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Supporting information for

Use of lithium aryloxides as promoters for preparation of α-hydroxy acid esters

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Crystallographic Data for Compounds 1-3.

Table S1. Crystal and data collection parameters for compounds **1-3**.

Crystal	**1**	**2**	**3**
Chemical formula	$C_{48}H_{42}Li_6O_{18}$	$C_{16}H_{15}LiO_6$	$C_{10}H_{15}LiO_5$
Formula Mass	948.45	310.22	222.16
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$Pna2_1$
a/Å	8.183 (4)	4.982 (3)	16.678 (4)
b/Å	12.029 (6)	11.477 (5)	10.147 (3)
c/Å	13.174 (8)	26.122 (6)	7.008 (2)
α/°	65.36 (2)		
β/°	75.12 (2)	94.98 (2)	
γ/°	84.37 (2)		
Unit cell volume/Å^3	1139.1 (11)	1488.0(12)	1186.0 (6)
Temperature/K	100(2)	100(2)	100(2)
Z	1	4	4
Radiation type	MoKα	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	0.103	0.105	0.821
No. of reflections measured	10125	10884	2830
No. of independent reflections	4925	3249	1508
No. of observed reflections ($I > 2\sigma(I)$)	3231	2110	1495
R_{int}	0.0538	0.0734	0.0106
Final R_1 values ($I > 2\sigma(I)$)	0.0635	0.0554	0.0303
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1313	0.1140	0.0858
Final R_1 values (all data)	0.1065	0.0989	0.0306
Final $wR(F^2)$ values (all data)	0.1559	0.1346	0.0861
Goodness of fit on F^2	1.034	1.031	1.091
Δρmax/eÅ^{-3}	0.28	0.28	0.23
Δρmin/eÅ^{-3}	-0.27	-0.25	-0.16

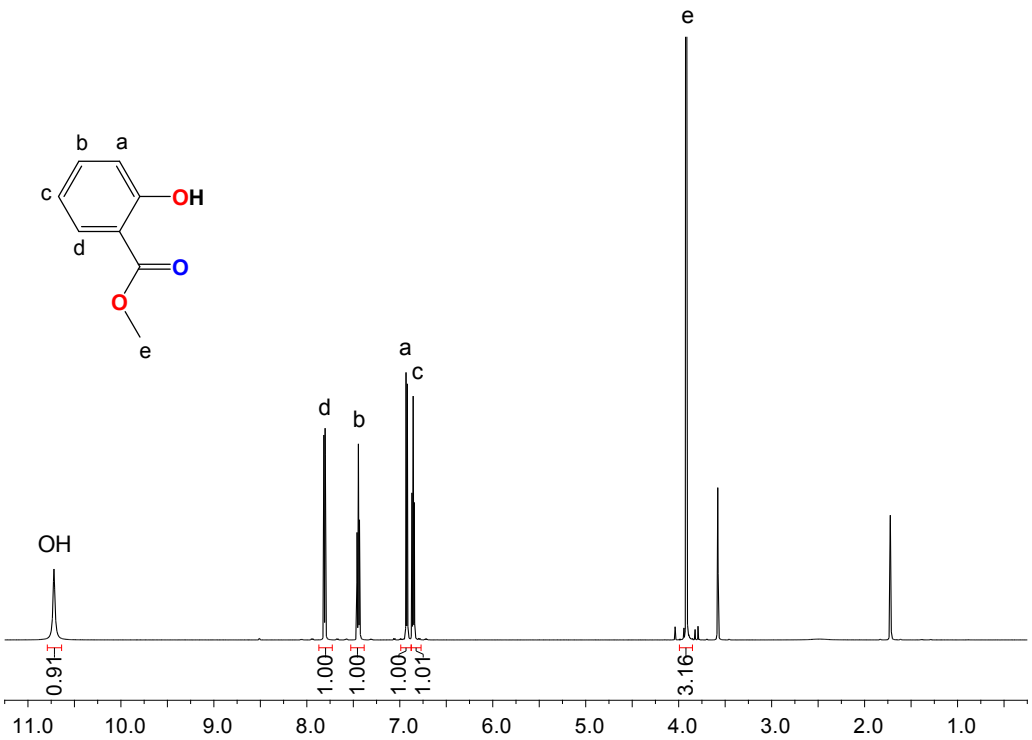

Fig. S1 ^{1}H NMR spectrum of ligand precursor MesalOH in THF-d_8.

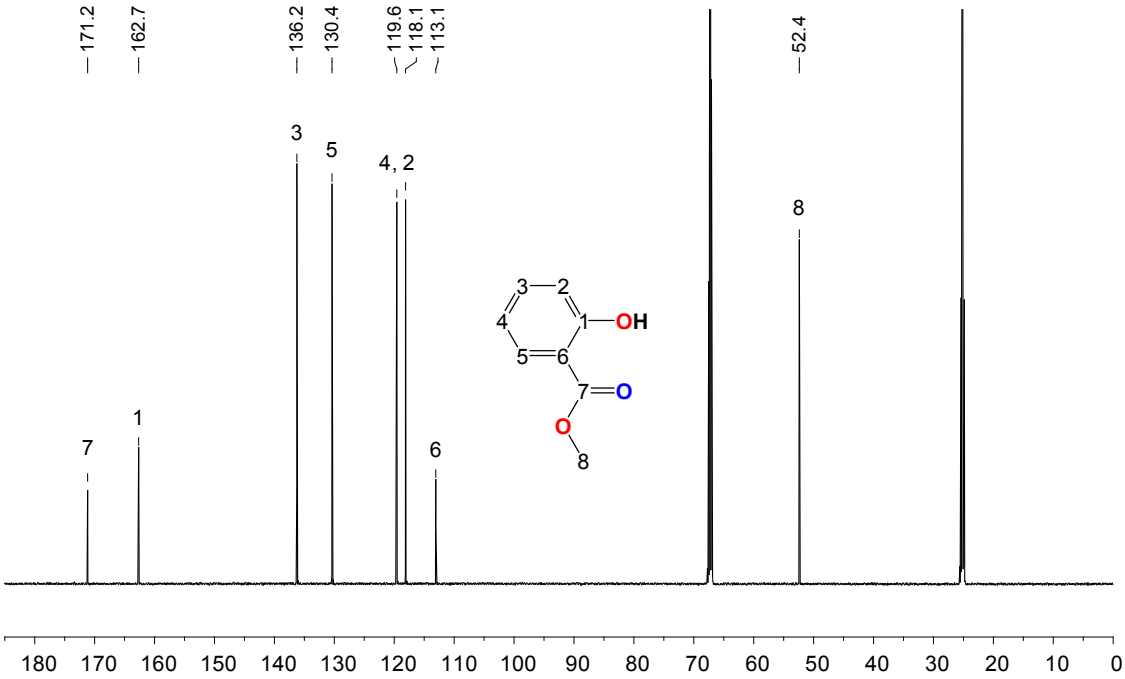

Fig. S2 ^{13}C NMR spectrum of ligand precursor MesalOH in THF-d_8.

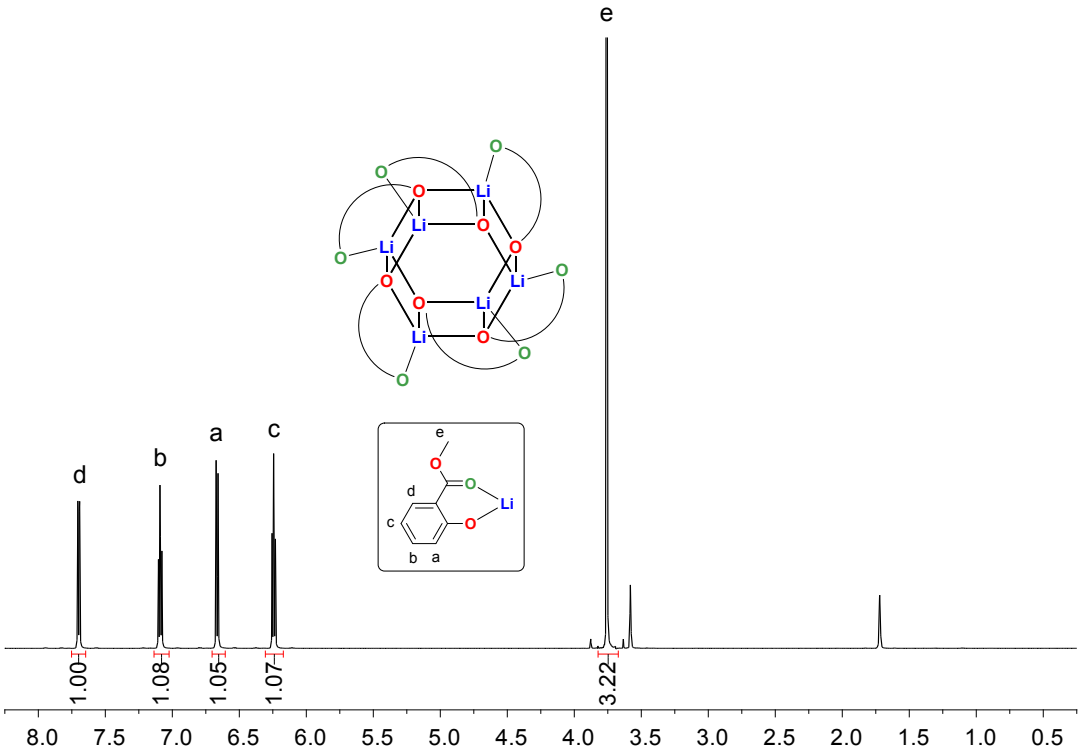

Fig. S3 ^{1}H NMR spectrum of **1** in THF-d_8.

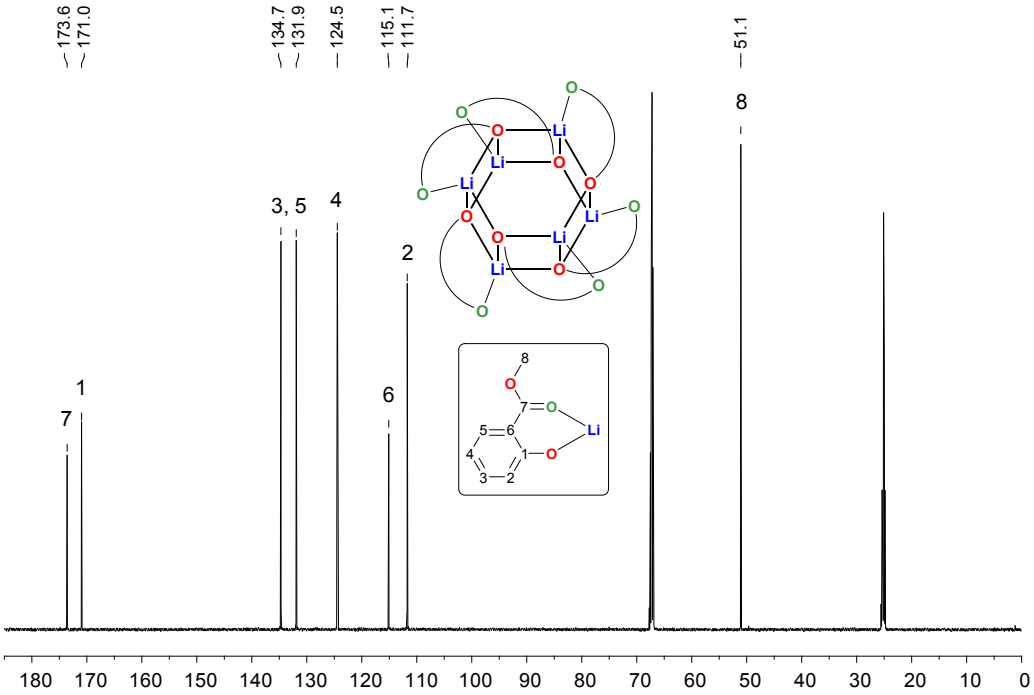

Fig. S4 ^{13}C NMR spectrum of **1** in THF-d_8.

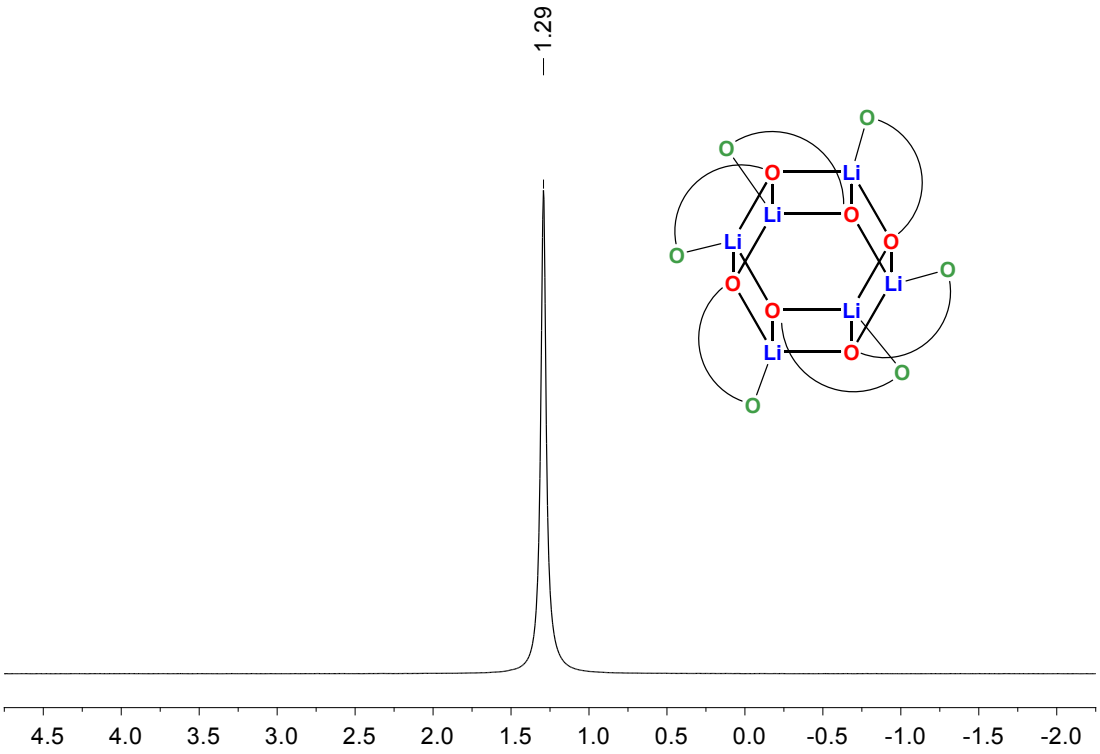

Fig. S5 ^{7}Li NMR spectrum of **1** in THF-d_8.

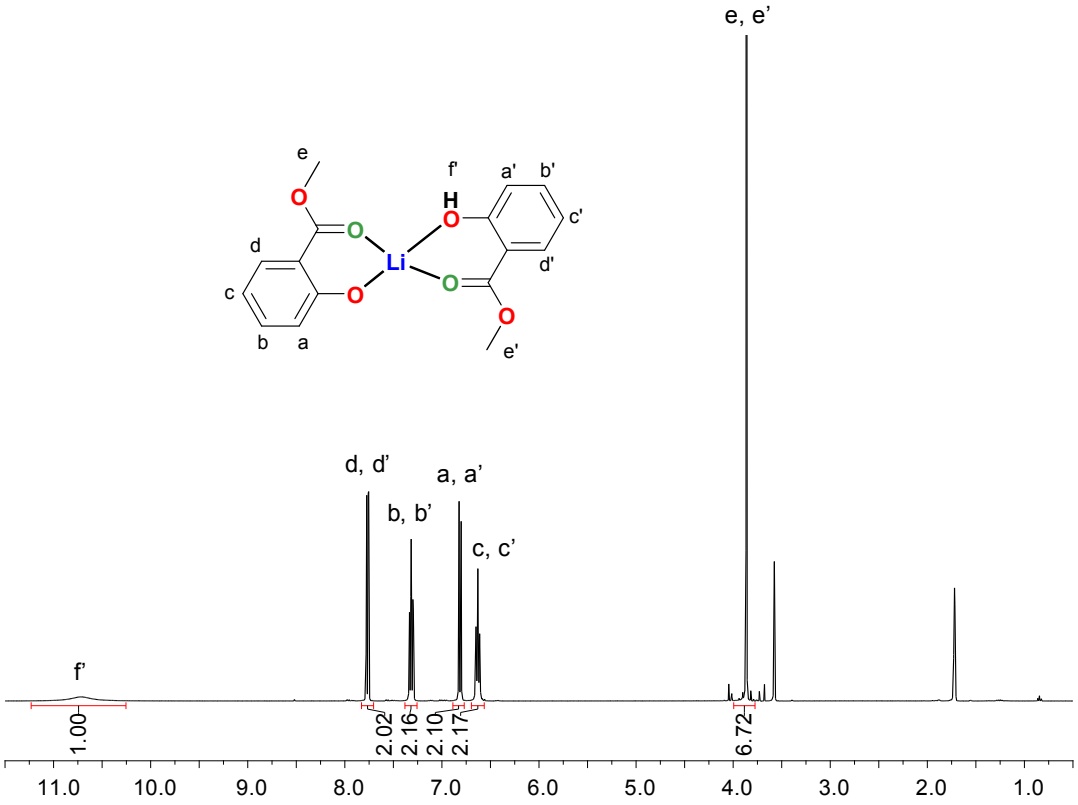

Fig. S6 ^{1}H NMR spectrum of **2** in THF-d_8.

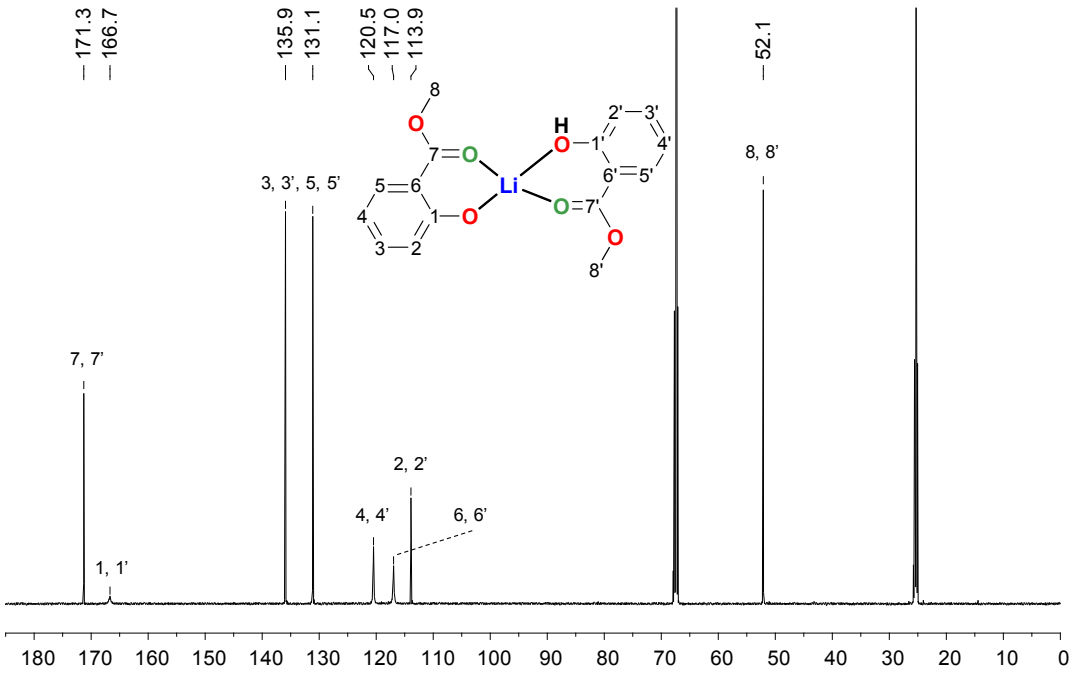

Fig. S7 ^{13}C NMR spectrum of **2** in THF-D8.

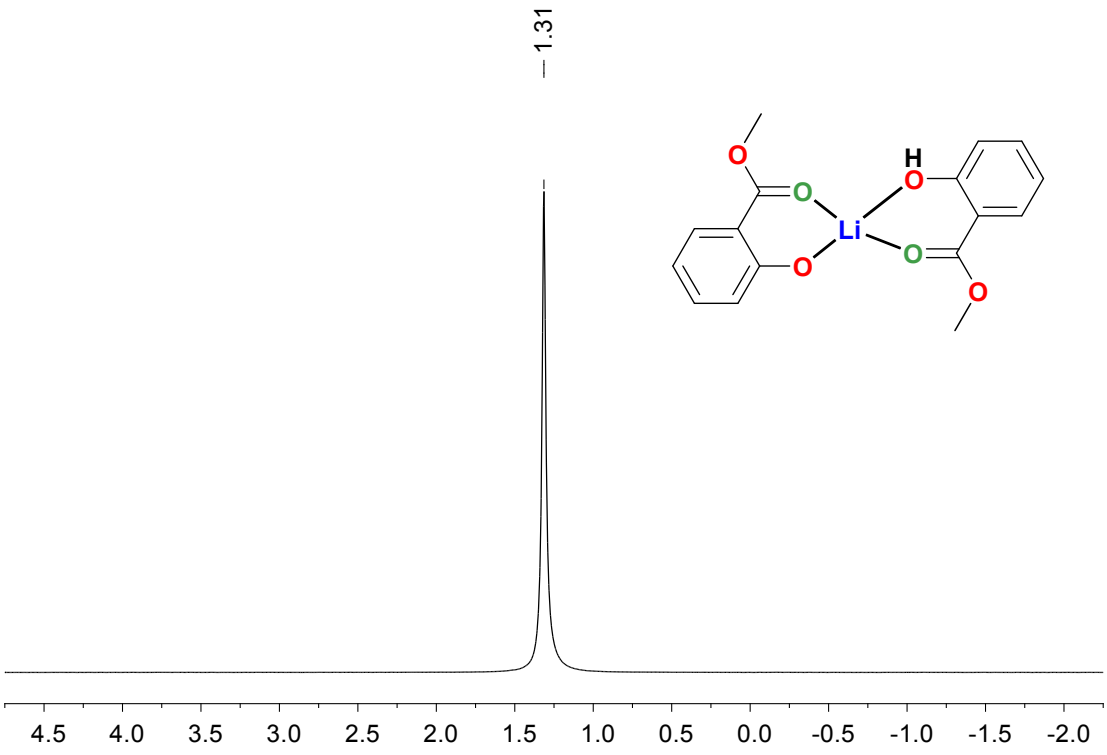

Fig. S8 ^{7}Li NMR spectrum of **2** in THF-d_8.

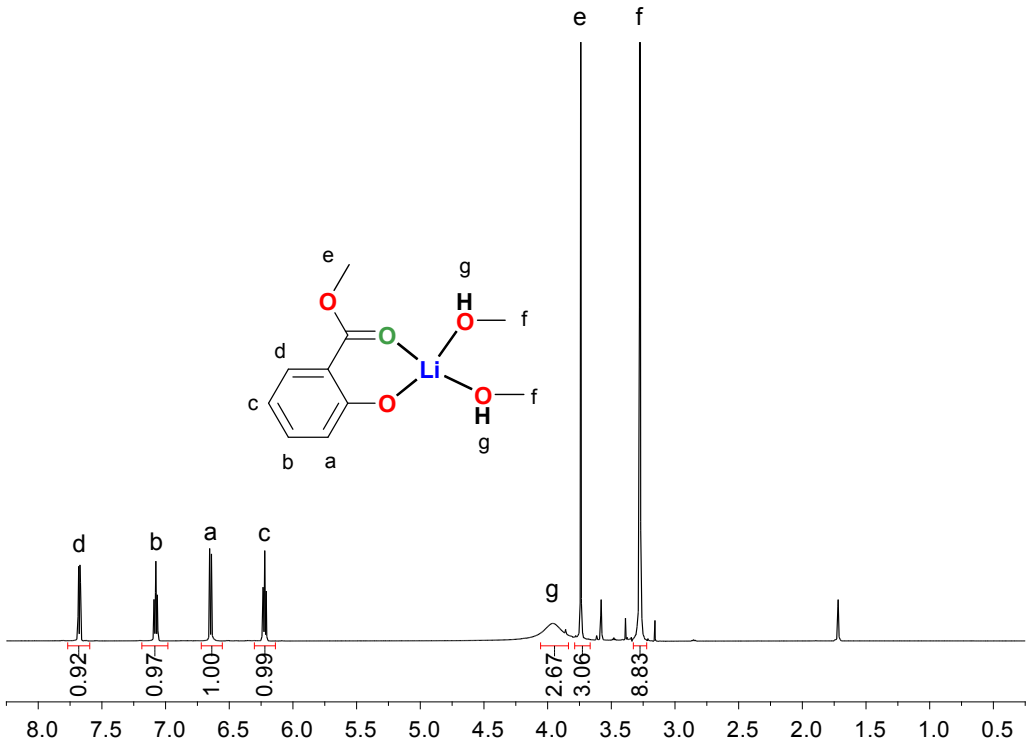

Fig. S9 ^{1}H NMR spectrum of **3** in THF-d_8.

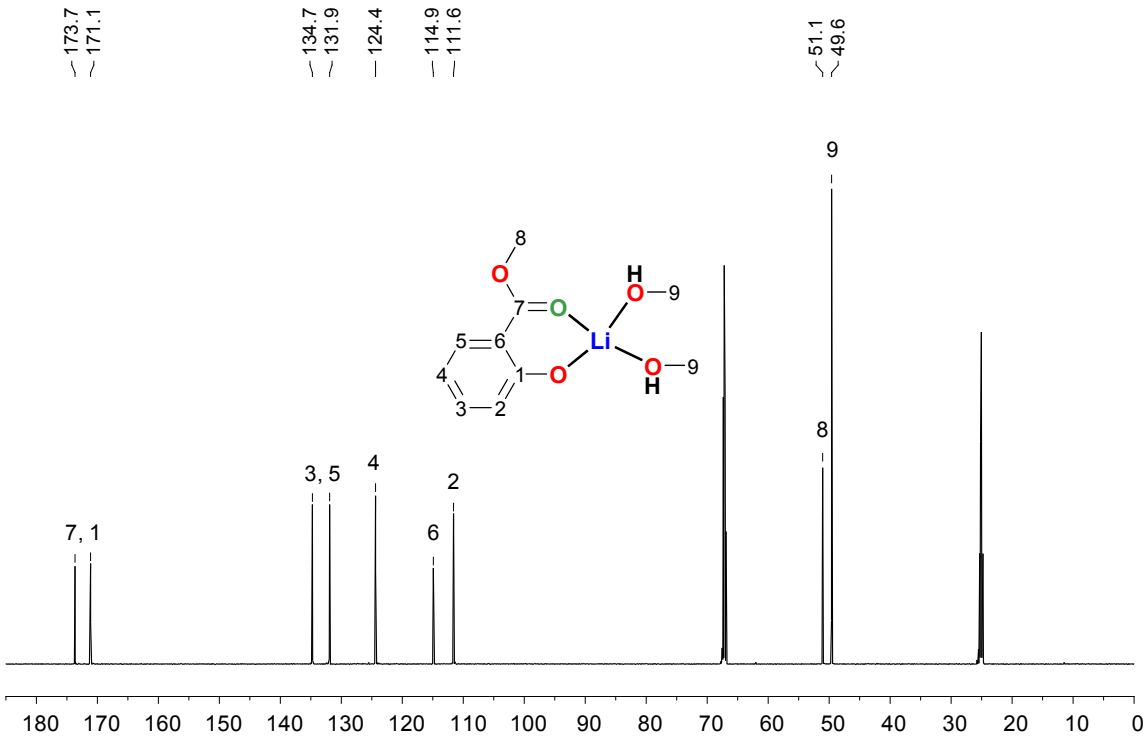

Fig. S10 ^{13}C NMR spectrum of **3** in THF-d_8.

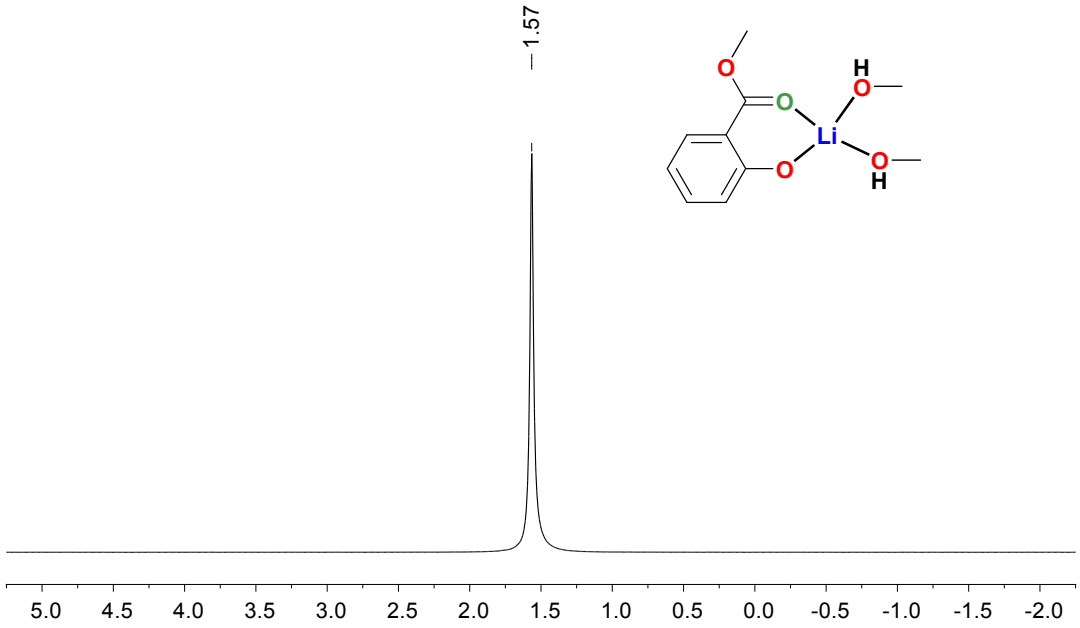

Fig. S11 ^{7}Li NMR spectrum of **3** in THF-d_8.

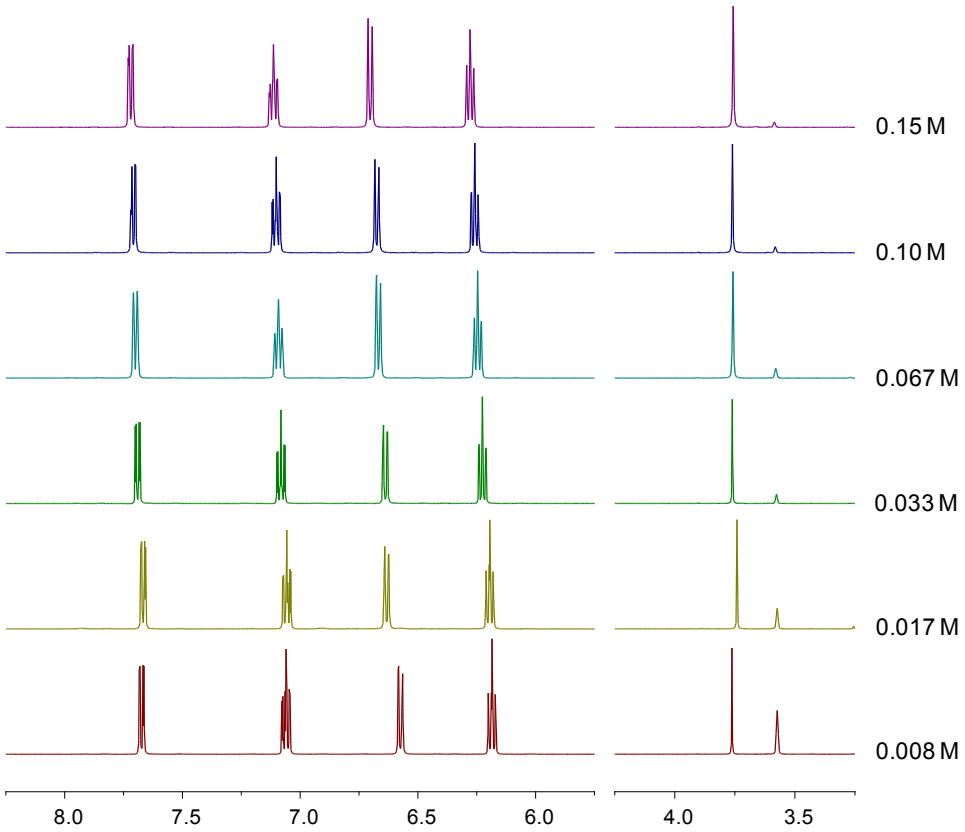

Fig. S12 Variable concentration ^{1}H NMR spectra of **1** in THF-d_8.

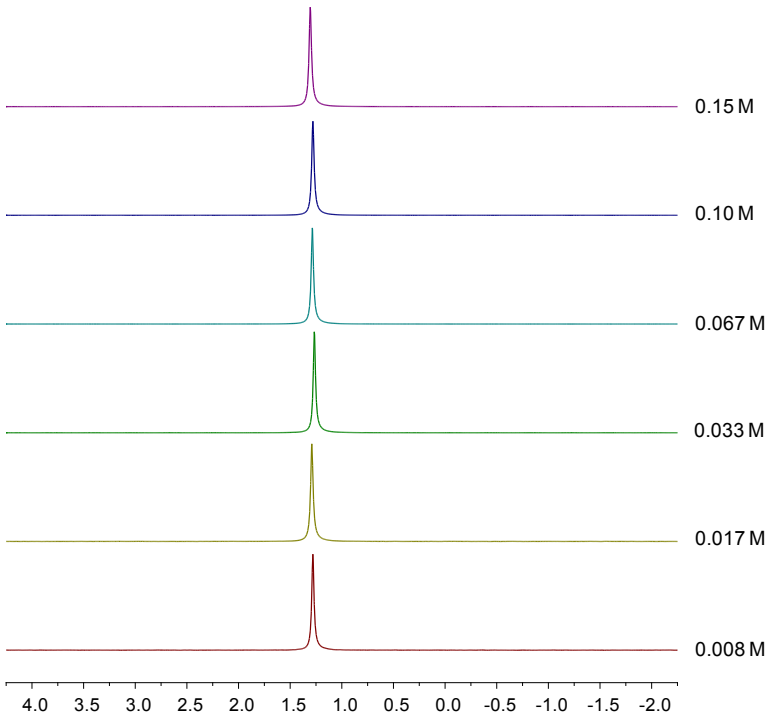

Fig. S13 Variable concentration ^{7}Li NMR spectra of **1** in THF-d_8.

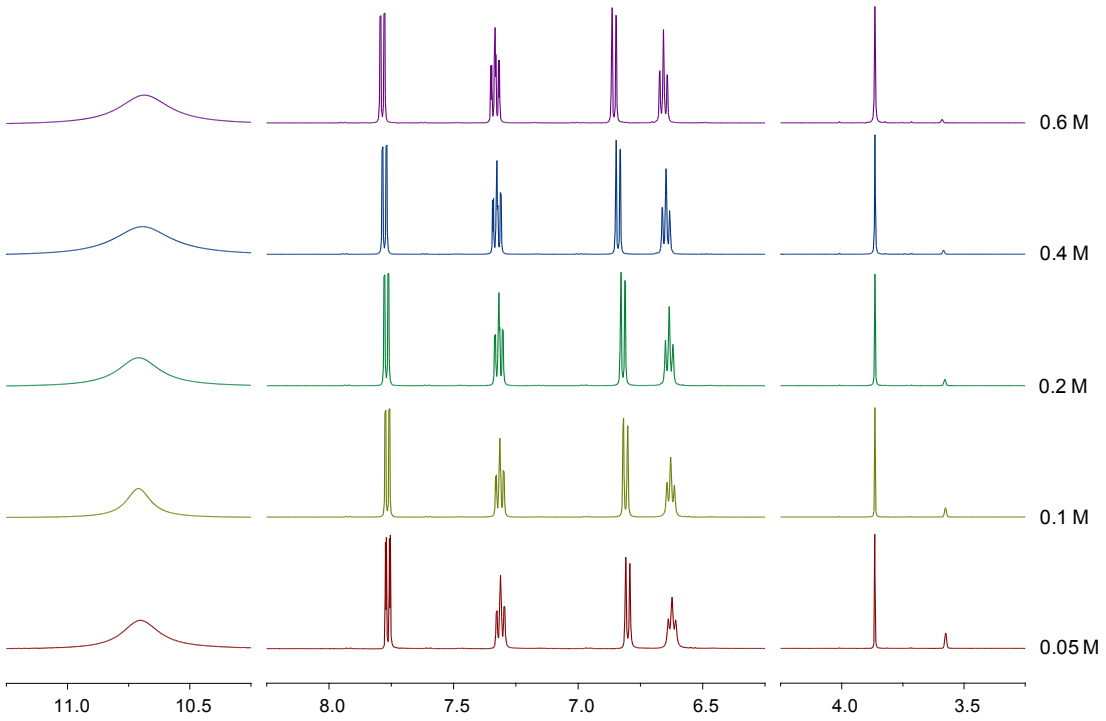

Fig. S14 Variable concentration ^{1}H NMR spectra of **2** in THF-d_8.

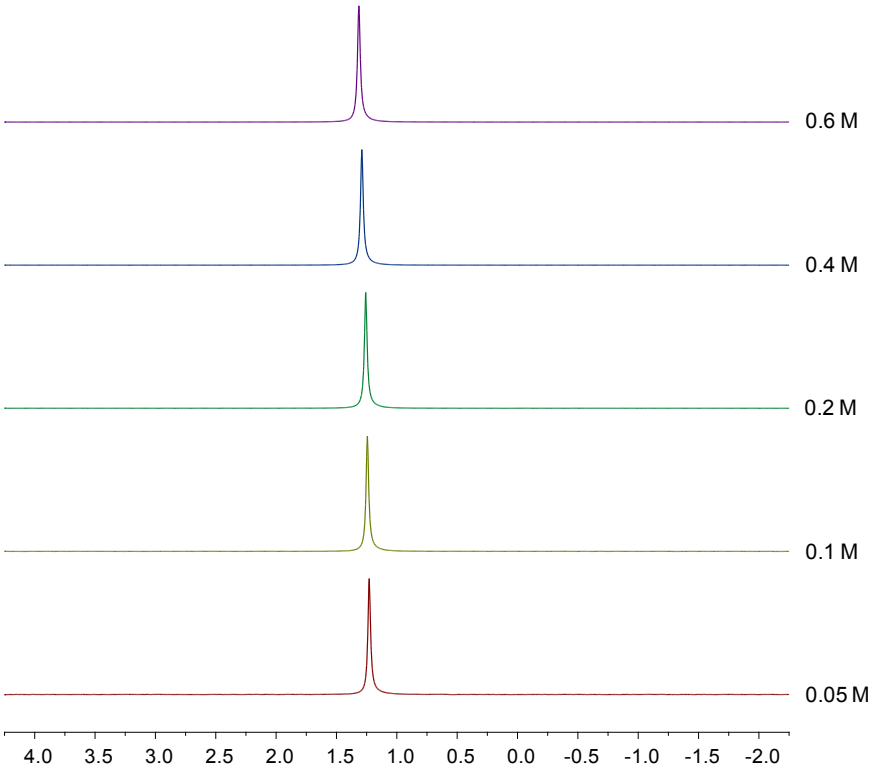

Fig. S15 Variable concentration ^{7}Li NMR spectra of **2** in THF-d_8.

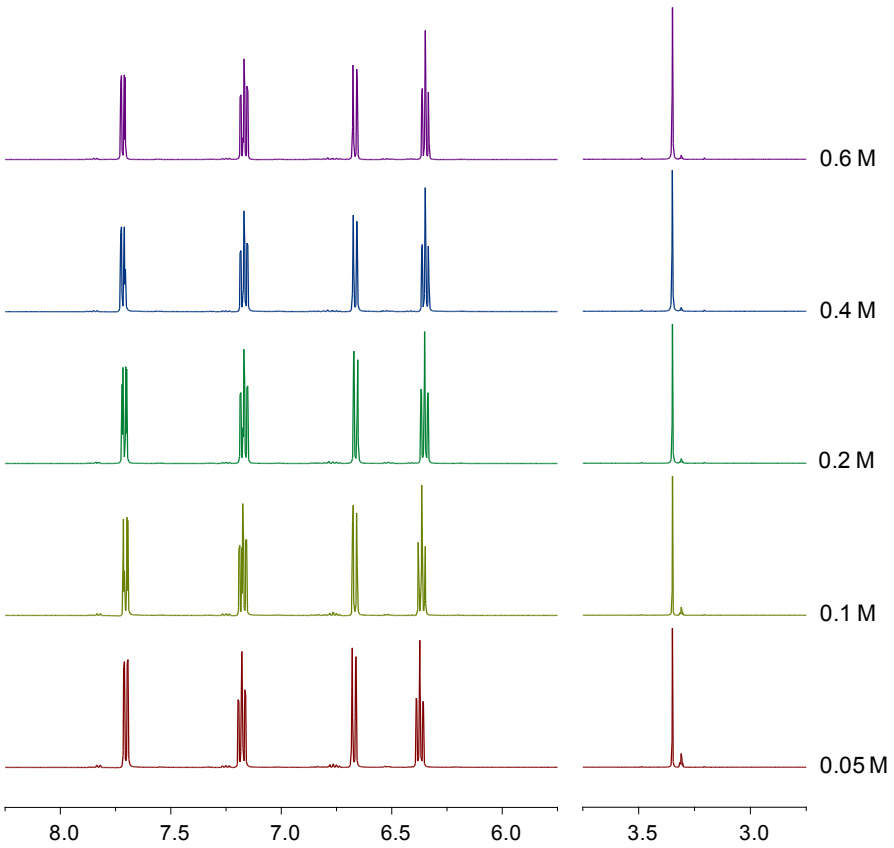

Fig. S16 Variable concentration ^{1}H NMR spectra of **3** in methanol-d$_4$.

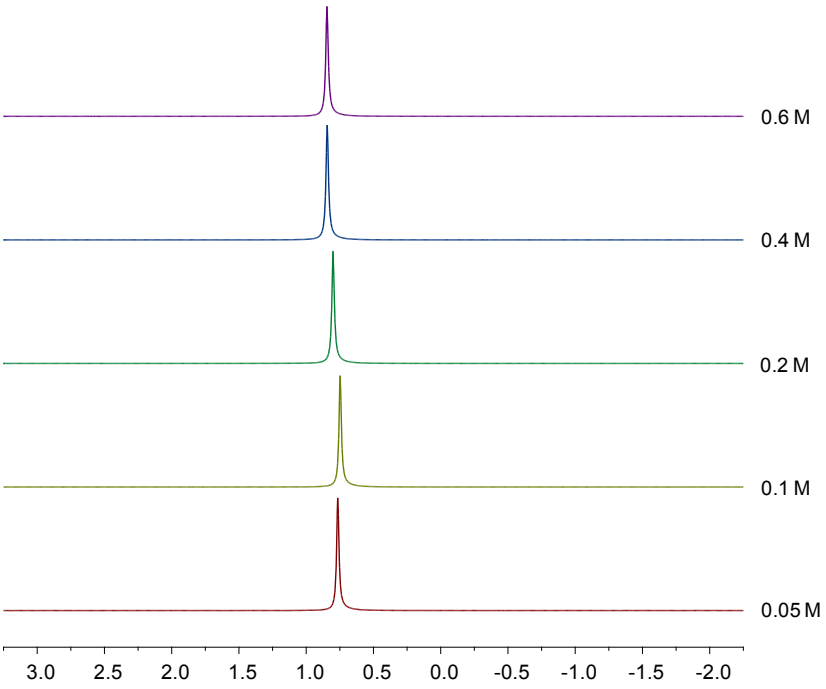

Fig. S17 Variable concentration ^{7}Li NMR spectra of **3** in methanol-d$_4$.

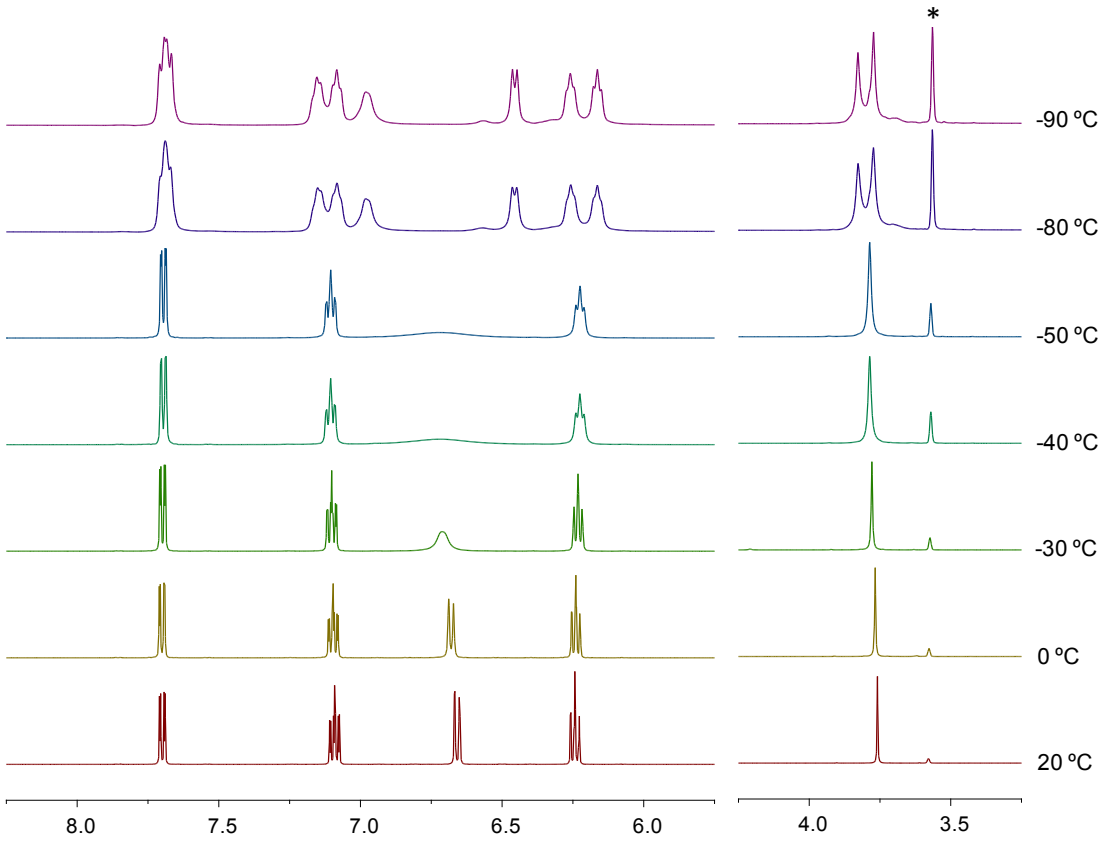

Fig. S18 Variable temperature ^{1}H NMR spectra of **1** (0.033M) in THF-d_8.

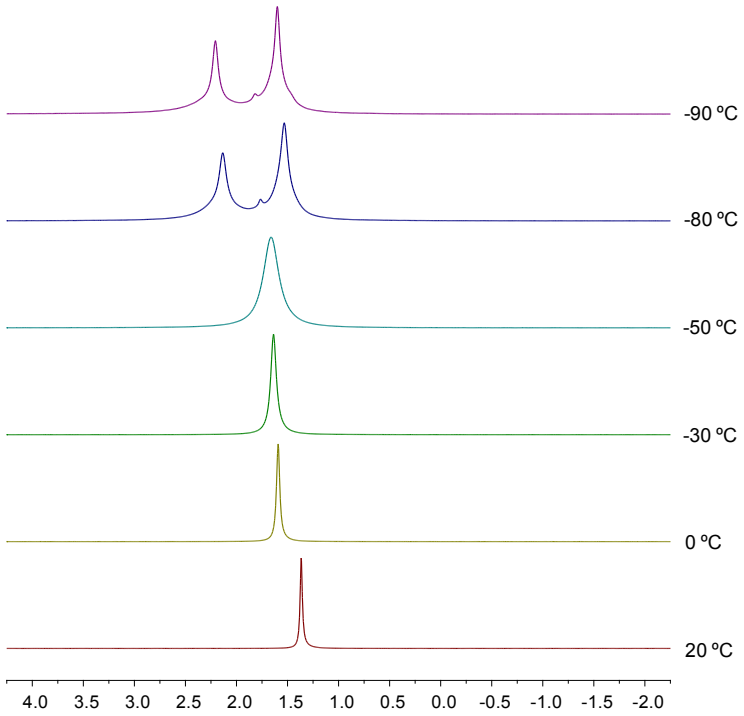

Fig. S19 Variable temperature ^{7}Li NMR spectra of **1** (0.033M) in THF-d_8.

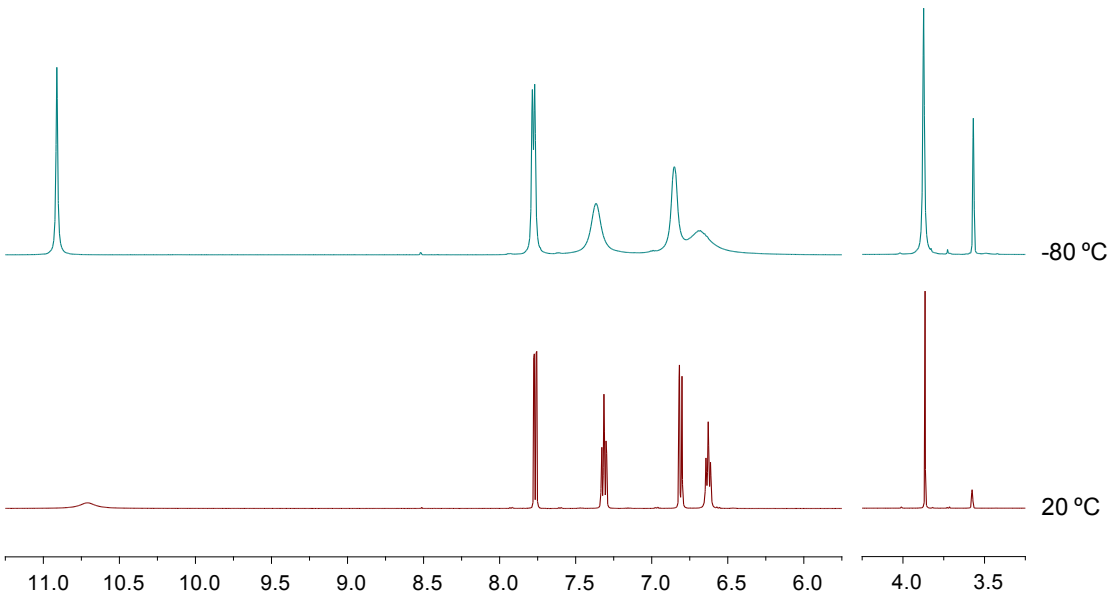

Fig. S20 Variable temperature ^{1}H NMR spectra of **2** (0.2 M) in THF-d_8.

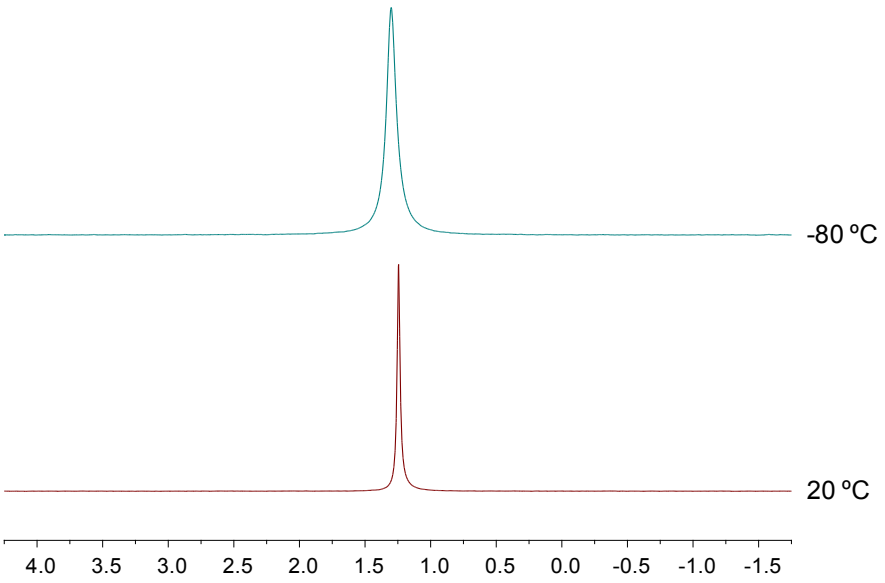

Fig. S21 Variable temperature ^{7}Li NMR spectra of **2** (0.2 M) in THF-d_8.

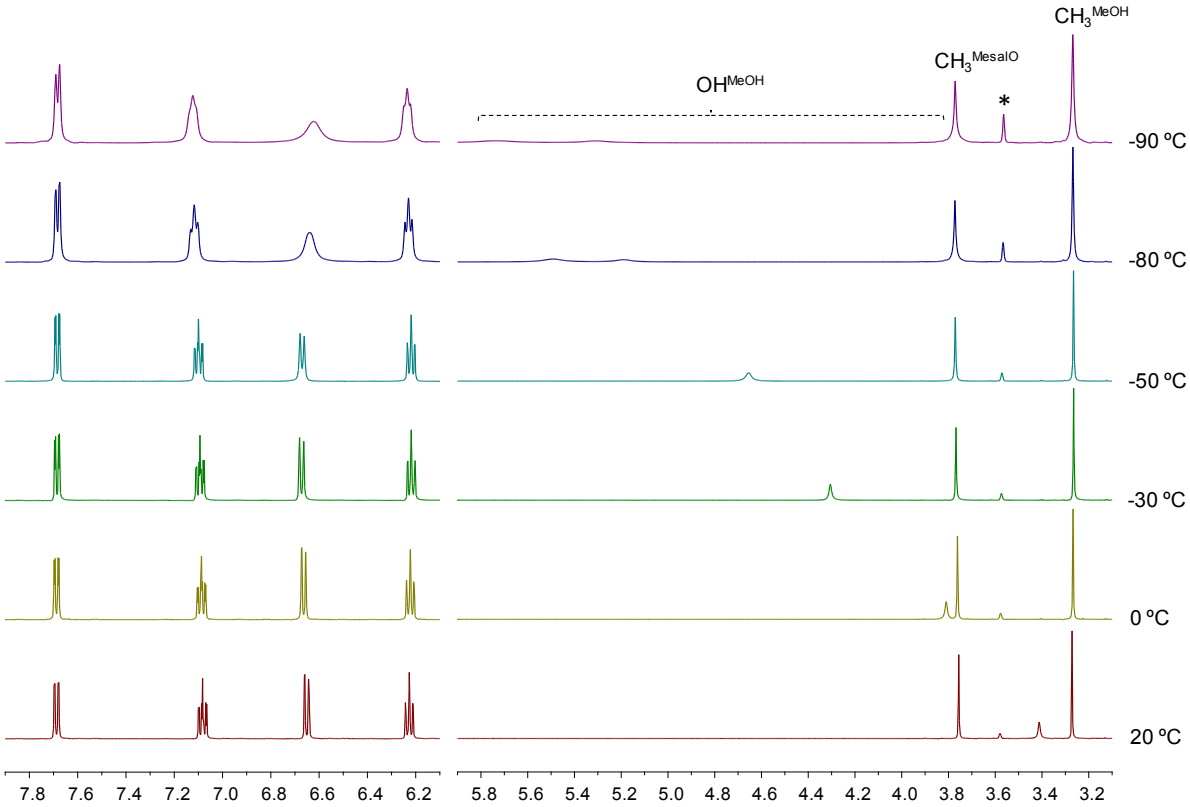

Fig. S22 Variable temperature ^{1}H NMR spectra of **3** (0.2 M) in THF-d_8.

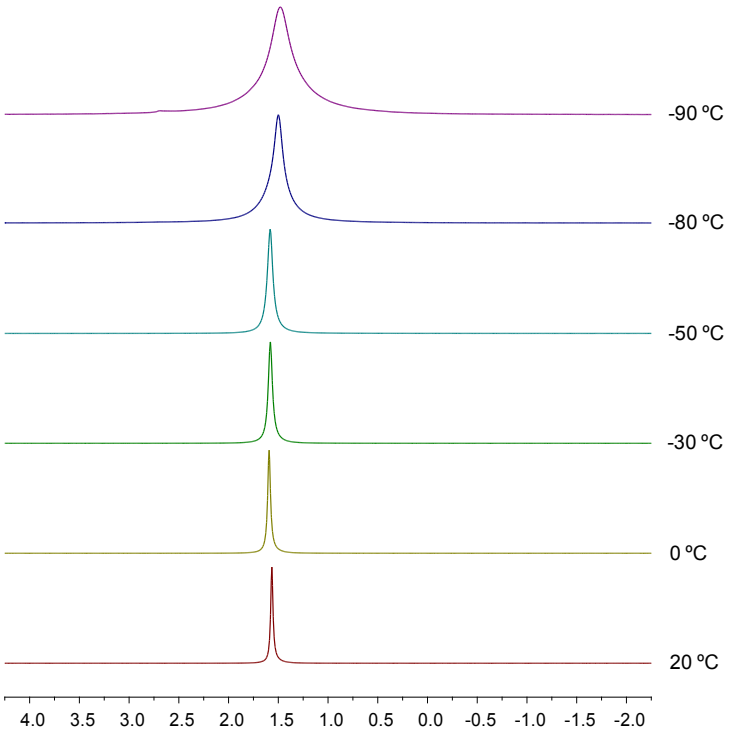

Fig. S23 Variable temperature ^{7}Li NMR spectra of **3** in THF-d_8.

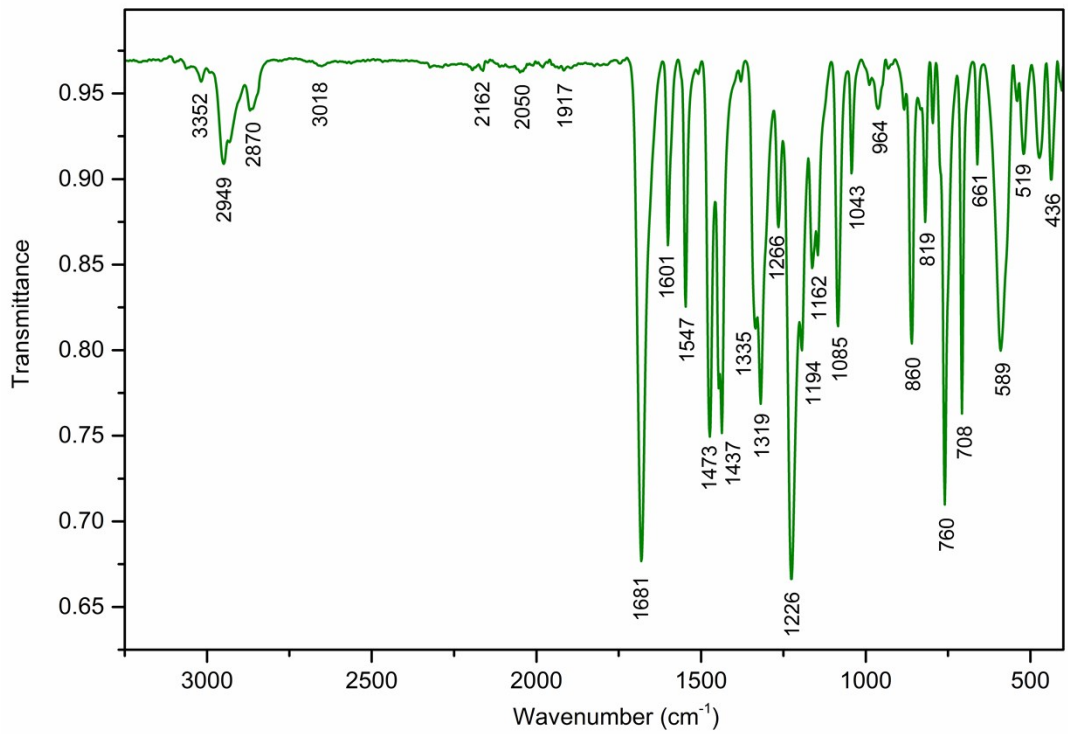

Fig. S24 FTIR-ATR spectra of **1**.

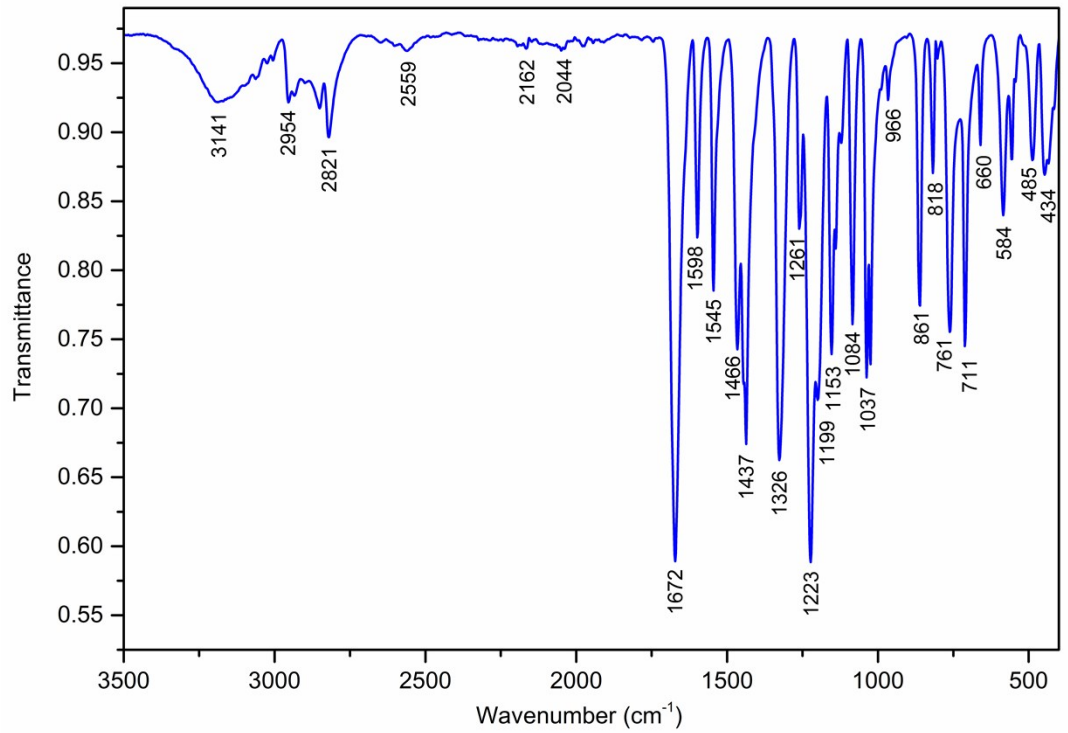

Fig. S25 FTIR-ATR spectra of **2**.

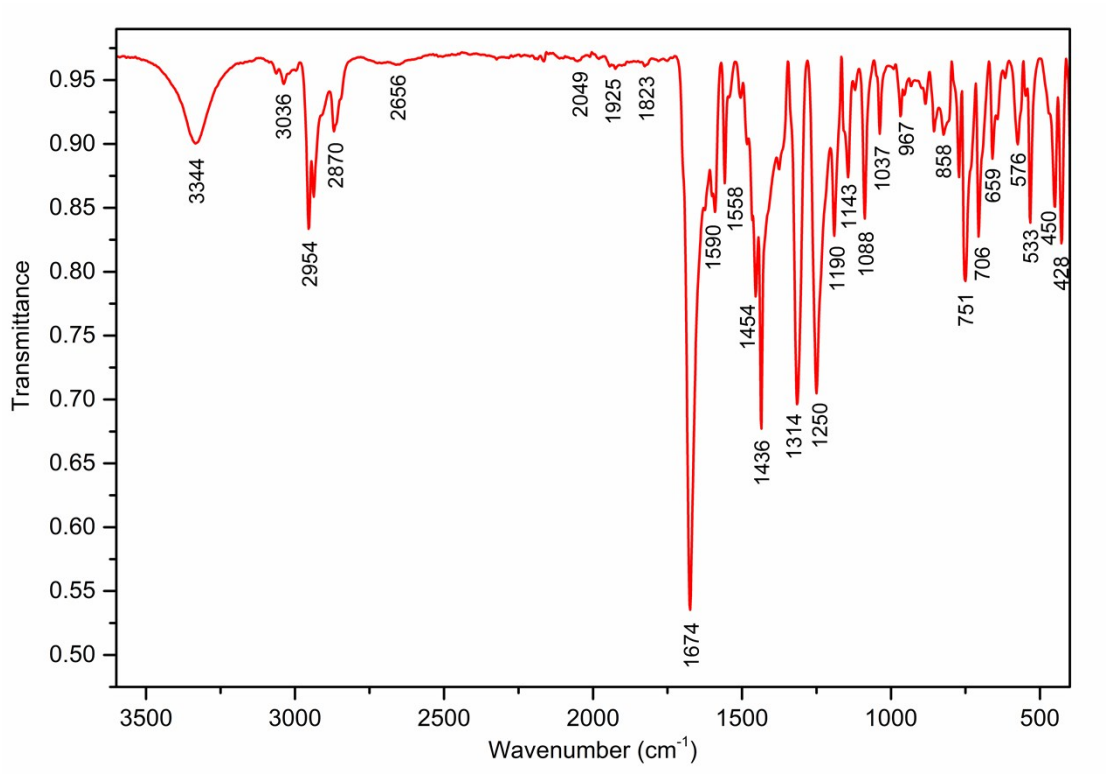

Fig. S26 FTIR-ATR spectra of **3**.

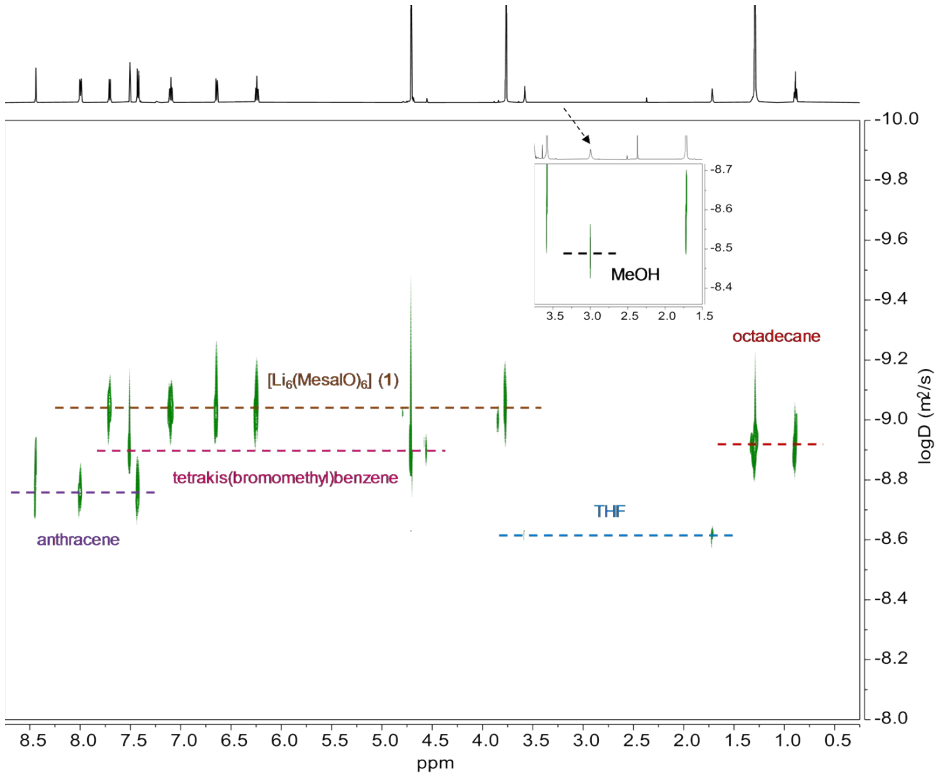

Fig. S27 ^{1}H DOSY NMR spectrum of a mixture of anthracene, octadecane, 1,2,4,5-tetrakis(bromomethyl)benzene and **1** in THF-d_8.

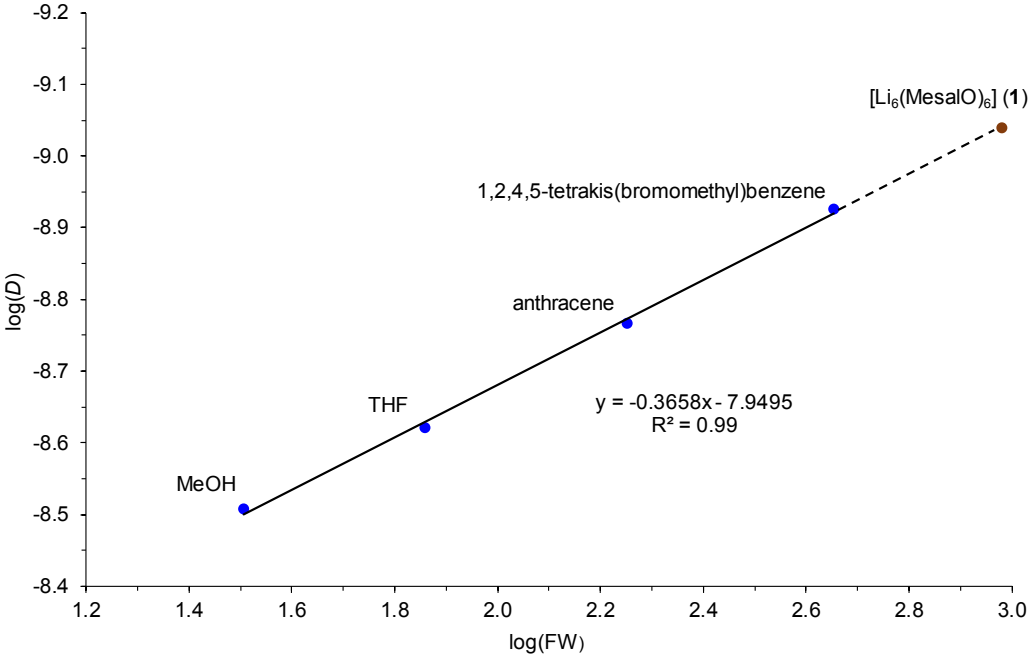

Fig. S28 Plot of diffusion coefficient (log*D*) versus formula weight (log Fw) of a mixture of THF, anthracene, octadecane, 1,2,4,5-tetrakis(bromomethyl)benzene and **1**. Octadecane reference was omitted due to a reveal much lower diffusion coefficient than expected, suggesting its aggregation in solution. Therefore, the residue MeOH was used as an additional reference.

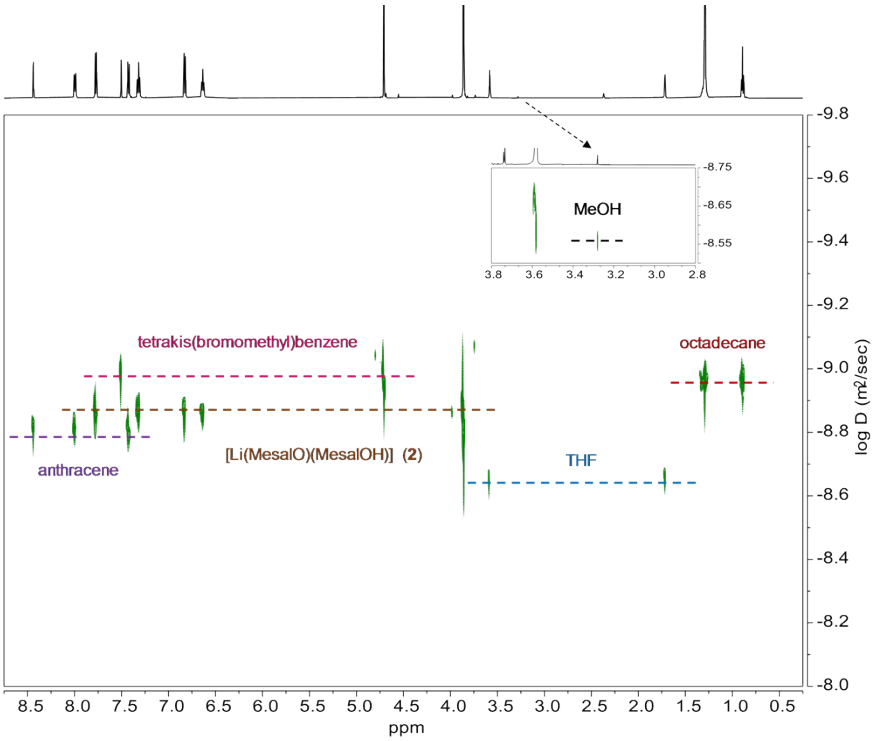

Fig. S29 ^{1}H DOSY NMR spectrum of a mixture of anthracene, octadecane, 1,2,4,5-tetrakis(bromomethyl)benzene and **2** in THF-d_8.

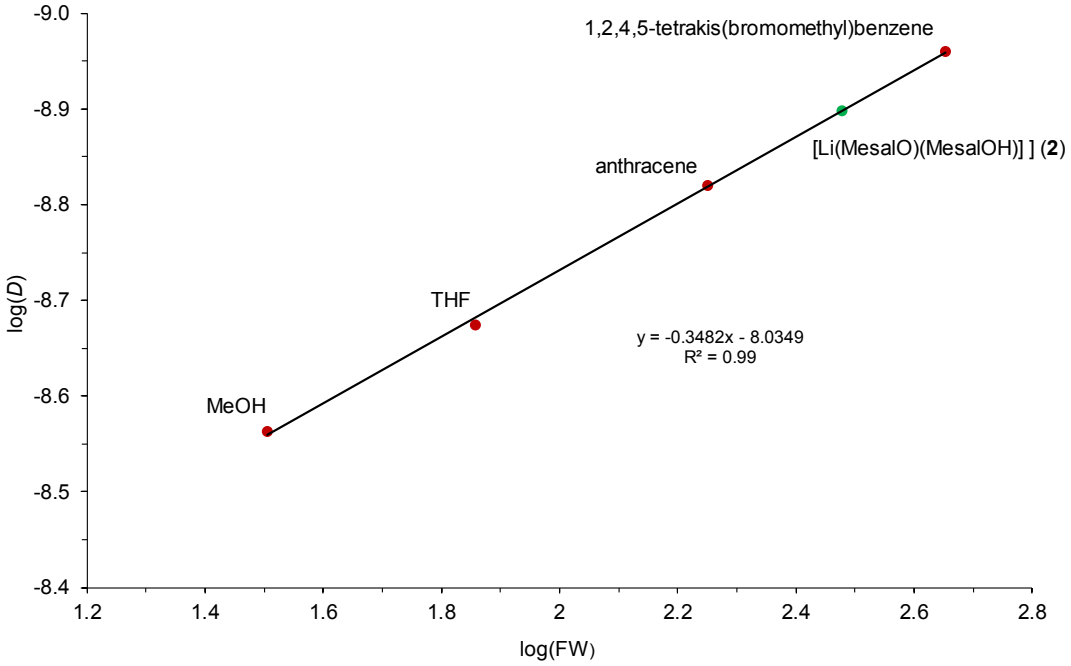

Fig. S30 Plot of diffusion coefficient (log*D*) versus formula weight (log Fw) of a mixture of THF, anthracene, octadecane, 1,2,4,5-tetrakis(bromomethyl)benzene and **2.** Octadecane was omitted and the residue MeOH was used as an additional reference.

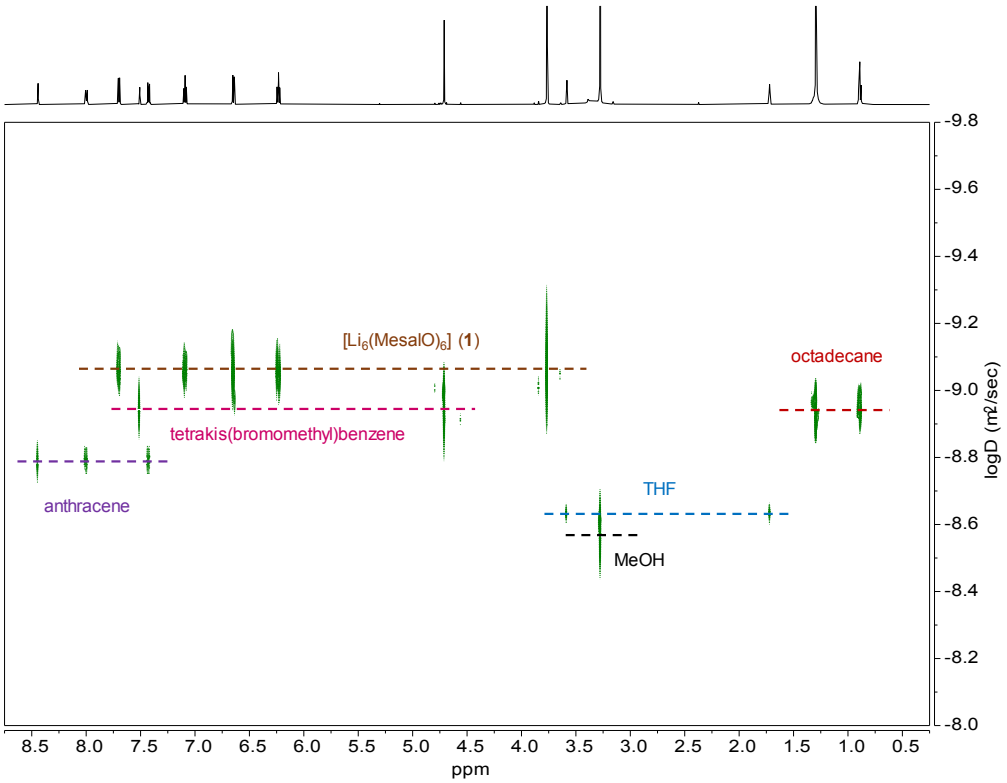

Fig. S31 ^{1}H DOSY NMR spectrum of a mixture of anthracene, octadecane, 1,2,4,5-tetrakis(bromomethyl)benzene and **3** in THF-d_8.

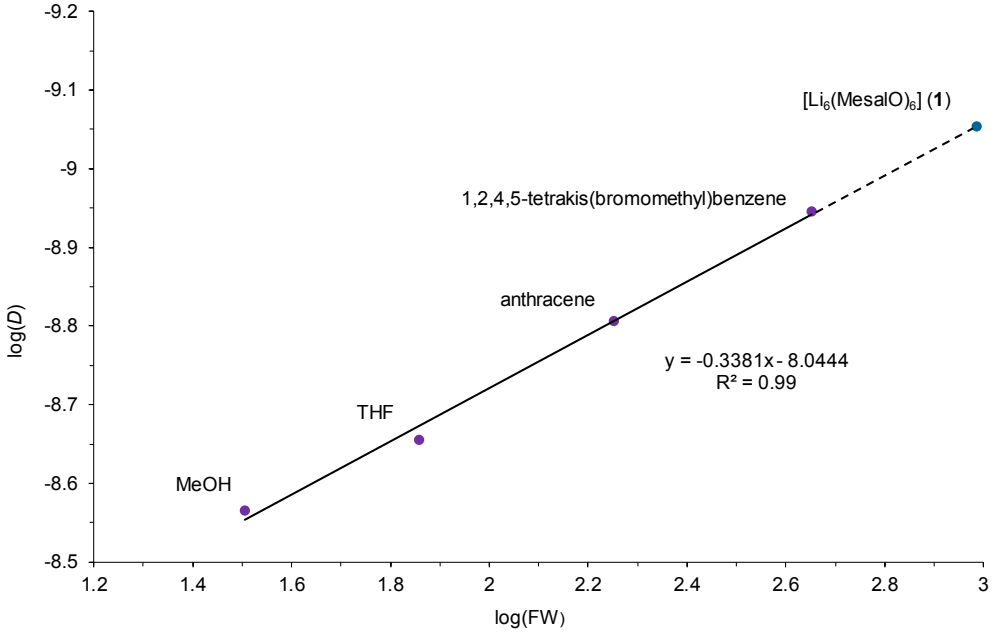

Fig. S32 Plot of diffusion coefficient (log*D*) versus formula weight (log Fw) of a mixture of THF, anthracene, octadecane, 1,2,4,5-tetrakis(bromomethyl)benzene and **3.** Octadecane reference was omitted due to a reveal much lower diffusion coefficient than expected.

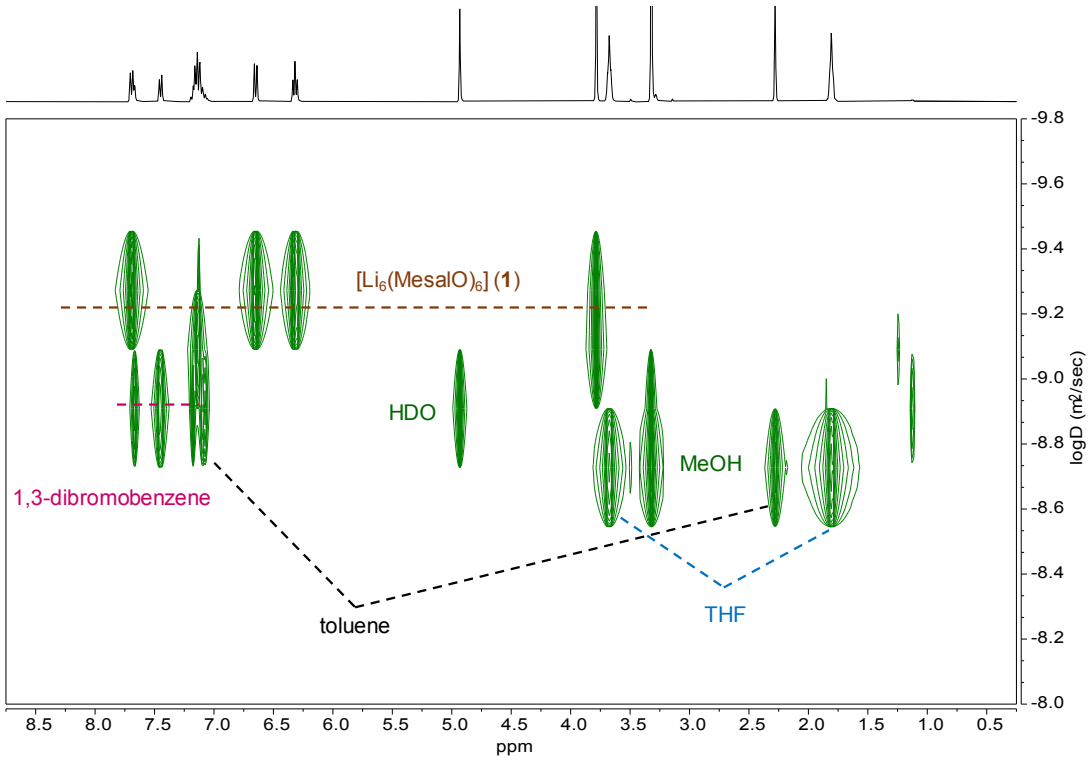

Fig. S33 ^{1}H DOSY NMR spectrum of a mixture of MeOH, THF, toluene, 1,3-dibromobenzene and **3** in methanol-d_4.

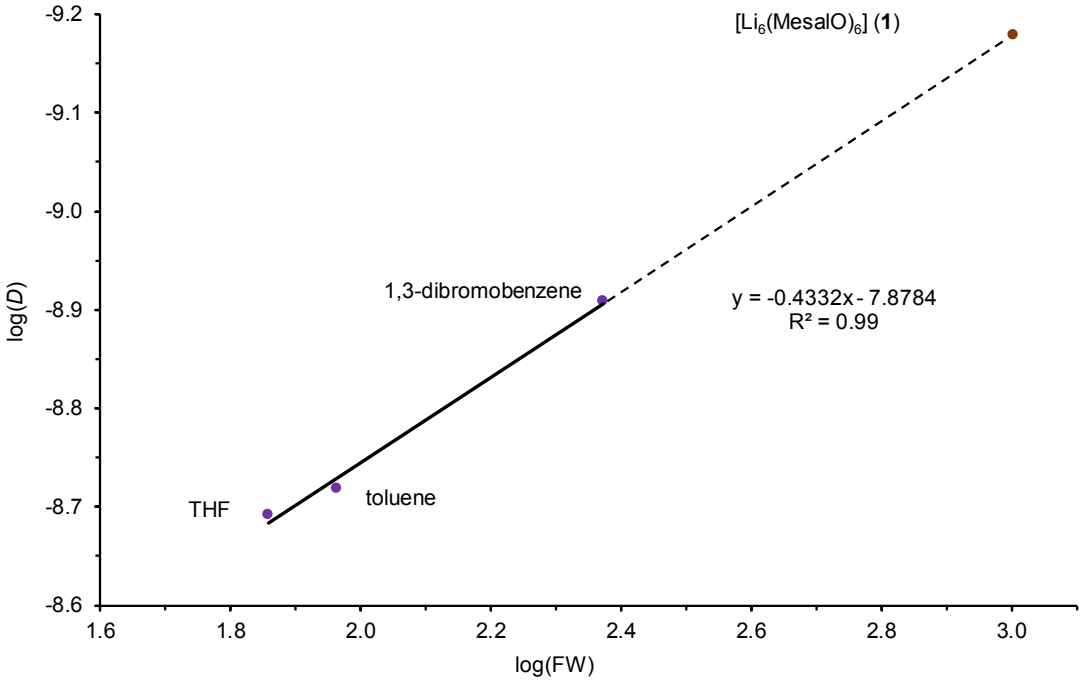

Fig. S34 Plot of diffusion coefficient (log*D*) versus formula weight (log Fw) of a mixture of MeOH, THF, toluene, 1,3-dibromobenzene and **3.**

Table. S2 Diffusion coefficients and estimated formula weight for **1-3** at 20 ºC.

No.	compound	10^{-10} *D* (m^2/s)	Fw (g/mol)	$Fw_{estimated}$ (g/mol)	solvent
1.	**1**	9.12	948.48	957	THF-d_8
2.	**2**	12.65	310.23	301	THF-d_8
3.	**3**	8.83	222.16	968	THF-d_8
4.	**3**	6.62	222.16	1005	methanol-d_4

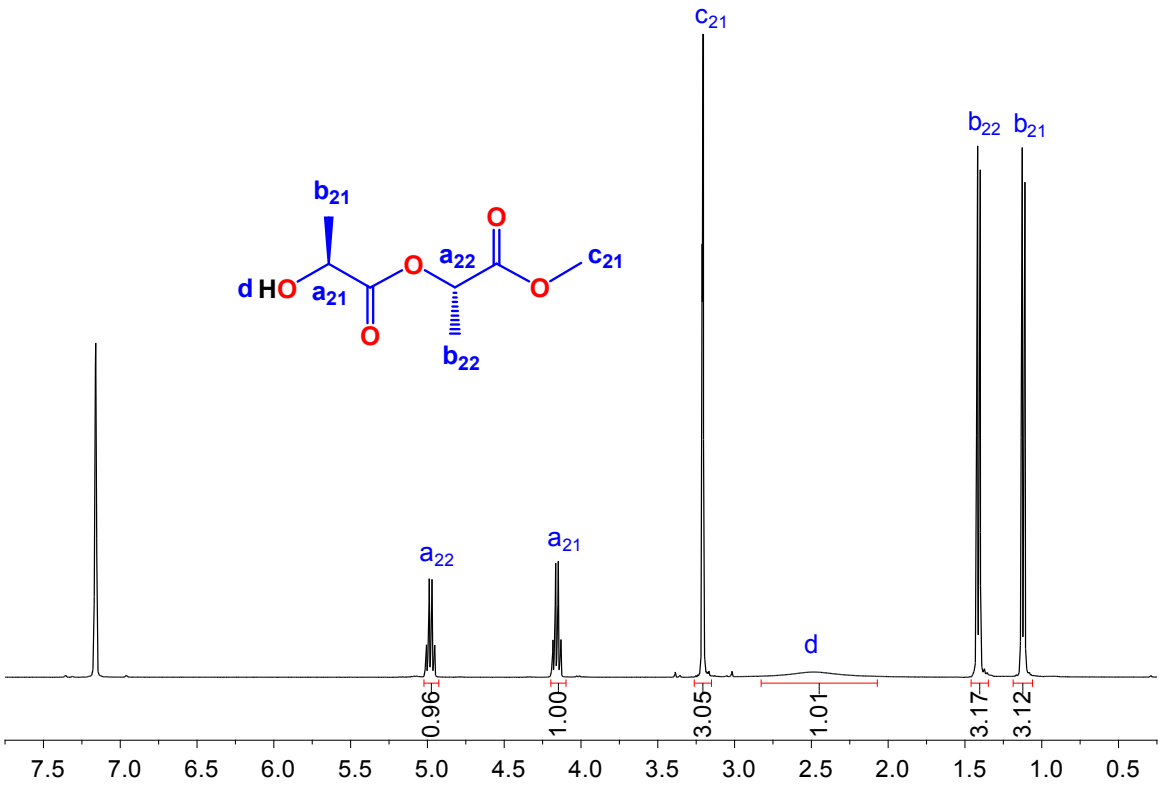

Fig. S35 ^{1}H NMR spectrum of MeL_2 in C_6D_6.

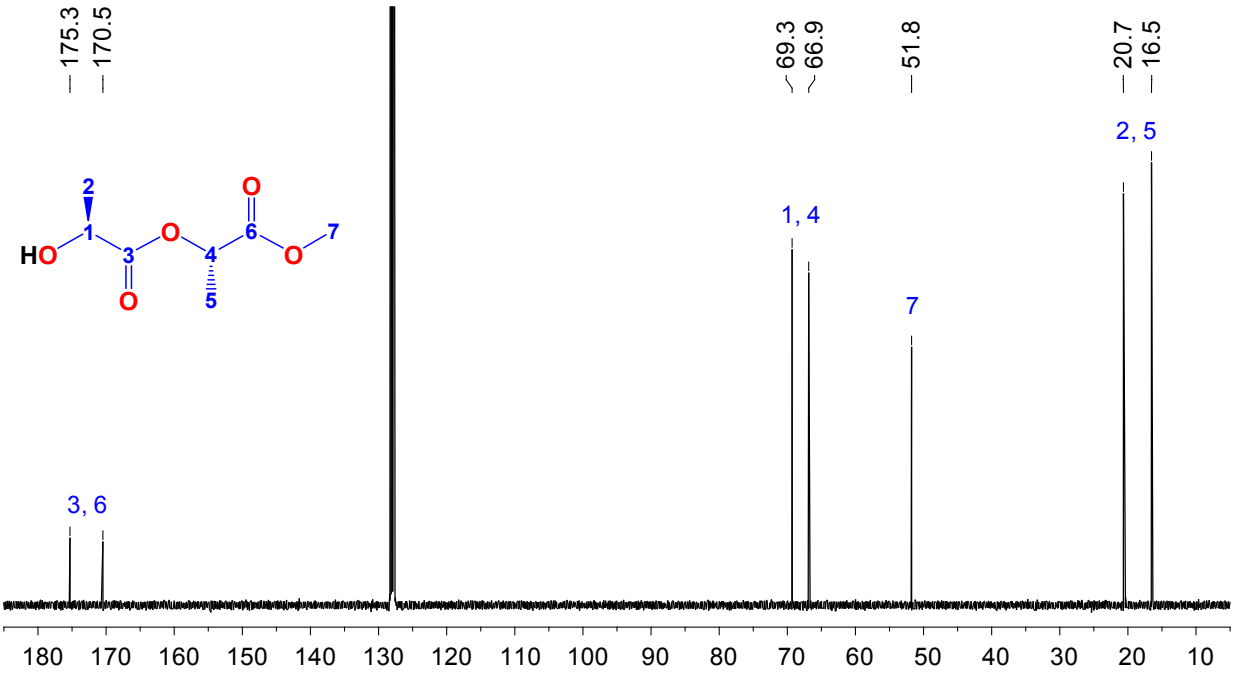

Fig. S36 ^{13}C NMR spectrum of MeL_2 in C_6D_6.

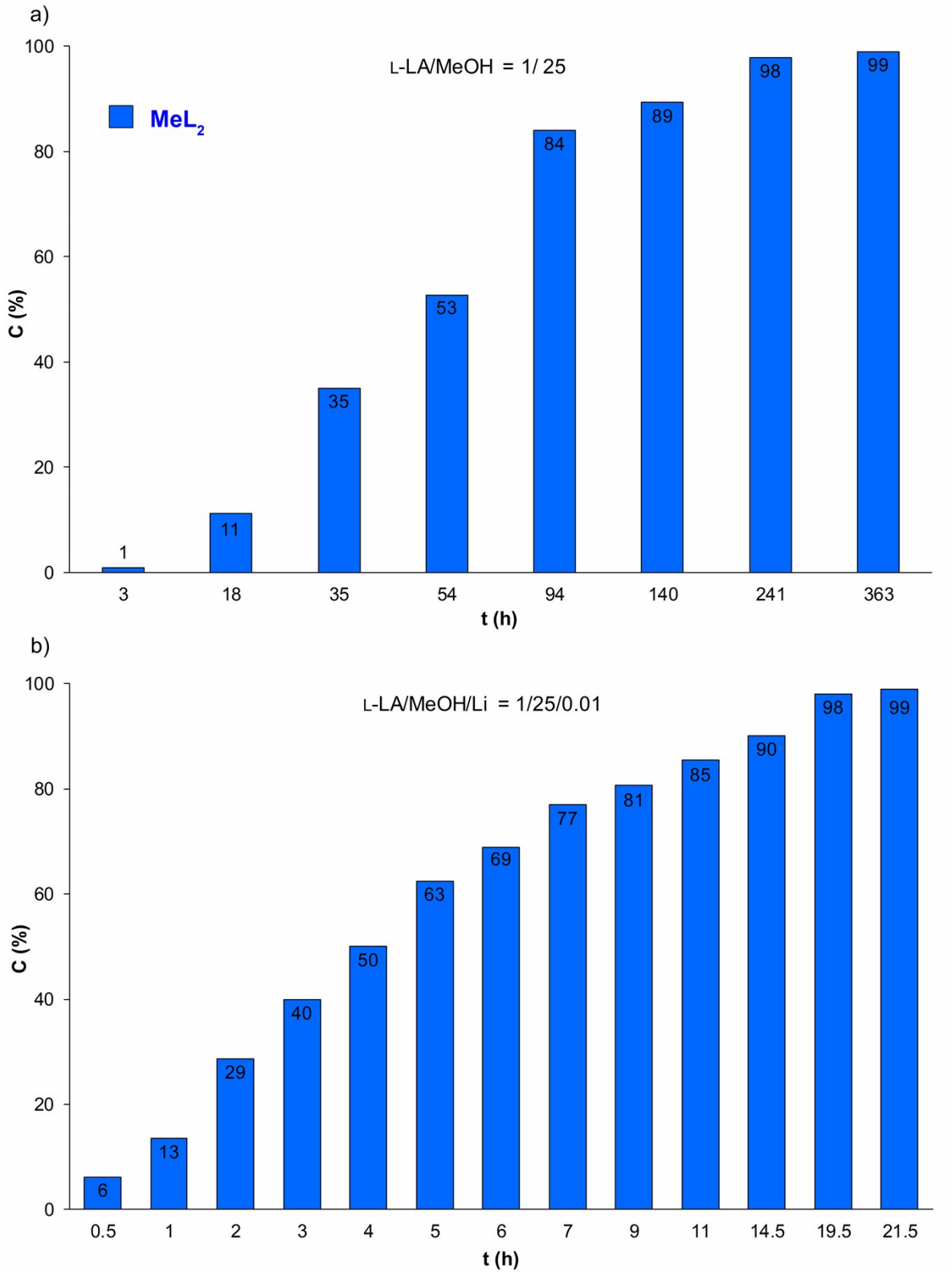

Fig. S37 Effect of reaction time on methanolysis of L-LA performed under catalyst-free conditions (a) or in presence of 0.167 mol% of **1** (b).

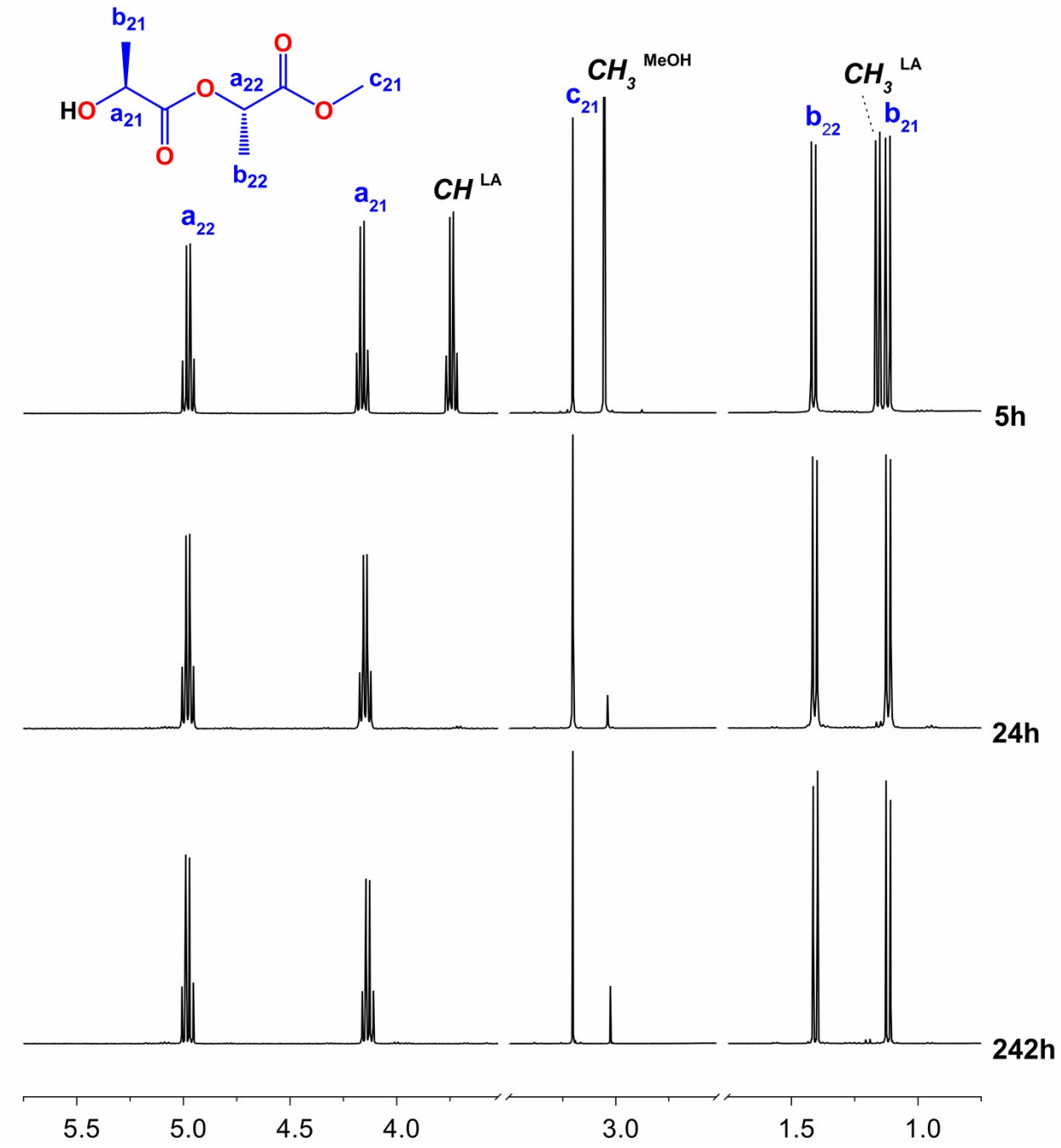

Fig. S38 ^{1}H NMR spectra in C_6D_6 of products of L-LA alcoholysis reaction performed in the in the presence of **1**.

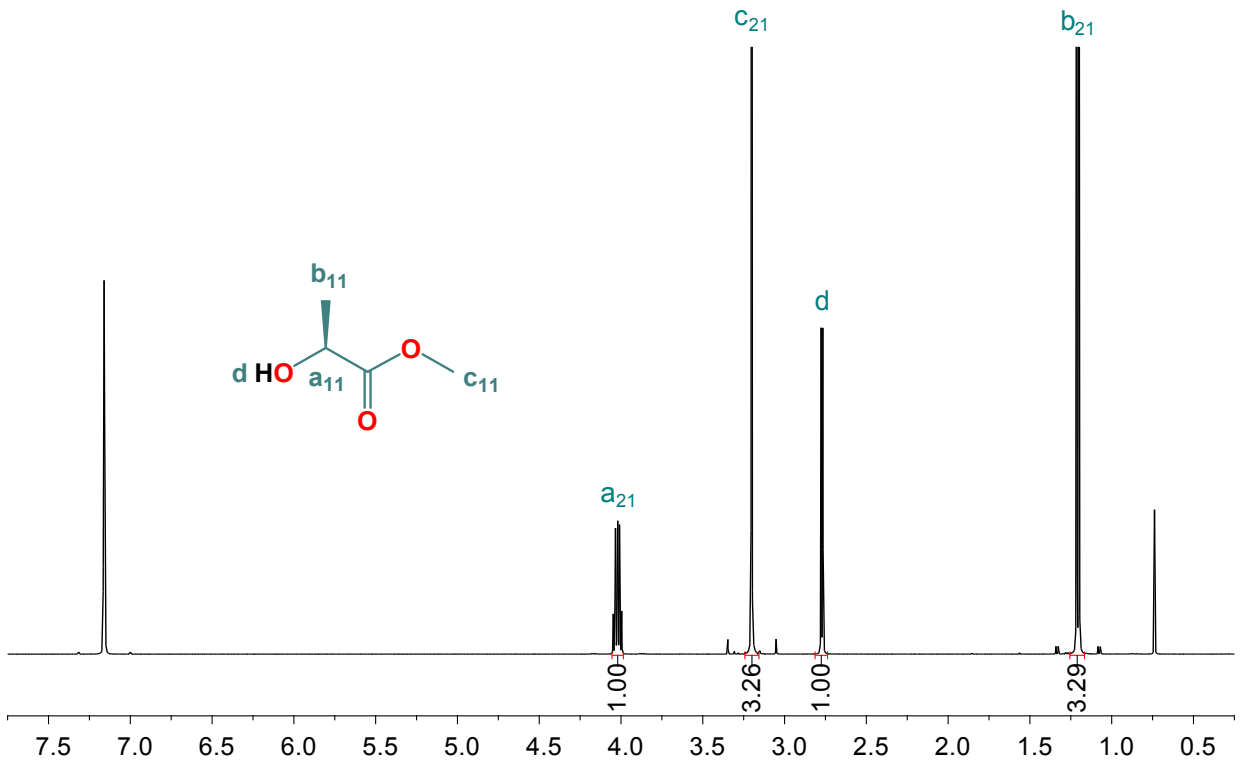

Fig. S39 ^{1}H NMR spectrum of MeL_1 in C_6D_6.

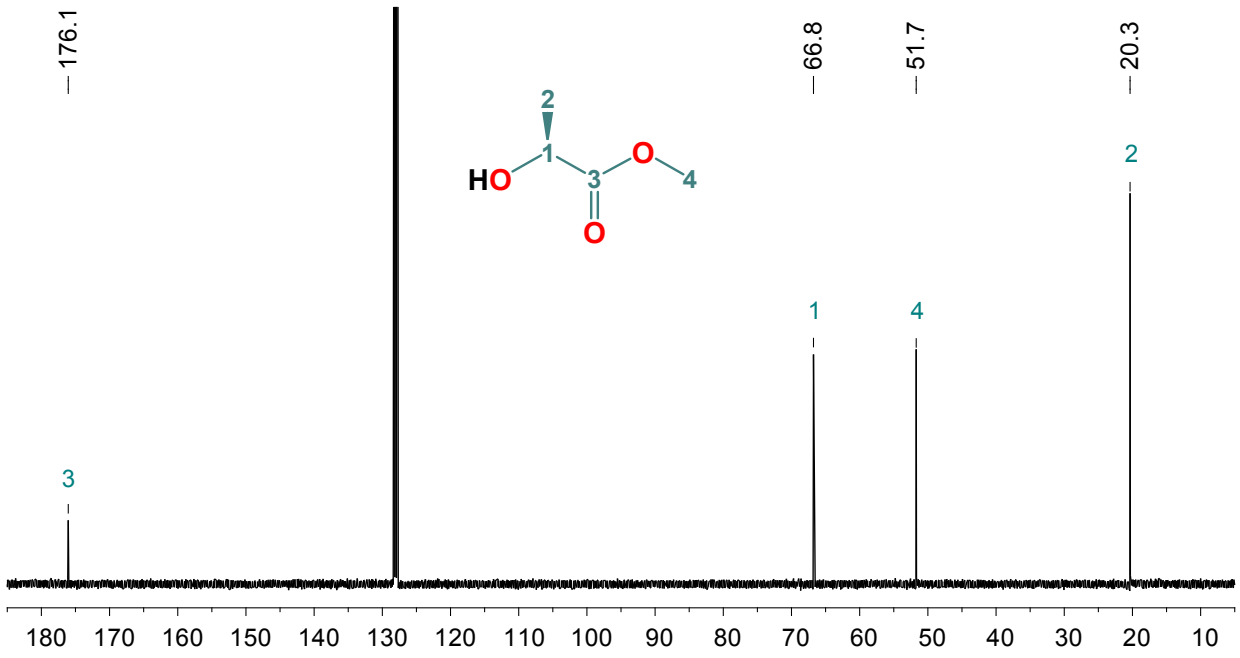

Fig. S40 ^{13}C NMR spectrum of MeL_1 in C_6D_6.

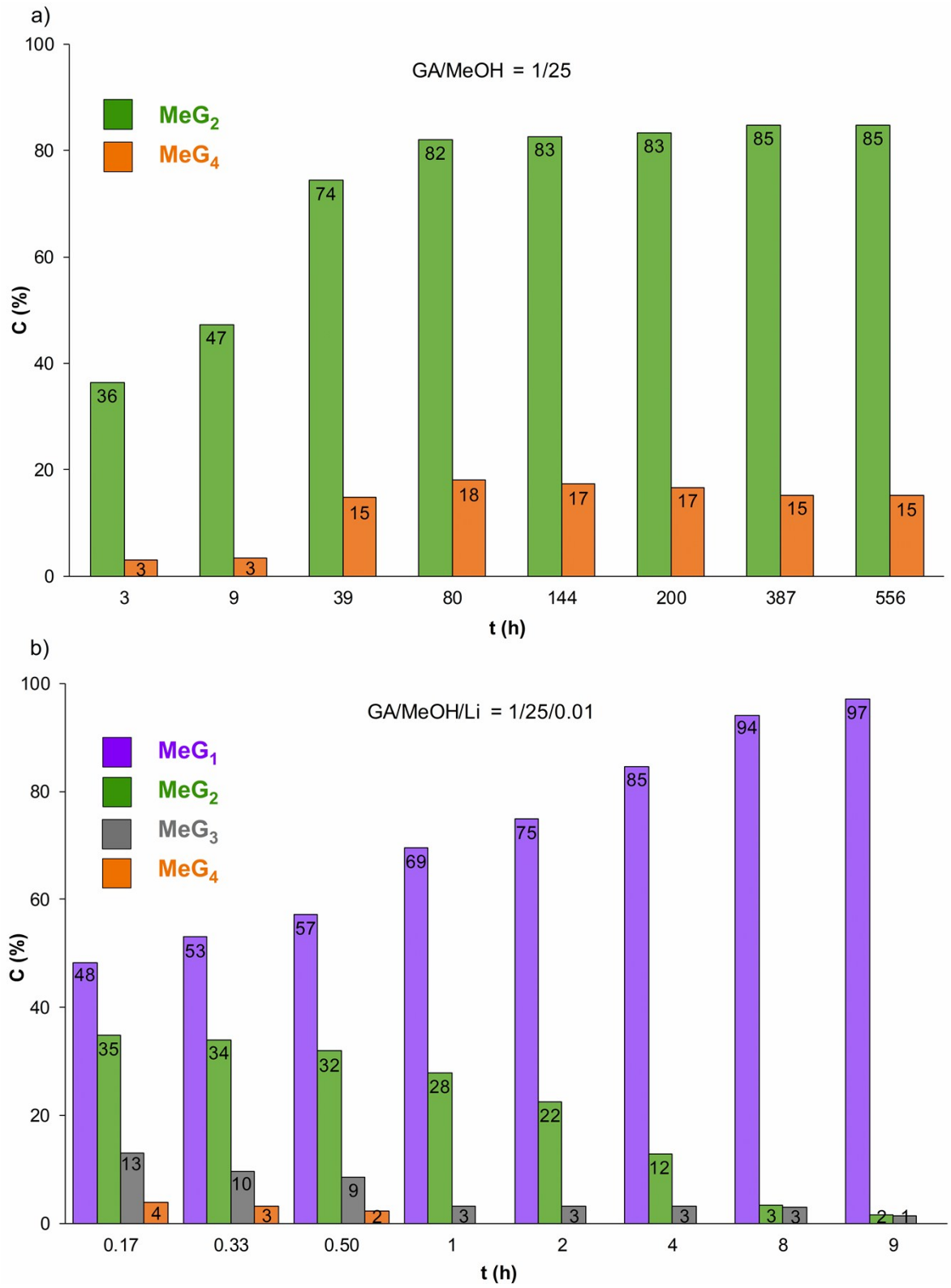

Fig. S41 Effects of reaction time on methanolysis of GA performed under catalyst-free conditions (a) or in presence of 0.167 mol% of **1** (b).

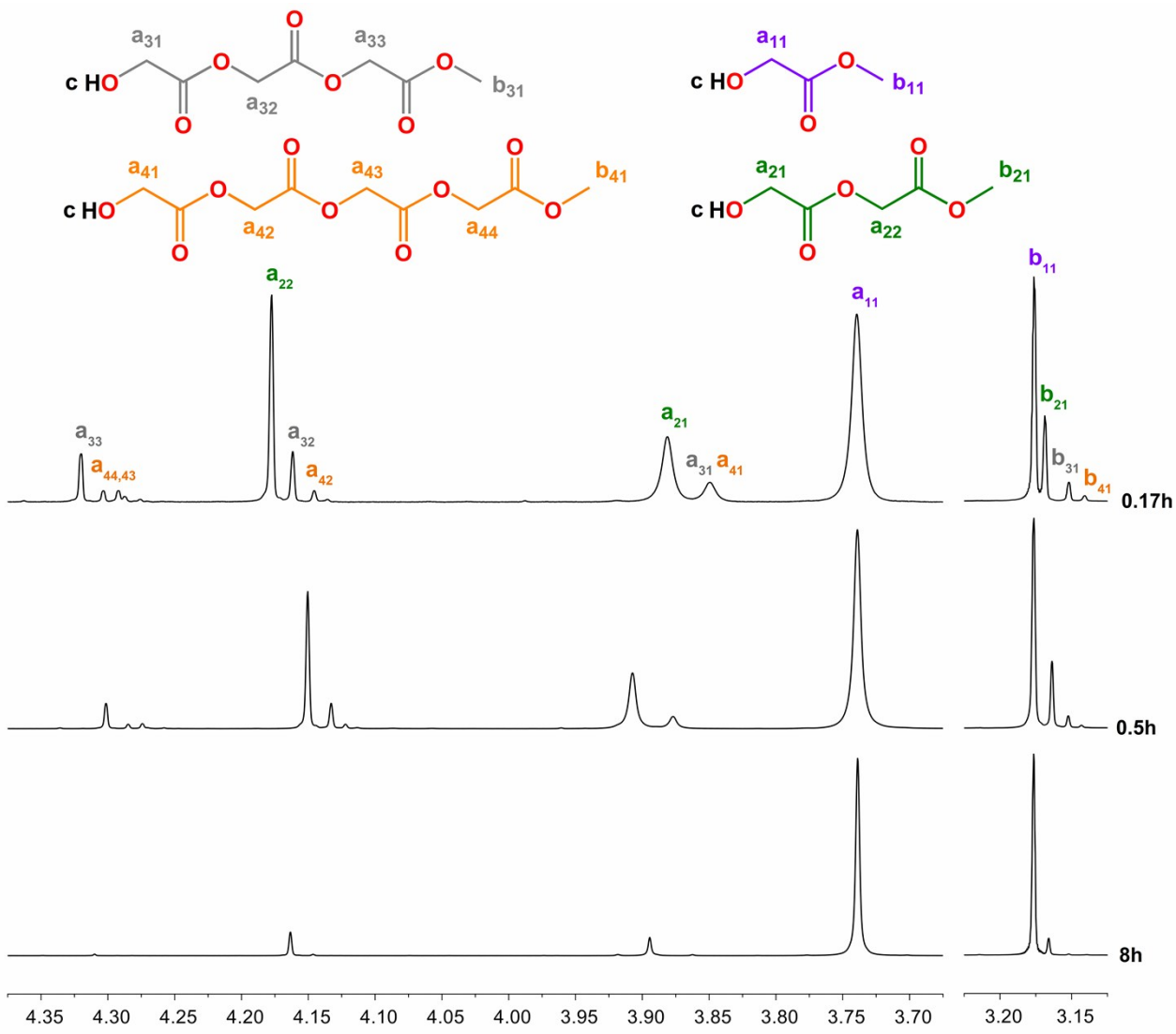

Fig. S42 ^{1}H NMR spectra in C_6D_6 of products of GA alcoholysis reaction performed in the in the presence of **1**.

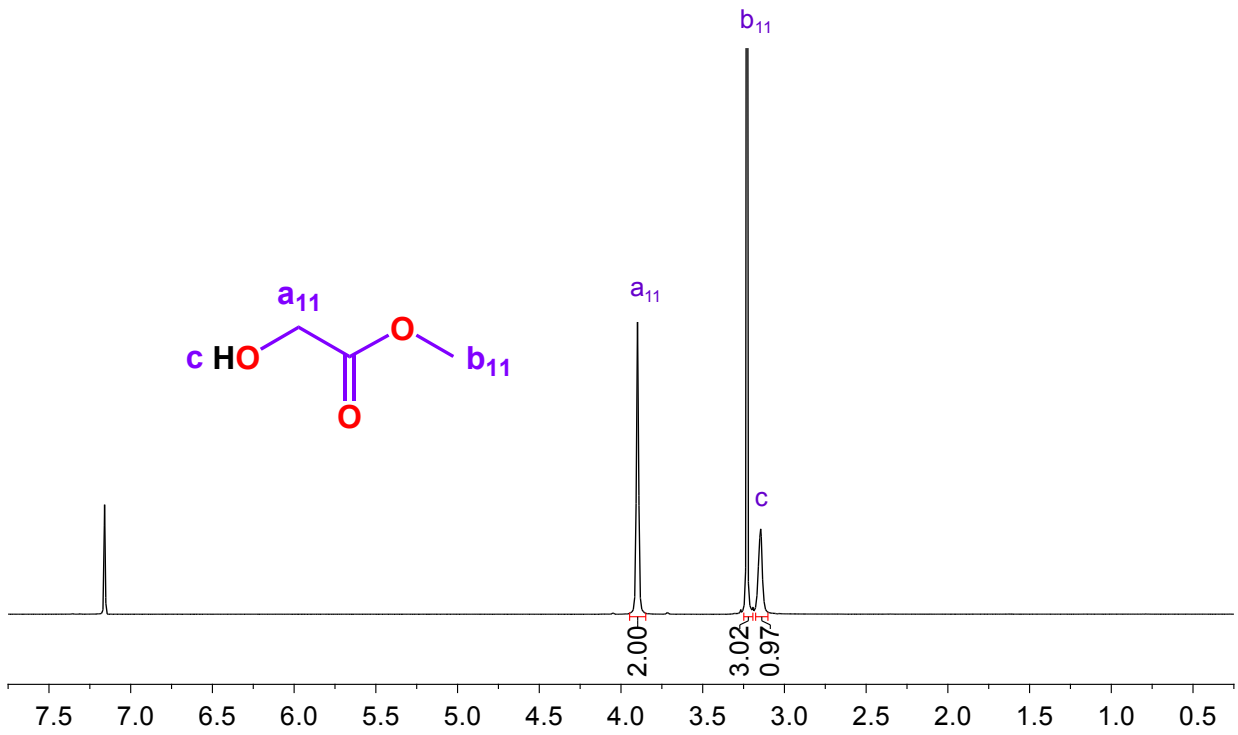

Fig. S43 ^{1}H NMR spectrum of MeG_1 in C_6D_6.

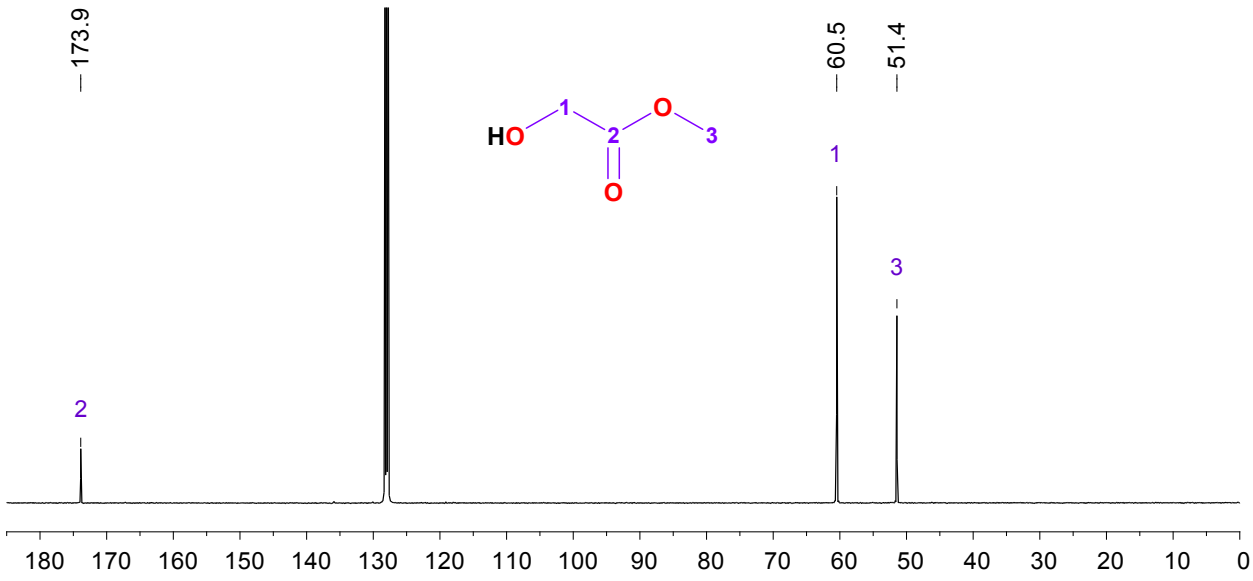

Fig. S44 ^{13}C NMR spectrum of MeG_1 in C_6D_6.

Table S3 Summary of catalyst free methanolysis of L-LA and GA.[a]

Entry	Ester	t(h)	MeY_2[b] (%)	MeY_4[b] (%)
1	L-LA	3	1	-
2	L-LA	18	11	-
3	L-LA	35	35	-
4	L-LA	54	53	-
5	L-LA	94	84	-
6	L-LA	140	89	-
7	L-LA	241	98	-
8	L-LA	363	99	-
9	GA	3	36	3
10	GA	8.5	47	3
11	GA	39	74	15
12	GA	80	82	18
13	GA	144	83	17
14	GA	200	83	17
15	GA	387	85	15
16	GA	556	85	15

[a]General reaction conditions: [GA(L-LA)] = 0.98 M, 10.7 mL of methanol as solvent, temperature 25 °C, in N_2 atmosphere, reactant stoichiometries GA(L-LA)/ROH = 1/25. [b]Obtained from ^{1}H NMR spectroscopic analysis, Y = lactate (L, 72 Da) or glycolate (G, 58 Da) unit.

Table S4 Summary of methanolysis of L-LA and GA performed in the presence of **1**.[a,b]

Entry	Ester	t(h)	MeY_1[c] (%)	MeY_2[c] (%)	MeY_3[c] (%)	MeY_4[c] (%)
1	L-LA	0.5	-	6	-	-
2	L-LA	1	-	13	-	-
3	L-LA	2	-	29	-	-
4	L-LA	3	-	40	-	-
5	L-LA	4	-	50	-	-
6	L-LA	5	-	63	-	-
7	L-LA	6	-	69	-	-
8	L-LA	7	-	77	-	-
9	L-LA	8	-	78	-	-
10	L-LA	9	-	81	-	-
11	L-LA	11	-	85	-	-
12	L-LA	14.5	-	90	-	-
13	L-LA	19.5	-	98	-	-
14	L-LA	21.5	-	99	-	-
15[b]	L-LA	0.25	90	10	-	-
16[b]	L-LA	0.5	95	5	-	-
17[b]	L-LA	1.5	97	3	-	-
18[b]	L-LA	2.5	99	1	-	-
19	GA	0.17	48	35	13	4
20	GA	0.33	53	34	10	3
21	GA	0.50	57	32	9	2
22	GA	1	69	28	3	-
23	GA	2	75	22	3	-
24	GA	4	85	13	3	-
25	GA	8	94	3	3	-
26	GA	9	97	2	1	-

[a]General reaction conditions: [GA(L-LA)] = 0.98 M, [**1**] = 1.63 mM, 10.7 mL of methanol as solvent, temperature 25 °C, in N_2 atmosphere, reactant stoichiometries GA(L-LA)/MeOH/Li = 1/25/0.01. [b]Reactions performed under reactant stoichiometry L-LA/MeOH/Li = 1/25/0.05. [c]Obtained from ^{1}H NMR spectroscopic analysis, Y = glycolate (G, 58 Da) or lactate (L, 72 Da) unit.