

**SUPPORTING INFORMATION**

**Title:** Domino Michael/Retro-Michael/Mukaiyama-Aldol Reactions of 1,3-Bis-Silyl Enol Ethers with 3-Acyl- and 3-Formylbenzopyrylium Triflates – Synthesis of Functionalised 2,4'-Dihydroxybenzophenones

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## Experimental Section

**General Comments.** All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI,  $\text{H}_2\text{O}$ ) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60-200 mesh) was used. The melting points are corrected.

### General procedure 1 (synthesis of benzophenones).

To the 3-formylchromone **1** (1.0 equiv.) was added  $\text{Me}_3\text{SiOTf}$  (0.3 equiv.) at 20 °C. After stirring for 10 min  $\text{CH}_2\text{Cl}_2$  (8 mL) was added, the solution was cooled to 0 °C and the 1,3-bis-silyl enol ether (1.3 equiv.) was added. The mixture was stirred for 12 h at 20 °C and was subsequently poured into an aqueous solution of hydrochloric acid (10%). The organic and the aqueous layer were separated and the latter was extracted with  $\text{Et}_2\text{O}$  (3 x 80 mL). The combined organic layers were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/ $\text{EtOAc}$  = 10:1 → 3:1).

### 1-[(2-Hydroxybenzoyl)-2-hydroxyphenyl]ethan-1-one (**3a**).

Starting with **1a** (200 mg, 1.15 mmol), Me<sub>3</sub>SiOTf (77 mg, 0.34 mmol) and 1,3-bis-silyl enol ether **2a** (365 mg, 1.49 mmol), **3a** was isolated as a colourless solid (127 mg, 43%), m.p. = 129 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.69 (s, 3 H, CH<sub>3</sub>), 6.91 (m, 1 H, Ar), 7.08 (d, *J* = 8.7 Hz, 1 H, Ar), 7.10 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1 H, Ar), 7.53 (m, 1 H, Ar), 7.58 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1 H, Ar), 7.86 (dd, *J* = 8.7 Hz, *J* = 2.2 Hz, 1 H, Ar), 8.20 (d, *J* = 2.1 Hz, 1 H, Ar), 11.78 (s, 1 H, OH), 12.68 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 26.8 (CH<sub>3</sub>), 118.5, 118.7, 118.8 (CH), 119.0, 119.3, 128.8 (C), 132.7, 133.2, 136.3, 137.4 (CH), 163.0, 165.5 (C-OH), 198.9, 204.5 (C=O). IR (KBr):  $\tilde{\nu}$  = 3081 (m), 2973 (m), 2925 (m), 1644 (s), 1626 (s), 1588 (s), 1482 (m), 1440 (m), 1423 (m), 1363 (s), 1295 (s), 1241 (s), 1221 (s), 1161 (m), 975 (m), 914 (w), 864 (w), 834 (s), 761 (s), 633 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 425 (3.16), 403 (3.17), 323 (3.93), 285 (4.02), 250 (4.30) nm. MS (EI, 70 eV): *m/z* (%) = 256 (M<sup>+</sup>, 70), 241 (14), 213 (9), 163 (17), 136 (6), 121 (100), 92 (14), 66 (22). Anal.: calcd. for C<sub>15</sub>H<sub>12</sub>O<sub>4</sub> (256.26): C 70.33, H 4.72; found: C 70.04, H 4.89.

### **(3-Benzoyl-4-hydroxyphenyl)-(2-hydroxyphenyl)methanone (3b).**

Starting with **1a** (209 mg, 1.2 mmol), Me<sub>3</sub>SiOTf (80 mg, 0.36 mmol) and 1,3-bis-silyl enol ether **2b** (478 mg, 1.6 mmol), **3b** was isolated as a colourless solid (233 mg, 61%), m.p. = 129 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.88 (m, 1 H, Ar), 7.05 (dd, *J* = 8.5 Hz, *J* = 0.8 Hz, 1 H, Ar), 7.24 (d, *J* = 8.6 Hz, 1 H, Ar), 7.55 (m, 5 H, Ar), 7.72 (m, 2 H, Ar), 7.90 (dd, *J* = 8.7 Hz, *J* = 2.2 Hz, 1 H, Ar), 8.06 (d, *J* = 2.2 Hz, 1 H, Ar), 11.76 (s, 1 H, OH), 12.44 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 118.6, 118.6 (CH), 118.6 (C), 118.7 (CH), 118.9, 128.6 (C), 128.6, 129.2, 132.6, 132.8, 135.8, 136.4 (CH), 137.0 (C), 137.2 (CH), 162.9, 166.3 (C-OH), 198.8, 201.2 (C=O). IR (KBr):  $\tilde{\nu}$  = 3065 (m), 1627 (s), 1576 (s), 1482 (s), 1450 (m), 1407 (w), 1346 (s), 1322 (m), 1284 (m), 1253 (s), 1234 (s), 1195 (m), 1158 (w), 921 (w), 849 (w), 830 (w), 807 (w), 759 (m), 739 (w), 705 (m), 660 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 336 (3.95), 261 (4.35) nm. MS (EI, 70 eV): *m/z* (%) = 318 (M<sup>+</sup>, 84), 281 (11), 225 (18),

197 (31), 147 (24), 121 (100), 77 (36), 51 (17). The exact molecular mass for C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>  $m/z = 318.0892 \pm 2$  ppm (M<sup>+</sup>) was confirmed by HRMS (EI, 70 eV).

### **Ethyl 5-(2-hydroxybenzoyl)salicylate (3c).**

Starting with **1a** (475 mg, 2.73 mmol), Me<sub>3</sub>SiOTf (182 mg, 0.82 mmol) and 1,3-bis-silyl enol ether **2c** (974 mg, 3.55 mmol), **3c** was isolated as a yellow solid (398 mg, 51%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.40$  (t,  $J = 7.0$  Hz, 3 H, CH<sub>3</sub>), 4.43 (q,  $J = 7.0$  Hz, 2 H, CH<sub>2</sub>), 6.92 (m, 1 H, Ar), 7.06 (br m, 3 H, Ar), 7.42 - 7.61 (m, 2 H, Ar), 8.27 (s, 1 H, Ar), 11.39 (s, 1 H, OH), 12.83 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta = 14.1$ , 62.1 (CH<sub>3</sub>), 112.5, 119.0, 129.0 (C), 117.7, 118.5, 118.7, 132.4, 132.9, 136.2, 136.6 (CH), 163.0, 164.7, 169.6 (C), 199.1 (C=O). IR (KBr):  $\tilde{\nu} = 3187$  (w), 3087 (w), 2987 (w), 2966 (w), 1683 (s), 1629 (s), 1589 (s), 1467 (m), 1444 (m), 1397 (m), 1343 (s), 1293 (s), 1242 (s), 1216 (s), 1176 (m), 1084 (m), 759 (s) cm<sup>-1</sup>. MS (EI, 70 eV):  $m/z$  (%) = 286 (M<sup>+</sup>, 100), 121 (94), 120 (86). Anal.: calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>5</sub> (286.29): C 67.31, H 4.93; found: C 66.88, H 5.18.

### **Methoxyethyl 5-(2-hydroxybenzoyl)salicylate (3d).**

Starting with **1a** (243 mg, 1.39 mmol), Me<sub>3</sub>SiOTf (101 mg, 0.42 mmol) and 1,3-bis-silyl enol ether **2d** (552 mg, 1.81 mmol), **3d** was isolated as a colourless solid (224 mg, 51%), m.p. = 69 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 3.41$  (s, 3 H, OCH<sub>3</sub>), 3.73 (m, 2 H, CH<sub>2</sub>OCH<sub>3</sub>), 4.54 (m, 2 H, OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 6.89 (dt,  $J = 7.6$  Hz,  $J = 1.1$  Hz, 1 H, Ar), 7.09 (m, 2 H, Ar), 7.52 (dt,  $J = 7.8$  Hz,  $J = 1.7$  Hz, 1 H, Ar), 7.57 (dd,  $J = 7.6$  Hz,  $J = 1.7$  Hz, 1 H, Ar), 7.85 (dd,  $J = 7.8$  Hz,  $J = 2.3$  Hz, 1 H, Ar), 8.32 (d,  $J = 2.2$  Hz, 1 H, Ar), 11.18 (s, 1 H, OH), 11.84 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta = 64.8$  (OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 70.0 (OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 95.0 (OCH<sub>3</sub>), 112.2 (C), 117.8, 118.5, 118.7 (CH), 119.0, 129.1 (C), 132.5, 132.9, 136.2, 136.7 (CH), 162.9, 164.6, 169.6 (C), 199.1 (C=O). IR (KBr):  $\tilde{\nu} = 3139$  (w), 2982 (w), 2899 (w), 1678 (s), 1628 (s), 1589 (s), 1485 (s), 1447 (m), 1417 (w), 1383 (m),

1343 (s), 1294 (s), 1259 (s), 1243 (s), 1217 (s), 1175 (m), 1126 (m), 1089 (m), 1029 (m), 846 (w), 794 (m), 762 (m), 731 (w), 633 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 283 (4.02), 263 (3.98), 235 (4.23), 214 (4.43) nm. MS (EI, 70 eV):  $m/z$  (%) = 316 ( $\text{M}^+$ , 60), 240 (39), 196 (17), 184 (10), 147 (17), 121 (100), 92 (24), 60 (60), 28 (5). The exact molecular mass for  $\text{C}_{17}\text{H}_{16}\text{O}_6$   $m/z = 316.0947 \pm 2$  ppm ( $\text{M}^+$ ) was confirmed by HRMS (EI, 70 eV).

### **Methyl 5-(2-hydroxybenzoyl)-3-methylsalicylate (3e).**

Starting with **1a** (350 mg, 2.01 mmol),  $\text{Me}_3\text{SiOTf}$  (134 mg, 0.60 mmol) and 1,3-bis-silyl enol ether **2e** (717 mg, 2.61 mmol), **3e** was isolated as colourless solid (322 mg, 56%), m.p. = 97 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.34$  (s, 3 H,  $\text{CH}_3$ ), 3.97 (s, 3 H,  $\text{OCH}_3$ ), 6.91 (dt,  $J = 7.6$  Hz,  $J = 1.1$  Hz, 1 H, Ar), 7.07 (dd,  $J = 7.9$  Hz,  $J = 1.0$  Hz, 1 H, Ar), 7.51 (m, 1 H, Ar), 7.56 (dd,  $J = 7.9$  Hz,  $J = 2.2$  Hz, 1 H, Ar), 7.74 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.11 (d,  $J = 2.2$  Hz, 1 H, Ar), 11.49 (s, 1 H, OH), 11.86 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.8$  ( $\text{CH}_3$ ), 52.7 ( $\text{OCH}_3$ ), 111.2 (C), 118.5, 118.7 (CH), 119.1, 127.5, 128.4 (C), 130.1, 133.0, 136.0, 136.9 (CH), 163.0, 163.3, (C-OH), 170.5, 194.4 (C=O). IR (KBr):  $\tilde{\nu} = 3100$  (m), 2957 (m), 2360 (w), 2340 (w), 1680 (s), 1625 (s), 1544 (s), 1473 (m), 1448 (s), 1359 (s), 1323 (m), 1304 (s), 1291 (s), 1264 (s), 1234 (s), 1219 (s), 1199 (s), 1173 (s), 1157 (s), 1132 (s), 1113 (m), 1002 (m), 869 (m), 797 (s)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 317 (3.92), 287 (3.99), 238 (4.31), 220 (4.33) nm. MS (EI, 70 eV):  $m/z$  (%) = 286 (100), 253 (32), 226 (12), 197 (18), 161 (24), 121 (84), 93 (10), 65 (16). Anal.: calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_5$  (286.29): C 67.16, H 4.93; found: C 67.39, H 5.32.

### **Ethyl 5-(2-hydroxybenzoyl)-3-ethylsalicylate (3f).**

Starting with **1a** (300 mg, 1.72 mmol),  $\text{Me}_3\text{SiOTf}$  (115 mg, 0.52 mmol) and 1,3-bis-silyl enol ether **2f** (680 mg, 2.24 mmol), **3f** was isolated as a colourless solid (286 mg, 53%), m.p. = 123 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.26$  (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.40 (t,  $J = 7.1$

Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.76 (q, *J* = 7.5 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 4.43 (q, *J* = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.91 (m, 1 H, Ar), 7.08 (dd, *J* = 8.4 Hz, *J* = 0.9 Hz, 1 H, Ar), 7.52 (m, 1 H, Ar), 7.60 (dd, *J* = 7.9 Hz, *J* = 1.6 Hz, 1 H, Ar), 7.73 (d, *J* = 2.2 Hz, 1 H, Ar), 8.14 (d, *J* = 2.2 Hz, 1 H, Ar), 11.62 (s, 1 H, OH), 11.91 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 15.5, 14.2 (CH<sub>3</sub>), 22.8, 61.9 (CH<sub>2</sub>), 111.6 (C), 118.5, 118.6 (CH), 119.2, 128.4 (C), 130.0 (CH), 133.1 (C), 133.1, 135.4, 136.0 (CH), 163.0, 163.1 (C-OH), 170.12, 199.6 (C=O). IR (KBr):  $\tilde{\nu}$  = 3083 (m), 3056 (m), 2987 (s), 2972 (s), 2908 (m), 2876 (m), 1673 (s), 1625 (s), 1592 (s), 1485 (m), 1448 (m), 1407 (m), 1310 (s), 1237 (s), 1206 (s), 1155 (m), 1112 (m), 1026 (s), 867 (w), 802 (m), 769 (s), 688 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): λ<sub>max</sub> (lg ε): 316 (3.90), 290 (3.95), 243 (4.21) nm. MS (EI, 70 eV): *m/z* (%) = 314 (75), 268 (31), 240 (71), 194 (54), 148 (36), 121 (100), 93 (15), 65 (18). The exact molecular mass for C<sub>18</sub>H<sub>18</sub>O<sub>5</sub> *m/z* = 314.1154±2 ppm (M<sup>+</sup>) was confirmed by HRMS (EI, 70 eV).

### **Methyl 3-propyl-5-(2-hydroxybenzoyl)salicylate (3g).**

Starting with **1a** (296 mg, 1.69 mmol), Me<sub>3</sub>SiOTf (122 mg, 0.51 mmol) and 1,3-bis-silyl enol ether **2g** (317 mg, 2.21 mmol), **3g** was isolated as a colourless solid (283 mg, 51%), m.p. = 125 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.98 (t, *J* = 7.3 Hz, 3 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.41 (t, *J* = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.60-1.72 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.70 (t, *J* = 7.4 Hz, 2 H, ArCH<sub>2</sub>), 4.43 (q, *J* = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.91 (m, 1 H, Ar), 7.08 (dd, *J* = 8.4 Hz, *J* = 1.1 Hz, 1 H, Ar), 7.51 (m, 1 H, Ar), 7.59 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 1 H, Ar), 7.70 (d, *J* = 2.2 Hz, 1 H, Ar), 8.15 (d, *J* = 2.3 Hz, 1 H, Ar), 11.61 (s, 1 H, OH), 11.90 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 13.9, 14.2 (CH<sub>3</sub>), 22.4 (CH<sub>2</sub>), 31.7 (Ar-CH<sub>2</sub>), 61.9 (OCH<sub>2</sub>CH<sub>3</sub>), 111.8 (C), 118.5, 118.6 (CH), 119.2, 128.3 (C), 130.1 (CH), 131.5 (C), 133.1, 136.1, 136.3 (CH), 163.0, 163.2 (C-OH), 170.2, 199.6 (C=O). IR (KBr):  $\tilde{\nu}$  = 3426 (m), 3091 (w), 3057 (w), 2991 (m), 2961 (m), 2931 (m), 2873 (m), 1673 (s), 1624 (s), 1590 (s), 1484 (m), 1448 (m), 1407 (m), 1381 (s), 1348 (s), 1328 (s), 1288 (s), 1264 (m), 1235 (s), 1208 (m), 1188 (s), 1154 (m),

1134 (w), 1024 (m), 867 (w), 810 (m), 802 (m), 766 (s)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 319 (3.91), 291 (3.95), 240 (4.24), 214 (4.46) nm. MS (EI, 70 eV):  $m/z$  (%) = 328 ( $\text{M}^+$ , 70), 285 (25), 254 (83), 208 (48), 162 (15), 121 (100), 93 (11), 66 (14), 28 (15). The exact molecular mass for  $\text{C}_{19}\text{H}_{20}\text{O}_5$   $m/z = 328.1311 \pm 2$  ppm ( $\text{M}^+$ ) was confirmed by HRMS (EI, 70 eV). Anal.: calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_5$  (328.37): C 69.50 H 6.14; found C 69.45, H 6.36.

### **Ethyl 3-allyl-5-(2-hydroxybenzoyl)salicylate (3h).**

Starting with **1a** (348 mg, 2.0 mmol),  $\text{Me}_3\text{SiOTf}$  (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2h** (817 mg, 2.6 mmol), **3h** was isolated as colourless solid (274 mg, 42%), m.p. = 111 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.41$  (t,  $J = 7.3$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 3.48 (m, 2 H,  $\text{CH}_2\text{CHCH}_2$ ), 4.44 (q,  $J = 7.3$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 4.98 - 5.18 (m, 2 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 6.00 (m, 1 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 6.90 (m, 1 H, Ar), 7.08 (dd,  $J = 7.3$  Hz,  $J = 1.0$  Hz, 1 H, Ar), 7.52 (m, 1 H, Ar), 7.58 (dd,  $J = 7.9$  Hz,  $J = 1.6$  Hz, 1 H, Ar), 7.73 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.17 (d,  $J = 2.2$  Hz, 1 H, Ar), 11.64 (s, 1H, OH), 11.89 (s, 1H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{CH}_3$ ), 33.6 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 62.0 ( $\text{OCH}_2\text{CH}_3$ ), 111.9 (C), 116.7 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 118.5, 118.6 (CH), 119.1, 128.5, 129.2 (C), 130.4, 133.0, 135.2, 136.1, 136.3 (CH), 162.8, 163.0 (C-OH), 170.0, 199.4 (C=O). IR (KBr):  $\tilde{\nu} = 3079$  (w), 3056 (w), 2992 (w), 2931 (w), 2909 (w), 1673 (s), 1624 (s), 1592 (s), 1484 (m), 1457 (m), 1408 (m), 1383 (m), 1347 (m), 1325 (m), 1288 (m), 1265 (m), 1236 (m), 1208 (m), 1191 (m), 1153 (m), 1132 (m), 1024 (w), 1024 (m), 914 (w), 870 (w), 810 (w), 785 (w), 766 (m), 736 (w), 704 (w), 659 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 317 (3.88), 288 (3.94), 243 (4.2) nm. MS (EI, 70 eV):  $m/z$  (%) = 326 ( $\text{M}^+$ , 8), 245 (37), 242 (84), 241 (40), 240 (10), 218 (31), 216 (74), 214 (35), 211 (11), 181 (9), 136 (100), 212 (14), 101 (29), 76 (31), 50 (15). Anal.: calcd. for  $\text{C}_{19}\text{H}_{18}\text{O}_5$  (326.35): C 69.93, H 5.56; found C 69.20, H 5.96.

### **Ethyl 3-butyl-5-(2-hydroxybenzoyl)salicylate (3i).**

Starting with **1a** (250 mg, 1.44 mmol), Me<sub>3</sub>SiOTf (96 mg, 0.43 mmol) and 1,3-bis-silyl enol ether **2i** (617 mg, 1.87 mmol), **3i** was isolated as yellow solid (306 mg, 62%), m.p. = 105 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.95 (t, *J* = 7.3 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.36 - 1.44 (br m, 5 H, CH<sub>2</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 1.64 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.72 (t, *J* = 7.6 Hz, 2 H, ArCH<sub>2</sub>), 4.43 (q, *J* = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.91 (m, 1 H, Ar), 7.08 (dd, *J* = 8.4 Hz, *J* = 0.9 Hz, 1 H, Ar), 7.52 (m, 1 H, Ar), 7.59 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1 H, Ar), 7.70 (dd, *J* = 2.3 Hz, *J* = 0.5 Hz, 1 H, Ar), 8.14 (d, *J* = 2.3 Hz, 1 H, Ar), 11.61 (s, 1 H, OH), 11.90 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 13.9, 14.1 (CH<sub>3</sub>), 22.5, 29.3, 31.3 (CH<sub>2</sub>), 61.9 (OCH<sub>2</sub>CH<sub>3</sub>), 111.7 (C), 118.4, 118.6 (CH), 119.2, 128.3 (C), 130.0 (CH), 131.7 (C), 133.0, 136.0, 136.2 (CH), 162.9, 163.1 (C-OH), 170.2, 199.5 (C=O). IR (KBr):  $\tilde{\nu}$  = 3089 (m), 2989 (m), 2961 (m), 2930 (m), 2868 (w), 1674 (s), 1624 (s), 1591 (s), 1485 (m), 1448 (m), 1405 (s), 1380 (s), 1348 (s), 1329 (s), 1307 (s), 1289 (s), 1265 (s), 1235 (s), 1209 (s), 1187 (s), 1155 (m), 1134 (w), 1027 (m), 888 (w), 804 (w), 767 (s) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): 320 (3.89), 291 (3.91), 240 (4.24), 215 (4.44) nm. MS (EI, 70 eV): *m/z* (%) = 342 (M<sup>+</sup>, 46), 309 (4), 285 (3), 268 (25), 222 (16), 148 (15), 121 (28), 74 (19), 43 (22). The exact molecular mass for C<sub>20</sub>H<sub>22</sub>O<sub>5</sub> *m/z* = 342.1467±2 ppm (M<sup>+</sup>) was confirmed by HRMS (EI, 70 eV).

### **Ethyl 3-octyl-5-(2-hydroxybenzoyl)salicylate (3j).**

Starting with **1a** (348 mg, 2.0 mmol), Me<sub>3</sub>SiOTf (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2j** (1.00 g, 2.6 mmol), **3j** was isolated as a yellow solid (343 mg, 43%), m.p. = 56 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.89 (t, *J* = 6.6 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.22 - 1.38 (br m, 10 H, CH<sub>2</sub>), 1.41 (t, *J* = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.63 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.71 (m, 2 H, ArCH<sub>2</sub>), 4.43 (q, *J* = 7.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.90 (m, 1 H, Ar), 7.08 (dd, *J* = 8.4 Hz, *J* = 1.0 Hz, 1 H, Ar), 7.51 (m, 1 H, Ar), 7.59 (dd, *J* = 8.1 Hz, *J* = 1.7 Hz, 1 H, Ar), 7.70 (d, *J* = 2.2 Hz, 1 H, Ar), 8.14 (d, *J* = 2.3 Hz, 1 H, Ar), 11.61 (s, 1 H, OH), 11.91 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 14.1, 14.2 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 29.2, 29.3, 29.4,

29.5, 29.6, 31.9 (CH<sub>2</sub>), 61.9 (OCH<sub>2</sub>CH<sub>3</sub>), 117.0 (C), 118.5, 118.6 (CH), 119.2, 128.3 (C), 130.0 (CH), 131.8 (C), 133.0, 136.0, 136.2 (CH), 163.0, 163.1 (C), 170.2, 199.3 (C=O). IR (KBr):  $\tilde{\nu}$  = 3084 (w), 2953 (m), 2927 (s), 2856 (m), 1674 (s), 1626 (s), 1593 (s), 1461 (m), 1405 (w), 1379 (m), 1348 (m), 1329 (w), 1290 (m), 1262 (m), 1236 (s), 1209 (m), 1189 (s), 1156 (w), 1132 (w), 804 (w), 767 (m), 704 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\max}$  (lg  $\epsilon$ ): 318 (3.89), 292 (3.92), 244 (4.20) nm. GC-MS:  $m/z$  (%) = 398 (M, 100), 353 (18), 324 (80), 285 (91), 253 (68), 197 (25), 121 (71), 93 (5). The exact molecular mass for C<sub>24</sub>H<sub>30</sub>O<sub>5</sub>  $m/z$  = 398.2093 $\pm$ 2 ppm (M<sup>+</sup>) was confirmed by HRMS (EI, 70 eV).

### **Ethyl 3-nonyl-5-(2-hydroxybenzoyl)salicylate (3k).**

Starting with **1a** (261 mg, 1.50 mmol), Me<sub>3</sub>SiOTf (100 mg, 0.45 mmol) and 1,3-bis-silyl enol ether **2k** (781 mg, 1.95 mmol), **3k** was isolated as a yellow solid (377 mg, 61%), m.p. = 59 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.88 (t,  $J$  = 6.9 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.20 - 1.34 (br m, 12 H, CH<sub>2</sub>), 1.39 (t,  $J$  = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.54 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.72 (t,  $J$  = 7.5 Hz, 2 H, ArCH<sub>2</sub>), 4.44 (q,  $J$  = 7.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.90 (m, 1 H, Ar), 7.08 (dd,  $J$  = 8.4 Hz,  $J$  = 1.0 Hz, 1 H, Ar), 7.51 (m, 1 H, Ar), 7.60 (dd,  $J$  = 8.0 Hz,  $J$  = 1.6 Hz, 1 H, Ar), 7.71 (d,  $J$  = 2.3 Hz, 1 H, Ar), 8.15 (d,  $J$  = 2.3 Hz, 1 H, Ar), 11.62 (s, 1 H, OH), 11.92 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.0, 14.1 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 29.2, 29.3, 29.4, 29.4, 29.5, 29.6 (CH<sub>2</sub>), 31.8 (ArCH<sub>2</sub>), 61.9 (OCH<sub>2</sub>CH<sub>3</sub>), 111.7 (C), 118.4, 118.5 (CH), 119.1, 128.2 (C), 129.9 (CH), 131.7 (C), 132.9, 135.9, 136.1 (CH), 162.9, 163.1 (C-OH), 170.1, 199.5 (C=O). IR (KBr):  $\tilde{\nu}$  = 3420 (w), 3089 (w), 2985 (m), 2927 (s), 2856 (s), 1675 (s), 1627 (s), 1593 (s), 1482 (m), 1457 (m), 1407 (m), 1378 (m), 1349 (m), 1328 (m), 1293 (s), 1264 (m), 1238 (s), 1207 (s), 1189 (s), 1157 (m), 1132 (w), 1027 (m), 871 (w), 804 (m), 764 (s), 738 (m), 701 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): 320 (3.94), 291 (3.97), 241 (4.28), 215 (4.50) nm. MS (EI, 70 eV):  $m/z$  (%) = 412 (M<sup>+</sup>, 100), 338 (20), 285 (33), 253 (32), 167 (20), 148 (59), 121 (67), 72 (10), 58 (23), 43 (23). C<sub>25</sub>H<sub>32</sub>O<sub>5</sub>.

### Ethyl 3-decyl-5-(2-hydroxybenzoyl)salicylate (**3l**).

Starting with **1a** (261 mg, 1.50 mmol), Me<sub>3</sub>SiOTf (100 mg, 0.45 mmol) and 1,3-bis-silyl enol ether **2l** (808 mg, 1.95 mmol), **3l** was isolated as a yellow solid (372 mg, 58%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.89 (t, *J* = 6.9 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.19 - 1.45 (br m, 14 H, CH<sub>2</sub>), 1.41 (t, *J* = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.62 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.71 (t, *J* = 7.5 Hz, 2 H, ArCH<sub>2</sub>), 4.43 (q, *J* = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.90 (m, 1 H, Ar), 7.07 (dd, *J* = 8.4 Hz, *J* = 0.9 Hz, 1 H, Ar), 7.51 (m, 1 H, Ar), 7.59 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1 H, Ar), 7.70 (d, *J* = 2.2 Hz, 1 H, Ar), 8.14 (d, *J* = 2.2 Hz, 1 H, Ar), 11.61 (s, 1 H, OH), 11.91 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 14.0, 14.1 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>CH<sub>3</sub>), 29.2, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 31.9 (CH<sub>2</sub>), 61.9 (OCH<sub>2</sub>CH<sub>3</sub>), 111.7 (C), 118.4, 118.6 (CH), 119.2, 128.2 (C), 129.9 (CH), 131.7 (C), 133.0, 135.9, 136.2 (CH), 162.9, 163.1 (C-OH), 170.1, 199.5 (C=O). IR (KBr):  $\tilde{\nu}$  = 3097 (m), 2954 (m), 2926 (s), 2855 (m), 1674 (s), 1627 (s), 1593 (s), 1484 (m), 1461 (m), 1403 (m), 1379 (s), 1349 (s), 1328 (m), 1292 (s), 1237 (s), 1210 (m), 1187 (s), 1156 (m), 1132 (w), 1024 (m), 802 (w), 764 (m), 736 (m), 704 (w), 661 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): 322 (3.85), 292 (3.87), 242 (4.20), 215 (4.41) nm. MS (EI, 70 eV): *m/z* (%) = 426 (M<sup>+</sup>, 16), 306 (3), 285 (4), 253 (5), 183 (3), 167 (4), 130 (1), 121 (11), 85 (2), 70 (2), 43 (8). HRMS (FT-ICR): calcd. for C<sub>26</sub>H<sub>35</sub>O<sub>5</sub> ([M+1]<sup>+</sup>): 427.24790; found: 427.24757.

### Ethyl 3-benzyl-5-(2-hydroxybenzoyl)salicylate (**3m**).

Starting with **1a** (348 mg, 2.0 mmol), Me<sub>3</sub>SiOTf (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2m** (948 mg, 2.6 mmol), **3m** was isolated as a colourless solid (268 mg, 48%), m.p. = 88 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.39 (t, *J* = 7.3 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 4.07 (s, 2 H, ArCH<sub>2</sub>), 4.43 (q, *J* = 7.3 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.85 (m, 1 H, Ar), 7.05 (dd, *J* = 8.3 Hz, *J* = 0.6 Hz, 1 H, Ar), 7.20 - 7.30 (m, 5 H, Ar), 7.46 - 7.53 (m, 2 H, Ar), 7.60 (d, *J* = 2.3 Hz, 1 H, Ar), 8.17 (d, *J* = 2.3 Hz, 1 H, Ar), 11.68 (s, 1 H, OH), 11.87 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5

MHz, CDCl<sub>3</sub>):  $\delta$  = 14.1 (CH<sub>3</sub>), 35.4 (ArCH<sub>2</sub>), 62.0 (OCH<sub>2</sub>CH<sub>3</sub>), 112.0 (C), 118.4, 118.6 (CH), 119.0 (C), 126.4 (CH), 128.4 (C), 128.5, 128.9 (CH), 130.3 (C), 130.5, 132.9, 136.1, 136.8 (CH), 139.5 (C), 162.9, 162.9 (C-OH), 176.0, 199.3 (C=O). IR (KBr):  $\tilde{\nu}$  = 3147 (w), 3065 (w), 3026 (w), 2912 (w), 1685 (s), 1627 (s), 1591 (s), 1486 (m), 1466 (m), 1379 (m), 1347 (s), 1298 (s), 1263 (s), 1238 (s), 1214 (m), 1175 (m), 1149 (s), 1105 (m), 1026 (m), 931 (w), 882 (w), 863 (w), 793 (m), 759 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\max}$  (lg  $\epsilon$ ): UV: 318 (3.91), 289 (3.95), 244 (4.24) nm. MS (EI, 70 eV):  $m/z$  (%) = 376 (M<sup>+</sup>, 25), 376 (100), 331 (11), 330 (34), 330 (34), 303 (14), 302 (62), 285 (19), 256 (19), 237 (5), 210 (21), 181 (12), 151 (20), 121 (90), 66 (17), 29 (15). HRMS (FT-ICR): calcd. for C<sub>23</sub>H<sub>21</sub>O<sub>5</sub> ([M+1]<sup>+</sup>): 377.13835; found: 377.13890.

#### **Ethyl 5-(2-hydroxybenzoyl-5-methyl)salicylate (3n).**

Starting with **1b** (132 mg, 0.70 mmol), Me<sub>3</sub>SiOTf (47 mg, 0.21 mmol) and 1,3-bis-silyl enol ether **2c** (250 mg, 0.91 mmol), **3n** was isolated as a colourless solid (120 mg, 57%), m.p. = 93 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.42 (t,  $J$  = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.55 (s, 3 H, CH<sub>3</sub>), 4.45 (q,  $J$  = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.99 (d,  $J$  = 8.7 Hz, 1 H, Ar), 7.10 (d,  $J$  = 8.7 Hz, 1 H, Ar), 7.34 (m, 2 H, Ar), 7.83 (dd,  $J$  = 8.7 Hz,  $J$  = 2.2 Hz, 1 H, Ar), 8.30 (d,  $J$  = 2.2 Hz, 1 H, Ar), 11.31 (s, 1 H, OH), 11.66 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.2 (OCH<sub>2</sub>CH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 62.0 (OCH<sub>2</sub>CH<sub>3</sub>), 112.5 (C), 117.7, 118.3 (CH), 118.7, 127.9, 129.2 (C), 132.4, 132.7, 136.6, 137.2 (CH), 160.9, 164.6 (C-OH), 169.7, 199.1 (C=O). IR (KBr):  $\tilde{\nu}$  = 3120 (m), 3071 (m), 2980 (s), 2972 (s), 2930 (m), 1672 (s), 1632 (s), 1611 (s), 1583 (s), 1482 (s), 1395 (m), 1376 (s), 1342 (s), 1290 (s), 1257 (s), 1209 (s), 1188 (s), 1148 (m), 1088 (m), 973 (w), 852 (w), 835 (m), 793 (m), 722 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\max}$  (lg  $\epsilon$ ): 348 (4.28), 283 (4.04), 266 (4.07), 236 (3.73) nm. MS (EI, 70 eV):  $m/z$  (%) = 300 (M<sup>+</sup>, 19), 289 (13), 260 (5), 223 (10), 191 (4), 178 (16), 135 (30), 113 (100), 103 (3), 77 (7). The

exact molecular mass for  $C_{17}H_{16}O_5$   $m/z = 300.0998 \pm 2$  ppm ( $M^+$ ) was confirmed by HRMS (EI, 70 eV).

**(3-Benzoyl-4-hydroxyphenyl)-(2-hydroxy-5-isopropylphenyl)methanone (3o).**

Starting with **1c** (250 mg, 1.16 mmol),  $Me_3SiOTf$  (77 mg, 0.34 mmol) and 1,3-bis-silyl enol ether **2b** (467 mg, 1.5 mmol), **3o** was isolated as a yellow solid (242 mg, 58%), m.p. = 128 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 1.13$  (d,  $J = 8.4$  Hz, 6 H,  $CH(CH_3)_2$ ), 2.13 (quint,  $J = 8.4$  Hz, 1 H,  $CH(CH_3)_2$ ), 6.98 (d,  $J = 8.5$  Hz, 1 H, Ar), 7.20 (d,  $J = 8.5$  Hz, 1 H, Ar), 7.37 (m, 1 H, Ar), 7.70 (m, 1 H, Ar), 7.92 (dd,  $J = 8.5$  Hz,  $J = 2.2$  Hz, 1 H, Ar), 8.08 (d,  $J = 2.2$  Hz, 1 H, Ar), 11.63 (s, 1 H, OH), 12.52 (s, 1 H, OH).  $^{13}C$  NMR (DEPT, 75.5 MHz,  $CDCl_3$ ):  $\delta = 23.9$  ( $CH(CH_3)_2$ ), 33.2 ( $CH(CH_3)_2$ ), 118.4 (CH), 118.5 (C), 118.7 (CH), 128.6 (C), 128.6 (CH), 128.7 (C), 128.9, 129.9, 132.5, 134.7, 135.8 (CH), 137.1 (C), 137.2 (CH), 139.0 (C), 161.1, 166.4 (C-OH), 198.7, 201.4 (C=O). IR (KBr):  $\tilde{\nu} = 3432$  (m), 2956 (s), 2929 (m), 1628 (s), 1598 (m), 158 (m), 1430 (s), 1349 (m), 1322 (m), 1294 (w), 1256 (s), 1225 (s), 1183 (w), 1041 (m), 1009 (m), 845 (s), 799 (m), 752 (w)  $cm^{-1}$ . UV-VIS ( $CH_3CN$ ):  $\lambda_{max}$  (lg  $\epsilon$ ): 338 (3.53), 263 (3.95), 226 (4.11) nm. MS (EI, 70 eV):  $m/z$  (%) = 360 ( $M^+$ , 100), 291 (45), 275 (18), 217 (49), 203 (15), 145 (31), 129 (31), 74 (93), 32 (15).

**Ethyl 5-(5-chloro-2-hydroxybenzoyl)salicylate (3p).**

Starting with **1d** (250 mg, 1.20 mmol),  $Me_3SiOTf$  (80 mg, 0.36 mmol) and 1,3-bis-silyl enol ether **2c** (428 mg, 1.56 mmol), **3p** was isolated as a yellow solid (169 mg, 46%), m.p. = 98.4 °C.  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta = 1.43$  (t,  $J = 7.5$  Hz, 3 H,  $OCH_2CH_3$ ), 4.46 (q,  $J = 7.5$  Hz, 2 H,  $OCH_2CH_3$ ), 7.05 (d,  $J = 8.7$  Hz, 1 H, Ar), 7.12 (d,  $J = 8.7$  Hz, 1 H, Ar), 7.46 (d,  $J = 8.7$  Hz,  $J = 2.6$  Hz, 1 H, Ar), 7.55 (d,  $J = 2.6$  Hz, 1 H, Ar), 7.84 (d,  $J = 8.7$  Hz,  $J = 2.6$  Hz, 1 H, Ar), 8.29 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.37 (s, 1 H, OH), 11.72 (s, 1 H, OH).  $^{13}C$  NMR (DEPT, 75.5 MHz,  $CDCl_3$ ):  $\delta = 14.2$  ( $CH_3$ ), 62.2 ( $CH_2$ ), 112.7 (C), 118.1 (CH), 119.7 (C),

120.2 (CH), 123.5, 128.3 (C), 131.8, 132.5, 136.0, 136.5 (CH), 161.5, 165.1, 169.5, 197.9 (C). IR (KBr):  $\tilde{\nu}$  = 3146 (m), 3092 (m), 2996 (m), 2943 (m), 2922 (s), 1684 (s), 1633 (s), 1606 (s), 1585 (s), 1472 (m), 1406 (m), 1378 (m), 1345(s), 1294 (m), 1267 (m), 1214 (m), 1116 (m), 1090 (m), 985 (m), 967 (m), 865 (m), 788 (m), 643 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 344 (3.73), 286 (3.97), 238 (4.20) nm. MS (EI, 70 eV):  $m/z$  (%) = 320 ( $\text{M}^+$ , 100), 274 (19), 253 (5), 237 (7), 209 (92), 166 (57), 154 (78), 120 (76), 91 (12), 70 (27), 43 (18). The exact molecular mass for  $\text{C}_{16}\text{H}_{13}\text{ClO}_5$   $m/z = 320.0452 \pm 2$  ppm ( $\text{M}^+$ ) was confirmed by HRMS (EI, 70 eV).

### **Ethyl 3-ethyl-5-(5-chloro-2-hydroxybenzoyl)salicylate (3q).**

Starting with **1d** (250 mg, 2.00 mmol),  $\text{Me}_3\text{SiOTf}$  (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2f** (786 mg, 2.60 mmol), **3q** was isolated as a yellow solid (383 mg, 55%), m.p. = 89 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.27 (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.42 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 2.76 (q,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 4.45 (q,  $J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 7.04 (d,  $J = 8.9$  Hz, 1 H, Ar), 7.46 (dd,  $J = 8.9$  Hz,  $J = 2.6$  Hz, 1 H, Ar), 7.58 (d,  $J = 2.6$  Hz, 1 H, Ar), 7.73 (d,  $J = 2.3$  Hz, 1 H, Ar), 8.14 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.60 (s, 1 H, OH), 11.76 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.5$ , 14.1 ( $\text{CH}_3$ ), 22.8 ( $\text{CH}_2\text{CH}_3$ ), 62.1 ( $\text{OCH}_2\text{CH}_3$ ), 111.7, 119.8 (C), 120.1 (CH), 123.4, 127.6 (C), 130.2, 132.0 (CH), 133.5 (C), 135.2, 135.8 (CH), 161.4, 163.4 (C-OH), 170.0, 198.4 (C=O). IR (KBr):  $\tilde{\nu}$  = 3099 (m), 3074 (m), 2988 (s), 2972 (s), 2938 (m), 2910 (m), 2875 (m), 1677 (s), 1628 (s), 1587 (s), 1465 (s), 1405 (s), 1377 (s), 1346 (s), 1323 (s), 1286 (s), 1265 (s), 1235 (s), 1187 (s), 1136 (m), 1115 (m), 1098 (m), 1025 (w), 927 (m), 826 (m), 801 (m), 759 (m), 711 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ): 343 (3.77), 297 (3.84), 219 (4.45) nm. MS (EI, 70 eV):  $m/z$  (%) = 348 ( $\text{M}^+$ , 50), 318 (7), 301 (23), 273 (32), 230 (4), 193 (100), 155 (42), 147 (75), 120 (32), 91 (19), 28 (41). The exact molecular mass for  $\text{C}_{18}\text{H}_{17}\text{ClO}_5$   $m/z = 348.0765 \pm 2$  ppm ( $\text{M}^+$ ) was confirmed by HRMS (EI, 70 eV).

**Ethyl 3-*n*-propyl-5-(5-chloro-2-hydroxybenzoyl)salicylate (3r).**

Starting with **1d** (417 mg, 2.0 mmol), Me<sub>3</sub>SiOTf (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2g** (819 mg, 2.6 mmol), **3r** was isolated as a colourless solid (334 mg, 46%), m.p. = 104 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.99 (t, *J* = 7.3 Hz, 3 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.42 (t, *J* = 7.2 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.67 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.71 (t, *J* = 7.3 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.45 (q, *J* = 7.2 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.04 (d, *J* = 8.9 Hz, 1 H, Ar), 7.46 (dd, *J* = 8.9 Hz, *J* = 2.6 Hz, 1 H, Ar), 7.58 (d, *J* = 2.3 Hz, 1 H, Ar), 7.70 (d, *J* = 2.6 Hz, 1 H, Ar), 8.15 (d, *J* = 2.3 Hz, 1 H, Ar), 11.66 (s, 1 H, OH), 11.76 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 13.9, 14.1 (CH<sub>3</sub>), 22.3, 31.6 (CH<sub>2</sub>), 62.1 (OCH<sub>2</sub>CH<sub>3</sub>), 111.9, 119.8 (C), 120.1 (CH), 123.4, 127.5 (C), 130.2 (CH), 131.9 (C), 132.0, 135.8, 136.1 (CH), 161.4, 163.5, (C-OH), 170.0, 198.4 (C=O). IR (KBr):  $\tilde{\nu}$  = 3082 (m), 2992 (m), 2960 (s), 2934 (m), 2875 (m), 1677 (s), 1635 (s), 1601 (s), 1574 (m), 1465 (s), 1405 (s), 1380 (s), 1350 (s), 1325 (s), 1286 (s), 1258 (s), 1228 (s), 1200 (s), 1179 (s), 1135 (m), 1121 (m), 1094 (m), 1023 (s), 891 (w), 868 (w), 823 (m), 798 (m), 777 (m), 759 (m), 715 (m), 688 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): 345 (3.78), 297 (3.86), 239 (4.25), 219 (4.48) nm. MS (EI, 70 eV): *m/z* (%) = 361 (M<sup>+</sup>, 53), 318 (11), 287 (46), 259 (6), 230 (3), 207 (100), 154 (42), 133 (29), 98 (8), 77 (9), 32 (9). The exact molecular mass for C<sub>19</sub>H<sub>19</sub>ClO<sub>5</sub> *m/z* = 362.0921±2 ppm (M<sup>+</sup>) was confirmed by HRMS (EI, 70 eV).

**Ethyl 2-ethyl-5-(5-nitro-2-hydroxybenzoyl)salicylate (3s).**

Starting with **1e** (250 mg, 1.14 mmol), Me<sub>3</sub>SiOTf (76 mg, 0.34 mmol) and 1,3-bis-silyl enol ether **2f** (448 mg, 1.48 mmol), **3s** was isolated as a yellow solid (246 mg, 63%), m.p. = 108 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.29 (t, *J* = 7.5 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.41 (t, *J* = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.78 (q, *J* = 7.5 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 4.45 (q, *J* = 7.5 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.19 (d, *J* = 9.2 Hz, 1 H, Ar), 7.78 (d, *J* = 2.3 Hz, 1 H, Ar), 8.19 (d, *J* = 2.3 Hz, 1 H, Ar), 8.39 (d, *J* = 9.2 Hz, *J* = 2.7 Hz, 1 H, Ar), 8.64 (d, *J* = 2.7 Hz, 1 H, Ar), 11.76 (s, 1 H, OH), 12.61 (s,

1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.5, 14.1$  ( $\text{CH}_3$ ), 22.7 ( $\text{CH}_2$ ), 62.2 ( $\text{OCH}_2$ ), 111.2, 117.9 (C), 119.5 (CH), 126.8 (C), 129.1, 130.5, 130.6 (CH), 134.0 (C), 135.2 (CH), 139.4, 164.1, 167.9, 169.9 (C), 198.1 (C=O). IR (KBr):  $\tilde{\nu} = 3007$  (w), 2976 (m), 2949 (m), 2924 (m), 2856 (m), 1674 (s), 1633 (s), 1614 (s), 1601 (s), 1582 (m), 1528 (m), 1477 (m), 1405 (m), 1379 (s), 1338 (s), 1317 (m), 1269 (s), 1240 (m), 1199 (s), 1179 (m), 1121 (w), 797 (m), 751 (w), 685 (w)  $\text{cm}^{-1}$ . GCMS:  $m/z$  (%) = 359 ( $\text{M}^+$ , 65), 313 (71), 285 (76), 253 (24), 207 (100), 166 (21), 135 (31), 73 (34). HRMS (FT-ICR): calcd. for  $\text{C}_{18}\text{H}_{18}\text{NO}_7$  ( $[\text{M}+1]^+$ ): 360.10832; found: 360.10778.

#### **Ethyl 5-(5-chloro-2-hydroxy-4-methylbenzoyl)salicylate (3t).**

Starting with **1f** (557 mg, 2.50 mmol),  $\text{Me}_3\text{SiOTf}$  (117 mg, 0.75 mmol) and 1,3-bis-silyl enol ether **2c** (892 mg, 3.25 mmol), **3t** was isolated as a yellow solid (469 mg, 56%), m.p. = 114 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.14$  (t,  $J = 6.9$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 2.40 (s, 3 H,  $\text{CH}_3$ ), 4.46 (q,  $J = 6.9$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 6.96 (s, 1 H, Ar), 7.10 (d,  $J = 8.7$  Hz, 1 H, Ar), 7.54 (s, 1 H, Ar), 7.82 (dd,  $J = 8.7$  Hz,  $J = 2.3$  Hz, 1 H, Ar), 8.28 (dd,  $J = 8.7$  Hz,  $J = 2.3$  Hz, 1 H, Ar), 11.33 (s, 1 H, OH), 11.75 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.2$  ( $\text{CH}_3$ ), 20.8 ( $\text{OCH}_2\text{CH}_3$ ), 62.1 ( $\text{OCH}_2\text{CH}_3$ ), 112.6 (C), 117.9, 120.6 (CH), 124.1, 128.5, 132.1 (C), 132.3, 132.4, 136.4 (CH), 145.4 (C), 161.4, 164.9 (C-OH), 169.5, 197.6 (C=O). IR (KBr):  $\tilde{\nu} = 3098$  (m), 2996 (m), 2964 (m), 1683 (s), 1635 (m), 1614 (s), 1586 (s), 1481 (s), 1451 (m), 1408 (m), 1374 (s), 1346 (s), 1299 (s), 1269 (s), 1232 (s), 1173 (m), 1133 (m), 1087 (m), 1019 (m), 876 (w), 789 (s), 760 (w), 731 (m), 679 (w), 644 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 344 (3.76), 285 (4.04), 269 (4.02), 223 (4.39), 207 (4.43) nm. MS (EI, 70 eV):  $m/z$  (%) = 335 ( $\text{M}^+$  [ $^{37}\text{Cl}$ ], 22), 333 ( $\text{M}^+$  [ $^{37}\text{Cl}$ ], 67), 288 (14), 168 (100), 120 (21), 77 (8), 32(9). Anal.: calcd. for  $\text{C}_{17}\text{H}_{14}\text{ClO}_5$  (333.75): C 60.95, H 4.22; found: C 61.36, 4.35.

#### **Ethyl 5-(5-chloro-2-hydroxy-4-methylbenzoyl)salicylate (3u).**

Starting with **1f** (250 mg, 1.12 mmol), Me<sub>3</sub>SiOTf (75 mg, 0.33 mmol) and 1,3-bis-silyl enol ether **2f** (441 mg, 1.45 mmol), **3u** was isolated as a yellow solid (185 mg, 51%), m.p. = 104 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.25 (t, *J* = 6.9 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.44 (t, *J* = 7.2 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.35 (s, 3 H, CH<sub>3</sub>), 2.74 (q, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 4.46 (q, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 6.97 (br s, 1 H, Ar), 7.57 (br s, 1 H, Ar), 7.71 (d, *J* = 2.1 Hz, 1 H, Ar), 8.13 (d, *J* = 2.2 Hz, 1 H, Ar), 11.63 (s, 1 H, OH), 11.80 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 13.5 (CH<sub>3</sub>), 14.2 (CH<sub>2</sub>CH<sub>3</sub>), 20.8 (OCH<sub>2</sub>CH<sub>3</sub>), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 62.0 (OCH<sub>2</sub>CH<sub>3</sub>), 111.7, 118.1 (C), 120.5 (CH), 124.0, 127.9 (C), 129.9, 132.4 (CH), 133.5 (C), 135.1 (CH), 145.3 (C), 161.4, 163.3 (C-OH), 170.1, 198.1 (C=O). IR (KBr):  $\tilde{\nu}$  = 3095 (m), 2993 (m), 2965 (s), 2926 (s), 2855 (m), 1680 (s), 1638 (m), 1589 (s), 1479 (m), 1457 (m), 1404 (m), 1381 (s), 1351 (s), 1320 (m), 1265 (s), 1236 (s), 1213 (m), 1181 (s), 1123 (m), 1041 (m), 1024 (m), 911 (w), 890 (w), 872 (w), 789 (s), 733(m), 747 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): λ<sub>max</sub> (lg ε): 284 (3.40), 247 (4.22) nm. GC-MS: *m/z* (%) = 362 (M<sup>+</sup>, 82), 316 (36), 288 (42), 253 (13), 194 (89), 169 (100), 147 (9), 120 (38), 77 (34). HRMS (FT-ICR): calcd. for C<sub>19</sub>H<sub>20</sub>ClO<sub>5</sub> ([M+1]<sup>+</sup>): 363.09938; found: 363.09939.

#### **Ethyl 3-ethyl-5-(2-hydroxy-3,5-dimethylbenzoyl)salicylate (3v).**

Starting with **1g** (344 mg, 1.70 mmol), Me<sub>3</sub>SiOTf (113 mg, 0.15 mmol) and 1,3-bis-silyl enol ether **2f** (668 mg, 2.21 mmol), **3v** was isolated as a colourless solid (267 mg, 46%), m.p. = 128 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.26 (t, *J* = 7.6 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.40 (t, *J* = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.24 (s, 3 H, CH<sub>3</sub>), 2.30 (s, 3 H, CH<sub>3</sub>), 2.75 (q, *J* = 7.5 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 4.43 (q, *J* = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.22 (m, 2 H, Ar), 7.72 (d, *J* = 2.2 Hz, 1H, Ar), 8.14 (d, *J* = 2.2 Hz, 1 H, Ar), 11.55 (s, 1 H, OH), 11.99 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 13.6, 14.18, 15.6, 20.5 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>), 61.9 (OCH<sub>2</sub>), 111.6, 118.2, 126.9, 127.1, 127.2, 128.8 (C), 130.0, 130.4 (CH), 135.4, 138.1 (CH), 159.3, 162.9 (C-OH), 170.2, 199.8 (C=O). IR (KBr):  $\tilde{\nu}$  = 2969 (m), 2936 (m), 2361 (w), 1720 (s), 1646 (s), 1618

(s), 1558 (w), 1456 (s), 1418 (s), 1377 (m), 1301 (m), 1242 (s), 1129 (m), 1096 (m), 1028 (m), 901 (w), 865 (w), 793 (w), 689 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 304 (3.70), 250 (4.09) nm. MS (EI, 70 eV):  $m/z$  (%) = 342 ( $\text{M}^+$ , 42), 295 (8), 267 (5), 175 (7), 148 (100), 120 (31), 91 (14), 65 (4). The exact molecular mass for  $\text{C}_{20}\text{H}_{22}\text{O}_5$   $m/z = 342.1467 \pm 2$  ppm ( $\text{M}^+$ ) was confirmed by HRMS (EI, 70 eV).

### **Ethyl 3-allyl-5-(2-hydroxy-3,5-dimethylbenzoyl)salicylate (3w).**

Starting with **1g** (404 mg, 2.0 mmol),  $\text{Me}_3\text{SiOTf}$  (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2h** (818 mg, 2.6 mmol), **3w** was isolated as a colourless solid (334 mg, 47%), m.p. = 84 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.41 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 2.23 (s, 3 H,  $\text{CH}_3$ ), 2.29 (s, 3 H,  $\text{CH}_3$ ), 3.47 (t,  $J = 6.6$  Hz, 2 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 4.43 (q,  $J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 5.08 - 5.16 (br m, 2 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.99 (m, 1 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 7.19 (d,  $J = 3.0$  Hz, 1 H, Ar), 7.21 (d,  $J = 3.0$  Hz, 1 H, Ar), 7.71 (d,  $J = 2.3$  Hz, 1 H, Ar), 8.17 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.61 (s, 1 H, OH), 11.99 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 ( $\text{OCH}_2\text{CH}_3$ ), 15.5, 20.4 (Ar $\text{CH}_3$ ), 33.5 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 61.9 ( $\text{OCH}_2\text{CH}_3$ ), 111.8, 116.6 (C), 118.1 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 126.9, 127.2, 128.79, 128.9 (C), 130.4, 130.4, 135.7, 136.4, 138.1 (CH), 159.3, 162.6 (C-OH), 170.1, 199.6 (C=O). IR (KBr):  $\tilde{\nu}$  = 3082 (m), 2987 (m), 2919 (m), 1675 (s), 1622 (s), 1585 (s), 1467 (m), 1430 (m), 1407 (s), 1381 (s), 1351 (s), 1332 (s), 1284 (s), 1262 (m), 1232 (s), 1196 (s), 1175 (m), 1058 (w), 1023 (m), 910 (w), 875 (w), 794 (m), 788 (m), 746 (w), 717 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 355 (3.70), 290 (3.98), 271 (3.98), 242 (4.19), 216 (4.38) nm. MS (EI, 70 eV):  $m/z$  (%) = 354 ( $\text{M}^+$  73), 309 (3), 307 (4), 280 (5), 206 (3), 187 (5), 160 (5), 148 (63), 147 (100) 120 (20), 77 (13), 32 (3), 29 (7). Anal.: calcd. for  $\text{C}_{21}\text{H}_{22}\text{O}_5$  (354.41): C 71.17, H 6.26; found: C 70.66, H 6.37.

### **1-(5-(3,5-Dichloro-2-hydroxybenzoyl)-2-hydroxyphenyl)ethan-1-one (3x).**

Starting with **1h** (250 mg, 1.01 mmol), Me<sub>3</sub>SiOTf (69 mg, 0.31 mmol) and 1,3-bis-silyl enol ether **2a** (326 mg, 1.34 mmol), **3x** was isolated as a yellow solid (134 mg, 52%), m.p. = 136 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 2.71 (s, 3 H, CH<sub>3</sub>), 7.13 (d, *J* = 8.7 Hz, 1 H, Ar), 7.50 (d, *J* = 2.5 Hz, 1 H, Ar), 7.62 (d, *J* = 2.5 Hz, 1 H, Ar), 7.85 (dd, *J* = 8.7 Hz, *J* = 2.2 Hz, 1 H, Ar), 8.21 (d, *J* = 2.2 Hz, 1 H, Ar), 12.09 (s, 1 H, OH), 12.75 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 26.8 (CH<sub>3</sub>), 118.9 (CH), 119.4, 120.3, 123.4, 124.4, 127.6 (C), 130.2, 133.5, 135.7, 137.2 (CH), 157.2, 166.2 (C-OH), 197.4, 204.3 (C=O). IR (KBr):  $\tilde{\nu}$  = 3425 (w), 3087 (m), 3067 (m), 3008 (w), 2926 (w), 2842 (w), 2789 (w), 1647 (s), 1618 (s), 1575 (s), 1486 (m), 1436 (s), 1369 (s), 1349 (s), 1324 (s), 1298 (s), 1260 (m), 1230 (s), 1189 (s), 1169 (s), 1140 (m), 993 (w), 851 (w), 822 (m), 792 (s), 793 (w), 756 (w), 739 (w), 633 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 289 (3.90), 248 (4.27), 230 (4.16) nm. MS (EI, 70 eV): *m/z* (%) = 324 (M<sup>+</sup> [<sup>35</sup>Cl, <sup>35</sup>Cl], 96), 309 (22), 246 (3), 189 (100), 163 (52), 136 (76), 121 (50), 106 (4), 92 (12), 77 (11), 64 (12), 43 (47), 39 (5). The exact molecular mass for C<sub>15</sub>H<sub>10</sub>Cl<sub>2</sub>O<sub>4</sub> *m/z* = 324.0452±2 ppm (M<sup>+</sup>) was confirmed by HRMS (EI, 70 eV).

#### **Ethyl 5-(3,5-dichloro-2-hydroxybenzoyl)salicylate (3y).**

Starting with **1h** (250 mg, 1.03 mmol), Me<sub>3</sub>SiOTf (67 mg, 0.31 mmol) and 1,3-bis-silyl enol ether **2c** (367 mg, 1.34 mmol), **3y** was isolated as a yellow solid (299 mg, 82%), m.p. = 125 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 1.43 (t, *J* = 7.8 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 4.47 (q, *J* = 7.8 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.13 (d, *J* = 8.7 Hz, 1 H, Ar), 7.50 (d, *J* = 2.4 Hz, 1 H, Ar), 7.61 (d, *J* = 2.4 Hz, 1 H, Ar), 7.84 (dd, *J* = 8.7 Hz, *J* = 2.3 Hz, 1 H, Ar), 8.29 (d, *J* = 2.3 Hz, 1 H, Ar), 11.41 (s, 1 H, OH), 12.19 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 14.2 (CH<sub>3</sub>), 62.3 (CH<sub>2</sub>), 112.7 (C), 118.2 (CH), 120.3, 123.3, 124.1, 127.8 (C), 130.4, 132.8, 135.5, 136.5 (CH), 157.2, 165.4, 169.4, 197.6 (C). IR (KBr):  $\tilde{\nu}$  = 3073 (m), 3008 (m), 2992 (m), 2949 (w), 2360 (w), 2340 (w), 1692 (s), 1625 (s), 1580 (s), 1486 (m), 1433(s), 1403 (s), 1374 (s), 1345 (s), 1324 (s), 1299 (s), 1267 (m), 1219 (s), 1186 (s), 1085 (m), 1013 (m), 995 (w), 880 (w),

839 (w), 792 (s), 754 (m), 720 (w), 641 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 347 (3.69), 291 (4.01), 232 (4.27) nm. MS (EI, 70 eV):  $m/z$  (%) = 354 ( $\text{M}^+$  [ $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ], 81), 308 (27), 188 (64), 166 (98), 147 (53), 120 (100), 92 (22), 53 (7). Anal.: calcd. for  $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{O}_5$  (355.17), C 54.10, H 3.40; found: C 54.40, H 3.89.

### **Ethyl 3-ethyl-5-(3,5-dichloro-2-hydroxybenzoyl)salicylate (3z).**

Starting with **1h** (376 mg, 1.55 mmol),  $\text{Me}_3\text{SiOTf}$  (103 mg, 0.46 mmol) and 1,3-bis-silyl enol ether **2f** (609 mg, 2.02 mmol), **3z** was isolated as a colourless solid (251 mg, 42%), m.p. = 130 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.27 (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.42 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 2.76 (q,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 4.45 (q,  $J = 7.5$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 7.52 (d,  $J = 2.4$  Hz, 1 H, Ar), 7.08 (d,  $J = 2.4$  Hz, 1 H, Ar), 7.73 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.13 (d,  $J = 2.2$  Hz, 1 H, Ar), 11.71 (s, 1 H, OH), 12.24 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.5, 14.2$  ( $\text{CH}_3$ ), 22.8 ( $\text{CH}_2\text{CH}_3$ ), 62.2 ( $\text{OCH}_2\text{CH}_3$ ), 111.8, 120.4, 123.2, 124.0, 127.2 (C), 130.4, 130.6 (CH), 133.7 (C), 135.2, 135.4 (CH), 157.2, 163.8 (C-OH), 169.9, 197.9 (C=O). IR (KBr):  $\tilde{\nu} = 3070$  (m), 2981 (m), 2939 (m), 1678 (s), 1623 (s), 1597 (s), 1460 (s), 1432 (s), 1403 (m), 1377 (s), 1346 (s), 1317 (s), 1292 (s), 1265 (s), 1237 (s), 1189 (s), 1175 (s), 1139 (m), 805 (w), 790 (m), 764 (w), 751 (m), 735 (w), 696 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 307 (3.90), 245 (4.24) nm. MS (EI, 70 eV):  $m/z$  (%) = 382 ( $\text{M}^+$  [ $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ], 30), 336 (23), 310 (23), 225 (17), 194 (100), 175 (15), 147 (59), 120 (20), 91 (13). Anal.: calcd. for  $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{O}_5$  (383.23): C 56.41, H 4.21; found: C 56.77, H 4.45.

### **Ethyl 3-ethyl-5-(3,5-dichloro-2-hydroxybenzoyl)salicylate (3aa).**

Starting with **1h** (300 mg, 1.23 mmol),  $\text{Me}_3\text{SiOTf}$  (83 mg, 0.37 mmol) and 1,3-bis-silyl enol ether **2g** (504 mg, 1.50 mmol), **3aa** was isolated as a colourless solid (253 mg, 52%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.99 (t,  $J = 7.3$  Hz, 3 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.42 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 1.63 - 1.75 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.71 (t,  $J = 7.3$  Hz, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.45

(q,  $J = 7.2$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 7.53 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.61 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.70 (d,  $J = 2.3$  Hz, 1 H, Ar), 8.15 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.69 (s, 1 H, OH), 12.23 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.9, 14.1$  ( $\text{CH}_3$ ), 22.3 ( $\text{CH}_2$ ), 31.6 (Ar- $\text{CH}_2$ ), 62.1 ( $\text{OCH}_2\text{CH}_3$ ), 111.9, 120.4, 123.2, 124.0, 127.0 (C), 130.5, 130.6 (CH), 132.1 (C), 135.4, 136.1 (CH), 157.2, 163.9 (C-OH), 169.9, 197.9 (C=O). IR (KBr):  $\tilde{\nu} = 3419$  (w), 3121 (m), 3077 (m), 2983 (m), 2964 (m), 2930 (m), 2871 (w), 1676 (s), 1622 (s), 1595 (s), 1578 (s), 1454 (m), 1428 (s), 1405 (s), 1380 (s), 1343 (s), 1319 (s), 1303 (s), 1284 (s), 1265 (s), 1231 (s), 1184 (s), 1141 (m), 1111 (m), 1020 (m), 883 (w), 790 (m), 771 (m), 749 (s), 715 (s), 699 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ): 346 (3.78), 307 (3.96), 219 (4.51) nm. MS (EI, 70 eV):  $m/z$  (%) = 396 ( $\text{M}^+$  [ $^{35}\text{Cl}, ^{35}\text{Cl}$ ], 10), 324 (4), 322 (7), 208 (17), 189 (6), 162 (4), 134 (4), 45 (11). Anal.: calcd. for  $\text{C}_{19}\text{H}_{18}\text{Cl}_2\text{O}_5$  (397.25) C 57.45, H 4.57; found: C 57.54, H 4.64.

### **Ethyl 3-allyl-5-(3,5-dichloro-2-hydroxybenzoyl)salicylate (3ab).**

Starting with **1h** (486 mg, 2.0 mmol),  $\text{Me}_3\text{SiOTf}$  (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2h** (818 mg, 2.6 mmol), **3ab** was isolated as a colourless solid (448 mg, 57%), m.p. = 94 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.43 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 3.49 (d,  $J = 6.7$  Hz, 2 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 4.46 (q,  $J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_2$ ), 5.15 (m, 2 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.98 (m, 1 H,  $\text{CH}_2-\text{CH}=\text{CH}_2$ ), 7.50 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.59 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.73 (d,  $J = 2.3$  Hz, 1 H, Ar), 8.16 (d,  $J = 2.3$  Hz, 1H, Ar), 11.73 (s, 1 H, OH), 12.22 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{OCH}_2\text{CH}_3$ ), 33.4 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 62.2 ( $\text{OCH}_2\text{CH}_3$ ), 112.0 (C), 117.0 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 120.3, 123.2, 124.0, 127.2, 129.8 (C), 130.5, 130.8 (CH, Ar), 134.9 ( $\text{CH}_2\text{CH}=\text{CH}_2$ ), 135.4, 136.1 (CH, Ar), 157.1, 163.5 (C-OH), 169.8, 197.7 (C=O). IR (KBr):  $\tilde{\nu} = 3080$  (m), 2987 (m), 2908 (w), 2880 (w), 1676 (s), 1624 (s), 1581 (s), 1456 (m), 1428 (s), 1405 (s), 1380 (s), 1344 (s), 1345 (s), 1301 (s), 1263 (s), 1232 (s), 1185 (s), 1174 (s), 1138 (m), 1022 (m), 915 (w), 804 (w), 789 (m), 772 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 348 (3.75), 304 (3.85), 219 (4.46) nm. MS (EI, 70 eV):  $m/z$  (%) = 394

( $M^+$  [ $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ], 4), 354 (1), 206 (4), 189 (3), 147 (3), 44 (8), 32 (25). Anal.: calcd. for  $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{O}_5$  (395.24): C 57.74, H 4.08; found: C 57.87, H 4.06.

**Ethyl 3-*n*-butyl-5-(3,5-dichloro-2-hydroxybenzoyl)salicylate (3ac).**

Starting with **1h** (486 mg, 2.0 mmol),  $\text{Me}_3\text{SiOTf}$  (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2i** (860 mg, 2.6 mmol), **3ac** was isolated as a colourless solid (435 mg, 53%), m.p. = 111 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.96 (t,  $J = 7.3$  Hz, 3 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.24 (m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.43 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 1.59 - 1.69 (br m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.73 (t,  $J = 7.5$  Hz, 2 H, Ar $\text{CH}_2$ ), 4.45 (q,  $J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 7.52 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.61 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.70 (d,  $J = 2.3$  Hz, 1 H, Ar), 8.14 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.69 (s, 1 H, OH), 12.23 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.9, 14.1$  ( $\text{CH}_3$ ), 22.5, 29.3, 31.3 ( $\text{CH}_2$ ), 62.1 ( $\text{OCH}_2\text{CH}_3$ ), 111.9, 120.4, 123.2, 124.0, 127.1 (C), 130.4, 130.6 (CH), 132.3 (C), 135.4, 136.1 (CH), 157.2, 163.9 (C-OH), 169.9, 197.9 (C=O). IR (KBr):  $\tilde{\nu} = 3122$  (m), 3080 (m), 2962 (m), 2930 (m), 2860 (w), 1675 (s), 1621 (s), 1595 (s), 1579 (s), 1460 (m), 1429 (s), 1406 (s), 1382 (s), 1344 (s), 1323 (s), 1297 (s), 1264 (s), 1234 (s), 1183 (s), 1142 (m), 1025 (m), 888 (w), 806 (w), 772 (w), 789 (m), 769 (w), 749 (m), 717 (m), 698 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ): 346 (3.76), 308 (3.86), 220 (4.44) nm. MS (EI, 70 eV):  $m/z$  (%) = 410 ( $M^+$  [ $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ], 14), 338 (5), 336 (7), 222 (25), 189 (5), 147 (2), 134(7), 32 (26). HRMS (FT-ICR): calcd. for  $\text{C}_{20}\text{H}_{21}\text{Cl}_2\text{O}_5$  ( $[M+1]^+$  [ $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ]): 411.07660; found: 411.07705.

**Ethyl 3-*n*-octyl-5-(3,5-dichloro-2-hydroxybenzoyl)salicylate (3ad).**

Starting with **1h** (486 mg, 2.0 mmol),  $\text{Me}_3\text{SiOTf}$  (133 mg, 0.6 mmol) and 1,3-bis-silyl enol ether **2j** (1.00 g, 2.6 mmol), **3ad** was isolated as a colourless solid (522 mg, 56%), m.p. = 80 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 0.89 (m, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.27 - 1.42 (br m, 10 H,  $\text{CH}_2$ ), 1.42 (t,  $J = 7.3$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 1.58 - 1.72 (br m, 2 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.72 (t,  $J = 7.1$  Hz,

2 H, ArCH<sub>2</sub>), 4.47 (q,  $J = 7.3$  Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.52 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.61 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.69 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.14 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.69 (s, 1 H, OH), 12.24 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta = 14.1, 14.2$  (CH<sub>3</sub>), 22.7, 29.2, 29.2, 29.4, 29.6, 29.8, 31.9 (CH<sub>2</sub>), 62.2 (OCH<sub>2</sub>CH<sub>3</sub>), 111.9, 120.5, 123.2, 124.1, 127.1 (C), 130.5, 130.6 (CH), 132.4 (C), 135.4, 136.0 (CH), 157.2, 163.9 (C-OH), 169.9, 197.9 (C=O). IR (KBr):  $\tilde{\nu} = 3119$  (w), 3077 (w), 2955 (m), 2926 (s), 2855 (m), 1678 (s), 1623 (m), 1582 (m), 1458 (m), 1424 (s), 1406 (m), 1381 (m), 1340 (m), 1324 (m), 1297 (m), 1263 (m), 1234 (s), 1187 (m), 1174 (m), 1174 (m), 1145 (m), 1019 (m), 884 (w), 850 (w), 843 (w), 806 (w), 789 (w), 769 (w), 751 (w), 732 (w), 713 (w), 701 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 306 (3.87), 243 (4.22) nm. MS (EI, 70 eV):  $m/z$  (%) = 466 (M<sup>+</sup> [<sup>35</sup>Cl, <sup>35</sup>Cl], 100), 423 (3), 394 (13), 392 (23), 323 (22), 322 (16), 321 (30), 279 (12), 278 (90), 232 (7), 188 (37), 147 (5), 134 (29), 74 (25), 29 (47). Anal.: calcd. for C<sub>24</sub>H<sub>28</sub>Cl<sub>2</sub>O<sub>5</sub> (467.39): C 61.67, H 6.04; found: C 61.97, H 6.04.

### **Ethyl 3-ethyl-5-(3,5-dibromo-2-hydroxybenzoyl)salicylate (3ae).**

Starting with **1i** (320 mg, 0.96 mmol), Me<sub>3</sub>SiOTf (64 mg, 0.29 mmol) and 1,3-bis-silyl enol ether **2f** (377 mg, 1.25 mmol), **3ae** was isolated as a yellow solid (512 mg, 54%), m.p. = 133 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 1.27$  (t,  $J = 7.5$  Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.43 (t,  $J = 7.2$  Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.76 (q,  $J = 7.5$  Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 4.47 (q,  $J = 7.2$  Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.70 (d,  $J = 2.3$  Hz, 1 H, Ar), 7.73 (d,  $J = 2.2$  Hz, 1 H, Ar), 7.89 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.13 (d,  $J = 2.3$  Hz, 1 H, Ar), 11.70 (s, 1 H, OH), 12.38 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta = 13.5, 14.2$  (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 62.1 (OCH<sub>2</sub>CH<sub>3</sub>), 110.2, 111.8, 113.2, 120.9, 127.1 (C), 130.5 (CH), 133.7 (C), 134.3, 135.2, 140.9 (CH), 158.5, 163.8 (C-OH), 169.9, 197.7 (C=O). IR (KBr):  $\tilde{\nu} = 3424$  (m), 3071 (m), 2971 (m), 2910 (w), 2876 (w), 1677 (s), 1624 (m), 1584 (m), 1424 (s), 1404 (m), 1377 (m), 1347 (s), 1316 (s), 1294 (s), 1262 (s), 1234 (s), 1189 (s), 1160 (s), 1128(w), 1026 (w), 789 (m), 703 (m) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):

$\lambda_{\max}$  (lg  $\epsilon$ ): 307 (3.89), 245 (4.26) nm. MS (EI, 70 eV):  $m/z$  (%) = 472 ( $M^+$  [ $^{81}\text{Br}$ ,  $^{79}\text{Br}$ ], 96), 428 (18), 398 (20), 279 (15), 194 (100), 175 (25), 147 (47), 84 (61), 43 (15). The exact molecular mass for  $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{O}_5$   $m/z = 469.9365 \pm 2$  ppm ( $M^+$  [ $^{79}\text{Br}$ ,  $^{79}\text{Br}$ ]) was confirmed by HRMS (EI, 70 eV).

### General procedure 2 (synthesis of benzophenones **3ah-aj**).

To 3-acetyl-4*H*-chromen-4-one **1j** (1.0 equiv.) was added  $\text{Me}_3\text{SiOTf}$  (0.3 equiv.) at 20 °C. After stirring for 10 min  $\text{CH}_2\text{Cl}_2$  (15 mL) was added, the solution cooled down to 0 °C and the 1,3-bis-silyl enol ether **2c,f,p** (1.3 equiv.) was added. The mixture was stirred for 12 h at 20 °C and was subsequently poured into an aqueous solution of hydrochloric acid (10%). The organic layer was separated and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 60 mL). The combined organic layers were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 20:1  $\rightarrow$  1:1) to give the methyl-substituted benzophenones **3ah-aj**.

### Ethyl 6-methyl-5-(2-hydroxybenzoyl)salicylate (**3ah**).

Starting with 3-acetyl-4*H*-chromen-4-one **1j** (178 mg, 0.95 mmol),  $\text{Me}_3\text{SiOTf}$  (63 mg, 0.29 mmol) and 1,3-bis-silyl enol ether **2c** (365 mg, 1.33 mmol), **3ah** was isolated as a colourless solid (120 mg, 42%), m.p. = 109 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.44 (t,  $J = 7.1$  Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 2.47 (s, 3 H,  $\text{CH}_3$ ), 4.47 (q,  $J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 6.8 (m, 1 H, Ar), 6.94 (d,  $J = 8.6$  Hz, 1 H, Ar), 7.05 (dd,  $J = 8.4$  Hz,  $J = 1.0$  Hz, 1 H, Ar), 7.26 (m, 2 H, Ar), 7.50 (m, 1 H, Ar), 11.44 (s, 1 H, OH), 12.20 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.1$  ( $\text{CH}_3$ ), 20.6 ( $\text{OCH}_2\text{CH}_3$ ), 62.2 ( $\text{OCH}_2\text{CH}_3$ ), 113.5 (C), 115.5, 118.3, 118.9 (CH), 120.9 (C), 131.4, 133.1, 133.5, 136.9 (CH), 139.1 (C), 163.2, 163.6 (C-OH), 171.3, 203.9 (C=O). IR (KBr):  $\tilde{\nu} = 3073$  (m), 3028 (m), 2987 (m), 2944 (m), 2913 (m), 1664 (s), 1628 (s), 1590 (s), 1476 (s), 1450 (m), 1399 (m), 1376 (s), 1335 (s), 1310 (s), 1289 (m), 1248

(s), 1205 (s), 1145 (m), 1114 (w), 1029 (w), 1000 (w), 936 (w), 842 (w), 807 (m), 765 (s), 645 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 325 (3.8), 254 (4.1), 213 (4.5) nm. MS (EI, 70 eV):  $m/z$  (%) = 300 ( $\text{M}^+$ , 100), 285 (38), 253 (81), 237 (36), 161 (26), 134 (52), 121 (73), 93 (20), 66 (24), 43 (16). Anal.: calcd. for  $\text{C}_{17}\text{H}_{16}\text{O}_5$  (300.32): C 67.99 H 5.37; found: C 67.85, H 5.35.

### **Ethyl 3-ethyl-6-methyl-5-(2-hydroxybenzoyl)salicylate (3ai).**

Starting with 3-acetyl-4*H*-chromen-4-one **1j** (473 mg, 2.5 mmol),  $\text{Me}_3\text{SiOTf}$  (167 mg, 0.75 mmol) and 1,3-bis-silyl enol ether **2f** (984 mg, 3.25 mmol), **3ai** was isolated as a yellow oil (394 mg, 48%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.11 (t,  $J = 7.6$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.33 (t,  $J = 7.1$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 2.33 (s, 3 H,  $\text{CH}_3$ ), 2.57 (q,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 4.37 (q,  $J = 7.1$  Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 6.72 (m, 2 H, Ar), 6.94 (dd,  $J = 8.4$  Hz,  $J = 0.9$  Hz, 1 H, Ar), 7.19 (dd,  $J = 8.0$  Hz,  $J = 1.7$  Hz, 1 H, Ar), 7.39 (m, 1 H, Ar), 11.65 (s, 1 H, OH), 12.16 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.36$  ( $\text{CH}_3$ ), 14.06 ( $\text{OCH}_2\text{CH}_3$ ), 20.48 ( $\text{CH}_2\text{CH}_3$ ), 22.75 ( $\text{CH}_2\text{CH}_3$ ), 62.00 ( $\text{OCH}_2\text{CH}_3$ ), 112.67 (C), 118.25, 118.88 (CH), 120.23, 130.15, 130.68 (C), 131.98, 133.49 (CH), 135.97 (C), 136.71 (CH), 161.73, 163.12 (C-OH), 171.73, 204.36 (C=O). IR (neat):  $\tilde{\nu} = 3042$  (m), 2971 (m), 2935 (m), 2876 (m), 1730 (m), 1658 (s), 1627 (s), 1610 (s), 1581 (s), 1481 (s), 1447(s), 1398 (s), 1374 (s), 1349 (s), 1284 (s), 1239 (s), 1203 (s), 1182 (s), 1154 (s), 1122 (m), 1078 (m), 1058 (m), 1022 (s), 943 (w), 908 (w), 867 (w), 813 (s), 759 (s), 711 (m), 681 (w), 629 (s)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 324 (3.85), 255 (4.21), 215 (4.48) nm. MS (EI, 70 eV):  $m/z$  (%) = 328 ( $\text{M}^+$ , 43), 313 (17), 281 (24), 267 (62), 238 (3), 162 (12), 121 (22), 84 (6), 58 (7). HRMS (FT-ICR): calcd. for  $\text{C}_{19}\text{H}_{21}\text{O}_5$  ( $[\text{M}+1]^+$ ): 329.13835; found: 329.13855.

### **Ethyl 3-(*n*-hexyl)-6-methyl-5-(2-hydroxybenzoyl)salicylate (3aj).**

Starting with 3-acetyl-4*H*-chromen-4-one **1j** (189 mg, 1.0 mmol),  $\text{Me}_3\text{SiOTf}$  (67 mg, 0.3 mmol) and 1,3-bis-silyl enol ether **2p** (466 mg, 1.3 mmol), **3aj** was isolated as a yellow oil

(138 mg, 36%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.87 (m, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.22 - 1.36 (m, 6 H,  $\text{CH}_2$ ), 1.40 (t,  $J$  = 7.2 Hz, 3 H,  $\text{OCH}_2\text{CH}_3$ ), 1.45 - 1.64 (m, 2 H,  $\text{CH}_2$ ), 2.42 (s, 3 H,  $\text{ArCH}_3$ ), 2.64 (t,  $J$  = 8.2 Hz, 2 H,  $\text{ArCH}_2$ ), 4.46 (q,  $J$  = 7.2 Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 6.81 (m, 1 H, Ar), 7.04 (dd,  $J$  = 8.4 Hz,  $J$  = 0.9 Hz, 1 H, Ar), 7.16 (s, 1 H, Ar), 7.83 (dd,  $J$  = 8.0 Hz,  $J$  = 1.7 Hz, 1 H, Ar), 7.46 - 7.52 (m, 1 H, Ar), 11.69 (s, 1 H, OH), 12.25 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.8, 8.9 ( $\text{CH}_3$ ), 15.2 ( $\text{OCH}_2\text{CH}_3$ ), 17.3, 23.8, 23.9, 24.4, 26.4 ( $\text{CH}_2$ ), 56.8 ( $\text{OCH}_2\text{CH}_3$ ), 107.6 (C), 113.06, 113.6 (CH), 115.1, 123.7, 125.3 (C), 127.6, 128.3 (CH), 130.8 (C), 131.5 (CH), 156.5, 157.9 (C-OH), 166.5, 199.1 (C=O). IR (KBr):  $\tilde{\nu}$  = 3039 (m), 2928 (s), 2859 (s), 1659 (s), 1625 (s), 1582 (s), 1478 (s), 1448 (m), 1397 (m), 1345 (s), 1286 (s), 1243 (s), 1183 (s), 1155 (s), 1121 (m), 1071 (w), 1022 (m), 943 (w), 812 (m), 759 (s), 718 (w), 629 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 324 (3.9), 255 (4.2), 213 (4.5) nm. MS (EI, 70 eV):  $m/z$  (%) = 384 ( $\text{M}^+$ , 100), 369 (54), 337 (31), 323 (40), 310 (48), 267 (34), 253 (15), 121 (32), 43 (11).

#### **5-(2-Hydroxybenzoyl)salicylic acid (4a).**

To an aqueous solution of KOH (381 mg in 190 mL water) was added salicylic acid **3c** (1.17 mmol, 336 mg). After stirring for 4 h at 80 °C the solution was poured on an aqueous solution of hydrochloric acid (1 M). The organic layer was separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (4 x 10 mL). The combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ), filtered and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-hexane/ $\text{EtOAc}$  = 3:1  $\rightarrow$  1:5) to give **4a** as a colourless solid (266 mg, 88%), m.p. = 171 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.12 (br s, 1 H, COOH), 6.94 (m, 2 H, Ar), 7.06 (d,  $J$  = 8.7 Hz, 1 H, Ar), 7.31 (dd,  $J$  = 7.6 Hz,  $J$  = 1.7 Hz, 1 H, Ar), 7.41 (m, 1 H, Ar), 7.89 (dd,  $J$  = 8.7 Hz,  $J$  = 2.3 Hz, 1 H, Ar), 8.15 (d,  $J$  = 2.3 Hz, 1 H, Ar), 10.18 (s, 1 H, Ar-OH), 12.60 (br s, 1 H, Ar-OH).  $^{13}\text{C}$  NMR (DEPT,  $[\text{D}_6]$ DMSO, 75.5 MHz):  $\delta$  = 113.2 (C), 116.5, 117.5, 119.1 (CH), 125.3, 128.6 (C), 129.8, 132.6, 133.0, 136.1 (CH),

156.0, 164.8 (C-OH), 171.2, 194.7 (C=O). IR (KBr):  $\tilde{\nu}$  = 3410 (m), 3113 (m), 3081 (m), 2930 (m), 2665 (m), 2605 (m), 1685 (s), 1628 (s), 1591 (s), 1487 (s), 1447 (s), 1341(s), 1305 (s), 1249 (s), 1231 (s), 1205 (s), 1161 (m), 1083(m), 979 (w), 847 (m), 796 (m), 758 (s), 695 (m), 667 (m), 631 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 283 (3.99), 263 (3.98), 233 (4.19), 212 (4.44) nm. MS (EI, 70 eV):  $m/z$  (%) = 258 ( $\text{M}^+$ , 3), 213 (2), 165 (2), 149 (2), 121 (6), 108 (17), 91 (4), 58 (4). HRMS (FT-ICR): calcd. for  $\text{C}_{14}\text{H}_{11}\text{O}_5$  ( $[\text{M}+1]^+$ ): 259.06010; found: 259.06005.

### **General procedure 3 (synthesis of salicylic acids 4b-e/g-j).**

The salicylic ester (45  $\mu\text{mol}$ ) was dissolved in DMSO (0.5 mL) and an aqueous solution of KOH (585  $\mu\text{mol}$ , 0.3 mL) was added at 20  $^\circ\text{C}$ . After stirring for 12 h an aqueous solution of hydrochloric acid (1 M, 600  $\mu\text{l}$ ) was added. The solvent was removed in vacuo to afford solid. The solid was suspended in water (2x) using an ultrasound bath to wash out KCl. The suspension was centrifuged and the aqueous layer was decanted and the remaining crude samples dried in speedvac vacuo to obtain the salicylic acid as a white solid in complete conversion. No further purification was necessary.

### **3-Methyl-5-(2-hydroxybenzoyl)salicylic acid (4b).**

Starting with **3e**, **4b** was isolated as a colourless solid.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ ): 2.20 (s, 3 H,  $\text{CH}_3$ ), 3.89 (br s, 1 H, COOH), 6.92 (t,  $J = 7.6$  Hz, 1 H, Ar), 6.98 (d,  $J = 8.0$  Hz, 1 H, Ar), 7.29 (dd,  $J = 7.6$  Hz,  $J = 1.5$  Hz, 1 H, Ar), 7.39 (td,  $J = 8.0$  Hz,  $J = 1.5$  Hz, 1 H, Ar), 7.81 (br s, 1 H, Ar), 7.99 (br s, 1 H, Ar), 10.21 (br s, 1 H, OH), 12.27 (br s, 1 H, OH). MS (ESI, negative mode): 271.2  $[\text{M}-\text{H}]$ .

### **3-Allyl-5-(2-hydroxybenzoyl)salicylic acid (4c).**

Starting with **3h**, **4c** was isolated as a colourless solid.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ ): 3.40 (d,  $J = 6.6$  Hz, 2 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.07 (dd,  $J = 9.8$  Hz,  $J = 1.5$  Hz, 1 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.96 (ddt,  $J = 16.9$  Hz,  $J = 9.8$  Hz,  $J = 6.6$  Hz, 1 H  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 5.09 (dd,  $J = 16.9$  Hz,  $J = 1.5$  Hz, 1 H,  $\text{CH}_2\text{CH}=\text{CH}_2$ ), 6.92 (t,  $J = 7.7$  Hz, 1 H, Ar), 6.98 (d,  $J = 8.2$  Hz, 1 H, Ar), 7.29 (dd,  $J = 7.7$  Hz,  $J = 1.5$  Hz, 1 H, Ar), 7.39 (td,  $J = 8.2$  Hz,  $J = 1.5$  Hz, 1 H, Ar), 7.82 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.01 (d,  $J = 2.2$  Hz, 1 H, Ar), 10.18 (s, 1 H, OH), 12.27 (br s, 1 H, OH). MS (ESI, negative mode): 297.3 [M-H].

### **3-Butyl-5-(2-hydroxybenzoyl)salicylic acid (4d).**

Starting with **3i**, **4d** was isolated as a colourless solid.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ ): 0.89 (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_3$ ), 1.31 (sext,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2$ ), 1.54 (quint,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2$ ), 2.63 (t,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2$ ), 3.83 (br s, 1 H, COOH), 6.92 (t,  $J = 7.6$  Hz, 1 H, Ar), 6.97 (d,  $J = 8.0$  Hz, 1 H, Ar), 7.29 (dd,  $J = 7.6$  Hz,  $J = 1.5$  Hz, 1 H, Ar), 7.39 (td,  $J = 8.0$  Hz,  $J = 1.5$  Hz, 1 H, Ar), 7.80 (d,  $J = 2.2$  Hz, 1 H, Ar), 7.99 (d,  $J = 2.2$  Hz, 1 H, Ar), 10.18 (s, 1 H, OH), 12.21 (br s, 1 H, OH). MS (ESI, negative mode): 313.3 [M-H].

### **3-Benzyl-5-(2-hydroxybenzoyl)salicylic acid (4e).**

Starting with **3m**, **4e** was isolated as a colourless solid.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ ): 3.72 (br s, 1 H, COOH), 3.99 (s, 2 H,  $\text{CH}_2$ ), 6.90 (t,  $J = 7.5$  Hz, 1 H, Ar), 6.95 (d,  $J = 8.0$  Hz, 1 H, Ar), 7.15-7.21 (m, 1 H, Ar), 7.38 (td,  $J = 8.0$  Hz,  $J = 1.3$  Hz, 1 H, Ar), 7.21-7.32 (m, 5 H, Ar), 7.81 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.00 (d,  $J = 2.2$  Hz, 1 H, Ar), 10.15 (s, 1 H, OH), 12.39 (br s, 1 H, OH). MS (ESI, negative mode): 347.3 [M-H].

### **5-(5-Chloro-4-methyl-2-hydroxybenzoyl)salicylic acid (4f).**

To a  $\text{CH}_2\text{Cl}_2$  solution (5 mL) of **3t** (0.26 mmol, 86 mg) was added  $\text{BBr}_3$  (1.20 mmol, 301 mg, 0.11 mL) at  $0^\circ\text{C}$ . The mixture was stirred for 12 h at  $20^\circ\text{C}$  and was subsequently poured into

an aqueous solution of hydrochloric acid (10%). The organic layer was separated and the aqueous layer was extracted with Et<sub>2</sub>O (4 x 10 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 3:1 → 1:5) to give **4f** as a colourless solid (65 mg, 82%), m.p. = 210 °C. <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO): δ = 2.32 (s, 3 H, CH<sub>3</sub>), 3.48 (br s, 2 H, Ar-OH, COOH), 6.93 (s, 1 H, Ar), 7.05 (d, *J* = 8.7 Hz, 1 H, Ar), 7.31 (s, 1 H, Ar), 7.88 (dd, *J* = 8.7 Hz, *J* = 2.3 Hz, 1 H, Ar), 8.13 (d, *J* = 2.3 Hz, 1 H, Ar), 10.27 (s, 1 H, Ar-OH). <sup>13</sup>C NMR (DEPT, 75.5MHz, [D<sub>6</sub>]DMSO): δ = 19.9 (CH<sub>3</sub>), 117.6 (CH), 118.9 (C), 118.9 (CH), 123.2, 125.0, 128.3 (C), 129.4, 133.1, 136.1 (CH), 139.9 (C), 154.5, 165.1 (C-OH), 171.1, 192.8 (C=O). IR (KBr):  $\tilde{\nu}$  = 3412 (m), 3070 (m), 2988 (m), 2929 (m), 1698 (s), 1931 (s), 1584 (s), 1479 (m), 1424 (m), 1354 (s), 1339 (s), 1304 (m), 1258 (s), 1215 (s), 1176 (s), 1082 (w), 843 (w), 793 (m), 752 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\max}$  (lg  $\epsilon$ ): 343 (3.81), 286 (4.02), 269 (4.01), 222 (4.39), 207 (4.44) nm. MS (EI, 70 eV): *m/z* (%) = 306 (M<sup>+</sup>, 15), 288 (2), 168 (23), 147 (5), 121 (3), 77 (5), 45 (4). HRMS (FT-ICR): calcd. for C<sub>15</sub>H<sub>12</sub>ClO<sub>5</sub> ([M+1]<sup>+</sup>): 307.03678; found: 307.03726.

### **3-Ethyl-5-(5-chloro-2-hydroxy-4-methylbenzoyl)salicylic acid (4g).**

Starting with **3u**, **4g** was isolated as a colourless solid. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): 1.16 (t, *J* = 7.6 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.31 (s, 3 H, CH<sub>3</sub>), 2.64 (q, *J* = 7.6 Hz, 2 H, CH<sub>2</sub>), 3.75 (br s, 1 H, COOH), 7.29 (s, 1 H, Ar), 6.92 (s, 1 H, Ar), 7.82 (d, *J* = 2.0 Hz, 1 H, Ar), 7.98 (d, *J* = 2.0 Hz, 1 H, Ar), 10.24 (s, 1 H, OH), 12.32 (br s, 1 H, OH). MS (ESI, negative mode): 333.3/335.2 [M-H]<sup>35Cl</sup>/[M-H]<sup>37Cl</sup>.

### **3-Ethyl-5-(2-hydroxy-3,4-dimethylbenzoyl)salicylic acid (4h).**

Starting with **3v**, **4h** was isolated as a colourless solid. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): 1.17 (t, *J* = 7.6 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.18 (s, 3 H, CH<sub>3</sub>), 2.19 (s, 3 H, CH<sub>3</sub>), 2.66 (q, *J* = 7.6 Hz, 2 H,

CH<sub>2</sub>), 3.69 (br s, 1 H, COOH), 7.09 (br s, 1 H, Ar), 7.23 (br s, 1 H, Ar), 7.77 (d,  $J = 2.2$  Hz, 1 H, Ar), 7.98 (d,  $J = 2.2$  Hz, 1 H, Ar), 10.77 (s, 1 H, OH), 12.26 (br s, 1 H, OH). MS (ESI, negative mode): 313.3 [M-H].

**3-Allyl-5-(2-hydroxy-3,4-dimethylbenzoyl)salicylic acid (4i).**

Starting with **3w**, **4i** was isolated as a colourless solid. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): 2.18 (s, 6 H, CH<sub>3</sub>), 3.41 (d,  $J = 6.3$  Hz, 2 H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.07 (dd,  $J = 10.3$  Hz,  $J = 1.7$  Hz, 1 H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.10 (dd,  $J = 16.9$  Hz,  $J = 1.7$  Hz, 1 H, CH<sub>2</sub>CH=CH<sub>2</sub>), 5.98 (ddt,  $J = 16.9$  Hz,  $J = 10.3$  Hz,  $J = 6.3$  Hz, 1 H, CH<sub>2</sub>CH=CH<sub>2</sub>), 7.23 (s, 1 H, Ar), 7.07 (s, 1 H, Ar), 7.75 (d,  $J = 2.2$  Hz, 1 H, Ar), 8.00 (d,  $J = 2.2$  Hz, 1 H, Ar), 10.74 (s, 1 H, OH), 12.27 (br s, 1 H, OH). MS (ESI, negative mode): 325.3 [M-H].

**3-Butyl-5-(3,5-dichloro-2-hydroxybenzoyl)salicylic acid (4j).**

Starting with **3ac**, **4j** was isolated as a colourless solid. <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): 0.88 (t,  $J = 7.3$  Hz, 3 H, CH<sub>3</sub>), 1.31 (sext,  $J = 7.3$  Hz, 2 H, CH<sub>2</sub>), 2.63 (t,  $J = 7.6$  Hz, 2 H, CH<sub>2</sub>), 1.53 (tt,  $J = 7.6$  Hz,  $J = 7.3$  Hz, 2 H, CH<sub>2</sub>), 3.99 (br s, 1 H, COOH), 7.33 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.72 (d,  $J = 2.5$  Hz, 1 H, Ar), 7.80 (d,  $J = 2.2$  Hz, 1 H, Ar), 7.96 (d,  $J = 2.2$  Hz, 1 H, Ar), 10.37 (s, 1 H, OH), 12.36 (br s, 1 H, OH). MS (ESI, negative mode): 381.3/383.2/385.2 [M-H]<sup>35/35Cl</sup>/[M-H]<sup>35/37Cl</sup>/[M-H]<sup>37/37Cl</sup>.

**3-Dimethylamino-1-(1-hydroxynaphthalen-2-yl)prop-2-en-1-one (6).**

To a THF solution (8 mL) of 1-(1'-hydroxynaphthalen-2'-yl)ethanone **5** (6.48 g, 35 mmol) was added diethoxy-*N,N*-dimethylmethanamine (5.15 g, 35 mmol) and the mixture was stirred for 12 h at 20 °C which resulted in formation of a solid. The solid was filtered off, washed with water and 3-dimethylamino-1-(1'-hydroxynaphthalen-2'-yl)-prop-2-en-1-one **6** was given as a yellow solid (7.51 g, 89%), m.p. = 172 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.99$  (s, 3 H,

NCH<sub>3</sub>), 3.19 (s, 3 H, NCH<sub>3</sub>), 5.83 (d,  $J = 12.2$  Hz, 1 H, C(O)CH=C), 7.20 (d,  $J = 8.8$  Hz, 1 H, Ar), 7.26 - 7.58 (br m, 2 H, Ar), 7.66 (d,  $J = 8.9$  Hz, 1 H, Ar), 7.72 (d,  $J = 7.6$  Hz, 1 H, Ar), 7.93 (d,  $J = 12.2$  Hz, 1 H, C=CHN(CH<sub>3</sub>)<sub>2</sub>), 8.44 (dd,  $J = 8.2$  Hz,  $J = 0.6$  Hz, 1 H, Ar), 15.85 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>):  $\delta = 41.2$  (N(CH<sub>3</sub>)<sub>2</sub>), 90.3 (CH), 113.2 (C), 117.1, 123.9, 124.1, 125.2 (CH), 125.9 (C), 127.2, 128.7 (CH), 136.5 (C), 154.5 (CH(N)), 162.6 (C-OH), 191.4 (C=O). IR (KBr):  $\tilde{\nu} = 3064$  (w), 2926 (w), 2880 (w), 2808 (w), 1914 (w), 1626 (s), 1555 (s), 1500 (s), 1465 (s), 1416 (s), 1388 (m), 1365 (s), 1333 (m), 1278 (s), 1245 (s), 1116 (m), 1199 (m), 1151 (m), 1110 (s), 1073 (m), 1020 (w), 981 (w), 939 (m), 863 (w), 794 (m), 772 (s), 603 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 385 (4.46), 373 (4.47), 350 (4.35), 276 (4.11), 266 (4.11), 241 (4.28), 218 (4.40) nm. MS (EI, 70 eV):  $m/z$  (%) = 241 (M<sup>+</sup>, 44), 223 (2), 197 (19), 170 (5), 141 (3), 127 (3), 114 (22), 72 (100), 56 (21), 42 (18). Anal.: calcd. for C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>: C 74.66 H 6.26 N 5.80; found: C 74.72, H 5.73 N 5.77.

### **3-Acetyl-4*H*-benzo[*h*]chromen-4-one (7).**

To an acetonitrile solution (300 mL) of 3-Dimethylamino-1-(1'-hydroxynaphthalen-2'-yl)-prop-2-en-1-one **6** (2.41 g, 10 mmol) were added pyridin (50 mL) and Acetanhydrid (4.08 g, 40 mmol) at 20 °C. After stirring for 6 h under reflux followed by strring for 12 h at 20 °C most of the solvent (250 mL) was removed in vacuo and an aqueous solution of hydrochloric acid (10%) was added. After adding CH<sub>2</sub>Cl<sub>2</sub> (40 mL) the layers were seperated and the aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (8 x 30 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, the filtrate was concentrated in vacuo and the residue was purified by column chromatography (silica gel, *n*-hexane/EtOAc = 5:1) to give 4*H*-benzo[*h*]chromen-4-one as a colourless solid (431 mg, 22%) and 3-acetyl-4*H*-benzo[*h*]chromen-4-one **7** as a yellow solid (1.13 g, 48%), m.p. = 175 °C. Analytical data for **7** are listed. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 2.80$  (s, 3 H, CH<sub>3</sub>), 7.68 - 7.78 (m, 2 H, Ar), 7.84 (d,  $J = 8.7$  Hz, 1 H, Ar), 7.96 (m, 1 H, Ar), 8.21 (d,  $J = 8.8$  Hz, 1 H, Ar), 8.49 (m, 1 H, Ar), 8.76 (s, 1 H, CH).

$^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 31.6 ( $\text{CH}_3$ ), 120.7 (C), 120.8 (CH), 121.9 (C), 122.2 (ArCH), 123.6, 123.9 (C), 126.4, 127.6, 128.2, 129.8 (ArCH), 136.1 (C), 160.5 (CH), 175.2, 196.8 (C=O). IR (KBr):  $\tilde{\nu}$  = 3110 (w), 3076 (m), 3012 (w), 2926 (w), 2362 (w), 1689 (s), 1643 (s), 1595 (m), 1552 (s), 1465 (m), 1443 (m), 1394 (s), 1362 (s), 1311 (s), 1264 (m), 1212 (m), 1154 (w), 1101 (s), 1024 (m), 972 (w), 889 (w), 795 (m), 769 (s), 648 (m)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (lg  $\epsilon$ ): 339 (3.69), 325 (3.69), 301 (3.81), 246 (4.55), 239 (4.52), 222 (4.42), 212 (4.38) nm. MS (EI, 70 eV):  $m/z$  (%) = 238 ( $\text{M}^+$ , 95), 223 (100), 196 (44), 171 (74), 139 (40), 126 (40), 113 (55), 88 (9), 64 (11), 53 (21), 43 (23). Anal.: calcd. for  $\text{C}_{15}\text{H}_{10}\text{O}_3$ : C 75.62 H 4.23; found: C 75.13, H 4.15.

#### General procedure 4 (synthesis of naphthophenones 8a-c).

To 3-acetyl-4*H*-benzo[*h*]chromen-4-one **7** (1.0 equiv.) was added  $\text{Me}_3\text{SiOTf}$  (0.3 equiv.) at 20 °C. Following general procedure **2** for the synthesis of methyl-substituted benzophenones the residue was purified by column chromatography (silica gel, n-hexane/EtOAc = 20:1  $\rightarrow$  5:1) to give the methyl-substituted benzophenones **8a-c**.

#### Methyl 3-(1-hydroxynaphthalen-2-carbonyl)-2-methylsalicylate (8a).

Starting with 3-Acetyl-4*H*-benzo[*h*]chromen-4-one **7** (238 mg, 1 mmol),  $\text{Me}_3\text{SiOTf}$  (67 mg, 1.3 mmol) and 1,3-bis-silyl enol ether **2q** (338 mg, 1.3 mmol), naphthophenone **8a** was given as a yellow solid (131 mg, 40%), m.p. = 135 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.47 (s, 3 H,  $\text{CH}_3$ ), 3.99 (s, 3 H,  $\text{OCH}_3$ ), 6.97 (d,  $J$  = 8.8 Hz, 1 H, Ar), 7.15 - 7.19 (m, 2 H, Ar), 7.35 (d,  $J$  = 8.6 Hz, 1 H, Ar), 7.56 (m, 1 H, Ar), 7.66 (m, 1 H, Ar), 7.74 (dd,  $J$  = 8.2 Hz,  $J$  = 0.7 Hz, 1 H, Ar), 8.52 (d,  $J$  = 8.1 Hz, 1 H, Ar), 11.38 (s, 1 H, OH), 14.04 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 20.6 ( $\text{CH}_3$ ), 52.6 ( $\text{OCH}_3$ ), 113.3, 113.8 (C), 115.6, 118.4, 124.5 (CH), 125.2 (C), 126.1, 126.9, 127.5, 130.6 (CH), 131.7 (C), 133.3 (CH), 137.6, 138.9 (C), 163.6, 163.8 (C-OH), 171.8, 203.5 (C=O). IR (KBr):  $\tilde{\nu}$  = 3056 (m), 3046 (m), 2957 (m),

1656 (s), 1628 (s), 1601 (s), 1503 (m), 1459 (s), 1417 (m), 1385 (s), 1335 (s), 1275 (s), 1251 (s), 1209 (s), 1145 (m), 1032 (m), 983 (m), 809 (s), 766 (m), 669 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 378 (3.94), 308 (4.08), 298 (4.19), 287 (4.13), 259 (4.66), 217 (4.67) nm. MS (EI, 70 eV):  $m/z$  (%) = 336 ( $\text{M}^+$ , 14), 289 (7), 247 (2), 231 (1), 189 (2), 170 (100), 134 (11), 113 (17), 77 (54), 51 (2). Anal.: calcd. for  $\text{C}_{20}\text{H}_{16}\text{O}_5$ : C 71.42 H 4.79; found: C 70.96, H 4.44.

### **Ethyl 3-(1-hydroxynaphthalen-2-carbonyl)-2-methylsalicylate (8b).**

Starting with 3-Acetyl-4*H*-benzo[*h*]chromen-4-one **7** (226 mg, 0.95 mmol),  $\text{Me}_3\text{SiOTf}$  (63 mg, 0.29 mmol) and 1,3-bis-silyl enol ether **2c** (340 mg, 1.24 mmol), naphthophenone **8b** was given as a yellow solid (119 mg, 36%), m.p. = 96 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.43 (t,  $J$  = 7.1 Hz, 1 H,  $\text{OCH}_2\text{CH}_3$ ), 2.49 (s, 3 H,  $\text{CH}_3$ ), 4.47 (q,  $J$  = 7.1 Hz, 2 H,  $\text{OCH}_2\text{CH}_3$ ), 6.97 (d,  $J$  = 8.6 Hz, 1 H, Ar), 7.16 (m, 2 H, Ar), 7.34 (d,  $J$  = 8.6 Hz, 1 H, Ar), 7.56 (m, 1 H, Ar), 7.65 (m, 1 H, Ar), 7.74 (dd,  $J$  = 7.5 Hz,  $J$  = 0.6 Hz, 1 H, Ar), 8.52 (d,  $J$  = 8.0 Hz, 1 H, Ar), 11.46 (s, 1 H, OH), 14.05 (s, 1 H, OH).  $^{13}\text{C}$  NMR (DEPT, 75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 ( $\text{CH}_3$ ), 20.7 ( $\text{OCH}_2\text{CH}_3$ ), 62.2 ( $\text{OCH}_2\text{CH}_3$ ), 113.5, 113.7 (C), 115.6, 118.3, 124.5 (CH), 125.2 (C), 126.1, 126.9, 127.5, 130.5 (CH), 131.7 (C), 133.1 (CH), 137.6, 138.9 (C), 163.6, 163.8 (C-OH), 171.3, 203.5 (C=O). IR (neat):  $\tilde{\nu}$  = 3306 (m), 2980 (s), 2932 (m), 2857 (m), 1661 (s), 1630 (s), 1603 (s), 1504 (s), 1464 (s), 1415 (s), 1389 (s), 1378 (s), 1334 (s), 1275 (s), 1252 (s), 1217 (s), 1175 (m), 1142 (s), 1103 (m), 1067 (w), 1030 (m), 1007 (m), 814 (s), 765 (s), 669 (w)  $\text{cm}^{-1}$ . UV-VIS ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  ( $\lg \epsilon$ ): 378 (3.77), 309 (3.94), 298 (4.03), 287 (3.96), 259 (4.42), 215 (4.49) nm. MS (EI, 70 eV):  $m/z$  (%) = 350 ( $\text{M}^+$ , 5), 186 (10), 170 (43), 151 (10), 114 (8), 86 (22), 84 (61), 72 (7), 157 (13), 43 (100). HRMS (FT-ICR): calcd. for  $\text{C}_{21}\text{H}_{19}\text{O}_5$  ( $[\text{M}+1]^+$ ): 351.12270; found: 351.12288.

### **Ethyl 3-octyl-5-(1-Hydroxynaphthalen-2-carbonyl)-2-methylsalicylate (8c).**

Starting with 3-Acetyl-4*H*-benzo[*h*]chromen-4-one **7** (80 mg, 0.33 mmol), Me<sub>3</sub>SiOTf (22 mg, 0.10 mmol) and 1,3-bis-silyl enol ether **2j** (160 mg, 0.43 mmol), naphthophenone **8c** was given as a yellow oil (50 mg, 33%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.87 (t, 3 H, *J* = 7.0 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.26 - 1.36 (m, 10 H, CH<sub>2</sub>), 1.43 (t, *J* = 7.1 Hz, 3 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.58 (m, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 2.45 (s, 3 H, CH<sub>3</sub>), 2.63 (t, *J* = 7.5 Hz, 2 H, ArCH<sub>2</sub>), 4.47 (q, *J* = 7.1 Hz, 2 H, OCH<sub>2</sub>CH<sub>3</sub>), 7.18 - 7.22 (m, 3 H, Ar), 7.57 (dd, *J* = 8.3 Hz, *J* = 1.3 Hz, 1 H, Ar), 7.65 (m, 1 H, Ar), 7.74 (d, *J* = 7.8 Hz, 1 H, Ar), 8.53 (d, *J* = 8.0 Hz, 1 H, Ar), 11.71 (s, 1 H, OH), 14.09 (s, 1 H, OH). <sup>13</sup>C NMR (DEPT, 75.5 MHz, CDCl<sub>3</sub>): δ = 14.1, 14.2 (CH<sub>3</sub>), 20.5 (OCH<sub>2</sub>CH<sub>3</sub>), 22.7, 29.1, 29.3, 29.5, 29.5, 29.8, 31.9 (CH<sub>2</sub>), 62.1 (OCH<sub>2</sub>CH<sub>3</sub>), 112.9, 113.9 (C), 118.3, 124.5 (CH), 125.5 (C), 126.0, 127.1, 127.5 (CH), 129.1 (C), 130.5 (CH), 130.9 (C), 132.9 (CH), 135.9, 137.6 (C), 161.8, 163.7 (C-OH), 171.9, 204.0 (C=O). IR (neat):  $\tilde{\nu}$  = 3394 (w), 2926 (s), 2856 (s), 1721 (m), 1657 (s), 1630 (s), 1607 (s), 1574 (s), 1504 (m), 1460 (s), 1416 (s), 1380 (s), 1329 (s), 1268 (s), 1241 (s), 1184 (s), 1153 (s), 1119 (s), 1083 (m), 1023 (s), 983 (m), 875 (w), 810 (s), 766 (m), 662 (w) cm<sup>-1</sup>. UV-VIS (CH<sub>3</sub>CN): λ<sub>max</sub> (lg ε): 377 (3.61), 309 (3.71), 298 (3.79), 287 (3.69), 259 (4.28), 219 (4.31) nm. MS (EI, 70 eV): *m/z* (%) = 462 (M<sup>+</sup>, 38), 447 (12), 401 (8), 317 (7), 292 (C<sub>18</sub>H<sub>27</sub>O<sub>3</sub><sup>+</sup>, 100), 246 (16), 161 (82).