Well-defined Poly(lactic acids) Containing Poly(ethylene glycol) Side-chains

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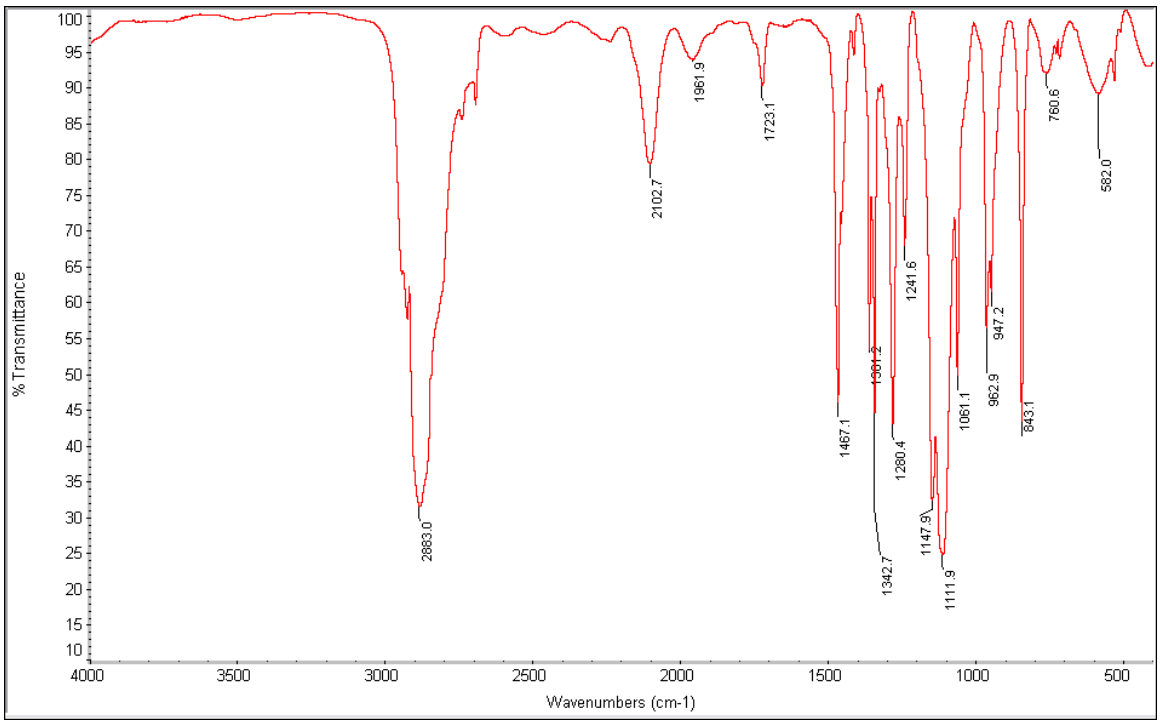
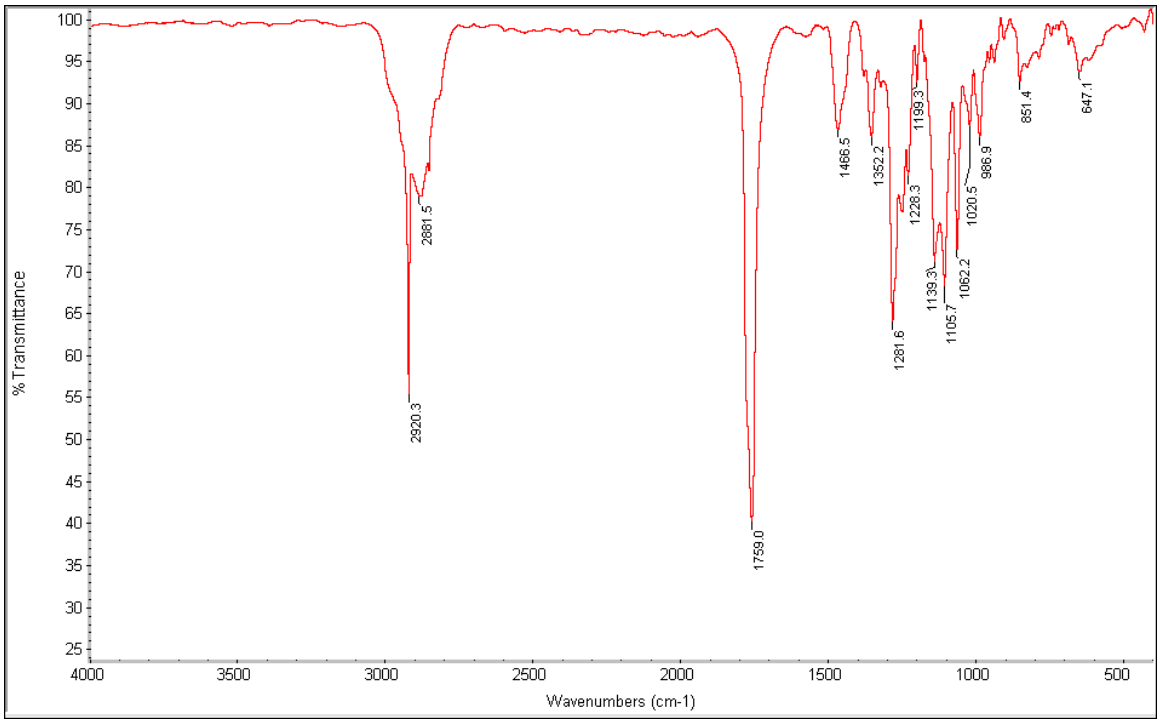
IR spectra

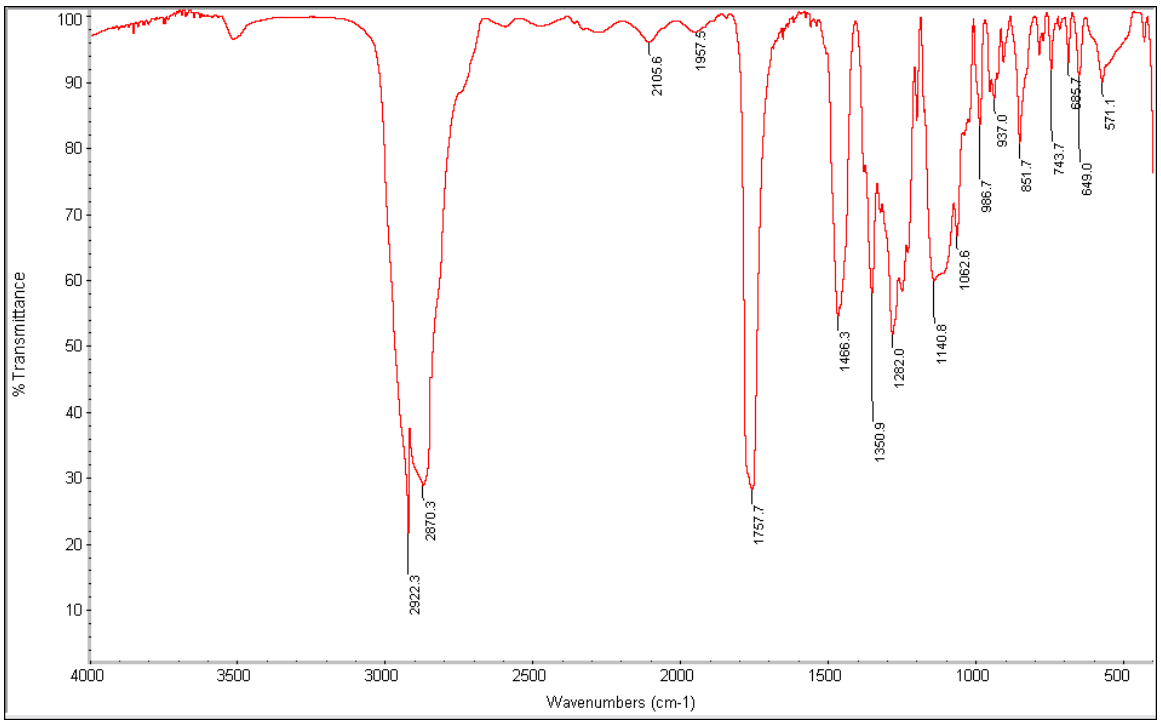
Azidopolyethylene glycol methyl ether (Mw~2000), PEG_{40}-N_3 (**3c**)



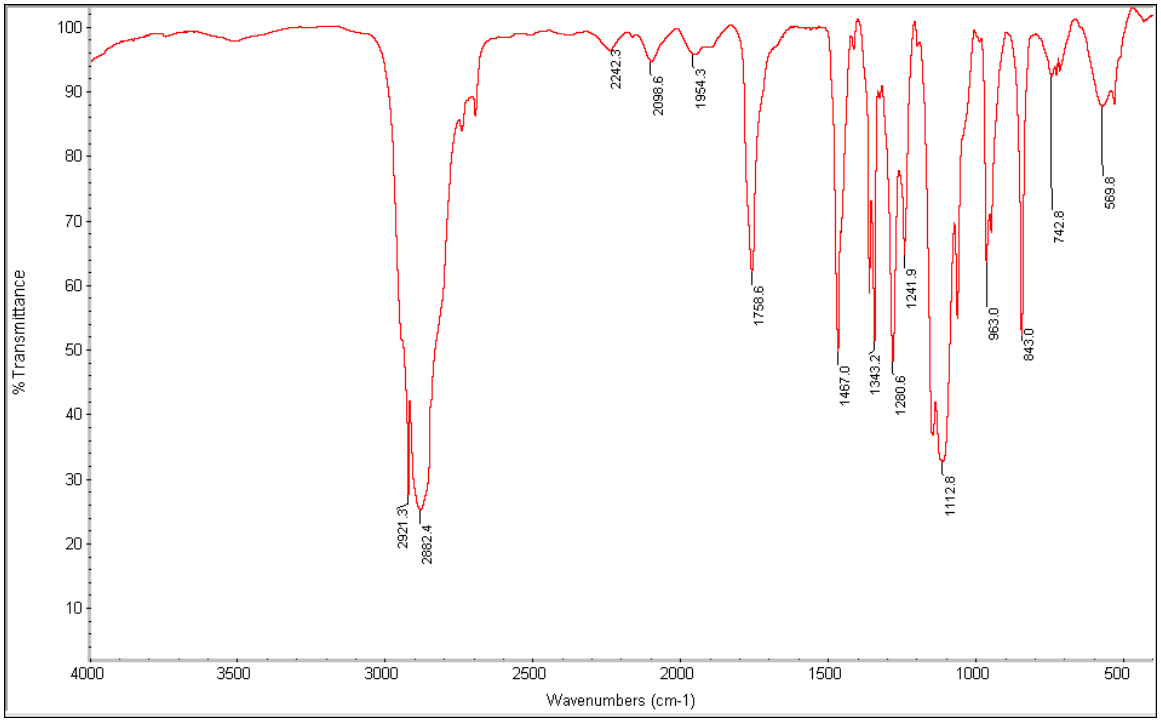
PEG_3-1,2,3-Δ^2-triazoline-spirolactide (**4a**)



PEG$_7$-1,2,3-Δ^2-triazoline-spirolactide (**4b**)



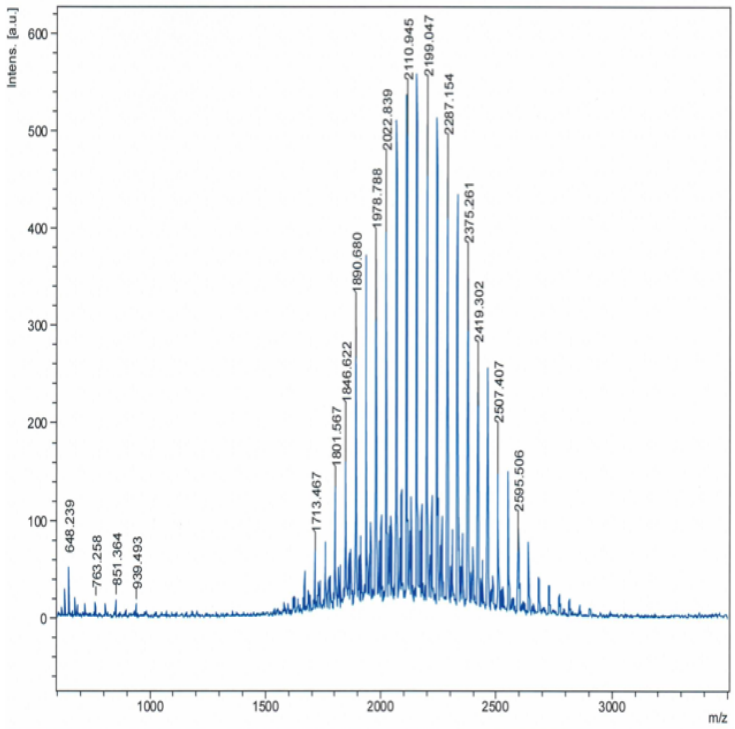
PEG$_{40}$-1,2,3-Δ^2-triazoline-spirolactide (**4c**).



Adamantyl-1,2,3-Δ^2-triazoline-spirolactide (**4d**)

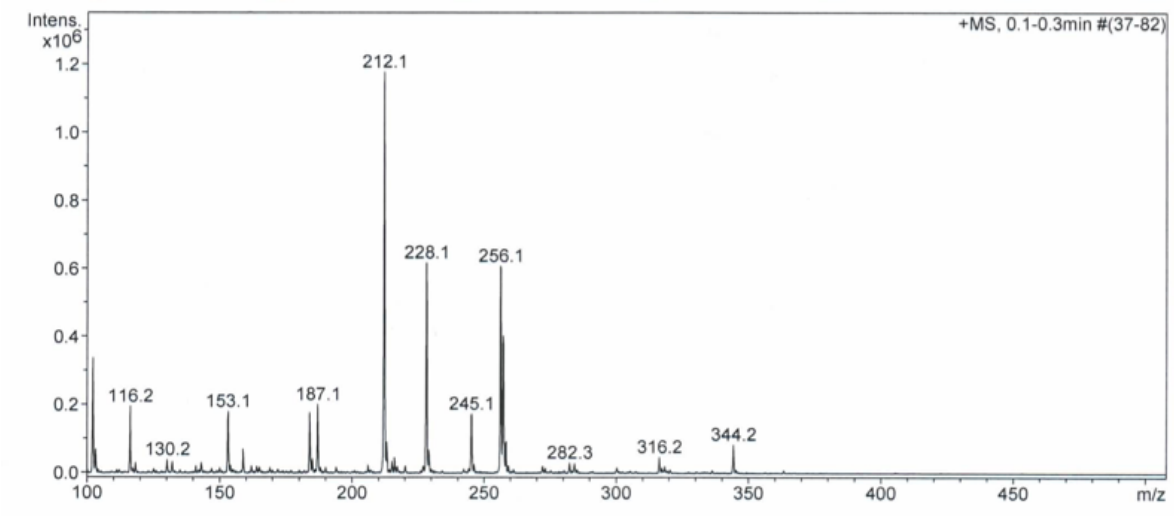
MALDI-TOF

PEG_{40}-spirolactide **4c** (theoric M_n ~2200)

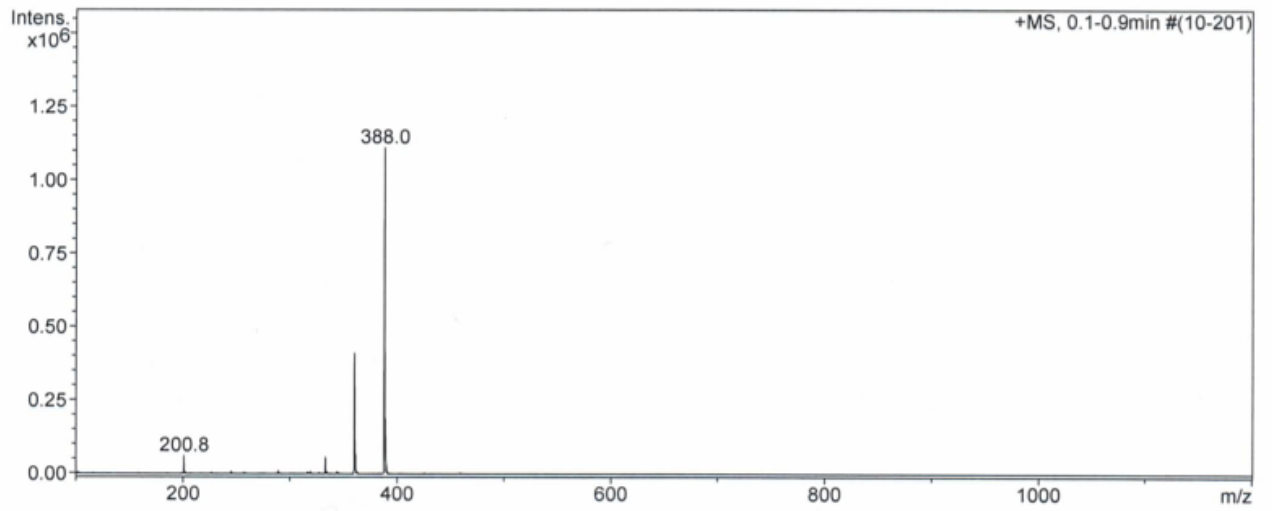


ESI mass spectra

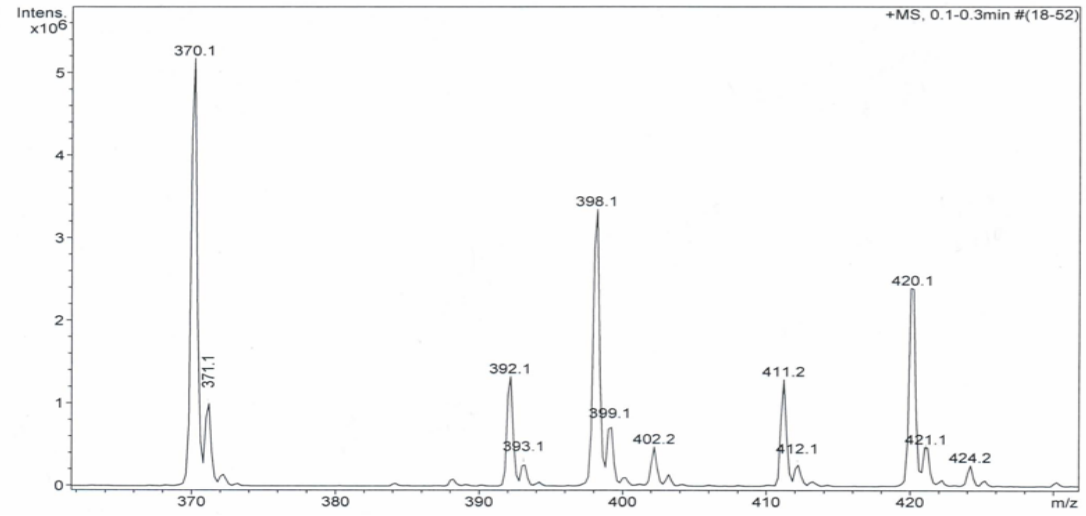
Azidotriethylene glycol methyl ether, PEG_3-N_3 (**3a**)
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_7H_{15}N_3O_3Na$ 212.2, found 212.1.
Mw ($C_7H_{15}N_3O_7$): 189.21. Eluent: MeOH/H_2O 90:10



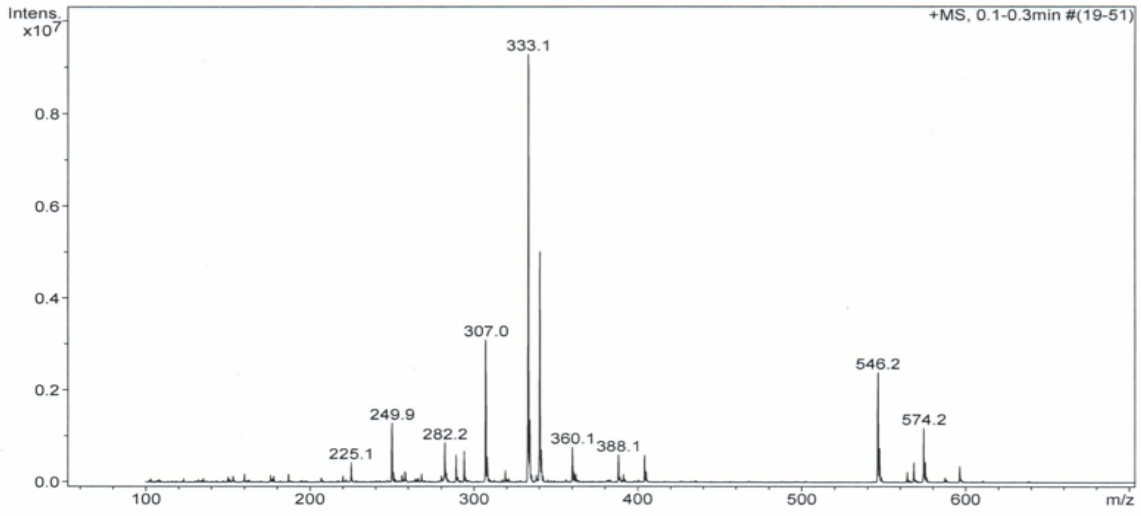
Azidoheptaethylene glycol methyl ether, PEG_7-N_3 (**3b**).
MS-ESI $(M+Na)^+$ m/z calcd. for $C_{15}H_{31}N_3O_7Na$ 388.41, found 388.0.
Mw ($C_{15}H_{31}N_3O_7$): 365.42. Eluent: MeOH/H_2O 90:10



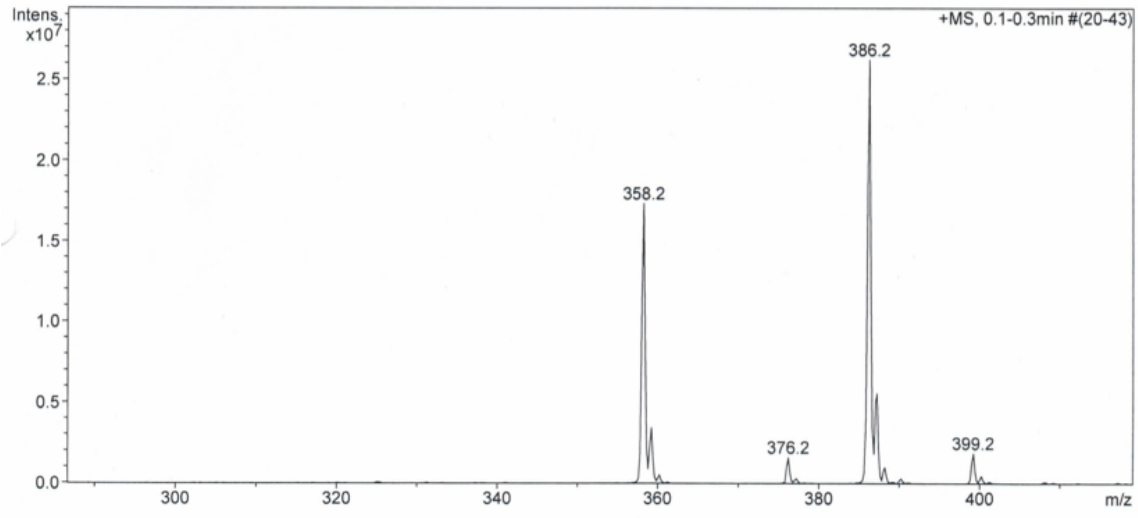
PEG$_3$-1,2,3-Δ^2-triazoline-spirolactide (**4a**)
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_{18}H_{27}N_3O_7Na$ 420.41, found 420.1
MS-ESI $(M+H)^+$ *m/z* calcd. for $C_{18}H_{28}N_3O_7$ 398.42, found 398.1
Mw ($C_{18}H_{27}N_3O_7$): 397.42. Eluent: ACN/H_2O 90:10



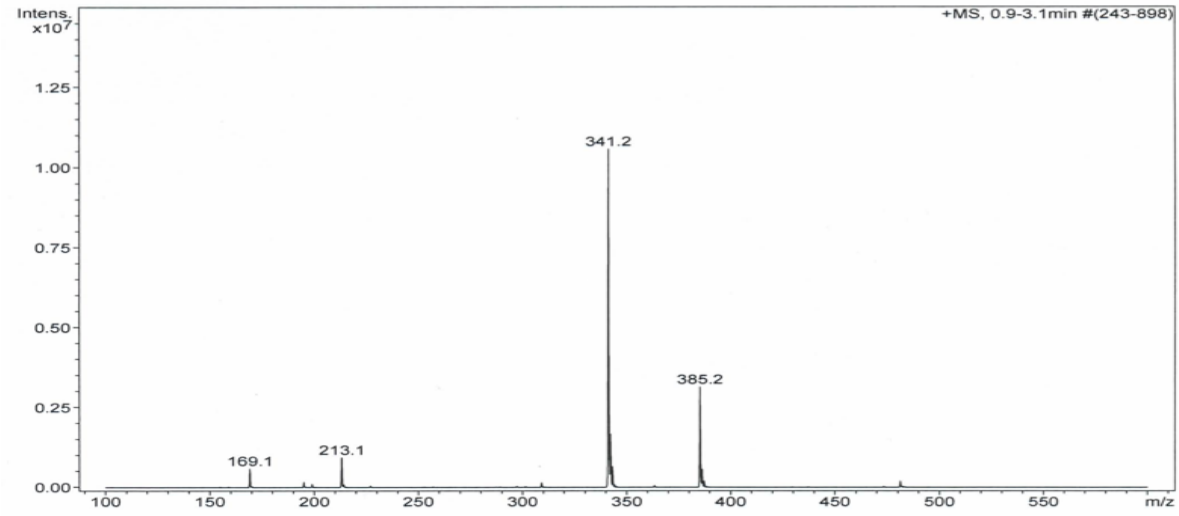
PEG$_7$-1,2,3-Δ^2-triazoline-spirolactide (**4b**)
MS-ESI $(M+H)^+$ *m/z* calcd. for $C_{26}H_{44}N_3O_{11}$ 574.63, found 574.2
Mw ($C_{26}H_{43}N_3O_{11}$): 573.63. Eluent: ACN/H_2O 90:10



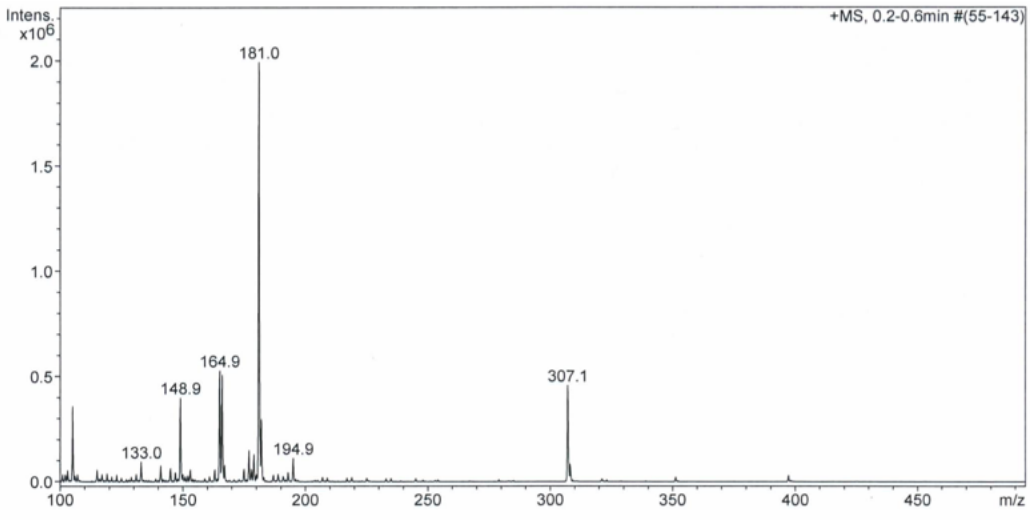
Adamantyl-1,2,3-Δ^2-triazoline-spirolactide (**4d**)
MS-ESI $(M+H)^+$ *m/z* calcd. for $C_{21}H_{28}N_3O_4$ 386.46, found 386.2
Mw ($C_{21}H_{27}N_3O_4$): 385.46. Eluent: ACN/H_2O 90:10



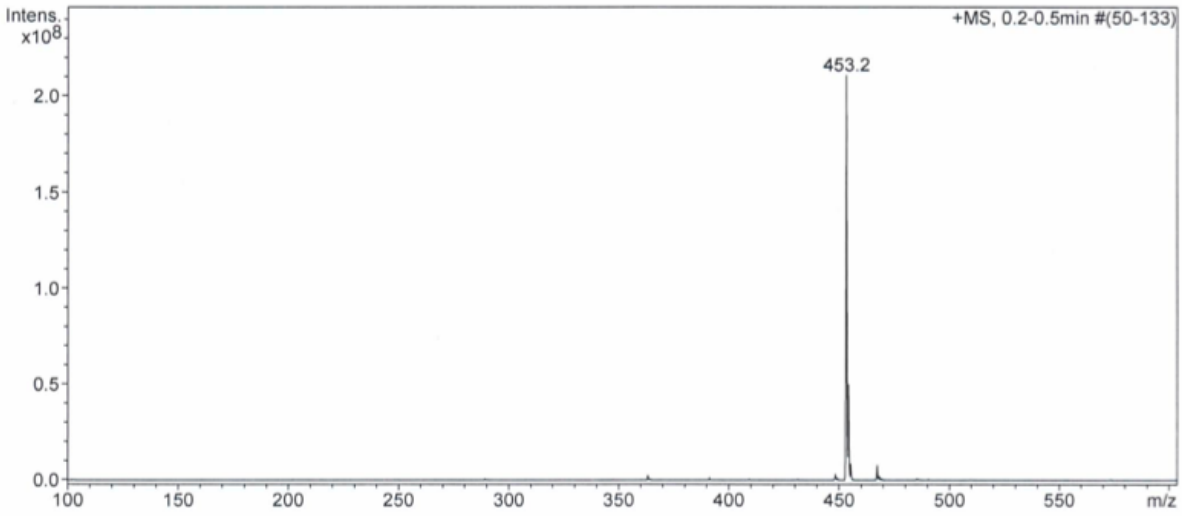
Triethylene glycol methyl ether *p*-tosylate, PEG_3-Ts (**6**)
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_{14}H_{22}O_6SNa$ 341.38, found 341.2
Mw ($C_{14}H_{22}O_6S$): 318.39. Eluent: ACN/H_2O 90:10



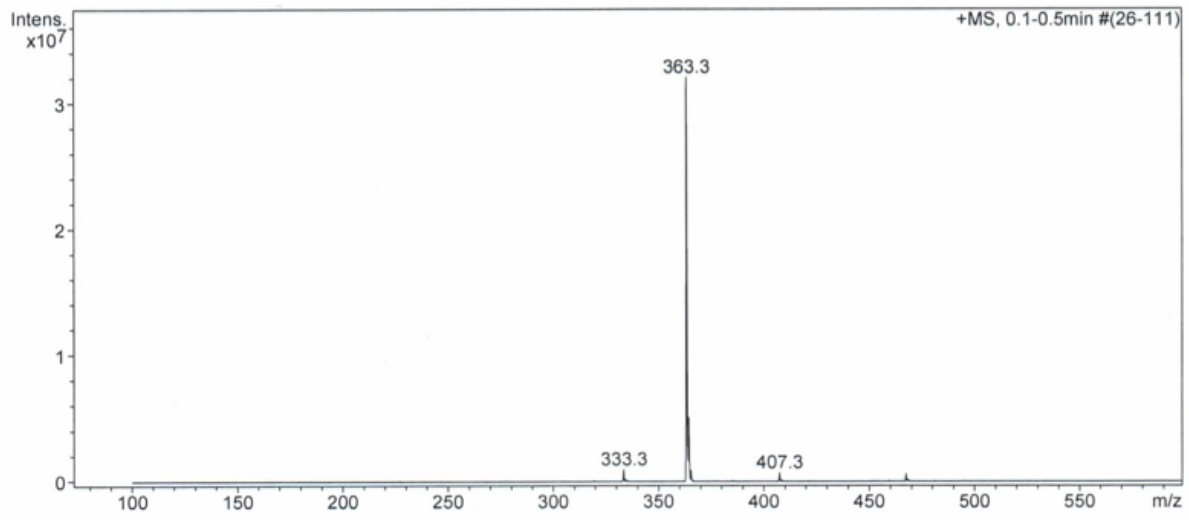
Tetraethylene glycol benzyl methyl ether, PEG_4-Bn (**7**):
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_{15}H_{24}O_5Na$ 307.34, found 307.1
Mw ($C_{15}H_{24}O_5$): 284.35. Eluent: MeOH/H_2O 90:10



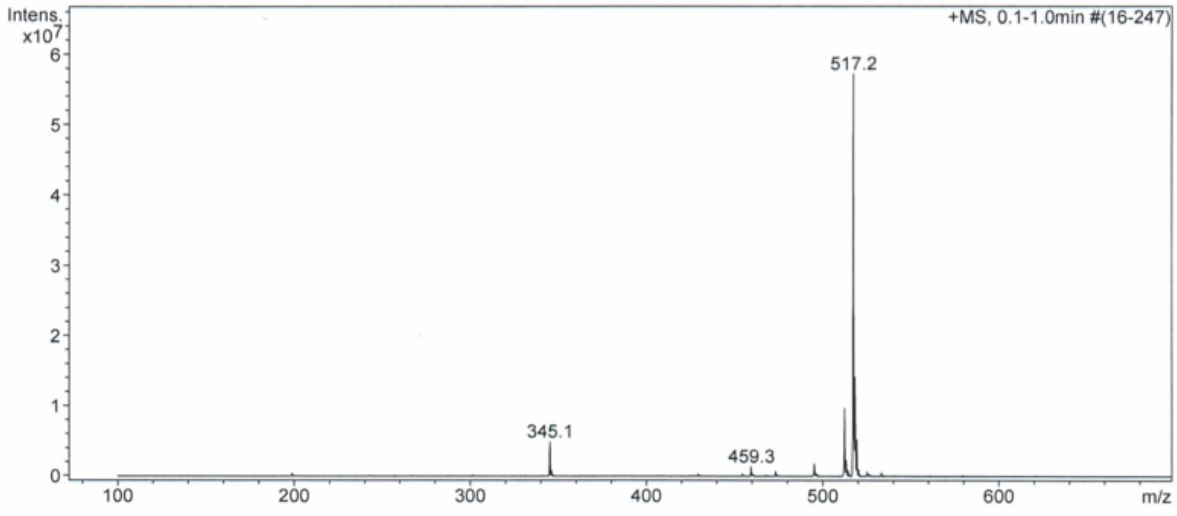
Heptaethylene glycol benzyl methyl ether, PEG_7-Bn (**8**)
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_{22}H_{38}O_8Na$ 453.52, found 453.2
Mw ($C_{22}H_{38}O_8$): 430.53. Eluent: MeOH/H_2O 90:10



Heptaethylene glycol methyl ether (**9**)
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_{15}H_{32}O_8Na$ 363.4, found 363.3
Mw ($C_{15}H_{32}O_8$): 340.41. Eluent: MeOH/H_2O 90:10

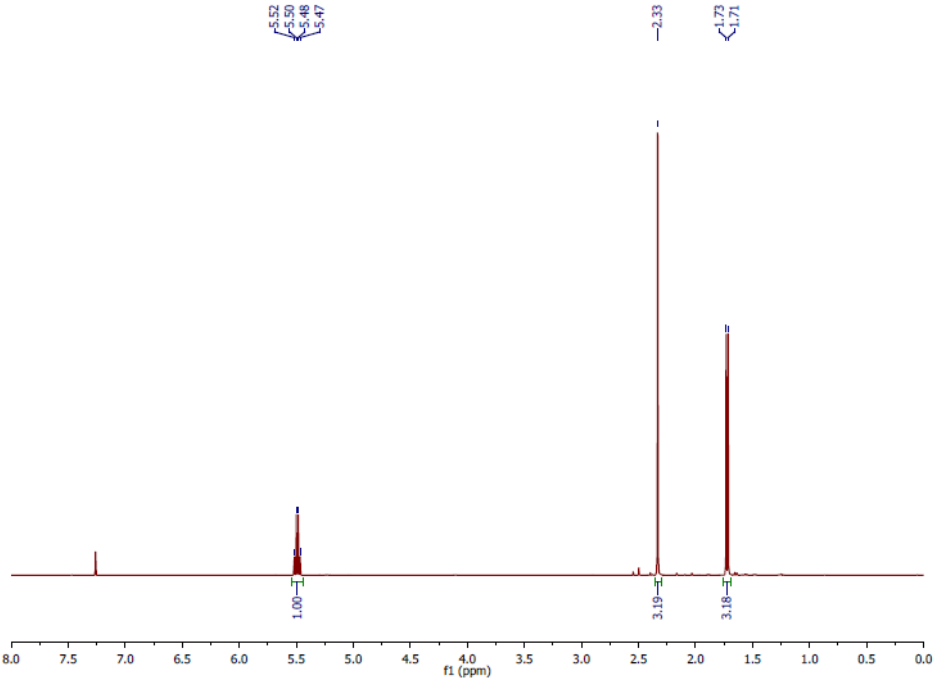


Heptaethylene glycol methyl ether *p*-tosylate, PEG_7-Ts (**10**)
MS-ESI $(M+Na)^+$ *m/z* calcd. for $C_{22}H_{38}O_4Na$ 517.59, found 517.2
Mw ($C_{22}H_{38}O_4$): 494.60. Eluent: MeOH/H_2O 90:10

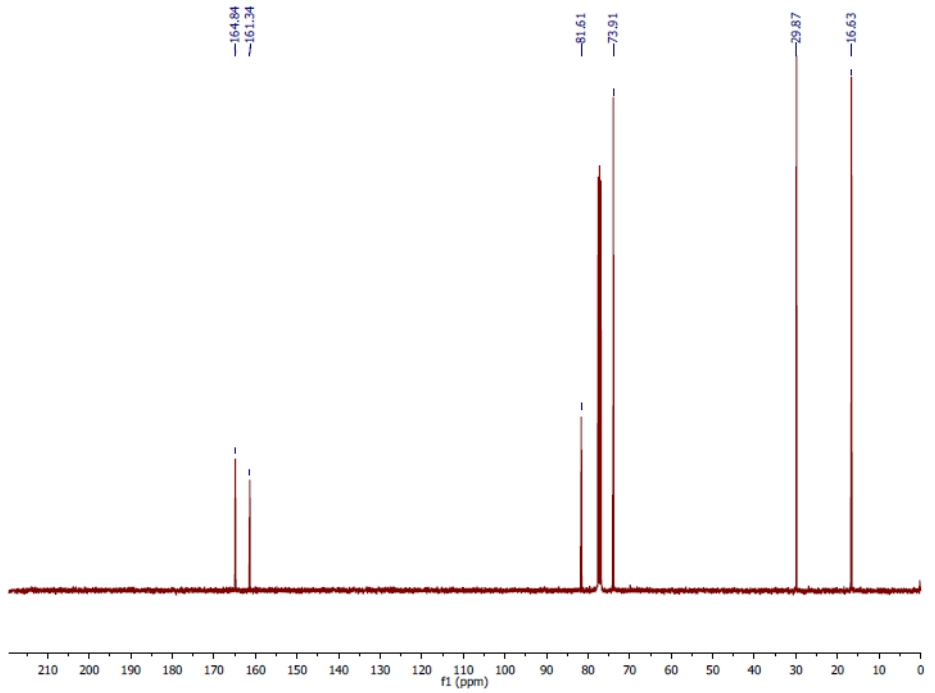


NMR spectra

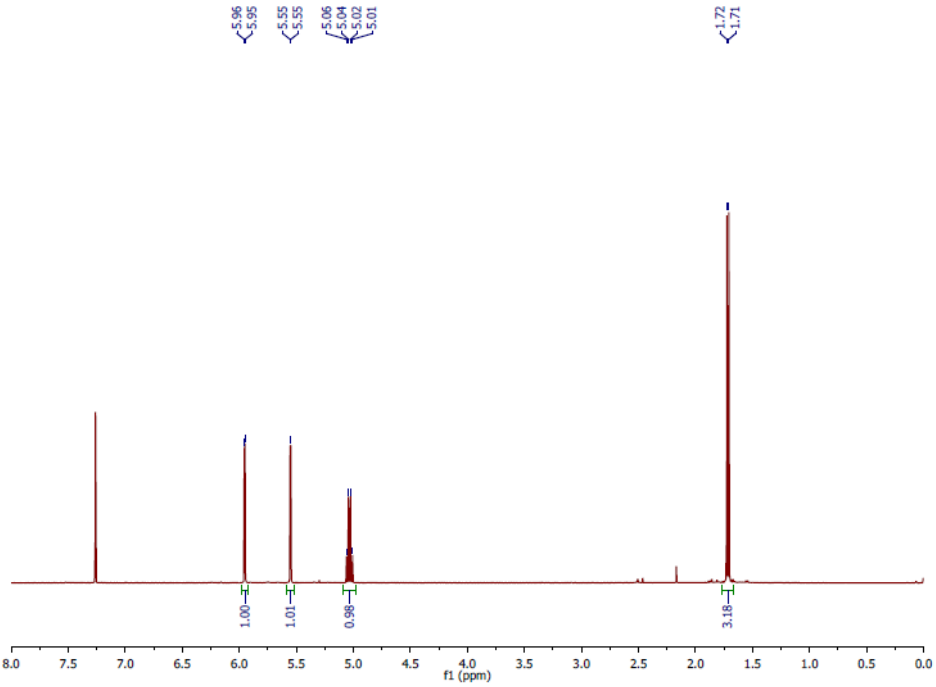
^{1}H-NMR spectrum of (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione in $CDCl_3$



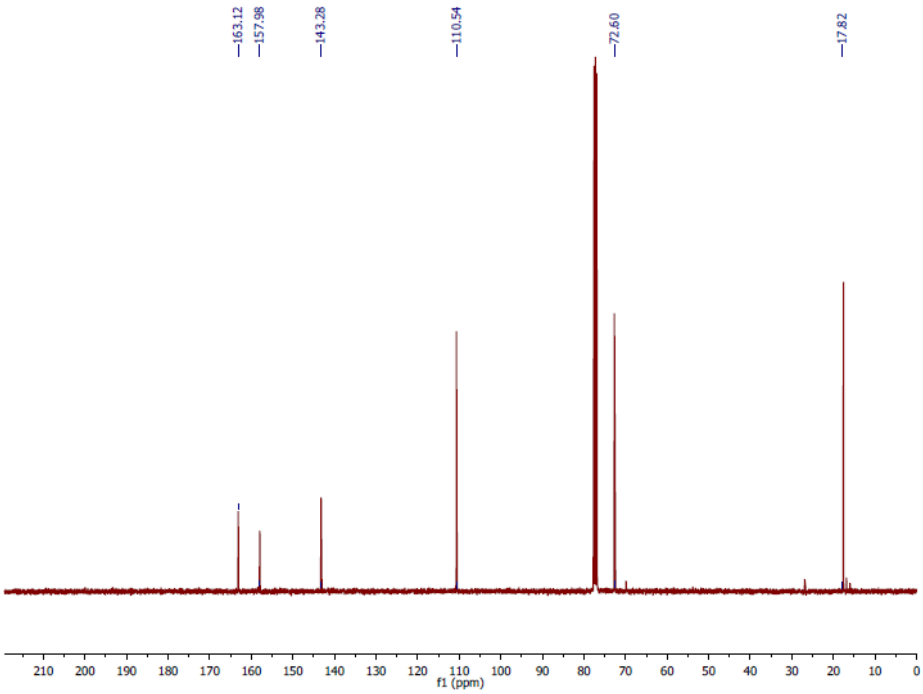
^{13}C-NMR spectrum of (3*S*, 6*S*)-3-bromo-3,6-dimethyl-1,4-dioxane-2,5-dione in $CDCl_3$



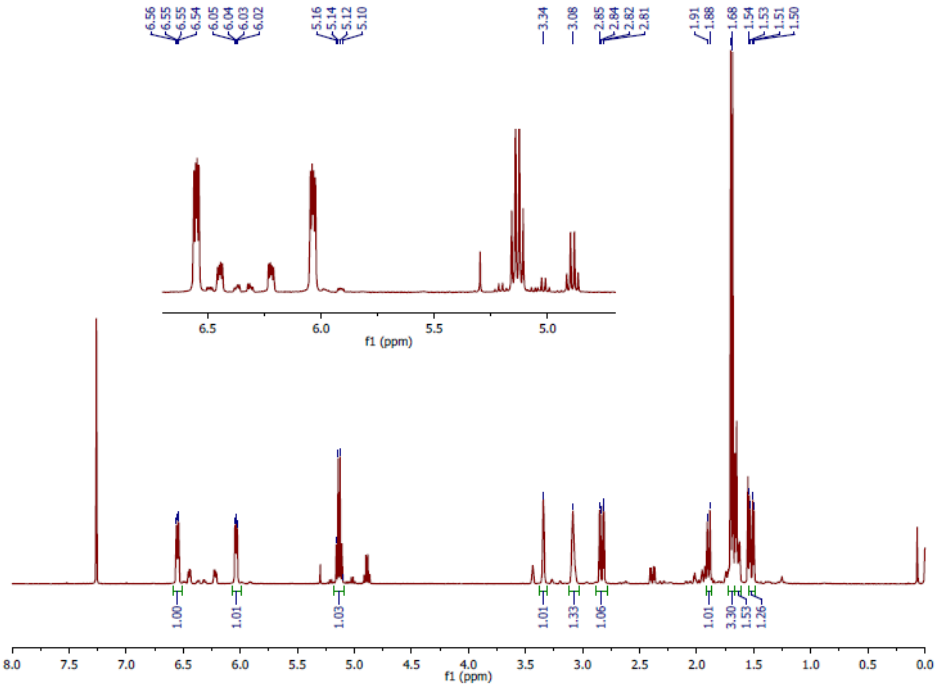
^{1}H-NMR spectrum of (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione (**1**) in $CDCl_3$



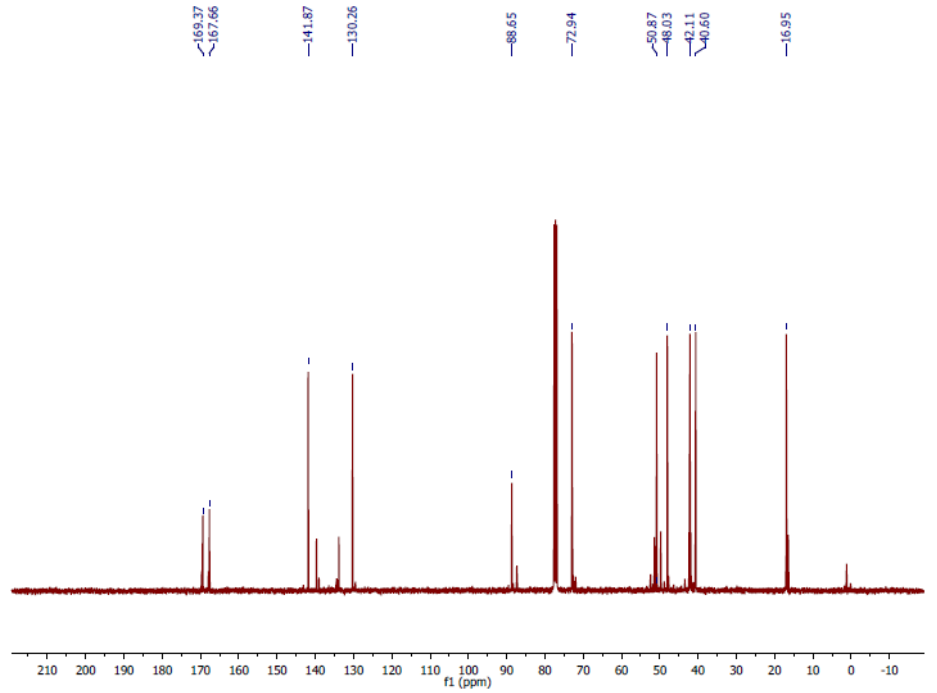
^{13}C-NMR spectrum of (6*S*)-3-methylene-6-methyl-1,4-dioxane-2,5-dione (**1**) in $CDCl_3$



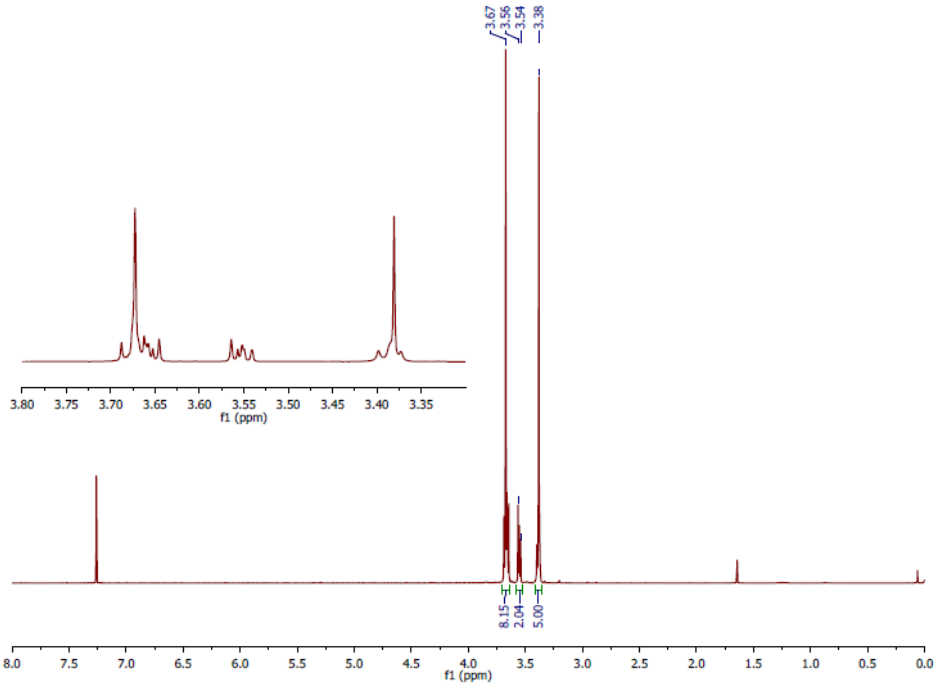
^{1}H-NMR spectrum of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hepta-5-ene] (**2**) in $CDCl_3$



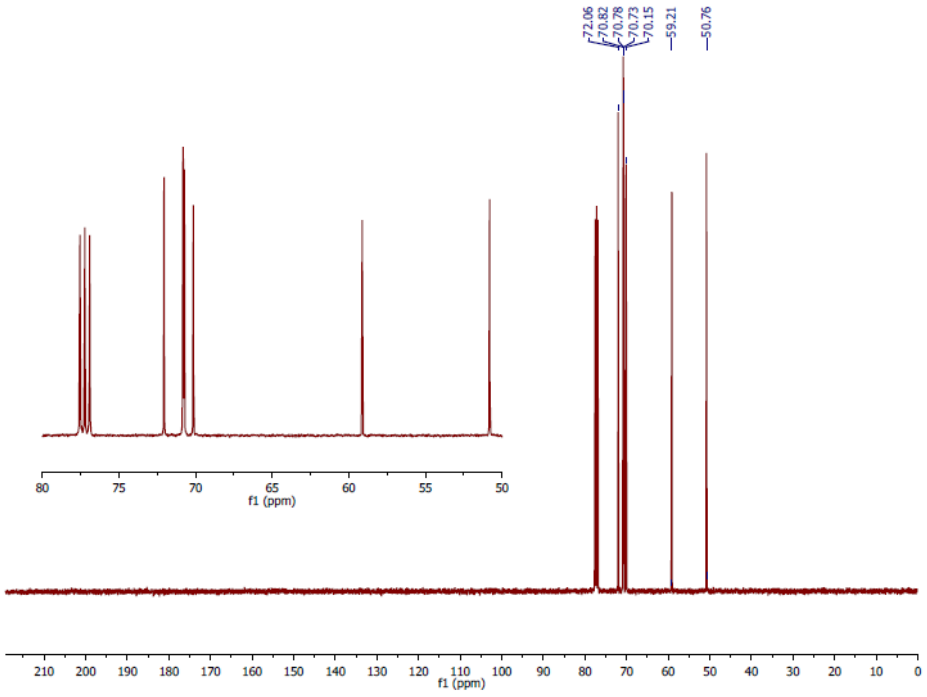
^{13}C-NMR spectrum of spiro[6-methyl-1,4-dioxane-2,5-dione-3,2'-bicyclo[2.2.1]hepta-5-ene] (**2**) in $CDCl_3$



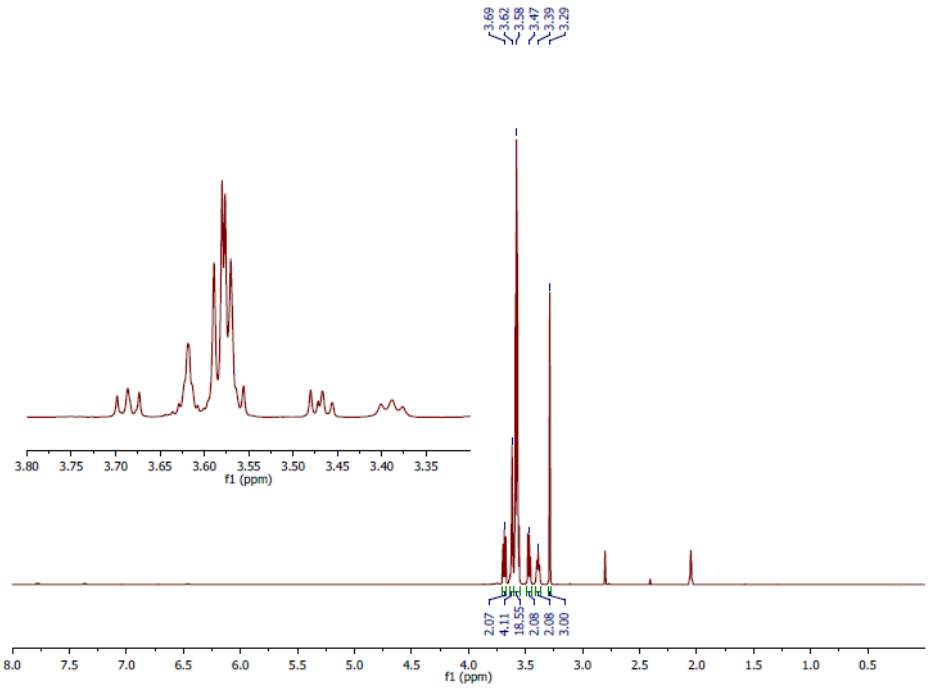
^{1}H-NMR spectrum of azidotriethylene glycol methyl ether, PEG_3-N_3 (**3a**), in $CDCl_3$



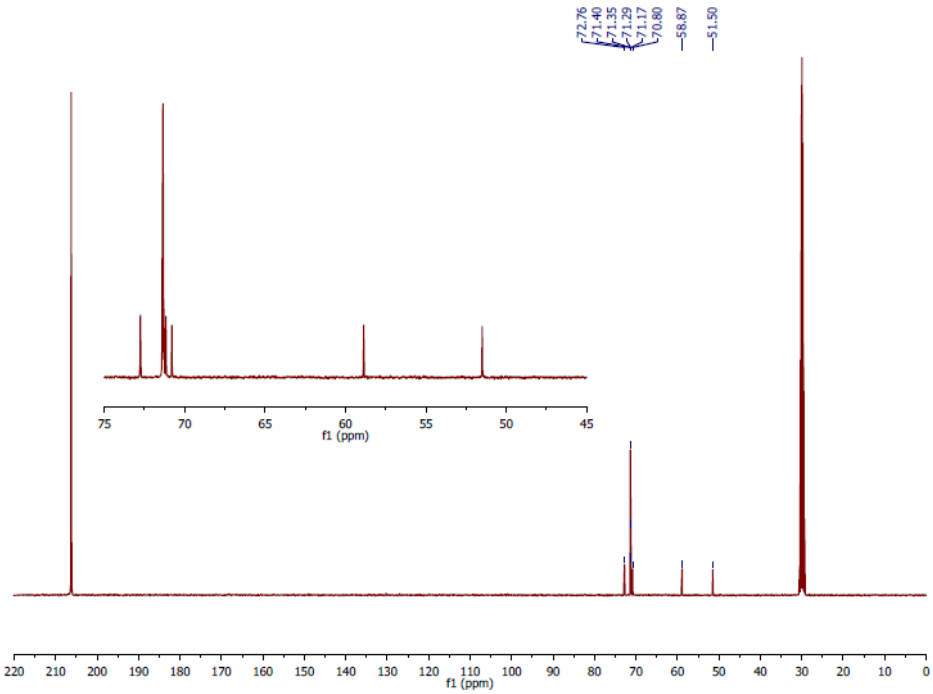
^{13}C-NMR spectrum azidotriethylene glycol methyl ether, PEG_3-N_3 (**3a**), in $CDCl_3$



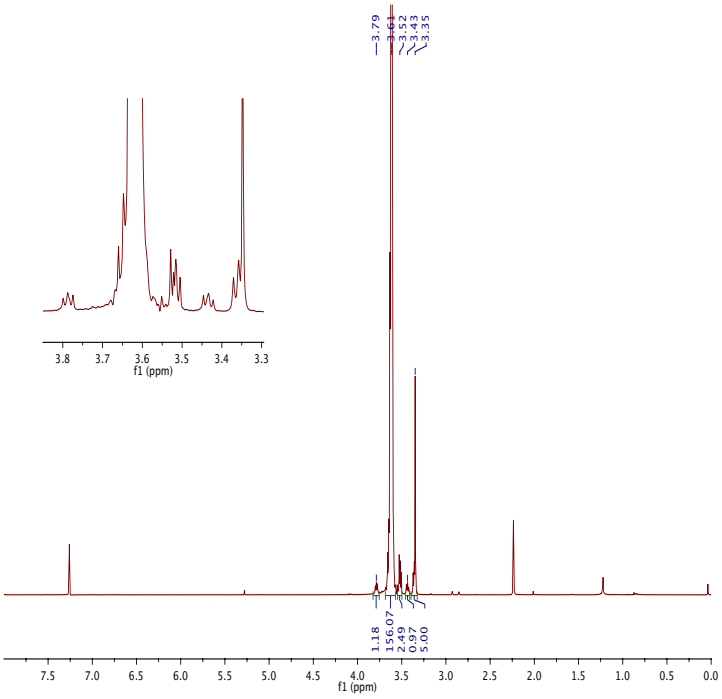
^{1}H-NMR spectrum azidoheptaethylene glycol methyl ether, PEG_7-N_3 (**3b**), in acetone-D_6



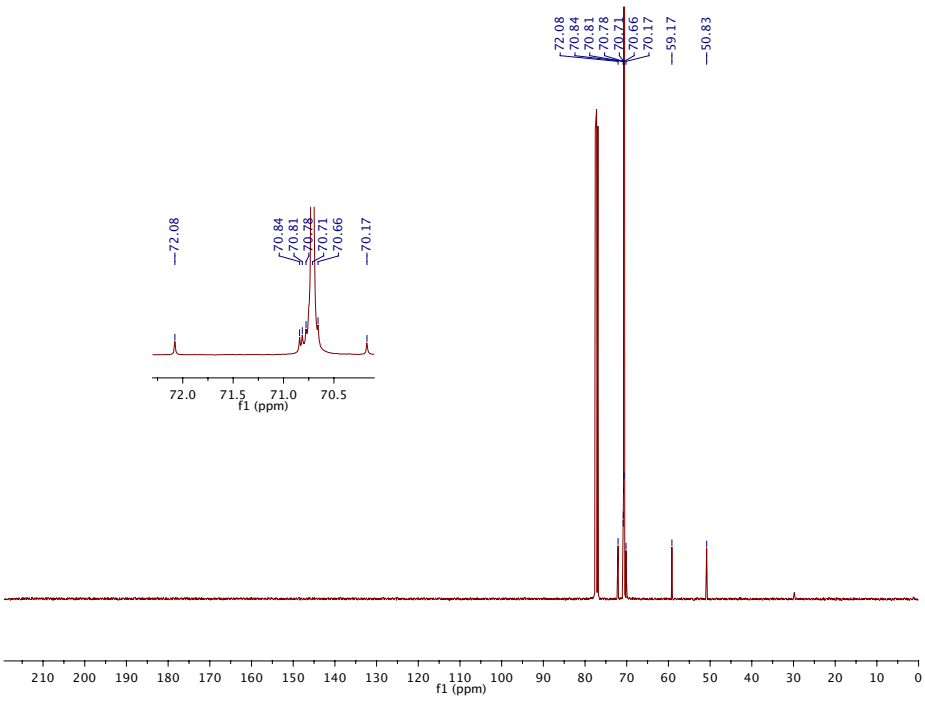
^{13}C-NMR spectrum azidoheptaethylene glycol methyl ether, PEG_7-N_3 (**3b**), in acetone-D_6



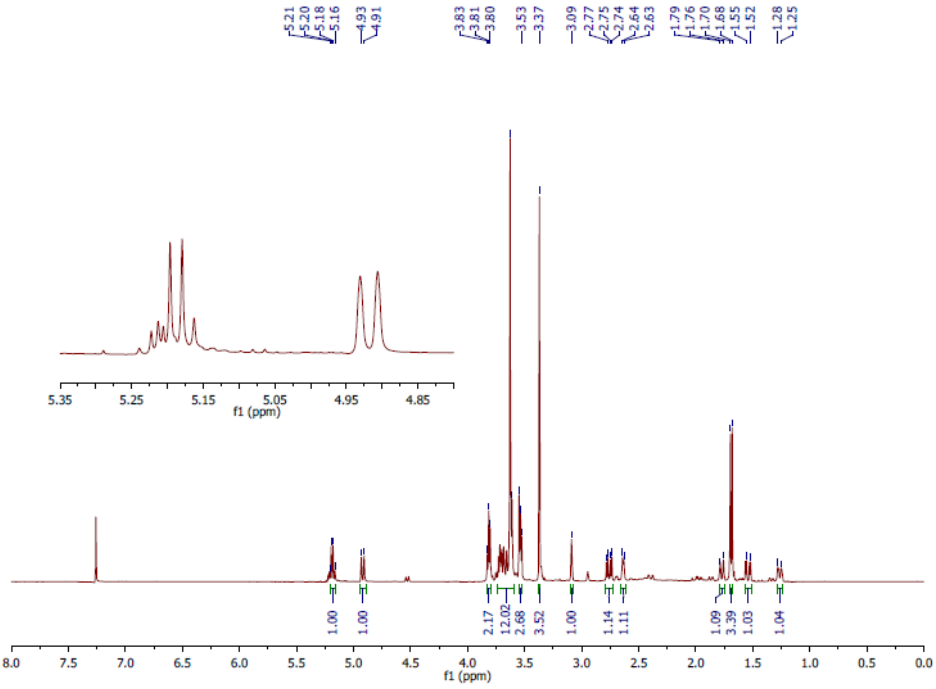
^{1}H-NMR spectrum azidopolyethylene glycol methyl ether (Mw~2000), PEG_{40}-N_3 (**3c**) in $CDCl_3$



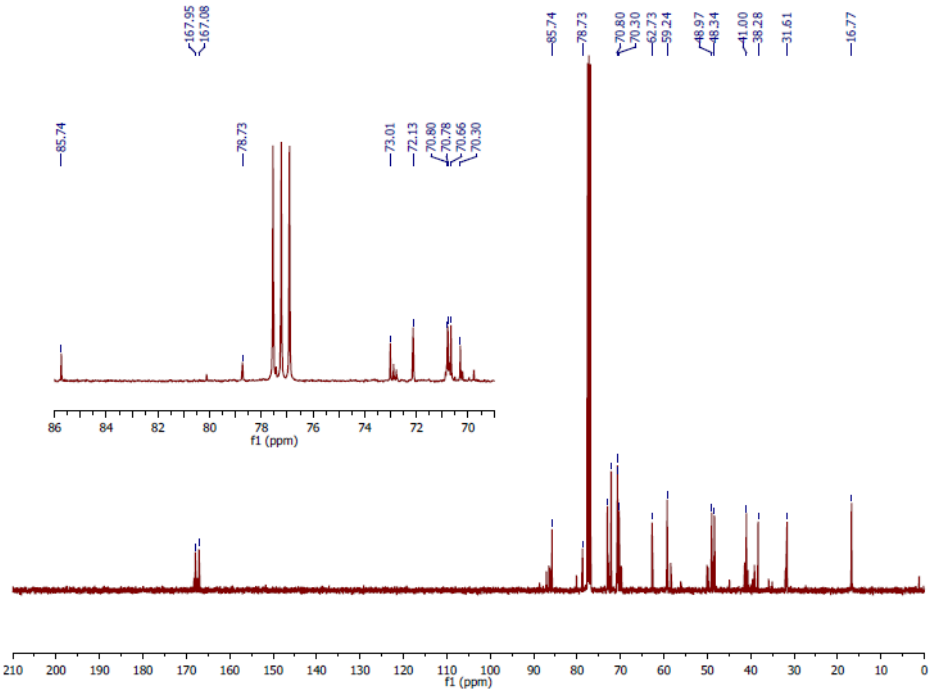
^{13}C-NMR spectrum azidopolyethylene glycol methyl ether (Mw~2000), PEG_{40}-N_3 (**3c**) in $CDCl_3$



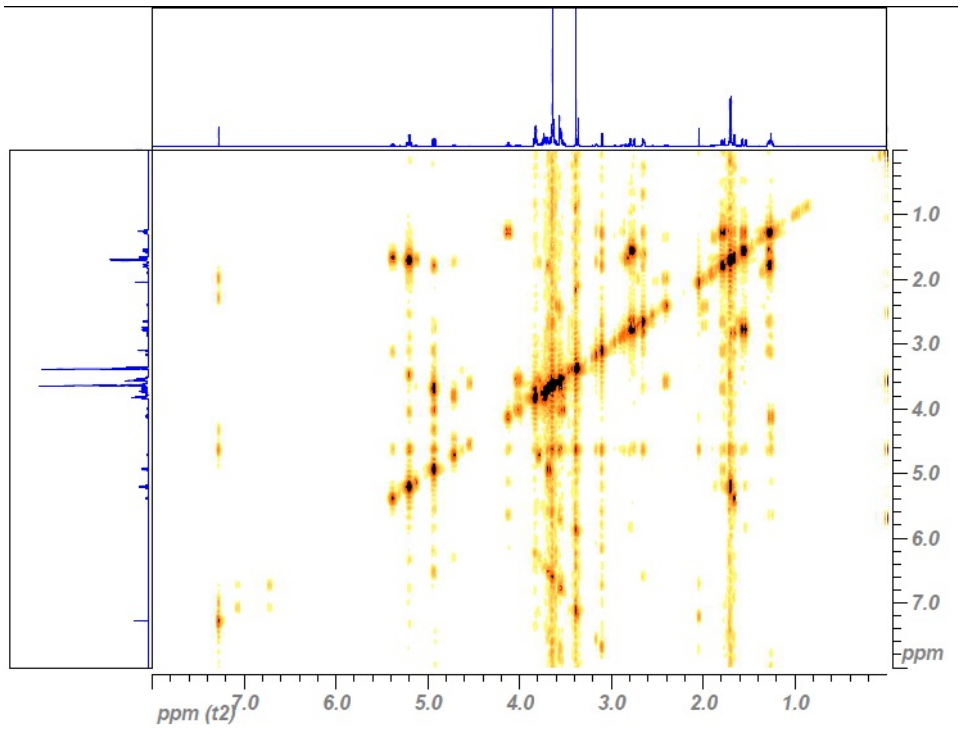
^{1}H-NMR spectrum PEG$_3$-spirolactide **4a** in $CDCl_3$



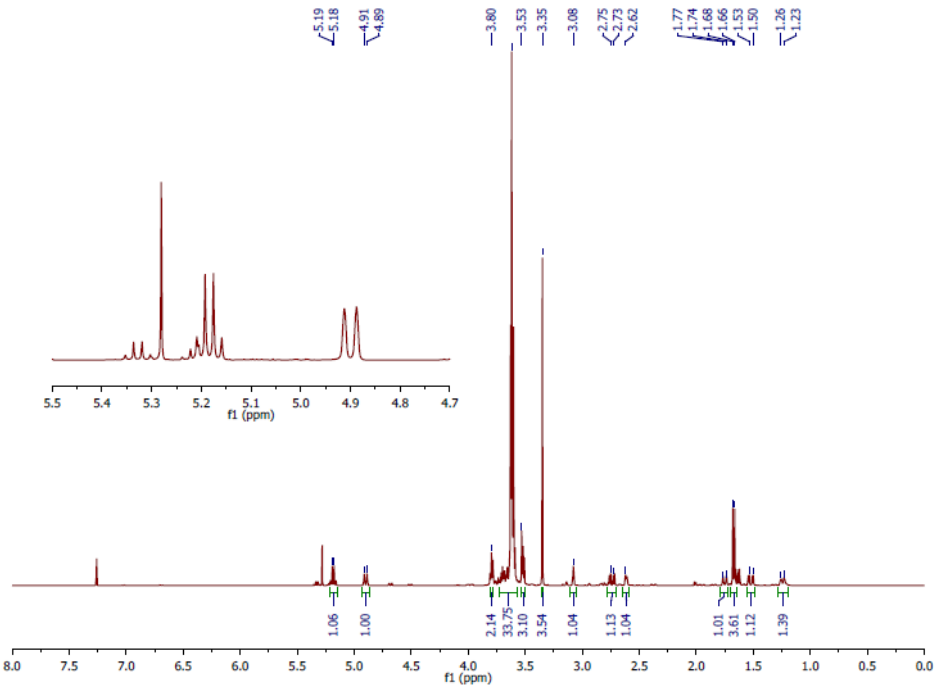
^{13}C-NMR spectrum PEG$_3$-spirolactide **4a** in $CDCl_3$



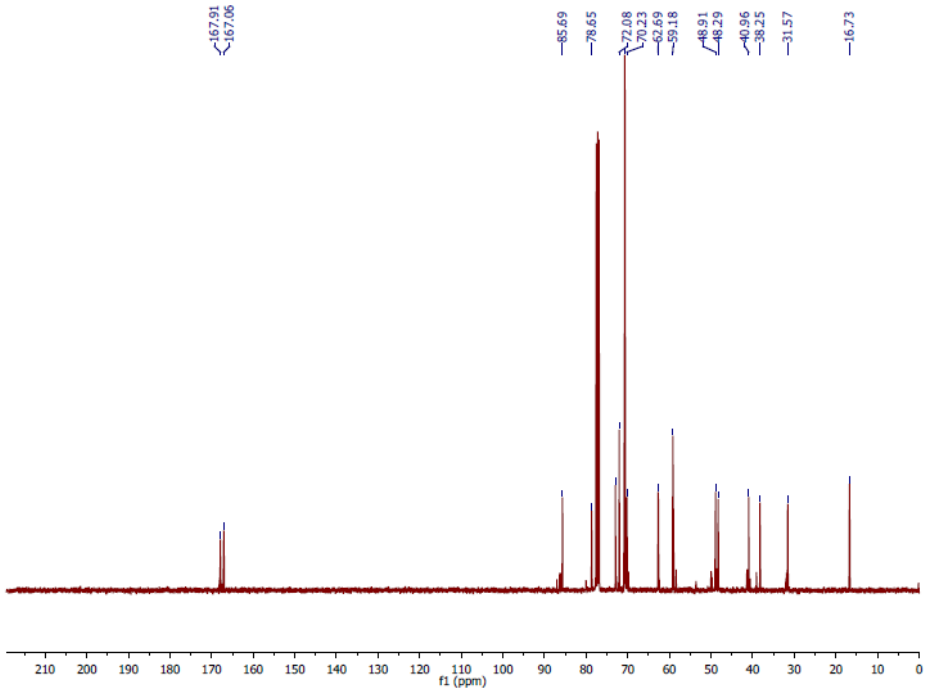
$^{1}H,^{1}H$-COSY spectrum of PEG_3-spirolactide **4a** in $CDCl_3$



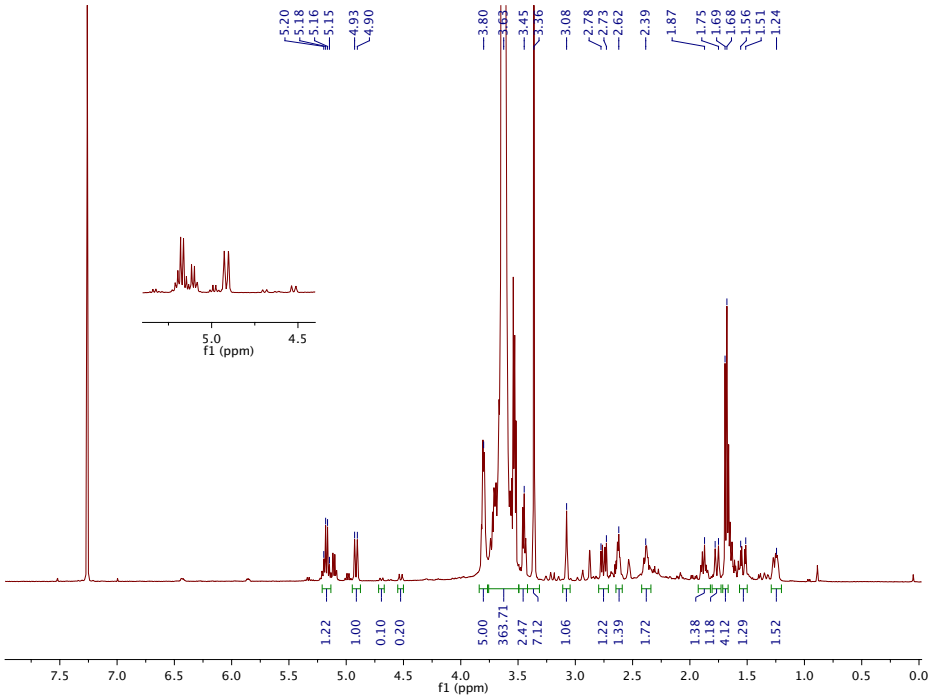
^{1}H-NMR spectrum of PEG$_7$-spirolactide **4b** in $CDCl_3$



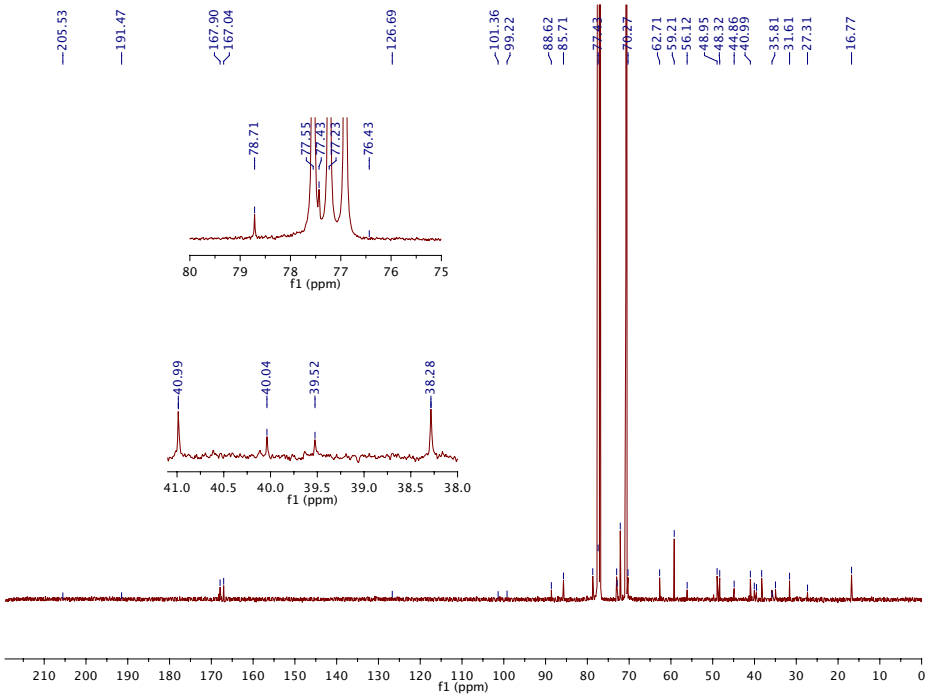
^{13}C-NMR spectrum of PEG$_7$-spirolactide **4b** in $CDCl_3$



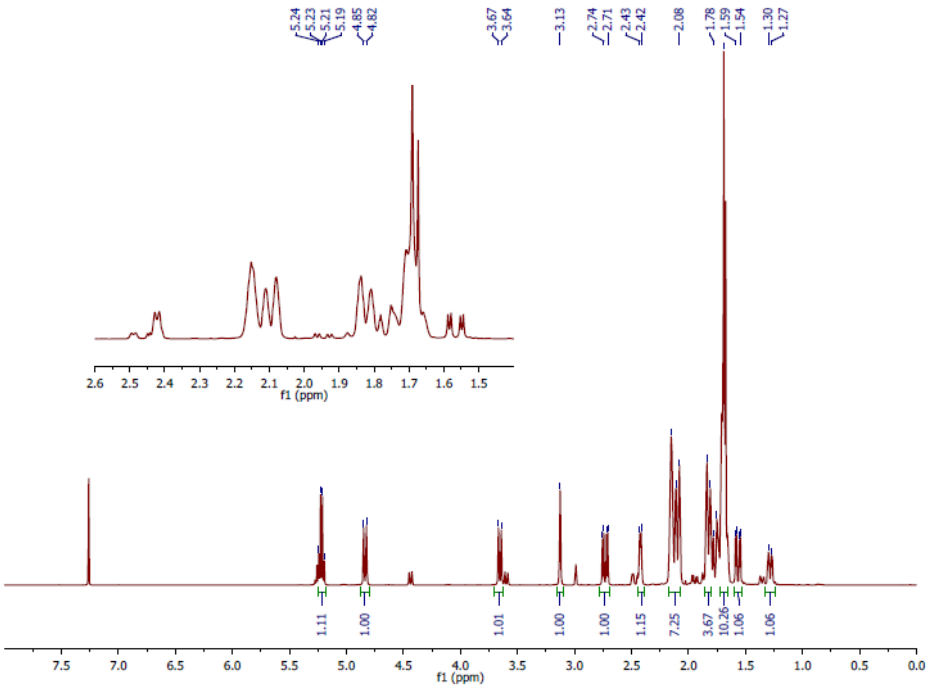
^{1}H-NMR spectrum of PEG_{40}-spirolactide **4c** in $CDCl_3$



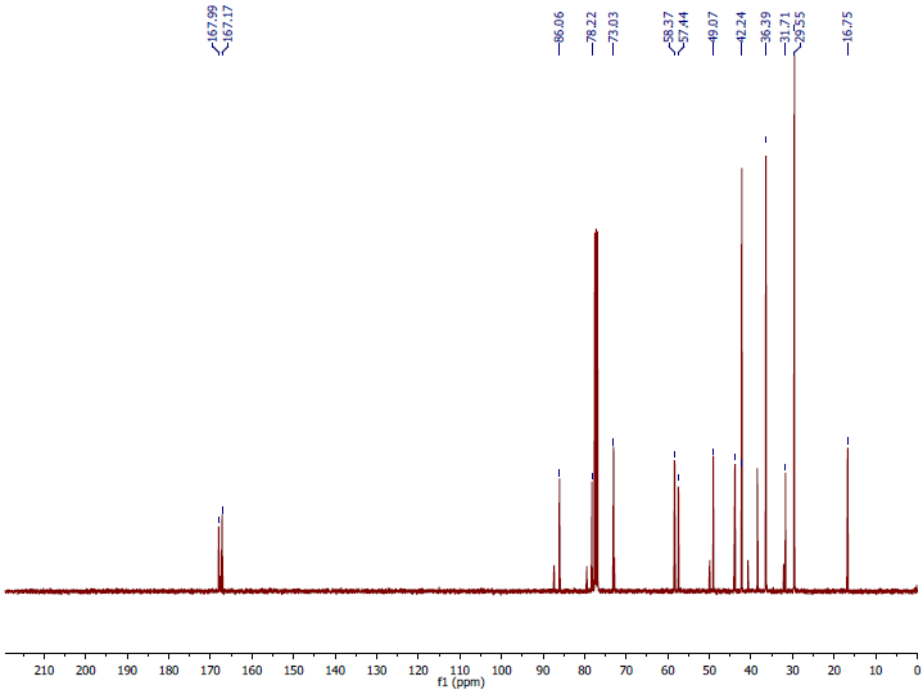
^{13}C-NMR spectrum of PEG_{40}-spirolactide **4c** in $CDCl_3$



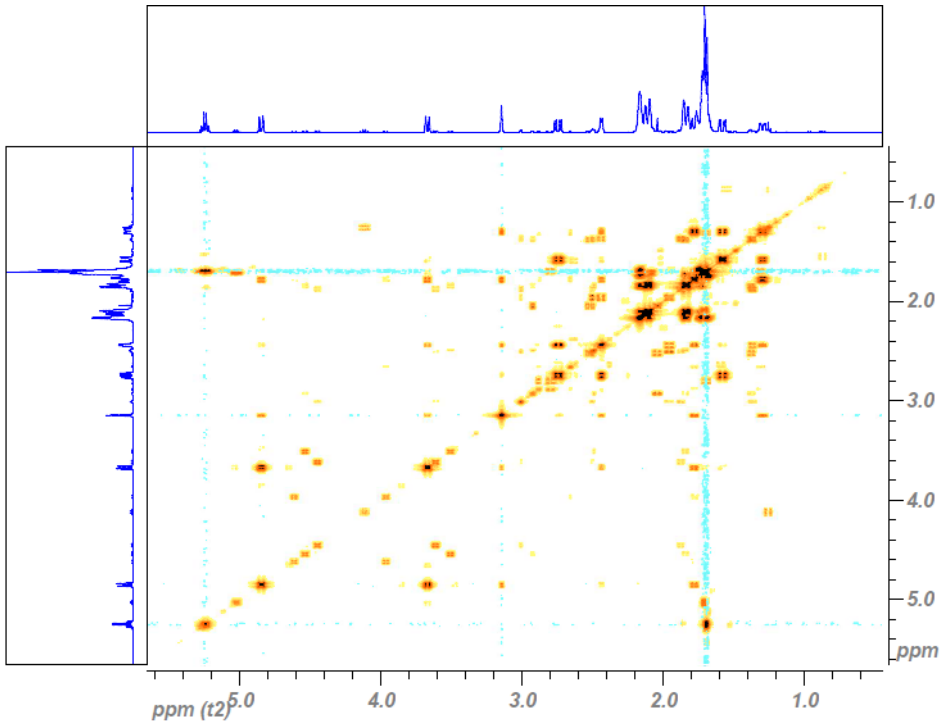
^{1}H-NMR spectrum of adamantyl-spirolactide **4d** in $CDCl_3$



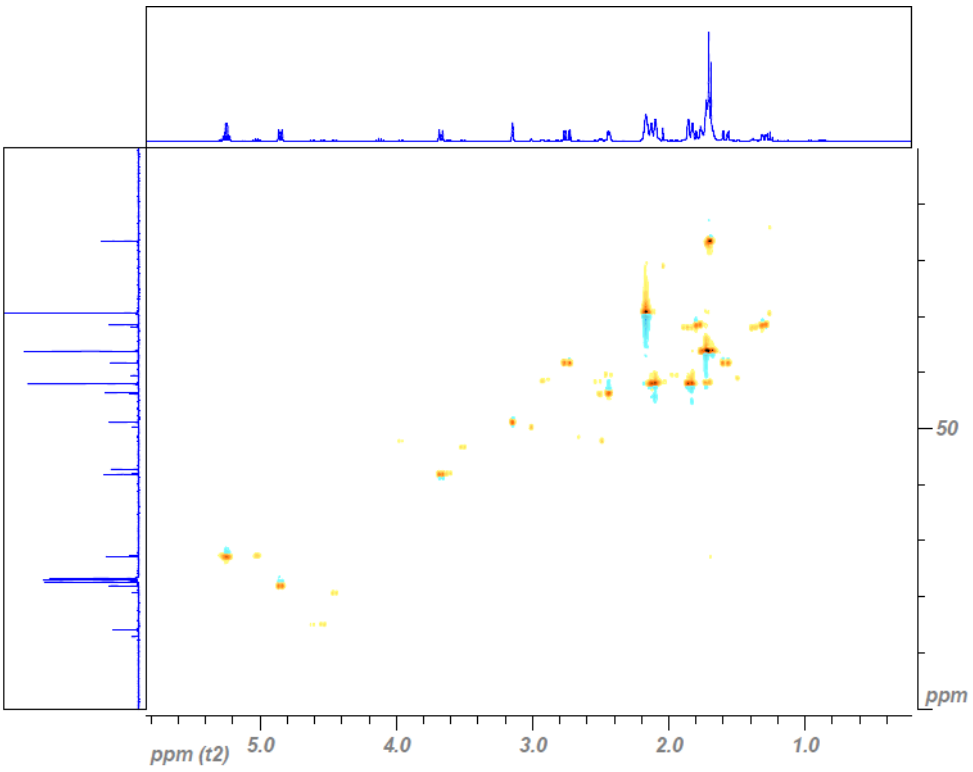
^{13}C-NMR spectrum of adamantyl-spirolactide **4d** in $CDCl_3$



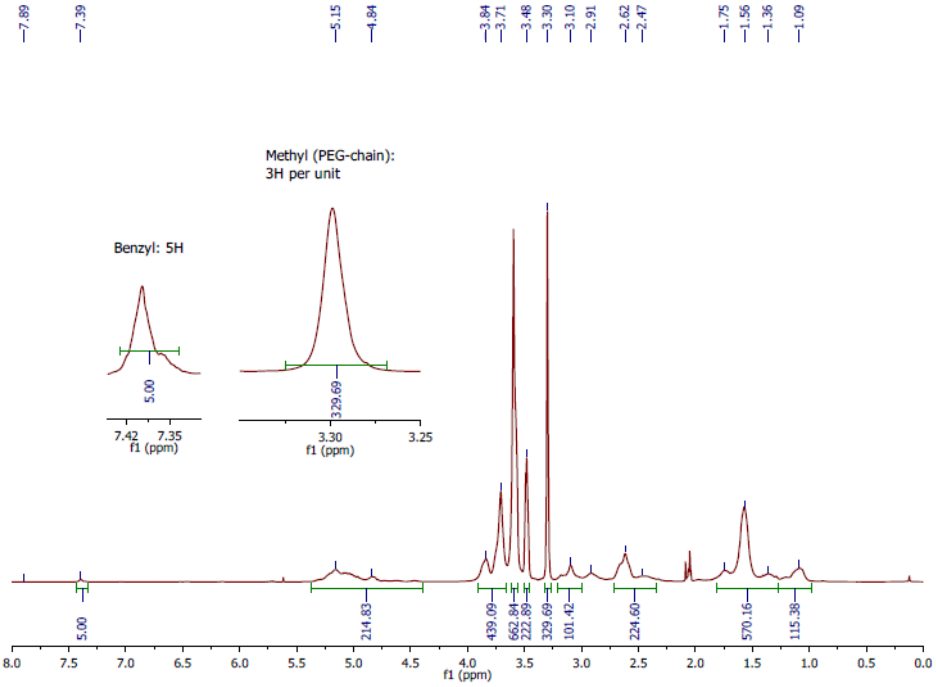
$^{1}H,^{1}H$-COSY spectrum of adamantyl-spirolactide **4d** in $CDCl_3$



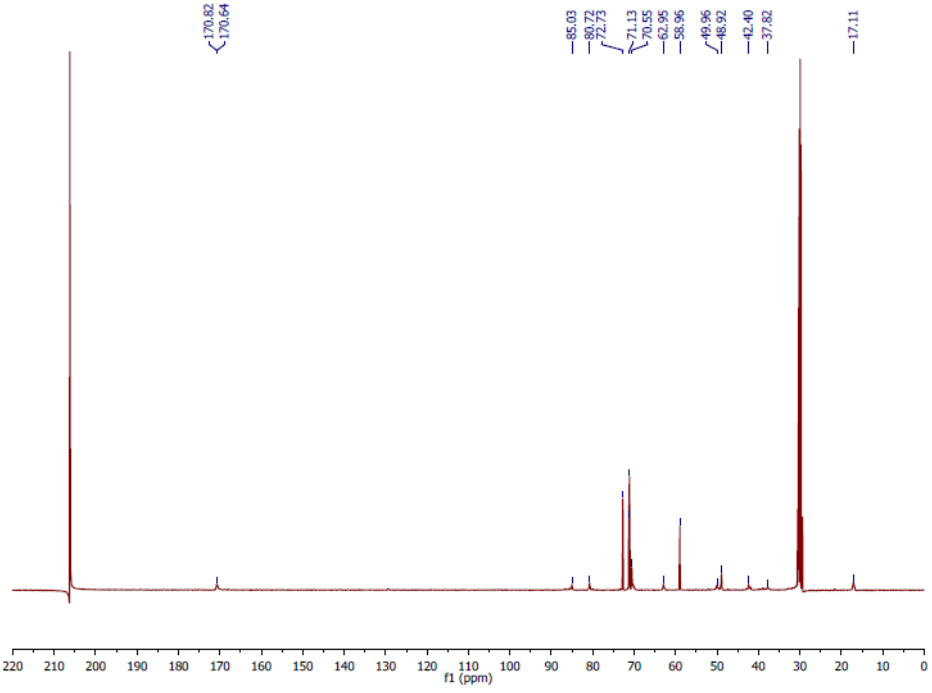
HSQC spectrum of adamantyl-spirolactide **4d** in $CDCl_3$



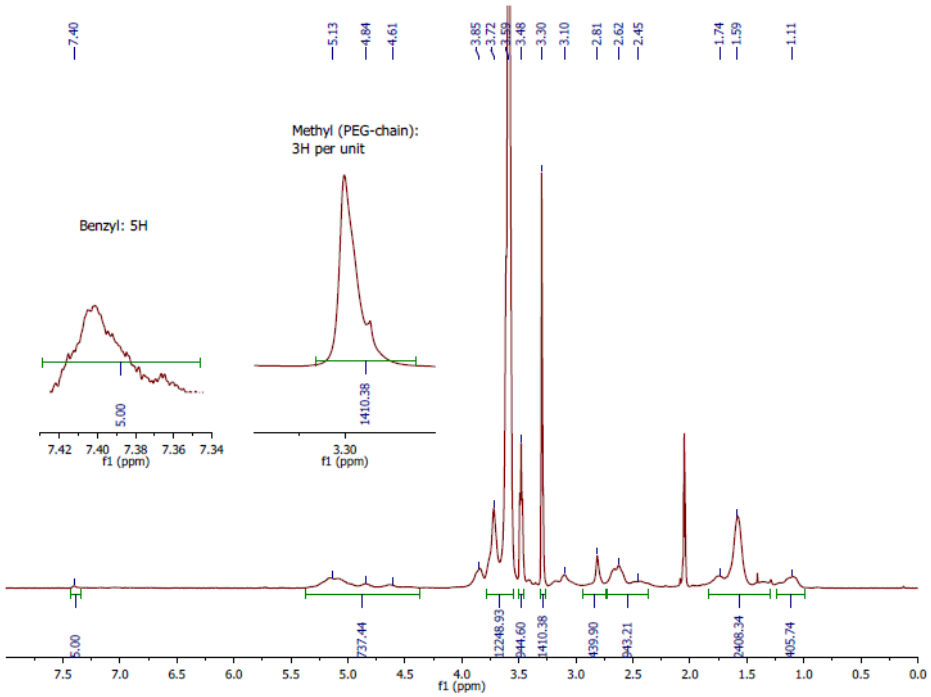
^{1}H-NMR spectrum of PEG$_3$-grafted PLA **5a** in acetone-D$_6$



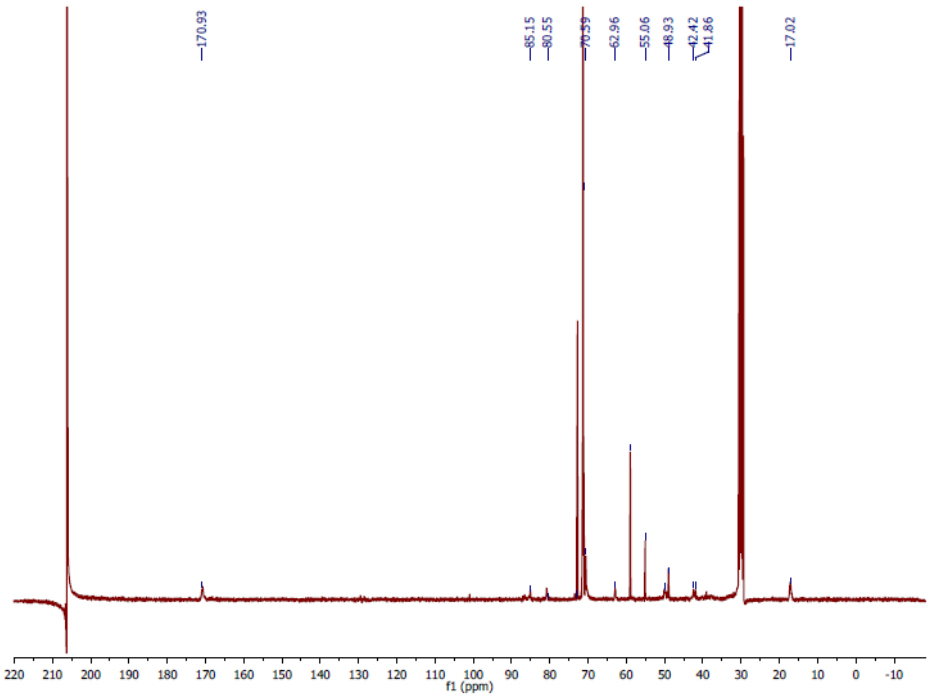
^{13}C-NMR spectrum PEG$_3$-grafted PLA **5a** in acetone-D$_6$



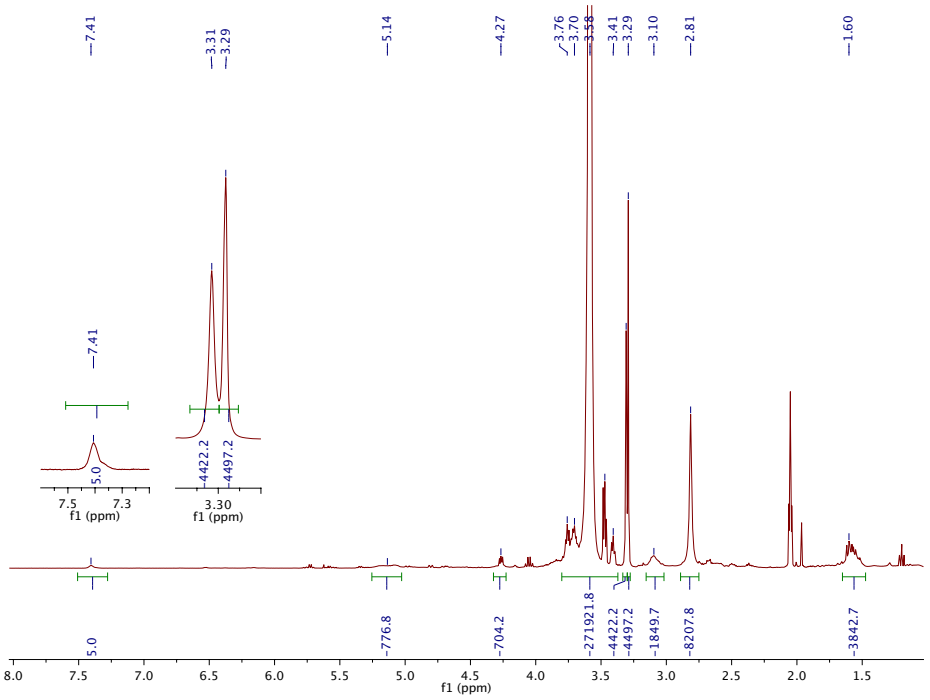
^{1}H-NMR spectrum of PEG$_7$-grafted PLA **5b** in acetone-D$_6$



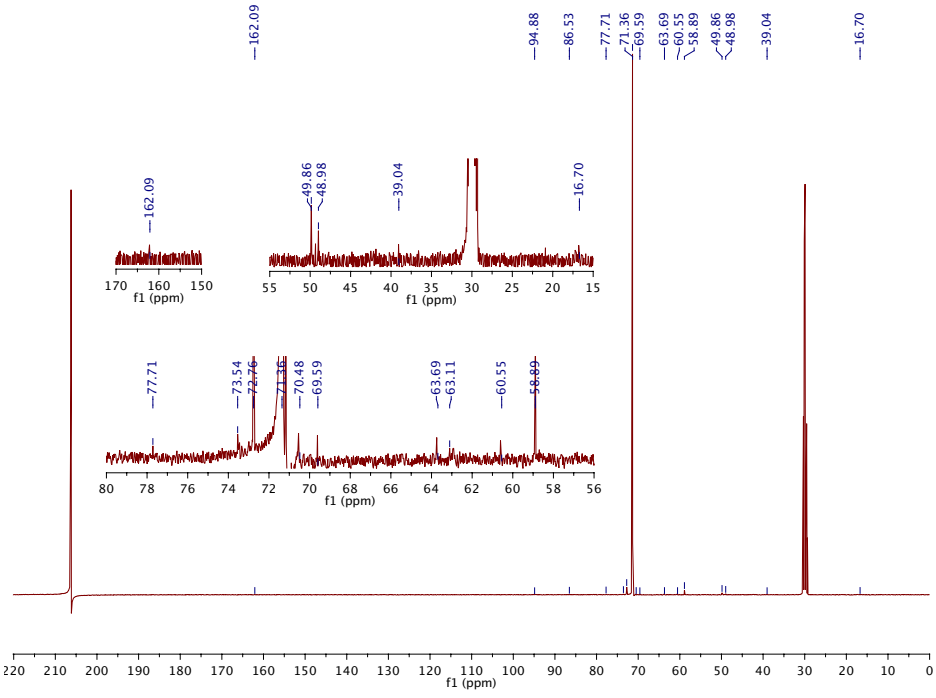
^{13}C-NMR spectrum of poly(PEG$_7$-PLA **5b** in acetone-D$_6$



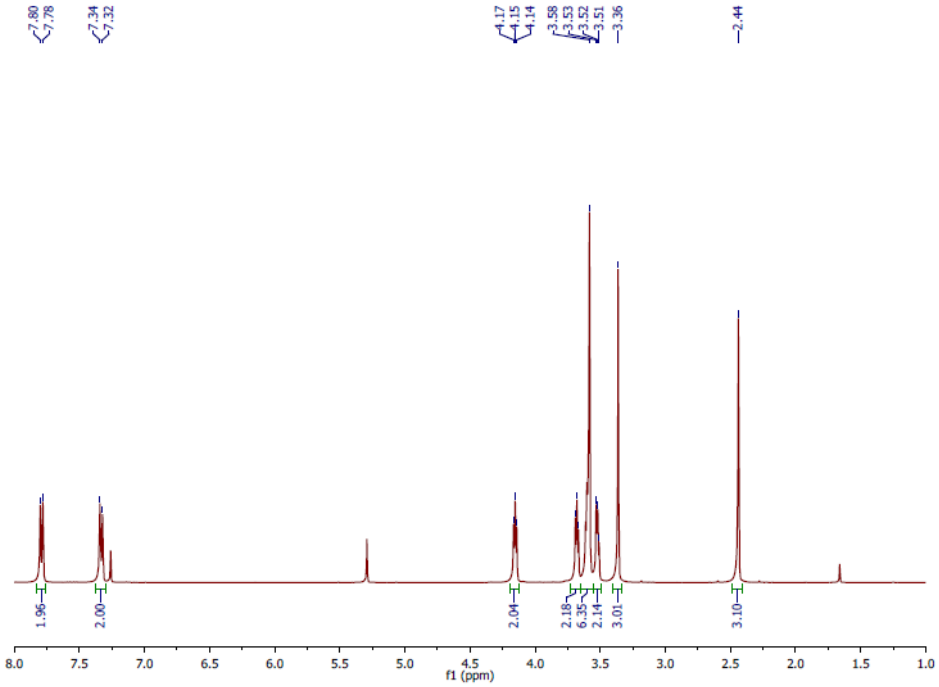
^{1}H-NMR spectrum of PEG$_{40}$-grafted PLA **5c** in acetone-D$_6$



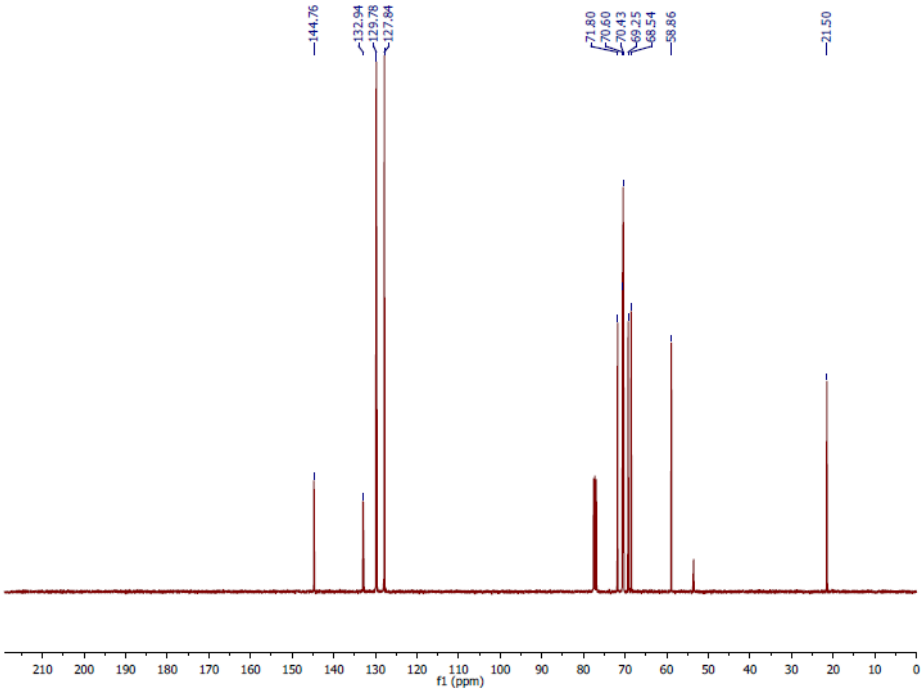
^{13}C-NMR spectrum of PEG$_{40}$-grafted PLA **5c** in acetone-D$_6$



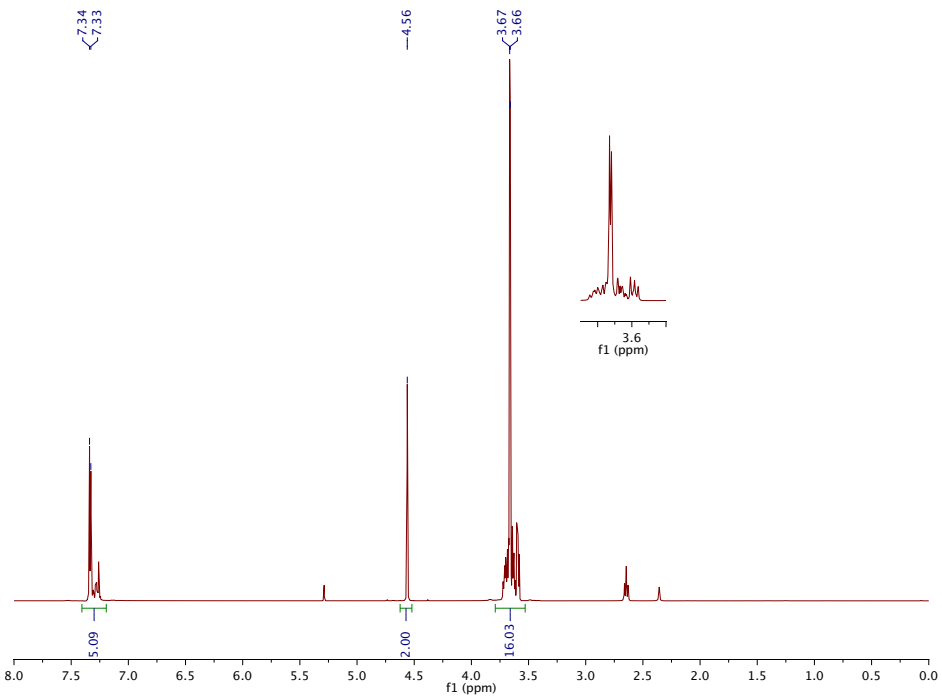
^{1}H-NMR spectrum of triethylene glycol methyl ether *p*-tosylate, PEG_3-Ts (**6**), in $CDCl_3$



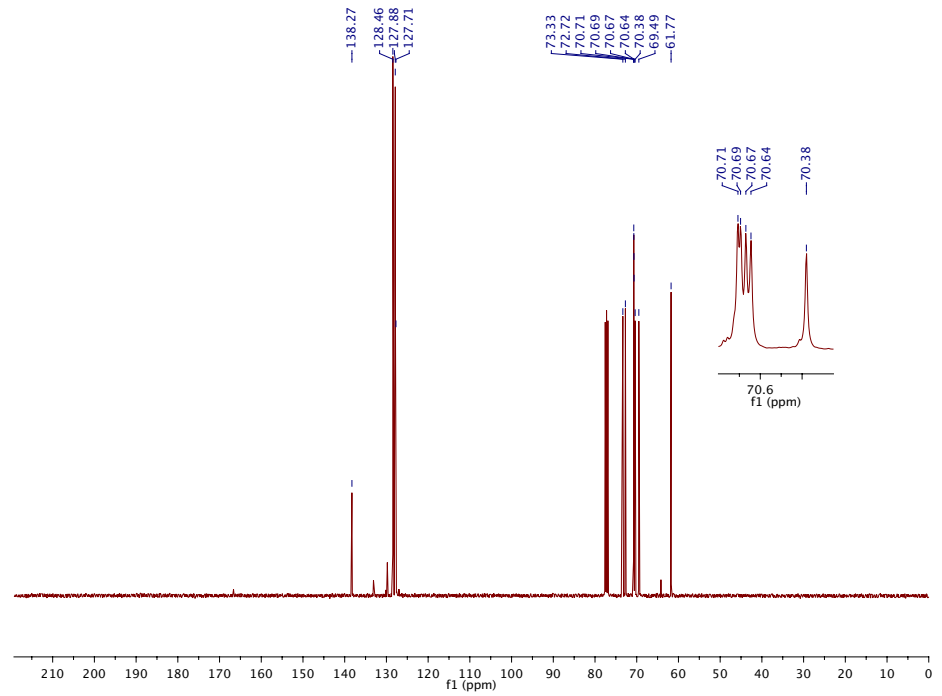
^{13}C-NMR spectrum of triethylene glycol methyl ether *p*-tosylate, PEG_3-Ts (**6**), in $CDCl_3$



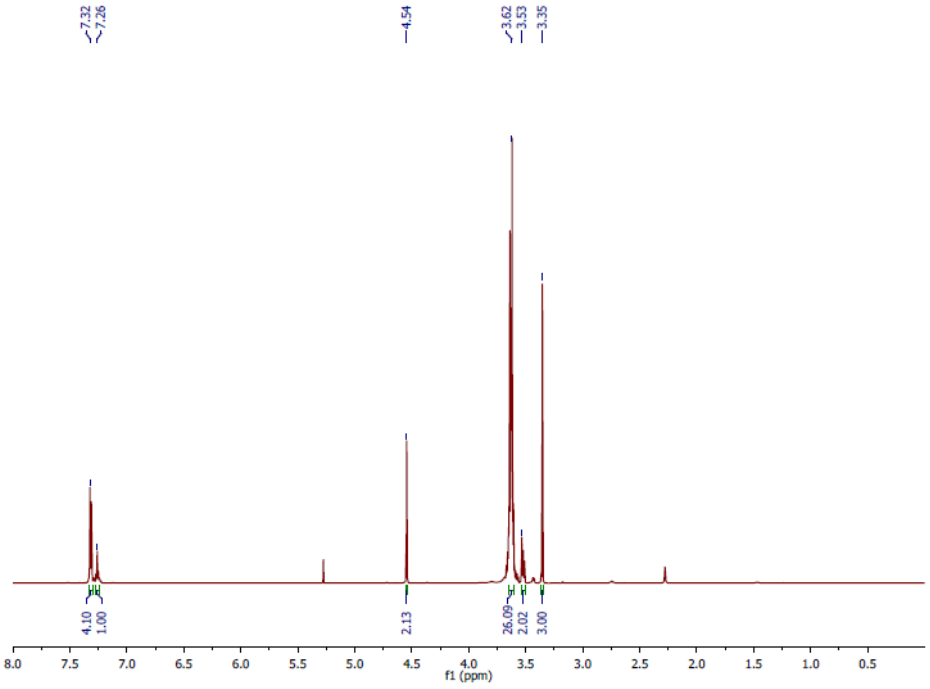
^{1}H-NMR spectrum of tetraethylene glycol benzyl ether, PEG_4-Bn (**7**), in $CDCl_3$



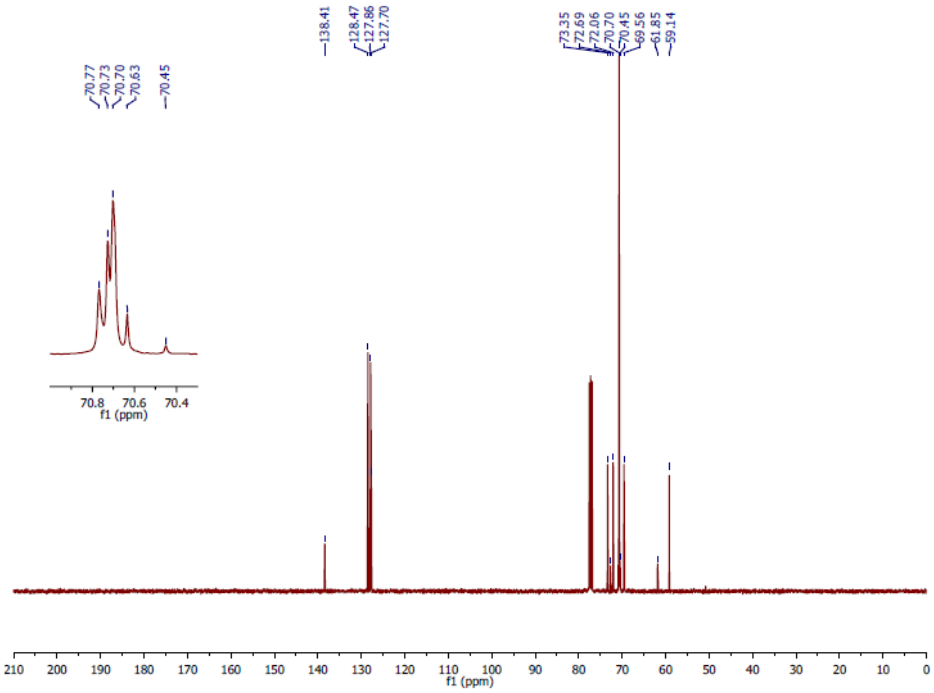
^{13}C-NMR spectrum tetraethylene glycol benzyl ether, PEG_4-Bn (**7**), in $CDCl_3$



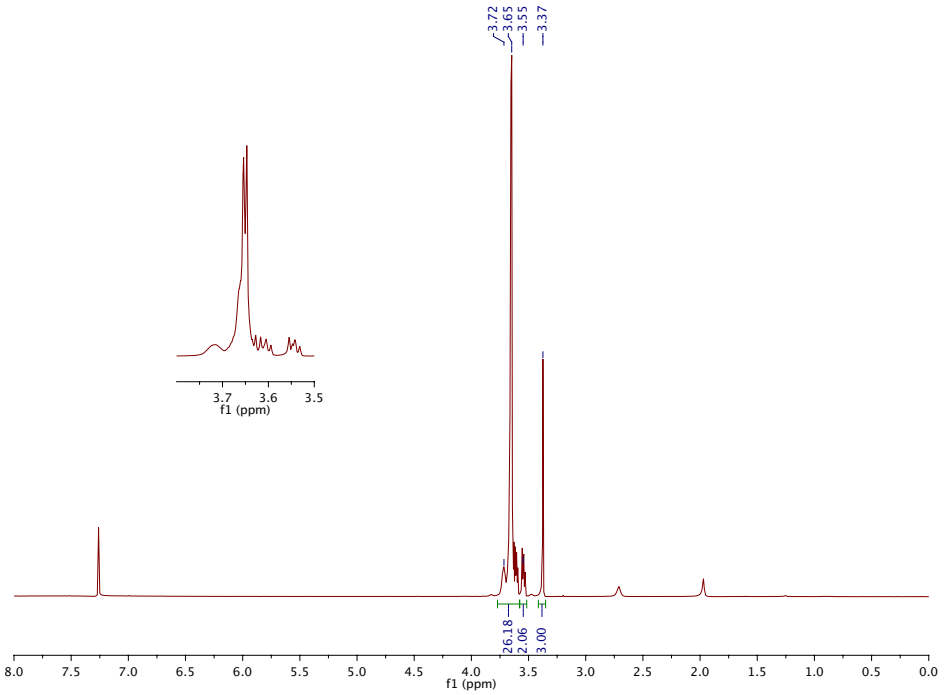
^{1}H-NMR spectrum of heptaethylene glycol benzyl methyl ether, PEG_7-Bn (**8**), in $CDCl_3$



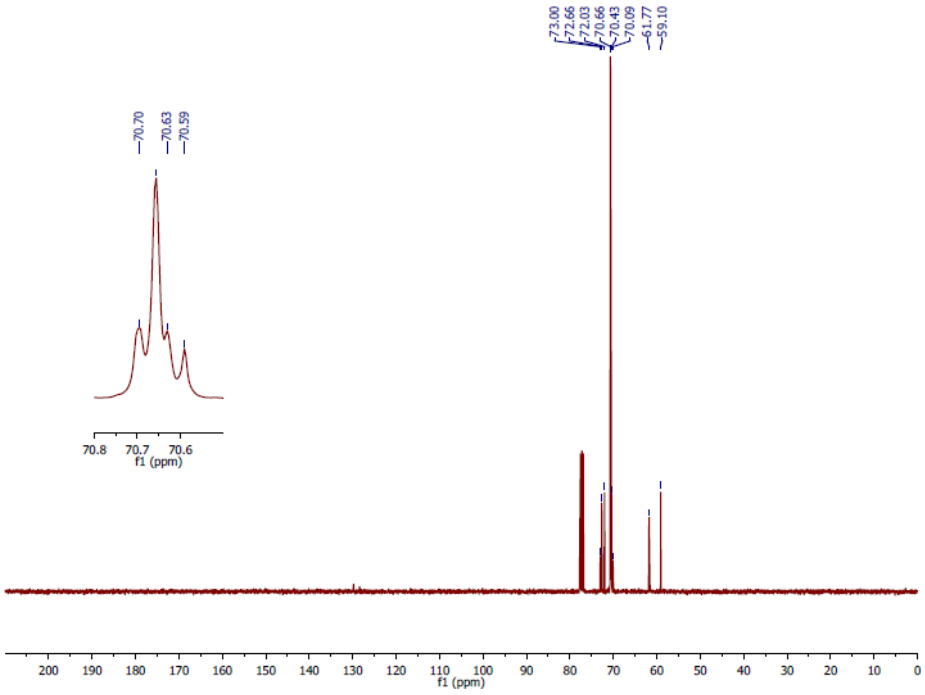
^{13}C-NMR spectrum of heptaethylene glycol benzyl methyl ether, PEG_7-Bn (**8**), in $CDCl_3$



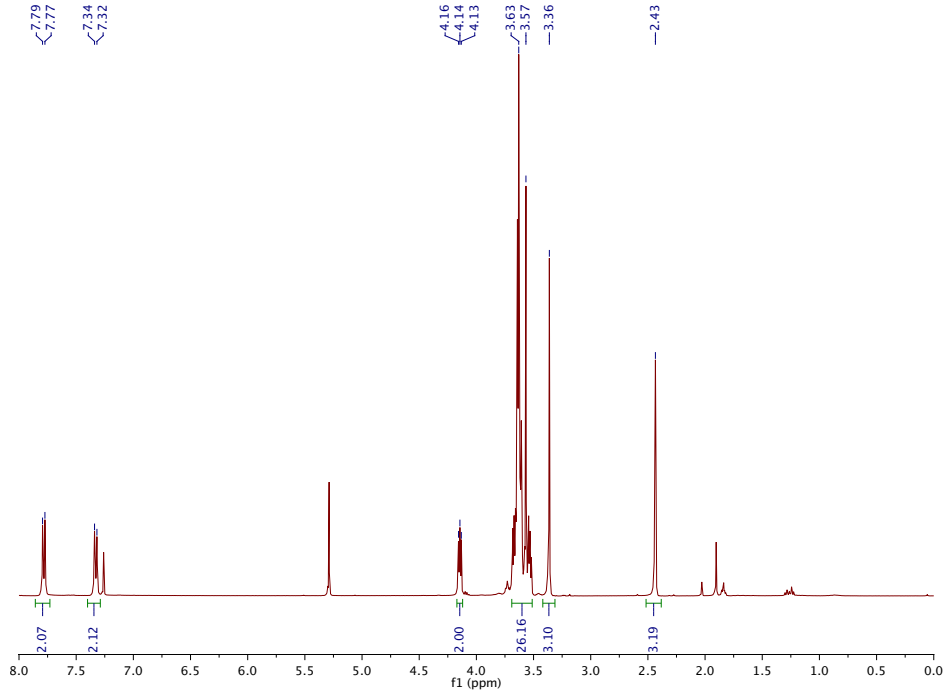
^{1}H-NMR spectrum of heptaethylene glycol methyl ether, PEG_7 (**9**), in $CDCl_3$



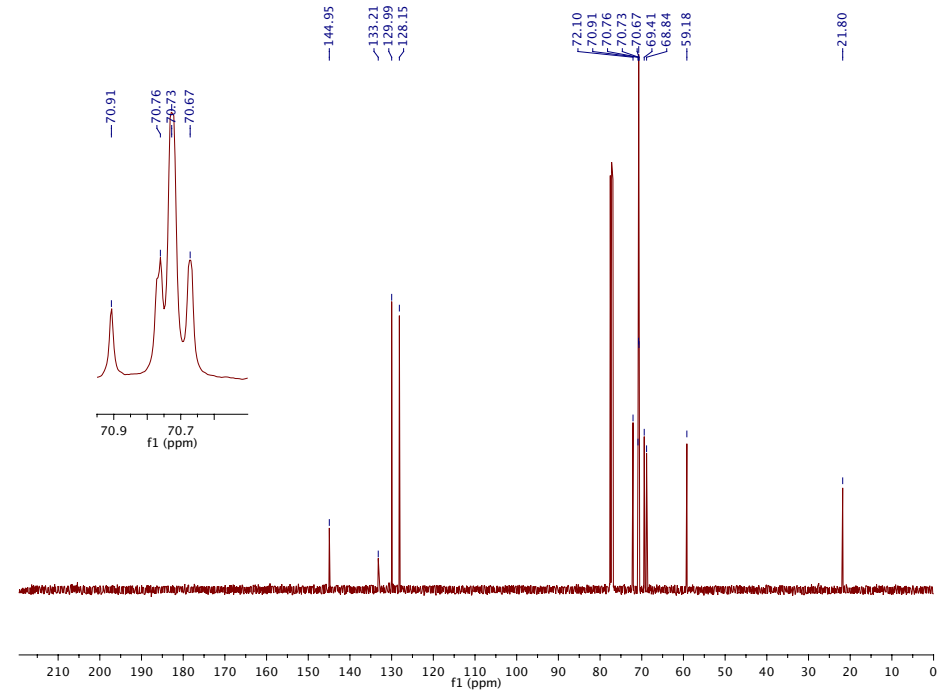
^{13}C-NMR spectrum of heptaethylene glycol methyl ether, PEG_7, (**9**) in $CDCl_3$



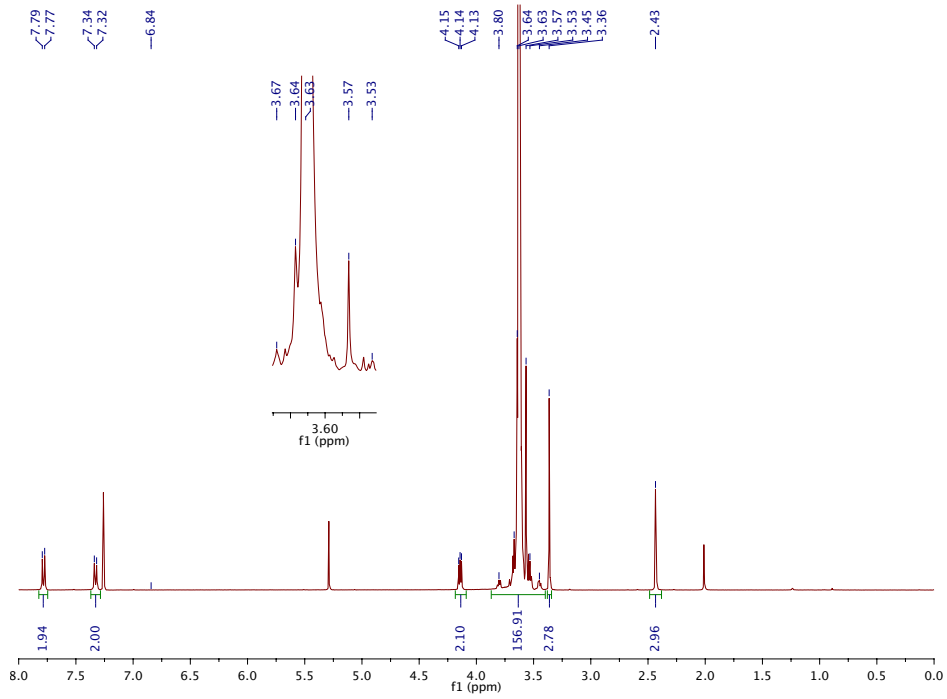
^{1}H-NMR spectrum of heptaethylene glycol methyl ether *p*-tosylate, PEG_7-Ts (**10**), in $CDCl_3$



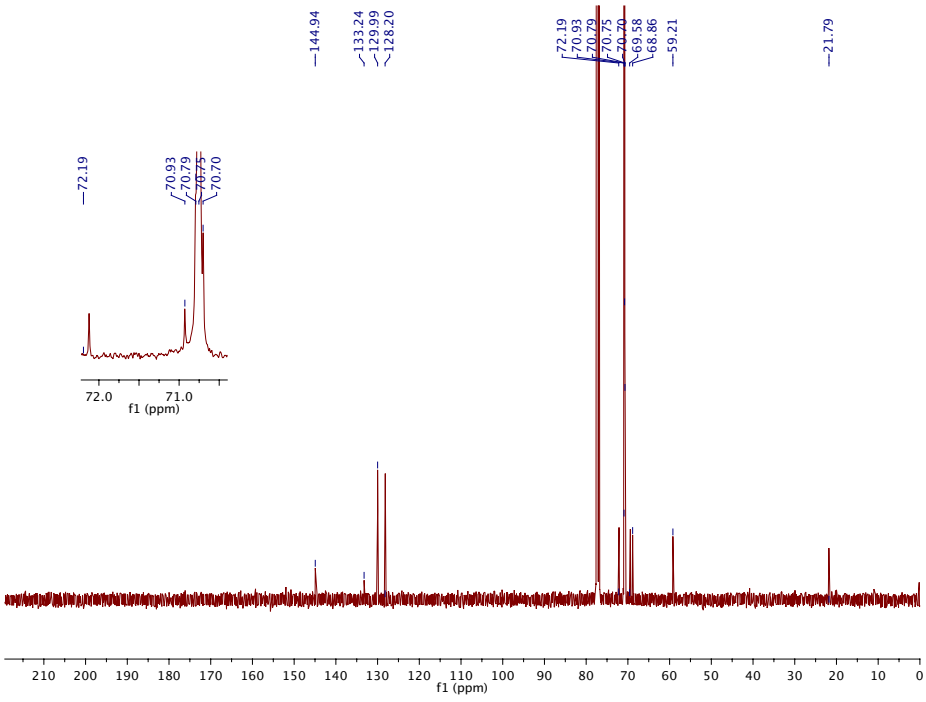
^{13}C-NMR spectrum of heptaethylene glycol methyl ether *p*-tosylate, PEG_7-Ts, (**10**) in $CDCl_3$



^{1}H-NMR spectrum of polyethylene glycol methyl ether *p*-tosylate (Mw~2000), PEG_{41}-Ts (**11**) in $CDCl_3$

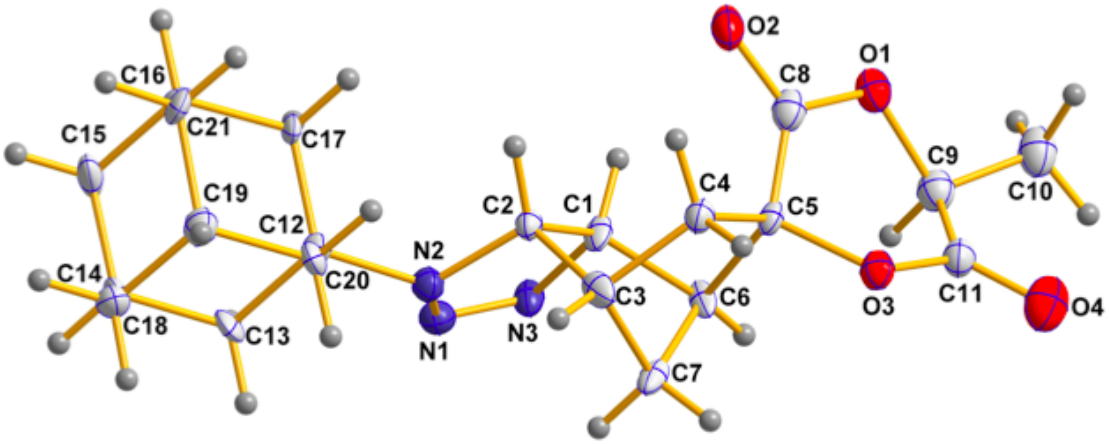


^{13}C-NMR spectrum of polyethylene glycol methyl ether *p*-tosylate (Mw~2000), PEG_{41}-Ts (**11**), in $CDCl_3$

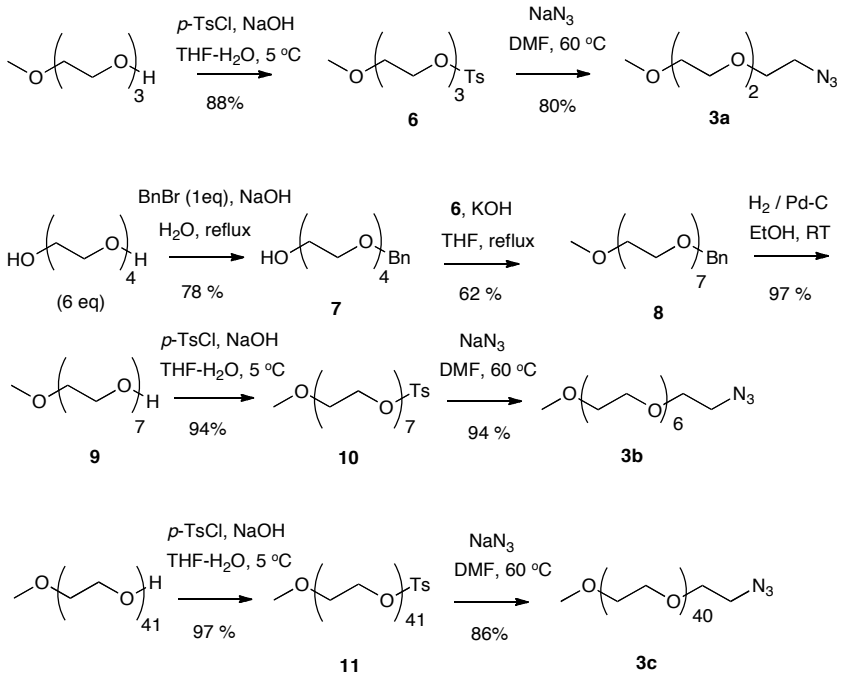


X-ray analysis

Crystal structure of the second isomer of azidomantane-spirolactide **4d**

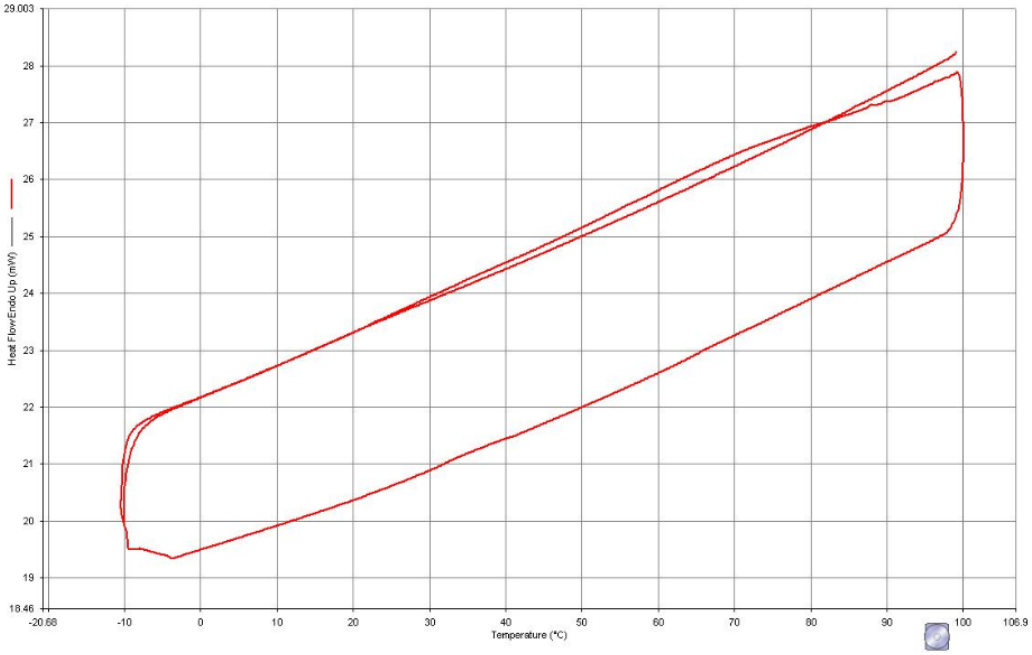


Scheme S1. Synthetic approach to PEG_n-azides **3a**, **3b**, and **3c**.

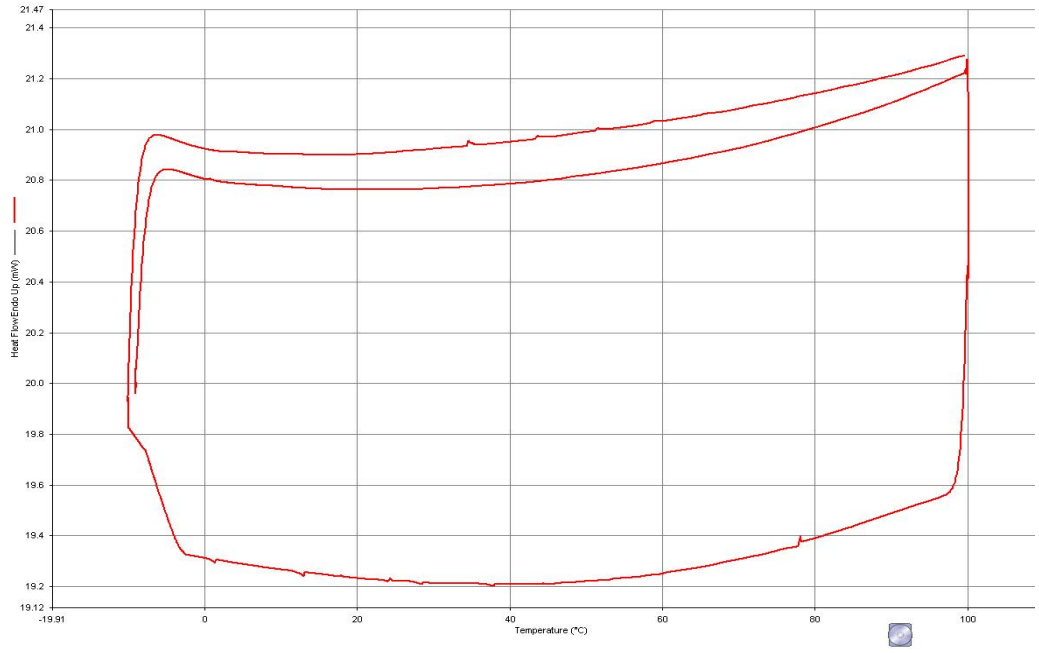


DSC measurements

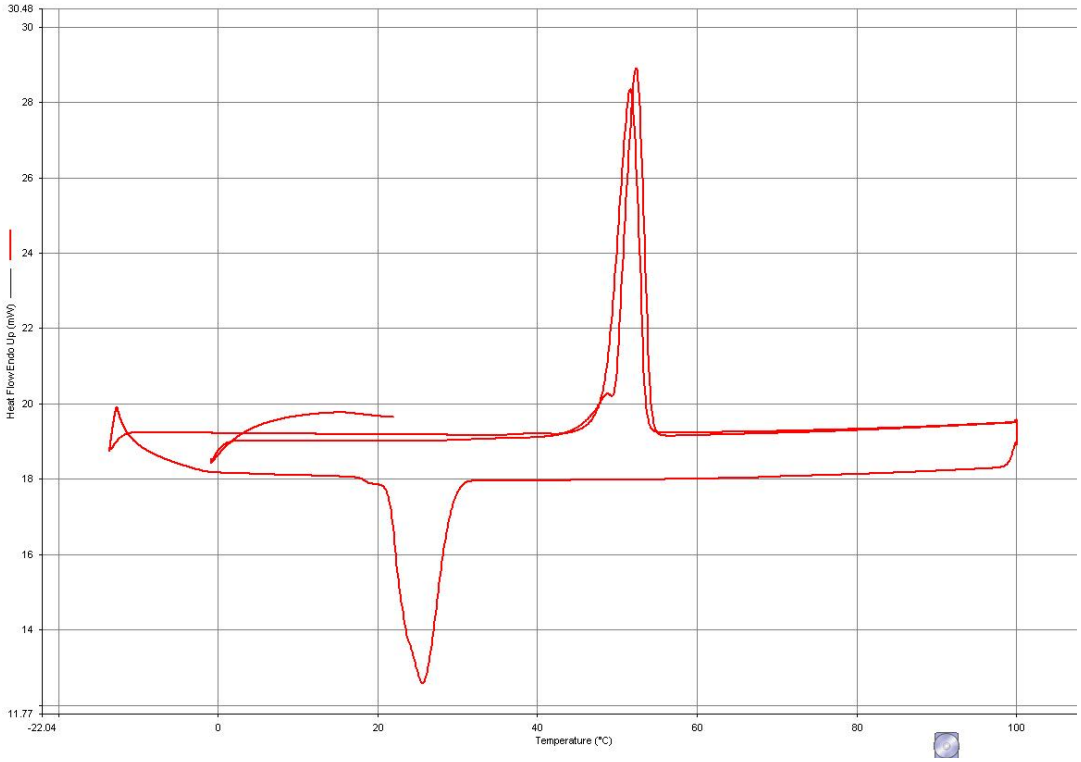
DSC curve of PEG_3-PLA (**5a**)



DSC curve of PEG_7-PLA (**5b**)



DSC curve of PEG_{40}-PLA (**5c**)

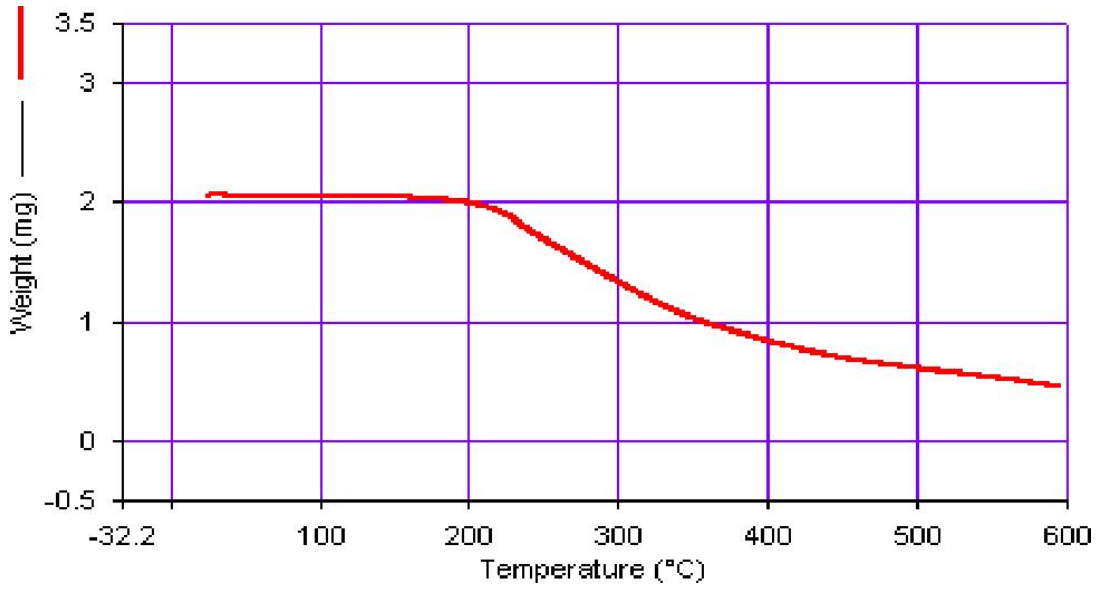


Thermogravimetric analysis (TGA)

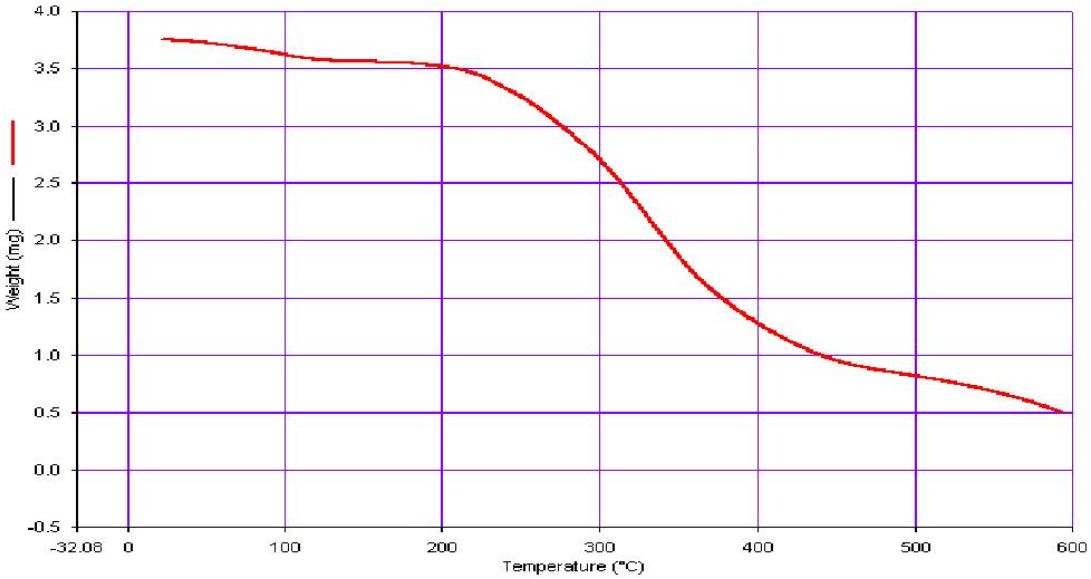
Table S1

Polymer	Decomposition temperature (°C)
PEG_3-PLA	T_o 215
5a	T_f 325
PEG_7-PLA	T_o 285
5b	T_f 386
PEG_{40}-PLA	T_o 332
5c	T_f 398

TGA of PEG_3-PLA (**5a**)



TGA of PEG_7-PLA (**5b**)



TGA of PEG_{40}-PLA (**5c**)