Regioselective Synthesis of 5-Alkylsalicylates, 5-Alkyl-2-hydroxy-acetophenones, and 5-Alkyl-2-hydroxy-benzophenones by [3+3] Cyclization of 1,3-Bis(Silyl Enol Ethers) with 2-Alkyl-1,1,3,3-tetraethoxypropanes

**Constantin Mamat,^a Stefan Büttner,^a Tiana Trabhardt,^a Christine Fischer,^{a, b}
and Peter Langer*^{a, b}**

^a *Institut für Chemie, Universität Rostock,*

Albert-Einstein-Str. 3a, 18059 Rostock, Germany

Fax: +49 381 4986412, E-mail: peter.langer@uni-rostock.de

^b *Leibniz-Institut für Katalyse e. V. an der Universität Rostock*

Albert-Einstein-Str. 29a, 18059 Rostock, Germany

Supporting Information

Table of Contents

General Procedures	S2
Analytical Data of compounds 6ab-bd	S2
¹ H and ¹³ C NMR spectra of compounds 6aa-bd	S18

General. ^1H and ^{13}C NMR spectra were measured in CDCl_3 at 250, 300, and 500 MHz, respectively. Chemical shifts are reported in parts per million using the solvent internal standard (chloroform, 7.26 and 77.0 ppm, respectively). Infrared resonance spectra were recorded on a FTIR spectrometer. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). Melting points are uncorrected. Analytical thin layer chromatography was performed on 0.20 mm 60 A silica gel plates. Column chromatography was performed on 60 A silica gel (60 – 200 mesh). All cyclization reactions were carried out in Schlenk tubes under an argon atmosphere using dried solvents. The appropriate acetals, enol ethers and substituted 1,1,3,3-tetraethoxypropanes were prepared as described in the literature.¹¹⁻¹⁴

General procedure for the synthesis of 6a-ad. To a CH_2Cl_2 solution (5 mL) of 1,3-bis(silyl enol ether) **5a-e** (2 equiv.) and of the respective 2-alkyl-1,1,3,3-tetraethoxypropane **4a-h** (1 equiv.) was added TiCl_4 (1 equiv.) at $-78\text{ }^\circ\text{C}$ under argon atmosphere. The temperature of this mixture was allowed to rise to $20\text{ }^\circ\text{C}$ during 14 h and, subsequently, an aqueous HCl solution (10%, 10 mL) was added. The organic layer was separated and the residue was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc = 50:1 to 20:1).

5-Ethyl-salicylic acid methylester (6a). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxybutane (**4b**) (0.500 g, 2.01 mmol), 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5a**) (1.11 g, 4.04 mmol) and TiCl_4 (0.22 mL, 2.01 mmol) in CH_2Cl_2 (4 mL) yielded **6a** as a yellow syrup (186 mg, 51%). $R_f = 0.4$ (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu} = 3206$ (w), 2964 (m), 1680 (s). ^1H NMR (250 MHz, CDCl_3): $\delta = 1.21$ (t, 3H, $^3J = 7.6$ Hz, CH_2CH_3), 2.58 (q, 2H, $^3J = 7.6$ Hz,

CH₂CH₃), 3.94 (s, 3H, OCH₃), 6.91 (d, 1H, ³J_{3,4} = 8.5 Hz, H-3), 7.30 (dd, 1H, ³J_{3,4} = 8.5 Hz, ⁴J_{4,6} = 2.2 Hz, H-4), 7.65 (d, 1H, ⁴J_{4,6} = 2.2 Hz, H-6), 10.58 (s, 1H, OH). ¹³C NMR (63 MHz, CDCl₃): δ = 15.7, 27.9, 52.2, 112.0, 117.4, 128.4, 134.9, 135.6, 159.7, 170.6. MS (EI, 70 eV): *m/z* (%) = 180 (M⁺, 40), 148 (100), 133 (79), 105 (16), 91 (12), 77 (17), 32 (49). HRMS (EI, 70 eV): calcd. for C₁₀H₁₂O₃ (M⁺): 180.0781; found: 180.0783.

5-*n*-Propyl-salicylic acid ethylester (6b). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxypentane (**4c**) (0.394 g, 1.50 mmol), 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5b**) (0.824 g, 3.00 mmol) and TiCl₄ (0.17 mL, 1.50 mmol) in CH₂Cl₂ (4 mL) yielded **6b** as a yellow syrup (157 mg, 50%). R_f = 0.4 (*n*-heptane/EtOAc = 2:1). IR (neat, cm⁻¹): $\tilde{\nu}$ = 3199 (m), 3172 (m), 2961 (s), 2932 (s), 2872 (s), 1675 (s). ¹H NMR (250 MHz, CDCl₃): δ = 0.93 (t, 3H, ³J = 7.3 Hz, ArCH₂CH₂CH₃), 1.42 (t, 3H, ³J = 7.1 Hz, OCH₂CH₃), 1.54-1.69 (m, 2H, ArCH₂CH₂CH₃), 2.52 (t, 2H, ³J = 7.6 Hz, ArCH₂CH₂CH₃), 4.40 (q, 2H, ³J = 7.1 Hz, OCH₂CH₃), 6.90 (d, 1H, ³J_{3,4} = 8.4 Hz, H-3), 7.27 (dd, 1H, ³J_{3,4} = 8.4 Hz, ⁴J_{4,6} = 2.3 Hz, H-4), 7.63 (d, 1H, ⁴J_{4,6} = 2.3 Hz, H-6), 10.68 (s, 1H, OH). ¹³C NMR (76 MHz, CDCl₃): δ = 13.6, 14.2, 24.6, 37.0, 61.3, 112.2, 117.3, 129.0, 133.2, 135.9, 159.8, 170.2. MS (EI, 70 eV): *m/z* (%) = 208 (M⁺, 32), 179 (27), 162 (68), 133 (100). HRMS (EI, 70 eV): calcd. for C₁₂H₁₆O₃ (M⁺): 208.10940, found: 208.10977.

5-*i*-Propyl-salicylic acid ethylester (6c). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxy-3-methylbutane (**4d**) (0.525 g, 2.00 mmol), 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5b**) (1.098 g, 4.00 mmol) and TiCl₄ (0.22 mL, 2.00 mmol) in CH₂Cl₂ (4 mL) yielded **6c** as a yellow syrup (148 mg, 36%). R_f = 0.4 (*n*-heptane/EtOAc = 2:1). IR (neat, cm⁻¹): $\tilde{\nu}$ = 3201 (m), 3174 (m), 2962 (s), 1676 (s). ¹H NMR (250 MHz, CDCl₃): δ = 1.23 (d, 6H, ³J = 6.9 Hz, ArCH(CH₃)₂), 1.43 (t, 3H, ³J = 7.1 Hz, OCH₂CH₃), 2.78-2.95 (m, 1H, ArCH(CH₃)₂), 4.41 (q, 2H, ³J = 7.1 Hz, OCH₂CH₃), 6.92 (d,

1H, $^3J_{3,4} = 8.6$ Hz, H-3), 7.33 (dd, 1H, $^3J_{3,4} = 8.6$ Hz, $^4J_{4,6} = 2.3$ Hz, H-4), 7.67 (d, 1H, $^4J_{4,6} = 2.3$ Hz, H-6), 10.68 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): $\delta = 14.2, 24.0, 33.2, 61.3, 112.1, 117.4, 127.0, 134.0, 139.4, 159.8, 170.2$.

5-*n*-Butyl-salicylic acid methylester (6d). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyhexane (**4e**) (0.500 g, 1.81 mmol), 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5a**) (1.24 g, 4.52 mmol) and TiCl_4 (0.19 mL, 1.81 mmol) in CH_2Cl_2 (4 mL) yielded **6d** as a yellow syrup (0.132 g, 35%). $R_f = 0.58$ (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu} = 3212$ (w), 2961 (m), 1681 (m). ^1H NMR (250 MHz, CDCl_3): $\delta = 0.92$ (t, 3H, $^3J = 7.3$ Hz, $\text{Ar}(\text{CH}_2)_3\text{CH}_3$), 1.20-1.43 (m, 2H, $\text{Ar}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 1.48-1.65 (m, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.54 (t, 2H, $^3J = 7.7$ Hz, $\text{ArCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.94 (s, 3H, OCH_3), 6.90 (d, 1H, $^3J_{3,4} = 8.5$ Hz, H-3), 7.28 (dd, 1H, $^3J_{3,4} = 8.5$ Hz, $^4J_{4,6} = 2.3$ Hz, H-4), 7.63 (d, 1H, $^4J_{4,6} = 2.3$ Hz, H-6), 10.58 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): $\delta = 13.9, 22.2, 33.7, 34.6, 52.1, 111.9, 117.3, 129.0, 133.5, 136.1, 159.7, 170.7$. MS (EI, 70 eV): m/z (%) = 208 (M^+ , 32), 176 (63), 165 (37), 133 (100), 105 (10), 77 (16). HRMS (EI, 70 eV): 208.10940; found: 208.109752.

5-*n*-Pentyl-salicylic acid ethylester (6e). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyheptane (**4f**) (0.436 g, 1.50 mmol), 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5b**) (0.824g, 3.00 mmol) and TiCl_4 (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6e** as a yellow syrup (0.127 g, 36%). $R_f = 0.58$ (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu} = 2958$ (s), 2930 (s), 2857 (s), 1676 (s). ^1H NMR (250 MHz, CDCl_3): $\delta = 0.89$ (t, 3H, $^3J = 6.7$ Hz, $\text{Ar}(\text{CH}_2)_4\text{CH}_3$), 1.27-1.37 (m, 4H, $\text{Ar}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$), 1.43 (t, 3H, $^3J = 7.1$ Hz, OCH_2CH_3), 1.50-1.66 (m, 2H, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.54 (t, 2H, $^3J = 7.8$ Hz, $\text{ArCH}_2(\text{CH}_2)_3\text{CH}_3$), 4.41 (q, 2H, $^3J = 7.1$ Hz, OCH_2CH_3), 6.90 (d, 1H, $^3J_{3,4} = 8.5$ Hz, H-3), 7.27 (dd, 1H, $^3J_{3,4} = 8.5$ Hz, $^4J_{4,6} = 2.3$ Hz, H-4),

7.63 (d, 1H, $^4J_{4,6}$ = 2.4 Hz, H-6), 10.67 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): δ = 14.0, 14.2, 22.5, 31.3, 31.4, 34.9, 61.3, 112.2, 117.3, 129.0, 133.5, 135.9, 159.7, 170.2. MS (EI, 70 eV): m/z (%) = 236 (M^+ , 31), 190 (67), 179 (41), 133 (100). Anal. calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3$ (236.14): C, 71.16; H, 8.53. Found: C, 70.89; H, 8.70.

5-*n*-Hexyl-salicylic acid methylester (6f). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyoctane (**4g**) (0.500 g, 1.64 mmol), 1-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5a**) (0.9 g, 3.28 mmol) and TiCl_4 (0.17 mL, 1.64 mmol) in CH_2Cl_2 (4 mL) yielded **6f** as a yellow syrup (0.132 g, 34%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3204 (m), 2928 (s), 1680 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.88 (t, 3H, 3J = 6.5 Hz, $\text{Ar}(\text{CH}_2)_5\text{CH}_3$), 1.24-1.38 (m, 6H, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.57 (qi, 2H, 3J = 7.5 Hz, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.53 (t, 2H, 3J = 7.5 Hz, $\text{ArCH}_2(\text{CH}_2)_4\text{CH}_3$), 3.94 (s, 3H, OCH_3), 6.90 (d, 1H, $^3J_{3,4}$ = 8.6 Hz, H-3), 7.27 (dd, 1H, $^3J_{3,4}$ = 8.6 Hz, $^4J_{4,6}$ = 2.3 Hz, H-4), 7.63 (d, 1H, $^4J_{4,6}$ = 2.3 Hz, H-6), 10.57 (s, 1H, OH). ^{13}C NMR (63 MHz, CDCl_3): δ = 14.0, 22.6, 28.8, 31.5, 31.7, 34.9, 52.2, 111.9, 117.3, 129.0, 133.6, 136.1, 159.6, 170.6. MS (EI, 70 eV): m/z (%) = 236 (M^+ , 33), 204 (65), 165 (51), 133 (100), 105 (9), 77 (14). HRMS (EI, 70 eV): calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3$ (M^+): 236.1407; found: 236.1403.

5-*n*-Heptyl-salicylic acid ethylester (6g). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxynonane (**4h**) (0.637 g, 2.00 mmol), 1-ethoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5b**) (1.098 g, 4.00 mmol) and TiCl_4 (0.22 mL, 2.00 mmol) in CH_2Cl_2 (4 mL) yielded **6g** as a yellow syrup (0.178 g, 34%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3201 (m), 3174 (m), 2956 (s), 2928 (s), 2856 (s), 1676 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.88 (t, 3H, 3J = 6.7 Hz, $\text{Ar}(\text{CH}_2)_6\text{CH}_3$), 1.21-1.38 (m, 8H, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.43 (t, 3H, 3J = 7.1 Hz, OCH_2CH_3), 1.49-1.65 (m, 2H, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 2.56 (t, 2H, 3J = 7.7 Hz, $\text{ArCH}_2(\text{CH}_2)_5\text{CH}_3$), 4.41 (q, 2H, 3J = 7.1 Hz,

OCH₂CH₃), 6.89 (d, 1H, ³J_{3,4} = 8.5 Hz, H-3), 7.27 (dd, 1H, ³J_{3,4} = 8.5 Hz, ⁴J_{4,6} = 2.3 Hz, H-4), 7.63 (d, 1H, ⁴J_{4,6} = 2.3 Hz, H-6), 10.67 (s, 1H, OH). ¹³C NMR (76 MHz, CDCl₃): δ = 14.0, 14.2, 22.6, 29.1, 29.1, 31.6, 31.8, 34.9, 61.3, 112.2, 117.3, 129.0, 133.4, 135.9, 159.7, 170.2. MS (EI, 70 eV): *m/z* (%) = 264 (M⁺, 34), 218 (67), 179 (52), 133 (100). HRMS (EI, 70 eV): calcd. for C₁₆H₂₄O₃ (M⁺): 264.17200; found: 264.17190.

2-Hydroxy-5-methyl-acetophenone (6h). Following the general procedure, the starting materials 1,1,3,3-tetraethoxy-2-methylpropane (**4a**) (0.500 g, 2.13 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (1.040 g, 4.26 mmol) and TiCl₄ (0.24 mL, 2.13 mmol) in CH₂Cl₂ (4 mL) yielded **6ah** as a yellow syrup (0.177 g, 55%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (nujol mull, cm⁻¹): $\tilde{\nu}$ = 1646 (s). ¹H NMR (250 MHz, CDCl₃): δ = 2.32 (s, 3H, ArCH₃), 2.62 (s, 3H, COCH₃), 6.88 (d, 1H, ³J_{3,4} = 8.5 Hz, H-3), 7.29 (dd, 1H, ³J_{3,4} = 8.5 Hz, ⁴J_{4,6} = 2.1 Hz, H-4), 7.51 (d, 1H, ⁴J_{4,6} = 2.0 Hz, H-6), 12.08 (s, 1H, OH). ¹³C NMR (63 MHz, CDCl₃): δ = 20.5, 26.6, 118.1, 119.3, 128.0, 130.4, 137.4, 160.3, 204.4. MS (EI, 70 eV): *m/z* (%) = 150 (M⁺, 49), 135 (100), 107 (16). HRMS (EI, 70 eV): calcd. for C₉H₁₀O₂ (M⁺): 150.06753; found: 150.06759.

5-Ethyl-2-hydroxy-acetophenone (6i). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxybutane (**4b**) (0.500 g, 2.01 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (1.200 g, 5.03 mmol) and TiCl₄ (0.22 mL, 2.01 mmol) in CH₂Cl₂ (4 mL) yielded **6i** as a yellow syrup (0.118 g, 36%). R_f = 0.44 (*n*-heptane/EtOAc = 2:1). IR (neat, cm⁻¹): $\tilde{\nu}$ = 2965 (w), 1643(s). ¹H NMR (250 MHz, CDCl₃): δ = 1.23 (t, 3H, ³J = 7.6 Hz, CH₂CH₃), 2.61 (q, 2H, ³J = 7.6 Hz, CH₂CH₃), 2.62 (s, 3H, COCH₃), 6.90 (d, 1H, ³J_{3,4} = 8.5 Hz, H-3), 7.32 (dd, 1H, ³J_{3,4} = 8.5 Hz, ⁴J_{4,6} = 2.0 Hz, H-4), 7.51 (d, 1H, ⁴J_{4,6} = 2.0 Hz, H-6), 12.11 (s, 1H, OH). ¹³C NMR (76 MHz, CDCl₃): δ = 15.7, 26.6, 27.9, 118.2, 119.4, 129.2, 134.5, 136.4, 160.4, 204.4. MS (EI, 70 eV): *m/z* (%) =

164 (M^+ , 41), 149 (100), 131 (18), 91 (9), 77 (12), 32 (37). HRMS (EI, 70 eV): calcd. for $C_{10}H_{12}O_2$ (M^+): 164.0832; found: 164.0832.

2-Hydroxy-5-*n*-propyl-acetophenone (6k). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxypentane (**4c**) (0.394 g, 1.50 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (0.733 g, 3.00 mmol) and $TiCl_4$ (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6k** as a yellow syrup (0.118 g, 36%). R_f = 0.44 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2960 (s), 2930 (s), 2872 (s), 1644 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.94 (t, 3H, 3J = 7.4 Hz, $(CH_2)_2CH_3$), 1.53-1.71 (m, 2H, $CH_2CH_2CH_3$), 2.55 (t, 2H, 3J = 7.6 Hz, $ArCH_2CH_2CH_3$), 2.63 (s, 3H, $COCH_3$), 6.90 (d, 1H, $^3J_{3,4}$ = 8.4 Hz, H-3), 7.30 (dd, 1H, $^3J_{3,4}$ = 8.4 Hz, $^4J_{4,6}$ = 2.2 Hz, H-4), 7.50 (d, 1H, $^4J_{4,6}$ = 2.2 Hz, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 13.6, 24.7, 26.6, 37.1, 118.1, 119.3, 129.9, 133.0, 136.9, 160.5, 204.5. MS (EI, 70 eV): m/z (%) = 178 (M^+ , 39), 163 (21), 149 (100), 131 (44). HRMS (EI, 70 eV): calcd. for $C_{11}H_{14}O_2$ (M^+): 178.09883; found: 178.09917.

2-Hydroxy-5-*i*-propyl-acetophenone (6l). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxy-3-methylbutane (**4d**) (0.525 g, 2.00 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (0.978 g, 4.00 mmol) and $TiCl_4$ (0.22 mL, 2.00 mmol) in CH_2Cl_2 (4 mL) yielded **6l** as a yellow syrup (0.078 g, 22%). R_f = 0.44 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2960 (s), 2900 (s), 2872 (s), 1644 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (d, 6H, 3J = 6.9 Hz, $ArCH(CH_3)_2$), 2.64 (s, 3H, $COCH_3$), 2.82-2.94 (m, 1H, $ArCH(CH_3)_2$), 6.92 (d, 1H, $^3J_{3,4}$ = 8.6 Hz, H-3), 7.37 (dd, 1H, $^3J_{3,4}$ = 8.6 Hz, $^4J_{4,6}$ = 2.3 Hz, H-4), 7.53 (d, 1H, $^4J_{4,6}$ = 2.3 Hz, H-6), 12.11 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 24.0, 26.6, 33.3, 118.3, 119.4, 127.8, 134.9, 139.2, 160.6, 204.4. MS (EI, 70 eV): m/z (%) = 178

(M^+ , 34), 163 (100), 145 (14). HRMS (EI, 70 eV): calcd. for $C_{11}H_{14}O_2$ (M^+): 178.09883; found: 178.09818.

5-*n*-Butyl-2-hydroxy-acetophenone (6m). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyhexane (**4e**) (0.500 g, 1.81 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (1.100 g, 4.54 mmol) and $TiCl_4$ (0.19 mL, 1.81 mmol) in CH_2Cl_2 (4 mL) yielded **6m** as a yellow syrup (0.125 g, 36%). R_f = 0.5 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2929 (s), 1643 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, 3H, 3J = 7.4 Hz, $Ar(CH_2)_3CH_3$), 1.23-1.44 (m, 2H, $Ar(CH_2)_2CH_2CH_3$), 1.50-1.65 (m, 2H, $ArCH_2CH_2CH_2CH_3$), 2.57 (t, 2H, 3J = 7.8 Hz, $ArCH_2(CH_2)_2CH_3$), 2.62 (s, 3H, $COCH_3$), 6.90 (d, 1H, $^3J_{3,4}$ = 8.6 Hz, H-3), 7.30 (dd, 1H, $^3J_{3,4}$ = 8.6 Hz, $^4J_{4,6}$ = 2.2 Hz, H-4), 7.50 (d, 1H, $^4J_{4,6}$ = 2.2 Hz, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.9, 26.6, 22.1, 33.7, 34.7, 118.1, 119.4, 129.8, 133.2, 136.8, 160.4, 204.4. MS (EI, 70 eV): m/z (%) = 192 (M^+ , 26), 177 (15), 149 (100), 135 (16), 131 (33), 86 (15), 84 (23), 77 (14). HRMS (EI, 70 eV): calcd. for $C_{12}H_{16}O_2$ (M^+): 192.1145; found: 192.1151.

2-Hydroxy-5-*n*-pentyl-acetophenone (6n). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyheptane (**4f**) (0.436 g, 1.50 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (0.733 g, 3.00 mmol) and $TiCl_4$ (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6n** as a yellow syrup (0.138 g, 45%). R_f = 0.5 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2957 (s), 2929 (s), 2857 (s), 1644 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, 3H, 3J = 6.7 Hz, $Ar(CH_2)_4CH_3$), 1.27-1.41 (m, 4H, $Ar(CH_2)_2(CH_2)_2CH_3$), 1.52-1.68 (m, 2H, $ArCH_2CH_2(CH_2)_2CH_3$), 2.56 (t, 2H, 3J = 7.8 Hz, $ArCH_2(CH_2)_3CH_3$), 2.63 (s, 3H, $COCH_3$), 6.90 (d, 1H, $^3J_{3,4}$ = 8.5 Hz, H-3), 7.30 (dd, 1H, $^3J_{3,4}$ = 8.6 Hz, $^4J_{4,6}$ = 2.2 Hz, H-4), 7.49 (d, 1H, $^4J_{4,6}$ = 2.2 Hz, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 14.0, 26.6, 22.5, 31.3, 31.3, 35.0, 118.1, 119.4, 129.8, 133.2, 136.8,

160.5, 204.4. MS (EI, 70 eV): m/z (%) = 206 (M^+ , 26), 191 (11), 149 (100), 131 (28). HRMS (EI, 70 eV): calcd. for $C_{13}H_{18}O_2$ (M^+): 206.13013; found: 206.13057.

5-*n*-Hexyl-2-hydroxy-acetophenone (6o). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyoctane (**4g**) (0.500 g, 1.64 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (0.8 g, 3.27 mmol) and $TiCl_4$ (0.17 mL, 1.64 mmol) in CH_2Cl_2 (4 mL) yielded **6o** as a yellow syrup (0.138 g, 45%). R_f = 0.56 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2928 (s), 1644 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 3H, 3J = 6.6 Hz, $Ar(CH_2)_5CH_3$), 1.23-1.40 (m, 6H, $Ar(CH_2)_2(CH_2)_3CH_3$), 1.50-1.68 (m, 2H, $ArCH_2CH_2(CH_2)_3CH_3$), 2.56 (t, 2H, 3J = 7.7 Hz, $ArCH_2(CH_2)_4CH_3$), 2.63 (s, 3H, $COCH_3$), 6.90 (d, 1H, $^3J_{3,4}$ = 8.6 Hz, H-3), 7.30 (dd, 1H, $^3J_{3,4}$ = 8.6 Hz, $^4J_{4,6}$ = 2.2 Hz, H-4), 7.50 (d, 1H, $^4J_{4,6}$ = 2.2 Hz, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 14.1, 26.7, 22.6, 28.8, 31.6, 31.7, 35.0, 118.2, 119.4, 129.8, 133.3, 136.7, 160.4, 204.5. MS (EI, 70 eV): m/z (%) = 220 (M^+ , 32), 205 (12), 149 (100), 131 (30), 77 (9), 43 (8). HRMS (EI, 70 eV): calcd. for $C_{14}H_{20}O_2$ (M^+): 220.1458; found: 220.1452.

5-*n*-Heptyl-2-hydroxy-acetophenone (6p). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxynonane (**4h**) (0.637 g, 2.00 mmol), 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**5c**) (0.978 g, 4.00 mmol) and $TiCl_4$ (0.22 mL, 2.00 mmol) in CH_2Cl_2 (4 mL) yielded **6p** as a yellow syrup (0.21 g, 45%). R_f = 0.56 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2956 (s), 2927 (s), 2856 (s), 1644 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.88 (t, 3H, 3J = 6.8 Hz, $Ar(CH_2)_6CH_3$), 1.21-1.38 (m, 8H, $Ar(CH_2)_2(CH_2)_4CH_3$), 1.50-1.67 (m, 2H, $ArCH_2CH_2(CH_2)_4CH_3$), 2.56 (t, 2H, 3J = 7.7 Hz, $ArCH_2(CH_2)_5CH_3$), 2.63 (s, 3H, $COCH_3$), 6.90 (d, 1H, $^3J_{3,4}$ = 8.5 Hz, H-3), 7.30 (dd, 1H, $^3J_{3,4}$ = 8.5 Hz, $^4J_{4,6}$ = 2.2 Hz, H-4), 7.49 (d, 1H, $^4J_{4,6}$ = 2.2 Hz, H-6), 12.10 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 14.1, 26.6, 22.6, 29.1, 31.6, 31.8, 35.0, 118.1, 119.4, 129.8, 133.2,

136.9, 160.4, 204.5. MS (EI, 70 eV): m/z (%) = 234 (M^+ , 54), 219 (17), 149 (100), 131 (46). HRMS (EI, 70 eV): calcd. for $C_{15}H_{22}O_2$ (M^+): 234.16143; found: 234.16157.

2-Hydroxy-5-methyl-benzophenone (6q). Following the general procedure, the starting materials 1,1,3,3-tetraethoxy-2-methylpropane (**4a**) (0.500 g, 2.13 mmol), 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (1.306 g, 4.26 mmol) and $TiCl_4$ (0.24 mL, 2.13 mmol) in CH_2Cl_2 (4 mL) yielded **6q** as a yellow solid (0.215 g, 48%). M.p. 81 °C; R_f = 0.56 (*n*-heptane/EtOAc = 2:1). IR (Nujol, cm^{-1}): $\tilde{\nu}$ = 1629 (s). 1H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3H, $ArCH_3$), 6.99 (d, 1H, $^3J_{3,4}$ = 8.4 Hz, H-3), 7.27-7.72 (m, 7H, Ph/Ar), 11.86 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 20.4, 118.1, 118.8, 127.7, 128.3, 129.1, 131.7, 133.2, 137.3, 138.1, 161.1, 201.5. MS (EI, 70 eV): m/z (%) = 212 (M^+ , 48), 211 (80), 135 (50), 105 (43), 77 (100). HRMS (EI, 70 eV): calcd. for $C_{14}H_{12}O_2$ (M^+): 212.08318; found: 212.08262.

5-Ethyl-2-hydroxy-benzophenone (6r). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxybutane (**4b**) (0.500 g, 2.01 mmol), 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (1.20 g, 4.01 mmol) and $TiCl_4$ (0.22 mL, 2.01 mmol) in CH_2Cl_2 (4 mL) yielded **6r** as a yellow syrup (0.143 g, 31%). R_f = 0.48 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2964 (m), 1631 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 1.17 (t, 3H, 3J = 7.6 Hz, CH_2CH_3), 2.56 (q, 2H, 3J = 7.6 Hz, CH_2CH_3), 6.90 (d, 1H, $^3J_{3,4}$ = 8.3 Hz, H-3), 7.32 (m, 7H, Ph/Ar), 11.86 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 15.7, 27.9, 118.2, 118.8, 128.3, 129.1, 131.8, 132.1, 134.3, 136.2, 138.1, 161.3, 201.6. MS (EI, 70 eV): m/z (%) = 226 (M^+ , 84), 225 ($M^+ - 1$, 100), 211 (15), 149 (28), 133 (42), 105 (22), 77 (37). HRMS (EI, 70 eV): calcd. for $C_{15}H_{13}O_2$ ($M^+ - 1$): 225.0910; found: 225.0907.

2-Hydroxy-5-*n*-propyl-benzophenone (6s). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyheptane (**4c**) (0.394 g, 1.50 mmol), 1-phenyl-1,3-

bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (0.920 g, 3.00 mmol) and TiCl_4 (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6s** as a yellow syrup (0.198 g, 55%). $R_f = 0.64$ (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu} = 3061$ (w), 2959 (s), 2930 (s), 2872 (s), 1631 (s). ^1H NMR (250 MHz, CDCl_3): $\delta = 0.90$ (t, 3H, $^3J = 7.2$ Hz, $\text{Ar}(\text{CH}_2)_2\text{CH}_3$), 1.47-1.66 (m, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_3$), 2.49 (t, 2H, $^3J = 7.5$ Hz, $\text{ArCH}_2\text{CH}_2\text{CH}_3$), 7.00 (d, 1H, $^3J_{3,4} = 8.6$ Hz, H-3), 7.31-7.71 (m, 7H, Ph/Ar), 11.85 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): $\delta = 13.6, 24.6, 37.0, 118.1, 118.8, 128.3, 129.1, 131.8, 132.7, 132.8, 136.7, 138.1, 161.3, 201.6$. MS (EI, 70 eV): m/z (%) = 240 (M^+ , 82), 211 (89), 163 (9), 133 (100). HRMS (EI, 70 eV): calcd. for $\text{C}_{16}\text{H}_{16}\text{O}_2$ (M^+): 240.11448; found: 240.11425.

5-*n*-Butyl-2-hydroxy-benzophenone (6t). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyhexane (**4e**) (0.500 g, 1.81 mmol), 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (1.40 g, 4.53 mmol) and TiCl_4 (0.19 mL, 1.81 mmol) in CH_2Cl_2 (4 mL) yielded **6t** as a yellow syrup (0.198 g, 43%). $R_f = 0.64$ (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu} = 3060$ (w), 2929 (s), 1631 (s). ^1H NMR (250 MHz, CDCl_3): $\delta = 0.90$ (t, 3H, $^3J = 7.3$ Hz, $\text{Ar}(\text{CH}_2)_3\text{CH}_3$), 1.23-1.40 (m, 2H, $\text{Ar}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$), 1.45-1.61 (m, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.51 (t, 2H, $^3J = 7.6$ Hz, $\text{ArCH}_2(\text{CH}_2)_2\text{CH}_3$), 7.00 (d, 1H, $^3J_{3,4} = 8.0$ Hz, H-3), 7.30-7.72 (m, 7H, Ar), 11.85 (s, 1H, OH). ^{13}C NMR (63 MHz, CDCl_3): $\delta = 13.9, 22.1, 33.6, 34.6, 118.1, 118.8, 128.3, 129.2, 131.2, 132.7, 132.9, 136.7, 138.1, 161.3, 201.6$. MS (EI, 70 eV): m/z (%) = 254 (M^+ , 79), 211 (100), 133 (95), 105 (23), 77 (37). HRMS (EI, 70 eV): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_2$ (M^+): 254.1301; found: 254.1293.

2-Hydroxy-5-*n*-pentyl-benzophenone (6u). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyheptane (**4f**) (0.436 g, 1.50 mmol), 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (0.920 g, 3.00 mmol) and TiCl_4 (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6u** as a yellow syrup (0.172 g, 43%). $R_f = 0.64$ (*n*-

heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2956 (s), 2928 (s), 2856 (s), 1631 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.88 (t, 3H, 3J = 6.7 Hz, $\text{Ar}(\text{CH}_2)_4\text{CH}_3$), 1.19-1.39 (m, 4H, $\text{Ar}(\text{CH}_2)_2(\text{CH}_2)_2\text{CH}_3$), 1.46-1.61 (m, 2H, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.50 (t, 2H, 3J = 7.7 Hz, $\text{ArCH}_2(\text{CH}_2)_3\text{CH}_3$), 7.00 (d, 1H, $^3J_{3,4}$ = 7.9 Hz, H-3), 7.31-7.72 (m, 7H, Ph/Ar), 11.85 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): δ = 14.0, 22.4, 31.2, 31.2, 34.8, 118.1, 118.8, 128.3, 129.2, 131.8, 132.7, 132.9, 136.7, 138.1, 161.3, 201.6. MS (EI, 70 eV): m/z (%) = 268 (M^+ , 68), 211 (10), 133 (85). HRMS (EI, 70 eV): calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$ (M^+): 268.14578; found: 268.14568.

5-*n*-Hexyl-2-hydroxy-benzophenone (6v). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyoctane (**4g**) (0.500 g, 1.64 mmol), 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (1.00 g, 3.26 mmol) and TiCl_4 (0.17 mL, 1.64 mmol) in CH_2Cl_2 (4 mL) yielded **6v** as a yellow syrup (0.157 g, 34%). R_f = 0.5 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3061 (m), 2927 (s), 1631 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.87 (t, 3H, 3J = 6.7 Hz, $\text{Ar}(\text{CH}_2)_5\text{CH}_3$), 1.20-1.43 (m, 6H, $\text{Ar}(\text{CH}_2)_2(\text{CH}_2)_3\text{CH}_3$), 1.44-1.65 (m, 2H, $\text{ArCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.51 (t, 2H, 3J = 7.6 Hz, $\text{ArCH}_2(\text{CH}_2)_4\text{CH}_3$), 6.95 (m, 8H), 10.57 (s, 1H, OH). ^{13}C NMR (63 MHz, CDCl_3): δ = 14.0, 22.6, 28.7, 31.4, 31.6, 34.9, 118.1, 118.8, 128.3, 129.2, 131.8, 132.7, 133.0, 136.7, 138.1, 161.3, 201.5. MS (EI, 70 eV): m/z (%) = 282 (M^+ , 50), 211 (100), 133 (72), 105 (18), 77 (21). HRMS (EI, 70 eV): calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_2$ (M^+): 282.1614; found: 282.1613.

5-*n*-Heptyl-2-hydroxy-benzophenone (6w). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxynonane (**4h**) (0.637 g, 2.00 mmol), 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**5d**) (1.228 g, 4.00 mmol) and TiCl_4 (0.22 mL, 2.00 mmol) in CH_2Cl_2 (4 mL) yielded **6aw** as a yellow syrup (0.321 g, 54%). R_f = 0.5 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3061 (m), 3028 (m), 2955 (s), 2927 (s), 2855 (s), 1631 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.87 (t, 3H, 3J = 6.8 Hz, $\text{Ar}(\text{CH}_2)_6\text{CH}_3$), 1.21-1.36

(m, 8H, Ar(CH₂)₂(CH₂)₄CH₃), 1.45-1.62 (m, 2H, ArCH₂CH₂(CH₂)₄CH₃), 2.50 (t, 2H, ³*J* = 7.7 Hz, ArCH₂(CH₂)₅CH₃), 7.00 (d, 1H, ³*J*_{3,4} = 8.1 Hz, H-3), 7.31-7.72 (m, 7H, Ph/Ar), 11.85 (s, 1H, OH). ¹³C NMR (76 MHz, CDCl₃): δ = 14.0, 22.6, 29.0, 29.1, 31.5, 31.8, 34.9, 118.1, 118.8, 128.3, 129.1, 131.8, 132.7, 132.9, 136.7, 138.1, 161.3, 201.5. MS (EI, 70 eV): *m/z* (%) = 296 (M⁺, 70), 211 (100), 133 (69). HRMS (EI, 70 eV): calcd. for C₂₀H₂₄O₂ (M⁺): 296.17708; found: 296.17780.

2-Hydroxy-3,5-dimethyl-propiophenone (6x). Following the general procedure, the starting materials 1,1,3,3-tetraethoxy-2-methylpropane (**4a**) (0.300 g, 1.28 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (0.698 g, 2.56 mmol) and TiCl₄ (0.14 mL, 1.28 mmol) in CH₂Cl₂ (4 mL) yielded **6x** as a yellow syrup (0.14 g, 61%). R_f = 0.5 (*n*-heptane/EtOAc = 2:1). IR (nujol mull, cm⁻¹): $\tilde{\nu}$ = 3694 (w), 3540 (w), 3477 (w), 1640 (s). ¹H NMR (250 MHz, CDCl₃): δ = 1.23 (t, 3H, ³*J* = 7.3 Hz, COCH₂CH₃), 2.23, 2.27 (2 s, 3H, ArCH₃), 3.03 (q, 2H, ³*J* = 7.3 Hz, COCH₂CH₃), 7.16 (s, 1H, H-4), 7.39 (s, 1H, H-6), 12.49 (s, 1H, OH). ¹³C NMR (76 MHz, CDCl₃): δ = 8.4, 15.4, 20.5, 31.6, 118.1, 127.0, 127.0, 127.2, 138.1, 158.8, 207.2. MS (EI, 70 eV): *m/z* (%) = 178 (M⁺, 32), 149 (100). HRMS (EI, 70 eV): calcd. for C₁₁H₁₄O₂ (M⁺): 178.09883; found: 178.09922.

5-Ethyl-2-hydroxy-3-methyl-propiophenone (6y). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxybutane (**4b**) (0.500 g, 2.01 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (1.10 g, 4.04 mmol) and TiCl₄ (0.22 mL, 2.01 mmol) in CH₂Cl₂ (4 mL) yielded **6y** as a yellow syrup (0.153 g, 40%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm⁻¹): $\tilde{\nu}$ = 3539 (w), 2966 (m), 1638 (s). ¹H NMR (250 MHz, CDCl₃): δ = 1.22 (t, 3H, ³*J* = 7.6 Hz, ArCH₂CH₃), 1.23 (t, 3H, ³*J* = 7.3 Hz, COCH₂CH₃), 2.25 (s, 3H, CH₃), 2.59 (q, 2H, ³*J* = 7.6 Hz, ArCH₂CH₃), 3.06 (q, 2H, ³*J* = 7.3 Hz, COCH₂CH₃), 7.18 (d, 1H, ⁴*J*_{4,6} = 1.6 Hz H-4), 7.40 (d, 1H, ⁴*J*_{4,6} = 1.6 Hz, H-6),

12.50 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): δ = 8.4, 14.7, 15.8, 28.1, 31.6, 118.2, 125.8, 127.3, 133.7, 136.9, 159.0, 207.3. MS (EI, 70 eV): m/z (%) = 192 (M^+ , 29), 163 (100), 91 (13), 77 (5). HRMS (EI, 70 eV): calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_2$ (M^+): 192.1145; found: 192.1142.

2-Hydroxy-3-methyl-5-*n*-propyl-propiophenone (6z). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxypentane (**4c**) (0.394 g, 1.50 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (0.818 g, 3.00 mmol) and TiCl_4 (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6z** as a yellow syrup (0.157 g, 51%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2960 (s), 2934 (s), 2873 (s), 1637 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.94 (t, 3H, 3J = 7.4 Hz, $\text{Ar}(\text{CH}_2)_2\text{CH}_3$), 1.23 (t, 3H, 3J = 7.3 Hz, COCH_2CH_3), 1.52-1.70 (m, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_3$), 2.24 (s, 3H, ArCH_3), 2.50 (t, 2H, 3J = 7.6 Hz, $\text{ArCH}_2\text{CH}_2\text{CH}_3$), 3.04 (q, 2H, 3J = 7.3 Hz, COCH_2CH_3), 7.16 (d, 1H, $^4J_{4,6}$ = 1.4 Hz, H-4), 7.39 (d, 1H, $^4J_{4,6}$ = 2.0 Hz, H-6), 12.51 (s, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3): δ = 8.4, 13.7, 15.5, 24.7, 31.6, 37.2, 118.1, 126.5, 127.1, 132.1, 137.5, 159.0, 207.3. MS (EI, 70 eV): m/z (%) = 206 (M^+ , 44), 177 (100). HRMS (EI, 70 eV): calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_2$ (M^+): 206.13013; found: 206.13058.

5-*n*-Butyl-2-hydroxy-3-methyl-propiophenone (6aa). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyhexane (**4e**) (0.5 g, 1.81 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (1.23 g, 4.51 mmol) and TiCl_4 (0.19 mL, 1.81 mmol) in CH_2Cl_2 (4 mL) yielded **6aa** as a yellow syrup (0.151g, 38%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2929 (s), 1636 (s). ^1H NMR (250 MHz, CDCl_3): δ = 0.93 (t, 3H, 3J = 7.2 Hz, $\text{Ar}(\text{CH})_3\text{CH}_3$), 1.23 (t, 3H, 3J = 7.3 Hz, COCH_2CH_3), 1.27-1.66 (m, 4H, $\text{ArCH}_2(\text{CH}_2)_4\text{CH}_3$), 2.24 (s, 3H, CH_3), 2.53 (t, 2H, 3J = 7.8 Hz, $\text{ArCH}_2(\text{CH}_2)_2\text{CH}_3$), 3.04 (q, 2H, 3J = 7.3 Hz, COCH_2CH_3), 7.17 (s, 1H, H-3), 7.39 (s, 1H, H-4), 12.51 (s, 1H, OH). ^{13}C NMR (63 MHz, CDCl_3): δ = 8.3, 13.9, 15.5, 22.3, 33.9, 34.8, 31.6, 118.1, 126.4, 127.1, 132.3,

137.4, 158.4, 207.3. MS (EI, 70 eV): m/z (%) = 220 (M^+ , 33), 191 (100), 177 (46), 159 (14), 91 (12), 77 (5). HRMS (EI, 70 eV): calcd. for $C_{14}H_{20}O_2$ (M^+): 220.1458; found: 220.1453.

2-Hydroxy-3-methyl-5-*n*-pentyl-propiophenone (6ab). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyheptane (**4f**) (0.436 g, 1.50 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (0.818 g, 3.00 mmol) and $TiCl_4$ (0.17 mL, 1.50 mmol) in CH_2Cl_2 (4 mL) yielded **6ab** as a yellow syrup (0.191 g, 54%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 957 (s), 2929 (s), 2857 (s), 1636 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, 3H, 3J = 6.9 Hz, $Ar(CH_2)_4CH_3$), 1.23 (t, 3H, 3J = 7.3 Hz, $COCH_2CH_3$), 1.28-1.38 (m, 4H, $Ar(CH_2)_2(CH_2)_2CH_3$), 1.50-1.66 (m, 2H, $ArCH_2CH_2(CH_2)_2CH_3$), 2.24 (s, 3H, $ArCH_3$), 2.52 (t, 2H, 3J = 7.7 Hz, $ArCH_2(CH_2)_3CH_3$), 3.04 (q, 2H, 3J = 7.3 Hz, $COCH_2CH_3$), 7.17 (d, 1H, $^4J_{4,6}$ = 1.5 Hz, H-4), 7.39 (d, 1H, $^4J_{4,6}$ = 2.1 Hz, H-6), 12.51 (s, 1H, OH). ^{13}C NMR (76 MHz, $CDCl_3$): δ = 8.4, 14.0, 15.5, 22.5, 31.4, 35.1, 31.6, 118.1, 126.4, 127.1, 132.3, 137.4, 158.9, 207.3. MS (EI, 70 eV): m/z (%) = 234 (M^+ , 36), 205 (100), 177 (59), 159 (15). HRMS (EI, 70 eV): calcd. for $C_{15}H_{22}O_2$ (M^+), 234.16143; found: 234.16086.

5-*n*-Hexyl-2-hydroxy-3-methyl-propiophenone (6ac). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxyoctane (**4g**) (0.500 g, 1.64 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (0.900 g, 3.28 mmol) and $TiCl_4$ (0.17 mL, 1.64 mmol) in CH_2Cl_2 (4 mL) yielded **6ac** as a yellow syrup (0.132 g, 32%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm^{-1}): $\tilde{\nu}$ = 2928 (s), 1636 (s). 1H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, 3H, 3J = 6.6 Hz, $Ar(CH_2)_5CH_3$), 1.24 (t, 3H, 3J = 7.3 Hz, $COCH_2CH_3$), 1.27-1.38 (m, 6H, $Ar(CH_2)_2(CH_2)_3CH_3$), 1.49-1.67 (m, 2H, $ArCH_2CH_2(CH_2)_3CH_3$), 2.24 (s, 3H, CH_3), 2.52 (t, 2H, 3J = 7.7 Hz, $ArCH_2(CH_2)_4CH_3$), 3.04 (q, 2H, 3J = 7.3 Hz, $COCH_2CH_3$), 7.17 (d, 1H, $^4J_{4,6}$ = 1.9 Hz, H-4), 7.39 (d, 1H, $^4J_{4,6}$ = 1.9 Hz, H-6), 12.51 (s, 1H, OH). ^{13}C NMR

(63 MHz, CDCl₃): δ = 8.4, 14.1, 15.5, 22.6, 28.9, 31.6, 31.7, 35.1, 31.7, 118.1, 126.4, 127.1, 132.4, 137.4, 158.9, 207.3. MS (EI, 70 eV): m/z (%) = 248 (M⁺, 68), 219 (100), 177 (100), 159 (28), 121 (10), 91 (22). HRMS (EI, 70 eV): calcd. for C₁₆H₂₄O₂ (M⁺): 248.1771; found: 248.1766.

5-*n*-Heptyl-2-hydroxy-3-methyl-propiophenone (6ad). Following the general procedure, the starting materials 2-diethoxymethyl-1,1-diethoxynonane (**4h**) (0.634 g, 2.00 mmol), 3,5-bis(trimethylsilyloxy)-2,4-heptadiene (**5e**) (1.092 g, 4.00 mmol) and TiCl₄ (0.22 mL, 2.00 mmol) in CH₂Cl₂ (4 mL) yielded **6ad** as a yellow syrup (0.33 g, 63%). R_f = 0.6 (*n*-heptane/EtOAc = 2:1). IR (neat, cm⁻¹): $\tilde{\nu}$ = 2956 (s), 2927 (s), 2856 (s), 1636 (s). ¹H NMR (250 MHz, CDCl₃): δ = 0.88 (t, 3H, ³*J* = 6.8 Hz, Ar(CH₂)₆CH₃), 1.19-1.37 (m, 8H, Ar(CH₂)₂(CH₂)₄CH₃), 1.23 (t, 3H, ³*J* = 7.3 Hz, COCH₂CH₃), 1.49-1.66 (m, 2H, ArCH₂CH₂(CH₂)₄CH₃), 2.23 (s, 3H, ArCH₃), 2.51 (t, 2H, ³*J* = 7.7 Hz, ArCH₂(CH₂)₆CH₃), 3.05 (q, 2H, ³*J* = 7.2 Hz, COCH₂CH₃), 7.16 (d, 1H, ⁴*J*_{4,6} = 1.8 Hz, H-4), 7.38 (d, 1H, ⁴*J*_{4,6} = 1.9 Hz, H-6), 12.51 (s, 1H, OH). ¹³C NMR (76 MHz, CDCl₃): δ = 8.4, 14.0, 15.5, 22.6, 29.1, 31.6, 31.8, 35.1, 31.7, 118.1, 126.4, 127.1, 132.3, 137.4, 158.9, 207.2. MS (EI, 70 eV): m/z (%) = 262 (M⁺, 10), 233 (100), 177 (68). HRMS (EI, 70 eV): calcd. for C₁₇H₂₆O₂ (M⁺): 262.19273; found: 262.19257.

5-Ethyl-salicylic acid methylester (6a) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

5-*n*-Propyl-salicylic acid ethylester (6b)¹H NMR, 250 MHz, CDCl₃ ¹³C NMR, 76 MHz, CDCl₃

5-*i*-Propyl-salicylic acid ethylester (6c) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Butyl-salicylic acid methylester (6d) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Pentyl-salicylic acid ethylester (6e)¹H NMR, 250 MHz, CDCl₃ ¹³C NMR, 76 MHz, CDCl₃

5-*n*-Hexyl-salicylic acid methylester (6f) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

5-*n*-Heptyl-salicylic acid ethylester (6g)¹H NMR, 250 MHz, CDCl₃ ¹³C NMR, 76 MHz, CDCl₃

2-Hydroxy-5-methyl-acetophenone (6h) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

5-Ethyl-2-hydroxy-acetophenone (6i) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

2-Hydroxy-5-*n*-propyl-acetophenone (6k) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

2-Hydroxy-5-*i*-propyl-acetophenone (6l) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Butyl-2-hydroxy-acetophenone (6m) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

2-Hydroxy-5-*n*-pentyl-acetophenone (6n) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Hexyl-2-hydroxy-acetophenone (6o) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Heptyl-2-hydroxy-acetophenone (6p) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

2-Hydroxy-5-methyl-benzophenone (6q) ^1H NMR, 300 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-Ethyl-2-hydroxy-benzophenone (6r) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

2-Hydroxy-5-*n*-propyl-benzophenone (6s) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Butyl-2-hydroxy-benzophenone (6t) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

2-Hydroxy-5-*n*-pentyl-benzophenone (6u) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Hexyl-2-hydroxy-benzophenone (6v) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

5-*n*-Heptyl-2-hydroxy-benzophenone (6w) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

2-Hydroxy-3,5-dimethyl-propiophenone (6x) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-Ethyl-2-hydroxy-3-methyl-propiophenone (6y) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

2-Hydroxy-3-methyl-5-*n*-propyl-propiophenone (6z) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Butyl-2-hydroxy-3-methyl-propiophenone (6aa) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

2-Hydroxy-3-methyl-5-*n*-pentyl-propiophenone (6ab) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3

5-*n*-Hexyl-2-hydroxy-3-methyl-propiophenone (6ac) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 63 MHz, CDCl_3

5-*n*-Heptyl-2-hydroxy-3-methyl-propiophenone (6ad) ^1H NMR, 250 MHz, CDCl_3 ^{13}C NMR, 76 MHz, CDCl_3