Lipase-catalysed polycondensation of levulinic acid derived diol-diamide monomers: access to new poly(ester-*co*-amide)s

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Supporting Information

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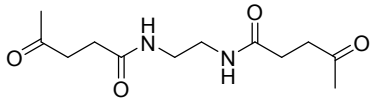
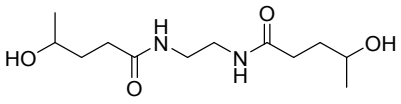
1. Characterization data of monomers

***N,N'*-(ethane-1,2-diyl)-bis-(4-oxopentanamide)** (**1a**).



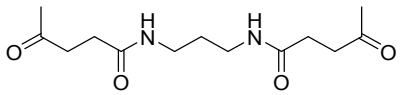
White solid (Yield= 77 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 2.08 (s, 6H, -C***H***$_3$), 2.26 (t, ^3J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.62 (t, ^3J= 6.9 Hz, 4H, -C***H***$_2$-CO-CH$_3$), 3.01-3.10 (m, 4H, -C***H***$_2$-NH-), 7.84 (s, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 29.1 (2C, -***C***H$_2$-CO-NH-), 29.7 (2C, -***C***H$_3$), 38.0 (2C, -***C***H$_2$-NH-), 38.4 (2C, -***C***H$_2$-CO-CH$_3$), 171.4 (2C, -NH-***C***=O-), 207.6 (2C, -***C***=O-).

***N,N'*-(ethane-1,2-diyl)-bis-(4-hydroxypentanamide) (2a).**



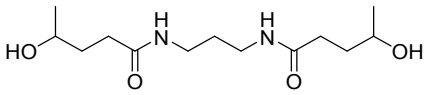
White solid (Yield= 67 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.02 (d, ^3J= 6.2 Hz, 6H, -C***H***$_3$), 1.43-1.62 (m, 4H, -C***H***$_2$-CH(OH)-), 2.00-2.19 (m, 4H, -C***H***$_2$-CO-NH-), 2.94-3.13 (m, 4H, -C***H***$_2$-NH-), 3.48-3.60 (m, 2H, -C***H***(OH)-), 4.45 (d, ^3J= 4.5 Hz, 2H, -O***H***), 7.79 (s, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 22.5 (2C, -***C***H$_3$), 31.1 (2C, -***C***H$_2$-CO-NH-), 33.8 (2C, -CH(OH)-***C***H$_2$-), 37.4 (2C, -***C***H$_2$-NH-), 64.5 (2C, -***C***H(OH)-), 171.8 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{12}H_{24}N_2O_4Na$: 283.1635 $[M+Na]^+$; found: 283.1634.

***N,N'*-(propane-1,3-diyl)-bis-(4-oxopentanamide) (1b).**



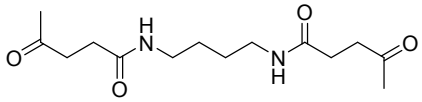
White solid (Yield= 69 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.43-1.54 (m, 2H, -C***H***$_2$-CH$_2$-NH-), 2.08 (s, 6H, -CH$_3$), 2.26 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.62 (t, ^{3}J= 6.9 Hz, 2H, -C***H***$_2$-CO-CH$_3$), 3.01 (m, 4H, -C***H***$_2$-NH-), 7.76 (s, *2*H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 29.1 (-***C***H$_2$-CH$_2$-NH-), 29.2 (2C, -***C***H$_2$-CO-NH-), 29.6 (2C, -***C***H$_3$), 36.3 (2C, -***C***H$_2$-NH-), 38.0 (2C, -***C***H$_2$-CO-CH$_3$), 171.0 (2C, -NH-***C***=O-), 207.4 (2C, -***C***=O-).

***N,N'*-(propane-1,3-diyl)-bis-(4-hydroxypentanamide) (2b).**



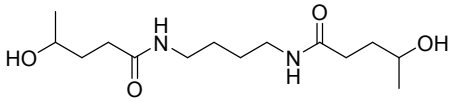
White solid (Yield= 79 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.02 (d, ^{3}J= 6.2 Hz, 6H, -C***H***$_3$), 1.38-1.61 (m, 6H, -C***H***$_2$-CH(OH)- and -C***H***$_2$-CH$_2$-NH-), 2.01-2.18 (m, 4H, -C***H***$_2$-CO-NH-), 2.97-3.04 (m, 4H, -C***H***$_2$-NH-), 3.50-3.60 (m, 2H, -C***H***(OH)-), 4.45 (d, ^{3}J= 4.7 Hz, 2H, -O***H***), 7.75 (s, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.5 (2C, -***C***H$_3$), 29.3 (-***C***H$_2$-CH$_2$-NH-), 32.1 (2C, -***C***H$_2$-CO-NH-), 34.9, (2C, -CH(OH)-***C***H$_2$-), 36.3 (2C, -***C***H$_2$-NH-), 65.4 (2C, -***C***H(OH)-), 172.3 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{13}H_{26}N_2O_4Na$: 297.1790 $[M+Na]^+$; found: 297.1790.

***N,N'*-(butane-1,4-diyl)-bis-(4-oxopentanamide) (1c).**



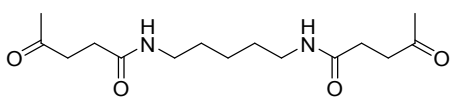
White solid (Yield= 95 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.34-1.38 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 2.09 (s, 6H, -C***H***$_3$), 2.27 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.63 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-CH$_3$), 2.98-3.05 (m, 4H, -C***H***$_2$-NH-), 7.83 (s, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 26.6 (2C, -***C***H$_2$-CH$_2$-NH-), 29.1 (2C, -***C***H$_2$-CO-NH-), 29.7 (2C, -***C***H$_3$), 38.1 (2C, -***C***H$_2$-NH-), 38.3 (2C, -***C***H$_2$-CO-CH$_3$), 171.1 (2C, -NH-***C***=O-), 207.6 (2C, -***C***=O-).

***N,N'*-(butane-1,4-diyl)-bis-(4-hydroxypentanamide) (2c).**



White solid (Yield= 81 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.03 (d, ^{3}J= 6.2 Hz, 6H, -C***H***$_3$), 1.33-1.37 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 1.44-1.62 (m, 4H, -C***H***$_2$-CH(OH)-), 1.98-2.19 (m, 4H, -C***H***$_2$-CO-NH-), 2.97-3.03 (m, 4H, -C***H***$_2$-NH-), 3.49-3.60 (m, 2H, -C***H***(OH)-), 4.42 (d, ^{3}J= 4.7Hz,2H, -O***H***), 7.72 (t, ^{3}J= 5.4 Hz, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.4 (2C, -***C***H$_3$), 26.7 (2C, -***C***H$_2$-CH$_2$-NH-), 32.0 (2C, -***C***H$_2$-CO-NH-), 34.9, (2C, -CH(OH)-***C***H$_2$-), 38.1 (2C, -***C***H$_2$-NH-), 65.5 (2C, -***C***H(OH)-), 172.2 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{14}H_{28}N_2O_4Na$ 311.1947: $[M+Na]^+$; found: 311.1944.

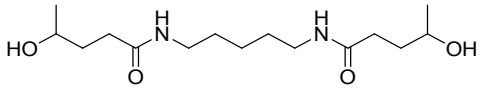
***N,N'*-(pentane-1,5-diyl)-bis-(4-oxopentanamide) (1d).**



White solid (Yield= 82 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.21-1.27 (m, 2H, -C***H***$_2$-CH$_2$-CH$_2$-NH-), 1.31-1.39 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 2.08 (s, 6H, -C***H***$_3$), 2.26 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.61 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-CH$_3$), 2.93-3.02 (m, 4H, -C***H***$_2$-NH-), 7.75 (s,

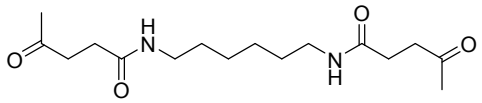
2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.7 (-***C***H$_2$-CH$_2$-CH$_2$-NH-), 28.8 (2C, -***C***H$_2$-CH$_2$-NH-), 29.1 (2C, -***C***H$_2$-CO-NH-), 29.6 (2C, -***C***H$_3$), 38.0 (2C, -***C***H$_2$-NH-), 39.5 (2C, -***C***H$_2$-CO-CH$_3$), 170.9 (2C, -NH-***C***=O-), 207.4 (2C, -***C***=O-).

_N,N'_-(pentane-1,5-diyl)-bis-(4-hydroxypentanamide) (2d).



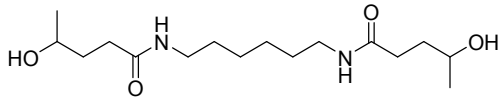
White solid (Yield= 69 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.03 (d, ^3J= 6.2 Hz, 6H, -C***H***$_3$), 1.17-1.27 (m, 2H, -C***H***$_2$-CH$_2$-CH$_2$-NH-), 1.31-1.42 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 1.45-1.60 (m, 4H, -C***H***$_2$-CH(OH)-), 2.00-2.18 (m, 4H, -C***H***$_2$-CO-NH-), 2.96-3.03 (m, 4H, -C***H***$_2$-NH-), 3.48-3.61 (m, 2H, -C***H***(OH)-), 4.42 (d, ^3J= 4.7 Hz, 2H, -O***H***), 7.70 (t, ^3J= 5.4 Hz, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.4 (2C, -***C***H$_3$), 23.8 (-***C***H$_2$-CH$_2$-CH$_2$-NH-), 28.8 (2C, -***C***H$_2$-CH$_2$-NH-), 32.0 (2C, -***C***H$_2$-CO-NH-), 34.9, (2C, -CH(OH)-***C***H$_2$-), 38.3 (2C, -***C***H$_2$-NH-), 65.4 (2C, -***C***H(OH)-), 172.1 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{15}H_{30}N_2O_4Na$: 325.2103 $[M+Na]^+$; found: 325.2101.

_N,N'_-(hexane-1,6-diyl)-bis-(4-oxopentanamide) (1e).



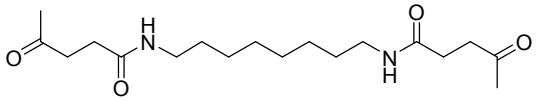
White solid (Yield= 93%).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.19-1.26 (m, 4H, -C***H***$_2$-CH$_2$-CH$_2$-NH-), 1.30-1.39 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 2.08 (s, 6H, -C***H***$_3$), 2.26 (t, ^3J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.61 (t, ^3J= 6.9 Hz, 4H, -C***H***$_2$-CO-CH$_3$), 2.96-3.02 (m, 4H, -C***H***$_2$-NH-), 7.75 (s, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 26.1 (2C, -***C***H$_2$-CH$_2$-CH$_2$-NH-), 29.1 (4C, -C***H***$_2$-CO-NH- and -***C***H$_2$-CH$_2$-NH-), 29.7 (2C, -***C***H$_3$), 38.1 (2C, -***C***H$_2$-NH-), 38.5 (2C, -***C***H$_2$-CO-CH$_3$), 171.0 (2C, -NH-***C***=O-), 207.6 (2C, -***C***=O-).

_N,N'_-(hexane-1,6-diyl)-bis-(4-hydroxypentanamide) (2e).



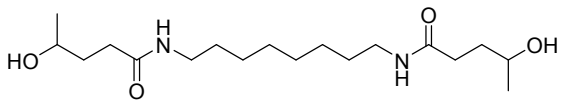
White solid (Yield= 81 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.03 (d, ^3J= 6.2 Hz, 6H, -C***H***$_3$), 1.18-1.28 (m, 4H, -C***H***$_2$-CH$_2$-CH$_2$-NH-), 1.30-1.41 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 1.46-1.58 (m, 4H, -C***H***$_2$-CH(OH)-), 2.00-2.18 (m, 4H, -C***H***$_2$-CO-NH-), 2.96-3.02 (m, 4H, -C***H***$_2$-NH-), 3.48-3.61 (m, 2H, -C***H***(OH)-), 4.42 (d, ^3J= 4.7 Hz, 2H, -O***H***), 7.70 (t, ^3J= 5.4 Hz, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.5 (2C, -***C***H$_3$), 26.1 (2C, -***C***H$_2$-CH$_2$-CH$_2$-NH-), 29.1 (2C, -***C***H$_2$-CH$_2$-NH-), 32.1 (2C, -***C***H$_2$-CO-NH-), 34.9, (2C, -CH(OH)-***C***H$_2$-), 38.3 (2C-***C***H$_2$-NH-), 65.5 (2C, -***C***H(OH)-), 172.2 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{16}H_{32}N_2O_4Na$: 339.2264 $[M+Na]^+$; found: 339.2260.

_N,N'_-(octane-1,8-diyl)-bis-(4-oxopentanamide) (1f).



White solid (Yield= 87 %).
^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.19-1.26 (m, 8H, -C***H***$_2$-C***H***$_2$-CH$_2$-CH$_2$-NH-), 1.29-1.40 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 2.07 (s, 6H, -C***H***$_3$), 2.25 (t, ^3J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.61 (t, ^3J= 6.9 Hz, 4H, -C***H***$_2$-CO-CH$_3$), 2.94-3.03 (m, 4H, -C***H***$_2$-NH-), 7.78 (s, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 26.4 (2C, -***C***H$_2$-CH$_2$-CH$_2$-CH$_2$-NH-), 28.8 (2C, -***C***H$_2$-CH$_2$-CH$_2$-NH-), 29.1 (2C, -C***H***$_2$-CO-NH-), 29.2 (2C, -***C***H$_2$-CH$_2$-NH-), 29.7 (2C, -***C***H$_3$), 38.1 (2C, -***C***H$_2$-NH-), 38.5 (2C, -***C***H$_2$-CO-CH$_3$), 171.0 (2C, -NH-***C***=O-), 207.6 (2C, -***C***=O-).

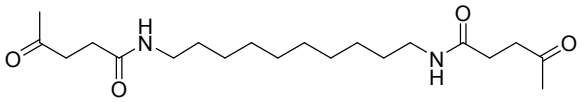
_N,N'_-(octane-1,8-diyl)-bis-(4-hydroxypentanamide) (2f).



White solid (Yield= 72 %).

^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.03 (d, ^{3}J= 6.2 Hz, 6H, -C***H***$_3$), 1.18-1.28 (m, 4H, -***C***H$_2$-CH$_2$-CH$_2$-NH-), 1.30-1.41 (m, 4H, -***C***H$_2$-CH$_2$-NH-), 1.46-1.58 (m, 4H, -C***H***$_2$-CH(OH)-), 2.00-2.18 (m, 4H, -C***H***$_2$-CO-NH-), 2.96-3.02 (m, 4H, -C***H***$_2$-NH-), 3.48-3.61 (m, 2H, -C***H***(OH)-), 4.42 (d, ^{3}J= 4.7 Hz, 2H, -O***H***), 7.70 (t, ^{3}J= 5.4 Hz, 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.5 (2C, -***C***H$_3$), 26.4 (2C, -***C***H$_2$-), 28.7 (2C, -***C***H$_2$-), 29.2 (2C, -***C***H$_2$-), 32.1 (2C, -***C***H$_2$-CO-NH-), 34.9, (2C, -CH(OH)-***C***H$_2$-), 38.4 (2C, -***C***H$_2$-NH-), 65.5 (2C, -***C***H(OH)-), 172.1 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{18}H_{36}N_2O_4Na$: 367.2566 [M+Na]$^{+}$; found: 367.2573.

***N,N'*-(decane-1,10-diyl)-bis-(4-oxopentanamide) (1g).**

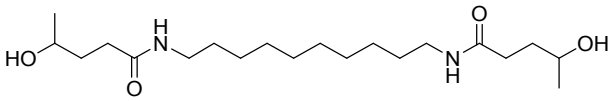


White solid (Yield= 78 %).

^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.19-1.26 (m, 16H, -C***H***$_2$-), 1.35 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 2.08 (s, 6H, -C***H***$_3$), 2.25 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-NH-), 2.61 (t, ^{3}J= 6.9 Hz, 4H, -C***H***$_2$-CO-CH$_3$), 2.99 (m, 4H, -C***H***$_2$-NH-), 7.75 (s, 2H, -N***H***-).

^{13}C NMR (75 MHz, CDCl$_3$, 300 K): δ (ppm) = 26.9 (2C, -CH$_2$-), 29.3 (2C, -CH$_2$-), 29.4 (2C, -CH$_2$-), 29.7 (2C, -CH$_2$-), 30.1 (2C, -CH$_3$), 30.2 (2C, -CH$_2$-), 38.8 (2C, -***C***H$_2$-NH-), 39.7 (2C, -***C***H$_2$-CO-CH$_3$), 171.9 (2C, -NH-C=O), 207.9 (2C, -C=O).

***N,N'*-(decane-1,10-diyl)-bis-(4-hydroxypentanamide) (2g).**



White solid (Yield= 88 %).

^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ (ppm)= 1.02 (d, ^{3}J= 6.2 Hz, 6H, -C***H***$_3$), 1.19-1.27 (m, 12H, -C***H***$_2$-), 1.29-1.43 (m, 4H, -C***H***$_2$-CH$_2$-NH-), 1.43-1.65 (m, 4H, -C***H***$_2$-CH(OH)-), 2.00-2.17 (m, 4H, -C***H***$_2$-CO-NH-), 2.96-3.02 (m, 4H, -C***H***$_2$-NH-), 3.45-3.62 (m, 2H, -C***H***(OH)-), 4.41 (d, ^{3}J= 4.7 Hz, 2H, -O***H***), 7.69 (t, ^{3}J= 5.4 Hz 2H, -N***H***-). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ (ppm)= 23.4 (2C, -***C***H$_3$), 26.4 (2C, -***C***H$_2$-), 28.7 (2C, -***C***H$_2$-), 28.9 (2C, -***C***H$_2$-), 29.1 (2C, -***C***H$_2$-), 32.0 (2C, -***C***H$_2$-), 34.9 (2C, -CH(OH)-***C***H$_2$-), 38.4 (2C, -***C***H$_2$-NH-), 65.4 (2C, -***C***H(OH)-), 172.1 (2C, -NH-***C***=O-). HRMS m/z calcd. for $C_{20}H_{40}N_2O_4Na$: 395.2886 [M+Na]$^{+}$; found: 395.2884.

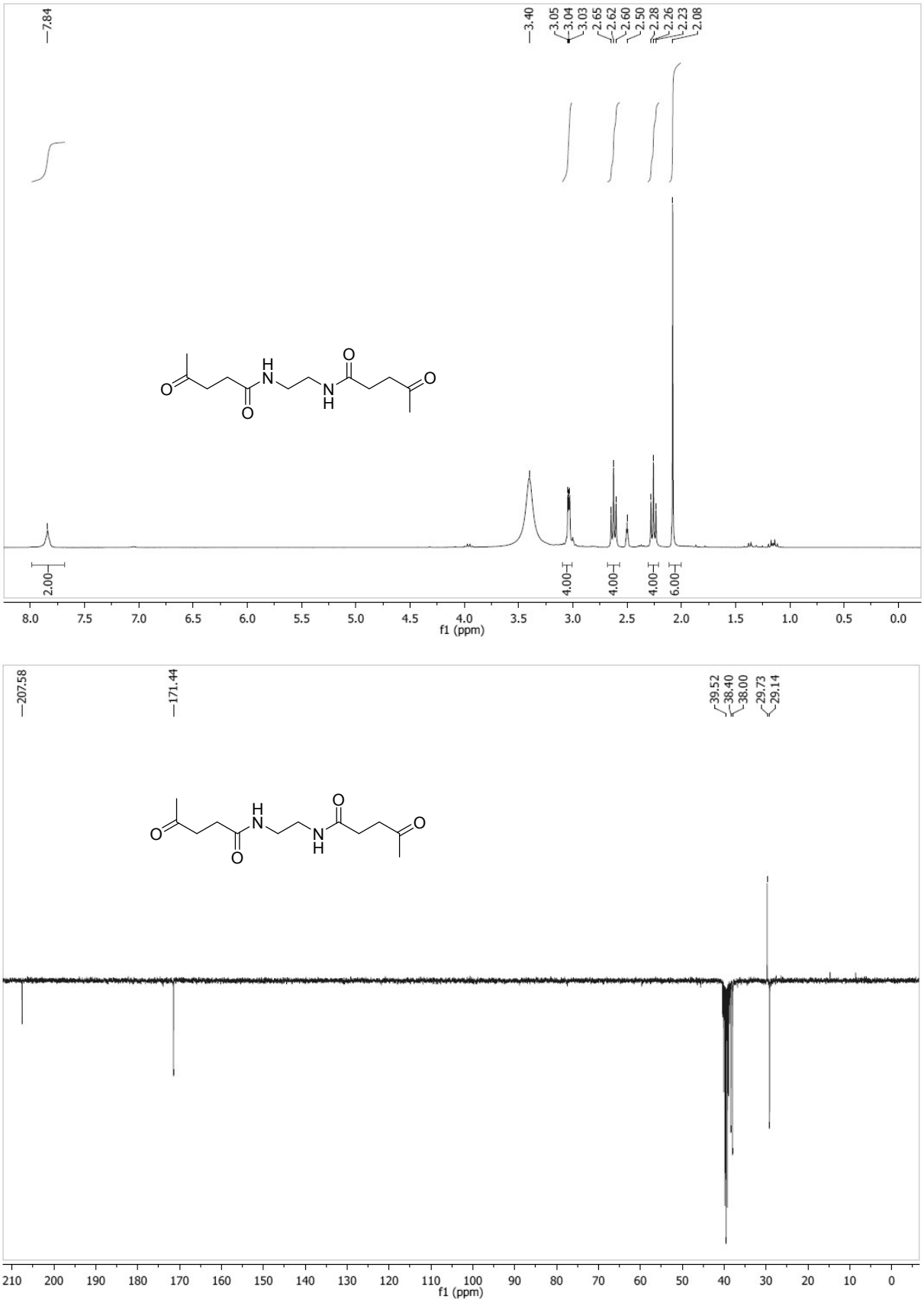


Fig. S1 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1a** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

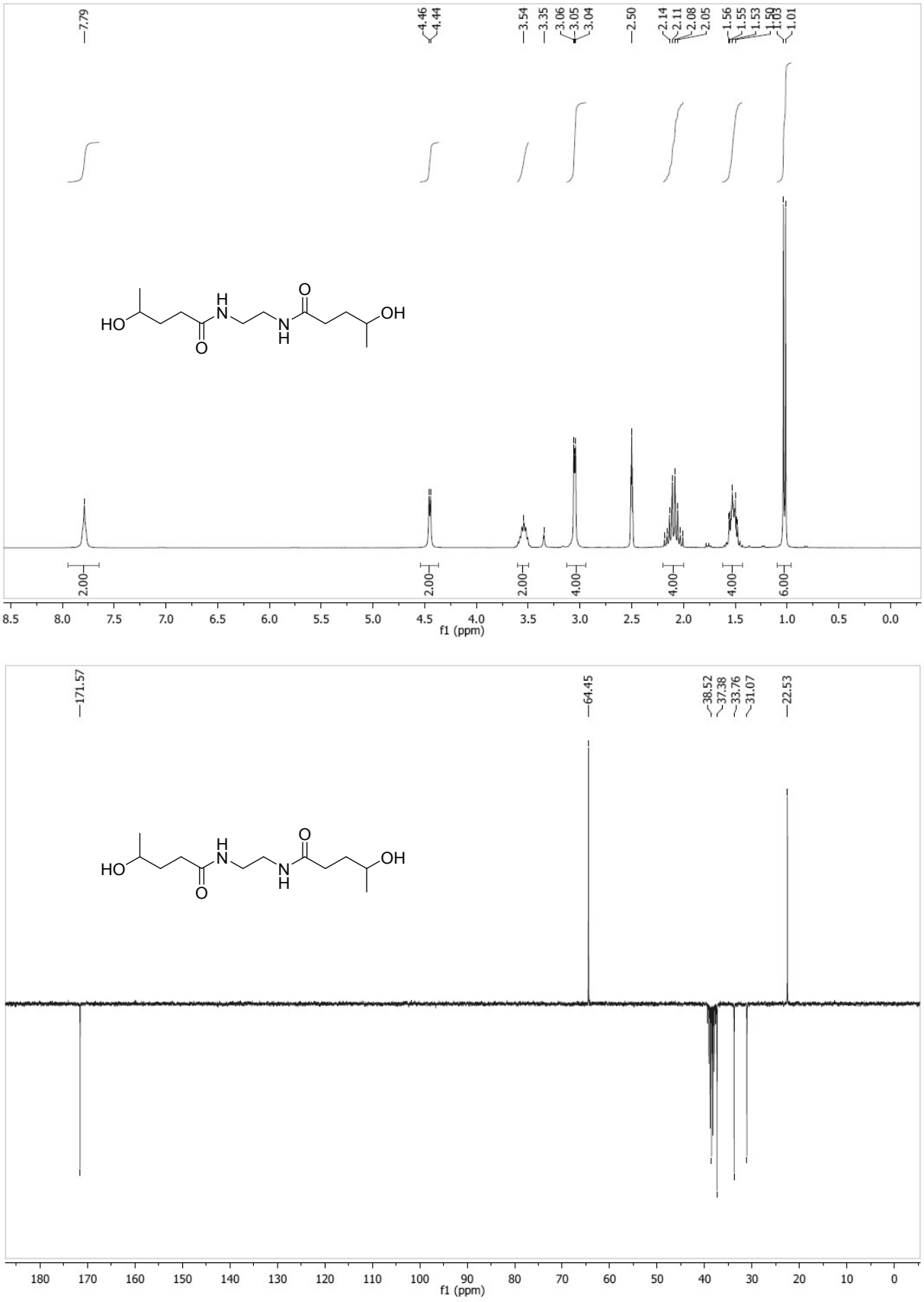


Fig. S2 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2a** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

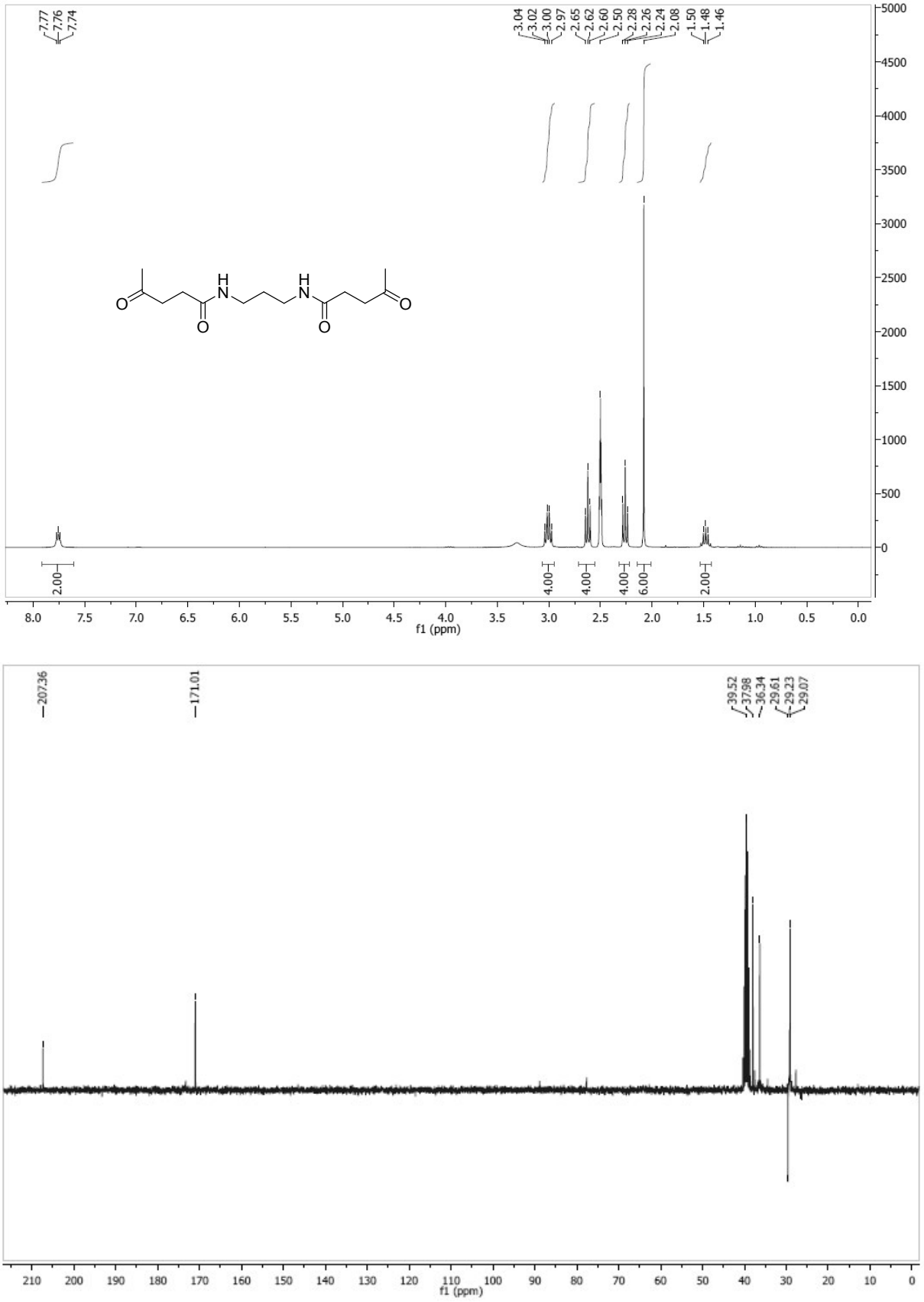


Fig. S3 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1b** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

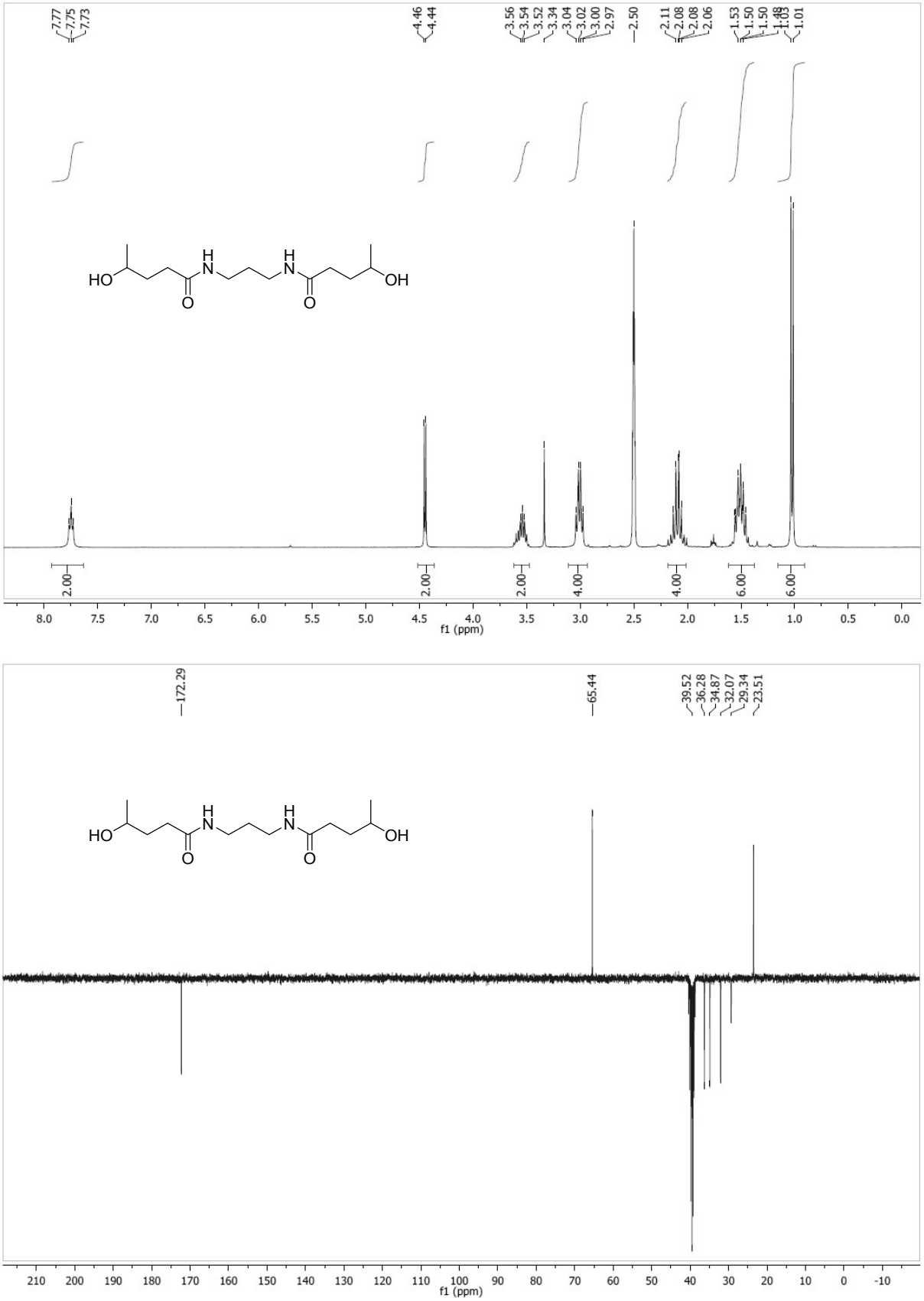


Fig. S4 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2b** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

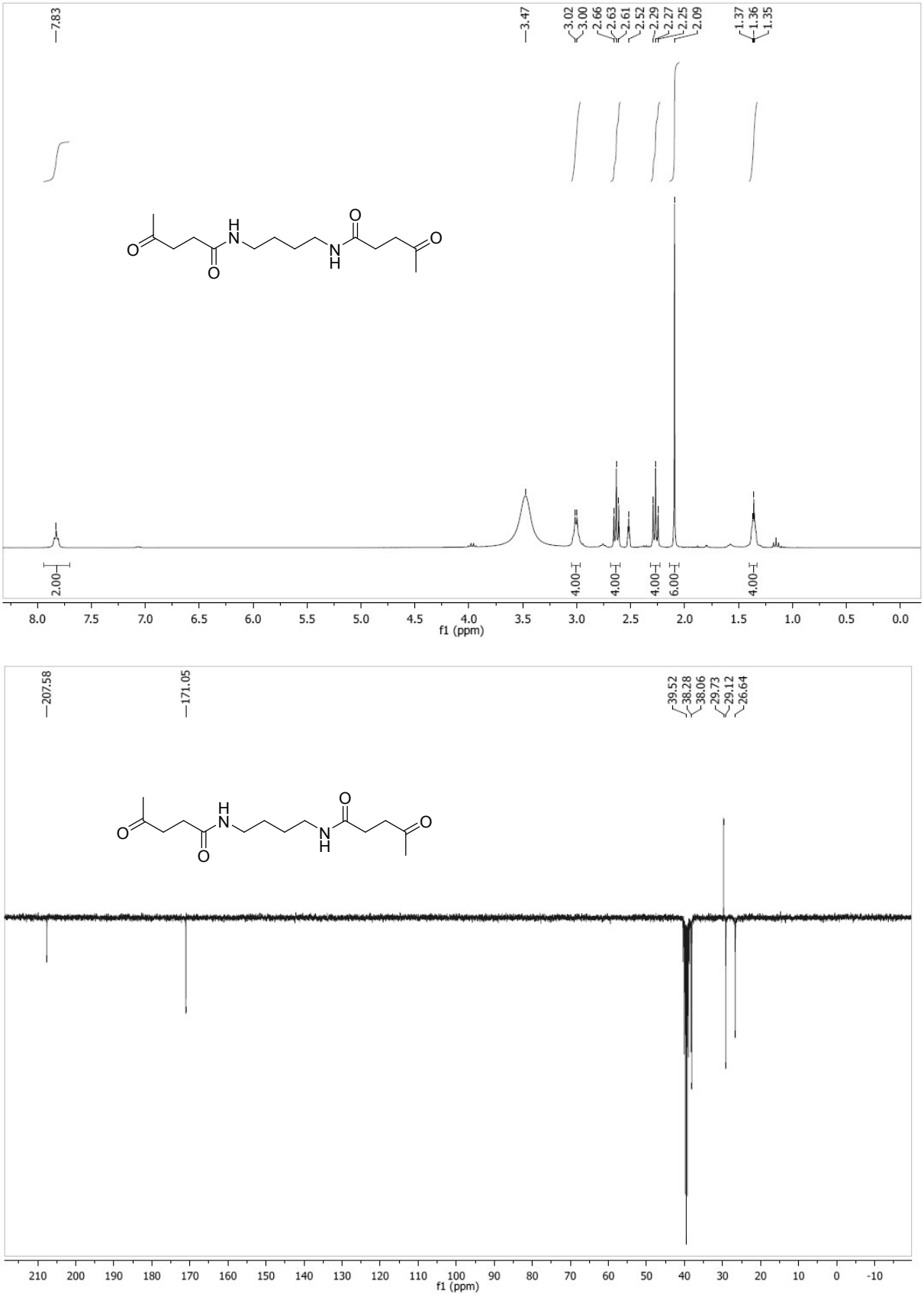


Fig. S5 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1c** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

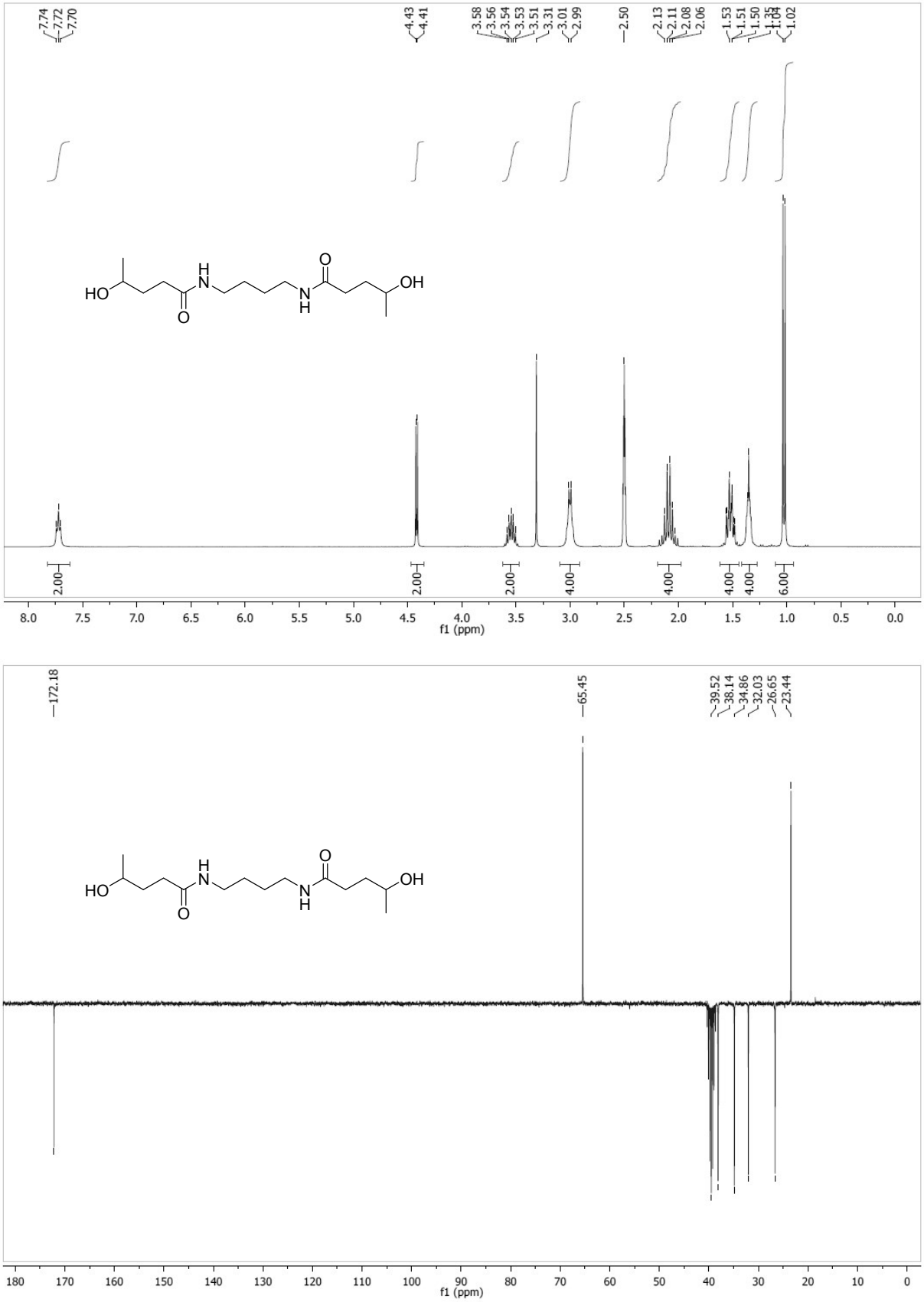


Fig. S6 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2c** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

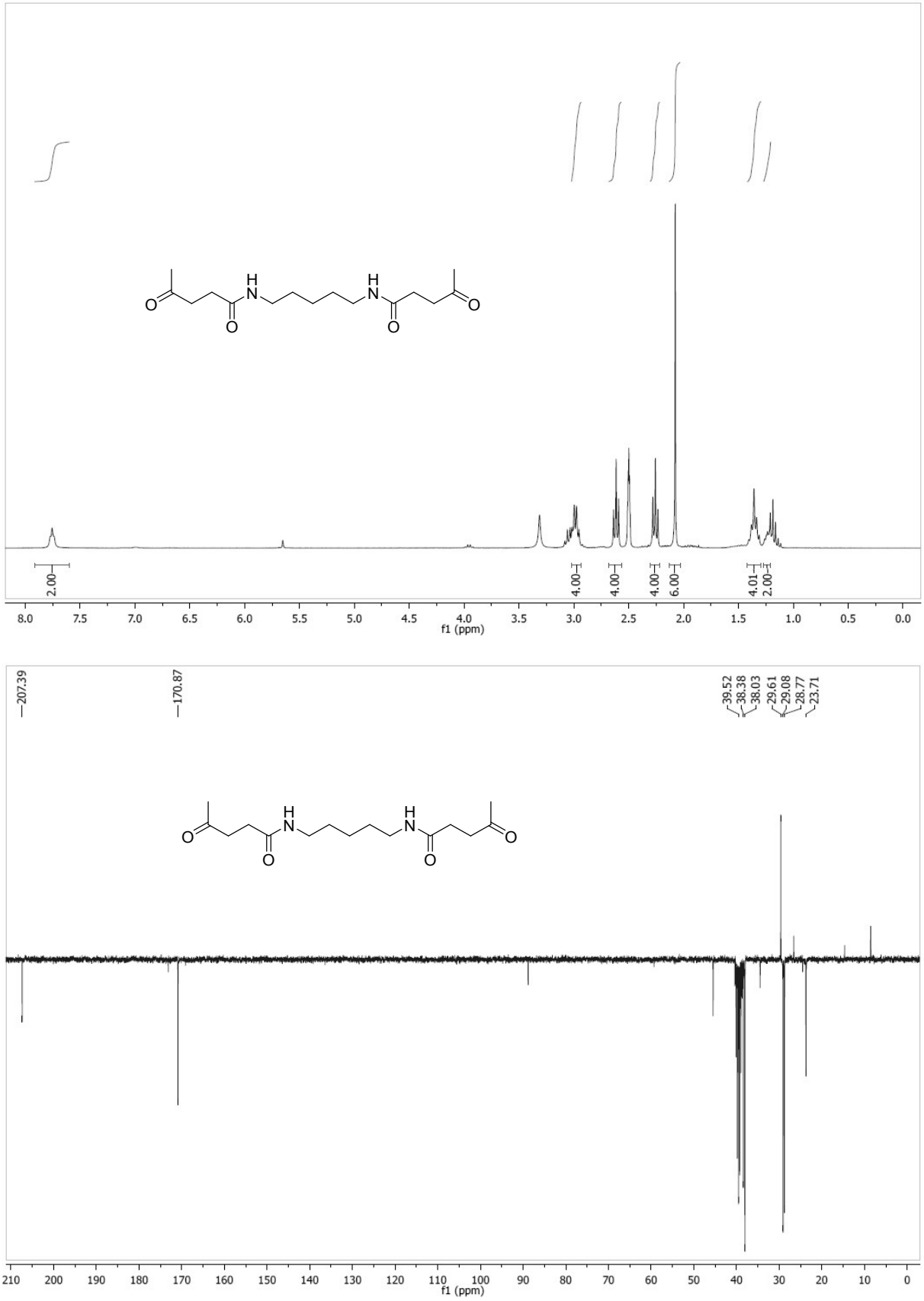


Fig. S7 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1d** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

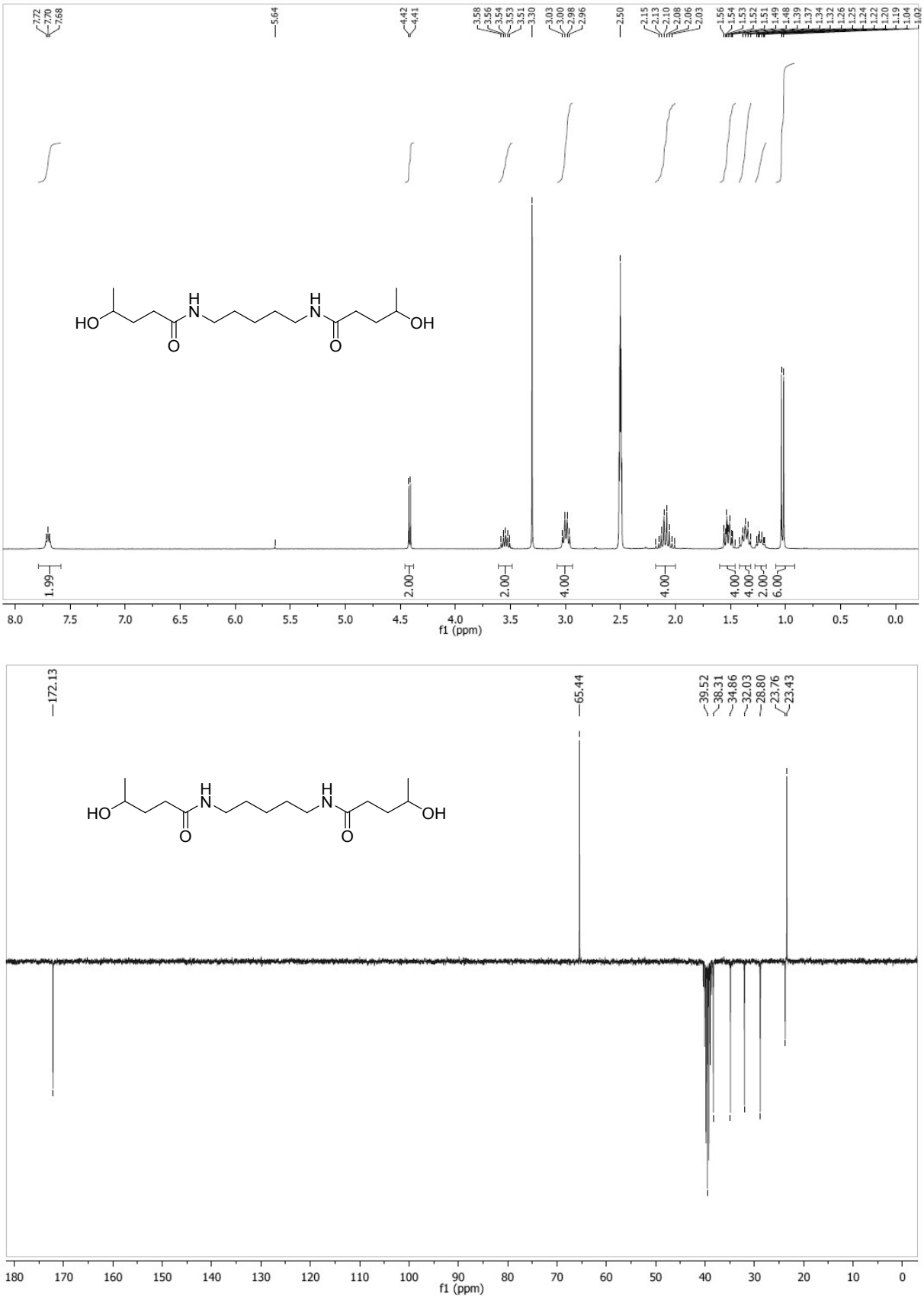


Fig. S8 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2d** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

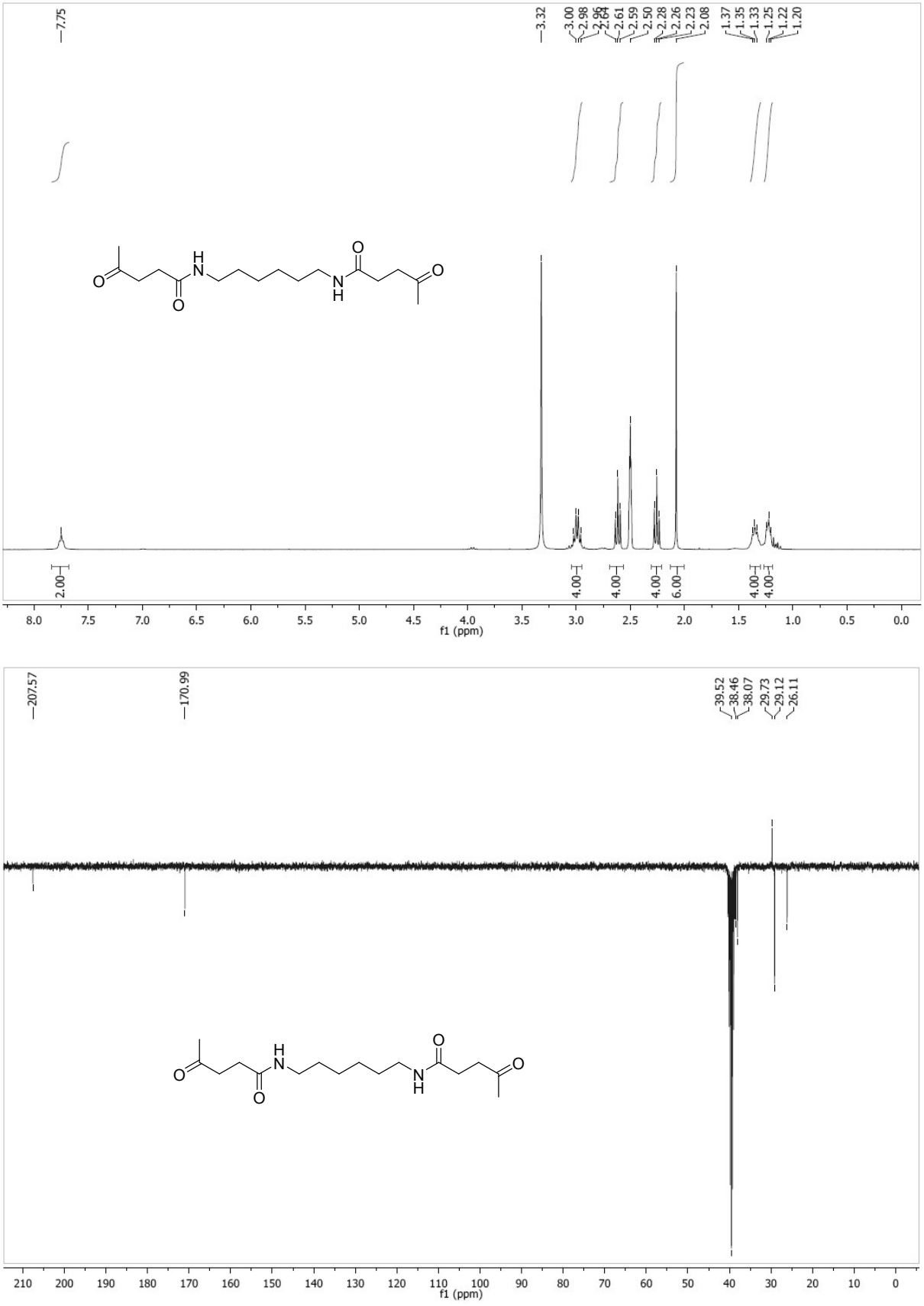


Fig. S9 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1e** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

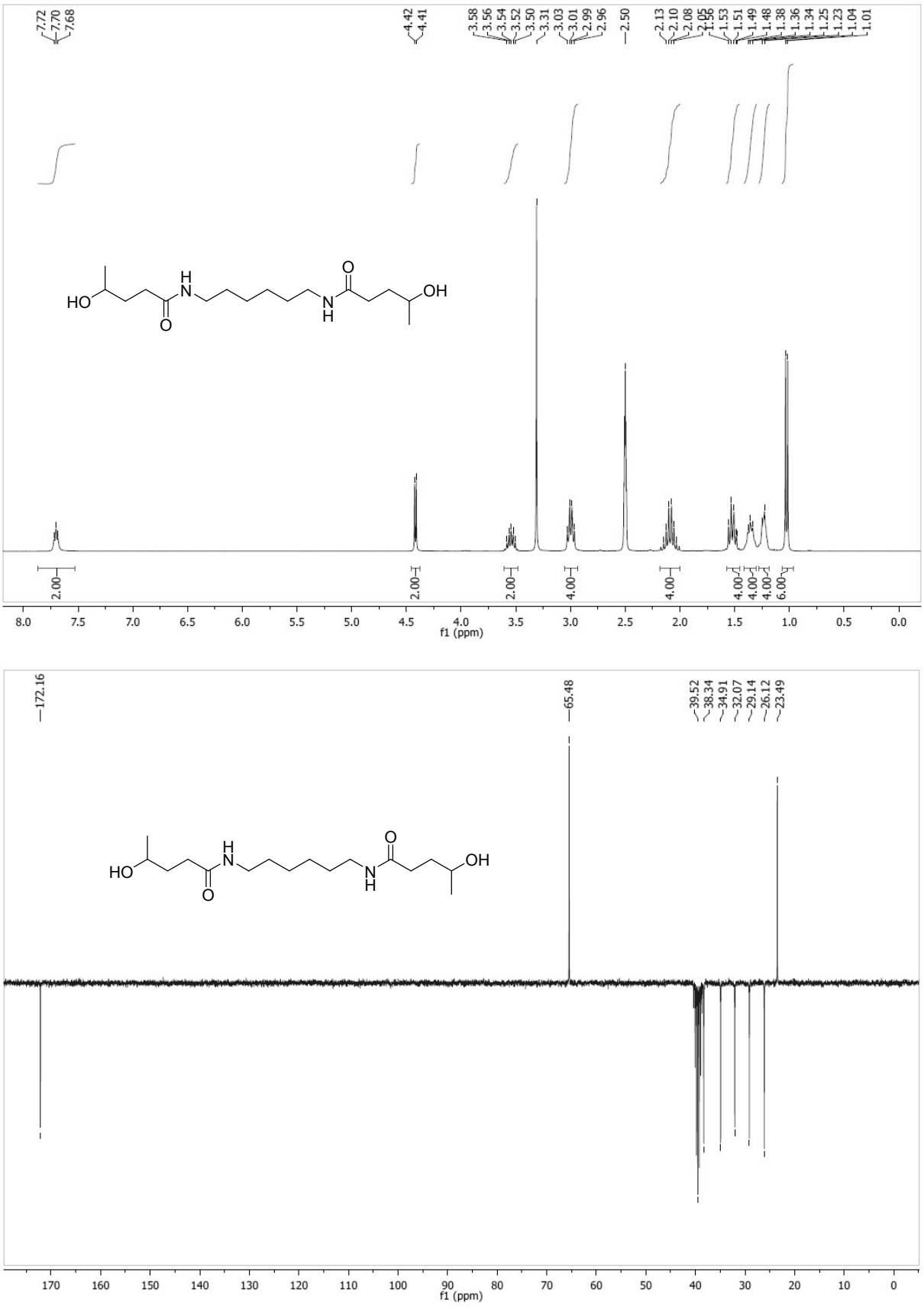


Fig. S10 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2e** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

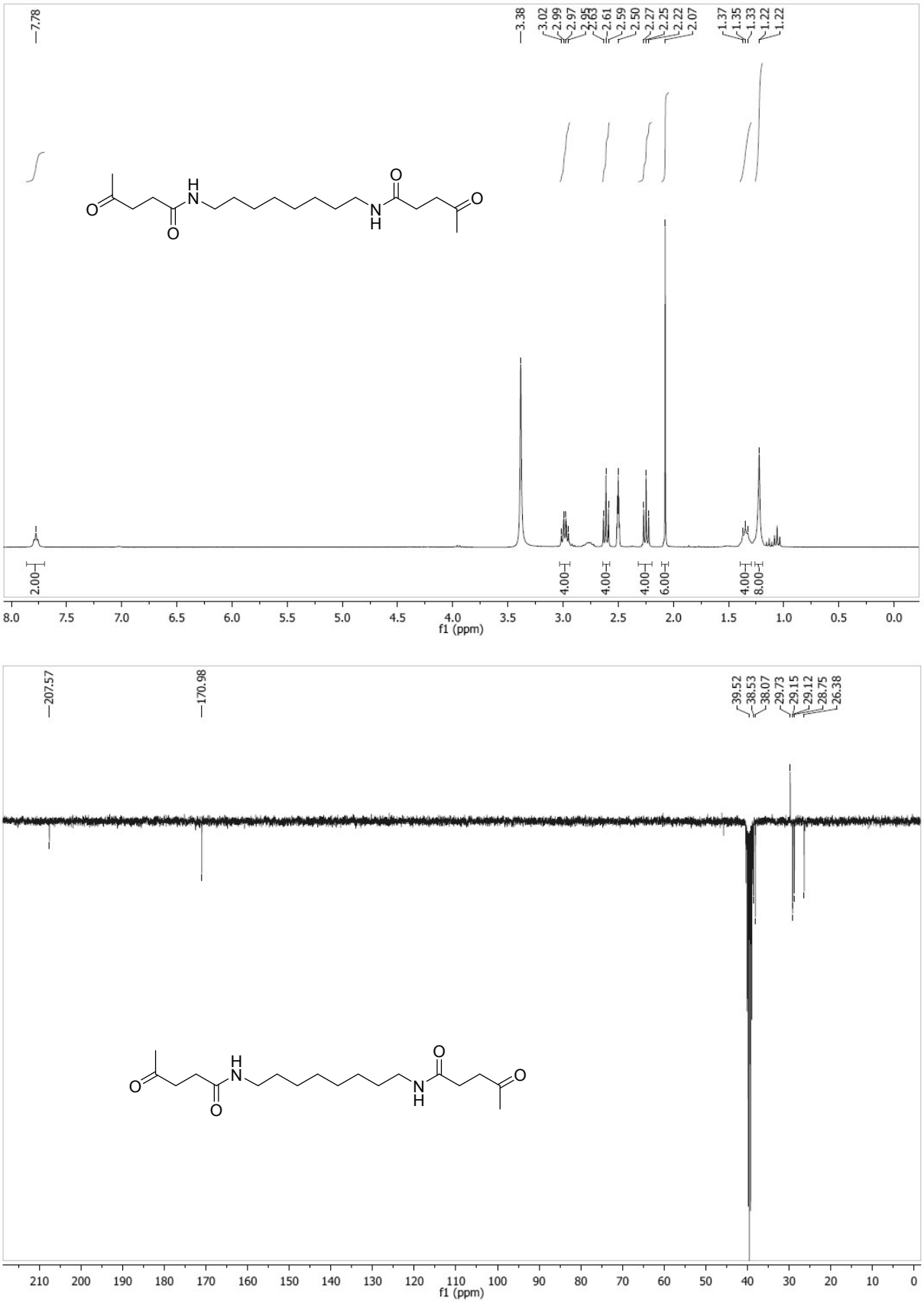


Fig. S11 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1f** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)

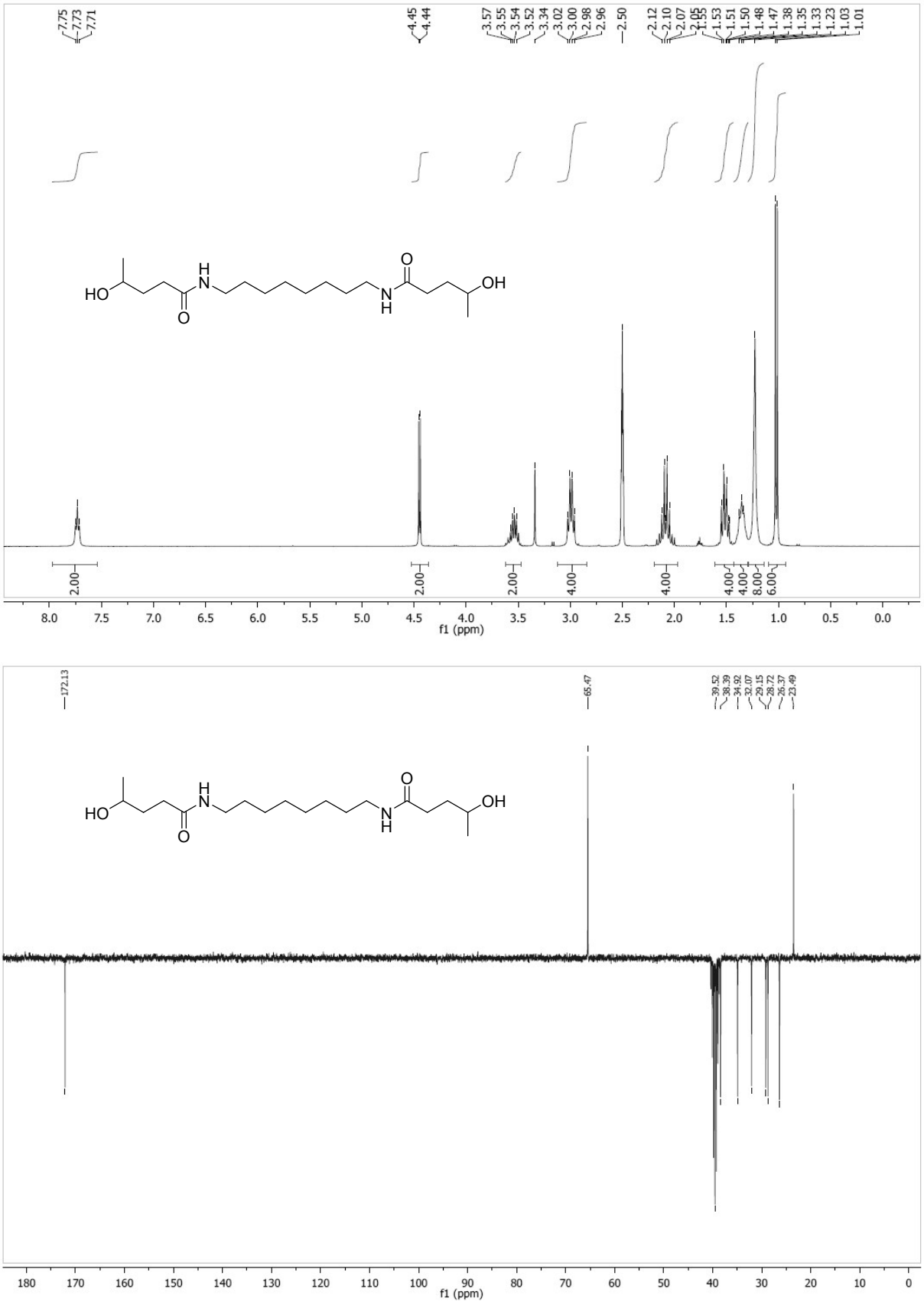
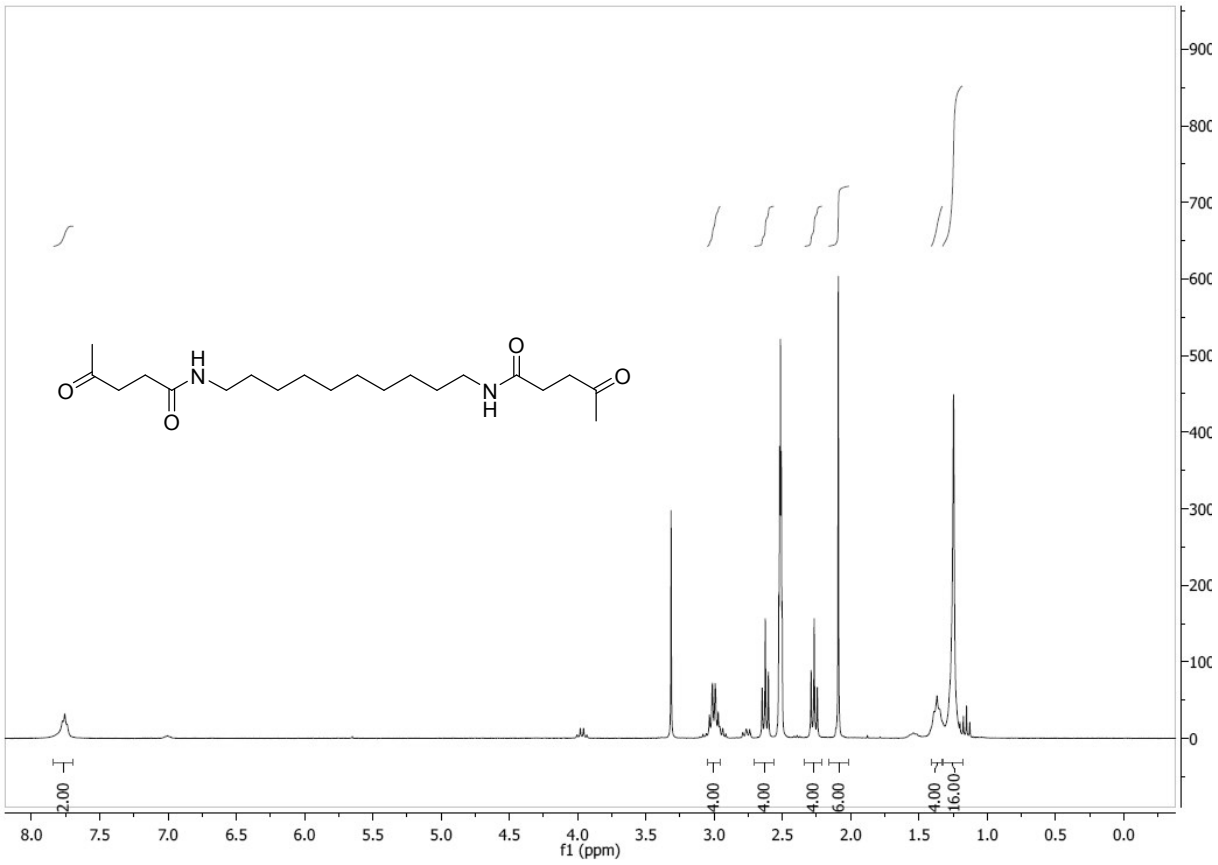


Fig. S12 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2f** (DMSO-d_6, 300 MHz and 75 MHz, 300 K)



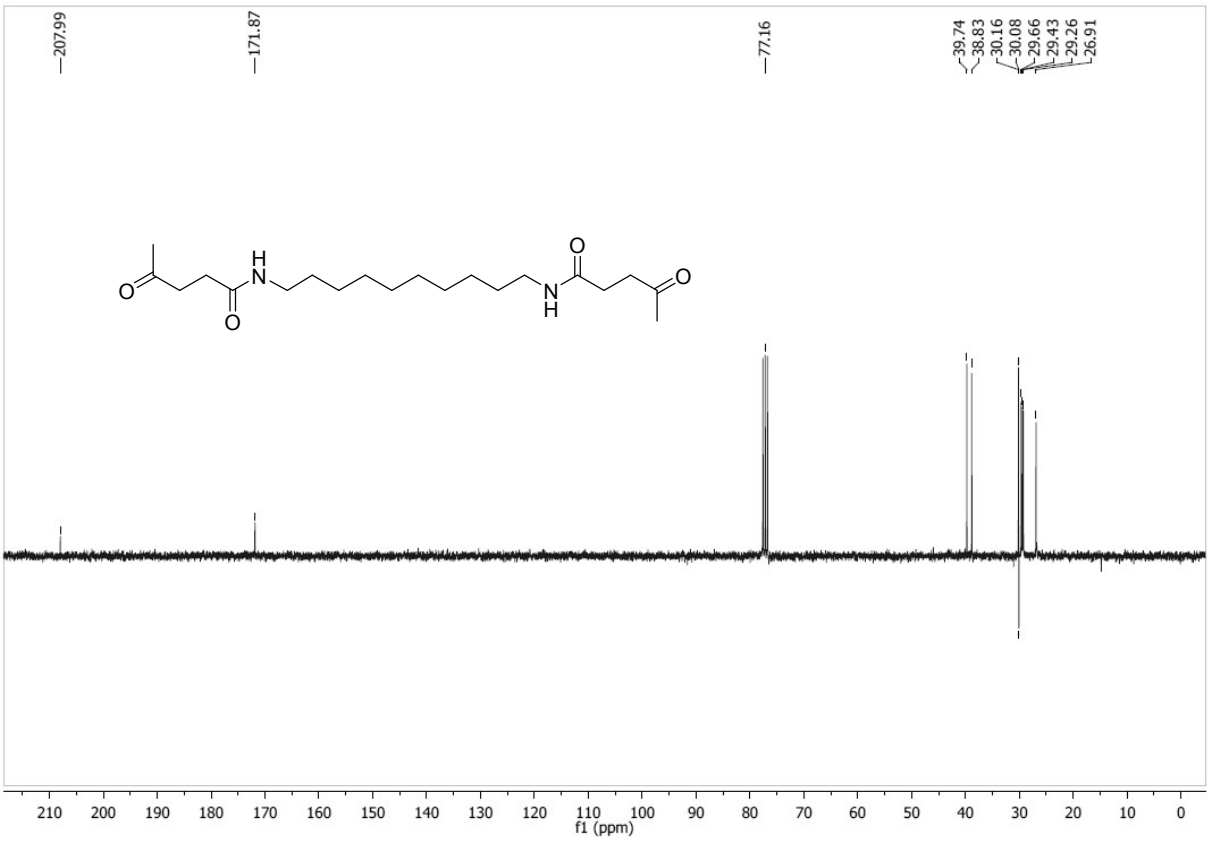


Fig. S13 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **1g** ($CDCl_3$, 300 MHz and 75 MHz, 300 K)

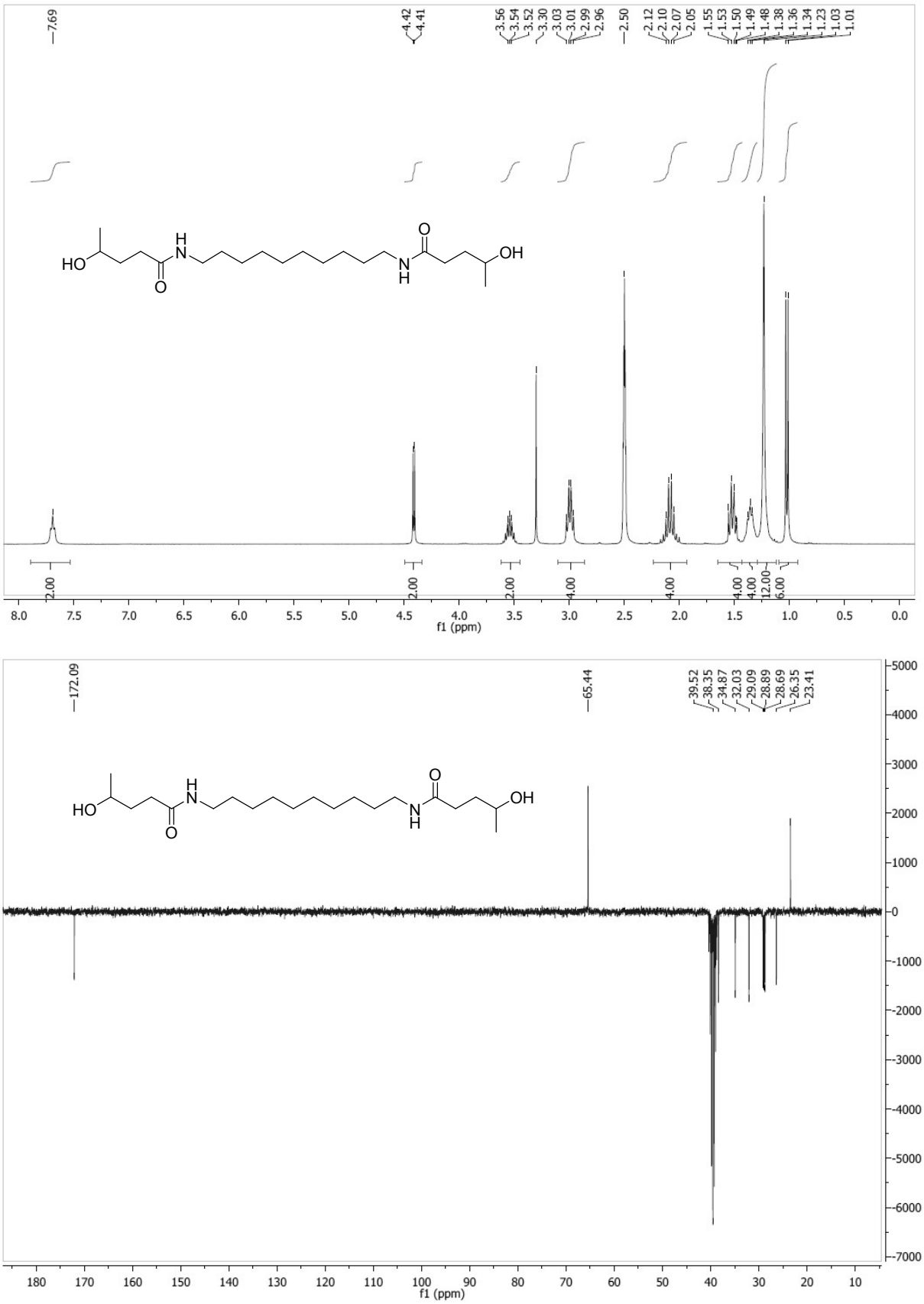


Fig. S14 ^{1}H (top) and DEPT ^{13}C (bottom) NMR spectra of **2g** (DMSO-d_6, 300MHz and 75MHz, 300 K)

2. MALDI-ToF and NMR spectra

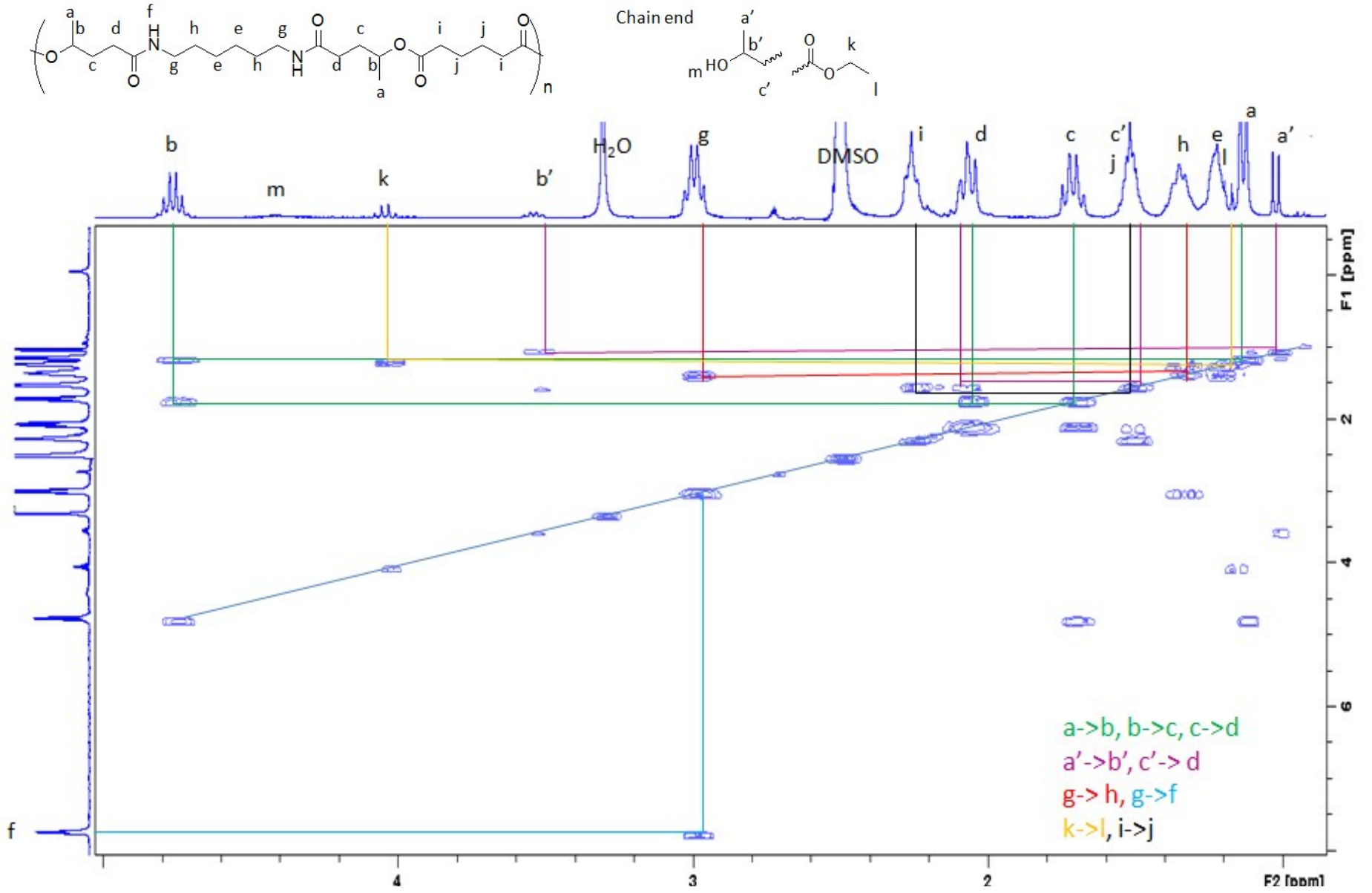


Fig. S15 COSY NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=6** (entry 2) by polycondensation in solution (DMSO-d_6, 300 MHz, 300 K)

[1] This sample was selected to show clearly the signals of the chain end to confirm the previous attributions

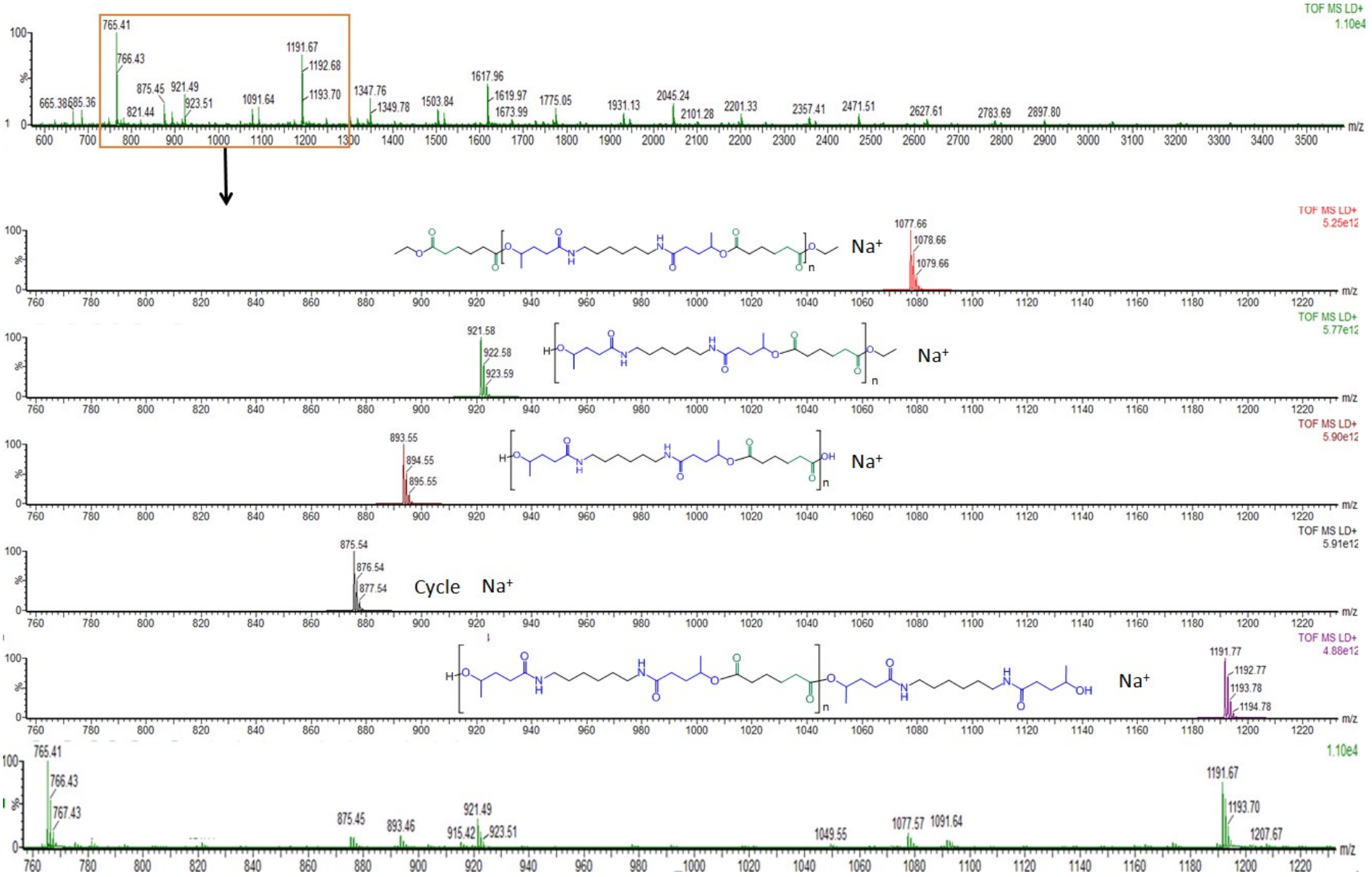


Fig. S16 MALDI-ToF analysis of poly(ester-*co*-amide) from diol-diamide **x=6** and diethyl adipate (entry 3)

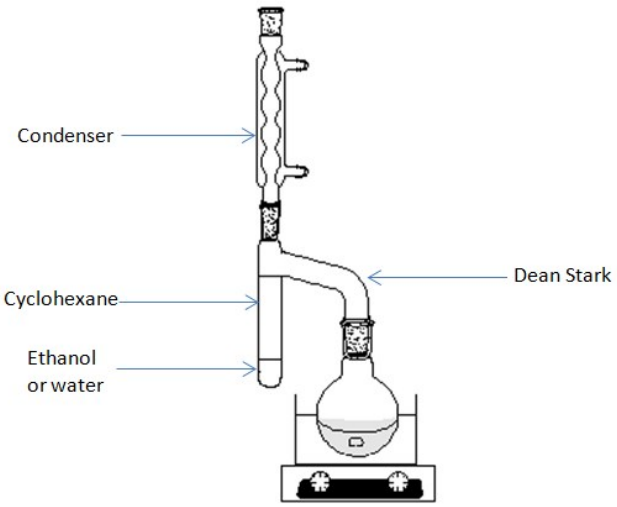


Fig. S17 Polymerisation with Dean Stark apparatus

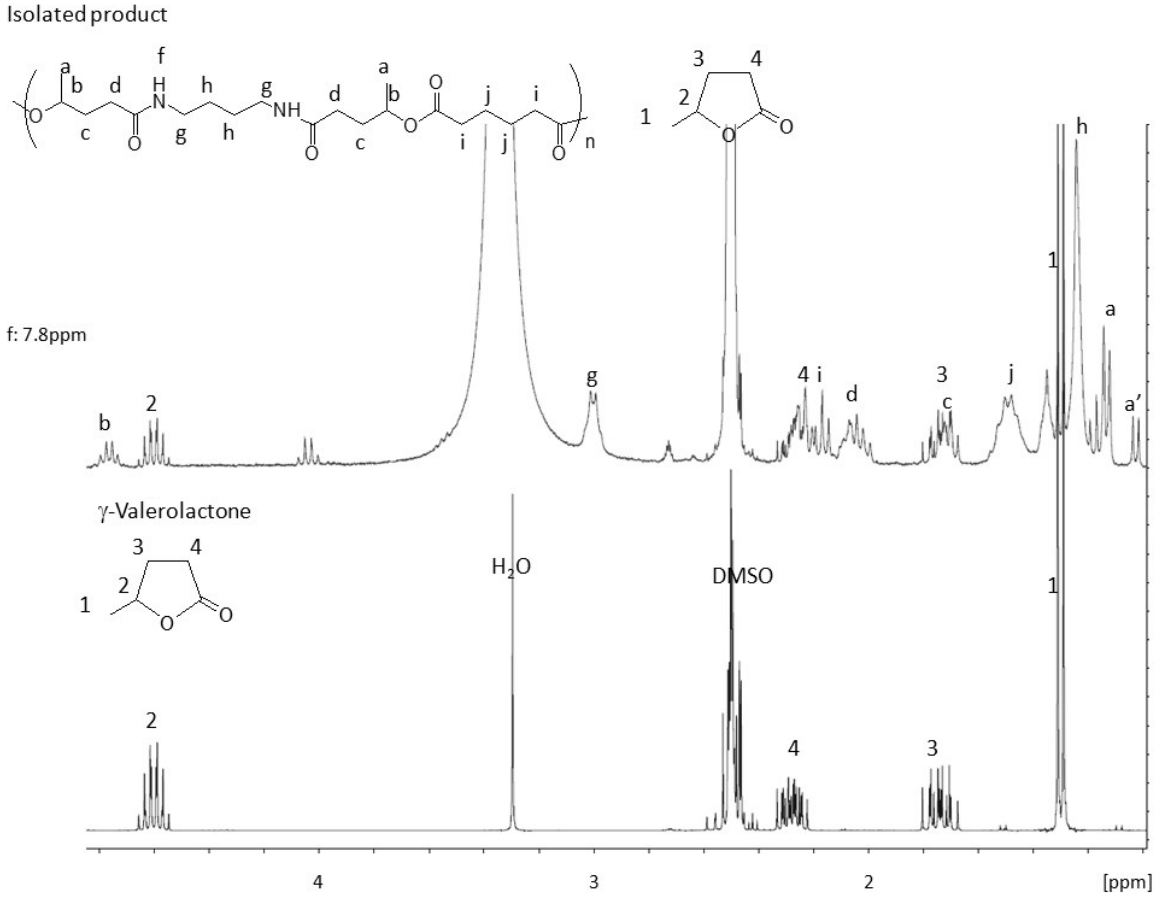


Fig. S18 Comparison of the ^{1}H NMR spectra (DMSO-d_6, 300 MHz) of the isolated product of polymerisation from diol-diamide **2c** (x=4) and adipic acid and of the γ-valerolactone

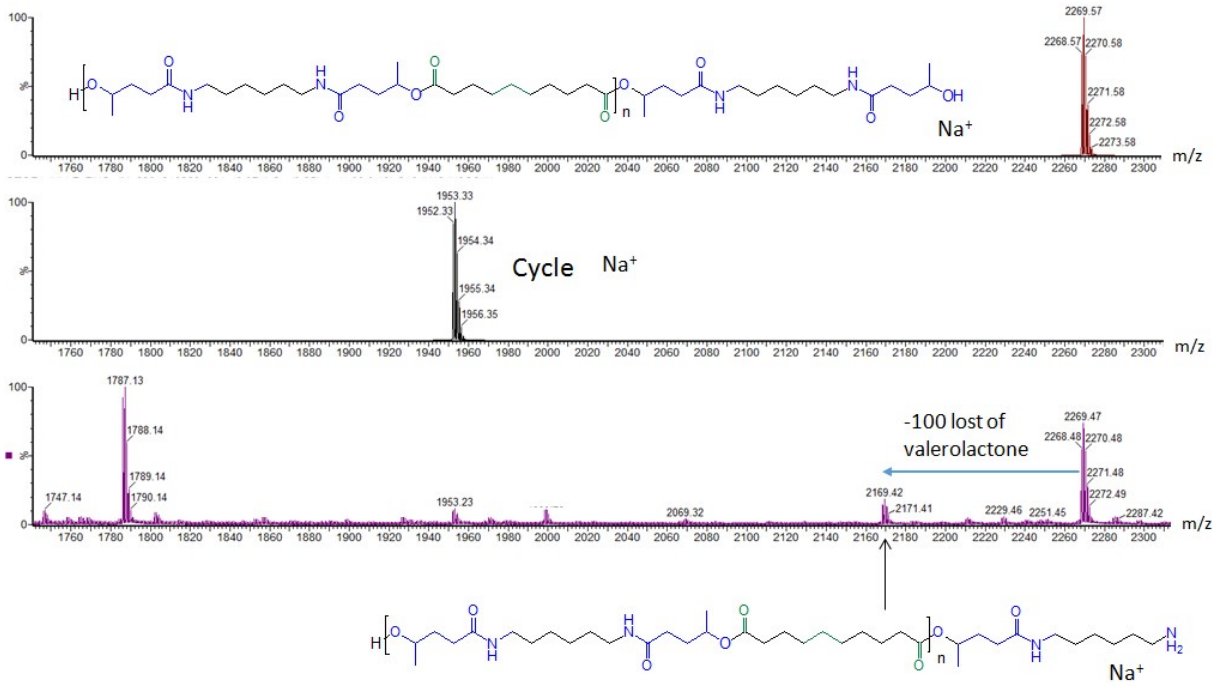


Fig. S19 MALDI-ToF analyse of poly(ester-*co*-amide) from diol-diamide **x=6** and sebacic acid (entry 7)

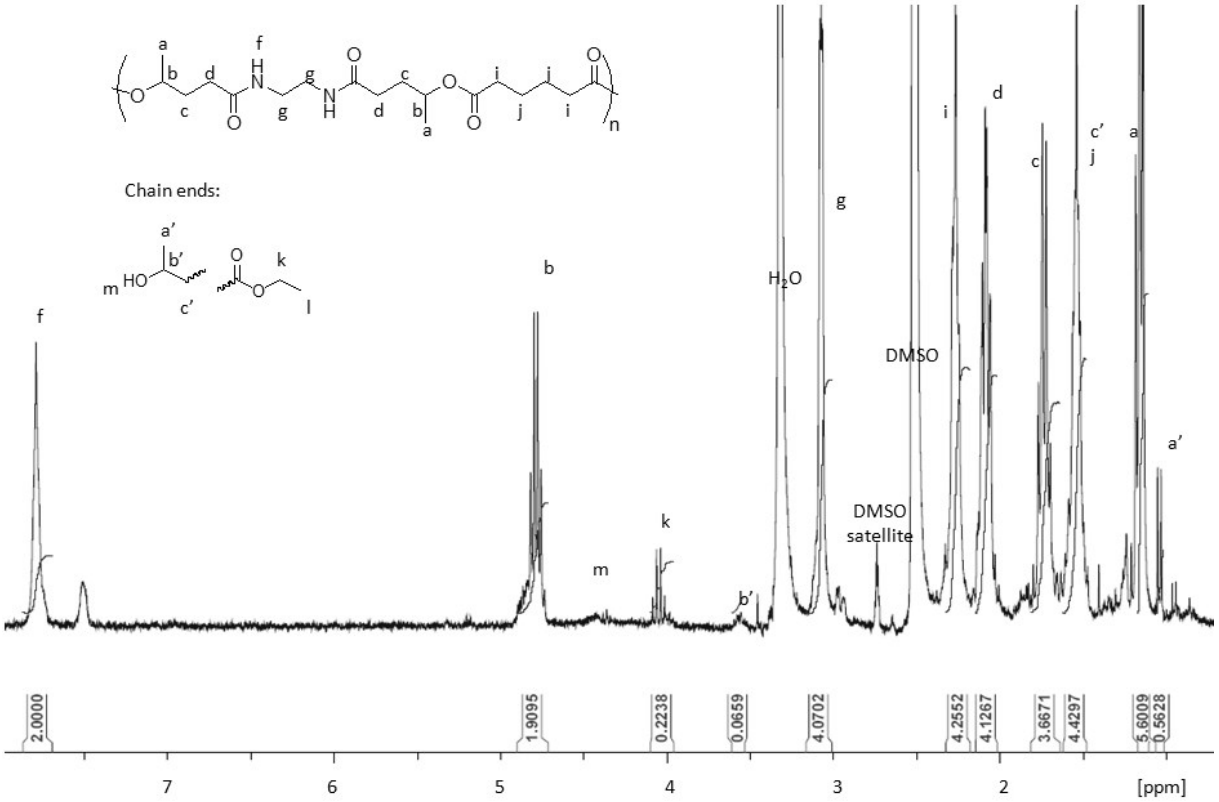


Fig. S20 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=2** (DMSO-d_6, 300 MHz, 300 K)

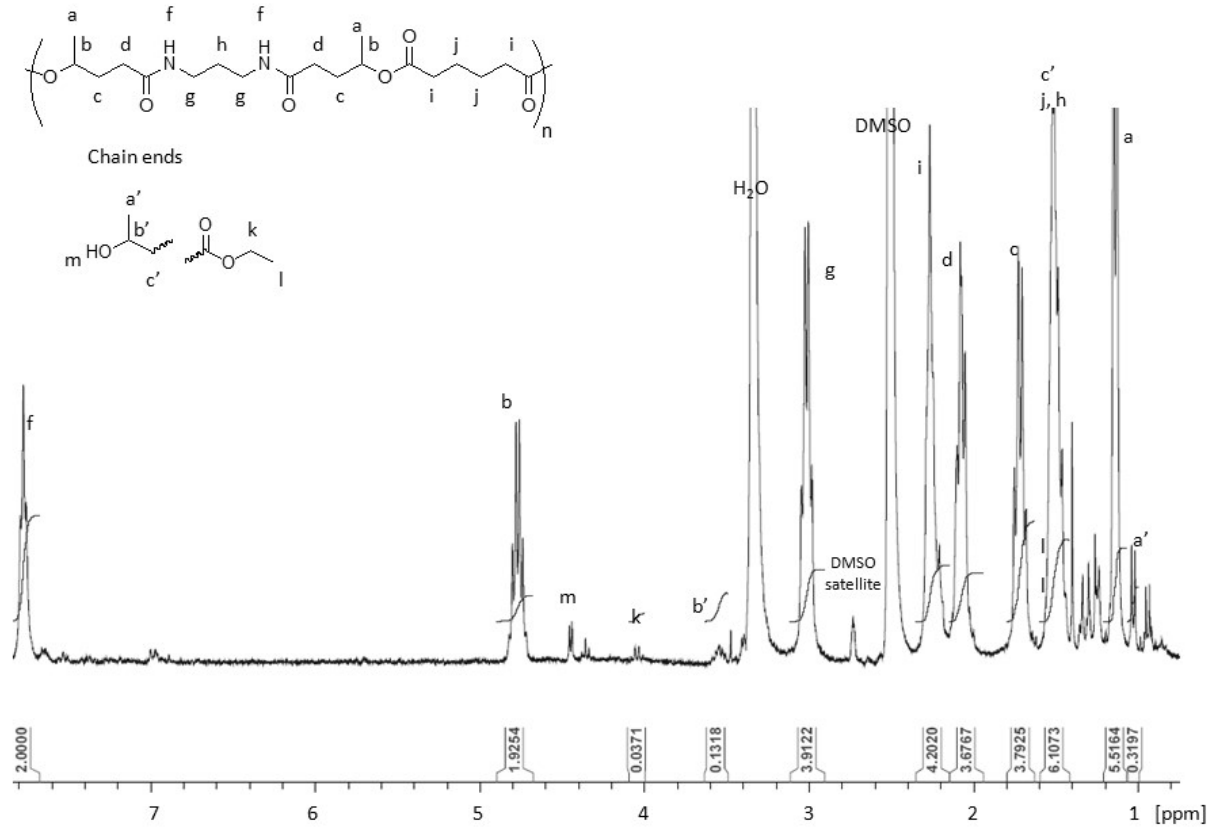


Fig. S21 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=3** (DMSO-d_6, 300 MHz, 300 K)

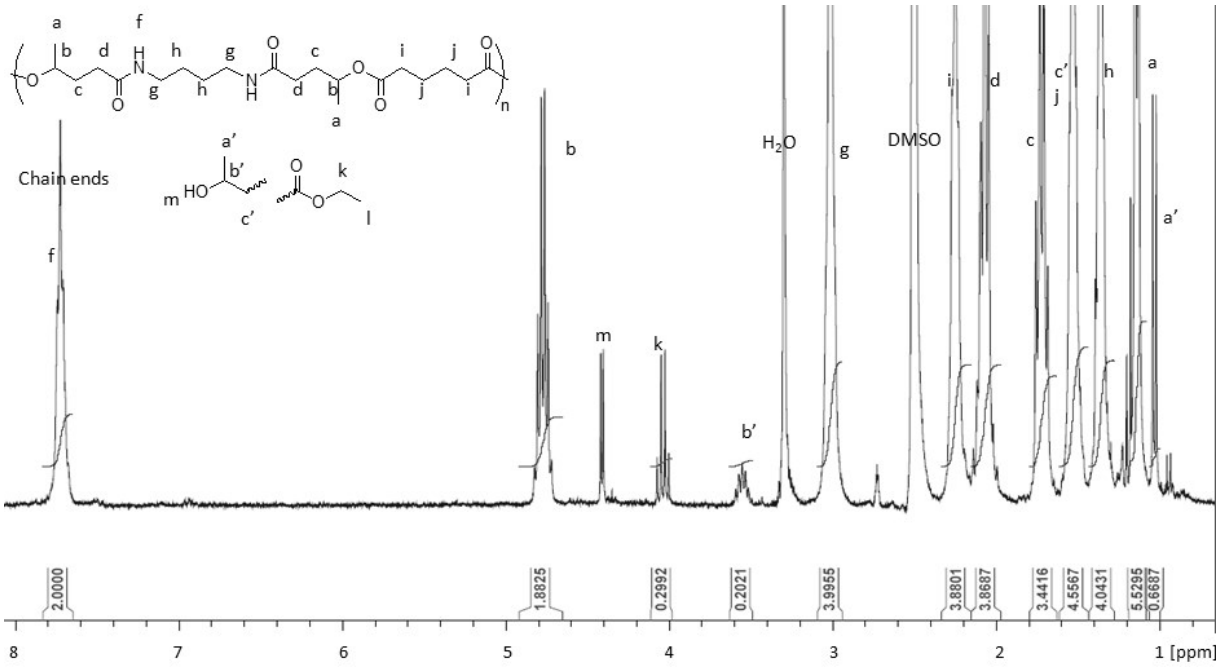


Fig. S22 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=4** (DMSO-d_6, 300 MHz, 300 K)

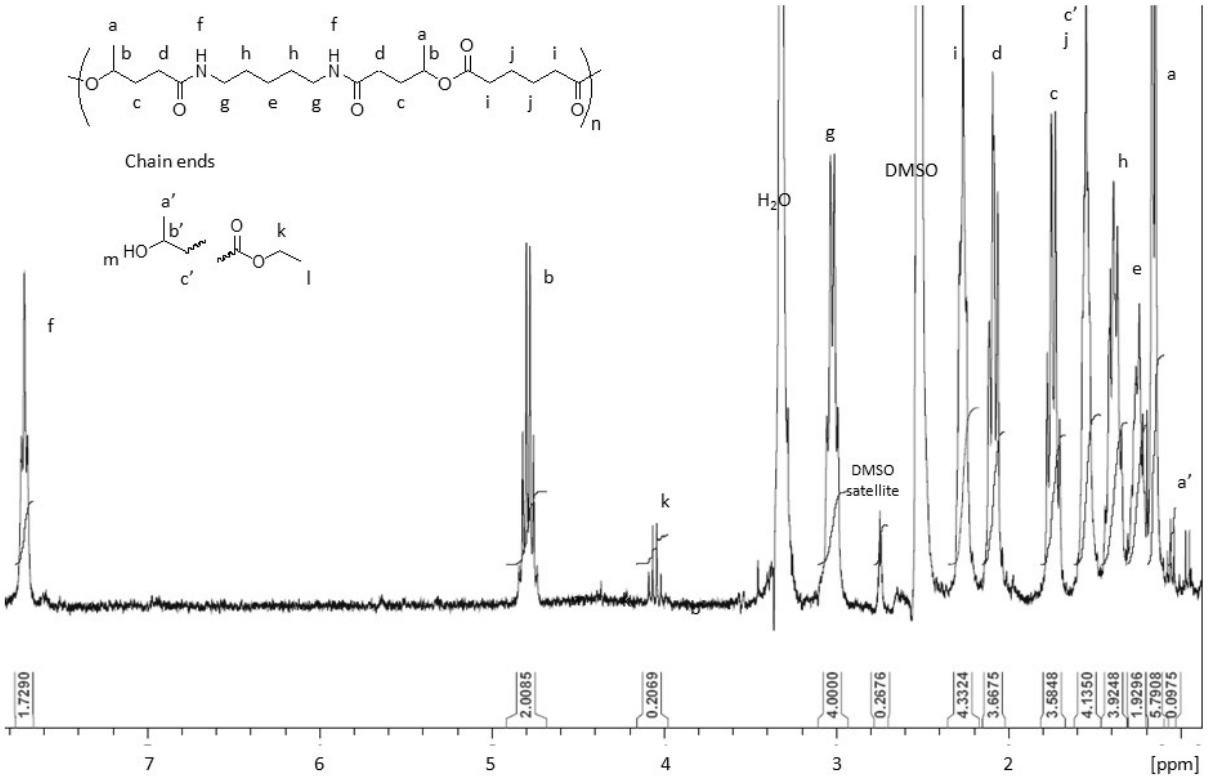


Fig. S23 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=5** (DMSO-d_6, 300 MHz, 300 K)

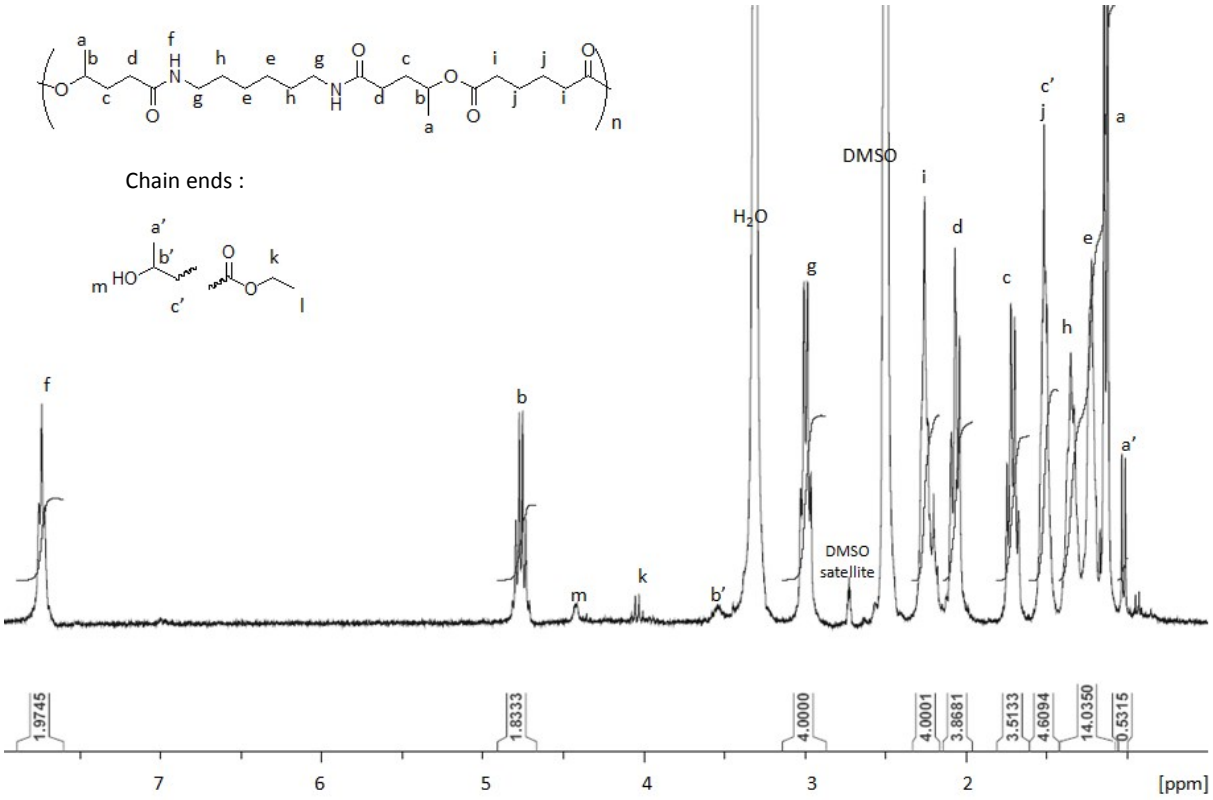


Fig. S24 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=6** (DMSO-d_6, 300 MHz, 300 K)

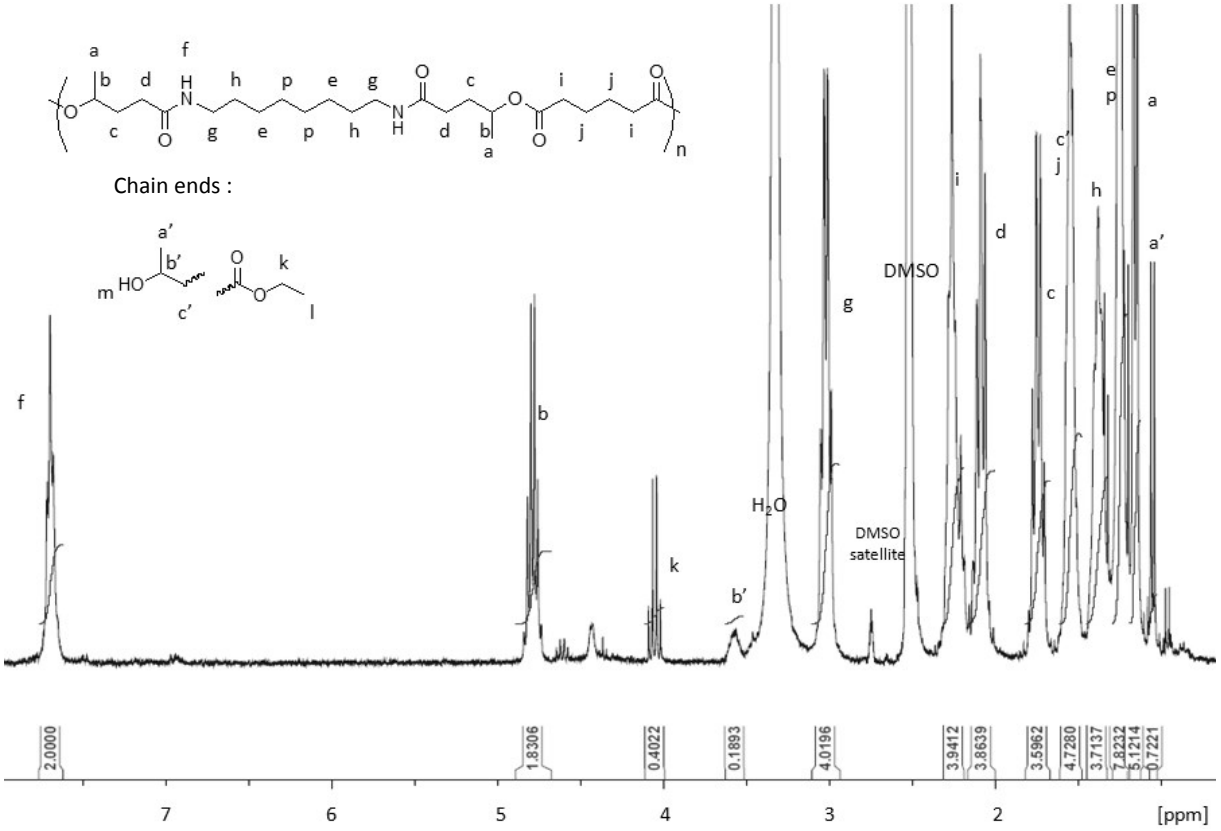


Fig. S25 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=8** (DMSO-d_6, 300 MHz, 300 K)

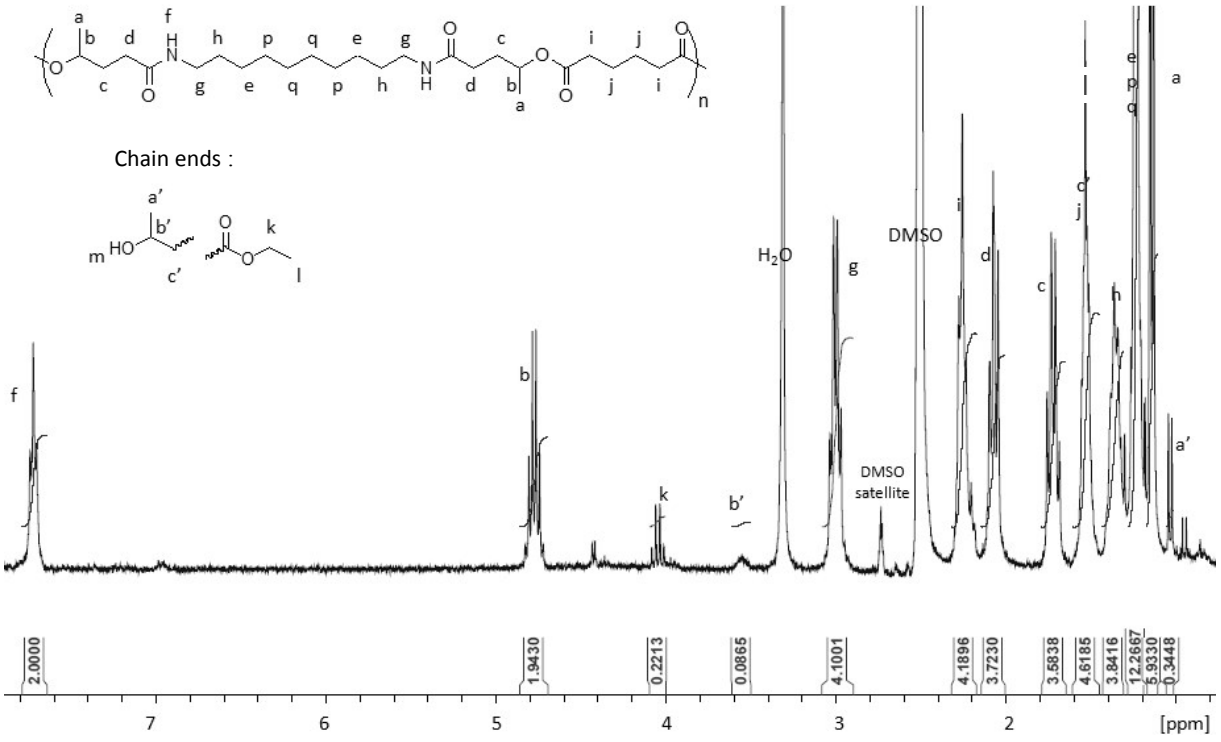


Fig. S26 ^{1}H NMR spectrum of poly(ester-*co*-amide) from diol-diamide **x=10** (DMSO-d_6, 300 MHz, 300 K)

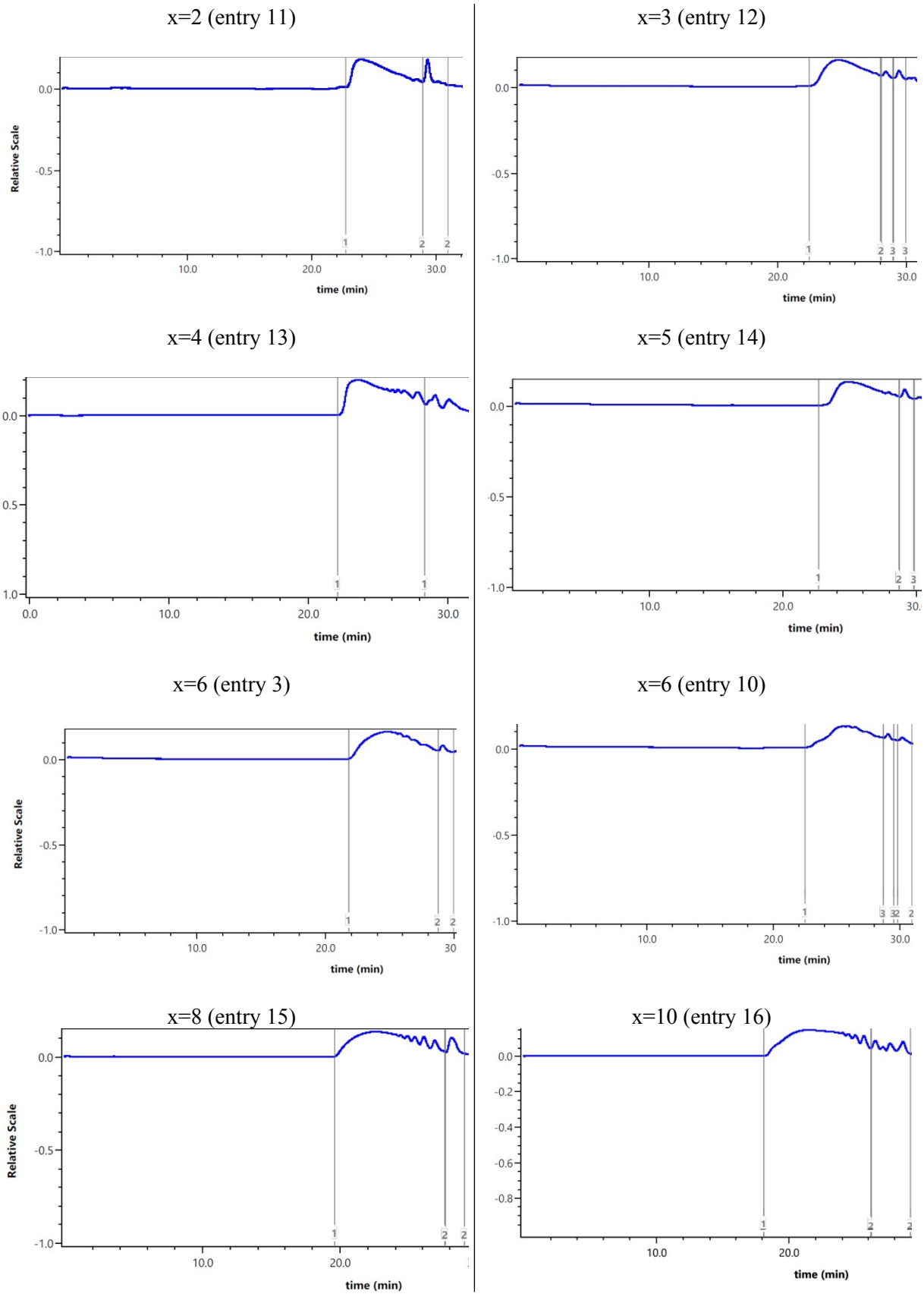


Fig. S27 SEC chromatograms of the reaction product obtained from diol-diamide and diethyl adipate ($CHCl_3$, 25°C, standard PS)

3. Influence of the medium concentration on polycondensation reactions

Table SI.1 Influence of the medium concentration on polycondensation reactions[a]

Entry	Diol diamide Number of carbons x	Concentration (mol/L) *vs* diol	Yield (%)	$M_{n\ SEC}$ (g/mol) [b]	$Đ_M$ [b]	Main peak [b,c] wt (%)	Corrected Yield (%)[d]	T_g (°C) [e]	T_c (°C) [e]	T_m (°C) [e]	$T_{deg\ 1}$ (°C) [f]	$T_{deg\ 2}$ (°C) [g]
11'	2	0.033	92	2,100	1.6	86	79	-10	/	/	187	355
11	2	0.10	81	1,500	1.4	88	71	-5	/	/		
12'	3	0.033	91	2,700	1.4	75	68	-10	/	/	198	360
12	3	0.10	92	2,300	1.4	91	84	-9	/	/		
13'	4	0.033	79	2,000	1.5	71	56	-2	/	/	201	365
13	4	0.10	65	2,300	1.6	86	56	0	/	/		
14'	5	0.033	94	1,300	1.6	79	75	-19	/	/	202	373
14	5	0.10	88	1,800	1.5	91	80	-10	/	/		
3	6	0.033	86	1,800	1.5	91	78	-13	/	/	205	375
10	6	0.10	90	3,300	1.5	92	83	-12	/	/		
15'	8	0.033	71	4,400	1.8	94	67	-22	71	89	180	376
15	8	0.10	85	4,200	1.8	91	78	-23	72	90		
16'	10	0.033	80	6,700	1.8	86	69	-15	20 and 55	97	203	378
16	10	0.10	71	7,200	1.6	91	65	-14	28 and 49	97		

[a] reaction at 81°C for 7 days in 20 mL or 60 mL of cyclohexane (respectively 0.1 and 0.033 mol/L *vs* diol), diol-diamide/diester (2 mmol/2 mmol), Novozyme 435 (10 % weight *vs.* monomers), Dean Stark apparatus with molecular sieves (replaced every 48h)

[b] SEC in chloroform at 25°C (polystyrene standards), M_n and $Đ_M$ for main peak

[c] main peak and secondary peaks distributions represent high M_n oligomers and small oligomers (M_n = 300-800 g/mol, $Đ_M$ = 1-1.3), respectively.
% by weight main peak = [area of main peak / (area of main peak + area of secondary peaks)] *100

[d] corrected yield = yield x main peak wt(%) / 100

[e] T_g, T_c (crystallization) and T_m (melting) determined by DSC on the second heating step.

[f] TGA temperatures at which 3 % of the mass was lost

[g] TGA temperatures for start of second degradation (inflection point of weight = f(T))

The polycondensation reaction gave higher corrected yield and higher M_n in lower volumes of solvent except for x=2 (entries 11-11')

4. DSC curves of polymers

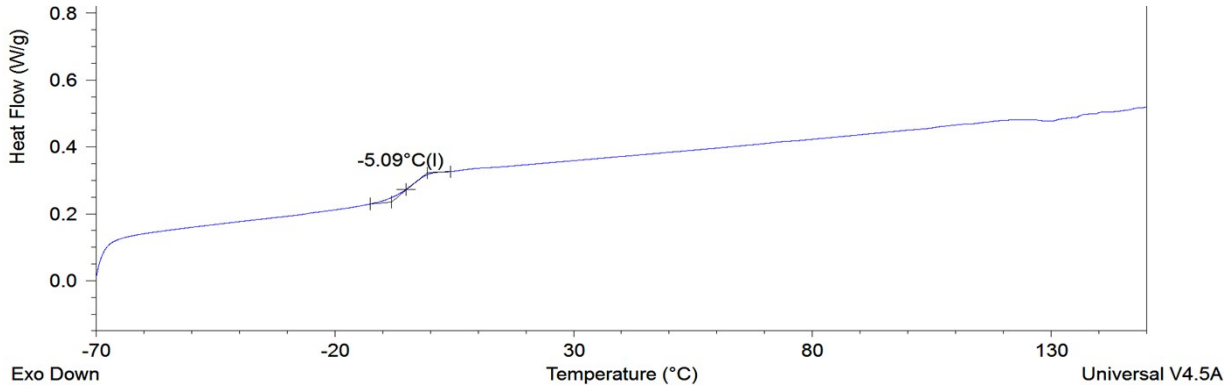


Fig. S28 DSC curve (second heating) of poly(ester-*co*-amide)s from diol-diamide **x=2**

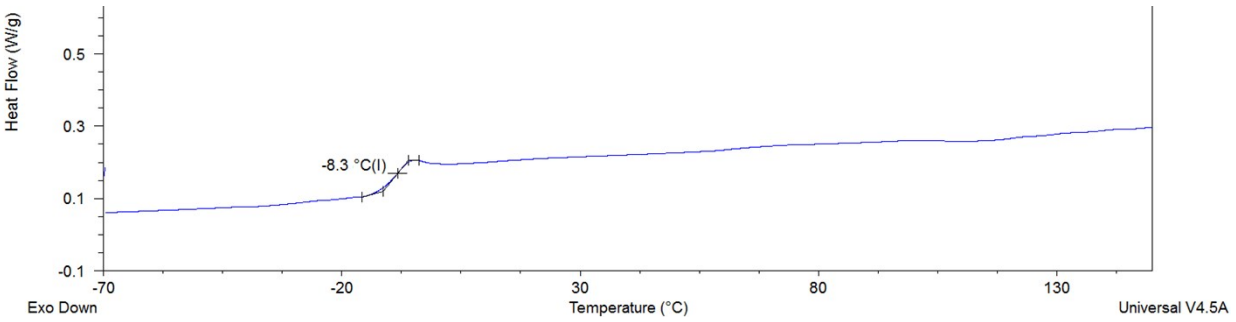


Fig. S29 DSC curve of poly(ester-*co*-amide)s from diol-diamide **x=3**

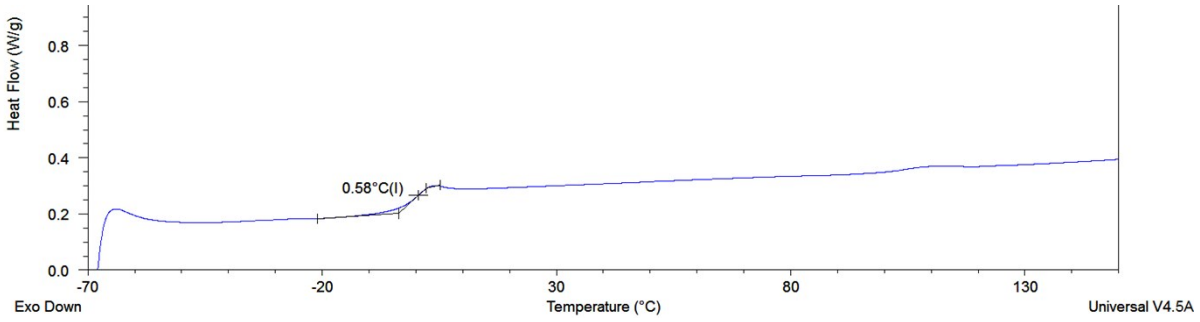


Fig. S30 DSC curve of poly(ester-*co*-amide)s from diol-diamide **x=4**

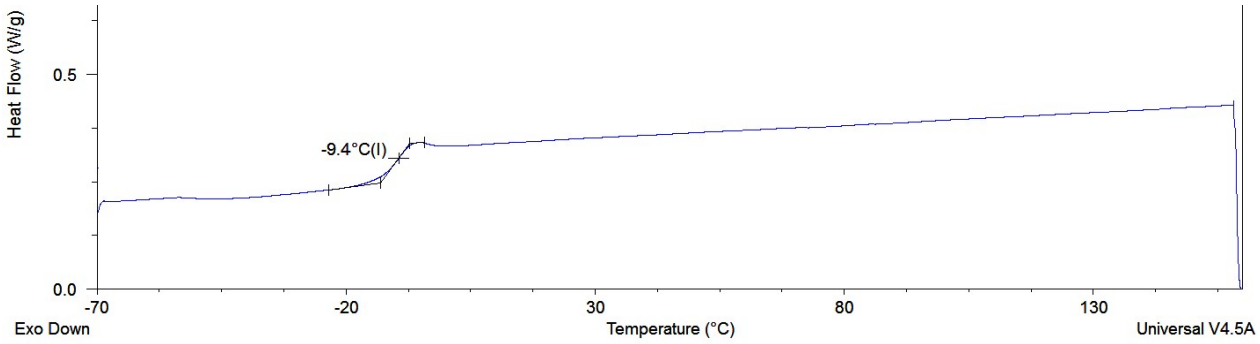


Fig. S31 DSC curve of poly(ester-*co*-amide)s from diol-diamide **x=5**

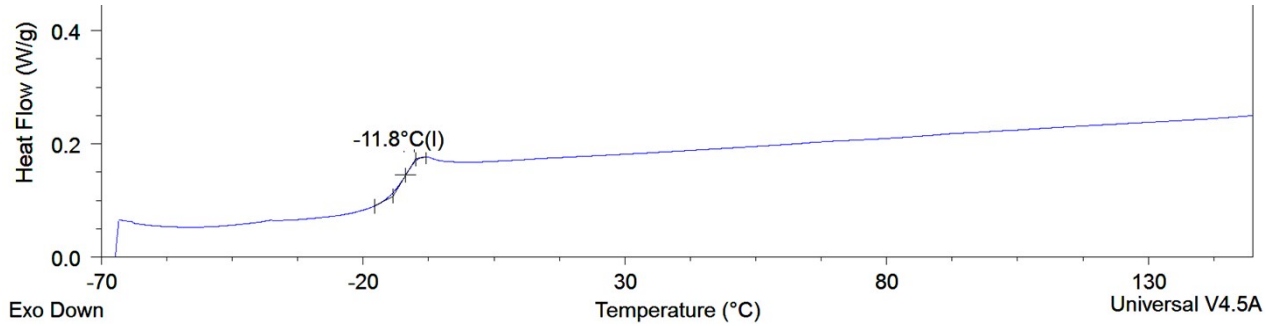


Fig. S32 DSC curve of poly(ester-*co*-amide)s from diol-diamide **x=6**

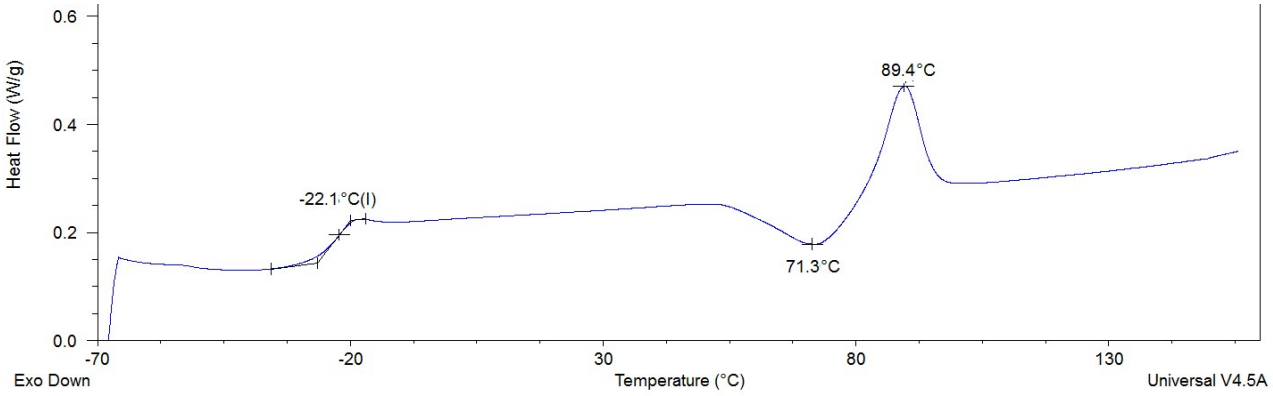


Fig. S33 DSC curve of poly(ester-*co*-amide)s from diol-diamide **x=8**

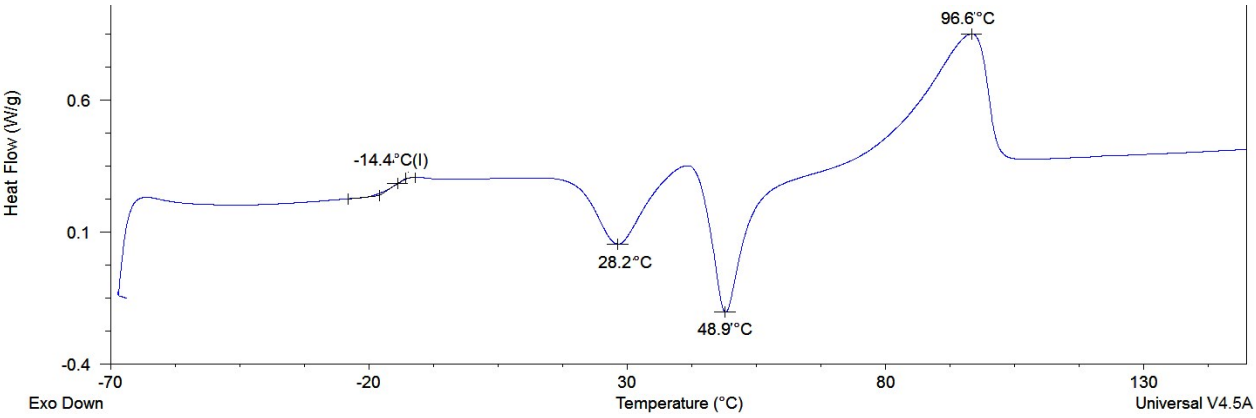


Fig. S34 DSC curve of poly(ester-*co*-amide)s (containing oligomers) from diol-diamide **x=10**

5. TGA curves of polymers

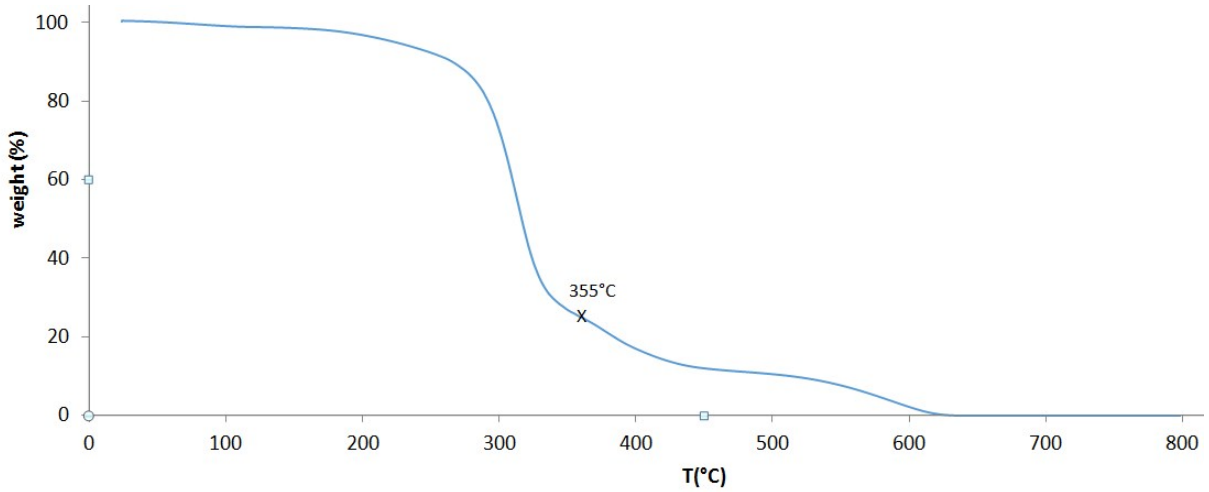


Fig. S35 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=2**

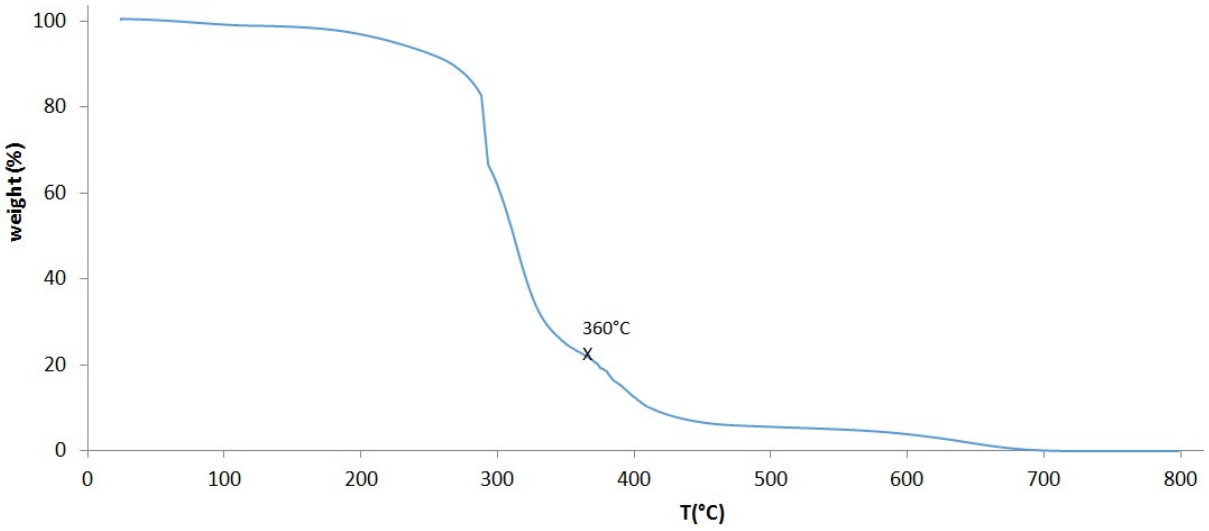


Fig. S36 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=3**

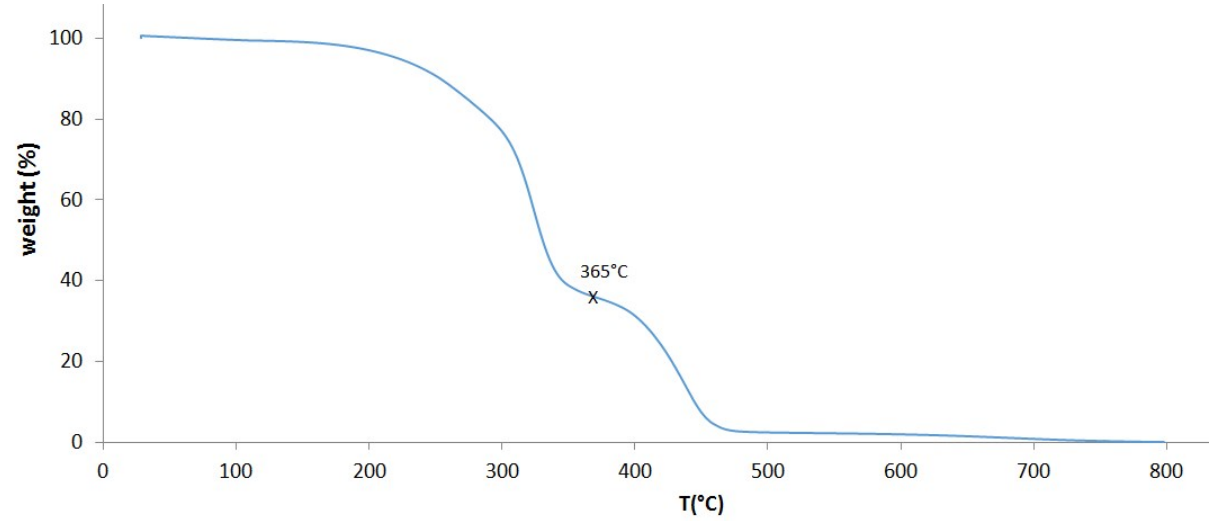


Fig. S37 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=4**

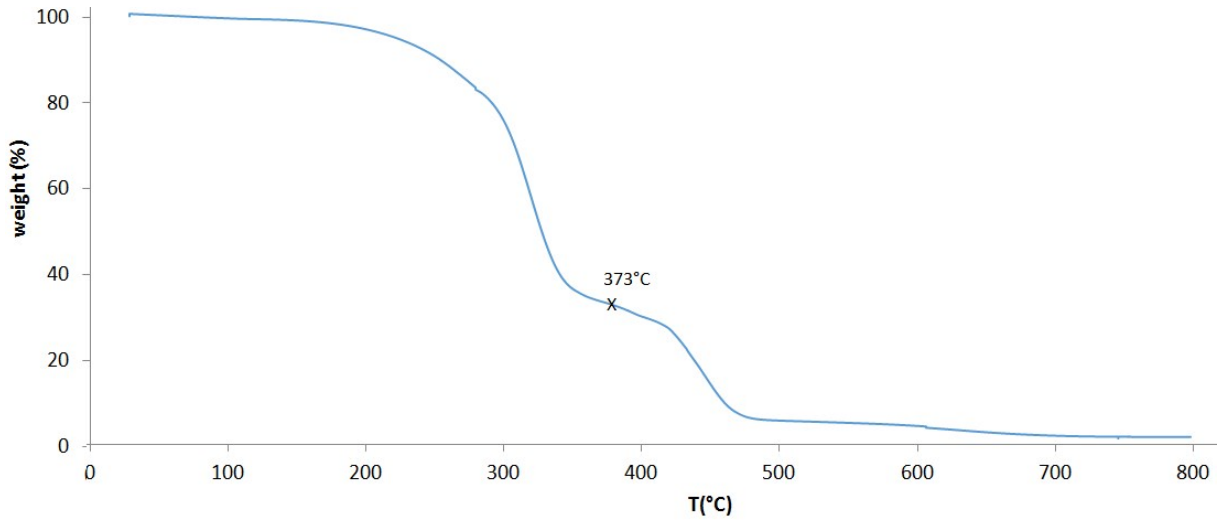


Fig. S38 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=5**

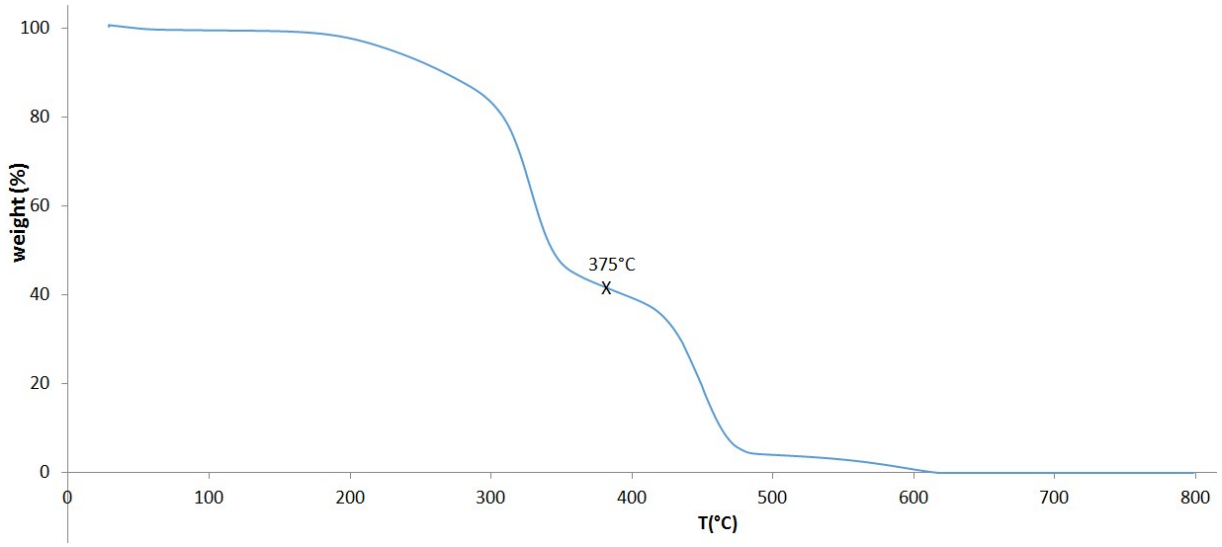


Fig. S39 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=6**

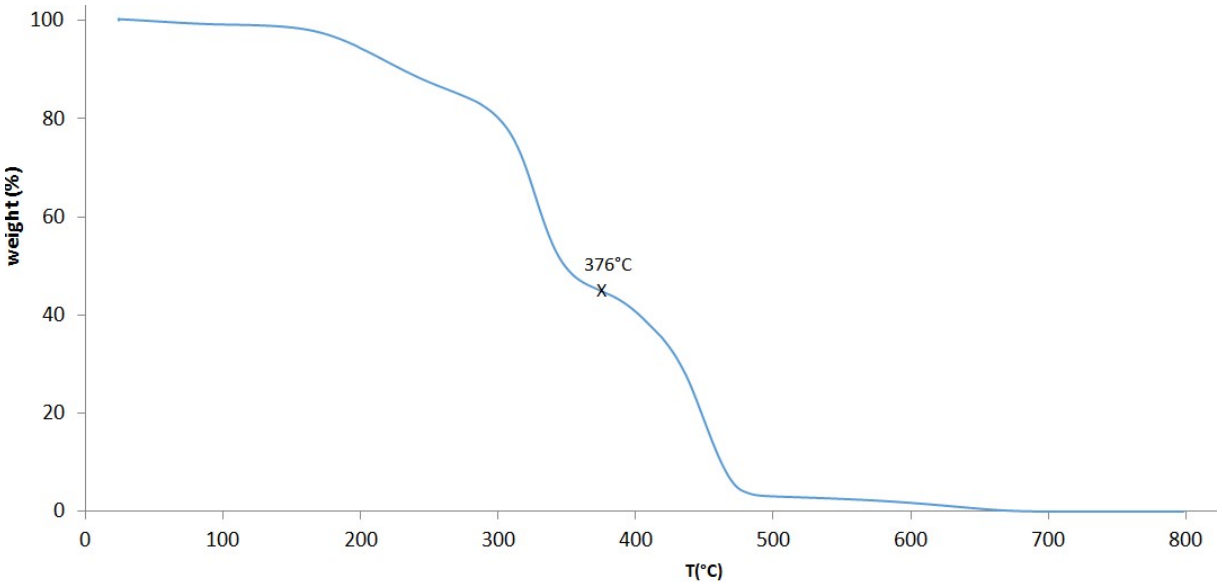


Fig. S40 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=8**

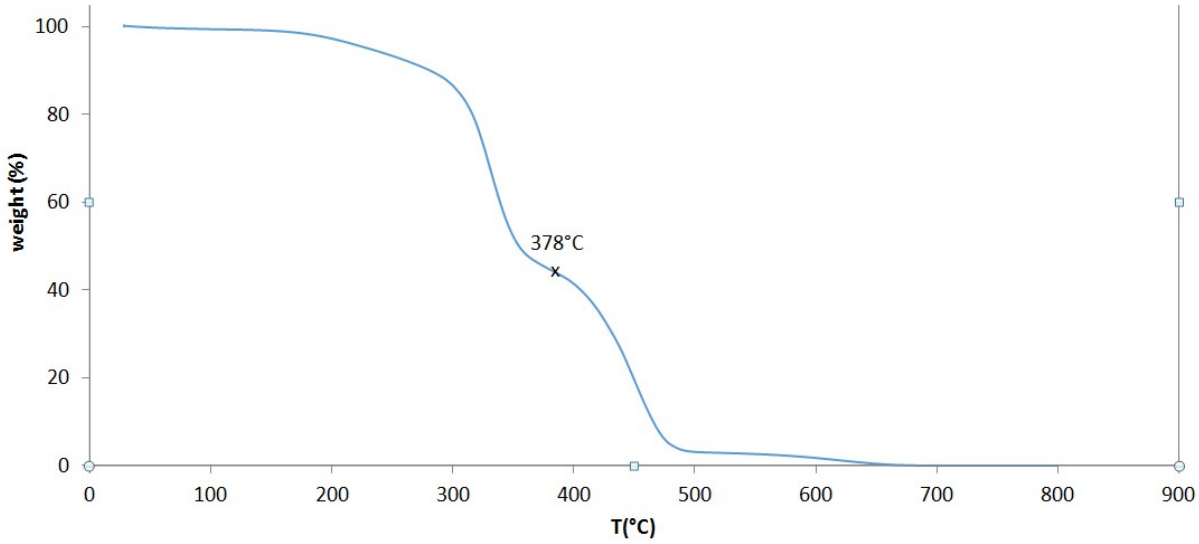


Fig. S41 TGA curve of poly(ester-*co*-amide)s from diol-diamide **x=10**