

Supplementary information

Enzymatic Synthesis of biobased Aliphatic-Aromatic Oligoesters Using 5,5'- Bis(hydroxymethyl)furoin as Building Block

Serena Baraldi,¹ Giancarlo Fantin,¹ Graziano Di Carmine,¹ Daniele Ragno,¹ Arianna Brandolese,¹
Alessandro Massi,¹ Olga Bortolini,¹ Nicola Marchetti,¹ and Pier Paolo Giovannini*¹

¹Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via L. Borsari, 46
44121 Ferrara (Italy)

e-mail: pierpaolo.giovannini@unife.it

Table of contents

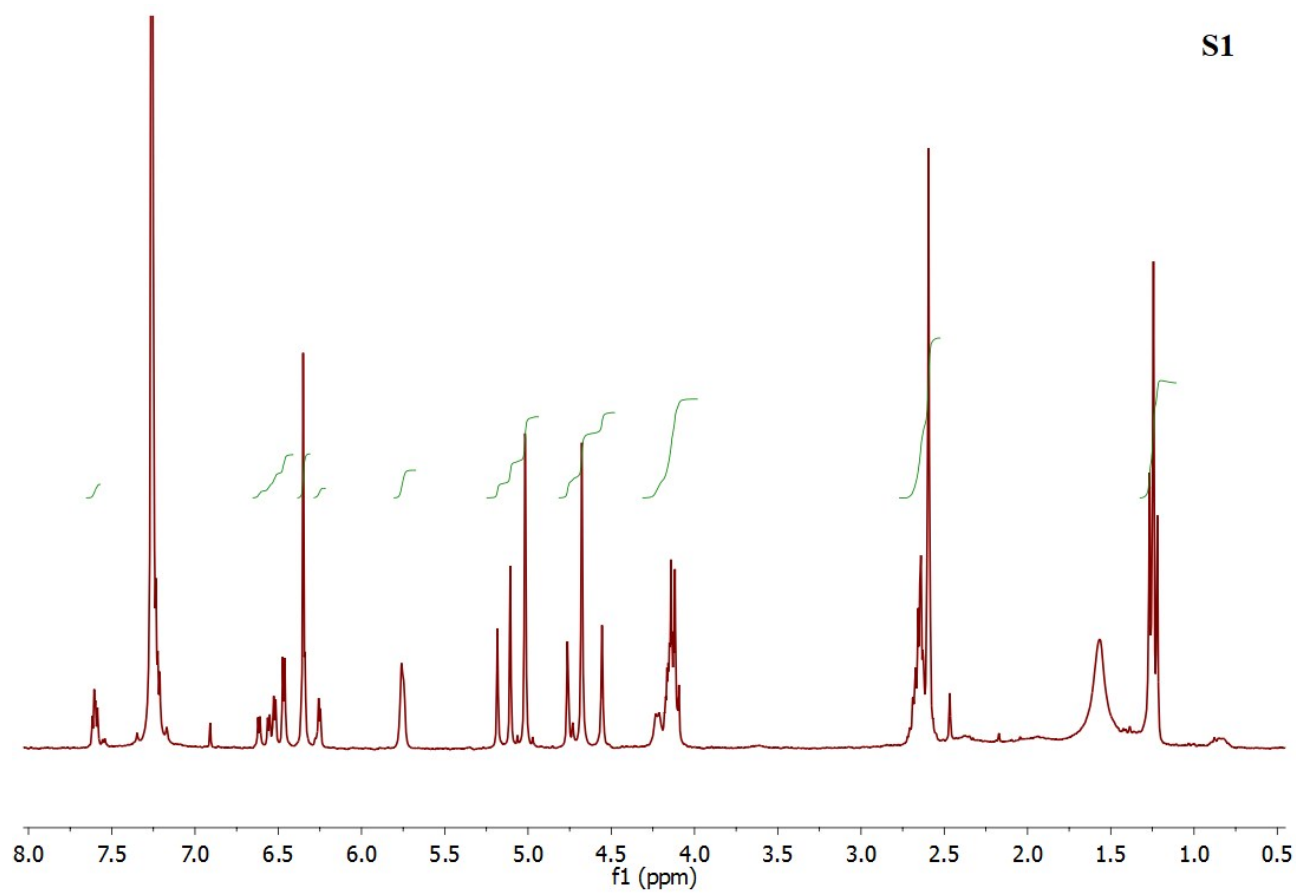
NMR spectra

¹ H NMR of the mixture of esters 1 , 2 and 3 after chromatography	S1
¹ H NMR of the reaction mixture after 1.5 h at 80 °C (760 mm Hg)	S2
¹ H NMR 2D COSY of the reaction mixture after 6 h at 80 °C (3h, 760 and 3h 300 mm Hg)	S3
¹ H NMR of the reaction mixture after 6 h at 50 °C and 4 h at 60 °C (at 18 mm Hg)	S4
¹ H NMR of the oligomers obtained from the reaction of DHMF with diethyl succinate	S5
¹³ C NMR of the oligomers obtained from the reaction of DHMF with diethyl succinate	S6
¹ H NMR of the mixture of esters 6 , 7 and 8 after chromatography	S7
¹ H NMR of the oligomers obtained from the reaction of DHMF with diethyl sebacate	S8
¹³ C NMR of the oligomers obtained from the reaction of DHMF with diethyl sebacate	S9

HPLC-MS chromatograms

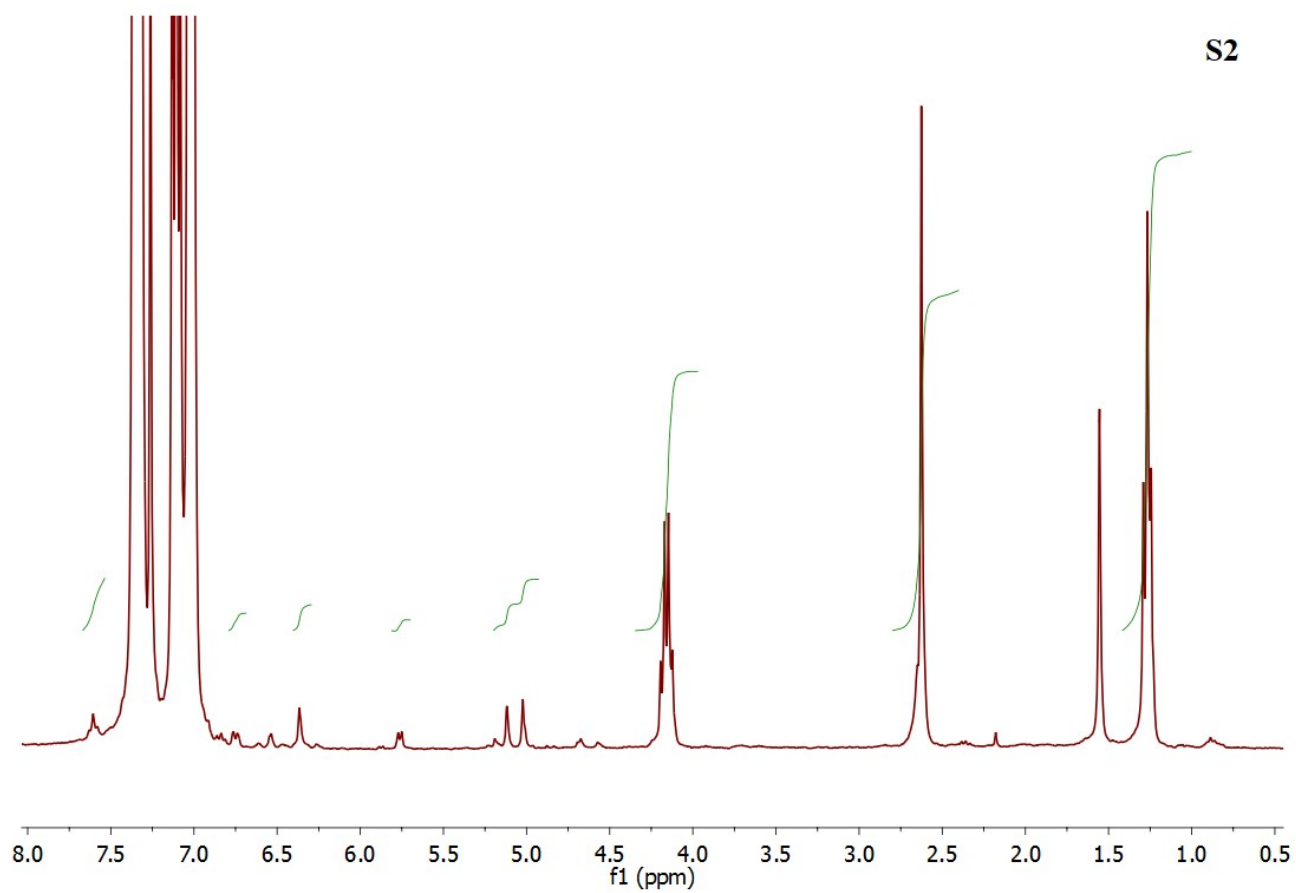
HPLC-MS of the mixture of products 1 , 2 and 3	S10
HPLC-MS of byproduct 5	S11
HPLC-MS of the oligomers mixture obtained from the reaction with diethyl succinate	S12
HPLC-MS of the mixture of products 6 , 7 and 8	S13
HPLC-MS of the oligomers mixture obtained from the reaction with diethyl sebacate	S14

S1

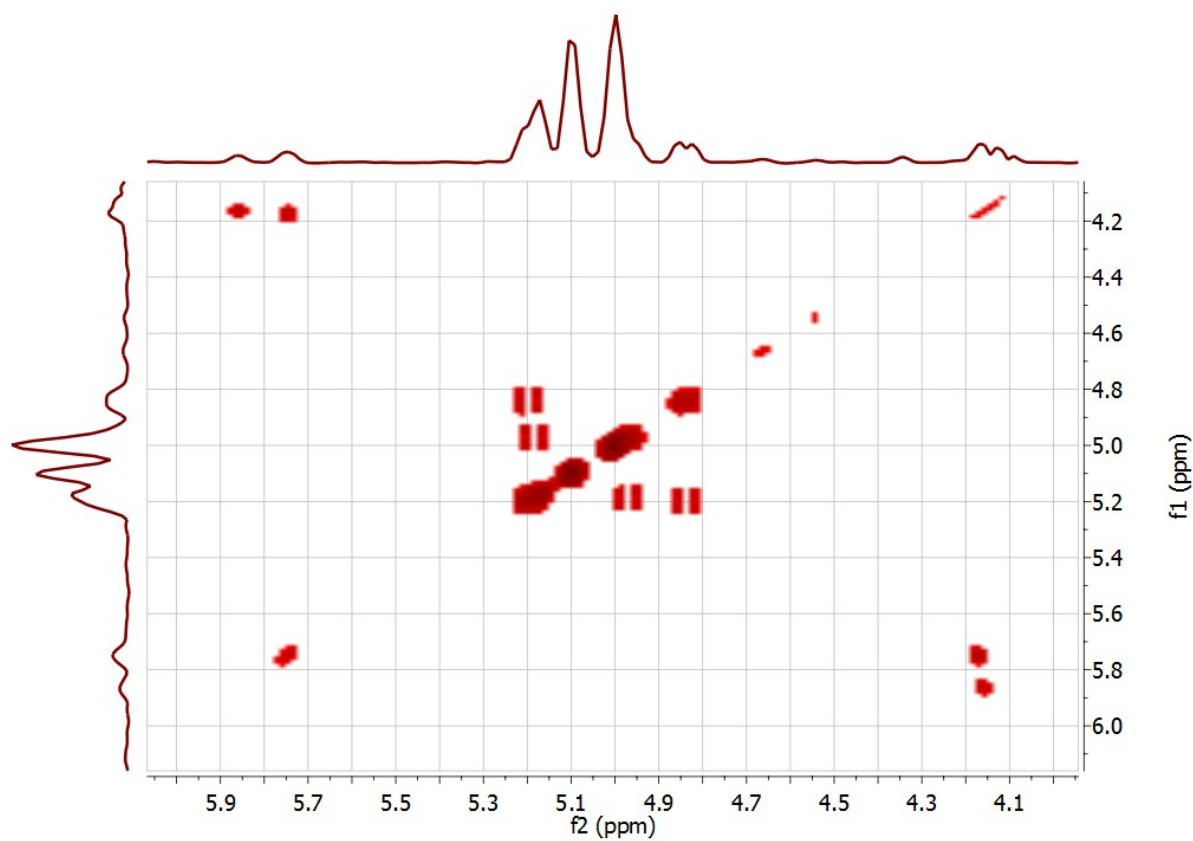
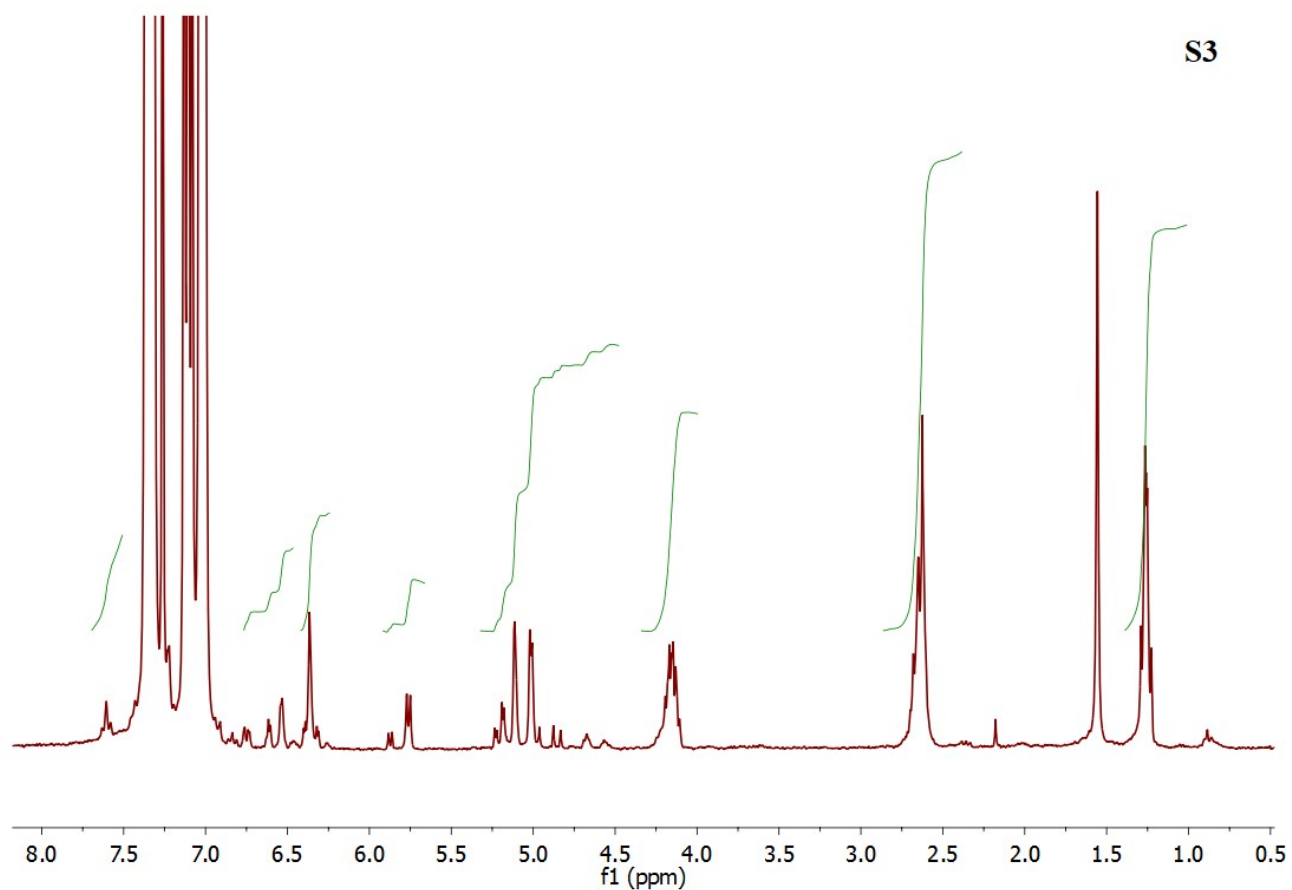


^1H NMR of the mixture of esters **1**, **2** and **3** after chromatography

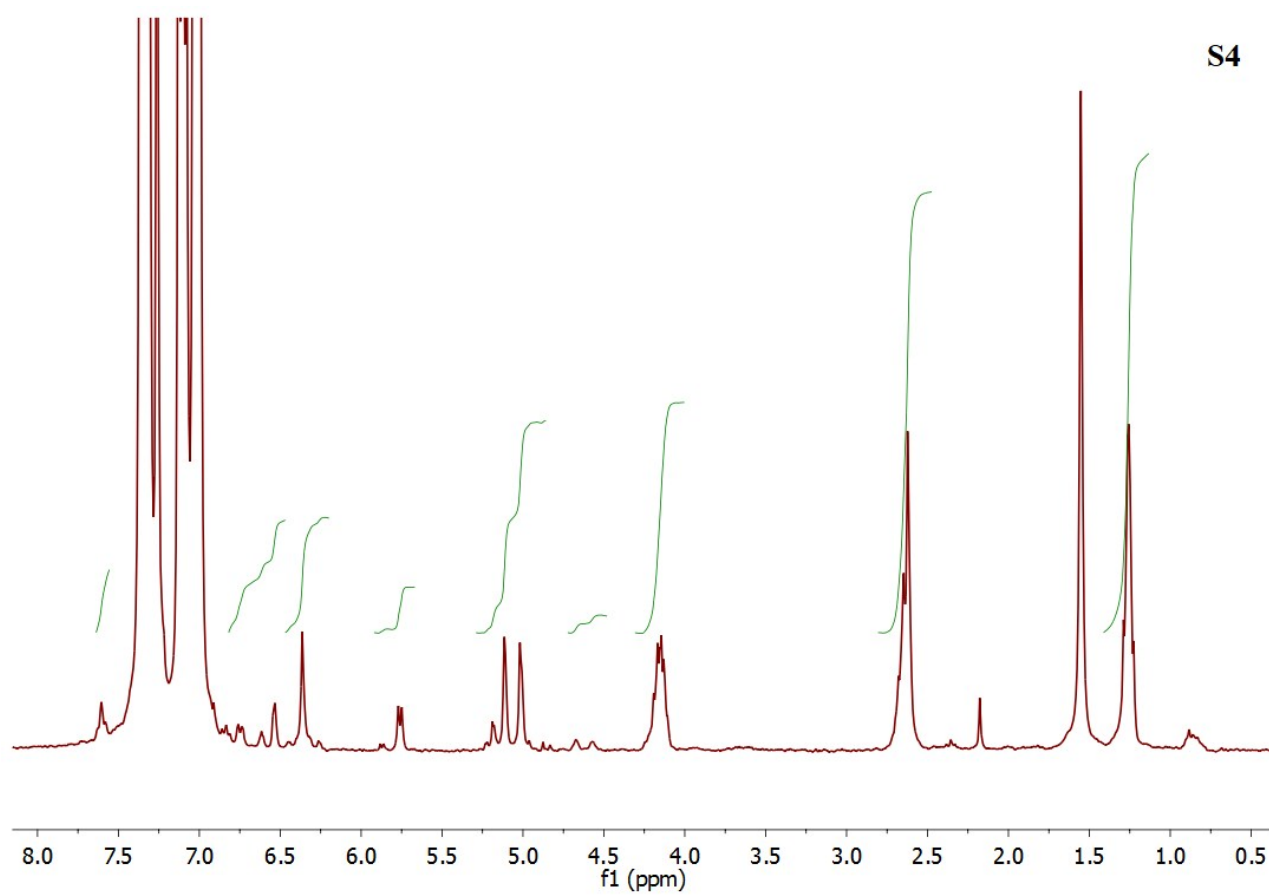
S2



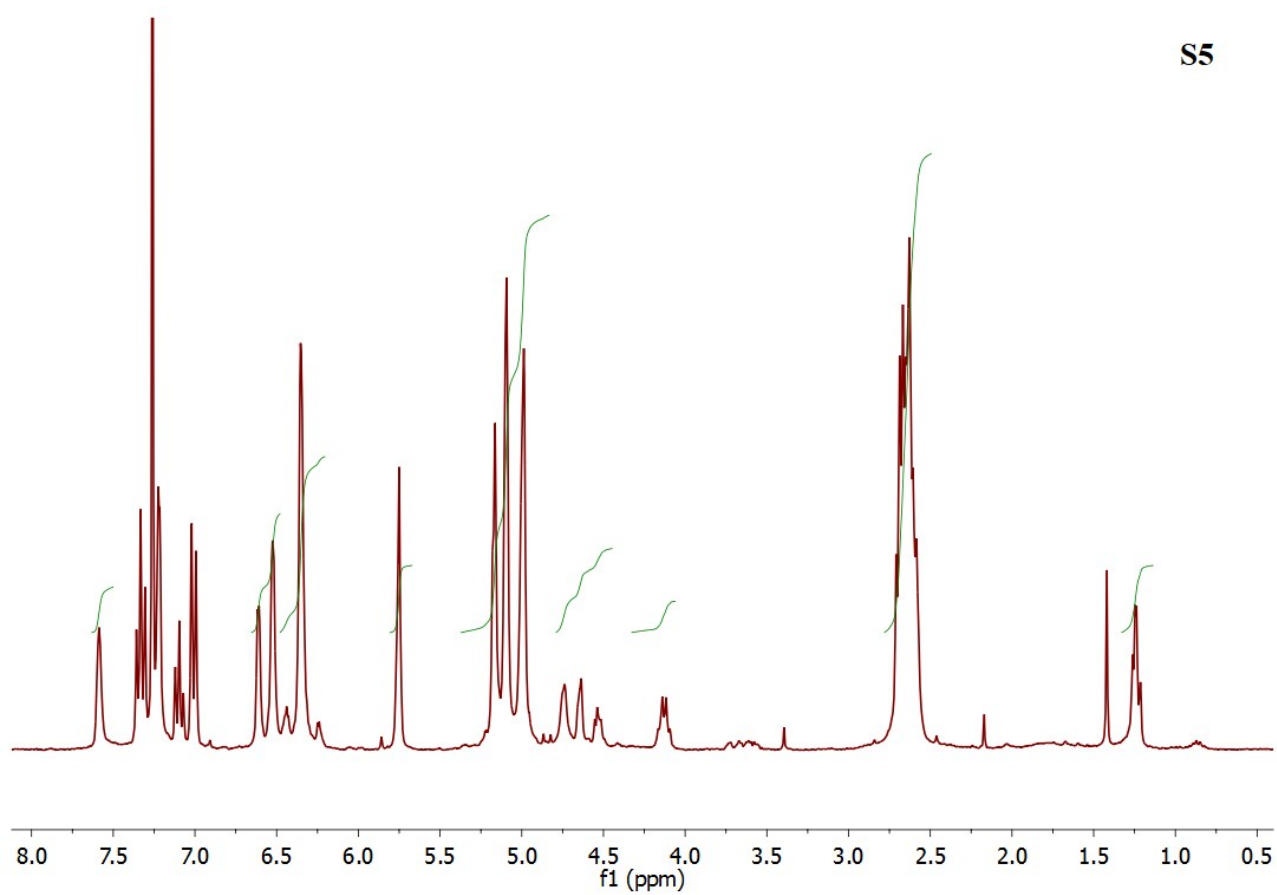
^1H NMR of the reaction mixture after 1.5 h at 80 °C (760 mm Hg)



¹H NMR and 2D COSY of the reaction mixture after 6 h at 80 °C (3h at 760 and 3h at 300 mm Hg)

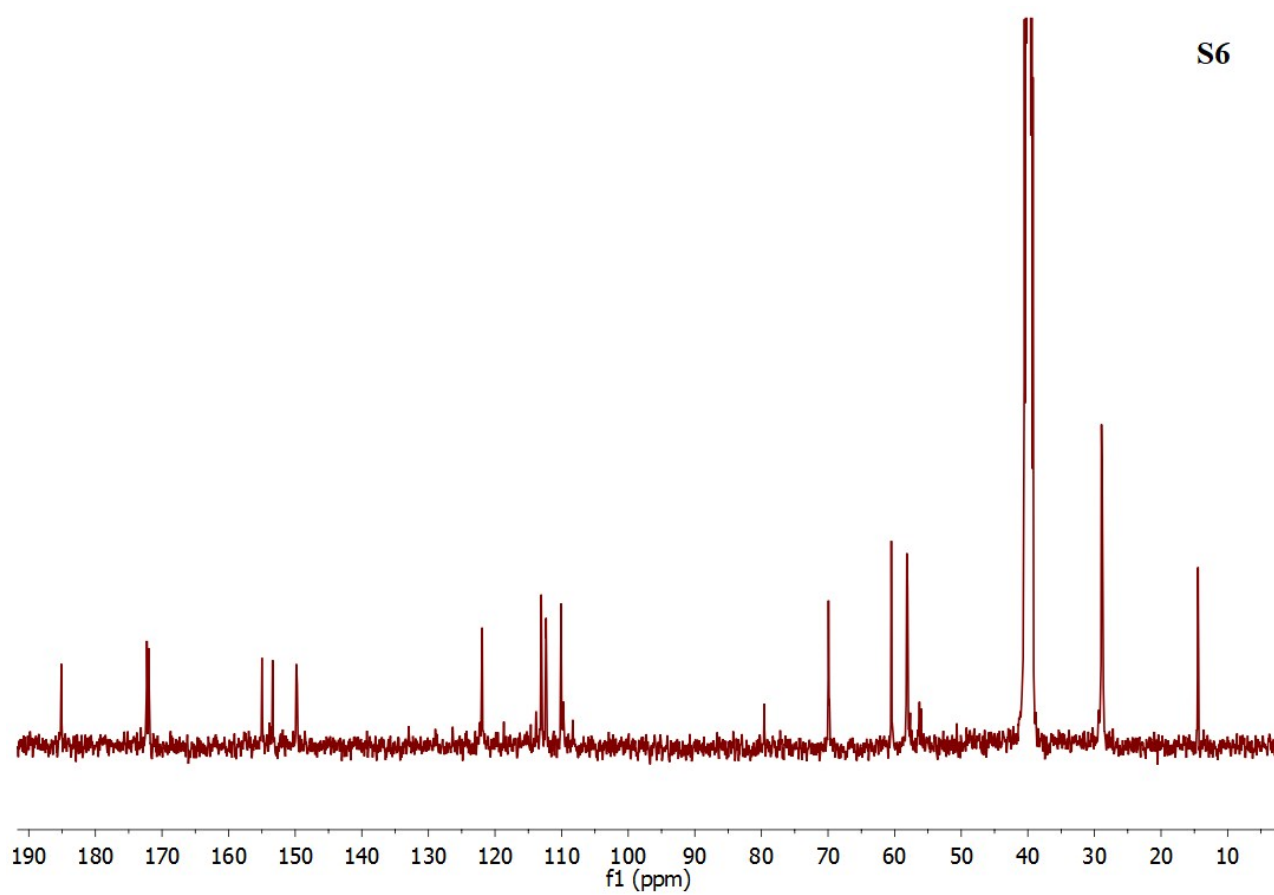


^1H NMR of the reaction mixture after 6 h at 50 °C and 4 h at 60 °C (at 18 mm Hg)

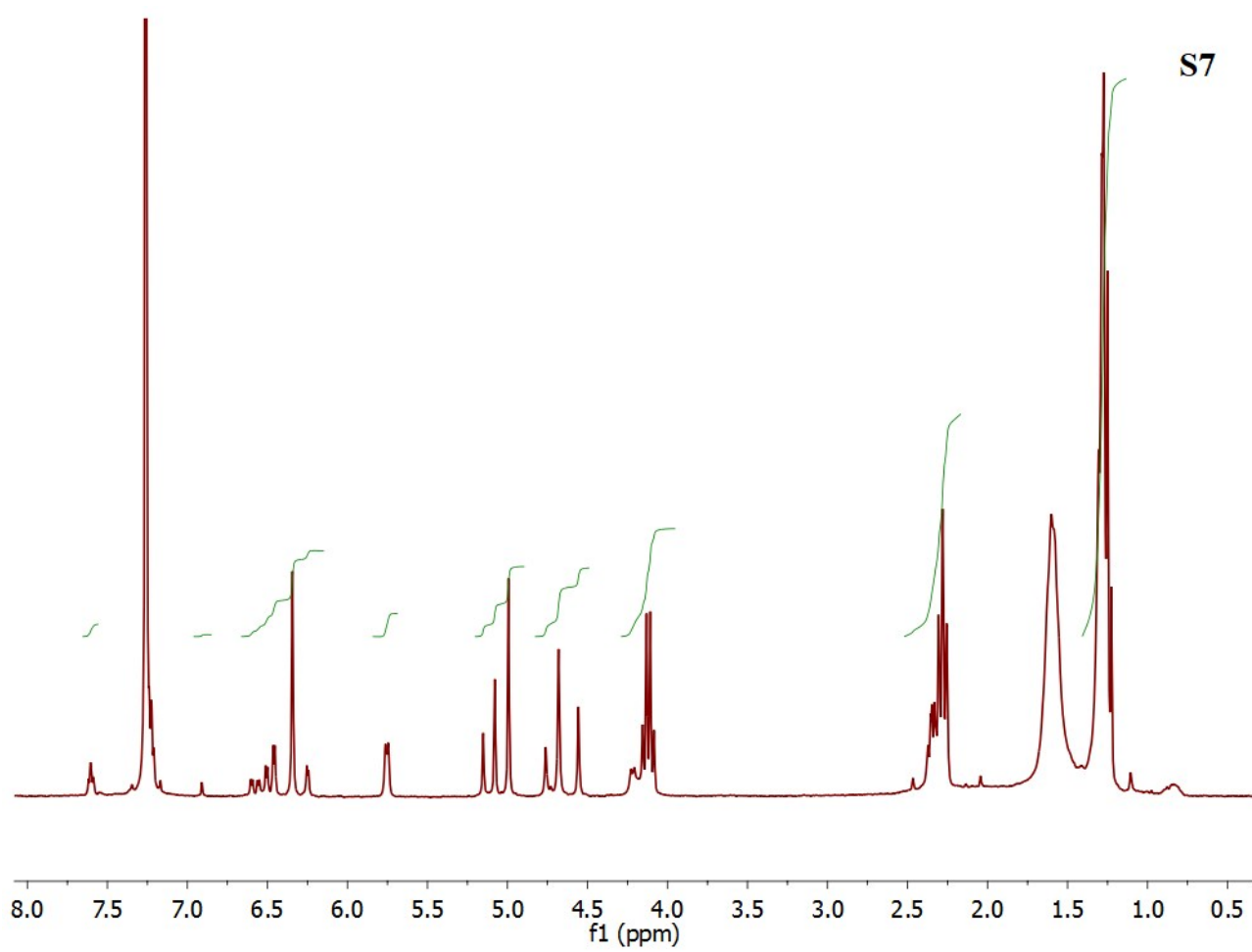


^1H NMR of the oligomers obtained from the reaction of DHMF with diethyl succinate

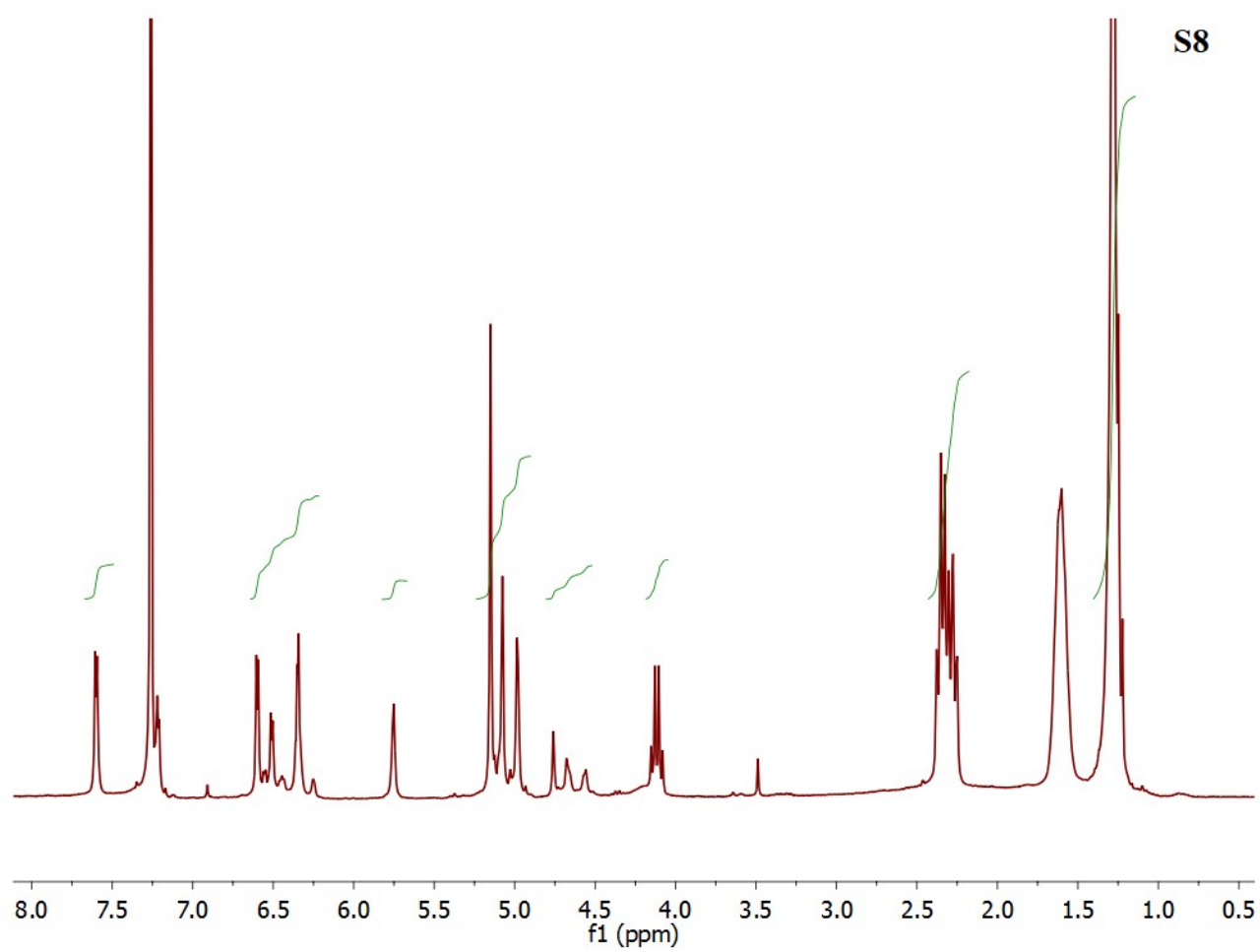
S6



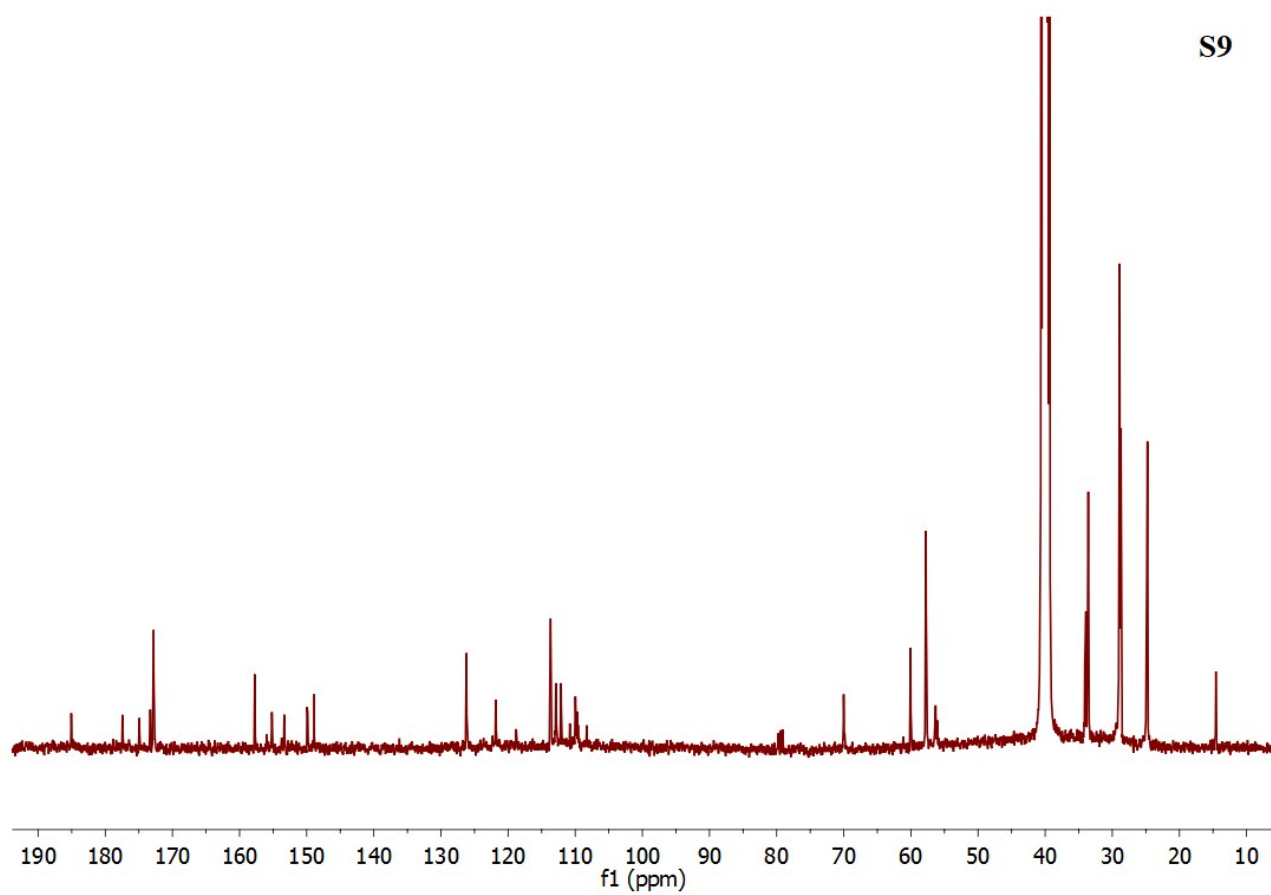
^{13}C NMR of the oligomers obtained from the reaction of DHMF with diethyl succinate



^1H NMR of the mixture of esters **6**, **7** and **8** after chromatography

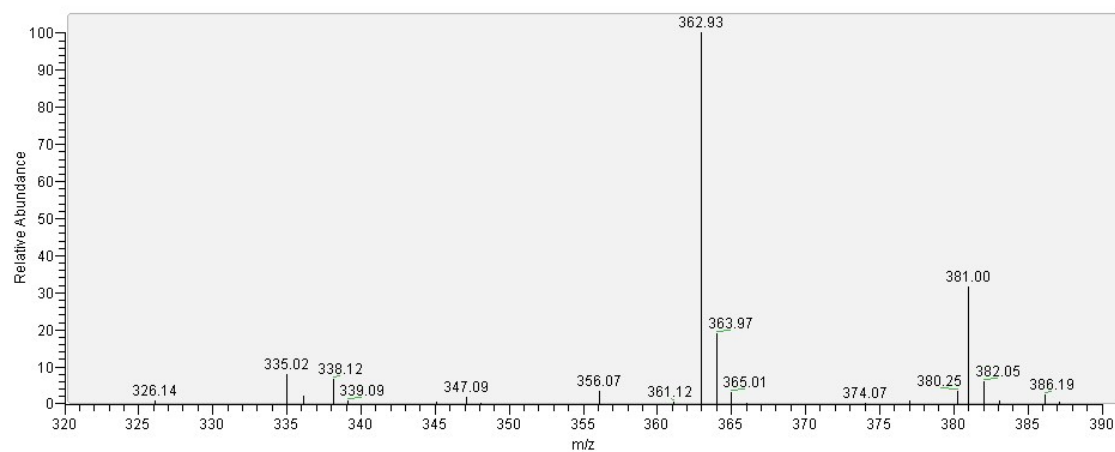
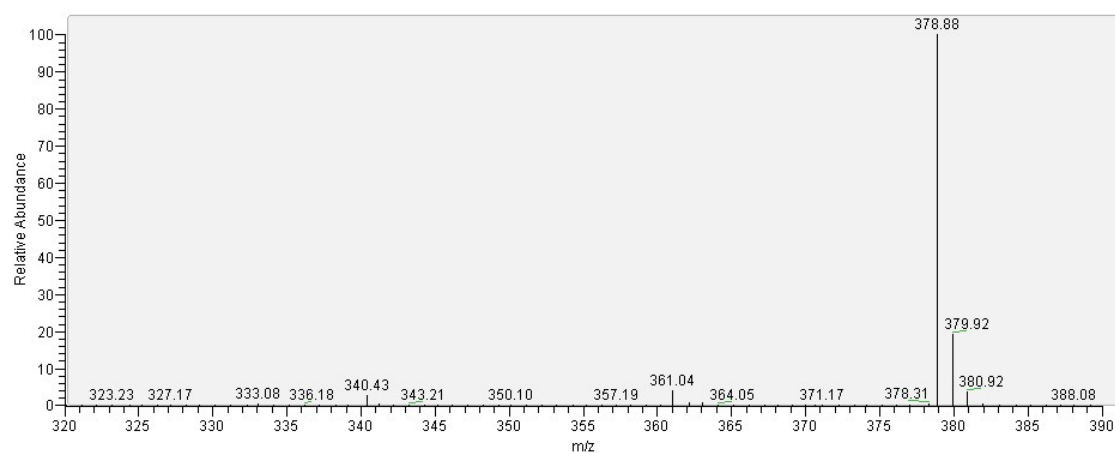
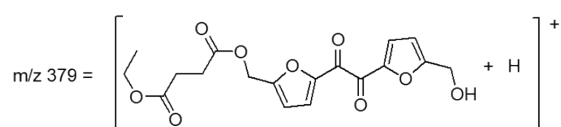
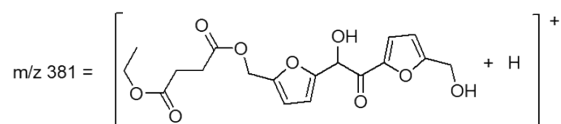
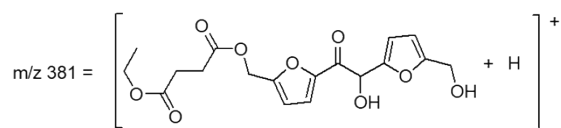
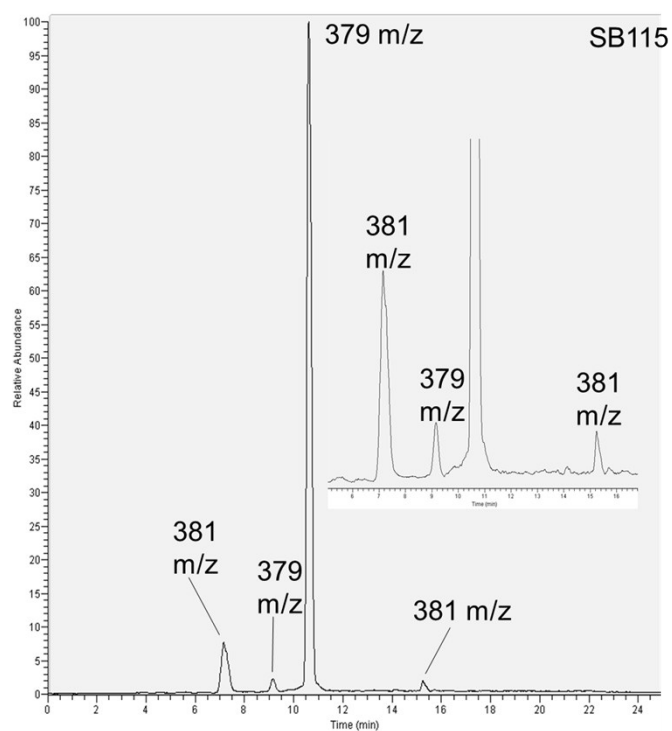


^1H NMR of the oligomers obtained from the reaction of DHMF with diethyl sebacate

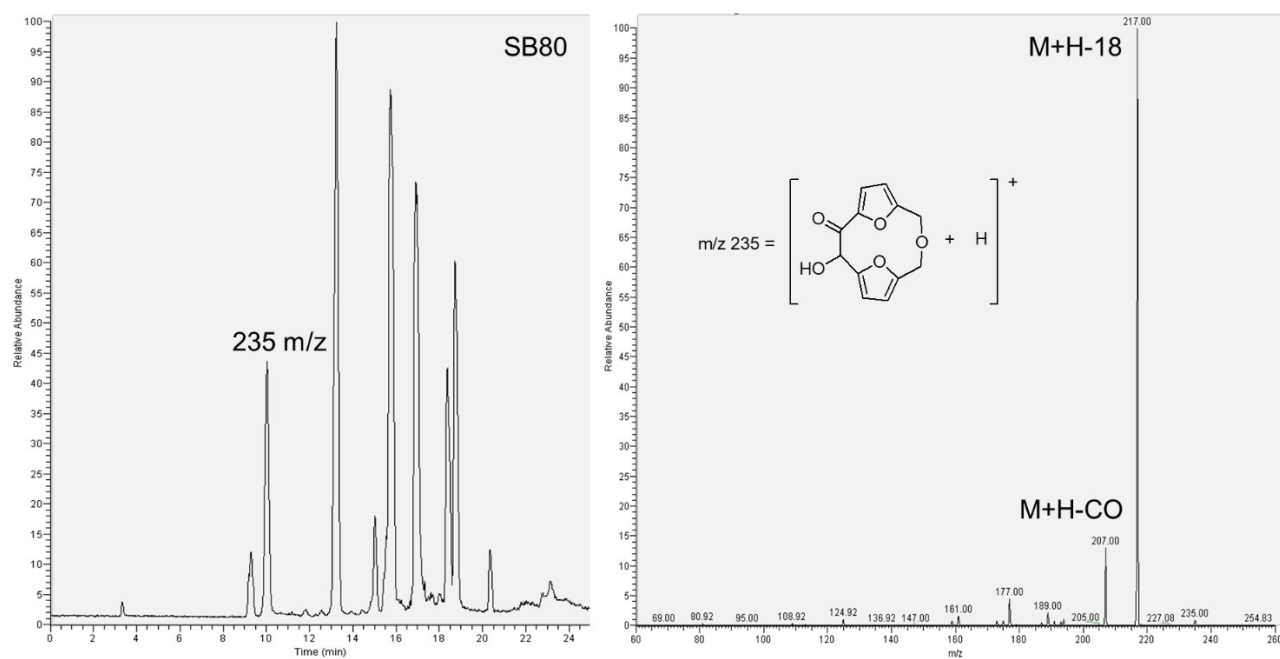


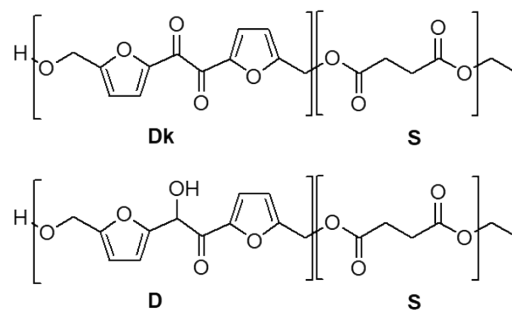
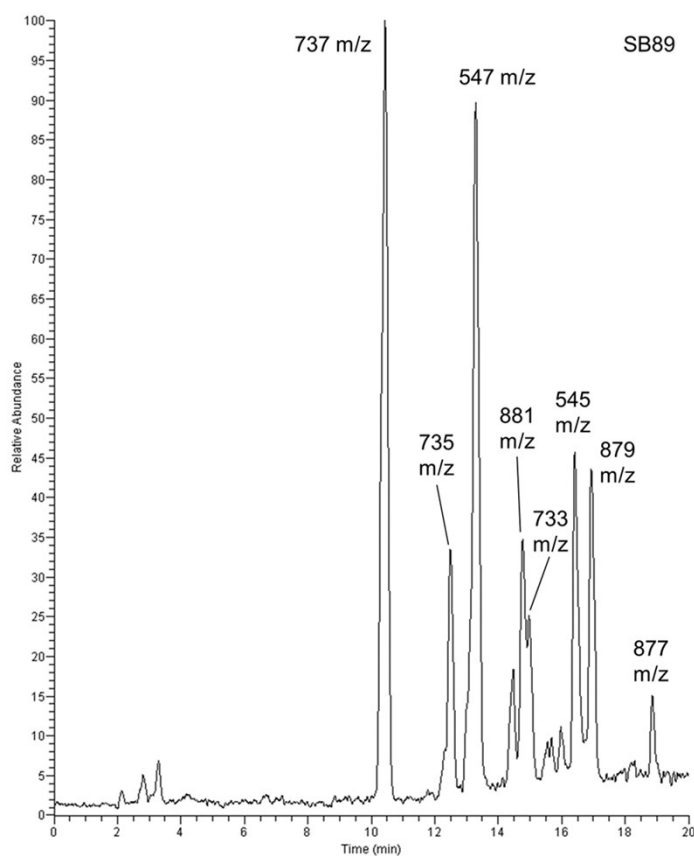
^{13}C NMR of the oligomers obtained from the reaction of DHMF with diethyl sebacate

S10



HPLC-MS of the mixture of products **1**, **2** and **3**

HPLC-MS of byproduct **5**



$$m/z\ 545 = [\text{Et-S-Dk-S-Et} + \text{Na}]^+$$

$$m/z\ 547 = [\text{Et-S-D-S-Et} + \text{Na}]^+$$

$$m/z\ 733 = [\text{H-Dk-S-Dk-S-Et} + \text{Na}]^+$$

$$m/z\ 735 = [\text{H-D-S-Dk-S-Et} + \text{Na}]^+$$

$$m/z\ 737 = [\text{H-D-S-D-S-Et} + \text{Na}]^+$$

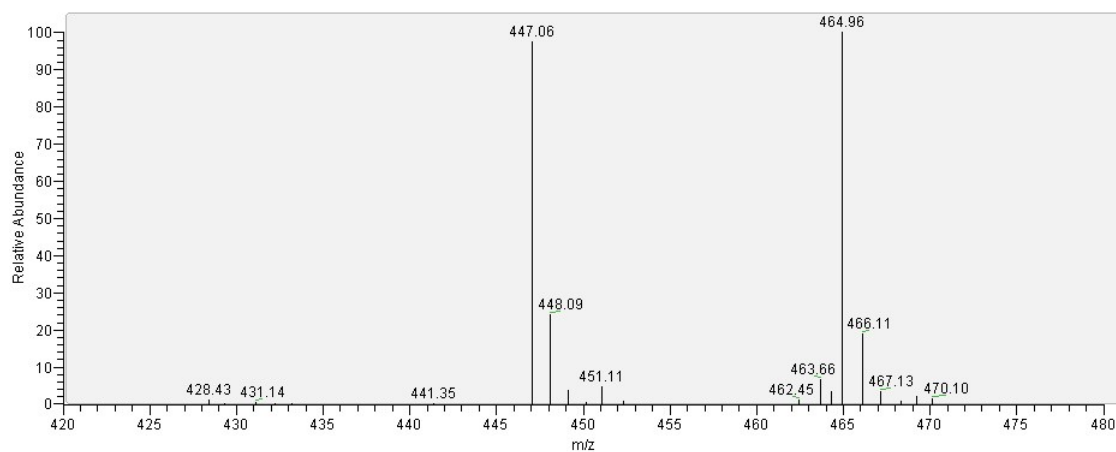
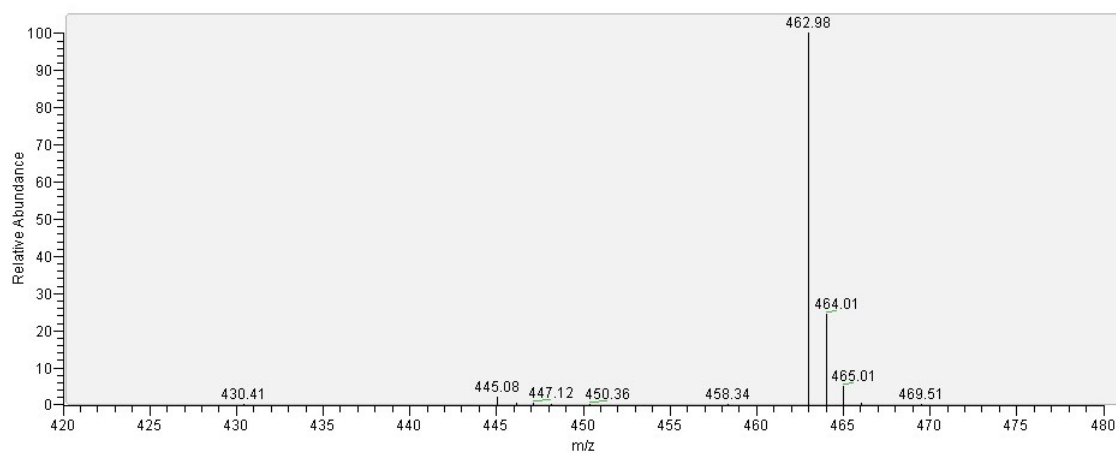
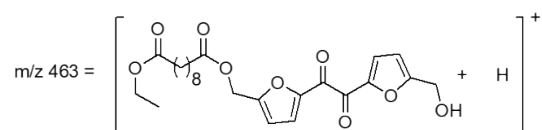
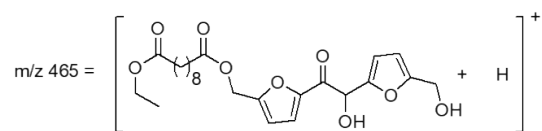
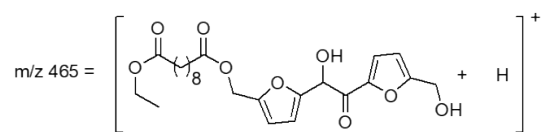
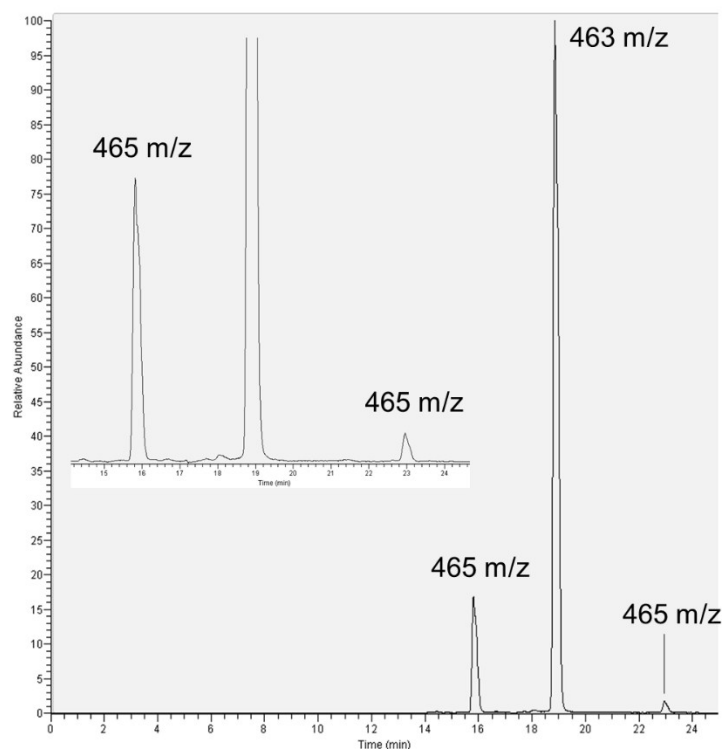
$$m/z\ 877 = [\text{Et-S-Dk-S-Dk-S-Et} + \text{Na}]^+$$

$$m/z\ 879 = [\text{Et-S-D-S-Dk-S-Et} + \text{Na}]^+$$

$$m/z\ 881 = [\text{Et-S-D-S-D-S-Et} + \text{Na}]^+$$

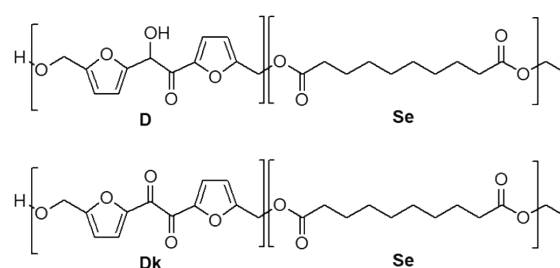
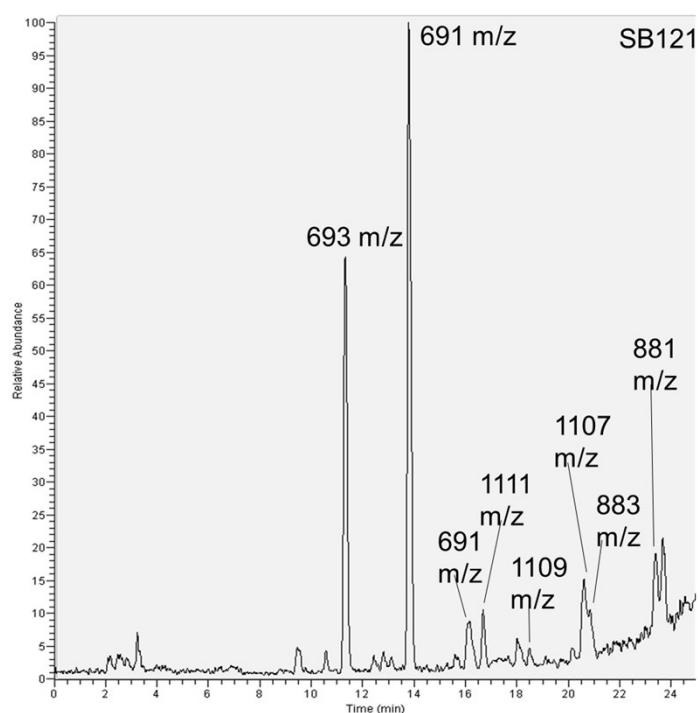
HPLC-MS of the oligomers mixture obtained from the reaction with diethyl succinate

S13



HPLC-MS of the mixture of products **6**, **7** and **8**

S14



- $m/z\ 691 = [\text{Et-Se-Dk-Se-Et} + \text{H}]^+$
- $m/z\ 693 = [\text{Et-Se-D-Se-Et} + \text{H}]^+$
- $m/z\ 881 = [\text{H-D-Se-Dk-Se-Et} + \text{H}]^+$
- $m/z\ 883 = [\text{H-D-Se-D-Se-Et} + \text{H}]^+$
- $m/z\ 1107 = [\text{Et-Se-Dk-Se-Dk-Se-Et} + \text{H}]^+$
- $m/z\ 1109 = [\text{Et-Se-Dk-Se-D-Se-Et} + \text{H}]^+$
- $m/z\ 1111 = [\text{Et-Se-D-Se-D-S-Et} + \text{H}]^+$

HPLC-MS of the oligomers mixture obtained from the reaction with diethyl sebacate