Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Narrowing Down Chain Length Effects on the Antibacterial Action of Guanylated Oligomers

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^{1}H and ^{13}C NMR analysis monomer

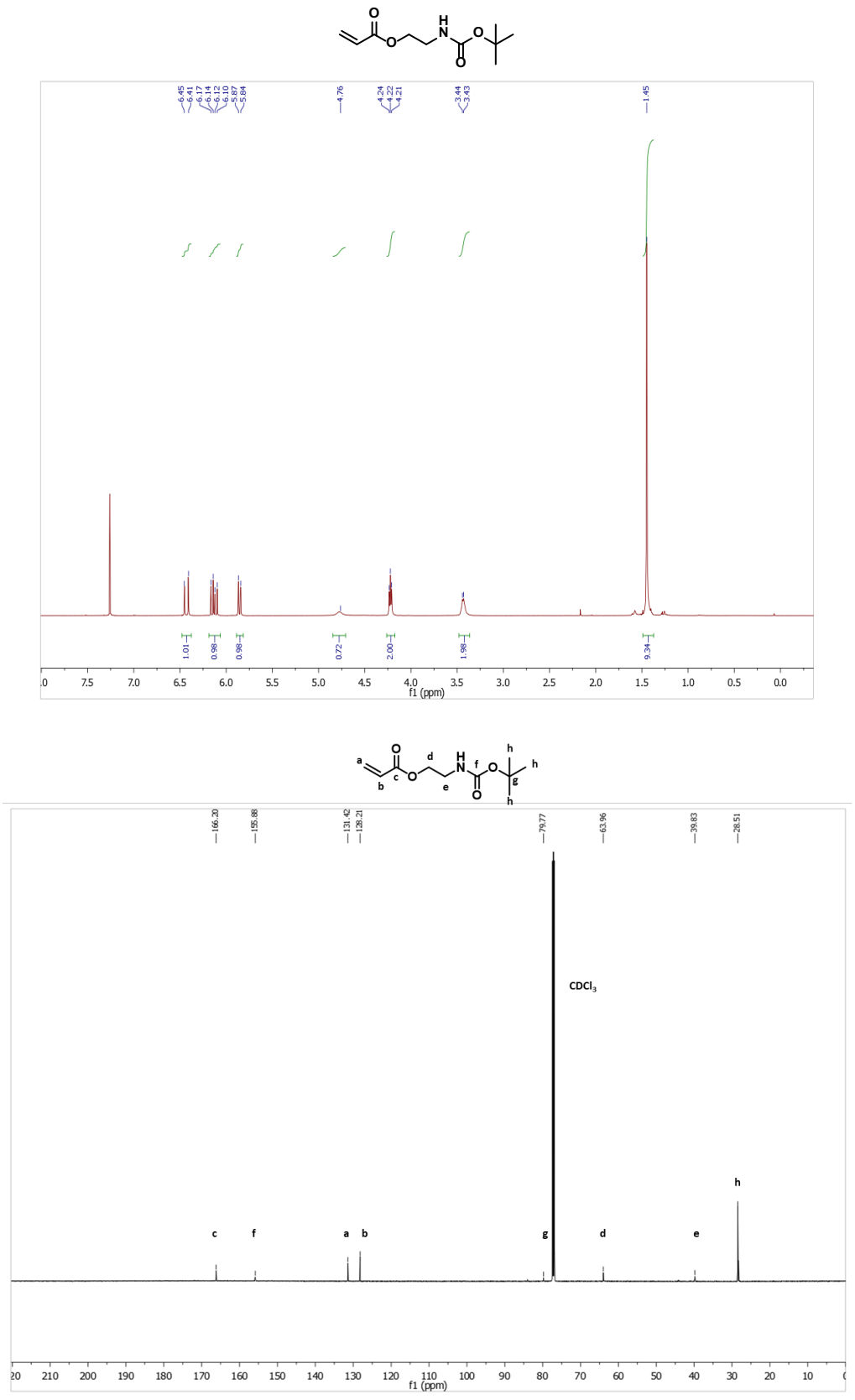

Figure S1: ^{1}H NMR (upper) and ^{13}C NMR (lower) of 2-Boc aminoethyl acrylate

^{1}H NMR analysis of discrete and disperse oligomers before/after thiol-ene reaction and deprotection

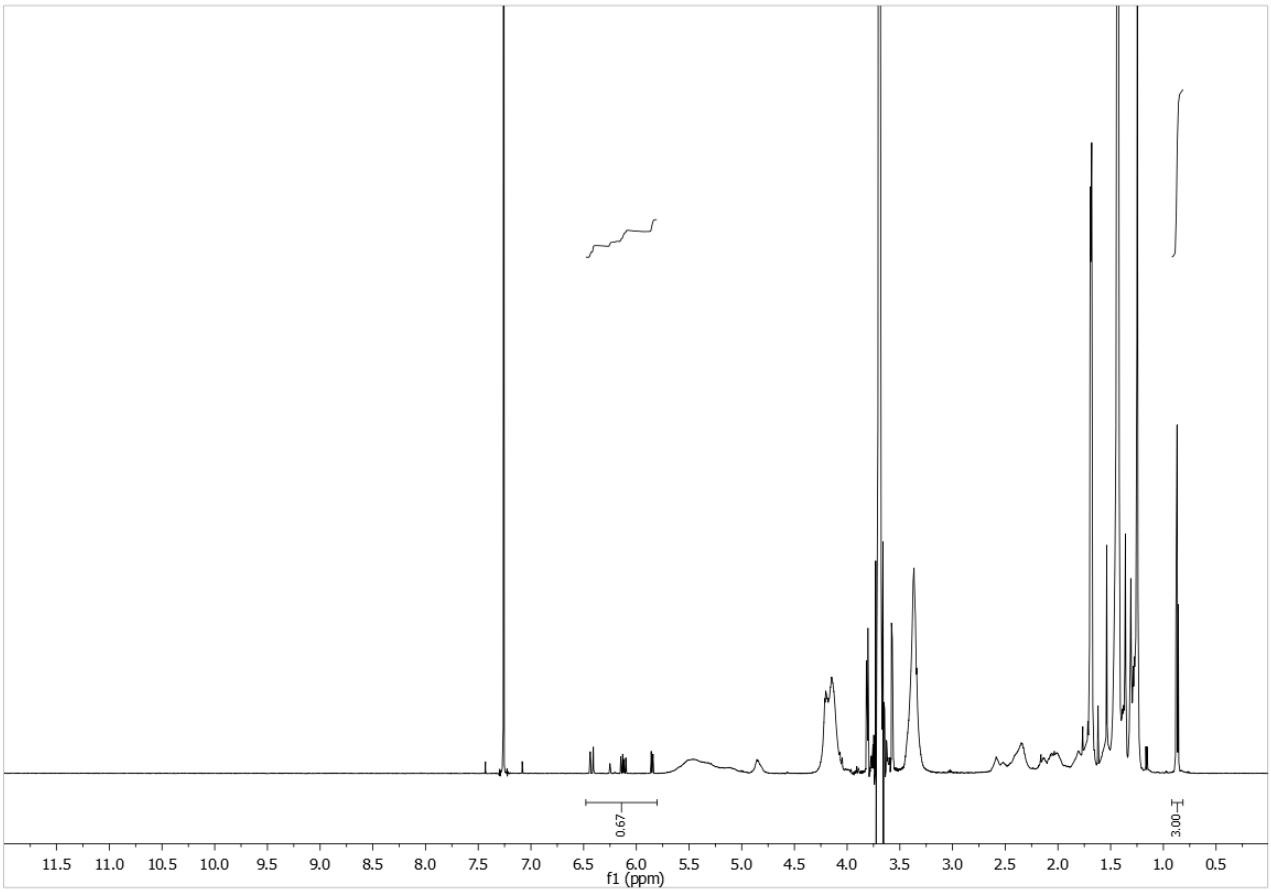

Figure S2: Determination of the monomer conversions of homopolymers of the different model monomers via ^{1}H NMR in $CDCl_3$: comparing the average integration of the vinyl peaks (monomer) to the integration of the endgroup as reference integrated for three protons. A reference sample at 0 minutes reaction time (T_0) was taken to which the vinyl integration were compared. The monomer conversion (p) was calculated using the following formula:

$$p = 1 - \left(\frac{\int I_{vinyl\ peaks\ T_r}}{\int I_{vinyl\ peaks\ T_0}}\right)$$

T_r represents the reaction time after which a sample was taken.

Table S1: Summarizing table of the DP, theoretical and exact masses of monodisperse oligomers isolated through FCC separation and boc deprotection. Exact masses were found on ESI-MS.

Insert	DP	Theoretical mass $(M + H^+)$	Exact mass $(M + H^+)$
1	5	921.486	921.474
2	6	1036.549	1036.550
3	7	1151.612	1151.613
4	8	1266.676	1266.674

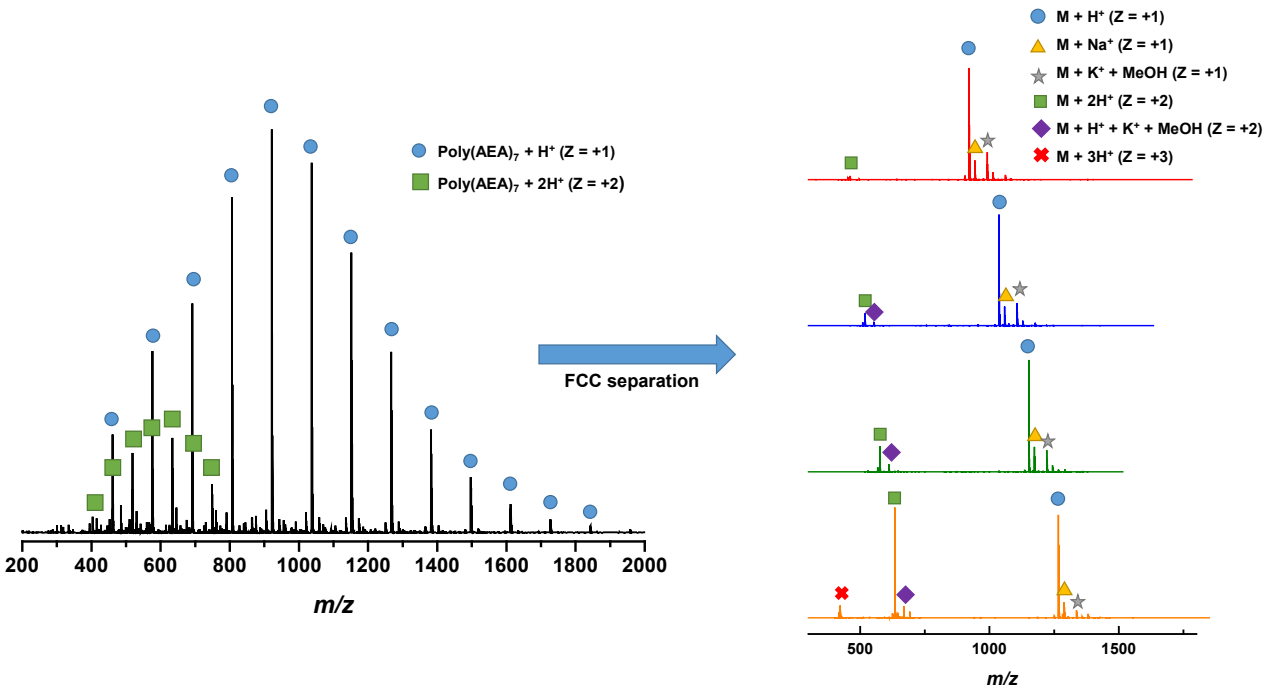

Figure S3: ESI-MS spectra of both crude (left) poly(AEA)$_7$ and isolated monodisperse oligomers (right) with 5 to 8 monomer insertions. Boc protection group removal was required prior to ESI-MS analysis to ensure proper ionization of the compounds.

Table S2: Summarizing table of the DP, theoretical and exact masses of monodisperse oligomers after end group modification through aminolysis and *in situ* thiolene coupling and subsequent boc deprotection.

Insert	DP	Theoretical mass $(M + H^+)$	Exact mass $(M + H^+)$
1	5	917.5628	917.5684
2	6	1032.6261	1032.6351
3	7	1147.6894	1147.6991
4	8	1262.7528	1262.7425

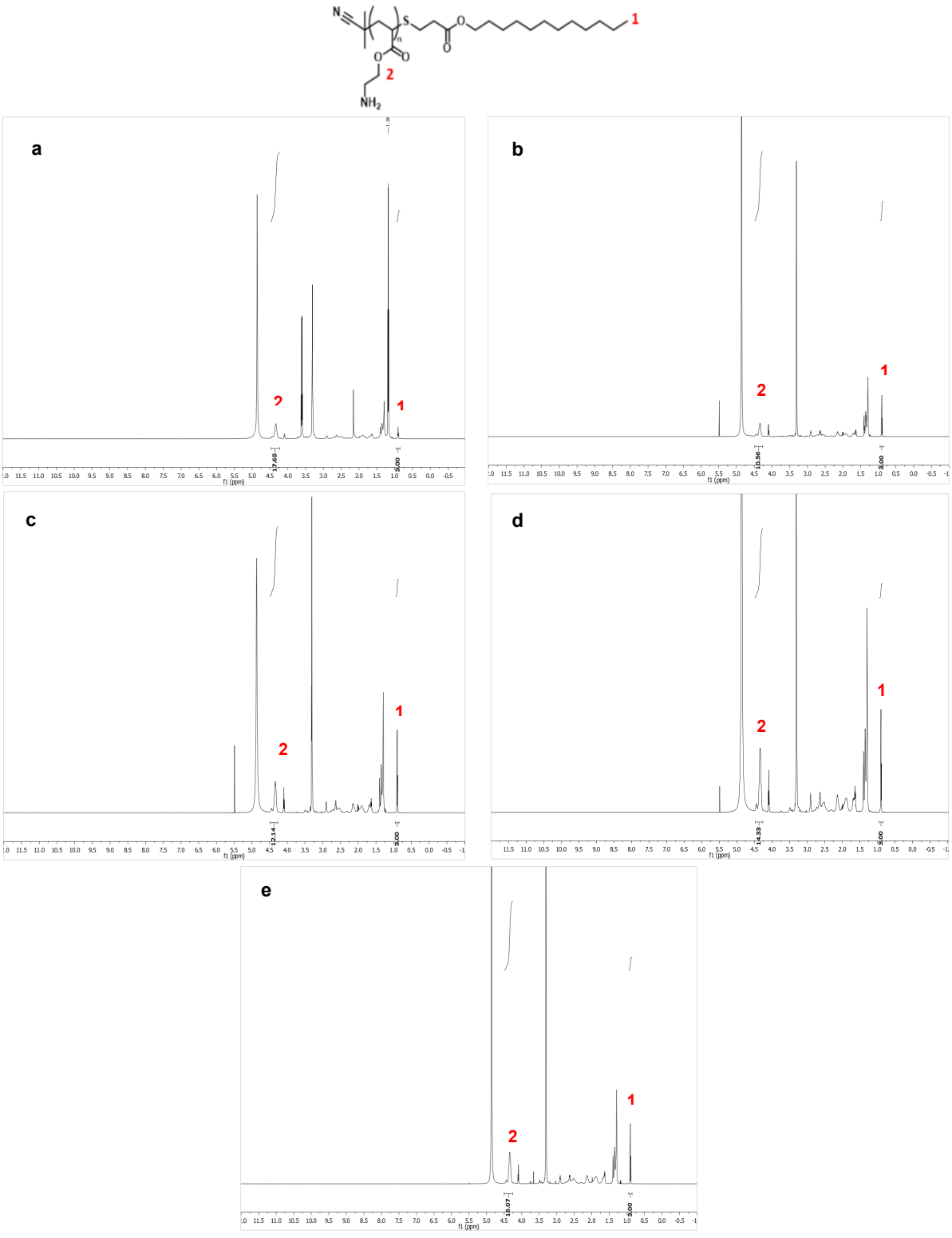

Figure S4: ^{1}H NMR of disperse (**a**) and discrete oligomers with 5 (**b**), 6 (**c**), 7 (**d**) or 8 (**e**) monomer insertions after end-group modification through aminolysis and a *in situ* thiolene coupling with dodecyl acrylate and subsequent deprotection with TFA. Complete Boc removal is confirmed by the absence of a singlet at 1.45 ppm indicative of the tert-butyl protons of Boc protection groups. All NMRs are measured in CD_3OD. The peaks at 1.18 and 3.6 ppm, in spectrum **a**, and at 5.49 ppm in spectrum **c** and **d** are residual peaks of diethyl ether and DCM respectively.

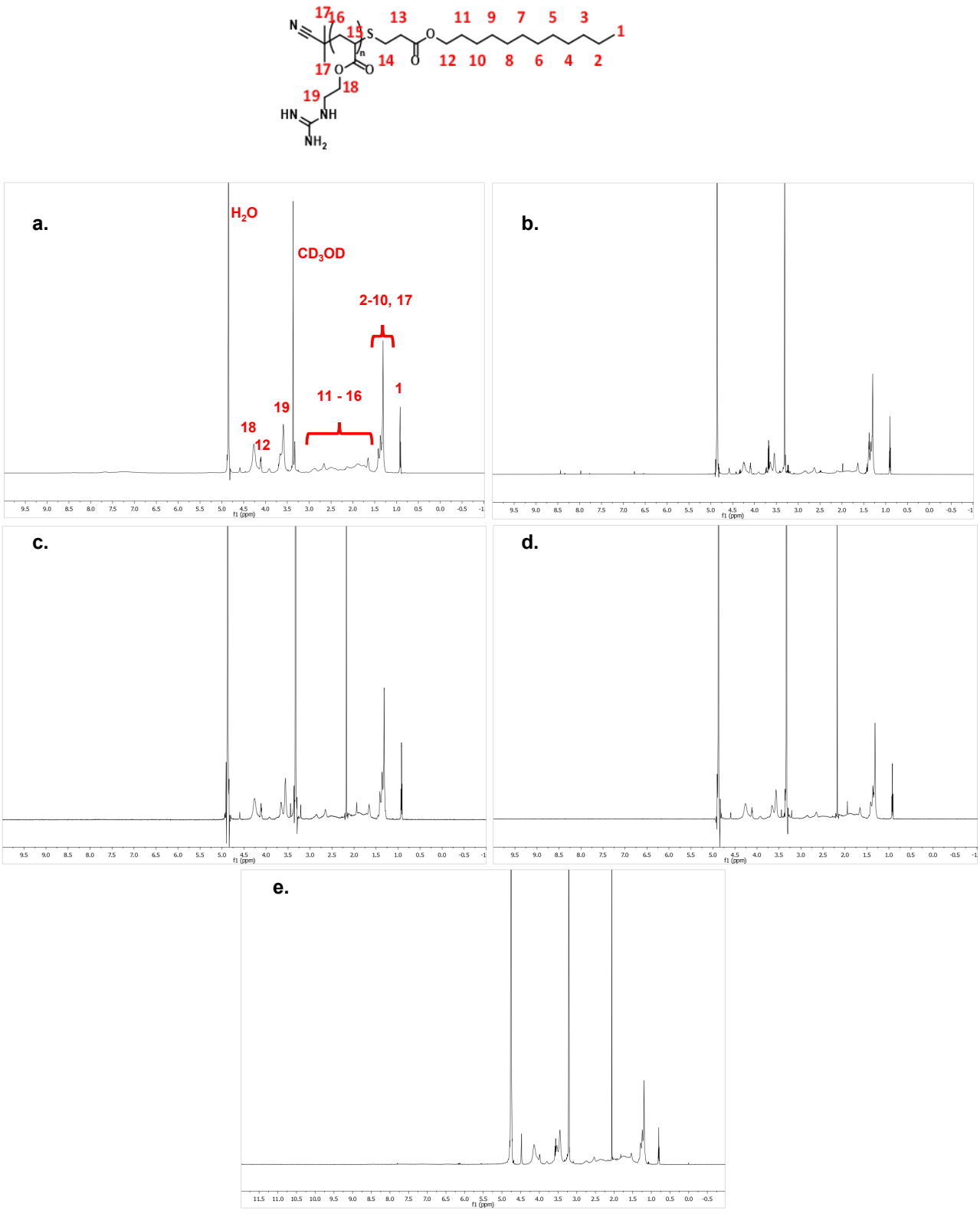

Figure S5: ^{1}H NMR of disperse (**a**) and discrete oligomers with 5 (**b**), 6 (**c**), 7 (**d**) or 8 (**e**) monomer insertions after guanylation. Conversion of primary amines to guanidines is confirmed by a shift in the proton signals adjacent to the functional groups (19) from from ~3.30 ppm (adjacent to amine) to 3.54 ppm (adjacent to guanidine). All NMRs are measured in CD_3OD. The peak at 2.16 ppm in spectrum **c** and **d** is a residual peak of acetone.

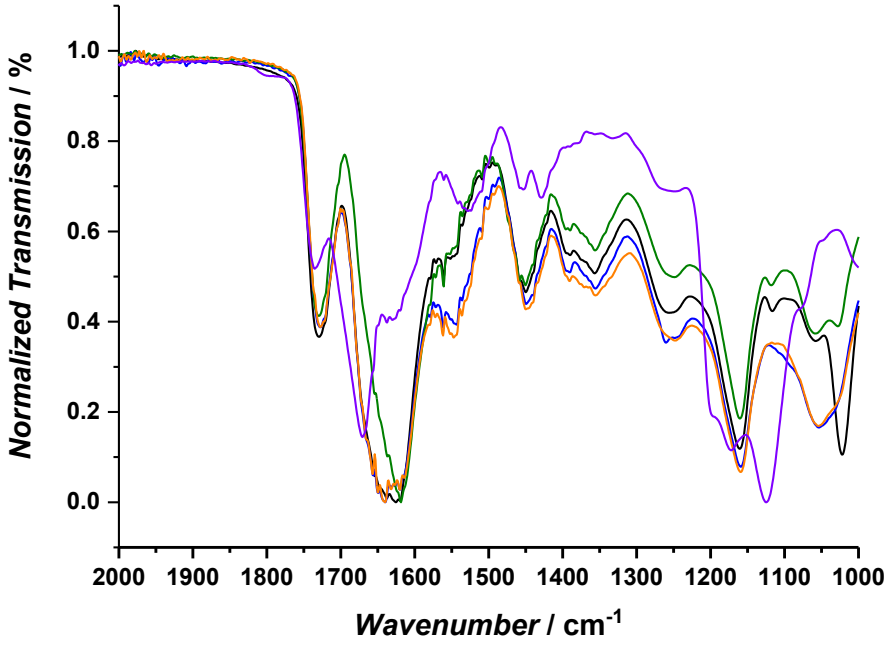

Figure S6: ATR FT-IR spectra of primary amine oligomer (purple) and of guanidine modified oligomers (black – orange). After guanylation, a new peak appears around 1639 cm^{-1} which is indicative of C=N stretching. In addition, no evidence of base induced isomerization of the oligomers is present with the FT-IR spectrum retaining a C=O stretch signal at 1718 cm^{-1} and C-O stretch at 1146 cm^{-1}, both indicating the presence of esters.