Synthetic aspects; numbering follows the main manuscript.

Synthesis of triflate (7)

A Schlenk tube was charged with 2-bromo-4,5-difluorophenol (1.64 ml, 3g, 1.44·10⁻² mol) under nitrogen and 9 ml of pyridine. The stirred solution is cooled to 0º C and then trifluoromethanesulfonic anhydride, 2.67 ml, is added very slowly through the rubber stopper via a syringe. The temperature is maintained at 0º C for 5 min and then allowed to warm to room temperature and stirred overnight (20-25 h).

The resulting mixture was poured into water and extracted with ethyl ether. The ether extract (upper phase) was washed sequentially with water, 10% aqueous hydrochloric acid solution (2x), water, and a concentrated sodium chloride solution, dried (MgSO₄), and concentrated to yield an oil. Chromatography (flash column, petroleum spirit 40-60ºC / EtOAc, 20:1) and solvent removing (rotavapor, 40º C, high vacuum, 3h, to remove all the EtOAc) afforded the desired product, 7, as a colourless liquid (3.2 g, 65%)

1H-NMR (CDCl₃, 400 MHz) δ ppm: 7.56 (t, J=8.46, 8.46 Hz, 1H); 7.28 (dd, J=6.85, 9.51 Hz, 1H). 13C{1H}-NMR (CDCl₃, 101 MHz) δ ppm: 149.5 (dd, 3JFC=12.9, 1JFC=256.1 Hz, 1C, C-F); 149.3 (dd, 3JFC=13.6, 1JFC=254.8 Hz, 1C, C-F); 142.4 (dd, 3JFC=3.9, 8.2 Hz, 1C, C-OTf); 122.3 (d, 2JFC =21.4 Hz, 1C, C-H); 118.5 (q, 1JFC=320.8 Hz, 1C, CF₃); 112.8 (d, 2JFC=21.9 Hz, 1C, C-H); 110.8 (dd, J=4.6, 7.5 Hz, 1C, C-Br).

19F{1H}-NMR (CDCl₃, 377 MHz) δ ppm: -72.9 (s, 3F, CF₃); -131.5 (d, 3JFF=21.3 Hz, 1F, C-F); -132.3 (d, 3JFF=21.3 Hz, 1F, C-F).

MS CI+(m/z) Found 339.8801 ([M]+) ; C₇H₂BrF₅O₂S requires 339.8828.

Triflate (2) was prepared similarly from 3-bromophenol as a light-coloured oil ; MS CI+(m/z) Found 339.8801 ([M]+) ; C₇H₂BrF₅O₂S requires 339.8828.

**Catalytic Experiments**

All the catalytic experiments were carried out under nitrogen in Schlenk tubes. Products were analyzed by $^{19}$F NMR and GC-MS spectroscopy.

**Suzuki reaction**

In a typical experiment, a Schlenk tube was charged with 4-methoxyphenylboronic acid (47 mg, 0.308 mmol, 5% excess), K$_3$PO$_4$ (124.4 mg, 0.586 mmol), LiBr (25 mg, 0.293 mmol) and PdCl$_2$(PPh$_3$)$_2$ (11 mg, 0.0147 mmol, 5% molar to aryl halide). Then, the schlenk tube was evacuated and refilled with nitrogen three times. Afterwards, it was charged with aryl halide-triflate (7) (100 mg, 0.293 mmol) under a nitrogen atmosphere and 3 ml of toluene and then heated at reflux temperature overnight (22 h). The resulting mixture was cooled and then filtered. Finally, the crude was analyzed by $^{19}$F NMR and GC/MS.

**Suzuki double-coupling experiments**

In the first experiment, previous procedure was followed but the amount of aryl halide-triflate (7) was halved to ensure (1:2) molar rate with regard to the boronic acid (50 mg, 0.147 mmol). 4-methoxyphenylboronic acid (47 mg, 0.308 mmol, 5% excess), K$_3$PO$_4$ (124.4 mg, 0.586 mmol) and PdCl$_2$(PPh$_3$)$_2$ (11 mg, 0.0147 mmol, 5% molar to aryl halide).

**Kumada reaction**

In a typical experiment, a Schlenk tube was charged with PhMgBr (0.117 mL, 3M solution, 0.352 mmol, 20% excess), LiBr (26 mg, 0.293 mmol) and PdCl$_2$(PPh$_3$)$_2$ (11 mg, 0.0147 mmol, 5% molar to aryl halide). Then, the Schlenk tube was evacuated and refilled with nitrogen three times. Afterwards, it was charged with aryl halide-triflate (7) (100 mg, 0.293 mmol) under a nitrogen atmosphere and 3 ml of toluene and then heated
at reflux temperature overnight (22 h). The resulting mixture was cooled and then filtered. Finally, the crude was analyzed by $^{19}$F NMR and GC/MS.

**Heck reaction**

In a typical experiment, a Schlenk tube was charged with sodium carbonate (47 mg, 0.440 mmol), dppp (12 mg, 0.0293 mmol, 10% molar to aryl halide) and Pd$_2$(dba)$_3$ (13 mg, 0.0147 mmol, 5% molar to aryl halide). Then, the Schlenk tube was evacuated and refilled with nitrogen three times. Afterwards, it was charged with 3 ml of toluene, butyl acrylate (56 mg, 0.440 mmol) and aryl halide-triflate (7) (100 mg, 0.293 mmol), both through a rubber septum under a nitrogen atmosphere and then the mixture was heated at reflux temperature overnight (22 h). The resulting mixture was cooled and then filtered. Finally, the reaction was analyzed by $^{19}$F NMR and GC/MS.

**Amination**

In a typical experiment, a Schlenk tube was charged with sodium tert-butoxide (39 mg, 0.410 mmol), dppp (6 mg, 0.0150 mmol, 10% molar to aryl halide) and Pd$_2$(dba)$_3$ (6.7 mg, 0.0073 mmol, 5% molar to aryl halide). Then, the Schlenk tube was evacuated and refilled with nitrogen three times. Afterwards, it was charged with 3 ml of toluene, morpholine (31 mg, 0.352 mmol) and aryl halide-triflate (7) (100 mg, 0.293 mmol), both through a rubber septum under a nitrogen atmosphere and then the mixture was heated at 80º C (22 h). The resulting mixture was cooled and then filtered. Finally, the crude was analyzed by $^{19}$F NMR and GC/MS.

(8) C$_{14}$H$_9$O$_4$F$_5$S $\text{GC-MS Cl}^+$(m/z): calcd for ([M + NH$_4$]$^+$): 368.0142, found: 368.0147; $^{19}$F-$^1$H-$^1$NMR (377 MHz, CDCl$_3$) $\delta$ ppm: -73.8 (s, 3F, CF$_3$); -134.8 (d, $^3$J$_{FF}$ = 21.8 Hz, 1F, C-F); -136.0 (d, $^3$J$_{FF}$ = 21.8 Hz, 1F, C-F).

(9) C$_{13}$H$_9$BrF$_2$O $\text{GC-MS Cl}^+$(m/z): calcd for ([M]$^+$): 297.9805, found: 297.9798; $^{19}$F-$^1$H-$^1$NMR (377 MHz, CDCl$_3$) $\delta$ ppm: -137.7 (d, $^3$J$_{FF}$ = 21.3 Hz, 1F); -138.8 (d, $^3$J$_{FF}$ = 20.9 Hz, 1F) (minor product).
(10) C_{20}H_{16}O_{2}F_{2} \text{ GC-MS CI+ (m/z): calcd for ([M]^+): 326.1118, found: 326.1117; }\text{^{19}F\{^1H\}-NMR (377 MHz, CDCl}_3\text{) }\delta \text{ ppm: -140.9 (s, 2F, C-F) (minor product).}

(11) C_{13}H_{7}O_{3}F_{5}S \text{ GC-MS CI+ (m/z): calcd for ([M]^+): 338.0036, found: 338.0031; }\text{^{19}F\{^1H\}-NMR (377 MHz, CDCl}_3\text{) }\delta \text{ ppm: -73.4 (s, 3F, CF}_3\text{); -133.0 (d, }^3J_{FF} = 21.8 \text{ Hz, 1F, C-F); -149.1 (dd, } J = 253.9, 14.2 \text{ Hz, C-F, 1C); 141.3 (dd, } J = 8.2, 3.3 \text{ Hz, C-OTf, 1C); 134.8 (t, } J = 6.3, 6.3 \text{ Hz, C-Ph, 1C); 133.9 (s, C^i\text{-Ph, 1C); 129.3 (s, C^o\text{-Ph, 2C); 129.0 (s, C^p\text{-Ph, 1C); 128.8 (s, C^s\text{-Ph, 2C); 119.7 (d, } J = 19.2 \text{ Hz, C-H, 1C); 118.3 (q, } J = 320.7, 320.7, 320.6 \text{ Hz, CF}_3\text{, 1C); 112.3 (d, } J = 21.1 \text{ Hz, C-H, 1C).}

(12) C_{13}H_{7}O_{3}F_{5}S \text{ }^{19}F\{^1H\}-NMR (377 MHz, CDCl}_3\text{) }\delta \text{ ppm: -137.1 (d, }^3J_{FF} = 21.7 \text{ Hz, 1F, C-F); -138.6 (d, }^3J_{FF} = 21.7 \text{ Hz, 1F, C-F) (minor product).}

(13) C_{18}H_{12}F_{2} \text{ GC-MS CI+ (m/z): calcd for ([M]^+): 266.0907, found: 266.0909; }\text{^{19}F\{^1H\}-NMR (377 MHz, CDCl}_3\text{) }\delta \text{ ppm: -140.2 (s, 2F, C-F).}^{3}

(15) C_{10}H_{10}BrF_{2}NO \text{ GC-MS CI+ (m/z): calcd for ([M]^+): 276.9914, found: 276.9904; }\text{^{19}F\{^1H\}-NMR (377 MHz, CDCl}_3\text{) }\delta \text{ ppm: -135.5 (d, }^3J_{FF} = 21.9 \text{ Hz, 1F, C-F); -141.1 (d, }^3J_{FF} = 21.9 \text{ Hz, 1F, C-F).}

(16) C_{13}H_{13}BrF_{2}O_{2} \text{ GC-MS CI+ (m/z): calcd for ([M+H]^+): 319.0145, found: 319.0134; }\text{^{19}F\{^1H\}-NMR (377 MHz, CDCl}_3\text{) }\delta \text{ ppm: -131.5 (d, }^3J_{FF} = 22.2 \text{ Hz, 1F, C-F); -136.6 (d, }^3J_{FF} = 22.2 \text{ Hz, 1F, C-F).}