

# Ring Opening Polymerization of Lactides and Lactones by Multimetallic Titanium Complexes Derived from the Acids $\text{Ph}_2\text{C}(\text{X})\text{CO}_2\text{H}$ ( $\text{X} = \text{OH}, \text{NH}_2$ )

Xin Zhang <sup>1</sup>, Timothy J. Prior <sup>1</sup>, Kai Chen <sup>2</sup>, Orlando Santoro <sup>1,3</sup> and Carl Redshaw <sup>1,\*</sup>

<sup>1</sup> Plastics Collaboratory, Department of Chemistry, University of Hull, Cottingham Road, Hull HU6 7RX, UK

<sup>2</sup> Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

<sup>3</sup> Dipartimento di Biotecnologie e Scienze della Vita, Università degli Studi dell'Insubria, 21100 Varese, Italy

\* Correspondence: c.redshaw@hull.ac.uk

## Contents

**Figure S1.** Harris notation and its application in describing these ligands.

**Figure S2.** Alternative view of **1**.

**Figure S3.** Coordination about the two independent Ti ions in **2**.

**Figure S4.** Alternate view (ORTEP) of **3** with atoms drawn as 25 % probability ellipsoids. Minor disorder and hydrogen atoms are omitted for clarity.

**Figure S5.** Asymmetric unit of **4** with atoms drawn as spheres of arbitrary radius. Each disorder component is illustrated; hydrogen atoms are not shown for clarity.

**Figure S6.** Alternative view of **5** with atoms drawn as 50% probability ellipsoids. For clarity hydrogen atoms have been omitted.

**Figure S7.** View of the crystal structure of **6** down *a*. Dashed lines show hydrogen bonds.

**Figure S8.** The two unique complexes in **7** composed of Ti1 and Ti2. Symmetry-equivalent atoms are generated by the following symmetry operations: \$1 = 1-x, 2-y, 2-z\$; \$2 = -x, 1-y, 1-z\$.

**Figure S9.** Two Ti cluster present in **8**. Symmetry operation used to generate equivalent atoms:  $i = 1-x, 1-y, 1-z$ .

**Figure S10.** Asymmetric unit of **9**. A portion of the infinite hydrogen bonded chain running parallel to the crystallographic *a* direction (left-right on the image) is shown as dashed lines.

**Figure S11.** Hydrogen-bonded chain within **10**. Dashed lines show hydrogen bonds.

**Figure S12.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **1** (Table 1, entry 1).

**Figure S13.** MALDI-TOF spectrum of PCL using **1** (Table 1, entry 1).

**Figure S14.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **2** (Table 1, entry 2).

**Figure S15.** MALDI-TOF spectrum of PCL using **2** (Table 1, entry 2).

**Figure S16.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **3** (Table 1, entry 3).

**Figure S17.** MALDI-TOF spectrum of PCL using **3** (Table 1, entry 3).

**Figure S18.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **4** (Table 1, entry 4).

**Figure S19.** MALDI-TOF spectrum of PCL using **4** (Table 1, entry 4).

**Figure S20.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **5** (Table 1, entry 5).

**Figure S21.** MALDI-TOF spectrum of PCL using **5** (Table 1, entry 5).

**Figure S22.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **6** (Table 1, entry 6).

**Figure S23.** MALDI-TOF spectrum of PCL using **6** (Table 1, entry 6).

**Figure S24.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **7** (Table 1, entry 7).

**Figure S25.** MALDI-TOF of PCL using **7** (Table 1, entry 7).

**Figure S26.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **9** (Table 1, entry 9).

**Figure S27.** MALDI-TOF of PCL using **9** (Table 1, entry 9).

**Figure S28.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **10** (Table 1, entry 10).

**Figure S29.** MALDI-TOF spectrum of PCL using **10** (Table 1, entry 10).

**Figure S30.** 3D time-resolved  $^1\text{H}$  NMR (400 MHz, toluene- $d_8$ ) of kinetics of *r*-LA using complex **7** (Table 3, entry 7).

**Figure S31.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **1** (Table 3, entry 1).

**Figure S32.** MALDI-TOF spectrum of PLA using **1** (Table 3, entry 1).

**Figure S33.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **2** (Table 3, entry 2).

**Figure S34.** MALDI-TOF spectrum of PLA using **2** (Table 3, entry 2).

**Figure S35.** MALDI-TOF spectrum of PLA using **3** (Table 3, entry 3).

**Figure S36.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **4** (Table 3, entry 4).

**Figure S37.** MALDI-TOF spectrum of PLA using **4** (Table 3, entry 4).

**Figure S38.** MALDI-TOF spectrum of PLA using **5** (Table 3, entry 5).

**Figure S39.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **7** (Table 3, entry 7).

**Figure S40.** MALDI-TOF spectrum of PLA using **7** (Table 3, entry 7).

**Figure S41.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **8** (Table 3, entry 8).

**Figure S42.** MALDI-TOF spectrum of PLA using **8** (Table 3, entry 8).

**Figure S43.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **9** (Table 3, entry 9).

**Figure S44.** MALDI-TOF spectrum of PLA using **9** (Table 3, entry 9).

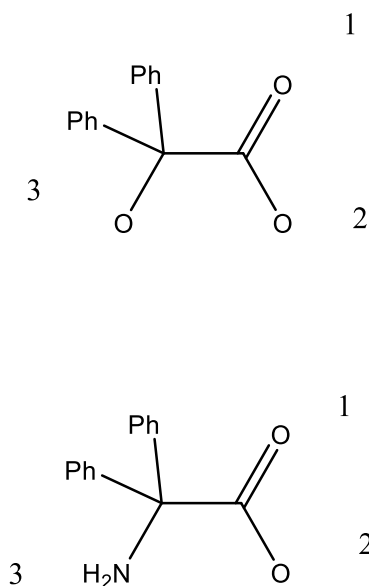
**Figure S45.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **1** (left) and **2** (right) (Table 3, entries 1 and 2).

**Figure S46.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **3** (left) and **4** (right) (Table 3, entries 3 and 4).

**Figure S47.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **5** (left) and **6** (right) (Table 3, entries 5 and 6).

**Figure S48.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **7** (left) and **8** (right) (Table 3, entries 7 and 8).

**Figure S49.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **9** (left) and **10** (right) (Table 3, entries 9 and 10).



**Figure S1.** Harris notation and its application in describing these ligands.

In line with the method of Harris, [S1] we have described the coordination of the benzilic acid in a systematic way. We have numbered each of the oxygen atoms in a consistent manner as shown above. The order in the Harris symbol reflects the binding of each atom in order. For example, [2.021] signifies the ligand binds to two metals, oxygen #1 does not bind, oxygen #2 binds to both metal ions, and oxygen #3 binds to one metal. It is notable that the same binding occurs for diphenyl glycine in each case, namely [1.011]. That is to say the dp<sub>g</sub> is chelating through O#2 and N#3.

In some cases it is necessary to remove ambiguity about which metal ions are bound and this is done through the use of subscripts to identify the metal ions. For example, [3.1<sub>1</sub>1<sub>2</sub>2<sub>13</sub>] would signify three unique bound metal ions; atom 1 binds M#1, atom 2 binds M#2, and atom 3 binds both M#1 and M#3.

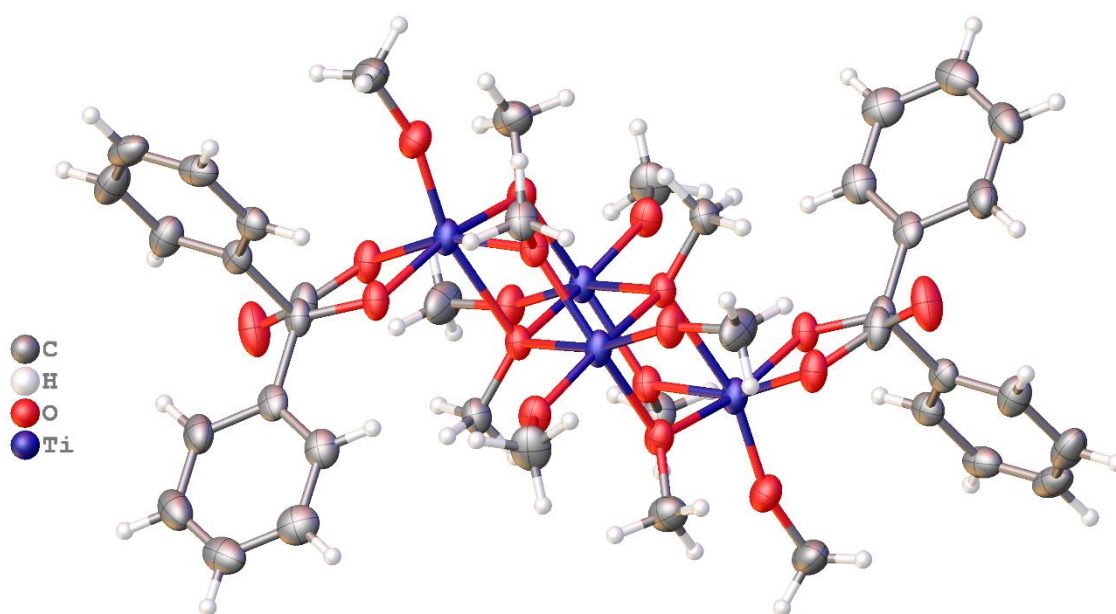


Figure S2. Alternative view of 1.

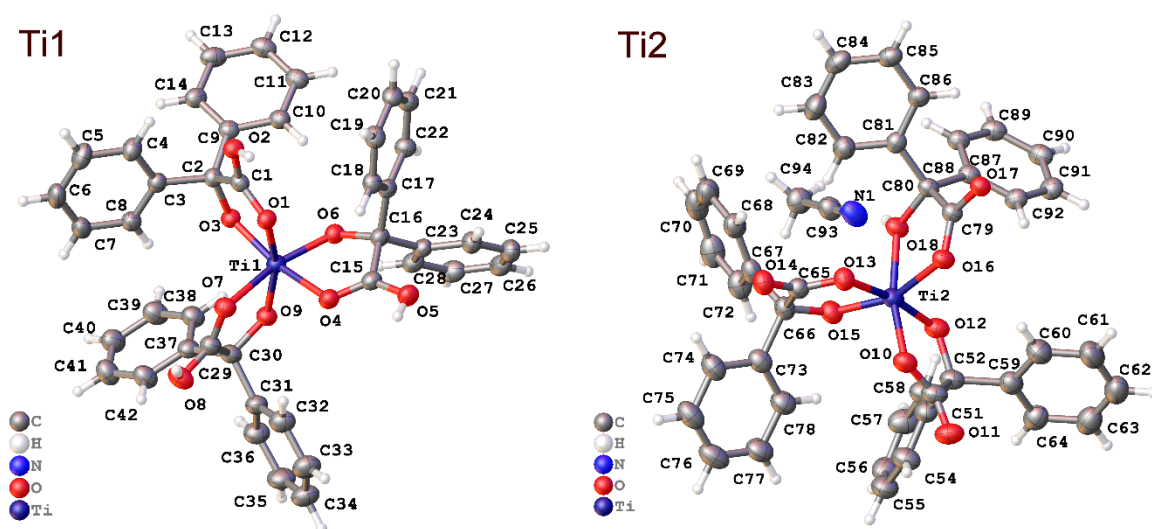
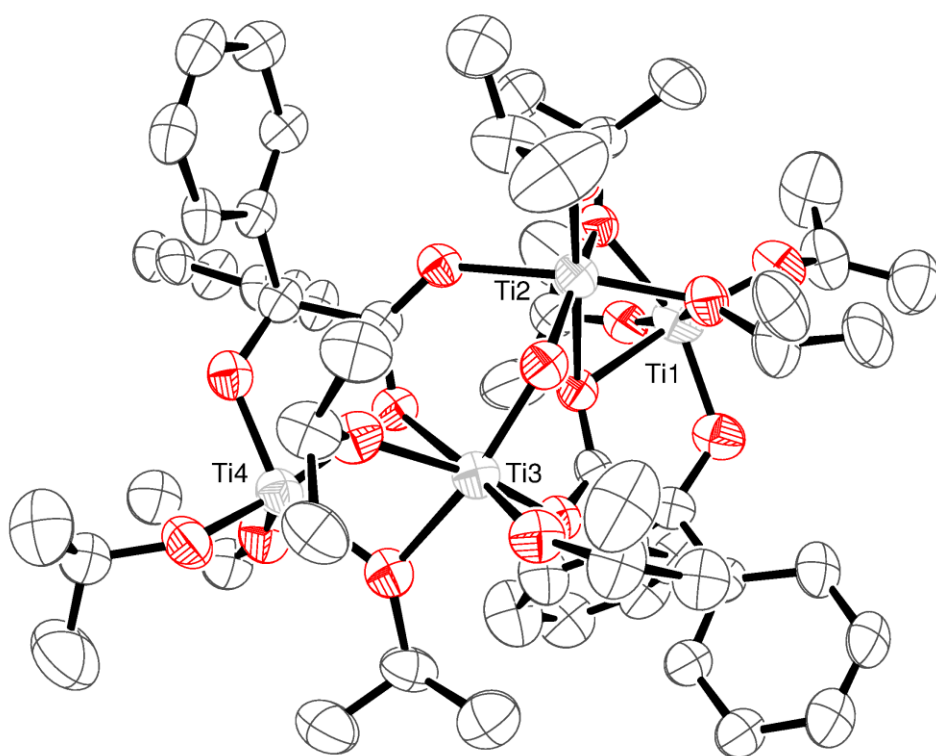
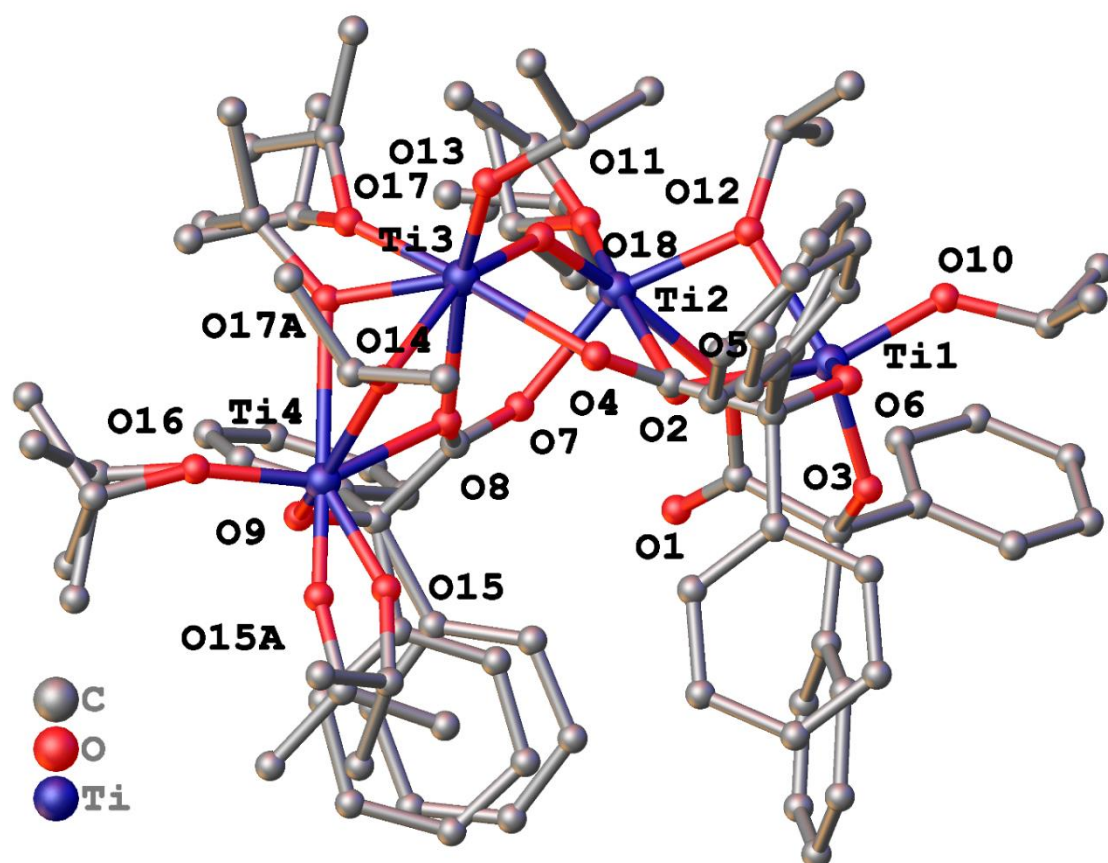


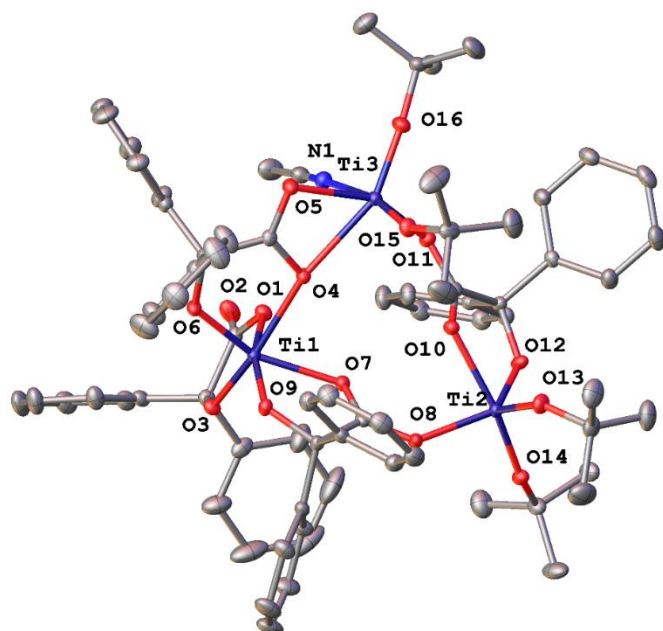
Figure S3. Coordination about the two independent Ti ions in 2.



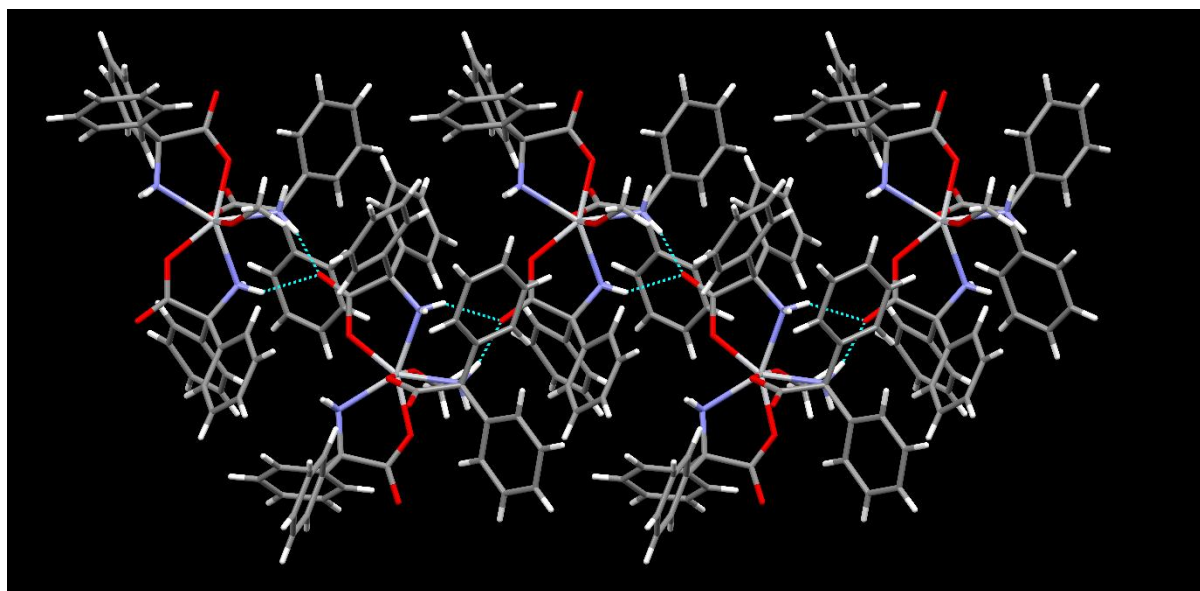
**Figure S4.** Alternate view (ORTEP) of **3** with atoms drawn as 25 % probability ellipsoids. Minor disorder and hydrogen atoms are omitted for clarity.



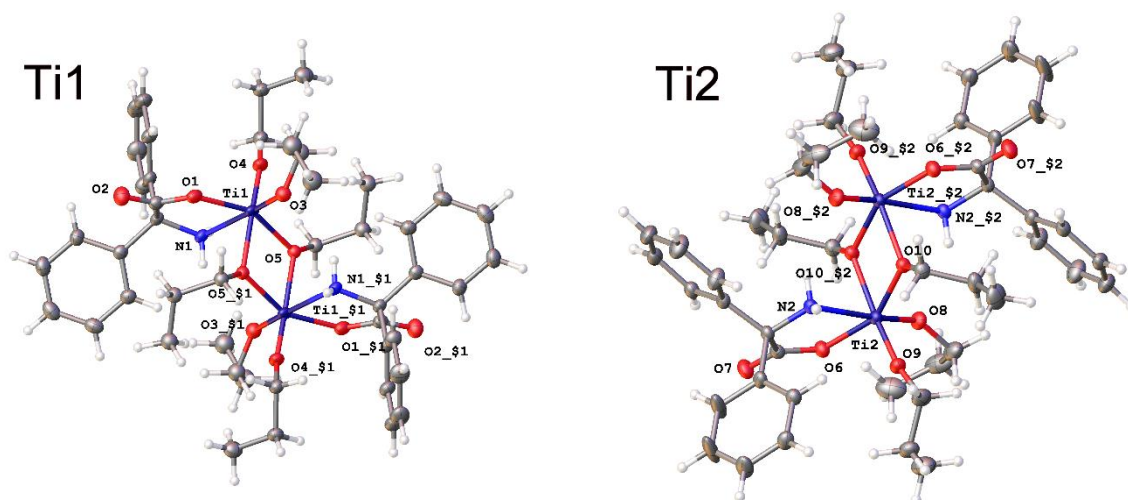
**Figure S5.** Asymmetric unit of 4 with atoms drawn as spheres of arbitrary radius. Each disorder component is illustrated; hydrogen atoms are not shown for clarity.



**Figure S6.** Alternative view of 5 with atoms drawn as 50% probability ellipsoids. For clarity hydrogen atoms have been omitted.

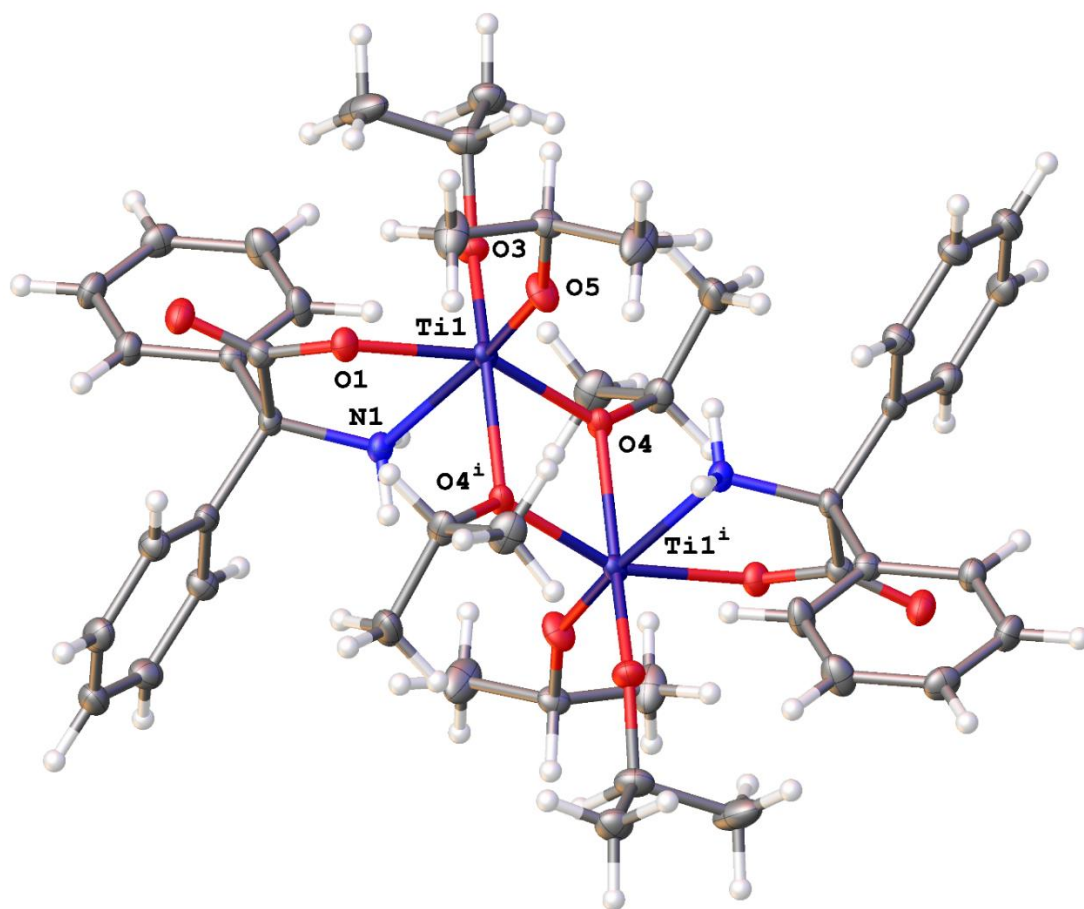


**Figure S7.** View of the crystal structure of **6** down *a*. Dashed lines show hydrogen bonds.

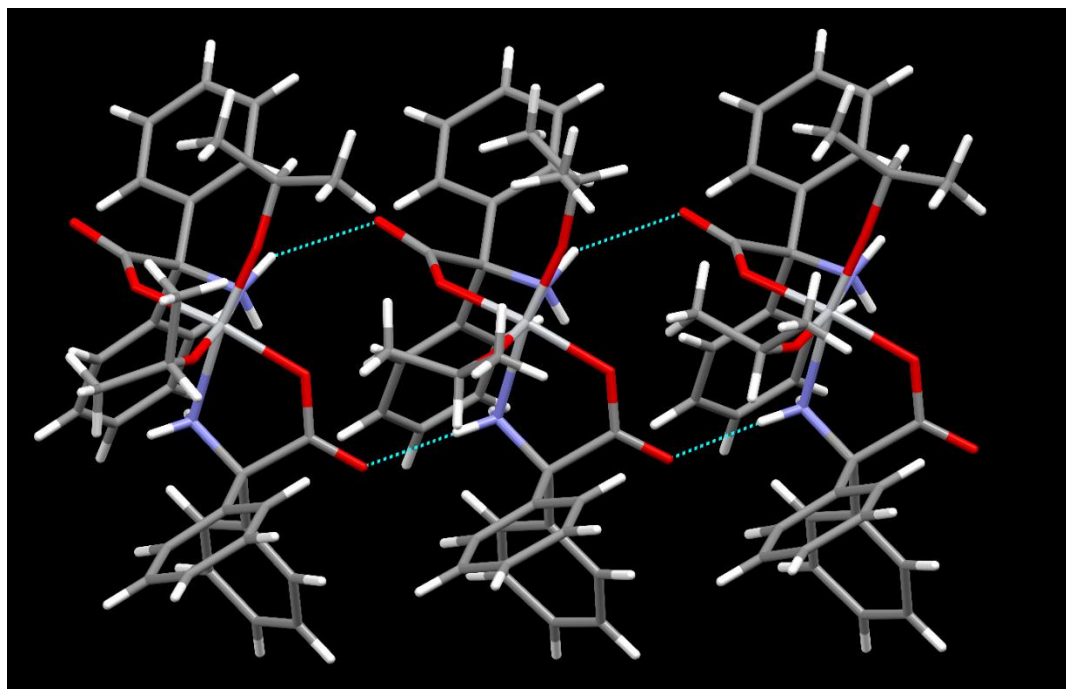


**Figure S8.** The two unique complexes in **7** composed of Ti1 and Ti2. Symmetry-equivalent atoms are generated by the following symmetry operations: \$1 = 1-x, 2-y, 2-z; \$2 = -x, 1-y, 1-z.



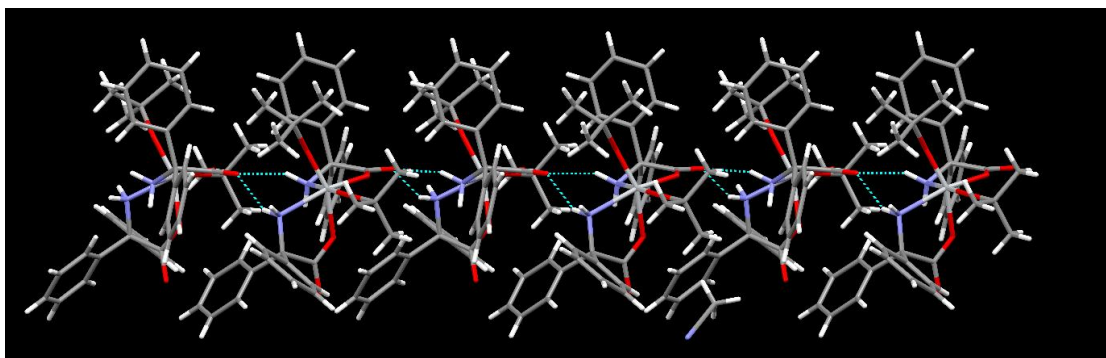


**Figure S9.** Two Ti cluster present in 8. Symmetry operation used to generate equivalent atoms:  $i = 1-x, 1-y, 1-z$ .

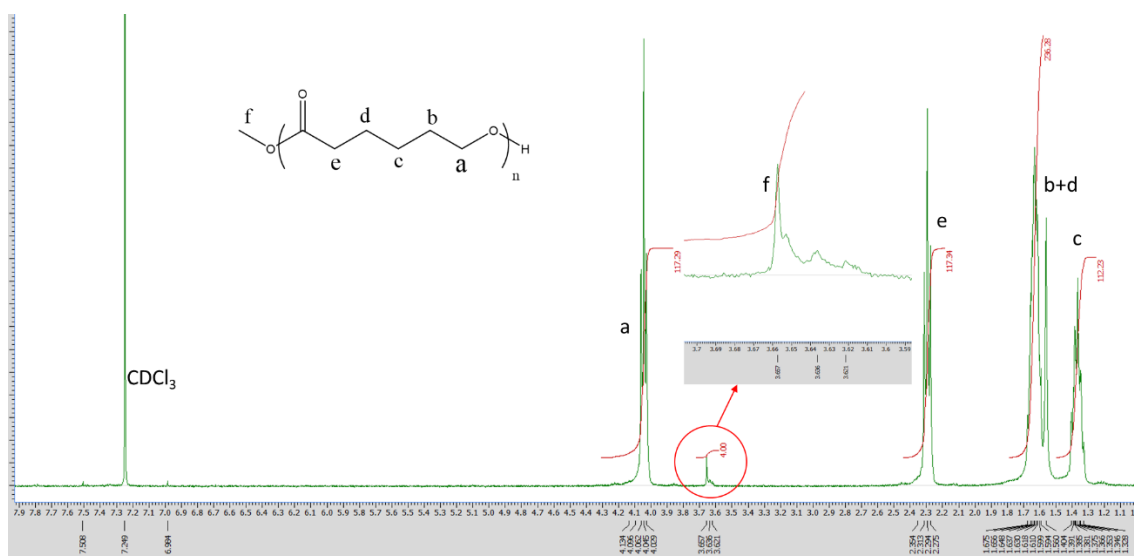


**Figure S10.** Asymmetric unit of 9. A portion of the infinite hydrogen bonded chain running parallel to the crystallographic *a* direction (left-right on the image) is shown as dashed lines.

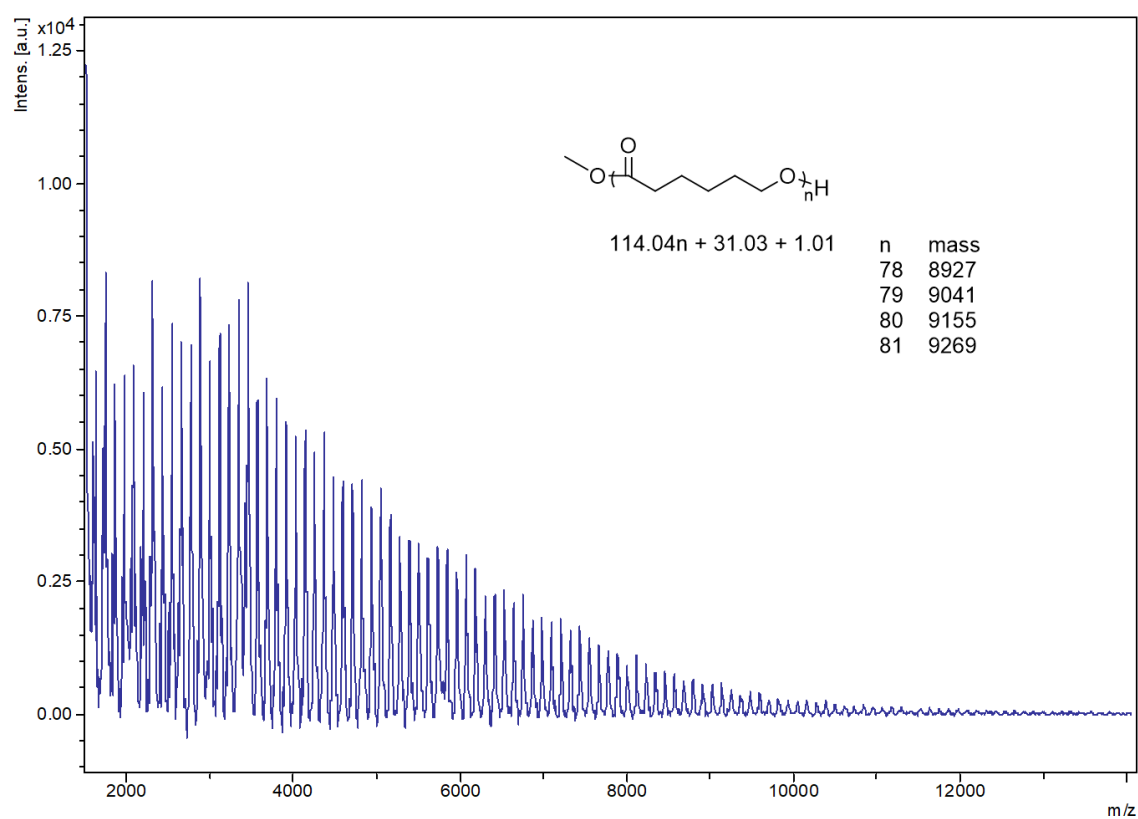




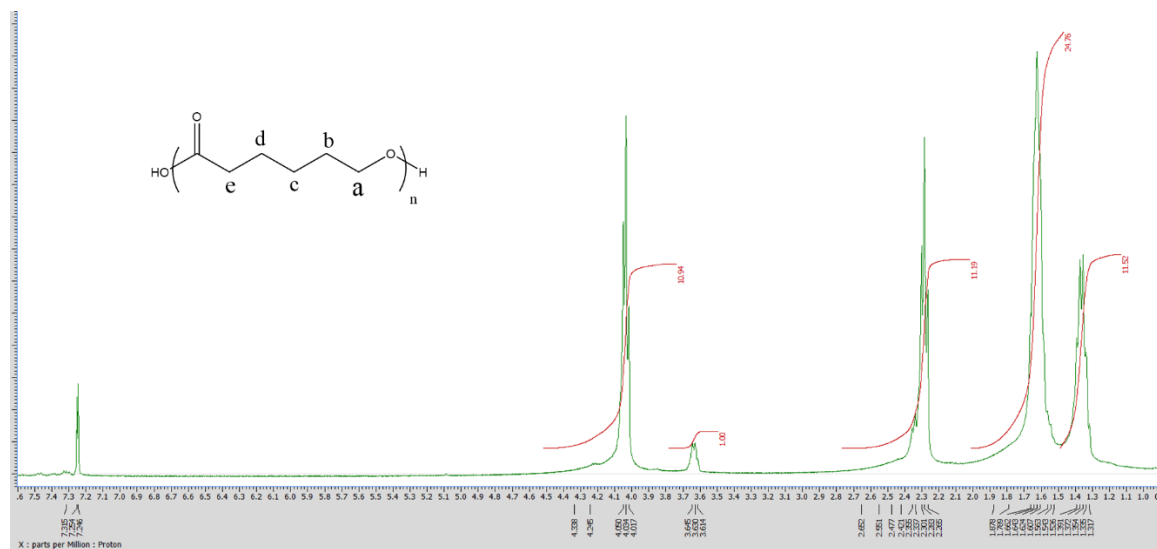
**Figure S11.** Hydrogen-bonded chain within **10**. Dashed lines show hydrogen bonds.



**Figure S12.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **1** (Table 1, entry 1).



**Figure S13.** MALDI-TOF spectrum of PCL using **1** (Table 1, entry 1).



**Figure S14.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **2** (Table 1, entry 2).

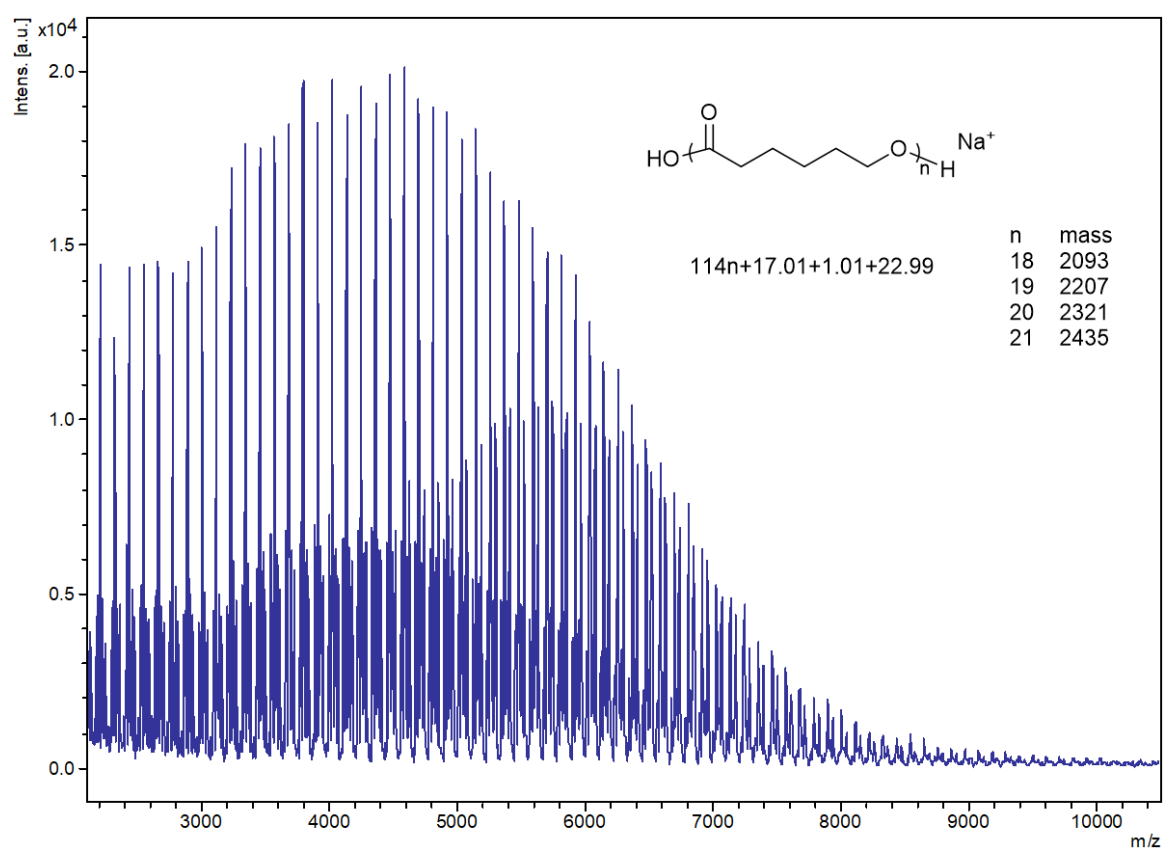


Figure S15. MALDI-TOF spectrum of PCL using **2** (Table 1, entry 2).

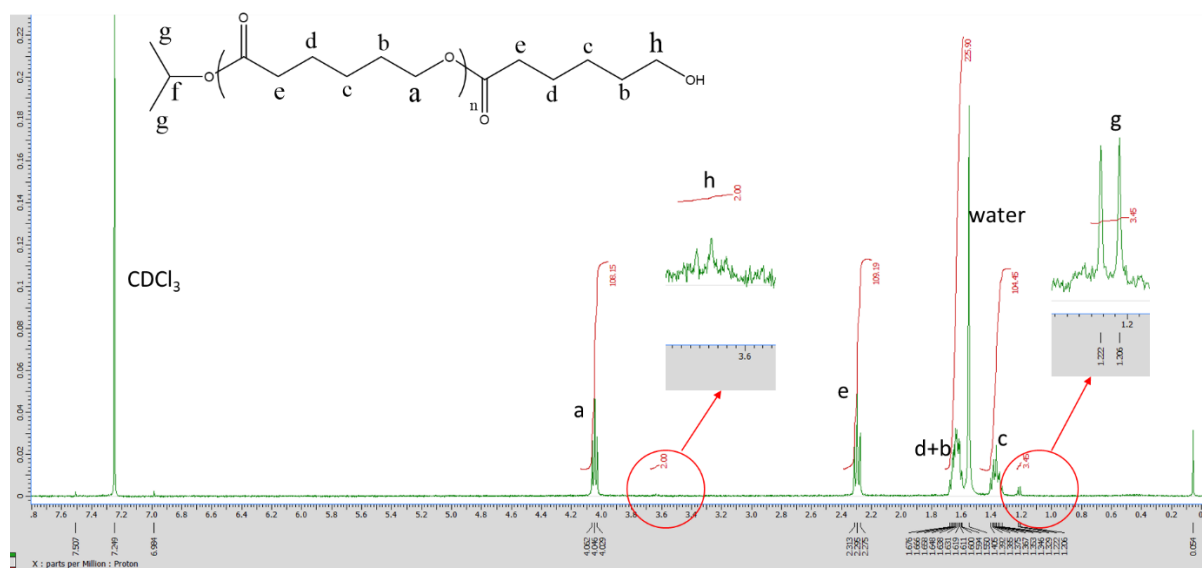


Figure S16.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **3** (Table 1, entry 3).

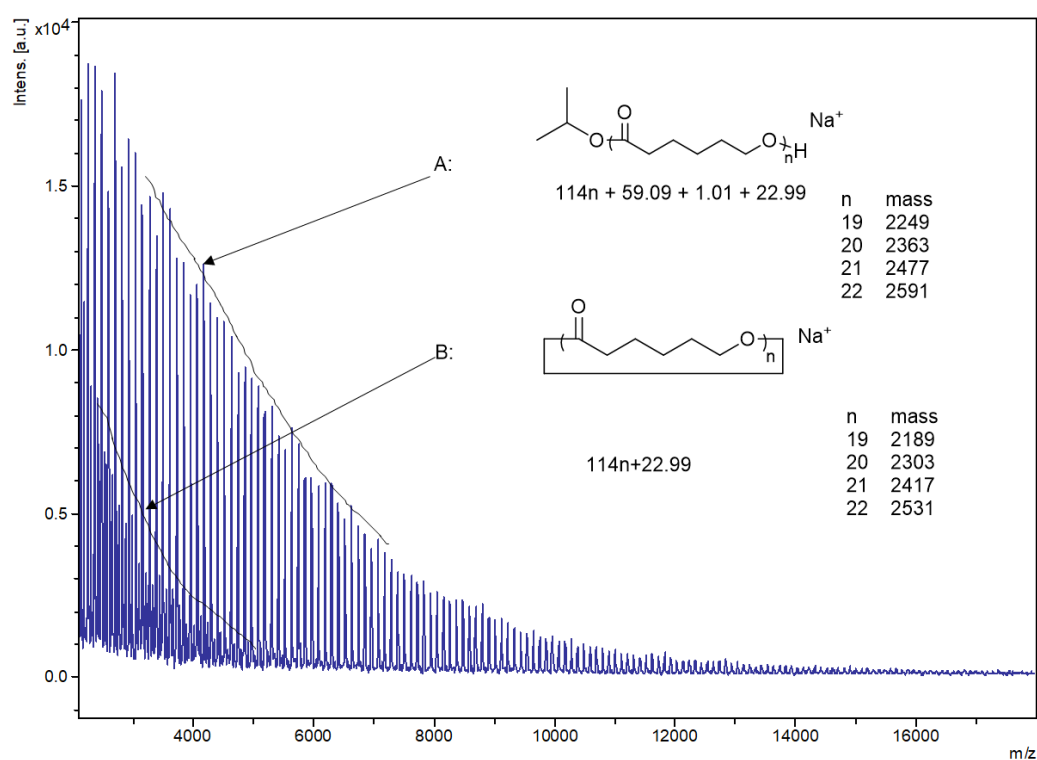


Figure S17. MALDI-TOF spectrum of PCL using **3** (Table 1, entry 3).

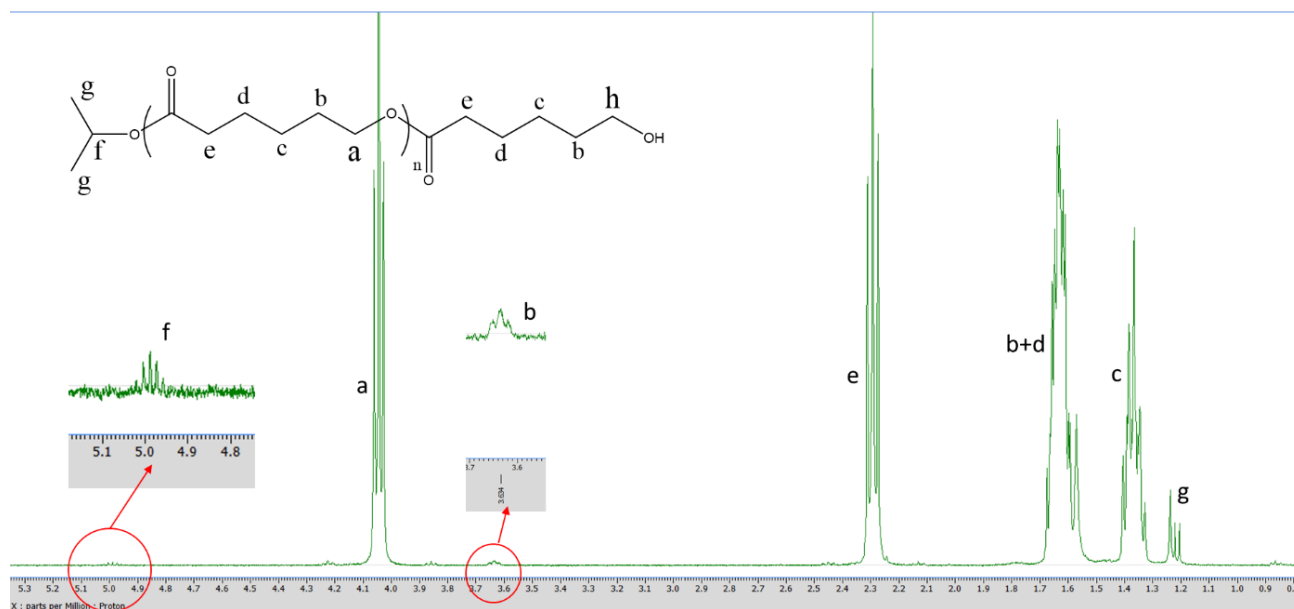
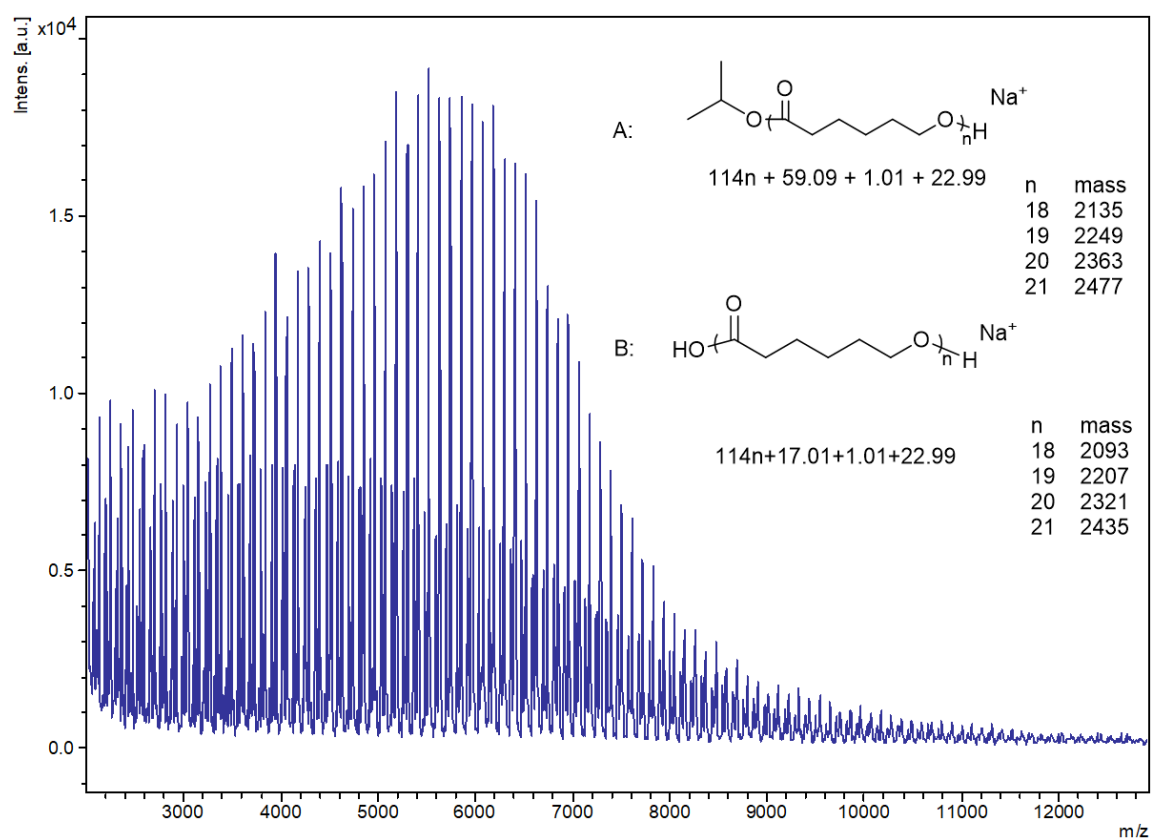
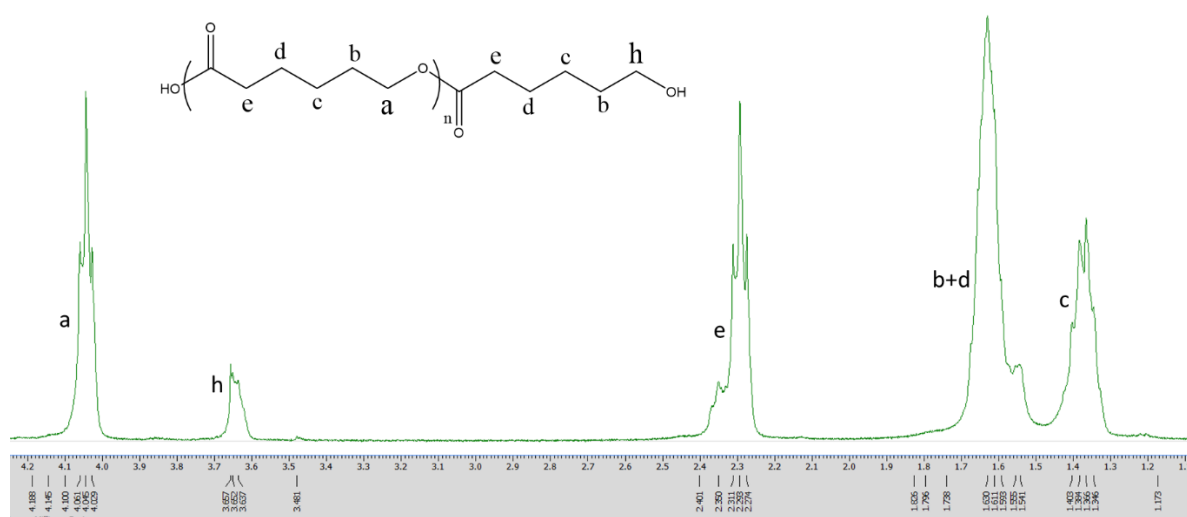


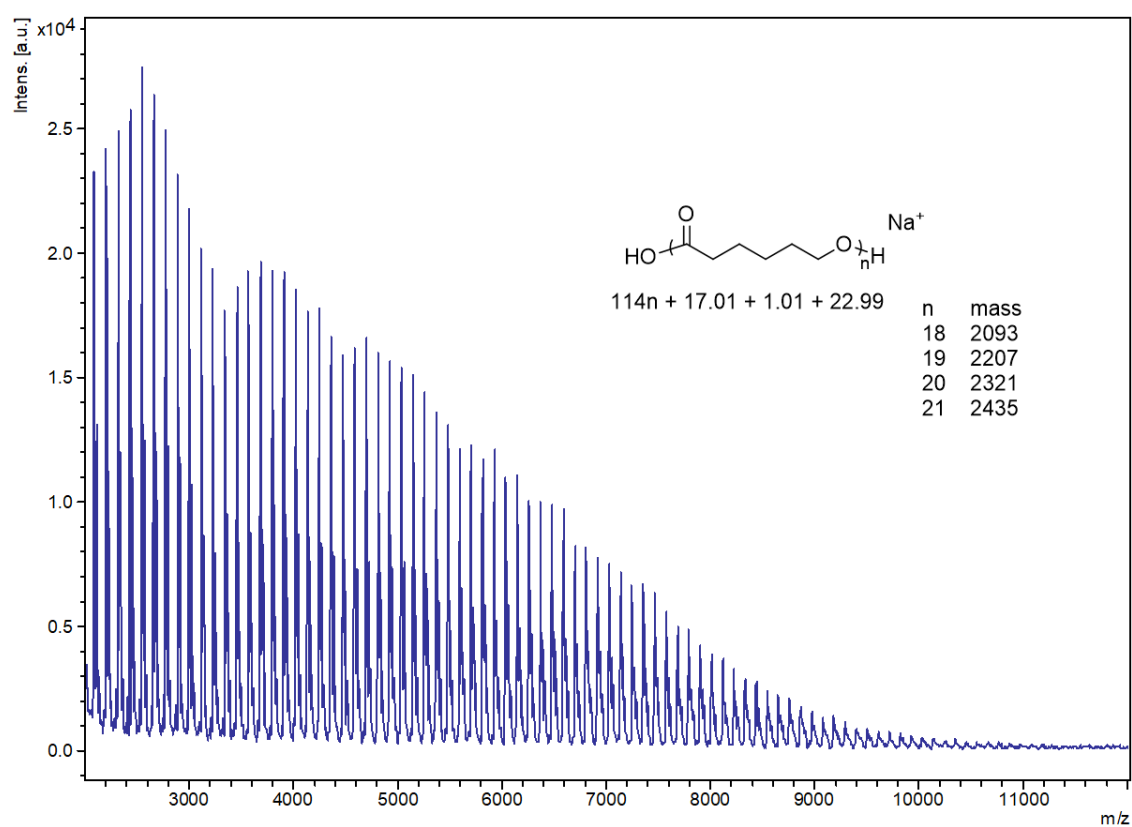
Figure S18.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **4** (Table 1, entry 4).



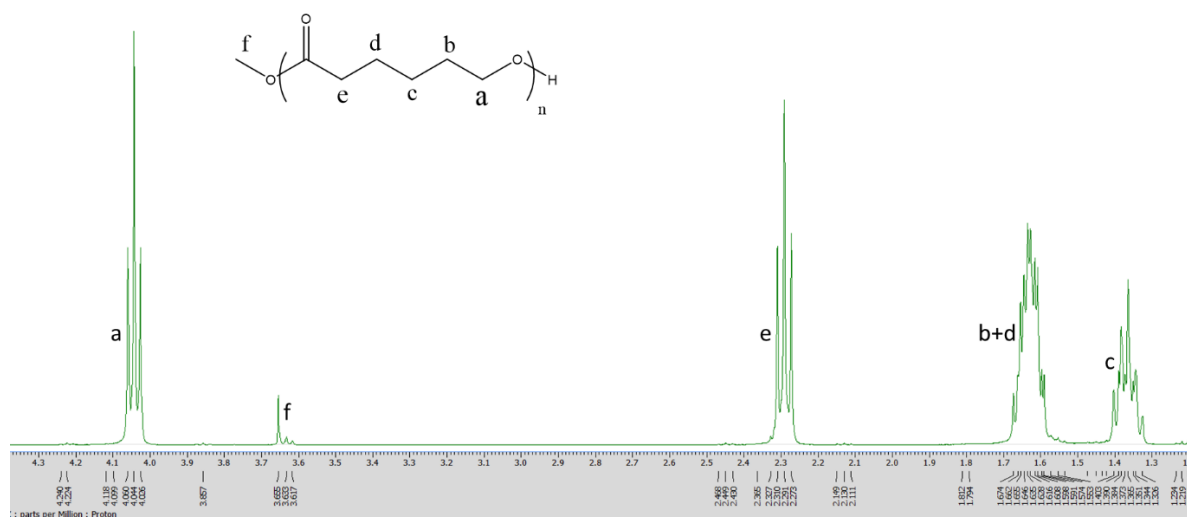
**Figure S19.** MALDI-TOF spectrum of PCL using **4** (Table 1, entry 4).



**Figure S20.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **5** (Table 1, entry 5).



**Figure S21.** MALDI-TOF spectrum of PCL using **5** (Table 1, entry 5).



**Figure S22.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **6** (Table 1, entry 6).



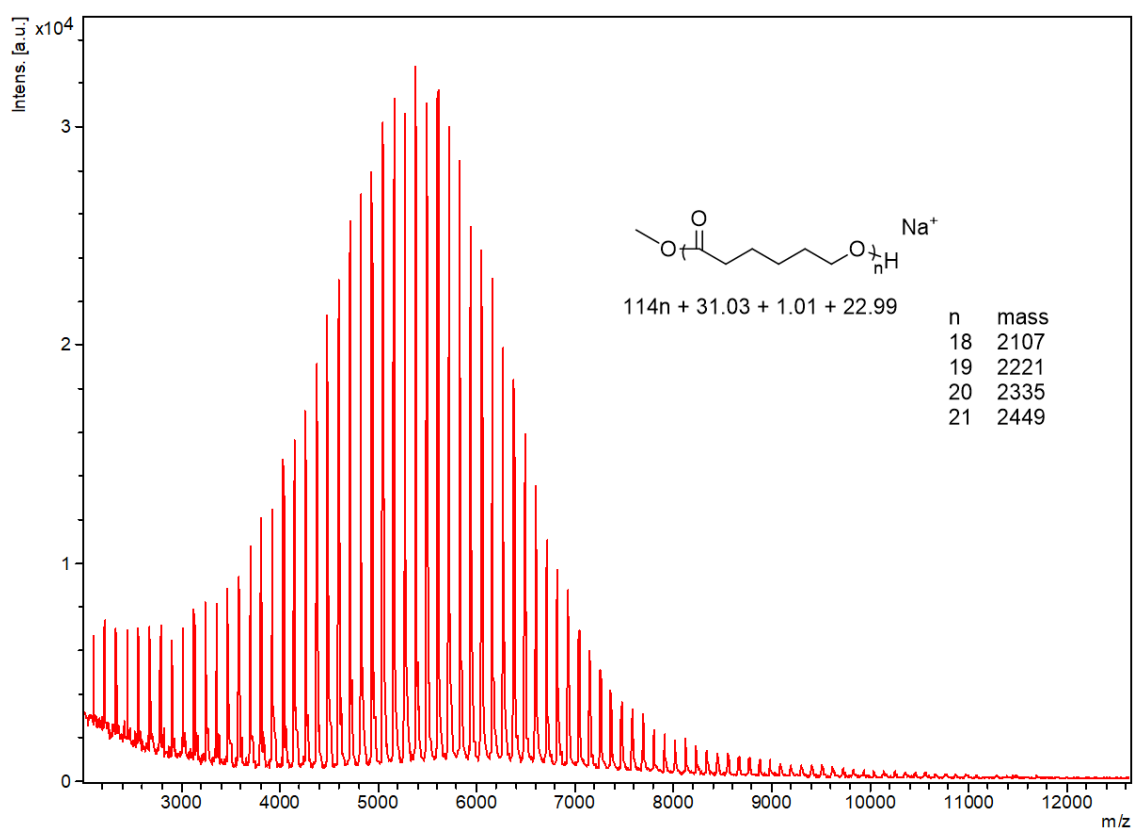


Figure S23. MALDI-TOF spectrum of PCL using **6** (Table 1, entry 6).

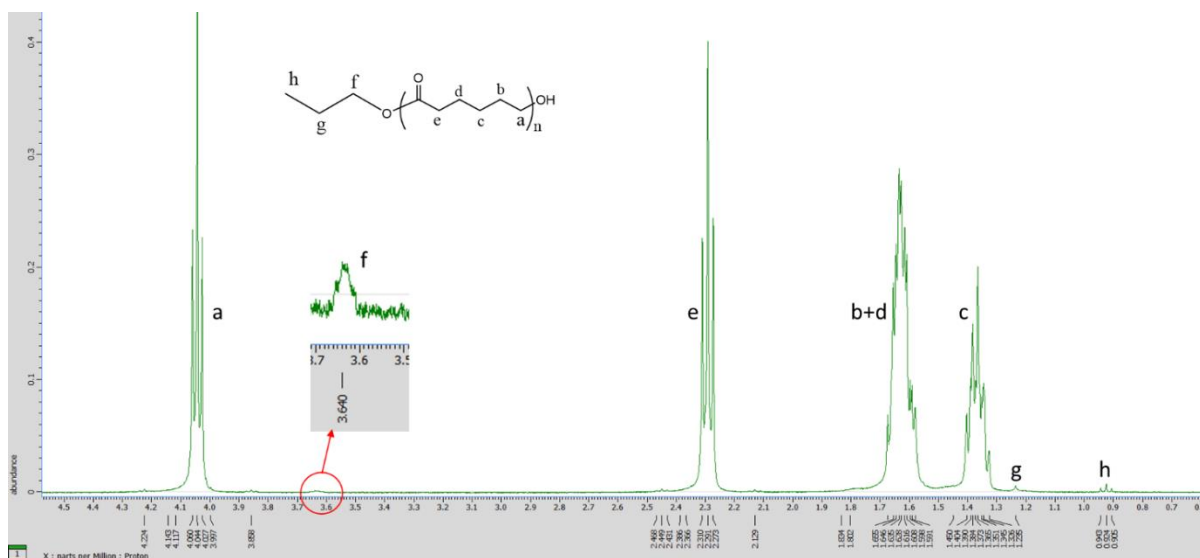


Figure S24. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **7** (Table 1, entry 7).

The figure displays the  $^1\text{H}$  NMR spectrum of a poly(ester amide) compound. The chemical structure is shown at the top, with protons labeled a through h. The spectrum below shows the corresponding peaks, with an inset providing a magnified view of the aromatic region (4.7-5.1 ppm).

**Chemical Structure:** The structure is a poly(ester amide) with the repeating unit:  $\text{[O-C(=O)-CH}_2\text{(d)-CH}_2\text{(c)-CH}_2\text{(b)-O-C(=O)-CH}_2\text{(e)-CH}_2\text{(d)-CH}_2\text{(c)-CH}_2\text{(b)-OH]}$ . The aromatic protons are labeled f and g.

**$^1\text{H}$  NMR Spectrum:** The spectrum shows several peaks corresponding to the protons in the structure:

- a:** Aromatic protons (f and g) in the aromatic region (4.7-5.1 ppm).
- e:** Methylene protons adjacent to the carbonyl group in the ester unit (2.3 ppm).
- b+d:** Methylene protons in the aliphatic chain (1.6 ppm).
- c:** Methylene protons in the aliphatic chain (1.3 ppm).
- g:** Aromatic protons (f and g) in the aromatic region (1.2 ppm).

The inset shows a magnified view of the aromatic region (4.7-5.1 ppm), highlighting the peaks for protons f and g.

**Figure S26.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PCL using **9** (Table 1, entry 9).

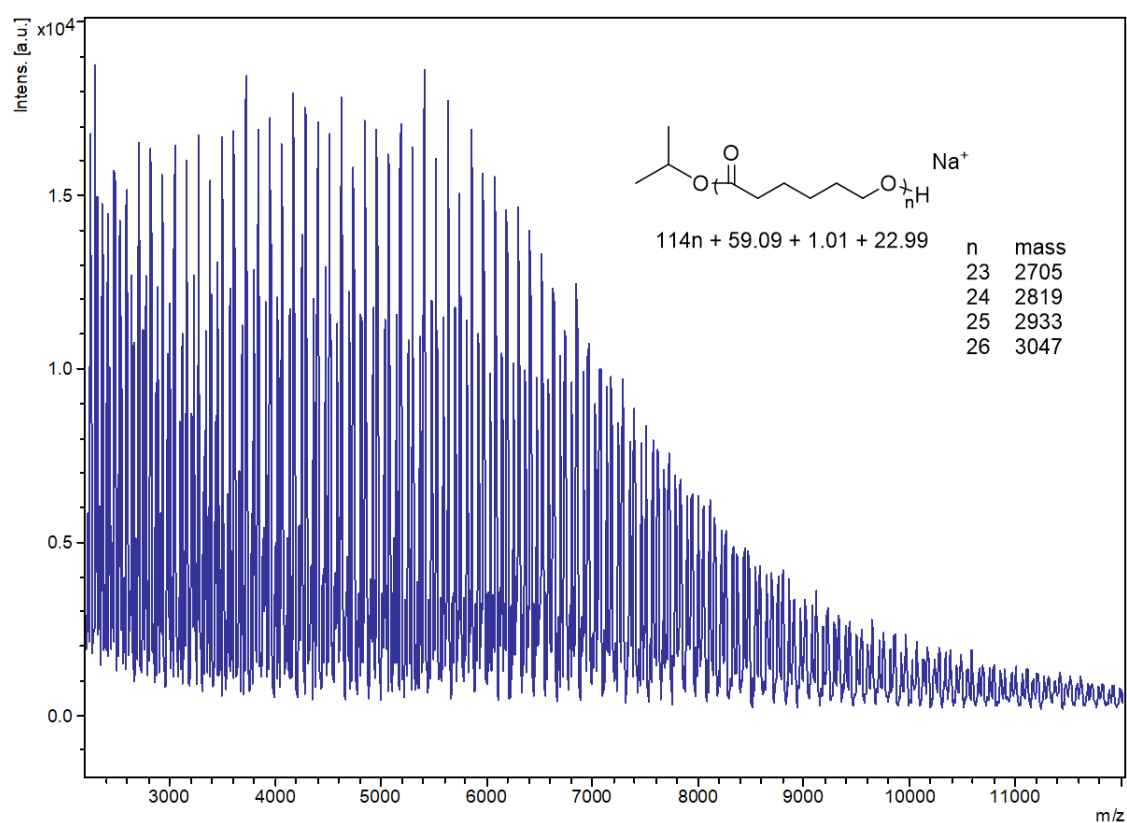


Figure S27. MALDI-TOF of PCL using **9** (Table 1, entry 9).

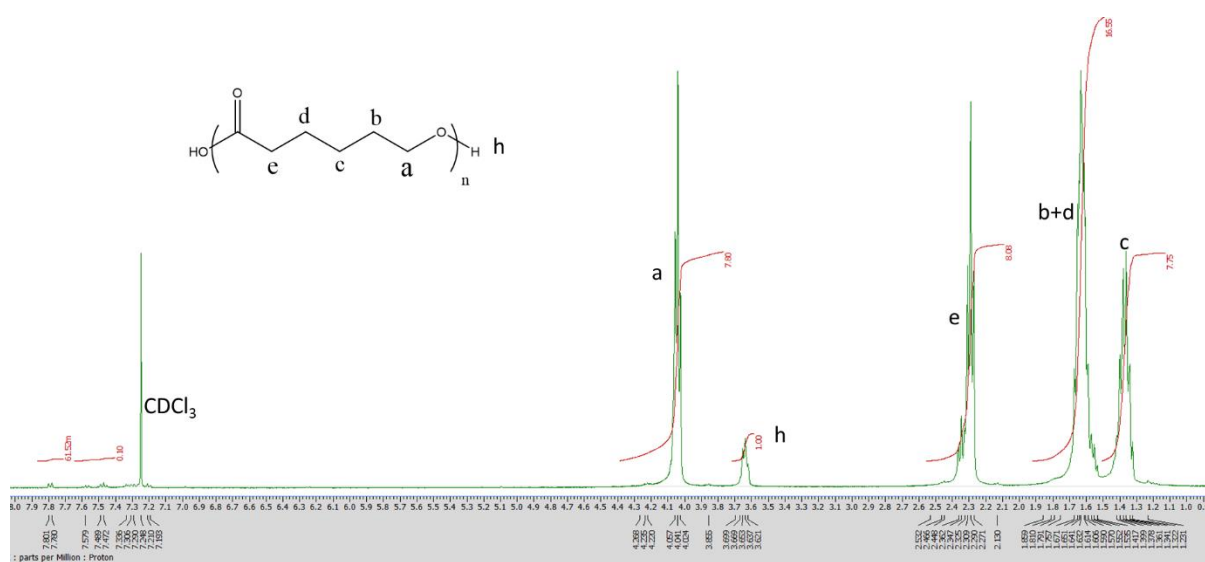


Figure S28. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PCL using **10** (Table 1, entry 10).

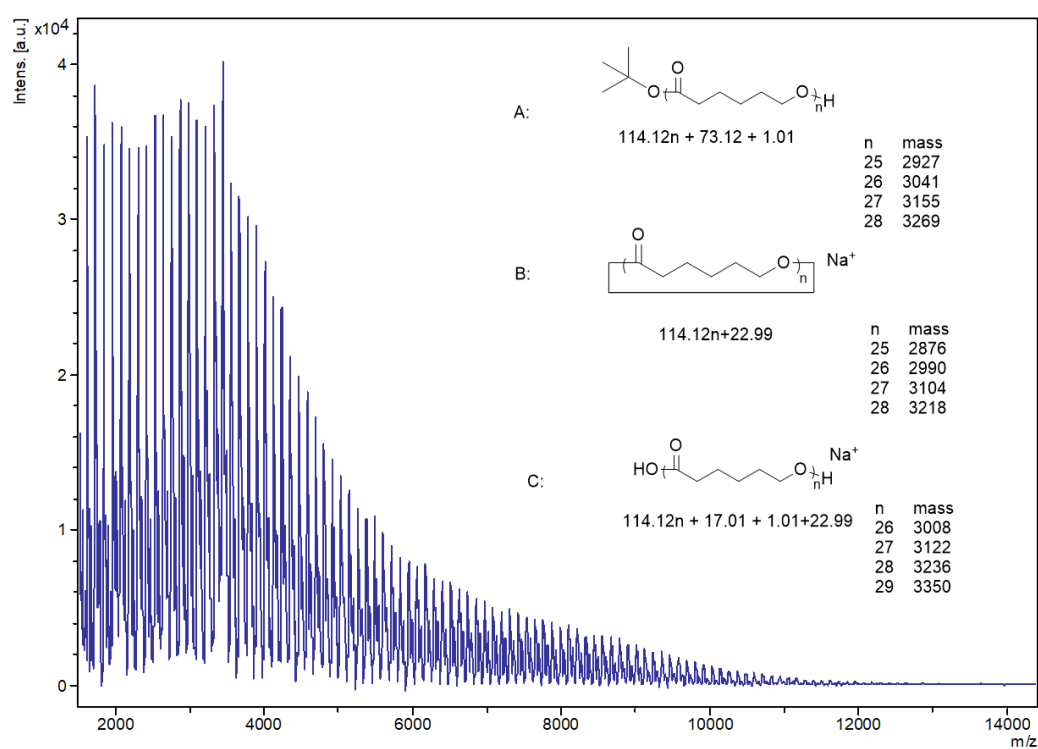


Figure S29. MALDI-TOF spectrum of PCL using **10** (Table 1, entry 10).

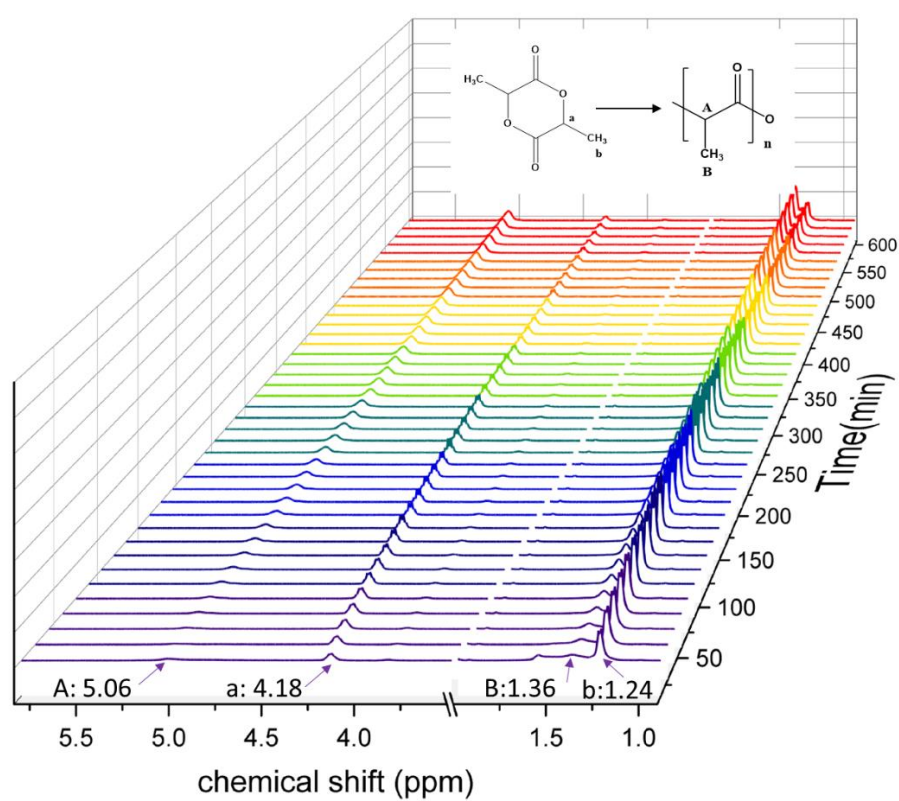


Figure S30. 3D time-resolved  $^1\text{H}$  NMR (400 MHz, toluene- $d_8$ ) of kinetics of *r*-LA using complex **7** (Table 3, entry 7).

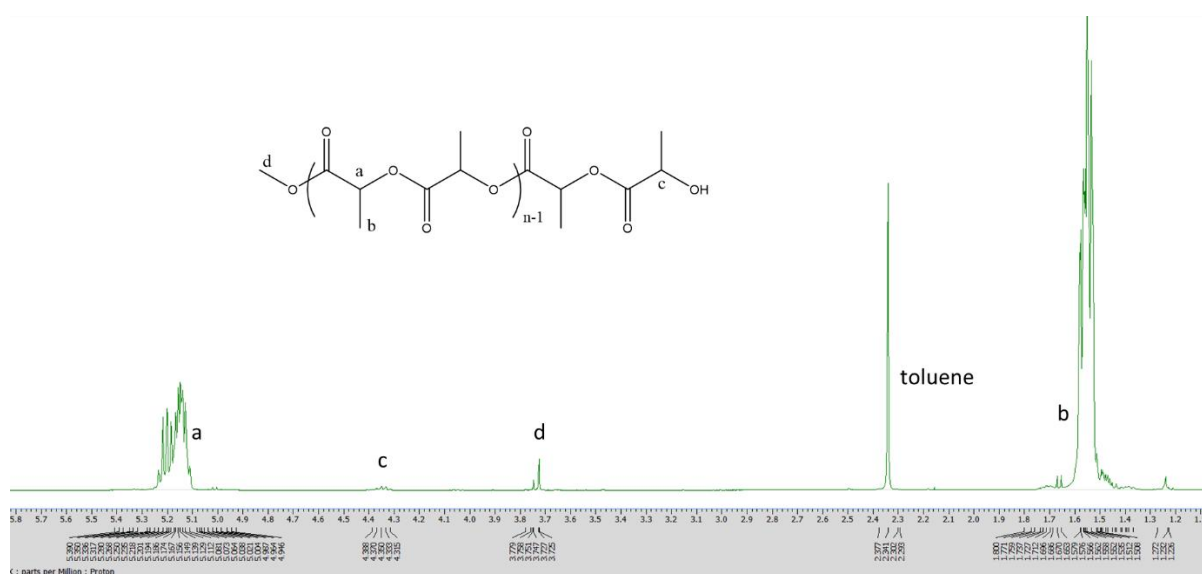


Figure S31.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using 1 (Table 3, entry 1).

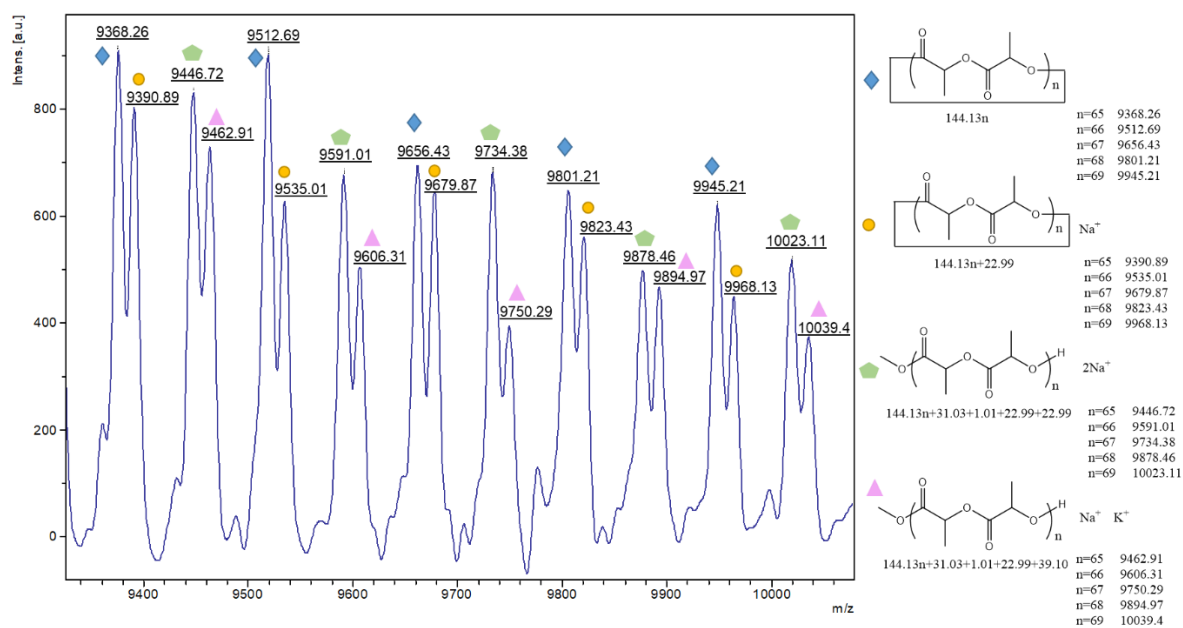
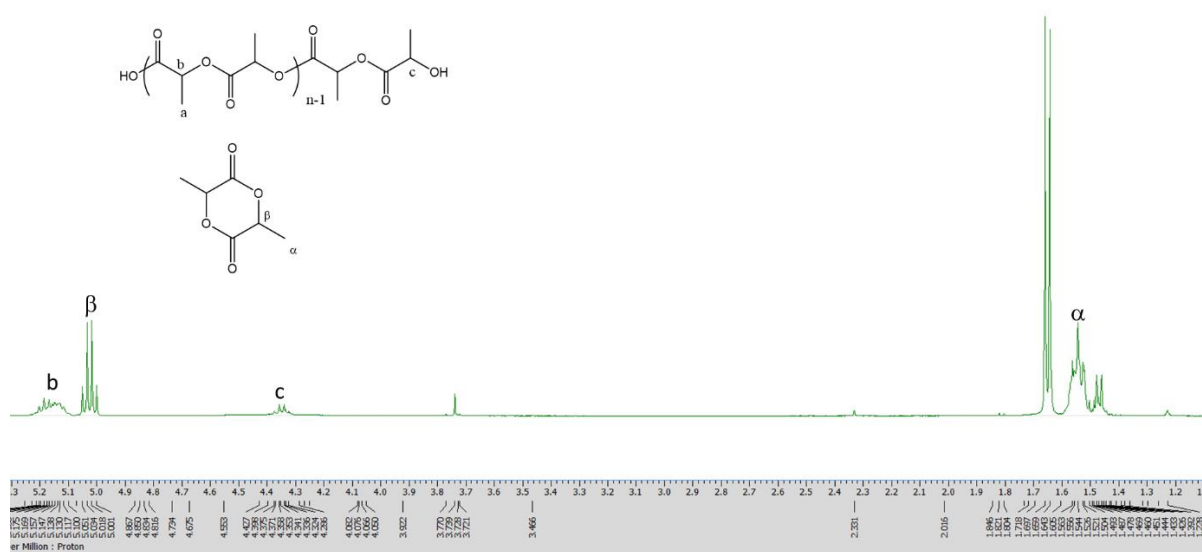
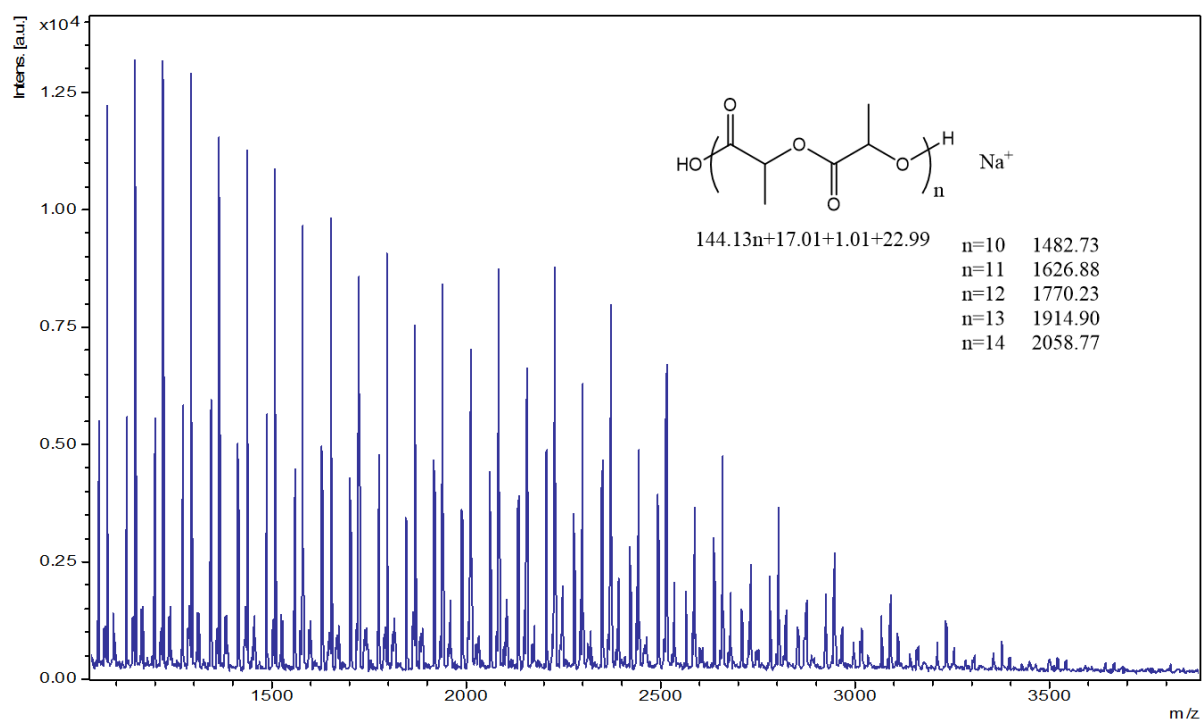


Figure S32. MALDI-TOF spectrum of PLA using 1 (Table 3, entry 1).



**Figure S33.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **2** (Table 3, entry 2).



**Figure S34.** MALDI-TOF spectrum of PLA using **2** (Table 3, entry 2).



Chemical structure of the polymer repeat unit and its <sup>1</sup>H NMR spectrum. The structure is a poly(ester) with a central repeat unit containing a methine proton labeled 'b'. The structure also shows a terminal unit with a methine proton labeled 'c' and a methyl group labeled 'd'. The spectrum shows peaks corresponding to these labels: 'b' at ~5.2 ppm, 'c' at ~4.3 ppm, 'd' at ~3.7 ppm, and 'e' at ~1.5 ppm. The x-axis is labeled 'parts per Million : Proton' and ranges from 5.4 to 1.2.

**Figure S36.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using **4** (Table 3, entry 4).

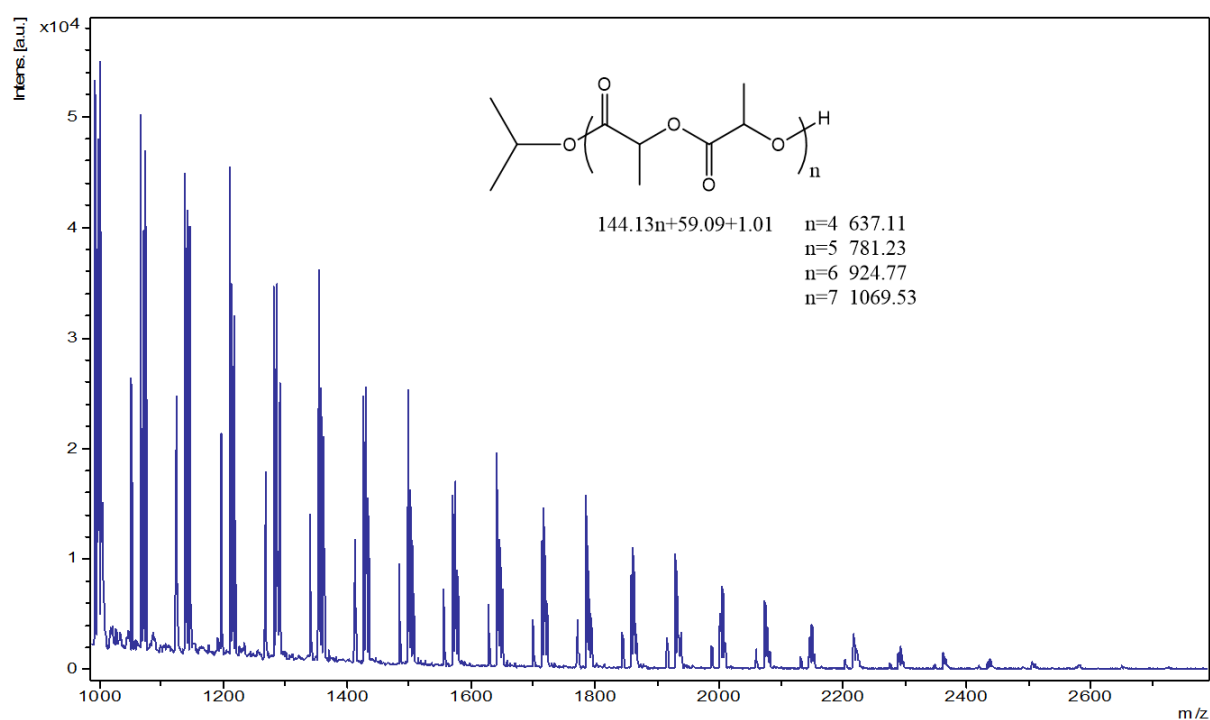


Figure S37. MALDI-TOF spectrum of PLA using 4 (Table 3, entry 4).

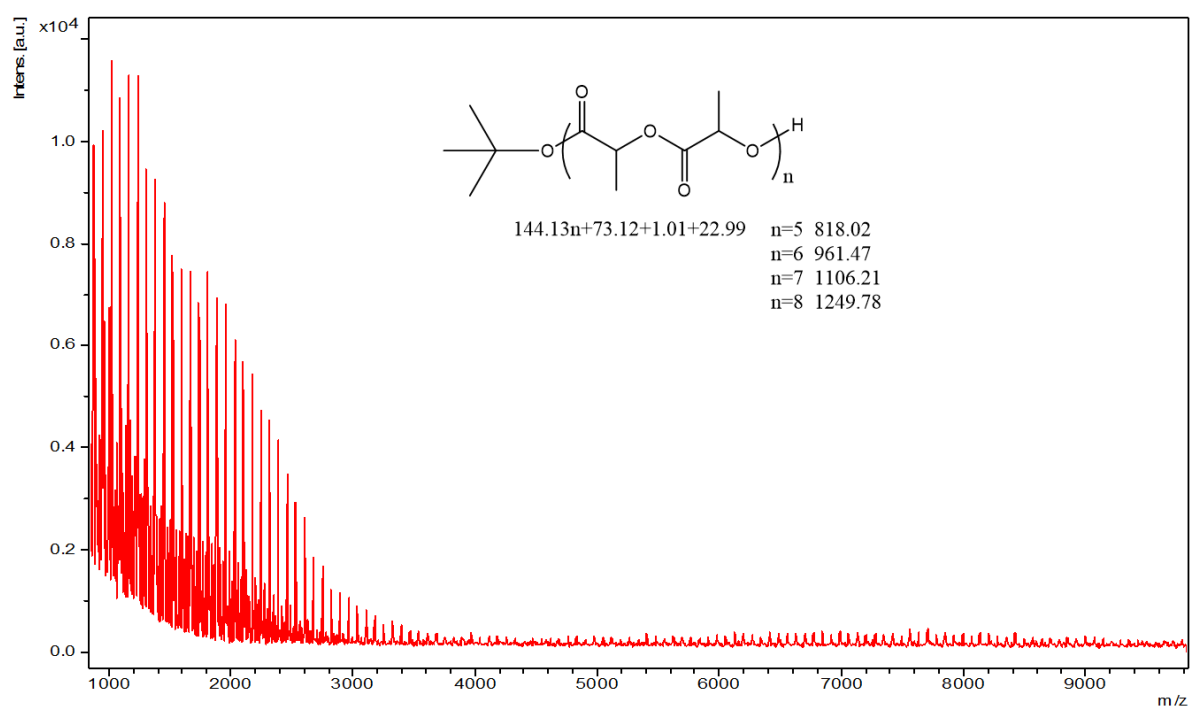
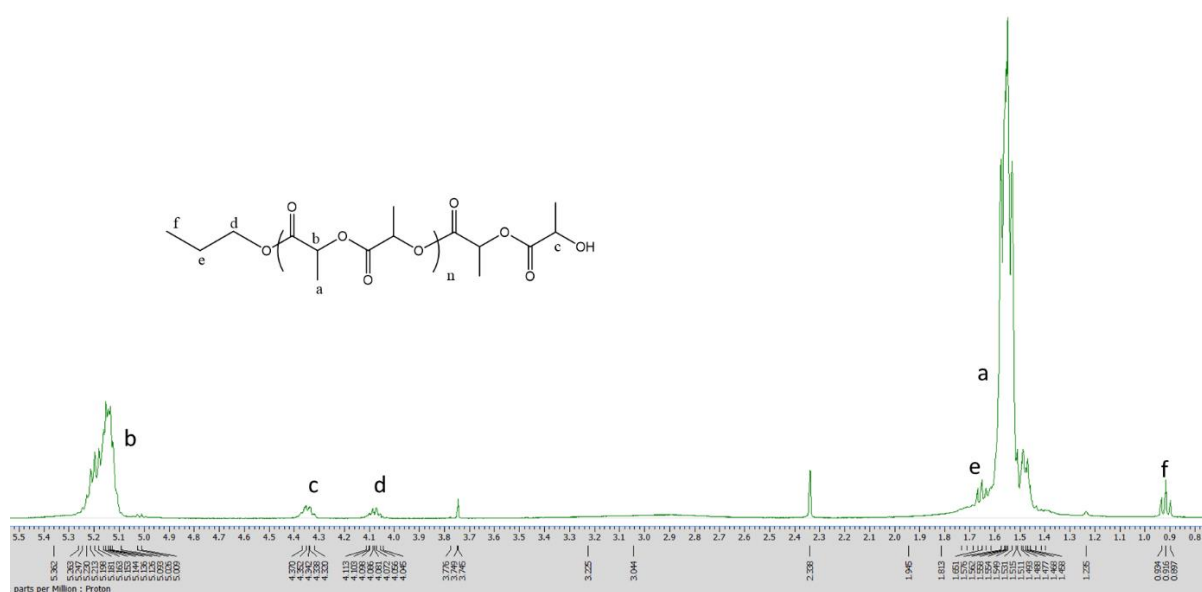
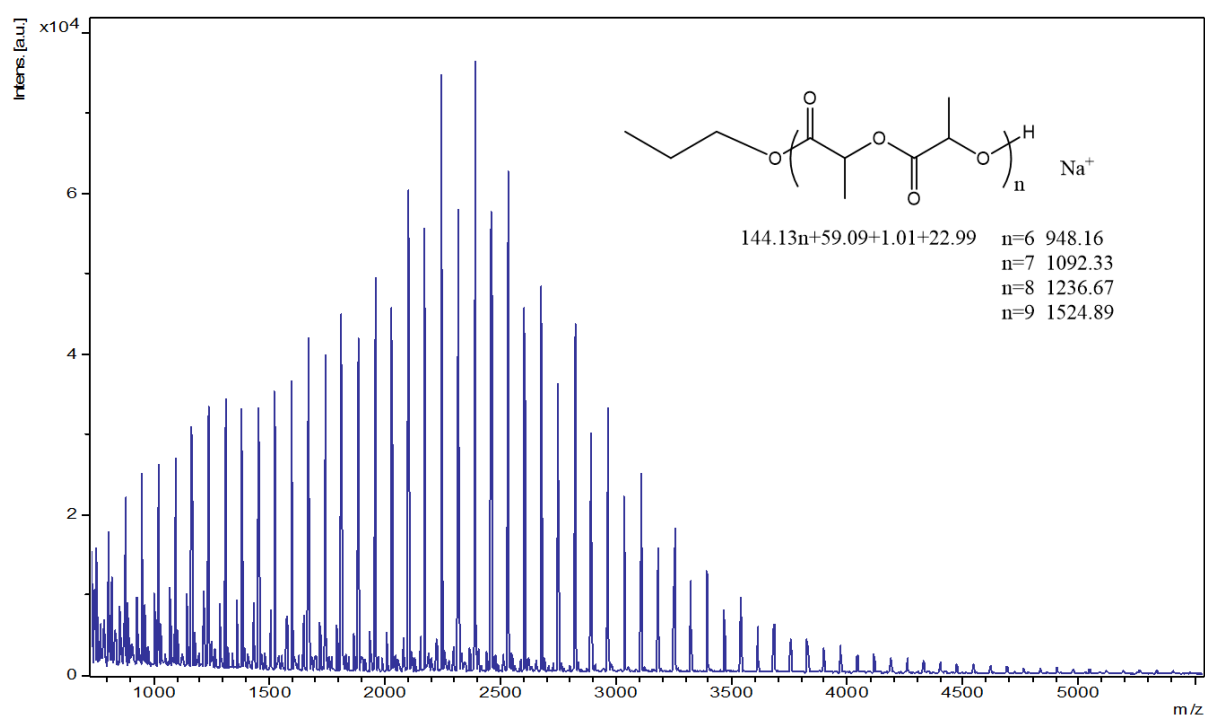


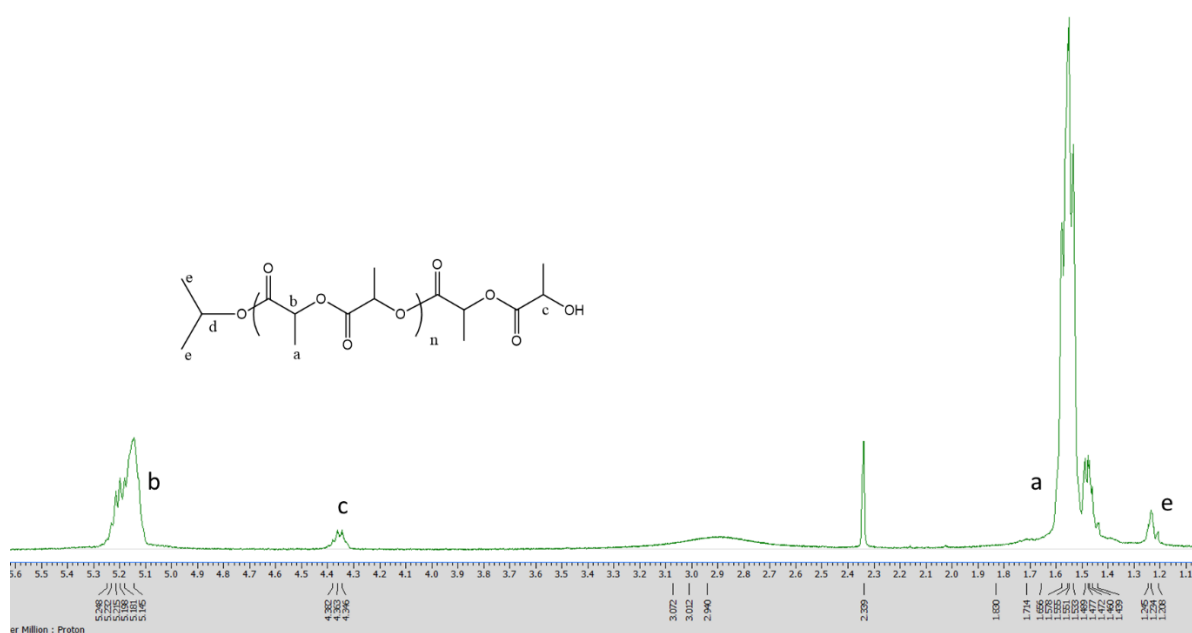
Figure S38. MALDI-TOF spectrum of PLA using 5 (Table 3, entry 5).



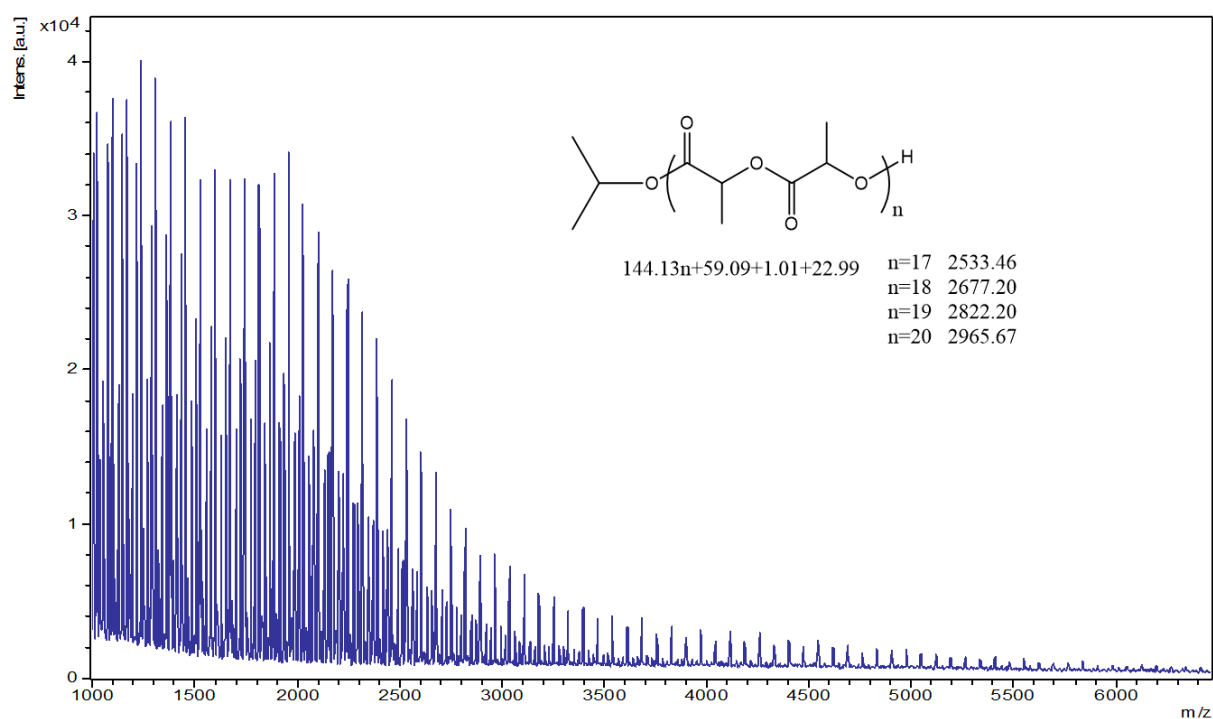
**Figure S39.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of PLA using 7 (Table 3, entry 7).



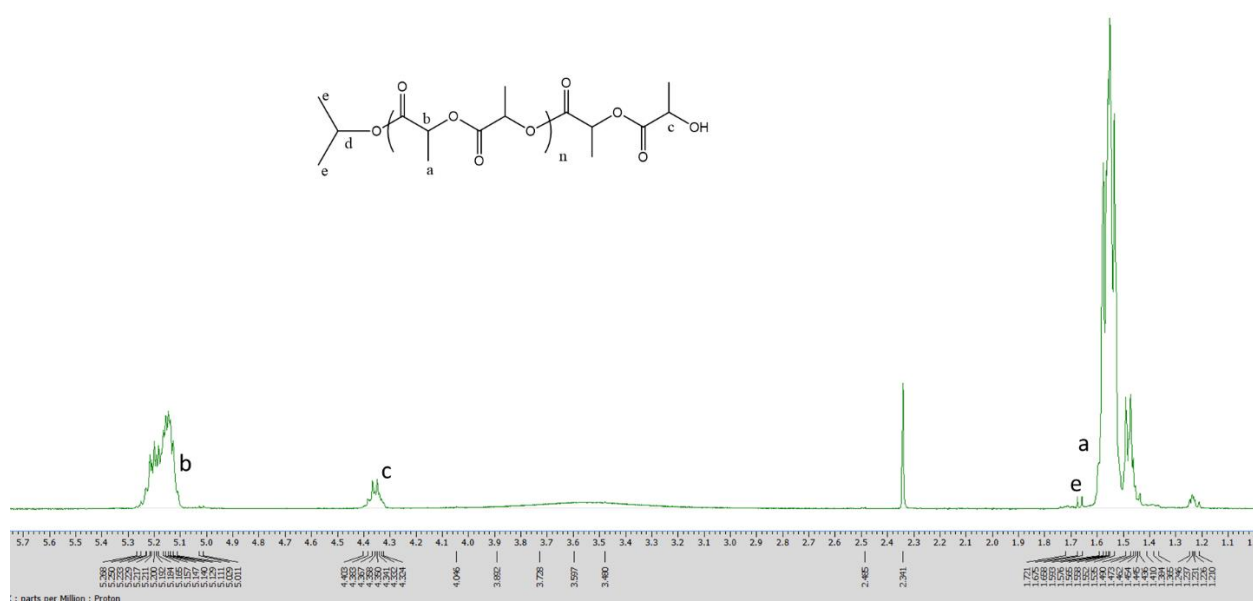
**Figure S40.** MALDI-TOF spectrum of PLA using 7 (Table 3, entry 7).



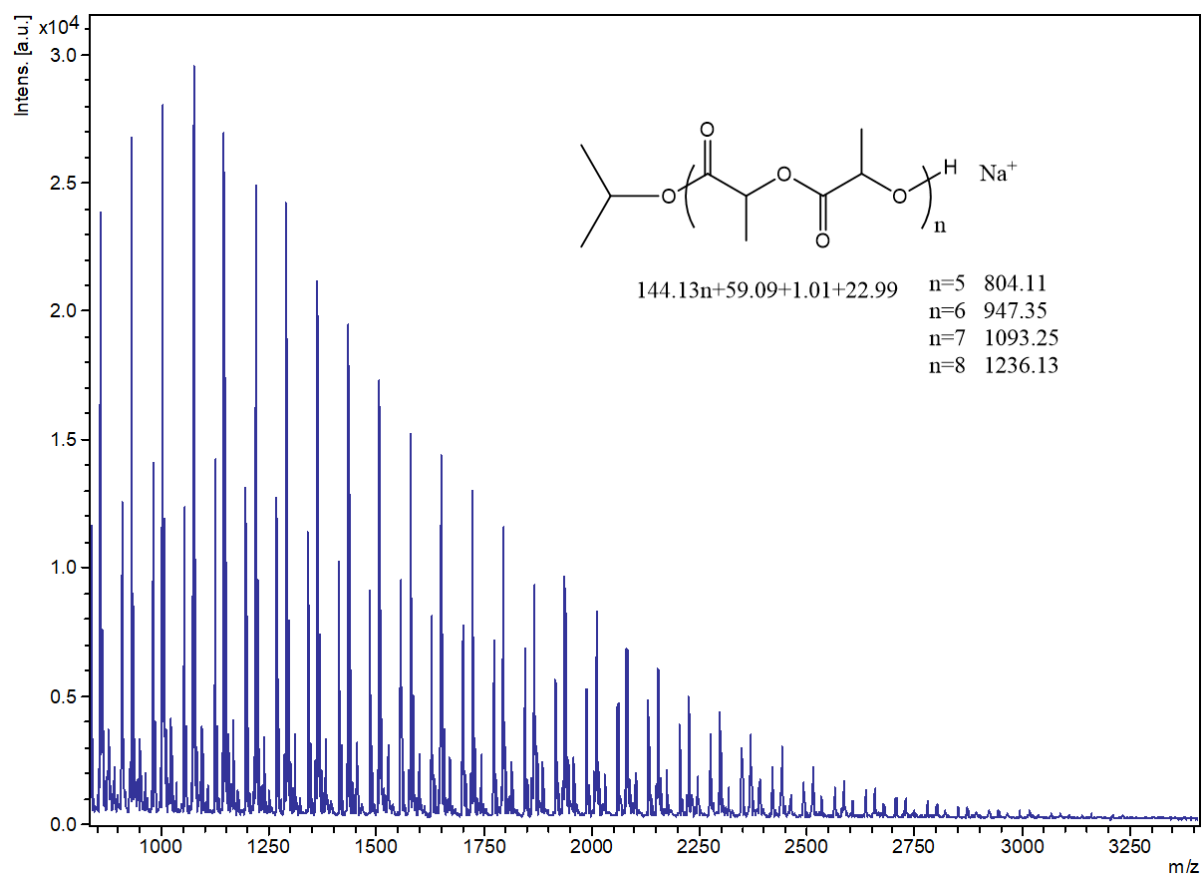
**Figure S41.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PLA using 8 (Table 3, entry 8).



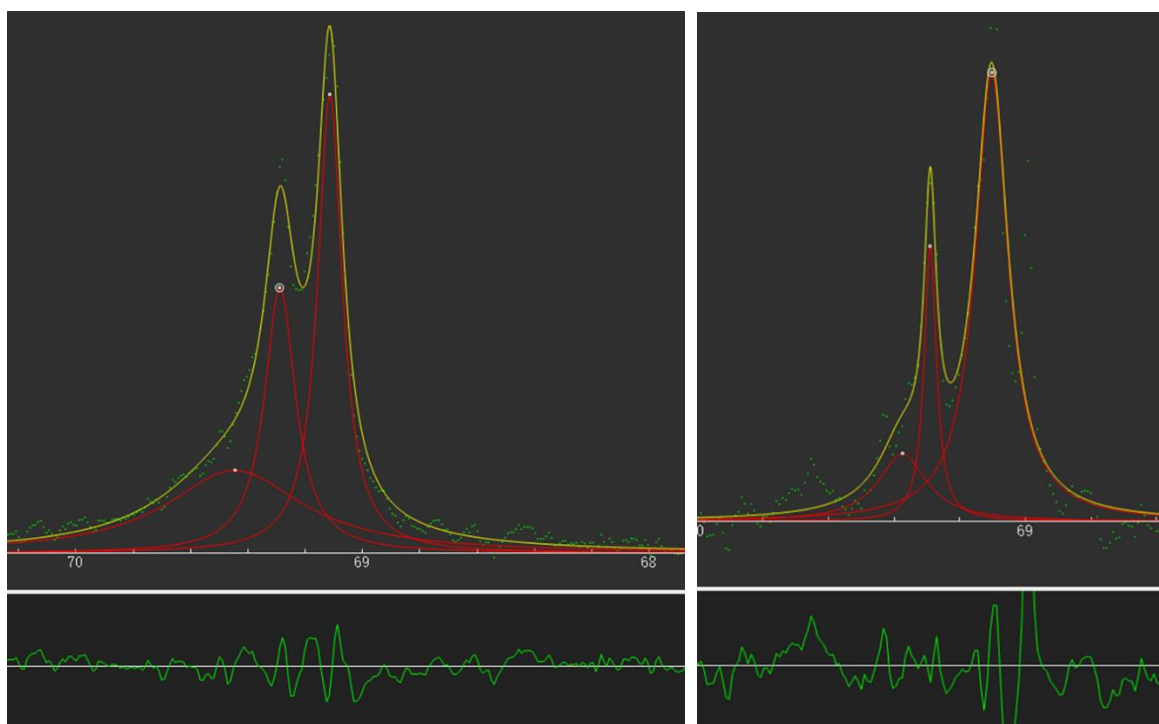
**Figure S42.** MALDI-TOF spectrum of PLA using 8 (Table 3, entry 8).



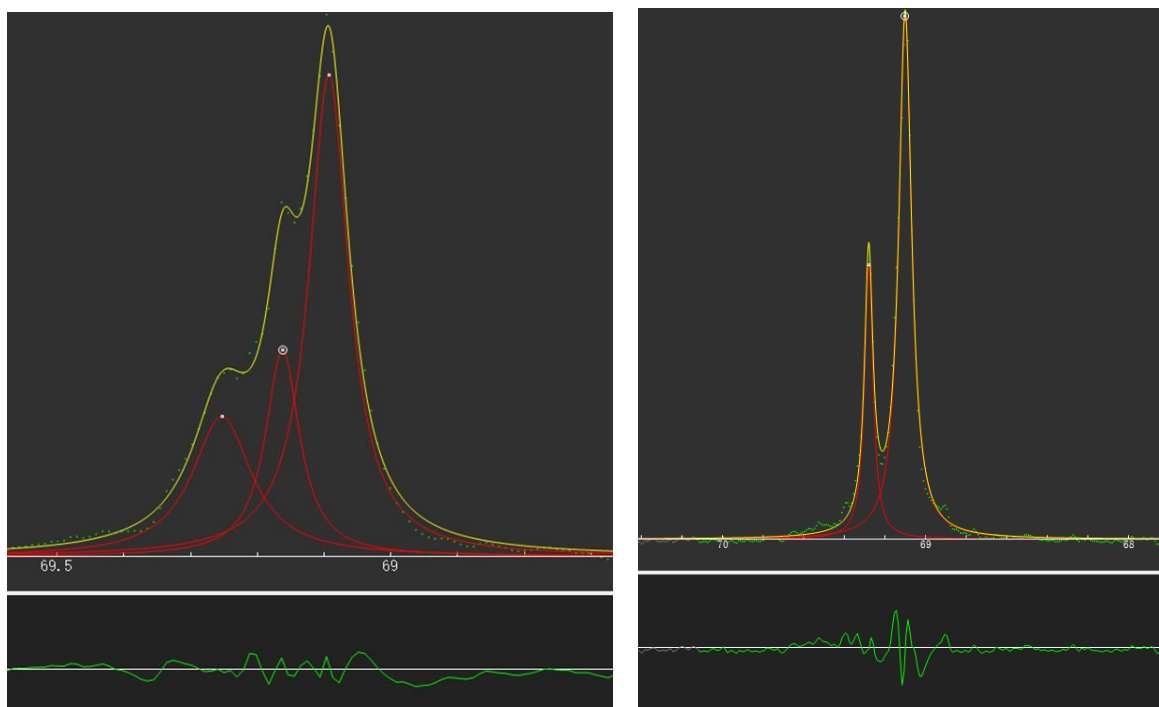
**Figure S43.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of PLA using **9** (Table 3, entry 9).



**Figure S44.** MALDI-TOF spectrum of PLA using **9** (Table 3, entry 9).

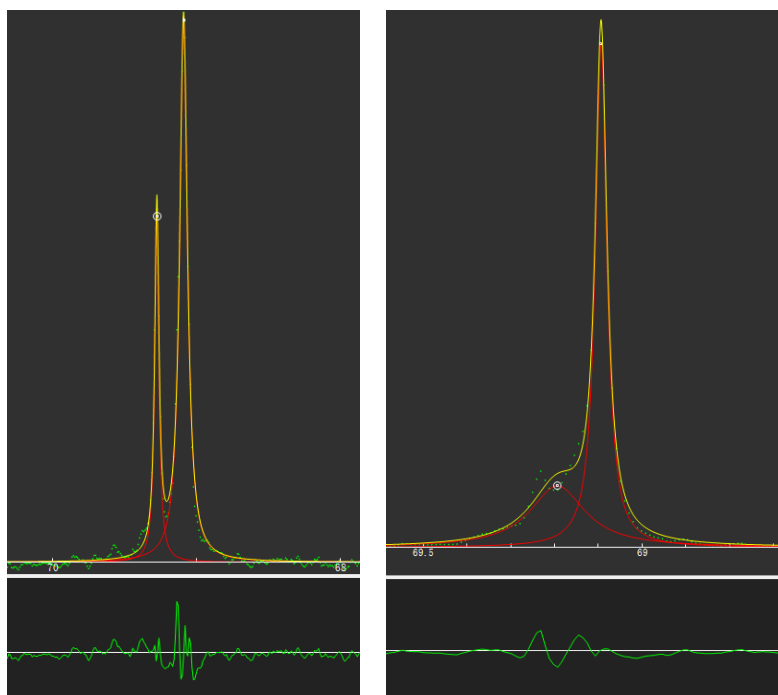


**Figure S45.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **1** (left) and **2** (right) (Table 3, entries 1 and 2).

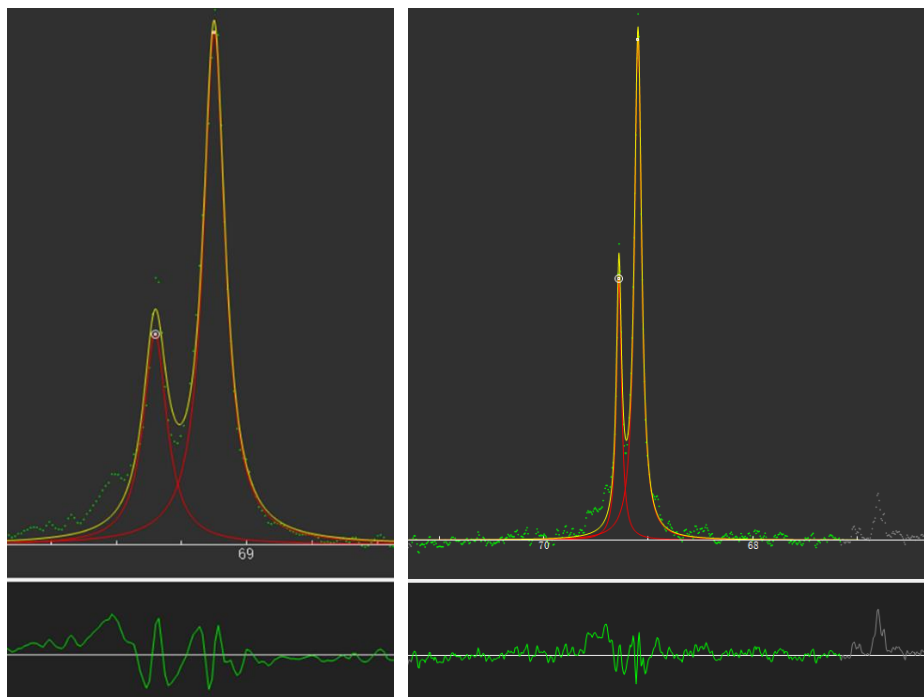


**Figure S46.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **3** (left) and **4** (right) (Table 3, entries 3 and 4).

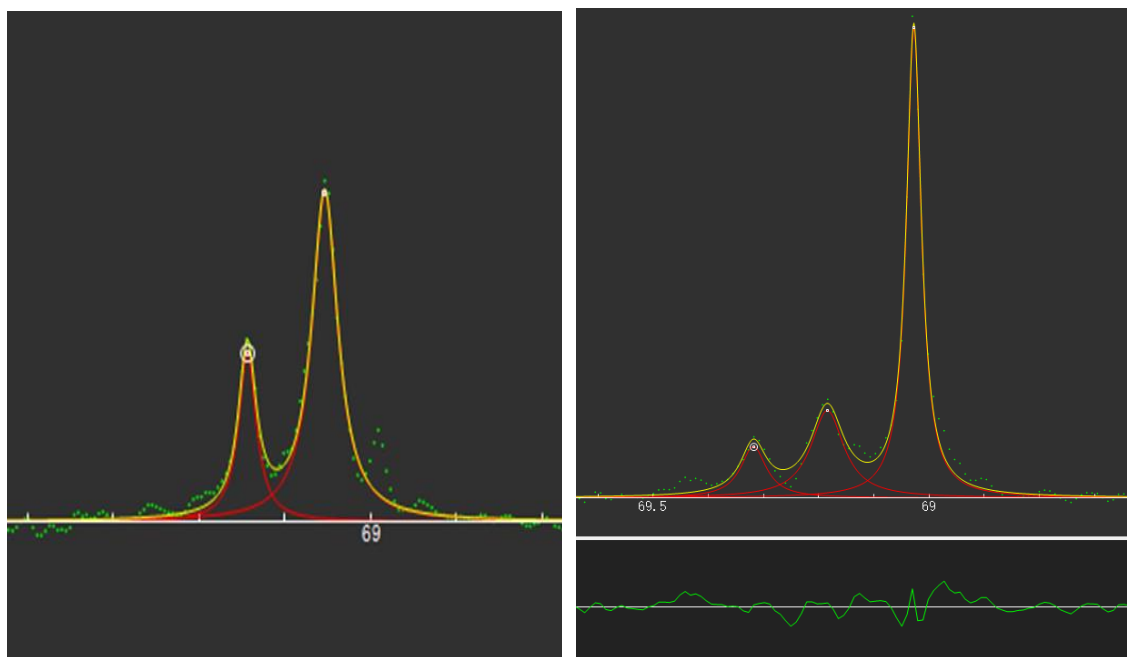




**Figure S47.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **5** (left) and **6** (right) (Table 3, entries 5 and 6).



**Figure S48.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **7** (left) and **8** (right) (Table 3, entries 7 and 8).



**Figure S49.**  $^{13}\text{C}$  NMR spectrum of methine carbon in PLA using **9** (left) and **10** (right) (Table 3, entries 9 and 10).

#### References

[S1] R. A. Coxall, S. G. Harris, D. K. Henderson, S. Parsons, P. A. Tasker, R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.* 2000, 14, 2349-2356.