***Supporting information***

**A Solvent-free Synthesis of 1-(4-Chlorophenyl)pyrazolidin-3-one in a Ball Mill**

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***General methods***

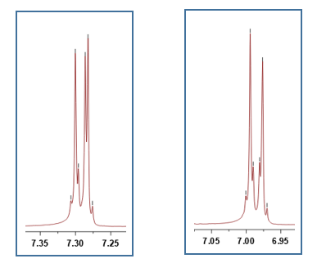
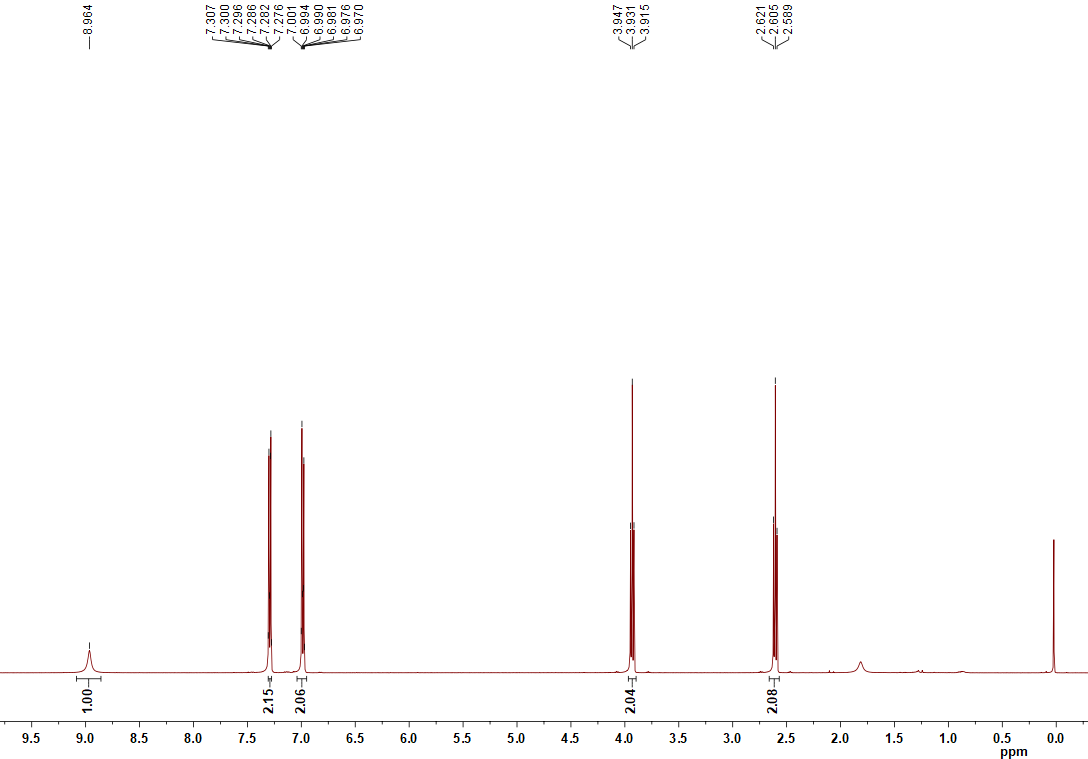
Flash chromatography (FC) was carried out using silica gel (200-300 mesh). Monitoring of reactions was performed by TLC on silica gel precoated on glass plates, and spots were visualized with UV light at 254nm.1H and 13C NMR were recorded in CDCl3 on Bruker AVANCE III (500 MHz for 1H NMR and 126 MHz for 13C NMR). TMS served as internal standard (δ = 0 ppm) for 1H NMR and CDCl3 was used as internal standard (δ = 77.0 ppm) for 13C NMR; 1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. IR were recorded on an EQUINOX 55. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6545 Q-TOF LCMS spectrometer equipped with an ESI source and controlled by using MassHunter software. All experiments were carried out under air. Reactions in the ball mill were conducted using a Fritsch Planetary Micro Mill model “Pulverisette 7”. The milling instrument accommodates two grinding bowls (45 mL) which are made of stainless steel.

***General procedure for the synthesis of 1-(4-Chlorophenyl)pyrazolidin-3-one***

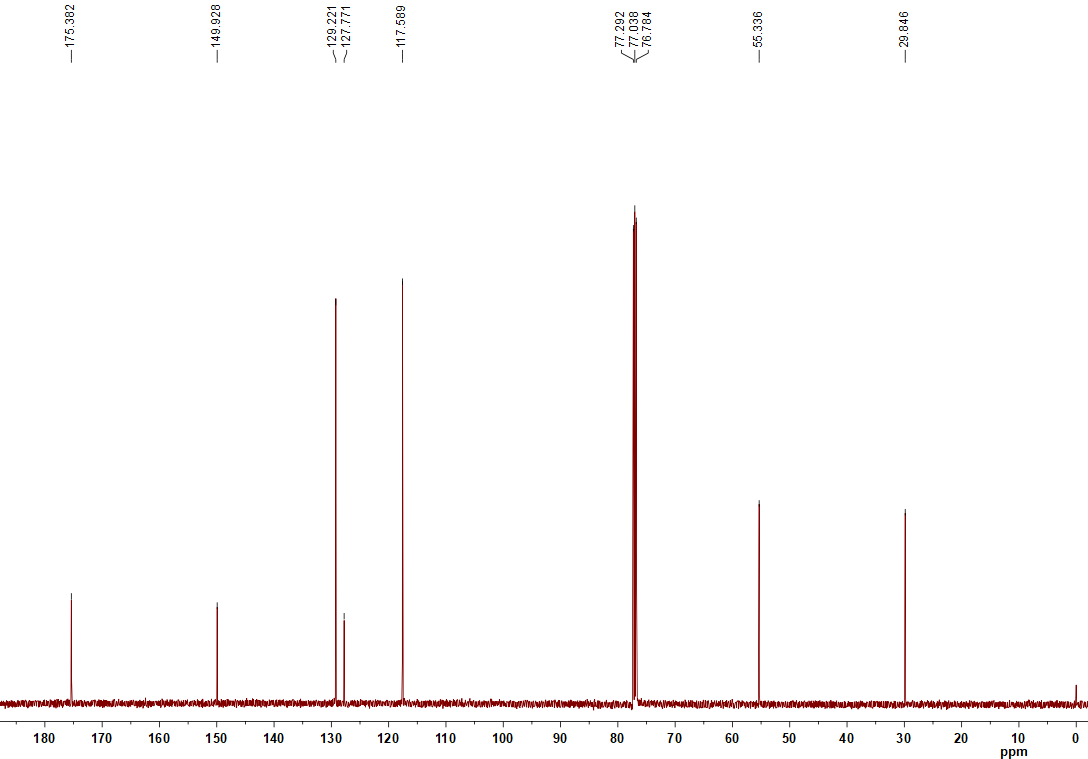
A clean, dry ball milling vessel was charged with 6 Φ10 mm stainless steel balls, 4-chlorophenylhydrazine (0.2 g), methyl acrylate (0.22 g, 1.8 mol equiv.) and KOH powder (0.2 g, 2.5 mol equiv.) were ball milled over periods of 12 cycles (1 cycle = 5 min. rotation + 4 min. pause). Afterwards, the vessel and the balls were rigorously washed with 30ml water; adjust to a pH of 7 using 5% HCl. The aqueous phase was extracted 3 times with ethyl acetate, and the combined organic phase were dried over Na2SO4, filtered off, and was concentrated to dryness under reduced pressure. The residue was purified via silica gel column chromatography.

***Characterization data***

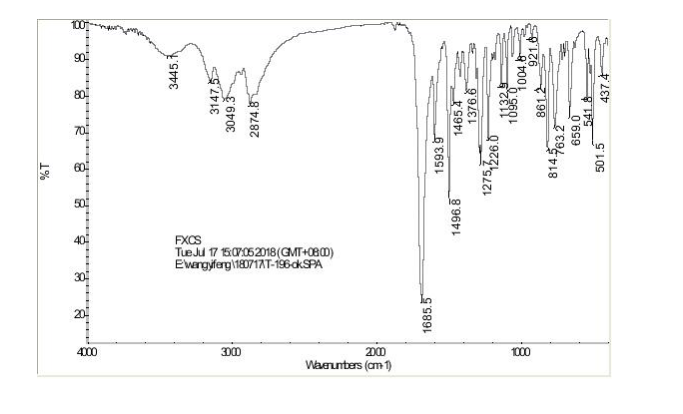
White solid; mp: 108.5-110.5 °C; 1H NMR (500 MHz, Chloroform-*d*) δ 8.96 (s, 1H, NH), 7.29 (m, part AA’ of the AA’BB’ system, *J* = 9.0 Hz, 3.0 Hz, 2H, H-2 and H-6, ClPh), 6.99 (m, part BB’ of the AA’BB’ system, *J* = 9.0 Hz, 3.0 Hz, 2H, H-3 and H-5, ClPh), 3.93 (t, *J* = 8.0 Hz, 2H, NCH2), 2.60 (t, *J* = 8.0 Hz, 2H, COCH2). 13C NMR (126 MHz, Chloroform-*d*) δ 175.38, 149.93, 129.22, 127.77, 117.59, 55.34, 29.85. IR (film) 1685, 1594, 1497, 1465, 1276 cm-1. HRMS (ESI) exact mass calculated for C9H8ClN2O ([M-H]-) requires m/z 195.0331. Found m/z 195.0327.

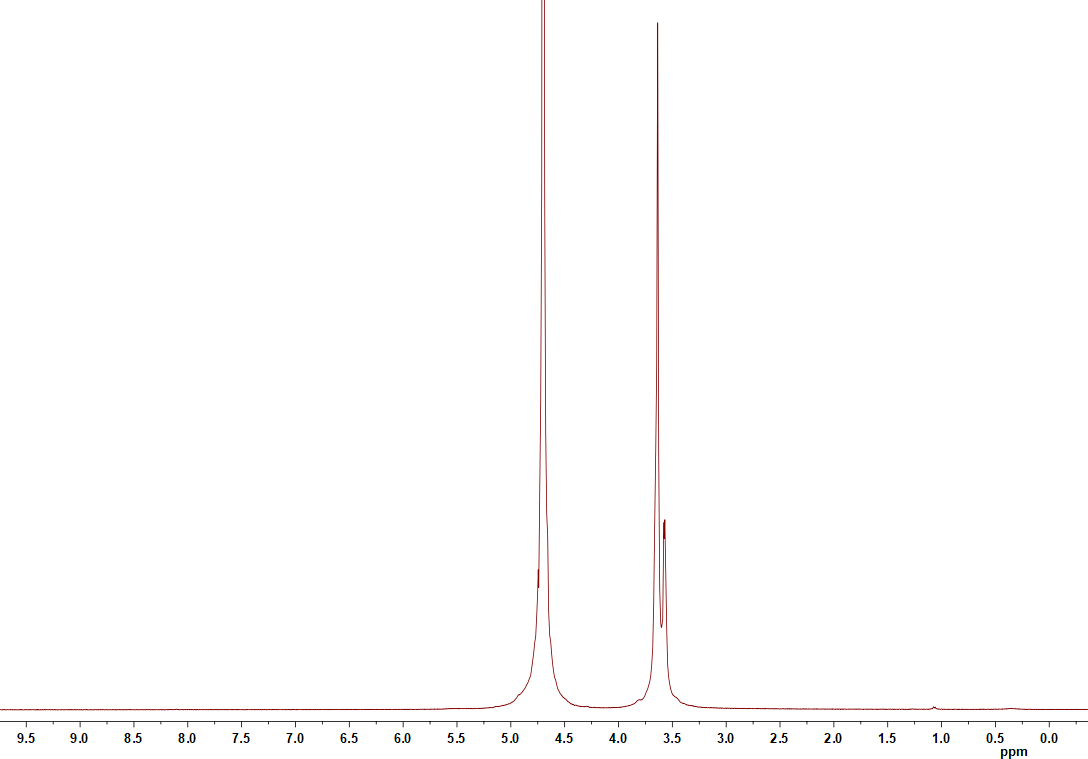
**Fig S1**: 1H-NMR spectra for 1-(4-Chlorophenyl)pyrazolidin-3-one



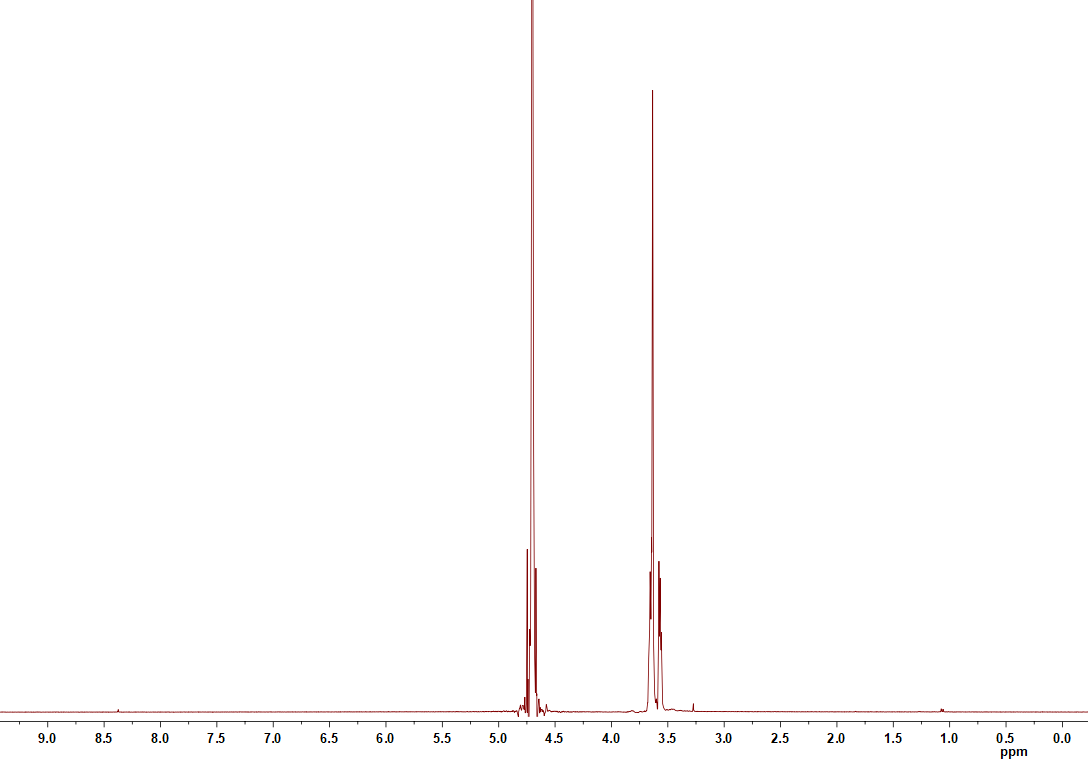
**Fig S2**: 13C-NMR spectra for 1-(4-Chlorophenyl)pyrazolidin-3-one



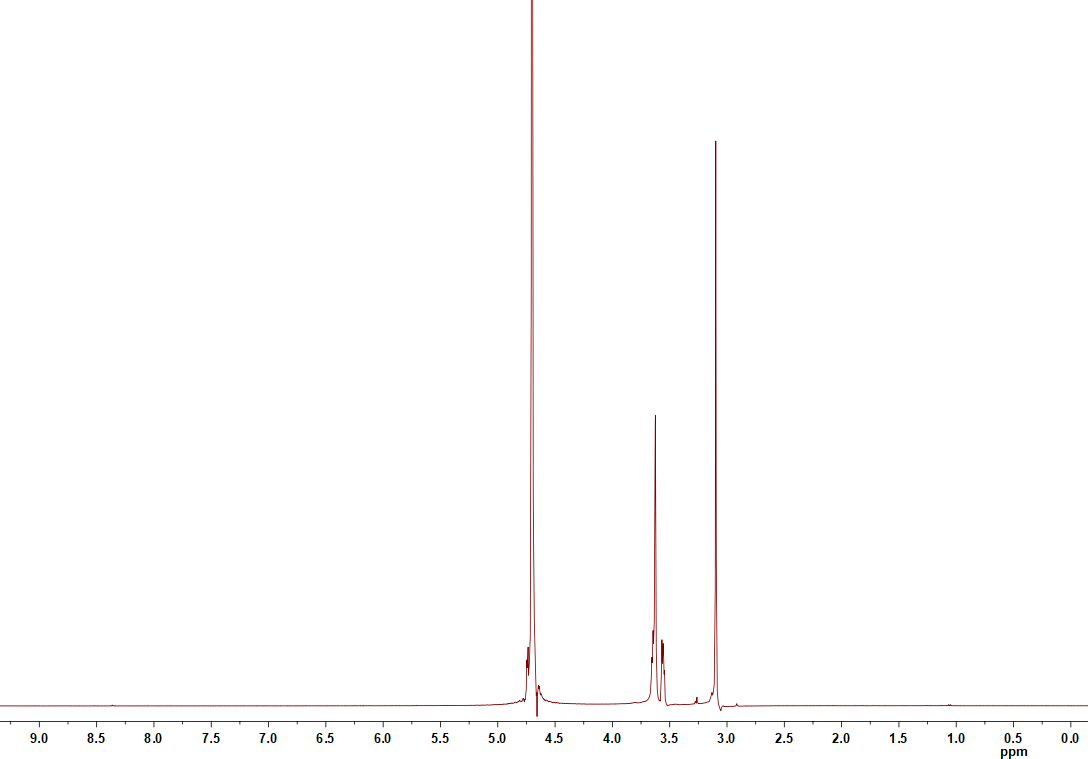
**Fig. S3:** FTIR spectrum of 1-(4-Chlorophenyl)pyrazolidin-3-one



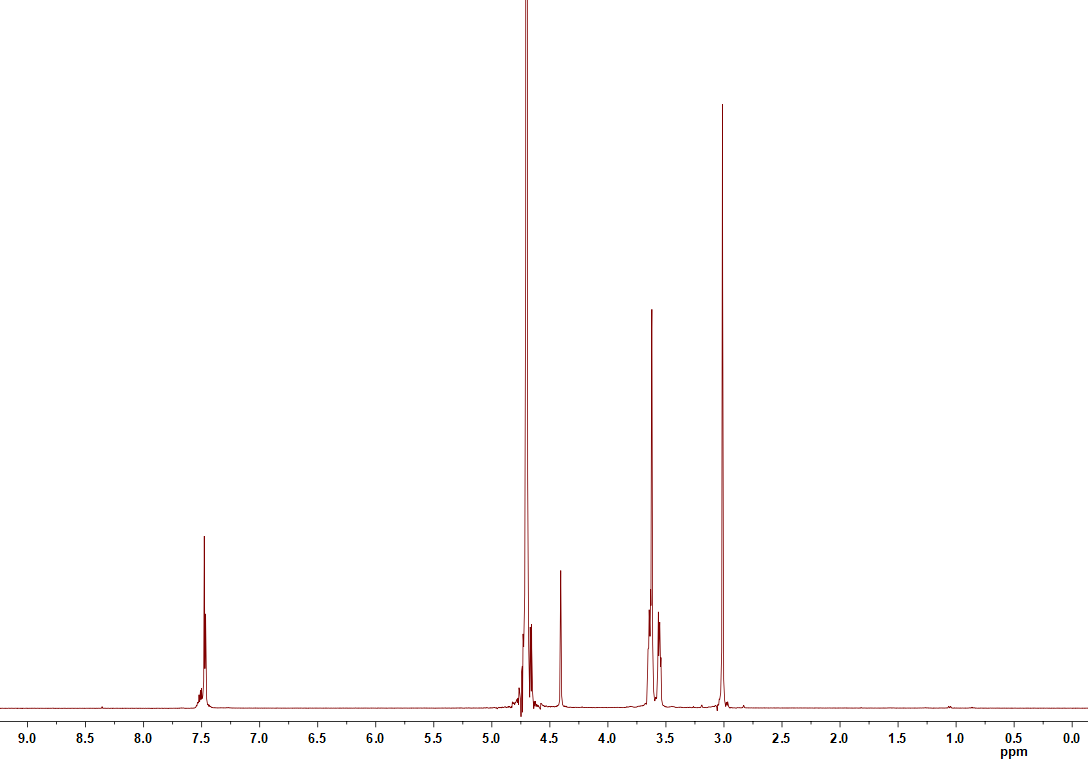
**Fig S4:** 1H-NMR spectra for PEG200



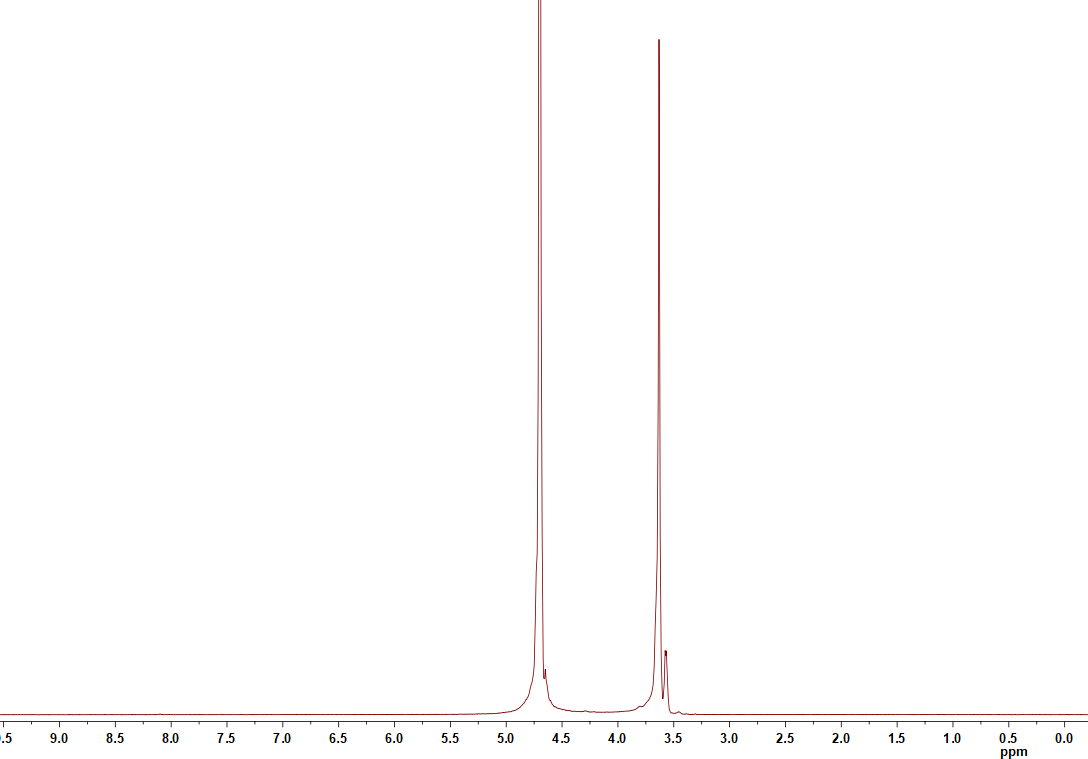
**Fig S5**: 1H-NMR spectra for [PEG200 K+][OH-]



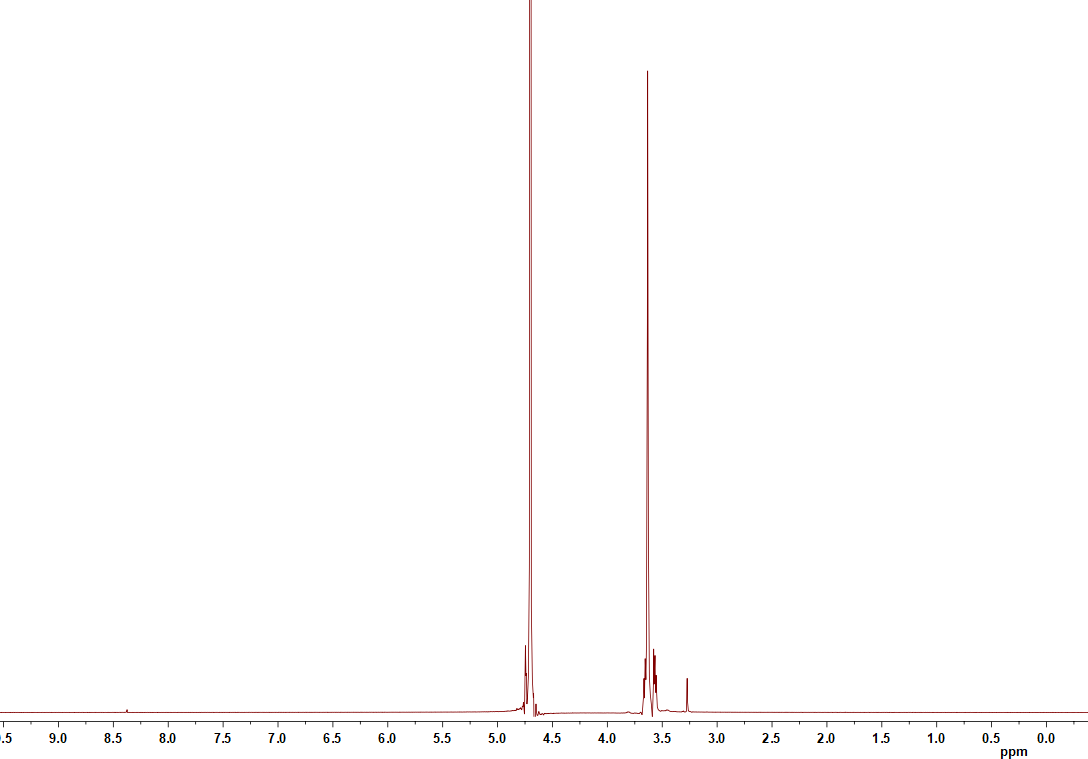
**Fig S6**: 1H-NMR spectra for 



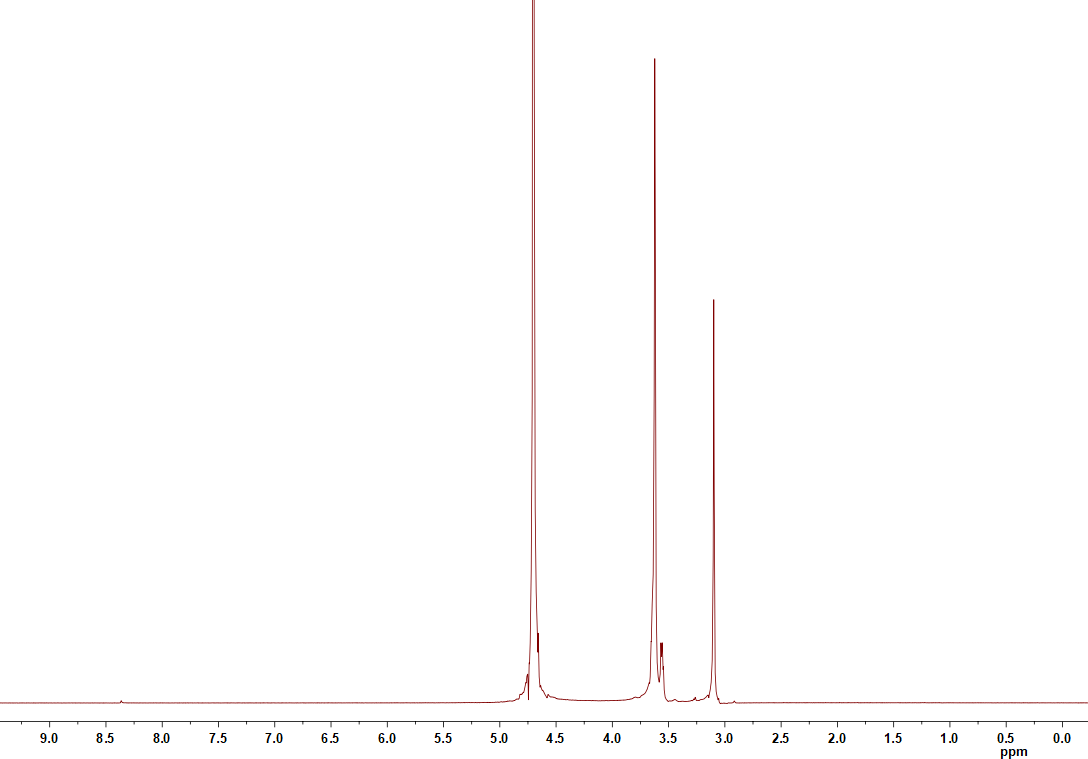
**Fig S7**: 1H-NMR spectra for 



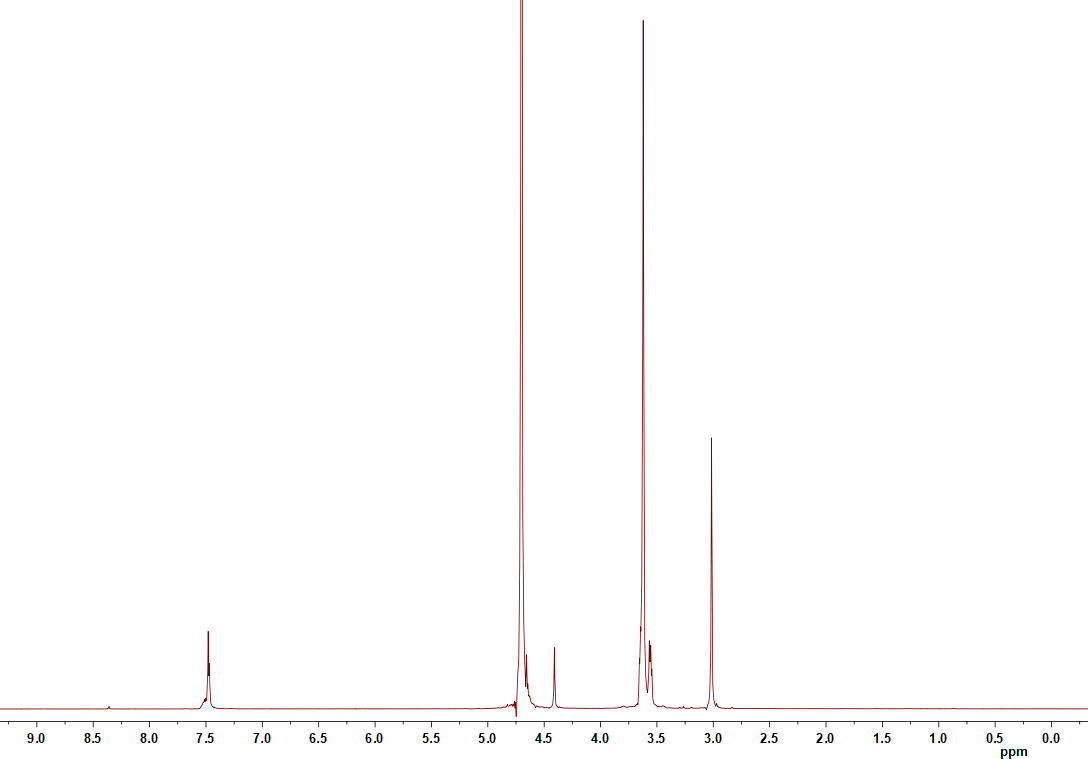
**Fig S8**: 1H-NMR spectra for PEG400



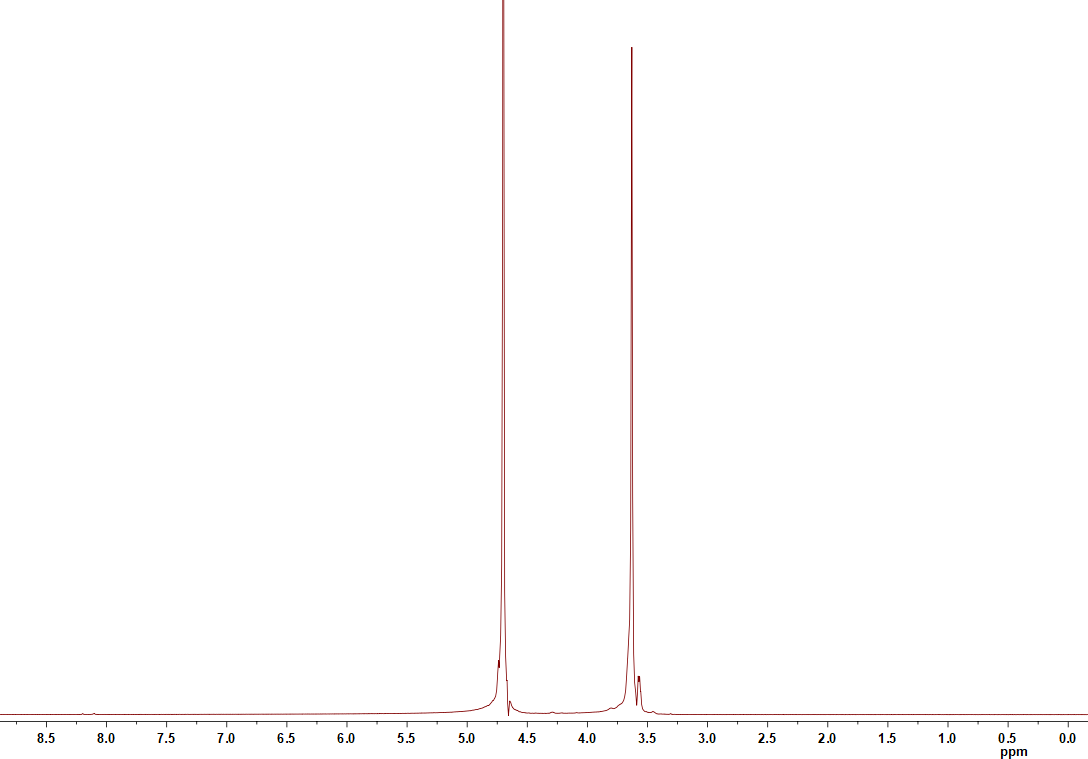
**Fig S9**: 1H-NMR spectra for [PEG400 K+][OH-]



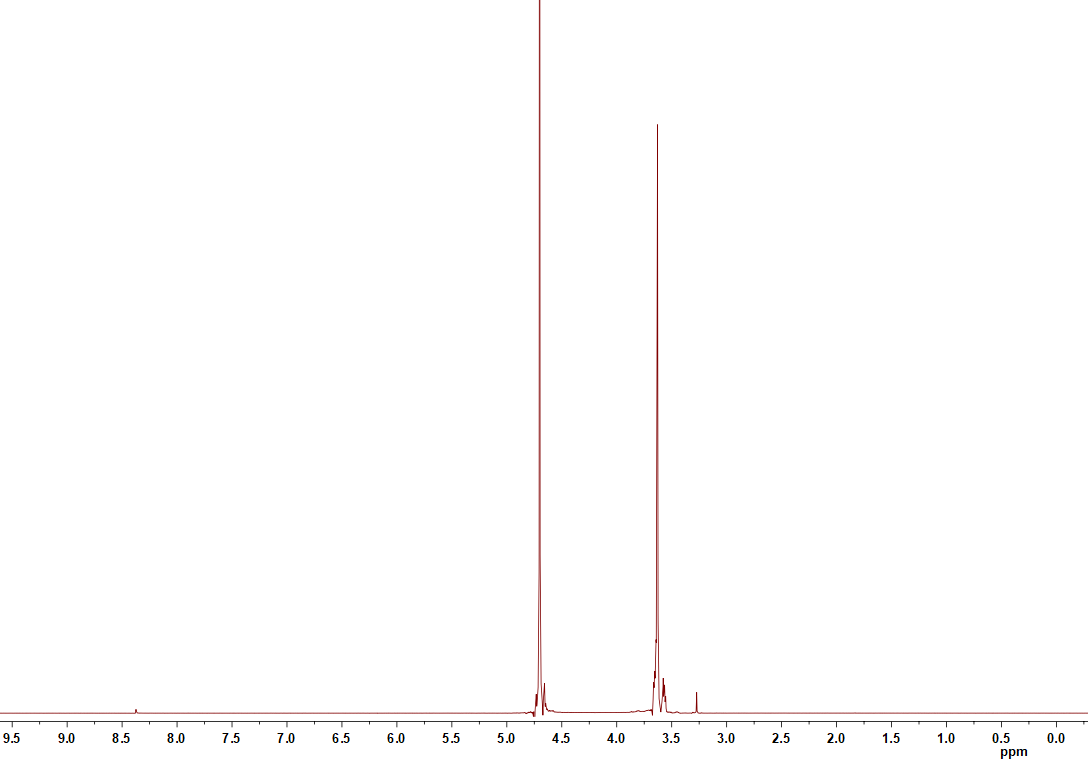
**Fig S10**: 1H-NMR spectra for 



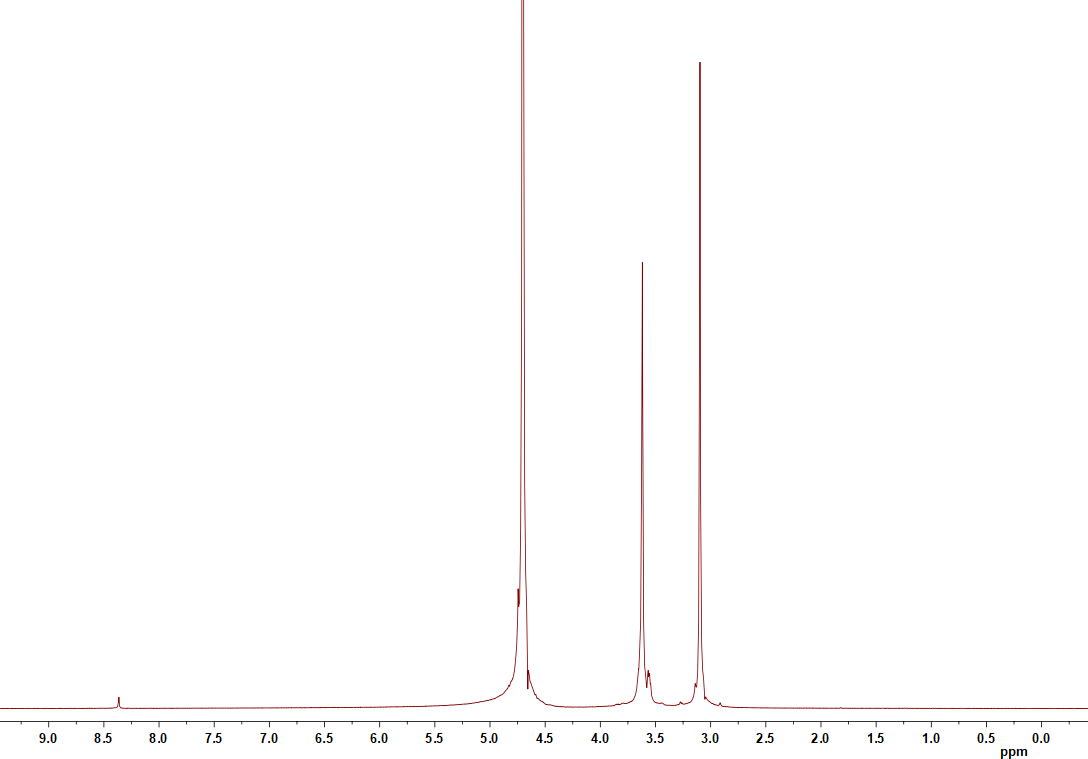
**Fig S11**: 1H-NMR spectra for 



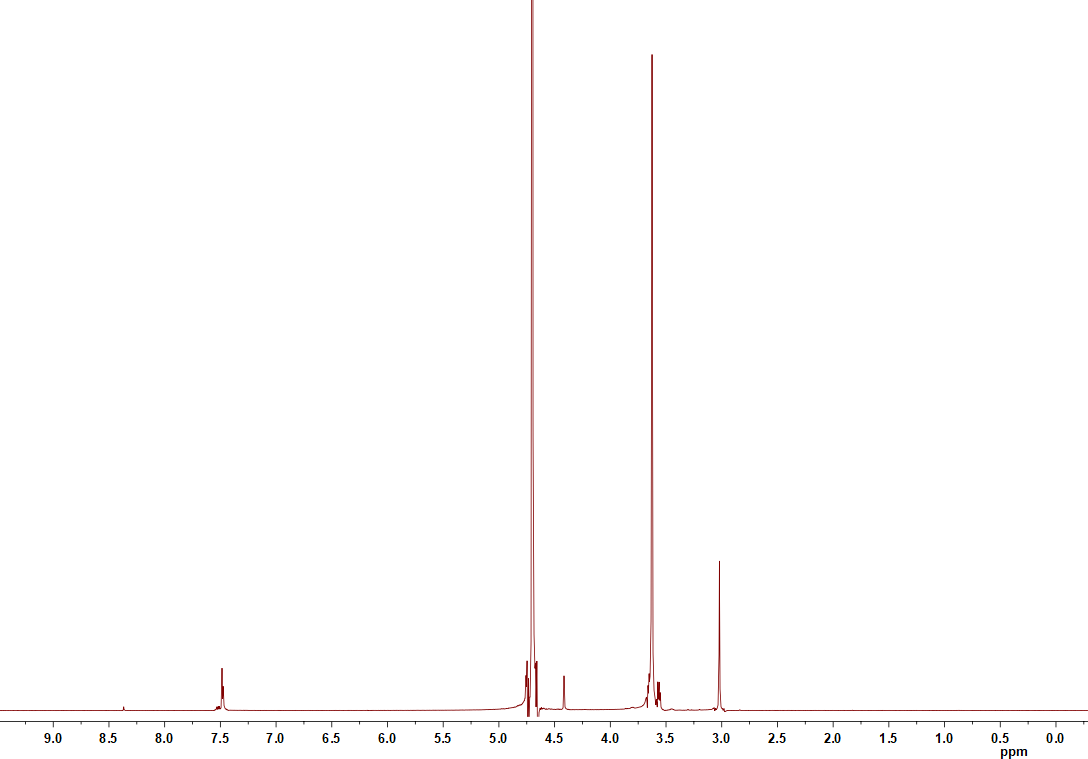
**Fig S12**: 1H-NMR spectra for PEG600



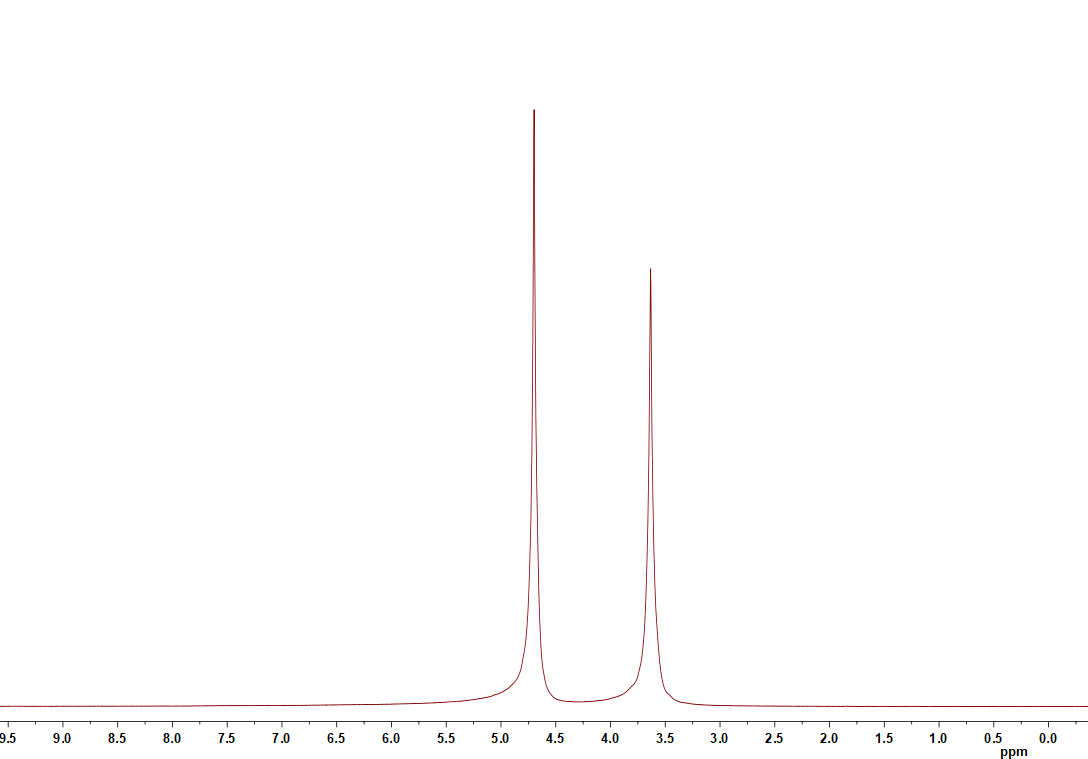
**Fig S13**: 1H-NMR spectra for [PEG600 K+][OH-]



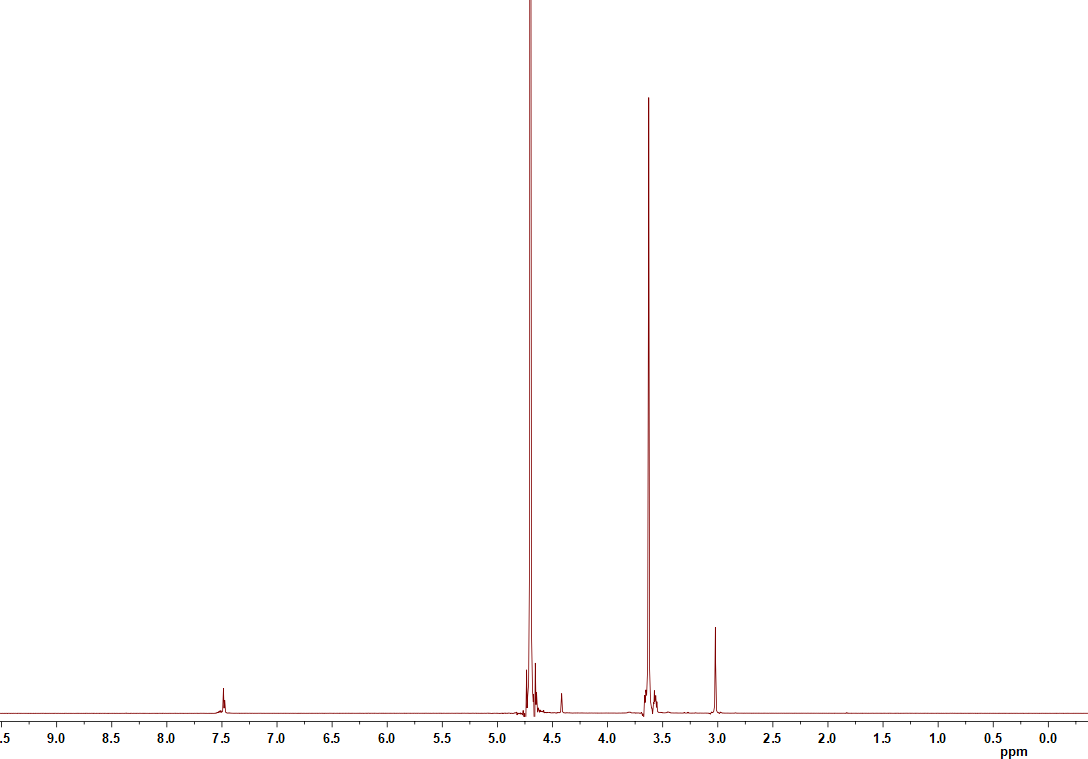
**Fig S14**: 1H-NMR spectra for 



**Fig S15**: 1H-NMR spectra for 



**Fig S16**: 1H-NMR spectra for PEG800



**Fig S17**: 1H-NMR spectra for 