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[3+3] Cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes—a new approach to diverse CF_3-substituted fluorenes, dibenzofurans, 9,10-dihydrophenanthrenes and 6*H*-benzo[*c*]chromenes

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ABSTRACT

Trifluoromethyl-substituted fluorenes, dibenzofurans, 9,10-dihydrophenanthrenes and 6*H*-benzo[*c*]chromenes were prepared by formal [3+3] cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes. The reactions proceeded with very good regioselectivity. The product distribution depends on the type of 1,3-dielectrophile employed and can be explained by electronic reasons.

1. Introduction

The trifluromethyl group is of great importance in organic and medicinal chemistry because CF_3-substituted molecules are chemically and metabolically stable.[1–4] In contrast, undesired enzymatic oxidations often occur in case of CH_3 groups and C–H bonds of arenes. Due to their metabolic stability and lipophilicity, the bioavailability of CF_3-substituted carba- and heterocycles is generally high. Besides medicinal chemistry, the trifluromethyl group also plays an important role for the development of catalysts soluble in fluorophilic solvent systems[5] and for the development of new organocatalysts.[6] Trifluoromethyl-substituted ring systems are synthetically available by reaction of aryl halides with trifluoromethylcopper[7] and by conversion of CX_3 into CF_3 groups.[8] An interesting alternative is based on cyclization reactions of fluorinated building blocks.[9] The cyclization of CF_3-substituted enones with hydrazones, amidines and enamines has been reported to give CF_3-substituted pyrazoles, pyrimidines and pyridines.[10,11] However, the synthesis of phenol derivatives using this approach is essentially restricted to one example, i.e., 2-acetyl-5-(trifluoromethyl) phenol, which was prepared from acetylacetone.[12] In fact, it has been demonstrated that β-ketoesters cannot be used.[12] In recent years, we have reported the regioselective synthesis of various trifluoromethyl- and perfluoroalkyl-substituted phenol derivatives based on formal [3+3] cyclocondensation of 1,3-bis(silyloxy)-1,3-butadienes with various fluorinated 1,3-dielectrophiles.[13] This strategy has been successfully applied to the synthesis of 5-methyl-3-(trifluoromethyl)phenols,[14] 5-aryl-3-(trifluoromethyl)phenols,[15] 5-hetaryl-3-(trifluoromethyl)phenols,[16] 5-alkyl-3-(perfluoroalkyl) phenols, 5-aryl-3-(perfluoroalkyl)-phenols[17] and 5-unsubstituted 3-(trifluoromethyl)phenols.[18] Herein, we report, for the first time, the application of our methodology to the synthesis of various pharmacologically relevant CF_3-substituted polycyclic ring systems, including fluorenes, dibenzofurans, dihydrophenanthrenes and 6*H*-benzo[*c*]chromenes. Interesting observations related to the regioselectivity are reported. The selectivity depends on the type of dielectrophile employed and can be rationalized by consideration of the electron distribution in the molecules. The starting materials, 1,3-bis(silyloxy)-1,3-butadienes, were prepared by known procedures.[19,20]

2. Results and discussion

2.1. Fluorenes

Parent fluorene has been isolated from coal tar and is used for the technical synthesis of fluorenone. Substituted fluorene

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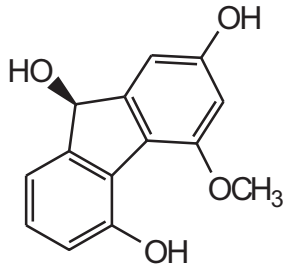
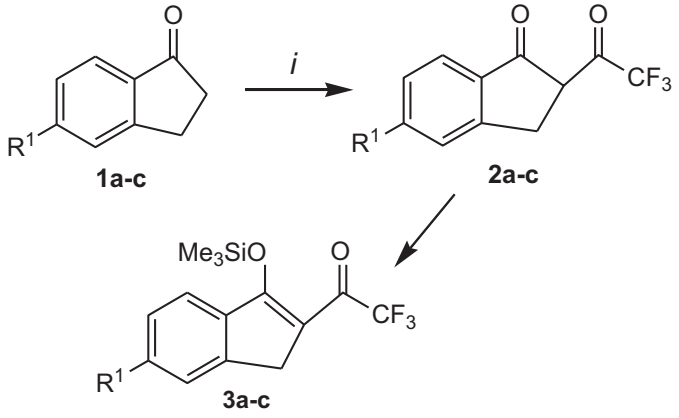
derivatives are present in various pharmaceuticals and pesticides[21] Fluorenes are important structural motifs of anti-cancer agents[22] and also occur in natural products, such as (9*R*)-4-methoxy-9*H*-fluorene-2,5-9-triol, which has been isolated from the orchidea *Dendrobium chrysotoxum* Lindl (Fig. 1).[23] The fluorene core structure also plays an important role in organic light emitting devices (OLED).[24] Fluorenes are synthetically available by functionalization of parent fluorene[25] and by intramolecular Friedel–Crafts acylation and subsequent reduction.[26]



(9R)-4-Methoxy-
9*H*-fluoren-2,5,9-triol

Fig. 1. A naturally occuring fluorene derivative.

The sodium methylate-mediated reaction of indan-1-ones **1a**–**c** with ethyl trifluoroacetate afforded the 2-trifluoroacetyl-indan-1-ones **2a**–**c** in good yields (Scheme 1, Table 1). The silylation of **2a**–**c** gave silyl enol ethers **3a**–**c**.



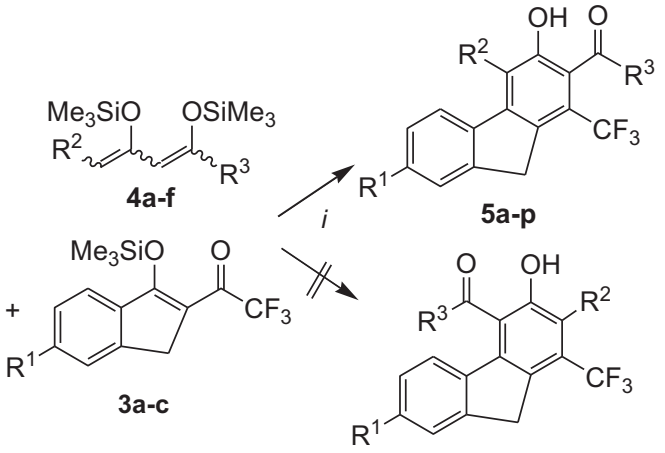
Scheme 1. Synthesis of **3a**–**c**. (i) Na, CH_3OH, F_3CCO_2Et, 0–20 °C, 16 h; (ii) NEt_3 (1.0 equiv), TMSOTf (0.95 equiv), $(C_2H_5)_2O$, 20 °C, 72 h.

Table 1
Synthesis of **3a**–**c**

2,3	R^1	% (**2**)[a]	% (**3**)[a]
a	H	56	84
b	Br	68	86
c	OCH_3	66	92

[a] Yields of isolated products.

The $TiCl_4$-mediated formal [3+3] cyclization of **4a**–**f** with **3a**–**c** afforded the CF_3-substituted fluorenes **5a**–**p** in 37–69% yield (Scheme 2, Table 2). The reaction proceeded by regioselective attack of the terminal carbon atom of the diene to the carbon atom attached to the silyloxy group and subsequent cyclization by attack of the central carbon atom of the diene to the keto group. The structure of product **5b** was confirmed by 2D NMR experiments (HMBC, NOESY) (Fig. 2). A diagnostic NOE is observed between the methyl group attached to one benzene moiety of the fluorene and the *ortho* hydrogen of the other benzene moiety. The structure of **5h** was independently confirmed by X-ray crystal structure analysis (Fig. 3). The molecule is flat. The carbonyl group is in plane with the phenyl moiety and an intramolecular hydrogen bond is observed with the hydroxyl group. In all reactions, only one regioisomer could be isolated. Analysis of the crude product mixture (before chromatographic purification) by TLC revealed that no significant amounts of the other regioisomer were formed. An exception is the formation of **5h** where the opposite regioisomer **5g** was isolated as a by-product in 24% yield. The synthesis of CF_3-substituted fluorenes has, to the best of our knowledge, not been reported so far.



Scheme 2. Synthesis of fluorenes **5a**–**p**. (i) $TiCl_4$, CH_2Cl_2, −78 to 20 °C, 16 h.

Table 2
Synthesis of **5a**–**p**

3	4	5	R^1	R^2	R^3	% (**5**)[a]
a	**a**	**a**	H	H	OCH_3	43
a	**b**	**b**	H	CH_3	OCH_3	48
a	**c**	**c**	H	C_2H_5	OCH_3	46
a	**d**	**d**	H	C_3H_7	OCH_3	54
a	**e**	**e**	H	OCH_3	OCH_3	67
a	**f**	**f**	H	H	CH_3	39
b	**a**	**h**	Br	H	OCH_3	41[b]
b	**b**	**j**	Br	CH_3	OCH_3	62
b	**c**	**k**	Br	C_2H_5	OCH_3	50
b	**d**	**l**	Br	C_3H_7	OCH_3	60
c	**a**	**m**	OCH_3	H	OCH_3	69
c	**b**	**n**	OCH_3	CH_3	OCH_3	50
c	**c**	**o**	OCH_3	C_2H_5	OCH_3	37
c	**d**	**p**	OCH_3	C_3H_7	OCH_3	43

[a] Yields of isolated products.
[b] The opposite regioisomer **5g** was isolated as a by-product in 24% yield.

2.2. Dibenzofurans

Substituted dibenzofurans occur as natural products. For example, 2-chloro-3,7-dihydroxy-1,9-dimethyldibenzofuran was isolated from the lychen *Lecanora cinereocarnea* and cytotoxic kehokorin A was isolated from the fungi *Trichia favoginea* var. *persimilis*. Usninic acid, which can be regarded as a dibenzofuran derivative, possesses antibiotic, antiviral, antileukaemic and anti-inflammatory activity.[27] Classic syntheses of benzofurans rely on the reaction of 4-bromophenols with arylhalides[28] and on $CuCl_2$-mediated reactions of phenols.[29]

The sodium methylate-mediated reaction of 3-coumaranone (**1d**) with ethyl trifluoroacetate afforded **2d** (Scheme 3). The silylation of **2d** gave silyl enol ether **3d**.

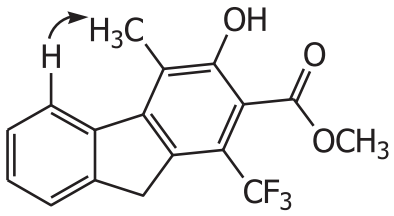


Fig. 2. Diagnostic NOESY interaction of **5b**.

methyl group attached to the aromatic ring and the aromatic carbon atom located next to the trifluoromethyl group. The structure could also be confirmed by inspection of the ^{13}C NMR spectra. In case of **5q**, the aromatic CH carbon atom appears as a quartet, due to its coupling with the trifluoromethyl group located in *ortho* position. This coupling would not be expected for the opposite regioisomer where the CH carbon is located *para* to the CF_3 group. In case of **5r**–**t**, a splitting to a quartet is observed for the ^{13}C NMR signals of the sp^3 hybridized carbon atoms located next to the aromatic ring. This splitting can be again explained by coupling of the alkyl group with the neighbouring CF_3 group. The structure of **5t** was independently confirmed by X-ray crystal structure analysis

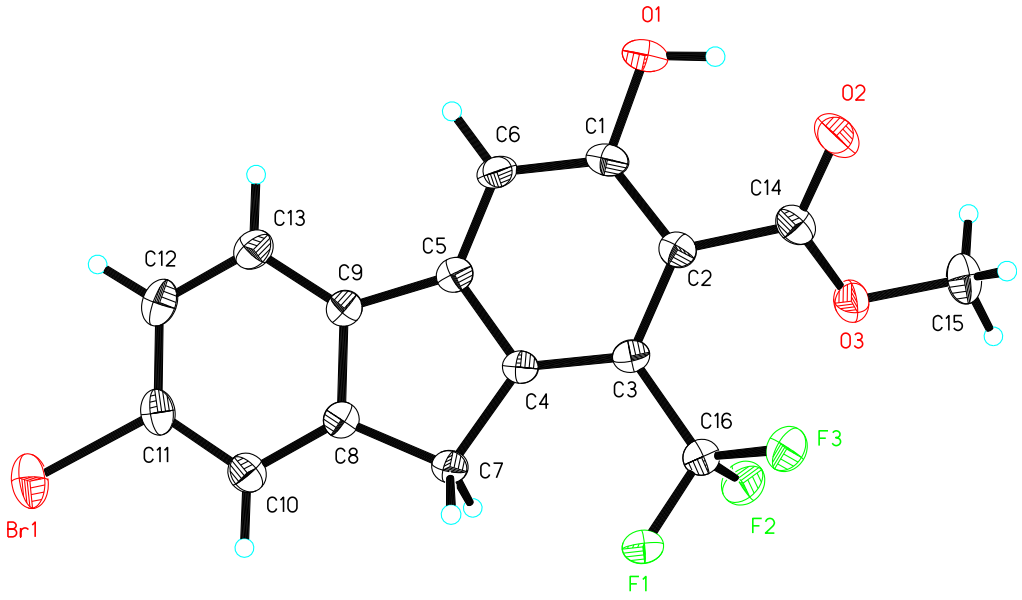
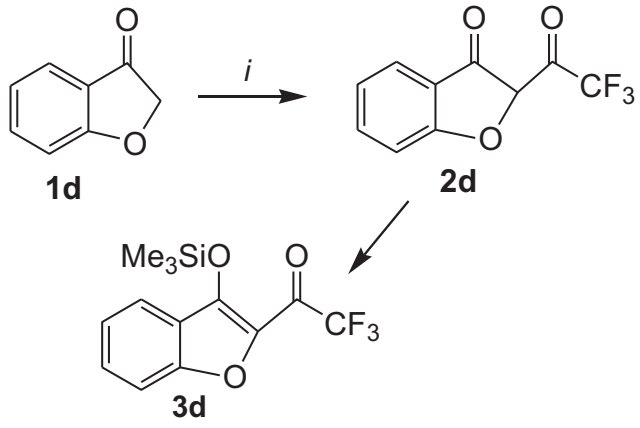
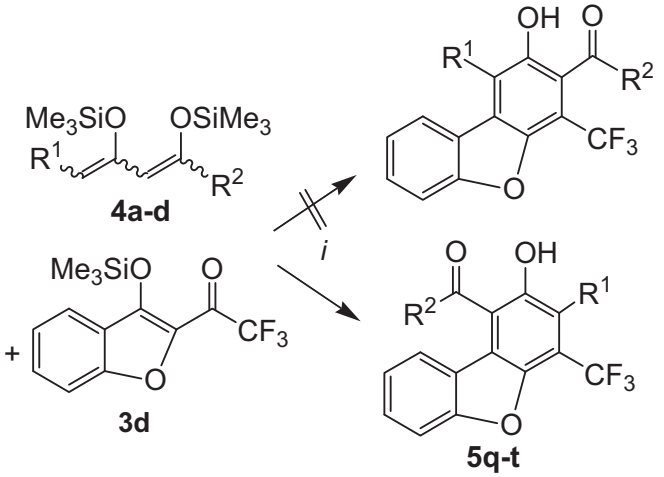


Fig. 3. Ortep plot of **5h** (50% probability level).



Scheme 3. Synthesis of **3d**. (i) Na, CH_3OH, F_3CCO_2Et, 0–20 °C, 16 h; (ii) NEt_3 (1.0 equiv), TMSOTf (0.95 equiv), $(C_2H_5)_2O$, 20 °C, 72 h.



Scheme 4. Synthesis of fluorenes **5q**–**t**; (i) $TiCl_4$, CH_2Cl_2, −78 to 20 °C, 16 h.

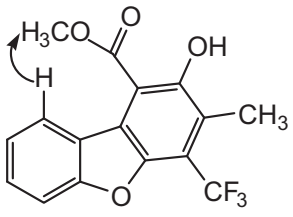
The $TiCl_4$-mediated formal [3+3] cyclization of **4a**–**d** with **3d** afforded the CF_3-substituted fluorenes **5q**–**t** in 31–51% yield (Scheme 4, Table 3). The reactions proceeded with very good regioselectivity by attack of the terminal carbon atom of the diene to the carbon atom attached to the silyloxy group and subsequent cyclization via the central carbon atom of the diene and the keto group. The other regioisomer could not be detected in the crude product mixture by TLC or ^1H NMR.

For compounds **5r** and **5s**, 2D NMR experiments were carried out to confirm the regioselectivity of cyclization (Fig. 4). Diagnostic $^1H,^1H$-NOESY correlations were observed between the methoxy group and the aromatic hydrogen atom of **5r**. The $^1H,^{13}C$-HMBC spectrum of **5r** revealed a coupling between the protons of the

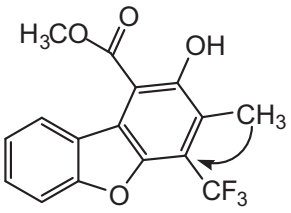
Table 3
Synthesis of **5q**–**t**

4	5	R^1	R^2	% (5)[a]
a	**q**	H	OCH_3	44
b	**r**	CH_3	OCH_3	48
c	**s**	C_2H_5	OCH_3	31
d	**t**	C_3H_7	OCH_3	51

[a] Yields of isolated products.



^{1}H,^{1}H-NOESY-correlations of **5r**

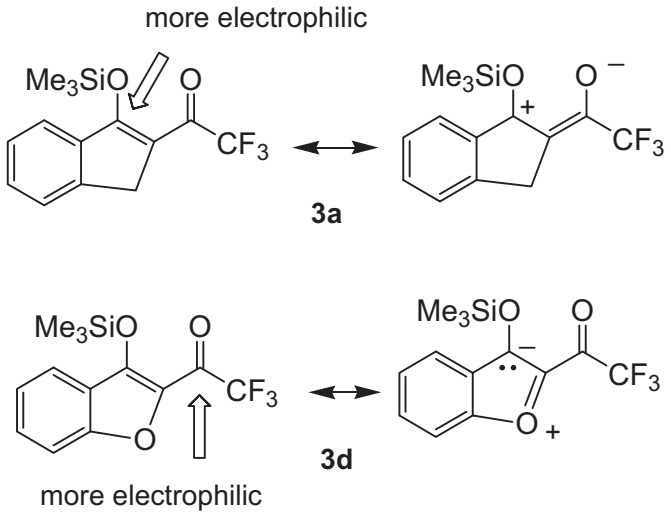


^{1}H,^{13}C-HMBC-correlations of **5r**

Fig. 4. Diagnostic NOESY and HMBC interactions of **5r**.

(Fig. 5). The molecule is, as expected, flat. The carbonyl group is in plane with the phenyl moiety and an intramolecular hydrogen bond is observed with the hydroxyl group.

The regioselectivity of the formation of fluorenes **5a**–**p** is opposite to the regioselectivity of the formation of dibenzofurans **5q**–**t**. This striking difference might be explained by the different



Scheme 5. Possible explanation of the different regioselectivities of the cyclization reactions of 1,3-bis(silyloxy)-1,3-butadienes **4** with **3a** and **3d**.

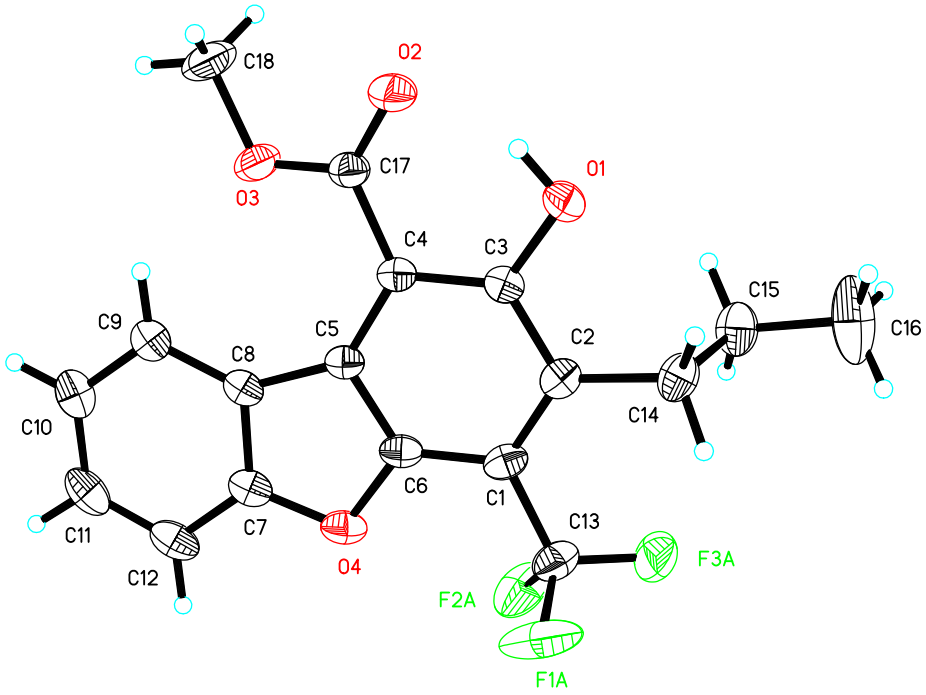


Fig. 5. Ortep plot of **5t** (50% probability level).

electronic nature of the 3-silyloxy-2-en-1-one systems of **3a**–**c** and **3d**. In case of **3a**–**c**, the carbon atom attached to the silyloxy group is more electrophilic than the carbonyl group. In case of **3d**, the electrophilicity of the carbon attached to the silyloxy group is decreased by the π-donating effect of the oxygen atom (Scheme 5).

2.3. 9,10-Dihydrophenanthrenes

The 9,10-dihydrophenanthrene core structure is present in various natural products. Examples include the sinensoles A–H isolated from *Spiranthes sinensis*[30] and the stemanthrenes A–C isolated from *Stemona* cf. *pierrei* (Fig. 6).[31] 9,10-Dihydrophenanthrenes are available by palladium- and nickel-catalyzed [2+2+2]-cycloadditions of alkenes with arynes.[32] Dihydrophenanthrenes have been prepared by nickel-catalyzed cross-coupling of iodo-substituted phenylethanols with iodo-xylenes.[33] We have reported the synthesis of dihydrophenanthrenes by $TiCl_4$-mediated [3+3]-cyclocondensation reactions.[34]

2-Trifluoroacetyltetralone (**2e**) was prepared from tetralone (**1e**). The silylation of **2e** gave silyl enol ether **3e** (Scheme 6). The cyclization of **3e** with diene **4a** afforded a separable mixture of 9,10-dihydrophenanthrene **5v** (32%) and its regioisomer **5u** (16%). Similar to the formation of fluorenes **3a**–**p**, the major product **5v** was formed by attack of the terminal carbon atom of the diene to the carbon atom attached to the silyloxy group. The synthesis of CF_3-substituted 9,10-dihydrophenanthrenes has, to the best of our knowledge, not yet been reported.

The structure of **5v** was independently confirmed by X-ray crystal structure analysis (Fig. 7). The molecular structure clearly shows that the biaryl system is twisted out of plane. The carbonyl group is twisted with regard to the phenyl moiety, due to steric reasons. In the ^{13}C NMR spectrum of **5v**, the aromatic quaternary

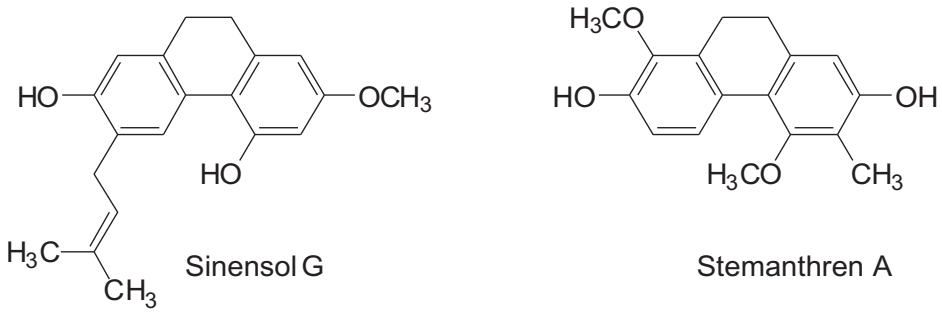
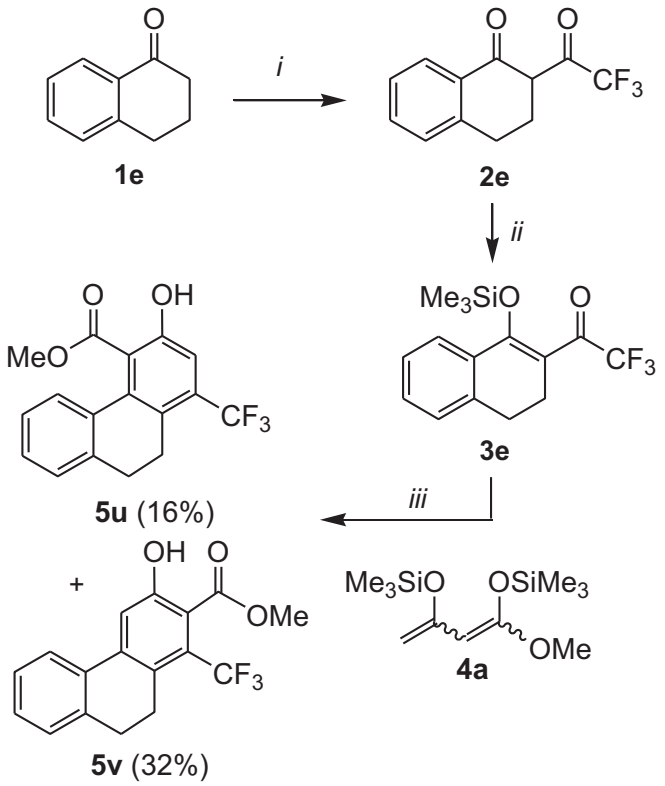


Fig. 6. Naturally occuring 9,10-dihydrophenanthrenes.



Scheme 6. Synthesis of **5u** and **5v**. (i) Na, CH_3OH, F_3CCO_2Et, 0–20 °C, 16 h; (ii) NEt_3 (1.0 equiv), TMSOTf (0.95 equiv), $(C_2H_5)_2O$, 20 °C, 72 h; (iii) $TiCl_4$, CH_2Cl_2, −78 to 20 °C, 16 h.

carbon atom attached to the ester group is splitted to a quartet, due to its coupling with the CF_3 group located in *ortho* position. In case of **5u**, the aromatic CH carbon appears as a quartet, due to coupling with the neighbouring CF_3 group.

2.4. Benzo[*c*]chromenes

Benzo[*c*]chromenes are very rare in nature. Δ^1-Tetrahydrocannabinol, a tetrahydro-benzo[*c*]chromene, represents a pharmacologically relevant natural product (Fig. 8).[21]

Our synthesis of benzo[*c*]chromenes started with chroman-4-one (**1f**), which was transformed to 2-trifluoroacetylchroman-4-one (**2f**). The silylation of **2f** gave **3f** (Scheme 7).

The cyclization of **3f** with dienes **4a**,**c**,**d** afforded the benzo[*c*]chromenes **5w**–**z** (Scheme 8, Table 4). In case of products **5y** and **5z**, only one regioisomer was isolated. The opposite regioisomer could not be detected in the crude product mixture. In contrast, product **5x** (48%) was isolated along with the regioisomeric by-product **5w** (18%). The regioselectivity can be explained by the fact that the heterocyclic oxygen atom is not directly connected to the double bond of the silyl enol ether moiety and thus exerts no electronic influence on the carbon atom attached to the silyloxy group. Therefore, the same regioselectivity is observed as in the case of fluorenes **5a**–**p**.

The structure of **5y** was confirmed by 2D NMR experiments. A NOE interaction was observed between the ethyl group and the neighbouring aromatic proton (Fig. 9). The structures of **5w** and **5x** were established based on the analysis of the coupling pattern of the ^{13}C NMR signals. In case of **5x**, the aromatic quaternary carbon atom attached to the ester group is splitted to a quartet, due to its coupling with the CF_3 group located in *ortho* position. In case of **5w**, the aromatic CH carbon appears as a quartet, due to coupling with the neighbouring CF_3 group. The structure of **5x** was independently confirmed by X-ray crystal structure analysis (Fig. 10). The two aryl groups of the molecule are slightly twisted out of plane. The

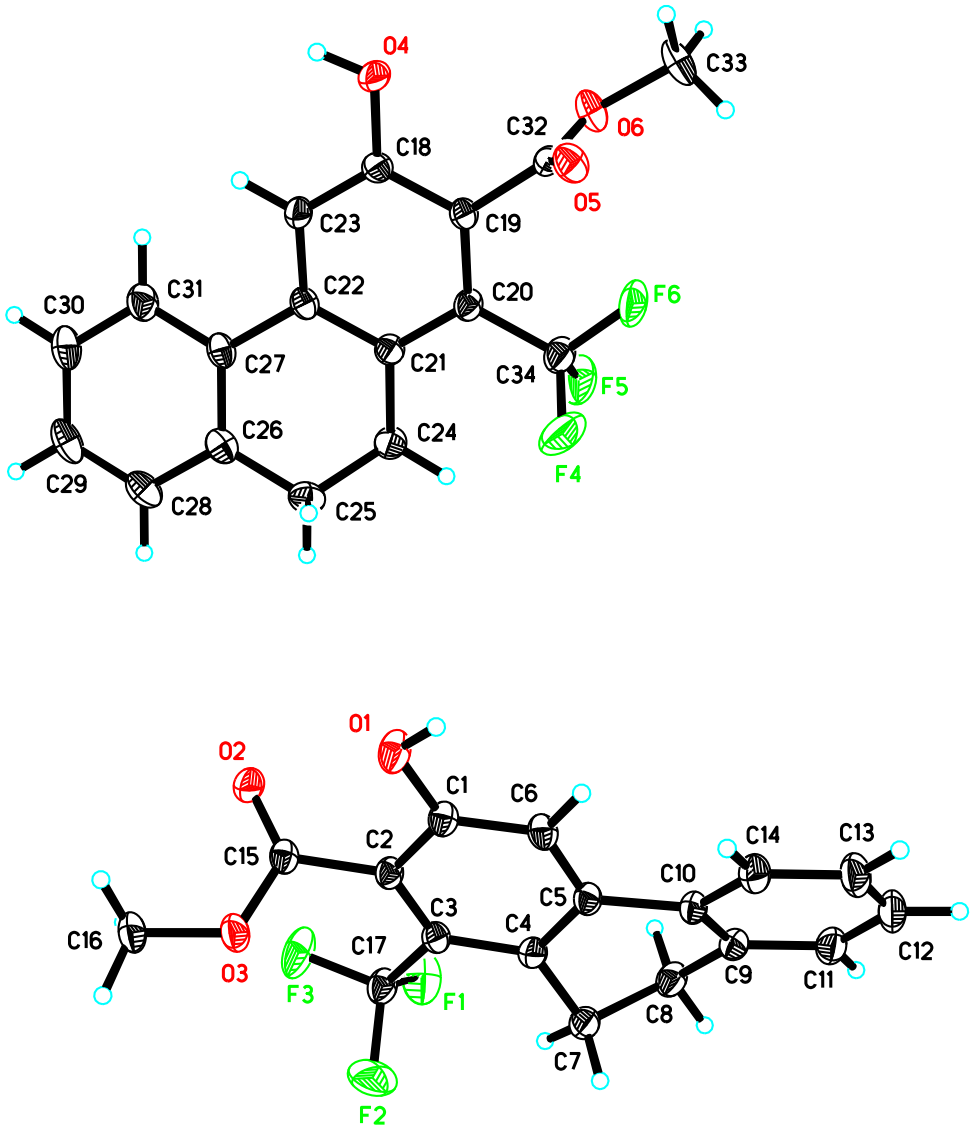


Fig. 7. Ortep plot of **5v** (50% probability level).

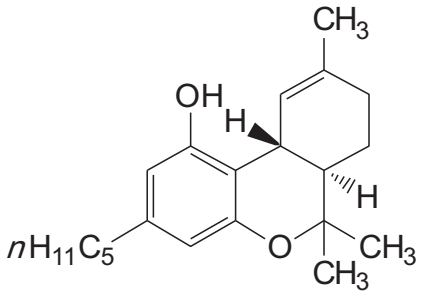
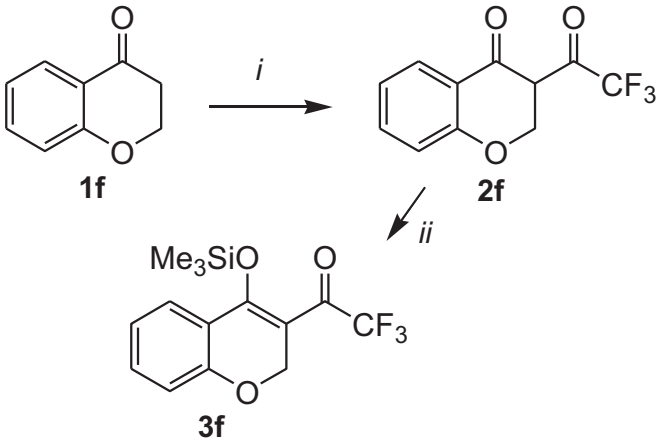


Fig. 8. Structure of Δ^1-tetrahydrocannabinol.

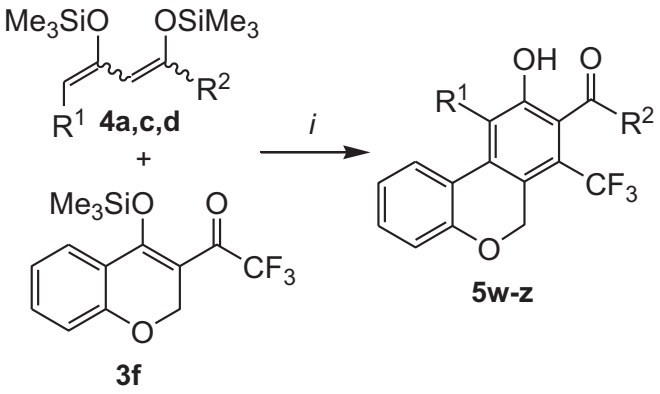
carbonyl group is twisted with regard to the plane of the phenyl moiety, due to steric reasons.

2.5. Suzuki–Miyaura cross-coupling reactions

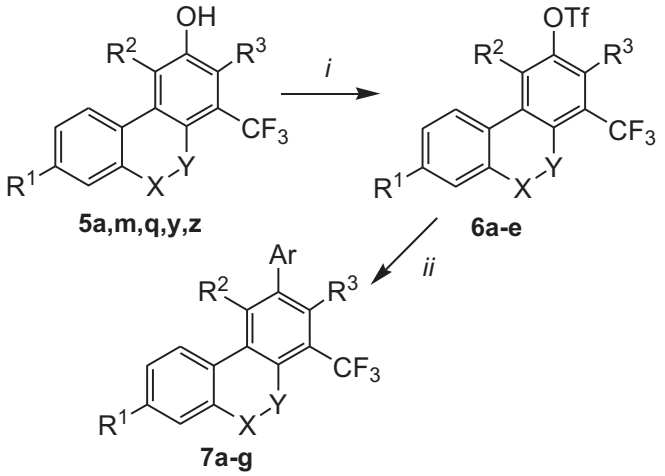
To broaden the diversity of the products, we studied whether the phenolic hydroxyl group could be replaced by aryl groups by Suzuki reactions of the corresponding aryl triflates. Fluorenes **5a** and **5m**, dibenzofuran **5q** and benzo[*c*]chromenes **5y**,**z** were transformed into their triflates **6a**–**e** (Scheme 9, Table 5). The Suzuki–Miyaura reaction of **6a**–**e** with arylboronic acids afforded the aryl-substituted products **7a**–**g** in good yields.



Scheme 7. Synthesis of **3f**. (i) Na, CH_3OH, F_3CCO_2Et, 0–20 °C, 16 h; (ii) NEt_3 (1.0 equiv), TMSOTf (0.95 equiv), $(C_2H_5)_2O$, 20 °C, 72 h.



Scheme 8. Synthesis of **5w–z**. (i) $TiCl_4$, CH_2Cl_2, −78 to 20 °C, 16 h.



Scheme 9. Suzuki–Miyaura cross-coupling reactions. (i) 1) Pyridine, CH_2Cl_2, −78 °C, 10 min; 2) Tf_2O, −78→0 °C, 4 h; (ii) $ArB(OH)_2$, K_3PO_4, $Pd(PPh_3)_4$, dioxane, 90 °C, 5 h.

Table 4
Synthesis of **5w–z**

4	5	X	R^1	R^2	R^3	% (**5**)[a]
a	**x**	O	H	H	OCH_3	48[b]
c	**y**	O	H	C_2H_5	OCH_3	53
d	**z**	O	H	C_3H_7	OCH_3	51

[a] Yields of isolated products.
[b] The opposite regioisomer **5w** was formed as a by-product in 18% yield.

Table 5
Suzuki–Miyaura cross-coupling reactions

5	6	7	X	Y	R^1	R^2	R^3	Ar	% (**6**)[a]	% (**7**)[a]
a	**a**	**a**	CH_2	—	H	H	CO_2CH_3	C_6H_5	95	68
m	**b**	**b**	CH_2	—	OCH_3	H	CO_2CH_3	4-MeC_6H_4	98	85
		c	CH_2	—	OCH_3	H	CO_2CH_3	4-ClC_6H_4		71
q	**c**	**d**	O	—	H	CO_2CH_3	H	C_6H_5	92	90
		e	O	—	H	CO_2CH_3	H	4-MeC_6H_4		99
y	**d**	**f**	CH_2	O	H	C_2H_5	CO_2CH_3	4-MeC_6H_4	98	95
z	**e**	**g**	CH_2	O	H	C_3H_7	CO_2CH_3	C_6H_5	95	59

[a] Yields of isolated products.

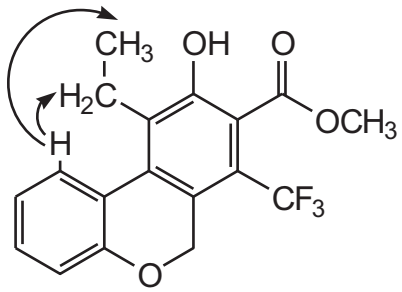


Fig. 9. Diagnostic NOESY interactions of **5y**.

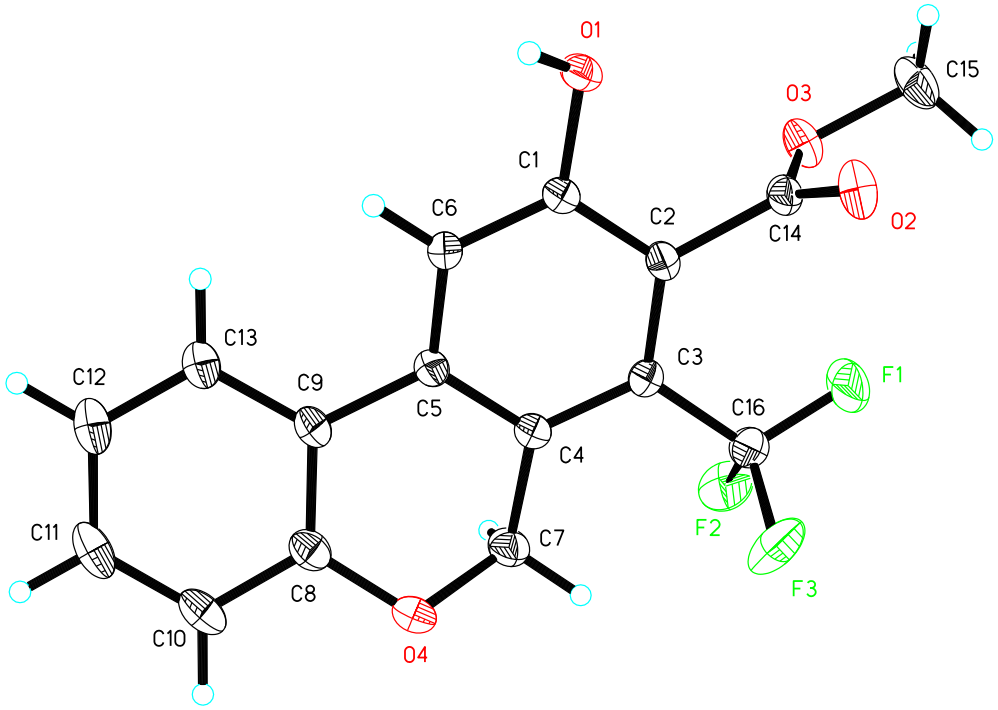


Fig. 10. Ortep plot of **5x** (50% probability level).

3. Conclusions

Trifluoromethyl-substituted fluorenes, dibenzofurans, 9,10-dihydrophenanthrenes and 6*H*-benzo[*c*]chromenes were prepared by formal [3+3] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes. The reactions proceeded with very good regioselectivity. The product distribution depends on the type of 1,3-dielectrophile employed. In case of the synthesis of fluorenes, 9,10-dihydrophenanthrenes and benzo[*c*]chromenes, the cyclizations proceed by attack of the terminal carbon of the diene to the carbon attached to the silyloxy group. In contrast, the carbonyl group is attacked first during the formation of dibenzofurans. This change of the selectivity can be explained by the π-donating effect of the oxygen atom. The hydroxyl group of the products could be replaced by aryl groups by Suzuki reactions of the aryl triflates. The methodology reported herein provides a convenient and regioselective approach to various CF_3-substituted polycyclic ring systems, which are not readily available by other methods. The products reported herein are of potential pharmacological relevance, due to their structural similarity to drugs and natural products.

4. Experimental section

4.1. General

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra, the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane) or electrospray ionization (ESI). For preparative scale chromatography, silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used. Crystallographic details are given in Ref. 35.

4.2. General procedure for the synthesis of diketones 2a–f

Sodium (1.2 equiv) was reacted with methanol (10.0 equiv) at 0 °C. To this freshly prepared sodium methylate suspension ethyl trifluoroacetate (1.0 equiv) has been added under stirring at 0 °C and stirring was continued for 30 min followed by addition of ketone **1a**–**f** (1.0 equiv). The reaction mixture was stirred for additional 14 h and then was worked up with hydrochloric acid (10%, 50 mL). The organic layer was separated and extracted with diethylether (3×40 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc 20:1).

*4.2.1. 5-Bromo-2-(2,2,2-trifluoroacetyl)-1-indanone (**2b**).* Starting with 5-bromo-1-indanone **1b** (5.00 g, 23.7 mmol), ethyl trifluoroacetate (3.366 g, 23.7 mmol), sodium (0.654 g, 28.4 mmol) and methanol (9.6 mL), product **2b** was isolated as a grey solid (4.958 g, 68%); mp=100–106 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=3.81 (s, 2H, C*H*$_2$), 7.62 (d, ^3J=8.2 Hz, 1H, Ar*H*), 7.68–7.75 (m, 2H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−72.8 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.0 (q, ^4J=2.2 Hz, *C*H$_2$), 109.3 (*C*), 118.2 (q, ^1J=280.1 Hz, *C*F$_3$), 124.7 (*C*H), 129.3 (*C*H), 129.8 (*C*), 131.6 (*C*H), 135.0 (*C*), 149.8 (*C*), 163.5 (q, ^2J=37.4 Hz, *C*CF$_3$), 191.4 (*CO*); IR (ATR, cm^{-1}): $\tilde{\nu}$=1689 (m), 1633 (m), 1598 (m), 1574 (w), 1538 (w), 1519 (w), 1504 (w), 1484 (w), 1469 (w), 1416 (w), 1386 (w), 1310 (m), 1261 (m), 1187 (m), 1171 (m), 1151 (m), 1132 (m), 1111 (m), 1056 (m), 1040 (w), 1008 (m); MS (EI, 70 eV): *m*/*z* (%)=308 (^{81}Br, M^+, 66), 306 (^{79}Br, M^+, 65), 239 (85), 237 (100), 211 (60), 209 (58), 102 (50); HRMS (EI, 70 eV): calcd for $C_{11}H_6^{79}BrF_3O_2$ (M^+): 305.94978, found 305.94986; calcd for $C_{11}H_6^{81}BrF_3O_2$ (M^+): 307.94773, found 307.94826.

*4.2.2. 5-Methoxy-2-(2,2,2-trifluoroacetyl)-1-indanone (**2c**).* Starting with 5-methoxy-1-indanone **1c** (5.00 g, 30.8 mmol), ethyl trifluoroacetate (4.380 g, 30.8 mmol), sodium (0.850 g, 37.0 mmol) and methanol (12.5 mL), product **2c** was isolated as a colourless solid (5.278 g, 66%); mp=107–108 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=3.76 (s, 2H, C*H*$_2$), 3.91 (s, 3H, C*H*$_3$), 6.95–7.03 (m, 2H, Ar*H*), 7.78 (dd, ^3J=7.5 Hz, ^4J=1.7 Hz, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−71.9 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.7 (q, ^4J=2.2 Hz, *C*H$_2$), 55.8 (OCH$_3$), 109.7 (*C*H), 110.3 (*C*), 115.9 (*C*H), 118.9 (q, ^1J=277.9 Hz, *C*F$_3$), 124.4 (*C*H), 129.5 (*C*), 152.4 (*C*), 156.9 (q, ^2J=37.3 Hz, *C*CF$_3$), 165.8 (*C*), 194.9 (*CO*); IR (ATR, cm^{-1}): $\tilde{\nu}$=3063 (w), 3018 (w), 2954 (w), 2908 (w), 2851 (w), 1684 (m), 1614 (m), 1578 (m), 1520 (w), 1486 (m), 1471 (m), 1453 (w), 1445 (w), 1425 (m), 1385 (w), 1334 (m), 1262 (m), 1208 (m), 1180 (m), 1161 (m), 1135 (s), 1107 (m), 1029 (m); MS (EI, 70 eV): *m*/*z* (%)=258 (M^+, 80), 189 (100), 174 (8), 161 (69), 146 (13), 118 (22); HRMS (EI, 70 eV): calcd for $C_{12}H_9F_3O_3$ (M^+): 258.04983, found 258.04998.

*4.2.3. 2-(2,2,2-Trifluoroacetyl)-3-coumaranone (**2d**).* Starting with 3-coumaranone **1d** (5.000 g, 37.3 mmol), ethyl trifluoroacetate (5.296 g, 37.3 mmol), sodium (1.028 g, 44.7 mmol) and methanol (15.1 mL), product **2d** was isolated as a red solid (3.186 g, 37%); mp=121–122 °C; ^1H NMR (300 MHz, $CDCl_3$): δ=7.36 (ddd, ^3J=8.0 Hz, ^3J=7.2 Hz, ^3J=0.9 Hz, 1H, Ar*H*), 7.51 (d, ^3J=8.6 Hz, 1H, Ar*H*), 7.66 (ddd, ^3J=8.5 Hz, ^3J=7.2 Hz, ^3J=1.3 Hz, 1H, Ar*H*), 7.83 (d, ^3J=8.0 Hz, 1H, Ar*H*), 8.71 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−75.0 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=113.3 (*C*H), 116.0 (q, ^1J=286.4 Hz, *C*F$_3$), 118.8 (*C*), 121.8 (*C*H), 124.0 (*C*H), 131.9 (*C*), 132.9 (*C*H), 156.0 (*C*), 159.5 (*C*), 172.2 (q, ^2J=38.8 Hz, *C*CF$_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$=3338 (w), 1666 (m), 1652 (m), 1614 (m), 1594 (m), 1553 (m), 1539 (m), 1504 (m), 1485 (w), 1480 (w), 1455 (m), 1435 (w), 1415 (w), 1392 (w), 1384 (w), 1372 (w), 1331 (w), 1294 (w), 1251 (m), 1229 (m), 1207 (m), 1189 (m), 1169 (m), 1134 (m), 1107 (m), 1009 (m), 993 (m); MS (EI, 70 eV): *m*/*z* (%)=230 (M^+, 74), 189 (4), 161 (100), 105 (26), 77 (15); HRMS (ESI, TOF/MS): calcd for $C_{10}H_4F_3O_3$ ($(M-H)^-$): 229.01180, found 229.01198.

4.3. General procedure for the synthesis of silyl enol ethers 3a–f

To a stirred diethyl ether solution (2 mL per 1.0 mmol of **2**) of **2a**–**f** (1.0 equiv) were added triethylamine (1.0 equiv) and TMSOTf (0.95 equiv) at 0 °C under an argon atmosphere. The solution was stirred for 30 min at 0 °C. The temperature of the reaction mixture was allowed to rise to 20 °C and the stirring was continued for 3 days. A liquid salt layer separated at the bottom of the flask. The upper layer (ether solution containing the product) was transferred to a dry flask by syringe under an argon atmosphere. Diethyl ether (1.5 mL per 1.0 mmol of **2**) was added to the liquid salt layer, the mixture was stirred for 2 min and the layers were allowed to separate in the period of 2 h. The ether solutions were combined and concentrated in vacuo to give silyl enol ethers **3a**–**f**, which were not further purified and, due to their unstable nature, were immediately used for the synthesis of phenols **5** (without detailed spectroscopic characterization).

*4.3.1. General procedure for the synthesis of products **5a**–**z**.* To a CH_2Cl_2 solution (4 mL) of 1,3-bis-silyl enol ether **4** (2.20 mmol) and 4-(silyloxy)alk-3-en-2-one **3** (2.00 mmol) was added $TiCl_4$ (2.20 mmol) at −78 °C under argon atmosphere. The temperature of the reaction mixture was allowed to rise to 20 °C during 14 h and, subsequently, hydrochloric acid (10%, 10 mL) was added. The

organic layer was separated and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc 20:1).

*4.3.2. Methyl 3-hydroxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5a**).* Starting with silyl enol ether **3a** (0.622 g, 2.07 mmol), 1,3-bis-silyl enol ether **4a** (0.573 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5a** was isolated as a colourless solid (0.272 g, 43%); mp=77–78 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.99 (s, 3H, OC*H*$_3$), 4.05 (q, *J*=2.5 Hz, 2H, C*H*$_2$), 7.35–7.45 (m, 2H, Ar*H*), 7.49–7.56 (m, 2H, Ar*H*), 7.72–7.80 (m, 1H, Ar*H*), 9.72 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−56.2 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=37.2 (q, *J*=4.1 Hz, *C*H$_2$), 52.9 (O*C*H$_3$), 110.8 (q, ^3J=2.3 Hz, *C*), 111.7 (*C*H), 121.0 (*C*H), 124.0 (q, ^1J=274.8 Hz, *C*F$_3$), 124.9 (*C*H), 126.2 (q, ^2J=32.7 Hz, *C*CF$_3$), 127.2 (*C*H), 129.2 (*C*H), 133.6 (q, *J*=2.4 Hz, *C*), 138.6 (*C*), 144.5 (q, *J*=1.7 Hz, *C*), 148.2 (*C*), 159.5 (*C*OH), 170.0 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3534 (m), 3424 (w), 3048 (w), 2960 (w), 2795 (w), 2726 (w), 2660 (w), 1705 (m), 1684 (m), 1651 (m), 1644 (m), 1616 (m), 1478 (m), 1440 (m), 1407 (m), 1315 (m), 1293 (m), 1264 (m), 1231 (m), 1206 (m), 1185 (m), 1157 (m), 1102 (s), 1021 (m); MS (EI, 70 eV): *m*/*z* (%)=308 (M$^+$, 54), 276 (100), 219 (18), 207 (68); HRMS (EI, 70 eV): calcd for $C_{16}H_{11}F_3O_3$ (M$^+$): 308.06548, found 308.06486.

*4.3.3. Methyl 3-hydroxy-4-methyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5b**).* Starting with silyl enol ether **3a** (0.598 g, 1.99 mmol), 1,3-bis-silyl enol ether **4b** (0.604 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product 5**b** was isolated as a pale yellow solid (0.309 g, 48%); mp=100–102 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.68 (s, 3H, Ar*C*H$_3$), 3.98 (s, 3H, O*C*H$_3$), 4.05–4.11 (m, 2H, C*H*$_2$), 7.38–7.45 (m, 2H, Ar*H*), 7.52–7.61 (m, 1H, Ar*H*), 8.00–8.07 (m, 1H, Ar*H*), 9.83 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−55.9 (C*F*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ=12.5 (Ar*C*H$_3$), 37.0 (q, *J*=3.7 Hz, *C*H$_2$), 52.9 (O*C*H$_3$), 109.9 (*C*), 122.9 (q, ^2J=32.5 Hz, *C*CF$_3$), 124.3 (*C*H), 124.3 (q, ^1J=274.3 Hz, *C*F$_3$), 124.7 (*C*H), 125.0 (*C*), 126.9 (*C*H), 128.2 (*C*H), 133.4 (*C*), 140.1 (*C*), 144.9 (*C*), 145.8 (*C*), 160.0 (*C*OH), 170.7 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3109 (w), 3034 (w), 3013 (w), 2955 (w), 2923 (w), 2853 (w), 1738 (w), 1667 (m), 1592 (w), 1440 (m), 1384 (m), 1366 (m), 1334 (m), 1313 (m), 1291 (m), 1251 (m), 1220 (m), 1206 (m), 1194 (m), 1162 (m), 1153 (m), 1113 (s), 1027 (m), 1003 (m); MS (EI, 70 eV): *m*/*z* (%)=322 (M$^+$, 55), 290 (67), 270 (100), 165 (23); HRMS (EI, 70 eV): calcd for $C_{17}H_{13}F_3O_3$ (M$^+$): 322.08113, found 322.08067. Anal. Calcd for $C_{17}H_{13}F_3O_3$ (322.28): C, 63.36; H, 4.07. Found: C, 62.83; H, 4.14.

*4.3.4. Methyl 4-ethyl-3-hydroxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5c**).* Starting with silyl enol ether **3a** (0.600 g, 2.00 mmol), 1,3-bis-silyl enol ether **4c** (0.635 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5c** was isolated as a pale yellow solid (0.309 g, 46%); mp=112–114 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.33 (t, ^3J=7.5 Hz, 3H, CH$_2$C*H*$_3$), 3.23 (q, ^3J=7.5 Hz, 2H, C*H*$_2$CH$_3$), 3.98 (s, 3H, O*C*H$_3$), 4.07–4.12 (m, 2H, C*H*$_2$), 7.36–7.48 (m, 2H, Ar*H*), 7.55–7.61 (m, 1H, Ar*H*), 7.97–8.03 (m, 1H, Ar*H*), 9.73 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−55.9 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.5 (ArCH$_2$*C*H$_3$), 19.4 (Ar*C*H$_2$CH$_3$), 37.0 (q, *J*=4.0 Hz, *C*H$_2$), 52.9 (O*C*H$_3$), 110.1 (q, *J*=2.2 Hz, *C*), 123.1 (q, ^2J=32.4 Hz, *C*CF$_3$), 124.1 (*C*H), 124.3 (q, ^1J=274.3 Hz, *C*F$_3$), 124.8 (*C*H), 127.2 (*C*H), 128.2 (*C*H), 131.4 (*C*), 133.8 (q, *J*=2.2 Hz, *C*), 139.4 (*C*), 145.0 (*C*), 145.2 (*C*), 156.8 (*C*OH), 170.7 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3432 (w), 3082 (w), 3024 (w), 2959 (w), 2935 (w), 2915 (w), 2873 (w), 2785 (w), 1712 (m), 1604 (w), 1574 (w), 1483 (w), 1462 (w), 1451 (w), 1436 (m), 1410 (m), 1397 (m), 1366 (m), 1327 (m), 1309 (m), 1293 (m), 1267 (m), 1218 (m), 1192 (m), 1160 (m), 1129 (m), 1107 (s), 1055 (m), 1037 (m), 1022 (m); MS (EI, 70 eV): *m*/*z* (%)=336 (M$^+$, 69), 304 (100), 284 (23), 276 (69), 207 (31); HRMS (EI, 70 eV): calcd for $C_{18}H_{15}F_3O_3$ (M$^+$): 336.09678, found 336.09615.

*4.3.5. Methyl 3-hydroxy-4-n-propyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5d**).* Starting with silyl enol ether **3a** (0.501 g, 1.67 mmol), 1,3-bis-silyl enol ether **4d** (0.666 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (3 mL), product **5d** was isolated as a pale yellow solid (0.317 g, 54%); mp=102–103 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.13 (t, ^3J=7.3 Hz, 3H, CH$_2$C*H*$_3$), 1.65–1.82 (m, 2H, C*H*$_2$CH$_3$), 3.10–3.21 (m, 2H, ArC*H*$_2$CH$_2$), 3.98 (s, 3H, O*C*H$_3$), 4.06–4.11 (m, 2H, C*H*$_2$), 7.35–7.47 (m, 2H, Ar*H*), 7.55–7.60 (m, 1H, Ar*H*), 7.90–7.96 (m, 1H, Ar*H*), 9.71 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−55.9 (C*F*$_3$); ^{13}C NMR (63 MHz, $CDCl_3$): δ=12.3 (Ar*C*H$_3$), 21.5 (*C*H$_2$), 27.9 (*C*H$_2$), 37.0 (q, *J*=4.0 Hz, ArCH$_2$Ar), 52.9 (O*C*H$_3$), 110.1 (q, *J*=2.3 Hz, *C*), 123.0 (q, ^2J=32.7 Hz, *C*CF$_3$), 124.0 (*C*H), 124.3 (q, ^1J=274.4 Hz, *C*F$_3$), 124.8 (*C*H), 127.1 (*C*H), 128.2 (*C*H), 130.1 (*C*), 133.8 (q, *J*=2.4 Hz, *C*), 139.5 (*C*), 145.0 (*C*), 145.4 (*C*), 156.9 (*C*OH), 170.7 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3420 (w), 3076 (w), 3022 (w), 2968 (w), 2957 (w), 2935 (w), 2918 (w), 2875 (w), 2792 (w), 1707 (m), 1602 (w), 1574 (w), 1464 (w), 1452 (w), 1436 (m), 1409 (m), 1399 (m), 1371 (m), 1331 (m), 1310 (m), 1288 (m), 1252 (m), 1217 (m), 1191 (m), 1158 (m), 1129 (m), 1109 (s), 1036 (m), 1012 (m); MS (EI, 70 eV): *m*/*z* (%)=350 (M$^+$, 68), 318 (100), 290 (73), 270 (26), 183 (17); HRMS (EI, 70 eV): calcd for $C_{19}H_{17}F_3O_3$ (M$^+$): 350.11243, found 350.11156. Anal. Calcd for $C_{19}H_{17}F_3O_3$ (350.33): C, 65.14; H, 4.89. Found: C, 64.75; H, 4.70.

*4.3.6. Methyl 3-hydroxy-4-methoxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5e**).* Starting with silyl enol ether **3a** (0.590 g, 1.96 mmol), 1,3-bis-silyl enol ether **4e** (0.639 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5e** was isolated as a pale yellow solid (0.446 g, 67%); mp=124–125 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.99 (s, 3H, O*C*H$_3$), 4.05–4.10 (m, 5H, ArO*C*H$_3$, C*H*$_2$), 7.34–7.48 (m, 2H, Ar*H*), 7.48–7.58 (m, 1H, Ar*H*), 8.11–8.20 (m, 1H, Ar*H*), 8.89 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−56.2 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=37.4 (q, *J*=3.6 Hz, *C*H$_2$), 53.0 (O*C*H$_3$), 60.3 (ArO*C*H$_3$), 113.7 (q, *J*=2.4 Hz, *C*), 120.7 (q, ^2J=32.8 Hz, *C*CF$_3$), 124.0 (q, ^1J=273.9 Hz, *C*F$_3$), 124.3 (*C*H), 124.5 (*C*H), 127.3 (*C*H), 128.4 (*C*H), 134.6 (q, ^3J=2.3 Hz, *C*), 137.8 (*C*), 138.3 (*C*), 143.8 (q, ^3J=1.4 Hz, *C*), 151.0 (*C*OH), 169.2 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3305 (w), 3054 (w), 3007 (w), 2946 (w), 2905 (w), 2837 (w), 1711 (m), 1607 (m), 1591 (m), 1487 (m), 1449 (m), 1419 (m), 1403 (m), 1392 (m), 1326 (m), 1302 (m), 1286 (m), 1222 (m), 1204 (m), 1183 (m), 1163 (m), 1134 (m), 1098 (m), 1065 (m), 1024 (m); MS (EI, 70 eV): *m*/*z* (%)=338 (M$^+$, 71), 306 (100), 278 (70), 249 (26), 207 (44), 181 (37); HRMS (EI, 70 eV): calcd for $C_{17}H_{13}F_3O_4$ (M$^+$): 338.07604, found 338.07545. Anal. Calcd for $C_{17}H_{13}F_3O_4$ (338.28): C, 60.36; H, 3.87. Found: C, 59.97; H, 4.02.

*4.3.7. 3-Hydroxy-2-(methylcarbonyl)-1-(trifluoromethyl)-9H-fluorene (**5f**).* Starting with silyl enol ether **3a** (0.594 g, 1.98 mmol), 1,3-bis-silyl enol ether **4f** (0.538 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5f** was isolated as a grey solid (0.225 g, 39%); mp=167–169 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.61 (s, 3H, COC*H*$_3$), 3.85 (s, 3H, O*C*H$_3$), 7.31–7.49 (m, 4H, Ar*H*), 7.64–7.75 (m, 1H, Ar*H*), 8.43 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−55.4 (C*F*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.1 (q, *J*=4.1 Hz, *C*H$_2$), 36.3 (*C*OCH$_3$), 111.9 (*C*), 120.6 (*C*H), 123.1 (q, ^3J=2.4 Hz, *C*), 124.1 (q, ^2J=32.2 Hz, *C*CF$_3$), 124.2 (q, ^1J=272.1 Hz, *C*F$_3$), 124.9 (*C*H), 127.1 (*C*H), 129.6 (*C*H), 133.4 (q, ^3J=2.5 Hz, *C*), 138.7 (*C*), 144.1 (*C*), 146.5 (*C*), 154.7 (*C*OH), 205.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3233 (w), 3063 (w), 2926 (w), 2789 (w), 2713 (w), 1682 (m), 1614 (m), 1514 (w), 1477 (m), 1456 (w), 1435 (m), 1403 (m), 1355 (m), 1324 (m), 1294 (m), 1285 (m), 1256 (m), 1212 (m), 1182 (m), 1152 (m), 1112 (m), 1081 (m); MS (EI, 70 eV): *m*/*z*

(%)=292 (M^+, 41), 277 (100), 229 (14), 201 (17); HRMS (EI, 70 eV): calcd for $C_{16}H_{11}F_3O_2$ (M^+): 292.07057, found 292.07067.

*4.3.8. Methyl 7-bromo-3-hydroxy-1-(trifluoromethyl)-9H-fluorene-4-carboxylate (**5g**).* Starting with silyl enol ether **3b** (0.567 g, 1.50 mmol), 1,3-bis-silyl enol ether **4a** (0.430 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5g** was isolated as a pale orange solid (0.137 g, 24%); mp=140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.96 (s, 2H, CH_2), 4.10 (s, 3H, OCH_3), 7.25 (s, 1H, Ar*H*), 7.45 (dd, ^3J=8.6 Hz, ^4J=2.0 Hz, 1H, Ar*H*), 7.68–7.71 (m, 1H, Ar*H*), 7.82 (d, ^3J=8.6 Hz, 1H, Ar*H*), 10.01 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−63.6 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=35.1 (*C*H_2), 52.5 (O*C*H_3), 111.7 (*C*), 113.7 (q, ^3J=4.9 Hz, *C*HCCF$_3$), 122.4 (*C*), 123.3 (q, ^1J=271.7 Hz, *C*F$_3$), 125.9 (*C*H), 127.9 (*C*H), 129.9 (*C*H), 131.4 (q, ^2J=32.7 Hz, *C*CF$_3$), 132.4 (q, J=1.8 Hz, *C*), 138.3 (*C*), 142.6 (*C*), 146.9 (*C*), 159.8 (*C*OH), 169.5 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3393 (m), 3107 (w), 3071 (w), 3045 (w), 3020 (w), 2960 (w), 2924 (w), 2852 (w), 2790 (w), 1747 (w), 1704 (m), 1611 (w), 1586 (m), 1487 (m), 1455 (w), 1439 (m), 1408 (m), 1401 (m), 1339 (m), 1312 (m), 1288 (m), 1263 (m), 1233 (m), 1204 (m), 1179 (m), 1153 (s), 1130 (m), 1121 (m), 1106 (s), 1097 (s), 1065 (m), 1007 (m); MS (EI, 70 eV): *m*/*z* (%)=388 (^{81}Br, M^+, 38), 386 (^{79}Br, M^+, 39), 356 (99), 354 (100), 275 (70), 247 (25), 219 (48); HRMS (EI, 70 eV): calcd for $C_{16}H_{10}^{79}BrF_3O_3$ (M^+): 385.97599, found 385.97686; calcd for $C_{16}H_{10}^{81}BrF_3O_3$ (M^+): 387.97395, found 387.97417. Anal. Calcd for $C_{16}H_{10}BrF_3O_3$ (387.15): C, 49.64; H, 2.60. Found: C, 49.55; H, 2.64.

*4.3.9. Methyl 7-bromo-3-hydroxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5h**).* Starting with silyl enol ether **3b** (0.567 g, 1.50 mmol), 1,3-bis-silyl enol ether **4a** (0.430 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5h** was isolated as a pale orange solid (0.236 g, 41%); mp=153–155 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.99 (s, 3H, OCH_3), 4.03 (q, J=2.7 Hz, 2H, CH_2), 7.47 (s, 1H, Ar*H*), 7.53 (dd, ^3J=8.2 Hz, ^4J=1.7 Hz, 1H, Ar*H*), 7.61 (d, ^3J=8.2 Hz, 1H, Ar*H*), 7.65–7.69 (m, 1H, Ar*H*), 9.73 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−56.2 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.9 (q, J=4.2 Hz, *C*H$_2$), 53.0 (O*C*H$_3$), 111.2 (q, ^3J=2.2 Hz, *C*), 111.8 (*C*H), 122.1 (*C*H), 123.3 (*C*), 123.8 (q, ^1J=272.2 Hz, *C*F$_3$), 126.3 (q, ^2J=32.9 Hz, *C*CF$_3$), 128.1 (*C*H), 130.5 (*C*H), 133.0 (q, J=2.5 Hz, *C*), 137.5 (*C*), 146.2 (*C*), 146.9 (*C*), 159.5 (*C*OH), 169.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3019 (w), 2964 (w), 1738 (w), 1668 (m), 1614 (w), 1587 (m), 1473 (w), 1443 (m), 1405 (w), 1383 (m), 1344 (m), 1288 (m), 1275 (m), 1254 (m), 1222 (m), 1207 (m), 1158 (m), 1149 (m), 1127 (s), 1061 (m); MS (EI, 70 eV): *m*/*z* (%)=388 (^{81}Br, M^+, 56), 386 (^{79}Br, M^+, 58), 356 (93), 354 (95), 287 (25), 285 (26), 275 (100), 247 (17), 219 (45); HRMS (EI, 70 eV): calcd for $C_{16}H_{10}^{79}BrF_3O_3$ (M^+): 385.97599, found 385.97606; calcd for $C_{16}H_{10}^{81}BrF_3O_3$ (M^+): 387.97395, found 387.97428. Anal. Calcd for $C_{16}H_{10}BrF_3O_3$ (387.15): C, 49.64; H, 2.60. Found: C, 49.40; H, 2.47.

*4.3.10. Methyl 7-bromo-3-hydroxy-4-methyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5j**).* Starting with silyl enol ether **3b** (0.648 g, 1.71 mmol), 1,3-bis-silyl enol ether **4b** (0.522 g, 1.90 mmol) and $TiCl_4$ (0.23 mL, 1.90 mmol) in CH_2Cl_2 (3 mL), product **5j** was isolated as a pale yellow solid (0.425 g, 62%); mp=141–143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.63 (s, 3H, ArCH_3), 3.98 (s, 3H, OCH_3), 4.01–4.05 (m, 2H, CH_2), 7.53 (dd, ^3J=8.4 Hz, ^4J=1.9 Hz, 1H, Ar*H*), 7.68 (d, ^4J=1.5 Hz, 1H, Ar*H*), 7.85 (d, ^3J=8.5 Hz, 1H, Ar*H*), 9.83 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.9 (CF_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ=12.4 (Ar*C*H$_3$), 36.7 (q, J=4.2 Hz, *C*H$_2$), 53.0 (O*C*H$_3$), 110.2 (q, ^3J=2.4 Hz, *C*), 122.5 (*C*), 123.0 (q, ^2J=32.5 Hz, *C*CF$_3$), 124.1 (q, ^1J=274.3 Hz, *C*F$_3$), 125.1 (*C*), 125.3 (*C*H), 127.9 (*C*H), 130.1 (*C*H), 132.8 (q, J=2.3 Hz, *C*), 138.9 (*C*), 144.6 (*C*), 146.7 (q, J=1.8 Hz, *C*), 157.1 (*C*OH), 170.5 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3412 (m), 3068 (w), 3008 (w), 2958 (w), 2922 (w), 2854 (w), 2784 (w), 1699 (m), 1598 (w), 1584 (w), 1479 (w), 1435 (m), 1395 (m), 1363 (m), 1327 (m), 1291 (m), 1278 (m), 1245 (m), 1217 (m), 1199 (m), 1155 (m), 1135 (m), 1112 (s), 1068 (m), 1025 (m), 1005 (m); MS (EI, 70 eV): *m*/*z* (%)=402 (^{81}Br, M^+, 59), 400 (^{79}Br, M^+, 61), 370 (98), 368 (96), 350 (97), 348 (100), 289 (32), 269 (28), 233 (39); HRMS (EI, 70 eV): calcd for $C_{17}H_{12}^{79}BrF_3O_3$ (M^+): 399.99164, found 399.99150; calcd for $C_{17}H_{12}^{81}BrF_3O_3$ (M^+): 401.98960, found 401.98959. Anal. Calcd for $C_{17}H_{12}BrF_3O_3$ (401.18): C, 50.90; H, 3.01. Found: C, 50.64; H, 2.82.

*4.3.11. Methyl 7-bromo-4-ethyl-3-hydroxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5k**).* Starting with silyl enol ether **3b** (0.562 g, 1.48 mmol), 1,3-bis-silyl enol ether **4c** (0.476 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5k** was isolated as a colourless solid (0.305 g, 50%); mp=173–174 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.30 (t, ^3J=7.5 Hz, 3H, CH_2CH_3), 3.17 (q, ^3J=7.5 Hz, 2H, CH_2CH$_3$), 3.98 (s, 3H, OCH_3), 4.04–4.08 (m, 2H, CH_2), 7.55 (dd, ^3J=8.5 Hz, ^4J=1.9 Hz, 1H, Ar*H*), 7.69–7.72 (m, 1H, Ar*H*), 7.83 (d, ^3J=8.5 Hz, 1H, Ar*H*), 9.74 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−56.0 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.4 (Ar*C*H$_2$CH$_3$), 19.3 (ArC*H*$_2$CH$_3$), 36.7 (q, J=4.2 Hz, *C*H$_2$), 53.0 (O*C*H$_3$), 110.5 (*C*), 122.5 (*C*), 123.2 (q, ^2J=32.8 Hz, *C*CF$_3$), 124.1 (q, ^1J=274.6 Hz, *C*F$_3$), 125.2 (*C*H), 128.0 (*C*H), 130.4 (*C*H), 131.5 (*C*), 133.3 (q, J=2.3 Hz, *C*), 138.3 (*C*), 144.1 (*C*), 146.9 (*C*), 156.9 (*C*OH), 170.5 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3429 (w), 2961 (w), 2938 (w), 2920 (w), 2875 (w), 2853 (w), 2782 (w), 1710 (m), 1599 (w), 1583 (w), 1481 (w), 1463 (w), 1454 (w), 1436 (m), 1421 (w), 1396 (m), 1369 (m), 1325 (m), 1310 (m), 1291 (m), 1268 (m), 1217 (m), 1193 (m), 1157 (m), 1134 (m), 1109 (s), 1069 (m), 1057 (m), 1025 (m); MS (EI, 70 eV): *m*/*z* (%)=416 (^{81}Br, M^+, 44), 414 (^{79}Br, M^+, 47), 384 (42), 382 (42), 364 (15), 362 (15), 303 (100), 275 (20); HRMS (EI, 70 eV): calcd for $C_{18}H_{14}^{79}BrF_3O_3$ (M^+): 414.00729, found 414.00710; calcd for $C_{18}H_{14}^{81}BrF_3O_3$ (M^+): 416.00525, found 416.00544. Anal. Calcd for $C_{18}H_{14}BrF_3O_3$ (415.20): C, 52.07; H, 3.40. Found: C, 52.25; H, 3.12.

*4.3.12. Methyl 7-bromo-3-hydroxy-4-n-propyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5l**).* Starting with silyl enol ether **3b** (0.560 g, 1.48 mmol), 1,3-bis-silyl enol ether **4d** (0.499 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5l** was isolated as a colourless solid (0.381 g, 60%); mp=127–129 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.11 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 1.61–1.77 (m, 2H, CH_2CH$_3$), 3.06–3.14 (m, 2H, ArCH_2CH$_2$), 3.98 (s, 3H, OCH_3), 4.03–4.07 (m, 2H, CH_2), 7.55 (dd, ^3J=8.5 Hz, ^4J=1.9 Hz, 1H, Ar*H*), 7.69–7.71 (m, 1H, Ar*H*), 7.75 (d, ^3J=8.5 Hz, 1H, Ar*H*), 9.72 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−56.0 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.3 (ArCH_3), 21.5 (*C*H$_2$), 27.9 (*C*H$_2$), 36.7 (q, J=4.0 Hz, ArCH_2Ar), 53.0 (O*C*H$_3$), 110.5 (*C*), 122.5 (*C*), 123.2 (q, ^2J=32.5 Hz, *C*CF$_3$), 124.1 (q, ^1J=274.4 Hz, *C*F$_3$), 125.1 (*C*H), 128.0 (*C*H), 130.3 (*C*), 130.4 (*C*H), 133.3 (q, J=2.2 Hz, *C*), 138.4 (*C*), 144.3 (*C*), 146.9 (q, J=0.8 Hz, *C*), 157.0 (*C*OH), 170.5 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3425 (w), 2957 (w), 2934 (w), 2875 (w), 1711 (m), 1599 (w), 1582 (w), 1477 (w), 1468 (w), 1454 (w), 1438 (m), 1420 (w), 1398 (m), 1373 (m), 1331 (m), 1311 (m), 1278 (m), 1251 (m), 1216 (m), 1193 (m), 1157 (m), 1135 (m), 1113 (s), 1073 (m), 1040 (m), 1011 (m); MS (EI, 70 eV): *m*/*z* (%)=430 (^{81}Br, M^+, 43), 428 (^{79}Br, M^+, 41), 398 (29), 396 (27), 369 (30), 367 (28), 317 (100), 289 (14), 232 (25); HRMS (EI, 70 eV): calcd for $C_{19}H_{16}^{79}BrF_3O_3$ (M^+): 428.02294, found 428.02296; calcd for $C_{19}H_{16}^{81}BrF_3O_3$ (M^+): 430.02090, found 430.02086. Anal. Calcd for $C_{19}H_{16}BrF_3O_3$ (429.23): C, 53.17; H, 3.76. Found: C, 52.89; H, 3.82.

*4.3.13. Methyl 3-hydroxy-7-methoxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5m**).* Starting with silyl enol ether **3c** (0.500 g, 1.51 mmol), 1,3-bis-silyl enol ether **4a** (0.430 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5m** was isolated as a orange solid (0.355 g, 69%); mp=134–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.87 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 3.99–4.04 (m, 2H, CH_2), 6.94 (dd, ^3J=8.5 Hz, ^4J=2.3 Hz, 1H, Ar*H*), 7.03–7.06 (m, 1H, Ar*H*), 7.38 (s, 1H, Ar*H*), 7.65 (d, ^3J=8.4 Hz, 1H, Ar*H*), 9.89 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−56.0 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$):

δ=37.3 (q, J=4.2 Hz, CH_2), 52.8 (OCH_3), 55.5 (OCH_3), 109.2 (q, ^3J=2.2 Hz, C), 109.7 (CH), 110.6 (CH), 114.0 (CH), 122.0 (CH), 124.1 (q, ^1J=274.8 Hz, CF_3), 126.0 (q, ^2J=32.6 Hz, CCF_3), 131.6 (C), 133.3 (q, J=2.5 Hz, C), 146.6 (q, J=1.8 Hz, C), 148.4 (C), 160.0 (COR), 161.1 (COR), 170.2 (CO); IR (ATR, cm^{-1}): $\tilde{\nu}$=3401 (w), 3020 (w), 2961 (w), 2935 (w), 2910 (w), 2838 (w), 1706 (w), 1652 (m), 1610 (m), 1594 (m), 1494 (m), 1450 (m), 1417 (m), 1403 (m), 1379 (m), 1331 (m), 1285 (m), 1267 (m), 1248 (m), 1212 (m), 1186 (m), 1151 (m), 1135 (m), 1121 (s), 1107 (s), 1092 (s), 1028 (m); HRMS (ESI, TOF/MS): calcd for $C_{17}H_{12}F_3O_4$ ($(M-H)^-$): 337.06932, found 337.06944.

*4.3.14. Methyl 3-hydroxy-7-methoxy-4-methyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5n**).* Starting with silyl enol ether **3c** (0.536 g, 1.62 mmol), 1,3-bis-silyl enol ether **4b** (0.494 g, 1.80 mmol) and $TiCl_4$ (0.20 mL, 1.80 mmol) in CH_2Cl_2 (3 mL), product **5n** was isolated as a pale yellow solid (0.287 g, 50%); mp=140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.62 (s, 3H, $ArCH_3$), 3.88 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.00–4.05 (m, 2H, CH_2), 6.95 (dd, ^3J=8.7 Hz, ^4J=2.5 Hz, 1H, ArH), 7.08 (d, ^4J=2.7 Hz, 1H, ArH), 7.91 (d, ^3J=8.7 Hz, 1H, ArH), 9.98 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.7 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.3 ($ArCH_3$), 37.0 (q, J=4.1 Hz, CH_2), 52.8 (OCH_3), 55.4 (OCH_3), 108.5 (q, ^3J=2.3 Hz, C), 109.7 (CH), 113.3 (CH), 122.6 (q, ^2J=32.4 Hz, CCF_3), 123.5 (C), 124.3 (q, ^1J=274.4 Hz, CF_3), 125.2 (CH), 132.9 (q, J=2.4 Hz, C), 133.0 (C), 145.9 (C), 147.1 (C), 157.3 (COR), 160.1 (COR), 170.8 (CO); IR (ATR, cm^{-1}): $\tilde{\nu}$=3082 (w), 3039 (w), 3001 (w), 2956 (w), 2937 (w), 2837 (w), 1738 (w), 1663 (m), 1620 (m), 1593 (m), 1490 (w), 1478 (w), 1456 (m), 1435 (m), 1408 (w), 1388 (m), 1362 (m), 1345 (m), 1305 (m), 1291 (m), 1254 (m), 1218 (m), 1166 (m), 1133 (m), 1111 (s), 1039 (m), 1028 (m), 1005 (m); MS (EI, 70 eV): m/z (%)=352 (M^+, 78), 320 (61), 300 (100), 249 (16); HRMS (EI, 70 eV): calcd for $C_{18}H_{15}F_3O_4$ (M^+): 352.09170, found 352.09187.

*4.3.15. Methyl 4-ethyl-3-hydroxy-7-methoxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5o**).* Starting with silyl enol ether **3c** (0.494 g, 1.50 mmol), 1,3-bis-silyl enol ether **4c** (0.476 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5o** was isolated as a colourless solid (0.201 g, 37%); mp=140–141 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.31 (t, ^3J=7.5 Hz, 3H, CH_2CH_3), 3.17 (q, ^3J=7.5 Hz, 2H, CH_2CH_3), 3.89 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.07 (s, 2H, CH_2), 6.97 (dd, ^3J=8.7 Hz, ^4J=2.5 Hz, 1H, ArH), 7.09 (d, ^4J=2.3 Hz, 1H, ArH), 7.88 (d, ^3J=8.7 Hz, 1H, ArH), 9.87 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.8 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.4 ($ArCH_2CH_3$), 19.3 ($ArCH_2CH_3$), 37.1 (q, J=4.1 Hz, CH_2), 52.8 (OCH_3), 55.5 (OCH_3), 108.8 (C), 109.8 (CH), 113.7 (CH), 122.8 (q, ^2J=32.4 Hz, CCF_3), 124.4 (q, ^1J=274.1 Hz, CF_3), 125.0 (CH), 129.9 (C), 132.3 (C), 133.4 (q, J=2.5 Hz, C), 145.3 (C), 147.3 (C), 157.1 (COR), 160.2 (COR), 170.8 (CO); IR (ATR, cm^{-1}): $\tilde{\nu}$=3075 (w), 3039 (w), 3007 (w), 2955 (w), 2933 (w), 2873 (w), 2845 (w), 1670 (m), 1619 (w), 1595 (w), 1492 (w), 1467 (w), 1436 (w), 1402 (w), 1372 (m), 1342 (m), 1305 (m), 1272 (m), 1263 (m), 1241 (m), 1214 (m), 1193 (w), 1161 (m), 1118 (s), 1068 (w), 1062 (w), 1039 (m), 1026 (m); MS (EI, 70 eV): m/z (%)=366 (M^+, 100), 319 (25), 306 (77), 291 (18); HRMS (EI, 70 eV): calcd for $C_{19}H_{17}F_3O_4$ (M^+): 366.10735, found 366.10708. Anal. Calcd for $C_{19}H_{17}F_3O_4$ (366.33): C, 62.29; H, 4.68. Found: C, 62.46; H, 4.90.

*4.3.16. Methyl 3-hydroxy-7-methoxy-4-n-propyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**5p**).* Starting with silyl enol ether **3c** (0.498 g, 1.51 mmol), 1,3-bis-silyl enol ether **4d** (0.499 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5p** was isolated as a pale yellow solid (0.249 g, 43%); mp=98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.12 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 1.63–1.79 (m, 2H, CH_2CH_3), 3.05–3.14 (m, 2H, $ArCH_2CH_2$), 3.88 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 4.02–4.06 (m, 2H, $ArCH_2Ar$), 6.97 (dd, ^3J=8.7 Hz, ^4J=2.5 Hz, 1H, ArH), 7.08 (d, ^4J=2.4 Hz, 1H, ArH), 7.81 (d, ^3J=8.7 Hz, 1H, ArH), 9.86 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.8 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.3 ($ArCH_3$), 21.4 (CH_2), 27.8 (CH_2), 37.1 (q, J=4.1 Hz, $ArCH_2Ar$), 52.8 (OCH_3), 55.5 (OCH_3), 108.7 (q, J=2.4 Hz, C), 109.7 (CH), 113.6 (CH), 122.8 (q, ^2J=32.2 Hz, CCF_3), 124.3 (q, ^1J=274.7 Hz, CF_3), 124.9 (CH), 128.7 (C), 132.4 (C), 133.4 (q, J=2.3 Hz, C), 145.5 (C), 147.3 (C), 157.3 (COR), 160.1 (COR), 170.8 (CO); IR (ATR, cm^{-1}): $\tilde{\nu}$=3338 (w), 3082 (w), 3005 (w), 2947 (w), 2928 (w), 2867 (w), 2843 (w), 2727 (w), 1738 (w), 1698 (m), 1687 (m), 1620 (m), 1598 (m), 148 (w), 1469 (m), 1441 (w), 1403 (w), 1373 (m), 1334 (m), 1310 (m), 1286 (m), 1255 (m), 1210 (m), 1163 (m), 1152 (m), 1109 (s), 1034 (m), 1007 (m); MS (EI, 70 eV): m/z (%)=380 (M^+, 100), 347 (18), 320 (100), 305 (13); HRMS (EI, 70 eV): calcd for $C_{20}H_{19}F_3O_4$ (M^+): 380.12300, found 380.12296. Anal. Calcd for $C_{20}H_{19}F_3O_4$ (380.36): C, 63.15; H, 5.03. Found: C, 62.93; H, 5.06.

*4.3.17. Methyl 2-hydroxy-4-(trifluoromethyl)dibenzo[b,d]furane-1-carboxylate (**5q**).* Starting with silyl enol ether **3d** (0.487 g, 1.61 mmol), 1,3-bis-silyl enol ether **4a** (0.469 g, 1.80 mmol) and $TiCl_4$ (0.20 mL, 1.80 mmol) in CH_2Cl_2 (3 mL), product **5q** was isolated as a colourless solid (0.221 g, 44%); mp=143–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.22 (s, 3H, OCH_3), 7.33–7.41 (m, 2H, ArH), 7.55 (dd, ^3J=8.2 Hz, ^3J=7.2 Hz, 1H, ArH), 7.65 (d, J=8.3 Hz, 1H, ArH), 8.33 (d, J=8.3 Hz, 1H, ArH), 11.21 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−62.4 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.6 (OCH_3), 108.8 (C), 112.2 (CH), 114.7 (q, ^3J=4.7 Hz, CH), 120.9 (q, ^2J=34.7 Hz, CCF_3), 122.2 (q, ^1J=272.9 Hz, CF_3), 122.4 (C), 123.1 (CH), 124.6 (CH), 125.2 (C), 128.8 (CH), 145.5 (C), 157.5 (C), 158.4 (COH), 170.1 (CO); IR (ATR, cm^{-1}): $\tilde{\nu}$=3141 (w), 3082 (w), 2970 (w), 1672 (m), 1626 (m), 1587 (w), 1504 (m), 1476 (m), 1447 (m), 1408 (m), 1358 (m), 1319 (m), 1279 (m), 1269 (m), 1246 (w), 1215 (s), 1176 (m), 1160 (m), 1146 (m), 1125 (s), 1115 (s), 1092 (s), 1026 (m), 1015 (m); MS (EI, 70 eV): m/z (%)=310 (M^+, 33), 278 (100), 250 (38); HRMS (EI, 70 eV): calcd for $C_{15}H_9F_3O_4$ (M^+): 310.04474, found 310.04476. Anal. Calcd for $C_{15}H_9F_3O_4$ (310.23): C, 58.07; H, 2.92. Found: C, 57.63; H, 2.90.

*4.3.18. Methyl 2-hydroxy-3-methyl-4-(trifluoromethyl)dibenzo[b,d]furane-1-carboxylate (**5r**).* Starting with silyl enol ether **3d** (0.457 g, 1.51 mmol), 1,3-bis-silyl enol ether **4b** (0.453 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5r** was isolated as a colourless solid (0.236 g, 48%); mp=126–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.52 (q, J=2.2 Hz, 3H, $ArCH_3$), 4.20 (s, 3H, OCH_3), 7.32 (ddd, ^3J=8.3 Hz, ^3J=7.1 Hz, ^4J=1.2 Hz, 1H, ArH), 7.50 (ddd, ^3J=8.3 Hz, ^3J=7.2 Hz, ^4J=1.2 Hz, 1H, ArH), 7.60 (d, ^3J=8.3 Hz, 1H, ArH), 8.22 (d, ^3J=8.3 Hz, 1H, ArH), 11.64 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.7 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.6 (q, J=3.1 Hz, $ArCH_3$), 52.5 (OCH_3), 107.5 (C), 111.9 (CH), 119.7 (q, ^2J=31.9 Hz, CCF_3), 121.4 (C), 122.3 (C), 122.8 (CH), 123.5 (q, ^1J=276.0 Hz, CF_3), 124.7 (CH), 126.5 (q, J=2.0 Hz, C), 128.1 (CH), 145.9 (C), 156.8 (C), 157.3 (COH), 170.7 (CO); IR (ATR, cm^{-1}): $\tilde{\nu}$=2959 (w), 1658 (m), 1626 (w), 1505 (w), 1471 (m), 1446 (m), 1406 (m), 1382 (m), 1356 (m), 1320 (m), 1291 (m), 1259 (m), 1235 (m), 1206 (m), 1186 (m), 1133 (s), 1105 (m), 1032 (m), 1016 (m); MS (EI, 70 eV): m/z (%)=324 (M^+, 48), 292 (100), 264 (44), 236 (50), 217 (11); HRMS (EI, 70 eV): calcd for $C_{16}H_{11}F_3O_4$ (M^+): 324.06039, found 324.06044.

*4.3.19. Methyl 3-ethyl-2-hydroxy-4-(trifluoromethyl)dibenzo[b,d]furane-1-carboxylate (**5s**).* Starting with silyl enol ether **3d** (0.455 g, 1.50 mmol), 1,3-bis-silyl enol ether **4c** (0.476 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5s** was isolated as a colourless solid (0.156 g, 31%); mp=144–145 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.28 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 3.01 (qq, ^3J=7.4 Hz, J=1.5 Hz, 2H, CH_2CH_3), 4.21 (s, 3H, OCH_3), 7.33 (ddd, ^3J=8.3 Hz, ^3J=7.2 Hz, ^4J=1.2 Hz, 1H, ArH), 7.50 (ddd, ^3J=8.4 Hz, ^3J=7.2 Hz, ^4J=1.3 Hz, 1H, ArH), 7.61 (d, ^3J=8.5 Hz, 1H, ArH), 8.24 (d, ^3J=8.3 Hz, 1H, ArH), 11.62 (s, 1H, OH); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.1 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1 (CH_2CH_3), 20.8 (q, J=2.7 Hz, $ArCH_2$), 52.5 (OCH_3), 107.8 (C), 111.9 (CH), 119.3 (q,

^2J=32.0 Hz, *C*CF_3), 121.6 (*C*), 122.3 (*C*), 122.8 (*C*H), 123.6 (q, ^1J=276.1 Hz, *C*F_3), 124.7 (*C*H), 128.2 (*C*H), 132.6 (q, *J*=1.9 Hz, *C*), 146.1 (*C*), 156.8 (*C*), 157.3 (*C*OH), 170.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3431 (w), 3142 (w), 3055 (w), 3012 (w), 2970 (w), 2960 (w), 2939 (w), 2878 (w), 1712 (w), 1667 (m), 1633 (w), 1621 (w), 1600 (w), 1582 (w), 1494 (w), 1455 (m), 1438 (m), 1397 (m), 1347 (m), 1273 (m), 1223 (m), 1202 (m), 1150 (m), 1138 (m), 1116 (s), 1075 (m), 1059 (m), 1035 (m), 1016 (m), 1001 (m); MS (EI, 70 eV): *m*/*z* (%)=338 (M^+, 53), 306 (100), 291 (19), 278 (75), 260 (25), 235 (17); HRMS (EI, 70 eV): calcd for $C_{17}H_{13}F_3O_4$ (M^+): 338.07604, found 338.07611. Anal. Calcd for $C_{17}H_{13}F_3O_4$ (338.28): C, 60.36; H, 3.87. Found: C, 60.23; H, 3.87.

*4.3.20. Methyl 2-hydroxy-3-n-propyl-4-(trifluoromethyl)dibenzo [b,d]furane-1-carboxylate (**5t**).* Starting with silyl enol ether **3d** (0.447 g, 1.48 mmol), 1,3-bis-silyl enol ether **4d** (0.499 g, 1.65 mmol) and $TiCl_4$ (0.18 mL, 1.65 mmol) in CH_2Cl_2 (3 mL), product **5t** was isolated as a colourless solid (0.265 g, 51%); mp=167–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.07 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 1.58–1.75 (m, 2H, CH_2CH_3), 2.89–2.99 (m, 2H, ArCH_2), 4.21 (s, 3H, OCH_3), 7.33 (ddd, ^3J=8.2 Hz, ^3J=7.1 Hz, ^4J=1.2 Hz, 1H, Ar*H*), 7.50 (ddd, ^3J=8.3 Hz, ^3J=7.1 Hz, ^4J=1.3 Hz, 1H, Ar*H*), 7.61 (d, ^3J=8.2 Hz, 1H, Ar*H*), 8.25 (d, ^3J=8.2 Hz, 1H, Ar*H*), 11.63 (s, 1H, O*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.1 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.5 (CH_2CH_3), 23.2 (CH_2CH_3), 29.4 (q, *J*=2.6 Hz, ArCH_2), 52.5 (OCH_3), 107.7 (*C*), 111.9 (*C*H), 119.4 (q, ^2J=31.9 Hz, *C*CF_3), 121.6 (*C*), 122.4 (*C*), 122.8 (*C*H), 123.6 (q, ^1J=276.2 Hz, *C*F_3), 124.7 (*C*H), 128.1 (*C*H), 131.4 (q, *J*=1.8 Hz, *C*), 146.1 (*C*), 156.8 (*C*), 157.5 (*C*OH), 170.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3052 (w), 3015 (w), 2961 (w), 2933 (w), 2875 (w), 1667 (m), 1621 (w), 1599 (w), 1582 (w), 1489 (w), 1469 (m), 1450 (m), 1440 (m), 1396 (m), 1347 (m), 1320 (m), 1272 (m), 1231 (m), 1213 (m), 1201 (m), 1150 (m), 1134 (m), 1117 (s), 1106 (s), 1084 (s), 1038 (m); MS (EI, 70 eV): *m*/*z* (%)=352 (M^+, 75), 320 (98), 291 (100), 251 (44), 235 (41), 206 (15); HRMS (EI, 70 eV): calcd for $C_{18}H_{15}F_3O_4$ (M^+): 352.09170, found 352.09202. Anal. Calcd for $C_{18}H_{15}F_3O_4$ (352.31): C, 61.37; H, 4.29. Found: C, 61.30; H, 3.89.

*4.3.21. Methyl 3-hydroxy-1-(trifluoromethyl)-9,10-dihydrophenanthrene-4-carboxylate (**5u**).* Starting with silyl enol ether **3e** (0.606 g, 1.93 mmol), 1,3-bis-silyl enol ether **4a** (0.573 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5u** was isolated as a pale yellow solid (0.097 g, 16%); mp=102–103 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.83 (s, 4H, CH_2), 3.68 (s, 3H, OCH_3), 7.06–7.11 (m, 1H, Ar*H*), 7.19–7.33 (m, 4H, Ar*H*), 9.28 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−61.5 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.8 (q, *J*=2.3 Hz, CH_2), 28.6 (CH_2), 52.1 (OCH_3), 113.9 (q, *J*=6.0 Hz, *C*H), 114.7 (*C*), 125.9 (*C*H), 127.3 (*C*H), 128.3 (*C*H), 128.7 (*C*H), 129.5 (*C*), 132.3 (q, ^2J=30.3 Hz, *C*CF_3), 133.2 (*C*), 138.2 (*C*), 138.7 (*C*), 157.4 (*C*OH), 171.2 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3334 (w), 3064 (w), 3032 (w), 3016 (w), 2955 (w), 2907 (w), 2853 (w), 1733 (m), 1609 (w), 1595 (w), 1574 (w), 1502 (w), 1456 (w), 1435 (m), 1412 (m), 1359 (m), 1334 (m), 1275 (m), 1264 (m), 1239 (m), 1219 (m), 1204 (m), 1193 (m), 1172 (m), 1146 (s), 1108 (s), 1093 (s), 1043 (m); MS (EI, 70 eV): *m*/*z* (%)=322 (M^+, 32), 290 (100), 262 (13), 233 (14), 165 (26); HRMS (EI, 70 eV): calcd for $C_{17}H_{13}F_3O_3$ (M^+): 322.08113, found 322.08111.

*4.3.22. Methyl 3-hydroxy-1-(trifluoromethyl)-9,10-dihydrophenanthrene-2-carboxylate (**5v**).* Starting with silyl enol ether **3e** (0.606 g, 1.93 mmol), 1,3-bis-silyl enol ether **4a** (0.573 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5v** was isolated as a colourless solid (0.196 g, 32%); mp=134–135 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=2.78–2.85 (m, 2H, CH_2), 2.94–3.02 (m, 2H, CH_2), 3.97 (s, 3H, OCH_3), 7.24–7.29 (m, 1H, Ar*H*), 7.30–7.37 (m, 2H, Ar*H*), 7.55 (s, 1H, Ar*H*), 7.68–7.73 (m, 1H, Ar*H*), 8.62 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−54.6 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=26.0 (q, *J*=3.7 Hz, CH_2), 28.4 (CH_2), 53.0 (OCH_3), 113.0 (q, *J*=2.8 Hz, *C*), 115.7 (*C*H), 123.9 (q, ^1J=275.1 Hz, *C*F_3), 124.7 (*C*H), 127.3 (*C*H), 127.5 (q, ^2J=30.4 Hz, *C*CF_3), 127.9 (*C*H), 129.2 (*C*H), 130.5 (*C*), 132.4 (*C*), 137.9 (*C*), 140.6 (*C*), 156.1 (*C*OH), 169.4 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3318 (m), 3027 (w), 2964 (w), 2905 (w), 2855 (w), 1699 (m), 1605 (m), 1573 (w), 1491 (w), 1439 (m), 1425 (m), 1327 (m), 1309 (m), 1280 (m), 1246 (m), 1217 (m), 1197 (m), 1186 (m), 1163 (m), 1145 (s), 1122 (s), 1042 (m), 1002 (m); MS (EI, 70 eV): *m*/*z* (%)=322 (M^+, 48), 290 (100), 262 (19), 215 (20), 165 (27); HRMS (EI, 70 eV): calcd for $C_{17}H_{13}F_3O_3$ (M^+): 322.08113, found 322.08123. Anal. Calcd for $C_{17}H_{13}F_3O_3$ (322.28): C, 63.36; H, 4.07. Found: C, 63.13; H, 4.14.

*4.3.23. Methyl 9-hydroxy-7-(trifluoromethyl)-6H-benzo[c]chromene-10-carboxylate (**5w**).* Starting with silyl enol ether **3f** (0.622 g, 1.98 mmol), 1,3-bis-silyl enol ether **4a** (0.573 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5w** was isolated as a colourless solid (0.112 g, 18%); mp=115–117 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.75 (s, 3H, OCH_3), 5.02–5.07 (m, 2H, CH_2), 6.97–7.19 (m, 3H, Ar*H*), 7.23–7.36 (m, 2H, Ar*H*), 9.31 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−61.4 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.3 (OCH_3), 65.4 (q, *J*=3.7 Hz, CH_2), 113.8 (q, ^3J=5.7 Hz, *C*H), 113.8 (*C*), 117.6 (*C*H), 121.6 (*C*H), 122.6 (*C*), 123.1 (q, ^1J=274.3 Hz, *C*F_3), 125.7 (*C*), 128.2 (*C*H), 130.2 (q, ^2J=31.9 Hz, *C*CF_3), 130.5 (*C*H), 133.7 (*C*), 156.0 (*C*), 158.4 (*C*OH), 170.4 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3235 (w), 3080 (w), 3034 (w), 2958 (w), 2923 (w), 2896 (w), 2855 (w), 1677 (m), 1606 (m), 1581 (m), 1494 (m), 1472 (m), 1441 (m), 1428 (m), 1386 (w), 1351 (m), 1309 (m), 1277 (m), 1235 (m), 1209 (m), 1177 (m), 1158 (m), 1152 (m), 1124 (s), 1112 (s), 1101 (s), 1040 (m), 1027 (m), 1010 (m); MS (EI, 70 eV): *m*/*z* (%)=324 (M^+, 48), 292 (100), 264 (18), 236 (15); HRMS (EI, 70 eV): calcd for $C_{16}H_{11}F_3O_4$ (M^+): 324.06039, found 324.06009. Anal. Calcd for $C_{16}H_{11}F_3O_4$ (324.25): C, 59.27; H, 3.42. Found: C, 59.37; H, 3.83.

*4.3.24. Methyl 9-hydroxy-7-(trifluoromethyl)-6H-benzo[c]chromene-8-carboxylate (**5x**).* Starting with silyl enol ether **3f** (0.622 g, 1.98 mmol), 1,3-bis-silyl enol ether **4a** (0.573 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5x** was isolated as a pale yellow solid (0.309 g, 48%); mp=152–153 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=3.97 (s, 3H, OCH_3), 5.17 (q, *J*=1.8 Hz, 2H, CH_2), 6.93–7.16 (m, 2H, Ar*H*), 7.28–7.38 (m, 1H, Ar*H*), 7.48 (s, 1H, Ar*H*), 7.69 (dd, ^3J=7.8 Hz, ^4J=1.5 Hz, 1H, Ar*H*), 9.04 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−54.2 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=53.1 (OCH_3), 65.5 (q, *J*=6.6 Hz, CH_2), 113.0 (q, ^3J=2.8 Hz, *C*), 114.0 (*C*H), 117.5 (*C*H), 121.0 (*C*), 122.7 (*C*H), 123.5 (q, ^1J=275.8 Hz, *C*F_3), 124.1 (*C*H), 124.6 (*C*), 126.4 (q, ^2J=32.0 Hz, *C*CF_3), 131.4 (*C*H), 136.3 (*C*), 155.3 (*C*), 157.7 (*C*OH), 169.0 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3307 (w), 3069 (w), 3024 (w), 2962 (w), 2923 (w), 2851 (w), 1698 (m), 1607 (m), 1503 (w), 1483 (m), 1462 (m), 1443 (m), 1423 (m), 1385 (w), 1367 (m), 1332 (m), 1306 (m), 1275 (m), 1260 (m), 1223 (m), 1188 (m), 1150 (m), 1127 (s), 1116 (m), 1045 (m), 1002 (m); MS (EI, 70 eV): *m*/*z* (%)=324 (M^+, 100), 292 (83), 263 (26), 236 (20), 223 (36); HRMS (EI, 70 eV): calcd for $C_{16}H_{11}F_3O_4$ (M^+): 324.06039, found 324.05948. Anal. Calcd for $C_{16}H_{11}F_3O_4$ (324.25): C, 59.27; H, 3.42. Found: C, 58.94; H, 3.64.

*4.3.25. Methyl 10-ethyl-9-hydroxy-7-(trifluoromethyl)-6H-benzo[c] chromene-8-carboxylate (**5y**).* Starting with silyl enol ether **3f** (0.620 g, 1.97 mmol), 1,3-bis-silyl enol ether **4c** (0.635 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5y** was isolated as a yellow solid (0.363 g, 53%); mp=102–103 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.46 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 2.97 (q, ^3J=7.4 Hz, 2H, CH_2CH_3), 3.97 (s, 3H, OCH_3), 5.01 (q, *J*=1.7 Hz, 2H, CH_2), 7.06–7.18 (m, 2H, Ar*H*), 7.35 (ddd, ^3J=7.7 Hz, ^3J=7.7 Hz, ^4J=1.5 Hz, 1H, Ar*H*), 7.72 (dd, ^3J=7.7 Hz, ^4J=1.2 Hz, 1H, Ar*H*), 9.24 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−53.8 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 ($ArCH_2CH_3$), 21.6 ($ArCH_2CH_3$), 53.1 (OCH_3), 66.9 (q, *J*=6.3 Hz, CH_2), 111.9 (q, ^3J=2.6 Hz, *C*), 117.5 (*C*H), 122.0 (*C*H), 122.8 (*C*), 123.2 (q,

^{2}J=31.9 Hz, *C*CF_3), 123.9 (q, ^{1}J=275.0 Hz, *C*F_3), 127.9 (*C*), 128.0 (*C*H), 130.4 (*C*H), 132.7 (*C*), 134.7 (*C*), 156.6 (*C*), 157.4 (*C*OH), 169.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3270 (w), 3043 (w), 3009 (w), 2961 (w), 2930 (w), 2871 (w), 1934 (w), 1688 (m), 1592 (m), 1489 (w), 1438 (m), 1410 (m), 1339 (m), 1280 (m), 1267 (m), 1236 (s), 1201 (m), 1165 (m), 1125 (s), 1112 (s), 1061 (m), 1041 (m), 1027 (m), 1001 (m); MS (EI, 70 eV): *m*/*z* (%)=352 (M^+, 84), 319 (15), 292 (100), 249 (10); HRMS (EI, 70 eV): calcd for $C_{18}H_{15}F_3O_4$ (M^+): 352.09170, found 352.09095. Anal. Calcd for $C_{18}H_{15}F_3O_4$ (352.31): C, 61.37; H, 4.29. Found: C, 60.90; H, 4.43.

*4.3.26. Methyl 9-hydroxy-10-n-propyl-7-(trifluoromethyl)-6H-benzo[c]chromene-8-carboxylate (**5z**).* Starting with silyl enol ether **3f** (0.633 g, 2.01 mmol), 1,3-bis-silyl enol ether **4d** (0.666 g, 2.20 mmol) and $TiCl_4$ (0.24 mL, 2.20 mmol) in CH_2Cl_2 (4 mL), product **5z** was isolated as a brownish solid (0.371 g, 51%); mp=112–113 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.12 (t, ^{3}J=6.3 Hz, 3H, CH_2CH_3), 1.76–1.95 (m, 2H, CH_2CH_3), 2.79–2.93 (m, 2H, ArCH_2), 3.97 (s, 3H, OCH_3), 5.01 (q, *J*=1.6 Hz, 2H, CH_2), 7.07–7.18 (m, 2H, Ar*H*), 7.35 (ddd, ^{3}J=7.7 Hz, ^{3}J=7.7 Hz, ^{4}J=1.5 Hz, 1H, Ar*H*), 7.64 (dd, ^{3}J=7.8 Hz, ^{4}J=1.4 Hz, 1H, Ar*H*), 9.24 (s, 1H, O*H*); ^{19}F NMR (235 MHz, $CDCl_3$): δ=−53.7 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.3 (CH_2CH_3), 22.5 (CH_2CH_3), 30.4 (ArCH_2), 53.1 (OCH_3), 66.8 (q, *J*=6.3 Hz, CH_2), 111.9 (q, ^{3}J=2.5 Hz, *C*), 117.5 (*C*H), 121.9 (*C*H), 122.8 (*C*), 123.2 (q, ^{2}J=31.8 Hz, *C*CF_3), 123.8 (q, ^{1}J=275.3 Hz, *C*F_3), 128.0 (*C*H), 130.4 (*C*H), 131.7 (*C*), 134.8 (*C*), 136.6 (*C*), 156.6 (*C*), 157.4 (*C*OH), 169.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3291 (w), 3042 (w), 3011 (w), 2963 (w), 2928 (w), 2866 (w), 1936 (w), 1693 (m), 1593 (m), 1558 (w), 1490 (m), 1473 (m), 1451 (m), 1438 (m), 1412 (m), 1347 (m), 1327 (m), 1299 (m), 1233 (m), 1201 (m), 1125 (s), 1113 (s), 1040 (m), 1015 (m); MS (EI, 70 eV): *m*/*z* (%)=366 (M^+, 56), 333 (8), 317 (7), 306 (100), 291 (14); HRMS (EI, 70 eV): calcd for $C_{19}H_{17}F_3O_4$ (M^+): 366.10735, found 366.10679. Anal. Calcd for $C_{19}H_{17}F_3O_4$ (366.33): C, 62.29; H, 4.68. Found: C, 61.77; H, 4.82.

4.4. General procedure for the synthesis of triflates 6a–e

To a stirred solution of benzoate (1.0 equiv) in CH_2Cl_2 (10 mL per 1.0 mmol of benzoate) pyridine (2.0 equiv) was added at −78 °C and the reaction mixture was stirred for 10 min followed by addition of trifluoromethanesulfonic anhydride (1.2 equiv). The temperature of the reaction mixture was allowed to rise to 0 °C over a period of 4 h. The solvent was removed in vacuo and the residue was purified by column chromatography (silica gel, CH_2Cl_2).

*4.4.1. Methyl 1-(trifluoromethyl)-3-(trifluoromethanesulfonyloxy)-9H-fluorene-2-carboxylate (**6a**).* Starting with benzoate **5a** (0.094 g, 0.305 mmol), pyridine (0.047 g, 0.6 mmol) and trifluoromethanesulfonic anhydride (0.102 g, 0.36 mmol) in CH_2Cl_2 (3 mL), product **6a** was isolated as a colourless solid (0.125 g, 95%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.00 (s, 3H, OCH_3), 4.15 (s, 2H, CH_2), 7.43–7.50 (m, 2H, Ar*H*), 7.59–7.63 (m, 1H, Ar*H*), 7.80–7.84 (m, 1H, Ar*H*), 7.86 (s, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−58.7 (CF_3), −73.6 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.9 (CH_2), 53.4 (OCH_3), 115.7 (*C*H), 120.9 (*C*H), 123.9 (*C*), 125.2 (*C*H), 126.0 (q, ^{2}J=33.4 Hz, *C*CF_3), 127.6 (*C*H), 129.6 (*C*H), 137.9 (*C*), 141.2 (*C*), 143.6 (*C*), 145.7 (*C*), 146.6 (*C*), 164.0 (*C*O).

*4.4.2. Methyl 7-methoxy-1-(trifluoromethyl)-3-(trifluoromethanesulfonyloxy)-9H-fluorene-2-carboxylate (**6b**).* Starting with benzoate **5m** (0.196 g, 0.579 mmol), pyridine (0.092 g, 1.16 mmol) and trifluoromethanesulfonic anhydride (0.197 g, 0.7 mmol) in CH_2Cl_2 (6 mL), product **6b** was isolated as a colourless solid (0.266 g, 98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.89 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2), 6.99 (dd, ^{3}J=8.5 Hz, ^{4}J=2.4 Hz, 1H, Ar*H*), 7.11 (d, ^{4}J=2.3 Hz, 1H, Ar*H*), 7.67–7.73 (m, 2H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−73.6 (CF_3), −58.7 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=36.9 (q, ^{4}J=2.6 Hz, CH_2), 53.4 (OCH_3), 55.6 (OCH_3), 110.1 (*C*H), 114.3 (*C*H), 114.6 (*C*H), 121.9 (*C*H), 122.6 (*C*), 125.7 (q, ^{2}J=33.5 Hz, *C*CF_3), 130.8 (*C*), 140.6 (q, ^{3}J=2.0 Hz, *C*), 145.8 (*C*), 145.9 (*C*), 146.7 (*C*), 161.4 (*C*), 164.1 (*C*O).

*4.4.3. Methyl 4-(trifluoromethyl)-2-(trifluoromethanesulfonyloxy)-dibenzo[b,d]furan-1-carboxylate (**6c**).* Starting with benzoate **5q** (0.161 g, 0.52 mmol), pyridine (0.082 g, 1.04 mmol) and trifluoromethanesulfonic anhydride (0.176 g, 0.62 mmol) in CH_2Cl_2 (5 mL), the product **6c** was isolated as a colourless solid (0.211 g, 92%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=4.16 (s, 3H, OCH_3), 7.39–7.48 (m, 1H, Ar*H*), 7.58–7.73 (m, 3H, Ar*H*), 8.18 (d, ^{3}J=8.0 Hz, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−73.2 (CF_3), −61.7 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=53.3 (OCH_3), 112.3 (*C*H), 116.5 (*C*), 117.6 (q, ^{2}J=36.0 Hz, *C*CF_3), 117.7 (q, ^{3}J=4.7 Hz, *C*H), 120.9 (*C*), 121.7 (q, ^{1}J=273.1 Hz, *C*F_3), 124.2 (*C*H), 124.2 (*C*H), 126.7 (*C*), 130.4 (*C*H), 141.7 (*C*), 150.9 (*C*), 157.8 (*C*), 163.3 (*C*O).

*4.4.4. Methyl 10-ethyl-7-(trifluoromethyl)-9-(trifluoromethanesulfonyloxy)-6H-benzo[c]chromene-8-carboxylate (**6d**).* Starting with benzoate **5y** (0.137 g, 0.391 mmol), pyridine (0.063 g, 0.8 mmol) and trifluoromethanesulfonic anhydride (0.135 g, 0.48 mmol) in CH_2Cl_2 (4 mL), product **6d** was isolated as a colourless solid (0.185 g, 98%); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.35 (t, ^{3}J=7.5 Hz, 3H, CH_2CH_3), 3.15 (q, ^{3}J=7.5 Hz, 2H, CH_2CH_3), 3.96 (s, 3H, OCH_3), 5.07 (q, *J*=1.4 Hz, 2H, ArCH_2), 7.13–7.20 (m, 2H, Ar*H*), 7.36–7.43 (m, 1H, Ar*H*), 7.61–7.66 (m, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.7 (CF_3), −73.0 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (CH_2CH_3), 22.0 (CH_2CH_3), 53.4 (OCH_3), 66.3 (q, *J*=5.6 Hz, ArCH_2), 117.8 (*C*H), 121.9 (*C*), 122.6 (*C*H), 123.2 (q, ^{2}J=32.3 Hz, *C*CF_3), 126.2 (*C*), 127.5 (*C*H), 131.1 (*C*H), 135.1 (*C*), 136.3 (*C*), 138.9 (*C*), 144.0 (*C*), 156.9 (*C*), 163.7 (*C*O).

*4.4.5. Methyl 10-n-propyl-7-(trifluoromethyl)-9-(trifluoromethanesulfonyloxy)-6H-benzo[c]chromene-8-carboxylate (**6e**).* Starting with benzoate **5z** (0.073 g, 0.199 mmol), pyridine (0.032 g, 0.4 mmol) and trifluoromethanesulfonic anhydride (0.068 g, 0.24 mmol) in CH_2Cl_2 (2 mL), product **6e** was isolated as a colourless solid (0.094 g, 95%); ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.03 (t, ^{3}J=7.3 Hz, 3H, CH_2CH_3), 1.61–1.80 (m, 2H, CH_2), 3.01–3.13 (m, 2H, CH_2), 3.95 (s, 3H, OCH_3), 5.06 (q, *J*=1.4 Hz, 2H, ArCH_2), 7.12–7.21 (m, 2H, Ar*H*), 7.34–7.44 (m, 1H, Ar*H*), 7.55–7.62 (m, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.7 (CF_3), −73.0 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (CH_2CH_3), 22.8 (CH_2), 30.6 (CH_2), 53.4 (OCH_3), 66.3 (q, *J*=5.6 Hz, ArCH_2), 117.8 (*C*H), 122.0 (*C*), 122.5 (*C*H), 123.1 (q, ^{2}J=32.3 Hz, *C*CF_3), 126.1 (*C*), 127.4 (*C*H), 131.1 (*C*H), 135.2 (*C*), 136.2 (*C*), 137.7 (*C*), 144.0 (*C*), 156.9 (*C*), 163.7 (*C*O).

4.5. General procedure for the synthesis of compounds 7a–g

A stirred solution of triflates **6a–e** (1.0 equiv), boronic acid (1.3 equiv), potassium phosphate (1.6 equiv) and tetrakis(-triphenylphosphine)palladium(0) (0.03 equiv) in dioxane (1 mL), was heated to 90 °C for 5 h. The reaction mixture was cooled to 20 °C and worked up with a saturated solution of ammonium chloride (5 mL). The organic layer was separated and extracted with diethylether (3×10 mL). The combined organic layers were dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, *n*-heptane/EtOAc 20:1).

*4.5.1. Methyl 3-phenyl-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**7a**).* Starting with triflate **6a** (0.108 g, 0.252 mmol), phenylboronic acid (0.040 g, 0.33 mmol), potassium phosphate (0.086 g, 0.40 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.009 g, 0.008 mmol) in dioxane (1 mL), product **7a** was

isolated as a colourless solid (0.061 g, 68%); mp=124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.65 (s, 3H, OCH_3), 4.18 (s, 2H, CH_2), 7.39–7.47 (m, 7H, Ar*H*), 7.58–7.64 (m, 1H, Ar*H*), 7.78–7.83 (m, 1H, Ar*H*), 7.92 (s, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−57.9 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=37.1 (q, J=2.6 Hz, *C*H$_2$), 52.4 (O*C*H$_3$), 120.4 (*C*H), 124.1 (q, ^1J=271.7 Hz, *C*F$_3$), 124.1 (q, ^2J=32.2 Hz, *C*CF$_3$), 124.4 (*C*H), 125.0 (*C*H), 127.2 (*C*H), 128.0 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 128.7 (*C*H), 129.7 (q, J=2.6 Hz, *C*), 139.1 (*C*), 139.5 (*C*), 140.2 (q, J=2.2 Hz, *C*), 140.4 (*C*), 143.5 (*C*), 144.2 (*C*), 168.4 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3031 (w), 3009 (w), 2948 (w), 2852 (w), 1723 (s), 1614 (w), 1498 (w), 1479 (w), 1451 (w), 1431 (m), 1403 (m), 1365 (m), 1297 (m), 1284 (m), 1263 (m), 1218 (m), 1204 (m), 1187 (m), 1171 (m), 1155 (m), 1142 (m), 1117 (s), 1041 (m), 1024 (m); MS (EI, 70 eV): m/z (%)=368 (M$^+$, 100), 337 (68), 317 (14), 309 (57), 288 (19), 239 (31); HRMS (EI, 70 eV): calcd for $C_{22}H_{15}F_3O_2$ (M$^+$): 368.10187, found 368.10217.

*4.5.2. Methyl 3-(4-tolyl)-7-methoxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**7b**).* Starting with triflate **6b** (0.071 g, 0.151 mmol), 4-tolylboronic acid (0.027 g, 0.20 mmol), potassium phosphate (0.051 g, 0.24 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.006 g, 0.005 mmol) in dioxane (1 mL), product **7b** was isolated as a colourless solid (0.053 g, 85%); mp=118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.42 (s, 3H, CH_3), 3.66 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.12 (s, 2H, CH_2), 6.96 (dd, ^3J=8.5 Hz, ^4J=2.4 Hz, 1H, Ar*H*), 7.13 (d, ^4J=2.0 Hz, 1H, Ar*H*), 7.24 (d, ^3J=8.0 Hz, 2H, Ar*H*), 7.32 (d, ^3J=8.1 Hz, 2H, Ar*H*), 7.67 (d, ^3J=8.5 Hz, 1H, Ar*H*), 7.77 (s, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−57.9 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.2 (*C*H$_3$), 37.1 (q, J=2.6 Hz, *C*H$_2$), 52.4 (O*C*H$_3$), 55.5 (O*C*H$_3$), 110.1 (*C*H), 113.7 (*C*H), 121.2 (*C*H), 123.5 (*C*H), 123.9 (q, ^2J=31.8 Hz, *C*CF$_3$), 124.1 (q, ^1J=274.9 Hz, *C*F$_3$), 128.4 (*C*), 128.5 (*C*H), 129.0 (*C*H), 132.1 (*C*), 136.8 (*C*), 137.7 (*C*), 139.5 (q, J=2.6 Hz, *C*), 140.5 (*C*), 144.2 (*C*), 145.5 (*C*), 160.5 (*C*), 168.6 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3000 (w), 2949 (w), 2923 (w), 2837 (w), 1733 (m), 1713 (m), 1610 (m), 1584 (w), 1557 (w), 1518 (w), 1489 (m), 1449 (m), 1426 (m), 1401 (m), 1363 (m), 1311 (m), 1298 (m), 1285 (m), 1259 (m), 1208 (m), 1173 (m), 1150 (s), 1117 (s), 1042 (m), 1024 (m); MS (EI, 70 eV): m/z (%)=412 (M$^+$, 100), 381 (40), 353 (18); HRMS (ESI-TOF/MS): calcd for $C_{24}H_{18}F_3O_3$ ((M−H)$^-$): 411.1214, found 411.1221.

*4.5.3. Methyl 3-(4-chlorophenyl)-7-methoxy-1-(trifluoromethyl)-9H-fluorene-2-carboxylate (**7c**).* Starting with triflate **6b** (0.071 g, 0.151 mmol), 4-chlorophenylboronic acid (0.031 g, 0.20 mmol), potassium phosphate (0.051 g, 0.24 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.006 g, 0.005 mmol) in dioxane (1 mL), product **7c** was isolated as a colourless solid (0.046 g, 71%); mp=134–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.66 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.12 (s, 2H, CH_2), 6.96 (dd, ^3J=8.5 Hz, ^4J=2.3 Hz, 1H, Ar*H*), 7.13 (d, ^4J=2.0 Hz, 1H, Ar*H*), 7.32–7.46 (m, 4H, Ar*H*), 7.68 (d, ^3J=8.5 Hz, 1H, Ar*H*), 7.73 (s, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−57.9 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=37.1 (q, J=2.6 Hz, *C*H$_2$), 52.5 (O*C*H$_3$), 55.5 (O*C*H$_3$), 110.1 (*C*H), 113.8 (*C*H), 121.3 (*C*H), 123.2 (*C*H), 124.0 (q, ^1J=274.9 Hz, *C*F$_3$), 124.1 (q, ^2J=32.1 Hz, *C*CF$_3$), 128.4 (q, J=2.6 Hz, *C*), 128.5 (*C*H), 130.0 (*C*H), 131.9 (*C*), 134.2 (*C*), 138.1 (*C*), 139.2 (*C*), 140.1 (q, J=2.2 Hz, *C*), 144.4 (*C*), 145.5 (*C*), 160.6 (*C*), 168.3 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3003 (w), 2951 (w), 2836 (w), 1732 (m), 1609 (m), 1585 (w), 1556 (w), 1488 (m), 1449 (m), 1427 (m), 1395 (m), 1364 (m), 1311 (m), 1296 (m), 1287 (m), 1266 (m), 1210 (m), 1174 (m), 1151 (m), 1117 (s), 1088 (m), 1040 (m), 1020 (m); MS (EI, 70 eV): m/z (%)=432 (M$^+$, 100), 401 (24), 373 (13), 366 (14), 199 (12); HRMS (ESI-TOF/MS): calcd for $C_{23}H_{17}ClF_3O_3$ ((M+H)$^+$): 433.0813, found 433.0808.

*4.5.4. Methyl 2-phenyl-4-(trifluoromethyl)dibenzo[b,d]furane-1-carboxylate (**7d**).* Starting with triflate **6c** (0.090 g, 0.203 mmol), phenylboronic acid (0.032 g, 0.26 mmol), potassium phosphate (0.068 g, 0.32 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.007 g, 0.006 mmol) in dioxane (1 mL), product **7d** was isolated as a colourless solid (0.068 g, 90%); mp=101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.76 (s, 3H, OCH_3), 7.37–7.51 (m, 6H, Ar*H*), 7.54–7.62 (m, 1H, Ar*H*), 7.67–7.68 (m, 2H, Ar*H*), 7.98 (d, ^3J=8.0 Hz, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−61.2 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.5 (O*C*H$_3$), 112.2 (*C*H), 116.0 (q, ^2J=34.5 Hz, *C*CF$_3$), 121.4 (*C*), 122.6 (*C*H), 122.8 (q, ^1J=271.4 Hz, *C*F$_3$), 123.7 (*C*H), 124.0 (*C*), 125.7 (q, ^3J=4.4 Hz, *C*H), 127.9 (*C*H), 128.5 (*C*H), 128.6 (*C*H), 129.0 (*C*H), 129.2 (*C*), 135.5 (*C*), 139.3 (*C*), 151.4 (*C*), 157.1 (*C*), 168.1 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3084 (w), 3037 (w), 2996 (w), 2945 (w), 2927 (w), 2854 (w), 1725 (m), 1599 (w), 1485 (m), 1475 (m), 1451 (w), 1430 (m), 1405 (m), 1359 (m), 1324 (m), 1308 (m), 1288 (m), 1270 (m), 1243 (m), 1212 (m), 1189 (m), 1157 (m), 1145 (m), 1116 (s), 1106 (s), 1075 (m), 1042 (m), 1026 (m), 1014 (m); MS (EI, 70 eV): m/z (%)=370 (M$^+$, 100), 339 (82), 291 (26), 242 (16); HRMS (EI, 70 eV): calcd for $C_{21}H_{13}F_3O_3$ (M$^+$): 370.08113, found 370.08086.

*4.5.5. Methyl 2-(4-tolyl)-4-(trifluoromethyl)dibenzo[b,d]furane-1-carboxylate (**7e**).* Starting with triflate **6c** (0.089 g, 0.200 mmol), 4-tolylboronic acid (0.035 g, 0.26 mmol), potassium phosphate (0.068 g, 0.32 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.007 g, 0.006 mmol) in dioxane (1 mL), product **7e** was isolated as a colourless solid (0.076 g, 99%); mp=108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.43 (s, 3H, ArCH_3), 3.80 (s, 3H, OCH_3), 7.24–7.30 (m, 2H, Ar*H*), 7.31–7.37 (m, 2H, Ar*H*), 7.37–7.43 (m, 1H, Ar*H*), 7.57 (ddd, ^3J=8.4 Hz, ^3J=7.3 Hz, ^4J=1.3 Hz, 1H, Ar*H*), 7.70 (d, ^3J=8.3 Hz, 1H, Ar*H*), 7.74 (s, 1H, Ar*H*), 7.97 (d, ^3J=8.0 Hz, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−61.2 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.2 (Ar*C*H$_3$), 52.6 (O*C*H$_3$), 112.2 (*C*H), 116.0 (q, ^2J=34.4 Hz, *C*CF$_3$), 121.5 (*C*), 122.5 (*C*H), 122.8 (q, ^1J=272.2 Hz, *C*F$_3$), 123.7 (*C*H), 123.9 (*C*), 125.7 (q, ^3J=4.4 Hz, *C*H), 128.4 (*C*H), 128.9 (*C*H), 129.4 (*C*), 129.1 (*C*H), 135.4 (*C*), 136.4 (*C*), 137.8 (*C*), 151.2 (q, J=1.8 Hz, *C*), 157.1 (*C*), 168.2 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3077 (w), 2959 (w), 2917 (w), 2851 (w), 2748 (w), 2529 (w), 1730 (m), 1658 (m), 1583 (m), 1467 (w), 1423 (m), 1380 (w), 1356 (m), 1277 (m), 1243 (s), 1212 (s), 1166 (s), 1152 (s), 1115 (m), 1071 (m); MS (EI, 70 eV): m/z (%)=384 (M$^+$, 100), 353 (67), 255 (13); HRMS (EI, 70 eV): calcd for $C_{22}H_{15}F_3O_3$ (M$^+$): 384.09678, found 384.09696.

*4.5.6. Methyl 10-ethyl-9-(4-tolyl)-7-(trifluoromethyl)-6H-benzo[c]chromene-8-carboxylate (**7f**).* Starting with triflate **6d** (0.075 g, 0.155 mmol), 4-tolylboronic acid (0.035 g, 0.26 mmol), potassium phosphate (0.068 g, 0.32 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.007 g, 0.006 mmol) in dioxane (1 mL), product **7f** was isolated as a colourless solid (0.063 g, 95%); mp=131–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.02 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 2.41 (s, 3H, OCH_3), 2.80 (q, ^3J=7.4 Hz, 2H, CH_2CH_3), 3.45 (s, 3H, OCH_3), 5.09–5.13 (m, 2H, ArCH_2), 7.07–7.17 (m, 4H, Ar*H*), 7.21 (d, ^3J=7.9 Hz, 2H, Ar*H*), 7.29–7.37 (m, 1H, Ar*H*), 7.75 (dd, ^3J=7.9 Hz, ^4J=1.4 Hz, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.3 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.2 (CH_2CH_3), 21.3 (*C*H$_3$), 24.4 (CH_2CH_3), 52.1 (O*C*H$_3$), 66.5 (q, J=5.1 Hz, Ar*C*H$_2$), 117.5 (*C*H), 119.6 (q, ^2J=31.2 Hz, *C*CF$_3$), 122.0 (*C*H), 123.1 (*C*), 123.8 (q, ^1J=275.4 Hz, *C*F$_3$), 127.6 (*C*H), 128.4 (*C*H), 130.0 (*C*H), 130.0 (*C*H), 132.2 (*C*), 132.2 (*C*), 134.0 (*C*), 134.5 (*C*), 137.6 (*C*), 141.3 (*C*), 143.6 (*C*), 157.0 (*C*), 167.8 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3033 (w), 2981 (w), 2942 (w), 2923 (w), 2876 (w), 2852 (w), 1721 (m), 1606 (w), 1584 (w), 1573 (w), 1556 (w), 1514 (w), 1487 (w), 1465 (m), 1446 (w), 1438 (w), 1421 (w), 1409 (w), 1378 (w), 1342 (m), 1331 (m), 1303 (m), 1271 (w), 1238 (m), 1207 (m), 1186 (m), 1173 (m), 1148 (m), 1117 (s), 1062 (m), 1040 (m), 1025 (m), 1015 (m); MS (EI, 70 eV): m/z (%)=426 (M$^+$, 100), 397 (14), 391 (12); HRMS (EI, 70 eV): calcd for $C_{25}H_{21}F_3O_3$ (M$^+$): 426.14373, found 426.14365.

*4.5.7. Methyl 9-phenyl-10-n-propyl-7-(trifluoromethyl)-6H-benzo[c]chromene-8-carboxylate (**7g**).* Starting with triflate **6e** (0.079 g,

0.158 mmol), phenylboronic acid (0.032 g, 0.26 mmol), potassium phosphate (0.068 g, 0.32 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.007 g, 0.006 mmol) in dioxane (1 mL), product **7g** was isolated as a colourless solid (0.040 g, 59%); mp=111–113 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.79 (t, ^3J=7.4 Hz, 3H, CH_2CH_3), 1.44–1.59 (m, 2H, CH_2), 2.77–2.90 (m, 2H, CH_2), 3.54 (s, 3H, OCH_3), 5.20–5.25 (m, 2H, $ArCH_2$), 7.19–7.29 (m, 2H, Ar*H*), 7.34–7.41 (m, 2H, Ar*H*), 7.41–7.57 (m, 4H, Ar*H*), 7.81 (dd, ^3J=7.9 Hz, ^4J=1.4 Hz, 1H, Ar*H*); ^{19}F NMR (282 MHz, $CDCl_3$): δ=−55.3 (CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8 (CH_2CH_3), 23.7 (CH_2), 33.4 (CH_2), 52.1 (OCH_3), 66.5 (q, J=5.1 Hz, $ArCH_2$), 117.5 (*C*H), 120.1 (q, ^2J=31.2 Hz, *C*CF_3), 122.0 (*C*H), 123.2 (*C*), 123.7 (q, ^1J=275.3 Hz, *C*F_3), 127.5 (*C*H), 127.7 (*C*H), 127.9 (*C*H), 130.0 (*C*H), 130.1 (*C*H), 131.9 (q, J=3.0 Hz, *C*), 132.5 (*C*), 134.6 (*C*), 137.1 (*C*), 141.3 (*C*), 142.2 (*C*), 157.0 (*C*), 167.7 (*C*O); IR (ATR, cm^{-1}): $\tilde{\nu}$=3058 (w), 3029 (w), 2992 (w), 2963 (w), 2946 (w), 2928 (w), 2870 (w), 1731 (m), 1605 (w), 1583 (w), 1553 (w), 1488 (m), 1465 (m), 1440 (m), 1421 (w), 1407 (w), 1377 (w), 1341 (m), 1309 (m), 1278 (m), 1233 (m), 1206 (m), 1174 (s), 1151 (m), 1122 (s), 1088 (m), 1076 (m), 1045 (m), 1016 (m); MS (EI, 70 eV): m/z (%)=426 (M^+, 100), 377 (21), 314 (10); HRMS (ESI-TOF/MS): calcd for $C_{25}H_{22}F_3O_3$ ($(M+H)^+$): 427.1516, found 427.1517.

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35. CCDC-865738–865741 contains all crystallographic details of this publication and is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; Fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk