SUPPORTING INFORMATION

Unexpected selectivity in the functionalization of

neat castor oil under benign catalyst-free conditions

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Materials and Methods

Materials

1,6-hexamethylene diisocyanate (HMDI, 98.0% purity) was purchased from Sigma-Aldrich, and castor oil (211 cSt at 40 °C) was obtained from Guinama (Spain). All materials were used as received without further purification.

Synthesis of pre-polymers

Castor oil (84, 75 or 68 parts by weight) and HMDI (16, 25 or 32 parts by weight, respectively) were combined, covered, and stirred at 200-300 rpm at room temperature for 24 hours to give the desired pre-polymer formulation. The nomenclature of the obtained formulations and their molar compositions are presented in Table 1 of the associated manuscript.

Chemical composition of castor oil

Fatty acid and cholesterol profiles in castor oil were determined according to the IUPAC Standard Methods. Results are as follows:

Fatty Acids	% Composition
Palmitic acid, 16:0	0.94
Stearic acid, 18:0	1.11
Oleic acid, 18:1 (9)	2.52
Vaccenic acid, 18:1 (11)	0.45
Linoleic acid, 18:2	3.88
Linolenic acid, 18:3	0.43
Ecosenoic acid, 20:1	0.26
Ricinoleic acid, 18:1-OH	89.91
Lesquerolic acid, 20:1-OH	0.49

Sterol	Composition (%)
Colesterol	0.28
Brasicasterol	0
24-metilencolesterol	0
Campesterol	10.94
Campestanol	0.32
Estigmasterol	20.71
Delta 7 campesterol	0
5,23 estigmastadienol	0
Clerosterol	0
B-Sitosterol	48.9
Sitostanol	1.3
5-Avenasterol	14.21
5,24-Estigmastadienol	2.54
7-Estigmasterol	0.31
7-Avenasterol	0.49
TOTAL (mg/Kg)	**1879**

Fourier Transform Infra-Red (FTIR)

Fourier Transform Infra-Red (FTIR) measurements were performed using a Jasco FT4200 infrared spectrometer (JASCO Inc., Tokyo, Japan) equipped with an attenuated total reflectance (ATR) system. Samples were loaded onto the ATR crystal area and the respective spectra obtained in the transmission mode over a scanning range of 4000–400 cm^{-1} for ~ 80 repeated scans at a resolution of 4 cm^{-1}. All spectra were transformed into the absorbance mode using the Spectra Manager software (version 2.10.2.1), baseline corrected and normalized to the CH_2 peak area.

Nuclear Magnetic Resonance: ^{1}H-NMR of quenched samples for quantitative comparisons

NCO-containing pre-polymers for ^{1}H-NMR measurements were dissolved in excess methanol at immediately following the synthesis reaction (i.e., at *t0*) in order to quench the unreacted isocyanate. Methanol was subsequently removed by evaporation at room temperature followed by drying under vacuum at room temperature for 24 hours.

[1]H spectra were acquired on a Bruker Avance 500 MHz spectrometer (Bruker, USA) equipped with a 5-mm Broadband Observe (BBFO) probe with z gradient. Spectra were acquired at 25 ºC over a 16- ppm spectral window with a 10 s recycle delay, 32 transients. Spectra were Fourier transformed, phase corrected, and baseline corrected. The spectral width was 10330.572 Hz for [1]H. Chemical shifts were referenced using $CDCl_3$ (δ(^{1}H) = 7.24 ppm) as solvent. Spectra were analysed using ACD/NMR Processor Academic Edition software (Version 12.01).

Qualitative Nuclear Magnetic Resonance: Supporting ^{13}C- and 2D-NMR for chemical characterization

^{1}H-^{1}H COSY, ^{13}C DEPT135 and ^{13}C NMR experiments were performed on a representative NCO-containing prepolymer (8416) as obtained immediately following processing; i.e., without prior NCO quenching. $CDCl_3$ was used as solvent, and all peaks were referenced relative to TMS. For the ^{1}H experiments, a 300 MHz spectrometer (Bruker, USA) was used, and for the ^{13}C experiments, a 400 MHz spectrometer spectrometer (Bruker, USA) was used. Spectra were analysed using ACD/NMR Processor Academic Edition software (Version 12.01).

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) measurements were performed using a Q50 model TGA (TA Instruments, New Castle, DE, USA) under constant nitrogen flow (sample flow 60 mL/min; balance flow 40 mL/min). Typically, 12-17 mg of pre-polymer were loaded onto a platinum pan and heated to 600 °C at a rate of 10 °C/min. TGA data were analysed using the 'TA Universal Analysis' software (Version 4.5A).

Rheology

Using a controlled-stress Physica MCR501 (Anton Paar, Austria) rheometer, viscosity flow curves were obtained by applying a stepped shear rate ramp in the shear rate range of 1 to 100 s^{-1} at 25 ºC using a rough plate–plate geometry (25 mm diameter, 0.5 mm gap).
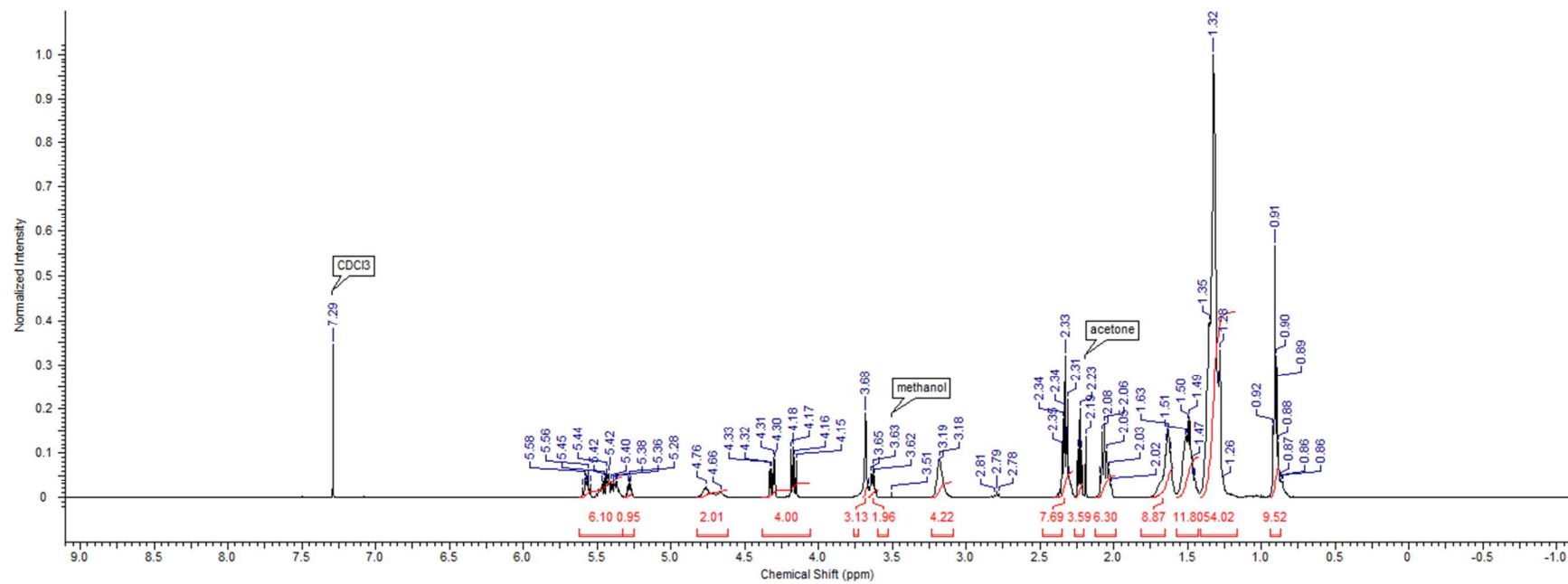
(a)

Figure S1: ^{1}H-NMR spectra of methanol-quenched NCO-containing prepolymers, obtained at 500 MHz and using CDCl$_3$ solvent. (a) 8416, (b) 7525, (c) 6832.
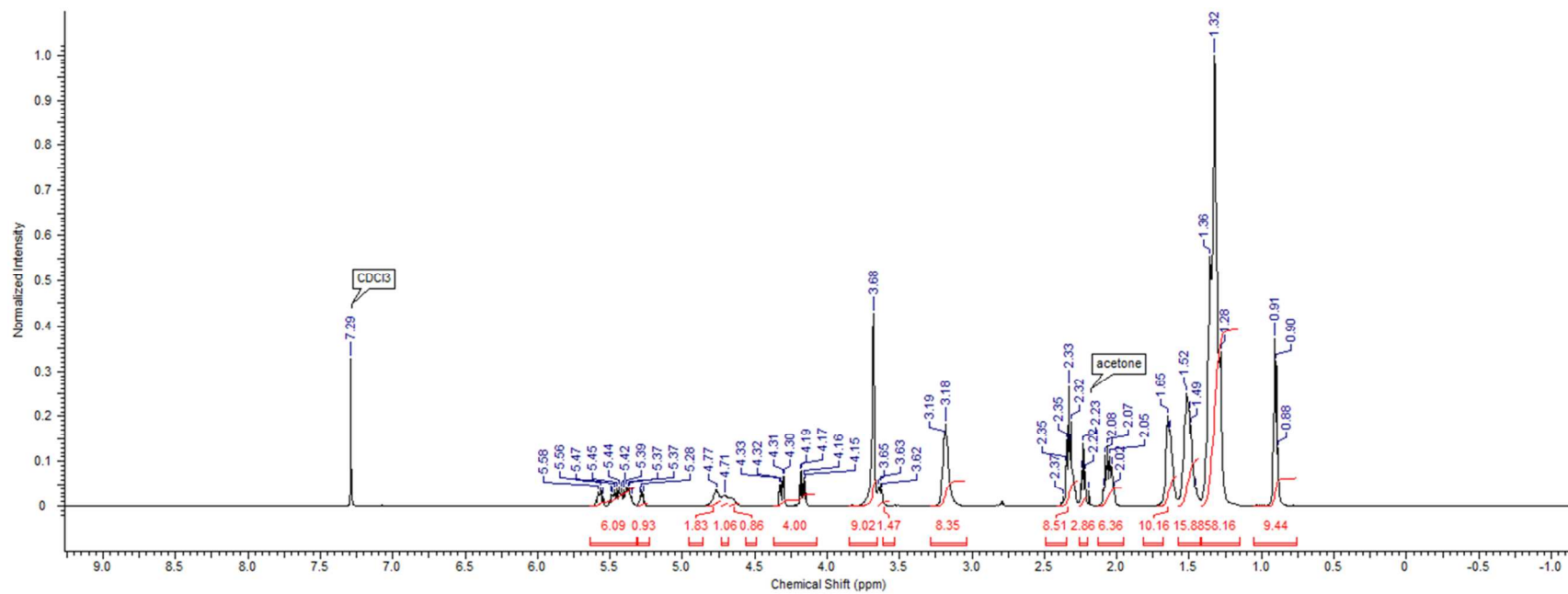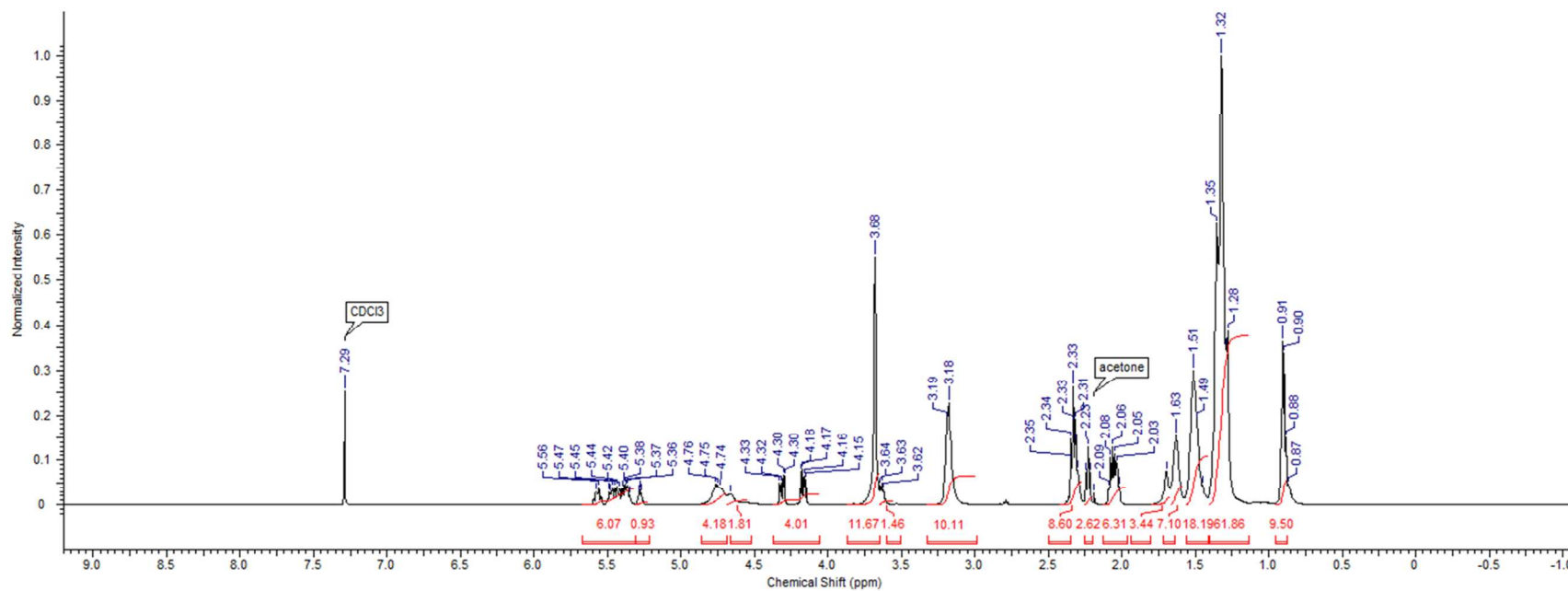
(b)

Figure S1 (cont'd): ^{1}H-NMR spectra of methanol-quenched NCO-containing prepolymers, obtained at 500 MHz and using CDCl$_3$

solvent. (a) 8416, (b) 7525, (c) 6832.

(c)

Figure S1 (cont'd): ^{1}H-NMR spectra of methanol-quenched NCO-containing prepolymers, obtained at 500 MHz and using CDCl$_3$ solvent. (a) 8416, (b) 7525, (c) 6832.

Table S1: Quantification of unreacted isocyanates and degree of castor oil functionalization of urethane pre-polymers, as obtained from methanol-quenched ^{1}H-NMR experiments.

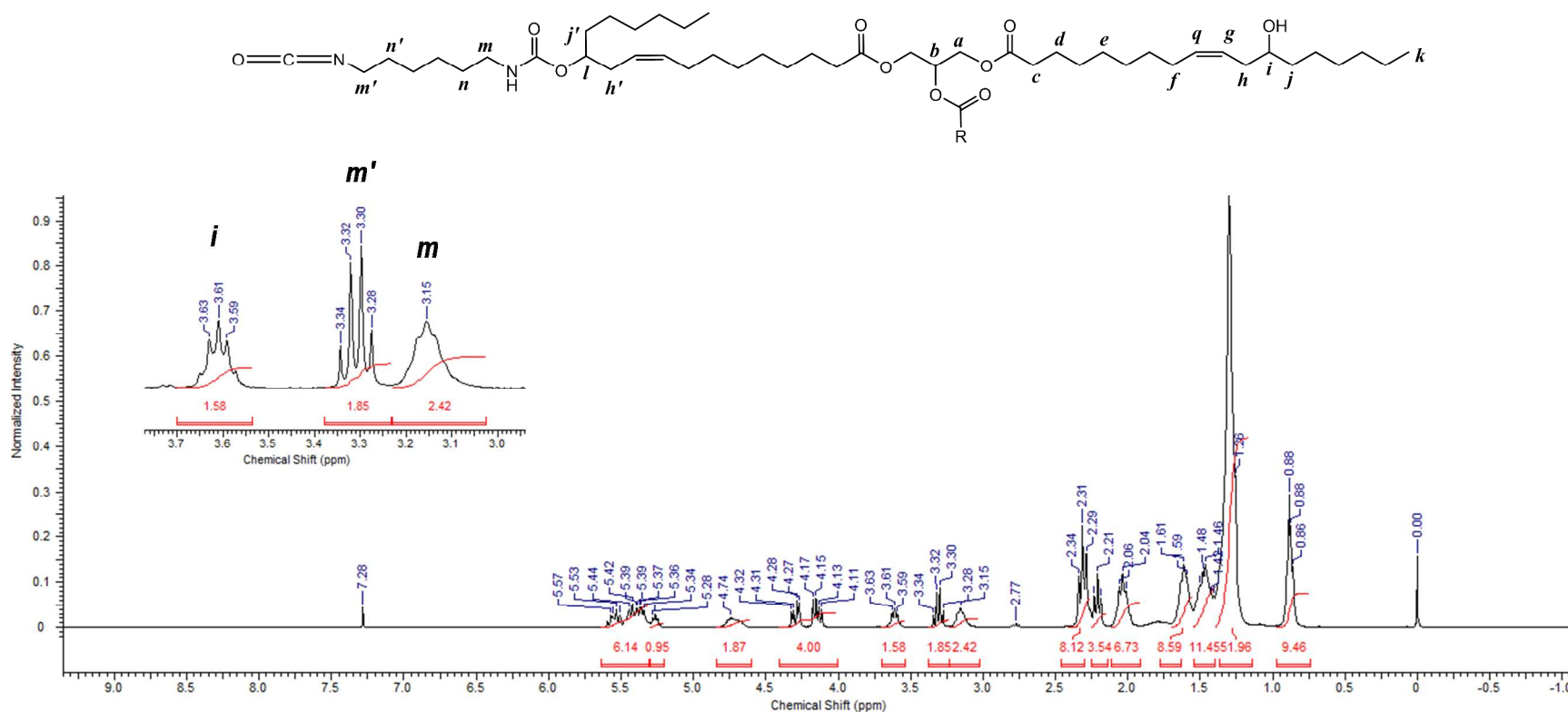|	8416	7525	6832
Total NCO (p/3)	1	3	4
Total NHCOO (m/2)	2	4	5
NHCOO from castor oil only (m/2 – p/3)	1	1	1

(a)

Figure S2: (a) ^{1}H-, (b) COSY-, (c) ^{13}C DEPT135, and (d) ^{13}C- NMR characterization of a representative NCO-containing prepolymer, obtained in CDCl₃ solvent at 300 and 400 MHz for ^{1}H and ^{13}C experiments, respectively.
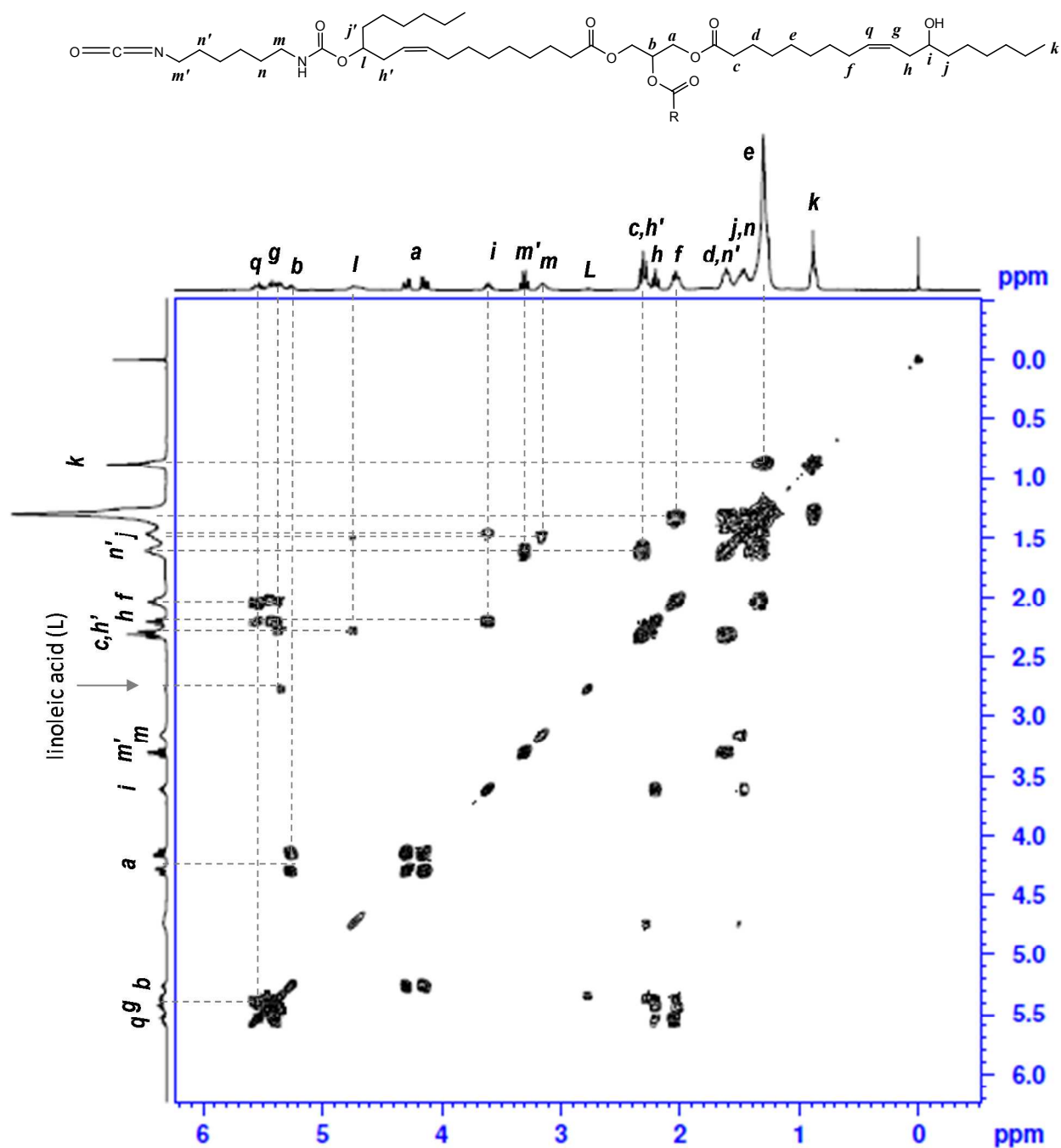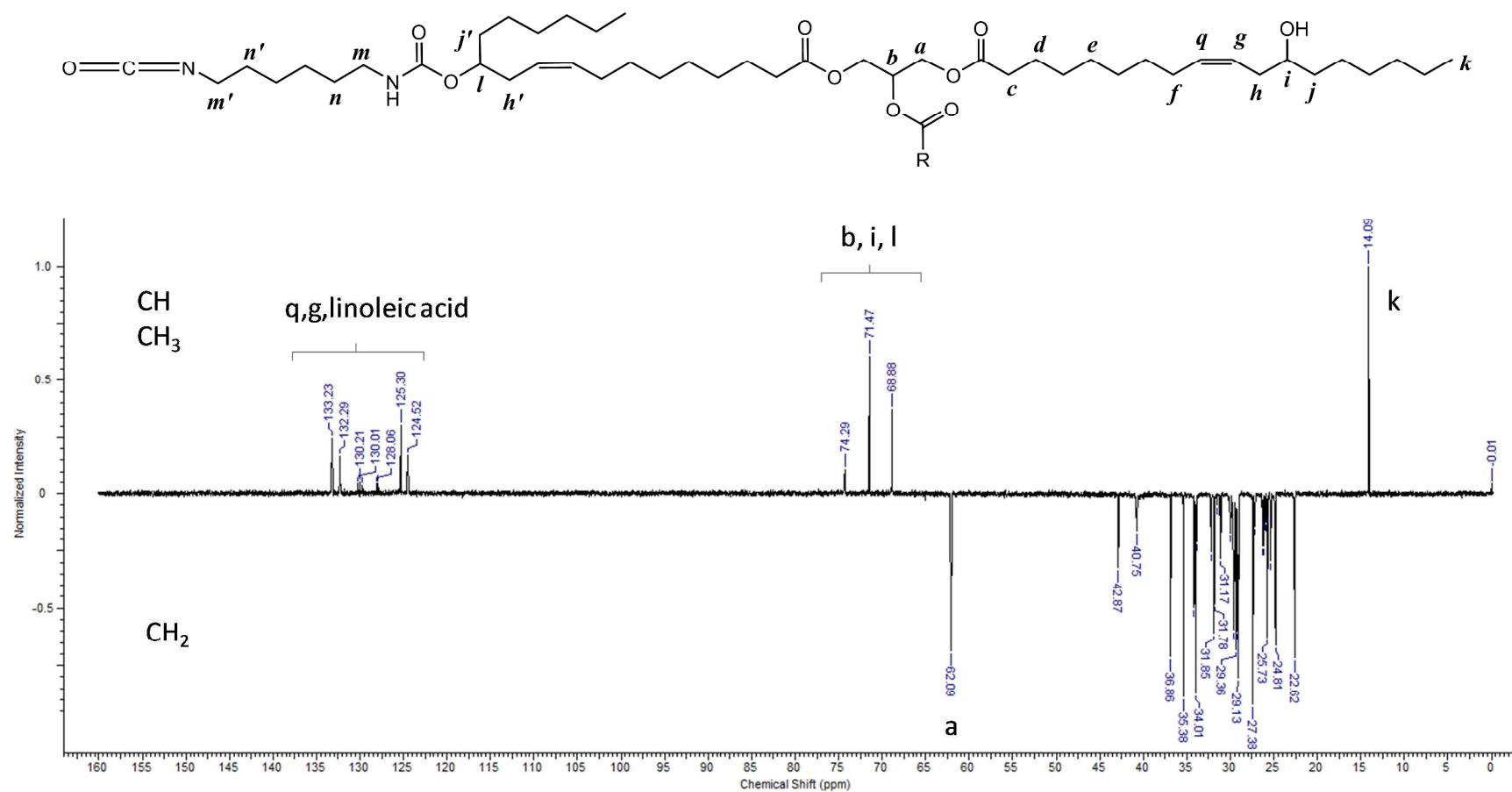
(b)

Figure S2 (cont'd): (a) ^{1}H-, (b) COSY-, (c) ^{13}C DEPT135, and (d) ^{13}C- NMR characterization of a representative NCO-containing prepolymer, obtained in CDCl$_3$ solvent at 300 and 400 MHz for ^{1}H and ^{13}C experiments, respectively.

(c)

Figure S2 (cont'd): (a) ^{1}H-, (b) COSY-, (c) ^{13}C DEPT135, and (d) ^{13}C- NMR characterization of a representative NCO-containing

prepolymer, obtained in CDCl$_3$ solvent at 300 and 400 MHz for ^{1}H and ^{13}C experiments, respectively.
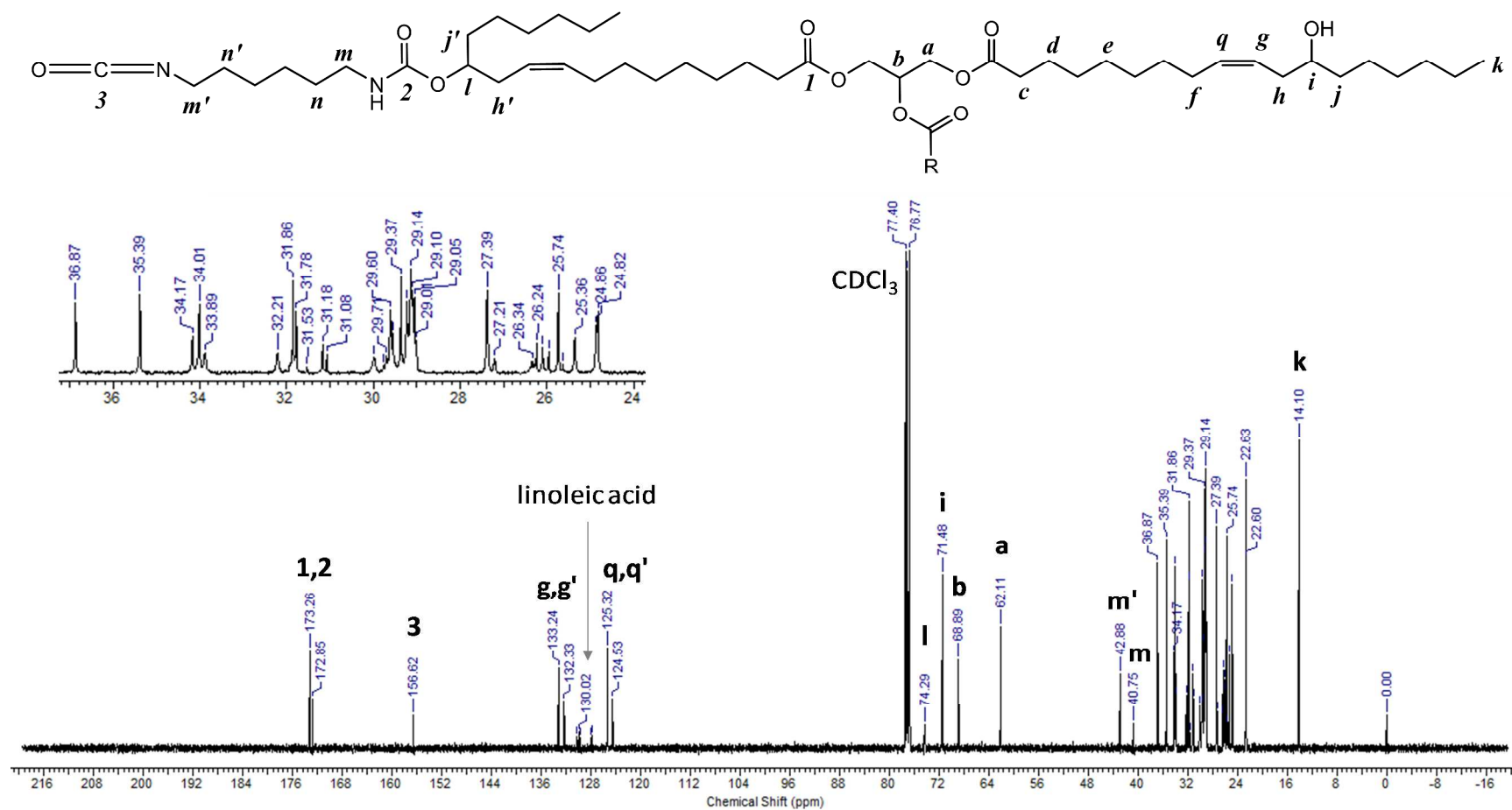
(d)

Figure S2 (cont'd): (a) ^{1}H-, (b) COSY-, (c) ^{13}C DEPT135, and (d) ^{13}C- NMR characterization of a representative NCO-containing prepolymer, obtained in CDCl$_3$ solvent at 300 and 400 MHz for ^{1}H and ^{13}C experiments, respectively.
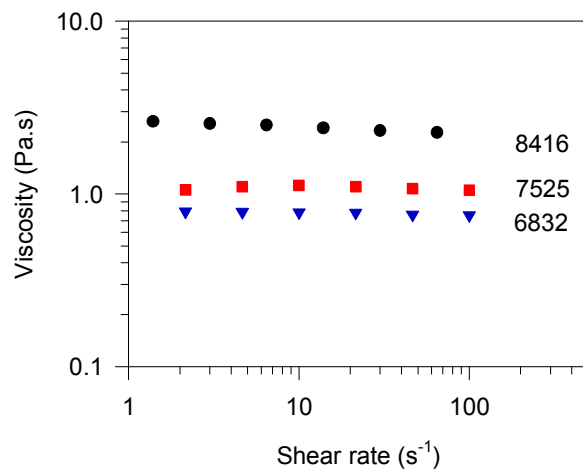
Figure S3: Viscosity flow curves of prepolymers showing decreasing viscosity with increasing

NCO content (prepolymer formulations in order of increasing NCO content: 8416 < 7525 <
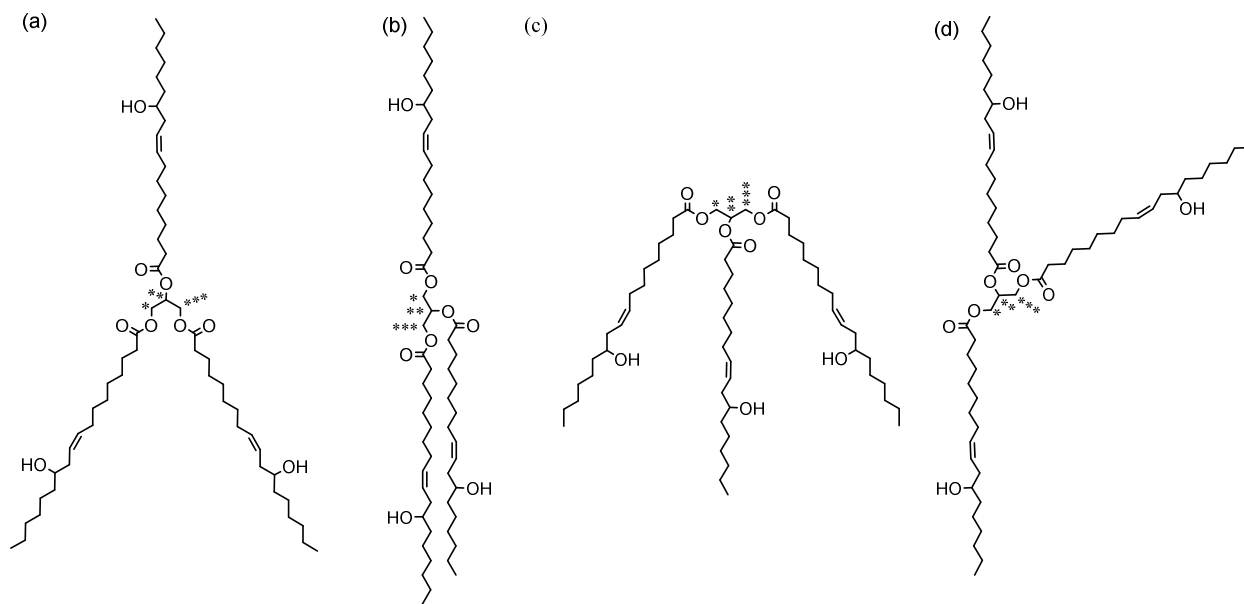
6832).

Figure S4: Conformations typically assumed by triglycerides, reproduced for ricinolein. (a)

Tuning fork; (b) Chair; (c) Trident; (d) Random fluid. *, ** and *** mark sn-1, sn-2 and sn-3

centers, respectively. Structures a-c are usually found in crystallized triglycerides, and structure d

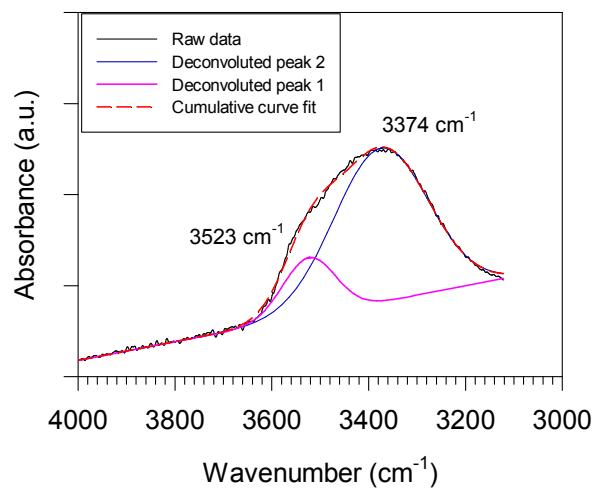shows a representative random structure as expected in fluids.

Figure S5: Deconvolution of FTIR OH peak of castor oil to show hydrogen bonded (3374 cm^{-1})

and non-hydrogen bonded (3523 cm^{-1}) OH peak contributions.