Supporting Information to

The Prins fluorination cyclisations: Preparation of 4-fluoro-pyran and piperidine heterocycles.

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Experimental and characterisation details of synthesised compounds
General method for the oxa-Prins reaction

Boron trifluoride diethyl etherate (0.5 mmol, 1.0 equiv) was added to a solution of the aldehyde (0.5 mmol, 1 equiv) in dichloromethane. After 5 min, the alcohol (0.5 mmol, 1 equiv) was added, and the mixture stirred for 5 h. Water and dichloromethane were then added and the layers were separated. The aqueous layer was extracted with dichloromethane, the organic layers dried, filtered and concentrated. The residue was then purified on silica.

General method for the aza-Prins reaction

Boron trifluoride diethyl etherate (0.5 mmol, 1.0 equiv) was added to a solution of the aldehyde (0.5 mmol, 1 equiv) in dichloromethane. After 5 min, the N-(tosyl)-N-but-3-ene (0.5 mmol, 1 equiv) was added, and the mixture stirred 36 h. Water and dichloromethane were then added and the layers were separated. The aqueous layer was extracted with dichloromethane, the organic layers dried, filtered and concentrated. The residue was then purified on silica.

General method for the oxa-Prins reaction under microwave conditions

Boron trifluoride diethyl etherate (0.5 mmol, 1.0 equiv) was added to a solution of the aldehyde (0.5 mmol, 1 equiv) in dichloromethane. After 5 min, the alcohol (0.5 mmol, 1 equiv) was added, and the mixture irradiated for 10 min with microwaves (100 W). Water and dichloromethane were then added and the layers were separated. The aqueous layer was extracted with dichloromethane, the organic layers dried, filtered and concentrated. The residue was then purified on silica.
General method for the aza-Prins reaction under microwave conditions

Boron trifluoride diethyl etherate (0.5 mmol, 1.0 equiv) was added to a solution of the aldehyde (0.5 mmol, 1 equiv) in dichloromethane. After 5 min, the \textit{N}-(tosyl)-\textit{N}-but-3-ene (0.5 mmol, 1 equiv) was added, and the mixture irradiated for 30 min by microwaves (100 W). Water and dichloromethane were then added and the layers were separated. The aqueous layer was extracted with dichloromethane, the organic layers dried, filtered and concentrated. The residue was then purified on silica.
2-(4-Nitrophenyl)-4-fluoropyrans syn-5a and anti-5a.

Products *syn*-5a and *anti*-5a were prepared according to the general procedure outlined for the oxa-Prins reaction from 4-nitrobenzaldehyde (76 mg, 0.5 mmol), but-3-en-1-ol 3 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product *syn*-5a was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a white solid (47 mg, 41%, microwave: 33 mg, 29%, at -20 °C: 70mg, 61%).

**NMR:** "H, 300 MHz (δ in ppm): 8.24-8.14 (2H, m, ar), 7.56-7.47 (2H, m, ar), 4.84 (1H, dtt, J= 49.0 Hz, 10.9 Hz, 4.9 Hz, CHF), 4.43 (1H, dt, J= 11.5 Hz, 1.8 Hz, OCHCH₂), 4.25 (1H, dtd, J= 11.9 Hz, 5.7 Hz, 1.8 Hz, OCHHCH₂), 3.58 (1H, tt, J= 12.3 Hz, 1.8 Hz, OCHHCH₂), 2.39 (1H, dtt, J= 12.3 Hz, 4.9 Hz, 2.1 Hz, OCHCHH), 2.20-2.09 (1H, m, OCH₂CHH), 1.86 (1H, tddd, J= 12.3 Hz, 11.1 Hz, 9.9 Hz, 5.3 Hz, OCH₂CHH), 1.67 (1H, dtd, J= 12.3 Hz, 11.5 Hz, 9.5, OCHCHH); "C, 75 MHz (δ in ppm): 148.6 (Cq, ar), 147.4 (Cq, ar), 126.4 (CH, ar), 123.6 (CH, ar), 88.7 (CH, d, J= 177.7 Hz, CHF), 76.4 (CH, d, J= 11.5 Hz, OCHCH₂), 65.3 (CH₂, d, J= 11.6 Hz, OCH₂CH₂), 40.4 (CH₂, d, J= 17.7 Hz, OCHCH₂), 32.6 (CH₂, d, J= 17.7 Hz, OCH₂CH₂); "F, 282 MHz (δ in ppm): -170.5 to -170.8 (m); HRMS m/z: [MH]⁺: 226.0879, calculated 226.0878; Mp: 80-82 °C; IR: ν<sub>max</sub> (neat)/cm⁻¹: 2976, 2942, 2853, 1521, 1348, 1320, 1181, 1133, 1078, 849.
Product **anti-5a** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a white solid (23 mg, 20%, microwave: 20 mg, 18%).

**NMR: ¹H, 300 MHz (δ in ppm):** 8.26-8.18 (2H, m, ar), 7.57-7.50 (2H, m, ar), 5.11 (1H, dtt, J = 47.7 Hz, 2.9 Hz, 2.6 Hz, CHF), 4.87 (1H, dd, J = 11.8 Hz, 2.2 Hz, OCHCH₂), 4.10-3.97 (2H, m, OC₂H₂CH₂), 2.21 (1H, dddt, J = 14.4 Hz, 10.7 Hz, 3.3 Hz, 2.2 Hz, OCHCHH), 2.06-1.87 (2H, m, OCH₂CH₂), 1.74 (1H, dddd, J = 43.0Hz, 14.1Hz, 5.9Hz, 2.2Hz, OCHCHH);

**13C, 75 MHz (δ in ppm):** 149.6 (Cq, ar), 147.3 (Cq, ar), 126.3 (CH, ar), 123.6 (CH, ar), 86.3 (CH, d, J = 169.6 Hz, CHF), 73.1 (CH, OCHCH₂), 63.0 (CH₂, d, J = 11.6 Hz, OCH₂CH₂), 38.7 (CH₂, d, J = 20.3 Hz, OCHCH₂), 30.4 (CH₂, d, J = 21.1 Hz, OCH₂CH₂);

**19F, 282 MHz (δ in ppm):** -185.7 to -186.3 (m);

**HRMS m/z:** [MH]⁺: 226.0874, calculated 226.0879;

**Mp:** 100-102 °C;

**IR:** νmax (neat)/cm⁻¹: 3080, 2974, 2852, 1514, 1345, 1207, 1150, 1069, 872, 857.

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2-(2-Fluorophenyl)-4-fluoropyrans **syn-5b** and **anti-5b**.

Products **syn-5b** and **anti-5b** were prepared according to the general procedure outlined for the oxa-Prins reaction from 2-fluorobenzaldehyde (53 µL, 0.5 mmol), but-3-en-1-ol 3 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

![syn-5b](image_url)

Product **syn-5b** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (50 mg, 50%).

**NMR: ¹H, 300 MHz (δ in ppm):** 7.50 (1H, td, J = 7.5 Hz, 5.6 Hz, ar), 7.32-7.23 (1H, m, ar), 7.17 (1H, td, J = 7.5 Hz, 1.2 Hz, ar), 7.03 (1H, ddd, J = 10.6 Hz, 8.2 Hz, 1.2 Hz, ar), 4.84 (1H, dtt, J = 49.2 Hz, 11.0 Hz, 5.0 Hz, CHF), 4.66 (1H, dt, J = 11.4 Hz, 1.7 Hz, OCHCH₂), 4.23 (1H, dtd, J = 12.0 Hz, 5.7 Hz, 1.7 Hz, OCHCH₂), 3.60 (1H, tt, J = 12.3 Hz, 1.9 Hz, OCHCH₂), 2.38 (1H, dt, J = 12.3 Hz, 5.0 Hz, 1.8 Hz, OCHCHH), 2.20-2.09 (1H, m, OCH₂CHH), 1.87 (1H, tddd, J = 12.5 Hz, 11.0 Hz, 10.1 Hz, 5.2 Hz,
OCH₂CH₂H), 1.72 (1H, dtd, J = 12.1 Hz, 11.0 Hz, 9.5 Hz, OCH₂CH₂H); ¹³C, 75 MHz (δ in ppm): 159.2 (Cq, d, J = 246.0 Hz, Car-F), 129.1 (CH, d, J = 8.0 Hz, ar), 128.4 (Cq, ar), 127.1 (CH, d, J = 4.2 Hz, ar), 124.4 (CH, d, J = 3.5 Hz, ar), 115.2 (CH, d, J = 21.7 Hz, ar), 89.0 (CH, d, J = 176.9 Hz, CHF), 71.4 (CH, dd, J = 12.6 Hz, 3.6 Hz, OCHCH₂), 65.5 (CH₂, d, J = 11.7 Hz, OCH₂CH₂), 39.5 (CH₂, d, J = 18.1 Hz, OCHCH₂), 32.9 (CH₂, d, J = 18.1 Hz, OCH₂CH₂); ¹⁹F, 282 MHz (δ in ppm): -120.3 to -120.4 (m), -170.3. -170.7 (m); HRMS m/z: [MH, -HF]⁺: 179.0871, calculated 179.0872; IR: νmax (neat)/cm⁻¹: 3047, 2961, 2932, 2855, 1589, 1494, 1455, 1230, 1183, 1159, 1084, 1044, 982.

Product anti-5b was isolated after purification on silica gel (hexane/diethylether, 8/2) as a colorless oil (10 mg, 10%).

**NMR: **¹H, 300 MHz (δ in ppm): 7.48 (1H, td, J = 7.5 Hz, 1.9 Hz, ar), 7.30-7.21 (1H, m, ar), 7.15 (1H, td, J = 7.5 Hz, 1.4 Hz, ar), 7.03 (1H, ddd, J = 10.5 Hz, 8.1 Hz, 1.4 Hz, ar), 5.09 (1H, dquint, J = 48.1 Hz, 2.9 Hz, CHF), 5.08 (1H, dd, J = 11.7 Hz, 2.0 Hz, OCHCH₂), 4.07-4.00 (2H, m, OCH₂CH₂), 2.28-2.16 (1H, m, OCHCH₂H), 2.07-1.69 (3H, m, OCH₂CH₂, OCHCH₂H); ¹³C, 75 MHz (δ in ppm): 159.2 (Cq, d, J = 246.0 Hz, Car-F), 129.2 (CH, d, J = 8.1 Hz, ar), 126.9 (CH, d, J = 4.0 Hz, ar), 126.4 (Cq, ar), 124.4 (CH, d, J = 3.5 Hz, ar), 115.3 (CH, d, J = 21.3 Hz, ar), 86.8 (CH, d, J = 169.1 Hz, CHF), 68.9 (CH, OCHCH₂), 63.3 (CH₂, OCH₂CH₂), 37.7 (CH₂, d, J = 22.3 Hz, OCHCH₂), 30.3 (CH₂, d, J = 24.4 Hz, OCH₂CH₂); ¹⁹F, 282 MHz (δ in ppm): -119.5 to -119.6 (m), -186.4 to -187.0 (m); HRMS m/z: [MH, -HF]⁺: 179.0874, calculated 179.0872; IR: νmax (neat)/cm⁻¹: 3017, 2918, 2852, 1589, 1491, 1460, 1270, 1183, 1135, 1089, 962.
2-(3-Fluorophenyl)-4-fluoropyrans *syn*-5c and *anti*-5c.

Products *syn*-5c and *anti*-5c were prepared according to the general procedure outlined for the oxa-Prins reaction from 3-fluorobenzaldehyde (55 µL, 0.5 mmol), but-3-en-1-ol 3 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product *syn*-5c was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (55 mg, 55%).

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.31-7.19 (1H, m, ar), 7.09-7.00 (2H, m, ar), 6.93 (1H, tdd, $J = 8.4$ Hz, 2.6 Hz, 1.1 Hz, ar), 4.76 (1H, dt, $J = 49.1$ Hz, 11.0 Hz, 5.0 Hz, CHF), 4.27 (1H, dt, $J = 11.5$ Hz, 1.8 Hz, OCHCH$_2$), 4.16 (1H, dtd, $J = 12.0$ Hz, 5.7 Hz, 1.8 Hz, OCHHCH$_2$), 3.50 (1H, tt, $J = 12.3$ Hz, 1.8 Hz, OCHHCH$_2$), 2.29 (1H, ddd, $J = 12.3$ Hz, 4.9 Hz, 2.1 Hz, OCHH-H), 2.13-2.01 (1H, m, OCH$_2$CHH), 1.79 (1H, tddd, $J = 12.5$ Hz, 11.0 Hz, 9.9 Hz, 5.0 Hz, OCH$_2$CHH), 1.65 (1H, dtd, $J = 12.2$ Hz, 11.3 Hz, 9.6 Hz, OCHCH-H); $^{13}$C, 75 MHz (δ in ppm): 162.8 (Cq, d, $J = 247.0$ Hz, Car-F), 143.9 (Cq, dd, $J = 8.6$ Hz, 1.2 Hz, ar), 129.9 (CH, d, $J = 8.2$ Hz, ar), 121.3 (CH, d, $J = 2.8$ Hz, ar), 114.6 (CH, d, $J = 21.9$ Hz, ar), 112.8 (CH, d, $J = 21.9$ Hz, ar), 89.2 (CH, d, $J = 176.2$ Hz, CHF), 77.0 (CH, d, $J = 12.7$ Hz, OCHCH$_2$), 65.4 (CH$_2$, d, $J = 11.5$ Hz, OCH$_2$CH$_2$), 40.5 (CH$_2$, d, $J = 17.3$ Hz, OCH$_2$CH$_2$), 32.9 (CH$_2$, d, $J = 17.3$ Hz, OCH$_2$CH$_2$); $^{19}$F, 282 MHz (δ in ppm): -113.3 to -113.4 (m), -170.3 to -170.7 (m); HRMS m/z: [MH, -HF]$^+$: 179.0870, calculated 179.0872; IR: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3017, 2919, 2854, 1590, 1491, 1448, 1272, 1186, 1138, 1073, 962.
Product **anti-5c** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (7 mg, 7%).

**NMR:** $^1$H, **300 MHz** ($\delta$ in ppm): 7.35-7.28 (1H, m, ar), 7.16-7.07 (2H, m, ar), 7.0-6.93 (1H, m, ar), 5.10 (1H, dq quint, $J_1$ = 47.8 Hz, 2.8 Hz, CH$_F$), 4.76 (1H, dd, $J_2$ = 12.2 Hz, 2.5 Hz, OCHCH$_2$), 4.05-3.99 (2H, m, OCH$_2$CH$_2$), 2.23-2.13 (1H, m, OCHC$_H$H), 1.79 (1H, dddd, $J_3$ = 43.5 Hz, 14.5 Hz, 11.5 Hz, 2.1 Hz, OCHCHH) ; $^{13}$C, **75 MHz** ($\delta$ in ppm): 162.9 (Cq, $J$ = 249.3 Hz, Car-F), 147.1 (Cq, ar), 129.9 (CH, d, $J_4$ = 9.7 Hz, ar), 121.2 (CH, d, $J_5$ = 2.8 Hz, ar), 114.4 (CH, d, $J_6$ = 22.5 Hz, ar), 112.7 (CH, d, $J_7$ = 22.5 Hz, ar), 86.7 (CH, d, $J_8$ = 169.1 Hz, CHF), 73.4 (CH, OCHCH$_2$), 63.1 (CH$_2$, OCH$_2$CH$_2$), 38.6 (CH$_2$, d, $J_9$ = 21.9 Hz, OCHCH$_2$), 30.5 (CH$_2$, d, $J_9$ = 21.9 Hz, OCH$_2$CH$_2$) ; $^{19}$F, **282 MHz** ($\delta$ in ppm): -113.4 to -113.5 (m), -186.1 to -186.5 (m) ; **HRMS** m/z: [MH, -HF]$^+$: 179.0882, calculated 179.0872; **IR:** $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3075, 2962, 2856, 1592, 1488, 1447, 1257, 1174, 1139, 1082, 984.

2-(4-Fluorophenyl)-4-fluoropyrans **syn-5d** and **anti-5d**.

Products **syn-5d** and **anti-5d** were prepared according to the general procedure outlined for the oxa-Prins reaction from 4-fluorobenzaldehyde (53 µL, 0.5 mmol), but-3-en-1-ol **3** (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

![syn-5d](image)

Product **syn-5d** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (49 mg, 49%).

**NMR:** $^1$H, **400 MHz** ($\delta$ in ppm): 7.37-7.30 (2H, m, ar), 7.08-7.01 (2H, m, ar), 4.82 (1H, dtt, $J_1$ = 49.1 Hz, 11.0 Hz, 5.9 Hz, CHF), 4.31 (1H, dt, $J_2$ = 11.6 Hz, 1.8 Hz, OCHCH$_2$), 4.21 (1H, dtd, $J_3$ = 11.9 Hz, 5.7 Hz, 1.7 Hz, OCHHCH$_2$), 3.57 (1H, tt, $J_4$ = 12.3 Hz, 1.8 Hz, OCHHCH$_2$), 2.32 (1H, dtt, $J_5$ = 12.3 Hz, 4.8 Hz, 2.1 Hz, OCHCHH), 2.17-2.09 (1H, m, OCH$_2$CHH), 1.85 (1H, tddd, $J_6$ = 12.5 Hz, 11.0 Hz, 9.9 Hz, 5.1 Hz, OCH$_2$CHH), 1.74 (1H, dtd, $J_7$ = 12.2 Hz, 11.3 Hz, 9.6 Hz, OCHCHH) ; $^{13}$C, **100 MHz** ($\delta$ in ppm): 162.3 (CH, d, $J_8$ = 249.0 Hz, ar), 137.9 (Cq, ar), 127.6 (CH, d, $J_9$ = 8.5 Hz, ar),
Product *anti-5d* was isolated after purification on silica gel (hexane-diethyl ether, 8/2) as a colorless oil (10 mg, 10%).

**NMR:** $^1$H, 400 MHz ($\delta$ in ppm): 7.36-7.30 (2H, m, ar), 7.08-7.00 (2H, m, ar), 5.10 (1H, dquint, $J$ = 48.0 Hz, 2.6 Hz, CHF), 4.74 (1H, dd, $J$ = 12.0 Hz, 2.3 Hz, OCHCH$_2$), 4.04-3.98 (2H, m, OCH$_2$CH$_2$), 2.20-2.10 (1H, m, OCHCHH), 2.06-1.8 (2H, m, OCH$_2$CH$_2$), 1.81 (1H, dddd, $J$ = 43.7 Hz, 14.4 Hz, 11.8 Hz, 2.2 Hz, OCHCHH); $^{13}$C, 100 MHz ($\delta$ in ppm): 162.1 (Cq, d, $J$ = 245.0 Hz), 137.9 (Cq, ar), 127.4 (CH, d, $J$ = 8.1 Hz, ar), 115.2 (CH, d, $J$ = 20.5 Hz, ar), 86.7 (CH, d, $J$ = 168.1 Hz, CHF), 73.4 (CH, OCHCH$_2$), 63.1 (CH$_2$, OCH$_2$CH$_2$), 38.6 (CH$_2$, d, $J$ = 20.7 Hz, OCHCH$_2$), 30.5 (CH$_2$, d, $J$ = 20.5 Hz, OCH$_2$CH$_2$); $^{19}$F, 376 MHz ($\delta$ in ppm): -115.4 to -115.5 (m), -186.1 to -186.5 (m); **HRMS m/z**: [MH, -HF]$^+$: 179.0874, calculated 179.0872; **IR**: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 2977, 2926, 1447, 1276, 1181, 1123, 1086, 977.

2-(2-Bromophenyl)-4-fluoropyrans *syn-5e* and *anti-5e*.

Products *syn-5e* and *anti-5e* were prepared according to the general procedure outlined for the oxa-Prins reaction from 2-bromobenzaldehyde (58 µL, 0.5 mmol), but-3-en-1-ol 3 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).
Product **syn-5e** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (68 mg, 52%, microwave: 87 mg, 67%).

**NMR: **$^1$H, 300 MHz ($\delta$ in ppm): 7.59-7.50 (2H, m, ar), 7.40-7.32 (1H, td, $J$= 7.5 Hz, 1.1 Hz, ar), 7.20-7.12 (1H, td, $J$= 7.8 Hz, 1.7 Hz, ar), 4.83 (1H, dtt, $J$= 49.0 Hz, 10.1 Hz, 5.0 Hz, CHF), 4.65 (1H, dt, $J$= 11.3 Hz, 1.9 Hz, OCHCH$_2$), 4.23 (1H, dtd, $J$= 11.7 Hz, 5.7 Hz, 1.6 Hz, OCHCHCH$_2$), 3.61 (1H, tt, $J$= 12.3 Hz, 1.8 Hz, OCHCHCH$_2$), 2.52 (1H, dtt, $J$= 12.3 Hz, 4.8 Hz, 2.1 Hz, OCHCHH$_2$), 2.20-2.09 (1H, m, OCH$_3$CH), 1.87 (1H, tddd, $J$= 12.5 Hz, 10.8 Hz, 10.0 Hz, 5.1 Hz, OCH$_2$CH$_2$), 1.54 (1H, dtd, $J$= 12.3 Hz, 11.3 Hz, 9.3 Hz, OCHCHH)$_2$; $^{13}$C, 75 MHz ($\delta$ in ppm): 140.5 (Cq, ar), 132.5 (CH, ar), 129.0 (CH, ar), 127.8 (CH, ar), 127.4 (CH, ar), 121.3 (Cq, ar), 88.9 (CH, d, $J$= 177.2 Hz, CHF), 76.7 (CH, d, $J$= 12.2 Hz, OCHCH$_2$), 65.4 (CH$_2$, d, $J$= 11.9 Hz, OCH$_2$CH$_2$), 39.2 (CH$_2$, d, $J$= 17.4 Hz, OCHCH$_2$), 32.9 (CH$_2$, d, $J$= 17.7 Hz, OCH$_2$CH$_2$); $^{19}$F, 376 MHz ($\delta$ in ppm): -170.1 to -170.5 (m); HRMS m/z: [MH, -HF]$^+$: 239.0072; 241.0061, calculated 239.0072, 241.0051; IR: $\nu_{\max}$ (neat)/cm$^{-1}$: 3067, 2962, 2854, 1568, 1473, 1440, 1371, 1249, 1158, 1082, 1082, 982, 754, 679.

Product **anti-5e** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (10 mg, 8%, microwave: 26 mg, 20%).

**NMR: **$^1$H, 300 MHz ($\delta$ in ppm): 7.57-7.50 (2H, m, ar), 7.38-7.30 (1H, m, ar), 7.17-7.10 (1H, m, ar), 5.10 (1H, dd, $J$= 11.6 Hz, 2.1 Hz, OCHCH$_2$), 5.09 (1H, dquint, $J$= 47.8 Hz, 2.8 Hz, CHF), 4.08-4.03 (2H, m, OCH$_2$CH$_2$), 2.45-2.33 (1H, m, OCHCHH)$_2$, 2.12-1.81 (2H, m, OCH$_2$CH$_2$), 1.60 (1H, dddd, $J$= 43.8 Hz, 14.4 Hz, 11.55 Hz, 2.1
Hz, OCHCHH); $^{13}$C, 75 MHz ($\delta$ in ppm): 141.5 (Cq, ar), 132.6 (CH, ar), 128.8 (CH, ar), 127.7 (CH, ar), 127.2 (CH, ar), 121.5 (Cq, ar), 86.5 (CH, d, $J$ = 168.9 Hz, CHF), 73.3 (CH, OCHCH$_2$), 63.2 (CH$_2$, OCH$_2$CH$_2$), 37.2 (CH$_2$, d, $J$ = 20.6 Hz, OCHCH$_2$), 30.6 (CH$_2$, d, $J$ = 19.9 Hz, OCH$_2$CH$_2$); $^{19}$F, 282 MHz ($\delta$ in ppm): -186.8 to -187.4 (m); HRMS m/z: [MH, -HF]$^+$: 239.0076; 241.0051, calculated 239.0072, 241.0051; IR: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3064, 2953, 2864, 1567, 1470, 1428, 1369, 1254, 1147, 1072, 1021, 982, 751, 705.

2-(3-Bromophenyl)-4-fluoropyrans syn-5f and anti-5f.

Products syn-5f and anti-5f were prepared according to the general procedure outlined for the oxa-Prins reaction from 3-bromobenzaldehyde (58 $\mu$L, 0.5 mmol), but-3-en-1-ol 3 (45 $\mu$L, 0.5 mmol) and boron trifluoride (65 $\mu$L, 0.5 mmol).

Product syn-5f was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (71 mg, 55%, microwave: 72 mg, 55%).

NMR: $^1$H, 300 MHz ($\delta$ in ppm): 7.56-7.53 (1H, m, ar), 7.44 (1H, dt, $J$ = 7.3 Hz, 1.9 Hz), 7.30-7.20 (2H, m, ar), 4.82 (1H, dtt, $J$ = 48.9 Hz, 11.0 Hz, 5.0 Hz, CHF), 4.30 (1H, dt, $J$ = 11.7 Hz, 2.0 Hz, OCHCH$_2$), 4.22 (1H, dtd, $J$ = 12.2 Hz, 5.6 Hz, 1.8 Hz, OCHHCH$_2$), 3.56 (1H, tt, $J$ = 12.2 Hz, 1.8 Hz, OCHHCH$_2$), 2.34 (1H, dtt, $J$ = 12.3 Hz, 5.0 Hz, 2.0 Hz, OCHCHH), 2.19-2.08 (1H, m, OCH$_2$CHH), 1.86 (1H, tddd, $J$ = 12.3Hz, 11.0 Hz, 9.8 Hz, 5.0 Hz, OCH$_2$CHH), 1.71 (1H, dtd, $J$ = 11.9 Hz, 11.5 Hz, 9.6 Hz, OCHHCH$_2$); $^{13}$C, 75 MHz ($\delta$ in ppm): 143.5 (Cq, ar), 130.8 (CH, ar), 130.0 (CH, ar), 128.9 (CH, ar), 124.3 (CH, ar), 122.5 (Cq, ar), 89.0 (CH, d, $J$ = 177.0 Hz, CHF), 76.9 (CH, d, $J$ = 12.4 Hz, OCHCH$_2$), 65.4 (CH$_2$, d, $J$ = 12.4 Hz, OCH$_2$CH$_2$), 40.5 (CH$_2$, d, $J$ = 17.8 Hz, OCH$_2$CH$_2$); $^{19}$F, 282 MHz ($\delta$ in ppm): -170.3 to -170.7 (m); HRMS m/z: [MH, -HF]$^+$: 239.0102; 241.0059, calculated
Product **anti-5f** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (15 mg, 11%, microwave: 34 mg, 26%).

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.56-7.51 (1H, m, ar), 7.41 (1H, dt, $J = 7.4$ Hz, 1.8 Hz, ar), 7.29-7.18 (2H, m, ar), 5.09 (1H, dquint, $J = 47.9$ Hz, 2.8Hz, CHF), 4.73 (1H, dd, $J = 11.7$ Hz, 2.2 Hz, OCHCH$_2$), 4.05-3.97 (2H, m, OCH$_2$CH$_2$), 2.24-2.10 (1H, m, OCHCHH), 2.09-1.82 (2H, m, OCH$_2$CH$_2$), 1.78 (1H, dddd, $J = 43.4$ Hz, 14.5 Hz, 11.7 Hz, 2.1 Hz OCHCHH); **$^{13}$C, 75 MHz (δ in ppm):** 144.5 (Cq, ar), 130.6 (CH, ar), 130.0 (CH, ar), 128.9 (CH, ar), 124.3 (CH, ar), 122.6 (Cq, ar), 86.6 (CH, d, $J = 169.0$ Hz, CHF), 73.3 (CH, OCHCH$_2$), 63.0 (CH$_2$, OCH$_2$CH$_2$), 38.6 (CH$_2$, d, $J = 21.1$ Hz, OCHCH$_2$), 30.5 (CH$_2$, d, $J = 20.0$ Hz, OCH$_2$CH$_2$); **$^{19}$F, 282 MHz (δ in ppm):** -186.0 to -186.7 (m); **HRMS m/z:** [MH, -HF]$^+$: 239.0076; 241.0051, calculated 239.0072, 241.0051; **IR:** $v_{\text{max}}$ (neat)/cm$^{-1}$: 3065, 2954, 2865, 1568, 1475, 1428, 1361, 1255, 1115, 1072, 1043, 867, 780, 689.

2-(4-Bromophenyl)-4-fluoropyrans **syn-5g** and **anti-5g**.

Products **syn-5g** and **anti-5g** were prepared according to the general procedure outlined for the oxa-Prins reaction from 4-bromobenzaldehyde (92 mg, 0.5 mmol), but-3-en-1-ol 3 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).
Product **syn-5g** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a white solid (92 mg, 71%, microwave: 71 mg, 55%).

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.53-7.45 (2H, m, ar), 7.26-7.20 (2H, m, ar), 4.81 (1H, dtt, $J$= 48.9 Hz, 11.0 Hz, 5.1 Hz, CHF), 4.29 (1H, dt, $J$= 11.6 Hz, 1.9 Hz, OCHCH$_2$), 4.21 (1H, dtt, $J$= 12.0 Hz, 5.8 Hz, 1.8 Hz, OCH$^2$CH$_2$), 3.56 (1H, tt, $J$= 12.3 Hz, 1.9 Hz, OCH$^2$CH$_2$), 2.32 (1H, dtt, $J$= 12.3 Hz, 4.8 Hz, 2.1 Hz, OCHCH$_2$H), 2.18-2.08 (1H, m, OCH$_2$CH$_2$), 1.85 (1H, tddd, $J$= 12.5 Hz, 11.0 Hz, 9.9 Hz, 5.1 Hz, OCH$_2$CH$_2$H), 1.79-1.62 (1H, m, OCHCH$_2$H); $^{13}$C, 75 MHz (δ in ppm): 140.3 (Cq, ar), 131.5 (Cq, ar), 127.5 (CH, ar), 121.6 (CH, ar), 89.1 (CH, d, $J$= 177.6 Hz, CHF), 77.0 (CH, d, $J$= 11.5 Hz, OCHCH$_2$), 65.4 (CH$_2$, d, $J$= 12.0 Hz, OCH$_2$CH$_2$), 40.4 (CH$_2$, d, $J$= 17.0 Hz, OCHCH$_2$), 32.8 (CH$_2$, d, $J$= 18.3 Hz, OCH$_2$CH$_2$); $^{19}$F, 282 MHz (δ in ppm): -170.1 to -170.7 (m); HRMS m/z: [MH, -HF]$^+$: 239.0072, 241.0057, calculated 239.0072, 241.0051; **Mp:** 36-38 °C; **IR:** $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3082, 2959, 2856, 1588, 1489, 1453, 1362, 1247, 1158, 1089, 978, 822, 589.

Product **anti-5g** was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (18 mg, 14%, microwave: 26 mg, 20%).

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.51-7.48 (2H, m, ar), 7.26-7.21 (2H, m, ar), 5.08 (1H, dquint, $J$= 48.1 Hz, 2.8 Hz, CHF), 4.72 (1H, dd, $J$= 11.8 Hz, 2.3 Hz, OCHCH$_2$), 4.04-3.98 (2H, m, OCH$_2$CH$_2$), 2.15 (1H, dddt, $J$= 14.6 Hz, 11.1 Hz, 3.3 Hz, 2.2 Hz, m OCHCH$_2$H), 2.06-1.63 (3H, m, OCH$_2$CH$_2$, OCHCH$_2$H); $^{13}$C, 75 MHz (δ in ppm): 145.9 (Cq, ar), 136.0 (Cq, ar), 131.5 (CH, ar), 127.4 (CH, ar), 86.5 (CH, d, $J$= 169.1 Hz, CHF), 73.4 (CH, OCHCH$_2$), 63.0 (CH$_2$, OCH$_2$CH$_2$), 38.7 (CH$_2$, d, $J$= 20.8 Hz,
OCHCH₂), 30.5 (CH₂, d, J= 21.5 Hz, OCH₂CH₂); \(^{19}F, 282 \text{ MHz (δ in ppm): -185.8 to -186.6 (m); HRMS m/z: [MH, -HF]⁺: 239.0077; 241.0052, calculated 239.0072, 241.0051; Mp: 39-41 °C; IR: \(ν_{\text{max}} \text{(neat)/cm}^{-1}: 3079, 2918, 2850, 1580, 1475, 1360, 1255, 1202, 1146, 1069, 1007, 814.}

2-(4-Methoxyphenyl)-4-fluoropyrans syn-5i and anti-5i.

Products syn-5i and anti-5i were prepared according to the general procedure outlined for the oxa-Prins reaction from 4-methoxybenzaldehyde (60 µL, 0.5 mmol), but-3-en-1-ol 3 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol). The product was isolated as a white solid as a mixture of diastereoisomers after purification on silica gel (hexane/diethyl ether, 8/2) (17 mg, 16%, mixture ratio syn/anti 2.5/1, microwave: 39 mg, 37%, mixture ratio syn/anti 1/1.9).

Product syn-5i, identified from the mixture of diastereoisomers:

**NMR:** \(^1H, 300 \text{ MHz (δ in ppm): 7.33-7.25 (2H, m, ar), 6.93-6.85 (2H, m, ar), 4.81 (1H, dtt, J= 49.2 Hz, 11.0 Hz, 5.0 Hz, CHF), 4.28 (1H, dt, J= 11.5 Hz, 2.0 Hz, OCHCH₂), 4.20 (1H, dtd, J= 12.0 Hz, 5.4 Hz, 1.7 Hz, OCHHCH₂), 3.81 (3H, s, OCH₃), 3.57 (1H, tt, J= 12.2 Hz, 2.0 Hz, OCHHCH₂), 2.31 (1H, dtt, J= 12.4 Hz, 5.0 Hz, 2.1 Hz, OCHCHH), 2.21-2.07 (1H, m, OCH₂CHH), 2.07-1.71 (2H, m, OCH₂CHH, OCHCHH); \(^{13}C, 75 \text{ MHz (δ in ppm): 158.0 (Cq, ar), 134.3 (Cq, ar), 127.2 (CH, ar), 113.8 (CH, ar), 89.4 (CH, d, J= 176.6 Hz, CHF), 77.6 (CH, OCHCH₂), 65.4 (CH₂, d, J= 12.4 Hz, OCH₂CH₂), 55.2 (CH₃, OCH₃), 40.3 (CH₂, d, J= 17.1 Hz, OCHCH₂), 32.9 (CH₂, d, J= 16.2 Hz, OCH₂CH₂); \(^{19}F, 282 \text{ MHz (δ in ppm): -169.9 to -170.3 (m); HRMS m/z: [MH]⁺: 211.1133, calculated 211.1134; IR of the mixture: \(ν_{\text{max}} \text{(neat)/cm}^{-1}: 3079, 2932, 2858, 1518, 1450, 1347, 1295, 1169, 1081, 951, 854, 586.**
Product \textit{anti-5i}, identified from the mixture of diastereoisomers:

\textbf{NMR: $^1$H, 300 MHz ($\delta$ in ppm):} 7.33-7.25 (2H, m, ar), 6.93-6.85 (2H, m, ar), 5.92 (1H, dquint, $J$= 48.0 Hz, 2.8 Hz, CHF), 4.71 (1H, dd, $J$= 11.6 Hz, 2.2 Hz, OCHCH$_2$), 4.04-3.97 (2H, m, OCH$_2$CH$_2$), 3.81 (3H, s, OCH$_3$), 2.21-2.07 (1H, m, OCHCHH), 2.07-1.71 (3H, m, OCH$_2$CH$_2$, OCHCHH); \textbf{$^{13}$C, 75 MHz ($\delta$ in ppm):} 159.0 (Cq, ar), 134.3 (Cq, ar), 127.1 (CH, ar), 113.8 (CH, ar), 86.9 (CH, d, $J$= 168.6 Hz, CHF), 73.7 (CH, OCHCH$_2$), 63.1 (CH$_2$, OCH$_2$CH$_2$), 55.2 (CH$_3$, OCH$_3$), 38.4 (CH$_2$, d, $J$= 20.7 Hz, OCHCH$_2$), 30.6 (CH$_2$, d, $J$= 20.7 Hz, OCH$_2$CH$_2$); \textbf{$^{19}$F, 282 MHz ($\delta$ in ppm):} -185.8 to -186.4 (m); \textbf{HRMS m/z: [MH]$^+$:} 211.1133, calculated 211.1134; \textbf{IR of the mixture: $\nu_{\text{max}}$ (neat)/cm$^{-1}$:} 3079, 2932, 2858, 1518, 1450, 1347, 1295, 1169, 1081, 951, 854, 586.

\textbf{2-Pentyl-4-fluoropyrans syn-5k and anti-5k.}

Products \textit{syn-5k} and \textit{anti-5k} were prepared according to the general procedure outlined for the oxa-Prins reaction from hexanal (61 $\mu$L, 0.5 mmol), but-3-en-1-ol (45 $\mu$L, 0.5 mmol) and boron trifluoride (65 $\mu$L, 0.5 mmol).

Product \textit{syn-5k} was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a pale yellow oil (42 mg, 48%, from microwave: 51 mg, 58%, at -20 °C: 57 mg, 66%).
Product anti-5k was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (20 mg, 23%, microwave: 26 mg, 30%).

NMR: $^1$H, 400 MHz (δ in ppm): 4.99 (1H, dquint, $J= 48.1$ Hz, 2.7 Hz, CHF), 3.88-3.76 (2H, m, OCH$_2$CH$_2$), 3.65 (1H, dddd, $J= 11.6$ Hz, 7.0 Hz, 4.4 Hz, 2.1 Hz, OCHCH$_2$), 1.90-1.70 (2H, m, OCHCH$_2$, OCH$_2$CH$_2$), 1.59-1.21 (10H, m, OCH$_2$CH$_2$, OCHCH$_2$, 4xCH$_2$ penty1, 0.89 (3H, t, $J = 7.13$ Hz, CH$_3$ penty1); $^{13}$C, 100 MHz (δ in ppm): 39.3 (CH, d, $J= 176.2$ Hz, CHF), 39.7 (CH, d, $J= 10.9$ Hz, OCHCH$_2$), 64.9 (CH$_2$, d, $J= 11.4$ Hz, OCH$_2$CH$_2$), 38.7 (CH$_2$, d, $J= 17.1$ Hz, OCHCH$_2$), 36.0 (CH$_2$, CH$_2$ penty1), 33.1 (CH$_2$, d, $J= 17.4$ Hz, OCH$_2$CH$_2$), 31.7 (CH$_2$, CH$_2$ penty1), 25.1 (CH$_2$, CH$_2$ penty1), 22.5 (CH$_2$, CH$_2$ penty1), 14 (CH$_3$, CH$_3$ penty1); $^{19}$F, 376 MHz (δ in ppm): -169.7 to -170.0 (m); HRMS m/z: [MH, -HF]$^+$: 155.1435, calculated 155.1436; IR: $\nu_{\text{max}}$(neat)/cm$^{-1}$: 2955, 2931, 2858, 1456, 1367, 1163, 1085, 1005.
2-Phenyl-4-fluoropyrans syn-5m and anti-5m.

Products syn-5m and anti-5m were prepared according to the general procedure outlined for the oxa-Prins reaction from freshly distilled benzaldehyde (50 µL, 0.5 mmol), but-3-en-1-ol 99 (45 µL, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

\[
\begin{align*}
&\text{syn-5m} \\
\end{align*}
\]

Product syn-5m was isolated after purification on silica gel as a single diastereoisomer (hexane/diethyl ether, 8/2) as a colorless oil (19 mg, 21%, microwave: 8 mg, 9%, at -20 °C: 54 mg, 59%).

**NMR:** $^1$H, 400 MHz ($\delta$ in ppm): 7.30-7.16 (5H, m, ar), 4.74 (1H, dtt, $J = 49.1$ Hz, 10.9 Hz, 5.0 Hz, CHF), 4.23 (1H, dt, $J = 11.6$ Hz, 1.8 Hz, OCHCH$_2$), 4.13 (1H, dtd, $J = 11.9$ Hz, 5.7 Hz, 1.8 Hz, OCHHCH$_2$), 3.48 (1H, tt, $J = 12.2$ Hz, 1.8 Hz, OCHHCH$_2$), 2.26 (1H, dtt, $J = 12.3$ Hz, 4.9 Hz, 2.1 Hz, OCHCHH), 2.04 (1H, dddt, $J = 12.3$ Hz, 6.9 Hz, 4.3 Hz, 2.0 Hz, OCH$_2$CHH), 1.86-1.60 (2H, m, OCHCHH, OCH$_2$CHH); $^{13}$C, 100 MHz ($\delta$ in ppm): 141.2 (Cq, ar), 128.4 (CH, ar), 127.8 (CH, ar), 125.8 (CH, ar), 89.3 (CH, d, $J = 176.9$ Hz, CHF), 77.8 (CH, d, $J = 11.3$ Hz, OCHCH$_2$), 65.4 (CH$_2$, d, $J = 11.9$ Hz, OCH$_2$CH$_2$), 40.5 (CH$_2$, d, $J = 17.0$ Hz, OCH$_2$CH$_2$), 32.9 (CH$_2$, d, $J = 17.6$ Hz, OCHCH$_2$); $^{19}$F, 376 MHz ($\delta$ in ppm): -169.9 to -170.4 (m); HRMS m/z: [MNa]$^+$: 203.0843, calculated 203.0848; IR: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3064, 3032, 2960, 2853, 1494, 1453, 1374, 1249, 1158, 1081, 980, 757, 699.

\[
\begin{align*}
&\text{anti-5m} \\
\end{align*}
\]

Product anti-5m was isolated as a mixture of diastereoisomers with 101r after purification on silica gel (hexane/diethyl ether, 8/2) as a colorless oil (32 mg, 35%, mixture ratio syn/anti 2.4/1, microwave: 47 mg, 52%, mixture ratio syn/anti 2.7/1).
From the mixture of diastereoisomers:

**NMR: **$^1$H, 300 MHz ($\delta$ in ppm): 7.29-7.17 (5H, m, ar), 5.01 (1H, dquint, $J = 48.1$ Hz, 3.2 Hz, CHF), 4.67 (1H, dd, $J = 11.9$ Hz, 2.6 Hz, OCHCH$_2$), 3.95-3.91 (2H, m, OCH$_2$CH$_2$), 3.07-2.13 (1H, m, OCH$_3$CH$_3$), 1.98-1.62 (3H, m, OCH$_2$CH$_2$, OCHCHH);

**$^{13}$C, 75 MHz ($\delta$ in ppm):** 142.2 (Cq, ar), 128.5 (CH, ar), 127.6 (CH, ar), 125.8 (CH, ar), 86.9 (CH, d, $J = 168.7$ Hz, CHF), 74.1 (CH, OCHCH$_2$), 63.1 (CH$_2$, OCH$_2$CH$_2$), 38.6 (CH$_2$, d, $J = 21.0$ Hz, OCHCH$_2$), 30.6 (CH$_2$, d, $J = 22.4$ Hz, OCH$_2$CH$_2$); $^{19}$F, 282 MHz ($\delta$ in ppm): -185.9 to -186.4 (m); HRMS m/z: [MNa]$^+$: 203.0846, calculated 203.0848; IR of the mixture of diastereoisomers: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3064, 2960, 2853, 1494, 1453, 1374, 1249, 1158, 1081, 980, 757, 699.

3-Fluoro-5-phenylpentan-1-ol 7.

Pd on charcoal (4 mg) was added to a solution of 2-phenyl-4-fluoropyran 5m (47 mg, 0.26 mmol) in acetic acid (4 mL) and perchloric acid (40 µL, 60% in water). The mixture was stirred under a hydrogen atmosphere for 16 h. The mixture was then filtered through celite and the product was extracted with ethyl acetate. The organic layer was dried, filtered and concentrated. The title compound was obtained after purification on silica (hexane/diethyl ether 7/3) as a colorless oil (41 mg, 70%).

**NMR: **$^1$H, 400 MHz ($\delta$ in ppm): 7.37-7.28 (2H, m, ar), 7.26-7.17 (3H, m, ar), 4.63 (1H, dtt, $J = 49.5$ Hz, 8.6 Hz, 3.6 Hz, CHF), 4.30-4.13 (2H, m, CH$_2$CH$_2$OH), 2.84 (1H, ddd, $J = 13.8$ Hz, 9.9 Hz, 5.5 Hz, PhCHHCH$_2$), 2.72 (1H, ddd, $J = 13.8$ Hz, 9.4 Hz, 7.1 Hz, PhCHHCH$_2$), 2.12-1.75 (7H, m, PhCH$_2$CH$_2$, HOCH$_2$CH$_2$, C=OCH$_3$); $^{13}$C, 100 MHz ($\delta$ in ppm): 171.0 (Cq, C=OCH$_3$), 141.2 (Cq, ar), 128.5 (CH, ar), 128.4 (CH, ar), 126.0 (CH, ar), 90.2 (CH, d, $J = 168.6$ Hz, CHF), 60.6 (CH, d, $J = 4.7$ Hz, CH$_2$CH$_2$OH), 36.9 (CH$_2$, d, $J = 21.0$ Hz, HOCH$_2$CH$_2$), 34.2 (CH$_2$, d, $J = 21.0$ Hz, PhCH$_2$CH$_2$), 31.2 (CH$_2$, d, $J = 4.7$ Hz, PhCH$_2$CH$_2$), 20.9 (CH$_3$, C=OCH$_3$); $^{19}$F, 376
MHz (δ in ppm): -185.1 to -185.7 (m); HRMS m/z: [MNa]+: 247.1109, calculated 247.1110; IR: ν max (neat)/cm⁻¹: 3027, 2932, 1739, 1385, 1365, 1248, 1046, 746, 700.0.

**trans-2-Vinylcyclohexanol 8.**

To a solution of cyclohexene oxide 10 (500 µL, 5 mmol) in diethyl ether (2 mL) at -20 °C, was added CuBr.Me₂S (102 mg, 0.5 mmol) and vinylmagnesium bromide (6 mL, 6 mmol). After 10h, the mixture was hydrolysed with a solution of saturated ammonium chloride and the layers separated. The aqueous layer was extracted with diethyl ether. The organic layers were dried, concentrated and purified on silica gel. Alcohol 8 was obtained as a colorless oil (447 mg, 71%)

NMR: ¹H, 400 MHz (δ in ppm): 5.68 (1H, ddd, J= 17.2 Hz, 10.2 Hz, 8.7 Hz, CH=CH₂), 5.16 (1H, ddd, J= 17.2 Hz, 1.9 Hz, 0.7 Hz, CH=CH₂), 5.12 (1H, dd, J= 10.2 Hz, 1.9 Hz, CH=CH₂), 3.24 (1H, td, J= 10.0 Hz, 4.4 Hz, CHO), 2.06-1.98 (1H, m, CHHCHOH), 1.96-1.84 (1H, m, CHCH=CH₂), 1.79-1.70 (2H, m, CHHCH₂CHOH or CHHCH₂CHOH, CHHCH=CH₂), 1.69-1.64 (1H, m, CHHCH₂CHOH or CHHCH₂CH₂CHOH), 1.31-1.15 (4H, CHHCHCH=CH₂, CHHCH₂CHOH, CHHCH₂CH₂CHOH, CHHCHOH); ¹³C, 100 MHz (δ in ppm): 140.8 (CH, CH=CH₂), 116.7 (CH₂, CH=CH₂), 72.7 (CH, CHO), 51.2 (CH, CHCH=CH₂), 33.8 (CH₂, CH₂CHOH), 31.1 (CH₂, CH₂CHCH=CH₂), 25.1, 24.7 (CH₂, CH₂CH₂CHOH, CH₂CH₂CH₂CHOH); LRMS m/z: [MNa]+: 149.1, calculated 149.1; IR: ν max (neat)/cm⁻¹: 3384, 2918, 2851, 1697, 1446, 1303, 1200, 1057.
4-Fluoro-2-phenyloctahydrochromene 9a.

Product 9a was prepared according to the general procedure outlined for the oxa-Prins reaction from benzaldehyde (102 µL, 1.0 mmol), 2-vinylcyclohexanol 8 (126 mg, 1.0 mmol) and boron trifluoride (126 µL, 0.1 mmol). The product was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a pale yellow oil (69 mg, 59%).

NMR: $^1$H, 300 MHz (δ in ppm): 7.39-7.33 (4H, m, ar), 7.31-7.27 (1H, m, ar), 4.46 (1H, dtd, $J$= 49.9 Hz, 10.4 Hz, 5.0 Hz, CHF), 4.44 (1H, dt, $J$= 11.82 Hz, 2.0 Hz, OCHArCH$_2$), 3.16 (1H, tdd, $J$= 10.4 Hz, 4.2 Hz, 1.5 Hz, OCHCH$_2$), 2.35 (1H, dtd, $J$= 12.4 Hz, 4.7 Hz, 2.0 Hz, OCHArCH=CH), 2.21 (1H, ddt, $J$= 13.3 Hz, 5.6 Hz, 3.0 Hz, CHFCHCH$_2$), 2.05 (1H, m, OCHCHCH$_2$), 1.91-1.81 (2H, m, CHFCH$_2$CHOAr and CHFCHCH$_2$CH$_2$), 1.80-1.72 (2H, m, CHFCH$_2$CH$_2$), 1.60-1.42 (2H, m, OCHCH$_2$CH$_2$, CHFCH$_2$), 1.40-1.24 (2H, m, OCHCH$_2$CH$_2$), 1.13-0.96 (1H, m, CHFCHCHHCH$_2$), 1.10-1.00 (1H, m, CHFCHCH$_2$CH$_2$); $^{13}$C, 75 MHz (δ in ppm): 136.3 (Cq, ar), 128.5 (CH, ar), 127.7 (CH, ar), 126.0 (CH, ar), 93.6 (CH, d, $J$= 177.7 Hz, CHF), 78.7 (CH, d, $J$= 8.8 Hz, OCHCH$_2$), 77.1 (CH, d, $J$= 12.5 Hz, OCHAr), 47.9 (CH, d, $J$= 16.9 Hz, CHFCHCH$_2$), 40.4 (CH$_2$, d, $J$= 17.4 Hz, CHFCH$_2$CHAr), 32.0 (CH$_2$, OCHCH$_2$CH$_2$), 26.9 (CH$_2$, CHFCH$_2$), 24.9 (CH$_2$, CHFCH$_2$CH$_2$CH$_2$ or CHFCHCH$_2$CH$_2$CH$_2$), 24.7 (CH$_2$, CHFCHCH$_2$CH$_2$CH$_2$ or CHFCHCH$_2$CH$_2$CH$_2$); $^{19}$F, 282 MHz (δ in ppm): -179.8 to -180.1 (m); HRMS m/z: [MNa]$^+$: 257.1318, calculated 257.1319; IR: $\nu_{max}$ (neat)/cm$^{-1}$: 3027, 2920, 2851, 1449, 1372, 1278, 1183, 1123, 1072, 1034, 997, 756, 698.
4-Fluoro-2-(4-nitrophenyl)octahydrochromene 9b.

Product 9b was prepared according to the general procedure outlined for the oxa-Prins reaction from 4-nitrobenzaldehyde (121 mg, 0.87 mmol), 2-vinyl-cyclohexanol 8 (110 mg, 0.87 mmol) and boron trifluoride (110 µL, 0.87 mmol). The title compound was isolated after purification on silica gel (hexane/diethyl ether, 8/2) as a white solid (80 mg, 57%).

NMR: $^1$H, 300 MHz ($\delta$ in ppm): 8.20 (2H, m, ar), 7.54 (2H, m, ar), 4.55 (1H, m, OCHArCH$_2$), 4.47 (1H, dtd, $J$= 49.6 Hz, 10.4 Hz, 4.9 Hz, CHF), 3.18 (1H, tdd, $J$= 10.3 Hz, 4.1 Hz, 1.4 Hz, OCHCH$_2$), 2.38 (1H, dtd, $J$= 12.3 Hz, 4.5 Hz, 2.3 Hz, OCHArCH=HCHF), 2.21 (1H, ddt, $J$= 13.2 Hz, 5.3 Hz, 3.0 Hz, CHFCHCHHCH$_2$), 2.10-2.00 (1H, m, OCHCHHCH$_2$), 1.91-1.81 (1H, m, OCHCH$_2$CH=HCH$_2$ or OCHCH$_2$CH=CH)$_2$, 1.81-1.68 (2H, m, OCHArCH=HCHF, OCHCH$_2$CH=HCH$_2$ or OCHCH$_2$CH=CH)$_2$, 1.60-1.39 (1H, m, OCHCH, OCHCHHCH$_2$), 1.39-1.18 (2H, m, OCHCH$_2$CH=HCH$_2$, OCHCH$_2$CH=CH)$_2$, 1.13-0.96 (1H, m, CHFCHCHHCH$_2$); $^{13}$C, 75 MHz ($\delta$ in ppm): 148.7 (Cq, ar), 147.3 (Cq, ar), 126.5 (CH, ar), 123.6 (CH, ar), 92.8 (CH, d, $J$= 178.8 Hz, CHF), 78.7 (CH, d, $J$= 9.3 Hz, OCHCH), 75.7 (CH, d, $J$= 12.0 Hz, OCHArCH$_2$), 47.7 (CH, d, $J$= 17.4 Hz, OCHCH), 40.4 (CH$_2$, d, $J$= 18.5 Hz, OCHArCH$_2$CHF), 31.9 (CH$_2$, CHFCHCH$_2$), 26.7 (CH$_2$, OCHCH$_2$CH$_2$), 24.8 (CH$_2$, OCHCH$_2$CH$_2$CH$_2$ or OCHCH$_2$CH$_2$CH$_2$), 24.5 (CH$_2$, OCHCH$_2$CH$_2$CH$_2$ or OCHCH$_2$CH$_2$CH$_2$); $^{19}$F, 282 MHz ($\delta$ in ppm): -181.6 to -182.0 (m); HRMS m/z: [M+Na]$^+$: 302.1170, calculated 302.1168; Mp: 77-79 °C; IR: $\nu$ (neat)/cm$^{-1}$: 3080, 2932, 2858, 1604, 1519, 1348, 1169, 1081, 1049, 854.
3-Ethyl-4-fluoro-2-(4-nitrophenyl)tetrahydropyran 12a.

Pyran 12a was prepared according to the general procedure outlined for the oxo-Prins reaction from 4-nitrobenzaldehyde (151 mg, 1 mmol), (E)-hex-3-en-1-ol 11a (118 µL, 1 mmol) and boron trifluoride (127 µL, 1 mmol). The title compound was obtained after purification on silica gel (hexane/diethyl ether, 8/2) as a white solid (67 mg, 53%).

**NMR:** $^1$H, 300 MHz (δ in ppm): 8.25-8.17 (2H, m, ar), 7.56-7.49 (2H, m, ar), 4.64 (1H, dtd, $J$= 49.2 Hz, 10.6 Hz, 4.9 Hz, CHF), 4.19-4.08 (2H, m, OCHCH, OCHCH$_2$), 3.57 (1H, tdd, $J$= 12.5 Hz, 2.1 Hz, 1.5 Hz, OCHHCH$_2$), 2.19 (1H, dddd, $J$= 12.2 Hz, 6.8 Hz, 4.9 Hz, 2.0 Hz, OCH$_2$CHH), 2.02 (1H, m, OCH$_2$CHH), 1.79 (1H, qt, $J$= 9.7 Hz, 4.9 Hz, OCHCH), 1.46-1.31 (1H, m, CHCHHCH$_3$), 1.28-1.17 (1H, m, CHCHHCH$_3$), 0.74 (3H, td, $J$= 7.6 Hz, 0.9 Hz, CH$_2$CH$_3$); $^{13}$C, 75 MHz (δ in ppm): 147.7 (Cq, ar), 146.9 (Cq, ar), 128.3 (CH, ar), 123.6 (CH, ar), 91.8 (CH, d, $J$= 178.8 Hz, CHF), 81.5 (CH, d, $J$= 9.9 Hz, OCHCH), 65.4 (CH$_2$, d, $J$= 12.9 Hz, OCH$_2$CH$_2$), 49.0 (CH, d, $J$= 17.4 Hz, OCHCH), 32.9 (CH$_2$, d, $J$= 18.5 Hz, OCH$_2$CH$_2$), 20.0 (CH$_2$, CH$_2$CH$_3$), 10.5 (CH$_3$, CH$_2$CH$_3$); $^{19}$F, 282 MHz (δ in ppm): -176.0 to -176.5 (m); HRMS m/z: [MNa]$^+$: 276.1015, calculated 276.1012; Mp: 81-83 °C; IR: $v_{max}$ (neat)/cm$^{-1}$: 3110, 3080, 2966, 2858, 1605, 1522, 1347, 1198, 1155, 1088, 1025, 852, 814.

3-Ethyl-4-fluoro-2-(4-nitrophenyl)tetrahydropyran 12b.
Pyran 12b was prepared according to the general procedure outlined for the oxa-Prins reaction from 4-nitrobenzaldehyde (151 mg, 1 mmol), (Z)-hex-3-en-1-ol 11b (118 µL, 1 mmol) and boron trifluoride (127 µL, 1 mmol). The title compound was obtained after purification on silica gel (hexane/diethyl ether, 8/2) as a white solid (68 mg, 54%).

**NMR:** $^1$H, 300 MHz ($\delta$ in ppm): 8.25-8.17 (2H, m, ar), 7.55-7.46 (2H, m, ar), 4.96 (1H, ddt, $J = 48.6$ Hz, $11.6$ Hz, $5.1$ Hz, $\text{CHF}$), 4.51 (1H, t, $J = 2.3$ Hz, $\text{OCHCH}$), 4.21 (1H, dtd, $J = 11.6$ Hz, 6.1 Hz, 1.5 Hz, $\text{OCHCH}_2$), 3.56 (1H, dddd, $J = 12.3$ Hz, 12.0 Hz, 2.9 Hz, 1.5 Hz, $\text{OCHCH}_2$), 2.23 (1H, m, $\text{OCHCH}$), 2.02 (1H, dddd, $J = 24.5$ Hz, 12.6 Hz, 8.2 Hz, 5.5 Hz, $\text{OCH}_2\text{CH}$), 1.95-1.85 (1H, m, $\text{OCH}_2\text{CH}$), 1.50 (1H, ddd, $J = 14.6$ Hz, 7.6 Hz, 4.9 Hz, $\text{OCHCHCH}_2$), 1.21 (1H, ddd, $J = 14.6$ Hz, 7.6 Hz, 5.8 Hz, $\text{OCHCHCH}_2$), 0.47 (3H, dt, $J = 7.6$ Hz, 0.8 Hz, $\text{OCHCH}_2\text{CH}_3$); $^{13}$C, 75 MHz ($\delta$ in ppm): 147.9 (Cq, ar), 146.0 (Cq, ar), 126.3 (CH, ar), 123.4 (CH, ar), 92.4 (CH, d, $J = 183.0$ Hz, $\text{CHF}$), 79.0 (CH, d, $J = 9.4$ Hz, $\text{OCHCH}$), 65.2 (CH$_2$, d, $J = 11.9$ Hz, $\text{OCH}_2\text{CH}_2$), 47.0 (CH, d, $J = 16.2$ Hz, $\text{OCHCH}$), 27.2 (CH$_2$, d, $J = 18.7$ Hz, $\text{OCH}_2\text{CH}_2$), 14.7 (CH$_2$, d, $J = 1.7$ Hz, $\text{CH}_2\text{CH}_3$), 14.4 (CH$_3$, d, $J = 1.8$ Hz, $\text{CH}_2\text{CH}_3$); $^{19}$F, 282 MHz ($\delta$ in ppm): -176.9 to -177.3 (m); HRMS m/z: [M+Na]$^+$: 276.1019, calculated 276.1012; Mp: 81-83 °C; IR: $v_{\text{max}}$ (neat)/cm$^{-1}$: 3112, 3080, 2966, 2876, 1601, 1519, 1346, 1171, 1104, 1072, 1026, 856.

$\text{N-Tosyl-3-butenylamine 13.}$

1-Bromobut-3-ene (1.01 ml, 10 mmol) was added to a solution of tosylamine (1.71g, 10 mmol), and potassium carbonate (1.65 g, 12 mmol) in acetone (100 mL). After 4h at reflux, the mixture was concentrated under vacuum, and water and diethyl ether were added. The layers were separated and the aqueous layer extracted with diethyl ether. The organic layers were dried, filtered and concentrated. The title compound was obtained after purification on silica (hexane/diethyl ether 6/4) as a pale yellow oil (922 mg, 41%).
NMR: $^1$H, 300 MHz (δ in ppm): 7.80-7.70 (2H, m, ar), 7.35-7.28 (2H, m, ar), 5.62 (1H, ddt, $J = 16.9$ Hz, 10.3 Hz, 6.8 Hz, CH$_2$=CH), 5.08-4.97 (2H, m, CH$_2$NH), 5.08-4.97 (2H, m, CH$_2$CH$_2$NH), 4.76 (1H, t broad, $J = 5.8$ Hz, NH), 3.00 (2H, td, $J = 6.8$ Hz, 5.8 Hz, CH$_2$C=CH), 2.42 (3H, m, ArCH$_3$), 2.19 (2H, qt, $J = 6.8$ Hz, 1.4 Hz, CHC=CH$_2$CH$_2$NH); $^{13}$C, 100 MHz (δ in ppm): 143.2 (Cq, ar), 138.1 (Cq, ar), 130.0 (CH, ar), 127.1 (CH, ar), 136.2 (CH, CH$_2$=CH), 116.4 (CH$_2$, CH$_2$=CH), 48.1 (CH$_2$, CH$_2$NHTs), 34.3 (CH$_2$, CH$_2$=CHCH$_2$), 21.5 (CH$_3$, arCH$_3$); LRMS m/z: [MH]$^+$: 225.1, calculated 225.1; IR: ν$_{max}$ (neat)/cm$^{-1}$: 3283, 3075, 2974, 2924, 2868, 1641, 1597, 1493, 1323, 1158, 1090, 1085, 990, 920, 813.

$N$-(Tosyl)-2-(4-nitrophenyl)-4-fluoropiperidines syn-14a and anti-14a.

Piperidines syn-14a and anti-14a were prepared according to the general procedure outlined for the aza-Prins reaction from 4-nitrobenzaldehyde (76 mg, 0.5 mmol), N-tosyl-3-butenylamine 13 (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product syn-14a was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a colorless oil (59 mg, 31%, microwave: 62 mg, 33%).

NMR: $^1$H, 400 MHz (δ in ppm): 8.28-8.18 (2H, m, ar), 7.79-7.73 (2H, m, ar), 7.58-7.52 (2H, m, ar), 7.40-7.34 (2H, m, ar), 5.42 (1H, s broad, NCHCH$_2$), 4.54 (1H, dtt, $J = 48.3$ Hz, 10.4 Hz, 4.5 Hz, C HF), 4.03-3.94 (1H, m, NCHHCH$_2$), 3.10-2.99 (1H, m, NCHHCH$_2$), 2.68-2.58 (1H, m, NCHCHH), 2.47 (3H, s, arCH$_3$), 1.98-1.86 (1H, m, NCH$_2$C=H), 1.79 (1H, dddd, $J = 13.8$ Hz, 10.8 Hz, 8.6 Hz, 5.7 Hz, NCHCHH), 1.49 (1H, ttd, $J = 12.5$ Hz, 10.2 Hz, 4.8 Hz, NCH$_2$CHH); $^{13}$C, 100 MHz (δ in ppm): 147.3 (Cq, ar), 145.8 (Cq, ar), 144.1 (Cq, ar), 137.2 (Cq, ar), 130.1 (CH, ar), 127.6 (CH, ar), 127.0 (CH, ar), 124.0 (CH, ar), 86.0 (CH, d, $J = 174.5$ Hz, CSF), 55.4 (CH, d, $J = 12.5$ Hz, OCHCH$_2$), 40.2 (CH$_2$, d, $J = 11.7$ Hz, OCH$_2$CH$_2$), 34.0 (CH$_2$, d, $J = 20.3$ Hz, NCHCH$_2$), 30.8 (CH$_2$, d, $J = 19.5$ Hz, NCH$_2$CH$_2$), 21.6 (CH$_3$, arCH$_3$); $^{19}$F, 376 MHz (δ
Product anti-14a was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a colorless oil (56 mg, 30%, microwave: 46 mg, 24%).

NMR: $^1$H, 300 MHz (δ in ppm): 8.19-8.12 (2H, m, ar), 7.77-7.71 (2H, m, ar), 7.53-7.46 (2H, m, ar), 7.36-7.29 (2H, m, ar), 5.35 (1H, d broad, $J= 6.6$ Hz, NCHCH$_2$), 4.90 (1H, dt, $J= 47.3$ Hz, 3.8 Hz, 2.2 Hz, CHF), 3.85 (1H, dd, $J= 14.6$ Hz, 4.6 Hz, NCH$\cdot$HCH$_2$), 3.35 (1H, ddd, $J= 14.6$ Hz, 12.9 Hz, 3.1 Hz, NCH$\cdot$HCH$_2$), 2.75-2.66 (1H, m NCHCHH), 2.45 (3H, s, arCH$_3$), 2.01 (1H, dddd, $J= 43.8$ Hz, 15.4 Hz, 6.9 Hz, 2.4 Hz, NCHCHH), 1.82-1.60 (2H, m, NCH$_2$CH$_2$); $^{13}$C, 100 MHz (δ in ppm): 147.3 (Cq, ar), 146.8 (Cq, ar), 143.9 (Cq, ar), 137.6 (Cq, ar), 130.0 (CH, ar), 127.4 (CH, ar), 126.9 (CH, ar), 123.8 (CH, ar), 85.9 (CH, d, $J= 172.6$ Hz, CHF), 52.9 (CH, s, OCHCH$_2$), 36.6 (CH$_2$, s, OCH$_2$CH$_2$), 32.1 (CH$_2$, d, $J= 19.7$ Hz, NCHCH$_2$), 28.8 (CH$_2$, d, $J= 21.2$ Hz, NCH$_2$CH$_2$), 21.6 (CH$_3$, arCH$_3$); $^{19}$F, 376 MHz (δ in ppm): -175.7 to -176.0 (m); HRMS m/z: [MNa]$^+$: 401.0956, calculated 401.0947; Mp: 148-150 °C; IR: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3081, 2940, 2851, 1598, 1519, 1494, 1345, 1158, 1091, 888.

$N$-(Tosyl)-2-pentyl-4-fluoropiperidines syn-14b and anti-14b.

Piperidines syn-14b and anti-14b were prepared according to the general procedure outlined for the aza-Prins reaction from hexanal (61 µL, 0.5 mmol), $N$-tosyl-3-butenylamine 13 (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol) to give the title compounds. The products were isolated as a mixture of diastereoisomer after purification on silica gel (hexane/diethyl ether, 7/3) as colorless oils (119 mg,
73%, mixture ratio syn/anti 2/1, microwave: 129 mg, 79%, mixture ratio syn/anti 1.9/1).

Analysis from the mixture of diastereoisomers syn-14b and anti-14b:

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.77-7.68 (2H, m, ar), 7.33-7.25 (2H, m, ar), 4.72 (1H, dtt, $J= 48.7$ Hz, 11.3 Hz, 4.9 Hz, CHF), 4.24-4.12 (1H, m, NCHCH$_2$), 4.05-3.88 (1H, m, NCHHCH$_2$), 3.03 (1H, dddd, $J= 14.9$ Hz, 13.1 Hz, 2.4 Hz, 1.2 Hz, NCHHCH$_2$), 2.42 (3H, s, arCH$_3$), 2.02-1.83 (2H, m, NCHCHH, NCH$_2$CHH), 173-1.12 (10H, m, NCH$_2$CHH, NCHCHH, 4xCH$_2$ pentyl), 0.87 (3H, t, $J= 6.7$ Hz, CH$_3$ pentyl); $^{13}$C, 75 MHz (δ in ppm): 143.7 (Cq, ar), 138.2 (Cq, ar), 129.8 (CH, ar), 126.9 (CH, ar), 87.0 (CH, d, $J= 173.0$ Hz, CHF), 53.6 (CH, d, $J= 13.0$ Hz, OCHCH$_2$), 38.7 (CH$_2$, d, $J= 12.3$ Hz, OCH$_2$CH$_2$), 34.2 (CH$_2$, d, $J= 18.2$ Hz, NCHCH$_2$), 32.2 (CH$_2$, pentyl), 31.4 (CH$_2$, pentyl), 31.2 (CH$_2$, d, $J= 21.7$ Hz, NCH$_2$CH$_2$), 26.0 (CH$_2$, pentyl), 22.4 (CH$_2$, pentyl), 21.5 (CH$_3$, arCH$_3$), 13.9 (CH$_3$, pentyl); $^{19}$F, 282 MHz (δ in ppm): -175.8 to -176.3 (m); HRMS m/z: [MNa]$^+$: 350.1559, calculated 350.1566; IR from the mixture of diastereoisomers: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 2952, 2918, 2851, 1457, 1331, 1300, 1200, 1144, 811.

Analysis from the mixture of diastereoisomers syn-14b and anti-14b:

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.77-7.68 (2H, m, ar), 7.33-7.25 (2H, m, ar), 4.83 (1H, dtt, $J= 47.5$ Hz, 3.0 Hz, 2.9 Hz, CHF), 4.05-3.88 (1H, m, NCHCH$_2$), 3.72 (1H, m, NCHHCH$_2$), 3.31 (1H, ddt, $J= 14.3$ Hz, 4.9 Hz, NCHHCH$_2$), 3.11 (1H, dddd, $J= 14.3$ Hz, 13.3 Hz, 2.8 Hz, NCHHCH$_2$), 2.41 (3H, s, arCH$_3$), 2.02-1.83 (1H, m, NCHCHH), 1.83-1.73 (1H, m,
NCH₂CHH), 1.73-1.12 (10H, m, NCH₂CHH, NCHCHH, 4xCH₂ pentyl), 0.85 (3H, t, J= 6.6 Hz, CH₃ pentyl); $^{13}$C, 75 MHz (δ in ppm): 143.0 (Cq, ar), 138.5 (Cq, ar), 129.6 (CH, ar), 126.9 (CH, ar), 87.0 (CH, d, J= 170.0 Hz, CHF), 51.4 (CH, OCHCH₂), 35.0 (CH₂, OCH₂CH₂), 32.2 (CH₂, pentyl), 31.9 (CH₂, d, J= 19.2 Hz, NCHCH₂), 31.1 (CH₂, pentyl), 29.2 (CH₂, d, J= 21.4 Hz, NCH₂CH₂), 26.4 (CH₂, pentyl), 22.4 (CH₂, pentyl), 21.4 (CH₃, arCH₃), 13.9 (CH₃, pentyl); $^{19}$F, 282 MHz (δ in ppm): -179.9 to -180.7 (m); HRMS m/z: [MNa]$^+$: 350.1559, calculated 350.1566; IR as a mixture of diastereoisomers: $ν_{max}$ (neat)/cm$^{-1}$: 2952, 2918, 2851, 1457, 1331, 1300, 1200, 1144, 811.

$\text{N-(Tosyl)-2-(4-bromophenyl)-4-fluoropiperidines syn-14c and anti-14c}$.

Piperidines syn-14c and anti-14c were prepared according to the general procedure outlined for the aza-Prins reaction from 4-bromobenzaldehyde (92 mg, 0.5 mmol), N-tosyl-3-butylamine 13 (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product syn-14c was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (72 mg, 35%, microwave: 90 mg, 44%).

**NMR: $^1$H, 400 MHz (δ in ppm):** 7.78-7.68 (2H, m, ar), 7.50-7.44 (2H, m, ar), 7.37-7.31 (2H, m, ar), 7.26-7.20 (2H, m, ar), 5.35 (1H, s broad, NCHCH₂), 4.57 (1H, dtt, J= 48.5 Hz, 10.8 Hz, 4.5 Hz, CHF), 4.02-3.92 (1H, m, NCHCHH₂), 3.66-3.57 (1H, m NCHCH₂), 2.62-2.55 (1H, m NCHCHH₂), 2.46 (3H, s, PhCH₃), 1.92-1.83 (1H, m, NCH₂CHH), 1.76-1.65 (1H, m, NCHCHH), 1.44 (1H, ttt, J= 12.6 Hz, 10.3 Hz, 4.8 Hz, NCH₂CHH); $^{13}$C, 100 MHz (δ in ppm): 143.8 (Cq, ar), 137.6 (Cq, ar), 136.9 (Cq, ar), 131.9 (CH, ar), 130.0 (CH, ar), 128.3 (CH, ar), 126.9 (CH, ar), 121.5 (Cq, ar), 86.4 (CH, d, J= 174.6 Hz, CHF), 55.2 (CH, d, J= 12.4 Hz, OCHCH₂), 39.9 (CH₂, d, J= 12.4 Hz, OCH₂CH₂), 33.5 (CH₂, d, J= 20.2 Hz, NCHCH₂), 30.9 (CH₂, d, J= 18.9 Hz,
NCH₂CH₂), 21.6 (CH₃, ArCH₃); ¹⁹F, 376 MHz (δ in ppm): -175.2 to -175.5 (m); HRMS m/z: [MNa]⁺: 434.0199, 436.0182, calculated 434.0202, 436.0181; Mp: 131-133 °C; IR: v max (neat)/cm⁻¹: 3058, 2935, 2862, 1594, 1485, 1342, 1155, 1093, 1009, 816, 668.

Product anti-14c was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (68 mg, 33%, microwave: 47 mg, 23%).

NMR: ¹H, 300 MHz (δ in ppm): 7.74-7.67 (2H, m, ar), 7.43-7.36 (2H, m, ar), 7.32-7.26 (2H, m, ar), 7.23-7.16 (2H, m, ar), 5.19 (1H, d broad, J = 6.4 Hz, NCHCH₂), 4.87 (1H, dtt, J = 47.6 Hz, 3.2 Hz, 3.0 Hz, CHF), 3.84-3.72 (1H, m, NCHHCH₂), 3.36 (1H, ddd, J = 14.5 Hz, 12.5 Hz, 3.4 Hz, NCHHCH₂), 2.67-2.53 (1H, m NCHC), 2.03 (1H, dddd, J = 43.0 Hz, 15.2 Hz, 6.7 Hz, 2.6 Hz, NCHCH₃), 1.82-1.71 (1H, m, NCH₂CHH), 1.70-1.53 (1H, m, NCH₂CHH); ¹³C, 75 MHz (δ in ppm): 143.5 (Cq, ar), 138.5 (Cq, ar), 137.8 (Cq, ar), 131.3 (CH, ar), 129.8 (CH, ar), 128.4 (CH, ar), 126.9 (CH, ar), 120.9 (Cq, ar), 86.0 (CH, d, J = 171.9 Hz, CHF), 52.9 (CH, s, OCHCH₂), 36.6 (CH₂, d, J = 1.5 Hz, OCH₂CH₂), 31.9 (CH₂, d, J = 19.0 Hz, NCHCH₂), 29.1 (CH₂, d, J = 18.0 Hz, NCH₂CH₂), 21.5 (CH₃, arCH₃); ¹⁹F, 282 MHz (δ in ppm): -181.2 to -181.7 (m); HRMS m/z: [MH, -HF]⁺: 392.0311, 394.0311, calculated 392.0320, 394.0299; Mp: 121-123 °C; IR: v max (neat)/cm⁻¹: 3058, 2952, 2873, 1594, 1488, 1339, 1158, 1094, 1009, 814, 671.

N-(Tosyl)-2-(3-bromophenyl)-4-fluoropiperidines syn-14d and anti-14d.

Piperidines syn-14d and anti-14d were prepared according to the general procedure outlined for the aza-Prins reaction from 3-bromobenzaldehyde (58 µL, 0.5 mmol), N-tosyl-3-butenylamine 13 (112 mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).
Product **syn-14d** was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (82 mg, 40%).

**NMR:** \(^1H, 300 \text{ MHz (δ in ppm)}\): 7.78-7.71 (2H, m, ar), 7.40-7.28 (4H, m, ar), 7.26-7.18 (2H, m, ar), 5.38 (1H, s broad, NCH\(\text{CH}_2\)), 4.58 (1H, dt, \(J = 48.5 \text{ Hz}, 10.8 \text{ Hz}, 4.4 \text{ Hz}, \text{CHF}\)), 4.06-3.94 (1H, m, NCH\(\text{HCH}_2\)), 3.10-2.97 (1H, m NCH\(\text{HCH}_2\)), 2.65-2.52 (1H, m NCH\(\text{HCH}_2\)), 2.46 (3H, s, ar\(\text{CH}_3\)), 1.95-1.82 (1H, m, NCH\(\text{CH}_2\)), 1.73 (1H, dddd, \(J = 13.4 \text{ Hz}, 11.1 \text{ Hz}, 8.7 \text{ Hz}, 5.6 \text{ Hz}, \text{NCHCH}_2\)), 1.44 (1H, ttd, \(J = 12.5 \text{ Hz}, 10.3 \text{ Hz}, 4.8 \text{ Hz}, \text{NCH}_2\text{CH}_2\)); \(^{13}C, 75 \text{ MHz (δ in ppm)}\): 143.8 (Cq, ar), 140.3 (Cq, ar), 137.6 (Cq, ar), 130.6 (CH, ar), 130.4 (CH, ar), 130.0 (CH, ar), 129.5 (CH, ar), 126.9 (CH, ar), 125.2 (CH, ar), 123.1 (Cq, ar), 86.3 (CH, d, \(J = 174.4 \text{ Hz}, \text{CHF}\)), 55.1 (CH, d, \(J = 12.3 \text{ Hz}, \text{OCHCH}_2\)), 40.0 (CH\(_2\), d, \(J = 12.2 \text{ Hz}, \text{OCH}_2\text{CH}_2\)), 33.6 (CH\(_2\), d, \(J = 19.6 \text{ Hz}, \text{NCHCH}_2\)), 31.0 (CH\(_2\), d, \(J = 19.3 \text{ Hz}, \text{NCH}_2\text{CH}_2\)), 21.6 (CH\(_3\), ar\(\text{CH}_3\)); \(^{19}F, 282 \text{ MHz (δ in ppm)}\): -175.6 to -176.0 (m); **HRMS m/z:** \([\text{MNa}]^+\): 434.0189, 436.0184, calculated 434.0202, 436.0181; **Mp:** 93-95 °C; **IR:** \(\nu_{\text{max}} \text{ (neat)/cm}^{-1}\): 3058, 3036, 2918, 2868, 1594, 1566, 1476, 1339, 1155, 1093, 1018, 811, 741, 660.

Product **anti-14d** was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (40 mg, 19%).

**NMR:** \(^1H, 400 \text{ MHz (δ in ppm)}\): 7.73-7.67 (2H, m, ar), 7.35-7.29 (3H, m, ar), 7.29-7.24 (2H, m, ar), 7.18-7.13 (1H, m, ar), 5.22 (1H, d broad, \(J = 6.4 \text{ Hz}, \text{NCHCH}_2\)), 4.88 (1H, dt, \(J = 47.5 \text{ Hz}, 3.5 \text{ Hz}, 2.8 \text{ Hz}, \text{CHF}\)), 3.85-3.76 (1H, m, NCH\(\text{HCH}_2\)), 3.38 (1H, dddd, \(J = 14.4 \text{ Hz}, 12.6 \text{ Hz}, 3.2 \text{ Hz}, \text{NCHCH}_2\)), 2.64-2.54 (1H, m NCH\(\text{HCH}_2\)), 2.44
N-(Tosyl)-2-(2-bromophenyl)-4-fluoropiperidines syn-14e and anti-14e.

Piperidines syn-14e and anti-14e were prepared according to the general procedure outlined for the aza-Prins reaction from 2-bromobenzaldehyde (58 µL, 0.5 mmol), N-tosyl-3-butenylamine 13 (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product syn-14e was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a colorless oil (51 mg, 25%).

NMR: $^1$H, 300 MHz (δ in ppm): 7.68-7.63 (2H, m, ar), 7.44 (1H, dd, $J= 8.0$ Hz, 1.5 Hz, ar), 7.36 (1H, dd, $J= 8.0$ Hz, 2.0 Hz, ar), 7.21-7.16 (3H, m, ar), 7.07-7.01 (1H, m, ar), 5.14 (1H, t, $J= 6.0$ Hz, NCHCH$_2$), 4.78 (1H, ddt, $J= 48.5$ Hz, 6.2 Hz, 3.8 Hz, CHF), 3.97-3.87 (1H, m, NCHHCH$_2$), 3.71 (1H, dt, $J= 13.9$ Hz, 5.1 Hz, NCHHCH$_2$), 2.41-2.29 (4H, s, NCHHCH, arCH$_3$), 2.18-2.05 (1H, m, NCHCHH), 2.01-1.82 (2H, NCH$_2$CH$_2$); $^{13}$C, 100 MHz (δ in ppm): 143.2 (Cq, ar), 140.3 (Cq, ar), 136.4 (Cq, ar), 133.1 (CH, ar), 129.5 (CH, ar), 129.4 (CH, ar), 127.3 (CH, ar), 127.3 (CH, ar), 127.2 (CH, ar), 122.0 (Cq, ar), 86.6 (CH, d, $J= 173.8$ Hz, CHF), 54.8 (CH, d, $J= 6.3$ Hz, OCHCH$_2$), 40.4 (CH$_2$, d, $J= 6.3$ Hz, OCH$_2$CH$_2$), 35.2 (CH$_2$, d, $J= 20.2$ Hz, NCHCH$_2$),

(3H, s, PhCH$_3$), 1.98 (1H, dddd, $J= 43.1$ Hz, 15.1 Hz, 6.8 Hz, 2.6 Hz, NCHCHH), 1.86-1.76 (1H, m, NCH$_2$CHH), 1.75-1.61 (1H, m, NCH$_2$CHH); $^{13}$C, 100 MHz (δ in ppm): 143.7 (Cq, ar), 142.0 (Cq, ar), 137.8 (Cq, ar), 130.0 (CH, ar), 129.9 (CH, ar), 129.8 (CH, ar), 129.7 (CH, ar), 126.9 (CH, ar), 125.3(CH, ar), 122.5 (Cq, ar), 86.0 (CH, d, $J= 172.2$ Hz, CHF), 52.9 (CH, s, OCHCH$_2$), 36.8 (CH$_2$, s, OCH$_2$CH$_2$), 32.3 (CH$_2$, d, $J= 19.3$ Hz, NCHCH$_2$), 29.2 (CH$_2$, d, $J= 21.2$ Hz, NCH$_2$CH$_2$), 21.6 (CH$_3$, ArCH$_3$); $^{19}$F, 376 MHz (δ in ppm): -181.4 to -181.9 (m); HRMS m/z: [MNa]$^+$: 434.0201, 436.0183, calculated 434.0202, 436.0181; Mp: 105-107 °C; IR: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3057, 2974, 2865, 1594, 1563, 1474, 1325, 1281, 1130, 1068, 886, 746, 710, 648.
Product **anti-14e** was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a colorless oil (49 mg, 24%).

**NMR:** $^1$H, 400 MHz ($\delta$ in ppm): 7.53-7.48 (2H, m, ar), 7.42 (1H, dd, $J$ = 8.0 Hz, 1.2 Hz, ar), 7.37 (1H, dd, $J$ = 7.8 Hz, 1.6 Hz, ar), 7.24-7.16 (3H, m, ar), 7.07 (1H, td, $J$ = 7.6 Hz, 1.6 Hz, ar), 5.21 (1H, dd, $J$ = 7.7 Hz, 5.1 Hz, NCH$_2$CH$_2$), 4.81 (1H, dtt, $J$ = 48.5 Hz, 6.4 Hz, 3.7 Hz, CHF), 3.81-3.70 (2H, m, NCH$_2$CH$_2$), 2.44-2.29 (4H, m NCHC$_H$H, arCH$_3$), 2.19-1.99 (2H, m, NCHC$_H$H, NCH$_2$CHH), 1.92-1.77 (1H, m, NCH$_2$CHH); $^{13}$C, 100 MHz ($\delta$ in ppm): 143.2 (Cq, ar), 139.4 (Cq, ar), 135.9 (Cq, ar), 133.1 (CH, ar), 129.3 (CH, ar), 128.8 (CH, ar), 128.8 (CH, ar), 127.3 (CH, ar), 127.2 (CH, ar), 122.9 (Cq, ar), 86.3 (CH, d, $J$ = 172.4 Hz, CHF), 55.8 (CH, d, $J$ = 6.7 Hz, OCHCH$_2$), 42.5 (CH$_2$, d, $J$ = 6.3 Hz, OCH$_2$CH$_2$), 35.8 (CH$_2$, d, $J$ = 20.7 Hz, NCHCH$_2$), 30.6 (CH$_2$, d, $J$ = 20.7 Hz, NCH$_2$CH$_2$), 21.5 (CH$_3$, arCH$_3$); $^{19}$F, 376 MHz ($\delta$ in ppm): -180.9 to -181.4 (m) ; HRMS m/z: [MNa]$^+$: 434.0195, 436.0186, calculated 434.0202, 436.0181; IR: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3022, 2985, 2845, 1558, 1281, 1182, 1057, 892, 760, 671.

**N-(Tosyl)-2-(4-fluorophenyl)-4-fluoropiperidines syn-14f and anti-14f.**

Piperidines **syn-14f** and **anti-14f** were prepared according to the general procedure outlined for the aza-Prins reaction from 4-fluorobenzaldehyde (53 µL, 0.5 mmol), **N-tosyl-3-butynlamine 13** (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).
Product **syn-14f** was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (78 mg, 44%, microwave: 66 mg, 38%).

**NMR:** $^1$H, 400 MHz (δ in ppm): 7.80-7.73 (2H, m, ar), 7.37-7.30 (4H, m, ar), 7.07-7.01 (2H, m, ar), 5.38 (1H, s broad, NCHCH$_2$), 4.60 (1H, dtt, $J$= 48.5 Hz, 10.9 Hz, 4.5 Hz, CHF), 4.03-3.93 (1H, m, NCHHCH$_2$), 3.03 (1H, dddd, $J$= 14.7 Hz, 12.7 Hz, 2.6 Hz, 1.3 Hz, NCHHCH$_2$), 2.66-2.56 (1H, m NCHHCH$_3$), 2.46 (3H, s, PhCH$_3$), 1.92-1.83 (1H, m, NCHHCH$_2$), 1.70 (1H, dddd, $J$= 13.4 Hz, 11.0 Hz, 8.7 Hz, 5.5 Hz, NCHHCH$_3$), 1.44 (1H, tt, $J$= 12.6 Hz, 10.3 Hz, 4.8 Hz, NCH$_2$CH$_3$); $^{13}$C, 100 MHz (δ in ppm): 162.0 (Cq, d, $J$= 249.8 Hz, ar), 143.7 (Cq, ar), 137.8 (Cq, ar), 134.5 (Cq, ar), 130.0 (CH, ar), 128.3 (CH, d, $J$= 8.0 Hz, ar), 126.9 (CH, ar), 115.7 (CH, d, $J$= 21.2 Hz, ar), 86.5 (CH, d, $J$= 173.1 Hz, CHF), 55.1 (CH, d, $J$= 13.1 Hz, OCHCH$_2$), 39.9 (CH$_2$, d, $J$= 13.5 Hz, OCH$_2$CH$_2$), 33.6 (CH$_2$, d, $J$= 19.6 Hz, NCHCH$_2$), 31.0 (CH$_2$, d, $J$= 19.6 Hz, NCH$_2$CH$_2$), 21.6 (CH$_3$, ArCH$_3$); $^{19}$F, 376 MHz (δ in ppm): -115.6 to -115.7 (m), -175.5 to -176.0 (m); HRMS m/z: [MNa]$^+$: 374.1001, calculated 374.1002; Mp: 111-113 °C; IR: $v$$_{max}$ (neat)/cm$^{-1}$: 3043, 2941, 2873, 1597, 1507, 1339, 1151, 1093, 838.

The product **anti-14f** was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a colorless oil (42 mg, 24%, microwave: 44 mg, 25%).

**NMR:** $^1$H, 400 MHz (δ in ppm): 7.75-7.67 (2H, m, ar), 7.35-7.25 (4H, m, ar), 7.02-6.91 (2H, m, ar), 5.22 (1H, d broad, $J$= 6.3 Hz, NCHCH$_2$), 4.87 (1H, dtt, $J$= 47.6 Hz, 3.4 Hz, 3.0 Hz, CHF), 3.83-3.72 (1H, m, NCHHCH$_2$), 3.37 (1H, ddd, $J$= 14.4 Hz, 12.6 Hz, 3.0 Hz, NCHHCH$_2$), 2.66-2.55 (1H, m NCHHCH$_3$), 2.44 (3H, s, PhCH$_3$), 1.96 (1H,
dddd, \( J = 43.2 \) Hz, 15.3 Hz, 6.8 Hz, 2.7 Hz, NCH\( \cdot \)H\( \cdot \)H), 1.81-1.70 (1H, m, NCH\( \cdot \)H\( \cdot \)H), 1.70-1.55 (1H, m, NCH\( \cdot \)H\( \cdot \)H); \( ^{13} \)C, 100 MHz (\( \delta \) in ppm): 161.7 (Cq, d, \( J = 245.6 \) Hz), 143.4 (Cq, ar), 137.9 (Cq, ar), 135.1 (Cq, d, \( J = 2.9 \) Hz, ar), 129.8 (CH, ar), 128.3 (CH, dd, \( J = 8.0 \) Hz, 2.5 Hz, ar), 126.9 (CH, ar), 115.0 (CH, d, \( J = 21.3 \) Hz, ar), 86.1 (CH, d, \( J = 172.4 \) Hz, CHF), 52.9 (CH, s, OCH\( \cdot \)CH\( \cdot \)H), 36.6 (CH\( \cdot \), OCH\( \cdot \)CH\( \cdot \)H), 32.0 (CH\( \cdot \), d, \( J = 19.3 \) Hz, NCH\( \cdot \)H\( \cdot \)H), 29.1 (CH\( \cdot \), d, \( J = 21.1 \) Hz, NCH\( \cdot \)H\( \cdot \)H), 21.5 (CH\( \cdot \), ArCH\( \cdot \)); \( ^{19} \)F, 376 MHz (\( \delta \) in ppm): -116.7 to 116.8 (m), -180.8 to -181.3 (m); HRMS m/z: \([\text{MNa}]^+\) 374.1001, calculated 374.1002; \( \text{Mp} \): 127-129 °C; IR: \( \nu_{max} \) (neat)/cm\(^{-1}\): 3043, 2920, 2873, 1597, 1508, 1328, 1152, 1071, 1032, 882.

\( N\)\((\text{Tosyl})\)-2-(3-fluorophenyl)-4-fluoropiperidines \( \text{syn-14g} \) and \( \text{anti-14g} \).

Piperidines \( \text{syn-14g} \) and \( \text{anti-14g} \) were prepared according to the general procedure outlined for the aza-Prins reaction from 3-fluorobenzaldehyde (55 µL, 0.5 mmol), \( N\)-tosyl-3-butenylamine \( 13 \) (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product \( \text{syn-14g} \) was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (78 mg, 44%).

NMR: \( ^1 \)H, 300 MHz (\( \delta \) in ppm): 7.81-7.74 (2H, m, ar), 7.39-7.32 (2H, m, ar), 7.30-7.22 (1H, m, ar), 7.18-7.11 (1H, m, ar), 7.09-7.01 (1H, m, ar), 7.01-6.92 (1H, m, ar), 5.41 (1H, s broad, NCH\( \cdot \)H\( \cdot \)H), 4.57 (1H, dtt, \( J = 48.5 \) Hz, 10.9 Hz, 4.5 Hz, CHF), 4.07-3.94 (1H, m, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 4.57 (1H, dtt, \( J = 48.5 \) Hz, 10.9 Hz, 4.5 Hz, CHF), 4.07-3.94 (1H, m, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 4.57 (1H, dtt, \( J = 48.5 \) Hz, 10.9 Hz, 4.5 Hz, CHF), 4.07-3.94 (1H, m, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 3.03 (1H, dddd, \( J = 14.9 \) Hz, 12.8 Hz, 2.9 Hz, 1.2 Hz, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 2.67-2.55 (1H, m NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 2.46 (3H, s, PhCH\( \cdot \)), 1.94-1.82 (1H, m, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 1.72 (1H, dddd, \( J = 13.4 \) Hz, 11.2 Hz, 8.6 Hz, 5.7 Hz, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H), 1.45 (1H, ttd, \( J = 12.7 \) Hz, 10.3 Hz, 4.9 Hz, NCH\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H\( \cdot \)H); \( ^{13} \)C, 75 MHz (\( \delta \) in ppm): 163.2 (Cq, d, \( J = 247.7 \) Hz, CHF), 143.7 (Cq, ar), 140.7 (Cq, d, \( J = 7.7 \) Hz, ar), 137.6 (Cq, ar), 130.4 (CH, d, \( J = 8.7 \) Hz, ar), 130.0 (CH, ar), 129.5 (CH, d, \( J = 8.7 \) Hz, ar), 126.9 (CH, ar), 114.4 (CH, t, \( J = 21.3 \) Hz, ar), 113.6 (CH, d, \( J = 22.7 \) Hz, ar), 86.4 (CH, d, \( J = \)
174.9 Hz, CHF), 55.2 (CH, d, J= 12.5 Hz, OCHCH2), 40.0 (CH2, d, J= 11.7 Hz, OCH2CH2), 33.6 (CH2, d, J= 20.5 Hz, NCHCH2), 30.9 (CH2, d, J= 19.0 Hz, NCH2CH2), 21.5 (CH3, arCH3); 19F, 376 MHz (δ in ppm): -112.0 to -112.1 (m), -175.0 - -175.3 (m); HRMS m/z: [MNa]+: 374.1002, calculated 374.1002; Mp: 101-103 °C; IR: v_max (neat)/cm⁻¹: 3065, 2944, 2877, 1614, 1590, 1488, 1341, 1160, 1096, 1019, 889, 736, 674.

Product anti-14g was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a white solid (39 mg, 22%).

**NMR: ¹H, 300 MHz (δ in ppm):** 7.70-7.69 (2H, m, ar), 7.35-7.28 (2H, m, ar), 7.24 (1H, dd, J= 8.0 Hz, 6.0 Hz, ar), 7.14-7.08 (1H, m, ar), 7.04-6.96 (1H, m, ar), 6.95-6.85 (1H, m, ar)5.26 (1H, d broad, J= 6.6 Hz, NCHCH2), 4.88 (1H, dtt, J= 47.3 Hz, 3.2 Hz, 2.8 Hz, CHF), 3.86-3.75 (1H, m, NCHCH2), 3.38 (1H, ddd, J= 14.4 Hz, 12.6 Hz, 3.3 Hz, NCHCH2), 2.68-2.55 (1H, m, NCHCH), 2.44- (3H, s, arCH3), 1.98 (1H, ddd, d, J= 43.6 Hz, 15.2 Hz, 6.9 Hz, 2.6 Hz, NCHCH), 1.82-1.72 (1H, m, NCH2CH), 1.71-1.53 (1H, m, NCH2CH); ¹³C, 75 MHz (δ in ppm): 162.8 (Cq, d, J= 246.2 Hz, CHF), 143.5 (Cq, ar), 142.3 (Cq, d, J= 6.7 Hz, ar), 137.8 (Cq, ar), 129.8 (CH, ar), 129.6 (CH, d, J= 8.3 Hz, ar), 126.9 (CH, ar), 122.1 (CH, t, J= 2.3 Hz, ar), 113.7 (CH, d, J= 21.0 Hz, ar), 113.6 (CH, dd, J= 2.9 Hz, 2.4 Hz, ar), 85.9 (CH, d, J= 172.2 Hz, CHF), 52.8 (CH, d, J= 6.7 Hz, OCHCH2), 36.6 (CH2, OCHCH2), 32.0 (CH2, d, J= 20.4 Hz, NCHCH2), 29.0 (CH2, d, J= 21.0 Hz, NCH2CH2), 21.5 (CH3, arCH3); 19F, 376 MHz (δ in ppm): -113.4 to 113.5 (m), -186.0 to -186.5 (m); HRMS m/z: [MNa]+: 374.1013, calculated 374.1002; Mp: 111-113 °C; IR: v_max (neat)/cm⁻¹: 2974, 2913, 2845, 1611, 1588, 1348, 1269, 1186, 1127, 1068, 903, 732, 654.
N-(Tosyl)-2-(4-methoxyphenyl)-4-fluoropiperidines \(\text{syn-14h}\) and \(\text{anti-14h}\).

Piperidines \(\text{syn-14h}\) and \(\text{anti-14h}\) were prepared according to the general procedure outlined for the aza-Prins reaction from 4-methoxybenzaldehyde (60 µL, 0.5 mmol), \(N\)-tosyl-3-butynylamine 13 (112 mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol).

Product \(\text{syn-14h}\) was isolated after purification on silica gel (hexane/diethyl ether, 7/3) as a pale yellow viscous oil (26 mg, 14%).

**NMR: \(^1\text{H}, 400 \text{ MHz (δ in ppm)}\):** 7.80-7.74 (2H, m, ar), 7.37-7.31 (2H, m, ar), 7.30-7.23 (2H, m, ar), 6.90-6.85 (2H, m, ar), 5.38 (1H, s broad, NCH\(_2\)CH\(_2\)), 4.64 (1H, dtt, \(J = 48.7 \text{ Hz}, 10.9 \text{ Hz}, 4.4 \text{ Hz}, \text{CHF}\)), 4.02-3.91 (1H, m, NCH\(_2\)CH\(_2\)), 3.81 (3H, s, OCH\(_3\)), 3.02 (1H, dddd, \(J = 14.9 \text{ Hz}, 12.7 \text{ Hz}, 2.6 \text{ Hz}, 1.0 \text{ Hz}, \text{NCH}\(_2\)CH\(_2\)), 2.67-2.58 (1H, m NCHCH\(_2\)), 2.46 (3H, s, arCH\(_3\)), 1.91-1.81 (1H, m NCHCH\(_2\)), 1.68 (1H, dddd, \(J = 13.2 \text{ Hz}, 11.2 \text{ Hz}, 9.0 \text{ Hz}, 5.7 \text{ Hz}, \text{NCHCH}\(_2\)), 1.43 (1H, ttd, \(J = 12.5 \text{ Hz}, 10.5 \text{ Hz}, 4.9 \text{ Hz}, \text{NCH}_2\text{CHHH}\)); \(^{13}\text{C}, 100 \text{ MHz (δ in ppm)}\): 158.8 (Cq, ar), 143.5 (Cq, ar), 138.0 (Cq, ar), 129.9 (CH, ar), 129.5 (Cq, ar), 127.7 (CH, ar), 126.9 (CH, ar), 114.2 (CH, ar), 86.8 (CH, d, \(J = 176.8 \text{ Hz, CHF}\)), 55.3 (CH\(_3\), OCH\(_3\)), 55.1 (CH, d, \(J = 12.9 \text{ Hz, OCHCH}_2\)), 39.8 (CH\(_2\), d, \(J = 12.5 \text{ Hz, OCH}_2\text{CH}_2\)), 33.5 (CH\(_2\), d, \(J = 19.6 \text{ Hz, NCHCH}_2\)), 31.1 (CH\(_2\), d, \(J = 18.3 \text{ Hz, NCH}_2\text{CH}_2\)), 21.5 (CH\(_3\), arCH\(_3\)); \(^{19}\text{F, 376 MHz (δ in ppm)}\): -175.5 to -175.8 (m); \(\text{HRMS m/z: [MNa]}^+\): 386.1201, calculated 386.1202; \(\text{IR of the mixture of diastereoisomers: } \nu_{\max (\text{neat})/\text{cm}^{-1}}:\) 2974, 2918, 2845, 1510, 1348, 1303, 1180, 1144, 1012, 881.
Product **anti-14h** was isolated as a mixture of diastereoisomers (syn/anti, 1/2.2) after purification on silica gel (hexane/diethyl ether, 7/3) as a pale yellow viscous oil (13 mg, 7%).

**NMR: ¹H, 400 MHz (δ in ppm):** 7.74-7.67 (2H, m, ar), 7.30-7.21 (4H, m, ar), 6.84-6.77 (2H, m, ar), 5.19 (1H, d broad, J= 6.2 Hz, NCHCH₂), 4.87 (1H, dtt, J= 47.8 Hz, 3.6 Hz, 2.7 Hz, CHF), 3.79 (3H, s, OCH₃), 3.77-3.70 (1H, m, NCH₂HCH₂), 3.40 (1H, ddd, J= 14.5 Hz, 12.2 Hz, 3.4 Hz, NCH₃HCH₂), 2.66-2.55 (1H, m NCH₂H), 2.43 (3H, s, arCH₃), 1.97 (1H, dddd, J= 42.6 Hz, 15.2 Hz, 6.8 Hz, 2.8 Hz, NCH₂CH), 1.82-1.74 (1H, m, NCH₂CH), 1.70-1.64 (1H, m, NCH₂CH); ¹³C, 100 MHz (δ in ppm): 148.6 (Cq, ar), 143.3 (Cq, ar), 138.0 (Cq, ar), 131.3 (Cq, ar), 129.7 (CH, ar), 127.9 (CH, ar), 127.0 (CH, ar), 113.5 (CH, ar), 86.3 (CH, d, J= 173.7 Hz, CHF), 55.2 (CH₃, OCH₃), 53.2 (CH, s, OCH₂CH₂), 36.7 (CH₂, OCH₂CH₂), 32.1 (CH₂, d, J= 19.9 Hz, NCH₂CH), 29.1 (CH₂, d, J= 19.6 Hz, NCH₂CH), 21.5 (CH₃, arCH₃); ¹⁹F, 376 MHz (δ in ppm): -180.1 to -180.6 (m); HRMS m/z: [MNa]+: 386.1208, calculated 386.1202; IR of the mixture of diastereoisomers: νₘₐₓ (neat)/cm⁻¹: 2952, 2918, 2845, 1608, 1591, 1337, 1303, 1146, 1090, 833.

**N-(Tosyl)-2-methyl-4-fluoropiperidines syn-14j and anti-14j.**

Piperidines **syn-14j** and **anti-14j** were prepared according to the general procedure outlined for the aza-Prins reaction from acetaldehyde (28 µL, 0.5 mmol), N-tosyl-3-butynlamine 13 (112mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol) to give the title compounds (99 mg, 73%, mixture ratio syn/anti 1.2/1, microwave: 104 mg, 77%, mixture ratio syn/anti 1.2/1).
Analysis from the mixture of diastereoisomers *syn-14j* and *anti-14j*:

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.75-7.66 (2H, m, ar), 7.34-7.24 (2H, m, ar), 4.77 (1H, dtt, $J=48.5$ Hz, 10.9 Hz, 4.7 Hz, CHF), 4.42-4.29 (1H, m, NCHCH$_2$), 3.94-3.79 (1H, m, NCHHCH$_2$), 3.10 (1H, ddd, $J=13.9$ Hz, 12.7 Hz, 2.7 Hz, 1.2 Hz, NCHHCH$_2$), 2.42 (3H, s, arCH$_3$), 2.08-1.96 (1H, m NCH$_2$CHH), 1.95-1.45 (3H, m, NCH$_2$CHH, NCHCH$_2$), 1.12, (3H, d, $J=7.1$ Hz, CHCH$_3$); $^{13}$C, 75 MHz (δ in ppm): 143.3 (Cq, ar), 137.6 (Cq, ar), 129.7 (CH, ar), 126.8 (CH, ar), 86.7 (CH, d, $J=173.0$ Hz, CHF), 49.0 (CH, d, $J=12.8$ Hz, OCHCH$_2$), 38.6 (CH$_2$, d, $J=12.5$ Hz, OCH$_2$CH$_2$), 36.7 (CH$_2$, d, $J=18.6$ Hz, NCHCH$_2$), 31.7 (CH$_2$, d, $J=19.1$ Hz, NCH$_2$CH$_2$), 21.4 (CH$_3$, arCH$_3$), 17.0 (CH$_3$, CHCH$_3$); $^{19}$F, 282 MHz (δ in ppm): 179.8 to 180.4 (m); HRMS m/z: [MNa]$^+$: 294.0942, calculated 294.0940; IR from the mixture of diastereoisomers: $v_{max}$ (neat)/cm$^{-1}$: 3058, 3030, 2941, 2873, 1594, 1348, 1331, 1160, 1001, 813.

Analysis from the mixture of diastereoisomers *syn-14j* and *anti-14j*:

**NMR:** $^1$H, 300 MHz (δ in ppm): 7.75-7.66 (2H, m, ar), 7.34-7.24 (2H, m, ar), 4.88 (1H, dtt, $J=47.3$ Hz, 3.1 Hz, 2.9 Hz, CHF), 4.29-4.16 (1H, m, NCHCH$_2$), 3.70 (1H, dd broad, $J=13.7$ Hz; 5.3 Hz, NCHHCH$_2$), 3.31 (1H, td, $J=13.1$ Hz, 2.7 Hz, NCHHCH$_2$), 2.41 (3H, s, arCH$_3$), 1.95-1.45 (4H, m, NCH$_2$CH$_2$, NCH$_2$CH$_2$), 1.17 (3H, dd, $J=7.2$ Hz, 1.8 Hz, CHCH$_3$); $^{13}$C, 75 MHz (δ in ppm): 143.1 (Cq, ar), 138.0 (Cq, ar), 129.6 (CH, ar), 126.8 (CH, ar), 86.8 (CH, d, $J=170.3$ Hz, CHF), 46.9 (CH, OCHCH$_2$), 34.7 (CH$_2$, OCH$_2$CH$_2$), 34.6 (CH$_2$, d, $J=18.9$ Hz, NCHCH$_2$), 29.8 (CH$_2$, d, $J=21.4$ Hz, NCH$_2$CH$_2$), 21.4 (CH$_3$, arCH$_3$), 17.9 (CH$_3$ CHCH$_3$); $^{19}$F, 282 MHz (δ in ppm): -179.8 to -180.4 (m); HRMS m/z: [MNa]$^+$: 294.0942, calculated 294.0940; IR from a
mixture of diastereoisomers: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 3058, 3030, 2941, 2873, 1594, 1348, 1331, 1160, 1001, 813.

*N*-Tosyl-2-isobutyl-4-fluoropiperidines *syn*-14k and *anti*-14k.

Piperidines *syn*-14k and *anti*-14k were prepared according to the general procedure outlined for the aza-Prins reaction from isobutyraldehyde (45 µL, 0.5 mmol), *N*-tosyl-3-butylethylamine 13 (112 mg, 0.5 mmol) and boron trifluoride (65 µL, 0.5 mmol). The product was isolated as a mixture of diastereoisomers after purification on silica gel (hexane/diethyl ether, 7/3) as a pale yellow oil (111 mg, 82%, mixture ratio *syn/*anti 1/1, microwave: 112 mg, 83%, mixture ratio *syn/*anti 1.2/1).

![syn-14k](attachment:structure.png)

Analysis from the mixture of diastereoisomers *syn*-14k and *anti*-14k:

**NMR**: $^1$H, 300 MHz ($\delta$ in ppm): 7.78-7.71 (2H, m, ar), 7.34-7.28 (2H, m, ar), 4.67 (1H, dtt, $J$ = 48.8 Hz, 11.3 Hz, 4.6 Hz, CHF), 4.04-3.92 (1H, m, NCHCH$_2$), 3.80-3.71 (1H, m, NCHCH$_2$), 2.99 (1H, dddd, $J$ = 15.3 Hz, 13.6 Hz, 2.7 Hz, 1.3 Hz, NCHCH$_2$), 2.44 (3H, s, arCH$_3$), 2.21-2.10 (1H, m NCHCHH), 1.93-1.75 (2H, m, NCH$_2$CHH, CH(CH$_3$)$_2$), 1.37-1.22 (2H, m, NCH$_2$CHH, NCHCHH), 0.95 (3H, d, $J$ = 6.8 Hz, CHCH$_3$), 0.81 (3H, d, $J$ = 6.77 Hz, CHCH$_3$); $^{13}$C, 75 MHz ($\delta$ in ppm): 143.3 (Cq, ar), 138.4 (Cq, ar), 129.8 (CH, ar), 126.9 (CH, ar), 86.9 (CH, d, $J$ = 172.2 Hz, CHF), 60.1 (CH, d, $J$ = 12.3 Hz, OCHCH$_2$), 39.1 (CH$_2$, d, $J$ = 12.5 Hz, OCH$_2$CH$_2$), 31.6 (CH$_2$, d, $J$ = 17.7 Hz, NCHCH$_2$), 30.8 (CH$_2$, d, $J$ = 19.2 Hz, NCH$_2$CH$_2$), 27.7 (CH, CH(CH$_3$)$_2$), 21.5 (CH$_3$, CHCH$_3$), 20.2 (CH$_3$, CHCH$_3$), 19.9 (CH$_3$, arCH$_3$); $^{19}$F, 282 MHz ($\delta$ in ppm): -174.4 to -174.9 (m); HRMS m/z: [MNa]$^+$: 322.1256, calculated 322.1253; IR from the mixture of diastereoisomers: $\nu_{\text{max}}$ (neat)/cm$^{-1}$: 2969, 2918, 2868, 1454, 1337, 1303, 1208, 1149, 1090, 818.
Analysis from the mixture of diastereoisomers *syn-14k* and *anti-14k*:

**NMR: **$^1$H, 300 MHz (δ in ppm): 7.77-7.70 (2H, m, ar), 7.35-7.28 (2H, m, ar), 4.79 (1H, dtt, $J$= 48.3 Hz, 2.9 Hz, 2.6 Hz, CHF), 3.80-3.67 (1H, NCHCH$_2$), 3.54 (1H, dd, $J$= 10.9 Hz, 6.2 Hz, NCHCH$_2$), 3.29 (1H, ddd, $J$= 15.0 Hz, 13.4 Hz, 3.0 Hz, NCHHCH$_2$), 2.41 (3H, s, arCH$_3$), 2.29-2.08 (2H, m, NCHCH, CH(CH$_3$)$_2$), 1.74-1.34 (3H, m, NCH$_2$CHH, NCH$_2$CHH, NCHCHH), 0.94 (3H, d, $J$= 6.5 Hz, CHCH$_3$), 0.85 (3H, d, $J$= 6.6 Hz, CHCH$_3$); $^{13}$C, 75 MHz (δ in ppm): 143.0 (Cq, ar), 138.6 (Cq, ar), 129.6 (CH, ar), 126.9 (CH, ar), 87.2 (CH, d, $J$= 170.0 Hz, CHF), 57.9 (CH, OCHCH$_2$), 35.5 (CH$_2$, OCH$_2$CH$_2$), 29.1 (CH$_2$, d, $J$= 19.8 Hz, NCHCH$_2$), 28.9 (CH, CH(CH$_3$)$_2$), 28.7 (CH$_2$, d, $J$= 20.7 Hz, NCH$_2$CH$_2$), 21.5 (CH$_3$, arCH$_3$), 20.7 (CH$_3$ CHCH$_3$), 20.1 (CH$_3$ CHCH$_3$); $^{19}$F, 282 MHz (δ in ppm): -181.4 to -182.2 (m); **HRMS m/z: **[MNa]+$^+$: 322.1256, calculated 322.1253; **IR: **$\nu_{\text{max}}$ (neat)/cm$^{-1}$: 2969, 2918, 2868, 1454, 1337, 1303, 1208, 1149, 1090, 818.