Electronic Supplementary Information

Metal-Free Transesterification Catalyzed by Tetramethylammonium Methyl Carbonate

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Appendix: $^1$H and $^{13}$C spectra.
1. General information.

$^1$H NMR spectra were measured on a JEOL ECS400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the $\delta$ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration, and assignment. $^{13}$C NMR spectra were measured on a JEOL ECS400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.00 ppm). $^{31}$P NMR spectra were measured on a JEOL ECS-400 (161 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the external standard ($\text{H}_3\text{PO}_4$ at 0 ppm). Optical rotations were measured on Rudolph Autopol IV digital polarimeter. The products were purified by column chromatography on silica gel (E. Merck Art. 9385; Kanto Chemical Co., Inc. 37560; Fuji Silysia Chemical LTD. Chromatorex-NH DM1020). High resolution mass spectral analyses were performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700 (FAB), JEOL JMS-T100GCV (EI), Bruker Daltonics micrOTOF-QII (ESI)). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. Melting points were measured on MPA100, Standard Research Systems. High performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-M20A and chiral column of Daicel CHIRALCEL, CHIRALPAK; AS-3 and OD-3. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO$_4$, and phosphomolybdic acid. $n$-Hexane, ethyl acetate, methyl acetate, dimethyl carbonate and were freshly distilled in prior to use. Anhydrous solvents, such as toluene, 2-propanol, methyl methacrylate (MMA), THF and DMF, were used as received commercially.

2. Preparation of phosphonium and ammonium salts.

$[\text{Me(}n\text{-octyl)}_3\text{P}]^+\text{[OCO}_2\text{Me}]^-$ (2a), $[\text{Me(}n\text{-octyl)}_3\text{N}]^+\text{[OCO}_2\text{Me}]^-$ (3a): These compounds were known and prepared by the reported procedure.$^{1,2}$ Prepared compounds (pale yellow liquids) were stored at room temperature in a sealed vial under an inert gas-atmosphere.

$[\text{Me}_2(\text{}n\text{-octyl})_2\text{N}]^+\text{[OCO}_2\text{Me}]^-$ (3b): A pale yellow solid. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 0.87 (t, $J = 6.9$ Hz, 6H), 1.19-1.34 (m, 20H), 1.58-1.66 (m, 4H), 2.97 (s, 6H), 3.15 (s, 3H), 3.19-3.23 (m, 4H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 13.8 (2C), 21.7 (2C), 22.1 (2C), 25.8 (2C), 28.5 (2C), 28.6 (2C), 31.2 (2C), 49.6 (2C), 50.7, 62.5 (2C), 155.7. IR (KBr) 3433, 2926, 2856, 1697, 1467, 1308, 1080 cm$^{-1}$. M.p. 66-74 °C.
[Me$_3$(n-octyl)N]$^+$[OCO$_2$Me]$^-$ (3c): A pale yellow solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 0.87 (t, $J = 6.4$ Hz, 3H), 1.21-1.34 (m, 10 H), 1.62-1.70 (m, 2H), 3.03 (s, 9H), 3.15 (s, 3H), 3.23-3.27 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 13.9, 22.1 (2C), 25.8, 28.6 (2C), 31.2, 50.9, 51.8 (3C), 65.0, 155.8. IR (KBr) 3411, 2926, 2857, 1654, 1481, 1301, 1080 cm$^{-1}$. M.p. 174-181 °C.

[Me$_4$N]$^+$[OCO$_2$Me]$^-$ (3d): To a solution of 10 wt. % tetramethylammonium hydroxide in methanol (2.7 mL, 2.5 mmol) was added dimethyl carbonate (2.1 mL, 25 mmol). The mixture was stirred under a nitrogen atmosphere at room temperature for 15 h. The volatiles were removed under reduced pressure to yield [Me$_4$N]$^+$[OCO$_2$Me]$^-$ quantitatively as a white solid. Obtained [Me$_4$N]$^+$[OCO$_2$Me]$^-$ was stored and handled in glovebox filled with argon. White solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 3.11 (s, 12H), 3.16 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 50.9, 54.3 (4C), 155.7. IR (KBr) 3432, 1654, 1488, 1447, 1403, 1312, 1083 cm$^{-1}$. M.p. 126-144 °C.

[Et$_4$N]$^+$[OCO$_2$Me]$^-$ (3e): Tetraethylammonium hydroxide in water (35 wt. %, 1.5 mL, 2.5 mmol) was fully concentrated, and then water was replaced by methanol (2 mL). Dimethyl carbonate (2.1 mL, 25 mmol) was added, and the mixture was stirred under a nitrogen atmosphere at room temperature for 15 h. The volatiles were removed under reduced pressure to yield [Et$_4$N]$^+$[OCO$_2$Me]$^-$ as a white solid quantitatively. Obtained [Et$_4$N]$^+$[OCO$_2$Me]$^-$ was stored and handled in glovebox filled with argon. White solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 1.13-1.17 (m, 12H), 3.15 (s, 3H), 3.20 (q, $J = 7.3$ Hz, 8H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 7.1 (4C), 50.9, 51.4 (4C), 155.7. IR (KBr) 3470, 2991, 1696, 1493, 1439, 1397, 1310, 1173, 1079 cm$^{-1}$. M.p. 210-215 °C.

[Me$_4$N]$^+$[OCO$_2$H]$^-$ (3f): A white solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 3.10 (s, 12 H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 54.4 (t, $J_{C-N} = 4.0$ Hz, 4C), 158.3. IR (KBr) 3019, 1655, 1488, 1404, 1008 cm$^{-1}$. M.p. 194-205 °C.

[Me$_4$N]$^+$[OH]$^-$ (3g) and [Me$_4$N]$^+$[Cl]$^-$ (3h): Commercially available.
3. General procedure for the La(NO₃)₃·H₂O–[Me(n-octyl)₃P][OCO₂Me]⁻ complex 1·2a₂-catalyzed transesterification in n-hexane.

A mixture of La(NO₃)₃·H₂O (1) (20.6 mg, 0.06 mmol) and methyltrioctylphosphonium methyl carbonate (2a) (55.3 mg, 0.12 mmol) in n-hexane (4 mL) was stirred at room temperature for 1–2 min. As soon as alcohol (2.0 mmol) was added, methyl ester (2.0 mmol) and 4,4′-di-tert-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added to the solution. The mixture was heated under azeotropic reflux conditions (bath temperature 90 °C). Methanol was removed through a Soxhlet extractor containing a cotton plug and activated 5Å molecular sieves (pellets, 1 g). After the azeotropic reflux for the indicated reaction time, the reaction mixture was allowed to cool to room temperature. To quench the catalyst, a drop of water was added, and the mixture was stirred for 5 min. The mixture was dried over MgSO₄, and the organic phase was concentrated under reduced pressure. The rough yield was determined by ¹H NMR analysis based on 4,4′-di-tert-butylbiphenyl as an internal standard, and the resultant residue was purified by silica gel column chromatography (eluent: n-hexane:EtOAc = 50:1 to 10:1) to give the desired product. The isolated yield was determined by the purified compound.

4. General procedure for the [R₄N][OCO₂Me]⁻ (3)-catalyzed transesterification in n-hexane.

To a solution of tetraalkylammonium methyl carbonate (3) (0.12 mmol) in n-hexane (4 mL), alcohol (2.0 mmol), methyl ester (2.0 mmol), and 4,4′-di-tert-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was heated under azeotropic reflux conditions (bath temperature 90 °C). Methanol was removed through a Soxhlet extractor containing a cotton plug and activated 5Å molecular sieves (pellets, 1 g). See Figure S1 for a typical reaction vessel in this transesterification. After the azeotropic reflux for the indicated reaction time, the reaction mixture was allowed to cool to room temperature. To remove the catalyst, the reaction mixture was filtered through flash silica pad using n-hexane–ethyl acetate (1:1) and the filtrate was
concentrated under reduced pressure. The rough yield was determined by \(^1\)H NMR analysis based on 4,4’-di-tert-butylibiphenyl as an internal standard, and the resultant residue was purified by silica gel column chromatography (eluent: \(n\)-hexane:EtOAc = 100:1 to 1:1) to give the desired product. The isolated yield was determined by the purified compound.

**General reaction conditions (solvent, boiling point, and bath temperature):**

- **n-Hexane** (4 mL), b.p. 69 °C, bath temperature 90 °C, azeotropic reflux with pellet MS 5Å.
- **Ethyl acetate** (4 mL), b.p. 77 °C, bath temperature 100 °C, azeotropic reflux with pellet MS 5Å.
- **Methyl acetate** (4 mL), b.p. 57 °C, bath temperature 70 °C, powdered MS 5Å in the flask.
- **Dimethyl carbonate** (4 mL), b.p. 67 °C, bath temperature 110 °C, azeotropic reflux with pellet MS 5Å.
- **Toluene** (4 mL), b.p. 110 °C, bath temperature 140 °C, azeotropic reflux with pellet MS 5Å.
- **2-Propanol** (4 mL), b.p. 82 °C, bath temperature 105 °C, azeotropic reflux with pellet MS 5Å.
- **THF** (4 mL), b.p. 66 °C, bath temperature 90 °C, azeotropic reflux with pellet MS 5Å.
- **Methyl methacrylate (MMA)** (4 mL), b.p. 110 °C, bath temperature 70 °C, powdered MS 5Å in the flask.
- **DMF** (4 mL), b.p. 153 °C, bath temperature 90 °C, powdered MS 5Å in the flask.

*Figure S1.* A typical reaction vessel in this transesterification.
5. Products in Table 1 and the related control experiments.

The generality of 3a-catalysis was briefly examined in comparison with our previous La(III) catalyst 1·2a2 in n-hexane (Scheme S1). As a result, chelating alcohols could be used and the corresponding esters 6b–d were obtained in high yields. Chelating esters also could be used (see 6e–g). In particular, the combination of chelating ester and chelating alcohol was tolerable, as seen in 6f. Sesamol, as a relatively nucleophilic phenol, could be used, although a reactive trifluoroethyl ester was used (see 6g).

Scheme S1. Transesterification with the use of ammonium salt catalyst 3a. The reaction was carried out under the standard conditions as seen in Table 1 unless otherwise noted. a Trifluoroethyl ester was used.

Benzyl 2-hydroxybenzoate (6a): Colorless oil. 1H NMR (400 MHz, CDCl3) δ 5.39 (s, 2H), 6.87 (t, J = 8.2 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 7.33-7.50 (m, 6H), 7.89 (d, J = 8.2 Hz, 1H), 10.75 (s, 1H). 13C NMR (100 MHz, CDCl3) δ 66.9, 112.3, 117.5, 119.1, 128.2 (2C), 128.5, 128.6 (2C), 129.9, 135.3, 135.7, 161.7, 169.9. IR (neat) 3188, 1674, 1485, 1299, 1250, 1213, 1157 cm⁻¹. HRMS (FAB+) calcd for C14H13O3 [M+H]+ 229.0859, found 229.0872.
2-(2-Ethoxyethoxy)ethyl benzoate (6b): Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.21 (t, $J = 6.9$ Hz, 3H), 3.53 (q, $J = 6.9$ Hz, 2H), 3.61 (m, 2H), 3.71 (m, 2H), 3.85 (m, 2H), 4.49 (m, 2H), 7.44 (t, $J = 8.3$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.2, 64.2, 66.8, 69.3, 69.9, 70.8, 128.4 (2C), 129.7 (2C), 130.2, 133.0, 166.6. IR (neat) 2870, 1719, 1275, 1110 cm$^{-1}$. HRMS (ESI+) calcd for C$_{13}$H$_{18}$NaO$_4$ [M+Na]$^+$ 261.1097, found 261.1095.

Pyridin-2-ylethyl benzoate (6c): Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.49 (s, 2H), 7.25 (dd, $J = 7.8$, 4.6 Hz, 1H), 7.42-7.48 (m, 3H), 7.59 (t, $J = 7.3$ Hz, 1H), 7.72 (td, $J = 7.8$, 1.8 Hz, 1H), 8.13 (d, $J = 4.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 67.3, 121.7, 122.9, 128.5 (2C), 129.8 (2C), 129.9, 133.3, 136.9, 149.6, 156.1, 166.3. IR (neat) 3064, 1722, 1594, 1451, 1276, 1113 cm$^{-1}$. HRMS (ESI+) calcd for C$_{13}$H$_{11}$NNaO$_2$ [M+Na]$^+$ 236.0682, found 236.0684.

Hexane-1,6-diyl dibenzoate (6d): White solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.49–1.57 (m, 2H), 1.77-1.85 (m, 4H), 4.34 (t, $J = 6.9$ Hz, 4H), 7.44 (t, $J = 7.8$ Hz, 4H), 7.56 (t, $J = 7.8$ Hz, 2H), 8.05 (d, $J = 7.8$ Hz, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 25.9 (2C), 28.7 (2C), 64.9 (2C), 128.4 (4C), 129.6 (4C), 130.4 (2C), 132.9 (2C), 166.7 (2C). IR (KBr) 3036, 1721, 1594, 1451, 1276, 1113 cm$^{-1}$. M.p. 53-55 °C. HRMS (ESI+) calcd for C$_{20}$H$_{22}$NaO$_4$ [M+Na]$^+$ 349.1410, found 349.1407.

Benzyl 1H-indole-2-carboxylate (6e): White solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 5.40 (s, 2H), 7.14 (t, $J = 6.9$ Hz 1H), 7.27-7.43 (m, 6H), 7.46 (d, $J = 6.4$ Hz, 2H), 7.68 (d, $J = 7.8$ Hz, 1H), 9.04 (brs, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 66.8, 109.3, 112.0, 120.9, 122.7, 125.6, 127.1, 127.5, 128.3 (2C), 128.5, 128.7 (2C), 135.8, 137.0, 161.9. IR (KBr) 3341, 1687, 1524, 1391, 1340, 1308, 1246, 1196 cm$^{-1}$. M.p. 136-137 °C. HRMS (ESI+) calcd for C$_{16}$H$_{13}$NNaO$_2$ [M+Na]$^+$ 274.0838, found 274.0835.
(Tetrahydrofuran-2-yl)methyl 2-hydroxybenzoate (6f): Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.73 (m, 1H), 1.89-2.02 (m, 2H), 2.08 (m, 1H), 3.84 (m, 1H), 3.94 (m, 1H), 4.23-4.34 (m, 2H), 4.41 (dd, $J = 11.0$, 3.2 Hz, 1H), 6.88 (t, $J = 8.2$ Hz, 1H), 6.98 (d, $J = 8.2$ Hz, 1H), 7.46 (t, $J = 8.2$ Hz, 1H), 7.88 (dd, $J = 8.2$, 1.8 Hz, 1H), 10.7 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 25.8, 28.1, 67.1, 68.6, 76.4, 112.4, 117.6, 119.2, 130.1, 135.8, 161.7, 170.1. IR (neat) 3187, 2976, 2873, 1676, 1614, 1486, 1301, 1251, 1215, 1159, 1083 cm$^{-1}$. HRMS (FAB+) calcd for C$_{12}$H$_{15}$O$_4$ [M+H]$^+$ 223.0970, found 223.0975.

Benzod[1,3]dioxol-5-yl picolinate (6g): Instead of methyl ester, trifluoroethyl ester was used as a starting material. Brown solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 6.02 (s, 2H), 6.71 (dd, $J = 8.3$, 2.3 Hz, 1H), 6.78 (d, $J = 2.3$ Hz, 1H), 6.83 (d, $J = 8.3$ Hz, 1H), 7.56 (ddd, $J = 7.8$, 4.6, 1.4 Hz, 1H), 7.92 (td, $J = 7.8$, 1.8 Hz, 1H), 8.27 (d, $J = 8.3$ Hz, 1H), 8.85 (d, $J = 4.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 101.8, 103.8, 108.1, 114.1, 125.9, 127.5, 137.2, 145.1, 145.6, 147.4, 148.1, 150.1, 164.2. IR (KBr) 1752, 1504, 1487, 1282, 1236, 1173, 1119, 1068 cm$^{-1}$. M.p. 72-73 °C. HRMS (FAB+) calcd for C$_{13}$H$_{10}$NO$_4$ [M+H]$^+$ 244.0610, found 244.0613.
6. Recovery and reuse of the catalyst in gram scale synthesis of 6b (Scheme 1).

A mixture of tetramethylammonium methyl carbonate (3) (9.0 mg, 0.060 mmol) in \( n \)-hexane (6 mL) was stirred at room temperature. (*) 2-(2-Ethoxyethoxy)ethanol (813 \( \mu \)L, 6.0 mmol), methyl benzoate (750 \( \mu \)L, 6.0 mmol), and 4,4’-di-tert-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added. The mixture was heated under azeotropic reflux conditions (bath temperature, 90 °C). Methanol was removed through a Soxhlet extractor containing a cotton plug and 5Å molecular sieves (pellets, 2 g). After the azeotropic reflux for 3 h, the reaction mixture was allowed to cool to 0 °C and stirred at that temperature for 5 min. After decantation of the insoluble and viscous catalyst at 0 °C (see Figure S2), clear supernatant involving a product 6b was separated by using a syringe, and the rough yield was determined by \(^1\)H NMR analysis based on the internal standard after partially sampling the solution and removal of volatiles. To the remaining residue involving the active catalyst, \( n \)-hexane (6 mL) was added for the next reaction. The procedure from (*) was repeated additional three times. The all separated solution was combined and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: \( n \)-hexane:EtOAc = 50:1 to 5:1) to give the desired product 6b (5.48 g, 96% yield).

![Figure S2. 3d-Derived viscous deposit in \( n \)-hexane at 0 °C](image)
7. Products in Table 2 and the related control experiments.

The catalytic performance of 3d (vs. 3a) was carefully examined for systematically-selected acyclic and cyclic alcohols in toluene (bp. 110 °C) under azeotropic reaction conditions (Scheme S2). As a result, 3a was still effective for sterically less-hindered alcohols. However, the yields of the corresponding bulkier products by 3a-catalysis gradually decreased, whereas 3d-catalysis continued to show high yields. Since the reactivity of sterically hindered alcohols would be inherently low, 3a-derived [Me(n-octyl)₃N][OR]⁺, rather than 3d-derived [Me₄N][OR], might readily decompose before the unlikely nucleophilic attack to ester 4b.

![Scheme S2](image)

**Scheme S2.** Transesterification of 4b with acyclic and cyclic alcohols with the use of 3d or 3a.

**Nonyl benzoate:** Colorless oil. $^1$H NMR (400 MHz, CDCl₃) δ 0.88 (t, $J = 6.2$ Hz, 3H), 1.20-1.50 (m, 12H), 1.76 (quintet, $J = 6.9$ Hz, 2H), 4.31 (t, $J = 6.9$ Hz, 2H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.55 (t, $J = 7.8$ Hz, 1H), 8.05 (d, $J = 7.6$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl₃) δ 14.2, 22.8, 26.1, 28.8, 29.3,
29.4, 29.6, 31.9, 65.2, 128.4 (2C), 129.6 (2C), 130.6, 132.9, 166.8. IR (neat) 2926, 2855, 1721, 1452, 1274, 1112 cm$^{-1}$. HRMS (EI) calcd for C$_{16}$H$_{24}$O$_2$ [M]$^+$ 248.1776, found 248.1776.

Nonan-2-yl benzoate:  
Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, $J$ = 6.9 Hz, 3H), 1.23-1.43 (m, 10H), 1.61 (m, 1H), 1.73 (m, 1H), 5.15 (sextet, $J$ = 6.4 Hz, 1H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.55 (t, $J$ = 7.6 Hz, 1H), 8.04 (d, $J$ = 7.8 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.2, 20.2, 22.7, 25.5, 29.3, 29.5, 31.9, 36.1, 71.8, 128.3 (2C), 129.6 (2C), 131.0, 132.7, 166.3. IR (neat) 2928, 2857, 1718, 1451, 1275, 1110 cm$^{-1}$. HRMS (EI) calcd for C$_{16}$H$_{24}$O$_2$ [M]$^+$ 248.1776, found 248.1779.

Nonan-3-yl benzoate:  
Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.86 (t, $J$ = 6.9 Hz, 3H), 0.95 (t, $J$ = 6.9 Hz, 3H), 1.20-1.45 (m, 8H), 1.63-1.74 (m, 2H), 1.70 (quintet, $J$ = 7.3 Hz, 2H), 5.08 (quintet, $J$ = 6.2 Hz, 1H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.55 (t, $J$ = 7.8 Hz, 1H), 8.06 (d, $J$ = 7.8 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 9.7, 14.1, 22.7, 25.4, 27.1, 29.3, 31.8, 33.8, 76.3, 128.3 (2C), 129.6 (2C), 130.9, 132.7, 166.5. IR (neat) 2930, 2858, 1718, 1451, 1275, 1109 cm$^{-1}$. HRMS (EI) calcd for C$_{16}$H$_{24}$O$_2$ [M]$^+$ 248.1776, found 248.1777.

Nonan-4-yl benzoate:  
Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87 (t, $J$ = 6.9 Hz, 3H), 0.93 (t, $J$ = 7.3 Hz, 3H), 1.25-1.50 (m, 8H), 1.55-1.75 (m, 4H), 5.15 (m, 1H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.55 (t, $J$ = 7.8 Hz, 1H), 8.05 (d, $J$ = 7.8 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 14.1, 18.7, 22.6, 25.1, 31.8, 34.3, 36.5, 74.9, 128.3 (2C), 129.6 (2C), 130.9, 132.7, 166.4. IR (neat) 2932, 2871, 1718, 1451, 1274, 1110 cm$^{-1}$. HRMS (FAB+) calcd for C$_{16}$H$_{25}$O$_2$ [M+H]$^+$ 249.1855, found 249.1859.

Nonan-5-yl benzoate (8):  
Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.88 (m, 6H), 1.33 (m, 8H), 1.66 (m, 4H), 5.13 (m, 1H), 7.43 (t, $J$ = 7.5 Hz, 2H), 7.54 (t, $J$ = 7.5 Hz, 1H), 8.05 (d, $J$ = 7.5 Hz,
\( ^{13} \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 13.9 \text{ (2C), 22.6 \text{ (2C), 27.4 \text{ (2C), 33.9 \text{ (2C), 75.0, 128.2 \text{ (2C), 129.5 \text{ (2C), 130.8, 132.6, 166.3. IR (neat) 2957, 2860, 1718, 1452, 1275, 1110 cm}^{-1}. HRMS (FAB+) calcd for C}_{16}H_{24}NaO_2 [M+Na]^+ 271.1674, found 271.1682.}

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\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Cyclopentyl benzoate:}^{14} \quad \text{Colorless oil. } \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 1.61-1.72 \text{ (m, 2H), 1.76-1.90 \text{ (m, 4H), 1.92-2.01 \text{ (m, 2H), 5.41 \text{ (m, 1H), 7.43 \text{ (t, } J = 7.8 \text{ Hz, 2H), 7.54 \text{ (t, } J = 7.8 \text{ Hz, 1H), 8.02 \text{ (d, } J = 7.8 \text{ Hz, 2H). } \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 23.9 \text{ (2C), 32.8 \text{ (2C), 77.7, 128.3 \text{ (2C), 129.5 \text{ (2C), 130.9, 132.7, 166.4. IR (neat) 2965, 1714, 1584, 1451, 1316, 1277, 1169, 1115, 1070,01026 cm}^{-1}. HRMS (ESI+) calcd for C}_{12}H_{14}NaO_2 [M+Na]^+ 213.0886, found 213.0891.}

\[
\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Cyclohexyl benzoate:}^{13} \quad \text{Colorless oil. } \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 1.00-2.10 \text{ (m, 10H), 5.03 \text{ (m, 1H), 7.40-7.48 \text{ (m, 2H), 7.52-7.60 \text{ (m, 1H), 8.02-8.08 \text{ (m, 2H). } \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 23.6 \text{ (2C), 25.4, 31.6 \text{ (2C), 73.0, 128.2 \text{ (2C), 129.4 \text{ (2C), 130.9, 132.6, 165.9. IR (neat) 2937, 2858, 1715, 1451, 1277, 1112, 1025 cm}^{-1}. HRMS (FAB+) calcd for C}_{13}H_{16}NaO_2 [M+Na]^+ 227.1048, found 227.1051.}

\[
\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Cycloheptyl benzoate:}^{15} \quad \text{Colorless oil. } \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 1.49-1.95 \text{ (m, 10H), 1.97-2.10 \text{ (m, 2H), 5.20 \text{ (m, 1H), 7.43 \text{ (t, } J = 7.8 \text{ Hz, 2H), 7.54 \text{ (t, } J = 7.8 \text{ Hz, 1H), 8.04 \text{ (d, } J = 7.8 \text{ Hz, 2H). } \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 23.0 \text{ (2C), 28.4 \text{ (2C), 33.9 \text{ (2C), 75.6, 128.3 \text{ (2C), 129.5 \text{ (2C), 131.1, 132.7, 166.0. IR (neat) 2929, 2859, 1714, 1451, 1275, 1114 cm}^{-1}. HRMS (FAB+) calcd for C}_{14}H_{18}NaO_2 [M+Na]^+ 241.1204, found 241.1209.}

\[
\text{Ph} \quad \text{O} \quad \text{O} \quad \text{Cyclooctyl benzoate:}^{16} \quad \text{Colorless oil. } \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 1.54-1.69 \text{ (m, 8H), 1.73-1.97 \text{ (m, 6H), 5.20 \text{ (m, 1H), 7.43 \text{ (t, } J = 7.8 \text{ Hz, 2H), 7.54 \text{ (t, } J = 7.8 \text{ Hz, 1H), 8.04 \text{ (d, } J = 7.8 \text{ Hz, 2H). } \text{C NMR (100 MHz, CDCl}_3 \text{)} \delta 23.0 \text{ (2C), 25.4, 27.2 \text{ (2C), 31.5 \text{ (2C), 75.7, 128.3 \text{ (2C), 129.6 \text{ (2C), 131.2,
132.7, 166.0. IR (neat) 2925, 2856, 1714, 1450, 1276, 1112 cm$^{-1}$. HRMS (FAB+) calcd for C$_{13}$H$_{20}$NaO$_2$ [M+Na]$^+$ 255.1361, found 255.1357.

![Cyclododecyl benzoate](image)

**Cyclododecyl benzoate:** $^{17}$ White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.26-1.46 (m, 18H), 1.59-1.74 (m, 2H), 1.79-1.88 (m, 2H), 5.26 (t, $J = 7.8$ Hz, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.8$ Hz, 1H), 8.04 (d, $J = 7.8$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.0 (2C), 23.3 (2C), 23.5 (2C), 24.1, 24.3 (2C), 29.2 (2C), 73.1, 128.4 (2C), 129.6 (2C), 131.1, 132.8, 166.4. IR (KBr) 2930, 2860, 1711, 1469, 1275, 1114 cm$^{-1}$. M.p. 42 °C. HRMS (FAB+) calcd for C$_{19}$H$_{28}$NaO$_2$ [M+Na]$^+$ 311.1987, found 311.1988.

8. **Products in Scheme 2.**

![Scheme 2](image)

**2-(Piperidin-4-yl)ethyl benzoate (10a):** $^{18}$ Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.20 (qd, $J = 12.4, 4.1$ Hz, 2H), 1.52-1.62 (m, 2H), 1.70-1.77 (m, 4H), 2.61 (td, $J = 12.4, 2.3$ Hz, 2H), 3.08 (d, $J = 11.9$ Hz, 2H), 4.38 (t, $J = 6.9$ Hz, 2H), 7.45 (t, $J = 7.3$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 8.04 (d, $J = 7.3$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 33.4, 33.5 (2C), 35.9, 46.7 (2C), 62.8, 128.4 (2C), 129.5 (2C), 130.4, 132.9, 166.6. IR (neat) 3413, 2922, 1715, 1602, 1451, 1315, 1276, 1114 cm$^{-1}$. HRMS (FAB+) calcd for C$_{14}$H$_{20}$NO$_2$ [M+H]$^+$ 234.1494, found 234.1497.

![Furan-2-carboxylate](image)

**2-(Phenylamino)ethyl furan-2-carboxylate (10b):** Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.53 (m, 2H), 3.99 (br, 1H), 4.52 (t, $J = 5.5$ Hz, 2H), 6.52 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.67 (dd, $J = 7.8, 0.9$ Hz, 2H), 6.74 (tt, $J = 7.3, 0.9$ Hz, 1H), 7.17-7.22 (m, 3H), 7.59 (dd, $J = 1.8, 0.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 42.9, 63.6, 111.9, 112.9 (2C), 117.9, 118.4, 129.3 (2C), 144.3, 146.5, 147.6, 158.7. IR (neat) 3403, 1721, 1604, 1509, 1474, 1297, 1180, 1119 cm$^{-1}$. HRMS (FAB+) calcd for C$_{13}$H$_{13}$NO$_3$ [M]$^+$ 231.0895, found 231.0891.
**Arecoline benzyl ester (10c):** Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.33-2.43 (m, 2H), 2.40 (s, 3H), 2.49 (t, $J = 5.5$ Hz, 2H), 3.17 (d, $J = 2.3$ Hz, 2H), 5.19 (s, 2H), 7.06 (m, 1H), 7.29-7.39 (m, 5H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 26.7, 45.8, 50.8, 53.2, 66.1, 128.0 (2C), 128.1, 128.5 (2C), 129.0, 136.1, 138.1, 165.6. IR (neat) 2941, 2786, 1710, 1654, 1456, 1398, 1289, 1264, 1142, 1091, 1027 cm$^{-1}$. HRMS (FAB+) calcd for C$_{14}$H$_{18}$NO$_2$ [M+H]$^+$ 232.1338, found 232.1336.

**TBSO**

(3R,3aR,6R,6aS)-6-((tert-Butyldimethylsilyl)oxy)hexahydrofuro[3,2-b]furan-3-yl 2-methoxy acetate (10d): Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.11 (s, 3H), 0.12 (s, 3H), 0.91 (s, 9H), 3.46 (s, 3H), 3.56 (t, $J = 8.3$ Hz, 1H), 3.85 (dd, $J = 8.3$, 6.4 Hz, 1H), 3.91 (dd, $J = 9.6$, 6.4 Hz, 1H), 4.00 (dd, $J = 9.6$, 6.4 Hz, 1H), 4.10 (s, 2H), 4.28 (m, 1H), 4.33 (t, $J = 5.0$ Hz, 1H), 4.69 (t, $J = 5.0$ Hz, 1H) 5.18 (q, $J = 6.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ –4.9, –4.7, 18.4, 25.9 (3C), 59.4, 69.5, 70.7, 72.4, 73.6, 74.5, 80.3, 81.8, 169.9. IR (neat) 2954, 2857, 1762, 1472, 1387, 1254, 1195, 1133, 1069, 1025 cm$^{-1}$. HRMS (FAB+) calcd for C$_{15}$H$_{28}$NaO$_6$Si [M+Na]$^+$ 355.1553, found 355.1550.

**MeO**

(2E,6E)-3,7,11-Trimethyldeca-2,6,10-trien-1-yl 6-methoxy-2,5,7,8-tetramethylchromane-2-carboxylate (10e): Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.59 (s, 1H), 1.68 (s, 3H), 1.85 (m, 1H), 1.95-2.08 (m, 8H), 2.08 (s, 3H), 2.15 (s, 3H), 2.18 (s, 3H), 2.39-2.52 (m, 2H), 2.60 (m, 1H), 3.61 (s, 3H), 4.56 (d, $J = 7.1$ Hz, 2H), 5.06-5.09 (m, 2H), 5.26 (t, $J = 7.1$, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 11.6, 11.8, 12.6, 16.0, 16.3, 17.7, 20.9, 25.4, 25.7, 26.2, 26.7, 30.5, 39.5, 39.7, 60.3, 61.8, 77.1, 117.2, 117.9, 122.9, 123.6, 124.3, 125.6, 127.9, 131.3, 135.4, 143.0, 147.8, 150.0, 173.7. IR (neat) 2928, 1751, 1730, 1456, 1404, 1375, 1286, 1254, 1195, 1168, 1139, 1104, 1015 cm$^{-1}$. HRMS (FAB+) calcd for C$_{30}$H$_{44}$O$_4$ [M]$^+$ 468.3240, found 468.3231.
Cholesterol-derived benzoyl ester (10f): White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.69 (s, 3H), 0.86 (d, $J$ = 6.3 Hz, 6H), 0.92 (d, $J$ = 6.3 Hz, 3H), 0.95-2.10 (m, 29H), 2.46 (d, $J$ = 8.1 Hz, 2H), 4.86 (m, 1H), 5.41 (d, $J$ = 4.5 Hz, 1H), 7.43 (t, $J$ = 6.9 Hz, 2H), 7.54 (t, $J$ = 6.9 Hz, 1H), 8.04 (d, $J$ = 6.9 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 11.8, 18.6, 19.3, 21.0, 22.5, 22.8, 23.8, 24.2, 27.8, 28.0, 28.2, 31.8, 31.9, 35.7, 36.1, 36.6, 37.0, 38.1, 39.4, 39.7, 42.2, 49.9, 56.0, 56.6, 74.5, 122.7, 128.2 (2C), 129.5 (2C), 130.7, 132.6, 139.6, 165.9. IR (KBr) 2943, 2864, 1713, 1273, 1113 cm$^{-1}$. M.p. 146-147 ºC (decomposition). HRMS (FAB+) calcd for C$_{34}$H$_{50}$NaO$_2$ [M+Na]$^+$ 513.3709, found 513.3703.

Benzyl diphenylphosphinate (10g): White solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.07 (d, $J$_{H-P} = 6.4 Hz, 2H), 7.29-7.38 (m, 5H), 7.42-7.48 (m, 4H), 7.50-7.55 (m, 2H), 7.81-7.86 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 66.3 (d, $J$_{C-P} = 5.7 Hz), 127.9 (2C), 128.3, 128.5 (2C), 128.6 (d, $J$_{C-P} = 13.3 Hz, 4C), 131.4 (d, $J$_{C-P} = 136.4 Hz, 2C), 131.8 (d, $J$_{C-P} = 9.5 Hz, 4C), 132.3 (d, $J$_{C-P} = 2.9 Hz, 2C), 136.4 (d, $J$_{C-P} = 7.6 Hz). $^{31}$P NMR (161 MHz, CDCl$_3$) $\delta$ 32.7. IR (KBr) 2884, 1591, 1497, 1484, 1459, 1440, 1384, 1314, 1209, 1130 cm$^{-1}$. M.p. 79 ºC. HRMS (FAB+) calcd for C$_{19}$H$_{18}$O$_2$P [M+H]$^+$ 309.1444, found 309.1057.

2',3'-O-(1-Methylethylidene)-adenosyl 5'-benzoate (10h): Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.43 (s, 3H), 1.64 (s, 3H), 4.48 (q, $J$ = 6.4 Hz, 1H), 4.59-4.67 (m, 2H), 5.18 (q, $J$ = 3.2 Hz, 1H), 5.49 (br, 2H), 5.59 (dd, $J$ = 6.2, 1.8 Hz, 1H), 6.11 (d, $J$ = 1.8 Hz, 1H), 7.38 (t, $J$ = 7.8 Hz, 2H), 7.54 (t, $J$ = 7.3 Hz, 1H), 7.89 (s, 1H), 7.91 (d, $J$ = 7.3 Hz, 2H), 8.33 (s, 1H). $^{13}$C NMR (100 MHz,
CDCl₃ δ 25.5, 27.2, 64.4, 81.7, 84.2, 85.1, 91.4, 114.7, 120.4, 128.4 (2C), 129.4, 129.6 (2C), 133.3, 139.6, 149.3, 153.2, 155.7, 166.1. IR (neat) 3322, 3168, 2988, 1720, 1645, 1599, 1475, 1375, 1273, 1209, 1092 cm⁻¹. HRMS (ESI+) calcd for C₂₀H₂₁N₅NaO₅ [M+Na]⁺ 434.1435, found 434.1424.

(S)-(1-Methylpyrrolidin-2-yl)methyl 1H-indole-2-carboxylate (10i): Pale yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 1.71-1.92 (m, 3H), 2.01 (m, 1H), 2.32 (dd, J = 9.6, 8.5, 2.3 Hz, 1H), 2.49 (s, 3H), 2.64 (m, 1H), 3.14 (t, J = 7.8 Hz, 1H), 4.32 (dd, J = 11.2, 5.0 Hz, 1H), 4.42 (dd, J = 11.0, 5.2 Hz, 1H), 7.15 (td, J = 7.8, 0.9 Hz, 1H), 7.25 (m, 1H), 7.32 (td, J = 8.3, 0.9, 1H), 7.43 (dd, J = 8.3, 0.9 Hz, 1H), 7.69 (dd, J = 7.8, 0.9 Hz, 1H), 9.53 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 22.8, 28.2, 41.4, 57.7, 66.3, 109.0, 112.1, 120.8, 122.6, 125.4, 127.3, 127.5, 137.1, 162.0. IR (neat) 3329, 2953, 2793, 1710, 1530, 1341, 1308, 1248, 1196, 1147 cm⁻¹. M.p. 83 °C. HRMS (FAB+) calcd for C₁₅H₁₉N₂O₂ [M+H]⁺ 259.1447, found 259.1443.

Trinonyl citrate (10j): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 0.86 (t, J = 6.9 Hz, 9H), 1.18-1.37 (brs, 36H), 1.57-1.67 (m, 6H), 2.79 (d, J = 15.6 Hz, 2H), 2.89 (d, J = 15.6 Hz, 2H), 4.07 (t, J = 6.9 Hz, 4H), 4.14 (s, 1H), 4.20 (t, J = 6.9 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 22.8 (3C), 25.8, 25.9 (2C), 28.4, 28.5 (2C), 29.3 (6C), 29.5 (3C), 31.9 (3C), 43.3 (2C), 65.2 (2C), 66.5, 73.2, 169.9 (2C), 173.5. IR (neat) 2925, 2855, 1741, 1467, 1343, 1190 cm⁻¹. HRMS (FAB+) calcd for C₃₃H₆₃O₇ [M+H]⁺ 571.4574, found 571.4568.

Quinidine-derived phenylpropanoate (10k): Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 1.39 (m, 1H), 1.59-1.68 (m, 2H), 1.70-1.81 (m, 2H), 2.25 (m, 1H), 2.66-3.01 (m, 8H), 3.25 (q, J = 7.3 Hz, 1H), 3.94 (s, 3H), 5.08 (d, J = 17.0 Hz, 1H), 5.12 (d, J = 9.6 Hz, 1H), 6.00 (ddd, J = 17.2, 10.3, 7.3 Hz, 1H), 6.51 (d, J = 6.0 Hz, 1H), 7.13-7.26 (m, 6H), 7.36 (d, J = 9.6 Hz, 1H), 7.37 (d, J = 7.3 Hz, 1H),
8.01 (d, J = 9.6 Hz, 1H), 8.67 (d, J = 4.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 23.4, 26.3, 27.8, 30.8, 36.0, 39.7, 49.2, 49.8, 55.6, 58.9, 73.6, 101.3, 114.9, 118.5, 121.9, 126.4, 127.0, 128.2 (2C), 128.6 (2C), 131.8, 140.0, 140.3, 143.6, 144.7, 147.5, 157.9, 171.9. IR (neat) 2937, 2871, 1739, 1621, 1508, 1474, 1454, 1432, 1361, 1227, 1147, 1081, 1030 cm$^{-1}$. HRMS (FAB+) calcd for C$_{29}$H$_{33}$N$_2$O$_3$ [M+H]$^+$ 457.2491, found 457.2508.

**Quinine-derived phenylpropanoate (10):** Pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.41 (m, 1H), 1.52 (m, 1H), 1.74-1.81 (m, 2H), 2.25 (m, 1H), 2.55-2.65 (m, 2H), 2.72 (m, 2H), 2.94 (t, J = 7.8 Hz, 2H), 3.47 (q, J = 8.2 Hz, 1H), 3.93 (s, 3H), 4.99 (dd, J = 10.5, 1.4 Hz, 1H), 5.00 (dd, J = 17.0, 1.4 Hz, 1H), 5.81 (ddd, J = 17.0, 10.5, 7.8 Hz, 1H), 6.47 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 6.4 Hz, 2H), 7.16-7.26 (m, 4H), 7.36 (dd, J = 9.2, 2.8 Hz, 1H), 7.40 (d, J = 2.8 Hz, 1H), 8.01 (d, J = 9.2 Hz, 1H), 8.68 (d, J = 4.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 24.2, 27.5, 27.8, 30.8, 35.9, 39.7, 42.4, 55.6, 56.6, 59.0, 73.8, 101.4, 114.5, 118.9, 121.8, 126.4, 127.0, 128.2 (2C), 128.5 (2C), 131.8, 140.0, 141.8, 143.5, 144.8, 147.5, 157.9, 172.0. IR (neat) 3375, 2941, 1739, 1621, 1508, 1361, 1228, 1079, 1030 cm$^{-1}$. HRMS (FAB+) calcd for C$_{29}$H$_{33}$N$_2$O$_3$ [M+H]$^+$ 457.2491, found 457.2473.

9. General procedure for the transesterification of α-amino acid esters (Scheme 2).

To a suspension of tetramethylammonium methyl carbonate (3d) (17.9 mg, 0.12 mmol) and activated powdered MS 5Å (1.0 g) in n-hexane (4 mL), benzyl alcohol (310 µL, 3.0 mmol), α-amino acid methyl ester (2.0 mmol), and 4,4’-di-tert-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was stirred at 50 °C by checking TLC. To remove the catalyst, reaction reaction mixture was filtered through a pad of NH silica gel (Fuji Silysia Chemical LTD. Chromatorex-NH DM1020) using n-hexane–ethyl acetate (1:1), and the filtrate was concentrated under reduced pressure. The rough yield was determined by $^1$H NMR analysis based on
4,4'-di-tert-butylbiphenyl as an internal standard, and the resultant residue was purified by NH silica gel column chromatography (eluent: n-hexane:EtOAc = 50:1 to 10:1) to give the desired product. The isolated yield and optical purity were determined by the purified compound.

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\text{Benzyl L-leucinate (10m):}\] Pale yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.91 (d, \(J = 6.9\) Hz, 3H), 0.93 (d, \(J = 6.4\) Hz, 3H), 1.40-1.62 (m, 4H), 1.77 (m, 1H), 3.51 (dd, \(J = 8.7, 5.5\) Hz, 1H), 5.13 (d, \(J = 12.4\) Hz, 1H), 5.17 (d, \(J = 12.4\) Hz, 1H), 7.31-7.04 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.8, 22.9, 24.7, 43.9, 52.9, 66.5, 128.2 (2C), 128.3, 128.5 (2C), 135.7, 176.5. IR (neat) 3380, 2956, 2870, 1735, 1607, 1456, 1367, 1269, 1167 cm\(^{-1}\). \([\alpha]_D^{25}\) = 5.6 (c 1.00, CHCl\(_3\), >99% ee). Chiral HPLC analysis; AS-3, \(n\)-hexane/\(i\)-PrOH = 9/1, 1.0 mL/min, \(t_R\) = 6.2 min (\(L\)) [7.6 min (\(D\)), not observed.]. HRMS (FAB+) calcd for C\(_{13}\)H\(_{20}\)NO\(_2\) [M+H]\(^+\) 222.1494, found 222.1494.

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\text{Benzyl L-methioninate (10n):}\] Pale yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.53 (brs, 2H), 1.82 (ddt, \(J = 13.7, 8.2, 6.9\) Hz, 1H), 2.05 (m, 1H), 2.07 (s, 3H), 2.60 (t, \(J = 6.9\) Hz, 2H), 3.63 (dd, \(J = 8.2, 5.0\) Hz, 1H), 5.15 (d, \(J = 14.7\) Hz, 1H), 5.18 (d, \(J = 15.1\) Hz, 1H), 7.32-7.40 (m, 5H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 15.4, 30.4, 33.9, 53.4, 66.7, 128.3 (2C), 128.4, 128.6 (2C), 135.6, 175.6. IR (neat) 3378, 2916, 1733, 1605, 1497, 1455 1283, 1170 cm\(^{-1}\). \([\alpha]_D^{25}\) = -8.8 (c 1.00, CHCl\(_3\), 97% ee). Chiral HPLC analysis; OD-3 \times 2, \(n\)-hexane/\(i\)-PrOH = 9/1, 1.0 mL/min, \(t_R\) = 30.2 min (minor, \(D\)), 32.7 min (major, \(L\)). HRMS (FAB+) calcd for C\(_{12}\)H\(_{18}\)NO\(_2\)S [M+H]\(^+\) 240.1058, found 240.1059.
10. Gram scale synthesis of 10e (Scheme 3).

To a solution of tetramethylammonium methyl carbonate (3d) (223 mg, 1.5 mmol, 6 mol%) in toluene (100 mL), trans,trans-farnesol (6.34 mL, 25.0 mmol), methyl ester (6.96 g, 25.0 mmol), and well-dried MS 5Å (25 g) were added at room temperature. The mixture was heated under azeotropic reflux conditions (bath temperature 140 °C). After the azeotropic reflux for 3 h, the reaction mixture was allowed to cool to room temperature. To remove the catalyst and MS 5Å, reaction mixture was filtered through flash silica pad using n-hexane–ethyl acetate (1:1) and the filtrate was concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: n-hexane:EtOAc = 100:1 to 1:1) to give the desired product (10.61 g, 91% yield). See Figure S3 for this reaction.

Figure S3. Gram scale synthesis of 10e.

3-O-Acetyl-1,2:5,6-di-O-isopropyldene-α-D-glucofuranose (10o):\(^{24}\) White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.31 (s, 3H), 1.33 (s, 3H), 1.41 (s, 3H), 1.52 (s, 3H), 2.11 (s, 3H), 4.00-4.10 (m, 2H), 4.19-4.25 (m, 2H), 4.50 (d, \(J = 3.7\) Hz, 1H), 5.25 (d, \(J = 2.3\) Hz, 1H), 5.88 (d, \(J = 3.6\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 21.0, 25.3, 26.2, 26.8, 26.9, 67.2, 72.5, 76.2, 79.7, 83.4, 105.1, 109.4, 112.3, 169.7. IR (KBr) 2993, 1748, 1374, 1228, 1077, 1025 cm\(^{-1}\). M.p. 57-60 °C. HRMS (FAB+) calcd for C\(_{14}\)H\(_{22}\)NaO\(_7\) [M+Na\(^+\)] 325.1258, found 325.1266.

6-O-Acetyl-1,2:3,4-di-O-isopropyldene-α-D-galactopyranose (10p):\(^{25}\) White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.33 (s, 3H), 1.34 (s, 3H), 1.45 (s, 3H), 1.52 (s, 3H), 2.09 (s, 3H), 4.03 (ddd, \(J = 7.8, 5.0, 1.8\) Hz, 1H), 4.19 (dd, \(J = 11.9, 7.8\) Hz, 1H), 4.24 (dd, \(J = 8.2, 1.8\) Hz, 1H), 4.29 (dd, \(J = 11.9, 4.6\) Hz, 1H), 4.33 (dd, \(J = 5.0, 2.8\) Hz, 1H), 4.62 (dd, \(J = 8.2, 2.8\) Hz, 1H), 5.55 (d, \(J = 4.6\) Hz, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 20.9, 24.5, 25.0, 25.9, 26.0, 63.5, 65.9, 70.4, 70.7, 71.1, 96.3, 108.8, 110.0, 171.0. IR (KBr) 3468, 1762, 1458, 1211 cm\(^{-1}\). M.p. 109-110 °C. HRMS (FAB+) calcd for C\(_{14}\)H\(_{22}\)NaO\(_7\) [M+Na\(^+\)] 325.1258, found 325.1275.

Propane-1,2,3-triyi triacetate (10q):\(^{26}\) Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.08 (s, 6H), 2.10 (s, 3H), 4.16 (dd, \(J = 11.9, 6.0\) Hz, 2H), 4.30 (dd, \(J = 11.9, 4.1\) Hz, 2H), 5.25 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 20.6 (2C), 20.8, 62.2 (2C), 69.0, 170.0, 170.4 (2C). IR (neat) 3468, 1743, 1644, 1372, 1222, 1049 cm\(^{-1}\). HRMS (ESI+) calcd for C\(_9\)H\(_{14}\)NaO\(_6\) [M+Na\(^+\)] 241.0683, found 241.0676.

1-Adamantyl methyl carbonate (10r):\(^{27}\) White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.66 (s, 6H), 2.11 (s, 6H), 2.19 (s, 3H), 3.70 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 30.8 (3C), 35.9 (3C), 40.9
(3C), 53.7, 81.7, 153.5. IR (KBr) 2911, 1744, 1445, 1311, 1254, 1045 cm⁻¹. M.p. 101-103 °C.
HRMS (FAB+) calcd for C₁₂H₁₉O₃ [M+H]+ 211.1334, found 211.1335.

**Dihydrolinaloyl methyl carbonate (10s):** Colorless oil. 
¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, J = 7.8 Hz, 3H), 1.43 (s, 3H), 1.60 (s, 3H), 1.67 (s, 3H), 1.70–2.04 (m, 6H), 3.70 (s, 3H), 5.09 (t, J = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 7.8, 17.4, 22.1, 22.8, 25.5, 30.5, 37.3, 53.8, 86.4, 123.7, 131.7, 153.8. IR (neat) 2973, 1744, 1440, 1377, 1263 cm⁻¹. HRMS (FAB+) calcd for C₁₂H₂₂NaO₃ [M+Na]+ 237.1467, found 237.1465.

**Isobornyl methacrylate (10t):** Colorless oil. 
¹H NMR (400 MHz, CDCl₃) δ 0.85 (s, 3H), 0.86 (s, 3H), 1.02 (s, 3H), 1.07-1.21 (m, 2H), 1.57 (m, 1H), 1.67-1.88 (m, 4H), 1.93 (s, 3H), 4.71 (m, 1H), 5.52 (d, J = 1.4 Hz, 1H), 6.07 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 18.4, 19.9, 20.1, 27.1, 33.7, 38.9, 45.1, 47.0, 48.9, 81.2, 125.0, 136.9, 166.9. IR (neat) 2955, 2879, 1717, 1638, 1455, 1327, 1298, 1163, 1054 cm⁻¹. HRMS (FAB+) calcd for C₁₄H₂₂NaO₂ [M+Na]+ 245.1517, found 245.1509.

**Bornyl methacrylate (10u):** Colorless oil. 
¹H NMR (400 MHz, CDCl₃) δ 0.86 (s, 3H), 0.89 (s, 3H), 0.93 (s, 3H), 1.01 (dd, J = 13.7, 3.2 Hz, 1H), 1.21-1.38 (m, 2H), 1.70 (t, J = 4.6 Hz 1H), 1.76 (m, 1H), 1.96 (s, 3H), 1.98 (m, 1H), 2.40 (m, 1H), 4.92 (ddd, J = 10.1, 3.2, 2.3 Hz, 1H), 5.55 (t, J = 1.4 Hz, 1H), 6.12 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.6, 18.4, 18.9, 19.8, 27.3, 28.1, 36.9, 45.0, 47.8, 49.0, 80.2, 125.0, 136.9, 167.8. IR (neat) 2955, 2880, 1718, 1454, 1326, 1303, 1173 cm⁻¹. HRMS (FAB+) calcd for C₁₂H₂₀NaO₂ [M+Na]+ 245.1517, found 245.1523.

**(1R,3r,5S)-8-Methyl-8-azabicyclo[3.2.1]octan-3-yl methacrylate (10v):** Colorless oil. 
¹H NMR
(400 MHz, CDCl$_3$) δ 1.73 (d, $J = 15.0$ Hz, 2H), 1.91-2.10 (m, 4H), 1.96 (s, 3H), 2.15 (dt, $J = 15.0$, 4.1 Hz, 2H), 2.29 (s, 3H), 3.11 (brs, 2H), 5.06 (t, $J = 5.3$ Hz, 1H), 5.57 (s, 1H), 6.09 (s, 1H).  

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 18.3, 25.7 (2C), 36.7 (2C), 40.5 (2C), 59.8, 67.7, 125.2, 136.9, 166.7.  IR (neat) 2943, 1715, 1448, 1316, 1296, 1170, 1063, 1036 cm$^{-1}$.  HRMS (FAB+) calcd for C$_{12}$H$_{20}$NO$_2$ [M+H]$^+$ 210.1494, found 210.1485.

2-Ethyl-2-((methacryloyloxy)methyl)propane-1,3-diy1 bis(2-methylacrylate) (10w).$^{30}$ Pale yellow oil.  

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.95 (t, $J = 7.8$ Hz, 3H), 1.58 (q, $J = 7.8$ Hz, 2H), 1.94 (s, 9H), 4.16 (s, 6H), 5.58 (s, 3H), 6.09 (s, 3H).  

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 7.5, 18.3 (3C), 23.5, 41.2, 64.4 (3C), 126.1 (3C), 136.0 (3C), 167.0 (3C).  IR (neat) 2967, 1724, 1638, 1455, 1322, 1294, 1154 cm$^{-1}$.  HRMS (FAB+) calcd for C$_{18}$H$_{26}$NaO$_6$ [M+Na]$^+$ 361.1627, found 361.1623.

Isopropyl tetracosanoate (10x):$^{31}$ White solid.  

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.88 (t, $J = 6.9$ Hz, 3H), 1.17-1.40 (m, 46H), 1.57-1.65 (m, 2H), 2.25 (t, $J = 7.8$ Hz, 2H), 5.00 (m, 1H).  

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.2, 21.9 (2C), 22.8, 25.1, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8 (13C), 32.0, 34.8, 67.4, 173.5.  IR (KBr) 2915, 2848, 1735, 1473, 1463, 1382, 1175, 1115 cm$^{-1}$.  M.p. 49-51 °C.  HRMS (ESI+) calcd for C$_{27}$H$_{54}$NaO$_2$ [M+Na]$^+$ 433.4016, found 433.3997.


$^1$H NMR (400 MHz, CDCl$_3$) δ 0.98 (t, $J = 7.3$ Hz, 3H), 1.23 (d, $J = 6.4$ Hz, 6H), 1.69 (quintet, $J = 7.3$ Hz, 2H), 2.05-2.14 (m, 4H), 2.28 (t, $J = 7.3$ Hz, 2H), 2.81-2.85 (m, 8H), 5.01 (m, 1H), 5.28-5.43 (m, 10H).  

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 14.4, 20.6, 21.9 (2C), 24.9, 25.6, 25.7 (3C), 26.6, 34.1, 67.5, 127.1, 127.9, 128.2 (2C), 128.3, 128.4, 128.6, 128.8, 129.1, 132.1, 173.2.  IR (neat) 3012, 2965, 2933, 1732, 1455, 1373, 1178, 1110 cm$^{-1}$.  HRMS (FAB+) calcd for C$_{23}$H$_{37}$O$_2$ [M+H]$^+$ 345.2794, found 345.2785.
**Diisopropyl adipate (10z):** Colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.23 (d, $J = 6.0$ Hz, 12H), 1.63-1.67 (m, 4H), 2.26-2.31 (m, 4H), 5.00 (septet, $J = 6.4$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.8 (4C), 24.4 (2C), 34.2 (2C), 67.4 (2C), 172.8 (2C). IR (neat) 2980, 1732, 1375, 1180, 1109 cm$^{-1}$. HRMS (FAB+) calcd for C$_{12}$H$_{22}$NaO$_4$ $^+ \ [M+Na]^+$ 253.1410, found 253.1419.

**12. Transesterification of triglycerides 11 in methanol (Scheme 5).**

To a suspension of ammonium salt 3d (9.0 mg, 0.060 mmol, 1 mol%) in methanol (99 mmol, 4 mL for 11a (1.5 M); 148 mmol, 6 mL for 11b (1.0 M)), tryglyceride 11 (6.0 mmol) was added at room temperature. The mixture was stirred under reflux conditions (bath temperature 90 °C), by checking TLC, for 2 h. After cooling to room temperature, water (30 mL) was added to the concentrated mixture, and the organic layer was extracted with ethyl acetate (30 mL $\times$ 3). Catalyst and released glycerol were completely removed through this extraction. The organic layer was washed with brine (30 mL) and combined extracts were dried over Na$_2$SO$_4$. The organic phase was concentrated under reduced pressure to give the desired product 12.

To a suspension of ammonium salt 3d (233 mg, 1.56 mmol, 1 mol%, 0.23 wt. %) in methanol (2.57 mol, 104 mL, 1.5 M based on 11a), trilaurin 11a (100 g, 156 mmol) was added at room temperature. The mixture was stirred under reflux conditions (bath temperature 90 °C), by checking TLC, for 2 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. Water (150 mL) was added to the concentrated mixture, and the organic layer was extracted with ethyl
acetate (100 mL × 3). Catalyst and released glycerol were completely removed through this extraction. The organic layer was washed with brine (100 mL) and combined extracts were dried over Na₂SO₄. The organic phase was concentrated under reduced pressure to give the desired product 12a (>99% yield, 100.6 g).

**Figure S4.** Gram scale synthesis of 12a.
**Methyl dodecanoate (12a):** With the use of 1 mol% of catalyst 3d (0.23 wt. %). Colorless oil. 
\[ ^1H \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 0.88 (t, J = 6.9 \text{ Hz}, 3\text{H}), 1.20-1.36 (m, 16\text{H}), 1.62 (quintet, J = 7.3 \text{ Hz}, 2\text{H}), 2.30 (t, J = 7.3 \text{ Hz}, 2\text{H}), 3.67 (s, 3\text{H}). \]
\[ ^{13}C \text{ NMR} (100 \text{ MHz, CDCl}_3) \delta 14.2, 22.8, 25.0, 29.2, 29.3, 29.4, 29.5, 29.7 (2\text{C}), 32.0, 34.2, 51.5, 174.4. \]
IR (neat) 2925, 2854, 1743, 1465, 1436, 1197, 1171 cm\(^{-1}\). HRMS (EI) calcd for C\(_{13}\)H\(_{26}\)O\(_2\) [M]+ 214.1933, found 214.1939.

**Methyl linoleate (12b):** With the use of 1 mol% of catalyst 3d (0.17 wt. %). Colorless oil. 
\[ ^1H \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta 0.89 (t, J = 6.4 \text{ Hz}, 3\text{H}), 1.24-1.40 (m, 14\text{H}), 1.62 (quintet, J = 7.3 \text{ Hz}, 2\text{H}), 2.05 (q, J = 6.9 \text{ Hz}, 4\text{H}), 2.30 (t, J = 7.3 \text{ Hz}, 2\text{H}), 2.77 (t, J = 6.4 \text{ Hz}, 2\text{H}), 3.67 (s, 3\text{H}), 5.29-5.43 (m, 4\text{H}). \]
\[ ^{13}C \text{ NMR} (100 \text{ MHz, CDCl}_3) \delta 14.2, 22.6, 25.0, 25.7, 27.3 (2\text{C}), 29.1 (2\text{C}), 29.2, 29.4, 29.7, 31.6, 34.2, 51.5, 128.0, 128.1, 130.1, 130.3, 174.4. \]
IR (neat) 3009, 2927, 2855, 1742, 1464, 1436, 1196, 1171 cm\(^{-1}\). HRMS (EI) calcd for C\(_{19}\)H\(_{34}\)O\(_2\) [M]+ 294.2559, found 294.2551.

### 13. Transesterification of diols 11 in MMA (Scheme 6).

**Selective mono-transesterification by using catalyst 2a** To a suspension of phosphonuium salt 2a (55.8 µL, 0.12 mmol) and activated powdered MS 5Å (1.0 g) in MMA (38 mmol, 4 mL, unless otherwise noted), diol 13 (2 mmol) and 4,4’-di-tert-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was stirred at that temperature, by checking TLC. After the removal of the most of MMA under reduced pressure, the rough yield was determined by \(^1H\) NMR analysis based on 4,4’-di-tert-butylbiphenyl as an internal standard. The resultant residue was purified by silica gel column chromatography (eluent: n-hexane:EtOAc = 50:1 to 10:1) to give the desired product 14.
[Selective di-transesterification by using catalyst 3d]  To a suspension of ammonium salt 3d (17.9 mg, 0.12 mmol) and activated powdered MS 5Å (1.0 g) in MMA (38 mmol, 4 mL, unless otherwise noted), diol 13 (2 mmol) and 4,4′-di-tert-butylbiphenyl (53.3 mg, 0.20 mmol) as an internal standard were added at room temperature. The mixture was stirred at 80 °C, by checking TLC. After the removal of the most of MMA under reduced pressure, the rough yield was determined by 1H NMR analysis based on 4,4′-di-tert-butylbiphenyl as an internal standard. The resultant residue was purified by silica gel column chromatography (eluent: n-hexane:EtOAc = 50:1 to 10:1) to give the desired product 15.

3-Hydroxy-3-methylbutyl methacrylate (14a): Colorless oil. 1H NMR (400 MHz, CDCl3) δ 1.29 (s, 6H), 1.90 (t, J = 6.9 Hz, 2H), 1.95 (dd, J = 1.4, 0.9 Hz, 3H), 4.34 (t, J = 6.9 Hz, 2H), 5.57 (quintet, J = 1.4 Hz, 1H), 6.09 (t, J = 1.4 Hz, 1H) [OH was not observed.]. 13C NMR (100 MHz, CDCl3) δ 18.3, 29.7 (2C), 41.6, 61.7, 70.0, 125.6, 136.3, 167.5. IR (neat) 3434, 2972, 1718, 1637, 1455, 1378, 1326, 1300, 1168 cm⁻¹. HRMS (FAB+) calcd for C9H17O3 [M+H]⁺ 173.1178, found 173.1175.

3-Methylbutane-1,3-diyl bis(2-methacrylate) (15a): Colorless oil. 1H NMR (400 MHz, CDCl3) δ 1.55 (s, 6H), 1.90 (t, J = 1.4 Hz, 3H), 1.93 (t, J = 1.4 Hz, 3H), 2.22 (t, J = 6.9 Hz, 2H), 4.27 (t, J = 6.9 Hz, 2H), 5.50 (quintet, J = 1.4 Hz, 1H), 5.55 (quintet, J = 1.4 Hz, 1H), 6.02 (t, J = 1.4 Hz, 1H), 6.09 (s, 1H). 13C NMR (100 MHz, CDCl3) δ 18.3, 18.4, 26.4 (2C), 39.3, 61.0, 81.0, 124.9, 125.6, 136.3, 137.6, 166.6, 167.4. IR (neat) 1716, 1637, 1454, 1331, 1298, 1142 cm⁻¹. HRMS (FAB+) calcd for C13H21O4 [M+H]⁺ 241.1440, found 241.1447.

3-Hydroxypentyl methacrylate (14b): Colorless oil. 1H NMR (400 MHz, CDCl3) δ 0.97 (t, J = 7.3 Hz, 3H), 1.45-1.56 (m, 2H), 1.72 (m, 1H), 1.87 (m, 1H), 1.95 (t, J = 1.4 Hz, 3H), 2.00 (d, J = 4.6 Hz, 1H), 3.63 (m, 1H), 4.24 (dt, J = 11.4, 5.5 Hz, 1H), 4.44 (ddd, J = 11.0, 8.7, 5.0 Hz, 1H), 5.58 (quintet, J = 1.4 Hz, 1H), 6.11 (s, 1H). 13C NMR (100 MHz, CDCl3) δ 9.9, 18.4, 30.3, 35.9, 62.1,
70.1, 125.7, 136.3, 167.8. IR (neat) 3427, 2964, 1717, 1637, 1456, 1323, 1299, 1172 cm\(^{-1}\). HRMS (FAB+) calcd for C\(_9\)H\(_7\)O\(_3\) [M+H]\(^+\) 173.1178, found 173.1179.

**Pentane-1,3-diyi bis(2-methylacrylate) (15b):** Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.92 (t, \(J = 7.3\) Hz, 3H), 1.67 (quintet, \(J = 6.9\) Hz, 2H), 1.94 (s, 6H), 1.99 (q, \(J = 6.0\) Hz, 2H), 4.16 (dt, \(J = 11.0, 6.9\) Hz, 1H), 4.24 (dt, \(J = 11.0, 6.0\) Hz, 1H), 5.02 (quintet, \(J = 6.0\) Hz, 1H), 5.55 (quintet, \(J = 1.4\) Hz, 2H), 6.10 (s, 2H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 9.4, 18.2, 18.3, 27.1, 32.5, 61.2, 72.6, 125.3, 125.5, 136.2, 136.5, 167.0, 167.3. IR (neat) 2970, 1719, 1637, 1454, 1322, 1296, 1165 cm\(^{-1}\). HRMS (FAB+) calcd for C\(_{13}\)H\(_{21}\)O\(_4\) [M+H]\(^+\) 241.1440, found 241.1435.

**4-Hydroxy-4-methylpentan-2-yl methacrylate (14c):** Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.23 (s, 3H), 1.24 (s, 3H), 1.31 (d, \(J = 6.0\) Hz, 3H), 1.69 (dd, \(J = 14.7, 3.2\) Hz, 1H), 1.94 (d, \(J = 0.9\) Hz, 3H), 1.95 (m, 1H), 2.01 (s, 1H), 5.23 (m, 1H), 5.57 (t, \(J = 1.4\) Hz, 1H), 6.09 (s, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.4, 21.8, 29.9 (2C), 49.1, 69.2, 70.1, 125.7, 136.7, 167.2. IR (neat) 3450, 2932, 2915, 1636, 1453, 1378, 1321, 1301, 1173, 1127 cm\(^{-1}\). HRMS (FAB+) calcd for C\(_{10}\)H\(_{19}\)O\(_3\) [M+H]\(^+\) 187.1334, found 187.1341.

**2-Methylpentane-2,4-diyi bis(2-methylacrylate) (15c):** 20 mL (189 mmol) of MMA (i.e., 0.1 \(M\) based on 13c) was used. Colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.27 (d, \(J = 6.0\) Hz, 3H), 1.49 (s, 3H), 1.51 (s, 3H), 1.87 (d, \(J = 0.9\) Hz, 3H), 1.91 (d, \(J = 0.9\) Hz, 3H), 2.07 (dd, \(J = 15.1, 3.2\) Hz, 1H), 2.30 (dd, \(J = 15.1, 8.7\) Hz, 1H), 5.23 (m, 1H), 5.47 (t, \(J = 1.8\) Hz, 1H), 5.53 (t, \(J = 1.8\) Hz, 1H), 5.99 (d, \(J = 0.9\) Hz, 1H), 6.06 (d, \(J = 0.9\) Hz, 1H). \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 18.4, 18.5, 21.7, 26.4, 27.2, 45.8, 68.1, 81.3, 124.9, 125.4, 136.8, 137.8, 166.8, 166.9. IR (neat) 2980, 1715, 1637, 1453, 1377, 1331, 1302, 1181, 1127 cm\(^{-1}\). HRMS (FAB+) calcd for C\(_{14}\)H\(_{23}\)O\(_4\) [M+H]\(^+\) 255.1596, found 255.1603.
14. $^1$H NMR experiments with ammonium catalyst and BnOH.

To determine whether or not the estimated active species $[\text{R}_4\text{N}]^+\text{[OR']}^-$ could be rapidly generated \textit{in situ}, $^1$H NMR (toluene-$d_8$) experiments were performed. Table S1 shows the results of $[\text{Me}(n\text{-octyl})_3\text{N}]^+[\text{OCO}_2\text{Me}]^-$ (3a) + BnOH (5a). Within 6 min at room temperature, $[\text{Me}(n\text{-octyl})_3\text{N}]^+[\text{OBn}]^-$ (S1) was generated in 87% conversion. After an additional 5 min at 50 °C, S1 was observed in 93% conversion. In contrast, $[\text{Me}(n\text{-octyl})_3\text{N}]^+\text{[Cl}^-\text{(S2}} + \text{BnOH (5a})$ did not provide S1 under the same conditions (Table S2). Overall, the active species would be quickly generated \textit{in situ} under our standard reaction conditions.

**Table S1.** $[\text{Me}(n\text{-octyl})_3\text{N}]^+[\text{OCO}_2\text{Me}]^-$ (3a) + BnOH (5a).

$[\text{Me}(n\text{-octyl})_3\text{N}]^+[\text{OCO}_2\text{Me}]^-$ (3a) (1 equiv) + BnOH (5a) (1 equiv) + 4,4'-di-tert-butylbiphenyl (0.1 equiv as an internal standard) + MS 5Å → $[\text{Me}(n\text{-octyl})_3\text{N}]^+[\text{OBn}]^-$ (S1) (toluene-$d_8$ (0.5 M)

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<th>$\text{OCO}_2\text{Me}]^-$ (%)$^a$</th>
<th>S1 (%)$^a$</th>
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<td>1</td>
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</table>

$^a$ Distribution was determined by $^1$H NMR based on internal standard.

**Table S2.** $[\text{Me}(n\text{-octyl})_3\text{N}]^+\text{[Cl}^-\text{(S2}} + \text{BnOH (5a})$.

$[\text{Me}(n\text{-octyl})_3\text{N}]^+\text{[Cl}^-\text{(S2}} (1$ equiv) + BnOH (5a) (1 equiv) + 4,4'-di-tert-butylbiphenyl (0.1 equiv as an internal standard) + MS 5Å → $[\text{Me}(n\text{-octyl})_3\text{N}]^+[\text{OBn}]^-$ (S1) (toluene-$d_8$ (0.5 M)

<table>
<thead>
<tr>
<th>entry</th>
<th>Conditions</th>
<th>5a (%)$^a$</th>
<th>S1 (%)$^a$</th>
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<tr>
<td>1</td>
<td>25 °C, 1 min</td>
<td>105</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>25 °C, 1 min + 25 °C, 5 min</td>
<td>104</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>25 °C, 1 min + 25 °C, 5 min + 50 °C, 5 min</td>
<td>104</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Distribution was determined by $^1$H NMR based on internal standard.
Figure S5. $^1$H NMR experiment of [Me($n$-octyl)$_3$N][OCO$_2$Me]$^-$ (3a) + BnOH (5a). (a) 3a at 25 °C. (b) 5a at 25 °C. (c) 3a + 5a at 25 °C, 1 min. (d) 3a + 5a at 25 °C, 1 min + 25 °C, 5 min. (e) 3a + 5a at 25 °C, 1 min + 25 °C, 5 min + 50 °C, 5 min.
Figure S6. $^1$H NMR experiment of $[\text{Me}(n\text{-octyl})_3\text{N}]^+\text{[Cl]}^- (\text{S2}) + \text{BnOH (5a)}$. (a) S2 at 25 °C. (b) 5a at 25 °C. (c) S2 + 5a at 25 °C, 1 min. (d) S2 + 5a at 25 °C, 1 min + 25 °C, 5 min. (e) S2 + 5a at 25 °C, 1 min + 25 °C, 5 min + 50 °C, 5 min.
15. Decomposition of catalyst 3a in the reaction of 4b and cyclohexanol.

We monitored the reaction of methyl benzoate 4b and cyclohexanol in toluene, n-hexane, or THF in the presence of catalyst [Me(n-octyl)3N][OCO2Me]− 3a under azeotropic reflux conditions. The results are shown in Figure S7. In toluene (bp. 110 °C), 3a decomposed within 1 h, and the yield of product (68% yield) did not change after 1 h. n-Hexane (bp. 69 °C) and THF (bp. 66 °C) showed similar reaction curves, and we did not observe a clear sign of the decomposition of 3a in either case. The reaction in n-hexane showed slightly better conversion than that in THF. Overall, catalyst 3a would decompose at a relatively high reflux temperature, such as in hexane, whereas 3a might be used without significant decomposition at a lower reflux temperature, such as in hexane or THF.

![Equation](image)

**Figure S7.** The reaction of 4b and cyclohexanol with the use of 3a in toluene, n-hexane, or THF.
16. Effect of the reaction temperature.

In the probe reaction of methyl benzoate 4b and cyclohexanol, we examined the reaction temperature (room temperature, 50 °C, and 70 °C) in the same solvent (Figure S8). Figure S8a shows the results in n-hexane (bp. 69 °C), and Figure S8b shows the results in THF (bp. 66 °C). In both cases, at 70 °C (bath temperature), the reaction proceeded smoothly and was almost finished within 6–8 h. At 50 °C (bath temperature), the reaction also proceeded smoothly, but was still ongoing after 20 h. Although n-hexane and THF have different chemical properties, the progress of the reaction might strongly depend on the reaction temperature since the reaction curves in n-hexane and THF were quite similar. Unfortunately, these reactions did not proceed in n-hexane and THF at room temperature. This representative result at room temperature would not deny the possibility of reactions of any other substrates at room temperature, because other reactions, such as shown in Scheme 6 using MMA, could be demonstrated at room temperature. The reaction proceedings strongly depend on alcohols (1° > 2° > 3°) as well as esters (excess (solvent) > 1 equivalent).

![Reaction scheme and graphs](image)

**Figure S8.** The reaction of 4b and cyclohexanol with the use of 3a in different temperatures in the same solvent (n-hexane and THF).
17. Screening of catalysts in \( n \)-hexane under azeotropic reflux conditions.

To exclude the effect of the decomposition of the catalysts and to evaluate only steric effects on the catalysts, we examined the reaction of \( 4b \) (1 equiv) and cyclohexanol (3 equiv) in \( n \)-hexane (bp. 69 °C) under azeotropic reflux conditions. The reaction was interrupted at 30 min, although the reaction was still proceeding at that time. As a result, phosphonium salt \( 2a \) was less effective than ammonium salts \( 3a–d \). Among ammonium salts \( 3a–d \), the yield was in the order \( 3a < 3b < 3c < 3d \). This order might agree with the size of the ammonium salts. Figure S9 summarized the results. Also see the screening of catalysts in toluene (bp. 111 °C).

![Chemical reaction](image)

**Conclusion:** The order of catalytic activity and chemical stability are both in the order \( 3a < 3b < 3c < 3d \).

**Figure S9.** The order of catalytic activity.
18. General catalyst screening.

Catalyst screening was conducted in a probe reaction between methyl salicylate 4a and benzyl alcohol 5a (Table S3, also see Table 1 in the paper). The present optimum ammonium salt 3d was also effective as well as 3a (entries 4 and 5). Basic metal salt catalysts, such as NaOt-Bu, NaOC₆H₄(4-t-Bu), and KOt-Bu, gave 6a in low to moderate yields (12–54%) (entries 6–9). Brønsted acid catalysts, such as p-TsOH and TfOH, were not effective (entries 10 and 11). Acidic metal salt catalysts, such as Sc(III), Ti(IV), Mn(II), Fe(II)/(III), Cu(II), Zn(II), Zr(IV), La(III), and Hf(IV), were not effective (entries 11–25).

### Table S3. Screening of catalysts.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2 La(Oi-Pr)₃ + HO(CH₂CH₂O)₂Me</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>1/2 La(NO₃)₃·H₂O (1) + [Me(n-octyl)₃P][OOC₂Me] (2a)</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>[Me(n-octyl)₃P][OOC₂Me] (2a)</td>
<td>87 (71)(^b)</td>
</tr>
<tr>
<td>4</td>
<td>[Me(n-octyl)₃N][OOC₂Me]⁻ (3a)</td>
<td>92 (79)(^b)</td>
</tr>
<tr>
<td>5</td>
<td>[Me₄N][OOC₂Me]⁻ (3d)</td>
<td>92 (79)(^b) (90)(^c)</td>
</tr>
<tr>
<td>6</td>
<td>NaOt-Bu</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>NaOC₆H₄(4-t-Bu)</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>KOt-Bu</td>
<td>54</td>
</tr>
<tr>
<td>9</td>
<td>p-TsOH</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>TfOH</td>
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</tr>
<tr>
<td>11</td>
<td>Sc(OTf)₃</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>Ti(Oi-Pr)₄</td>
<td>17</td>
</tr>
<tr>
<td>13</td>
<td>TiCl₄</td>
<td>0</td>
</tr>
<tr>
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<td>Mn(OAc)₂</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>Fe(OTf)₂</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>Fe(OTf)₃</td>
<td>0</td>
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<tr>
<td>17</td>
<td>Cu(OAc)₂</td>
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<td>18</td>
<td>Zn(OAc)₂</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>Zn(OCOCF₃)₂</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>Zn₄(OCOCF₃)₆O</td>
<td>7</td>
</tr>
<tr>
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<td>24</td>
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<td>6</td>
</tr>
<tr>
<td>25</td>
<td>HfCl₄(thf)₂</td>
<td>9</td>
</tr>
</tbody>
</table>

\(^a\) The reaction was carried out with 4a (2 mmol), 5a (2 mmol), and catalyst (6 mol%) in \(n\)-hexane at 90 °C (bath temperature) for 2 h under azeotropic reflux conditions with MS 5Å. \(^b\) Yield of 6a for 30 min. \(^c\) Reaction was conducted in the presence of 1 mol% of 3d for 1 h.

We examined whether or not molecular sieves (MS) are necessary in a probe reaction of 4b and 7 with the use of catalyst 3d (Scheme S3). As a result, 8 was obtained in 97% yield in the presence of MS 5Å, while 8 was obtained in 87% yield in the absence of MS 5Å. Therefore, MS 5Å is necessary in this equilibrium reaction to remove methanol. We consistently used MS 5Å, although MS 3Å and MS 4Å showed the same performance (97% yield).

![Scheme S3. Effect of molecular sieves.](image)

with MS 3Å: 97% yield
with MS 4Å: 97% yield
with MS 5Å: 97% yield
without MS: 87% yield
20. References.

$\text{OH} \quad \text{O} \quad \text{O} \quad \text{Ph}$

(6a)

$^1\text{H NMR, 400 MHz, CDCl}_3$

$^1\text{C NMR, 100 MHz, CDCl}_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$\text{H NMR, 400 MHz, CDCl}_3$

$\text{C NMR, 100 MHz, CDCl}_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 100 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

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$^1$H NMR, 400 MHz, CDCl$_3$

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\(^1\)H NMR, 400 MHz, CDCl\(_3\)

\(^{13}\)C NMR, 100 MHz, CDCl\(_3\)
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 100 MHz, CDCl$_3$
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$^{13}$C NMR, 100 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$
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$^1$H NMR, 400 MHz, CDCl$_3$

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\[ \text{(14c)} \]

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\[^{13}\text{C} \text{NMR, 100 MHz, CDCl}_3\]
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 100 MHz, CDCl$_3$