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Oligomers based on cyanoacrylic acid esters

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^{1}H NMR spectra were recorded on a Bruker Avance-400 pulse spectrometer (operating frequency 400.13 MHz) in CDCl3.^{13}C NMR was recorded on a Bruker CXP-200 instrument with an operating frequency of 50.32 MHz at a temperature of 297 K.

MALDI - ToF mass spectrum was recorded using a Bruker Daltonics Ultraflex TOF time-of-flight mass spectrometer in the reflective and linear modes in the corresponding mass range.2,5-dihydroxybenzoic acid was used as a matrix.

Dynamic light scattering was studied on Nanotrack Flex instrument.

The starting materials were obtained from commercial sources and used without purification.

Synthesis of ethyl 2-cyano-3-(hexyloxy)propanoate (**1**).

Hydroquinone (0.05 g, 0.5 mmol), *p*-toluenesulfonic acid (0.05 g, 0.3 mmol) and 2-cyanoacrylic acid (0.05 g, 0.56 mmol) were placed into a 50 ml two-necked round-bottom flask equipped with a magnetic stirrer and SO_2 inlet and outlet system. Then ethyl 2-cyanoacrylate (1.2 ml, 10 mmol) was added. Hexyl alcohol 1.4 ml (11 mmol) was added dropwise with stirring and continuous passage of SO_2. After 1 hour, the SO_2 capillary was removed, the flask was closed, and the mixture was stirred for 5 hours without heating. The liquid product was filtered and excess hexyl alcohol was distilled off in vacuum without heating.

^{1}H NMR ($CDCl_3$) δ: 0.92 (t, 3 H, CH_3), 1.33 (t, 3 H, CH_3), 1.34-1.42 (m, 8 H, CH_2), 1.57-1.61 (m, 2 H, O-CH_2-C(CN)), 3.67 (t, 1 H, CH(CN)), 4.33-4.39 (m, 2H, CH2 O-CH_2-CH_3). Found (%): C, 61.65; H, 7.60; N, 7.04. Calc. for $C_{12}H_{21}ON$ (%): C, 63.44; H, 9.25; N 6.17.

Ethyl 2-cyano-3-(octyloxy)propanoate (**2**), **ethyl 2-cyano-3-(decyloxy)propanoate** (**3**) and **ethyl 2-cyano-3-(dodecyloxy)propanoate** (**4**)were obtained by a similar procedure.

Table S1.

	N, %		C, %		H, %	
Compound	Found	Calc.	Found	Calc.	Found	Calc.
2	5.45	5.49	65.98	65.88	9.32	9.8
3	3.79	4.95	69.18	67.84	10.49	10.25
4	3.34	4.52	70.84	69.68	10.64	10.32

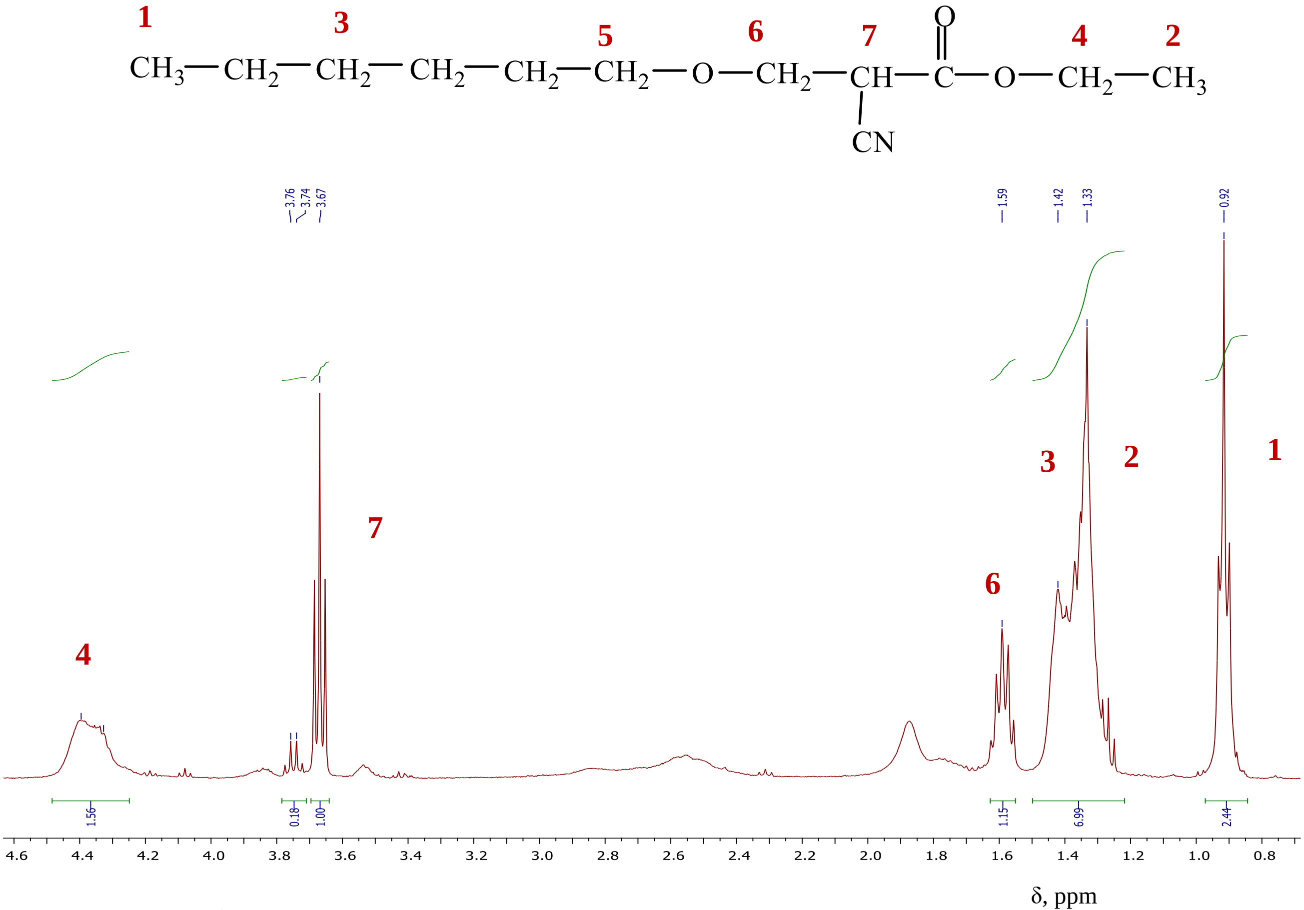

Figure S1. ^{1}H NMR spectrum of the compound 1.

Figure S2 shows the ^{13}C NMR spectrum of the reaction product of hexanol and ethyl 2-cyanoacrylate (**1**). The spectrum of compound **1** contains signals of the carbonyl group 161.95 ppm. The shift of the signal relative to the carbonyl group of cyanoacrylic acid is caused by the presence of a donor ethoxy substituent of the ester group. The signal at 143.75 ppm, related to the carbon atom at the double bond of ethyl 2-cyanoacrylate, is absent in the spectrum. The signal at 141.47 ppm most likely refers to the CH group of the ABC system formed after the addition of hexanol at the double bond. An intense signal at 113.98 ppm belongs to the carbon of the nitrile group. At the same time, the spectrum does not contain the signal of the quaternary carbon atom at the double bond 113.98 ppm, which is characteristic of the starting ethyl 2-cyanoacrylate. Spectrum of **1** contains also signals of the main carbon chain of the hexanol substituent: the signal of the methyl group at 14.41 ppm and of the CH_2 groups of the main chain: 22.97 ppm, 25.68 ppm, 31.52 ppm and 32.52 ppm.

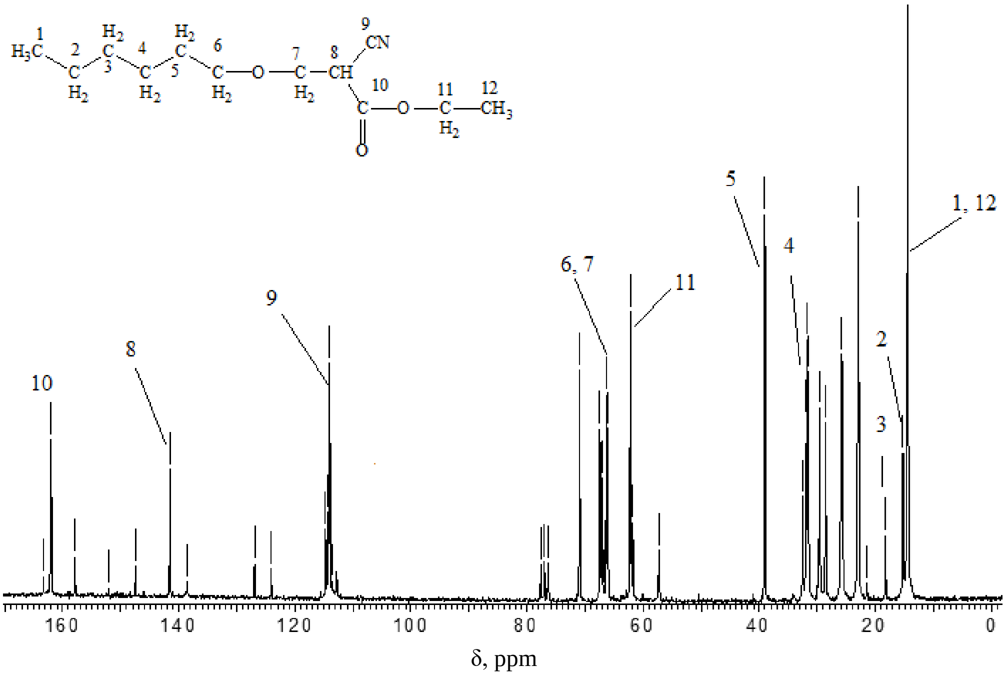

Figure S2. ^{13}C NMR spectrum of compound **1**.

In addition, the spectrum contains two types of signals of CH_2O groups: 62.25 ppm related to the CH_2O group of the ethyl radical of the ester group, as well as 66.05-66.14 ppm, attributed to CH_2O group attached to the double bond and 66.32 ppm, attributed to CH_2O group of the alkyl substituent attached to the double bond.

The preparation of the oligomer O1 from compound 1.

Compound **1** (1 ml) was added dropwise with stirring to distilled water (5 ml). A two-phase system consisting of an aqueous suspension and a transparent layer of hexyl alcohol was formed. The layers were separated using a separating funnel, then additionally washed from alcohol residues with chloroform. The resulting suspension was dried from water on a rotary evaporator.

The other oligomers **O2**, **O3** and **O4** were prepared by a similar procedure.

Obtaining capsules of oligo(ethyl-2-cyanoacrylate).

The reaction product of ethyl 2-cyanoacrylate and alkanol (1 ml) was added dropwise with stirring to distilled water (5 ml). A two-phase system was formed consisting of an aqueous suspension and a transparent layer of alcohol immiscible with water. The layers were separated with a separating funnel. The suspension was lyophilized to leave a powder of oligo(ethyl 2-cyanoacrylate) capsules.

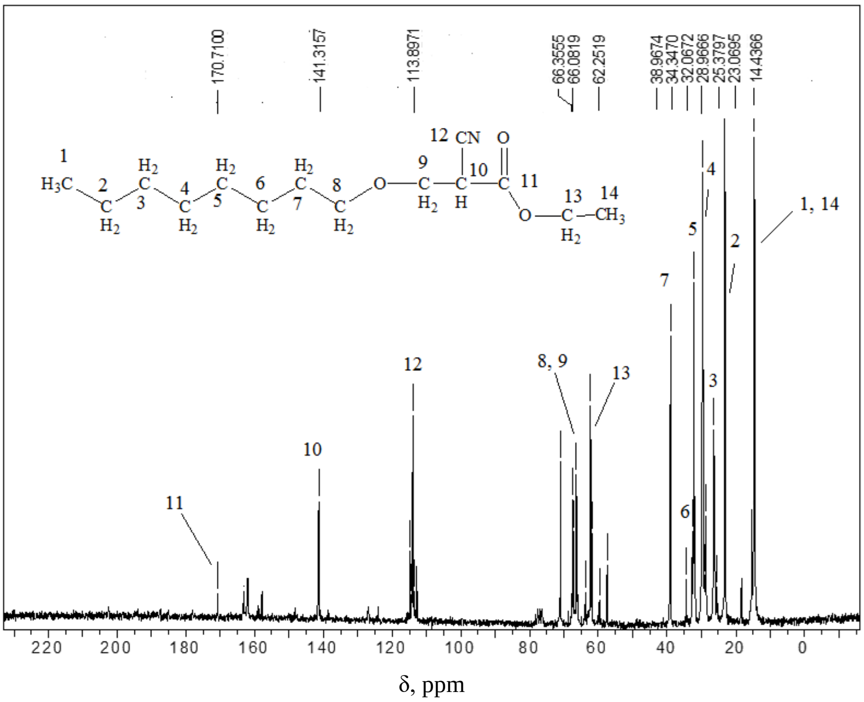

Figure S3. C^{13} NMR spectrum of the adduct of ethyl 2-cyanoacrilate and octanol (**2**)

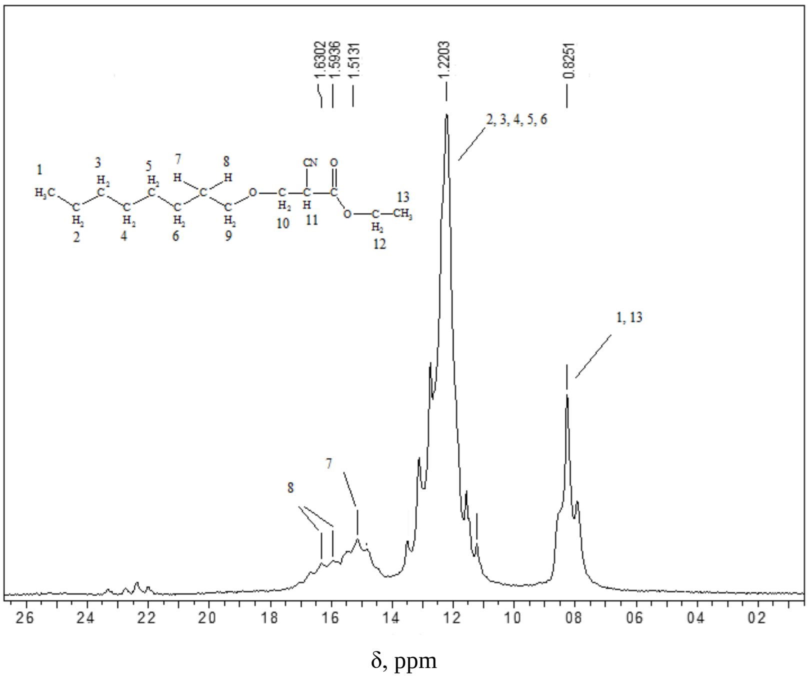

Figure S4. ^{1}H NMR spectrum of compound **2**, range from 0 to 2 ppm

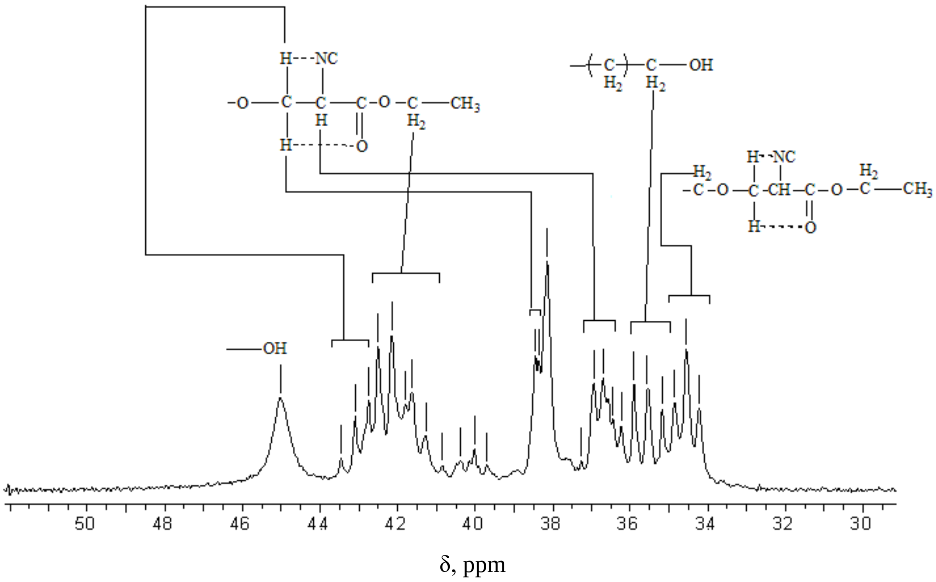

Figure S5. ^{1}H NMR spectrum of compound **2**, range from 3 to 5 ppm.

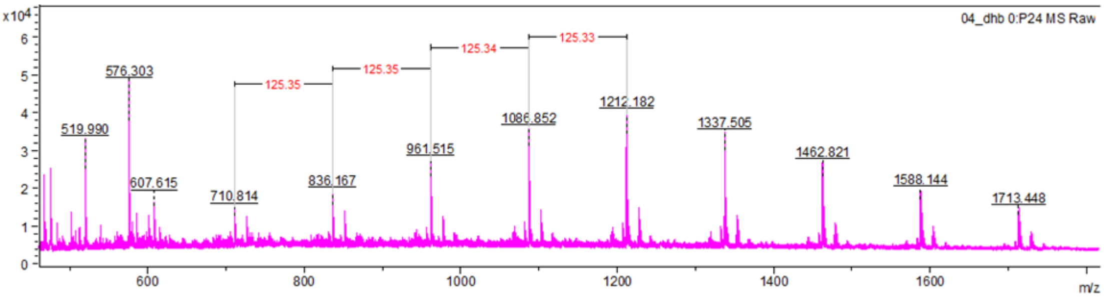

Figure S6. MALDI-TOF MS spectrum of the **O2** oligomer

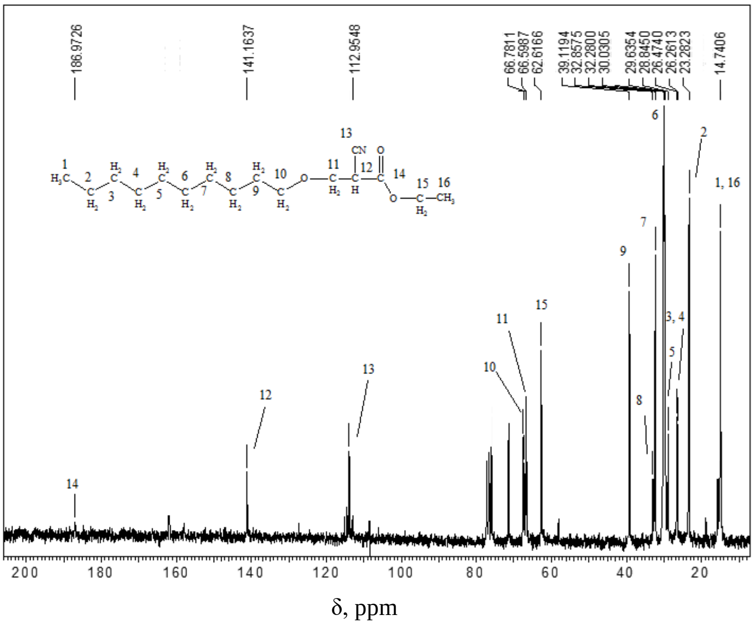

Figure S7. ^{13}C NMR spectrum of compound **3**.

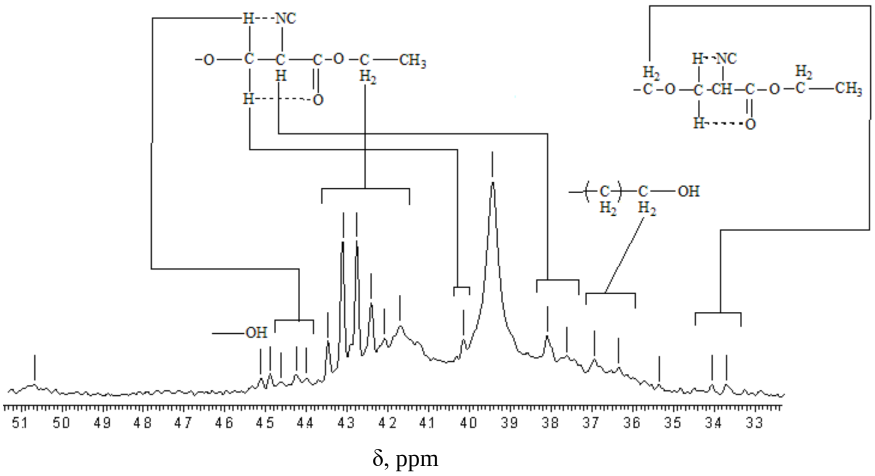

Figure S8.^{1}H NMR spectrum of compound **3**, range from 3 to 5 ppm.

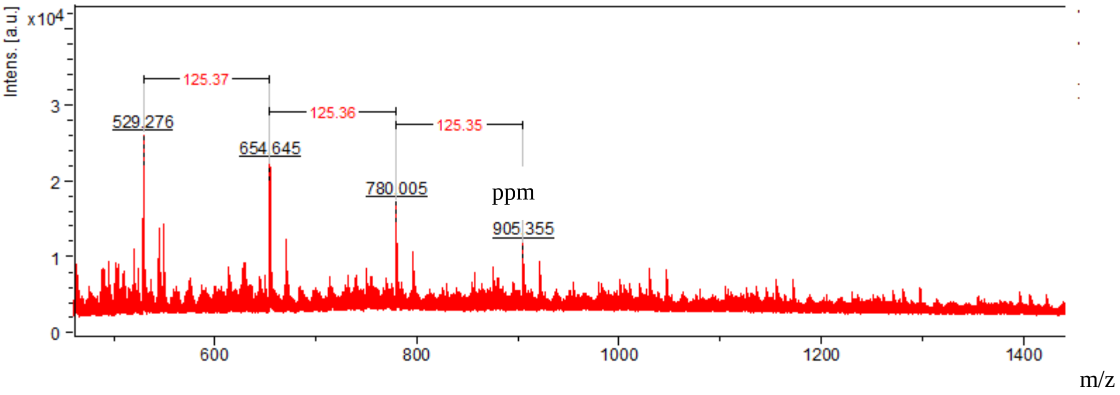

Figure S9. MALDI-TOF MS spectrum of the **O3** oligomer

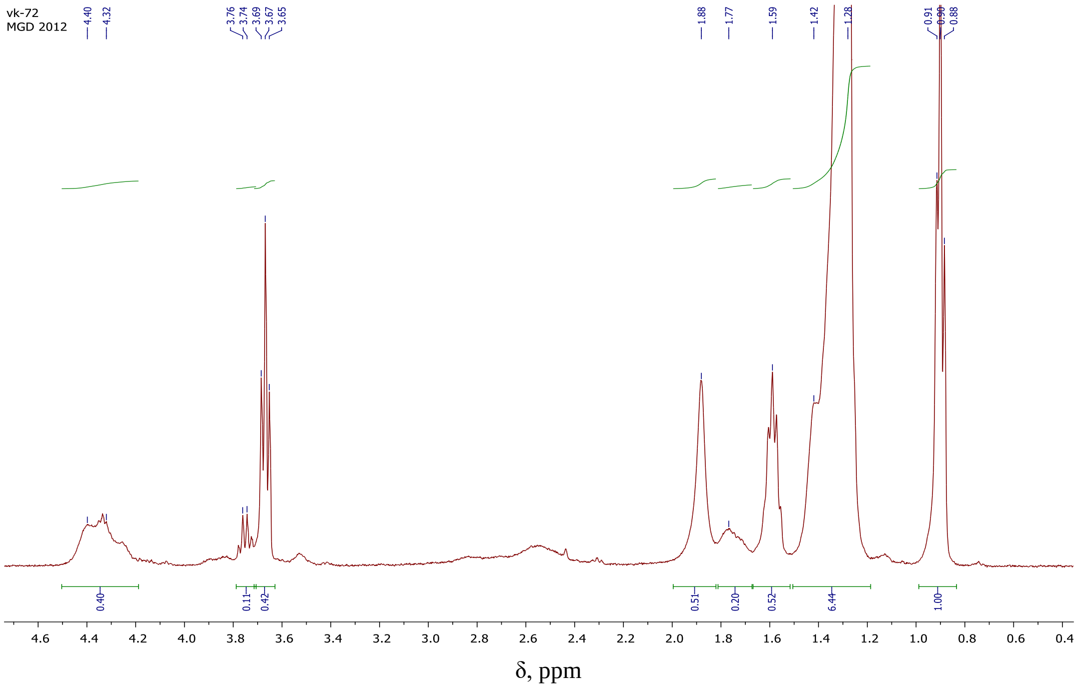

Figure S10. ^{1}H NMR spectrum of compound **4.**

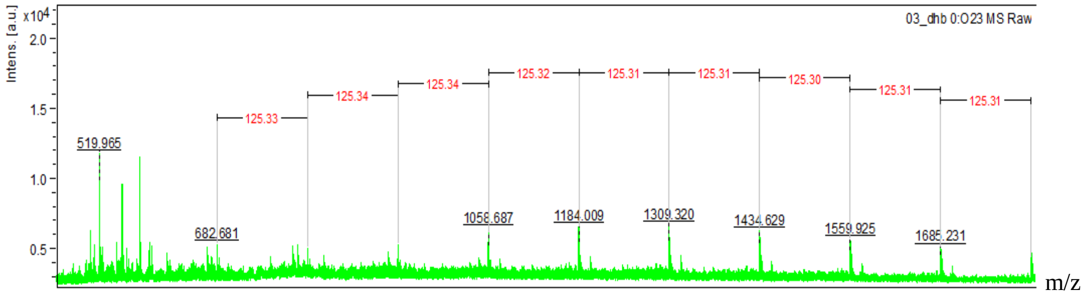

Figure S11. MALDI-TOF MS spectrum of the **O4** oligomer