Electronic Supplementary Information

Synthesis of the bis potassium salts of 5-hydroxy-3-oxo-pent-4-enoic acids and their use for the efficient preparation of 4-hydroxy-2H-pyran-2-ones and other heterocycles

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General methods
All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Temperatures are reported as inner temperatures. Tetrahydrofuran was continuously refluxed and freshly distilled from sodium/benzophenone under argon, ethanol was dried with sodium / diethyl phthalate and distilled. Solvents used for extraction and purification were distilled prior to use. n-BuLi was titrated prior to use with sec-BuOH in Xylene and 1,10-phenanthroline as an indicator. TLC was performed on aluminium-backed plates coated with silica gel 60 with F254 indicator (Macherey & Nagel). Compounds were visualised by UV light (254 nm) or with FeCl₃ as a solution in ethanol. Flash column chromatography was carried out on silica gel 60 M, 230 - 400 mesh (Macherey & Nagel). Melting points obtained on the Büchi melting point apparatus B-545 with open capillary tubes are uncorrected. ¹H (¹³C) NMR spectra were recorded at 500 (125.7) and 300 (75.4) MHz on a Varian UnityInova spectrometer with CDCl₃ (δ = 7.26 ppm in ¹H NMR spectra and δ = 77.0 ppm in ¹³C NMR spectra), DMSO-d₆ (δ = 2.49 ppm in ¹H NMR spectra and δ = 39.7 ppm in ¹³C NMR spectra), D₂O (δ = 4.65 ppm in ¹H NMR spectra), and acetone-d₆ (δ = 2.04 ppm in ¹H NMR spectra and δ = 29.8 ppm in ¹³C NMR spectra), as internal standards. HSQC-, HMBC- and COSY spectra were recorded on a Varian UnityInova (500 MHz). Low-resolution electron impact mass spectra (EI-LRMS) and exact mass electron impact mass spectra (HRMS) were obtained at 70 eV on a Finnigan MAT 8200 instrument. The intensities are reported as percentages relative to the base peak after the corresponding m/z value.
IR spectra were measured on a Perkin-Elmer Spectrum One (FT-IR-spectrometer). UV/VIS spectra were recorded with a Varian Cary 50. All commercially available reagents were used without
further purification unless otherwise indicated and were purchased from Sigma-Aldrich Chemical Co., Acros Organics or Lancaster Organics.

**General procedure for the preparation of the N-acyl-2-methyl aziridines 8**

The N-acyl-2-methyl aziridines were prepared from their corresponding acyl chlorides following a known procedure. The aziridines were purified by vacuum distillation or by flash chromatography on silica gel. No elementary analyses or high resolution mass spectra were recorded because toxicity was suspected.

**N-Propionyl-2-methyl aziridine (8a):** Colourless oil. Bp 52 - 53°C / 18 mbar. R<sub>f</sub> = 0.47 (SiO<sub>2</sub>, PE / EtOAc = 10 : 1). IR (ATR): ν = 2976 (w), 2939 (vw), 1690 (vs), 1462 (m), 1406 (s), 1372 (s), 1280 (m), 1181 (s), 1162 (w), 1136 (w), 1108 (w), 1074 (w), 1040 (w), 1017 (w), 963 (m), 901 (w), 811 (w), 743 (w) cm<sup>-1</sup>. UV/VIS (MeOH): λ<sub>max</sub> (lg ε) = 234 nm (2.53). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 2.44 - 2.47 (m, 1 H), 2.40 (q, 2 H, <sup>3</sup>J = 7.6 Hz), 2.30 (d, 1 H, <sup>3</sup>J = 5.6 Hz), 1.91 (d, 1 H, <sup>3</sup>J = 3.2 Hz), 1.30 (d, 3 H, <sup>3</sup>J = 5.6 Hz), 1.14 (t, 3 H, <sup>3</sup>J = 7.5 Hz). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): δ (ppm) 187.0, 32.9, 31.5, 30.3, 18.0, 9.4. LRMS (EI, 70 eV): m/z (%) = 113 (1) [M<sup>+</sup>], 98 (1), 84 (4), 69 (4), 57 (100), 56 (92), 41 (45).

**N-Butyryl-2-methyl aziridine (8b):** Colourless oil. Bp 64°C / 18 mbar. R<sub>f</sub> = 0.49 (SiO<sub>2</sub>, PE / EtOAc = 10 : 1). IR (ATR): ν = 2964 (w), 2933 (vw), 2875 (vw), 1690 (vs), 1405 (s), 1372 (m), 1289 (w), 1179 (vs), 1089 (w), 985 (w), 919 (m), 816 (vw), 693 (vw) cm<sup>-1</sup>. UV/VIS (MeOH): λ<sub>max</sub> (lg ε) = 236 nm (2.68). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 2.48 - 2.43 (m, 1 H), 2.35 (q, 2 H, <sup>3</sup>J = 7.5 Hz, <sup>4</sup>J = 1.3 Hz), 2.31 (d, 1 H, <sup>3</sup>J = 5.9 Hz), 1.91 (d, 1 H, <sup>3</sup>J = 3.4 Hz), 1.66 (sext, 2 H, <sup>3</sup>J = 7.3 Hz), 1.30 (d, 3 H, <sup>3</sup>J = 5.4 Hz), 0.94 (t, 3 H, <sup>3</sup>J = 7.3 Hz). <sup>13</sup>C NMR (125.7 MHz, CDCl<sub>3</sub>): δ (ppm) 186.2, 39.1, 32.8, 31.5, 18.8, 18.0, 14.1. LRMS (EI, 70 eV): m/z (%) = 127 (1) [M<sup>+</sup>], 112 (1), 99 (4), 84 (6), 71 (23), 57 (56), 56 (71), 43 (100), 41 (68).

**N-Isobutyryl-2-methyl aziridine (8c):** Colourless oil. Bp 59°C / 19 mbar. R<sub>f</sub> = 0.55 (SiO<sub>2</sub>, PE / EtOAc = 10 : 1). IR (ATR): ν = 2970 (m), 2931 (w), 2874 (vw), 1688 (vs), 1469 (m), 1405 (s), 1384 (m), 1371 (m), 1353 (w), 1276 (s), 1188 (s), 1161 (m), 1124 (w), 1096 (w), 1035 (vw), 985 (w), 915 (w), 871 (vw), 847 (vw), 795 (vw), 766 (vw) cm<sup>-1</sup>. UV/VIS (MeOH): λ<sub>max</sub> (lg ε) = 238 nm
(2.70). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 2.62 (sept, 1 H, $^3J = 6.9$ Hz), 2.48 - 2.43 (m, 1 H), 2.32 (d, 1 H, $^3J = 5.9$ Hz), 1.90 (d, 1 H, $^3J = 3.5$ Hz), 1.31 (d, 3 H, $^3J = 5.6$ Hz), 1.18 (t, 6 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 190.2, 36.5, 33.0, 31.2, 19.9, 19.7, 18.0. LRMS (EI, 70 eV): $m/z$ (%) = 127 (1) [M$^+$], 112 (1), 98 (1), 84 (8), 71 (11), 57 (34), 56 (57), 43 (100), 41 (78).

$N$-Pivaloyl-2-methyl aziridine (8d): Colourless oil. Bp 55 - 56°C / 17 mbar. R$_f$ = 0.62 (SiO$_2$, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu}$ = 2931 (w), 2871 (vw), 1682 (vs), 1480 (m), 1461 (m), 1404 (s), 1365 (m), 1297 (s), 1247 (w), 1159 (s), 1121 (vs), 1084 (w), 1035 (vw), 972 (m), 938 (vw), 904 (w), 813 (vw), 796 (vw), 776 (w), 673 (vw)$^1$ cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 244 nm (2.67). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 2.44 - 2.40 (m, 1 H). 2.38 (d, 1 H, $^3J = 6.1$ Hz), 1.84 (d, 1 H, $^3J = 3.6$ Hz), 1.32 (d, 3 H, $^3J = 5.3$ Hz), 1.23 (s, 9 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 192.2, 41.3, 34.2, 31.1, 28.2, 18.0. LRMS (EI, 70 eV): $m/z$ (%) = 141 (4) [M$^+$], 126 (3), 117 (< 1), 98 (12), 84 (12), 69 (3), 57 (100), 56 (34), 43 (3), 41 (91).

$N$-Benzoyl-2-methyl aziridine (8e): Colourless oil. R$_f$ = 0.34 (SiO$_2$, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu}$ = 3061 (w), 2996 (vw), 2968 (vw), 2930 (vw), 1668 (vs), 1600 (w), 1490 (vw), 1466 (w), 1449 (m), 1405 (s), 1370 (m), 1315 (vs), 1295 (vs), 1227 (s), 1156 (m), 1139 (vw), 1121 (vw), 1110 (vw), 1070 (m), 1026 (w), 959 (s) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 239 (4.14), 275 nm (3.25). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.02 (d, 2 H, $^3J = 7.3$ Hz), 7.54 (t, 1 H, $^3J = 7.3$ Hz), 7.45 (t, 2 H, $^3J = 7.7$ Hz), 2.59 - 2.55 (m, 1 H), 2.54 (d, 1 H, $^3J = 5.8$ Hz), 2.14 (d, 1 H, $^3J = 3.6$ Hz), 1.39 (d, 3 H, $^3J = 5.3$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 179.3, 133.5, 132.6, 129.0, 128.4, 34.6, 32.1, 17.7. LRMS (EI, 70 eV): $m/z$ (%) = 161 (2) [M$^+$], 160 (24), 146 (1), 120 (35), 117 (4), 105 (100), 91 (4), 77 (89), 56 (83), 51 (74).

$N$-(3,4-Dimethoxybenzoyl)-2-methyl aziridine (8f): Mp 65°C. R$_f$ = 0.42 (SiO$_2$, PE / EtOAc = 7 : 3). IR (ATR): $\tilde{\nu}$ = 3005 (vw), 2962 (vw), 2940 (vw), 2614 (vw), 2026 (vw), 1739 (w), 1662 (vs), 1598 (m), 1586 (m), 1510 (s), 1470 (m), 1450 (m), 1417 (s), 1405 (s), 1371 (w), 1348 (w), 1298 (s), 1266 (vs), 1238 (vs), 1216 (vs), 1179 (m), 1165 (m), 1155 (m), 1144 (w), 1087 (w), 1022 (vs), 981 (w), 909 (m), 880 (s), 839 (m), 823 (w), 774 (vs), 761 (vs), 729 (w), 678 (w)$^1$ cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 268 (4.06), 296 nm (3.90). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.67 (dd, 1
H, $^3J = 8.2$ Hz, $^4J = 1.9$ Hz), 7.54 (d, 1 H, $^3J = 1.9$ Hz), 6.90 (d, 1 H, $^3J = 8.6$ Hz), 3.94 (s, 3 H), 3.93 (s, 3 H), 2.56 - 2.52 (m, 2 H), 2.10 (d, 1 H, $^3J = 3.0$ Hz), 1.40 (d, 3 H, $^3J = 5.6$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 179.2, 153.0, 148.9, 126.5, 123.3, 111.8, 110.5, 56.3, 56.2, 35.0, 32.3, 18.1. LRMS (EI, 70 eV): m/z (%) = 221 (61) [M$^+$], 206 (2), 190 (< 1), 177 (5), 165 (100), 144 (3), 137 (20), 122 (22), 107 (18), 94 (14), 92 (21), 79 (51), 77 (40), 51 (36).

$\textbf{N-(3,4,5-Trimethoxybenzoyl)-2-methyl aziridine (8g):}$ Mp 61°C. $R_t = 0.51$ (SiO$_2$, PE / EtOAc = 7 : 3). IR (ATR): $\tilde{\nu} = 3071$ (vw), 3006 (vw), 2965 (vw), 2946 (vw), 2833 (vw), 1994 (vw), 1663 (vs), 1584 (s), 1502 (s), 1462 (s), 1431 (w), 1415 (vs), 1404 (s), 1368 (w), 1330 (vs), 1282 (m), 1234 (vs), 1204 (m), 1183 (m), 1164 (s), 1154 (s), 1121 (vs), 1001 (vs), 909 (w), 886 (vs), 846 (w), 832 (w), 799 (vw), 771 (vs), 742 (m), 676 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 268 (4.06), 296 nm (3.90). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.29 (s, 2 H), 3.91 (s, 9 H), 2.58 - 2.52 (m, 2 H), 2.12 (d, 1 H, $^3J = 3.3$ Hz), 1.41 (d, 3 H, $^3J = 5.6$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 179.1, 153.2, 142.2, 128.9, 106.6, 61.2, 56.4, 35.1, 32.4, 18.1. LRMS (EI, 70 eV): m/z (%) = 251 (70) [M$^+$], 195 (100).

$\textbf{N-(2-Furoyl)-2-methyl aziridine (8h):}$ Pale yellow oil. $R_t = 0.34$ (SiO$_2$, PE / EtOAc = 8 : 2). IR (ATR): $\tilde{\nu} = 3121$ (vw), 2998 (vw), 2971 (vw), 2932 (vw), 1660 (vs), 1575 (m), 1566 (w), 1468 (s), 1442 (w), 1406 (vs), 1392 (m), 1371 (m), 1312 (vs), 1247 (w), 1228 (w), 1177 (vs), 1154 (m), 1101 (m), 1083 (m), 1012 (s), 964 (m), 920 (s), 884 (m), 867 (w), 835 (w), 760 (vs), 656 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 220 (3.73), 260 nm (4.10). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.55 (s, 1 H), 7.16 (d, 1 H, $^3J = 3.4$ Hz), 6.50 (dd, 1 H, $^3J = 3.4$ Hz, $^3J = 1.5$ Hz), 2.68 - 2.63 (m, 1 H), 2.54 (d, 1 H, $^3J = 5.9$ Hz), 2.12 (d, 1 H, $^3J = 3.9$ Hz), 1.40 (d, 3 H, $^3J = 5.6$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 169.7, 148.6, 146.0, 117.1, 112.1, 34.8, 32.2, 18.0. LRMS (EI, 70 eV): m/z (%) = 151 (34) [M$^+$], 123 (19), 110 (48), 95 (95), 81 (21), 67 (14), 56 (100), 41 (28), 39 (79).

$\textbf{N-(3-Furoyl)-2-methyl aziridine (8i):}$ Pale yellow oil. $R_t = 0.43$ (SiO$_2$, PE / EtOAc = 8 : 2). IR (ATR): $\tilde{\nu} = 3131$ (vw), 2997 (vw), 2969 (vw), 2932 (vw), 1665 (vs), 1569 (m), 1506 (w), 1466 (w), 1442 (w), 1405 (s), 1371 (m), 1320 (vs), 1252 (w), 1173 (s), 1155 (vs), 1117 (w), 1073 (m), 1036 (w), 1010 (m), 983 (w), 932 (s), 873 (vs), 832 (m), 792 (w), 766 (vs), 741 (s), 577 (w) cm$^{-1}$. 4
UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 247 nm (3.63). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.02 (s, 1 H), 7.43 (t, 1 H, $^3$$J$ = 1.6 Hz), 6.74 (d, 1 H, $^3$$J$ = 1.5 Hz), 2.60 - 2.55 (m, 1 H), 2.51 (d, 1 H, $^3$$J$ = 5.9 Hz), 2.06 (d, 1 H, $^3$$J$ = 3.7 Hz), 1.37 (d, 3 H, $^3$$J$ = 5.6 Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 174.6, 146.8, 143.7, 122.9, 109.4, 34.1, 31.8, 17.8. LRMS (EI, 70 eV): $m/z$ (%) = 151 (18) [M$^+$], 136 (2), 123 (20), 122 (12), 110 (6), 95 (100), 81 (1), 67 (13), 56 (80), 39 (55).

$N$-(2-Thenoyl)-2-methyl aziridine (8j): Pale yellow oil. $R_f$ = 0.35 (SiO$_2$, PE / EtOAc = 9 : 1). IR (ATR): $\tilde{\nu}$ = 3091 (vw), 2996 (vw), 2969 (vw), 2929 (vw), 1651 (vs), 1519 (w), 1456 (w), 1415 (vs), 1403 (vs), 1369 (w), 1358 (s), 1291 (vs), 1230 (s), 1202 (w), 1154 (w), 1112 (vw), 1083 (w), 1071 (m), 1045 (w), 951 (w), 937 (m), 902 (vw), 850 (s), 823 (vw), 807 (vw), 790 (vw), 761 (vs), 749 (s), 717 (vs) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 256 (3.98), 276 nm (3.94). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.77 (d, 1 H, $^3$$J$ = 3.7 Hz), 7.55 (d, 1 H, $^3$$J$ = 5.1 Hz), 7.11 (t, 1 H, $^3$$J$ = 4.4 Hz), 2.67-2.62 (m, 1 H), 2.59 (d, 1 H, $^3$$J$ = 5.9 Hz), 2.12 (d, 1 H, $^3$$J$ = 3.7 Hz), 1.42 (d, 3 H, $^3$$J$ = 5.4 Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 173.6, 138.3, 132.00, 131.96, 127.8, 35.3, 32.3, 17.8. LRMS (EI, 70 eV): $m/z$ (%) = 167 (36) [M$^+$], 152 (< 1), 140 (1), 126 (64), 111 (100), 83 (46), 56 (92).

$N$-Nicotinoyl-2-methyl aziridine (8k): The raw material was purified via silica gel flash chromatography with diethyl ether as the eluent. Note that this compound is extremely sensitive. After exposure to air the colourless oil rapidly oxidizes to a brown oil; after 4 h an almost black resin was obtained. On the other hand, this compound is relatively stable in a solution of, for example, THF (3 M) stored at low temperatures (-20°C).

$R_f$ = 0.67 (SiO$_2$, CHCl$_3$ / MeOH = 20 : 1). IR (ATR): $\tilde{\nu}$ = 2979 (vw), 2931 (vw), 1669 (s), 1586 (m), 1466 (w), 1417 (m), 1406 (s), 1371 (w), 1326 (vs), 1304 (vs), 1230 (m), 1193 (w), 1159 (m), 1114 (m), 1098 (m), 1024 (m), 958 (m), 889 (vw), 859 (vw), 794 (vw), 725 (w), 703 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 225 (3.99), 265 nm (3.63). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 9.22 (d, 2 H, $^3$$J$ = 2.0 Hz), 8.75 (dd, 1 H, $^3$$J$ = 4.8 Hz, $^4$$J$ = 1.6 Hz), 8.26 (td, 1 H, $^3$$J$ = 7.9 Hz, $^4$$J$ = 1.9 Hz), 7.39 (dd, 1 H, $^3$$J$ = 7.9 Hz, $^3$$J$ = 5.0 Hz), 2.66 - 2.60 (m, 1 H), 2.57 (d, 1 H, $^3$$J$ = 5.7 Hz), 2.18 (d, 1 H, $^3$$J$ = 3.5 Hz), 1.40 (d, 3 H, $^3$$J$ = 5.5 Hz). $^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ (ppm) 177.4, 153.1, 150.4, 136.4, 129.1, 123.4, 34.8, 32.2, 17.6. LRMS (EI, 70 eV): $m/z$ (%) = 162 (6) [M$^+$], 161 (21), 147 (8), 134 (18), 118 (2), 106 (96), 78 (93), 56 (100), 51 (80).
**N-Isonicotinoyl-2-methyl aziridine (8l):** Due to the sensitivity of this compound an alternative procedure was developed. 305 mg (2.5 mmol) DMAP was added to a suspension of 3 g (24.4 mmol) isonicotinic acid in 80 ml of dry CH$_2$Cl$_2$, which was then treated with 2.1 ml (30 mmol) 2-methylaziridine and finally a solution of 5.16 g (25 mmol) DCC in 20 ml CH$_2$Cl$_2$ at 0°C. The resulting mixture was stirred at 0°C for 3 h, then the cooling bath was removed and the white slurry stirred for an additional 12 h at rt. The precipitate was filtered off and washed with one portion of CH$_2$Cl$_2$ (50 ml). The filtrates were combined and the volatiles carefully removed in vacuo (heating should be avoided). The residue was immediately submitted to flash chromatography on silica gel with diethyl ether as the eluent. 2.84 g (17.6 mmol, 72 %) N-Isonicotinoyl-2-methylaziridine (8k) was obtained as a colourless oil that quickly turned brown. The material can be stored as a solution in THF at -20°C (see 8k).

R$_f$ = 0.37 (SiO$_2$, Et$_2$O). IR (ATR): $\tilde{\nu}$ = 2969 (vw) 1672 (s), 1594 (m), 1556 (m), 1466 (w), 1406 (s), 1371 (w), 1326 (v), 1304 (vs), 1230 (m), 1159 (m), 1098 (w), 1062 (w), 993 (m), 964 (m), 850 (s), 760 (vs), 719 (m), 700 (s), 665 (m) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 217 (3.91), 235 (3.67), 272 nm (3.37). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 8.77 (dd, 2 H, $^3J$ = 4.5 Hz, $^4J$ = 1.5 Hz), 7.79 (dd, 2 H, $^3J$ = 4.5 Hz, $^4J$ = 1.5 Hz), 2.67 - 2.59 (m, 1 H), 2.19 (d, 1 H, $^3J$ = 3.5 Hz), 1.40 (d, 3 H, $^3J$ = 5.3 Hz). $^{13}$C NMR (75.4 MHz, CDCl$_3$): $\delta$ (ppm) 177.7, 150.9, 140.6, 122.5, 35.1, 32.6, 17.9. LRMS (EI, 70 eV): $m/z$ (%) = 162 (12) [M$^+$], 161 (22), 147 (2), 134 (13), 118 (7), 106 (63), 78 (73), 56 (100), 51 (67).

**N-Capryloyl-2-methyl aziridine (8m):** Colourless liquid. Bp 91 – 92°C / 0.29 mbar. R$_f$ = 0.26 (SiO$_2$, PE / EtOAc = 20 : 1). IR (ATR): $\tilde{\nu}$ = 2926 (vs), 2856 (vs), 1693 (vs), 1467 (m), 1405 (s), 1373 (m), 1282 (m), 1234 (vs), 1173 (m), 1104 (w), 1037 (w), 984 (w), 915 (w), 724 (w) cm$^{-1}$. UV/VIS (MeOH); $\lambda_{max}$ (lg $\varepsilon$) = 242 (2.56). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 2.47 - 2.42 (m, 1 H), 2.35 (dt, 2 H, $^3J$ = 7.5 Hz, $^4J$ = 1.3 Hz), 2.30 (d, 1 H, $^4J$ = 6.0 Hz), 1.90 (d, 1 H, $^3J$ = 3.3 Hz), 1.62 (quint, 2 H, $^3J$ = 7.3 Hz), 1.30 - 1.25 (m, 8 H), 1.29 (d, 3 H, $^3J$ = 5.4 Hz), 0.86 (t, 3 H, $^3J$ = 7.1 Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 186.4, 37.2, 32.8, 31.9, 31.5, 29.5, 29.2, 25.4, 22.8, 18.0, 14.3. LRMS (EI, 70 eV): $m/z$ (%) = 183 (1.5) [M$^+$], 182 (1), 168 (2), 154 (8), 149 (3), 126 (6), 112 (33), 99 (100), 84 (6), 57 (89), 43 (20). HRMS (EI, M$^+$): Calcd. for C$_{11}$H$_{21}$NO: 183.1623. Found: 183.1618. Anal. calcd. for C$_{11}$H$_{21}$NO: C 72.08, H 11.55, N 7.64. Found: C 72.16, H 11.61, N 7.60.
N-Palmitinoyl-2-methyl aziridine (8n): Colourless solid. Mp 41°C. R_f = 0.46 (SiO2, PE / EtOAc = 8 : 2). IR (ATR): ν = 2959 (w), 2911 (vs), 2848 (s), 1684 (vs), 1471 (s), 1415 (m), 1390 (m), 1348 (w), 1331 (w), 1316 (w), 1298 (w), 1216 (w), 1195 (w), 1183 (m), 1158 (w), 1140 (w), 1112 (w), 1092 (w), 1029 (w), 1010 (w), 996 (w), 906 (w), 778 (w), 737 (w), 716 (s) cm⁻¹. UV/VIS (MeOH); λ_max (lg ε) = 243 (3.20). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 2.49 - 2.44 (m, 1 H), 2.37 (dt, 2 H, ³J = 7.6 Hz, ⁴J = 1.2 Hz), 2.31 (d, 1 H, ³J = 5.9 Hz ), 1.91 (d, 1 H, ³J = 3.4 Hz), 1.67 - 1.61 (m, 2 H), 1.32 - 1.25 (m, 24 H), 1.31 (d, 3 H, ³J = 5.4 Hz), 0.87 (t, 3 H, ³J = 6.8 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 186.4, 37.3, 32.9, 32.2, 31.5, 29.92 (2×C), 29.91 (2×C), 29.89 (2×C), 29.8, 29.7, 29.6 (2×C), 25.4, 22.9, 18.0, 14.3. LRMS (EI, 70 eV): m/z (%) = 295 (5) [M⁺], 294 (4), 280 (5), 266 (5), 252 (6), 239 (16), 224 (3), 210 (4), 196 (4), 182 (5), 168 (7), 154 (10), 126 (11), 112 (52), 99 (88), 84 (54), 71 (64), 57 (100), 43 (76). HRMS (EI, M⁺): Calcd. for C₁₉H₃₇NO: 295.2875. Found: 295.2875. Anal. calcd. for C₁₉H₃₇NO: C 77.23, H 12.62, N 4.74. Found: C 77.22, H 12.62, N 4.74.

General procedure for the preparation of the 5-hydroxy-3-oxo-pent-4-enolic acid ethyl esters 1
The 5-hydroxy-3-oxo-pent-4-enolic acid ethyl esters 1 were prepared from the N-acyl aziridines 8 by modifying a known procedure.⁶a
Method A) With NaH/n-BuLi: 1.90 g (14.63 mmol) ethyl acetoacetate were added dropwise to a suspension of 386 mg (16.1 mmol) NaH and 80 ml THF at rt (beware of vigorous evolution of hydrogen) and the resulting mixture stirred for 1 h at rt. The clear solution was cooled down to -10°C and 10.1 ml of a n-BuLi solution (16.1 mmol, 1.6 M in n-Hexan) were added dropwise. The resulting yellow solution was stirred for 15 min at -10°C, and then a solution of 12.7 mmol N-acyl-2-methyl aziridine in 30 ml THF was added within 20 min. The resulting mixture was allowed to warm to 0°C and stirred for another 3 h. The mixture was poured into 300 ml of saturated NH₄Cl solution under vigorous stirring, and the organic phase was separated. The aqueous phase was extracted three times with EtOAc and the organic phases were combined. After washing with water and brine the organic phase was dried over MgSO₄ and the volatiles were removed in vacuo. The residue was then submitted to flash chromatography.
Method B) With 2 equivalents of LDA: 46.8 ml of a n-BuLi solution (63.65 mmol, 1.36 M in n-hexane) were added to a solution of 9.12 ml (65.01 mmol) diisopropylamine in 50 ml THF at -10°C with stirring within 30 min, and the resulting solution was stirred at -10°C for another 30 min. The reaction mixture was cooled down to -78°C, and a solution of 3.94 g (30.31 mmol) ethyl acetoacetate in 10 ml of THF was added dropwise. The acetone/dry-ice cooling bath was replaced by an ice bath; the yellow solution was allowed to warm to 0°C and stirred at this temperature for 10 min. Then a solution of 27.56 mmol N-acyl-2-methyl aziridine 8 in 20 ml of THF was added dropwise and the resulting mixture stirred for 3 h at 0°C. The mixture was then poured into 300 ml of saturated NH₄Cl solution, and the organic phase was separated. The aqueous phase was extracted three times with EtOAc and the organic phases were combined. After washing with water, followed by brine and drying over MgSO₄ the volatiles were removed in vacuo and the residue subjected to flash chromatography.

The 1D and 2D NMR spectra (¹H, ¹³C, HSQC, HMBC, COSY, ROESY) indicated that all esters mainly exist as a mixture of 3 tautomers in CDCl₃ solution. The tautomers were identified as 5-hydroxy-3-oxo-pent-4-enoic acid ethyl ester, 3,5-dioxo-pentanoic acid ethyl ester and 3-hydroxy-5-oxo-pent-2-enoic acid ethyl ester. Their structures were confirmed by detailed NMR studies (HSQC-, HMBC- or COSY correlation spectra). The ratios of the individual tautomers were determined by analysis of the integrals of the proton signals.

5-Hydroxy-3-oxo-hept-4-enoic acid ethyl ester (1a): (Method A). Colourless liquid. Rₜ = 0.52 (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): ν = 2982 (vw), 2941 (vw), 1736 (vs), 1599 (vs), 1447 (w), 1411 (w), 1368 (m), 1322 (s), 1253 (vs), 1144 (vs), 1064 (w), 1029 (vs), 938 (m), 897 (w), 857 (w), 807 (w), 771 (m), 658 (vw) cm⁻¹. UV/VIS (MeOH): λ_max (lg ε) = 273 nm (3.73). ¹H NMR (500 MHz, CDCl₃): δ(ppm) 15.10 (bs, 1 H), 5.60 (s, 1 H), 4.19 (q, 2 H, ³J = 7.1 Hz), 3.32 (s, 2 H), 2.33 (q, 2 H, ³J = 7.5 Hz), 1.27 (t, 3 H, ³J = 7.1 Hz), 1.13 (t, 3 H, ³J = 7.6 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 194.5, 186.7, 167.6, 99.1, 61.4, 45.1, 31.0, 14.0, 9.5. 3,5-Dioxo-heptanoic acid ethyl ester: ¹H NMR (500 MHz, CDCl₃): δ(ppm) 4.17 (overlapping, q, 2 H, ³J = 7.1 Hz), 3.72 (s, 2 H), 3.55 (s, 2 H), 2.53 (q, 2 H, ³J = 7.3 Hz), 1.26 (overlapping, t, 3 H, ³J = 7.1 Hz), 1.06 (t, 3 H, ³J = 7.3 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 204.3, 197.0, 167.0, 61.5, 56.2, 49.4, 37.0, 14.0, 7.4. 3-Hydroxy-5-oxo-hept-2-enoic acid ethyl ester: ¹H NMR (500 MHz, CDCl₃): δ(ppm) 12.10 (bs, 1 H), 5.10 (s, 1 H), 3.25 (s, 2 H), 2.56 (overlapping, q, 2 H, ³J = 7.1 Hz). ¹³C
NMR (125.7 MHz, CDCl₃): $\delta$ (ppm) 205.1*, 170.9*, 92.3, 60.3, 48.8, 35.9, 14.2. LRMS (EI, 70 eV): $m/z$ (%) = 186 (15) [M⁺], 157 (51), 141 (12), 130 (10), 115 (64), 99 (72), 84 (12), 57 (80), 29 (100). HRMS (EI, M⁺): Calcd. for C₉H₁₄O₄: 186.0892. Found: 186.0863. Anal. calcd. for C₉H₁₄O₄: C 58.05, H 7.58. *From HMBC spectra

5-Hydroxy-3-oxo-oct-4-enoic acid ethyl ester (1b): (Method A). Colourless liquid. $R_f = 0.58$ (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu}$ = 2966 (vw), 2937 (vw), 2876 (vw), 1737 (vs), 1599 (vs), 1447 (w), 1410 (w), 1368 (m), 1320 (s), 1254 (vs), 1147 (vs), 1096 (m), 1030 (vs), 922 (w), 897 (w), 860 (w), 774 (m) cm⁻¹. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 276 nm (3.86). $^1$H NMR (500 MHz, CDCl₃): $\delta$ (ppm) 15.12 (bs, 1 H), 5.59 (s, 1 H), 4.19 (q, 2 H, $^3J = 7.0$ Hz), 3.33 (s, 2 H), 2.27 (t, 2 H, $^3J = 7.5$ Hz), 1.63 (sext, 2 H, $^3J = 7.4$ Hz), 1.27 (t, 3 H, $^3J = 7.0$ Hz), 0.95 (t, 3 H, $^3J = 7.4$ Hz). $^{13}$C NMR (125.7 MHz, CDCl₃): $\delta$ (ppm) 192.9, 187.5, 167.6, 99.8, 61.4, 45.3, 39.6, 19.1, 14.1, 13.6. 3,5-Dioxo-octanoic acid ethyl ester: $^1$H NMR (500 MHz, CDCl₃): $\delta$ (ppm) 4.18 (overlapping, q, 2 H, $^3J = 7.0$ Hz), 3.72 (s, 2 H), 3.55 (s, 2 H), 2.49 (t, 2 H, $^3J = 7.4$ Hz), 1.62 (overlapping, sext, 2 H, $^3J = 7.3$ Hz), 1.27 (overlapping, t, 3 H, $^3J = 7.0$ Hz), 0.93 (overlapping, t, 3 H, $^3J = 7.4$ Hz). $^{13}$C NMR (125.7 MHz, CDCl₃): $\delta$ (ppm) 203.9, 197.0, 167.0, 61.5, 56.5, 49.4, 45.6, 16.8, 14.0, 13.5. 3-Hydroxy-5-oxo-oct-2-enoic acid ethyl ester: $^1$H NMR (500 MHz, CDCl₃): $\delta$ (ppm) 12.1 (bs, 1 H), 5.1 (s, 1 H), 3.24 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl₃): $\delta$ (ppm) 92.7, 49.9. LRMS (EI, 70 eV): $m/z$ (%) = 200 (10) [M⁺], 157 (92), 129 (10), 115 (100), 84 (10), 69 (47), 55 (9), 43 (73), 29 (54). HRMS (EI, M⁺): Calcd. for C₁₀H₁₆O₄: 200.1049. Found: 200.1023. Anal. calcd. for C₁₀H₁₆O₄: C 59.99, H 8.05. Found: C 60.19, H 8.13.

5-Hydroxy-6-methyl-3-oxo-hept-4-enoic acid ethyl ester (1c): (Method B). Colourless liquid. $R_f = 0.58$ (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu}$ = 2974 (w), 2937 (w), 2876 (vw), 1737 (vs), 1596 (vs), 1466 (m), 1410 (w), 1387 (m), 1322 (s), 1254 (vs), 1150 (vs), 1096 (m), 1030 (vs), 912 (m), 843 (w), 778 (m) cm⁻¹. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 2966 (vw), 2937 (vw), 2876 (vw), 1737 (vs), 1599 (vs), 1447 (w), 1410 (w), 1368 (m), 1320 (s), 1254 (vs), 1147 (vs), 1096 (m), 1030 (vs), 922 (w), 897 (w), 860 (w), 774 (m) cm⁻¹. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 276 nm (3.86). $^1$H NMR (500 MHz, CDCl₃): $\delta$ (ppm) 15.20 (bs, 1 H), 5.61 (s, 1 H), 4.20 (q, 2 H, $^3J = 7.1$ Hz), 3.34 (s, 2 H), 2.47 (sept, 1 H, $^3J = 7.0$ Hz), 1.28 (t, 3 H, $^3J = 7.1$ Hz), 1.15 (d, 6 H, $^3J = 7.0$ Hz). $^{13}$C NMR (125.69 MHz, CDCl₃): $\delta$ (ppm) 197.7, 187.9, 167.8, 98.0, 61.6, 45.6, 36.5, 19.5, 14.3. 6-Methyl-3,5-dioxo-heptanoic acid ethyl ester: $^1$H NMR (500 MHz, CDCl₃): $\delta$ (ppm) 4.18 (overlapping, q, 2 H, $^3J = 7.2$ Hz), 3.79 (s, 2 H), 3.56 (s, 2 H), 2.68 (sept, 1 H, $^3J = 7.0$ Hz), 1.27 (overlapping, t, 3 H, $^3J = 7.1$ Hz).
Hz), 1.13 (d, 6 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 208.0, 197.6, 167.3, 61.7, 54.5, 49.6, 42.1, 17.9, 14.3. **3-Hydroxy-6-methyl-5-oxo-hept-2-enoic acid ethyl ester:** $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 12.09 (bs, 1 H), 5.07 (s, 1 H), 3.32 (s, 2 H), 2.75 (sept, 1 H, $^3J = 6.9$ Hz), 1.13 (d, 6 H, $^3J = 7.0$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 208.2, 172.5, 171.0, 92.5, 47.0, 41.2, 18.2. LRMS (EI, 70 eV): $m/z$ (%) = 200 (15) [M$^+$], 185 (2), 157 (74), 129 (17), 115 (72), 84 (11), 69 (48), 43 (100), 29 (39). HRMS (EI, M$^+$): Calcd. for C$_{10}$H$_{16}$O$_4$: 200.1049. Found: 200.1048. Anal. calcd. for C$_{10}$H$_{16}$O$_4$: C 59.99, H 8.05. Found: C 59.89, H 8.02.

5-Hydroxy-6,6-dimethyl-3-oxo-hept-4-enoic acid ethyl ester (1d): (Method B). Colourless liquid. $R_f = 0.60$ (SiO$_2$, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu} = 2971$ (w), 2874 (vw), 1738 (vs), 1595 (vs), 1480 (w), 1464 (w), 1411 (vv), 1395 (vv), 1366 (m), 1321 (m), 1279 (m), 1251 (s), 1219 (s), 1136 (vs), 1097 (w), 1060 (vw), 1030 (vs), 941 (w), 900 (w), 862 (vw), 788 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 276 nm (3.32). $^1$H NMR (500 MHz, CDCl$_3$): 15.46 (bs, 1 H), 5.70 (s, 1 H), 4.20 (q, 2 H, $^3J = 7.3$ Hz), 3.35 (s, 2 H), 1.27 (t, 3 H, $^3J = 7.2$ Hz), 1.17 (s, 9 H). $^{13}$C NMR (125.69 MHz, CDCl$_3$): 199.7, 188.4, 167.9, 96.1, 61.6, 45.8, 39.1, 27.4, 14.3. **6,6-Dimethyl-3,5-dioxo-heptanoic acid ethyl ester:** $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 4.17 (overlapping, q, 2 H, $^3J = 7.2$ Hz), 3.83 (s, 2 H), 3.56 (s, 2 H), 1.27 (t, 3 H, $^3J = 7.2$ Hz), 1.15 (s, 9 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 208.0*, 198.1, 167.5, 61.7, 51.3, 49.5, 45.3, 26.2, 14.3. LRMS (EI, 70 eV): $m/z$ (%) = 214 (11) [M$^+$], 199 (5), 169 (24), 157 (94), 127 (79), 115 (89), 111 (91), 84 (47), 69 (90), 57 (75), 43 (100), 29 (73). HRMS (EI, M$^+$): Calcd. for C$_{11}$H$_{18}$O$_4$: 214.1205. Found: 214.1215. Anal. calcd. for C$_{11}$H$_{18}$O$_4$: C 61.66, H 8.47. Found: C 61.50, H 8.47. *from HMBC spectra

5-Hydroxy-3-oxo-5-phenyl-pent-4-enoic acid ethyl ester (1e): (Method B): Colourless liquid. $R_f = 0.66$ (SiO$_2$, PE / EtOAc = 8 : 2). IR (ATR): $\tilde{\nu} = 2983$ (vv), 2939 (vv), 1734 (vs), 1679 (w), 1599 (vs), 1571 (vs), 1457 (m), 1413 (w), 1367 (w), 1267 (vs), 1248 (vs), 1179 (s), 1150 (s), 1027 (vs), 1001 (w), 956 (w), 843 (w), 811 (vv), 759 (vs), 686 (vs) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 247 nm (3.32), 312 (4.16). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 15.78 (bs, 1 H), 7.95 - 7.93 (m, 2 H), 7.55-7.52 (m, 1 H), 7.47 - 7.44 (m, 2 H), 6.30 (s, 1 H), 4.23 (q, 2 H, $^3J = 7.2$ Hz), 3.48 (s, 2 H), 1.30 (t, 3 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 189.3, 182.6, 167.6, 134.1, 132.6, 128.7, 127.1, 96.7, 61.5, 45.9, 14.1. **3,5-Dioxo-5-phenyl-pentanoic acid ethyl ester:** $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.95 - 7.93 (m, 2 H), 7.62 - 7.59 (m, 1 H), 7.50 - 7.47
(overlapping, m, 2 H), 4.29 (s, 2 H), 4.18 (q, 2 H, $^3J = 7.2$ Hz), 3.65 (s, 2 H), 1.25 (t, 3 H, $^3J = 7.2$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 197.3, 193.8, 167.1, 133.9, 128.8, 128.6, 53.1, 49.2, 14.0. 3-Hydroxy-5-oxo-5-phenyl-pent-2-enoic acid ethyl ester: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 12.20 (s, 1 H), 5.14 (s, 1H). LRMS (EI): $m/z$ (%) = 234 (21) [M$^+$], 216 (3), 205 (4), 188 (12), 160 (55), 147 (83), 105 (100), 77 (52), 69 (55), 51 (19), 29 (22). HRMS (EI, M$^+$): Calcd. for C$_{10}$H$_{16}$O$_4$: 234.0892. Found: 234.0890.

5-(3,4-Dimethoxy-phenyl)-5-hydroxy-3-oxo-pent-4-enoic acid ethyl ester (1f): (Method A). White solid. Mp 48°C. R$_f$ = 0.41 (SiO$_2$, PE / EtOAc = 7 : 3). IR (ATR): $\tilde{\nu}$ = 3463 (vw), 3084 (vw), 2994 (vw), 2970 (vw), 2944 (vw), 2835 (vw), 2688 (vw), 2605 (vw), 2161 (vw), 2030 (vw), 1839 (vw), 1802 (vw), 1739 (vs), 1593 (vs), 1572 (vs), 1511 (vs), 1466 (vs), 1434 (vs), 1200 (m), 1361 (m), 1341 (m), 1291 (m), 1257 (vs), 1151 (vs), 1136 (vs), 1092 (vs), 1015 (vs), 941 (vs), 896 (vs), 814 (s), 780 (vs), 765 (vs), 747 (vs), 735 (vs) cm$^{-1}$. UV/VIS (MeOH): $\lambda$$_{max}$ (lg $\varepsilon$) = 234 nm (4.04), 280 (3.82), 341 (4.23). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 16.01 (bs, 1 H, enolic H), 7.51 (dd, 1 H, $^3J = 8.5$ Hz, $^4J = 2.2$ Hz), 7.44 (d, 1 H, $^4J = 2.0$ Hz), 6.90 (d, 1 H, $^3J = 8.3$ Hz), 6.23 (s, 1 H), 4.22 (q, 2 H, $^3J = 7.0$ Hz), 3.94 (s, 6 H), 3.44 (s, 2 H), 1.29 (t, 3 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 186.5, 184.3, 168.0, 153.3, 149.3, 127.4, 121.7, 110.7, 109.9, 96.3, 61.7, 56.3, 45.4, 14.4. 5-(3,4-Dimethoxy-phenyl)-3,5-dioxo-pentanoic acid ethyl ester: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.55 (dd, 1 H, $^3J = 8.3$ Hz, $^4J = 2.0$ Hz), 4.23 (s, 2 H), 4.17 (overlapping, q, 2 H, $^3J = 7.3$ Hz), 3.93 (s, 6 H), 3.63 (s, 2 H), 1.25 (t, 3 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 197.8, 192.3, 154.3, 149.4, 129.6, 124.1, 110.5, 110.4, 56.4, 53.4, 49.4, 14.3. LRMS (EI, 70 eV): $m/z$ (%) = 294 (87) [M$^+$], 248 (51), 220 (33), 207 (46), 165 (100), 139 (24), 124 (29), 107 (8), 77 (12), 69 (24), 29 (15). HRMS (EI, M$^+$): Calcd. for C$_{15}$H$_{16}$O$_6$: 294.1104. Found: 294.1103.

5-Hydroxy-3-oxo-5-(3,4,5-trimethoxy-phenyl)-pent-4-enoic acid ethyl ester (1g): (Method A). White solid. Mp 51°C. R$_f$ = 0.37 (SiO$_2$, PE / EtOAc = 7 : 3). IR (ATR): $\tilde{\nu}$ = 3457 (vv), 3101 (vv), 3007 (w), 2981 (w), 2944 (w), 2927 (w), 2833 (w), 2638 (vw), 1738 (vs), 1572 (vs), 1500 (s), 1461 (s), 1429 (m), 1410 (m), 1361 (w), 1320 (s), 1261 (s), 1236 (s), 1211 (m), 1186 (m), 1165 (m), 1125 (vs), 1089 (s), 1031 (s), 993 (vs), 964 (s), 947 (s), 918 (w), 867 (w), 856 (m), 821 (m), 787 (w), 769 (s), 757 (s), 725 (s), 671 (m) cm$^{-1}$. UV/VIS (MeOH): $\lambda$$_{max}$ (lg $\varepsilon$) = 228 nm (4.11), 328...
(4.20). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 16.05 (bs, 1 H), 7.17 (s, 2 H), 6.27 (2, 1 H), 4.22 (q, 2 H, 3J = 7.1 Hz), 3.958 (s, 6 H), 3.955 (s, 3 H), 3.51 (s, 2 H), 1.34 (t, 3 H, 3J = 7.0 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 187.7, 183.7, 167.9, 153.5, 142.5, 129.8, 104.8, 96.8, 61.7, 61.2, 56.5, 45.7, 14.4. 3,5-Dioxo-5-(3,4,5-trimethoxy-phenyl)-pentanoic acid ethyl ester: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.21 (s, 2 H), 4.25 (s, 2 H), 4.18 (overlapping, q, 2 H, 3J = 7.0 Hz), 3.67 (s, 2 H), 1.25 (t, 3 H, 3J = 7.0 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 197.6, 192.6, 167.4, 153.4*, 143.6*, 131.4*, 106.4*, 61.2, 53.7, 49.3, 14.3. LRMS (EI, 70 eV): m/z (%) = 324 (96) [M⁺], 278 (58), 258 (41), 237 (47), 195 (100), 154 (45), 69 (13). HRMS (EI, M⁺): Calcd. for C₁₆H₂₀O₇: 324.1209. Found: 324.1203. * Due to overlapping proton signals, signals could not be unambiguously assigned by HSQC/HMBC.

5-Furan-2-yl-5-hydroxy-3-oxo-pent-4-enoic acid ethyl ester (1h): (Method A). Yellow solid. Mp 39°C. Rf = 0.55 (SiO₂, PE / EtOAc = 8 : 2). IR (ATR): ν = 3472 (m), 2994 (w), 2115 (vw), 1720 (vs), 1662 (w), 1674, 1569 (s), 1506 (vs), 1479 (s), 1458 (vs), 1366 (w), 1322 (m), 1277 (m), 1245 (m), 1226 (w), 1184 (w), 1161 (w), 1136 (vs), 1112 (m), 1032 (w), 1020 (m), 970 (m), 949 (w), 925 (vw), 884 (m), 860 (w), 788 (w), 769 (s), 749 (vs), 681 (m) cm⁻¹. UV/VIS (MeOH): λmax (lg ε) = 218 nm (3.68), 273 (3.86), 327 (4.01). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 15.22 (bs, 1 H), 7.58 (s, 1 H), 7.17 (d, 1 H, 3J = 3.6 Hz), 6.55 (d, 1 H, 3J = 3.3 Hz), 6.18 (s, 1 H), 4.22 (q, 2 H, 3J = 7.1 Hz), 3.41 (s, 2 H), 1.29 (t, 3 H, 3J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 185.4, 175.3, 167.8, 150.1, 146.6, 116.5, 112.9, 96.6, 61.8, 44.9, 14.3. 5-Furan-2-yl-3,5-dioxo-pentanoic acid ethyl ester: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.61 (s, 1 H), 7.28 (d, 1 H, 3J = 3.6 Hz), 6.56 (d, 1 H, 3J = 3.4 Hz), 4.19 (overlapping, q, 2 H, 3J = 7.4 Hz), 4.12 (s, 2 H), 3.63 (s, 2 H), 1.26 (overlapping, t, 3 H, 3J = 7.2 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 196*, 180*, 168*, 147.5, 119.0, 113.1, 53.2, 49.6, 14.3. 3-Hydroxy-5-oxo-5-furan-2-yl-pent-2-enoic acid ethyl ester: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 11.62 (s, 1 H), 5.17 (bs, 1 H). LRMS (EI, 70 eV): m/z (%) = 224 (30) [M⁺], 178 (43), 150 (23), 137 (100), 110 (23), 95 (90), 69 (38), 39 (24), 29 (36). HRMS (EI, M⁺): Calcd. for C₁₁H₁₂O₅: 224.0685. Found: 224.0666. Anal. calcd. for C₁₁H₁₂O₅: C 58.93, H 5.39. Found: C 58.76, H 5.46. *From HMBC spectra.

5-Furan-3-yl-5-hydroxy-3-oxo-pent-4-enoic acid ethyl ester (1i): (Method A). Yellow liquid. Rf = 0.44 (SiO₂, PE / Et₂O = 1 : 1). IR (ATR): ν = 3456 (vw), 3134 (w), 2983 (w), 1734 (vs), 1671
(m), 1602 (vs), 1509 (m), 1446 (w), 1407 (w), 1368 (m), 1303 (s), 1253 (s), 1155 (vs), 1075 (m), 1028 (s), 1012 (m), 968 (w), 935 (w), 873 (w), 827 (w), 785 (s), 743 (s) cm⁻¹. UV/VIS (MeOH): λ_max (lg ε) = 213 nm (3.87), 304 (4.03). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 15.32 (bs, 1 H), 8.01 (dd, 1 H, ³J = 1.5 Hz, ⁴J = 0.7 Hz), 7.45 (overlapping), 6.68 (dd, 1 H, ³J = 1.8 Hz, ⁴J = 0.7 Hz), 5.94 (s, 1 H), 4.21 (q, 2 H, ³J = 7.0 Hz), 3.40 (s, 2 H), 1.29 (t, 3 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 187.2, 178.7, 167.6, 145.8, 144.3, 123.8, 107.9, 97.6, 61.5, 45.2, 14.1.

5-Furan-3-yl-3,5-dioxo-pentanoic acid ethyl ester:

1H NMR (500 MHz, CDCl₃): δ (ppm) 15.32 (bs, 1 H), 8.01 (dd, 1 H, ³J = 1.5 Hz, ⁴J = 0.7 Hz), 7.45 (overlapping), 6.68 (dd, 1 H, ³J = 1.8 Hz, ⁴J = 0.7 Hz), 5.94 (s, 1 H), 4.21 (q, 2 H, ³J = 7.0 Hz), 3.40 (s, 2 H), 1.29 (t, 3 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 187.2, 178.7, 167.6, 145.8, 144.3, 123.8, 107.9, 97.6, 61.5, 45.2, 14.1.

3-Hydroxy-5-oxo-5-furan-3-yl-pent-2-enoic acid ethyl ester:

1H NMR (500 MHz, CDCl₃): δ (ppm) 15.32 (bs, 1 H), 8.01 (dd, 1 H, ³J = 1.5 Hz, ⁴J = 0.7 Hz), 7.45 (overlapping), 6.68 (dd, 1 H, ³J = 1.8 Hz, ⁴J = 0.7 Hz), 5.94 (s, 1 H), 4.21 (q, 2 H, ³J = 7.0 Hz), 3.40 (s, 2 H), 1.29 (t, 3 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 187.2, 178.7, 167.6, 145.8, 144.3, 123.8, 107.9, 97.6, 61.5, 45.2, 14.1.

5-Hydroxy-3-oxo-5-thiophen-2-yl-pent-4-enoic acid ethyl ester (1j):

Yellow solid. Mp 34°C. Rₚ = 0.41 (SiO₂, PE / EtOAc = 8 : 2). IR (ATR): ν ~ 3111 (w), 3081 (w), 2978 (w), 2928 (w), 2928 (w), 1892 (vw), 1842 (vw), 1726 (vs), 1632 (s), 1571 (w), 1465 (m), 1446 (m), 1406 (s), 1371 (m), 1334 (s), 1302 (w), 1273 (vs), 1230 (m), 1180 (vs), 1162 (vs), 1092 (w), 1072 (s), 1026 (vs), 1015 (w), 948 (s), 875 (s), 863 (s), 823 (w), 788 (s), 753 (m), 734 (vs), 670 (w) cm⁻¹. UV/VIS (MeOH): λ_max (lg ε) = 213 nm (3.87), 304 (4.03). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 15.32 (bs, 1 H), 8.01 (dd, 1 H, ³J = 1.5 Hz, ⁴J = 0.7 Hz), 7.45 (overlapping), 6.68 (dd, 1 H, ³J = 1.8 Hz, ⁴J = 0.7 Hz), 5.94 (s, 1 H), 4.21 (q, 2 H, ³J = 7.0 Hz), 3.40 (s, 2 H), 1.29 (t, 3 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 187.2, 178.7, 167.6, 145.8, 144.3, 123.8, 107.9, 97.6, 61.5, 45.2, 14.1.

3-Hydroxy-5-oxo-5-thiophen-2-yl-pent-2-enoic acid ethyl ester: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 15.32 (bs, 1 H), 8.01 (dd, 1 H, ³J = 1.5 Hz, ⁴J = 0.7 Hz), 7.45 (overlapping), 6.68 (dd, 1 H, ³J = 1.8 Hz, ⁴J = 0.7 Hz), 5.94 (s, 1 H), 4.21 (q, 2 H, ³J = 7.0 Hz), 3.40 (s, 2 H), 1.29 (t, 3 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 187.2, 178.7, 167.6, 145.8, 144.3, 123.8, 107.9, 97.6, 61.5, 45.2, 14.1.
ester: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 12.17 (s, 1 H), 7.79 (dd, 1 H, $^3J = 3.8$ Hz, $^4J = 1.2$ Hz), 5.17 (bs, 1 H), 3.76 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 134.0, 92.8, 45.9. LRMS (EI, 70 eV): $m/z$ (%) = 240 (53) [M$^+$], 194 (37), 166 (69), 153 (89), 126 (18), 111 (100), 69 (73), 39 (46), 29 (44). HRMS (EI, M$^+$): Calcd. for C$_{11}$H$_{12}$O$_4$S: 240.0456. Found: 240.0449. Anal. calcd. for C$_{11}$H$_{12}$O$_4$S: C 54.99, H 5.03, S 13.35. Found: C 55.17, H 5.03, S 13.10.

5-Hydroxy-3-oxo-5-pyridin-3-yl-pent-4-enoic acid ethyl ester (1k): (Method B). As purification of this compound via flash chromatography was somehow difficult, an alternative work-up procedure was developed. After evaporation of the volatiles the residue was dissolved in ether. 200 ml of petroleum ether ($-20^\circ$C) was added and the resulting mixture vigorously shaken. The ester precipitated immediately and the lumps were triturated with a glass rod. The petroleum ether was decanted. Again, the solid was digerated twice with petroleum ether, and then decanted. After drying the pure product was obtained as an orange solid. Mp 38$^\circ$C. R$_f = 0.54$ (SiO$_2$, EtOAc). IR (ATR): $\tilde{\nu} =$ 3127 (w), 2987 (w), 1714 (vs), 1585 (vs), 1474 (m), 1419 (m), 1366 (m), 1281 (s), 1251 (s), 1173 (s), 1141 (m), 1211 (m), 1084 (m), 1022 (s), 948 (s), 875 (w), 846 (m), 793 (vs), 727 (w), 702 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 236 nm (3.77), 309 (4.08). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 15.56 (bs, 1 H), 9.06 (d, 1 H, $^4J = 1.6$ Hz), 8.73 (d, 1 H, $^3J = 4.5$ Hz), 8.15 (d, 1 H, $^3J = 8.1$ Hz), 7.40 (dd, 1 H, $^3J = 8.1$ Hz, $^3J = 4.9$ Hz), 6.31 (s, 1 H), 4.22 (q, 2 H, $^3J = 7.1$ Hz), 3.49 (s, 2 H), 1.29 (t, 3 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 190.0, 180.0, 167.3, 152.8, 148.2, 134.5, 129.9, 123.6, 97.2, 61.6, 45.9, 14.1. 3,5-Dioxo-5-pyridin-3-yl-pentanoic acid ethyl ester: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 9.14 (s, 1 H), 8.81 (d, 1 H, $^3J = 4.9$ Hz), 8.23 (d, 1 H, $^3J = 8.1$ Hz), 7.44 (dd, 1 H, $^3J = 6.2$ Hz, $^3J = 4.9$ Hz), 4.31 (s, 2 H), 4.19 (overlapping, q, 2 H, $^3J = 7.3$ Hz), 3.65 (s, 2 H), 1.26 (overlapping, t, 3 H, $^3J = 7.1$ Hz). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 54.8, 50.1. LRMS (EI, 70 eV): $m/z$ (%) = 235 (29) [M$^+$], 218 (< 1), 206 (2), 189 (22), 162 (88), 148 (100), 106 (94), 78 (78), 69 (42), 51 (52), 29 (57). HRMS (EI, M$^+$): Calcd. for C$_{12}$H$_{13}$NO$_4$: 235.0845. Found: 235.0836.

5-Hydroxy-3-oxo-5-pyridin-4-yl-pent-4-enoic acid ethyl ester (1l): (Method B). Same workup procedure as described for 1k. Yellow solid. Mp 43$^\circ$C. R$_f = 0.45$ (SiO$_2$, EtOAc). IR (ATR): $\tilde{\nu} =$ 3120 (vw), 3067 (vw), 3036 (vw), 2998 (w), 2963 (w), 2488 (w), 1724 (vs), 1610 (m), 1587 (m), 1547 (m), 1496 (w), 1445 (w), 1418 (w), 1383 (w), 1363 (w), 1290 (m), 1244 (s), 1215 (m), 1172
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(w), 1143 (s), 1069 (m), 992 (m), 887 (w), 847 (m), 820 (w), 801 (vs), 769 (s), 693 (w), 678 (w) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{max} (lg \varepsilon) = 221 \text{ nm (3.86)}, 307 \text{ (4.10)}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 15.30 (bs, 1 H), 8.75 (d, 2 H, \(^3J = 6.1 \text{ Hz}\)), 7.66 (dd, 2 H, \(^3J = 4.7 \text{ Hz}, \(^4J = 1.5 \text{ Hz}\)), 6.34 (s, 1 H), 4.22 (q, 2 H, \(^3J = 7.1 \text{ Hz}\)), 3.51 (s, 2 H), 1.28 (t, 3 H, \(^3J = 7.1 \text{ Hz}\)).

\(^13\)C NMR (125.7 MHz, CDCl\(_3\)): \(\delta\) (ppm) 192.0, 178.1, 167.1, 150.1, 141.0, 120.2, 97.8, 61.3, 46.5, 14.1.

**3,5-Dioxo-5-pyridin-4-yl-pentanoic acid ethyl ester**: \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.83 (d, 2 H, \(^3J = 5.8 \text{ Hz}\)), 7.71 (d, 2 H, \(^3J = 6.2 \text{ Hz}\)), 4.29 (s, 2 H), 4.18 (overlapping, q, 2 H, \(^3J = 7.1 \text{ Hz}\)), 3.63 (s, 2 H), 1.28 (overlapping, t, 3 H, \(^3J = 7.1 \text{ Hz}\)).

**2-Hexyl-5-hydroxy-3-oxo-dodec-4-enoic acid ethyl ester (10a)**: (Method B). Colourless oil. \(R_t = 0.61 \text{ (SiO\(_2\), PE / EtOAc = 20 : 1)}\). IR (ATR): \(\tilde{\nu} = 2927 \text{ (vs)}, 2857 \text{ (vs)}, 1738 \text{ (s)}, 1599 \text{ (s)}, 1456 \text{ (m)}, 1367 \text{ (s)}, 1229 \text{ (s)}, 1216 \text{ (w)}, 1113 \text{ (m)}, 1036 \text{ (w)}, 938 \text{ (w)}, 777 \text{ (w)}, 725 \text{ (vw)} \text{ cm}^{-1}\). UV/VIS (MeOH): \(\lambda_{max} (lg \varepsilon) = 278 \text{ nm (4.05)}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 15.22 (s, 1 H, enolic H), 5.57 (s, 1 H), 4.17 (q, 2 H, \(^3J = 7.0 \text{ Hz}\)), 3.22 (t, 1 H, \(^3J = 7.3 \text{ Hz}\)), 2.27 (t, 2 H, \(^3J = 7.7 \text{ Hz}\)), 1.93 - 1.86 (m, 1 H), 1.84 - 1.76 (m, 1 H), 1.59 (quint, 2 H, \(^3J = 7.4 \text{ Hz}\)), 1.39 - 1.24 (m, 16 H), 1.25 (t, 3 H, \(^3J = 7.1 \text{ Hz}\)), 0.87 (t, 3 H, \(^3J = 7.0 \text{ Hz}\)), 0.86 (t, 3 H, \(^3J = 7.0 \text{ Hz}\)).

\(^13\)C NMR (125.7 MHz, CDCl\(_3\)): \(\delta\) (ppm) 192.9, 192.1, 170.7, 98.8, 61.4, 55.9, 37.9, 31.9, 31.7, 29.6, 29.4, 29.2 (2×C), 27.6, 26.0, 22.82, 22.76, 14.33, 14.27, 14.24.

**2-Hexyl-5-hydroxy-3-oxo-dodec-4-enoic acid ethyl ester**:

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 3.71 (d, 1 H, \(^2J = 15.1 \text{ Hz}\)), 3.61 (d, 1 H, \(^2J = 15.1 \text{ Hz}\)), 3.53 (t, 1 H, \(^3J = 7.3 \text{ Hz}\)), 2.49 (t, 3 H, \(^3J = 7.4 \text{ Hz}\)).

\(^13\)C NMR (125.7 MHz, CDCl\(_3\)): \(\delta\) (ppm) 204.1, 199.5, 169.8, 61.7, 59.8, 43.8, 31.9, 31.7, 29.2, 28.2, 27.4, 23.6.

**2-Hexyl-3-hydroxy-5-oxo-dodec-2-enoic acid ethyl ester**:

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 3.71 (d, 1 H, \(^2J = 15.1 \text{ Hz}\)), 3.61 (d, 1 H, \(^2J = 15.1 \text{ Hz}\)), 3.53 (t, 1 H, \(^3J = 7.3 \text{ Hz}\)), 2.49 (t, 3 H, \(^3J = 7.4 \text{ Hz}\)).

\(^13\)C NMR (125.7 MHz, CDCl\(_3\)): \(\delta\) (ppm) 204.1, 199.5, 169.8, 61.7, 59.8, 43.8, 31.9, 31.7, 29.2, 28.2, 27.4, 23.6.
5-Hydroxy-2-(3-methyl-but-2-enyl)-3-oxo-icos-4-enoic acid ethyl ester (10b): (Method B).

Colourless oil. 

IR (ATR): \( \nu \approx 2923 \) (vs), 2853 (s), 1738 (vs), 1599 (vs), 1455 (m), 1368 (w), 1330 (w), 1237 (w), 1186 (m), 1150 (s), 1039 (m), 933 (w), 859 (w), 773 (w), 721 (w) cm\(^{-1}\).

UV/VIS (MeOH): \( \lambda_{\text{max}} \) (\( \varepsilon \)) = 279 nm (3.98).

\( ^1H \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) 15.20 (s, 1 H, enolic H), 5.57 (s, 1 H), 5.03 (t, 1 H, \( ^3J = 7.1 \) Hz), 4.17 (q, 2 H, \( ^3J = 7.2 \) Hz), 3.24 (t, 1 H, \( ^3J = 7.7 \) Hz), 2.63 - 2.55 (m, 1 H), 2.53 - 2.46 (m, 1 H), 2.27 (t, 2 H, \( ^3J = 7.7 \) Hz), 1.67 (s, 3 H), 1.62 (s, 3 H), 1.59 (quint, 2 H, \( ^3J = 7.3 \) Hz), 1.28 - 1.23 (m, 27 H), 0.87 (t, 3 H, \( ^3J = 7.0 \) Hz).

\( ^13C \) NMR (125.7 MHz, CDCl\(_3\)): \( \delta \) (ppm) 192.9, 191.7, 170.3, 134.9, 120.1, 99.0, 61.5, 56.0, 37.9, 32.2, 29.92 (2\( \times \)), 29.90 (2\( \times \)), 29.88 (2\( \times \)), 29.8, 29.7, 29.59, 29.56, 29.4, 28.3, 26.1, 26.0, 22.9, 18.0, 14.3. 2-(3-Methyl-but-2-enyl)-3,5-dioxo-icosanoic acid ethyl ester: \( ^1H \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) 3.70 (d, 1 H, \( ^2J = 15.3 \) Hz), 3.62 (d, 1 H, \( ^3J = 15.3 \) Hz), 3.57 (t, 1 H, \( ^3J = 7.4 \) Hz).

\( ^13C \) NMR (125.7 MHz, CDCl\(_3\)): \( \delta \) (ppm) 204.0, 199.3, 169.4, 135.2, 119.7, 99.0, 61.7, 59.6, 56.4, 43.8, 29.3, 27.1, 27.0, 23.6, 18.0.

General procedure for the preparation of the bis potassium salts of 5-hydroxy-3-oxo-pent-4-enoic acids

The bis potassium salts of 3-oxo-5-hydroxy-pent-4-enoic acids 3 were prepared from the 5-hydroxy-3-oxo-pent-4-enoic acid ethyl esters 1 as follows: A solution of 5-hydroxy-3-oxo-pent-4-enoic acid ethyl ester 1 (R\(_1\) = Et, 4.11 mmol) in 3 ml absolute ethanol was added dropwise to a solution of 1.30 g (22.62 mmol) KOH in 9 ml absolute ethanol at rt. The reaction mixture was stirred for 30 min at rt; after a few minutes a solid started to precipitate. To complete the precipitation the reaction mixture was stored at -20°C for 12 h. The precipitate was filtered off, washed with approx. 5 ml of cold (-10°C) absolute ethanol and 100 ml of diethyl ether, and then dried.

NMR spectra were recorded in D\(_2\)O because all the compounds were only soluble in water. As the protons 2-H\(_2\), 4-H and partially 6-H were exchanged the bis potassium salts were transformed into their corresponding acids (see next chapter). No sufficient mass spectra (ESI) of the bis potassium salts could be obtained using ESI. However, a mass spectrum of the bis potassium salt of 5-hydroxy-6,6-dimethyl-3-oxo-hept-4-enoic acid (3d) could be obtained by using the ESI-TOF
method, representing all the bis potassium salts. No melting points could be recordered as all compounds decompose at temperatures higher than 220°C without melting.

**Bis potassium salt of 5-hydroxy-3-oxo-hept-4-enoic acid (3a):** IR (ATR): $\tilde{\nu} = 3328$ (vw), 2967 (vw), 2160 (vw), 1593 (vs), 1574 (vs), 1504 (w), 1436 (vs), 1419 (vs), 1371 (vs), 1324 (m), 1259 (w), 1159 (s), 1060 (w), 999 (w), 960 (w), 935 (m), 870 (s), 802 (w), 761 (s), 668 (vw) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 277 nm (3.88). $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 2.26 (bs, 2 H), 0.92 (t, 3 H, $^3J = 7.6$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 17.0, 10.8.

**Bis potassium salt of 5-hydroxy-3-oxo-oct-4-enoic acid (3b):** IR (ATR): $\tilde{\nu} = 2958$ (vw), 2871 (vw), 2160 (vw), 1574 (vs), 1500 (w), 1423 (vs), 1373 (vs), 1256 (w), 1160 (s), 1069 (vw), 1039 (vw), 971 (vw), 941 (m), 907 (vw), 879 (m), 835 (w), 761 (m), 663 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 325 nm (3.91). $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 2.20 (bs, 2 H, H-6), 1.44 - 1.36 (sext, 2 H, $^3J = 7.3$ Hz), 0.77 (t, 3 H, $^3J = 7.4$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 187.0, 42.5, 22.2, 16.1.

**Bis potassium salt of 5-hydroxy-6-methyl-3-oxo-hept-4-enoic acid (3c):** IR (ATR): $\tilde{\nu} = 2965$ (w), 2923 (vw), 2866 (vw), 2159 (vw), 1573 (vs), 1508 (vw), 1463 (s), 1433 (vs), 1382 (s), 1325 (vs), 1260 (s), 1166 (s), 1084 (w), 965 (vw), 938 (m), 907 (m), 854 (s), 757 (s), 678 (s), 659 (m) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 277 nm (3.98). $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 0.88 (d, 3 H, $^3J = 6.8$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 190.5, 39.8, 22.3.

**Bis potassium salt of 5-hydroxy-6,6-dimethyl-3-oxo-hept-4-enoic acid (3d):** IR (ATR): $\tilde{\nu} = 2955$ (w), 2159 (vw), 1574 (vs), 1542 (w), 1502 (w), 1423 (vs), 1383 (s), 1373 (s), 1358 (s), 1274 (m), 1244 (w), 1220 (w), 1172 (s), 1155 (w), 1132 (vw), 1021 (vw), 964 (vw), 939 (m), 871 (s), 833 (w), 771 (m), 759 (m), 700 (vw), 657 (m) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 278 nm (3.99), $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 0.95 (s, 9 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 43.6, 30.3. LRMS (ESI-TOF): $m/z$ (%) = 185 (34) [M-2K, +H]$^+$, 141 (100). HRMS ($\mu$-TOF, M$^+$+H): Calcd. for C$_9$H$_{13}$O$_4$: 185.0819, Found: 185.0813.
Bis potassium salt of 5-hydroxy-3-oxo-5-phenyl-pent-4-enoic acid (3e): IR (ATR): $\tilde{\nu} = 3231$ (vw), 2162 (vw), 1591 (s), 1566 (vs), 1501 (w), 1450 (vs), 1413 (vs), 1381 (vs), 1303 (w), 1278 (m), 1232 (w), 1203 (w), 1181 (w), 1161 (w), 1081 (w), 1066 (vw), 1024 (w), 999 (vw), 971 (m), 935 (vw), 882 (w), 861 (m), 809 (w), 759 (m), 746 (m), 710 (s), 686 (m) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 246 nm (3.77), 313 (4.17). The compound exists as a mixture of 3 tautomers in D$_2$O.

Tautomer 1: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 7.62 (d, 2 H, $^3J = 7.3$ Hz), 7.38-7.31 (m, 3 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 130.4, 128.5, 127.0.

Tautomer 2: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 7.85 (d, 2 H, $^3J = 7.8$ Hz), 7.44-7.40 (m, 3 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 134.3, 129.0.

Tautomer 3: $^1$H NMR (500 MHz, D$_2$O) $\delta$ (ppm): 7.74 (d, 2 H, $^3J = 7.8$), 7.56 (t, 2 H, $^3J = 7.6$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 131.4, 128.7.

Bis potassium salt of 5-(3,4-dimethoxy-phenyl)-5-hydroxy-3-oxo-pent-4-enoic acid (3f): IR (ATR): $\tilde{\nu} = 3227$ (vw), 2930 (vw), 1609 (w), 1591 (vs), 1568 (vs), 1495 (w), 1455 (vs), 1430 (vs), 1372 (vs), 1262 (vs), 1215 (m), 1198 (m), 1156 (w), 1131 (w), 1071 (vw), 1021 (s), 974 (m), 935 (w), 919 (vw), 858 (vw), 820 (w), 764 (s), 753 (m), 696 (vw), 666 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 233 nm (3.91), 333 (4.09). The compound exists as a mixture of 2 tautomers in D$_2$O.

Tautomer 1: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 7.28 (d, 1 H, $^3J = 8.3$ Hz), 7.25 (s, 1 H), 6.87 (d, 1 H, $^3J = 8.3$ Hz), 3.75 (s, 3 H), 3.73 (s, 3 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 204.7, 155.8, 150.4, 131.9, 127.2, 113.2, 112.6, 58.4, 58.1. Tautomer 2: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 7.17 (s, 1 H), 6.80 (d, 1 H, $^4J = 8.3$ Hz), 3.68 (s, 6 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 125.7, 123.5, 113.4, 112.9, 58.4, 58.3.

Bis potassium salt of 5-(3,4,5-trimethoxy-phenyl)-5-hydroxy-3-oxo-pent-4-enoic acid (3g): IR (ATR): $\tilde{\nu} = 3224$ (w), 3009 (vw), 2958 (vw), 2930 (vw), 2831 (w), 2160 (w), 2032 (w), 1637 (w), 1609 (m), 1591 (s), 1568 (vs), 1454 (vs), 1446 (vs), 1427 (vs), 1372 (vs), 1322 (m), 1262 (s), 1217 (m), 1198 (s), 1166 (w), 1155 (m), 1131 (s), 1104 (w), 1072 (w), 1022 (m), 1002 (w), 975 (m), 935(w), 920 (w), 883 (w), 859 (w), 821 (w), 764 (s), 753 (s), 732 (w), 705 (w), 667 (m). cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 222 nm (4.10), 326 (4.23). The compound exists as a mixture of 2 tautomers in D$_2$O.

Tautomer 1: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 6.95 (s, 2 H), 3.76 (s, 6 H), 3.65 (s, 3 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 185.5, 178.6, 152.2, 138.4, 132.1, 104.7, 97.8,
61.0, 56.2, 50.1. **Tautomer 2: **$^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 7.10 (s, 2 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$(ppm) 201.9, 191.6, 177.6, 139.2, 132.7, 106.2, 56.1.

**Bis potassium salt of 5-furan-2-yl-5-hydroxy-3-oxo-pent-4-enoic acid (3h):** IR (ATR): $\tilde{\nu}$ = 3326 (vw), 2160 (vw), 1607 (vs), 1562 (vs), 1511 (vs), 1477 (vs), 1454 (m), 1430 (m), 1387 (m), 1275 (s), 1244 (w), 1170 (s), 1153 (w), 1080 (w), 1051 (w), 1016 (m), 965 (w), 944 (w), 920 (m), 884 (m), 851 (m), 806 (vw), 754 (vs), 737 (s), 692 (m) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 215 nm (3.84), 306 (4.04). The compound exists as a mixture of 2 tautomers in D$_2$O. **Tautomer 1:** $^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 7.48 (s, 1 H); 6.89 (bs, 1 H), 6.44 (bs, 1 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$(ppm) 150.0, 113.0, 112.1. **Tautomer 2:** $^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 7.68 (d, 1 H, $^3J$ = 1.5 Hz), 7.37 (d, 1 H, $^3J$ = 3.9 Hz), 6.56 (dd, 1 H, $^3J$ = 3.7 Hz, $^3J$ = 1.7 Hz).

**Bis potassium salt of 5-furan-3-yl-5-hydroxy-3-oxo-pent-4-enoic acid (3i):** IR (ATR): $\tilde{\nu}$ = 3439 (w), 3223 (w), 2078 (vw), 1648 (w), 1590 (vs), 1572 (vs), 1553 (vs), 1435 (vs), 1379 (vs), 1411 (vs), 1291 (m), 1264 (w), 1228 (w), 1193 (m), 1157 (s), 1148 (s), 1123 (w), 1067 (m), 1010 (w), 974 (m), 945 (w), 930 (m), 867 (m), 824 (w), 760 (vs), 730 (w), 661 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 223 nm (3.31), 275 (3.64), 326 (3.98). The compound exists as a mixture of 2 tautomers. **Tautomer 1:** $^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 7.82 (s, 1 H), 7.38 (s, 1 H), 6.60 (s, 1 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$(ppm) 147.0 (C-2'), 146.6, 132.4, 111.7. **Tautomer 2:** $^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 8.23 (s, 1 H), 7.48 (s, 1 H), 6.67 (s, 1 H).

**Bis potassium salt of 5-hydroxy-3-oxo-5-thiophen-2-yl-pent-4-enoic acid (3j):** IR (ATR): $\tilde{\nu}$ = 3661 (vw), 3407 (vw), 3219 (w), 2376 (vw), 2355 (vw), 2345 (vw), 2331 (vw), 2322 (vw), 2161 (vw), 1648 (w), 1571 (vs), 1441 (vs), 1416 (vs), 1423 (vs), 1379 (vs), 1345 (s), 1279 (s), 1228 (s), 1194 (m), 1143 (m), 1081 (w), 1068 (w), 1026 (w), 970 (m), 932 (vw), 873 (vw), 852 (m), 754 (s), 714 (m), 705 (s), 667 (w), 661 (w) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{max}$ (lg $\varepsilon$) = 263 nm (3.73), 329 (4.00). The compound exists as a mixture of 2 tautomers. **Tautomer 1:** $^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 7.47 (d, 2 H, $^3J$ = 3.4 Hz), 7.44 (d, 1 H, $^3J$ = 4.9 Hz), 7.01 (t, 1 H, $^3J$ = 4.3 Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$(ppm) 136.2, 129.8, 128.3, 127.7. **Tautomer 2:** $^1$H NMR (500 MHz, D$_2$O): $\delta$(ppm) 7.82 (d, 1 H, $^3J$ = 3.9 Hz), 7.77 (d, 1 H, $^3J$ = 4.6 Hz), 7.12 (t, 1 H, $^3J$ = 4.4 Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$(ppm) 135.7, 129.2.
Bis potassium salt of 5-hydroxy-3-oxo-5-pyridin-3-yl-pent-4-enoic acid (3k): IR (ATR): $\tilde{\nu} = 3289$ (w), 2960 (vw), 2933 (vw), 1616 (s), 1597 (vs), 1583 (s), 1572 (s), 1488 (vs), 1461 (vs), 1403 (vs), 1379 (vs), 1322 (w), 1290 (w), 1244 (w), 1185 (w), 1166 (s), 1090 (s), 1038 (w), 1028 (w), 967 (w), 948 (w), 857 (m), 821 (w), 797 (w), 735 (vs), 704 (s), 659 (sv) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 236 nm (3.79), 312 (4.11). The compound exists as a mixture of 2 tautomers. Tautomer 1: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 8.68 (s, 1 H), 8.40 (dd, 1 H, $^3J = 5.0$ Hz, $^4J = 1.3$ Hz), 7.98 (d, 1 H, $^3J = 7.8$ Hz), 7.35 (dd, 1 H, $^3J = 7.9$ Hz, $^4J = 5.0$ Hz), 3.35 (bs, 2 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 202.3, 177.6, 153.0, 149.0, 137.2, 132.5, 124.5. Tautomer 2: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 8.94 (s, 1 H), 8.60 (d, 1 H, $^3J = 4.9$ Hz), 8.23 (d, 1 H, $^3J = 7.8$ Hz), 7.46 (dd, 1 H, $^3J = 8.0$ Hz, $^4J = 4.9$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 150.6, 149.2, 137.8, 124.0.

Bis potassium salt of 5-hydroxy-3-oxo-4-pyridin-3-yl-pent-4-enoic acid (3l): IR (ATR): $\tilde{\nu} = 1594$ (vs), 1571 (s), 1549 (s), 1506 (w), 1439 (vs), 1423 (vs), 1383 (vs), 1317 (w), 1236 (m), 1217 (m), 1181 (s), 1147 (m), 1089 (w), 1057 (w), 999 (w), 968 (m), 936 (w), 876 (m), 847 (m), 803 (w), 761 (vs), 737 (m), 706 (s), 689 (m), 665 (vw) cm$^{-1}$. UV/VIS (MeOH): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 221 nm (3.89), 313 (4.08). The compound exists as a mixture of 3 tautomers. Tautomer 1: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 8.37 (d, 2 H, $^3J = 6.2$ Hz), 7.46 (d, 2 H, $^3J = 5.0$ Hz), 3.28 (bs, 2 H). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 193.3, 183.0, 178.2, 149.0, 121.7. Tautomer 2: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 8.57 (d, 2 H, $^3J = 5.0$ Hz), 7.69 (d, 2 H, $^3J = 5.1$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): $\delta$ (ppm) 151.0, 122.1. Tautomer 3: $^1$H NMR (500 MHz, D$_2$O): $\delta$ (ppm) 8.46 (d, 2 H, $^3J = 5.7$ Hz), 7.59 (d, 2 H, $^3J = 5.1$ Hz). $^{13}$C NMR (125.7 MHz, D$_2$O): 150.0, 123.2.

General procedure for the preparation of the 5-hydroxy-3-oxo-pent-4-enoic acids 3
The 5-hydroxy-3-oxo-pent-4-enoic acids 2 were prepared from their bis potassium salts 3.

Method A) With HCl: A solution of 0.35 mmol bis potassium salt 3 in 1 ml distilled water was acidified with 1 N HCl to pH 2 at 0°C. The aqueous phase was extracted three times with cold (0°C) chloroform and the organic phases were combined. After drying over MgSO$_4$ the volatiles were removed in vacuo (without heating). As the NMR spectra indicate the obtained residue was pure.
**Method B) With tartaric acid:** 4 ml of a cold (2°C) saturated tartaric acid solution were added to a solution of 0.83 mmol bis potassium salt in 2 ml of distilled water at 0°C, then chloroform was added (4 ml, 0°C cold) and the resulting mixture vigorously shaken for 2 min. The precipitate potassium hydrogen tartrate was removed by suction over a frit and the organic phase then separated from the filtrate. The aqueous phase was twice extracted with ice cold chloroform and the organic phases were combined. After drying over MgSO₄ the volatiles were removed in vacuo.

As the ¹H NMR spectrum indicated the crude product was pure. The ¹H NMR spectrum shows that all acids exist as mixtures of mainly 3 tautomers, i.e. the 5-hydroxy-3-oxo-pent-4-enoic acid, the 3,5-dioxo pentanoic acid and traces of the 3-hydroxy-5-oxo-pent-2-enoic acid. The ratios of the single tautomers was determined by analysis of the integrals of the proton signals.

### 5-Hydroxy-3-oxo-hept-4-enoic acid (2a): (Method B)

Colourless oil. Rₚ = 0.22 (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): ʋ = 2980 (w), 2942 (w), 1711 (vs), 1603 (vs), 1407 (m), 1379 (m), 1288 (s), 1175 (s), 1143 (s), 892 (s), 807 (s), 767(s) cm⁻¹. UV/VIS (CH₃CN): λₘₐₓ (lg ε) = 276 nm (3.89). ¹H NMR (500 MHz, CDCl₃): δ(ppm) 14.85 (bs, 1 H), 9.77 (bs, 1 H), 5.61 (s, 1 H), 3.41 (s, 2 H), 2.36 (q, 2 H, ³J = 7.5 Hz), 1.16 (t, 3 H, ³J = 7.5 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 193.8, 188.2, 172.0, 99.2, 44.2, 30.7, 9.7. **3,5-Dioxo-heptanoic acid:** ¹H NMR (500 MHz, CDCl₃): δ(ppm) 3.75 (s, 2 H), 3.64 (s, 2 H), 2.55 (q, 2 H, ³J = 7.3 Hz), 1.07 (t, 3 H, ³J = 7.3 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 197.0, 170.5, 56.2, 48.7, 37.1, 14.0, 7.4. **3-Hydroxy-5-oxo-hept-2-enoic acid:** ¹H NMR (500 MHz, CDCl₃): δ(ppm) 11.75 (bs, 1 H), 5.13 (s, 1 H), 3.31 (s, 2 H), 2.57 (overlapping, q, 2 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 91.9, 49.1, 36.6. LRMS (EI, 70 eV): m/z (%) = 158 (15) [M⁺], 140 (12), 129 (40), 116 (22), 111 (43), 99 (38), 87 (23), 85 (34), 69 (55), 57 (92), 43 (100), 29 (75). HRMS (EI, M⁺): Calcd. for C₇H₁₀O₄: 157.0662. Found: 157.0684.

### 5-Hydroxy-3-oxo-oct-4-enoic acid (2b): (Method A)

Colourless oil. Rₚ = 0.13 (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): ʋ = 2973 (m), 1715 (vs), 1598 (vs), 1386 (w), 1208 (s), 1137 (s), 1081 (m), 917 (s), 790 (m) cm⁻¹. UV/VIS (CH₃CN): λₘₐₓ (lg ε) = 275 nm (3.92). ¹H NMR (500 MHz, CDCl₃): δ(ppm) 14.90 (bs, 1 H), 10.65 (bs, 1 H), 5.60 (s, 1 H), 3.41 (s, 2 H), 2.28 (q, 2 H, ³J = 7.6 Hz), 1.64 (sext, 2 H, ³J = 7.4 Hz), 0.95 (t, 3 H, ³J = 7.4 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 192.5, 188.5, 172.3, 99.2, 44.5, 39.3, 19.2, 9.9. **3,5-Dioxo-octanoic acid:** ¹H NMR (500 MHz, CDCl₃): δ(ppm) 3.75 (s, 2 H), 3.64 (s, 2 H), 2.55 (q, 2 H, ³J = 7.3 Hz), 1.07 (t, 3 H, ³J = 7.3 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 197.0, 170.5, 56.2, 48.7, 37.1, 14.0, 7.4. **3-Hydroxy-5-oxo-oct-2-enoic acid:** ¹H NMR (500 MHz, CDCl₃): δ(ppm) 11.75 (bs, 1 H), 5.13 (s, 1 H), 3.31 (s, 2 H), 2.57 (overlapping, q, 2 H, ³J = 7.1 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ(ppm) 91.9, 49.1, 36.6. LRMS (EI, 70 eV): m/z (%) = 160 (15) [M⁺], 142 (12), 129 (40), 116 (22), 111 (43), 99 (38), 87 (23), 85 (34), 69 (55), 57 (92), 43 (100), 29 (75). HRMS (EI, M⁺): Calcd. for C₈H₁₀O₄: 161.0813. Found: 161.0816.
MHz, CDCl₃): δ (ppm) 3.74 (s, 2 H), 3.63 (s, 2 H), 2.24 (t, 2 H, 3J = 7.4 Hz), 1.60 (overlapping, sext, 2 H, 3J = 7.4 Hz), 0.91 (t, 3 H, 3J = 7.4 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 197.0, 171.9, 56.5, 48.8, 40.0, 16.8, 13.4. LRMS (EI, 70 eV): m/z (%) = 172 (1) [M⁺], 154 (< 1), 129 (9), 128 (13), 111 (10), 87 (5), 85 (41), 71 (15), 44 (100), 28 (20). HRMS (EI, M⁺): Calcd. for C₈H₁₂O₄: 172.0736. Found: 172.0746.

5-Hydroxy-6-methyl-3-oxo-hept-4-enoic acid (2c): (Method A). Colourless oil. Rₜ = 0.24 (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): ν = 2973 (m), 1715 (vs), 1595 (vs), 1386 (w), 1208 (s), 1137 (s), 1082 (m), 920 (s), 791 (m) cm⁻¹. UV/VIS (CH₃CN): λmax (lg ε) = 275 nm (3.92). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 14.95 (bs, 1 H), 8.71 (bs, 1 H), 5.61 (s, 1 H), 3.42 (s, 2 H), 2.50 (sept, 1 H, 3J = 7.0 Hz), 1.16 (d, 6 H, 3J = 7.0 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 197.2, 189.2, 172.2, 98.1, 44.6, 36.2, 19.5. 6-Methyl-3,5-dioxo-heptanoic acid: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 3.80 (s, 2 H), 3.65 (s, 2 H), 2.68 (sept, 1 H, 3J = 7.0 Hz), 1.13 (d, 6 H, 3J = 7.0 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 197.7, 172.0, 54.6, 48.9, 42.2, 17.9. 3-Hydroxy-6-methyl-5-oxo-hept-2-enoic acid: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 11.78 (bs, 1 H), 5.12 (bs, 1 H), 2.74 (overlapping, sept, 1 H, 3J = 7.0 Hz), 1.13 (overlapping). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 91.8, 47.1, 18.2. LRMS (EI, 70 eV): m/z (%) = 172 (1) [M⁺], 128 (25), 113 (3), 111 (5), 85 (100), 71 (5), 69 (6), 58 (2), 43 (68), 28 (17). HRMS (EI, M⁺): Calcd. for C₈H₁₂O₄: 172.0736. Found: 172.0753.

5-Hydroxy-6,6-dimethyl-3-oxo-hept-4-enoic acid (2d): (Method A). Colourless oil. Rₜ = 0.41 (SiO₂, PE / EtOAc = 10 : 1). IR (ATR): ν = 2970 (m), 1715 (vs), 1386 (w), 1265 (m), 1138 (s), 897 (m), 788 (m), 750 (w) cm⁻¹. UV/VIS (CH₃CN): λmax (lg ε) = 276 nm (3.92). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 15.15 (bs, 1 H), 5.69 (s, 1 H), 3.45 (s, 2 H), 1.19 (s, 9 H). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 198.7, 190.1, 171.0, 96.0, 44.3, 38.6, 27.2. 6,6-Dimethyl-3,5-dioxo-heptanoic acid: ¹H NMR (500 MHz, CDCl₃): δ (ppm) 3.84 (s, 2 H), 3.66 (s, 2 H), 1.17 (s, 9 H). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 51.1, 48.2, 25.9. LRMS (EI, 70 eV): m/z (%) = 186 (8) [M⁺], 142 (12), 129 (63), 111 (50), 85 (69), 69 (34), 57 (100), 43 (56), 28 (31). HRMS (EI, M⁺): Calcd. for C₉H₁₄O₄: 186.0892. Found: 186.0882.
5-Hydroxy-3-oxo-5-phenyl-pent-4-enoic acid (2e): (Method A). White solid. Mp 79°C. Rf = 0.26 (SiO2, PE / EtOAc = 10 : 1). 1H NMR (500 MHz, CDCl3): δ (ppm) 15.54 (bs, 1 H), 8.84 (bs, 1 H), 7.90 - 7.88 (m, 2 H), 7.57 - 7.54 (m, 1 H), 7.49 - 7.45 (m, 2 H), 6.29 (s, 1 H), 3.57 (s, 2 H). 13C NMR (125.7 MHz, CDCl3): δ (ppm) 190.3, 182.4, 172.3, 134.1, 133.2, 129.0, 127.4, 97.1, 45.3.

3,5-Dioxo-5-phenyl-pentanoic acid: 1H NMR (500 MHz, CDCl3): δ (ppm) 8.10 - 8.08 (m, 2 H), 7.63 - 7.60 (m, 1 H), 7.49 - 7.45 (overlapping, m, 2 H), 4.31 (s, 2 H), 3.75 (s, 2 H). 13C NMR (125.7 MHz, CDCl3): δ (ppm) 172.2, 134.4, 133.8, 130.5, 128.7, 53.4, 48.8.

3-Hydroxy-5-oxo-5-phenyl-pent-2-enoic acid: 1H NMR (500 MHz, CDCl3): δ (ppm) 11.82 (bs, 1 H), 7.94 - 7.93 (m, 1 H), 5.19 (s, 1 H). LRMS (EI, 70 eV): m/z (%) = 206 (6) [M+], 162 (67), 147 (65), 105 (100), 77 (74), 69 (64), 51 (36), 44 (42), 27 (5).

5-(3,4-Dimethoxy-phenyl)-5-hydroxy-3-oxo-pent-4-enoic acid (2f): (Method A). Pale yellow solid. Mp 98 - 100°C. Rf = 0.41 (SiO2, PE / EtOAc = 7 : 3). IR (ATR): ν = 2938 (w), 1717 (s), 1593 (s), 1511 (vs), 1462 (s), 1438 (s), 1335 (m), 1261 (vs), 1134 (vs), 1080 (m), 1017 (vs), 957 (w), 873 (w), 766 (vs), 733 (m) cm⁻¹. UV/VIS (CH3CN): λ max (lg ε) = 233 nm (4.09), 331 (4.20).

5-(3,4-Dimethoxy-phenyl)-5-hydroxy-3-oxo-pent-4-enoic acid (2g): (Method A). White solid. Mp 116°C. Rf = 0.41 (SiO2, PE / EtOAc = 7 : 3). IR (ATR): ν = 2944 (w), 1706 (s), 1577 (s), 1502 (s), 1457 (m), 1428 (s), 1319 (s), 1276 (s), 1174 (m), 1121 (vs), 1092 (vs), 996 (vs), 910 (m), 862 (m), 841 (w), 769 (vs), 709 (m), 673 (w) cm⁻¹. UV/VIS (CH3CN): λ max (lg ε) = 223 nm (4.02), 331 (4.12). 1H NMR (500 MHz, CDCl3): δ (ppm) 15.67 (bs, 1 H), 8.89 (s, 1 H), 7.14 (s, 2 H), 6.22 (s, 1 H). 13C NMR (125.7 MHz, CDCl3): δ (ppm) 248 (< 1), 222 (100), 207 (24), 191 (20), 165 (98), 139 (30), 124 (44), 77 (15), 69 (26). HRMS (EI, M⁺): Calcd. for C13H14O6: 266.0790. Found: 266.0779. *From HMBC spectra.

5-(3,4,5-Trimethoxy-phenyl)-5-hydroxy-3-oxo-pent-4-enoic acid (2h): (Method A). White solid. Mp 116°C. Rf = 0.41 (SiO2, PE / EtOAc = 7 : 3). IR (ATR): ν = 2944 (w), 1706 (s), 1577 (s), 1502 (s), 1457 (m), 1428 (s), 1319 (s), 1276 (s), 1174 (m), 1121 (vs), 1092 (vs), 996 (vs), 910 (m), 862 (m), 841 (w), 769 (vs), 709 (m), 673 (w) cm⁻¹. UV/VIS (CH3CN): λ max (lg ε) = 223 nm (4.02), 331 (4.12). 1H NMR (500 MHz, CDCl3): δ (ppm) 15.67 (bs, 1 H), 8.89 (s, 1 H), 7.14 (s, 2 H), 6.22 (s, 1 H). 13C NMR (125.7 MHz, CDCl3): δ (ppm) 248 (< 1), 222 (100), 207 (24), 191 (20), 165 (98), 139 (30), 124 (44), 77 (15), 69 (26). HRMS (EI, M⁺): Calcd. for C13H14O6: 266.0790. Found: 266.0779. *From HMBC spectra.
H), 3.94 (s, 9 H), 3.58 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 188.9, 182.9, 171.9, 153.5, 142.8, 129.0, 104.9, 96.9, 61.3, 56.6, 44.8. 

5-(3,4,5-Trimethoxyphenyl)-3,5-dioxo-pentanoic acid: $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.29 (s, 2 H), 4.36 (s, 2 H), 3.93 (s, 9 H), 3.74 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 106.4, 48.6. 

5-(3,4,5-Trimethoxyphenyl)-3-hydroxy-5-oxo-pent-2-enoic acid: $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 12.0 (s, 1 H), 7.35 (s, 2 H), 5.26 (s, 1 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 107.7. LRMS (EI, 70 eV): $m/z$ (%) = 296 (1) [M$^+$], 252 (100), 237 (23), 221 (24), 195 (75), 169 (14), 154 (40), 137 (9), 109 (6), 85 (10), 69 (14), 44 (31). HRMS (EI, M$^+$): Calcd. for C$_{14}$H$_{16}$O$_7$: 296.0896. Found: 296.0888.

5-Furan-2-yl-5-hydroxy-3-oxo-pent-4-enoic acid (2h): (Method A). Yellow solid. Mp 87°C. $R_f = 0.22$ (SiO$_2$, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu} = 2930$ (m), 1698 (vs), 1609 (vs), 1466 (m), 1402 (s), 1299 (s), 1241 (s), 1228 (s), 1191 (s), 1161 (m), 1092 (m), 1030 (w), 903 (s), 881 (vs), 798 (s), 767 (vs), 735 (vs) cm$^{-1}$. UV/VIS (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 224 nm (3.18), 273 (3.63), 319 (3.92). $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 15.00 (bs, 1 H), 10.33 (bs, 1 H), 7.59 (d, 1 H, $^{3}J = 1.0$ Hz), 7.20 (d, 1 H, $^{3}J = 3.6$ Hz), 6.57 (dd, 1 H, $^{3}J = 1.6$ Hz, $^{3}J = 3.6$ Hz), 6.19 (s, 1 H), 3.49 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 186.1, 174.1, 172.4, 149.3, 146.7, 116.7, 112.8, 96.4, 44.0. 

5-Furan-2-yl-3,5-dioxo-pentanoic acid: $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 7.62 (s, 1 H), 4.14 (s, 2 H), 3.72 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 196.4, 147.5, 119.0, 112.9, 52.8, 48.6. 

5-Furan-2-yl-3-hydroxy-5-oxo-pent-2-enoic acid: $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 11.80 (s, 1 H), 5.22 (s, 1 H), 3.42 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 147.3, 116.3, 112.7, 91.6, 44.8. LRMS (EI, 70 eV): $m/z$ (%) = 196 (12) [M$^+$], 178 (7), 152 (49), 137 (44), 124 (12), 110 (49), 95 (100), 69 (30). HRMS (EI, M$^+$): Calcd. for C$_9$H$_8$O$_5$: 196.0372. Found: 196.0372.

5-Furan-3-yl-5-hydroxy-3-oxo-pent-4-enoic acid (2i): (Method A). Yellow solid. Mp 57°C. $R_f = 0.29$ (SiO$_2$, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu} = 3133$ (m), 1714 (vs), 1570 (vs), 1515 (m), 1415 (s), 1310 (s), 1237 (m), 1149 (s), 1063 (m), 1001 (m), 971 (s), 937 (vs), 872 (vs), 852 (vs), 780 (vs), 710 (vs) cm$^{-1}$. UV/VIS (CH$_3$CN): $\lambda_{\text{max}}$ (lg $\varepsilon$) = 212 nm (3.93), 303 (4.10). $^{1}$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 15.08 (bs, 1 H), 10.41 (bs, 1 H), 8.04 (s, 1 H), 7.47 (t, 1 H, $^{3}J = 1.6$ Hz), 6.68 (d, 1 H, $^{3}J = 1.8$ Hz), 5.94 (s, 1 H), 3.50 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 185.2, 178.8, 172.5, 149.4, 146.9, 115.0, 114.7, 112.8, 36.5, 44.8.
5-Furan-3-yl-3,5-dioxo-pentanoic acid: 
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 8.09 (s, 1 H), 7.46 (overlapping, 1 H), 6.77 (d, 1 H, $^3J = 1.5$ Hz), 4.06 (s, 2 H), 3.71 (s, 2 H) $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 148.7, 144.8, 108.5, 55.0, 48.4.

5-Furan-3-yl-3-hydroxy-5-oxo-pent-2-enoic acid: 
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 11.80 (bs, 1 H), 8.11 (s, 1 H), 6.79 (s, 1 H, $^3J = 1.5$ Hz), 5.21 (s, 1 H), 3.65 (s, 2 H). LRMS (EI, 70 eV): $m/z$ (%) = 196 (19) [M$^+$], 178 (1), 152 (12), 137 (22), 123 (10), 110 (18), 95 (100), 69 (40). 


5-Hydroxy-3-oxo-5-thiophen-2-yl-pent-4-enoic acid (2j): (Method A). Yellow solid. Mp 96°C. 

$R_t = 0.18$ (SiO$_2$, PE / EtOAc = 10 : 1). IR (ATR): $\tilde{\nu} = 3096$ (m), 2927 (w), 1700 (vs), 1563 (vs), 1517 (s), 1400 (vs), 1274 (s), 1235 (vs), 1185 (vs), 1072 (w), 947 (m), 860 (vs), 937 (vs), 787 (vs), 727 (vs), 680 (vs) cm$^{-1}$. UV/VIS (CH$_3$CN): $\lambda_{max}$ (lg $\varepsilon$) = 263 nm (3.88), 321 (4.10). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 15.35 (bs, 1 H), 10.17 (bs, 1 H), 7.73 (d, 1 H, $^3J = 4.0$ Hz), 7.64 (d, 1 H, $^3J = 5.0$ Hz), 7.15 (t, 1 H, $^3J = 4.0$ Hz), 6.15 (s, 1 H), 3.49 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 183.9, 180.4, 172.8, 140.1, 133.5, 131.3, 128.7, 97.2, 43.7. 3,5-Dioxo-5-thiophen-2-yl-pentanoic acid: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 4.22 (s, 2 H), 3.75 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 196.7, 186.0, 176.4, 143.3, 135.9, 134.1, 128.8, 54.0, 48.7. 3-Hydroxy-5-oxo-5-thiophen-2-yl-pent-2-enoic acid: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ (ppm) 11.82 (bs, 1 H), 5.24 (s, 1 H), 3.81 (s, 2 H). $^{13}$C NMR (125.7 MHz, CDCl$_3$): $\delta$ (ppm) 91.9, 46.1. LRMS (EI, 70 eV): $m/z$ (%) = 212 (3) [M$^+$], 194 (2), 168 (73), 153 (44), 135 (12), 126 (20), 111 (100), 84 (23), 69 (48), 43 (33). HRMS (EI, M$^+$): Calcd. for C$_8$H$_9$O$_4$S: 212.0143. Found: 212.0148.

General procedure for the preparation of substituted 4-hydroxy-2H-pyran-2-ones 4

The 6-substituted 4-hydroxy-2-pyrones 4 were prepared from the bis potassium salts 3 as follows: 305 µl (4.1 mmol) TFA was added to a vigorously stirred suspension of 1.86 mmol bis potassium salt 3 in 10 ml TFAA at -20°C. The clear solution that formed after a few minutes was allowed to warm up to 0°C and stirred. The reaction was monitored by TLC. After 2 h the starting material was completely consumed. Excess TFA/TFAA was removed by distillation under normal pressure. Remaining traces of TFA could be removed azeotropically with toluene. The residue was poured into 50 ml of vigorously stirred ice water, and the pyrone 4 precipitated immediately. For complete precipitation the crude product was stored at 4°C for 12 h. The precipitate was filtered, washed
with water and dried. For 4a-d, the aqueous solution was saturated with sodium chloride and extracted four times with CH₂Cl₂. The combined organic phases were washed with water and dried over MgSO₄. The volatiles were removed in vacuo and the residue submitted to flash chromatography on silica gel.

6-Ethyl-4-hydroxy-2H-pyran-2-one (4a): Colourless solid. Mp 83°C. Rᵣ = 0.46 (SiO₂, CH₂Cl₂ / MeOH = 20 : 1). IR (ATR): ν = 2982 (w), 2947 (w), 2840 (w), 2665 (w), 1650 (m), 1614 (s), 1538 (s), 1445 (s), 1384 (s), 1366 (s), 1311 (m), 1267 (m), 1240 (vs), 1185 (m), 1140 (vs), 1072 (w), 1022 (w), 1010 (w), 993 (w), 935 (w), 884 (vs), 810 (vs), 783 (m), 726 (s), 727 (w), 696 (w), 661 (w) cm⁻¹. UV/VIS (MeOH): λ_max (lg ε) = 288 nm (3.75). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 11.25 (bs, 1H), 6.01 (t, 1 H, ⁴J = 1.0 Hz), 5.59 (d, 1 H, ⁴J = 2.0 Hz), 2.53 (q, 2 H, ³J = 7.5 Hz), 1.21 (t, 3 H, ³J = 7.3 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 173.1, 168.7, 168.6, 100.8, 90.0, 27.1, 11.0. LRMS (EI, 70 eV): m/z (%) = 140 (52) [M⁺], 111 (92), 99 (22), 69 (100), 57 (33), 55 (22). HRMS (EI, M⁺): Calcd. for C₇H₈O₃: 140.0474. Found: 140.0476. Anal. calcd. for C₇H₈O₃: C 60.00, H 5.75. Found: C 59.79, H 5.45.

6-Propyl-4-hydroxy-2H-pyran-2-one (4b): Colourless solid. Mp 94°C. Rᵣ = 0.50 (SiO₂, CH₂Cl₂ / MeOH = 20 : 1). IR (ATR): ν = 2966 (w), 2939 (w), 2881 (w), 2825 (w), 2750 (w), 2521 (w), 1648 (m), 1597 (s), 1573 (vs), 1532 (vs), 1503 (vs), 1458 (m), 1421 (m), 1383 (w), 1340 (s), 1303 (s), 1275 (vs), 1240 (vs), 1186 (s), 1137 (s), 997 (w), 923 (vs), 878 (vs), 828 (vs), 760 (w), 728 (w), 690 (m) cm⁻¹. UV/VIS (MeOH): λ_max (lg ε) = 288 nm (3.75). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 11.02 (bs, 1H), 5.99 (s, 1 H), 5.58 (s, 1 H), 2.45 (t, 2 H, ³J = 7.5 Hz), 1.71 - 1.63 (sext, 2 H, ³J = 7.5 Hz), 0.95 (t, 3 H, ³J = 7.4 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 172.9, 168.6, 167.3, 101.7, 90.0, 35.7, 20.3, 13.6. LRMS (EI, 70 eV): m/z (%) = 154 (52) [M⁺], 139 (4), 126 (55), 111 (100), 97 (24), 84 (43), 69 (91), 55 (21). HRMS (EI, M⁺): Calcd. for C₈H₁₀O₃: 154.0630. Found: 154.0635.

6-Isopropyl-4-hydroxy-2H-pyran-2-one (4c): Colourless solid. Mp 89°C. Rᵣ = 0.62 (SiO₂, CH₂Cl₂ / MeOH = 20 : 1). IR (ATR): ν = 2970 (w), 2932 (w), 2877 (w), 2600 (w), 2556 (w), 2036 (w), 1653 (s), 1627 (vs), 1550 (vs), 1432 (vs), 1388 (s), 1340 (w), 1316 (m), 1288 (w), 1238 (vs), 1205 (m), 1171 (s), 1133 (s), 1074 (s), 994 (w), 973 (m), 963 (m), 930 (w), 894 (s), 856 (s),
828 (vs), 802 (vs), 726 (s), 695 (w) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{\text{max}}\) (lg \(\varepsilon\)) = 283 nm (3.84).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 11.18 (bs, 1H), 6.00 (s, 1 H), 5.59 (s, 1 H), 2.74 (sept, 1 H, \(^3J = 7.0\) Hz), 1.22 (d, 6 H, \(^3J = 6.8\) Hz). 13C NMR (125.7 MHz, CDCl\(_3\)): \(\delta\) (ppm) 172.9, 171.9, 168.4, 99.3, 89.8, 32.6, 20.1, 19.8. LRMS (EI, 70 eV): \(m/z\) (%) = 154 (64) [M\(^+\)], 139 (< 1), 126 (38), 111 (100), 97 (11), 84 (10), 69 (89), 55 (41). HRMS (EI, M\(^+\)): Calcd. for C\(_8\)H\(_{10}\)O\(_3\): 154.0630. Found: 154.0626. Anal. calcd. for C\(_8\)H\(_{10}\)O\(_3\): C 62.33, H 6.54. Found: C 62.47, H 6.53.

\(6\)-\(\text{tert}\)-Butyl-4-hydroxy-2\(\text{H}\)-pyran-2-one (4d): Colourless solid. Mp 139°C. \(R_f = 0.43\) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 20 : 1). IR (ATR): \(\tilde{\nu}\) = 3098 (w), 2976 (w), 2936 (w), 2876 (w), 2729 (vw), 2678 (v), 2609 (v), 1781 (v), 1678 (s), 1652 (vs), 1579 (vs), 1483 (m), 1466 (m), 1450 (vs), 1431 (vs), 1392 (s), 1360 (m), 1309 (m), 1255 (w), 1229 (vs), 1218 (vs), 1179 (vs), 1108 (vs), 1036 (w), 994 (w), 956 (s), 892 (m), 839 (s), 819 (s), 805 (m), 760 (cm\(^{-1}\)). UV/VIS (MeOH): \(\lambda_{\text{max}}\) (lg \(\varepsilon\)) = 282 nm (3.86). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) (ppm) 11.04 (bs, 1H), 6.03 (d, 1 H, \(^4J = 2.2\) Hz), 5.57 (d, 1 H, \(^4J = 2.0\) Hz), 1.26 (s, 9 H). 13C NMR (125.7 MHz, CDCl\(_3\)): \(\delta\) (ppm) 174.3, 173.0, 168.4, 98.6, 89.9, 36.3, 28.0. LRMS (EI, 70 eV): \(m/z\) (%) = 168 (29) [M\(^+\)], 140 (3), 125 (5), 111 (100), 83 (4), 69 (25), 57 (35). HRMS (EI, M\(^+\)): Calcd. for C\(_9\)H\(_{12}\)O\(_3\): 168.0786. Found: 168.0772. Anal. calcd. for C\(_9\)H\(_{12}\)O\(_3\): C 64.27, H 7.19. Found: C 64.17, H 7.17.

4-Hydroxy-6-phenyl-2\(\text{H}\)-pyran-2-one (4e): Colourless solid. Mp 244°C. \(R_f = 0.75\) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 10 : 1). IR (ATR): 3676 (w), 2988 (w), 2902 (w), 2734 (w), 2602 (w), 2549 (w), 1640 (w), 1606 (s), 1578 (m), 1543 (vs), 1495 (s), 1455 (s), 1423 (vs), 1320 (w), 1254 (s), 1226 (vs), 1174 (vs), 1104 (w), 1072 (s), 1029 (w), 998 (w), 926 (w), 873 (m), 828 (m), 805 (vs), 773 (vs), 723 (m), 690 (s), 680 (m), 662 (w), 627 (m), 575 (vs), 546 (w), 536 (w), 525 (w) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{\text{max}}\) (lg \(\varepsilon\)) = 220 nm (4.20), 235 (4.23), 318 (4.07). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 11.90 (bs, 1H), 7.84 - 7.82 (m, 2 H), 7.51 - 7.50 (m, 3 H), 6.74 (d, 1 H, \(^4J = 1.7\) Hz), 5.38 (d, 1 H, \(^4J = 2.0\) Hz). 13C NMR (125.7 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) 171.3, 163.8, 160.7, 131.8, 131.6, 129.8, 126.1, 99.1, 90.3. LRMS (EI, 70 eV): \(m/z\) (%) = 188 (83) [M\(^+\)], 160 (62), 147 (19), 131 (7), 111 (5), 105 (100), 77 (51), 69 (35), 51 (21). HRMS (EI, M\(^+\)): Calcd. for C\(_{11}\)H\(_8\)O\(_3\): 188.0474. Found: 188.0466.

\(6\)-(3,4-Dimethoxy-phenyl)-4-hydroxy-2\(\text{H}\)-pyran-2-one (4f): Yellow solid. Mp 228°C. \(R_f = 0.34\) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 10 : 1). IR (ATR): \(\tilde{\nu}\) = 2957 (w), 2837 (w), 2616 (w), 2035 (w), 1807
(w), 1637 (m), 1622 (s), 1585 (m), 1560 (w), 1512 (vs), 1476 (w), 1465 (m), 1454 (s), 1436 (vs), 1404 (vs), 1346 (w), 1324 (w), 1265 (vs), 1231 (vs), 1190 (w), 1174 (s), 1143 (vs), 1081 (w), 1023 (s), 1001 (w), 961 (w), 900 (w), 875 (vs), 855 (w), 810 (w), 793 (vs), 768 (m), 684 (w), 657 (s) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{\text{max}} (\log \varepsilon) = 214\) nm (4.48), 278 (3.89), 331 (4.26). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta (\text{ppm}) 11.72\) (bs, 1H), 7.42 (dd, 1H, \(^3J = 6.6\) Hz, \(^4J = 0.9\) Hz), 7.33 (d, 1H, \(^4J = 1.7\) Hz), 7.06 (d, 1H, \(^3J = 8.6\) Hz), 6.70 (d, 1H, \(^4J = 1.7\) Hz), 5.33 (d, 1H, \(^4J = 1.5\) Hz), 3.83 (s, 3H), 3.81 (s, 3H). \(^{13}\)C NMR (125.7 MHz, DMSO-\(d_6\)): \(\delta (\text{ppm}) 171.5, 163.8, 161.0, 151.9, 149.6, 124.2, 119.5, 112.4, 109.2, 97.7, 89.4, 56.4, 56.3\). LRMS (EI, 70 eV): \(m/z\) (%) = 248 (100) \([\text{M}^+\]), 220 (14), 206 (35), 191 (2), 149 (2), 124 (4), 119 (3), 92 (4), 69 (11), 51 (5). HRMS (EI, M\(^+\)): Calcd. for C\(_{13}\)H\(_{12}\)O\(_5\): 248.0685. Found: 248.0665.

4-Hydroxy-6-(3,4,5-trimethoxy-phenyl)-2H-pyran-2-one (4g): Yellow solid. Mp 185 - 188°C. \(R_f = 0.30\) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 20 : 1). IR (ATR): \(\tilde{\nu} = 3507\) (w), 2948 (w), 2841 (w), 2616 (w), 1671 (s), 1631 (m), 1590 (s), 1573 (s), 1503 (vs), 1442 (vs), 1419 (vs), 1346 (vs), 1316 (w), 1287 (w), 1244 (s), 1211 (w), 1196 (w), 1182 (w), 1127 (w), 1035 (w), 1000 (m), 982 (m), 903 (w), 847 (w), 821 (vs), 800 (s), 759 (w), 727 (w), 688 (w), 664 (w) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{\text{max}} (\log \varepsilon) = 220\) nm (4.58), 281 (3.95), 325 (4.21). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta (\text{ppm}) 11.80\) (bs, 1H), 7.10 (s, 2H), 6.82 (d, 1H, \(^4J = 1.5\) Hz), 5.36 (d, 1H, \(^4J = 1.5\) Hz), 3.85 (s, 6H), 3.71 (s, 3H). \(^{13}\)C NMR (125.7 MHz, DMSO-\(d_6\)): \(\delta (\text{ppm}) 171.4, 163.7, 160.6, 153.9, 140.5, 127.2, 103.7, 99.0, 89.9, 60.5, 56.8\). LRMS (EI, 70 eV): \(m/z\) (%) = 278 (100) \([\text{M}^+\]), 263 (5), 250 (5), 236 (51), 221 (8), 195 (43), 69 (14). HRMS (EI, M\(^+\)): Calcd. for C\(_{14}\)H\(_{14}\)O\(_6\): 278.0790. Found: 278.0788.

6-Furan-2-yl-4-hydroxy-2H-pyran-2-one (4h): Yellow solid. Mp 230°C. \(R_f = 0.71\) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 10 : 1). IR (ATR): \(\tilde{\nu} = 3146\) (w), 2972 (w), 2798 (w), 2753 (w), 2655 (w), 2611 (w), 2572 (w), 2160 (w), 1979 (vw), 1763 (w), 1716 (s), 1650 (s), 1622 (s), 1584 (s), 1569 (m), 1546 (vs), 1501 (m), 1463 (m), 1421 (w), 1402 (w), 1379 (w), 1350 (w), 1314 (w), 1273 (w), 1252 (w), 1228 (vs), 1163 (m), 1108 (w), 1069 (w), 1041 (w), 1017 (vs), 895 (m), 883 (s), 866 (w), 827 (vs), 817 (vs), 748 (vs), 721 (vs), 688 (w), 670 (w) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{\text{max}} (\log \varepsilon) = 330\) nm (4.09). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta (\text{ppm}) 11.91\) (bs, 1H), 7.91 (d, 1H, \(^3J = 1.2\) Hz), 7.07 (d, 1H, \(^3J = 3.4\) Hz), 6.69 (dd, 1H, \(^3J = 3.5\) Hz, \(^3J = 1.8\) Hz), 6.41 (d, 1H, \(^4J = 2.0\) Hz), 5.32 (d, 1H, \(^4J = 2.0\) Hz). \(^{13}\)C NMR (125.7 MHz, DMSO-\(d_6\)): \(\delta (\text{ppm}) 175.4, 167.5, 157.4, 151.3, 150.8, 117.9, 117.2,

6-Furan-3-yl-4-hydroxy-2H-pyran-2-one (4i): Yellow solid. Mp 223°C. Rₜ = 0.32 (SiO₂, CH₂Cl₂ / MeOH = 15 : 1). IR (ATR): ν ~ 3112 (w), 2730 (w), 2514 (w), 1655 (s), 1615 (s), 1558 (s), 1536 (vs), 1427 (vs), 1374 (s), 1337 (w), 1277 (vs), 1180 (s), 1159 (vs), 1109 (m), 1076 (m), 1014 (s), 996 (w), 980 (m), 908 (s), 827 (m), 807 (vs), 731 (m), 689 (w), 668 (s) cm⁻¹. UV/VIS (MeOH): λmax (lg ε) = 263 nm (3.61), 313 (3.98). ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 11.78 (bs, 1 H), 8.25 (s, 1 H), 7.80 (t, 1 H, 3J = 1.8 Hz), 6.95 (d, 1 H, 3J = 1.0 Hz), 6.48 (d, 1 H, 4J = 2.0 Hz), 5.30 (d, 1 H, 4J = 2.0 Hz). ¹³C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 170.6, 162.9, 155.7, 145.2, 143.0, 119.9, 107.7, 98.0, 89.2. LRMS (EI, 70 eV): m/z (%) = 178 (86) [M⁺], 150 (35), 137 (13), 136 (14), 122 (6), 121 (5), 95 (100), 69 (40). HRMS (EI, M⁺): Calcd. for C₉H₆O₄: 178.0266. Found: 178.0245. Anal. calcd. for C₉H₆O₄: C 60.68, H 3.39. Found: C 60.47, H 3.51.

6-Thiophen-2-yl-4-hydroxy-2H-pyran-2-one (4j): Yellow solid. Mp 225°C. Rₜ = 0.38 (SiO₂, CH₂Cl₂ / MeOH = 15 : 1). IR (ATR): ν ~ 2950 (w), 2812 (w), 2762 (w), 2717 (w), 2651 (w), 2587 (w), 2161 (w), 2025 (w), 1757 (w), 1717 (s), 1628 (s), 1567 (s), 1524 (s), 1482 (m), 1365 (m), 1306 (s), 1269 (m), 1229 (m), 1190 (m), 1076 (m), 1058 (s), 1037 (s), 999 (w), 914 (w), 862 (w), 816 (s), 793 (w), 748 (w), 720 (m), 703 (vs), 688 (m) cm⁻¹. UV/VIS (MeOH): λmax (lg ε) = 248 nm (4.12), 336 (4.13). ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) 11.85 (bs, 1H), 7.81 (d, 1H, 3J = 4.9 Hz), 7.75 (d, 1H, 3J = 3.4 Hz), 7.20 (t, 1H, 3J = 4.3 Hz), 6.62 (d, 1H, 4J = 1.7 Hz), 5.32 (d, 1H, 4J = 2.0 Hz). ¹³C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 170.6, 162.5, 156.2, 134.6, 130.3, 128.9, 127.8, 96.9, 89.1. LRMS (EI, 70 eV): m/z (%) = 194 (93) [M⁺], 166 (38), 153 (14), 137 (4), 111 (100), 83 (8), 69 (31). HRMS (EI, M⁺): Calcd. for C₉H₆O₃S: 194.0038, Found: 194.0031.

4-Hydroxy-6-pyridin-3-yl-2H-pyran-2-one (4k): Yellow solid. Mp 194°C. Rₜ = 0.41 (SiO₂, CH₂Cl₂ / MeOH = 10 : 1). IR (ATR): ν = 3018 (w), 3016 (w), 2550 (w), 2164 (w), 2032 (w), 1726 (s), 1632 (s), 1561 (vs), 1483 (w), 1457 (w), 1366 (w), 1344 (w), 1324 (m), 1297 (m), 1270 (m), 1249 (w), 1224 (vs), 1196 (vs), 1183 (vs), 1146 (vs), 1124 (vs), 1078 (m), 1008 (w), 995 (m),
928 (w), 918 (w), 842 (s), 828 (vs), 795 (s), 773 (vs), 687 (s) cm⁻¹. UV/VIS (MeOH): λ_{max} (lg ε) = 229 nm (4.06), 259 (3.40), 318.0 (3.87). 1H NMR (500 MHz, DMSO-d₆): δ (ppm) 12.07 (bs, 1H), 9.09 (d, 1 H, ^3J = 1.4 Hz), 8.73 (dd, 1 H, ^3J = 5.0 Hz), 8.35 (td, 1 H, ^3J = 9.1 Hz, ^4J = 1.8 Hz), 7.66 (dd, 1 H, ^3J = 8.2 Hz, ^3J = 5.0 Hz), 6.95 (d, 1 H, ^4J = 1.8 Hz), 5.45 (d, 1 H, ^4J = 1.8 Hz). 13C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 171.0, 163.3, 157.8, 150.4, 145.9, 135.5, 128.5, 125.3, 100.9, 91.1. LRMS (EI, 70 eV): m/z (%) = 189 (97) [M⁺], 161 (100), 148 (38), 132 (8), 111 (21), 106 (64), 78 (52), 69 (73), 51 (57). HRMS (EI, M⁺): Calcd. for C₁₀H₇O₃N: 189.0399. Found: 189.0409.

4-Hydroxy-6-pyridin-4-yl-2H-pyran-2-one (4l): Yellow solid. Mp 232°C. Rf = 0.41 (SiO₂, CH₂Cl₂ / MeOH = 10 : 1). IR (ATR): ν = 3436 (w), 3070 (w), 2544 (w), 2139 (w), 1731 (m), 1675 (m), 1625 (s), 1528 (w), 1424 (w), 1383 (w), 1358 (w), 1336 (w), 1313 (m), 1299 (m), 1248 (w), 1229 (s), 1189 (s), 1137 (s), 1104 (m), 1071 (s), 1005 (m), 992 (w), 917 (w), 861 (w), 829 (vs), 789 (s), 725 (s), 715 (m), 666 (m) cm⁻¹. UV/VIS (MeOH): λ_{max} (lg ε) = 227 nm (3.99), 322 (3.81). 1H NMR (500 MHz, DMSO-d₆): δ (ppm) 12.30 (bs, 1H), 8.80 (d, 2 H, ^3J = 4.6 Hz), 7.94 (d, 2 H, ^3J = 5.1 Hz), 7.12 (s, 1 H), 5.53 (d, 1 H, ^4J = 1.7 Hz). 13C NMR (125.7 MHz, DMSO-d₆): δ (ppm) 175.1, 167.6, 161.6, 153.9, 145.3, 125.2, 107.6, 96.9. LRMS (EI, 70 eV): m/z (%) = 189 (100) [M⁺], 161 (62), 148 (26), 132 (5), 111 (14), 106 (53), 78 (24), 69 (45), 51 (29). HRMS (EI, M⁺): Calcd. for C₁₀H₇NO₃: 189.0426. Found: 189.0440.

6-Heptyl-3-hexyl-4-hydroxy-2H-pyran-2-one (11a): A solution of 2.00 g (5.88 mmol) of 10a in 5 ml of absolute ethanol was added dropwise to a solution of 1.03 g (32.34 mmol) potassium hydroxide in 25 ml of absolute ethanol. The resulting mixture was stirred for 2 h at rt and the excess ethanol removed in vacuo. The residue was dissolved in 20 ml distilled water and poured into a vigorously stirred mixture of 150 ml tartaric acid solution (4°C, 6 g tartaric acid in 100 ml water) and 150 ml cold (-20°C) dichloromethane. The resulting mixture was stirred for 10 min. The precipitate potassium hydrogen tartrate was filtered off and washed with 200 ml cold (-20°C) dichloromethane. The filtrates were combined and the organic phase was separated. The aqueous phase was saturated with sodium chloride and extracted three times with dichloromethane. The organic phases were combined and dried over magnesium sulphate. The volatiles were removed in vacuo (Note: A temperature of 4°C should not be exceeded because the acid may decarboxylate), and the residue was dissolved in 45 ml cold (-20°C) TFAA. The resulting mixture was stirred for 2
h at -20°C and the excess TFA/TFAA distilled off under normal pressure. Traces of TFA were removed azeotropically with toluene. The raw material was submitted to flash chromatography (SiO₂, PE / EtOAc = 6 : 4). 1.21 g (4.1 mmol, 70 %) **11a** was obtained as a white solid. 

Mp 88°C. Rₗ = 0.61 (SiO₂, PE / EtOAc = 1 : 1). IR (ATR): ν = 3674 (w), 2957 (w), 2921 (m), 2657 (w), 1784 (w), 1663 (m), 1630 (s), 1549 (s), 1433 (s), 1406 (vs), 1292 (m), 1255 (m), 1232 (w), 1172 (m), 1130 (w), 1099 (w), 1066 (w), 1027 (w), 998 (m), 860 (w), 797 (w), 759 (w), 722 (w) cm⁻¹. UV/VIS (MeOH): λₘₐₓ (lg ε) = 292 nm (3.94). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.17 (s, 1 H), 2.44 (t, 2 H, ³J = 7.6 Hz), 2.44 (t, 2 H, ³J = 7.6 Hz), 1.62 (quint, 2 H, ³J = 7.4 Hz), 1.49 (quint, 2 H, ³J = 7.4 Hz), 1.36-1.26 (m, 14 H), 0.87 (t, 3 H, ³J = 6.8 Hz), 0.86 (t, 3 H, ³J = 6.6 Hz). ¹³C NMR (125.7 MHz, CDCl₃): δ (ppm) 168.7, 167.3, 164.0, 103.7, 101.0, 33.7, 32.0, 31.9, 29.6, 29.21, 29.16, 28.3, 27.0, 23.3, 22.9, 22.8, 14.3, 14.2. LRMS (EI, 70 eV): m/z (%) = 294 (24) [M⁺], 277 (4), 265 (5), 251 (15), 237 (23), 224 (100), 223 (78), 210 (12), 195 (54), 168 (20), 153 (21), 126 (20), 55 (33). HRMS (EI, M⁺): Calcd. for C₁₈H₃₀O₃: 294.2195. Found: 294.2206. Anal. calcd. for C₁₈H₃₀O₃: C 73.43, H 10.27. Found: C 73.55, H 10.20.

**4-Hydroxy-3-(3-methyl-but-2-enyl)-6-pentadecyl-2H-pyran-2-one (11c):** At rt a solution of 1.80 g (4.11 mmol) **10b** in 2 ml of absolute ethanol was added dropwise to a solution of 1.39 g (23.71 mmol) potassium hydroxide and the resulting mixture stirred for 2 h. Ethanol was removed in vacuo and the residue dissolved in 30 ml of distilled water. This solution was poured into a vigorously stirred mixture of 250 ml tartaric acid solution (10 g tartaric acid dissolved in 100 ml water, then cooled to 2°C) and 250 ml of cold (-20°C) dichloromethane. After stirring for another 10 min the precipitate potassium hydrogen tartrate was filtered off and washed with 200 ml cold dichloromethane. The filtrates were collected and the organic phase was separated. The aqueous phase was saturated with sodium chloride and then extracted twice with cold dichloromethane. The organic phases were combined and dried over anhydrous magnesium sulphate. The volatiles were removed in vacuo; temperatures exceeding 4°C should be avoided. The residue was immediately suspended in 25 ml of cold (-20°C) acetic anhydride. Then 500 µl (6.2 mmol) of pyridine were added and the resulting mixture stirred at 0°C for 2 h (after addition of pyridine a white solid started to separate). For complete precipitation the mixture was stored at -20°C for 12 h and the white solid was filtered off. Precipitated pyrone **11b** was set aside; the excess Ac₂O/AcOH of the filtrate was removed in vacuo. The residue was dissolved in 20 ml of
methanol. After addition of 542 mg (3.92 mmol) potassium carbonate the resulting mixture was stirred for 2 h at rt. The excess methanol was removed in vacuo and the residue dissolved in 30 ml of water (due to partial precipitation of the pyrone 11c the solution turned turbid). After this suspension was acidified to pH 3 with glacial acetic acid, the product 11c started to deposit. The white solid was collected on a Büchner funnel, washed with water and dried. 140 mg (0.37 mmol) of 11c were obtained. The precipitate (set aside previously) was dissolved in 50 ml of methanol. After addition of 3.08 g (21.85 mmol) potassium carbonate the resulting mixture was stirred at rt for 2 h. Excess methanol was removed in vacuo and the residue suspended in 50 ml water. The complete precipitation of 11c was accomplished by acidifying the mixture to pH 3 with glacial acetic acid. The product was collected on a Büchner funnel, washed with water and dried. An additional 1.16 g (2.97 mmol) 11c were isolated as a white solid. The total yield of 11c was 1.30 g (3.34 mmol, 80 %).

Mp 99°C. Rf = 0.61 (SiO2, PE / EtOAc = 1 : 1). IR (ATR): \(\tilde{\nu} = 3155 \, \text{cm}^{-1}\) (w), 2956 (w), 2916 (vs), 2850 (s), 1664 (s), 1645 (vs), 1587 (vs), 1472 (w), 1426 (m), 1401 (vs), 1303 (w), 1283 (w), 1265 (w), 1251 (m), 1187 (w), 1149 (vw), 1108 (m), 1030 (w), 1001 (m), 981 (w), 902 (w), 859 (m), 843 (w), 810 (w), 781 (w), 753 (m), 717 (m), 697 (w) cm\(^{-1}\). UV/VIS (MeOH): \(\lambda_{\text{max}} \, (\lg \varepsilon) = 292 \, \text{nm} (3.77)\). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta \, (\text{ppm}) = 6.05 \, (s, \, 1 \, H), \, 5.27 \, (t, \, 1 \, H, \, ^3J = 7.3 \, Hz), \, 3.19 \, (d, \, 2 \, H, \, ^3J = 7.2 \, Hz), \, 2.41 \, (t, \, 2 \, H, \, ^3J = 7.6 \, Hz), \, 1.76 \, (s, \, 3 \, H), \, 1.71 \, (s, \, 3 \, H), \, 1.61 \, (\text{quint}, \, 2 \, H, \, ^3J = 7.3 \, Hz), \, 1.33 - 1.25 \, (m, \, 24 \, H), \, 0.87 \, (t, \, 3 \, H, \, ^3J = 6.7 \, Hz)\). \(^{13}\)C NMR (125.7 MHz, CDCl\(_3\)): \(\delta \, (\text{ppm}) = 167.6, \, 167.2, \, 164.0, \, 134.9, \, 121.1, \, 101.9, \, 100.9, \, 33.8, \, 32.2, \, 29.92 \, (2\times), \, 29.90 \, (3\times), \, 29.9, \, 29.7, \, 29.6, \, 29.5, \, 29.3, \, 27.1, \, 26.0, \, 22.9, \, 22.7, \, 18.2, \, 14.3\). LRMS (EI, 70 eV): \(m/z \, (\%) = 390 \, (100) \, [M^+]\), 375 (21), 361 (3), 347 (28), 335 (42), 151 (10), 123 (5), 109 (9), 69 (22), 55 (18), 41 (31). HRMS (EI, \(M^+\)): Calcd. for C\(_{25}\)H\(_{42}\)O\(_3\): 390.3134. Found: 390.3113. Anal. calcd. for C\(_{25}\)H\(_{42}\)O\(_3\): C 76.88, H 10.84. Found: C 76.77, H 10.82.

(5-Phenyl-1\(H\)-pyrazol-3-yl)-acetic acid (12): A solution of 400 mg (1.42 mmol) 4e in 6 ml distilled water and 107 mg (1.56 mmol) hydrazine monohydrochloride was heated under reflux for 2 h. After cooling, the solution was acidified to pH 3 and the product started to deposit. For complete precipitation the mixture was stored at 4°C for 12 h. The solid was collected on a Büchner funnel and washed with water to neutral. After drying 265 mg (1.31 mmol) (5-Phenyl-1\(H\)-pyrazol-3-yl)-acetic acid (12) were obtained.
White solid. Mp 173 - 174°C. \( R_f = 0.58 \) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 10 : 3). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) 12.66 (bs, 1 H), 7.74 (d, 2 H, \(^3\)J = 7.3 Hz), 7.40 (t, 2 H, \(^3\)J = 7.5 Hz), 7.28 (t, 1 H, \(^3\)J = 7.3 Hz), 6.55 (s, 1 H), 3.41 (s, 2 H). \(^13\)C NMR (125.7 MHz, CDCl\(_3\)): \( \delta \) (ppm) 172.2, 147.5, 142.2, 132.6, 129.5, 128.2, 125.7, 102.8, 33.4. LRMS (EI, 70 eV): \( m/z \) (%) = 202 (100) [M\(^+\)], 185 (7), 158 (81), 157 (82), 128 (78), 102 (14), 77 (24), 51 (19).

**5-Phenyl-isoxazol-3-yl)-acetic acid (13):** A solution of 728 mg (2.58 mmol) 4e in 4 ml distilled water and 197 mg (2.84 mmol) hydroxylamine hydrochloride was warmed at 50°C for 2 h. After cooling 1 \( N \) hydrochloric acid was added dropwise until pH 3 was reached. The mixture was then stored at 4°C for 12 h for complete precipitation and the solid collected on a Büchner funnel. After washing with water and drying 378 mg (1.86 mmol, 72 %) (5-Phenyl-isoxazol-3-yl)-acetic acid were obtained as an almost white solid.

Mp 170°C. \( R_f = 0.43 \) (SiO\(_2\), CH\(_2\)Cl\(_2\) / MeOH = 15 : 1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) (ppm) 11.14 (bs, 1 H), 7.86 (dd, 2 H, \(^3\)J = 7.8 Hz, \(^4\)J = 1.4 Hz), 7.55 - 7.48 (m, 3 H), 6.87 (s, 1 H), 3.80 (s, 2 H). \(^13\)C NMR (125.7 MHz, CDCl\(_3\)): \( \delta \) (ppm) 169.8, 169.7, 159.0, 130.4, 129.4, 127.8, 125.8, 100.9, 31.5. LRMS (EI, 70 eV): \( m/z \) (%) = 203 (100) [M\(^+\)], 159 (37), 131 (12), 105 (87), 77 (68), 51 (23).