SUPPORTING INFORMATION FOR:

Synthesis of non-isocyanate poly(hydroxy)urethanes from bis(cyclic carbonates) and polyamines.

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Structural characterization of PHUs and hydroxycarbamates

PHU 1a: ^{1}H-NMR (500 MHz, DMSO-d$_6$): 7.11 (d, J_{HH} = 5.7Hz, 1H, $NH_{urethane}$), 4.89 (d, J_{HH} = 5.1 Hz, 1H, *secondary OH*), 4.75 (t, J_{HH} = 5.5 Hz, 1H, *primary OH*), 4.67 (m, 1H), 3.89 (m, 2H), 3.73 (dd, J_{HH} = 10.4, 5.2 Hz, 1H), 3.46 (m, 2H,), 3.39 (m, 4H, $CH_2^{\alpha}{}_{BGDC}$), 3.33 (m, 4H), 2.96 (s, 4H, $CH_2^{\alpha}{}_{BDA}$), 1.51 (s, 4H, $CH_2^{\beta}{}_{BGDC}$), 1.37 (s, 4H, $CH_2^{\beta}{}_{BDA}$). ^{13}C-NMR (500 MHz, DMSO-d$_6$): 156.7 (C=O$_{urethane}$), 73.6, 72.4, 70.9 ($C^{\alpha}{}_{BGDC}$), 69.7, 68.3, 66, 60.6, 40.4 ($C^{\alpha}{}_{BDA}$), 27.2 ($C^{\beta}{}_{BDA}$), 26.4 ($C^{\beta}{}_{BGDC}$). IR: ν (C=O)$_{amide}$ = 1699 cm^{-1}; ν (NH) $_{amide}$ = 1533 cm^{-}1, ν (C–O)$_{urethane}$= 1252 cm^{-1}.

PHU 1b: ^{1}H-NMR (400 MHz, DMSO-d$_6$): 7.11 (s, 1H, NH$_{urethane}$), 4.90 (s, 1H, *OH*), 4.67 (s, 1H), 3.88 (m, 2H), 3.74 (s, 2H), 3.57 (s, 1H, CH_2^{α}-NH$_{isophorone}$), 3.46 (s, 2H), 3.39 (s, 2H, $CH_2^{\alpha}{}_{BGDC}$), 3.32 (s, 2H), 2.72 (d, $J_{H\text{-}H}$ = 5.7 Hz, 2H, CH^{β}-NH$_{isophorone}$), 1.52 (s, 2H, $CH_2^{\beta}{}_{BGDC}$), 0.93 (m, 11H, CH_3, CH_2 isophorone). ^{13}C-NMR (400 MHz, DMSO-d$_6$): 157 (C=O$_{urethane}$), 73.7, 72.4, 70.9 ($C^{\alpha}{}_{BGDC}$), 69.7, 68.3, 66, 60.6, 55 (C^{η}-NH$_{isophorone}$), 47.4 ($C_{isophorone}$), 43.9 (C^{α}-NH$_{isophorone}$), 35.5 ($C_{isophorone}$), 28.4 ($C_{isophorone}$), 26.4($C^{\beta}{}_{BGDC}$), 23.7 ($C_{isophorone}$). IR: ν (C=O)$_{amide}$ = 1695 cm^{-1}; ν (NH)$_{amide}$ = 1537 cm^{-1}, ν (C–O)$_{urethane}$ = 1243 cm^{-1}.

PHU 1c: ^{1}H-NMR (500 MHz, DMSO-d$_6$): 7.11 (s, 1H, NH$_{urethane}$), 4.89 (s, 1H, *secondary OH*), 4.75 (s, 1H, *primary OH*), 4.67 (m, 1H), 3.88 (ddd, , J_{HH} = 15.2, 10.9, 6 Hz), 3.73 (m, 2H), 3.46 (s, 2H), 3.39 (s, 2H, $CH_2^{\alpha}{}_{BGDC}$), 3.32 (s, 2H), 2.95 (d, J_{HH} = 5.1 Hz, 1H), 2.80 (d, J_{HH} = 3.6 Hz, 4H, CH^{σ}-NH$_{diamine}$), 1.67 (d, J_{HH} = 12.9 Hz, 2H), 1.51 (d, J_{HH} = 5.9 Hz, 4H, $CH_2^{\beta}{}_{BGDC}$), 1.37 (s, 2H, CH_2^{β}-NH$_{diamine}$), 1.27 (dd, J_{HH} = 13, 8.1Hz, 1H), 1.13 (m, 1H), 0.73 (m, 1H), 0.47 (q, J_{HH} = 12.2 Hz, 1H). ^{13}C-NMR (500 MHz, DMSO-d$_6$): 156.9 (C=O$_{urethane}$), 73.5, 72.4, 70.9 ($C^{\alpha}{}_{BGDC}$), 69.7, 68.3, 66, 60.6, 47.3 (C^{α}-NH$_{diamine}$), 38 (C^{β}-NH$_{diamine}$), 30.8 ($C_{diamine}$), 26.4 ($C^{\beta}{}_{BGDC}$). IR: ν (C=O)$_{amide}$ = 1695 cm^{-1}; ν (NH)$_{amide}$ = 1538 cm^{-1}, ν (C–O)$_{urethane}$ = 1251 cm^{-1}.

PHU 1d: ^{1}H-NMR (400 MHz, DMSO-d$_6$): 7.67 (s, 1H, NH$_{urethane}$), 7.26 (t, J_{HH} = 7.7Hz, 1H, $Ph_{\eta\text{-}xylene}$), 7.13 (d, J_{HH} = 7.2 Hz, 3H, $Ph_{\alpha\text{-}xylene}$), 4.92 (s, 1H, *secondary OH*), 4.78 (s, 1H, *primary OH*), 4.72 (m, 1H), 4.16 (d, J_{HH} = 5.8 Hz, 2H, CH_2^{α}-NH$_{\eta}$-xylene), 3.93 (ddd, , J_{HH} = 17.2, 11, 5.3 Hz, 2H), 3.76 (s, 1H), 3.48 (s, 2H), 3.39 (s, 2H, $CH_2^{\alpha}{}_{BGDC}$), 3.34 (s, 2H), 1.52 (s, 4H, $CH_2^{\beta}{}_{BGDC}$). ^{13}C-NMR (500 MHz, DMSO-d$_6$): 157 (C=O$_{urethane}$), 140.3 ($Ph_{\eta\text{-}xylene}$), 128.7 ($Ph_{\eta\text{-}xylene}$), 126.7 ($Ph_{\eta\text{-}xylene}$), 126 ($Ph_{\eta\text{-}xylene}$), 73.9, 72.4, 70.9 ($C^{\alpha}{}_{BGDC}$), 69.7, 68.3, 66.2, 60.6, 44.3 (C^{α}-NH$_{\eta}$-xylene), 26.4 ($C^{\beta}{}_{BGDC}$). IR: ν (C=O)$_{amide}$ = 1695 cm^{-1}; ν (NH)$_{amide}$ = 1533 cm^{-1}, ν (C–O)$_{urethane}$ = 1247 cm^{-1}.

PHU 1e: ^{1}H-NMR (500 MHz, DMSO-d$_6$): 7.15 (s, 1H, NH$_{urethane}$), 4.68 (dt, $J_{H\text{-}H}$ = 10; 4.9 Hz, 1H), 3.90 (ddd, , J_{HH} = 17.8, 10, 7 Hz, 2H), 3.75 (m, 1H), 3.46 (s, 2H), 3.39 (s, 2H, $CH_2^{\alpha}{}_{BGDC}$), 3.32 (d, J_{HH} = 5.4Hz, 2H), 3.01 (d, J_{HH} = 5.6Hz, 4H, CH_2^{α}-NH$_{urethane}$), 2.55 (m, 2H, CH_2^{α}-NH$_{triamine}$), 2.45 (m, 4H, CH_2^{β}-NH$_{urethane}$), 2.38 (dd, J_{HH} = 13.1, 6.7 Hz, 2H, CH_2^{β}-NH$_{triamine}$), 1.52 (m, 2H, $CH_2^{\beta}{}_{BGDC}$). ^{13}C-NMR (500 MHz, DMSO-d$_6$): 156.9 (C=O$_{urethane}$), 73.9, 72.4, 70.9 ($C^{\alpha}{}_{BGDC}$), 69.7, 68.2, 66.2, 60.6, 58.4

(C^{β}-$NH_{urethane}$), 54.4 (C^{β}-$NH_{triamine}$), 40 (C^{α}-$NH_{triamine}$), 39.5(CH_2^{α}-$NH_{urethane}$), 26.4 (C^{β}BGDC). IR: ν (C=O)amide = 1696 cm^{-1}; ν (NH)amide = 1532 cm^{-1}, ν (C–O)urethane = 1251 cm^{-1}.

PHU 1f: ^{1}H-NMR (500 MHz, DMSO-d_6): 7.13 (s, 1H, NHurethane), 6.21 (s, 1H, NH_{urea}), 4.65 (s, 1H), 3.86 (m, 2H), 3.82 (m, 1H, CH^{α}-$NH_{L\text{-}lysine}$), 3.75 (m, 1H), 3.46 (s, 2H), 3.39 (s, 2H, CH_2^{α}BGDC), 3.32 (d, J_{HH} = 5.4Hz, 2H), 3.26-3.3.20 (m, 8H, *DBU*), 2.91 (d, J_{HH} = 5.4 Hz, 4H, CH_2^{α}-$NH_{L\text{-}lysine}$), 2.61 (d, J_{HH} = 5.4 Hz, 2H, *DBU*), 1.85 (m, 2H, *DBU*), 1.64-1.60 (m, 4H, *DBU*), 1.51 (s, 2H, CH_2^{β}BGDC), 1.32 (m, 4H, CH_2^{β}-$NH_{L\text{-}lysine}$), 1.19 (s, 2H, CH_2^{δ}-$NH_{L\text{-}lysine}$). ^{13}C-NMR (500 MHz, DMSO-d_6): 174.1(C=O_{L}-lysine), 164.7 (*DBU*), 156.7 (C=Ourethane), 155.8 (C=Ourea), 73.9, 72.4, 70.9 (C^{α}BGDC), 69.7, 68.2, 66.0, 60.6, 56.0 (C^{α}-$NH_{L\text{-}lysine}$), 53.4 (*DBU*), 48.22 (*DBU*), 40.9 (C^{α}-$NH_{L\text{-}lysine}$), 32.9 (C^{β}-$NH_{L\text{-}lysine}$), 32.7 (*DBU*), 30.0 (C^{β}-$NH_{L\text{-}lysine}$), 27.0(*DBU*), 26.4 (C^{η}BGDC), 24.5 (*DBU*), 22.8 (C^{γ}-$NH_{L\text{-}lysine}$), 20.2 (*DBU*). IR: ν (C=O)amide = 1697 cm^{-1} ; ν (C=O)urea = 1646 cm^{-1}, ν (NH)amide = 1537 cm^{-1}, ν (C–O)urethane = 1245 cm^{-1}.

Hydroxycarbamate 2: ^{1}H-NMR (400 MHz, DMSO-d_6): 7.11 (d, $J_{H\text{-}H}$ = 5.5Hz, 1H, NHurethane), 4.94 (m, 2H, CH cyclic carbonate), 4.75 (t, $J_{H\text{-}H}$ = 5.5 Hz, 1H, *primary OH*), 4.67 (m, 1H), 4.52 (t, J_{HH} = 8.4Hz, 2H, $CH_{2,\text{cyclic carbonate}}$), 4.25 (dd, J_{HH} = 8.2, 5.9Hz, 2H, $CH_{2,\text{cyclic carbonate}}$), 4.09 (q, J_{HH} = 5.2 Hz, 1H, *secondary OH*), 3.89 (dd, J_{HH} = 27.1, 5.3Hz, 2H), 3.74 (m, 1H), 3.59 (ddd, J_{HH} = 15.6, 11.5, 3.4Hz, 4H), 3.46 (m, 2H), 3.39 (m, 4H, CH_2^{σ}BGDC), 3.33 (m, 2H), 2.95 (s, 4H, CH_2^{α}BDA), 1.53 (s, 4H, CH_2^{β}BGDC), 1.37 (s, 4H, CH_2^{η}BDA). ^{13}C-NMR (400 MHz, DMSO-d_6): 156.7 (C=Ourethane), 155.4 (C=Ocyclic carbonate), 76.0 (CHcyclic carbonate), 73.6, 72.4, 71.0, 70.9 (C^{α}BGDC), 70.0, 68.3, 66.6 ($CH_{2,\text{ cyclic carbonate}}$), 66.0, 60.6, 40.4 ($C^{\alpha}$BDA), 27.2 ($CH_2^{\beta}$BDA), 26.1 ($CH_2^{\beta}$BGDC). IR: ν (C=O)cyclic carbonate = 1787 cm^{-1}, ν (C=O)amide = 1692 cm^{-1}; ν (NH)amide = 1525 cm^{-1}, ν (C–O)urethane = 1249, 1049 cm^{-1}.

Analysis found:	C: 50.5 %	H: 7.5 %	N: 3.9 %
Calculated:	C: 50.3 %	H: 7.2 %	N: 4.2 %

Hydroxycarbamate 3: ^{1}H-NMR (400 MHz, DMSO-d_6): 7.11 (s, 1H, NHurethane), 4.68 (m, 1H), 3.88 (ddd, , J_{HH}= 17.1, 11, 5.4Hz, 4H, *2*), 3.73 (m, 1H), 3.46 (m, 2H, *11*), 3.39 (m, 4H, CH_2^{α}BGDC), 3.32 (m, 4H), 2.95 (dd, J_{HH}= 12.6, 6.5Hz, 4H, CH_2^{α}BDA), 2.5 (m, 4H, CH_2^{α}BDA,urethane), 1.51 (d, J_{HH}= 4.6Hz, 4H, CH_2^{β}BGDC), 1.35 (m, 4H, CH_2^{β}BDA,BDA urethane *3*). ^{13}C-NMR (400 MHz, DMSO-d_6): 156.7 (C=Ourethane), 73.5, 72.4, 70.9 (C^{α}BGDC), 69.7, 68.3, 66.0, 60.6, 41.9 (C^{α}BDA, urethane), 40.4 (C^{α}BDA), 31.1 (C^{β}BDA, urethane) 27.5 (C^{β}BDA), 26.4 (C^{β}BGDC). IR: ν (O–H) = 3340 cm^{-1}, ν (C=O)amide = 1687 cm^{-1}; ν (NH)amide = 1535 cm^{-1}, ν (C–O)urethane = 1248, 1109 cm^{-1}.

Analysis found:	C: 52.7 %	H: 9.5 %	N: 11.4 %
Calculated:	C: 52.5 %	H: 9.2 %	N: 11.7 %

Figure S1. ^{1}H-NMR spectrum of PHU **1a** in DMSO-d$_6$.

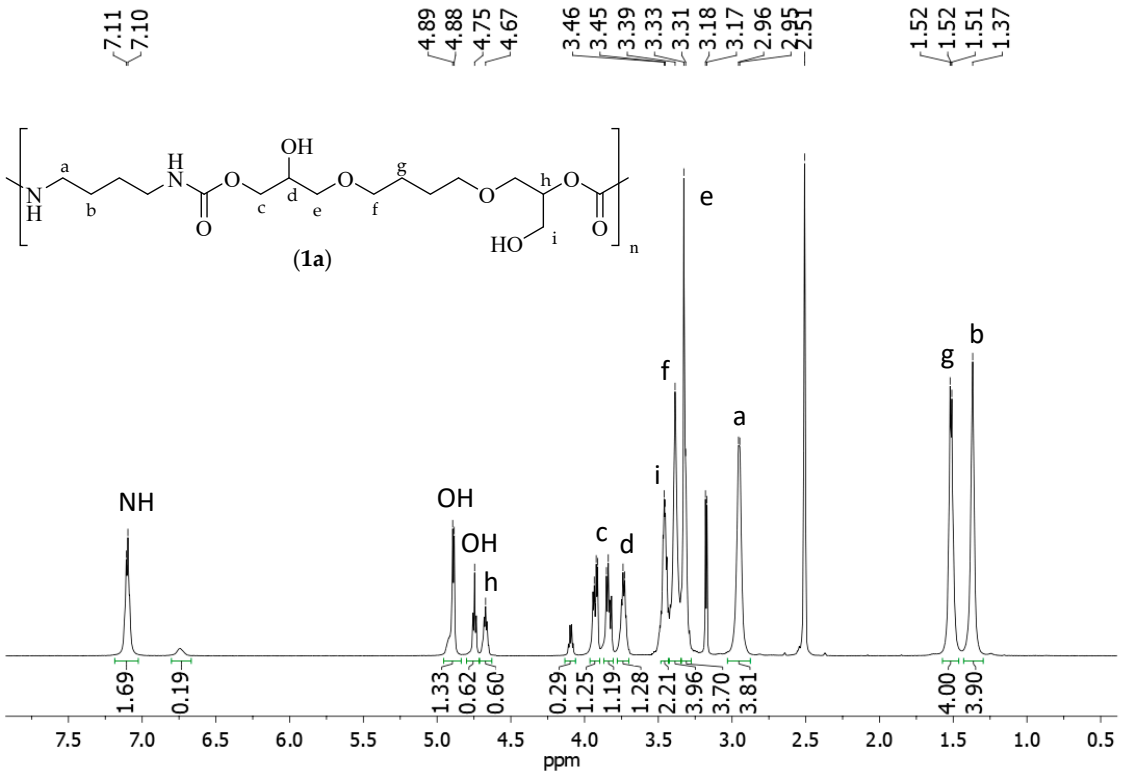

Figure S2. ^{13}C-{^{1}H}-NMR spectrum of PHU **1a** in DMSO-d$_6$.

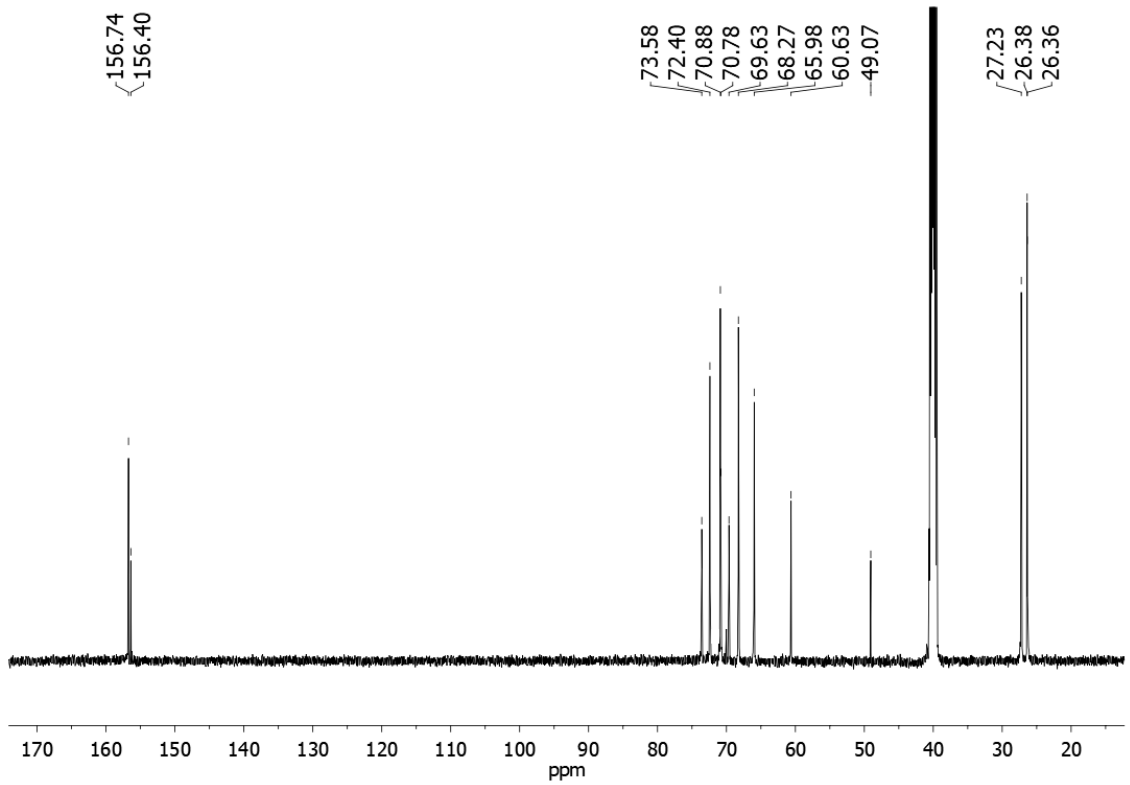

Figure S3. IR spectrum of PHU **1a**.

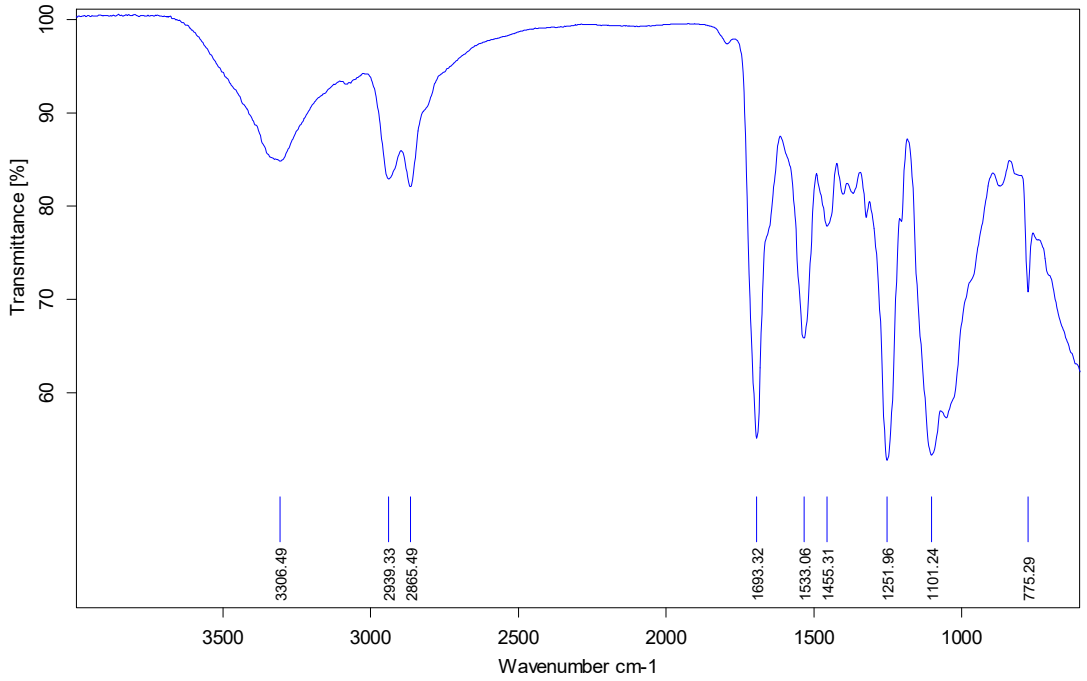

Figure S4. DSC thermogram of PHU **1a**.

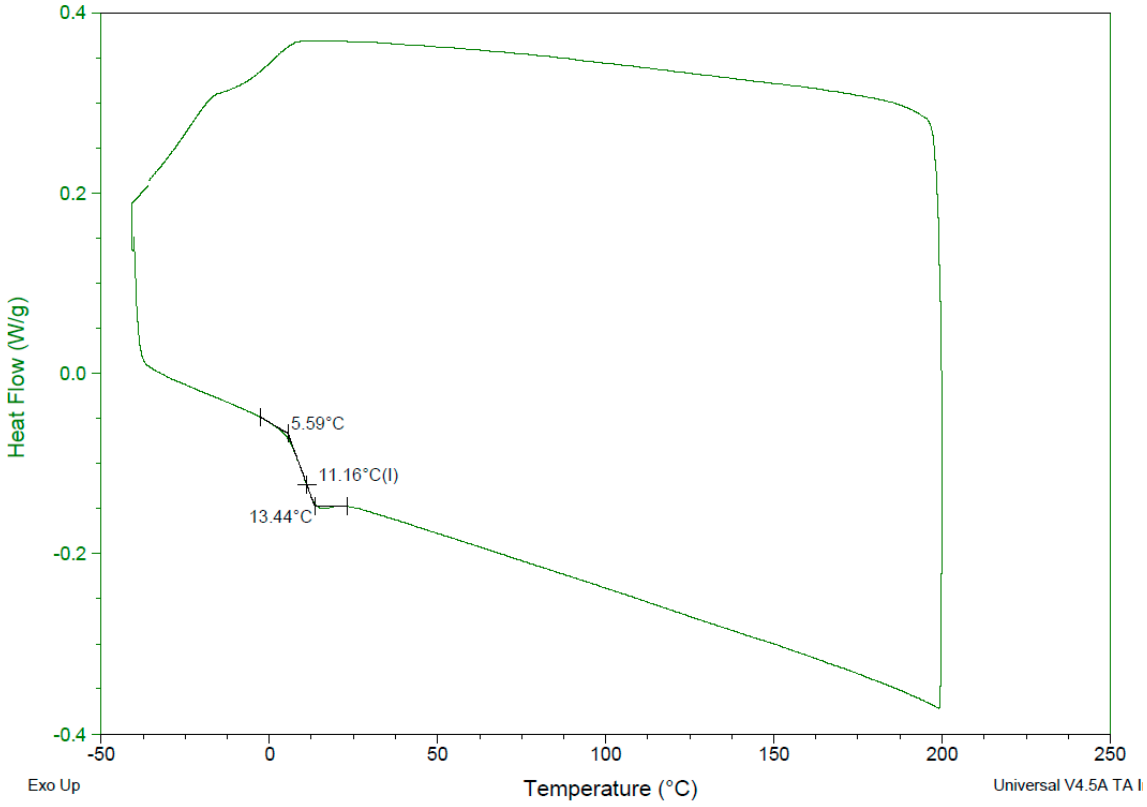

Figure S5. TGA thermogram of PHU **1a**.

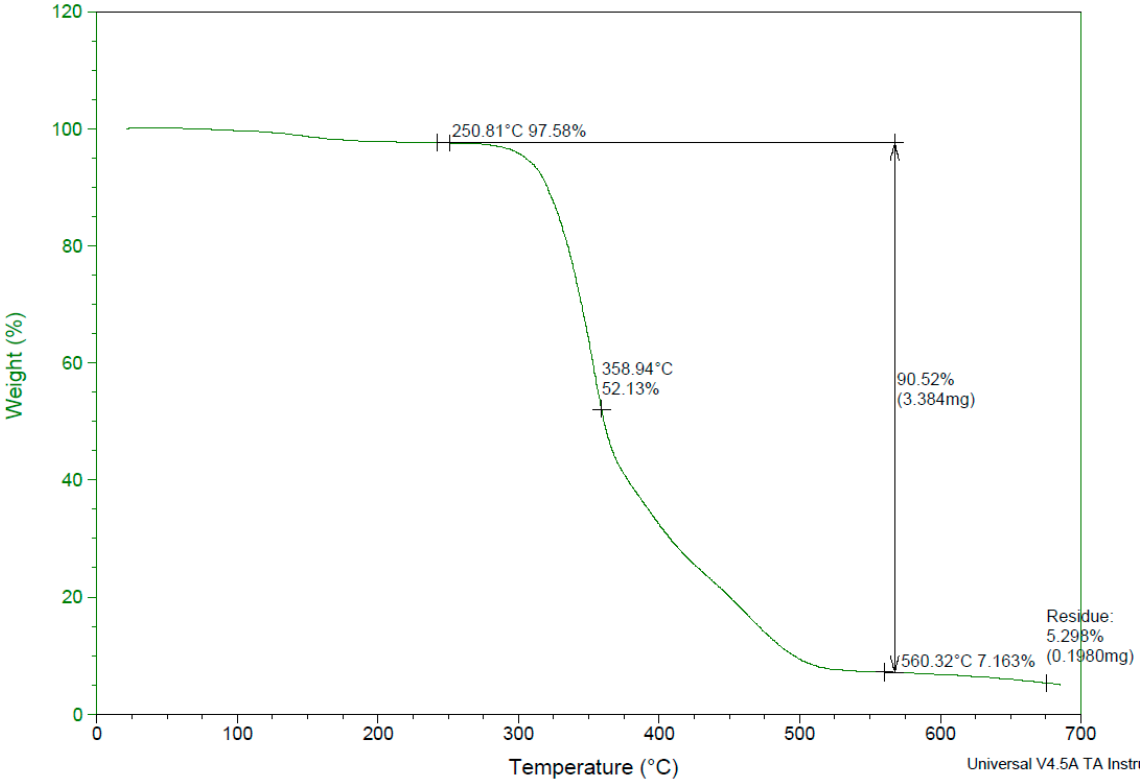

Figure S6. ^{1}H-NMR spectrum of PHU **1b** in DMSO-d$_6$.

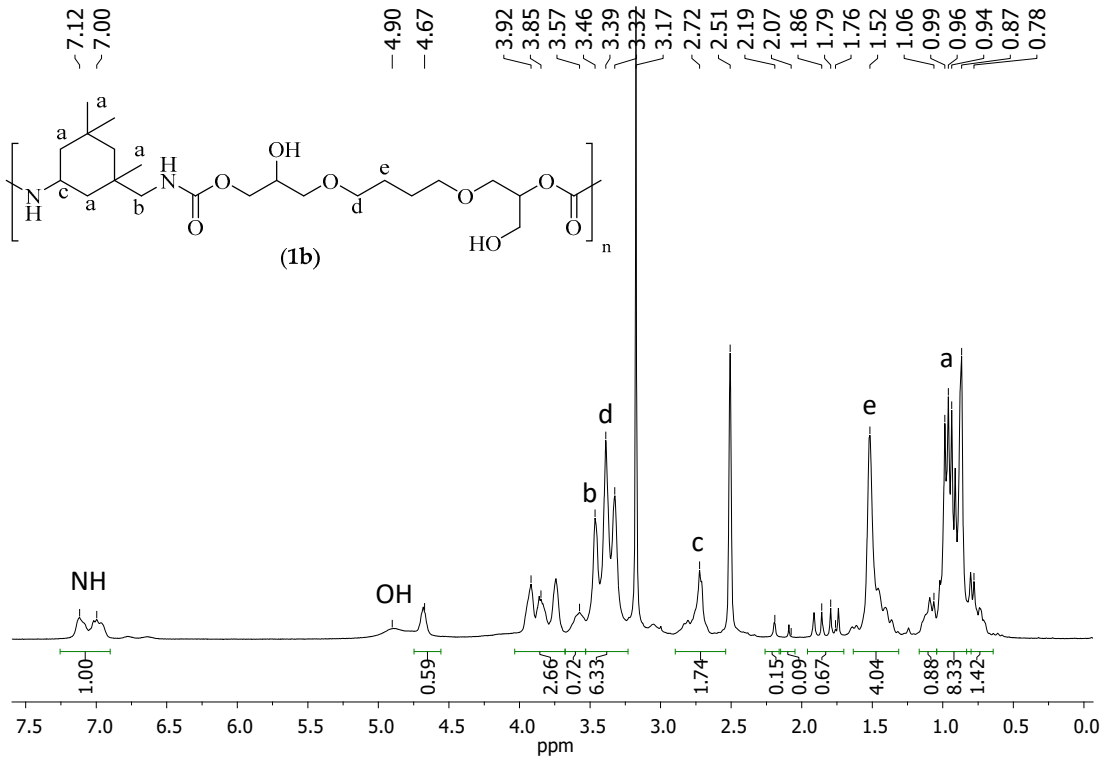

Figure S7. ^{13}C-{^{1}H}-NMR spectrum of PHU **1b** in DMSO-d_6.

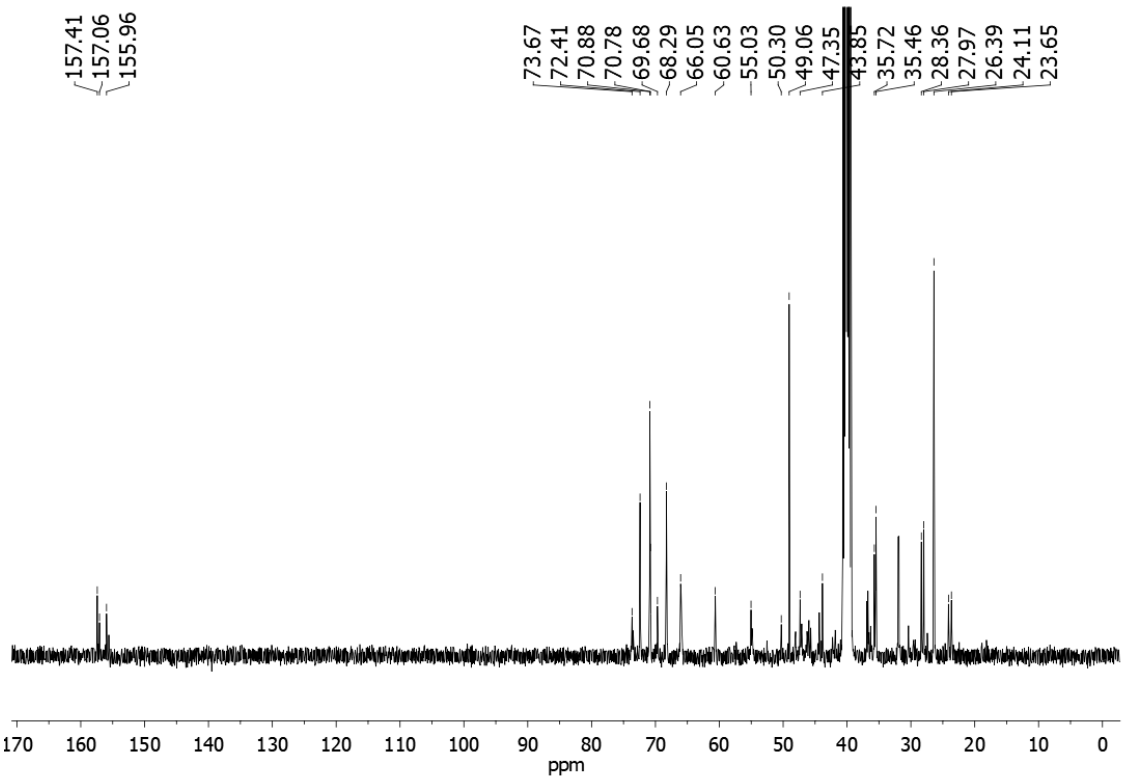

Figure S8. IR spectrum of PHU **1b**.

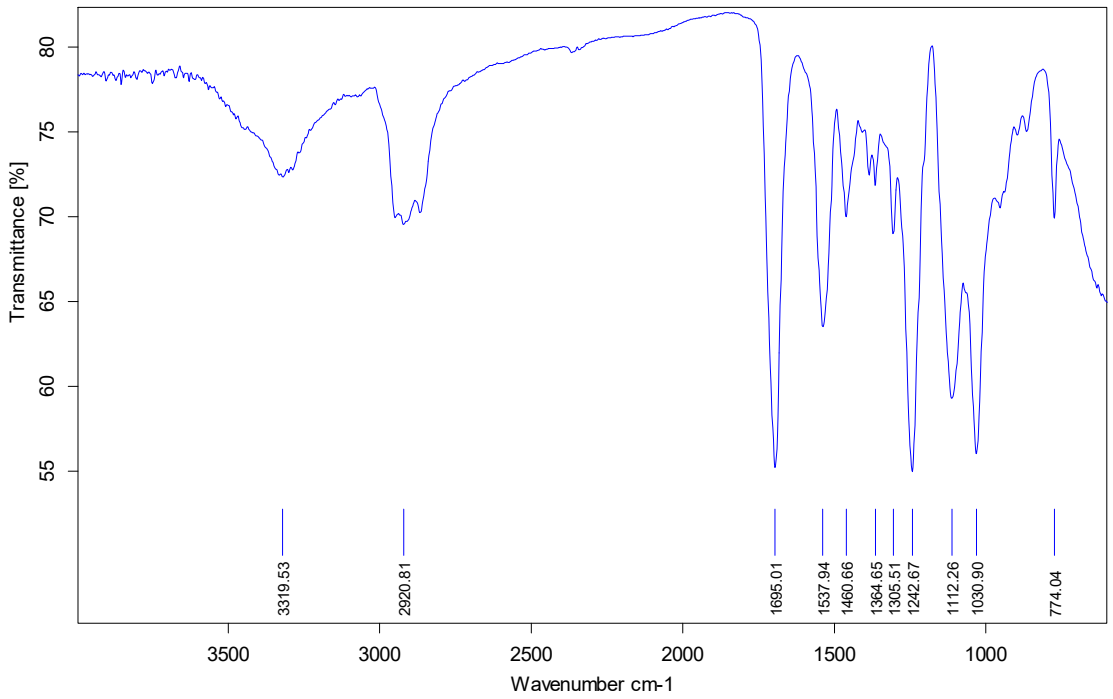

Figure S9. MALDI-ToF spectrum of PHU **1b**.

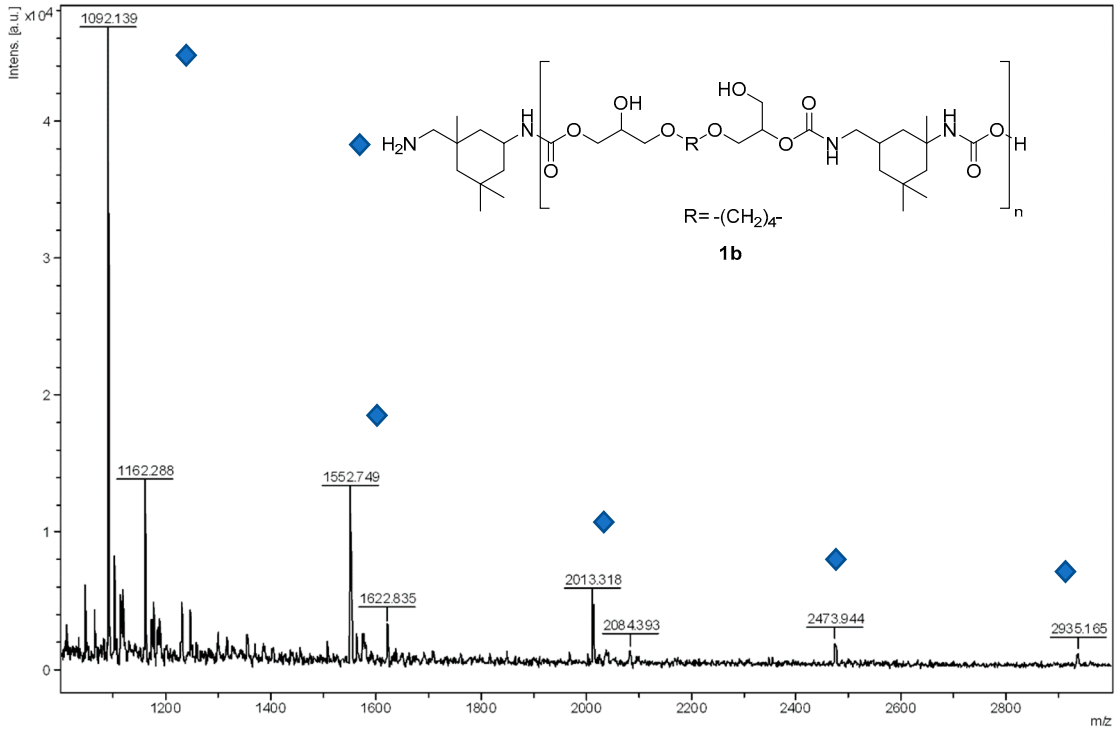

Figure S10. DSC thermogram of PHU **1b**.

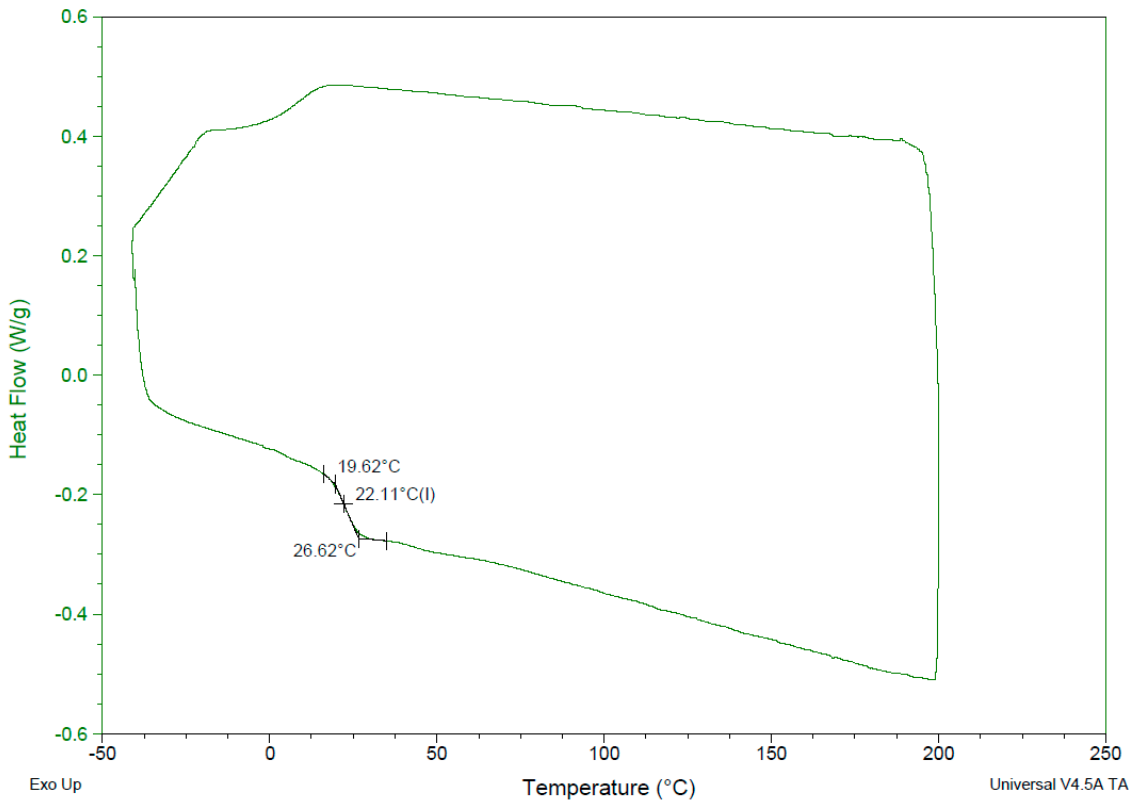

Figure S11. TGA thermogram of PHU **1b**.

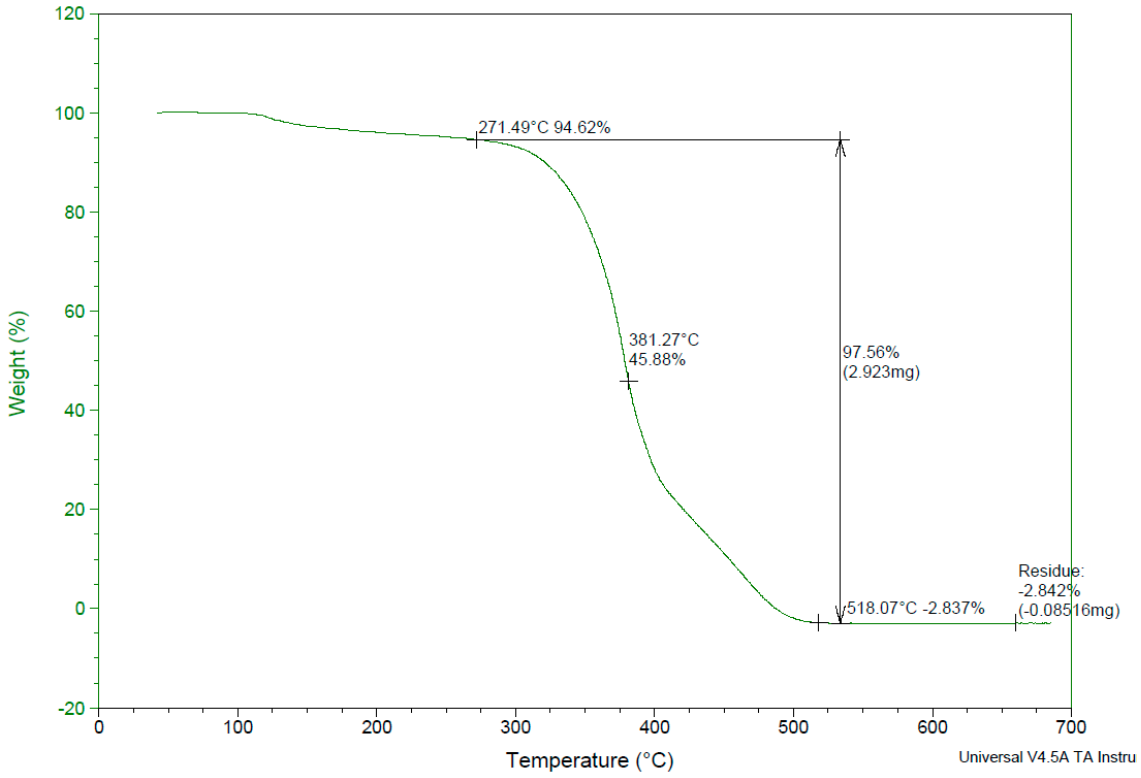

Figure S12. ^{1}H-NMR spectrum of PHU **1c** in DMSO-d$_6$.

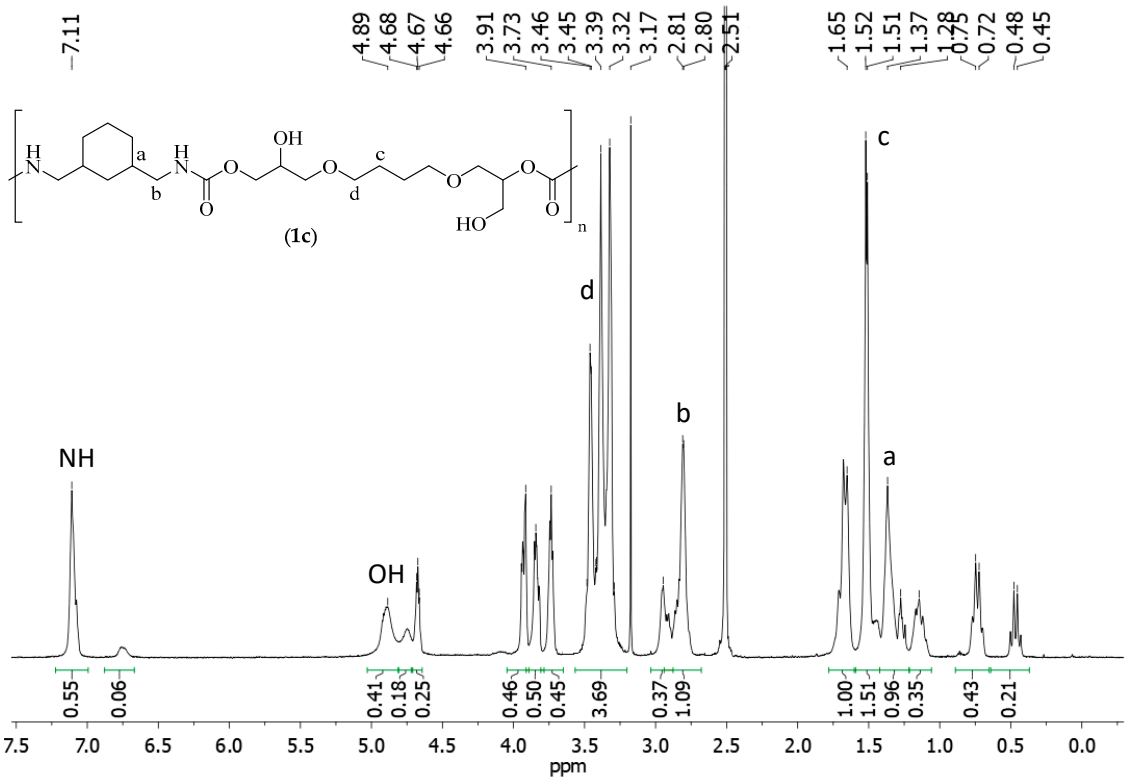

Figure S13. ^{13}C-{^{1}H}-NMR spectrum of PHU **1c** in DMSO-d_6.

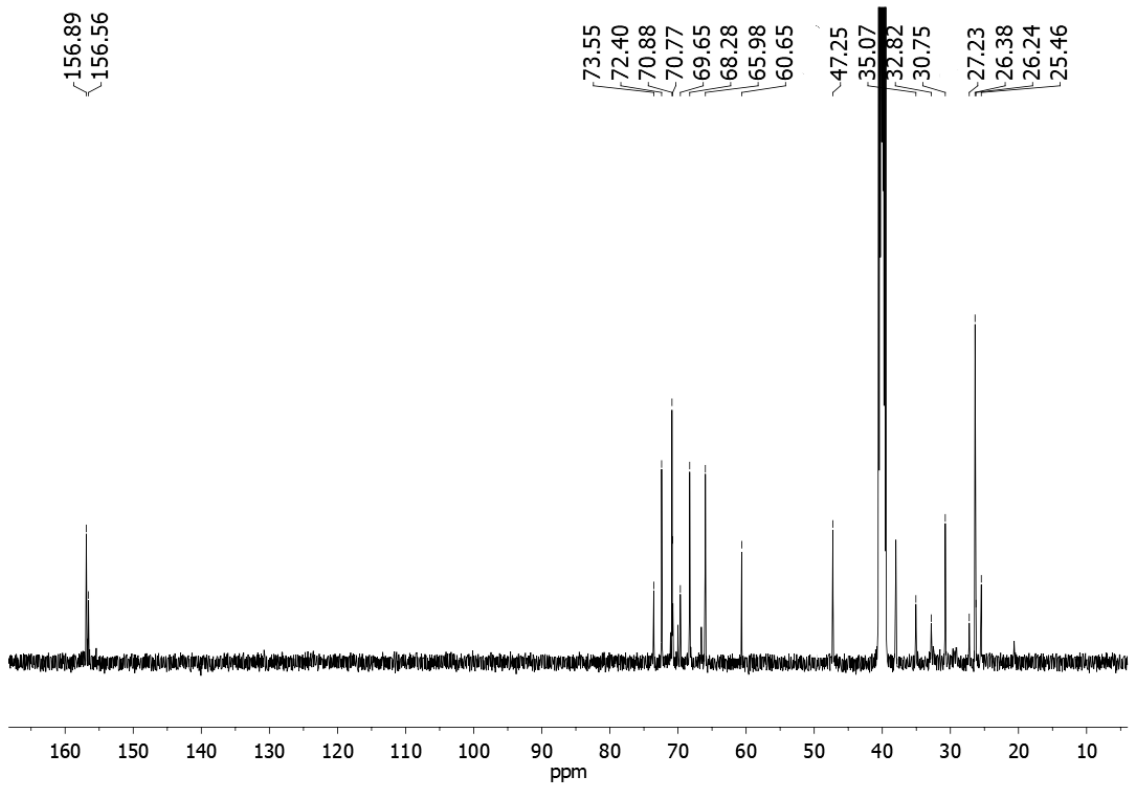

Figure S14. IR spectrum of PHU **1c**.

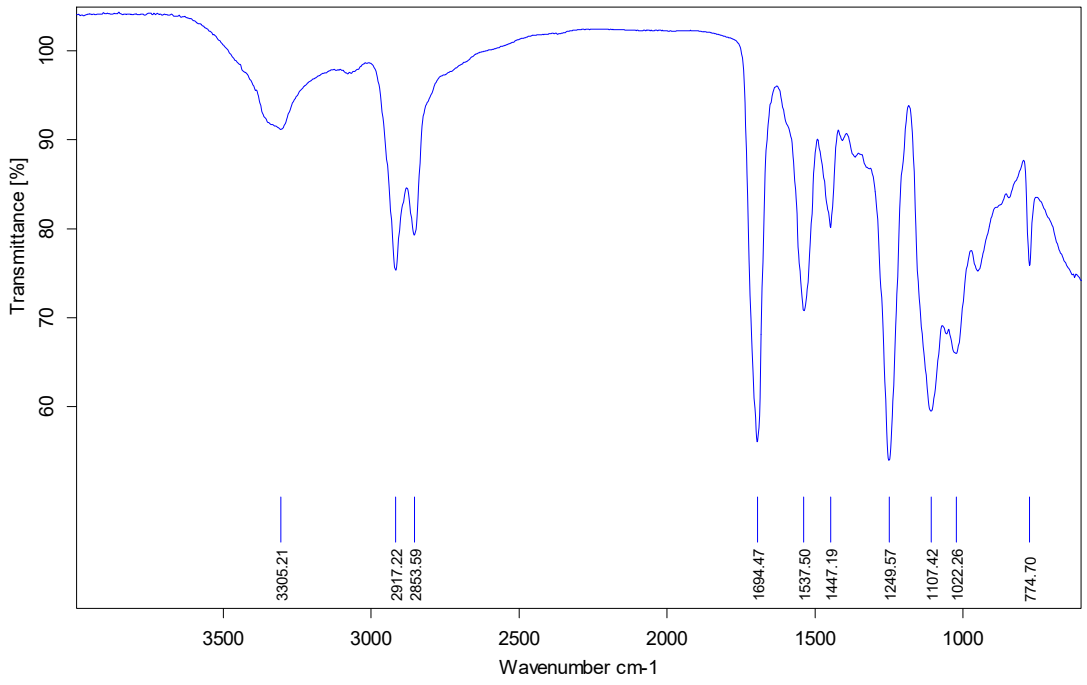

Figure S15. DSC thermogram of PHU **1c**.

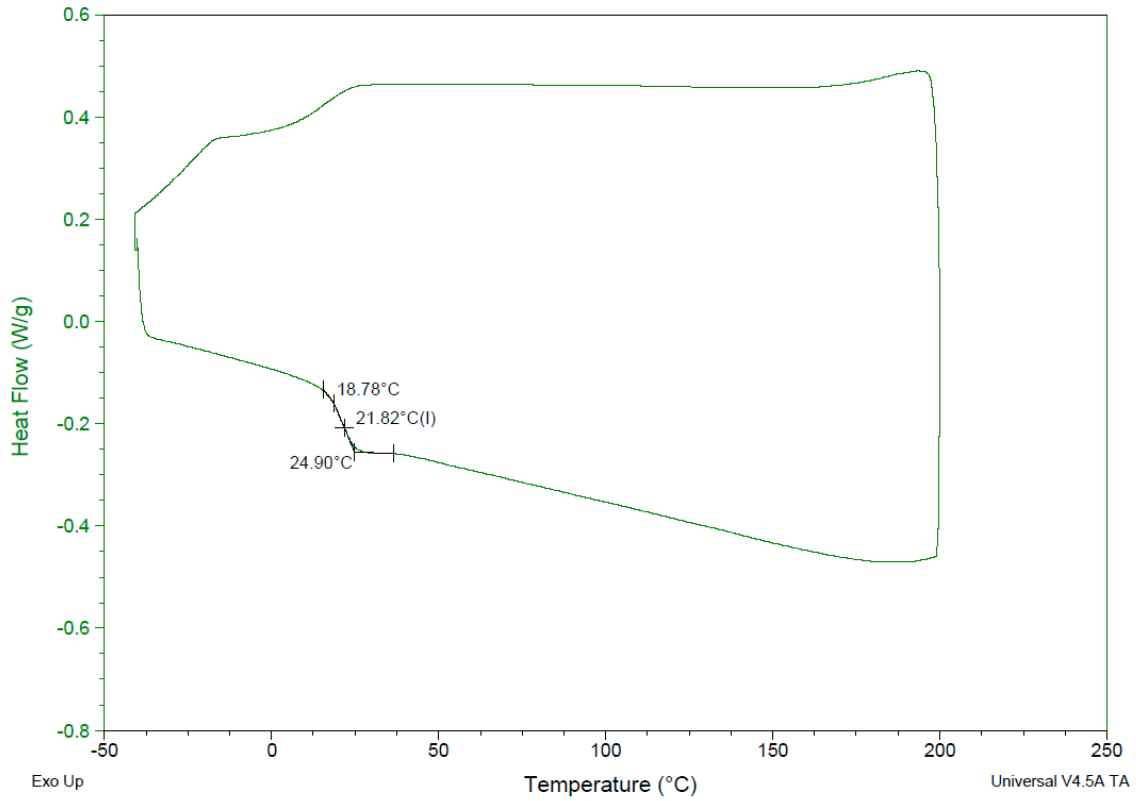

Figure S16. TGA thermogram of PHU **1c**.

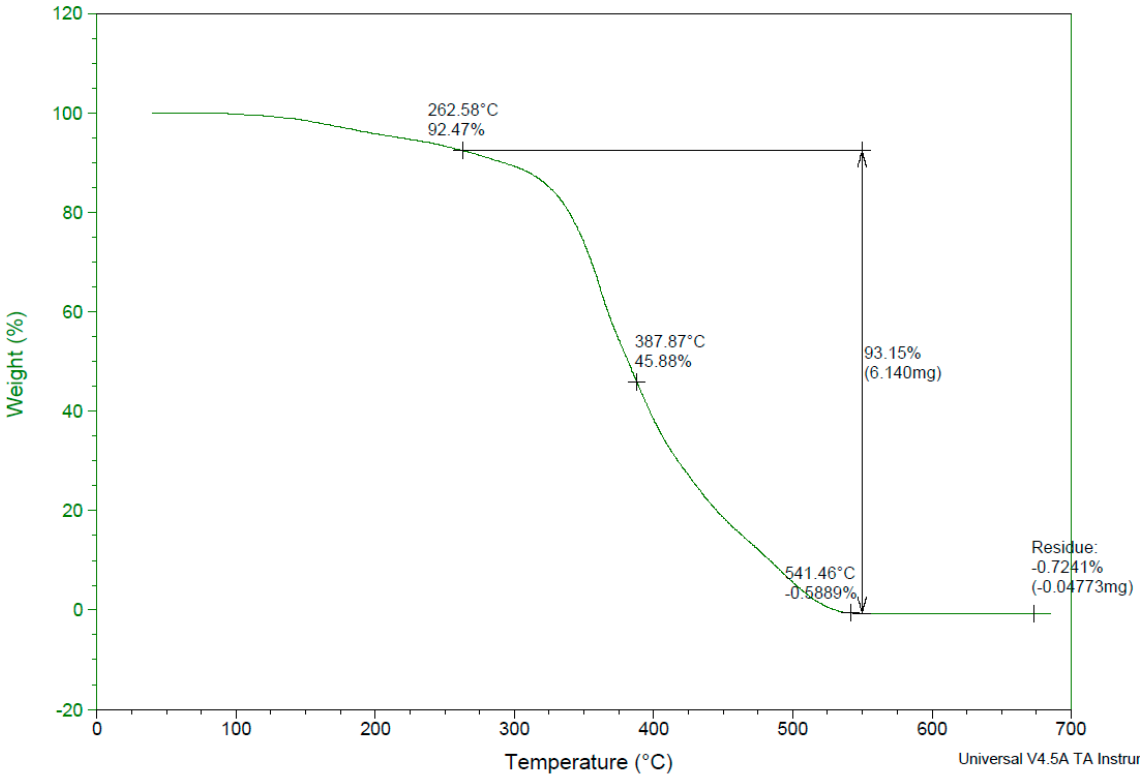

Figure S17. [1]H-NMR spectrum of PHU **1d** in DMSO-d6.

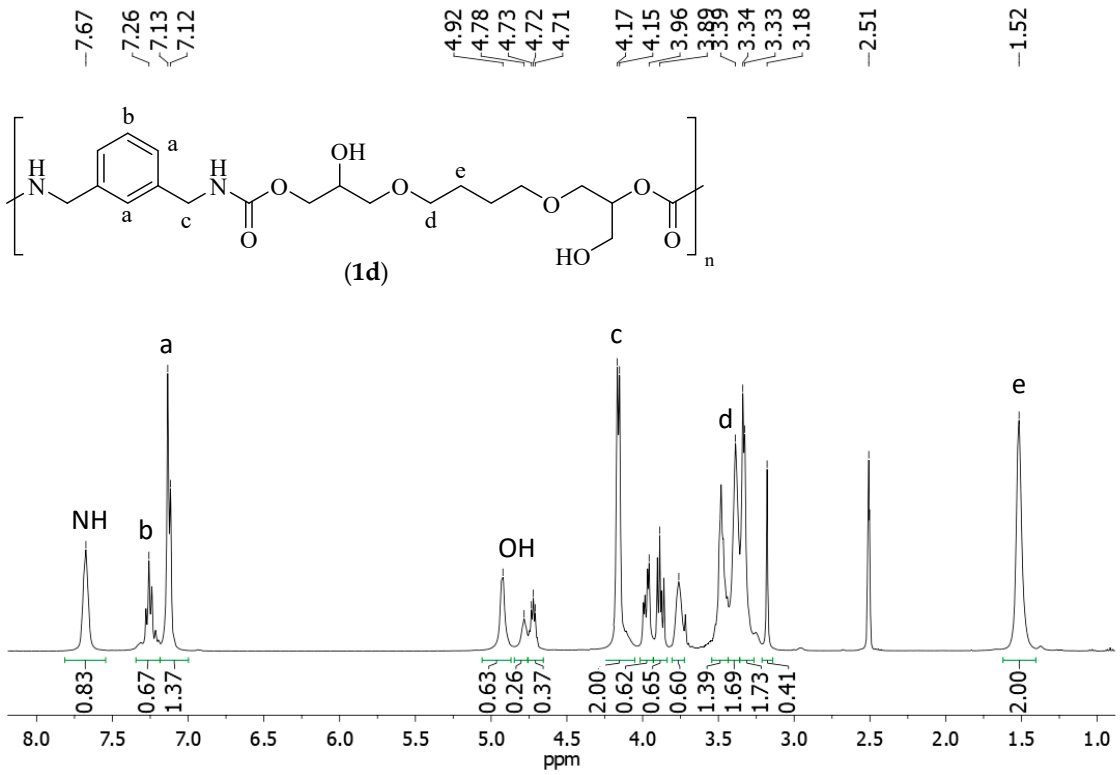

Figure S18. [13]C-{[1]H}-NMR spectrum of PHU **1d** in DMSO-d6.

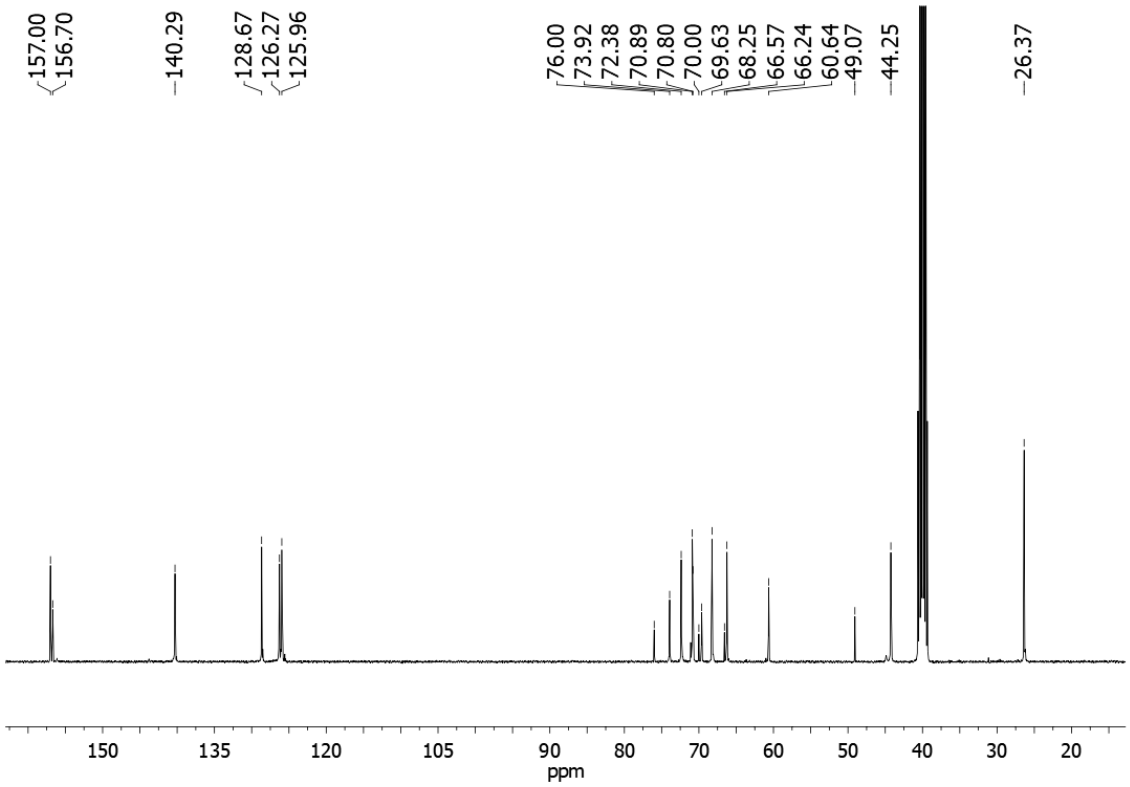

Figure S19. IR spectrum of PHU **1d**.

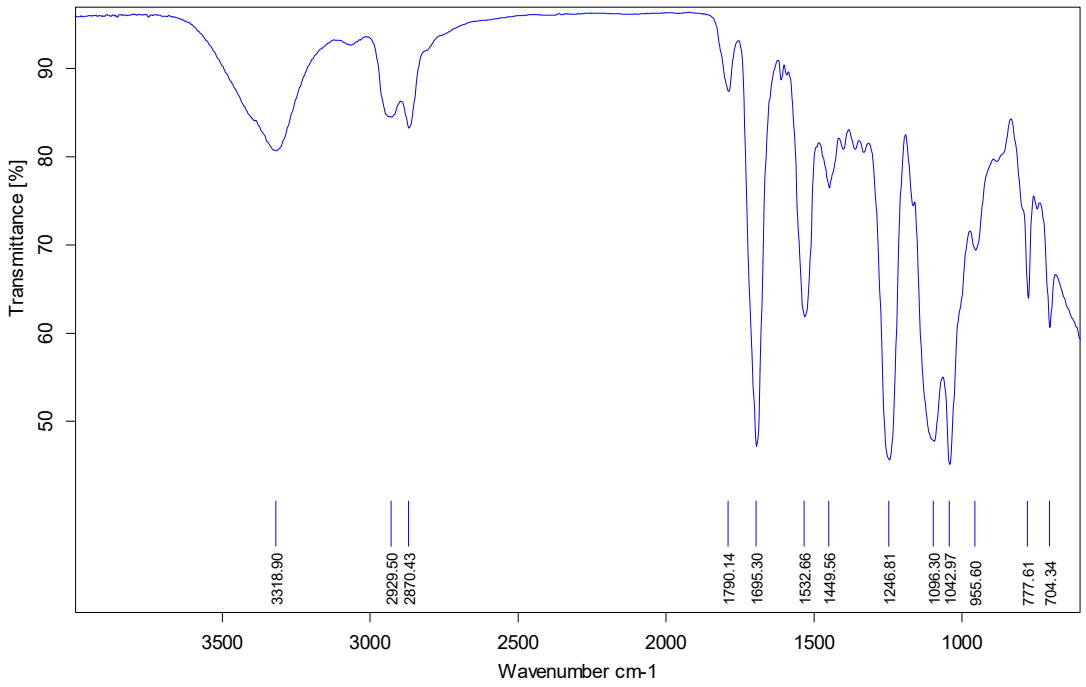

Figure S20. GPC trace of PHU **1d**.

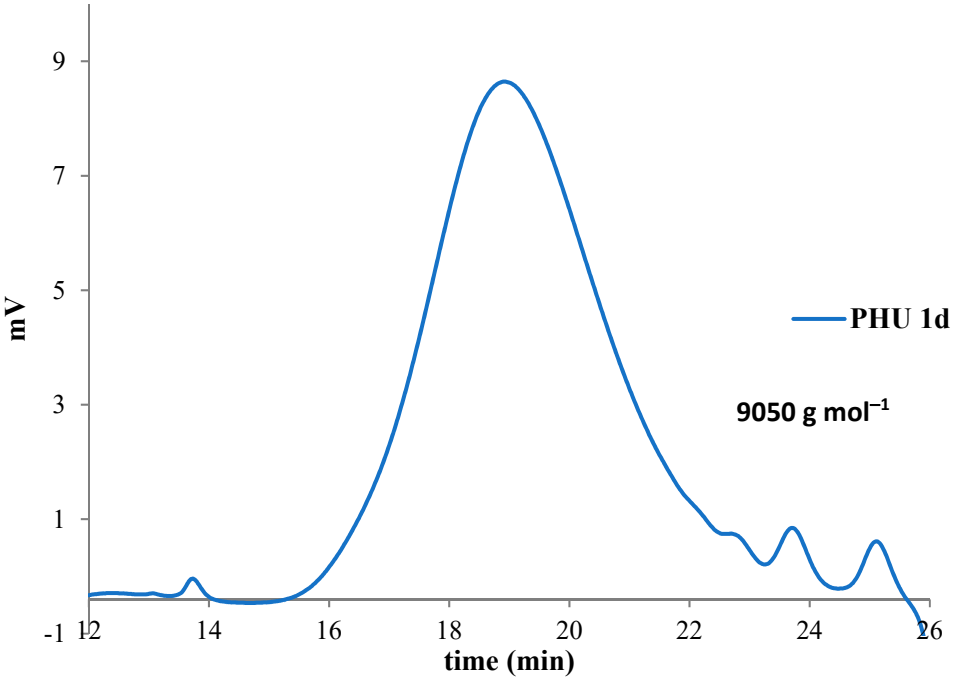

Figure S21. DSC thermogram of PHU **1d**.

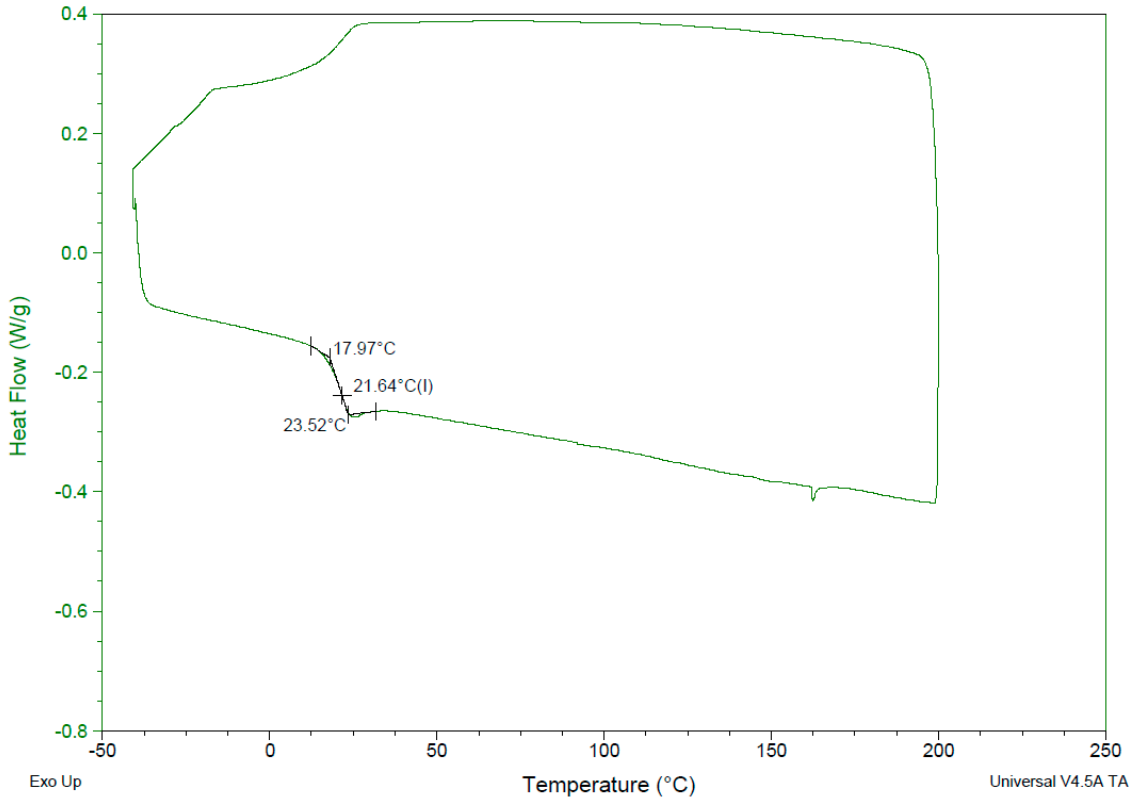

Figure S22. TGA thermogram of PHU **1d**.

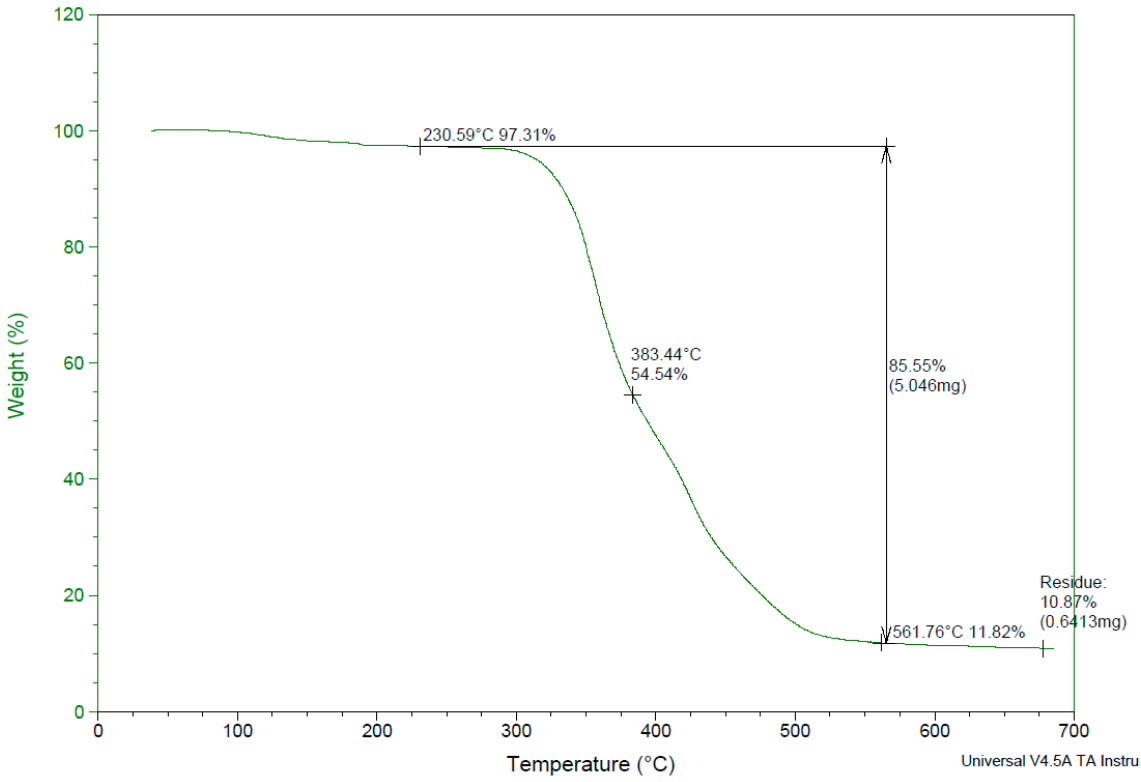

Figure S23. [1]H-NMR spectrum of PHU **1e** in DMSO-d6.

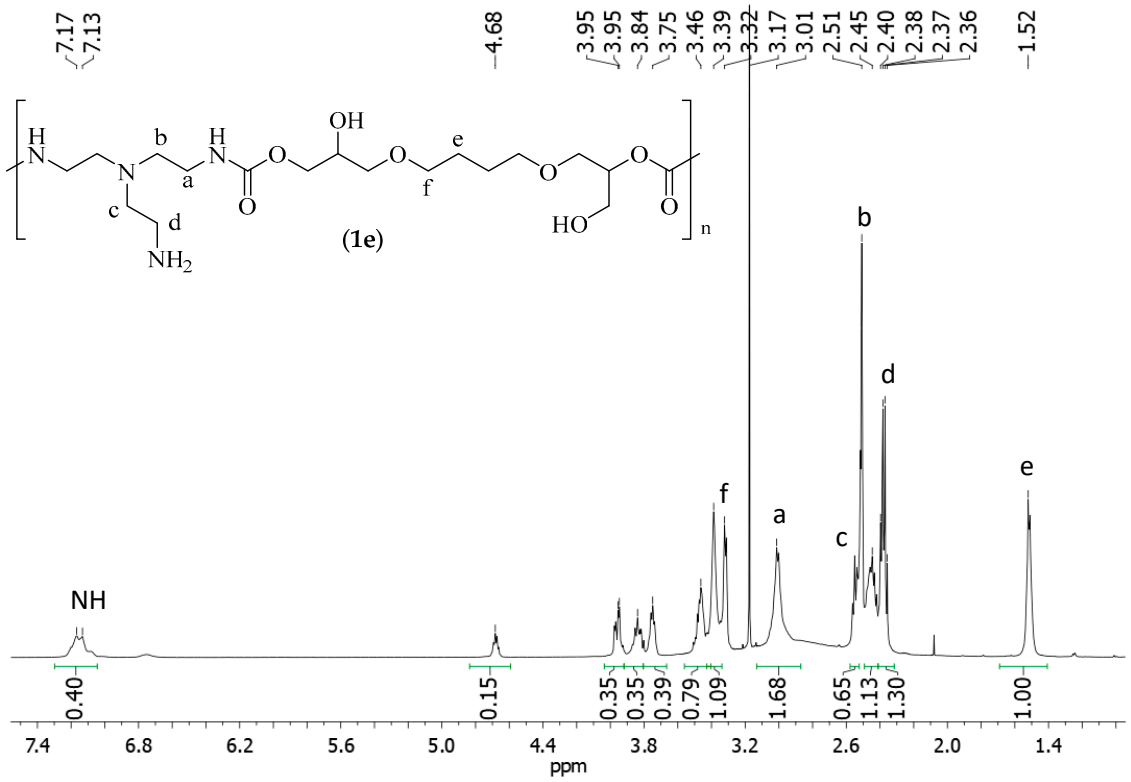

Figure S24. [13]C-{[1]H}-NMR spectrum of PHU **1e** in DMSO-d6.

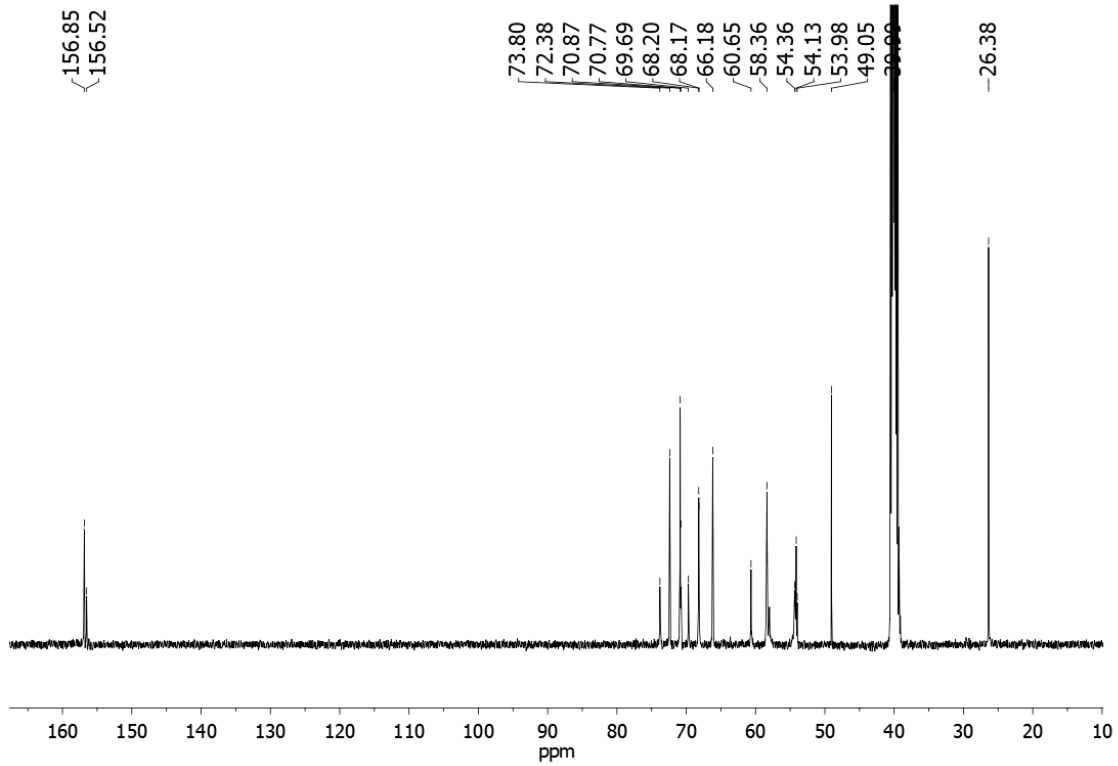

Figure S25. IR spectrum of PHU **1e**.

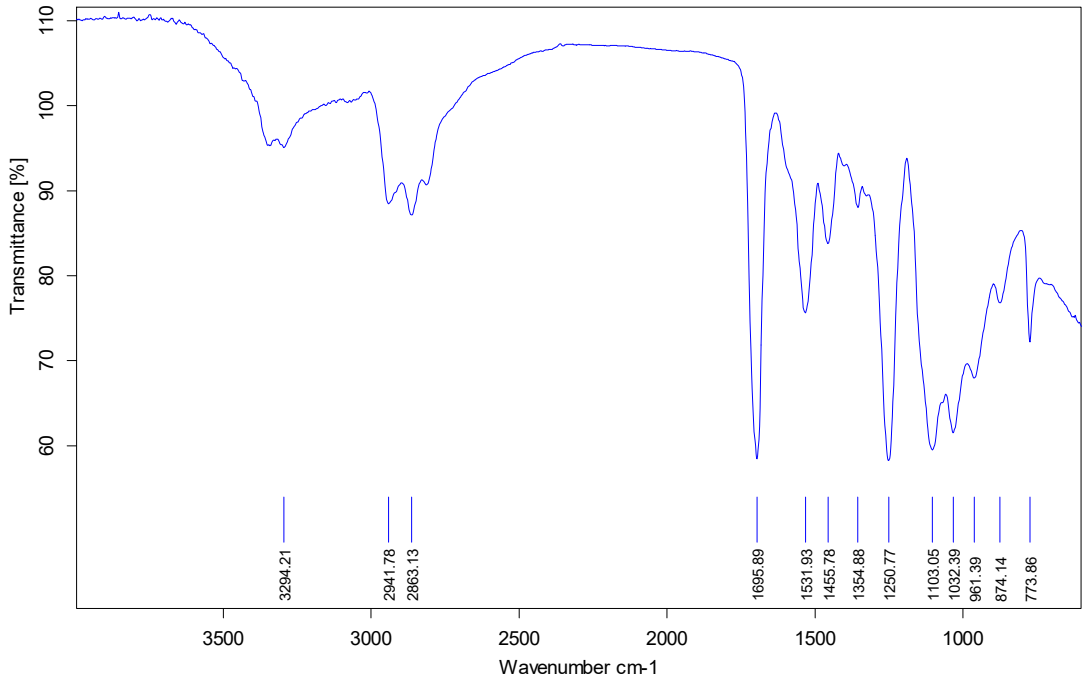

Figure S26. DSC thermogram of PHU **1e**.

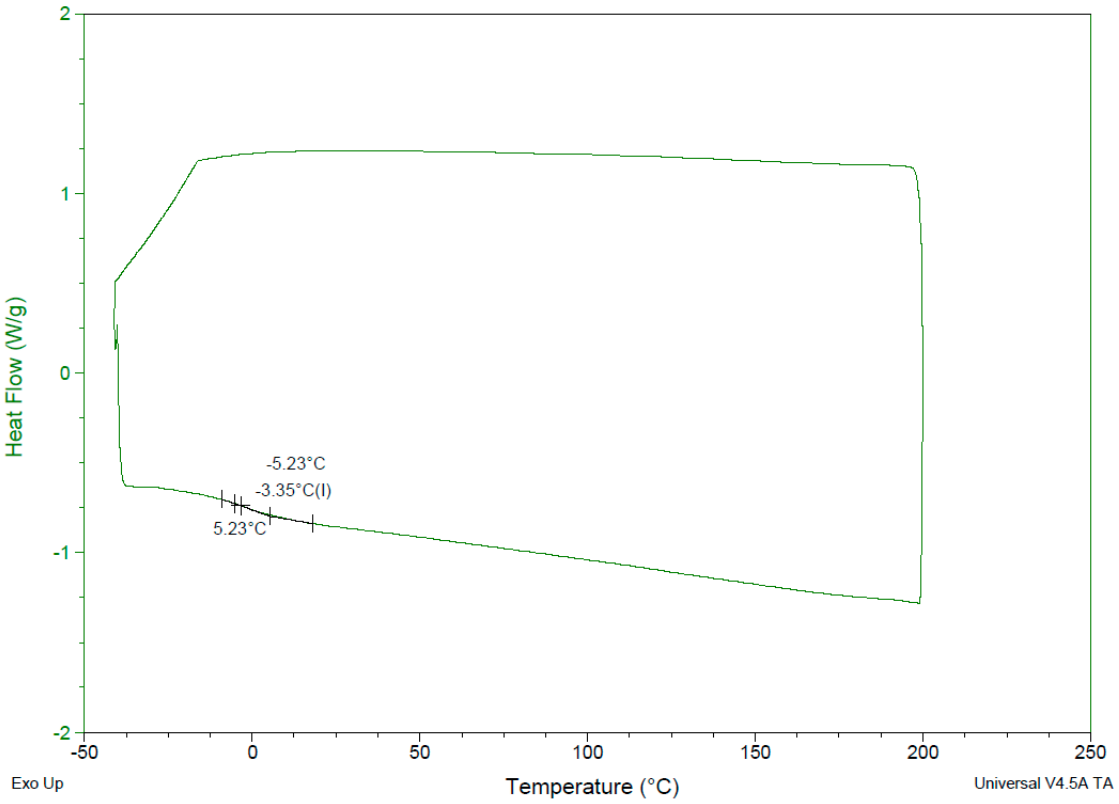

Figure S27. TGA thermogram of PHU **1e**.

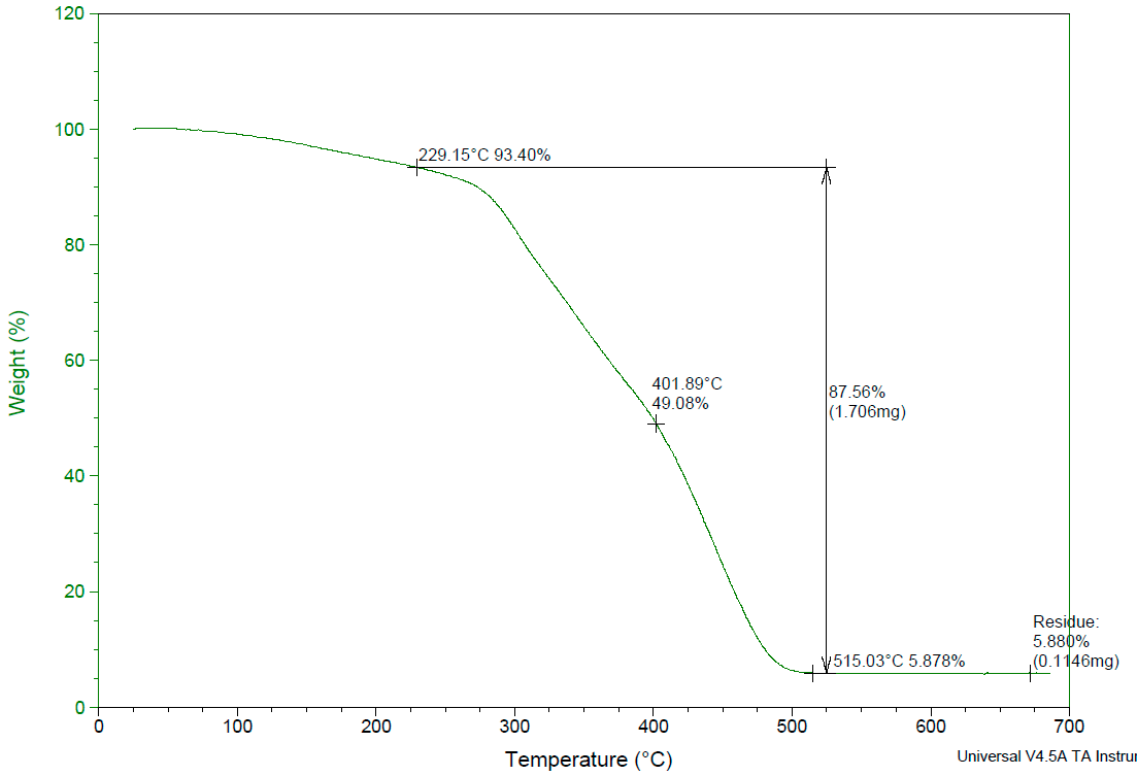

Figure S28. IR spectrum of PHU **1e** crosslinked (0.66 eq. tris-(aminoethyl)amine).

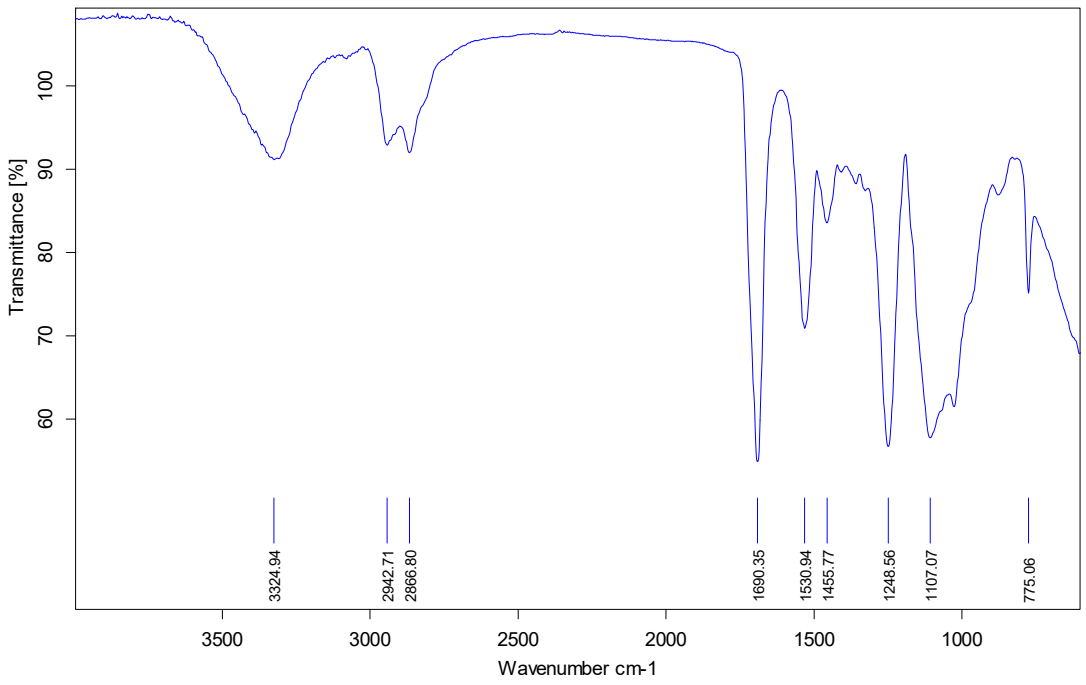

Figure S29. DSC thermogram of PHU **1e** crosslinked (0.66 eq. tris-(aminoethyl)amine).

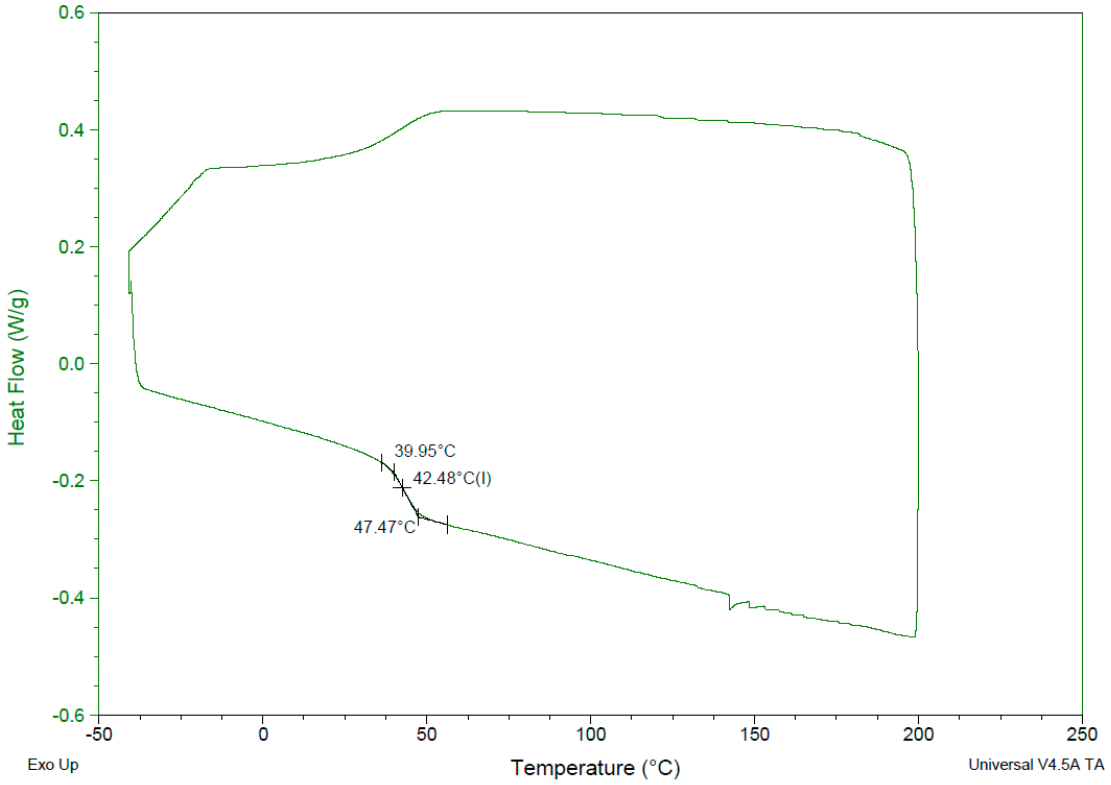

Figure S30. TGA thermogram of PHU **1e** crosslinked (0.66 eq. tris-(aminoethyl)amine).

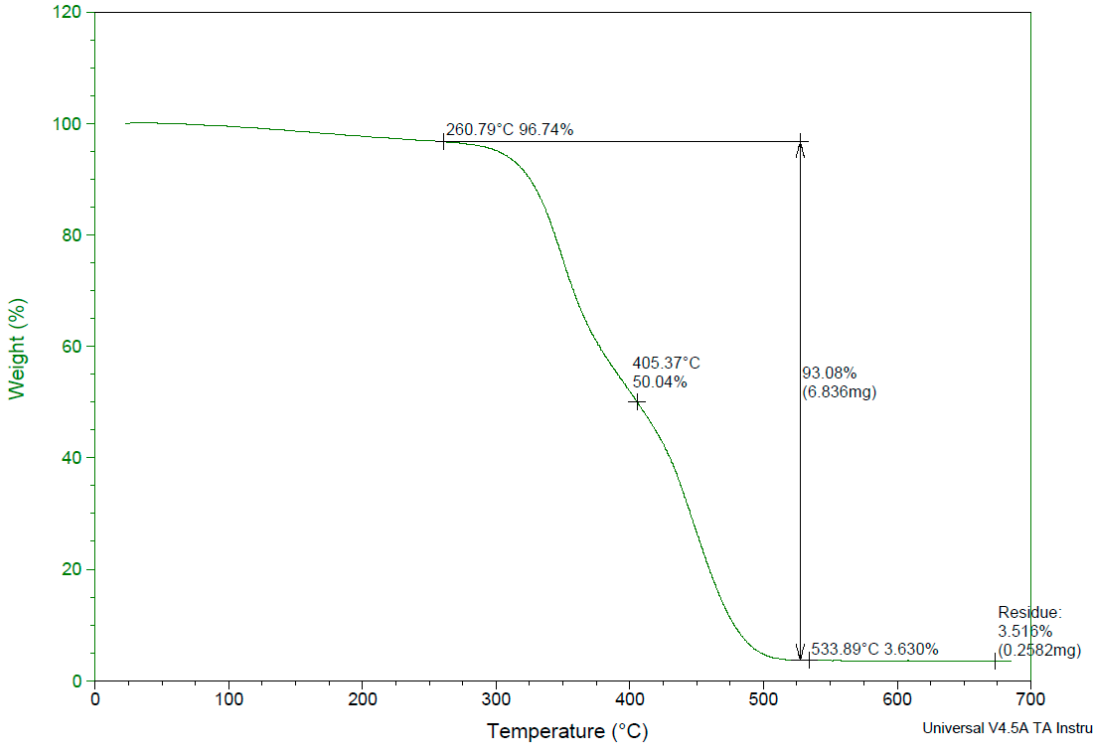

Figure S31. ^{1}H-NMR spectrum of PHU **1f** in DMSO-d$_6$.

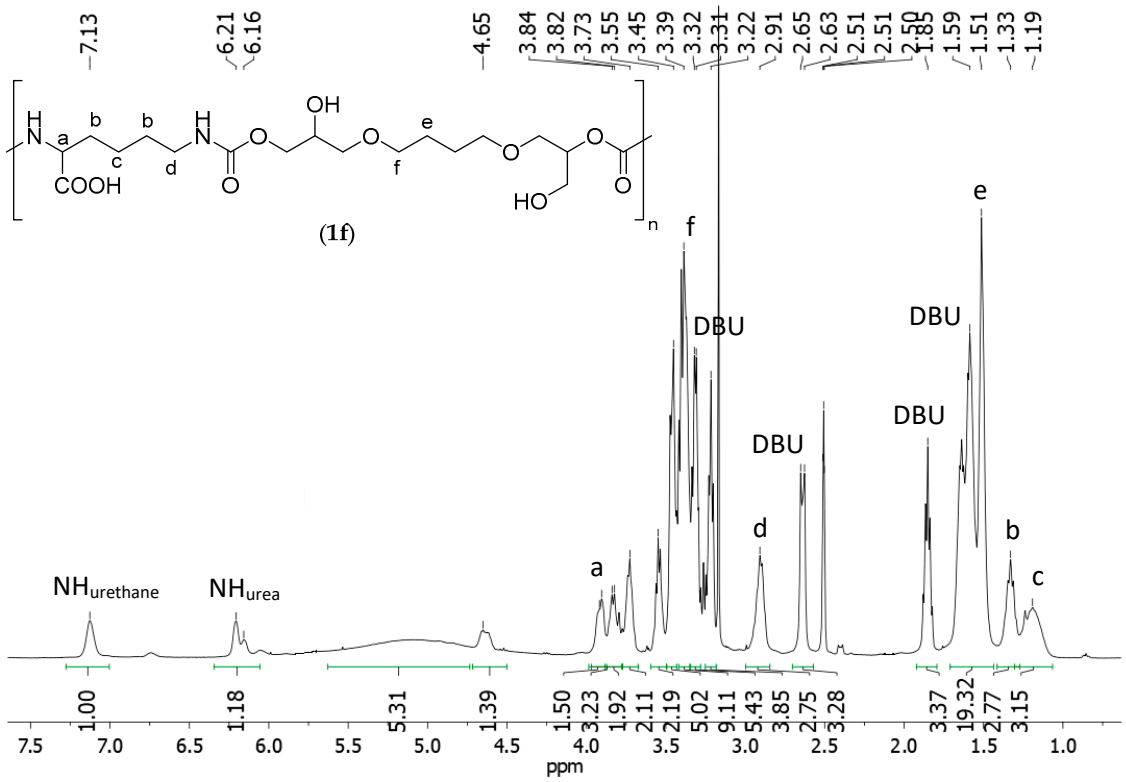

Figure S32. ^{13}C-{^{1}H}-NMR spectrum of PHU **1f** in DMSO-d$_6$.

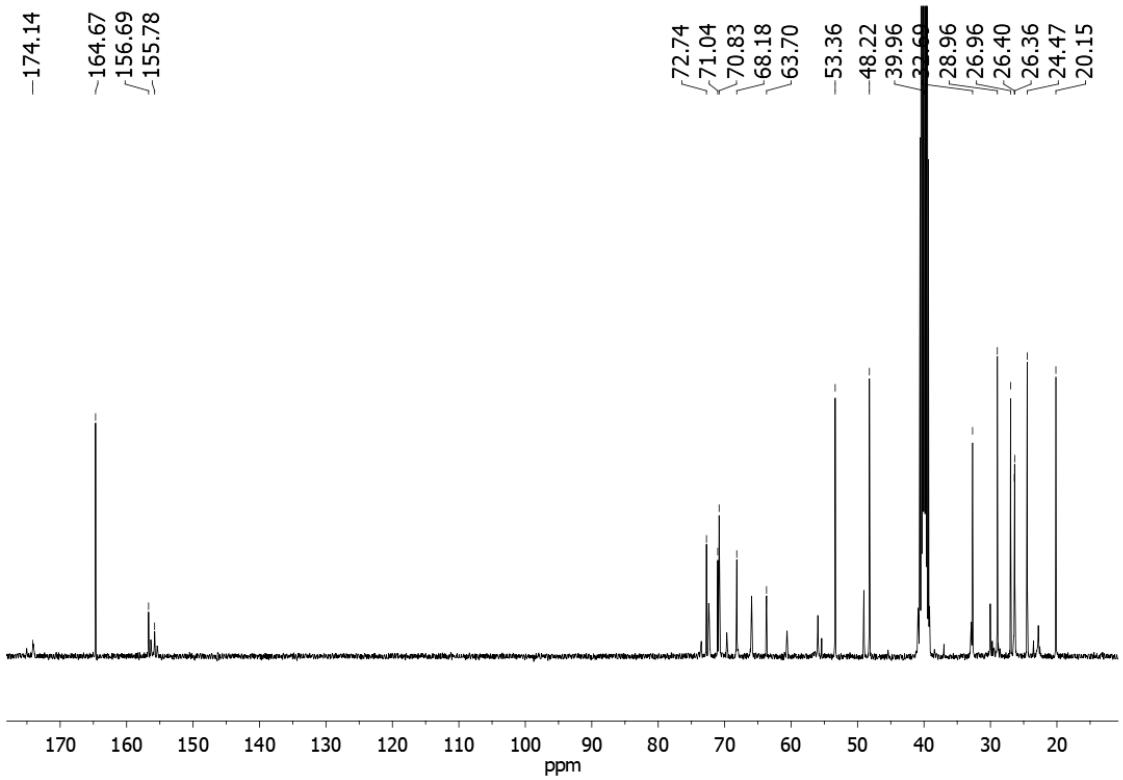

Figure S33. IR spectrum of PHU **1f**.

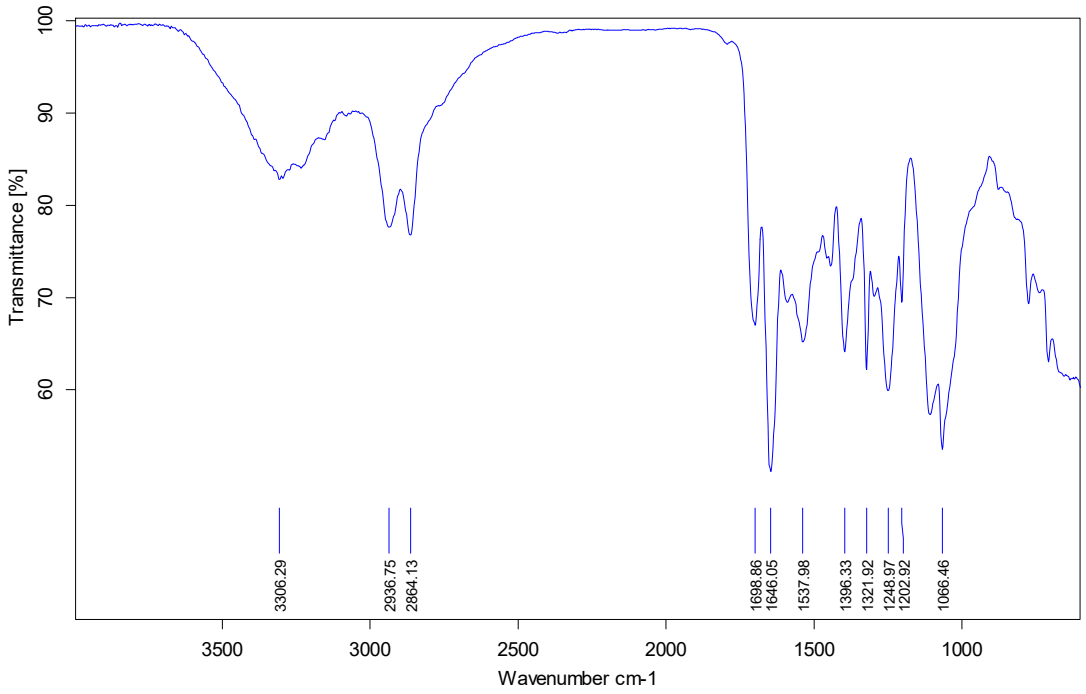

Figure S34. GPC trace of PHU **1f**.

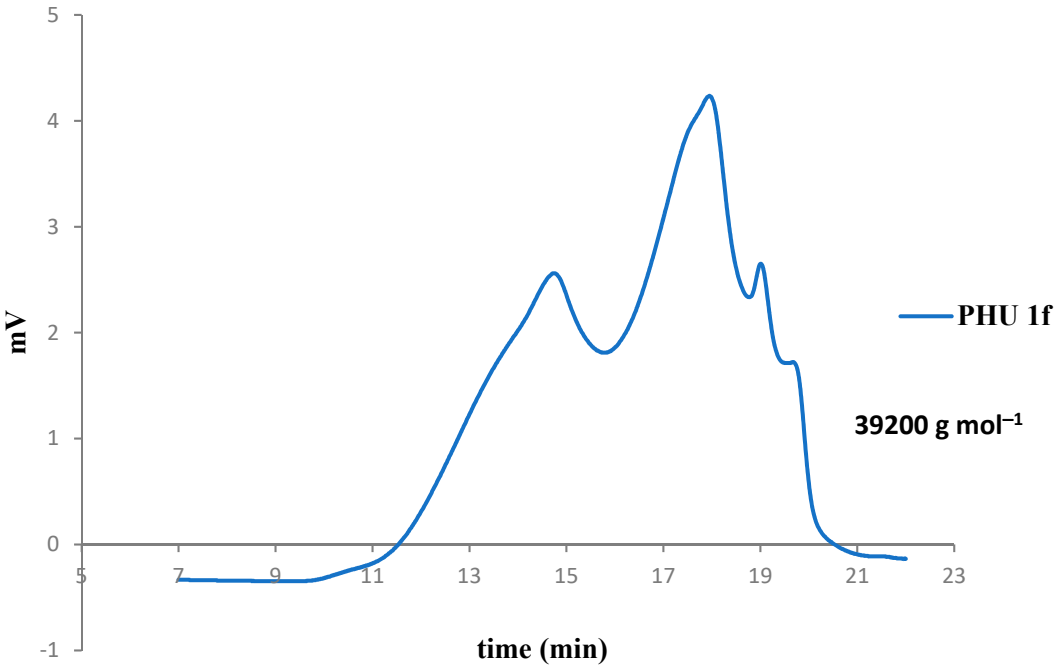

Figure S35. DOSY spectrum of PHU **1f.**

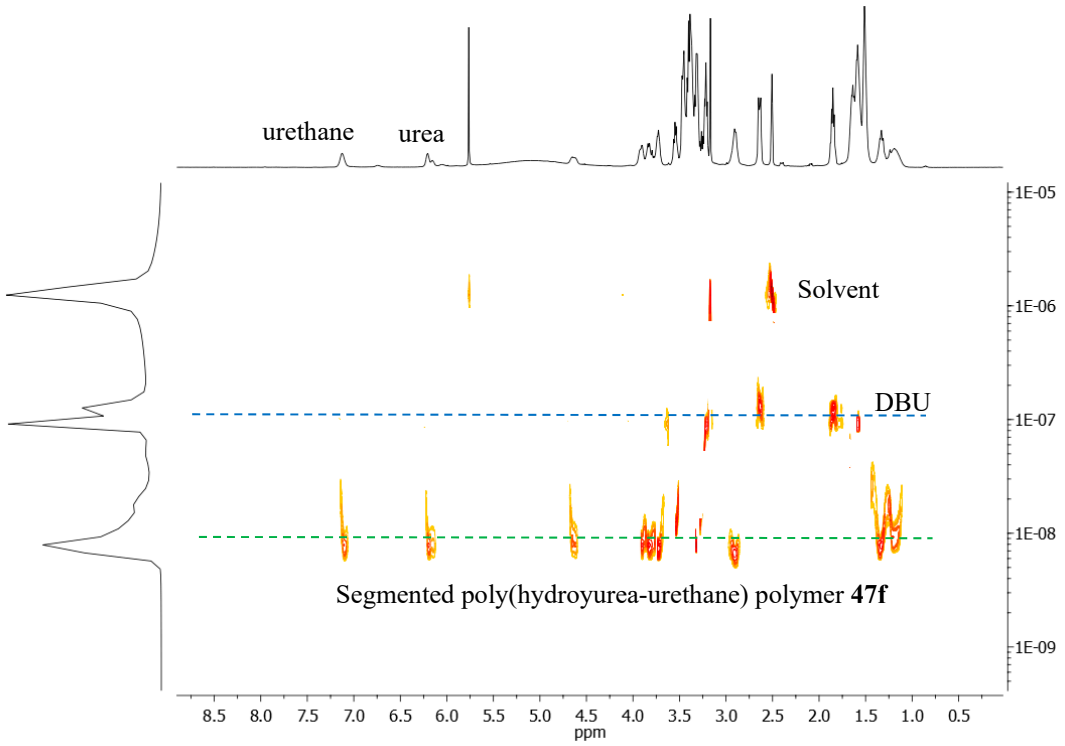

Figure S36. DSC thermogram of PHU **1f.**

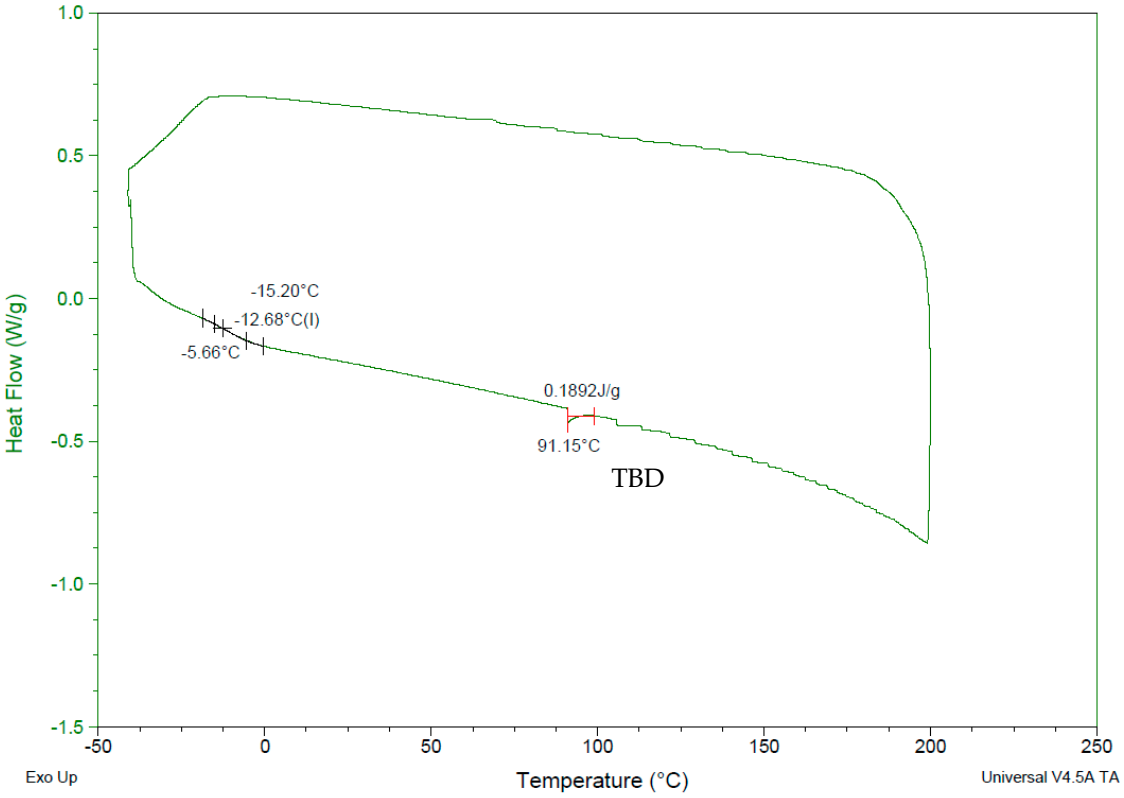

Figure S37. TGA thermogram of PHU **1f.**

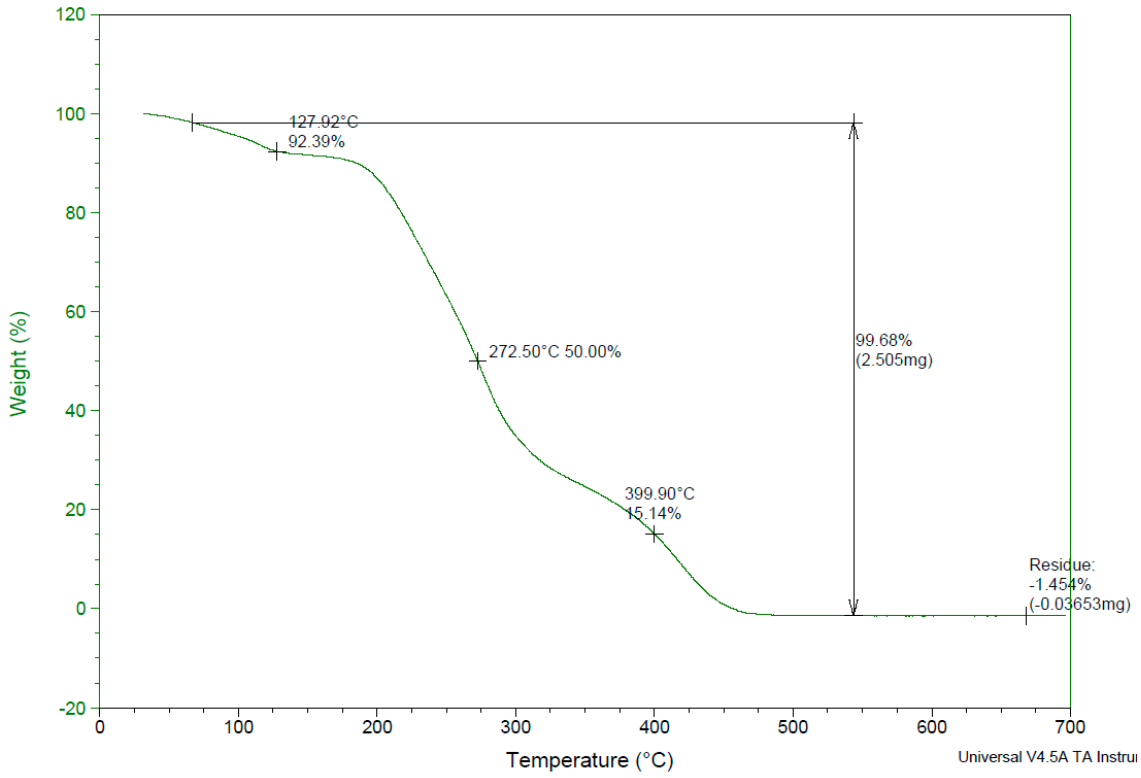

Figure S38. ^{1}H-NMR spectrum of hydroxycarbamate **2** in DMSO-d$_6$.

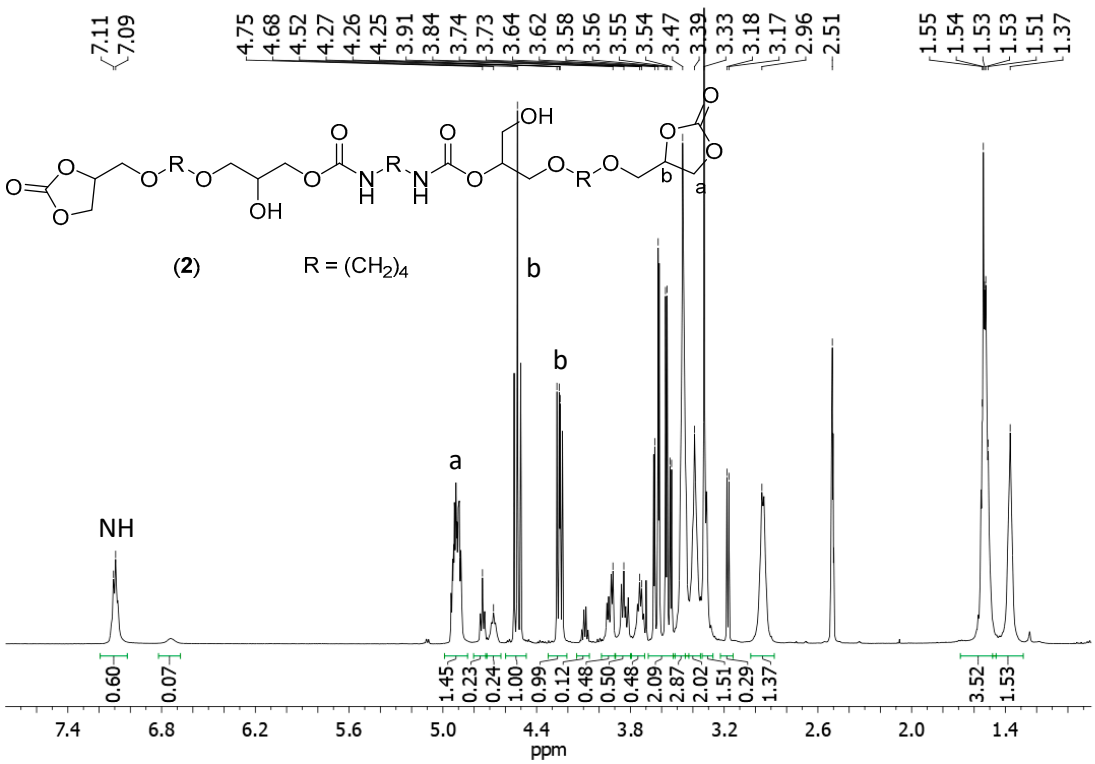

Figure S39. ^{13}C-{^{1}H}-NMR spectrum of hydroxycarbamate **2** in DMSO-d_6.

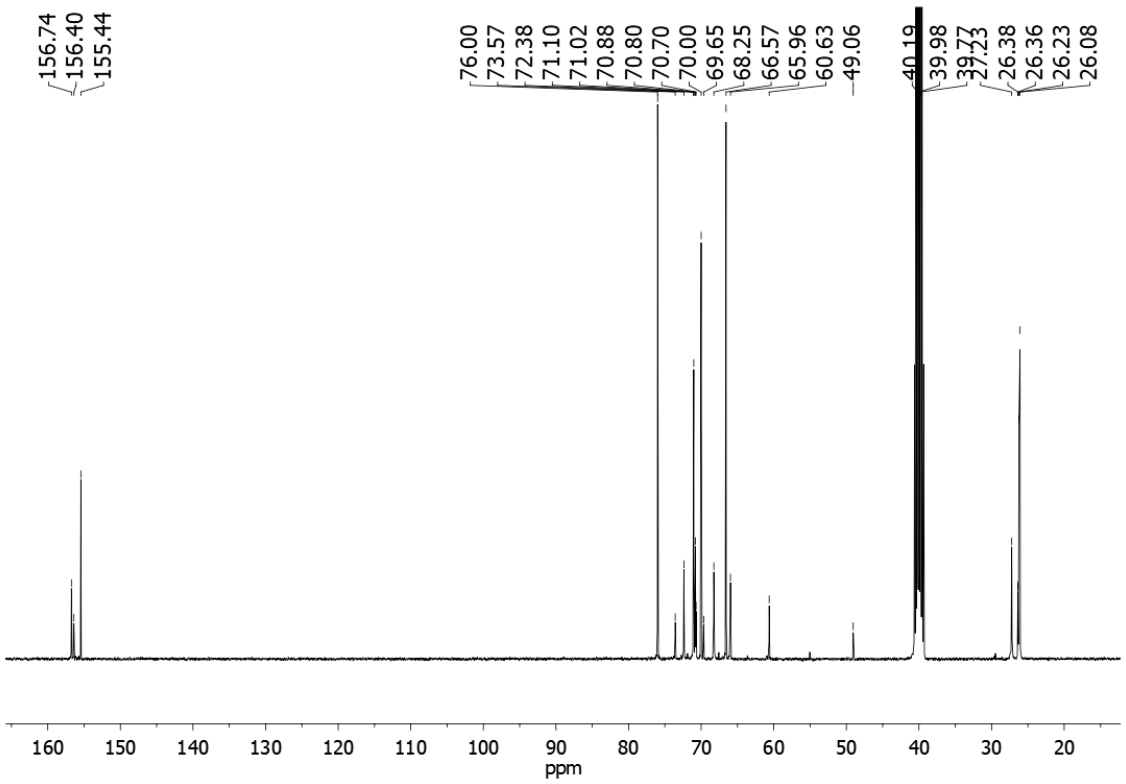

Figure S40. IR spectrum of hydroxycarbamate **2**.

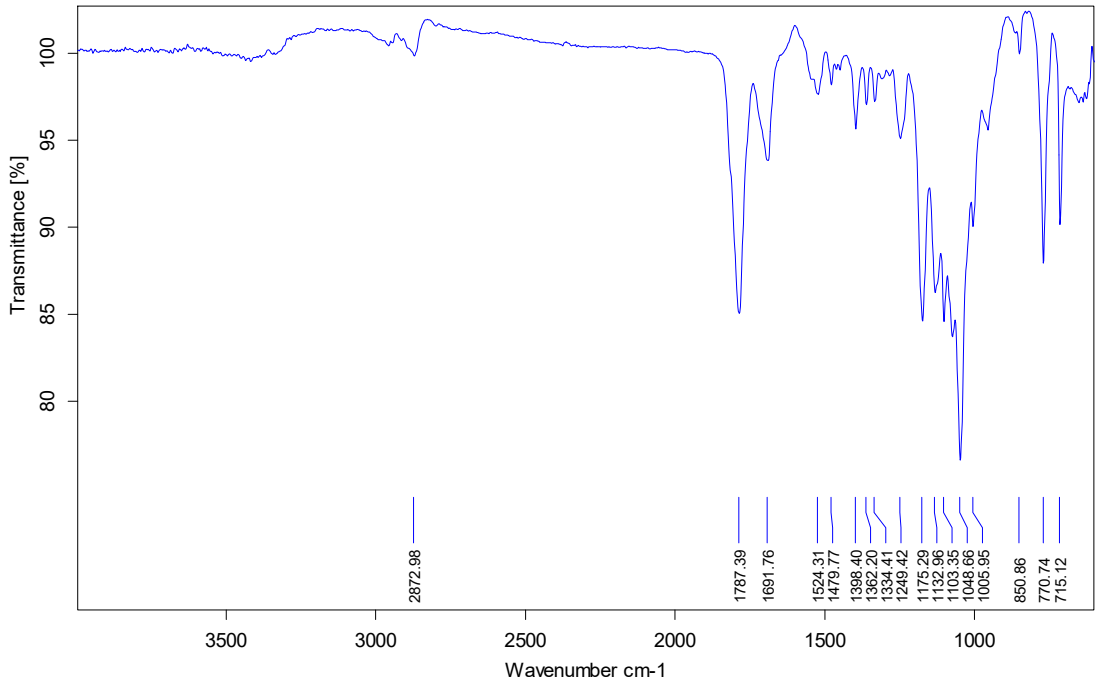

Figure S41. MALDI-ToF spectrum of hydroxycarbamate **2**.

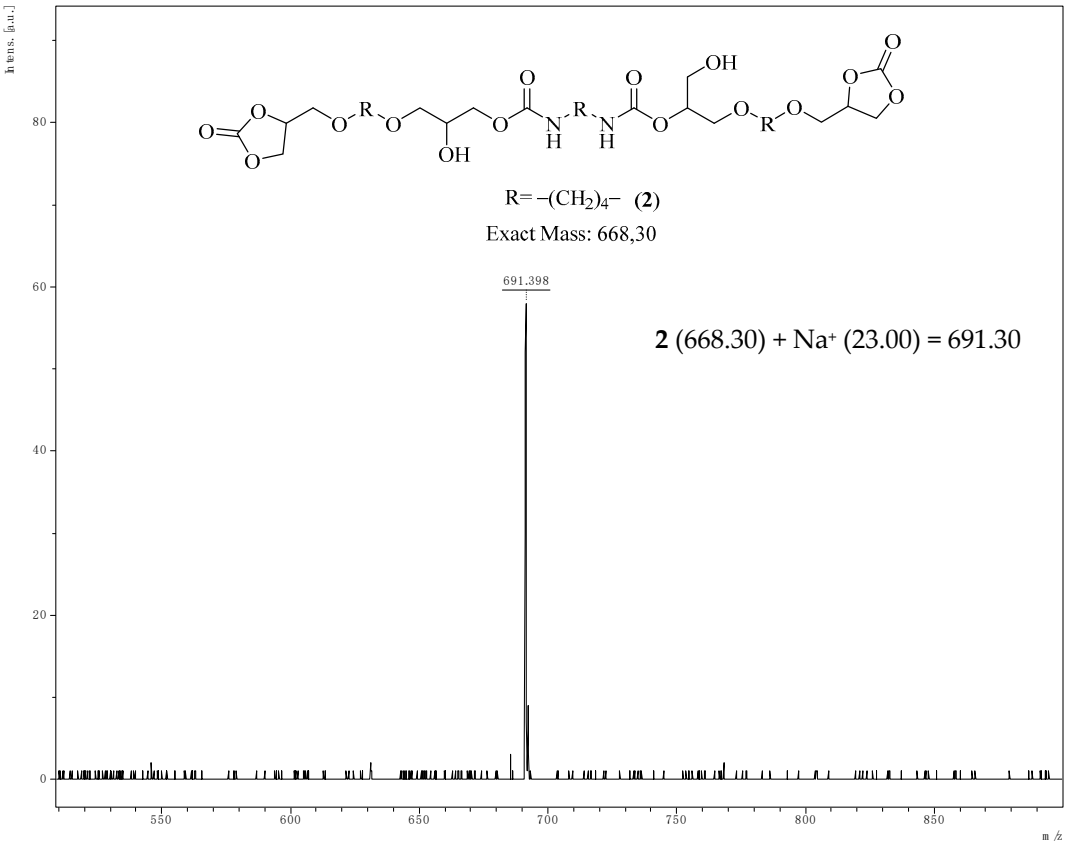

Figure S42. ^{1}H-NMR spectrum of hydroxycarbamate **3** in DMSO-d$_6$.

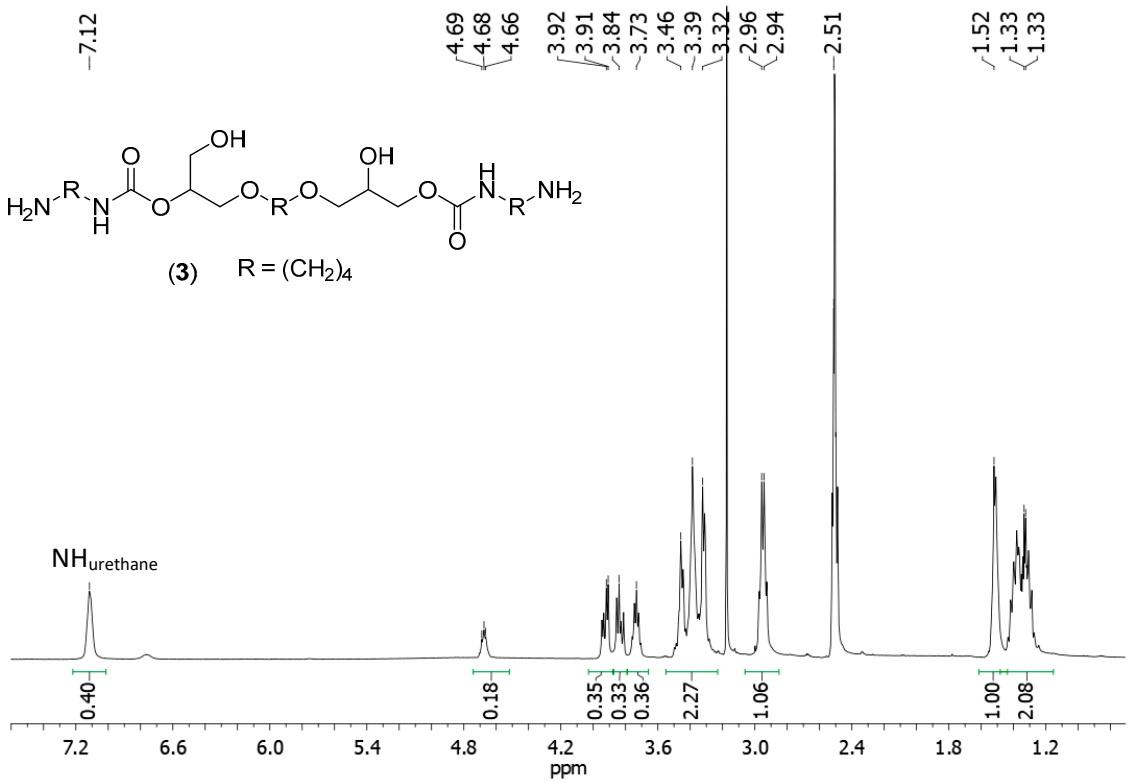

Figure S43. ^{13}C-{^{1}H}-NMR spectrum of hydroxycarbamate **3** in DMSO-d_6.

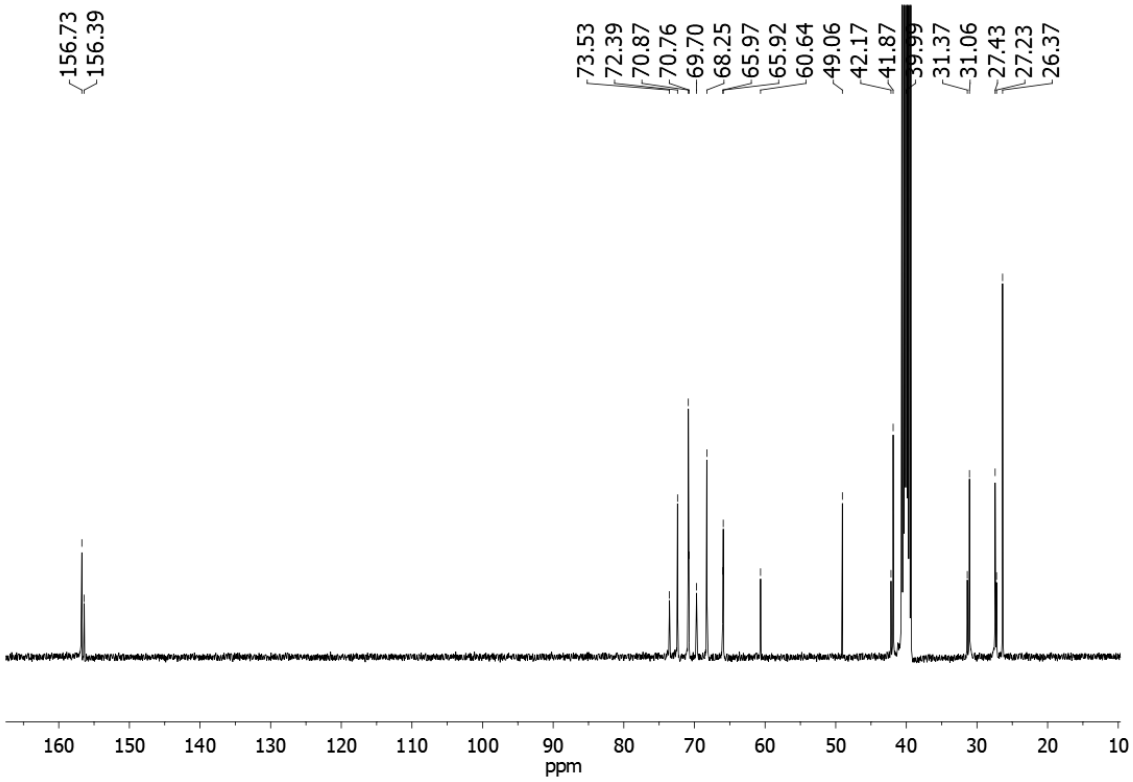

Figure S44. IR spectrum of hydroxycarbamate **3**.

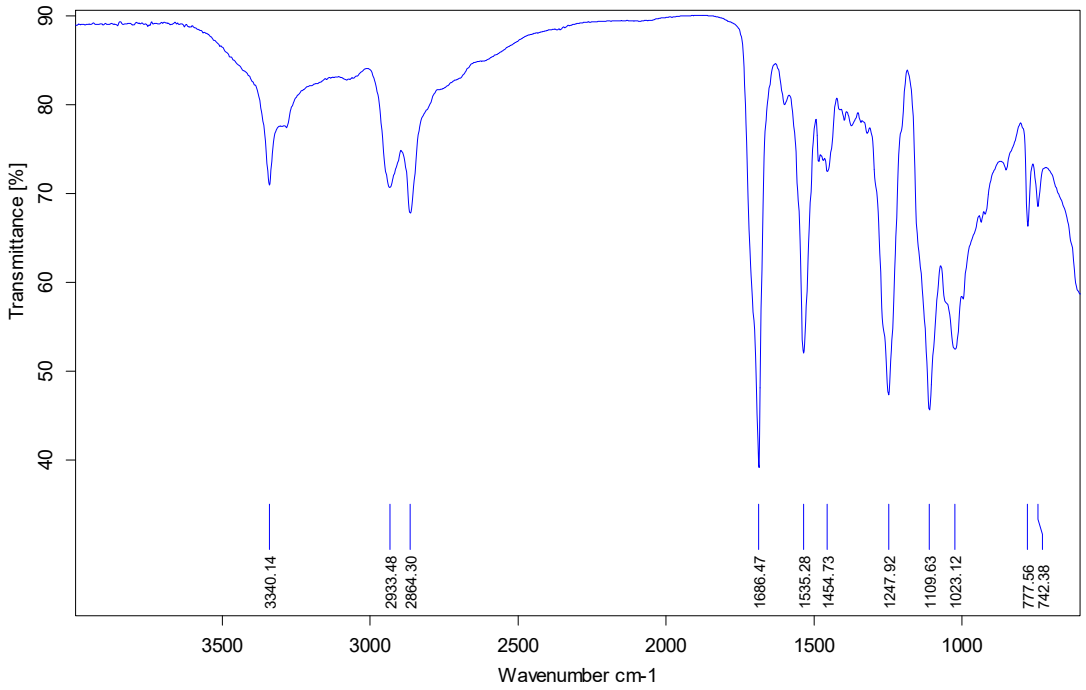

Figure S45. MALDI-ToF spectrum of hydroxycarbamate **3**.