Supplementary Information (SI) for Polymer Chemistry.

Supplementary Information

Development of redox-active polycaprolactone and its electrochemical redox behavior in aqueous media

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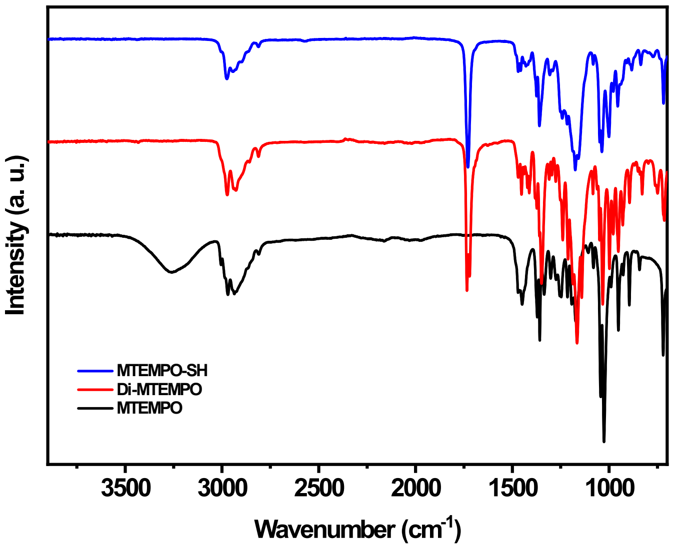


Fig. S1. FT-IR analysis of **MTEMPO**, **Di-MTEMPO**, and **MTEMPO-SH**.

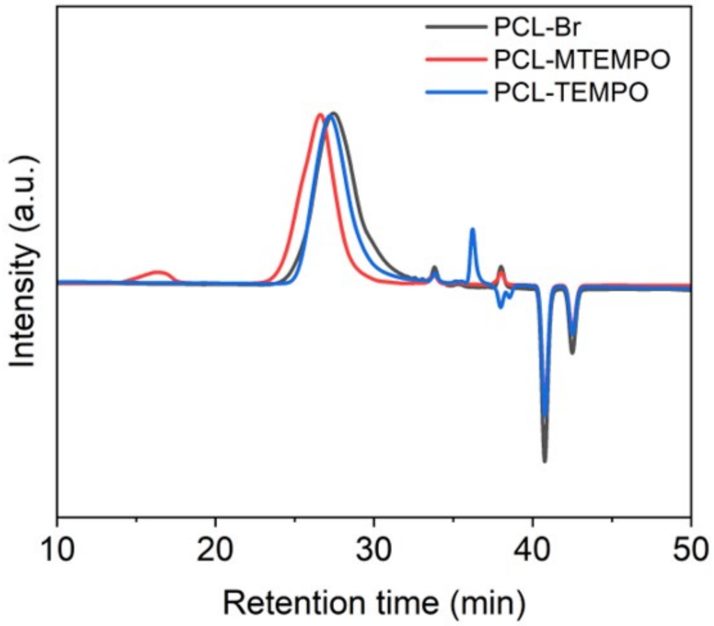


Fig. S2. SEC profiles of **PCL-Br**, **PCL-MTEMPO**, and **PCL-TEMPO**.

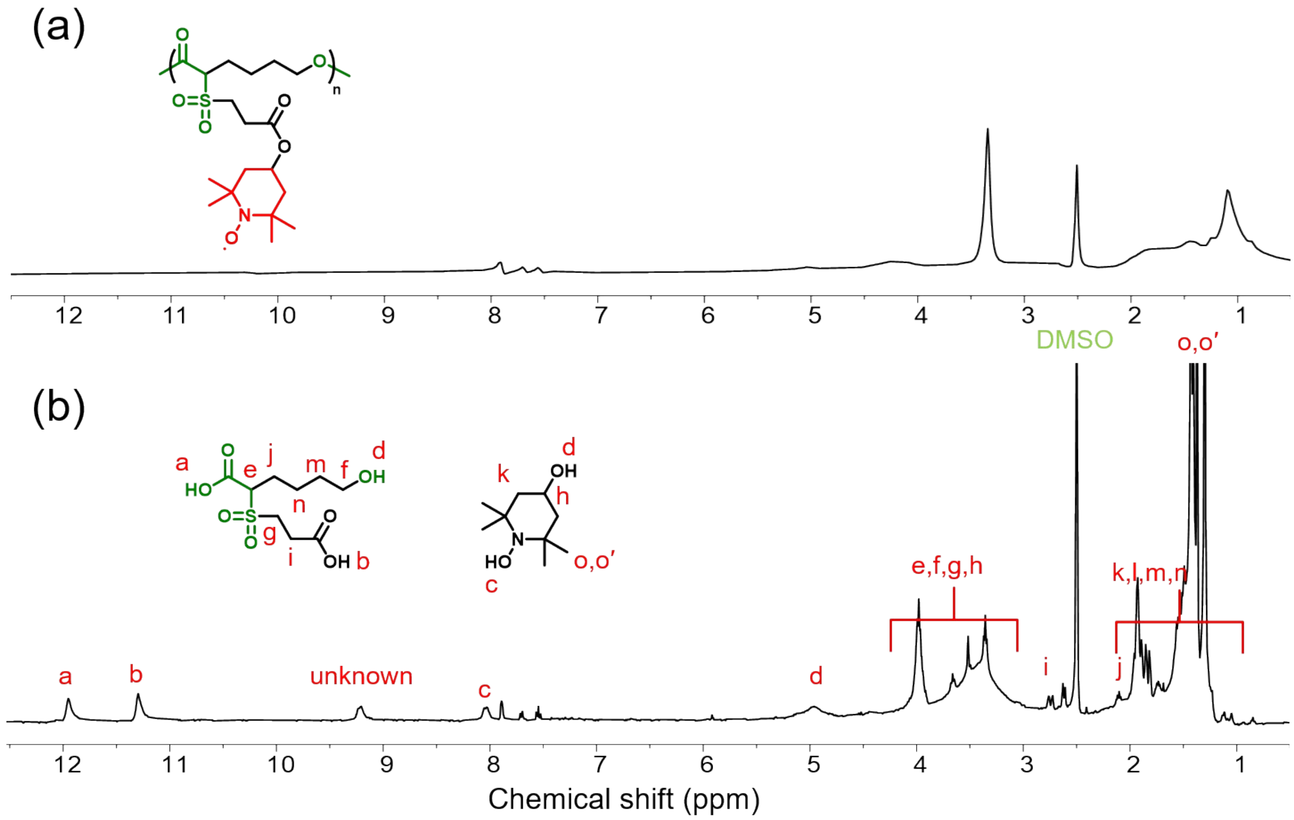


Fig. S3. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **PCL-TEMPO** before (a) and after (b) degradation with KOH in MeOH at 90 ºC for 12 h.

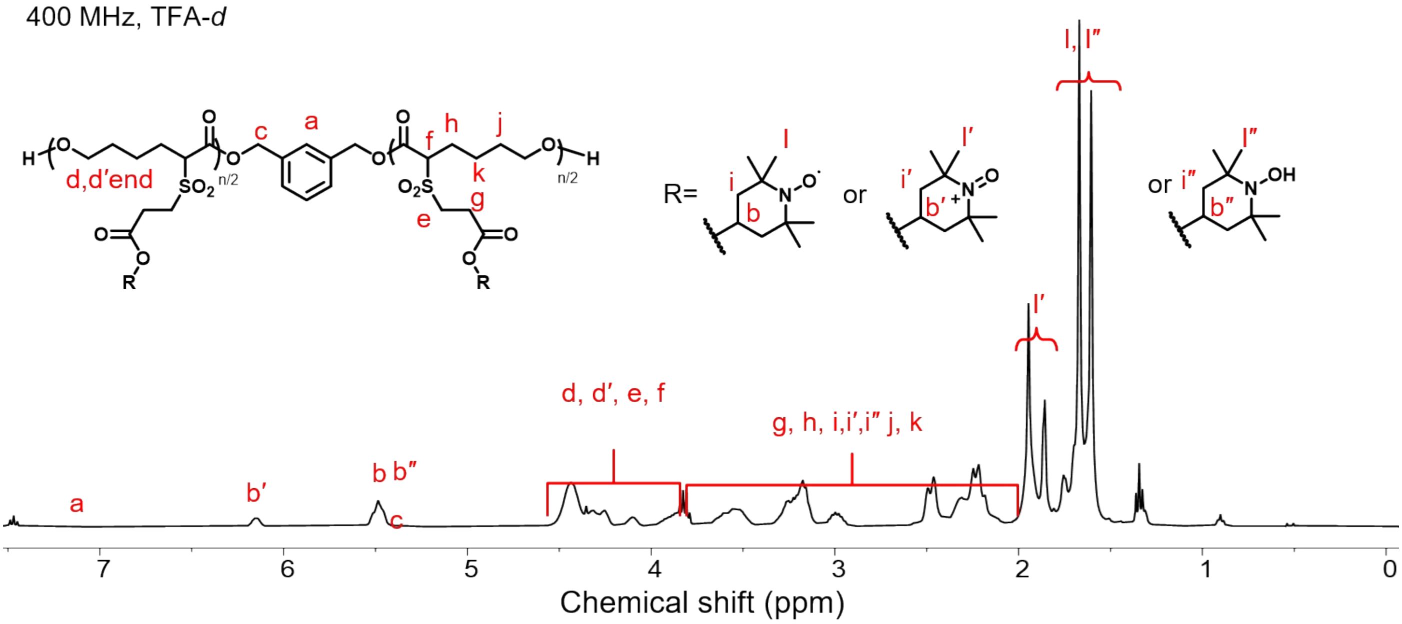


Fig. S4. ^{1}H NMR (400 MHz, TFA-d) spectrum of **PCL-TEMPO**.

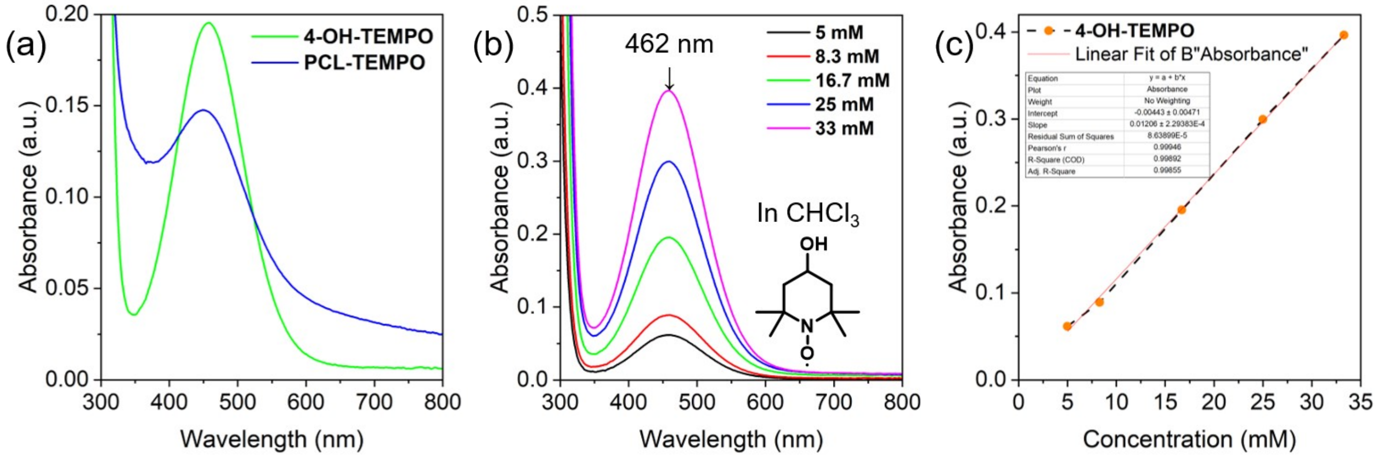


Fig. S5. (a) UV-Vis spectra of **PCL-TEMPO** (16.7 mM of repeating unit) and 4-OH-TEMPO (16.7 mM) in $CHCl_3$. (b) UV-Vis spectra of 4-OH-TEMPO in $CHCl_3$ with different molar concentration, and (c) calibration curve showing that amount of nitroxide radical is linearly proportional to its absorbance peak at 462 nm.

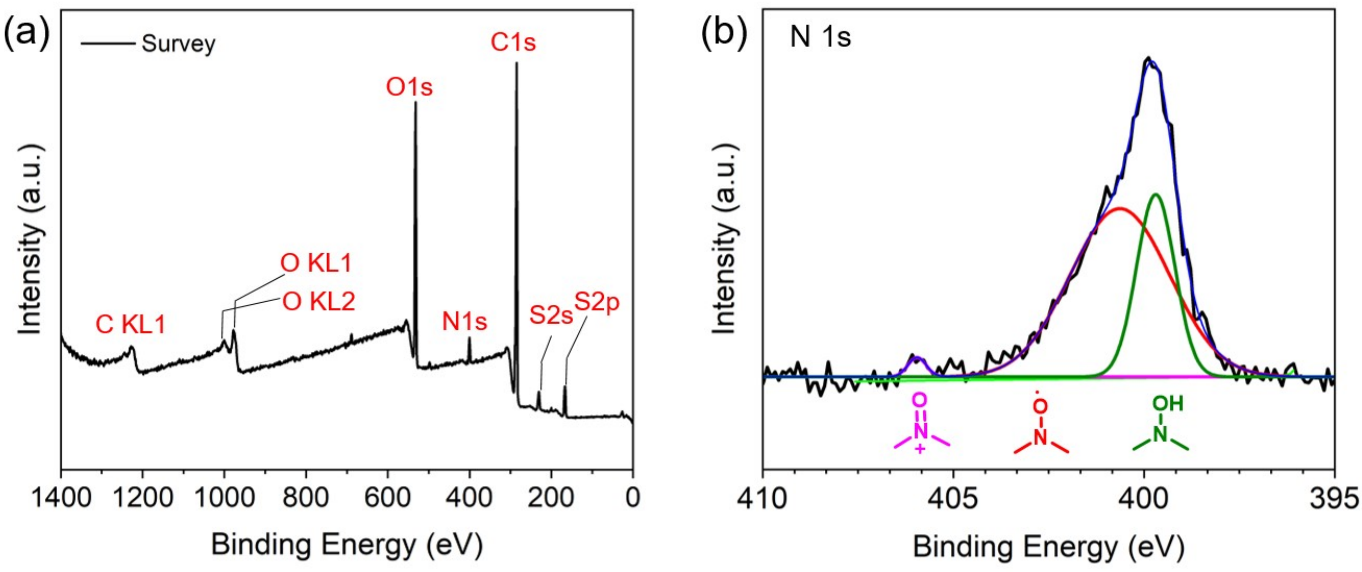


Fig. S6. XPS spectra of **PCL-TEMPO**(a) survey scan and (b) high-resolution spectrum of N1s.

Table S1. Composition of N1s based on high-resolution XPS spectrum of N1s (Fig. S5b).

	eV	**Area**	**%**
N1s Scan A	406	152.16689	1.5
N1s Scan B	400.6	7172.81354	69.5
N1s Scan C	399.7	2990.19031	29.0

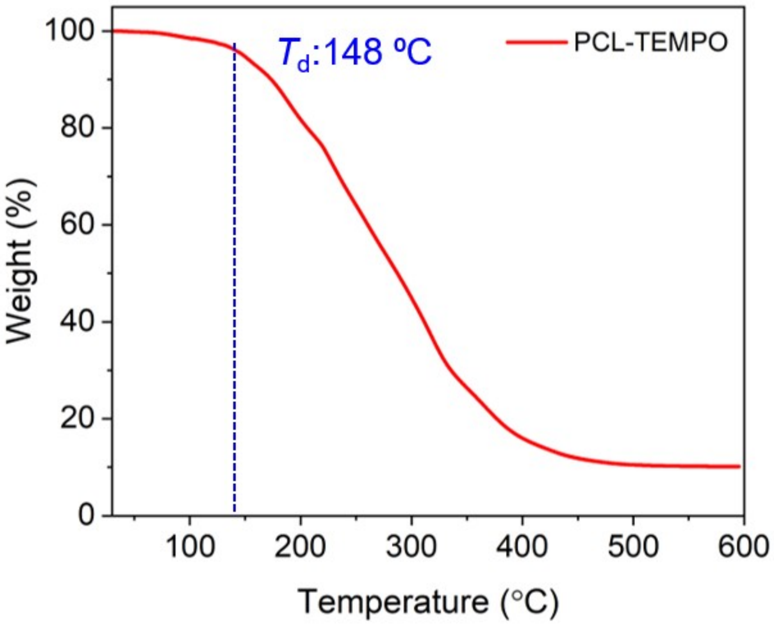


Fig. S7. Thermal stability study of PLC-TEMPO; T_d of **PCL-TEMPO** was observed at 148 ºC. The degradation temperature of **PCL-TEMPO** exceeded the slurry electrode's drying temperature (80 ºC).

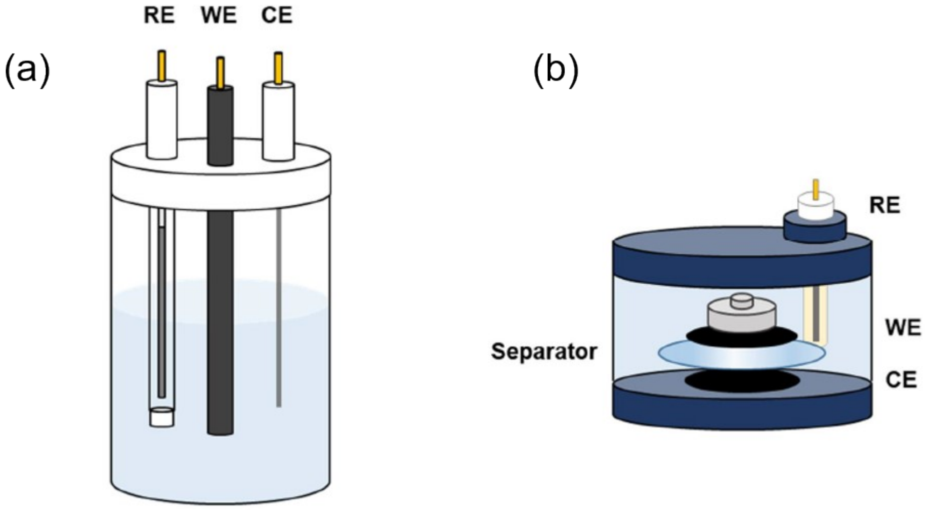


Fig. S8. Illustrations of (a) an open-and (b) a compact-cell for electrochemical analysis.

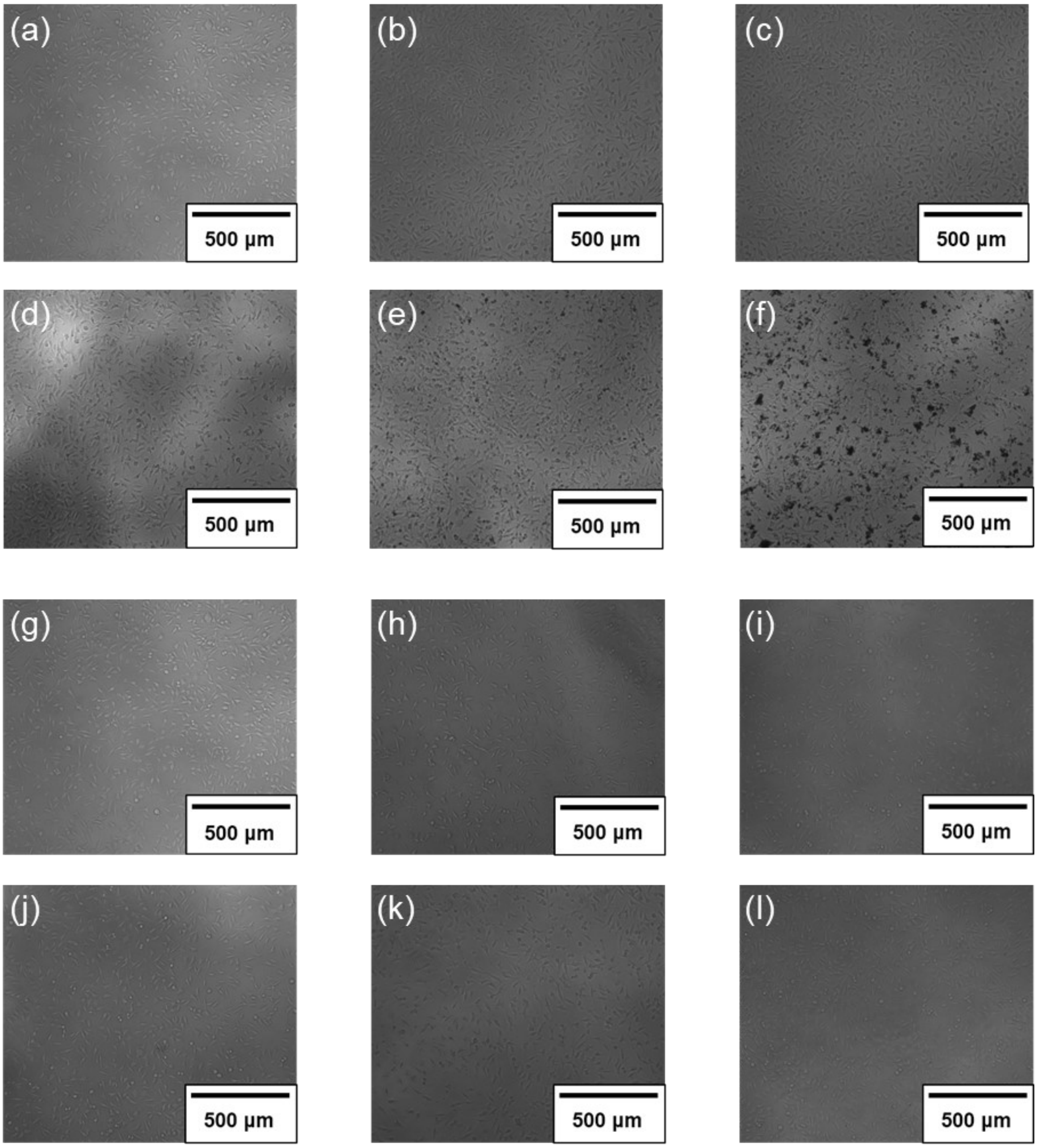


Fig. S9. (a-f) Optical cells images cultured with **PCL-TEMPO**. (a) without **PCL-TEMPO**, (b) 0.01 µM **PCL-TEMPO**, (c) 0.1 µM **PCL-TEMPO**, (d) 1 µM **PCL-TEMPO**, (e) 10 µM **PCL-TEMPO**, (f) 100 µM **PCL-TEMPO** (magnification 20×). (g-l) Optical cells images cultured with degraded **PCL-TEMPO** g) without degraded **PCL-TEMPO**, (h) 0.01 µM degraded **PCL-TEMPO**, (i) 0.1 µM degraded **PCL-TEMPO**, (j) 1 µM degraded **PCL-TEMPO**, (k) 10 µM degraded **PCL-TEMPO**, (l) 100 µM degraded **PCL-TEMPO** (magnification 20×). Statistical significance between two groups was assessed by an unpaired t-test and $P < 0.05$ was considered to be not statistically significant.

Theoretical Capacity Calculation

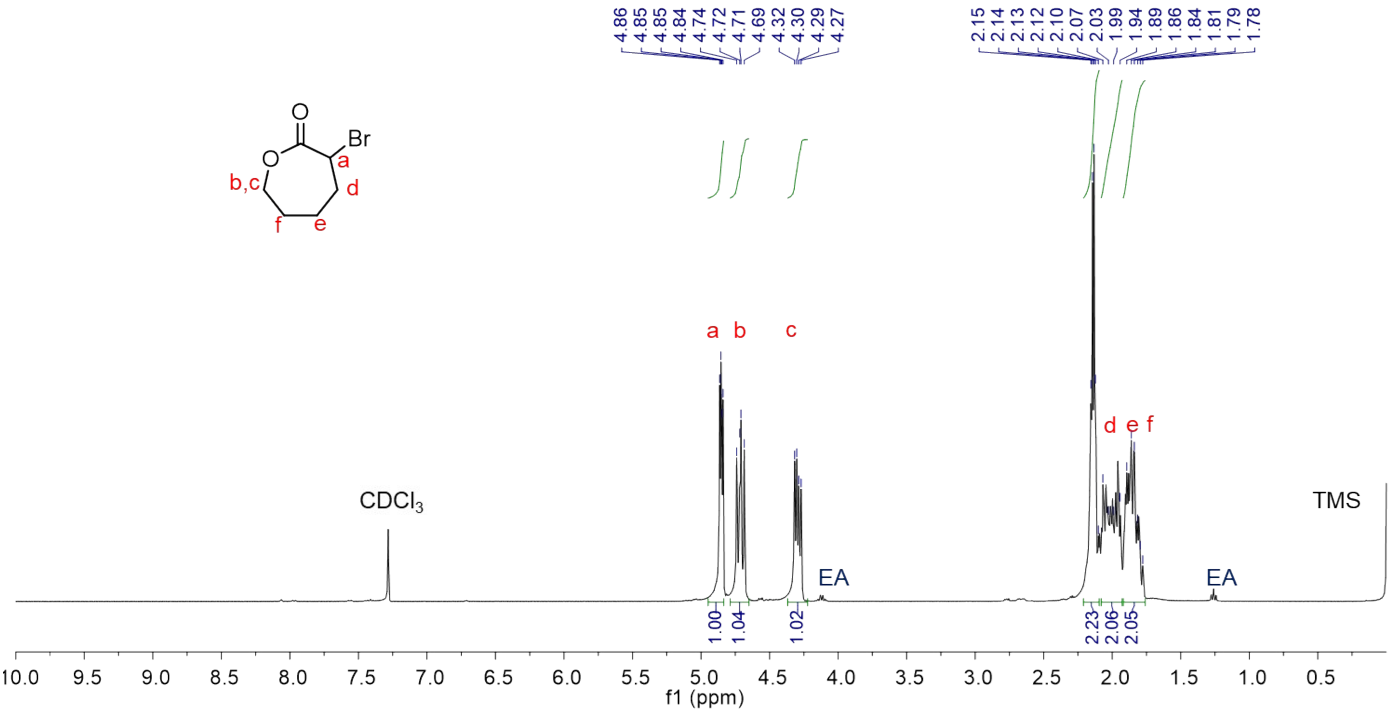
The theoretical gravimetric capacity of **PCL-TEMPO** was calculated using

$$Theoretical\ capacity\ = \left(\frac{nF}{3600\ M}\right) \times 1000\left(\frac{mA \cdot h}{g}\right)$$

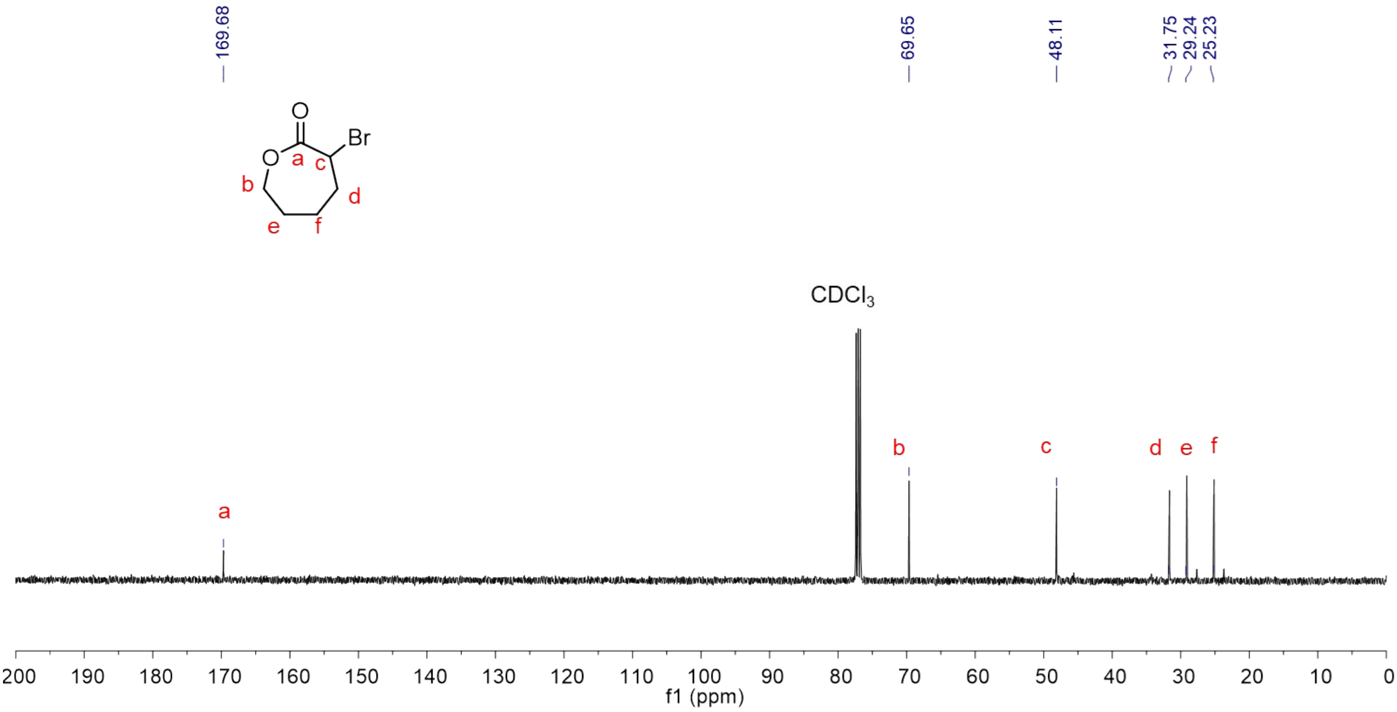
Equation S1

Where n is the moles of electrons transferred per molecule of repeat unit, F is Faraday constant (≈ 96,485 s·A·mol^{-1}), M is the molar mass (g·mol^{-1}) of the molecule of polymer repeat unit. Capacity was calculated using the discharged state for pendant group, TEMPO. The theoretical capacity was 66.26 mA·h·g^{-1}.

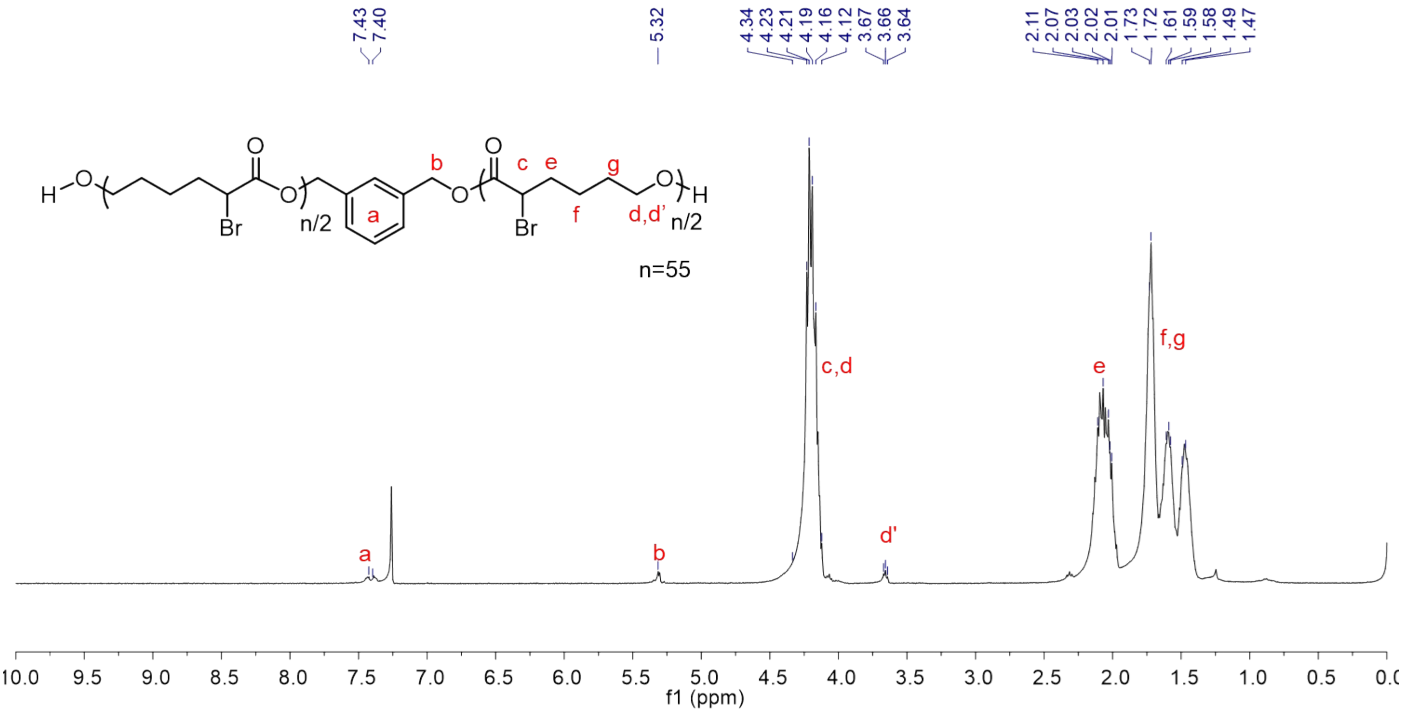
Spectral copies of ^{1}H and ^{13}C NMR



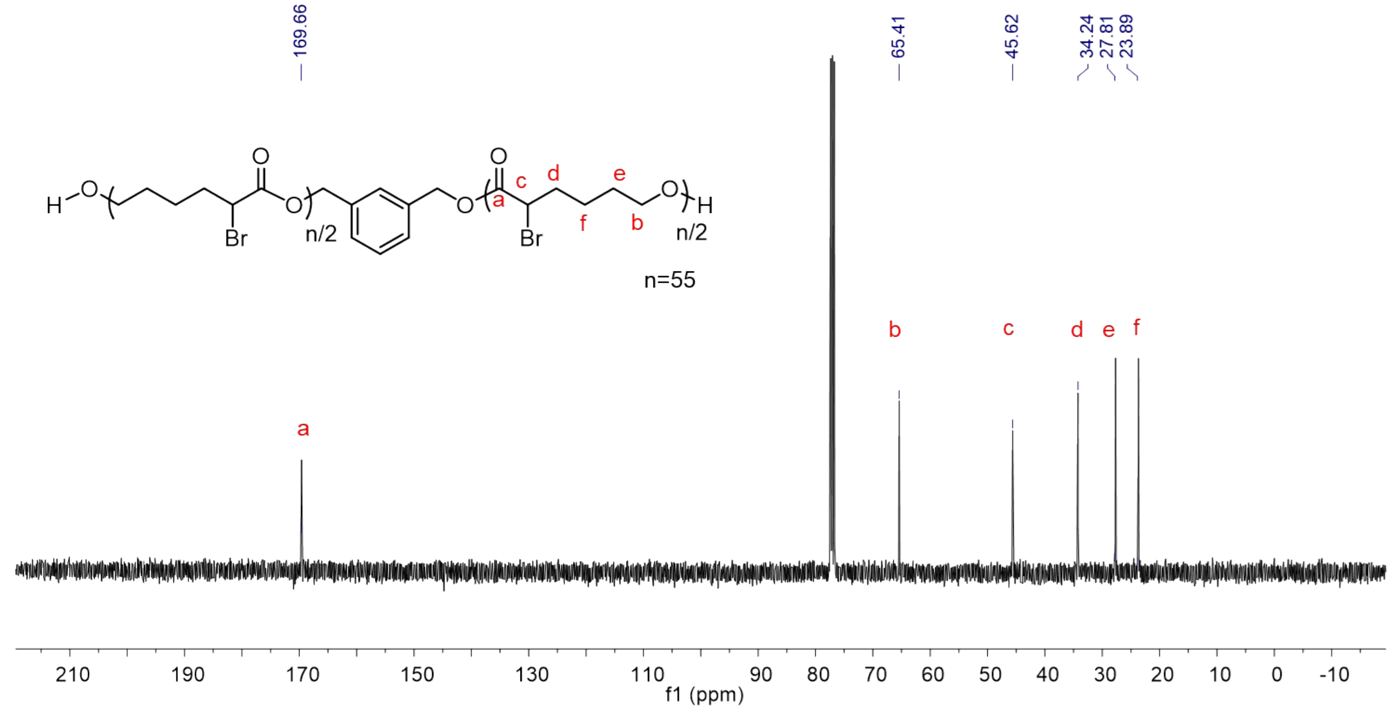
^{1}H NMR of **CL-Br** in $CDCl_3$ (400 MHz)



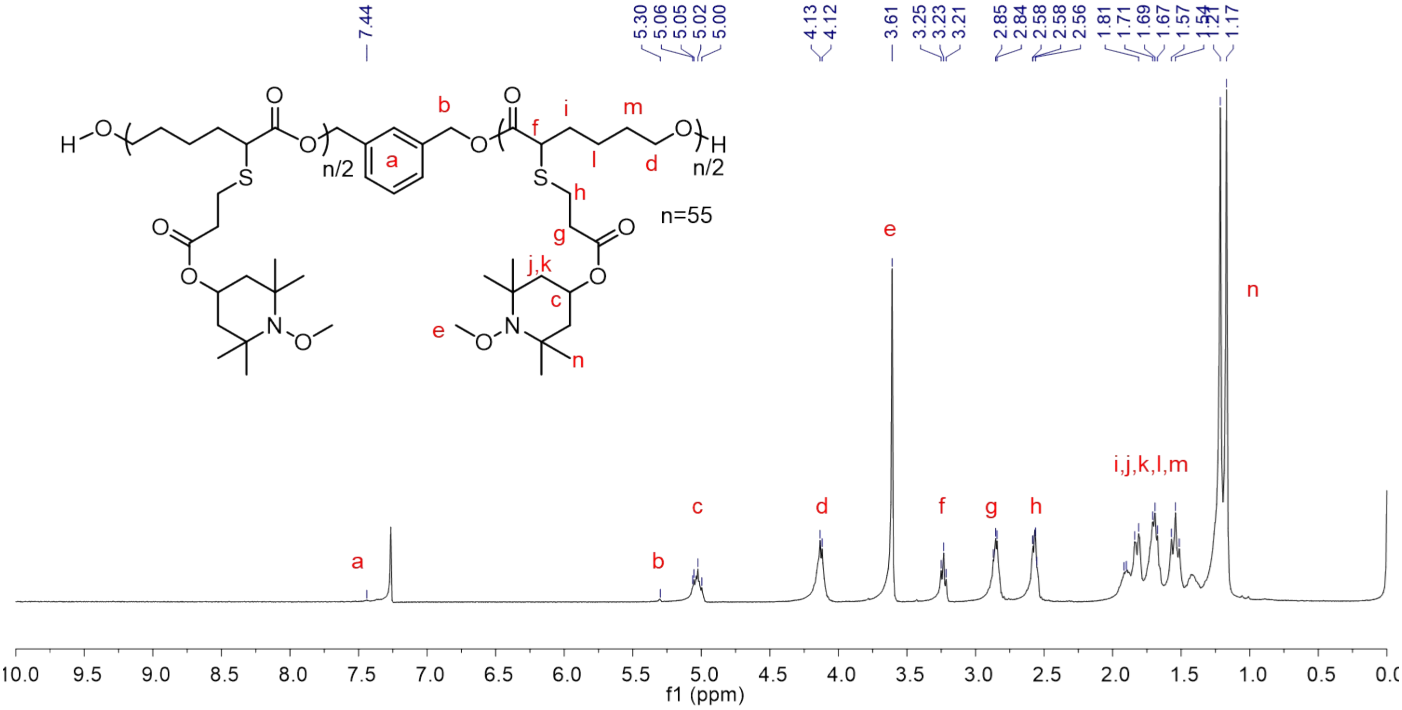
^{13}C NMR of **CL-Br** in $CDCl_3$ (101 MHz)



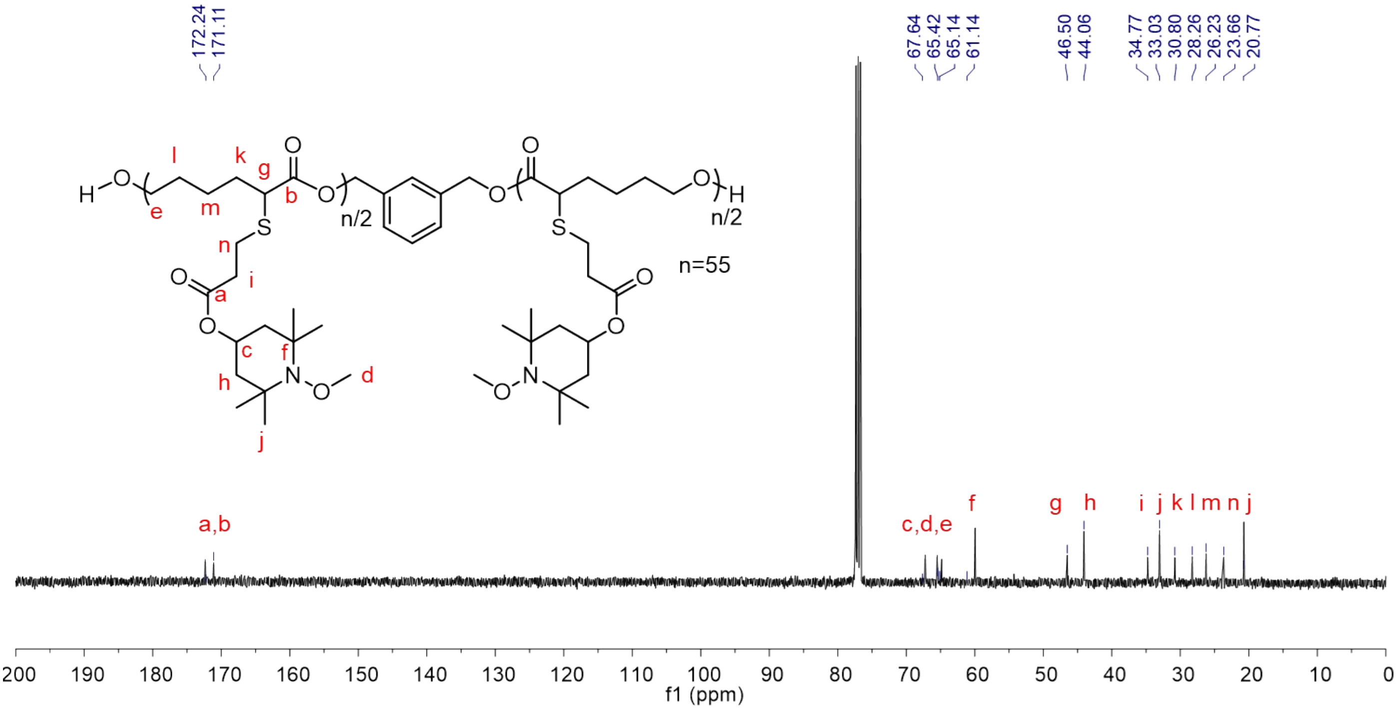
^{1}H NMR of **PCL-Br** in $CDCl_3$ (400 MHz)



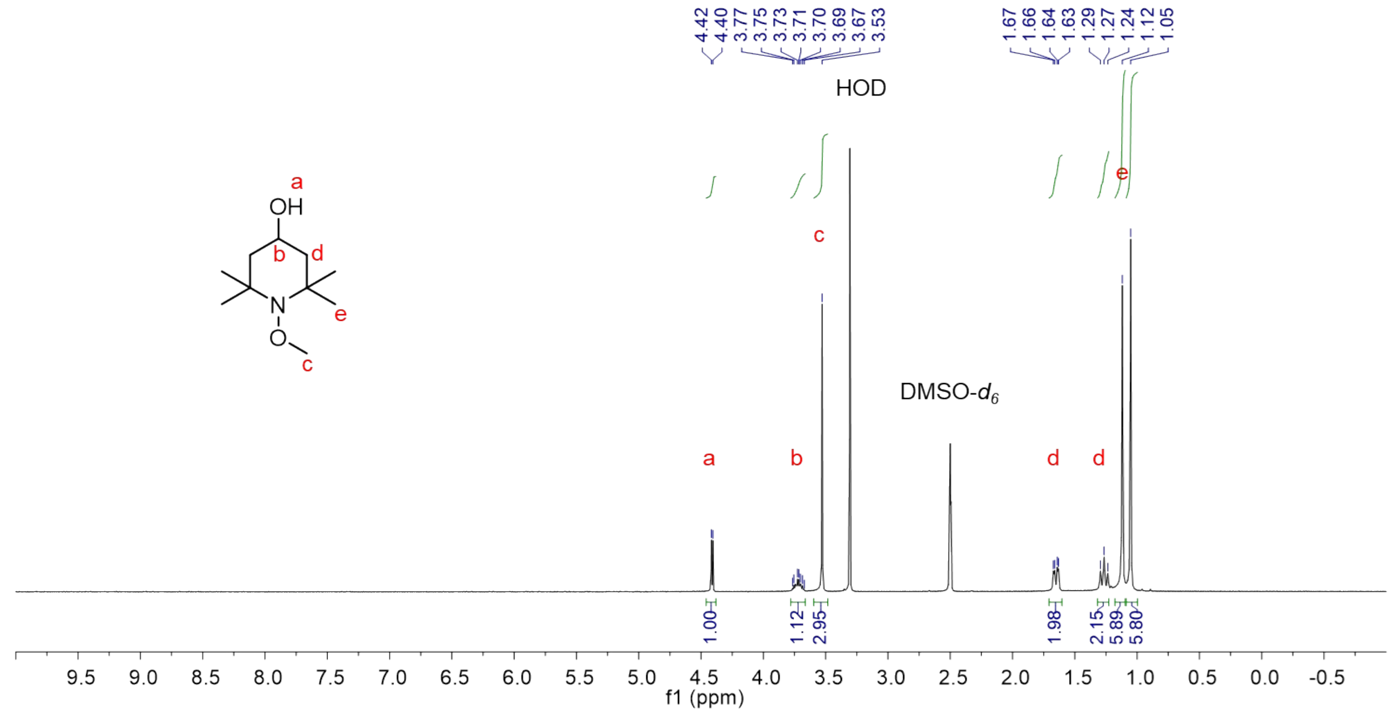
^{13}C NMR of **PCL-Br** in $CDCl_3$ (101 MHz)



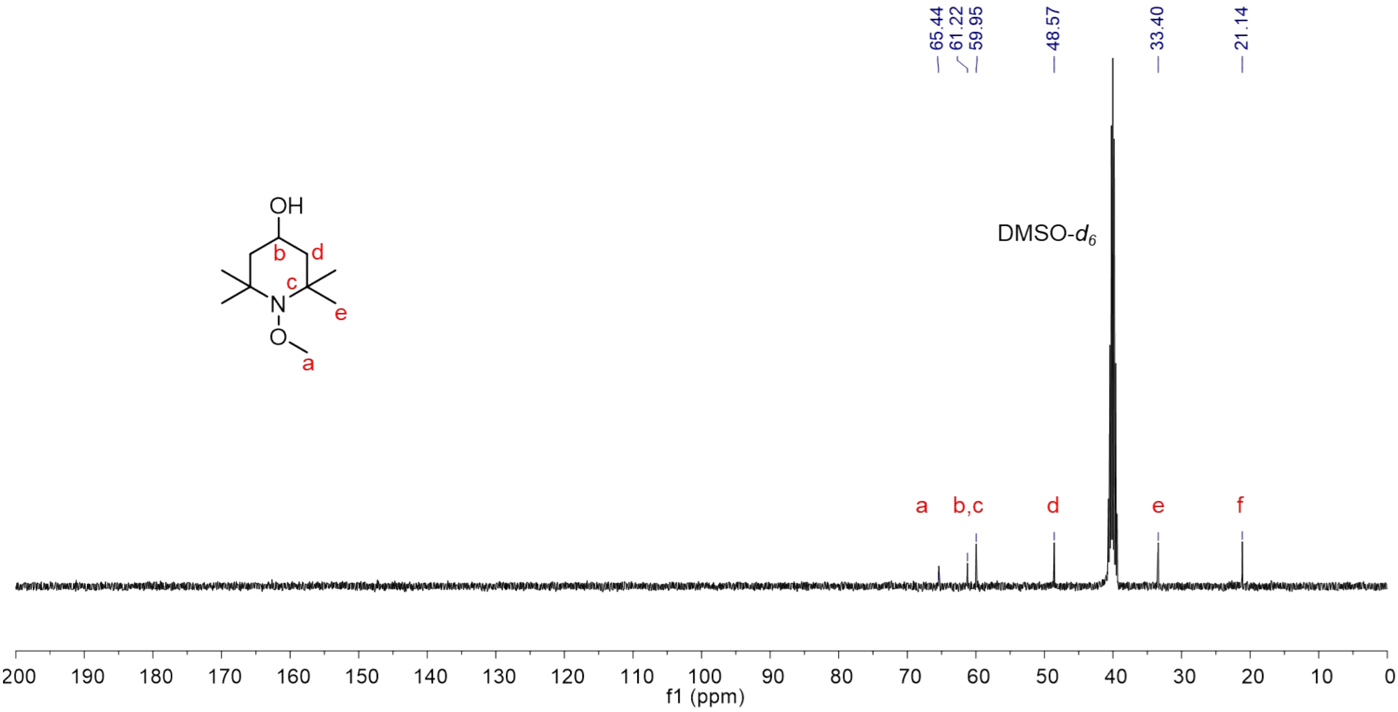
^{1}H NMR of **PCL-MTEMPO** in $CDCl_3$ (400 MHz)



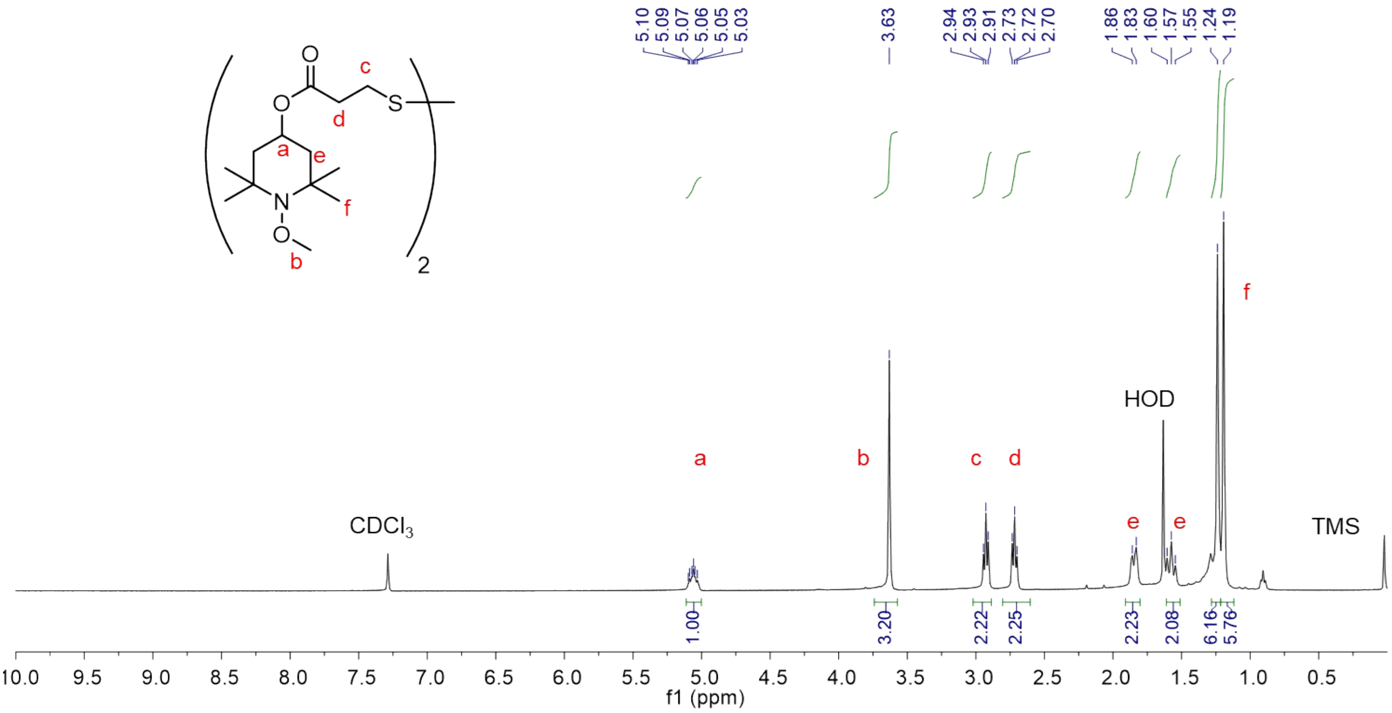
^{13}C NMR of **PCL-MTEMPO** in $CDCl_3$ (101 MHz)



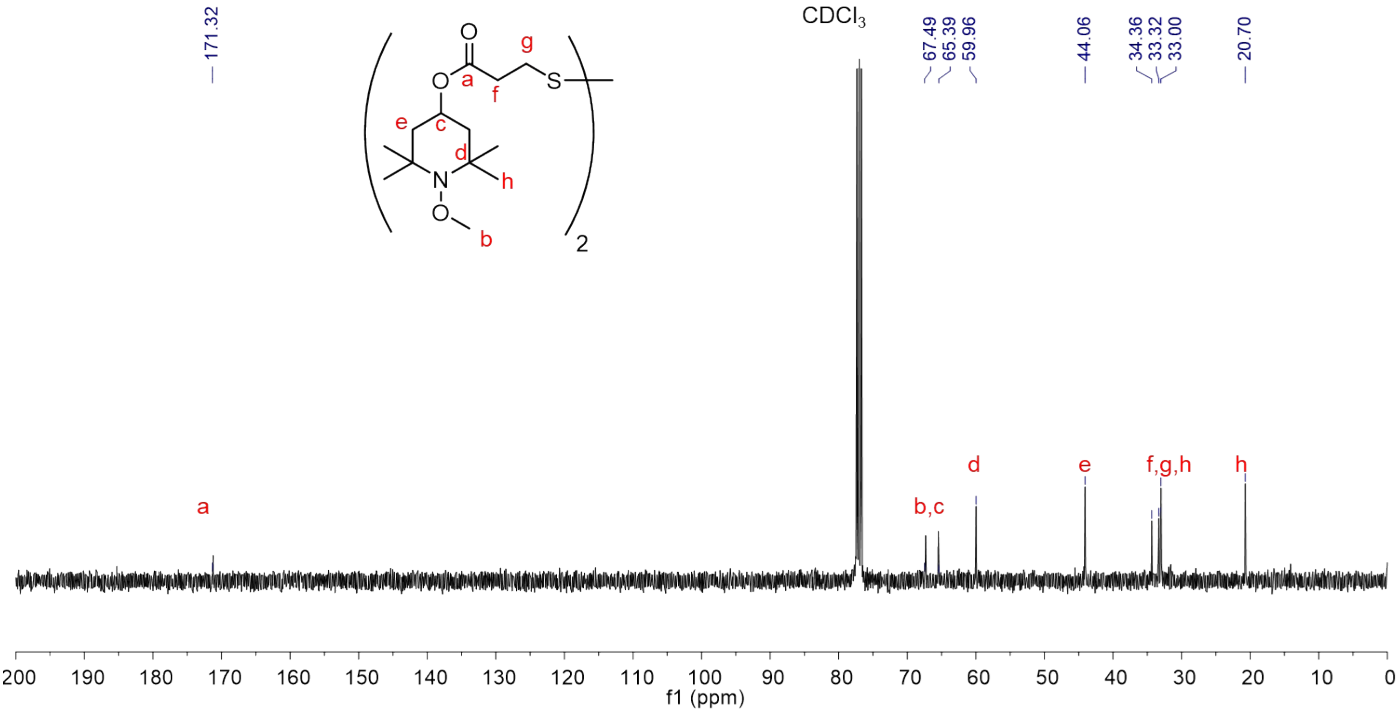
^{1}H NMR of **MTEMPO** in DMSO-d_6 (400 MHz)



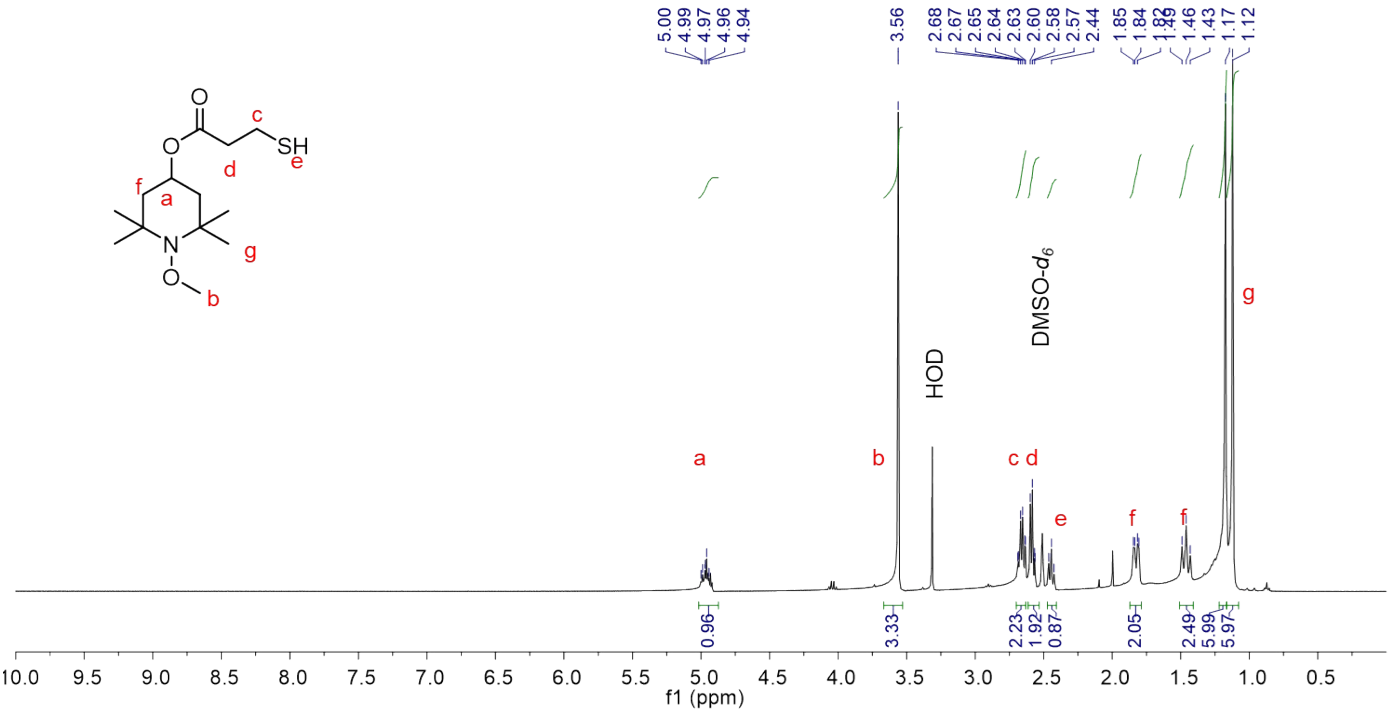
^{13}C NMR of **MTEMPO** in DMSO-d_6 (101 MHz)



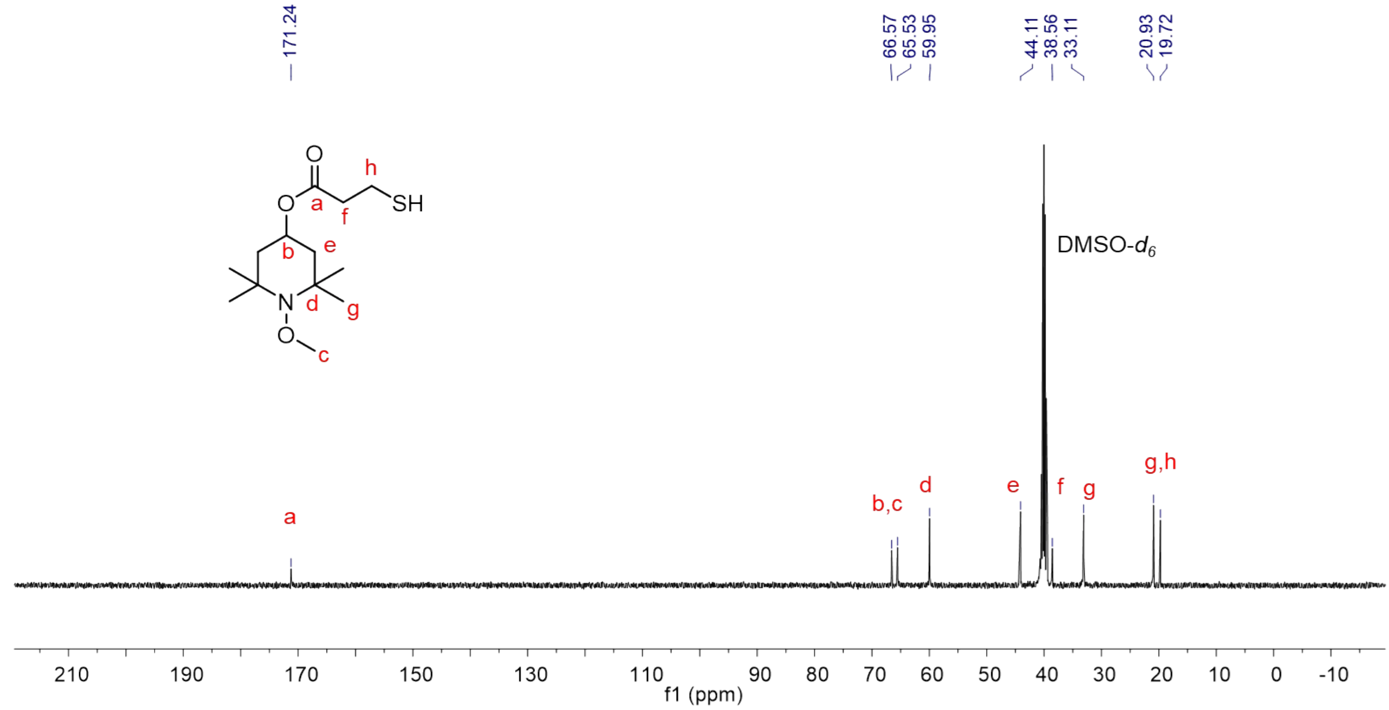
^{1}H NMR of **Di-MTEMPO** in $CDCl_3$ (400 MHz)



^{13}C NMR of **Di-MTEMPO** in $CDCl_3$ (101 MHz)



^{1}H NMR of **MTEMPO-SH** in DMSO-d_6 (400 MHz)



^{13}C NMR of **MTEMPO-SH** in DMSO-d_6 (101 MHz)