Supporting information

Organocatalysis by Hydrogen-Bonding: A New Approach to Controlled/Living Polymerization of α-Amino acid *N*-carboxyanhydrides

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Figure S1. Full ^{1}H NMR spectra of **TU-S**, **Glu-NCA** and **TU-S**/**Glu-NCA** mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S2. Full ^{1}H NMR spectrum of **TU-S**/**Glu-NCA** mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S3. The molecular weight of obtained PBLG as a function of monomer/initiator ratio ($[M]_0/[I]_0$) in polymerization of Glu-NCA initiated by **DMEA**/**TU-S**.

Figure S4. (a) $M_{n,SEC\text{-}LS}$ and PDI versus conversion (polymerization time in parentheses) for the ROP of Glu-NCA initiated by **DMEA**/TU-S; (b) SEC profiles (RI signals) of samples taken at different time during ROP of Glu-NCA initiated by **DMEA**/TU-S (conditions:[Glu-NCA]/[**DMEA**]/[TU-S]=240/1/2, $[Glu\text{-}NCA]_0$ = 0.19M; DCM,25 ^{o}C).

Figure S5. SEC traces of polypeptides from polymerizations initiated by **DMEA** in the presence of TU-S in different solvents.

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Figure S7. Full ^{1}H NMR spectrum of **TU-S**/**DMEA-TMS'** mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S8. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **DMEA/TU-S** (500M, 25^{o}C, $CDCl_3/CF_3COOD$ (2:1)).

Figure S9. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **MDEA/TU-S** (500M, 25^{o}C, $CDCl_3/CF_3COOD$ (2:1)).

Figure S10. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **TEA/TU-S** (500M, 25^{o}C, $CDCl_3/CF_3COOD$ (2:1)).

Figure S11. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **THEED/TU-S** (500M, 25^{o}C, $CDCl_3/CF_3COOD$ (2:1)).

Figure S12. Full ^{1}H NMR spectrum of **TU-S**/**DMEA** mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S13. Full ^{1}H NMR spectrum of **TU-S**/methyl 2-amino-2-phenylacetate (**MAP**) (1:1) mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S14. Full ^{1}H NMR spectra of **TU-S**, **THEED** and **TU-S**/**THEED** (1:1) mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S15. Full ^{1}H NMR spectra of **TU-S**, **THEED-TMS'** and **TU-S**/**THEED-TMS'** (1:1) mixture (500M, 25^{o}C, CD_2Cl_2).

Figure S16. Full ^{1}H NMR spectra of **THEED** and **THEED-TMS'** (500M, 25^{o}C, CD_2Cl_2).

Figure S17. SEC traces of polypeptides from polymerizations initiated by **THEED** in the presence of TU-S in different solvents.

Figure S18. The molecular weight of obtained PBLG as a function of monomer/initiator ratio ($[M]_0/[I]_0$) in polymerization of Glu-NCA initiated by **THEED**/**TU-S**.

Figure S19. SEC traces of polypeptides obtained from ROP initiated by **THEED/TU-S** in Table 1.

Figure S20. Kinetics of the ROP of Glu-NCA promoted by **THEED**/**TU-S** ([M]=0.19M, [Glu-NCA]/[**THEED**]=120, [**TU-S**]/[**THEED**]=1, 2, 3, and 5, 25^{o}C, DCM, the automatic sampling interval of *in situ* IR is 10 seconds).

Figure S21. ln($[NCA]_0/[NCA]_t$) vs. time for the ROP of Glu-NCA initiated by **THEED**/**TU-S** ([M]=0.19M, [Glu-NCA]/[**TU-S**]/[**THEED**]=120/(2+2)/1, 25^{o}C, DCM) and corresponding 3D kinetic behavior profile from *in situ* IR (the sampling interval of *in situ* IR is 10 seconds).

Figure S22. Mark-Houwink-Sakurada plots of PBLGs obtained from the ROP of Glu-NCA initiated by three different initiators.

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Figure S24. Full ^{13}C NMR spectrum of **DMEA-TMS'**(125M, 25^{o}C, CD_2Cl_2).

Figure S25. Full ^{1}H NMR spectrum of **MDEA-TMS'**(500M, 25^{o}C, CD_2Cl_2).

Figure S26. Full ^{13}C NMR spectrum of **MDEA-TMS'**(125M, 25^{o}C, CD_2Cl_2).

Figure S27. Full ^{1}H NMR spectrum of **TEA-TMS'**(500M, 25^{o}C, CD_2Cl_2).

Figure S28. Full ^{13}C NMR spectrum of **TEA-TMS'**(125M, 25^{o}C, CD_2Cl_2).

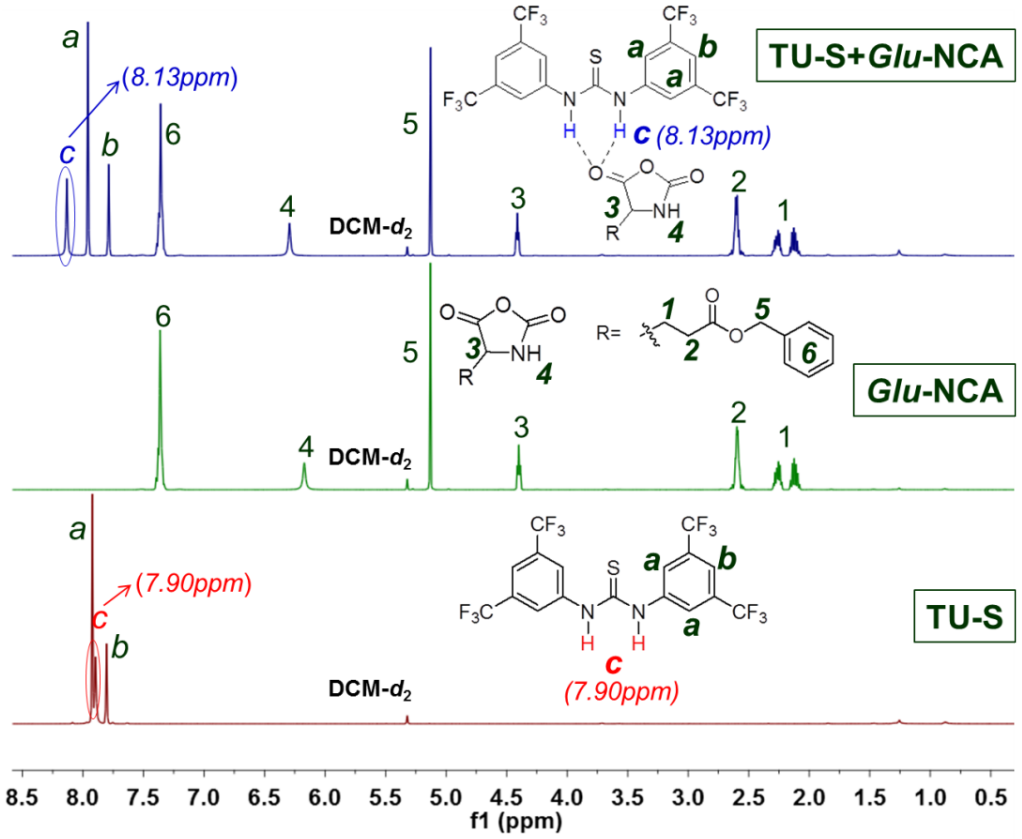
Figure S29. ^{1}H NMR spectrum of **THEED-TMS'** (600M, 25^{o}C, CD_2Cl_2)

Figure S30. ^{13}C NMR spectrum of **THEED-TMS'**(150M, 25^{o}C, CD_2Cl_2)

Figure S31. Full ^{1}H NMR spectrum of **TU-S** (500M, 25^{o}C, CD_2Cl_2).

Figure S32. Full ^{1}H NMR spectrum of **Glu-NCA** (500M, 25^{o}C, CD_2Cl_2).

Figure S33. Full ^{1}H NMR spectrum of **DMEA**(500M, 25^{o}C, CD_2Cl_2).



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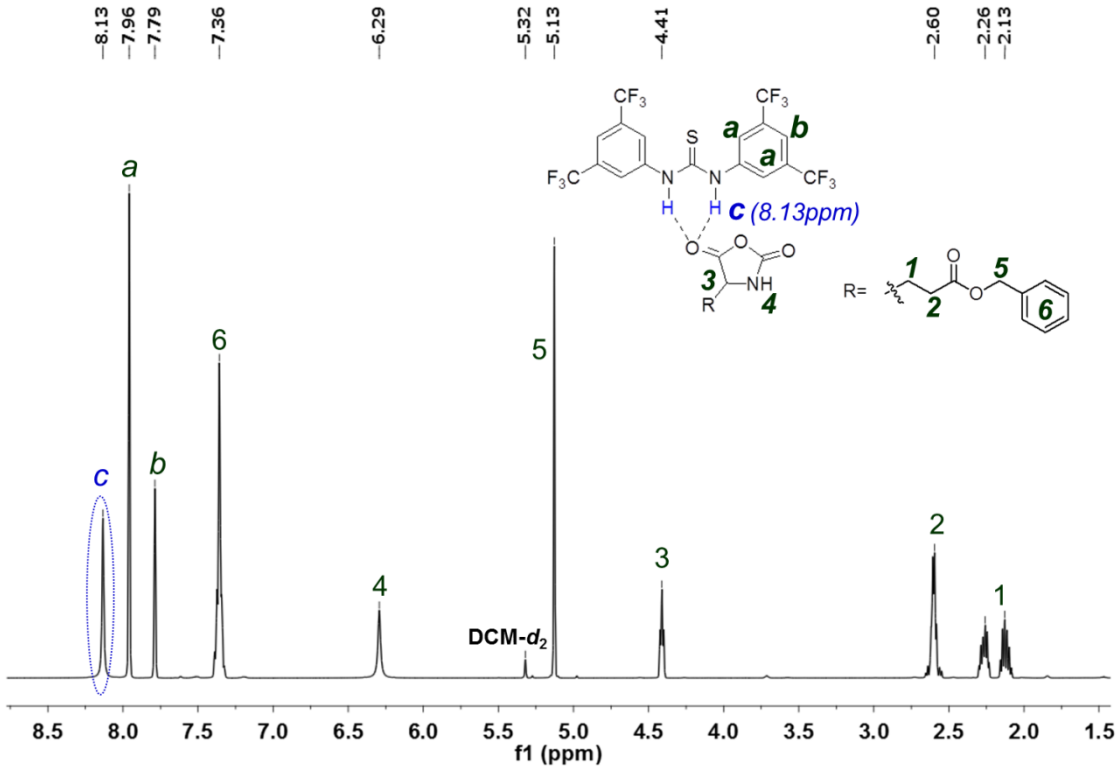


Figure S2. Full ^{1}H NMR spectrum of **TU-S/Glu-NCA** mixture (500M, 25^{o}C, CD_2Cl_2).

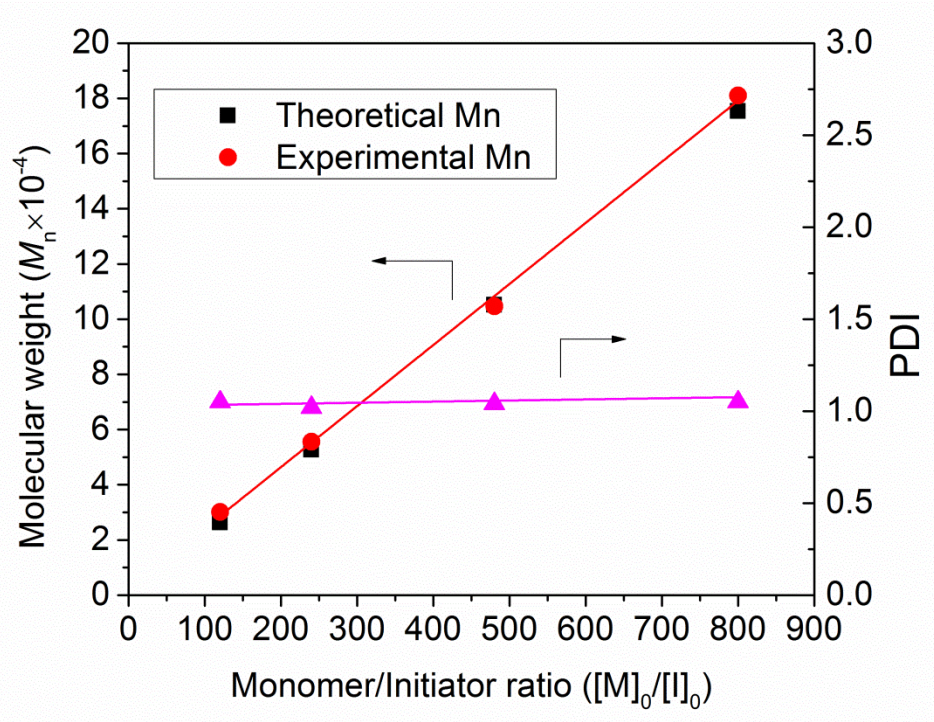
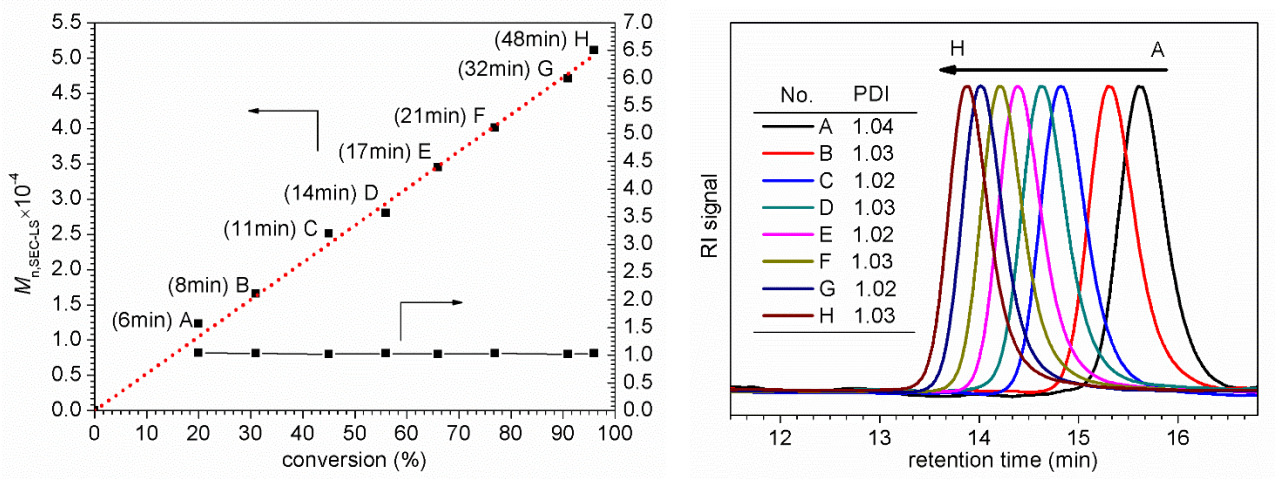


Figure S3. The molecular weight of obtained PBLG as a function of monomer/initiator ratio ($[M]_0/[I]_0$) in polymerization of Glu-NCA initiated by **DMEA**/**TU-S**.



(a) (b)

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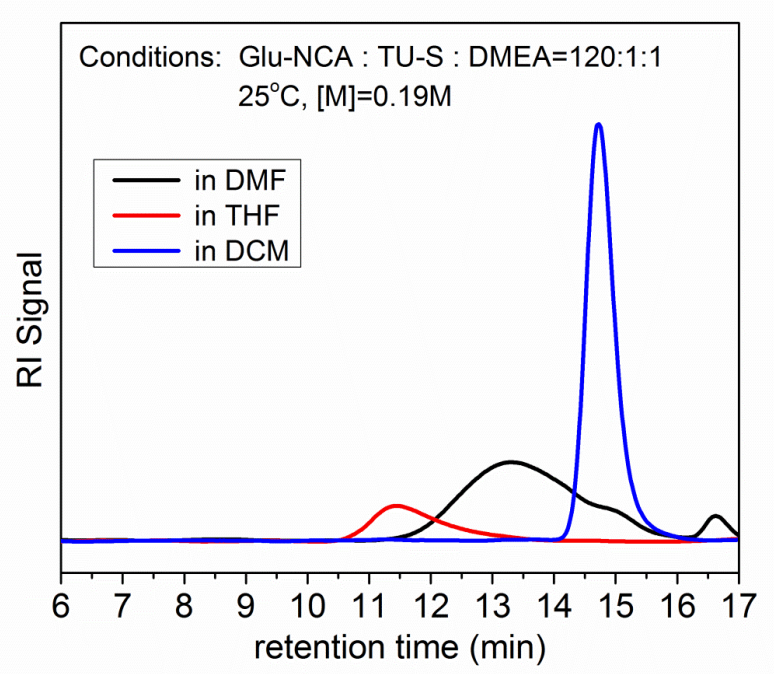


Figure S5. SEC traces of polypeptides from polymerizations initiated by **DMEA** in the presence of TU-S in different solvents.

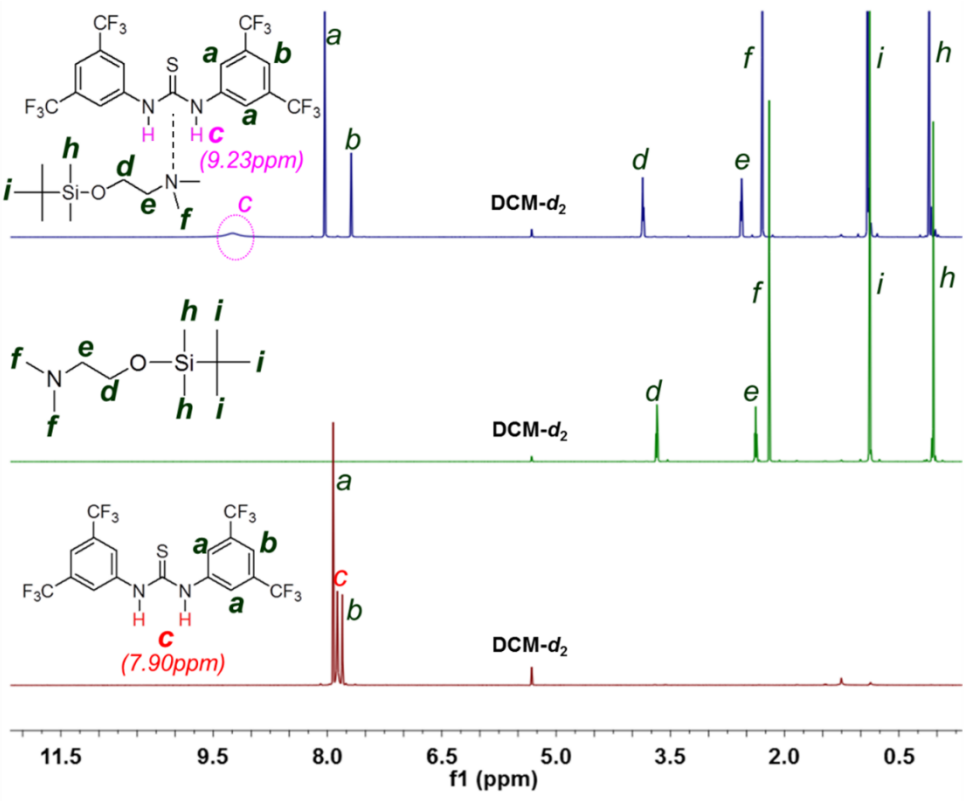


Figure S6. Full ^{1}H NMR spectra of **TU-S**, **DMEA-TMS'** and **TU-S/DMEA-TMS'** mixture (500M, 25°C, CD_2Cl_2).

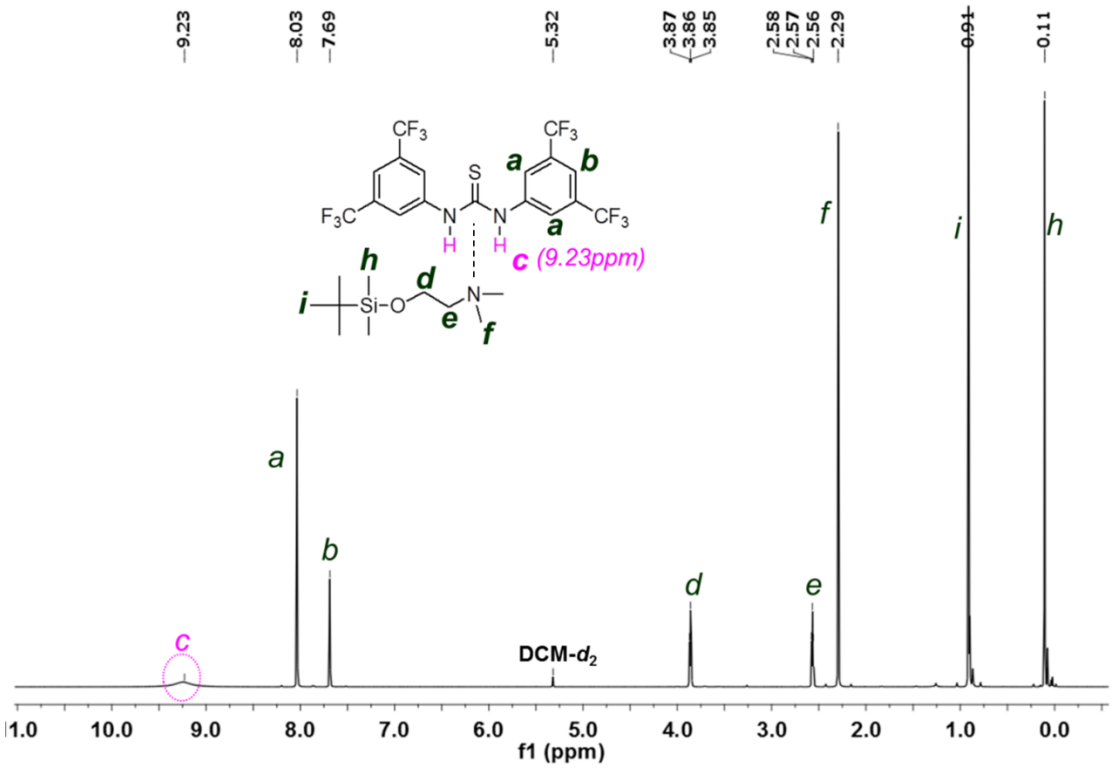


Figure S7. Full ^{1}H NMR spectrum of **TU-S/DMEA-TMS'** mixture (500M, 25^{o}C, CD_2Cl_2).

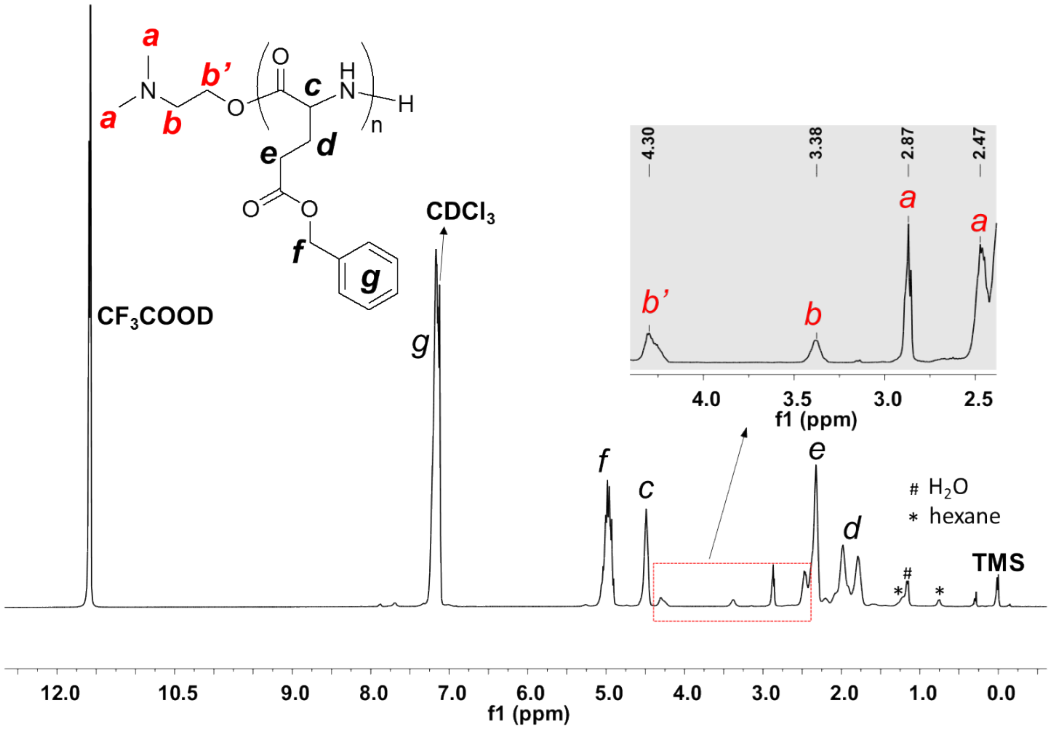


Figure S8. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **DMEA/TU-S** (500M, 25^{o}C, $CDCl_3/CF_3COOD$ (2:1)).

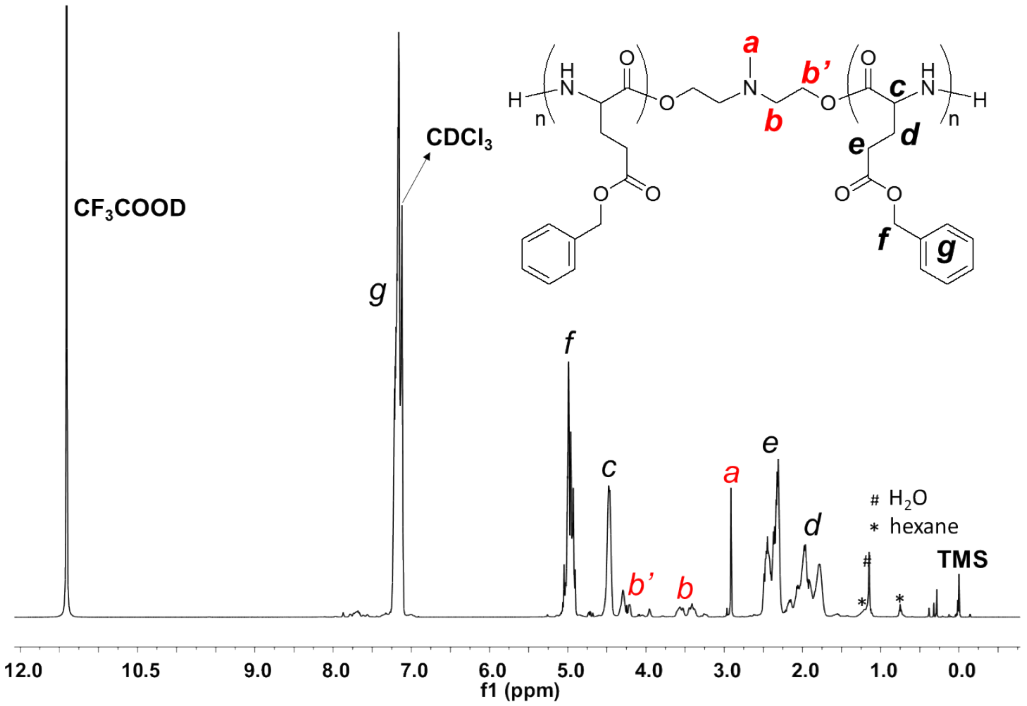


Figure S9. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **MDEA/TU-S** (500M, 25°C, $CDCl_3/CF_3COOD$ (2:1)).

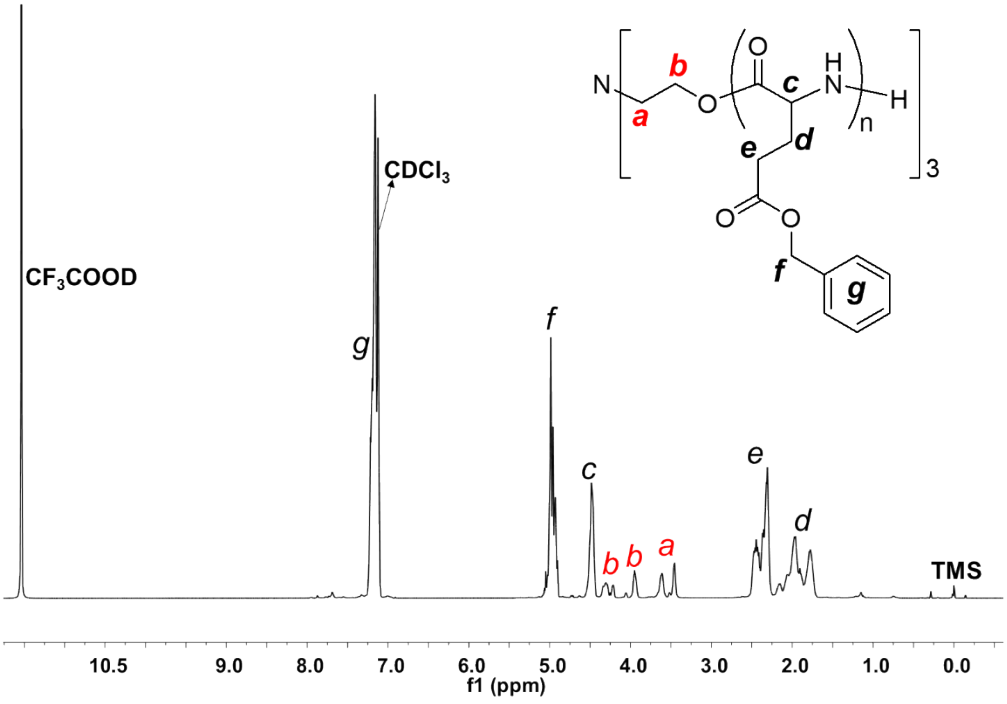


Figure S10. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **TEA/TU-S** (500M, 25°C, $CDCl_3/CF_3COOD$ (2:1)).

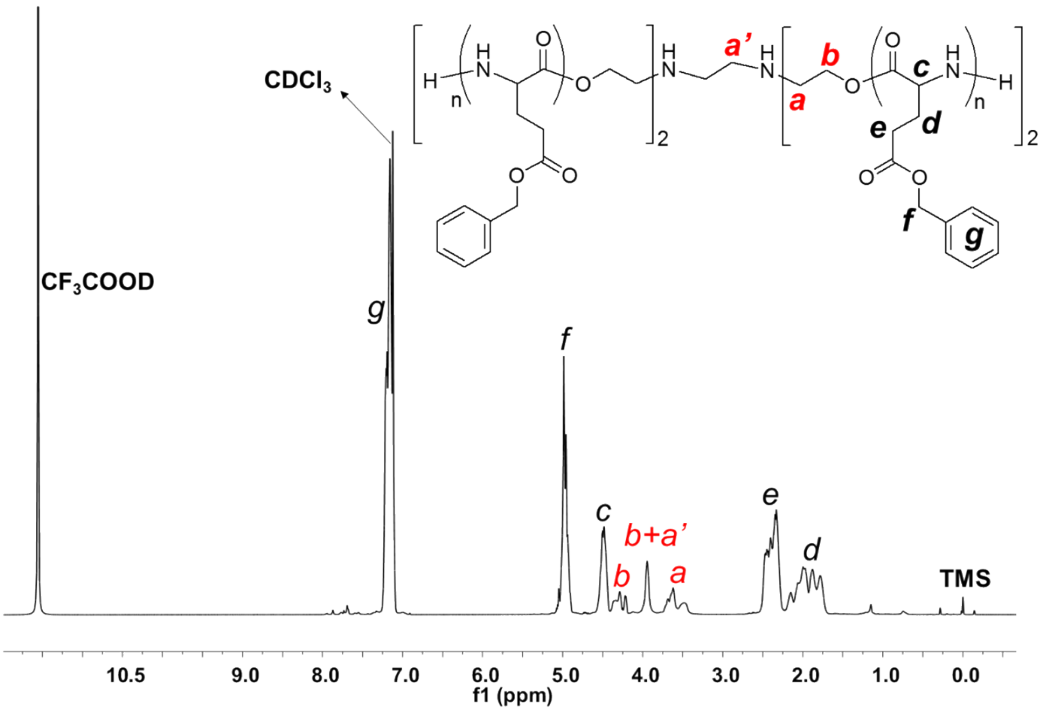


Figure S11. ^{1}H NMR spectrum of $PBLG_{15}$ from ROP of Glu-NCA initiated by **THEED/TU-S** (500M, 25^{o}C, $CDCl_3$/CF_3COOD (2:1)).

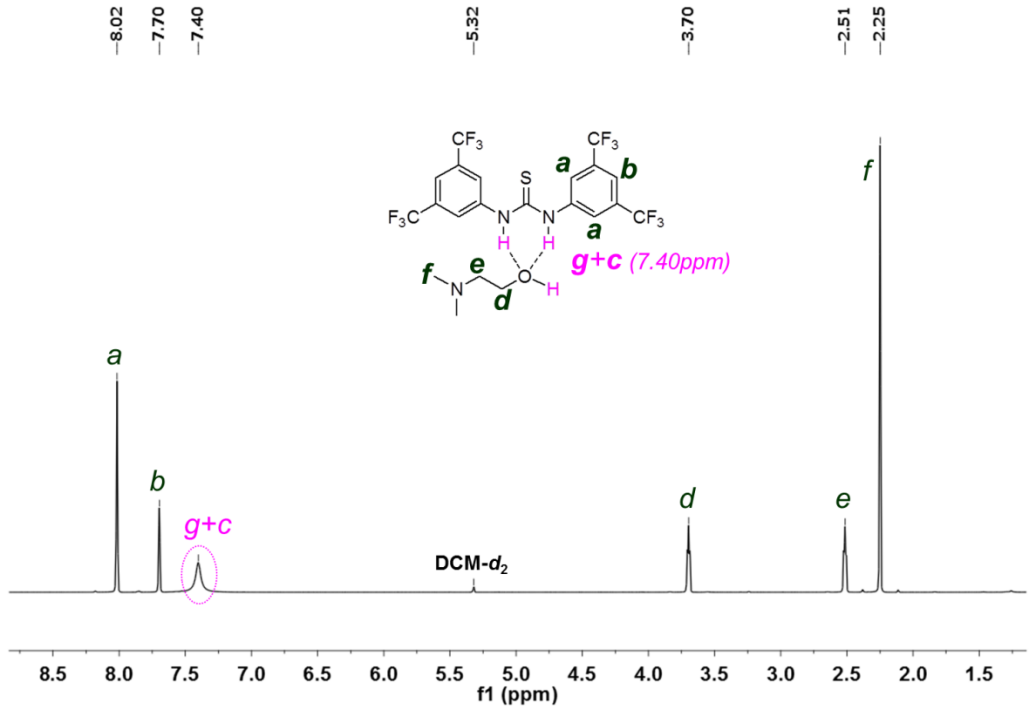


Figure S12. Full ^{1}H NMR spectrum of **TU-S/DMEA** mixture (500M, 25^{o}C, CD_2Cl_2).

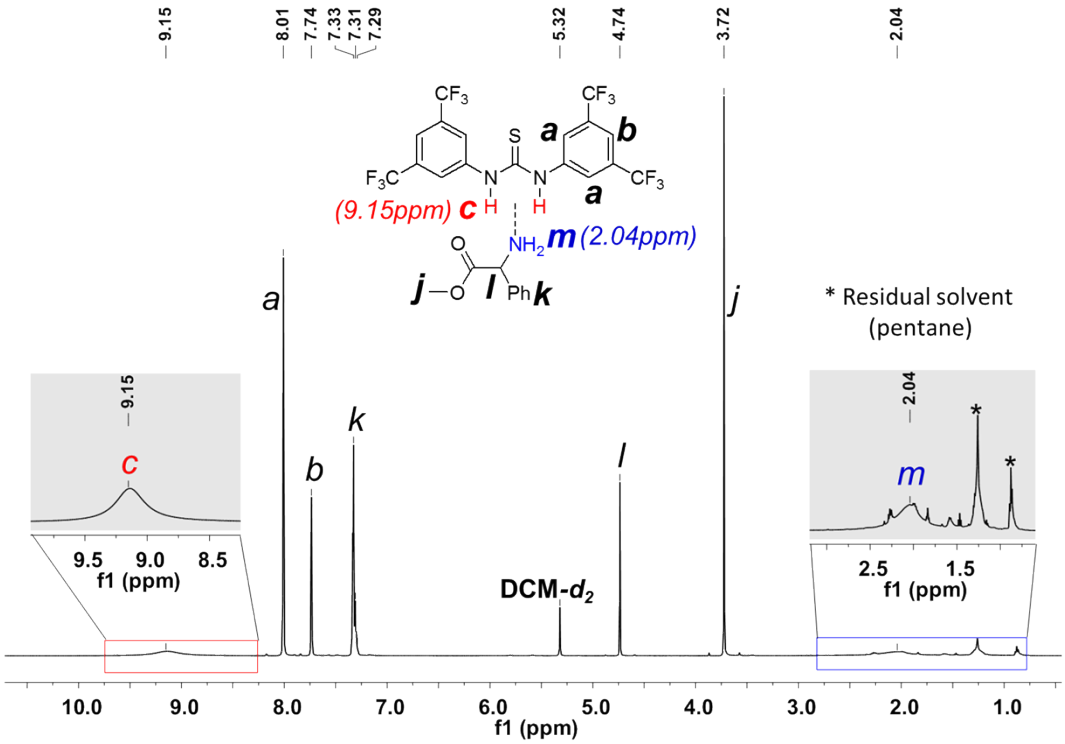


Figure S13. Full ^{1}H NMR spectrum of **TU-S**/methyl 2-amino-2-phenylacetate (**MAP**) (1:1) mixture (500M, 25^{o}C, CD_2Cl_2).

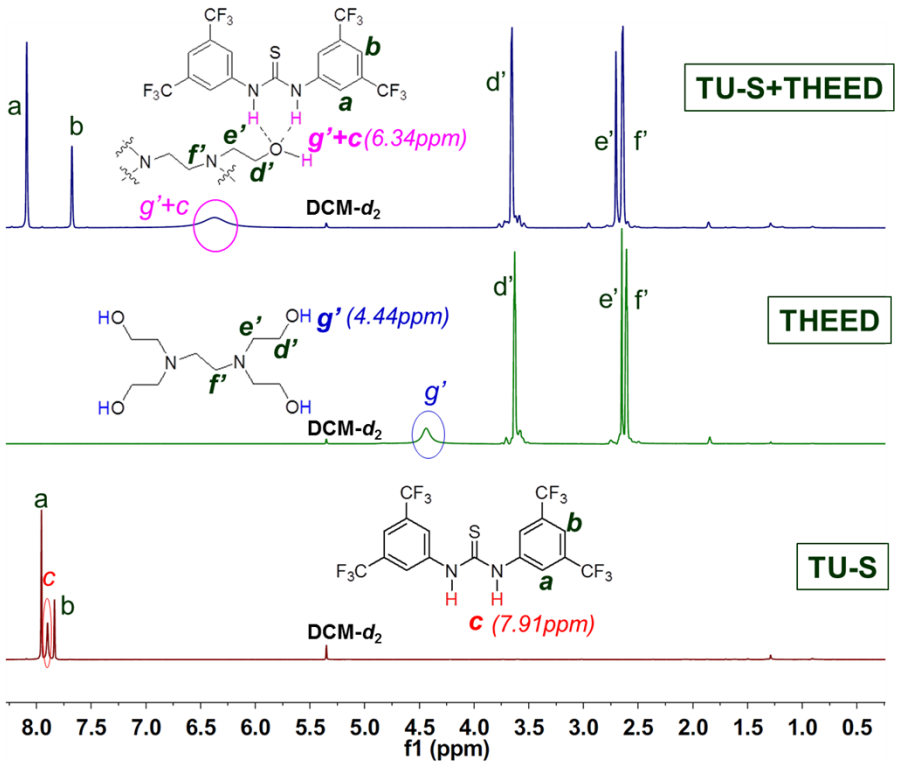


Figure S14. Full ^{1}H NMR spectra of **TU-S**, **THEED** and **TU-S**/**THEED** (1:1) mixture (500M, 25^{o}C, CD_2Cl_2).

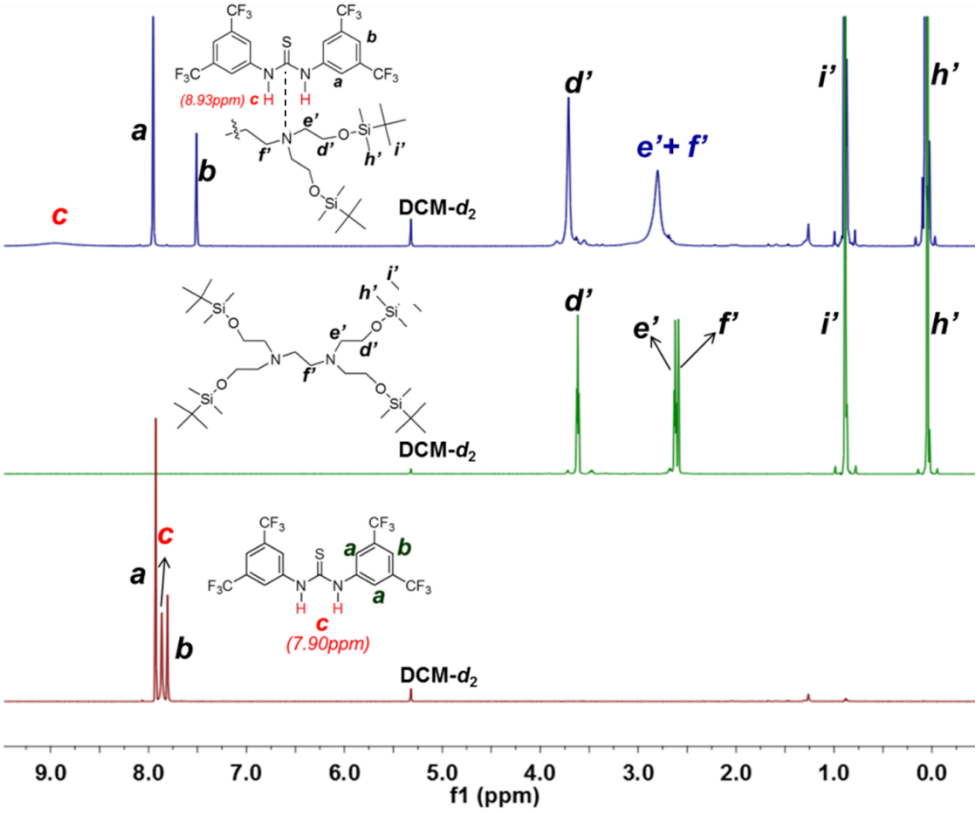


Figure S15. Full ^{1}H NMR spectra of **TU-S**, **THEED-TMS'** and **TU-S/THEED-TMS'** (1:1) mixture (500M, 25^{o}C, CD_2Cl_2).

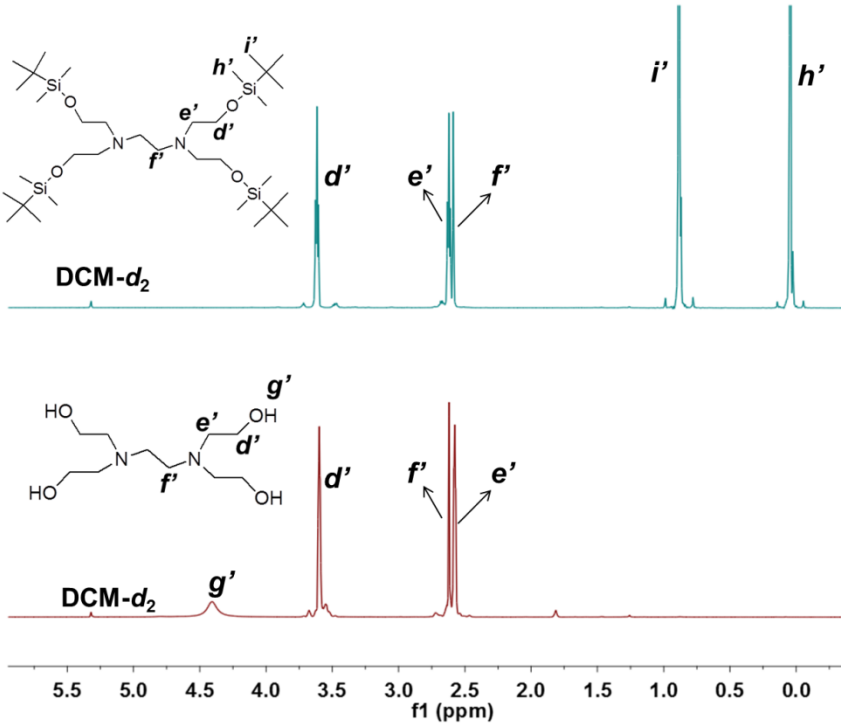


Figure S16. Full ^{1}H NMR spectra of **THEED** and **THEED-TMS'** (500M, 25^{o}C, CD_2Cl_2).

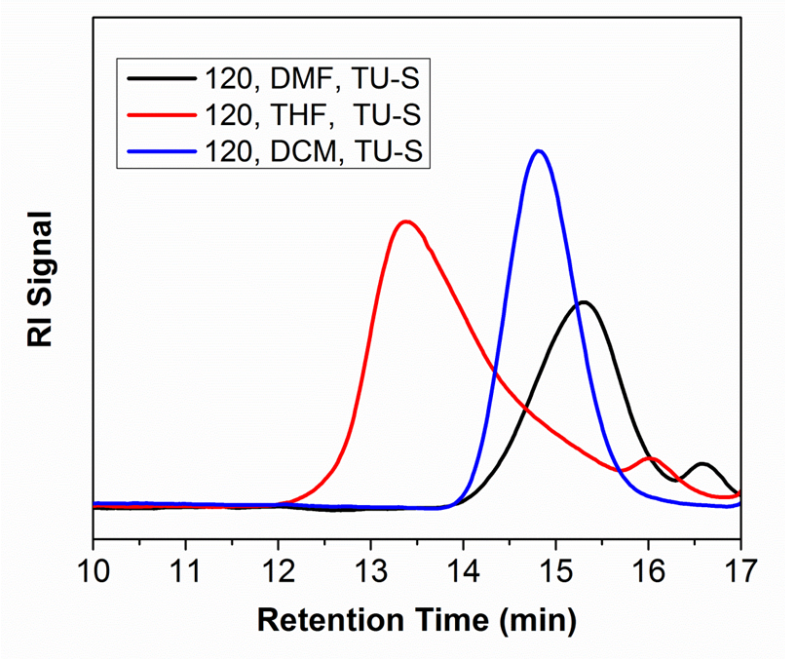
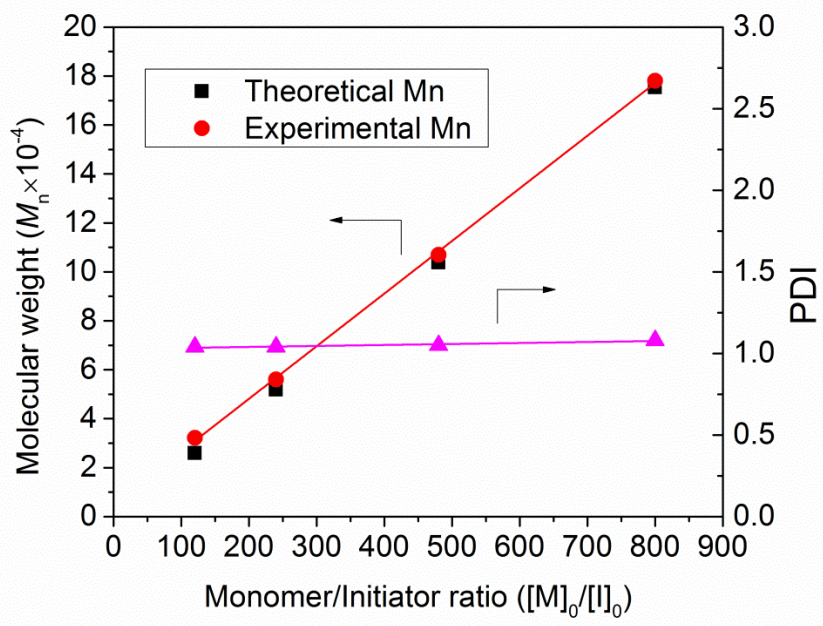


Figure S17. SEC traces of polypeptides from polymerizations initiated by **THEED** in the presence of TU-S in different solvents.



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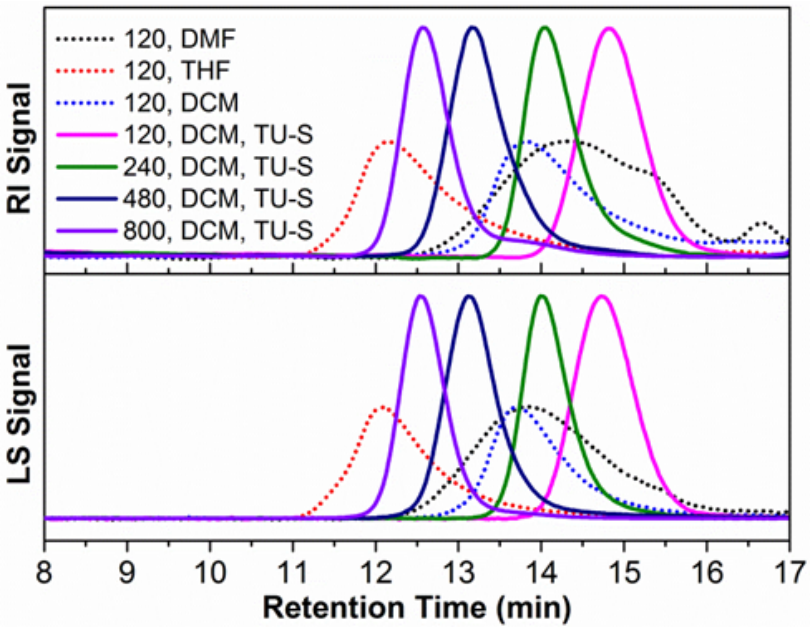

Figure S19. SEC traces of polypeptides obtained from ROP initiated by **THEED/TU-S** in Table 1.

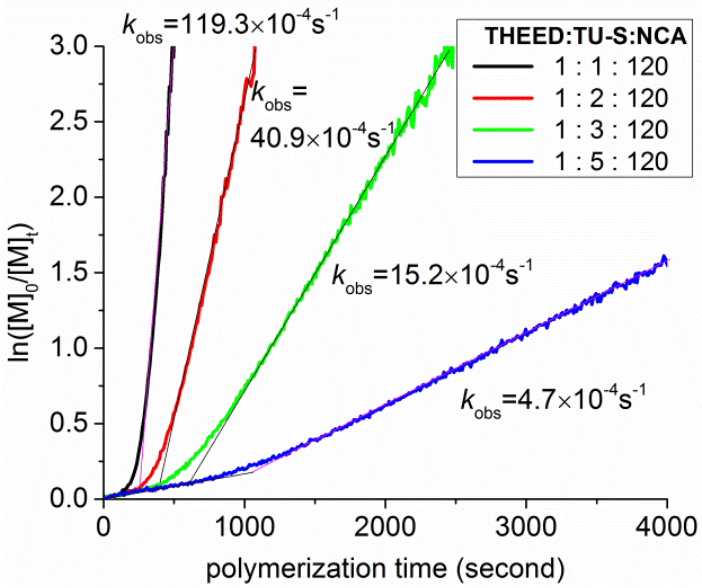

Figure S20. Kinetics of the ROP of Glu-NCA promoted by **THEED/TU-S** ([M]=0.19M, [Glu-NCA]/[**THEED**]=120, [**TU-S**]/[**THEED**]=1, 2, 3, and 5, 25°C, DCM, the automatic sampling interval of *in situ* IR is 10 seconds).

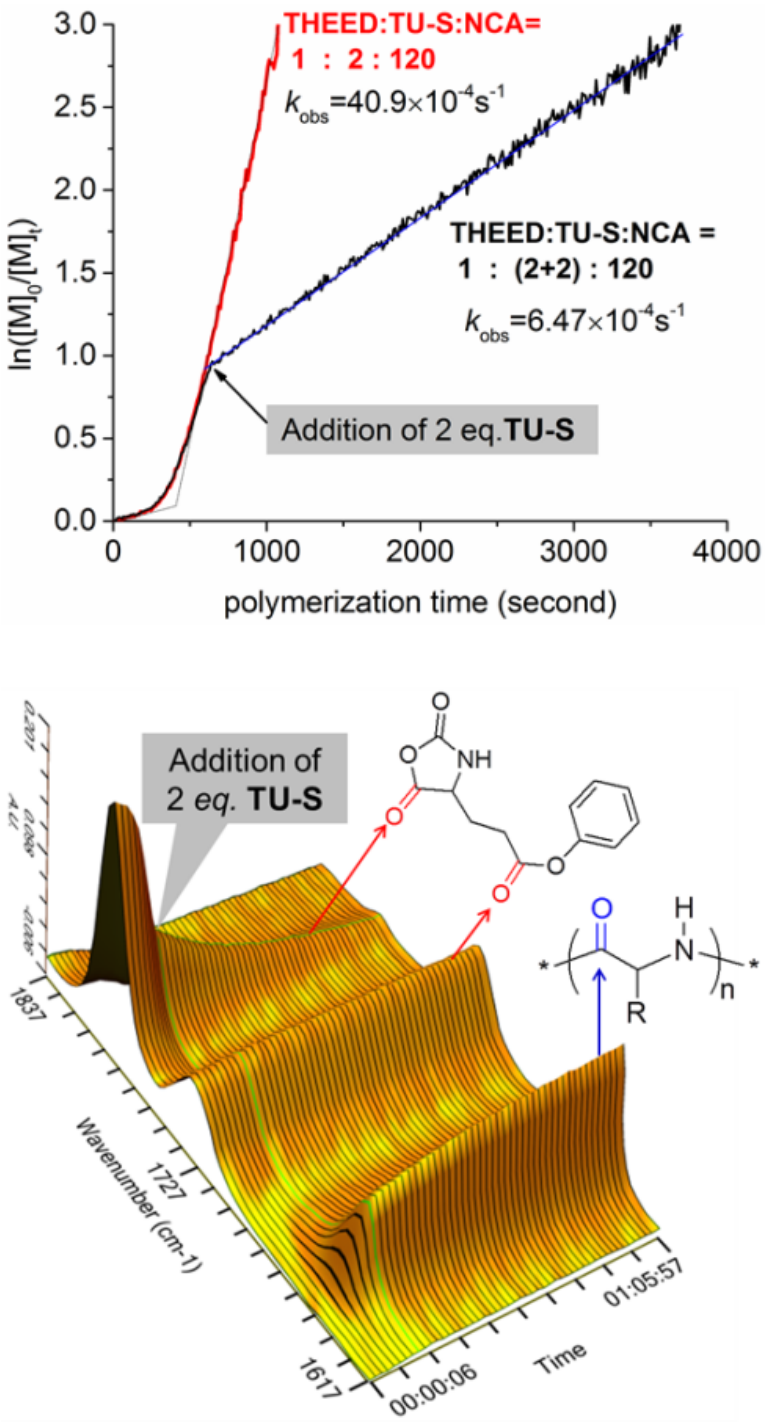

Figure S21. ln([NCA]$_0$/([NCA]$_t$) vs. time for the ROP of Glu-NCA initiated by **THEED**/**TU-S** ([M]=0.19M, [Glu-NCA]/[**TU-S**]/[**THEED**]=120/(2+2)/1, 25^{o}C, DCM) and corresponding 3D kinetic behavior profile from *in situ* IR (the sampling interval of *in situ* IR is 10 seconds).

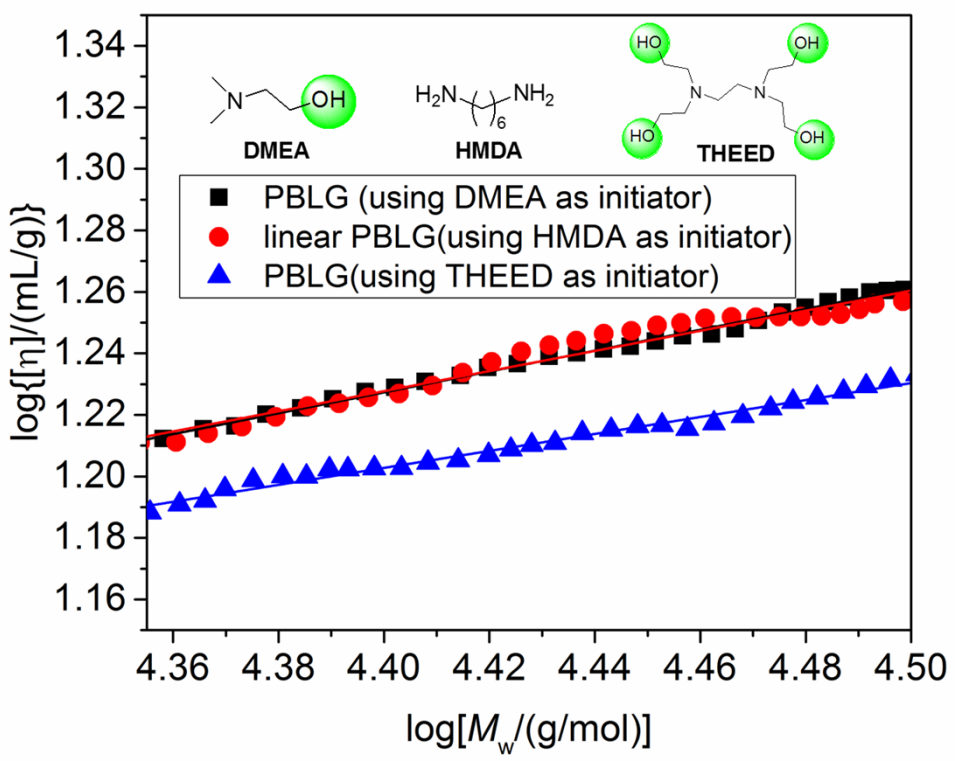

Figure S22. Mark-Houwink-Sakurada plots of PBLGs obtained from the ROP of Glu-NCA initiated by three different initiators.

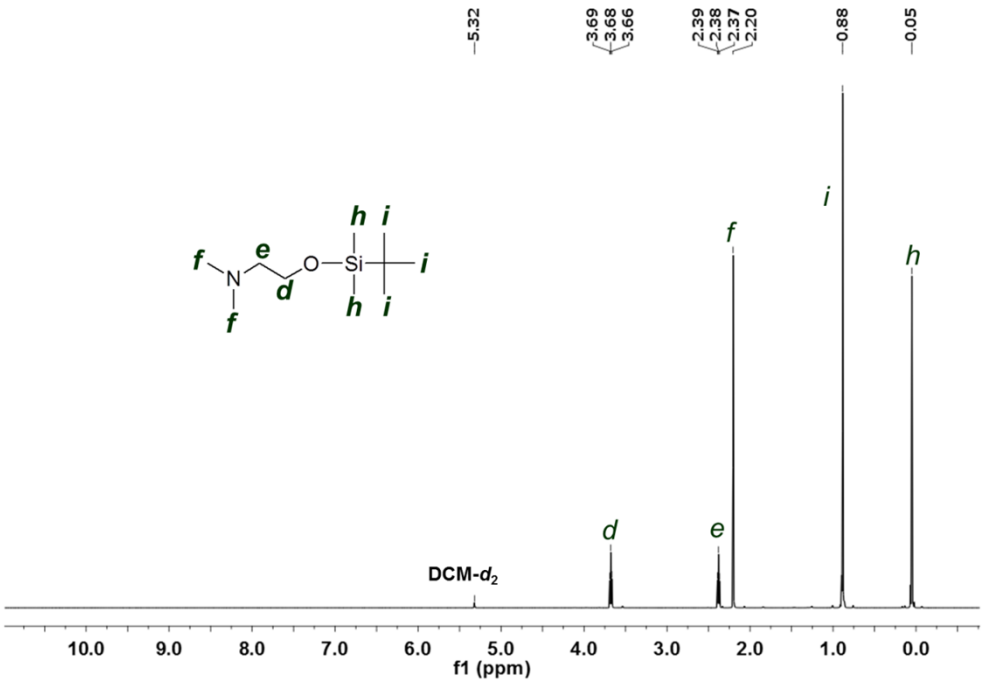

Figure S23. Full ^{1}H NMR spectrum of **DMEA-TMS'**(500M, 25^{o}C, CD_2Cl_2).

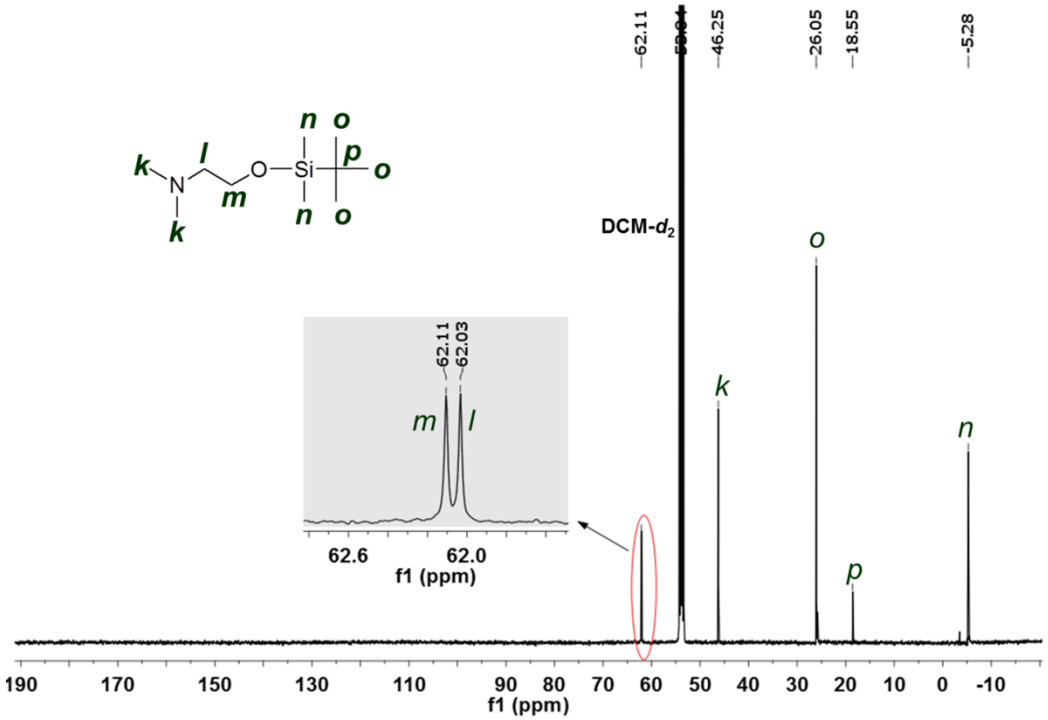

Figure S24. Full ^{13}C NMR spectrum of **DMEA-TMS'**(125M, 25°C, CD_2Cl_2).

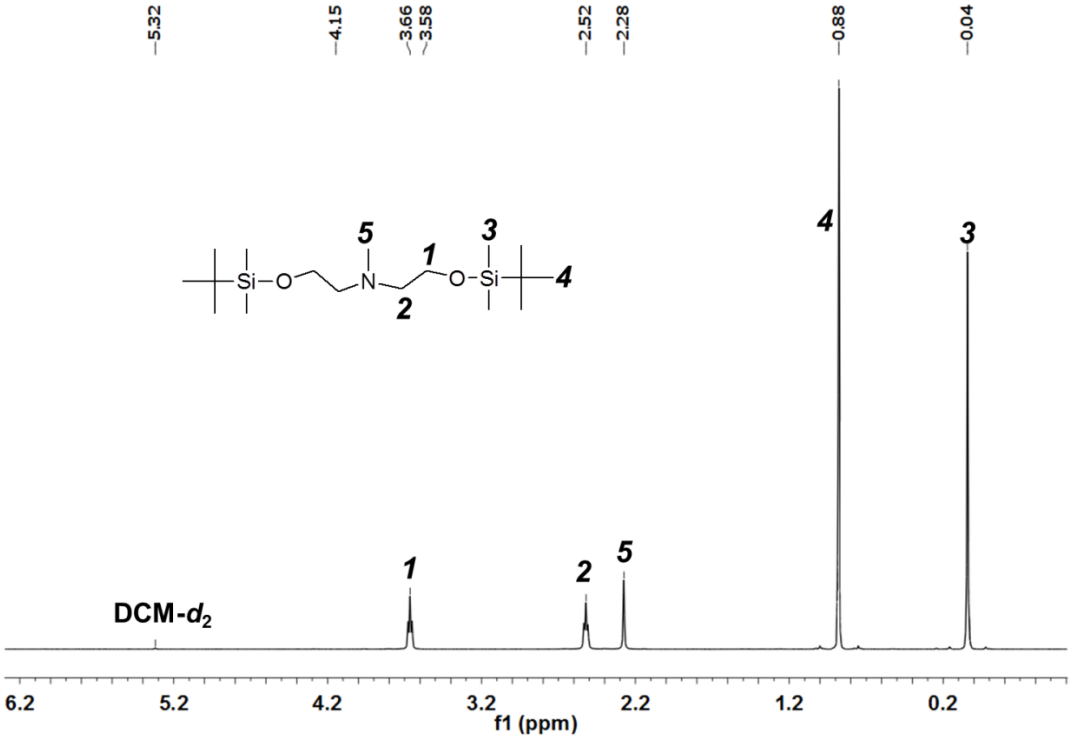

Figure S25. Full ^{1}H NMR spectrum of **MDEA-TMS'**(500M, 25°C, CD_2Cl_2).

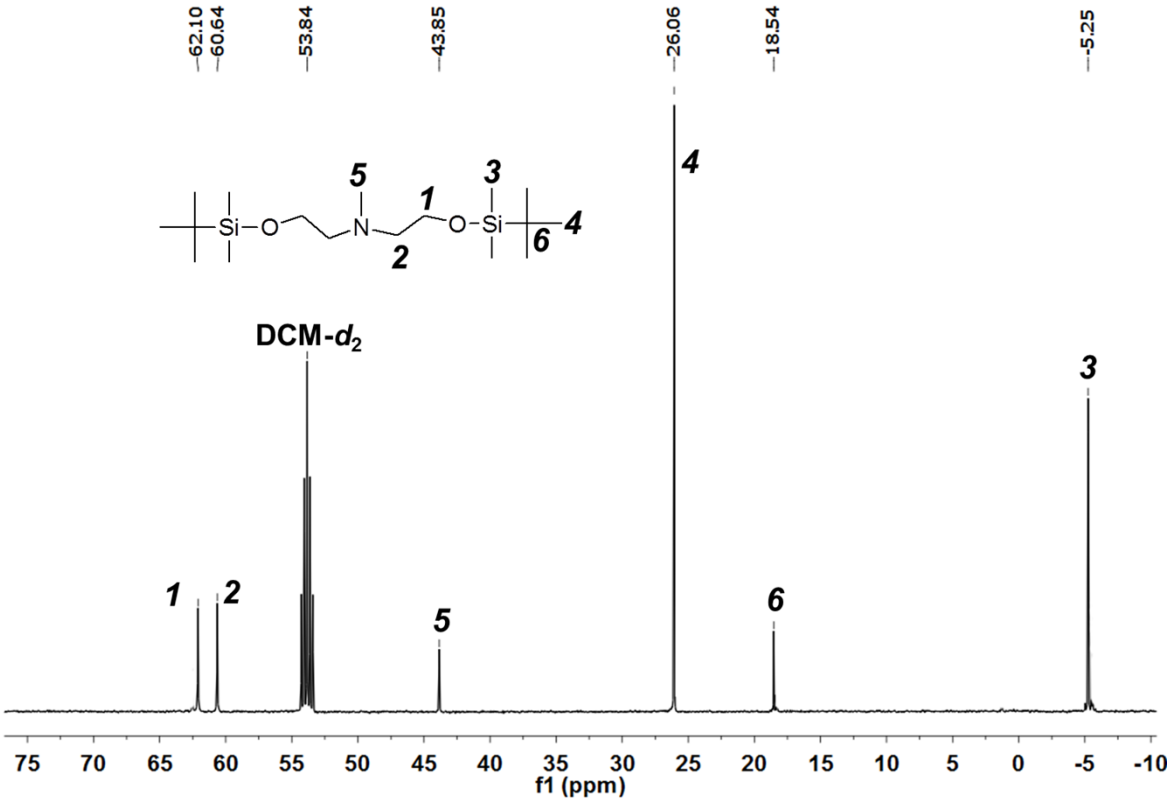

Figure S26. Full ^{13}C NMR spectrum of **MDEA-TMS'**(125M, 25°C, CD_2Cl_2).

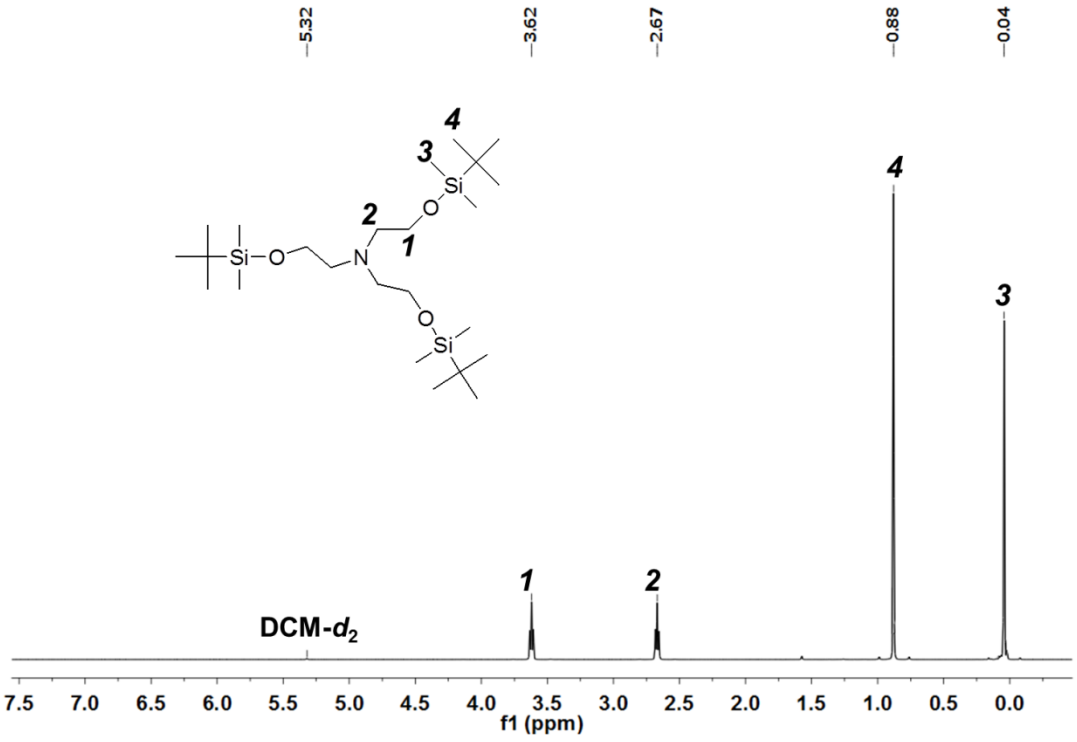

Figure S27. Full ^{1}H NMR spectrum of **TEA-TMS'**(500M, 25°C, CD_2Cl_2).

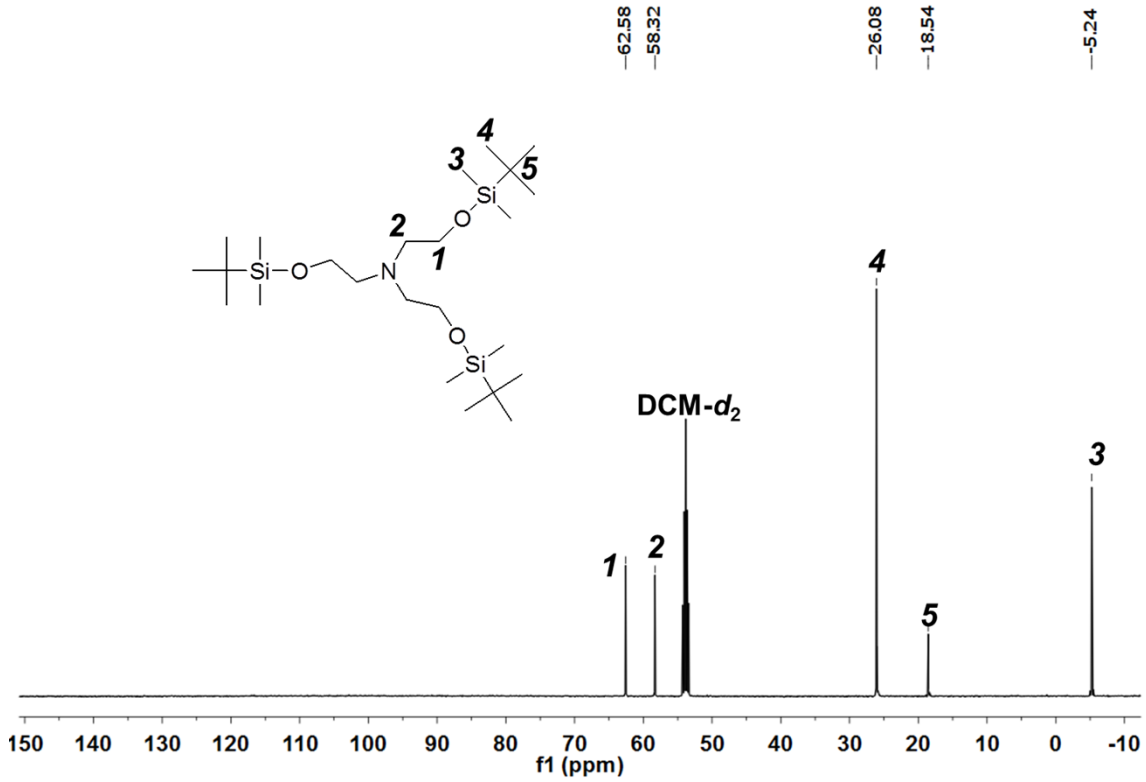

Figure S28. Full ^{13}C NMR spectrum of **TEA-TMS'**(125M, 25°C, CD_2Cl_2).

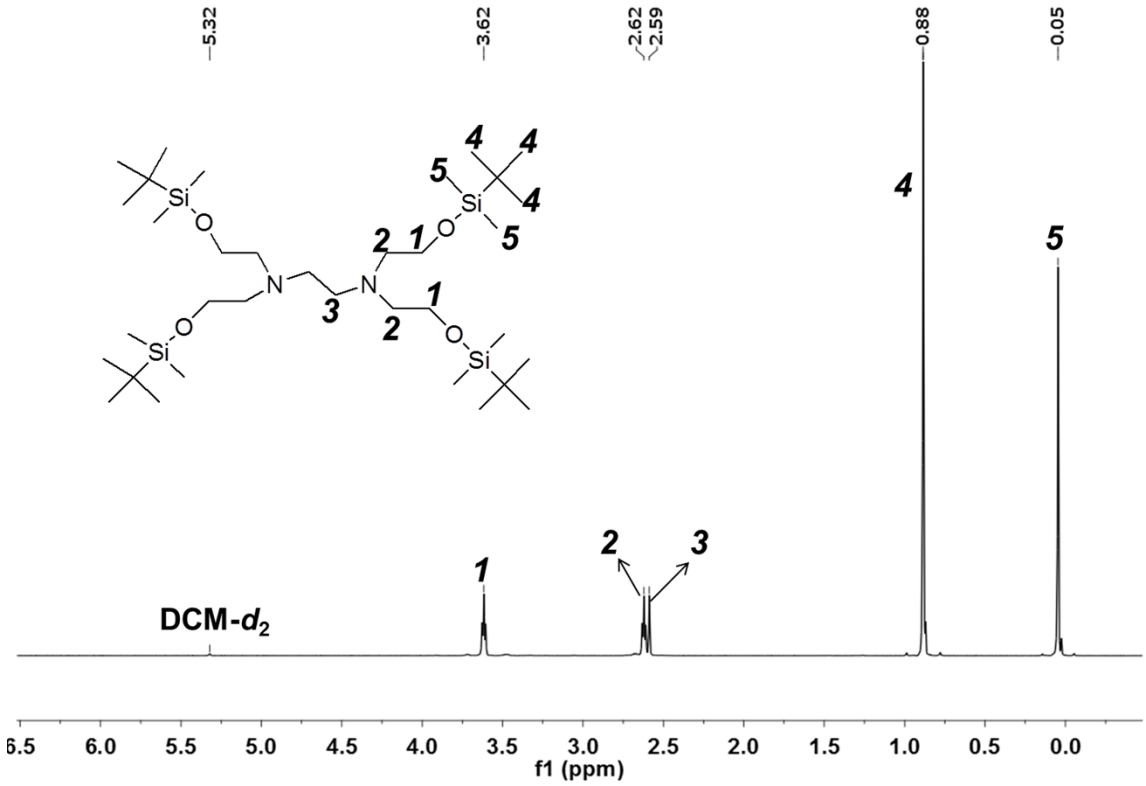

Figure S29. ^{1}H NMR spectrum of **THEED-TMS'** (600M, 25°C, CD_2Cl_2)

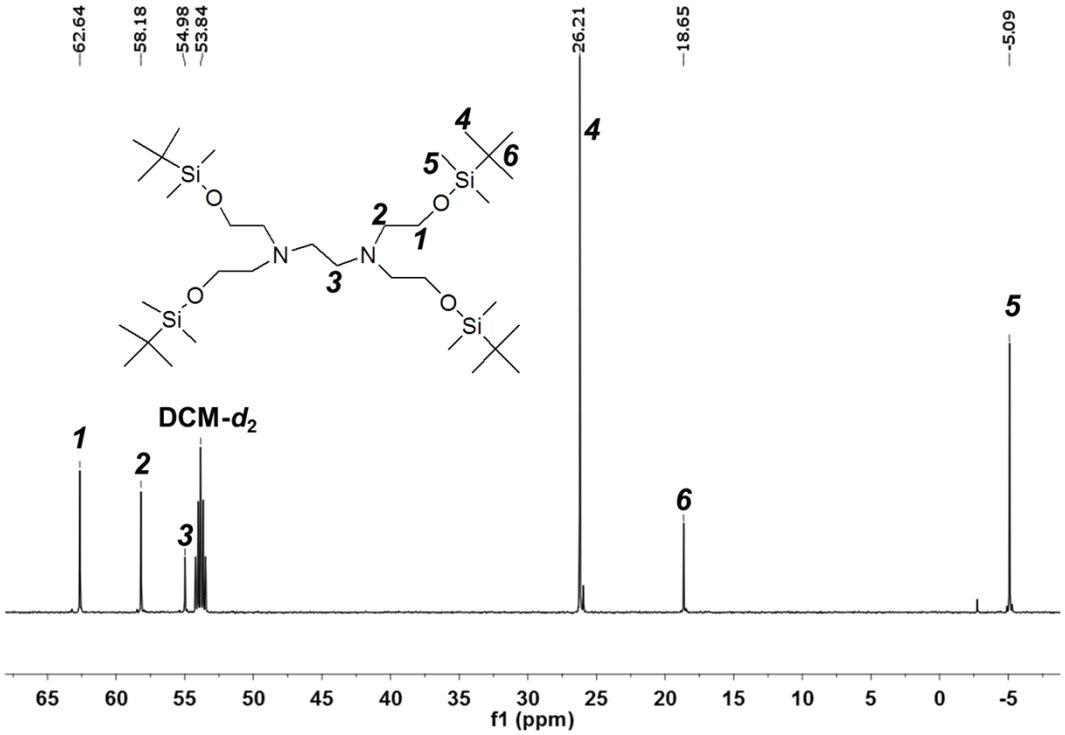

Figure S30. ^{13}C NMR spectrum of **THEED-TMS'**(150M, 25°C, CD_2Cl_2)

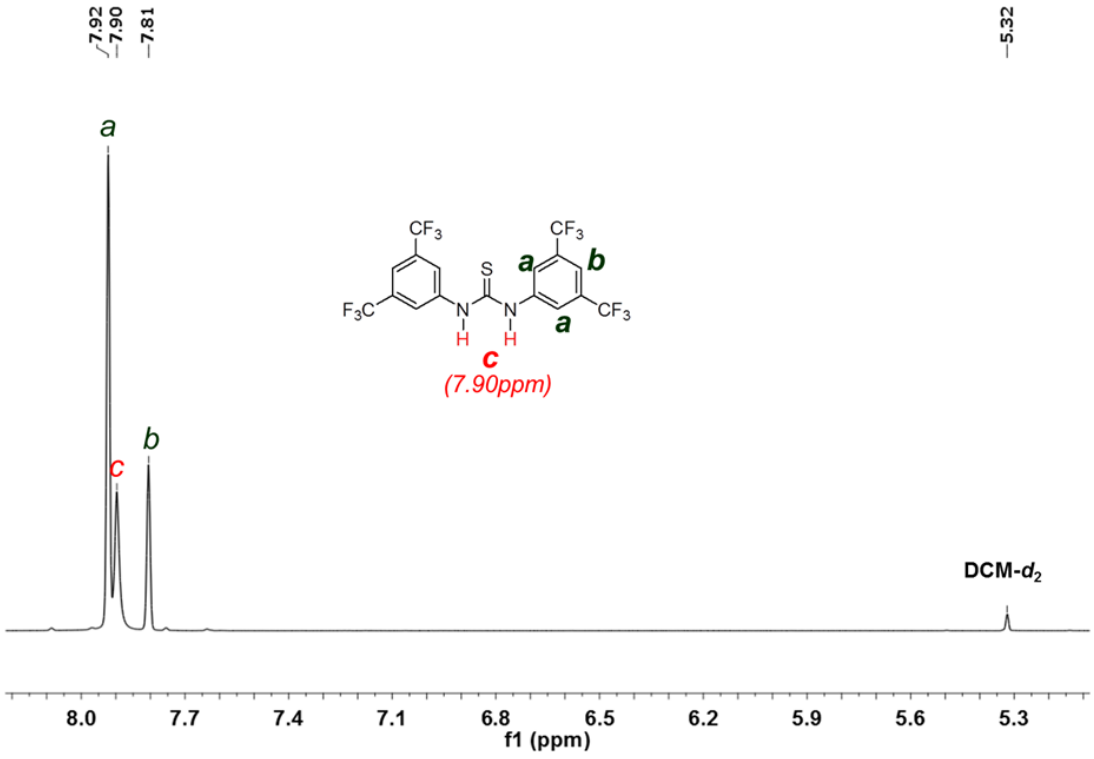

Figure S31. Full ^1H NMR spectrum of **TU-S** (500M, 25°C, CD_2Cl_2).

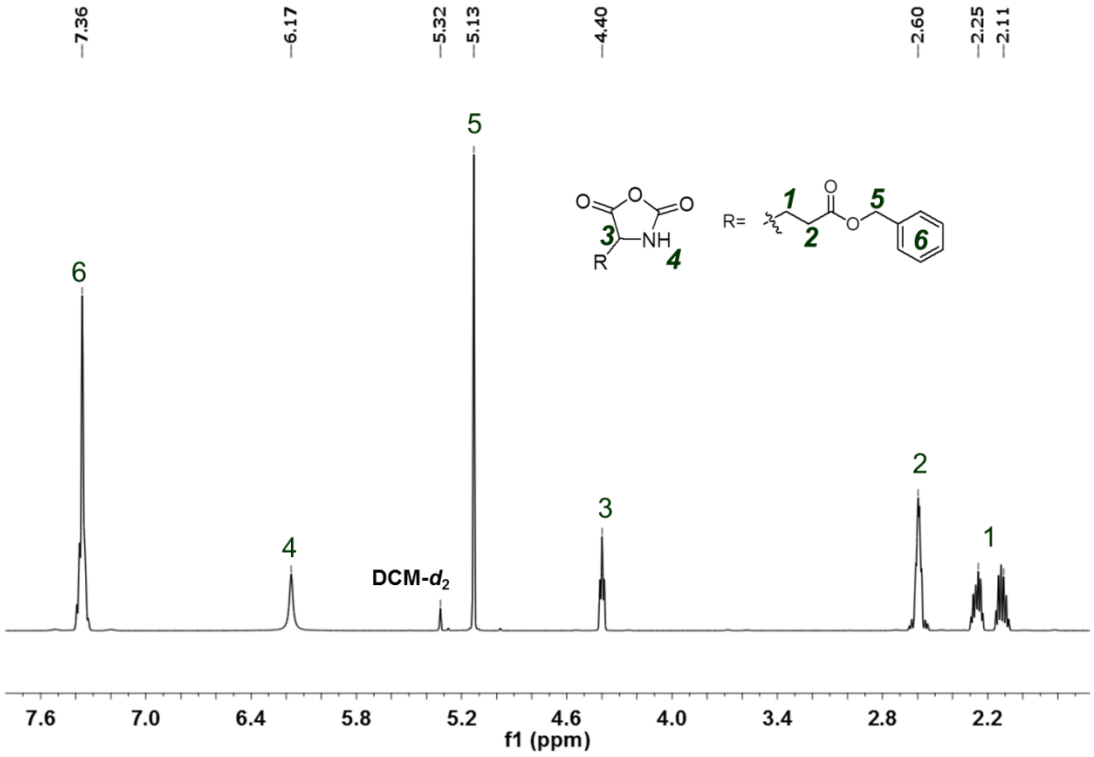

Figure S32. Full ^{1}H NMR spectrum of **Glu-NCA** (500M, 25^{o}C, CD_2Cl_2).

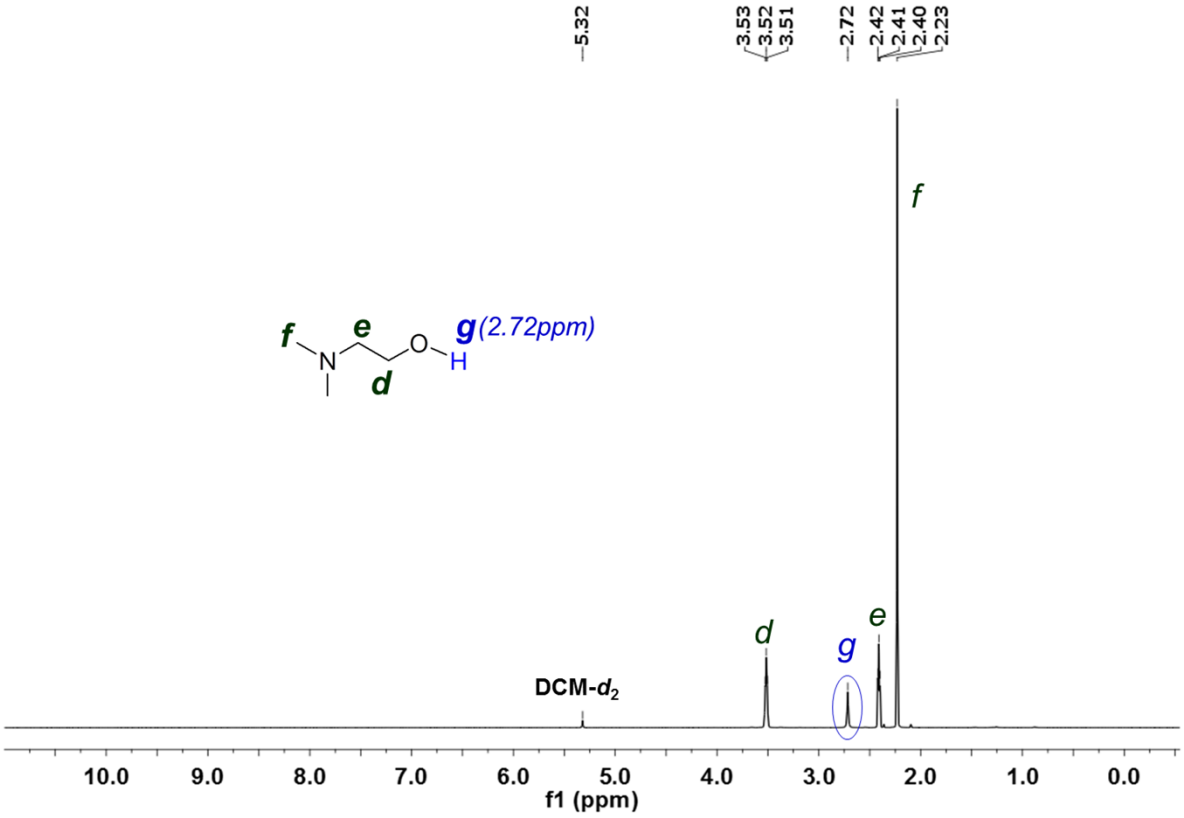

Figure S33. Full ^{1}H NMR spectrum of **DMEA**(500M, 25^{o}C, CD_2Cl_2).