Supporting information for

Use of group 13 aryloxides for the synthesis of green chemicals and oxide materials

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Crystallographic Data for Compounds 1-6.

Table S1A. Crystal and data collection parameters for compounds **1**-**3a**.

Crystal	**1**	**1a**	**2**	**3**	**3a**·1.5(C_7H_8)
Chemical formula	$C_{24}H_{21}AlO_9$	$C_{27}H_{27}AlO_9$	$C_{20}H_{26}Ga_2O_6$	$C_{48}H_{42}AlLi_3O_{18}$	$C_{64.5}H_{66}AlLi_3O_{18}$
Formula Mass	480.39	522.46	501.85	954.61	1176.97
Crystal system	Triclinic	Trigonal	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{3}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	7.280 (2)	13.171 (3)	7.273 (2)	11.879 (2)	12.554 (2)
b/Å	12.680 (3)		8.766 (2)	23.291 (4)	12.981 (2)
c/Å	13.008 (3)	8.265 (2)	9.548 (3)	17.296 (3)	19.250 (3)
α/°	107.20(5)		79.92 (4)		99.50 (2)
β/°	90.44 (5)		67.77 (5)	105.41 (3)	92.51 (2)
γ/°	93.43 (5)		69.97 (4)		102.89 (2)
Unit cell volume/Å^3	1144.6 (6)	1241.7 (6)	528.7 (3)	4613.3 (15)	3005.4 (9)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Z	2	2	1	4	2
Radiation type	MoKα	MoKα	CuKα	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	0.14	0.14	3.41	0.12	0.09
No. of reflections measured	12092	2905	8060	31006	66491
No. of independent reflections	4247	1766	1869	9619	10927
No. of observed reflections ($I > 2\sigma(I)$)	2506	1525	1857	7110	10409
R_{int}	0.0826	0.0187	0.020	0.0392	0.0208
Final R_1 values ($I > 2\sigma(I)$)	0.0874	0.0366	0.0208	0.0421	0.0305
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1958	0.0885	0.0557	0.0802	0.0816
Final R_1 values (all data)	0.1470	0.0444	0.0210	0.0686	0.0317
Final $wR(F^2)$ values (all data)	0.2368	0.0951	0.0558	0.898	0.0825
Goodness of fit on F^2	1.082	1.096	1.070	1.023	1.034
Δρmax/eÅ^{-3}	0.68	0.25	0.32	0.27	0.26
Δρmin/eÅ^{-3}	-0.31	-0.32	-0.35	-0.33	-0.25

Table S1B. Crystal and data collection parameters for compounds **4-6**.

Crystal	**4**	**6**·2.25H_2O
Chemical formula	$C_{22}H_{28}GaLiO_7$	$C_{18}H_{25.5}GaLiO_{9.25}$
Formula Mass	481.10	466.54
Crystal system	Triclinic	Orthorhombic
Space group	*P*$\bar{1}$	*Cmc*2_1
a/Å	9.966 (5)	15.235 (4)
b/Å	21.841 (3)	21.548 (5)
c/Å	21.886 (3)	6.698 (2)
α/°	88.11 (2)	
β/°	80.20 (2)	
γ/°	77.02 (3)	
Unit cell volume/Å^3	4574 (3)	2198.8 (10)
Temperature/K	100(2)	100(2)
Z	8	4
Radiation type	CuKα	MoKα
Absorption coefficient, μ/mm^{-1}	1.98	1.296
No. of reflections measured	16730	4302
No. of independent reflections	12376	1618
No. of observed reflections ($I > 2\sigma(I)$)	10144	927
R_{int}	0.0469	0.1503
Final R_1 values ($I > 2\sigma(I)$)	0.0817	0.0756
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2215	0.1025
Final R_1 values (all data)	0.0988	0.1534
Final $wR(F^2)$ values (all data)	0.2438	0.1296
Goodness of fit on F^2	1.16	1.01
Δρmax/eÅ^{-3}	1.35	0.58
Δρmin/eÅ^{-3}	-0.69	-0.51

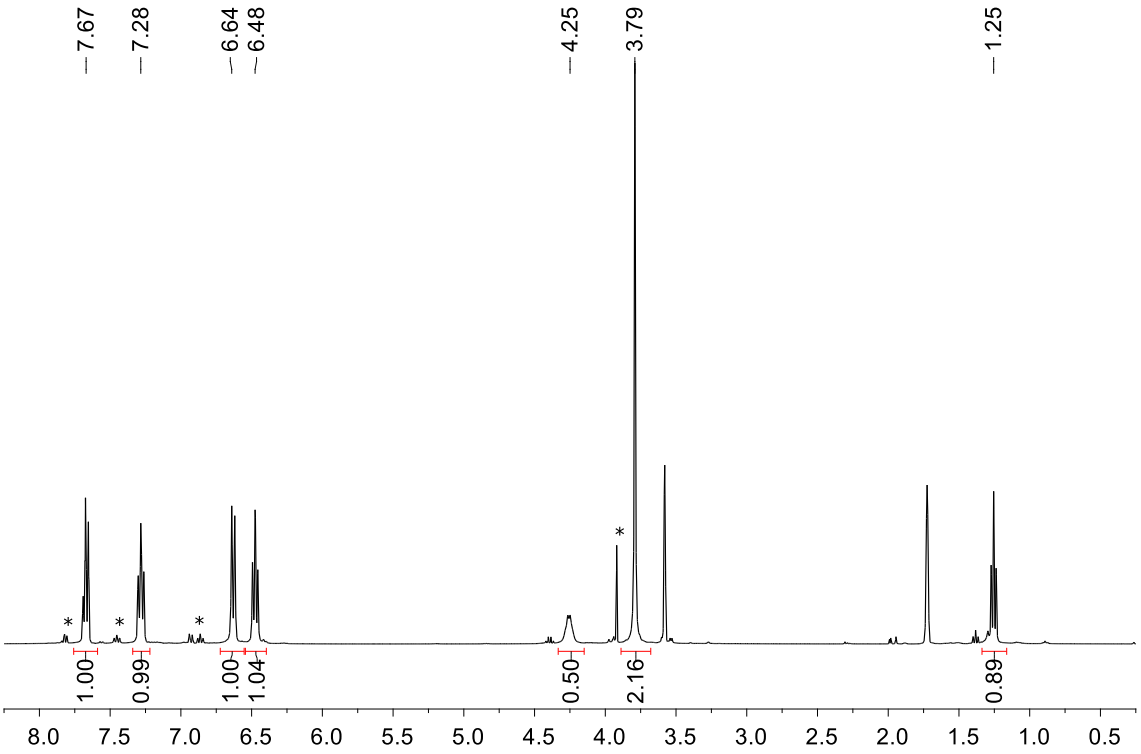

Figure S1. ^{1}H NMR spectrum of **1** in THF-d_8. * - assigned signals from MesalOH residues.

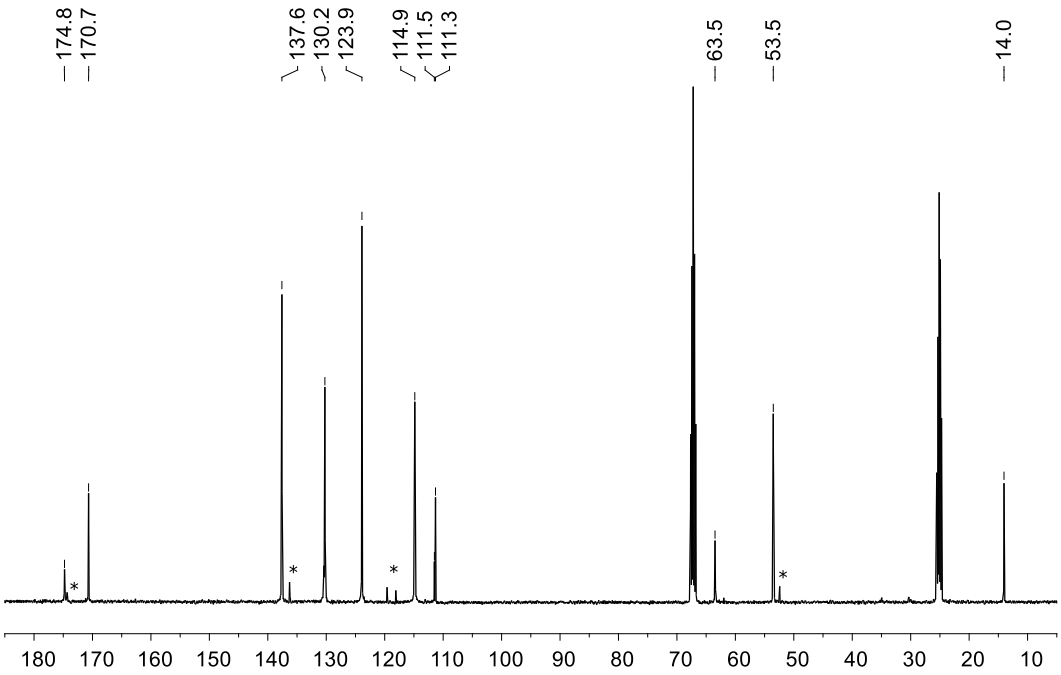

Figure S2. ^{13}C{^{1}H} NMR spectrum of **1** in THF-d_8. * - assigned signals from MesalOH residues. Signals at 53.5 and 14.0 ppm arise from the ethyl group in ethyl salicylate ligands formed during recrystallization of **1** from EtOH.

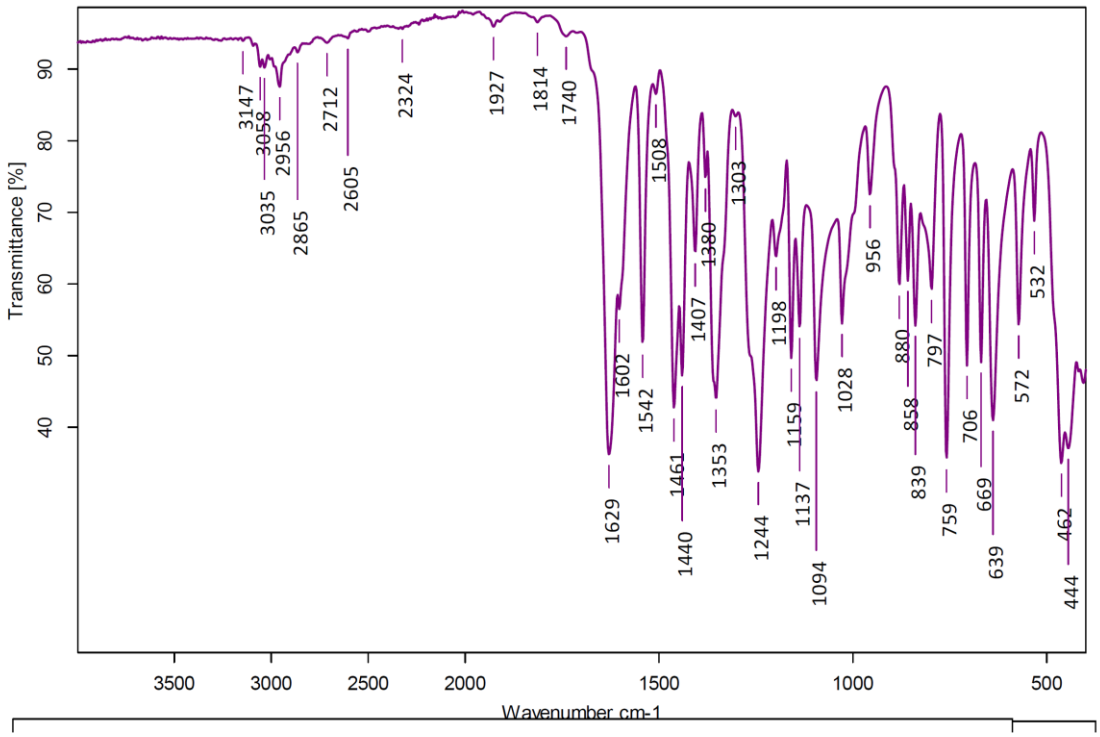

Figure S3. FTIR-ATR spectrum of **1**.

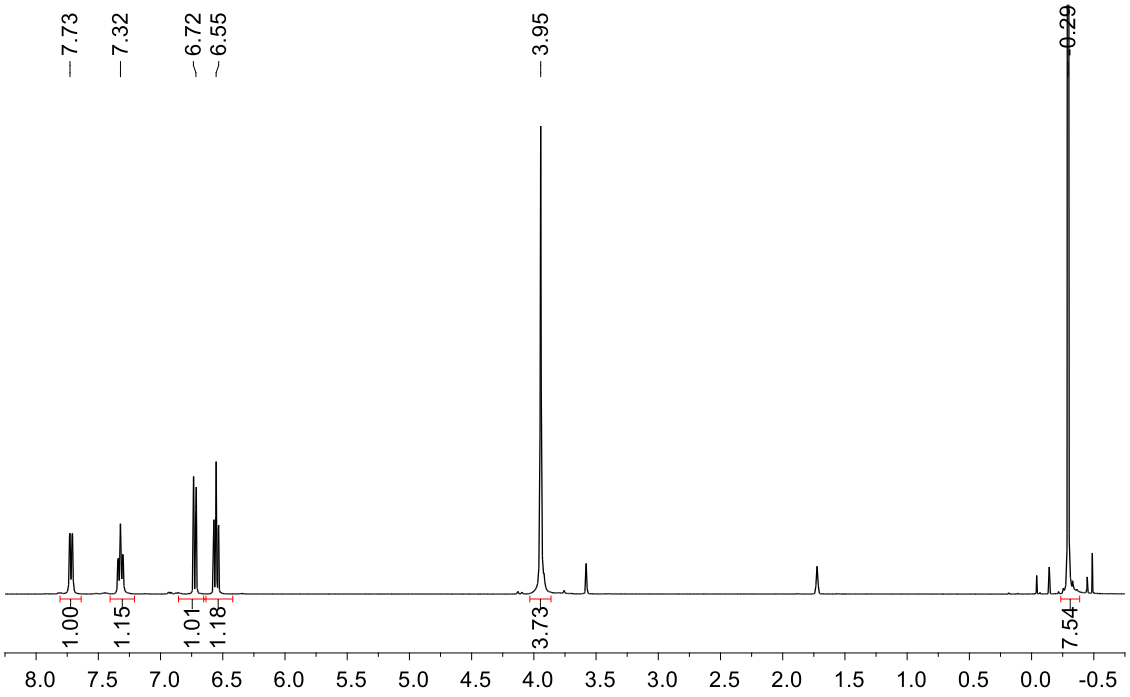

Figure S4. ^{1}H NMR spectrum of **2** in THF-d_8.

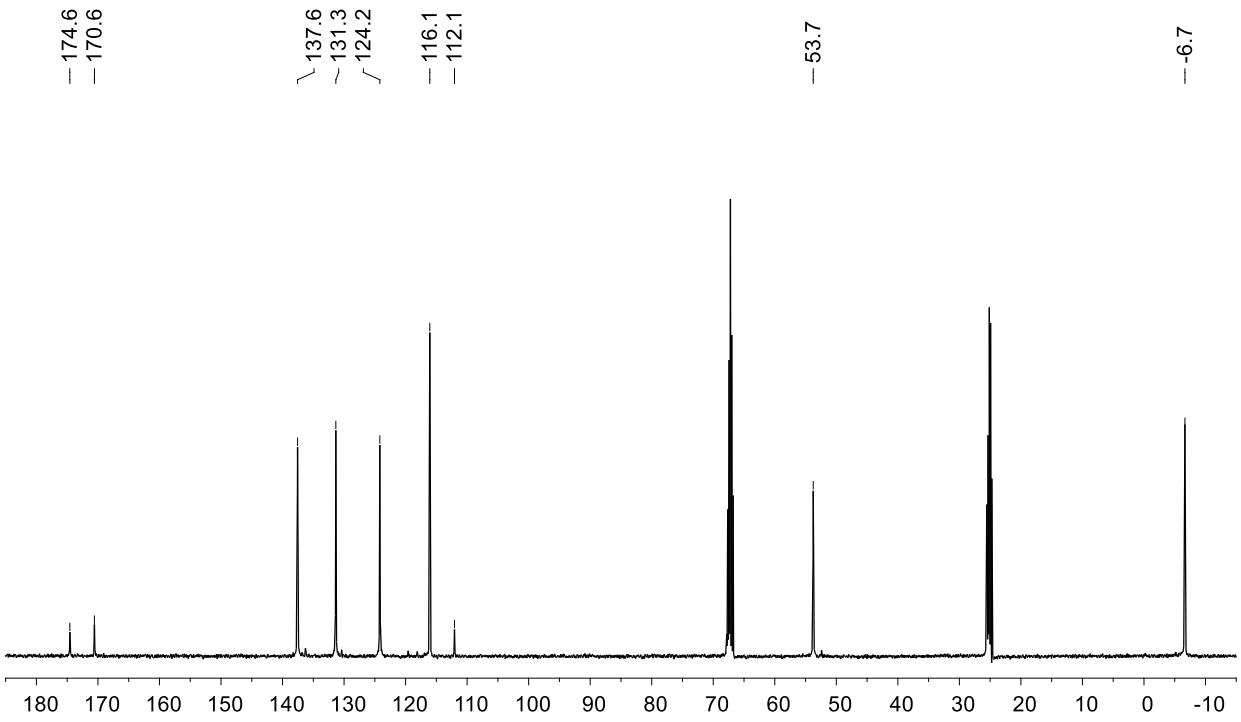

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in THF-d_8.

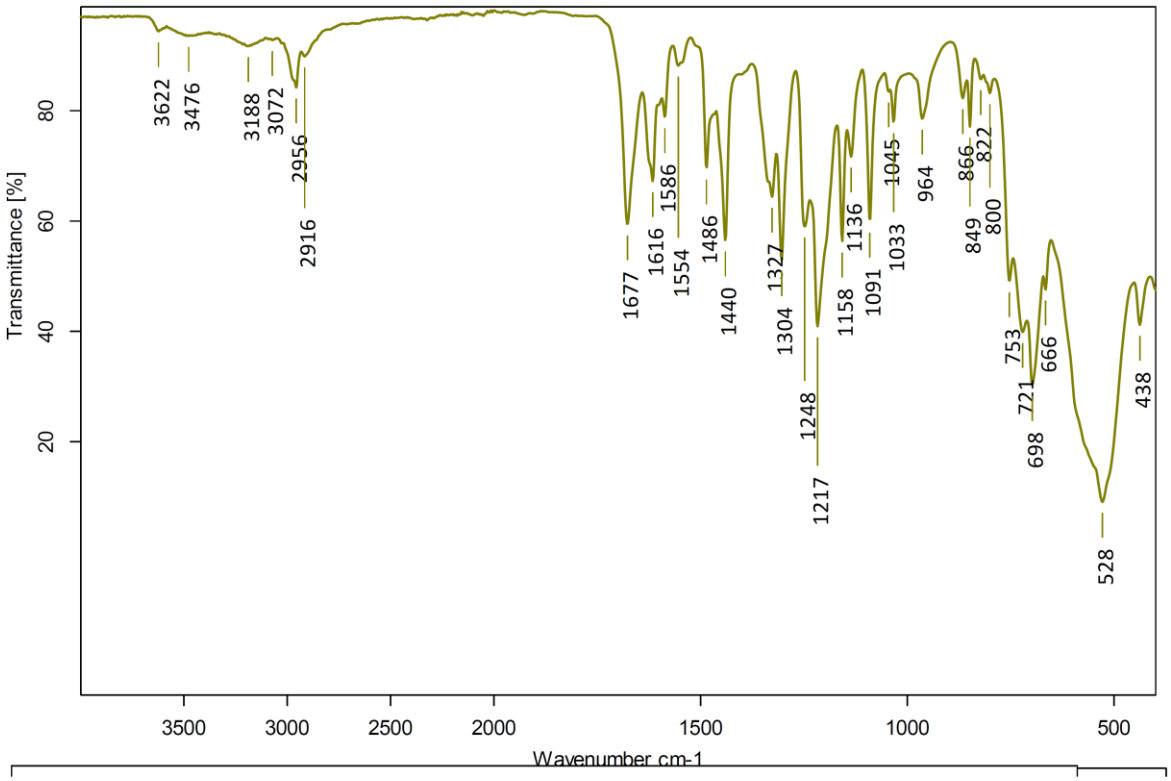

Figure S6. FTIR-ATR spectrum of **2**.

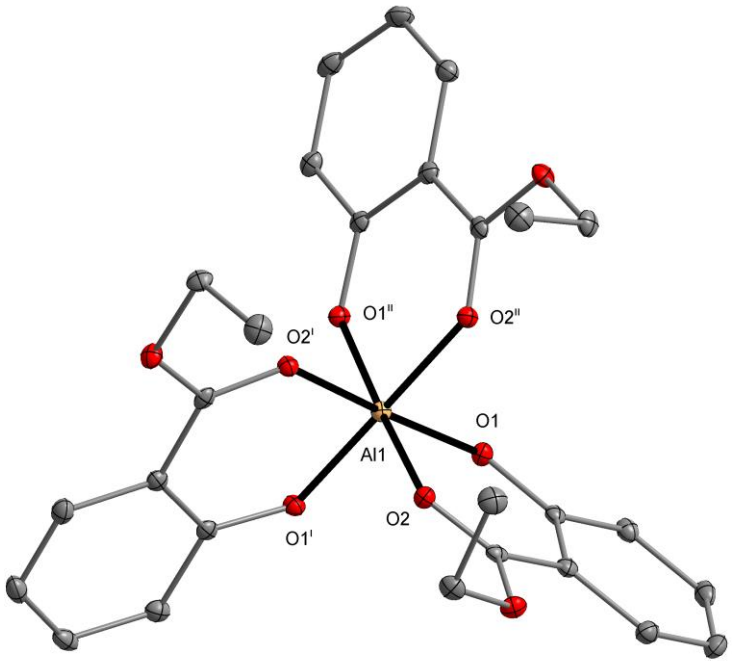

Figure S7. Molecular structure of [Al(EtsalO)$_3$] (**1a**). The displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity [symmetry codes: (i) 1−*x*+*y*, 1−*x*, *z;* (ii) 1−*y*, *x*−*y*, *z*].

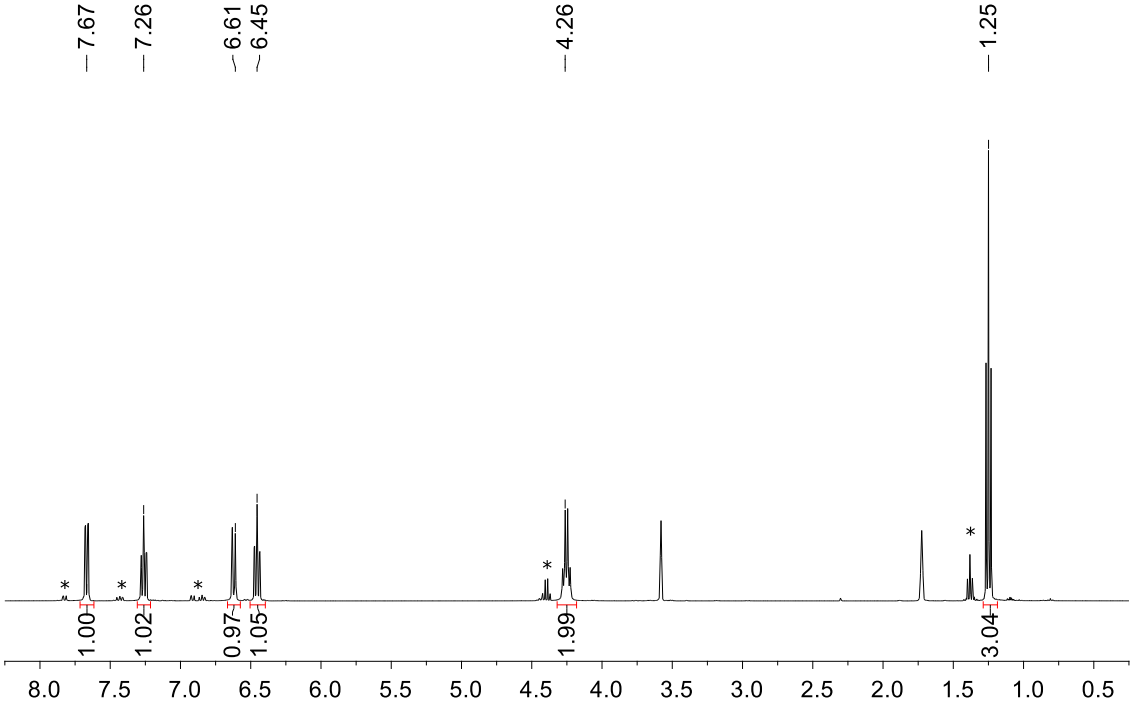

Figure S8. ^{1}H NMR spectrum of **1a** in THF-d$_8$. * - assigned signals from EtsalOH residues.

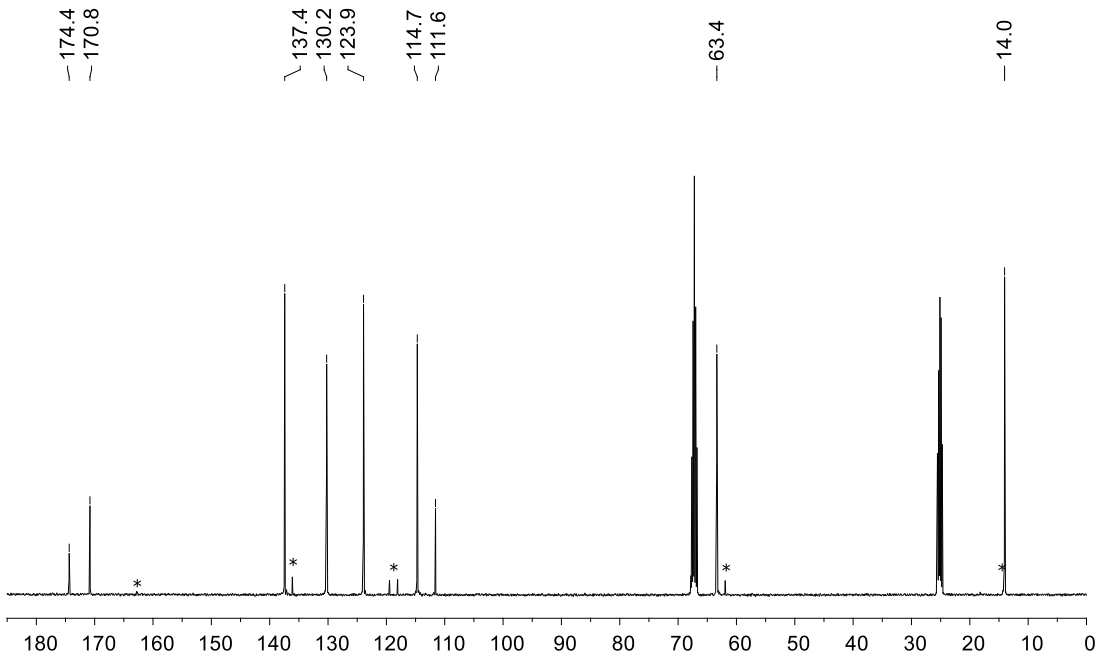

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in THF-d_8. * - assigned signals from EtsalOH residues.

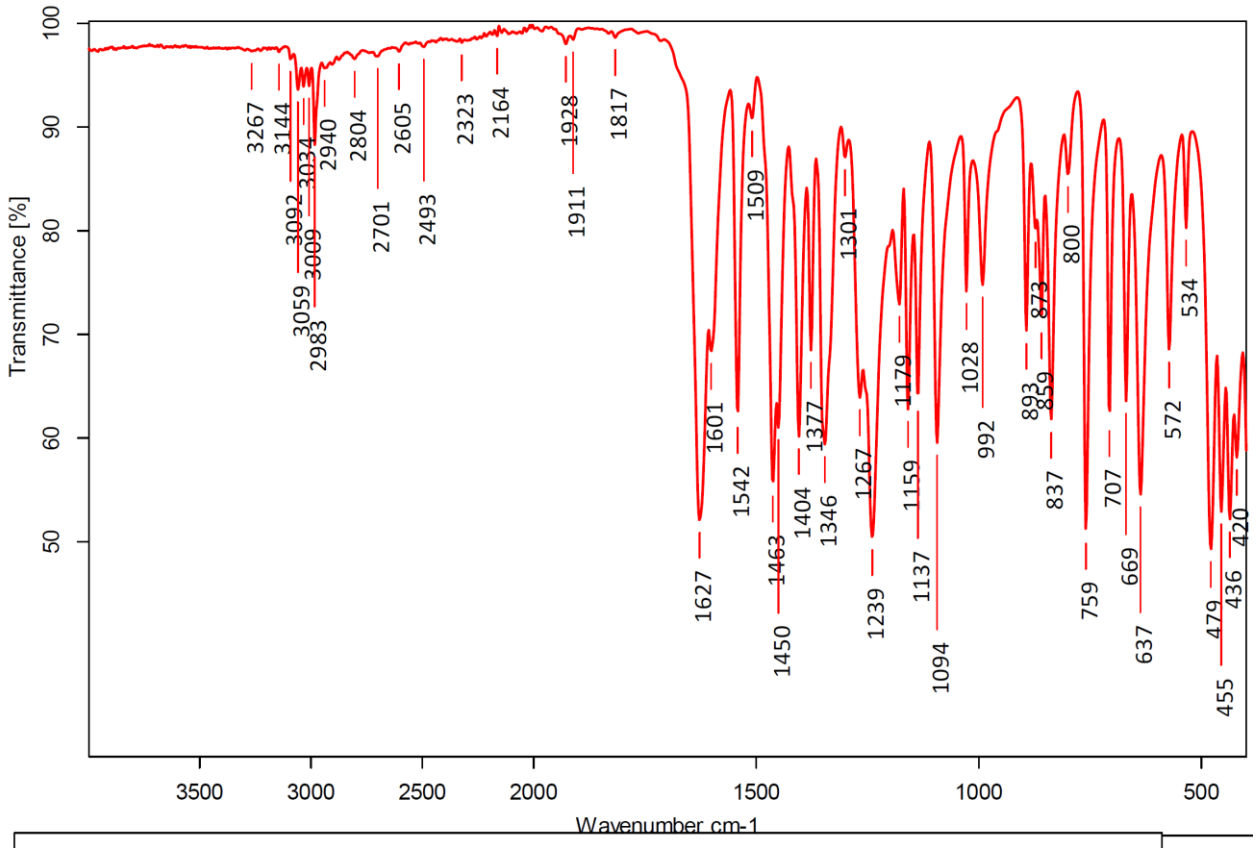

Figure S10. FTIR-ATR spectrum of **1a**.

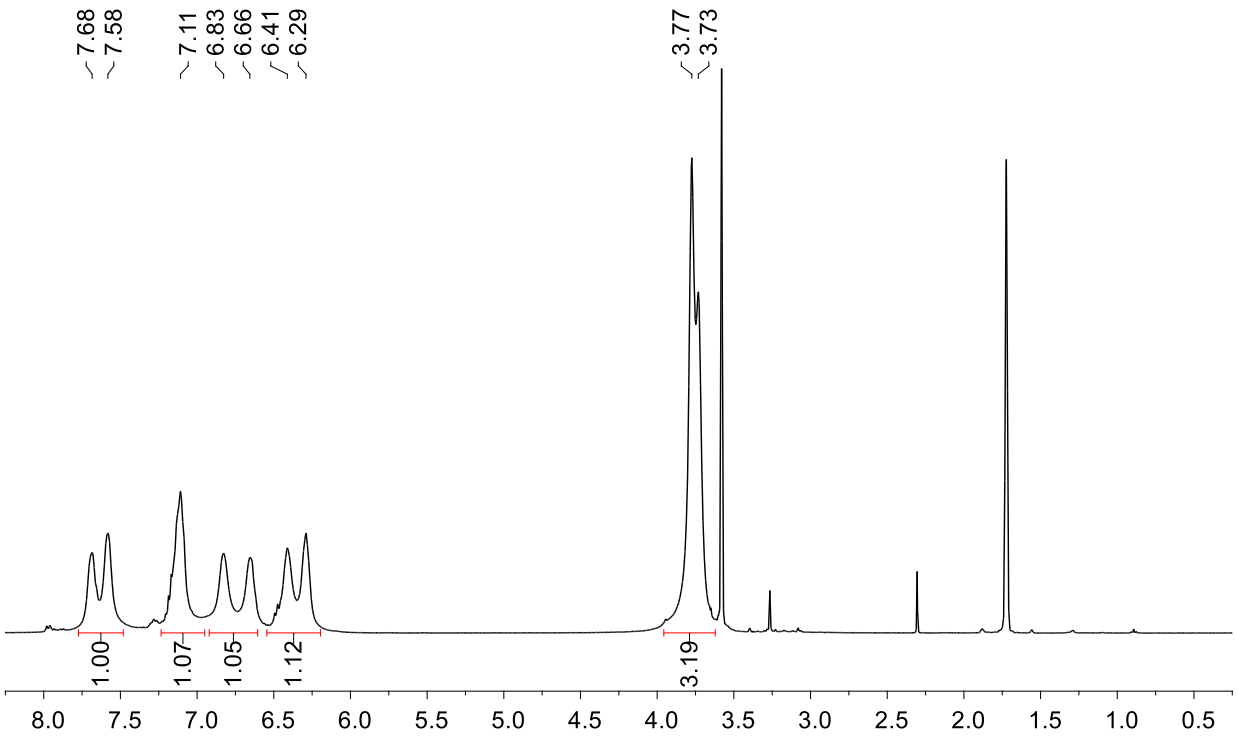

Figure S11. ^{1}H NMR spectrum of **3** in THF-d_8.

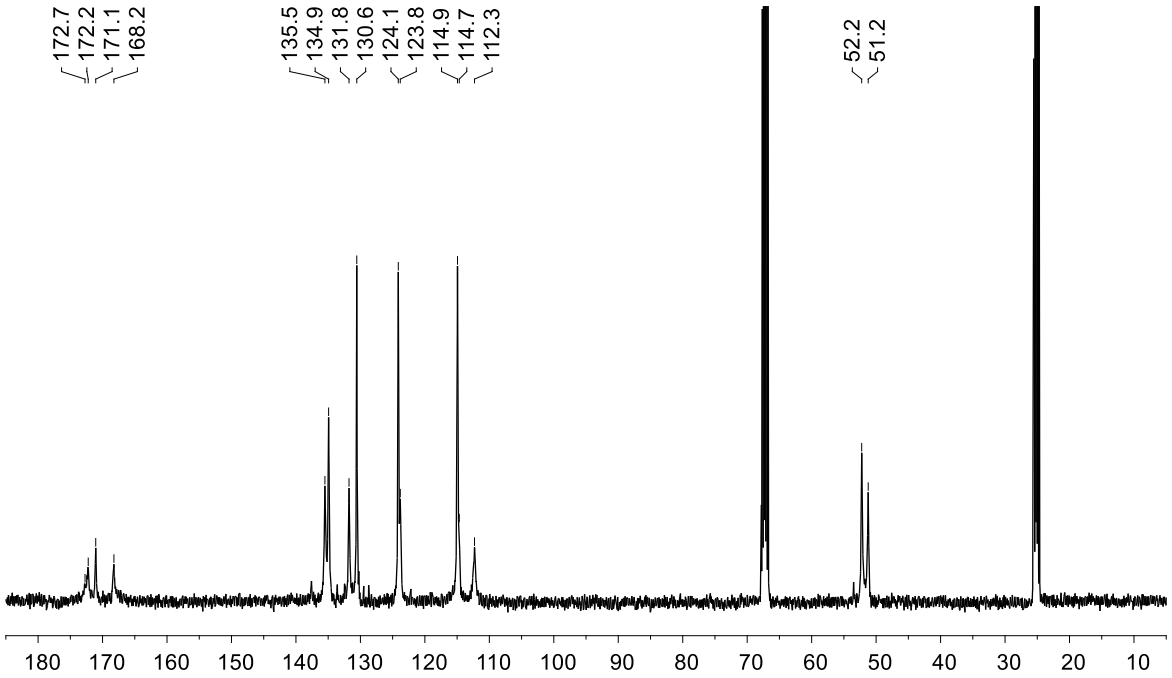

Figure S12. ^{13}C{^{1}H} NMR spectrum of **3** in THF-d_8.

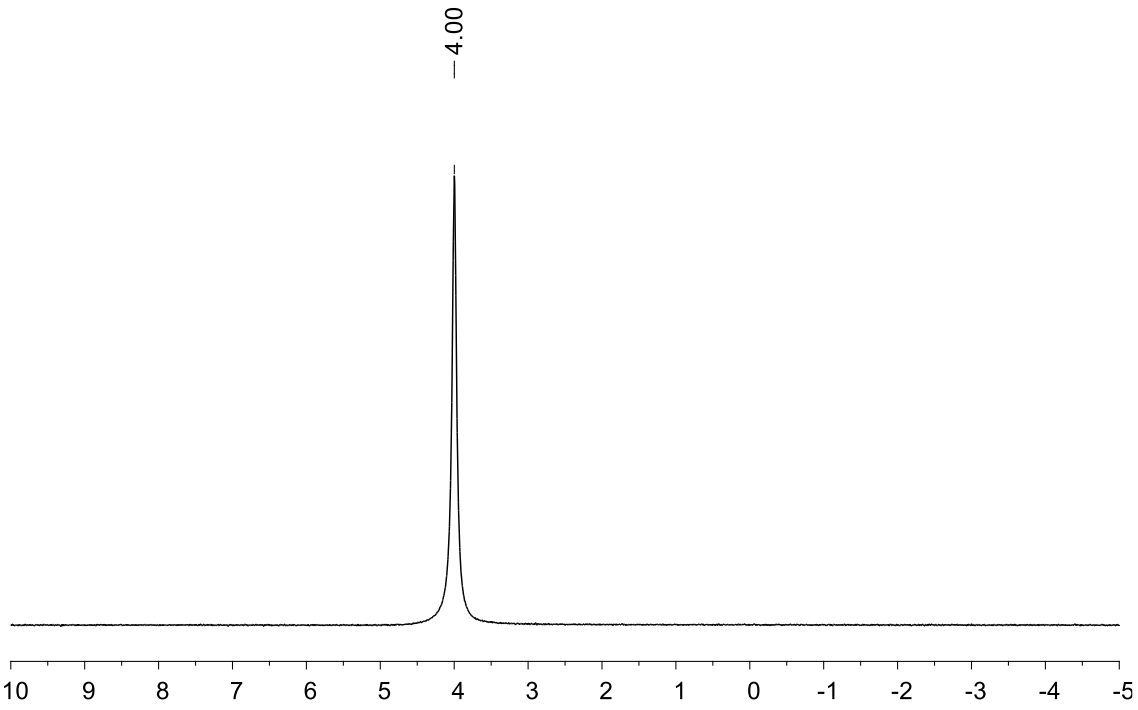

Figure S13. ^{7}Li NMR spectrum of **3** in THF-d_8.

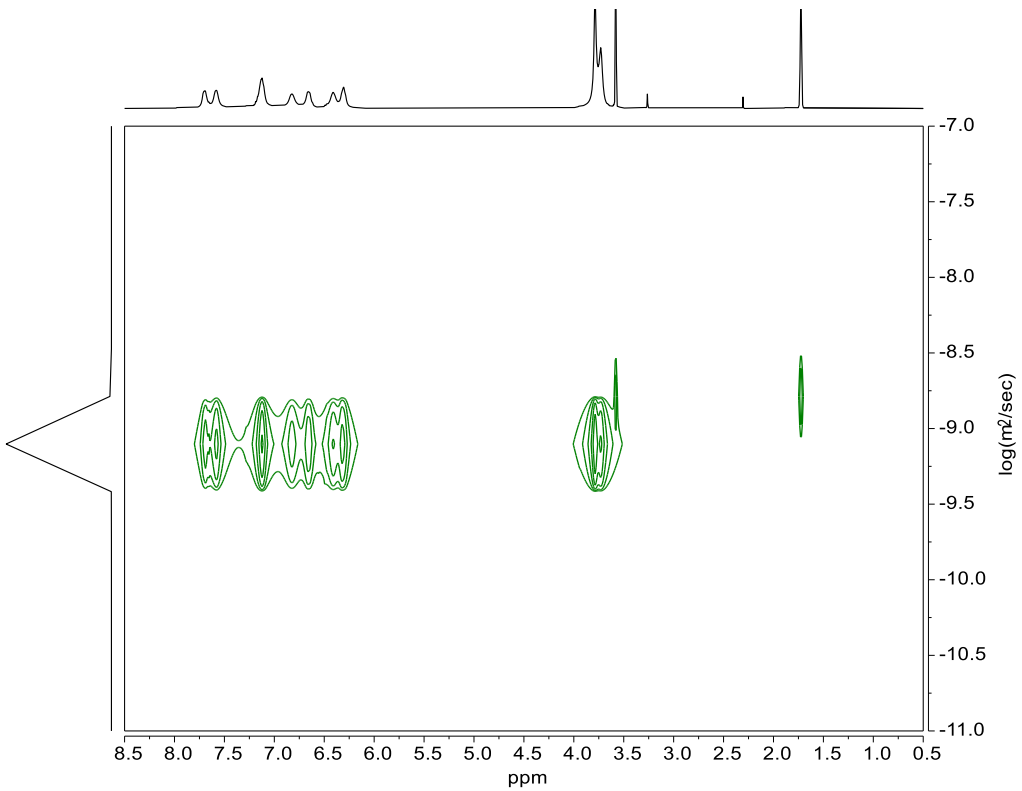

Figure S14. ^{1}H-DOSY NMR spectrum of **3** in THF-d_8.

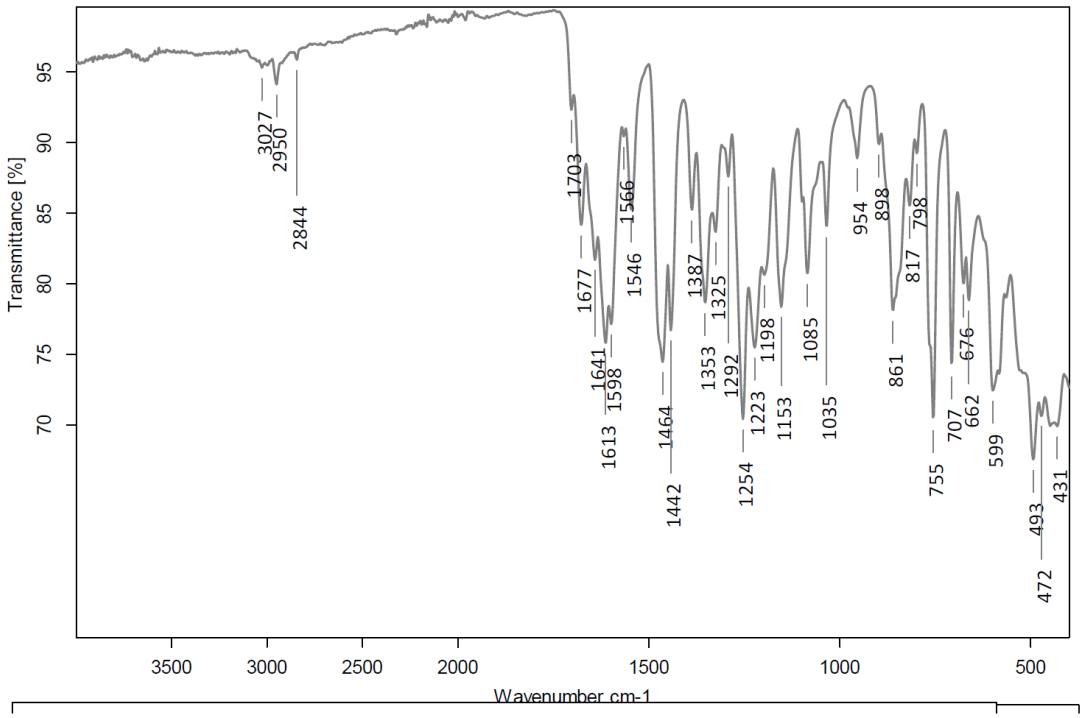

Figure S15. FTIR-ATR spectrum of **3**.

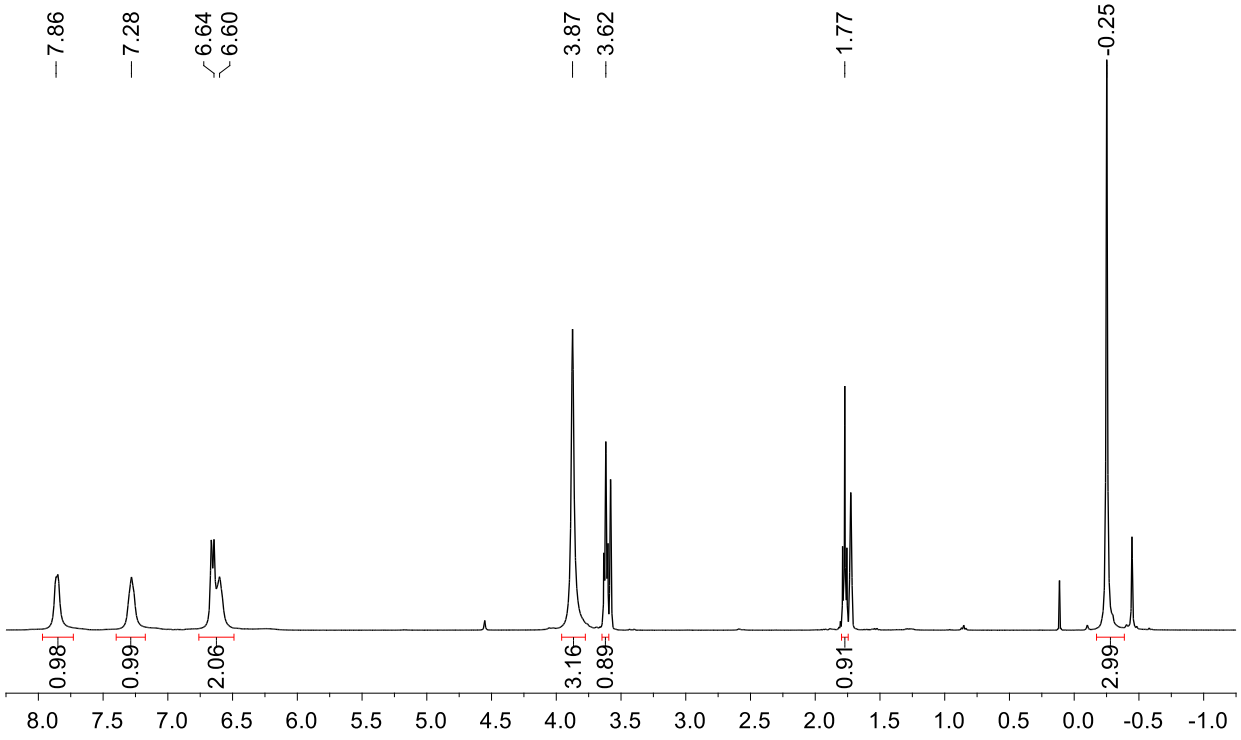

Figure S16. ^{1}H NMR spectrum of **4** in THF-d_8.

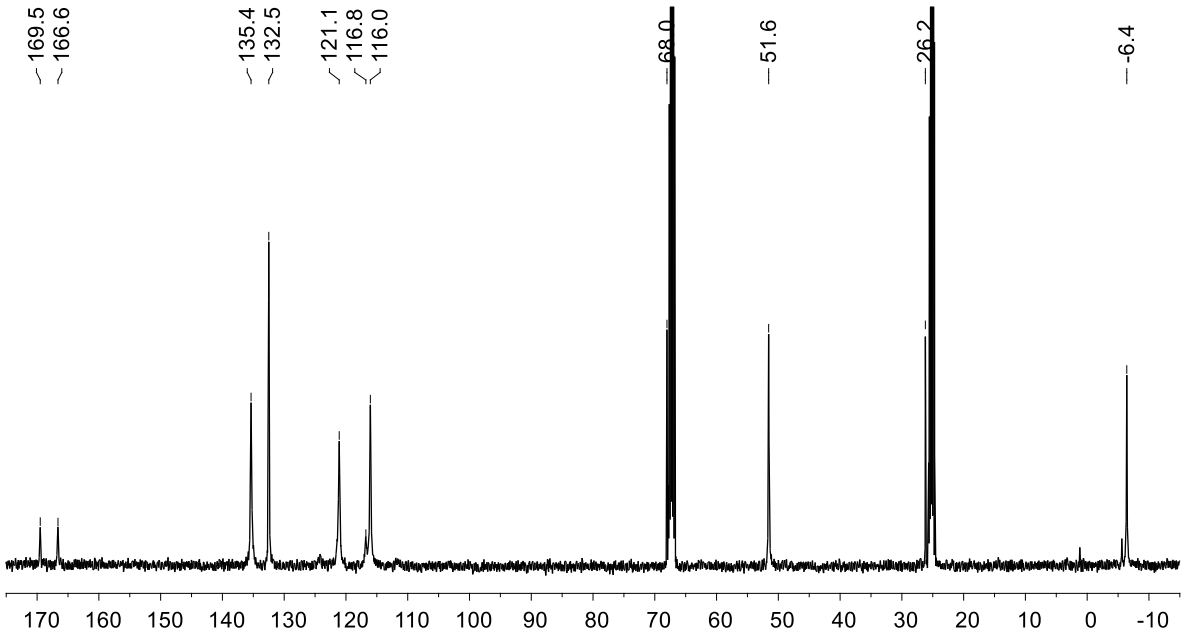

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in THF-d_8.

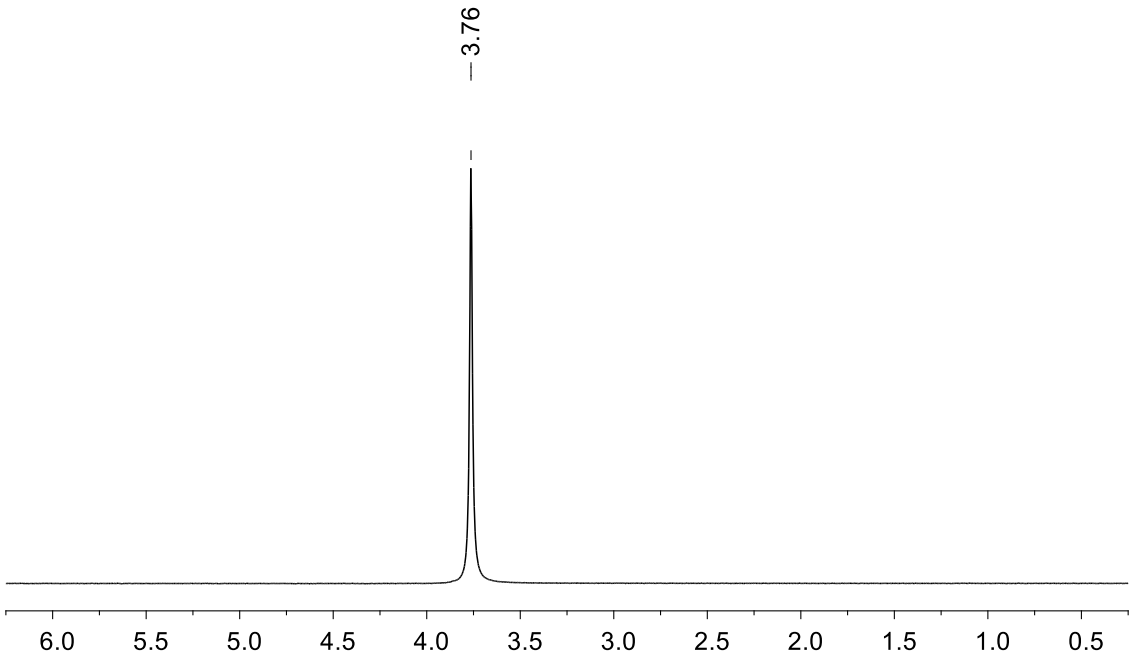

Figure S18. ^{7}Li NMR spectrum of **4** in THF-d_8.

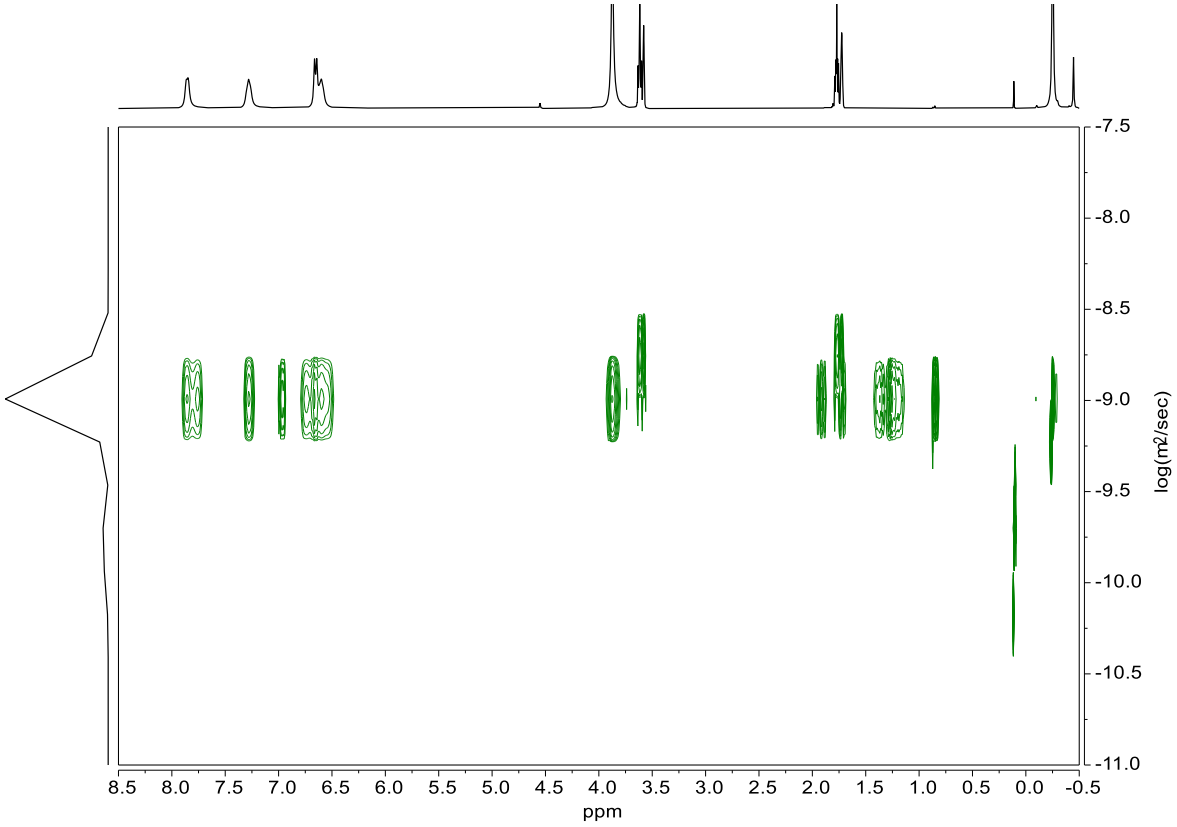

Figure S19. ^{1}H-DOSY NMR spectrum of **4** in THF-d_8.

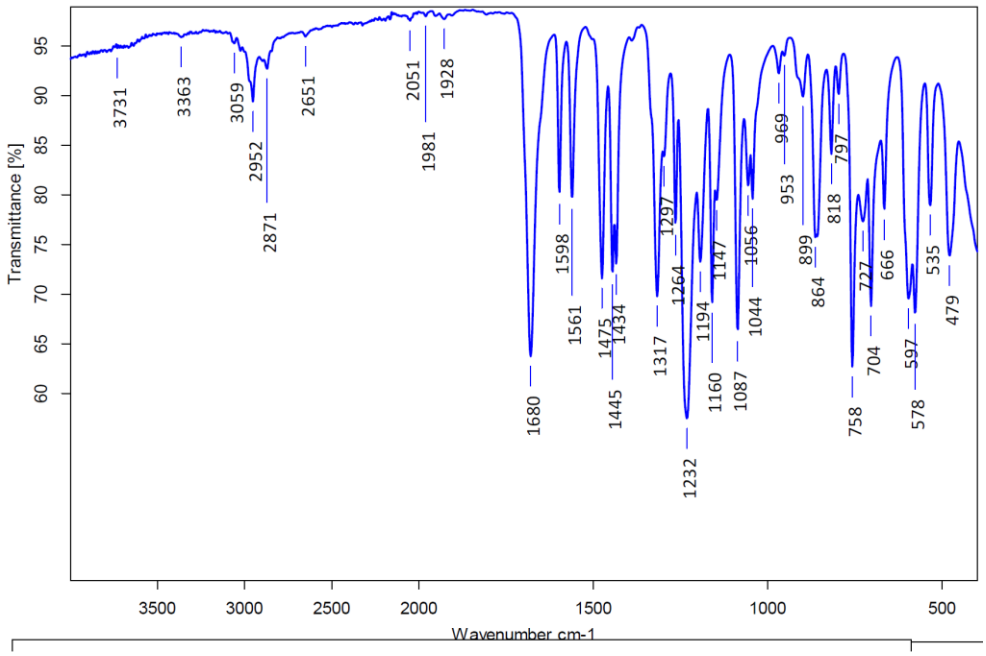

Figure S20. FTIR-ATR spectrum of **4**.

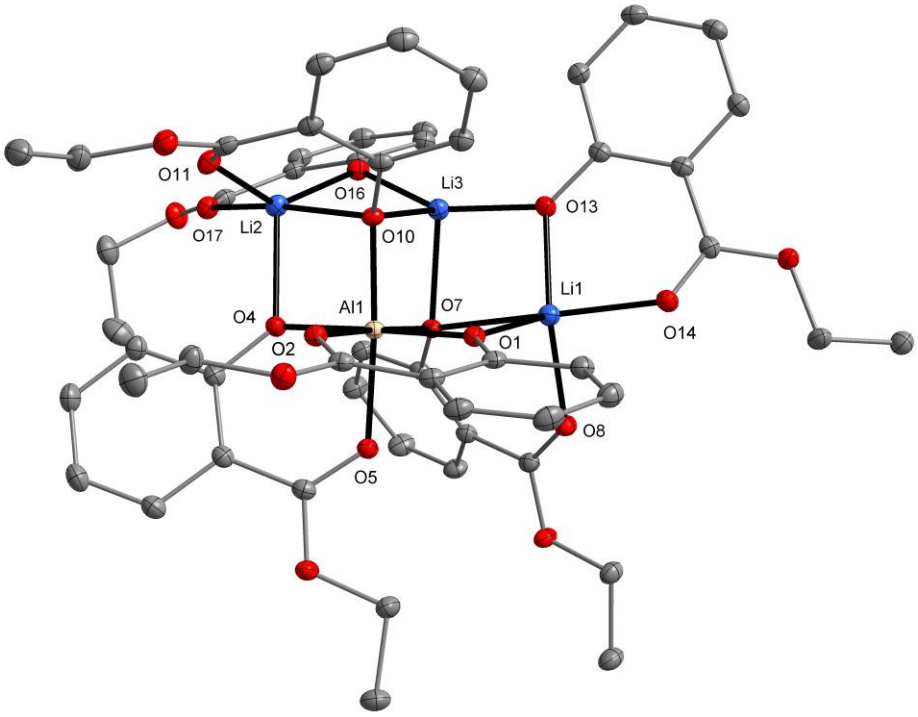

Figure S21. Molecular structure of [$AlLi_3(EtsalO)_6$] (**3a**). The displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for the sake of clarity.

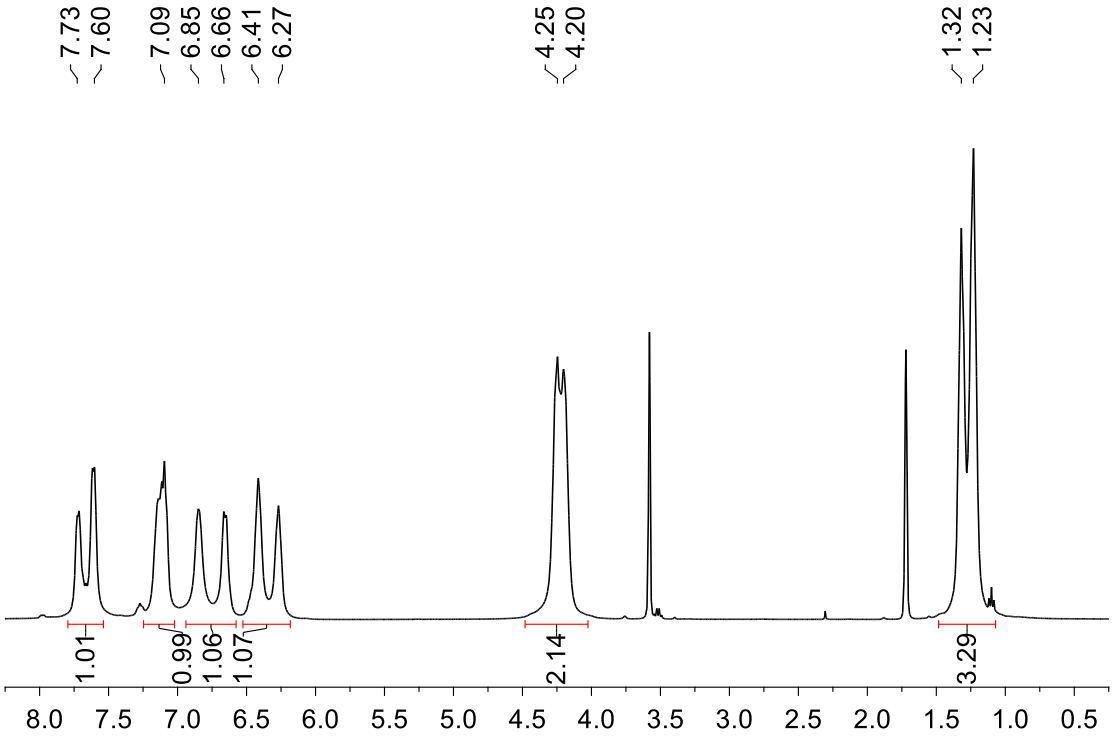

Figure S22. ^{1}H NMR spectrum of **3a** in THF-d_8.

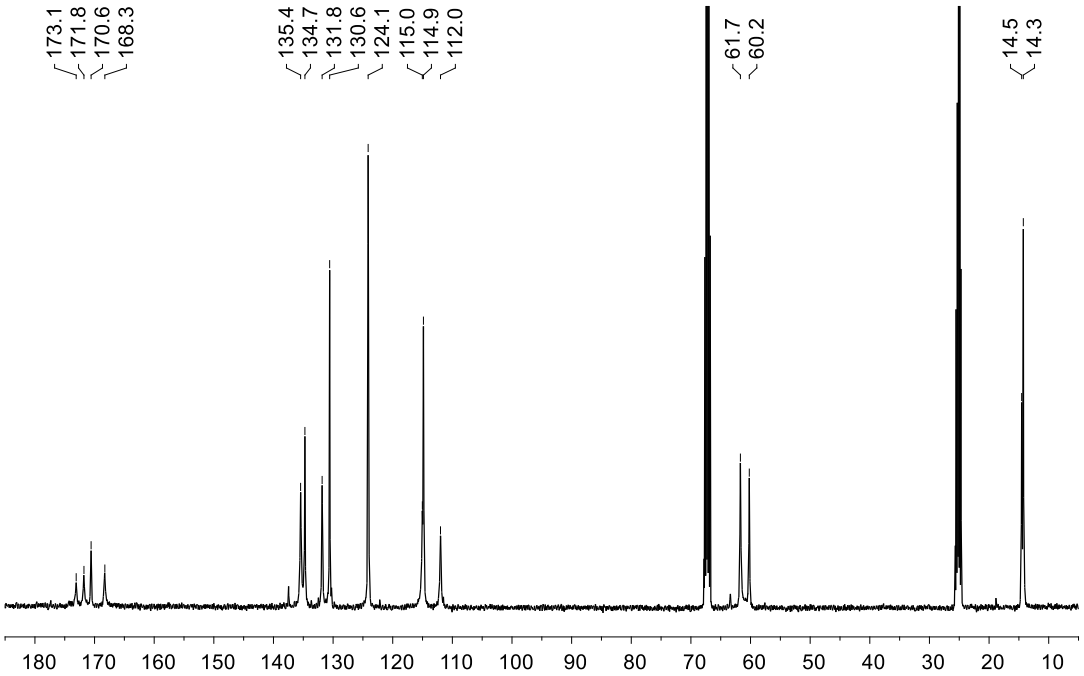

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in THF-d_8.

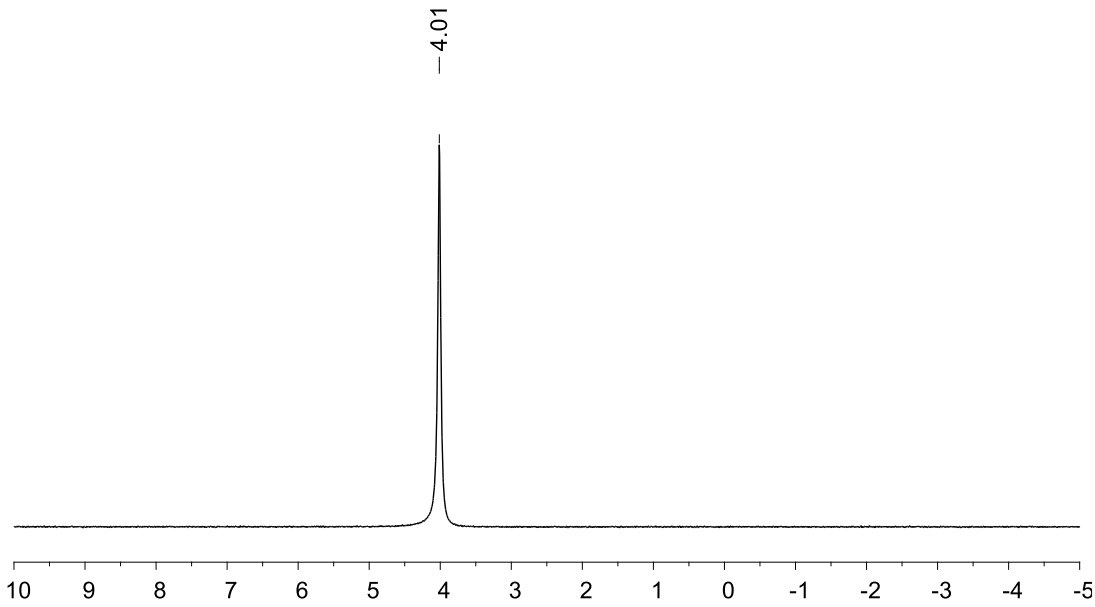

Figure S24. ^{7}Li NMR spectrum of **3a** in THF-d_8.

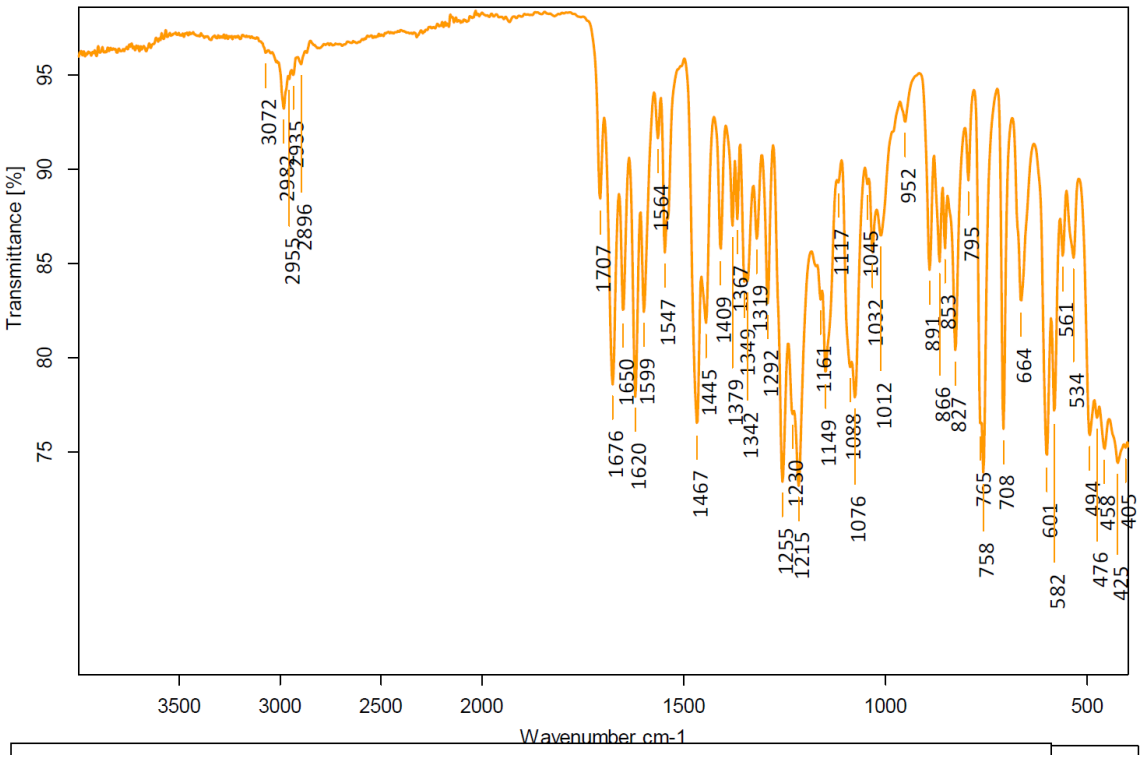

Figure S25. FTIR-ATR spectrum of **3a**

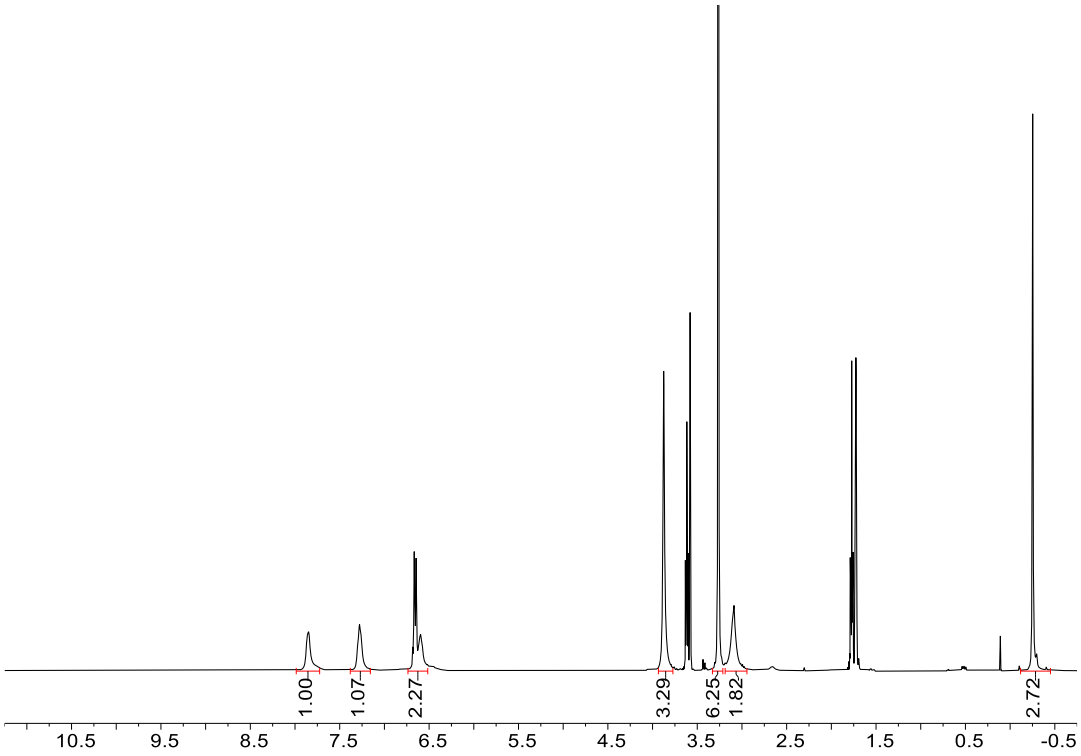

Figure S26. ^{1}H NMR spectrum of reaction of **4** with four molar equiv of MeOH in THF-d_8.

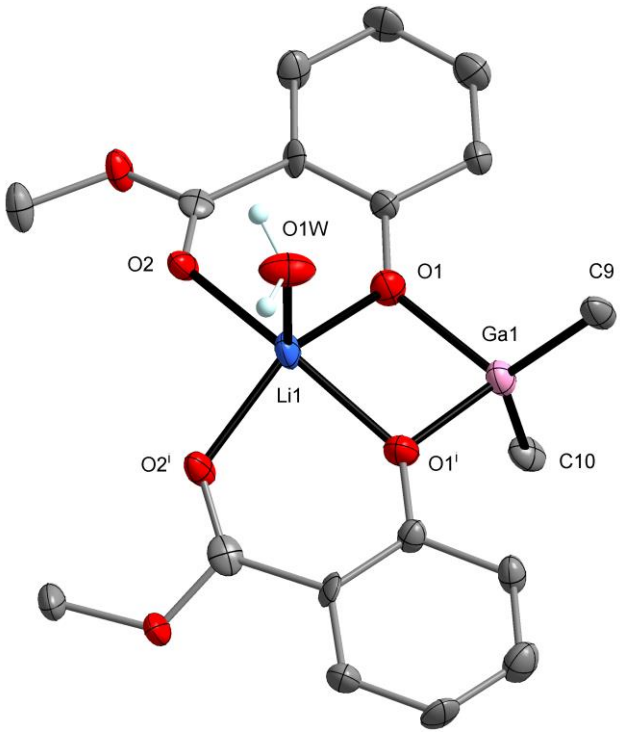

Figure S27. Molecular structure of [$Me_2GaLi(MesalO)_2(H_2O)$] (**6**). The displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

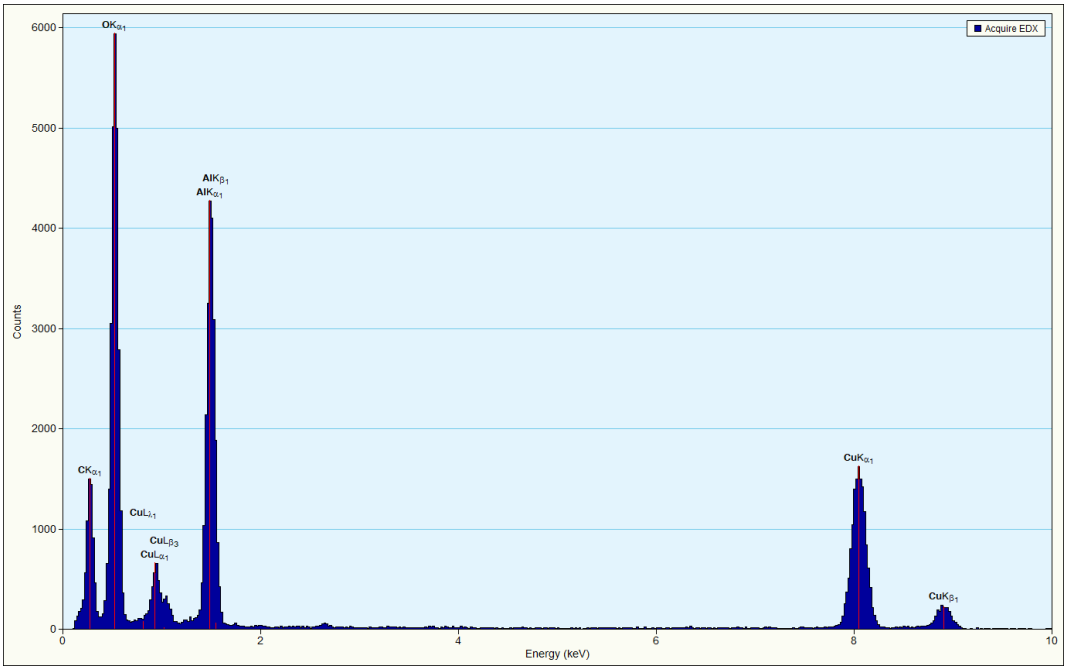

Figure S28. EDX analysis of γ-$LiAlO_2$ prepared by calcination of **3** at 850 °C. The EDX cannot detect the lithium element due to its lightweight. The copper and carbon elements come from the use of copper-carbon grids.

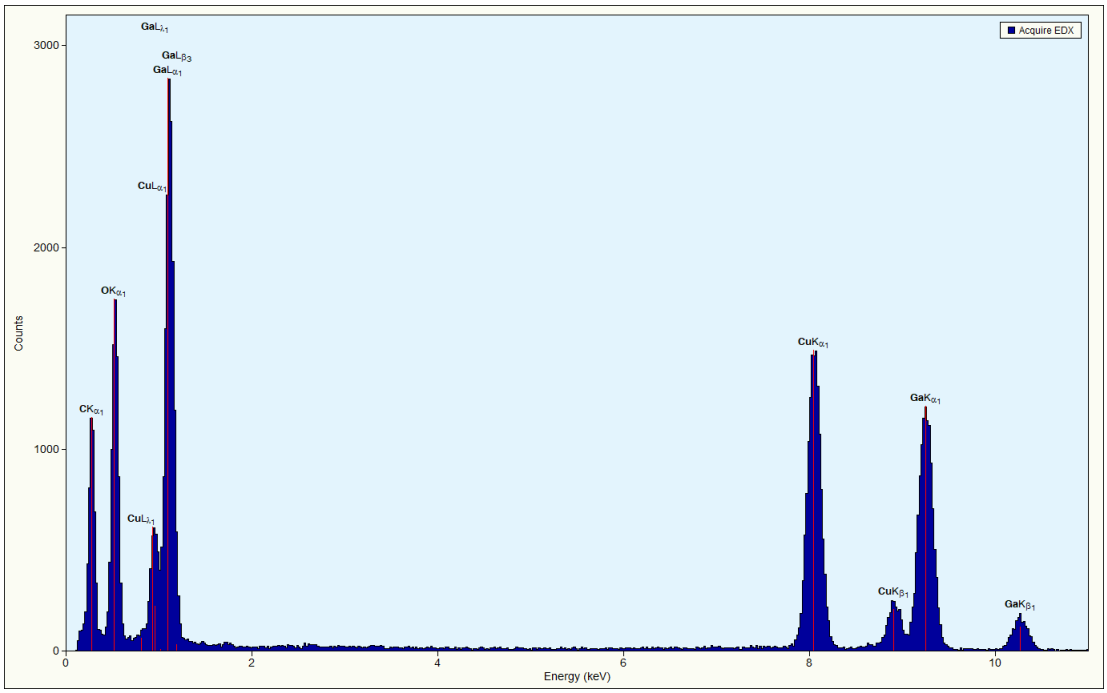

Figure S29. EDX analysis of β-$LiGaO_2$ prepared by calcination of **4** at 850 °C. The EDX cannot detect the lithium element due to its lightweight. The copper and carbon elements come from the use of copper-carbon grids.

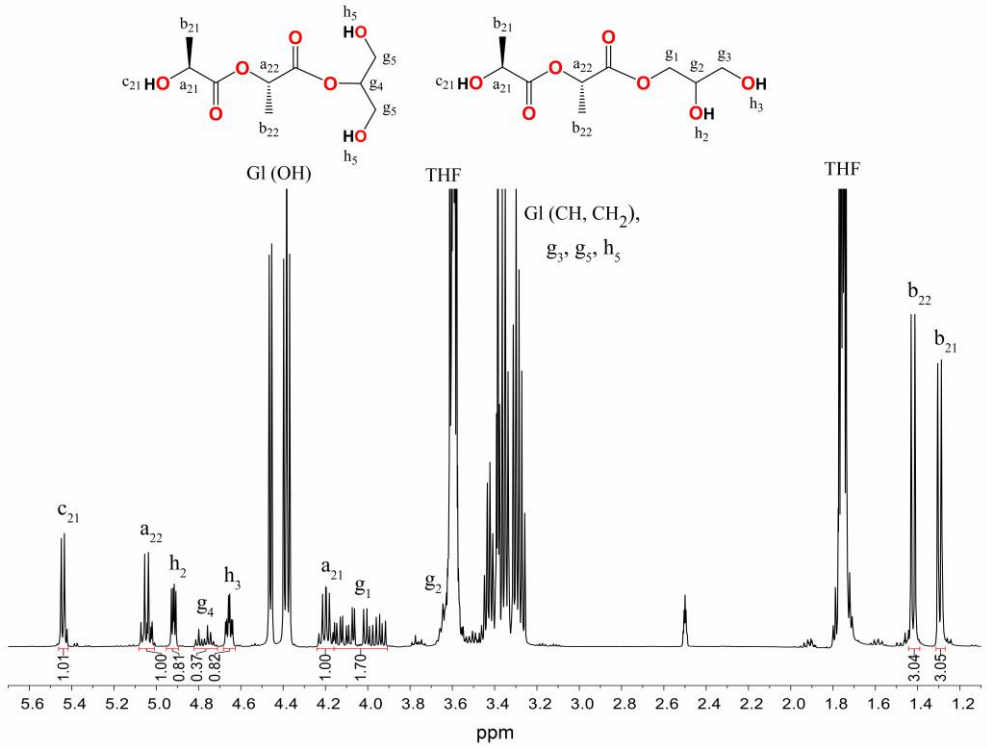

Figure S30. ^{1}H NMR spectrum in DMSO-d_6 of GlL_2 formed in L-LA alcoholysis reaction in the absence of catalyst source.

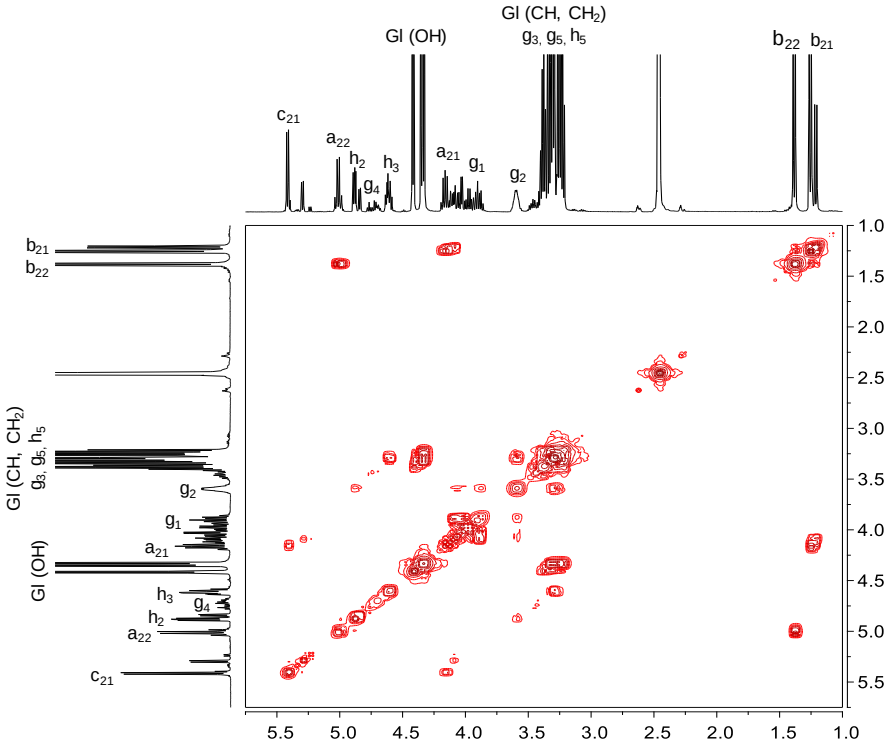

Figure S31. ^{1}H-^{1}H COSY NMR spectrum in DMSO-d_6 of mixture GlL_2 and GlL_1 received in the presence of **4**.

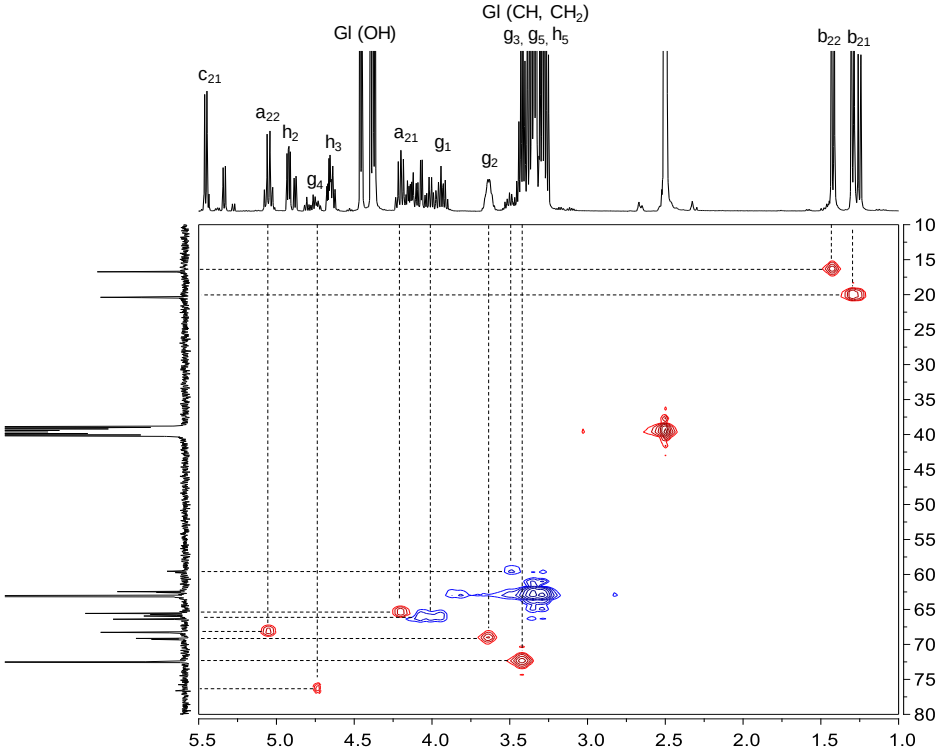

Figure S32. ^{1}H-^{13}C HSQC NMR spectrum in DMSO-d_6 of GlL_2 and GlL_1 mixture received in the presence of **4**.

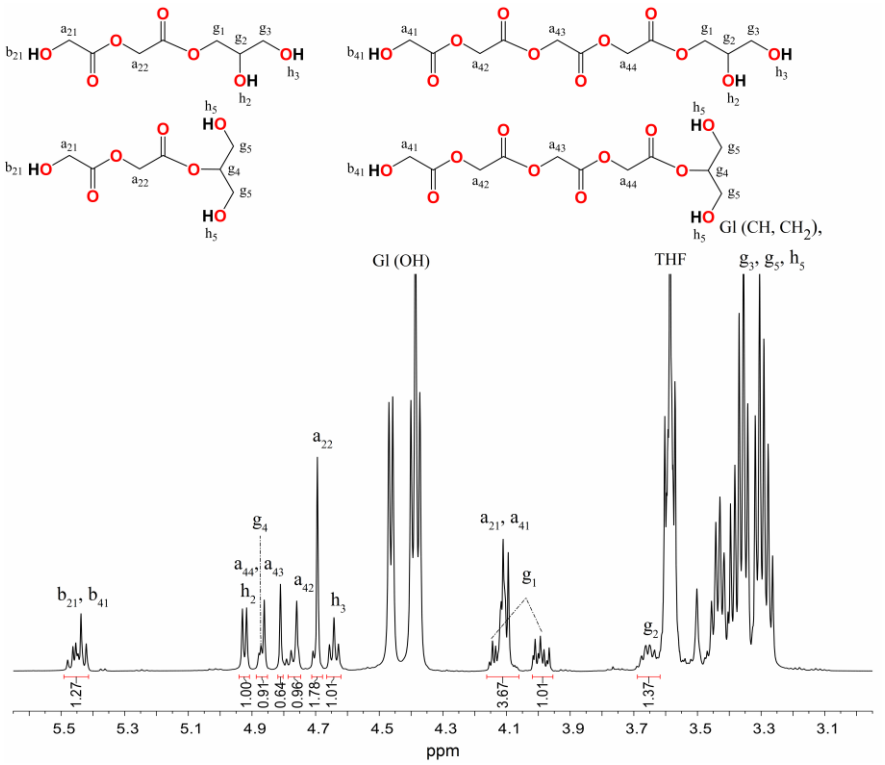

Figure S33. ^{1}H NMR spectrum in DMSO-d_6 of GlG_2 and GlG_4 formed in the alcoholysis reaction of a GA in the absence of catalyst source.

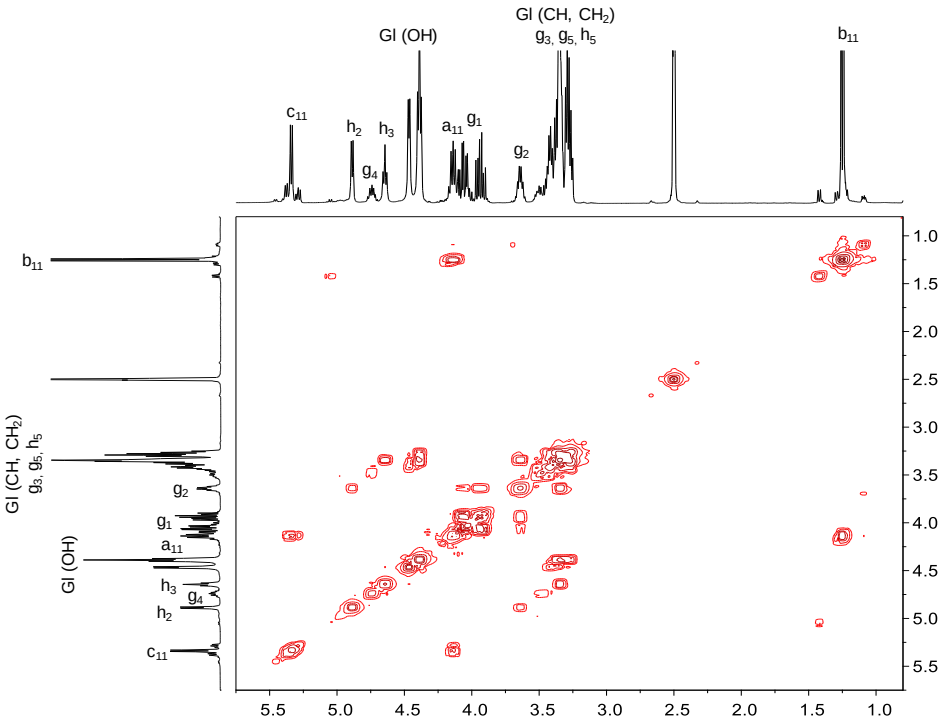

Figure S34. ^{1}H-^{1}H COSY NMR spectrum in DMSO-d_6 of GlL_1 formed in L-LA alcoholysis reaction in the presence of **3**.

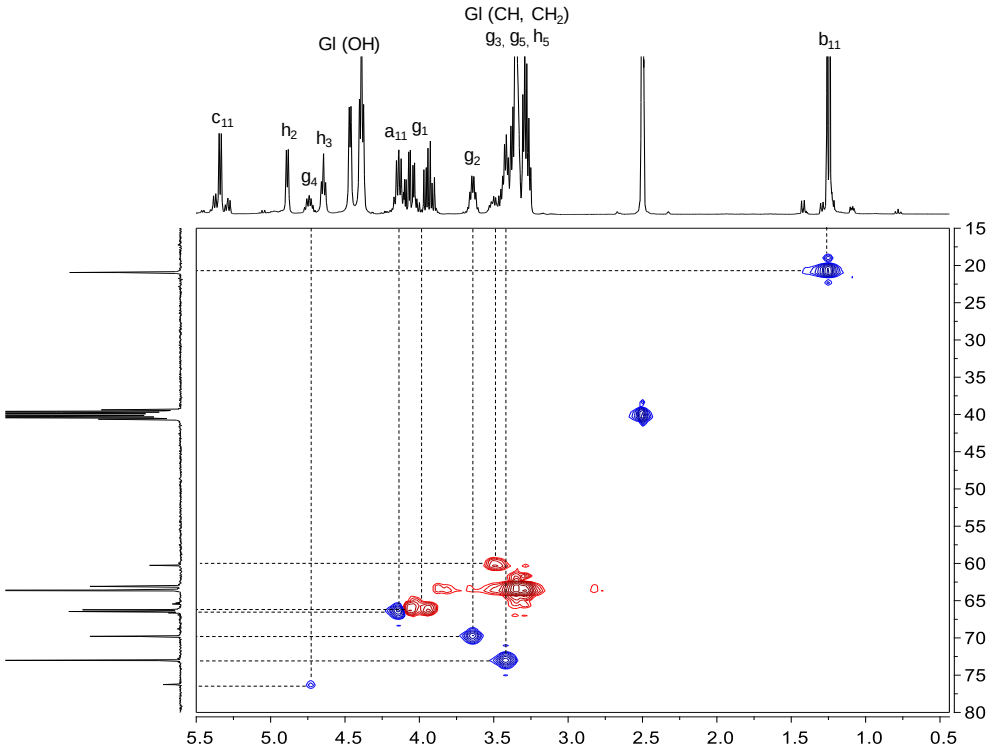

Figure S35. ^{1}H-^{13}C HSQC NMR spectrum in DMSO-d_6 of GlL_1 formed in L-LA alcoholysis reaction in the presence of **3**.

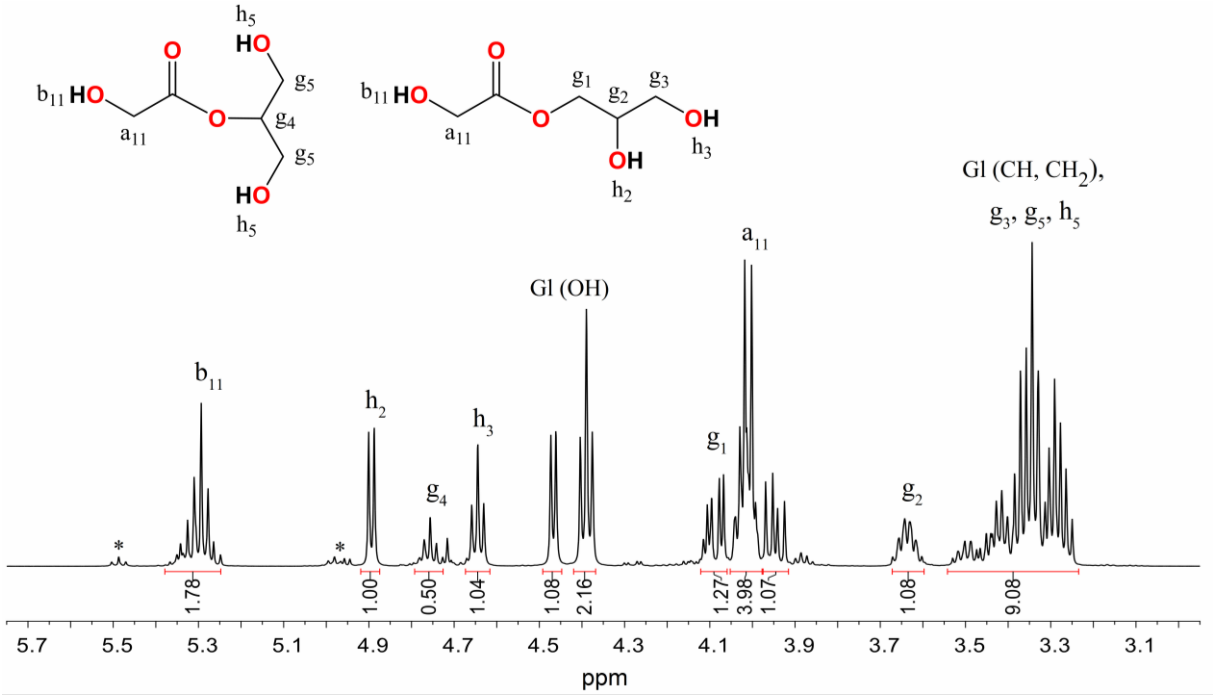

Figure S36. ^{1}H NMR spectrum in DMSO-d_6 of GlG_1 and GlG_n.formed in GA alcoholysis reaction in the presence of **5**. * - assigned signals from GlG_n.

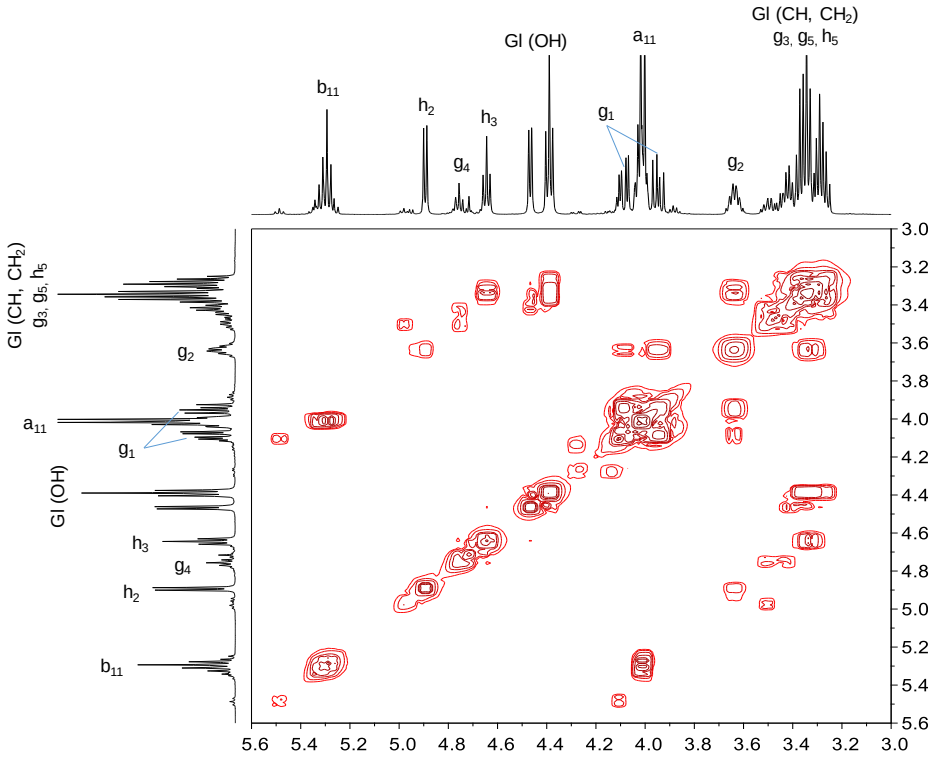

Figure S37. ^{1}H-^{1}H COSY NMR spectrum in DMSO-d_6 of GlG_1 formed in GA alcoholysis reaction in the presence of **5**.

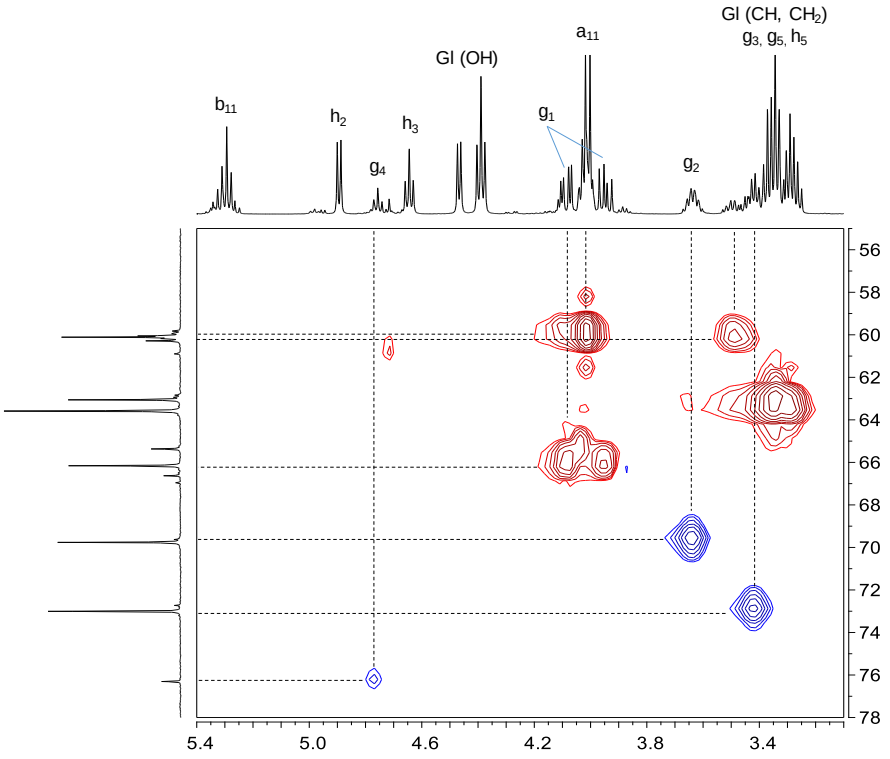

Figure S38. ^{1}H-^{13}C HSQC NMR spectrum in DMSO-d_6 of GlG_1 formed in GA alcoholysis reaction in the presence of **5**.

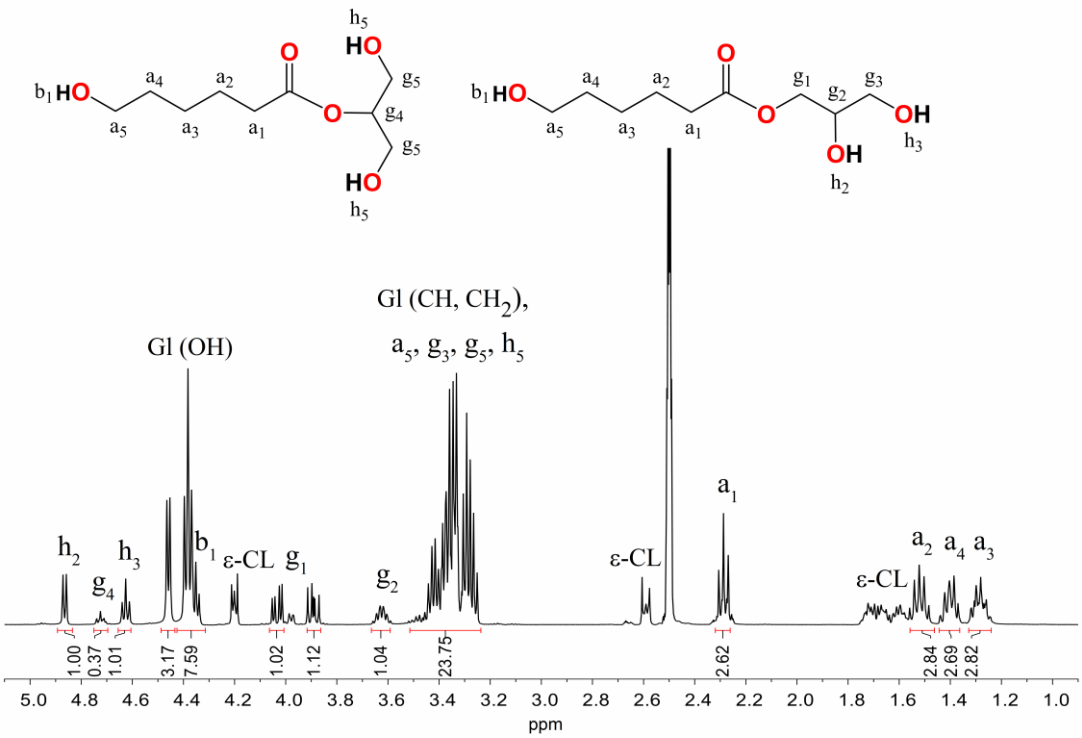

Figure S39. ^{1}H NMR spectrum in DMSO-d$_6$ of GlCL$_1$ formed in ε-CL alcoholysis reaction in the presence of **5**.

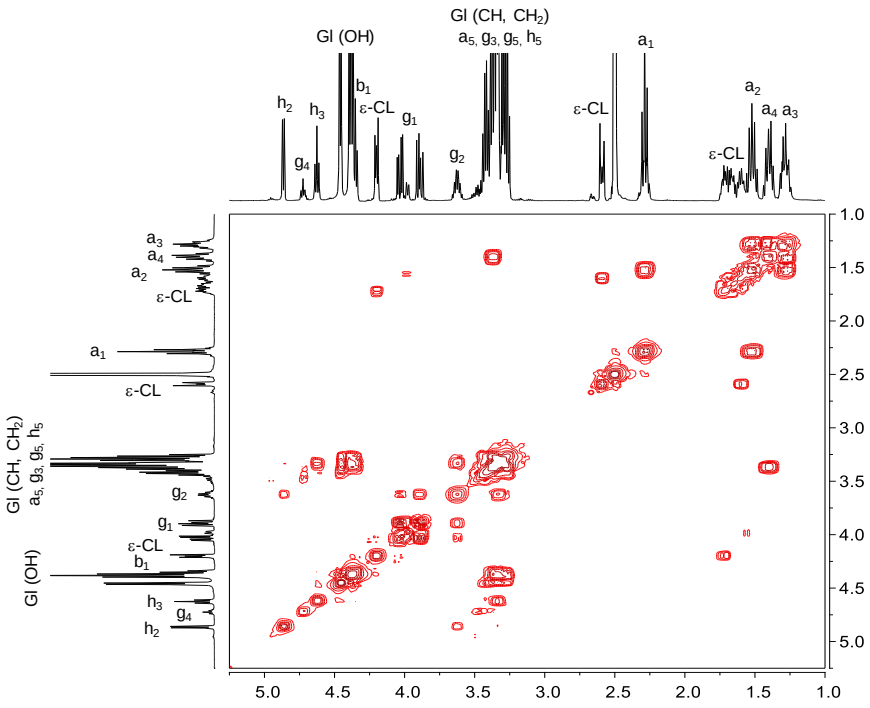

Figure S40. ^{1}H-^{1}H COSY NMR spectrum in DMSO-d$_6$ of GlCL$_1$ formed in ε-CL alcoholysis reaction in the presence of **5**.

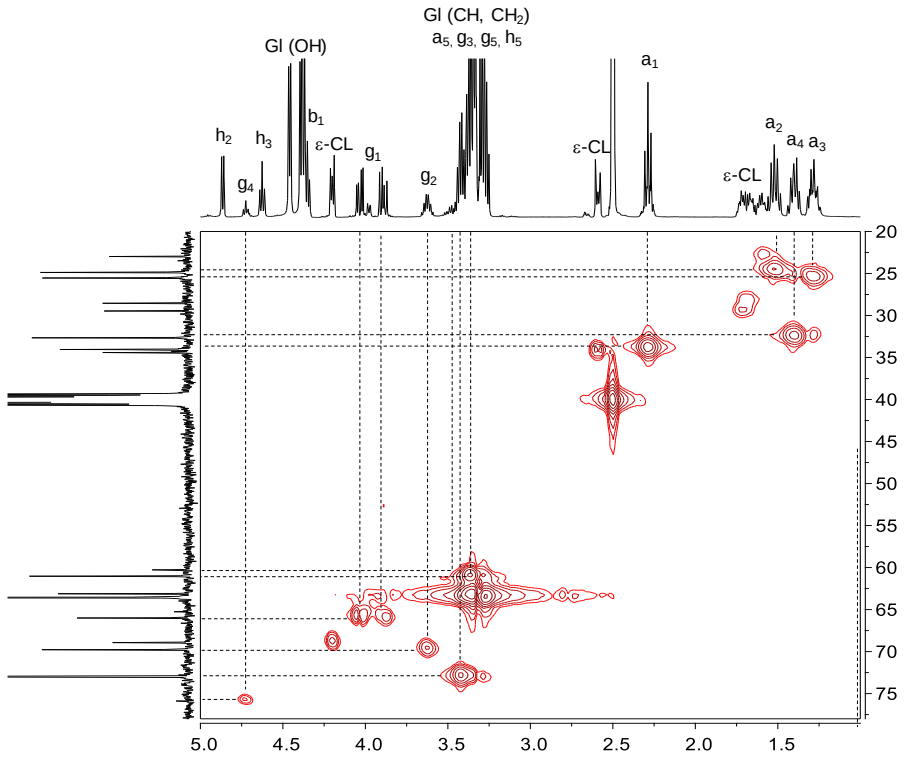

Figure S41. ^{1}H-^{13}C HSQC NMR spectrum in DMSO-d_6 of $GlCL_1$ formed in ε-CL alcoholysis reaction in the presence of **5**.

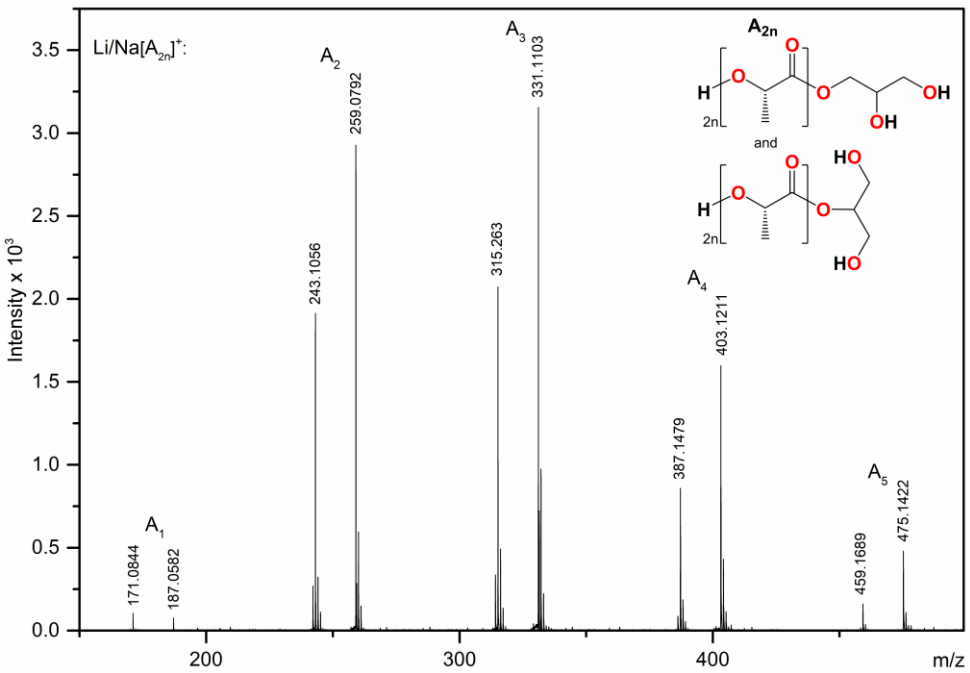

Figure S42. ESI-MS spectrum of GlL_1 and its polycondensation products.

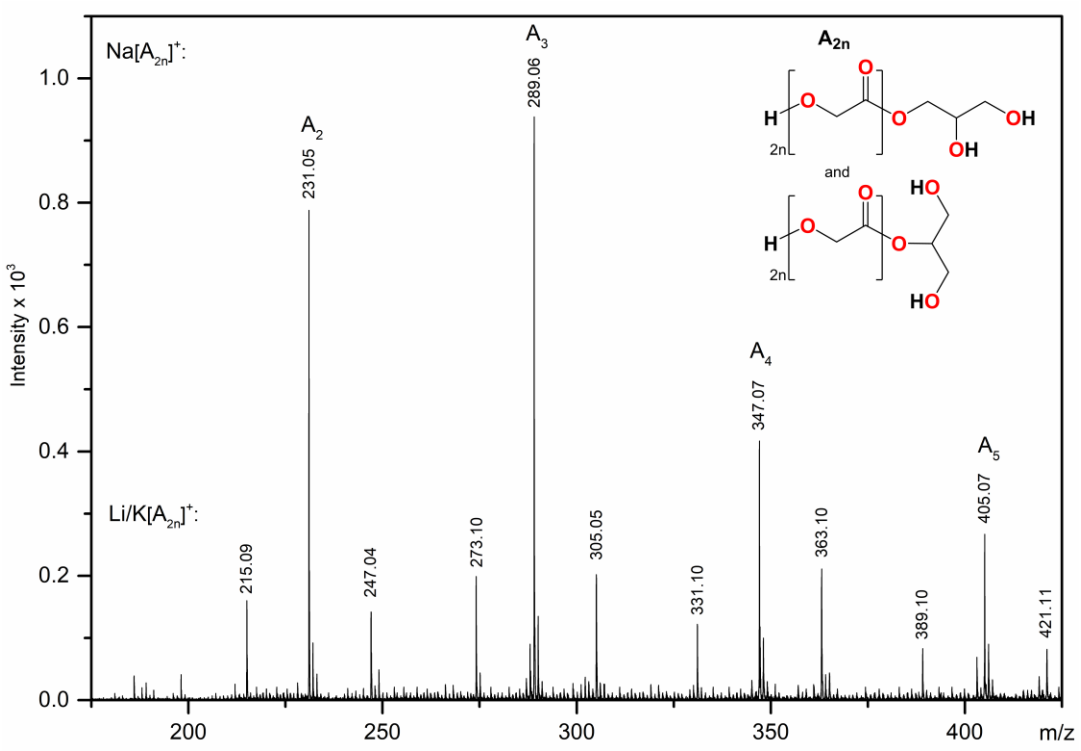

Figure S43. ESI-MS spectrum of the mixture of GlG_1 and GlG_n.

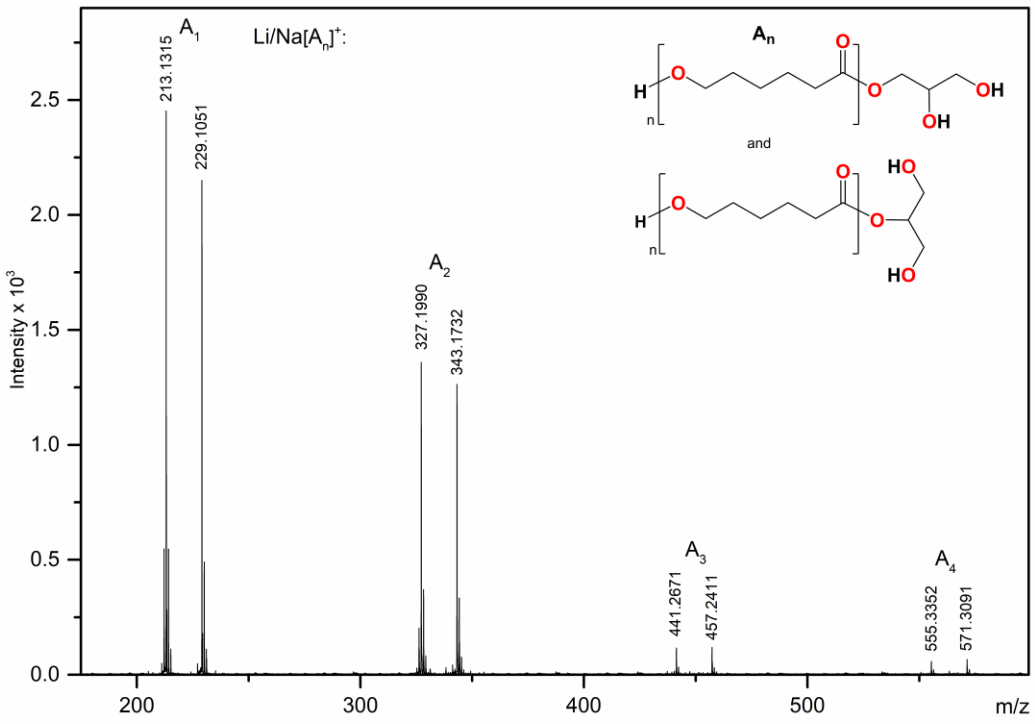

Figure S44. ESI-MS spectrum of $GlCL_1$ and its polycondensation products.

Table S2. Summary of catalyst-free alcoholysis of L-LA and ε-CL.[a]

Entry	Ester	Ester/Gl	t(h)	GlCL[b] (%)	GlL_2[b] (%)
1	L-LA	1/1	58	-	6
2	L-LA	1/1	120	-	14
3	L-LA	1/1	145	-	18
4	L-LA	1/1	168	-	22
5	L-LA	1/1	196	-	25
6	L-LA	1/1	216	-	28
7	L-LA	1/1	240	-	30
8	L-LA	1/1	312	-	35
9	L-LA	1/1	360	-	37
10	L-LA	1/1	576	-	43
11	L-LA	1/2	5	-	6
12	L-LA	1/2	22	-	13
13	L-LA	1/2	58	-	41
14	L-LA	1/2	120	-	64
15	L-LA	1/2	145	-	67
16	L-LA	1/2	168	-	70
17	L-LA	1/2	312	-	85
18	L-LA	1/2	360	-	86
19	L-LA	1/2	480	-	92
20	L-LA	1/2	576	-	93
21	L-LA	1/3	5	-	11
22	L-LA	1/3	8	-	27
23	L-LA	1/3	22	-	31
24	L-LA	1/3	58	-	60
25	L-LA	1/3	120	-	76
26	L-LA	1/3	145	-	87
27	L-LA	1/3	168	-	93
28	L-LA	1/3	196	-	99
29	ε-CL	1/2	167	1	-
30	ε-CL	1/3	168	2	-
31	ε-CL	1/3	312	2	-

[a]General reaction conditions: [L-LA(ε-CL)] = 0.53 M, 20 ml of THF as solvent, temperature 25 °C, under N_2 atmosphere, reactant stoichiometries L-LA(ε-CL)/Gl = 1/1-3. [b]Obtained from ^{1}H NMR spectroscopic analysis.

Table S3. Summary of catalyst-free alcoholysis of GA.[a]

Entry	Ester	Ester/Gl	t(h)	GlG_2[b] (%)	GlG_4[b] (%)
1	GA	1/1	3	2	0
2	GA	1/1	8	2	1
3	GA	1/1	32	5	2
4	GA	1/1	50	7	3
5	GA	1/1	72	11	7
6	GA	1/1	168	18	15
7	GA	1/1	216	19	18
8	GA	1/1	312	20	18
9	GA	1/1	408	22	21
10	GA	1/2	3	3	0
11	GA	1/2	8	6	1
12	GA	1/2	32	17	10
13	GA	1/2	50	24	15
14	GA	1/2	72	31	28
15	GA	1/2	168	40	43
16	GA	1/2	216	43	43
17	GA	1/2	312	44	45
18	GA	1/3	3	8	3
19	GA	1/3	8	31	20
20	GA	1/3	32	38	33
21	GA	1/3	50	41	34
22	GA	1/3	72	48	42
23	GA	1/3	168	55	44
24	GA	1/3	216	55	44
25	GA	1/3	312	57	43

[a]General reaction conditions: [GA] = 0.53 M, 20 ml of THF as solvent, temperature 25 °C, under N_2 atmosphere, reactant stoichiometries GA/Gl = 1/1-3. [b]Obtained from ^{1}H NMR spectroscopic analysis.

Table S4. Summary of alcoholysis of L-LA in the presence of **1**-**5**.[a]

Entry	Ester	Ester/Gl/M	Catalyst	t(min)	GlL_1[b] (%)	GlL_2[b] (%)	GlL_n[b] (%)
1	L-LA	1/3/0.01	**1**	4200	-	43	-
2	L-LA	1/3/0.01	**2**	4200	-	45	-
3	L-LA	1/3/0.01	**3**	4200	-	67	-
4	L-LA	1/3/0.01	**4**	4200	-	65	-
5	L-LA	1/3/0.01	**5**	2	5	89	6
6	L-LA	1/3/0.01	**5**	5	7	84	9
7	L-LA	1/3/0.01	**5**	7	9	83	8
8	L-LA	1/3/0.01	**5**	10	10	80	10
9	L-LA	1/3/0.01	**5**	15	11	79	10
10	L-LA	1/3/0.01	**5**	17	14	76	10
11	L-LA	1/3/0.01	**5**	20	15	75	10
12	L-LA	1/3/0.01	**5**	27	18	74	8
13	L-LA	1/3/0.01	**5**	30	22	72	6
14	L-LA	1/3/0.01	**5**	50	28	66	6
15	L-LA	1/3/0.01	**5**	90	34	61	5
16	L-LA	1/3/0.01	**5**	120	36	58	6
17	L-LA	1/3/0.01	**5**	180	43	52	5
18	L-LA	1/3/0.01	**5**	360	49	47	4
19	L-LA	1/3/0.01	**5**	480	50	46	4
20	L-LA	1/3/0.02	**5**	15	45	52	3
21	L-LA	1/3/0.02	**5**	30	49	46	5
22	L-LA	1/3/0.02	**5**	45	55	43	2
23	L-LA	1/3/0.02	**5**	60	63	35	2
24	L-LA	1/3/0.02	**5**	120	73	24	3
25	L-LA	1/3/0.02	**5**	180	77	21	2
26	L-LA	1/3/0.02	**5**	330	79	19	2
27	L-LA	1/3/0.02	**5**	450	80	18	2
28	L-LA	1/3/0.05	**3**	2	21	77	2
29	L-LA	1/3/0.05	**3**	5	27	71	1
30	L-LA	1/3/0.05	**3**	20	34	65	1
31	L-LA	1/3/0.05	**3**	30	62	37	1
32	L-LA	1/3/0.05	**4**	2	4	90	6
33	L-LA	1/3/0.05	**4**	5	5	90	5
34	L-LA	1/3/0.05	**4**	20	7	89	4
35	L-LA	1/3/0.05	**4**	30	8	90	2

[a]General reaction conditions: [L-LA] = 0.53 M, 8 ml of THF as solvent, temperature 25 °C, under N_2 atmosphere, reactant stoichiometries L-LA/Gl/M = 1/3/0.01 – 0.05. [b]Obtained from ^{1}H NMR spectroscopic analysis.

Table S5. Summary of alcoholysis of GA in the presence of **1**-**5**.[a]

Entry	Ester	Ester/Gl/M	Catalyst	t(min)	GlG_1[b] (%)	GlG_2[b] (%)	GlG_n[b] (%)
1	GA	1/3/0.01	**1**	1	3	55	40
2	GA	1/3/0.01	**1**	3	7	59	33
3	GA	1/3/0.01	**1**	8	4	54	41
4	GA	1/3/0.01	**1**	15	4	55	39
5	GA	1/3/0.01	**1**	30	4	56	40
6	GA	1/3/0.01	**1**	120	6	53	40
7	GA	1/3/0.01	**1**	480	9	51	39
8	GA	1/3/0.01	**1**	530	15	48	37
9	GA	1/3/0.01	**2**	530	2	44	50
10	GA	1/3/0.01	**3**	1	48	36	15
11	GA	1/3/0.01	**3**	3	58	29	12
12	GA	1/3/0.01	**3**	8	70	25	5
13	GA	1/3/0.01	**3**	15	79	16	5
14	GA	1/3/0.01	**3**	30	85	13	2
15	GA	1/3/0.01	**3**	120	87	11	2
16	GA	1/3/0.01	**3**	480	87	11	2
17	GA	1/3/0.01	**4**	1	25	47	28
18	GA	1/3/0.01	**4**	3	34	45	21
19	GA	1/3/0.01	**4**	8	43	39	18
20	GA	1/3/0.01	**4**	15	52	37	11
21	GA	1/3/0.01	**4**	30	65	24	11
22	GA	1/3/0.01	**4**	60	75	17	8
23	GA	1/3/0.01	**4**	120	81	15	4
24	GA	1/3/0.01	**4**	480	85	11	4
25	GA	1/3/0.01	**4**	530	88	8	4
26	GA	1/3/0.01	**5**	5	28	41	31
27	GA	1/3/0.01	**5**	7	37	35	28
28	GA	1/3/0.01	**5**	10	42	33	25
29	GA	1/3/0.01	**5**	12	44	33	23
30	GA	1/3/0.01	**5**	15	49	32	19
31	GA	1/3/0.01	**5**	20	52	30	17
32	GA	1/3/0.01	**5**	25	62	26	12
33	GA	1/3/0.01	**5**	30	63	26	11
34	GA	1/3/0.01	**5**	40	67	23	10
35	GA	1/3/0.01	**5**	60	75	17	8
36	GA	1/3/0.01	**5**	90	76	18	6
37	GA	1/3/0.01	**5**	120	83	12	5
38	GA	1/3/0.01	**5**	180	83	12	5
39	GA	1/3/0.01	**5**	420	86	10	4

[a]General reaction conditions: [GA] = 0.53 M, 8 ml of THF as solvent, temperature 25 °C, under N_2 atmosphere, reactant stoichiometries GA/Gl/M = 1/3/0.01. [b]Obtained from ^{1}H NMR spectroscopic analysis.

Table S6. Summary of alcoholysis of ε-CL in the presence of **1**-**5**.[a]

Entry	Ester	Ester/Gl/M	Catalyst	t(min)	$GlCL_1$[b] (%)
1	ε-CL	1/2/0.01	**5**	7	17
2	ε-CL	1/2/0.01	**5**	20	19
3	ε-CL	1/2/0.01	**5**	40	22
4	ε-CL	1/2/0.01	**5**	60	27
5	ε-CL	1/2/0.01	**5**	90	29
6	ε-CL	1/2/0.01	**5**	180	44
7	ε-CL	1/2/0.01	**5**	240	54
8	ε-CL	1/2/0.01	**5**	300	57
9	ε-CL	1/2/0.02	**1**	1140	1
10	ε-CL	1/2/0.02	**1**	5760	1
11	ε-CL	1/2/0.02	**2**	1140	<1
12	ε-CL	1/2/0.02	**2**	5760	<1
13	ε-CL	1/2/0.02	**3**	120	40
14	ε-CL	1/2/0.02	**3**	240	66
15	ε-CL	1/2/0.02	**3**	1140	98
16	ε-CL	1/2/0.02	**4**	120	34
17	ε-CL	1/2/0.02	**4**	240	44
18	ε-CL	1/2/0.02	**4**	1140	81
19	ε-CL	1/2/0.02	**5**	10	22
20	ε-CL	1/2/0.02	**5**	30	64
21	ε-CL	1/2/0.02	**5**	60	77
22	ε-CL	1/2/0.02	**5**	96	97
23	ε-CL	1/2/0.02	**5**	120	98
24	ε-CL	1/2/0.08	**3**	30	14
25	ε-CL	1/2/0.08	**3**	60	23
26	ε-CL	1/2/0.08	**3**	120	28
27	ε-CL	1/2/0.08	**3**	240	49
28	ε-CL	1/2/0.08	**3**	300	60
29	ε-CL	1/2/0.08	**4**	30	16
30	ε-CL	1/2/0.08	**4**	60	34
31	ε-CL	1/2/0.08	**4**	120	38
32	ε-CL	1/2/0.08	**4**	240	68
33	ε-CL	1/2/0.08	**4**	300	77

[a]General reaction conditions: [ε-CL] = 0.53 M, 8 ml of THF as solvent, temperature 25 °C, under N_2 atmosphere, reactant stoichiometries ε-CL/Gl/M = 1/2/0.01 – 0.08. [b]Obtained from ^{1}H NMR spectroscopic analysis.

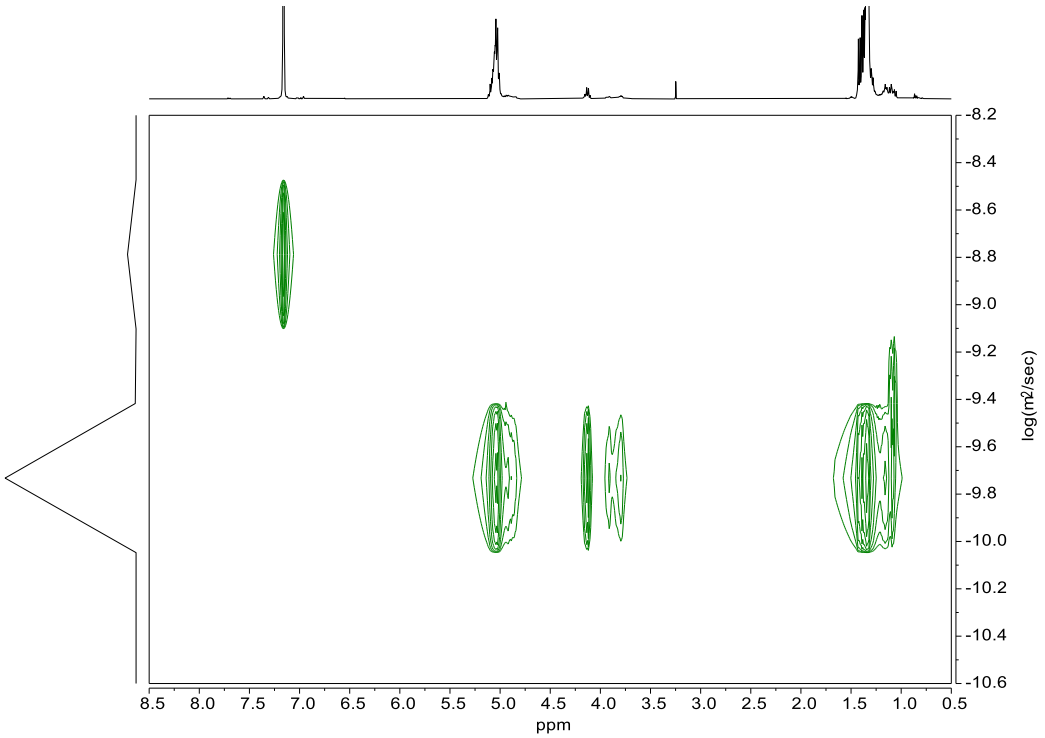

Figure S45. ^{1}H-DOSY NMR spectrum in C_6D_6 of PLLA synthesized using **5**.

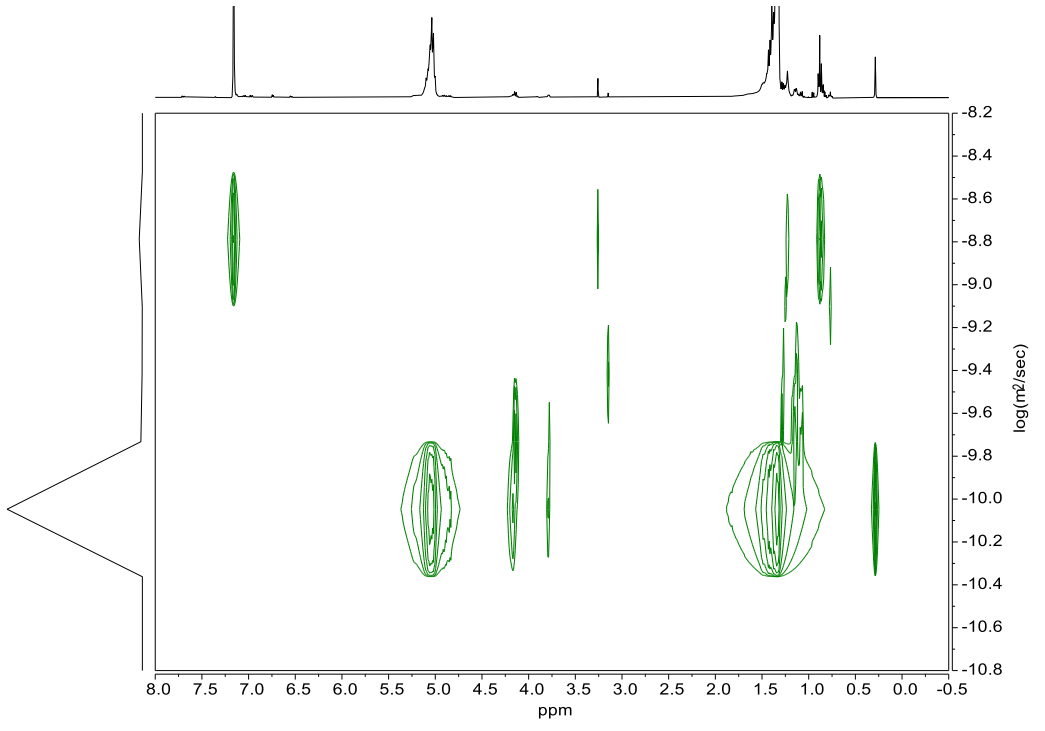

Figure S46. ^{1}H-DOSY NMR spectrum in C_6D_6 of PLLA synthesized using **3**.

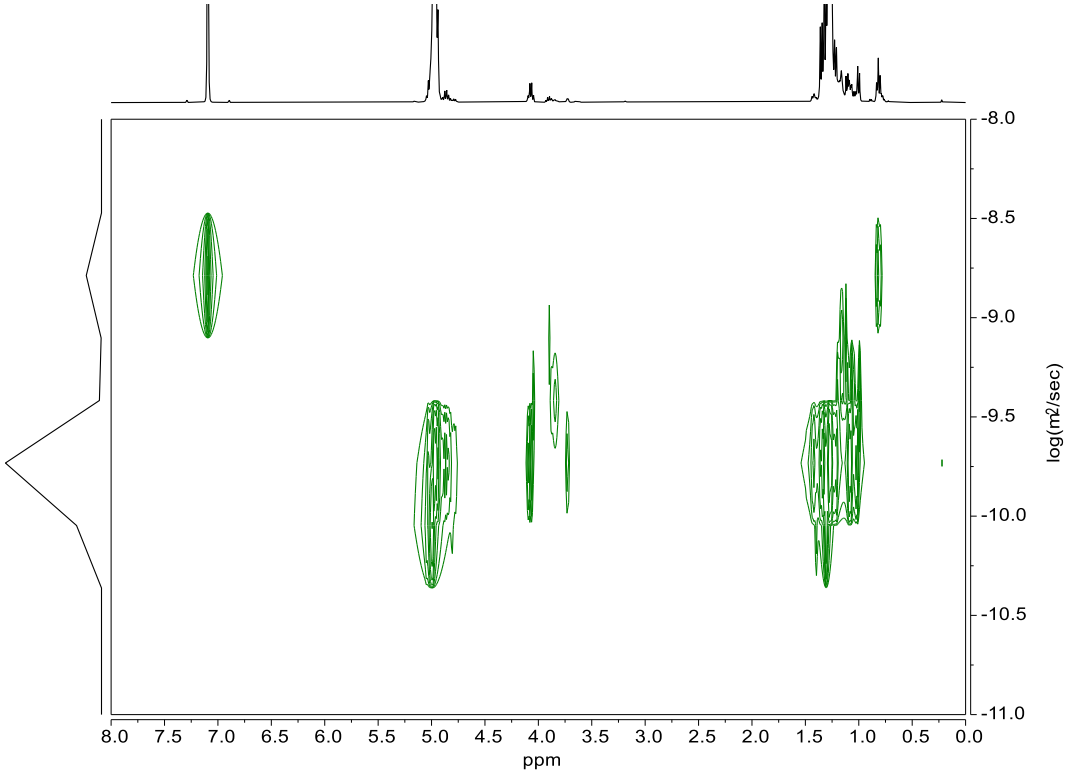

Figure S47. ^{1}H-DOSY NMR spectrum in C_6D_6 of PLLA synthesized using **4**.

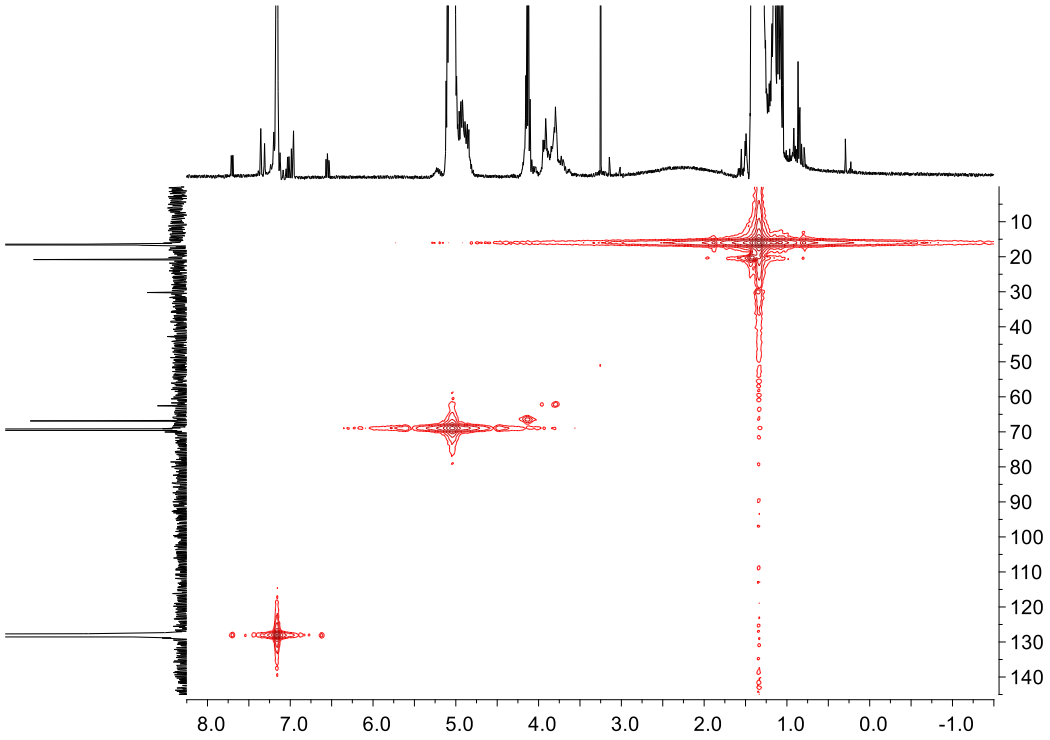

Figure S48. ^{1}H-^{13}C HMQC spectrum in C_6D_6 of PLLA synthesized in the presence of **4**.

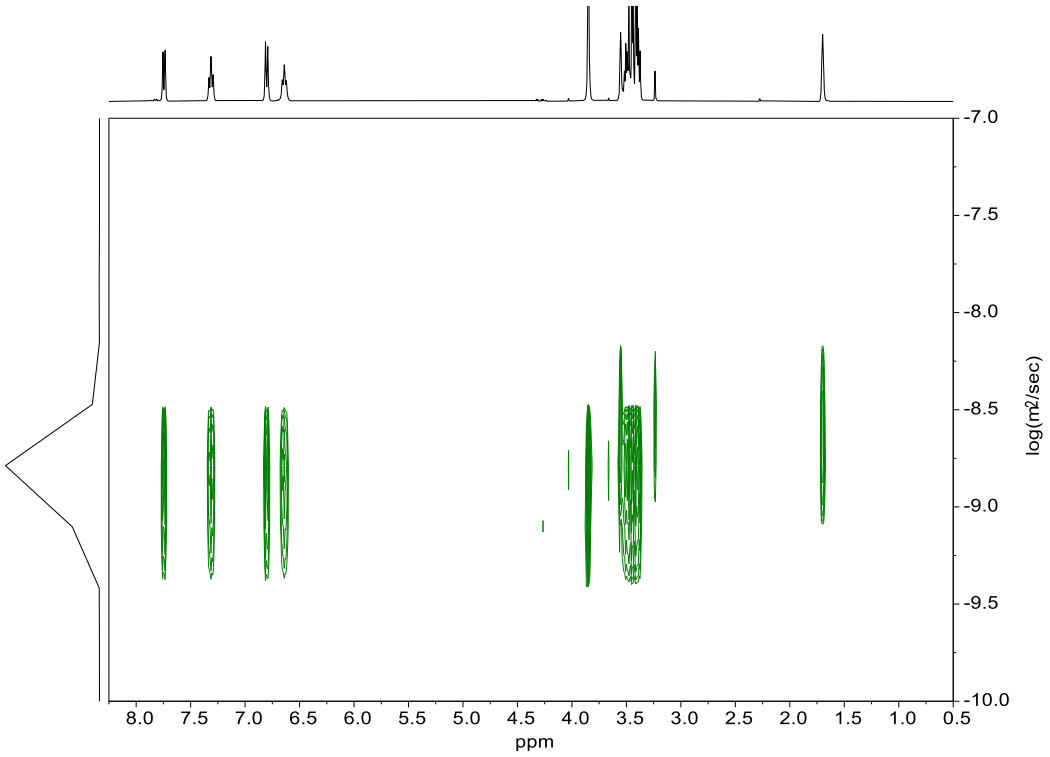

Figure S49. ^{1}H-DOSY NMR spectrum of the mixture of **3** and Gl in THF-d_8.

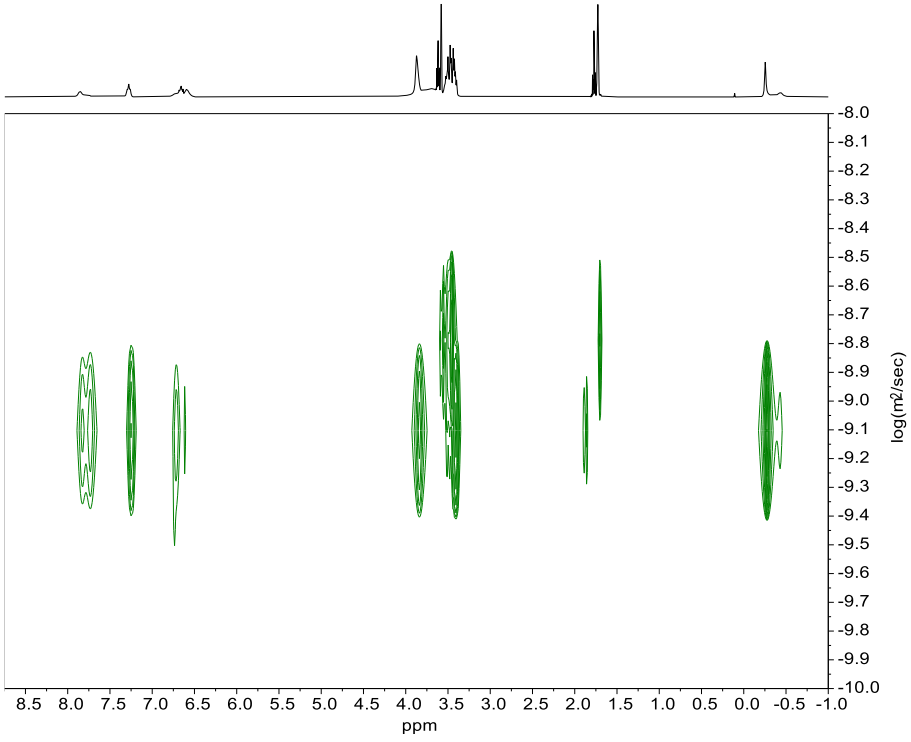

Figure S50. ^{1}H-DOSY NMR spectrum of the mixture of **4** and Gl in THF-d_8.

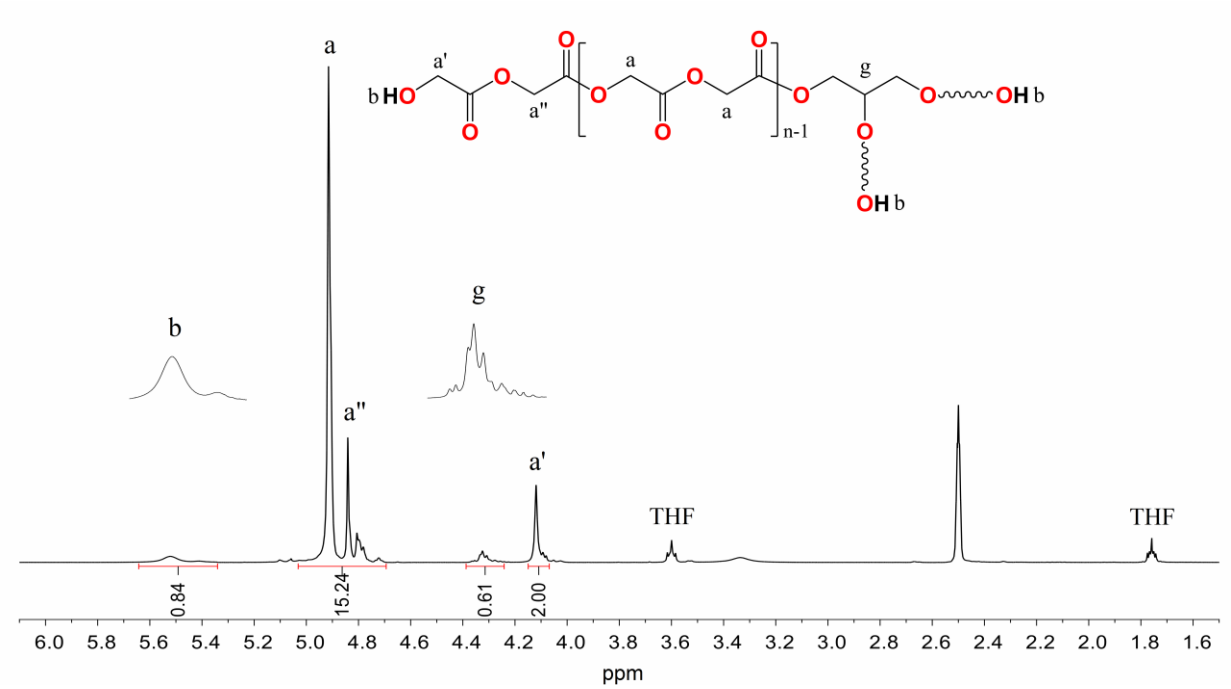

Figure S51. ^{1}H NMR spectrum of PGA in DMSO-d_6 synthesized using **4**.

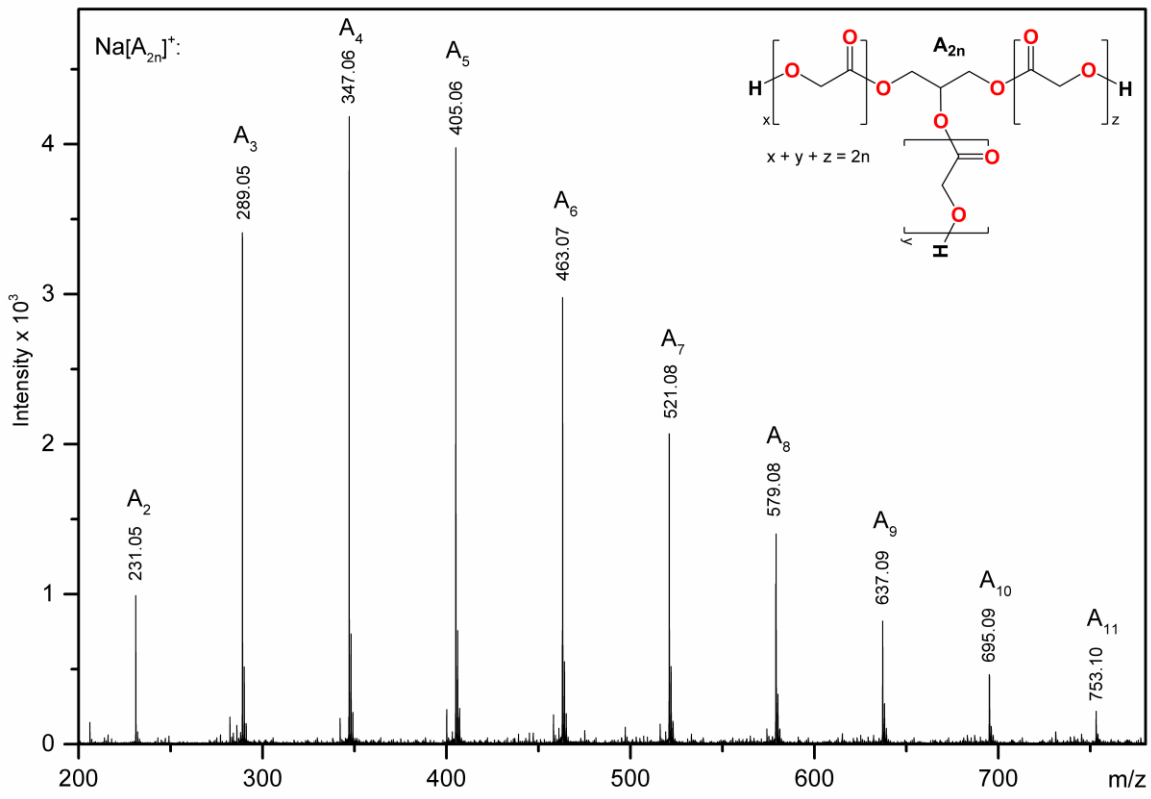

Figure S52. ESI-MS spectrum of PGA synthesized using **4**.

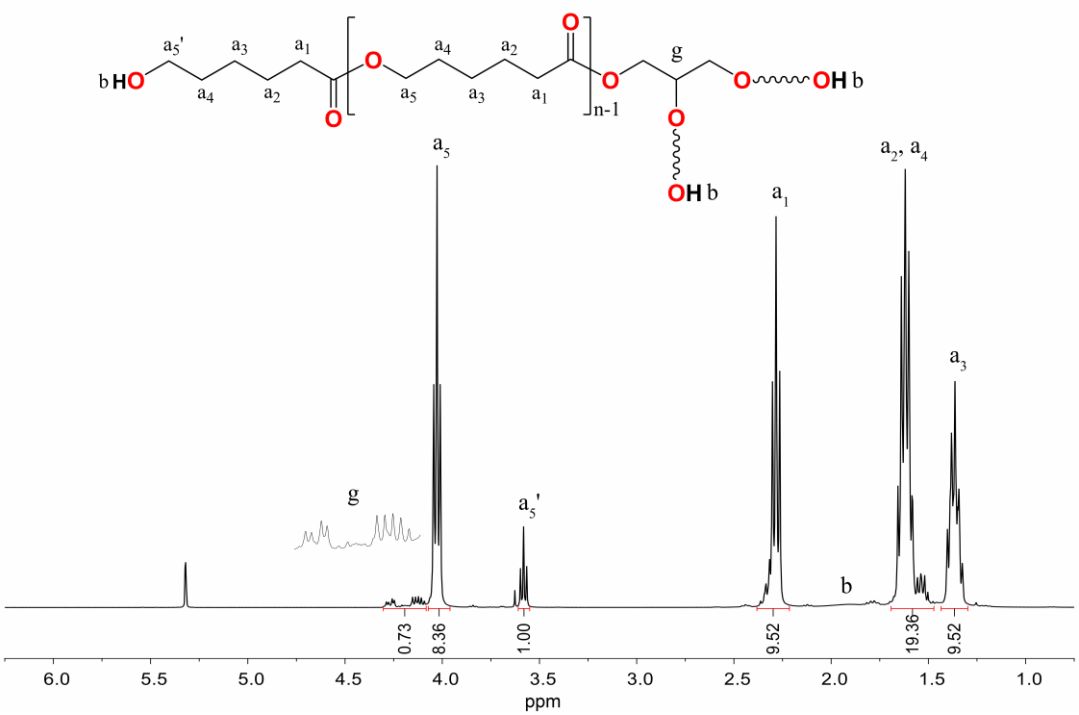

Figure S53. ^{1}H NMR spectrum of 3-arm PCL in CD_2Cl_2.

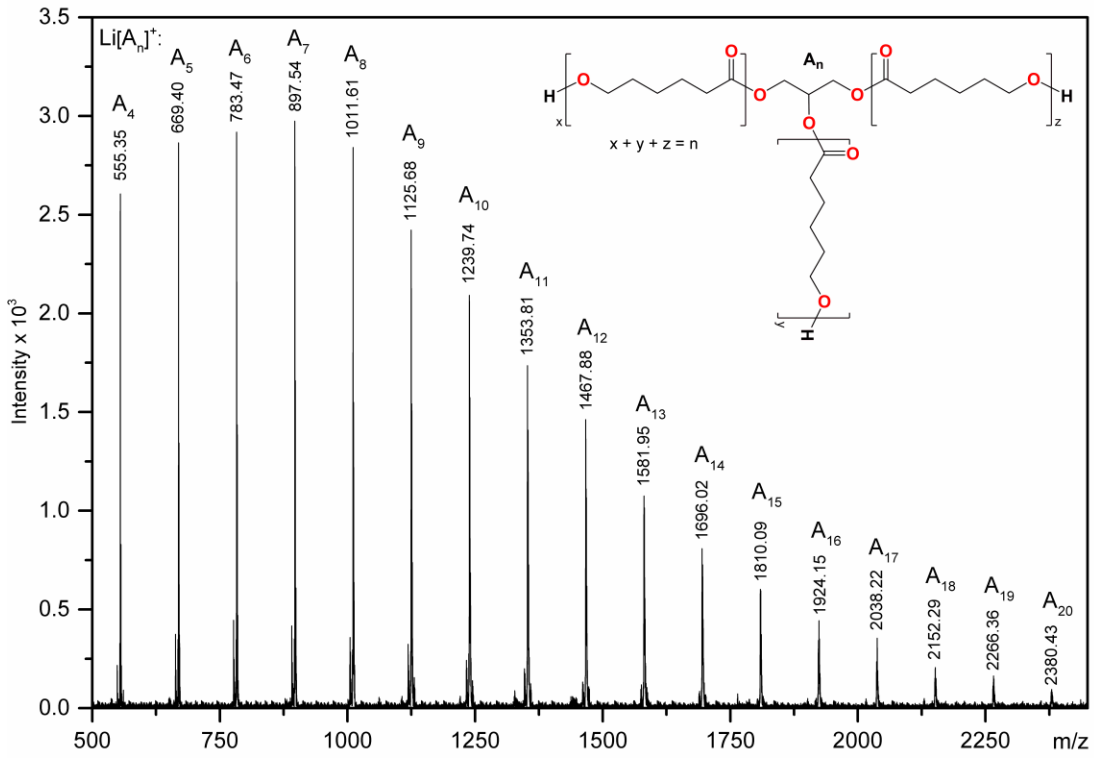

Figure S54. ESI-MS spectrum of 3-arm PCL.