

Supporting informations for:

A High-Throughput, Low Volume Enzyme Assay on Solid Support.

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A. Experimental part:

All reagent were purchased from Fluka or Aldrich or synthesized by following procedures. Chromatography was performed with SDS silicagel 60 (0.040-0.064 mm). TLC was performed with fluorescent F254 glass plates. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with Bruker Ac-200, AC-300 or Varian Gemini 200 spectrometer in CDCl_3 . Melting points were determined with Buchi 510 melting point and are uncorrected. Fluorescence was readed with Spectramax geminiXS with SOFTmax PRO 4.0. Enzymes were dispersed by Gilson 233XL on-line column switching and Gilson 402 syringe pump with Gilson 735 sampler software v. 5.20. For clustering analysis was used Vista software <http://forrest.psych.unc.edu/research/>.

General procedure for the synthesis of esters 1a/b – 16a/b. A solution of umbelliferone or 4-Methyl-umbelliferone (1.23 mmol) in anhydrous THF (3 mL) was treated with NaH (118 mg, 55 % suspension in oil, 2.3 equiv.). After 30 min at 25°C, the reaction was cooled to 0°C and the acyl chloride (1.85 mmol, 1.5 equiv.) was added as a solution in dry THF (1 mL). After 2 h at 25°C, reaction mixture was poured into aq. 1M HCl (50 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic phase was dried over Na_2SO_4 , evaporated and the residue was purified by flash chromatography to give ester **1a/b-16a/b**.

General procedure for the synthesis of oxymethyl ethers 17b-20b and 20a. A solution of umbelliferone or 4-Methyl-umbelliferone (1.85 mmol) in anhydrous THF (3 mL) was treated with NaH (118 mg, 55% suspension in oil, 1.5 equiv.). After 30 min at 25°C reaction was cooled to -60°C and the alkylating agent (iodomethyl or bromomethyl ester)¹ was added as a solution in anhydrous THF (1 mL). The temperature was maintained at -60°C for 5h, then slowly raised to 25°C overnight. The reaction mixture was then poured into aq. 1M HCl (50 mL) and extacted with CH_2Cl_2 (2 x 50 mL). The organic phase was dried over Na_2SO_4 , evaporated, and the residue was purified by flash chromatography to give the acyloxymethyl ethers **17b-20b** and **20a**.

7-(Propylcarbonyl)oxy-2H-1-benzopyran-2-on (1a): white solid; m.p. 68-70°C; yield: 170 mg (0.74 mmol, 62%); ^1H NMR (300 MHz, CDCl_3): δ =7.63 (d, J=6.9 Hz, 1H), 7.4 (d, J= 8.4 Hz, 1H), 7.07 (d, J=2.6 Hz, 1H), 7.04 (dd, J=5.4; 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.8 (h, J=7.5 Hz, 2H), 1.08 (t, J=7.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ =142.8, 128.5, 118.4, 115.9, 110.1, 36.2, 18.3, 13.5; MS (EI)= 232 [M]⁺

¹ N. Bensel, M. T. Reymond, J.-L. Reymond, *Chem. Eur. J.* **2001**, 7, 4604.

7-(Propylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (1b): white solid; m.p. 86°C; yield: 152 mg (0.62 mmol, 51%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.11 (dd, J=5.4; 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.27 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.44 (s, 3H), 1.8 (h, J=7.5 Hz, 2H), 1.08 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171, 160.8, 154.7, 153.5, 152, 125, 118.3, 117, 114, 110.5, 36, 30, 18.7, 18.3, 13; MS (EI)= 246 [M]⁺

7-(Isobutyroyl)oxy-2H-1-benzopyran-2-on (2a): white solid; yield: 180 mg (0.77 mmol, 63%); m.p. 102-103°C; ¹H NMR (300 MHz, CDCl₃): δ=7.69 (d, J=6.9 Hz, 1H), 7.48 (d, J= 8.4 Hz, 1H), 7.08 (d, J=2.6 Hz, 1H), 7.04 (dd, J=8.4; 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.84 (m, 1H) 1.34 (d, J=7 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ=176.6, 160.8, 154.7, 153.5, 143.1, 128, 118.3, 116.3, 115, 110.5, 39.2, 27.4; MS (EI)= 232 [M]⁺

7-(Isobutyroyl) 4-methyl-oxy-2H-1-benzopyran-2-on (2b): white solid; yield: 100 mg (0.41 mmol, 34%); m.p. 85°C; ¹H NMR (300 MHz, CDCl₃): δ=7.63 (d, J=6.9 Hz, 1H), 7.12 (d, J= 8.4 Hz, 1H), 7.08 (d, J=2.6 Hz, 1H), 6.28 (s, 1H), 2.8 (m, 1 H), 2.45 (s, 3H), 1.38 (d, J=7 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ=174.6, 160.8, 154.7, 153.5, 151.1, 125, 118.3, 114.3, 110.5, 34.2, 18; MS (EI)= 246 [M]⁺

7-Pivaloyl-2H-1-benzopyran-2-on (3a): white solid; yield: 288 mg (0.97 mmol, 78%); m.p. 139°C; ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.49 (d, J= 8.4 Hz, 1H), 7.1 (d, J=2.6 Hz, 1H), 7.02 (dd, J=8.4; 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 1.38 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=174.6, 160.8, 159.7, 155.5, 143.1, 129, 114.3, 114, 113, 103.5, 33.2, 22.4; MS (EI)= 246 [M]⁺

7-Pivaloyl-4-methyl-oxy-2H-1-benzopyran-2-on (3b): white solid; yield: 220 mg (0.84 mmol, 70%); m.p. 87°C; ¹H NMR (300 MHz, CDCl₃): δ=7.62 (d, J=6.9 Hz, 1H), 7.09 (d, J= 8.4 Hz, 1H), 7.06 (dd, J=8.4; 2.6 Hz, 1H), 6.28 (d, J= 9.6 Hz, 1H), 2.97 (s, 3H), 1.39 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ=160.5, 154.5, 153.6, 151.9 125.2, 118.0, 117.6, 114.4, 110.3, 39.2, 27.0, 18.7; MS (EI)= 260 [M]⁺

7-(cyclobutylcarbonyl)oxy-2H-1-benzopyran-2-on (4a): white solid; m.p. 96-98°C ; yield: 230 mg (0.94 mmol, 78%); ¹H NMR (300 MHz, CDCl₃): δ=7.72 (d, J=6.9 Hz, 1H), 7.5 (d, J= 8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.04 (dd, J=5.4; 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 3.4 (p, J=3.5 Hz 1H), 2.4 (m, 4H), 2 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ=173.6, 160.8, 154.7, 153, 142.1, 128, 118.3, 116.5, 115, 110.5, 38.6, 25.6, 18; MS (EI)= 244 [M]

7-(cyclobutylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (4b): white solid; m.p. 74-76°C; yield: 220 mg (0.85 mmol, 71%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.13 (d, J=1.6 Hz, 1H), 7.07 (dd, J=5.4; 2.6 Hz, 1H), 6.28 (d, J=1.2 Hz), 3.4 (p, J=3.5 Hz 1H), 2.4 (s, 3H), 2.4 (m, 4H), 2 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ=173.2, 160.5, 154.1, 153.3, 151.9, 125.3, 118.0, 117.6, 114.4, 110.3, 38.0, 25.2, 18.5, 18.4; MS (EI)= 258 [M]⁺

7-(Pentylcarbonyl)oxy-2H-1-benzopyran-2-on (5a): white solid; m.p. 50°C; yield: 160 mg (0.61 mmol, 51%); ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.5 (d, J= 8.4 Hz, 1H), 7.12 (d, J=2.6 Hz, 1H), 7.06 (dd, J=5.4; 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.78 (p, J=6.5 Hz, 2H), 1.4 (m, 4H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171.6, 160.8, 154.7, 153.1, 142, 128.3, 118.5, 116, 115, 110, 34, 31, 22, 13; MS (EI)= 260 [M]⁺

7-(Pentylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (5b): white solid; m.p. 60°C; yield: 170 mg (0.62 mmol, 51%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.09 (dd, J=5.4; 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.28 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.44 (s, 3H), 1.78 (p, J=6.5 Hz, 2H), 1.4 (m, 4H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=173.6, 160.4, 154.1, 153.1, 151.9, 125.3, 118.1, 117.7, 114.4, 110.4, 34.2, 31.2, 24.4, 22.2, 18.7, 13.9; MS (EI)= 274 [M]⁺

7-(cyclohexylcarbonyl)oxy-2H-1-benzopyran-2-on (6a): white solid; m.p. 118-120°C ; yield: 250 mg (0.92 mmol, 76%); ¹H NMR (300 MHz, CDCl₃): δ=7.72 (d, J=6.9 Hz, 1H), 7.5 (d, J= 8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.04 (dd, J=5.4, 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.5 (p, J=1.2 1H), 2.5 (s, 1H), 1.6 (m, 8 H), 1.1 (t, J=6.9 3 H), 0.9 (t, J=5.2 3H) ¹³C NMR (75 MHz, CDCl₃): δ=173.6, 160.8, 154.7, 142.1, 128, 118.3, 116.5, 115, 110.5, 43, 28.6, 25.6, 25.4; MS (EI)= 272 [M]⁺

7-(cyclohexylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (6b): white solid; m.p. 70-73°C; yield: 160 mg (0.56 mmol, 46%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.1 (dd, J=5.4; 2.6 Hz, 1H), 7.04 (d, J=1.6 Hz, 1H), 6.28 (d, J=1.2 Hz), 2.5 (p, J=1.2 1H), 2.5 (s, 1H), 2.4 (s, 3H), 1.6 (m, 8 H), 1.1 (t, J=6.9 3 H), 0.9 (t, J=5.2 3H); ¹³C NMR (75 MHz, CDCl₃): δ=173.6, 160.8, 154.7, 153.5, 151.1, 125, 118.3, 117.5, 114, 110.5, 43, 28, 25, 24.8, 18; MS (EI)= 286 [M]⁺

7-(Heptylcarbonyl)oxy-2H-1-benzopyran-2-on (7a): white solid; m.p. 54–56°C; yield: 300 mg (0.95 mmol, 79%); ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.6 (d, J=8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.07 (dd, J=5.4; 2.6 Hz, 1H), 6.4 (d, J=9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.78 (p, J=6.5 Hz, 2H), 1.33 (m, 8H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=154.6, 142.8, 128.5, 115.9, 110.3, 34.3, 31.6, 30.9, 29.0, 28.8, 24.7, 22.5, 14.0; MS (EI)= 288 [M]⁺

7-(Heptylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (7b): white solid; m.p. 35°C; yield: 285 mg (0.94 mmol, 78%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J=8.4 Hz, 1H), 7.12 (dd, J=5.4, 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.28 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.45 (s, 3H), 1.78 (p, J=6.5 Hz, 2H), 1.3 (m, 8H), 0.94 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171.5, 160.4, 154.1, 153.2, 151.9, 125.3, 118.1, 117.6, 114.3, 110.3, 34.3, 31.6, 28.9, 24.7, 22.5, 18.6, 14.0; MS (EI)= 302 [M]⁺

7-(Hept-3-ylcarbonyl)oxy-2H-1-benzopyran-2-on (8a): Colourless oil; yield: 280 mg (0.97 mmol, 81%); ¹H NMR (300 MHz, CDCl₃): δ=7.72 (d, J=6.9 Hz, 1H), 7.6 (d, J=8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.04 (dd, J=5.4; 2.6 Hz, 1H), 6.4 (d, J=9.6 Hz, 1H), 2.5 (p, J=1.2 1H) 2.3 (m, 2H), 1.6 (m, 8 H), 1.1 (t, J=6.9 3 H), 0.9 (t, J=5.2 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171.6, 160.8, 154.7, 153.5, 142.1, 128, 118.3, 116.5, 115, 110.5, 48, 31, 29.6, 24.8, 25.6, 22, 13, 11; MS (EI)= 288 [M]⁺

7-(Hept-3-ylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (8b): Colourless oil; yield: 120 mg (0.40 mmol, 33%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J=8.4 Hz, 1H), 7.1 (dd, J=5.4; 2.6 Hz, 1H), 7.04 (d, J=1.6 Hz, 1H), 6.28 (d, J=1.2 Hz), 2.5 (p, J=1.2 1H), 2.4 (s, 3H), 1.6 (m, 8 H), 1.1 (t, J=6.9 3 H), 0.9 (t, J=5.2 3H); ¹³C NMR (75 MHz, CDCl₃): δ=181.4, 174.2, 160.4, 154.1, 153.3, 151.9, 47.3, 31.6, 29.6, 25.4, 22.5, 18.7, 13.9, 11.8; MS (EI)= 302 [M]⁺

7-(Nonylcarbonyl)oxy-2H-1-benzopyran-2-on (9a): white solid; m.p. 58°C; yield: 300 mg (0.95 mmol, 79%); ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.5 (d, J=8.4 Hz, 1H), 7.12 (d, J=2.6 Hz, 1H), 7.08 (dd, J=5.4, 2.6 Hz, 1H), 6.4 (d, J=9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.78 (p, J=6.5 Hz, 2H), 1.3 (m, 12H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171.6, 160.8, 154.7, 153.1, 142, 128.3, 118.5, 116, 115, 110, 34, 31, 29.3, 29.22, 29.20, 29.03, 24, 22, 14; MS (EI)= 316 [M]⁺

7-(Nonylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (9b): white solid; m.p. 46°C; yield: 215 mg (0.65 mmol, 54%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J=8.4 Hz, 1H), 7.12 (dd, J=5.4, 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.28 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.45 (s, 3H), 1.78 (p, J=6.5 Hz, 2H), 1.3 (m, 12H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=181.4, 174.6, 160.8, 154.7, 153.1, 142, 128.3, 118.5, 116, 115, 110, 34, 31, 29.3, 29.22, 29.20, 29.03, 24, 22, 14; MS (EI)= 330 [M]⁺

7-(Undecanylcarbonyl)oxy-2H-1-benzopyran-2-on (10a): white solid; m.p. 65–67°C; yield: 190 mg (0.55 mmol, 46%); ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.6 (d, J=8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.07 (dd, J=5.4, 2.6 Hz, 1H), 6.4 (d, J=9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.78 (p, J=6.5 Hz, 2H), 1.33 (m, 16H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171.6, 160.8, 154.7, 153.1, 142, 128.3, 118.5, 116, 115, 110, 34, 31, 29.59, 29.43, 29.22, 29.06, 24.79, 22, 14; MS (EI)= 344 [M]⁺

7-(Undecanylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (10b): white solid; m.p. 56–59°C; yield: 285 mg (0.34 mmol, 28%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J=8.4 Hz, 1H), 7.12 (dd, J=5.4; 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.28 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.45 (s, 3H), 1.78 (p, J=6.5 Hz, 2H), 1.3 (m, 16H), 0.92 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171; 160.8; 154.7; 153.5; 151.9; 125; 118.3; 117; 114; 110.5; 34.3; 31.9; 29.59; 29.44; 29.32; 29.22; 29.06; 24.78; 22.6; 18.7; 18.3; 14; MS (EI)= 358 [M]⁺

7-(Tridecanylcarbonyl)oxy-2H-1-benzopyran-2-on (11a): white solid; m.p. 62–63°C; yield: 210 mg (0.56 mmol, 47%); ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.6 (d, J=8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.07 (dd, J=5.4; 2.6 Hz, 1H), 6.4 (d, J=9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.78 (p, J=6.5 Hz, 2H), 1.33 (m, 20H), 0.92 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171.6, 160.8, 154.7, 153.1, 142, 128.3, 118.5, 116, 110, 34, 31.9, 29.69, 29.67, 29.65, 29.63, 29.59, 29.44, 29.35, 29.23, 29.06, 24, 22, 14; MS (EI)= 372 [M]⁺

7-(Tridecanylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (11b): white solid; m.p. 55–58°C; yield: 230 mg (0.60 mmol, 50%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J=8.4 Hz, 1H), 7.12 (dd, J=5.4, 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.29 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.4 (s, 3H), 1.78 (p, J=6.5 Hz, 2H), 1.33 (m, 20H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171, 160.8, 154.7, 153.5, 151.9, 125, 118.3, 117, 114, 110.5, 34.3, 31.9, 29.67, 29.63, 29.59, 29.44, 29.43, 29.35, 29.24, 29.06, 24.6, 22.6, 18.7, 14; MS (EI)= 386 [M]⁺

7-(Pentadecanoylcarbonyl)oxy-2H-1-benzopyran-2-on (12a): white solid; m.p. 75-76°C; yield: 190 mg (0.48 mmol, 40%); ¹H NMR (300 MHz, CDCl₃): δ=7.7 (d, J=6.9 Hz, 1H), 7.6 (d, J= 8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.07 (dd, J=5.4, 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.6 (t, J=7.3 Hz 2H), 1.78 (p, J=6.5 Hz, 2H), 1.33 (m, 24H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (300 MHz, CDCl₃): δ=180.0, 171.8, 171.6, 160.5, 153.2, 125.3, 118.1, 114.8, 110.4, 34.3, 34.0, 31.9, 29.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 24.8, 24.6, 23.6, 22.6, 18.7, 14.1; MS (EI)= 400 [M]⁺

7-(Pentadecanoylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (12b): white solid; m.p. 60-63°C; yield: 280 mg (0.68 mmol, 56%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.12 (dd, J=5.4, 2.6 Hz, 1H), 7.06 (d, J=1.4 1H), 6.29 (d, J=1.2 Hz), 2.6 (t, J=7.3 Hz 2H), 2.58 (s, 3H), 1.78 (p, J=6.5 Hz, 2H), 1.33 (m, 24H), 0.95 (t, J=7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=171, 160.8, 154.7, 153.5, 151.9, 125, 118.3, 117, 114, 110.5, 34.3, 33.9, 31.9, 29.69, 29.68, 29.65, 29.59, 29.44, 29.36, 29.07, 24.78, 24.7, 22.6, 18.7, 14; MS (EI)= 414 [M]⁺

7-(Heptadecanoylcarbonyl)oxy-2H-1-benzopyran-2-on (13a): white solid; yield: 200 mg (0.77 mmol, 63%); m.p. 75°C; ¹H NMR (300 MHz, CDCl₃): δ=7.72 (d, J=6.9 Hz, 1H), 7.51 (d, J= 8.4 Hz, 1H), 7.13 (d, J=2.6 Hz, 1H), 7.04 (dd, J=8.4; 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.6 (t, J=7.4 2H) 1.7 (p, J=7.5 Hz, 2H), 1.2 (m, 28 H), 0.89 (t, J=6.9 3 H); ¹³C NMR (75 MHz, CDCl₃): δ=171.6, 160.8, 154.7, 153.5, 142.1, 128, 118.3, 116.5, 116, 110.5, 34.2, 32, 29.67, 29.65, 29.59, 29.44, 29.35, 29.23, 29.06, 24.8, 22.6; 14; MS (EI)= 430 [M]⁺

7-(Heptadecanoylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (13b): white solid; yield: 40 mg (0.09 mmol, 7.5%); m.p. 63-65°C ; ¹H NMR (300 MHz, CDCl₃): δ=7.63 (d, J=6.9 Hz, 1H), 7.13 (dd, J=8.4; 2.6 Hz, 1H), 7.1 (d, J= 8.4 Hz, 1H), 6.29 (d, J= 9.6 Hz, 1H), 2.6 (t, J=7.4 2H), 2.2 (s, 3H), 1.7 (p, J=7.5 Hz, 2H), 1.2 (m, 28 H), 0.89 (t J=6.9 3 H); ¹³C NMR (75 MHz, CDCl₃): δ=168.6, 160.8, 154.7, 153.5, 152.1, 125, 118.3, 117.5, 114, 110.5, 70.2, 69.9, 64; 45, 30.2, 29.67, 27.06, 26, 24.8, 21.6, 18; MS (EI)= 446 [M]⁺

7-(Phenylcarbonyl)oxy-2H-1-benzopyran-2-on (14a): white solid; yield: 110 mg (0.41 mmol, 34%); m.p. 158°C ; ¹H NMR (300 MHz, CDCl₃): δ=8.2 (dd, J=7.1; J=1.3 Hz, 1H), 7.7 (d, J=9.2 Hz 1H), 7.69 (t, J= 2.4 Hz, 1H), 7.58 (dd, J=7.35; J=2 Hz, 2H), 7.5 (t, J=1.6 Hz, 1H), 7.2 (dd J=8.4, 2.6 Hz 1H), 6.4 (d, J= 9.6 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ=164.6, 160.8, 154.7, 153.5, 142.1, 134, 128, 118.3, 116.7, 116.1, 110.5; MS (EI)= 266 [M]⁺

7-(Phenylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (14b): white solid; yield: 180 mg (0.64 mmol, 54%); m.p. 155°C ; ¹H NMR (300 MHz, CDCl₃): δ=8.2 (dd, J=7.1, J=1.3 Hz, 1H), 7.7 (d, J=9.2 Hz 2H), 7.5 (t, J= 2.4 Hz, 2H), 7.28 (d, J=2.2 Hz, 1H), 7.2 (dd J=8.4; 2.6 Hz 1H), 6.3 (d, J= 1.2 Hz, 1H), 2.4 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=164.5, 160.5, 154.2, 153.4, 151.9, 134.0, 130.3, 128.8, 128.7, 125.4, 118.2, 117.9, 224.5, 110.6, 18.7; MS (EI)= 280 [M]⁺

7-(Phenyl-methylcarbonyl)oxy-2H-1-benzopyran-2-on (15a): white solid; m.p. 95-96°C ; yield: 240 mg (0.86 mmol, 71%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J=9.6 Hz, 1H), 7.37 (d, J= 8.6 Hz, 1H), 7.29 (m, 5H), 7, (d, J=2.2 Hz, 1H), 6.9 (dd, J=5.4; 2.6 Hz, 1H), 6.3 (d, J= 9.6 Hz, 1H), 3.7 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ=169.6, 160.8, 154.7, 153, 142.1, 132, 129.36, 129.31, 128.55, 127, 118.3, 116.7, 116.1, 110, 41; MS (EI)= 280 [M]⁺

7-(Phenyl-methylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (15b): white solid; m.p. 85-87°C; yield: 200 mg (0.68 mmol, 57%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.41 (m, 5H), 7.11 (d, J=1.6 Hz, 1H), 7.07 (dd, J=5.4, 2.6 Hz, 1H), 6.28 (d, J=1.2 Hz), 3.9 (s, 2H), 2.44 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ=169, 160.8, 132.9, 129.36, 129.32, 128.8, 127.6, 114, 125, 117.9, 117.8, 114, 110, 41; MS (EI)= 294 [M]⁺

7-(Adamant-1-ylcarbonyl)oxy-2H-1-benzopyran-2-on (16a): white solid; m.p. 157-158°C; yield: 250 mg (0.77 mmol, 64%); ¹H NMR (300 MHz, CDCl₃): δ=7.73 (d, J=6.9 Hz, 1H), 7.5 (d, J= 8.4 Hz, 1H), 7.1 (d, J=2.6 Hz, 1H), 7.04 (dd, J=5.4, 2.6 Hz, 1H), 6.4 (d, J= 9.6 Hz, 1H), 2.09 (m, 6H), 1.8 (m, 3H), 1.6 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ=175.6, 160.8, 154.7, 153, 142.1, 128, 118.3, 116.5, 115, 110.5, 38.67, 36, 27; MS (EI)= 324 [M]⁺

7-(Adamant-1-ylcarbonyl)-4-methyl-oxy-2H-1-benzopyran-2-on (16b): white solid; m.p. 155-158°C; yield: 310 mg (0.85 mmol, 71%); ¹H NMR (300 MHz, CDCl₃): δ=7.6 (d, J= 8.4 Hz, 1H), 7.13 (d, J=1.6 Hz, 1H), 7.07 (dd, J=5.4, 2.6 Hz, 1H), 6.28 (d, J=1.2 Hz), 3.4 (p, J=3.5 Hz 1H), 2.47 (s, 3H), 2.4 (m, 4H), 2 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ=175.6, 160.8, 154.7, 153.5, 151.1, 125, 118.3, 114, 110.5, 41, 38, 36, 27, 18; MS (EI)= 338[M]⁺

7-[(Ethylcarbonyloxymethyl)-4-methyl-oxy-2H-1-benzopyran-2-on (17b): white solid; yield: 110 mg (0.44 mmol, 24%); m.p. 83°C; ¹H NMR (300 MHz, CDCl₃): δ=7.67 (d, J=6.9 Hz, 1H), 7.42 (d, J= 8.4 Hz, 1H), 7.03 (d, J=2.6 Hz, 1H), 6.95 (dd, J=8.4; 2.6 Hz, 1H), 6.31 (d, J= 9.6 Hz, 1H), 5.82 (s, 2H), 2.42 (q, J=7.4 Hz, 2H), 2.4 (s, 3H), 1.19 (t, J=7.4 Hz 3H); ¹³C NMR: (75 MHz, CDCl₃): δ=171, 169.6, 160.8, 159.7, 155.5, 143.1, 129, 114.3, 114, 113.5, 103.5, 84.7, 27.4, 8.7; MS (EI)= 262 [M]⁺

7-[(iso-Propylcarbonyloxymethyl) 4-methyl-oxy-2H-1-benzopyran-2-on (18b): white solid; yield: 160 mg (0,57 mmol, 51%); m.p. 50°C; ¹H NMR (300 MHz, CDCl₃): δ=7.54 (d, J=6.9 Hz, 1H), 6.99 (d, J= 8.4 Hz, 1H), 6.94 (d, J=2.6 Hz, 1H), 6.16 (d, J= 1.1 Hz, 1H), 5.8 (s, 2H), 2.62 (q, J=7.4 Hz, 1H), 2.3 (s, 3H), 1.17 (d, J=6.9 Hz 6H); ¹³C NMR (75 MHz, CDCl₃): δ=175.6, 160.9, 159.5, 154.9, 152.2, 125.7, 115.1, 113.2, 112.9, 103.4, 84.7, 33.9, 18.6; MS (EI)= 276 [M]⁺

7-[(Cyclopropylcarbonyloxymethyl)-4-methyl-oxy-2H-1-benzopyran-2-on (19b): white solid; yield: 90 mg (0.33 mmol, 18%); m.p. 97°C; ¹H NMR (300 MHz, CDCl₃): δ=7.67 (d, J=6.9 Hz, 1H), 7.42 (d, J= 8.4 Hz, 1H), 7.03 (d, J=2.6 Hz, 1H), 6.95 (dd, J=8.4; 2.6 Hz, 1H), 6.31 (d, J= 9.6 Hz, 1H), 5.82 (s, 2H), 2.42 (s, 3H), 1.67 (m, 1H), 1.08 (m, 1H), 0.97 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ=173.6, 160.2, 159.5, 154.9, 152.2, 125.5, 115.1, 113.2, 112.9, 103.4, 84.7, 18.6, 12.7, 92.7; MS (EI)= 274 [M]⁺

7-(nonylcarbonyloxymethyl)oxy-2H-1-benzopyran-2-on (20a): white solid; yield: 220 mg (0.64 mmol, 52%); m.p. 85-87°C ; ¹H NMR (300 MHz, CDCl₃): δ=7.69 (d, J=6.9 Hz, 1H), 7.44 (d, J= 8.4 Hz, 1H), 7.04 (d, J=2.6 Hz, 1H), 6.9 (dd, J=8.4, 2.6 Hz, 1H), 6.3 (d, J= 9.6 Hz, 1H), 5.8 (s, 2H), 2.4 (t, J=6.4 Hz, 2H) 1.23 (m, 14H), 0.88 (t, J=5.6); ¹³C NMR (75 MHz, CDCl₃): δ=172.4, 160.8, 159.7, 143.1, 128.9, 114.2, 113.9, 113.5, 103.4, 84.5, 34.1, 31.8, 29.19, 29.17, 28.9, 24.6, 22.6, 14.0; MS (EI)= 346 [M]⁺

7-(nonylcarbonyloxymethyl)-4-methyl-oxy-2H-1-benzopyran-2-on (20b): white solid; yield: 148 mg (0,41 mmol, 34%); m.p. 64°C; ¹H NMR (300 MHz, CDCl₃): δ=7.56 (d, J=6.9 Hz, 1H), 7.04 (d, J= 2.2 Hz, 1H), 7 (dd, J=6.9, 2.2 Hz, 1H), 6.2 (d, J= 1.3 Hz, 1H), 5.8 (s, 2H), 2.43 (s, 1H), 2.4 (t, J=6.4 Hz, 2H) 1.23 (m, 14H), 0.88 (t, J=5.6); ¹³C NMR (75 MHz, CDCl₃): δ=172.4, 160.9, 159.7, 154.5, 152.1, 125, 115.3, 113.3, 112, 103.5, 84.2, 37.4, 34, 31.8, 29.3, 29.1, 25, 24.6, 22.6, 18.6, 14; MS (EI)= 360 [M]⁺

B. Table S1. Abbreviation list and commercial source of lipases and esterases.

number	product number	short cut	enzyme name
1	F 46061	TBE	Thermoanaerobium brockii est.
2	F 46069	HrLE	horse liver est.
3	F 46054	BTE	Bacillus thermoglucosidasius est.
4	F 46071	SCE	Saccharomyces cerevisiae est.
5	F 46059	MME	Mucor miehei est.
6	F 46056	CLE	Candida lipolytica est.
7	F 62333	CVL	Cromobacterium visc. lipoprotein lip.
8	F 62321	PFL	Pseudomonas florescens lip.
9	F 62310	RNL	Rhizopus niveus lip.
10	F 62308	PRL	Penicillium roqueforti lip.
11	F 62300	HPL	hog pancreatic lip.
12	F 62294	ANL1	Aspergillus niger lip
13	F 62299	CAL	Candida antarctica lip.
14	F 73416	AOL	Aspergillus oryzae lip.
15	F 62316	CCL	Candida cylindraceae lip.
16	F 62298	MML	Mucor miehei lip.
17	F 62309	PCL2	Pseudomonas cepacia lip.
18	F 62303	CLL	Candida lipolytica lip.
19	F 62336	PSBL	Pseudomonas sp. B lipoprotein lip.
20	F 62304	MJL	Mucor javanicus lip.
21	F 62291	RML	Rhizomucor miehei lip.
22	F 62306	WGL	wheat germ lip.
23	Chyralzyme roche	E2	pig liver est.
24	Chyralzyme roche	E1	pig liver est.
25	Chyralzyme roche	L9	Mucor miehei
26	Chyralzyme roche	L8	Thermomyces lanuginosa
27	Chyralzyme roche	L7	pig pancreas lip
28	Chyralzyme roche	L6	Pseudomonas sp.
29	Chyralzyme roche	L5	Candida antarctica
30	Chyralzyme roche	L3	Candida rugosa
31	Chyralzyme roche	L2	Candida antarctica fraction B
32	Chyralzyme roche	L10	Alcaligines sp.
33	Chyralzyme roche	L3P	Candida rugosa purified
34	Sigma L-3126	PPL	porcine pancreas lip.
35	F 46062	BSE	Bacillus sp est.









































































