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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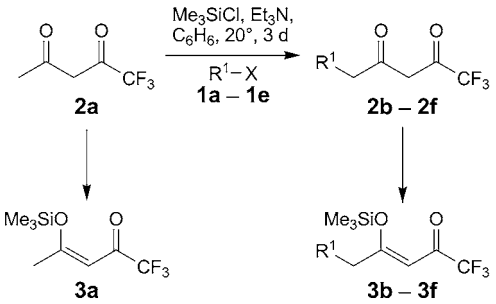
Functionalized 5-alkyl-3-(trifluoromethyl)phenols were prepared by formal [3 + 3] cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 1,1,1-trifluoro-4-(silyloxy)alk-3-en-2-ones derived from 1,1,1-trifluoroalkane-2,4-diones. The latter were prepared by condensation of the dianion of 1,1,1-trifluoropentane-2,4-dione 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-dienes[1]) 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 R^1 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 CF_3-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*).

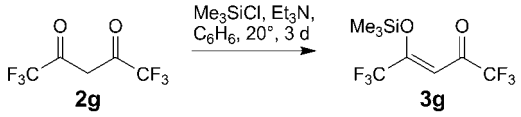
Table 1. *Synthesis of* **3a**–**3f**



R^1	Compound	Yield of **2** [%][a])	Compound	Yield of **3** [%][a])
C_6H_{13}	**2b**	42	**3b**	94
$Cl(CH_2)_6$	**2c**	49	**3c**	77
C_8H_{17}	**2d**	59	**3d**	92
$C_{10}H_{21}$	**2e**	41	**3e**	95
$C_{12}H_{25}$	**2f**	55	**3f**	93

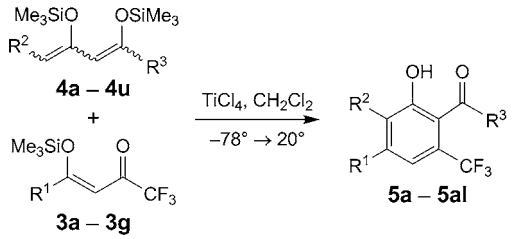
[a]) Yields of isolated products.

Scheme. *Synthesis of* **3g**



The $TiCl_4$ 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 CF_3 group in *ortho* position to the ester (or Ac) group. The other possible regioisomers (CF_3 group *para* to the ester group) could not be detected in the crude product mixture (^{1}H-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_4H_9	MeO	49
3a	**4e**	**5e**	Me	C_6H_{13}	MeO	31
3a	**4f**	**5f**	Me	$Cl(CH_2)_6$	MeO	50
3a	**4g**	**5g**	Me	C_7H_{15}	MeO	47
3a	**4h**	**5h**	Me	C_8H_{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_7H_{15}	H	MeO	66
3b	**4b**	**5r**	C_7H_{15}	Me	MeO	65
3b	**4q**	**5s**	C_7H_{15}	Et	MeO	66
3b	**4r**	**5t**	C_7H_{15}	Pr	MeO	57
3b	**4p**	**5u**	C_7H_{15}	H	Me	80
3b	**4s**	**5v**	C_7H_{15}	MeO	MeO	60
3c	**4m**	**5w**	$Cl(CH_2)_7$	H	EtO	44
3d	**4a**	**5x**	C_9H_{19}	H	MeO	32
3d	**4b**	**5y**	C_9H_{19}	Me	MeO	66
3d	**4q**	**5z**	C_9H_{19}	Et	MeO	60
3d	**4p**	**5aa**	C_9H_{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_6H_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.

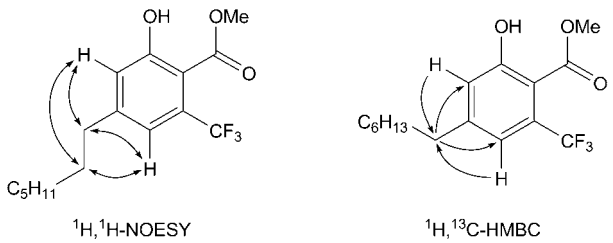


Fig. 1. *NOESY and HMBC of* **5q**

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.

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[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.

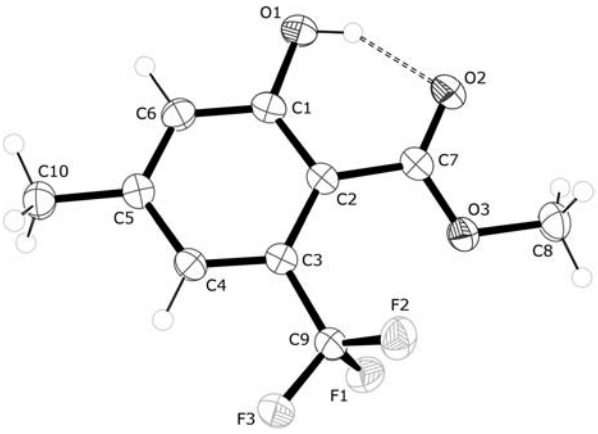

Fig. 2. *Crystal structure of* **5a**

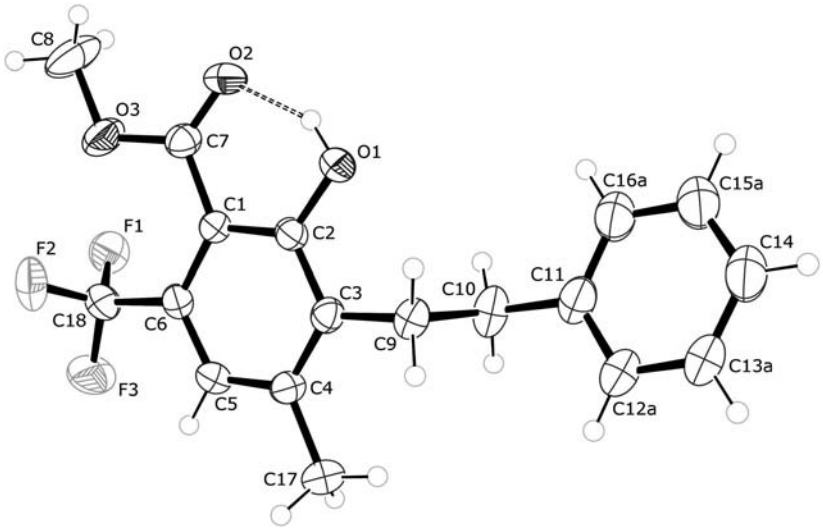

Fig. 3. *Crystal structure of* **5k**

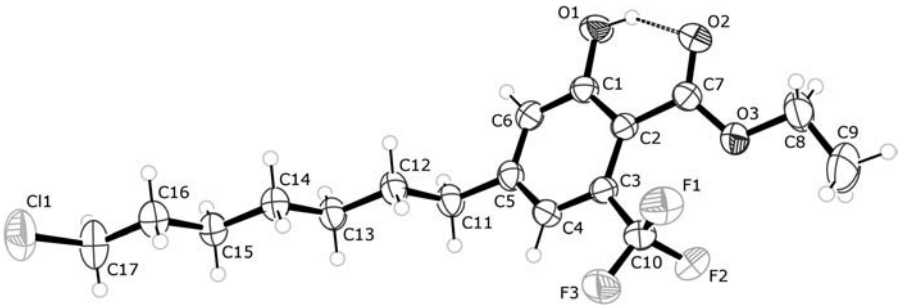

Fig. 4. *Crystal structure of* **5w**

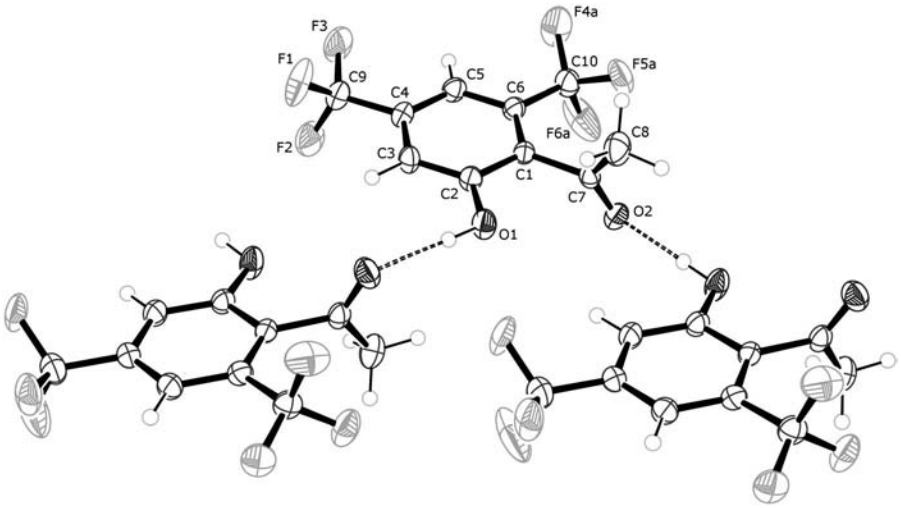

Fig. 5. *Crystal structure and intermolecular interactions of* **5al**

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**) $^{i}Pr_2NH$ (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 $^{i}Pr_2NH$ (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°/0.9 Torr. IR (ATR): 3117*w*, 2958*w*, 2929*m*, 2858*w*, 1594*m*, 1459*m*, 1379*w*, 1277*w*, 1197*m*, 1150*s*, 1107*m*. ^{1}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}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}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^+, $C_{11}H_{17}F_3O_2^+$; 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 $^{i}Pr_2NH$ (2.1 ml, 14.93 mmol) in THF (16 ml), **2c** was isolated as a colorless liquid (0.864 g, 49%) by CC. ^{1}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}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}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^+, $C_{11}H_{16}ClF_3O_2^+$; 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 $^{i}Pr_2NH$ (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°/0.6 Torr. IR (ATR): 2956*w*, 2926*m*, 2856*w*, 1595*m*, 1459*m*, 1378*w*, 1276*w*, 1197*m*, 1151*s*, 1107*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7,

Me); 1.20–1.40 (*m*, 6 CH_2); 1.58–1.73 (*m*, CH_2); 2.43 (*t*, *J* = 7.6, $COCH_2CH_2$); 5.91 (*s*, CH). ^{13}C-NMR (75 MHz): 14.1 (Me); 22.6 (CH_2); 25.5 (CH_2); 29.1 (CH_2); 29.2 (CH_2); 29.2 (CH_2); 29.3 (CH_2); 31.8 (CH_2); 38.4 (CH_2); 95.6 (*q*, ^3J = 2.0, CH); 117.0 (*q*, ^1J = 283.0, CF_3); 175.7 (*q*, ^2J = 36.2, $COCF_3$); 197.6 (CO). ^{19}F-NMR (282 MHz): −76.7 (CF_3). EI-MS (70 eV): 266 (5, M^+), 197 (34), 167 (30), 154 (100), 139 (73). HR-EI-MS (70 eV): 266.1491 (M^+, $C_{13}H_{21}F_3O_2^+$; 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 ^{i}Pr$_2$NH (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*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, Me); 1.20–1.38 (*m*, 8 CH_2); 1.59–1.71 (*m*, CH_2); 2.43 (*t*, *J* = 7.6, $COCH_2CH_2$); 5.91 (*s*, CH). ^{13}C-NMR (75 MHz): 14.1 (Me); 22.7 (CH_2); 25.5 (CH_2); 29.1 (CH_2); 29.2 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 31.9 (CH_2); 38.4 (CH_2); 95.6 (*q*, ^3J = 1.8, CH); 117.0 (*q*, ^1J = 283.7, CF_3); 175.7 (*q*, ^2J = 36.2, $COCF_3$); 197.6 (CO). ^{19}F-NMR (282 MHz): −76.7 (CF_3). EI-MS (70 eV): 294 (4, M^+), 228 (28), 167 (29), 154 (100), 139 (66). HR-EI-MS (70 eV): 294.1805 (M^+, $C_{15}H_{25}F_3O_2^+$; calc. 294.1807).

1,1,1-Trifluoroheptadecane-2,4-dione (**2f**). Starting with **1** (4.623 g, 30 mmol), 1-iododododecane (8.887 g, 30 mmol), BuLi (27.6 ml of a 2.5M soln. in hexanes), and ^{i}Pr$_2$NH (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*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, Me); 1.19–1.39 (*m*, 10 CH_2); 1.58–1.70 (*m*, CH_2); 2.43 (*t*, *J* = 7.6, $COCH_2CH_2$); 5.91 (*s*, CH). ^{13}C-NMR (75 MHz): 14.1 (Me); 22.7 (CH_2); 25.5 (CH_2); 29.1 (CH_2); 29.2 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.7 (CH_2); 31.9 (CH_2); 38.4 (CH_2); 95.6 (*q*, ^3J = 1.8, CH); 117.0 (*q*, ^1J = 283.5, CF_3); 175.7 (*q*, ^2J = 36.2, $COCF_3$); 197.6 (CO). ^{19}F-NMR (282 MHz): −76.7 (CF_3). 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, $C_{17}H_{29}F_3O_2^+$; calc. 322.2120).

General Procedure for the Synthesis of Compounds **3a**–**3g**. To a stirred Et_2O soln. (2 ml per 1.0 mmol of **2**) of **2a**–**2g** (1.0 equiv.) were added Et_3N (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 (Et_2O soln., containing the product) was transferred to a dry flask by syringe under Ar. Et_2O (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 Et_2O 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 CH_2Cl_2 soln. (5 ml) of **4** (2.4 mmol) and **3** (2.2 mmol) was added $TiCl_4$ (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 CH_2Cl_2 (3 × 20 ml). The combined org. layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by CC (SiO_2; 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 $TiCl_4$ (0.26 ml, 2.4 mmol) in CH_2Cl_2 (5 ml), **5a** was isolated as a white solid (0.390 g, 76%). M.p. 68–69°. IR (Nujol): 1671*m* (ν(C=O)). ^{1}H-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). ^{13}C-NMR (63 MHz): 21.5 (Me); 52.7 (MeO); 120.4 (*q*, ^3J = 7, CH); 122.0 (CH); 123.1 (*q*, ^1J = 274, CF_3); 130.1 (*q*, ^2J = 32, CCF_3); 145.1 (C); 147.3 (C); 162.0 (COH); 169.7 (CO). ^{19}F-NMR (235 MHz): −58.8 (CF_3). EI-MS (70 eV): 234 (31, M^+), 202 (100). Anal. calc. for $C_{10}H_9F_3O_3$ (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 $TiCl_4$ (0.1 ml, 1.0 mmol) in CH_2Cl_2 (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*. ^{1}H-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). ^{13}C-NMR (100 MHz): 11.9, 20.5 (2 Me); 52.7 (MeO); 107.7 (C); 120.4 (*q*, ^3J = 6.7, CH); 123.6 (*q*, ^1J = 271.0, CF_3); 126.8 (*q*, ^2J = 31.5, CCF_3); 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 $C_{11}H_{11}F_3O_3$ (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°. R_f (heptanes/AcOEt 3:2) 0.78. IR (ATR): 2958*w*, 1660*s*, 1613*w*, 1439*m*, 1394*w*, 1341*w*, 1239*w*, 1126*w*, 959*w*, 815*w*, 728*s*. ^{1}H-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, CCF_3); 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 $C_{13}H_{14}ClF_3O_3$ (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): 3657*m*, 2970*m*, 2929*m*, 2868*m*, 1928*s*, 1674*m*, 1612*m*, 1576*m*, 1440*m*, 1382*s*, 1342*w*, 1305*w*, 1236*w*, 1194*m*, 1141*w*, 1046*w*, 1005*w*, 974*w*, 935*w*, 873*w*, 841*w*, 812*s*, 751*m*, 710*m*, 677*m*, 659*m*, 582*m*, 553*m*, 540*s*. ^{1}H-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 (*Me*Ar); 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, CCF_3); 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^+, $C_{14}H_{17}F_3O_3^+$; 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°. R_f (hexane/CH_2Cl_2 3:2) 0.88. IR (ATR): 2952*w*, 2924*m*, 2855*w*, 1660*s*, 1613*w*, 1439*m*, 1342*m*, 1305*m*, 1127*m*, 955*s*, 884*m*, 814*m*, 711*s*. ^{1}H-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, CCF_3); 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 $C_{16}H_{21}F_3O_3$ (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): 3640*w*, 2945*m*, 2852*m*, 1936*s*, 1673*m*, 1612*m*, 1576*s*, 1440*m*, 1383*s*, 1340*s*, 1291*w*, 1236*w*, 1194*s*, 1140*w*, 1099*w*, 1047*s*, 975*m*, 936*m*, 874*m*, 843*m*, 813*m*, 729*m*, 710*m*, 677*m*, 654*m*, 582*m*, 555*m*, 540*s*. ^{1}H-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 (*Me*Ar); 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, CCF_3); 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^+, $C_{16}H_{20}ClF_3O_3^+$; calc. 352.1048). Anal. calc. for $C_{16}H_{20}ClF_3O_3$ (352.78): C 54.47, H 5.71; found: C 54.4, H 5.93.

Methyl 3-Heptyl-2-hydroxy-4-methyl-6-(trifluormethyl)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°. IR (KBr): 3452*w*, 2958*w*, 2921*w*, 2848*w*, 1663*w*, 1614*s*, 1578*m*, 1473*m*, 1463*m*, 1440*m*, 1396*s*, 1347*m*, 1311*m*, 1294*m*, 1272*m*, 1243*m*, 1203*m*, 1190*m*, 1162*s*, 1135*s*, 1050*m*, 1002*m*, 985*m*, 961*m*, 936*m*, 909*m*, 885*m*, 844*m*, 816*m*, 795*s*, 773*m*, 735*m*, 712*m*, 678*m*, 658*m*, 556*s*, 538*m*, 485*s*. ^{1}H-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 (*Me*Ar); 23.0,

27.0, 28.8, 29.5, 30.3, 32.2 (6 CH_2); 53.0 (MeO); 108.3 (C); 121.1 (*q*, $^3J = 6.8$, CH); 123.9 (*q*, $^1J = 272.7$, CF_3); 127.2 (*q*, $^2J = 31.8$, *C*CF_3); 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): 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^+, $C_{17}H_{23}F_3O_3^+$; calc. 332.1599). Anal. calc. for $C_{17}H_{23}F_3O_3$ (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 $TiCl_4$ (0.1 ml, 1.0 mmol) in CH_2Cl_2 (2 ml), **5h** was isolated as a slight yellow solid (0.090 g, 26%). M.p. 49–51°. R_f (hexane/CH_2Cl_2 3:2) 0.80. IR (ATR): 2957*w*, 2923*m*, 2852*w*, 1660*s*, 1613*s*, 1473*s*, 1461*w*, 1439*m*, 1343*m*, 1304*m*, 1128*m*, 964*m*, 934*m*, 814*m*, 711*s*. ^{1}H-NMR (300 MHz): 0.88 (*t*, $J = 6.7$, Me); 1.26–1.55 (*m*, 6 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, 29.3, 29.4, 30.0, 31.9 (7 CH_2); 52.6 (MeO); 107.9 (C); 120.7 (*q*, $^3J = 6.7$, CH); 123.5 (*q*, $^1J = 271.0$, CF_3); 126.8 (*q*, $^2J = 31.7$, *C*CF_3); 134.4, 142.4 (2 C); 160.0 (COH); 170.3 (CO). ^{19}F-NMR (282 MHz): −58.2 (CF_3). EI-MS (70 eV): 346 (21, M^+), 300 (17), 299 (100), 229 (12), 216 (63), 215 (41), 196 (40). Anal. calc. for $C_{18}H_{25}F_3O_3$ (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 $TiCl_4$ (0.24 ml, 2.2 mmol) in CH_2Cl_2 (5 ml), **5j** was isolated as a colorless solid (0.444 g, 68%). M.p. 57–58°. IR (neat): 3644*m*, 3076*m*, 3023*m*, 2950*m*, 2852*m*, 1932*s*, 1672*m*, 1612*s*, 1577*m*, 1497*m*, 1440*m*, 1396*m*, 1383*s*, 1344*s*, 1302*w*, 1236*w*, 1194*m*, 1140*w*, 1088*w*, 1068*w*, 1030*w*, 962*w*, 936*w*, 907*w*, 875*w*, 843*w*, 813*s*, 745*m*, 700*m*, 659*m*, 621*m*, 579*m*, 540*m*, 494*s*. ^{1}H-NMR (300 MHz): 2.34 (*s*, Me); 3.97 (*s*, MeO); 4.12 (*s*, CH_2); 7.14–7.27 (*m*, 6 arom. H); 11.12 (*s*, OH). ^{13}C-NMR (75 MHz): 20.8 (*Me*Ar); 32.2 (CH_2); 53.2 (MeO); 108.7 (C); 121.3 (*q*, $^3J = 6.7$, CH); 123.8 (*q*, $^1J = 273.3$, CF_3); 127.8 (*q*, $^2J = 30.6$, *C*CF_3); 126.5, 128.5, 128.8, 139.3 (Ph); 132.4 (C); 144.1 (C); 160.5 (COH); 170.6 (CO). ^{19}F-NMR (282 MHz): −58.3 (CF_3). 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^+, $C_{17}H_{15}F_3O_3^+$; calc. 324.0973). Anal. calc. for $C_{17}H_{15}F_3O_3$ (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 $TiCl_4$ (0.1 ml, 1.0 mmol) in CH_2Cl_2 (2 ml), **5k** was isolated as a white solid (0.145 g, 43%). M.p. 70–71°. R_f (hexane/CH_2Cl_2 3:2) 0.68. IR (ATR): 3086*w*, 3026*w*, 2949*w*, 2857*w*, 1673*m*, 1604*m*, 1494*w*, 1440*m*, 1309*s*, 1231*m*, 1121*s*, 949*s*, 878*m*, 695*s*. ^{1}H-NMR (300 MHz): 2.21 (*s*, Me); 2.80 (*t*, $J = 7.8$, CH_2); 2.99 (*t*, $J = 8.1$, CH_2); 3.97 (*s*, MeO); 7.08 (*s*, 1 arom. H); 7.18–7.31 (*m*, 5 arom. H); 11.15 (*s*, OH). ^{13}C-NMR (75 MHz): 19.9 (Me); 29.0, 34.4 (2 CH_2); 52.7 (MeO); 108.0 (C); 120.7 (*q*, $^3J = 6.4$, CH); 123.5 (*q*, $^1J = 271.1$, CF_3); 126.0 (Ph); 127.2 (*q*, $^2J = 31.5$, *C*CF_3); 128.4, 128.5 (Ph); 133.1, 141.8, 142.8 (3 C); 160.2 (COH); 170.3 (CO). ^{19}F-NMR (282 MHz): −58.2 (CF_3). EI-MS (70 eV): 338 (21, M^+), 306 (21), 247 (22), 216 (11), 215 (100), 91 (44). Anal. calc. for $C_{18}H_{17}F_3O_3$ (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 $TiCl_4$ (0.24 ml, 2.2 mmol) in CH_2Cl_2 (5 ml), **5l** was isolated as a colorless oil (0.479 g, 68%). IR (neat): 3644*m*, 3076*m*, 3023*m*, 2950*m*, 2852*m*, 1932*s*, 1672*m*, 1612*s*, 1577*m*, 1497*m*, 1440*m*, 1396*m*, 1383*s*, 1344*s*, 1302*w*, 1236*w*, 1194*m*, 1140*w*, 1088*w*, 1068*w*, 1030*w*, 962*w*, 936*w*, 907*w*, 875*w*, 843*w*, 813*s*, 745*m*, 700*m*, 659*m*, 621*m*, 579*m*, 540*m*, 494*s*. ^{1}H-NMR (300 MHz): 1.84, 1.88 (*tt*, $J = 7.8$, $CH_2CH_2CH_2$); 2.29 (*s*, Me); 2.75 (*t*, $J = 8.2$, 2 CH_2Ar); 3.97 (*s*, MeO); 7.11 (*s*, 1 arom. H); 7.18–7.31 (*m*, 5 arom. H); 11.06 (*s*, OH). ^{13}C-NMR (75 MHz): 20.2 (*Me*Ar); 26.6, 30.1, 36.4 (3 CH_2); 53.0 (MeO); 108.3 (C); 121.1 (*q*, $^3J = 6.7$, CH); 123.9 (*q*, $^1J = 272.9$, CF_3); 127.4 (*q*, $^2J = 31.7$, *C*CF_3); 126.2, 128.6, 128.7 (Ph); 134.2 (C); 142.4 (C); 142.9 (C); 160.4 (COH); 170.6 (CO). ^{19}F-NMR (282 MHz): −58.2 (CF_3). 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^+, $C_{19}H_{19}F_3O_3^+$; calc. 352.1281). Anal. calc. for $C_{19}H_{19}F_3O_3$ (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 $TiCl_4$ (0.26 ml, 2.4 mmol) in CH_2Cl_2 (5 ml), **5m** was isolated as a colorless solid (0.220 g, 40%). M.p. 28°. IR (Nujol): 1672 (ν(C=O)). ^{1}H-NMR (300 MHz): 1.41 (*t*, $J = 7.6$,

MeCH_2O); 2.38 (*s*, Me); 4.43 (*q*, *J* = 7.2, MeC*H*$_2$O); 7.01 (*s*, CH); 7.13 (*s*, CH); 10.90 (*s*, OH). ^{13}C-NMR (63 MHz): 13.4 (*Me*CH_2); 21.5 (Me); 62.3 (CH_2); 108.6 (C); 120.4 (*q*, ^3J = 7, CH); 122.0 (CH); 123.2 (*q*, ^1J = 275, CF_3); 130.1 (*q*, ^2J = 34, *C*CF_3); 145.0 (C); 162.1 (COH); 169.3 (CO). ^{19}F-NMR (282 MHz): − 58.0 (CF_3). EI-MS (70 eV): 248 (16, M^+), 202 (100). Anal. calc. for $C_{11}H_{11}F_3O_3$ (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 $TiCl_4$ (0.26 ml, 2.4 mmol) in CH_2Cl_2 (5 ml), **5n** was isolated as a colorless oil (0.430 g, 75%). IR (Nujol): 1669 (ν(C=O)). ^{1}H-NMR (250 MHz): 1.40 (*t*, *J* = 7.6, *Me*CH_2O); 2.21 (*s*, Me); 2.33 (*s*, Me); 4.43 (*q*, *J* = 7.2, MeC*H*$_2$O); 7.11 (*s*, CH); 11.21 (*s*, OH). ^{13}C-NMR (63 MHz): 11.9 (*Me*Ar); 13.5 (*Me*Ar); 20.5 (*Me*CH_2O); 62.3 (CH_2O); 108.0 (*q*, ^3J = 2, C); 120.4 (*q*, *J* = 7, CH); 123.6 (*q*, ^1J = 274, CF_3); 126.8 (*q*, ^2J = 32, *C*CF_3); 129.7 (C); 142.8 (C); 160.1 (COH); 169.9 (CO). ^{19}F-NMR (235 MHz): − 57.7 (CF_3). EI-MS (70 eV): 262 (29, M^+), 216 (55). HR-EI-MS (70 eV): 262.0809 (M^+, $C_{12}H_{13}F_3O_3^+$; calc. 262.0817). Anal. calc. for $C_{12}H_{13}F_3O_3$ (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 $TiCl_4$ (0.26 ml, 2.4 mmol) in CH_2Cl_2 (5 ml), **5o** was isolated as a colorless oil (0.435 g, 72%). IR (Nujol): 1669 (ν(C=O)). ^{1}H-NMR (250 MHz): 1.13 (*t*, *J* = 7.5, *Me*CH_2Ar); 1.40 (*t*, *J* = 7.5, *Me*CH_2O); 2.36 (*s*, Me); 2.73 (*q*, *J* = 7.4, MeC*H*$_2$Ar); 4.42 (*q*, *J* = 7.2, MeC*H*$_2$O); 7.10 (*s*, CH); 11.16 (*s*, OH). ^{13}C-NMR (63 MHz): 12.6 (*Me*CH_2); 13.5 (*Me*CH_2O); 19.6 (*Me*Ar); 62.3 (CH_2O); 108.3 (C); 120.7 (*q*, ^3J = 7, CH); 123.5 (*q*, ^1J = 272, CF_3); 126.8 (*q*, ^2J = 32, *C*CF_3); 135.5 (C); 142.0 (C); 160.0 (COH); 169.9 (CO). ^{19}F-NMR (235 MHz): − 57.7 (CF_3). EI-MS (70 eV): 276 (39, M^+), 230 (86). HR-EI-MS (70 eV): 276.0958 (M^+, $C_{13}H_{15}F_3O_3^+$; 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 $TiCl_4$ (0.26 ml, 2.4 mmol) in CH_2Cl_2 (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)). ^{1}H-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). ^{13}C-NMR (63 MHz): 21.5 (Me), 31.4 (*q*, *J* = 6, CO*Me*); 118.9 (*q*, ^3J = 2, *C*); 119.9 (*q*, ^3J = 6, CH); 122.3 (CH); 123.7 (*q*, ^1J = 274, CF_3); 128.7 (*q*, ^2J = 30, *C*CF_3); 144.3 (C); 158.8 (COH); 204.9 (CO). ^{19}F-NMR (235 MHz): − 55.3 (CF_3). EI-MS (70 eV): 218 (24, M^+), 203 (100). HR-EI-MS (70 eV): 218.0545 (M^+, $C_{10}H_9F_3O_2^+$; 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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (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*. ^{1}H-NMR (250 MHz): 0.88 (*t*, *J* = 6.9, *Me*C_6H_{12}); 1.18–1.41 (*m*, 4 CH_2); 1.51–1.72 (*m*, C*H*$_2$CH$_2$Ar); 2.62 (*t*, *J* = 7.7, C*H*$_2$Ar); 3.97 (*s*, MeO); 7.01 (*s*, 1 arom. H); 7.13 (*s*, 1 arom. H); 10.76 (*s*, OH). ^{13}C-NMR (75 MHz): 14.0 (*Me*CH_2); 22.6 (CH_2); 29.0 (CH_2); 29.1 (CH_2); 30.4 (CH_2); 31.7 (CH_2); 35.9 (*C*H$_2$Ar); 52.7 (MeO); 108.4 (*q*, ^3J = 1.2, *C*CO_2Me); 119.8 (*q*, ^3J = 6.7, *C*HCCF_3); 121.3 (*C*HCOH); 123.4 (*q*, ^1J = 273.7, CF_3); 130.1 (*q*, ^2J = 31.7, *C*CF_3); 150.1 (*C*C_7H_{15}); 162.0 (COH); 169.7 (CO). ^{19}F-NMR (282 MHz): − 58.8 (CF_3). EI-MS (70 eV): 318 (17, M^+), 286 (28), 215 (13), 202 (100), 173 (10). HR-EI-MS (70 eV): 318.1436 (M^+, $C_{16}H_{21}F_3O_3^+$; calc. 318.1443. Anal. calc. for $C_{16}H_{21}F_3O_3$ (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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (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*. ^{1}H-NMR (300 MHz): 0.89 (*t*, *J* = 6.9, *Me*C_6H_{12}); 1.22–1.40 (*m*, 4 CH_2); 1.49–1.62 (*m*, C*H*$_2$CH$_2$Ar); 2.24 (*s*, Me); 2.64 (*t*, *J* = 7.9, C*H*$_2$Ar); 3.96 (*s*, MeO); 7.10 (*s*, 1 arom. H); 11.10 (*s*, OH). ^{13}C-NMR (125 MHz): 11.6 (*Me*Ar); 14.0 (*Me*CH_2); 22.6 (CH_2); 29.1 (CH_2); 29.5 (CH_2); 30.0 (CH_2); 31.8 (CH_2); 34.1 (*C*H$_2$Ar); 52.6 (MeO); 107.6 (*C*COOMe); 119.7 (*q*, ^3J = 6.7, *C*HCCF_3); 123.7 (*q*, ^1J = 273.4, CF_3); 126.9 (*q*, ^2J = 31.7, *C*CF_3); 129.3 (*C*Me); 147.5 (*C*C_7H_{15}); 160.4 (COH); 170.3 (CO). ^{19}F-NMR (282 MHz): − 58.6 (CF_3). EI-MS (70 eV): 332 (34, M^+), 300 (100), 229 (74), 216 (86), 187 (16). HR-EI-MS (70 eV): 332.1595 (M^+, $C_{17}H_{23}F_3O_3^+$; 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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5s** was isolated

as a pale red oil (0.351 g, 66%). IR (ATR): 2957*w*, 2928*m*, 2873, 2857*w*, 1671*m*, 1609*w*, 1439*m*, 1400*w*, 1337*m*, 1292*s*, 1247*s*, 1228*s*, 1194*m*, 1136*s*, 1111*s*, 1062*m*. ^{1}H-NMR (300 MHz): 0.89 (*t*, *J* = 7.0, *Me*C$_6$H$_{12}$); 1.15 (*t*, *J* = 7.5, *Me*CH$_2$Ar); 1.22–1.44 (*m*, 4 CH$_2$); 1.50–1.64 (*m*, C*H*$_2$CH$_2$Ar); 2.60–2.68 (*m*, CH$_2$C*H*$_2$Ar); 2.73 (*q*, *J* = 7.5, MeC*H*$_2$Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). ^{13}C-NMR (63 MHz): 13.5 (*Me*CH$_2$); 14.0 (*Me*CH$_2$); 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 (*C*H$_2$Ar); 52.6 (MeO); 107.8 (*C*COOMe); 120.0 (*q*, ^3J = 6.7, *C*HCCF$_3$); 123.6 (*q*, ^1J = 272.7, CF$_3$); 127.0 (*q*, ^2J = 31.7, *C*CF$_3$); 135.1 (*C*C$_2$H$_5$); 146.9 (*C*C$_7$H$_{15}$); 160.2 (COH); 170.3 (CO). ^{19}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^+, C$_{18}$H$_{25}$F$_3$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$_2$Cl$_2$ (3 ml), **5t** was isolated as a yellow oil (0.321 g, 57%). IR (ATR): 2957*w*, 2927*m*, 2872*m*, 2857*w*, 1671*m*, 1610*m*, 1573*m*, 1456*w*, 1439*w*, 1399*w*, 1334*w*, 1302*m*, 1283*s*, 1222*s*, 1193*m*, 1135*s*, 1091*m*. ^{1}H-NMR (300 MHz): 0.89 (*t*, *J* = 7.0, *Me*C$_6$H$_{12}$); 1.01 (*t*, *J* = 7.4, *Me*CH$_2$CH$_2$Ar); 1.24–1.41 (*m*, 4 CH$_2$); 1.50–1.62 (*m*, 2 *H*$_2$CH$_2$Ar); 2.59–2.71 (*m*, 2 C*H*$_2$Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). ^{13}C-NMR (75 MHz): 14.1 (*Me*CH$_2$); 14.5 (*Me*CH$_2$); 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 (*C*COOMe); 119.9 (*q*, ^3J = 6.7, *C*HCCF$_3$); 123.6 (*q*, ^1J = 272.7, CF$_3$); 127.0 (*q*, ^2J = 31.6, *C*CF$_3$); 133.8 (*C*C$_3$H$_7$); 147.2 (*C*C$_7$H$_{15}$); 160.4 (COH); 170.4 (CO). ^{19}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^+, C$_{19}$H$_{27}$F$_3$O$_3^+$; calc. 360.1912). Anal. calc. for C$_{19}$H$_{27}$F$_3$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$_2$Cl$_2$ (3 ml), **5u** was isolated as a pale red solid (0.371 g, 80%). M.p. 82–83°. IR (ATR): 3331*w*, 2958*w*, 2927*m*, 2857*w*, 1688*w*, 1615*m*, 1586*m*, 1464*w*, 1435*w*, 1356*w*, 1323*w*, 1280*w*, 1265*w*, 1234*w*, 1191*w*, 1158*m*, 1143*m*, 1120*s*, 1023*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.9, *Me*C$_6$H$_{12}$); 1.21–1.38 (*m*, 4 CH$_2$); 1.55–1.68 (*m*, C*H*$_2$CH$_2$Ar); 2.57–2.65 (*m*, C*H*$_2$Ar, COMe); 6.98 (*s*, 1 arom. H); 7.07 (*s*, 1 arom. H); 10.04 (*s*, OH). ^{13}C-NMR (75 MHz): 14.0 (*Me*CH$_2$); 22.6 (CH$_2$); 29.0 (CH$_2$); 29.1 (CH$_2$); 30.5 (CH$_2$); 31.4 (*q*, ^5J = 5.4, CO*Me*); 31.7 (CH$_2$); 35.8 (CH$_2$); 119.1 (*C*COMe); 119.3 (*q*, ^3J = 5.8, *C*HCCF$_3$); 121.5 (COHCH); 123.8 (*q*, ^1J = 273.6, CF$_3$); 128.7 (*q*, ^2J = 31.1, *C*CF$_3$); 149.3 (*C*C$_7$H$_{15}$); 158.7 (COH); 204.8 (CO). ^{19}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^+, C$_{16}$H$_{21}$F$_3$O$_2^+$; calc. 302.1494). Anal. calc. for C$_{16}$H$_{21}$F$_3$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$_2$Cl$_2$ (3 ml), **5v** was isolated as a red oil (0.297 g, 60%). IR (ATR): 2956*w*, 2927*m*, 2857*m*, 1746*w*, 1673*m*, 1609*m*, 1574*w*, 1441*w*, 1412*w*, 1363*w*, 1328*w*, 1274*w*, 1262*w*, 1197*w*, 1178*m*, 1133*s*, 1063*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*C$_6$H$_{12}$); 1.20–1.40 (*m*, 4 CH$_2$); 1.50–1.67 (*m*, C*H*$_2$CH$_2$Ar); 2.65 (*t*, *J* = 7.8, C*H*$_2$Ar); 3.91 (*s*, MeO); 3.97 (*s*, MeO); 7.12 (*s*, 1 arom. H); 10.63 (*s*, OH). ^{13}C-NMR (75 MHz): 14.0 (*Me*CH$_2$); 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 (*C*COOMe); 120.1 (*q*, ^3J = 6.7, *C*HCCF$_3$); 123.4 (*q*, ^1J = 272.7, CF$_3$); 124.3 (*q*, ^2J = 32.0, *C*CF$_3$); 140.9 (*C*OMe); 149.2 (*C*C$_7$H$_{15}$); 155.0 (COH); 169.6 (CO). ^{19}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^+, C$_{17}$H$_{23}$F$_3$O$_4^+$; calc. 348.1548). Anal. calc. for C$_{17}$H$_{23}$F$_3$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$_2$Cl$_2$ (4 ml), **5w** was isolated as a colorless solid (0.303 g, 44%). IR (Nujol): 1689*w*, 1621*m*, 1577*w*, 1488*w*, 1402*w*, 1326*w*, 1310*w*, 1287*w*, 1215*m*, 1173*m*, 1142*m*, 1128*s*, 1020*s*, 1010*s*, 1001*m*. ^{1}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, C*H*$_2$O); 7.00 (*d*, ^4J = 1.2, 1 arom. H); 7.12 (*d*, ^4J = 1.2, 1 arom. H); 10.89 (*s*, OH). ^{13}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$_2$O); 108.7 (C); 119.7 (*q*, ^3J = 6.7, *C*HCCF$_3$); 121.2 (CH); 123.4 (*q*, ^1J = 273.6, CF$_3$); 130.1 (*q*, ^2J = 31.8, *C*CF$_3$); 149.6 (C); 162.2 (COH); 169.2 (CO). ^{19}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): 2957*w*, 2918*m*, 2851*w*, 1678*m*, 1620*m*, 1579*m*, 1487*m*, 1461*w*, 1441*w*, 1362*w*, 1339*w*, 1285*m*, 1261*m*, 1220*m*, 1206*w*, 1170*m*, 1126*s*, 1092*s*, 1024*s*, 1002*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.8, *Me*C_8H_{16}); 1.21–1.36 (*m*, 6 CH_2); 1.55–1.67 (*m*, C$H_2$$CH_2$Ar); 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 (*Me*CH_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 (*C*H_2Ar); 52.7 (MeO); 108.4 (*C*COOMe); 119.7 (*q*, ^3J = 6.7, *C*HCCF_3); 121.3 (*C*HCOH); 123.4 (*q*, ^1J = 273.1, CF_3); 130.1 (*q*, ^2J = 31.7, *C*CF_3); 150.1 (*C*C_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 solid (0.230 g, 66%). M.p. 43–44°. IR (ATR): 2920*m*, 2851*w*, 1663*m*, 1612*m*, 1581*m*, 1462*m*, 1437*w*, 1401*w*, 1346*w*, 1286*w*, 1257*w*, 1237*m*, 1204*w*, 1190*w*, 1165*w*, 1144*w*, 1127*w*, 1114*m*, 1055*w*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*C_8H_{16}); 1.22–1.40 (*m*, 6 CH_2); 1.49–1.61 (*m*, C$H_2$$CH_2$Ar); 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 (*Me*Ar); 14.1 (*Me*CH_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 (*C*H_2Ar); 52.7 (MeO); 107.5 (*C*COOMe); 119.7 (*q*, ^3J = 6.7, *C*HCCF_3); 123.6 (*q*, ^1J = 272.7, CF_3); 126.9 (*q*, ^2J = 31.7, *C*CF_3); 129.2 (*C*Me); 147.5 (*C*C_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): 2956*w*, 2925*m*, 2855*w*, 1671*m*, 1611, 1574*w*, 1439, 1399, 1336*m*, 1291*s*, 1248, 1232, 1193*m*, 1135*s*, 1062*m*. ^{1}H-NMR (300 MHz): 0.89 (*t*, *J* = 6.7, *Me*C_8H_{16}); 1.16 (*t*, *J* = 7.5, *Me*CH_2Ar); 1.22–1.44 (*m*, 6 CH_2); 1.51–1.63 (*m*, C$H_2$$CH_2$Ar); 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 (*Me*CH_2); 14.0 (*Me*CH_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 (*C*H_2Ar); 52.6 (MeO); 107.9 (*C*COOMe); 120.0 (*q*, ^3J = 6.6, *C*HCCF_3); 123.7 (*q*, ^1J = 272.9, CF_3); 126.9 (*q*, ^2J = 31.6, *C*CF_3); 135.1 (*C*C_2H_5); 146.9 (*C*C_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): 3325*w*, 2923*w*, 2853*w*, 1688*w*, 1615*m*, 1586*m*, 1466*w*, 1435*w*, 1355*w*, 1322*w*, 1268*w*, 1235*w*, 1191*w*, 1158*m*, 1120*s*, 1022*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*C_8H_{16}); 1.20–1.38 (*m*, 6 CH_2); 1.55–1.69 (*m*, C$H_2$$CH_2$Ar); 2.57–2.65 (*m*, C$H_2$Ar, CO*Me*); 6.98 (*s*, 1 arom. H); 7.08 (*s*, 1 arom. H); 10.07 (*s*, OH). ^{13}C-NMR (75 MHz): 14.1 (*Me*CH_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, *C*COMe); 119.3 (*q*, ^3J = 5.9, *C*HCCF_3); 121.6 (COHCH); 123.8 (*q*, ^1J = 273.6, CF_3); 128.7 (*q*, ^2J = 31.2, *C*CF_3); 149.3 (*C*C_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): 2957*w*, 2917*w*, 2849*w*, 1680*m*, 1620*m*,

1579*m*, 1487*w*, 1460*w*, 1441*w*, 1362*w*, 1337*w*, 1302*w*, 1286*m*, 1240*w*, 1216*w*, 1205*m*, 1167*m*, 1127*s*, 1092*m*, 1023*w*, 1003*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*$C_{10}H_{20}$); 1.21–1.36 (*m*, 8 CH_2); 1.54–1.68 (*m*, CH_2CH_2Ar); 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}C-NMR (75 MHz): 14.1 (*Me*CH_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 (*C*COOMe); 119.7 (*q*, ^3J = 6.7, *C*HCCF$_3$); 121.3 (*C*HCOH); 123.4 (*q*, ^1J = 273.3, CF_3); 130.1 (*q*, ^2J = 31.7, *C*CF_3); 150.1 ($CC_{11}H_{23}$); 162.0 (COH); 169.7 (CO). ^{19}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^+, $C_{20}H_{29}F_3O_3^+$; calc. 374.2069). Anal. calc. for $C_{20}H_{29}F_3O_3$ (374.44): C 64.15, H 7.81; found: C 64.51, 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): 2918*w*, 2850*w*, 1663*m*, 1612*m*, 1580*w*, 1461*w*, 1437*w*, 1401*w*, 1346*w*, 1285*w*, 1245*w*, 1229*w*, 1205*w*, 1190*w*, 1165*w*, 1143*m*, 1128*s*, 1114*s*, 1062*s*, 1012*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*$C_{10}H_{20}$); 1.21–1.39 (*m*, 8 CH_2); 1.48–1.62 (*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); 11.11 (*s*, OH). ^{13}C-NMR (125 MHz): 11.7 (*Me*Ar); 14.1 (*Me*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); 29.6 (CH_2); 30.0 (CH_2); 31.9 (CH_2); 34.1 (CH_2Ar); 52.6 (MeO); 107.6 (*C*COOMe); 119.7 (*q*, ^3J = 6.7, *C*HCCF$_3$); 123.6 (*q*, ^1J = 272.8, CF_3); 126.9 (*q*, ^2J = 31.7, *C*CF_3); 129.2 (*C*Me); 147.5 ($CC_{11}H_{23}$); 160.4 (COH); 170.3 (CO). ^{19}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^+, $C_{21}H_{31}F_3O_3^+$; calc. 388.2225). Anal. calc. for $C_{21}H_{31}F_3O_3$ (388.46): C 64.93, H 8.04; found: C 64.87, H 8.40.

Methyl 3-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): 2924*w*, 2854*w*, 1671*m*, 1611*m*, 1574*w*, 1439*w*, 1399*w*, 1336*m*, 1292*s*, 1247*s*, 1231*s*, 1193*m*, 1136*s*, 1062*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*$C_{10}H_{20}$); 1.15 (*t*, *J* = 7.5, *Me*CH_2Ar); 1.21–1.43 (*m*, 8 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); 11.05 (*s*, OH). ^{13}C-NMR (63 MHz): 13.5 (*Me*CH_2); 14.1 (*Me*CH_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 (*C*COOMe); 120.0 (*q*, ^3J = 6.7, *C*HCCF$_3$); 123.6 (*q*, ^1J = 272.7, CF_3); 127.0 (*q*, ^2J = 31.7, *C*CF_3); 135.1 (CC_2H_5); 146.9 ($CC_{11}H_{23}$); 160.2 (COH); 170.3 (CO). ^{19}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^+, $C_{22}H_{33}F_3O_3^+$; calc. 402.2382). Anal. calc. for $C_{22}H_{33}F_3O_3$ (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): 2949*w*, 2914*w*, 2864*w*, 2847*w*, 1661*m*, 1611*m*, 1578*m*, 1484*w*, 1464*w*, 1440*w*, 1398*w*, 1355*w*, 1306*w*, 1284*w*, 1263*w*, 1243*w*, 1226*w*, 1206*w*, 1193*w*, 1167*w*, 1145*m*, 1131*s*, 1117*s*, 1092*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*$C_{10}H_{20}$); 1.01 (*t*, *J* = 7.4, *Me*CH_2CH_2Ar); 1.22–1.42 (*m*, 8 CH_2); 1.49–1.63 (*m*, 2 CH_2CH_2Ar); 2.59–2.71 (*m*, 2 CH_2Ar); 3.96 (*s*, MeO); 7.11 (*s*, 1 arom. H); 11.05 (*s*, OH). ^{13}C-NMR (75 MHz): 14.1 (*Me*CH_2); 14.5 (*Me*CH_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 (*C*COOMe); 119.9 (*q*, ^3J = 6.7, *C*HCCF$_3$); 123.6 (*q*, ^1J = 272.6, CF_3); 127.0 (*q*, ^2J = 31.7, *C*CF_3); 133.8 (CC_3H_7); 147.2 ($CC_{11}H_{23}$); 160.4 (COH); 170.4 (CO). ^{19}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^+, $C_{23}H_{35}F_3O_3^+$; calc. 416.2538). Anal. calc. for $C_{23}H_{35}F_3O_3$ (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): 3306*w*, 2921*w*, 2852*w*, 1691*m*, 1651*w*, 1615*m*, 1586*m*, 1504*m*, 1464*w*, 1435*w*, 1355*w*, 1326*w*, 1269*w*, 1236*w*, 1191*m*, 1142*m*, 1120*s*, 1022*m*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*$C_{10}H_{20}$); 1.21–1.36 (*m*, 8 CH_2); 1.56–1.68 (*m*, CH_2CH_2Ar); 2.57–2.65 (*m*, ArCH_2, CO*Me*); 6.98 (*s*, 1 arom. H); 7.08 (*s*, 1 arom. H); 10.09 (*s*, OH). ^{13}C-NMR (75 MHz): 14.1 (*Me*CH_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

(CH_2); 31.4 (q, $^5J = 5.2$, CO*Me*); 31.9 (CH_2); 35.7 (CH_2); 119.1 (q, $^3J = 5.8$, *C*HCCF$_3$); 119.5 (q, $^3J = 1.6$, *C*COMe); 121.4 (COHCH); 123.8 (q, $^1J = 273.5$, CF_3); 128.6 (q, $^2J = 31.2$, *C*CF$_3$); 149.1 (*C*C$_{11}$H$_{23}$); 158.4 (COH); 204.9 (CO). ^{19}F-NMR (282 MHz): -55.4 (CF_3). EI-MS (70 eV): 358 (48, M^+), 343 (100), 218 (56). HR-EI-MS (70 eV): 358.2118 (M^+, $C_{20}H_{29}F_3O_2^+$; 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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ag** was isolated as a orange solid (0.202 g, 34%). M.p. 58–59°. IR (ATR): 2957*w*, 2917*s*, 2877*s*, 2849*s*, 1680*s*, 1619*m*, 1580*m*, 1487*w*, 1461*w*, 1441*w*, 1428*w*, 1365*m*, 1338*s*, 1307*s*, 1288*m*, 1281*s*, 1218*s*, 1206*m*, 1170*m*, 1138*m*, 1126*s*, 1093*m*, 1035*m*, 1021*w*, 1004*m*. ^{1}H-NMR (300 MHz): 0.88 (t, $J = 6.7$, *Me*C$_{12}$H$_{24}$); 1.18–1.38 (m, 10 CH_2); 1.55–1.69 (m, C*H*$_2$CH$_2$Ar); 2.61 (t, $J = 7.7$, CH$_2$Ar); 3.97 (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 (*Me*CH$_2$); 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); 29.6 (CH_2); 29.7 (CH_2); 30.4 (CH_2); 31.9 (CH_2); 35.9 (*C*H$_2$Ar); 52.7 (MeO); 108.4 (*C*COOMe); 119.7 (q, $^3J = 6.7$, *C*HCCF$_3$); 121.3 (*C*HCOH); 123.4 (q, $^1J =$ 273.5, CF_3); 130.1 (q, $^2J = 31.8$, *C*CF$_3$); 150.1 (*C*C$_{13}$H$_{27}$); 162.0 (COH); 169.7 (CO). ^{19}F-NMR (282 MHz): -58.8 (CF_3). 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^+, $C_{22}H_{33}F_3O_3^+$; calc. 402.2382). Anal. calc. for $C_{22}H_{33}F_3O_3$ (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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ah** was isolated as a colorless solid (0.220 g, 35%). M.p. 57–58°. IR (ATR): 2917*w*, 2849*w*, 1663*m*, 1612*m*, 1580*m*, 1486*w*, 1461*w*, 1437*w*, 1401*w*, 1346*m*, 1311*w*, 1285*w*, 1252*w*, 1237*w*, 1219*w*, 1204*w*, 1190*w*, 1165*w*, 1144*w*, 1128*w*, 1115*w*, 1063*m*, 1030*w*, 1011*m*. ^{1}H-NMR (300 MHz): 0.88 (t, $J = 6.7$, *Me*C$_{12}$H$_{24}$); 1.19–1.42 (m, 10 CH_2); 1.49–1.61 (m, C*H*$_2$CH$_2$Ar); 2.24 (s, Me); 2.64 (t, $J = 7.9$, C*H*$_2$Ar); 3.96 (s, MeO); 7.10 (s, 1 arom. H); 11.11 (s, OH). ^{13}C-NMR (75 MHz): 11.7 (*Me*Ar); 14.1 (*Me*CH$_2$); 22.7 (CH_2); 29.4 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.7 (CH_2); 30.0 (CH_2); 31.9 (CH_2); 34.1 (*C*H$_2$Ar); 52.6 (MeO); 107.6 (*C*COOMe); 119.7 (q, $^3J = 6.8$, *C*HCCF$_3$); 123.6 (q, $^1J = 273.0$, CF_3); 126.9 (q, $^2J = 31.6$, *C*CF$_3$); 129.2 (*C*Me); 147.5 (*C*C$_{13}$H$_{27}$); 160.4 (COH); 170.3 (CO). ^{19}F-NMR (282 MHz): -58.6 (CF_3). 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^+, $C_{23}H_{35}F_3O_3^+$; calc. 416.2538). Anal. calc. for $C_{23}H_{35}F_3O_3$ (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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5ai** was isolated as a colorless solid (0.284 g, 43%). M.p. 34–35°. IR (ATR): 2987*w*, 2957*w*, 2916*w*, 2849*w*, 1663*m*, 1610*m*, 1575*m*, 1465*m*, 1453*w*, 1436*w*, 1398*w*, 1345*w*, 1294*w*, 1251*w*, 1235*m*, 1216*m*, 1203*w*, 1190*w*, 1163*w*, 1144*w*, 1132*w*, 1076*w*, 1063*m*. ^{1}H-NMR (300 MHz): 0.88 (t, $J = 6.7$, *Me*C$_{12}$H$_{24}$); 1.15 (t, $J = 7.5$, *Me*CH$_2$Ar); 1.22–1.43 (m, 10 CH_2); 1.51–1.63 (m, C*H*$_2$CH$_2$Ar); 2.64 (t, $J = 8.0$, CH$_2$C*H*$_2$Ar); 2.73 (q, $J = 7.5$, MeC*H*$_2$Ar); 3.96 (s, MeO); 7.11 (s, 1 arom. H); 11.05 (s, OH). ^{13}C-NMR (75 MHz): 13.5 (*Me*CH$_2$); 14.1 (*Me*CH$_2$); 19.5 (CH_2); 22.7 (CH_2); 29.4 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.6 (CH_2); 29.7 (CH_2); 29.7 (CH_2); 31.0 (CH_2); 31.9 (CH_2); 33.3 (*C*H$_2$Ar); 52.6 (MeO); 107.8 (*C*COOMe); 120.0 (q, $^3J = 6.7$, *C*HCCF$_3$); 123.6 (q, $^1J = 272.7$, CF_3); 127.0 (q, $^2J = 31.6$, *C*CF$_3$); 135.1 (*C*C$_2$H$_5$); 146.9 (*C*C$_{13}$H$_{27}$); 160.2 (COH); 170.3 (CO). ^{19}F-NMR (282 MHz): -58.6 (CF_3). EI-MS (70 eV): 430 (35, M^+), 398 (49), 369 (12), 243 (100), 230 (28). HR-EI-MS (70 eV): 430.2688 (M^+, $C_{24}H_{37}F_3O_3^+$; 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 $TiCl_4$ (0.18 ml, 1.65 mmol) in CH_2Cl_2 (3 ml), **5aj** was isolated as a colorless solid (0.298 g, 45%). M.p. 46–47°. IR (ATR): 2949*w*, 2914*w*, 2864*w*, 2846*w*, 1661*m*, 1611*m*, 1579*m*, 1484*w*, 1464*w*, 1441*w*, 1399*w*, 1356*w*, 1307*w*, 1285*w*, 1250*w*, 1232*w*, 1218*w*, 1194*w*, 1168*w*, 1145*m*, 1131*s*, 1118*s*, 1093*m*, 1080*m*, 1038*w*. ^{1}H-NMR (300 MHz): 0.88 (t, $J = 6.7$, *Me*C$_{12}$H$_{24}$); 1.01 (t, $J = 7.4$, *Me*CH$_2$CH$_2$Ar); 1.22–1.42 (m, 10 CH_2); 1.48–1.63 (m, 2 C*H*$_2$CH$_2$Ar); 2.58–2.71 (m, 2 C*H*$_2$Ar); 3.96 (s, MeO); 7.10 (s, 1 arom. H); 11.05 (s, OH). ^{13}C-NMR (75 MHz): 14.1 (*Me*CH$_2$); 14.5 (*Me*CH$_2$); 22.5 (CH_2); 22.7 (CH_2); 28.3 (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); 29.7 (CH_2); 30.9 (CH_2); 31.9 (CH_2); 33.4 (CH_2); 52.6 (MeO); 107.7 (*C*COOMe); 119.9 (q, $^3J = 6.7$, *C*HCCF$_3$); 123.7 (q, $^1J = 272.2$, CF_3); 127.0 (q, $^2J = 31.8$, *C*CF$_3$); 133.8 (*C*C$_3$H$_7$); 147.3 (*C*C$_{13}$H$_{27}$);

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^+, $C_{25}H_{39}F_3O_3^+$; calc. 444.2851). Anal. calc. for $C_{25}H_{39}F_3O_3$ (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): 3185*w*, 2920*w*, 2850*w*, 1654*w*, 1614*w*, 1596*w*, 1580*w*, 1467*w*, 1448*w*, 1433*w*, 1352*w*, 1326*w*, 1318*w*, 1276*w*, 1250*w*, 1190*w*, 1172*w*, 1153*m*, 1124*s*, 1073*s*, 1025*w*. ^{1}H-NMR (300 MHz): 0.88 (*t*, *J* = 6.7, *Me*$C_{12}H_{24}$); 1.19–1.41 (*m*, 10 CH_2); 1.57–1.71 (*m*, C*H*$_2$CH_2Ar); 2.64 (*t*, *J* = 7.4, C*H*$_2$Ar); 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 (*Me*CH_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); 29.7 (CH_2); 30.9 (CH_2); 31.9 (CH_2); 35.7 (CH_2); 118.9 (*q*, ^3J = 4.5, *C*HCCF_3); 120.1 (CH); 121.4 (*C*COMe); 123.4 (*q*, ^1J = 274.8, CF_3); 128.5 (CH); 129.2 (*q*, ^2J = 31.6, *C*CF_3); 129.6 (CH); 133.9 (CH); 137.7 (C); 147.4 (*C*$C_{13}H_{27}$); 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^+, $C_{27}H_{35}F_3O_2^+$; calc. 448.2589). Anal. calc. for $C_{27}H_{35}F_3O_2$ (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): 3379*m*, 3020*m*, 2927*m*, 2855*w*, 1703*s*, 1628*s*, 1601*s*, 1513*w*, 1445*m*, 1388*s*, 1365*m*, 1274*s*, 1241*m*, 1184*m*, 1155*s*, 1107*s*, 952*s*, 880*m*. ^{1}H-NMR (300 MHz): 2.64 (*s*, Me); 7.38 (*s*, C*H*C–OH); 7.47 (*s*, CF_3CCHCCF_3); 8.69 (br *s*, OH). ^{13}C-NMR (75.5 MHz): 31.7 (*q*, ^5J = 3.7, Me); 115.1 (*m*, CF_3C*C*HCCF_3); 118.1 (*q*, ^5J = 3.7, *C*HC–OH); 122.6 (*q*, ^1J = 273.0, CF_3); 122.9 (*q*, ^1J = 274.0, CF_3); 127.9 (*C*COMe); 129.3 (*q*, ^2J = 33.0, CF_3*C*C); 133.8 (*q*, ^2J = 33.9, CF_3*C*CH); 155.6 (COH); 204.1 (*C*OMe). ^{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 $C_{10}H_6F_6O_2$ (272.14): C 44.13, H 2.22; found: C 44.00, H 2.41.

REFERENCES

[1] P. Langer, *Synthesis* **2002**, 441.
[2] C. Mamat, T. Pundt, A. Schmidt, P. Langer, *Tetrahedron Lett.* **2006**, *47*, 2183.
[3] S. Büttner, A. Riahi, I. Hussain, M. A.Yawer, M. Lubbe, A. Villinger, H. Reinke, C. Fischer, P. Langer, *Tetrahedron* **2009**, *65*, 2124.
[4] I. Hussain, A. Riahi, M. A. Yawer, A. Villinger, C. Fischer, H. Görls, P. Langer, *Org. Biomol. Chem.* **2008**, *6*, 3542.
[5] S. Büttner, M. Lubbe, H. Reinke, C. Fischer, P. Langer, *Tetrahedron* **2008**, *64*, 7968.
[6] C. Mamat, T. Pundt, T. H. T. Dang, R. Klassen, H. Reinke, M. Köckerling, P. Langer, *Eur. J. Org. Chem.* **2008**, 492.
[7] T.-H. Chan, P. Brownbridge, *J. Am. Chem. Soc.* **1980**, *102*, 3534; G. A. Molander, K. O. Cameron, *J. Am. Chem. Soc.* **1993**, *115*, 830.
[8] V. T. H. Nguyen, E. Bellur, B. Appel, P. Langer, *Synthesis* **2006**, 2865.
[9] V. T. H. Nguyen, B. Appel, P. Langer, *Tetrahedron* **2006**, *62*, 7674.

Received February 2, 2012