Supplementary Information

General Information

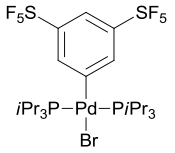
All reactions were done in an argon atmosphere. Benzene-d_6, tetrahydrofurane-d_8 (thf-d_8), *n*-hexane and tetrahydrofurane (thf) were dried by stirring over Na/K and then distilled. The complexes [Pd(Me)$_2$(tmeda)], [Pd(P*i*Pr$_3$)$_2$] (**1**) and the triisopropylphosphine were prepared according to literature procedures.[1] 3,5-bis(pentafluorosulfanyl)-1-bromobenzene (**2**), 3-pentafluorosulfanyl-1-iodobenzene (**4**), and 4-pentafluorosulfanyl-1-bromobenzene (**6**) were purchased from *Apollo Scientific*. All other reagents were either purchased from *Sigma Aldrich* or *abcr*.

Microanalyses were performed with a HEKAtech Euro EA Elemental Analyzer. The NMR spectra were recorded at 300 K on a Bruker DPX 300 or a Bruker Avance III 300 NMR spectrometer. The ^{1}H NMR chemical shifts were referenced to residual benzene-d_5 at δ = 7.16 ppm or thf-d_7 at δ = 3.58 ppm. The ^{13}C{^{1}H} NMR chemical shifts were referenced to benzene-d_6 at δ 128.06 ppm. The ^{19}F NMR and ^{31}P{^{1}H} spectra were referenced to external $CFCl_3$ at δ = 0.0 ppm, and 85% H_3PO_4 at δ = 0.0 ppm. The EI mass spectra were recorded with an AMD MSI 604 Concept 1H at 70 eV. GC/MS spectra were measured at an Agilent 6890N gas-phase chromatograph (Agilent 19091S-433 Hewlett-Packard) and an Agilent 5973 Network mass selective detector at 70 eV. HRMS (ESI) analyses were carried out with a Micromass Q-TOF II spectrometer.

The crystallographic data collections of complex **11** and compound **9** and **15** were performed with a BRUKER D8 VENTURE area detector, Mo-*K*α radiation (λ = 0.71073 Å). Multi-scan absorption corrections implemented in SADABS[2] were applied to the data. The structures were solved by intrinsic phasing method (SHELXT-2013)[3] and refined by full-matrix least square procedures based on F^2 with all measured reflections (SHELXL-2013)[4] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. Diffraction data of complexes **3**, **5** and **7** were collected with a STOE IPDS 2θ diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 100 K. The structures were solved by direct methods (SHELXS-97)[5] and refined with full-matrix least-square methods on F^2 (SHELXL-97, SHELXL-2013)[4, 6]. The hydrogen atoms were placed at calculated positions and refined by using a riding model. Crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

TON are defined as number of borylation steps based on the amount of aromatic substrate.

Synthesis of *trans*-[Pd(Br){3,5-$(SF_5)_2C_6H_3$}($PiPr_3$)$_2$] (3)



3

A solution of [Pd($PiPr_3$)$_2$] (**1**) (144.0 mg, 0.337 mmol) in *n*-hexane (10 mL) was treated with 3,5-bis(pentafluorosulfanyl)-1-bromobenzene (**2**) (138.0 mg, 0.337 mmol) and the reaction mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo and the colourless solid was sparsely washed with *n*-hexane (1 mL) to give 179.0 mg (69%) of **3**.

^{1}H NMR (300.1 MHz, benzene-d_6): δ = 8.26 (s, 2H, CH_{ar}), 7.92 (s, 1H, CH_{ar}), 2.20 (dsept, $^3J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 7.3 Hz, 6H, PC*H*CH_3), 1.04 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 21.2 Hz, 36H, PCHC*H*$_3$) ppm; the $^3J_{H,H}$ coupling constant was obtained from a ^{1}H{^{31}P} NMR spectrum.**^{13}C{^{1}H} NMR** (75.5 MHz, thf-d_8): 157.4 (t, J_{CP} = 5 Hz), 151.9 (quin, J_{CF} = 15 Hz), 138.7 (s), 117.8 (br), 25.2 (vt, J_{CP} = 11 Hz), 19.7 (s). **^{31}P{^{1}H} NMR** (121.5 MHz, benzene-d_6): δ = 32.1 (s) ppm. **^{19}F NMR** (282.4 MHz, benzene-d_6): δ = 83.9 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 151 Hz, 2F), 62.9 (B_4 part, apparent d coupling $^2J_{FF}$ = 151 Hz, 8F) ppm. **HR ESI-MS**, *m/z* calcd. for $C_{24}H_{45}F_{10}P_2PdS_2^+$ $[M]^+$: 755.1313, found: 755.1308. **Elemental analysis** (%) calcd. for $C_{24}H_{45}BrF_{10}P_2PdS_2$: calc.: C 34.48, H 5.43, S 7.76; found: C 35.14, H 5.50, S 7.24.

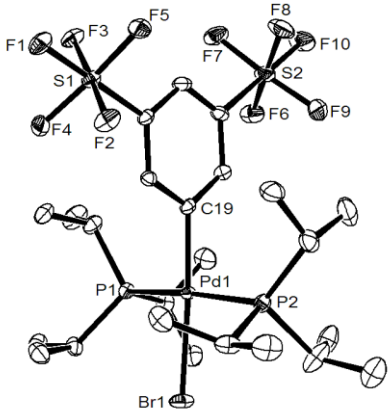
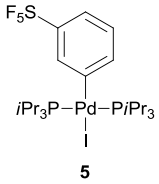


Figure S 1 Molecular structure of **3 (**ORTEP; ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]:Pd(1)-C(19) 2.011(2); Pd(1)-Br(1) 2.5067(3); Pd(1)-P(1) 2.3557(5); Pd(1)-P(2) 2.3597(5); Br(1)-Pd(1)-C(19) 173.51(6); Br(1)-Pd(1)-P(1) 90.203(16).

Synthesis of *trans*-[Pd(I)(3-$SF_5C_6H_4$)(P*i*Pr_3)$_2$] (5)



5

A solution of [Pd(P*i*Pr_3)$_2$] (**1**) (129.0 mg, 0.302 mmol) in *n*-hexane (10 mL) was treated with 3-pentafluorosulfanyl-1-iodobenzene (**4**) (37 µL, 0.302 mmol, ρ = 2.7 g/mL) and the reaction mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo and the colourless solid was sparsely washed with *n*-hexane (1 mL) to give 40.0 mg (18%) of (**5**).

^{1}H NMR (300.1 MHz, benzene-d_6): δ = 8.07 (s, 1H, CH_{ar}), 7.44 (d, $^2J_{HH}$ = 7.6 Hz, 1H, CH_{ar}), 7,14 (m, 1H, CH_{ar}), 6.65 (t, $^2J_{HH}$ = 7.6 Hz, 1H, CH_{ar}), 2.39 (dsept, $^3J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 7.0 Hz, 6H, PC*H*CH_3), 1.08 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 21.4 Hz, 36H, PCHC*H*$_3$) ppm; the $^3J_{H,H}$ coupling constant was obtained from a ^{1}H{^{31}P} NMR spectrum. **^{31}P{^{1}H} NMR** (121.5 MHz, benzene-d_6): δ = 31.1 (s) ppm. **^{19}F NMR** (282.4 MHz, benzene-d_6): δ = 86.9 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 150 Hz, 1F), 62.8 (B_4 part, apparent d coupling $^2J_{FF}$ = 150 Hz, 4F) ppm. **HR ESI-MS**, *m/z* calcd. for $C_{24}H_{46}F_5P_2PdS^+$ $[M]^+$: 629.1750, found: 629.1745. **Elemental analysis** (%) calcd. for $C_{24}H_{46}F_5IP_2PdS$: calc.: C 38.08, H 6.13, S 4.24; found: C 38.69, H 6.13, S 3.85.

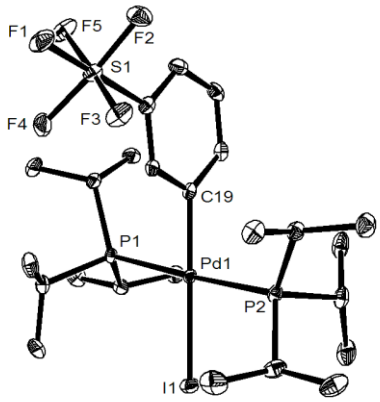
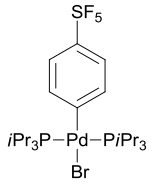


Figure S 3 Molecular structure of **5 (**ORTEP; ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]:Pd(1)-C(19) 2.014(2); Pd(1)-I(1) 2.7009(2); Pd(1)-P(1) 2.3788(6); Pd(1)-P(2) 2.3607(6); I(1)-Pd(1)-C(19) 178.35(6); I(1)-Pd(1)-P(1) 91.312(15).

Synthesis of *trans*-[Pd(Br)(4-$SF_5C_6H_4$)(P*i*Pr_3)$_2$] (7)



7

A solution of [Pd(P*i*Pr_3)$_2$] (**1**) (225.0 mg, 0.527 mmol) in *n*-hexane (10 mL) was treated with 4-pentafluorosulfanyl-1-bromobenzene (**6**) (82 µL, 0.527 mmol) and the reaction mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo and the colourless solid was sparsely washed with *n*-hexane to give 102.0 mg (27%) of (**7**).

^{1}H NMR (300.1 MHz, benzene-d_6): δ = 7.44 (d, $^2J_{HH}$ = 8.1 Hz, 2H, CH_{ar}), 7.25 (d, $^2J_{HH}$ = 8.3 Hz, 2H, CH_{ar}), 2.25 (dsept, $^3J_{HH}$ = 7.1 Hz, $^2J_{HP}$ = 7.1 Hz, 6H, PC*H*CH_3), 1.07 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 21.1 Hz, 36H, PCHC*H*$_3$) ppm; the $^3J_{HH}$ coupling constant was obtained from a ^{1}H{^{31}P} NMR spectrum. **^{31}P{^{1}H} NMR** (121.5 MHz, benzene-d_6): δ = 31.4 (s) ppm. **^{19}F NMR** (282.4 MHz, benzene-d_6): δ = 87.4 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 149 Hz, 1F), 62.9 (B_4 part, apparent d coupling $^2J_{FF}$ = 149 Hz, 4F) ppm. **HR ESI-MS**, *m/z* calcd. for $C_{24}H_{46}F_5P_2PdS^+$ $[M]^+$: 629.1750, found: 629.1745. **Elemental analysis** (%) calcd. for $C_{24}H_{46}BrF_5P_2PdS$: calc.: C 40.60, H 6.53, S 4.52; found: C 41.04, H 6.50, S 3.96.

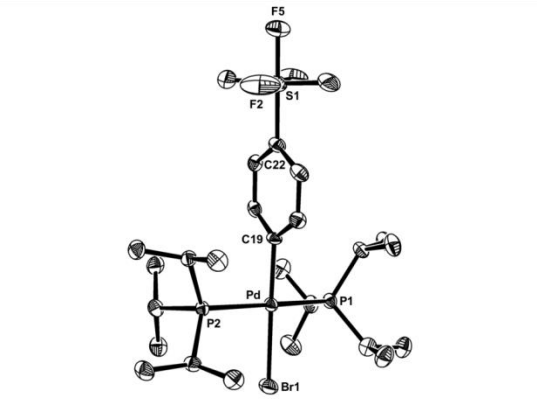


Figure S 4 Molecular structure of **7 (**ORTEP; ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]:Pd(1)-C(19) 1.993(4); Pd(1)-Br(1) 2.4753(5); Pd(1)-P(1) 2.3258(11); Pd(1)-P(2) 2.3392(10); Br(1)-Pd(1)-C(19) 177.63(13); Br(1)-Pd(1)-P(1) 89.01(3).

Treatment of *trans*-[Pd(I)(3-$SF_5C_6H_4$)(P*i*Pr_3)$_2$] (5) with B_2pin_2

A solution of **5** (10 mg, 0.013 mmol) in benzene-d_6 (0.6 mL) in a NMR tube was treated with B_2pin_2 (3.3 mg, 0.013 mmol). The mixture was then heated to 60° C for 16 h. The ^{19}F, ^{1}H spectra revealed the presence of 1-Bpin-3-$SF_5C_6H_4$ (**8**) in a ratio of **5** : **8** of 1:1.2 and traces of (3-$SF_5C_6H_4$)$_2$ (**9**). The borylation product **8** as well as **9** could not be isolated from the reaction

mixture. The analytical data are listed below. GC-MS analysis confirmed the formation of I-Bpin, *m/z* [M-CH_3]: 240.

Treatment of *trans*-[Pd(Br)(4-$SF_5C_6H_4$)(P*i*Pr$_3$)$_2$] (7) with B_2pin_2

A solution of **7** (79.4 mg, 0.112 mmol) in thf-d_8 (0.6 mL) in a NMR tube was treated with B_2pin_2 (28.4 mg, 0.112 mmol) and the reaction mixture was heated to 60° C for 48 h. ^{19}F and ^1H NMR spectra revealed the presence of 1-Bpin-4-$SF_5C_6H_4$ (**10**) in a ratio of **7** : **10** of 1:0.5. The borylation product **10** could not be isolated from the reaction mixture. The analytical data are listed below.

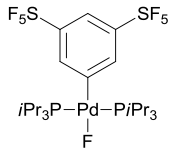
Treatment *trans*-[Pd(Br){3,5-(SF_5)$_2$$C_6H_3$}(P*i*Pr$_3$)$_2$] (3) with B_2pin_2

Complex **3** (20 mg, 0.049 mmol) and B_2pin_2 (12 mg, 0.049 mmol) were in a NMR tube dissolved in thf-d_8 (0.5 mL). The reaction mixture was heated to 60° C for 16 h. The ^{19}F, ^1H and $^{31}P\{^1H\}$NMR spectra revealed no conversion. .

Treatment of *trans*-[Pd(Br){3,5-(SF_5)$_2$$C_6H_3$}(P*i*Pr$_3$)$_2$] (3) with CsF

To a solution of **3** (53.0 mg, 0.063 mmol) in thf-d_8 (0.6 mL) in a NMR tube, CsF (125 mg, 1.001 mmol) was added. The reaction mixture was heated at 60 °C for 16 h. The $^{31}P\{^1H\}$NMR spectra revealed the formation of *trans*-[Pd(F){3,5-(SF_5)$_2$$C_6H_3$}(P*i*Pr$_3$)$_2$] (**11**) (7 %). The analytical data are listed below.

Synthesis of *trans*-[Pd(F){3,5-(SF_5)$_2$$C_6H_3$}(P*i*Pr$_3$)$_2$] (11)



11

Complex **3** (100 mg, 0.120 mmol) and AgF (500 mg, 3.94 mmol) were in a NMR tube suspended in thf-d_8 (0.5 mL). The reaction mixture was exposed in absence of light to ultrasound for 3 h at 60° C. The NMR spectra confirmed the formation of **11**. The solution was filtered and the filtrate stirred additionally over CsF for 16 h to remove HF impurities. The solution was filtered and the solvent was removed from the filtrate in vacuo. The solid was recrystallized in *n*-hexane (1 mL) affording 64 mg (69%) of **11**.

^{1}H NMR (300.1 MHz, thf-d_8): δ = 8.10 (s, 2H, CH_{ar}), 7.65 (s, 1H, CH_{ar}), 2.22 (dsept, $^3J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 7.3 Hz, 6H, PC*H*CH_3), 1.29 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 21.0 Hz, 36H, PCHC*H*$_3$) ppm; the $^3J_{HH}$ coupling constant was obtained from a $^1H\{^{31}P\}$ NMR spectrum.

$^{31}P\{^{1}H\}$ NMR (121.5 MHz, thf-d_8): δ = 32.4 (d, $^{2}J_{P,F}$ = 14 Hz) ppm. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 83.3 (AB_4, A part, apparent quin coupling $^{2}J_{FF}$ = 150 Hz, 1F), 62.0 (B_4 part, apparent d coupling $^{2}J_{FF}$ = 150 Hz, 4F), -316.7 (t, $^{2}J_{PF}$ = 14 Hz, PdF) ppm. **HR ESI-MS**, *m/z* calcd. for $C_{24}H_{45}F_{10}P_2PdS_2^+$ $[M]^+$: 755.1313, found: 755.1308.

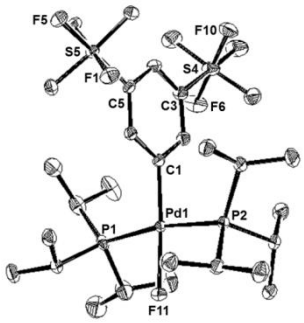
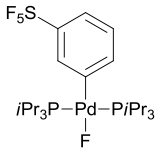


Figure S 2 Molecular structure of **11 (**ORTEP; ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd(1)-C(1) 1.9879(17); Pd(1)-F(11) 2.0412(12); Pd(1)-P(1) 2.3288(6); Pd(1)-P(2) 2.3397(6); F(11)-Pd(1)-C(1) 176.35(6); F(11)-Pd(1)-P(1) 88.03(04).

Synthesis of *trans*-[Pd(F)(3-$SF_5C_6H_4$)(P*i*Pr_3)$_2$] (12)

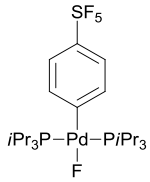


12

Complex **5** (3.5 mg, 0.005 mmol) and AgF (22.0 mg, 0.014 mmol) were in a NMR tube suspended in thf-d_8 (0.5 mL). The reaction mixture was exposed in absence of light to ultrasound for 3 h at 60°C. The NMR spectra confirmed the formation of **12**. The solution was filtered and the filtrate stirred additionally over CsF for 16 h to remove HF impurities. The solution was filtered and the solvent was removed from the filtrate in vacuo. The solid was recrystallized in *n*-hexane (1 mL).

^{1}H NMR (300.1 MHz, thf-d_8): δ = 7.59 (d, $^{2}J_{HH}$ = 8.1 Hz, 2H, CH_{ar}), 7.39 (d, $^{2}J_{HH}$ = 8.3 Hz, 2H, CH_{ar}), 2.27 (dsept, $^{3}J_{HH}$ = 7.1 Hz, $^{2}J_{HP}$ = 7.1 Hz, 6H, PC*H*CH_3), 1.10 (dd, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HP}$ = 21.1 Hz, 36H, PCHC*H*$_3$) ppm; the $^{3}J_{HH}$ coupling constant was obtained from a $^{1}H\{^{31}P\}$ NMR spectrum.**$^{31}P\{^{1}H\}$ NMR** (121.5 MHz, thf-d_8): δ = 32.4 (d, $^{2}J_{PF}$ = 13 Hz) ppm. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 82.4 (AB_4, A part, apparent coupling $^{2}J_{FF}$ = 150 Hz, 1 F), 60.0 (B_4 part, d, $^{2}J_{FF}$ = 150 Hz, 4 F), -311.2- (-311.5) (m, Pd*F*) ppm.

Synthesis of *trans*-[Pd(F)(4-$SF_5C_6H_4$)(P*i*Pr_3)$_2$] (13)



13

Complex **7** (45 mg, 0.0634 mmol) and AgF (220 mg, 1.734 mmol) were in a NMR tube suspended in thf-d_8 (0.5 mL). The reaction mixture was exposed in absence of light to ultrasound for 3 h at 60° C. The NMR spectra confirmed the formation of **13**. The solution was filtered and the filtrate stirred additionally over CsF for 16 h to remove HF impurities. The solution was filtered and the solvent was removed from the filtrate in vacuo. The solid was recrystallized in *n*-hexane (1 mL) affording 32 mg (78%) of **13**.

^{1}H NMR (300.1 MHz, thf-d_8): δ = 7.69 (d, $^2J_{HH}$ = 8.1 Hz, 2H, CH_{ar}), 7.29 (d, $^2J_{HH}$ = 8.3 Hz, 2H, CH_{ar}), 2.27 (dsept, $^3J_{HH}$ = 7.0 Hz, $^2J_{HP}$ = 7.0 Hz, 6H, PC*H*CH_3), 1.33 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 20.2 Hz, 36H, PCHC*H*$_3$) ppm; the $^3J_{HH}$ coupling constant was obtained from a ^{1}H{^{31}P} NMR spectrum. **^{31}P{^{1}H} NMR** (121.5 MHz, thf-d_8): δ = 34.1 (d, $^2J_{PF}$ = 13 Hz) ppm. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 86.9 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 149 Hz, 1F), 62.8 (B_4 part, apparent d coupling $^2J_{FF}$ = 149 Hz, 4F), - 306.6 (br s, PdF) ppm.

Treatment of *trans*-[Pd(F){3,5-(SF_5)$_2$$C_6H_3$}(P*i*$Pr_3$)$_2$] (11) with B_2pin_2

Complex **11** (11 mg, 0.0142 mmol) and B_2pin_2 (1.8 mg, 0.0071 mmol) were in a NMR tube dissolved in thf-d_8 (0.5 mL). The reaction mixture was then heated to 60 °C. The ^{19}F, ^{1}H NMR spectra revealed new datasets in addition to the signals of **11**, which corresponded to the borylation product **14** and traces of the homocoupling product **15**. The borylation product **14** as well as **15** could not be isolated from the reaction mixture. The analytical data are listed below.

Treatment of *trans*-[Pd(F){3,5-(SF_5)$_2$$C_6H_3$}(P*i*$Pr_3$)$_2$] (11) with B_2pin_2 and P*i*Pr_3

Complex **11** (20 mg, 0.026 mmol) and B_2pin_2 (7 mg, 0.026 mmol) were in a NMR tube dissolved in thf-d_8 (0.5 mL). P*i*Pr_3 (5 µL, 0.026 mmol) was added to the solution. The reaction mixture was first kept for 16 h at room temperature and then warmed to 60° C and stirred for another 16 h. ^{19}F, ^{1}H and ^{31}P{^{1}H}NMR spectra revealed no conversion of **11**.

Treatment *trans*-[Pd(Br){3,5-(SF_5)$_2$$C_6H_3$}(P*i*$Pr_3$)$_2$] (3) with KOAc

In a NMR tube KOAc (5 mg, 0.0478 mmol) and **3** (41 mg, 0.049 mmol) were suspended in thf-d_8 (0.5 mL). The reaction mixture was first kept for 16 h at room temperature and then warmed to 60° C and stirred for another 16 h. The ^{19}F, ^{1}H and $^{31}P\{^{1}H\}$NMR spectra revealed no conversion.

Catalytic reaction of 3,5-bis(pentafluorosulfanyl)-1-bromobenzene (2), B_2pin_2 in the presence of one eq CsF.

In a Young NMR tube, equipped with a thf-d_8/TMS capillary as external standard, [Pd(Me)$_2$(tmeda)] (3.1 mg, 0.012 mmol) was dissolved in thf-d_8 (0.5 mL). P*i*Pr$_3$ (4.7 µL, 0.024 mmol), **2** (50 mg 0.122 mmol), B_2pin_2 (31 mg, 0.122 mmol) and CsF (19 mg, 0.122 mmol) were added to the solution. The reaction mixture was heated to 80° C for 7 d. The ^{1}H NMR spectra revealed a new broad signal for the borylation product **14** and of the homocoupling product **15**. The intense overlap of the signals does not allow an assignment of the signals. The solvent was removed from the reaction mixture in vacuo. The residue was sublimed at room temperature for 6 h affording 7 mg (1%) of **15** as white crystals, which were analyzed by X-Ray crystal structure analysis.

Analytical data for (3,5-(SF$_5$)$_2$C$_6$H$_3$)$_2$ (**15**): **^{1}H NMR** (300.1 MHz, thf-d_8): δ = 8.39 (broad s, 2H, CH$_{ar}$), 8,32 (broad s, 4H, CH$_{ar}$) ppm. **$^{13}C\{^{1}H\}$ NMR** (75.5 MHz, thf-d_8): δ = 154.5 (quin, J_{CF} = 20 Hz), 141.8 (s), 130.3-130.1 (m), 125.0-124.7 (m) ppm. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 79.1 (AB$_4$, A part, apparent quin coupling $^{2}J_{FF}$ = 152 Hz, 4F), 60.0 (B$_4$ part, apparent d coupling $^{2}J_{FF}$ = 152 Hz, 16F) ppm. **GC-MS**, *m/z* [M]: 658. The analytical data for **14** are listed below.

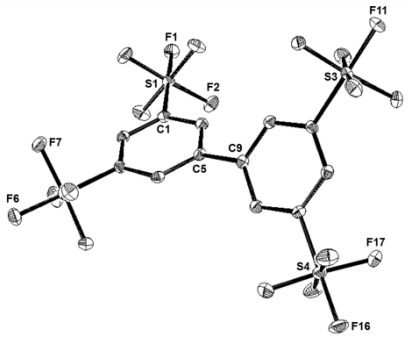


Figure S 5 ORTEP diagram of **15**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) **15**: C(5)-C(9) 1.4881(17); C(1)-S(1) 1.8083(13); S(1)-F(1) 1.5787(8); S(1)-F(2) 1.5885(9); C(4)-C(5)-C(9) 121.97(11); C(1)-S(1)-F(2) 91.84(5); F(1)-S(1)-F(2) 88.04(5).

Catalytic reaction of 3,5-bis(pentafluorosulfanyl)-1-bromobenzene (2), five eq B_2pin_2 in the presence of one eq CsF.

In a Young NMR tube, equipped with a thf-d_8/TMS capillary as external standard, [Pd(Me)$_2$(tmeda)] (3.1 mg, 0.012 mmol) was dissolved in thf-d_8 (0.5 mL). P*i*Pr$_3$ (4.7 µL,

0.024 mmol), **2** (50 mg, 0.122 mmol), B_2pin_2 (155 mg, 0.611 mmol) and CsF (19 mg, 0.122 mmol) were added. The reaction mixture was heated to 80° C. After 7 d the NMR spectroscopic analysis of the reaction solution indicated a complete conversion of **2**. The ^1H and ^{19}F NMR spectra revealed a new dataset corresponding to the borylated product **14** Yield: 80 % (according to the ^1H NMR spectrum).

Analytical data for 1-Bpin-3,5-$(SF_5)_2C_6H_4$ (**14**): **^1H NMR** (300.1 MHz, thf-d_8): δ = 8.37 (s, 1H, CH_{ar}), 8.31 (s, 2H, CH_{ar}), the signals corresponding to the methyl group of the Bpin unit are covered by the resonances for B_2pin_2. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 81.1 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 152 Hz, 1F), 62.0 (AB_4, B_4 part, apparent d coupling $^2J_{FF}$ = 152 Hz, 4F) ppm. **$^{11}B\{^1H\}$ NMR** (96.3 MHz, thf-d_8): δ = 32 (s, br) ppm. **EI-MS**: *m/z* calcd. for $C_{12}H_{15}BF_{10}O_2S_2^+$ $[M]^+$: 456.0447, found: 456.0446; **GC-MS**, *m/z* [M]: 456, [M-CH_3]: 441.

Catalytic reaction of 3-pentafluorosulfanyl-1-iodobenzene (4), B_2pin_2 in the presence of P*i*Pr$_3$

In a NMR tube, equipped with a thf-d_8/TMS capillary as external standard, $[Pd(Me)_2(tmeda)]$ (4 mg, 0.015 mmol) was dissolved in thf-d_8 (0.5 mL). P*i*Pr$_3$ (5.8 µL, 0.030 mmol), 3-pentafluorsulfanyl-1-iodobenzene (**4**) (18.5 µL, 0.151 mmol), B_2pin_2 (38.4 mg, 0.151 mmol) and CsF (23 mg, 0.151 mmol) were added. The reaction mixture was heated to 60° C. The NMR spectroscopic data of the reaction mixture revealed that **4** was converted into (3-$SF_5C_6H_4)_2$ (**9**) as the main product. The solvent was removed from the reaction mixture in vacuo. The residue was sublimed at room temperature for 6 h affording 6 mg (10%) of **9** · B_2pin_2 as colourless crystals, which were analyzed by X-Ray crystal structure analysis.

Analytical data for $(3\text{-}SF_5C_6H_4)_2$ (**9**): **^1H NMR** (300.1 MHz, thf-d_8): δ = 8.09-8.08 (m, 1H, CH_{ar}), 7.94-7.89 (m, 2H, CH_{ar}), 7.73-7.68 (m, 1H, CH_{ar}) ppm. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 82.3 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 152 Hz, 1F), 60.3 (B_4 part, apparent d coupling $^2J_{FF}$ = 152 Hz, 4F) ppm. **GC-MS**, *m/z* [M]: 406.

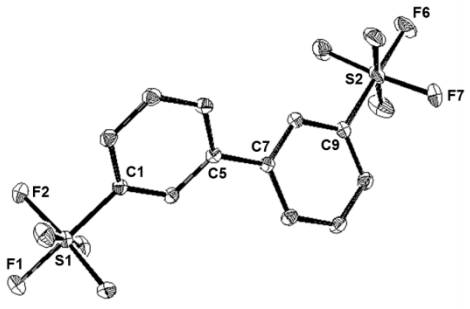


Figure S 6 ORTEP diagram of **9**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) **9**: C(5)-C(7) 1.4832(14); C(1)-S(1) 1.8026(11); S(1)-F(1) 1.5904(8); S(1)-F(2) 1.5909(8); C(6)-C(5)-C(7) 120.12(9); C(1)-S(1)-F(2) 92.60(4); F(1)-S(1)-F(2) 87.73(4).

Catalytic reaction of 3-pentafluorosulfanyl-1-iodobenzene (4) and B_2pin_2 in the presence of P*t*Bu_3

In a Young NMR tube, equipped with a thf-d_8/TMS capillary as external standard, [Pd(Me)$_2$(tmeda)] (4 mg, 0.015 mmol) was dissolved in thf-d_8 (0.5 mL). P*t*Bu_3 (7.3 µL, 0.030 mmol), 3-pentafluorsulfanyl-1-iodobenzene (**4**) (18.5 µL, 0.151 mmol), B_2pin_2 (38.4 mg, 0.151 mmol) and CsF (46 mg, 0.303 mmol) were added. The reaction mixture was heated to 80° C. After 48 h at 80 °C the ^{1}H NMR spectra revealed a conversion to the borylation product **8** of 71% and for the homocoupling product **9** 21%.

Analytical data of **8**: **^{1}H NMR** (300.1 MHz, thf-d_8): δ = 8.12 (broad s, 1H, CH_{ar}) ppm. The other signals corresponding to the aromatic protons could not be assigned, because of overlapping signals. **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 82.4 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 152 Hz, 1F), 60.0 (B_4 part, apparent d coupling $^2J_{FF}$ = 152 Hz, 4F) ppm. **^{11}B{^{1}H} NMR** (96.3 MHz, thf-d_8): δ = 33 (s, br) ppm. **EI-MS**: *m/z* calcd. for $C_{12}H_{16}BF_5O_2S^+$ $[M]^+$: 330.0884, found: 330.0884. **GC-MS**, *m/z* [M]: 330, [M-CH_3]: 315.

Catalytic reaction of 4-pentafluorosulfanyl-1-bromobenzene (6) and B_2pin_2

In a Young NMR tube, equipped with a thf-d_8/TMS capillary as external standard, [Pd(Me)$_2$(tmeda)] (4.5 mg, 0,017 mmol) was dissolved in thf-d_8 (0.5 mL). P*t*Bu_3 (8.6 µL, 0.035 mmol), 4-pentafluorsulfanyl-1-bromobenzene (**6**) (27 µL, 0.177 mmol), B_2pin_2 (44.8 mg, 0.177 mmol) and CsF (27 mg, 0.177 mmol) were added. The reaction mixture was heated to 80° C for 7 d. The NMR spectroscopic data of the reaction mixture revealed 80% conversion and the formation of 1-Bpin-(4-$SF_5C_6H_4$) (**10**) as well as of (3-$SF_5C_6H_4$)$_2$ (**16**). The ratio of the borylation product **10** and the homocoupling product **16** could not be determined, because of the intense overlap of the signals in the reaction mixture. The borylation product **10** as well as **16** could not be isolated from the reaction mixture.

Analytical data of **10** and **16**: **^{1}H NMR** (300.1 MHz, thf-d_8): δ = 7.95 (br, CH_{ar}), 7.90 (br, CH_{ar}), 7.81 (br, CH_{ar}), 7.71 (br, CH_{ar}), 1.12 (br, CH_3) ppm. **GC-MS**, *m/z* [M] **10**: 330, [M-CH_3]: 315, *m/z* [M] **16**: 406.

Additional analytical data of **10**: **^{19}F NMR** (282.4 MHz, thf-d_8): δ = 81.8 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 151 Hz, 1F), 81.7 (AB_4, A part, apparent quin coupling $^2J_{FF}$ = 151 Hz, 1F), 60.1 (B_4 part, apparent d coupling $^2J_{FF}$ = 151 Hz, 4F), 60.0 (B_4 part, apparent d coupling $^2J_{FF}$ = 151 Hz, 4F) ppm. **^{11}B{^{1}H} NMR** (96.3 MHz, thf-d_8): δ = 33 (s, br) ppm.

Table S1 Crystallographic data.

Compound	**3**	**5**	**7**	**11**	**9**	**15**
emperical formulae	$C_{24}H_{44}BrF_{10}P_2PdS_2$	$C_{24}H_{46}IF_5P_2PdS$	$C_{24}H_{46}BrF_5P_2PdS$	$C_{24}H_{44}F_{11}P_2PdS_2$	$C_{12}H_8F_{10}S_2$	$C_{18}H_{18}B_1F_{20}O_2S_2$
molecular weight [g/mol]	834.96	756.91	709.92	775.06	406.30	392.69
cryst. system	triclinic, $P\bar{1}$	monoclinic, $P\,2_1/m$	monoclinic, $P\,2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P\,2_1/n$	triclinic, $P\bar{1}$
a [Å]	10.6334(7)	14.4952(5)	9.3877(5)	10.779(2)	12.1389(18)	9.9552(9)
b [Å]	12.3442(8)	12.5053(4)	12.7766(5)	12.164(3)	8.7547(12)	11.1590(9)
c [Å]	12.6391(8)	18.0453(6)	26.0735(15)	12.241(3)	13.5608(19)	13.6383(11)
α [°]	102.884(3)			80.079(8)		73.775(3)
β [°]	91.323(2)	112.2440(10)	108.762(4)	89.555(7)	100.440(5)	71.961(3)
γ [°]	90.704(2)			88.284(8)		76.711(3)
V [$Å^3$]	161.56(18)	3027.58(18)	2961.2(8)	1580.3(6)	1417.3(3)	1366.1(2)
Z	2	4	4	2	4	4
density [g/cm^3]	1.715	1.661	1.592	1.629	1.904	1.909
F(000)	842	1520	1448	792	808	782
R_{int}	0.0370	0.0428	0.1608	0.0328	0.0335	0.0338
Total nr. of refl.	79663	27669	37275	76927	33804	62428
indep. refl.	8102	8842	6024	9266	6217	7382
refl. with I>2σ(l)	7638	7332	5223	8632	5049	6460
parameters	374	319	319	373	217	410
θ-range [°]	2.50 - 28.42	2.44-31.44	3.189- 26.483	2.53- 30.08	2.49-34.98	2.67-29.15
R_1	0.0272	0.0317	0.0490	0.0299	0.0394	0.0283
wR_2	0.0651	0.0743	0.1427	0.0749	0.0957	0.0692
R_1 (all data)	0.0293	0.0432	0.0584	0.0328	0.0536	0.0356
wR_2 (all data)	0.0661	0.0805	0.1536	0.0769	0.1022	0.0727
GoF	1.035	1.009	1.022	1.063	1.059	1.042
completeness	0.997	0.997	0.997	0.997	0.994	0.997
largest diff. peak / hole [eÅ]	1.802/-1.102	2.110/-1.160	1.084/-1.030	2.675/-1.174	0.699/-0.323	0.514/-0.308
CCDC	1439131	1439132	1439133	1439135	1439134	1439136

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