Supporting Information

Highly regio- and diastereoselective Cu-catalyzed hydroborylation and hydrosilylation of difluorocyclopropenes with B$_2$pin$_2$ and Me$_2$PhSi-Bpin

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1. General information

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. All gem-difluorocyclopropenes were prepared according to previously reported procedures. Toluene and other solvents were dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. \(^1\)H NMR and \(^13\)C NMR spectra were recorded on a 400 spectrometer (400 MHz for \(^1\)H and 100 MHz for \(^13\)C, respectively) using TMS as internal standard. The \(^19\)F NMR spectra were obtained using a 400 spectrometer (376 MHz). CDCl\(_3\) was used as the NMR solvents. High resolution mass spectra (HRMS) were acquired in the electron impact mode (EI) using a TOF mass analyzer. High-resolution mass spectra (ESI) were recorded with a MicroMass LCTTM spectrometer. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

2. The substrates 1a–q used in this reaction

![Chemical Structures](image)

The gem-difluorocyclopropenes 1a–q were prepared according to the reported procedure.\(^1\)
3. Table S1 The influence of the amounts of B$_2$pin$_2$, CuCl, Xantphos and NaOtBu on the yield of the reaction$^a$

![Diagram](image)

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$^a$Reaction conditions: 1a (0.2 mmol), MeOH (2.0 equiv), toluene (2 mL), rt, 12 h, Ar. $^b$Yields are determined by GC analysis based on 1a.

4. General procedures for the synthesis of target compounds

4.1 Cu-catalyzed hydroborylation of various difluorocyclopropenes

An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), B$_2$pin$_2$ 2a (101.6 mg, 0.4 mmol, 2.0 equiv), NaOttBu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of gem-difluorocyclopropenes 1a–q (0.2 mmol) in toluene (0.5 mL) was added, followed by addition of MeOH (12.8 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H$_2$O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na$_2$SO$_4$, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate as eluent to afford the pure target compounds 3aa–qa.

4.2 Cu-catalyzed hydrosilylation of various difluorocyclopropenes

An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), PhMe$_2$Si–Bpin 2b (78.6 mg, 0.3 mmol, 1.5 equiv), NaOttBu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of gem-difluorocyclopropenes 1a–d, 1f–h, 1k–o, 1q (0.2 mmol) in toluene
(0.5 mL) was added, followed by addition of MeOH (12.8 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H₂O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate as eluent to afford the pure target compounds 3ab–db, 3fb–hb, 3kb–ob, 3qb.

5. Hydroboration of 1a on a 5.0 mmol scale

An oven dried 100 mL reaction vial containing a stirring bar was charged with CuCl (49.5 mg, 0.5 mmol, 10 mol%), Xantphos (433.5 mg, 0.75 mmol, 15 mol%), B₂pin₂ 2a (2.54 g, 10.0 mmol, 2.0 equiv), NaOᵗBu (57.6 mg, 0.6 mmol, 12 mol%) and toluene (40 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of gem-difluorocyclopropenes 1a (910 mg, 5.0 mmol, 1.0 equiv) in toluene (5 mL) was added, followed by addition of MeOH (320 mg, 10.0 mmol, 2.0 equiv) in toluene (5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H₂O (30 mL) and extracted with ethyl acetate (20 mL×3). The organic layer was separated and dried over Na₂SO₄, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate as eluent to afford the pure target compounds 3aa.

6. Deuterated experiments (b and c)

An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), B₂pin₂ 2a (101.6 mg, 0.4 mmol, 2.0 equiv), NaOᵗBu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of gem-difluorocyclopropenes 1a (36.4 mg, 0.2 mmol, 1.0 equiv) in toluene (0.5 mL) was added, followed by addition of D₂O (8.0 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H₂O.
(20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na$_2$SO$_4$, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate as eluent to afford the deuterated 3aa with 53% deuterium content (determined by $^1$H NMR).

$^1$H NMR spectrum of deuterated 3aa

An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), B$_2$pin$_2$ 2a (101.6 mg, 0.4 mmol, 2.0 equiv), NaO$_{t\ Bu}$ (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of gem-difluorocyclopropenes 1a (36.4 mg, 0.2 mmol, 1.0 equiv) in toluene (0.5 mL) was added, followed by addition of MeOD (13.2 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H$_2$O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na$_2$SO$_4$, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using n-hexane/ethyl acetate as eluent to afford the deuterated 3aa with 78% deuterium content (determined by $^1$H NMR).
One-pot synthesis of trans-difluorocyclopropyl MIDA boronate 4

An oven dried 25 mL reaction vial containing a stirring bar was charged with CuCl (5.0 mg, 0.05 mmol, 10 mol%), Xantphos (43.4 mg, 0.075 mmol, 15 mol%), B<sub>2</sub>pin<sub>2</sub> 2a (254.0 mg, 1.0 mmol, 2.0 equiv), NaOtbu (5.8 mg, 0.06 mmol, 12 mol%) and toluene (4.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of gem-difluorocyclopropenes 1a (91.0 mg, 0.5 mmol, 1.0 equiv) in toluene (0.5 mL) was added, followed by addition of MeOH (32.0 mg, 1.0 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was filtered and evaporated under vacuum.

The solution of MIDA (441 mg, 3.0 mmol, 6.0 equiv) in DMSO (10 mL) was added to the mixture and was stirred at 110 °C for 12 h under an argon atmosphere. After the completion of reaction, the reaction mixture was quenched with H<sub>2</sub>O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over
Na$_2$SO$_4$, filtered and evaporated under vacuum. Recrystallization with Et$_2$O to afford the pure product 4.

8. Analytical data of compounds

trans-2-(2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3aa). Yield 97% (60.1 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06 (d, $J$ = 8.8 Hz, 2H), 6.77 (d, $J$ = 8.8 Hz, 2H), 3.70 (s, 3H), 2.84 (dd, $J$ = 11.2, 9.6 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.16–1.12 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.7, 127.9, 124.8, 113.6 (dd, $^1J_{CF}$ = 286.9, 281.4 Hz), 112.8, 83.1, 54.2, 29.8 (dd, $^2J_{CF}$ = 11.0, 10.5 Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −125.2 (ddd, $^3J_{HF}$ = 11.2, 4.5 Hz, 1F), −135.4 (dd, $J_{FF}$ = 145.9 Hz, $^3J_{HF}$ = 16.2 Hz, 1F); HRMS (EI): calcd for C$_{16}$H$_{21}$BF$_2$O$_3$ [M]$^+$: 310.1552, found: 310.1553.

trans-2-(2,2-Difluoro-3-(3-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba). Yield 99% (61.4 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24–7.20 (m, 1H), $\delta$ 6.82–6.78 (m, 2H), 6.76 (s, 1H), 3.78 (s, 3H), 2.94 (t, $J$ = 9.6 Hz, 1H), 1.35–1.31 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.7, 135.4, 129.4, 120.2, 114.5 (dd, $^1J_{CF}$ = 286.7, 282.0 Hz), 113.7, 112.6, 84.2, 55.2, 31.5 (dd, $^2J_{CF}$ = 11.2, 10.4 Hz), 24.8, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −124.7 (ddd, $J_{FF}$ = 146.3 Hz, $^3J_{HF}$ = 11.6, 4.9 Hz, 1F), −135.4 (dd, $J_{FF}$ = 145.9 Hz, $^3J_{HF}$ = 16.2 Hz, 1F); HRMS (EI): calcd for C$_{16}$H$_{21}$BF$_2$O$_3$ [M]$^+$: 310.1552, found: 310.1551.

trans-2-(2,2-Difluoro-3-(2-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ca). Yield 78% (48.4 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25–7.22 (m, 1H), 7.09 (d, $J$ = 7.2 Hz, 1H), 6.92–6.87 (m, 1H), 6.87 (d, $J$ = 8.4 Hz, 1H), 3.84 (s, 3H), 3.09 (t, $J$ = 10.8 Hz, 1H), 1.28 (s, 12 H), 1.24–1.19 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7, 128.4, 127.7, 122.4, 120.3, 115.2 (dd, $^1J_{CF}$ = 286.5, 280.7 Hz), 110.3, 84.0, 55.5, 26.8
trans-2-(3-(3,4-Dimethoxyphenyl)-2,2-difluorocyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane  (3da).

 Yield 70% (47.6 mg), yellow solid, m.p.: 98.6–100.3 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.82 (d, $J = 8.0$ Hz, 1H), 6.78–6.76 (m, 1H), 6.73 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.92 (dd, $J = 11.2, 9.2$ Hz, 1H), 1.29 (s, 6H), 1.28 (s, 6H), 1.24–1.22 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.9, 148.3, 126.3, 120.0, 114.6 (dd, $^1J_{CF} = 287.0, 281.6$ Hz), 111.2, 111.1, 84.2, 55.9, 55.9, 31.1 (t, $^2J_{CF} = 10.9$ Hz), 24.9, 24.6 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –124.9 – –125.3 (m, 1F), –135.3 (dd, $^1J_{FF} = 145.5$ Hz, $^3J_{HF} = 15.8$ Hz, 1F). HRMS (EI): calcd for C$_{17}$H$_{23}$BF$_2$O$_4$ [M$^+$]: 340.1657, found: 340.1658.

trans-2-(2,2-Difluoro-3-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane  (3ea). Yield 87% (48.7 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33–7.27 (m, 3H), 7.21 (d, $J = 7.2$ Hz, 2H), 2.96 (t, $J = 10.4$ Hz, 1H), 1.36–1.33 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.0, 128.4, 127.8, 127.2, 114.5 (dd, $^1J_{CF} = 286.8, 281.8$ Hz), 84.2, 31.5 (t, $^2J_{CF} = 10.5$ Hz), 24.9, 24.6 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –124.9 – –125.3 (m, 1F), –135.3 (dd, $^1J_{FF} = 145.5$ Hz, $^3J_{HF} = 15.8$ Hz, 1F). HRMS (EI): calcd for C$_{17}$H$_{23}$BF$_2$O$_4$ [M$^+$]: 340.1657, found: 340.1658.

trans-2-(2,2-Difluoro-3-(p-tolyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane  (3fa). Yield 82% (48.2 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.06–7.01 (m, 4H), 2.85 (dd, $J = 10.8, 9.6$ Hz, 1H), 2.25 (s, 3H), 1.24–1.23 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.8, 129.8, 128.1, 126.7, 113.5 (dd,
\[^1J_{CF} = 286.8, 281.7 \text{ Hz}, \ 83.1, 30.2 \ (t, ^2J_{CF} = 11.2 \text{ Hz}), \ 23.8, 23.5, 20.0 \ (\text{Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the } ^{11}B \text{ nucleus}); ^19F \text{ NMR (376 MHz, CDCl}_3) \delta -125.0 \ (\text{ddd, } ^{1}J_{HF} = 146.1 \text{ Hz, } ^3J_{HF} = 11.6, 4.5 \text{ Hz, 1F}), -135.4 \ (\text{dd, } J_{FF} = 146.0 \text{ Hz, } ^3J_{HF} = 15.9 \text{ Hz, 1F}); \text{HRMS (EI): calcd for } C_{16}H_{21}BF_2O_2 [M]^+: 294.1603, \text{ found: 294.1604.}\]

\[\text{trans-2-} (3-\{(1,1'-\text{Biphenyl})-4-\text{-yl})-2,2-\text{difluorocyclopropyl})-4,4,5,5-\text{tremethyl-1,3,2-dioxaborolane} \ (3ga). \text{ Yield 95\% (67.6 mg), white solid, m.p.: 115.6–117.3 \text{ °C; } ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.58–7.53 \ (m, 4H), 7.44–7.40 \ (m, 2H), 7.35–7.33 \ (m, 1H), 7.29 \ (d, J = 8.0 \text{ Hz, 2H}), 3.03 \ (dd, J = 11.2, 9.6 \text{ Hz, 1H}), 1.36 \ (ddd, J = 15.6, 9.2, 4.4 \text{ Hz, 1H}), 1.29 \ (s, 6H), 1.28(s, 6H); ^13C \text{ NMR (100 MHz, CDCl}_3) \delta 140.7, 140.2, 133.1, 128.8, 128.3, 127.4, 127.2, 127.1, 114.5 \ (\text{dd, } ^1J_{CF} = 287.1, 281.8 \text{ Hz), 84.3, 31.3 \ (t, ^2J_{CF} = 10.9 \text{ Hz), 24.9, 24.6 \ (\text{Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the } ^{11}B \text{ nucleus); } ^19F \text{ NMR (376 MHz, CDCl}_3) \delta -124.7 \ (\text{ddd, } ^{1}J_{HF} = 146.4 \text{ Hz, } ^3J_{HF} = 11.4, 4.4 \text{ Hz, 1F}), -135.4 \ (\text{dd, } J_{FF} = 146.4 \text{ Hz, } ^3J_{HF} = 15.8 \text{ Hz, 1F}); \text{HRMS (EI): calcd for } C_{21}H_{23}BF_2O_2S [M]^+: 356.1759, \text{ found: 356.1758.}\]

\[\text{trans-2-} (2,2-\text{Difluoro-3-}(4-(methylthio)phenyl)cyclopropyl)-4,4,5,5-\text{tremethyl-1,3,2-dioxaborolane} \ (3ha). \text{ Yield 63\% (41.0 mg), yellow oil; } ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.13 \ (d, J = 8.4 \text{ Hz, 2H}), 7.06 \ (d, J = 8.4 \text{ Hz, 2H}, 2.84 \ (t, J = 10.0 \text{ Hz, 1H}), 2.38 \ (s, 3H), 1.21 \ (s, 6H), 1.19 \ (s, 6H), 1.17–1.12 \ (m, 1H); ^13C \text{ NMR (100 MHz, CDCl}_3) \delta 136.3, 129.7, 127.3, 125.7, 113.4 \ (\text{dd, } ^1J_{CF} = 287.2, 281.7 \text{ Hz), 83.2, 29.9 \ (dd, ^2J_{CF} = 11.4, 10.4 \text{ Hz), 23.8, 23.5, 14.9 \ (\text{Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the } ^{11}B \text{ nucleus); } ^19F \text{ NMR (376 MHz, CDCl}_3) \delta -124.9 \ (\text{ddd, } J_{FF} = 146.3 \text{ Hz, } ^3J_{HF} = 11.3, 4.5 \text{ Hz, 1F}), -135.4 \ (\text{dd, } J_{FF} = 146.3 \text{ Hz, } ^3J_{HF} = 15.8 \text{ Hz, 1F}); \text{HRMS (EI): calcd for } C_{16}H_{21}BF_2O_2S [M]^+: 326.1323, \text{ found: 326.1324.}\]

\[\text{trans-2-} (3-(4-Bromophenyl)-2,2-\text{difluorocyclopropyl})-4,4,5,5-\text{tremethyl-1,3,2-dioxaborolane} \ (3ia). \text{ Yield 92\% (65.9 mg), white solid, m.p.: 77.3–78.8 \text{ °C; } ^1H \text{ NMR (400 MHz, CDCl}_3) \delta 7.43 \ (d, J = 8.4 \text{ Hz, 2H}), 7.08 \ (d, J = 8.4 \text{ Hz, 2H), 2.90 \ (dd, J = 11.2, 9.6 \text{ Hz, 1H}), 1.28 \ (s, 6H), 1.27 \ (s, 6H), 1.26–1.23 \ (m, 1H); ^13C \text{ NMR (100 MHz, CDCl}_3)\]
δ 133.0, 131.5, 129.6, 121.1, 114.1 (dd, $^1J_{CF} = 288.2, 281.7$ Hz), 84.3, 30.8 (dd, $^2J_{CF} = 11.6, 10.2$ Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = 125.0 (dddd, $^1J_{FF} = 146.6$ Hz, $^3J_{HF} = 11.3, 3.8$ Hz, 1F), –135.3 (ddddd, $^1J_{FF} = 146.6$ Hz, $^3J_{HF} = 15.8$ Hz, 1F); HRMS (EI): calcd for C$_{15}$H$_{18}$BBrF$_2$O$_2$ [M]$^+$: 358.0551, found: 358.0552.

**trans-2-(3-(3-Bromophenyl)-2,2-difluorocyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ja).** Yield 62% (44.0 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, $^1J_{CF} = 8.0$ Hz, 1H), 7.37 (s, 1H), 7.20–7.16 (m, 1H), 7.14 (d, $^1J_{CF} = 7.6$ Hz, 1H), 2.91 (t, $^1J_{CF} = 10.4$ Hz, 1H), 1.33–1.31 (m, 1H), 1.29 (s, 6H), 1.27 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.3, 131.0, 130.3, 129.9, 126.5, 122.5, 114.1 (dd, $^1J_{CF} = 287.1, 281.9$ Hz), 84.4, 30.8 (dd, $^2J_{CF} = 11.7, 10.2$ Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = –124.9 (ddd, $^1J_{FF} = 147.0$ Hz, $^3J_{HF} = 11.3, 4.5$ Hz, 1F), –135.1 (dd, $^1J_{FF} = 147.0$ Hz, $^3J_{HF} = 16.2$ Hz, 1F); HRMS (EI): calcd for C$_{15}$H$_{18}$BBrF$_2$O$_2$ [M]$^+$: 358.0551, found: 358.0555.

**trans-2-(2,2-Difluoro-3-(4-fluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ka).** Yield 80% (47.6 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.11–7.08 (m, 2H), 6.93–6.89 (m, 2H), 2.85 (t, $^1J_{CF} = 10.4$ Hz, 1H), 1.16–1.13 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.0 (d, $^1J_{CF} = 245.8$ Hz), 128.6 (d, $^1J_{CF} = 2.6$ Hz), 128.4 (d, $^1J_{CF} = 8.1$ Hz), 124.3 (d, $^1J_{CF} = 21.6$ Hz), 113.2 (d, $^1J_{CF} = 286.8, 281.3$ Hz), 83.2, 29.6 (t, $^2J_{CF} = 11.3$ Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = –115.2 – –115.3 (m, 1F), –125.3 (dddd, $^1J_{FF} = 146.7$ Hz, $^3J_{HF} = 11.4, 4.4$ Hz, 1F), –135.4 (dd, $^1J_{FF} = 146.7$ Hz, $^3J_{HF} = 16.0$ Hz, 1F); HRMS (EI): calcd for C$_{15}$H$_{18}$BF$_3$O$_2$ [M]$^+$: 298.1352, found: 298.1351.

**trans-Methyl-4-(2,2-difluoro-3-(4-fluorophenyl)cyclopropyl)benzoate (3la).** Yield 75% (50.7 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, $^1J_{CF} = 8.0$ Hz, 2H), 7.28 (d, $^1J_{CF} = 8.4$ Hz, 2H), 3.91 (s, 3H), 2.99 (t, $^1J_{CF} = 10.0$ Hz, 1H), 1.38 (dddd, $^1J = 16.0, 9.6, 4.8$ Hz, 1H), 1.29 (s, 6H), 1.28 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.1 (d, $^1J_{CF} = 245.8$ Hz), 128.8 (d, $^1J_{CF} = 2.6$ Hz), 128.3 (d, $^1J_{CF} = 8.1$ Hz), 124.5 (d, $^1J_{CF} = 21.6$ Hz), 112.6 (d, $^1J_{CF} = 286.8, 281.3$ Hz), 83.2, 29.6 (t, $^2J_{CF} = 11.3$ Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) δ = –115.2 – –115.3 (m, 1F), –125.3 (dddd, $^1J_{FF} = 146.7$ Hz, $^3J_{HF} = 11.4, 4.4$ Hz, 1F), –135.4 (dd, $^1J_{FF} = 146.7$ Hz, $^3J_{HF} = 16.0$ Hz, 1F); HRMS (EI): calcd for C$_{16}$H$_{21}$BF$_3$O$_2$ [M]$^+$: 298.1352, found: 298.1351.
MHz, CDCl$_3$ δ 166.8, 139.3, 129.6, 129.0, 127.8, 114.1 (dd, $^3J_{CF} = 287.5, 282.0$ Hz), 84.4, 52.1, 31.3 (t, $^2J_{CF} = 10.5$ Hz), 24.8, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}B$ nucleus]; $^{19}F$ NMR (376 MHz, CDCl$_3$) δ −124.6 (ddd, $^3J_{FF} = 146.6$ Hz, $^3J_{HF} = 11.3, 4.5$ Hz, 1F), −135.3 (dd, $^3J_{FF} = 146.6$ Hz, $^3J_{HF} = 15.8$ Hz, 1F); HRMS (EI): calcd for C$_{17}$H$_{21}$BF$_2$O$_4$ [M$^+$]: 338.1501, found: 338.1502.

**trans-4-(2,2-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzonitrile (3ma).** Yield 68% (41.5 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 2.98 (t, $J = 10.0$ Hz, 1H), 1.40–1.32 (m, 1H), 1.29 (s, 6H), 1.28 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.6, 132.2, 128.5, 118.6, 113.8 (dd, $^3J_{CF} = 288.2, 282.1$ Hz), 111.0, 84.5, 31.2 (dd, $^3J_{CF} = 11.9, 9.9$ Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}B$ nucleus]; $^{19}F$ NMR (376 MHz, CDCl$_3$): δ −124.6 (ddd, $^3J_{FF} = 147.7$ Hz, $^3J_{HF} = 11.0, 4.6$ Hz, 1F), −135.2 (dd, $^3J_{FF} = 147.7$ Hz, $^3J_{HF} = 15.9$ Hz, 1F); HRMS (EI): calcd for C$_{16}$H$_{18}$BF$_2$NO$_2$ [M$^+$]: 305.1399, found: 305.1401.

**trans-2-(2,2-Difluoro-3-(3-nitrophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3na).** Yield 74% (48.1 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, $J = 8.0$ Hz, 1H), 8.09 (s, 1H), 7.56 (d, $J = 7.6$ Hz, 1H), 7.52–7.48 (m, 1H), 3.05 (t, $J = 10.0$ Hz, 1H), 1.40 (dd, $J = 16.0, 9.2, 4.4$ Hz, 1H), 1.30 (s, 6H), 1.29 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.3, 136.2, 134.0, 129.4, 122.9, 122.2, 113.7 (dd, $^3J_{CF} = 287.8, 281.7$ Hz), 84.5, 30.6 (dd, $^3J_{CF} = 12.0, 10.0$ Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}B$ nucleus]; $^{19}F$ NMR (376 MHz, CDCl$_3$): δ −125.1 (ddd, $^3J_{FF} = 147.8$ Hz, $^3J_{HF} = 10.9, 3.8$ Hz, 1F), −135.1 (dd, $J_{FF} = 147.8$ Hz, $^3J_{HF} = 15.8$ Hz, 1F); HRMS (EI): calcd for C$_{14}$H$_{15}$BF$_2$NO$_4$ [M-CH$_3$]$^+$: 310.1062, found: 310.1062.

**trans-2-(2,2-Difluoro-3-(naphthalen-2-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3oa).** Yield 91% (60.0 mg), white solid, m.p.: 60.2–61.9 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72–7.69 (m, 3H), 7.59 (s, 1H), 7.39–7.33 (m, 2H), 7.25 (d, $J = 8.4$ Hz, 1H), 3.05 (t, $J = 10.4$ Hz, 1H), 1.41–1.34 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H); $^{13}$C NMR
(100 MHz, CDCl$_3$) $\delta$ 132.2, 131.5, 130.3, 127.0, 126.6, 125.6, 125.2, 124.9, 124.8, 113.6 (dd, $^1J_{CF} = 287.0$, 282.0 Hz), 83.2, 30.6 (t, $^2J_{CF} = 10.5$ Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –124.6 (ddd, $^1J_{FF} = 146.2$ Hz, $^3J_{HF} = 11.6$, 4.5 Hz, 1F), –135.0 (dd, $^1J_{FF} = 146.2$ Hz, $^3J_{HF} = 15.8$ Hz, 1F); HRMS (EI): calcd for C$_{19}$H$_{21}$BF$_2$O$_2$ [M$^+$]: 330.1604, found: 330.1604.

**trans-2-(2,2-Difluoro-3-(thiophen-3-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3pa).** Yield 63% (36.0 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28–7.26 (m, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 6.95 (d, $J = 4.8$ Hz, 1H), 2.96 (t, $J = 10.8$ Hz, 1H), 1.20 (dd, $J = 16.0$, 9.2, 4.4 Hz, 1H), 1.28 (s, 6H), 1.27 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 134.9, 127.1, 125.7, 121.8, 114.6 (dd, $^1J_{CF} = 286.9$, 282.3 Hz), 84.2, 27.3 (dd, $^2J_{CF} = 12.3$, 10.5 Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –126.2 (ddd, $^1J_{FF} = 146.3$ Hz, $^3J_{HF} = 11.3$, 4.8 Hz, 1F), –134.4 (dd, $^1J_{FF} = 146.6$ Hz, $^3J_{HF} = 16.1$ Hz, 1F); HRMS (EI): calcd for C$_{13}$H$_{17}$BF$_2$O$_2$S [M$^+$]: 286.1010, found: 286.1011.

**trans-3-(2,2-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)propyl benzoate (3qa).** Yield 42% (30.7 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.0$ Hz, 2H), 7.57–7.54 (m, 1H), 7.46–7.42 (m, 2H), 4.32 (t, $J = 6.4$ Hz, 2H), 1.93–1.86 (m, 2H), 1.84–1.78 (m, 1H), 1.69–1.63 (m, 1H), 1.56–1.49 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.03 (ddd, $J = 11.9$, 6.5, 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.6, 132.8, 130.4, 129.6, 128.3, 116.5 (t, $^1J_{CF} = 282.4$ Hz), 84.1, 64.6, 27.7 (d, $J = 2.3$ Hz), 25.8 (d, $J = 6.2$ Hz), 24.8, 24.3, 20.1 (t, $^2J_{CF} = 10.1$ Hz) [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –126.2 (ddd, $J_{FF} = 146.6$ Hz, $^3J_{HF} = 11.3$, 4.8 Hz, 1F), –134.4 (dd, $J_{FF} = 146.3$ Hz, $^3J_{HF} = 16.1$ Hz, 1F); HRMS (EI): calcd for C$_{19}$H$_{25}$BF$_2$O$_4$ [M$^+$]: 366.1814, found: 366.1807.

**trans-(2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl)dimethyl(phenyl)silane (3ab).** Yield 97% (61.7 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58–7.55 (m, 2H), 7.39–7.37 (m, 3H), 7.15 (d, $J = 8.8$ Hz, 2H), 6.84...
trans-(2,2-Difluoro-3-(3-methoxyphenyl)cyclopropyl)dimethyl(phenyl)silane (3bb). Yield 99% (62.9 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49–7.47 (m, 2H), 7.30–7.29 (m, 3H), 7.14–7.10 (m, 1H), 6.70 (d, $J = 8.0$ Hz, 2H), 6.64 (s, 1H), 3.67 (s, 3H), 2.52 (t, $J = 10.0$ Hz, 1H), 1.15 (ddd, $J = 17.6$, 9.6, 8.0 Hz, 1H), 0.34 (s, 3H), 0.33 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.6, 137.2, 133.8, 129.5, 128.4, 128.1 (t, $J_{CF} = 2.6$ Hz), 128.0, 123.4, 120.3, 116.1 (t, $J_{CF} = 282.6$ Hz), 110.2, 55.4, 25.9 (t, $J_{CF} = 11.1$ Hz), 18.0 (dd, $J_{CF} = 18.0$, 4.4 Hz), $-2.8$, $-3.2$; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-122.7$ (ddd, $J_{FF} = 147.0$ Hz, $J_{HF} = 9.4$, 9.0 Hz, 1F), $-131.5$ (dd, $J_{FF} = 145.7$ Hz, $J_{HF} = 9.8$ Hz, 1F), $-132.3$ (dd, $J_{FF} = 146.6$ Hz, $J_{HF} = 17.3$ Hz, 1F); HRMS (EI): calcd for C$_{18}$H$_{20}$F$_2$OSi [M]$^+$: 318.1251, found: 318.1253.

trans-(2,2-Difluoro-3-(2-methoxyphenyl)cyclopropyl)dimethyl(phenyl)silane (3cb). Yield 87% (55.3 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60–7.58 (m, 2H), 7.38–7.37 (m, 3H), 7.25–7.21 (m, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 6.90–6.87 (m, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 3.81 (s, 3H), 2.76 (t, $J = 10.4$ Hz, 1H), 1.15 (ddd, $J = 18.0$, 10.4, 8.0 Hz, 1H), 0.43 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7, 137.2, 133.8, 129.5, 128.4, 128.1 (t, $J_{CF} = 2.6$ Hz), 128.0, 123.4, 120.3, 116.1 (t, $J_{CF} = 282.6$ Hz), 110.2, 55.4, 25.9 (t, $J_{CF} = 11.1$ Hz), 18.0 (dd, $J_{CF} = 18.0$, 4.4 Hz), $-2.8$, $-3.2$; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-123.7$ (dd, $J_{FF} = 145.0$ Hz, $J_{HF} = 9.4$, 9.0 Hz, 1F), $-132.3$ (dd, $J_{FF} = 146.6$ Hz, $J_{HF} = 17.3$ Hz, 1F); HRMS (EI): calcd for C$_{18}$H$_{20}$F$_2$OSi [M]$^+$: 318.1251, found: 318.1250.

trans-(3-(3,4-Dimethoxyphenyl)-2,2-difluorocyclopropyl)dimethyl(phenyl)silane (3db). Yield 77% (53.6 mg),
colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59–7.57 (m, 2H), 7.39–7.37 (m, 3H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 6.68 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.60 (t, $J = 10.4$ Hz, 1H), 1.17 (ddd, $J = 17.6$, 10.0, 8.0 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.9, 148.2, 136.9, 133.7, 129.6, 128.1, 127.2, 120.0, 115.5 (t, $^{1}J_{CF} = 283.9$ Hz), 111.4, 111.1, 55.9, 55.8, 30.4 (t, $^{2}J_{CF} = 11.2$ Hz), 19.1 (dd, $^{2}J_{CF} = 18.3$, 4.3 Hz), –2.9, –3.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –123.1 (ddd, $^{1}J_{FF} = 146.3$ Hz, $^{3}J_{HF} = 9.0$, 9.0 Hz, 1F), –132.0 (dd, $^{3}J_{HF} = 146.3$ Hz, $^{3}J_{HF} = 17.3$, 1F); HRMS (EI): calcd for C$_{19}$H$_{22}$F$_{2}$O$_{2}$Si $[M]^{+}$: 348.1357, found: 348.1355.

**trans-(2,2-Difluoro-3-(p-tolyl)cyclopropyl)dimethyl(phenyl)silane** (**3fb**). Yield 87% (52.5 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50–7.48 (m, 2H), 7.31–7.29 (m, 3H), 7.03 (d, $J = 8.0$ Hz, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 2.52 (t, $J = 10.4$ Hz, 1H), 2.24 (s, 3H), 1.18–1.09 (m, 1H), 0.34 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.8, 135.7, 132.7, 130.6 (d, $^{3}J_{CF} = 1.7$ Hz), 128.5, 128.1, 126.9, 126.7, 114.4 (t, $^{1}J_{CF} = 283.7$ Hz), 29.5 (t, $^{2}J_{CF} = 11.2$ Hz), 20.0, 17.8 (dd, $^{2}J_{CF} = 18.3$, 4.3 Hz), –3.9, –4.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –123.0 (ddd, $^{1}J_{FF} = 146.6$ Hz, $^{3}J_{HF} = 9.4$, 9.0 Hz, 1F), –132.3 (dd, $^{3}J_{HF} = 146.6$ Hz, $^{3}J_{HF} = 17.3$, 1F).

**trans-(3-(1,1'-Biphenyl)-4-yl)-2,2-difluorocyclopropyl)dimethyl(phenyl)silane** (**3gb**). Yield 85% (61.9 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50–7.47 (m, 3H), 7.45–7.42 (m, 3H), 7.33–7.28 (m, 5H), 7.24–7.20 (m, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.57 (t, $J = 10.4$ Hz, 1H), 1.19 (ddd, $J = 17.6$, 10.0, 8.0 Hz, 1H), 0.35 (s, 3H), 0.34 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.7, 140.1, 136.8, 133.9 (d, $J = 1.3$ Hz), 133.8, 129.7, 128.9, 128.4, 128.2, 127.4, 127.2, 127.1, 115.5 (t, $^{1}J_{CF} = 283.7$ Hz), 30.7 (t, $^{2}J_{CF} = 11.3$ Hz), 19.4 (dd, $^{2}J_{CF} = 18.2$, 3.8 Hz), –2.8, –3.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –122.7 (dt, $J_{FF} = 147.4$ Hz, $^{3}J_{HF} = 9.4$, 9.0 Hz, 1F), –132.1 (dd, $J_{HF} = 147.4$ Hz, $^{3}J_{HF} = 17.3$, 1F); HRMS (EI): calcd for C$_{23}$H$_{22}$F$_{2}$Si $[M]^{+}$: 364.1459, found: 364.1461.

**trans-(2,2-Difluoro-3-(4-(methylthio)phenyl)cyclopropyl)dimethyl(phenyl)silane** (**3hb**). Yield 75% (50.1 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56–7.55 (m, 2H), 7.39–7.36 (m, 3H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 2.58 (t, $J = 10.4$ Hz, 1H), 2.45 (s, 3H), 1.20 (ddd, $J = 17.6$, 9.6, 8.4 Hz, 1H), 0.42 (s, 3H), 0.41 (s,
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.3, 136.7, 133.7, 131.6, 129.6, 128.4, 128.1, 126.7, 115.3 (t, $^{1}J_{CF} = 283.9$ Hz), 30.4 (t, $^{2}J_{CF} = 11.3$ Hz), 19.2 (dd, $^{3}J_{CF} = 18.2$, 4.1 Hz), 15.9, $-2.9$, $-3.3$; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-147.0$ Hz, $^{1}J_{HF} = 9.4$, 9.0 Hz, 1F), $-132.2$ (dd, $J_{FF} = 147.0$ Hz, $^{2}J_{HF} = 17.3$ Hz, 1F); HRMS (EI): calcd for C$_{18}$H$_{20}$F$_{2}$Si $[M]^+$: 334.1023, found: 334.1022.

$^{3}$kb

trans-(2,2-Difluoro-3-(4-fluorophenyl)cyclopropyl)dimethyl(phenyl)silane (3kb). Yield 82% (50.2 mg), colourless oil; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57–7.55 (m, 2H), 7.41–7.36 (m, 3H), 7.14 (dd, $J = 8.8$, 5.6 Hz, 2H), 7.00–6.96 (m, 2H), 2.59 (t, $J = 10.4$ Hz, 1H), 1.18 (ddd, $J = 17.6$, 10.0, 8.0 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.0 (d, $^{1}J_{CF} = 244.2$ Hz), 136.7, 133.7, 130.5 (d, $J = 2.9$ Hz), 129.7, 129.5 (d, $J = 8.0$ Hz), 128.1, 115.4 (d, $^{2}J_{CF} = 21.5$ Hz), 115.2 (t, $^{1}J_{CF} = 283.3$ Hz), 30.0 (t, $^{2}J_{CF} = 11.3$ Hz), 19.4 (dd, $^{2}J_{CF} = 18.4$, 4.2 Hz), $-2.9$, $-3.3$; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-153.3$ – $-154.4$ (m, 1F), $-123.4$ (dd, $J_{FF} = 147.4$ Hz, $^{1}J_{HF} = 9.8$, 9.8 Hz, 1F), $-132.2$ (dd, $J_{FF} = 147.4$ Hz, $^{2}J_{HF} = 17.7$ Hz, 1F); HRMS (EI): calcd for C$_{17}$H$_{16}$F$_{2}$O$_{2}$Si $[M-HF]^+$: 286.0989, found: 286.0998.

$^{3}$lb

trans-Methyl-4-(3-(dimethyl(phenyl)silyl)-2,2-difluorocyclopropyl)benzoate (3lb). Yield 83% (57.4 mg), colourless oil; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.56–7.54 (m, 2H), 7.40–7.37 (m, 3H), 7.25 (d, $J = 8.0$ Hz, 2H), 3.90 (s, 3H), 2.64 (t, $J = 10.0$ Hz, 1H), 1.30 (ddd, $J = 17.6$, 10.0, 8.4 Hz, 1H), 0.44 (s, 3H), 0.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.8, 140.2 (d, $J = 1.7$ Hz), 136.4, 133.7, 129.7, 129.7, 128.9, 128.1, 127.8, 115.1 (t, $^{1}J_{CF} = 284.1$ Hz), 52.1, 30.9 (t, $^{2}J_{CF} = 11.3$ Hz), 20.0 (dd, $^{3}J_{CF} = 18.2$, 3.9 Hz), $-2.9$, $-3.4$; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-122.5$ (dt, $J_{FF} = 147.8$ Hz, $^{2}J_{HF} = 9.0$ Hz, 1F), $-132.1$ (dd, $J_{FF} = 147.8$ Hz, $^{3}J_{HF} = 17.3$ Hz, 1F); HRMS (EI): calcd for C$_{19}$H$_{20}$F$_{2}$O$_{2}$Si $[M-HF]^+$: 346.1201, found: 346.1200.

$^{3}$mb

trans-4-(3-(Dimethyl(phenyl)silyl)-2,2-difluorocyclopropyl)benzonitrile (3mb). Yield 53% (33.2 mg), yellow oil; $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.4$ Hz, 2H), 7.55–7.53 (m, 2H), 7.42–7.36 (m, 3H), 7.27 (d, $J = 8.0$ Hz,
trans-(2,2-Difluoro-3-(3-nitrophenyl)cyclopropyl)dimethyl(phenyl)silane (3nb). Yield 82% (54.6 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 (d, $J = 7.6$ Hz, 1H), 8.04 (s, 1H), 7.57–7.55 (m, 2H), 7.52–7.45 (m, 2H), 7.41–7.39 (m, 3H), 2.68 (t, $J = 9.6$ Hz, 1H), 1.37–1.28 (m, 1H), 0.46 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.4, 137.1 (d, $J = 1.7$ Hz), 136.1, 133.9, 133.7, 129.9, 129.4, 128.2, 122.1, 114.6 (t, $J_{CF} = 284.2$ Hz), 30.2 (t, $J_{CF} = 11.3$ Hz), 20.1 (dd, $J_{CF} = 18.5$, 3.9 Hz), –3.0, –3.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –123.2 (dt, $J_{FF} = 148.9$ Hz, $J_{HF} = 8.3$ Hz, 1F), –132.10 (dd, $J_{FF} = 148.9$ Hz, $J_{HF} = 17.7$ Hz, 1F); HRMS (EI): calcd for C$_{18}$H$_{17}$F$_2$NSi $[M]^+$: 313.1098, found: 313.1096.

trans-(2,2-Difluoro-3-(naphthalen-2-yl)cyclopropyl)dimethyl(phenyl)silane (3ob). Yield 98% (66.2 mg), yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79–7.74 (m, 3H), 7.63 (s, 1H), 7.59–7.58 (m, 2H), 7.44–7.43 (m, 2H), 7.39–7.37 (m, 3H), 7.30 (d, $J = 8.4$ Hz, 1H), 2.79 (t, $J = 10.0$ Hz, 1H), 1.37 (ddd, $J = 17.6$, 9.6, 8.4 Hz, 1H), 0.46 (s, 3H), 0.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.9, 133.8, 133.4, 132.6, 132.3 (d, $J = 1.7$ Hz), 129.7, 128.2, 128.2, 127.7, 126.7, 126.4, 126.1, 125.9, 115.6 (t, $J_{CF} = 284.0$ Hz), 31.1 (t, $J_{CF} = 11.2$ Hz), 19.4 (dd, $J_{CF} = 18.2$, 4.2 Hz), –2.8, –3.2; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –123.2 (dt, $J_{FF} = 147.0$ Hz, $J_{HF} = 9.0$ Hz, 1F), –131.9 (dd, $J_{FF} = 147.0$ Hz, $J_{HF} = 17.3$ Hz, 1F); HRMS (EI): calcd for C$_{21}$H$_{20}$F$_2$Si $[M]^+$: 338.1301, found: 338.1301.

trans-3-(3-(Dimethyl(phenyl)silyl)-2,2-difluorocyclopropyl)propyl benzoate (3qb). Yield 74% (55.3 mg), colourless oil; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95–7.93 (m, 2H), 7.46–7.43 (m, 3H), 7.36–7.32 (m, 2H), 7.28–7.27 (m, 3H), 4.22 (t, $J = 6.4$ Hz, 2H), 1.76–1.70 (m, 2H), 1.69–1.60 (m, 1H), 1.56–1.47 (m, 1H), 1.42–1.34 (m, 1H), 0.45 (ddd, $J = 17.2$, 9.6, 7.6 Hz, 1H), 0.26 (s, 3H), 0.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.5, 137.1, 133.6, 132.9,
130.3, 129.5, 129.4, 128.4, 128.0, 117.3 (dd, $J_{CF} = 283.3, 281.2$ Hz), 64.1, 28.2 (d, $J = 2.0$ Hz), 25.8 (dd, $J_{CF} = 11.2, 9.9$ Hz), 25.0 (d, $J = 1.9$ Hz), 18.1 (dd, $J_{CF} = 18.6, 4.9$ Hz), –2.9, –3.4; $^{19}$F NMR (376 MHz, CDCl$_3$) δ –125.4 (d, $J_{FF} = 148.5$ Hz, 1F), –134.25 (dd, $J_{FF} = 148.9$ Hz, $J_{HF} = 17.3$ Hz, 1F); HRMS (EI): calcd for C$_{21}$H$_{24}$F$_2$O$_2$Si [M]$^+$: 374.1514, found: 374.1513.

**trans-2-(2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4).** Yield 75% (127.1 mg), white solid; $^1$H NMR (400 MHz, DMSO-d$_6$) δ 7.21 (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 4.31 (dd, $J = 32.0, 17.2$ Hz, 2H), 4.08 (dd, $J = 16.8, 11.6$ Hz, 2H), 3.74 (s, 3H), 2.95 (s, 3H), 2.70 (t, $J = 10.4$ Hz, 1H), 1.51 (ddd, $J = 17.2, 9.6, 5.2$ Hz, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$) δ 169.1, 168.3, 158.1, 128.7, 125.9, 115.8 (dd, $J_{CF} = 287.7, 279.5$ Hz), 113.7, 61.9, 61.8, 55.0, 46.6, 28.5 (t, $J_{CF} = 10.6$ Hz) [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the $^{11}$B nucleus]; $^{19}$F NMR (376 MHz, DMSO-d$_6$) δ –127.0 (ddd, $J_{FF} = 145.8$ Hz, $J_{HF} = 11.3, 4.9$ Hz, 1F), –134.1 (dd, $J_{FF} = 145.8$ Hz, $J_{HF} = 17.6, 4.1$ Hz, 1F); HRMS (ESI): calcd for C$_{15}$H$_{15}$BF$_2$NO$_3$ [M–H]$^-$: 338.1011, found: 338.1010.

9. References

10. $^1$H, $^{13}$C, $^{19}$F NMR and HRMS (EI) spectra of target compounds

$^1$H NMR spectrum of 3aa

$^{13}$C NMR spectrum of 3aa
$^{19}$F NMR spectrum of 3aa

HRMS (EI) of 3aa
$^1$H NMR spectrum of 3ba
$^{13}$C NMR spectrum of 3ba

$^{19}$F NMR spectrum of 3ba
HRMS (EI) of 3ba

\[ \text{H NMR spectrum of 3ca} \]
$^{13}$C NMR spectrum of 3ca

$^{19}$F NMR spectrum of 3ca
HRMS (EI) of 3ca

\[ ^1H \text{NMR spectrum of 3da} \]
$^{13}$C NMR spectrum of 3da

$^{19}$F NMR spectrum of 3da
HRMS (EI) of 3da

$^1$H NMR spectrum of 3ea
$^{13}$C NMR spectrum of 3ea

$^{19}$F NMR spectrum of 3ea
$^{1}H$ NMR spectrum of 3fa

$^{13}C$ NMR spectrum of 3fa
\[ ^{19}\text{F NMR spectrum of 3fa} \]

\[ \text{HRMS (EI) of 3fa} \]
$^1$H NMR spectrum of 3ga

$^{13}$C NMR spectrum of 3ga
$^{19}$F NMR spectrum of 3ga

HRMS (EI) of 3ga
$^1$H NMR spectrum of 3ha

$^{13}$C NMR spectrum of 3ha
$^1$H NMR spectrum of 3ia

$^{13}$C NMR spectrum of 3ia
$^{19}$F NMR spectrum of 3ia

HRMS (EI) of 3ia
$^1$H NMR spectrum of 3ja

$^{13}$C NMR spectrum of 3ja
$^{19}$F NMR spectrum of 3ja

HRMS (EI) of 3ja
$^1$H NMR spectrum of 3ka

$^{13}$C NMR spectrum of 3ka
$^{19}$F NMR spectrum of 3ka

HRMS (EI) of 3ka
$^1$H NMR spectrum of 3la

$^{13}$C NMR spectrum of 3la
$^19$F NMR spectrum of 3la

HRMS (EI) of 3la
$^1$H NMR spectrum of 3ma

$^{13}$C NMR spectrum of 3ma
$^{19}$F NMR spectrum of 3ma

HRMS (EI) of 3ma
\(^1\)H NMR spectrum of 3na

\(^{13}\)C NMR spectrum of 3na
$^{19}$F NMR spectrum of 3na

HRMS (EI) of 3na
$^1$H NMR spectrum of 3oa

$^{13}$C NMR spectrum of 3oa
$^{19}$F NMR spectrum of 3oa
HRMS (EI) of 3oa

$^1$H NMR spectrum of 3pa
$^{13}$C NMR spectrum of 3pa

$^{19}$F NMR spectrum of 3pa
HRMS (EI) of 3pa

'H NMR spectrum of 3qa
$^{13}$C NMR spectrum of 3qa

$^{19}$F NMR spectrum of 3qa
HRMS (EI) of 3qa

H NMR spectrum of 3ab
$^{13}$C NMR spectrum of 3ab

$^{19}$F NMR spectrum of 3ab
HRMS (EI) of 3ab

\[ \text{[Image of HRMS spectrum]} \]

\[ \text{\textsuperscript{1}H NMR spectrum of 3bb} \]

\[ \text{[Image of 
\textsuperscript{1}H NMR spectrum]} \]
$^{13}$C NMR spectrum of 3bb

$^{19}$F NMR spectrum of 3bb
HRMS (EI) of 3bb

$^1$H NMR spectrum of 3cb

$^{13}$C NMR spectrum of 3cb
$^{19}$F NMR spectrum of 3cb

HRMS (EI) of 3cb
$^1$H NMR spectrum of 3db

$^{13}$C NMR spectrum of 3db
$^{19}\text{F NMR spectrum of 3db}$

$\text{HRMS (EI) of 3db}$
$^1$H NMR spectrum of 3fb

$^{13}$C NMR spectrum of 3fb
$^{19}$F NMR spectrum of 3fb

$^1$H NMR spectrum of 3gb
$^{13}$C NMR spectrum of 3gb

$^{19}$F NMR spectrum of 3gb
HRMS (EI) of 3gb

1H NMR spectrum of 3hb
$^{13}$C NMR spectrum of 3hb

$^{19}$F NMR spectrum of 3hb
HRMS (EI) of 3hb

$^1$H NMR spectrum of 3kb
$^{13}$C NMR spectrum of 3kb

$^{19}$F NMR spectrum of 3kb
HRMS (EI) of 3kb

$^1$H NMR spectrum of 3lb
$^{13}$C NMR spectrum of 3lb

$^{19}$F NMR spectrum of 3lb
$^1$H NMR spectrum of 3mb

$^{13}$C NMR spectrum of 3mb
$^{19}$F NMR spectrum of 3mb

HRMS (EI) of 3mb
\(^1\)H NMR spectrum of 3nb

\[^{13}\]C NMR spectrum of 3nb
$^{19}$F NMR spectrum of 3nb

HRMS (EI) of 3nb
$^1$H NMR spectrum of 3ob

$^{13}$C NMR spectrum of 3ob
$^{19}$F NMR spectrum of 3ob

HRMS (EI) of 3ob
$^1$H NMR spectrum of 3qb

![H NMR spectrum of 3qb](image)

$^{13}$C NMR spectrum of 3qb

![C NMR spectrum of 3qb](image)
$^{19}$F NMR spectrum of 3qb

HRMS (EI) of 3qb
$^1$H NMR spectrum of 4 (DMSO-$d_6$)

$^{13}$C NMR spectrum of 4 (DMSO-$d_6$)
$^{19}$F NMR spectrum of 4 (DMSO-$d_6$)

HRMS (ESI) of 3qb