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

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In this work, a hexanuclear lithium compound, $[Li_6(MesalO)_6]$ (**1**), supported by a chelating ligand, namely methyl salicylato (MesalOH), was used as a precursor for preparation of the monomeric lithium aryloxides [Li(MesalO)(MesalOH)] (**2**) and $[Li(MesalO)(MeOH)_2]$ (**3**) *via* reactions with MesalOH or MeOH. These aryloxides were characterized by single-crystal X-ray diffraction, and spectroscopic and other analytical methods. The diffusion-ordered ^{1}H NMR measurements revealed the retention of solid-state structures of **1** and **2** in THF-d_8 solution. Experimental data obtained for **3** showed its decomposition into compound **1** and free MeOH. Compound **1** generated from **3** was also used as a catalyst for the alcoholysis of L-lactide (L-LA) and glycolide (GA) for the preparation of α-hydroxy acid esters. We established that during methanolysis in the presence of **1**, L-LA was selectively transformed into methyl (*S*,*S*)-*O*-lactyllactate (**MeL$_2$**), and GA was converted to methyl glycolate (**MeG$_1$**) and oligoglycolate esters **MeG$_n$** (n = 2, 3, and 4).

Introduction

Lithium alkoxides are the largest and most important group of alkali–metal alkoxo and aryloxo derivatives. They have numerous practical applications in organic, polymer, and materials chemistry. Simple lithium alkoxides [Li(OR)] (R = Et, iPr, *sec*-Bu, and *t*Bu) are commonly used as precursors for chemical vapor deposition of lithium-containing layers[1] and sol–gel processes.[2–4] They have been used as electrolyte additives to improve the low-temperature performances of rechargeable lithium-ion electrochemical cells, and enable extension of operating temperatures to as low as −40 °C.[5] Lithium alkoxides are also important components of the superbases commonly used in synthetic and polymer chemistry, which are synthesized by metal interchange reactions between organolithium compounds (LiR) and heavier-alkali–metal alkoxides ([M(OR′)], M = Na, K, Rb, and Cs). The reactivities of such systems are considerably greater than those of the parent compounds, and depend on the type of reaction, the solvents used, and the superbase structures, *i.e.*, monomeric or mixed-metal aggregated species.[6] [Li(O^{t}Bu)] is particularly useful as a catalyst or reagent in organic synthesis,[7] and an initiator in the polymerizations of lactones,[8,9] acrylamides,[10] hydroxyalkyl acrylates, and methacrylates.[11] It is also an effective promotor for C–C bond formation by α-alkylation of ketones with ROH under transition-metal-free conditions.[12] Lithium(quinolin-8-olato), which has strong blue-light electroluminescence, good film formability, and excellent electron mobility or a low turn-on voltage, has been investigated as a promising emitter[13] or interfacial material for the electron-transporting[14] and electron-injecting layers[15] in organic light-emitting diodes. Lithium pyridylphenolate complexes have similar applications.[16] Tetranuclear lithium aryloxide cubane clusters are effective building blocks for the construction of crystalline porous materials for gas storage.[17] Lithium aryloxides supported by aminophenolate or bis(phenolate) ligands have been intensively investigated as efficient initiators in the ring-opening polymerization (ROP) of heterocyclic monomers to give biodegradable polymers with numerous applications in the biomedical and food-packaging industries.[18,19] In addition to their use in ROP, cyclic esters can be used as precursors for the synthesis of a wide range of α-hydroxy acid esters, which are important eco-friendly chemicals, *i.e.*, green solvents.[20,21] They have many commercial applications, *e.g.*, as high-grade clean solvents, paint and ink additives, preservatives and flavors, and ingredients in pharmaceutical or skin-care formulations.[22,23] Alkyl lactates and glycolates are particularly useful and are promising alternatives to classical petrochemical solvents. These esters can be synthesized by alcoholysis of L-lactide (L-LA) and glycolide (GA) initiated by simple metal alkoxides.

The development of inexpensive methods for the synthesis of stable and well-defined lithium aryloxide compounds is

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† Electronic supplementary information (ESI) available: NMR, IR, and crystallographic data for **1–3**; NMR data for time monitoring of alcoholysis reactions and obtained esters (PDF). CCDC 1944070–1944072. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt03631h

therefore particularly important to enable their practical use in catalytic reactions.

Here, we report the preparation and characterization of the hexanuclear aryloxylithium compound $[Li_6(MesalO)_6]$ (**1**), which is supported by the industrially used methyl salicylato ligand (MesalOH).[24,25] We also examined the stability of **1** by using MesalOH and MeOH as solvating agents. In this study, we obtained two new monomeric lithium aryloxides, namely [Li(MesalO)(MesalOH)] (**2**) and $[Li(MesalO)(MeOH)_2]$ (**3**). We also showed that **1** is an effective catalyst for the alcoholysis of heterocyclic esters, *i.e.*, L-LA and GA, to give a family of environmentally friendly α-hydroxy acid esters in excellent yields and under ambient conditions.

Results and discussion

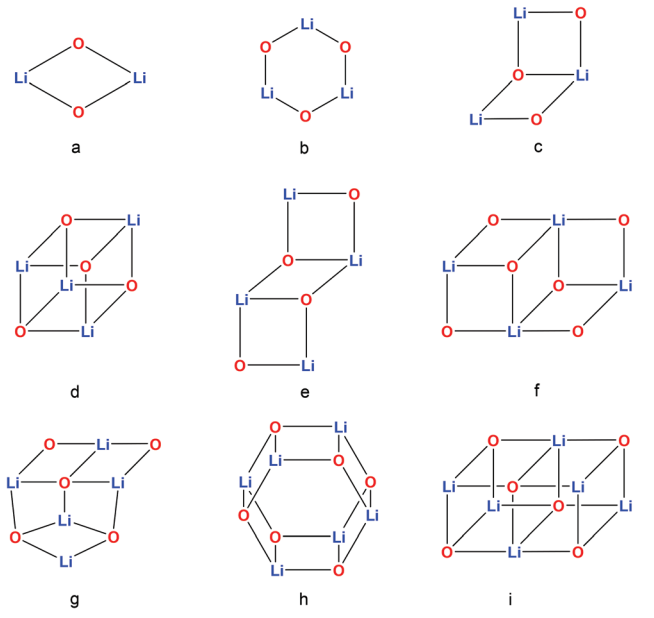
Synthesis and characterization of lithium compounds 1–3

In the solid state, lithium aryloxides usually exist as various aggregates with structures varying from dimers to hexamers, as shown in Scheme 1. The structural diversity of lithium aryloxides results from the coordinating ability, and steric or electronic effects, of the ligands used. Boyle and colleagues studied *ortho*-substituted lithium phenoxides and reported that steric hindrance at this position strongly affected the final [Li(OAr)] structure by reducing the bridging capacity of the OAr ligands.[26] Other factors responsible for the degree of aggregation were the donor solvent basicity and solvation with strong bases, which result in the formation of smaller aggregates. Most previously reported structures are based on various types of central core structure: Li_2O_2 rings;[27] Li_3O_3 hexagons[28] and chairs;[29] Li_4O_4 cubanes[30] and ladders,[31] Li_4O_6 double-open dicubanes;[32] Li_5O_5 aggregates, and Li_6O_6 hexagonal prisms[33] and dicubanes[34] (Scheme 1a–i).

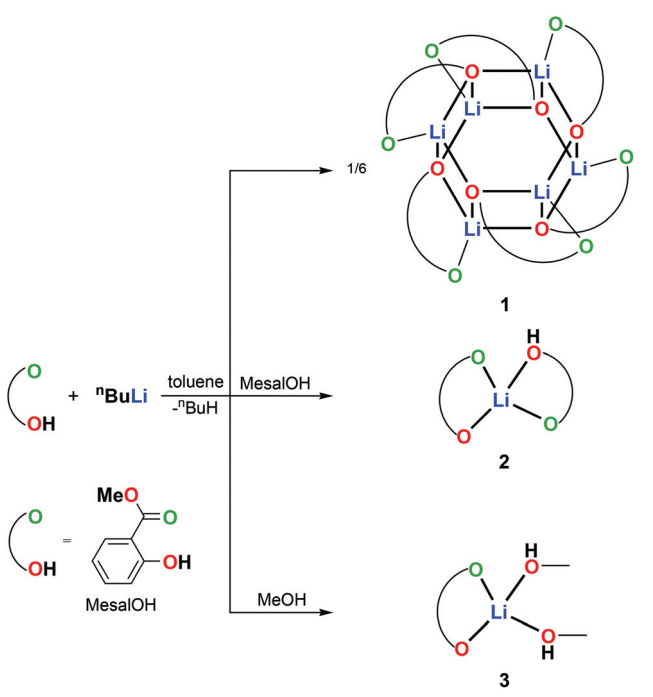
Scheme 2 shows that the reaction of MesalOH (1 equiv.) with ^{n}BuLi (1 equiv.) under butane evolution in toluene afforded a new lithium compound, $[Li_6(MesalO)_6]$ (**1**, 64%).

Single-crystal X-ray diffraction data (XRD, ESI, Table S1†) show that in the solid form compound **1** is a centrosymmetric hexanuclear cluster based on a hexagonal-prismatic $Li_6(\mu^3\text{-}O)_6$ core structure. The structure of **1** (Fig. 1) consists of two stacked Li_3O_3 units; this is a common structural motif in lithium coordination chemistry and has been found in $[Li_6(OPh)_6(THF)_6]$[35], $[Li_6(OAr)_6]$ (ArO^- = 2,6-dimethoxyphenolato[36] or quinolin-8-olato[37] anions), and $[Li_6(L)_2]$ (L^{3-} = cage-shaped triphenolato anions[38]). The Li_3O_3 unit is nearly planar with a maximum deviation of 0.058 Å from a plane drawn through this six-membered ring. The lithium ions are four-coordinated with O_4 donor sets from three MesalO ligands. Continuous-shape measurement (CShM)[39] analysis of the LiO_4 polyhedrons confirmed the presence of axially vacant trigonal bipyramidal coordination environments around the Li1 and Li3 atoms or a tetrahedral environment around Li2, as confirmed by the shape parameters: S(vTBPY-4) = 2.431 for Li1 and 2.326 for Li3, or S(T-4) = 2.444 for Li2. The lengths of the Li–O(aryloxo) bonds within the Li_3O_3 ring, *i.e.*, 1.883(5)–1.946(5) Å, are much shorter than those between the rings, which range from 2.043(5) to 2.075(5) Å.

In lithium chemistry, the use of strong donor solvents generally leads to the formation of smaller aggregates. For example, [Li(OPh)] crystallizes as a hexamer or tetramer from THF and as a dimer from pyridine.[26] However, it has never



Scheme 1 Common lithium aryloxide core structures: Li_2O_2 ring (a); Li_3O_3 hexagon (b), and chair (c); Li_4O_4 cubane (d) and ladder (e); Li_4O_6 defective dicubane (f); Li_5O_5 aggregate (g); and Li_6O_6 hexagonal prism (h) and dicubane (i).



Scheme 2 Synthesis of compounds **1–3**.

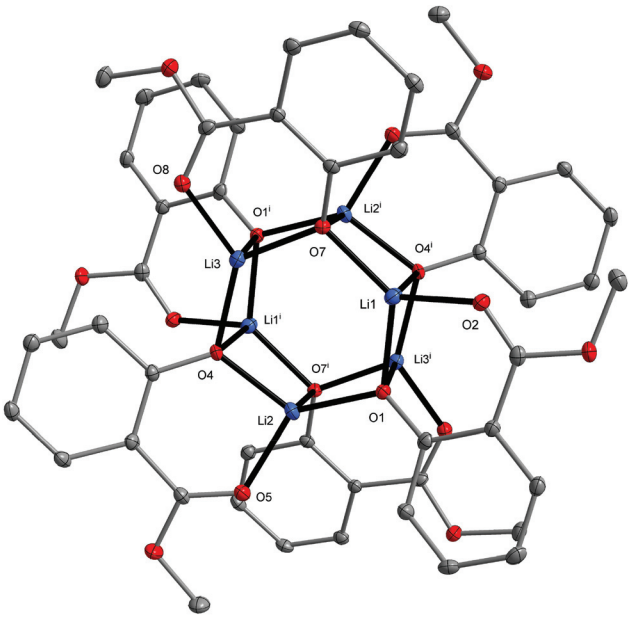


Fig. 1 Molecular structure of $[Li_6(MesalO)_6]$ (**1**). Displacement ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

been observed that the use of simple donor solvents leads to the formation of well-defined monomeric species. We therefore chose cluster **1** as the starting material for the synthesis of monomeric lithium aryloxides *via* reactions with MesalOH and MeOH. The addition of MesalOH (6 equiv.) to a THF solution of **1** led to breakage of the hexanuclear structure and formation of a monomeric lithium compound, [Li(MesalO)(MesalOH)] (**2**, 57%). The XRD data for **2** (Fig. 2) indicate that the Li1 atom is tetrahedrally coordinated with O_4 donor sets from one MesalO and one MesalOH ligand. The Li–O bond lengths, *i.e.*, 1.892(4)–1.931(4) Å, are similar to those in **1**.

When a similar reaction was performed in the presence of MeOH, the monomeric in solid state lithium aryloxide $[Li(MesalO)(MeOH)_2]$ (**3**, 61%) was obtained (Fig. 3). The structures of **2** and **3** are based on the same motif, in which a lithium ion coordinated with a bidentate aryloxide ligand is solvated by two oxygen donor atoms from one MesalOH or two

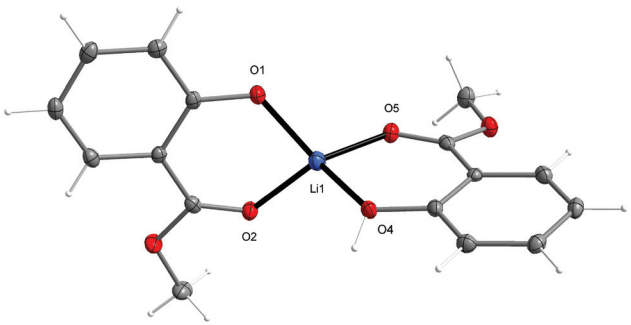


Fig. 2 Molecular structure of [Li(MesalO)(MesalOH)] (**2**). Displacement ellipsoids are drawn at 30% probability level.

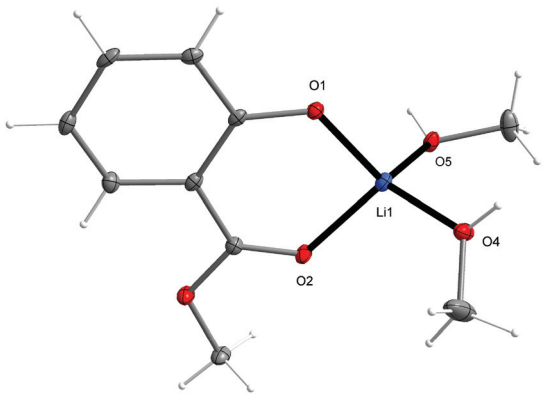


Fig. 3 Molecular structure of $[Li(MesalO)(MeOH)_2]$ (**3**). Displacement ellipsoids are drawn at 30% probability level.

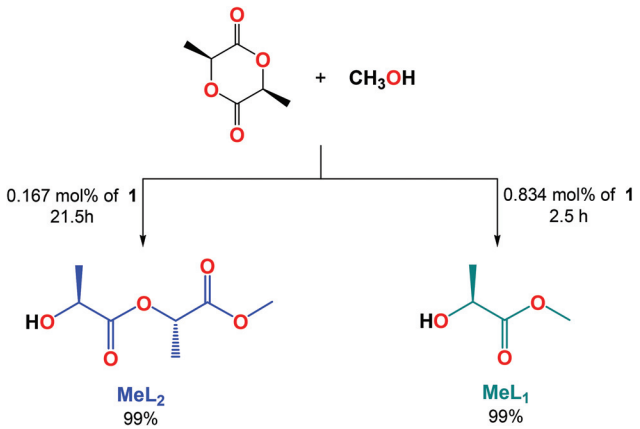
MeOH molecules; this is crucial for the formation of non-aggregated lithium species. CShM analysis showed a large departure from an ideal tetrahedron for the coordination environment around Li1 in **2**, as confirmed by the shape parameters, *i.e.*, S(T-4) = 3.121 for **2** and 0.784 for **3**. This is also clearly reflected in the O–Li–O bond angles, which range from 90.75(18)° to 126.89(19)° for **2** and from 93.97(14)° to 115.41(19)° for **3**. The Li–O distances, *i.e.*, 1.887(3)–1.949(4) Å, are typical and are in good agreement with previously reported values for lithium aryloxides.[40,41]

In the field of structural chemistry, the presence of monomeric tetracoordinated lithium centers surrounded by four oxygen donors is typical of ionic compounds such as *t*-butanol solvates of lithium halides, *i.e.*, $[Li(^tBuOH)_4]X$ (X = Cl, Br, and I).[42] It is worth noting that formation of solvated mononuclear lithium aryloxides $[Li(OAr)(solv)_x]$ is relatively limited. They have often been proposed as catalysts or reagents but well-defined examples of such compounds are rare. The only examples of monomeric lithium aryloxides are those obtained when bulky phenolato,[43,44] biphenolato,[45] bis- and tris-phenolato,[46,47] or calixarene[48] ligands have been used in the presence of strong N/O-donor solvents such as THF, Et_2O, acetone, tetramethylethylenediamine and pentamethyldiethylenetriamine. Several mononuclear lithium compounds supported by aminophenolate[49,50] or aminobisphenolate[51] ligands have been reported.

Compounds **1–3** were characterized by ^1H, ^{13}C, and ^7Li NMR, and FTIR-ATR spectroscopies, and elemental analysis (ESI, Fig. S1–S26†). The ^1H NMR spectrum of **1** shows only one set of signals at 7.70–6.24 and 3.76 ppm, arising from the aromatic and methyl protons of MesalO ligands (ESI, Fig. S3†). The ^7Li NMR spectrum of **1** exhibits one sharp singlet at δ_{Li} 1.29 ppm indicating the presence of one-equivalent environments for the lithium atoms (ESI, Fig. S5†). These NMR observations suggested that compound **1** had a C_3 symmetry, consistent with the XRD structure. The performed variable concentration ^1H and ^7Li NMR study did not provide any additional information (ESI, Fig. S12 and S13†). When VT ^1H NMR study was performed for **1**, at −80 °C the split of reso-

nances of protons of MesalO ligands for two set of signals at 7.15/7.08, 6.97/6.45, 6.26/6.16 and 3.82/3.77 with 1 : 1 ratio was observed (ESI, Fig. S18†). The ^{7}Li NMR spectrum of **1** at −80 °C also showed two main peaks at 2.13 and 1.53 ppm (ESI, Fig. S19†). The VT ^{1}H and ^{7}Li NMR spectra of **2** and **3** did not show any significant differences in the resonances of MesalO ligand or lithium ion, suggesting the presence of only one equivalent species in solution (ESI, Fig. S20–S23†).

Finally, the diffusion-ordered ^{1}H NMR spectroscopy (DOSY) was used to estimate the formula weight (FW) of the species present in solution, by use of known internal references and correlate their molecular weights with relative diffusion coefficients (D) through the linear regression plot of the logarithms of D against the FWs of the references. The DOSY ^{1}H NMR spectrum of **1** revealed the retention of hexanuclear solid-state structure in THF-d_8 solution (ESI, Fig. S27†). The estimated molecular weights of 961 g mol^{-1} for **1** was practically identical with the value of 948.5 g mol^{-1} calculated from the molecular formula (ESI, Fig. S28 and Table S2†). The calculated molecular weights of 301 g mol^{-1} for **2** correspond to its solid-state structure, and confirmed the presence of mononuclear species in solution (ESI, Fig. S29 and S30, Table S2†). The DOSY ^{1}H NMR analysis of **3** revealed that in THF-d_8 solution at room temperature lithium ion lost coordinated MeOH molecules, and hexanuclear cluster **1** and free MeOH were generated, as verified by the presence of two different D coefficients equal to 27.2 × 10^{-10} m^2 s^{-1} for free MeOH and 8.83 × 10^{-10} m^2 s^{-1} for **1** (ESI, Fig. S31 and S32, Table S2†). However VT ^{1}H and ^{7}Li NMR spectra of **3** at temperature below −80 did not show characteristic resonances pattern observed for **1**. When DOSY ^{1}H NMR spectrum of **3** was recorded in methanol-d_4 also the presence of signals associated with hexanuclear compound **1** was observed (ESI, Fig. S33 and S34, Table S2†).

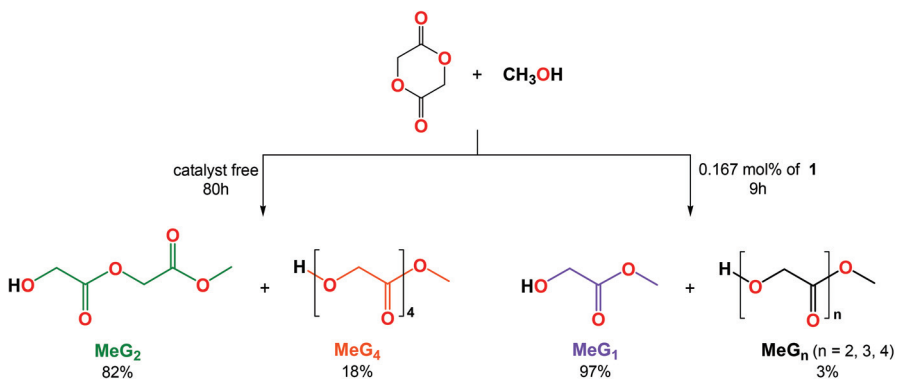


Scheme 3 Catalytic switching of L-LA alcoholysis reaction.

Synthesis of α-hydroxy acid esters

Alcoholysis reactions of heterocyclic esters, namely L-LA and GA, were investigated for the synthesis of various lactyl and glycolyl derivatives (Schemes 3 and 4). Typical reactions were performed in MeOH solution at room temperature using 25 equiv. of alcohol per equivalent of lactone. For both diesters, we first conducted control experiments in the absence of a catalyst source. ^{1}H NMR spectroscopic monitoring of L-LA alcoholysis over time showed that after 94 h, 84% conversion of L-LA to methyl (*S*,*S*)-*O*-lactyllactate (**MeL$_2$**) had been achieved. The ^{1}H NMR spectra show characteristic resonance signals at 4.98, 4.16, 1.41, and 1.12 ppm from the methine and methyl protons of **MeL$_2$**, and the resonances for the methyl ester and hydroxyl groups at 3.20 and 2.47 ppm (Fig. 4, and ESI Fig. S35 and S36†). Electro-spray ionization mass spectrometry (ESI-MS) studies confirmed the presence in the reaction mixtures of lactic acid oligomers separated by increments of 72 Da, with methyl ester end-groups (Fig. 5). Graphical analysis of these results (ESI, Fig. S37a†) showed that 98% conversion was achieved after 241 h. When the reaction was continued for another 122 h, a slight increase in L-LA conversion to **MeL$_2$** was observed and no other lactate derivatives were detected (ESI, Table S3†).

This suggests that under catalyst-free conditions MeOH reacts with L-LA to give only the ring-opened product **MeL$_2$**. An alternative method was reported by Claborn, who synthesized alkyl lactyllactates (AL$_2$) from crude LA, anhydrous alcohols, aromatic solvents, and acid catalysts at 70–90 °C and reaction times of 6–8 h.[52,53] Formation of AL$_2$ as one of the main pro-



Scheme 4 Proposed courses of GA alcoholysis performed under catalyst-free conditions and with catalytic amount of **1**.

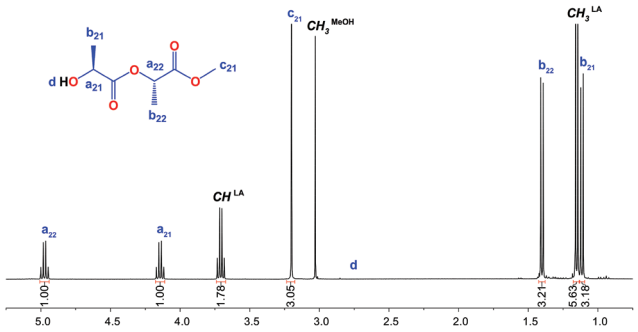


Fig. 4 ^{1}H NMR spectrum in C_6D_6 of products of L-LA alcoholysis reaction performed under catalyst-free conditions.

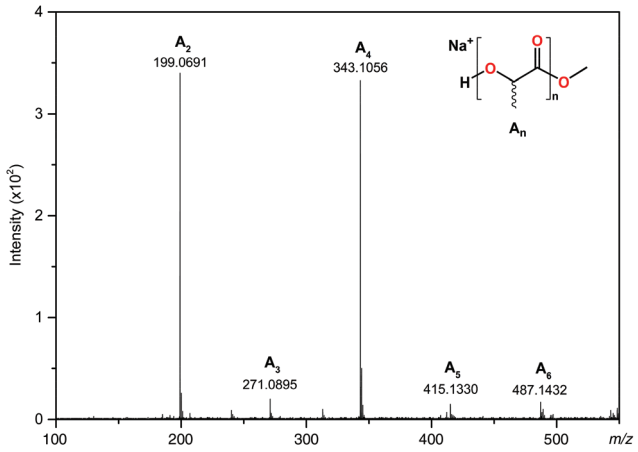


Fig. 5 ESI mass spectrum of sodium-cationized methyl oligolactates formed during L-LA alcoholysis under catalyst-free conditions.

ducts, in yields of up to *ca.* 40%, has also been observed during solvothermal alcoholysis of poly(lactic acid).[54] Once we had identified a suitable system for the alcoholysis of L-LA to **MeL$_2$**, we investigated the use of **1** as a catalyst to achieve high product yields in short periods of time. However when we carefully investigated the synthesis of **1** *in situ* by the reaction of MesalOH with ^{n}BuLi (1 : 1) the formation of several species in solution was observed. Therefore, we used compound **3** as catalyst precursor because of its easy synthesis in crystalline form and generation of **1** in pure form in solution. An L-LA alcoholysis study performed at a reactant stoichiometry of L-LA/MeOH/Li = 1/25/0.01 showed that in the first 22 h only selective formation of **MeL$_2$** occurred (ESI, Table S4†). The results (ESI, Fig. S37b†) show that L-LA conversion greater than 90% was achieved after 14.5 h. We did not observe the formation of any other products, even when the reaction time was extended to 242 h (ESI, Fig. S38†).

A comparison of these results with those for catalyst-free reactions shows that the use of 0.167 mol% of **1** enabled 99% conversion to be achieved 16 times faster (ESI, Fig. S37†). The obtained results are consistent with those previously reported by Phomphrai and colleagues for the alcoholysis of cyclic esters mediated by group 1 metal alkoxides synthesized *in situ* from metal bis(trimethylsilyl)amides.[55] They observed that the final conversions of L-LA to **MeL$_2$** after 60 min at room temperature were 48%, 60%, and 84% for $MN(SiMe_3)_2$, where M = Li, Na, and K, respectively. However, the reactions stopped after 10 to 30 min because of the formation of metal alkoxide aggregates of the type $[M(OR)]_n$, and increasing the reaction time did not increase the L-LA conversion. When we increased the amount of **1** in the reaction system five-fold, complete conversion of L-LA to a mixture of methyl (*S*)-lactate (**MeL$_1$**) (90%) and **MeL$_2$** (10%) was achieved in 0.25 h. After 2.5 h the amount of synthesized **MeL$_1$** increased to 99%. The ^{1}H NMR spectrum of **MeL$_1$** in Fig. 6 shows resonance signals from the methine and methyl protons of the lactate unit at 4.03 and 1.21 ppm, and from the methyl ester and hydroxyl groups at 3.20 and 2.47 ppm. The increased amount of catalyst enables the methanolysis reaction to switch toward the synthesis of **MeL$_1$** as the main product, as shown in Scheme 3 (ESI, Fig. S39 and S40†). This reaction step is similar to those previously reported by us in the magnesium aminophenolate-mediated transesterification of AL_2 to AL, which occurs after complete conversion of L-LA.[56] This is the first time that controlled switching of the reaction course toward the synthesis of **MeL$_2$** or **MeL$_1$** caused by changing the amount of catalyst has been observed.

When we examined GA alcoholysis in the absence of a catalyst, a mixture of methyl glycolylglycolate (**MeG$_2$**) and methyl tris(glycolyl)glycolate (**MeG$_4$**) was obtained (ESI, Table S3†).

For example, after 80 h, the GA conversions to **MeG$_2$**/**MeG$_4$** were 82%/18% and these values did not change when the reaction time was extended to 200 or even 556 h. ^{1}H NMR spectroscopic analysis of the obtained products showed six different methylene peaks, at 4.19 and 3.93 ppm, from **MeG$_2$**, and at 4.32, 4.31, 4.16, and 3.90 ppm, from **MeG$_4$**, as shown in Fig. 7. ESI-MS showed the presence of glycolic acid oligomers terminated by methyl ester end-groups, separated by a mass of

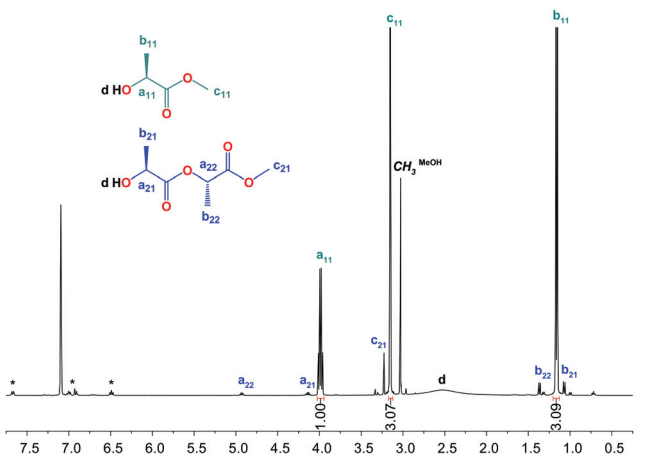


Fig. 6 ^{1}H NMR spectrum in C_6D_6 of products of L-LA alcoholysis performed in presence of 0.834 mol% of **1**. *Assigned signals from aromatic protons of **1**.

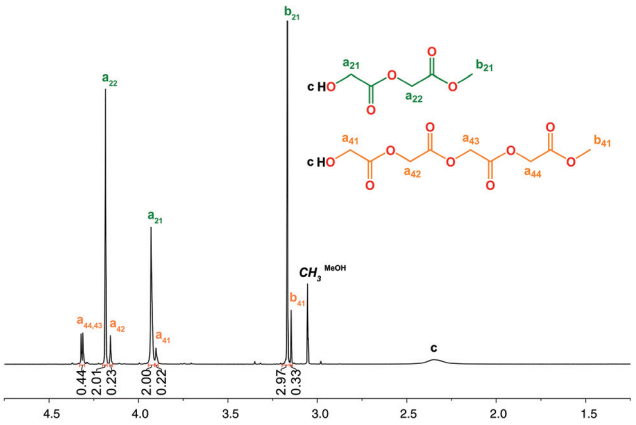


Fig. 7 ^{1}H NMR spectrum in C_6D_6 of products of GA alcoholysis performed under catalyst-free conditions.

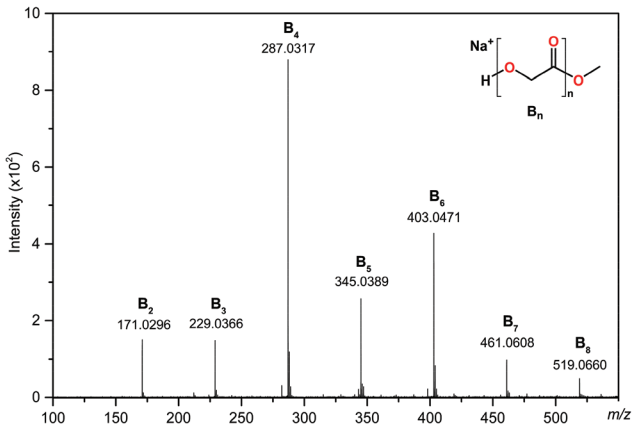


Fig. 8 ESI mass spectrum of sodium-cationized methyl oligoglycolates formed during GA alcoholysis under catalyst-free conditions.

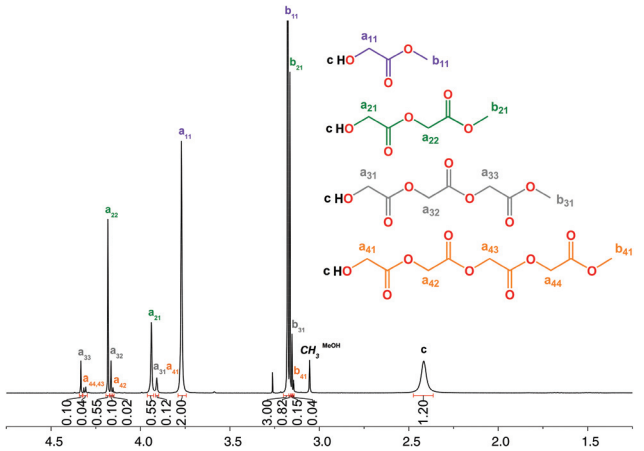


Fig. 9 ^{1}H NMR spectrum in C_6D_6 of products of GA alcoholysis performed in presence of **1**.

58 Da. The most intensive peak, with a value of 287.0317, corresponds to an adduct of **MeG$_4$** with sodium ions, *i.e.*, Na $\{H[O(CH_2)CO]_4OCH_3\}^+$ (Fig. 8).

These results show that under similar conditions GA alcoholysis to **MeG$_2$** is faster than L-LA alcoholysis to **MeL$_2$** (ESI, Fig. S37a and S41a†). The GA conversion reached 47% after 9 h, whereas 54% conversion of L-LA was achieved after 53 h. The main difference between the reactions is that L-LA was selectively ring opened to give only **MeL$_2$**, whereas GA methanolysis led to a mixture of **MeG$_2$** and **MeG$_4$** esters. The **MeG$_4$** ester was formed by the reaction of GA with **MeG$_2$**, which proceeds as long as GA is present in the reaction mixture. When this reaction ends, neither MeOH nor **MeG$_2$** can attack the linear **MeG$_4$**, as shown by its constant presence in the reaction mixture over a wide time period, *i.e.*, from 39 to 556 h.

When the same reaction was performed with compound **1**, with a stoichiometry of GA/MeOH/Li = 1/25/0.01, methyl glycolate (**MeG$_1$**) and several oligoglycolate esters, including **MeG$_2$**, **MeG$_3$** and **MeG$_4$**, were formed, as shown in Scheme 4 and Fig. 9 (ESI, Table S4†). After 10 min, GA conversion was complete, with formation of 48% **MeG$_1$**, 35% **MeG$_2$**, 13% **MeG$_3$**, and 4% **MeG$_4$**. These results (ESI, Fig. S41b†) show that as the reaction progressed, the amount of **MeG$_n$** (n = 2–4) esters decreased, with simultaneous increases in the amount of the final product **MeG$_1$** (ESI, Fig. S42†). In this reaction, compound **1** acts as a catalyst in ring opening of GA through alcoholysis and actively participates in the transesterification of methyl oligoglycolate esters to **MeG$_1$** (ESI, Fig. S42 and S43†). We also found that during the investigated reaction, the slowest step was the transformation of **MeG$_2$** to **MeG$_1$**; for example, after 1 h, the GA conversions to **MeG$_1$**/**MeG$_2$** were 69%/28%, after 4 h they were 85%/12%, and after 9 h the values were 97%/2%. This synthesis of **MeG$_3$** is analogous to that previously described for **MeG$_4$**, and is achieved by alcoholysis of GA by **MeG$_1$**. When we increased the amount of **1** in the reaction system two-fold, conversion of GA to a mixture of **MeG$_1$**/**MeG$_2$** reached 81%/17% after 5 min, 97%/2% after 10 min and 98%/1% after 15 min.

The main difference between the alcoholysis reactions of the two studied cyclic esters in the presence of 0.167 mol% of **1** is that L-LA is selectively ring opened to give only **MeL$_2$**, whereas for GA, after ring opening, **MeG$_2$** reacts with MeOH to give **MeG$_1$**. Both **MeG$_2$** and **MeG$_1$** participate actively in ring opening of GA, which leads to formation of **MeG$_3$** and **MeG$_4$**.

Conclusion

In this study, we demonstrated the synthesis of well-defined, monomeric in solid state lithium aryloxides, *i.e.*, [Li(MesalO)(MesalOH)] (**2**) and [Li(MesalO)(MeOH)$_2$] (**3**), by reaction of the hexanuclear precursor [Li$_6$(MesalO)$_6$] (**1**) with MesalOH or MeOH. We revealed the retention of solid-state structures of **1** and **2** in THF-d$_8$ solution. We showed that mononuclear in solid state compound **3** in THF-d$_8$ or methanol-d$_4$ solution undergoes transformation into **1** and free MeOH. We showed that compound **1** generated from **3** is an effective catalyst for

the alcoholysis of L-LA and GA. We established that during methanolysis in the presence of 0.167 mol% of **1**, L-LA was selectively ring opened to give only methyl (*S*,*S*)-*O*-lactyllactate (**MeL$_2$**), whereas GA was converted to the methyl glycolate (**MeG$_1$**) and oligoglycolate esters **MeG$_n$** (n = 2, 3, and 4). A five-fold increase in the amount of catalyst in the L-LA alcoholysis switched the reaction course toward the synthesis of methyl (*S*)-lactate (**MeL$_1$**) as the main product. In the absence of a catalyst source, L-LA was transformed to **MeL$_2$**, whereas GA was converted to a mixture of **MeG$_2$** and **MeG$_4$** esters. This is the first time that this has been observed.

We believe that the current results represent an important advance in the synthesis of new alkyl lactate and glycolate derivatives *via* cyclic ester alcoholysis mediated by metal alkoxides/aryloxides. Our study will be helpful in the design of new efficient catalysts for the selective transformation of lactones or hydroxy acid oligomers to alkyl α-hydroxy acid esters for industrial applications.

Experimental section

Materials and methods

All syntheses were performed under a dry nitrogen atmosphere, using standard Schlenk techniques. Reagents were purified by standard methods: toluene, hexane, tetrahydrofuran were distilled over Na; CH_2Cl_2 was distilled over P_2O_5, CH_3OH was distilled over Mg. L-Lactide and glycolide were three times recrystallized from toluene and kept under P_2O_5. All chemical reagents were purchased from commercial sources: THF-d_8, methyl salicylate, L-lactide, glycolide and ^{n}BuLi solution 1.6 M in hexanes (Aldrich, St Louis, MO, USA), toluene, hexane, THF, THF-d_8, CH_2Cl_2, CH_3OH, CD_3OD and C_2H_5OH (Carl Roth). ^{1}H and ^{13}C NMR spectra were recorded at room temperature using Bruker Avance 600 MHz and Jeol JNM-ECZ 400 MHz spectrometers. Chemical shifts are reported in ppm and referenced to the residual protons in deuterated solvents. The ^{7}Li spectra were referenced to a 0.1 M solution of $LiNO_3$ in D_2O. Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra were recorded on a Bruker Vertex 70 Vacuum spectrometer. Elemental analysis was performed with a PerkinElmer 2400 CHN elemental analyzer.

Characterization of ligand precursor methyl salicylate (MesalOH)

^{1}H NMR (THF-d_8, 600 MHz): δ 10.72 (s, 1H, OH), 7.81 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 7.45 (ddd, J = 8.5, 7.4, 1.6 Hz, 1H, ArH), 6.93 (dd, J = 8.5, 1.2 Hz, 1H, ArH), 6.86 (ddd, J = 8.0, 7.4, 1.2, 1H, ArH), 3.92 (s, 3H, CH_3). ^{13}C NMR (THF-d_8, 151 MHz) δ 171.2 (1C, C═O), 162.7 (1C, C–OH), 136.3 (1C, ArH), 130.4 (1C, ArH), 119.6 (1C, ArH), 118.1 (1C, ArH), 113.1 (1C, Ar), 52.4 (1C, CH_3). FTIR-ATR (cm^{-1}): 3186 (m), 2955 (w), 2901 (vw), 2854 (vw), 2049 (vw), 1937 (vw), 1674 (vs), 1614 (s), 1585 (m), 1485 (s), 1465 (m), 1439 (s), 1404 (w), 1327 (s), 1302 (vs), 1251 (s), 1211 (vs), 1194 (s), 1156 (vs), 1133 (s), 1089 (vs), 1032 (m), 962 (m), 865 (w), 848 (s), 800 (m), 754 (vs), 721 (s), 699 (vs), 665 (s), 562 (m), 529 (s), 511 (m), 438 (m).

Synthesis of [Li$_6$(MesalO)$_6$] (1)

LiBu (5 mL, 8 mmol) was added dropwise to a solution of MesalOH (1.04 mL, 8 mmol) in 20 mL toluene. The mixture was stirred at room temperature for 2 h. Then, the volume was reduced to 10 mL and the white precipitate was filtered off, washed with hexane (3 × 10 mL), and dried under vacuum. Single crystals of **1** for XRD analysis were obtained as a result of recrystallization from CH_2Cl_2 during the two-month crystallization period. The crystals were filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield 0.81 g (64%). Anal. calcd for $C_{48}H_{42}O_{18}Li_6$: C, 60.78; H, 4.46. Found: C, 60.82; H, 4.49. ^{1}H NMR (THF-d_8, 600 MHz): δ 7.70 (dd, J = 8.0, 1.9 Hz, 6H, ArH), 7.09 (ddd, J = 8.7, 6.8, 1.9 Hz, 6H, ArH), 6.67 (dd, J = 8.7, 1.1 Hz, 6H, ArH), 6.24 (ddd, J = 8.0, 6.8, 1.1 Hz, 6H, ArH), 3.76 (s, 18H, CH_3). ^{13}C NMR (THF-d_8, 151 MHz) δ 173.6 (6C, C═O), 171.0 (6C, C–OLi), 134.7 (6C, ArH), 131.9 (6C, ArH), 124.5 (6C, ArH), 115.1 (6C, ArH), 111.7 (6C, Ar), 51.1 (6C, CH_3). ^{7}Li NMR (THF-d_8, 155 MHz): δ 1.29. FTIR-ATR (cm^{-1}): 3352 (vw), 3018 (vw), 2949 (w), 2870 (w), 2653 (vw), 2323 (vw), 2194 (vw), 2162 (vw), 2050 (vw), 1981 (vw), 1917 (vw), 1681 (vs), 1601 (m), 1547 (s), 1508 (vw), 1473 (s), 1446 (s), 1437 (s), 1379 (vw), 1335 (s), 1319 (s), 1266 (m), 1226 (vs), 1194 (s), 1162 (m), 1146 (m), 1085 (s), 1043 (m), 989 (vw), 964 (w), 933 (vw), 884 (vw), 860 (s), 819 (m), 797 (w), 760 (vs), 708 (s), 661 (m), 589 (s), 541 (w), 519 (m), 472 (m), 436 (m), 405 (w).

Synthesis of [Li(MesalO)(MesalOH)] (2)

LiBu (5 mL, 8 mmol) was added dropwise to a solution of MesalOH (2.08 mL, 16 mmol) in 20 mL toluene. The mixture was stirred at room temperature for 6 h. Then, the volume was reduced to 5 mL and the colorless oil was precipitated with hexane (10 mL), and then filtered of, washed with hexane (3 × 10 mL), and dried under vacuum. Single crystals of **2** for XRD analysis were obtained as a result of recrystallization from THF during the one week crystallization period. The crystals were filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield 1.41 g (57%). Anal. calcd for $C_{16}H_{15}O_6Li$: C, 61.95; H, 4.81. Found: C, 62.02; H, 4.89. Compound **2** were also easily synthesized by recrystallization of **1** from MesalOH solution. ^{1}H NMR (THF-d_8, 600 MHz): δ 10.70 (s, 1H, OH), 7.77 (dd, J = 8.0, 1.8 Hz, 2H, ArH), 7.32 (ddd, J = 8.7, 7.1, 1.8 Hz, 2H, ArH), 6.81 (dd, J = 8.7, 1.0 Hz, 1H, ArH), 6.63 (m, 2H, ArH), 3.86 (s, 6H, CH_3). ^{13}C NMR (THF-d_8, 151 MHz): δ 171.3 (2C, C═O), 166.7 (2C, C–OLi), 135.9 (2C, ArH), 131.1 (2C, ArH), 120.5 (2C, ArH), 117.0 (2C, ArH), 113.9 (2C, ArH), 52.1 (2C, CH_3). ^{7}Li NMR (THF-d_8, 155 MHz): δ 1.31. FTIR-ATR (cm^{-1}): 3334 (m), 3037 (vw), 2996 (vw), 2954 (m), 2937 (m), 2870 (w), 2715 (vw), 2655 (vw), 2165 (vw), 2054 (vw), 1925 (vw), 1825 (vw), 1674 (vs), 1624 (m), 1590 (m), 1558 (w), 1505 (vw), 1483 (w), 1466 (m), 1454 (m), 1436 (s), 1376 (w), 1314 (s), 1250 (s), 1190 (m), 1143 (w), 1119 (vw), 1088 (m), 1037 (w), 967 (w), 954 (vw), 884 (w), 855 (w), 823 (w), 772 (m), 751 (m), 706 (m), 659 (m), 641 (w), 616 (vw), 575 (m), 549 (w), 533 (m), 470 (w), 450 (m), 428 (m).

Synthesis of [Li(MesalO)(MeOH)$_2$] (3)

LiBu (5 mL, 8 mmol) was added dropwise to a solution of MesalOH (2.08 mL, 16 mmol) in 20 mL toluene/methanol mixture (1 : 1). The mixture was stirred at room temperature for 5 h. Then, the volume was reduced to 10 mL and the colorless crystals were obtained from concentrated mother liquor. The crystals were filtered off, washed with hexane (3 × 5 mL), and dried under vacuum. Yield 1.08 g (61%). Anal. calcd for $C_{10}H_{15}O_5Li$: C, 54.06; H, 6.81. Found: C, 54.11; H, 6.84. Compound **3** can be also easily synthesized by recrystallization of **1** from MeOH. ^{1}H NMR (THF-d$_8$, 600 MHz): δ 7.68 (dd, J = 8.1, 1.9 Hz, 1H, ArH), 7.08 (ddd, J = 8.7, 6.8, 2.0 Hz, 1H, ArH), 6.65 (dd, J = 8.7, 1.1 Hz, 1H, ArH), 6.22 (m, 1H, ArH), 3.96 (s, 2H, OH^{MeOH}), 3.74 (s, 3H, CH_3), 3.28 (s, 6H, CH_3^{MeOH}). ^{13}C NMR (THF-d$_8$, 151 MHz) δ 173.6 (1C, C═O), 171.0 (1C, C–OLi), 134.7 (1C, ArH), 131.9 (1C, ArH), 124.5 (1C, ArH), 115.1 (1C, ArH), 111.7 (1C, Ar), 51.1 (1C, CH_3), 49.6 (2C, CH_3^{MeOH}). ^{7}Li NMR (THF-d$_8$, 155 MHz): δ 1.57. FTIR-ATR (cm^{-1}): 3141 (m), 2954 (m), 2935 (m), 2851 (m), 2821 (m), 2652 (vw), 2603 (vw), 2565 (vw), 2323 (vw), 2194 (vw), 2166 (vw), 2050 (vw), 1978 (vw), 1917 (vw), 1825 (vw), 1783 (vw), 1744 (vw), 1672 (vs), 1598 (m), 1545 (m), 1466 (s), 1445 (s), 1437 (s), 1326 (s), 1261 (m), 1223 (vs), 1199 (s), 1153 (s), 1140 (m), 1121 (w), 1084 (m), 1037 (s), 1025 (s), 966 (w), 861 (m), 818 (w), 802 (vw), 761 (s), 711 (s), 660 (w), 584 (m), 556 (w), 544 (vw), 485 (m), 447 (m), 434 (m), 415 (w).

Cyclic esters alcoholysis procedure

The typical alcoholysis procedure for synthesis of various alkyl lactate or glycolate derivatives was as follows. For the catalyst free reactions GA (1.22 g, 10.5 mmol) or L-LA (1.51 g, 10.5 mmol) was added to a 10.7 mL of MeOH at a stoichiometry of GA(L-LA)/MeOH = 1/25 (ESI, Table S2†). For GA and L-LA alcoholysis reaction in the presence of catalyst a solution of **3** (0.0233 g, 0.105 mmol) in MeOH (1 mL) was added to a solution of GA (1.22 g, 10.5 mmol) or L-LA (1.51 g, 10.5 mmol) in MeOH (9.7 mL) at a stoichiometry of GA(L-LA)/MeOH/Li = 1/25/0.01 (SI, Table S3†). The reaction mixture was stirred for the prescribed time. Next MeOH was removed under vacuum and the conversion yields of GA and L-LA were determined by ^{1}H NMR spectroscopy.

Methyl (*S*)-lactate (MeL$_1$)

^{1}H NMR (C_6D_6, 400 MHz): 4.03 (q, J = 6.9 Hz, 1H, CH), 3.21 (s, 3H, OCH_3), 2.45 (s, 1H, OH), 1.21 (d, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6, 101 MHz): δ 176.1 (1C, C═O), 66.8 (1C, CH), 51.7 (1C, OCH_3), 20.3 (1C, CH_3). FTIR-ATR (cm^{-1}): 3437 (m), 2986 (w), 2957 (w), 2892 (vw), 2850 (vw), 1732 (vs), 1452 (m), 1438 (m), 1372 (w), 1269 (m), 1214 (s), 1124 (vs), 1084 (m), 1046 (s), 978 (m), 917 (w), 842 (w), 757 (w), 678 (vw), 492 (vw).

Methyl (*S*,*S*)-*O*-lactyllactate (MeL$_2$)

^{1}H NMR (C_6D_6, 400 MHz): δ 4.98 (q, J = 7.1 Hz, 1H, CH), 4.16 (q, J = 6.9 Hz, 1H, CH), 3.20 (s, J = 1.1 Hz, 3H, OCH_3), 2.47 (s, 1H, OH), 1.41 (d, J = 6.9 Hz, 3H, CH_3), 1.12 (d, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (C_6D_6, 101 MHz): δ 175.3 (1C, C═O), 170.5 (1C, C═O), 69.3 (1C, CH), 66.9 (1C, CH), 51.8 (1C, OCH_3), 20.7 (1C, CH_3), 16.5 (1C, CH_3). MS-ESI found 199.0691, $C_7H_{12}O_5Na^+$ requires 199.0582. FTIR-ATR (cm^{-1}): 3472 (m), 2991 (w), 2957 (w), 2885 (w), 2850 (vw), 1739 (vs), 1451 (m), 1378 (w), 1356 (w), 1308 (w), 1274 (m), 1197 (s), 1122 (vs), 1095 (vs), 1046 (s), 977 (m), 937 (w), 902 (vw), 865 (w), 848 (w), 748 (w), 666 (vw), 449 (vw).

Methyl glycolate (MeG$_1$)

^{1}H NMR (C_6D_6, 400 MHz): δ 3.77 (s, 2H, CH_2), 3.18 (s, 3H, OCH_3), 2.42 (s, 1H, OH). ^{13}C NMR (C_6D_6, 101 MHz): δ 173.9 (1C, C═O), 60.5 (1C, CH_2), 51.4 (1C, OCH_3). FTIR-ATR (cm^{-1}): 3424 (m), 3005 (vw), 2957 (w), 2913 (vw), 2848 (vw), 1736 (vs), 1436 (m), 1376 (w), 1279 (m), 1212 (s), 1089 (vs), 977 (m), 888 (w), 847 (w), 697 (w), 576 (w), 449 (w), 410 (vw).

Methyl glycolylglycolate (MeG$_2$)

^{1}H NMR (C_6D_6, 400 MHz): δ 4.18 (s, 2H, CH_2), 3.94 (s, 2H, CH_2), 3.16 (s, 3H, OCH_3), 2.42 (s, 1H, OH). ^{13}C NMR (C_6D_6, 101 MHz): δ 172.7 (1C, C═O), 167.5 (1C, C═O), 60.6 (1C, CH_2), 60.4 (1C, CH_2), 51.6 (1C, OCH_3). MS-ESI found 171.0296, $C_5H_8O_5Na^+$ requires 171.0269. FTIR-ATR (cm^{-1}): 3484 (m), 3009 (vw), 2959 (w), 2857 (vw), 1740 (vs), 1440 (m), 1427 (m), 1384 (m), 1293 (w), 1171 (s), 1094 (s), 1047 (m), 1005 (m), 970 (m), 881 (w), 850 (w), 716 (w), 695 (w), 570 (w), 510 (vw), 444 (vw).

Methyl bis-(glycolyl)glycolate (MeG$_3$)

^{1}H NMR (C_6D_6, 400 MHz): δ 4.33 (s, 2H, CH_2), 4.16 (s, 2H, CH_2), 3.91 (s, 2H, CH_2), 3.15 (s, 3H, OCH_3), 2.42 (s, 1H, OH). MS-ESI found 229.0366, $C_7H_{10}O_7Na^+$ requires 229.0324.

Methyl tris-(glycolyl)glycolate (MeG$_4$)

^{1}H NMR (C_6D_6, 400 MHz): δ 4.32 (s, 2H, CH_2), 4.31 (s, 2H, CH_2), 4.15 (s, 2H, CH_2), 3.88 (s, 2H, CH_2), 3.14 (s, 3H, OCH_3), 2.42 (s, 1H, OH). MS-ESI found 287.0317, $C_9H_{12}O_9Na^+$ requires 287.0379.

Crystallography

XRD data were collected at 100 K using a KUMA KM4 CCD or Agilent SuperNova Dual, Atlas diffractometer.[57] The experimental details and the crystal data are given in Table S1.† The structures were solved by direct methods and refined by full-matrix least-squares on F^2, using the SHELXTL package.[58] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were positioned geometrically and added to the structure factor calculations, but were not refined. The molecular graphics were created using Diamond, version 3.1e.[59] Crystallographic data for the structural analyses reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC), numbers CCDC 1944070–1944072.†

Conflicts of interest

The authors declare no competing financial interests.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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