Supporting Information

Solvothermal Alcoholysis Routes for Recycling Polylactide Waste as Lactic Acid Esters

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Table S1. The specifications of PLA resin used in alcoholysis reaction.

PLA used	M_n (kDa)[a]	M_w (kDa)[a]	PDI[a]	T_m (°C)[b]	T_{id} (°C)[b]	T_{max} (°C)[b]	Sn (mg/kg)[c]
PLLA Ingeo™ 2003D	102.6	137.9	1.34	150.9	331.5	354.9	6.8; 7.5
PLLA Naturesse® cup	73.5	100.1	1.37	152.3	328.5	355.1	15.9; 16.6
PDLA PURASORB® PD24	115.7	181.6	1.57	176.3	332.2	358.3	3.5; 3.6
PDLLA BIOCOP®	64.2	81.1	1.26	-	267.7	316.8	2.5; 2.6[d]

[a] Obtained from SEC analysis with MALLS detector. [b]Obtained from TGA/DTA analysis; T_m - melting point; T_{id} - initial temperature of degradation, T_{max} - temperature of maximum rate of degradation. [c] Sn content for 1kg of PLA, determined by ICP-OES technique. [d] Zr content for 1kg of PLA.

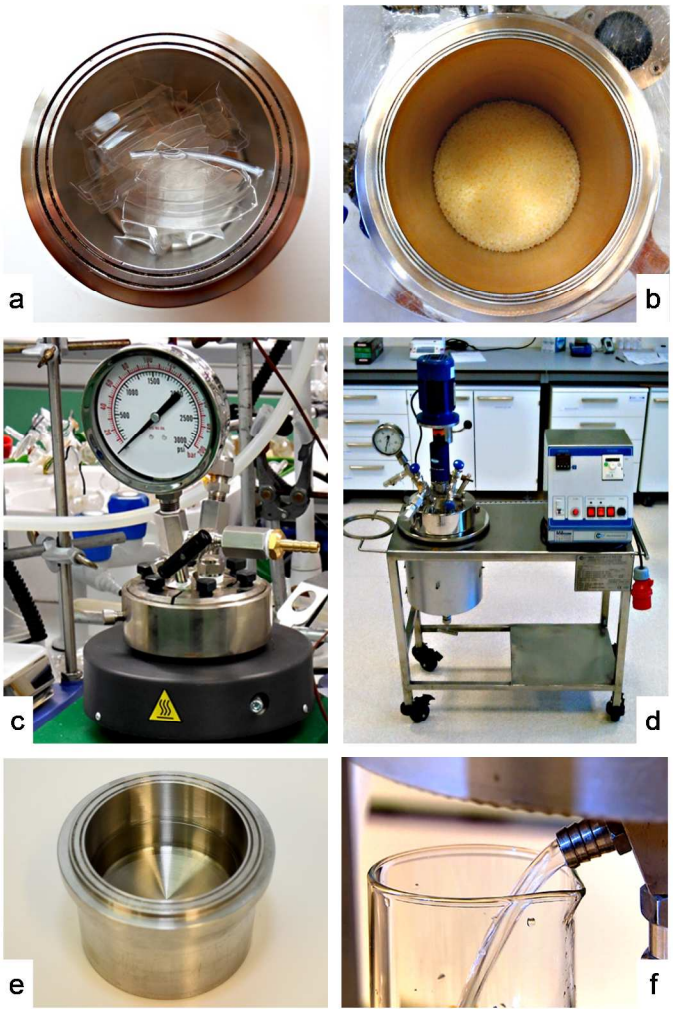

Figure S1. Reaction vessels loading with PLA residues of disposable packaging (a) or commercial granules (b). Pressure reactor with a capacity of 150 mL (c) or 5 L (d) loading with substrates. The liquid post reaction mixtures (e-f).

Table S2. Alcoholysis reaction of PLLA.[a]

No.	T (°C)	*la*/EtOH[b]	C_{EL} (%)[c]	C_{EL2} (%)[c]	P_{max} (bar)[d]
1	260	1/10	99	1	107
2	240	1/10	99	1	50
3	220	1/10	98	2	37
4	200	1/10	76	17	26
5	180	1/10	5	2	18
6	260	1/4	96	4	42
7	240	1/4	93	6	40
8	220	1/4	90	9	36
9	200	1/4	51	32	25
10	180	1/4	4	4	16
11	260	1/2	77	18	34
12	240	1/2	76	21	32
13	220	1/2	65	27	30
14	200	1/2	36	38	25
15	180	1/2	3	5	15
16	260	1/1	50	30	24
17	240	1/1	48	38	22
18	220	1/1	44	40	20
19	200	1/1	27	44	20
20	180	1/1	2	7	12

[a] Alcoholysis conditions: 10 g of PLLA (Ingeo™ 2003D) and from 8.1 to 81.1 mL of EtOH. Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants, through 1h. [b] Calculated based on the amount of EtOH per ester unit (*la*) in the polymer. [c] Obtained from ^{1}H NMR analysis according equation $C_{EL} = [EL]/[PLLA]_0$ and $C_{EL2} = 2[EL_2]/[PLLA]_0$. [d] The maximum pressure in the reactor observed throughout the course of the reaction.

Table S3. Alcoholysis reaction of PDLA and PDLLA.[a]

No.	T (°C)	PLA	*la*/EtOH[b]	C_{EL} (%)[c]	C_{EL2} (%)[c]	P_{max} (bar)[d]
1	260	PDLA	1/10	98	2	62
2	200	PDLA	1/10	55	27	33
3	260	PDLA	1/4	88	11	40
4	220	PDLA	1/4	58	30	31
5	200	PDLA	1/4	41	32	26
6	260	PDLA	1/2	71	18	28
7	200	PDLA	1/2	32	37	22
8	260	PDLA	1/1	40	26	14
9	200	PDLA	1/1	28	43	10
10	220	PDLLA	1/4	96	2	28
11	220	PDLLA	1/2	81	11	18
12	200	PDLLA	1/1	31	50	6

[a] Alcoholysis conditions: 5 g of PLA (PDLA PURASORB® PD24, PDLLA BIOCOP®) and from 4.1 to 40.6 mL of EtOH. Reaction performed using pressure reactor with a capacity of 150 ml, under N_2 atmosphere and autogenous pressure of reactants, through 1h. [b] Calculated based on the amount of EtOH per ester unit (*la*) in the polymer. [c] Obtained from ^{1}H NMR analysis according equation $C_{EL} = [EL]/[PLA]_0$ and $C_{EL2} = 2[EL_2]/[PLA]_0$. [d] The maximum pressure in the reactor observed throughout the course of the reaction.

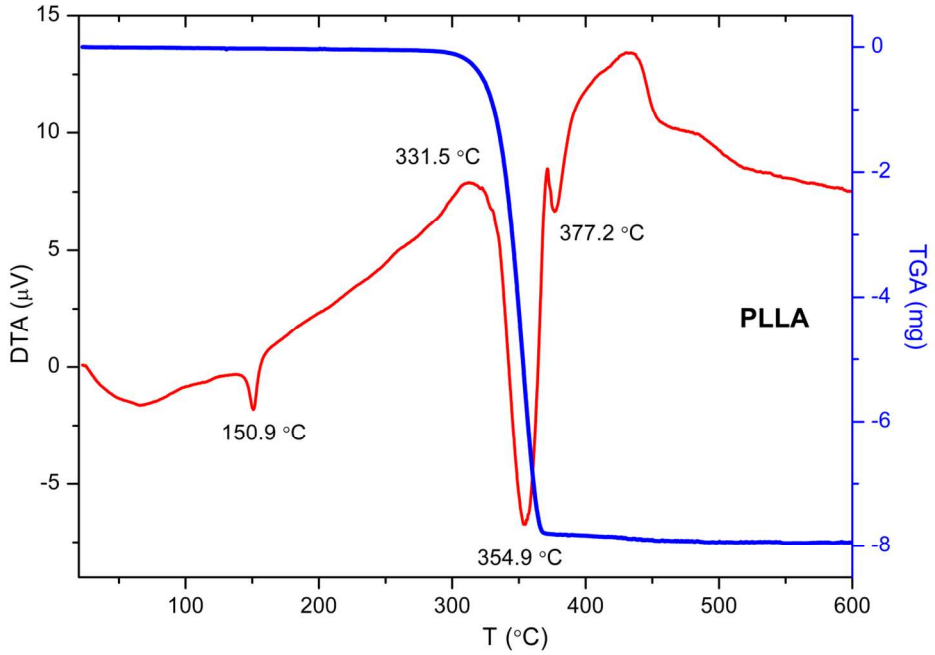

Figure S2. TGA-DTA thermograms of PLLA.

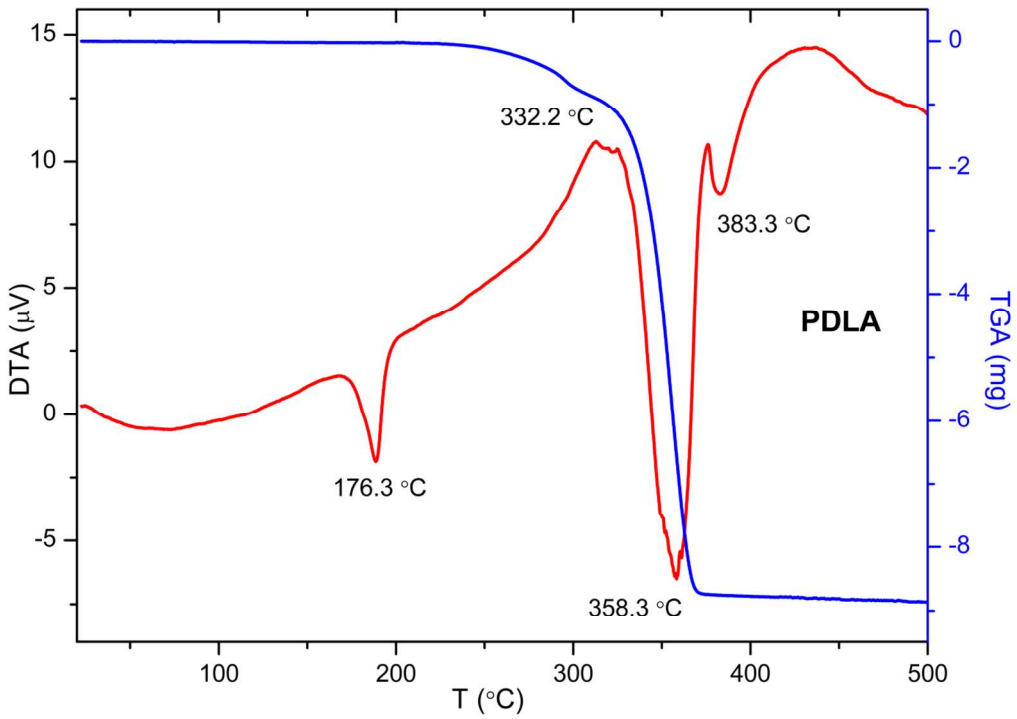

Figure S3. TGA-DTA thermograms of PDLA.

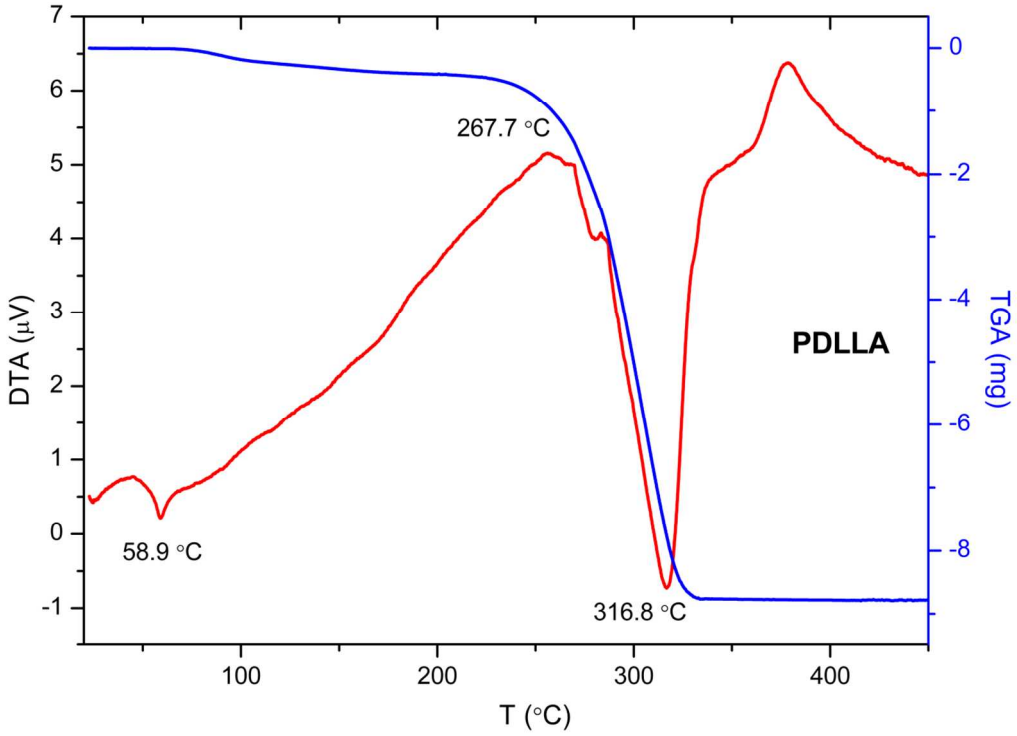

Figure S4. TGA-DTA thermograms of PDLLA.

Table S4. Alcoholysis reaction of PLLA using $MgBu_2$ as precatalyst.[a]

No.	T (°C)	*la*/EtOH/Mg[b]	C_{EL} (%)[c]	C_{EL2} (%)[c]	P_{max} (bar)[d]
1	200	1/10/0.01	98	2	24
2	180	1/10/0.01	98	2	15
3	160	1/10/0.01	97	3	10
4	140	1/10/0.01	96	4	6
5	120	1/10/0.01	96	4	<6
6	100	1/10/0.01	88	9	<6
7[e]	80	1/10/0.01	10	0	<6
8	200	1/4/0.01	98	2	19
9	180	1/4/0.01	96	4	12
10	160	1/4/0.01	95	5	8
11	140	1/4/0.01	95	5	6
12	120	1/4/0.01	84	6	<6
13[e]	100	1/4/0.01	71	8	<6
14[e]	80	1/4/0.01	8	0	<6
15	200	1/2/0.01	90	9	11
16	180	1/2/0.01	89	9	8
17	160	1/2/0.01	88	11	6
18	150	1/2/0.01	77	12	<6
19	140	1/2/0.01	70	13	<6
20	120	1/2/0.01	60	10	<6
21[e]	100	1/2/0.01	43	6	<6
22[e]	80	1/2/0.01	9	0	<6
23	220	1/1/0.01	66	22	8
24	200	1/1/0.01	65	22	7
25	180	1/1/0.01	61	23	6
26	160	1/1/0.01	47	15	<6
27	140	1/1/0.01	35	7	<6
28[e]	120	1/1/0.01	26	6	<6
29[e]	100	1/1/0.01	23	6	<6
30[e]	80	1/1/0.01	9	0	<6

[a] Alcoholysis conditions: 1.39 mL of $MgBu_2$, 10 g of PLLA (Ingeo™ 2003D) and from 8.1 to 81.1 mL of EtOH. Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants, through 1h. [b] Calculated based on the amount of EtOH per ester unit (*la*) in the polymer. [c] Obtained from ^{1}H NMR analysis according equation C_{EL} = [EL]/[PLLA]$_0$ and C_{EL2} = 2[EL$_2$]/[PLLA]$_0$. [d] The maximum pressure in the reactor observed throughout the course of the reaction. [e] Calculated based on ^{1}H NMR analysis and the amount of isolated solid PLLA.

Table S5. Alcoholysis reaction of PLA using as starting material PLLA cup, PDLA and PDLLA resins and $MgBu_2$ as precatalyst.[a]

No.	T (°C)	*la*/EtOH/Mg[b]	C_{EL} (%)[c]	C_{EL2} (%)[c]	P_{max} (bar)[d]
1[e]	200	1/4/0.01	91	5	18
2[e]	200	1/2/0.01	83	15	12
3[e]	200	1/1/0.01	48	30	10
4[f]	200	1/4/0.01	97	2	7
5[g]	200	1/4/0.01	94	6	19

[a] Alcoholysis conditions: 1.39 mL of $MgBu_2$, 10 g of PLA (PLLA Naturesse® cup, PDLA PURASORB® PD24, PDLLA BIOCOP®) and from 8.1 to 32.4 mL of EtOH. Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants, through 1h. [b] Calculated based on the amount of EtOH per ester unit (*la*) in the polymer. [c] Obtained from ^{1}H NMR analysis according equation C_{EL} = [EL]/[PLA]$_0$ and C_{EL2} = 2[EL$_2$]/[PLA]$_0$. [d] The maximum pressure in the reactor observed throughout the course of the reaction. [e e-g] Using as starting material PLLA cup (*e*), PDLLA (*f*) or PDLA (*g*).

Table S6. Alcoholysis reaction of PLLA conducted at varying amounts of $MgBu_2$.[a]

No.	*la*/EtOH/Mg[b]	C_{EL} (%)[c]	C_{EL2} (%)[c]	P_{max} (bar)[d]
1	1/4/0.01	98	2	19
2	1/4/0.0075	88	4	20
3	1/4/0.005	76	12	21
4	1/4/0.0025	68	19	23
5	1/2/0.01	90	9	11
6	1/2/0.0075	78	14	13
7	1/2/0.005	54	23	20
8	1/2/0.0025	47	29	22

[a]Alcoholysis conditions: from 0.35 to 1.39 mL of $MgBu_2$, 10 g of PLLA (Ingeo™ 2003D) and from 16.2 to 32.4 mL of EtOH. Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants, at temperature of 200 °C, through 1h. [b] Calculated based on the amount of EtOH per ester unit (*la*) in the polymer. [c] Obtained from ^{1}H NMR analysis according equation C_{EL} = [EL]/[PLLA]$_0$ and C_{EL2} = 2[EL$_2$]/[PLLA]$_0$. [d] The maximum pressure in the reactor observed throughout the course of the reaction.

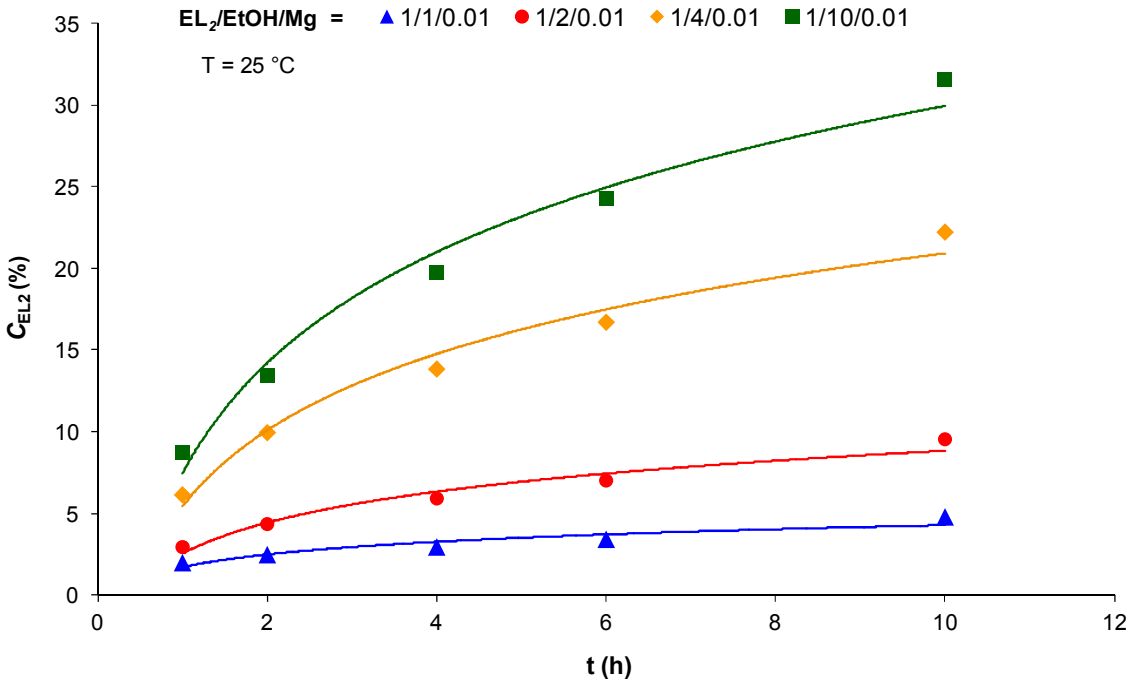

Figure S5. Effect of alcohol amount on the ethanolysis of EL_2 at 25 °C.

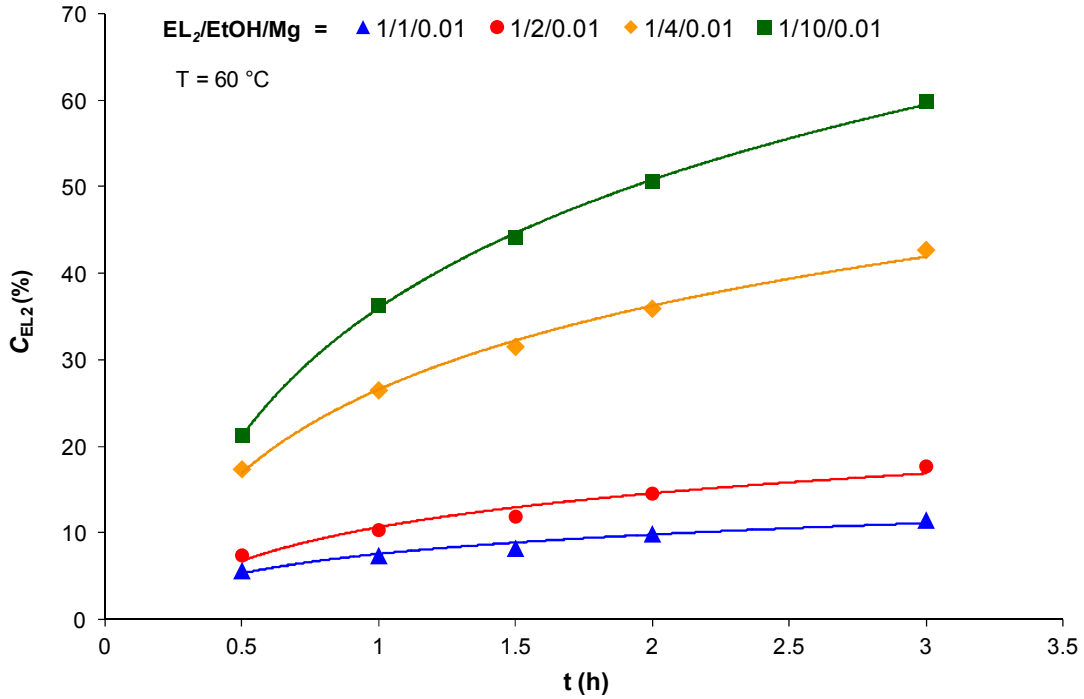

Figure S6. Effect of alcohol amount on the ethanolysis of EL_2 at 60 °C.

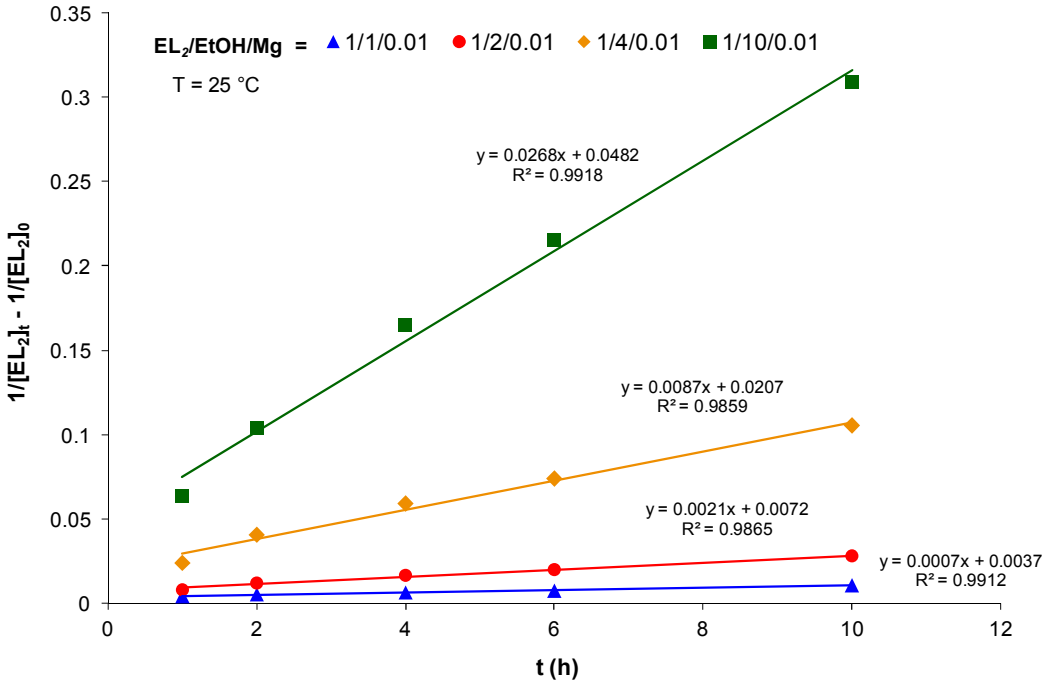

Figure S7. Linear plots of $1/[EL_2]_t - 1/[EL_2]_0$ vs time demonstrating the second order dependence on monomer concentration, study performed at 25 °C.

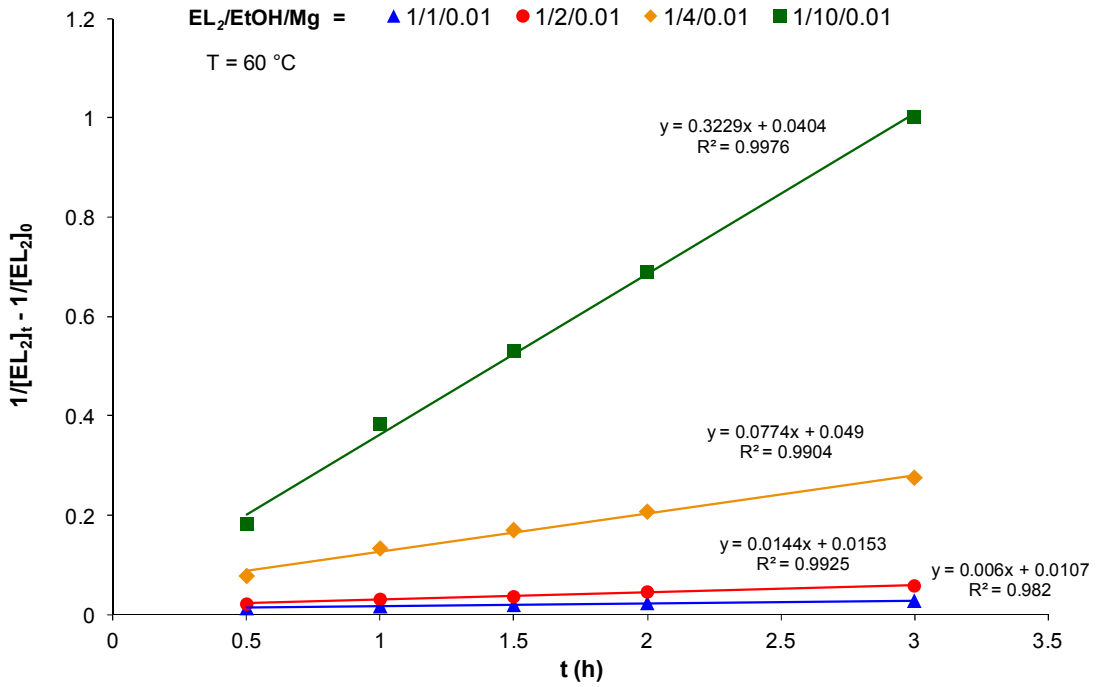

Figure S8. Linear plots of $1/[EL_2]_t - 1/[EL_2]_0$ vs time demonstrating the second order dependence on monomer concentration, study performed at 60 °C.

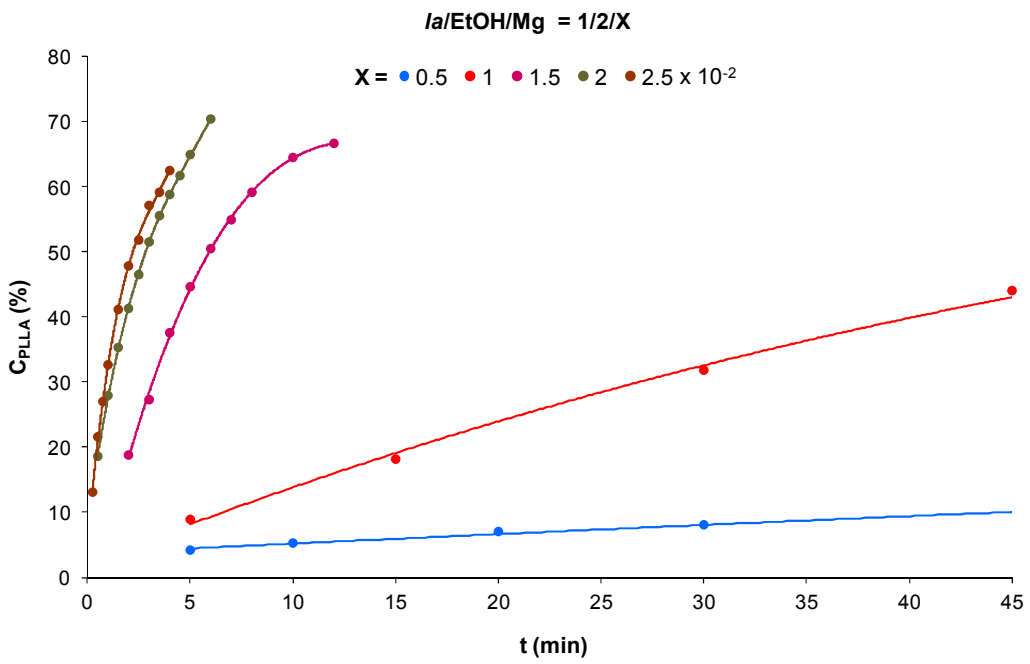

Figure S9. Effect of catalyst amount on the alcholysis of PLLA at reactants stoichiometry *la*/EtOH/Mg = 1/2/0.005, 0.01, 0.015, 0.02, 0.025 ($[la]_0$ = 0.5 M; [Mg] = 2.5, 5, 7.5, 10, 12.5 mM in toluene at 90 °C).

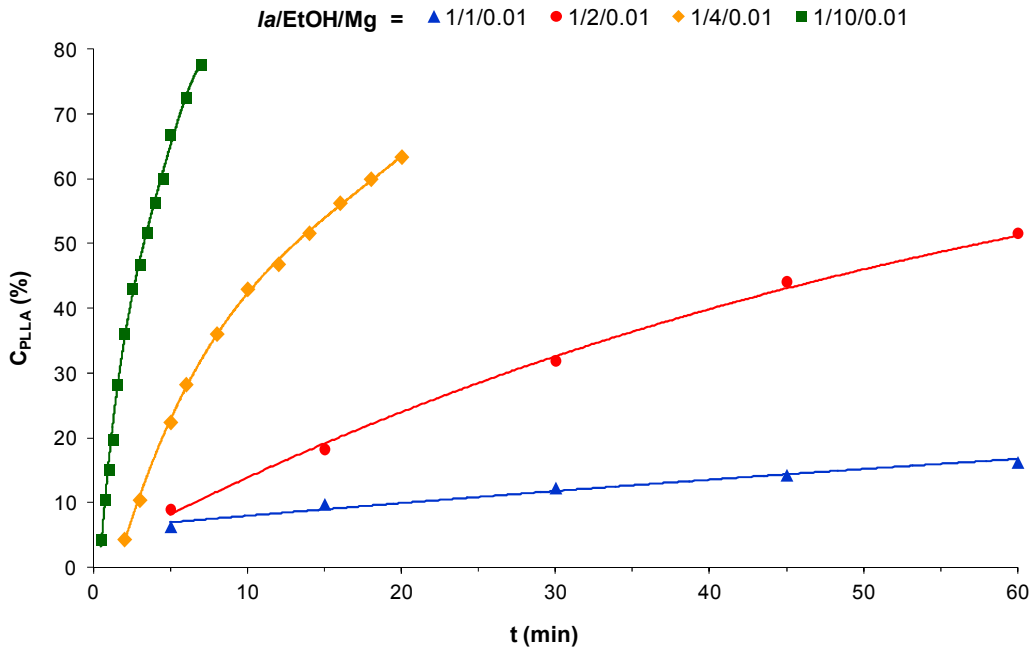

Figure S10. Effect of alcohol amount on the PLLA alcoholysis at reactants stoichiometry *la*/EtOH/Mg = 1/1, 2, 4, 10/0.01 ($[la]_0$ = 0.5 M; [EtOH] = 0.5, 1, 2, 5 M in toluene at 90 °C).

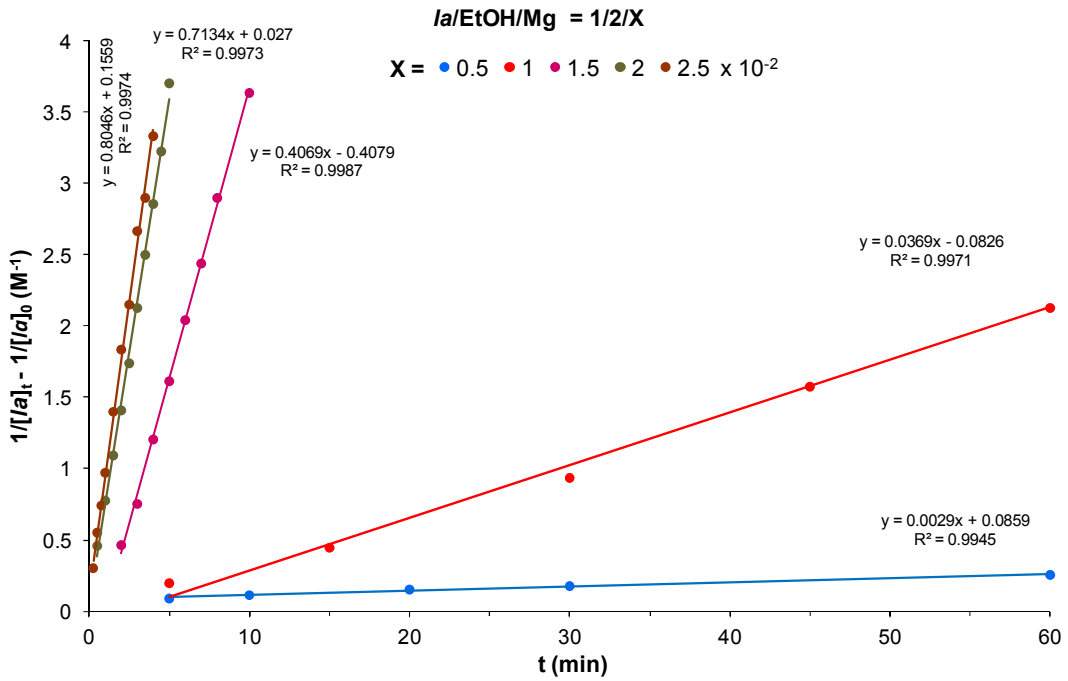

Figure S11. Linear plots of ($1/[la]_t$ - $1/[la]_0$) *vs.* time for the PLLA alcoholysis at reactants stoichiometry *la*/EtOH/Mg = 1/2/0.005, 0.01, 0.015, 0.02, 0.025 ($[la]_0$ = 0.5 M; [Mg] = 2.5, 5, 7.5, 10, 12.5 mM in toluene at 90 °C).

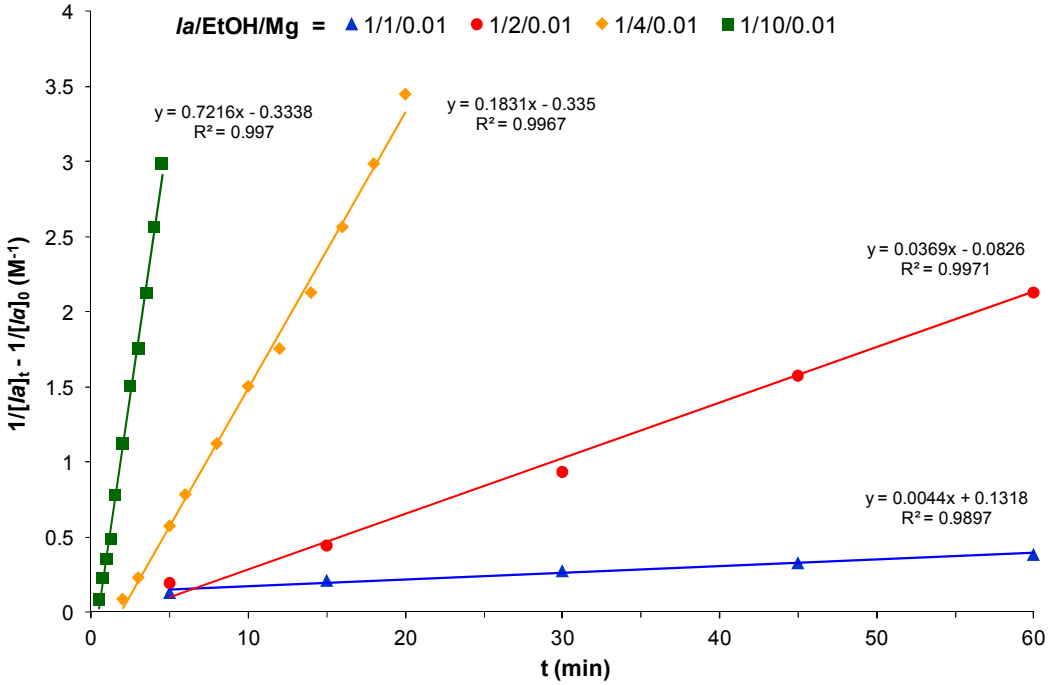

Figure S12. Linear plots of ($1/[la]_t$ - $1/[la]_0$) *vs.* time for the PLLA alcoholysis at reactants stoichiometry *la*/EtOH/Mg = 1/1, 2, 4, 10/0.01 ($[la]_0$ = 0.5 M; [EtOH] = 0.5, 1, 2, 5 M in toluene at 90 °C).

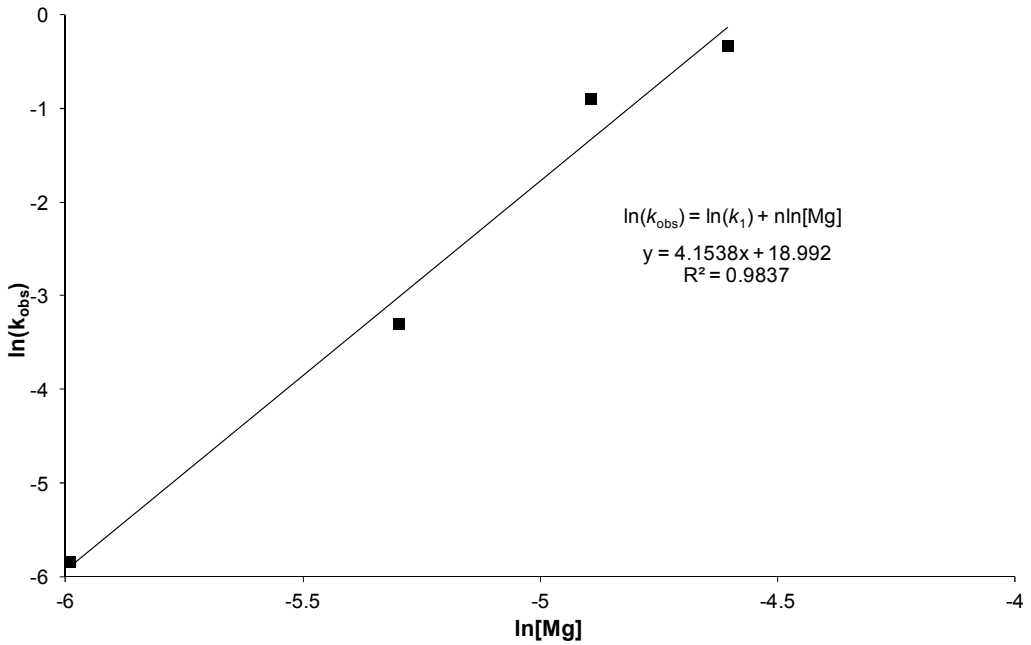

Figure S13. Plot of ln(k_{obs}) *vs*. ln[Mg] for the PLLA alcoholysis.

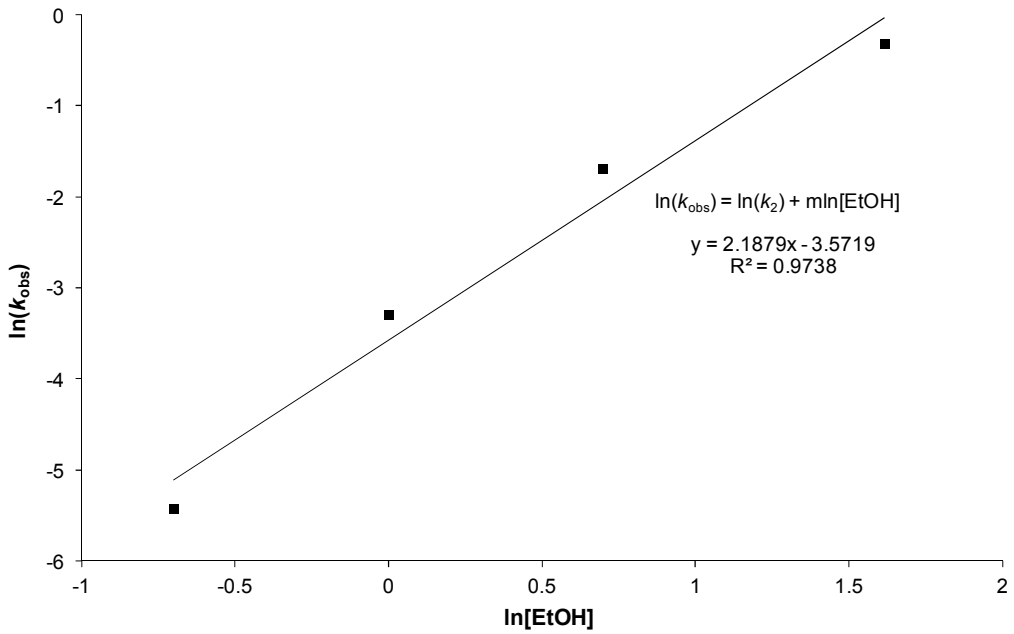

Figure S14. Plot of ln(k_{obs}) *vs*. ln[EtOH] for the PLLA alcoholysis.

Table S7. Alcoholysis reaction of PLLA using different butanol isomers or sterically hindered cyclic alcohols and phenol.[a]

No.	ROH	T (°C)	C_{AL} (%)[b]	C_{AL2} (%)[b]	P_{max} (bar)[c]
1	iBuOH	200	76	17	8
2	iBuOH	160	42	8	<6
3	nBuOH	200	53	19	7
4	nBuOH	160	29	8	<6
5	sBuOH	200	41	26	9
6	sBuOH	160	28	9	<6
7	tBuOH	200	6	1	23
8	tBuOH	160	4	4	8
9	CypOH	200	27	14	<6
10	CypOH	160	8	5	<6
11	CyOH	200	29	6	<6
12	CyOH	160	6	0	<6
13	PhOH	200	0	0	<6
14	PhOH	160	0	0	<6

[a] Alcoholysis conditions: *la*/ROH/Mg = 1/2/0.01, 10g of PLLA (IngeoTM 2003D). Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants. [b] Obtained from ^{1}H NMR analysis according equation C_{AL} = [AL]/[PLLA]$_0$ and C_{AL2} = 2[AL$_2$]/[PLLA]$_0$. [c] The maximum pressure in the reactor observed throughout the course of the reaction.

Table S8. Alcoholysis reaction of PLLA using electron rich and poor alcohols.[a]

No.	ROH	T (°C)	C_{AL} (%)[b]	C_{AL2} (%)[b]	P_{max} (bar)[c]
1	$(CH_3)_2NCH_2CH_2OH$	200	98	0	7
2	$(CH_3)_2NCH_2CH_2OH$	160	83	14	<6
3	$CH_3OCH_2CH_2OH$	200	75	19	<6
4	$CH_3OCH_2CH_2OH$	160	42	8	<6
5	$CH_3OCH_2CH_2OH$	140	28	8	<6
6	$PhCH_2CH_2OH$	200	37	11	<6
7	$PhCH_2CH_2OH$	160	12	3	<6
8	$PhCH_2OH$	200	15	11	<6
9	$PhCH_2OH$	160	3	0	<6
10	CF_3CH_2OH	200	26	24	21
11	CF_3CH_2OH	160	19	17	10
12	CF_3CH_2OH	140	10	8	<6
13	CCl_3CH_2OH	200	6	9	<6
14	CCl_3CH_2OH	160	0	0	<6
15[d]	CBr_3CH_2OH	160	-	-	85

[a] Alcoholysis conditions: *la*/ROH/Mg = 1/2/0.01, 10g of PLLA (IngeoTM 2003D). Reaction performed using pressure reactor with a capacity of 150 mL, under N_2 atmosphere and autogenous pressure of reactants. [b] Obtained from ^{1}H NMR analysis according equation C_{AL} = [AL]/[PLLA]$_0$ and C_{AL2} = 2[AL$_2$]/[PLLA]$_0$. [c] The maximum pressure in the reactor observed throughout the course of the reaction. [d] Deconstruction under heating

Table S9. Crystal and data collection parameters for compounds **1-2.**

	1	**2**
Chemical formula	$C_{16}H_{30}CaO_{12}$	$C_{20}H_{40}CaCl_2O_{12}$
Formula Mass	454.48	583.50
Crystal system	Monoclinic	Triclinic
Space group	*C2*	*P*1
a/Å	19.697(3)	8.768(7)
b/Å	5.855(2)	9.508(6)
c/Å	9.532(3)	10.629(10)
α/°		97.45(3)
β/°	95.80 (2)	100.88(3)
γ/°		117.39(3)
Unit cell volume/$Å^3$	1093.7(5)	748.4(11)
Temperature/K	80(2)	100(2)
Z	2	1
Radiation type	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	0.344	3.908
No. of reflections measured	4054	5453
No. of independent reflections	1892	3523
No. of obsevred reflections ($I > 2\sigma(I)$)	1350	3338
R_{int}	0.0826	0.0574
Final R_1 values ($I > 2\sigma(I)$)	0.0993	0.0565
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1847	0.1434
Final R_1 values (all data)	0.1457	0.0604
Final $wR(F^2)$ values (all data)	0.2125	0.1614
Goodness of fit on F^2	1.121	1.074
Δρmax/e$Å^{-3}$	0.74	0.52
Δρmin/e$Å^{-3}$	-0.46	-0.63

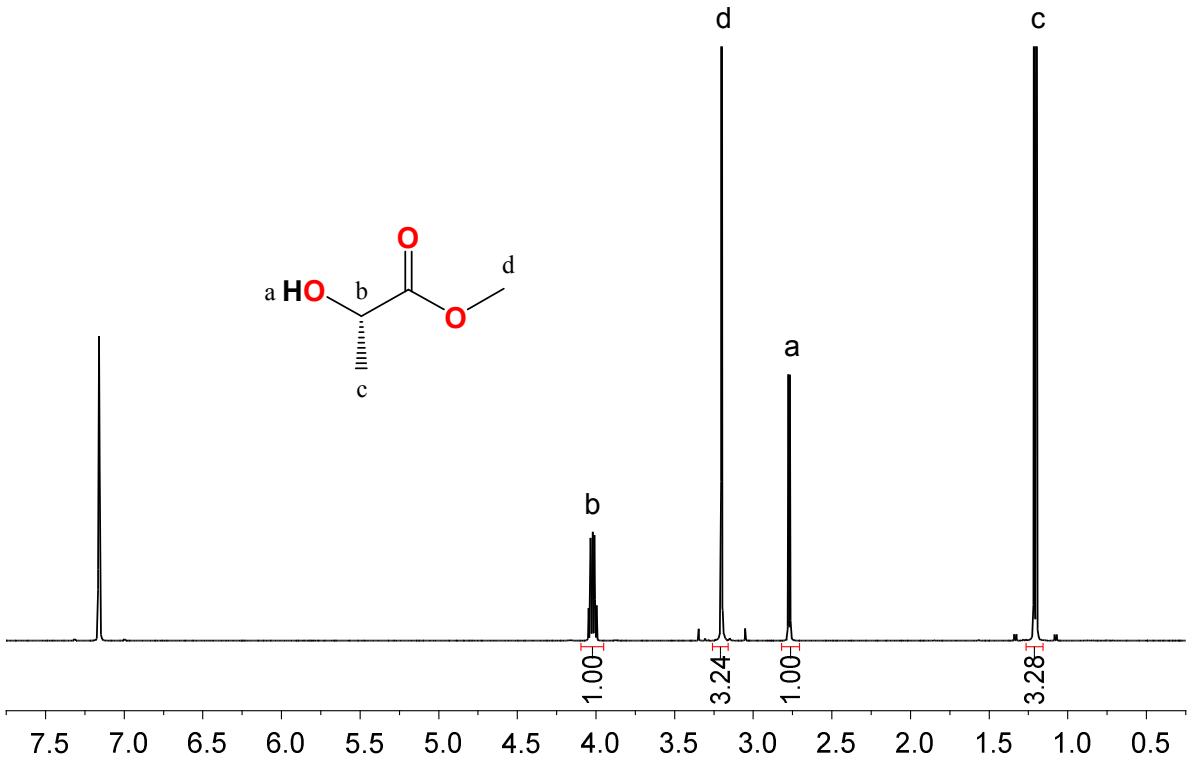

Figure S15. ^{1}H NMR spectrum of methyl L-lactate in C_6D_6.

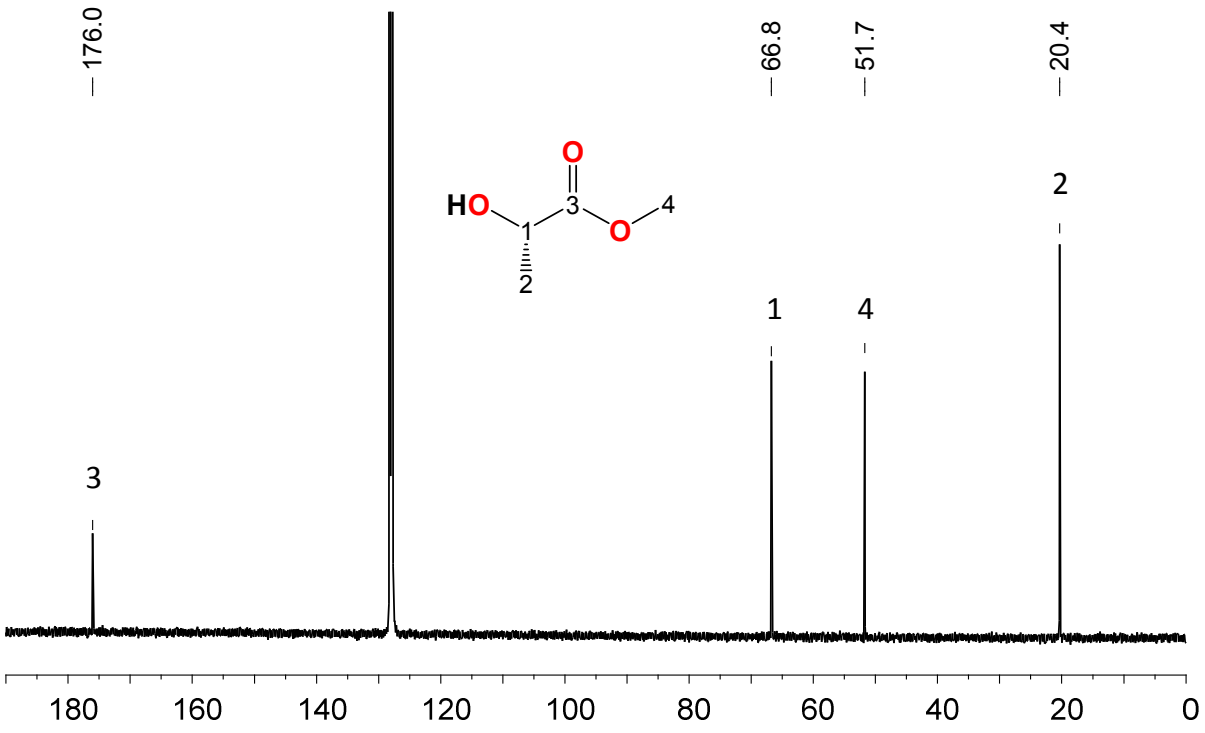

Figure S16. ^{13}C NMR spectrum of methyl L-lactate in C_6D_6.

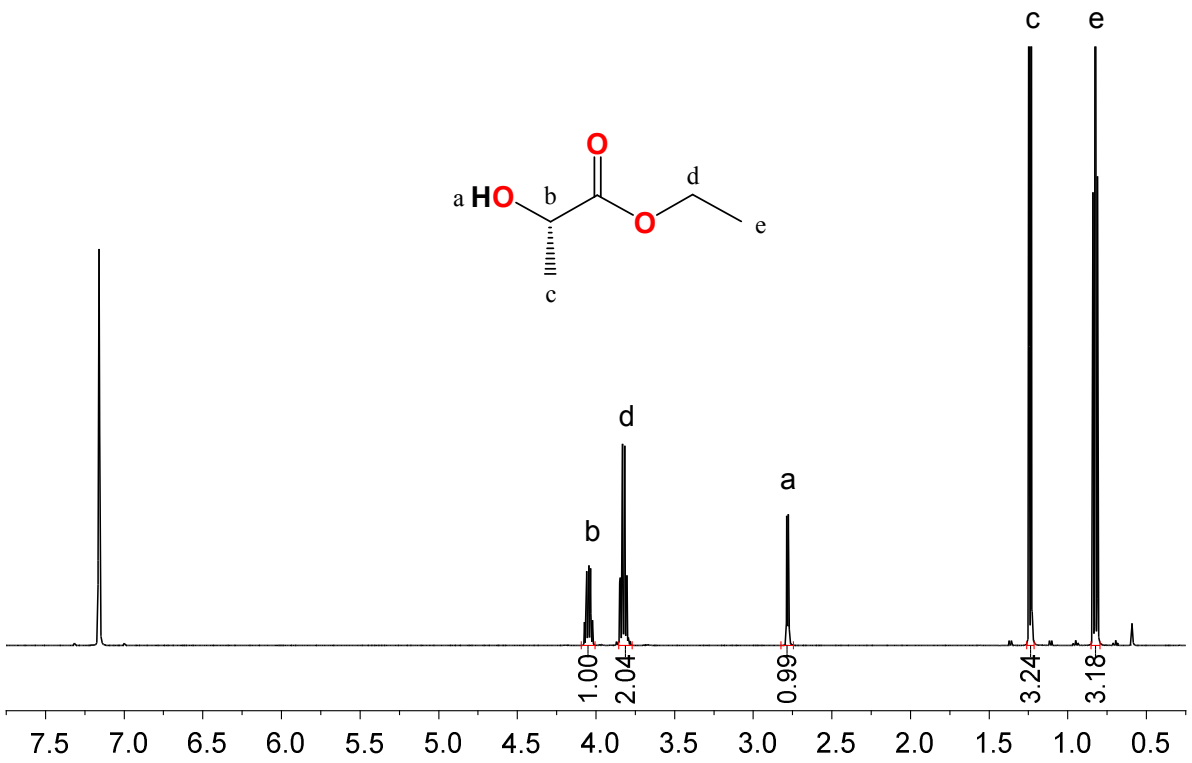

Figure S17. ^{1}H NMR spectrum of ethyl L-lactate in C_6D_6.

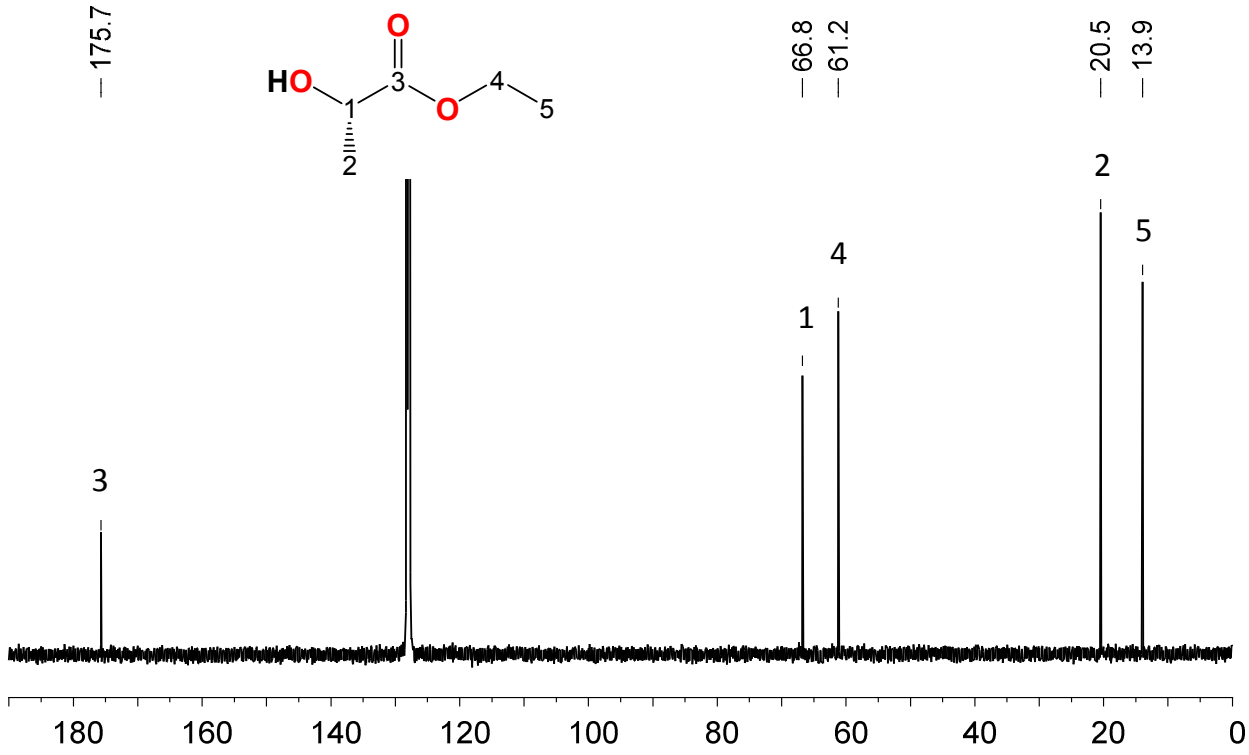

Figure S18. ^{13}C NMR spectrum of ethyl L-lactate in C_6D_6.

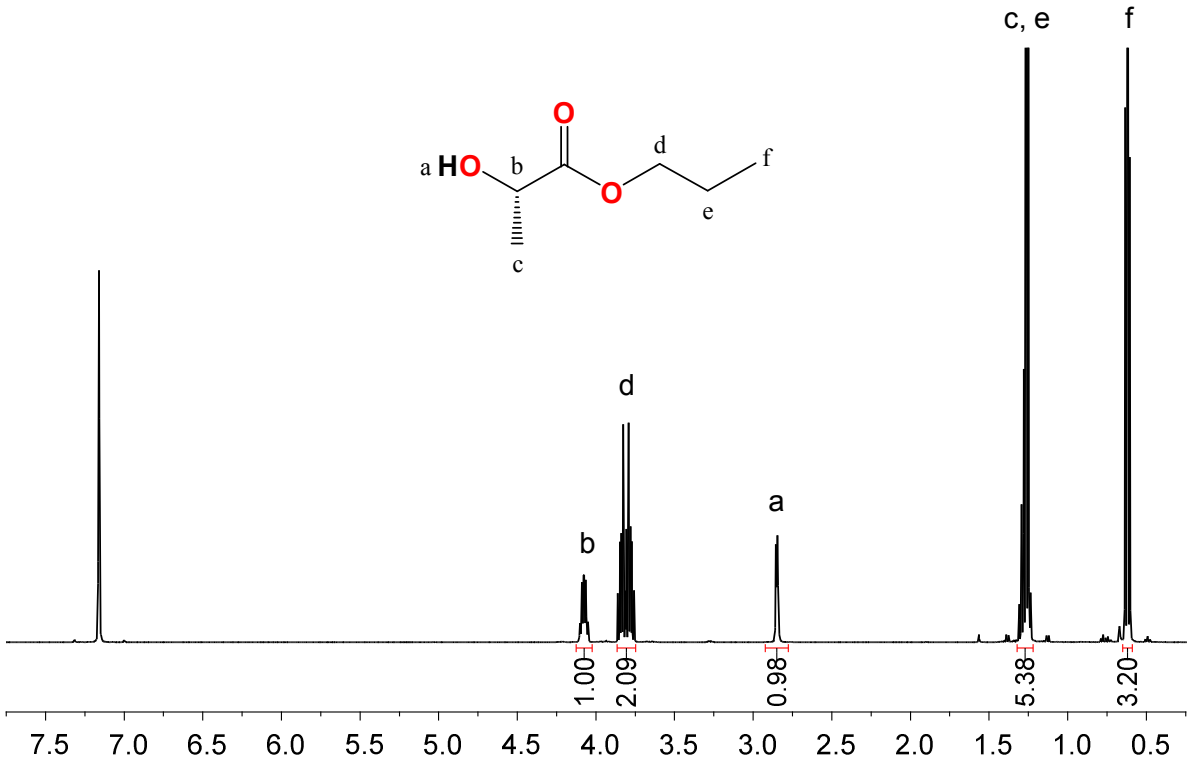

Figure S19. ^{1}H NMR spectrum of n-propyl L-lactate in C_6D_6.

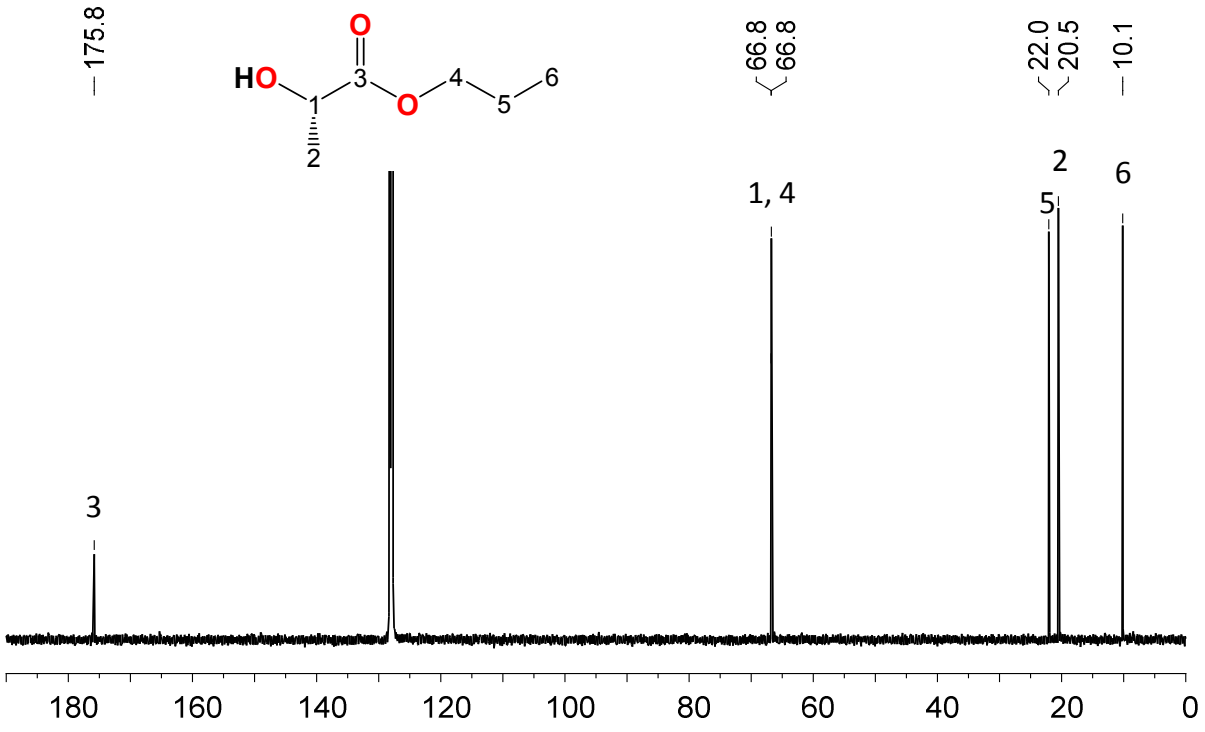

Figure S20. ^{13}C NMR spectrum of n-propyl L-lactate in C_6D_6.

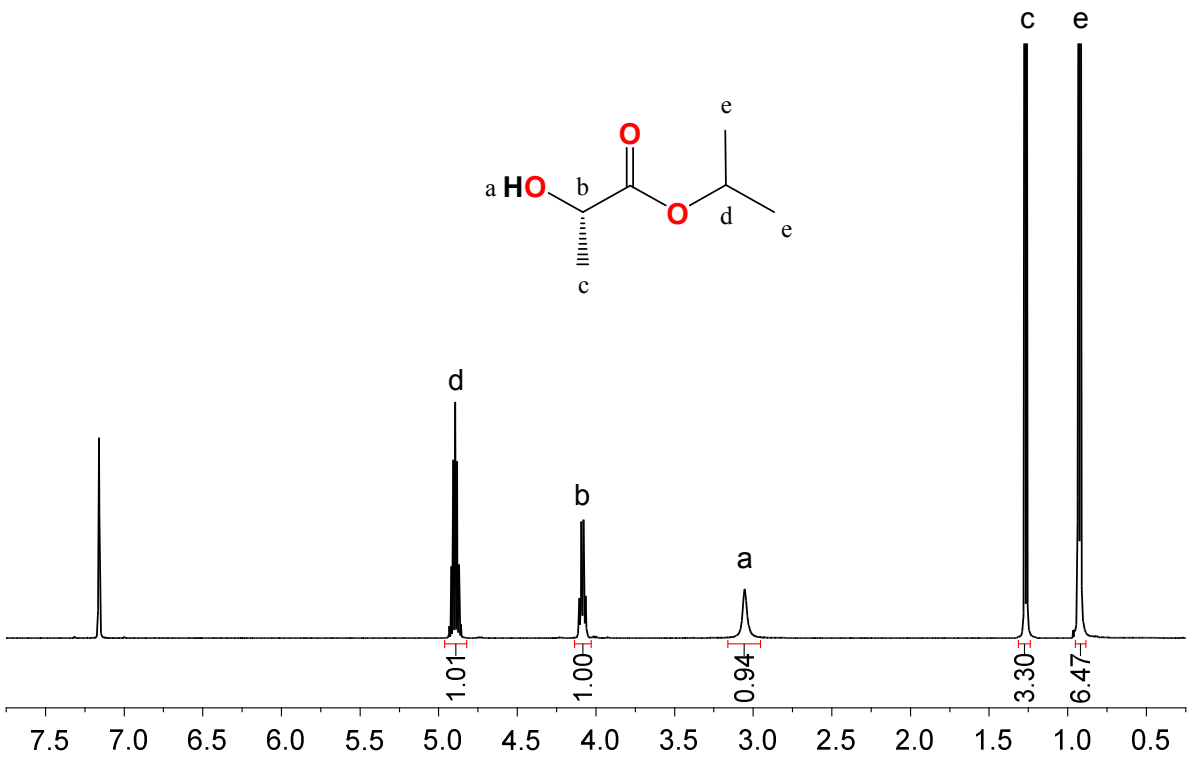

Figure S21. ^{1}H NMR spectrum of isopropyl L-lactate in C_6D_6.

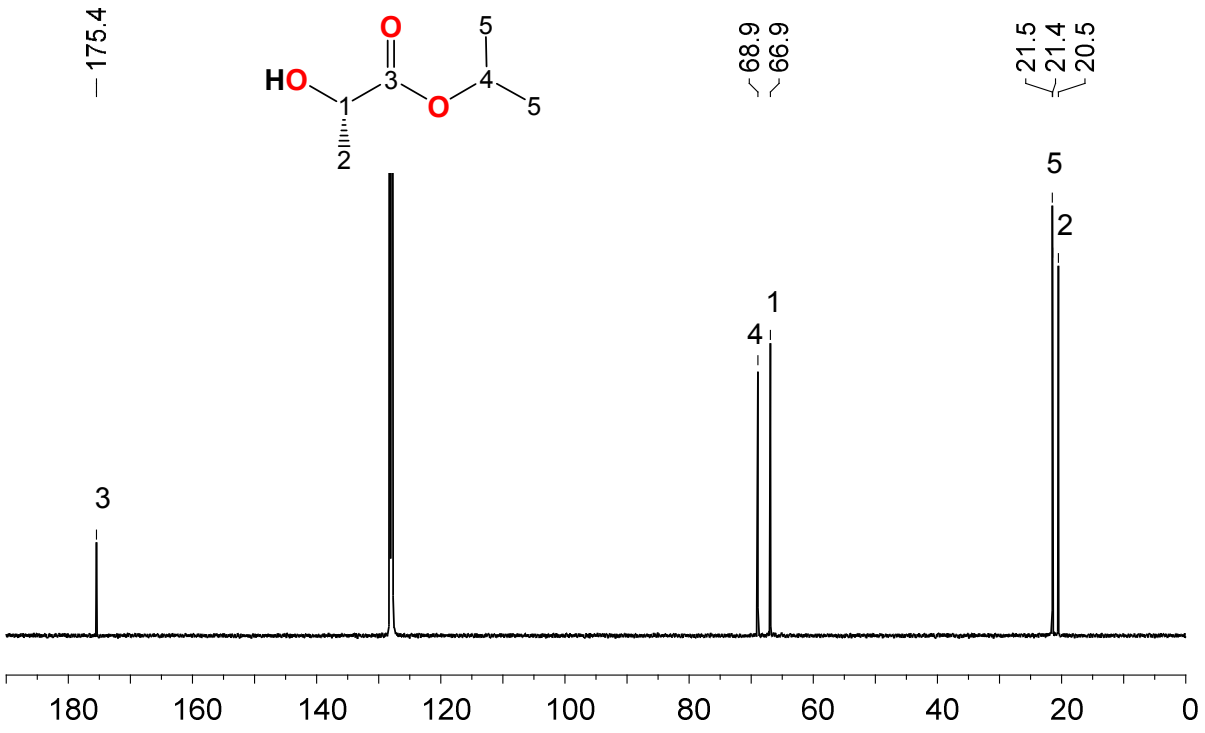

Figure S22. ^{13}C NMR spectrum of isopropyl L-lactate in C_6D_6.

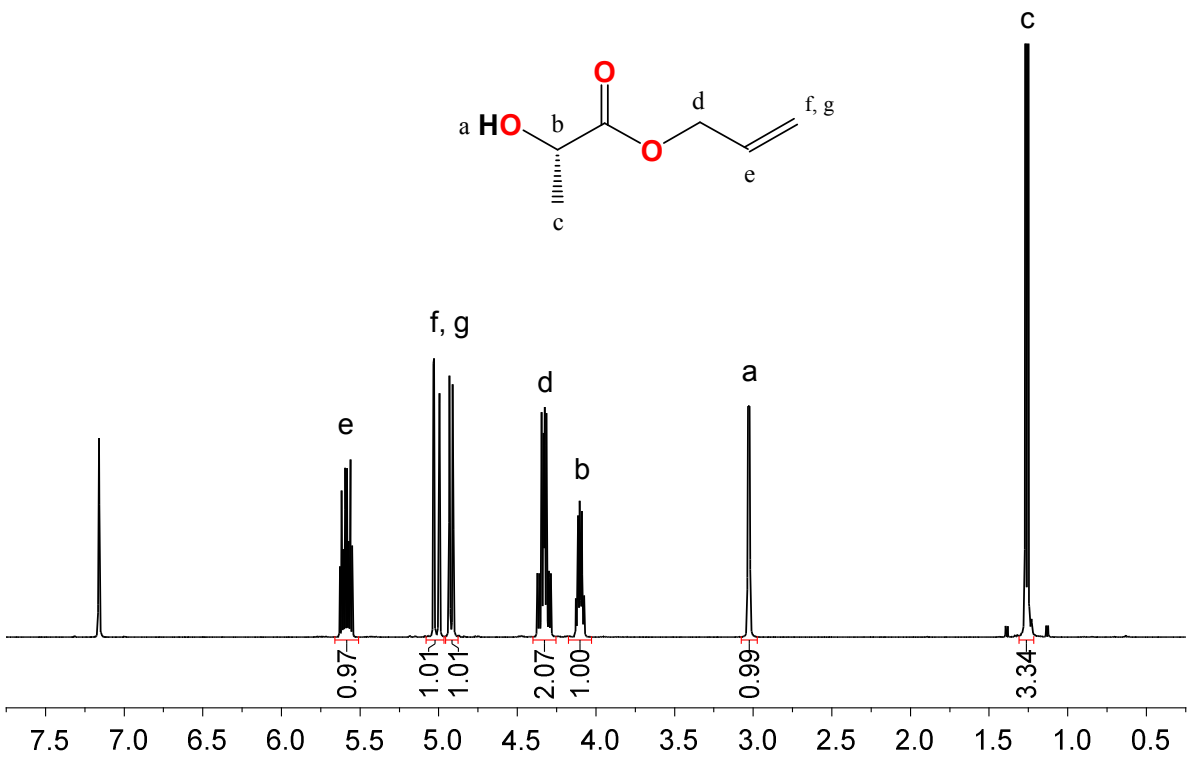

Figure S23. ^{1}H NMR spectrum of allyl L-lactate in C_6D_6.

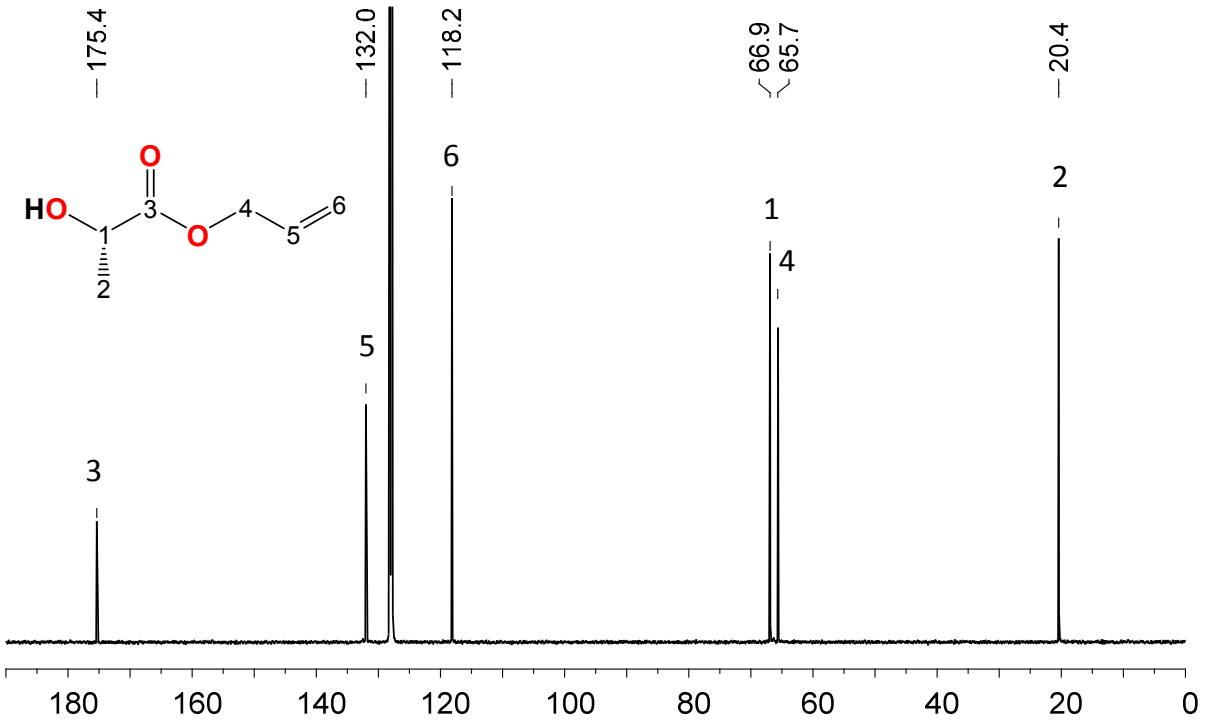

Figure S24. ^{13}C NMR spectrum of allyl L-lactate in C_6D_6.

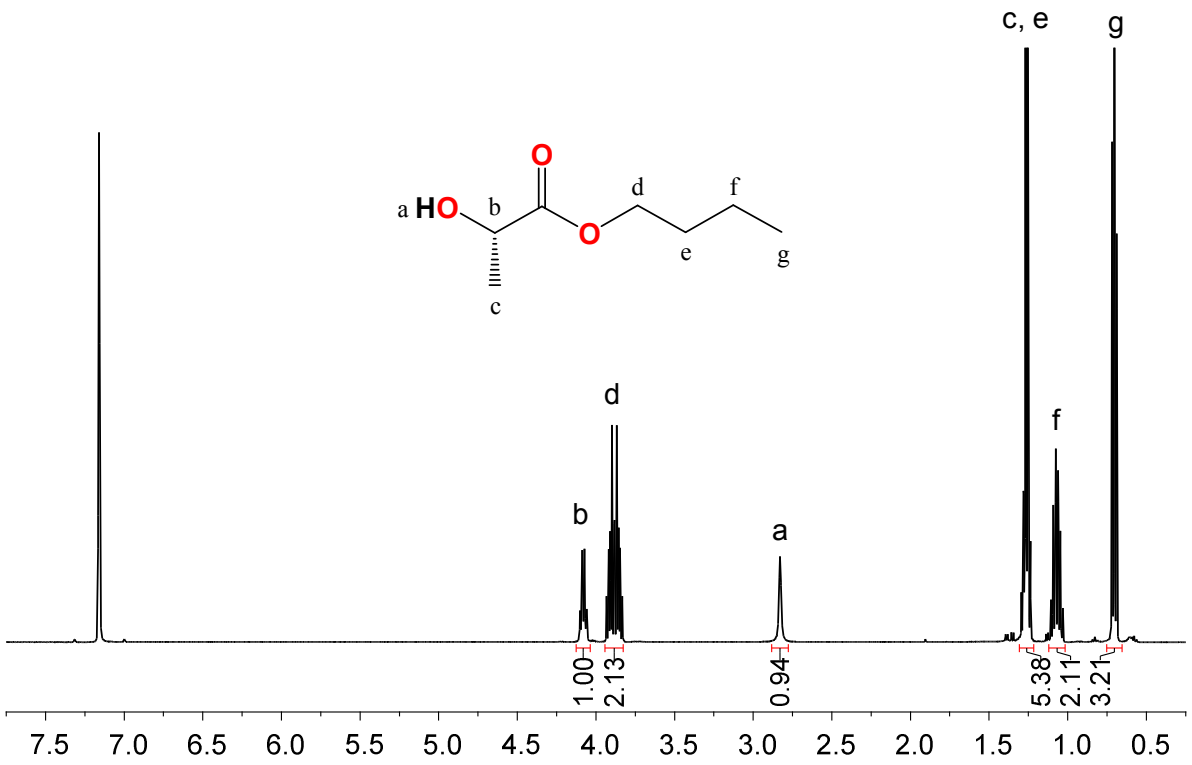

Figure S25. ^{1}H NMR spectrum of butyl L-lactate in C_6D_6.

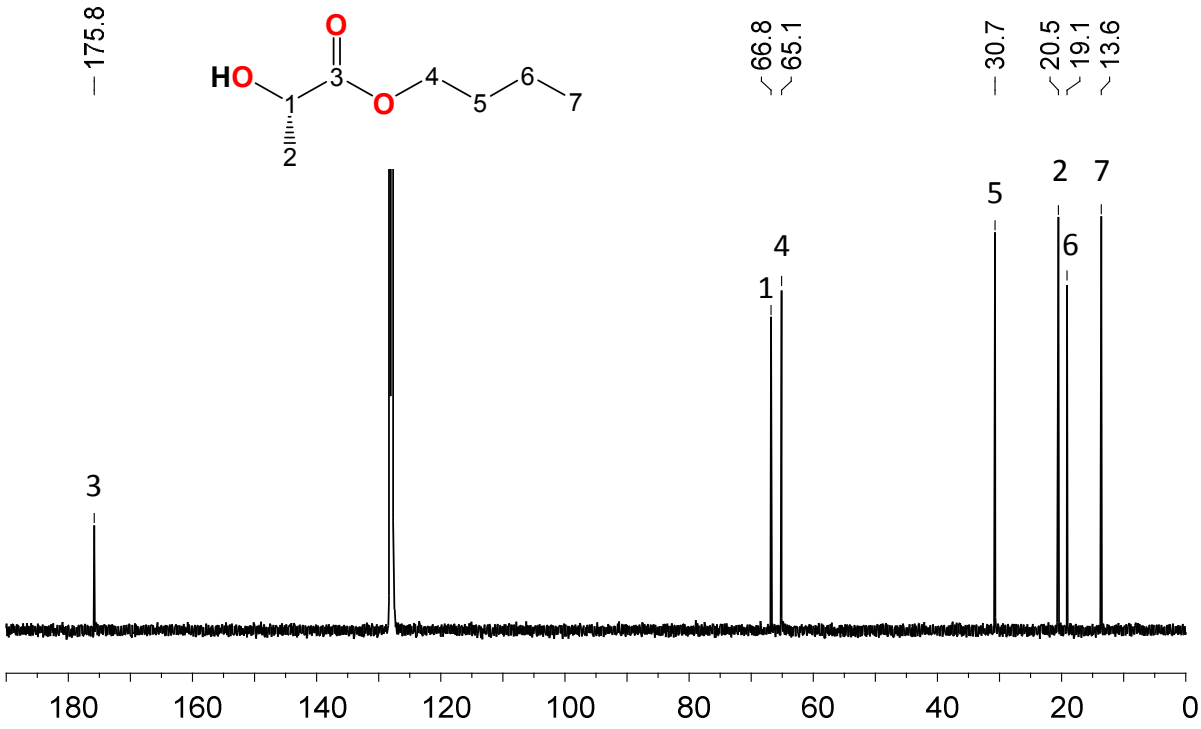

Figure S26. ^{13}C NMR spectrum of butyl L-lactate in C_6D_6.

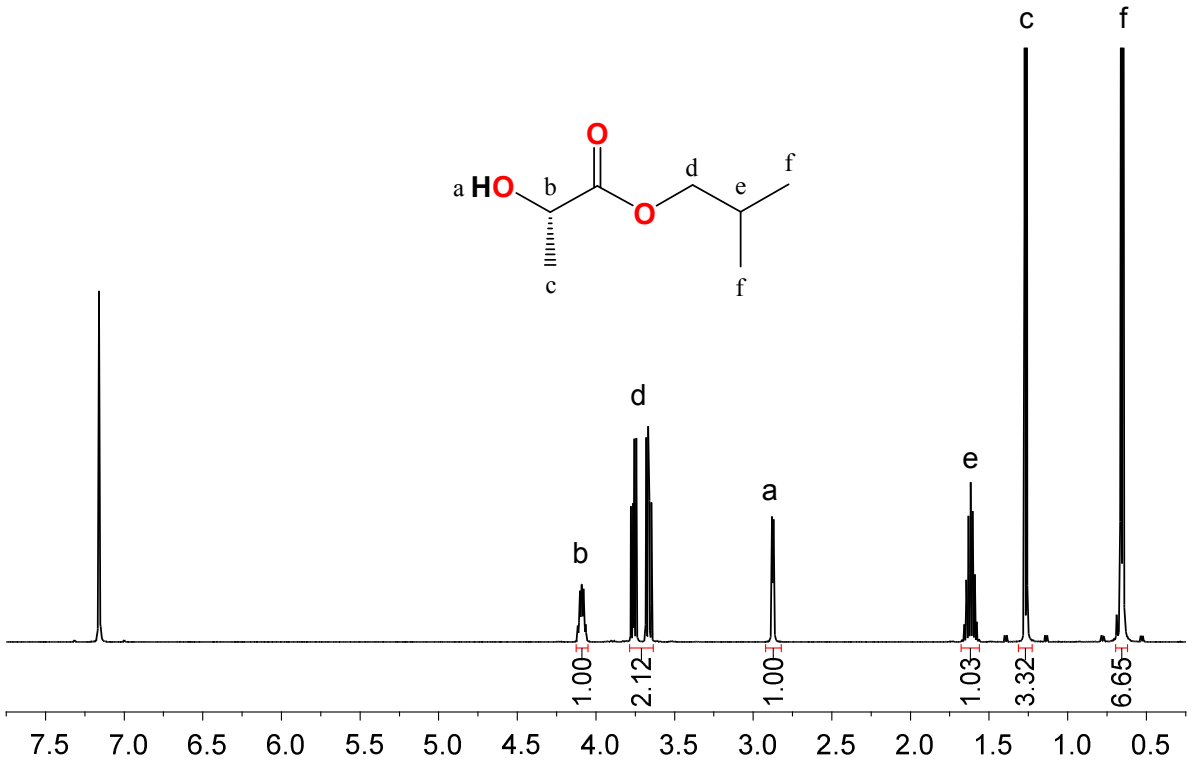

Figure S27. ^{1}H NMR spectrum of isobutyl L-lactate in C_6D_6.

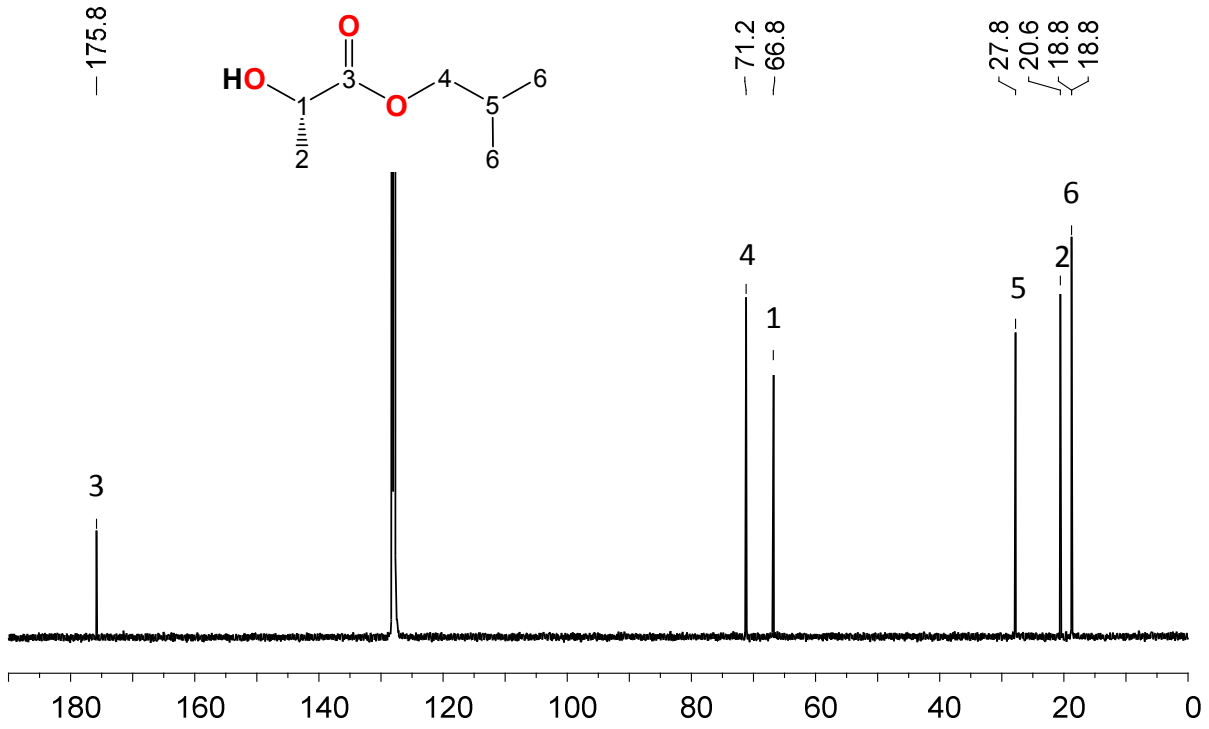

Figure S28. ^{13}C NMR spectrum of isobutyl L-lactate in C_6D_6.

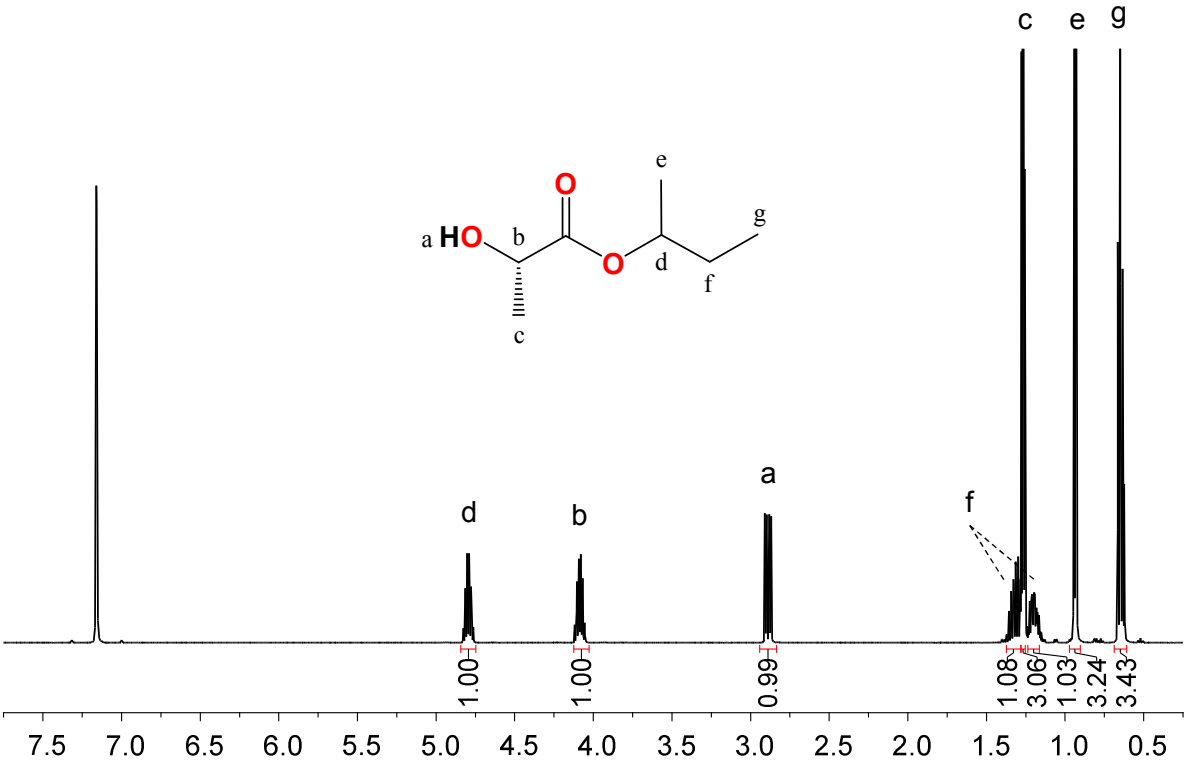

Figure S29. ^{1}H NMR spectrum of sec-butyl L-lactate in C_6D_6.

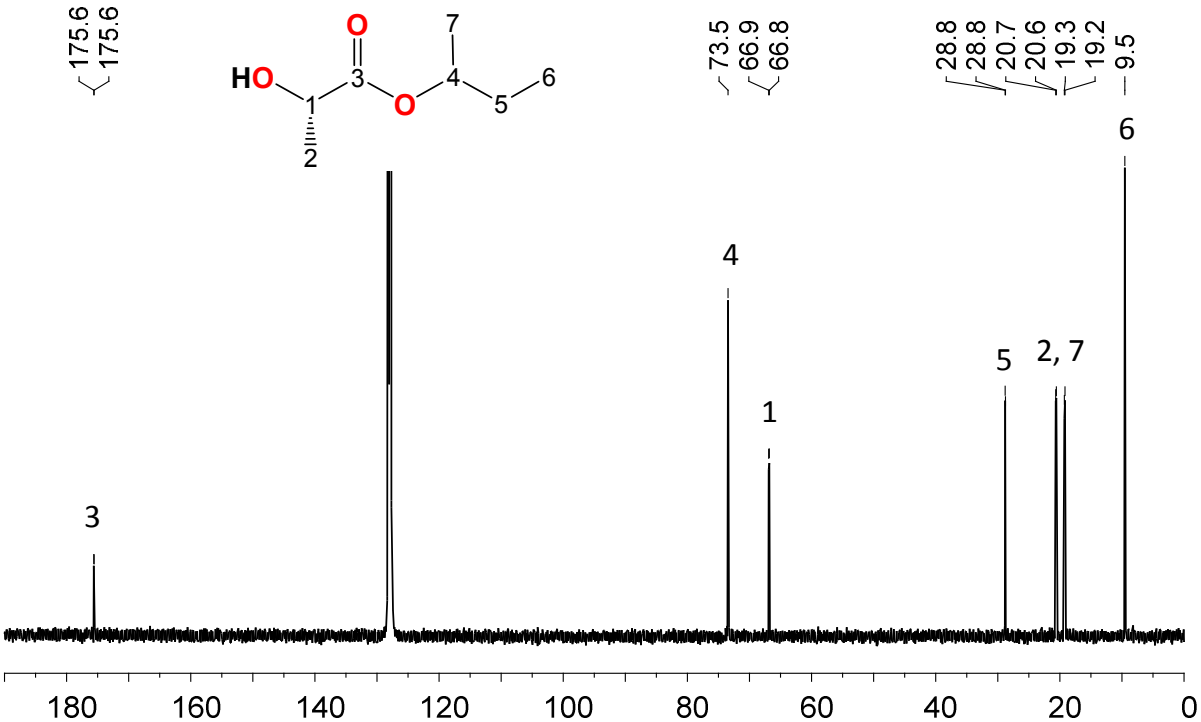

Figure S30. ^{13}C NMR spectrum of sec-butyl L-lactate in C_6D_6.

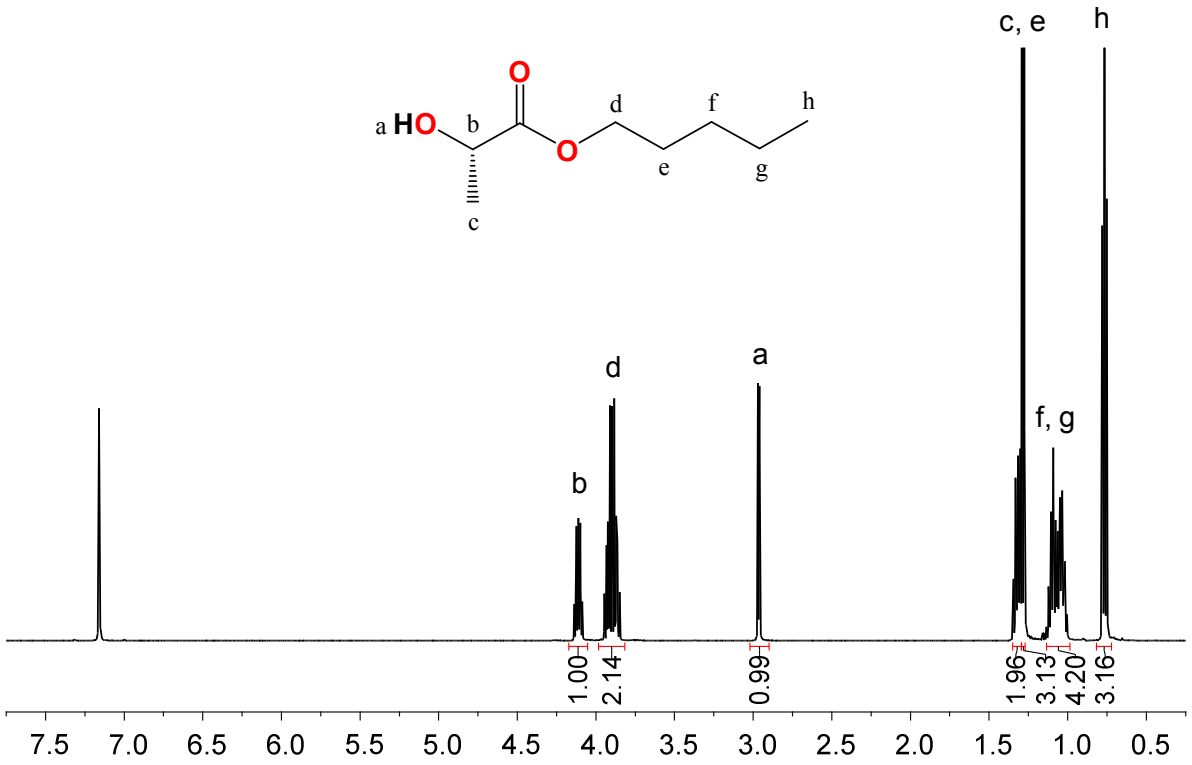

Figure S31. ^{1}H NMR spectrum of n-pentyl L-lactate in C_6D_6.

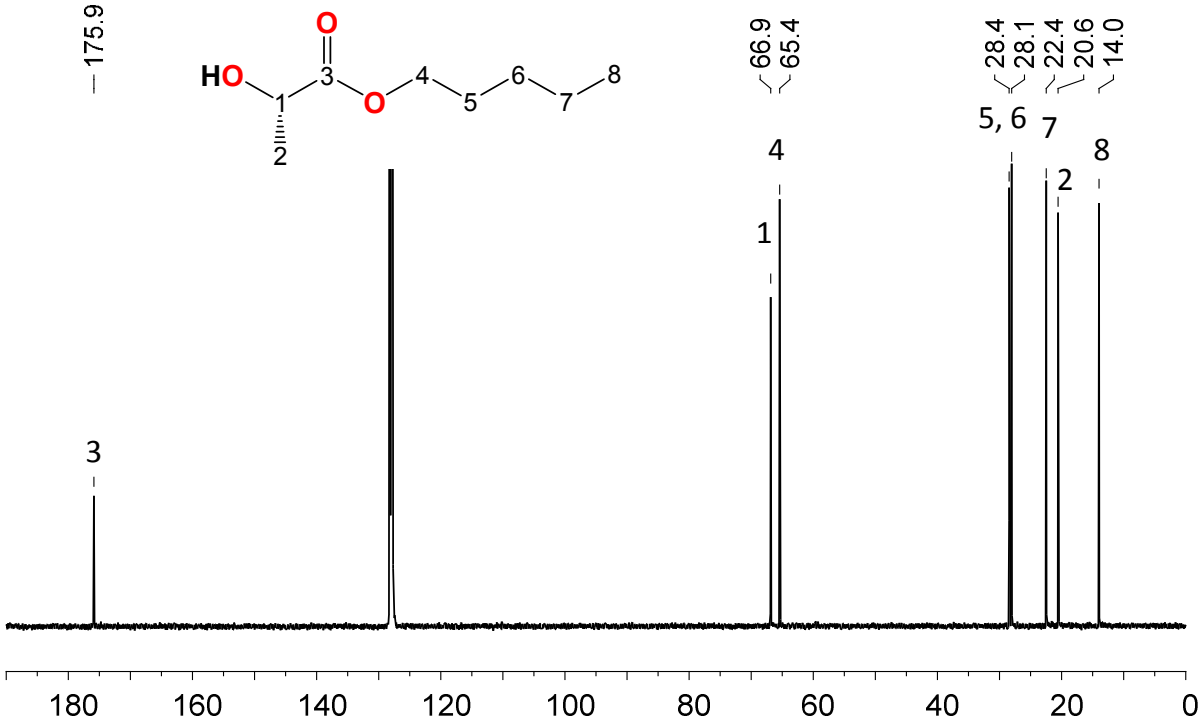

Figure S32. ^{13}C NMR spectrum of n-pentyl L-lactate in C_6D_6.

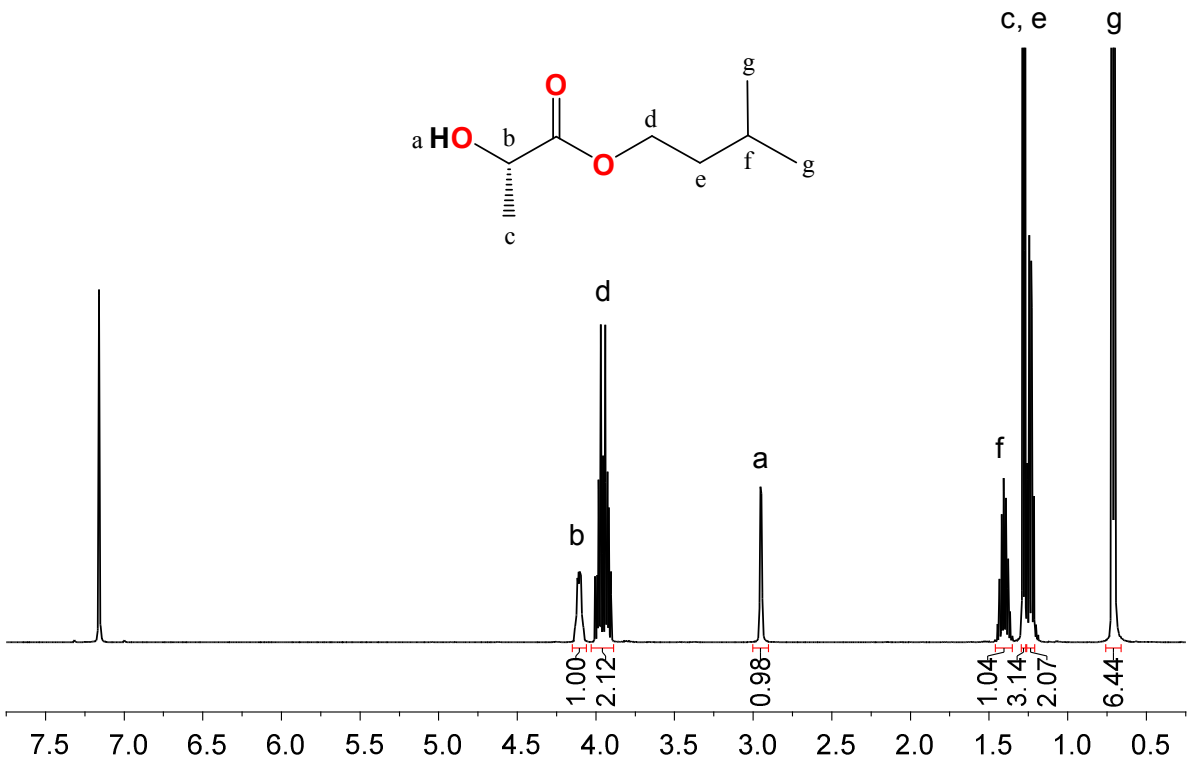

Figure S33. ^{1}H NMR spectrum of isopentyl L-lactate in C_6D_6.

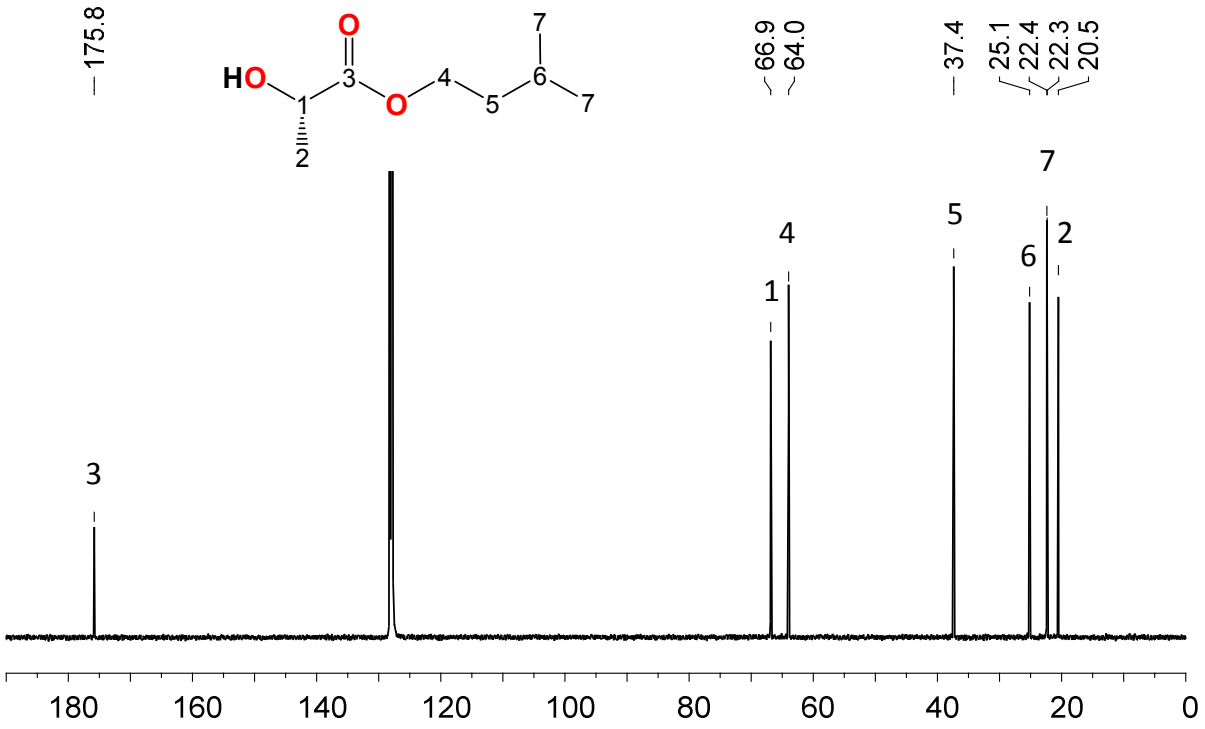

Figure S34. ^{13}C NMR spectrum of isopentyl L-lactate in C_6D_6.

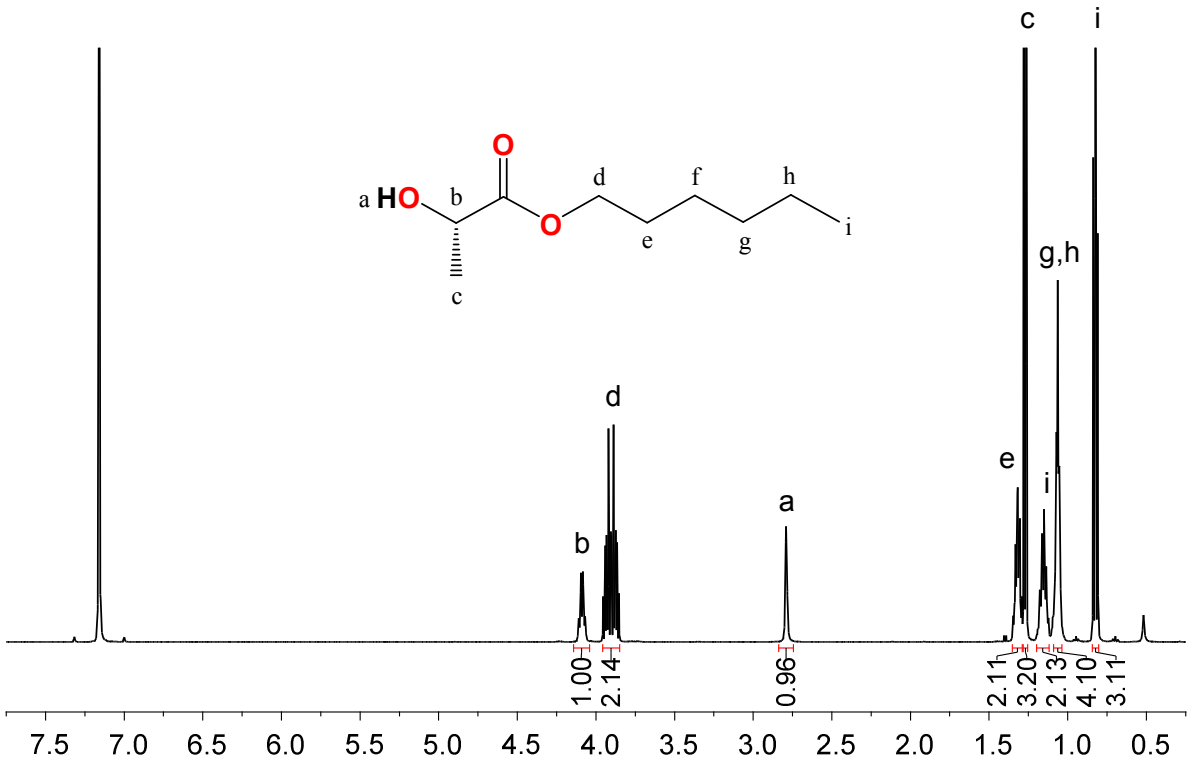

Figure S35. ^{1}H NMR spectrum of n-hexyl L-lactate in C_6D_6.

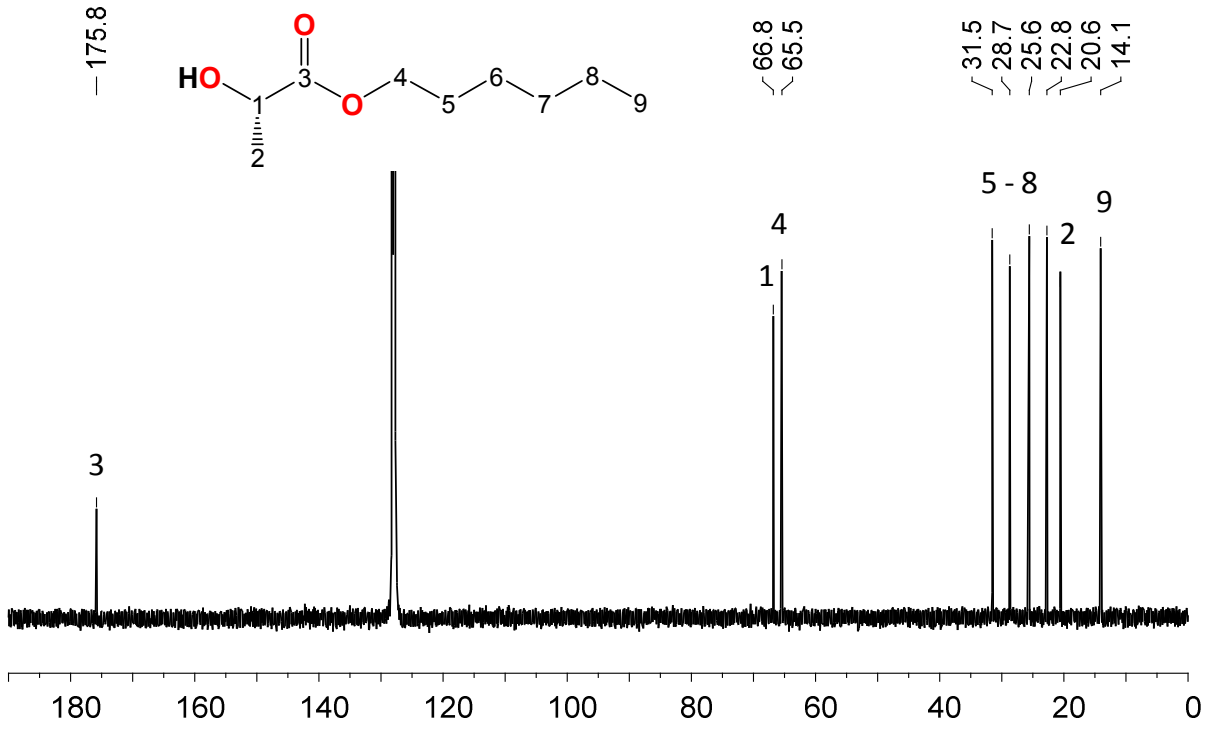

Figure S36. ^{13}C NMR spectrum of n-hexyl L-lactate in C_6D_6.

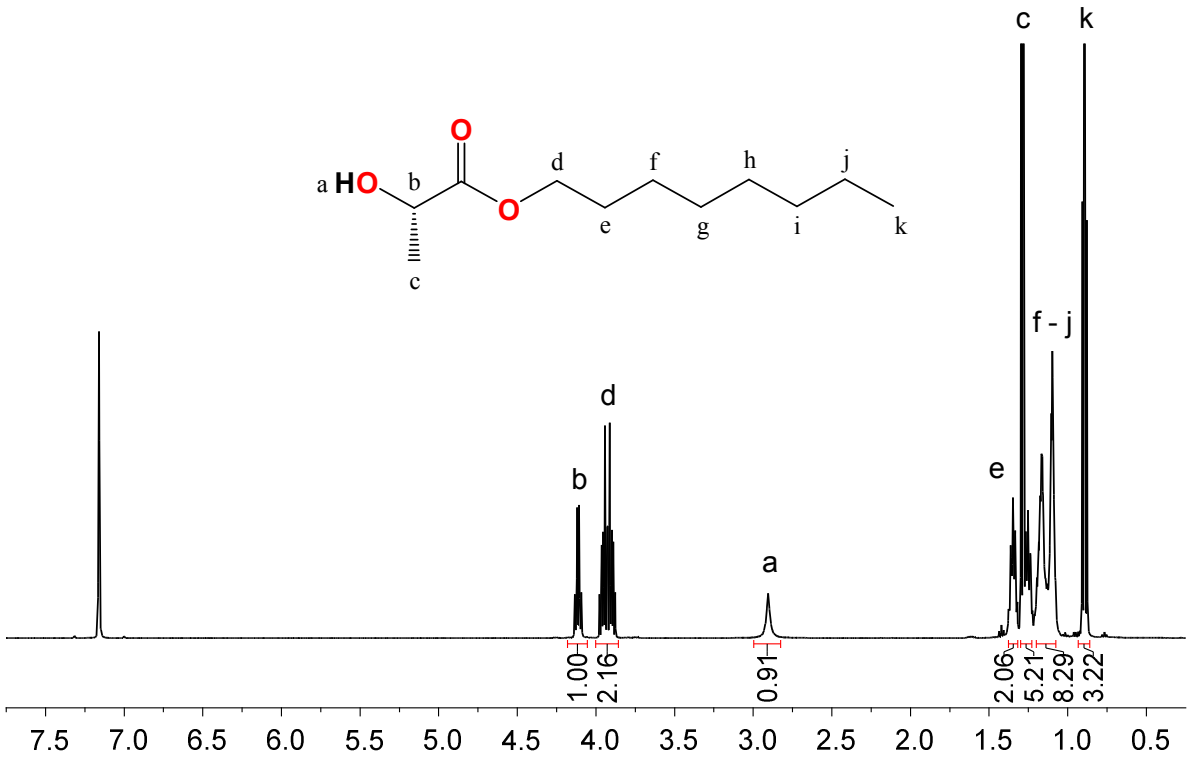

Figure S37. ^{1}H NMR spectrum of n-octyl L-lactate in C_6D_6.

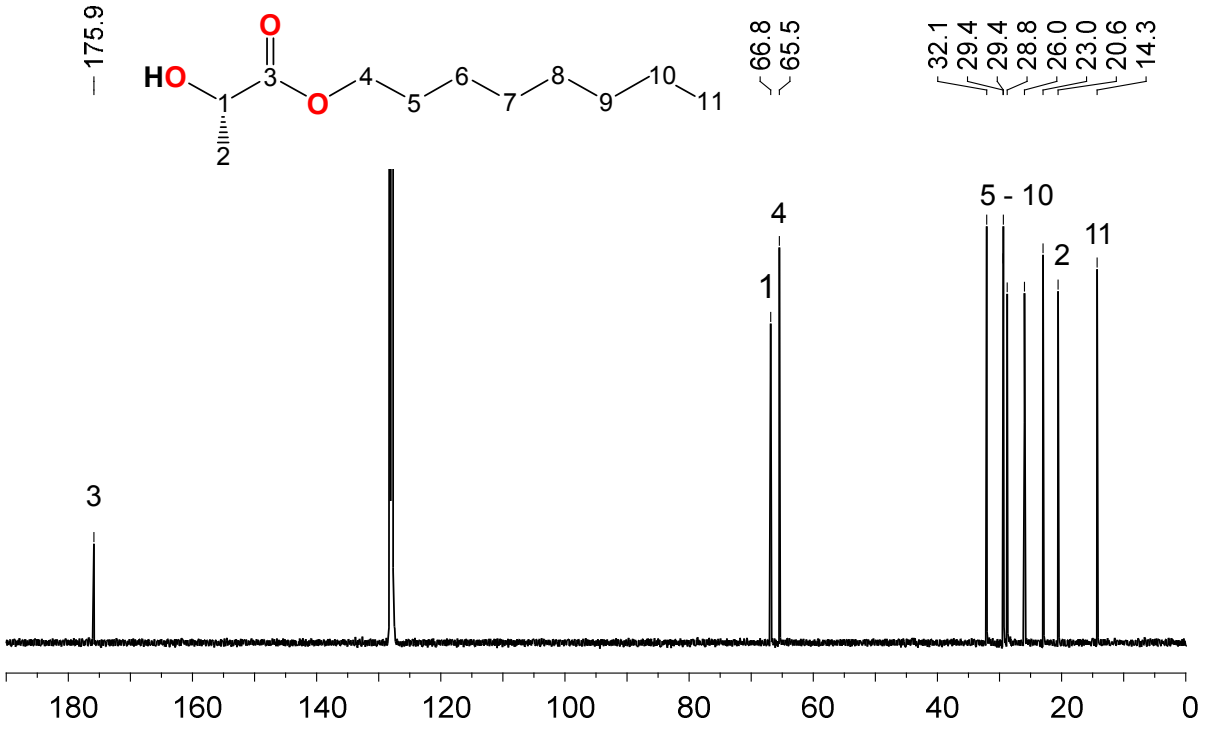

Figure S38. ^{13}C NMR spectrum of n-octyl L-lactate in C_6D_6.

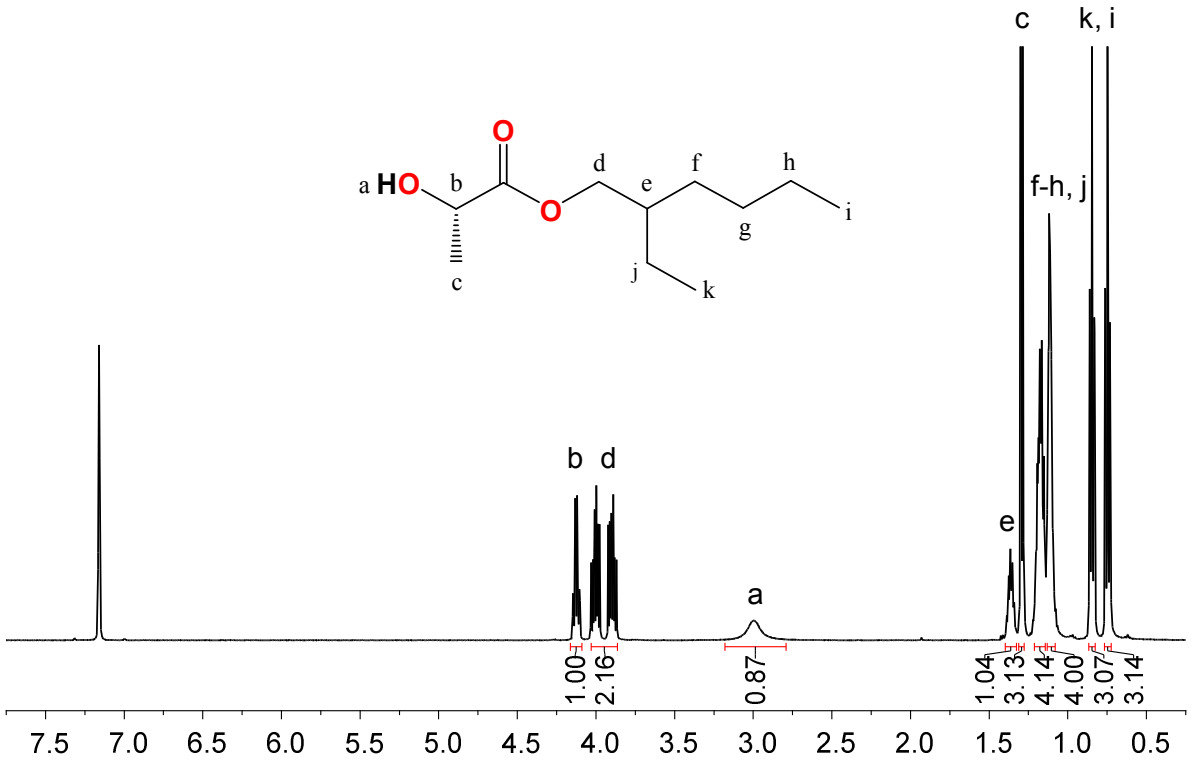

Figure S39. ^{1}H NMR spectrum of 2-etylhexyl L-lactate in C_6D_6.

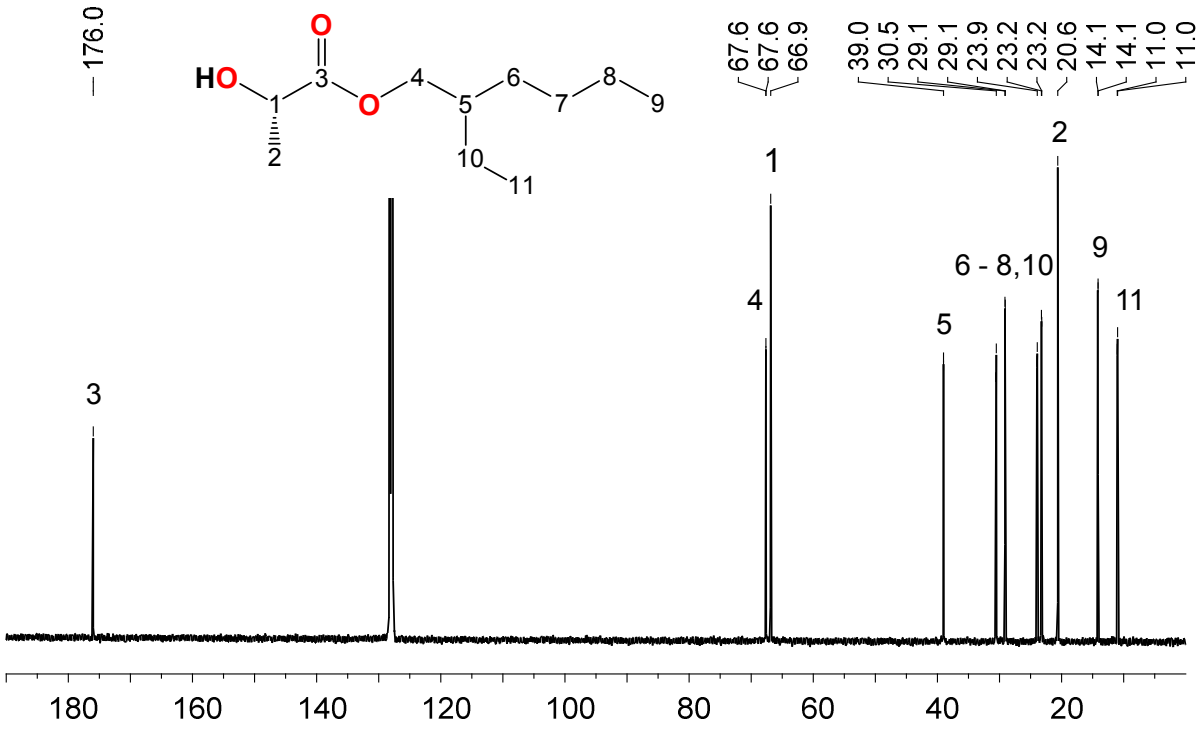

Figure S40. ^{13}C NMR spectrum of 2-etylhexyl L-lactate in C_6D_6.

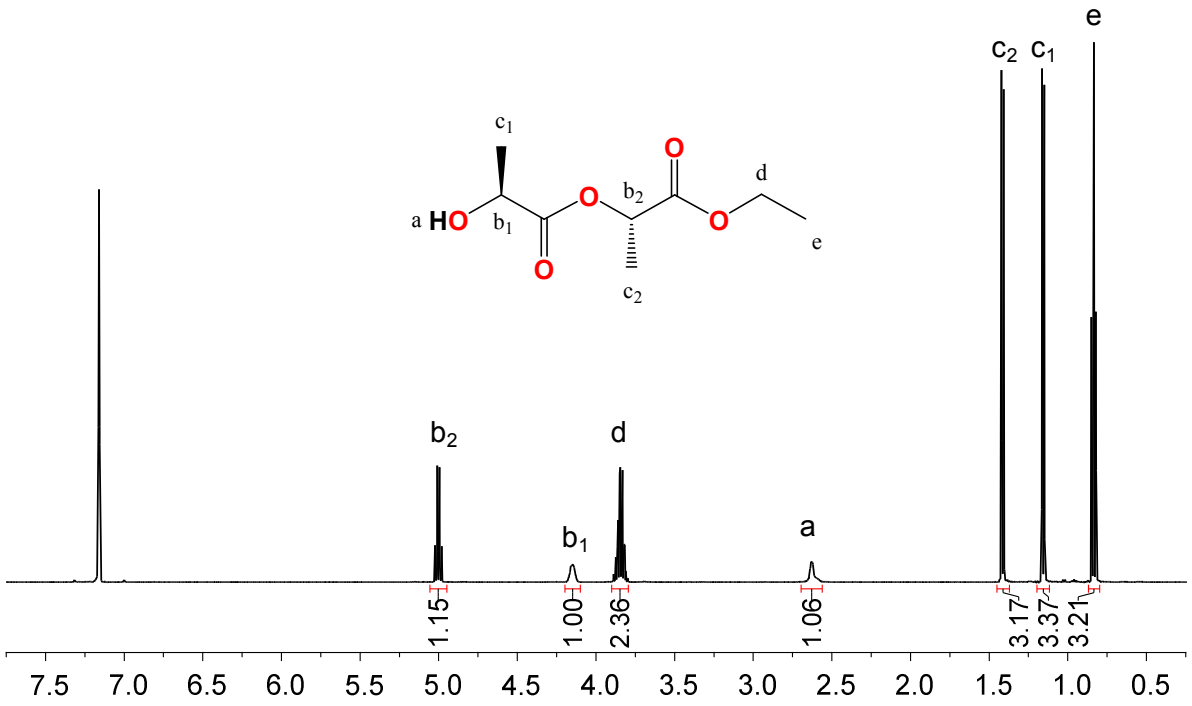

Figure S41. ^{1}H NMR spectrum of ethyl L-lactyllactate in C_6D_6.

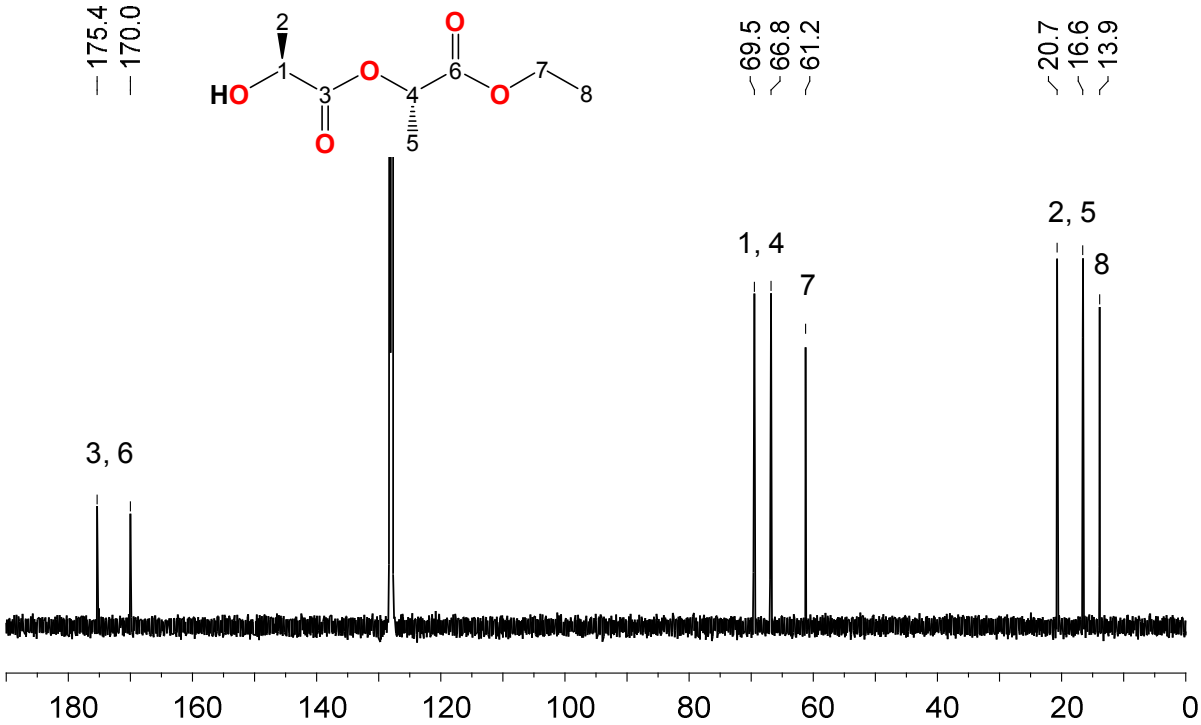

Figure S42. ^{13}C NMR spectrum of ethyl L-lactyllactate in C_6D_6.