Diversity-Oriented Synthesis of 1-Hydroxy-2,4-benzodioates by Regioselective [3+3] Cyclocondensations of 1,3-Bis(silyloxy)-1,3-butadienes with 3-Alkoxycarbonyl-2-en-1-ones

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Supporting Information

Experimental Section

General Comments. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For $^1$H and $^{13}$C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063-0.200 mm, 70 – 230 mesh) was used.

General procedure for the synthesis of 1-hydroxy-2,4-benzodioates 4a-o. To a CH$_2$Cl$_2$ solution (2 mL / 1.0 mmol of 3) of 3 (1.0 equiv.) was added 1 (1.0 equiv.) and,
subsequently, TiCl₄ (1.0 equiv.) at −78 °C. The temperature of the solution was allowed
to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid
(10%, 20 mL) and the organic and the aqueous layer were separated. The later was
extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried (Na₂SO₄),
filtered and the filtrate was concentrated in vacuo. The residue was purified by
chromatography (silica gel, n-heptane / EtOAc) to give product 4.

1-Ethyl 3-methyl 4-hydroxy-2,6-dimethylisophthalate (4a): Starting with 3
(0.489 g, 2.0 mmol) and 1a (0.521 g, 2.0 mmol), 4a was isolated after chromatography
(silica gel, heptanes/EtOAc) as an orange oil (0.149 g, 30%). ¹H NMR (CDCl₃, 250 MHz):
δ = 1.36 (t, ³J = 7.1 Hz, 3H, OCH₂C₃H₃), 2.25 (s, 3H, CH₃), 2.44 (s, 3H, CH₃), 3.94 (s, 3H,
OCH₃), 4.36 (q, ³J = 7.1 Hz, 2H, OCH₂CH₃), 6.69 (s, 1H, CHAr), 11.23 (s, 1H, OH). ¹³C
NMR (CDCl₃, 75 MHz): δ = 14.2 (OCH₂CH₃), 20.0, 20.2 (CH₃), 52.2 (OCH₃), 61.1
(OCH₂CH₃), 110.4 (C₂Ar), 116.9 (CH₂Ar), 128.6, 137.8, 141.8 (C₄Ar), 162.6 (COH), 169.7 (CO),
171.7 (CO). IR (neat, cm⁻¹): ̃v = 3421 (br, w), 2983 (m), 2956 (m), 1725 (s), 1666 (s), 1606
(m), 1579 (m), 1444 (s), 1360 (s), 1234 (s), 1259 (s), 1232 (s), 1185 (s), 1115 (s), 1053 (m),
1036 (m). MS (GC/MS, 70 eV): m/z (%) = 252 (M⁺, 27), 220 (100), 207 (28), 175 (61).

Diethyl 4-hydroxy-2,5,6-trimethylisophthalate (4b): Starting with 3
(0.305 g, 1.25 mmol) and 1b (0.325 g, 1.25 mmol), 4b was isolated after chromatography
(silica gel, heptanes/EtOAc) as a slightly yellow solid (167 mg, 48%), mp. = 66-67 °C. ¹H NMR
(CDCl₃, 250 MHz): δ = 1.44 - 1.35 (m, 6H, 2OCH₂CH₃), 2.17 (s, 3H, PhCH₃), 2.21 (s, 3H,
PhCH₃), 2.44 (s, 3H, PhCH₃), 4.38 (q, ³J = 7.0 Hz, 2H, OCH₂CH₃), 4.43 (q, ³J = 7.0 Hz,
2H, OCH₂CH₃), 11.68 (s, 1H, OH). ¹³C NMR (CDCl₃, 75 MHz): δ = 11.5 (CH₃), 14.1, 14.2
(OCH₂CH₃), 17.5, 20.1, (CH₃), 61.1 (OCH₂CH₃), 61.7 (OCH₂CH₃), 110.0, 123.2, 128.6,
133.8, 139.2 (C₂Ar), 160.7 (COH), 170.1, 171.9, (CO). IR (Nujol, cm⁻¹): ̃v = 1722 (s), 1656 (s),
1598 (m), 1576 (m). MS (EI, 70 eV): m/z (%) = 280 (M⁺, 37), 235 (60), 234 (100), 206 (87),
189 (34), 178 (48), 177 (26). Anal.: calcd. for C₁₅H₂₀O₅ (280.32): C, 64.27; H, 7.19. Found:
C, 64.04; H, 7.40.
Diethyl 5-ethyl-4-hydroxy-2,6-dimethylisophthalate (4c): Starting with 3 (0.305 g, 1.25 mmol) and 1c (0.378 g, 1.25 mmol), 4c was isolated after chromatography (silica gel, heptanes/EtOAc) as colourless oil (0.181 g, 49%). $^1$HNMR (CDCl$_3$, 250 MHz): $\delta = 1.10$ (t, $^3J \text{ } = 7.6$ Hz, 3H, CH$_2$C$_3$H$_3$), 1.44 – 1.36 (m, 6H, 2 OCH$_2$C$_3$H$_3$), 2.24 (s, 3H, PhCH$_3$), 2.43 (s, 3H, PhCH$_3$), 2.70 (q, $^3J \text{ } = 7.6$ Hz, 2H, CH$_2$C$_3$H$_3$), 4.38 (q, $^3J \text{ } = 7.0$ Hz, 2H, OCH$_2$C$_3$H$_3$), 4.42 (q, $^3J \text{ } = 7.0$ Hz, 2H, OCH$_2$C$_3$H$_3$), 11.63 (s, 1H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 13.0$, 14.1, 14.2, 16.6, 19.3, 20.2 (CH$_3$), 61.1, 61.7 (OCH$_2$C$_3$H$_3$), 110.2, 128.8, 129.2, 134.0, 138.5 (CAr), 160.6 (COH), 170.6, 171.8 (CO). IR (neat, cm$^{-1}$): $\tilde{\nu} = 3422$ (br, m), 2938 (s), 2937 (s), 2970 (m), 2875 (m), 1727 (s), 1656 (s), 1600 (s), 1574 (s). MS (EI, 70 eV): m/z (%) = 294 (M+, 20), 249 (25), 248 (37), 220 (100), 203 (15), 192 (31). Anal.: calcd. for C$_{16}$H$_{22}$O$_5$ (294.34): C, 65.29; H, 7.53. Found: C, 65.27; H, 7.68.

1-Ethyl 3-methyl 5-hexyl-4-hydroxy-2,6-dimethylisophthalate (4d). Starting with 3 (0.488 g, 2.0 mmol) and 1d (0.757 g, 2.2 mmol), 4d was isolated after chromatography (silica gel, heptanes/EtOAc) as a colourless viscous oil (0.236 g, 35%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.81$ (t(br), $^3J \text{ } = 7.4$ Hz, 3 H, CH$_3$), 1.19 – 1.25 (m, 8 H, 4 CH$_2$), 1.31 (t, $^3J \text{ } = 7.6$ Hz, 3 H, OCH$_2$CH$_3$), 2.16 (s, 3 H, PhCH$_3$), 2.34 (s, 3 H, PhCH$_3$), 2.59 (t, $^3J \text{ } = 7.4$ Hz, 2 H, PhCH$_2$), 3.88 (s, 3 H, OCH$_3$), 4.32 (q, $^3J \text{ } = 7.6$ Hz, 2 H, OCH$_2$CH$_3$), 11.40 (s, 1 H, OH). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 15.2$, 15.3, 18.0, 21.0 (CH$_3$), 23.7, 27.3, 29.7, 32.4, 34.4 (CH$_2$), 53.6 (OCH$_3$), 62.3 (OCH$_2$CH$_3$), 111.1, 129.3, 130.0, 135.1, 140.0 (CAr), 161.9 (COH), 171.8, 173.5 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu} = 2962$ (m), 1723 (m), 1663 (m), 1439 (m), 1394 (m), 1229 (s), 1194 (s), 1151 (s), 1033 (m), 844 (w), 723 (w). GC-MS (EI, 70 eV): m/z (%) = 336 ([M$^+$], 49), 289 (100), 276 (87), 259 (19), 234 (54), 206 (31), 187 (43), 178 (13), 159 (6), 91 (9), 77 (8), 43 (7). HRMS (EI): Calcd. for C$_{19}$H$_{28}$O$_5$: 336.19313; found: 336.19263.

1-Ethyl 3-methyl 4-hydroxy-2,6-dimethyl-5-nonylisophthalate (4e). Starting with 3 (0.488 g, 2.0 mmol) and 1e (0.850 g, 2.2 mmol), 4e was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellowish oil (0.302 g, 40%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.80$ (t(br), $^3J \text{ } = 7.3$ Hz, 3 H, (CH$_2$)$_8$CH$_3$), 1.19 - 1.24 (m, 14 H, 7 CH$_2$), 1.31 (t, $^3J \text{ } = 7.3$ Hz, 3 H, OCH$_2$CH$_3$), 2.15 (s, 3 H, PhCH$_3$), 2.34 (s, 3 H, PhCH$_3$), 2.57 (t, $^3J \text{ } = 6.7$ Hz, 2 H, PhCH$_2$), 3.87 (s, 3 H, OCH$_3$), 4.30 (q, $^3J \text{ } = 7.1$ Hz, 2 H, OCH$_2$CH$_3$), 11.48 (s, 1 H, OH).
$^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.0$, 14.1, 16.8, 20.0 (CH$_3$), 22.6, 26.1, 28.8, 29.3, 29.5, 29.6, 29.9, 31.8 (CH$_2$), 52.2 (OCH$_3$), 61.3 (OCH$_2$), 109.9 (CCOOCH$_3$), 128.1 (COOC$_2$H$_5$), 128.8, 133.8, 138.8 (C$_{Ar}$), 160.7 (COH), 170.6, 172.3 (CO). IR (neat, cm$^{-1}$): $v = 2953$ (w), 2922 (m), 2852 (w), 1725 (m), 1598 (w), 1572 (w), 1439 (m), 1411 (w), 1362 (m), 1328 (m), 1267 (m), 1217 (s), 1192 (m), 1155 (m), 1123 (m), 1094 (w), 1073 (w), 1033 (m), 972 (w), 858 (w), 809 (m), 756 (w), 684 (w), 662 (w), 580 (w), 541 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 378 ([M$^+$], 52), 333 (20), 332 (118), 331 (100), 329 (17), 318 (29), 301 (10), 275 (14), 235 (10), 234 (60), 233 (38), 206 (41), 187 (24). HRMS (EI): Calcd. for C$_{22}$H$_{34}$O$_5$ ([M$^+$]): 378.240088; found: 378.239837.

1-Ethyl 3-methyl 5-decyl-4-hydroxy-2,6-dimethylisophthalate (4f). Starting with 3 (0.488 g, 2.0 mmol) and 1 (0.881 g, 2.2 mmol), 4f was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellowish oil (0.321 g, 41%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.80$ (t, $^3$$J = 7.3$ Hz, 3 H, (CH$_2$)$_9$CH$_3$), 1.13 - 1.23 (m, 16 H, 8 CH$_2$), 1.30 (t, $^3$$J = 7.3$ Hz, 3 H, OCH$_2$CH$_3$), 2.15 (s, 3 H, PhCH$_3$), 2.33 (s, 3 H, PhCH$_3$), 2.57 (t, $^3$$J = 6.7$ Hz, 2 H, PhCH$_2$), 3.87 (s, 3 H, OCH$_3$), 4.30 (q, $^3$$J = 7.2$ Hz, 2 H, OCH$_2$CH$_3$), 11.47 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.0$, 14.1, 16.8, 20.0 (CH$_3$), 22.6, 26.1, 28.8, 29.3, 29.5, 29.6, 29.9, 31.8 (CH$_2$), 52.2 (OCH$_3$), 61.3 (OCH$_2$), 109.9 (CCOOCH$_3$), 128.1 (COOC$_2$H$_5$), 128.8, 133.8, 138.9 (C$_{Ar}$), 160.7 (COH), 170.6, 172.3 (CO). IR (neat, cm$^{-1}$): $v = 2953$ (w), 2922 (m), 2852 (w), 1725 (m), 1657 (m), 1598 (w), 1572 (w), 1439 (m), 1411 (w), 1362 (m), 1328 (m), 1267 (m), 1217 (s), 1192 (m), 1155 (m), 1123 (m), 1094 (w), 1073 (w), 1033 (m), 972 (w), 858 (w), 809 (m), 756 (w), 684 (w), 662 (w), 580 (w), 541 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 378 ([M$^+$], 52), 333 (20), 332 (118), 331 (100), 329 (17), 318 (29), 301 (10), 275 (14), 235 (10), 234 (60), 233 (38), 206 (41), 187 (24). HRMS (EI): Calcd. for C$_{22}$H$_{34}$O$_5$ ([M$^+$]): 378.240088; found: 378.239837.

3-Ethyl 5-methyl 6-hydroxy-2,4,4'-trimethylbiphenyl-3,5-dicarboxylate (4g). Starting with 3 (0.488 g, 2.0 mmol) and 1g (0.771 g, 2.2 mmol), 4g was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellowish oil (0.260 g, 38%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 1.24$ (t, $^3$$J = 7.0$ Hz, 3 H, OCH$_2$CH$_3$), 1.90 (s, 3 H, PhCH$_3$), 2.27 (s, 3 H, PhCH$_3$), 2.36 (s, 3 H, PhCH$_3$), 3.83 (s, 3 H, OCH$_3$). 4.26 (q, $^3$$J = 7.0$ Hz, 2 H, ...
OCH$_2$CH$_3$), 6.94 - 6.97 (m, 2 H, CH$_2$Ar), 7.02 - 7.08 (m, 2 H, CH$_2$Ar), 11.18 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 14.1, 18.2, 20.1, 21.2 (CH$_3$), 52.3 (OCH$_3$), 61.2 (OCH$_2$), 110.6 (CCOOCH$_3$), 128.8 (C$_{Ar}$), 129.0 (CCOOCC$_2$H$_5$), 129.2 (2 CH$_{Ar}$), 129.7 (2 CH$_{Ar}$), 133.0 (C$_{Ar}$), 135.8, 137.0, 139.5 (C$_{Ar}$), 160.1 (COH), 170.1, 171.9 (CO). IR (neat, cm$^{-1}$): $\nu =$ 2954 (w), 2929 (w), 2871 (w), 1721 (m), 1598 (w), 1568 (w), 1513 (w), 1438 (m), 1363 (w), 1213 (s), 1203 (s), 1098 (m), 1075 (w), 1035 (m), 958 (w), 923 (w), 842 (w), 821 (w), 809 (m), 760 (w), 729 (w), 710 (w), 686 (w), 666 (w), 611 (w), 580 (w), 539 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 342 ([M$^+$], 50), 310 (100), 297 (17), 282 (22), 265 (13), 253 (12), 236 (11), 209 (16), 165 (14), 119 (5), 43 (5). HRMS (EI): Calcd. for C$_{20}$H$_{22}$O$_5$ ([M$^+$]): 342.14618; found: 342.146101.

3-Ethyl 5-methyl 4'-chloro-6-hydroxy-2,4-dimethyl-biphenyl-3,5-dicarboxylate (4h). Starting with 3 (0.488 g, 2.0 mmol) and 1h (0.816 g, 2.2 mmol), 4h was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellowish oil (0.270 g, 37%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta =$ 1.16 (t, $^3$J = 6.9 Hz, 3 H, OCH$_2$CH$_3$), 1.78 (s, 3 H, PhCH$_3$), 2.27 (s, 3 H, PhCH$_3$), 3.74 (s, 3 H, OCH$_3$), 4.16 (q, $^3$J = 6.9 Hz, 2 H, OCH$_2$CH$_3$), 6.89 - 6.93 (m, 2 H, 2 CH$_{Ar}$), 7.02 - 7.08 (m, 2 H, 2 CH$_{Ar}$), 11.26 (S, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 15.1, 19.1, 21.2 (CH$_3$), 53.3 (OCH$_3$), 62.2 (OCH$_2$), 111.5 (CCOOCH$_3$), 128.7 (C$_{Ar}$), 129.6 (2 CH$_{Ar}$), 129.9 (CCOOCC$_2$H$_5$), 132.2 (2 CH$_{Ar}$), 134.3, 135.5, 137.4, 140.3 (C$_{Ar}$), 160.0 (COH), 170.8, 172.8 (CO). IR (neat, cm$^{-1}$): $\nu =$ 2954 (w), 2930 (w), 2871 (w), 1722 (m), 1658 (m), 1604 (w), 1591 (w), 1571 (w), 1491 (w), 1438 (m), 1408 (w), 1363 (w), 1329 (m), 1204 (s), 1100 (m), 1086 (m), 1034 (m), 1014 (m), 985 (w), 957 (w), 831 (m), 809 (m), 758 (w), 689 (w), 665 (w), 612 (w), 579 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 364 ([M$^+$], $^{37}$Cl, 12), 362 ([M$^+$], $^{35}$Cl, 39), 332 ($^{37}$Cl, 29), 331 (23), 330 ($^{35}$Cl, 100), 317 (15), 302 (18), 285 (12), 274 (8), 165 (14), 128 (6), 86 (9), 43 (5). HRMS (EI): Calcd. for C$_{19}$H$_{19}$ClO$_5$ ([M$^+$], $^{35}$Cl): 362.09155; found: 362.090638.

3-Ethyl 5-methyl 6-hydroxy-4'-methoxy-2,4-dimethyl-biphenyl-3,5-dicarboxylate (4i). Starting with 3 (0.488 g, 2.0 mmol) and 1i (0.806 g, 2.2 mmol), 4i was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellowish oil (0.245 g, 34%). $^1$H NMR
(250 MHz, CDCl₃): δ = 1.32 (t, 3J = 7.1 Hz, 3 H, OCH₂CH₃), 1.96 (s, 3 H, PhCH₃), 2.42 (s, 3 H, PhCH₃), 3.77 (s, 3 H, OCH₃), 3.89 (s, 3 H, OCH₃), 4.32 (q, 3J = 6.9 Hz, 2 H, OCH₂CH₃), 6.88 - 6.93 (m, 2 H, 2 CHAr), 7.02 - 7.08 (m, 2 H, 2 CHAr), 11.26 (s, 1 H, OH).

13C NMR (CDCl₃, 75 MHz): δ = 14.2, 18.2, 20.1 (CH₃), 52.3, 55.3 (OCH₃), 61.2 (OCH₂), 110.6 (CCOOCH₃), 113.9 (2 CHAr), 128.1 (C₆H₅), 128.7 (CCOOC₂H₅), 128.9 (C₆H₅), 130.9 (2 CHAr), 135.8, 139.7 (C₆H₅), 158.8 (C₆H₅), 160.2 (COH), 170.2, 171.9 (CO).

IR (neat, cm⁻¹): ν = 3033 (w), 2995 (w), 2953 (w), 2906 (w), 2835 (w), 1719 (m), 1656 (w), 1608 (w), 1509 (s), 1439 (m), 1364 (w), 1331 (m), 1300 (w), 1242 (s), 1207 (s), 1174 (s), 1100 (m), 1073 (w), 1030 (s), 985 (w), 956 (w), 830 (m), 810 (m), 764 (w), 686 (w), 637 (w), 581 (w), 555 (w), 526 (m). GC-MS (EI, 70 eV): m/z (%) = 358 (M⁺, 5), 326 (10), 270 (21), 121 (100), 78 (6).

HRMS (EI): Calcd. for C₂₀H₂₂O₆ ([M⁺]: 358.14109; found: 358.140227.

1-Ethyl 3-methyl 4-hydroxy-5-methoxy-2,6-dimethylisophthalate (4j): Starting with 3 (0.305 g, 1.25 mmol) and 1j (0.363 g, 1.25 mmol), 4j was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellow oil (0.230 g, 65%).

1H NMR (CDCl₃, 250 MHz): δ = 1.39 (t, 3J = 7.3 Hz, 3 H, OCH₂CH₃), 2.23 (s, 3 H, PhCH₃), 2.41 (s, 3 H, PhCH₃), 3.97 (s, 3 H, OCH₃), 3.98 (s, 3 H, OCH₃), 4.38 (q, 3J = 7.3 Hz, 2 H, OCH₂CH₃), 11.30 (s, 1 H, OH), 13C NMR (CDCl₃, 75 MHz): δ = 13.3, 14.2, 19.8 (CH₃), 52.4, 60.1 (OCH₃), 61.3 (OCH₂CH₃), 111.8, 128.4, 131.7, 134.0, 144.7 (C₆H₅), 156.1 (COH), 169.5, 171.7 (CO).

IR (neat, cm⁻¹): ν̃ = 3422 (br, w), 2982 (m), 2957 (w), 2939 (m), 2838 (s), 1726 (s), 1683 (s), 1600 (m), 1578 (m). MS (EI, 70 eV): m/z (%) = 282 (M⁺, 35), 250 (93), 237 (23), 222 (100), 205 (26), 194 (43). Anal.: calcd. for C₁₄H₁₈O₆ (282.29): C, 59.57; H, 6.43. Found: C, 59.65; H, 6.44.

Diethyl 4-hydroxy-2,6-dimethyl-5-phenoxyisophthalate (4k). Starting with 3 (0.366 g, 1.5 mmol) and 1k (0.577 g, 1.6 mmol), 4k was isolated after chromatography (silica gel, n-heptane/EtOAc) as reddish viscous oil (0.260 g, 48%).

1H NMR (250 MHz, CDCl₃): δ = 1.31 (t, 3J = 7.4 Hz, 3 H, OCH₂CH₃), 1.34 (t, 3J = 7.6 Hz, 3 H, OCH₂CH₃), 2.07 (s, 3 H, PhCH₃), 2.42 (s, 3 H, PhCH₃), 2.43 (q, 3J = 7.3 Hz, 2 H, OCH₂CH₃), 4.37 (q, 3J = 7.4 Hz, 2 H, OCH₂CH₃), 6.76 (d, 3J = 7.4 Hz, 2 H, CHAr), 6.89 (m, 1 H, CHAr), 6.94 (m, 2 H, CHAr), 11.27 (s, 1 H, OH). 13C NMR (62 MHz, CDCl₃): δ = 12.7, 13.1, 19.0, 19.2 (CH₃),
Diethyl 4-hydroxy-2,6-dimethyl-5-(2-tolyloxy)isophthalate (4l). Starting with 3 (0.488 g, 2.0 mmol) and 1l (0.837 g, 2.2 mmol), 4l was isolated after chromatography (silica gel, n-heptane/EtOAc) as a reddish viscous oil (0.312 g, 42%). 1H NMR (250 MHz, CDCl3): δ = 1.32 (t, 3J = 7.2 Hz, 3 H, OCH2CH3), 1.35 (t, 3J = 7.4 Hz, 3 H, OCH2CH3), 2.05 (s, 3 H, PhCH3), 2.24 (s, 3 H, PhCH3), 2.43 (s, 3 H, PhCH3), 4.35 (q, 3J = 7.4 Hz, 2 H, OCH2CH3), 4.38 (q, 3J = 7.6 Hz, 2 H, OCH2CH3), 6.54 (s, 1 H, CHAr), 6.56 (m, 2 H, 2 CHAr), 6.75 (d, 3J = 7.5 Hz, 1 H, CHAr), 11.20 (s, 1 H, OH). 13C NMR (62 MHz, CDCl3): δ = 15.6, 16.0, 16.1, 21.9, 23.3 (CH3), 63.2, 64.0 (CH2), 113.1 (CHAr), 114.2 (CAr), 117.1, 124.7, 130.5 (CHAr), 131.3 135.4, 136.8, 140. 9, 141.6 (CAr), 157.8 (COH), 159.4 (CAr), 171.1, 172.8 (CO). IR (neat, cm⁻¹): v = 2979 (w), 1723 (s), 1658 (s), 15 86 (m), 1444 (s), 1367 (m), 1321 (s), 1218 (s), 1139 (s), 1032 (s), 939 (m), 771 (m), 686 (m). MS (EI, 70 eV): m/z (%) = 372 ([M⁺], 33), 326 (49), 297 (84), 281 (12), 254 (13), 225 (4), 119 (100). HRMS (EI): Calcd. for C21H24O6: 372.15673; found: 372.15665.

Diethyl 4-hydroxy-2,6-dimethyl-5-(3-tolyloxy)isophthalate (4m). Starting with 3 (0.488 g, 2.0 mmol) and 1m (0.836 g, 2.2 mmol), 4m was isolated after chromatography (silica gel, n-heptane/EtOAc) as a reddish viscous oil (0.382 g, 51%). 1H NMR (250 MHz, CDCl3): δ = 1.31 (t, 3J = 7.4 Hz, 3 H, OCH2CH3), 1.35 (t, 3J = 7.6 Hz, 3 H, OCH2CH3), 2.07 (s, 3 H, PhCH3), 2.22 (s, 3 H, PhCH3), 2.42 (s, 3 H, PhCH3), 4.36 (q, 3J = 7.2 Hz, 2 H, OCH2CH3), 4.38 (q, 3J = 7.6 Hz, 2 H, OCH2CH3), 6.56 (m, 2 H, 2 CHAr), 6.72 (d, 3J = 7.6 Hz, 1 H, CHAr), 7.06 (m, 1 H, CHAr), 11.25 (s, 1 H, OH). 13C NMR (62 MHz, CDCl3): δ = 13.7, 14.1, 14.2, 20.0, 21.4 (CH3), 61.4, 61.8 (CH2), 111.5 (CHAr), 112.3 (CAr), 115.3, 122.8 (CHAr), 128.6 (CAr), 129.2 (CHAr), 133.5, 135.0, 139.0, 139.7 (CAr), 155.9 (COH), 157.5 (CAr), 169.3, 170.9 (CO). IR (neat, cm⁻¹): v = 1660 (s), 1619 (m), 1452 (s), 1343 (s), 1219
3-Acetyl-4-hydroxy-2,6-dimethyl-benzoic acid ethylester (4n): Starting with 3 (0.305 g, 1.25 mmol) and 1n (0.305 g, 1.25 mmol), 4n was isolated after chromatography (silica gel, n-heptane/EtOAc) as a yellow oil (0.113 g, 38%). 1H NMR (CDCl3, 250 MHz): \( \delta = 1.39 \ (t, ^3J = 7.0 \ Hz, 3H, OCH_2CH_3), 2.27 \ (s, 3H, PhCH_3), 2.49 \ (s, 3H, PhCH_3), 2.63 \ (s, 3H, PhCH_3) \), 4.39 \ (q, ^3J = 7.0 \ Hz, 2H, OCH_2CH_3), 6.69 \ (s, 1H, CH_Ar), 11.83 \ (s, 1H, OH). 13C NMR (CDCl3, 75 MHz): \( \delta = 14.2, 20.1, 20.6, 33.1 \ (CH_3), 61.3 \ (OCH_2CH_3), 117.5 \ (CH_Ar), 120.6, 128.4, 136.1, 142.3 \ (C_Ar), 161.8 \ (COH), 169.5, 205.7 \ (CO). IR (neat, cm\(^{-1}\)): \( \tilde{\nu} = 3337 \ (s, \text{br}), 2982 \ (s), 2935 \ (m), 2909 \ (m), 2874 \ (w), 1722 \ (s), 1695 \ (s), 1631 \ (s), 1599 \ (s). \) MS (EI, 70 eV): \( m/z \ (%) = 236 \ (M^+, 60), 221 \ (100), 207 \ (37), 193 \ (83), 191 \ (79), 175 \ (42), 91 \ (35). \) Anal.: calcd. for C\(_{13}H_{16}O_4\) (236.26): C, 66.09; H, 6.83. Found: C, 66.05; H, 6.90.

3-Benzoyl-4-hydroxy-2,6-dimethyl-benzoic acid ethylester (4o). Starting with 3 (0.305 g, 1.25 mmol) and 1o (0.386 g, 1.25 mmol), 4o was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellow oil (0.135 g, 36%). 1H NMR (CDCl3, 250 MHz): \( \delta = 1.36 \ (t, ^3J = 7.0 \ Hz, 3H, OCH_2CH_3), 1.96 \ (s, 3H, PhCH_3), 2.32 \ (s, 3H, PhCH_3), 4.35 \ (q, ^3J = 7.0 \ Hz, 2H, OCH_2CH_3), 7.73 – 7.42 \ (m, 5H, 5 CH_Ar), 6.73 \ (s, 1H, CH_Ar), 8.66 \ (s, 1H, OH). 13C NMR (CDCl3, 63 MHz): \( \delta = 14.2, 19.8, 20.1 \ (CH_3), 61.2 \ (OCH_2CH_3), 116.3 \ (CH_Ar), 121.6, 128.1 \ (C_Ar), 128.8 \ (2 CH_Ar), 129.1 \ (2 CH_Ar), 133.2 \ (CH_Ar), 135.7, 139.4, 140.9 \ (C_Ar), 158.1 \ (COH), 169.4, 200.1 \ (CO). \) IR (KBr, cm\(^{-1}\)): \( \tilde{\nu} = 3305 \ (w, \text{br}), 2979 \ (w), 2972 \ (s), 1712 \ (s), 1667 \ (s), 1595 \ (s), 1448 \ (m), 1363 \ (m), 1309 \ (m), 1283 \ (m), 1228 \ (s), 1174 \ (s), 1132 \ (s), 1052 \ (m), 937 \ (w), 922 \ (s), 851 \ (m), 806 \ (w), 758 \ (w), 711 \ (s), 686 \ (s), 622 \ (s), 587 \ (m). \) MS (EI, 70 eV): \( m/z \ (%) = 299 \ ([M+1]^+, 9), 298 \ ([M^+]^+, 51), 251 \ (100), 224 \ (18), 193 \ (10), 175 \ (17), 105 \ (32), 91 \ (9), 77 \ (26). \) HRMS (EI, 70 eV): calcd. for C\(_{18}H_{18}O_4\) (M\(^+\)): 298.1200, found: 298.1193.
**Typical experimental procedure for the synthesis of 7a-ae.** To a CH$_2$Cl$_2$ solution (2 mL / 1 mmol of 6a-e) of 6a-e was added 1 (1.1 mmol) and, subsequently, TiCl$_4$ (1.1 mmol) at −78 °C. The temperature of the solution was allowed to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The latter was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic layers were dried (Na$_2$SO$_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, heptanes / EtOAc) to give 7a-ae.

**Dimethyl 4-hydroxy-2-methylisophthalate (7a).** Starting with 6a (0.237 g, 1.5 mmol) and 1a (0.429 g, 1.7 mmol), 7a was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.144 g, 43%), mp. = 88 - 90 °C. $^1$H NMR (250 MHz, CDCl$_3$): δ = 2.63 (s, 3 H, PhCH$_3$), 3.79 (s, 3 H, OCH$_3$), 3.91 (s, 3 H, OCH$_3$), 6.78 (d, $^3$J = 8.7 Hz, 1 H, CH$_{Ar}$), 7.76 (d, $^3$J = 8.9 Hz, 1 H, CH$_{Ar}$), 10.98 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ = 20.0 (CH$_3$), 52.0, 52.5 (OCH$_3$), 114.5 (CCOOCH$_3$), 115.2 (CH$_{Ar}$), 123.9 (CCOOCH$_3$), 135.8 (CH$_{Ar}$), 143.6 (C$_{Ar}$), 163.9 (COH), 168.0, 171.7 (CO). IR (KBr, cm$^{-1}$): v = 3339 (w), 2989 (w), 2959 (w), 2924 (w), 2853 (w), 1715 (m), 1688 (m), 1651 (m), 1583 (m), 1537 (m), 1430 (m), 1386 (m), 1321 (m), 1243 (m), 1195 (s), 1151 (s), 1050 (m), 1018 (m), 960 (m), 944 (m), 858 (m), 797 (s), 754 (m), 707 (s), 652 (m), 560 (m). GC-MS (EI, 70 eV): m/z (%) = 224 ([M]$^+$, 31), 193 (30), 192 (100), 161 (56), 160 (26), 149 (13), 133 (12), 132 (12), 105 (10), 77 (15), 51 (11). HRMS (EI): Calcd. for C$_{11}$H$_{12}$O$_5$ ([M]$^+$): 224.06792; found: 224.067341.

**Dimethyl 4-hydroxy-2,5-dimethylisophthalate (7b).** Starting with 6a (0.237 g, 1.5 mmol) and 1p (0.457 g, 1.7 mmol), 7b was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.205 g, 57%), mp. = 110 - 112 °C. $^1$H NMR (250 MHz, CDCl$_3$): δ = 2.15 (s, 3 H, PhCH$_3$), 2.60 (s, 3 H, PhCH$_3$), 3.78 (s, 3 H, OCH$_3$), 3.90 (s, 3 H, OCH$_3$), 7.75 (s, 1 H, CH$_{Ar}$), 11.22 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ = 15.7, 19.8 (CH$_3$), 51.9, 52.4 (OCH$_3$), 113.7 (CCOOCH$_3$), 123.0 (C$_{Ar}$), 124.0 (CCOOCH$_3$), 136.3 (CH$_{Ar}$), 140.6 (C$_{Ar}$), 162.4 (COH), 168.2, 172.1 (CO). IR (KBr, cm$^{-1}$): v = 3349 (w), 2992 (w), 2989 (w), 2959 (w), 2924 (w), 2853 (w), 1715 (m), 1688 (m), 1651 (m), 1583 (m), 1537 (m), 1430 (m), 1386 (m), 1321 (m), 1243 (m), 1195 (s), 1151 (s), 1050 (m), 1018 (m), 960 (m), 944 (m), 858 (m), 797 (s), 754 (m), 707 (s), 652 (m), 560 (m).
3-Ethyl 1-methyl 5-ethyl-4-hydroxy-2-methylisophthalate (7c). Starting with 6a (0.237 g, 1.5 mmol) and 1c (0.499 g, 1.7 mmol), 7c was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.200 g, 50%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 1.05$ (t, $^3J = 7.5$ Hz, 3 H, CH$_2$CH$_3$), 1.27 (t, $^3J = 6.7$ Hz, 3 H, OCH$_2$CH$_3$), 2.48 (q, $^3J = 7.3$ Hz, 2 H, CH$_2$CH$_3$), 2.52 (s, 3 H, PhCH$_3$), 3.71 (s, 3 H, OCH$_3$), 4.30 (q, $^3J = 7.0$ Hz, 2 H, OCH$_2$CH$_3$), 7.55 (s, 1 H, CH Ar), 11.21 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 13.5$, 14.1, 19.9 (CH$_3$), 23.1 (CH$_2$), 52.0 (OCH$_3$), 62.2 (OCH$_2$), 114.3 (CCOOCH$_3$)$_2$, 123.4 (CCOOCH$_3$)$_2$, 129.8 (C$_{Ar}$), 134.9 (CH$_{Ar}$), 140.8 (C$_{Ar}$), 162.5 (COH), 168.5, 171.9 (CO). IR (neat, cm$^{-1}$): $\nu = 2967$ (w), 2874 (w), 1718 (m), 1565 (m), 1580 (w), 1429 (m), 1396 (w), 1372 (m), 1326 (m), 1261 (m), 1227 (s), 1199 (s), 1154 (s), 1095 (w), 1043 (m), 1019 (m), 959 (w), 844 (w), 809 (m), 780 (m), 743 (w), 650 (m), 535 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 266 ([M$^+$], 25), 221 (17), 220 (63), 193 (12), 192 (100), 189 (15), 177 (10), 77 (11), 29 (7). HRMS (EI): Calcd. for C$_{14}$H$_{18}$O$_5$ ([M$^+$]): 266.11488; found: 266.115159.

Dimethyl 5-butyl-4-hydroxy-2-methylisophthalate (7d). Starting with 6a (0.237 g, 1.5 mmol) and 1q (0.522 g, 1.7 mmol), 7d was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.218 g, 52%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.85$ (t, $^3J = 7.5$ Hz, 3 H, (CH$_2$)$_3$CH$_3$), 1.25 – 1.35 (m, 2 H, CH$_2$), 1.48 – 1.53 (m, 2 H, CH$_2$), 2.54 (t, $^3J = 7.5$ Hz, 2 H, PhCH$_2$), 2.58 (s, 3 H, PhCH$_3$), 3.79 (s, 3 H, OCH$_3$), 3.90 (s, 3 H, OCH$_3$), 7.62 (s, 1 H, CH Ar), 11.21 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 12.9$, 18.9 (CH$_3$), 21.5, 28.9, 30.4 (CH$_2$), 50.9, 51.5 (OCH$_3$), 113.0 (CCOOCH$_3$), 122.1 (C$_{Ar}$), 127.6 (CCOOCH$_3$), 134.8 (CH$_{Ar}$), 139.6 (C$_{Ar}$), 161.1 (COH), 167.4, 171.2 (CO). IR (neat, cm$^{-1}$): $\nu = 3024$ (w), 2989 (w), 2957 (w), 2932 (w), 2865 (w), 1713 (s), 1659 (m), 1608 (w), 1579 (w), 1431 (s), 1377 (w), 1337 (m), 1259 (m), 1228 (s), 1199 (s), 1152 (s), 1049 (m), 994 (m), 962 (m), 894 (m), 872 (w), 808 (m), 767 (m), 653 (m), 544 (w). GC-MS (EI, 70 eV): $m/z$ (%)
Dimethyl 5-hexyl-4-hydroxy-2-methylisophthalate (7e). Starting with 6a (0.237 g, 1.5 mmol) and 1d (0.568 g, 1.7 mmol), 7e was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.254 g, 55%). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.72 (t, J = 7.5 \text{ Hz}, 3 \text{ H}, (\text{CH}_2)_5\text{CH}_3), 1.11 - 1.20 (m, 6 \text{ H}, 3 \text{ CH}_2), 1.40 - 1.47 (m, 2 \text{ H}, \text{CH}_2), 2.44 (t, J = 7.5 \text{ Hz}, 2 \text{ H}, \text{PhCH}_2), 2.51 (s, 3 \text{ H}, \text{PhCH}_3), 3.71 (s, 3 \text{ H}, \text{OCH}_3), 3.82 (s, 3 \text{ H}, \text{OCH}_3), 7.54 (s, 1 \text{ H}, \text{CH Ar}), 11.13 (s, 1 \text{ H}, \text{OH}). \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta = 14.0, 19.8 (\text{CH}_3), 22.6, 29.1, 29.2, 29.7, 31.7 (\text{CH}_2), 51.9, 52.4 (\text{OCH}_3), 113.9 (\text{CCOOCH}_3), 123.1 (\text{C}_\text{Ar}), 128.7 (\text{CCOOCH}_3), 135.7 (\text{C}_\text{Ar}), 140.5 (\text{C}_\text{Ar}), 162.0 (\text{COH}), 168.3, 172.2 (\text{CO}).\) IR (neat, cm\(^{-1}\)): \(v = 3400 (w), 2952 (w), 2923 (w), 2853 (w), 1720 (m), 1659 (m), 1608 (w), 1580 (w), 1432 (m), 1335 (m), 1227 (s), 1194 (s), 1150 (s), 1045 (m), 990 (m), 961 (w), 889 (w), 809 (w), 779 (m), 723 (w), 651 (m), 555 (w). GC-MS (EI, 70 eV): \(m/z (\%) = 308 ([M]^+, 37), 277 (23), 276 (20), 259 (16), 248 (40), 247 (31), 245 (11), 233 (13), 220 (10), 219 (17), 217 (14), 207 (16), 206 (100), 205 (33), 178 (35), 173 (42), 91 (10), 77 (10), 43 (8).\) HRMS (EI): Calcd. for C\(_{17}\)H\(_{24}\)O\(_5\) ([M]^+): 308.161683; found: 308.161283.

Dimethyl 5-hexyl-4-hydroxy-2-methylisophthalate (7f). Starting with 6a (0.237 g, 1.5 mmol) and 1r (0.591 g, 1.7 mmol), 7f was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.246 g, 51%). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.78 (t, J = 7.5 \text{ Hz}, 3 \text{ H}, (\text{CH}_2)_6\text{CH}_3), 1.18 - 1.22 (m, 8 \text{ H}, 4 \text{ CH}_2), 1.48 - 1.54 (m, 2 \text{ H}, \text{CH}_2), 2.53 (t, J = 7.5 \text{ Hz}, 2 \text{ H}, \text{PhCH}_2), 2.58 (s, 3 \text{ H}, \text{PhCH}_3), 3.79 (s, 3 \text{ H}, \text{OCH}_3), 3.89 (s, 3 \text{ H}, \text{OCH}_3), 7.62 (s, 1 \text{ H}, \text{CH Ar}), 11.22 (s, 1 \text{ H}, \text{OH}).\(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta = 13.0, 18.8 (\text{CH}_3), 21.6, 27.7, 27.8, 28.2, 28.7, 30.8 (\text{CH}_2), 50.9, 51.4 (\text{OCH}_3), 112.9 (\text{CCOOCH}_3), 122.1 (\text{C}_\text{Ar}), 127.6 (\text{CCOOCH}_3), 134.7 (\text{C}_\text{Ar}), 139.6 (\text{C}_\text{Ar}), 161.1 (\text{COH}), 167.4, 171.4 (\text{CO}).\) IR (neat, cm\(^{-1}\)): \(v = 3400 (w), 2952 (w), 2923 (w), 2853 (w), 1720 (m), 1659 (m), 1610 (w), 1579 (w), 1433 (m), 1379 (w), 1336 (m), 1228 (s), 1195 (s), 1152 (s), 1046 (m), 997 (w), 889 (w), 809 (m), 779 (m), 723 (w), 651 (m), 555 (w). GC-MS (EI, 70 eV): \(m/z (\%) = 322 ([M]^+, 33), 291 (23), 290 (19), 273 (14), 262 (32), 247 (29), 233 (11), 231 (14), 219 (17), 207 (17), 206 (100), 205 (23), 189 (19), 178 (40), 173 (34), 91 (10), 77 (11).\) HRMS (EI): Calcd. for C\(_{13}\)H\(_{20}\)O\(_5\) ([M]^+): 280.13053; found: 280.130756.
206 (100), 205 (33), 178 (33), 173 (40), 91 (10), 77 (9), 43 (10), 29 (8). HRMS (EI): Calcd. for C_{18}H_{26}O_{5} ([M]^+): 322.17748; found: 322.177264.

**Dimethyl 4-hydroxy-2-methyl-5-octylisophthalate (7g).** Starting with 6a (0.237 g, 1.5 mmol) and 1s (0.614 g, 1.7 mmol), 7g was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.241 g, 48%). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.80 (t, ^3J = 7.5 \text{ Hz}, 3 \text{ H}, (\text{CH}_2)_7\text{CH}_3), 1.15 – 1.23 (m, 10 \text{ H}, 5 \text{ CH}_2), 1.51 – 1.53 (m, 2 \text{ H}, \text{CH}_2), 2.54 (t, ^3J = 7.7 \text{ Hz}, 2 \text{ H}, \text{PhCH}_2), 2.59 (s, 3 \text{ H}, \text{PhCH}_3), 3.80 (s, 3 \text{ H}, \text{OCH}_3), 3.90 (s, 3 \text{ H}, \text{OCH}_3), 7.62 (s, 1 \text{ H}, \text{CH}_{\text{Ar}}), 11.21 (s, 1 \text{ H}, \text{OH}). \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta = 14.0, 19.8 (\text{CH}_3), 22.6, 29.2, 29.4, 29.5, 29.6, 29.7, 31.8 (\text{CH}_2), 51.9, 52.4 (\text{OCH}_3), 113.9 (\text{CCOOCH}_3), 123.1 (\text{CAr}), 128.8 (\text{CCOOCH}_3), 135.7 (\text{CAr}), 140.6 (\text{CAr}), 162.0 (\text{COH}), 168.4, 172.1 (\text{CO}). \text{IR (neat, cm}^{-1})\): \(v = 2952 (w), 2924 (w), 2853 (w), 1720 (m), 1699 (m), 1605 (w), 1552 (w), 1434 (m), 1377 (w), 1336 (m), 1229 (s), 1202 (s), 1153 (s), 1045 (m), 996 (w), 911 (w), 809 (m), 759 (m), 700 (m), 652 (w), 566 (w). \text{GC-MS (EI, 70 eV): m/z} \%(\text{[M]+}) = 336 (35), 305 (20), 304 (14), 287 (13), 276 (32), 247 (34), 245 (17), 233 (12), 219 (18), 207 (15), 206 (100), 205 (30), 178 (33), 173 (39), 91 (11), 43 (10), 41 (10), 29 (7). HRMS (EI): Calcd. for C_{19}H_{28}O_{5} ([M]^+): 336.19313; found: 336.193115.

**Dimethyl 4-hydroxy-2-methyl-5-nonylbenzene-1,3-dioate (7h).** Starting with 6a (0.237 g, 1.5 mmol) and 1e (0.522 g, 1.7 mmol), 7h was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.273 g, 52%), mp. 56 - 57 °C. \(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 0.80 (t, ^3J = 7.3 \text{ Hz}, 3 \text{ H}, (\text{CH}_2)_8\text{CH}_3), 1.19 – 1.26 (m, 6 \text{ CH}_2), 1.47 – 1.55 (m, 2 \text{ H}, \text{CH}_2), 2.54 (t, ^3J = 7.2 \text{ Hz}, 2 \text{ H}, \text{PhCH}_2), 2.59 (s, 3 \text{ H}, \text{PhCH}_3), 3.80 (s, 3 \text{ H}, \text{OCH}_3), 3.90 (s, 3 \text{ H}, \text{OCH}_3), 7.62 (s, 1 \text{ H}, \text{CH}_{\text{Ar}}), 11.20 (s, 1 \text{ H}, \text{OH}). \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \(\delta = 13.1, 18.8 (\text{CH}_3), 21.6, 28.2, 28.3, 28.4, 28.5, 28.7, 29.9, 30.9 (\text{CH}_2), 50.9, 51.4 (\text{OCH}_3), 112.9 (\text{CCOOCH}_3), 122.1 (\text{CCOOCH}_3), 127.6 (\text{CAr}), 134.7 (\text{CAr}), 139.6 (\text{CAr}), 161.0 (\text{COH}), 167.3, 171.2 (\text{CO}). \text{IR (KBr, cm}^{-1})\): \(v = 3000 (w), 2954 (m), 2914 (m), 2851 (m), 1709 (m), 1665 (m), 1607 (w), 1579 (m), 1471 (m), 1437 (w), 1426 (w), 1382 (w), 1335 (m), 1252 (w), 1229 (s), 1210 (s), 1194 (s), 1149 (s), 1045 (m), 1003 (m), 986 (m), 972 (m), 961 (m), 920 (m), 887 (s), 802 (m), 791 (m), 781 (m), 743 (m), 714 (m), 659 (m), 610 (m), 561 (w). \text{GC-MS (EI, 70 eV): m/z} \%(\text{[M]+}) = 350 ([M]^+, 34), 319 (20), 290 (24), 259 (15), 247
3-(2-Methoxyethyl) 1-methyl 4-hydroxy-2-methylbenzene-1,3-dioate (7i). Starting with 6a (0.237 g, 1.5 mmol) and 1t (0.479 g, 1.7 mmol), 7i was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.193 g, 48%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 2.66$ (s, 3 H, PhCH$_3$), 3.36 (s, 3 H, OCH$_3$), 3.66 (t, $^3$J = 4.9 Hz, 2 H, OCH$_2$CH$_2$OCH$_3$), 3.80 (s, 3 H, OCH$_3$), 4.47 (t, $^3$J = 4.7 Hz, 2 H, OCH$_2$CH$_2$OCH$_3$), 6.78 (d, $^3$J = 8.7 Hz, 1 H, CH$_{Ar}$), 7.78 (d, $^3$J = 9.0 Hz, 1 H, CH$_{Ar}$), 10.51 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 20.6$ (CH$_3$), 52.7, 59.6 (OCH$_3$), 65.2, 70.5 (OCH$_2$), 115.9 (CH$_{Ar}$), 116.0 (CCOOCH$_2$CH$_2$OCH$_3$), 124.7 (CCOOCH$_3$), 136.5 (CH$_{Ar}$), 144.3 (C$_{Ar}$), 164.0 (COH), 168.6, 171.1 (CO). IR (KBr, cm$^{-1}$): $v =$ 3281 (w), 2951 (w), 2924 (w), 2851 (w), 1716 (m), 1661 (w), 1588 (m), 1470 (w), 1434 (w), 1378 (w), 1315 (w), 1224 (m), 1200 (m), 1048 (s), 1028 (s), 955 (m), 868 (m), 834 (m), 804 (m), 783 (m), 709 (m), 653 (m), 608 (m), 543 (m). GC-MS (EI, 70 eV): m/z (%) = 268 ([M$^+$], 17), 237 (8), 192 (100), 161 (32), 133 (5), 105 (6), 77 (7), 59 (11), 45 (5). HRMS (EI): Calcd. for C$_{13}$H$_{16}$O$_6$ ([M$^+$]: 268.09414; found: 268.094150.

Dimethyl 2-hydroxy-4,4'-dimethylbiphenyl-3,5-dicarboxylate (7j). Starting with 6a (0.237 g, 1.5 mmol) and 1g (0.403 g, 1.65 mmol), 7j was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.250 g, 53 %), mp. = 83 - 85 °C. $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 2.32$ (s, 3 H, PhCH$_3$), 2.65 (s, 3 H, PhCH$_3$), 3.80 (s, 3 H, OCH$_3$), 3.93 (s, 3 H, OCH$_3$), 7.15 – 7.19 (m, 2 H, 2 CH$_{Ar}$), 7.34 – 7.37 (m, 2 H, 2 CH$_{Ar}$), 7.83 (s, 1 H, CH$_{Ar}$), 11.04 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 18.9, 20.2$ (CH$_3$), 51.0, 51.6 (OCH$_3$), 114.3 (CCOOCH$_3$), 122.6 (CCOOCH$_3$), 126.9 (C$_{Ar}$), 128.0 (2 CH$_{Ar}$), 128.2 (2 CH$_{Ar}$), 132.6 (C$_{Ar}$), 135.4 (C$_{Ar}$), 136.4, 141.0 (C$_{Ar}$), 159.5 (COH), 167.0, 171.0 (CO). IR (KBr, cm$^{-1}$): $v =$ 3027 (w), 3012 (w), 2953 (w), 2924 (w), 2853 (w), 1771 (w), 1718 (m), 1684 (w), 1663 (m), 1653 (m), 1636 (w), 1616 (w), 1608 (w), 1576 (w), 1558 (w), 1540 (w), 1533 (w), 1516 (w), 1507 (w), 1497 (w), 1489 (w), 1472 (w), 1456 (w), 1436 (m), 1399 (w), 1338 (m), 1240 (m), 1209 (m), 1103 (w), 1052 (w), 1028 (w), 958 (w), 910 (w), 822 (w), 783 (w), 733 (m), 668 (w), 650 (w), 617 (w), 608 (w), 567 (w), 541 (w). GC-MS (EI,
70 eV): m/z (%) = 314 ([M+], 42), 282 (100), 267 (5), 251 (14), 239 (16), 222 (13), 195 (14), 165 (13), 152 (12), 132 (12), 119 (29), 105 (18), 91 (19), 69 (22), 57 (29), 43 (20).

HRMS (EI): Calcd. for C_{18}H_{18}O_{5} ([M]+): 314.11488; found: 314.114827

**Dimethyl 4'-chloro-2-hydroxy-4-methylbiphenyl-3,5-dicarboxylate (7k).** Starting with 6a (0.237 g, 1.5 mmol) and 1h (0.612 g, 1.7 mmol), 7k was isolated after chromatography (silica gel, heptanes/EtOAc) as brownish crystals (0.241 g, 48%), mp. = 160 - 161 °C. \(^{1}H\) NMR (250 MHz, CDCl\(_3\)): \(\delta = 2.65\) (s, 3 H, PhCH\(_3\)), 3.80 (s, 3 H, OCH\(_3\)), 3.93 (s, 3 H, OCH\(_3\)), 7.28 – 7.33 (m, 2 H, 2 CH\(_{Ar}\)), 7.38 – 7.43 (m, 2 H, 2 CH\(_{Ar}\)), 7.81 (s, 1 H, CH\(_{Ar}\)), 11.36 (s, 1 H, OH). \(^{13}C\) NMR (CDCl\(_3\), 75 MHz): \(\delta = 19.1\) (CH\(_3\)), 51.1, 51.7 (OCH\(_3\)), 114.0 (CCOOCH\(_3\)), 122.9 (CCOOCH\(_3\)), 125.6 (C\(_{Ar}\)), 127.4 (2 CH\(_{Ar}\)), 129.6 (2 CH\(_{Ar}\)), 132.6, 134.0 (C\(_{Ar}\)), 141.8 (C\(_{Ar}\)), 159.7 (COH), 166.8, 171.0 (CO). IR (KBr, cm\(^{-1}\)): \(v = 3000\) (w), 2951 (w), 1716 (m), 1662 (m), 1603 (m), 1579 (m), 1562 (w), 1520 (m), 1439 (m), 1425 (m), 1389 (m), 1375 (m), 1323 (m), 1301 (m), 1239 (m), 1194 (s), 1171 (s), 1105 (m), 1085 (m), 1051 (m), 1025 (m), 1010 (m), 949 (m), 926 (m), 876 (m), 825 (m), 806 (m), 782 (m), 771 (m), 746 (m), 719 (m), 675 (m), 650 (m), 629 (m), 613 (m), 540 (m). GC-MS (EI, 70 eV): m/z (%) = 336 ([M+], 37Cl, 6), 334 ([M+], 35Cl, 17), 302 (100), 296 (20), 270 (12), 242 (7), 215 (4), 152 (11), 125 (8), 104 (6), 86 (10), 43 (9). HRMS (EI): Calcd. for C\(_{17}\)H\(_{15}\)O\(_{5}\)Cl ([M]+): 334.06025; found: 334.059873.

**Dimethyl 4-hydroxy-5-methoxy-2-methylbenzene-1,3-dioate (7l).** Starting with 6a (0.237 g, 1.5 mmol) and 1j (0.360 g, 1.7 mmol), 7l was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.198 g, 52%). \(^{1}H\) NMR (250 MHz, CDCl\(_3\)): \(\delta = 2.45\) (s, 3 H, PhCH\(_3\)), 3.76 (s, 3 H, OCH\(_3\)), 3.79 (s, 3 H, OCH\(_3\)), 7.32 (s, 1 H, CH\(_{Ar}\)), 9.41 (s, 1 H, OH). \(^{13}C\) NMR (CDCl\(_3\), 75 MHz): \(\delta = 18.7\) (CH\(_3\)), 52.0, 52.6, 56.2 (OCH\(_3\)), 115.5 (CH\(_{Ar}\)), 117.6 (CCOOCH\(_3\)), 122.3 (CCOOCH\(_3\)), 133.4, 145.3 (C\(_{Ar}\)), 151.6 (COH), 167.7, 170.4 (CO). IR (KBr, cm\(^{-1}\)): \(v = 3400\) (w), 3001 (w), 2951 (w), 2842 (w), 1713 (m), 1662 (m), 1610 (w), 1587 (m), 1492 (m), 1433 (m), 1385 (w), 1357 (m), 1305 (m), 1282 (m), 1200 (s), 1167 (s), 1082 (s), 1048 (m), 1029 (s), 959 (m), 914 (w), 886 (m), 858 (w), 806 (w), 780 (m), 730 (m), 688 (w), 671 (w), 647 (w), 621 (w), 592 (w), 553 (w). GC-MS (EI, 70 eV): m/z (%) = 254 ([M+], 38), 222 (100), 207 (4), 194 (53), 179 (20), 163

**Dimethyl 2-ethyl-4-hydroxy-5-methylisophthalate (7m).** Starting with \( 6\text{b} \) (0.258 g, 1.5 mmol) and \( 1\text{p} \) (0.457 g, 1.7 mmol), 7m was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.196 g, 52%). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 1.14 \) (t, \( \text{J} = 7.7 \text{ Hz}, 3 \text{ H, CH}_2\text{CH}_3 \)), 2.21 (s, 3 H, PhCH\(_3\)), 3.09 (q, \( \text{J} = 7.1 \text{ Hz}, 2 \text{ H, CH}_2\text{CH}_3 \)), 3.79 (s, 3 H, OCH\(_3\)), 3.91 (s, 3 H, OCH\(_3\)), 7.63 (s, 1 H, CH\(_{\text{Ar}}\)), 11.14 (s, 1 H, OH). \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \( \delta = 14.8, 15.0 \) (CH\(_3\)), 24.2 (CH\(_2\)), 50.9, 51.5 (OCH\(_3\)), 112.2 (CCOOCH\(_3\)), 121.5 (C\(_{\text{Ar}}\)), 123.4 (CCOOCH\(_3\)), 136.0 (CH\(_{\text{Ar}}\)), 145.6 (C\(_{\text{Ar}}\)), 161.4 (COH), 167.3, 171.2 (CO). IR (neat, cm\(^{-1}\)): \( \nu = 2952 \) (w), 2930 (w), 2854 (w), 1719 (m), 1658 (m), 1610 (w), 1578 (w), 1432 (m), 1380 (w), 1333 (m), 1300 (m), 1277 (m), 1225 (s), 1192 (s), 1149 (s), 1071 (m), 1017 (m), 983 (m), 886 (w), 813 (m), 776 (m), 732 (m), 675 (m), 644 (m). GC-MS (EI, 70 eV): \( m/z \% = 252 \) ([M]+, 32), 221 (27), 220 (100), 189 (24), 177 (11), 170 (12), 161 (11), 160 (19), 133 (9), 132 (10), 103 (9), 77 (14). HRMS (EI): Calcd. for \( \text{C}_{13}\text{H}_{16}\text{O}_{5} \) ([M]+): 252.09923; found: 252.099203.

**3-Ethyl 1-methyl 2,5-diethyl-4-hydroxyisophthalate (7n).** Starting with \( 6\text{b} \) (0.258 g, 1.5 mmol) and \( 1\text{c} \) (0.499 g, 1.7 mmol), 7n was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.210 g, 50%). \(^1\)H NMR (250 MHz, CDCl\(_3\)): \( \delta = 1.11-1.19 \) (m, 6 H, 2 CH\(_3\)), 1.37 (t, \( \text{J} = 7.4 \text{ Hz}, 3 \text{ H, OCH}_2\text{CH}_3 \)), 2.58 (q, \( \text{J} = 7.4 \text{ Hz}, 2 \text{ H, PhCH}_2 \)), 3.11 (q, \( \text{J} = 7.5 \text{ Hz}, 2 \text{ H, PhCH}_2 \)), 3.79 (s, 3 H, OCH\(_3\)), 4.39 (q, \( \text{J} = 7.4 \text{ Hz}, 2 \text{ H, OCH}_2\text{CH}_3 \)), 7.63 (s, 1 H, CH\(_{\text{Ar}}\)), 11.22 (s, 1 H, OH). \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \( \delta = 13.4, 13.9, 15.2 \) (CH\(_3\)), 21.9, 23.9, 50.9 (CH\(_2\)), 61.1 (OCH\(_2\)), 112.4 (CCOOCH\(_2\text{H}_5\)), 121.6 (CCOOCH\(_3\)), 129.0 (C\(_{\text{Ar}}\)), 134.0 (C\(_{\text{Ar}}\)), 145.3 (C\(_{\text{Ar}}\)), 161.0 (COH), 167.3, 170.6 (CO). IR (neat, cm\(^{-1}\)): \( \nu = 2968 \) (w), 2935 (w), 2875 (w), 1722 (m), 1657 (m), 1608 (w), 1578 (w), 1429 (w), 1373 (w), 1323 (w), 1274 (m), 1229 (m), 1200 (m), 1156 (w), 1093 (w), 1061 (w), 1021 (w), 979 (w), 909 (w), 847 (w), 818 (w), 733 (m), 648 (w). GC-MS (EI, 70 eV): \( m/z \% = 280 \) ([M]+, 36), 249 (11), 235 (23), 234 (100), 206 (17), 203 (20), 191 (16), 175 (11), 174 (37), 147 (15), 146 (16), 91 (13), 77 (10). HRMS (EI): Calcd. for \( \text{C}_{15}\text{H}_{20}\text{O}_{5} \) ([M]+): 280.13053; found: 280.130632.
Dimethyl 5-butyl-2-ethyl-4-hydroxyisophthalate (7o). Starting with 6b (0.258 g, 1.5 mmol) and 1q (0.522 g, 1.7 mmol), 7o was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.229 g, 52%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.86$ (t, $^3J = 7.4$ Hz, 3 H, (CH$_2$)$_3$CH$_3$), 1.14 (t, $^3J = 7.4$ Hz, 3 H, CH$_2$CH$_3$), 1.25 – 1.34 (m, 2 H, CH$_2$), 1.45 – 1.54 (m, 2 H, CH$_2$), 2.55 (t, $^3J = 7.6$ Hz, 2 H, PhCH$_2$), 3.08 (q, $^3J = 7.4$ Hz, 2 H, PhCH$_2$), 3.78 (s, 3 H, OCH$_3$), 3.91 (s, 3 H, OCH$_3$), 7.62 (s, 1 H, CH$_{Ar}$), 11.08 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 13.9$, 16.0 (CH$_3$), 22.6, 25.1, 29.6, 31.4 (CH$_2$), 51.9, 52.5 (OCH$_3$), 113.4 (CCOOCH$_3$), 122.6 (C$_{Ar}$), 128.8 (CCOOCH$_3$), 135.9 (C$_{Ar}$), 146.4 (C$_{Ar}$), 162.0 (COH), 168.2, 172.1 (CO). IR (neat, cm$^{-1}$): $\nu = 2954$ (w), 2930 (w), 2873 (w), 2256 (w), 1721 (m), 1662 (m), 1606 (w), 1579 (w), 1434 (m), 1337 (w), 1276 (m), 1228 (m), 1202 (m), 1153 (w), 1068 (w), 986 (w), 908 (m), 816 (w), 732 (s), 648 (w). GC-MS (EI, 70 eV): m/z (%) = 294 ([M$^+$], 47), 263 (27), 262 (41), 247 (12), 245 (23), 233 (18), 231 (20), 221 (14), 220 (100), 219 (26), 203 (55), 192 (13), 187 (28), 160 (15), 159 (11), 131 (11), 103 (12), 91 (13), 77 (14). HRMS (EI): Calcd. for C$_{16}$H$_{22}$O$_5$ ([M$^+$]): 294.14618; found: 294.146337.

Dimethyl 2-ethyl-5-hexyl-4-hydroxyisophthalate (7p). Starting with 6b (0.258 g, 1.5 mmol) and 1d (0.568 g, 1.7 mmol), 7p was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.251 g, 52%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.79$ (t, $^3J = 7.6$ Hz, 3 H, (CH$_2$)$_5$CH$_3$), 1.13 (t, $^3J = 7.4$ Hz, 3 H, CH$_2$CH$_3$), 1.21 – 1.29 (m, 6 H, 3 CH$_2$), 1.46 – 1.53 (m, 2 H, CH$_2$), 2.53 (t, $^3J = 7.6$ Hz, 2 H, PhCH$_2$), 2.99 (q, $^3J = 7.3$ Hz, 2 H, PhCH$_2$), 3.78 (s, 3 H, OCH$_3$), 3.90 (s, 3 H, OCH$_3$), 7.61 (s, 1 H, CH$_{Ar}$), 11.08 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.0$, 16.0, (CH$_3$), 22.6, 25.0, 29.1, 29.2, 29.8, 31.7 (CH$_2$), 51.9, 52.5 (OCH$_3$), 113.3 (CCOOCH$_3$), 122.6 (C$_{Ar}$), 128.8 (CCOOCH$_3$), 135.9 (C$_{Ar}$), 146.4 (C$_{Ar}$), 161.9 (COH), 168.2, 172.1 (CO). IR (neat, cm$^{-1}$): $\nu = 2953$ (w), 2930 (w), 2873 (w), 2255 (w), 1719 (m), 1660 (m), 1606 (w), 1578 (w), 1433 (m), 1334 (m), 1272 (m), 1227 (s), 1200 (s), 1151 (m), 1087 (w), 1068 (w), 1047 (w), 992 (w), 906 (s), 816 (w), 729 (s), 648 (m). GC-MS (EI, 70 eV): m/z (%) = 323 (10), 322 ([M$^+$], 50), 291 (28), 290 (38), 273 (25), 262 (11), 261 (43), 259 (16), 247 (11), 234 (11), 233 (21), 231 (49), 221 (16), 220 (100), 219 (31), 205 (10), 192 (14), 187 (31), 160 (15), 131 (11), 103 (11), 91 (12), 77 (11). HRMS (EI): Calcd. for C$_{18}$H$_{26}$O$_5$ ([M$^+$]): 322.17748; found: 322.177229.
Dimethyl 2-ethyl-5-heptyl-4-hydroxyisophthalate (7q). Starting with 6b (0.258 g, 1.5 mmol) and 1r (0.591 g, 1.7 mmol), 7q was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.257 g, 51%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.81$ (t, $^3J = 7.6$ Hz, 3 H, (CH$_2$)$_6$CH$_3$), 1.14 (t, $^3J = 7.6$ Hz, 3 H, CH$_2$CH$_3$), 1.20 – 1.27 (m, 8 H, 4 CH$_2$), 1.49 – 1.54 (m, 2 H, CH$_2$), 2.53 (t, $^3J = 7.6$ Hz, 2 H, PhCH$_2$), 3.08 (q, $^3J = 7.4$ Hz, 2 H, PhCH$_2$), 3.79 (s, 3 H, OCH$_3$), 3.91 (s, 3 H, OCH$_3$), 7.62 (s, 1 H, CH$_{Ar}$), 11.08 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.1$, 16.0, (CH$_3$), 22.6, 25.1, 29.1, 29.2, 29.4, 29.8, 31.8 (CH$_2$), 51.9, 52.5 (OCH$_3$), 113.2 (CCOOCH$_3$), 122.7 (C$_{Ar}$), 129.0 (CCOOCH$_3$), 136.2 (CH$_{Ar}$), 146.6 (C$_{Ar}$), 162.3 (COH), 168.4, 172.2 (CO). IR (neat, cm$^{-1}$): $v = 2953$ (w), 2927 (m), 2855 (w), 2258 (w), 1722 (m), 1662 (m), 1606 (w), 1579 (w), 1434 (m), 1335 (w), 1275 (m), 1228 (m), 1202 (m), 1152 (w), 1069 (w), 990 (w), 908 (m), 816 (w), 733 (m), 648 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 337 (10), 336 ([M]+, 45), 305 (26), 304 (35), 287 (24), 275 (10), 273 (15), 262 (10), 261 (41), 247 (11), 246 (49), 234 (10), 233 (20), 221 (18), 220 (100), 205 (10), 192 (15), 161 (10), 160 (13), 159 (11), 131 (11), 103 (10), 91 (11), 43 (10). HRMS (EI): Calcd. for C$_{19}$H$_{28}$O$_5$ ([M]+): 336.19313; found: 336.193054.

Dimethyl 2-ethyl-4-hydroxy-5-octylisophthalate (7r). Starting with 6b (0.258 g, 1.5 mmol) and 1s (0.614 g, 1.7 mmol), 7r was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellow oil (0.263 g, 50%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.79$ (t, $^3J = 7.5$ Hz, 3 H, (CH$_2$)$_7$CH$_3$), 1.13 (t, $^3J = 7.6$ Hz, 3 H, CH$_2$CH$_3$), 1.22 – 1.36 (m, 10 H, 5 CH$_2$), 1.47 – 1.56 (m, 2 H, CH$_2$), 2.52 (t, $^3J = 7.6$ Hz, 2 H, PhCH$_2$), 3.06 (q, $^3J = 7.5$ Hz, 2 H, PhCH$_2$), 3.79 (s, 3 H, OCH$_3$), 3.90 (s, 3 H, OCH$_3$), 7.62 (s, 1 H, CH$_{Ar}$), 11.07 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 13.7$, 15.9, (CH$_3$), 22.1, 25.1, 28.9, 29.0, 29.2, 29.3, 29.8, 31.6 (CH$_2$), 51.6, 52.4 (OCH$_3$), 112.8 (CCOOCH$_3$), 121.7 (C$_{Ar}$), 128.7 (CCOOCH$_3$), 135.9 (CH$_{Ar}$), 146.1 (C$_{Ar}$), 161.9 (COH), 167.7, 171.9 (CO). IR (neat, cm$^{-1}$): $v = 2954$ (w), 2925 (m), 2854 (w), 2255 (w), 1745 (w), 1711 (w), 1658 (m), 1604 (w), 1569 (w), 1462 (w), 1329 (w), 1231 (w), 1153 (w), 908 (m), 845 (w), 734 (s), 649 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 350 (10), 318 (12), 228 (28), 220 (20), 155 (10), 130 (10), 129 (44), 116 (100), 111 (11), 101 (10), 98 (11), 97 (15), 95 (12), 85 (21), 83 (16), 81 (17), 71 (30), 69 (40), 57 (43), 55
(26), 43 (32), 41 (19). HRMS (ESI, [M-H]−): calcd. for C_{26}H_{29}O_{5}: 349.20205; found: 349.20192.

**Dimethyl 2-ethyl-4-hydroxy-5-nonylbenzene-1,3-dioate (7s).** Starting with 6b (0.258 g, 1.5 mmol) and 1e (0.638 g, 1.65 mmol), 7s was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellow oil (0.278 g, 51%). 1H NMR (250 MHz, CDCl3): δ = 0.81 (t, 3J = 6.5 Hz, 3 H, (CH2)8CH3), 1.14 (t, 3J = 7.0 Hz, 3 H, CH3), 1.18 – 1.25 (m, 12 H, 6 CH2), 1.49 – 1.54 (m, 2 H, CH2), 2.54 (t, 3J = 7.0 Hz, 2 H, PhCH2), 3.08 (q, 3J = 7.5 Hz, 2 H, PhCH2), 3.80 (s, 3 H, OCH3), 3.91 (s, 3 H, OCH3), 7.62 (s, 1 H, CHAr), 11.08 (s, 1 H, OH). 13C NMR (CDCl3, 75 MHz): δ = 13.2, 15.1 (CH3), 21.7, 24.1, 26.4, 28.2, 28.3, 28.5, 28.8, 30.3, 30.8 (CH2), 50.9, 51.5 (OCH3), 112.3 (CCOOCH3), 121.6 (CCOOCH3), 127.8 (CAr), 135.0 (CHAr), 145.5 (CAr), 161.0 (COH), 167.4, 171.1 (CO). IR (KBr, cm⁻¹): v = 2925 (s), 2854 (m), 1749 (w), 1717 (m), 1662 (m), 1617 (w), 1577 (w), 1559 (w), 1540 (w), 1507 (w), 1456 (w), 1436 (m), 1331 (w), 1273 (w), 1229 (m), 1203 (m), 1153 (w), 1070 (w), 994 (w), 909 (m), 817 (w), 734 (m), 668 (w), 649 (w). GC-(EI, 70 eV): m/z (%) = 364 ([M+], 47), 332 (49), 315 (19), 273 (41), 242 (21), 220 (100), 187 (21), 160 (9), 129 (26), 116 (54), 97 (12), 85 (7), 69 (11), 57 (14), 43 (16). HRMS (EI): Calcd. for C_{21}H_{32}O_{5} ([M+]: 364.22443; found: 364.223933.

**Dimethyl 5-decyl-2-ethyl-4-hydroxybenzene-1,3-dioate (7t).** Starting with 6b (0.258 g, 1.5 mmol) and 1f (0.661 g, 1.65 mmol), 7t was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellow oil (0.278 g, 49%). 1H NMR (250 MHz, CDCl3): δ = 0.80 (t, 3J = 6.6 Hz, 3 H, (CH2)9CH3), 1.13 (t, 3J = 8.6 Hz, 3 H, CH3), 1.16 – 1.24 (m, 14 H, 7 CH2), 1.46 – 1.54 (m, 2 H, CH2), 2.53 (t, 3J = 7.6 Hz, 2 H, PhCH2), 3.08 (q, 3J = 7.4 Hz, 2 H, PhCH2), 3.79 (s, 3 H, OCH3), 3.91 (s, 3 H, OCH3), 7.62 (s, 1 H, CHAr), 11.08 (s, 1 H, OH). 13C NMR (CDCl3, 75 MHz): δ = 13.1, 15.3 (CH3), 21.8, 24.2, 28.2, 28.3, 28.4, 28.5, 28.6, 28.7, 28.8, 30.9, (CH2), 50.8, 51.5 (OCH3), 112.5 (CCOOCH3), 121.8 (CCOOCH3), 127.9 (CAr), 134.9 (CHAr), 145.5 (CAr), 161.0 (COH), 167.4, 171.2 (CO). IR (KBr, cm⁻¹): v = 2953 (m), 2925 (s), 2854 (m), 1749 (w), 1717 (m), 1662 (m), 1617 (w), 1577 (w), 1559 (w), 1540 (w), 1507 (w), 1456 (w), 1436 (m), 1331 (w), 1273 (w), 1229 (m), 1203 (m), 1153 (w), 1070 (w), 994 (w), 909 (m), 817 (w), 734 (m), 668 (w), 649 (w). GC-MS (EI, 70 eV): m/z (%) = 378 ([M+], 43), 363 (3), 346 (48), 329 (19), 311.
Dimethyl 4-ethyl-2-hydroxy-4'-methylbiphenyl-3,5-dicarboxylate (7u). Starting with 6b (0.258 g, 1.5 mmol) and 1g (0.525 g, 1.7 mmol), 7u was isolated after chromatography (silica gel, heptanes/EtOAc) as a light red oil (0.250 g, 51%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 1.19 (t, $^3J = 7.5$ Hz, 3 H, CH$_2$CH$_3$), 2.31 (s, 3 H, PhCH$_3$), 3.11 (q, $^3J = 7.5$ Hz, 2 H, CH$_2$CH$_3$), 3.79 (s, 3 H, OCH$_3$), 3.93 (s, 3 H, OCH$_3$), 7.15 - 7.19 (m, 2 H, 2 CH$_{Ar}$), 7.33 - 7.36 (m, 2 H, 2 CH$_{Ar}$), 7.82 (s, 1 H, CH$_{Ar}$), 10.60 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ = 15.9, 21.2 (CH$_3$), 25.2 (CH$_2$), 52.0, 52.7 (OCH$_3$), 115.2 (CCOOCH$_3$), 122.9 (C$_{Ar}$), 127.9 (CCOOCH$_3$), 129.1 (2 CH$_{Ar}$), 129.5 (2 CH$_{Ar}$), 133.5 (C$_{Ar}$), 136.5 (CH$_{Ar}$), 137.5, 147.5 (C$_{Ar}$), 160.0 (COH), 167.7, 171.6 (CO). IR (neat, cm$^{-1}$): $\nu$ = 2950 (w), 2874 (w), 1719 (m), 1660 (m), 1605 (m), 1561 (m), 1431 (m), 1397 (m), 1332 (m), 1293 (m), 1231 (s), 1198 (s), 1174 (s), 1081 (m), 1029 (m), 961 (m), 932 (m), 822 (m), 778 (m), 745 (m), 680 (w), 656 (m), 539 (m). GC-MS (EI, 70 eV): $m/z$ (%) = 328 ([M]+, 40), 297 (47), 296 (100), 253 (12), 165 (7). HRMS (EI): Calcd. for C$_{19}$H$_{20}$O$_5$ ([M]+): 328.13053; found: 328.130425.

Dimethyl 4-hydroxy-5-methyl-2-propylisophthalate (7v). Starting with 6c (0.279 g, 1.5 mmol) and 1p (0.457 g, 1.7 mmol), 7v was isolated after chromatography (silica gel, heptanes/EtOAc) as a light red oil (0.203 g, 51%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta$ = 0.85 (t, $^3J = 8.2$ Hz, 2 H, CH$_2$CH$_2$CH$_3$), 2.98 (t, $^3J = 7.5$ Hz, 3 H, CH$_2$CH$_2$CH$_3$), 3.73 (s, 3 H, OCH$_3$), 3.86 (s, 3 H, OCH$_3$), 7.58 (s, 1 H, CH$_{Ar}$), 11.09 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ = 14.5, 15.8 (CH$_3$), 22.3, 33.6 (CH$_2$), 51.9, 52.6 (OCH$_3$), 113.2 (CCOOCH$_3$), 122.9 (C$_{Ar}$), 124.4 (CCOOCH$_3$), 136.8 (CH$_{Ar}$), 145.2 (C$_{Ar}$), 162.4 (COH), 168.3, 172.3 (CO). IR (neat, cm$^{-1}$): $\nu$ = 2953 (w), 2927 (w), 2855 (w), 1720 (m), 1658 (m), 1609 (w), 1580 (w), 1432 (m), 1379 (w), 1331 (m), 1265 (m), 1222 (s), 1192 (s), 1150 (s), 1063 (m), 1017 (m), 985 (m), 912 (w), 843 (w), 813 (m), 760 (m), 731 (m), 678 (w), 647 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 266 ([M]+, 28), 235 (29), 234 (100),
219 (12), 203 (24), 187 (14), 178 (14), 177 (9), 175 (11), 163 (9), 157 (8), 147 (9), 91 (10), 77 (8). HRMS (EI): Calcd. for C_{14}H_{18}O_{5} ([M]+): 266.11488; found: 266.114914.

3-Ethyl 1-methyl 5-ethyl-4-hydroxy-2-propylisophthalate (7w). Starting with 6c (0.279 g, 1.5 mmol) and 1c (0.499 g, 1.65 mmol), 7w was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.233 g, 53%). 1H NMR (250 MHz, CDCl_3): δ = 0.76 (t, 3J = 7.5 Hz, 3 H, (CH_2)_2CH_3), 0.99 (t, 3J = 7.5 Hz, 3 H, CH_2CH_3), 1.23 (t, 3J = 7.4 Hz, 3 H, OCH_2CH_3), 1.32 – 1.47 (m, 2 H, CH_2CH_2CH_3), 2.44 (q, 3J = 7.6 Hz, 2 H, PhCH_2CH_3), 2.91 (q, 3J = 7.4 Hz, 2 H, PhCH_2CH_2), 3.65 (s, 3 H, OCH_3), 4.25 (q, 3J = 7.6 Hz, 2 H, OCH_2CH_3), 7.48 (s, 1 H, CH Ar), 11.08 (s, 1 H, OH). 13C NMR (CDCl_3, 75 MHz): δ = 14.8, 15.3, 15.8 (CH_3), 24.2, 26.5, 34.9 (CH_2), 53.2 (OCH_3), 63.4 (OCH_2CH_3), 114.7 (CCOOCH_2CH_3), 124.1 (C Ar), 131.3 (CCOOCH_3), 136.3 (CH Ar), 146.1 (C Ar), 163.4 (COH), 169.7, 173.0 (CO). IR (neat, cm⁻¹): ν = 2963 (w), 2933 (w), 2872 (w), 2255 (w), 1716 (m), 1655 (m), 1578 (w), 1428 (w), 1396 (w), 1373 (w), 1321 (w), 1298 (w), 1263 (w), 1223 (s), 1154 (m), 1097 (w), 1054 (w), 1020 (w), 971 (w), 906 (m), 868 (w), 845 (w), 818 (w), 729 (s), 648 (w), 581 (w). GC-MS (EI, 70 eV): m/z (%) = 294 ([M]+, 38), 263 (14), 249 (22), 248 (100), 233 (17), 230 (14), 217 (21), 215 (11), 198 (17), 192 (48), 191 (11), 177 (12), 173 (12), 171 (13), 115 (10), 91 (13), 77 (10). HRMS (EI): Calcd. for C_{16}H_{22}O_{5} ([M]+): 294.14618; found: 294.146042.

Dimethyl 5-butyl-4-hydroxy-2-propylisophthalate (7x). Starting with 6c (0.279 g, 1.5 mmol) and 1q (0.522 g, 1.7 mmol), 7x was isolated after chromatography (silica gel, heptanes/EtOAc) as a light yellowish oil (0.236 g, 51%). 1H NMR (250 MHz, CDCl_3): δ = 0.82 - 0.93 (m, 6 H, 2 CH_3), 1.25 – 1.35 (m, 2 H, (CH_2)_2CH_2CH_3), 1.45 – 1.55 (m, 4 H, 2 CH_2), 2.54 (t, 3J = 7.4 Hz, 2 H, PhCH_2), 3.03 (t, 3J = 7.4 Hz, 2 H, PhCH_2), 3.79 (s, 3 H, OCH_3), 3.91 (s, 3 H, OCH_3), 7.61 (s, 1 H, CH Ar), 11.07 (s, 1 H, OH). 13C NMR (CDCl_3, 75 MHz): δ = 13.9, 14.6 (CH_3), 22.6, 25.3, 29.5, 31.4, 33.6 (CH_2), 51.9, 52.5 (OCH_3), 113.4 (CCOOCH_3), 122.8 (C Ar), 128.7 (CCOOCH_3), 135.9 (CH Ar), 145.0 (C Ar), 161.9 (COH), 168.3, 172.1 (CO). IR (neat, cm⁻¹): ν = 2955 (w), 2930 (w), 2871 (w), 2255 (w), 1719 (m), 1661 (m), 1606 (w), 1579 (w), 1434 (m), 1335 (w), 1297 (w), 1265 (w), 1226 (m), 1199 (m), 1153 (m), 1088 (w), 1063 (w), 999 (w), 907 (m), 816 (w), 731 (s), 649 (w). GC-MS (EI, 70
**Dimethyl 5-hexyl-4-hydroxy-2-propylisophthalate (7y).** Starting with 6c (0.279 g, 1.5 mmol) and 1d (0.568 g, 1.7 mmol), 7y was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.227 g, 45%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.80$ (t, $^3J = 7.4$ Hz, 3 H, (CH$_2$)$_5$CH$_3$), 0.90 (t, $^3J = 7.4$ Hz, 3 H, (CH$_2$)$_2$CH$_3$), 1.17 – 1.32 (m, 6 H, 3 CH$_2$), 1.43 – 1.56 (m, 4 H, 2 CH$_2$), 2.53 (t, $^3J = 7.4$ Hz, 2 H, PhCH$_2$), 3.03 (t, $^3J = 7.5$ Hz, 2 H, PhCH$_2$), 3.78 (s, 3 H, OCH$_3$), 3.90 (s, 3 H, OCH$_3$), 7.61 (s, 1 H, CH Ar), 11.07 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.0$, 14.6 (CH$_3$), 22.6, 25.3, 29.1, 29.2, 29.8, 31.7, 33.6 (CH$_2$), 51.9, 52.6 (OCH$_3$), 113.7 (C COOCH$_3$), 122.9 (C Ar), 128.8 (C COOCH$_3$), 136.0 (CH$_{Ar}$), 145.0 (C$_{Ar}$), 162.3 (CO), 168.4, 172.3 (CO). IR (neat, cm$^{-1}$): $\nu = 2954$ (w), 2927 (m), 2857 (w), 2255 (w), 1720 (m), 1660 (m), 1606 (w), 1579 (w), 1433 (m), 1331 (w), 1298 (w), 1261 (w), 1226 (s), 1199 (s), 1152 (m), 1092 (w), 1062 (w), 995 (w), 972 (w), 907 (m), 816 (w), 731 (s), 649 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 337 (34), 336 ([M$^+$], 98), 306 (19), 305 (91), 304 (96), 303 (14), 289 (21), 288 (13), 287 (75), 276 (23), 275 (89), 274 (14), 273 (76), 262 (18), 261 (37), 249 (11), 248 (54), 247 (72), 246 (17), 245 (87), 244 (13), 235 (55), 234 (100), 233 (88), 229 (12), 219 (22), 217 (14), 216 (32), 215 (32), 206 (11), 205 (13), 203 (18), 202 (23), 201 (44), 192 (13), 191 (24), 189 (11), 187 (14), 184 (14), 178 (37), 175 (18), 174 (12), 173 (22), 159 (11), 157 (14), 147 (12), 146 (10), 145 (13), 115 (12), 91 (12). HRMS (EI): Calcd. for C$_{19}$H$_{28}$O$_5$ ([M$^+$]): 336.19313; found: 336.192594.

**Dimethyl 5-heptyl-4-hydroxy-2-propylisophthalate (7z).** Starting with 6c (0.279 g, 1.5 mmol) and 1r (0.591 g, 1.7 mmol), 7z was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.227 g, 46%). $^1$H NMR (250 MHz, CDCl$_3$): $\delta = 0.79$ (t, $^3J = 7.6$ Hz, 3 H, (CH$_2$)$_6$CH$_3$), 0.91 (t, $^3J = 7.5$ Hz, 3 H, (CH$_2$)$_2$CH$_3$), 1.13 – 1.30 (m, 8 H, 4 CH$_2$), 1.45 – 1.58 (m, 4 H, 2 CH$_2$), 2.54 (t, $^3J = 7.6$ Hz, 2 H, PhCH$_2$), 3.03 (t, $^3J = 7.5$ Hz, 2 H, PhCH$_2$), 3.79 (s, 3 H, OCH$_3$), 3.91 (s, 3 H, OCH$_3$), 7.61 (s, 1 H, CH Ar), 11.07 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.0$, 14.6 (CH$_3$), 22.7, 25.4, 29.1, 29.5, 29.6, 29.8, 30.1, 31.7, 33.6 (CH$_2$), 51.9, 52.6 (OCH$_3$), 113.7 (C COOCH$_3$), 122.9 (C Ar), 128.8 (C COOCH$_3$), 136.0 (CH$_{Ar}$), 145.0 (C$_{Ar}$), 162.3 (CO), 168.4, 172.3 (CO). IR (neat, cm$^{-1}$): $\nu = 2954$ (w), 2927 (m), 2857 (w), 2255 (w), 1720 (m), 1660 (m), 1606 (w), 1579 (w), 1433 (m), 1331 (w), 1298 (w), 1261 (w), 1226 (s), 1199 (s), 1152 (m), 1092 (w), 1062 (w), 995 (w), 972 (w), 907 (m), 816 (w), 731 (s), 649 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 337 (34), 336 ([M$^+$], 98), 306 (19), 305 (91), 304 (96), 303 (14), 289 (21), 288 (13), 287 (75), 276 (23), 275 (89), 274 (14), 273 (76), 262 (18), 261 (37), 249 (11), 248 (54), 247 (72), 246 (17), 245 (87), 244 (13), 235 (55), 234 (100), 233 (88), 229 (12), 219 (22), 217 (14), 216 (32), 215 (32), 206 (11), 205 (13), 203 (18), 202 (23), 201 (44), 192 (13), 191 (24), 189 (11), 187 (14), 184 (14), 178 (37), 175 (18), 174 (12), 173 (22), 159 (11), 157 (14), 147 (12), 146 (10), 145 (13), 115 (12), 91 (12). HRMS (EI): Calcd. for C$_{19}$H$_{28}$O$_5$ ([M$^+$]): 336.19313; found: 336.192594.
31.8, 33.6 (CH₂), 51.9, 52.5 (OCH₃), 113.6 (CCOOCH₃), 122.8 (CAr), 128.8 (CCOOCH₃), 135.8 (CH₃Ar), 145.0 (CAr), 162.1 (COH), 168.4, 172.2 (CO). IR (neat, cm⁻¹): ν = 2954 (w), 2926 (m), 2855 (w), 1720 (m), 1661 (m), 1607 (w), 1578 (w), 1434 (m), 1329 (m), 1298 (w), 1262 (w), 1199 (m), 1152 (w), 1093 (w), 1063 (w), 994 (w), 908 (w), 816 (w), 732 (s), 649 (w). GC-MS (EI, 70 eV): m/z (%) = 351 (13), 350 ([M]+, 56), 319 (41), 318 (43), 301 (34), 289 (10), 287 (36), 276 (12), 275 (50), 262 (10), 261 (12), 259 (43), 248 (11), 247 (25), 235 (17), 234 (100), 233 (44), 219 (11), 216 (12), 203 (11), 202 (12), 201 (21), 191 (14), 178 (12), 173 (14), 145 (10). HRMS (EI): Calcd. for C₂₀H₃₀O₅ ([M]+): 350.20878; found: 350.208521.

**Dimethyl 4-hydroxy-5-octyl-2-propylisophthalate (7aa).** Starting with 6c (0.279 g, 1.5 mmol) and 1s (0.614 g, 1.7 mmol), 7aa was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.246 g, 45%). ¹H NMR (250 MHz, CDCl₃): δ = 0.80 (t, 3J = 7.4 Hz, 3 H, (CH₂)₇CH₃), 0.90 (t, 3J = 7.6 Hz, 3 H, (CH₂)₂CH₃), 1.17 – 1.30 (m, 10 H, 5 CH₂), 1.46 – 1.57 (m, 4 H, 2 CH₂), 2.53 (t, 3J = 7.6 Hz, 2 H, PhCH₂), 3.03 (t, 3J = 7.5 Hz, 2 H, PhCH₂), 3.79 (s, 3 H, OCH₃), 3.90 (s, 3 H, OCH₃), 7.61 (s, 1 H, CHAr), 11.07 (s, 1 H, OH). ¹³C NMR (CDCl₃, 75 MHz): δ = 14.0, 14.6 (CH₃), 22.6, 25.3, 29.1, 29.2, 29.4, 29.5, 29.8, 31.8, 33.6 (CH₂), 51.8, 52.5 (OCH₃), 113.7 (CCOOCH₃), 123.1 (CAr), 129.0 (CCOOCH₃), 136.1 (CHAr), 145.4 (CAr), 162.1 (COH), 168.2, 172.2 (CO). IR (neat, cm⁻¹): ν = 2954 (w), 2926 (m), 2855 (w), 2256 (w), 1721 (w), 1662 (m), 1606 (w), 1579 (w), 1434 (m), 1331 (w), 1298 (w), 1262 (w), 1227 (m), 1200 (m), 1152 (w), 1094 (w), 1062 (w), 995 (w), 908 (m), 817 (w), 733 (s), 649 (w). GC-MS (EI, 70 eV): m/z (%) = 364 ([M]+, 47), 333 (42), 332 (73), 315 (28), 301 (33), 289 (11), 276 (21), 275 (74), 273 (53), 261 (13), 248 (17), 247 (32), 235 (26), 234 (100), 233 (69), 228 (16), 219 (14), 217 (11), 216 (22), 215 (10), 203 (13), 202 (16), 201 (32), 191 (14), 185 (11), 184 (11), 179 (11), 178 (25), 175 (14), 173 (17), 158 (10), 157 (12), 155 (13), 147 (10), 145 (10), 130 (11), 129 (45), 117 (13), 116 (85), 115 (11), 101 (10), 98 (11), 91 (11), 85 (19), 83 (12), 81 (10), 71 (30), 69 (25), 57 (42), 55 (23). HRMS (EI): Calcd. for C₂₁H₃₂O₅ ([M]+): 364.22443; found: 364.224478.

**Dimethyl 4-hydroxy-5-nonyl-2-propylbenzene-1,3-dioate (7ab).** Starting with 6c (0.279 g, 1.5 mmol) and 1e (0.638 g, 1.7 mmol), 7ab was isolated after chromatography...
(silica gel, heptanes/EtOAc) as a yellowish oil (0.284 g, 50%). $^1$H NMR (250 MHz, CDCl$_3$): 
$\delta =$ 0.80 (t, $^3J = 6.4$ Hz, 3 H, (CH$_2$)$_9$CH$_3$), 0.91 (t, $^3J = 7.5$ Hz, 3 H, (CH$_2$)$_2$CH$_3$), 1.15 – 1.26 (m, 14 H, 7 CH$_2$), 1.52 – 1.54 (m, 2 H, CH$_2$), 2.54 (t, $^3J = 7.5$ Hz, 2 H, PhCH$_2$), 3.00 – 3.06 (m, 2 H, PhCH$_2$), 3.79 (s, 3 H, OCH$_3$), 3.91 (s, 3 H, OCH$_3$), 7.61 (s, 1 H, CH$_{Ar}$), 11.07 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 13.0, 13.9 (CH$_3$), 21.9, 24.4, 26.1, 28.2, 28.3, 28.5, 28.8, 30.3, 30.9 32.6 (CH$_2$), 50.9, 51.5 (OCH$_3$), 112.6 (CCOOCH$_3$), 121.9 (CCOOCH$_3$), 127.9 (C$_{Ar}$), 135.1 (CH$_{Ar}$), 144.2 (C$_{Ar}$), 161.2 (COH), 167.6, 171.2 (CO). IR (KBr, cm$^{-1}$): $v =$ 2954 (m), 2925 (s), 2854 (m), 1722 (m), 1662 (m), 1608 (w), 1578 (w), 1435 (m), 1330 (w), 1299 (w), 1262 (m), 1227 (s), 1200 (m), 1153 (m), 1094 (w), 1063 (w), 995 (w), 908 (m), 817 (w), 733 (s), 650 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 378 ([M$^+$], 50), 368 (5), 346 (57), 329 (21), 275 (40), 242 (22), 234 (100), 201 (17), 178 (18), 158 (12), 129 (37), 116 (78), 97 (16), 85 (12), 69 (17), 57 (23), 43 (21). HRMS (EI): Calcd. for C$_{22}$H$_{34}$O$_5$ ([M$^+$]): 378.24008; found: 378.239947.

**Dimethyl 5-decyl-4-hydroxy-2-propylbenzene-1,3-dioate (7ac).** Starting with 6c (0.279 g, 1.5 mmol) and 1f (0.661 g, 1.7 mmol), 7ac was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.323 g, 55%). $^1$H NMR (250 MHz, CDCl$_3$): 
$\delta =$ 0.80 (t, $^3J = 6.5$ Hz, 3 H, (CH$_2$)$_9$CH$_3$), 0.91 (t, $^3J = 7.2$ Hz, 3 H, (CH$_2$)$_2$CH$_3$), 1.16 – 1.26 (m, 16 H, 8 CH$_2$), 1.49 – 1.54 (m, 2 H, CH$_2$), 2.53 (t, $^3J = 7.7$ Hz, 2 H, PhCH$_2$), 3.01 – 3.06 (m, 2 H, PhCH$_2$), 3.79 (s, 3 H, OCH$_3$), 3.91 (s, 3 H, OCH$_3$), 7.61 (s, 1 H, CH$_{Ar}$), 11.07 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 13.9, 14.7 (CH$_3$), 22.7, 25.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7,29.8, 31.9, 33.8 (CH$_2$), 51.9, 52.7 (OCH$_3$), 113.3 (CCOOCH$_3$), 122.9 (CCOOCH$_3$), 128.8 (C$_{Ar}$), 136.0 (CH$_{Ar}$), 145.1 (C$_{Ar}$), 162.0 (COH), 168.4, 172.2 (CO). IR (KBr, cm$^{-1}$): $v =$ 2954 (m), 2955 (m), 2854 (m), 1723 (m), 1662 (m), 1606 (w), 1579 (w), 1434 (m), 1331 (w), 1298 (w), 1261 (w), 1227 (m), 1200 (m), 1152 (w), 1095 (w), 1061 (w), 996 (w), 908 (w), 817 (w), 734 (m), 650 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 392 ([M$^+$], 50), 360 (43), 343 (20), 301 (30), 275 (31), 247 (20), 234 (100), 219 (8), 201 (15), 178 (18), 145 (7), 116 (12), 91 (5), 69 (4), 55 (7), 43 (11). HRMS (EI): Calcd. for C$_{23}$H$_{36}$O$_5$ ([M$^+$]): 392.25573; found: 392.255638.
6-Ethyl 2-methyl 3-hydroxy-4-methylbiphenyl-2,6-dicarboxylate (7ad). Starting with 6d (0.372 g, 1.5 mmol) and 1p (0.457 g, 1.7 mmol), 7ad was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.272 g, 58%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 1.17 (t, $^3$$J$ = 7.0 Hz, 3 H, OCH$_2$CH$_3$), 2.24 (s, 3 H, PhCH$_3$), 3.89 (s, 3 H, OCH$_3$), 4.14 (q, $^3$$J$ = 7.5 Hz, 2 H, OCH$_2$CH$_3$), 7.02 - 7.06 (m, 3 H, 3 CH$_{Ar}$), 7.33 - 7.36 (m, 2 H, 2 CH$_{Ar}$), 7.88 (s, 1 H, CH$_{Ar}$), 11.04 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 14.0, 15.8 (CH$_3$), 51.9 (OCH$_3$), 61.4 (OCH$_2$), 112.7 (CCOOCH$_3$), 123.9 (CCOOC$_2$H$_5$), 126.0 (C$_{Ar}$), 128.2 (CH$_{Ar}$), 128.4 (2 CH$_{Ar}$), 128.7 (2 CH$_{Ar}$), 133.7 (CH$_{Ar}$), 135.6, 135.9 (C$_{Ar}$), 167.5 (COH), 171.4, 173.1 (CO). IR (KBr, cm$^{-1}$): $\nu$ = 3059 (w), 2981 (w), 2953 (w), 2905 (w), 2872 (w), 1737 (m), 1686 (m), 1662 (m), 1578 (m), 1494 (w), 1381 (w), 1366 (m), 1264 (m), 1193 (s), 1148 (s), 1076 (m), 1022 (m), 998 (m), 942 (w), 870 (w), 814 (m), 755 (m), 687 (s), 647 (m), 572 (m). GC-MS (EI, 70 eV): $m/z$ (%) = 314 ([M]$^+$, 51), 283 (20), 282 (100), 254 (22), 253 (96), 237 (27), 210 (12), 209 (47), 208 (23), 181 (10), 153 (15), 152 (10). HRMS (EI): Calcd. for C$_{18}$H$_{18}$O$_5$ ([M]$^+$): 314.11488; found: 314.114952.

Diethyl 4-ethyl-3-hydroxybiphenyl-2,6-dicarboxylate (7ae). Starting with 6d (0.372 g, 1.5 mmol) and 1c (0.499 g, 1.7 mmol), 7ae was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.308 g, 60%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 0.57 (t, $^3$$J$ = 7.3 Hz, 3 H, OCH$_2$CH$_3$), 0.77 (t, $^3$$J$ = 7.4 Hz, 3 H, OCH$_2$CH$_3$), 1.16 (t, $^3$$J$ = 7.3 Hz, 3 H, PhCH$_2$CH$_3$), 2.61 (q, $^3$$J$ = 7.5 Hz, 2 H, PhCH$_2$CH$_3$), 3.74 – 3.85 (m, 4 H, 2 OCH$_2$CH$_3$), 6.99 – 7.04 (m, 2 H, 2 CH$_{Ar}$), 7.17 - 7.19 (m, 3 H, 3 CH$_{Ar}$), 7.62 (s, 1 H, CH$_{Ar}$), 11.17 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta =$ 12.8, 13.4, 13.6 (CH$_3$), 22.9, 60.7, 61.3 (CH$_2$), 113.0 (CCOOCH$_3$), 124.5 (CCOOC$_2$H$_5$), 126.6 (CH$_{Ar}$), 127.1 (2 CH$_{Ar}$), 128.3 (2 CH$_{Ar}$), 131.9 (CH$_{Ar}$), 134.4, 141.2, 142.3 (C$_{Ar}$), 161.5 (COH), 168.4, 171.3 (CO). IR (KBr, cm$^{-1}$): $\nu$ = 3058 (w), 2978 (w), 2935 (w), 2874 (w), 2254 (w), 1708 (m), 1657 (m), 1602 (w), 1571 (w), 1443 (m), 1398 (w), 1367 (m), 1329 (m), 1306 (m), 1281 (m), 1265 (m), 1214 (s), 1178 (s), 1125 (m), 1095 (w), 1066 (w), 1020 (m), 907 (m), 884 (w), 866 (w), 819 (w), 763 (w), 728 (s), 698 (s), 669 (w), 648 (w). GC-MS (EI, 70 eV): $m/z$ (%) = 342 ([M]$^+$, 35), 297 (16), 296 (51), 268 (19), 267 (100), 251 (12), 223 (36), 222 (11), 165 (13), 152 (13). HRMS (EI): Calcd. for C$_{20}$H$_{22}$O$_5$ ([M]$^+$): 342.14618; found: 342.146145.
LUBBE MD 036, 1H, CDCl3

OH
O
H3C
CH3
OCH2CH3

H3C
OCH2CH3

4c

CH3
OCH2CH3

CH3
OCH2CH3

OH
O
H3C
CH3
O
OCH2CH3

4c

LUBBE MD 036, 13C

Correct Data Parameters
NAME: MD036
NORM: 1

Analysis Parameters
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REPOL: 5
USER: ESI

Nuclear Overhauser
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Integrals

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Nuclear Overhauser
NOE = 4

Integrals
### Compound 4f

- **Formula:** H_3C(H_2C_2)_2OH O
- **Structure:** ![Structure Image]

### Compound 4i

- **Formula:** HCO_3C_6H_5OH O
- **Structure:** ![Structure Image]
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| GB | 0 |
| PC | 1.40 |

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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MeOOC–[CH2]3–COOMe

7 d

MeOOC–[CH2]3–COOMe

7 d
MeOOC
\(\overset{\text{COOMe}}{\text{(CH}_2\text{)}}\text{OH}\)
\(\overset{\text{7e}}{\text{MeOOC}}\)

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- PULPROG: zg30
- TD: 65536
- SOLVENT: CDCl3
- NS: 16
- DS: 2
- SWH: 5165.289 Hz
- FIDRES: 0.078816 Hz
- AQ: 6.3439350 sec
- RG: 575
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- DE: 10.00 usec
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- D1: 1.00000000 sec
- TD0: 1

**F1 - Processing parameters**
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- SF: 250.1300386 MHz

**F2 - Processing parameters**
- SI: 32768
- SF: 62.8952390 MHz

**Supplementary Material (ESI) for Organic & Biomolecular Chemistry**
This journal is (c) The Royal Society of Chemistry 2009
MeOOC
\[
\text{OH}
\]
\[7\text{l}\]

MeOOC
\[
\text{COOMe}
\]
\[7\text{m}\]

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2009
Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2009
H$_2$CO$_3$C$_6$H$_9$O$_7$
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- **TD** | 65536
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- **NS** | 2048
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**Channel f1**

- **NUC1** | 13C
- **P1** | 10.00 usec
- **PL1** | -0.50 dB
- **PL1W** | 33.25691986 W
- **SFO1** | 75.4752953 MHz

**Channel f2**

- **CPDPRG2** | waltz16
- **NUC2** | 1H
- **PCPD2** | 72.00 usec
- **PL2** | 0.00 dB
- **PL12** | 17.00 dB
- **PL13** | 17.00 dB
- **PL2W** | 11.25325108 W
- **PL12W** | 0.22453187 W
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**F2 - Processing parameters**

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**CO2**

**CH2**

**CH3**

**OH**

**H3**

**CO2**

**CH3**

**H3**

**CO2**

**CH2**

**CH3**

**OH**

**H3**

**CO2**

**CH2**

**CH3**

**OH**

**H3**