

Regioselective [3 + 3] Cyclization of 1,3-Bis(silyloxy)buta-1,3-dienes with 1,1,1-Trifluoro-4-(silyloxy)alk-3-en-2-ones: New and Convenient Synthesis of Functionalized 5-Alkyl-3-(trifluoromethyl)phenols

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Functionalized 5-alkyl-3-(trifluoromethyl)phenols were prepared by formal [3 + 3] cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 1,1,1-trifluoro-4-(silyloxy)alk-3-en-2-ones derived from 1,1,1-trifluoroalkane-2,4-diones. The latter were prepared by condensation of the dianion of 1,1,1-trifluoropentane-2,4-dione with alkyl halides.

Introduction. – In 2006, we published a preliminary communication related to the synthesis of 5-methyl-3-(trifluoromethyl)phenols by formal [3 + 3] cyclocondensation of 1,3-bis(silyloxy)buta-1,3-dienes¹⁾ with 1,1,1-trifluoro-4-(silyloxy)prop-3-en-2-one [2]. This methodology was later extended to the synthesis of 5-aryl-3-(trifluoromethyl)phenols [3], 5-hetaryl-3-(trifluoromethyl)phenols [4], 5-alkyl-3-(perfluoroalkyl)phenols, and 5-aryl-3-(perfluoroalkyl)phenols [5]. We also reported the synthesis of 5-unsubstituted 3-(trifluoromethyl)phenols by cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 4-ethoxy-1,1,1-trifluoroalk-3-en-2-ones [6]. Here, we report full details of the synthesis of functionalized 5-alkyl-3-(trifluoromethyl)phenols by cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 1,1,1-trifluoro-4-(silyloxy)alk-3-en-2-ones. With regard to our preliminary communication [2], the preparative scope has been considerably extended. While the method was initially restricted to the synthesis of 5-methyl-3-(trifluoromethyl)phenols, we were able to realize the synthesis of various 5-alkyl-3-(trifluoromethyl)phenols. In this context, we report an efficient synthesis of the required starting materials, 1,1,1-trifluoroalkane-2,4-diones, by condensation of the dianion of 1,1,1-trifluoropentane-2,4-dione with alkyl halides. While in our preliminary communication only very few variations of substituent R¹ were studied, the present paper includes a variety of different groups. In addition, chloroalkyl substituents were introduced in different position of the molecule.

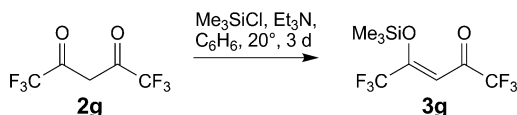
¹⁾ For a review of 1,3-bis(silyl enol ethers) in general, see [1].

Results and Discussion. – The condensation of the dianion of 1,1,1-trifluoropentane-2,4-dione (**2a**) with alkyl iodides **1a–1e** afforded the 1,1,1-trifluoroalkane-2,4-diones **2b–2f** in 41–59% yield (*Table 1*). 1,1,1-Trifluoro-4-(trimethylsilyloxy)alk-3-en-2-ones **3a–3f** were prepared by silylation of the corresponding CF₃-substituted 1,3-diones **2a–2f**. The reactions with simple aliphatic alkyl iodides afforded products **3b** and **3d–3f** in excellent yields (92–95%). 1,3-Dione **3c**, containing a remote Cl substituent, was isolated in 77% yield. Commercially available 1,1,1,3,3,3-hexafluoropentane-2,4-dione (**2g**) was transformed to **3g** (*Scheme*).

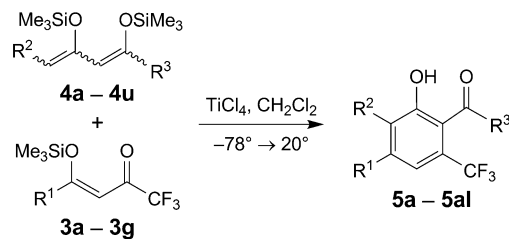
Table 1. Synthesis of **3a–3f**

R ¹	Compound	Yield of 2 [%] ^{a)}	Compound	Yield of 3 [%] ^{a)}
C ₆ H ₁₃	2b	42	3b	94
Cl(CH ₂) ₆	2c	49	3c	77
C ₈ H ₁₇	2d	59	3d	92
C ₁₀ H ₂₁	2e	41	3e	95
C ₁₂ H ₂₅	2f	55	3f	93

^{a)} Yields of isolated products.

Scheme. Synthesis of **3g**

The TiCl₄ mediated cyclization of **3a–3g** with 1,3-bis(silyloxy)buta-1,3-dienes **4a–4u**, prepared by known procedures [7–9], afforded the desired 5-alkyl-3-(trifluoromethyl)phenols **5a–5al** in 26–76% yield (*Table 2*). For reaction optimization, (high) concentration and stoichiometric amounts of the starting materials, and low temperature (–78°) were decisive. All products were formed with excellent regioselectivity and contained the CF₃ group in *ortho* position to the ester (or Ac) group. The other possible regioisomers (CF₃ group *para* to the ester group) could not be detected in the crude product mixture (¹H-NMR evidence). In some cases, the product yields were moderate, due to practical problems. The individual quality (purity) of the enones and dienes, which cannot be purified owing to their labile nature, played an important role.

Table 2. *Synthesis of 5-Alkyl-3-(trifluoromethyl)phenols 5a–5al*

3	4	5	R ¹	R ²	R ³	Yield of 5 [%] ^{a)}
3a	4a	5a	Me	H	MeO	76
3a	4b	5b	Me	Me	MeO	48
3a	4c	5c	Me	Cl(CH ₂) ₃	MeO	49
3a	4d	5d	Me	C ₄ H ₉	MeO	49
3a	4e	5e	Me	C ₆ H ₁₃	MeO	31
3a	4f	5f	Me	Cl(CH ₂) ₆	MeO	50
3a	4g	5g	Me	C ₇ H ₁₅	MeO	47
3a	4h	5h	Me	C ₈ H ₁₇	MeO	26
3a	4j	5j	Me	PhCH ₂	MeO	69
3a	4k	5k	Me	Ph(CH ₂) ₂	MeO	43
3a	4l	5l	Me	Ph(CH ₂) ₃	MeO	68
3a	4m	5m	Me	H	EtO	40
3a	4n	5n	Me	Me	EtO	75
3a	4o	5o	Me	Et	EtO	72
3a	4p	5p	Me	H	Me	60
3b	4a	5q	C ₇ H ₁₅	H	MeO	66
3b	4b	5r	C ₇ H ₁₅	Me	MeO	65
3b	4q	5s	C ₇ H ₁₅	Et	MeO	66
3b	4r	5t	C ₇ H ₁₅	Pr	MeO	57
3b	4p	5u	C ₇ H ₁₅	H	Me	80
3b	4s	5v	C ₇ H ₁₅	MeO	MeO	60
3c	4m	5w	Cl(CH ₂) ₇	H	EtO	44
3d	4a	5x	C ₉ H ₁₉	H	MeO	32
3d	4b	5y	C ₉ H ₁₉	Me	MeO	66
3d	4q	5z	C ₉ H ₁₉	Et	MeO	60
3d	4p	5aa	C ₉ H ₁₉	H	Me	62
3e	4a	5ab	C ₁₁ H ₂₃	H	MeO	39
3e	4b	5ac	C ₁₁ H ₂₃	Me	MeO	51
3e	4q	5ad	C ₁₁ H ₂₃	Et	MeO	47
3e	4t	5ae	C ₁₁ H ₂₃	Pr	MeO	49
3e	4p	5af	C ₁₁ H ₂₃	H	Me	67
3f	4a	5ag	C ₁₃ H ₂₇	H	MeO	34
3f	4b	5ah	C ₁₃ H ₂₇	Me	MeO	35
3f	4q	5ai	C ₁₃ H ₂₇	Et	MeO	43
3f	4t	5aj	C ₁₃ H ₂₇	Pr	MeO	45
3f	4u	5ak	C ₁₃ H ₂₇	H	C ₆ H ₅	66
3g	4a	5al	CF ₃	H	Me	35

^{a)} Yield of isolated products.

In some cases, hydrolysis of the starting materials is observed during the reaction. In addition, TiCl_4 -mediated oxidative dimerization of the diene gives rise to the formation of side-products. Both ester-, Ac- and PhCO(Bz) -substituted phenols were successfully prepared. While dienes **4p** and **4u** were prepared from acetyl- and benzoylacetone, respectively, all other dienes were prepared from β -keto esters. Despite the fact that, in general, the reactivity of dienes derived from 1,3-diones is lower than the reactivity of dienes derived from β -keto esters, excellent yields were obtained for the products derived from **4p** and **4u**. Likewise, substituents R^1 and R^2 do not have a major influence on the yield. Interestingly, products **5c**, **5f**, and **5w**, containing a side chain at C(5) or C(6) with a remote Cl substituent, were isolated in acceptable yields. In fact, we have observed earlier that dienes containing a remote Cl substituent can be successfully employed in formal $[3+3]$ cyclizations [9].

The structure of **5q** was established by 2D-NMR experiments (NOESY and HMBC) (Fig. 1). Additional evidence was obtained from analysis and comparison of the C,F coupling pattern for all derivatives. The structures of **5a**, **5k**, **5w**, and **5al** were independently confirmed by X-ray crystal-structure analyses (Figs. 2–5)². Inspection of the crystal lattice of **5al** revealed that the H-atom of the OH group is involved in intermolecular bonds to the C=O groups of adjacent molecules.

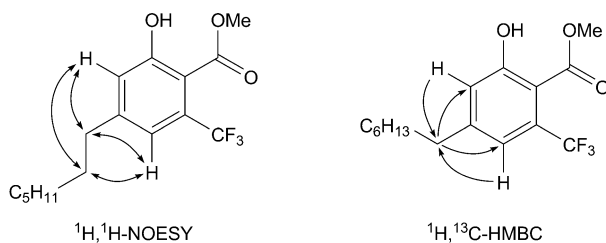
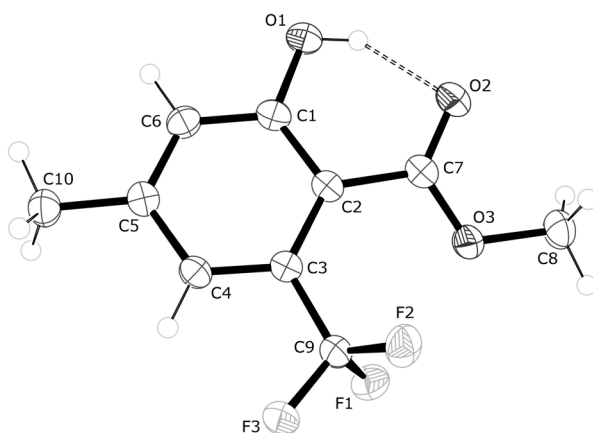
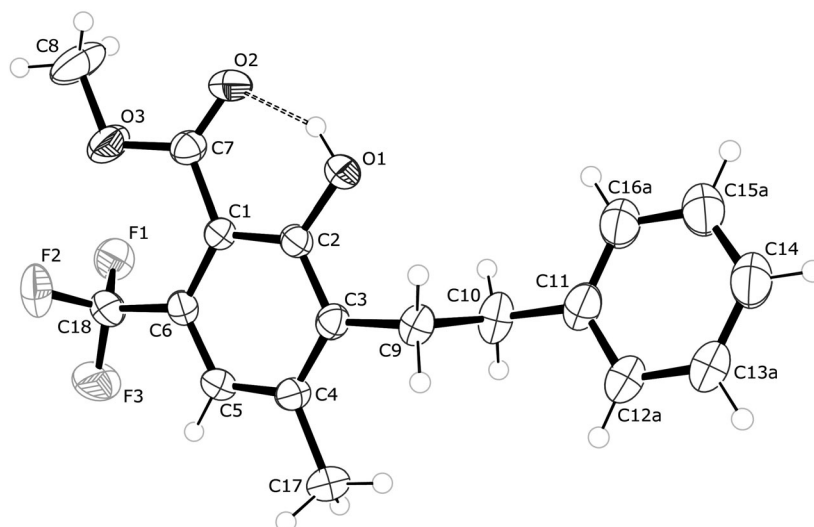
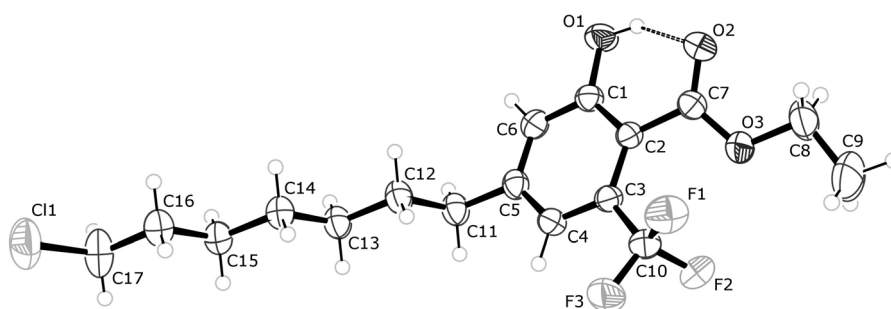


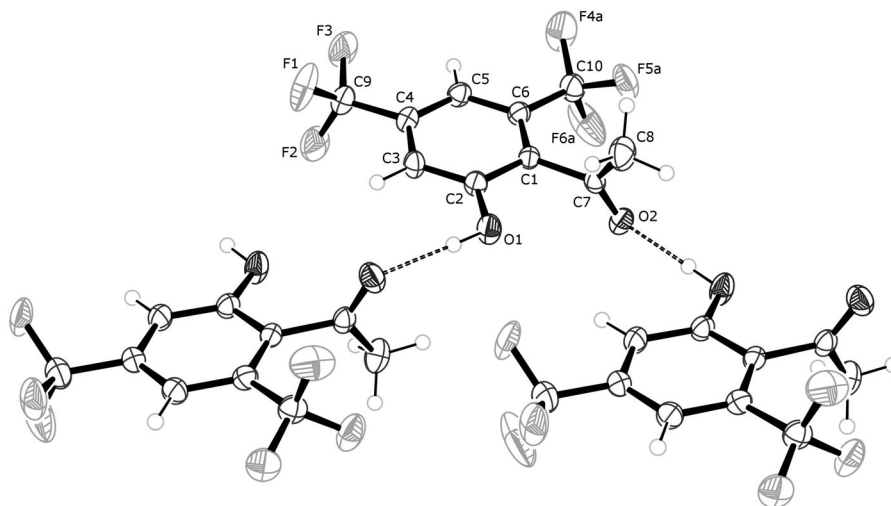
Fig. 1. NOESY and HMBC of **5q**

Compounds **5a**–**5al** show some interesting spectroscopic features. The ^{19}F -NMR chemical-shift values of all compounds containing an ester group are in the range of 58–59 ppm, while for compounds with an Ac group the signals are observed in the range of 55–56 ppm. The chemical shift is influenced by through-bond or through-space interactions with the neighboring group.

In conclusion, we have reported a versatile synthesis of 5-alkyl-3-(trifluoromethyl)phenols by cyclization reactions of 1,3-bis(silyloxy)buta-1,3-dienes. The starting materials, 1,1,1-trifluoroalkane-2,4-diones, were prepared by condensation of the dianion of 1,1,1-trifluoropentane-2,4-dione with alkyl halides.

²) CCDC-884948–884951 contain all crystallographic details of this publication and are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html, or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk.

Fig. 2. Crystal structure of **5a**Fig. 3. Crystal structure of **5k**Fig. 4. Crystal structure of **5w**

Fig. 5. Crystal structure and intermolecular interactions of **5al**

Experimental Part

General Procedure for the Synthesis of Diones 2b–2f. To a soln. of BuLi (2.3 equiv.) in THF (3 ml per 1.0 mmol of **1**) $^i\text{Pr}_2\text{NH}$ (2.3 equiv.) was added at 0° , and the mixture was stirred for 30 min, followed by dropwise addition of 1,1,1-trifluoropentane-2,4-dione (1.0 equiv.) and subsequent stirring for additional 60 min at 0° . The mixture then was cooled to -78° and the iodoalkane (1.0 equiv.) was added. The temp. of the mixture was allowed to rise to 20° during 14 h, and, subsequently, HCl (10%, 40 ml) was added. The org. layer was separated and extracted with Et_2O (3×40 ml). The combined org. layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (CC; SiO_2 ; heptane/ AcOEt 20:1) or by distillation.

1,1,1-Trifluoroundecane-2,4-dione (2b). Starting with 1,1,1-trifluoropentane-2,4-dione (**1**; 4.623 g, 30 mmol), 1-iodohexane (6.362 g, 30 mmol), BuLi (27.6 ml of a 2.5M soln. in hexanes), and $^i\text{Pr}_2\text{NH}$ (9.7 ml, 69 mmol) in THF (90 ml), **2b** was isolated as a colorless liquid (2.968 g, 42%) by distillation. B.p. $73-75^\circ/0.9$ Torr. IR (ATR): 3117w, 2958w, 2929m, 2858w, 1594m, 1459m, 1379w, 1277w, 1197m, 1150s, 1107m. $^1\text{H-NMR}$ (250 MHz): 0.88 (t, $J = 6.7$, Me); 1.21–1.41 (m, 4 CH_2); 1.57–1.73 (m, CH_2); 2.43 (t, $J = 7.6$, COCH_2CH_2); 5.91 (s, CH). $^{13}\text{C-NMR}$ (75 MHz): 14.0 (Me); 22.6 (CH_2); 25.5 (CH_2); 28.9 (CH_2); 29.0 (CH_2); 31.6 (CH_2); 38.4 (CH_2); 95.6 (q, $^3J = 1.9$, CH); 117.0 (q, $^1J = 282.8$, CF_3); 175.6 (q, $^2J = 36.2$, COCF_3); 197.6 (CO). $^{19}\text{F-NMR}$ (235 MHz): -76.7 (CF_3). EI-MS (70 eV): 238 (6, M^+), 196 (13), 169 (48), 154 (100), 139 (90). HR-EI-MS (70 eV): 238.1176 (M^+ , $\text{C}_{11}\text{H}_{17}\text{F}_3\text{O}_2^+$; calc. 238.1181).

11-Chloro-1,1,1-trifluoroundecane-2,4-dione (2c). Starting with **1** (1.000 g, 6.49 mmol), 1-chloro-6-iodohexane (1.600 g, 6.49 mmol), BuLi (6.0 ml of a 2.5M soln. in hexanes), and $^i\text{Pr}_2\text{NH}$ (2.1 ml, 14.93 mmol) in THF (16 ml), **2c** was isolated as a colorless liquid (0.864 g, 49%) by CC. $^1\text{H-NMR}$ (250 MHz): 1.21–1.84 (m, 5 CH_2); 2.41 (t, $J = 7.6$, CH_2); 3.55 (t, $J = 7.6$, CH_2); 5.93 (s, CH). $^{13}\text{C-NMR}$ (75 MHz): 25.3 (CH_2); 26.6 (CH_2); 28.5 (CH_2); 28.9 (CH_2); 32.4 (CH_2); 38.4 (CH_2); 45.0 (CH_2); 95.7 (CH); 117.0 (q, $^1J = 283.0$, CF_3); 175.3 (CCF_3); 197.4 (CO). $^{19}\text{F-NMR}$ (235 MHz): -76.7 (CF_3). EI-MS (70 eV): 272 (3, M^+), 203 (22), 167 (27), 154 (100), 139 (68), 85 (44). HR-EI-MS (70 eV): 272.0788 (M^+ , $\text{C}_{11}\text{H}_{16}\text{ClF}_3\text{O}_2^+$; calc. 272.0791).

1,1,1-Trifluorotridecane-2,4-dione (2d). Starting with **1** (1.541 g, 10 mmol), 1-iodooctane (2.401 g, 10 mmol), BuLi (9.2 ml of a 2.5M soln. in hexanes), and $^i\text{Pr}_2\text{NH}$ (3.2 ml, 23 mmol) in THF (30 ml), **2d** was isolated as a colorless liquid (1.569 g, 59%) by distillation. B.p. $95-99^\circ/0.6$ Torr. IR (ATR): 2956w, 2926m, 2856w, 1595m, 1459m, 1378w, 1276w, 1197m, 1151s, 1107m. $^1\text{H-NMR}$ (300 MHz): 0.88 (t, $J = 6.7$,

Me); 1.20–1.40 (*m*, 6 CH₂); 1.58–1.73 (*m*, CH₂); 2.43 (*t*, *J* = 7.6, COCH₂CH₂); 5.91 (*s*, CH). ¹³C-NMR (75 MHz): 14.1 (Me); 22.6 (CH₂); 25.5 (CH₂); 29.1 (CH₂); 29.2 (CH₂); 29.2 (CH₂); 29.3 (CH₂); 31.8 (CH₂); 38.4 (CH₂); 95.6 (*q*, ³*J* = 2.0, CH); 117.0 (*q*, ¹*J* = 283.0, CF₃); 175.7 (*q*, ²*J* = 36.2, COCF₃); 197.6 (CO). ¹⁹F-NMR (282 MHz): –76.7 (CF₃). EI-MS (70 eV): 266 (5, *M*⁺), 197 (34), 167 (30), 154 (100), 139 (73). HR-EI-MS (70 eV): 266.1491 (*M*⁺, C₁₃H₂₁F₃O₂⁺; calc. 266.1494).

1,1,1-Trifluoropentadecane-2,4-dione (2e). Starting with **1** (6.164 g, 40 mmol), 1-iododecane (10.727 g, 40 mmol), BuLi (36.8 ml of a 2.5M soln. in hexanes), and ³Pr₂NH (12.9 ml, 92 mmol) in THF (120 ml), **2e** was isolated as a colorless liquid (4.814 g, 41%) by CC and subsequent distillation. B.p. 110°/0.2 Torr. IR (ATR): 2924*w*, 2855*w*, 1595*m*, 1459*m*, 1377*w*, 1277*w*, 1198*m*, 1151*s*, 1107*m*. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, Me); 1.20–1.38 (*m*, 8 CH₂); 1.59–1.71 (*m*, CH₂); 2.43 (*t*, *J* = 7.6, COCH₂CH₂); 5.91 (*s*, CH). ¹³C-NMR (75 MHz): 14.1 (Me); 22.7 (CH₂); 25.5 (CH₂); 29.1 (CH₂); 29.2 (CH₂); 29.3 (CH₂); 29.4 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 31.9 (CH₂); 38.4 (CH₂); 95.6 (*q*, ³*J* = 1.8, CH); 117.0 (*q*, ¹*J* = 283.7, CF₃); 175.7 (*q*, ²*J* = 36.2, COCF₃); 197.6 (CO). ¹⁹F-NMR (282 MHz): –76.7 (CF₃). EI-MS (70 eV): 294 (4, *M*⁺), 228 (28), 167 (29), 154 (100), 139 (66). HR-EI-MS (70 eV): 294.1805 (*M*⁺, C₁₅H₂₅F₃O₂⁺; calc. 294.1807).

1,1,1-Trifluoroheptadecane-2,4-dione (2f). Starting with **1** (4.623 g, 30 mmol), 1-iodododecane (8.887 g, 30 mmol), BuLi (27.6 ml of a 2.5M soln. in hexanes), and ³Pr₂NH (9.7 ml, 69 mmol) in THF (90 ml), **2f** was isolated as a colorless liquid (5.316 g, 55%) by CC and subsequent distillation. B.p. 112–115°/0.08 Torr. IR (ATR): 2923*w*, 2854*w*, 1596*m*, 1465*m*, 1377*w*, 1277*w*, 1198*m*, 1152*s*, 1107*m*. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, Me); 1.19–1.39 (*m*, 10 CH₂); 1.58–1.70 (*m*, CH₂); 2.43 (*t*, *J* = 7.6, COCH₂CH₂); 5.91 (*s*, CH). ¹³C-NMR (75 MHz): 14.1 (Me); 22.7 (CH₂); 25.5 (CH₂); 29.1 (CH₂); 29.2 (CH₂); 29.3 (CH₂); 29.4 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.7 (CH₂); 31.9 (CH₂); 38.4 (CH₂); 95.6 (*q*, ³*J* = 1.8, CH); 117.0 (*q*, ¹*J* = 283.5, CF₃); 175.7 (*q*, ²*J* = 36.2, COCF₃); 197.6 (CO). ¹⁹F-NMR (282 MHz): –76.7 (CF₃). EI-MS (70 eV): 322 (5, *M*⁺), 253 (21), 192 (19), 167 (32), 154 (100), 139 (57). HR-EI-MS (70 eV): 322.2110 (*M*, C₁₇H₂₉F₃O₂⁺; calc. 322.2120).

General Procedure for the Synthesis of Compounds 3a–3g. To a stirred Et₂O soln. (2 ml per 1.0 mmol of **2**) of **2a–2g** (1.0 equiv.) were added Et₃N (1.0 equiv.) and TMSOTf (0.95 equiv.) at 0° under Ar. The soln. was stirred for 30 min at 0°. The temp. of the mixture was allowed to rise to 20°, and stirring was continued for 3 d. A liquid salt layer separated at the bottom of the flask. The upper layer (Et₂O soln., containing the product) was transferred to a dry flask by syringe under Ar. Et₂O (1.5 ml per 1.0 mmol of **2**) was added to the liquid salt layer, the mixture was stirred for 2 min, and the layers were allowed to separate in a period of 2 h. The Et₂O solns. were combined and concentrated *in vacuo* to give **3a–3f**, which were not further purified and, due to their unstable nature, immediately used for the synthesis of phenols **5** (without detailed spectroscopic characterization).

General Procedure for the Synthesis of 5-Alkyl-3-(trifluoromethyl)phenols 5a–5al. To a CH₂Cl₂ soln. (5 ml) of **4** (2.4 mmol) and **3** (2.2 mmol) was added TiCl₄ (2.4 mmol) at –78° under Ar. The temp. of the mixture was allowed to rise to 20° during 14 h, and, subsequently, HCl (10%, 20 ml) was added. The org. layer was separated and extracted with CH₂Cl₂ (3 × 20 ml). The combined org. layers were dried (Na₂SO₄), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by CC (SiO₂; heptane/AcOEt 20:1).

Methyl 2-Hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5a). Starting with **3a** (0.498 g, 2.2 mmol), **4a** (0.625 g, 2.4 mmol), and TiCl₄ (0.26 ml, 2.4 mmol) in CH₂Cl₂ (5 ml), **5a** was isolated as a white solid (0.390 g, 76%). M.p. 68–69°. IR (Nujol): 1671*m* (*ν*(C=O)). ¹H-NMR (250 MHz): 2.38 (*s*, Me); 3.97 (*s*, MeO); 7.01 (*s*, 1 arom. H); 7.13 (*s*, 1 arom. H); 10.76 (*s*, OH). ¹³C-NMR (63 MHz): 21.5 (Me); 52.7 (MeO); 120.4 (*q*, ³*J* = 7, CH); 122.0 (CH); 123.1 (*q*, ¹*J* = 274, CF₃); 130.1 (*q*, ²*J* = 32, CCF₃); 145.1 (C); 147.3 (C); 162.0 (COH); 169.7 (CO). ¹⁹F-NMR (235 MHz): –58.8 (CF₃). EI-MS (70 eV): 234 (31, *M*⁺), 202 (100). Anal. calc. for C₁₀H₉F₃O₃ (234.17): C 51.29, H 3.87; found: C 50.93, H 4.24.

Methyl 2-Hydroxy-3,4-dimethyl-6-(trifluoromethyl)benzoate (5b). Starting with **3a** (0.226 g, 1.0 mmol), **4b** (0.549 g, 2.0 mmol), and TiCl₄ (0.1 ml, 1.0 mmol) in CH₂Cl₂ (2 ml), **5b** was isolated as a white solid (0.120 g, 48%). M.p. 56–58°. *R*_f (heptanes/AcOEt 3:2) 0.80. IR (ATR): 3030*w*, 2970*w*, 2861*w*, 1660*s*, 1612*w*, 1439*w*, 1390*m*, 1341*m*, 1125*m*, 1099*m*, 933*m*, 809*m*, 707*s*. ¹H-NMR (300 MHz): 2.22 (*s*, Me); 2.33 (*s*, Me); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.08 (*s*, OH). ¹³C-NMR (100 MHz): 11.9, 20.5 (2 Me); 52.7 (MeO); 107.7 (C); 120.4 (*q*, ³*J* = 6.7, CH); 123.6 (*q*, ¹*J* = 271.0, CF₃); 126.8 (*q*, ²*J* = 31.5, CCF₃); 129.7,

142.9 (C); 160.0 (COH); 170.3 (CO). ^{19}F -NMR (282 MHz): -58.2 (CF_3). EI-MS (70 eV): 248 (30, M^+), 217 (16), 216 (40), 197 (11), 196 (100). Anal. calc. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_3$ (248.07): C 53.23, H 4.47; found: C 53.31, H 4.50.

Methyl 3-(3-Chloropropyl)-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5c). Starting with **3a** (0.226 g, 1.0 mmol), **4c** (0.674 g, 2.0 mmol), and TiCl_4 (0.1 ml, 1.0 mmol) in CH_2Cl_2 (2 ml), **5c** was isolated as a white solid (0.152 g, 49%). M.p. $56-58^\circ$. R_f (heptanes/AcOEt 3:2) 0.78. IR (ATR): 2958w, 1660s, 1613w, 1439m, 1394w, 1341w, 1239w, 1126w, 959w, 815w, 728s. ^1H -NMR (300 MHz): 1.98–2.05 (m, CH_2); 2.05 (s, Me); 2.86 (t, $J = 7.8$, CH_2Ar); 3.60 (t, $J = 6.4$, CH_2Cl); 3.96 (s, MeO); 7.12 (s, 1 arom. H); 11.12 (s, OH). ^{13}C -NMR (75 MHz): 20.0 (Me); 24.0, 31.1, 45.0 (3 CH_2); 52.7 (MeO); 108.0 (C); 120.9 (q , $^3J = 6.7$, CH); 123.4 (q , $^1J = 271.0$, CF_3); 127.5 (q , $^2J = 31.7$, CCF₃); 132.4, 142.9 (C); 160.1 (COH); 170.2 (CO). ^{19}F -NMR (282 MHz): -58.3 (CF_3). EI-MS (70 eV): 310 (15, M^+), 244 (13), 243 (100), 216 (17), 215 (14), 196 (17). Anal. calc. for $\text{C}_{13}\text{H}_{14}\text{ClF}_3\text{O}_3$ (310.70): C 50.25, H 4.54; found: C 50.49, H 4.72.

Methyl 3-Butyl-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5d). Starting with **3a** (0.975 g, 4.31 mmol), **4d** (1.500 g, 4.74 mmol), and TiCl_4 (0.52 ml, 4.7 mmol) in CH_2Cl_2 (5 ml), **5d** was isolated as a colorless liquid (0.611 g, 49%). IR (neat): 3657m, 2970m, 2929m, 2868m, 1928s, 1674m, 1612m, 1576m, 1440m, 1382s, 1342w, 1305w, 1236w, 1194m, 1141w, 1046w, 1005w, 974w, 935w, 873w, 841w, 812s, 751m, 710m, 677m, 659m, 582m, 553m, 540s. ^1H -NMR (300 MHz): 0.95 (t, $J = 7.1$, Me), 1.35–1.54 (m, 2 CH_2); 2.36 (s, Me); 2.69 (t, $J = 7.6$, CH_2Ar); 3.96 (s, MeO); 7.10 (s, 1 arom. H); 11.02 (s, OH). ^{13}C -NMR (75 MHz): 14.3 (Me); 20.3 (MeAr); 23.4, 26.7, 30.9 (3 CH_2); 53.0 (MeO); 108.3 (C); 121.1 (q , $^3J = 6.4$, CH); 123.9 (q , $^1J = 273.3$, CF_3); 127.3 (q , $^2J = 28.3$, CCF₃); 134.8 (C), 142.8 (C); 160.4 (COH); 170.7 (CO). ^{19}F -NMR (282 MHz): -58.2 (CF_3). EI-MS (70 eV): 291 (6, M^+), 290 (37), 259 (12), 258 (10), 244 (13), 243 (100), 241 (17), 229 (18), 217 (8), 216 (69), 215 (44), 197 (7), 196 (62), 187 (9), 159 (9), 109 (9). HR-EI-MS (70 eV): 290.1122 (M^+ , $\text{C}_{14}\text{H}_{17}\text{F}_3\text{O}_3^+$; calc. 290.1130).

Methyl 3-Hexyl-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5e). Starting with **3a** (0.226 g, 1.0 mmol), **4e** (0.689 g, 2.0 mmol), and TiCl_4 (0.1 ml, 1.0 mmol) in CH_2Cl_2 (2 ml), **5e** was isolated as a slightly yellow solid (0.100 g, 31%). M.p. $40-41^\circ$. R_f (hexane/ CH_2Cl_2 3:2) 0.88. IR (ATR): 2952w, 2924m, 2855w, 1660s, 1613w, 1439m, 1342m, 1305m, 1127m, 955s, 884m, 814m, 711s. ^1H -NMR (300 MHz): 0.89 (t, $J = 6.9$, Me); 1.25–1.52 (m, 4 CH_2); 2.35 (s, Me); 2.68 (t, $J = 7.8$, CH_2Ar); 3.95 (s, MeO); 7.10 (s, 1 arom. H); 11.01 (s, OH). ^{13}C -NMR (75 MHz): 14.1, 20.0 (2 Me); 22.6, 26.6, 28.4, 29.6, 31.7 (5 CH_2); 52.6 (MeO); 107.9 (C); 120.7 (q , $^3J = 6.7$, CH); 123.6 (q , $^1J = 271.2$, CF_3); 126.8 (q , $^2J = 31.5$, CCF₃); 134.4, 142.4 (C); 160.0 (COH); 170.3 (CO). ^{19}F -NMR (282 MHz): -58.2 (CF_3). EI-MS (70 eV): 318 (26, M^+), 272 (15), 271 (100), 229 (13), 216 (66), 215 (44), 196 (46). Anal. calc. for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{O}_3$ (318.33): C 60.37, H 6.65; found: C 60.44, H 6.66.

Methyl 3-(6-Chlorohexyl)-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5f). Starting with **3a** (0.814 g, 3.60 mmol), **4f** (1.500 g, 3.96 mmol), and TiCl_4 (0.43 ml, 4.0 mmol) in CH_2Cl_2 (5 ml), **5f** was isolated as a colorless oil (0.633 g, 50%). IR (neat): 3640w, 2945m, 2852m, 1936s, 1673m, 1612m, 1576s, 1440m, 1383s, 1340s, 1291w, 1236w, 1194s, 1140w, 1099w, 1047s, 975m, 936m, 874m, 843m, 813m, 729m, 710m, 677m, 654m, 582m, 555m, 540s. ^1H -NMR (300 MHz): 1.36–1.57 (m, 3 CH_2); 1.77, 1.81 (tt, $J = 6.9$, 6.7, CH_2); 2.36 (s, Me); 2.69 (t, $J = 7.6$, CH_2Ar); 3.54 (t, $J = 6.7$, CH_2Cl); 3.96 (s, MeO); 7.11 (s, 1 arom. H); 11.03 (s, OH). ^{13}C -NMR (75 MHz): 20.3 (MeAr); 26.8, 27.1, 28.5, 29.5, 32.9, 45.4 (6 CH_2); 53.0 (MeO); 108.3 (C); 121.1 (q , $J = 6.8$, CH); 123.9 (q , $^1J = 272.8$, CF_3); 127.3 (q , $^2J = 31.7$, CCF₃); 134.5 (C); 142.8 (C); 160.4 (COH); 170.7 (CO). ^{19}F -NMR (282 MHz): -58.3 (CF_3). EI-MS (70 eV): 355 (2, M^+ , ^{37}Cl), 353 (5, M^+ , ^{35}Cl), 352 (26), 320 (16), 307 (22), 306 (11), 305 (67), 285 (32), 243 (11), 229 (14), 217 (12), 216 (100), 215 (54), 197 (7), 196 (59), 187 (10), 159 (8). HR-EI-MS (70 eV): 352.1041 (M^+ , $\text{C}_{16}\text{H}_{20}\text{ClF}_3\text{O}_3^+$; calc. 352.1048). Anal. calc. for $\text{C}_{16}\text{H}_{20}\text{ClF}_3\text{O}_3$ (352.78): C 54.47, H 5.71; found: C 54.4, H 5.93.

Methyl 3-Heptyl-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5g). Starting with **3a** (0.860 g, 3.80 mmol), **4g** (1.500 g, 4.18 mmol), and TiCl_4 (0.46 ml, 4.2 mmol) in CH_2Cl_2 (5 ml), **5g** was isolated as a white solid (0.600 g, 47%). M.p. $47-48^\circ$. IR (KBr): 3452w, 2958w, 2921w, 2848w, 1663w, 1614s, 1578m, 1473m, 1463m, 1440m, 1396s, 1347m, 1311m, 1294m, 1272m, 1243m, 1203m, 1190m, 1162s, 1135s, 1050m, 1002m, 985m, 961m, 936m, 909m, 885m, 844m, 816m, 795s, 773m, 735m, 712m, 678m, 658m, 556s, 538m, 485s. ^1H -NMR (300 MHz): 0.89 (t, $J = 6.8$, Me); 1.29–1.55 (m, 5 CH_2); 2.36 (s, Me); 2.68 (t, $J = 7.8$, CH_2Ar); 3.96 (s, MeO); 7.10 (s, CH); 11.02 (s, OH). ^{13}C -NMR (75 MHz): 14.4 (Me); 20.3 (MeAr); 23.0,

27.0, 28.8, 29.5, 30.3, 32.2 (6 CH₂); 53.0 (MeO); 108.3 (C); 121.1 (*q*, ³*J* = 6.8, CH); 123.9 (*q*, ¹*J* = 272.7, CF₃); 127.2 (*q*, ²*J* = 31.8, CCF₃); 134.8 (C); 142.8 (C); 160.4 (COH); 170.7 (CO). ¹⁹F-NMR (282 MHz): – 58.2 (CF₃). EI-MS (70 eV): 333 (5, *M*⁺), 332 (26), 301 (10), 286 (17), 285 (100), 283 (10), 243 (9), 229 (14), 216 (68), 215 (42), 196 (46), 187 (7). HR-EI-MS (70 eV): 332.1597 (*M*⁺, C₁₇H₂₃F₃O₃⁺; calc. 332.1599). Anal. calc. for C₁₇H₂₃F₃O₃ (332.36): C 61.43, H 6.98; found: C 61.2, H 6.90.

Methyl 2-Hydroxy-4-methyl-3-octyl-6-(trifluoromethyl)benzoate (5h). Starting with **3a** (0.226 g, 1.0 mmol), **4h** (0.754 g, 2.0 mmol), and TiCl₄ (0.1 ml, 1.0 mmol) in CH₂Cl₂ (2 ml), **5h** was isolated as a slight yellow solid (0.090 g, 26%). M.p. 49–51°. *R*_f (hexane/CH₂Cl₂ 3:2) 0.80. IR (ATR): 2957w, 2923m, 2852w, 1660s, 1613s, 1473s, 1461w, 1439m, 1343m, 1304m, 1128m, 964m, 934m, 814m, 711s. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, Me); 1.26–1.55 (*m*, 6 CH₂); 2.35 (*s*, Me); 2.68 (*t*, *J* = 7.8, CH₂Ar); 3.95 (*s*, MeO); 7.10 (*s*, 1 arom. H); 11.01 (*s*, OH). ¹³C-NMR (75 MHz): 14.1, 20.0 (2 Me); 22.6, 26.6, 28.4, 29.3, 29.4, 30.0, 31.9 (7 CH₂); 52.6 (MeO); 107.9 (C); 120.7 (*q*, ³*J* = 6.7, CH); 123.5 (*q*, ¹*J* = 271.0, CF₃); 126.8 (*q*, ²*J* = 31.7, CCF₃); 134.4, 142.4 (2 C); 160.0 (COH); 170.3 (CO). ¹⁹F-NMR (282 MHz): – 58.2 (CF₃). EI-MS (70 eV): 346 (21, *M*⁺), 300 (17), 299 (100), 229 (12), 216 (63), 215 (41), 196 (40). Anal. calc. for C₁₈H₂₅F₃O₃ (346.38): C 62.41, H 7.27; found: C 62.44, H 7.50.

Methyl 3-Benzyl-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5j). Starting with **3a** (0.453 g, 2.0 mmol), **4j** (0.771 g, 2.2 mmol), and TiCl₄ (0.24 ml, 2.2 mmol) in CH₂Cl₂ (5 ml), **5j** was isolated as a colorless solid (0.444 g, 68%). M.p. 57–58°. IR (neat): 3644m, 3076m, 3023m, 2950m, 2852m, 1932s, 1672m, 1612s, 1577m, 1497m, 1440m, 1396m, 1383s, 1344s, 1302w, 1236w, 1194m, 1140w, 1088w, 1068w, 1030w, 962w, 936w, 907w, 875w, 843w, 813s, 745m, 700m, 659m, 621m, 579m, 540m, 494s. ¹H-NMR (300 MHz): 2.34 (*s*, Me); 3.97 (*s*, MeO); 4.12 (*s*, CH₂); 7.14–7.27 (*m*, 6 arom. H); 11.12 (*s*, OH). ¹³C-NMR (75 MHz): 20.8 (*MeAr*); 32.2 (CH₂); 53.2 (MeO); 108.7 (C); 121.3 (*q*, ³*J* = 6.7, CH); 123.8 (*q*, ¹*J* = 273.3, CF₃); 127.8 (*q*, ²*J* = 30.6, CCF₃); 126.5, 128.5, 128.8, 139.3 (Ph); 132.4 (C); 144.1 (C); 160.5 (COH); 170.6 (CO). ¹⁹F-NMR (282 MHz): – 58.3 (CF₃). EI-MS (70 eV): 325 (11, *M*⁺), 324 (61), 304 (11), 293 (34), 292 (100), 291 (23), 284 (23), 272 (50), 271 (30), 269 (49), 264 (56), 263 (43), 244 (10), 215 (21), 201 (15), 195 (12), 165 (25), 152 (10). HR-EI-MS (70 eV): 324.0964 (*M*⁺, C₁₇H₁₅F₃O₃⁺; calc. 324.0973). Anal. calc. for C₁₇H₁₅F₃O₃ (324.29): C 62.96, H 4.66; found: C 63.4, H 4.72.

Methyl 2-Hydroxy-4-methyl-3-(2-phenylethyl)-6-(trifluoromethyl)benzoate (5k). Starting with **3a** (0.226 g, 1.0 mmol), **4k** (0.729 g, 2.0 mmol), and TiCl₄ (0.1 ml, 1.0 mmol) in CH₂Cl₂ (2 ml), **5k** was isolated as a white solid (0.145 g, 43%). M.p. 70–71°. *R*_f (hexane/CH₂Cl₂ 3:2) 0.68. IR (ATR): 3086w, 3026w, 2949w, 2857w, 1673m, 1604m, 1494w, 1440m, 1309s, 1231m, 1121s, 949s, 878m, 695s. ¹H-NMR (300 MHz): 2.21 (*s*, Me); 2.80 (*t*, *J* = 7.8, CH₂); 2.99 (*t*, *J* = 8.1, CH₂); 3.97 (*s*, MeO); 7.08 (*s*, 1 arom. H); 7.18–7.31 (*m*, 5 arom. H); 11.15 (*s*, OH). ¹³C-NMR (75 MHz): 19.9 (Me); 29.0, 34.4 (2 CH₂); 52.7 (MeO); 108.0 (C); 120.7 (*q*, ³*J* = 6.4, CH); 123.5 (*q*, ¹*J* = 271.1, CF₃); 126.0 (Ph); 127.2 (*q*, ²*J* = 31.5, CCF₃); 128.4, 128.5 (Ph); 133.1, 141.8, 142.8 (3 C); 160.2 (COH); 170.3 (CO). ¹⁹F-NMR (282 MHz): – 58.2 (CF₃). EI-MS (70 eV): 338 (21, *M*⁺), 306 (21), 247 (22), 216 (11), 215 (100), 91 (44). Anal. calc. for C₁₈H₁₇F₃O₃ (338.32): C 63.90, H 5.06; found: C 64.06, H 5.01.

Methyl 2-Hydroxy-4-methyl-3-(3-phenylpropyl)-6-(trifluoromethyl)benzoate (5l). Starting with **3a** (0.453 g, 2.0 mmol), **4l** (0.833 g, 2.2 mmol), and TiCl₄ (0.24 ml, 2.2 mmol) in CH₂Cl₂ (5 ml), **5l** was isolated as a colorless oil (0.479 g, 68%). IR (neat): 3644m, 3076m, 3023m, 2950m, 2852m, 1932s, 1672m, 1612s, 1577m, 1497m, 1440m, 1396m, 1383s, 1344s, 1302w, 1236w, 1194m, 1140w, 1088w, 1068w, 1030w, 962w, 936w, 907w, 875w, 843w, 813s, 745m, 700m, 659m, 621m, 579m, 540m, 494s. ¹H-NMR (300 MHz): 1.84, 1.88 (*tt*, *J* = 7.8, CH₂CH₂CH₂); 2.29 (*s*, Me); 2.75 (*t*, *J* = 8.2, 2 CH₂Ar); 3.97 (*s*, MeO); 7.11 (*s*, 1 arom. H); 7.18–7.31 (*m*, 5 arom. H); 11.06 (*s*, OH). ¹³C-NMR (75 MHz): 20.2 (*MeAr*); 26.6, 30.1, 36.4 (3 CH₂); 53.0 (MeO); 108.3 (C); 121.1 (*q*, ³*J* = 6.7, CH); 123.9 (*q*, ¹*J* = 272.9, CF₃); 127.4 (*q*, ²*J* = 31.7, CCF₃); 126.2, 128.6, 128.7 (Ph); 134.2 (C); 142.4 (C); 142.9 (C); 160.4 (COH); 170.6 (CO). ¹⁹F-NMR (282 MHz): – 58.2 (CF₃). EI-MS (70 eV): 353 (9, *M*⁺), 352 (42), 321 (13), 320 (15), 229 (12), 228 (10), 217 (11), 216 (100), 215 (18), 208 (32), 196 (64), 193 (15), 105 (18), 91 (21). HR-EI-MS (70 eV): 352.1277 (*M*⁺, C₁₉H₁₉F₃O₃⁺; calc. 352.1281). Anal. calc. for C₁₉H₁₉F₃O₃ (352.35): C 64.77, H 5.44; found: C 64.9, H 5.52.

Ethyl 2-Hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5m). Starting with **3a** (0.453 g, 2.2 mmol), **4m** (0.659 g, 2.4 mmol), and TiCl₄ (0.26 ml, 2.4 mmol) in CH₂Cl₂ (5 ml), **5m** was isolated as a colorless solid (0.220 g, 40%). M.p. 28°. IR (Nujol): 1672 (ν(C=O)). ¹H-NMR (300 MHz): 1.41 (*t*, *J* = 7.6,

MeCH₂O); 2.38 (s, Me); 4.43 (*q*, *J* = 7.2, *MeCH₂O*); 7.01 (s, CH); 7.13 (s, CH); 10.90 (s, OH). ¹³C-NMR (63 MHz): 13.4 (*MeCH₂*); 21.5 (Me); 62.3 (CH₂); 108.6 (C); 120.4 (*q*, ³*J* = 7, CH); 122.0 (CH); 123.2 (*q*, ¹*J* = 275, CF₃); 130.1 (*q*, ²*J* = 34, CCF₃); 145.0 (C); 162.1 (COH); 169.3 (CO). ¹⁹F-NMR (282 MHz): – 58.0 (CF₃). EI-MS (70 eV): 248 (16, *M*⁺), 202 (100). Anal. calc. for C₁₁H₁₁F₃O₃ (248.20): C 53.23, H 4.47; found: C 52.85, H 4.69.

Ethyl 2-Hydroxy-3,4-dimethyl-6-(trifluoromethyl)benzoate (5n). Starting with **3a** (0.453 g, 2.2 mmol), **4n** (0.692 g, 2.4 mmol), and TiCl₄ (0.26 ml, 2.4 mmol) in CH₂Cl₂ (5 ml), **5n** was isolated as a colorless oil (0.430 g, 75%). IR (Nujol): 1669 (*ν*(C=O)). ¹H-NMR (250 MHz): 1.40 (*t*, *J* = 7.6, *MeCH₂O*); 2.21 (s, Me); 2.33 (s, Me); 4.43 (*q*, *J* = 7.2, *MeCH₂O*); 7.11 (s, CH); 11.21 (s, OH). ¹³C-NMR (63 MHz): 11.9 (*MeAr*); 13.5 (*MeAr*); 20.5 (*MeCH₂O*); 62.3 (CH₂O); 108.0 (*q*, ³*J* = 2, C); 120.4 (*q*, *J* = 7, CH); 123.6 (*q*, ¹*J* = 274, CF₃); 126.8 (*q*, ²*J* = 32, CCF₃); 129.7 (C); 142.8 (C); 160.1 (COH); 169.9 (CO). ¹⁹F-NMR (235 MHz): – 57.7 (CF₃). EI-MS (70 eV): 262 (29, *M*⁺), 216 (55). HR-EI-MS (70 eV): 262.0809 (*M*⁺, C₁₂H₁₃F₃O₃⁺; calc. 262.0817). Anal. calc. for C₁₂H₁₃F₃O₃ (262.23): C 54.96, H 5.00; found: C 54.46, H 4.99.

Ethyl 3-Ethyl-2-hydroxy-4-methyl-6-(trifluoromethyl)benzoate (5o). Starting with **3a** (0.453 g, 2.2 mmol), **4o** (0.726 g, 2.4 mmol), and TiCl₄ (0.26 ml, 2.4 mmol) in CH₂Cl₂ (5 ml), **5o** was isolated as a colorless oil (0.435 g, 72%). IR (Nujol): 1669 (*ν*(C=O)). ¹H-NMR (250 MHz): 1.13 (*t*, *J* = 7.5, *MeCH₂Ar*); 1.40 (*t*, *J* = 7.5, *MeCH₂O*); 2.36 (s, Me); 2.73 (*q*, *J* = 7.4, *MeCH₂Ar*); 4.42 (*q*, *J* = 7.2, *MeCH₂O*); 7.10 (s, CH); 11.16 (s, OH). ¹³C-NMR (63 MHz): 12.6 (*MeCH₂*); 13.5 (*MeCH₂O*); 19.6 (*MeAr*); 62.3 (CH₂O); 108.3 (C); 120.7 (*q*, ³*J* = 7, CH); 123.5 (*q*, ¹*J* = 272, CF₃); 126.8 (*q*, ²*J* = 32, CCF₃); 135.5 (C); 142.0 (C); 160.0 (COH); 169.9 (CO). ¹⁹F-NMR (235 MHz): – 57.7 (CF₃). EI-MS (70 eV): 276 (39, *M*⁺), 230 (86). HR-EI-MS (70 eV): 276.0958 (*M*⁺, C₁₃H₁₅F₃O₃⁺; calc. 276.0973).

1-[2-Hydroxy-4-methyl-6-(trifluoromethyl)phenyl]ethanone (5p). Starting with **3a** (0.453 g, 2.2 mmol), **4p** (0.587 g, 2.4 mmol), and TiCl₄ (0.26 ml, 2.4 mmol) in CH₂Cl₂ (5 ml), **5p** was isolated as a colorless solid (0.290 g, 60%). M.p. 120–121°. IR (Nujol): 3311 (*ν*(OH)), 1687 (*ν*(C=O)). ¹H-NMR (250 MHz): 2.37 (s, Me); 2.62 (*q*, *J* = 1.8, COMe); 6.98 (s, CH); 7.07 (s, CH); 10.04 (s, OH). ¹³C-NMR (63 MHz): 21.5 (Me); 31.4 (*q*, *J* = 6, COMe); 118.9 (*q*, ³*J* = 2, C); 119.9 (*q*, ³*J* = 6, CH); 122.3 (CH); 123.7 (*q*, ¹*J* = 274, CF₃); 128.7 (*q*, ²*J* = 30, CCF₃); 144.3 (C); 158.8 (COH); 204.9 (CO). ¹⁹F-NMR (235 MHz): – 55.3 (CF₃). EI-MS (70 eV): 218 (24, *M*⁺), 203 (100). HR-EI-MS (70 eV): 218.0545 (*M*⁺, C₁₀H₉F₃O₂⁺; calc. 218.0555).

Methyl 4-Heptyl-2-hydroxy-6-(trifluoromethyl)benzoate (5q). Starting with **3b** (0.458 g, 1.48 mmol), **4a** (0.430 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5q** was isolated as a red solid (0.308 g, 66%). M.p. 35–36°. IR (ATR): 2958*m*, 2855*w*, 1679*m*, 1620*m*, 1580*m*, 1487*m*, 1461*w*, 1441*w*, 1362*w*, 1338*w*, 1286*w*, 1204*m*, 1170*m*, 1127*s*, 1026*w*, 1004*m*. ¹H-NMR (250 MHz): 0.88 (*t*, *J* = 6.9, *MeC₆H₁₂*); 1.18–1.41 (*m*, 4 CH₂); 1.51–1.72 (*m*, CH₂CH₂Ar); 2.62 (*t*, *J* = 7.7, CH₂Ar); 3.97 (s, MeO); 7.01 (s, 1 arom. H); 7.13 (s, 1 arom. H); 10.76 (s, OH). ¹³C-NMR (75 MHz): 14.0 (*MeCH₂*); 22.6 (CH₂); 29.0 (CH₂); 29.1 (CH₂); 30.4 (CH₂); 31.7 (CH₂); 35.9 (CH₂Ar); 52.7 (MeO); 108.4 (*q*, ³*J* = 1.2, CCO₂Me); 119.8 (*q*, ³*J* = 6.7, CHCCF₃); 121.3 (CHCOH); 123.4 (*q*, ¹*J* = 273.7, CF₃); 130.1 (*q*, ²*J* = 31.7, CCF₃); 150.1 (CC₇H₁₅); 162.0 (COH); 169.7 (CO). ¹⁹F-NMR (282 MHz): – 58.8 (CF₃). EI-MS (70 eV): 318 (17, *M*⁺), 286 (28), 215 (13), 202 (100), 173 (10). HR-EI-MS (70 eV): 318.1436 (*M*⁺, C₁₆H₂₁F₃O₃⁺; calc. 318.1443). Anal. calc. for C₁₆H₂₁F₃O₃ (318.33): C 60.37, H 6.65; found: C 60.48, H 6.67.

Methyl 4-Heptyl-2-hydroxy-3-methyl-6-(trifluoromethyl)benzoate (5r). Starting with **3b** (0.466 g, 1.50 mmol), **4b** (0.453 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5r** was isolated as a pale red oil (0.322 g, 65%). IR (ATR): 2956*w*, 2927*m*, 2857*w*, 1671*m*, 1611*m*, 1578*w*, 1440*w*, 1400*w*, 1329*m*, 1280*s*, 1245*s*, 1232*s*, 1194*m*, 1134*s*, 1077*s*, 1012*m*. ¹H-NMR (300 MHz): 0.89 (*t*, *J* = 6.9, *MeC₆H₁₂*); 1.22–1.40 (*m*, 4 CH₂); 1.49–1.62 (*m*, CH₂CH₂Ar); 2.24 (s, Me); 2.64 (*t*, *J* = 7.9, CH₂Ar); 3.96 (s, MeO); 7.10 (s, 1 arom. H); 11.10 (s, OH). ¹³C-NMR (125 MHz): 11.6 (*MeAr*); 14.0 (*MeCH₂*); 22.6 (CH₂); 29.1 (CH₂); 29.5 (CH₂); 30.0 (CH₂); 31.8 (CH₂); 34.1 (CH₂Ar); 52.6 (MeO); 107.6 (CCO₂Me); 119.7 (*q*, ³*J* = 6.7, CHCCF₃); 123.7 (*q*, ¹*J* = 273.4, CF₃); 126.9 (*q*, ²*J* = 31.7, CCF₃); 129.3 (CMe); 147.5 (CC₇H₁₅); 160.4 (COH); 170.3 (CO). ¹⁹F-NMR (282 MHz): – 58.6 (CF₃). EI-MS (70 eV): 332 (34, *M*⁺), 300 (100), 229 (74), 216 (86), 187 (16). HR-EI-MS (70 eV): 332.1595 (*M*⁺, C₁₇H₂₃F₃O₃⁺; calc. 332.1599).

Methyl 3-Ethyl-4-heptyl-2-hydroxy-6-(trifluoromethyl)benzoate (5s). Starting with **3b** (0.480 g, 1.55 mmol), **4q** (0.476 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5s** was isolated

as a pale red oil (0.351 g, 66%). IR (ATR): 2957w, 2928m, 2873, 2857w, 1671m, 1609w, 1439m, 1400w, 1337m, 1292s, 1247s, 1228s, 1194m, 1136s, 1111s, 1062m. $^1\text{H-NMR}$ (300 MHz): 0.89 (*t*, $J = 7.0$, $\text{MeC}_6\text{H}_{12}$); 1.15 (*t*, $J = 7.5$, MeCH_2Ar); 1.22–1.44 (*m*, 4 CH_2); 1.50–1.64 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.60–2.68 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.73 (*q*, $J = 7.5$, MeCH_2Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). $^{13}\text{C-NMR}$ (63 MHz): 13.5 (MeCH_2); 14.0 (MeCH_2); 19.5 (CH_2); 22.6 (CH_2); 29.1 (CH_2); 29.6 (CH_2); 30.9 (CH_2); 31.7 (CH_2); 33.3 (CH_2Ar); 52.6 (MeO); 107.8 (CCOOMe); 120.0 (*q*, $^3J = 6.7$, CHCCF_3); 123.6 (*q*, $^1J = 272.7$, CF_3); 127.0 (*q*, $^2J = 31.7$, CCF_3); 135.1 (CC_7H_{15}); 146.9 (CC_7H_{15}); 160.2 (COH); 170.3 (CO). $^{19}\text{F-NMR}$ (282 MHz): –58.6 (CF_3). EI-MS (70 eV): 346 (25, M^+), 314 (70), 285 (11), 243 (100), 230 (19). HR-EI-MS (70 eV): 346.1751 (M^+ , $\text{C}_{18}\text{H}_{25}\text{F}_3\text{O}_3^+$; calc. 346.1756).

Methyl 4-Heptyl-2-hydroxy-3-propyl-6-(trifluoromethyl)benzoate (5t). Starting with **3b** (0.489 g, 1.58 mmol), **4r** (0.499 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5t** was isolated as a yellow oil (0.321 g, 57%). IR (ATR): 2957w, 2927m, 2872m, 2857w, 1671m, 1610m, 1573m, 1456w, 1439w, 1399w, 1334w, 1302m, 1283s, 1222s, 1193m, 1135s, 1091m. $^1\text{H-NMR}$ (300 MHz): 0.89 (*t*, $J = 7.0$, $\text{MeC}_6\text{H}_{12}$); 1.01 (*t*, $J = 7.4$, $\text{MeCH}_2\text{CH}_2\text{Ar}$); 1.24–1.41 (*m*, 4 CH_2); 1.50–1.62 (*m*, 2 $\text{H}_2\text{CH}_2\text{Ar}$); 2.59–2.71 (*m*, 2 CH_2Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). $^{13}\text{C-NMR}$ (75 MHz): 14.1 (MeCH_2); 14.5 (MeCH_2); 22.5 (CH_2); 22.6 (CH_2); 28.3 (CH_2); 29.1 (CH_2); 29.6 (CH_2); 30.9 (CH_2); 31.7 (CH_2); 33.4 (CH_2); 52.6 (MeO); 107.7 (CCOOMe); 119.9 (*q*, $^3J = 6.7$, CHCCF_3); 123.6 (*q*, $^1J = 272.7$, CF_3); 127.0 (*q*, $^2J = 31.6$, CCF_3); 133.8 (CC_7H_7); 147.2 (CC_7H_{15}); 160.4 (COH); 170.4 (CO). $^{19}\text{F-NMR}$ (282 MHz): –58.6 (CF_3). EI-MS (70 eV): 360 (25, M^+), 328 (78), 285 (8), 257 (100), 229 (18). HR-EI-MS (70 eV): 360.1908 (M^+ , $\text{C}_{19}\text{H}_{27}\text{F}_3\text{O}_3^+$; calc. 360.1912). Anal. calc. for $\text{C}_{19}\text{H}_{27}\text{F}_3\text{O}_3$ (360.41): C 63.32, H 7.55; found: C 63.40, H 7.52.

1-[4-Heptyl-2-hydroxy-6-(trifluoromethyl)phenyl]ethanone (5u). Starting with **3b** (0.478 g, 1.54 mmol), **4p** (0.403 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5u** was isolated as a pale red solid (0.371 g, 80%). M.p. 82–83°. IR (ATR): 3331w, 2958w, 2927m, 2857w, 1688w, 1615m, 1586m, 1464w, 1435w, 1356w, 1323w, 1280w, 1265w, 1234w, 1191w, 1158m, 1143m, 1120s, 1023m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.9$, $\text{MeC}_6\text{H}_{12}$); 1.21–1.38 (*m*, 4 CH_2); 1.55–1.68 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.57–2.65 (*m*, CH_2Ar , COMe); 6.98 (*s*, 1 arom. H); 7.07 (*s*, 1 arom. H); 10.04 (*s*, OH). $^{13}\text{C-NMR}$ (75 MHz): 14.0 (MeCH_2); 22.6 (CH_2); 29.0 (CH_2); 29.1 (CH_2); 30.5 (CH_2); 31.4 (*q*, $^5J = 5.4$, COMe); 31.7 (CH_2); 35.8 (CH_2); 119.1 (CCOMe); 119.3 (*q*, $^3J = 5.8$, CHCCF_3); 121.5 (COHCH); 123.8 (*q*, $^1J = 273.6$, CF_3); 128.7 (*q*, $^2J = 31.1$, CCF_3); 149.3 (CC_7H_{15}); 158.7 (COH); 204.8 (CO). $^{19}\text{F-NMR}$ (282 MHz): –55.4 (CF_3). EI-MS (70 eV): 302 (13, M^+), 287 (100), 218 (10). HR-EI-MS (70 eV): 302.1488 (M^+ , $\text{C}_{16}\text{H}_{21}\text{F}_3\text{O}_2^+$; calc. 302.1494). Anal. calc. for $\text{C}_{16}\text{H}_{21}\text{F}_3\text{O}_2$ (302.33): C 63.56, H 7.00; found: C 63.30, H 7.20.

Methyl 4-Heptyl-2-hydroxy-3-methoxy-6-(trifluoromethyl)benzoate (5v). Starting with **3b** (0.441 g, 1.42 mmol), **4s** (0.479 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5v** was isolated as a red oil (0.297 g, 60%). IR (ATR): 2956w, 2927m, 2857m, 1746w, 1673m, 1609m, 1574w, 1441w, 1412w, 1363w, 1328w, 1274w, 1262w, 1197w, 1178m, 1133s, 1063m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.7$, $\text{MeC}_6\text{H}_{12}$); 1.20–1.40 (*m*, 4 CH_2); 1.50–1.67 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.65 (*t*, $J = 7.8$, CH_2Ar); 3.91 (*s*, MeO); 3.97 (*s*, MeO); 7.12 (*s*, 1 arom. H); 10.63 (*s*, OH). $^{13}\text{C-NMR}$ (75 MHz): 14.0 (MeCH_2); 22.6 (CH_2); 29.1 (CH_2); 29.4 (CH_2); 30.1 (CH_2); 30.2 (CH_2); 31.7 (CH_2); 52.8 (MeO); 60.6 (MeO); 110.4 (CCOOMe); 120.1 (*q*, $^3J = 6.7$, CHCCF_3); 123.4 (*q*, $^1J = 272.7$, CF_3); 124.3 (*q*, $^2J = 32.0$, CCF_3); 140.9 (COMe); 149.2 (CC_7H_{15}); 155.0 (COH); 169.6 (CO). $^{19}\text{F-NMR}$ (282 MHz): –58.4 (CF_3). EI-MS (70 eV): 348 (28, M^+), 316 (100), 245 (89), 225 (180), 204 (14). HR-EI-MS (70 eV): 348.1543 (M^+ , $\text{C}_{17}\text{H}_{23}\text{F}_3\text{O}_4^+$; calc. 348.1548). Anal. calc. for $\text{C}_{17}\text{H}_{23}\text{F}_3\text{O}_4$ (348.36): C 58.61, H 6.65; found: C 58.55, H 6.76.

Ethyl 4-(7-Chloroheptyl)-2-hydroxy-6-(trifluoromethyl)benzoate (5w). Starting with **3c** (0.650 g, 1.88 mmol), **4m** (1.035 g, 3.77 mmol), and TiCl_4 (0.21 ml, 1.88 mmol) in CH_2Cl_2 (4 ml), **5w** was isolated as a colorless solid (0.303 g, 44%). IR (Nujol): 1689w, 1621m, 1577w, 1488w, 1402w, 1326w, 1310w, 1287w, 1215m, 1173m, 1142m, 1128s, 1020s, 1010s, 1001m. $^1\text{H-NMR}$ (300 MHz): 1.29–1.50 (*m*, Me, 3 CH_2); 1.57–1.69 (*m*, CH_2); 1.70–1.83 (*m*, CH_2); 2.62 (*t*, $J = 7.7$, CH_2); 3.53 (*t*, $J = 6.7$, CH_2); 4.43 (*q*, $J = 7.2$, CH_2O); 7.00 (*d*, $^4J = 1.2$, 1 arom. H); 7.12 (*d*, $^4J = 1.2$, 1 arom. H); 10.89 (*s*, OH). $^{13}\text{C-NMR}$ (125 MHz): 13.5 (Me); 26.7 (CH_2); 28.6 (CH_2); 28.9 (CH_2); 30.3 (CH_2); 32.5 (CH_2); 35.8 (CH_2); 45.0 (CH_2); 62.4 (CH_2O); 108.7 (C); 119.7 (*q*, $^3J = 6.7$, CHCCF_3); 121.2 (CH); 123.4 (*q*, $^1J = 273.6$, CF_3); 130.1 (*q*, $^2J = 31.8$, CCF_3); 149.6 (C); 162.2 (COH); 169.2 (CO). $^{19}\text{F-NMR}$ (282 MHz): –58.0 (CF_3). EI-MS

(70 eV): 366 (18, M^+), 320 (29), 285 (12), 215 (13), 202 (100), 173 (16). HR-EI-MS (70 eV): 366.1200 (M^+ , $C_{17}H_{22}ClF_3O_3^+$; calc. 366.1210).

Methyl 2-Hydroxy-4-nonyl-6-(trifluoromethyl)benzoate (5x). Starting with **3d** (0.322 g, 0.95 mmol), **4a** (0.287 g, 1.10 mmol), and $TiCl_4$ (0.12 ml, 1.10 mmol) in CH_2Cl_2 (2 ml), **5x** was isolated as a colorless solid (0.107 g, 32%). M.p. 46–47°. IR (ATR): 2957w, 2918m, 2851w, 1678m, 1620m, 1579m, 1487m, 1461w, 1441w, 1362w, 1339w, 1285m, 1261m, 1220m, 1206w, 1170m, 1126s, 1092s, 1024s, 1002m. 1H -NMR (300 MHz): 0.88 (t, $J = 6.8$, MeC_8H_{16}); 1.21–1.36 (m, 6 CH_2); 1.55–1.67 (m, CH_2CH_2Ar); 2.61 (t, $J = 7.7$, CH_2Ar); 3.96 (s, MeO); 7.01 (s, 1 arom. H); 7.13 (s, 1 arom. H); 10.76 (s, OH). ^{13}C -NMR (75 MHz): 14.1 ($MeCH_2$); 22.7 (CH_2); 29.1 (CH_2); 29.2 (CH_2); 29.3 (CH_2); 29.5 (CH_2); 30.4 (CH_2); 31.9 (CH_2); 35.9 (CH_2Ar); 52.7 (MeO); 108.4 ($CCOOMe$); 119.7 (q, $^3J = 6.7$, $CHCCF_3$); 121.3 ($CHCOH$); 123.4 (q, $^1J = 273.1$, CF_3); 130.1 (q, $^2J = 31.7$, CCF_3); 150.1 (CC_9H_{19}); 162.0 (COH); 169.7 (CO). ^{19}F -NMR (282 MHz): –58.8 (CF_3). EI-MS (70 eV): 346 (34, M^+), 314 (57), 234 (19), 215 (58), 202 (100), 173 (14). HR-EI-MS (70 eV): 346.1757 (M^+ , $C_{18}H_{25}F_3O_3^+$; calc. 346.1756). Anal. calc. for $C_{18}H_{25}F_3O_3$ (346.38): C 62.41, H 7.27; found: C 62.28, H 7.28.

Methyl 2-Hydroxy-3-methyl-4-nonyl-6-(trifluoromethyl)benzoate (5y). Starting with **3d** (0.328 g, 0.97 mmol), **4b** (0.302 g, 1.10 mmol), and $TiCl_4$ (0.12 ml, 1.10 mmol) in CH_2Cl_2 (2 ml), **5y** was isolated as a colorless oil (0.230 g, 66%). M.p. 43–44°. IR (ATR): 2920m, 2851w, 1663m, 1612m, 1581m, 1462m, 1437w, 1401w, 1346w, 1286w, 1257w, 1237m, 1204w, 1190w, 1165w, 1144w, 1127w, 1114m, 1055w. 1H -NMR (300 MHz): 0.88 (t, $J = 6.7$, MeC_8H_{16}); 1.22–1.40 (m, 6 CH_2); 1.49–1.61 (m, CH_2CH_2Ar); 2.24 (s, Me); 2.64 (t, $J = 7.9$, CH_2Ar); 3.96 (s, MeO); 7.10 (s, 1 arom. H); 11.10 (s, OH). ^{13}C -NMR (125 MHz): 11.7 ($MeAr$); 14.1 ($MeCH_2$); 22.7 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 30.0 (CH_2); 31.9 (CH_2); 34.1 (CH_2Ar); 52.7 (MeO); 107.5 ($CCOOMe$); 119.7 (q, $^3J = 6.7$, $CHCCF_3$); 123.6 (q, $^1J = 272.7$, CF_3); 126.9 (q, $^2J = 31.7$, CCF_3); 129.2 (CMe); 147.5 (CC_9H_{19}); 160.4 (COH); 170.3 (CO). ^{19}F -NMR (282 MHz): –58.6 (CF_3). EI-MS (70 eV): 360 (37, M^+), 328 (100), 229 (80), 216 (82), 187 (18). HR-EI-MS (70 eV): 360.1908 (M^+ , $C_{19}H_{27}F_3O_3^+$; calc. 360.1912). Anal. calc. for $C_{19}H_{27}F_3O_3$ (360.41): C 63.32, H 7.55; found: C 63.24, H 7.84.

Methyl 3-Ethyl-2-hydroxy-4-nonyl-6-(trifluoromethyl)benzoate (5z). Starting with **3d** (0.340 g, 1.00 mmol), **4q** (0.317 g, 1.10 mmol), and $TiCl_4$ (0.12 ml, 1.10 mmol) in CH_2Cl_2 (2 ml), **5z** was isolated as a colorless oil (0.224 g, 60%). IR (ATR): 2956w, 2925m, 2855w, 1671m, 1611, 1574w, 1439, 1399, 1336m, 1291s, 1248, 1232, 1193m, 1135s, 1062m. 1H -NMR (300 MHz): 0.89 (t, $J = 6.7$, MeC_8H_{16}); 1.16 (t, $J = 7.5$, $MeCH_2Ar$); 1.22–1.44 (m, 6 CH_2); 1.51–1.63 (m, CH_2CH_2Ar); 2.64 (t, $J = 7.9$, CH_2CH_2Ar); 2.73 (q, $J = 7.5$, $MeCH_2Ar$); 3.96 (s, MeO); 7.11 (s, 1 arom. H); 11.06 (s, OH). ^{13}C -NMR (125 MHz): 13.5 ($MeCH_2$); 14.0 ($MeCH_2$); 19.5 (CH_2); 22.6 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.7 (CH_2); 30.9 (CH_2); 31.9 (CH_2); 33.3 (CH_2Ar); 52.6 (MeO); 107.9 ($CCOOMe$); 120.0 (q, $^3J = 6.6$, $CHCCF_3$); 123.7 (q, $^1J = 272.9$, CF_3); 126.9 (q, $^2J = 31.6$, CCF_3); 135.1 (CC_2H_5); 146.9 (CC_9H_{19}); 160.2 (COH); 170.3 (CO). ^{19}F -NMR (282 MHz): –58.6 (CF_3). EI-MS (70 eV): 374 (26, M^+), 342 (75), 313 (13), 243 (100), 230 (23). HR-EI-MS (70 eV): 374.2063 (M^+ , $C_{20}H_{29}F_3O_3^+$; calc. 374.2069). Anal. calc. for $C_{20}H_{29}F_3O_3$ (374.44): C 64.15, H 7.81; found: C 64.06, H 7.96.

1-[2-Hydroxy-4-nonyl-6-(trifluoromethyl)phenyl]ethanone (5aa). Starting with **3d** (0.326 g, 0.96 mmol), **4p** (0.269 g, 1.10 mmol), and $TiCl_4$ (0.12 ml, 1.10 mmol) in CH_2Cl_2 (2 ml), **5aa** was isolated as a pale orange solid (0.197 g, 62%). M.p. 67–68°. IR (ATR): 3325w, 2923w, 2853w, 1688w, 1615m, 1586m, 1466w, 1435w, 1355w, 1322w, 1268w, 1235w, 1191w, 1158m, 1120s, 1022m. 1H -NMR (300 MHz): 0.88 (t, $J = 6.7$, MeC_8H_{16}); 1.20–1.38 (m, 6 CH_2); 1.55–1.69 (m, CH_2CH_2Ar); 2.57–2.65 (m, CH_2Ar , COMe); 6.98 (s, 1 arom. H); 7.08 (s, 1 arom. H); 10.07 (s, OH). ^{13}C -NMR (75 MHz): 14.1 ($MeCH_2$); 22.6 (CH_2); 29.1 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.4 (CH_2); 30.5 (CH_2); 31.4 (q, $^5J = 5.5$, COMe); 31.8 (CH_2); 35.8 (CH_2); 119.0 (q, $J = 1.6$, COMe); 119.3 (q, $^3J = 5.9$, $CHCCF_3$); 121.6 (COHCH); 123.8 (q, $^1J = 273.6$, CF_3); 128.7 (q, $^2J = 31.2$, CCF_3); 149.3 (CC_9H_{19}); 158.9 (COH); 204.8 (CO). ^{19}F -NMR (282 MHz): –55.4 (CF_3). EI-MS (70 eV): 330 (15, M^+), 315 (100), 218 (14). HR-EI-MS (70 eV): 330.1800 (M^+ , $C_{18}H_{25}F_3O_2^+$; calc. 330.1807). Anal. calc. for $C_{18}H_{25}F_3O_2$ (330.39): C 65.44, H 7.63; found: C 65.42, H 7.60.

Methyl 2-Hydroxy-6-(trifluoromethyl)-4-undecylbenzoate (5ab). Starting with **3e** (0.580 g, 1.58 mmol), **4a** (0.430 g, 1.65 mmol), and $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ab** was isolated as a pale yellow solid (0.230 g, 39%). M.p. 53–54°. IR (ATR): 2957w, 2917w, 2849w, 1680m, 1620m,

1579m, 1487w, 1460w, 1441w, 1362w, 1337w, 1302w, 1286m, 1240w, 1216w, 1205m, 1167m, 1127s, 1092m, 1023w, 1003m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.7$, $\text{MeC}_{10}\text{H}_{20}$); 1.21–1.36 (*m*, 8 CH_2); 1.54–1.68 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.61 (*t*, $J = 7.7$, CH_2Ar); 3.97 (*s*, MeO); 7.01 (*s*, 1 arom. H); 7.13 (*s*, 1 arom. H); 10.76 (*s*, OH). $^{13}\text{C-NMR}$ (75 MHz): 14.1 (MeCH_2); 22.7 (CH_2); 29.1 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 30.4 (CH_2); 31.9 (CH_2); 35.9 (CH_2Ar); 52.7 (MeO); 108.4 (CCOOMe); 119.7 (*q*, $^3J = 6.7$, CHCCF_3); 121.3 (CHCOH); 123.4 (*q*, $^1J = 273.3$, CF_3); 130.1 (*q*, $^2J = 31.7$, CCF_3); 150.1 ($\text{CC}_{11}\text{H}_{23}$); 162.0 (COH); 169.7 (CO). $^{19}\text{F-NMR}$ (282 MHz): -58.8 (CF_3). EI-MS (70 eV): 374 (46, M^+), 342 (46), 234 (32), 215 (90), 202 (100), 189 (14), 173 (20). HR-EI-MS (70 eV): 374.2060 (M^+ , $\text{C}_{20}\text{H}_{29}\text{F}_3\text{O}_3^+$; calc. 374.2069). Anal. calc. for $\text{C}_{20}\text{H}_{29}\text{F}_3\text{O}_3$ (374.44): C 64.15, H 7.81; found: C 64.51, H 7.83.

Methyl 2-Hydroxy-3-methyl-6-(trifluoromethyl)-4-undecylbenzoate (5ac). Starting with **3e** (0.559 g, 1.53 mmol), **4b** (0.453 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ac** was isolated as a colorless solid (0.303 g, 51%). M.p. 49–50°. IR (ATR): 2918w, 2850w, 1663m, 1612m, 1580w, 1461w, 1437w, 1401w, 1346w, 1285w, 1245w, 1229w, 1205w, 1190w, 1165w, 1143m, 1128s, 1114s, 1062s, 1012m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.7$, $\text{MeC}_{10}\text{H}_{20}$); 1.21–1.39 (*m*, 8 CH_2); 1.48–1.62 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.24 (*s*, Me); 2.64 (*t*, $J = 7.9$, CH_2Ar); 3.96 (*s*, MeO); 7.10 (*s*, 1 arom. H); 11.11 (*s*, OH). $^{13}\text{C-NMR}$ (125 MHz): 11.7 (MeAr); 14.1 (MeCH_2); 22.7 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 30.0 (CH_2); 31.9 (CH_2); 34.1 (CH_2Ar); 52.6 (MeO); 107.6 (CCOOMe); 119.7 (*q*, $^3J = 6.7$, CHCCF_3); 123.6 (*q*, $^1J = 272.8$, CF_3); 126.9 (*q*, $^2J = 31.7$, CCF_3); 129.2 (CMe); 147.5 ($\text{CC}_{11}\text{H}_{23}$); 160.4 (COH); 170.3 (CO). $^{19}\text{F-NMR}$ (282 MHz): -58.6 (CF_3). EI-MS (70 eV): 388 (50, M^+), 356 (71), 33 (12), 287 (13), 229 (100), 216 (66), 203 (18), 187 (25). HR-EI-MS (70 eV): 388.2219 (M^+ , $\text{C}_{21}\text{H}_{31}\text{F}_3\text{O}_3^+$; calc. 388.2225). Anal. calc. for $\text{C}_{21}\text{H}_{31}\text{F}_3\text{O}_3$ (388.46): C 64.93, H 8.04; found: C 64.87, H 8.40.

Methyl 2-Ethyl-2-hydroxy-6-(trifluoromethyl)-4-undecylbenzoate (5ad). Starting with **3e** (0.529 g, 1.44 mmol), **4q** (0.476 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ad** was isolated as a colorless oil (0.274 g, 47%). IR (ATR): 2924w, 2854w, 1671m, 1611m, 1574w, 1439w, 1399w, 1336m, 1292s, 1247s, 1231s, 1193m, 1136s, 1062m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.7$, $\text{MeC}_{10}\text{H}_{20}$); 1.15 (*t*, $J = 7.5$, MeCH_2Ar); 1.21–1.43 (*m*, 8 CH_2); 1.51–1.63 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.64 (*t*, $J = 7.9$, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.73 (*q*, $J = 7.5$, MeCH_2Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). $^{13}\text{C-NMR}$ (63 MHz): 13.5 (MeCH_2); 14.1 (MeCH_2); 19.5 (CH_2); 22.7 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.7 (CH_2); 30.9 (CH_2); 31.9 (CH_2); 33.3 (CH_2Ar); 52.6 (MeO); 107.8 (CCOOMe); 120.0 (*q*, $^3J = 6.7$, CHCCF_3); 123.6 (*q*, $^1J = 272.7$, CF_3); 127.0 (*q*, $^2J = 31.7$, CCF_3); 135.1 (CC_2H_5); 146.9 ($\text{CC}_{11}\text{H}_{23}$); 160.2 (COH); 170.3 (CO). $^{19}\text{F-NMR}$ (282 MHz): -58.6 (CF_3). EI-MS (70 eV): 402 (27, M^+), 370 (59), 341 (13), 243 (100), 230 (26). HR-EI-MS (70 eV): 402.2374 (M^+ , $\text{C}_{22}\text{H}_{33}\text{F}_3\text{O}_3^+$; calc. 402.2382). Anal. calc. for $\text{C}_{22}\text{H}_{33}\text{F}_3\text{O}_3$ (402.49): C 65.65, H 8.26; found: C 65.63, H 8.58.

Methyl 2-Hydroxy-3-propyl-6-(trifluoromethyl)-4-undecylbenzoate (5ae). Starting with **3e** (0.537 g, 1.47 mmol), **4r** (0.499 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ae** was isolated as a pale yellow solid (0.297 g, 49%). M.p. 38–39°. IR (ATR): 2949w, 2914w, 2864w, 2847w, 1661m, 1611m, 1578m, 1484w, 1464w, 1440w, 1398w, 1355w, 1306w, 1284w, 1263w, 1243w, 1226w, 1206w, 1193w, 1167w, 1145m, 1131s, 1117s, 1092m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.7$, $\text{MeC}_{10}\text{H}_{20}$); 1.01 (*t*, $J = 7.4$, $\text{MeCH}_2\text{CH}_2\text{Ar}$); 1.22–1.42 (*m*, 8 CH_2); 1.49–1.63 (*m*, 2 $\text{CH}_2\text{CH}_2\text{Ar}$); 2.59–2.71 (*m*, 2 CH_2Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). $^{13}\text{C-NMR}$ (75 MHz): 14.1 (MeCH_2); 14.5 (MeCH_2); 22.5 (CH_2); 22.7 (CH_2); 28.3 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.7 (CH_2); 30.9 (CH_2); 31.9 (CH_2); 33.4 (CH_2); 52.6 (MeO); 107.7 (CCOOMe); 119.9 (*q*, $^3J = 6.7$, CHCCF_3); 123.6 (*q*, $^1J = 272.6$, CF_3); 127.0 (*q*, $^2J = 31.7$, CCF_3); 133.8 (CC_3H_7); 147.2 ($\text{CC}_{11}\text{H}_{23}$); 160.4 (COH); 170.4 (CO). $^{19}\text{F-NMR}$ (282 MHz): -58.6 (CF_3). EI-MS (70 eV): 416 (31, M^+), 384 (100), 341 (11), 257 (100), 229 (21). HR-EI-MS (70 eV): 416.2535 (M^+ , $\text{C}_{23}\text{H}_{35}\text{F}_3\text{O}_3^+$; calc. 416.2538). Anal. calc. for $\text{C}_{23}\text{H}_{35}\text{F}_3\text{O}_3$ (416.52): C 66.32, H 8.47; found: C 66.40, H 8.77.

1-[2-Hydroxy-6-(trifluoromethyl)-4-undecylphenyl]ethanone (5af). Starting with **3e** (0.541 g, 1.48 mmol), **4p** (0.403 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5af** was isolated as a orange solid (0.353 g, 67%). M.p. 57–58°. IR (ATR): 3306w, 2921w, 2852w, 1691m, 1651w, 1615m, 1586m, 1504m, 1464w, 1435w, 1355w, 1326w, 1269w, 1236w, 1191m, 1142m, 1120s, 1022m. $^1\text{H-NMR}$ (300 MHz): 0.88 (*t*, $J = 6.7$, $\text{MeC}_{10}\text{H}_{20}$); 1.21–1.36 (*m*, 8 CH_2); 1.56–1.68 (*m*, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.57–2.65 (*m*, ArCH_2 , COMe); 6.98 (*s*, 1 arom. H); 7.08 (*s*, 1 arom. H); 10.09 (*s*, OH). $^{13}\text{C-NMR}$ (75 MHz): 14.1 (MeCH_2); 22.7 (CH_2); 29.2 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 30.5

(CH₂); 31.4 (*q*, ⁵*J* = 5.2, COMe); 31.9 (CH₂); 35.7 (CH₂); 119.1 (*q*, ³*J* = 5.8, CHCCF₃); 119.5 (*q*, ³*J* = 1.6, CCOMe); 121.4 (COHCH); 123.8 (*q*, ¹*J* = 273.5, CF₃); 128.6 (*q*, ²*J* = 31.2, CCF₃); 149.1 (CC₁₁H₂₃); 158.4 (COH); 204.9 (CO). ¹⁹F-NMR (282 MHz): –55.4 (CF₃). EI-MS (70 eV): 358 (48, *M*⁺), 343 (100), 218 (56). HR-EI-MS (70 eV): 358.2118 (*M*⁺, C₂₀H₂₉F₃O₃⁺; calc. 358.2114).

Methyl 2-Hydroxy-4-tridecyl-6-(trifluoromethyl)benzoate (5ag). Starting with **3f** (0.582 g, 1.47 mmol), **4a** (0.430 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5ag** was isolated as a orange solid (0.202 g, 34%). M.p. 58–59°. IR (ATR): 2957w, 2917s, 2877s, 2849s, 1680s, 1619m, 1580m, 1487w, 1461w, 1441w, 1428w, 1365m, 1338s, 1307s, 1288m, 1281s, 1218s, 1206m, 1170m, 1138m, 1126s, 1093m, 1035m, 1021w, 1004m. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, MeC₁₂H₂₄); 1.18–1.38 (*m*, 10 CH₂); 1.55–1.69 (*m*, CH₂CH₂Ar); 2.61 (*t*, *J* = 7.7, CH₂Ar); 3.97 (*s*, MeO); 7.01 (*s*, 1 arom. H); 7.13 (*s*, 1 arom. H); 10.76 (*s*, OH). ¹³C-NMR (75 MHz): 14.1 (MeCH₂); 22.7 (CH₂); 29.1 (CH₂); 29.3 (CH₂); 29.4 (CH₂); 29.5 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.7 (CH₂); 30.4 (CH₂); 31.9 (CH₂); 35.9 (CH₂Ar); 52.7 (MeO); 108.4 (CCOOMe); 119.7 (*q*, ³*J* = 6.7, CHCCF₃); 121.3 (CHCOH); 123.4 (*q*, ¹*J* = 273.5, CF₃); 130.1 (*q*, ²*J* = 31.8, CCF₃); 150.1 (CC₁₃H₂₇); 162.0 (COH); 169.7 (CO). ¹⁹F-NMR (282 MHz): –58.8 (CF₃). EI-MS (70 eV): 402 (59, *M*⁺), 370 (35), 234 (42), 215 (88), 202 (100), 189 (17), 173 (24). HR-EI-MS (70 eV): 402.2378 (*M*⁺, C₂₂H₃₃F₃O₃⁺; calc. 402.2382). Anal. calc. for C₂₂H₃₃F₃O₃ (402.49): C 65.65, H 8.26; found: C 65.88, H 8.59.

Methyl 2-Hydroxy-3-methyl-4-tridecyl-6-(trifluoromethyl)benzoate (5ah). Starting with **3f** (0.596 g, 1.51 mmol), **4b** (0.453 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5ah** was isolated as a colorless solid (0.220 g, 35%). M.p. 57–58°. IR (ATR): 2917w, 2849w, 1663m, 1612m, 1580m, 1486w, 1461w, 1437w, 1401w, 1346m, 1311w, 1285w, 1252w, 1237w, 1219w, 1204w, 1190w, 1165w, 1144w, 1128w, 1115w, 1063m, 1030w, 1011m. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, MeC₁₂H₂₄); 1.19–1.42 (*m*, 10 CH₂); 1.49–1.61 (*m*, CH₂CH₂Ar); 2.24 (*s*, Me); 2.64 (*t*, *J* = 7.9, CH₂Ar); 3.96 (*s*, MeO); 7.10 (*s*, 1 arom. H); 11.11 (*s*, OH). ¹³C-NMR (75 MHz): 11.7 (MeAr); 14.1 (MeCH₂); 22.7 (CH₂); 29.4 (CH₂); 29.4 (CH₂); 29.5 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.7 (CH₂); 30.0 (CH₂); 31.9 (CH₂); 34.1 (CH₂Ar); 52.6 (MeO); 107.6 (CCOOMe); 119.7 (*q*, ³*J* = 6.8, CHCCF₃); 123.6 (*q*, ¹*J* = 273.0, CF₃); 126.9 (*q*, ²*J* = 31.6, CCF₃); 129.2 (CMe); 147.5 (CC₁₃H₂₇); 160.4 (COH); 170.3 (CO). ¹⁹F-NMR (282 MHz): –58.6 (CF₃). EI-MS (70 eV): 416 (63, *M*⁺), 384 (59), 366 (21), 315 (12), 229 (100), 216 (66), 203 (20), 187 (28). HR-EI-MS (70 eV): 416.2531 (*M*⁺, C₂₃H₃₅F₃O₃⁺; calc. 416.2538). Anal. calc. for C₂₃H₃₅F₃O₃ (416.52): C 66.32, H 8.47; found: C 66.23, H 8.56.

Methyl 3-Ethyl-2-hydroxy-4-tridecyl-6-(trifluoromethyl)benzoate (5ai). Starting with **3f** (0.599 g, 1.52 mmol), **4q** (0.476 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5ai** was isolated as a colorless solid (0.284 g, 43%). M.p. 34–35°. IR (ATR): 2987w, 2957w, 2916w, 2849w, 1663m, 1610m, 1575m, 1465m, 1453w, 1436w, 1398w, 1345w, 1294w, 1251w, 1235m, 1216m, 1203w, 1190w, 1163w, 1144w, 1132w, 1076w, 1063m. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, MeC₁₂H₂₄); 1.15 (*t*, *J* = 7.5, MeCH₂Ar); 1.22–1.43 (*m*, 10 CH₂); 1.51–1.63 (*m*, CH₂CH₂Ar); 2.64 (*t*, *J* = 8.0, CH₂CH₂Ar); 2.73 (*q*, *J* = 7.5, MeCH₂Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). ¹³C-NMR (75 MHz): 13.5 (MeCH₂); 14.1 (MeCH₂); 19.5 (CH₂); 22.7 (CH₂); 29.4 (CH₂); 29.4 (CH₂); 29.5 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.6 (CH₂); 29.7 (CH₂); 29.7 (CH₂); 31.0 (CH₂); 31.9 (CH₂); 33.3 (CH₂Ar); 52.6 (MeO); 107.8 (CCOOMe); 120.0 (*q*, ³*J* = 6.7, CHCCF₃); 123.6 (*q*, ¹*J* = 272.7, CF₃); 127.0 (*q*, ²*J* = 31.6, CCF₃); 135.1 (CC₁₃H₂₇); 146.9 (CC₁₃H₂₇); 160.2 (COH); 170.3 (CO). ¹⁹F-NMR (282 MHz): –58.6 (CF₃). EI-MS (70 eV): 430 (35, *M*⁺), 398 (49), 369 (12), 243 (100), 230 (28). HR-EI-MS (70 eV): 430.2688 (*M*⁺, C₂₄H₃₇F₃O₃⁺; calc. 430.2695).

Methyl 2-Hydroxy-3-propyl-4-tridecyl-6-(trifluoromethyl)benzoate (5aj). Starting with **3f** (0.593 g, 1.50 mmol), **4r** (0.499 g, 1.65 mmol), and TiCl₄ (0.18 ml, 1.65 mmol) in CH₂Cl₂ (3 ml), **5aj** was isolated as a colorless solid (0.298 g, 45%). M.p. 46–47°. IR (ATR): 2949w, 2914w, 2864w, 2846w, 1661m, 1611m, 1579m, 1484w, 1464w, 1441w, 1399w, 1356w, 1307w, 1285w, 1250w, 1232w, 1218w, 1194w, 1168w, 1145m, 1131s, 1118s, 1093m, 1080m, 1038w. ¹H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, MeC₁₂H₂₄); 1.01 (*t*, *J* = 7.4, MeCH₂CH₂Ar); 1.22–1.42 (*m*, 10 CH₂); 1.48–1.63 (*m*, 2 CH₂CH₂Ar); 2.58–2.71 (*m*, 2 CH₂Ar); 3.96 (*s*, MeO); 7.10 (*s*, 1 arom. H); 11.05 (*s*, OH). ¹³C-NMR (75 MHz): 14.1 (MeCH₂); 14.5 (MeCH₂); 22.5 (CH₂); 22.7 (CH₂); 28.3 (CH₂); 29.4 (CH₂); 29.4 (CH₂); 29.5 (CH₂); 29.7 (CH₂); 29.7 (CH₂); 29.7 (CH₂); 29.7 (CH₂); 29.7 (CH₂); 30.9 (CH₂); 31.9 (CH₂); 33.4 (CH₂); 52.6 (MeO); 107.7 (CCOOMe); 119.9 (*q*, ³*J* = 6.7, CHCCF₃); 123.7 (*q*, ¹*J* = 272.2, CF₃); 127.0 (*q*, ²*J* = 31.8, CCF₃); 133.8 (CC₁₃H₂₇); 147.3 (CC₁₃H₂₇);

160.4 (COH); 170.4 (CO). ^{19}F -NMR (282 MHz): -58.6 (CF_3). EI-MS (70 eV): 444 (M^+ , 32), 412 (88), 257 (100), 229 (22). HR-EI-MS (70 eV): 444.2844 (M^+ , $\text{C}_{25}\text{H}_{39}\text{F}_3\text{O}_3^+$; calc. 444.2851). Anal. calc. for $\text{C}_{25}\text{H}_{39}\text{F}_3\text{O}_3$ (444.57): C 67.54, H 8.84, found: C 67.84, H 9.31.

[2-Hydroxy-4-tridecyl-6-(trifluoromethyl)phenyl](phenyl)methanone (**5ak**). Starting with **3f** (0.596 g, 1.51 mmol), **4u** (0.506 g, 1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ak** was isolated as a yellow solid (0.445 g, 66%). M.p. 62–63°. IR (ATR): 3185w, 2920w, 2850w, 1654w, 1614w, 1596w, 1580w, 1467w, 1448w, 1433w, 1352w, 1326w, 1318w, 1276w, 1250w, 1190w, 1172w, 1153m, 1124s, 1073s, 1025w. ^1H -NMR (300 MHz): 0.88 (t, $J = 6.7$, $\text{MeC}_{12}\text{H}_{24}$); 1.19–1.41 (m, 10 CH_2); 1.57–1.71 (m, $\text{CH}_2\text{CH}_2\text{Ar}$); 2.64 (t, $J = 7.4$, CH_2Ar); 6.50 (s, OH); 6.95 (s, 1 arom. H); 7.11 (s, 1 arom. H); 7.41–7.48 (m, 2 arom. H); 7.59 (tt, $J = 7.4$, $^4J = 1.7$, 1 arom. H); 7.72–7.79 (m, 2 arom. H). ^{13}C -NMR (75 MHz): 14.1 (MeCH_2); 22.7 (CH_2); 29.2 (CH_2); 29.4 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.7 (CH_2); 29.7 (CH_2); 29.7 (CH_2); 29.7 (CH_2); 30.9 (CH_2); 31.9 (CH_2); 35.7 (CH_2); 118.9 (q, $^3J = 4.5$, CHCCF_3); 120.1 (CH); 121.4 (CCOMe); 123.4 (q, $^1J = 274.8$, CF_3); 128.5 (CH); 129.2 (q, $^2J = 31.6$, CCF_3); 129.6 (CH); 133.9 (CH); 137.7 (C); 147.4 ($\text{CC}_{13}\text{H}_{27}$); 154.5 (COH); 196.8 (CO). ^{19}F -NMR (282 MHz): -56.7 (CF_3). EI-MS (70 eV): 448 (100, M^+), 427 (61), 280 (28), 260 (23), 105 (97). HR-EI-MS (70 eV): 448.2580 (M^+ , $\text{C}_{27}\text{H}_{35}\text{F}_3\text{O}_2^+$; calc. 448.2589). Anal. calc. for $\text{C}_{27}\text{H}_{35}\text{F}_3\text{O}_2$ (448.56): C 72.30, H 7.86; found: C 72.37, H 7.79.

1-[2-Hydroxy-4,6-bis(trifluoromethyl)phenyl]ethanone (**5al**). Starting with **3g** (1.5 mmol), **4p** (1.65 mmol), and TiCl_4 (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5al** was isolated as a yellow oil (35%). IR (KBr): 3379m, 3020m, 2927m, 2855w, 1703s, 1628s, 1601s, 1513w, 1445m, 1388s, 1365m, 1274s, 1241m, 1184m, 1155s, 1107s, 952s, 880m. ^1H -NMR (300 MHz): 2.64 (s, Me); 7.38 (s, CHC-OH); 7.47 (s, $\text{CF}_3\text{CCHCCF}_3$); 8.69 (br s, OH). ^{13}C -NMR (75.5 MHz): 31.7 (q, $^5J = 3.7$, Me); 115.1 (m, $\text{CF}_3\text{CCHCCF}_3$); 118.1 (q, $^5J = 3.7$, CHC-OH); 122.6 (q, $^1J = 273.0$, CF_3); 122.9 (q, $^1J = 274.0$, CF_3); 127.9 (CCOMe); 129.3 (q, $^2J = 33.0$, CF_3CC); 133.8 (q, $^2J = 33.9$, CF_3CCH); 155.6 (COH); 204.1 (COMe). ^{19}F -NMR (235.4 MHz): -56.9 (s, CF_3), -63.6 (s, CF_3). EI-MS (70 eV): 272 (17, M^+), 257 (100), 209 (37), 181 (23), 131 (18), 69 (32). Anal. calc. for $\text{C}_{10}\text{H}_6\text{F}_6\text{O}_2$ (272.14): C 44.13, H 2.22; found: C 44.00, H 2.41.

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