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Regioselective Synthesis of Fluorinated Phenols, Biaryls, 6*H*-Benzo[*c*]chromen-6-ones and Fluorenones Based on Formal [3+3] Cyclizations of 1,3-Bis(silyl enol ethers)

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A variety of fluorinated phenols, biaryls, 6*H*-benzo[*c*]chromen-6-ones and fluorenones were prepared based on regioselective [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 2-fluoro-3-silyloxy-2-en-1-ones.

Introduction

The fluoro group represents, due to its unique stereoelectronic properties, a very important substituent in organic and medicinal chemistry.[1] While the fluorine atom is relatively small, its high electronegativity results in a dramatic change of the electronic situation and of the reactivity of the molecule. This plays an important role in drug–receptor interactions. Notably, the increased lipophilicity of fluoro-substituted molecules also improves their transport in vivo. It is noteworthy that, due to the high chemical and biological stability of the fluoro group, undesirable metabolic transformations are often avoided. Therefore, the synthesis of fluoro-substituted arenes and hetarenes plays an important role in drug discovery.[1,2] A great variety of pharmaceuticals, such as well known ciprofloxacin, ofloxacin, and norfloxacin, contain a fluoroarene moiety.[3] Aryl fluorides are also present in natural products. This includes, for example, 4-fluorozaragozic acid A or fluorinated carbazole alkaloids.[4] Organic fluoro compounds show very good solubility in fluorophilic solvents. Therefore, they are used as ligands[5] for catalytic reactions in fluorous biphasic systems and supercritical carbon dioxide.[6] The unique electronic properties of fluorinated arenes are used also for applications in organocatalysis.[7,8]

Aryl fluorides are available by reaction of arenes with strong electrophilic fluorination agents (such as fluorine or xenon fluorides).[9] However, these reagents are difficult to obtain or handle, dangerous, or (in some cases) very expensive. Selectfluor represents an "easy-to-handle", commercially available electrophilic fluorination agent.[10] However, the fluorination of non-activated arenes was reported to be unsuccessful (low conversion).[10,11] The fluorination of (activated) anisole has been reported to proceed with 72% conversion. However, a 1:1 regioisomeric mixture of 2- and 4-fluoroanisol was formed.[11] The reaction of Selectfluor with phenols has been reported to give 4-fluorocyclohexadienones.[12] The functionalization of simple fluorinated arenes, such as 4-fluorophenol, by electrophilic substitution reactions has been widely explored.[13] However, these transformations are often low-yielding and proceed with low regioselectivity. In addition, the synthesis of heavily substituted benzene derivatives is not an easy task. A different approach to aryl fluorides relies on cyclization reactions of fluorinated synthetic building blocks. For example, aryl fluorides were prepared by [4+2] cycloaddition reactions of 2-fluoro-1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene, 2-fluoro-3-methoxybuta-1,3-diene and related dienes with alkenes or alkynes.[14] Portella et al. reported the synthesis of fluorophenols by annulation reactions of 2,2-difluoro-1,5-diketones which were prepared from acylsilanes, trimethyl(trifluoromethyl)silane and enones.[15]

The formal [3+3] cyclization of 1,3-bis(silyl enol ethers) with 1,3-dielectrophiles, first reported by Chan and coworkers,[16] provides a convenient approach to various arenes.[17,18] Recently, we reported the application of this method to the synthesis of aryl fluorides based on [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 2-fluoro-3-(silyloxy)-2-en-1-ones.[19] Herein we report full details of these studies. With regard to our preliminary communication, the preparative scope was considerably extended. In addition, we wish to report the application of our methodology to the synthesis of fluorinated 6*H*-benzo[*c*]chromen-6-ones (biaryl

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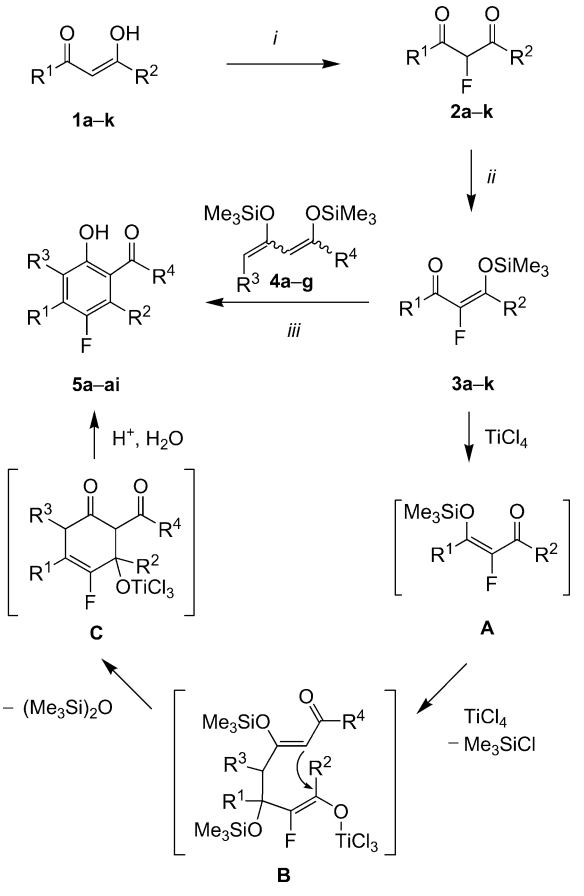
lactones, dibenzo[*b*,*d*]pyran-6-ones) and fluorenones. The chemistry outlined herein offers a convenient and regioselective approach to a variety of functionalised and sterically encumbered aryl fluorides which are not readily available by other methods.

Results and Discussion

2-Fluoro-1,3-diones are available by reaction of 1,3-diketones with fluorine,[20] *N*-fluorobis(trifluoromethyl)sulfonimide,[21] and Selectfluor.[22] Our starting point was the synthesis of a variety of novel 2-fluoro-1,3-diones that were required for our studies. The reaction of Selectfluor with 1,3-diones **1a**–**k** afforded the 2-fluoro-1,3-diones **2a**–**k**, which were transformed by reaction with Me_3SiCl/NEt_3, into the 2-fluoro-3-(silyloxy)-2-en-1-ones **3a**–**k** (Scheme 1, Table 1). The $TiCl_4$-mediated formal [3+3] cyclization of **3a**–**k** with 1,3-bis(silyl enol ethers) **4a**–**g**, prepared from the corresponding 1,3-dicarbonyl compounds in one or two steps[23], afforded the novel fluorinated phenols and biaryls **5a**–**ai** in moderate to good yields.



Scheme 1. Synthesis of fluorinated phenols and biaryls **5a**–**ai**; conditions: *i*: method A: Selectfluor, microwave, 10 min, 82 °C, CH_3CN; method B: reflux, 4 h; *ii*: Me_3SiCl, NEt_3, C_6H_6, 20 °C; *iii*: $TiCl_4$, CH_2Cl_2, –78→20 °C.

The best yields were obtained when the reaction was carried out in high concentration. The use of Me_3SiOTf or $BF_3{\cdot}OEt_2$, rather than $TiCl_4$, was unsuccessful (no conversion or decomposition, respectively). Notably, products **5i**–**ai** were formed with excellent regioselectivity. The formation of the opposite regioisomer could not be detected. The results can be explained by the following mechanism:[16,18] Silyl enol ether **3** undergoes a $TiCl_4$-mediated 1,5-silyl shift to give intermediate **A**. The $TiCl_4$-mediated conjugate addition of the 1,3-bis(silyl enol ether) **4** onto **A** gives intermediate **B** (Mukaiyama–Michael reaction). The cyclization proceeds by attack of the central carbon of **4** onto the carbonyl group (Mukaiyama aldol reaction). Aromatization by an elimination reaction (before or during the aqueous workup) leads to the final product. The yields seem to mainly depend on the quality of the starting materials and on the handling of each individual experiment. The structures of **5y** and **5z** were independently confirmed by X-ray crystal structure analysis (see Figures 1 and 2).[24]

6*H*-Benzo[*c*]chromen-6-ones (dibenzo[*b*,*d*]pyran-6-ones, biaryl lactones) are of considerable pharmacological relevance and occur in various natural products. This includes, for example, autumnariol,[25] autumnariniol,[26] alternariol,[27] or altenusiol.[28] 6*H*-Benzo[*c*]chromen-6-ones represent specific inhibitors of the growth of endothelial cells[29] and estrogen receptors.[30] Ellagic acid and coruleoellagic acid, isolated both as glycosides and aglycons, contain an additional lactone bridge.[31] Dibenzo[*c*,*d*]chromen-6-ones (benzo[*d*]naphthopyran-6-ones) can be regarded as benzo-annulated 6*H*-benzo[*c*]chromen-6-ones. They are present in a number of antibiotics and antitumor agents which have been isolated from Streptomyces (e.g. the gilvocarcins, chrysomycins and ravidomycins).[32] Recently, we reported the synthesis of 6*H*-benzo[*c*]chromen-6-ones by reaction of 1,3-bis(silyl enol ethers) with benzopyrylium triflates.[33] A recent approach to 6*H*-benzo[*c*]chromen-6-ones relies on the [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 1-(2-methoxyphenyl)-1-(trimethylsilyloxy)alk-1-en-3-ones, and subsequent lactonization.[34] The combination of this method with the chemistry reported herein provides a convenient access to 10-fluoro-6*H*-benzo[*c*]chromen-6-ones. The synthesis of this type of fluorinated core structure has, to the best of our knowledge, not yet been reported. Treatment of biaryls **5m**–**r** with BBr_3 and subsequent addition of an aqueous solution of potassium *tert*-butoxide (KO*t*Bu) afforded the novel fluorinated dibenzo[*b*,*d*]pyran-6-ones **6a**–**f** (Scheme 2, Table 2). The formation of the products proceeds by cleavage of the arylmethyl ether and subsequent base-mediated lactonization. The structure of **6d** was investigated by crystal structure analysis.[35]

1-Hydroxyfluorenones are interesting lead structures in medicinal chemistry and are also present in nature (e.g. in the natural products dengibsin, dengibsinin, and dendroflorin).[36] Fluorinated fluorenones[37] are of specific interest in current medicinal chemistry. For example, it was shown that 4-fluorofluorenones possess antagonistic in vitro activity to human progesterone receptor B (hPR-B) in co-transfected CV-1 cells (IC_{50} = 158 nM).[38] Recently, we re-

Table 1. Synthesis of 4-fluorophenols **5a**–**ai**.

4	1,2,3	5	R^1	R^2	R^3	R^4	% Yield **2**[a]	% Yield **3**[a]	% Yield **5**[a]
a	**a**	**a**	Et	Et	H	OMe	71	98	54
b	**a**	**b**	Et	Et	H	OEt			42
d	**a**	**c**	Et	Et	H	Me			50
e	**a**	**d**	Et	Et	H	Ph			52
a	**b**	**e**	Ph	Ph	H	OMe	77	89	82
b	**b**	**f**	Ph	Ph	H	OEt			68
d	**b**	**g**	Ph	Ph	H	Me			30
c	**b**	**h**	Ph	Ph	H	$O(CH_2)_2OMe$			51
a	**c**	**i**	Me	Ph	H	OMe	88	98	40
c	**c**	**j**	Me	Ph	H	$O(CH_2)_2OMe$			42
d	**c**	**k**	Me	Ph	H	Me			31
e	**c**	**l**	Me	Ph	H	Ph			40
a	**d**	**m**	Me	2-$(MeO)C_6H_4$	H	OMe	72	99	44
f	**d**	**n**	Me	2-$(MeO)C_6H_4$	Me	OMe			54
g	**d**	**o**	Me	2-$(MeO)C_6H_4$	Et	OEt			44
a	**e**	**p**	*n*Pr	2-$(MeO)C_6H_4$	H	OMe	90	79	35
f	**e**	**q**	*n*Pr	2-$(MeO)C_6H_4$	Me	OMe			34
g	**e**	**r**	*n*Pr	2-$(MeO)C_6H_4$	Et	OEt			55
a	**f**	**s**	Me	2-MeC_6H_4	H	OMe	46	65	44
g	**f**	**t**	Me	2-MeC_6H_4	Et	OEt			40
a	**g**	**u**	Me	2-ClC_6H_4	H	OMe	42	80	26
f	**g**	**v**	Me	2-ClC_6H_4	Me	OMe			38
g	**g**	**w**	Me	2-ClC_6H_4	Et	OEt			38
a	**h**	**x**	Me	4-ClC_6H_4	H	OMe	58	70	30
f	**h**	**y**	Me	4-ClC_6H_4	Me	OMe			32
g	**h**	**z**	Me	4-ClC_6H_4	Et	OEt			44
a	**i**	**aa**	Me	4-FC_6H_4	H	OMe	46	82	32
f	**i**	**ab**	Me	4-FC_6H_4	Me	OMe			40
g	**i**	**ac**	Me	4-FC_6H_4	Et	OEt			35
a	**j**	**ad**	Me	1-naphthoyl	H	OMe	37	71	31
f	**j**	**ae**	Me	1-naphthoyl	Me	OMe			37
g	**j**	**af**	Me	1-naphthoyl	Et	OEt			42
a	**k**	**ag**	*n*Pr	2-naphthoyl	H	OMe	64	74	30
f	**k**	**ah**	*n*Pr	2-naphthoyl	Me	OMe			34
g	**k**	**ai**	*n*Pr	2-naphthoyl	Et	OEt			35

[a] Isolated yields.

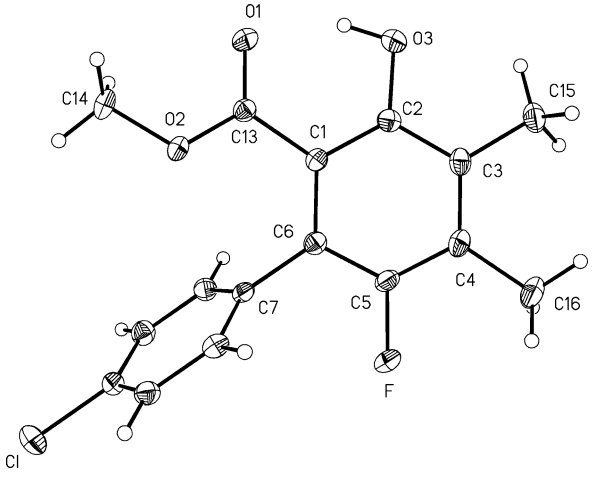


Figure 1. ORTEP plot of **5y**.

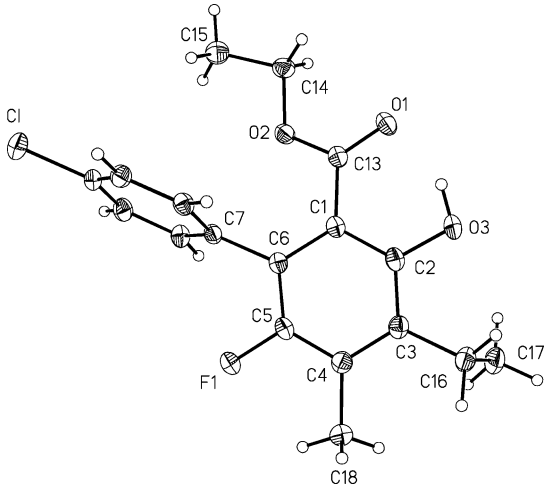
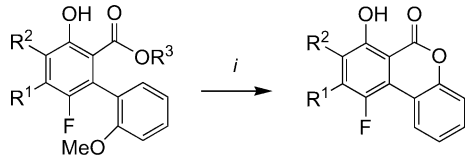


Figure 2. ORTEP plot of **5z**.

ported a new approach to fluorenones based on Suzuki cross-coupling reactions of salicylates and subsequent acid-mediated Friedel–Crafts-type acylation.[39] Chan et al. reported the synthesis of 1-hydroxy-3-methylfluorenone by reaction of methyl 6-phenylsalicylate with concentrated sulfuric acid.[16]



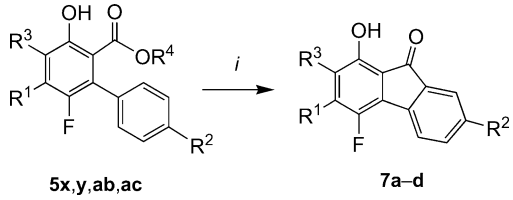
Scheme 2. Synthesis of dibenzo[*b*,*d*]pyran-6-ones **6a**–**f**; conditions: *i*: 1) BBr_3 (4 equiv.), CH_2Cl_2, 0→20 °C, 18 h, 2) KO*t*Bu, H_2O, 15 min, 20 °C.

Table 2. Synthesis of dibenzo[*b*,*d*]pyran-6-ones **6a**–**f**.

5	6	R^1	R^2	R^3	% Yield **6**[a]
m	**a**	Me	H	Me	91
n	**b**	Me	Me	Me	84
o	**c**	Me	Et	Et	75
p	**d**	*n*Pr	H	Me	47
q	**e**	*n*Pr	Me	Me	55
r	**f**	*n*Pr	Et	Et	67

[a] Isolated yields.

The combination of the Friedel–Crafts reaction with the chemistry reported herein provides a convenient approach to a variety of functionalized 4-fluorofluorenones which are not readily available by other methods. In fact, the novel 1-hydroxy-4-fluorofluorenones **7a**–**d** were obtained in good yields by simple treatment of 6-arylsalicylates **5x**,**y**,**ab**,**ac** with concentrated sulfuric acid (Scheme 3, Table 3).



Scheme 3. Synthesis of fluorenones **7a**–**d**; conditions: *i*: concd. H_2SO_4, 20 °C, 1 h.

Table 3. Synthesis of fluorenones **7a**–**d**.

5	7	R^1	R^2	R^3	R^4	% Yield **7**[a]
x	**a**	Me	Cl	H	Me	77
y	**b**	Me	Cl	Me	Me	75
ab	**c**	Me	F	Me	Me	74
ac	**d**	Me	F	Et	Et	69

[a] Isolated yields.

Conclusions

In conclusion, we have reported the synthesis of variety of fluorinated phenols, biaryls, 6*H*-benzo[*c*]chromen-6-ones and fluorenones based on regioselective [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 2-fluoro-3-(silyloxy)-2-en-1-ones. The reactions provide a convenient approach to various fluorinated arenes which are not readily available by other methods. The starting materials are readily available by fluorination of 1,3-diketones with Selectfluor.

Experimental Section

General: ^{1}H NMR spectra were taken in $CDCl_3$ at 250, 300, or 500 MHz. ^{13}C NMR spectra were taken in $CDCl_3$ at 62.5, 75, or 125 MHz. Chemical shifts are reported in parts per million using the solvent as internal standard (chloroform, δ = 7.26 and 77.0 ppm, respectively). Infrared spectra were recorded with an FTIR spectrometer. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). Melting points are uncorrected. CH_2Cl_2 (anhydrous, 99.8%) was purchased directly from ACROS and used without further purification, $TiCl_4$ was purchased from Aldrich. Analytical thin-layer chromatography was performed on 0.20 mm 60 A silica gel plates. Column chromatography was performed on 60-Å silica gel (60–200 mesh). All cyclization reactions were carried out in Schlenk tubes under argon using dried solvents. Crystallographic data were collected with a Bruker Apex-X8 with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were refined in the model at geometrically calculated positions and refined using a riding model.

General Procedure for the Synthesis of 1,3-Dicarbonyl Compounds 1: To a stirred solution of LDA (75 mmol) in THF (1.2 mL/1 mmol of LDA) was added the ketone (50 mmol) at –78 °C. After the solution was stirred for 1 h, the acid chloride (60 mmol) was added. The temperature of the solution was allowed to rise to 20 °C during 12 h. A saturated solution of NH_4Cl was added, the layers were separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined organic layers were dried (Na_2So_4) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc, 30:1→20:1) to give **1**. Compounds **1a**–**c** are commercially available. The syntheses of **1d**,[40] **1e**,[41] **1f**,[42] **1h**,[43] and **1i**[44] have been previously reported.

4-(2-Chlorophenyl)-4-hydroxy-3-buten-2-one (1g): Starting with LDA (75 mmol), acetone (2.904 g, 50.0 mmol) and 2-chlorobenzoyl chloride (10.501 g, 60.0 mmol) in THF (62.5 mL), **1g** (2.514 g, 25%) was isolated as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.09 (s, 3 H, CH_3), 5.95 (s, 1 H, CH), 7.23 (m, 1 H, CH_{ClPh}), 7.27 (m, 1 H, CH_{ClPh}), 7.32 (m, 1 H, CH_{ClPh}), 7.48 (m, 1 H, CH_{ClPh}), 15.64 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.8 (CH_3), 102.2 (CH), 127.4, 130.3 (CH_{ClPh}), 130.6 (C_{ClPh}), 131.1, 132.1 (CH_{ClPh}), 135.9 (C_{ClPh}), 185.0 (COH), 193.1 (*C*OCH_3) ppm. IR (neat): $\tilde{\nu}$ = 2964 (w), 1762 (m), 1602 (s), 1434 (s), 1291 (m), 1099 (m), 1046 (s), 952 (m), 766 (s), 535 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 196 (^{37}Cl, 1) $[M]^+$, 181 (10), 161 (100), 139 (26), 111 (11), 85 (9), 75 (10), 69 (15), 43 (13). HRMS (EI): calcd. for $C_{10}H_9ClO_2$ ($[M]^+$, ^{35}Cl) 196.02856; found 196.02830.

4-Hydroxy-4-(1-naphthyl)-3-buten-2-one (1j): Starting with LDA (65.5 mmol), acetone (2.904 g, 50.0 mmol) and 1-naphthoyl chloride (11.400 g, 60.0 mmol) in THF (62.5 mL), **1j** (4.563 g, 43%) was isolated as a yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, $COCH_3$), 6.14 (s, 1 H, CH), 7.45–7.62 (m, 4 H, CH_{Naph}), 7.88–8.07 (m, 2 H, CH_{Naph}), 8.48–8.52 (m, 1 H, CH_{Naph}), 16.14 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.8 (CO*C*H_3), 97.4 (CH), 125.1, 125.2, 126.7, 126.8, 127.7, 128.9 (CH_{Naph}), 130.5 (C_{Naph}), 132.4 (CH_{Naph}), 134.2, 134.6 (C_{Naph}), 189.6 (COH), 197.3 (*C*OCH_3) ppm. IR (neat): $\tilde{\nu}$ = 2927 (w), 1745 (s), 1715 (s), 1590 (s), 1472 (m), 1435 (s), 1360 (m), 1292 (s), 1254 (m), 1119 (m), 1053 (m), 964 (w), 845 (w), 765 (m), 742 (m), 606 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 212 (99) $[M]^+$, 197 (56), 179

(43), 169 (72), 155 (85), 141 (26), 127 (100), 115 (14), 101 (9), 85 (18), 77 (14), 69 (31), 63 (9), 51 (6), 43 (27).

1-Hydroxy-1-(2-naphthyl)-1-hexen-3-one (1k): Starting with LDA (65.5 mmol), 2-pentanone (4.306 g, 50.0 mmol) and 2-naphthoyl chloride (11.400 g, 60.0 mmol) in THF (62.5 mL), **1k** (7.449 g, 62%) was isolated as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.56–1.64 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.28 (t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 6.18 (s, 1 H, CH), 7.35–7.39 (m, 2 H, CH_{Naph}), 7.66–7.70 (m, 2 H, CH_{Naph}), 7.73 (m, 1 H, CH_{Naph}), 7.74 (m, 1 H, CH_{Naph}), 8.27 (s, 1 H, CH_{Naph}), 16.21 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4 ($CH_2CH_2CH_3$), 18.1 ($CH_2CH_2CH_3$), 40.0 ($CH_2CH_2CH_3$), 95.3 (CH), 121.1, 125.5 (CH_{Naph}), 126.5, 126.8 (C_{Naph}), 126.9, 127.2, 128.1 (CH_{Naph}), 131.1 (C_{Naph}), 131.6, 134.0 (CH_{Naph}), 182.1 (COH), 195.5 ($COCH_2CH_2CH_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (m), 2873 (w), 1631 (s), 1465 (m), 1386 (m), 1278 (w), 1152 (w), 953 (w), 781 (s), 746 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 240 (82) [M]$^+$, 211 (22), 197 (100), 170 (19), 155 (95), 127 (67), 101 (5), 77 (9), 69 (77), 43 (10). HRMS (EI): calcd. for $C_{16}H_{16}O_2$ 240.11448; found 240.11470.

General Procedure for the Synthesis of Fluorinated 1,3-Dicarbonyl Compounds 2a–c: A stirred solution of **1a**–**c** (16 mmol) and Selectfluor (16 mmol) in acetonitrile (2 mL/1 mmol of **1**) was irradiated (microwave) at 82 °C for 10 min. The solution was cooled to room temperature and filtered. The solvent was removed in vacuo and the residue was purified by vacuum distillation to give **2a**–**c**. The syntheses of **2b**[22] and **2c**[45] have been previously reported.

General Procedure for the Synthesis of Fluorinated 1,3-Dicarbonyl Compounds 2d–k: A stirred solution of **1d**–**k** (16 mmol) and Selectfluor (16 mmol) in acetonitrile (2 mL/1 mmol of **1**) was refluxed for 4 h. After cooling, the precipitate was filtered, and the filtrate was diluted with water. The organic layer was separated, and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo, and the residue was purified by chromatography (silica gel, *n*-heptane/dichloromethane) to give the fluorinated 1,3-dicarbonyl compounds **2d**–**k**.

2-Fluoro-1-(2-methoxyphenyl)-1,3-butanedione (2d): Starting with **1d** (3.088 g, 16.1 mmol) and Selectfluor (5.695 g, 16.1 mmol) in acetonitrile (32 mL), **2d** (2.500 g, 73%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 6.06 (d, $^2J_{H,F}$ = 48.0 Hz, 1 H, CH), 6.86–6.89 (m, 2 H, CH_{Ar}), 7.43 (m, 1 H, CH_{Ar}), 7.55 (m, 1 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1 ($COCH_3$), 55.8 (OCH_3), 97.9 (d, ^1J = 194.9 Hz, CF), 112.1, 121.5 (CH_{Ar}), 125.0 ($C_{Ar}OCH_3$), 131.7 (CH_{Ar}), 135.5 (d, ^4J = 3.5 Hz, CH_{Ar}), 170.1 (d, ^3J = 26.9 Hz, C_{Ar}), 193.4 (d, ^2J = 21.0 Hz, $COCFCOCH_3$), 199.6 (d, ^2J = 22.5 Hz, $COCFCOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –191.1 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (m), 2874 (w), 1726 (s), 1600 (s), 1489 (s), 1301 (s), 1254 (s), 1163 (m), 1081 (s), 962 (w), 757 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 210 (50) [M$^+$], 135 (100), 120 (2), 108 (2), 92 (11), 77 (22), 63 (4), 43 (8). HRMS (EI): calcd. for $C_{16}H_{11}FO_3$ 210.06867; found 286.06820.

2-Fluoro-1-(2-methoxyphenyl)-1,3-hexanedione (2e): Starting with **1e** (0.881 g, 4.0 mmol) and Selectfluor (1.417 g, 4.0 mmol) in acetonitrile (8 mL), **2e** (0.808 g, 90%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 1.55–1.63 (m, 2 H, $CH_2CH_2CH_2CH_3$), 2.58 (br. t, ^3J = 7.2 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 3.82 (s, 3 H, OCH_3), 5.93 (d, $^2J_{H,F}$ = 45.9 Hz, 1 H, CH), 6.96 (d, ^3J = 8.5 Hz, 1 H, CH_{Ar}), 7.01 (d, ^3J = 7.6 Hz, 1 H, CH_{Ar}), 7.46–7.52 (m, 1 H, CH_{Ar}), 7.62–7.66 (m, 1 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 ($COCH_2CH_2CH_3$), 16.6 (d, ^4J = 1.2 Hz, $COCH_2CH_2CH_3$), 40.9 ($COCH_2CH_2CH_3$), 55.9 (OCH_3), 97.8 (d, ^1J = 194.9 Hz, $COCFCOCH_2CH_2CH_3$), 112.1, 121.4 (CH_{Ar}), 125.1 ($C_{Ar}OCH_3$), 131.0, 135.4 (CH_{Ar}), 169.7 (d, ^3J = 27.0 Hz, C_{Ar}), 193.4 (d, ^2J = 20.6 Hz, $COCFCOCH_2CH_2CH_3$), 201.8 (d, ^2J = 21.5 Hz, $COCFCOCH_2CH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –192.8 (CF) ppm. IR (neat): $\tilde{\nu}$ = 2966 (s), 2877 (m), 1731 (s), 1686 (s), 1599 (s), 1486 (s), 1438 (s), 1290 (s), 1248 (s), 1163 (s), 1019 (s), 971 (m), 759 (s), 651 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 238 (3) [M$^+$], 207 (10), 168 (5), 135 (100), 92 (16) (8) 77, 64 (3), 43 (10). HRMS (EI): calcd. for $C_{13}H_{15}FO_3$ 238.09997; found 238.09972.

2-Fluoro-1-(2-methylphenyl)-1,3-butanedione (2f): Starting with **1f** (2.0618 g, 12.6 mmol) and Selectfluor (4.4 g, 12.6 mmol) in acetonitrile (25 mL), **2f** (1.123 g, 46%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (br. s, 3 H, CH_3), 2.42 (s, 3 H, $CH_{3,Ar}$), 5.75 (d, $^2J_{H,F}$ = 50.1 Hz, 1 H, CH), 7.21 (m, 1 H, CH_{Tol}), 7.33 (m, 1 H, CH_{Tol}), 7.35 (m, 1 H, CH_{Tol}), 7.60 (m, 1 H, CH_{Tol}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 ($COCH_3$), 28.6 ($CH_{3,Tol}$), 95.8 (d, ^1J = 196.5 Hz, CF), 124.6 (CH_{Tol}), 127.1 ($CCH_{3,Tol}$), 131.2, 131.6 (CH_{Tol}), 139.7 (d, ^4J = 3.6 Hz, CH_{Tol}), 165.1 (C_{Tol}), 172.0 (d, ^2J = 20.7 Hz, $COCFCOCH_3$), 187.1 (d, ^2J = 22.8 Hz, $COCFCOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –187.1 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3065 (w), 2929 (m), 1713 (s), 1692 (s), 1602 (m), 1571 (m), 1457 (m), 1296 (s), 1101 (m), 958 (w), 765 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 194 (5) [M$^+$], 179 (39), 159 (5), 131 (12), 119 (100), 103 (6), 91 (66), 77 (5), 65 (17), 51 (5), 43 (19), 39 (6). HRMS (EI): calcd. for $C_{11}H_{11}FO_2$ 194.07376; found 194.07356.

1-(2-Chlorophenyl)-2-fluoro-1,3-butanedione (2g): Starting with **1g** (0.393 g, 2.0 mmol) and Selectfluor (0.708 g, 2.0 mmol) in acetonitrile (4 mL), **2g** (0.180 g, 42%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 5.79 (d, $^2J_{H,F}$ = 49.3 Hz, 1 H, CH), 7.29 (m, 1 H, CH_{ClPh}), 7.31 (m, 1 H, CH_{ClPh}), 7.39 (m, 1 H, CH_{ClPh}), 7.55 (m, 1 H, CH_{ClPh}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.0 ($COCH_3$), 96.0 (d, ^1J = 198.9 Hz, CF), 123.1, 124.5 (CH_{ClPh}), 125.7 (CCl_{ClPh}), 127.7, 133.6 (CH_{ClPh}), 168.7 (d, ^3J = 24.6 Hz, C_{ClPh}), 191.8 (d, ^2J = 20.3 Hz, $COCFCOCH_3$), 199.1 (d, ^2J = 22.7 Hz, $COCFCOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –190.2 (CF) ppm. IR (neat): $\tilde{\nu}$ = 3420 (w), 2925 (w), 1735 (s), 1683 (s), 1509 (s), 1358 (m), 1286 (s), 1122 (m), 1063 (m), 970 (w), 780 (s) cm^{-1}.

1-(4-Chlorophenyl)-2-fluoro-1,3-butanedione (2h): Starting with **1h** (3.933 g, 20.0 mmol) and Selectfluor (7.085 g, 20.0 mmol) in acetonitrile (40 mL), **2h** (2.5 g, 58%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 5.90 (d, $^2J_{H,F}$ = 49.9 Hz, 1 H, CH), 7.36 (m, 2 H, CH_{ClPh}), 7.79 (m, 2 H, CH_{ClPh}) ppm. IR (KBr): $\tilde{\nu}$ = 3106 (w), 1924 (w), 1740 (m), 1689 (s), 1590 (s), 1488 (m), 1360 (s), 1179 (s), 1093 (s), 836 (s), 729 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 216 (^{37}Cl, 5) [M]$^+$, 214 (^{35}Cl, 15) [M]$^+$, 199 (3), 179 (13), 159 (3), 141 (^{37}Cl, 34), 139 (^{35}Cl, 100), 113 (^{37}Cl, 14), 111 (^{35}Cl, 41), 87 (6), 75 (20), 50 (6), 43 (23). HRMS (EI): calcd. for $C_{10}H_8ClFO_2$ ([M]$^+$, ^{35}Cl) 214.01914; found 214.01846.

2-Fluoro-1-(4-fluorophenyl)-1,3-butanedione (2i): Starting with **1i** (0.360 g, 2.0 mmol) and Selectfluor (0.708 g, 2.0 mmol) in acetonitrile (4 mL), **2i** (0.185 g, 46%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 5.90 (d, $^2J_{H,F}$ = 50.1 Hz, 1 H, CH), 7.07 (m, 2 H, CH_{FPh}), 7.96–7.98 (m, 2 H, CH_{FPh}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7 ($COCH_3$), 96.6 (d, ^1J = 198.0 Hz, $COCFCOCH_3$), 115.1 (d, ^3J = 22.2 Hz, $2CH_{FPh}$), 128.9 (d, ^3J = 4.4 Hz, C_{FPh}), 131.6 (d, ^4J = 3.3 Hz, $2CH_{FPh}$), 165.5 (d, ^1J = 256.2 Hz, CF_{FPh}), 187.7 (d, ^2J = 19.2 Hz, $COCFCOCH_3$), 199.4 (d, ^2J = 23.6 Hz, $COCFCOCH_3$) ppm. IR

(neat): $\tilde{\nu}$ = 3079 (m), 2929 (m), 1738 (s), 1693 (s), 1599 (s), 1507 (s), 1414 (s), 1360 (s), 1240 (s), 1160 (s), 1013 (m), 851 (s), 610 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 198 (12) [M^+], 183 (4), 123 (100), 107 (3), 95 (42), 75 (15), 43 (17). HRMS (EI): calcd. for $C_{10}H_8F_2O_2$ 198.04869; found 198.139023.

2-Fluoro-1-(1-naphthyl)-1,3-butanedione (2j): Starting with **1j** (0.480 g, 2.0 mmol) and Selectfluor (0.708 g, 2.0 mmol) in acetonitrile (4 mL), **2j** (0.193 g, 37%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, CH_3), 5.84 (d, $^2J_{H,F}$ = 49.9 Hz, 1 H, CH), 7.37–7.39 (m, 4 H, CH_{Naph}), 7.82–7.86 (m, 2 H, CH_{Naph}), 8.51–8.54 (m, 1 H, CH_{Naph}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5 ($CO\mathit{C}H_3$), 97.5 (d, ^1J = 200.4 Hz, $CO\mathit{C}FCOCH_3$), 127.1, 130.3, 130.5, 130.9 (CH_{Naph}), 131.8, 132.1 (C_{Naph}), 132.2, 132.8, 133.4 (CH_{Naph}), 167.7 (d, ^3J = 26.8 Hz, C_{Naph}), 188.8 (d, ^2J = 28.4 Hz, $\mathit{C}OCFCOCH_3$), 199.5 (d, ^2J = 23.1 Hz, $COCF\mathit{C}OCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –185.6 (CF) ppm. IR (neat): $\tilde{\nu}$ = 3400 (br., w), 3072 (w), 2927 (w), 1716 (s), 1590 (s), 1472 (m), 1435 (s), 1360 (m), 1291 (m), 1126 (m), 1053 (m), 743 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 230 (25) [M^+], 210 (5), 195 (5), 167 (12), 155 (100), 139 (12), 127 (82), 101 (5), 77 (7), 43 (11).

2-Fluoro-1-(2-naphthyl)-1,3-hexanedione (2k): Starting with **1k** (0.480 g, 2.0 mmol) and Selectfluor (0.708 g, 2.0 mmol) in acetonitrile (4 mL), **2k** (0.331 g, 64%) was isolated as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 7.6 Hz, 3 H, $CH_2CH_2C\mathit{H}_3$), 1.49–1.57 (m, 2 H, $CH_2C\mathit{H}_2CH_3$), 2.58 (br. t, ^3J = 8.0 Hz, 2 H, $C\mathit{H}_2CH_2CH_3$), 5.84 (d, $^2J_{H,F}$ = 48.4 Hz, 1 H, CH), 7.78–7.81 (m, 4 H, CH_{Naph}), 8.41 (m, 1 H, CH_{Naph}), 8.49 (m, 2 H, CH_{Naph}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 ($COCH_2CH_2\mathit{C}H_3$), 16.6 (d, ^4J = 1.6 Hz, $COCH_2\mathit{C}H_2CH_3$), 40.5 ($CO\mathit{C}H_2CH_2CH_3$), 97.1 (d, ^1J = 197.7 Hz, $CO\mathit{C}FCOCH_2CH_2CH_3$), 124.5 (d, ^4J = 197.7 Hz, CH_{Naph}), 127.4, 128.2, 129.1, 129.8, 130.4 (CH_{Naph}), 132.6 (C_{Naph}), 133.0 (CH_{Naph}), 136.5 (C_{Naph}), 165.7 (d, ^3J = 19.7 Hz, C_{Naph}), 190.6 (d, ^2J = 18.9 Hz, $\mathit{C}OCFCOCH_2CH_2CH_3$), 203.2 (d, ^2J = 22.6 Hz, $COCF\mathit{C}OCH_2CH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –190.7 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3060 (w), 2965 (m), 2876 (w), 1732 (m), 1686 (s), 1629 (s), 1596 (m), 1467 (m), 1281 (m), 1126 (m), 1098 (m), 864 (w), 755 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 258 (27) [M^+], 229 (12), 215 (5), 188 (19), 155 (100), 127 (54), 101 (3), 71 (10), 43 (15). HRMS (EI): calcd. for $C_{16}H_{15}FO_2$ 258.10506; found 258.10470.

General Procedure for the Synthesis of Silyl Enol Ethers 3: To a stirred benzene solution (2.5 mL/1 mmol of **2**) of **2** (10 mmol) was added triethylamine (16 mmol). After the solution was stirred for 2 h, chlorotrimethylsilane (18 mmol) was added. After the solution was stirred for 72 h, the solvent was removed in vacuo and hexane (25 mL) was added to the residue to give a suspension. The latter was filtered under argon. The filtrate was concentrated in vacuo to give silyl enol ethers **3**.

3-Fluoro-4-(2-methoxyphenyl)-4-(trimethylsilyloxy)-3-buten-2-one (3d): Starting with benzene (30 mL), **2d** (2.502 g, 11.9 mmol), triethylamine (1.926 g, 19.0 mmol) and chlorotrimethylsilane (2.326 g, 21.4 mmol), **3d** was isolated as a yellowish oil (3.322 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.10–0.11 [m, 9 H, $Si(CH_3)_3$], 1.90 (s, 3 H, CH_3), 3.73 (s, 3 H, OCH_3), 6.87 (m, 1 H, CH_{Ar}), 6.90 (m, 1 H, CH_{Ar}), 7.12–7.14 (m, 1 H, CH_{Ar}) 7.32 (m, 1 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [$OSi(\mathit{C}H_3)_3$], 25.8 ($CO\mathit{C}H_3$), 55.0 ($C_{Ar}O\mathit{C}H_3$), 110.6, 120.0 (CH_{Ar}), 123.4 ($\mathit{C}_{Ar}OCH_3$), 130.3, 131.1 (CH_{Ar}), 143.3 (C), 145.8 (d, ^1J = 240.4 Hz, CF), 156.7 (C_{Ar}), 190.3 (d, ^2J = 27.5 Hz, $\mathit{C}OCH_3$) ppm.

2-Fluoro-1-(2-methoxyphenyl)-1-(trimethylsilyloxy)-1-hexen-3-one (3e): Starting with benzene (39 mL), **2e** (3.079 g, 12.9 mmol), triethylamine (2.090 g, 20.6 mmol) and chlorotrimethylsilane (2.524 g, 23.2 mmol), **3e** was isolated as a yellowish oil (3.163 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 [m, 9 H, $Si(CH_3)_3$], 0.76 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2C\mathit{H}_3$), 1.44–1.47 (m, 2 H, $CH_2C\mathit{H}_2CH_3$), 2.30 (br. t, ^3J = 7.2 Hz, 2 H, $C\mathit{H}_2CH_2CH_3$), 3.71 (s, 3 H, OCH_3), 6.83 (d, ^3J = 8.2 Hz, 1 H, CH_{Ar}), 6.90 (d, ^3J = 7.6 Hz, 1 H, CH_{Ar}), 7.11 (dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 1 H, CH_{An}), 7.31 (dd, ^3J = 7.6 Hz, ^4J = 0.9 Hz, 1 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [$OSi(\mathit{C}H_3)_3$], 13.1 ($COCH_2CH_2\mathit{C}H_3$), 16.6 (d, ^4J = 1.2 Hz, $COCH_2\mathit{C}H_2CH_3$), 40.7 ($CO\mathit{C}H_2CH_2CH_3$), 54.8 ($CO\mathit{C}H_3$), 110.5, 119.8 (CH_{Ar}), 123.6 ($\mathit{C}_{Ar}OCH_3$), 130.2, 130.7 (CH_{Ar}), 134.6 (C), 145.6 (d, ^1J = 243.2 Hz, CF), 156.6 (d, ^3J = 9.9 Hz, C_{Ar}), 193.2 (d, ^2J = 28.5 Hz, $\mathit{C}OCH_2CH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –145.9 (CF) ppm.

[2-Fluoro-3-methyl-1-(2-methylphenyl)-1,3-butadienyloxy]trimethylsilane (3f): Starting with benzene (18 mL), **2f** (1.123 g, 5.8 mmol), triethylamine (0.936 g, 9.2 mmol) and chlorotrimethylsilane (1.131 g, 10.5 mmol), **3f** was isolated as a yellowish oil (1.001 g, 65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 [m, 9 H, $Si(CH_3)_3$], 2.11 (s, 3 H, $CH_{3,Tol}$), 7.12 (m, 2 H, CH_{Tol}), 7.18 (m, 2 H, C_{Tol}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [$OSi(\mathit{C}H_3)_3$], 18.5 ($CO\mathit{C}H_3$), 27.1 ($CH_{3,Tol}$), 125.1, 127.6, 128.8, 129.8 (CH_{Tol}), 131.0 ($\mathit{C}CH_{3,Tol}$), 136.0 (d, ^3J = 2.7 Hz, C_{Tol}), 143.5 (C), 145.6 (d, ^1J = 241.0 Hz, $\mathit{C}FCOCH_3$), 189.2 (d, ^2J = 24.4 Hz, $\mathit{C}OCH_3$) ppm.

4-(2-Chlorophenyl)-3-fluoro-4-(trimethylsilyloxy)-3-buten-2-one (3g): Starting with benzene (26 mL), **2g** (2.281 g, 10.6 mmol), triethylamine (1.719 g, 17.0 mmol) and chlorotrimethylsilane (2.076 g, 19.1 mmol), **3g** was isolated as a yellowish oil (2.432 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 [m, 9 H, $Si(CH_3)_3$], 1.97 (s, 3 H, CH_3), 7.38 (m, 1 H, CH_{ClPh}), 7.40 (m, 1 H, CH_{ClPh}), 7.50 (m, 1 H, CH_{ClPh}), 7.54 (m, 1 H, CH_{ClPh}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [$OSi(\mathit{C}H_3)_3$], 27.6 ($CO\mathit{C}H_3$), 126.2, 129.1, 130.1, 131.8 (CH_{ClPh}), 132.5, 133.4 (C_{ClPh}), 143.5 (d, ^2J = 12.6 Hz, 1 C), 145.2 (d, ^1J = 244.7 Hz, $\mathit{C}FCOCH_3$), 190.1 (d, ^2J = 29.7 Hz, $\mathit{C}OCH_3$) ppm.

4-(4-Chlorophenyl)-3-fluoro-4-(trimethylsilyloxy)-3-buten-2-one (3h): Starting with benzene (35 mL), **2h** (2.511 g, 11.6 mmol), triethylamine (1.885 g, 18.6 mmol) and chlorotrimethylsilane (2.277 g, 18.6 mmol), **3h** was isolated as a yellowish oil (2.183 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 [m, 9 H, $Si(CH_3)_3$], 2.09 (s, 3 H, CH_3), 7.19 (m, 2 H, CH_{ClPh}), 7.56 (m, 2 H, CH_{ClPh}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [$OSi(\mathit{C}H_3)_3$], 19.0 ($CO\mathit{C}H_3$), 127.7, 129.7, 129.8, 130.0 (CH_{ClPh}), 135.4 (C), 137.4 ($\mathit{C}Cl_{ClPh}$), 144.7 (d, ^1J = 237.4 Hz, $\mathit{C}FCOCH_3$), 149.9 (d, ^3J = 12.1 Hz, C_{ClPh}), 185.1 (d, ^2J = 29.4 Hz, $\mathit{C}OCH_3$) ppm.

3-Fluoro-4-(4-fluorophenyl)-4-(trimethylsilyloxy)-3-buten-2-one (3i): Starting with benzene (26 mL), **2i** (2.064 g, 10.4 mmol), triethylamine (1.684 g, 16.7 mmol) and chlorotrimethylsilane (2.034 g, 18.7 mmol), **3i** was isolated as a yellowish oil (2.306 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.23 [m, 9 H, $Si(CH_3)_3$], 2.20 (s, 3 H, CH_3), 7.03 (m, 2 H, CH_{FPh}), 7.76–7.78 (m, 2 H, CH_{FPh}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.4 [$OSi(\mathit{C}H_3)_3$], 19.0 ($CO\mathit{C}H_3$), 114.6 (d, ^2J = 21.5 Hz, $2CH_{FPh}$), 130.8 (d, ^2J = 6.9 Hz, $2CH_{FPh}$), 144.8 (d, ^1J = 237.9 Hz, $\mathit{C}FCOCH_3$), 146.4 (C), 149.7 (d, ^3J = 12.2 Hz, C_{FPh}), 164.5 (d, ^1J = 252.5 Hz, CF_{FPh}), 185.5 (d, ^2J = 29.1 Hz, $COCF\mathit{C}OCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –144.1 (CF) ppm.

3-Fluoro-4-(1-naphthyl)-4-(trimethylsilyloxy)-3-buten-2-one (3j): Starting with benzene (24 mL), **2j** (2.425 g, 9.4 mmol), triethylamine (1.520 g, 15.0 mmol) and chlorotrimethylsilane (1.836 g, 16.9 mmol), **3j** was isolated as a yellowish oil (2.016 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 [m, 9 H, $Si(CH_3)_3$], 1.94 (br. s,

3 H, CH_3), 7.56 (m, 4 H, CH_{Naph}), 7.92 (m, 3 H, CH_{Naph}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [OSi(CH_3)$_3$], 27.2 (COCH_3), 124.1, 124.4, 125.6, 125.7 (CH_{Naph}), 126.3 (d, ^3J = 11.8 Hz, C_{Naph}), 126.4 (CH_{Naph}), 127.2, 127.8 (C_{Naph}), 127.9, 129.7 (CH_{Naph}), 144.3 (C), 145.9 (d, ^1J = 242.6 Hz, CFCOCH$_3$), 189.8 (d, ^2J = 26.7 Hz, COCH$_3$) ppm.

2-Fluoro-1-(2-naphthyl)-1-(trimethylsilyloxy)-1-hexen-3-one (3k): Starting with benzene (19 mL), **2k** (1.9155 g, 7.4 mmol), triethylamine (1.200 g, 11.8 mmol) and chlorotrimethylsilane (1.449 g, 13.3 mmol), **3k** was isolated as a yellowish oil (1.813 g, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.10–0.24 [m, 9 H, Si(CH_3)$_3$], 0.91 (t, ^3J = 7.2 Hz, 3 H, CH$_2$CH$_2$CH_3), 1.54–1.62 (m, 2 H, CH$_2$CH_2CH$_3$), 2.57 [br. t, ^3J = 8.5 Hz, 2 H, CH_2CH$_2$CH$_3$], 7.37 (m, 1 H, CH_{Naph}), 7.39 (m, 1 H, CH_{Naph}), 7.69–7.78 (m, 4 H, CH_{Naph}), 8.26 (m, 1 H, CH_{Naph}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1 [OSi(CH_3)$_3$], 13.1 (COCH$_2$CH$_2$$CH_3$), 19.6 (d, ^4J = 2.7 Hz, COCH$_2$$CH_2CH_3$), 33.3 (CO$CH_2CH_2CH_3$), 124.4, 127.0, 127.1, 127.3, 128.7, 128.8, 129.7 (CH_{Naph}), 131.7, 134.4 (C_{Naph}), 134.5 (C), 145.0 (d, ^1J = 238.4 Hz, CFCOCH$_2$CH$_2$CH$_3$), 152.8 (d, ^3J = 10.7 Hz, C_{Naph}), 186.9 (d, ^2J = 29.7 Hz, COCH$_2$CH$_2$CH$_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –142.9 (CF) ppm.

General Procedure for the Synthesis of Fluorinated Phenols and Biaryls 5: To a CH_2Cl_2 solution of silyl enol ether **3** (1.0 equiv.) and 1,3-bis(silyl enol ether) **4** (1.0 equiv.) was added dropwise $TiCl_4$ (1.09 equiv.) at –78 °C under argon atmosphere. The solution was stirred at –78 °C for 30 min and then warmed to 20 °C during 18 h. To the solution was added hydrochloric acid (10%). The organic layer was separated and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography (silica gel, *n*-heptane/EtOAc) to give products **5**.

Methyl 2,4-Diethyl-3-fluoro-6-hydroxybenzoate (5a): Starting with bis(silyl enol ether) **4a** (0.588 g, 2.26 mmol), $TiCl_4$ (0.50 mL, 4.52 mmol) in CH_2Cl_2 (5 mL) and silyl enol ether **3a** (0.493 g, 2.26 mmol), **5a** was isolated (0.274 g, 54%) by column chromatography as a yellowish oil (R_f = 0.45, silica gel, *n*-heptane/EtOAc = 10:1). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.4 Hz, 3 H, CH$_2$CH_3), 1.21 (t, ^3J = 7.6 Hz, 3 H, CH$_2$CH_3), 2.63 (ddq, ^3J = 7.6 Hz, $^4J_{F,H}$ = 1.2 Hz, $^4J_{H,H}$ = 0.7 Hz, 2 H, CH_2CH$_3$), 2.93 (dq, ^3J = 7.4 Hz, $^4J_{F,H}$ = 3.2 Hz, 2 H, CH_2CH$_3$), 3.89 (s, 3 H, OCH$_3$), 6.68 (dt, $^4J_{H,F}$ = 6.6 Hz, $^4J_{H,H}$ = 0.7 Hz, 1 H, Ar), 10.85 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.5, 14.9 (CH$_2$$CH_3$), 20.7 (d, ^3J = 6.5 Hz, CH$_2$CH$_3$), 22.7 (d, ^3J = 4.1 Hz, CH$_2$CH$_3$), 52.2 (OCH$_3$), 109.7 (d, ^3J = 3.5 Hz, CCOOCH$_3$), 115.5 (d, ^3J = 5.3 Hz, CH_{Ar}), 132.1 (d, ^2J = 18.2 Hz, CCF), 138.9 (d, ^2J = 20.5 Hz, CCF), 152.6 (d, ^1J = 234.2 Hz, CF), 158.3 (d, ^4J = 1.8 Hz, COH), 171.4 (d, ^4J = 3.2 Hz, COOCH$_3$) ppm. ^{19}F NMR (235 MHz, Cl_3CF): δ = –133.0 (CF) ppm. IR (neat): $\tilde{\nu}$ = 3101 (br., m), 2973 (m), 2939 (m), 2879 (m), 1733 (m), 1668 (br., s), 1626 (s), 1574 (m), 1437 (s), 1326 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 226 (19) [M$^+$], 195 (18), 194 (100), 151 (58). HRMS (EI, 70 eV): calcd. for $C_{12}H_{15}FO_3$ [M$^+$] 226.09997; found: 226.10022.

Ethyl 2,4-Diethyl-3-fluoro-6-hydroxybenzoate (5b): Starting with bis(silyl enol ether) **4b** (0.905 g, 3.3 mmol), $TiCl_4$ (0.620 g, 3.3 mmol) in CH_2Cl_2 (6 mL) and silyl enol ether **3a** (0.654 g, 3.0 mmol), **5b** was isolated (0.302 g, 42%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.5 Hz, 6 H, CH$_2$CH_3), 1.43 (t, ^3J = 7.0 Hz, 3 H, OCH$_2$CH_3), 2.62 (dq, ^3J = 7.6 Hz, $^4J_{F,H}$ = 3.5 Hz, 2 H, CH_2CH$_3$), 2.90 (ddq, ^3J = 7.4 Hz, $^4J_{F,H}$ = 1.2 Hz, $^4J_{H,H}$ = 0.9 Hz, 2 H, CH_2CH$_3$), 4.43 (q, ^3J = 7.2 Hz, 2 H, OCH_2CH$_3$), 6.68 (d, $^4J_{H,F}$ = 3.0 Hz, 1 H, CH), 10.90 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.4 (d, ^4J = 0.6 Hz, CH$_2$$CH_3$), 12.9 (CH$_2$$CH_3$), 13.6 (OCH$_2$$CH_3$), 19.6 (d, ^3J = 6.6 Hz, CH$_2$CH$_3$), 21.6 (d, ^3J = 3.5 Hz, CH$_2$CH$_3$), 60.7 (OCH$_2$CH$_3$), 108.8 (d, ^3J = 3.3 Hz, C_{Ar}), 114.5 (d, ^3J = 6.6 Hz, CH_{Ar}), 131.0 (d, ^2J = 18.0 Hz, C_{Ar}), 137.7 (d, ^2J = 20.7 Hz, C_{Ar}), 151.6 (d, ^1J = 232.7 Hz, CF_{Ar}), 157.3 (d, ^4J = 1.7 Hz, COH_{Ar}), 169.9 (d, ^4J = 3.0 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –133.2 (CF) ppm. IR (neat): $\tilde{\nu}$ = 2977 (s), 2877 (m), 1663 (s), 1625 (s), 1463 (s), 1373 (s), 1253 (s), 1204 (s), 1081 (s), 1010 (m), 914 (m), 743 (m) cm^{-1}. MS (CI, 70 eV): *m*/*z* (%) = 240 (19) [M]$^+$, 194 (100), 166 (3), 151 (33), 123 (3), 109 (4). HRMS (EI): calcd. for $C_{13}H_{17}FO_3$ 240.11562; found 240.11598.

1-(2,4-Diethyl-3-fluoro-6-hydroxyphenyl)-1-ethanone (5c): Starting with bis(silyl enol ether) **4d** (0.714 g, 3.3 mmol), $TiCl_4$ (0.620 g, 3.3 mmol) in CH_2Cl_2 (6 mL) and silyl enol ether **3a** (0.654 g, 3.0 mmol), **5c** was isolated (0.315 g, 50%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 1.75 (t, ^3J = 7.7 Hz, 6 H, CH$_2$CH_3), 2.67 (s, 3 H, COCH$_3$), 2.87 (ddq, ^3J = 7.7 Hz, $^4J_{F,H}$ = 1.4 Hz, $^4J_{H,H}$ = 0.8 Hz, 2 H, CH_2CH$_3$), 2.93 (dq, ^3J = 7.4 Hz, $^4J_{F,H}$ = 3.2 Hz, 2 H, CH_2CH$_3$), 6.85 (d, $^4J_{H,F}$ = 2.6 Hz, 1 H, CH_{Ar}), 11.80 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 13.4 (d, ^4J = 0.9 Hz, CH$_2$$CH_3$), 15.1 (CH$_2$$CH_3$), 20.6 ($CH_2CH_3$), 22.6 ($CH_2CH_3$), 32.1 (CO$CH_3$), 116.2 (d, ^3J = 3.3 Hz, CH_{Ar}), 119.7 (d, ^3J = 2.2 Hz, CCOCH$_{3,Ar}$), 130.2 (d, ^2J = 16.6 Hz, C_{Ar}), 139.1 (d, ^2J = 20.5 Hz, C_{Ar}), 152.7 (d, ^1J = 233.7 Hz, CF_{Ar}), 157.3 (COH_{Ar}), 204.9 (d, ^4J = 3.1 Hz, COCH$_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –132.0 (CF) ppm. IR (neat): $\tilde{\nu}$ = 3350 (br.), 2972 (s), 2878 (m), 1684 (s), 1432 (s), 1359 (s), 1233 (s), 1202 (s), 1089 (m), 841 (m), 661 (w), 562 (w) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 210 (32) [M$^+$], 195 (100), 117 (16), 166 (4), 149 (4), 133 (3), 109 (7). HRMS (EI): calcd. for $C_{12}H_{15}FO_2$ 210.10506; found 210.10486.

(2,4-Diethyl-3-fluoro-6-hydroxyphenyl)(phenyl)methanone (5d): Starting with bis(silyl enol ether) **4e** (1.011 g, 3.3 mmol), $TiCl_4$ (0.620 g, 3.3 mmol) CH_2Cl_2 (6 mL) and silyl enol ether **3a** (0.654 g, 3.0 mmol), **5d** was isolated (0.422 g, 52%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^1H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH_3), 1.25 (t, ^3J = 7.5 Hz, 3 H, CH$_2$CH_3), 2.38 (dq, ^3J = 7.4 Hz, $^4J_{F,H}$ = 3.3 Hz, 2 H, CH_2CH$_3$), 2.66 (ddq, ^3J = 7.6 Hz, $^4J_{F,H}$ = 1.4 Hz, $^4J_{H,H}$ = 1.0 Hz, 2 H, CH_2CH$_3$), 6.69 (d, $^4J_{H,F}$ = 5.0 Hz, 1 H, CH_{Ar}), 7.26 (m, 2 H, CH_{Ph}), 7.42 (m, 1 H, CH_{Ph}), 7.78 (m, 2 H, CH_{Ph}), 10.85 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (d, ^4J = 1.5 Hz, CH$_2$$CH_3$), 14.9 (d, ^4J = 3.0 Hz, CH$_2$$CH_3$), 20.9 (d, ^3J = 3.7 Hz, CH$_2$CH$_3$), 22.4 (d, ^3J = 3.7 Hz, CH$_2$CH$_3$), 13.6 (OCH$_2$$CH_3$), 115.6 (d, ^3J = 3.6 Hz, CH_{Ar}), 122.1 (d, ^3J = 3.0 Hz, C_{Ar}), 128.6 (2 CH_{Ph}), 129.2 (CH_{Ph}), 130.2 (d, ^2J = 18.0 Hz, C_{Ar}), 133.3 (CH_{Ph}), 136.0 (d, ^2J = 20.2 Hz, C_{Ar}), 138.9 (C_{Ph}), 152.1 (d, ^4J = 2.2 Hz, COH_{Ar}), 153.3 (d, ^1J = 235.5 Hz, CF_{Ar}), 199.1 (d, ^4J = 3.0 Hz, CO_{Ar}) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –133.3 (CF) ppm. IR (neat): $\tilde{\nu}$ = 3381 (m, br.), 2970 (m), 2930 (s), 2852 (m), 1661 (s), 1597 (m), 1450 (s), 1430 (s), 1241 (s), 1060 (m), 842 (m), 689 (m) cm^{-1}. GC-MS (CI, 70 eV): *m*/*z* (%) = 271 (100) [M – 1]$^+$, 256 (50), 239 (51), 228 (17), 211 (5), 151 (8), 128 (7), 105 (15), 77 (31). HRMS (CI): calcd. for $C_{17}H_{16}FO_2$ [M – 1]$^+$ 271.11288; found 271.11252.

Methyl 6-Fluoro-3-hydroxy-5-phenylbiphenyl-2-carboxylate (5e): Starting with bis(silyl enol ether) **4a** (0.414 g, 1.59 mmol), $TiCl_4$ (0.298 g, 1.59 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3b** (0.500 g, 1.59 mmol), **5e** was isolated (0.430 g, 82%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a

reddish solid (m.p. 114–115 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.46 (s, 3 H, OCH_3), 7.12 (d, ^4J = 6.6 Hz, 1 H, Ar), 7.20–7.50 (m, 8 H, Ph), 7.53–7.63 (m, 2 H, Ph), 10.64 (s, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 111.6 (d, ^3J = 1.8 Hz, *C*$COOCH_{3,Ar}$), 118.2 (br. s, CH_{Ar}), 127.4 (2CH_{Ph}), 127.7 (2CH_{Ph}), 128.5 (2CH_{Ph}), 128.6 (2CH_{Ph}), 128.9 (br. s, CH_{Ph}), 129.1 (d, ^4J = 2.9 Hz, CH_{Ph}), 131.1 (d, ^2J = 20.5 Hz, C_{Ar}), 134.7 (d, ^3J = 1.4 Hz, C_{Ph}), 135.6 (br. s, C_{Ph}), 135.9 (d, ^2J = 17.6 Hz, C_{Ar}), 150.0 (d, ^1J = 238.3 Hz, CF), 157.4 (d, ^4J = 2.4 Hz, COH), 170.6 (^4J = 2.4 Hz, *C*$OOCH_3$) ppm. ^{19}F NMR (235 MHz, Cl_3CF): δ = –127.6 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1669 (m), 1616 (m), 1601 (m), 1336 (m), 1254 (m), 1222 (m), 1208 (m), 1114 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 322 (62) [M$^+$], 291 (30), 290 (100), 262 (34), 233 (48). HRMS (EI, 70 eV): calcd. for $C_{20}H_{15}FO_3$ 322.09997; found 322.09939.

Ethyl 6-Fluoro-3-hydroxy-5-phenylbiphenyl-2-carboxylate (5f): Starting with bis(silyl enol ether) **4b** (0.366 g, 1.59 mmol), $TiCl_4$ (0.298 g, 1.59 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3b** (0.500 g, 1.59 mmol), **5f** a was isolated (0.363 g, 68%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 97–98 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.73 (t, ^3J = 7.0 Hz, 3 H, OCH_2CH_3), 3.97 (q, ^3J = 8.0 Hz, 2 H, OCH_2CH_3), 7.12 (d, $^4J_{H,F}$ = 6.7 Hz, 1 H, CH_{Ar}), 7.24–7.26 (m, 2 H, CH_{Ph}), 7.28–7.48 (m, 6 H, CH_{Ph}), 7.57–7.62 (m, 2 H, CH_{Ph}), 10.80 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 12.9 (OCH_2CH_3), 61.3 (OCH_2CH_3), 111.7 (d, ^3J = 1.9 Hz, C_{Ar}), 118.1 (d, ^3J = 2.5 Hz, CH_{Ar}), 127.2 (CH_{Ph}), 127.6 (2CH_{Ph}), 128.5 (4CH_{Ph}), 129.0 (4CH_{Ph}), 131.1 (d, ^2J = 20.2 Hz, C_{Ar}), 134.7 (C_{Ph}), 135.7 (d, ^2J = 16.5 Hz, C_{Ar}), 149.9 (d, ^1J = 234.1 Hz, CF_{Ar}), 157.5 (d, ^4J = 2.1 Hz, COH_{Ar}), 170.1 (d, ^4J = 1.5 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –134.0 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1665 (m), 1615 (w), 1558 (w), 1505 (w), 1319 (m), 1249 (m), 1226 (m), 1179 (m), 1111 (m), 1075 (w), 902 (w), 865 (w), 760 (s), 697 (s) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 336 (35) [M]$^+$, 290 (100), 262 (27), 233 (36), 157 (3), 131 (3). $C_{21}H_{17}FO_3$ (336.37): calcd. C 74.99, H 5.09; found C 74.63, H 5.24.

(6-Fluoro-3-hydroxy-5-phenylbiphenyl-2-yl)-1-ethanone (5g): Starting with bis(silyl enol ether) **4d** (0.344 g, 1.59 mmol), $TiCl_4$ (0.298 g, 1.59 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3b** (0.500 g, 1.59 mmol), **5g** was isolated (0.146 g, 30%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 65–66 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.81 (s, 3 H, $COCH_3$), 7.20 (d, $^4J_{H,F}$ = 6.7 Hz, 1 H, CH_{Ar}), 7.35–7.62 (m, 10 H, CH_{Ph}), 11.70 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 31.6 ($CO*C*H_3$), 118.8 (d, ^3J = 2.7 Hz, CH_{Ar}), 120.3 (C_{Ph}), 128.4, 128.6, 128.7, 128.7, 128.9, 128.9, 129.0, 129.7, 129.8, 130.0 (CH_{Ph}), 134.5 (d, ^3J = 4.3 Hz, C_{Ar}), 134.7 (d, ^2J = 22.1 Hz, C_{Ar}), 136.2 (d, ^2J = 17.2 Hz, C_{Ar}), 147.0 (C_{Ph}), 149.5 (d, ^1J = 236.0 Hz, CF_{Ar}), 157.3 (d, ^4J = 1.4 Hz, COH_{Ar}), 205.8 (d, ^4J = 3.3 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –128.8 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1681 (w), 1637 (s), 1551 (m), 1500 (w), 1364 (s), 1292 (m), 1245 (m), 1210 (s), 1073 (w), 880 (m), 776 (m), 698 (s), 671 (w), 506 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 306 (100) [M$^+$], 291 (81), 273 (6), 228 (21), 183 (5), 153 (5), 153 (3), 133 (3), 105 (93), 77 (41). HRMS (EI): calcd. for $C_{20}H_{15}FO_2$ 306.10506; found 306.10517.

(2-Methoxyethyl) 6-Fluoro-3-hydroxy-5-phenylbiphenyl-2-carboxylate (5h): Starting with bis(silyl enol ether) **4c** (0.484 g, 1.59 mmol), $TiCl_4$ (0.298 g, 1.59 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3b** (0.500 g, 1.59 mmol), **5h** was isolated (0.297 g, 51%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 61–62 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.01 (t, ^3J = 5.0 Hz, 2 H, $OCH_2CH_2OCH_3$), 3.18 (s, 3 H, OCH_3), 4.08 (t, ^3J = 5.0 Hz, 2 H, $OCH_2CH_2OCH_3$), 7.12 (d, $^4J_{H,F}$ = 6.7 Hz, 1 H, CH_{Ar}), 7.26 (m, 2 H, CH_{Ph}), 7.31–7.34 (m, 6 H, CH_{Ph}), 7.56–7.61 (m, 2 H, CH_{Ph}), 10.60 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 58.6 ($OCH_{3,Ar}$), 64.0 ($OCH_2CH_2OCH_3$), 69.1 ($OCH_2CH_2OCH_3$), 111.6 (d, ^3J = 2.3 Hz, C_{Ar}), 118.2 (d, ^3J = 3.4 Hz, CH_{Ar}), 127.4 (4CH_{Ph}), 128.5 (4CH_{Ph}), 129.0 (2CH_{Ph}), 131.0 (d, ^2J = 23.7 Hz, C_{Ar}), 134.6 (d, ^3J = 2.3 Hz, C_{Ph}), 135.7 (C_{Ph}), 135.8 (d, ^2J = 18.2 Hz, C_{Ar}), 150.0 (d, ^1J = 284.0 Hz, CF_{Ar}), 157.4 (d, ^4J = 2.0 Hz, COH_{Ar}), 169.9 (d, ^4J = 3.4 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.6 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1661 (s), 1612 (m), 1318 (s), 1251 (s), 1201 (s), 1134 (m), 1114 (m), 1025 (m), 778 (m), 755 (s), 700 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 366 (59) [M$^+$], 305 (20), 290 (100), 262 (37), 233 (30), 149 (4). $C_{22}H_{19}FO_4$ (366.39): calcd. C 72.12, H 5.23; found C 71.79, H 5.26.

Methyl 6-Fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5i): Starting with bis(silyl enol ether) **4a** (0.620 g, 2.38 mmol), $TiCl_4$ (0.26 mL, 2.38 mmol) in CH_2Cl_2 (5 mL) and silyl enol ether **3c** (0.600 g, 2.38 mmol), **5i** was isolated (0.247 g, 40%) by column chromatography as a yellowish solid; R_f = 0.22 (silica gel, *n*-heptane/EtOAc = 5:1), m.p. 67–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29 (d, $^4J_{H,F}$ = 2.2 Hz, 3 H, CH_3), 3.42 (s, 3 H, OCH_3), 6.85 (d, $^4J_{H,F}$ = 6.5 Hz, 1 H, CH_{Ar}), 7.14–7.23 (m, 2 H, CH_{Ph}), 7.33–7.40 (m, 3 H, CH_{Ph}), 10.61 (s, 1 H, OH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 15.4 (d, $^3J_{Me,F}$ = 3.7 Hz, CH_3), 51.7 (OCH_3), 110.2 (d, ^3J = 1.8 Hz, *C*$COOCH_3$), 118.9 (d, ^3J = 4.5 Hz, CH_{Ar}), 127.2 (2CH_{Ph}), 127.6 (2CH_{Ph}), 128.9 (d, ^4J = 1.8 Hz, CH_{Ph}), 129.7 (d, ^2J = 19.0 Hz, C_{Ar}), 133.3 (d, ^2J = 21.0 Hz, *C*CH_3), 135.7 (C_{Ph}), 151.6 (d, ^1J = 235.5 Hz, CF), 157.4 (d, ^4J = 2.5 Hz, COH), 170.8 (d, ^4J = 2.5 Hz, *C*$OOCH_3$) ppm. ^{19}F NMR (235 MHz, Cl_3CF): δ = –127.5 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1670 (s), 1622 (m), 1574 (m), 1329 (s), 1216 (s), 1194 (s), 1073 (m), 1012 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 260 (34) [M$^+$], 229 (18), 228 (100), 200 (38), 171 (17). HRMS (EI, 70 eV): calcd. for $C_{15}H_{13}FO_3$ 260.08432; found 260.08377. $C_{15}H_{13}FO_3$ (260.26): calcd. C 69.22, H 5.03; found C 69.14, H 5.11.

(2-Methoxyethyl) 6-Fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5j): Starting with bis(silyl enol ether) **4c** (0.724 g, 2.38 mmol), $TiCl_4$ (0.446 g, 2.38 mmol) in CH_2Cl_2 (5 mL) and silyl enol ether **3c** (0.600 g, 2.38 mmol), **5j** was isolated (0.304 g, 42%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.23 (d, $^4J_{H,F}$ = 1.5 Hz, 3 H, CH_3), 2.97 (t, ^3J = 5.7 Hz, 2 H, $OCH_2CH_2OCH_3$), 3.16 (s, 3 H, OCH_3), 4.04 (t, ^3J = 5.0 Hz, 2 H, $OCH_2CH_2OCH_3$), 6.85 (d, $^4J_{H,F}$ = 7.5 Hz, 1 H, CH_{Ar}), 7.19 (s, 1 H, CH_{Ph}), 7.26 (m, 2 H, CH_{Ph}), 7.35–7.41 (m, 2 H, CH_{Ph}), 11.60 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.4 (d, ^3J = 4.3 Hz, $CH_{3,Ar}$), 58.6 (OCH_3), 63.8 ($OCH_2CH_2OCH_3$), 69.0 ($OCH_2CH_2OCH_3$), 110.1 (C_{Ph}), 118.9 (d, ^3J = 4.8 Hz, CH_{Ar}), 127.0 (2CH_{Ph}), 127.5 (2CH_{Ph}), 129.0 (CH_{Ph}), 129.6 (d, ^2J = 23.2 Hz, C_{Ar}), 133.2 (d, ^2J = 25.5 Hz, C_{Ar}), 135.9 (C_{Ar}), 151.6 (d, ^1J = 279.7 Hz, CF_{Ar}), 157.4 (d, ^4J = 3.0 Hz, COH_{Ar}), 170.0 (d, ^4J = 3.0 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.5 (CF) ppm. IR (neat): $\tilde{\nu}$ = 3403 (br.), 2927 (w), 1737 (s), 1667 (s), 1623 (w), 1465 (m), 1378 (m), 1240 (s), 1219 (s), 1130 (m), 1026 (w), 757 (m), 699 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 304 (61) [M$^+$], 288 (100), 200 (41), 171 (9), 152 (5). $C_{17}H_{17}FO$ (256.32): calcd. C 67.10, H 5.63; found C 67.78, H 5.82.

1-(6-Fluoro-3-hydroxy-5-methylbiphenyl-2-yl)-1-ethanone (5k): Starting with bis(silyl enol ether) **4d** (0.515 g, 2.38 mmol), $TiCl_4$ (0.446 g, 2.38 mmol) in CH_2Cl_2 (5 mL) and silyl enol ether **3c** (0.600 g, 2.38 mmol), **5k** was isolated (0.180 g, 31%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 57–59 °C). ^{1}H NMR (250 MHz, $CDCl_3$): δ =

1.75 (s, 3 H, $COCH_3$), 2.30 (s, 3 H, $CH_{3,Ar}$), 6.85 (d, $^4J_{H,F}$ = 2.6 Hz, 1 H, CH_{Ar}), 7.26–7.33 (m, 2 H, CH_{Ph}), 7.44–7.47 (m, 3 H, CH_{Ph}), 11.80 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.5 ($CO\mathit{C}H_3$), 31.6 ($CH_{3,Ar}$), 117.3 ($\mathit{C}COCH_{3,Ar}$), 119.5 (d, ^3J = 4.1 Hz, CH_{Ar}), 123.6 (C_{Ph}), 128.5 (2CH_{Ph}), 128.8 (2CH_{Ph}), 130.0 (CH_{Ph}), 133.8 (d, ^2J = 22.3 Hz, $\mathit{C}CH3_{Ar}$), 145.0 (d, ^2J = 34.7 Hz, $\mathit{C}CH_{3Ar}$), 151.2 (d, ^1J = 233.7 Hz, CF_{Ar}), 157.5 (COH_{Ar}), 205.7 ($\mathit{C}OCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –128.4 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3060 (m), 2928 (m), 1634 (s), 1568 (m), 1469 (s), 1361 (s), 1293 (s), 1207 (s), 1020 (m), 879 (s), 771 (s), 702 (s), 645 (m), 594 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 244 (100) [M^+], 229 (89), 211 (21), 183 (30), 165 (11), 152 (12), 133 (4), 115 (4), 97 (5). $C_{15}H_{13}FO_2$ (244.26): calcd. C 73.76, H 5.36; found C 73.66, H 5.51.

(6-Fluoro-3-hydroxy-5-methylbiphenyl-2-yl) Phenyl Ketone (5l): Starting with bis(silyl enol ether) **4e** (0.729 g, 2.38 mmol), $TiCl_4$ (0.446 g, 2.38 mmol) in CH_2Cl_2 (5 mL) and silyl enol ether **3c** (0.600 g, 2.38 mmol), **5l** was isolated (0.291 g, 40%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 151–152 °C). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.36 (t, $^3J_{H,F}$ = 2.2 Hz, 3 H, $CH_{3,Ar}$), 6.94 (d, $^4J_{H,F}$ = 6.2 Hz, 1 H, CH_{Ar}), 6.99–7.26 (m, 8 H, CH_{Ph}), 7.31–7.35 (m, 2 H, CH_{Ph}), 9.22 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.6 (d, ^3J = 4.5 Hz, $CH_{3,Ar}$), 119.0 (d, ^3J = 4.6 Hz, CH_{Ar}), 120.2 (d, ^3J = 2.1 Hz, C_{Ar}), 127.5 (2CH_{Ph}), 127.6 (2CH_{Ph}), 129.0 (4CH_{Ph}), 130.9 (CH_{Ph}), 131.9 (CH_{Ph}), 132.0 (d, ^2J = 17.3 Hz, C_{Ar}), 132.5 (C_{Ar}), 134.0 (C_{Ph}), 149.4 (C_{Ph}), 151.3 (d, ^1J = 286.2 Hz, CF_{Ar}), 154.9 (d, ^4J = 2.1 Hz, COH_{Ar}), 200.6 (d, ^4J = 4.1 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –113.7 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 3389 (s), 3270 (s), 1663 (s), 1594 (m), 1500 (w), 1326 (m), 1276 (s), 1248 (m), 1201 (m), 1073 (w), 847 (s), 690 (w) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 306 (84) [M^+], 305 (100), 287 (4), 229 (23), 220 (6), 200 (6), 183 (6), 153 (5). HRMS (EI): calcd. for $C_{20}H_{15}FO_2$ 306.10506; found 306.10443.

Methyl 6-Fluoro-3-hydroxy-2′-methoxy-5-methylbiphenyl-2-carboxylate (5m): Starting bis(silyl enol ether) **4a** (0.852 g, 3.3 mmol), $TiCl_4$ (0.620 g, 3.3 mmol) in CH_2Cl_2 (6 mL) and silyl enol ether **3d** (0.847 g, 3.0 mmol), **5m** was isolated (0.383 g, 44%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 105–107 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.22 (br. s, 3 H, CH_3), 3.37 (s, 3 H, OCH_3), 3.65 (s, 3 H, $COO\mathit{C}H_3$), 6.85 (d, $^4J_{H,F}$ = 8.1 Hz, 1 H, CH_{Ar}), 6.92 (dd, ^3J = 7.4 Hz, ^4J = 0.9 Hz, 1 H, CH_{Ar}), 7.01–7.04 (m, 1 H, CH_{Ar}), 7.19–7.23 (m, 1 H, CH_{Ar}), 7.25–7.28 (m, 1 H, CH_{Ar}), 10.57 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (d, ^3J = 3.6 Hz, CH_3), 50.6 ($OCH_{3,Ar}$), 54.4 ($COO\mathit{C}H_3$), 109.2 (d, ^3J = 9.6 Hz, CH_{Ar}), 110.0 ($\mathit{C}COOCH_{3,Ar}$), 117.8 (d, ^4J = 4.2 Hz, CH_{Ar}), 119.0 (CH_{Ar}), 123.6 ($\mathit{C}OCH_{3,Ar}$), 124.8 (d, ^2J = 19.5 Hz, $\mathit{C}CF_{Ar}$), 127.9, 129.2 (CH_{Ar}), 132.1 (d, ^2J = 21.5 Hz, $\mathit{C}CH_{3,Ar}$), 150.6 (d, ^1J = 233.0 Hz, CF_{Ar}), 155.4 (C_{Ar}), 156.2 (d, ^4J = 2.1 Hz, COH_{Ar}), 169.7 (d, ^4J = 2.1 Hz, $\mathit{C}OOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.9 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3012 (w), 2844 (w), 1662 (s), 1499 (m), 1459 (s), 1378 (s), 1239 (s), 1106 (m), 1074 (m), 1025 (m), 806 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 290 (50) [M^+], 258 (100), 241 (6), 229 (26), 187 (10), 159 (6), 133 (8). HRMS (EI): calcd. for $C_{16}H_{15}FO_4$ 290.09489; found 290.09473.

Methyl 6-Fluoro-3-hydroxy-2′-methoxy-4,5-dimethylbiphenyl-2-carboxylate (5n): Starting with bis(silyl enol ether) **4f** (0.898 g, 3.3 mmol), $TiCl_4$ (0.620 g, 3.3 mmol) in CH_2Cl_2 (6 mL) and silyl enol ether **3d** (0.847 g, 3.0 mmol), **5n** was isolated (0.494 g, 54%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 98–100 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.17 (br. s, 6 H, CH_3), 3.36 (s, 3 H, $OCH_{3,Ar}$), 3.64 (s, 3 H, $COOCH_3$), 6.84 (dd, ^3J = 8.1 Hz, ^4J = 0.9 Hz, 1 H, CH_{Ar}), 6.91 (dd, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1 H, CH_{Ar}), 7.01–7.04 (m, 1 H, CH_{Ar}), 7.23 (ddd, ^3J = 8.1 Hz, ^3J = 8.1 Hz, ^4J = 1.8 Hz, 1 H, CH_{Ar}), 10.91 (s, 1 H, OH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.7 (d, ^4J = 2.3 Hz, CH_3), 11.1 (d, ^3J = 5.8 Hz, $\mathit{C}CH_{3,Ar}$), 50.6 ($O\mathit{C}H_{3,Ar}$), 54.6 ($COO\mathit{C}H_3$), 108.6 (d, ^3J = 2.9 Hz, $\mathit{C}COOCH_{3,Ar}$), 109.1, 119.0 (CH_{Ar}), 121.6 (d, ^2J = 20.4 Hz, $\mathit{C}CF_{Ar}$), 124.0 ($\mathit{C}OCH_{3,Ar}$), 125.0 (d, ^3J = 3.4 Hz, C_{Ar}), 124.0 (CH_{Ar}), 129.4 (d, ^4J = 1.7 Hz, CH_{Ar}), 130.4 (d, ^2J = 19.8 Hz, $FC\mathit{C}CH_{3,Ar}$), 150.2 (d, ^1J = 232.2 Hz, CF_{Ar}), 154.5 (d, ^3J = 1.7 Hz, $\mathit{C}CH_{3Ar}$), 155.5 (COH_{Ar}), 170.3 (d, ^4J = 3.3 Hz, $\mathit{C}OOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.8 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3016 (w), 2960 (m), 2841 (w), 1660 (s), 1621 (m), 1499 (m), 1437 (s), 1340 (s), 1248 (s), 1228 (s), 1095 (s), 903 (m), 805 (s), 749 (s), 639 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 304 (39) [M^+], 272 (71), 257 (100), 241 (60), 229 (22), 213 (9), 199 (10), 183 (14), 165 (12), 149 (40), 112 (16), 97 (21), 83 (30), 69 (65), 57 (64). HRMS (EI): calcd. for $C_{17}H_{17}FO_4$ 304.11054; found 304.10978. $C_{17}H_{17}FO_4$ (304.32): calcd. C 67.09, H 5.63; found C 67.22, H 5.62.

Ethyl 4-Ethyl-6-fluoro-3-hydroxy-2′-methoxy-5-methylbiphenyl-2-carboxylate (5o): Starting with bis(silyl enol ether) **4f** (0.357 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3d** (0.424 g, 1.5 mmol), **5o** was isolated (0.220 g, 33%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 81–83 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.64 (t, ^3J = 7.2 Hz, 3 H, $CH_2C\mathit{H_3}$), 1.09 (t, ^3J = 7.4 Hz, 3 H, $OCH_2C\mathit{H_3}$), 2.19 (br. s, 3 H, CH_3), 2.68 (q, ^3J = 7.4 Hz, 2 H, $\mathit{C}H_2CH_3$), 3.64 (s, 3 H, $OC\mathit{H_{3,Ar}}$), 3.86 (q, ^3J = 7.2 Hz, 2 H, $COOC\mathit{H}_2CH_3$), 6.82 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}), 6.86–6.91 (m, 1 H, CH_{Ar}), 6.99 (d, ^3J = 7.4 Hz, 1 H, CH_{Ar}), 7.23 (ddd, ^3J = 8.1 Hz, ^3J = 7.4 Hz, ^4J = 1.7 Hz, 1 H, CH_{Ar}), 10.99 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.4 ($CH_2\mathit{C}H_3$), 11.9 ($COOCH_2\mathit{C}H_3$), 12.0 (d, ^3J = 11.2 Hz, CH_3), 18.6 (d, ^4J = 1.6 Hz, $\mathit{C}H_2CH_3$), 54.5 ($O\mathit{C}H_{3,Ar}$), 59.7 ($COO\mathit{C}H_2CH_3$), 109.0 (d, ^3J = 2.9 Hz, $\mathit{C}COOCH_2CH_{3,Ar}$), 109.3, 119.1 ($CH_{Ar}$), 121.5 (d, ^2J = 20.4 Hz, $\mathit{C}CF_{Ar}$), 124.0 ($\mathit{C_{Ar}}OCH_3$), 127.5 (CH_{Ar}), 129.4 (d, ^4J = 1.7 Hz, CH_{Ar}), 129.6 (d, ^2J = 19.2 Hz, $\mathit{C_{Ar}}CH_3$), 130.9 (d, ^3J = 3.5 Hz, C_{Ar}), 150.4 (d, ^1J = 232.1 Hz, CF_{Ar}), 154.5 (d, ^3J = 1.7 Hz, $\mathit{C_{Ar}}CH_2CH_3$), 155.7 (COH_{Ar}), 169.9 (d, ^4J = 3.4 Hz, $\mathit{C}OOCH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.5 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (w, br.), 3058 (w), 2970 (m), 2933 (m), 2873 (m), 1653 (s), 1615 (m), 1499 (m), 1466 (m), 1398 (s), 1326 (s), 1276 (s), 1243 (s), 1225 (s), 1080 (m), 1029 (m), 752 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 332 (44) [M^+], 286 (86), 271 (75), 255 (100), 228 (8), 213 (9), 199 (17), 183 (16), 152 (9), 133 (6), 69 (12). HRMS (EI): calcd. for $C_{19}H_{21}FO_4$ 332.14184; found 332.14174. $C_{19}H_{21}FO_3$ (316.37): calcd. C 68.66, H 6.36; found C 68.83, H 6.81.

Methyl 6-Fluoro-3-hydroxy-2′-methoxy-5-propylbiphenyl-2-carboxylate (5p): Starting with bis(silyl enol ether) **4a** (0.568 g, 2.2 mmol), $TiCl_4$ (0.414 g, 2.2 mmol) in CH_2Cl_2 (4 mL) and silyl enol ether **3e** (0.621 g, 2.0 mmol), **5p** was isolated (0.229 g, 35%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 67–70 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2C\mathit{H_3}$), 1.53 (m, 2 H, $CH_2C\mathit{H}_2CH_3$), 2.48 (br. t, ^3J = 7.2 Hz, 2 H, $\mathit{C}H_2CH_2CH_3$), 3.31 (s, 3 H, $OC\mathit{H_{3,Ar}}$), 3.58 (s, 3 H, $COOC\mathit{H_3}$), 6.71 (d, $^4J_{H,F}$ = 6.4 Hz, 1 H, CH_{Ar}), 6.79 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1 H, CH_{Ar}), 6.85 (ddd, ^3J = 7.4, 7.4 Hz, ^4J = 0.9 Hz, 1 H, CH_{Ar}), 6.97 (m, 1 H, CH_{Ar}), 7.18 (ddd, ^3J = 8.1, 8.1 Hz, ^4J = 1.7 Hz, 1 H, CH_{Ar}), 10.50 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 ($CH_2CH_2\mathit{C}H_3$), 21.6 (d, ^4J = 1.1 Hz, $CH_2\mathit{C}H_2CH_3$), 30.5 (d, ^3J =

2.2 Hz, $CH_2CH_2CH_3$), 50.6 (OCH_3), 54.5 ($COOCH_3$), 109.3 (CH_{Ar}), 109.8 (d, ^3J = 2.3 Hz, $CCO_2CH_2CH_3$), 116.9 (d, ^3J = 2.9 Hz, CH_{Ar}), 119.1 (CH_{Ar}), 123.7 ($COCH_3$), 124.9 (d, ^2J = 19.8 Hz, CCF_{Ar}), 127.8 (CH_{Ar}), 129.3 (d, ^4J = 1.7 Hz, CH_{Ar}), 136.5 (d, ^2J = 19.8 Hz, $CCH_2CH_2CH_3$), 150.4 (d, ^1J = 233.8 Hz, CF_{Ar}), 155.5 (COH_{Ar}), 156.3 (d, ^3J = 2.9 Hz, C_{Ar}), 169.8 (d, ^4J = 2.9 Hz, CO_2CH_3) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –128.2 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3067 (w), 2959 (s), 2873 (m), 1669 (s), 1622 (m), 1583 (w), 1499 (m), 1435 (s), 1332 (s), 1239 (s), 1110 (m), 1028 (m), 847 (m), 752 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 318 (36) [M$^+$], 286 (100), 258 (29), 243 (4), 229 (5), 215 (9), 186 (4), 159 (5), 133 (3). HRMS (EI): calcd. for $C_{18}H_{19}FO_4$ 318.12619; found 318.12680.

Methyl 6-Fluoro-3-hydroxy-2′-methoxy-4-methyl-5-propylbiphenyl-2-carboxylate (5q): Starting with bis(silyl enol ether) **4f** (0.598 g, 2.2 mmol), $TiCl_4$ (0.414 g, 2.2 mmol) in CH_2Cl_2 (4 mL) and silyl enol ether **3e** (0.621 g, 2.0 mmol), **5q** was isolated (0.228 g, 34%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 62–64 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.44 (m, 2 H, $CH_2CH_2CH_3$), 2.13 (s, 3 H, CH_3), 2.54 (br. t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_3$), 3.30 (s, 3 H, OCH_3), 3.58 (s, 3 H, $COOCH_3$), 6.78 (d, ^4J = 7.6 Hz, 1 H, CH_{Ar}), 6.84 (ddd, ^3J = 7.4, 7.4 Hz, ^4J = 0.9 Hz, 1 H, CH_{Ar}), 6.98 (m, 1 H, CH_{Ar}), 7.17 (ddd, ^3J = 8.1, 8.1 Hz, ^4J = 1.7 Hz, 1 H, CH_{Ar}), 10.85 (s, 1 H, OH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (d, ^4J = 2.3 Hz, CH_3), 15.9 ($CH_2CH_2CH_3$), 24.5 ($CH_2CH_2CH_3$), 30.5 (d, ^3J = 3.6 Hz, $CH_2CH_2CH_3$), 53.5 ($OCH_{3,Ar}$), 57.5 ($COOCH_3$), 111.8 (d, ^3J = 2.9 Hz, $CCOOCH_3$), 112.2, 122.0 (CH_{Ar}), 124.6 (d, ^2J = 21.0 Hz, CCF_{Ar}), 127.0 ($COCH_3$), 127.6 (d, ^3J = 4.0 Hz, C_{Ar}), 130.6 (CH_{Ar}), 132.4 (d, ^4J = 1.7 Hz, CH_{Ar}), 137.8 (d, ^2J = 19.2 Hz, $CCH_2CH_2CH_{3,Ar}$), 153.3 (d, ^1J = 232.1 Hz, CF_{Ar}), 157.6 (COH_{Ar}), 158.1 (d, ^3J = 2.3 Hz, $CCH_{3,Ar}$), 173.3 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.1 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3421 (m, br.), 3009 (w), 2956 (m), 1659 (s), 1616 (m), 1500 (w), 1411 (s), 1338 (s), 1266 (s), 1220 (s), 1137 (m), 1025 (m), 750 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 332 (47) [M$^+$], 300 (100), 285 (27), 269 (13), 257 (38), 241 (17), 199 (10), 133 (3). HRMS (EI): calcd. for $C_{19}H_{21}FO_4$ 332.14184; found 332.14206.

Ethyl 4-Ethyl-6-fluoro-3-hydroxy-2′-methoxy-5-propylbiphenyl-2-carboxylate (5r): Starting with bis(silyl enol ether) **4f** (0.499 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3e** (0.467 g, 1.5 mmol), **5r** was isolated (0.286 g, 55%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.59 (t, ^3J = 7.0 Hz, 3 H, $CH_2CH_2CH_3$), 0.86 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.07 (t, ^3J = 7.4 Hz, 3 H, OCH_2CH_3), 1.46 (m, 2 H, $CH_2CH_2CH_3$), 2.53 (q, ^3J = 7.8 Hz, 2 H, CH_2CH_3), 2.62 (br. s, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_3$), 3.58 (s, 3 H, $OCH_{3,Ar}$), 3.80 (q, ^3J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 6.77 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1 H, CH_{Ar}), 6.83 (ddd, ^3J = 7.4, 7.4 Hz, ^4J = 1.1 Hz, 1 H, CH_{Ar}), 6.96 (dd, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1 H, CH_{Ar}), 7.17 (ddd, ^3J = 8.1, 8.1 Hz, ^4J = 1.7 Hz, 1 H, CH_{Ar}), 10.91 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8 (CH_2CH_3), 15.8 ($CH_2CH_2CH_3$), 16.0 ($COOCH_2CH_3$), 21.5 (d, ^4J = 1.6 Hz, CH_2CH_3), 25.4 (d, ^4J = 1.1 Hz, $CH_2CH_2CH_3$), 30.2 (d, ^3J = 3.3 Hz, $CH_2CH_2CH_3$), 57.7 ($OCH_{3,Ar}$), 62.6 ($COOCH_2CH_3$), 112.1 (d, ^3J = 2.9 Hz, $CCOOCH_2CH_{3Ar}$), 112.3, 120.0 (CH_{An}), 124.8 (d, ^2J = 20.9 Hz, CCF_{Ar}), 127.4 ($C_{Ar}OCH_3$), 130.4 (CH_{Ar}), 132.4 (d, ^4J = 1.7 Hz, CH_{Ar}), 133.4 (d, ^3J = 3.5 Hz, C_{Ar}), 137.1 (d, ^3J = 18.6 Hz, $C_{Ar}CH_2CH_2CH_3$), 153.4 (d, ^1J = 232.7 Hz, CF_{Ar}), 157.7 (d, ^3J = 1.7 Hz, CCH_2CH_{3Ar}), 158.6 (COH_{Ar}), 172.8 (d, ^4J = 2.5 Hz, $COOCH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.8 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 2958 (s), 2870 (m), 1655 (s), 1616 (m), 1503 (m), 1468 (m), 1415 (m), 1399 (m), 1246 (s), 1233 (s), 1097 (m), 750 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 360 (56) [M$^+$], 314 (100), 299 (50), 283 (67), 271 (31), 199 (8). HRMS (EI): calcd. for $C_{21}H_{25}FO_4$ 360.17314; found 360.17255.

Methyl 6-Fluoro-3-hydroxy-2′,5-dimethylbiphenyl-2-carboxylate (5s): Starting with bis(silyl enol ether) **4a** (0.426 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3f** (0.360 g, 1.5 mmol), **5s** was isolated (0.180 g, 44%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (br. s, 3 H, $CH_{3,Tol}$), 2.30 (br. s, 3 H, CH_3), 3.41 (s, 3 H, $COOCH_3$), 6.84 (d, $^4J_{H,F}$ = 6.4 Hz, 1 H, CH_{Ar}), 6.97 (d, ^3J = 7.4 Hz, 1 H, CH_{Tol}), 7.21 (m, 1 H, CH_{Tol}), 7.22–7.24 (m, 2 H, CH_{Tol}), 10.79 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8 (d, ^3J = 3.6 Hz, $CH_{3,Tol}$), 20.1 (CH_3), 50.3 ($COOCH_3$), 110.3 (d, ^3J = 2.7 Hz, $C_{Ar}CO_2CH_3$), 118.9 (d, ^3J = 4.3 Hz, CH_{Ar}), 125.5, 127.8, 128.9 (CH_{Tol}), 129.4 ($CCH_{3,Tol}$), 129.6 (d, ^4J = 3.5 Hz, CH_{Tol}), 133.9 (d, ^2J = 21.5 Hz, CCF_{Ar}), 136.0 (d, ^2J = 13.9 Hz, $C_{Ar}CH_3$), 139.6 (C_{Tol}), 151.8 (d, ^1J = 232.7 Hz, CF_{Ar}), 158.2 (d, ^4J = 2.3 Hz, COH_{Ar}), 171.1 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.8 (CF_{Ar}) ppm. IR (neat): $\tilde{\nu}$ = 2925 (m), 2875 (w), 1669 (s), 1624 (w), 1437 (m), 1334 (m), 1240 (s), 1221 (s), 1077 (m), 846 (m), 755 (m), 644 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 274 (29) [M$^+$], 242 (100), 214 (10), 199 (11), 183 (6), 171 (16), 136 (3). HRMS (EI): calcd. for $C_{16}H_{15}FO_3$ 274.09997; found 274.10009.

Ethyl 4-Ethyl-6-fluoro-3-hydroxy-2′,5-dimethylbiphenyl-2-carboxylate (5t): Starting with bis(silyl enol ether) **4g** (0.495 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3f** (0.360 g, 1.5 mmol), **5s** was isolated (0.185 g, 40%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.72 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.23 (t, ^3J = 7.4 Hz, 3 H, $COOCH_2CH_3$), 2.12 (s, 3 H, $CH_{3,Tol}$), 2.32 (br. s, 3 H, $CH_{3,Ar}$), 2.82 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 3.95 (q, ^3J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 7.03 (d, ^3J = 7.4 Hz, 1 H, CH_{Tol}), 7.17–7.23 (m, 1 H, CH_{Tol}), 7.26–7.28 (m, 2 H, CH_{Tol}), 11.29 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8 (d, ^3J = 6.1 Hz, $CH_{3,Tol}$), 13.2 (CH_2CH_3), 13.5 ($COOCH_2CH_3$), 20.0 (d, ^4J = 2.2 Hz, CH_2CH_3), 20.2 ($CH_{3,Tol}$), 61.3 ($COOCH_2CH_3$), 109.7 (d, ^3J = 2.9 Hz, $C_{Ar}COOCH_2CH_3$), 125.5 (CH_{Tol}), 126.3 ($CCH_{3,Tol}$), 126.6 (C_{Tol}), 127.6 (CH_{Tol}), 129.1 (d, ^4J = 1.1 Hz, CH_{Tol}), 129.5 (CH_{Tol}), 131.3 (d, ^2J = 19.8 Hz, CCF_{Ar}), 132.3 (d, ^3J = 3.5 Hz, $C_{Ar}CH_2CH_3$), 136.5 (d, ^2J = 19.5 Hz, $C_{Ar}CH_3$), 151.6 (d, ^1J = 231.0 Hz, CF_{Ar}), 156.5 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.1 (d, ^4J = 3.2 Hz, $COOCH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.5 (CF_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2926 (s), 2855 (w), 1661 (s), 1616 (w), 1456 (m), 1374 (m), 1328 (m), 1272 (m), 1226 (s), 1214 (s), 1170 (w), 1038 (w), 759 (m), 734 (m), 450 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 316 (39) [M$^+$], 270 (43), 255 (100), 237 (11), 213 (4), 183 (12), 165 (6). HRMS (EI): calcd. for $C_{19}H_{21}FO_3$ 316.14692; found 316.14730.

Methyl 2′-Chloro-6-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5u): Starting with bis(silyl enol ether) **4a** (0.426 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3g** (0.429 g, 1.5 mmol), **5u** was isolated (0.118 g, 26%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a reddish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (br. s, 3 H, CH_3), 3.38 (s, 3 H, $COOCH_3$), 6.81 (d, $^4J_{H,F}$ = 6.6 Hz, 1 H, CH_{Ar}), 7.06–7.08 (m, 1 H, CH_{ClPh}), 7.19–7.22 (m, 2 H, CH_{ClPh}), 7.34–7.37 (m, 1 H, CH_{ClPh}), 10.82 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (d, ^3J = 3.9 Hz, CH_3), 51.0 ($COOCH_3$), 108.7 (d,

^3J = 1.7 Hz, $C_{Ar}COOCH_3$), 118.7 (d, ^3J = 3.4 Hz, CH_{Ar}), 125.2 (d, ^2J = 19.8 Hz, CCF_{Ar}), 127.7 ($3CH_{Ph}$), 129.4 (d, ^4J = 1.1 Hz, CH_{Ph}), 132.1 (d, ^3J = 1.1 Hz, C_{Ph}), 132.7 (d, ^2J = 21.0 Hz, $C_{Ar}CH_3$), 133.9 (CCl_{ClPh}), 150.4 (d, ^1J = 234.4 Hz, CF_{Ar}), 156.9 (d, ^4J = 2.3 Hz, COH_{Ar}), 169.3 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.4 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1674 (s), 1632 (w), 1376 (s), 1331 (s), 1215 (s), 1074 (m), 858 (m), 760 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 296 (^{37}Cl, 3) [M$^+$], 294 (^{35}Cl, 9) [M$^+$], 259 (100), 234 (15), 199 (21), 170 (24), 151 (4), 129 (4), 85 (9), 75 (4). HRMS (EI): calcd. for $C_{15}H_{12}ClFO_3$ ([M]$^+$, ^{35}Cl) 294.04535; found 294.04604.

Methyl 2′-Chloro-6-fluoro-3-hydroxy-4,5-dimethylbiphenyl-2-carboxylate (5v): Starting with bis(silyl enol ether) **4f** (0.448 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3g** (0.429 g, 1.5 mmol), **5v** was isolated (0.177 g, 38%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 76–78 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.19 (br. s, 6 H, CH_3), 3.38 (s, 3 H, $COOCH_3$), 7.06–7.09 (m, 2 H, CH_{ClPh}), 7.18–7.21 (m, 2 H, CH_{ClPh}), 11.19 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3 (d, ^4J = 2.9 Hz, CH_3), 12.6 (d, ^3J = 5.2 Hz, CH_3), 52.4 ($COOCH_3$), 109.0 (d, ^3J = 2.6 Hz, $C_{Ar}COOCH_3$), 123.8 (d, ^2J = 21.0 Hz, CCF_{Ar}), 126.5 (d, ^4J = 1.1 Hz, CH_{ClPh}), 127.5 (d, ^3J = 3.5 Hz, $C_{Ar}CH_3$), 128.9, 129.1, 131.0 (CH_{ClPh}), 132.3 (d, ^2J = 19.8 Hz, $C_{Ar}CH_3$), 133.7 (d, ^3J = 1.1 Hz, C_{ClPh}), 135.7 (CCl_{ClPh}), 151.5 (d, ^1J = 232.1 Hz, CF_{Ar}), 156.7 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.4 (d, ^4J = 3.4 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.4 (CF) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 310 (^{37}Cl, 5) [M$^+$], 308 (^{35}Cl, 15) [M$^+$], 273 (38), 241 (100), 213 (7), 183 (15), 170 (9), 136 (5), 82 (3). HRMS (EI): calcd. for $C_{16}H_{16}ClFO_3$ ([M]$^+$, ^{35}Cl) 308.06100; found 308.06159.

Ethyl 2′-Chloro-4-ethyl-6-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5w): Starting with bis(silyl enol ether) **4g** (0.494 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3g** (0.405 g, 1.5 mmol), **5w** was isolated (0.192 g, 38%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a reddish viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.49 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 0.93 (t, ^3J = 7.6 Hz, 3 H, $COOCH_2CH_3$), 2.20 (br. s, 3 H, CH_3), 2.52 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 3.72 (q, ^3J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 6.90–6.93 (m, 1 H, CH_{ClPh}), 6.99–7.06 (m, 2 H, CH_{ClPh}), 7.16–7.19 (m, 1 H, CH_{ClPh}), 11.12 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8 (d, ^3J = 5.8 Hz, CCH_3), 13.2 (CH_2CH_3), 13.4 ($COOCH_2CH_3$), 20.1 (d, ^4J = 2.3 Hz, CH_2CH_3), 61.4 ($COOCH_2CH_{3,Ar}$), 109.4 (d, ^3J = 2.3 Hz, $C_{Ar}COOCH_2CH_3$), 123.9 (d, ^2J = 21.0 Hz, CCF_{Ar}), 126.4, 128.8, 129.1 (CH_{ClPh}), 131.0 (d, ^4J = 1.7 Hz, CH_{ClPh}), 131.6 (d, ^2J = 19.2 Hz, $C_{Ar}CH_3$), 133.3 (d, ^3J = 2.9 Hz, $C_{Ar}CH_2CH_3$), 133.9 (d, ^3J = 1.1 Hz, C_{ClPh}), 136.1 (CCl_{ClPh}), 151.6 (d, ^1J = 232.7 Hz, CF_{Ar}), 156.6 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.0 (d, ^4J = 2.9 Hz, $COOCH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.1 (CF) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 338 (^{37}Cl, 4) [M$^+$], 336 (^{35}Cl, 14) [M$^+$], 301 (27), 292 (^{37}Cl, 5), 290 (^{35}Cl, 16), 275 (^{37}Cl, 4), 273 (^{35}Cl, 11), 255 (100), 247 (4), 207 (4), 183 (15), 170 (4). HRMS (EI): calcd. for $C_{18}H_{18}ClFO_3$ ([M]$^+$, ^{35}Cl) 336.09230; found 336.09156.

Methyl 4′-Chloro-6-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5x): Starting with bis(silyl enol ether) **4a** (0.568 g, 2.2 mmol), $TiCl_4$ (0.414 g, 2.2 mmol) in CH_2Cl_2 (4 mL) and silyl enol ether **3h** (0.574 g, 2.0 mmol), **5x** was isolated (0.171 g, 30%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (br. s, 3 H, CH_3), 3.39 (s, 3 H, $COOCH_3$), 6.78 (d, $^4J_{H,F}$ = 6.4 Hz, 1 H, CH_{Ar}), 7.03–7.06 (m, 2 H, CH_{ClPh}), 7.27–7.30 (m, 2 H, CH_{ClPh}), 11.59 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (d, ^3J = 3.7 Hz, CH_3), 50.8 ($COOCH_3$), 108.8 (d, ^3J = 1.7 Hz, $C_{Ar}COOCH_3$), 118.3 (d, ^3J = 3.5 Hz, CH_{Ar}), 126.8 (d, ^4J = 1.1 Hz, $2CH_{ClPh}$), 127.3 (d, ^2J = 19.2 Hz, CCF_{Ar}), 129.2 ($2CH_{ClPh}$), 132.3 (d, ^2J = 14.5 Hz, $C_{Ar}CH_3$), 132.6 (C_{ClPh}), 133.1 (CCl_{ClPh}), 150.5 (d, ^1J = 234.3 Hz, CF_{Ar}), 156.6 (d, ^4J = 1.8 Hz, COH_{Ar}), 169.5 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.4 (CF) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 296 (^{37}Cl, 11) [M$^+$], 294 (^{35}Cl, 31) [M$^+$], 264 (^{37}Cl, 32), 262 (^{35}Cl, 100), 236 (^{37}Cl, 8), 234 (^{35}Cl, 24), 199 (11), 170 (24), 151 (3), 85 (9). HRMS (EI): calcd. for $C_{15}H_{12}ClFO_3$ ([M]$^+$, ^{35}Cl) 294.04535; found 294.04581.

Methyl 4′-Chloro-6-fluoro-3-hydroxy-4,5-dimethylbiphenyl-2-carboxylate (5y): Starting with bis(silyl enol ether) **4f** (0.598 g, 2.2 mmol), $TiCl_4$ (0.414 g, 2.2 mmol) in CH_2Cl_2 (4 mL) and silyl enol ether **3h** (0.574 g, 2.0 mmol), **5y** was isolated (0.198 g, 32%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a yellowish solid (m.p. 87–92 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (br. s, 6 H, CH_3), 3.35 (s, 3 H, $COOCH_3$), 6.99–7.02 (m, 2 H, CH_{ClPh}), 7.22–7.25 (m, 2 H, CH_{ClPh}), 10.89 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2 (d, ^4J = 2.9 Hz, CH_3), 12.5 (d, ^3J = 5.8 Hz, $C_{Ar}CH_3$), 52.2 ($COOCH_3$), 109.2 (d, ^3J = 2.9 Hz, $C_{Ar}COOCH_3$), 125.4 (d, ^2J = 19.8 Hz, CCF_{Ar}), 127.0 (d, ^3J = 3.4 Hz, $C_{Ar}CH_3$), 128.2 ($2CH_{ClPh}$), 130.8 ($2CH_{ClPh}$), 132.1 (d, ^2J = 19.8 Hz, $C_{Ar}CH_3$), 133.3 (C_{ClPh}), 135.0 (CCl_{ClPh}), 151.6 (d, ^1J = 232.7 Hz, CF_{Ar}), 156.3 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.5 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.4 (CF) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 310 (^{37}Cl, 10) [M$^+$], 308 (^{35}Cl, 30) [M$^+$], 278 (^{37}Cl, 19), 276 (^{35}Cl, 54), 261 (7), 241 (100), 233 (6), 213 (8), 183 (15), 170 (12), 136 (5). HRMS (EI): calcd. for $C_{16}H_{14}ClFO_3$ ([M]$^+$, ^{35}Cl) 308.06100; found 308.06178.

Ethyl 4′-Chloro-4-ethyl-6-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5z): Starting with bis(silyl enol ether) **4g** (0.660 g, 2.2 mmol), $TiCl_4$ (0.414 g, 2.2 mmol) in CH_2Cl_2 (4 mL) and silyl enol ether **3h** (0.574 g, 2.0 mmol), **5z** was isolated (0.297 g, 44%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a yellowish solid (m.p. 73–75 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.69 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 1.09 (t, ^3J = 7.4 Hz, 3 H, $COOCH_2CH_3$), 2.20 (br. s, 3 H, CH_3), 2.69 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 3.89 (q, ^3J = 7.2 Hz, 2 H, $COOCH_2CH_3$), 7.03–7.07 (m, 2 H, CH_{ClPh}), 7.25–7.30 (m, 2 H, CH_{ClPh}), 11.01 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.7 (CH_2CH_3), 13.3 (d, ^3J = 9.0 Hz, CH_3), 14.3 ($COOCH_2CH_3$), 20.0 (d, ^3J = 2.3 Hz, CH_2CH_3), 61.5 ($COOCH_2CH_3$), 109.6 (d, ^3J = 2.4 Hz, $C_{Ar}COOCH_2CH_3$), 125.7 (d, ^2J = 20.4 Hz, CCF_{Ar}), 128.1 ($2CH_{ClPh}$), 130.0 ($2CH_{ClPh}$), 131.3 (d, ^2J = 19.2 Hz, $C_{Ar}CH_3$), 133.0 (d, ^3J = 2.9 Hz, $C_{Ar}CH_2CH_3$), 133.3 (C_{ClPh}), 135.3 (CCl_{ClPh}), 151.7 (d, ^1J = 232.7 Hz, CF_{Ar}), 156.3 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.1 (d, ^4J = 2.9 Hz, $COOCH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.0 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 2973 (m), 2875 (w), 1660 (s), 1616 (w), 1797 (m), 1395 (s), 1375 (s), 1331 (s), 1226 (s), 1106 (m), 1086 (s), 1017 (m), 823 (s), 810 (m), 514 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 338 (^{37}Cl, 10) [M$^+$], 336 (^{35}Cl, 29) [M$^+$], 292 (^{37}Cl 14), 290 (^{35}Cl. 40) , 275 (12), 255 (100), 237 (8), 212 (3), 183 (17), 170 (4). HRMS (EI): calcd. for $C_{18}H_{18}ClFO_3$ ([M]$^+$,^{35}Cl) 336.09230; found 336.09218.

Methyl 4′,6-Difluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5aa): Starting with bis(silyl enol ether) **4a** (0.426 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3i** (0.405 g, 1.5 mmol), **5aa** was isolated (0.135 g, 32%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a

colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (br. s, 3 H, CH_3), 3.38 (s, 3 H, COOCH_3), 6.77 (d, $^4J_{H,F}$ = 6.4 Hz, 1 H, CH_{Ar}), 6.96–7.01 (m, 2 H, CH_{FPh}), 7.04–7.09 (m, 2 H, CH_{FPh}), 10.57 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (d, ^3J = 3.9 Hz, CH_3), 50.8 (COOCH_3), 109.0 (d, ^3J = 1.7 Hz, C_{Ar}-$COOCH_3$), 113.6 (d, ^2J = 21.9 Hz, 2CH_{FPh}), 118.1 (d, ^3J = 4.4 Hz, CH_{Ar}), 127.5 (d, ^2J = 19.2 Hz, CCF_{Ar}), 129.4 (d, ^4J = 1.7 Hz, CH_{FPh}), 129.6 (d, ^4J = 1.1 Hz, CH_{FPh}), 130.5 (d, ^3J = 3.4 Hz, C_{FPh}), 132.4 (d, ^2J = 21.5 Hz, $C_{Ar}CH_3$), 150.7 (d, ^1J = 233.8 Hz, CF_{Ar}), 156.6 (d, ^4J = 1.7 Hz, COH_{Ar}), 161.1 (d, ^1J = 244.3 Hz, CF_{FPh}), 169.6 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.5 (CF_{Ar}), –115.5 (CF_{FPh}) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 278 (32) [M$^+$], 246 (100), 218 (41), 201 (3), 189 (16), 170 (8), 151 (3), 133 (2), 85 (4). HRMS (EI): calcd. for $C_{15}H_{12}F_2O_3$ 278.07490; found 278.07532.

Methyl 4′,6-Difluoro-3-hydroxy-4,5-dimethylbiphenyl-2-carboxylate (5ab): Starting with bis(silyl enol ether) **4f** (0.448 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3i** (0.405 g, 1.5 mmol), **5ab** was isolated (0.177 g, 40%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (br. s, 6 H, CH_3), 3.32 (s, 3 H, COOCH_3), 6.92–6.96 (m, 2 H, CH_{FPh}), 6.99–7.03 (m, 2 H, CH_{FPh}), 10.86 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.2 (d, ^4J = 2.3 Hz, CH_3), 12.5 (d, ^3J = 5.7 Hz, CCH_3), 52.1 (COOCH_3), 109.5 (d, ^3J = 2.5 Hz, C_{Ar}-$COOCH_3$), 114.9 (d, ^2J = 21.4 Hz, 2CH_{FPh}), 125.7 (d, ^2J = 20.4 Hz, CCF_{Ar}), 126.9 (d, ^3J = 3.6 Hz, C_{FPh}), 131.0 (d, ^4J = 1.8 Hz, CH_{FPh}), 131.1 (d, ^4J = 1.2 Hz, CH_{FPh}), 132.0 (d, ^2J = 19.5 Hz, $C_{Ar}CH_3$), 132.4 (d, ^3J = 3.5 Hz, $C_{Ar}CH_3$), 151.8 (d, ^1J = 231.9 Hz, CF_{Ar}), 155.8 (d, ^4J = 1.8 Hz, COH_{Ar}), 162.5 (d, ^1J = 244.1 Hz, CF_{FPh}), 171.6 (d, ^4J = 3.1 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.5 (CF_{Ar}), –115.5 (CF_{FPh}) ppm. IR (KBr): $\tilde{\nu}$ = 2926 (m), 2875 (w), 1665 (s), 1616 (w), 1515 (s), 1440 (s), 1334 (s), 1259 (m), 1219 (s), 1174 (m), 1096 (m), 1015 (m), 833 (m), 805 (m), 586 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 292 (64) [M$^+$], 260 (100), 245 (81), 231 (9), 217 (43), 183 (17), 170 (5), 151 (3). HRMS (EI): calcd. for $C_{16}H_{14}F_2O_3$ 292.09055; found 292.09034.

Ethyl 4-Ethyl-4′,6-difluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (5ac): Starting with bis(silyl enol ether) **4g** (0.495 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3i** (0.405 g, 1.5 mmol), **5ac** was isolated (0.170 g, 35%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.69 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.09 (t, ^3J = 7.4 Hz, 3 H, $COOCH_2CH_3$), 2.19 (br. s, 3 H, CH_3), 2.69 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 3.88 (q, ^3J = 7.0 Hz, 2 H, $COOCH_2CH_3$), 6.95–7.02 (m, 2 H, CH_{FPh}), 7.04–7.11 (m, 2 H, CH_{FPh}), 11.00 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8 (d, ^3J = 2.3 Hz, CH_3), 13.4 (CH_2CH_3), 13.5 ($COOCH_2CH_3$), 20.0 (d, ^4J = 2.3 Hz, CH_2CH_3), 61.4 ($COOCH_2CH_3$), 109.8 (d, ^3J = 1.7 Hz, $C_{Ar}COOCH_2CH_3$), 114.7, 115.7 (CH_{FPh}), 125.9 (d, ^2J = 20.4 Hz, CCF_{Ar}), 131.0 (d, ^2J = 1.1 Hz, CH_{FPh}), 131.1 (d, ^2J = 2.3 Hz, CH_{FPh}), 131.3 (d, ^2J = 20.4 Hz, CCF_{Ar}), 132.7 (d, ^3J = 3.5 Hz, C_{FPh}), 132.8 (d, ^3J = 2.9 Hz, CCH_2CH_{Ar}), 151.9 (d, ^1J = 232.7 Hz, CF_{Ar}), 156.2 (d, ^4J = 1.7 Hz, COH_{Ar}), 162.5 (d, ^1J = 243.7 Hz, CF_{FPh}), 171.2 (d, ^4J = 3.5 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.1 (CF_{Ar}), –115.9 (CF_{FPh}) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 320 (64) [M$^+$], 274 (88), 256 (100), 231 (34), 201 (24), 183 (23), 170 (6), 151 (4), 133 (3). HRMS (EI): calcd. for $C_{18}H_{18}F_2O_3$ 320.17071; found 320.12229.

Methyl 3-Fluoro-6-hydroxy-4-methyl-2-(1-naphthyl)benzoate (5ad): Starting with bis(silyl enol ether) **4a** (0.426 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3j** (0.454 g, 1.5 mmol), **5ad** was isolated (0.135 g, 31%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a reddish solid (m.p. 119–121 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (br. s, 3 H, CH_3), 3.01 (s, 3 H, COOCH_3), 6.88 (dd, ^3J = 6.6 Hz, ^4J = 0.7 Hz, 1 H, CH_{Naph}), 7.17 (dd, ^3J = 7.0 Hz, ^4J = 1.3 Hz, 1 H, CH_{Naph}), 7.29–7.32 (m, 1 H, CH_{Naph}), 7.35 (m, 1 H, CH_{Ar}), 7.37–7.39 (m, 1 H, CH_{Naph}), 7.41–7.44 (m, 1 H, CH_{Naph}), 7.76–7.81 (m, 2 H, CH_{Naph}), 10.82 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (d, ^3J = 3.5 Hz, CH_3), 50.6 (COOCH_3), 109.7 (d, ^3J = 2.3 Hz, $C_{Ar}COOCH_3$), 118.4 (d, ^3J = 3.5 Hz, CH_{Ar}), 123.9, 124.1, 124.5, 125.0, 125.1, 126.6 (CH_{Naph}), 126.7 (d, ^2J = 15.7 Hz, CCF_{Ar}), 127.1 (CH_{Naph}), 131.1, 132.1, 132.5 (C_{Naph}), 132.7 (d, ^2J = 12.2 Hz, $FCCCH_{3,Ar}$), 151.1 (d, ^1J = 233.8 Hz, CF_{Ar}), 156.9 (d, ^4J = 2.3 Hz, COH_{Ar}), 169.6 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.6 (CF_{Ar}) ppm. IR (Nujol): $\tilde{\nu}$ = 1665 (m), 1463 (s), 1376 (s), 1335 (m), 1225 (m), 1080 (w), 953 (w), 789 (m), 551 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 310 (38) [M$^+$], 278 (100), 249 (18), 233 (8), 220 (15), 155 (3), 110 (10). HRMS (EI): calcd. for $C_{19}H_{15}FO_3$ 310.09997; found 310.10006.

Methyl 3-Fluoro-6-hydroxy-4,5-dimethyl-2-(1-naphthyl)benzoate (5ae): Starting with bis(silyl enol ether) **4f** (0.448 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3j** (0.454 g, 1.5 mmol), **5ae** was isolated (0.180 g, 37%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a reddish solid (m.p. 88–91 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.12 (br. s, 3 H, CH_3), 2.17 (br. s, 3 H, CH_3), 2.92 (s, 3 H, COOCH_3), 7.10 (dd, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1 H, CH_{Naph}), 7.19–7.19 (m, 1 H, CH_{Naph}), 7.30–7.32 (m, 2 H, CH_{Naph}), 7.66–7.72 (m, 3 H, CH_{Naph}), 11.15 (s, 1 H, OH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1 (d, ^4J = 2.3 Hz, CH_3), 13.4 (d, ^3J = 5.8 Hz, CCH_3), 52.8 (COOCH_3), 111.0 (d, ^3J = 2.9 Hz, $CCOOCH_{3Ar}$), 125.7 (d, ^2J = 21.5 Hz, CCF_{Ar}), 126.2, 126.4, 126.7, 127.1 (CH_{Naph}), 127.5 (d, ^4J = 1.1 Hz, CH_{Naph}), 127.9 (d, ^3J = 3.4 Hz, $C_{Ar}CH_3$), 128.6, 129.3 (CH_{Naph}), 133.1 (d, ^2J = 19.8 Hz, $C_{Ar}CH_3$), 133.5, 134.4, 135.3 (CH_{Naph}), 152.9 (d, ^1J = 231.5 Hz, CF_{Ar}), 155.5 (d, ^4J = 1.7 Hz, COH_{Ar}), 172.4 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –124.0 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1664 (s), 1457 (s), 1377 (s), 1339 (s), 1260 (s), 1226 (s), 1098 (m), 924 (w), 779 (s), 432 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 324 (36) [M$^+$], 292 (100), 277 (18), 249 (10), 233 (8), 220 (17), 162 (4), 110 (8). HRMS (EI): calcd. for $C_{20}H_{17}FO_3$ 324.11562; found 324.11546.

Ethyl 3-Ethyl-5-fluoro-2-hydroxy-4-methyl-6-(1-naphthyl)benzoate (5af): Starting with bis(silyl enol ether) **4g** (0.495 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3j** (0.454 g, 1.5 mmol), **5af** was isolated (0.223 g, 42%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a reddish solid (m.p. 68–72 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.16 (t, ^3J = 7.5 Hz, 3 H, $COOCH_2CH_3$), 2.56 (br. s, 3 H, $CH_{3,Ar}$), 2.68 (q, ^3J = 7.6 Hz, 2 H, CH_2CH_3), 3.58 (q, ^3J = 7.3 Hz, 2 H, $COOCH_2CH_3$), 7.11 (m, 1 H, CH_{Naph}), 7.21–7.26 (m, 4 H, CH_{Naph}), 7.68–7.76 (m, 2 H, CH_{Naph}), 11.10 (s, 1 H, OH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.9 (d, ^3J = 5.6 Hz, $CH_{3,Ar}$), 12.6 ($CH_2CH_{3,Ar}$), 13.5 ($COOCH_2$-$CH_{3,Ar}$), 20.1 (d, ^4J = 1.6 Hz, $CH_2CH_{3,Ar}$), 61.1 ($COOCH_2CH_{3,Ar}$), 110.4 (d, ^3J = 2.3 Hz, $C_{Ar}COOCH_2CH_3$), 125.0 (d, ^2J = 21.5 Hz, CCF_{Ar}), 125.4 (d, ^4J = 1.1 Hz, CH_{Naph}), 125.8, 125.9, 126.2, 126.6, 127.7, 128.4 (CH_{Naph}), 131.5 (d, ^2J = 19.2 Hz, $C_{Ar}CH_3$), 132.9 (d, ^3J = 2.9 Hz, $C_{Ar}CH_2CH_3$), 133.1, 133.6 (C_{Naph}), 134.8 (d, ^4J = 1.1 Hz, CCH_{3Ar}), 152.3 (d, ^1J = 231.5 Hz, CF_{Ar}), 156.6 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.1 (d, ^4J = 3.5 Hz, $COOCH_{3,Ar}$) ppm. ^{19}F

NMR (235 MHz, $CDCl_3$): δ = –124.0 (CF) ppm. IR (Nujol): $\tilde{\nu}$ = 1663 (s), 1460 (s), 1357 (s), 1327 (m), 1206 (m), 1109 (w), 1041 (w), 790 (m), 641 (w) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 352 (36) [M^+], 306 (34), 291 (100), 273 (5), 220 (13), 162 (2), 110 (2). HRMS (EI): calcd. for $C_{22}H_{21}FO_3$ 352.14692; found 352.14689.

Methyl 3-Fluoro-6-hydroxy-2-(2-naphthyl)-4-propylbenzoate (5ag): Starting with bis(silyl enol ether) **4a** (0.424 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3k** (0.495 g, 1.5 mmol), **5ag** was isolated (0.143 g, 30%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.54–1.62 (m, 2 H, $CH_2CH_2CH_3$), 2.53 (t, ^3J = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 3.21 (s, 3 H, $COOCH_3$), 6.80 (d, $^4J_{H,F}$ = 6.3 Hz, 1 H, CH_{Ar}), 7.22 (dd, CH_{Naph}, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 1 H,), 7.37–7.40 (m, 2 H, CH_{Naph}), 7.58 (m, 1 H, CH_{Naph}), 7.71–7.77 (m, 3 H, CH_{Naph}), 10.58 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2 ($CH_2CH_2CH_3$), 23.1 (d, ^4J = 1.1 Hz, $CH_2CH_2CH_3$), 32.0 (d, ^3J = 1.7 Hz, $CH_2CH_2CH_3$), 52.1 ($COOCH_3$), 110.7 (d, ^3J = 1.7 Hz, $C_{Ar}COOCH_3$), 118.7 (d, ^4J = 2.8 Hz, CH_{Naph}), 125.6 (CH_{Naph}), 126.4 (d, ^3J = 5.2 Hz, CH_{Ar}), 127.3, 128.1, 128.4, 129.7 (CH_{Naph}), 129.9, 130.2 (C_{Naph}), 131.3 (CH_{Naph}), 132.9 (d, ^3J = 1.7 Hz, C_{Naph}), 133.5 (d, ^3J = 19.2 Hz, CCF_{Ar}), 138.2 (d, ^3J = 19.8 Hz, $C_{Ar}CH_2CH_2CH_3$), 152.0 (d, ^1J = 234.4 Hz, CF_{Ar}), 158.0 (d, ^4J = 2.0 Hz, COH_{Ar}), 171.2 (d, ^4J = 2.9 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –128.8 (CF) ppm. IR (neat): $\tilde{\nu}$ = 2960 (s), 2872 (w), 1668 (s), 1619 (w), 1437 (s), 1332 (s), 1234 (s), 1092 (m), 819 (m), 787 (m), 746 (m), 478 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 338 (50) [M^+], 306 (100), 278 (44), 249 (31), 220 (32), 207 (5), 169 (6), 125 (5), 110 (9). HRMS (EI): calcd. for $C_{21}H_{19}FO_3$ 338.13127; found 338.13136.

Methyl 3-Fluoro-6-hydroxy-5-methyl-2-(2-naphthyl)-4-propylbenzoate (5ah): Starting with bis(silyl enol ether) **4f** (0.448 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3k** (0.495 g, 1.5 mmol), **5ah** was isolated (0.180 g, 34%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless solid (m.p. 87–90 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, ^3J = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.39–1.52 (m, 2 H, $CH_2CH_2CH_3$), 2.16 (s, 3 H, CH_3), 2.55 (br. t, ^3J = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 3.16 (s, 3 H, $COOCH_3$), 7.18 (dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, 1 H, CH_{Naph}), 7.31–7.34 (m, 2 H, CH_{Naph}), 7.54 (m, 1 H, CH_{Naph}), 7.65–7.72 (m, 3 H, CH_{Naph}), 10.89 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.2 (d, ^4J = 2.3 Hz, CH_3), 12.6 ($CH_2CH_2CH_3$), 21.8 (d, ^4J = 1.1 Hz, $CH_2CH_2CH_3$), 27.8 (d, ^3J = 3.9 Hz, $CH_2CH_2CH_3$), 50.9 ($COOCH_3$), 107.9 (d, ^3J = 2.9 Hz, $C_{Ar}COOCH_3$), 124.4, 124.5 (CH_{Naph}), 124.7 (d, ^2J = 19.8 Hz, CCF_{Ar}), 125.1 ($C_{Ar}CH_3$), 125.4, 126.2, 126.3, 126.3, 126.5 (CH_{Naph}), 130.9, 131.6, 132.1 (C_{Naph}), 134.6 (d, ^2J = 19.2 Hz, $C_{Ar}CH_2CH_2CH_3$), 150.4 (d, ^1J = 232.7 Hz, CF_{Ar}), 154.7 (d, ^4J = 1.7 Hz, COH_{Ar}), 169.9 (d, ^4J = 3.5 Hz, $COOCH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.7 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 2959 (m), 2871 (w), 1664 (s), 1617 (w), 1440 (s), 1414 (s), 1331 (s), 1264 (s), 1224 (s), 1115 (w), 1017 (m), 895 (w), 819 (m), 744 (m), 475 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 352 (47) [M^+], 320 (100), 305 (37), 292 (15), 277 (20), 249 (4), 220 (17), 176 (7), 146 (6), 116 (5). HRMS (EI): calcd. for $C_{22}H_{21}FO_3$ 352.14692; found 352.14732.

Ethyl 3-Ethyl-5-fluoro-2-hydroxy-6-(2-naphthyl)-4-propylbenzoate (5ai): Starting with bis(silyl enol ether) **4g** (0.484 g, 1.6 mmol), $TiCl_4$ (0.310 g, 1.6 mmol) in CH_2Cl_2 (3 mL) and silyl enol ether **3k** (0.495 g, 1.5 mmol), **5ai** was isolated (0.204 g, 35%) by column chromatography (silica gel, *n*-heptane/EtOAc = 30:1→20:1) as a colourless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.31 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 0.91 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.13 (t, ^3J = 7.4 Hz, 3 H, $COOCH_2CH_3$), 1.45–1.58 (m, 2 H, $CH_2CH_2CH_3$), 2.59 (br. t, ^3J = 8.0 Hz, 2 H, $CH_2CH_2CH_3$), 2.67 (t, ^3J = 8.0 Hz, 2 H, CH_2CH_3), 3.74 (q, ^3J = 7.2 Hz, 2 H, $COOCH_2CH_3$), 7.25 (dd, ^3J = 8.3 Hz, ^4J = 1.5 Hz, 1 H, CH_{Naph}), 7.35–7.40 (m, 2 H, CH_{Naph}), 7.57 (m, 1 H, CH_{Naph}), 7.68–7.79 (m, 3 H, CH_{Naph}), 11.00 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1 ($CH_2CH_2CH_3$), 14.4 (CH_2CH_3), 14.7 ($COOCH_2CH_3$), 20.0 (d, ^4J = 1.6 Hz, $CH_2CH_2CH_3$), 23.9 (d, ^4J = 1.1 Hz, CH_2CH_3), 28.8 (d, ^3J = 3.3 Hz, $CH_2CH_2CH_3$), 61.3 ($COOCH_2CH_3$), 110.2 (d, ^3J = 2.9 Hz, $C_{Ar}COOCH_2CH_3$), 126.1, 126.3 (CH_{Naph}), 127.0 (d, ^2J = 20.4 Hz, CCF_{Ar}), 127.3, 128.0 (CH_{Naph}), 128.1 (d, ^4J = 1.6 Hz, CH_{Naph}), 128.2 (d, ^4J = 1.1 Hz, CH_{Naph}), 128.2 (CH_{Naph}), 132.3 (d, ^3J = 3.5 Hz, $C_{Ar}CH_2CH_3$), 132.8, 133.4 (C_{Naph}), 134.3 (d, ^4J = 1.1 Hz, C_{Naph}), 135.9 (d, ^2J = 18.6 Hz, $FCCCH_2CH_2CH_{3,Ar}$), 152.1 (d, ^1J = 232.7 Hz, CF_{Ar}), 156.5 (d, ^4J = 1.7 Hz, COH_{Ar}), 171.3 (d, ^4J = 3.5 Hz, $COOCH_2CH_3$) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –127.4 (CF) ppm. IR (neat): $\tilde{\nu}$ = 2964 (s), 2873 (m), 1660 (s), 1613 (m), 1507 (m), 1416 (s), 1373 (s), 1328 (s), 1257 (s), 1243 (s), 1210 (s), 1164 (m), 1030 (m), 819 (m), 749 (s), 477 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 380 (65) [M^+], 334 (100), 305 (10), 291 (39), 273 (37), 246 (5), 176 (5), 152 (3), 131 (3), 116 (3). HRMS (EI): calcd. for $C_{24}H_{25}FO_3$ 380.17822; found 380.17793.

General Procedure for the Synthesis of Fluorinated Biaryl Lactones 6: To a CH_2Cl_2 solution of **5** was added BBr_3 (4.0 equiv.) at 0 °C. The solution was warmed to 20 °C during 18 h. To the solution was added an aqueous solution of KO*t*Bu (0.1 M), and the solution was stirred for 15 min. The organic and the aqueous layers were separated and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The product was purified by chromatography (silica gel; *n*-heptane/EtOAc = 20:1).

10-Fluoro-7-hydroxy-9-methyl-6*H*-benzo[*c*]chromen-6-one (6a): Starting with **5m** (0.060 g, 0.21 mmol) in CH_2Cl_2 (5 mL), BBr_3 (0.207 g, 0.83 mmol) and KO*t*Bu (10 mL, 0.1 M aqueous solution), **6a** was isolated as a colourless solid (0.046 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.33 (br. s, 3 H, CH_3), 6.81 (d, $^4J_{H,F}$ = 5.9 Hz, 1 H, CH_{Ar}), 7.24–7.26 (m, 1 H, CH_{Ar}), 7.28 (m, 1 H, CH_{Ar}), 7.38–7.43 (m, 1 H, CH_{Ar}), 8.35–8.39 (m, 1 H, CH_{Ar}), 11.21 (s, 1 H, OH) ppm. ^{13}C NMR (62 MHz, $CDCl_3$): δ = 15.7 (d, ^3J = 6.2 Hz, CH_3), 103.4 (d, ^3J = 3.7 Hz, CCO_{Ar}), 115.4 (d, ^3J = 5.2 Hz, CH_{Ar}), 117.2 (CH_{Ar}), 118.3 (d, ^3J = 4.9 Hz, CH_{Ar}), 120.5 (d, ^3J = 11.2 Hz, C_{Ar}), 125.2 (d, ^4J = 2.5 Hz, CH_{Ar}), 127.4 (d, ^2J = 22.9 Hz, C_{Ar}), 130.3 (d, ^4J = 2.5 Hz, CH_{Ar}), 136.8 (d, ^2J = 20.5 Hz, $C_{Ar}CH_3$), 149.9 (CO_{Ar}), 150.5 (d, ^1J = 241.1 Hz, CF_{Ar}), 158.1 (d, ^4J = 2.5 Hz, COH_{Ar}), 164.5 (d, ^4J = 3.1 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.7 (CF_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2954 (w), 2853 (w), 1672 (s), 1607 (m), 1455 (w), 1432 (w), 1278 (m), 1206 (s), 1104 (m), 1065 (m), 758 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 244 (100) [M^+], 229 (17), 216 (11), 196 (9), 159 (9), 133 (12), 69 (5), 57 (4). HRMS (EI): calcd. for $C_{14}H_{19}FO_3$ 244.05302; found 244.05258.

10-Fluoro-7-hydroxy-8,9-dimethyl-6*H*-benzo[*c*]chromen-6-one (6b): Starting with **5n** (0.060 g, 0.20 mmol) in CH_2Cl_2 (5 mL), BBr_3 (0.197 g, 0.78 mmol) and KO*t*Bu (10 mL, 0.1 M aqueous solution), **6b** was isolated as a colourless solid (0.043 g, 84%), m.p. 151–154 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 2.28 (br. s, 3 H, CH_3), 7.25–7.28 (m, 2 H, CH_{Ar}), 7.36–7.42 (m, 1 H, CH_{Ar}), 8.35–8.40 (m, 1 H, CH_{Ar}), 11.60 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.7 (d, ^4J = 2.2 Hz, CH_3), 12.3 (d, ^3J = 7.8 Hz, CH_3), 102.5 (d, ^3J = 5.2 Hz, CCO_{Ar}), 116.3 (d, ^3J = 5.2 Hz, C_{Ar}), 117.2 (CH_{Ar}), 117.7 (d, ^2J = 12.8 Hz, CCF_{Ar}), 125.2

(CH_{Ar}), 126.3 (d, ^3J = 4.0 Hz, $C_{Ar}CH_3$), 127.4 (CH_{Ar}), 129.8 (d, ^4J = 2.3 Hz, CH_{Ar}), 135.3 (d, ^2J = 19.2 Hz, $C_{Ar}CH_3$), 149.8 (CO_{Ar}), 150.3 (d, ^1J = 241.1 Hz, CF_{Ar}), 156.4 (d, ^4J = 1.7 Hz, COH_{Ar}), 165.1 (d, ^4J = 3.4 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.4 (CF_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2962 (m), 2925 (m), 2854 (w), 1677 (s), 1622 (w), 1606 (m), 1440 (s), 1335 (m), 1270 (s), 1179 (s), 1095 (s), 1228 (s), 1022 (m), 799 (s), 757 (s) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 258 (100) [M$^+$], 243 (25), 229 (4), 215 (3), 199 (3), 183 (4), 170 (4), 152 (3). HRMS (EI): calcd. for $C_{15}H_{11}FO_3$ 258.06867; found 258.06807.

8-Ethyl-10-fluoro-7-hydroxy-9-methyl-6*H*-benzo[*c*]chromen-6-one (6c): Starting with **5o** (0.060 g, 0.18 mmol) in CH_2Cl_2 (5 mL), BBr_3 (0.180 g, 0.72 mmol) and KO*t*Bu (10 mL, 0.1 M aqueous solution), **6c** was isolated as a colourless solid (0.037 g, 75%), m.p. 119–121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 2.34 (br. s, 3 H, CH_3), 2.74 (q, ^3J = 7.2 Hz, 2 H, CH_2CH_3), 7.19 (m, 1 H, CH_{Ar}), 7.29–7.30 (m, 1 H, CH_{Ar}), 7.37–7.43 (m, 1 H, CH_{Ar}), 8.39–8.43 (m, 1 H, CH_{Ar}), 11.60 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.7 (d, ^3J = 8.7 Hz, CH_3), 11.9 (CH_2CH_3), 18.5 (d, ^4J = 2.3 Hz, CH_2CH_3), 103.4 (d, ^3J = 4.4 Hz, CCO_{Ar}), 115.5 (d, ^3J = 5.2 Hz, C_{Ar}), 116.3 (CH_{Ar}), 117.1 (d, ^2J = 12.8 Hz, CCF_{Ar}), 124.2, 126.5 (CH_{Ar}), 128.9 (d, ^4J = 2.3 Hz, CH_{Ar}), 131.3 (d, ^3J = 3.5 Hz, $C_{Ar}CH_2CH_3$), 133.8 (d, ^2J = 14.9 Hz, $C_{Ar}CH_3$), 148.0 (CO_{Ar}), 148.3 (d, ^1J = 241.0 Hz, CF_{Ar}), 155.4 (d, ^4J = 1.7 Hz, COH_{Ar}), 164.4 (d, ^4J = 3.4 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –124.7 (CF_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 2967 (m), 2876 (w), 1672 (s), 1608 (m), 1563 (w), 1413 (s), 1339 (s), 1287 (s), 1268 (s), 1178 (s), 1164 (s), 872 (m), 768 (s), 738 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 272 (42) [M$^+$], 257 (100), 229 (2), 170 (4), 152 (3), 133 (2). HRMS (EI): calcd. for $C_{16}H_{13}FO_3$ 272.08432; found 272.08386.

10-Fluoro-7-hydroxy-9-propyl-6*H*-benzo[*c*]chromen-6-one (6d): Starting with **5p** (0.148 g, 0.46 mmol) in CH_2Cl_2 (8 mL), BBr_3 (0.465 g, 1.85 mmol) and KO*t*Bu (20 mL, 0.1 M aqueous solution), **6d** was isolated as a colourless solid (0.060 g, 47%), m.p. 88–90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 1.57–1.70 (m, 2 H, $CH_2CH_2CH_3$), 2.65 (br. t, ^3J = 7.2 Hz, 2 H, $CH_2CH_2CH_3$), 6.82 (d, $^4J_{H,F}$ = 5.7 Hz, 1 H, CH_{Ar}), 7.24–7.26 (m, 1 H, CH_{Ar}), 7.27 (m, 1 H, CH_{Ar}), 7.37–7.43 (m, 1 H, CH_{Ar}), 8.37–8.41 (m, 1 H, CH_{Ar}), 11.22 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 ($CH_2CH_2CH_3$), 21.7 (d, ^4J = 1.1 Hz, $CH_2CH_2CH_3$), 30.8 (d, ^3J = 3.9 Hz, $CH_2CH_2CH_3$), 102.7 (d, ^3J = 4.0 Hz, CCO_{Ar}), 115.3 (d, ^3J = 5.2 Hz, C_{Ar}), 116.7 (d, ^3J = 3.4 Hz, CH_{Ar}), 120.0 (d, ^2J = 12.2 Hz, CCF_{Ar}), 124.3, 126.5, 126.8 (CH_{Ar}), 129.4 (d, ^4J = 1.1 Hz, CH_{Ar}), 140.3 (d, ^2J = 19.2 Hz, $C_{Ar}CH_2CH_2CH_3$), 148.5 (d, ^1J = 243.2 Hz, CF_{Ar}), 149.1 (CO_{Ar}), 157.4 (d, ^4J = 2.0 Hz, COH_{Ar}), 163.8 (d, ^4J = 2.9 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –125.7 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3054 (w), 2965 (m), 2870 (m), 1700 (s), 1629 (m), 1569 (m), 1447 (m), 1435 (s), 1276 (s), 1203 (s), 1106 (s), 952 (w), 756 (s), 735 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 272 (100) [M$^+$], 257 (10), 244 (96), 215 (21), 199 (10), 183 (3), 170 (11), 157 (7), 133 (9). HRMS (EI): calcd. for $C_{18}H_{19}FO_4$ 272.08432; found 272.08412.

10-Fluoro-7-hydroxy-8-methyl-9-propyl-6*H*-benzo[*c*]chromen-6-one (6e): Starting with **5q** (0.100 g, 0.30 mmol) in CH_2Cl_2 (8 mL), BBr_3 (0.30 g, 1.20 mmol) and KO*t*Bu (10 mL, 0.1 M aqueous solution), **6e** was isolated as a colourless solid (0.052 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 1.44–1.60 (m, 2 H, $CH_2CH_2CH_3$), 2.14 (s, 3 H, CH_3), 2.70 (br. t, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_3$), 7.23 (m, 1 H, CH_{Ar}), 7.25 (m, 1 H, CH_{Ar}), 7.33–7.39 (m, 1 H, CH_{Ar}), 8.46–8.78 (m, 1 H, CH_{Ar}), 11.60 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.4 (d, ^4J = 2.2 Hz, CH_3), 13.1 ($CH_2CH_2CH_3$), 21.5 (d, ^4J = 1.9 Hz, $CH_2CH_2CH_3$), 27.7 (d, ^3J = 5.4 Hz, $CH_2CH_2CH_3$), 101.7 (d, ^3J = 5.2 Hz, CCO_{Ar}), 115.4 (d, ^3J = 5.2 Hz, C_{Ar}), 116.2 (CH_{Ar}), 116.9 (d, ^2J = 12.8 Hz, CCF_{Ar}), 124.2 (CH_{Ar}), 125.4 (d, ^3J = 4.0 Hz, $C_{Ar}CH_3$), 126.5 (CH_{Ar}), 128.8 (d, ^4J = 2.3 Hz, CH_{Ar}), 138.7 (d, ^2J = 18.0 Hz, $C_{Ar}CH_2CH_2CH_3$), 148.9 (CO_{Ar}), 149.4 (d, ^1J = 241.4 Hz, CF_{Ar}), 155.8 (d, ^4J = 1.7 Hz, COH_{Ar}), 164.2 (d, ^4J = 3.4 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.9 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 2968 (s), 2926 (s), 2853 (m), 1678 (s), 1604 (m), 1456 (m), 1426 (s), 1339 (m), 1281 (s), 1178 (s), 1119 (m), 871 (m), 763 (s), 729 (m) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 286 (100) [M$^+$], 271 (47), 258 (47), 243 (12), 229 (6), 215 (2), 199 (7), 183 (6), 170 (7), 152 (5), 133 (4). HRMS (EI): calcd. for $C_{17}H_{15}FO_3$ 286.09997; found 286.09965.

8-Ethyl-10-fluoro-7-hydroxy-9-propyl-6*H*-benzo[*c*]chromen-6-one (6f): Starting with **5r** (0.124 g, 0.35 mmol) in CH_2Cl_2 (6 mL), BBr_3 (0.124 g, 0.35 mmol) and KO*t*Bu (10 mL, 0.1 M aqueous solution), **6f** was isolated as a colourless solid (0.069 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, ^3J = 7.2 Hz, 3 H, $CH_2CH_2CH_3$), 1.13 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.51–1.64 (m, 2 H, $CH_2CH_2CH_3$), 2.70 (q, ^3J = 8.2 Hz, 2 H, CH_2CH_3), 2.75 (br. t, ^3J = 8.3 Hz, 2 H, $CH_2CH_2CH_3$), 7.24–7.29 (m, 2 H, CH_{Ar}), 7.36–7.42 (m, 1 H, CH_{Ar}), 8.39–8.43 (m, 1 H, CH_{Ar}), 11.62 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7 (CH_2CH_3), 13.2 ($CH_2CH_2CH_3$), 18.5 (d, ^4J = 1.6 Hz, CH_2CH_3), 22.5 (d, ^4J = 1.1 Hz, $CH_2CH_2CH_3$), 27.7 (d, ^3J = 5.8 Hz, $CH_2CH_2CH_3$), 102.0 (d, ^3J = 4.6 Hz, CCO_{Ar}), 115.5 (d, ^3J = 5.2 Hz, C_{Ar}), 116.3 (CH_{Ar}), 117.1 (d, ^2J = 12.8 Hz, CCF_{Ar}), 124.2, 126.5 (CH_{Ar}), 128.9 (d, ^4J = 1.7 Hz, CH_{Ar}), 131.1 (d, ^3J = 3.5 Hz, $C_{Ar}CH_2CH_3$), 138.3 (d, ^2J = 18.0 Hz, $C_{Ar}CH_2CH_2CH_3$), 149.0 (CO_{Ar}), 149.7 (d, ^1J = 242.0 Hz, CF_{Ar}), 155.8 (d, ^4J = 1.1 Hz, COH_{Ar}), 164.4 (d, ^4J = 3.5 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –126.3 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 2961 (s), 2929 (m), 2870 (m), 1686 (s), 1608 (m), 1410 (s), 1336 (m), 1278 (m), 1171 (s), 1114 (s), 1092 (m), 891 (w), 752 (s) cm^{-1}. GC-MS (EI, 70 eV): *m*/*z* (%) = 300 (100) [M$^+$], 285 (74), 272 (7), 257 (70), 244 (18), 229 (5), 199 (7), 183 (8), 170 (6), 152 (3), 133 (3). HRMS (EI): calcd. for $C_{18}H_{17}FO_3$ 300.11562; found 300.11481.

General Procedure for the Synthesis of Fluorinated Fluorenones 7: A solution of **5** (1 mmol) in concentrated sulfuric acid (12 mL) was stirred at room temperature for one hour. To the solution was added water, and it was stirred for a further 15 minutes. The organic and the aqueous layers were separated, and the latter was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The product was purified by chromatography (silica gel; *n*-heptane/EtOAc = 20:1) to give **7**.

7-Chloro-4-fluoro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7a): Starting with **5x** (0.031 g, 0.105 mmol) and concd. sulfuric acid (1.2 mL), **7a** was isolated as a yellow solid (0.021 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.22 (d, ^4J = 1.3 Hz, 3 H, CH_3), 6.52 (d, ^3J = 5.9 Hz, 1 H, CH_{Ar}), 7.18 (m, 1 H, CH_{ClPh}), 7.38 (d, ^3J = 8.0 Hz, 1 H, CH_{ClPh}), 7.52 (m, 1 H, CH_{ClPh}), 8.02 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 16.0 (d, ^3J = 4.0 Hz, CH_3), 112.3 (d, ^2J = 24.0 Hz, $C_{Ar}CH_3$), 116.4 (d, ^3J = 4.6 Hz, C_{ClPh}), 121.1 (CH_{ClPhr}), 124.9 (d, ^4J = 1.7 Hz, CH_{ClPh}), 125.2 (d, ^3J = 3.5 Hz, CH_{Ar}), 134.6 (CH_{ClPh}), 136.3 (C_{ClPh}), 138.4 (d, ^2J = 19.0 Hz, C_{Ar}), 145.0 (C_{Ar}), 152.4 (C_{ClPh}), 153.8 (COH_{Ar}), 163.6 (d, ^1J = 250.5 Hz, CF_{Ar}), 193.7 (CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –131.7 (CF_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3423 (br., m), 2973 (m), 2851 (w), 1698 (s), 1636 (w), 1605 (m), 1456 (m), 1310 (m), 1270 (m), 1180 (s), 1088 (m), 793 (m), 580 (w) cm^{-1}. GC-MS (EI,

70 eV): *m/z* (%) = 264 (^{37}Cl, 34) [M$^+$], 262 (^{35}Cl, 100) [M$^+$], 235 (^{37}Cl, 3), 233 (^{35}Cl, 8), 199 (13), 170 (23), 151 (3), 131 (3), 99 (6), 85 (9). HRMS (EI): calcd. for $C_{14}H_8ClFO_2$ ([M]$^+$, ^{35}Cl) 262.01914; found 262.01891.

7-Chloro-4-fluoro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (7b): Starting with **5y** (0.036 g, 0.12 mmol) and concd. sulfuric acid (1.39 mL), **7a** was isolated as a yellow solid (0.024 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, CH_3), 2.12 (br. s, 3 H, CH_3), 7.33 (dd, ^3J = 8.0 Hz, ^4J = 1.9 Hz, 1 H, CH_{ClPh}), 7.42 (m, 1 H, CH_{ClPh}), 7.46 (d, ^3J = 1.8 Hz, 1 H, CH_{ClPh}), 8.32 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.5 (d, ^4J = 1.7 Hz, CH_3), 12.5 (d, ^3J = 5.2 Hz, CH_3), 115.4 (d, ^3J = 5.2 Hz, $C_{Ar}CH_3$), 123.5 (d, ^2J = 17.4 Hz, $C_{Ar}CH_3$), 124.7, 125.2 (CH_{ClPh}), 129.3 (d, ^4J = 2.3 Hz, C_{ClPh}), 134.7 (d, ^2J = 28.5 Hz, C_{Ar}), 134.9 (CH_{ClPh}), 136.0 (C_{ClPh}), 136.2 (d, ^3J = 5.8 Hz, C_{ClPh}), 140.1 (C_{Ar}), 150.5 (d, ^1J = 244.9 Hz, CF_{Ar}), 152.5 (COH_{Ar}), 194.3 (CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –129.5 (CF_{Ar}) ppm. IR (KBr): $\tilde{\nu}$ = 3414 (br., s), 2923 (m), 2852 (m), 1696 (s), 1636 (w), 1604 (m), 1453 (s), 1382 (w), 1288 (s), 1274 (s), 1170 (s), 1078 (m), 1021 (m), 878 (w), 793 (m), 743 (m), 629 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 278 (^{37}Cl, 37) [M$^+$], 276 (^{35}Cl, 100) [M$^+$], 263 (^{37}Cl, 12), 261 (^{35}Cl, 40), 235 (^{37}Cl, 3), 233 (^{35}Cl, 10), 213 (5), 207 (23), 183 (17), 170 (11), 138 (6), 91 (11). HRMS (EI): calcd. for $C_{15}H_{10}ClFO_2$ ([M]$^+$, ^{35}Cl) 276.03479; found 276.03481.

4,7-Difluoro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (7c). Starting with **5ab** (0.078g, 0.27 mmol) and concd. sulfuric acid (3.2 mL), **7c** was isolated as a yellow solid (0.069 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CH_3), 2.01 (d, $^4J_{H,F}$ = 2.1 Hz, 3 H, CH_3), 7.00 (ddd, ^3J = 8.5, 8.7 H, ^4J = 2.5 Hz, 1 H, CH_{FPh}), 7.14 (dd, ^3J = 7.2 Hz, ^4J = 2.4 Hz, 1 H, CH_{FPh}), 7.38 (dd, ^3J = 8.1 Hz, ^4J = 2.5 Hz, 1 H, CH_{FPh}), 8.24 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 11.4 (d, ^4J = 1.7 Hz, CH_3), 12.4 (d, ^3J = 5.8 Hz, CH_3), 112.0 (d, ^2J = 22.7 Hz, CH_{FPh}), 115.8 (d, ^3J = 5.2 Hz, $C_{Ar}CH_3$), 121.1 (d, ^2J = 22.7 Hz, $C_{Ar}CH_3$), 123.5 (d, ^3J = 18.6 Hz, CH_{FPh}), 125.3 (CH_{FPh}), 128.5 (d, ^3J = 1.1 Hz, C_{FPh}), 136.0 (d, ^2J = 16.3 Hz, C_{Ar}), 136.7 (d, ^3J = 8.1 Hz, C_{FPh}), 137.6 (d, ^3J = 1.7 Hz, C_{Ar}), 150.2 (d, ^1J = 244.3 Hz, CF_{FPh}), 152.4 (COH_{Ar}), 163.3 (d, ^1J = 248.4 Hz, CF_{Ar}), 194.0 (d, ^4J = 2.3 Hz, CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –131.1 (CF_{Ar}), –111.9 (CF_{FPh}) ppm. GC-MS (EI, 70 eV): *m/z* (%) = 260 (100) [M$^+$], 245 (51), 231 (7), 217 (13), 201 (9), 183 (14), 130 (4).

2-Ethyl-4,7-difluoro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7d): Starting with **5ac** (0.037 mg, 0.12 mmol) and concd. sulfuric acid (1.38 mL), **7d** was isolated as a yellow solid (0.022 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 2.16 (s, 3 H, CH_3), 2.57 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 7.06 (ddd, ^3J = 8.5, 8.5 Hz, ^4J = 2.4 Hz, 1 H, CH_{FPh}), 7.20 (dd, ^3J = 5.1 Hz, ^4J = 0.3 Hz, 1 H, CH_{FPh}), 7.48 (dd, ^3J = 8.1 Hz, ^4J = 3.6 Hz, 1 H, CH_{FPh}), 8.31 (s, 1 H, OH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 9.5 (CH_2CH_3), 11.2 (CH_3), 17.0 (d, ^4J = 2.3 Hz, CH_2CH_3), 109.6 (d, ^2J = 23.3 Hz, CH_{FPh}), 113.8 ($C_{Ar}CH_2CH_3$), 118.8 (d, ^2J = 22.7 Hz, CH_{FPh}), 121.4 (d, ^4J = 16.3 Hz, $CCH_{3,FPh}$), 123.2 (CH_{FPh}), 126.3 (C_{Ar}), 133.1 (d, ^2J = 17.4 Hz, C_{Ar}), 134.6 (C_{FPh}), 135.4 (C_{FPh}), 148.1 (d, ^1J = 244.3 Hz, C_{FPh}), 150.1 (COH_{Ar}), 161.0 (d, ^1J = 248.4 Hz, CF_{Ar}), 191.9 (CO) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –129.8 (CF_{Ar}), –111.8 (CF_{FPh}) ppm. IR (KBr): $\tilde{\nu}$ = 3445 (br., m), 2975 (w), 2939 (m), 2852 (w), 1684 (s), 1603 (w), 1485 (m), 1265 (m), 1095 (m), 837 (w), 598 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 274 (43) [M$^+$], 259 (100), 231 (6), 201 (8), 183 (7), 122 (2). HRMS (EI): calcd. for $C_{16}H_{12}FO_2$ 274.07999; found 274.07954.

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