Supplementary Information

Synthesis and Characterization of Amphiphilic Cyclic Diblock Copolypeptoids from *N*-Heterocyclic Carbene-Mediated Zwitterionic Polymerization of *N*-Substituted *N*-carboxyanhydride

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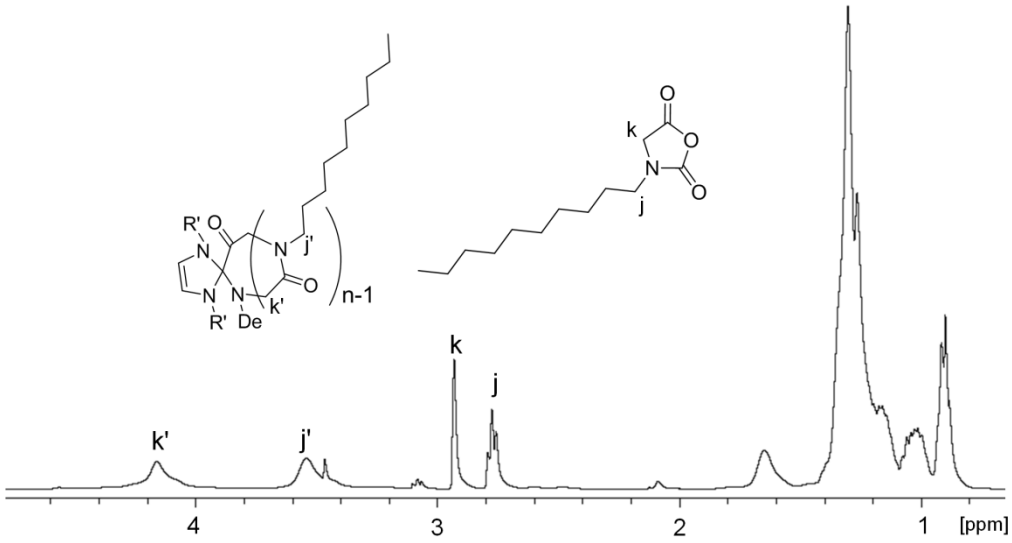

Figure S1. Representative ^{1}H NMR spectrum of a NHC-mediated polymerization of M_1 at 70 ^{o}C in toluene-d_8 showing the formation of cyclic poly(*N*-decyl-glycine) (*c*-PNDG) and unreacted M_1 ($[M_1]_0$:$[NHC]_0$ = 50:1, $[M_1]_0$ = 0.4 M, reaction time = 62 m).

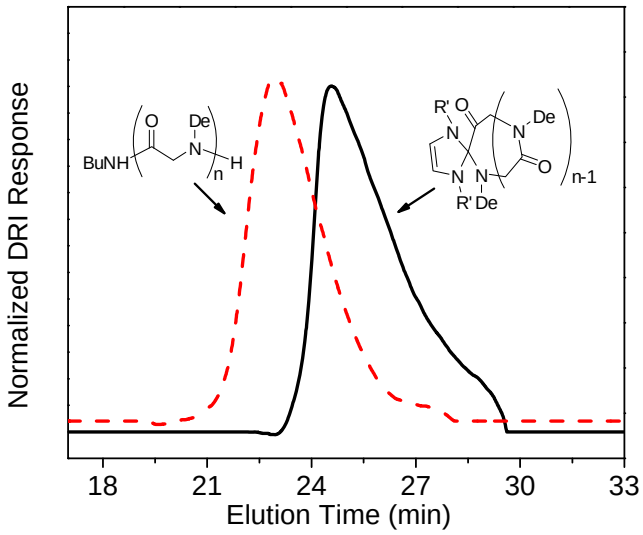

Figure S2. SEC chromatograms of a high MW *c*-PNDG sample (M_n = 20.4 kg·mol^{-1}, PDI = 1.20) (—) and its linear analog (*l*-PNDG) (M_n = 20.8 kg·mol^{-1}, PDI = 1.09) (---) that were independently prepared from the NHC-mediated and $BuNH_2$-initiated polymerization of M_2, respectively.

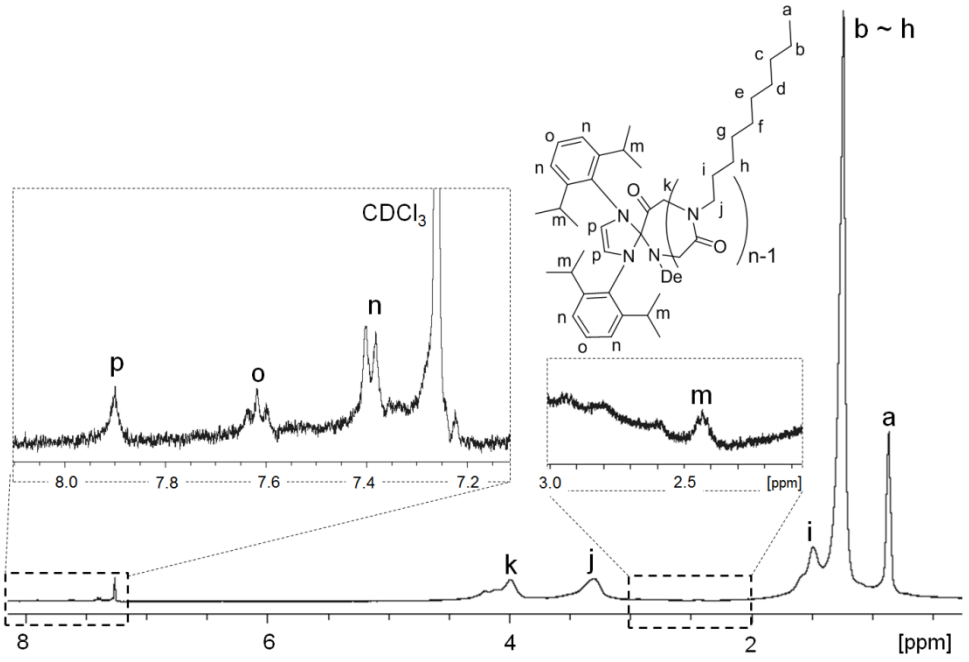

Figure S3. ^{1}H NMR spectrum of a low MW *c*-PNDG in $CDCl_3$/CF_3COOD where proton resonances of the NHC are notably visible.

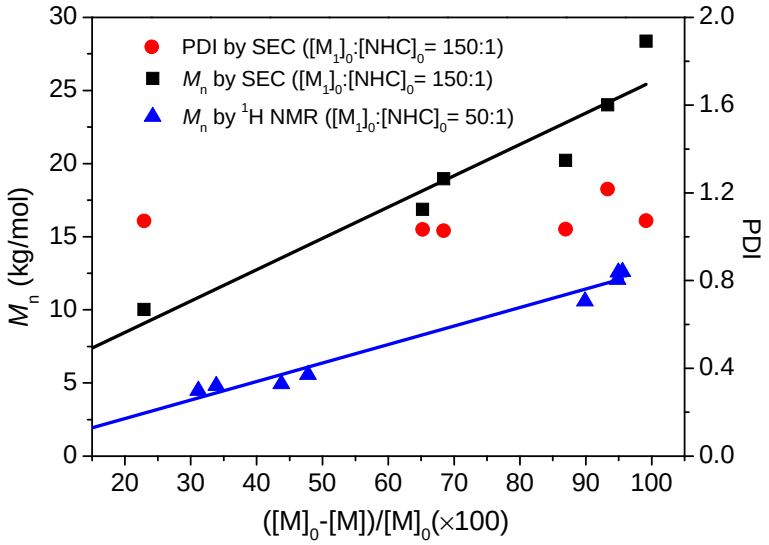

Figure S4. The plot of polymer molecular weights [M_n: ■ determined by SEC-MALS-DRI or ▲ ^{1}H NMR analysis and PDI (●) of *c*-PNDGs versus conversion for the NHC-mediated polymerization of M_2 in THF at 70 °C ($[M_2]_0$:$[I]_0$ = 150:1 or 50:1, $[M_2]_0$=0.4 M). [Note: aliquots of the polymerization solution ($[M_2]_0$:$[I]_0$ = 150:1) was taken, filtered and directly injected into SEC columns for the MW determination over the course of reaction].

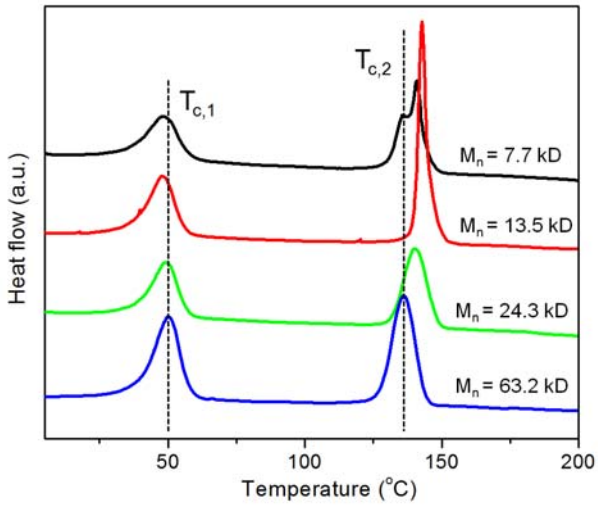

Figure S5. DSC thermograms of *c*-PNDGs having different molecular weights collected from the first cooling cycle.

Table S1. Crystallization temperature and heat of fusion of *c*-PNDGs of various MWs.

M_n (kg·mol^{-1})	$T_{c,1}$ (°C)	$T_{c,2}$ (°C)	$\Delta H_{c,1}$ (J·g^{-1})	$\Delta H_{c,2}$ (J·g^{-1})
7.7	48.8	140.8	37.3	44.6
13.5	47.7	145.6	40.5	50.8
24.3	49.5	139.7	36.7	42.8
63.2	49.8	135.8	37.4	39.8

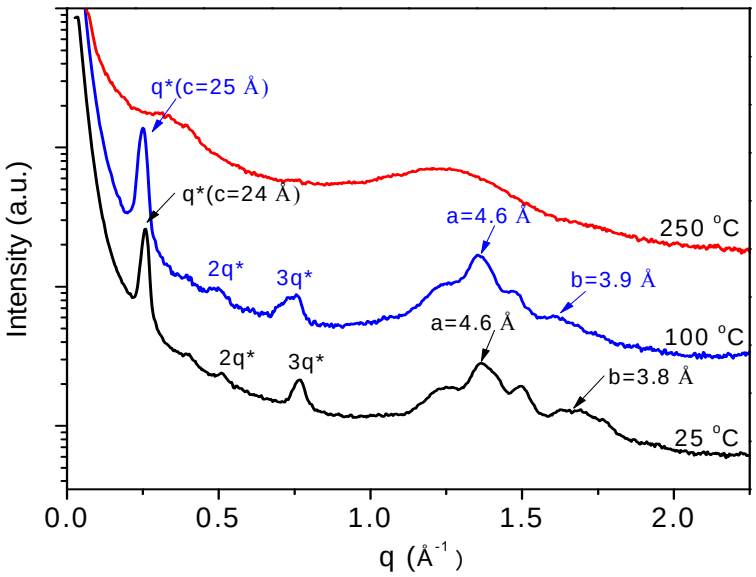

Figure S6. WAXS diffractograms of as-prepared *c*-PNDG (M_n = 7.7 kg·mol^{-1}, PDI=1.26) without thermal annealing in the solid state at 25, 100 and 250 °C.

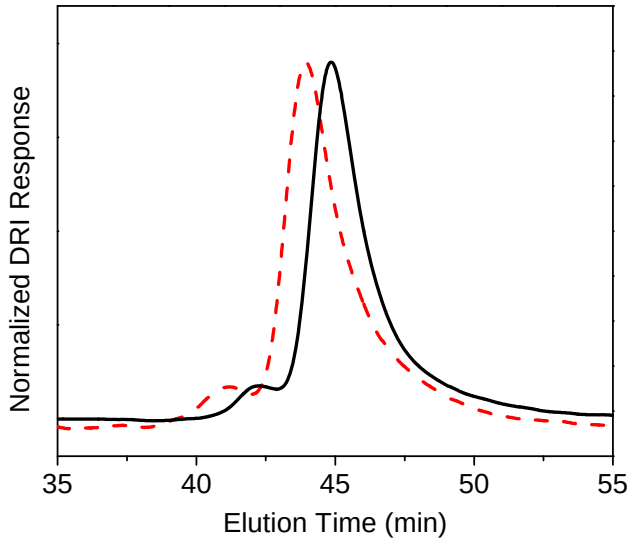

Figure S7. SEC-DRI chromatograms of cyclic poly(*N*-methyl-glycine)$_{105}$ (—) and cyclic poly(*N*-methyl-glycine)$_{105}$-*b*-poly(*N*-decyl-glycine)$_{15}$ diblock copolymers (---) prepared from sequential NHC-mediated polymerization of M_2 and M_1.

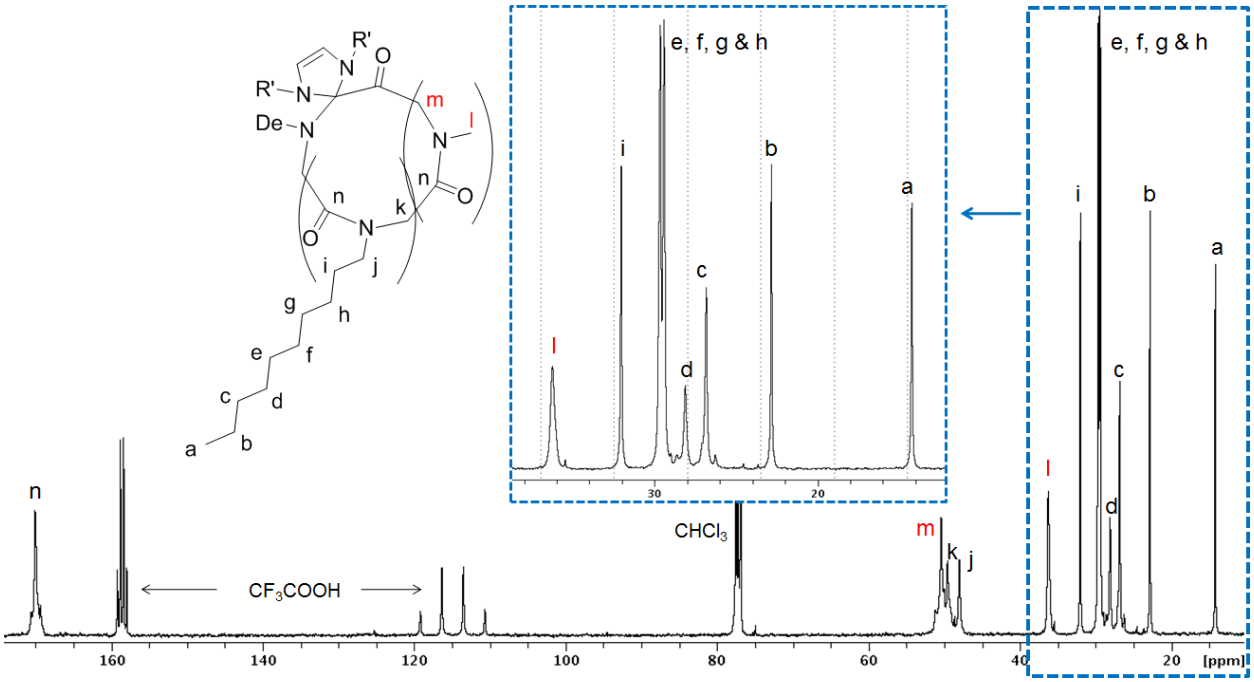

Figure S8. $^{13}C\{^{1}H\}$ NMR spectra of cyclic poly(*N*-Me-glycine)$_{105}$-*b*-poly(*N*-De-glycine)$_{50}$ (*c*-PNMG$_{105}$-*b*-PNDG$_{50}$) in $CDCl_3/CF_3COOD$.

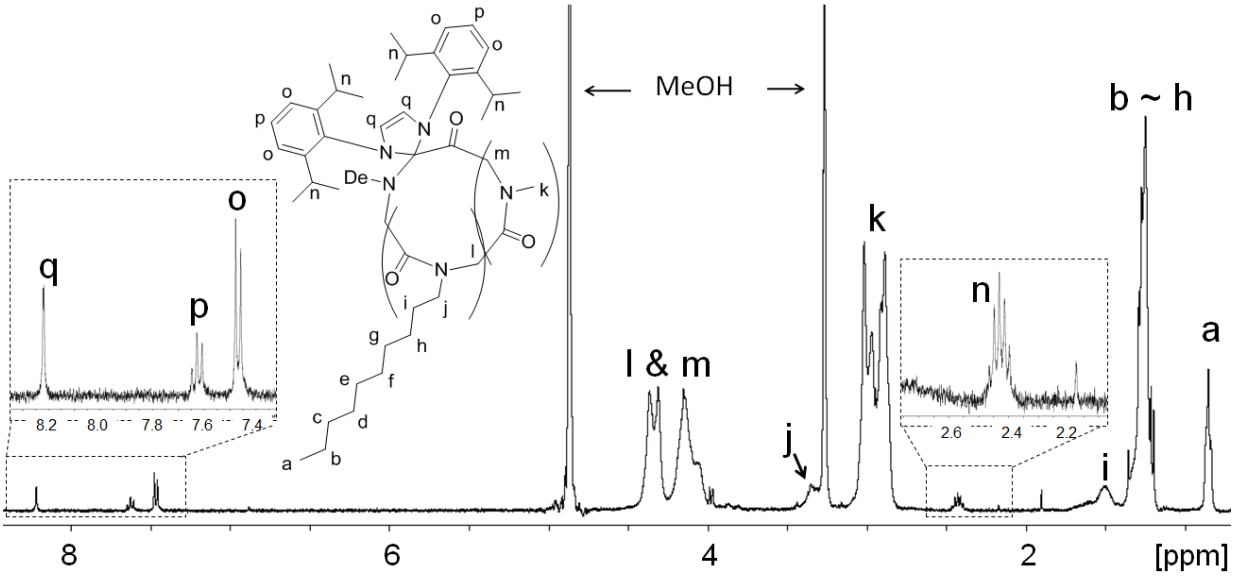

Figure S9. ^{1}H NMR spectrum of a low MW cyclic poly(*N*-Me-glycine)-*b*-poly(*N*-De-glycine) diblock copolymer (*c*-PNMG$_{72}$-*b*-PNDG$_{8}$) in CD_3OD, where proton resonances of the NHC are notably visible.

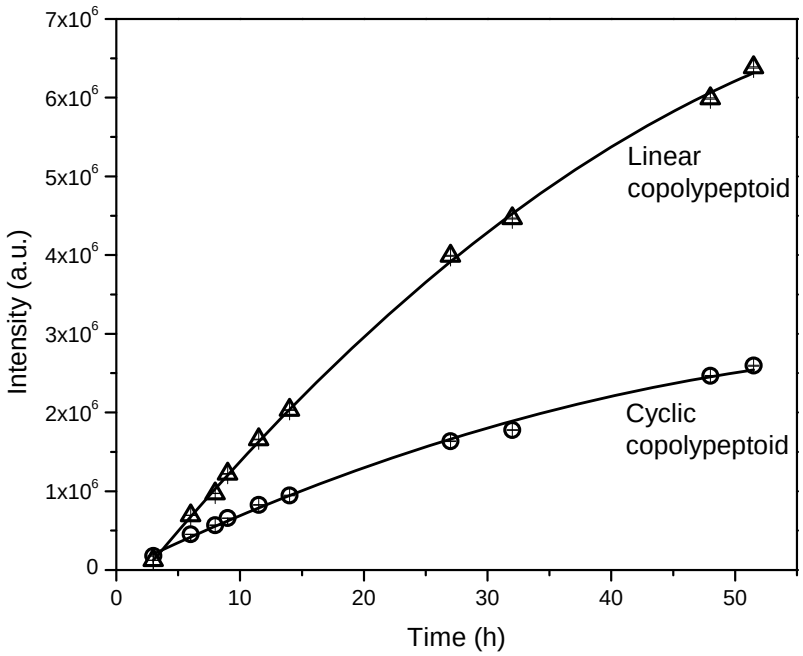

Figure S10. Turbidity measurements of both linear and cyclic block copolypeptoid solutions in methanol over the first 2 d after preparation.

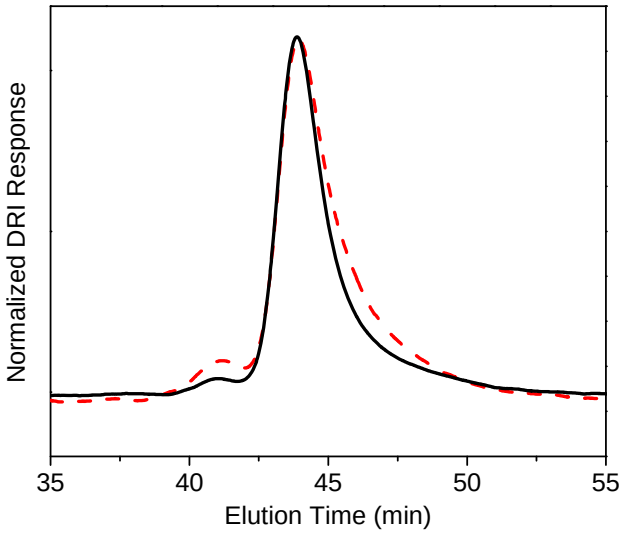

Figure S11. SEC-DRI chromatograms of cyclic poly(*N*-methyl-glycine)$_{105}$-*b*-poly(*N*-decyl-glycine)$_{15}$ obtained after 17 d in room temperature methanol (---) and the original sample (—).

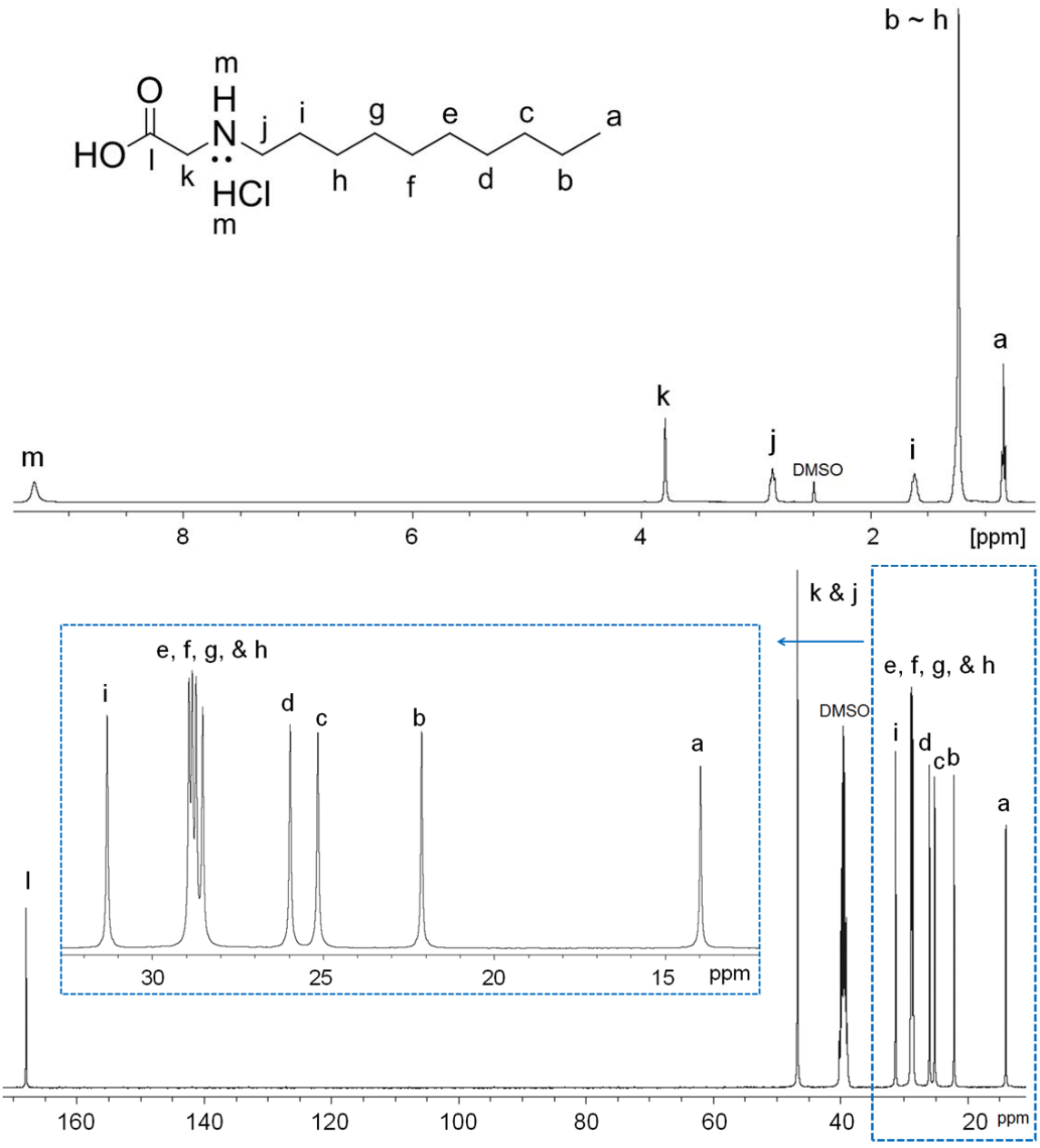

Figure S12. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 2-(*n*-decylamino)acetic acid hydrochloride (**1**) in DMSO-d_6.

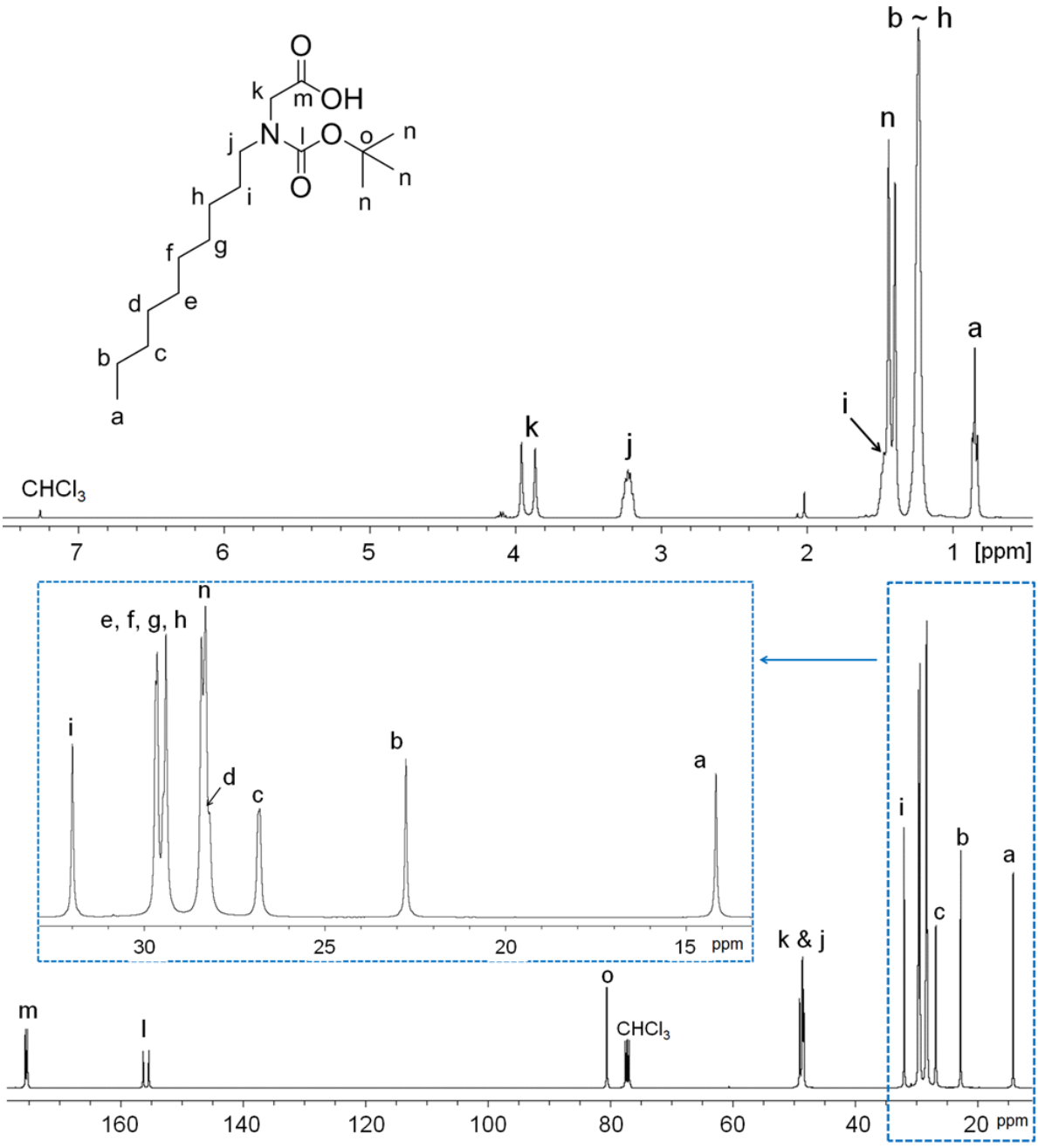

Figure S13. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 2-(*N*,*N*-*tert*-butoxycarbonyl-*n*-decylamino)acetic acid (**2**) in $CDCl_3$.