

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

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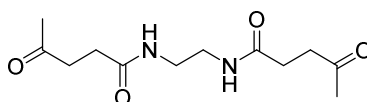
Supporting Information

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1. Characterization data of monomers

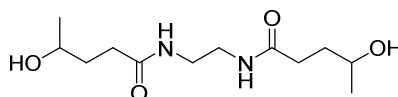
N,N'-(ethane-1,2-diyl)-bis-(4-oxopentanamide) (1a).



White solid (Yield= 77 %).

¹H NMR (300 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 2.08 (s, 6H, -CH₃), 2.26 (t, ³J= 6.9 Hz, 4H, -CH₂-CO-NH-), 2.62 (t, ³J= 6.9 Hz, 4H, -CH₂-CO-CH₃), 3.01-3.10 (m, 4H, -CH₂-NH-), 7.84 (s, 2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 29.1 (2C, -CH₂-CO-NH-), 29.7 (2C, -CH₃), 38.0 (2C, -CH₂-NH-), 38.4 (2C, -CH₂-CO-CH₃), 171.4 (2C, -NH-C=O-), 207.6 (2C, -C=O-).

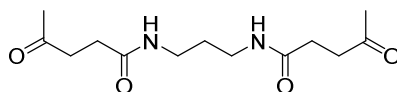
N,N'-(ethane-1,2-diyl)-bis-(4-hydroxypentanamide) (2a).



White solid (Yield= 67 %).

¹H NMR (300 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 1.02 (d, ³J= 6.2 Hz, 6H, -CH₃), 1.43-1.62 (m, 4H, -CH₂-CH(OH)-), 2.00-2.19 (m, 4H, -CH₂-CO-NH-), 2.94-3.13 (m, 4H, -CH₂-NH-), 3.48-3.60 (m, 2H, -CH(OH)-), 4.45 (d, ³J= 4.5 Hz, 2H, -OH), 7.79 (s, 2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 22.5 (2C, -CH₃), 31.1 (2C, -CH₂-CO-NH-), 33.8 (2C, -CH(OH)-CH₂-), 37.4 (2C, -CH₂-NH-), 64.5 (2C, -CH(OH)-), 171.8 (2C, -NH-C=O-). HRMS m/z calcd. for C₁₂H₂₄N₂O₄Na: 283.1635 [M+Na]⁺; found: 283.1634.

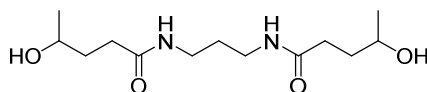
***N,N'*-(propane-1,3-diyl)-bis-(4-oxopentanamide) (1b).**



White solid (Yield= 69 %).

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

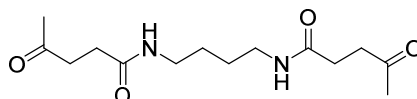
***N,N'*-(propane-1,3-diyl)-bis-(4-hydroxypentanamide) (2b).**



White solid (Yield= 79 %).

^1H NMR (300 MHz, DMSO- d_6 , 300 K): δ (ppm)= 1.02 (d, $^3J= 6.2$ Hz, 6H, $-\text{CH}_3$), 1.38-1.61 (m, 6H, $-\text{CH}_2\text{-CH(OH)-}$ and $-\text{CH}_2\text{-CH}_2\text{-NH-}$), 2.01-2.18 (m, 4H, $-\text{CH}_2\text{-CO-NH-}$), 2.97-3.04 (m, 4H, $-\text{CH}_2\text{-NH-}$), 3.50-3.60 (m, 2H, $-\text{CH(OH)-}$), 4.45 (d, $^3J= 4.7$ Hz, 2H, $-\text{OH}$), 7.75 (s, 2H, $-\text{NH-}$). ^{13}C NMR (75 MHz, DMSO- d_6 , 300 K): δ (ppm)= 23.5 (2C, $-\text{CH}_3$), 29.3 ($-\text{CH}_2\text{-CH}_2\text{-NH-}$), 32.1 (2C, $-\text{CH}_2\text{-CO-NH-}$), 34.9, (2C, $-\text{CH(OH)-CH}_2\text{-}$), 36.3 (2C, $-\text{CH}_2\text{-NH-}$), 65.4 (2C, $-\text{CH(OH)-}$), 172.3 (2C, $-\text{NH-C=O-}$). HRMS m/z calcd. for $\text{C}_{13}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$: 297.1790 [$\text{M}+\text{Na}$] $^+$; found: 297.1790.

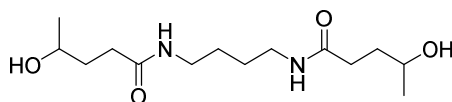
***N,N'*-(butane-1,4-diyl)-bis-(4-oxopentanamide) (1c).**



White solid (Yield= 95 %).

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

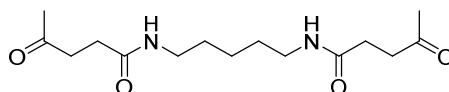
***N,N'*-(butane-1,4-diyl)-bis-(4-hydroxypentanamide) (2c).**



White solid (Yield= 81 %).

^1H NMR (300 MHz, DMSO- d_6 , 300 K): δ (ppm)= 1.03 (d, $^3J= 6.2$ Hz, 6H, $-\text{CH}_3$), 1.33-1.37 (m, 4H, $-\text{CH}_2\text{-CH}_2\text{-NH-}$), 1.44-1.62 (m, 4H, $-\text{CH}_2\text{-CH(OH)-}$), 1.98-2.19 (m, 4H, $-\text{CH}_2\text{-CO-NH-}$), 2.97-3.03 (m, 4H, $-\text{CH}_2\text{-NH-}$), 3.49-3.60 (m, 2H, $-\text{CH(OH)-}$), 4.42 (d, $^3J= 4.7$ Hz, 2H, $-\text{OH}$), 7.72 (t, $^3J= 5.4$ Hz, 2H, $-\text{NH-}$). ^{13}C NMR (75 MHz, DMSO- d_6 , 300 K): δ (ppm)= 23.4 (2C, $-\text{CH}_3$), 26.7 (2C, $-\text{CH}_2\text{-CH}_2\text{-NH-}$), 32.0 (2C, $-\text{CH}_2\text{-CO-NH-}$), 34.9, (2C, $-\text{CH(OH)-CH}_2\text{-}$), 38.1 (2C, $-\text{CH}_2\text{-NH-}$), 65.5 (2C, $-\text{CH(OH)-}$), 172.2 (2C, $-\text{NH-C=O-}$). HRMS m/z calcd. for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}_4\text{Na}$ 311.1947: [$\text{M}+\text{Na}$] $^+$; found: 311.1944.

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

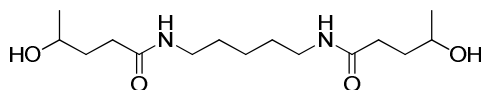


White solid (Yield= 82 %).

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

2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 23.7 (-CH₂-CH₂-CH₂-NH-), 28.8 (2C, -CH₂-CH₂-NH-), 29.1 (2C, -CH₂-CO-NH-), 29.6 (2C, -CH₃), 38.0 (2C, -CH₂-NH-), 39.5 (2C, -CH₂-CO-CH₃), 170.9 (2C, -NH-C=O-), 207.4 (2C, -C=O-).

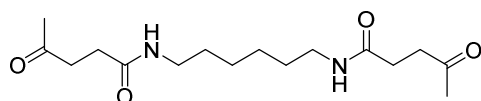
***N,N'*-(pentane-1,5-diyl)-bis-(4-hydroxypentanamide) (2d).**



White solid (Yield= 69 %).

¹H NMR (300 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 1.03 (d, ³J= 6.2 Hz, 6H, -CH₃), 1.17-1.27 (m, 2H, -CH₂-CH₂-CH₂-NH-), 1.31-1.42 (m, 4H, -CH₂-CH₂-NH-), 1.45-1.60 (m, 4H, -CH₂-CH(OH)-), 2.00-2.18 (m, 4H, -CH₂-CO-NH-), 2.96-3.03 (m, 4H, -CH₂-NH-), 3.48-3.61 (m, 2H, -CH(OH)-), 4.42 (d, ³J= 4.7 Hz, 2H, -OH), 7.70 (t, ³J= 5.4 Hz, 2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 23.4 (2C, -CH₃), 23.8 (-CH₂-CH₂-CH₂-NH-), 28.8 (2C, -CH₂-CH₂-NH-), 32.0 (2C, -CH₂-CO-NH-), 34.9, (2C, -CH(OH)-CH₂-), 38.3 (2C, -CH₂-NH-), 65.4 (2C, -CH(OH)-), 172.1 (2C, -NH-C=O-). HRMS m/z calcd. for C₁₅H₃₀N₂O₄Na: 325.2103 [M+Na]⁺; found: 325.2101.

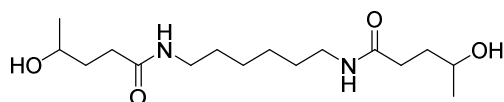
***N,N'*-(hexane-1,6-diyl)-bis-(4-oxopentanamide) (1e).**



White solid (Yield= 93%).

¹H NMR (300 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 1.19-1.26 (m, 4H, -CH₂-CH₂-CH₂-NH-), 1.30-1.39 (m, 4H, -CH₂-CH₂-NH-), 2.08 (s, 6H, -CH₃), 2.26 (t, ³J= 6.9 Hz, 4H, -CH₂-CO-NH-), 2.61 (t, ³J= 6.9 Hz, 4H, -CH₂-CO-CH₃), 2.96-3.02 (m, 4H, -CH₂-NH-), 7.75 (s, 2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 26.1 (2C, -CH₂-CH₂-CH₂-NH-), 29.1 (4C, -CH₂-CO-NH- and -CH₂-CH₂-NH-), 29.7 (2C, -CH₃), 38.1 (2C, -CH₂-NH-), 38.5 (2C, -CH₂-CO-CH₃), 171.0 (2C, -NH-C=O-), 207.6 (2C, -C=O-).

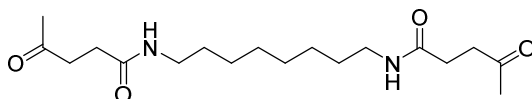
***N,N'*-(hexane-1,6-diyl)-bis-(4-hydroxypentanamide) (2e).**



White solid (Yield= 81 %).

¹H NMR (300 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 1.03 (d, ³J= 6.2 Hz, 6H, -CH₃), 1.18-1.28 (m, 4H, -CH₂-CH₂-CH₂-NH-), 1.30-1.41 (m, 4H, -CH₂-CH₂-NH-), 1.46-1.58 (m, 4H, -CH₂-CH(OH)-), 2.00-2.18 (m, 4H, -CH₂-CO-NH-), 2.96-3.02 (m, 4H, -CH₂-NH-), 3.48-3.61 (m, 2H, -CH(OH)-), 4.42 (d, ³J= 4.7 Hz, 2H, -OH), 7.70 (t, ³J= 5.4 Hz, 2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 23.5 (2C, -CH₃), 26.1 (2C, -CH₂-CH₂-CH₂-NH-), 29.1 (2C, -CH₂-CH₂-NH-), 32.1 (2C, -CH₂-CO-NH-), 34.9, (2C, -CH(OH)-CH₂-), 38.3 (2C, -CH₂-NH-), 65.5 (2C, -CH(OH)-), 172.2 (2C, -NH-C=O-). HRMS m/z calcd. for C₁₆H₃₂N₂O₄Na: 339.2264 [M+Na]⁺; found: 339.2260.

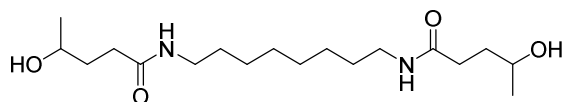
***N,N'*-(octane-1,8-diyl)-bis-(4-oxopentanamide) (1f).**



White solid (Yield= 87 %).

¹H NMR (300 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 1.19-1.26 (m, 8H, -CH₂-CH₂-CH₂-CH₂-NH-), 1.29-1.40 (m, 4H, -CH₂-CH₂-NH-), 2.07 (s, 6H, -CH₃), 2.25 (t, ³J= 6.9 Hz, 4H, -CH₂-CO-NH-), 2.61 (t, ³J= 6.9 Hz, 4H, -CH₂-CO-CH₃), 2.94-3.03 (m, 4H, -CH₂-NH-), 7.78 (s, 2H, -NH-). ¹³C NMR (75 MHz, DMSO-*d*₆, 300 K): δ (ppm)= 26.4 (2C, -CH₂-CH₂-CH₂-CH₂-NH-), 28.8 (2C, -CH₂-CH₂-CH₂-NH-), 29.1 (2C, -CH₂-CO-NH-), 29.2 (2C, -CH₂-CH₂-NH-), 29.7 (2C, -CH₃), 38.1 (2C, -CH₂-NH-), 38.5 (2C, -CH₂-CO-CH₃), 171.0 (2C, -NH-C=O-), 207.6 (2C, -C=O-).

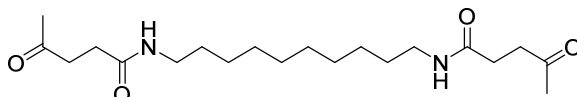
***N,N'*-(octane-1,8-diyl)-bis-(4-hydroxypentanamide) (2f).**



White solid (Yield= 72 %).

^1H NMR (300 MHz, DMSO- d_6 , 300 K): δ (ppm)= 1.03 (d, 3J = 6.2 Hz, 6H, - CH_3), 1.18-1.28 (m, 4H, - CH_2 - CH_2 - CH_2 -NH-), 1.30-1.41 (m, 4H, - CH_2 - CH_2 -NH-), 1.46-1.58 (m, 4H, - CH_2 -CH(OH)-), 2.00-2.18 (m, 4H, - CH_2 -CO-NH-), 2.96-3.02 (m, 4H, - CH_2 -NH-), 3.48-3.61 (m, 2H, -CH(OH)-), 4.42 (d, 3J = 4.7 Hz, 2H, -OH), 7.70 (t, 3J = 5.4 Hz, 2H, -NH-). ^{13}C NMR (75 MHz, DMSO- d_6 , 300 K): δ (ppm)= 23.5 (2C, - CH_3), 26.4 (2C, - CH_2 -), 28.7 (2C, - CH_2 -), 29.2 (2C, - CH_2 -), 32.1 (2C, - CH_2 -CO-NH-), 34.9, (2C, -CH(OH)- CH_2 -), 38.4 (2C, - CH_2 -NH-), 65.5 (2C, -CH(OH)-), 172.1 (2C, -NH-C=O-). HRMS m/z calcd. for $\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_4\text{Na}$: 367.2566 [M+Na] $^+$; found: 367.2573.

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

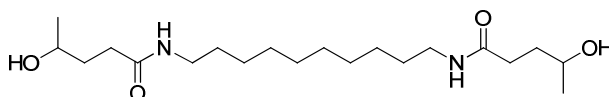


White solid (Yield= 78 %).

^1H NMR (300 MHz, DMSO- d_6 , 300 K): δ (ppm)= 1.19-1.26 (m, 16H, - CH_2 -), 1.35 (m, 4H, - CH_2 - CH_2 -NH-), 2.08 (s, 6H, - CH_3), 2.25 (t, 3J = 6.9 Hz, 4H, - CH_2 -CO-NH-), 2.61 (t, 3J = 6.9 Hz, 4H, - CH_2 -CO- CH_3), 2.99 (m, 4H, - CH_2 -NH-), 7.75 (s, 2H, -NH-).

^{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, - CH_2 -NH-), 39.7 (2C, - CH_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 %).

^1H NMR (300 MHz, DMSO- d_6 , 300 K): δ (ppm)= 1.02 (d, 3J = 6.2 Hz, 6H, - CH_3), 1.19-1.27 (m, 12H, - CH_2 -), 1.29-1.43 (m, 4H, - CH_2 - CH_2 -NH-), 1.43-1.65 (m, 4H, - CH_2 -CH(OH)-), 2.00-2.17 (m, 4H, - CH_2 -CO-NH-), 2.96-3.02 (m, 4H, - CH_2 -NH-), 3.45-3.62 (m, 2H, -CH(OH)-), 4.41 (d, 3J = 4.7 Hz, 2H, -OH), 7.69 (t, 3J = 5.4 Hz 2H, -NH-). ^{13}C NMR (75 MHz, DMSO- d_6 , 300 K): δ (ppm)= 23.4 (2C, - CH_3), 26.4 (2C, - CH_2 -), 28.7 (2C, - CH_2 -), 28.9 (2C, - CH_2 -), 29.1 (2C, - CH_2 -), 32.0 (2C, - CH_2 -), 34.9 (2C, -CH(OH)- CH_2 -), 38.4 (2C, - CH_2 -NH-), 65.4 (2C, -CH(OH)-), 172.1 (2C, -NH-C=O-). HRMS m/z calcd. for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{O}_4\text{Na}$: 395.2886 [M+Na] $^+$; found: 395.2884.

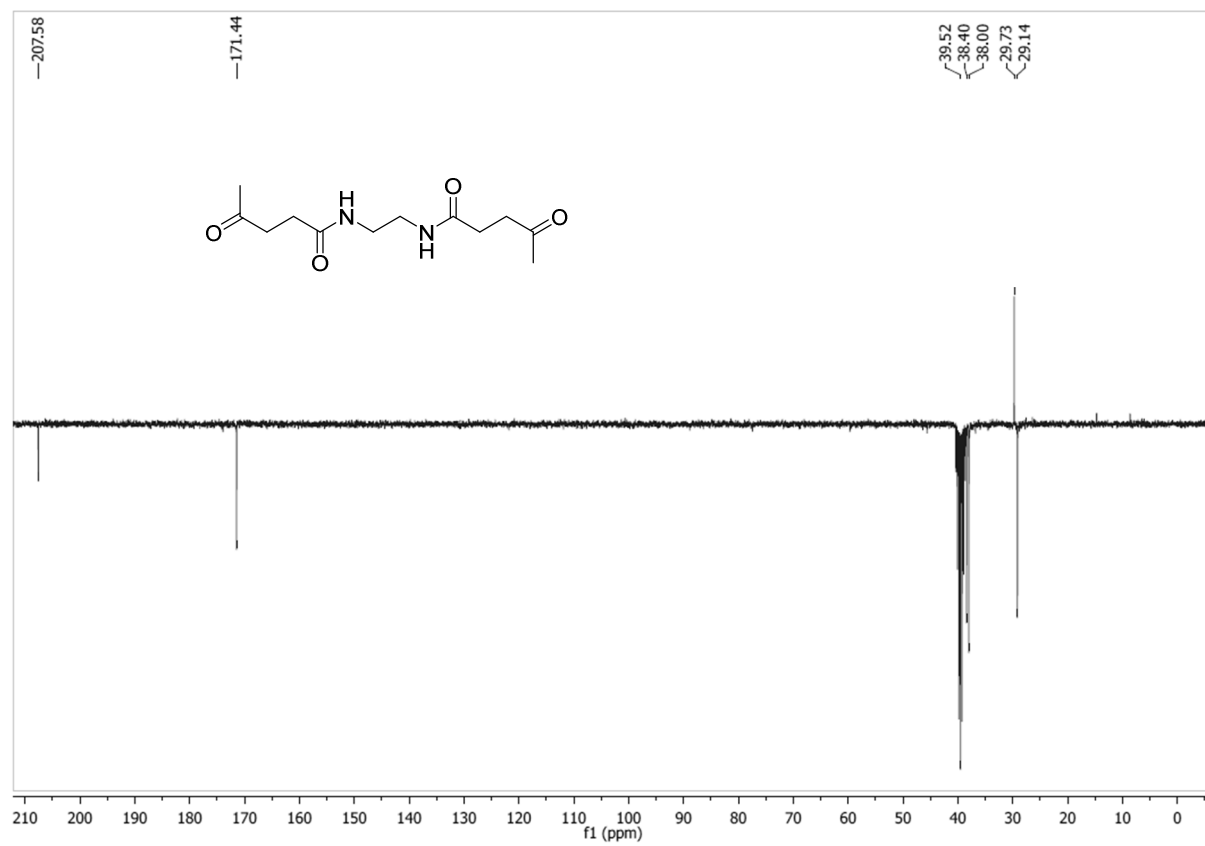
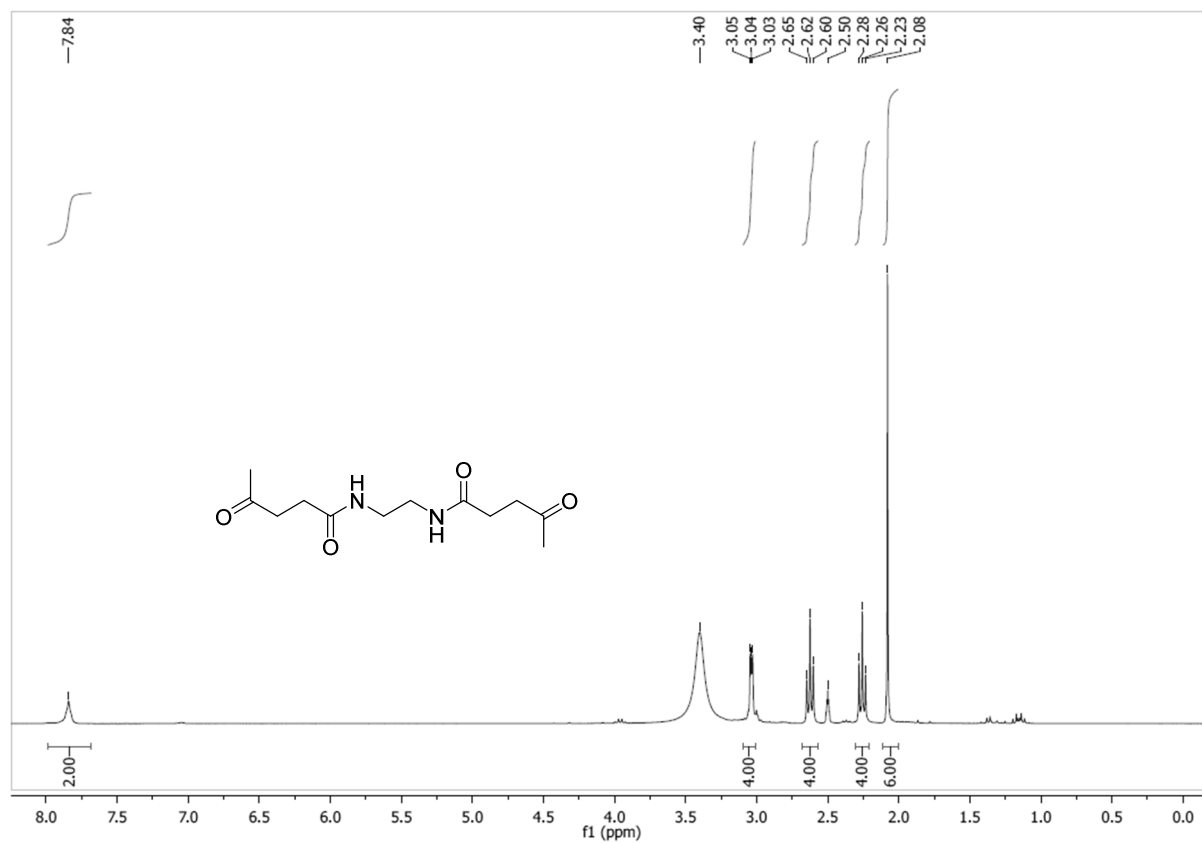


Fig. S1 ^1H (top) and DEPT ^{13}C (bottom) NMR spectra of **1a** (DMSO- d_6 , 300 MHz and 75 MHz, 300 K)

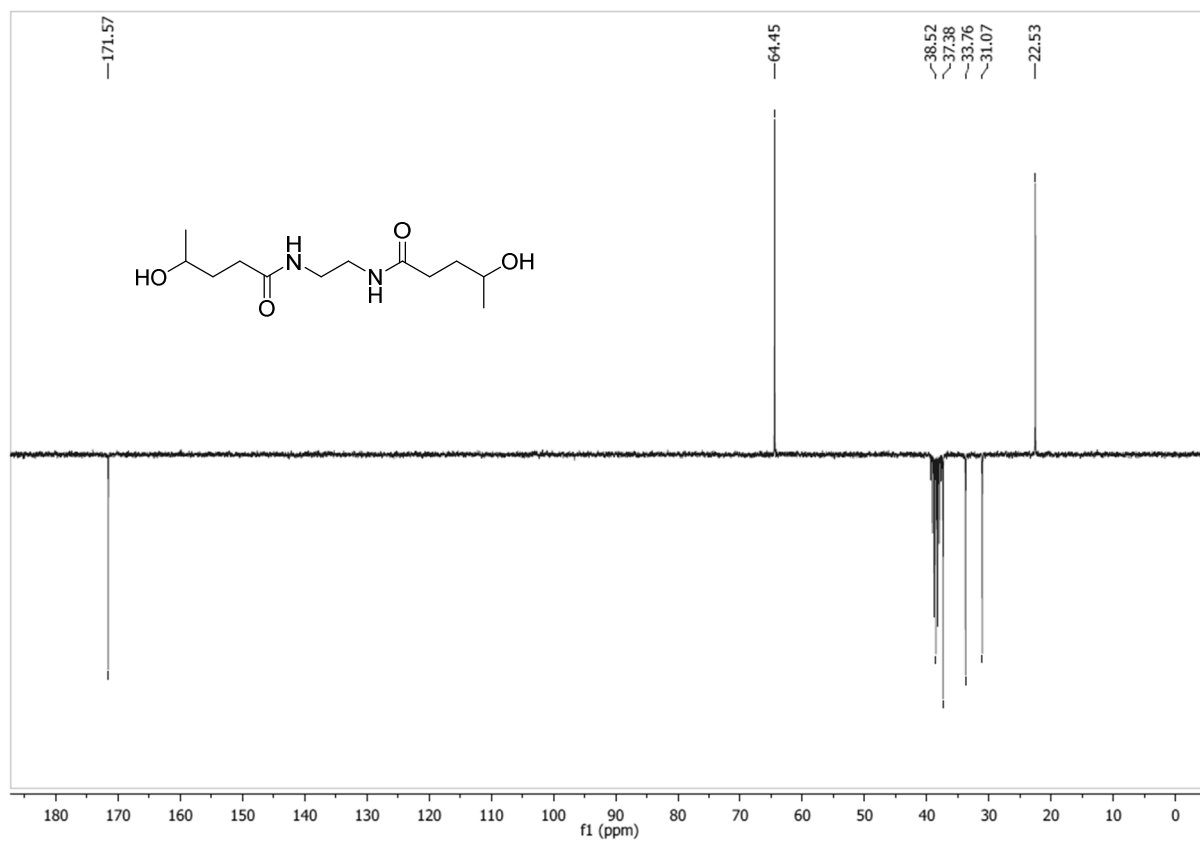
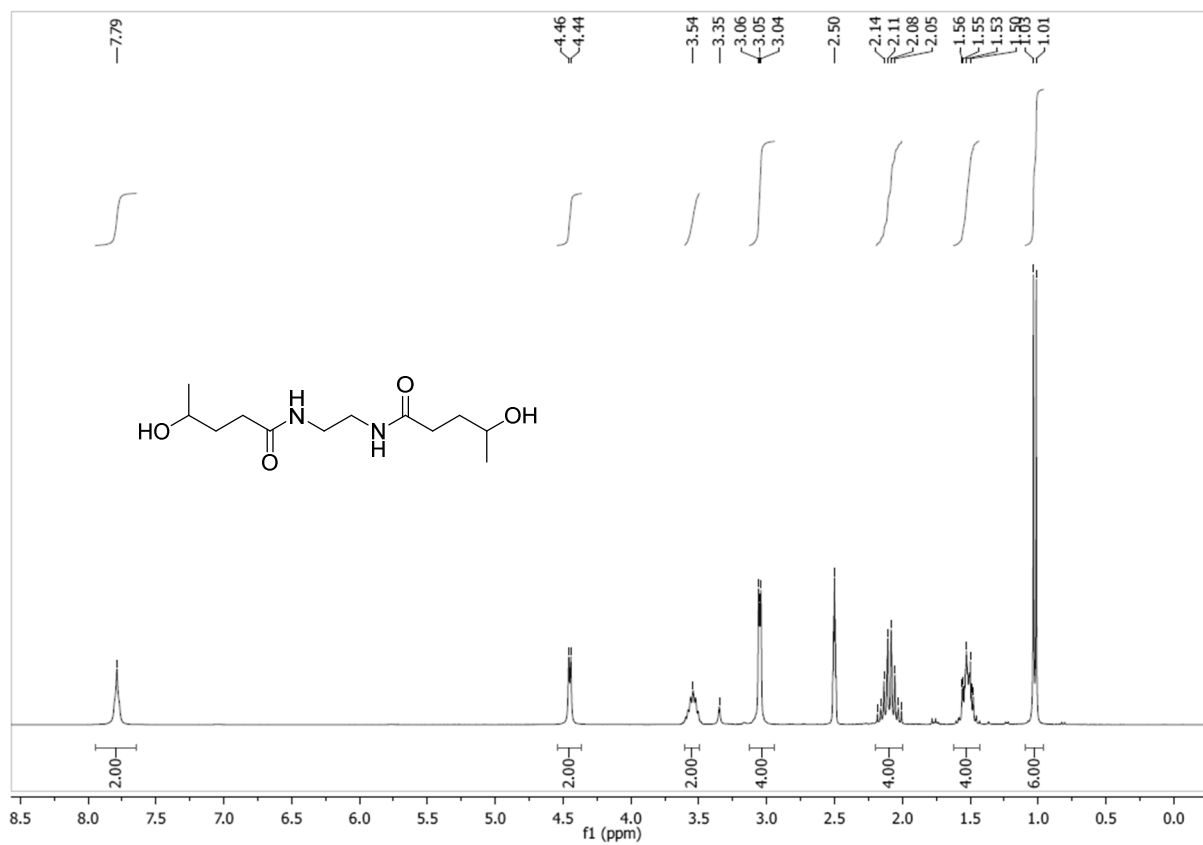


Fig. S2 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **2a** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

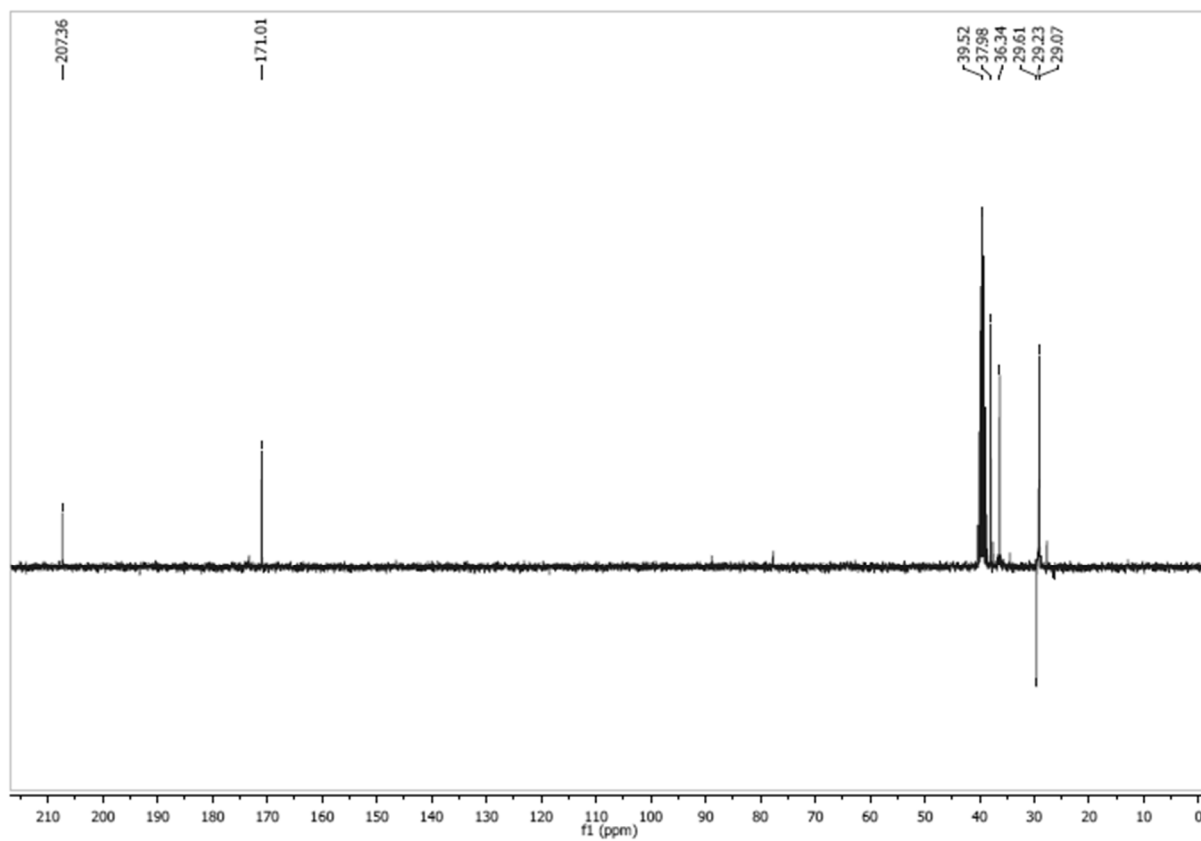
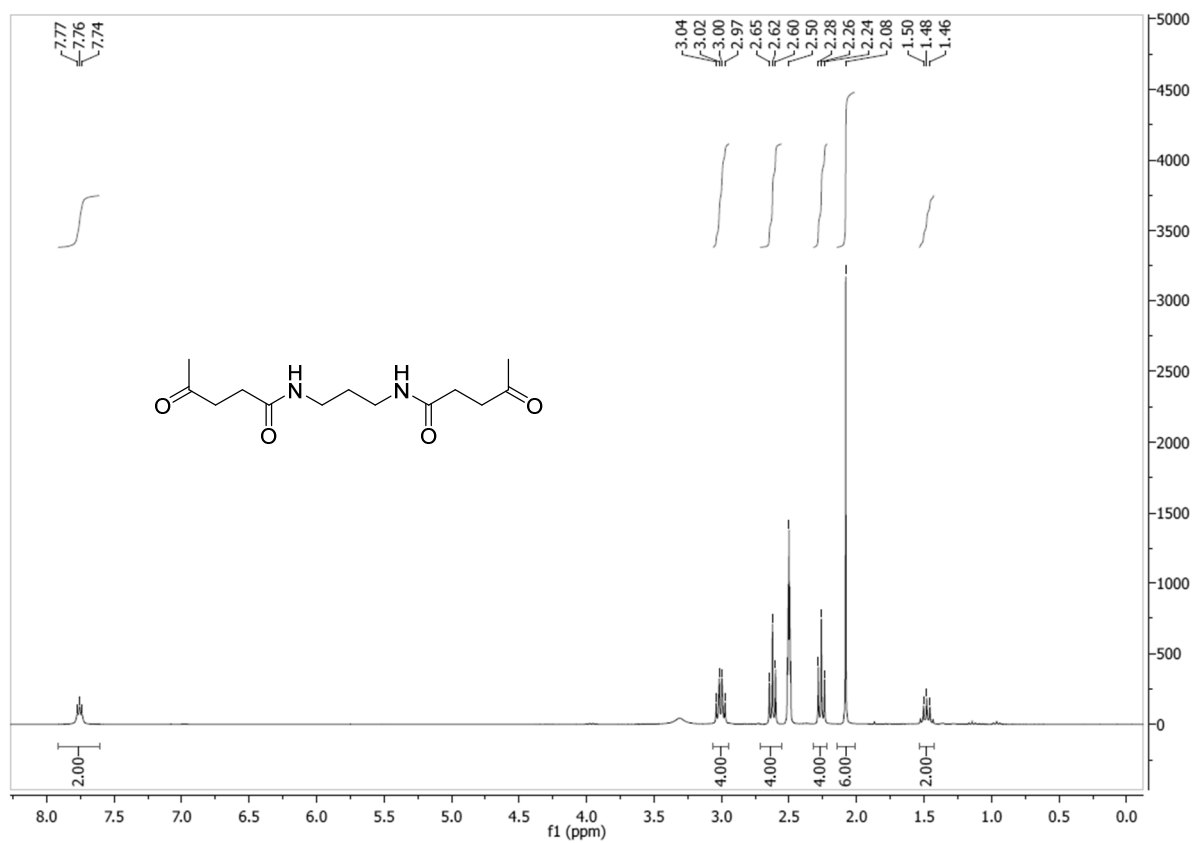


Fig. S3 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **1b** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

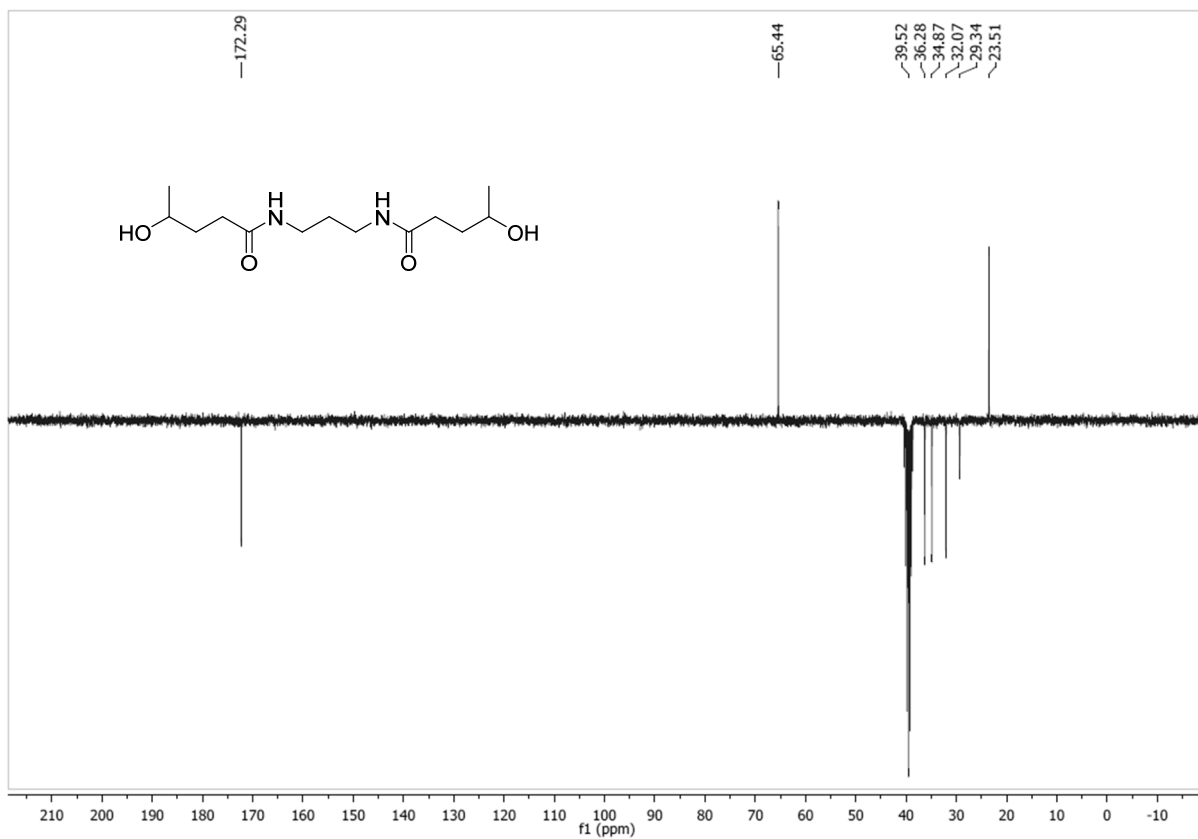
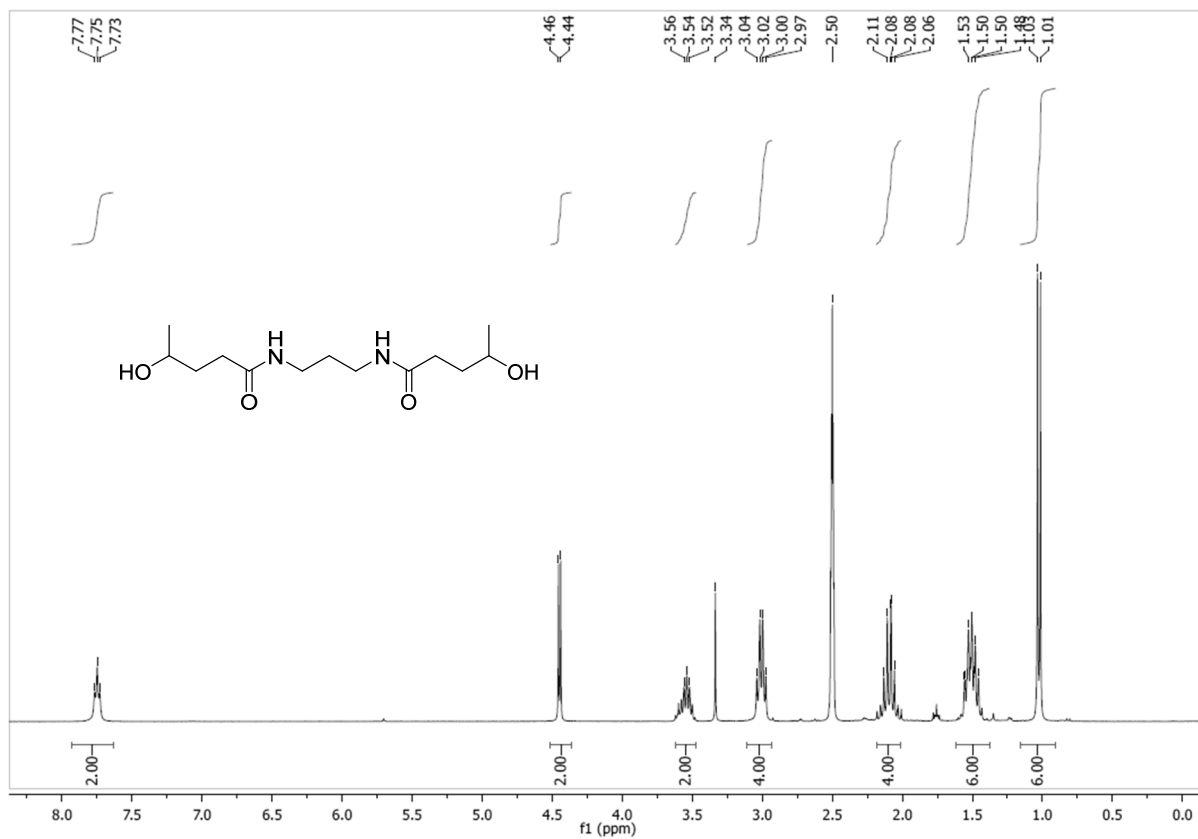


Fig. S4 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **2b** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

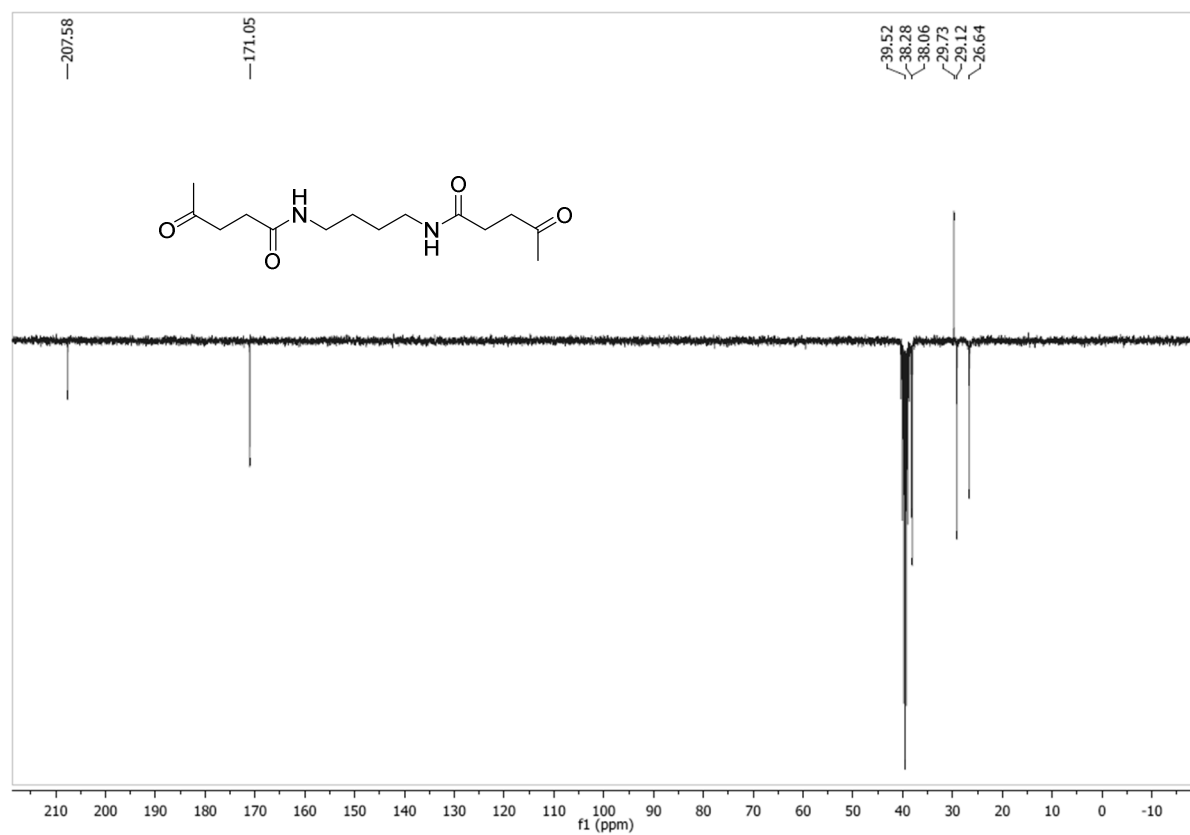
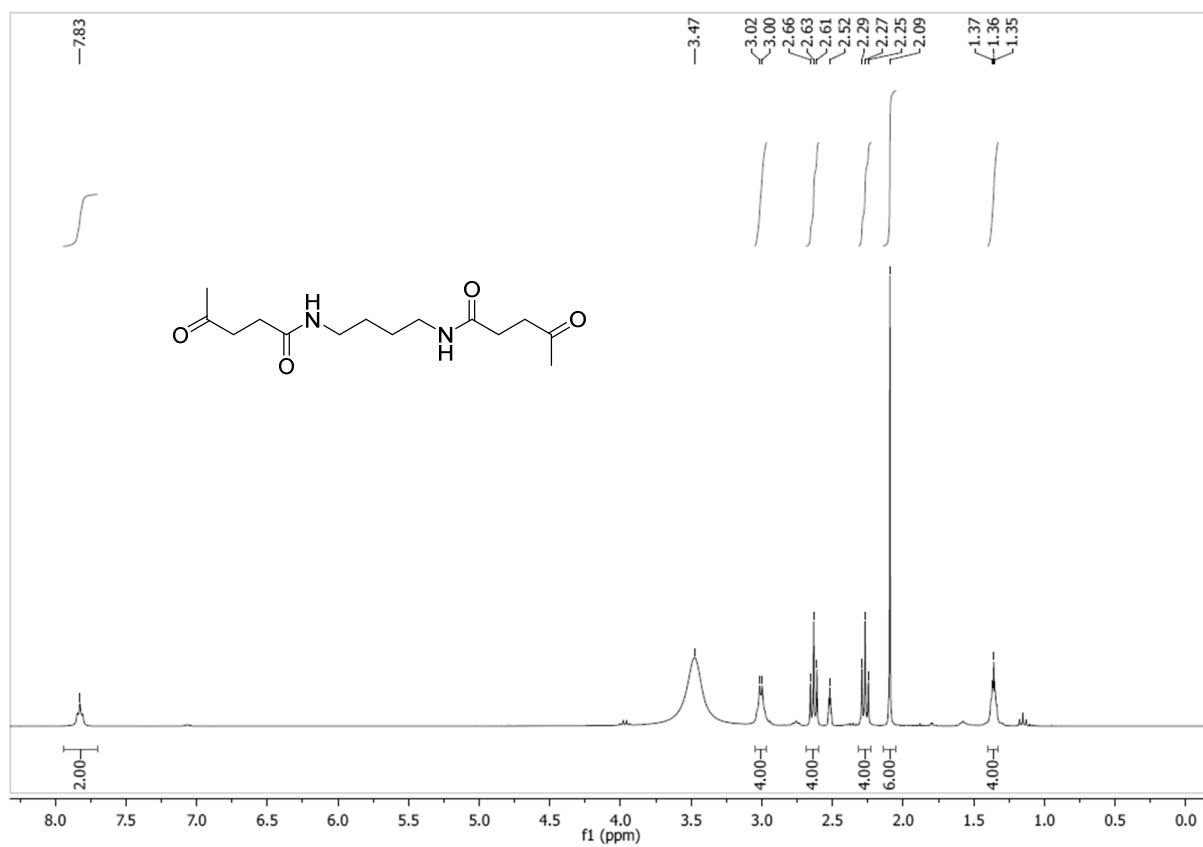


Fig. S5 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **1c** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

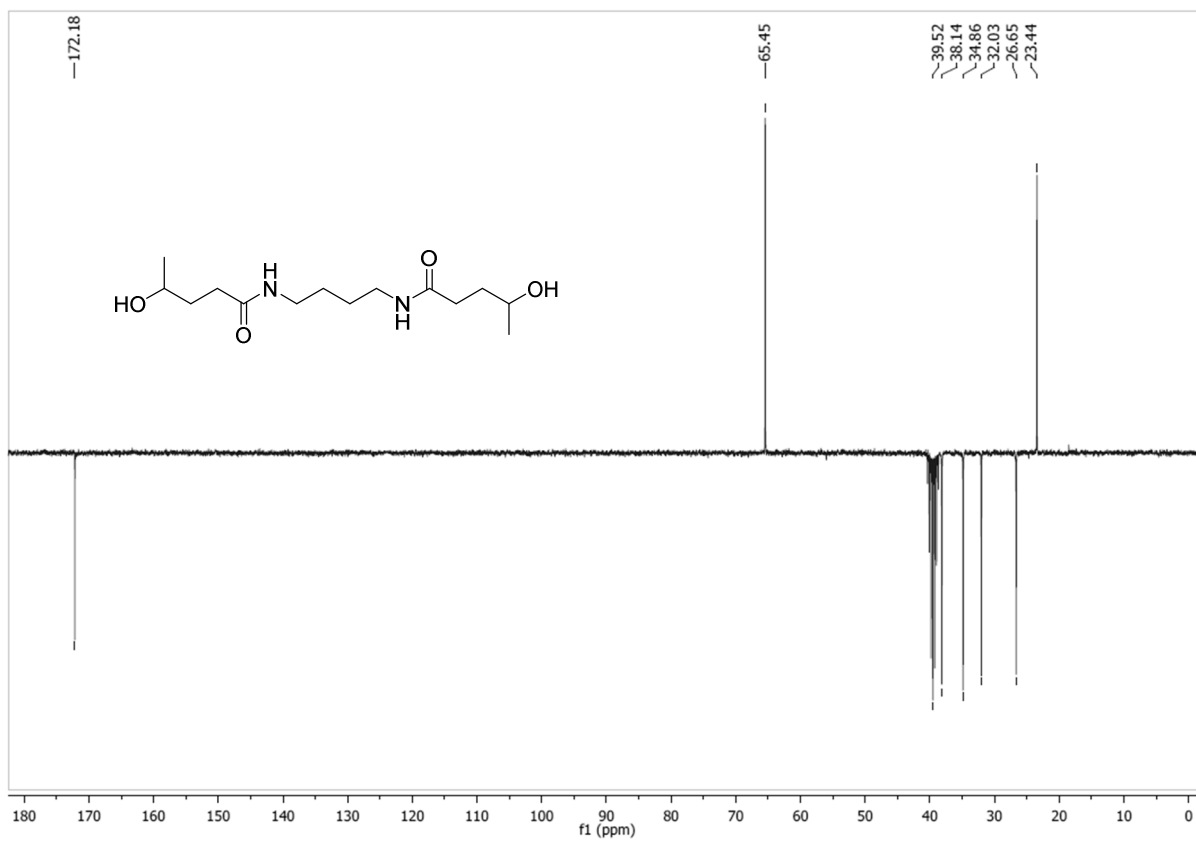
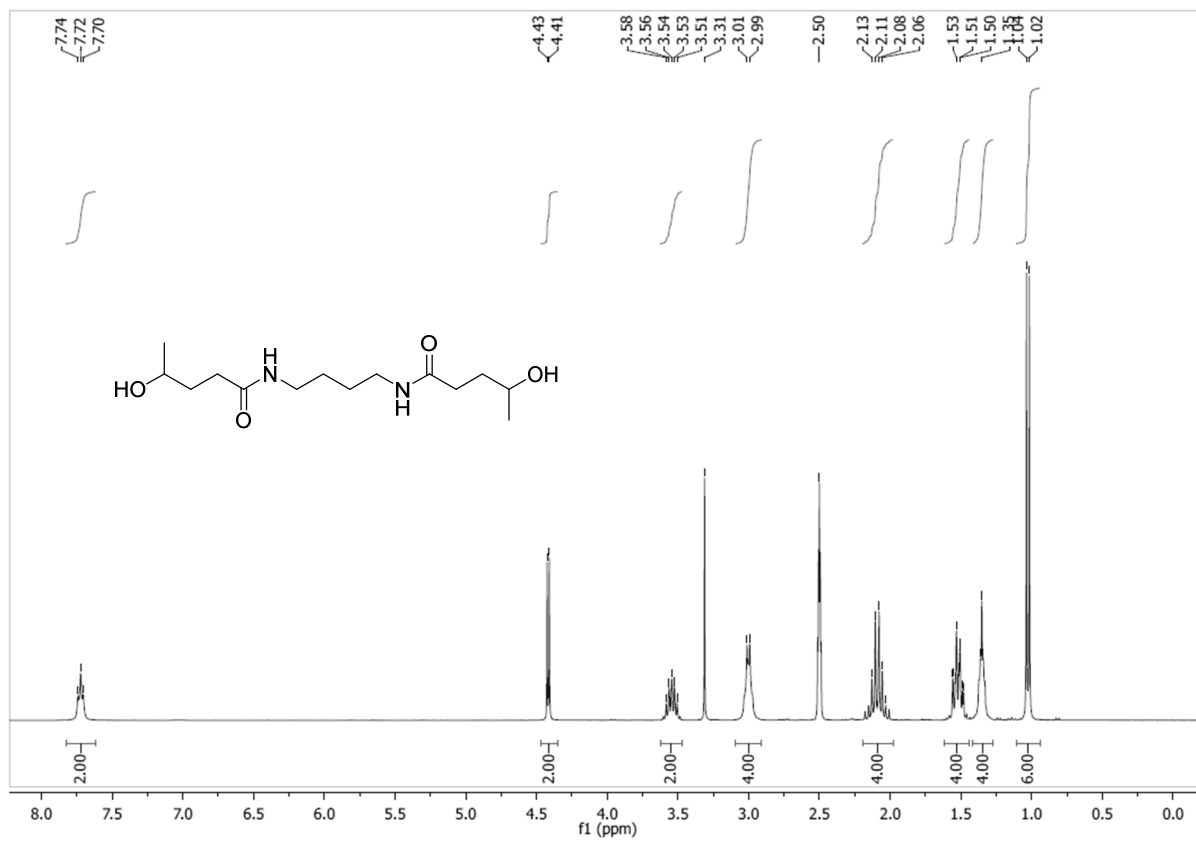


Fig. S6 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **2c** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

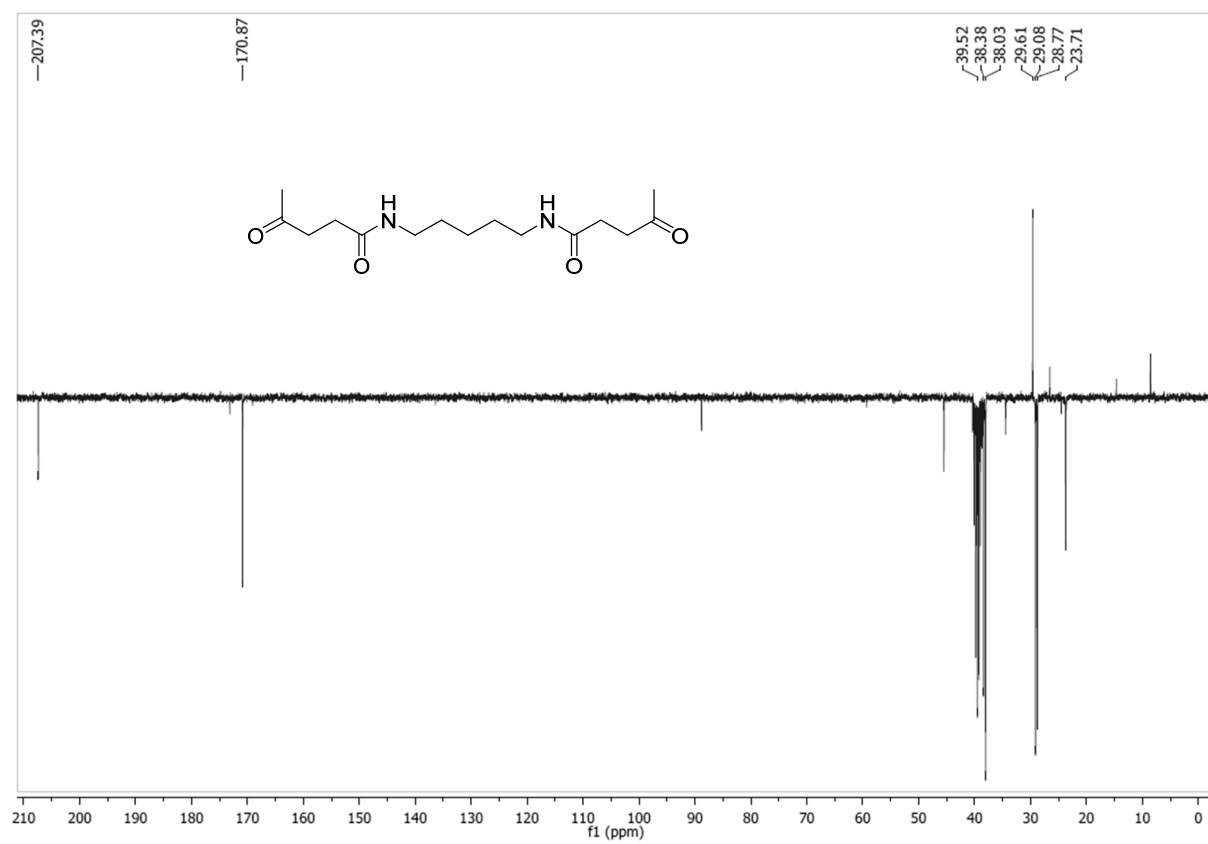
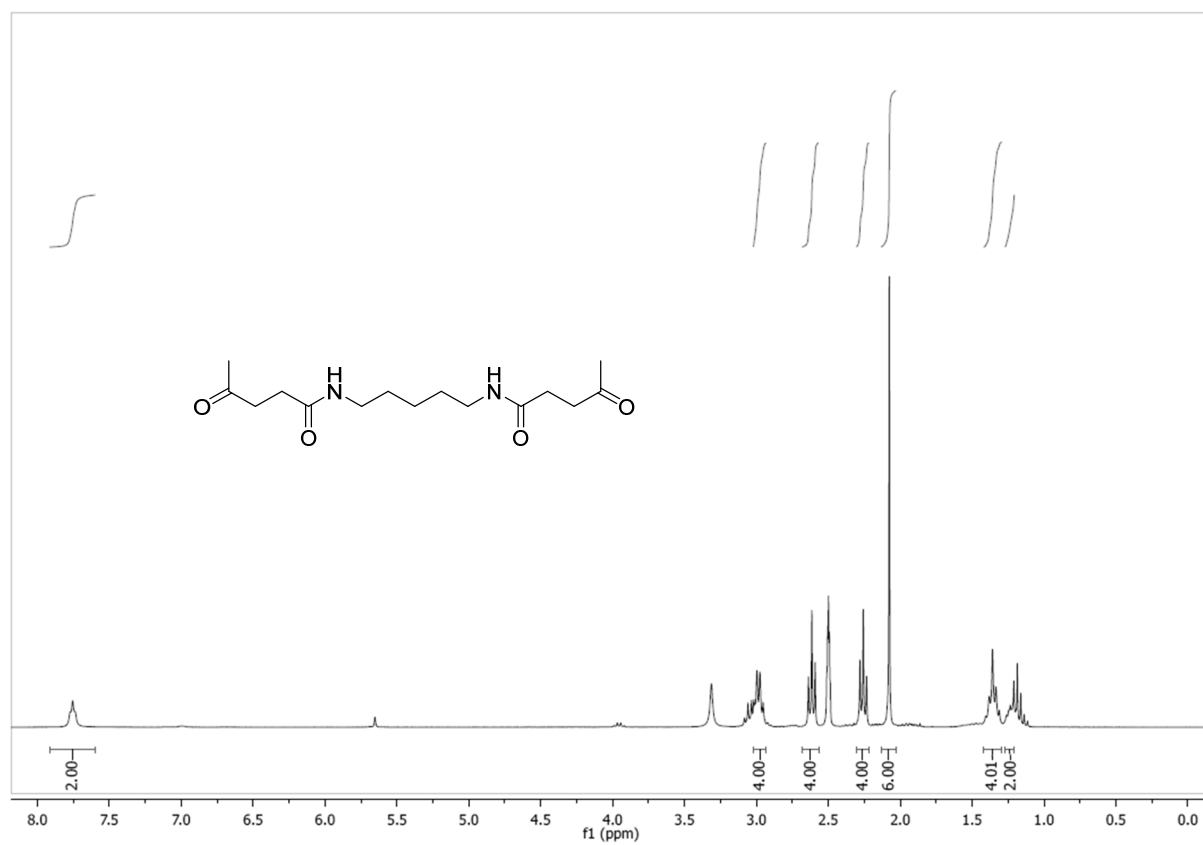


Fig. S7 ^1H (top) and DEPT ^{13}C (bottom) NMR spectra of **1d** (DMSO- d_6 , 300 MHz and 75 MHz, 300 K)

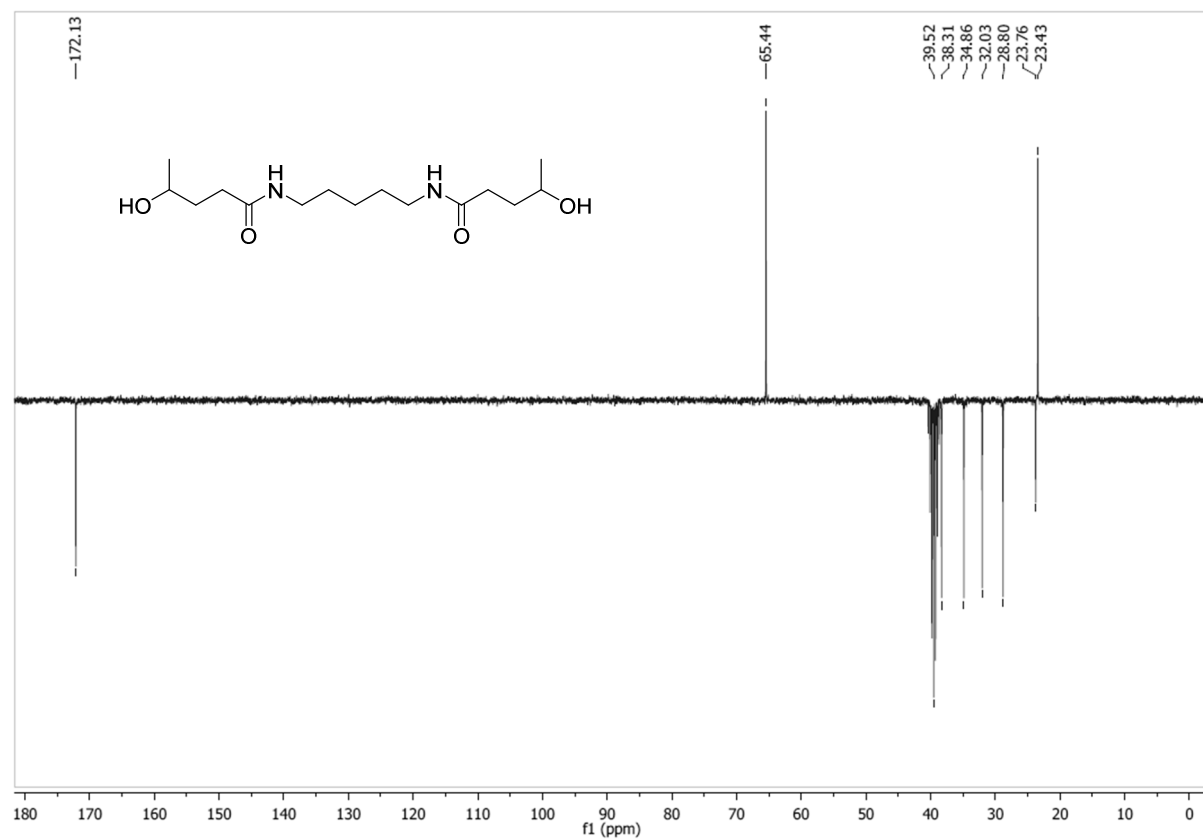
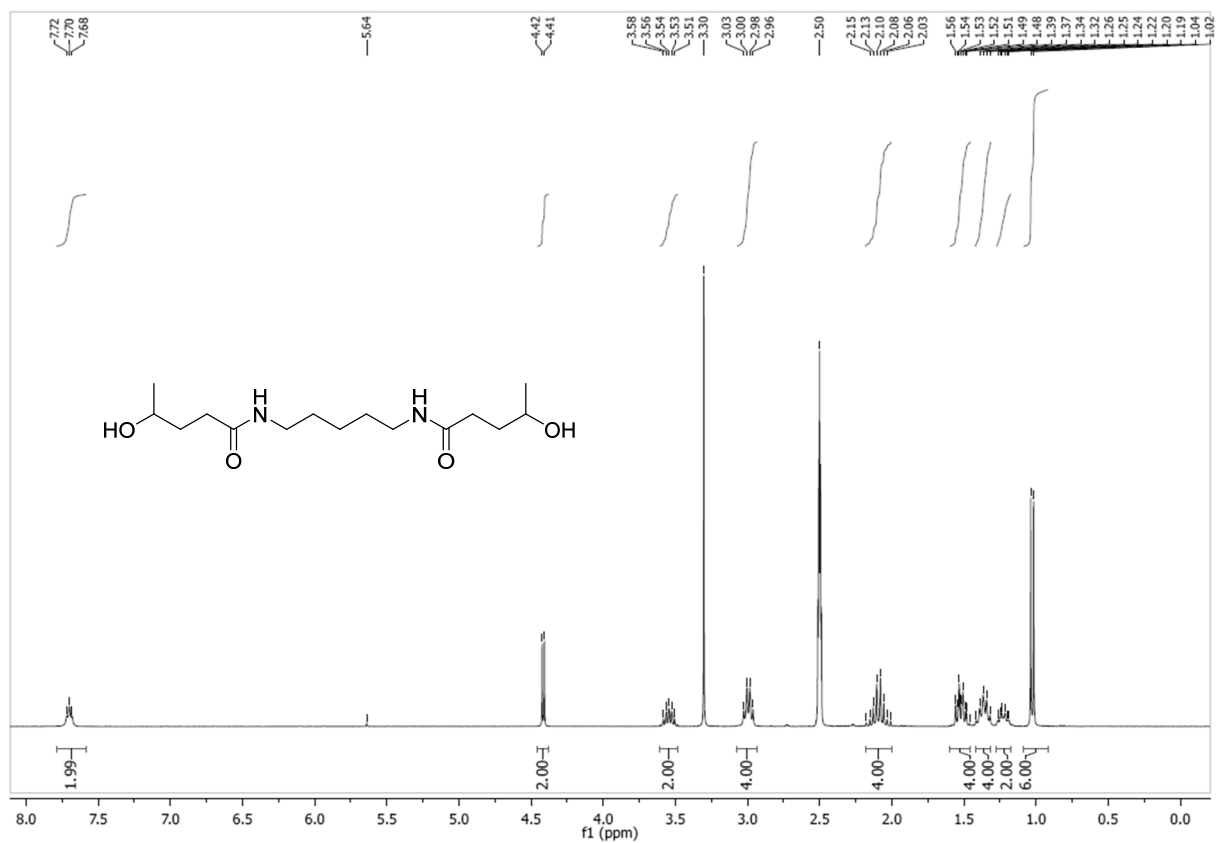


Fig. S8 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **2d** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

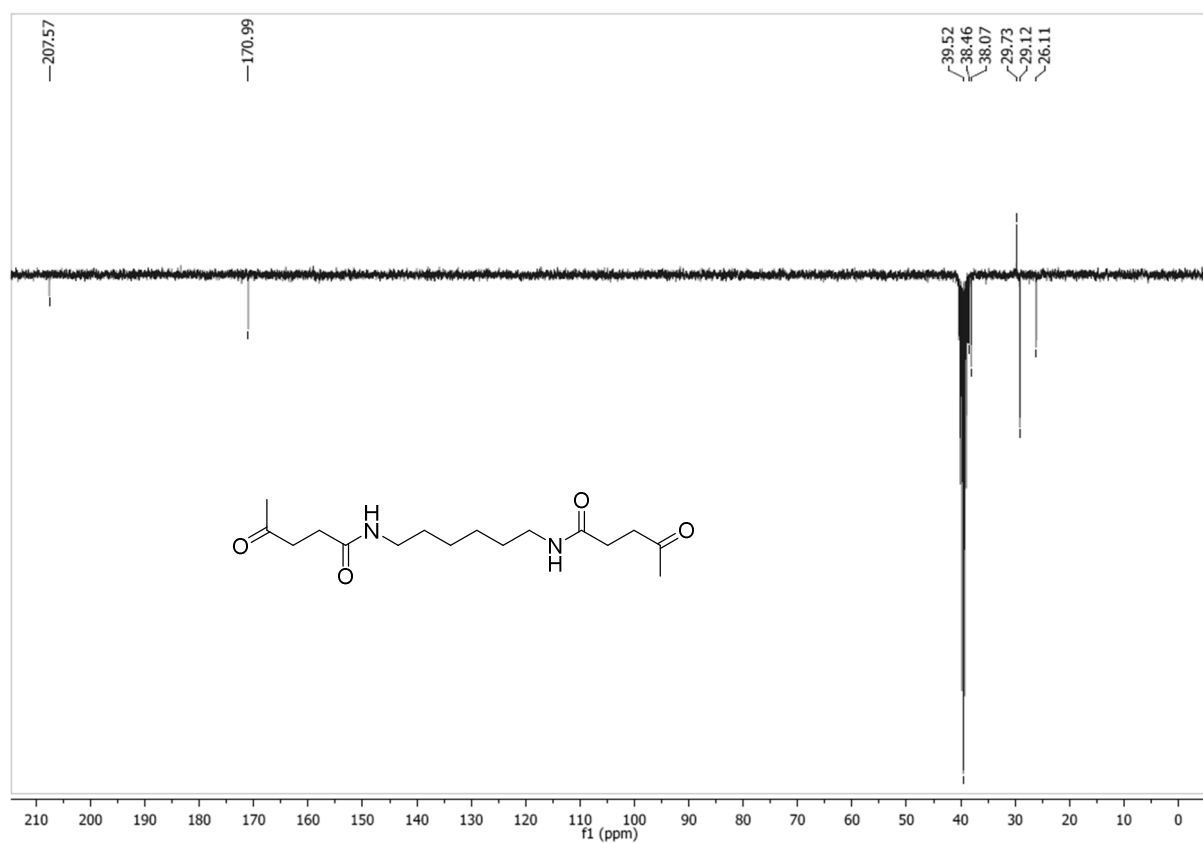
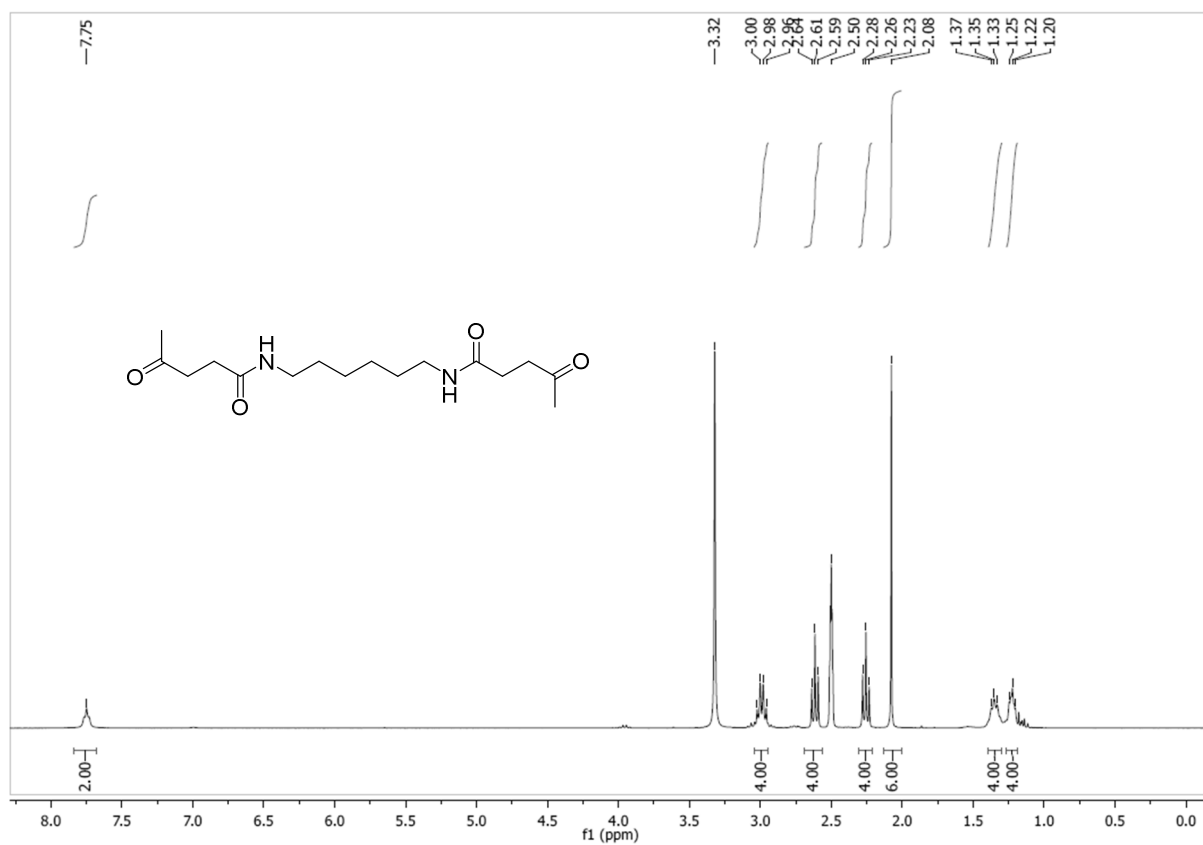


Fig. S9 ^1H (top) and DEPT ^{13}C (bottom) NMR spectra of **1e** (DMSO- d_6 , 300 MHz and 75 MHz, 300 K)

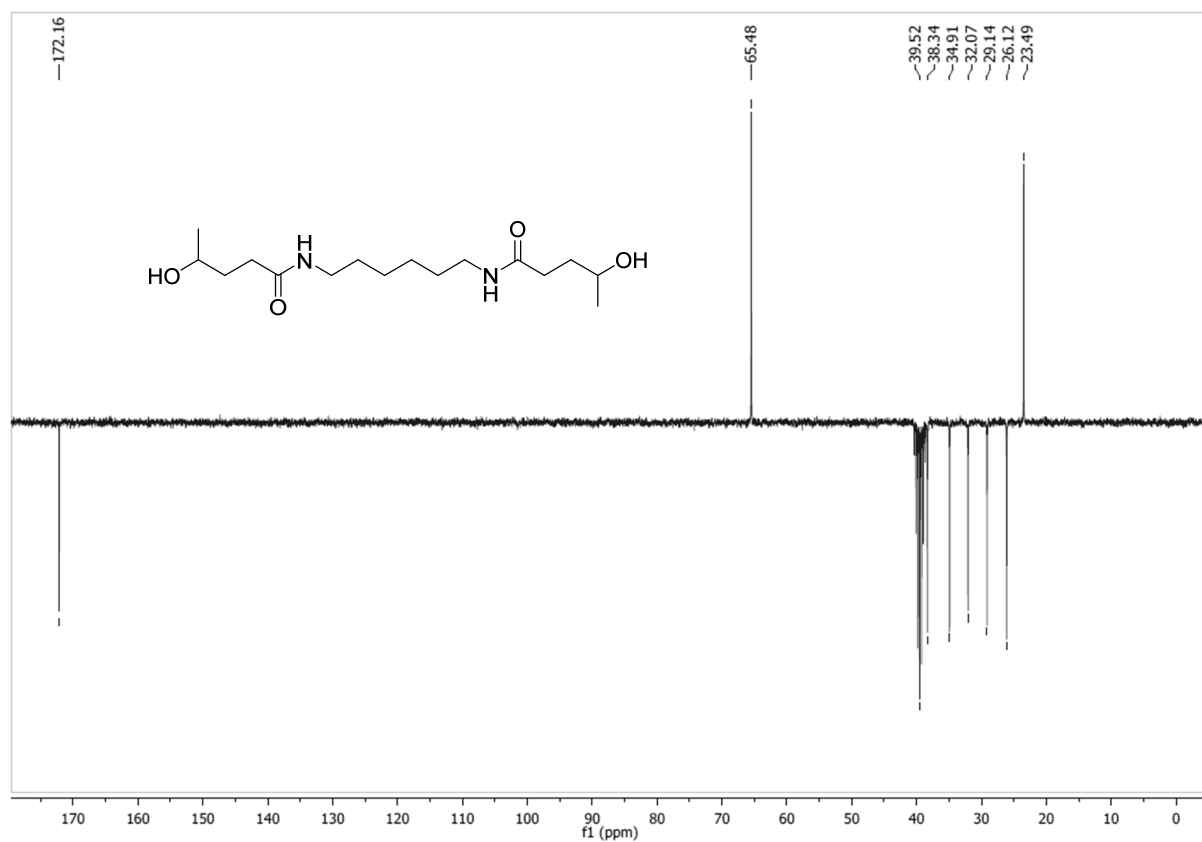
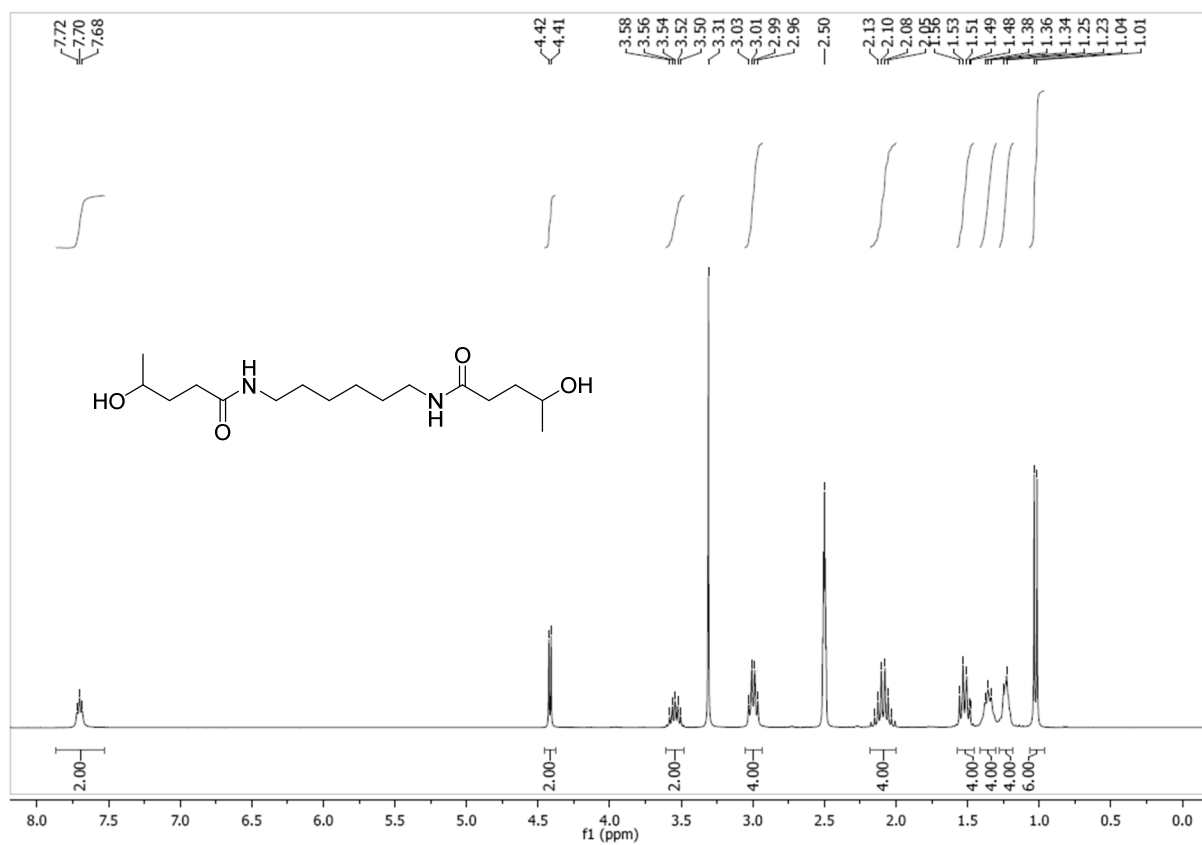


Fig. S10 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of 2e (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

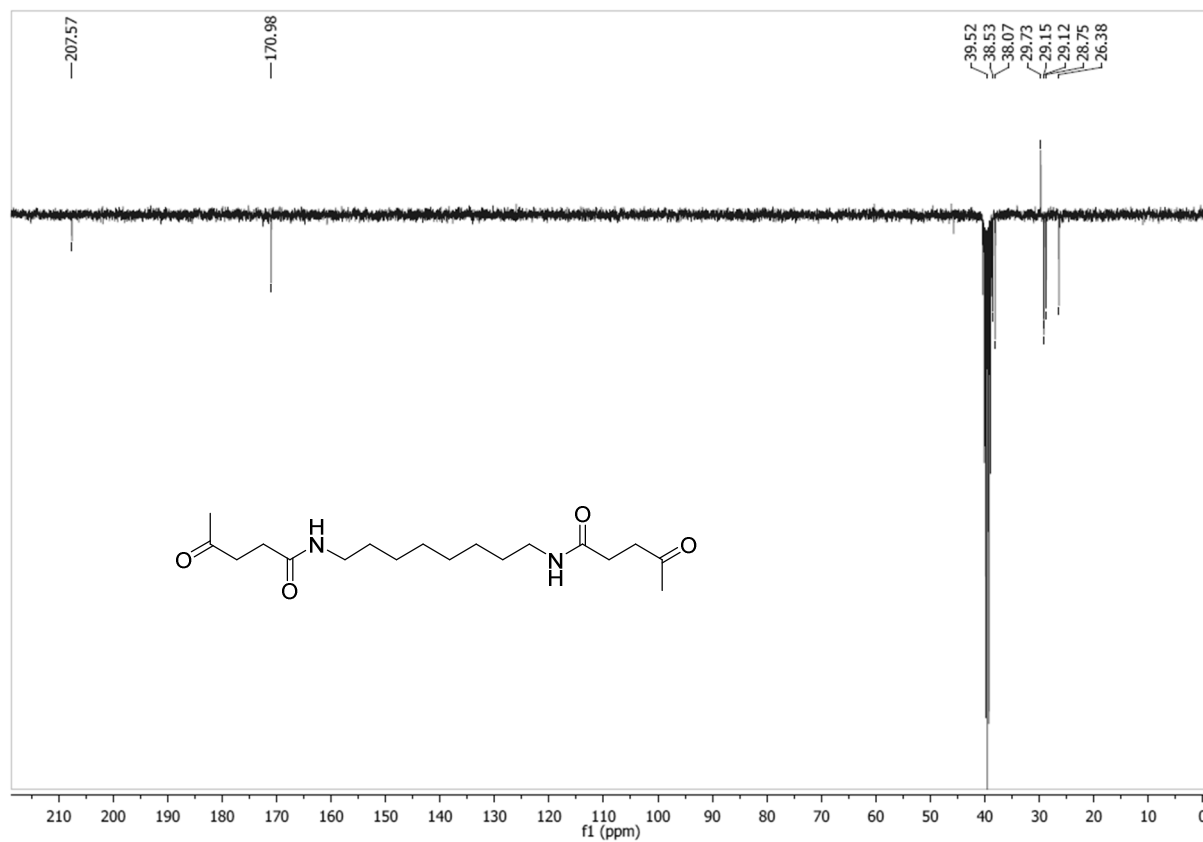
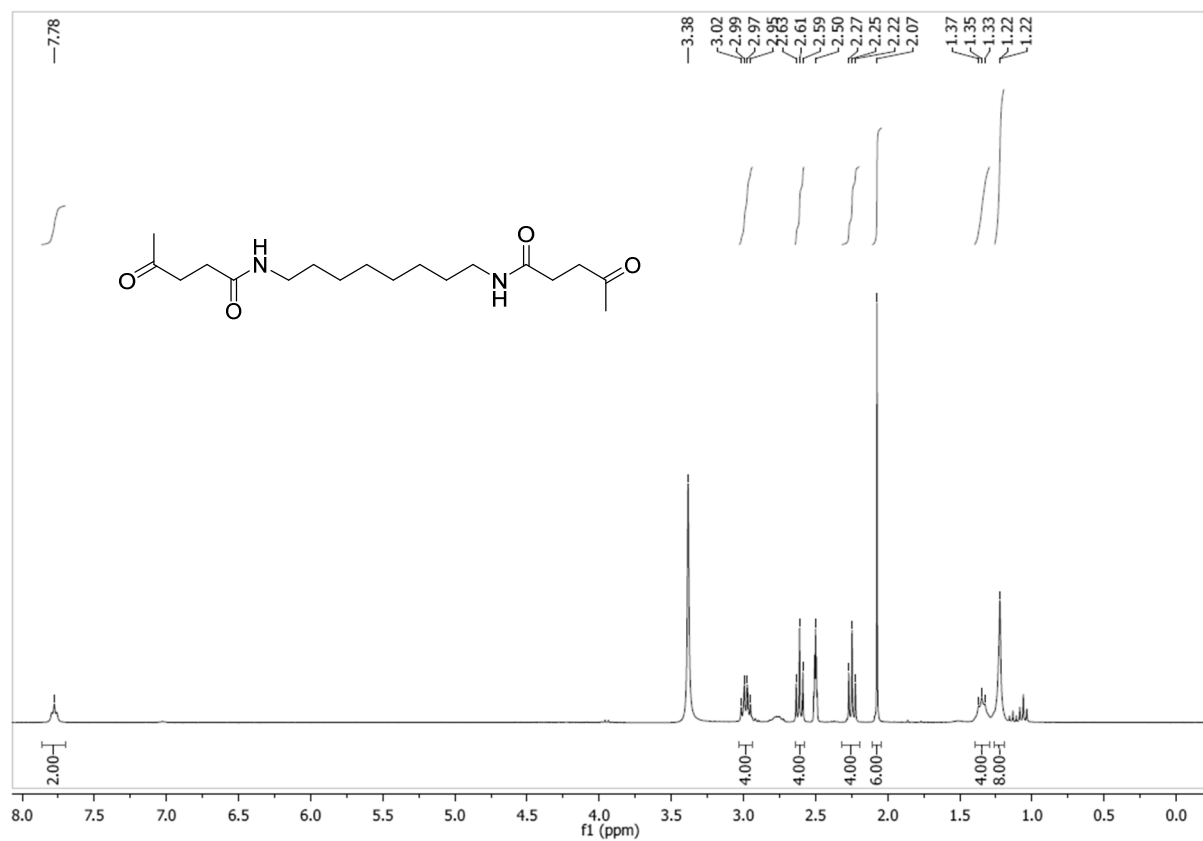


Fig. S11 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **1f** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

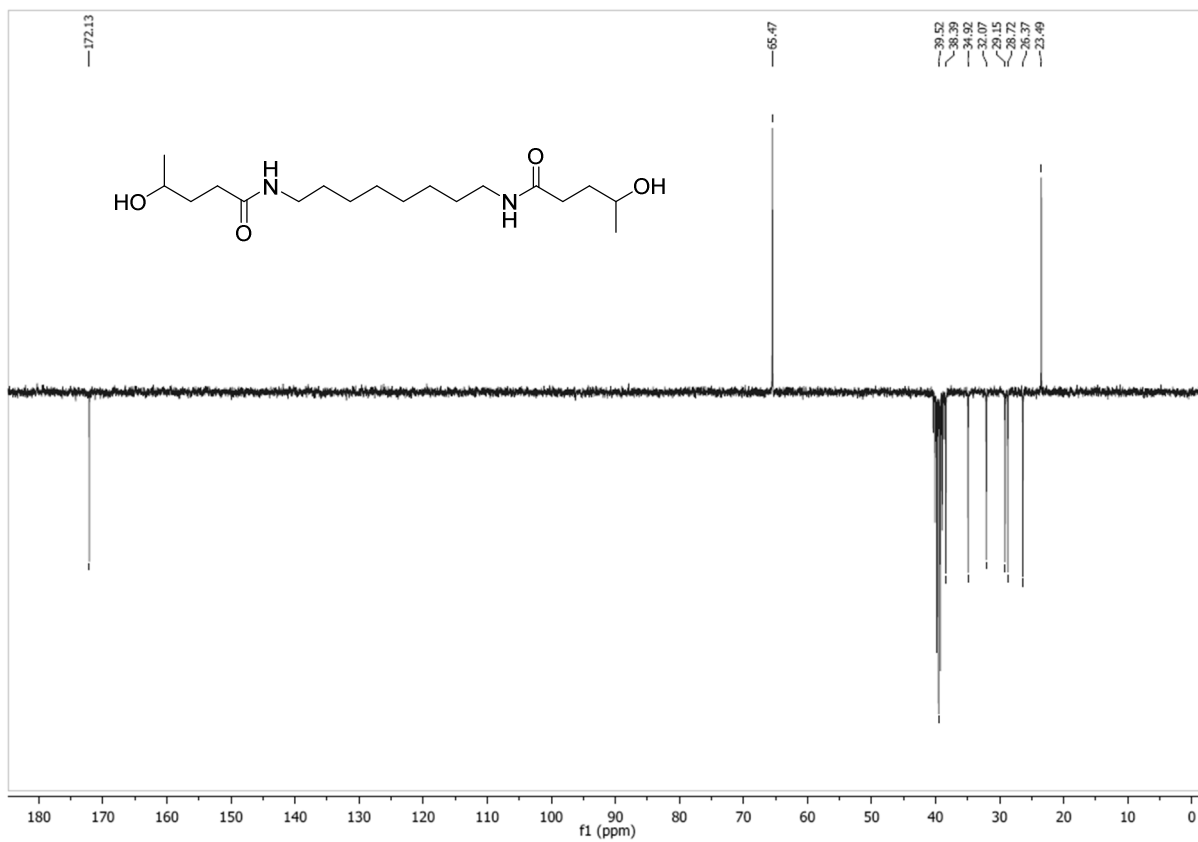
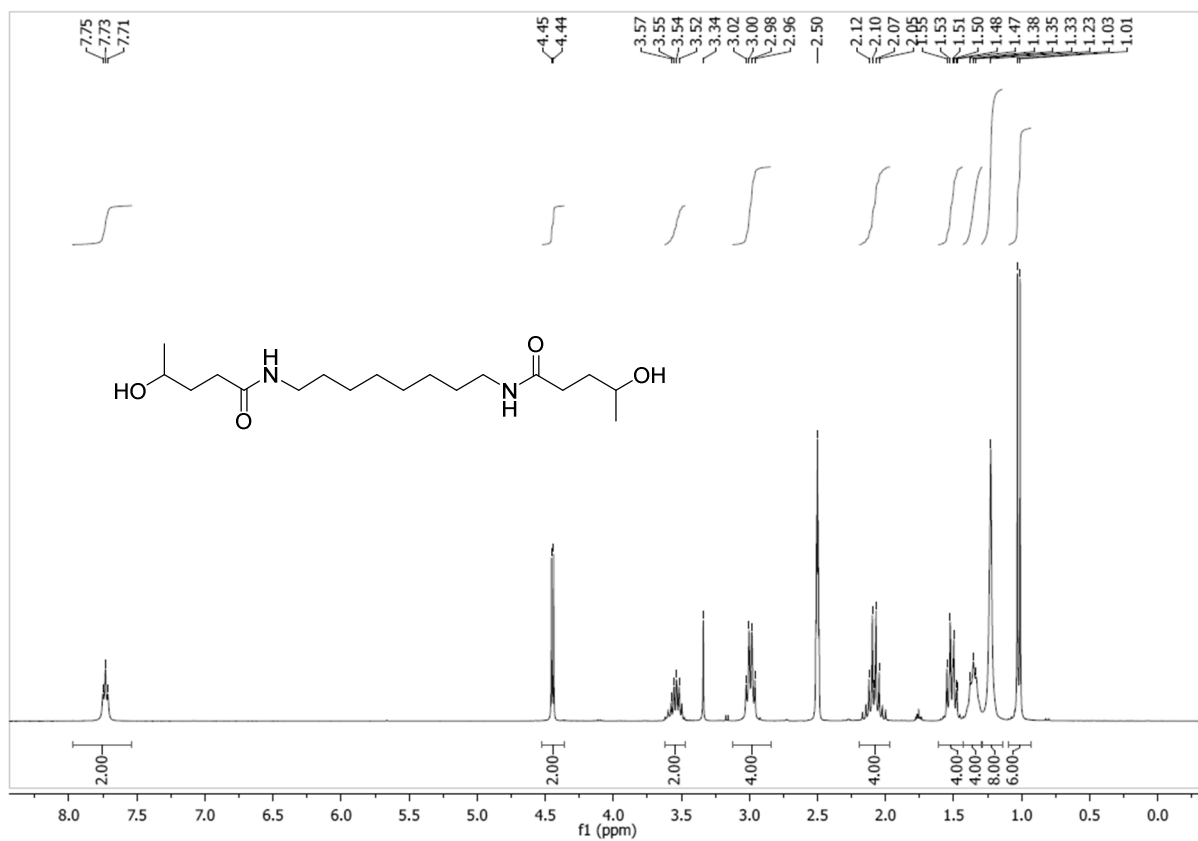


Fig. S12 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **2f** (DMSO-*d*₆, 300 MHz and 75 MHz, 300 K)

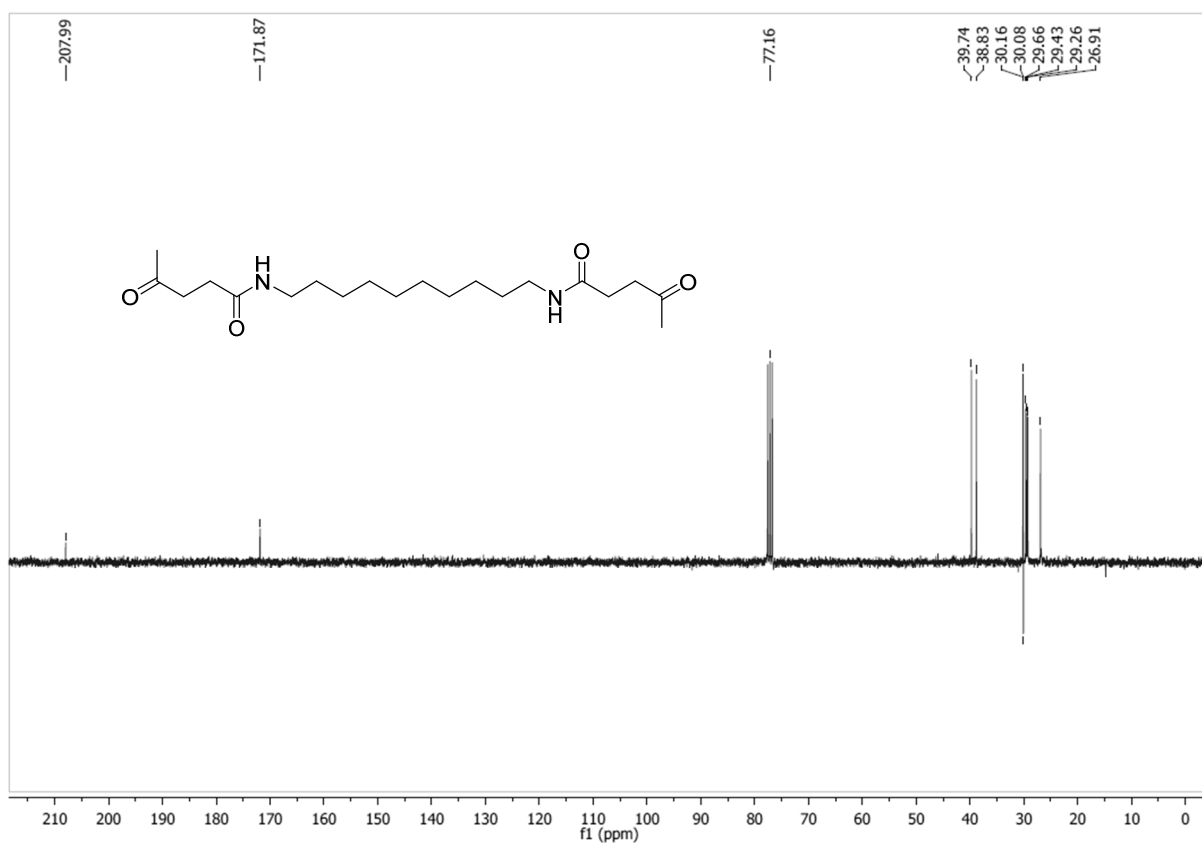
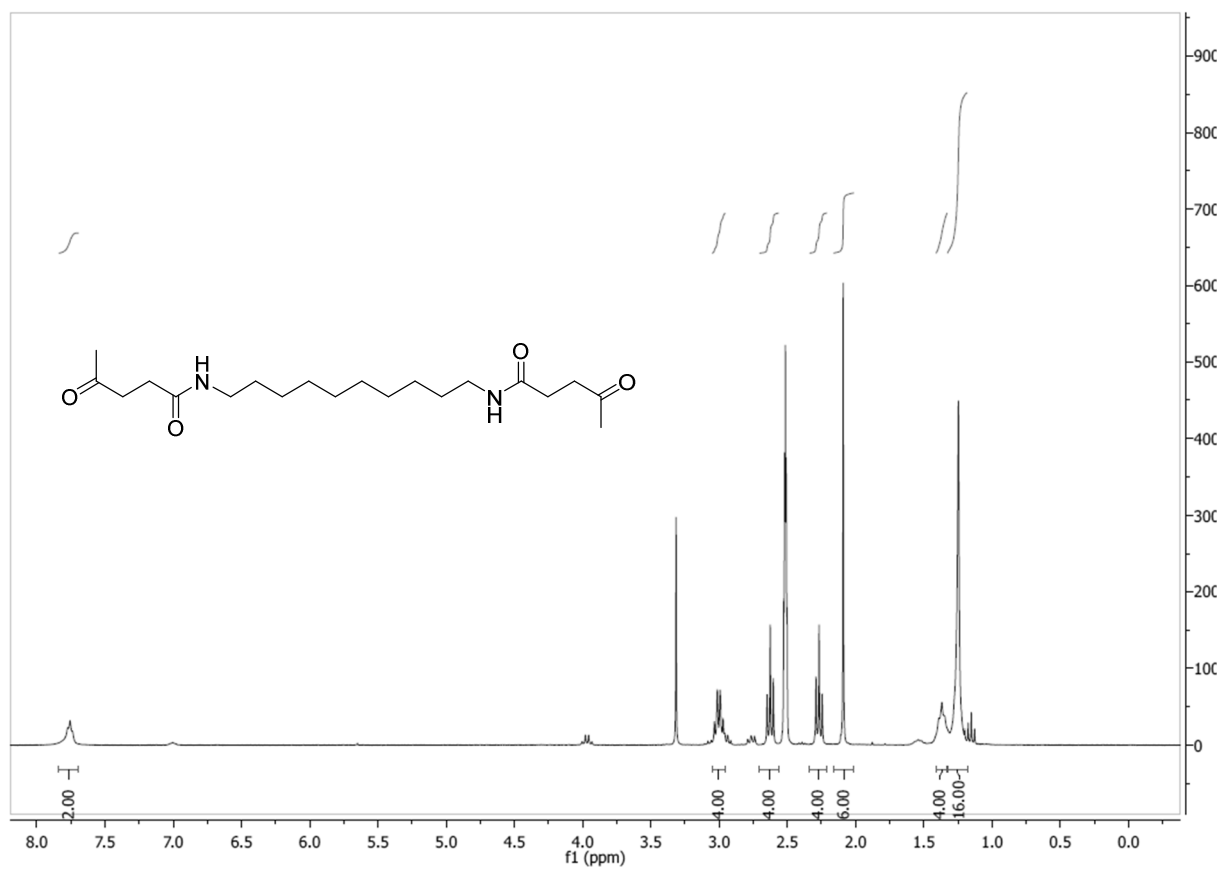


Fig. S13 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **1g** (CDCl₃, 300 MHz and 75 MHz, 300 K)

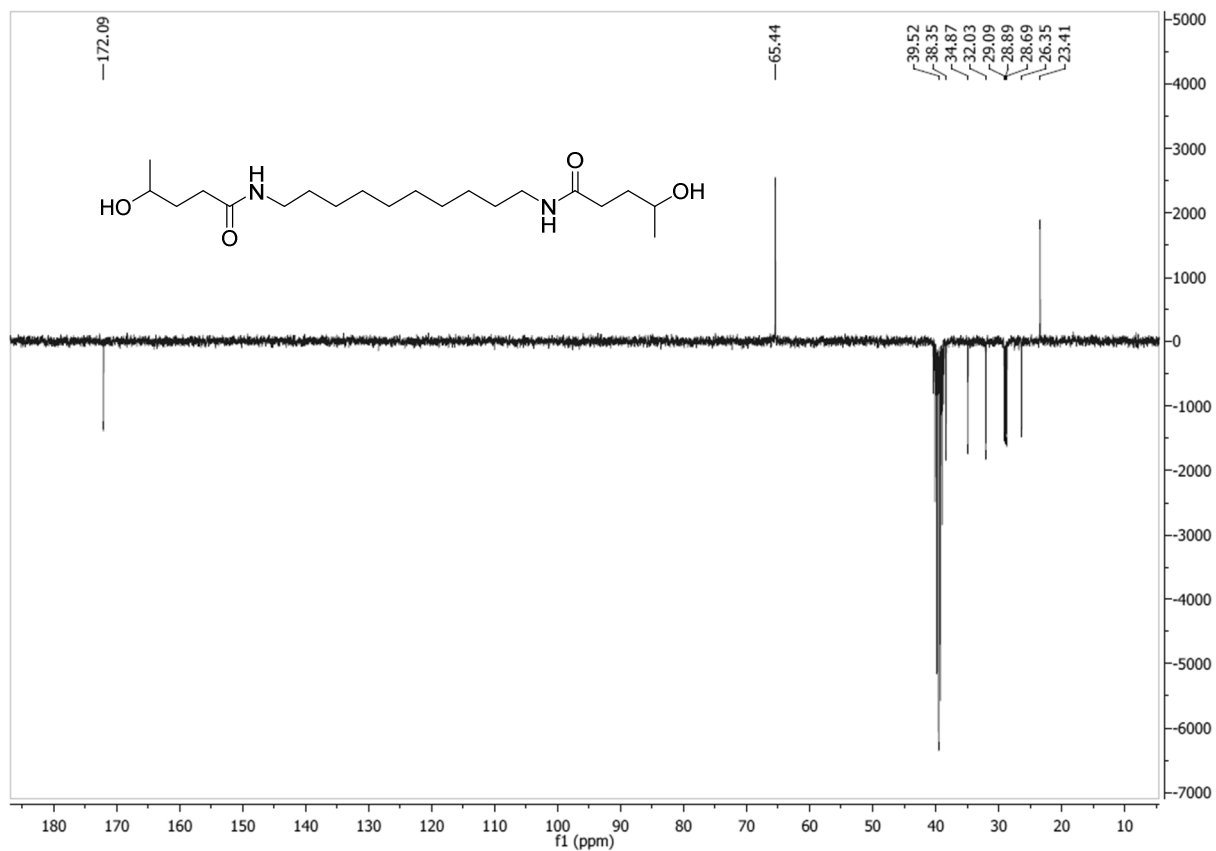
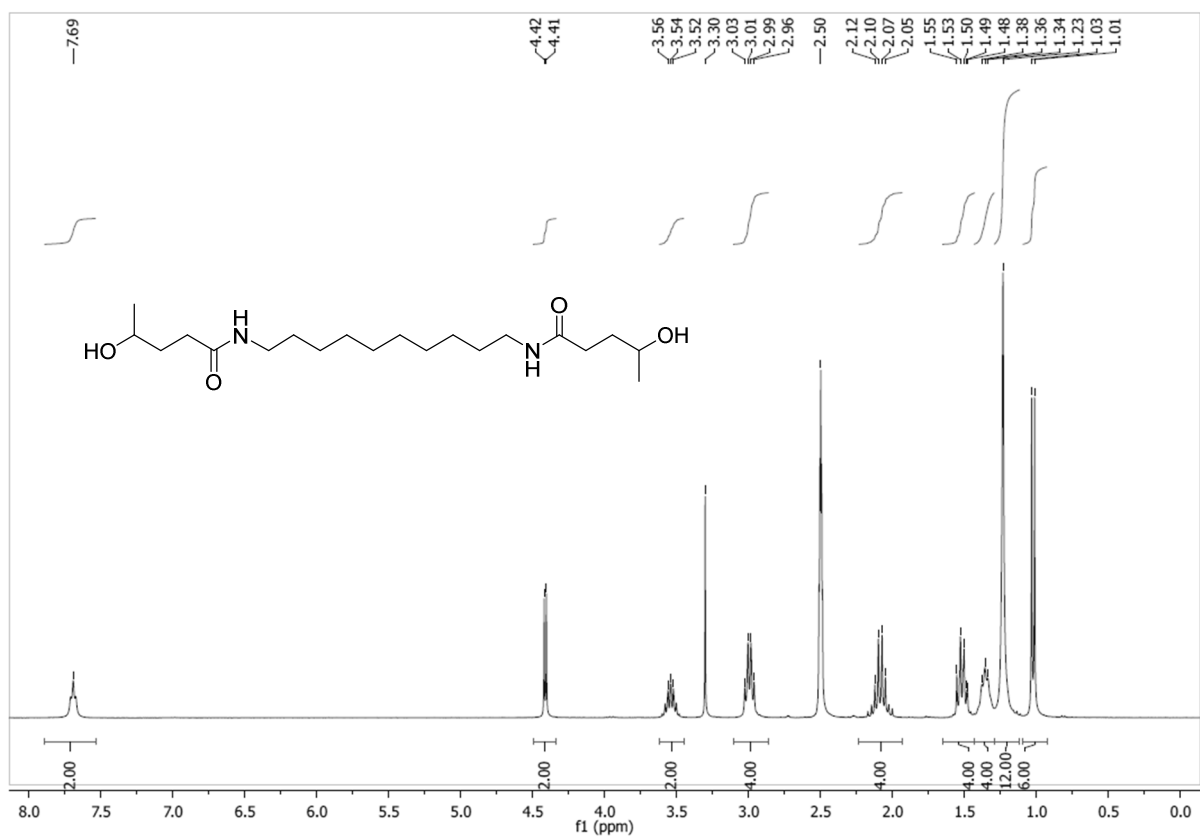


Fig. S14 ¹H (top) and DEPT ¹³C (bottom) NMR spectra of **2g** (DMSO-*d*₆, 300MHz and 75MHz, 300 K)

2. MALDI-ToF and NMR spectra

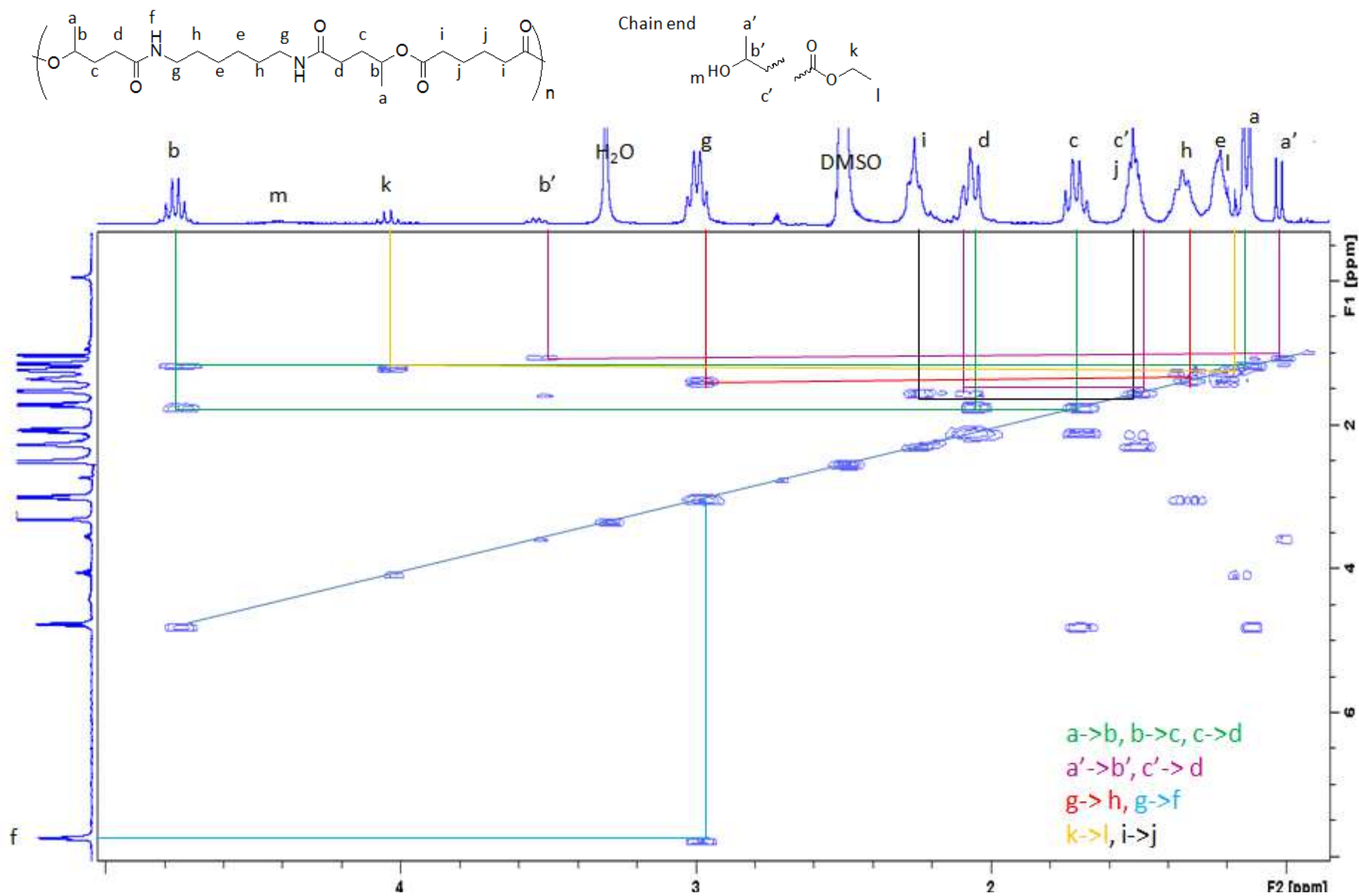


Fig. S15 COSY NMR spectrum of poly(ester-co-amide) from diol-diamide $x=6$ (entry 2) by polycondensation in solution (DMSO- d_6 , 300 MHz, 300 K)

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

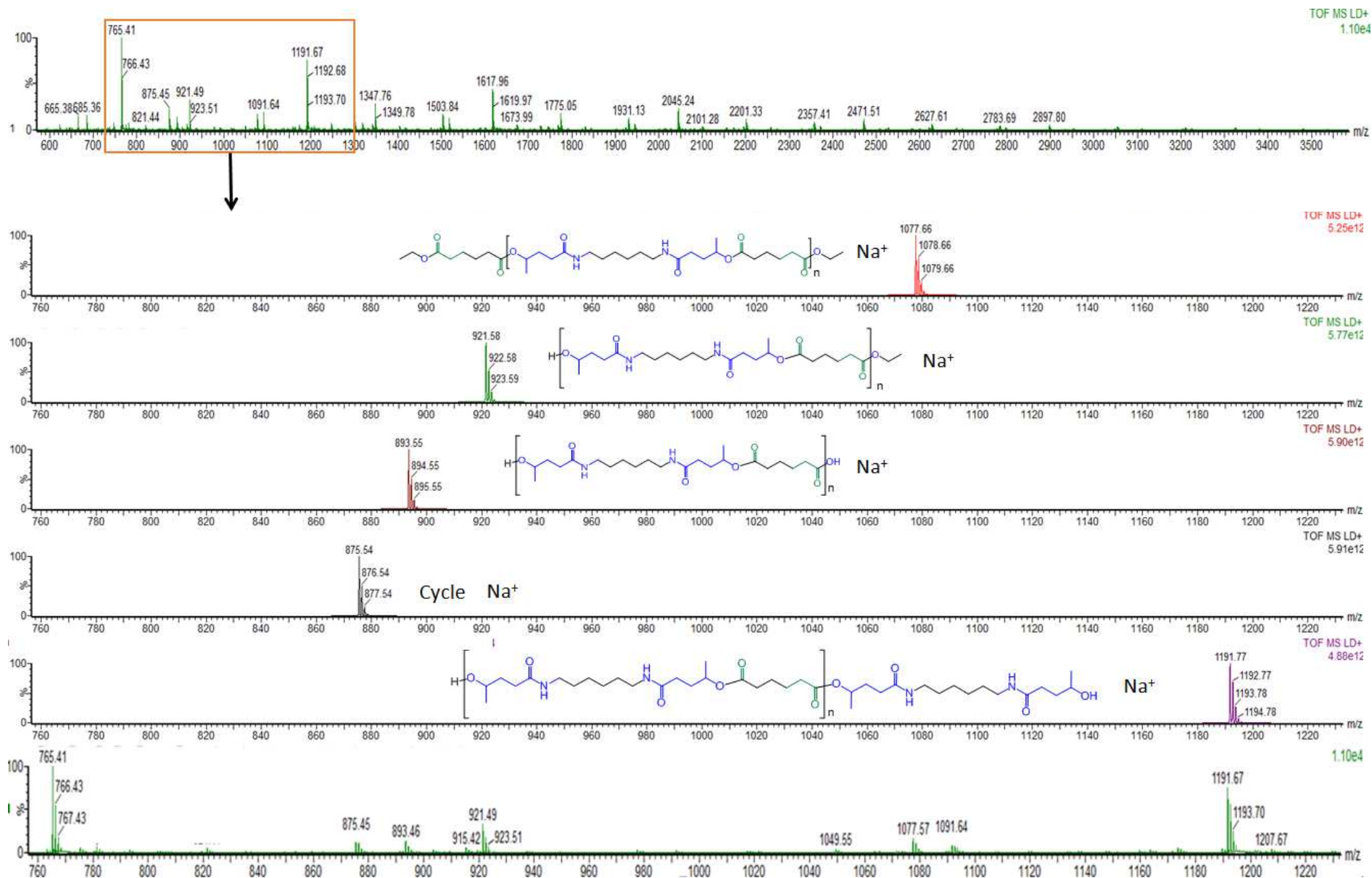


Fig. S16 MALDI-ToF analysis of poly(ester-co-amide) from diol-diamide $x=6$ and diethyl adipate (entry 3)

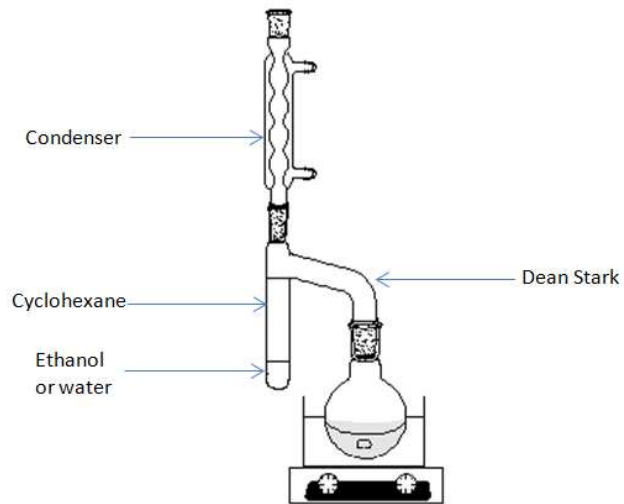


Fig. S17 Polymerisation with Dean Stark apparatus

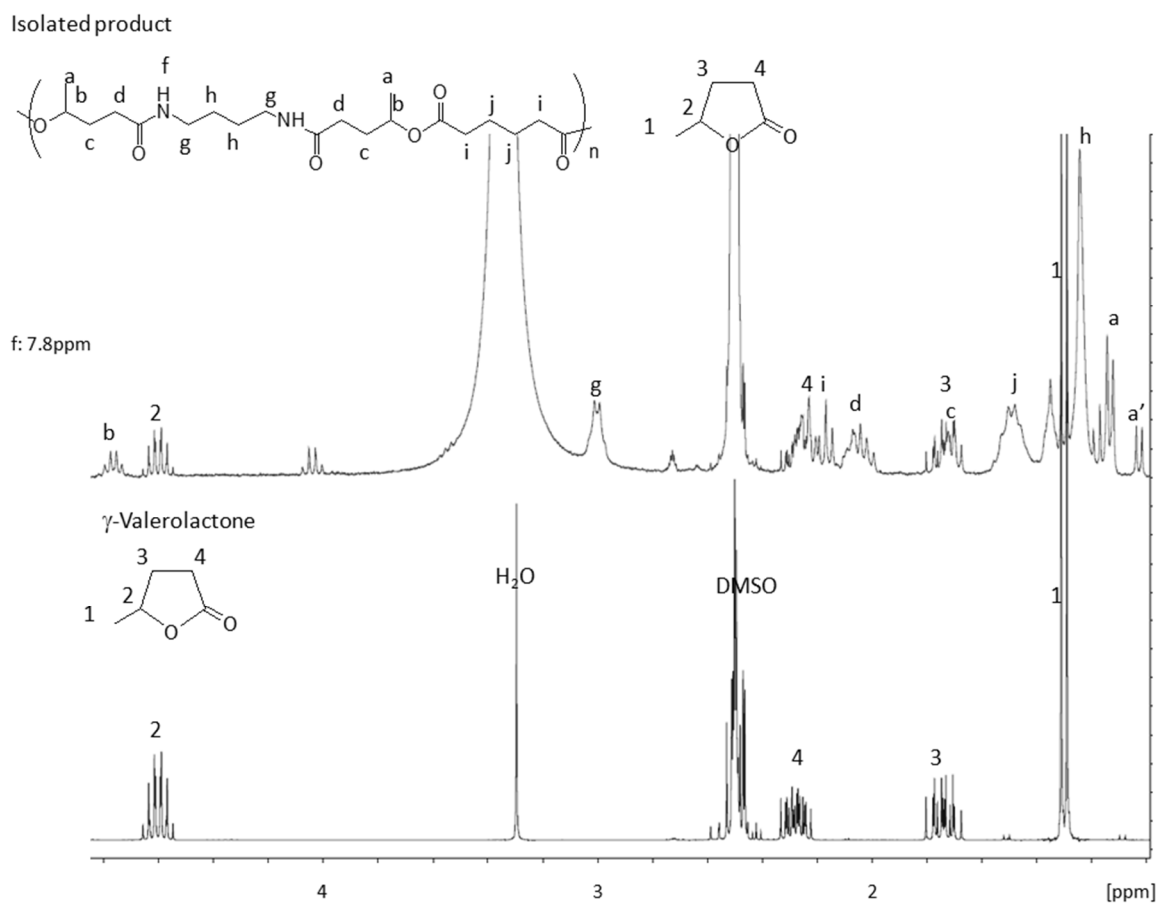


Fig. S18 Comparison of the ^1H NMR spectra (DMSO-d_6 , 300 MHz) of the isolated product of polymerisation from diol-diamide **2c** ($x=4$) and adipic acid and of the γ -valerolactone

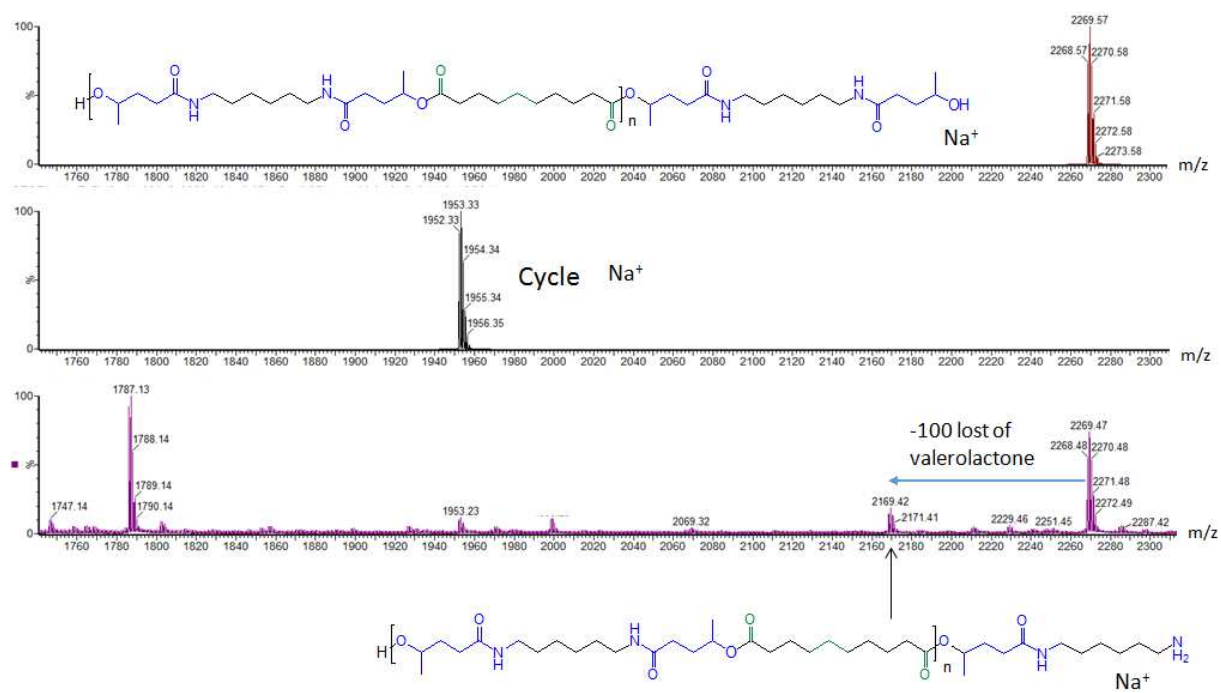
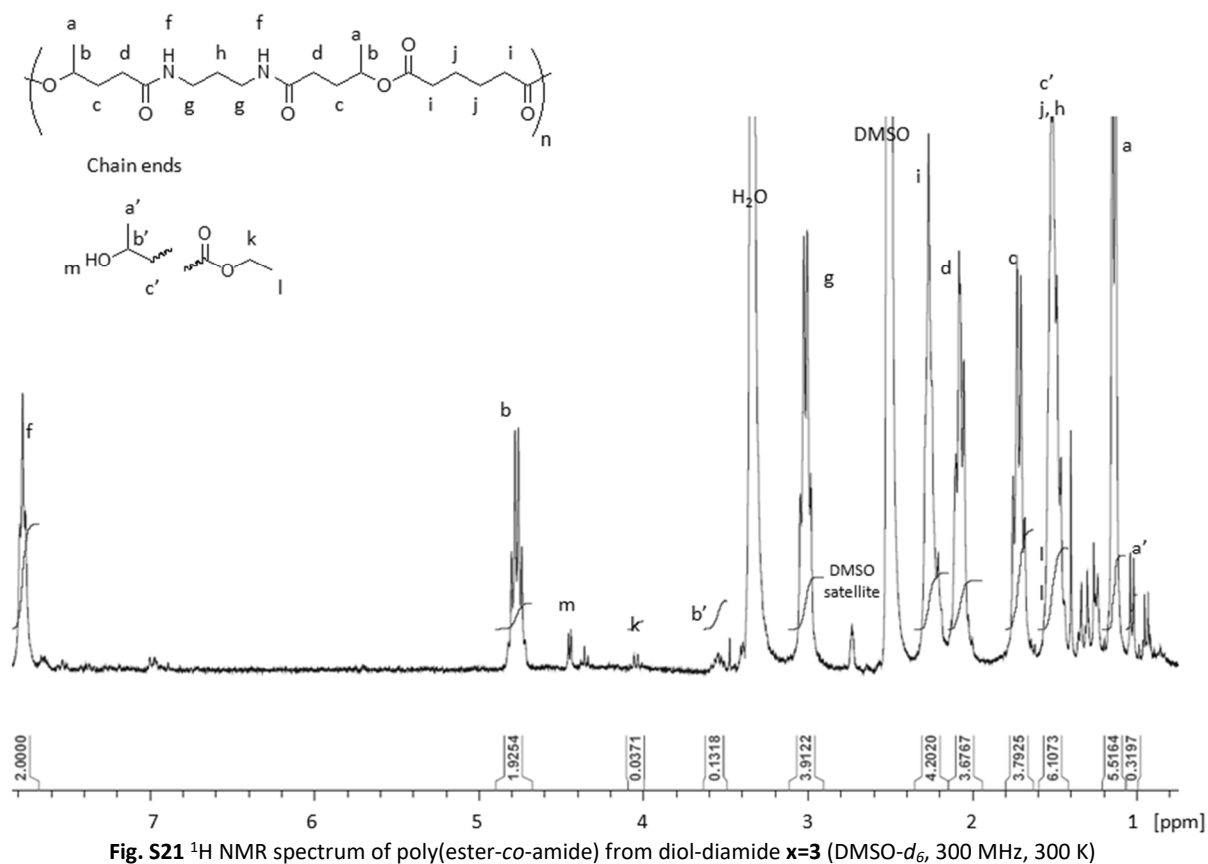
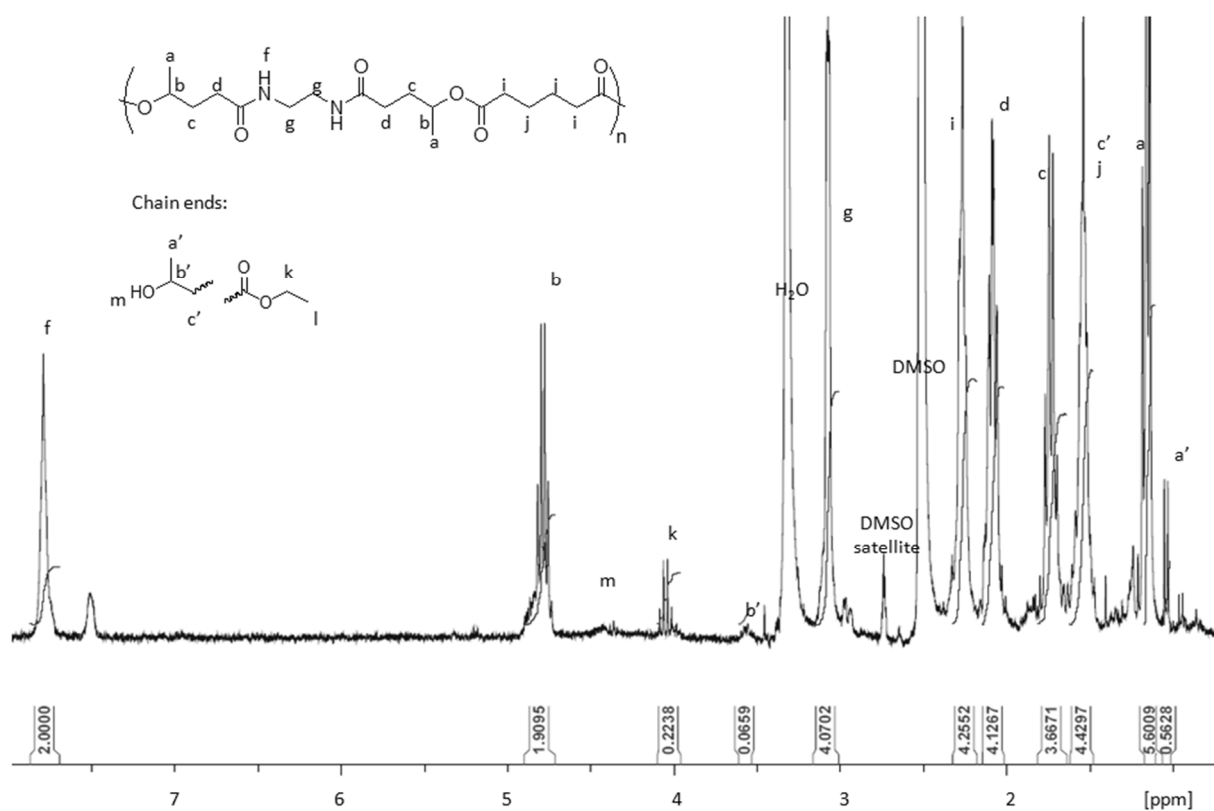


Fig. S19 MALDI-ToF analyse of poly(ester-co-amide) from diol-diamide $x=6$ and sebacic acid (entry 7)



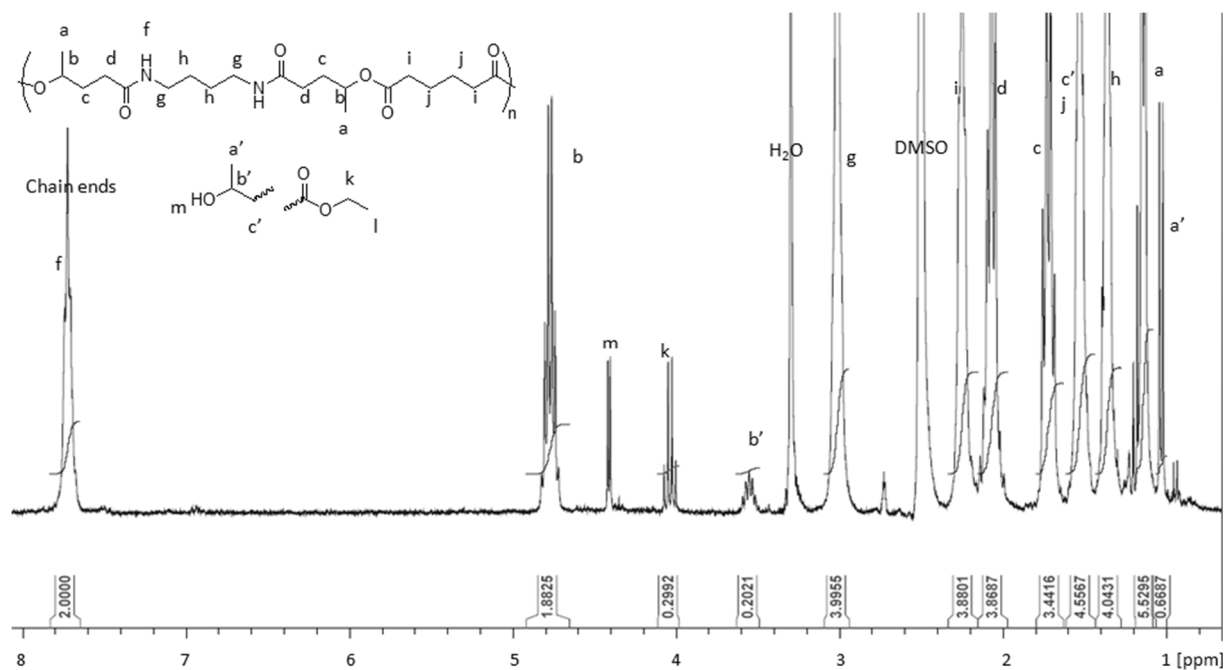


Fig. S22 ^1H NMR spectrum of poly(ester-co-amide) from diol-diamide $x=4$ (DMSO- d_6 , 300 MHz, 300 K)

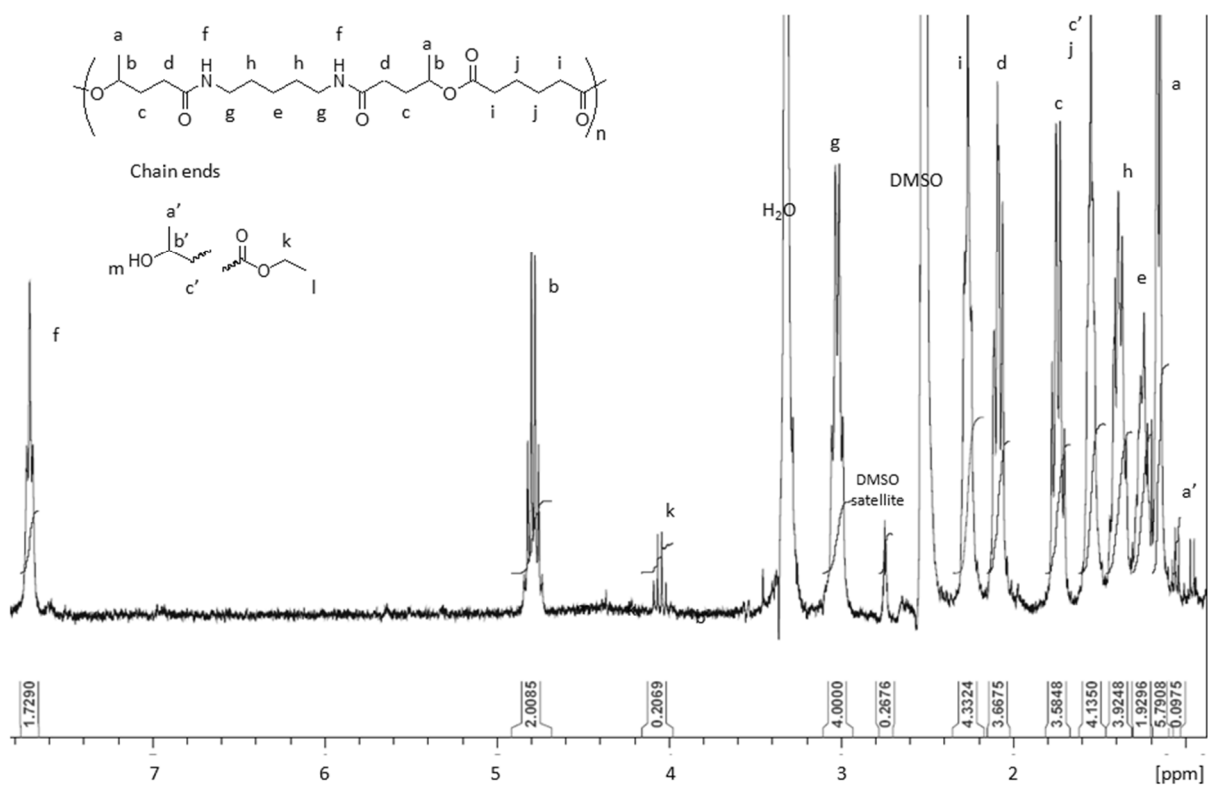


Fig. S23 ^1H NMR spectrum of poly(ester-co-amide) from diol-diamide $x=5$ (DMSO- d_6 , 300 MHz, 300 K)

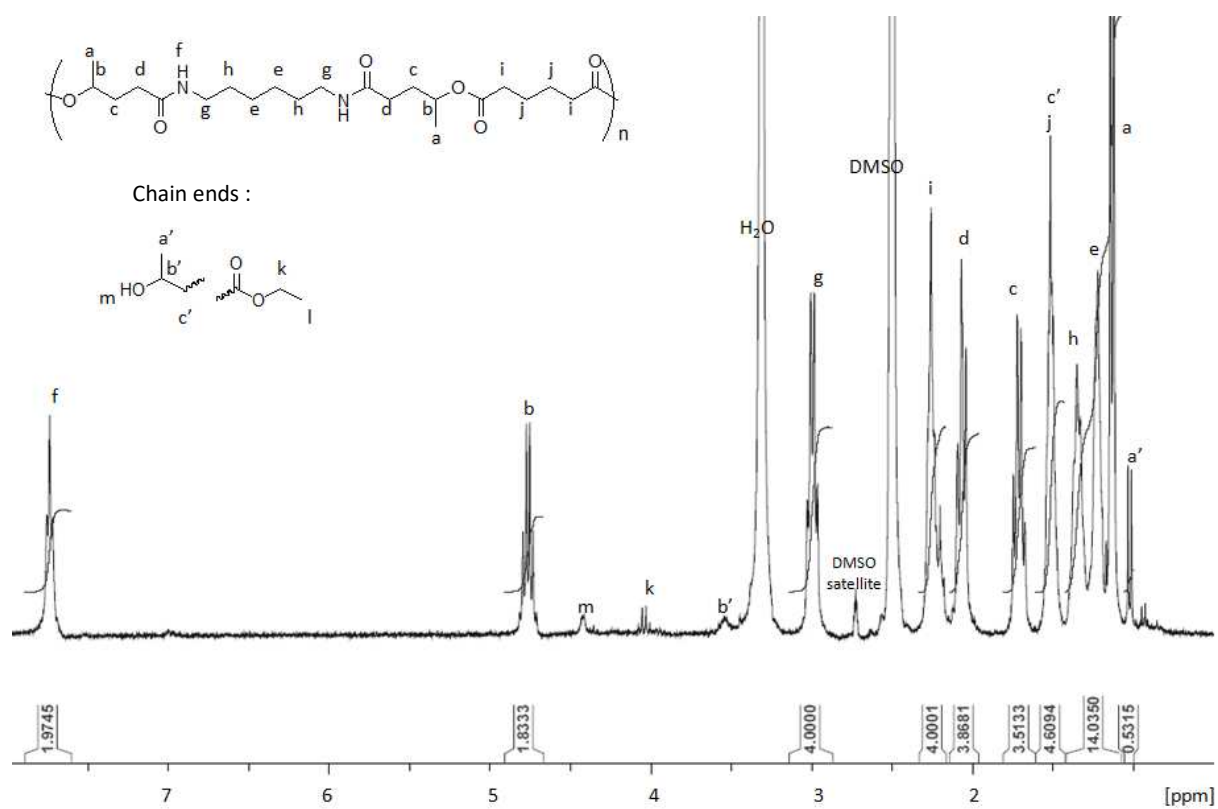


Fig. S24 ^1H NMR spectrum of poly(ester-co-amide) from diol-diamide $x=6$ (DMSO- d_6 , 300 MHz, 300 K)

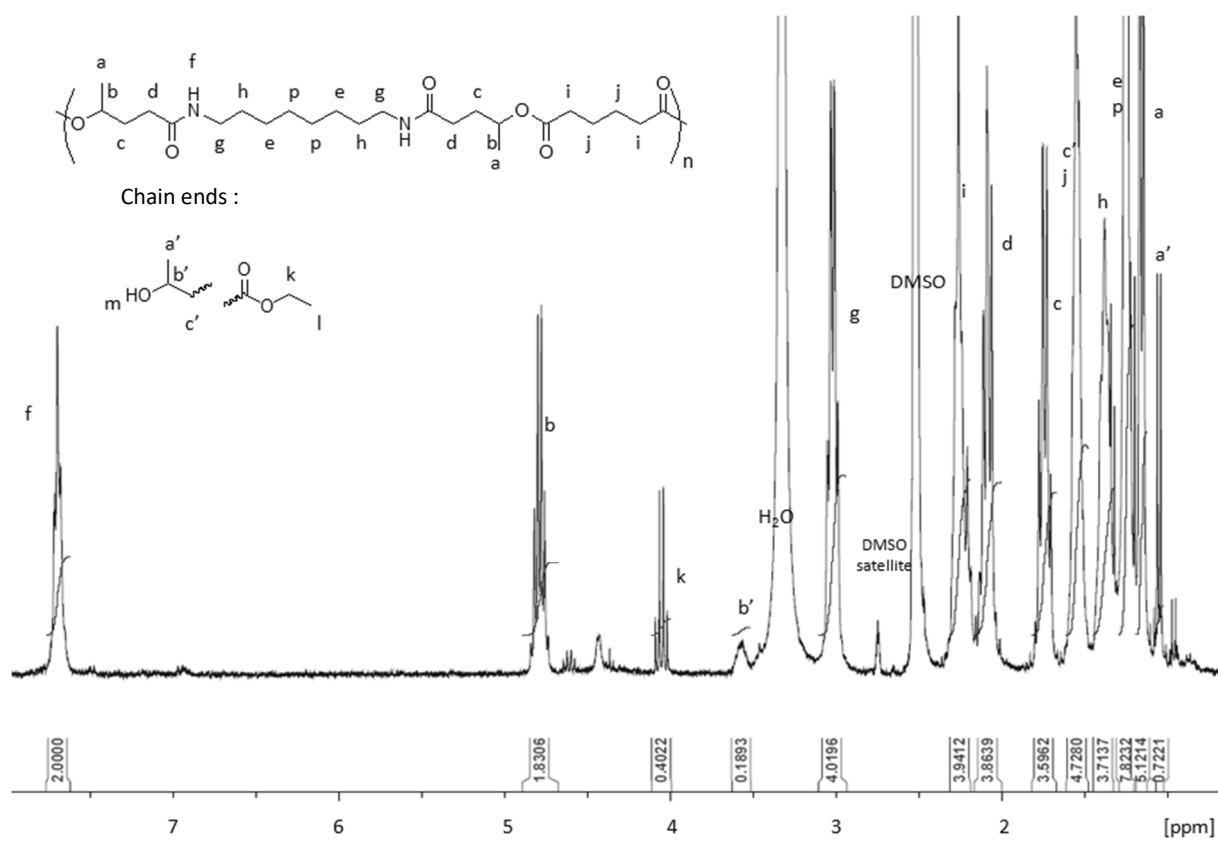


Fig. S25 ^1H NMR spectrum of poly(ester-co-amide) from diol-diamide $x=8$ (DMSO- d_6 , 300 MHz, 300 K)

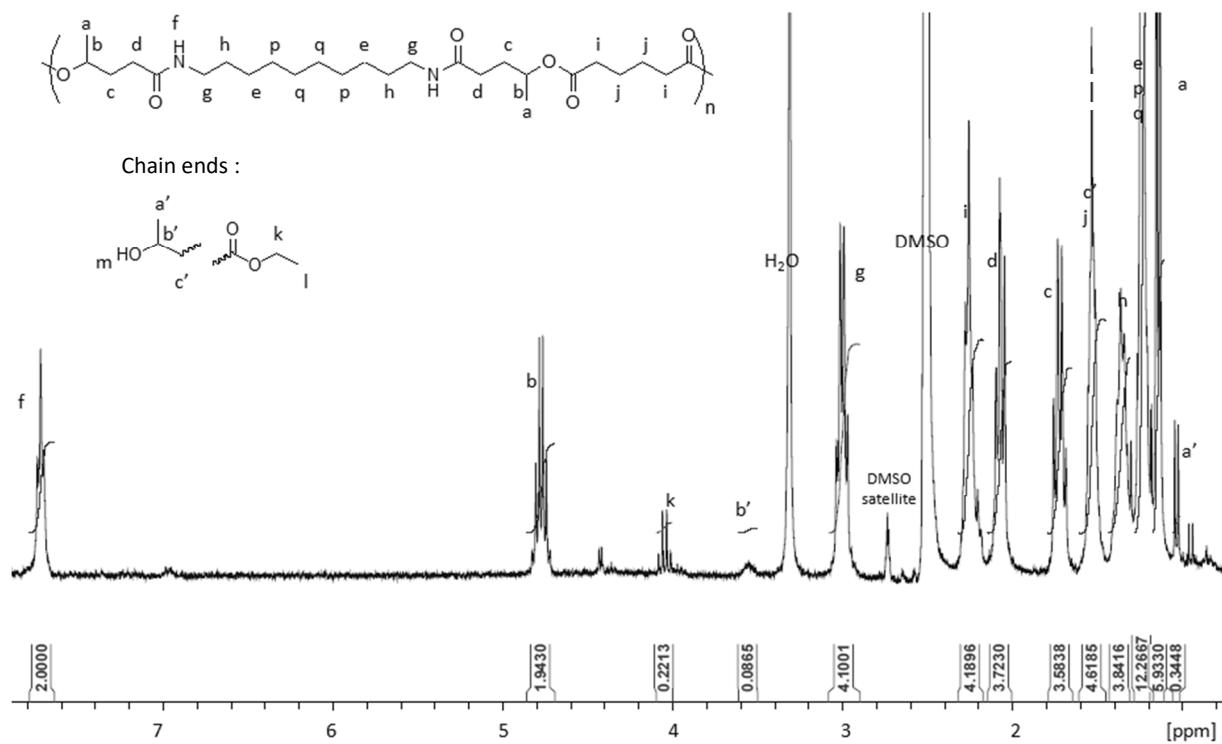


Fig. S26 ¹H NMR spectrum of poly(ester-co-amide) from diol-diamide $x=10$ (DMSO- d_6 , 300 MHz, 300 K)

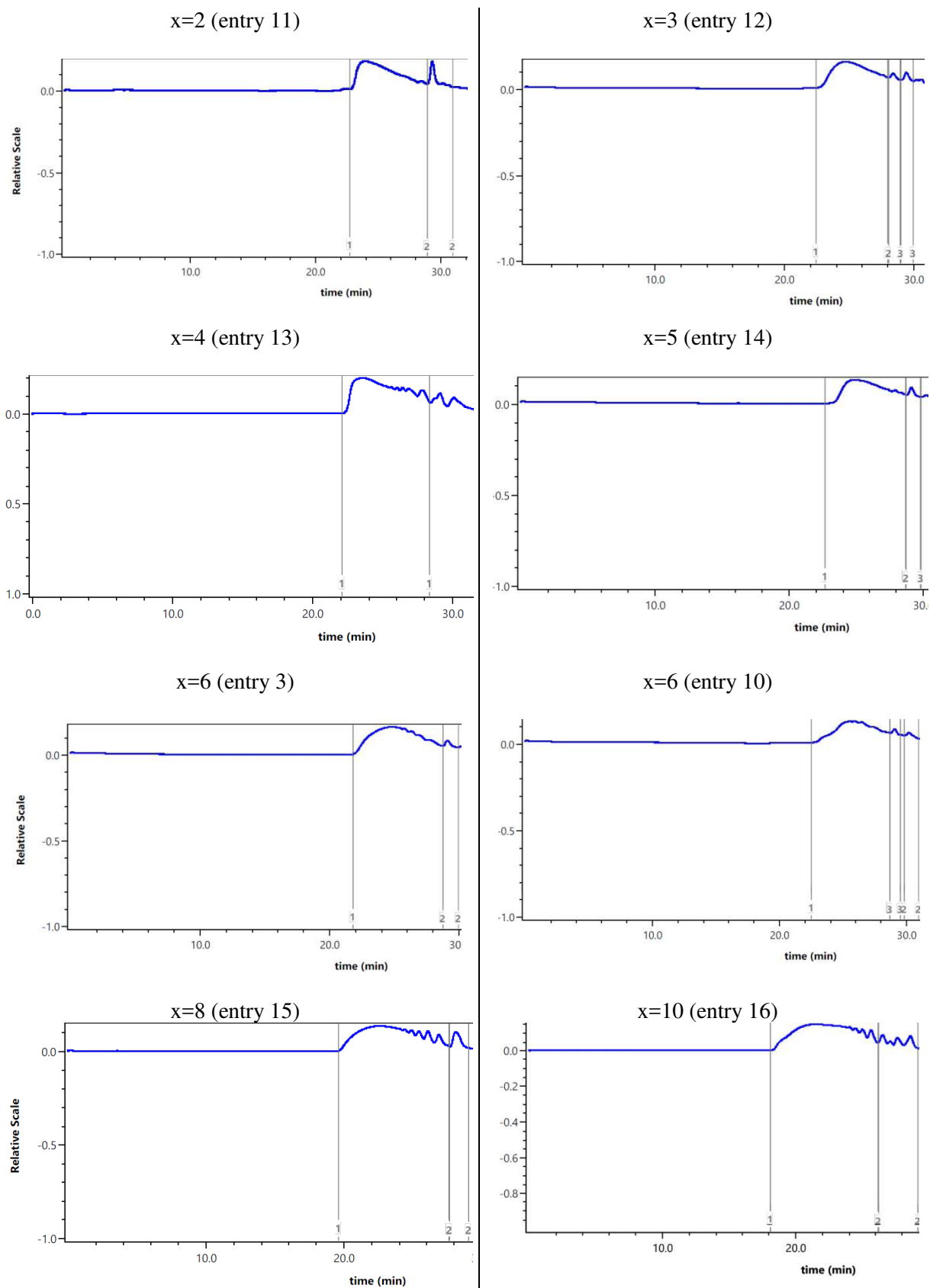


Fig. S27 SEC chromatograms of the reaction product obtained from diol-diamide and diethyl adipate (CHCl_3 , 25°C , standard PS)

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	D_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	/	/		
11	2	0.10	81	1,500	1.4	88	71	-5	/	/	187	355
12'	3	0.033	91	2,700	1.4	75	68	-10	/	/		
12	3	0.10	92	2,300	1.4	91	84	-9	/	/	198	360
13'	4	0.033	79	2,000	1.5	71	56	-2	/	/		
13	4	0.10	65	2,300	1.6	86	56	0	/	/	201	365
14'	5	0.033	94	1,300	1.6	79	75	-19	/	/		
14	5	0.10	88	1,800	1.5	91	80	-10	/	/	202	373
3	6	0.033	86	1,800	1.5	91	78	-13	/	/		
10	6	0.10	90	3,300	1.5	92	83	-12	/	/	205	375
15'	8	0.033	71	4,400	1.8	94	67	-22	71	89		
15	8	0.10	85	4,200	1.8	91	78	-23	72	90	180	376
16'	10	0.033	80	6,700	1.8	86	69	-15	20 and 55	97		
16	10	0.10	71	7,200	1.6	91	65	-14	28 and 49	97	203	378

^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 D_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, $D_M = 1-1.3$), 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

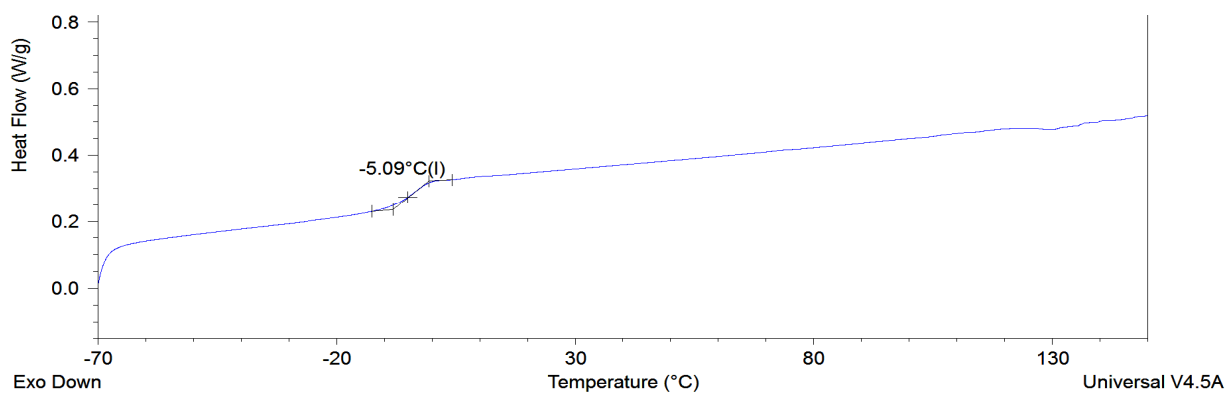


Fig. S28 DSC curve (second heating) of poly(ester-co-amide)s from diol-diamide $x=2$

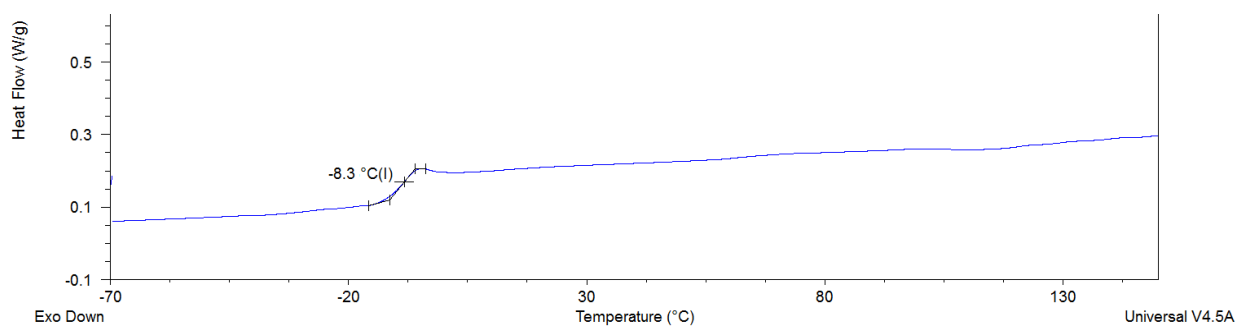


Fig. S29 DSC curve of poly(ester-co-amide)s from diol-diamide $x=3$

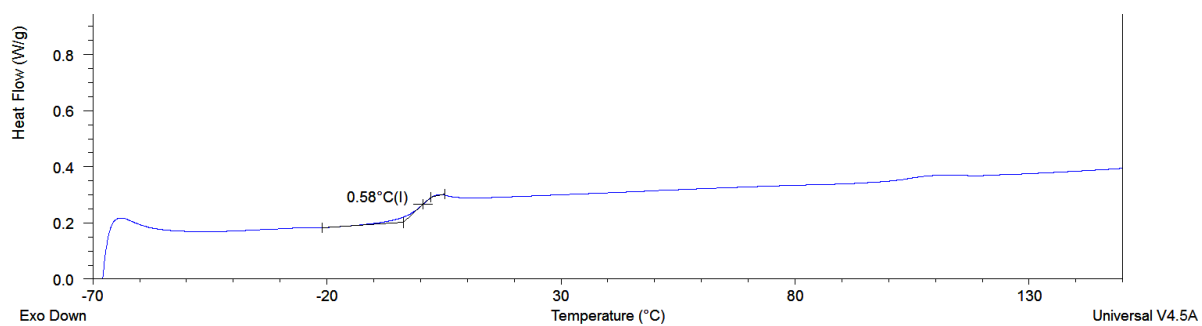


Fig. S30 DSC curve of poly(ester-co-amide)s from diol-diamide $x=4$

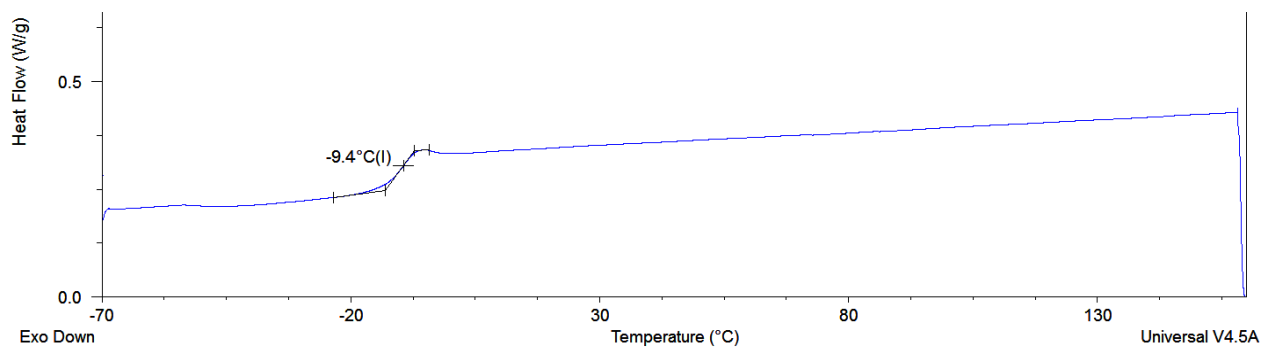


Fig. S31 DSC curve of poly(ester-co-amide)s from diol-diamide x=5

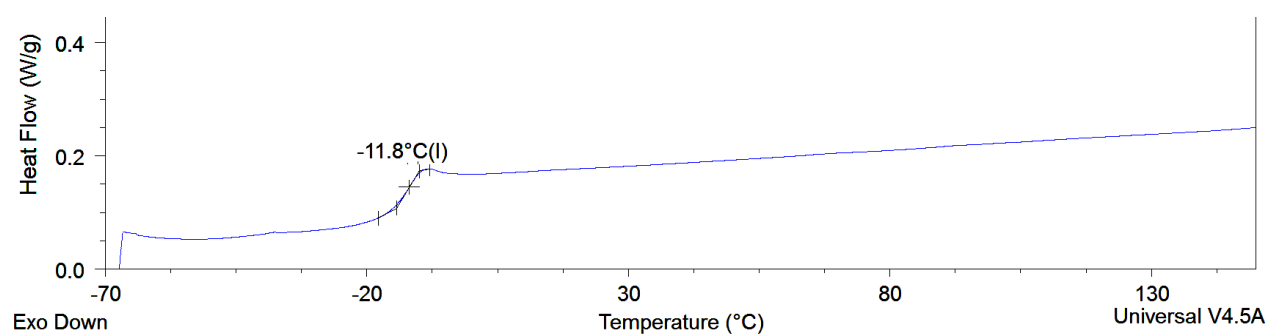


Fig. S32 DSC curve of poly(ester-co-amide)s from diol-diamide x=6

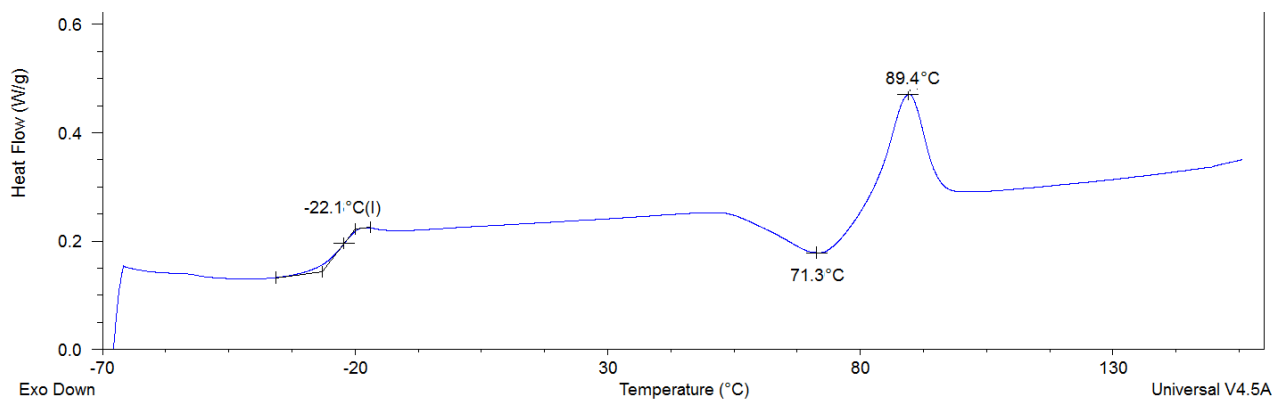


Fig. S33 DSC curve of poly(ester-co-amide)s from diol-diamide x=8

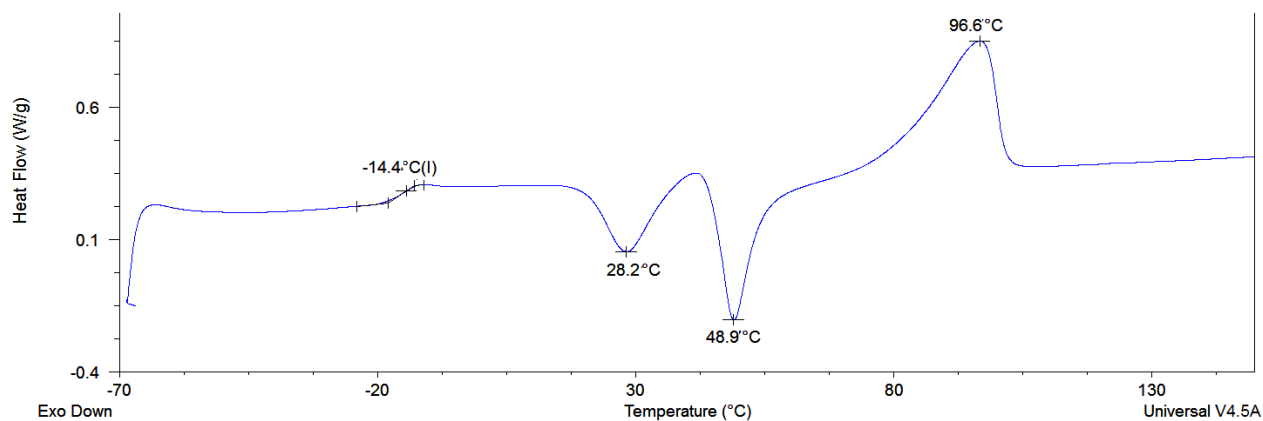


Fig. S34 DSC curve of poly(ester-co-amide)s (containing oligomers) from diol-diamide $x=10$

5. TGA curves of polymers

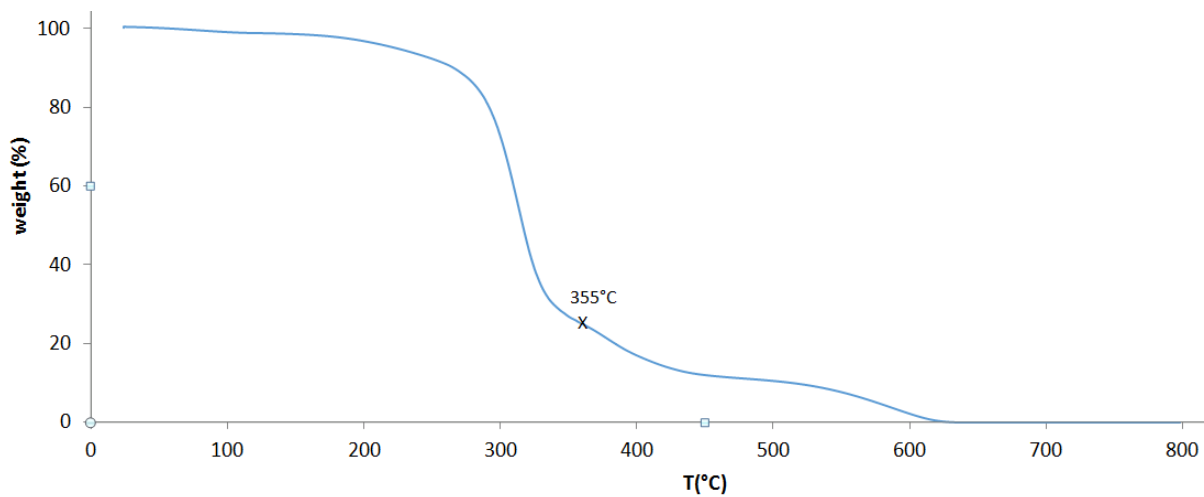


Fig. S35 TGA curve of poly(ester-co-amide)s from diol-diamide $x=2$

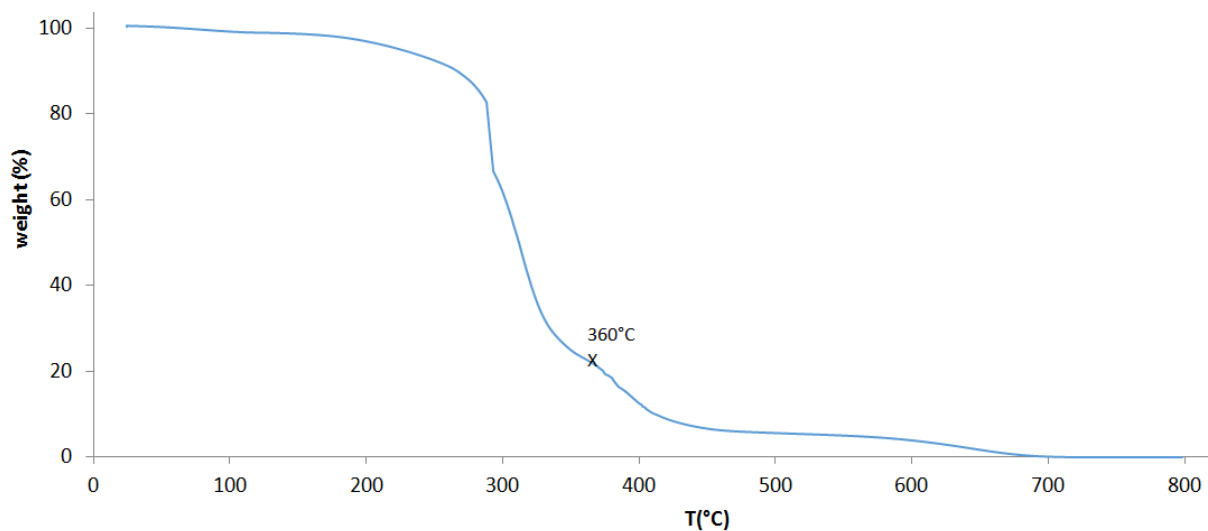


Fig. S36 TGA curve of poly(ester-co-amide)s from diol-diamide $x=3$

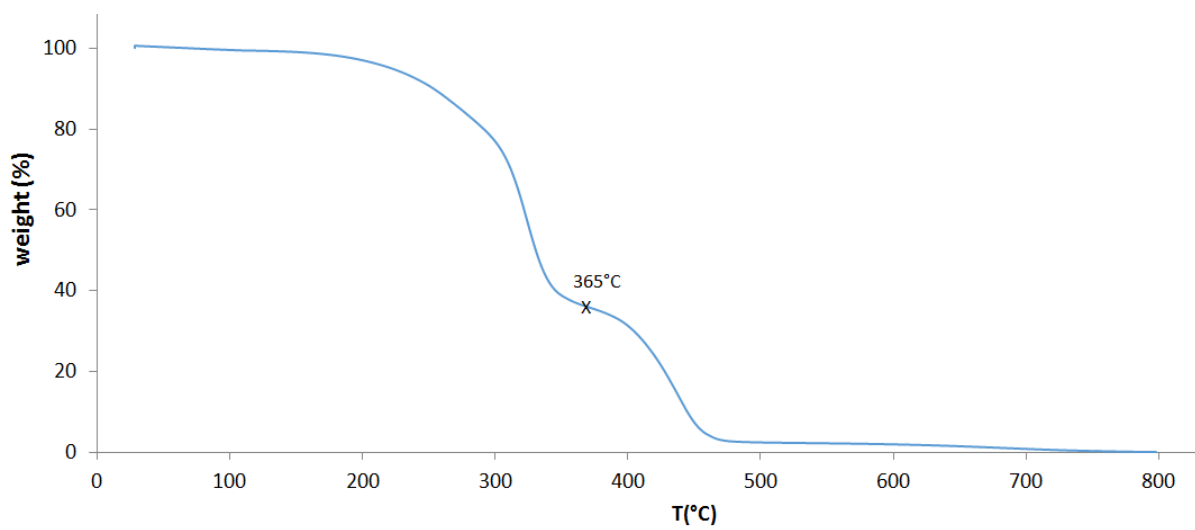


Fig. S37 TGA curve of poly(ester-co-amide)s from diol-diamide $x=4$

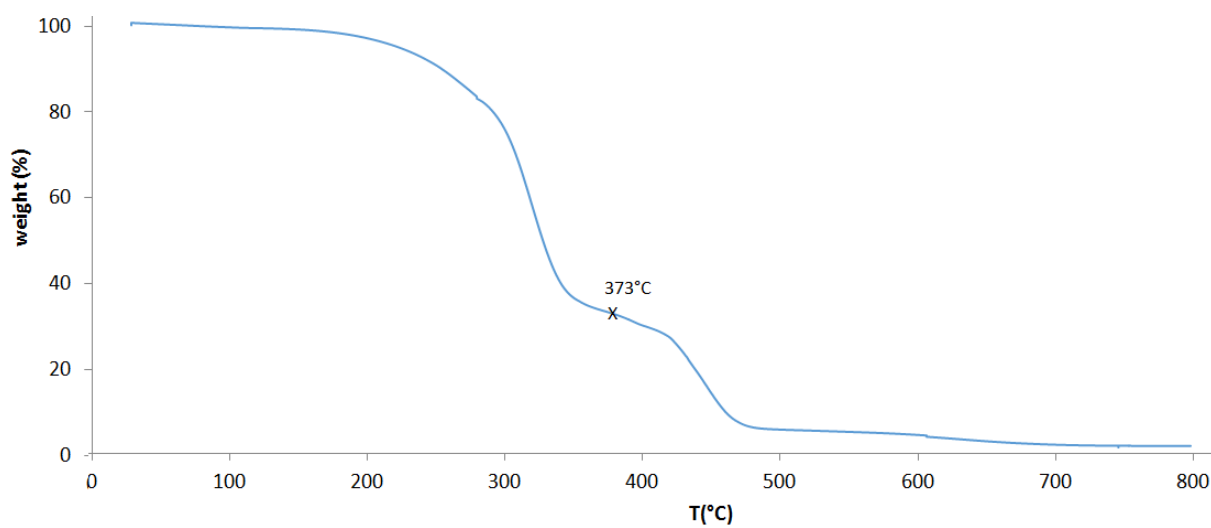


Fig. S38 TGA curve of poly(ester-co-amide)s from diol-diamide $x=5$

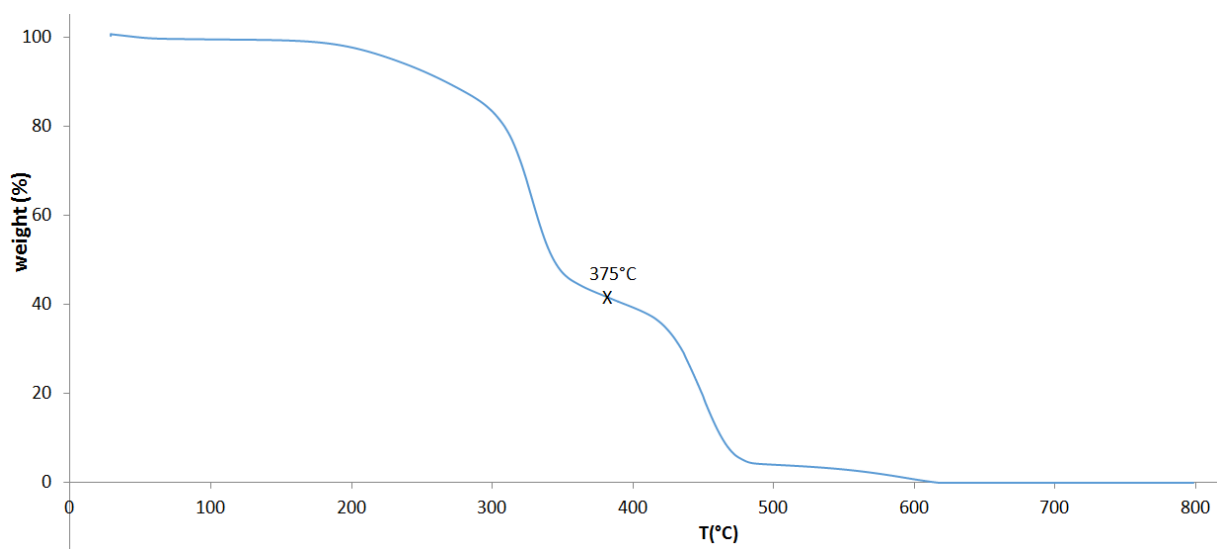


Fig. S39 TGA curve of poly(ester-co-amide)s from diol-diamide $x=6$

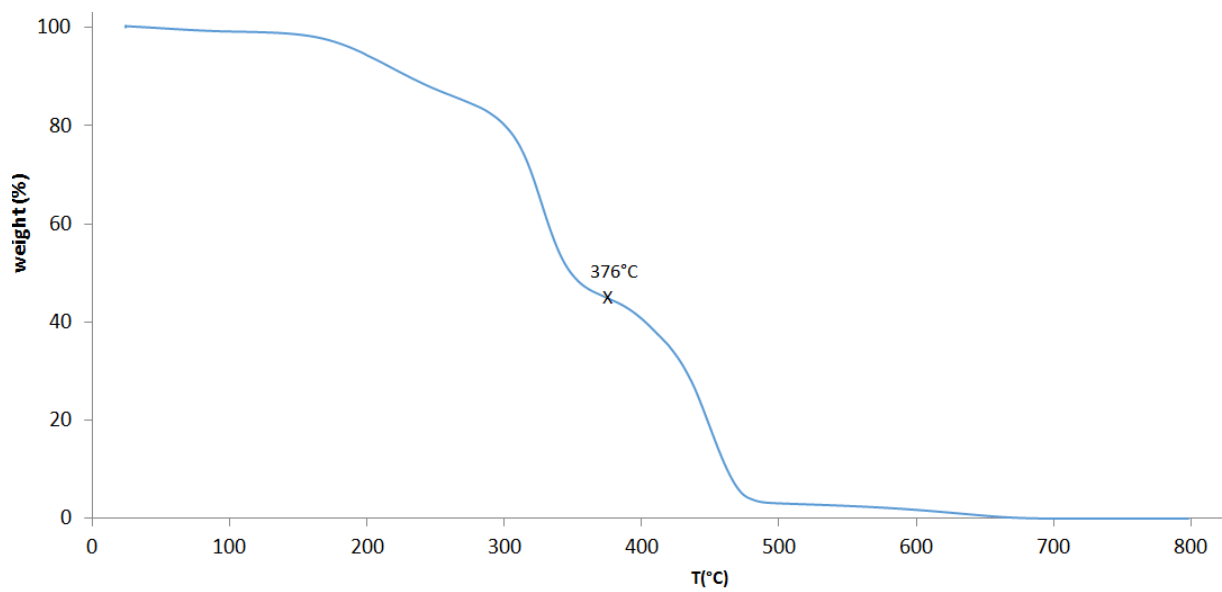


Fig. S40 TGA curve of poly(ester-co-amide)s from diol-diamide $x=8$

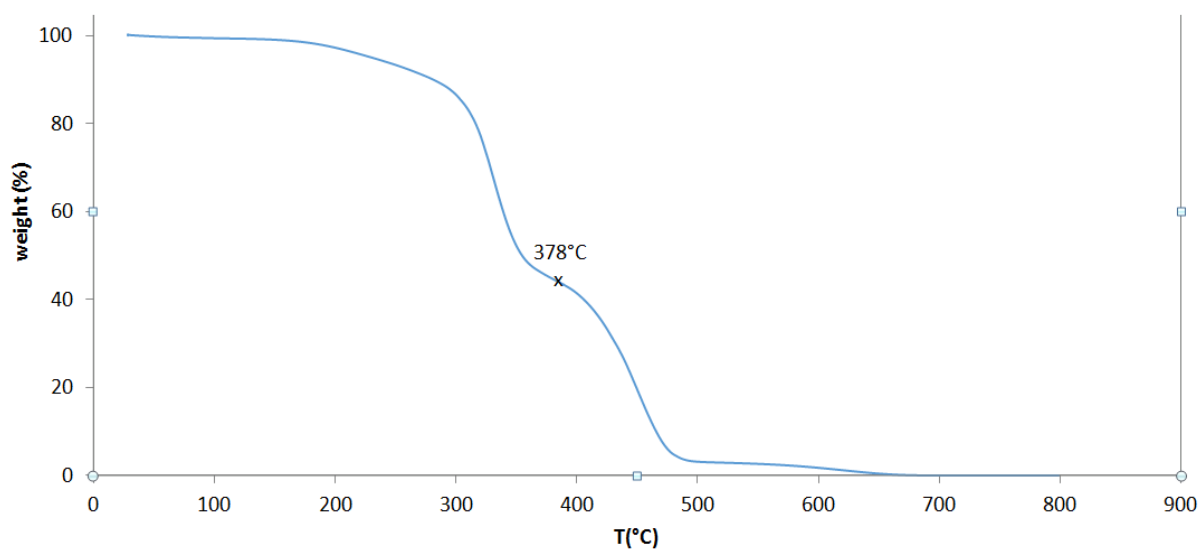


Fig. S41 TGA curve of poly(ester-co-amide)s from diol-diamide $x=10$