Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Enhancement of metallo-supramolecular dissociation kinetics in telechelic terpyridine-capped poly(ethylene glycol) assemblies in the semi-dilute regime

Electronic Supplementary Information

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Chemicals:

Compound	CAS number	Supplier	Purity
pEG-4K pEG-6K pEG-8K pEG-10K pEG-12K	25322-68-3	Sigma Aldrich	not provided[1]
Sodium hydride (60% in mineral oil)	7646-69-7	Sigma Aldrich	60%
Epichlorohydrin	106-89-8	Acros Organics	99%
Sodium azide	26628-22-8	Sigma Aldrich	99%
Ammonium chloride	12125-02-9	Acros Organics	99.5%
Potassium carbonate	584-08-7	Acros Organics	≥ 99%
2,6-Bis(2-pyridyl)-4(1*H*)-pyridone	128143-88-4	TCI Chemicals	> 98%
Propargyl bromide (80 wt% in toluene)	106-96-7	Acros Organics	79–87% (propargyl bromide) 13–27% (toluene)
Diaminoethane	107-15-3	Sigma Aldrich	≥ 99%
Di-*tert*-butyl dicarbonate	24424-99-5	Sigma Aldrich	≥ 98%
Dimethyl maleic anhydride	766-39-2	Alfa Aesar	≥ 97%
Trifluoroacetic acid	76-05-1	Alfa Aesar	99 %
4-Nitrophenyl chloroformate	7693-46-1	Alfa Aesar	97%

[1]: Purity information is not provided by the manufacturer. According to the specification sheet, all pEG compounds contain ≤ 1% of water and ≤ 0.2% of sulphated ash. An IR spectrum confirms the chemical structure. Coloured impurities were quantified via UV spectroscopy at $\lambda = 260$ nm (absorption ≤ 0.1) and $\lambda = 280$ nm (absorption ≤ 0.04).

Alternative Figure 4:

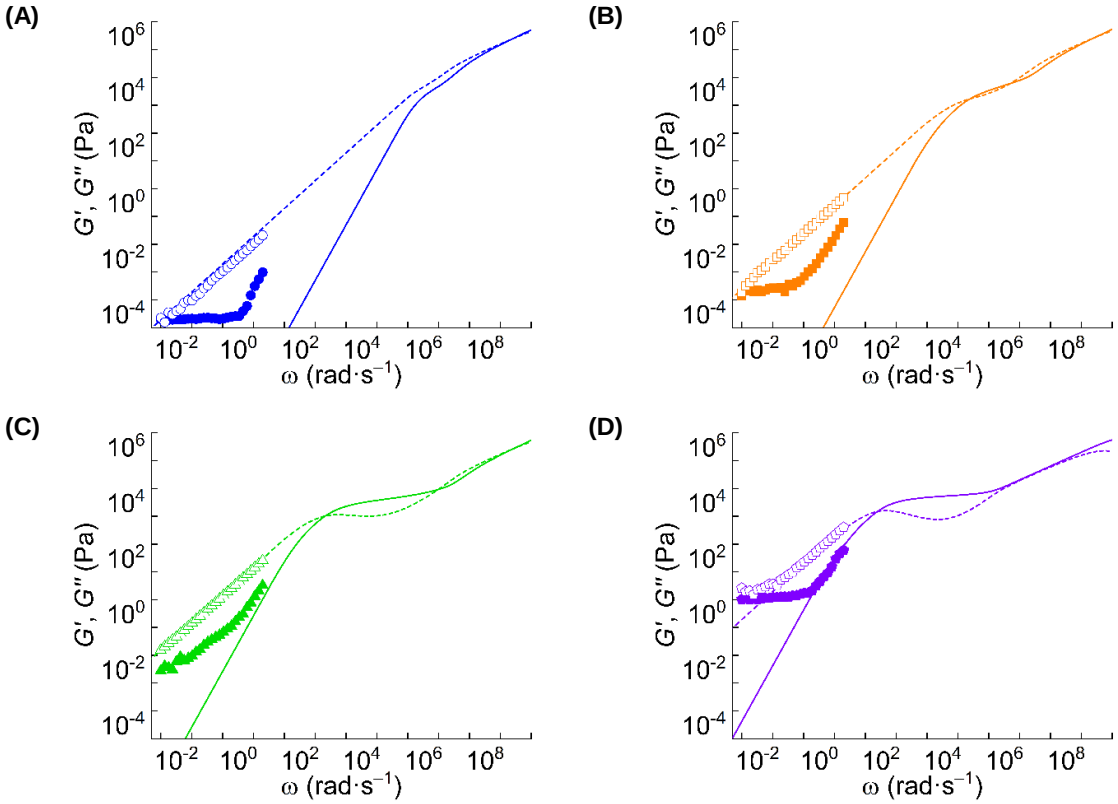

Figure 1. Alternative representation of the frequency-dependent storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, of semi-dilute solutions of pEG-*β*-hydroxy-*α*-terpyridine precursor chains (blue symbols/lines), the metallo-supramolecular chain-extended compound with Zn^{2+} ions (orange symbols/lines), representative of a weak transient bond, and Ni^{2+} ions (green symbols/lines), representative of a strong transient bond, as the linking agent, as well as the covalently chain-extended compound (purple symbols/lines). The precursor chains have a molar mass of M_w = 6 kg·mol^{-1} and were probed at 5x their overlap-concentration $5 \cdot c^* = 200$ g·L^{-1} in an isochoric mixture of chloroform and methanol. The experimentally determined storage moduli $G'(\omega)$ are denoted by full symbols, the loss moduli $G''(\omega)$ are denoted by open symbols, whereas values calculated by the TMA model are denoted by solid lines for the storage moduli $G'(\omega)$ and dashed lines for the loss moduli $G''(\omega)$.

^{1}H-NMR Spectra:

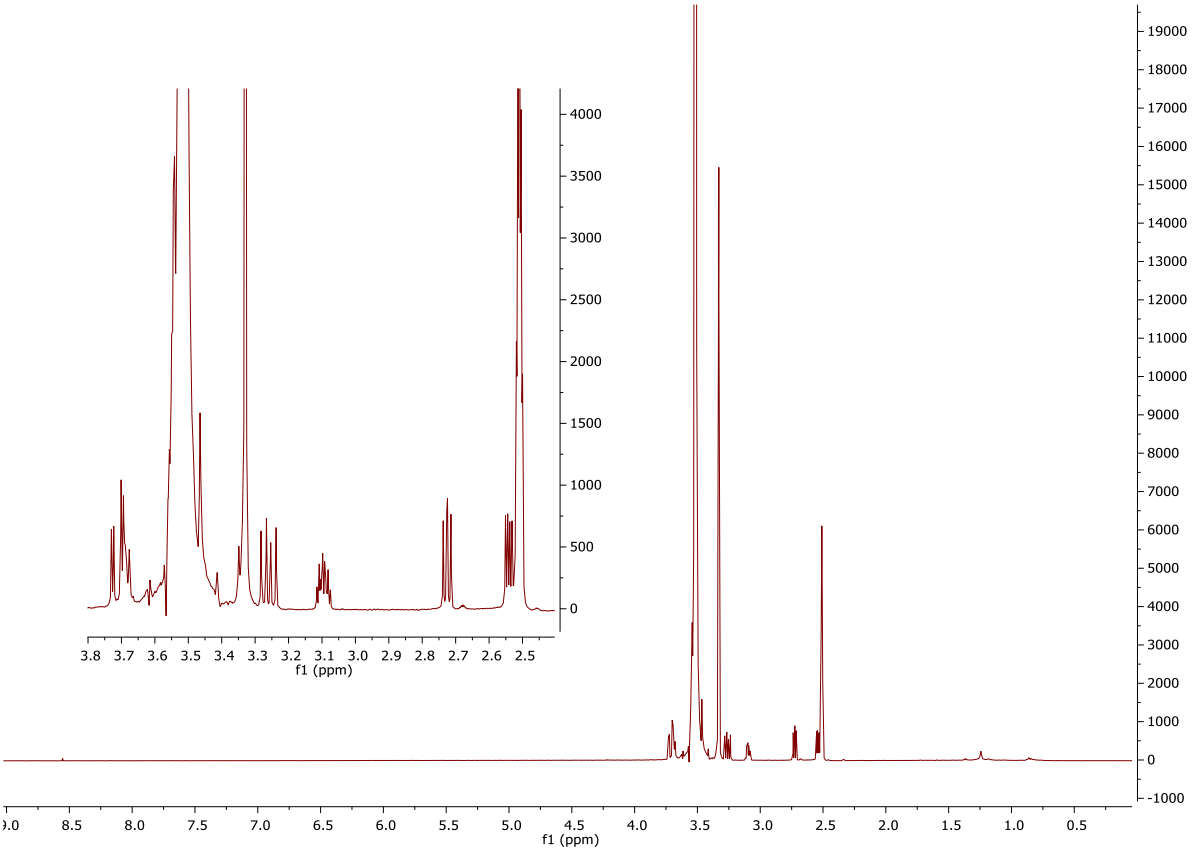

Figure 2. Full ^{1}H-NMR spectrum of pEG-epoxide, 4000 g·mol^{-1}. The solvent is DMSO-d_6.

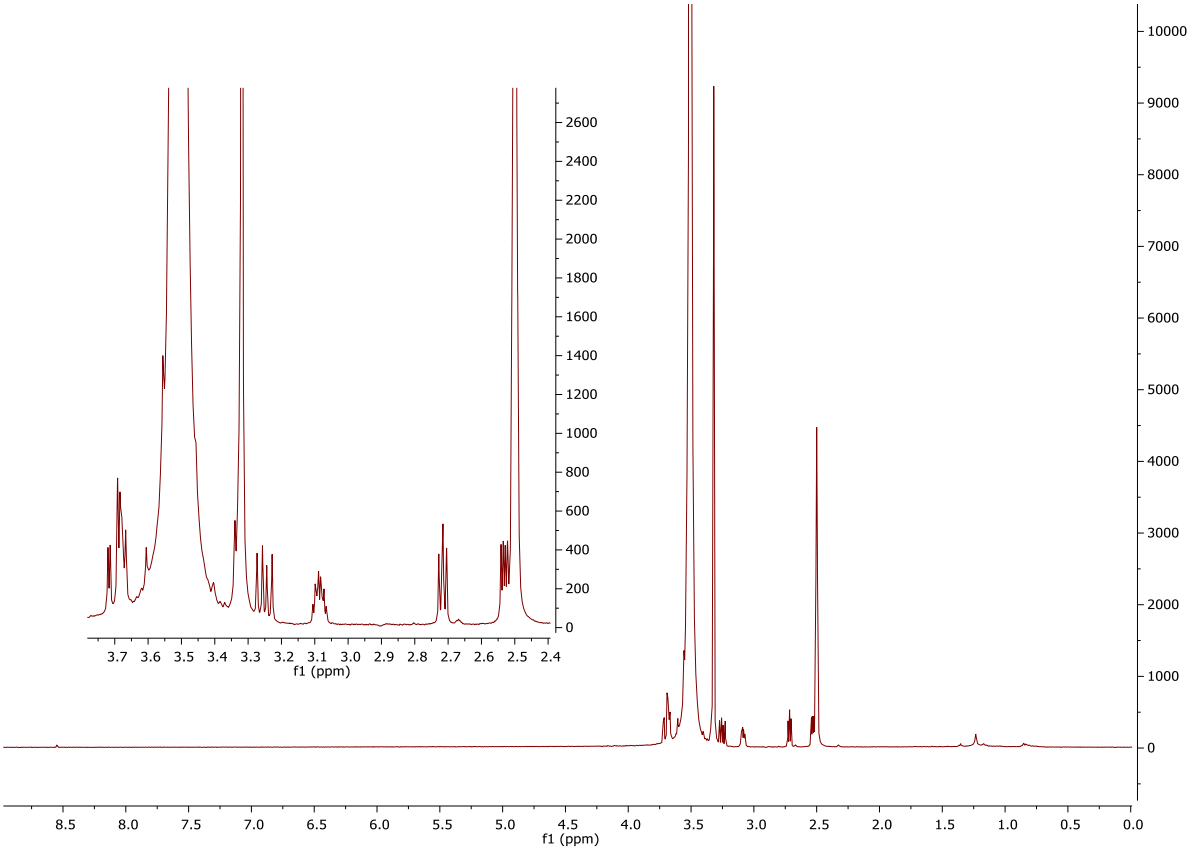

Figure 3. Full ^{1}H-NMR spectrum of pEG-epoxide, 6000 g·mol^{-1}. The solvent is DMSO-d_6.

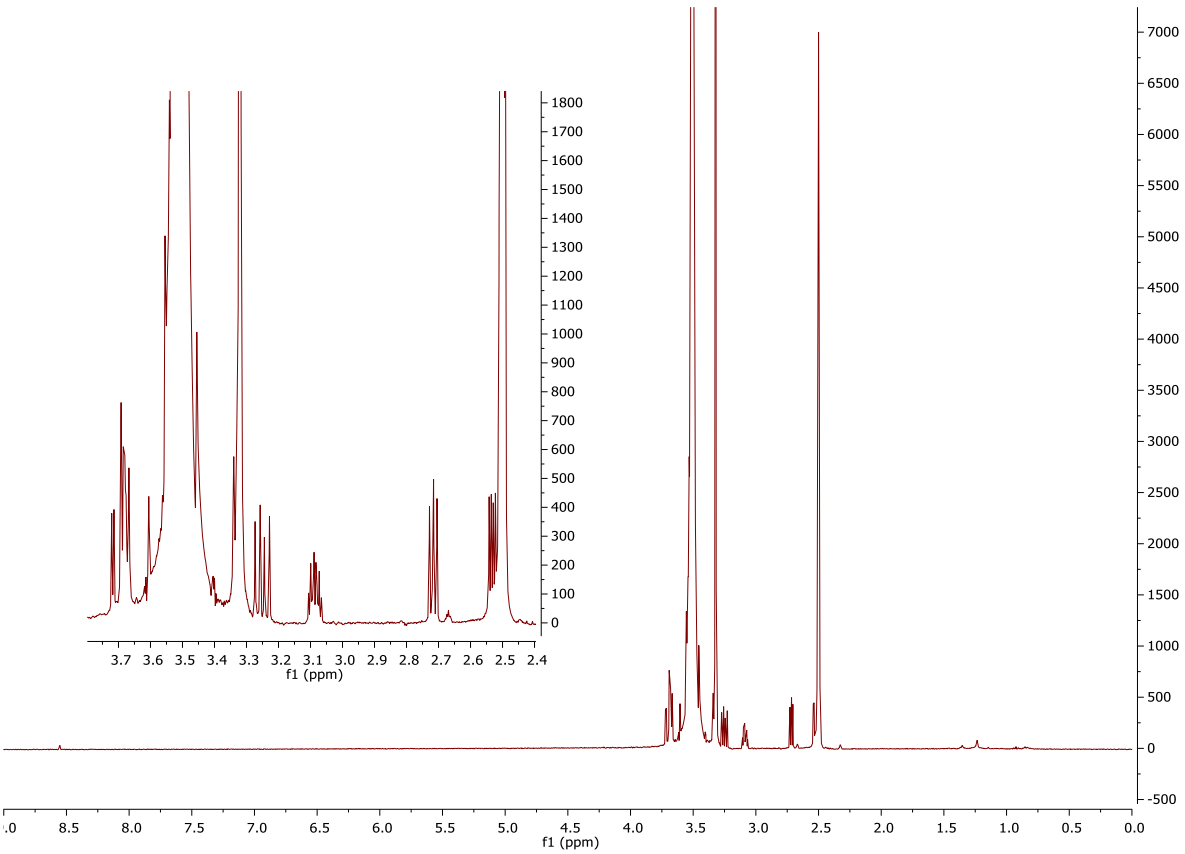

Figure 4. Full ^{1}H-NMR spectrum of pEG-epoxide, 6000 g·mol^{-1}. The solvent is DMSO-d_6.

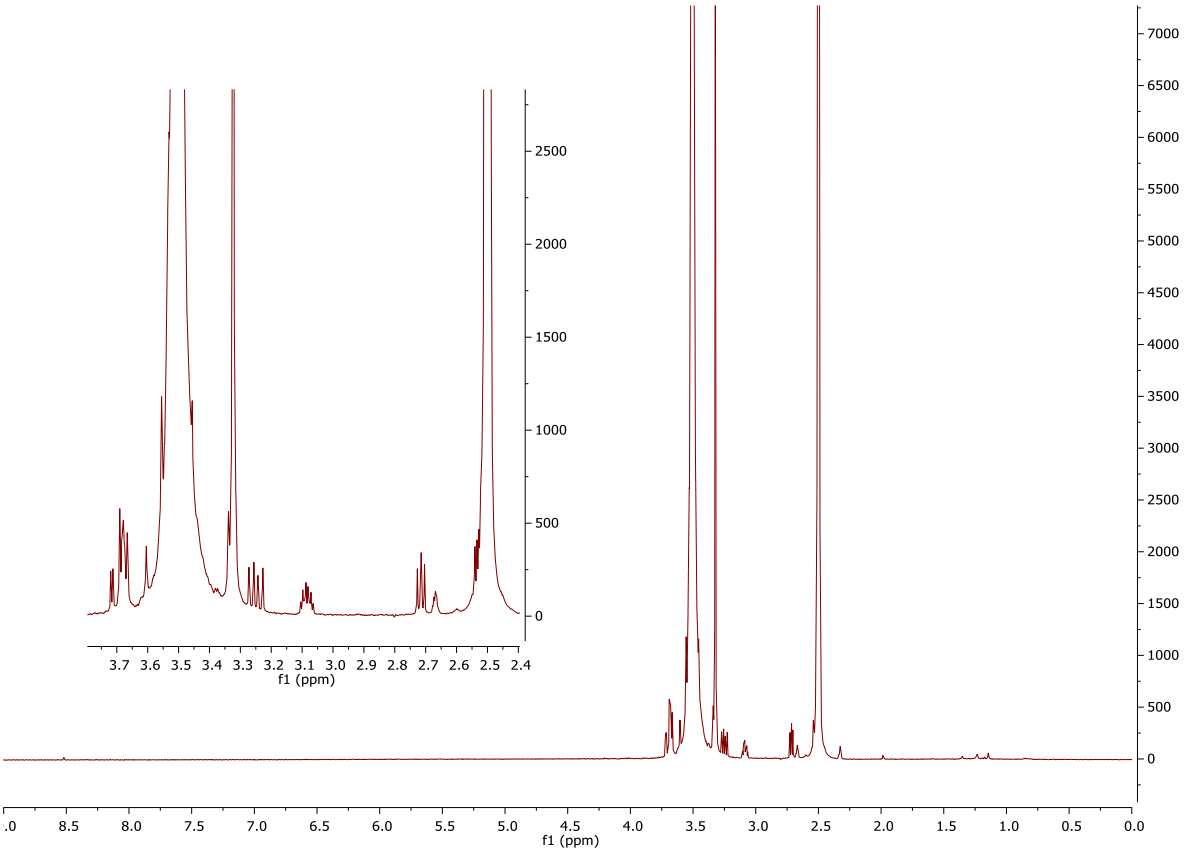

Figure 5. Full ^{1}H-NMR spectrum of pEG-epoxide, 10000 g·mol^{-1}. The solvent is DMSO-d_6.

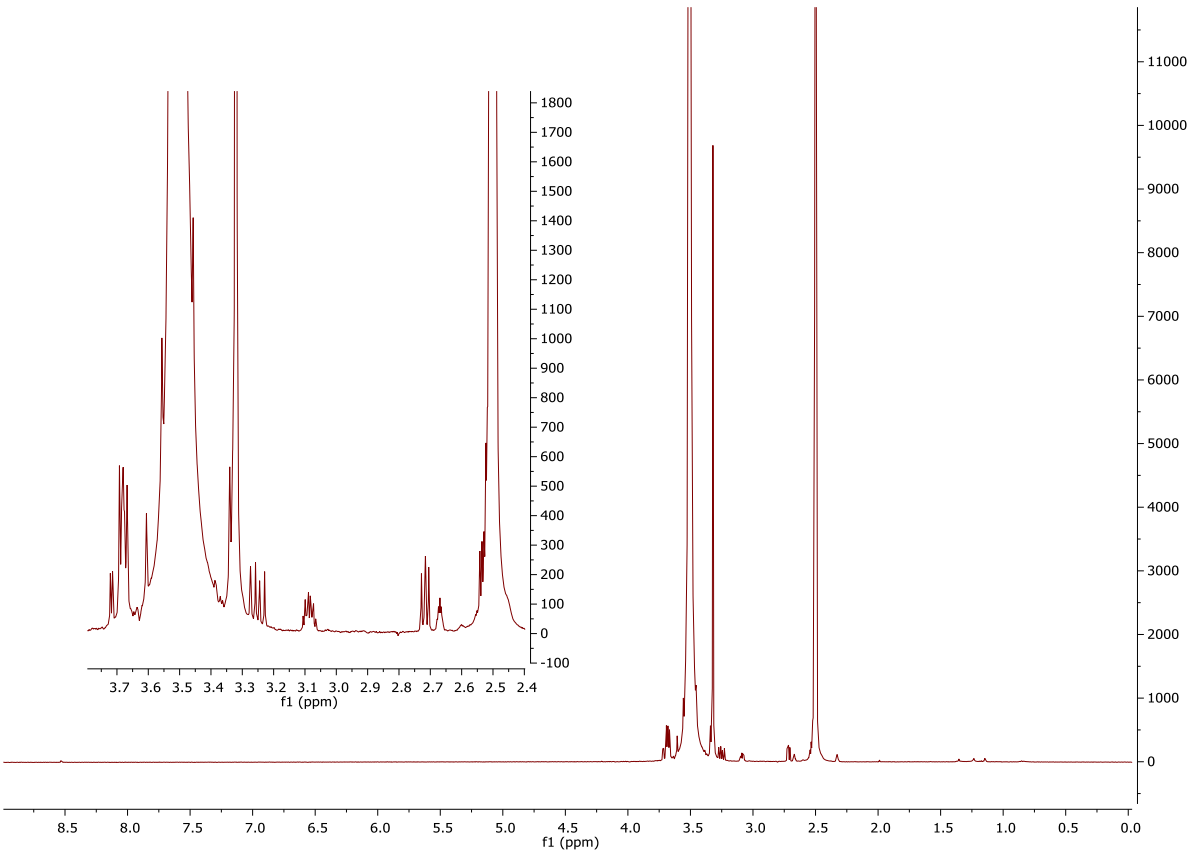

Figure 6. Full ^{1}H-NMR spectrum of pEG-epoxide, 12000 g·mol^{-1}. The solvent is DMSO-d_6.

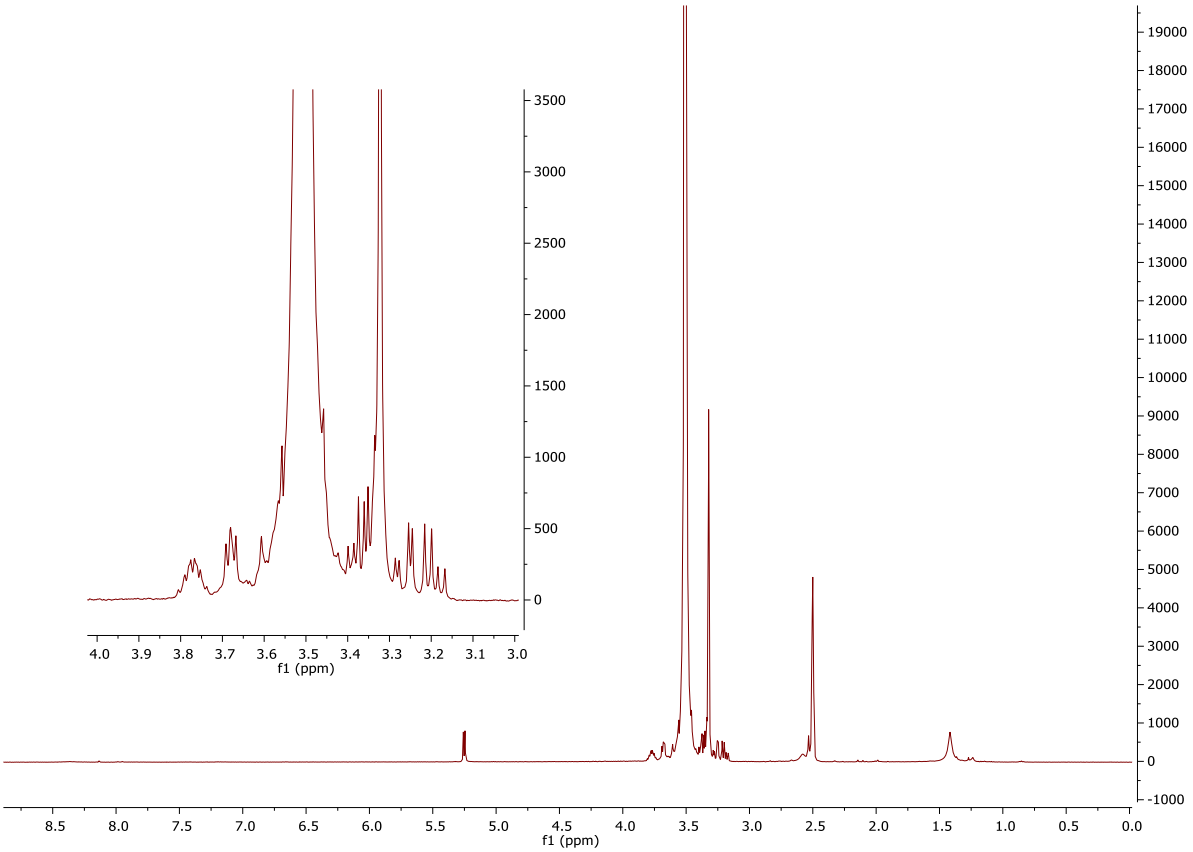

Figure 7. Full ^{1}H-NMR spectrum of pEG-hydroxy-azide, 4000 g·mol^{-1}. The solvent is DMSO-d_6.

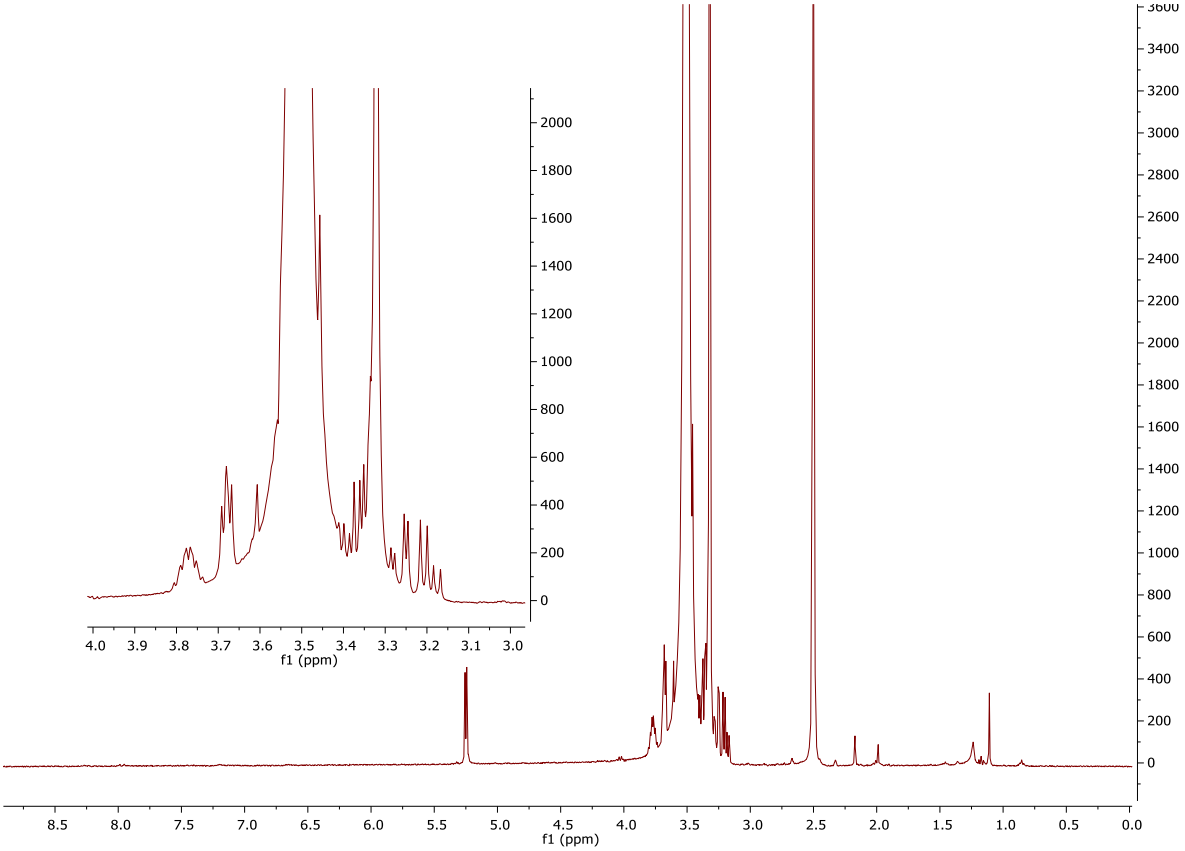

Figure 8. Full ^{1}H-NMR spectrum of pEG-hydroxy-azide, 6000 g·mol^{-1}. The solvent is DMSO-d_6.

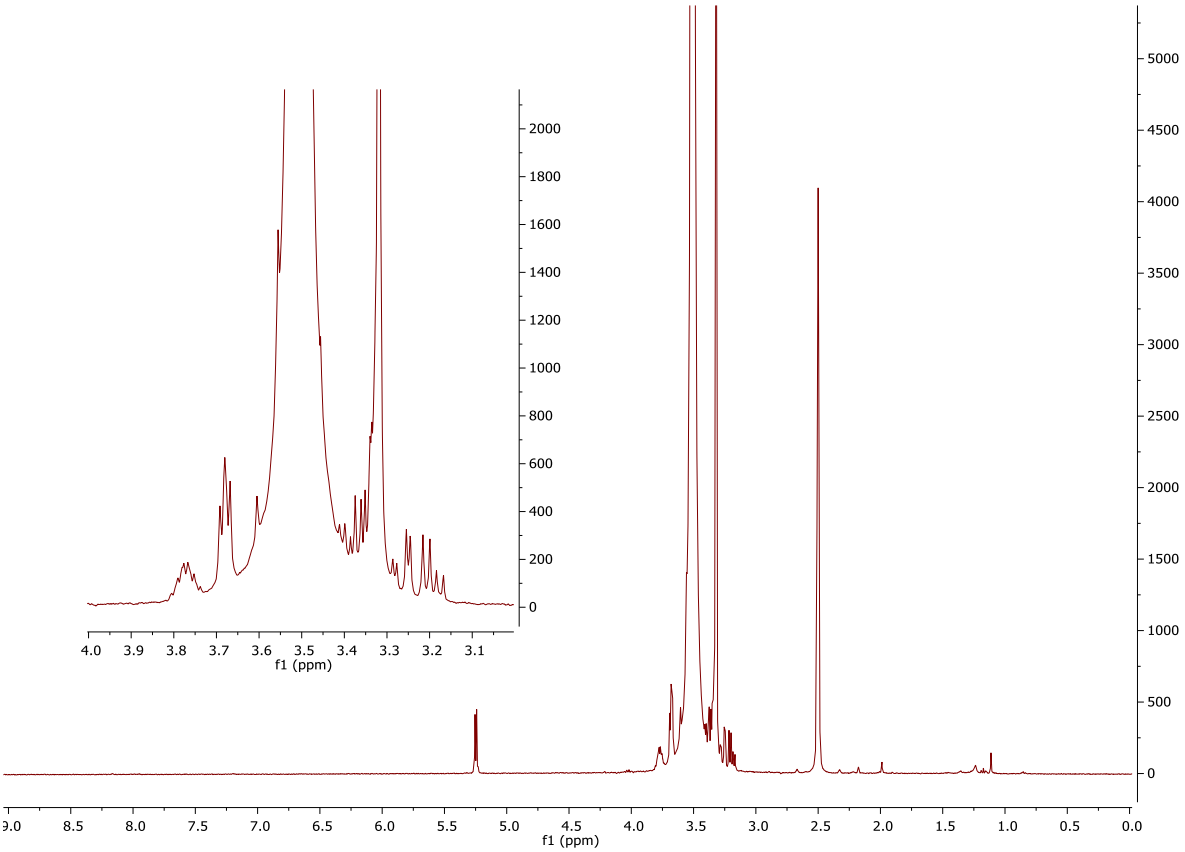

Figure 9. Full ^{1}H-NMR spectrum of pEG-hydroxy-azide, 8000 g·mol^{-1}. The solvent is DMSO-d_6.

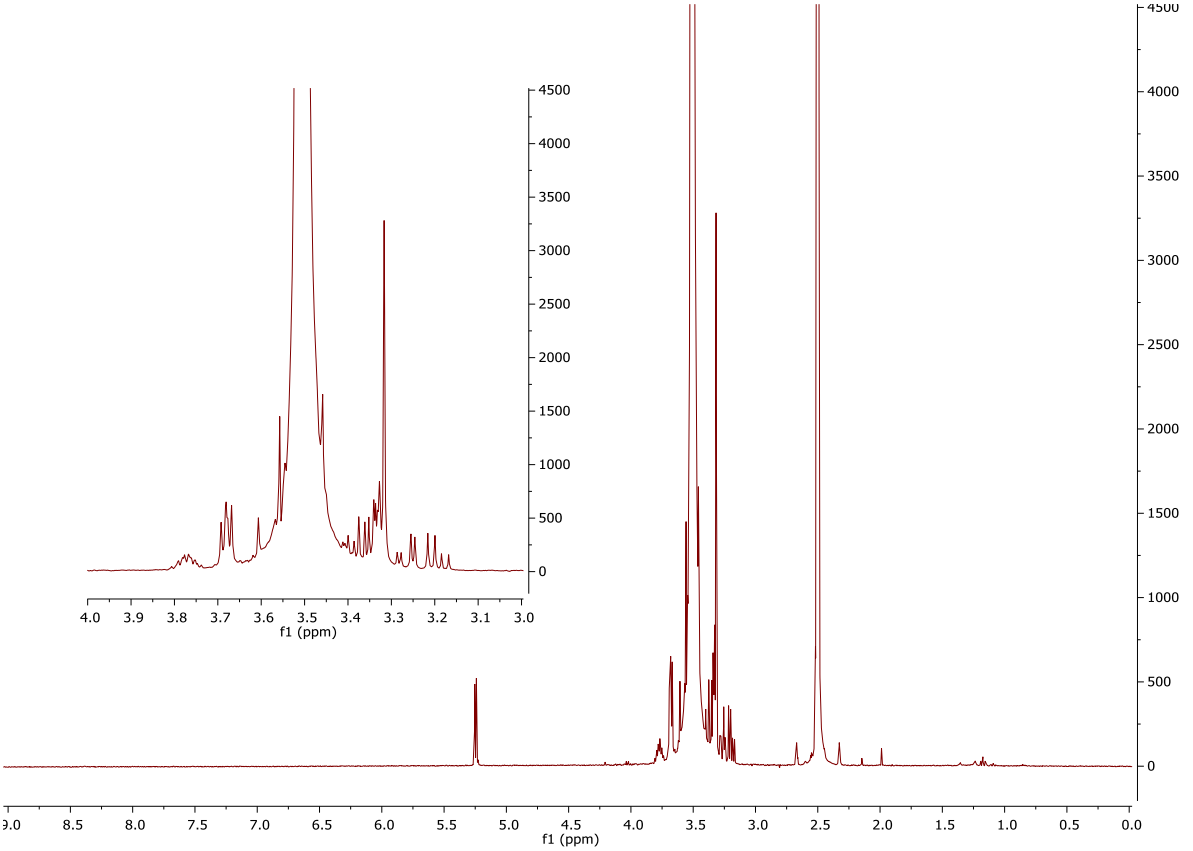

Figure 10. Full ^{1}H-NMR spectrum of pEG-hydroxy-azide, 10000 g·mol^{-1}. The solvent is DMSO-d$_6$.

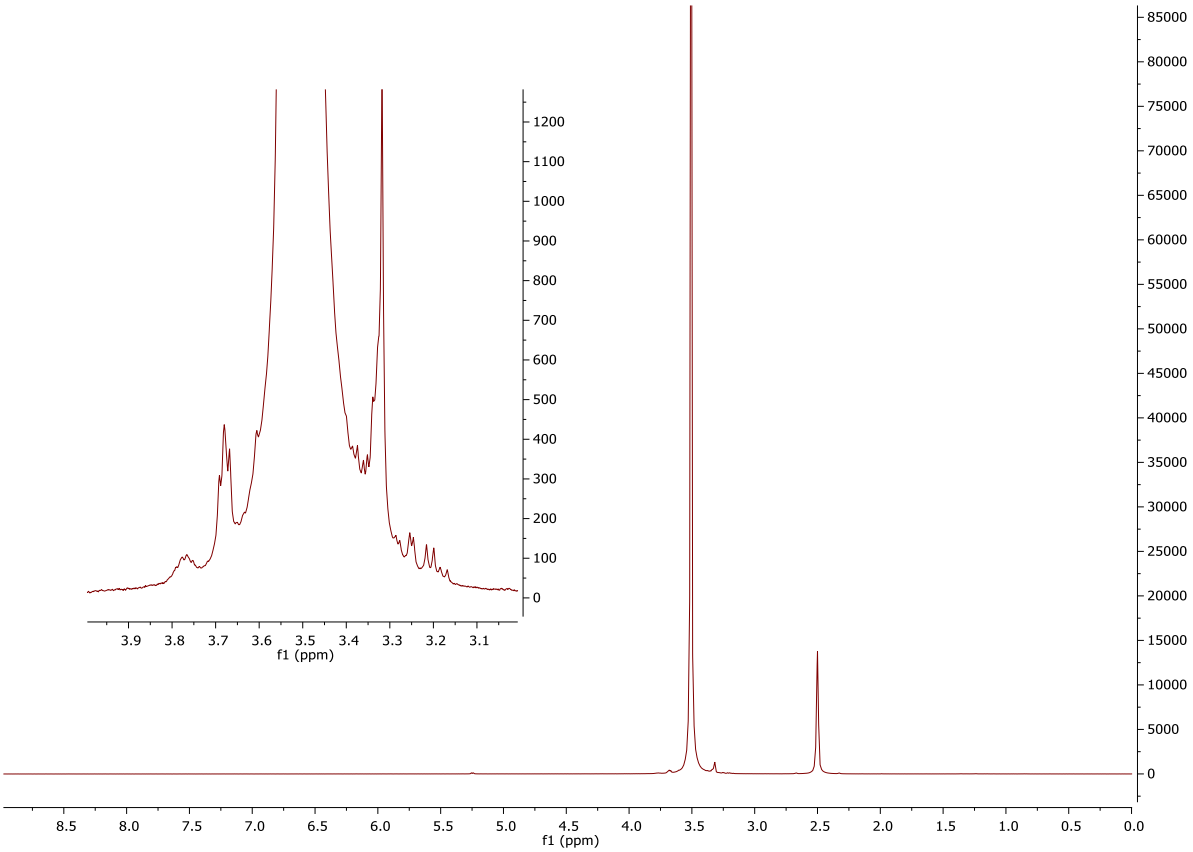

Figure 11. Full ^{1}H-NMR spectrum of pEG-hydroxy-azide, 12000 g·mol^{-1}. The solvent is DMSO-d$_6$.

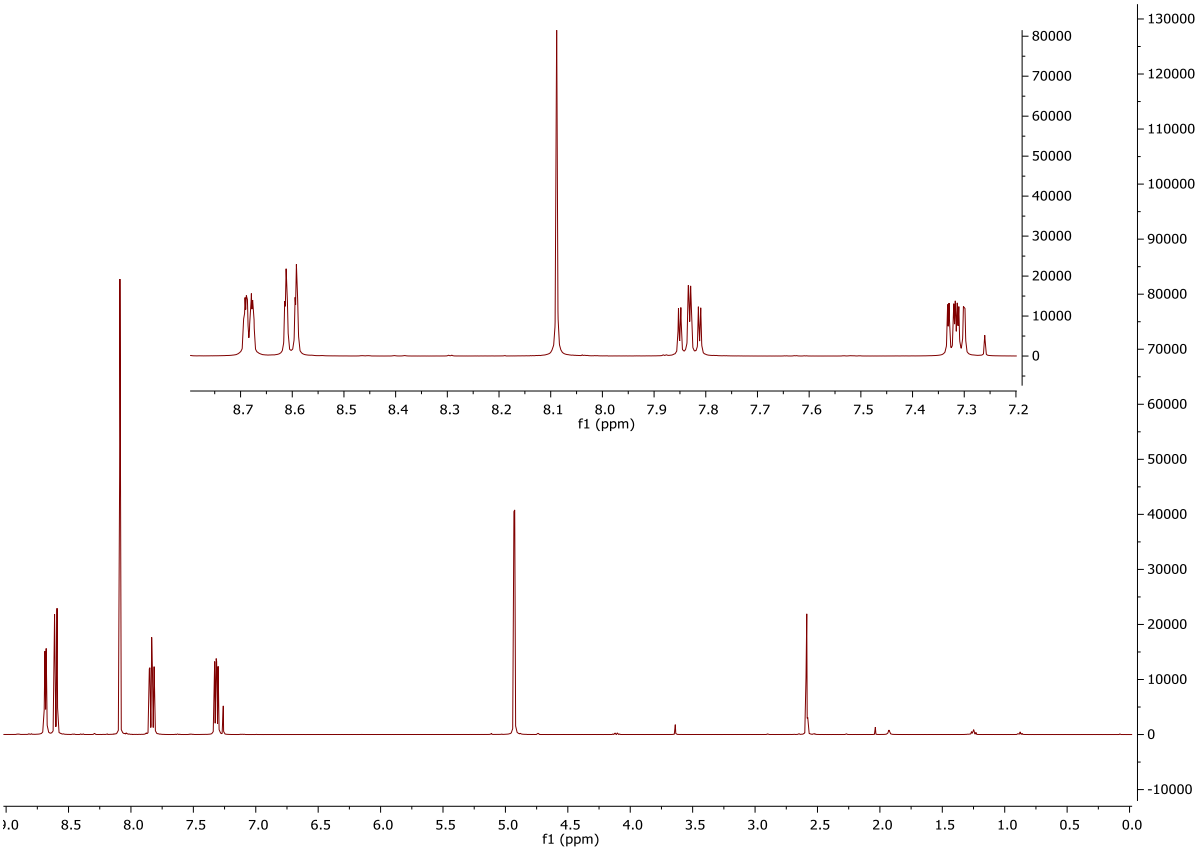

Figure 12. Full ^{1}H-NMR spectrum of propargyl-terpyridine. The solvent is $CDCl_3$.

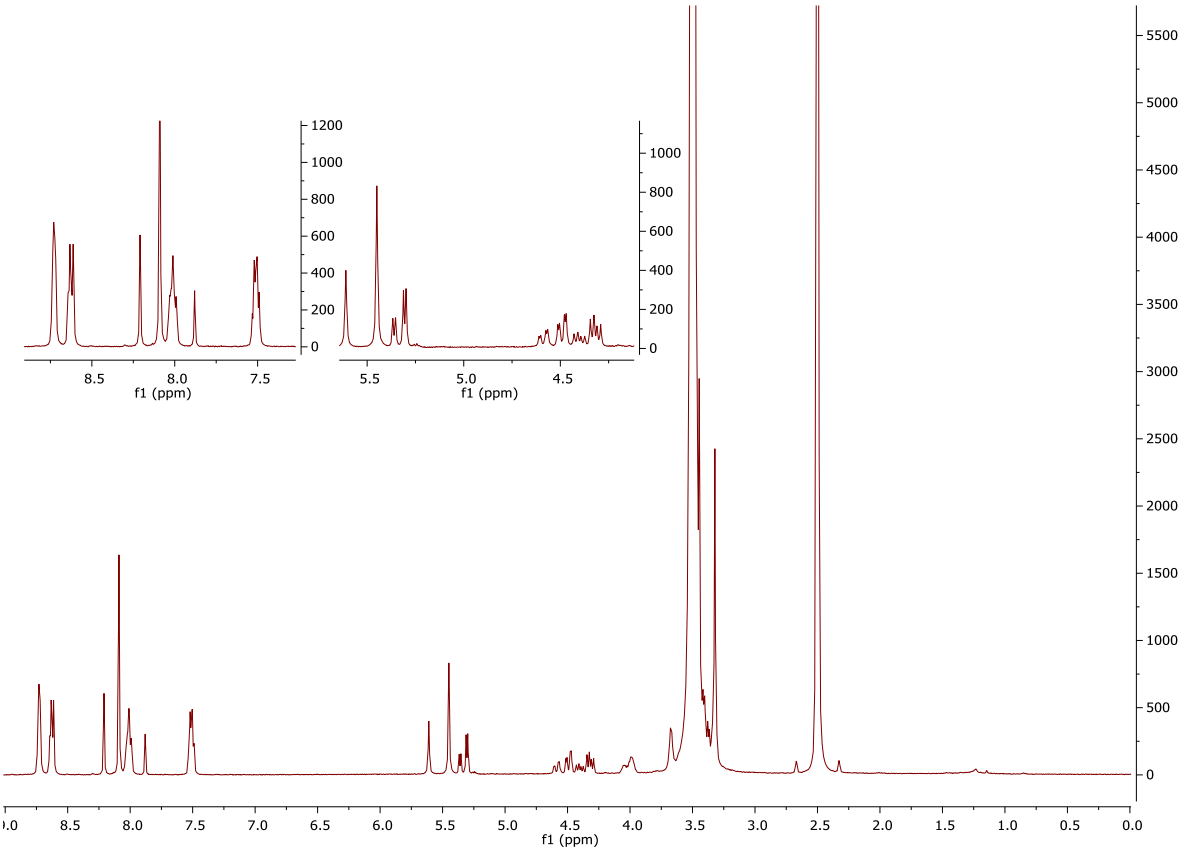

Figure 13. Full ^{1}H-NMR spectrum of pEG-hydroxy-terpyridine, 4000 g·mol^{-1}. The solvent is DMSO-d_6.

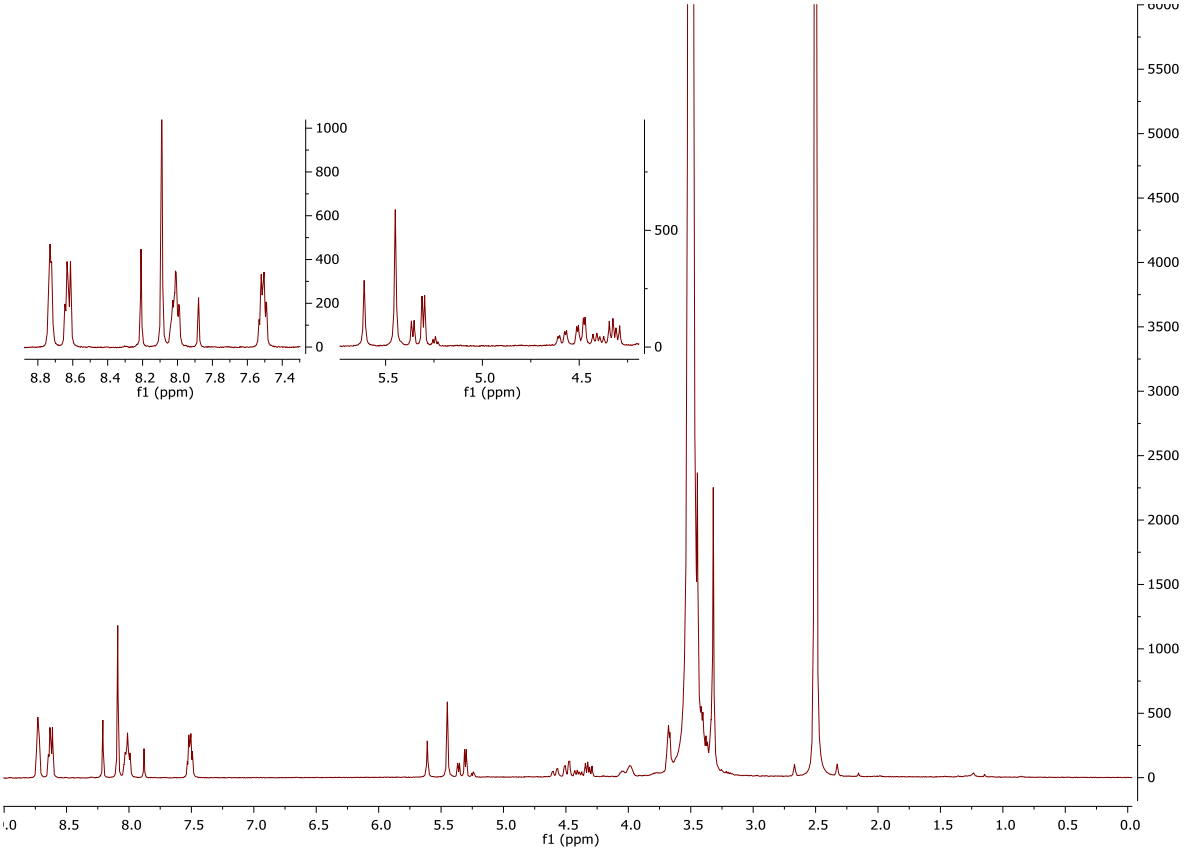

Figure 14. Full ^{1}H-NMR spectrum of pEG-hydroxy-terpyridine, 6000 g·mol^{-1}. The solvent is DMSO-d_6.

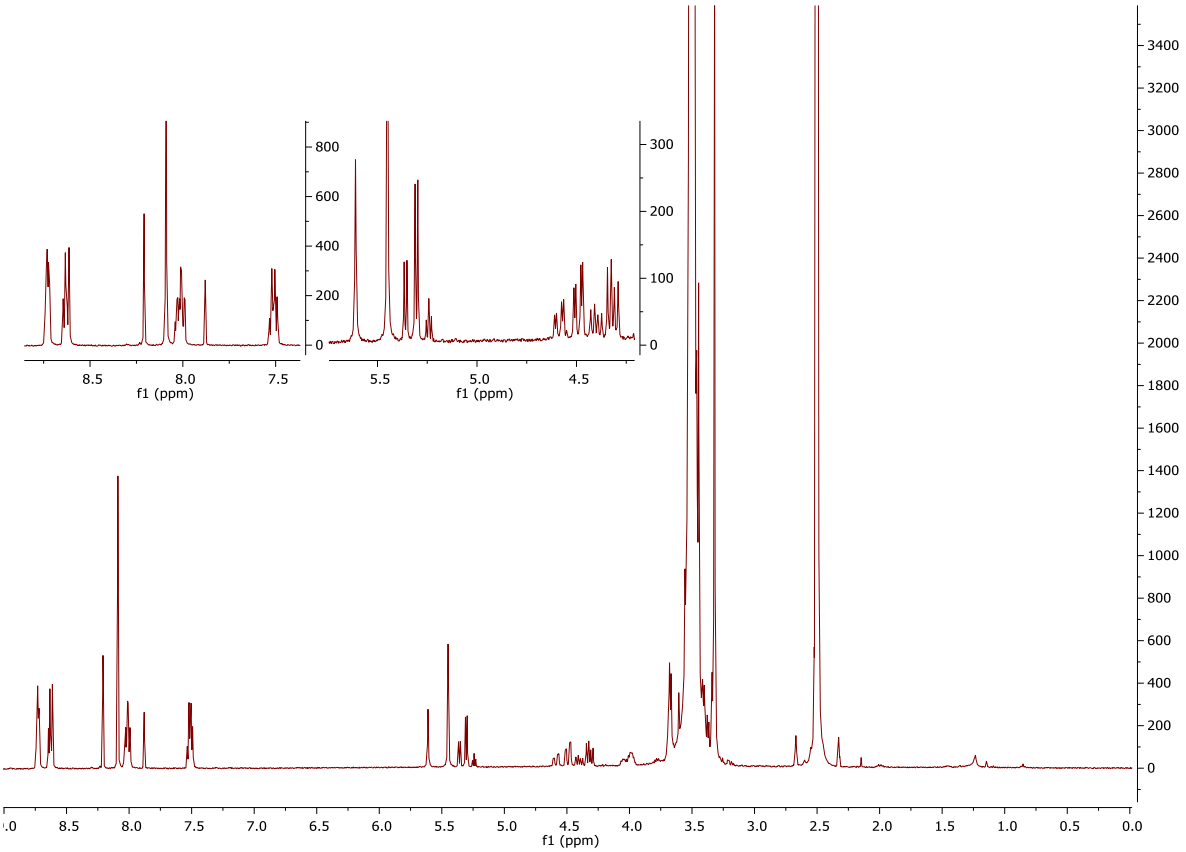

Figure 15. Full ^{1}H-NMR spectrum of pEG-hydroxy-terpyridine, 8000 g·mol^{-1}. The solvent is DMSO-d_6.

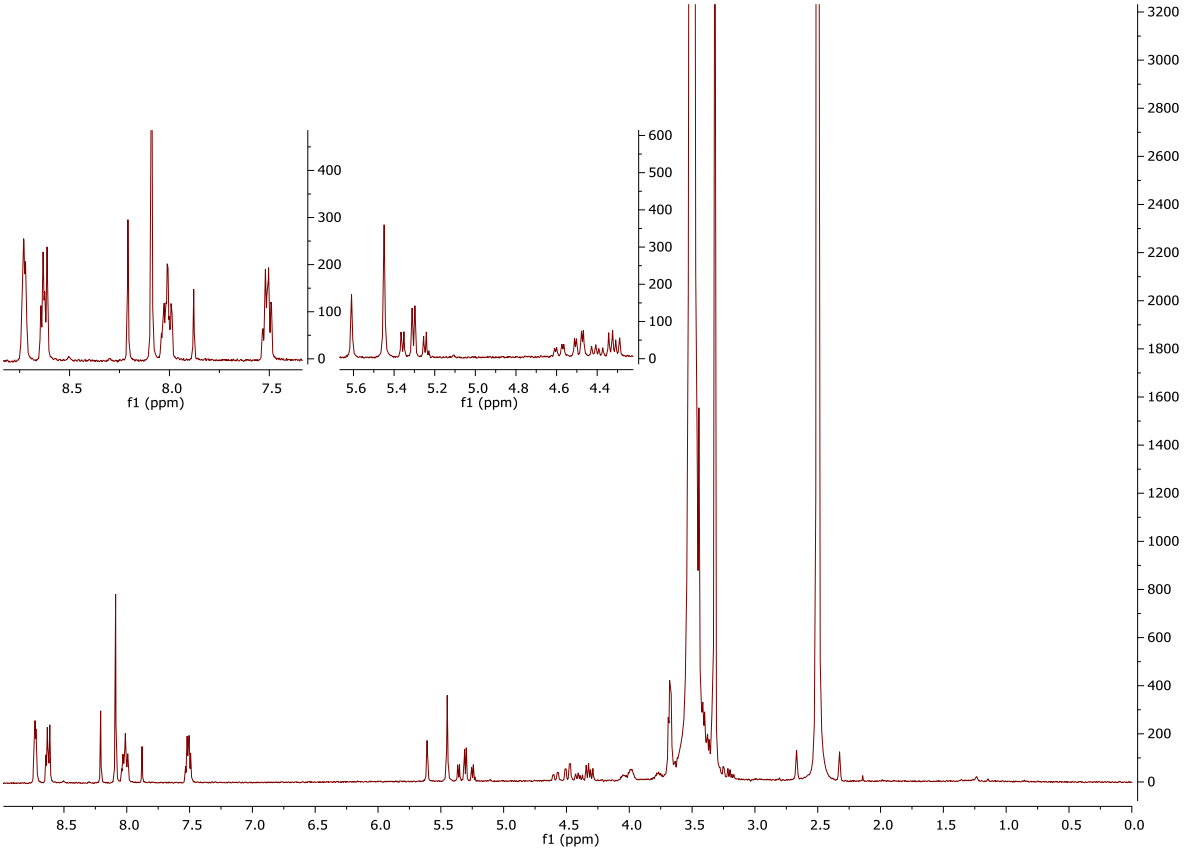

Figure 16. Full ^{1}H-NMR spectrum of pEG-hydroxy-terpyridine, 10000 g·mol^{-1}. The solvent is DMSO-d$_6$.

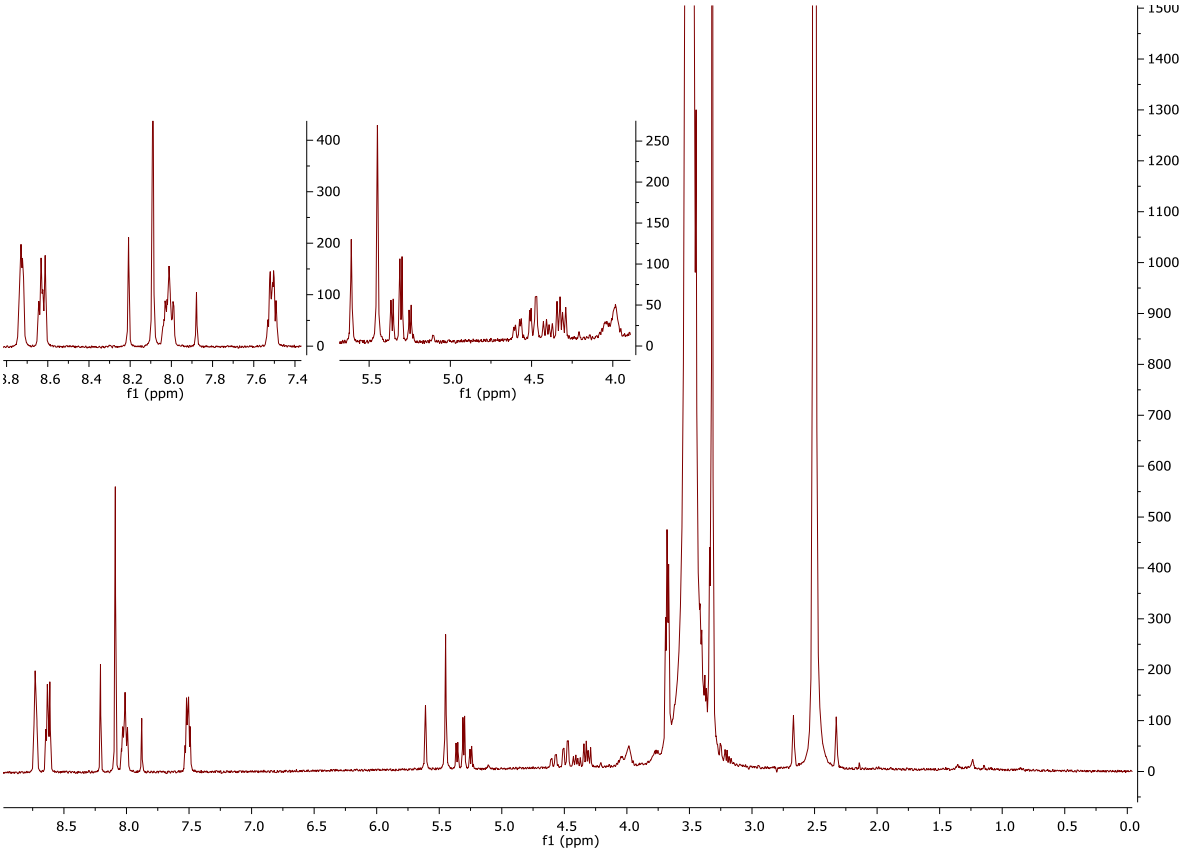

Figure 17. Full ^{1}H-NMR spectrum of pEG-hydroxy-terpyridine, 12000 g·mol^{-1}. The solvent is DMSO-d$_6$.

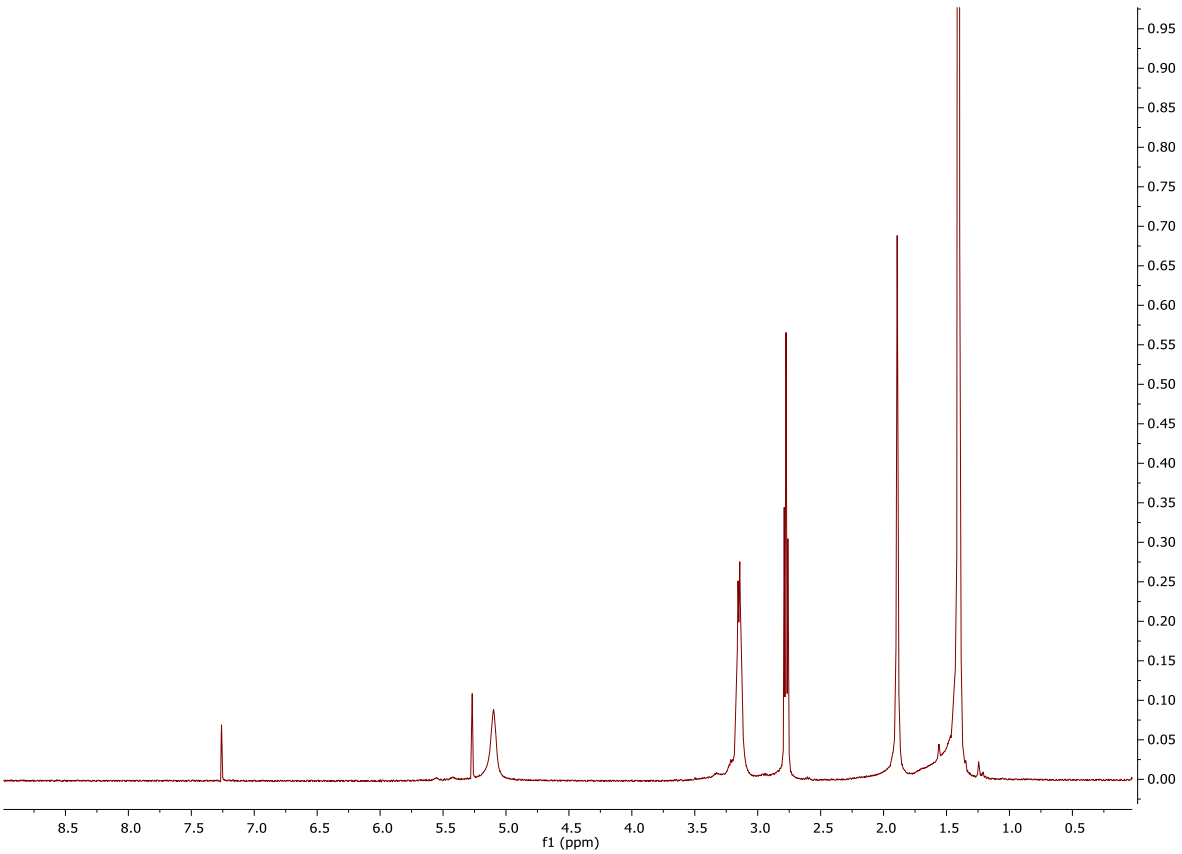

Figure 18. Full ^{1}H-NMR spectrum of *Tert*-butyl (2-aminoethyl)carbamate. The solvent is $CDCl_3$.

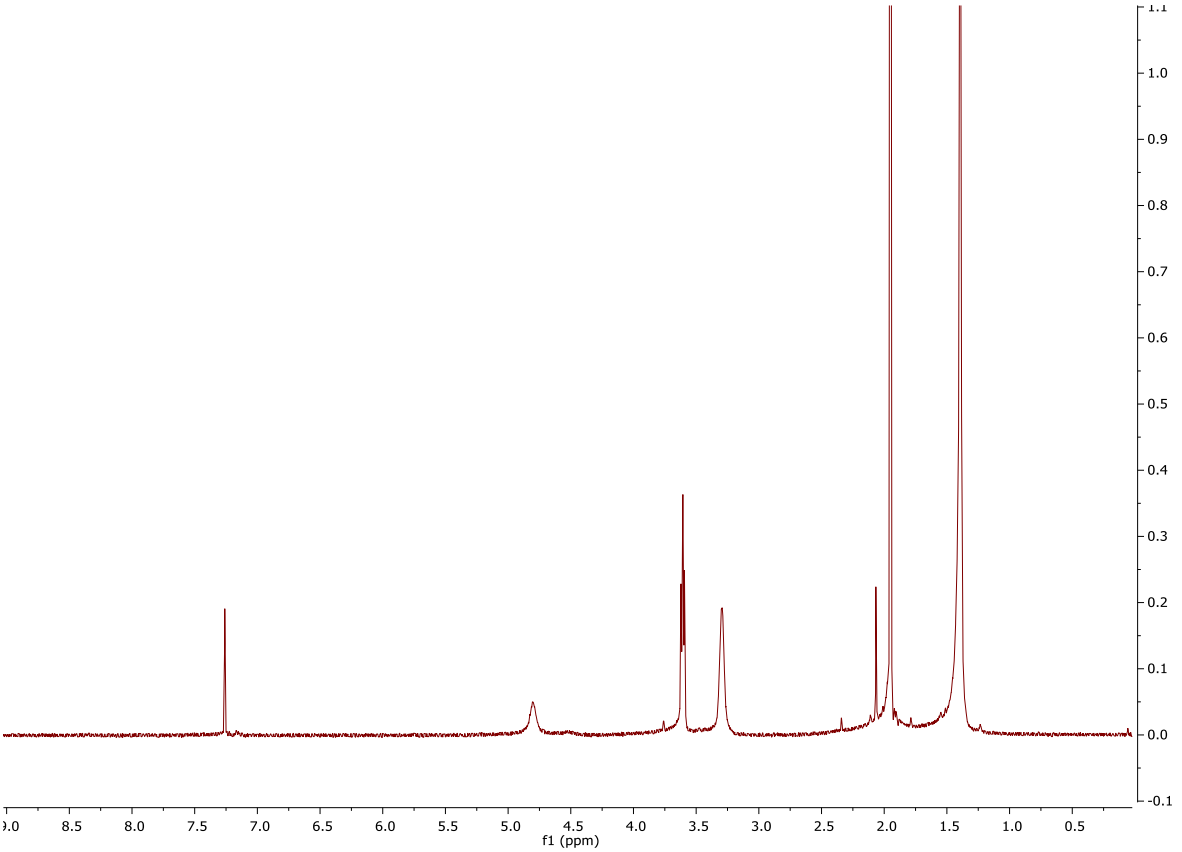

Figure 19. Full ^{1}H-NMR spectrum of *Tert*-butyl (2-(3,4-dimethyl-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)ethyl)carbamate. The solvent is $CDCl_3$.

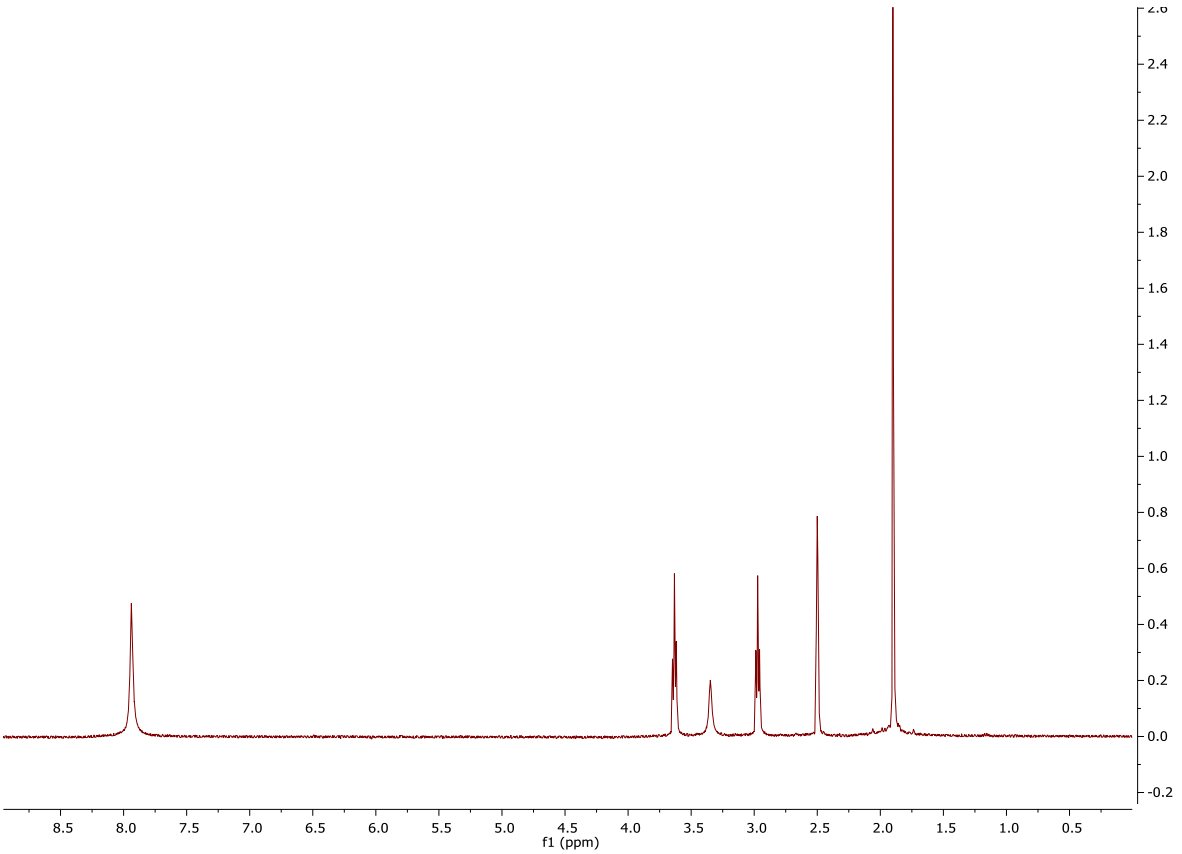

Figure 20. Full ^{1}H-NMR spectrum of 1-(2-Aminoethyl)-3,4-dimethyl-1*H*-pyrrole-2,5-dione trifluoroacetate. The solvent is $CDCl_3$.

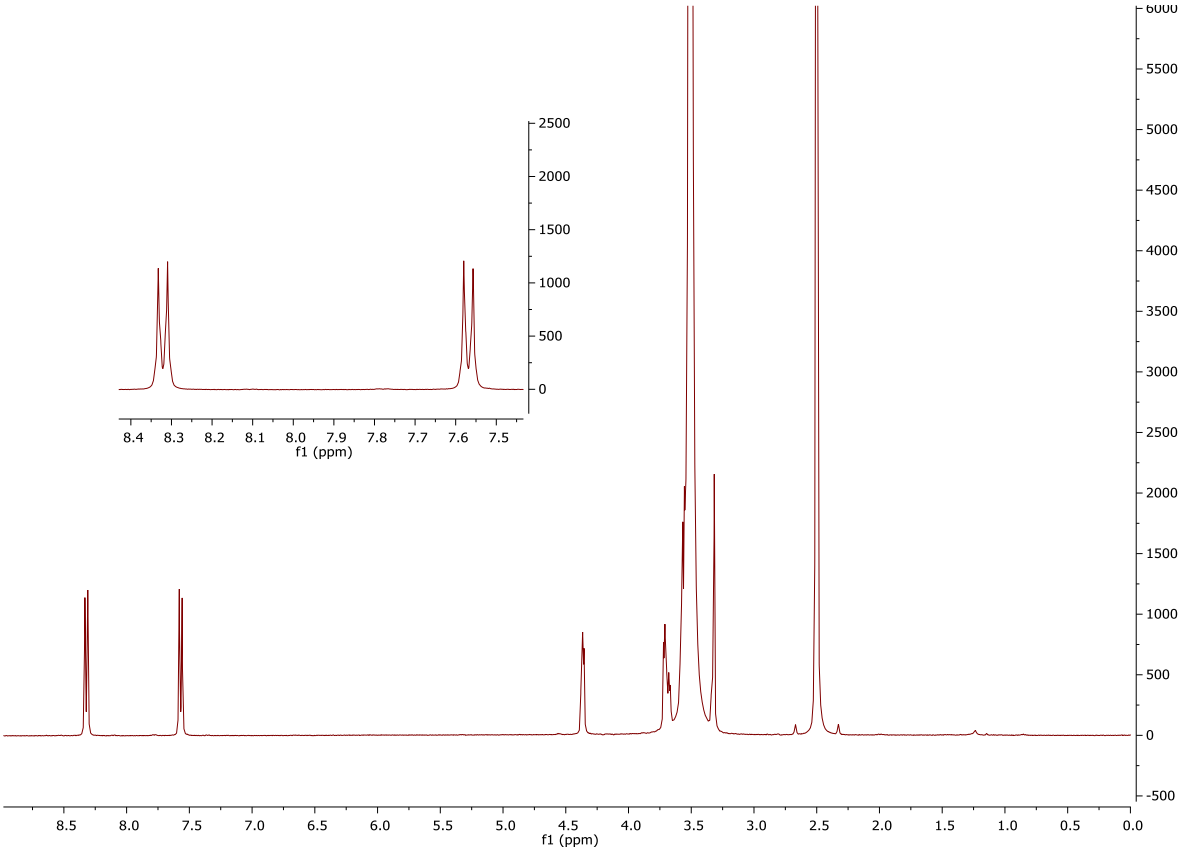

Figure 21. Full ^{1}H-NMR spectrum of pEG-*p*-nitrophenylcarbonate, 4000 g·mol^{-1}. The solvent is DMSO-d_6.

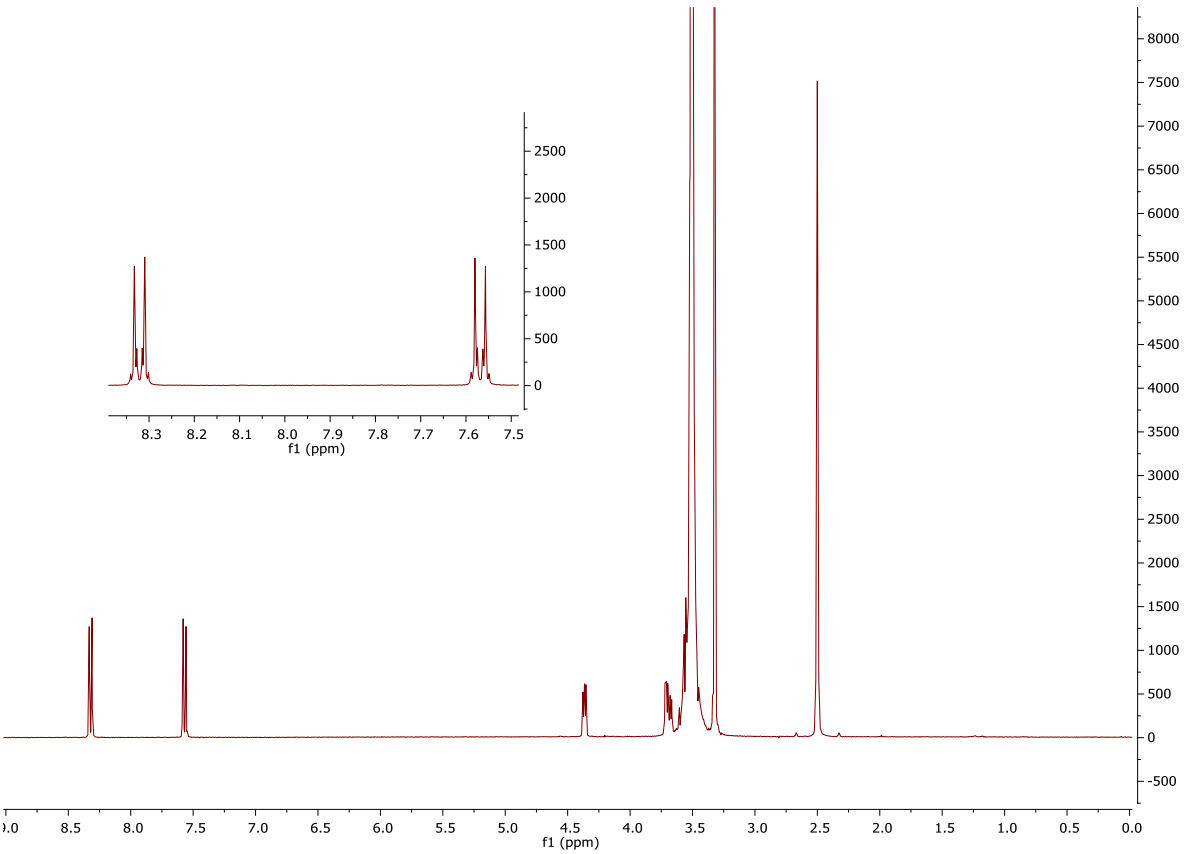

Figure 22. Full ^{1}H-NMR spectrum of pEG-*p*-nitrophenylcarbonate, 6000 g·mol^{-1}. The solvent is DMSO-d_6.

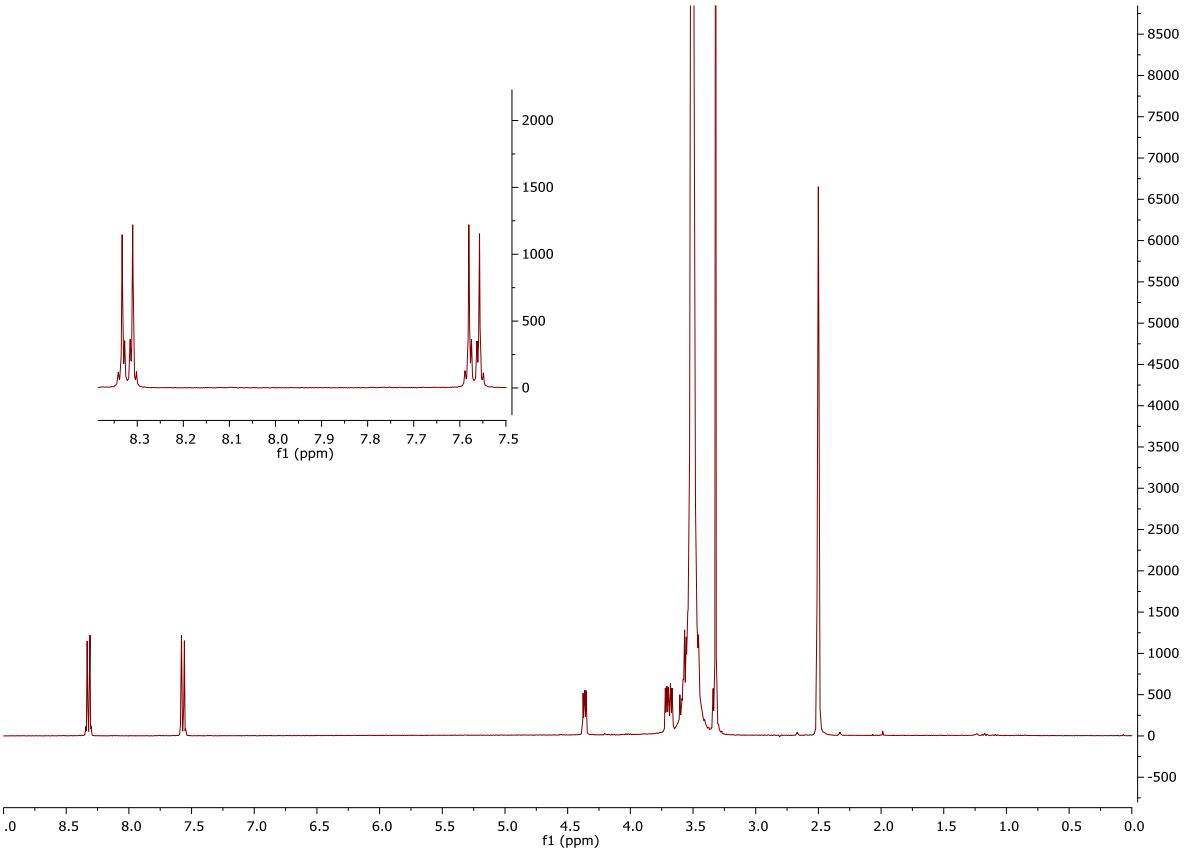

Figure 23. Full ^{1}H-NMR spectrum of pEG-*p*-nitrophenylcarbonate, 8000 g·mol^{-1}. The solvent is DMSO-d_6.

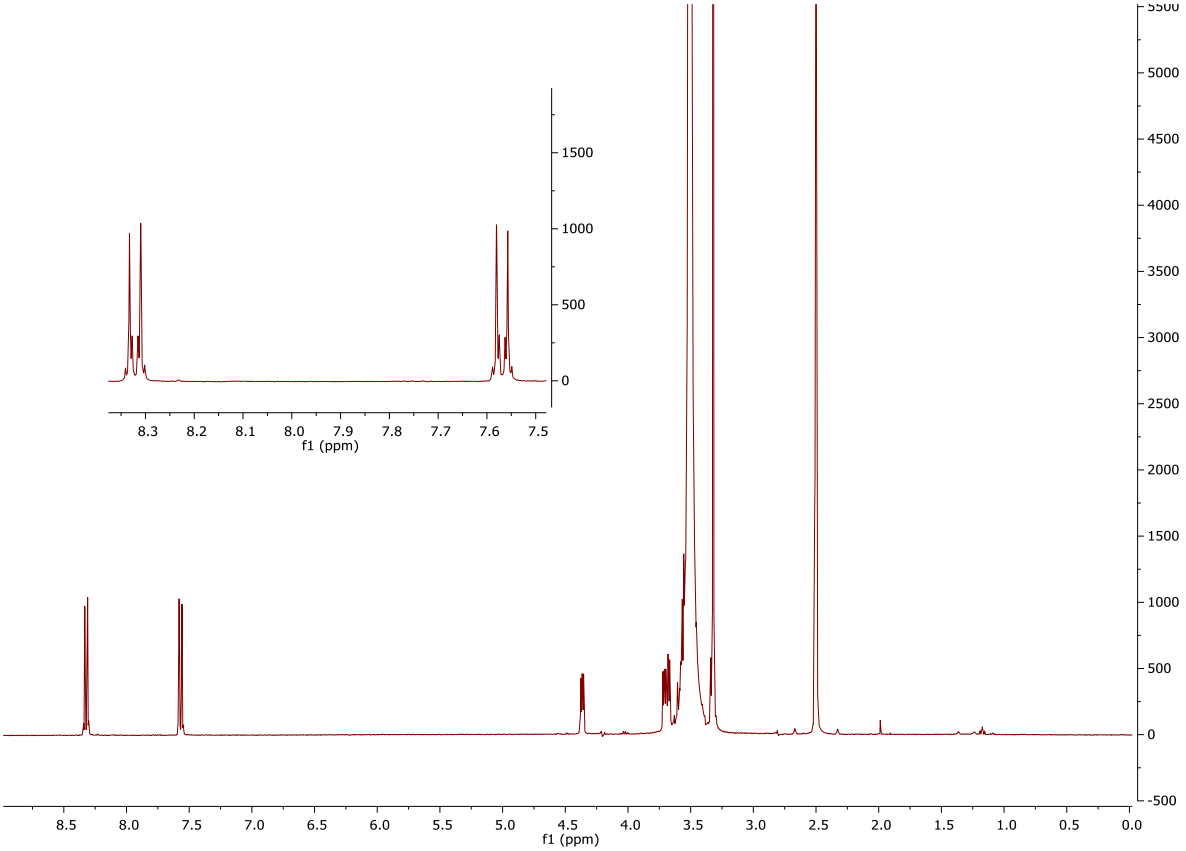

Figure 24. Full ^{1}H-NMR spectrum of pEG-*p*-nitrophenylcarbonate, 10000 g·mol^{-1}. The solvent is DMSO-d_6.

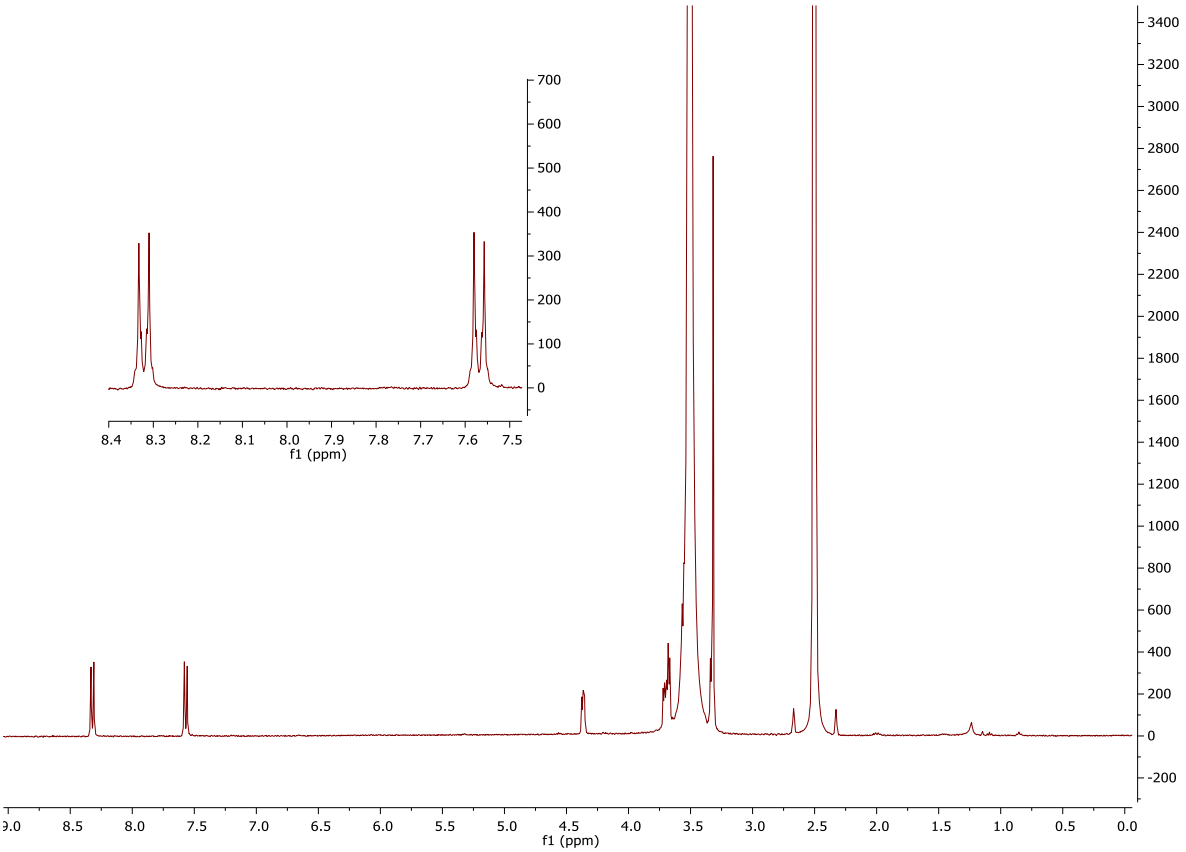

Figure 25. Full ^{1}H-NMR spectrum of pEG-*p*-nitrophenylcarbonate, 12000 g·mol^{-1}. The solvent is DMSO-d_6.

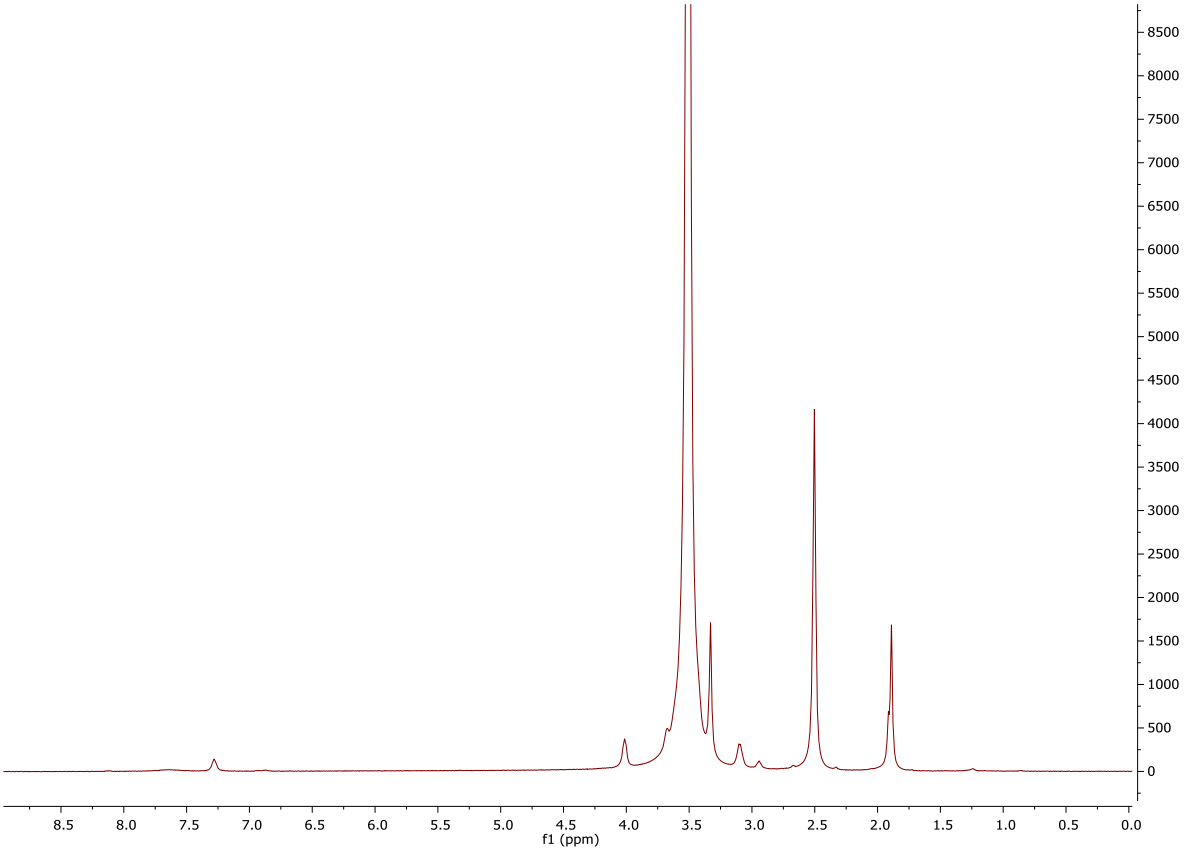

Figure 26. Full ^{1}H-NMR spectrum of pEG-DMMI, 4000 g·mol^{-1}. The solvent is DMSO-d_6.

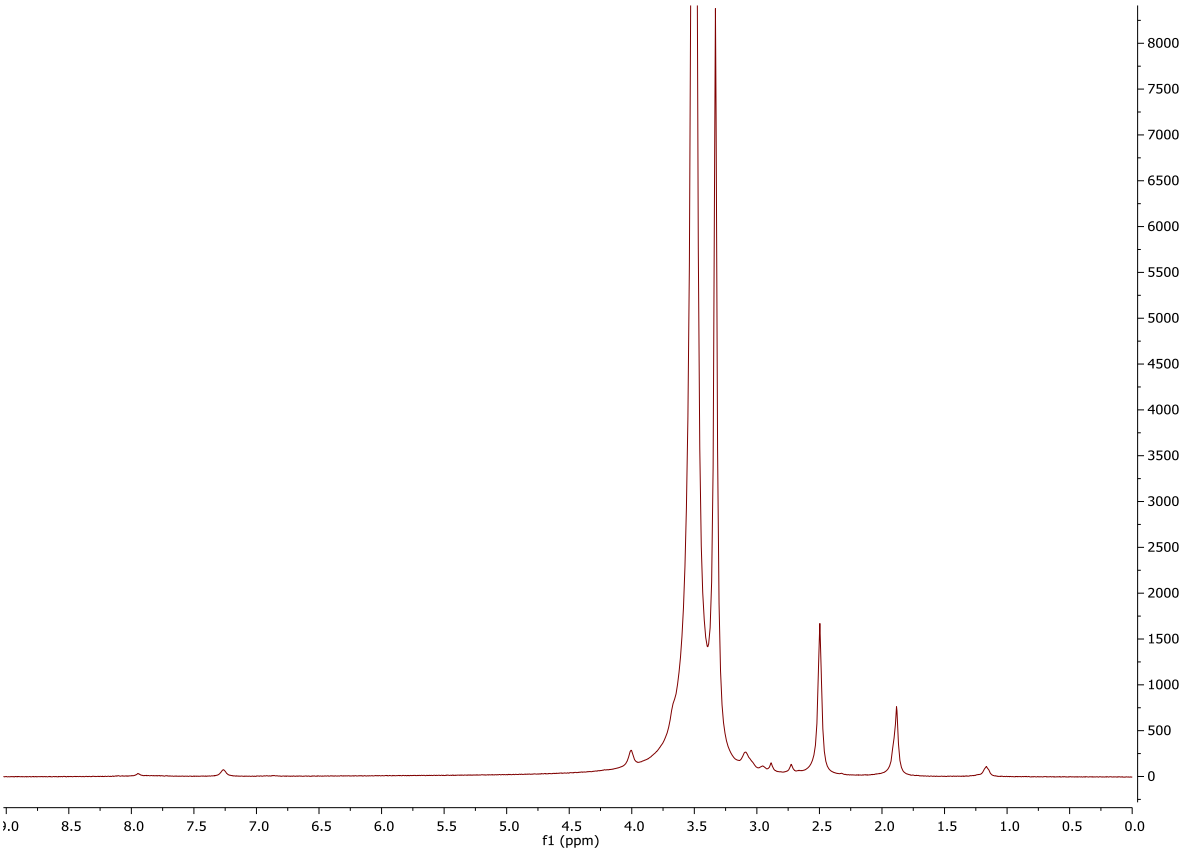

Figure 27. Full ^{1}H-NMR spectrum of pEG-DMMI, 6000 g·mol^{-1}. The solvent is DMSO-d_6.

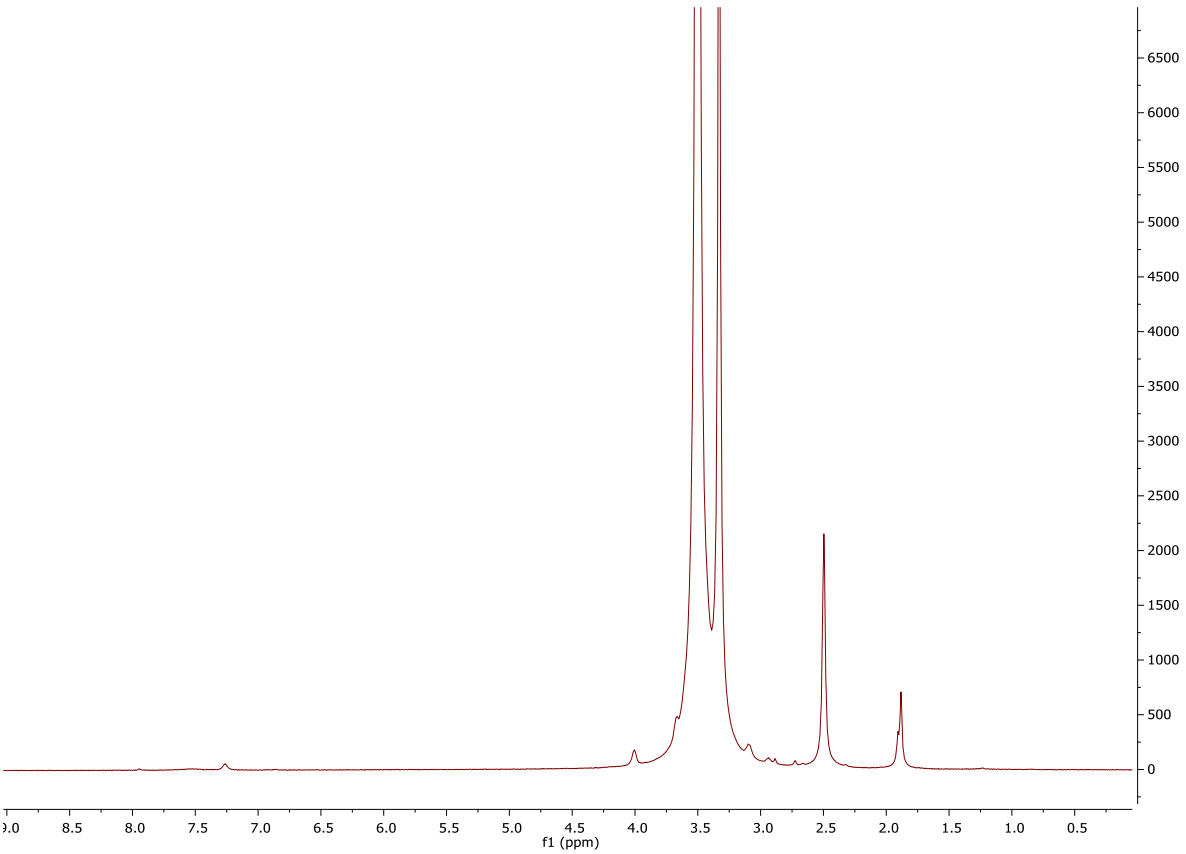

Figure 28. Full ^{1}H-NMR spectrum of pEG-DMMI, 8000 g·mol^{-1}. The solvent is DMSO-d_6.

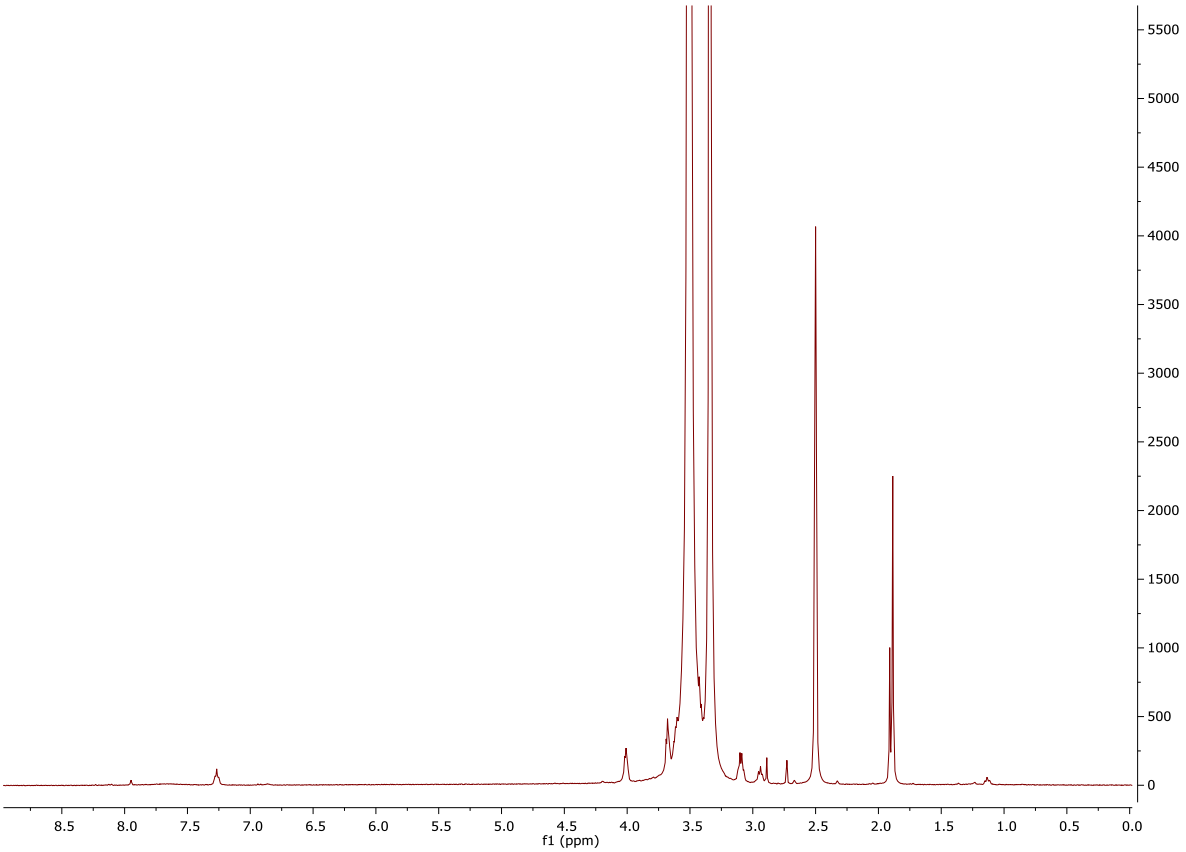

Figure 29. Full ^{1}H-NMR spectrum of pEG-DMMI, 10000 g·mol^{-1}. The solvent is DMSO-d_6.

pEG-DMMI, 12000 g·mol^{-1}:

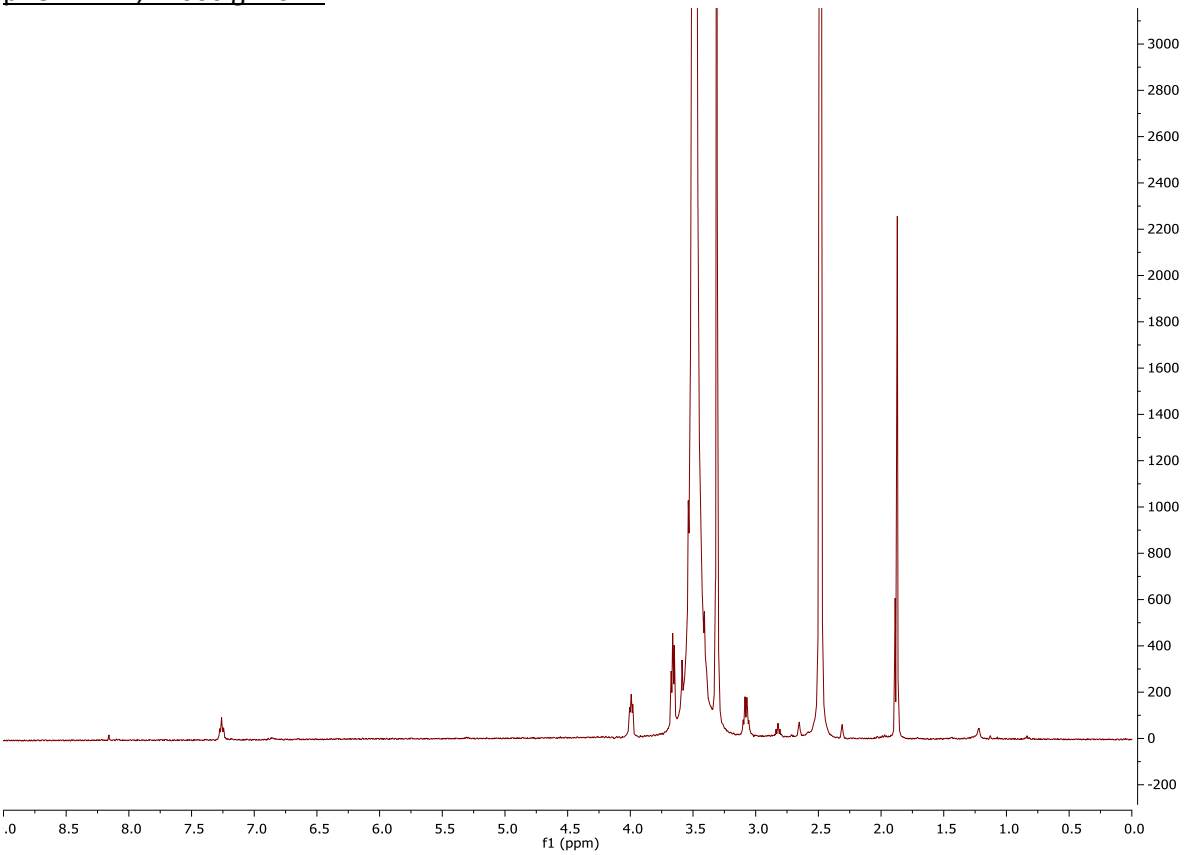

Figure 30. Full ^{1}H-NMR spectrum of pEG-DMMI, 12000 g·mol^{-1}. The solvent is DMSO-d_6.