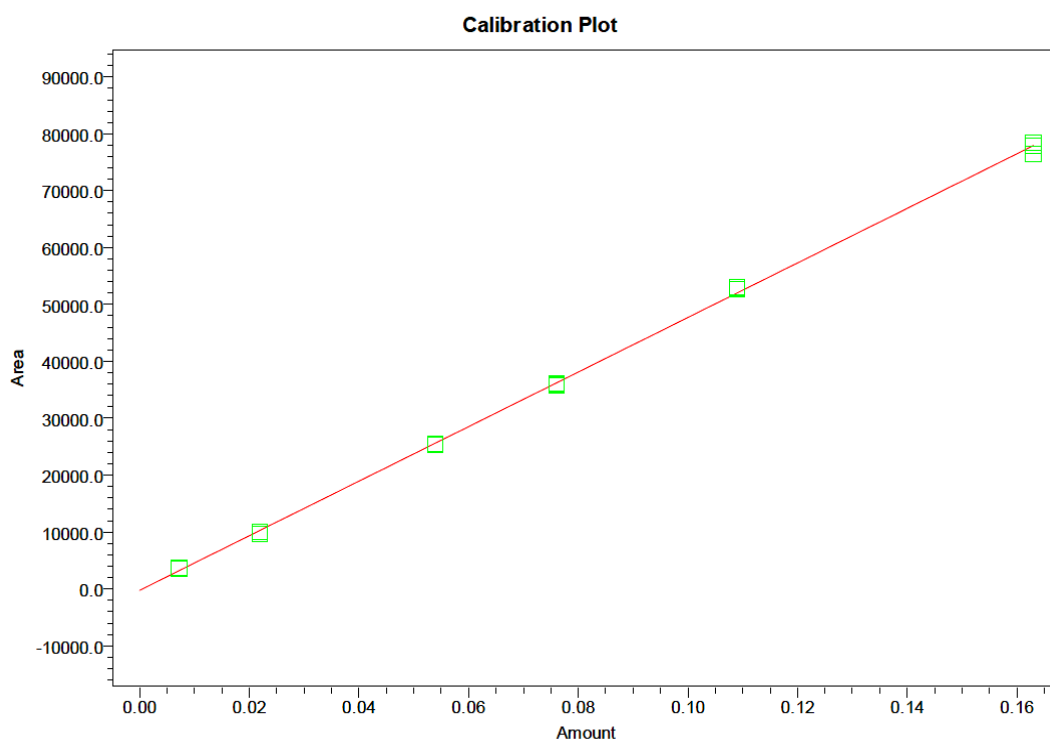


**Direct Ring-Opening of Lactide with Amines: Application to the  
Organo-catalyzed Preparation of Amide End-capped PLA and to the  
Removal of Residual Lactide from PLA Samples**

**Aurélie Alba, Olivier Thillaye du Boullay, Blanca Martin-Vaca, and Didier Bourissou**

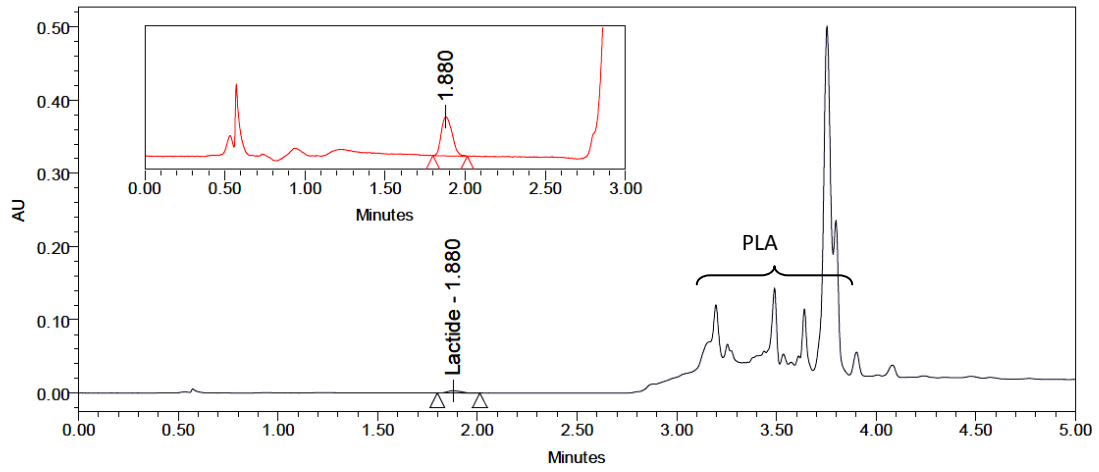
**Supporting Information**



Peak: Lactide

	Name	Level	X Value	Response	Calc. Value	% Deviation	Manual	Ignore
1	Lactide		0.007200	3592.235192	0.008022	11.412	No	No
2	Lactide		0.007200	3726.890829	0.008302	15.312	No	No
3	Lactide		0.007200	3625.995601	0.008092	12.390	No	No
4	Lactide		0.022000	9699.338751	0.020757	-5.651	No	No
5	Lactide		0.022000	10024.467088	0.021435	-2.570	No	No
6	Lactide		0.022000	9671.656553	0.020699	-5.914	No	No
7	Lactide		0.054000	25559.164730	0.053829	-0.317	No	No
8	Lactide		0.054000	25311.661100	0.053313	-1.273	No	No
9	Lactide		0.054000	25305.533605	0.053300	-1.296	No	No
10	Lactide		0.076000	36155.158356	0.075924	-0.100	No	No
11	Lactide		0.076000	36010.160182	0.075622	-0.497	No	No
12	Lactide		0.076000	35716.606653	0.075010	-1.303	No	No
13	Lactide		0.109000	52944.279895	0.110934	1.775	No	No
14	Lactide		0.109000	52981.988656	0.111013	1.847	No	No
15	Lactide		0.109000	52745.373564	0.110520	1.394	No	No
16	Lactide		0.163000	78399.513246	0.164015	0.623	No	No
17	Lactide		0.163000	76466.904377	0.159985	-1.849	No	No
18	Lactide		0.163000	77830.246978	0.162828	-0.105	No	No

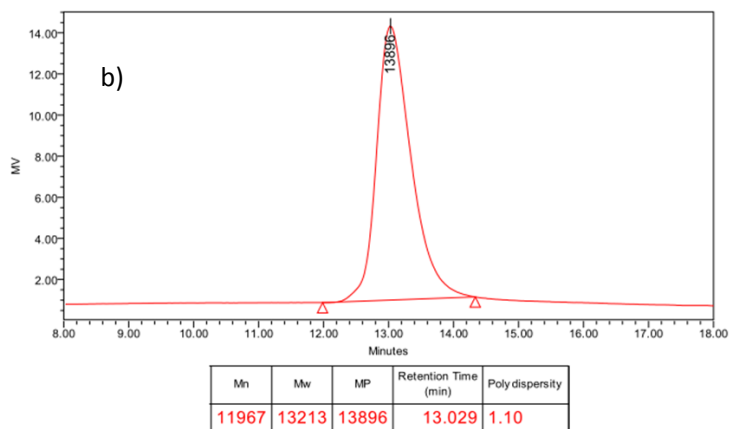
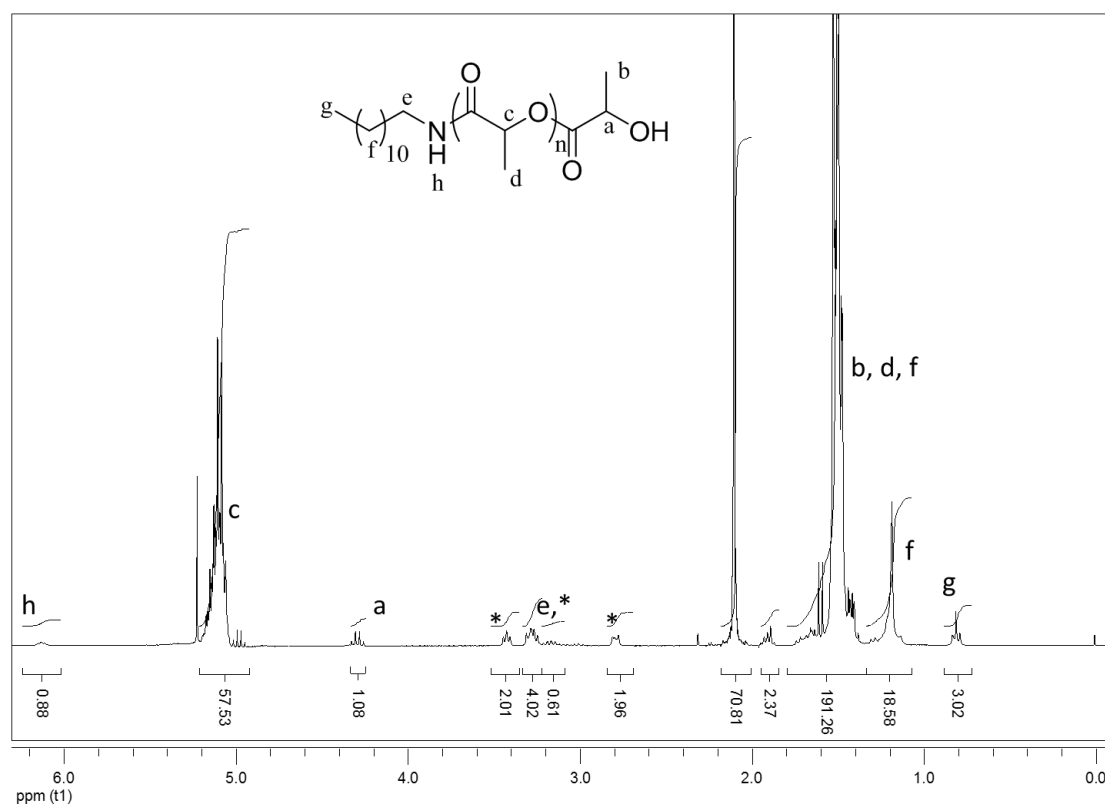
**Figure S1.** Calibration plot for the UPLC titration of lactide content in PLA samples



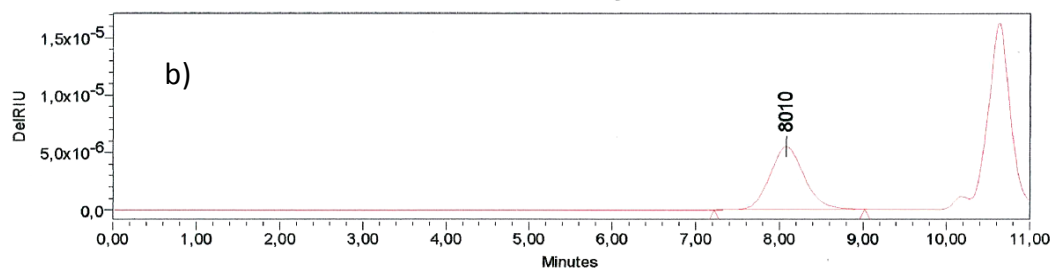
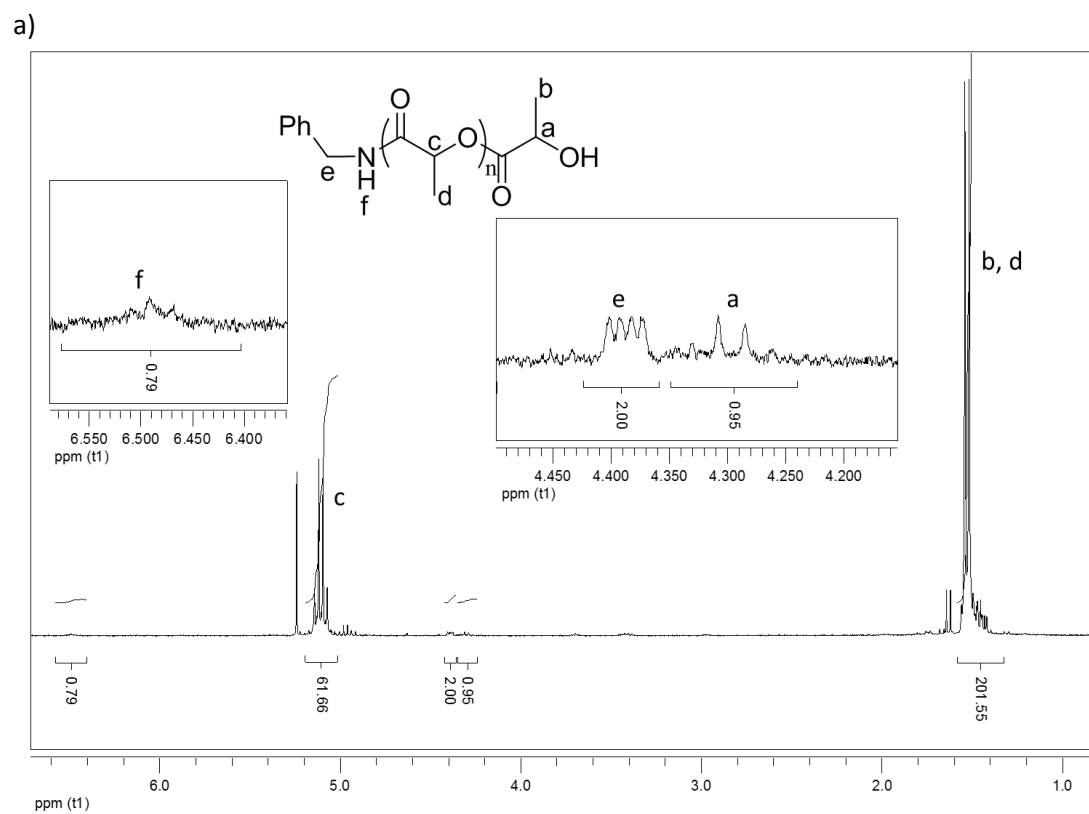
	Echantillon	Injection Volume (ul)	Injection	Nom	RT	Aire	Concentration	Units
1	BM1 106	1.00	1	Lactide	1.880	14098	0.02993	mg/mL
2	BM1 106	1.00	2	Lactide	1.873	13669	0.02903	mg/mL
9	BM1 106	1.00	1	Lactide	1.912	14135	0.03001	mg/mL

**Figure S2.** Titration of lactide content (0.46%) by UPLC in a PLA sample. Picks appearing between 2.8 and 4.3 minutes correspond to the PLA chains.

a)



**Figure S3.** a) <sup>1</sup>H NMR spectra of dodecyl amine end-capped PLA formed after ROP of 30 equiv. of lactide (\*DBU). b) SEC trace of dodecyl amine end-capped PLA formed after ROP of 60 equiv. of lactide.

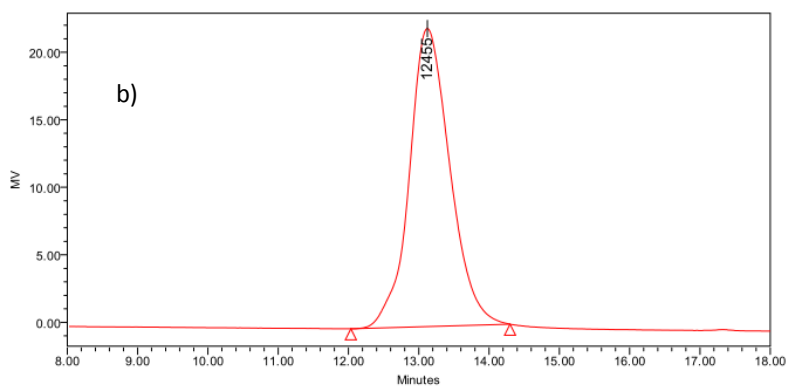
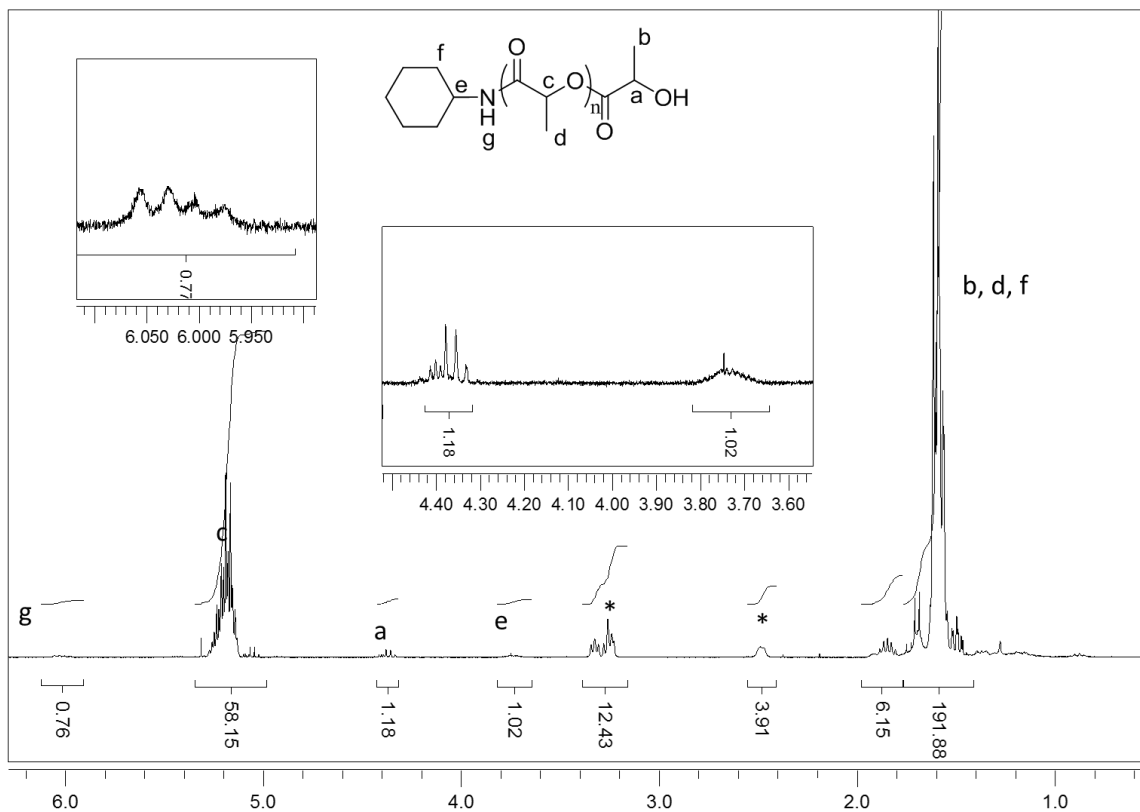


GPC Sample Results

	Retention Time	Mn	Mw	MP	Polydispersity
1	8,078	7263	8114	8010	1,12

**Figure S4.** a)  $^1\text{H}$  NMR spectra of benzyl amine end-capped PLA formed after ROP of 30 equiv. of lactide. b) SEC trace of benzyl amine end-capped PLA formed after ROP of 30 equiv. of lactide.

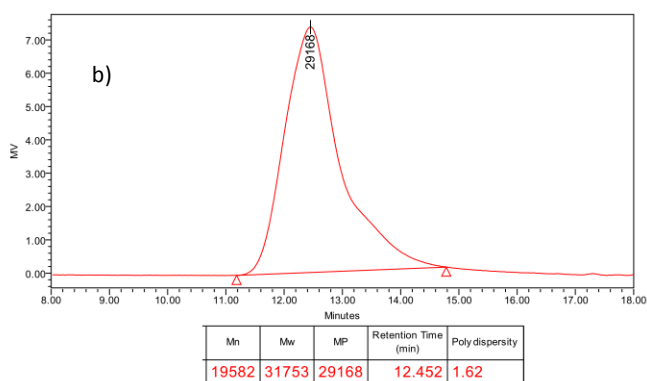
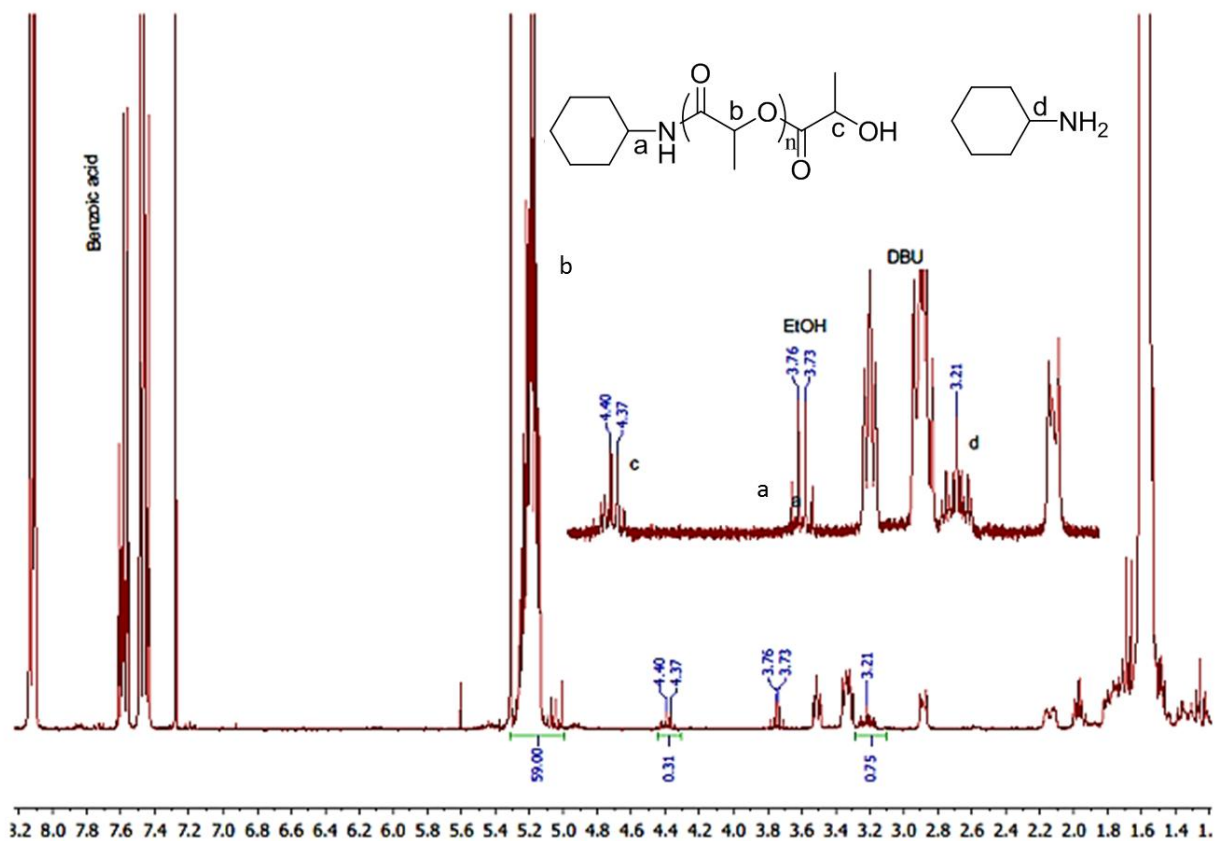
a)



Mn	Mw	MP	Retention Time (min)	Poly dispersity
11280	12555	12455	13.123	1.11

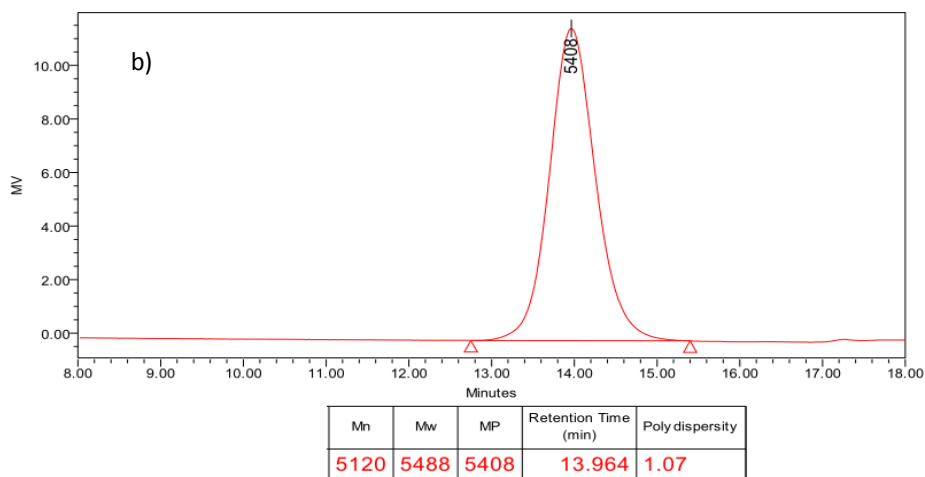
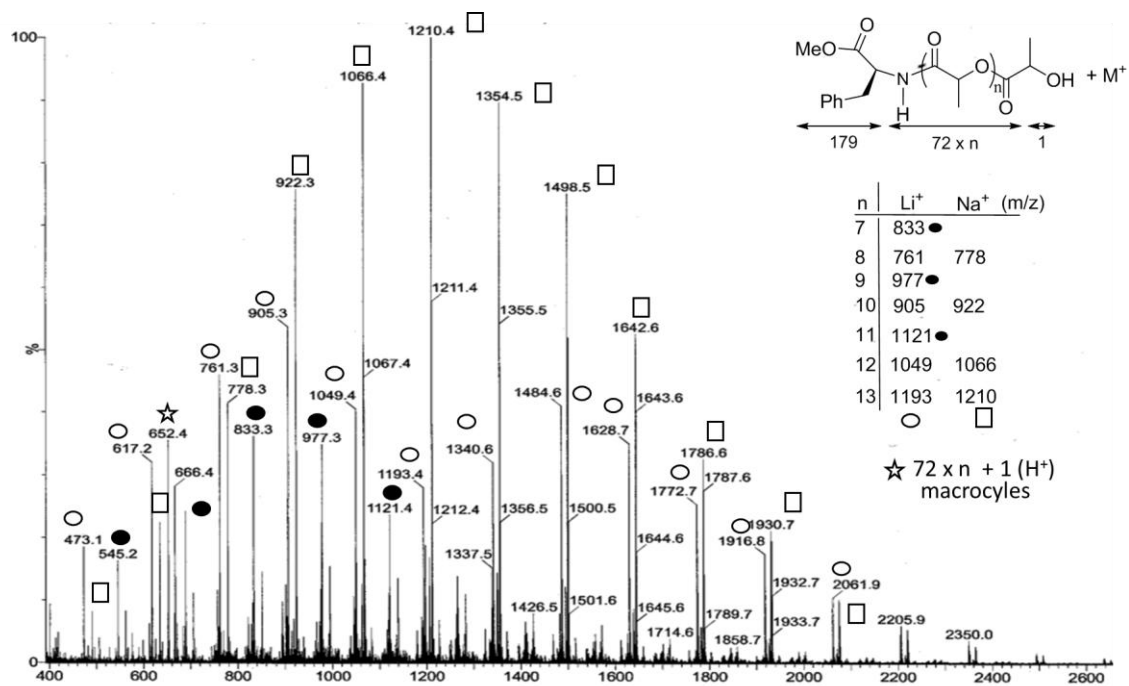
**Figure S5.** a)  $^1\text{H}$  NMR spectra of cyclohexyl amine end-capped PLA formed after ROP of 30 equiv. of lactide (\*DBU). b) SEC trace of cyclohexyl amine end-capped PLA formed after ROP of 50 equiv. of lactide.

a)



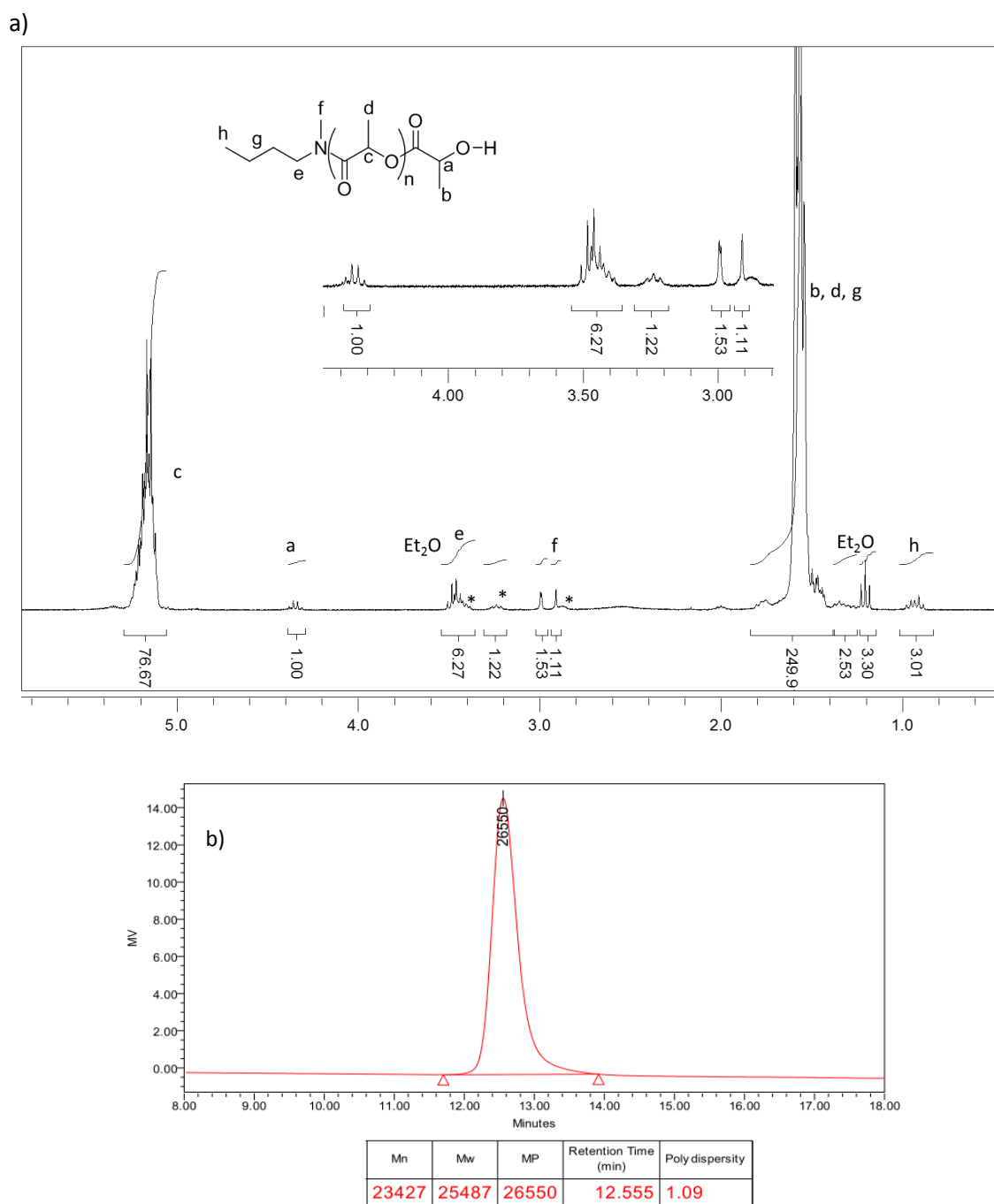
**Figure S6.**  $^1\text{H}$  NMR spectra of the reaction crude after ROP of 30 equiv. of lactide with simultaneous addition of DBU and cyclohexyl amine and catalyst deactivation by addition of benzoic acid. b) SEC trace of this reaction crude.

a)

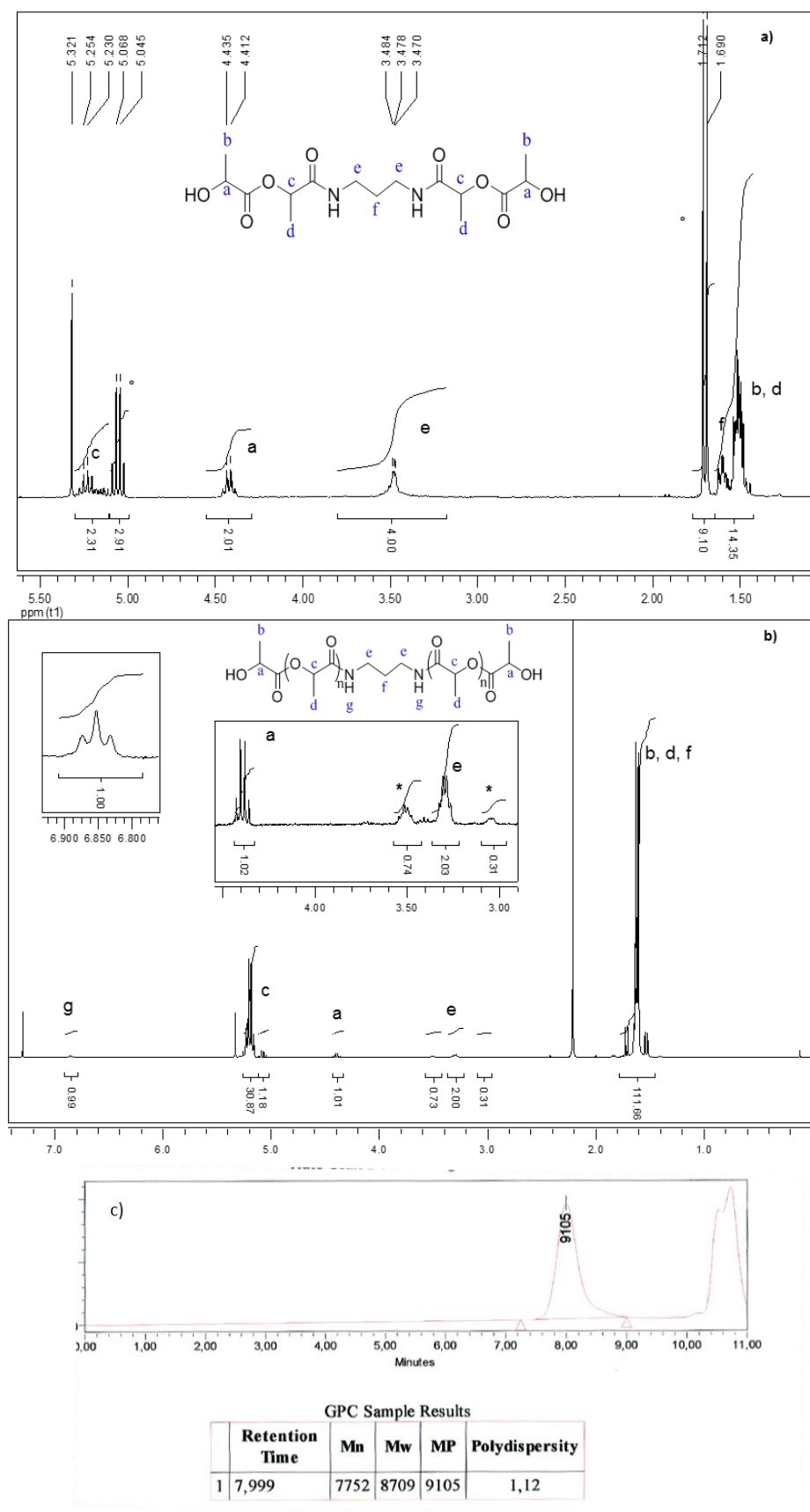


**Figure S7.** a) ESI-MS spectra of a methyl ester phenyl alanine end-capped PLA (DP = 10). b) SEC trace of a methyl ester phenyl alanine end-capped PLA (DP = 25)

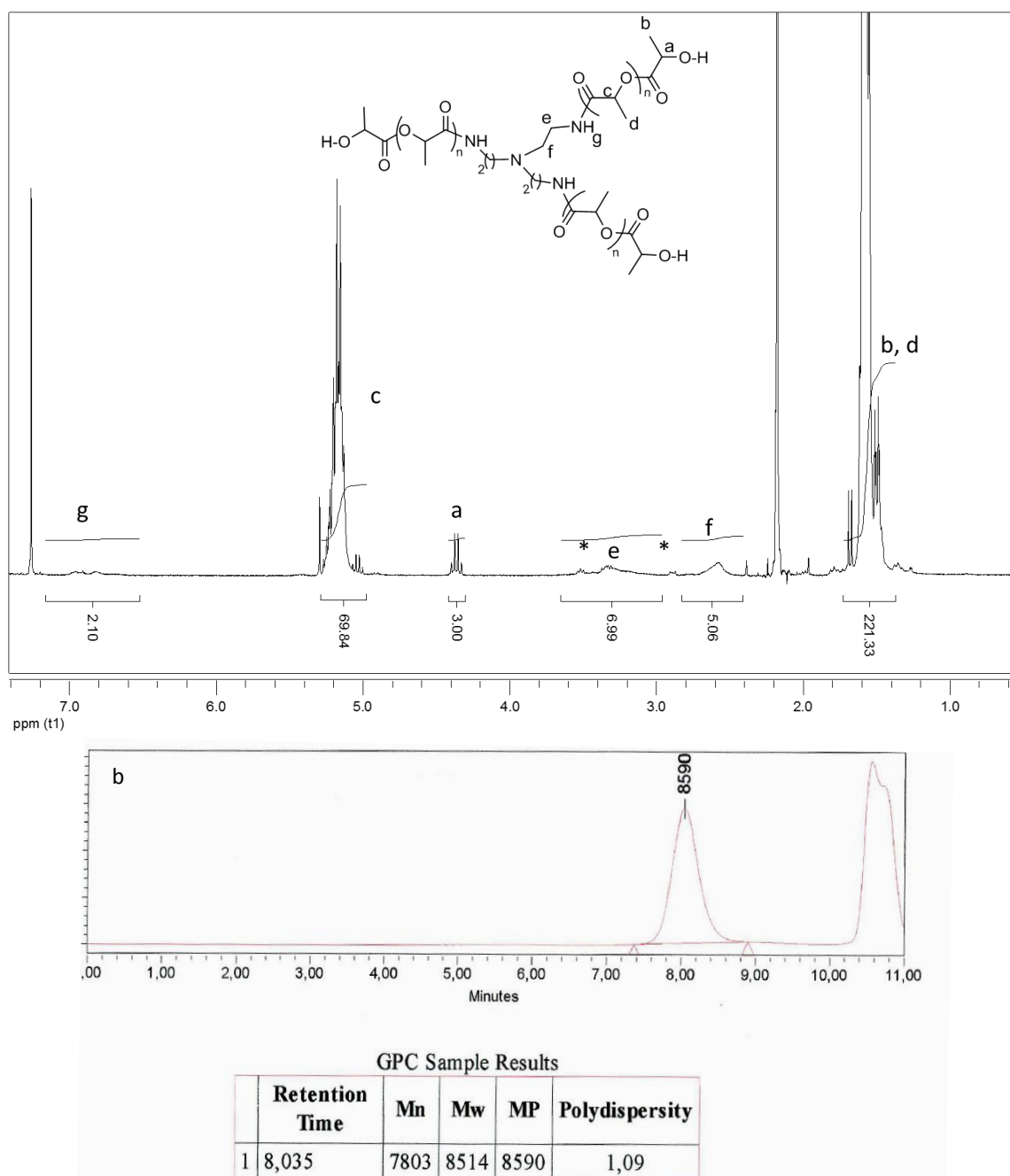




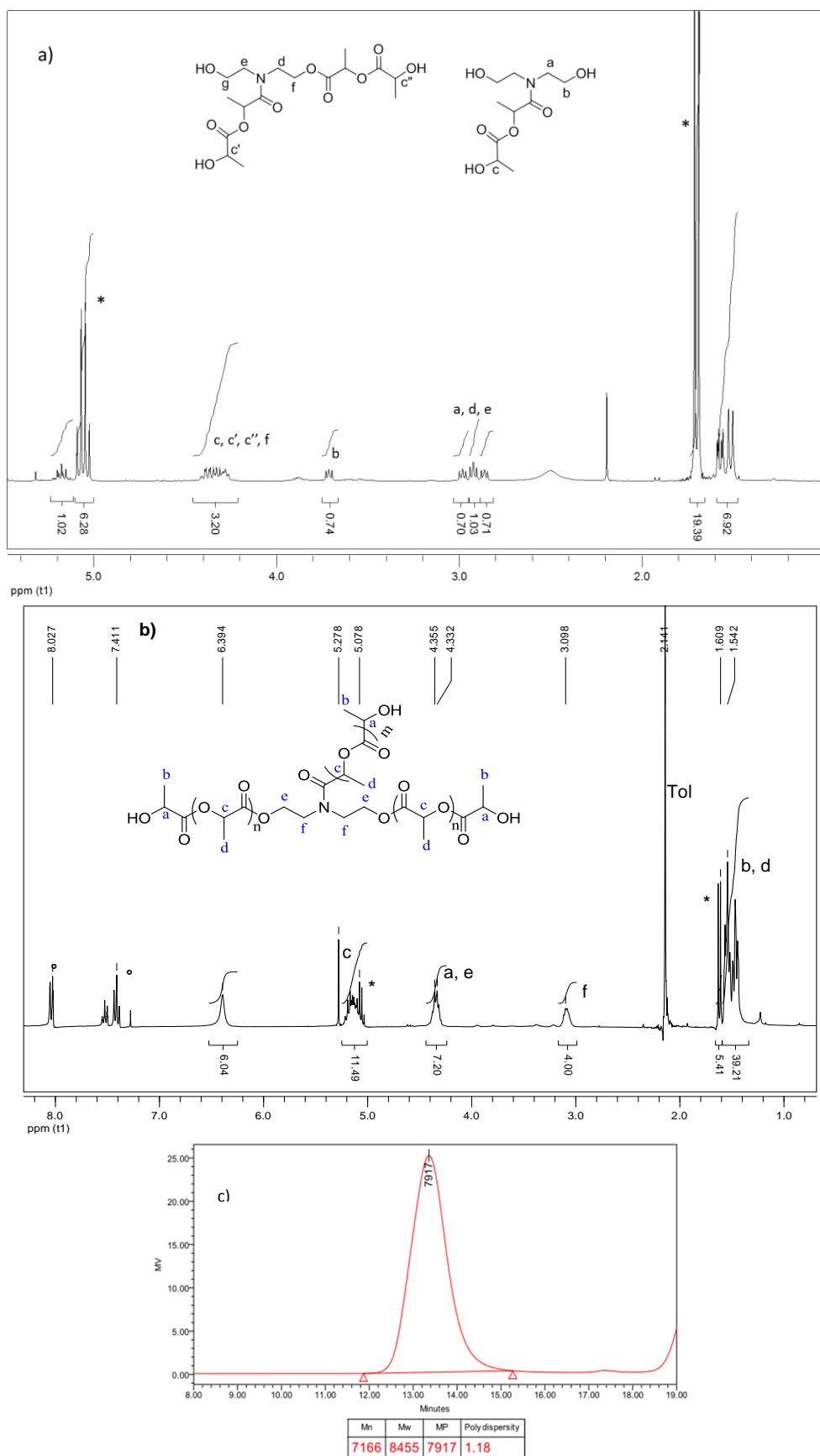
**Figure S8.** a) <sup>1</sup>H NMR spectrum of a *N*-methyl butylamine end-capped PLA (DP = 30). b) SEC trace of a *N*-methyl butylamine end-capped PLA (DP = 100).



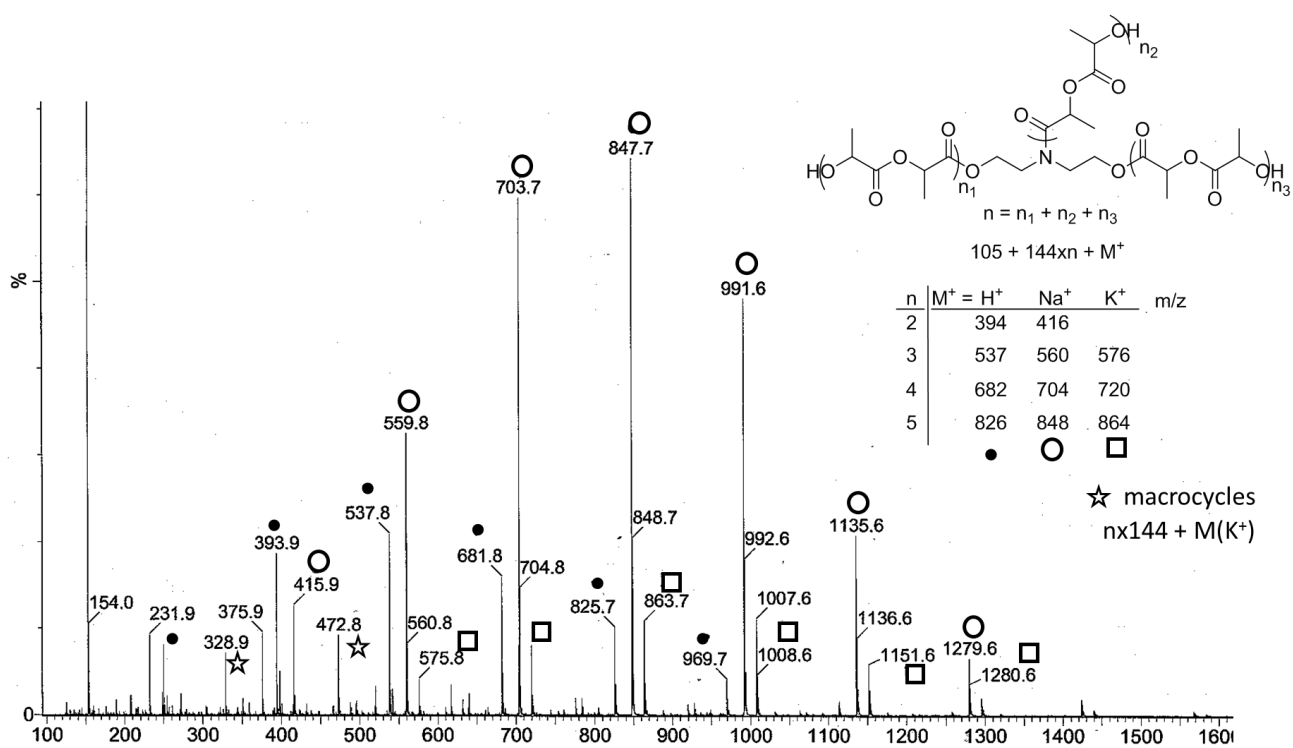
**Figure S9.** <sup>1</sup>H NMR spectra of: a) the adduct formed by reaction of propanediamine with 3.5 equiv of lactide, and b) telechelic PLA formed after ROP of 30 equiv. of lactide. ° unreacted lactide, \*DBU. c) SEC trace of a telechelic PLA formed after ROP of 30 equiv. of lactide with propanediamine



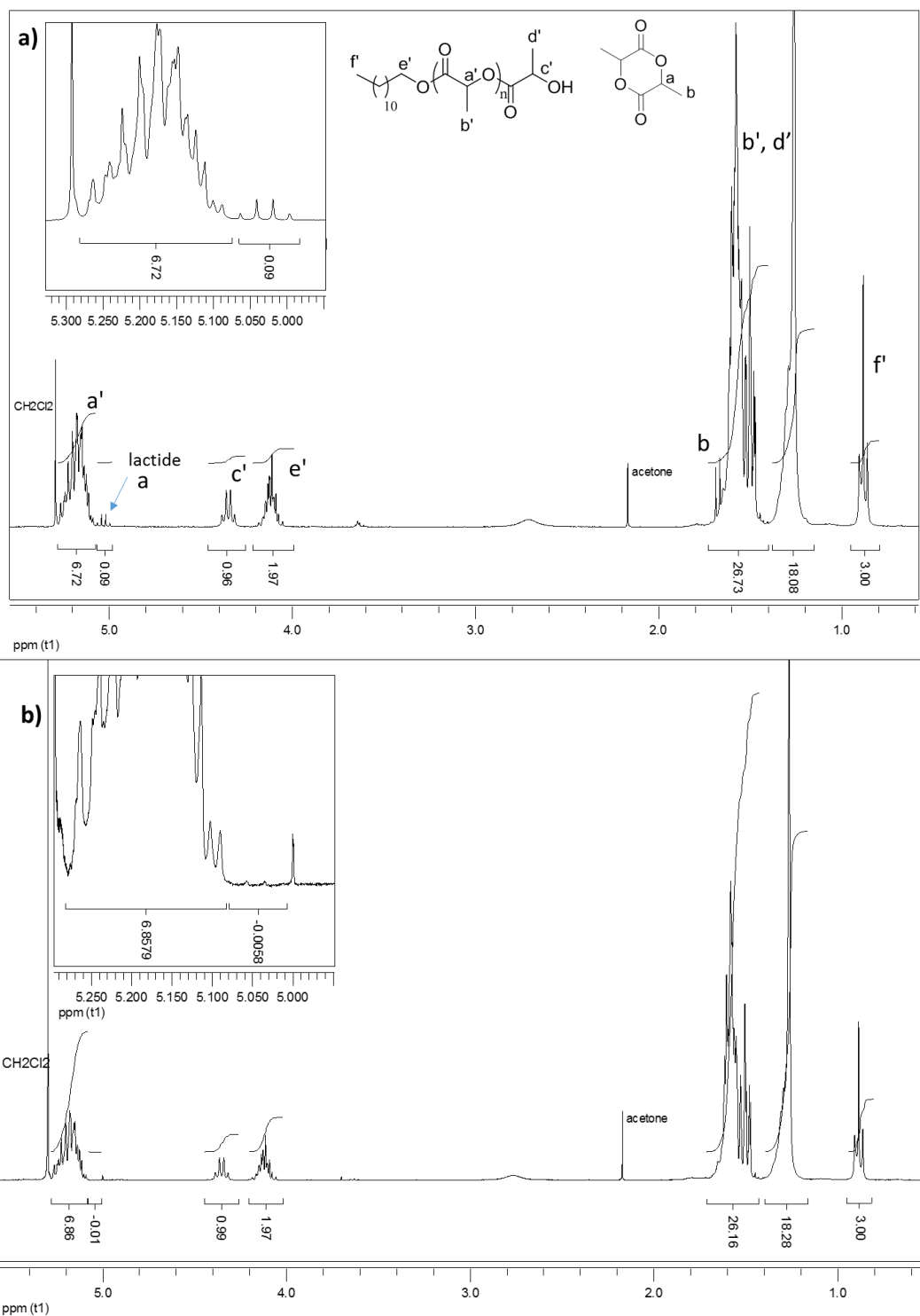
**Figure S10.** a)  $^1\text{H}$  NMR spectrum of the star shaped PLA formed after ROP of 30 equiv. of lactide with tris(2-aminoethyl)amine (\*DBU). b) SEC trace of the star shaped PLA formed after ROP of 30 equiv. of lactide with tris(2-aminoethyl)amine



**Figure S11.**  $^1\text{H}$  NMR spectra of the adducts formed by reaction of diethanolamine with 3.5 equiv of lactide and b) the star shaped PLA formed after ROP of 7 equiv. of lactide with diethanolamine (\*lactide; ° Toluene). c) SEC trace of the star shaped PLA formed after ROP of 30 equiv. of lactide with diethanolamine



**Figure S12.** ESI-MS spectra of a star shaped PLA formed after ROP of 30 equiv. of lactide with diethanolamine

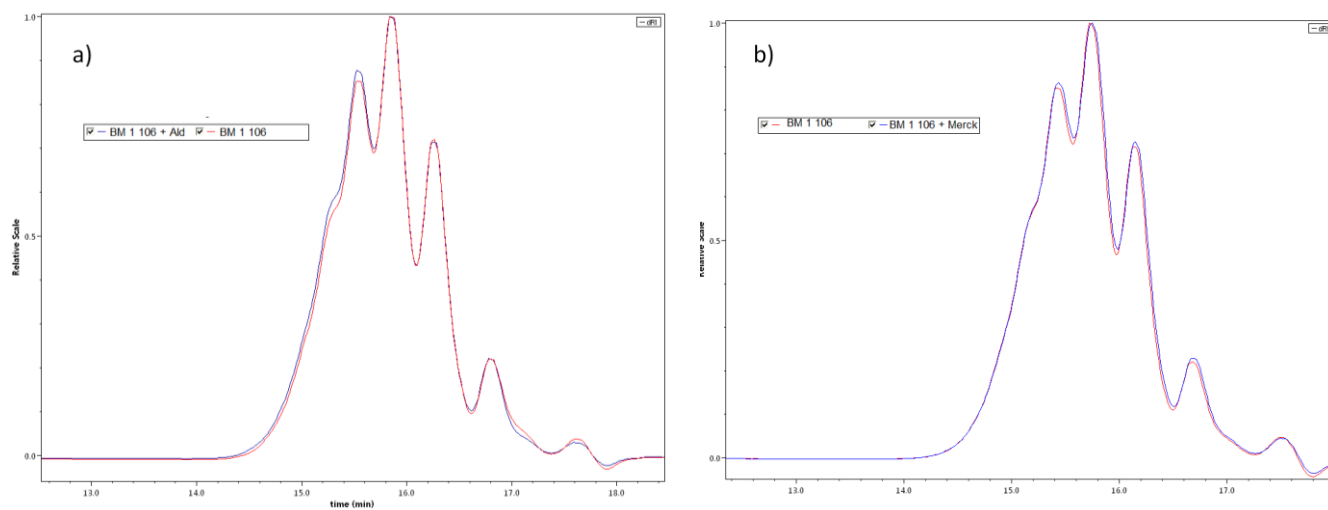


**Figure S13.**  $^1\text{H}$  NMR spectra of a dodecyl ester-end capped PLA sample before (a) /after (b) treatment with A

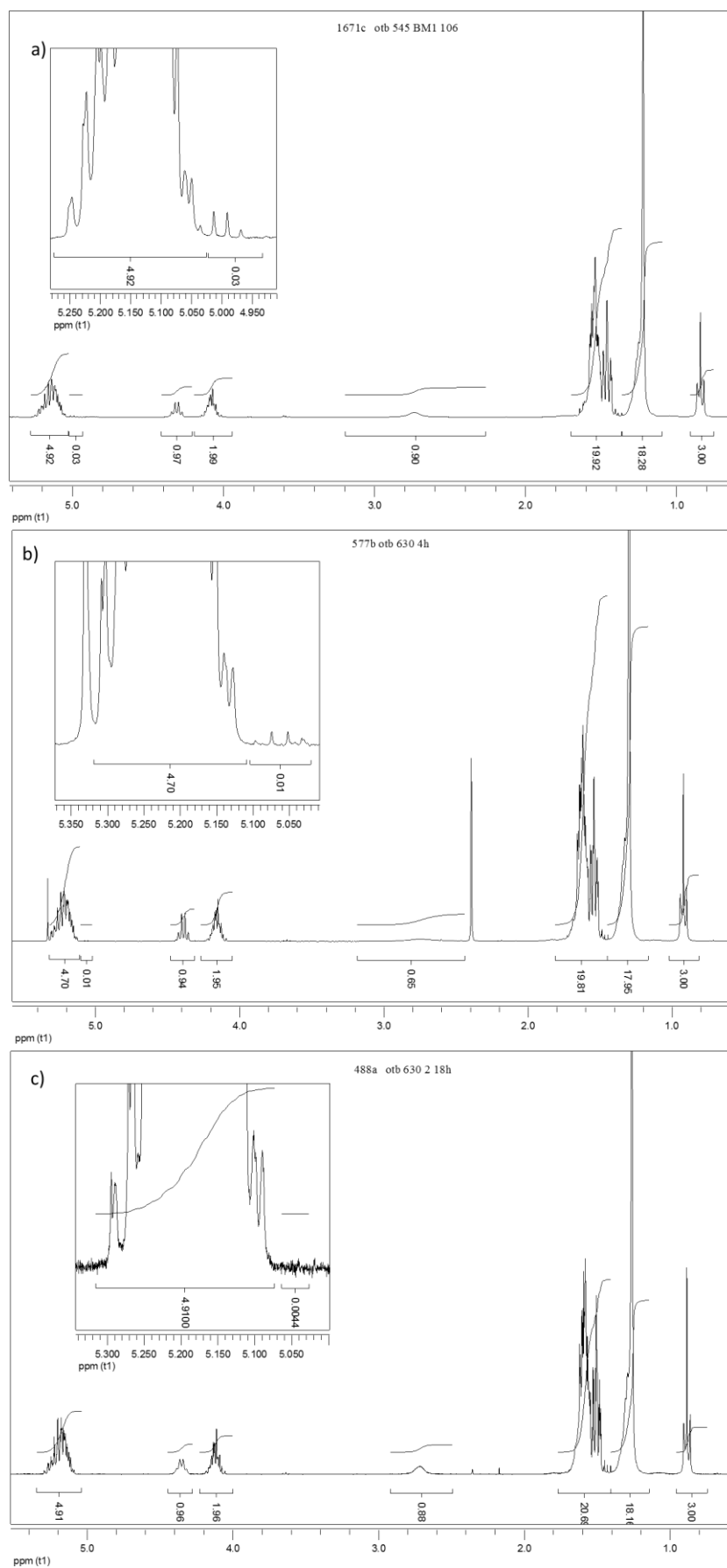
**Table S1.** SEC analysis of a PLA sample (BM106) before and after treatment with the supported amines

PLA Sample	$M_n$	$\mathcal{D}$
BM 1 106	990	1.17
BM 1 106 + Aldrich ( <b>A</b> )	1000	1.16
BM 1 106 + TCI ( <b>B</b> )	810 <sup>1</sup>	1.17
BM 1 106 + Merck ( <b>C</b> )	980	1.18

<sup>1</sup>analysis carried out on a different high-speed liquid chromatograph, PLA sample before treatment  $M_n = 810$ .

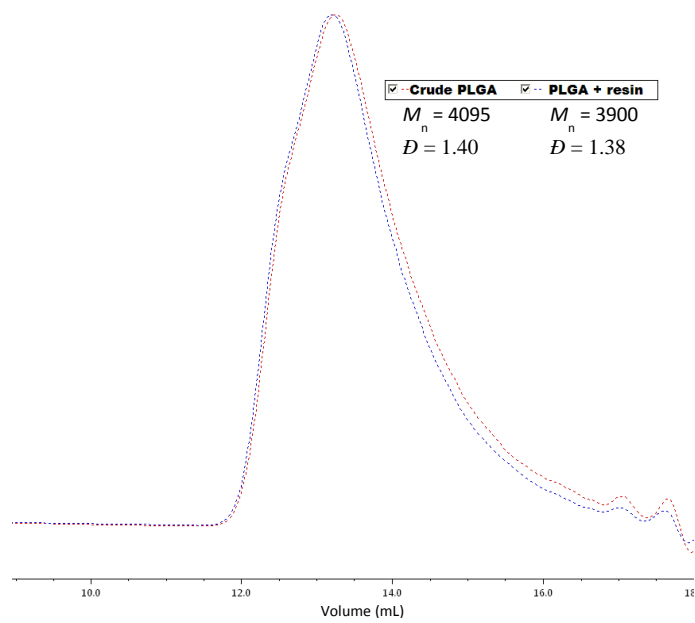


**Figure S14.** Overlay of SEC traces of a PLA sample before (red) /after (blue) treatment with **A** (a) and **C** (b)



**Figure S15.**  $^1\text{H}$  NMR spectra of a dodecyl ester-end capped PLA sample before (a) and after 2h (b) and 4h (c) treatment with **A**





**Figure S16.** Overlay of SEC traces of a PLGA sample before (red) and after (blue) treatment with **B** during 18 h