Novel Aromatic Fluoroolefins via Fluoro-Julia–Kocienski Olefination

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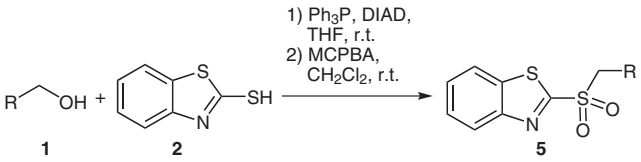
Abstract: Fluoroolefins, which play an increasingly important role as peptide mimics in pharmaceuticals and as crop protection agents, are generated using a fluoro-Julia–Kocienski olefination. Their preparation can easily be accomplished using a Mitsunobu reaction and subsequent oxidation to generate the required benzothiazolyl sulfones. The key step of this process was the electrophilic α-fluorination of the sulfone with *N*-fluorobenzenesulfonimide. The last stage of the successful synthesis of the fluoroolefins was the modified Julia–Kocienski olefination under basic conditions. Further functionalization was followed with the application of a Suzuki reaction.

Key words: fluorine, olefination, sulfones, heterocycles, cross-coupling

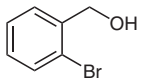
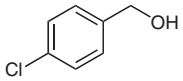
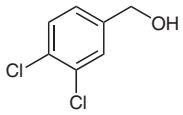
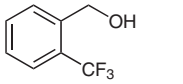
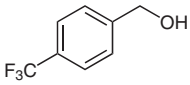
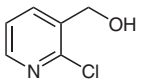
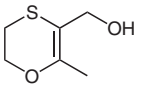
The incorporation of fluorine atoms in organic compounds results in the modifications of several fields of action.[1] Changes in biological activity are often observed when fluorine is introduced into new compounds of medicinal interest.[2] These advantages of fluorine are illustrated by the prominence of organofluorine compounds and the importance of new synthetic approaches for their synthesis.[3–7] Fluoroolefins have been successfully prepared and used as precursors of medicines, agrochemicals, and modified pheromones.[8] In particular, among the large variety of peptidomimetics, the monofluorinated olefins described in this article are considered to be excellent surrogates for amide bonds.[9] One of the most efficient strategies to install a C=C bond is the Julia olefination and the method modified by Kocienski and co-workers.[10,11] The combination of this well established olefination and fluorine chemistry leads to useful building blocks for various research areas like drug discovery.

We herein present some modifications of a methodology for the synthesis fluoroolefins, as previously developed by Gosh and Zajc.[12] In contrast to the reported syntheses we started our route in a different way. Instead of a nucleophilic substitution of benzyl chlorides with 2-mercaptobenzothiazole a Mitsunobu reaction of benzylic alcohols **1** as the first step for the synthesis was chosen (Scheme 1). The use of a slight excess of 2-mercaptobenzothiazole (**2**), triphenylphosphine, and diisopropyl azodicarboxylate (DIAD) furnished the desired products **3** (not shown) between moderate to excellent yields (49–97%, Table 1). Alcohol **1f** was prepared from 2-chloronicotinic acid (**4**) by simple reduction with BH_3·THF.[13,14]



Scheme 1 Mitsunobu reaction of **1** and following oxidation

Table 1 Mitsunobu Reaction and Following Oxidation of Alcohols **1**

Entry	**1**		**3**	Yield (%)	**5**	Yield (%)
1	**1a**		**3a**	97	**5a**	94
2	**1b**		**3b**	75	**5b**	78
3	**1c**		**3c**	92	**5c**	82
4	**1d**		**3d**	90	**5d**	86
5	**1e**		**3e**	61	**5e**	quant
6	**1f**		**3f**	96	**5f**	56
7	**1g**		**3g**	49[a]	**5g**	0[b]

[a] See Figure 1.
[b] Decomposition of the starting material was observed.

A by-product **6** was isolated in the case of alcohol **1g**, which explains the modest yield of the main product **3g** (Figure 1). Under the previously mentioned Mitsunobu conditions substitution of the nitrogen atom instead of the sulfur atom of 2-mercaptobenzothiazole took place.[15]

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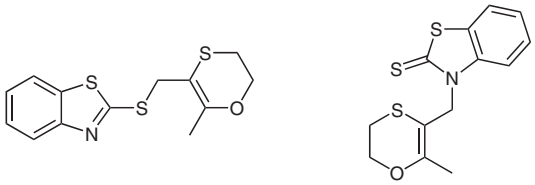


Figure 1 Product **3g** and by-product **6**, isolated during the Mitsunobu reaction of **1g**

Wicha et al. also observed this side reaction with an allylic alcohol, so it was envisaged that the use of the Mitsunobu reaction is limited to nonallylic alcohols.

Next, the oxidation reaction of sulfides **3** to the corresponding sulfones **5** was explored. Gratifyingly, *m*-chloroperbenzoic acid (MCPBA) led to good to excellent yields of the sulfones (Scheme 1 and Table 1). Oxone was less efficient. The reaction was carried out with 3 equivalents of the oxidizing reagent. Use of smaller amounts of MCPBA led to chiral sulfoxides as by-products, which could be easily detected by ^{1}H NMR spectroscopy. Furthermore, in the case of the pyridine derivative **5f** no pyridine *N*-oxide was observed, although MCPBA can be used for the preparation of such compounds.[16]

The general structure of sulfones was confirmed by conducting an X-ray structural determination on **5a** (Figure 2, see experimental for details).

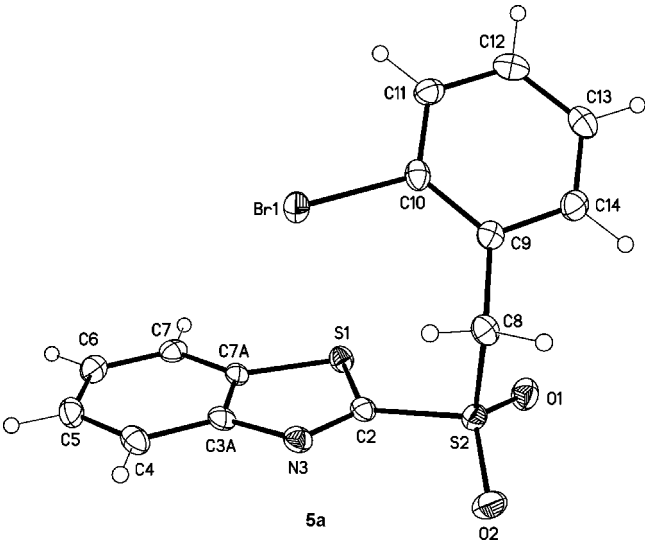
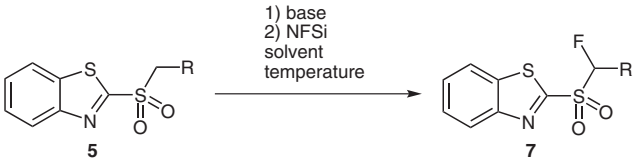


Figure 2 X-ray crystal structure of **5a**

The key step of our synthetic route was the introduction of one fluorine atom to the BT-sulfone (BT = benzothiazolyl, Scheme 2). The deprotonation-fluorination reaction was optimized in terms of base, solvent and temperature. *N*-Fluorobenzenesulfonimide (NFSi) proved to be the fluorinating agent of choice as already found earlier.[12,17,18]

Sulfone **5a** was taken as a model system and different reaction conditions were investigated. First attempt was carried out with lithium diisopropylamide (LDA) as base and toluene as solvent. The reaction was stirred at –78 °C for



Scheme 2 Electrophilic fluorination of sulfones **5**

three hours and gave product **7a** in 56% yield (Table 2, entry 1). Next, attempts were made to increase the yield by a longer reaction time, but the observed yield was lower than before (Table 2, entries 2, 3). No product could be isolated by increasing the ratio of LDA to substrate (Table 2, entry 4). Change of base to LiHMDS and solvent to THF were not successful either (Table 2, entry 5). As alternative reaction conditions, sodium hydride in acetonitrile as solvent was tested at higher temperature and led to an increased yield of fluorosulfone **7a** (74%, Table 2, entry 6). The fluorosulfones **7b**, **7e**, and **7f** were synthesized under similar reaction conditions (Table 2). Sodium hydride and NFSi were used in small excesses of 1.22 and 1.23 equivalents. The fluorinated products could be isolated in 33% to 58% yield. In case of sulfone **7d**, only the use of LDA and toluene led to acceptable 49% yield (Table 2, entry 8). Pyridine derivative **7f** could be isolated in 56% yield.

Table 2 Electrophilic Fluorination

Entry	5	Base	Solvent	Temp (°C)	Time (h)	Product 7	Yield (%)
1	**5a**	LDA	toluene	–78	3	**7a**	56
2	**5a**	LDA	toluene	–78	15	**7a**	28
3	**5a**	LDA	toluene	–78	48	**7a**	12
4	**5a**	LDA[a]	toluene	–78	24	**7a**	0
5	**5a**	LiHMDS	THF	–78	3	**7a**	0
6	**5a**	NaH	MeCN	–30	24	**7a**	74
7	**5b**	NaH	MeCN	–30	24	**7b**	58
8	**5d**	LDA	toluene	–78	3	**7d**	49
9	**5e**	NaH	MeCN	–30	48	**7e**	33
10	**5f**	NaH	MeCN	–30	24	**7f**	56

[a] Two equivalents.

During the electrophilic monofluorination of sulfone **5c** under the optimized conditions, traces of the monofluorinated sulfone **7c** and the difluorinated sulfone **8c** were isolated. The crystal structure of **7c/8c** (Figure 3) shows an occupancy disorder between the (additionally position disordered) monofluorinated sulfone **7c** and the difluorinated sulfone **8c** in the ratio of 3:1. The difluorinated compound is probably formed due to the small excess of the fluorination species.

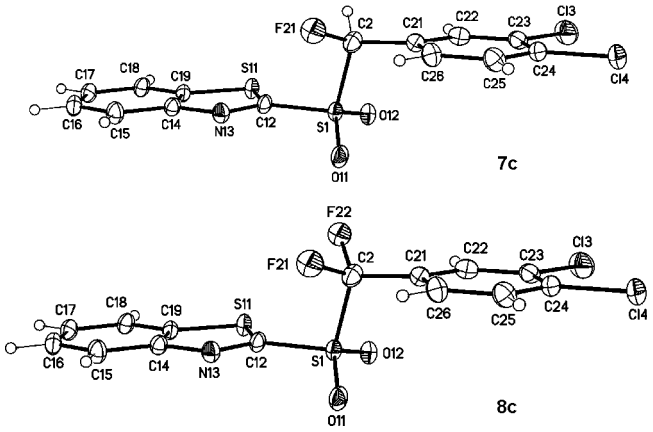
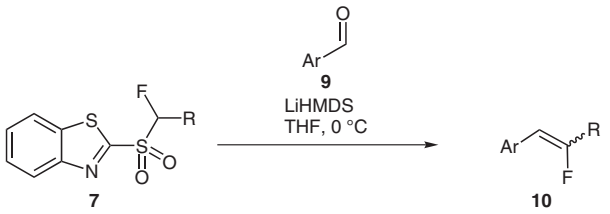


Figure 3 Top: molecular structure of monofluorinated sulfone **7c**; bottom: molecular structure of difluorinated sulfone **8c**

With the fluorosulfones in hand, the Julia–Kocienski olefination was examined with a range of aldehydes under 'Barbier-like' conditions (the base is added to a mixture of the aldehyde and sulfone). Reaction of the fluorosulfones **7** with a selection of functionalized (het)aryl aldehydes **9** gave the fluoro(hetero) stilbenes **10** in moderate to good yields (Scheme 3, Table 3); *E* and/or *Z*-isomers were formed depending on the substitution pattern.



Scheme 3 Olefination of fluorosulfones **7** with aldehydes **9**

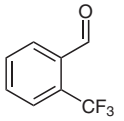
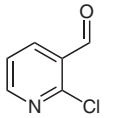
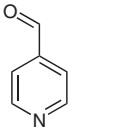
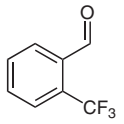
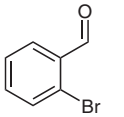
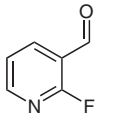
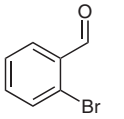
We next turned our attention to the preparation of fluorostilbenes bearing one substituted aromatic ring and one heterocyclic unit. Therefore, the reaction was carried out with a small excess of fluorosulfones **7** (1.20 equiv) and an excess of LiHMDS (2.40 equiv). The appropriate solvent was THF and the optimal temperature was 0 °C as Gosh and Zajc had reported earlier.[12]

The fluoroolefins **10a–c** (Table 3, entries 1–3) and **10f**,**g** (Table 3, entries 6, 7) were mostly obtained as the *E*-isomers. If a mixture was obtained, the *E*/*Z* ratio varied between 6.2:1 and 2.4:1. Only the vinyl fluorides **10d** and **10e** (Table 3, entries 5, 7) were predominantly isolated as the *Z*-isomers.

A Suzuki reaction was used to achieve further functionalization of the brominated fluoro(hetero)stilbenes.[23–25] The reactions provided the biaryl systems **11a**,**b** and **e** in moderate to excellent yields (25–86%, Figure 4). Biaryl **11b** could be isolated in 25% yield. As catalyst palladium acetate and triphenylphosphine were employed, the reaction was carried out in DMF and potassium carbonate was used as base.[24] As mentioned before, the fluoroolefin **10b** was isolated only as the *E*-isomer. After the Suzuki cross-coupling, the *E*/*Z*-ratio was determined to be 1.0 to 1.6. Double bond isomerizations are described in radical or photochemical processes.[26] But it is also known that the isomerization can be induced under palladium(II) catalysis,[27] which presumably appears during the Suzuki coupling of **10b**. Indeed, the biaryl **11e** could be prepared under the same condition in 86% yield, but the isomerization of the double bond did still occur. Due to this fact, the reaction conditions were changed and the reaction of **10a** and 4-chlorophenylboronic acid was carried out using $Pd(PPh_3)_4$ as catalyst, saturated aqueous Na_2CO_3 as base, and a mixture of dimethoxyethane and ethanol as solvent.[25] The desired product **11a** could be obtained in 75% yield and no isomerization of the double bound was observed.

In conclusion, we have presented here the application of a fluoro-Julia–Kocienski method for the generation of (hetero)arylfluorostilbenes and synthetic alternatives of the procedure developed by Gosh and Zajc. We successfully applied several aromatics with various functional groups

Table 3 Olefination Reaction (Scheme 3)

Entry	Sulfone **7**	Aldehyde	Product **10**	*E*/*Z* ratio[a,b]	Yield (%)[a]
1	**7a**	**9a** 	**10a**	3.4:1.0	61
2	**7a**	**9b**[c] 	**10b**	only *E*	57
3	**7a**	**9c** 	**10c**	4.5:1.0	51
4	**7b**	**9a** 	**10d**	0.4:1.0	65
5	**7d**	**9d** 	**10e**	only *Z*	20
6	**7e**	**9e** 	**10f**	6.2:1.0	85
7	**7f**	**9d** 	**10g**	2.4:1.0	60

[a] Isomers are separable in some cases. Combined yields are given.
[b] Geometry ascertained using NMR spectroscopy.[12,19,20]
[c] Aldehyde **9b** was obtained by oxidation of alcohol **1f** using DMP as oxidizing species.[21,22]

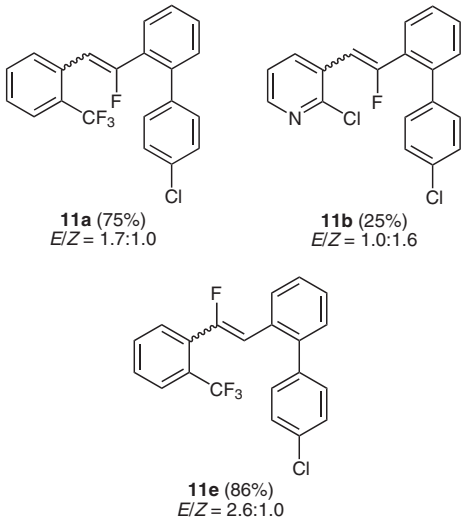


Figure 4 Synthesized biaryls **11a**, **b**, and **e**

and heterocyclic compounds like pyridine derivatives. Furthermore, we succeeded in the Suzuki cross-coupling of brominated fluoroolefins with 4-chlorophenylboronic acid leading to functionalized biaryls, which provides a higher diversity of products.

All reagents, except **1f** and **9b**, were purchased from ABCR, Apollo Scientific, Merck, Sigma-Aldrich and Thermo Fisher Scientific and used without further purification. The starting materials **1f**[13] and **9b**[22] were prepared according to literature. Solvents were dried and purified by standard methods. For TLC, aluminum foils layered with silica gel (silica gel 60 F_{254}) produced by Merck were used. Column chromatography was performed employing Merck silica gel 60 under flash conditions (EtOAc, *c*Hex = cyclohexane). Unless otherwise indicated, all solvent ratios are given as v/v. ^{1}H, ^{13}C and ^{19}F NMR spectra were measured with a Bruker Avance 400 (400 MHz, 100 MHz, and 376 MHz, respectively) spectrometer. $CDCl_3$ was used as solvent and residual $CHCl_3$/$CDCl_3$ as shift reference: δ ($CHCl_3$) = 7.26 ppm, δ ($CDCl_3$) = 77.0 ppm. ^{19}F NMR spectra were recorded with an external standard. IR spectra were recorded with Bruker FTIR device IFS 88. EI-MS, FAB-MS, FAB-HRMS, and HR-EIMS spectra were recorded on a Finnigan MAT 95 instrument; elemental analyses were performed using an Elementar Vario Micro device.

(2-Chloropyridin-3-yl)methanol (1f)[13]
Colorless solid. Yield: 0.417 g (2.89 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.67 (d, *J* = 5.4 Hz, 2 H, CH_2), 7.17 (m, 1 H, ArH-5), 7.79 (m, 1 H, ArH-4), 8.18 (dd, *J* = 1.7, 4.7 Hz, 1 H, ArH-6).

2-Chloropyridin-3-carbaldehyde (9b)[22]
Light yellow solid. Yield: 0.245 g (1.72 mmol, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (ddd, *J* = 0.6, 4.8, 7.6 Hz, 1 H, ArH-5), 8.24 (dd, *J* = 2.1, 7.7 Hz, 1 H, ArH-4), 8.62 (dd, *J* = 2.1, 4.7 Hz, 1 H, ArH-6), 10.45 (d, *J* = 0.6 Hz, 1 H, CHO).

Benzothiazole Sulfides 3; General Procedure
To a solution of 2-mercaptobenzothiazole (**2**; 1.10 equiv), Ph_3P (1.10 equiv), and the corresponding alcohol **1** (0.279–2.84 mmol, 1.00 equiv) in anhyd THF (14.5 mL/mmol **1**) was added DIAD (1.10 equiv) dropwise. The reaction mixture was stirred for 15 h at r.t. The solvent was removed under reduced pressure and the resulting yellow residue was purified by column chromatography on silica gel (*c*Hex–EtOAc) to afford the title compounds **3** (Table 1).

2-(2-Bromobenzylthio)benzo[*d*]thiazole (3a)
Yield: 0.874 g (2.59 mmol, 97%); yellow oil; R_f = 0.62 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3441, 3061, 1640, 1460, 1427, 1309, 1239, 1026, 994 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.75 (s, 2 H, CH_2), 7.14 (dt, *J* = 1.7, 7.7 Hz, 1 H, ArH-5′), 7.25 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH-4′), 7.28–7.32 (m, 1 H, ArH-3′), 7.43 (ddd, *J* = 1.2, 7.3, 8.3 Hz, 1 H, ArH-6′), 7.60 (ddd, *J* = 1.4, 8.2, 11.3 Hz, 2 H, ArH-5,6), 7.76 (dd, *J* = 0.5, 1.1 Hz, 1 H, ArH-4), 7.92 (ddd, *J* = 0.5, 0.9, 8.1 Hz, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9, 121.0, 121.6, 124.3, 124.8, 126.0, 127.6, 129.4, 131.3, 133.0, 135.5, 136.1, 153.1, 166.0.

MS (70 eV, EI): *m*/*z* (%) = 337/335 (48/45, [M^+]), 256 (100, [$C_{14}H_{10}NS_2^+$]), 223 (43), 171/169 (56/59, [$C_7H_6Br^+$]), 90 (34).

HR-EIMS: *m*/*z* calcd for $C_{14}H_{10}BrNS_2$: 334.9438; found: 334.9432.

Anal. Calcd for $C_{14}H_{10}BrNS_2$: C, 50.00; H, 3.00; N, 4.17; S, 19.07. Found: C, 50.07; H, 3.06; N, 4.36; S, 18.97.

2-(4-Chlorobenzylthio)benzo[*d*]thiazole (3b)
Yield: 0.275 g (0.938 mmol, 75%); white solid; R_f = 0.46 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3083 (w), 3063 (w), 2926 (w), 1950 (vw), 1912 (w), 1794 (w), 1595 (w), 1558 (w), 1492 (m), 1456 (m), 1426 (m), 1405 (w), 1309 (w), 1274 (w), 1239 (w), 1192 (w), 1123 (w), 1094 (m), 1078 (w), 1017 (m), 1003 (m), 973 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.56 (s, 2 H, CH_2), 7.27–7.33 (m, 3 H, ArH-6,2′,6′), 7.28–7.45 (m, 2 H, ArH-3′,5′), 7.43 (m, 1 H, ArH-5), 7.75 (d, *J* = 7.8 Hz, 1 H, ArH-4), 7.90 (d, *J* = 8.1 Hz, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.8, 121.0, 121.6, 124.4, 126.1, 128.8, 130.5, 133.6, 134.9, 135.3, 153.0, 165.8.

MS (70 eV, EI): *m*/*z* (%) = 293/292/291 (40/15/94, [M^+]), 260/259/258 (11/5/32, [M – S^+]), 173 (25), 171 (26), 127/126/125 (30/6/100, [$C_7H_6Cl^+$]).

HR-EIMS: *m*/*z* calcd for $C_{14}H_{10}ClNS_2$: 290.9943; found: 290.9945.

Anal. Calcd for $C_{14}H_{10}ClNS_2$: C, 57.62; H, 3.45; N, 4.80; S, 21.98. Found: C, 57.45; H, 3.41; N, 4.76; S, 21.85.

2-(3,4-Dichlorobenzylthio)benzo[*d*]thiazole (3c)
Yield: 0.443 g (1.15 mmol, 92%); yellow oil; R_f = 0.36 (*c*Hex–EtOAc, 19:1).

IR (KBr): 3856, 3772, 3448, 3061, 3029, 2926, 2850, 2290, 1901, 1781, 1711, 1592, 1561, 1469, 1427, 1309, 1275, 1239, 1204, 1133, 1076, 1032, 1018, 998 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.53 (s, 2 H, CH_2), 7.32 (dt, *J* = 4.5, 10.7 Hz, 2 H, ArH-5,6), 7.38 (d, *J* = 8.3 Hz, 1 H, ArH-5′), 7.44 (m, 1 H, ArH-6′), 7.58 (d, *J* = 2.0 Hz, 1 H, ArH-3′), 7.75 (d, *J* = 8.0 Hz, 1 H, ArH-4), 7.90 (d, *J* = 8.1 Hz, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.1, 121.0, 121.6, 124.5, 126.1, 128.4, 130.5, 131.1, 131.7, 132.5, 135.3, 136.9, 152.9, 165.2.

MS (70 eV, EI): *m*/*z* (%) = 329/327/325 (5/20/28, [M^+]), 292 (9, [M – S^+]), 163/161/159 (2/16/25, [$C_7H_5Cl_2^+$]), 43 (100).

HR-EIMS: *m*/*z* calcd for $C_{14}H_9Cl_2NS_2$: 324.9553; found: 324.9554.

Anal. Calcd for $C_{14}H_9Cl_2NS_2$: C, 51.54; H, 2.78; N, 4.29; S, 19.66. Found: C, 51.87; H, 2.90; N, 4.35; S, 19.42.

2-[2-(Trifluoromethyl)benzylthio]benzo[*d*]thiazole (3d)
Yield: 0.832 g (2.56 mmol, 90%); colorless oil; R_f = 0.59 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3065, 1943, 1607, 1584, 1497, 1459, 1428, 1316, 1240, 1179 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.84 (s, 2 H, CH_2), 7.32 (ddd, *J* = 1.2, 7.4, 8.3 Hz, 1 H, ArH-4′), 7.37 (t, *J* = 7.7 Hz, 1 H, ArH-6), 7.44 (ddd, *J* = 1.2, 7.4, 8.3 Hz, 1 H, ArH-3′), 7.49 (t, *J* = 7.6 Hz, 1 H, ArH-5), 7.68 (d, *J* = 7.8 Hz, 1 H, ArH-4), 7.75 (d, *J* = 2.9 Hz, 1 H, ArH-7), 7.74–7.78 (m, 1 H, ArH-5′), 7.92 (m, 1 H, ArH-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.7, 121.1, 121.6, 122.9, 124.4, 126.1, 126.2, 127.8, 128.6, 128.9, 131.8, 132.3, 135.4, 153.0, 166.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –59.3.

MS (70 eV, EI): *m*/*z* (%) = 325 (96, $[M^+]$), 159 (100, $[C_8H_6F_3^+]$), 109 (36).

HR-EIMS: *m*/*z* calcd for $C_{15}H_{10}F_3NS_2$: 325.0206; found: 325.0209.

Anal. Calcd for $C_{15}H_{10}F_3NS_2$: C, 55.37; H, 3.10; N, 4.30; S, 19.71. Found: C, 55.43; H, 3.23; N, 4.45; S, 19.31.

2-[4-(Trifluoromethyl)benzylthio]benzo[*d*]thiazole (3e)
Yield: 0.248 g (0.763 mmol, 61%); white solid; mp 183 °C; R_f = 0.35 (*c*Hex–EtOAc, 19:1).

IR (KBr): 3071, 2925, 2307, 1958, 1921, 1799, 1615, 1589, 1559, 1458, 1427, 1412, 1332, 1310, 1237, 1172, 1155, 1122, 1097, 1070, 1019, 1004, 979 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.64 (s, 2 H, CH_2), 7.29–7.34 (m, 1 H, ArH-6), 7.44 (ddd, *J* = 1.2, 7.4, 8.3 Hz, 1 H, ArH-5), 7.58 (s, 4 H, ArH-2′,3′,5′,6′), 7.76 (d, *J* = 8.0 Hz, 1 H, ArH-4), 7.91 (d, *J* = 8.1 Hz, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.8, 121.1, 121.6, 124.0, 124.5, 125.6, 126.1, 129.4, 129.9, 135.4, 140.7, 153.0, 165.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.5.

MS (70 eV, EI): *m*/*z* (%) = 325 (100, $[M^+]$), 292 (44, $[M - S^+]$), 159 (50, $[C_8H_6F_3^+]$).

HR-EIMS: *m*/*z* calcd for $C_{15}H_{10}F_3NS_2$: 325.0206; found: 325.0209.

Anal. Calcd for $C_{15}H_{10}F_3NS_2$: C, 55.37; H, 3.10; N, 4.30; S, 19.71. Found: C, 55.36; H, 3.12; N, 4.16; S, 20.05.

2-[(2-Chloropyridin-3-yl)methylthio]benzo[*d*]thiazole (3f)
Yield: 0.786 g (0.268 mmol, 96%); yellow oil; R_f = 0.38 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3068, 2993, 2951, 2913, 2736, 2621, 1919, 1793, 1562, 1458, 1427, 1408, 1259, 1239 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.70 (s, 2 H, CH_2), 7.18 (dd, *J* = 7.6, 4.8 Hz, 1 H, ArH-5′), 7.31 (t, *J* = 7.6 Hz, 1 H, ArH-6), 7.43 (ddd, *J* = 1.2, 7.4, 8.3 Hz, 1 H, ArH-5), 7.75 (d, *J* = 8.5 Hz, 1 H, ArH-4), 7.90 (d, *J* = 8.1 Hz, 1 H, ArH-4′), 8.00 (dd, *J* = 1.9, 7.6 Hz, 1 H, ArH-7), 8.30 (dd, *J* = 1.9, 4.8 Hz, 1 H, ArH-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.3, 121.1, 121.6, 122.6, 124.5, 126.2, 131.7, 135.5, 139.7, 148.7, 151.3, 152.9, 165.2.

MS (70 eV, EI): *m*/*z* (%) = 292.1/294.1 (66/27, $[M^+]$), 257.1 (100, $[C_{13}H_9N_2S_2^+]$), 224 (27), 126/128 (59/17, $[C_6H_5ClN^+]$).

HR-EIMS: *m*/*z* calcd for 291.9895; found 291.9897.

Anal. Calcd for $C_{13}H_9ClN_2S_2$: C, 53.32; H, 3.10; N, 9.57; S, 21.90. Found: C, 53.74; H, 3.06; N, 9.94; S, 21.81.

2-[(2-Methyl-5,6-dihydro-1,4-oxathiin-3-yl)methylthio]benzo[*d*]thiazole (3g)
Yield: 0.248 g (0.833 mmol, 49%); yellow solid; R_f = 0.59 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3064, 2923, 2881, 1718, 1639, 1491, 1466, 1428, 1371, 1313, 1240, 1143, 1078, 1005 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.89 (s, 3 H, CH_3), 2.90 (m, 2 H, SCH_2), 4.10 (s, 2 H, CH_2), 4.16 (m, 2 H, OCH_2), 7.20 (m, 1 H, ArH-5), 7.32 (m, 1 H, ArH-6), 7.66 (dd, *J* = 0.8, 7.7 Hz, 1 H, ArH-4), 7.78 (dd, *J* = 0.8, 8.0 Hz, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 25.9, 37.3, 65.6, 95.3, 120.9, 121.4, 124.2, 125.9, 135.2, 146.7, 152.9, 166.4.

MS (70 eV, EI): *m*/*z* (%) = 295 (7, $[M^+]$), 262 (21, $[M^+ - SH]$, 208 (39), 167 (100, $[C_7H_5NS_2^+]$), 129 (65, $[C_6H_9OS^+]$), 103 (64).

3-[(2-Methyl-5,6-dihydro-1,4-oxathiin-3-yl)methyl]benzo[*d*]thiazole-2(3*H*)-thione (6)
Isolated as the by-product together with **3g**. Yield: 0.156 g (0.527 mmol, 31%); yellow oil; R_f = 0.47 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3422, 3063, 2966, 2927, 2876, 1737, 1642, 1458, 1429, 1367, 1223, 1137 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, CH_3), 2.88 (m, 2 H, SCH_2), 4.20 (m, 2 H, OCH_2), 5.26 (s, 2 H, NCH_2), 7.30 (t, *J* = 8.1 Hz, 1 H, ArH-6), 7.34 (d, *J* = 7.5 Hz, 1 H, ArH-7), 7.37 (t, *J* = 7.4 Hz, 1 H, ArH-5), 7.47 (d, *J* = 8.2 Hz, 1 H, ArH-4).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.7, 25.5, 47.5, 65.3, 96.1, 112.8, 121.2, 124.7, 126.7, 127.2, 136.1, 154.5, 190.2.

MS (70 eV, EI): *m*/*z* (%) = 295 (47, $[M^+]$), 262 (25, $[M - SH^+]$), 166 (28, $[C_7H_4NS_2^+]$), 129 (100, $[C_6H_9OS^+]$), 43 (86, $[C_2H_3O^+]$).

HR-EIMS: *m*/*z* calcd for $C_{13}H_{13}NOS_3$: 295.0159; found: 295.0160.

Benzothiazole Sulfones 5; General Procedure
A solution of benzothiazole sulfide **3** (0.455–8.02 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL/mmol **3**) was cooled to 0 °C and MCPBA (3.00 equiv) was added portion by portion. The reaction mixture was stirred for additional 10 min at 0 °C and allowed to warm to r.t. and stirred for 5 h. The mixture was quenched with sat. aq $NaHCO_3$ (10 mL/mmol **3**) and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL/mmol **3**), and the combined organic layers were washed with H_2O (10 mL/mmol **3**) and brine (10 mL/mmol **3**), dried (Na_2SO_4), and the solvent removed under reduced pressure. Purification of the crude product by column chromatography on silica gel (*c*Hex–EtOAc) gave the pure products **5** (Table 1).

2-(2-Bromobenzylsulfonyl)benzo[*d*]thiazole (5a)
Yield: 2.76 g (7.54 mmol, 94%); brown solid; R_f = 0.26 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3064, 2995, 2941, 1959, 1921, 1795, 1701, 1569, 1467 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.00 (s, 2 H, CH_2), 7.21 (dt, *J* = 1.7, 7.6 Hz, 1 H, ArH-4′), 7.29 (dt, *J* = 1.3, 7.5 Hz, 1 H, ArH-5′), 7.45 (dd, *J* = 1.7, 7.7 Hz, 1 H, ArH-3′), 7.53 (dd, *J* = 1.3, 8.0 Hz, 1 H, ArH-6′), 7.57–7.68 (m, 2 H, ArH-5,6), 7.94 (dd, *J* = 0.6, 8.0 Hz, 1 H, ArH-7), 8.25 (dd, *J* = 0.6, 8.2 Hz, 1 H, ArH-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.5, 122.3, 125.6, 126.1, 126.9, 127.7, 127.9, 128.1, 130.9, 133.1, 133.4, 137.3, 152.7, 164.8.

MS (70 eV, EI): *m*/*z* (%) = 367/369 (0.12/0.13, $[M^+]$), 288 (100, $[C_{14}H_{10}NO_2S_2^+]$), 170/169 (70/68, $[C_7H_6Br^+]$), 90 (33, $[C_7H_6^+]$).

HR-EIMS: *m*/*z* calcd for $C_{14}H_{10}BrNO_2S_2$: 366.9336; found: 366.9336.

Anal. Calcd for $C_{14}H_{10}BrNO_2S_2$: C, 45.66; H, 2.74; N, 3.80; S, 17.41. Found: C, 45.49; H, 2.87; N, 3.63; S, 16.59.

2-(4-Chlorobenzylsulfonyl)benzo[*d*]thiazole (5b)
Yield: 0.237 g (0.728 mmol, 78%); white solid; R_f = 0.42 (*c*Hex–EtOAc, 4:1).

IR (KBr): 3070, 3031, 2990, 2941, 1918, 1793, 1594, 1554, 1491, 1475, 1455, 1406, 1332, 1316, 1279, 1234, 1146, 1127, 1088, 1015, 946 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.73 (s, 2 H, CH_2), 7.22–7.30 (m, 4 H, Ar-H-2′,3′,5′,6′), 7.60 (m, 1 H, ArH-6), 7.66 (m, 1 H, ArH-5), 7.97 (d, *J* = 7.9 Hz, 1 H, ArH-7), 8.26 (d, *J* = 8.0 Hz, 1 H, ArH-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.2, 122.3, 124.9, 125.5, 127.7, 128.1, 129.2, 132.4, 135.6, 137.0, 152.5, 164.8.

MS (70 eV, EI): *m*/*z* (%) = 325/324/323 (8/3/21, [M^+]), 260/259/258 (14/12/36, [M – SO_2^+]), 127/126/125 (32/7/100, [$C_6H_7Cl^+$]).

HR-EIMS: *m*/*z* calcd for $C_{14}H_{10}ClNO_2S_2$: 322.9841; found: 322.9844.

Anal. Calcd for $C_{14}H_{10}ClNO_2S_2$: C, 54.71; H, 3.28; N, 4.56; S, 20.86. Found: C, 54.71; H, 3.23; N, 4.60; S, 20.87.

2-(3,4-Dichlorobenzylsulfonyl)benzo[*d*]thiazole (5c)
Yield: 0.275 g (0.768 mmol, 82%); white solid; R_f = 0.28 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3071, 2993, 2936, 2445, 2324, 1965, 1934, 1802, 1679, 1554, 1469, 1419, 1395, 1327, 1274, 1244, 1200, 1150, 1087 (m), 1030 (m), 984 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.71 (s, 2 H, CH_2), 7.12 (dd, *J* = 2.1, 8.3 Hz, 1 H, ArH-5′), 7.36 (d, *J* = 8.3 Hz, 1 H, ArH-6′), 7.41 (d, *J* = 2.1 Hz, 1 H, ArH-3′), 7.61 (ddd, *J* = 1.3, 7.3, 8.3 Hz, 1 H, ArH-6), 7.67 (ddd, *J* = 1.3, 7.3, 8.3 Hz, 1 H, ArH-5), 7.98 (dd, *J* = 0.7, 7.4 Hz, 1 H, ArH-7), 8.25 (dd, *J* = 0.7, 7.7 Hz, 1 H, ArH-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.6, 122.4, 125.5, 126.4, 127.8, 128.3, 130.2, 130.8, 132.9, 133.1, 133.9, 136.9, 152.4, 164.7.

MS (70 eV, EI): *m*/*z* (%) = 361/359/357 (4/16/21, [M^+]), 294/293/292 (32/22/43, [M – SO_2^+]), 161/159 (63/100, [$C_7H_5Cl_2^+$]).

HR-EIMS: *m*/*z* calcd for $C_{14}H_9Cl_2NO_2S_2$: 356.9451; found: 356.9449.

Anal. Calcd for $C_{14}H_9Cl_2NO_2S_2$: C, 46.93; H, 2.53; N, 3.91; S, 17.90. Found: C, 46.57; H, 2.54; N, 3.90; S, 17.51.

2-(2-Trifluoromethyl)benzylsulfonylbenzo[*d*]thiazole (5d)
Yield: 1.01 g (2.81 mmol, 86%); colorless solid; R_f = 0.14 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3065, 2987, 2945, 1958, 1924, 1805, 1466, 1418, 1332, 1316, 1121 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.99 (s, 2 H, CH_2), 7.51 (t, *J* = 7.6 Hz, 1 H, ArH-4′), 7.50–7.72 (m, 5 H, ArH-5,6,3′,5′,6′), 7.99 (dd, *J* = 0.7, 8.0 Hz, 1 H, ArH-7), 8.25 (dd, *J* = 0.6, 8.1 Hz, 1 H, ArH-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.2, 122.3, 124.7, 125.7, 126.9, 127.8, 128.2, 129.5, 130.2, 130.5, 132.2, 133.5, 137.1, 152.6, 165.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.2.

MS (70 eV, EI): *m*/*z* (%) = 357 (13, [M^+]), 292 (57), 159 (100, [$C_8H_6F_3^+$]), 134 (13, [$C_7H_4NS^+$]), 109 (33).

HR-EIMS: *m*/*z* calcd for $C_{15}H_{10}F_3NO_2S_2$: 357.0105; found: 357.0107.

Anal. Calcd for $C_{15}H_{10}F_3NO_2S_2$: C, 50.41; H, 2.82; N, 3.92; S, 17.94. Found: C, 50.79; H, 3.19; N, 3.79; S, 17.27.

2-(4-Trifluoromethyl)benzylsulfonylbenzo[*d*]thiazole (5e)
Yield: 0.170 g (0.455 mmol, >99%); white solid; R_f = 0.15 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3435, 3007, 2955, 2473, 2297, 1962, 1936, 1890, 1799, 1701, 1619, 1552, 1470, 1420, 1334, 1266, 1239, 1152, 1128, 1070, 1021, 960, 945, 854 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.82 (s, 2 H, CH_2), 7.43 (d, *J* = 8.1 Hz, 2 H, ArH-2′,6′), 7.56 (d, *J* = 8.1 Hz, 2 H, ArH-3′,5′), 7.61 (ddd, *J* = 1.3, 7.3, 8.3 Hz, 1 H, ArH-6), 7.67 (ddd, *J* = 1.3, 7.2, 8.4 Hz, 1 H, ArH-5), 7.97 (dd, *J* = 0.9, 7.6 Hz, 1 H, ArH-4), 8.26 (dd, *J* = 0.7, 7.8 Hz, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.3, 122.4, 123.7, 125.5, 125.8, 127.9, 128.3, 130.4, 131.1, 131.6, 136.9, 152.5, 164.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.9.

MS (70 eV, EI): *m*/*z* (%) = 359/358/357 (2/4/28, [M^+]), 294/293/292 (9/36/100, [M – SO_2^+]), 159 (70, [$C_8H_6F_3^+$]).

HR-EIMS: *m*/*z* calcd for $C_{15}H_{10}N_2O_4S_2$: 357.0105; found: 357.0108.

2-(2-Chloropyridin-3-yl)methylsulfonylbenzo[*d*]thiazole (5f)
Yield: 0.285 g (0.879 mmol, 56%); beige solid; R_f = 0.10 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3930, 3819, 3073, 2949, 2908, 2789, 2494, 2445, 2273, 1954, 1925, 1584, 1562, 1470, 1417, 1203 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 4.95 (s, 2 H, CH_2), 7.30 (dd, *J* = 4.8, 7.7 Hz, 1 H, ArH-5′), 7.59–7.68 (m, 2 H, ArH-5,6), 7.90 (dd, *J* = 1.9, 7.7 Hz, 1 H, ArH-4′), 7.99 (d, *J* = 8.2 Hz, 1 H, ArH-7), 8.23 (d, *J* = 7.8, 1 H, ArH-4), 8.40 (dd, *J* = 1.9, 4.8 Hz, 1 H, ArH-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 57.7, 122.3, 122.5, 122.9, 125.7, 127.9, 128.4, 137.2, 141.7, 150.4, 152.4, 152.6, 164.1.

MS (70 eV, EI): *m*/*z* (%) = 324/326 (0.06/0.03, [M^+]), 289 (100, [$C_{13}H_9N_2S_2O_2^+$]), 259 (21), 225 (45), 126 (70, [$C_6H_5ClN^+$]).

HR-EIMS: *m*/*z* calcd for $C_{13}H_9ClN_2O_2S_2$: 323.9794; found: 323.9797.

Anal. Calcd for $C_{13}H_9ClN_2O_2S_2$: C, 48.07; H, 2.79; N, 8.62; S, 19.74. Found: C, 48.07; H, 2.93; N, 8.68; S, 19.44.

Electrophilic Fluorination; 2-[(2-Bromophenyl)fluoromethylsulfonyl]benzo[*d*]thiazole (7a); Typical Procedure
Under argon, sulfone **5a** (0.200 g, 0.540 mmol, 1.00 equiv) was dissolved in anhyd MeCN (15 mL) and cooled to –30 °C. To the reaction mixture, NaH (26.0 mg, 0.660 mmol, 1.20 equiv, 60% in mineral oil) was added. After 15 min, solid NFSi (0.208 g, 0.660 mmol, 1.20 equiv) was added. The mixture was stirred at this temperature for 20 h, warmed to r.t., and stirred for additional 4 h. The mixture was quenched with brine (5 mL), the layers were separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (10 mL), H_2O (10 mL) and brine (10 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure. Column chromatography (silica gel, *c*Hex–EtOAc, 19:1) yielded **7a** (0.154 g, 0.400 mmol, 74%) as a colorless solid; R_f = 0.35 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3418, 3073, 2962, 2862, 2494, 2435, 2335, 1949, 1913, 1590, 1467, 1348, 1156 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, *J* = 45.4 Hz, 1 H, CHF), 7.41 (dt, *J* = 1.5, 7.5 Hz, 1 H, ArH-5′), 7.46 (dt, *J* = 1.1, 7.7 Hz, 1 H, ArH-4′), 7.62–7.76 (m, 3 H, ArH-5,6,3′), 7.75 (dd, *J* = 1.7, 7.7 Hz, 1 H, ArH-6′), 8.05 (dd, *J* = 1.4, 7.3 Hz, 1 H, ArH-7), 8.33 (dd, *J* = 1.4, 7.8 Hz, 1 H, ArH-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 100.3, 122.3, 124.7, 125.9, 126.7, 127.9, 128.5, 130.4, 133.0, 133.5, 137.6, 152.9, 162.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –169.8.

MS (70 eV, EI): *m/z* (%) = 385/387 (0.2/0.2, [M$^+$]), 321/322/324 (19/17/2, [$C_{14}H_9BrFNS^+$]), 242 (58), 187/189 (100/69, [$C_7H_5BrF^+$]), 134 (17, [$C_7H_4NS^+$]).

HR-EIMS: *m/z* calcd for $C_{14}H_9BrFNO_2S_2$: 384.9242; found: 384.9239.

Anal. Calcd for $C_{14}H_9BrFNO_2S_2$: C, 43.53; H, 2.35; N, 3.63; S, 16.60. Found: C, 43.70; H, 2.66; N, 3.54; S, 16.25.

2-[(4-Chlorophenyl)fluoromethylsulfonyl]benzo[*d*]thiazole (7b)
Yield: 0.123 g (0.358 mmol, 58%); white solid; R_f = 0.41 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3092, 3065, 2952, 2551, 2492, 2436, 2304, 2028, 1964, 1919, 1796, 1735, 1595, 1552, 1490, 1464, 1409, 1350, 1318, 1278, 1262, 1238, 1221, 1155, 1088, 1049, 1014, 924 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (d, *J* = 45.7 Hz, 1 H, CHF), 7.47 (d, *J* = 8.3 Hz, 2 H, ArH-3′,5′), 4.57 (d, *J* = 8.6 Hz, 2 H, ArH-2′,6′), 7.62–7.71 (m, 2 H, ArH-5,6), 8.05 (m, 1 H, ArH-4), 8.28 (m, 1 H, ArH-7).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.2, 122.3, 125.7, 127.9, 128.5, 129.2, 129.6, 129.7, 132.3, 137.5, 138.0, 152.8, 162.4.

MS (FAB): *m/z* (%) = 344/343/342 [M + H$^+$], 278 [M + H – SO_2^+], 197 [$C_7H_4NO_2S_2^+$], 182.

FAB-HRMS: *m/z* calcd for $C_{14}H_{10}ClFNO_2S_2$: 341.9825; found: 341.9821.

2-{Fluoro-[2-(trifluoromethyl)phenyl]methylsulfonyl}benzo[*d*]thiazole (7d)
Yield: 0.255 g (0.681 mmol, 49%); colorless solid; R_f = 0.45 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3100, 2022, 1795, 1605, 1552, 1465, 1414, 1353, 1316, 1281, 1159, 1127 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, $J_{H,F}$ = 45.8 Hz, 1 H, CHF), 7.67 (m, 3 H, ArH-7,3′,4′), 7.76 (t, *J* = 7.3 Hz, 1 H, ArH-5′), 7.84 (d, *J* = 7.6 Hz, 1 H, ArH-4), 8.07 (t, *J* = 7.2 Hz, 2 H, ArH-5,6), 8.34 (d, *J* = 7.8 Hz, 1 H, ArH-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 97.1, 122.1, 122.3, 124.8, 125.1, 126.0, 126.7, 128.0, 128.6, 130.8, 131.9, 132.4, 137.5, 152.8, 162.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –164.0, –56.8.

MS (70 eV, EI): *m/z* (%) = 375 (1, [M$^+$]), 310 (38), 242 (18), 177 (100, [$C_8H_5F_4^+$]), 127 (9).

HR-EIMS: *m/z* calcd for $C_{15}H_9F_4NO_2S_2$: 375.0010; found: 375.0007.

Anal. Calcd for $C_{15}H_9F_4NO_2S_2$: C, 48.00; H, 2.42; N, 3.73; S, 17.08. Found: C, 48.15; H, 2.47; N, 3.69; S, 17.62.

2-{Fluoro-[4-(trifluoromethyl)phenyl]methylsulfonyl}benzo[*d*]thiazole (7e)
Yield: 0.035 g (0.092 mmol, 33%); white solid; R_f = 0.16 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3068, 2962, 2439, 1939, 1815, 1729, 1620, 1552, 1464, 1419, 1351, 1319, 1236, 1158, 1137, 1065, 1018, 964, 854, 796, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.71 (d, *J* = 46.0 Hz, 1 H, CHF), 7.68 (m, 2 H, ArH-5,6), 7.77 (s, 4 H, ArH-2′,3′,5′,6′), 8.07 (m, 1 H, ArH-7), 8.29 (m, 1 H, ArH-4).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.0, 122.4, 125.8, 125.8, 126.5, 128.0, 128.6, 128.7, 128.7, 130.2, 133.5, 137.5, 152.8, 162.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –174.4, –62.8.

MS (70 eV, EI): *m/z* (%) = 375 (1, [M$^+$]), 311 (51, [M – SO_2H^+]), 177 (100, [$C_8H_5F_4^+$]), 127 (18).

HR-EIMS: *m/z* calcd for $C_{15}H_9F_4NO_2S_2$: 375.0010; found: 375.0008.

2-[(2-Chloropyridin-3-yl)fluoromethylsulfonyl]benzo[*d*]thiazole (7f)
Yield: 0.060 g (0.174 mmol, 56%); white solid; R_f = 0.09 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3087, 2922, 2855, 2639, 2501, 2263, 1955, 1925, 1801, 1714, 1578, 1461, 1409, 1352, 1320, 1282, 1232, 1159, 1118, 1078, 1041, 964, 926, 850, 808, 762, 737, 725 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, *J* = 45.6 Hz, 1 H, CHF), 7.43 (dd, *J* = 7.7, 4.8 Hz, 1 H, ArH-4′), 7.63–7.71 (m, 2 H, ArH-4,7), 8.08 (m, 1 H, ArH-6′), 8.13 (ddd, *J* = 1.9, 3.5, 7.8 Hz, 1 H, ArH-5′), 8.34 (ddd, *J* = 1.4, 3.2, 7.7 Hz, 1 H, ArH-6), 8.62 (ddd, *J* = 1.8, 4.7, 25.8 Hz, 1 H, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 97.6, 122.6, 122.3 (+, C-Ar-4), 122.8, 125.9, 128.0, 128.7, 137.5, 139.1, 151.3, 152.3, 152.8, 161.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –172.3.

MS (70 eV, EI): *m/z* (%) = 342 (0.2, [M$^+$]), 307 (3, [M – Cl$^+$]), 261 (37), 243 (67), 162 (61), 144 (100, [$C_6H_4ClFN^+$]).

HR-EIMS: *m/z* calcd for $C_{13}H_8FClN_2O_2S_2$: 341.9699; found: 341.9703.

Fluoroolefins 10; General Procedure
Fluorinated BT-sulfone **7** (1.20 equiv) and aldehyde **9** (0.080–0.510 mmol, 1.00 equiv) were dissolved in anhyd THF (33 mL/mmol **9**) at 0 °C. To the mixture, LiHMDS (2.40 equiv) was added dropwise and stirred 1.5 h at 0 °C. The reaction was quenched with sat. aq $NaHCO_3$ (10 mL/mmol **9**) and extracted with EtOAc (3 × 30 mL/mmol **9**). The combined organic layers were washed with brine (10 mL/mmol **9**) and dried (Na_2SO_4). The solvent was evaporated and the crude product was purified by column chromatography (*c*Hex–EtOAc).

1-Bromo-2-{1-fluoro-2-[2-(trifluoromethyl)phenyl]vinyl}benzene (10a)
Yield: 0.064 g (0.220 mmol, 61%); colorless oil.

***Z*-Isomer**
R_f = 0.50 (*c*Hex).

IR (KBr): 3073, 1672, 1605, 1490, 1454, 1315, 1163, 1121 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (dd, $J_{H,F}$ = 1.8, 34.8 Hz, 1 H, CH=CF), 7.29 (m, 1 H, ArH-5′), 7.39 (dt, *J* = 1.0, 7.6 Hz, 2 H, ArH-4,5), 7.48 (d, *J* = 7.2 Hz, 1 H, ArH-6′), 7.52 (t, *J* = 7.7 Hz, 1 H, ArH-4′), 7.60 (d, *J* = 8.0 Hz, 1 H, ArH-6), 7.70 (d, *J* = 7.9 Hz, 1 H, ArH-3), 8.02 (d, *J* = 7.9 Hz, 1 H, ArH-3′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 106.9, 121.9, 122.8, 125.6, 125.9, 127.4, 127.9, 128.3, 130.83, 131.1, 131.2, 131.8, 133.8, 134.1, 157.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.7, –59.9.

MS (70 eV, EI): *m/z* (%) = 344 (26, [M$^+$]), 245 (66), 196 (100).

HR-EIMS: *m/z* calcd for $C_{15}H_9BrF_4$: 343.9823; found: 343.9821.

***E*-Isomer**
R_f = 0.60 (*c*Hex).

IR (KBr): 3071, 1679, 1591, 1577, 1469, 1429, 1317, 1282, 1222, 1190, 1165, 1124 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (dd, $J_{H,F}$ = 2.1, 17.2 Hz, 1 H, CH=CF), 6.94 (d, *J* = 7.5 Hz, 1 H, ArH-3), 7.20 (m, 5 H, ArH-4,5,6,4′,5′), 7.63 (d, *J* = 7.6 Hz, 2 H, ArH-3′,6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.7, 123.6, 124.2, 125.8, 127.3, 127.5, 128.6, 130.8, 131.3, 131.5, 131.9, 132.4, 133.3, 133.4, 158.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –87.0, –60.4.

MS (70 eV, EI): *m*/*z* (%) = 344 (67, [M^+]), 245 (66), 196 (100).

HR-EIMS: *m*/*z* calcd for $C_{15}H_9BrF_4$: 343.9823; found: 343.927.

Anal. Calcd for $C_{15}H_9BrF_4$: C, 52.02; H, 2.63. Found: C, 51.97; H, 2.90.

(*E*)-3-[2-(2-Bromophenyl)-2-fluorovinyl]-2-chloropyridine (10b)

Yield: 0.037 g (0.120 mmol, 57%); yellow oil; R_f = 0.35 (*c*Hex–EtOAc, 5:1).

IR (KBr): 3450, 3056, 2926, 1674, 1578, 1558, 1471, 1431, 1397, 1348, 1179, 1091 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.70 (d, $J_{H,F}$ = 16.7 Hz, 1 H, CH=CF), 6.92 (dd, *J* = 4.7, 7.7 Hz, 1 H, ArH-3′), 7.07 (ddd, *J* = 0.5, 1.8, 7.6 Hz, 1 H, ArH-6′), 7.27–7.30 (m, 3 H, ArH-4,5,5′), 7.62–7.66 (m, 1 H, ArH-4′), 8.19 (dd, *J* = 1.9, 4.7 Hz, 1 H, ArH-6).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.9, 122.1, 123.4, 127.8, 128.7, 131.8, 132.0, 132.5, 133.5, 138.0, 148.2, 154.4, 160.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –84.1.

MS (70 eV, EI): *m*/*z* (%) = 311/313/315 (61/80/19, [M^+]), 232 (14, [$C_{13}H_8ClFN^+$]), 197 (100, [$C_{13}H_8FN^+$]), 85 (27).

HR-EIMS: *m*/*z* calcd for $C_{13}H_8NBrClF$: 310.9512; found: 310.9510.

4-[2-(2-Bromophenyl)-2-fluorovinyl]pyridine (10c)

Yield: 0.031 g (0.112 mmol, 51%); colorless oil; R_f = 0.29 (*c*Hex–EtOAc, 1:1).

IR (KBr): 3440, 3057, 2922, 2850, 1713, 1678, 1630, 1597, 1563, 1492, 1468, 1385, 1223, 1188, 1096, 1075, 1026, 992 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.12 (d, *J* = 36.7 Hz, 1 H, CH=CF), 6.48 (d, *J* = 17.8 Hz, 1 H, CHCF), 6.81 (d, *J* = 4.2 Hz, 2 H_{arom}), 7.28–7.41 (m, 4 H_{arom}), 7.50 (d, *J* = 4.1 Hz, 2 H_{arom}), 7.55 (dd, *J* = 7.7, 1.5 Hz, 1 H_{arom}), 7.66–7.74 (m, 3 H_{arom}), 8.39 (br s, 2 H_{arom}), 8.64 (br s, 2 H_{arom}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.4, 110.0, 121.5, 121.7, 127.5, 128.0, 128.3, 129.5, 130.7, 131.4, 131.8, 132.1, 133.6, 133.9, 140.6, 141.0, 149.7, 150.0, 151.1, 159.6, 160.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –90.2, –80.7.

MS (70 eV, EI): *m*/*z* (%) = 279/278/277 (42/7/42, [M^+]), 199/198 (14/100, [M – Br^+]), 170 (31).

HR-EIMS: *m*/*z* calcd for $C_{13}H_9BrFN$: 279.9902; found: 279.9900.

1-[2-(4-Chlorophenyl)-2-fluorovinyl]-2-(trifluoromethyl)benzene (10d)

Yield: 0.062 g (0.135 mmol, 65%); colorless oil; R_f = 0.77 (*c*Hex).

IR (KBr): 3471, 2075, 2924, 1904, 1655, 1598, 1577, 1543, 1496, 1456, 1404, 1354, 1316, 1209, 1162, 1122, 1095, 1064, 1036, 1011, 957, 887 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.55 (dq, *J* = 1.7, 36.4 Hz, 1 H, CH=CF), 6.59 (dq, *J* = 1.8, 19.6 Hz, 1 H, CH=CF), 7.06 (d, *J* = 6.9 Hz, 1 H_{arom}), 7.12 (d, *J* = 3.8 Hz, 1 H_{arom}), 7.09–7.16 (m, 1 H_{arom}), 7.24–7.40 (m, 7 H_{arom}), 7.33 (d, *J* = 8.8 Hz, 1 H_{arom}), 7.46–7.52 (m, 1 H_{arom}), 7.63 (d, *J* = 7.6 Hz, 1 H_{arom}), 7.62–7.65 (m, 2 H_{arom}), 7.90 (d, *J* = 7.9 Hz, 1 H_{arom}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.5, 106.6, 124.3, 124.5, 125.9, 126.0, 126.1, 126.2, 127.0, 127.3, 127.4, 127.7, 128.1, 128.6, 129.0, 129.0, 129.4, 129.5, 129.7, 131.0, 131.1, 131.7, 131.8, 131.9, 135.6, 135.6, 157.2, 157.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –113.8, –97.2, – 61.4, –59.8.

MS (70 eV, EI): *m*/*z* (%) = 302/301/300 (32/16/100, [M^+]), 283/282/281 (1/4/2, [M – F^+]), 265 (5, [M – Cl^+]), 245 (15), 196 (28).

HR-EIMS: *m*/*z* calcd for $C_{15}H_9ClF_4$: 300.0328; found: 300.0331.

(*Z*)-1-Bromo-2-{2-fluoro-2-[2-(trifluoromethyl)phenyl]vinyl}benzene (10e)

Yield: 0.035 g (0.102 mmol, 20%); colorless oil; R_f = 0.35 (*c*Hex).

IR (KBr): 3449, 3069, 1670, 1605, 1578, 1494, 1314, 1174, 1136 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.41 (d, $J_{H,F}$ = 35.4 Hz, 1 H, CH=CF), 7.16 (dt, *J* = 1.6, 7.8 Hz, 1 H, ArH-5), 7.36 (t, *J* = 7.6 Hz, 1 H, ArH-4), 7.56 (t, *J* = 7.6 Hz, 1 H, ArH-4′), 7.62 (dd, *J* = 1.1, 8.0 Hz, 2 H, ArH-3,6), 7.67 (t, *J* = 8.8 Hz, 1 H, ArH-5′), 7.78 (d, *J* = 7.7 Hz, 1 H, ArH-3′), 7.95 (dd, *J* = 1.6, 7.9 Hz, 1 H, ArH-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.6, 123.5, 123.8, 126.8, 127.5, 128.7, 129.1, 129.9, 130.7, 131.1, 131.6, 131.9, 132.7, 132.8, 165.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –60.7, –84.8.

MS (70 eV, EI): *m*/*z* (%) = 344/345/346 (61/60/9, [M^+]), 245 (36, [$C_{15}H_8F_3^+$]), 196 (100, [$C_{14}H_9F^+$]), 58 (29), 43 (61).

HR-EIMS: *m*/*z* calcd for $C_{15}H_9BrF_4$: 343.9823; found: 343.9826.

Anal. Calcd for $C_{15}H_9BrF_4$: C, 52.20; H, 2.63. Found: C, 52.30; H, 2.73.

2-Fluoro-3-{2-fluoro-2-[4-(trifluoromethyl)phenyl]vinyl}pyridine (10f)

Yield: 0.019 g (0.068 mmol, 85%); yellow solid; R_f = 0.19 (*c*Hex–EtOAc, 19:1).

IR (KBr): 3065, 2928, 1930, 1668, 1618, 1600, 1565, 1517, 1431, 1409, 1325, 1249, 1167, 1130, 1069, 1016, 976, 888, 849 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.48 (d, *J* = 19.4 Hz, 1 H, CH=CF), 6.62 (d, *J* = 38.3 Hz, 1 H, CH=CF), 7.04 (m, 1 H_{arom}), 7.23 (ddd, *J* = 1.7, 4.9, 7.4 Hz, 1 H_{arom}), 7.47 (dddd, *J* = 0.8, 1.9, 7.5, 9.5 Hz, 1 H_{arom}), 7.51 (d, *J* = 8.7 Hz, 2 H_{arom}), 7.60 (d, *J* = 8.6 Hz, 2 H_{arom}), 7.62–7.72 (m, 3 H_{arom}), 7.79 (d, *J* = 8.4 Hz, 1 H_{arom}), 7.94 (ddd, *J* = 2.0, 7.5, 9.3 Hz, 1 H_{arom}), 8.12 (d, *J* = 4.8 Hz, 1 H_{arom}), 8.21 (ddd, *J* = 1.0, 1.9, 4.9 Hz, 1 H_{arom}), 8.38 (ddd, *J* = 1.9, 7.8, 9.7 Hz, 1 H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 102.7, 107.0, 121.1, 121.4, 121.8, 122.7, 123.6, 123.8, 124.9, 125.4, 125.6, 125.8, 126.0, 128.3, 130.8, 131.9, 132.0, 134.4, 135.2, 140.4, 143.5, 147.1, 158.6, 160.2, 160.7, 162.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.5, –92.0, –71.0, –68.2, –63.5, –63.0.

MS (70 eV, EI): *m*/*z* (%) = 287/286/285 (1/14/100, [M^+]), 267/266 (6/46, [M – F^+]), 217/216 (2/11, [M – CF_3^+]), 145 (1, [$C_7H_4F_3^+$]).

HR-EIMS: *m*/*z* calcd for $C_{14}H_8F_5N$: 285.0576; found: 285.0579.

3-[2-(2-Bromophenyl)-1-fluorovinyl]-2-chloropyridine (10g)

Yield: 0.024 g (0.078 mmol, 60%); colorless oil; R_f = 0.19 (*Z*), 0.25 (*E*) (*c*Hex–EtOAc, 99:1).

IR (KBr): 3436, 3056, 2925, 2853, 1925, 1676, 1579, 1558, 1469, 1437, 1398, 1349, 1277, 1230, 1180, 1134, 1101, 1061, 1036, 1025, 1005, 947, 877 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75–6.88 (m, 3 H, CH=CF, H_{arom}), 6.99–7.07 (m, 3 H_{arom}), 7.18 (m, 2 H_{arom}), 7.37 (dd, *J* = 7.2 Hz, 1 H_{arom}), 7.48–7.58 (m, 3 H_{arom}), 7.63 (d, *J* = 8.0 Hz, 1 H_{arom}), 7.95 (d, *J* = 7.7 Hz, 1 H_{arom}), 8.34–8.42 (m, 2 H, ArH-6).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.7, 113.4, 122.2, 122.3, 124.1, 124.3, 127.4, 127.5, 129.0, 129.2, 129.4, 130.3, 130.3, 130.8, 132.4, 132.6, 132.8, 132.9, 133.1, 138.3, 139.3, 139.7, 140.8, 150.7, 153.8, 155.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –104.5, –92.8.

MS (70 eV, EI): *m*/*z* (%) = 315/313/311 (17/66/54, [M^+]), 278/276 (18/18), 232 (6, [M – Br^+]), 197 (100).

HR-EIMS: *m*/*z* calcd for $C_{13}H_8BrClFN$: 310.9512; found: 310.9511.

Suzuki Coupling Reaction; 4′-Chloro-2-{2-fluoro-2-[2-(trifluoromethyl)phenyl]vinyl}biphenyl (11e); Typical Procedure

Under argon, fluoroolefin **10e** (20.0 mg, 0.060 mmol, 1.00 equiv), 4-chlorophenylboronic acid (**12**; 24.0 mg, 0.140 mmol, 2.40 equiv), $Pd(OAc)_2$ (1.0 mg, 0.003 mmol, 0.050 equiv), Ph_3P (3.0 mg (0.009 mmol, 0.150 equiv), K_2CO_3 (25.0 mg, 0.180 mmol, 3.00 equiv) were dissolved in anhyd DMF (5 mL). The flask containing the reaction mixture was evacuated and flushed with argon. The mixture was heated 3 d at 90 °C, quenched with aq 1 M HCl (5 mL), and extracted with Et_2O (3 × 15 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. Column chromatography (silica gel, *c*Hex) of the crude product afforded **11e** (20.0 mg, 0.052 mmol, 86%, *E*/*Z* = 2.6:1.0) as a colorless oil; R_f = 0.41 (*c*Hex, *E*-isomer), 0.36 (*c*Hex, *Z*-isomer).

IR (KBr): 3084, 3053, 3026, 2926, 1912, 1844, 1668, 1604, 1579, 1494, 1471, 1448, 1396, 1315, 1175, 1125, 1105 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.86 [d, *J* = 35.8 Hz, 1 H, (*Z*)-CH=CF], 6.58 [d, *J* = 19.9 Hz, 1 H, (*E*)-CH=CF] 7.31–7.61 (m, 20 H_{arom}), 7.73 (d, *J* = 7.5 Hz, 1 H, *Z*-H_{arom}), 7.76 (d, *J* = 7.7 Hz, 1 H, *E*-H_{arom}), 7.81 (d, *J* = 7.7 Hz, 1 H, *E*-H_{arom}), 7.99 (d, *J* = 7.8 Hz, 1 H, *Z*-H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 109.4, 111.1, 111.8, 112.1, 122.6, 124.7, 126.8, 126.9, 127.1, 127.3, 127.4, 127.5, 127.9, 128.2, 128.3, 128.4, 128.6, 127.7, 128.6, 129.0, 129.0, 129.7, 129.9, 130.0, 130.2, 130.8, 130.9, 131.0, 131.9, 132.1, 132.7, 133.2, 133.4, 139.8, 155.8, 156.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –97.6, –85.7, –60.7, –60.1.

MS (70 eV, EI): *m*/*z* (%) = 376/377/378 (91/12/23, [M^+]), 341 (8, [$C_{21}H_{13}F_4^+$]), 301 (100), 199 (15).

HR-EIMS: *m*/*z* calcd for $C_{21}H_{13}ClF_4$: 376.0641; found: 376.0645.

4′-Chloro-2-{1-fluoro-2-[2-(trifluoromethyl)phenyl]vinyl}biphenyl (11a)

Yield: 0.022 g (0.105 mmol, 75%); colorless oil; R_f = 0.37 (*c*Hex).

IR (KBr): 3448, 2927, 1671, 1605, 1475, 1452, 1317, 1166, 1127 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.22 [dd, $J_{H,F}$ = 1.8, 35.0 Hz, 1 H, (*Z*)-CH=CF], 6.53 [dd, $J_{H,F}$ = 2.3, 18.9 Hz, 1 H, (*E*)-CH=CF], 6.83 (d, *J* = 7.3 Hz, 1 H_{arom}), 6.94 (d, *J* = 8.0 Hz, 1 H_{arom}), 7.05–7.64 (m, 18 H_{arom}), 7.70 (d, *J* = 7.8 Hz, 1 H_{arom}), 7.88 (d, *J* = 7.4 Hz, 1 H_{arom}), 8.67 (d, *J* = 8.2 Hz, 1 H_{arom}), 8.69 (d, *J* = 8.9 Hz, 1 H_{arom}).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 106.1, 107.7, 122.5, 122.5, 124.4, 125.8, 126.8, 127.3, 127.4, 127.4, 127.8, 127.8, 128.2, 128.3, 128.6, 129.1, 129.6, 129.7, 130.1, 130.3, 130.4, 130.7, 130.8, 131.1, 131.3, 131.5, 131.7, 132.4, 133.5, 133.2, 138.5, 139.5, 139.7, 140.9, 146.7, 161.4, 162.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –96.0, –82.9, –60.6, –60.11.

MS (70 eV, EI): *m*/*z* (%) = 376 (67, [M^+]), 341 (68, [$C_{21}H_{13}F_4^+$]), 301 (100).

HR-EIMS: *m*/*z* calcd for $C_{21}H_{13}ClF_4$: 376.0641; found: 376.0640.

Anal. Calcd for $C_{21}H_{13}ClF_4$: C, 66.94; H, 3.48. Found: C, 66.86; H, 3.74.

2-Chloro-3-[2-(4′-chlorobiphenyl-2-yl)-2-fluorovinyl]pyridine (11b)

Yield: 8.00 mg (0.025 mmol, 25%); yellow oil; R_f = 0.32 (*c*Hex–EtOAc, 10:1).

IR (KBr): 3060, 2926, 1720, 1664, 1557, 1476, 1444, 1396, 1287, 1179, 1090 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.18 [d, $J_{H,F}$ = 37.0 Hz, 1 H, (*Z*)-CH=CF], 6.47 [d, $J_{H,F}$ = 19.2 Hz, 1 H, (*E*)-CH=CF], 6.86–8.31 (m, 22 H_{arom}).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 100.3, 105.4, 121.7, 121.8, 122.0, 122.3, 122.6, 124.8, 126.9, 127.8, 128.2, 128.6, 128.8, 129.4, 129.8, 130.1, 130.2, 130.4, 130.5, 130.7, 130.9, 131.1, 131.3, 131.9, 133.5, 133.6, 138.3, 138.5, 138.6, 139.3, 139.4, 139.7, 147.8, 148.4, 148.1, 149.7, 160.0, 167.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –95.3, –91.9.

MS (70 eV, EI): *m*/*z* (%) = 343/344/345 (41/8/27, [M^+]), 308 (26, [$C_{19}H_{12}ClFN^+$]), 272 (100), 254 (25, [$C_{19}H_{12}N^+$]).

HR-EIMS: *m*/*z* calcd for $C_{19}H_{12}Cl_2NF$: 343.0330; found: 343.0329.

Crystal Structure Determinations of 5a and 7c/8c[28]

All single-crystal X-ray diffraction studies were carried out on a Bruker-Nonius APEXII diffractometer (**5a**, Figure 2) or a Bruker-Nonius Kappa-CCD diffractometer (**8c**, Figure 3) at 123(2) K using MoKα radiation (λ = 0.71073 Å). Direct methods (SHELXS-97) were used for structure solution and refinement was carried out using SHELXL-97 (full-matrix least-squares on F^2). Non-hydrogen atoms were refined anisotropically (except disordered F atoms in **7c/8c**), hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. The crystal structure of **7c/8c** shows disorder of the F atoms. There is a sit occupancy disorder of the difluorinated sulfone **8c** and the (additionally positional disordered) monofluorinated sulfone **7c** in the ratio 1:3.

5a

Colorless crystals, $C_{14}H_{10}BrNO_2S_2$, *M* = 368.26, crystal size 0.20 × 0.16 × 0.08 mm, monoclinic, space group $P2_1/n$ (No. 14), *a* = 10.2305(4) Å, *b* = 11.0139(3) Å, *c* = 12.0621(5) Å, *b* = 96.008(2)°, *V* = 1351.66(9) $Å^3$, *Z* = 4, *r* (calc) = 1.810 Mg m^{-3}, *F*(000) = 736, *m* = 3.349 mm^{-1}, 6039 reflexes ($2\theta_{max}$ = 50°), 2352 unique [R_{int} = 0.036], 181 parameters, *R*1 (*I* > 2σ(*I*)) = 0.028, *wR2* (all data) = 0.070, S = 1.07, largest diff. peak and hole 0.555 and –0.466 e $Å^{-3}$.

7c/8c

Colorless crystals, $C_{14}H_{7.75}Cl_2F_{1.25}NO_2S_2 \cdot [0.75(C_{14}H_8Cl_2FNO_2S_2) \cdot 0.25(C_{14}H_7Cl_2F_2NO_2S_2)]$, *M* = 380.73, crystal size 0.50 × 0.20 × 0.15 mm, monoclinic, space group $P2_1/n$ (No. 14), *a* = 10.003(2) Å, *b* = 22.940(4) Å, *c* = 13.138(2) Å, *b* = 102.00(2)°, *V* = 2948.9(9) $Å^3$, *Z* = 8, *r* (calc) = 1.715 Mg m^{-3}, *F*(000) = 1536, *m* = 0.742 mm^{-1}, 19480 reflexes ($2\theta_{max}$ = 55°), 6714 unique [R_{int} = 0.031], 395 parameters, 18 restraintes, *R*1 (*I* > 2σ(*I*)) = 0.040, *wR2* (all data) = 0.097, S = 1.06, largest diff. peak and hole 1.019 and –0.731 e $Å^{-3}$.

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(28) Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 755487 (**5a**) and CCDC 755489 (**7c/8c**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK [Fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].