Supporting Information for

Functionalization of Enzymatically Synthesized Rigid Poly(itaconate)s *via* Post-Polymerization aza-Michael Addition of Primary Amines

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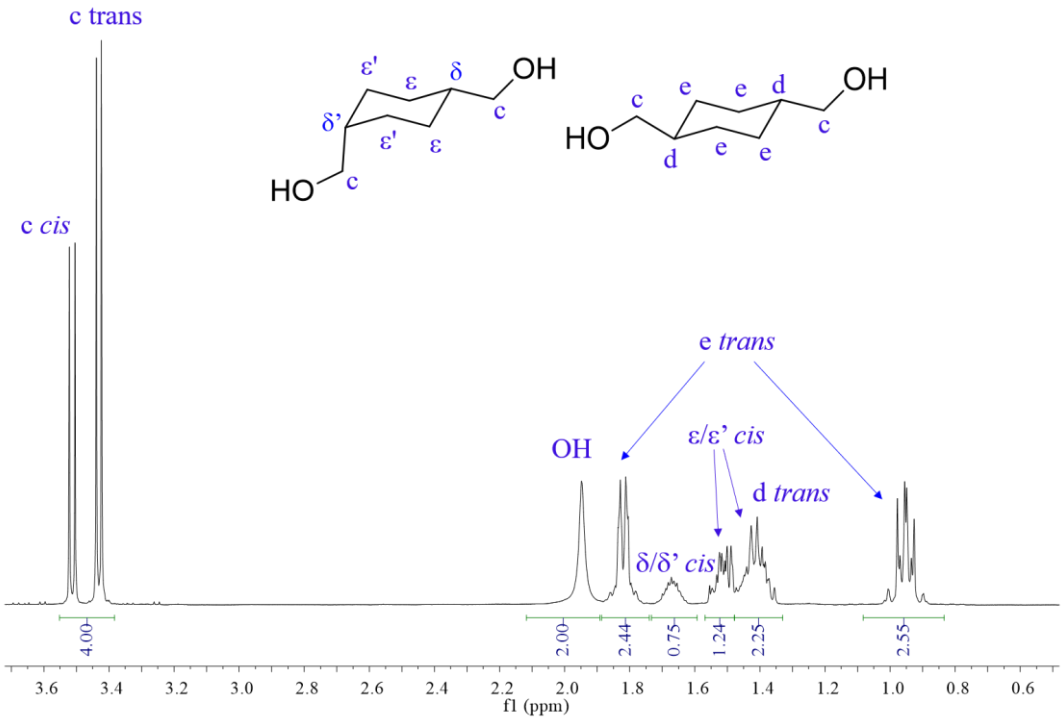


Figure S1. ^{1}H-NMR spectrum of 1,4-cyclohexanedimethanol in $CDCl_3$.
^{1}H-NMR (270 MHz, $CDCl_3$). δ 3.51 (d,2H), δ 3.43 (d,2H), δ 1.95 (s,2H), δ 1.82 (m,4H), δ 1.67 (m,4H), δ 1.51 (m,8H overlapping), δ 1.42 (m,4H overlapping), δ 0.95 (m,4H). Please, notice that the relative presence of the cis and trans forms are different, as showed by ^{1}H-NMR.

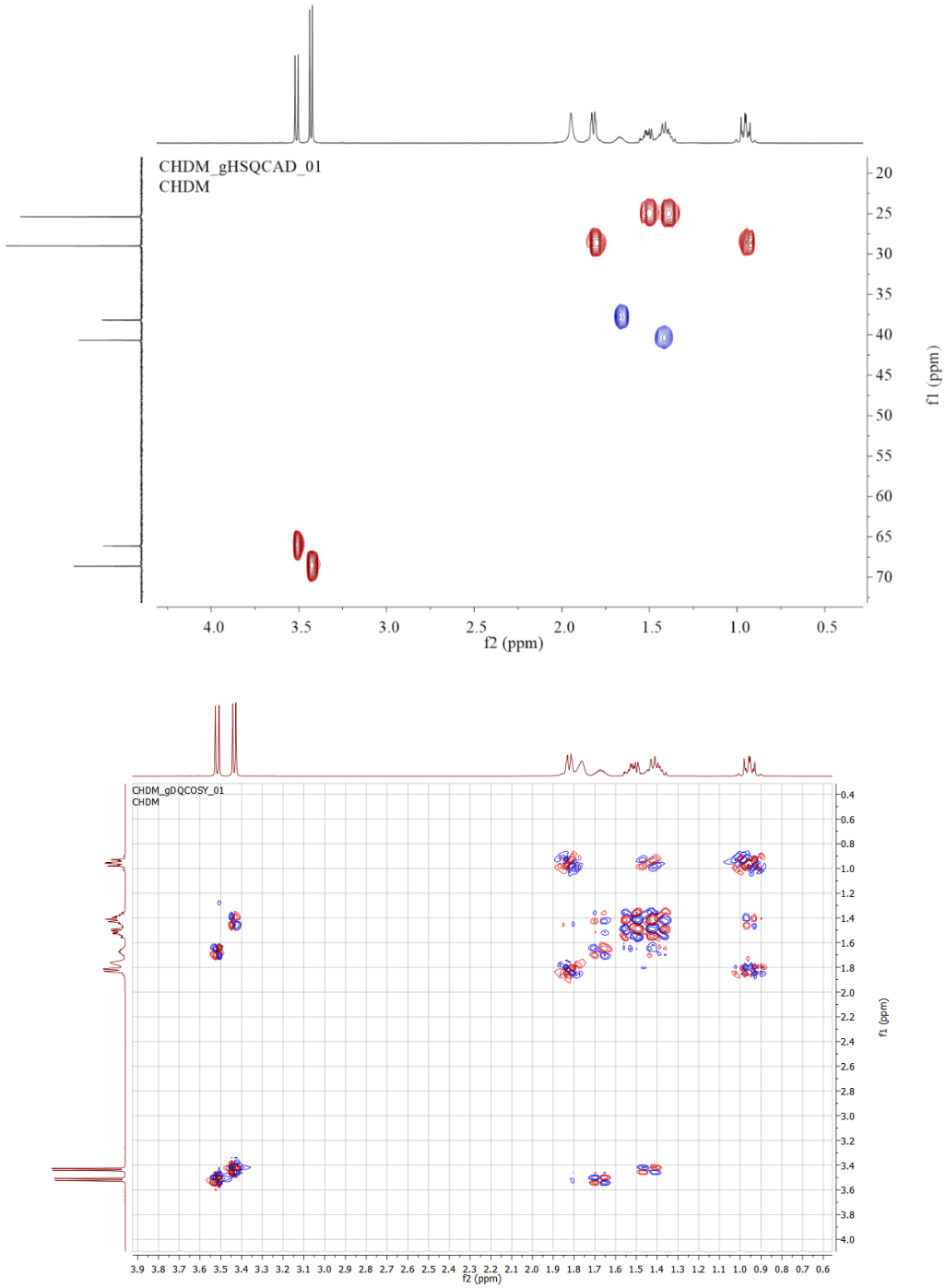


Figure S2. HSQC (top) and COSY (bottom) spectra of 1,4-cyclohexanedimethanol in $CDCl_3$.

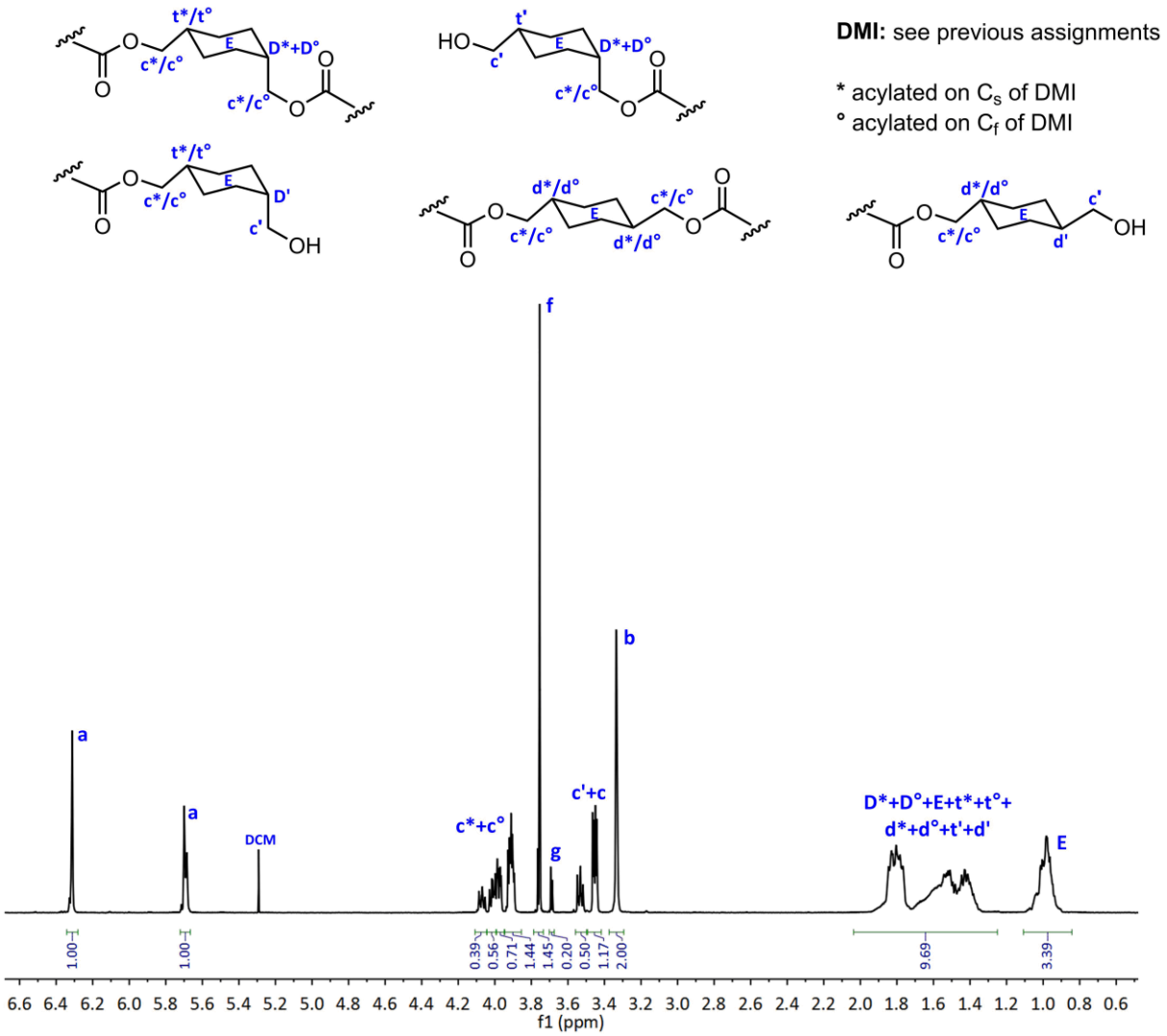


Figure S3. ^{1}H-NMR spectrum of poly(1,4-cyclohexanedimethanol itaconate) in $CDCl_3$. The reaction was catalyzed by CaLB (135 U per g of monomers) on Relizyme® EC-EP after 72 h. The reaction yields were calculated as described below (letters corresponds to the integration area of the ascribed signal):
Esterified OH groups of CHDM: [(*c**+*c*°)/4H]; Esterified OH groups of CHDM on carbonyl 1 (C_{slow}) of DMI: (*c**/4H); Esterified OH groups of CHDM on carbonyl 6 (C_{fast}) of DMI: (*c*°/4H); Reacted C_{slow} of DMI: [(3H-*f*)/3H]; Reacted C_{fast} of DMI: [(3H-g)/3H].

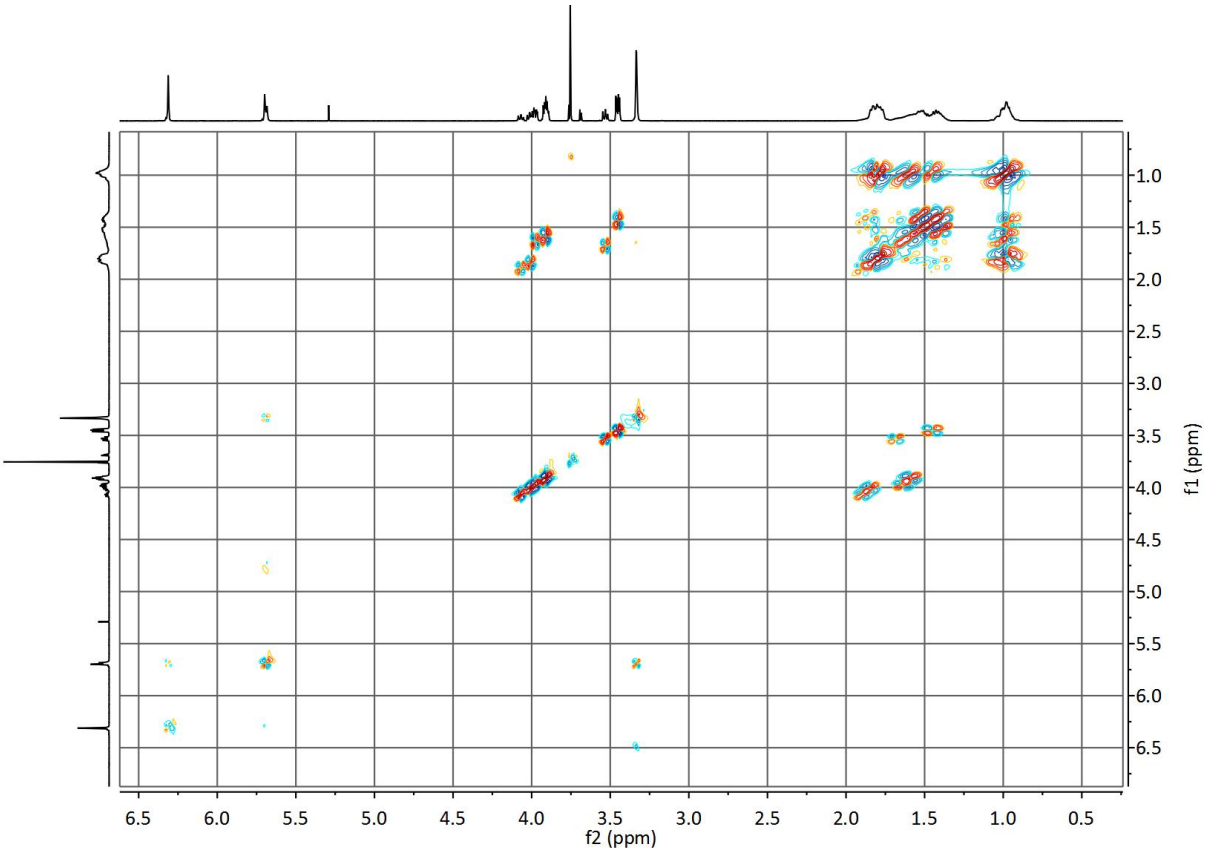


Figure S4. DQ-COSY spectrum in $CDCL_3$ of the polycondensation between DMI and CHDM catalyzed by CaLB (135 U per g of monomers) on Relizyme® EC-EP after 72 h.

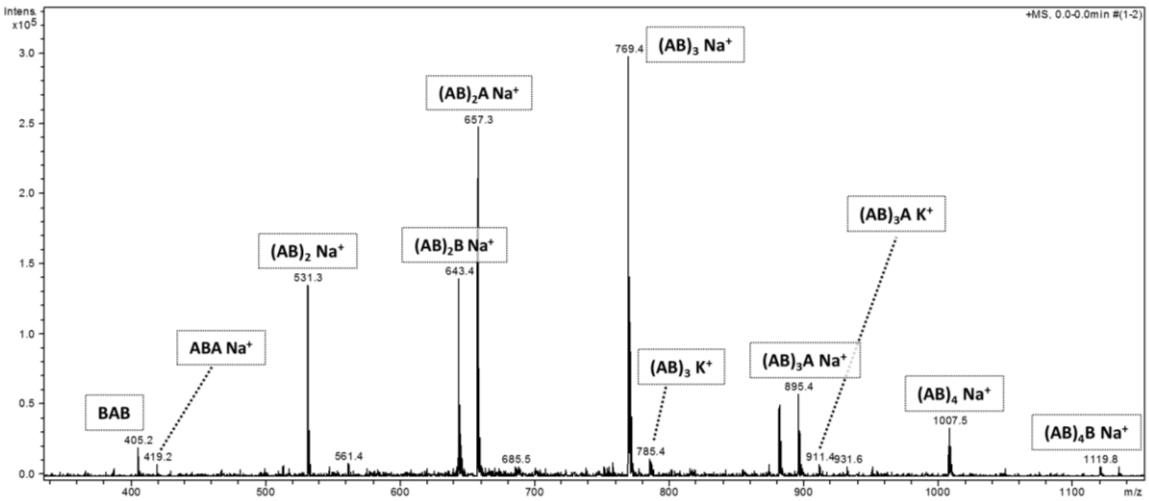


Figure S5. Positive ESI-MS spectrum of the polycondensation between DMI and CHDM catalyzed by CaLB (135 U per g of monomers) on Relizyme® EC-EP after 72h. The spectrum was recorded with a m/z target of 1000. A= DMI; B= CHDM.

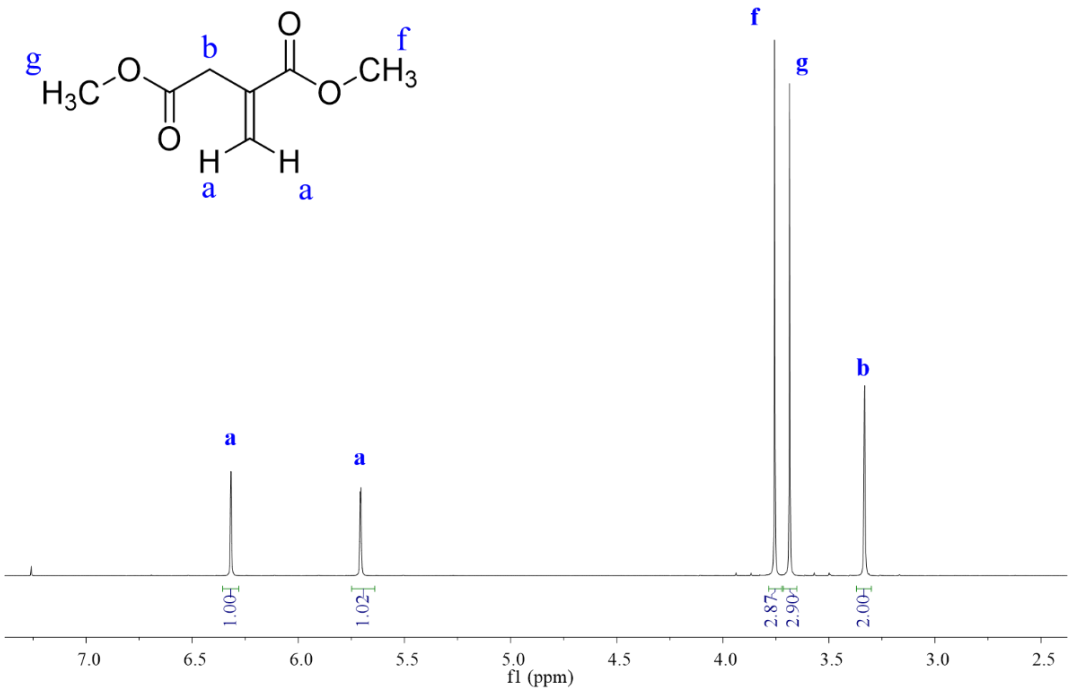
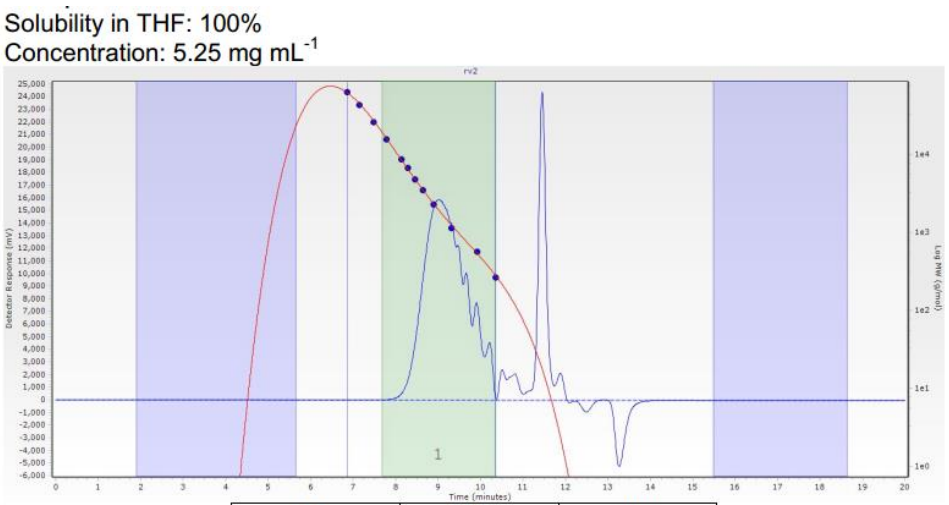


Figure S6. ^{1}H-NMR spectrum of pure DMI in $CDCl_3$.
^{1}H-NMR (270 MHz, $CDCl_3$). δ 6.35 (d,1H), δ 5.74 (m, 1H), δ 3.79 (s,3H), δ 3.73 (s,3H), δ 3.37 (d, 2H).



M_n	M_w	PDI
1141	1835	1.608

Peak at 11.5 min THF

Figure S7. GPC chromatogram in THF of the polycondensation between DMI and BDO catalyzed by CaLB (297 U per g of monomers) on Relizyme® EC-EP after 72h.

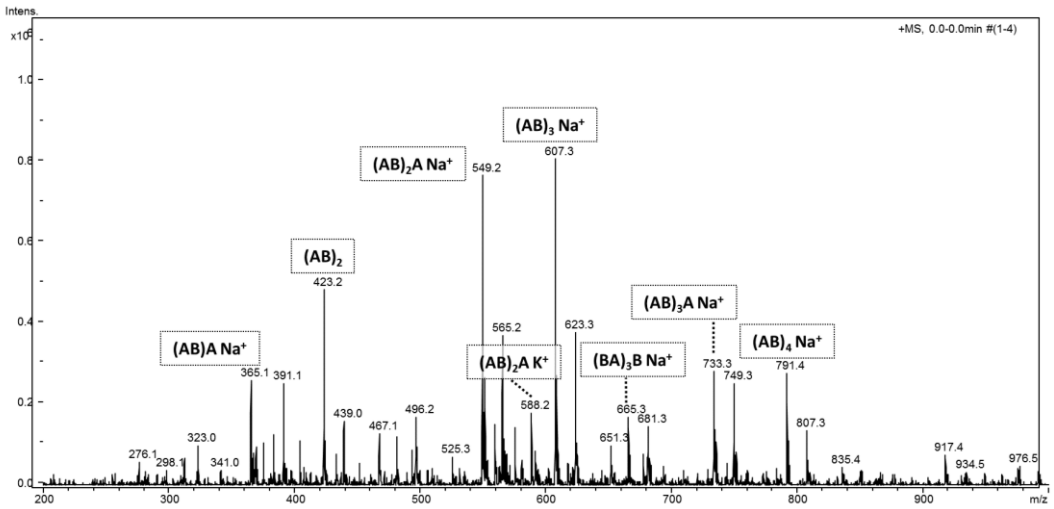


Figure S8. Positive ESI-MS spectrum of the polycondensation between DMI and BDO catalyzed by CaLB (297 U per g of monomers) on Relizyme® EC-EP. The spectrum was recorded with a m/z target of 1000. A= DMI; B= BDO.

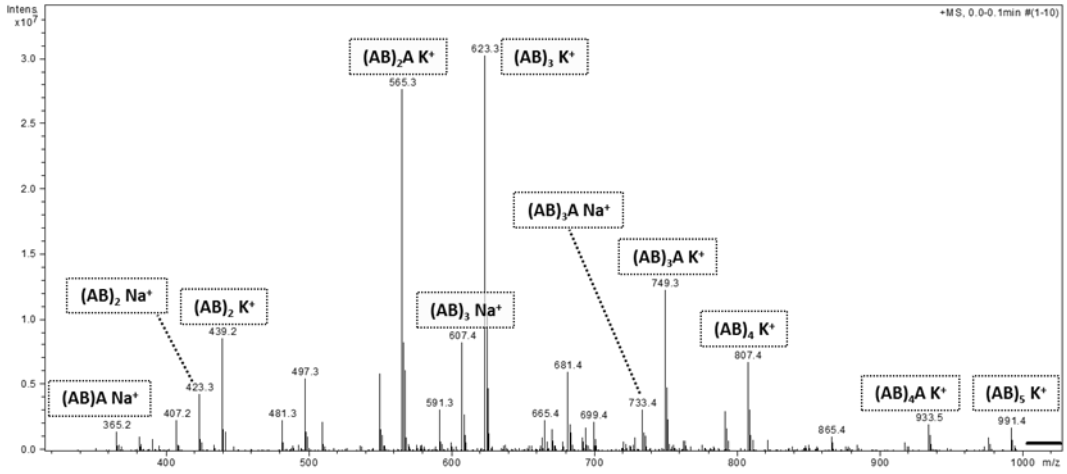
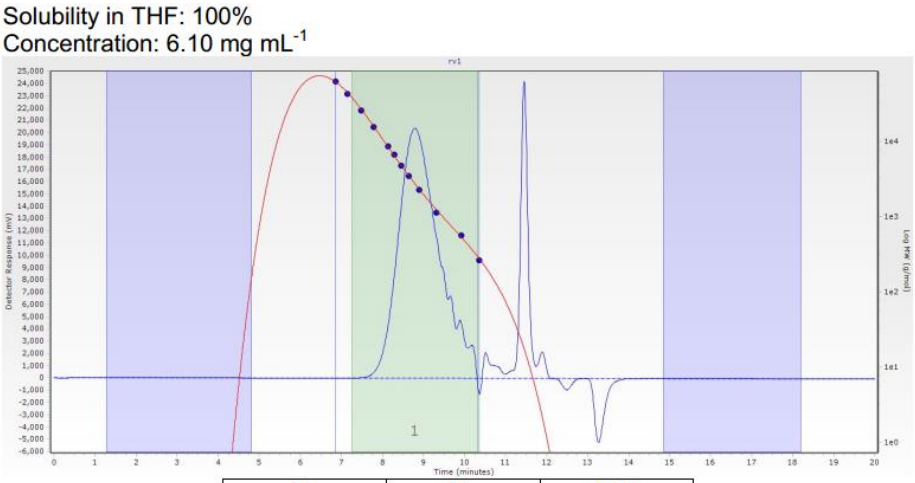


Figure S9. Positive ESI-MS spectrum of the polycondensation between DMI and BDO catalyzed by CaLB (158 U per g of monomers) on rice husk. The spectrum was recorded with a m/z target of 1000. A= DMI; B= BDO.



M_n	M_w	PDI
1628	2859	1.756

Figure S10. GPC chromatogram in THF of the polycondensation between DMI and BDO catalyzed by CaLB (158 U per g of monomers) on rice husk after 72 h.

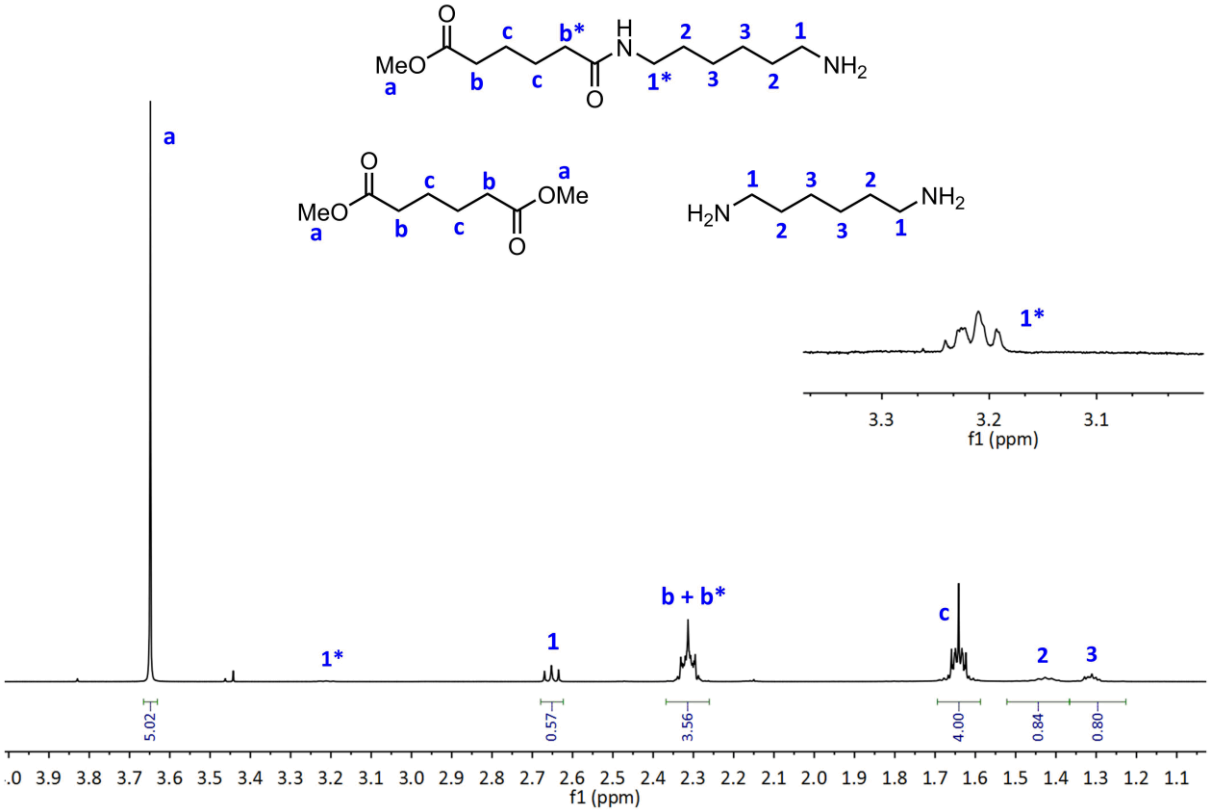


Figure S11. ^{1}H-NMR spectrum of the crude reaction mixture at 20 h of the reaction of DMA with HMDA. The reaction yield were calculated by substracting the area of the aminic methylenes NH_2CH_2 (signal *1*, 4H) from their theorical initial area of 0.8H (in proportion to DMA). The resulting area corresponds to the area of the reacted aminic methylenes, which is then rapported to the 4 hydrogens composing this signal.
^{1}H-NMR (270 MHz, $CDCl_3$). δ 3.65 (s, 3H), δ 3.21 (q, 2H), δ 2.66 (t, 2H), δ 2.31 (m,6H), δ 1.64 (m, 4H), δ 1.43 (m, 4H), δ 1.31 (m, 4H).

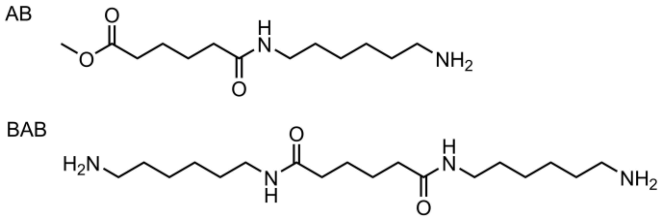


Figure S12. Structures of the products detected in positive ESI-MS spectra at 3 and 20 h for the reaction between DMA and HMDA

Table S1. Molar mass and m/z of the products and starting materials found in ESI-MS positive ion mass spectra at t 3h and 20h for the reaction between DMA and HMDA.

		m/z (Da)		
	Molar mass (Da)	**+ H^+**	**+ Na^+**	**+ K^+**
DMA	174.19	x	197.0	x
HMDA	116.2	117.2	139	x
AB	258.35	259.2	280.2	296.2
BAB	342.51	343.3	x	x

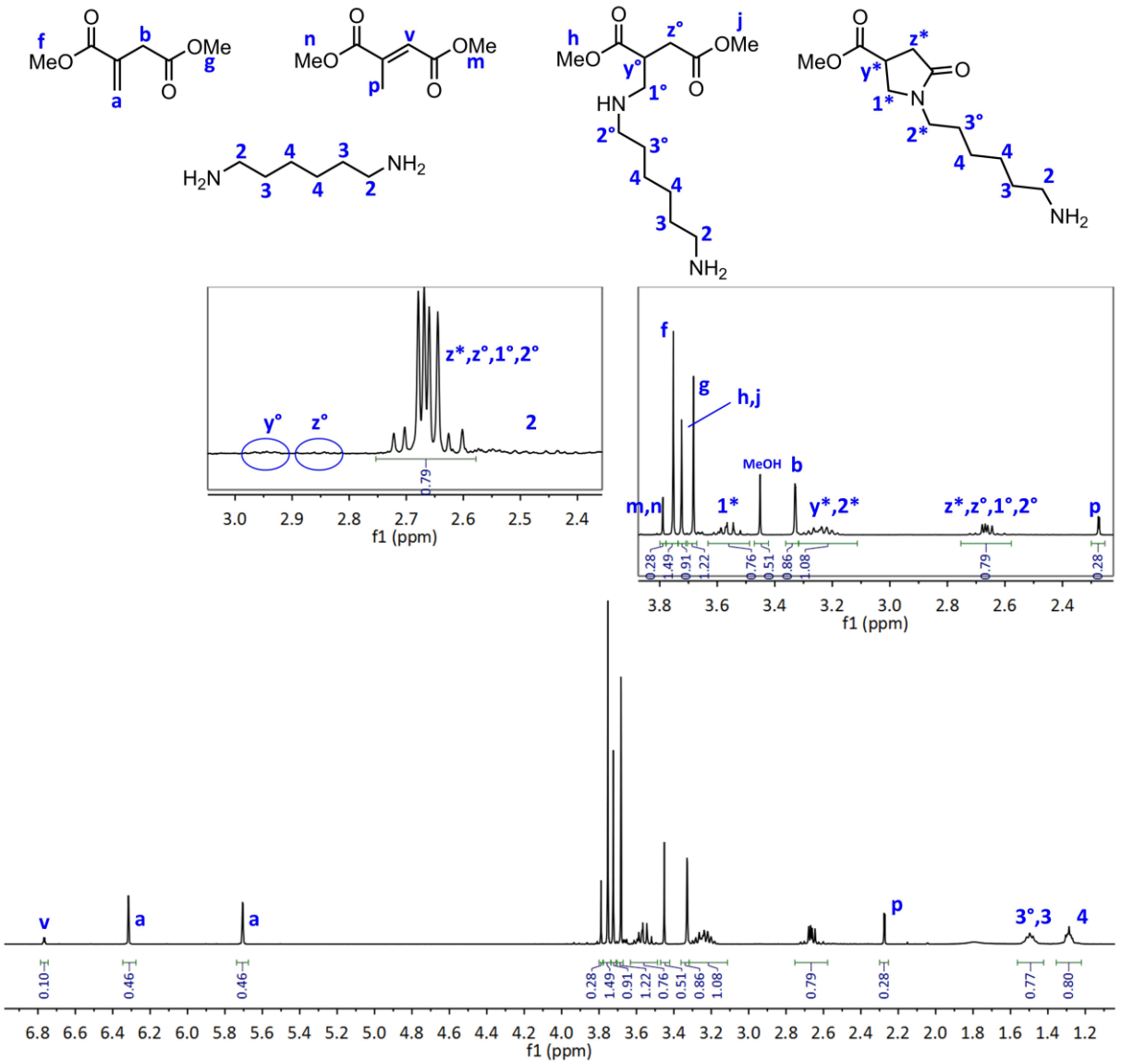


Figure S13. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 20h of the reaction of DMI with HMDA with zooms from 3.9 ppm to 2.3 ppm. The reaction yields were calculated as described below (letters corresponds to the integration area of the ascribed signal):
Reacted C=C double bonds: {[100%-(a+a)/2H]}; Lactamization: (*1**/2H); Isomerization: (*p*/3H); Mono- or bis-adducts: [(0.79-1*)/3H]; Unreacted DMI: [(a+a)/2H].
^{1}H-NMR (270 MHz, $CDCl_3$). δ 6.77 (m, 1H), δ 5.70 (m, 1H), δ 3.79 (singlets overlapping,6H), δ 3.75 (s,3H), δ 3.72 (singlets overlapping,6H), δ 3.68 (s,3H), δ 3.56 (m, 2H), δ 3.45 (s,3H), δ 3.33 (d,2H), δ 3.24 (m,3H), δ 2.95 (m,1H), δ 2.85 (m,1H), δ 2.66 (multiplets overlapping, 7H), δ 2.55 (m,4H), δ 2.28 (d,3H), δ 1.50 (overlapping multiplets,4H), δ 1.29 (m,4H).

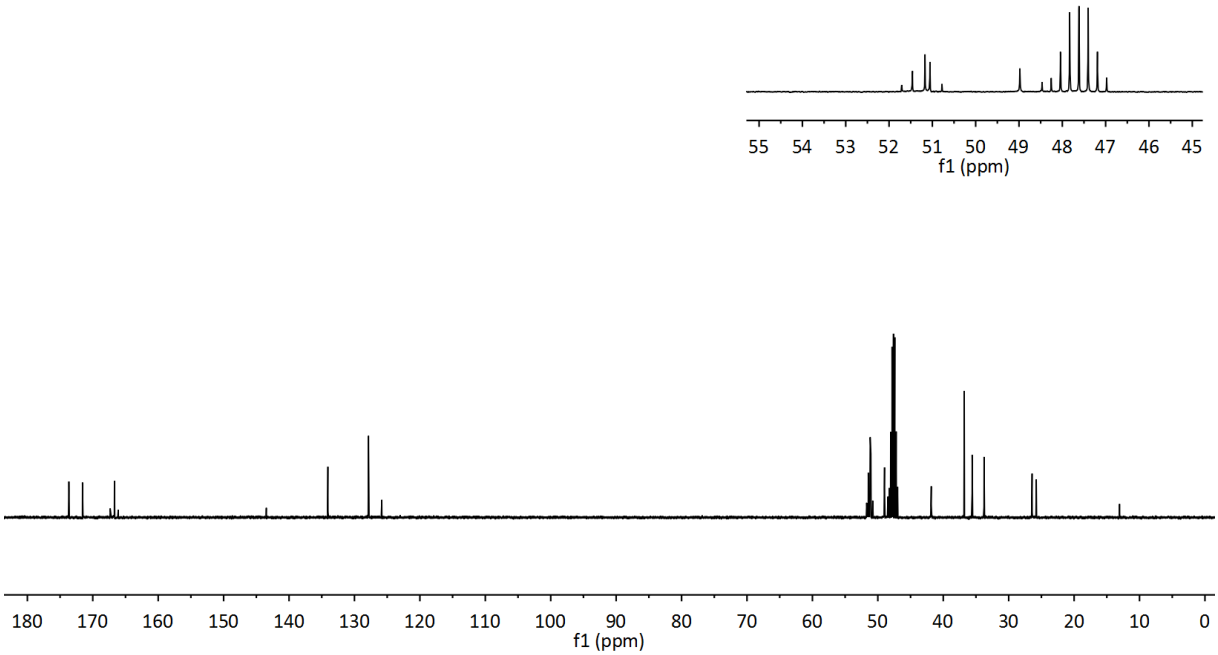


Figure S14. ^{13}C-NMR spectrum in CD_3OD of the crude reaction mixture at 20h of the reaction of DMI with HMDA with zoom from 55 ppm to 45 ppm.
^{13}C-NMR (270 MHz, CD_3OD). δ: 173.65; 173.62; 171.57; 167.31; 166.78; 166.08; 143.41; 134.04; 127.83; 125.82; 51.69; 51.45; 51.16; 51.06; 50.78; 48.98; 48.46; 48.25; 48.03; 47.82; 47.60; 47.40; 47.19; 46.98; 41.85; 41.83; 37.68; 35.58; 33.76; 13.04

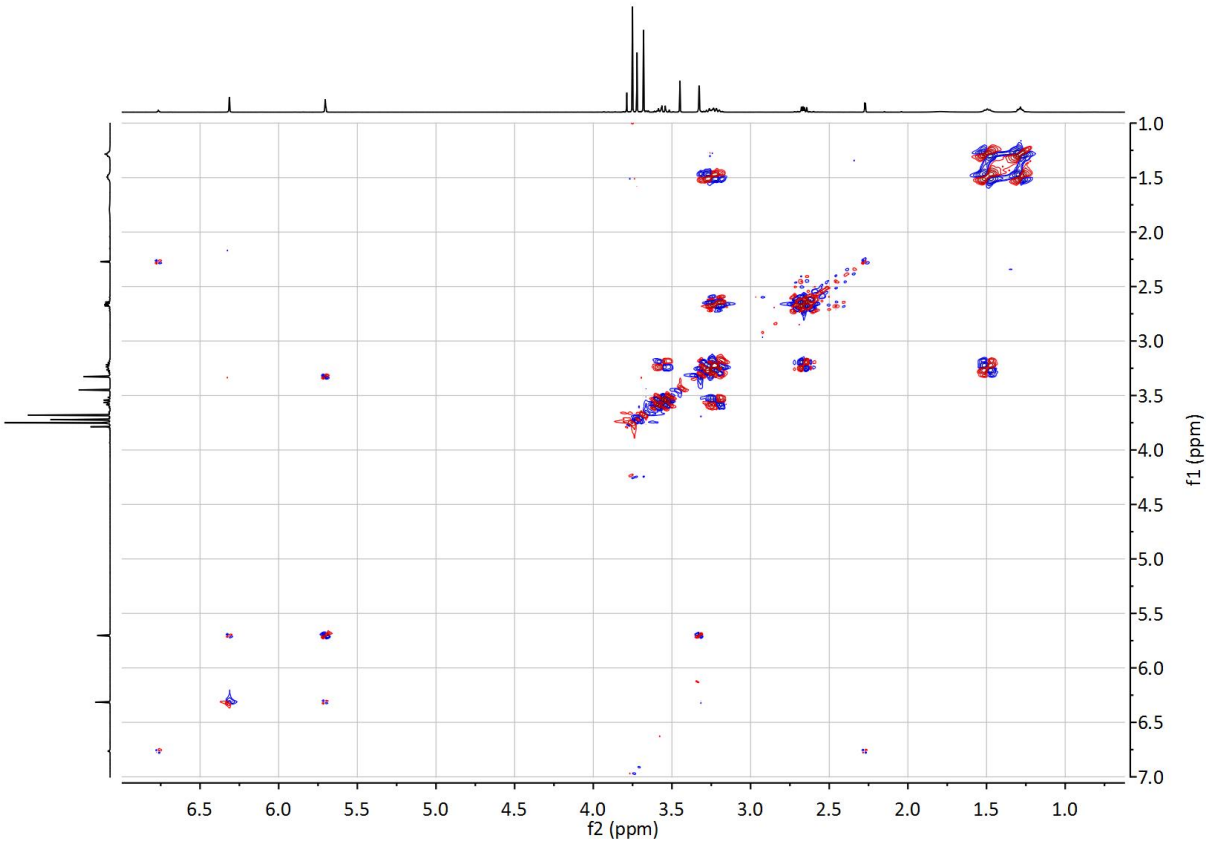


Figure S15. DQ-COSY spectrum in $CDCl_3$ of the crude reaction mixture at 20 h of the reaction of DMI with HMDA.

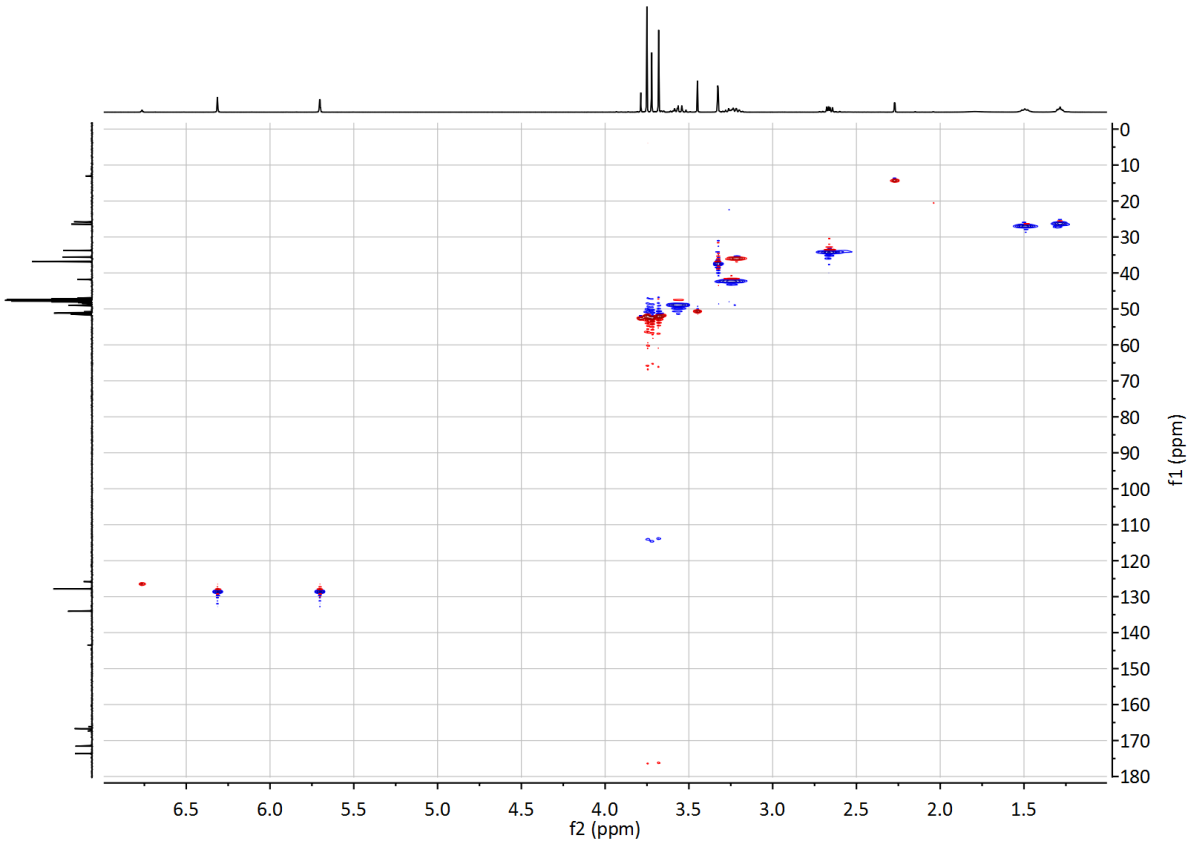


Figure S16. HSQC-AD spectrum in $CDCl_3$ of the crude reaction mixture at 20 h of the reaction of DMI with HMDA.

Table S2. Molar mass and m/z of the products and starting materials found in ESI-MS positive ion mass spectra at 3 and 20 h for the reaction between DMI and HMDA.

		m/z (Da)		
	Molar mass (Da)	**+ H^+**	**+ Na^+**	**+ K^+**
DMI	158.15	159.0	181.0	x
HMDA	116.2	x	x	x
1M/2M	432	433.2	x	x
3M	274	275.2	x	x
4M/5M	400	401.2	x	x
6M	558	559.3	x	x
7M	242	243.1; 243.2; 244.2	x	x
8M	368	369.2	391.2	x

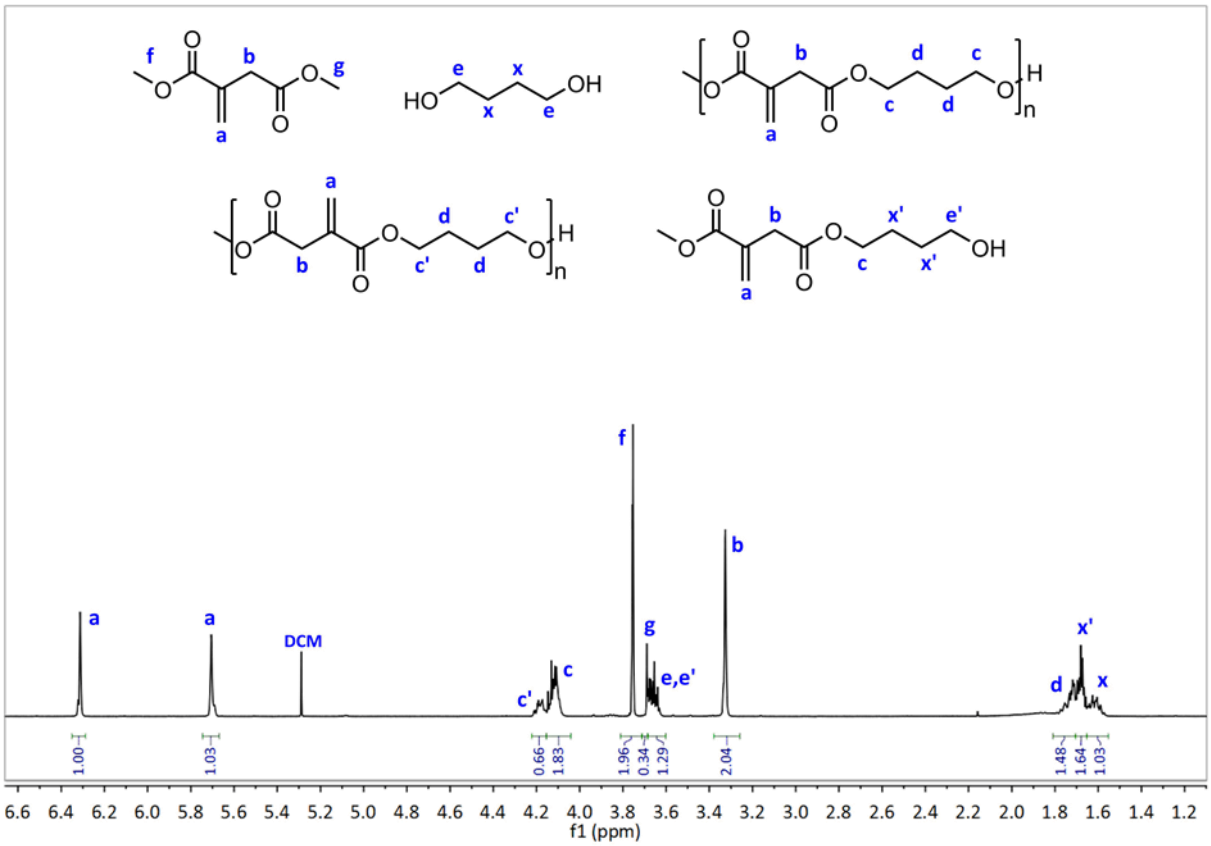


Figure S17. ^{1}H-NMR spectrum of the polycondensation between DMI and BDO catalyzed by CaLB on Relizyme® EC-EP. The reaction yields were calculated as described below (letters corresponds to the integration area of the ascribed signal): Esterified OH groups of BDO: [(*c*+*c'*)/4H]; Esterified OH groups of BDO on carbonyl 1 (C_{slow}) of DMI: (*c'*/4H); Esterified OH groups of BDO on carbonyl 6 (C_{fast}) of DMI: (*c*/4H); Reacted C_{slow} of DMI: [(3H-*f*)/3H]; Reacted C_{fast} of DMI: [(3H-g)/3H]. To be noticed: the integration of signal *g* cannot be considered precise since it is partially overlapping with signal *e* and *e'*.
^{1}H-NMR (270 MHz, $CDCl_3$). δ 6.31 (d,1H), δ 5.70 (m,1H), δ 4.14 (m,4H), δ 3.75 (s,3H), δ 3.69 (s,1H-overlapping), δ 3.32 (d,2H), δ 1.68 (m,4H)

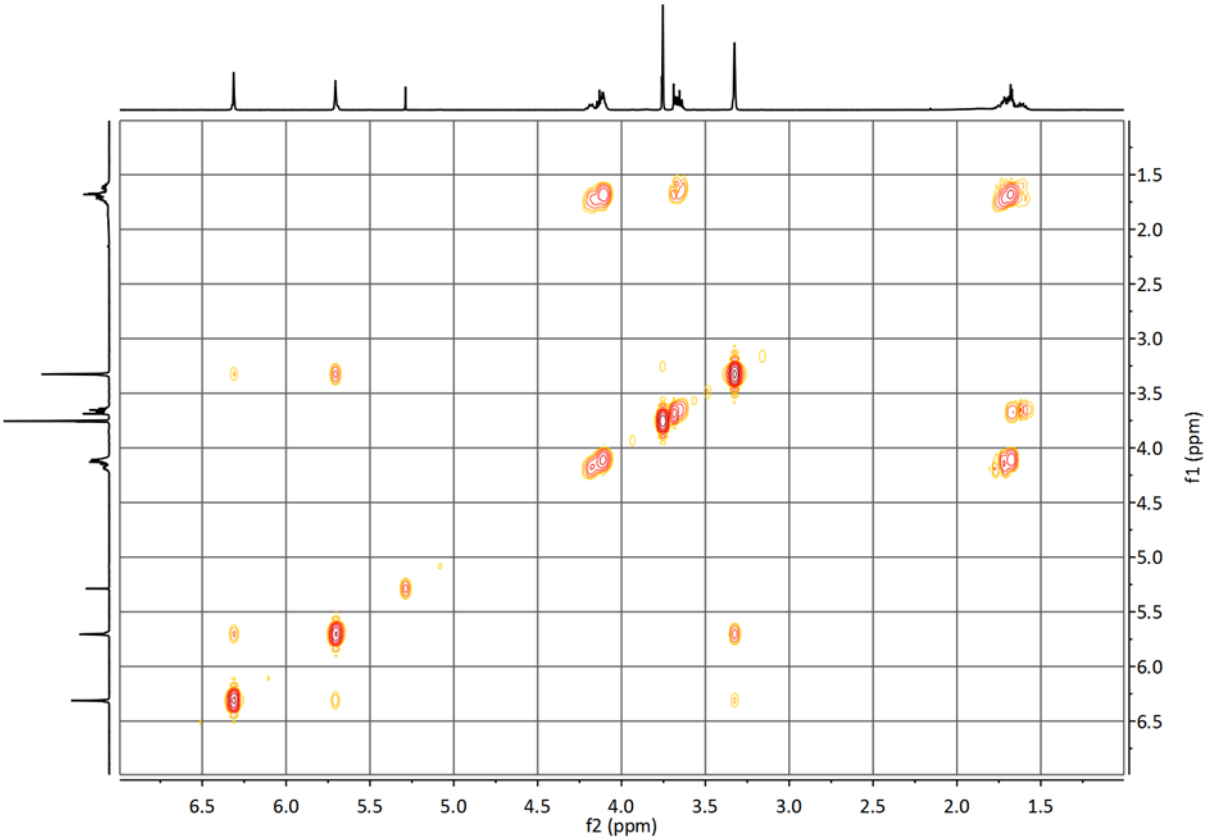


Figure S18. DQ-COSY spectrum of the polycondensation between DMI and BDO catalyzed by CaLB on Relizyme® EC-EP.

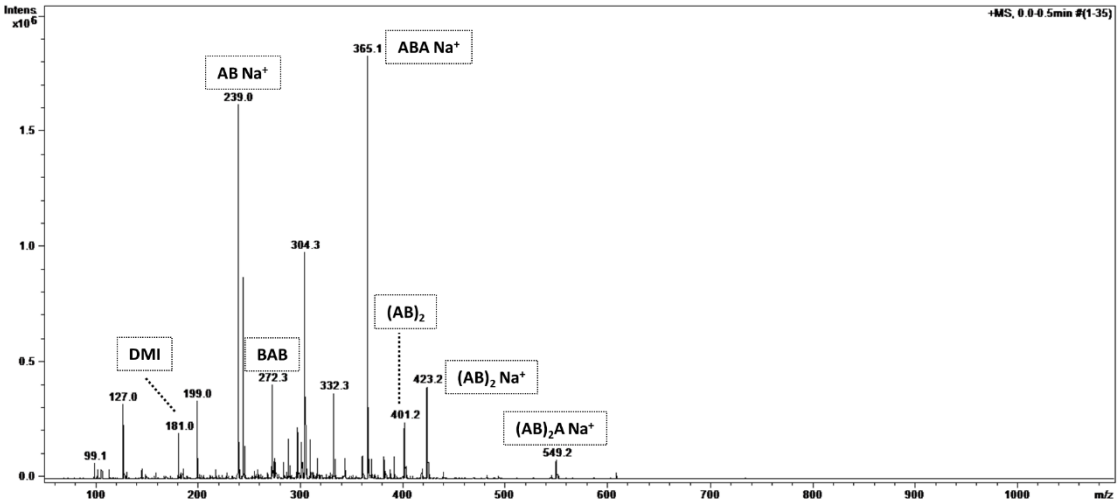


Figure S19. Positive ESI-MS spectrum of the polycondensation between DMI and BDO catalyzed by CaLB on Relizyme® EC-EP. The spectrum was recorded with a m/z target of 130. A= DMI; B= BDO.

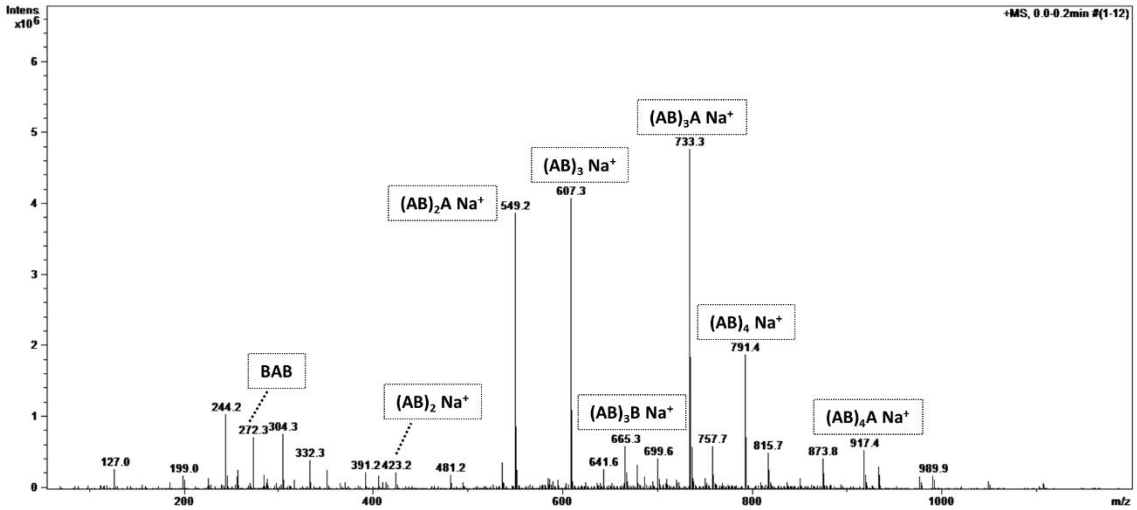


Figure S20. Positive ESI-MS spectrum of the polycondensation between DMI and BDO catalyzed by CaLB on Relizyme® EC-EP. The spectrum was recorded with a m/z target of 1000. A= DMI; B= BDO.

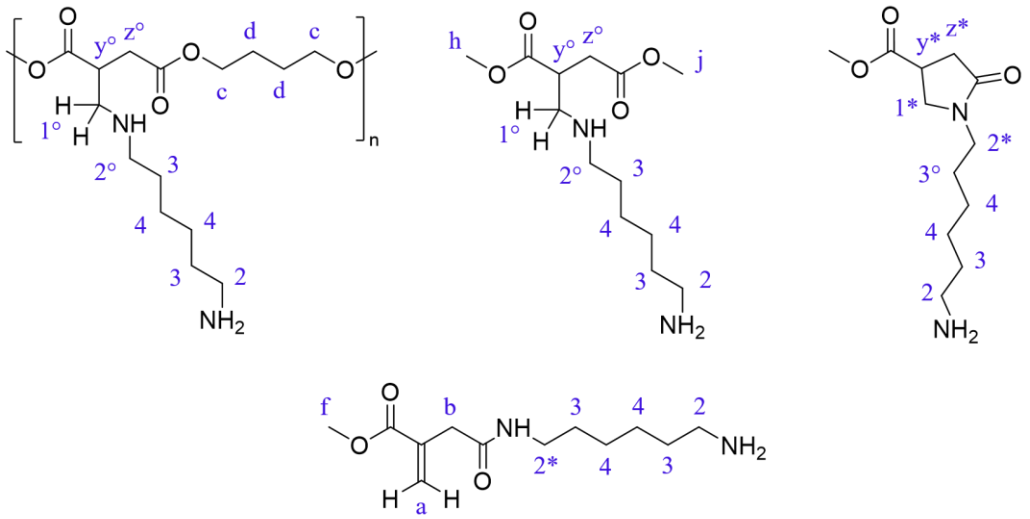


Figure S21. Structures of the possible products of the addition of HMDA (calculated on double bond presence in the oligomer) to PBI.

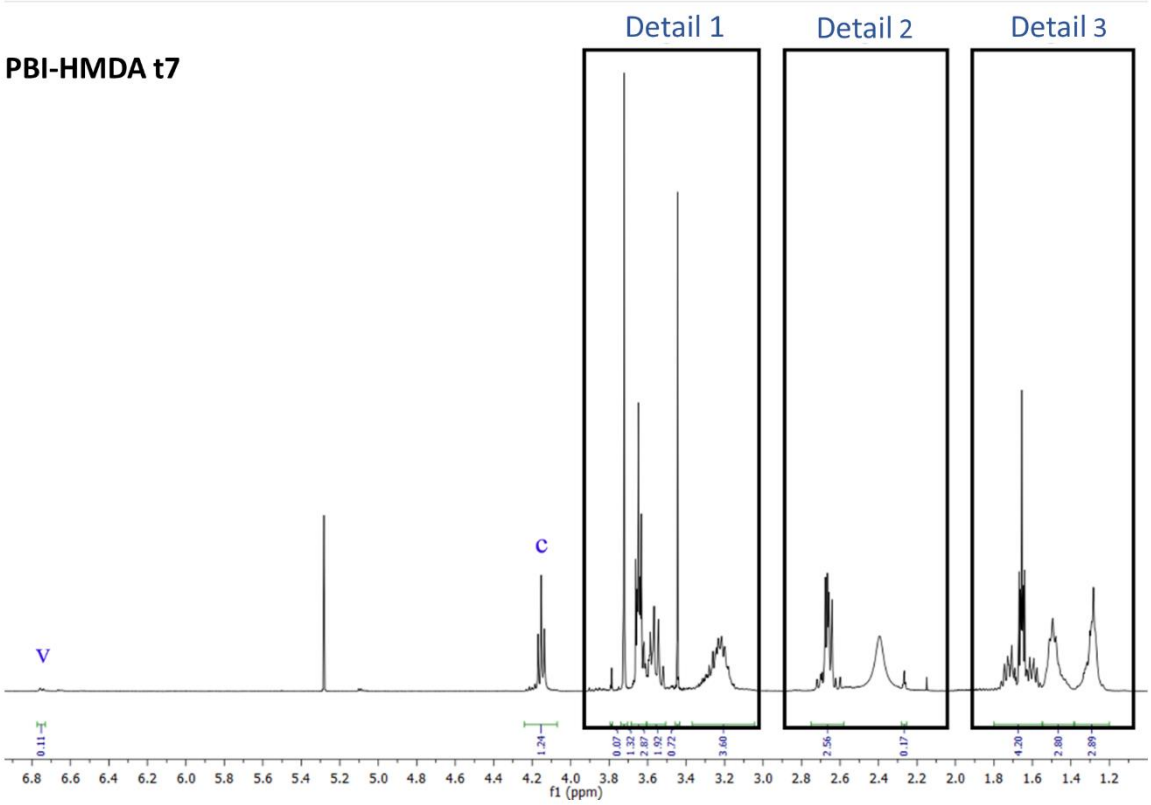
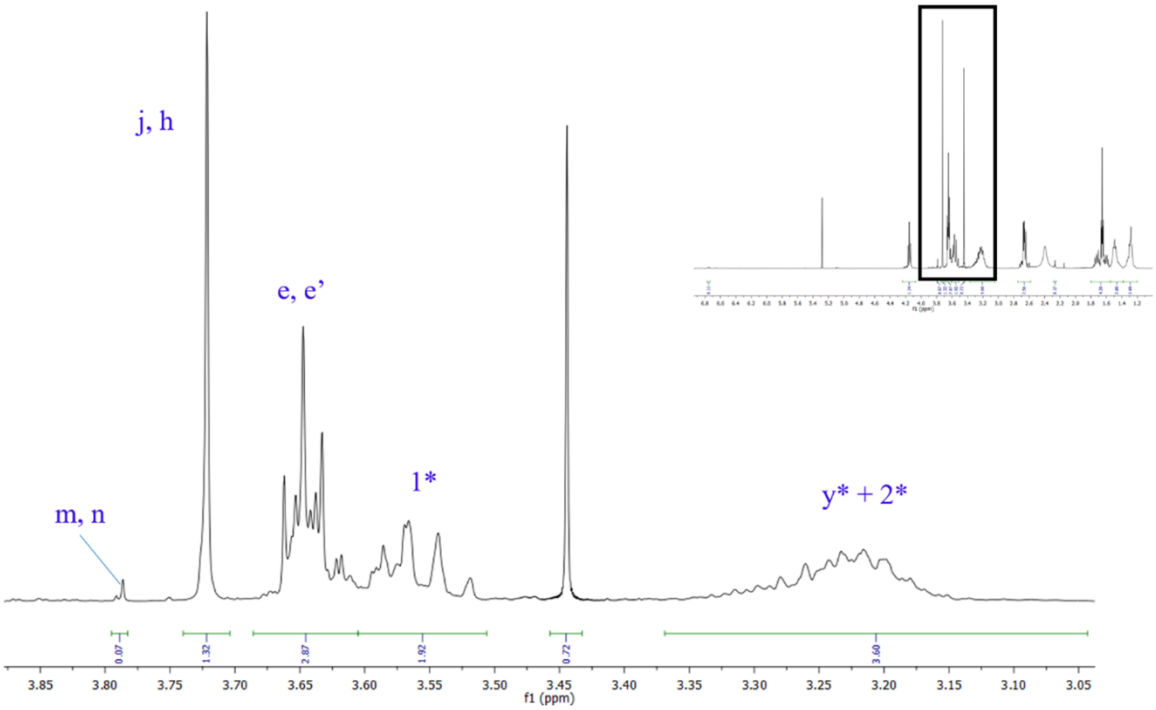
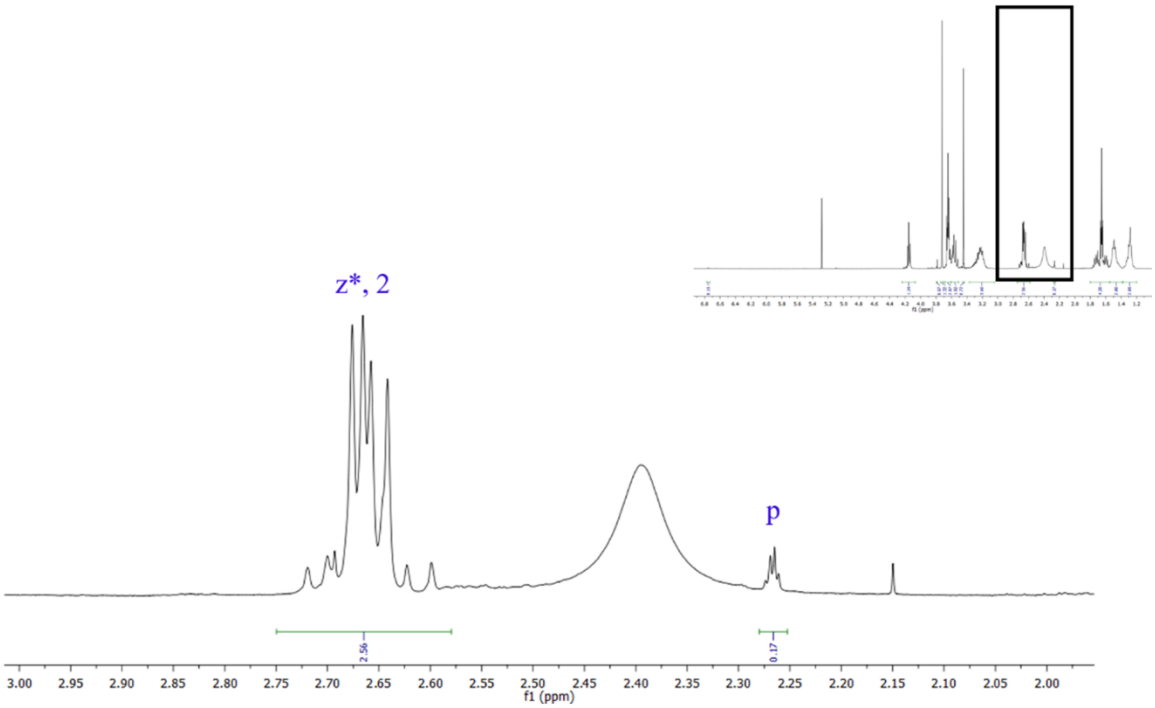


Figure S22. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between HMDA and PBI. For protons' assignments, see previous assignments for the DMI monomer and its isomers.

Detail 1



Detail 2



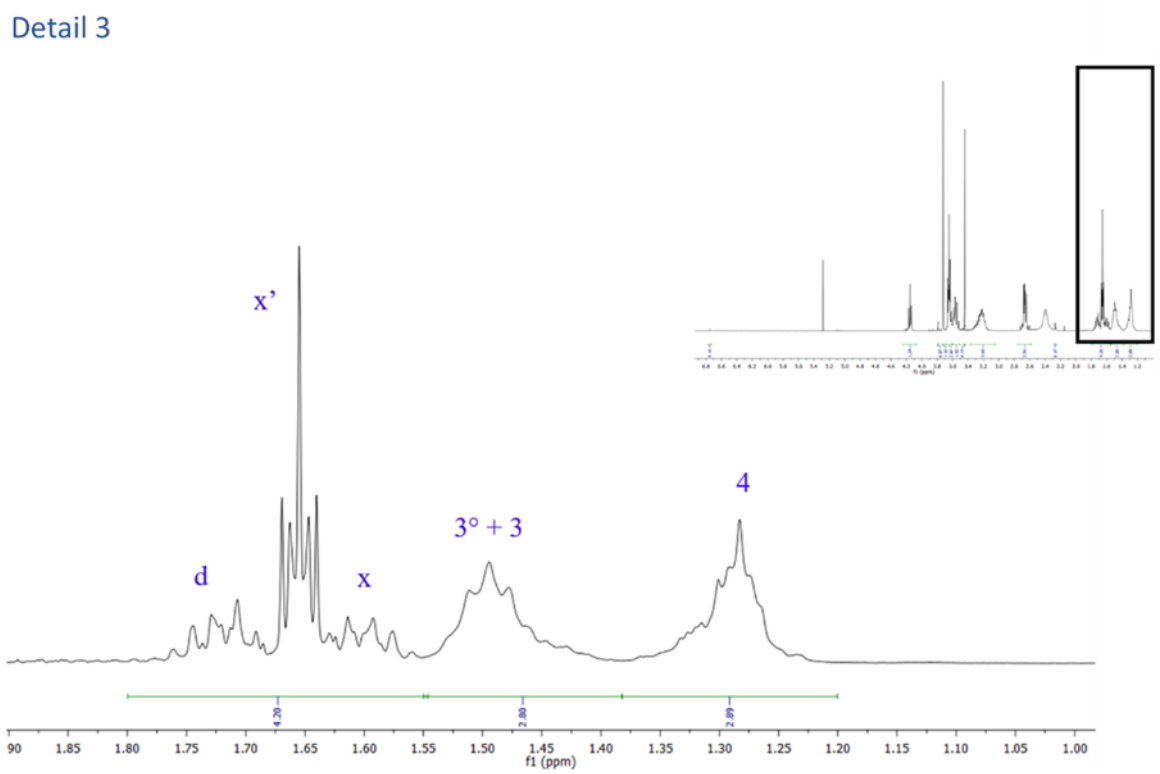


Figure S23. Zooms into detailed peaks of the ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between HMDA and PBI. For protons' assignments, see previous assignments for the DMI monomer and its isomers.

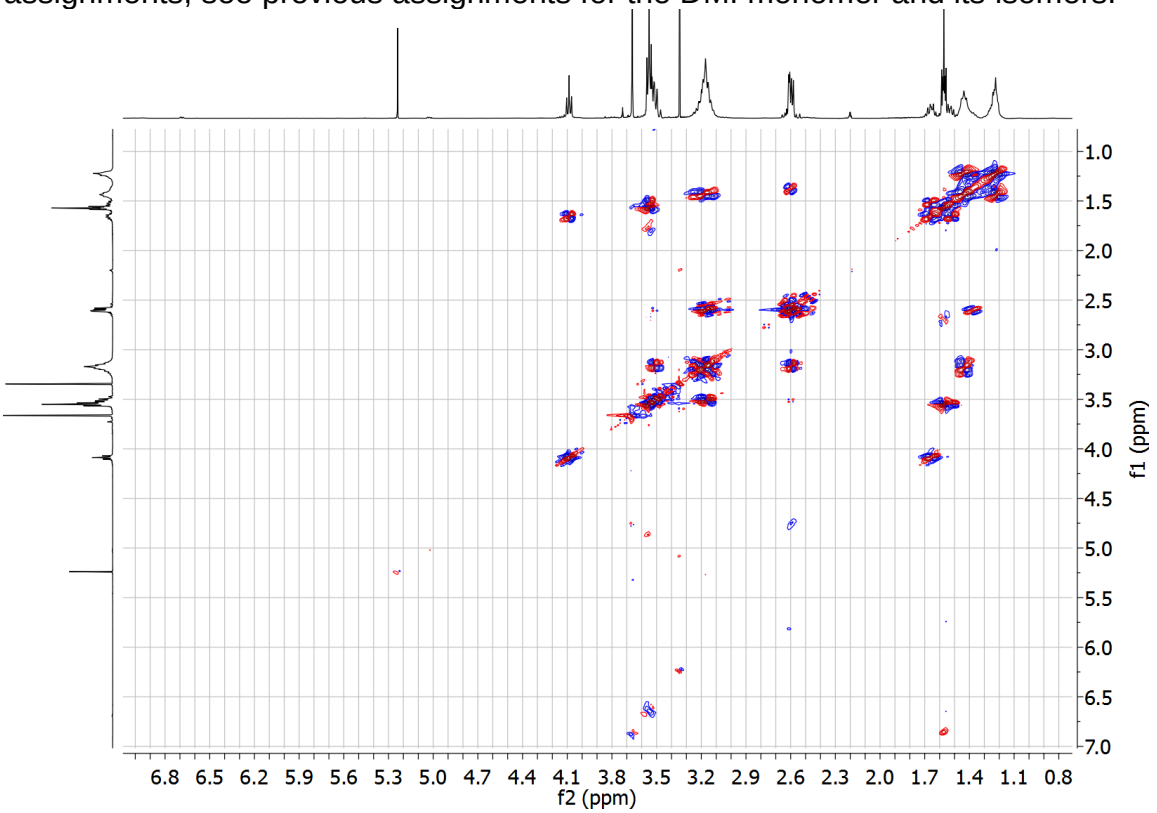


Figure S24. DQ-COSY spectrum of the crude reaction mixture at 456 min of the reaction between PBI and HMDA.

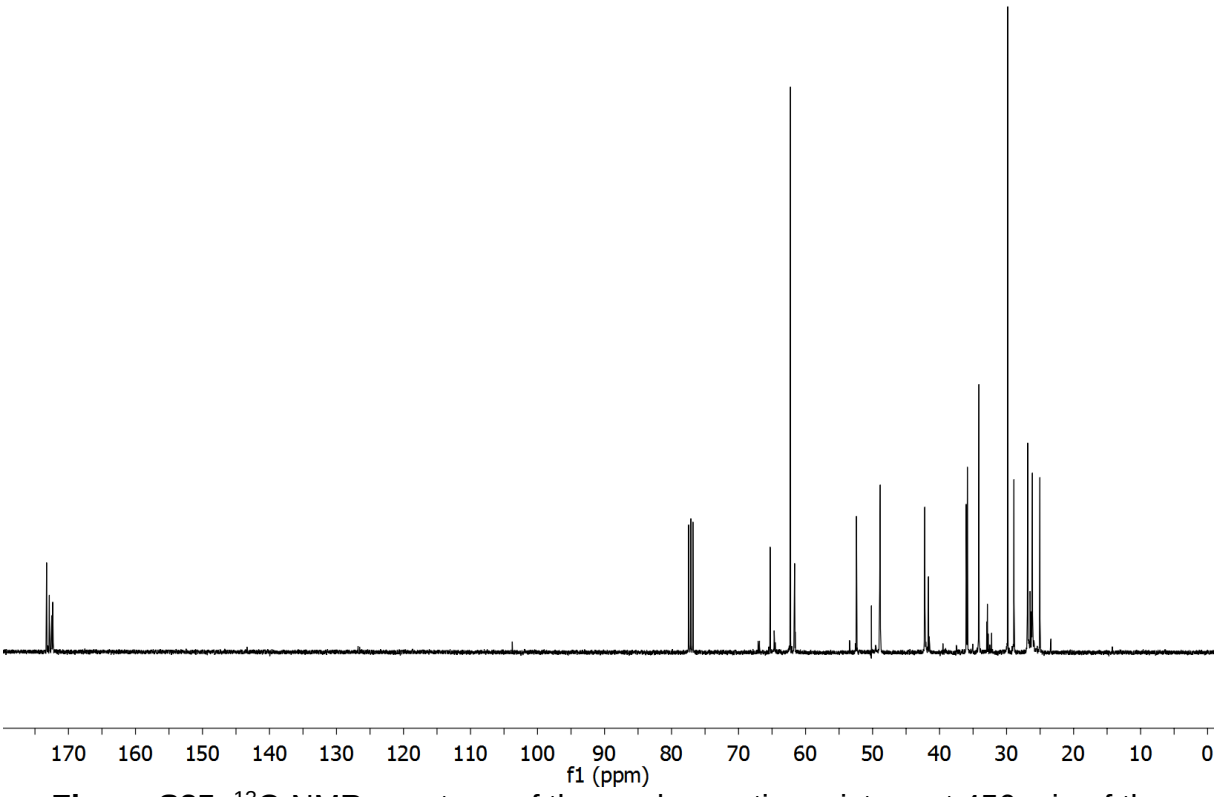


Figure S25. ^{13}C-NMR spectrum of the crude reaction mixture at 456 min of the reaction between PBI and HMDA in $CDCl_3$.

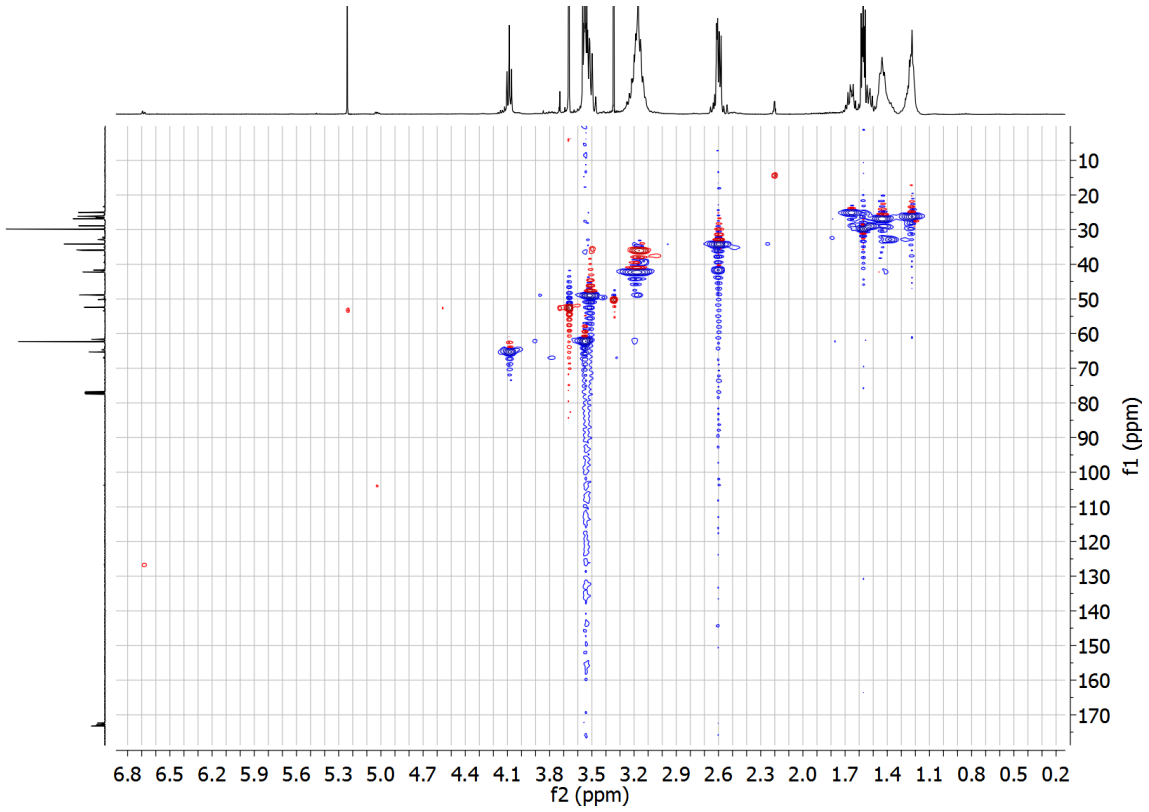


Figure S26. HSQC-AD spectrum of the crude reaction mixture at 456 min of the reaction between PBI and HMDA in $CDCl_3$.

Table S3. RP-HPLC gradient used for the analysis of the aza-Michael addition of HMDA to the oligomer PBI.		
Time (min)	**H_2O + 0.05% v/v TFA (%)**	**ACN + 0.05% v/v TFA (%)**
0	60	40
5 (injection)	60	40
15	60	40
25	40	60
40	40	60
55	60	40
50	60	40
Signals with registered with DAD detector: Red trace: 215nm and reference wavelength at 330 nm; green trace: 260 nm and reference wavelength at 330 nm; blue trace: 700 nm and reference wavelength at 500 nm. Double bond (chromophore) absorption max: 215 nm.		

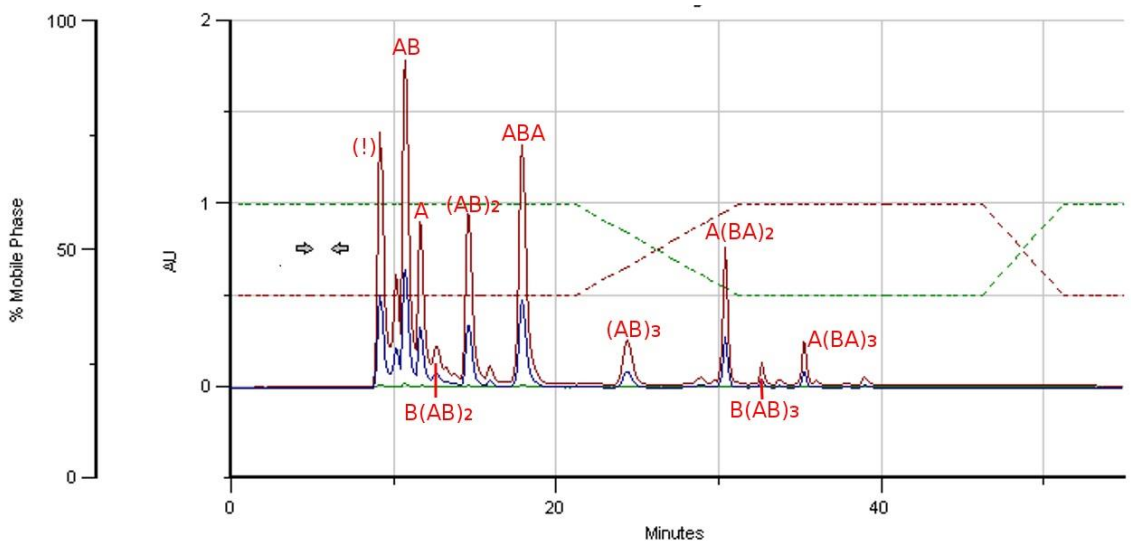


Figure S27. HPLC chromatogram of the crude reaction mixture at time 0 min of the reaction between HMDA and PBI.

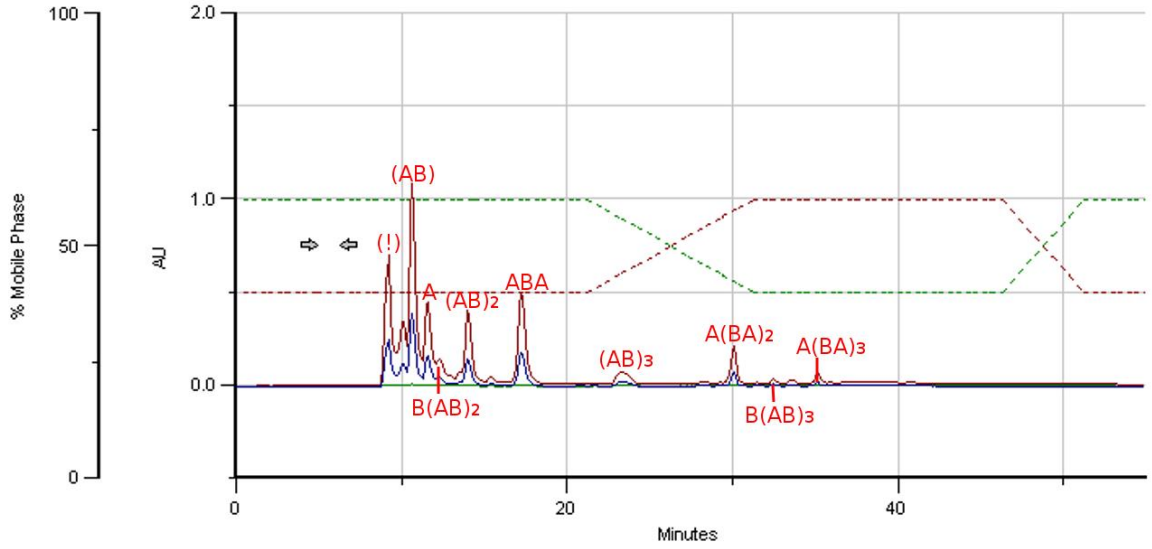


Figure S28. HPLC chromatogram of the crude reaction mixture at time 60 min of the reaction between HMDA and PBI.

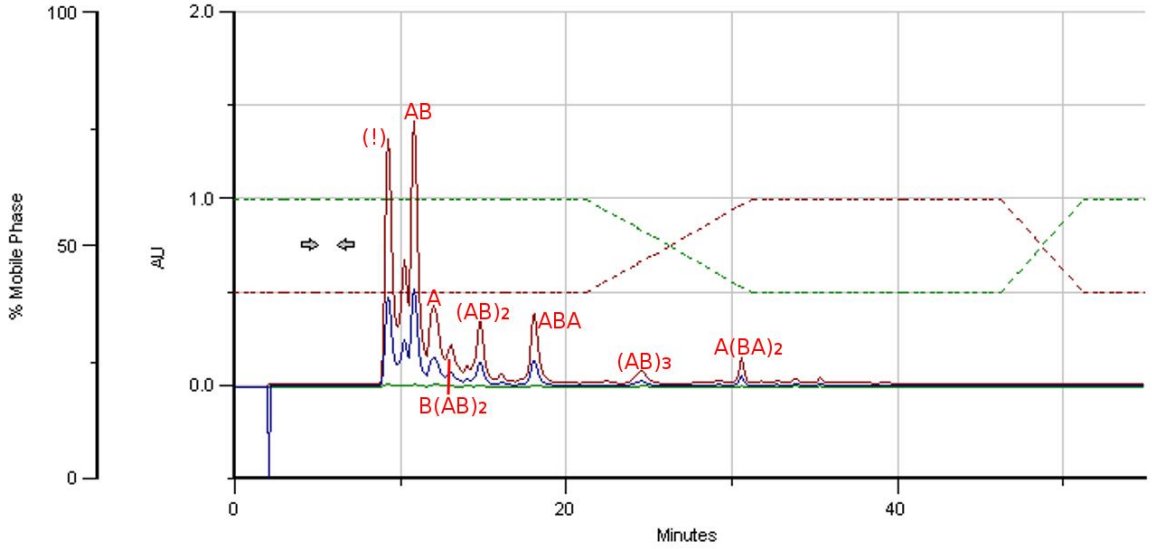


Figure S29. HPLC chromatogram of the crude reaction mixture at time 150 min of the reaction between HMDA and PBI.

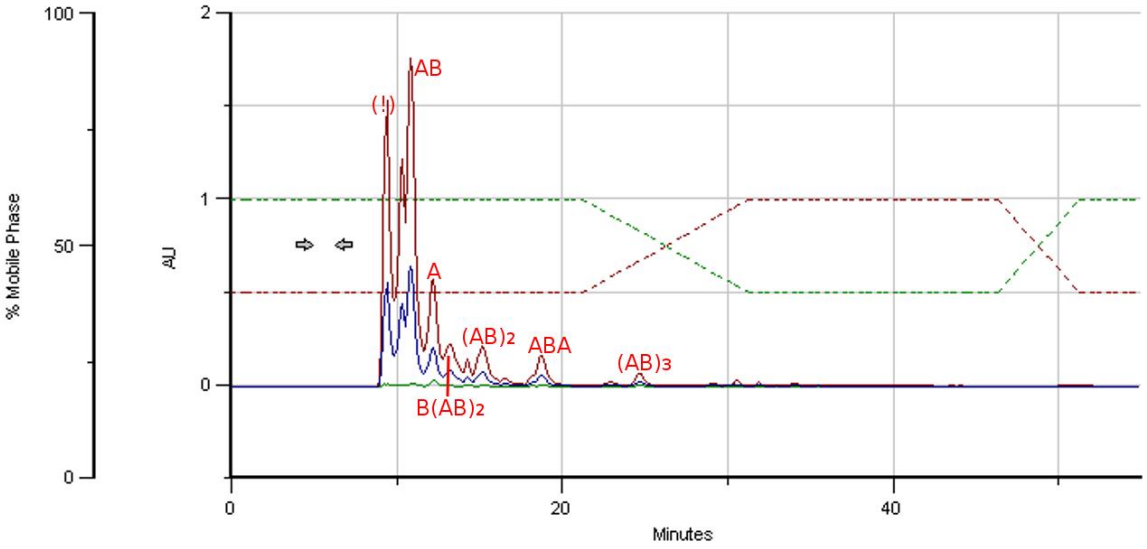


Figure S30. HPLC chromatogram of the crude reaction mixture at time 210 min of the reaction between HMDA and PBI.

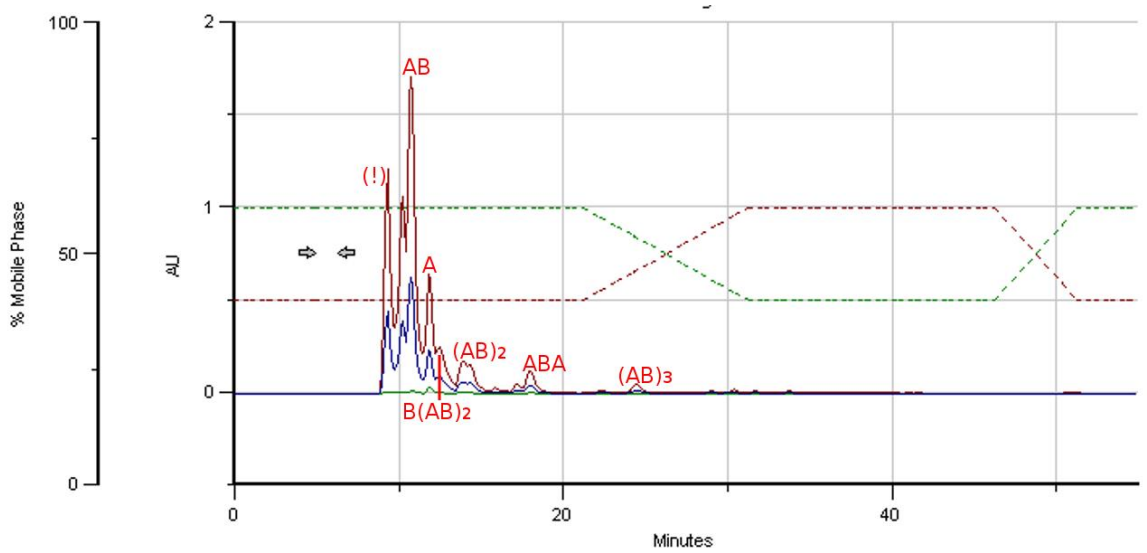


Figure S31. HPLC chromatogram of the crude reaction mixture at time 270 min of the reaction between HMDA and PBI.

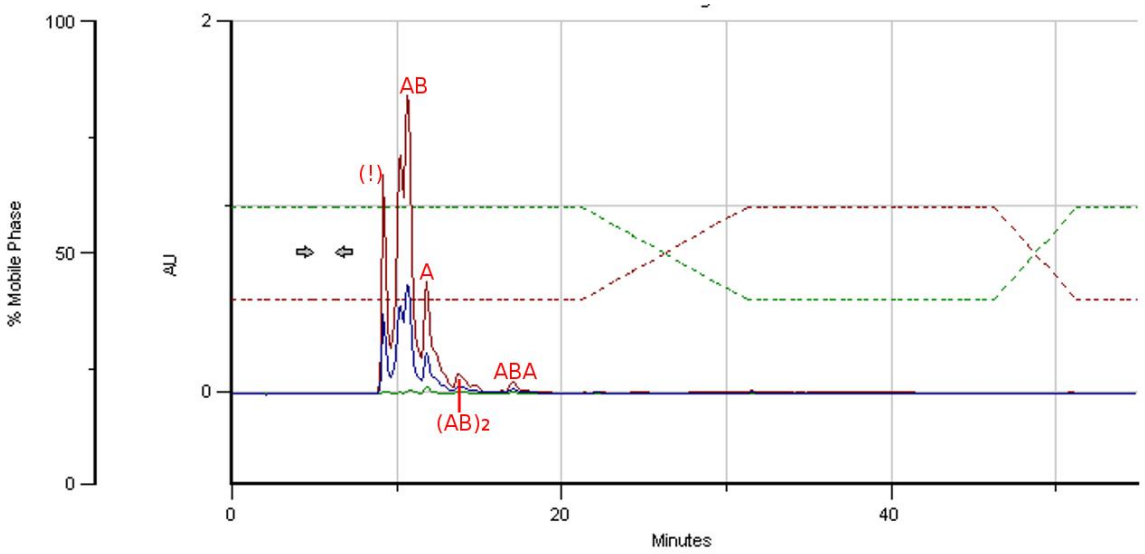


Figure S32. HPLC chromatogram of the crude reaction mixture at time 345 min of the reaction between HMDA and PBI.

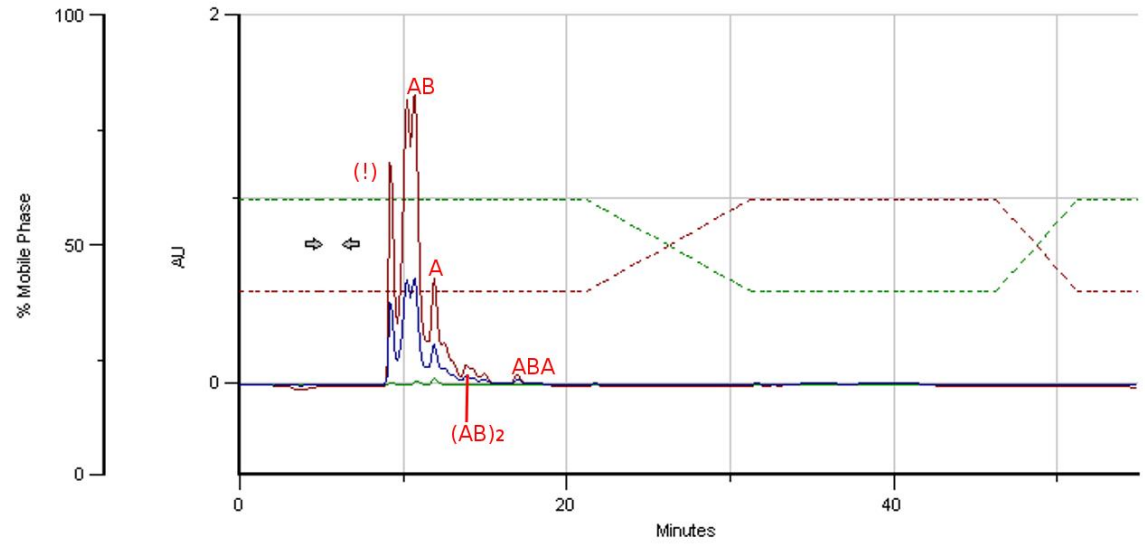


Figure S33. HPLC chromatogram of the crude reaction mixture at time 456 min of the reaction between HMDA and PBI.

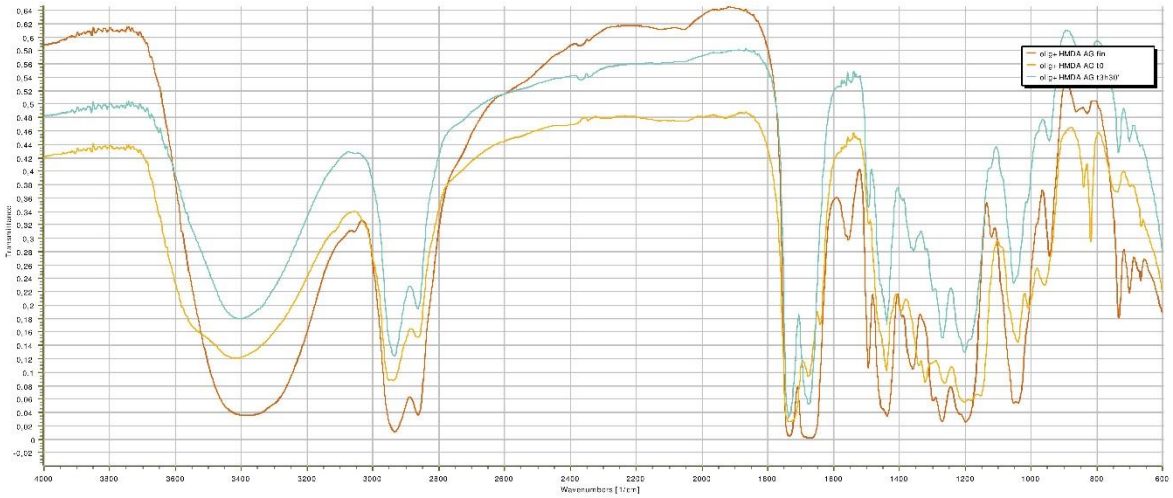


Figure S34. IR spectrum of the crude reaction mixture of theaddition of HMDA to PBI at different reaction times (orange: 0 min- 20% HMDA; cyan: 150 min- 40% HMDA; red: 456 min- 60% HMDA).

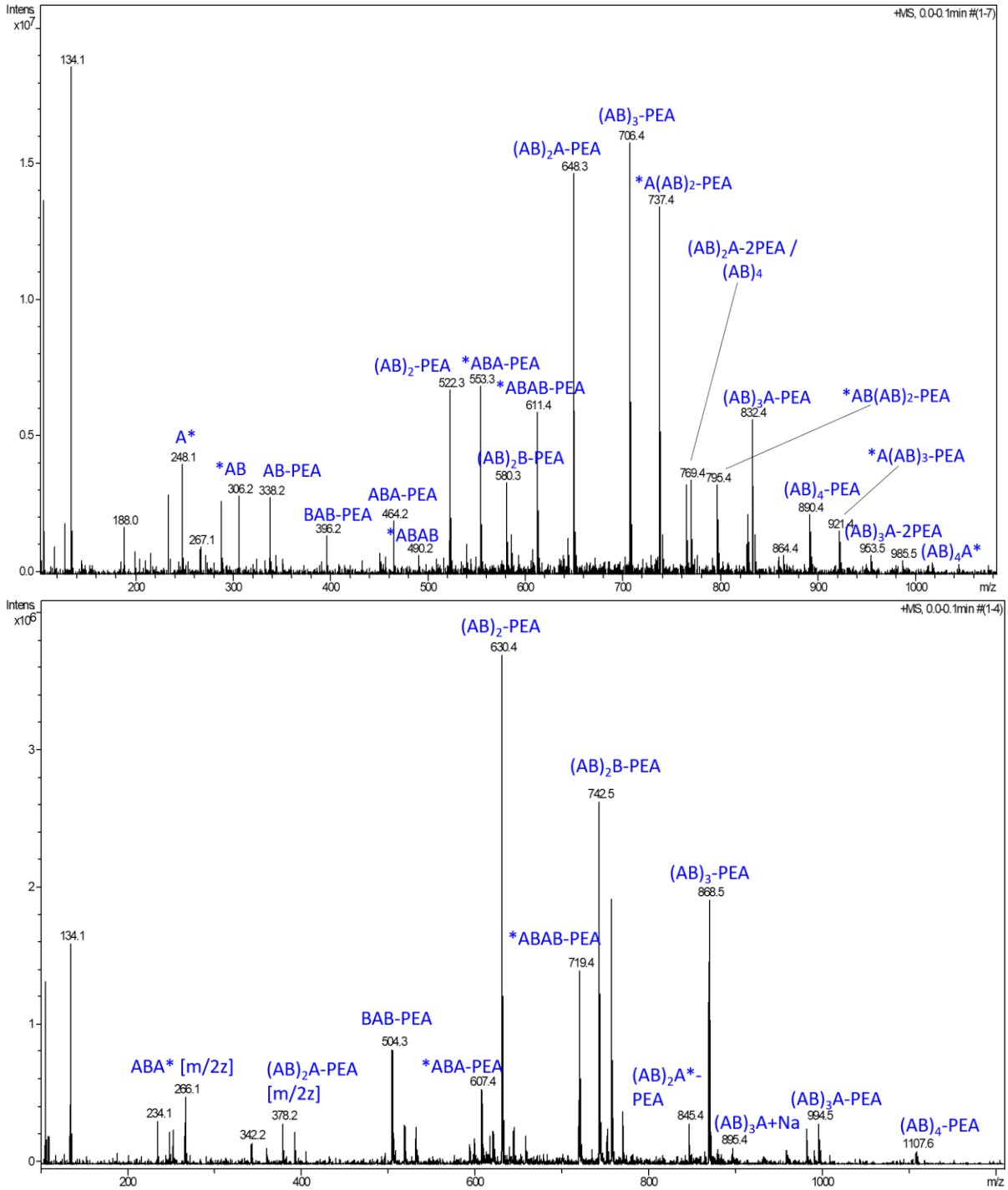


Figure S35. ESI-MS spectra 456min of the aza-Addition of PEA to PBI (left) and PCI (right). A: DMI; B diol; * stays for a lactam ring; the straight line connections indicate a crosslink. Target mass 1000 m/z.

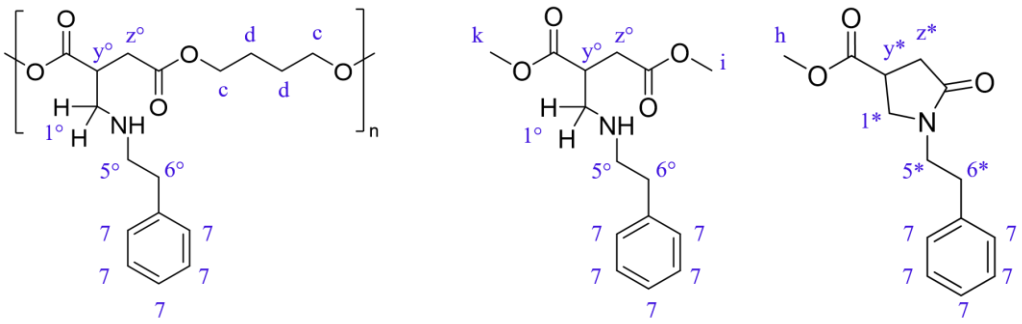


Figure S36. Structures of the possible products of the addition of PEA to PBI.

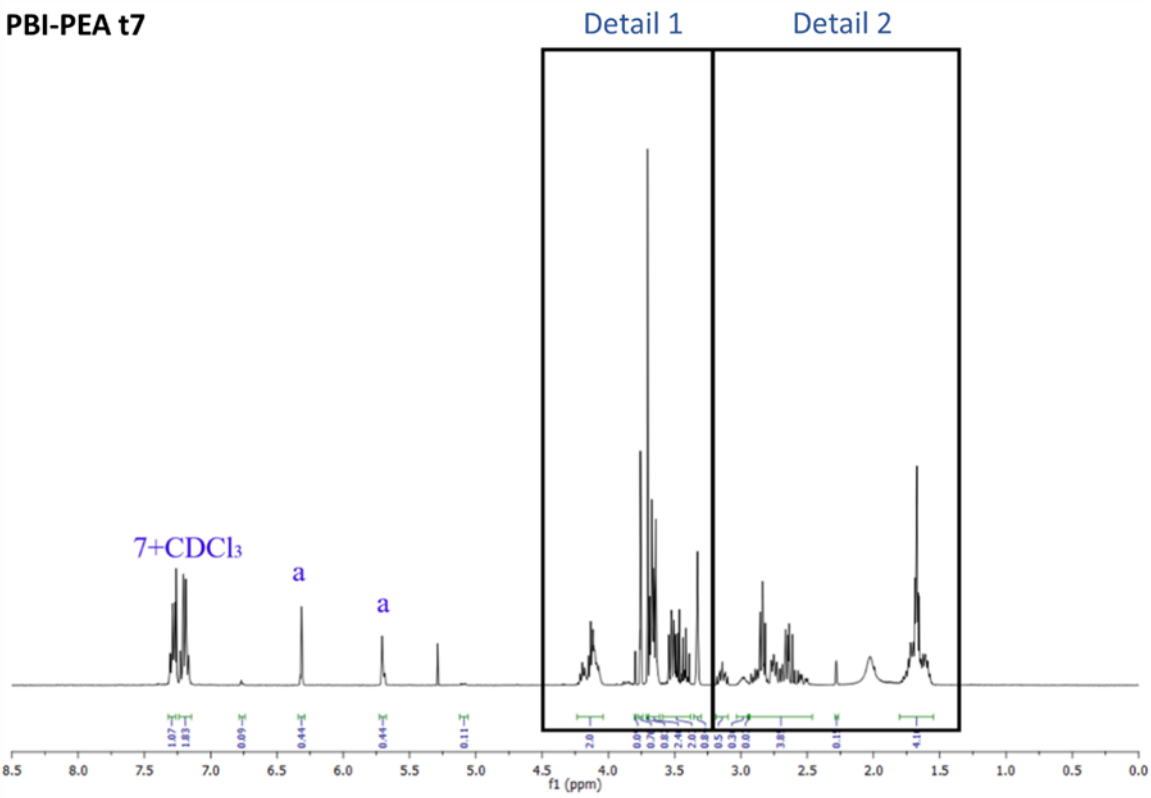


Figure S37. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between PEA and PBI. For protons' assignments, see S23 and previous assignments for the DMI monomer and its isomers.

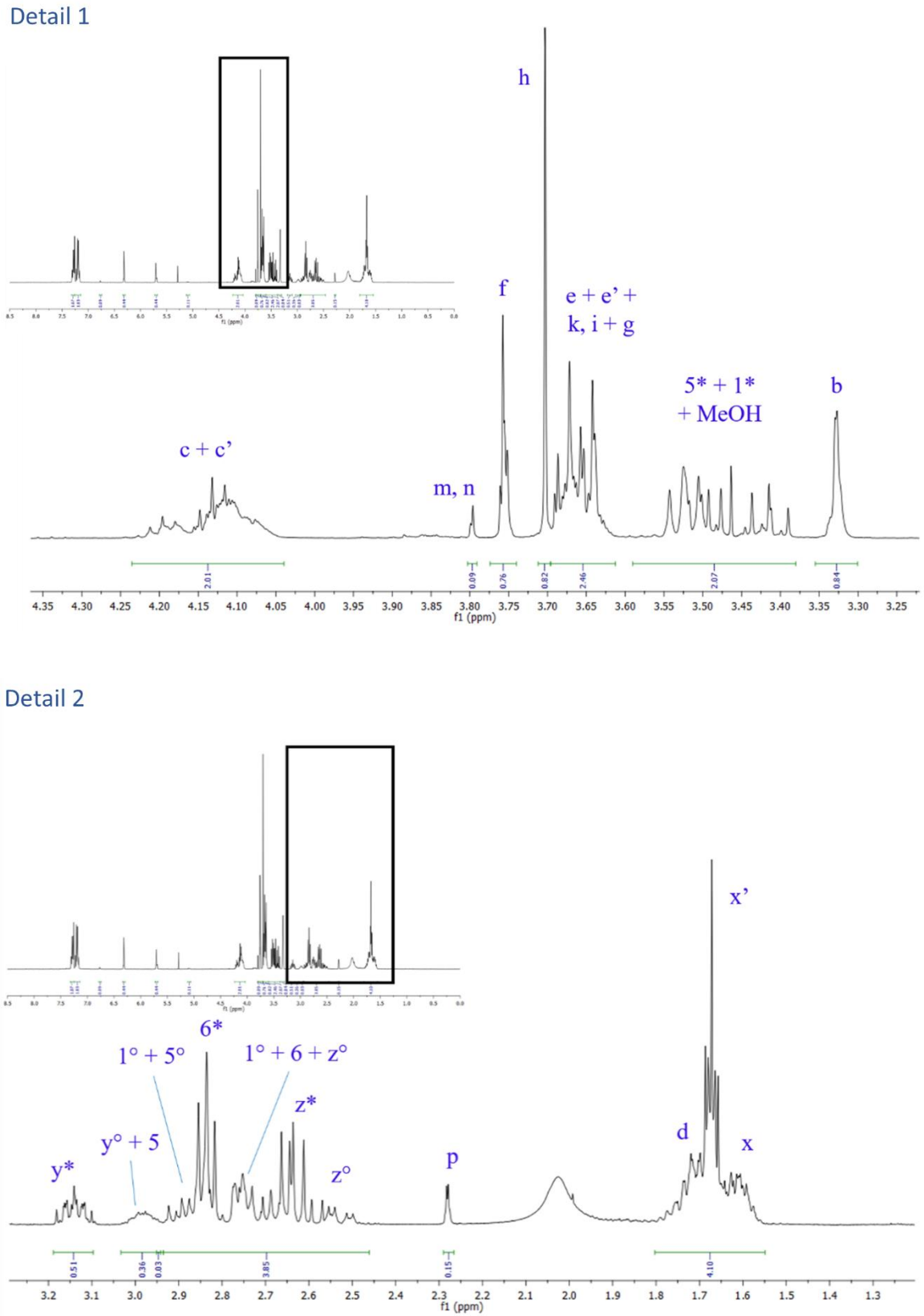


Figure S38. Zooms into detailed peaks of the ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between PEA and PBI. For protons' assignments, see previous assignments for the DMI monomer and its isomers.

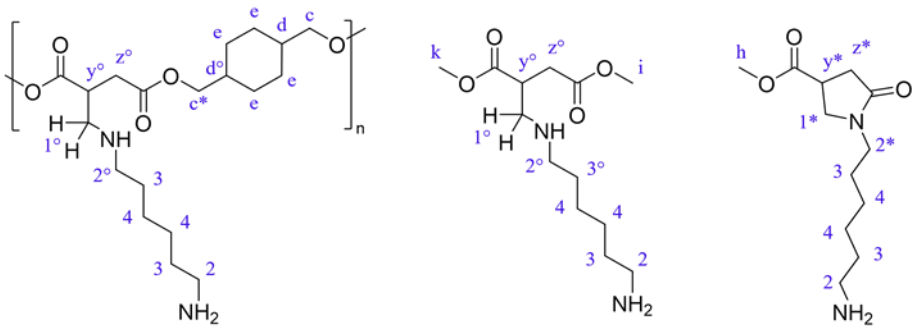


Figure S39. Structures of the possible products of the addition of HMDA to PCI.

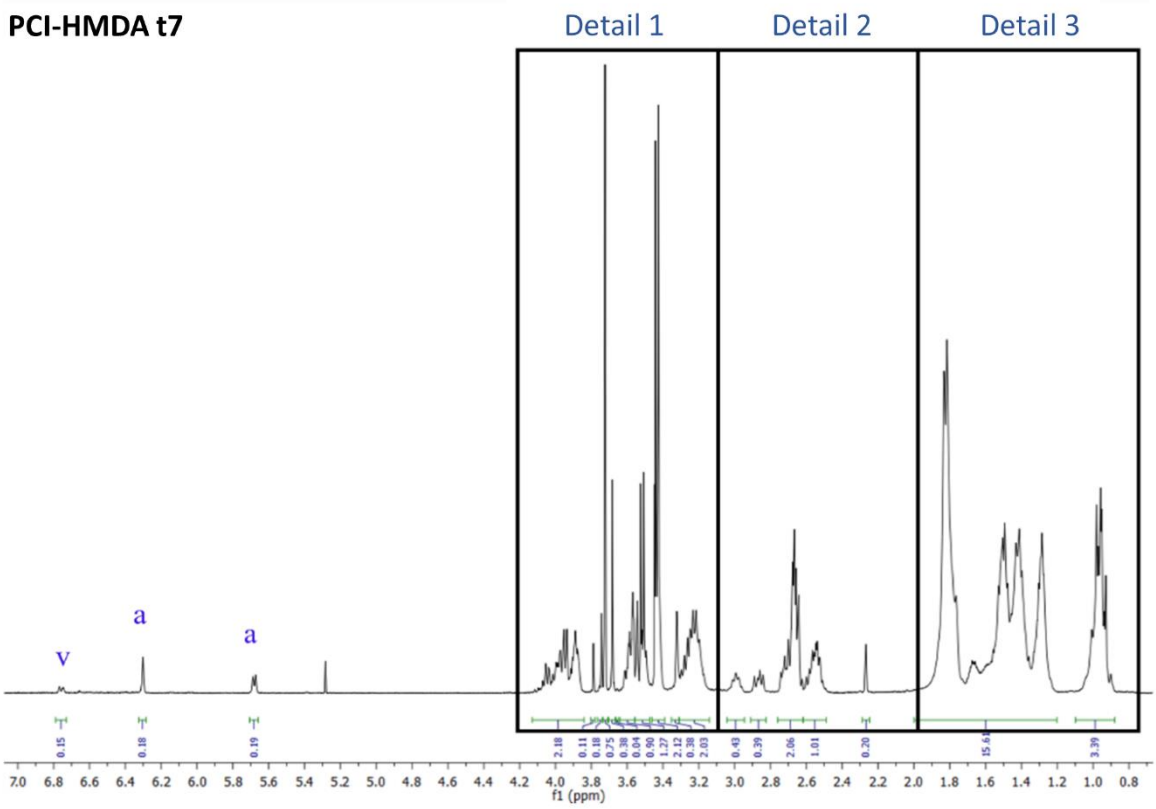
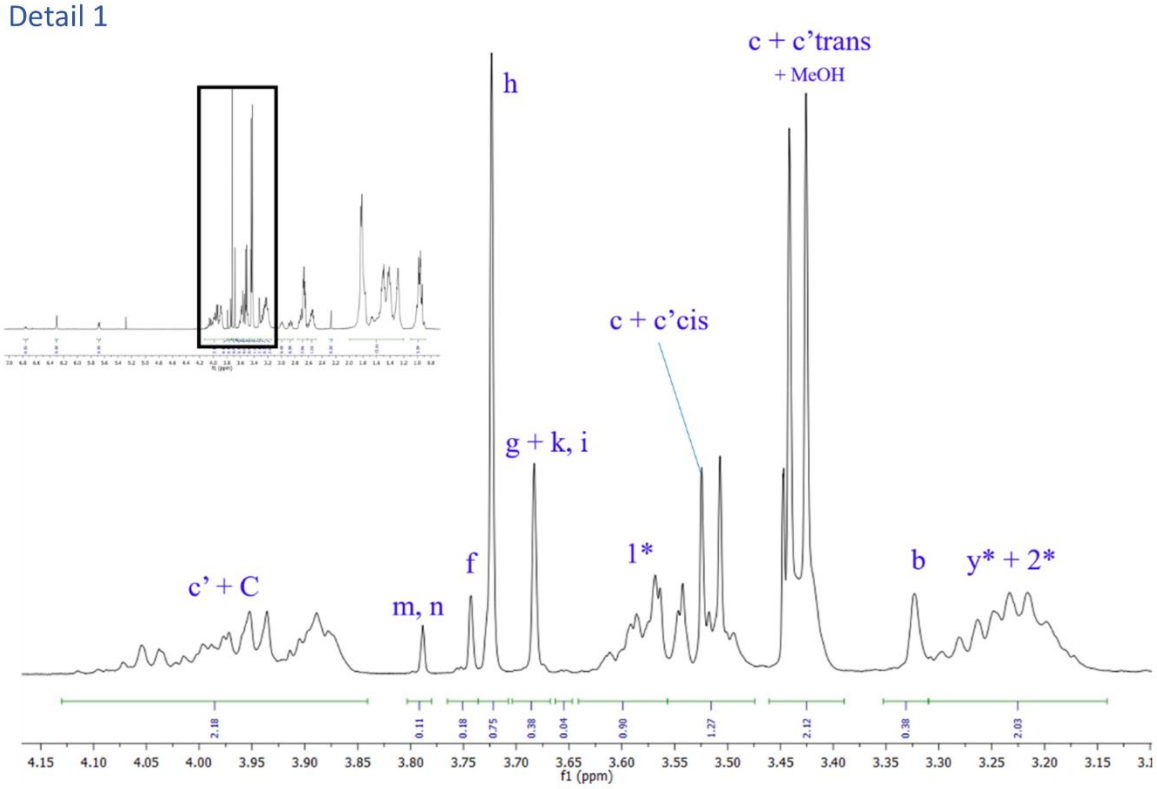
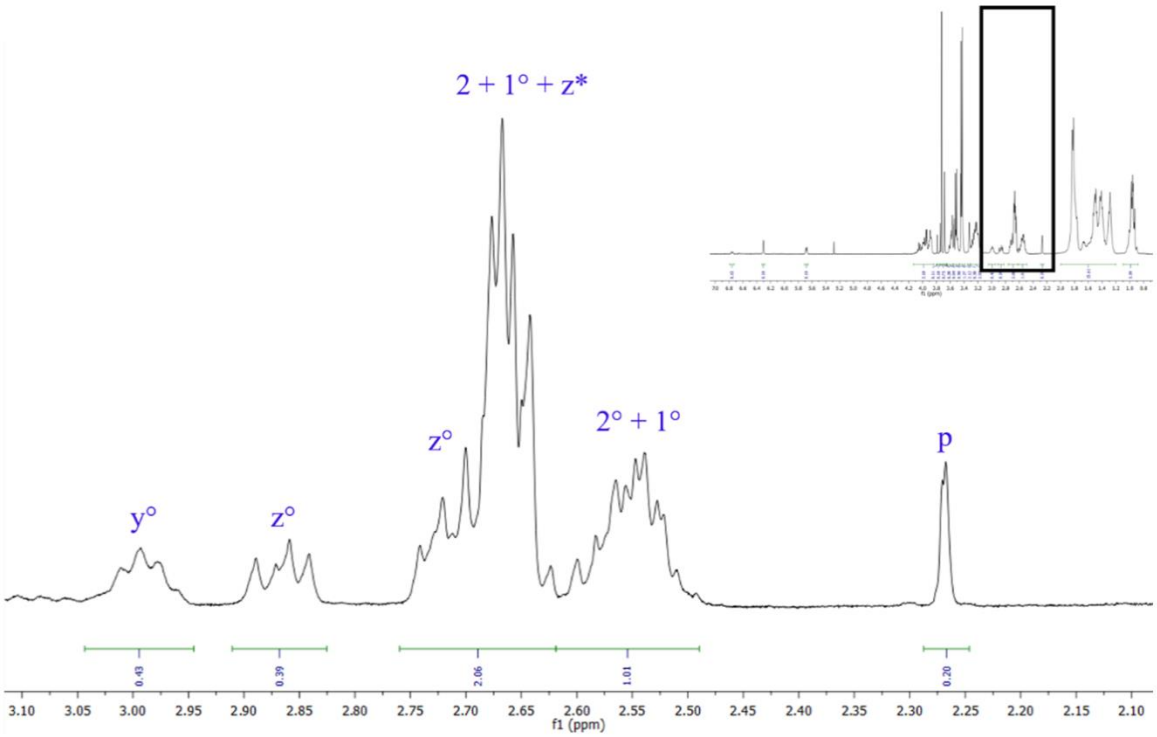


Figure S40. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between HMDA and PCI. For protons' assignments, see previous assignments for the DMI monomer and its isomers.

Detail 1



Detail 2



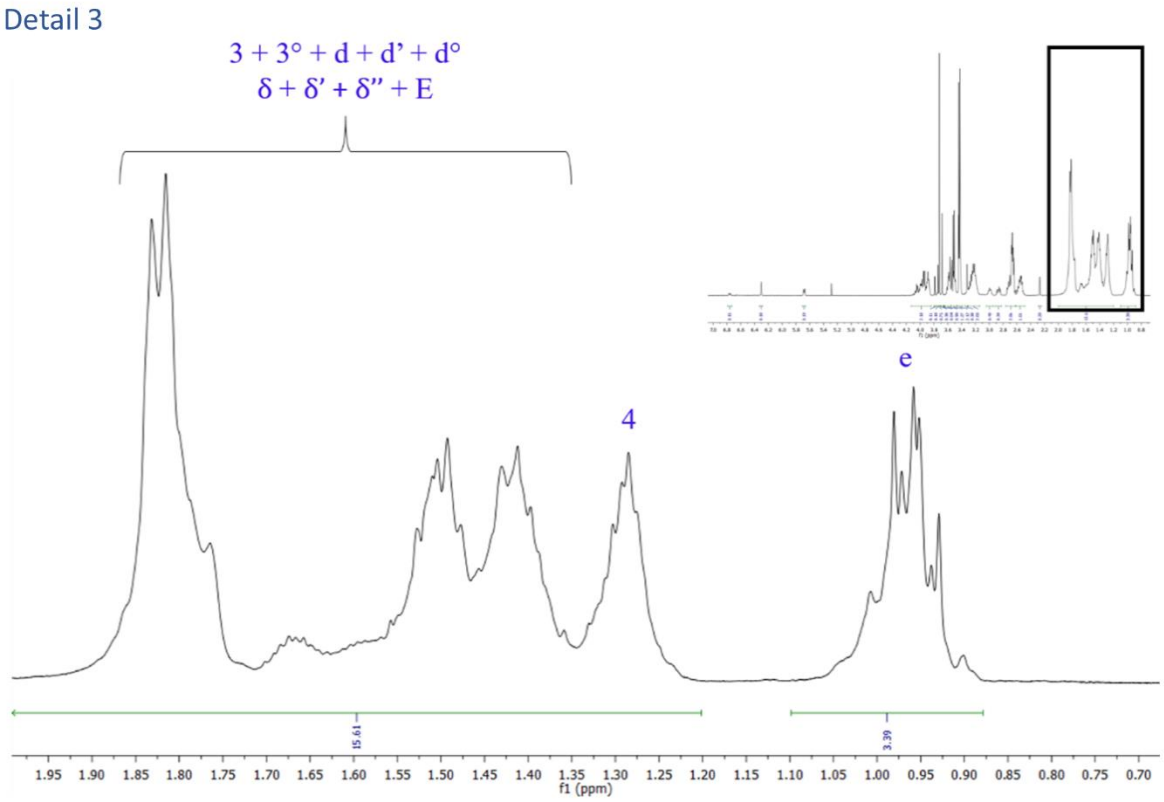


Figure S41. Zooms into detailed peaks of the ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between HMDA and PCI. For protons' assignments, see previous assignments for the DMI monomer and its isomers.

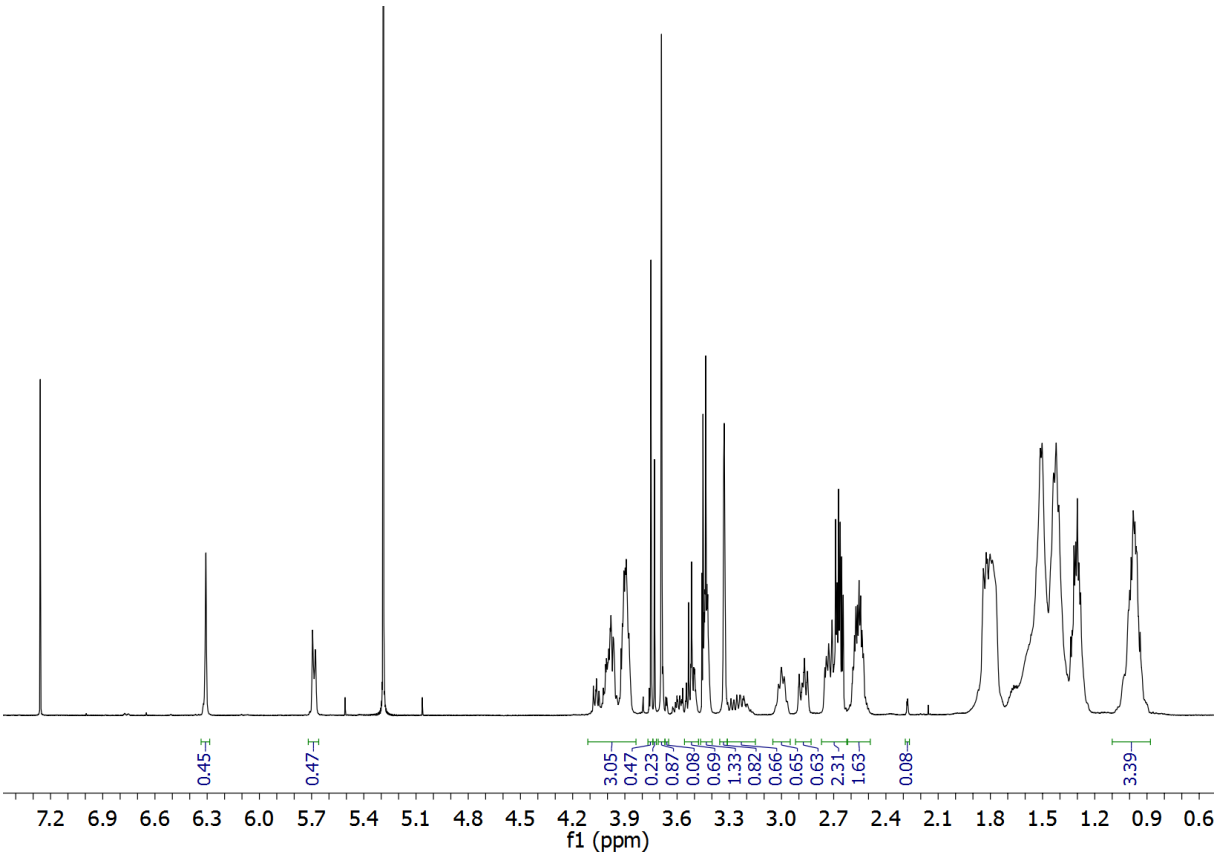


Figure S42. ^{1}H-NMR spectrum of the crude reaction mixture at 456 min of the reaction between HMDA and PCI in DCM. For protons' assignments, see previous assignments for the solvent-less reaction, for DMI monomer and its isomers. Spectra was recorded using $CDCl_3$ as the solvent.

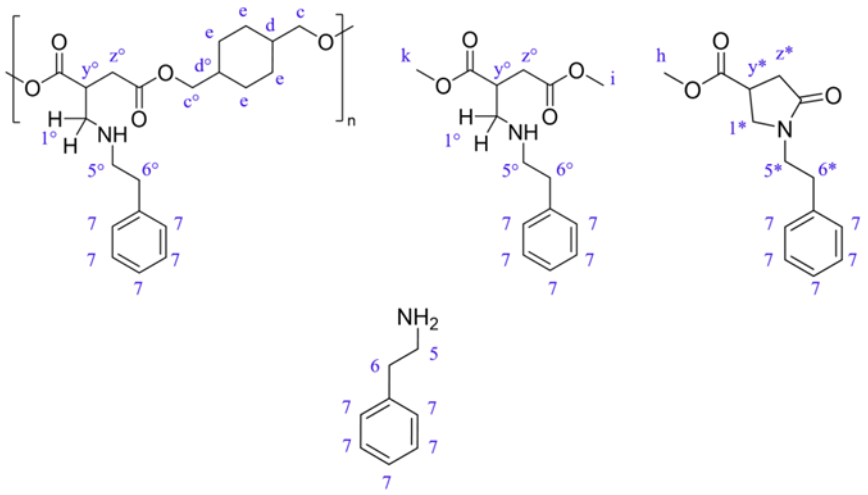


Figure S43. Structures of the possible PEA to PCI addition products.

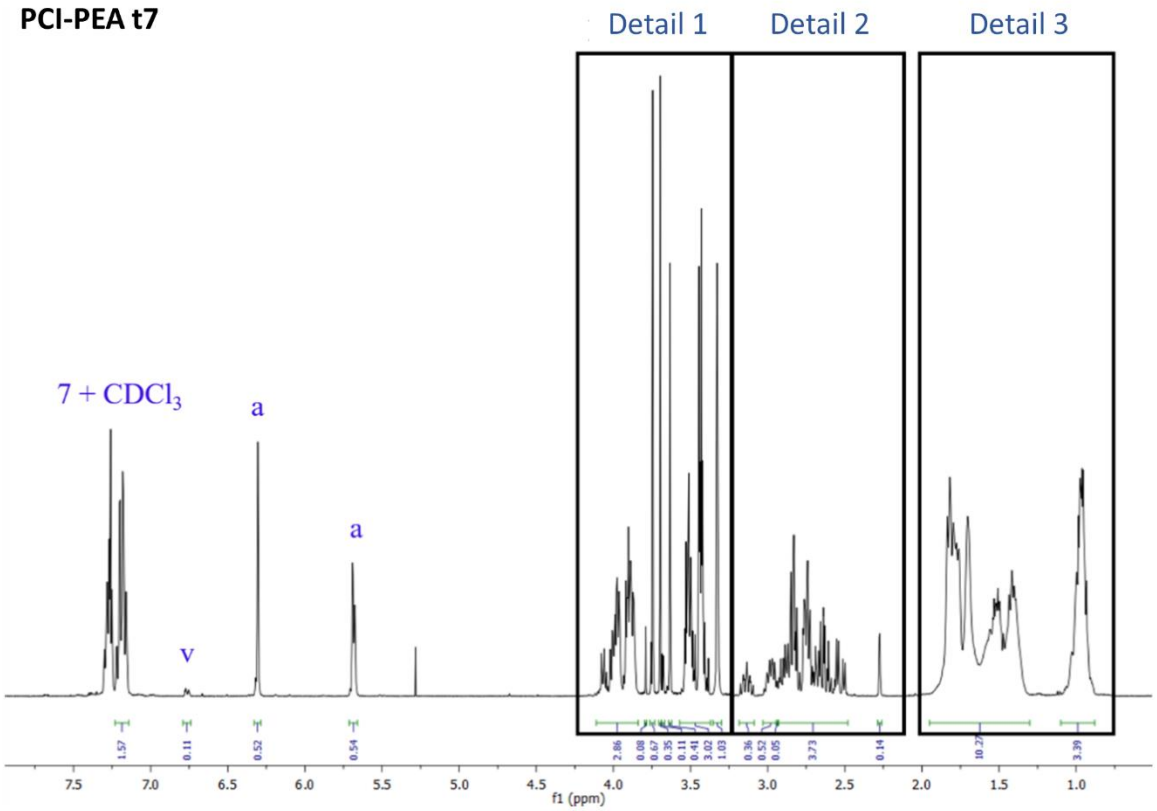
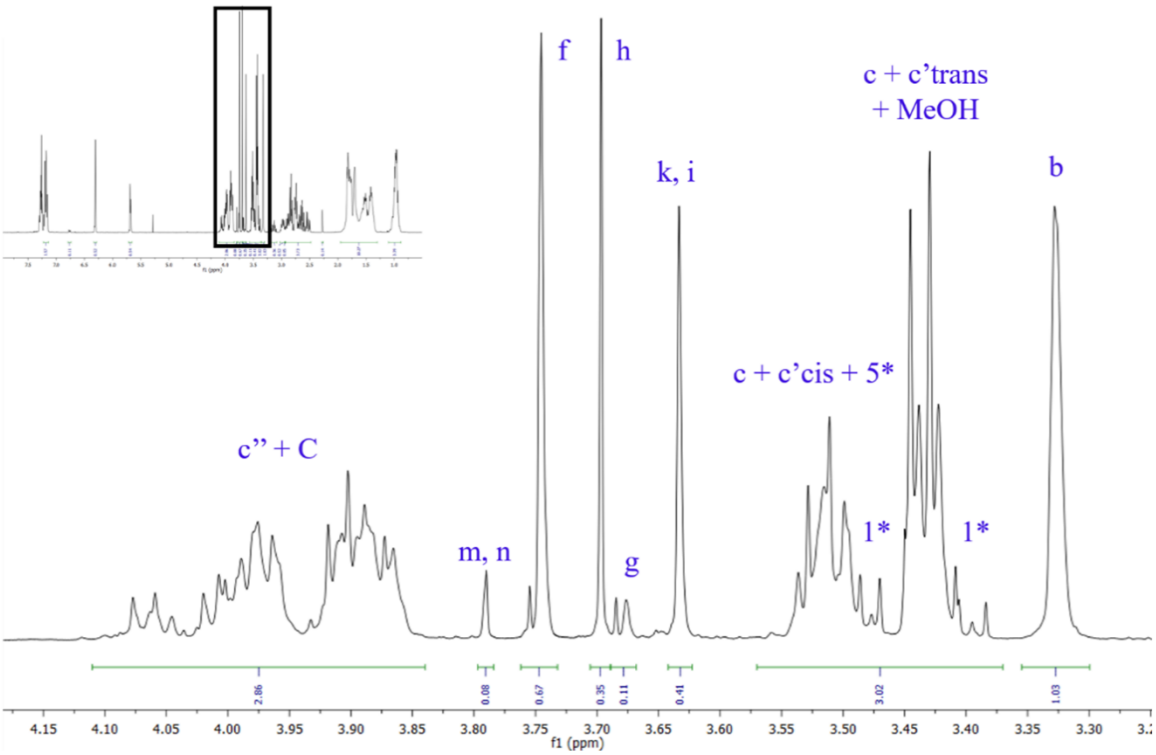
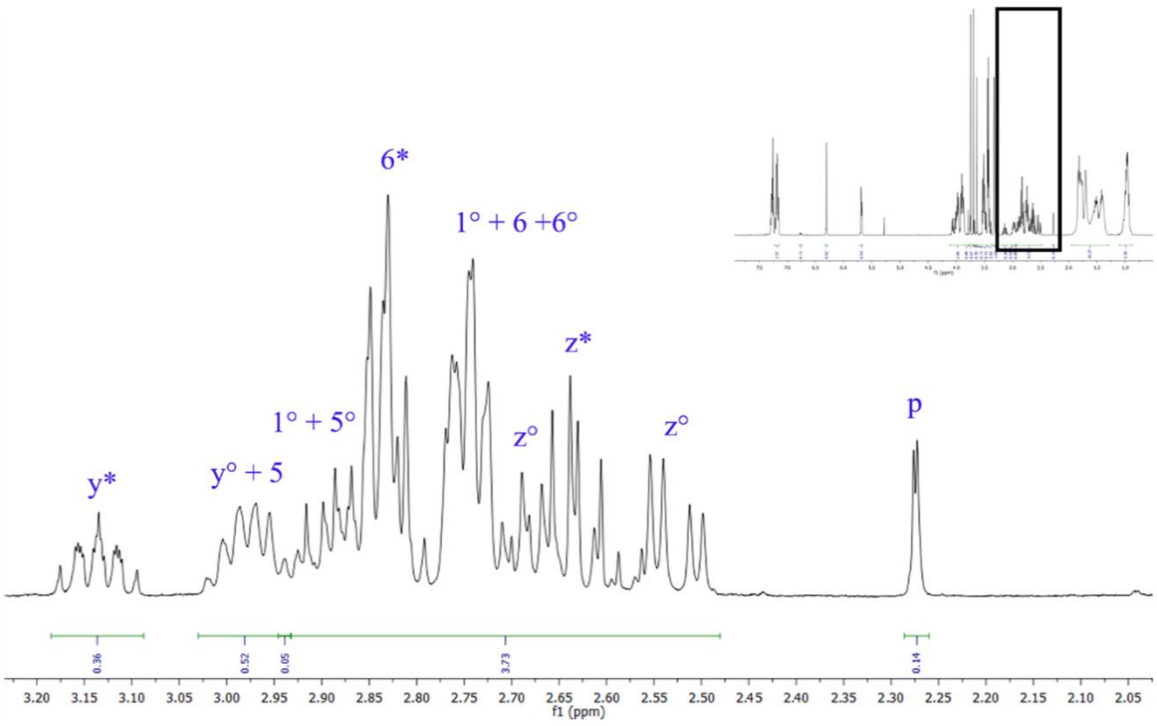


Figure S44. ^{1}H-NMR spectrum of the crude reaction mixture at 456 min of the reaction between PEA and PCI recorded in $CDCl_3$. For protons' assignments, see previous assignments for DMI monomer and its isomers.

Detail 1



Detail 2



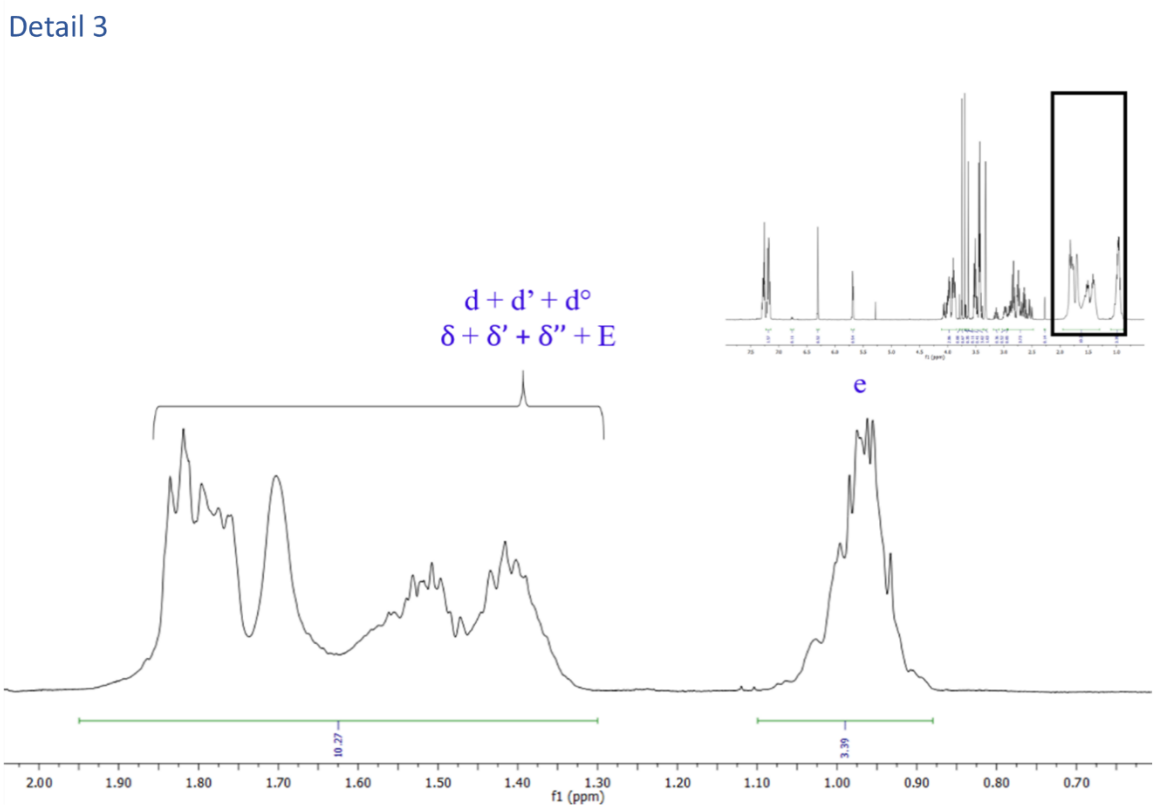


Figure S45. Zooms into detailed peaks of the ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 456 min of the reaction between PEA and PCI. For protons' assignments, see previous assignments for the DMI monomer and its isomers.

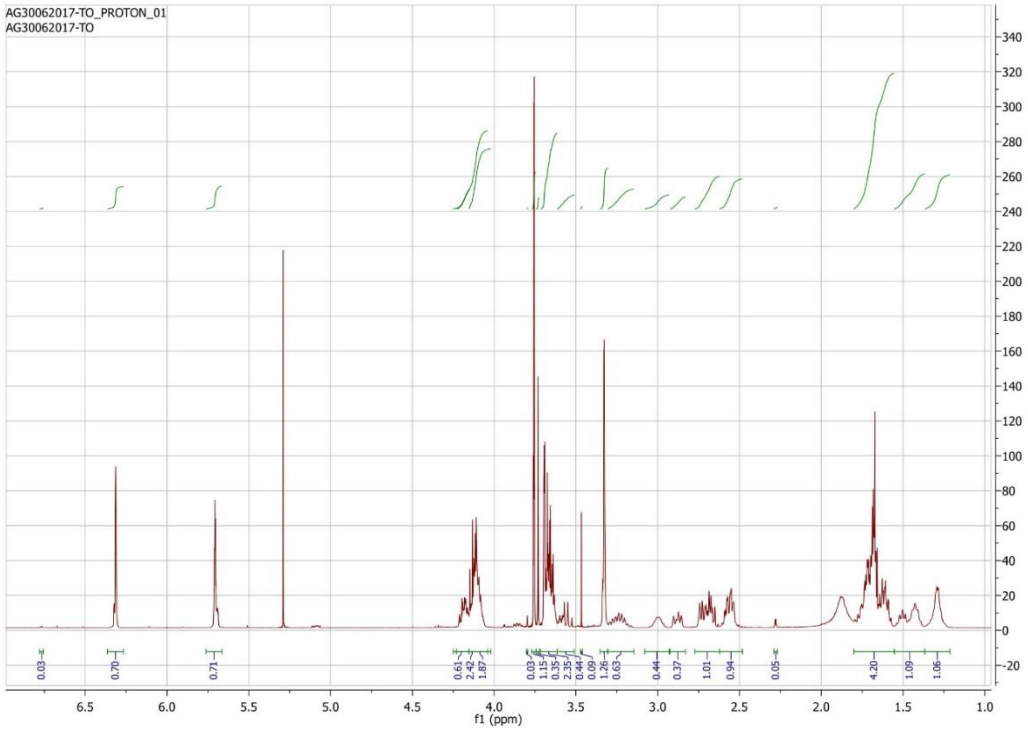


Figure S46. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 3 min of the reaction between HMDA and PBI.

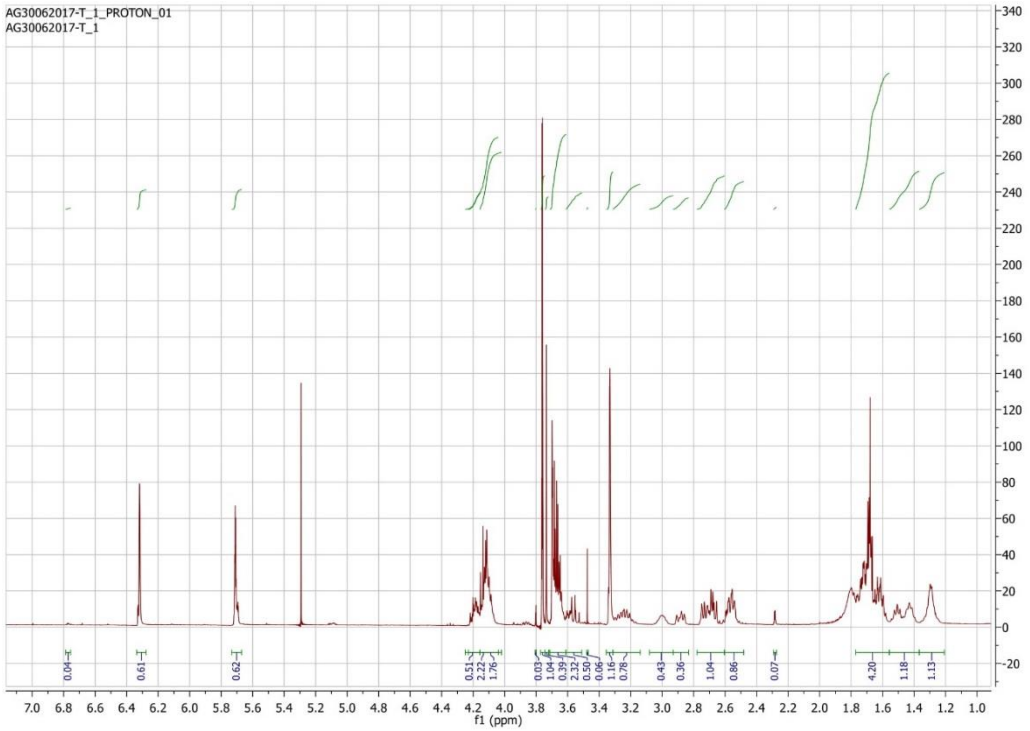


Figure S47. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 60 min of the reaction between HMDA and PBI.

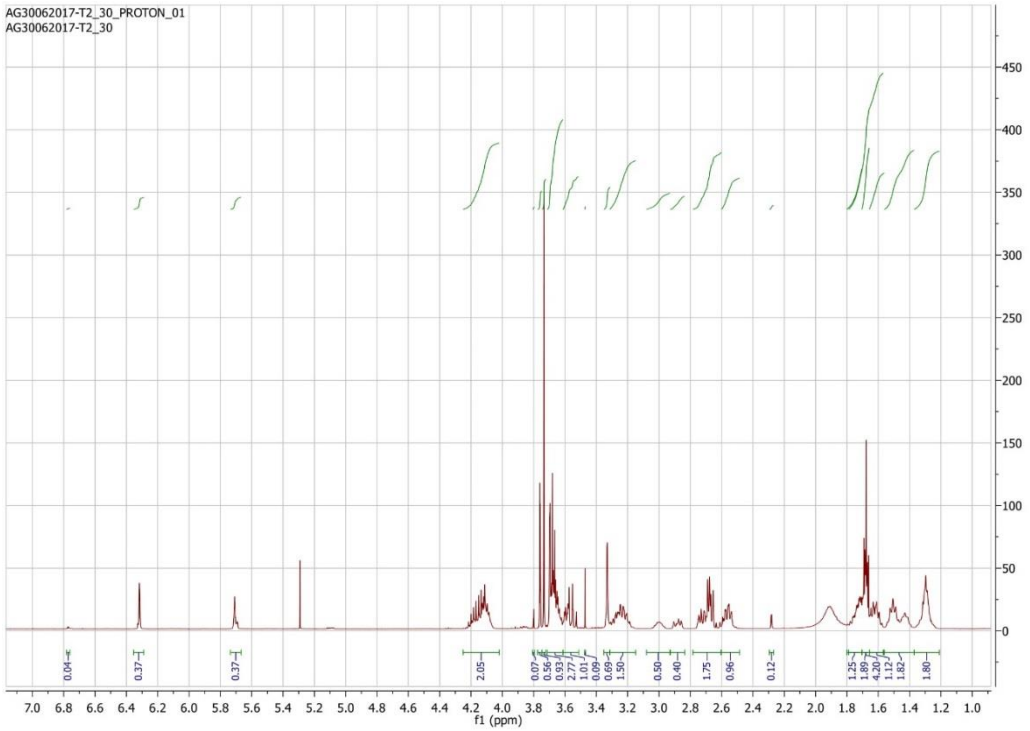


Figure S48. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 150 min of the reaction between HMDA and PBI.

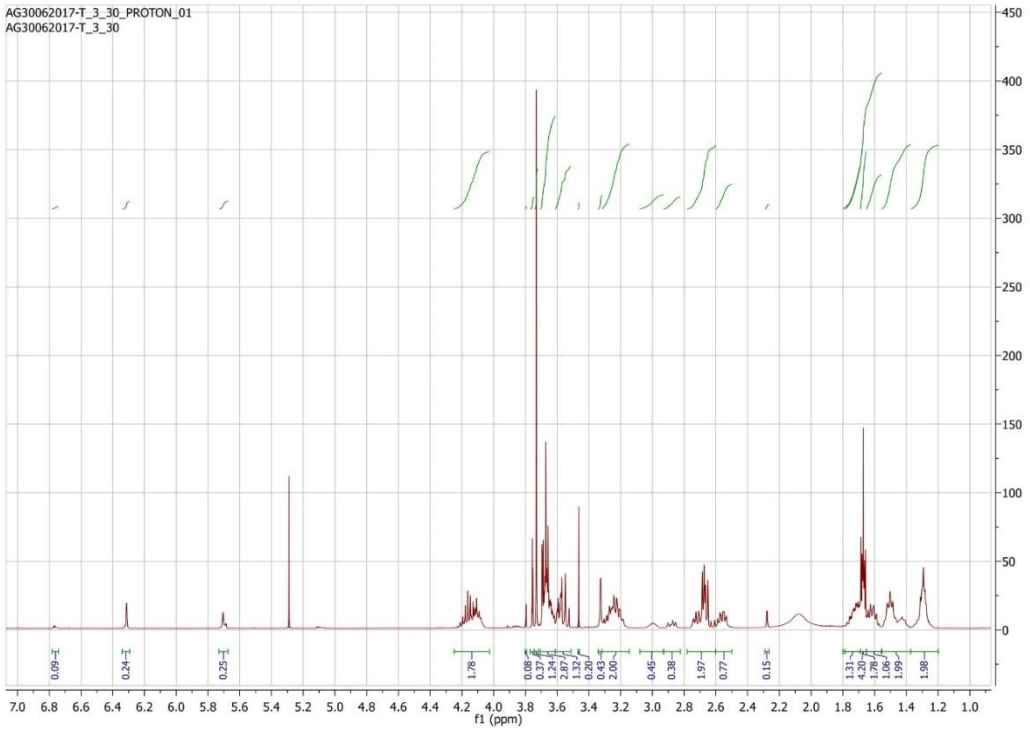


Figure S49. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 210 min of the reaction between HMDA and PBI.

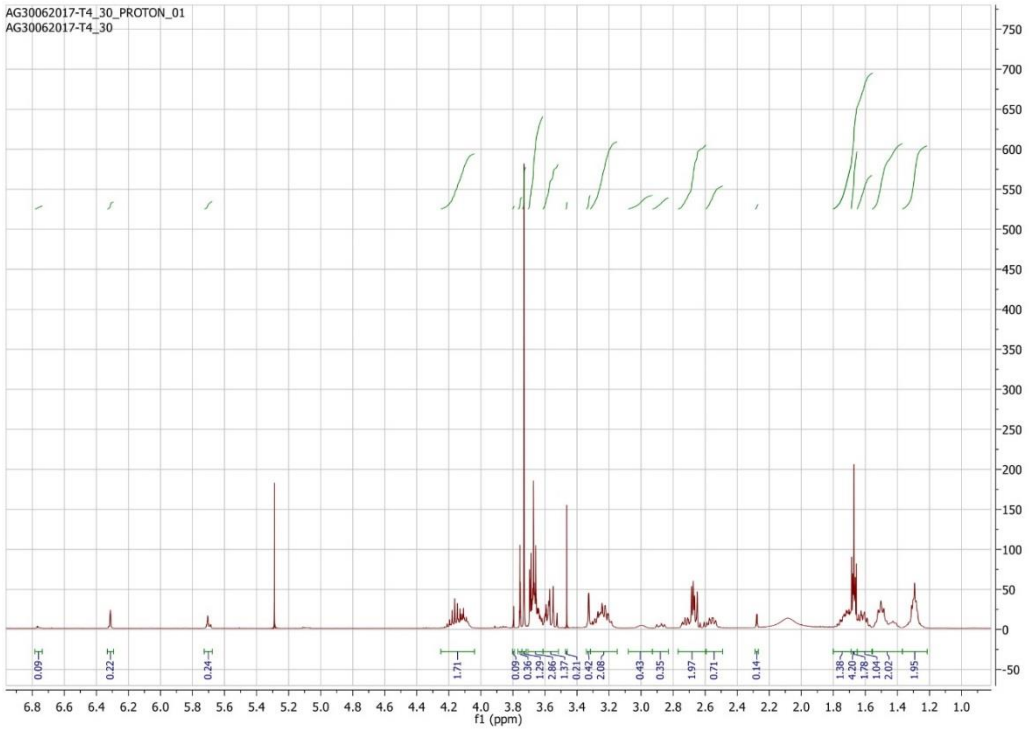


Figure S50. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 270 min of the reaction between HMDA and PBI.

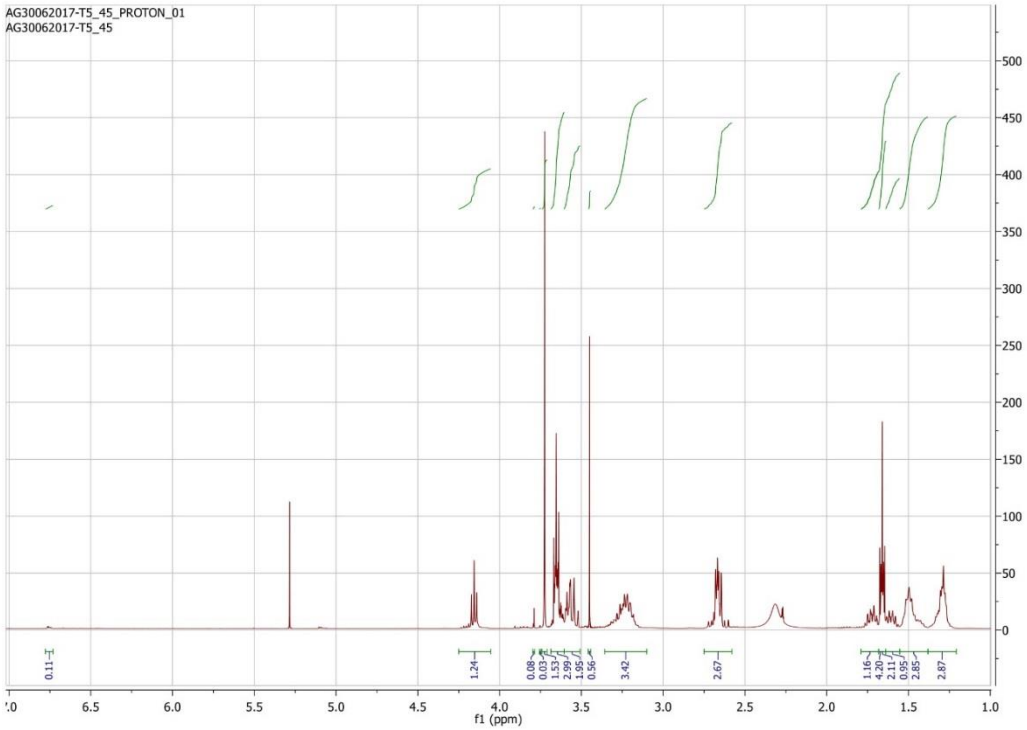


Figure S51. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 345 min of the reaction between HMDA and PBI.

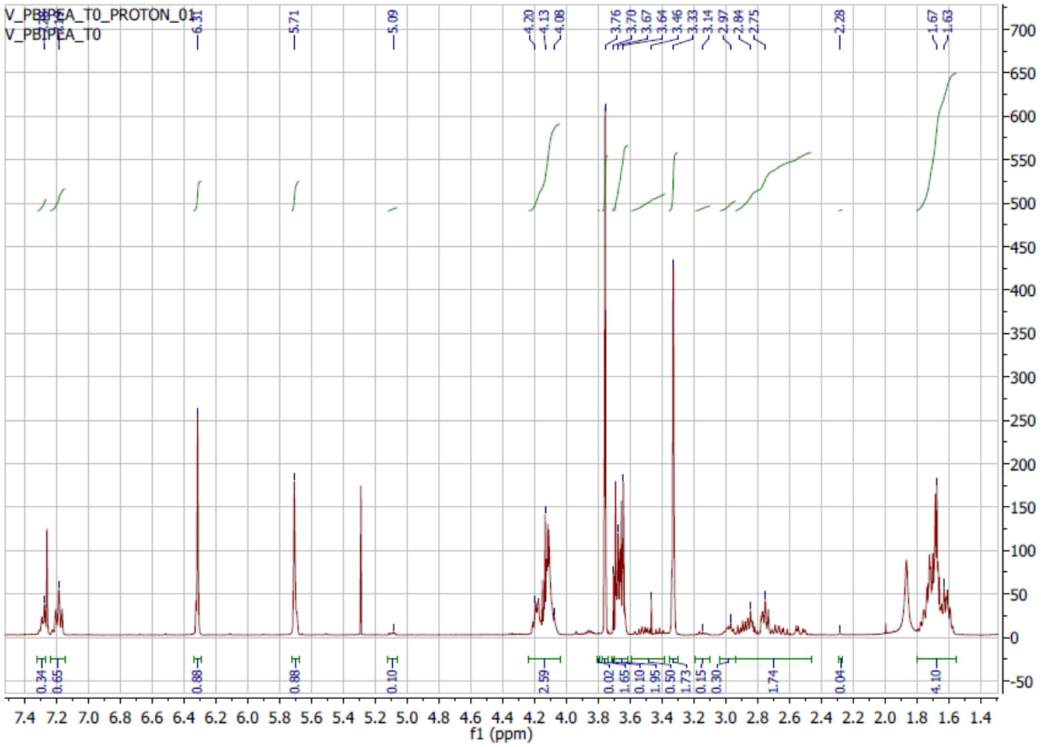


Figure S52. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 3 min of the reaction between PEA and PBI.

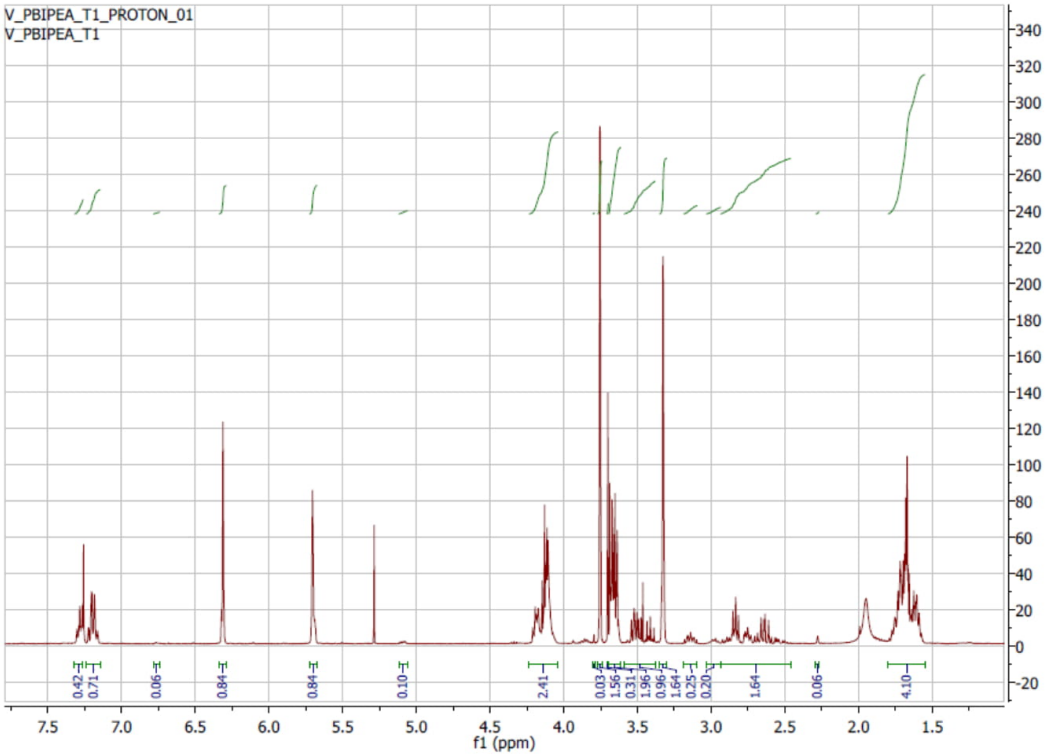


Figure S53. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 60 min of the reaction between PEA and PBI.

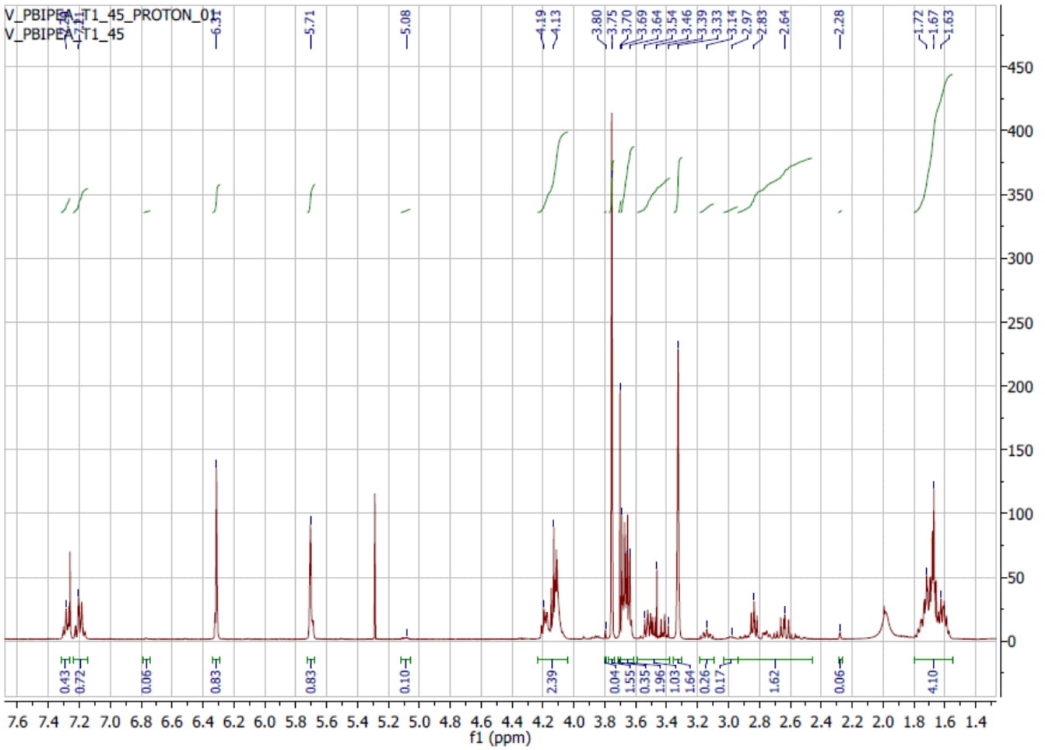


Figure S54. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 105 min of the reaction between PEA and PBI.

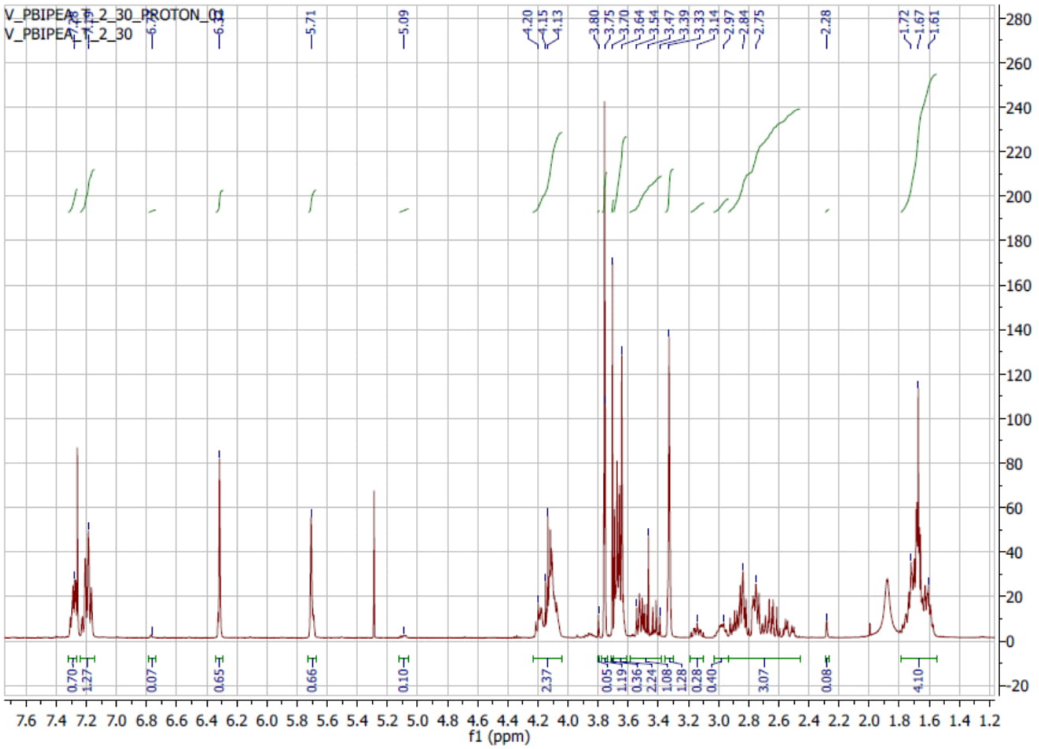


Figure S55. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 150 min of the reaction between PEA and PBI.

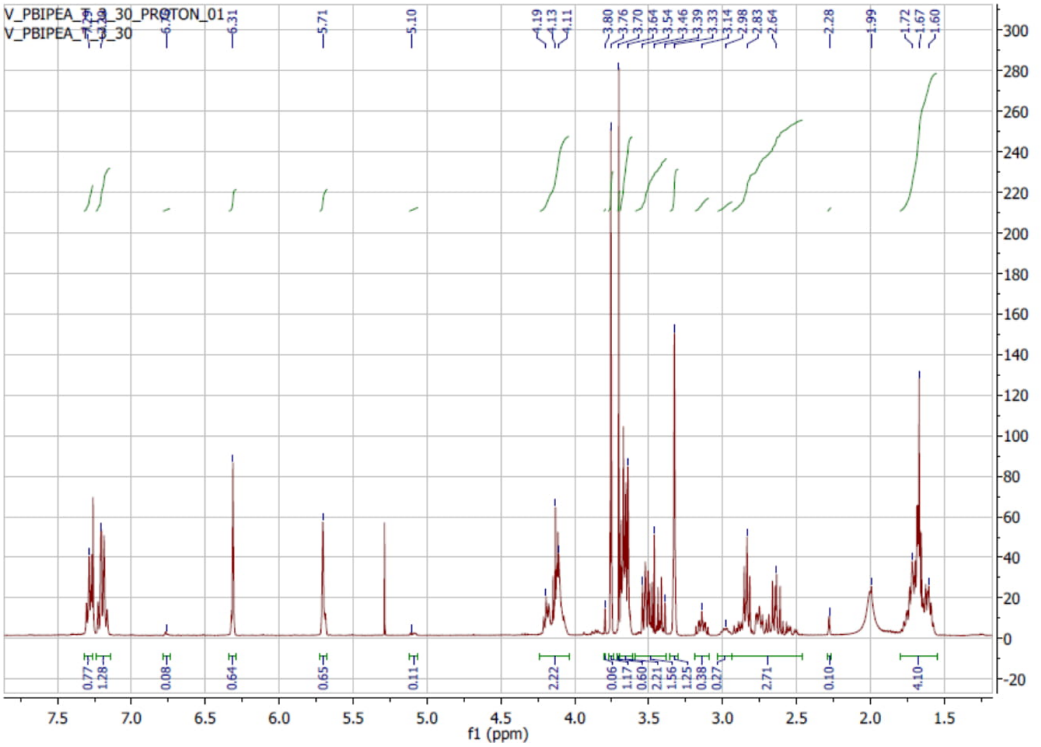


Figure S56. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 210 min of the reaction between PEA and PBI.

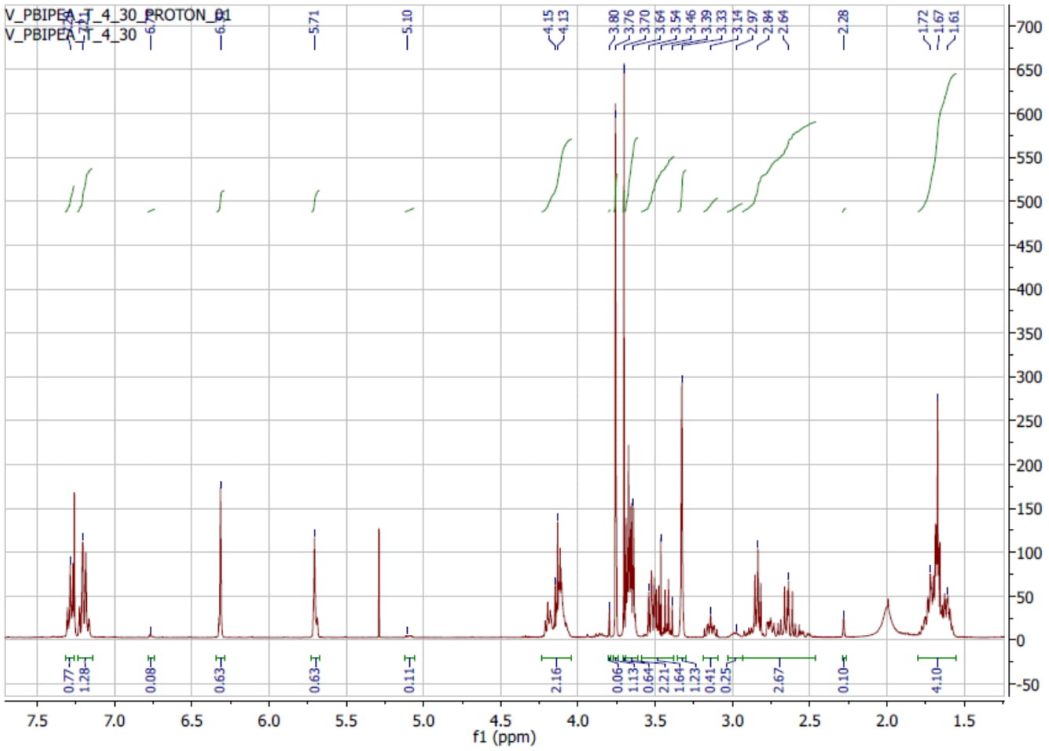


Figure S57. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 270 min of the reaction between PEA and PBI.

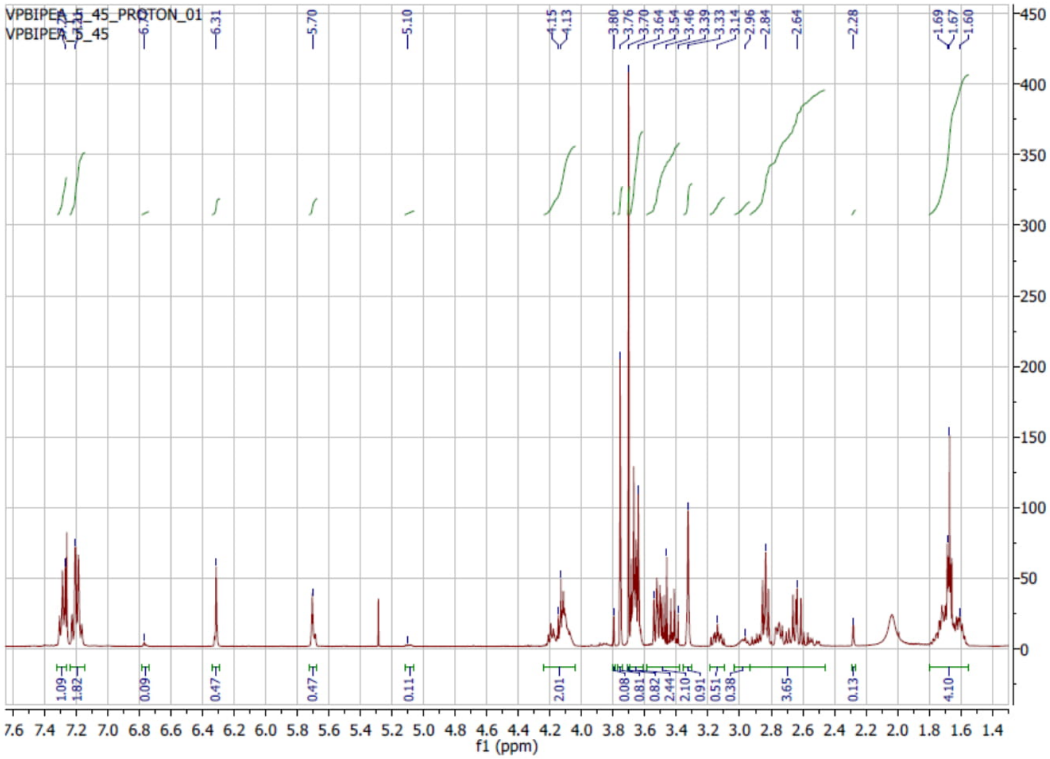


Figure S58. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 345 min of the reaction between PEA and PBI.

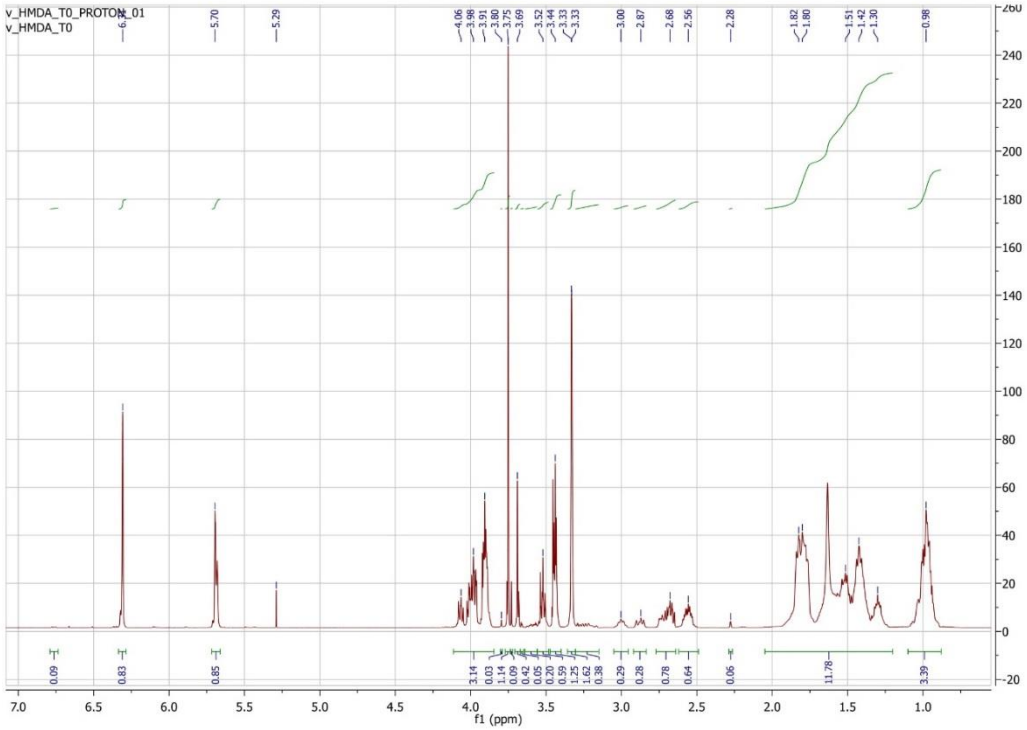


Figure S59. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 3 min of the reaction between HMDA and PCI.

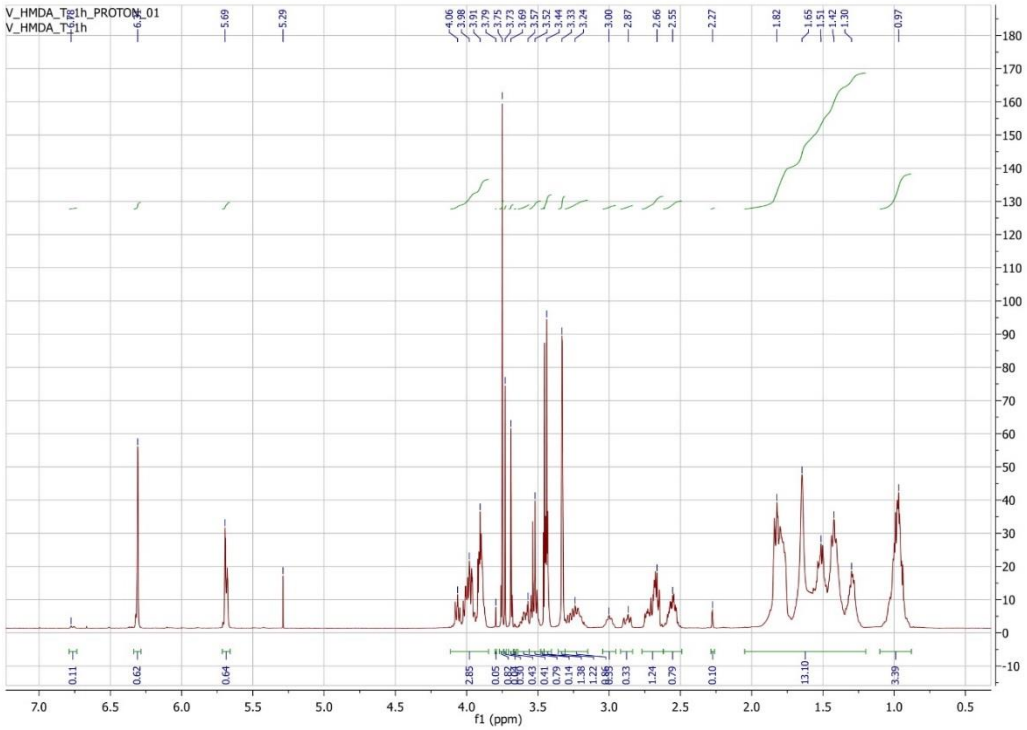


Figure S60. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 60 min of the reaction between HMDA and PCI.

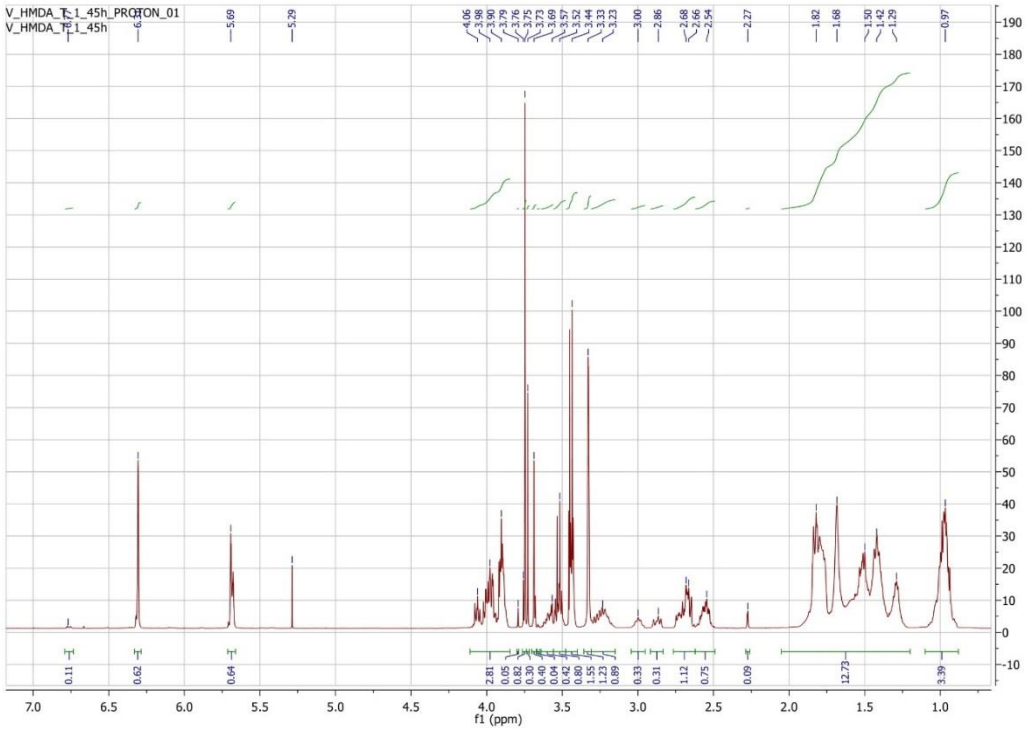


Figure S61. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 105 min of the reaction between HMDA and PCI.

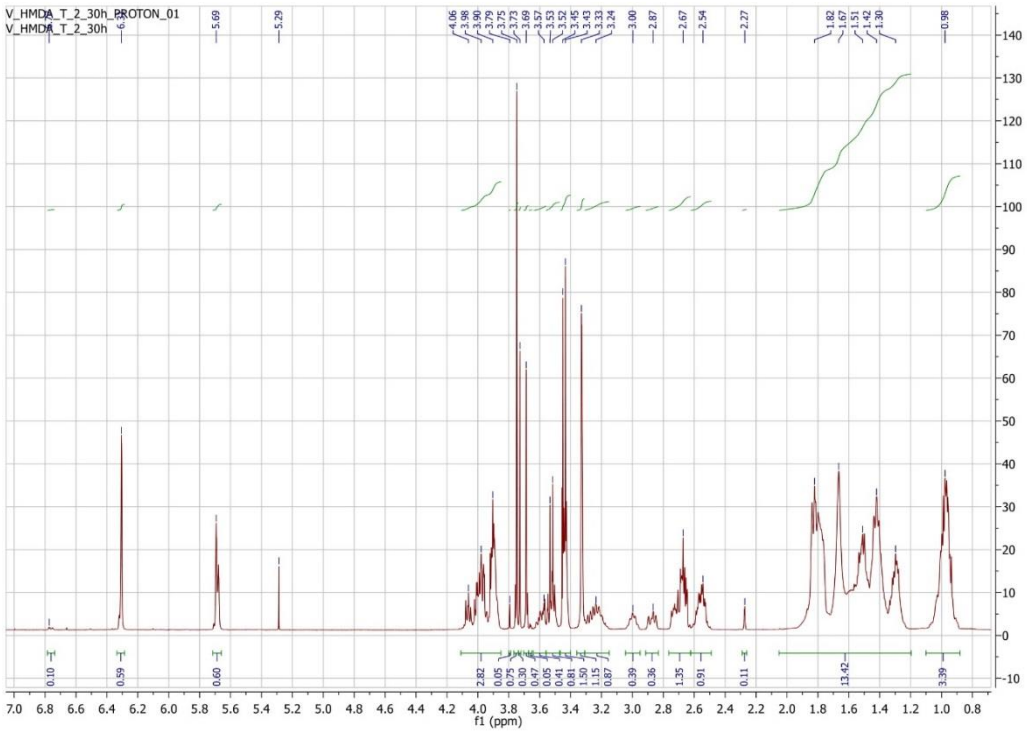


Figure S62. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 150 min of the reaction between HMDA and PCI.

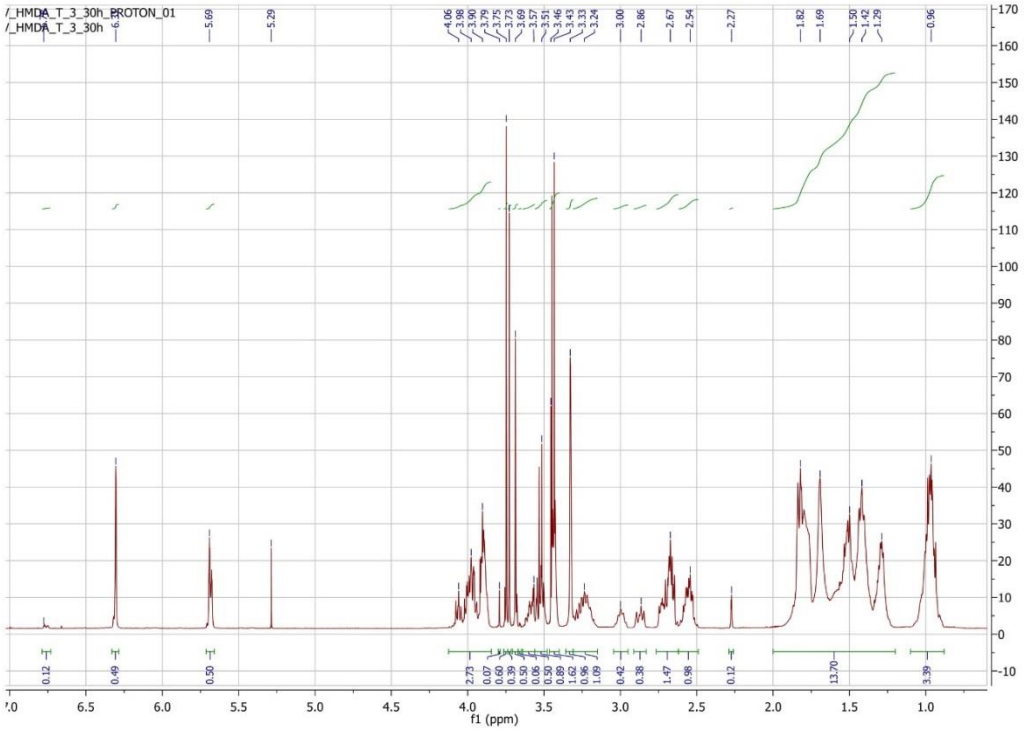


Figure S63. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 210 min of the reaction between HMDA and PCI.

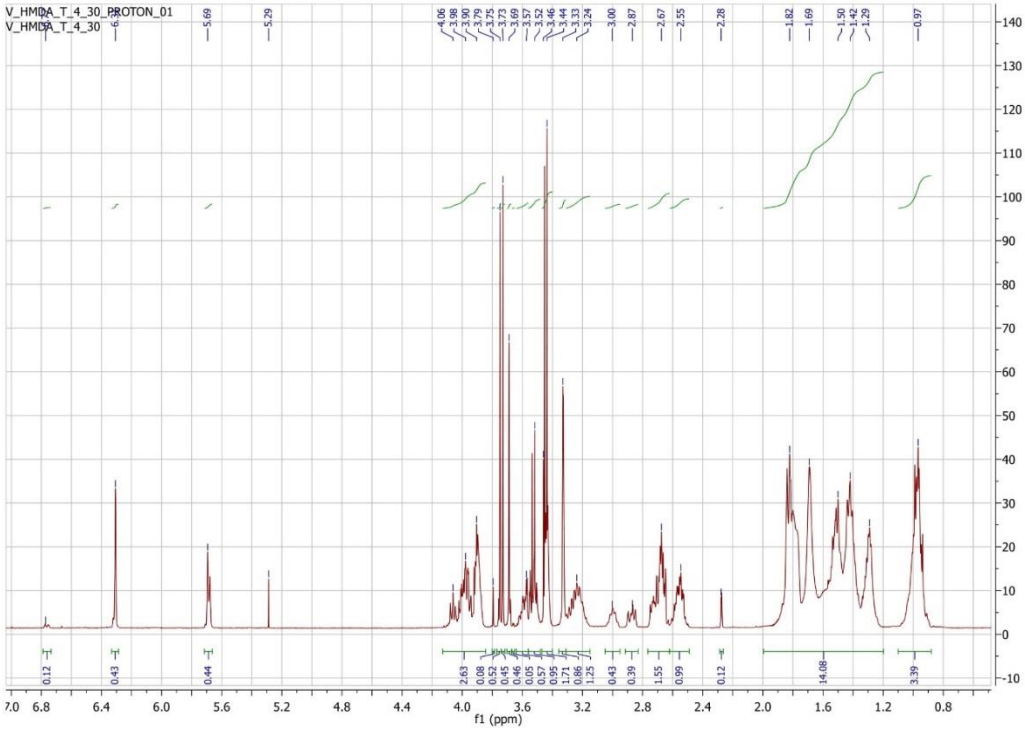


Figure S64. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 270 min of the reaction between HMDA and PCI.

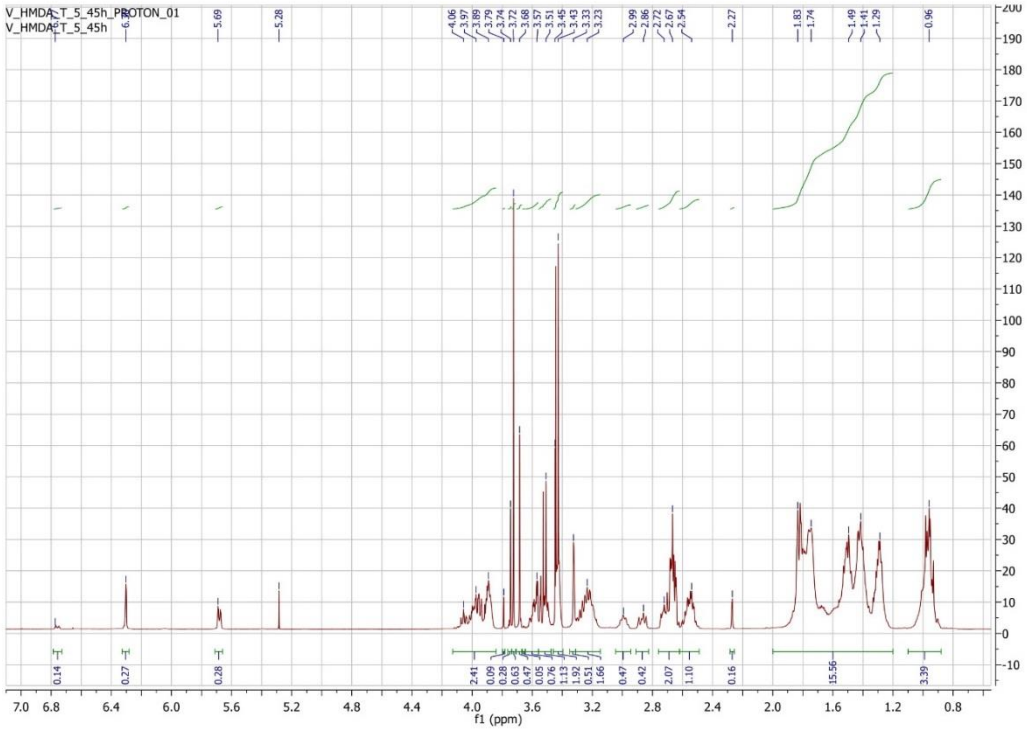


Figure S65. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 345 min of the reaction between HMDA and PCI.

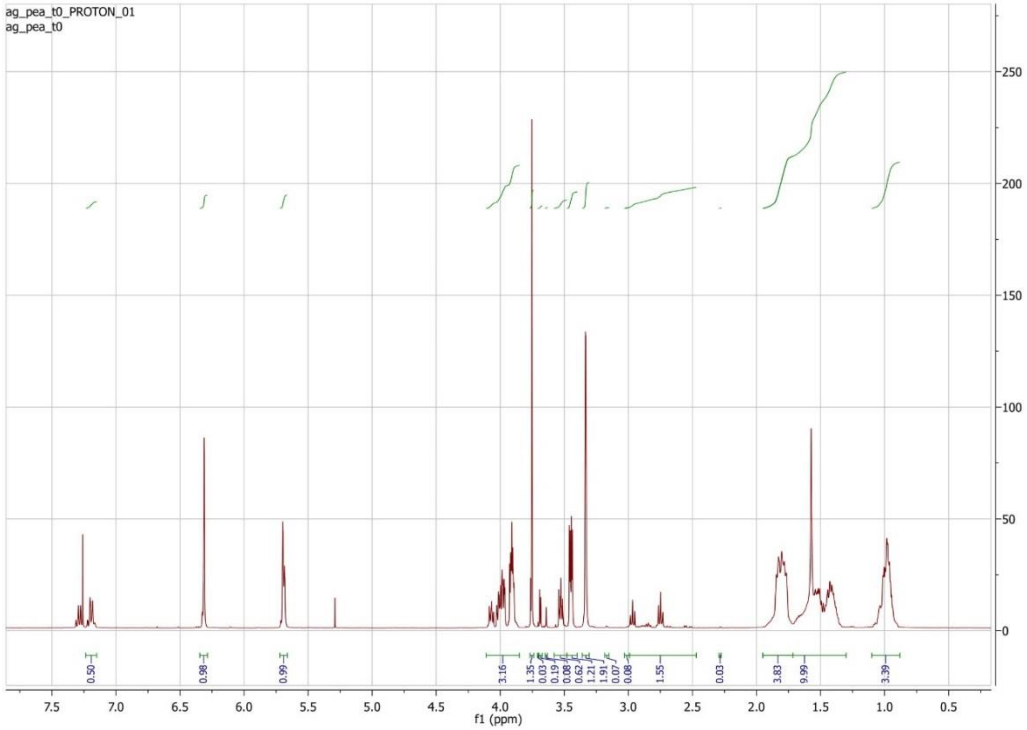


Figure S66. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 3 min of the reaction between PEA and PCI.

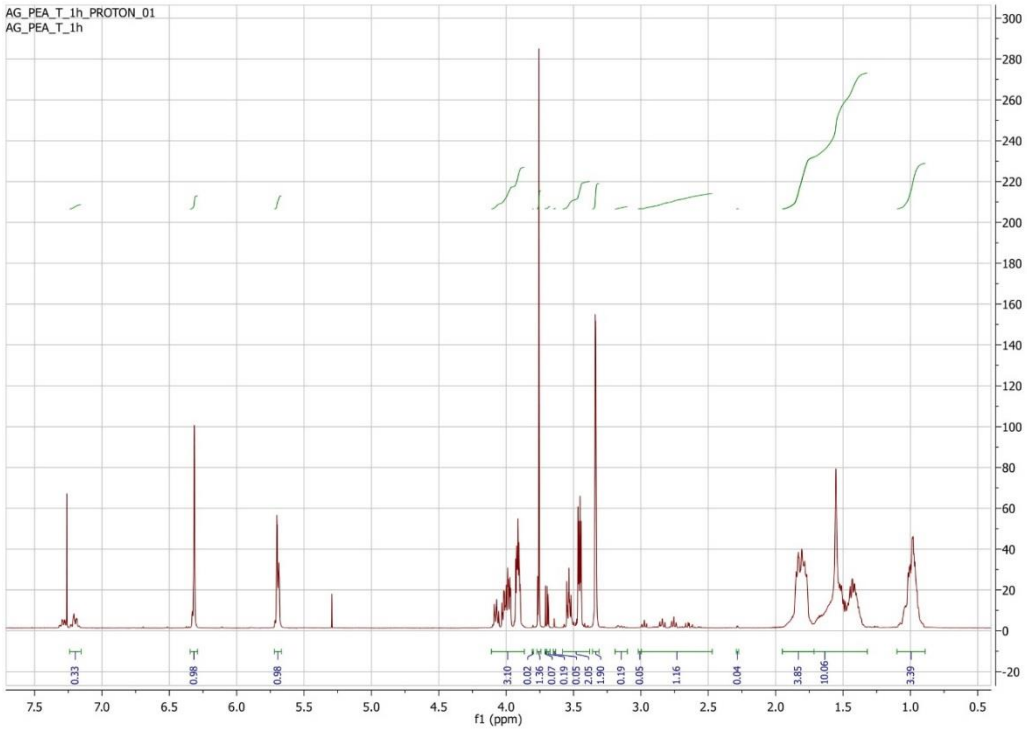


Figure S67. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 60 min of the reaction between PEA and PCI.

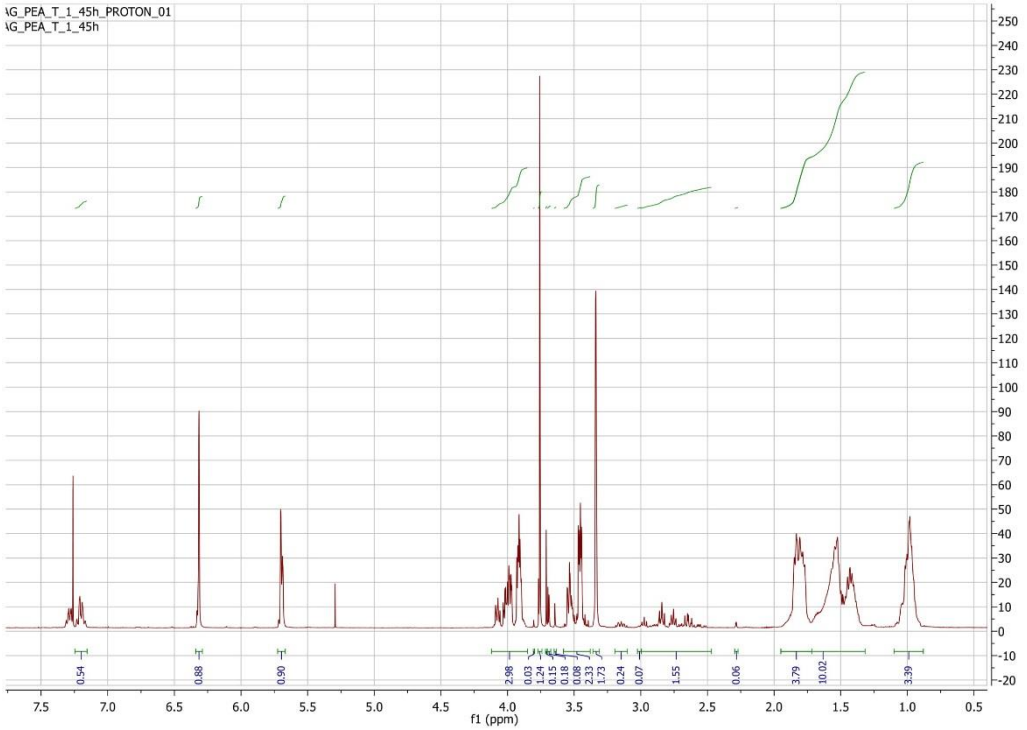


Figure S68. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 105 min of the reaction between PEA and PCI.

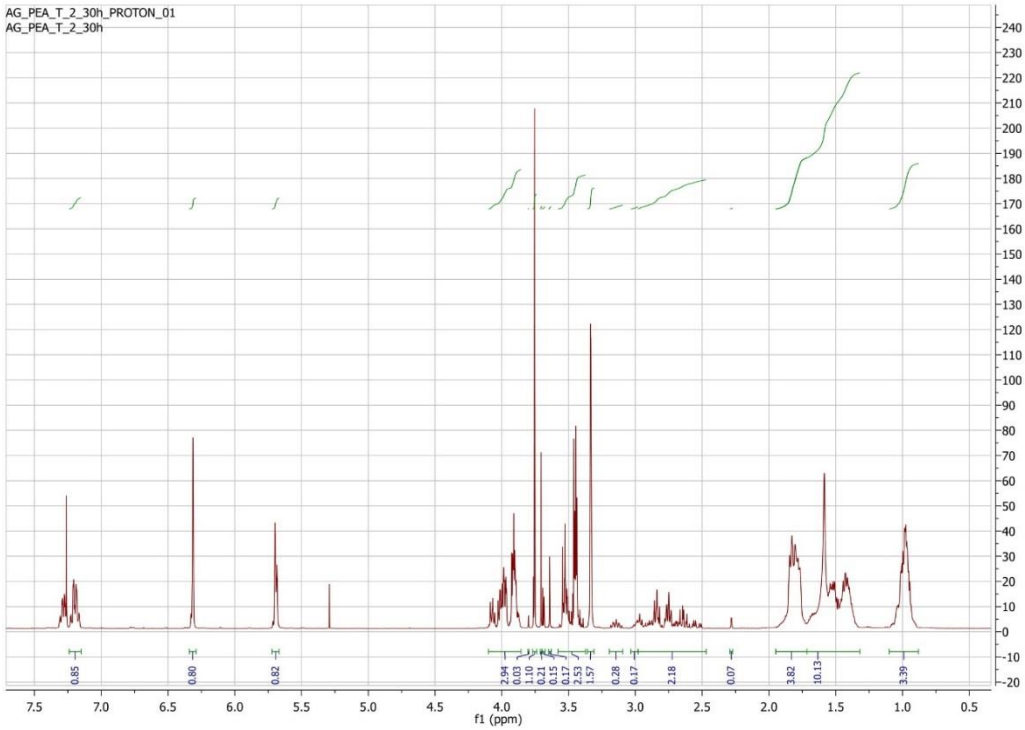


Figure S69. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 150 min of the reaction between PEA and PCI.

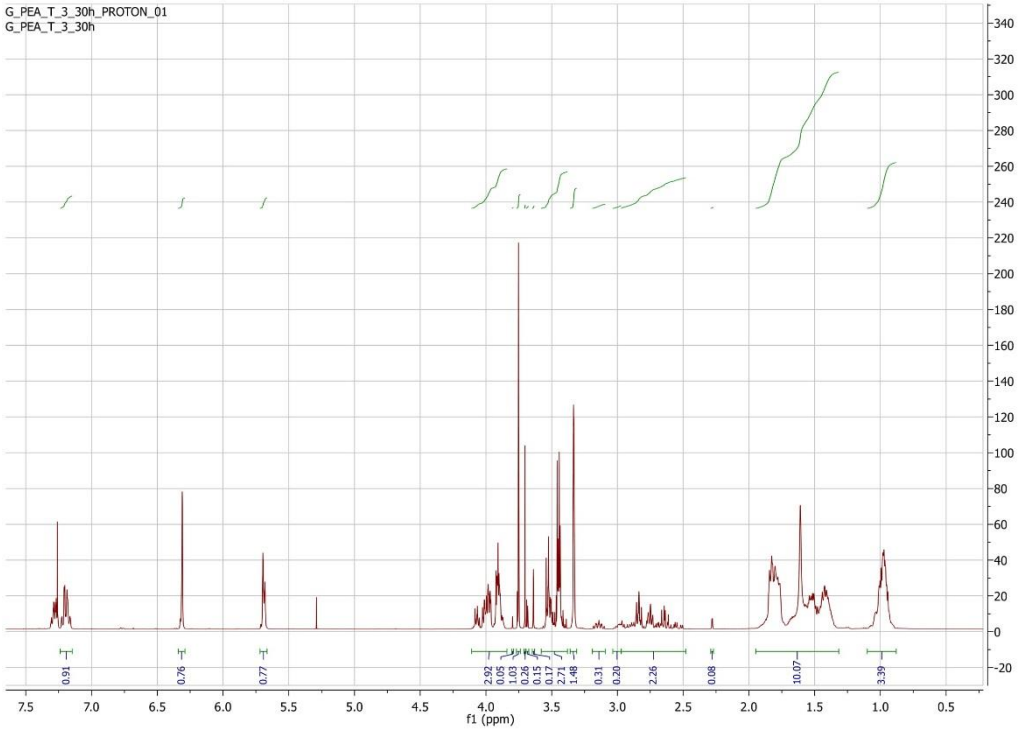


Figure S70. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 210 min of the reaction between PEA and PCI.

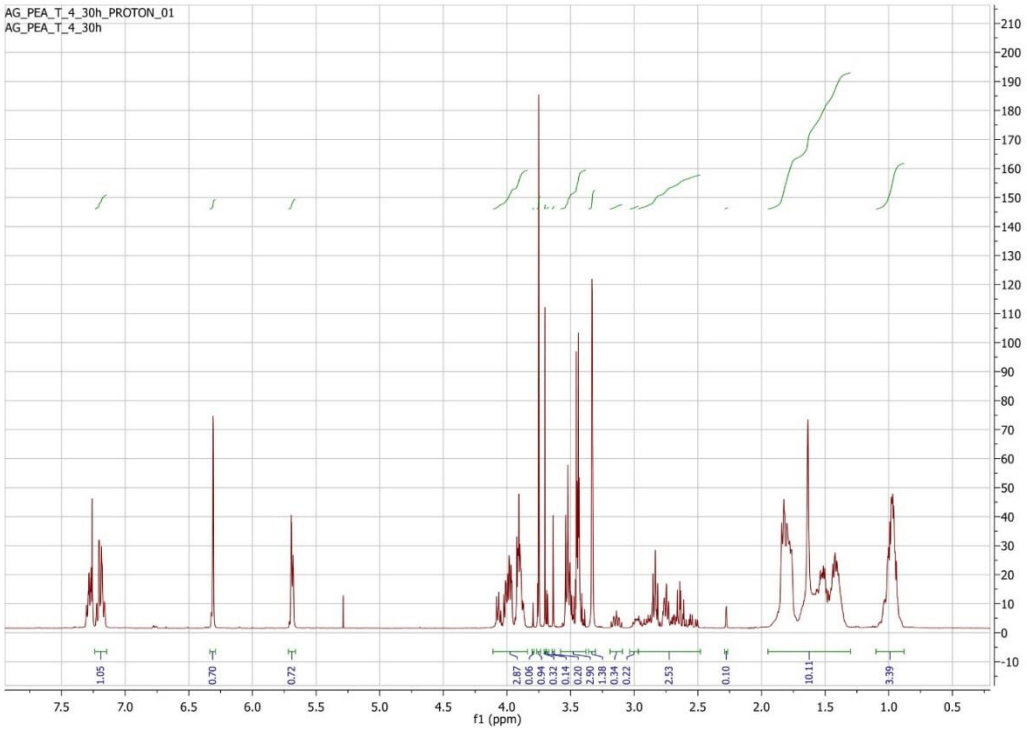


Figure S71. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 270 min of the reaction between PEA and PCI.

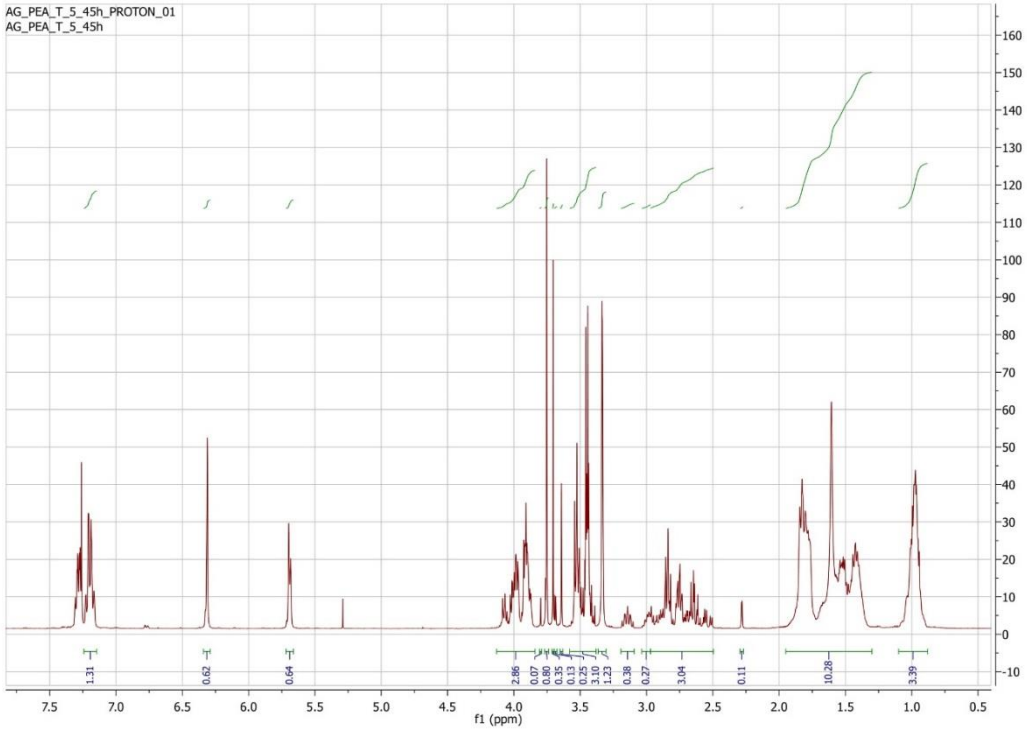


Figure S72. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 345 min of the reaction between PEA and PCI.

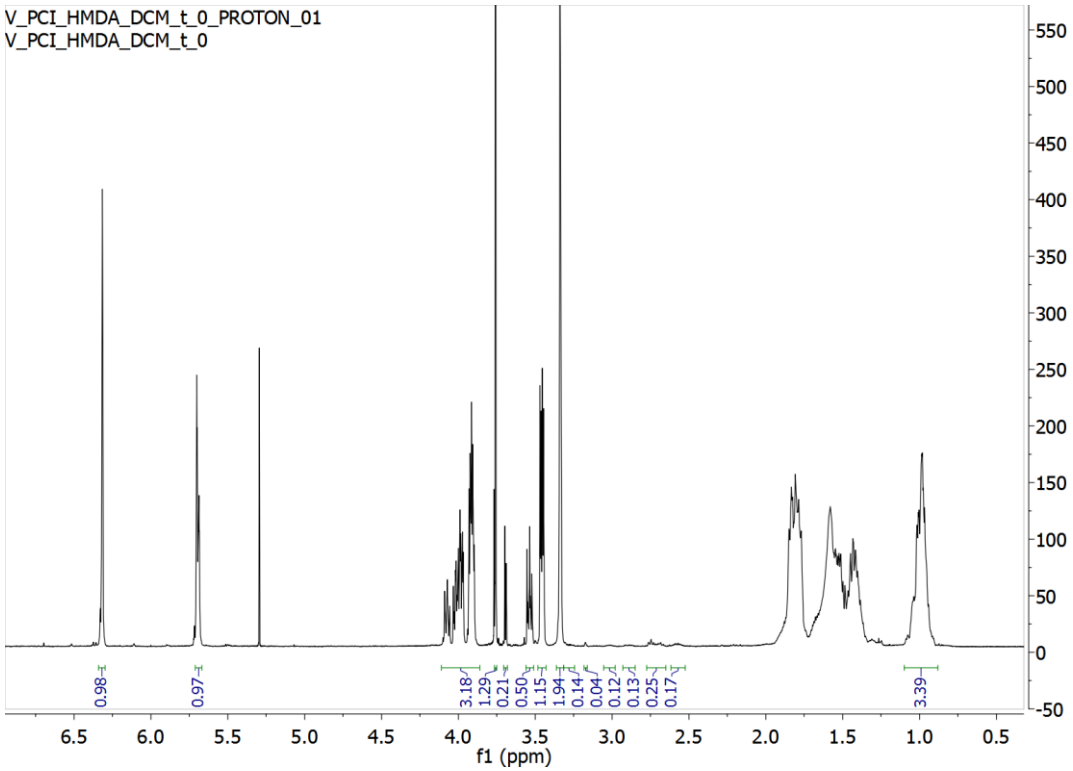


Figure S73. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 3 min of the reaction between HMDA and PCI in DCM.

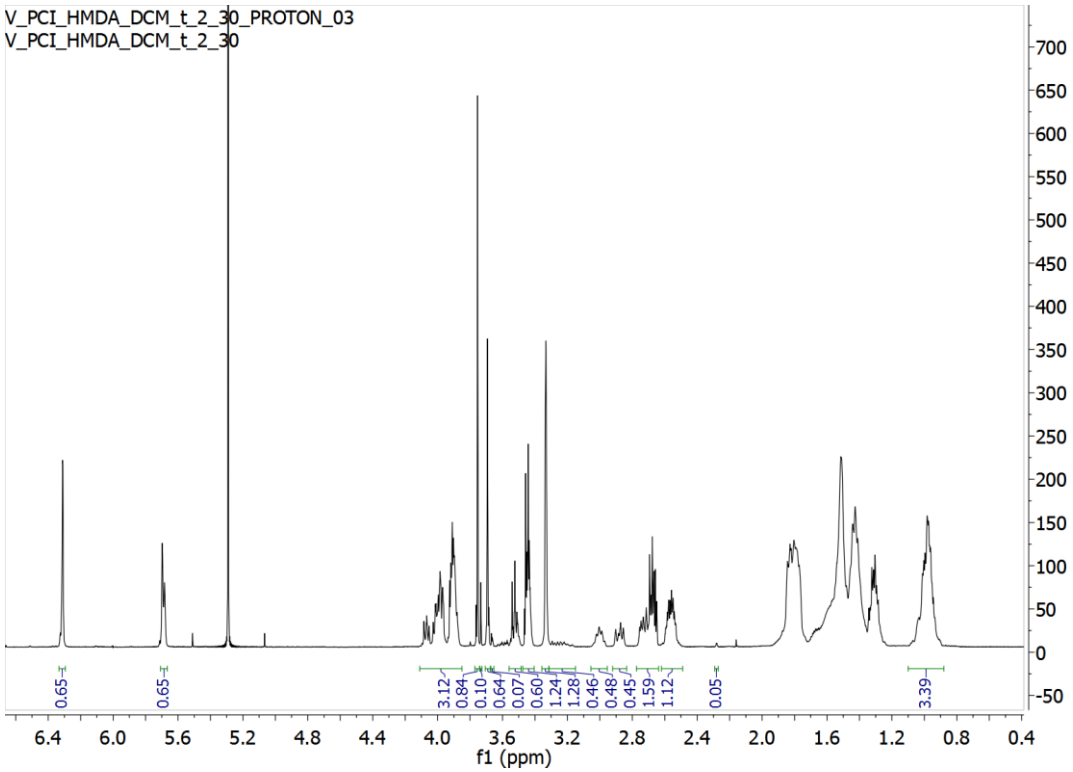


Figure S74. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 150 min of the reaction between HMDA and PCI in DCM.

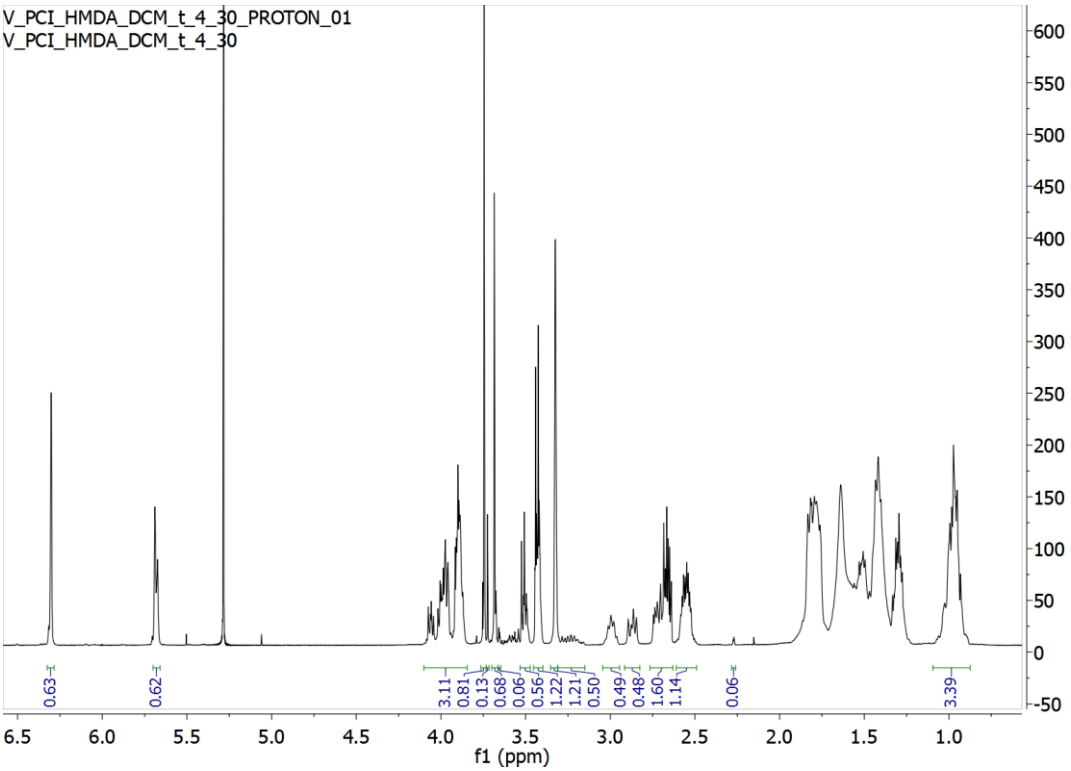


Figure S75. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 270 min of the reaction between HMDA and PCI in DCM.

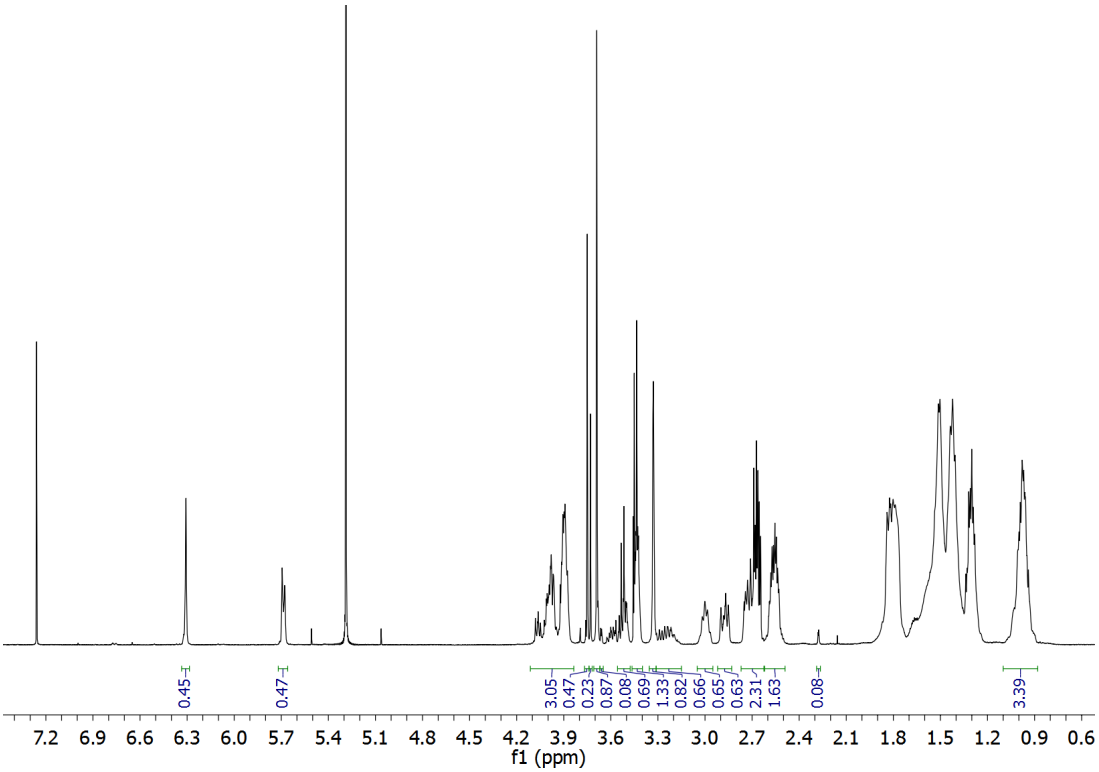


Figure S76. ^{1}H-NMR spectrum in $CDCl_3$ of the crude reaction mixture at 465 min of the reaction between HMDA and PCI in DCM.

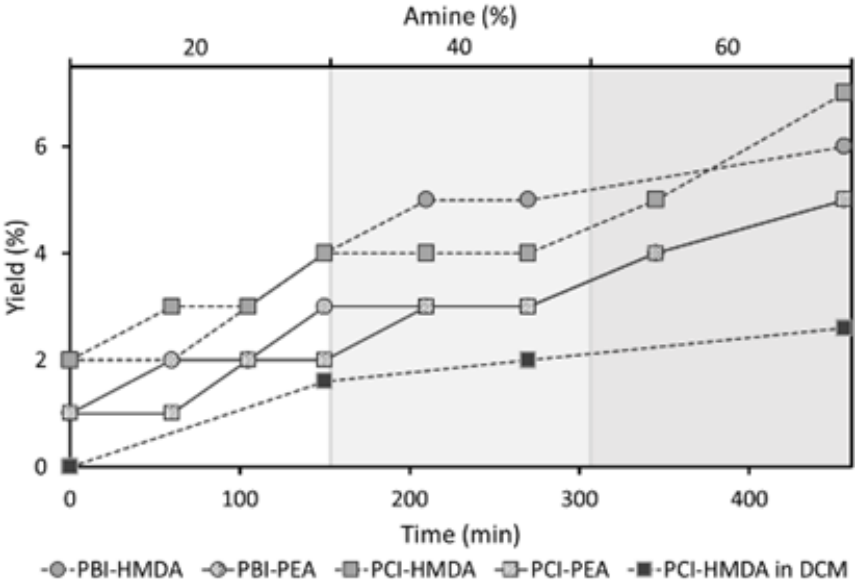


Figure S77. Double bond isomerization caused by the addition of PEA or HMDA to PCI and PBI. PCI: squares, PBI: circles. PEA: pattern fill and solid conjunction line, HMDA: grey fill and dashed conjunction line. The percentage of amine present is represented by a gradient of grey coloured blocks