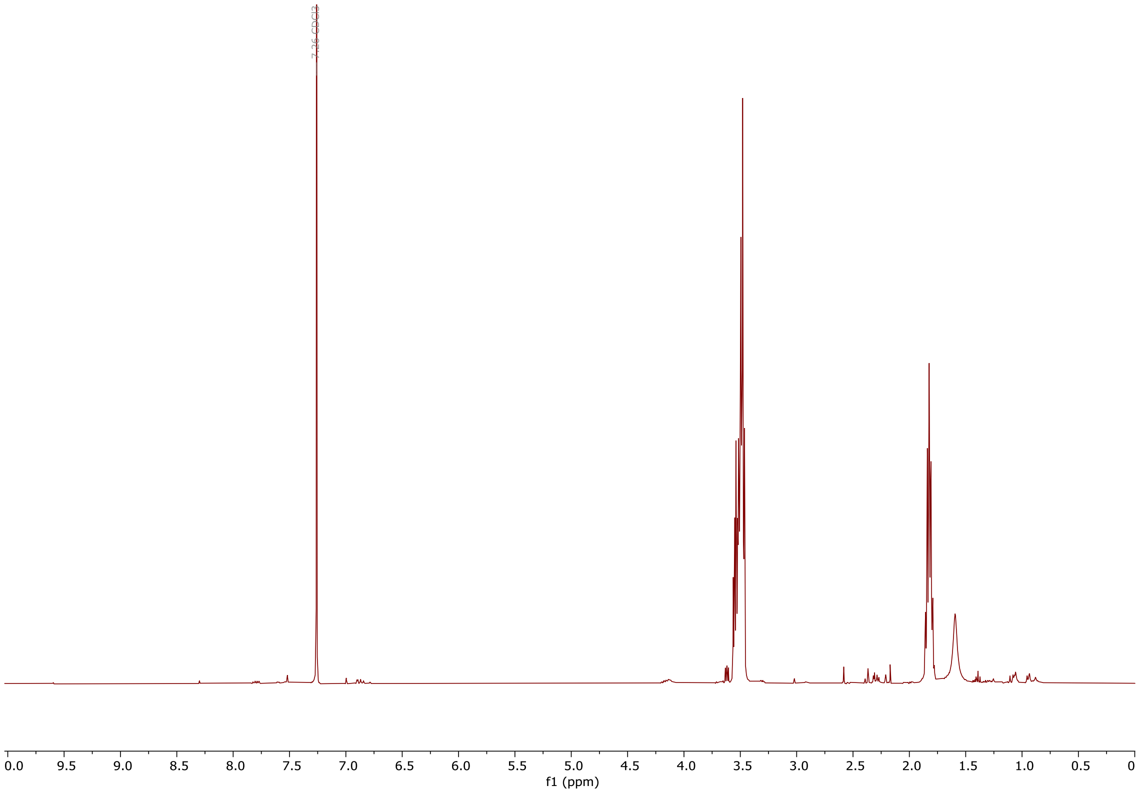
## $^1$H-NMR spectrum of polyurethane film 5-5%



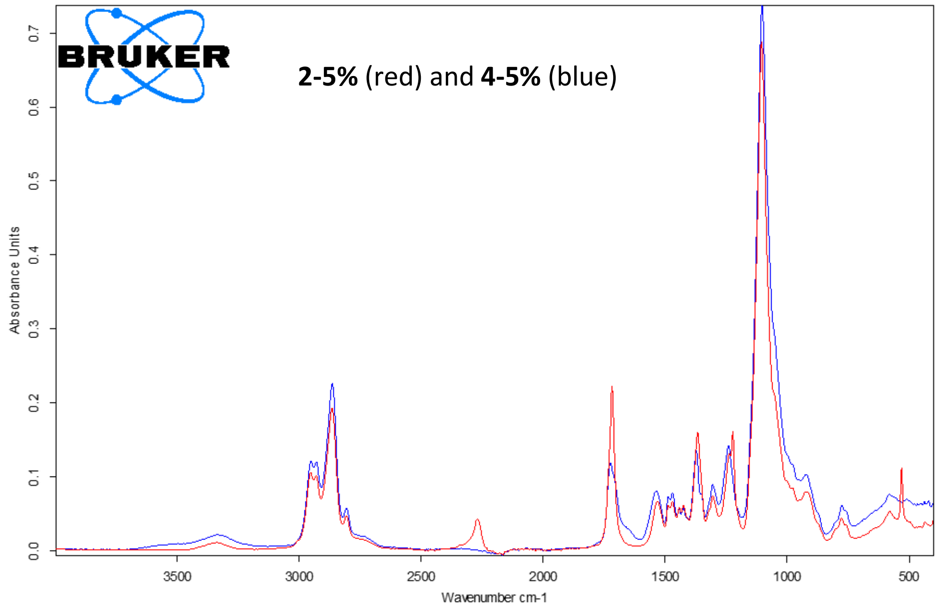
## $^1$H-NMR spectrum of polyurethane 3-10%



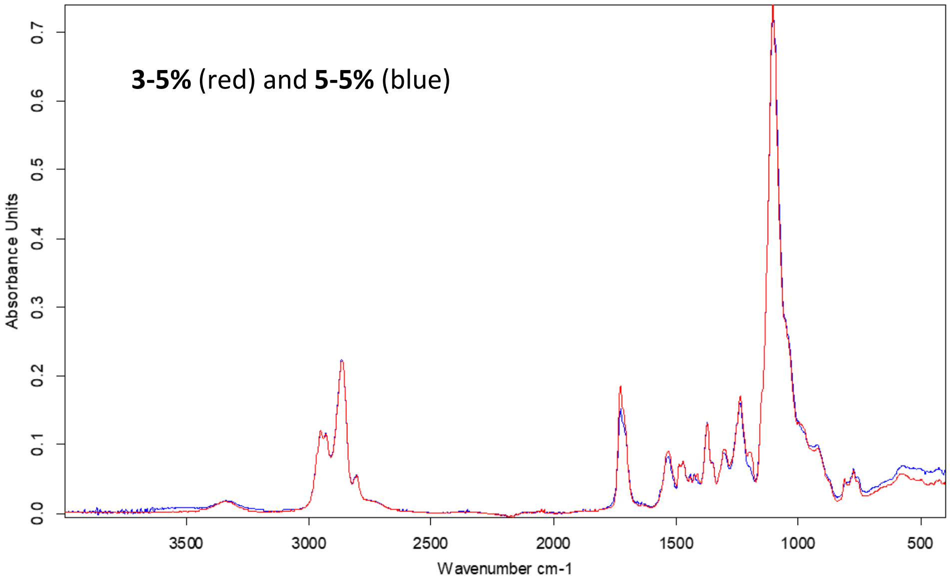
## $^1$H-NMR spectrum of polyurethane film 5-10%



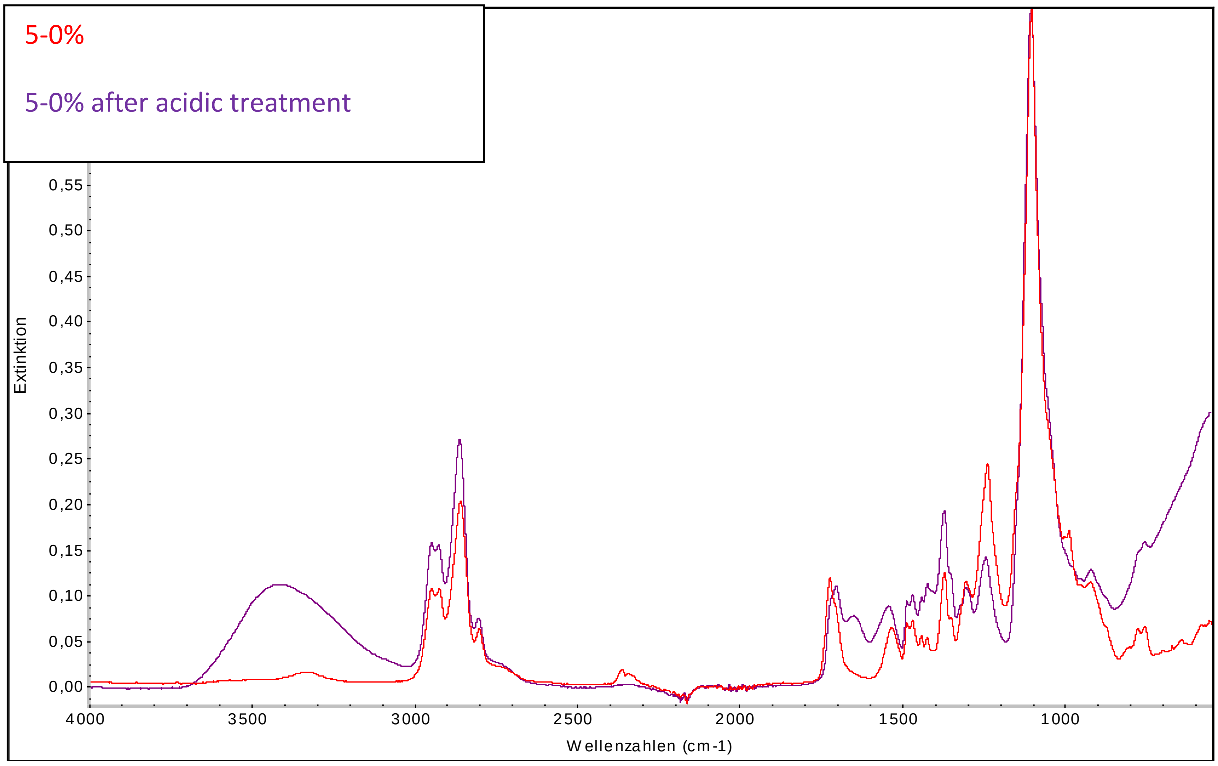
## S7.2 sample FTIR spectra of polyurethanes type A before (2-5%) and after (4-5%) curing

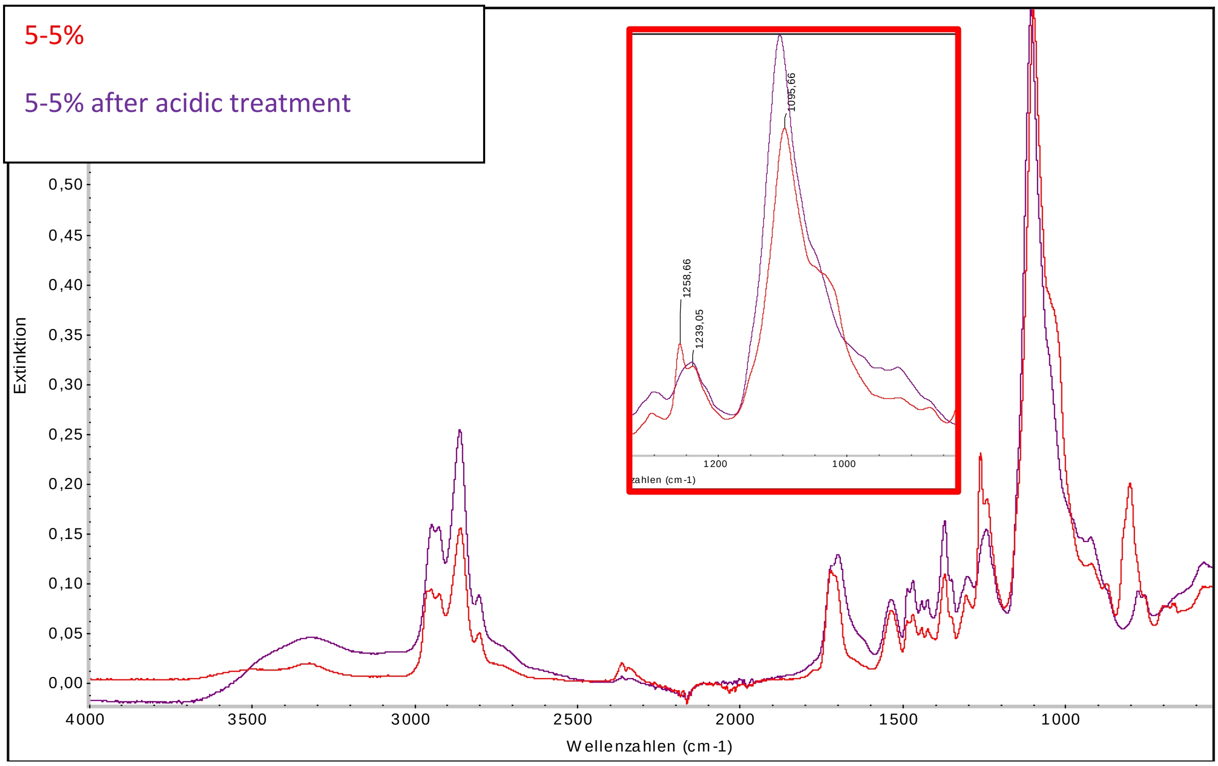


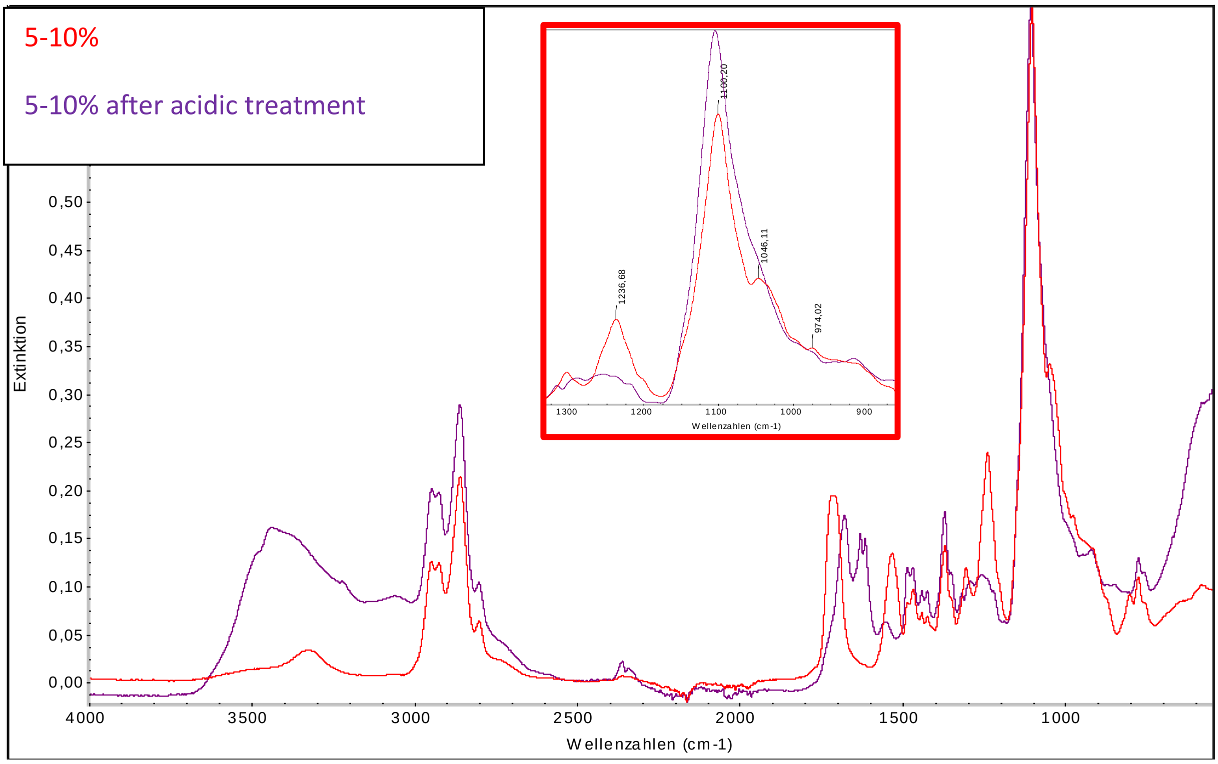
## S7.3 sample FTIR spectra of polyurethanes type A before (3-5%) and after (5-5%) curing



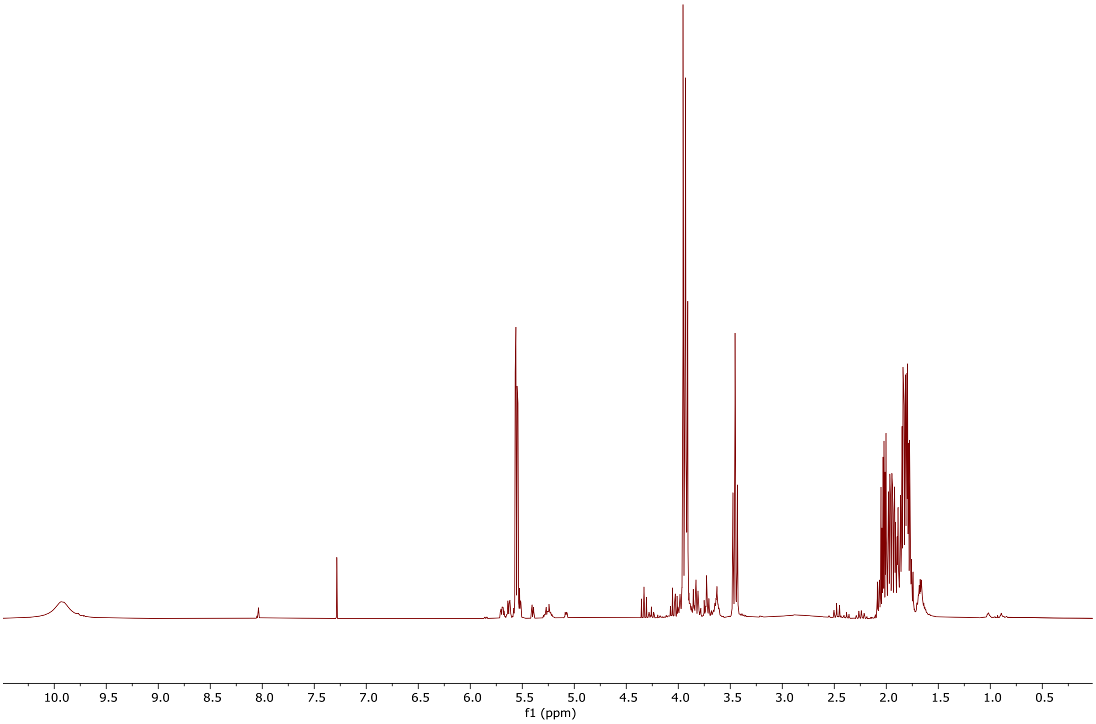
## S8 IR spectra of films 5 before and after cleavage in 5 M HCl in EtOH/$H_2O$



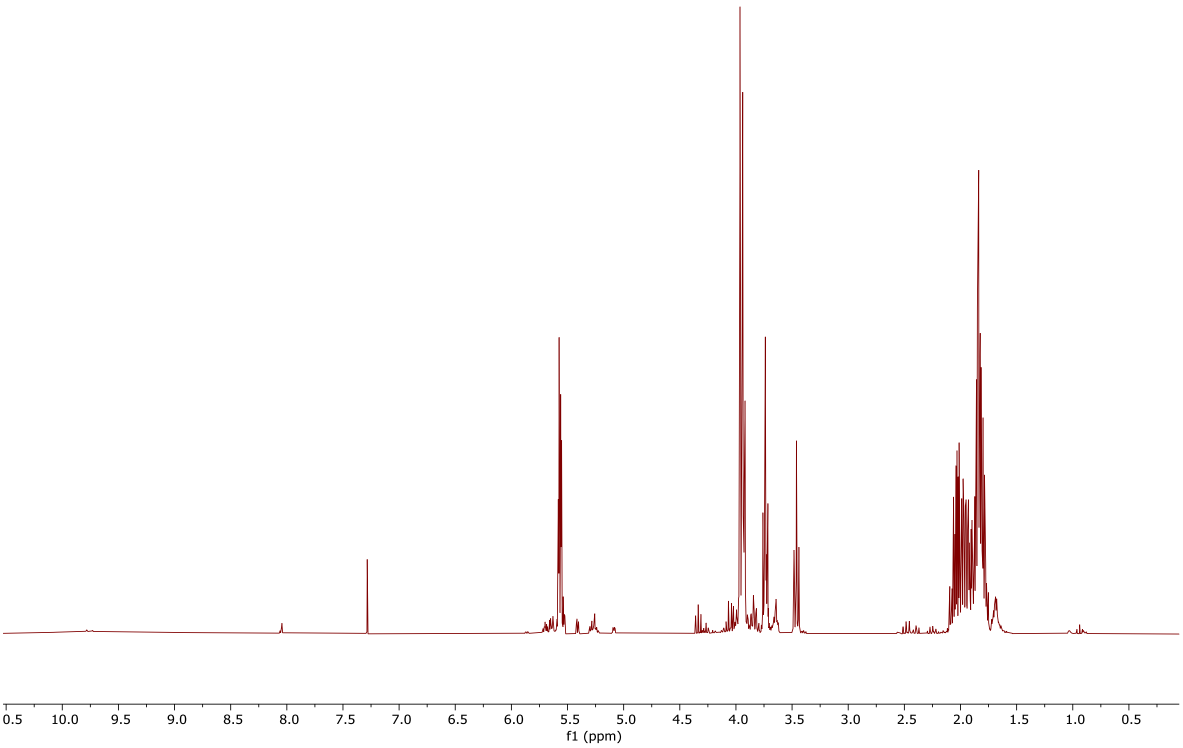




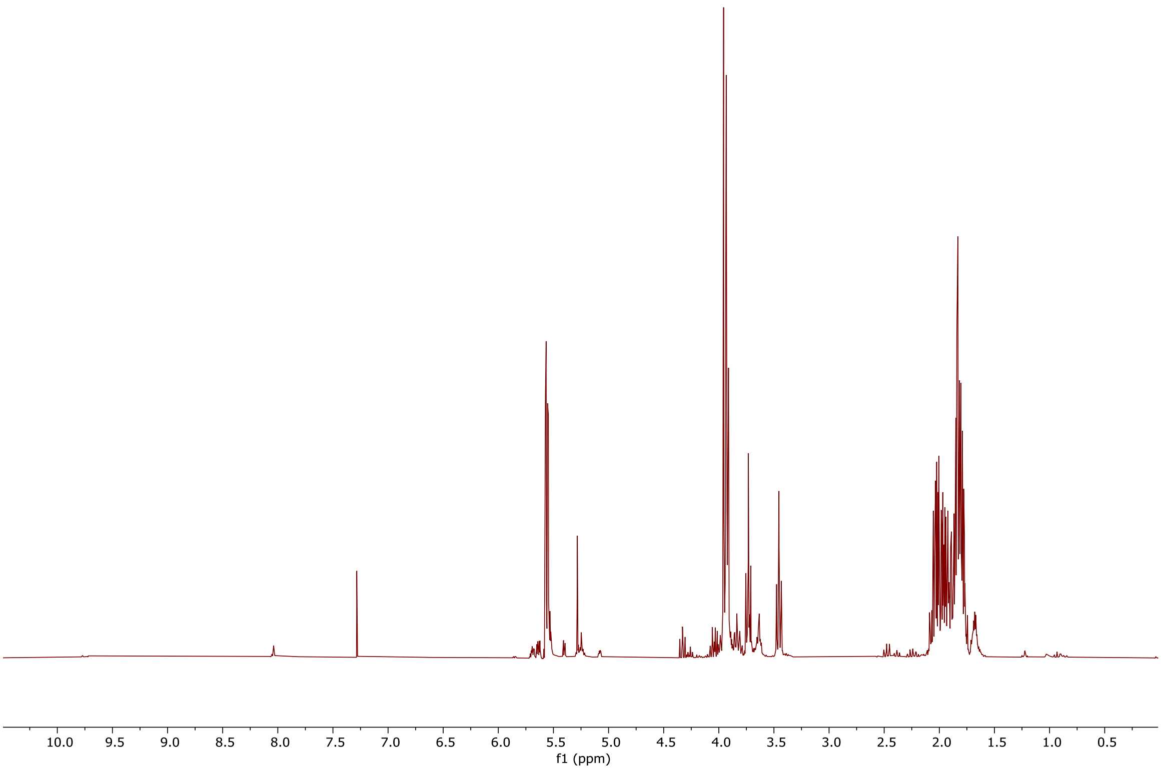
## S9 NMR spectra of films 5 after cleavage in 5M HCl / EtOH / $H_2O$



**$^1$H-NMR of film 5-0% after cleavage**



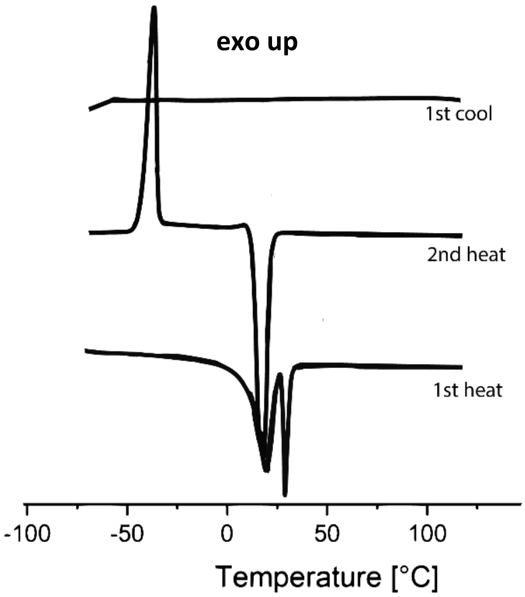
**$^1$H-NMR of film 5-5% after cleavage**



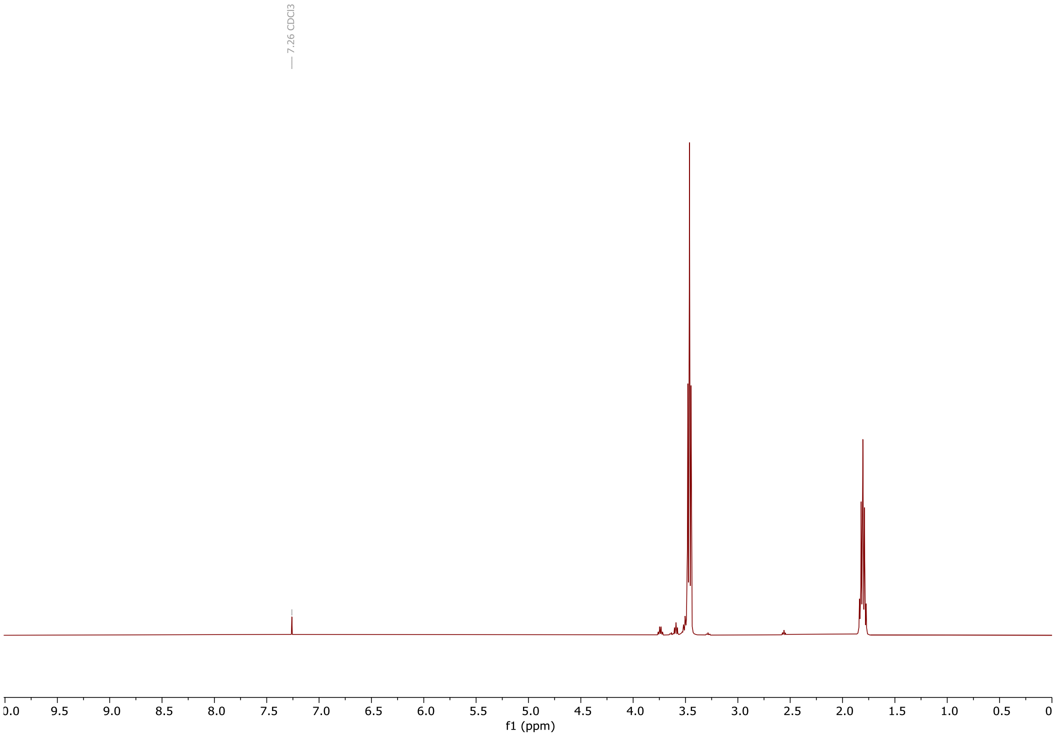
**$^1$H-NMR of film 5-10% after cleavage**

# S10 Analytical data for pure velvetol H2700

## S10.1 DSC traces of velvetol H2700

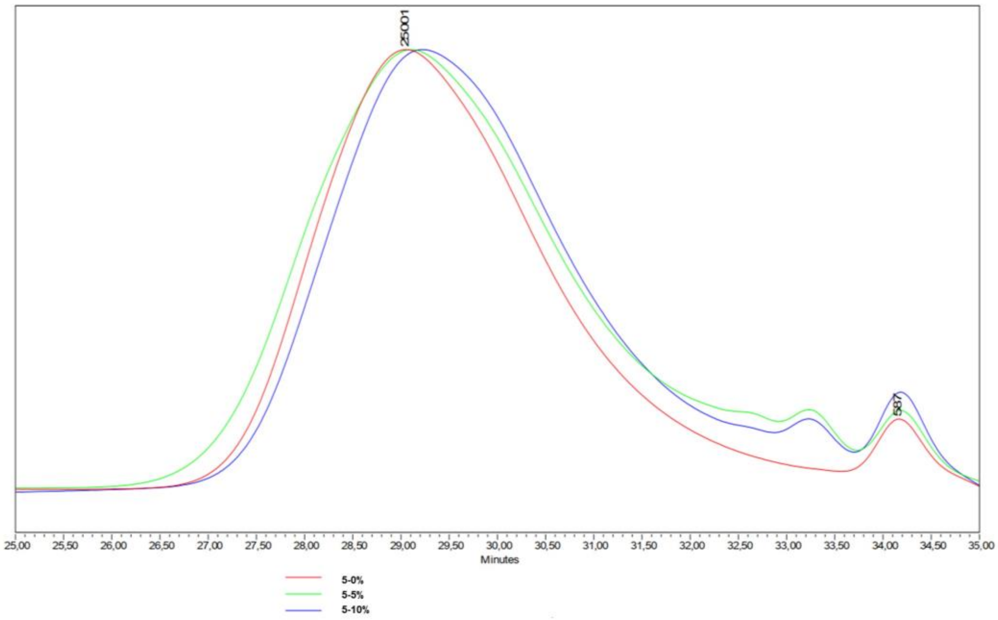


## S10.2 $^1$H-NMR spectrum of velvetol H2700



## S11. APC-GPC chromatograms

### S11.1 PUs 3



### S11.2 Visually dissolved samples after treatment in HCl/EtOH/$H_2O$.