JOC Article

Synthesis of Trifluoromethyl-Substituted Arenes, Cyclohexenones and Pyran-4-ones by Cyclocondensation of 1,3-Bis(silyloxy)-1,3-butadienes with 4,4-Dimethoxy-1,1,1-trifluorobut-3-en-2-one: Influence of the Lewis Acid on the Product Distribution

Alina Bunescu,[†,‡] Sebastian Reimann,[†,‡] Mathias Lubbe,[†] Anke Spannenberg,[‡] and Peter Langer*[,†,‡]

Institut für Chemie, Universität Rostock, Albert-Einstein-Strausse 3a, 18059 Rostock, Germany, and Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Strausse 29a, 18059 Rostock, Germany

peter.langer@uni-rostock.de

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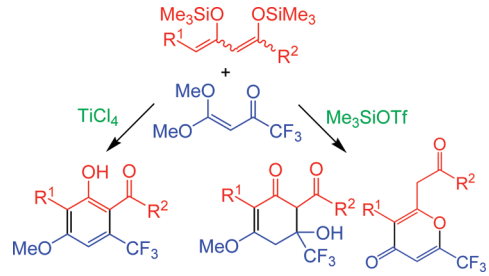

The $TiCl_4$-mediated formal [3 + 3] cyclocondensation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 4,4-dimethoxy-1,1,1-trifluorobut-3-en-2-one afforded a variety of functionalized 4-methoxy-6-(trifluoromethyl)salicylates and 3-methoxy-5-(trifluoromethyl)phenols with very good regioselectivity. The Me_3SiOTf-mediated cyclization of 1,3-bis(trimethylsilyloxy)-1,3-butadienes, containing no substituent located at carbon atom C-4 of the diene ($R^1 = H$), resulted in the formation of trifluoromethyl-substituted pyran-4-ones. In contrast, trifluoromethylated cyclohexenones were formed when dienes were employed which do contain a substituent located at carbon C-4 ($R^1 \neq H$).

Introduction

Trifluoromethyl-substituted arenes and hetarenes are of considerable importance in the field of medicinal chemistry.[1] While the sizes of the CH_3 and CF_3 groups are similar, the high electronegativity of the latter results in a dramatic change of the reactivity and polarity. The increased lipophilicity of CF_3-substituted molecules often results in a better transport of the drug in vivo which can play an important role in drug-receptor interactions. Due to the high chemical and biological stability of the CF_3 group, undesirable metabolic transformations are often reduced. Besides, CF_3-substituted molecules play an important role as ligands[2] for catalytic reactions in fluorous biphase systems,[3] as organocatalysts,[4] and as liquid crystals.[5]

* To whom correspondence should be addressed. Fax: 00 49 381 49864112. Tel: 0049 381 4986410.
† Institut für Chemie.
‡ Leibniz-Institut für Katalyse e. V.

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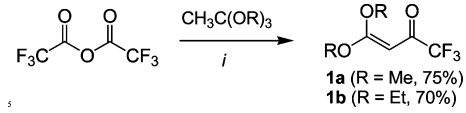
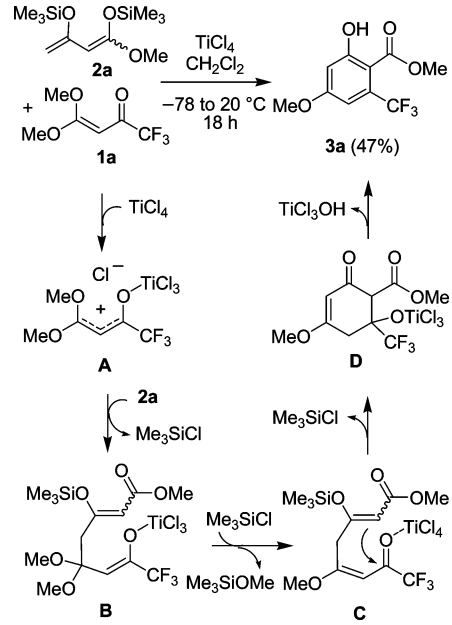
Trifluoromethyl-substituted arenes and hetarenes are available, for example, by reaction of aryl halides with trifluoromethylcopper.[6,7] However, this reagent is rather unstable and can decompose in reactions with "difficult" substrates. In addition, the synthesis of the required aromatic starting materials can be a difficult task. Other syntheses rely on the transformation of carboxylic acids or CX_3 into CF_3 groups, but these reactions often work only for specific substrates. An alternative strategy relies on the employment of suitable CF_3-containing building blocks.[8] In this context, cyclocondensations,[9,10] condensations of metalated (trifluoromethyl)arenes,[11] Diels−Alder reactions,[12] and cyclizations of enamines with 1,1,1,5,5,5-hexafluoroacetylacetone have been developed.[13] We have recently reported[14] the synthesis of CF_3-substituted salicylates by formal [3 + 3] cyclizations[15,16] of 1,3-bis(silyloxy)-1,3-butadienes[17] with 4-ethoxy-1,1,1-trifluoroalk-3-en-2-ones. Despite its preparative utility, the scope of this method is limited to products containing no functional group located at carbon atoms C3 or C-5.[18] However, biologically active molecules often contain a hydroxy or methoxy group at one of these positions, because they are related to naturally occurring polyketides. Recently, we have reported the $TiCl_4$-mediated cyclocondensation of 1,3-bis(silyloxy)-1,3-butadienes with 4,4-dimethoxy-1,1,1-trifluorobut-3-en-2-one.[19] These reactions provide a convenient and regioselective approach to 4-methoxy-6-(trifluoromethyl)salicylates. Herein, we report full details of this study. In addition, we report, for the first time, the influence of the Lewis acid on the product distribution. The Me_3SiOTf-mediated cyclization of 1,3-bis(trimethylsilyloxy)-1,3-butadienes, containing no substituent located at carbon atom C-4 of the diene ($R^1 = H$), resulted in the formation of trifluoromethyl-substituted pyran-4-ones. In contrast, trifluoromethylated cyclohexenones were formed when dienes were employed which do contain a substituent located at carbon C-4 ($R^1 \neq H$). The synthesis of pyran-4-ones from 1,3-bis(trimethylsilyloxy)-1,3-butadienes has, to the best of our knowledge, not been previously reported.

SCHEME 1. Synthesis of 1a,b[a]



[a] Conditions: *i*, pyridine, $CHCl_3$, 20 °C, 12 h.

SCHEME 2. Possible Mechanism of the Formation of 3a[a]



[a] Conditions: *i*, $TiCl_4$, CH_2Cl_2, −78 → 20 °C.

TABLE 1. Optimization of the Synthesis of 3a

n (**1**) [mmol]	*n* (**2a**) [mmol]	*V* (CH_2Cl_2) [mL]	yield (**3a**)[a] [%]
1	1	1	34
1	1	2	38
1	1	5	26
1	1	10	19
1	1.5	2	40
1	2	2	47

[a] Yields of isolated products.

Results and Discussion

The reactions of trifluoroacetic anhydride with 1,1,1-trimethoxy- and triethoxyethane afford 4,4-dimethoxy-1,1,1-trifluorobut-3-en-2-one (**1a**) and 4,4-diethoxy-1,1,1-trifluorobut-3-en-2-one (**1b**) (Scheme 1).[20] 1,3-Bis(silyloxy)-1,3-butadienes **2a**−**t** are prepared according to the literature from the corresponding β-ketoesters in two steps.[16,21,22]

The $TiCl_4$-mediated reaction of **1a** with 1,3-bis(silyloxy)-1,3-butadiene **2a** affords 4-methoxy-6-(trifluoromethyl)salicylate **3a** in 47% yield (Scheme 2). During the optimization (Table 1), the concentration, the temperature and the stoichiometry play an important role. The best yield is obtained when the solution is slowly warmed from −78 to 20 °C, when the reaction is

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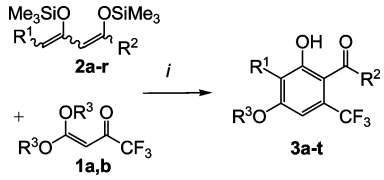
SCHEME 3. Synthesis of 3a−t[a]



[a] Conditions: *i*, $TiCl_4$, CH_2Cl_2, −78 → 20 °C.

TABLE 2. Synthesis of 3a−t

1	2	3	R^1	R^2	R^3	yield (**3**) [%][a]
a	**a**	**a**	H	OMe	Me	47
b	**a**	**b**	H	OMe	Et	31
a	**b**	**c**	H	OEt	Me	34
a	**c**	**d**	H	OBn	Me	32
a	**d**	**e**	H	O*i*Pr	Me	36
a	**e**	**f**	H	$O(CH_2)_2OMe$	Me	35
a	**f**	**g**	Me	OMe	Me	34
a	**g**	**h**	Me	Et	Me	31
a	**h**	**i**	Et	OEt	Me	44
a	**i**	**j**	Allyl	OMe	Me	42
a	**j**	**k**	*n*Pr	OMe	Me	41
a	**k**	**l**	*n*Bu	OMe	Me	40
a	**l**	**m**	*n*Hex	OMe	Me	30
a	**m**	**n**	*n*Oct	OMe	Me	30
a	**n**	**o**	*n*Undec	OMe	Me	30
a	**o**	**p**	$(CH_2)_2Ph$	OMe	Me	38
a	**p**	**q**	$(CH_2)_3Ph$	OMe	Me	43
a	**q**	**r**	OMe	OMe	Me	50
b	**q**	**s**	OMe	OMe	Et	33
a	**r**	**t**	$(CH_2)_3Cl$	OMe	Me	57

[a] Yields of isolated products.

carried out in a highly concentrated solution, and when an excess (2.0 equiv) of **2a** is employed.

The formation of **3a** can be explained by reaction of **1a** with $TiCl_4$ to give **A** containing an allylic carbon unit. The attack of the terminal carbon atom of **2a** onto **A** affords intermediate **B**. The elimination of Me_3SiOMe (intermediate **C**) and subsequent cyclization gives intermediate **D** (Scheme 2). The elimination of titanium hydroxide (before or during the aqueous workup) and aromatization results in the formation of product **3a**. Product **3a**, containing the CF_3 group located *ortho* to the ester group, is formed with excellent regioselectivity. The formation of the other regioisomer, containing the CF_3 group located *para* to the ester group, is not observed. The moderate yield can be explained by $TiCl_4$-mediated oxidative dimerization of the diene. This type of process has been previously reported.[23]

The $TiCl_4$-mediated reactions of **1a**,**b** with 1,3-bis(silyloxy)-1,3-butadienes **2a**−**r** afford the 4-methoxy-6-(trifluoromethyl)-salicylates **3a**−**f** and **3h**−**t** and the 3-methoxy-5-(trifluoromethyl)phenol **3g** in moderate yields (Scheme 3, Table 2). The products are not readily available by other methods. Better yields are obtained for enone **1a** than for **1b** (**3a** and **3b**, **3r** and **3s**). The yields also depend on the type of diene employed. However, no clear trend is observed.

The structures of the products are confirmed by spectroscopic methods. The structure of **3e** is independently confirmed by X-ray crystal structure analysis (see Supporting Information).

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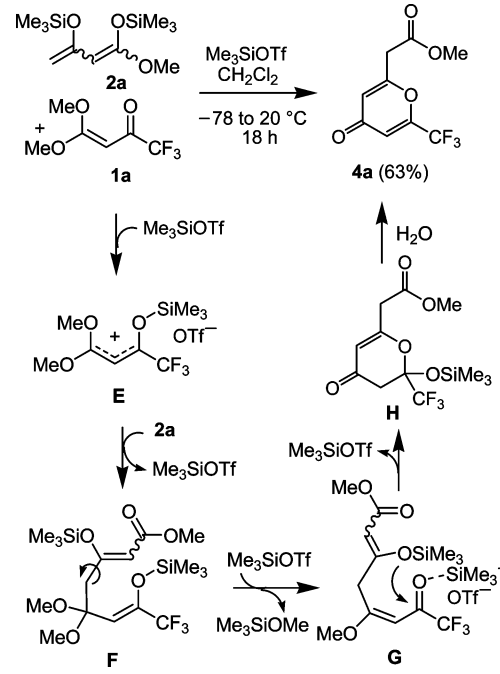
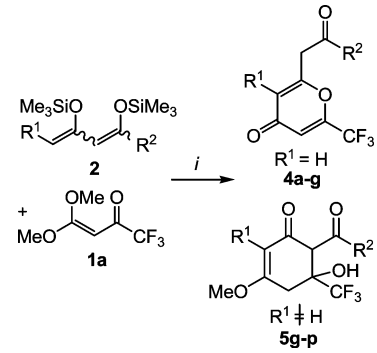
SCHEME 4. Possible Mechanism of the Formation of 4a



SCHEME 5. Synthesis of 4a−g and 5g−p[a]



[a] Conditions: *i*, Me_3SiOTf, CH_2Cl_2, −78 → 20 °C.

The reaction of **1a** with 1,3-bis(silyloxy)-1,3-butadiene **2a**, carried out in the presence of Me_3SiOTf (1.0 equiv) rather than $TiCl_4$, results in the formation of pyran-4-one **4a** in 63% yield (Scheme 4).

The formation of **4a** presumably proceeds by formation of allylic cation **E**. The attack of the terminal carbon atom of **2a** onto **E** gives intermediate **F**. The elimination of Me_3SiOMe (intermediate **G**) and subsequent cyclization via the oxygen rather than the carbon atom gives intermediate **H**. The elimination of silanol (before or during the aqueous workup) results in the formation of pyran-4-one **4a**. The formation of product **3a** is *not* observed.

The Me_3SiOTf-mediated reactions of **1a** with 1,3-bis(silyloxy)-1,3-butadienes **2a**−**e** and **2s**, all containing no substituent located at carbon atom C-4 of the diene (R^1 = H), afford pyran-4-ones **4a**−**f** in 32−69% yield (Scheme 5, Table 3). The reaction conditions have been optimized for the synthesis of derivative **4d** (Table 4). The best yield is obtained when an excess of **2d** is employed. In contrast to the $TiCl_4$-mediated syntheses of salicylates **3**, which are carried out in a highly concentrated solution, the yield of **4d** can be significantly improved when the reaction is carried out in a more dilute solution.

TABLE 3. Synthesis of 4a−g and 5g−p

2	4,5	R^1	R^2	yield (**4**) (%)[a]	yield (**5**) (%)[a]
a	**a**	H	OMe	63	0
b	**b**	H	OEt	69	0
c	**c**	H	OBn	32	0
d	**d**	H	O*i*Pr	64	0
e	**e**	H	$O(CH_2)_2OMe$	40	0
s	**f**	H	O*i*Bu	64	0
f	**g**	Me	OMe	12	38
t	**h**	Et	OMe	0	50
u	**i**	Cl	OMe	0	44
v	**j**	*n*-Pent	OEt	0	39
w	**k**	*n*-Hep	OEt	0	35
m	**l**	*n*-Oct	OMe	0	62
x	**m**	*n*-Non	OMe	0	57
y	**n**	*n*-Dodec	OMe	0	58
z	**o**	*n*-Hexadec	OMe	0	54
aa	**p**	$(CH_2)_2$*i*Pr	OMe	0	55

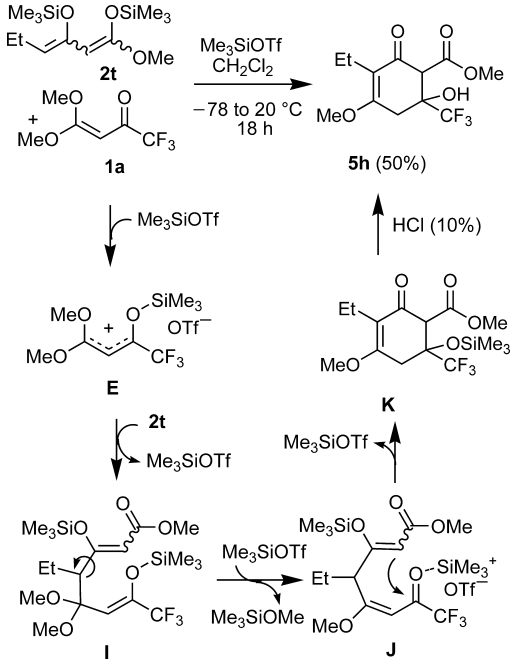
[a] Yields of isolated products.

TABLE 4. Optimization of the Synthesis of 4d

n (**1a**) (mmol)	*n* (**2d**) (mmol)	*V* (CH_2Cl_2) (mL)	yield (**4d**) (%)[a]
1	2	1	42
1	2	2	50
1	2	10	64
1	2	15	60
1	1	15	31

[a] Yields of isolated products.

SCHEME 6. Possible Mechanism of the Formation of 5h



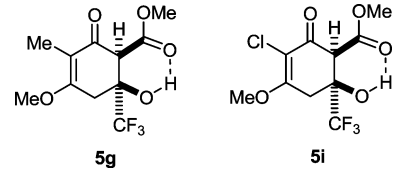
The Me_3SiOTf-mediated reactions of **1a** with 1,3-bis(silyloxy)-1,3-butadienes **2m** and **2t**−**aa**, which contain an alkyl or a chloride group located at carbon C-4 of the diene moiety ($R^1 \neq H$), afford the cyclohexenones **5g**−**p** in 38−62% yield (Scheme 5, Table 3). The formation of product **5h** can be explained by a mechanism related to the one suggested for the formation of products **4** (Scheme 6). The reaction of diene **2t** with intermediate **E** affords intermediate **I** which is transformed into intermediate **J**. Intermediates **I** and **J** are closely related to intermediates **F** and **G** (*vide supra*). The cyclization of **J** proceeds via the carbon atom. The formation of pyran-4-ones **4** is *not* observed. This might be explained by the steric influence of the ethyl group (R^1 = Et) which results in a change of the conformation of intermediate **J** with regard to **G** (allylic strain). In contrast to the formation of salicylates **3**, no elimination of the hydroxyl group and aromatization occurs. This result is surprising since the aromatization should be a facile process. It might be explained by the assumption that intermediate **D**, containing a titanium alkoxide moiety, readily undergoes an elimination of $TiCl_3OH$ and aromatization *before* the aqueous work up (*vide supra*). In contrast, intermediate **K**, containing a silanolate moiety, is more stable and no elimination occurs. The addition of hydrochloric acid (10%) (aqueous work up) results in cleavage of Si−O bond, but no elimination and aromatization occurs. The stability of compounds **5** might be explained by the presence of the electron-withdrawing CF_3 group. The rate of the acid-mediated elimination of water is decreased because a cation located next to the CF_3 group is expected to be unstable and an elimination requires more drastic conditions.

TABLE 5. Optimization of the Synthesis of 4g and 5g

n (**1a**) (mmol)	*n* (**2f**) (mmol)	*V* (CH_2Cl_2) (mL)	yield (**4g**) (%)[a]	yield (**5g**) (%)[a]
1	1	2	10	15
1	1	10	9	20
1	2	10	12	38
1	3	10	10	12
1	2	5	24	19
1	2	15	12	26

[a] Yields of isolated products.

SCHEME 7. Relative Configuration of 5g and 5i



The cyclization of **1a** with diene **2f** is of special interest because both pyran-4-one **4g** (12%) and cyclohexenone **5g** (38%) can be isolated. This might be explained by the fact that the steric influence of the methyl group (R^1 = Me) is relatively small. The influence of the reaction conditions on the product distribution has been studied for this reaction (Table 5). The best yield of **5g** is observed when 2.0 equiv of **2f** is used and when the cyclization is carried out in a relatively dilute solution. The yield decreases when 1.0 or 3.0 equiv of the diene is employed.

The structures of all products are confirmed by spectroscopic methods. The structure of **4a** is independently confirmed by X-ray crystal structure analysis (see Supporting Information).

The structures of **5g**, and **5i** are independently confirmed by X-ray crystal structure analyses (see Supporting Information). The X-ray structures of **5g**, and **5i** allow to unambiguously prove the relative configuration of these molecules. The hydroxyl and the ester group are located *cis* to eachother and an intramolecular hydrogen bond O−H···O is present (Scheme 7). In solution, only one major isomer is present. In some cases, a small amount of the minor isomer can be detected.

Under the conditions of mass spectrometry (EI, electron ionization), elimination of water from cyclohexenones **5** is observed and only the molecular ions of the aromatized products can be detected. The correct molecular ions are observed when the measurements are carried out using the milder ESI technique (electrospray ionization).

Conclusions

In conclusion, we report the $TiCl_4$-mediated formal [3 + 3] cyclocondensation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 4,4-dimethoxy-1,1,1-trifluorobut-3-en-2-one. These reactions allow for a convenient synthesis of a variety of functionalized 4-methoxy-6-(trifluoromethyl)salicylates with very good regioselectivity. The Me_3SiOTf-mediated cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes, containing no substituent located at carbon atom C-4 of the diene (R^1 = H), result in a cyclization via the oxygen atom and formation of pyran-4-ones. The reasons for the influence of the Lewis acid on the regioselectivity of cyclization remain unclear at present. Trifluoromethyl-substituted cyclohexenones are formed in the Me_3SiOTf-mediated cyclization of 1,3-bis(trimethylsilyloxy)-1,3-butadienes which contain a substituent located at carbon C-4 ($R^1 \neq$ H).

Experimental Section

General Comments. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063−0.200 mm, 70−230 mesh) was used. 1,3-Bis(silyloxy)-1,3-butadienes **2a**−**aa** were prepared according to the literature from the corresponding β-ketoesters in two steps.[16,21,22]

4,4-Dimethoxy-1,1,1-trifluorobut-3-en-2-one (1a). To a stirred dichloromethane solution (10 mL) of trimethyl orthoacetate (1.202 g, 10.0 mmol) and pyridine (1.820 g, 23.0 mmol) was dropwise added trifluoroacetic acid anhydride (4.201 g, 20 mmol) at 0 °C, and the mixture was subsequently stirred for 24 h at 20 °C. The mixture was washed with an aqueous solution of sodium carbonate (5%, 20 mL>). The organic layer was dried (sodium sulfate), filtered and the solvent and the pyridine were removed in vacuo to give **1a** as a light-yellow solid (1.350 g, 74%); mp = 52−53 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 3H), 3.97 (s, 3H), 4.98 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5, 57.7, 72.1, 116.8 (q, J_{C-F} = 292.4 Hz), 172.3, 175.9 (q, J_{C-F} = 32.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ = −77.3. MS (EI, 70 eV): *m/z* (%): 184 (M^+, 8), 139 (3), 115 (100), 103 (5), 69 (88), 59 (10). HRMS (EI, 70 eV): Calcd for $C_6H_7F_3O_3$ (M^+) 184.03394, found 184.034018.

The synthesis of **1b** has been previously reported.[20]

General Procedure for the Synthesis of 3a−t. To a CH_2Cl_2 solution (2 mL/1 mmol of **1a**,**b**) of **1a**,**b** (1.0 mmol) was added **2a**−**r** (2.0 mmol) and, subsequently, $TiCl_4$ (0.1 mL, 1.0 mmol) at −78 °C. The temperature of the solution was allowed to warm to 20 °C during 12−14 h with stirring. To the solution was added HCl (10%, 10 mL), and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by chromatography.

Methyl 2-Hydroxy-4-methoxy-6-(trifluoromethyl)benzoate (3a). Starting with **1a** (0.184 g, 1.0 mmol), **2a** (0.521 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3a** was isolated as a light-yellow solid (0,117 g, 47%); mp = 66−67 °C; R_F = 0.73 (heptane/EtOAc = 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.85, 3.95 (s, 3H), 6.62, 6.69 (s, 1H), 11.41 (s, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 52.5, 55.8, 103.0, 103.6, 109.3 (q, J_{C-F} = 7.3 Hz), 123.0 (q, J_{C-F} = 273.3 Hz), 131.8 (q, J_{C-F} = 32.5 Hz), 163.6, 165.1, 169.7. ^{19}F NMR (235 MHz, $CDCl_3$): δ = −59.3. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2985 (w), 2960 (w), 2923 (w), 2856 (w), 1662 (s), 1615 (s), 1593 (s), 1440 (s). MS (EI, 70 eV): *m/z* (%): 250 (M^+, 40), 219 (39), 218 (100), 190 (42), 175 (36), 147 (13). Anal. Calcd for $C_{10}H_9F_3O_4$ (250.17): C, 48.01; H, 3.63. Found: C, 48.28; H, 3.62.

Methyl 2-Hydroxy-4-ethoxy-6-(trifluoromethyl)benzoate (3b). Starting with **1b** (213 mg, 1.0 mmol), **2a** (0.521 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product**3b** was isolated as a colorless solid (0.082 g, 31%); mp = 62−63 °C; R_F = 0.78 (heptane/EtOAc = 1:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.44 (t, ^3J = 7.0 Hz, 3H), 3.95 (s, 3H), 4.07 (q, ^3J = 7.0 Hz, 2H), 6.59, 6.89 (s, 1H), 11.45 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 52.5, 64.2, 102.8, 104.0, 109.7 (q, J_{C-F} = 7.1 Hz), 123.1 (q, J_{C-F} = 273.4 Hz), 131.8 (q, J_{C-F} = 31.9 Hz), 162.9, 165.1, 169.8. ^{19}F NMR (235 MHz, $CDCl_3$): δ = −59.3. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2986 (w), 2957 (w), 2902 (w), 2857 (w), 1664 (s), 1618 (s), 1585 (s), 1438 (s). MS (EI, 70 eV): *m/z* (%): 264 (M^+, 58), 233 (27), 232 (100), 205 (31), 204 (99), 176 (67). Anal. Calcd for $C_{11}H_{11}F_3O_4$ (264.20): C, 50.01; H, 4.20. Found: C, 50.33; H, 4.20.

Ethyl 2-Hydroxy-4-methoxy-6-(trifluoromethyl)benzoate (3c). Starting with **1a** (0.184 g, 1.0 mmol), **2b** (0.549 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3c** was isolated as a white solid (0.090 g, 34%); mp = 83−84 °C; R_F = 0.64 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.40 (t, ^3J = 7.2 Hz, 3H), 3.85 (s, 3H), 4.41 (q, ^3J = 7.1 Hz, 2H), 6.60 (d, ^4J = 2.4 Hz, 1H), 6.89 (d, ^4J = 2.4 Hz, 1H), 11.59 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 55.7, 62.1, 103.3, 103.6, 109.3 (q, J_{C-F} = 7.2 Hz), 123.1 (q, J_{C-F} = 271.5 Hz), 131.8 (q, J_{C-F} = 32.0 Hz), 163.4, 165.2, 169.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2984 (w), 1650 (m), 1618 (m), 1591 (m), 1467 (w), 1447 (w), 1424 (m), 1371 (m), 1282 (s), 1238 (s), 1207 (s), 1125 (s), 1038 (s), 985 (s), 869 (s), 803 (s), 711 (s). GC-MS (EI, 70 eV): *m/z* (%): 264 (M^+, 31), 219 (32), 218 (100), 190 (35), 175 (22). Anal. Calcd for $C_{11}H_{11}F_3O_4$ (264.20): C, 50.01; H, 4.20. Found: C, 50.15; H, 4.22.

Benzyl 2-Hydroxy-4-methoxy-6-(trifluoromethyl)benzoate (3d). Starting with **1a** (0.184 g, 1.0 mmol), **2c** (0.673 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3d** was isolated as a slightly yellow solid (0.100 g, 32%); mp = 44−46 °C; R_F = 0.60 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3H), 5.35 (s, 2H), 6.56 (d, ^4J = 2.5 Hz, 1H), 6.84 (d, ^4J = 2.5 Hz, 1H), 7.32−7.42 (m, 5H), 11.50 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.7, 67.9, 103.0, 103.6, 109.4 (q, J_{C-F} = 7.1 Hz), 123.0 (q, J_{C-F} = 271.9 Hz), 128.5, 128.6, 128.8, 131.7 (q, J_{C-F} = 32.0 Hz), 134.5, 163.6, 165.4, 169.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3074 (w), 2969 (w), 1655 (m), 1620 (m), 1372 (m), 1322 (m), 1274 (m), 1210 (s), 1127 (s), 985 (s), 863 (s), 799 (m), 741 (s). GC-MS (EI, 70 eV): *m/z* (%): 326 (M^+, 14), 91 (100). HRMS (EI, 70 eV): calcd for $C_{16}H_{13}F_3O_4$ (M^+) 326.07604, found 326.07538.

Isopropyl 2-Hydroxy-4-methoxy-6-(trifluoromethyl)-benzoate (3e). Starting with **1a** (0.184 g, 1.0 mmol), **2d** (0.577 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3e** was isolated as a slightly yellow solid (0.100 g, 36%); mp = 45−47 °C; R_F = 0.69 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.36 (s, 3H), 1.38 (s, 3H), 3.84 (s, 3H), 5.22−5.35 (m, 1H), 6.59 (d, ^4J = 2.5 Hz, 1H), 6.88 (d, ^4J = 2.5 Hz, 1H), 11.70 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 55.7, 70.5, 103.6, 103.7, 109.2 (q, J_{C-F} = 7.2 Hz), 123.1 (q, J_{C-F} = 271.7 Hz), 131.7 (q, J_{C-F} = 32.0 Hz), 163.3, 165.2, 168.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −57.6. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2978 (w), 1654 (m), 1618 (m), 1590 (w), 1467 (w), 1446 (w), 1426 (w), 1365 (s), 1278 (s), 1207 (s), 1125 (s), 1037 (s), 985 (s), 803 (s), 713 (s). GC-MS (EI, 70 eV): *m/z* (%): 278 (M^+, 14), 236 (16), 219 (29), 218 (100). Anal. Calcd for $C_{12}H_{13}F_3O_4$ (278.22): C, 51.80; H, 4.71. Found: C, 51.55; H, 4.58.

2-Methoxyethyl 2-hydroxy-4-methoxy-6-(trifluoromethyl)-benzoate (3f). Starting with **1a** (0.184 g, 1.0 mmol), **2e** (0.609 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3f** was isolated as a white solid (0.103 g, 35%); mp = 57−58 °C; R_F = 0.49 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$):

δ = 3.40 (s, 3H, OCH_3), 3.72 (t, ^3J = 4.8 Hz, 2H), 3.85 (s, 3H), 4.49 (t, ^3J = 4.8 Hz, 2H), 6.60 (2 × d, ^4J = 2.7 Hz, 1H), 6.89 (2 × d, ^4J = 2.7 Hz, 1H), 11.28 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.7, 58.9, 64.7, 69.6, 103.3, 103.6, 109.3 (q, J_{C-F} = 7.0 Hz), 123.1 (q, J_{C-F} = 272.0 Hz), 131.7 (q, J_{C-F} = 32.0 Hz), 163.5, 164.9, 168.9. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.3. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3096 (w), 2935 (w), 2824 (w), 1650 (m), 1598 (m), 1431 (m), 1376 (s), 1336 (s), 1285 (s), 1244 (s), 1212 (s), 1128 (s), 1025 (s), 986 (s), 891 (s), 808 (s), 715 (s). GC-MS (EI, 70 eV): *m/z* (%): 294 (M^+, 20), 236 (19), 219 (71), 218 (100), 190 (22), 171 (15), 59 (19). Anal. Calcd for $C_{12}H_{13}F_3O_5$ (294.22): C, 48.99; H, 4.45. Found: C, 48.72; H, 4.46.

Methyl 2-Hydroxy-4-methoxy-3-methyl-6-(trifluoromethyl)-benzoate (3g). Starting with **1a** (0.184 g, 1.0 mmol), **2f** (0.549 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3g** was isolated as a white solid (0.091 g, 34%); mp = 65−67 °C; R_F = 0.88 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 6.86 (s, 1H), 11.26 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.3, 52.5, 55.8, 102.5 (q, J_{C-F} = 7.0 Hz), 104.0, 117.7, 123.5 (q, J_{C-F} = 271.6 Hz), 128.9 (q, J_{C-F} = 31.6 Hz), 160.7, 161.3, 170.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2959 (w), 2866 (w), 1657 (s), 1607 (w), 1586 (w), 1439 (m), 1286 (s), 1248 (s), 1121 (s), 999 (s), 842 (s), 713 (s). GC-MS (EI, 70 eV): *m/z* (%): 264 (M^+, 72), 233 (45), 232 (100), 231 (14), 214 (16), 212 (60), 204 (68), 203 (18), 202 (28), 185 (15). Anal. Calcd for $C_{11}H_{11}F_3O_4$ (264.20): C, 50.01; H, 4.20. Found: C, 50.06; H, 4.22.

3-Methyl-2-hydroxy-4-methoxy-6-(trifluoromethyl)-propiophenone (3h). Starting with **1a** (0.184 g, 1.0 mmol), **2g** (0.545 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3h** was isolated as a slightly yellow solid (0.080 g, 30%); mp = 95−98 °C; R_F = 0.64 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, ^{3} = 7.2 Hz, 3H), 2.13 (s, 3H), 2.88 (q, ^3J = 7.3 Hz, 2H), 3.90 (s, 3H), 6.76 (s, 1H), 9.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.4, 9.1, 36.9 (q, J_{C-F} = 5 Hz), 55.8, 101.6 (q, J_{C-F} = 5.6 Hz), 115.7, 117.9, 124.0 (q, J_{C-F} = 271.6 Hz), 126.9 (q, J_{C-F} = 31.3 Hz), 157.0, 159.9, 208.5. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −54.7. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3338 (w), 2931 (w), 1679 (m), 1606 (m), 1587 (m), 1455 (w), 1408 (w), 1347 (s), 1241 (s), 1117 (s), 837 (s), 705 (m). GC-MS (EI, 70 eV): *m/z* (%): 262 (M^+, 13), 233 (100), 185 (17). Anal. Calcd for $C_{12}H_{13}F_3O_3$ (262.23): C, 54.96; H, 5.00. Found: C, 54.88; H, 5.34.

Ethyl 3-Ethyl-2-hydroxy-4-methoxy-6-(trifluoromethyl)-benzoate (3i). Starting with **1a** (0.184 g, 1.0 mmol), **2h** (0.605 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3i** was isolated as a white solid (0.130 g, 44%); mp = 50−51 °C; R_F = 0.77 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 7.5 Hz, 3H), 1.39 (t, ^3J = 7.0 Hz, 3H), 2.70 (q, ^3J = 7.4 Hz, 2H), 3.90 (s, 3H), 4.41 (q, ^3J = 7.1 Hz, 2H), 6.86 (s, 1H), 11.32 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 13.5, 16.4, 55.7, 62.1, 102.7 (q, J_{C-F} = 7.2 Hz), 104.5, 123.6, 123.6 (q, J_{C-F} = 271.5 Hz), 129.0 (q, J_{C-F} = 31.7 Hz), 160.4, 161.2, 169.7. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −57.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2984 (m), 2950 (m), 1655 (s), 1609 (w), 1584 (w), 1468 (w), 1451 (w), 1398 (m), 1321 (s), 1247 (s), 1123 (s), 1021 (m), 846 (s), 808 (s), 713 (s). GC-MS (EI, 70 eV): *m/z* (%): 292 (M^+, 54), 247 (39), 246 (100), 231 (29), 226 (48), 218 (77), 208 (16), 200 (15), 175 (17). Anal. Calcd for $C_{13}H_{15}F_3O_4$ (292.25): C, 53.43; H, 5.17. Found: C, 53.25; H, 5.05.

Methyl 3-Allyl-2-hydroxy-4-methoxy-6-(trifluoromethyl)-benzoate (3j). Starting with **1a** (0.184 g, 1.0 mmol), **2i** (0.601 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3j** was isolated as a colorless oil (0.123 g, 42%); R_F = 0.78 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.45 (dt, ^3J = 6.1 Hz, 2H), 3.90 (s, 3H), 3.94 (s, 3H) 4.96−5.04 (m, 2H), 5.87−5.97 (m, 1H), 6.88 (s, 1H), 11.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.2, 52.6, 55.9, 102.8 (q, J_{C-F} = 7.0 Hz), 104.4, 115.1, 119.4, 123.4 (q, J_{C-F} = 271.6 Hz), 129.7 (q, J_{C-F} = 31.6 Hz), 134.9, 160.7, 161.2, 170.0. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.3. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2956 (w), 1667 (m), 1608 (m), 1439 (m), 1404 (m), 1293 (s), 1245 (s), 1203 (s), 1127 (s), 1004 (m), 845 (m), 715 (m). GC-MS (EI, 70 eV): *m/z* (%): 290 (M^+, 26), 270 (12), 259 (20), 258 (37), 243 (100), 230 (16), 215 (37). HRMS (EI, 70 eV): calcd for $C_{13}H_{13}F_3O_4$ (M^+) 290.07604, found 290.07604.

Methyl 2-Hydroxy-4-methoxy-3-propyl-6-(trifluoromethyl)-benzoate (3k). Starting with **1a** (0.184 g, 1.0 mmol), **2j** (0.605 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3k** was isolated as a slightly yellow solid (0.120 g, 41%); mp = 43−45 °C; R_F = 0.77 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, ^3J = 7.3 Hz, 3H), 1.46−1.59 (m, 2H), 2.66 (t, ^3J = 7.6 Hz, 2H), 3.89 (s, 3H), 3.94 (s, 3H), 6.86 (s, 1H), 11.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 21.6, 24.9, 52.5, 55.7, 102.7 (q, J_{C-F} = 7.0 Hz), 104.2, 122.2, 123.5 (q, J_{C-F} = 271.5 Hz), 129.0 (q, J_{C-F} = 31.7 Hz), 160.7, 161.3, 170.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2961 (w), 2866 (w), 1659 (m), 1611 (w), 1582 (w), 1441 (m), 1405 (m), 1320 (m), 1246 (s), 1127 (s), 1000 (m), 849 (s), 715 (s). GC-MS (EI, 70 eV): *m/z* (%): 292 (M^+, 53), 261 (28), 260 (72), 245 (29), 243 (17), 232 (71), 231 (100), 229 (17), 212 (13), 204 (23), 201 (15), 181 (31). Anal. Calcd for $C_{13}H_{15}F_3O_4$ (292.25): C, 53.43; H, 5.17. Found: C, 53.54; H, 5.17.

Methyl 3-Butyl-2-hydroxy-4-methoxy-6-(trifluoromethyl)-benzoate (3L). Starting with **1a** (0.184 g, 1.0 mmol), **2k** (0.633 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3l** was isolated as a white solid (0.102 g, 40%); mp = 29−30 °C; R_F = 0.71 (*n*-hexane/CH_2Cl_2 = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.2 Hz, 3H), 1.29−1.57 (m, 4H), 2.68 (t, ^3J = 7.6 Hz, 2H), 3.89 (s, 3H), 3.94 (s, 3H), 6.86 (s, 1H), 11.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.8, 22.9, 30.5, 52.5, 55.7, 102.7 (q, J_{C-F} = 7.0 Hz), 104.2, 122.5, 123.5 (q, J_{C-F} = 271.2 Hz), 129.0 (q, J_{C-F} = 31.7 Hz), 160.7, 161.2, 170.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2958 (w), 2938 (w), 2860 (w), 1664 (m), 1586 (w), 1436 (m), 1403 (m), 1320 (m), 1250 (s), 1125 (s), 850 (s), 808 (s), 715 (m). GC-MS (EI, 70 eV): *m/z* (%): 306 (M^+, 39), 275 (15), 257 (15), 245 (23), 243 (52), 232 (100), 231 (78), 212 (18), 204 (25), 181 (24). Anal. Calcd. for $C_{14}H_{17}F_3O_4$ (306.28): C, 54.90; H, 5.59. Found: C, 55.02; H, 5.64.

Methyl 3-Hexyl-2-hydroxy-4-methoxy-6-(trifluoromethyl)-benzoate (3m). Starting with **1a** (0.184 g, 1.0 mmol), **2 L** (0.689 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product**3m** was isolated as a white solid (0.100 g, 30%); mp = 34−35 °C; R_F = 0.74 (*n*-hexane/CH_2Cl_2 = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.7 Hz, 3H), 1.25−1.56 (m, 8H), 2.67 (t, ^3J = 7.5 Hz, 2H), 3.89 (s, 3H), 3.94 (s, 3H) 6.86 (s, 1H), 11.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 23.0, 28.3, 29.4, 31.7, 52.5, 55.7, 102.7 (q, J_{C-F} = 7.0 Hz), 104.1, 122.5, 123.5 (q, J_{C-F} = 271.5 Hz), 128.9 (q, J_{C-F} = 31.7 Hz), 160.7, 161.2, 170.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2931 (w), 2851 (w), 1671 (m), 1601 (m), 1501 (w), 1439 (m), 1404 (m), 1306 (s), 1246 (s), 1148 (s), 1117 (s), 1001 (m), 933 (m), 845 (s), 717 (m). GC-MS (EI, 70 eV): *m/z* (%): 334 (M^+, 31), 303 (14), 285 (12), 271 (64), 245 (18), 232 (100), 231 (89), 212 (17), 204 (23), 181 (24). Anal. Calcd for $C_{16}H_{21}F_3O_4$ (334.33): C, 57.48; H, 6.33. Found: C, 57.43; H, 6.25.

Methyl 2-Hydroxy-4-methoxy-6-(trifluoromethyl)-3-octyl-benzoate (3n). Starting with **1a** (0.184 g, 1.0 mmol), **2m** (0.754 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3n** was isolated as a white solid (0.110 g, 30%); mp = 38−39 °C; R_F = 0.62 (*n*-hexane/CH_2Cl_2 = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.7 Hz, 3H), 1.26−1.56 (m, 12H), 2.66 (t, ^3J = 7.5 Hz, 2H), 3.89 (s, 3H), 3.94 (s, 3H) 6.86 (s, 1H), 11.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 23.0, 28.3, 29.2, 29.4, 29.7, 31.9, 52.5, 55.7, 102.6 (q, J_{C-F} = 7.0 Hz), 104.1, 122.5, 123.5 (q, J_{C-F} = 271.5 Hz), 128.9 (q, J_{C-F} = 31.5 Hz), 160.6, 161.2, 170.1. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2918 (m), 2849 (m), 1656 (m), 1611 (w), 1584 (w), 1463 (w), 1441 (m), 1320 (s), 1250 (s), 1207 (s), 1126 (s), 1010 (w), 933

(m), 717 (s). GC-MS (EI, 70 eV): *m/z* (%): 362 (M^+, 28), 331 (15), 313 (12), 299 (69), 245 (17), 233 (12), 232 (100), 231 (87), 212 (15), 204 (20), 181 (19). HRMS (EI, 70 eV): calcd for $C_{18}H_{25}F_3O_4$ (M^+) 362.16995, found 362.16995.

Methyl 2-Hydroxy-4-methoxy-6-(trifluoromethyl)-3-undecylbenzoate (3o). Starting with **1a** (0.184 g, 1.0 mmol), **2n** (0.829 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3o** was isolated as a white solid (0.120 g, 30%); mp = 55−56 °C; R_F = 0.50 (*n*-hexane/CH_2Cl_2 = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.7 Hz, 3H), 1.25−1.55 (m, 18H), 2.66 (t, ^3J = 7.6 Hz, 2H), 3.89 (s, 3H), 3.94 (s, 3H), 6.86 (s, 1H), 11.18 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.6, 23.0, 28.3, 29.3, 29.5, 29.6, 29.6, 29.7, 29.8, 31.9, 52.5, 55.7, 102.6 (q, J_{C-F} = 7.0 Hz), 104.1, 122.5, 123.5 (q, J_{C-F} = 271.5 Hz), 128.9 (q, J_{C-F} = 31.5 Hz), 160.6, 161.2, 170.1. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2914 (m), 2894 (m), 1656 (m), 1610 (w), 1584 (w), 1465 (w), 1441 (m), 1316 (s), 1251 (s), 1207 (s), 1127 (s), 933 (m), 716 (s). GC-MS (EI, 70 eV): *m/z* (%): 404 (M^+, 24), 373 (12), 355 (13), 342 (14), 341 (67), 245 (16), 233 (14), 232 (100), 231 (87), 212 (14), 204 (18), 181 (18). Anal. Calcd for $C_{21}H_{31}F_3O_4$ (404.21): C, 62.36; H, 7.73. Found: C, 62.19; H, 7.93.

Methyl 2-Hydroxy-4-methoxy-3-phenethyl-6-(trifluoromethyl)-benzoate (3p). Starting with **1a** (0.184 g, 1.0 mmol), **2o** (0.729 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3p** was isolated as a white solid (0.136 g, 39%); mp = 62−63 °C; R_F = 0.61 (*n*-hexane/CH_2Cl_2 = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.77 (t, ^3J = 8.1 Hz, 2H), 2.99 (t, ^3J = 8.1 Hz, 2H), 3.81 (s, 3H), 3.95 (s, 3H), 6.84 (s, 1H), 7.18−7.28 (m, 5H), 11.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 34.3, 52.6, 55.7, 102.7 (q, J_{C-F} = 7.2 Hz), 104.2, 121.3, 123.4 (q, J_{C-F} = 271.5 Hz), 125.8, 128.1, 128.5, 129.3 (q, J_{C-F} = 32.0 Hz), 142.3 (Ph), 160.7, 161.3, 170.1. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3085 (w), 3027 (w), 2947 (w), 2861 (w), 1668 (m), 1600 (m), 1496 (w), 1440 (m), 1404 (m), 1317 (s), 1247 (s), 1127 (s), 997 (m), 844 (s), 656 (s). GC-MS (EI, 70 eV): *m/z* (%): 354 (M^+, 15), 263 (23), 232 (11), 231 (100), 181 (12), 91 (15). Anal. Calcd for $C_{18}H_{17}F_3O_4$ (354.32): C, 61.02; H, 4.84. Found: C, 61.16; H, 4.87.

Methyl 2-Hydroxy-4-methoxy-3-(phenylpropyl)-6-(trifluoromethyl)benzoate (3q). Starting with **1a** (0.184 g, 1.0 mmol), **2p** (0.757 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3q** was isolated as a slightly yellow solid (0.160 g, 43%); mp = 50−52 °C; R_F = 0.59 (*n*-hexane/CH_2Cl_2 = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78−1.89 (m, 2H), 2.65−2.77 (m, 4H), 3.87 (s, 3H), 3.94 (s, 3H), 6.85 (s, 1H), 7.13−7.29 (m, 5H), 11.21 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9, 29.7, 35.9, 52.6, 55.7, 102.6 (q, J_{C-F} = 7.0 Hz), 104.2, 121.9, 123.4 (q, J_{C-F} = 271.5 Hz), 125.6, 128.1, 128.3, 129.1 (q, J_{C-F} = 31.7 Hz), 142.5, 160.7, 161.2, 170.0. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3029 (w), 2971 (w), 2930 (w), 2863 (w), 1667 (m), 1606 (w), 1579 (w), 1511 (w), 1441 (m), 1320 (s), 1249 (s), 1125 (s), 998 (m), 847 (s), 697 (s). MS (EI, 70 eV): *m/z* (%): 368 (M^+, 100), 337 (35), 336 (37), 245 (77), 244 (42), 233 (32), 232 (96), 231 (89), 224 (67), 212 (44), 209 (36), 204 (51), 181 (22), 118 (31), 105 (51), 104 (22), 92 (13), 91 (46). Anal. Calcd for $C_{19}H_{19}F_3O_4$ (368.35): C, 61.95; H, 5.20. Found: C, 62.29; H, 5.32.

Methyl 2-Hydroxy-3,4-dimethoxy-6-(trifluoromethyl)-benzoate (3r). Starting with **1a** (0.184 g, 1.0 mmol), **2q** (0.581 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3r** was isolated as a slightly yellow solid (0.140 g, 50%); mp = 60−62 °C; R_F = 0.67 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.93 (s, 3H), 3.95 (s, 3H), 3.96 (s, 3H), 6.90 (s, 1H), 10.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.7, 56.1, 60.7, 103.6 (q, J_{C-F} = 6.7 Hz), 106.9, 123.1 (q, J_{C-F} = 271.1 Hz), 125.3 (q, J_{C-F} = 32.2 Hz), 138.8, 154.8, 155.0, 168.8. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −58.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2961 (w), 2855 (w), 1683 (m), 1602 (m), 1413 (m), 1256 (s), 1109 (s), 1023 (s), 963 (s), 922 (s), 840 (s), 709 (s). GC-MS (EI, 70 eV): *m/z* (%): 280 (M^+, 54), 249 (39), 248 (83), 247 (14), 220 (100), 219 (44), 205 (35), 189 (15), 188 (34), 93 (15). Anal. Calcd for $C_{11}H_{11}F_3O_5$ (280.20): C, 47.15; H, 3.96. Found: C, 47.11; H, 3.89.

Methyl 2-Hydroxy-4-ethoxy-3methoxy-6-(trifluoromethyl)-benzoate (3s). Starting with **1b** (213 mg, 1.0 mmol), **2q** (0.581 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3s** was isolated as a colorless solid (0.097 mg, 33%); mp = 61−62 °C; R_F = 0.68 (heptane/EtOAc = 1:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48 (t, ^3J = 7.1 Hz, 3H), 3.94, 3.95 (s, 3H), 4.17 (q, ^3J = 7.1 Hz, 2H), 6.88 (s, 1H), 10.11 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 52.7, 60.7, 64.9, 104.8 (q, J_{C-F} = 7.1 Hz), 107.0, 123.3 (q, J_{C-F} = 272.9 Hz), 125.2 (q, J_{C-F} = 32.5 Hz), 139.1, 154.2, 154.9, 168.8. ^{19}F NMR (235 MHz, $CDCl_3$): δ = −58.7. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2986 (w), 2947 (w), 2899 (w), 2852 (w), 1665 (s), 1600 (s), 1573 (m), 1436 (s). MS (EI, 70 eV): *m/z* (%): 294 (M^+, 63), 263 (45), 262 (100), 247 (16), 234 (67), 233 (63), 206 (74), 205 (83). Anal. Calcd for $C_{12}H_{13}F_3O_5$ (294.22): C, 48.99; H, 4.45. Found: C, 49.32; H, 4.77.

Methyl 3-(Chloropropyl)-2-hydroxy-4-methoxy-6-(trifluoromethyl)benzoate (3t). Starting with **1a** (0.184 g, 1.0 mmol), **2r** (0.674 g, 2.0 mmol) and $TiCl_4$ (0.1 mL, 1.0 mmol) in CH_2Cl_2 (2 mL), product **3t** was isolated as a white solid (0.185 g, 57%); mp = 46−50 °C; R_F = 0.68 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95−2.04 (m, 2H), 2.82 (t, ^3J = 7.3 Hz, 2H), 3.54 (t, ^3J = 7.0 Hz, 2H), 3.91 (s, 3H), 3.95 (s, 3H), 6.87 (s, 1H), 11.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 31.4, 44.8, 52.6, 55.8, 102.6 (q, J_{C-F} = 7.2 Hz), 104.3, 120.4, 123.3 (q, J_{C-F} = 271.7 Hz), 129.6 (q, J_{C-F} = 32.0 Hz), 160.8, 161.3, 170.0. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −58.3. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3010 (w), 2961 (w), 2854 (w), 1660 (m), 1605 (w), 1438 (m), 1398 (w), 1247 (s), 1142 (s), 1125 (s), 1102 (s), 1004 (s), 848 (s), 714 (s). GC-MS (EI, 70 eV): *m/z* (%): 326 (M^+, 14), 260 (12), 259 (100), 232 (25), 231 (21). HRMS (EI, 70 eV): calcd for $C_{13}H_{14}ClF_3O_4$ (M^+) 326.05272, found 326.05208.

General Procedure for the Synthesis of 4a−g and 5g−p. To a CH_2Cl_2 solution (10 mL/1 mmol of **1**) of **1** (1 mmol) was added **2** (2 mmol) and, subsequently, Me_3SiOTf (0.18 mL, 1 mmol) at −78 °C. The temperature of the solution was allowed to warm to 20 °C during 12−14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The latter was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography.

Methyl 2-(6-(Trifluoromethyl)-4-oxo-4H-pyran-2-yl)acetate (4a). Starting with **1a** (0.184 g, 1.0 mmol), **2a** (0.520 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product **4a** was isolated as a yellow solid (0.148 g, 63%); mp = 83−85 °C; R_F = 0.22 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 2H), 3.78 (s, 3H), 6.38 (d, ^4J = 2.2 Hz, 1H), 6.69 (d, ^4J = 2.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.8, 52.9, 114.6 (q, J_{C-F} = 2.5 Hz), 117.5, 118.2 (q, J_{C-F} = 271.9 Hz), 152.8 (q, J_{C-F} = 39.5 Hz), 161.3, 166.9, 177.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −71.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 2969 (w), 2940 (w), 1726 (s), 1672 (s), 1626 (s), 1440 (m), 1415 (m), 1342 (m), 1201 (s), 1139 (s), 1090 (s), 979 (s), 917 (s), 719 (m). GC-MS (EI, 70 eV): *m/z* (%): 236 (M^+, 100), 205 (10), 192 (65), 189 (13), 149 (68), 123 (17), 99 (29), 95 (19), 69 (55), 59 (98), 39 (13). Anal. Calcd for $C_9H_7F_3O_4$ (236.14): C, 45.78; H, 2.90. Found: C, 45.83; H, 3.03.

Ethyl 2-(6-(Trifluoromethyl)-4-oxo-4H-pyran-2-yl)acetate (4b). Starting with **1a** (0.184 g, 1.0 mmol), **2b** (0.549 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **4b** was isolated as a yellow solid (0.172 g, 69%); mp = 73−75 °C; R_F = 0.31 (*n*-heptane/EtOAc = 3:2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, ^3J = 7.2 Hz, 3H), 3.62 (s, 2H), 4.24 (q, ^3J = 7.3 Hz, 2H), 6.38 (d, ^4J = 2.3 Hz, 1H), 6.69 (d, ^4J = 2.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 39.2, 62.1, 114.6 (q, J_{C-F} = 2.6 Hz), 117.5, 120.0 (q, J_{C-F} = 272.3 Hz), 152.6 (q, J_{C-F} = 39.7 Hz), 161.6, 166.4, 177.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −71.2. IR

(ATR, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 2990 (w), 2974 (w), 2936 (w), 1722 (s), 1673 (s), 1627 (s), 1414 (m), 1367 (s), 1334 (s), 1282 (s), 1143 (s), 916 (s), 719 (s). GC-MS (EI, 70 eV): *m/z* (%): 250 (M^+, 56), 205 (25), 203 (10), 178 (100), 177 (13), 149 (52), 139 (22), 99 (22), 69 (50), 39 (10). Anal. Calcd for $C_{10}H_9F_3O_4$ (250.17): C, 48.01; H, 3.63. Found: C, 48.16; H, 3.79.

Benzyl 2-(6-(Trifluoromethyl)-4-oxo-4H-pyran-2-yl)acetate (4c). Starting with **1a** (0.184 g, 1.0 mmol), **2c** (0.673 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product **4c** was isolated as a yellow oil (0.099 g, 32%); R_F = 0.30 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 2H), 5.20 (s, 2H), 6.36, (d, ^4J = 2.2 Hz, 1H), 6.67 (d, ^4J = 2.2 Hz, 1H), 7.31−7.40 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.0, 67.7, 114.6 (q, J_{C-F} = 2.5 Hz), 117.6, 118.1 (q, J_{C-F} = 272.2 Hz), 128.3, 128.6, 128.7, 134.6, 153.0 (q, J_{C-F} = 39.5 Hz), 161.2, 166.2, 177.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −71.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 2938 (w), 1740 (m), 1674 (s), 1641 (m), 1619 (m), 1498 (w), 1362 (w), 1274 (s), 1147 (s), 1083 (s), 968 (m), 877 (m), 696 (s). GC-MS (EI, 70 eV): *m/z* (%): 312 (M^+, 0.71), 178 (59), 91 (100), 65 (10). HRMS (EI, 70 eV): calcd for $C_{15}H_{11}F_3O_4$ (M^+) 312.06039, found 312.06008.

Isopropyl 2-(6-(Trifluoromethyl)-4-oxo-4H-pyran-2-yl)acetate (4d). Starting with **1a** (0.184 g, 1.0 mmol), **2d** (0.577 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product **4d** was isolated as a yellow oil (0.170 g, 64%); R_F = 0.33 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25(s, 3H), 1.28 (s, 3H), 3.60 (s, 2H), 5.04−5.13 (m, 1H), 6.37 (d, ^4J = 2.1 Hz, 1H), 6.69 (d, ^4J = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 39.6, 70.0, 114.7 (q, J_{C-F} = 2.7 Hz), 117.5, 118.2 (q, J_{C-F} = 272.0 Hz), 153.1 (q, J_{C-F} = 39.5 Hz), 161.9, 166.0, 177.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −71.3. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3076 (w), 2985 (w), 2940 (w), 1735 (m), 1674 (s), 1643 (m), 1410 (w), 1361 (m), 1274 (s), 1201 (s), 1148 (s), 1083 (s), 961 (m), 876 (m), 721 (w). GC-MS (EI, 70 eV): *m/z* (%): 264 (M^+, 9), 205 (38), 178 (36), 177 (11), 149 (38), 99 (11), 69 (19), 43 (100), 41 (19). Anal. Calcd for $C_{11}H_{11}F_3O_4$ (264.20): C, 50.01; H, 4.20. Found: C, 50.16; H, 4.55.

2-Methoxyethyl 2-(6-(trifluoromethyl)-4-oxo-4H-pyran-2-yl)acetate (4e). Starting with **1a** (0.183 g, 1.0 mmol), **2e** (0.549 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product**4e** was isolated as a yellow oil (0.112 g, 40%); R_F = 0.36 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3H), 3.61 (t, ^3J = 4.5 Hz, 2H), 3.67 (s, 2H), 4.34 (t, ^3J = 4.5 Hz, 2H), 6.39 (d, ^4J = 2.1 Hz, 1H), 6.69 (d, ^4J = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.0, 59.0, 64.1, 70.2, 114.7 (q, J_{C-F} = 2.3 Hz), 117.7, 118.2 (q, J_{C-F} = 271.5 Hz), 152.9 (q, J_{C-F} = 39.0 Hz), 161.4, 166.6, 177.5. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −71.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3057 (w), 2928 (w), 2897 (w), 2849 (w), 2825 (w), 1741 (s), 1675 (s), 1642 (m), 1620 (w), 1362 (m), 1275 (s), 1199 (m), 1150 (s), 1084 (s), 1032 (m), 974 (m), 877 (s), 722 (s). GC-MS (EI, 70 eV): *m/z* (%): 280 (M^+, 2), 250 (15), 222 (20), 178 (87), 161 (11), 149 (56), 99 (19), 69 (29), 58 (33), 45 (100), 43 (11), 29 (16). Anal. Calcd for $C_{11}H_{11}F_3O_5$ (280.02): C, 47.15; H, 3.96. Found: C, 47.14; H, 4.31.

Isobutyl 2-(6-(Trifluoromethyl)-4-oxo-4H-pyran-2-yl)acetate (4f). Starting with **1a** (0.184 g, 1.0 mmol), **2s** (0.605 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product **4d** was isolated as a brownish oil (0.178 g, 64%); R_F = 0.40 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91(s, 3H), 0.93 (s, 3H), 1.88−2.01 (m, 1H), 3.63 (s, 2H), 3.96 (d, ^3J = 6.6 Hz, 2H), 6.38 (d, ^4J = 2.4 Hz, 1H), 6.69 (d, ^4J = 2.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 27.5, 39.2, 72.0, 114.6 (q, J_{C-F} = 1.9 Hz), 117.5, 118.2 (q, J_{C-F} = 272.1 Hz), 152.8 (q, J_{C-F} = 39.6 Hz), 161.6, 166.4, 177.4. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −71.1. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3076 (w), 2965 (w), 2878 (w), 1740 (m), 1675 (s), 1644 (m), 1620 (w), 1471 (w), 1361 (m), 1274 (s), 1201 (s), 1150 (s), 1084 (s), 973 (m), 876 (m), 721 (m). GC-MS (EI, 70 eV): *m/z* (%): 278 (M^+, 2), 223 (100), 205 (24), 178 (60), 177 (12), 149 (64), 99 (17), 69 (24), 57 (51), 56 (15), 41 (39), 39 (12), 29 (15). Anal. Calcd for $C_{12}H_{13}F_3O_4$ (278.22): C, 51.80; H, 4.71. Found: C, 51.84; H, 4.82.

Methyl 6-(Trifluoromethyl)-6-hydroxy-4-methoxy-3-methyl-2-oxocyclohex-3-enecarboxylate (5g). Starting with **1a** (0.184 g, 1.0 mmol), **2f** (0.549 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product **5g** was isolated as a light-yellow solid (0.107 g, 38%); mp = 123−126 °C; R_F = 0.49 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.72−1.74 (m, 3H), 2.78 (brd, ^2J = 17.6 Hz, 1H), 2.95 (d, ^2J = 17.5 Hz, 1H), 3.69 (s, 0.5 H), 3.70 (s, 0.5H), 3.88 (s, 3H), 3.89 (s, 3H), 5.49 (s, 0.5H), 5.50 (s, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 7.3, 30.4, 52.9, 53.1, 55.7, 74.1 (q, J_{C-F} = 29.1 Hz), 113.4, 124.5 (q, J_{C-F} = 286.4 Hz), 166.4, 171.3, 188.4. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3428 (w), 3013 (w), 2965 (w), 2926 (w), 2867 (w), 1739 (s), 1648 (m), 1613 (s), 1461 (w), 1440 (w), 1164 (s), 1117 (s), 1063 (s), 972 (s), 688 (m). GC-MS (EI, 70 eV): *m/z* (%): 282 (M^+, 4), 264 (100), 233 (16), 232 (41), 220 (32), 212 (18), 207 (27), 205 (40), 204 (22), 189 (16), 181 (31), 175 (14), 83 (20), 69 (36) 59 (20), 43 (15). Anal. Calcd for $C_{11}H_{13}F_3O_5$ (282.21): C, 46.81; H, 4.64. Found: C, 46.88; H, 4.63.

Methyl 6-(Trifluoromethyl)-3-ethyl-6-hydroxy-4-methoxy-2-oxocyclohex-3-enecarboxylate (5 h). Starting with **1a** (0.184 g, 1.0 mmol), **2t** (0.577 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5h** was isolated as a white solid (0.146 g, 50%); mp = 106−110 °C; R_F = 0.42 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.4 Hz, 3H), 1.21−2.48 (m, 2H), 2.78 (brd, ^2J = 17.7 Hz, 1H), 2.94 (d, ^2J = 17.7 Hz, 1H), 3.68 (s, 0.5H), 3.70 (s, 0.5H), 3.89 (s, 3H), 5.50 (s, 0.5H), 5.51 (s, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 15.6, 30.3, 52.9, 53.1, 55.7, 74.1 (q, J_{C-F} = 28.7 Hz), 119.6, 124.5 (q, J_{C-F} = 279.0 Hz), 166.3, 171.4, 188.0. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3437 (w), 3021 (w), 2963 (w), 2942 (w), 2879 (w), 1741 (s), 1649 (m), 1611 (s), 1441 (w), 1413 (w), 1250 (s), 1165 (s), 1132 (s), 1120 (s), 986 (s), 659 (m). GC-MS (EI, 70 eV): *m/z* (%):296 (M^+, 2), 278 (30), 246 (14), 220 (11), 219 (100), 195 (13), 83 (13), 69 (19). Anal. Calcd for $C_{12}H_{15}F_3O_5$ (396.24): C, 48.65; H, 5.10. Found: C, 48.70; H, 5.12.

Methyl 6-(Trifluoromethyl)-3-chloro-6-hydroxy-4-methoxy-2-oxocyclohex-3-enecarboxylate (5i). Starting with **1a** (0.184 g, 1.0 mmol), **2u** (0.589 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), product**5i** was isolated as a light-yellow solid (0.134 g, 44%); mp = 108−109 °C; R_F = 0.34 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.93 (d, ^2J = 17.7 Hz, 1H), 3.09 (d, ^2J = 17.4 Hz, 1H), 3.81 (s, 1H), 3.91, 4.04 (s, 3H), 5.53 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.2, 53.6, 53.6, 57.2, 75.4 (q, J_{C-F} = 29.3 Hz), 109.6, 124.4 (q, J_{C-F} = 285.8 Hz), 166.0, 170.1, 181.8. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.0. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3430 (m), 3018 (w), 2962 (w), 2937 (m), 2873 (w), 1733 (s), 1661 (m), 1591 (s), 1349 (w), 1265 (m), 1341 (m), 1185 (s), 955 (s), 845 (m), 664 (s). GC-MS (EI, 70 eV): *m/z* (%): 302 (M^+, 2), 286 (16), 284 (52), 242 (27), 240 (100), 227 (17), 212 (12), 210 (11), 197 (22), 174 (17), 131 (10), 103 (11), 69 (56), 59 (44). HRMS (ESI): calcd for $C_{18}H_{28}F_3O_5$ ($M+H^+$) 303.02416, found 303.02477.

Ethyl 6-(Trifluoromethyl)-6-hydroxy-4-methoxy-2-oxo-3-pentylcyclohex-3-enecarboxylate (5j). Starting with **1a** (0.184 g, 1.0 mmol), **2v** (0.689 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5j** was isolated as a yellow solid (0.138 g, 39%); mp = 73−75 °C; R_F = 0.42 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 6.9 Hz, 3H), 1.25−1.38 (m, 9H), 2.19−2.34 (m, 2H), 2.77 (brd, ^2J = 17.4 Hz, 1H), 2.94 (d, ^2J = 17.4 Hz, 1H), 3.64 (s, 1H), 3.87 (s, 3H), 4.35 (q, ^3J = 7.2 Hz, 2H), 5.59 (s, 0.5H), 5.60 (s, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 14.0, 22.1, 22.4, 27.9, 30.3, 31.7, 52.9, 55.6, 62.5, 74.1 (q, J_{C-F} = 28.5 Hz), 118.4, 124.6 (q, J_{C-F} = 285.0 Hz), 166.3, 171.0, 188.3. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3439 (w), 2959 (w), 2932 (w), 2873 (w), 2849 (w), 1735 (s), 1648 (m), 1612 (s), 1463 (w), 1414 (w), 1336 (m), 1250 (m), 1171 (s), 1122 (s), 1024 (s), 946 (m), 657 (m). GC-MS (EI,

70 eV): *m/z* (%):352 (M^+, 1), 334 (13), 314 (12), 257 (20), 233 (15), 232 (24), 231 (22), 206 (15), 205 (100), 69 (11). Anal. Calcd for $C_{16}H_{23}F_3O_5$ (352.35): C, 54.54; H, 6.58. Found: C, 54.64; H, 6.64.

Ethyl 6-(Trifluoromethyl)-3-heptyl-6-hydroxy-4-methoxy-2-oxocyclohex-3-enecarboxylate (5k). Starting with **1a** (0.184 g, 1.0 mmol), **2w** (0.754 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5k** was isolated as a slightly yellow solid (0.133 g, 35%); mp = 20−25 °C; R_F = 0.58 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, ^3J = 6.8 Hz, 3H), 1.25−1.38 (m, 13H), 2.19−2.31 (m, 2H), 2.77 (brd, ^2J = 17.7 Hz, 1H), 2.94 (d, ^2J = 17.4 Hz, 1H), 3.64 (s, 1H), 3.87 (s, 3H), 4.35 (dq, ^3J = 7.2 Hz, 2H), 5.59 (s, 0.5H), 5.60 (s, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 14.0, 22.1, 22.6, 28.3, 29.1, 29.5, 30.3, 31.8, 52.9, 55.6, 62.5, 74.1 (q, J_{C-F} = 28.7 Hz), 118.4, 124.6 (q, J_{C-F} = 285.0 Hz), 166.3, 171.0, 188.3. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3427 (w), 2960 (w), 2927 (w), 2856 (w), 1722 (m), 1638 (w), 1605 (s), 1446 (w), 1426 (w), 1375 (m), 1245 (s), 1171 (s), 1122 (s), 1016 (m), 656 (m). GC-MS (EI, 70 eV): *m/z* (%):380 (M^+, 1), 362 (21), 342 (15), 285 (31), 233 (17), 232 (50), 231 (37), 206 (16), 205 (100), 204 (12), 29 (10). ESI: calcd for $C_{18}H_{28}F_3O_5$ ($M+H^+$) 381.1883, found 381.1884; calcd for $C_{18}H_{27}F_3NaO_5$ ($M+Na^+$) 403.1702, found 403.1705. Anal. Calcd for $C_{18}H_{27}F_3O_5$ (380.40): C, 56.83; H, 7.15. Found: C, 56.89; H, 7.19.

Methyl 6-(Trifluoromethyl)-6-hydroxy-4-methoxy-3-octyl-2-oxocyclohex-3-enecarboxylate (5 L). Starting with **1a** (0.184 g, 1.0 mmol), **2m** (0.745 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5 L** was isolated as a yellow solid (0.236 g, 62%); mp = 77−79 °C; R_F = 0.62 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.7 Hz, 3H), 1.24−1.31 (m, 12H), 2.21−2.31 (m, 2H), 2.77 (brd, ^2J = 17.6 Hz, 1H), 2.94 (d, ^2J = 17.6 Hz, 1H), 3.68 (s, 0.5H), 3.70 (s, 0.5H), 3.87 (s, 3H), 3.88 (s, 3H), 5.50 (s, 0.5H), 5.51 (s, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.2, 22.6, 28.2, 29.2, 29.4, 29.5, 30.3, 31.8, 53.0, 53.1, 55.6, 74.1 (q, J_{C-F} = 29.0 Hz), 118.4, 124.5 (q, J_{C-F} = 285.0 Hz), 166.3, 171.4, 188.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3438 (m), 3025 (w), 2958 (w), 2928 (m), 2854 (w), 1739 (s), 1650 (m), 1612 (s), 1461 (w), 1438 (m), 1341 (m), 1258 (s), 1166 (s), 1123 (s), 1069 (m), 974 (m), 659 (m). GC-MS (EI, 70 eV): *m/z* (%):380 (M^+, 1), 362 (28), 342 (17), 232 (27), 219 (18), 205 (100), 69 (17). ESI: calcd for $C_{18}H_{28}F_3O_5$ ($M+H^+$) 381.1883, found 381.1880; calcd for $C_{18}H_{27}F_3NaO_5$ ($M+Na^+$) 403.1702, found 403.1704. Anal. Calcd for $C_{18}H_{27}F_3O_5$ (380.40): C, 56.83; H, 7.15. Found: C, 56.84; H, 7.12.

Methyl 6-(Trifluoromethyl)-6-hydroxy-4-methoxy-3-nonyl-2-oxocyclohex-3-enecarboxylate (5m). Starting with **1a** (0.184 g, 1.0 mmol), **2x** (0.745 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5m** was isolated as a yellow solid (0.225 g, 57%); mp = 63−64 °C; R_F = 0.53 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.7 Hz, 3H), 1.24−1.31 (m, 14H), 2.25−2.27 (m, 2H), 2.77 (brd, ^2J = 17.7 Hz, 1H), 2.94 (d, ^2J = 17.6 Hz, 1H), 3.68 (s, 0.5H), 3.70 (s, 0.5H), 3.87 (s, 3H), 3.88 (s, 3H), 5.50 (s, 0.5H), 5.51 (s, 0.5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.2, 22.6, 28.2, 29.3, 29.4, 29.5, 29.6, 30.3, 31.8, 53.0, 53.1, 55.6, 74.1 (q, J_{C-F} = 28.9 Hz), 118.4, 124.5 (q, J_{C-F} = 286.9 Hz), 166.3, 171.4, 188.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3439 (m), 3025 (w), 2958 (w), 2925 (m), 2855 (w), 1739 (s), 1651 (m), 1613 (s), 1461 (w), 1438 (w), 1248 (s), 1167 (s), 1123 (s), 975 (m), 659 (m). GC-MS (EI, 70 eV): *m/z* (%):394 (M^+, 1), 376 (41), 356 (23), 345 (15), 313 (70), 263 (16), 259 (15), 245 (18), 233 (17), 232 (100), 231 (84), 219 (21), 212 (15), 205 (99), 204 (19), 181 (19), 69 (16). ESI: calcd for $C_{19}H_{30}F_3O_5$ ($M+H^+$) 395.2039, found 395.2042; calcd for $C_{19}H_{29}F_3NaO_5$ ($M+Na^+$) 417.1859, found 417.1860. Anal. Calcd for $C_{19}H_{29}F_3O_5$ (394.20): C, 57.86; H, 7.41. Found: C, 57.78; H, 7.30.

Methyl 6-(Trifluoromethyl)-3-dodecyl-6-hydroxy-4-methoxy-2-oxocyclohex-3-enecarboxylate (5n). Starting with **1a** (0.184 g, 1.0 mmol), **2y** (0.857 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5n** was isolated as a yellow solid (0.252 g, 58%); mp = 74−76 °C; R_F = 0.63 (*n*-heptane/EtOAc = 3:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 6.8 Hz, 3H), 1.24−1.29 (m, 20H), 2.20−2.32 (m, 2H), 2.77 (brd, ^2J = 17.6 Hz, 1H), 2.94 (d, ^2J = 17.6 Hz, 1H), 3.68 (s, 0.5H), 3.70 (s, 0.5H), 3.87 (s, 3H), 3.88 (s, 3H), 5.49 (s, 0.5H), 5.50 (s, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.2, 22.6, 28.2, 29.3, 29.4, 29.6 (m), 30.3, 31.9, 52.9, 53.1, 55.6, 74.1 (q, J_{C-F} = 28.7 Hz), 118.4, 124.7 (q, J_{C-F} = 284.9 Hz), 166.3, 171.4, 188.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3413 (w), 2953 (w), 2916 (m), 2848 (m), 1734 (m), 1656 (m), 1614 (s), 1463 (w), 1439 (w), 1245 (s), 1160 (s), 1140 (s), 1119 (s), 664 (m). ESI: calcd for $C_{22}H_{36}F_3O_5$ ($M+H^+$) 437.2509, found 437.2510; calcd for $C_{22}H_{35}F_3NaO_5$ ($M+Na^+$) 459.2328, found 459.2327. Anal. Calcd for $C_{22}H_{35}F_3O_5$ (436.51): C, 60.53; H, 8.08. Found: C, 60.74; H, 8.08.

Methyl 6-(Trifluoromethyl)-3-hexadecyl-6-hydroxy-4-methoxy-2-oxocyclohex-3-enecarboxylate (5o). Starting with **1a** (0.184 g, 1.0 mmol), **2z** (0.969 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5o** was isolated as a yellow solid (0.264 g, 54%); mp = 82−84 °C; R_F = 0.69 (*n*-heptane/EtOAc = 3:2). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.8 Hz, 3H), 1.24−1.31 (m, 28H), 2.20−2.32 (m, 2H), 2.77 (brd, ^2J = 18.0 Hz, 1H), 2.94 (d, ^2J = 17.6 Hz, 1H), 3.68 (s, 1H), 3.86 (s, 3H), 3.88 (s, 3H), 5.49 (s, 0.5H), 5.50 (s, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 22.2, 22.6, 28.2, 29.3, 29.4, 29.6 (m), 30.3, 31.9, 52.9, 53.1, 55.6, 74.1 (q, J_{C-F} = 28.7 Hz), 118.4, 124.5 (q, J_{C-F} = 285.0 Hz), 166.3, 171.4, 188.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3413 (w), 2952 (w), 2916 (s), 2847 (s), 1735 (m), 1655 (m), 1613 (s), 1462 (m), 1439 (m), 1245 (s), 1161 (s), 1140 (s), 1120 (s), 664 (m). GC-MS (EI, 70 eV): *m/z* (%):492 (M^+, 1), 475 (11), 474 (48), 454 (15), 423 (15), 411 (55), 474 (48), 442 (22), 411 (55), 263 (16), 233 (25), 232 (100), 231 (83), 205 (83). ESI: calcd for $C_{26}H_{44}F_3O_5$ ($M+H^+$) 493.3135, found 493.3134; calcd for $C_{26}H_{43}F_3NaO_5$ ($M+Na^+$) 515.2954, found 515.2955. Anal. Calcd for $C_{26}H_{43}F_3O_5$ (492.61): C, 63.39; H, 8.80. Found: C, 63.71; H, 8.87.

Methyl 6-(Trifluoromethyl)-6-hydroxy-3-isopentyl-4-methoxy-2-oxocyclohex-3-enecarboxylate (5p). Starting with **1a** (0.184 g, 1.0 mmol), **2aa** (0.661 g, 2.0 mmol) and Me_3SiOTf (0.18 mL, 1.0 mmol) in CH_2Cl_2 (10 mL), **5p** was isolated as a yellow solid (0.193 g, 55%); mp = 90−92 °C; R_F = 0.60 (*n*-heptane/EtOAc = 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3H), 0.89 (s, 3H), 1.14−1.28 (m, 2H), 1.45−1.54 (m, 1H), 2.22−2.32 (m, 2H), 2.77 (brd, ^2J = 17.7 Hz, 1H), 2.94 (d, ^2J = 17.7 Hz, 1H), 3.68 (s, 0.5H), 3.70 (s, 0.5H), 3.87 (s, 3H), 3.88 (s, 3H), 5.50 (s, 0.5H), 5.51 (s, 0.5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.2, 22.4, 22.5, 28.1, 30.3, 37.3, 53.0, 53.1, 55.6, 74.1 (q, J_{C-F} = 28.7 Hz), 118.6, 124.5 (q, J_{C-F} = 284.7 Hz), 166.3, 171.4, 188.2. ^{19}F-NMR (282 MHz, $CDCl_3$): δ = −81.2. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3435 (w), 2959 (w), 2933 (w), 2876 (w), 2853 (w), 1740 (s), 1650 (m), 1612 (s), 1452 (w), 1439 (w), 1342 (m), 1249 (s), 1168 (s), 1140 (s), 1124 (s), 1041 (m), 978 (m), 658 (m). GC-MS (EI, 70 eV): *m/z* (%):338 (M^+, 2), 320 (32), 300 (17), 288 (11), 273 (10), 263 (16), 261 (18), 260 (11), 251 (13), 245 (16), 244 (18), 237 (14), 233 (14), 232 (73), 231 (35), 219 (17), 206 (12), 205 (100), 181 (10), 159 (15), 153 (10), 69 (23), 59 (15), 43 (12), 41 (11). Anal. Calcd for $C_{15}H_{21}F_3O_5$ (338.32): C, 53.25; H, 6.26. Found: C, 53.37; H, 6.61.

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Supporting Information Available: Copies of NMR spectra, crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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