Supplementary Information

(2-Fluoroallyl)boronates: new reagents for diastereoselective 2-fluoroallylboration of aldehydes

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1. General information

All reagents were purchased from Acros, Aldrich or Alfa Aesar and used without further purification. B_2pin_2 of 98% quality was ordered from Alfa Aesar. $[(2\text{-MeAll})PdCl]_2$ was prepared by bubbling of dry CO though a solution of $PdCl_2$, LiCl and methallyl chloride in $MeOH/H_2O$.[1] Benzaldehyde, octanal and isovaleraldehyde were distilled prior to use, other aldehydes were used without purification. CH_2Cl_2, DCE and MeCN were distilled over P_2O_5 under argon atmosphere, stored over Linde type molecular sieves (3A for MeCN, 4A for CH_2Cl_2 and DCE) and degassed prior to use. THF was distilled over $LiAlH_4$, stored over 4A Linde type molecular sieves and degassed prior to use. Silica gel 60 (40–63 μm, Merck) was used for column chromatography. TLC analysis was made on standard Merck plates with F_{254}-inducator using UV or $KMnO_4$ solution for visualization. GC analysis was performed on Chromatec Crystal 2000M gas chromatographer (capillary column Macherey-Nagel OPTIMA-1, 30 m x 0.25 mm, 100% polydimethylsiloxane (0.25 μm), carrier gas – He, detector – FID). ^1H and ^{13}C NMR were recorded on Bruker AC-200 (200.1 and 50.3 MHz, respectively), Bruker AVANCE II 300 (300.1 and 75.4 MHz, respectively) or Bruker AMX-400 (400.1 MHz and 100.6 MHz, respectively) in $CDCl_3$ containing TMS as an internal standard or in DMSO-d_6. ^{19}F NMR were recorded on Bruker AC-200 (188.3 MHz) or Bruker AVANCE II 300 (282.4 MHz) in $CDCl_3$. Chemical shifts in $CDCl_3$ are reported relative to internal C_6F_6 (δ = -162.2 ppm). ^1H, ^{13}C and ^{19}F homo- and heteronuclear correlations were recorded on Bruker AVANCE II 300. Quantitative ^{19}F and $^{19}F\{^1H\}$-NMR analyses were performed on Bruker AC-200 (188.3 MHz) on (^1H,^{19}F)-selective probe using 30° pulse, 3.0 sec relaxation delay and 16 scans, for $^{19}F\{^1H\}$ experiments inversed gate decoupling was used. GC/MS analysis was performed on Chromatec Crystal 5000.1 gas chromatographer (capillary column Macherey-Nagel OPTIMA-1, 30 m x 0.25 mm, 100% polydimethylsiloxane (0.25 μm), carrier gas – He) equipped with Thermo DSQ II mass-detector (EI, 70 eV, 200°C). Melting points were determined on Stuart SMP10 and reported uncorrected. HRMS were recorded on Bruker micrOTOF equipment using electro-spray ionization (ESI). Elemental analyses were made in Laboratory of microanalysis IOC RAS on Perkin-Elmer Series II 2400 CHN Analyzer.

2. Synthesis of 2-fluoroallyl chlorides

General procedure (cyclopropanation)

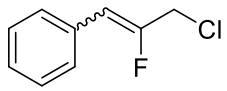
1-Phenyl- and 1-(4-fluorophenyl)-2-chloro-2-fluorocyclopropanes, 7-chloro-7-fluoro-bicyclo[4.1.0]heptane, 1,1-dimethyl- and *trans*-1,2-dimethyl-3-chloro-3-fluorocyclopropanes were obtained by the previously published general procedure [2,3]:

To a well-stirred by an overhead stirrer (> 1000 rpm) mixture of alkene (1 equiv.), $CHCl_2F$ (2–5 equiv.), TEBAC (0.02 equiv.) and CH_2Cl_2 (0.25 mL per 1 mmol of alkene) cooled by ice bath, a saturated solution of KOH (4–10 equiv.) was added dropwise. The reaction mixture was stirred further for 5–10 hours, while the reaction progress was controlled by GC. Then, it was diluted with water and extracted with CH_2Cl_2. In cases of slow phase separation, a mixture was filtered through a short pad of silica gel. Combined organic layers were dried over $CaCl_2$. The solvent was distilled off and the residue was redistilled under reduced pressure.

General procedure (isomerization)

A mixture of a cyclopropane (up to 0.5 mol), CuCl (0.20 equiv.) and abs. MeCN (0.25–1 mL/mmol) was heated at 100°C in a sealed screw-cap vial (for small scale experiments) or in a glass liner in a stainless steel autoclave (for large scale experiments) for 5–72 hours. The reaction progress was monitored by GC. After the reaction complete, it was diluted with Et_2O and ca. 1 M HCl. The organic layer was washed with water and brine and then dried over $MgSO_4$. Removing of a solvent (rotary evaporator or atmospheric pressure distillation) gave a mixture of isomeric 2-fluoroallyl chlorides which was purified by column chromatography on silica (for small scale) or fractionated under reduced pressure (for large scale).

(*Z*,*E*)-2-Fluorocinnamyl chloride (1a) (lit. [2,3])



Obtained by the general procedure from 85.2 g (0.50 mol) of 2-chloro-2-fluoro-1-phenyl-cyclopropane **S1a**, 4.96 g (0.050 mol) of CuCl and 125 mL after heating at 120°C for 12 hours. After aqueous work-up, 83.4 g of crude *Z*,*E*-**1a** as a light brown oil were obtained (98%, *Z*/*E* = 88/12). This material was used directly without additional purification.

Otherwise, it can be redistilled under reduced pressure on a short Vigreux column (100 mm) to give 63.0 g of *Z*,*E*-**1a** (*Z*/*E* = 91/9) as a colorless liquid (74% yield, 78–80°C / 5 mmHg).

A sample of *E*-**1a** with *Z*/*E* ratio of 25/75 used in Scheme 2 of the Main Article was obtained as one of the fractions during attempts to isolate pure (*Z*)-isomer from above mixture by fractional distillation on a 200 mm Vigreux column.

NMR data are fully consistent with previously published [3].

(*Z*)-Isomer *Z*-**1a**

^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 4.29 (d, 2H, CH_2Cl, *J* = 18.7 Hz), 5.92 (d, 1H, =CH-, *J* = 36.4 Hz), 7.25-7.75 (m, 5H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** -109.5 (dt, *J* = 36.4, 18.7 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 43.2 (d, CH_2Cl, *J* = 31.6 Hz), 110.6 (d, -CH=, *J* = 7.7 Hz), 128.2 (d, CH-arom., *J* = 2.3 Hz), 128.7 (s, CH-arom.), 129.0 (d, CH-arom., *J* = 7.5 Hz), 132.2 (d, C-arom., *J* = 3.5 Hz), 154.4 (d, -CF=, *J* = 264 Hz). **MS (EI) *m*/*z*** 170/172 ($[M]^+$, 40/14), 135 ($[M-Cl]^+$, 100), 133 (31), 115 (55).

(*E*)-Isomer *E*-**1a**

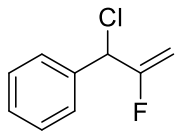
^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 4.38 (d, 2H, CH_2Cl, *J* = 21.8 Hz), 6.58 (d, 1H, =CH-, *J* = 18.7 Hz), 7.25-7.75 (m, 5H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** -105.1 (td, *J* = 21.8, 18.7 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 39.3 (d, CH_2Cl, *J* = 31.6 Hz), 113.1 (d, -CH=, *J* = 25.8 Hz), 128.0 (s, CH-arom.), 128.5 (d, CH-arom., *J* = 2.7 Hz), 128.9 (s, CH-arom.), 132.6 (s, C-arom.), 156.2 (d, -CF=, *J* = 252 Hz). **MS (EI) *m*/*z*** 170/172 ($[M]^+$, 41/14), 135 ($[M-Cl]^+$, 100), 133 (34), 115 (58).

(*Z*)-2-Fluorocinnamyl chloride (*Z*-1a)

For preparation of isomerically pure *Z*-**1a** following procedure was used:

115.8 g of *Z*,*E*-**1a** (*Z*/*E* = 91/9), prepared as above, were kept overnight in a freezer (-18°C). The solids formed were collected, affording 96.3 g of *Z*,*E*-**1a** with *Z*/*E* = 94/6. This procedure was repeated once again affording 88.1 g of *Z*,*E*-**1a** with *Z*/*E* = 96/4. The residues of (*E*)-isomer were distilled off on a Vigreux column (200 mm) equipped with a liquid dividing distillation head. Totally, 27.5 g of *Z*,*E*-**1a** with *Z*/*E* = 88/12 distilled at 94–97°C / 6 mmHg were collected. Next, a liquid dividing head was removed, and the residue was distilled on a Vigreux column (100 mm) affording 53.9 g of pure *Z*-**1a** (*Z*/*E* > 99.9, bp 103–104°C / 7 mmHg, a GC ratio between peaks of (*Z*)- and (*E*)-isomers was 99.94/0.06).

2-Fluoro-1-phenylallyl chloride (1'a)



Gas phase pyrolysis in a flow reactor was used for isomerization of 2-chloro-2-fluoro-1-phenylcyclopropane **S1a**.

The reactor — a quartz tube (length = 300 mm, i.d. = 15 mm) filled with pieces of quartz. Heated by a one-zone vertical tube furnace (length 250mm). The temperature was measured at the center of the reactor and was set to 515°C. Constant stream of N_2 — 4 L/h, was used. A solution of 37.4 g of **S1a** in 110 mL of CH_2Cl_2 was added by a pistol pump with the rate of 0.40 mL/min. The resulting black solution was concentrated on a rotary evaporator affording 21.6 g of a mixture that contained based on GC: 2% of **S1a** (*syn/anti* = 1/1), 67% of *Z*-**1a**, 26% of *E*-**1a** and 5% of **1'a**. It was subjected to a distillation on a 200 mm column packed with metal springs and equipped with heating mantle and liquid dividing distillation head (a reflux ratio was maintained at 20–30 : 1). The distillation was carried out at 3 mmHg. Metal springs used are known to give large pressure drop in a column. So, the vacuum in the distillation flask should be low. Therefore, high temperatures in an oil bath (160°C) and the column (80°C) were required. Totally, 7.1 g of a distillate with bp 59–61°C were collected, that contained: 4% of *Z*-**1a**, 10% of *E*-**1a** and 86% of **1'a**. The quantity of **1'a** formed clearly indicated that reversible isomerization between *Z,E*-**1a** and **1'a** had occurred during the distillation, that was induced by metal packing. Isomer **1'a** has the lowest boiling point and therefore was distilled out.

Obtained mixture was redistilled on a spiral-tube column (150 mm) collecting the fraction with bp 59.5–60.5°C at 5 mmHg. 1.51 g of **1'a** with NMR purity 97% were obtained (other 3% are *Z/E*-**1a** in the ratio of 2/1).

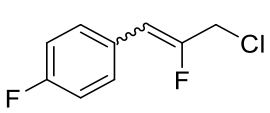
It should be noted that GC is not appropriate method to control **1'a** purity due to partial isomerization of **1'a** into more stable *Z/E*-**1a** in an injector of a gas chromatographer. However, decreasing of an injector temperature to 200°C and using of 1 μL of a dilute sample of **1'a** (ca. 1 mg/mL) allowed to obtain the GC ratio **1'a**/*Z*-**1a**/*E*-**1a** of 96/2/2.

^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 4.81 (dd, 1H, $=CH_2$ (*trans*- to F), *J* = 46.6, 3.6 Hz), 4.97 (dd, 1H, $=CH_2$ (*cis*- to F), *J* = 16.0, 3.6 Hz), 5.58 (d, 1H, CHCl, *J* = 13.3 Hz), 7.25–7.75 (m, 5H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –103.8 (ddd, *J* = 46.6, 16.0, 13.3 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 59.0 (d, CHCl, *J* = 31.6 Hz), 94.2 (d, $=CH_2$, *J* = 18.8 Hz), 127.9 (s, CH-arom.), 128.8 (s, CH-arom.), 129.1 (s, CH-arom.), 136.8 (s, CH-arom.), 162.7 (d, –CF=, *J* = 260 Hz). **MS (EI) *m/z*** 170/172 ([M^+], 15/5), 135 ([M^+–Cl], 100), 133 (32), 115 (58).

2-Fluoro-3-(4-fluorophenyl)allyl chloride (1b)

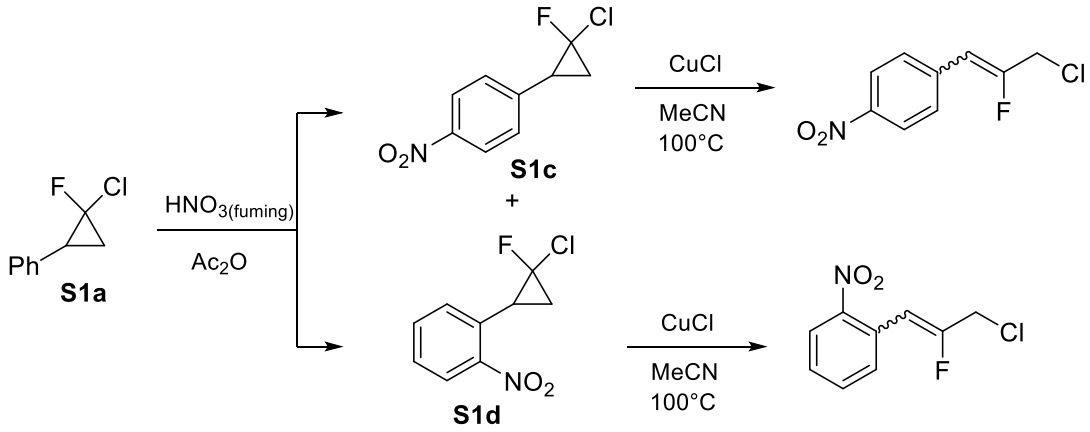
According to the general procedure, a mixture of 750 mg (4.0 mmol) of **S1b**, 80 mg (0.80 mmol) of CuCl and 2.0 mL of MeCN was heated at 80°C for 72 hours. After isolation 731 mg of

1b were obtained (*Z*/*E* = 79/21, 97% yield). NMR data are fully consistent with previously published [3].



^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 4.21 (d, 2H, CH_2Cl, *Z*-**1b**, *J* = 18.6 Hz), 4.22 (d, 2H, CH_2Cl, *E*-**1b**, *J* = 18.6 Hz), 5.81 (d, 1H, CH=, *Z*-**1b**, *J* = 36.4 Hz), 6.41 (d, 1H, CH=, *E*-**1b**, *J* = 18.1 Hz), 6.95–7.15 (m, 2H, arom.), 7.40–7.55 (m, 2H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –105.5 (td, 1F, CF=, *E*-**1b**, *J* = 18.6, 18.1 Hz), –110.7 (dt, 1F, CF=, *Z*-**1b**, *J* = 36.4, 18.6 Hz), –112.4 (m, 1F, *Z*-**1b**, arom.), –113.2 (m, *E*-**1b**, 1F, arom.). **MS (EI) *m*/*z*** 188/190 ([M^+], 28/10), 153 ([M^+–Cl], 100), 151 (28), 133 (70).

2-Fluoro-3-(4-nitrophenyl)allyl chloride (1c) and
2-Fluoro-3-(2-nitrophenyl)allyl chloride (1d)



To Ac_2O (16 mL) with stirring at –60°C under stream of argon, fuming HNO_3 (4.0 mL, 97 mmol) and 2-chloro-2-fluoro-1-phenylcyclopropane **S1a** (3.21 g, 18.8 mmol) were added dropwise. The reaction mixture was slowly warmed to –20°C over 30 min, and stirred at this temperature for 3 hours, and after that poured dropwise into 100 mL of hot water (50–60°C) under vigorous stirring. Resulting mixture was extracted with Et_2O; ethereal layers were washed with satd. $NaHCO_3$ and brine, dried over $MgSO_4$, concentrated on a rotary evaporator affording 3.82 g of almost pure mixture of *ortho*- and *para*-isomers **S1c** and **S1d** as a yellow oil (**S1c**/**S1d** = 57/43). Isomers were separated by column chromatography on silica gel (40–60 μm, 100 : 1, *n*-hexane/EtOAc = 5/1):

para-Isomer **S1c** — 2.77 g of a yellowish oil (68% yield, *syn*/*anti* = 59/41)

ortho-Isomer **S1d** — 1.02 g of a yellowish oil (25% yield, *syn*/*anti* = 54/46)

para-Isomer **S1c**

^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 1.73 (m, 1H, *syn*-**S1c**), 1.88–2.01 (m, 2H, *anti*-**S1c**), 2.14 (ddd, 1H, *syn*-**S1c**, *J* = 15.4, 11.4, 8.0 Hz), 2.79 (m, 1H, *anti*-**S1c**), 2.97 (ddd, 1H, *syn*-**S1c**, *J* =

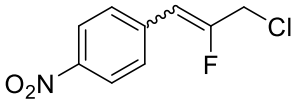
16.3, 11.4, 8.6 Hz), 7.34–7.45 (m, 2H, arom.), 8.15–8.26 (m, 2H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –128.7 (td, *syn*-**S1c**, *J* = 15.8, 6.1 Hz), –148.9 (m, *anti*-**S1c**).

ortho-Isomer **S1d**

^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 1.63 (ddd, 1H, *syn*-**S1d**, *J* = 8.9, 7.9, 5.4 Hz), 1.72–1.98 (m, 2H, *anti*-**S1d**), 2.14 (ddd, 1H, *syn*-**S1d**, *J* = 14.6, 11.2, 7.9 Hz), 3.12–3.23 (m, 1H, *anti*-**S1d**), 3.28–3.50 (m, 1H, *syn*-**S1d**), 7.29–7.56 (m, 2H, arom.), 7.56–7.70 (m, 1H, arom.), 7.99–8.16 (m, 1H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –131.4 (td, *syn*-**S1d**, *J* = 15.5, 5.3 Hz), –146.0 (dd, *anti*-**S1d**, *J* = 16.0, 8.3 Hz).

2-Fluoro-3-(4-nitrophenyl)allyl chloride (1c)

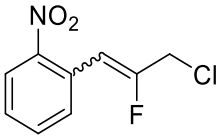
According to the general procedure, a mixture of **S1c** (428.8 mg, 2.0 mmol), CuCl (41.1 mg, 0.42 mmol) and 2.0 mL of MeCN was heated at 100°C for 20 hours. After column chromatography (25 : 1, *n*-hexane/EtOAc = 4/1), **1c** was obtained as a colorless solid (400.8 mg, 93% yield, *Z*/*E* = 87/13, mp 82–86°C).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 4.24 (d, 2H, CH_2Cl, *E*-**1c**, *J* = 22.6 Hz), 4.25 (d, 2H, CH_2Cl, *Z*-**1c**, *J* = 17.7 Hz), 5.98 (d, 1H, -CH=, *Z*-**1c**, *J* = 35.1 Hz), 6.48 (d, 1H, -CH=, *E*-**1c**, *J* = 17.5 Hz), 7.44–7.49 (m, 2H, arom., *E*-**1c**), 7.62–7.70 (m, 2H, arom., *Z*-**1c**), 8.16–8.22 (m, 2H, arom., *Z*-**1c**), 8.22–8.27 (m, 2H, arom., *E*-**1c**). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –99.7 (td, *E*-**1c**, *J* = 22.5, 17.8 Hz), –104.04 (dt, *Z*-**1c**, *J* = 35.2, 17.7 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 38.7 (d, CH_2Cl, *E*-**1c**, *J* = 31.7 Hz), 42.3 (d, CH_2Cl, *Z*-**1c**, *J* = 31.6 Hz), 108.6 (d, -CH=, *Z*-**1c**, *J* = 7.2 Hz), 111.4 (d, -CH=, *E*-**1c**, *J* = 28.0 Hz), 123.8 (s, 2CH, arom., *Z*-**1c**), 124.1 (s, 2CH, arom., *E*-**1c**), 129.3 (d, 2CH, arom., *E*-**1c**, *J* = 2.7 Hz), 129.5 (d, 2CH, arom., *Z*-**1c**, *J* = 8.0 Hz), 138.7 (d, C-arom., *Z*-**1c**, *J* = 3.5 Hz), 139.4 (d, C-arom., *E*-**1c**, *J* = 12.1 Hz), 146.9 (d, $C(NO_2)$, *Z*-**1c**, *J* = 2.8 Hz), 147.2 (s, $C(NO_2)$, *E*-**1c**), 157.2 (d, -CF=, *Z*-**1c**, *J* = 271 Hz), 158.1 (d, -CF=, *E*-**1c**, *J* = 258 Hz).

2-Fluoro-3-(2-nitrophenyl)allyl chloride (1d)

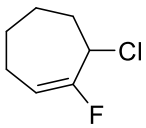
According to the general procedure, a mixture of **S1d** (330.2 mg, 1.5 mmol), CuCl (41.3 mg, 0.42 mmol) and 1.5 mL of MeCN was heated at 100°C for 7 days. After column chromatography (25 : 1, *n*-hexane/EtOAc = 10/1), **1d** was obtained as a yellow oil which solidifies upon storage at r.t. (281.4 mg, 85% yield, *Z*/*E* = 86/14, mp 49–52°C).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 4.10 (d, 2H, CH_2Cl, *E*-**1d**, *J* = 21.7 Hz), 4.24 (d, 2H, CH_2Cl, *Z*-**1d**, *J* = 17.8 Hz), 6.44 (d, 1H, -CH=, *Z*-**1d**, *J* = 33.5 Hz, 1H), 6.79 (d, 1H, -CH=, *E*-**1d**, *J* = 17.0 Hz, 1H), 7.44 (m, 1H, arom., *Z*-**1d**), 7.49–7.57 (m, 2H, arom., *E*-**1d**), 7.61 (m, 1H, arom., *Z*-**1d)**, 7.69 (m, 1H, arom., *E*-**1d)**, 7.79 (m, 1H, arom., *Z*-**1d**), 7.99 (m, 1H, arom., *Z*-**1d**), 8.12 (m, 1H, arom., *E*-**1d**). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –103.7 (td, *E*-**1d**, *J* = 21.7, 16.7 Hz), –109.0 (dt, *Z*-**1d**, *J* = 33.8, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 38.7 (d, CH_2Cl, *E*-**1d**, *J* = 31.0 Hz), 42.3 (d, CH_2Cl, *Z*-**1d**, *J* = 31.4 Hz), 105.3 (d, -CH=, *Z*-**1d**, *J* = 6.8 Hz), 110.0 (d, -CH=, *E*-**1d**, *J* = 31.0 Hz), 124.8 (s, CH-arom., *Z*-**1d**), 125.3 (s, CH-arom., *E*-**1d**), 126.6 (d, C-arom., *Z*-**1d**, *J* = 2.1 Hz), 128.1 (d, C-arom., *E*-**1d**, *J* = 12.7 Hz), 128.8 (s, CH-arom., *Z*-**1d**), 129.4 (s, CH-arom., *E*-**1d**), 131.4 (d, CH-arom., *E*-**1d**, *J* = 1.7 Hz), 131.8 (d, CH-arom., *Z*-**1d**, *J* = 9.3 Hz), 133.1 (s, CH-arom., *Z*-**1d**), 133.9 (s, CH-arom., *E*-**1d**), 147.9 (s, $C(NO_2)$, *Z*-**1d**), 148.1 (s, $C(NO_2)$, *E*-**1d**), 156.2 (d, -CF=, *Z*-**1d**, *J* = 268 Hz), 156.8 (d, -CF=, *E*-**1d**, *J* = 256 Hz).

3-Chloro-2-fluorocycloheptene (1e)

According to the general procedure, a mixture of 31.4 g (210 mmol) of 7-chloro-7-fluoro-bicyclo[4.1.0]heptane **S1e** (*endo*-Cl/*exo*-Cl = 65/35; only *endo*-Cl isomer reacts), 4.19 g (42.4 mmol) of CuCl and 100 mL of MeCN was stirred at 120°C for 2 hours. After aqueous work-up, solvents were removed by atmospheric pressure distillation. The residue was distilled under reduced pressure on a 100 mm Vigreux column. The fraction with bp 70–80°C / 53 mmHg was collected, affording 25.4 g of a mixture containing 21% of *exo*-Cl-**S1e**, 3% of *endo*-Cl-**S1e** and 75% of **1e**. This mixture was used without additional purification. NMR data are fully consistent with previously published [3].

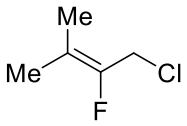


^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 1.45–2.28 (m, 8H, $4CH_2$), 4.73 (m, 1H, CHCl), 5.57 (m, 1H, =CH–). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –100.6 (m). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 22.6 (d, CH_2, *J* = 9.8 Hz), 23.3 (s, CH_2), 22.7 (s, CH_2), 32.6 (d, CH_2, *J* = 8.2 Hz), 58.8 (d, CHCl, *J* = 33.4 Hz), 111.4 (d, =CH–, *J* = 22.2 Hz), 159.6 (d, =CF–, *J* = 246 Hz). **MS (EI) *m/z*** 148, 150 ($[M^+]$, 29, 10), 113 ($[M–Cl]^+$, 64), 112 ($[M–HCl]^+$, 30), 97 (100), 93 (31), 91 (23), 85 (37), 77 (21), 72 (26).

2-Fluoro-3,3-dimethylallyl chloride (1f)

According to the general procedure, a mixture of 19.6 g (160 mmol) of 2-chloro-2-fluoro-1,1-dimethylcyclopropane **S1f**, 795 mg (8.0 mmol) of CuCl, 340 mg (8.0 mmol) of LiCl and 40 mL of MeCN was stirred at 80°C for 36 hours. After aqueous work-up, solvents were removed

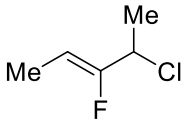
by atmospheric pressure distillation. The residue was fractionally distilled under reduced pressure on a 200 mm Vigreux column. The fraction with bp 66–67°C / 110 mmHg was collected, affording 12.2 g of **1f** (62% yield). NMR data are fully consistent with previously published [3].



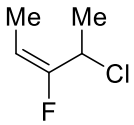
^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 1.71 (m, 6H, $2CH_3$), 4.20 (d, 2H, CH_2Cl, *J* = 22.4 Hz). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –117.2 (t, *J* = 22.4 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 15.9 (d, CH_3, *J* = 7.4 Hz), 17.5 (d, CH_3, *J* = 4.1 Hz), 39.0 (d, CH_2Cl, *J* = 34.4 Hz), 115.0 (d, Me_2C=, *J* = 16.7 Hz), 149.3 (d, CF=, *J* = 239 Hz). **MS (EI) *m*/*z*** 122, 124 ([M^+], 32, 12), 87 ([M^+–Cl], 100), 59 (50), 41 (49).

2-Fluoro-1,3-dimethylallyl chloride (1g)

According to the general procedure, a mixture of 9.80 g (80 mmol) of 3-chloro-3-fluoro-*trans*-1,2-dimethylcyclopropane **S1g**, 790 mg (8.0 mmol) of CuCl and 40 mL of MeCN was stirred at 80°C for 24 hours. After aqueous work-up, solvents were removed by atmospheric pressure distillation. The residue was distilled under atmospheric pressure on a 100 mm Vigreux column, affording 8.72 g of **1g** (89% yield, *Z*/*E* = 92/8, 110–111°C). NMR data are fully consistent with previously published [3].

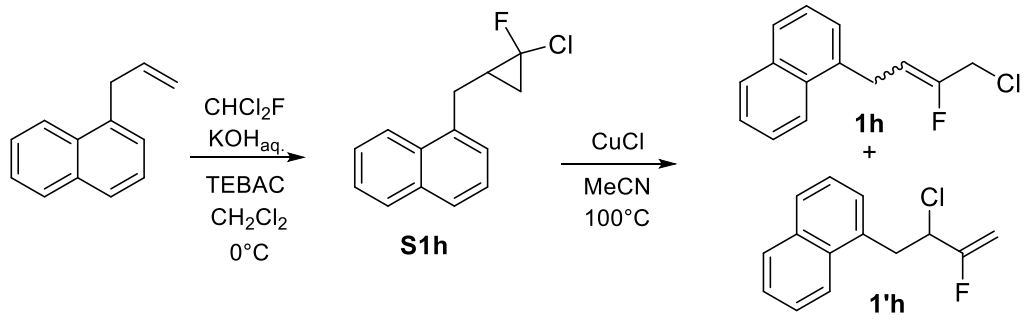


^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 1.61–1.67 (m, 6H, $2CH_3$), 4.51 (dq, 1H, CHCl, *J* = 18.5, 6.8 Hz), 4.95 (dq, 1H, CH=, *J* = 35.1, 6.9 Hz). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –123.2 (ddq, *J* = 35.1, 18.5, 2.5 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 8.9 (d, CH_3, *J* = 4.5 Hz), 21.9 (d, CH_3, *J* = 3.0 Hz), 54.4 (d, CHCl, *J* = 29.8 Hz), 102.8 (d, -CH=, *J* = 15.6 Hz), 158.0 (d, CF, *J* = 252 Hz). **MS (EI) *m*/*z*** 122, 124 ([M^+], 24, 7), 107, 109 ([M^+–CH_3], 6, 2), 87 ([M^+–Cl], 100), 59 (49).



^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 1.59–1.65 (m, 6H, $2CH_3$), 4.91 (dq, 1H, CHCl, *J* = 27.2, 7.0 Hz), 5.17 (dq, 1H, -CH=, *J* = 19.5, 7.5 Hz). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –123.6 (ddq, *J* = 27.2, 19.5, 2.8 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** 10.3 (d, CH_3, *J* = 8.2 Hz), 21.4 (d, CH_3, *J* = 3.0 Hz), 49.6 (d, CHCl, *J* = 29.8 Hz), 103.3 (d, CH=, *J* = 15.6 Hz), (=*CF- signal missed due to low intensity*). **MS (EI) *m*/*z*** 122, 124 ([M^+], 34, 12), 107, 109 ([M^+–CH_3], 6, 2), 87 ([M^+–Cl], 100), 59 (39).

1-(4-Chloro-3-fluorobut-2-en-1-yl)naphthalene (1h) and
1-(2-chloro-3-fluorobut-3-en-1-yl)naphthalene (1'h)



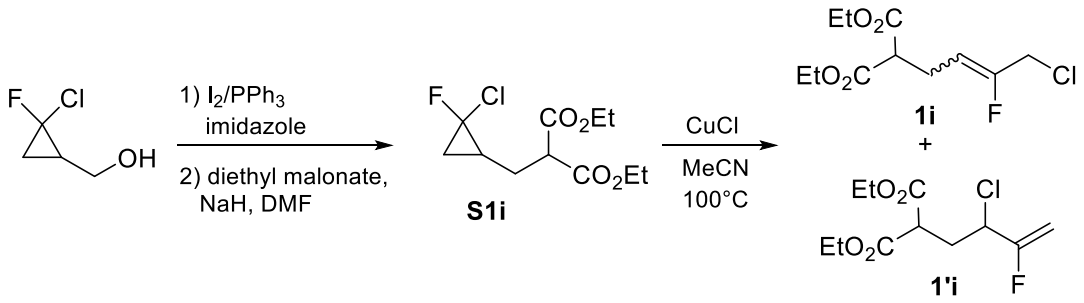
According to the general procedure, a mixture of 4.20 g of 1-allylnaphthalene (25 mmol), 15 g of $CHCl_2F$ (0.15 mol), a saturated solution of 15 g of KOH (ca. 0.2 mol) in ca. 10 mL of water, 114 mg of TEBAC (0.50 mmol) and 12 mL of CH_2Cl_2 was vigorously stirred for 5 hours. The conversion of 20% was achieved. After aqueous work-up, residual 1-allylnaphthalene was distilled off using 'bulb-to-bulb' distillation (0.1 mmHg, bath temp. 100°C to 130°C). The residue was purified by column chromatography on 25 g of silica eluting with petroleum ether affording **S1h** as a colorless oil (197 mg, 3% yield, *syn*/*anti* = 58/42).

^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 1.05 (td, 1H, *syn*-**S1h**, CH_2-cycloprop., *J* = 7.7, 6.1 Hz), 1.25–1.38 (m, 1H, *anti*-**S1h**, CH_2-cycloprop.), 1.39–1.50 (m, 1H, *anti*-**S1h**, CH_2-cycloprop.), 1.67 (ddd, 1H, *syn*-**S1h**, CH_2-cycloprop., *J* = 15.9, 11.3, 7.4 Hz, 1H), 1.85–2.14 (m, 1H+1H, both isomers, CH_2-cycloprop.), 3.10 (ddd, 1H, *syn*-**S1h**, $ArCH_2$, *J* = 15.7, 7.2, 2.8 Hz), 3.20 (ddd, 1H, *anti*-**S1h**, $ArCH_2$, *J* = 15.7, 7.1, 1.3 Hz), 3.37 (dd, 1H+1H, both isomers, $ArCH_2$, *J* = 15.7, 6.7 Hz), 7.38–7.57 (m, 4H, arom.), 7.71–7.79 (m, 1H, arom.), 7.84–7.89 (m, 1H, arom.), 7.97–8.04 (m, 1H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –130.7 (dd, *syn*-**S1h**, *J* = 15.4, 15.4 Hz), –150.9 (dd, *anti*-**S1h**, *J* = 16.2, 6.3 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 21.6 (d, *anti*-**S1h**, CH_2-cycloprop., *J* = 10.4 Hz), 21.7 (d, *syn*-**S1h**, CH_2-cycloprop., *J* = 11.1 Hz), 25.3 (d, *syn*-**S1h**, CH-cycloprop., *J* = 10.3 Hz), 27.7 (d, *anti*-**S1h**, CH-cycloprop., *J* = 11.1 Hz), 30.0 (d, *anti*-**S1h**, $ArCH_2$, *J* = 5.4 Hz), 32.3 (d, *syn*-**S1h**, $ArCH_2$, *J* = 1.1 Hz), 93.5 (d, *anti*-**S1h**, CFCl, *J* = 287 Hz), 96.1 (d, *syn*-**S1h**, CFCl, *J* = 286 Hz), 123.3 (s, arom.), 125.6 (s, arom.), 125.7 (s, arom.), 125.7 (s, arom.), 126.2 (s, arom.), 127.3 (s, arom.), 127.3 (s, arom.), 128.9 (s, arom.), 128.9 (s, arom.), 131.8 (s, arom.), 133.9 (s, arom.), 135.2 (s, arom.), 135.3 (s, arom.), 135.6 (s, arom.). **MS (EI, 70 eV) *m/z*** 234/236 ([M^+], 49/15), 199 (43), 193 (48), 179 (66), 165 (26), 154 (85), 153 (100), 141 (82), 128 (14), 115 (60), 89 (12), 76 (17), 63 (10).

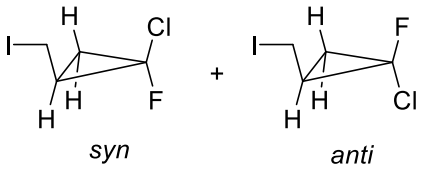
According to the general procedure, a mixture of **S1h** (120.5 mg, 0.51 mmol), CuCl (12.5 mg, 0.13 mmol) and 0.50 mL of MeCN was heated at 100°C for 68 hours. After column chromatography (25 : 1, *n*-hexane/benzene = 10/1), **1h,1'h** was obtained as a colorless oil (110.3 mg, 92% yield, *Z*-**1h**/*E*-**1h**/**1'h** = 47/37/16).

^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 3.59 (dd, 1H in Naphth-CH_2, **1'h**, *J* = 14.3, 7.2 Hz), 3.73 (dd, 1H in Naphth-CH_2, **1'h**, *J* = 14.3, 7.6 Hz), 3.76 (d, 2H, Naphth-CH_2, *E*-**1h**, *J* = 7.9 Hz, 2H), 3.87 (dd, 2H, Naphth-CH_2, *Z*-**1h**, *J* = 7.4, 1.8 Hz), 4.01 (d, 2H, CH_2Cl, *Z*-**1h**, *J* = 18.1 Hz), 4.21 (d, 2H, CH_2Cl, *E*-**1h**, *J* = 21.4 Hz), 4.39 (dd, 1H, =CH_2, **1'h**, *J* = 46.9, 3.4 Hz), 4.63 (dd, 1H, =CH_2, **1'h**, *J* = 15.4, 3.4 Hz), 4.67 (dt, 1H, CHCl, **1'h**, *J* = 21.1, 7.6 Hz), 5.16 (dt, 1H, -CH=, *Z*-**1h**, *J* = 33.8, 7.4 Hz), 5.58 (dt, 1H, -CH=, *E*-**1h**, *J* = 18.5, 7.9 Hz), 7.26–7.56 (m, 4H, arom.), 7.69–7.78 (m, 1H, arom.), 7.80–7.87 (m, 1H, arom.), 7.90–8.01 (m, 1H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –108.5 (dddt, *E*-**1h**, *J* = 21.3, 19.8, 18.6, 1.3 Hz), –111.3 (ddd, **1'h**, *J* = 46.9, 20.8, 15.4 Hz), –116.1 (dtt, *Z*-**1h**, *J* = 33.8, 18.2, 1.9). **^{13}C NMR (100.6 MHz, $CDCl_3$) δ:** 27.8 (d, Naphth-CH_2, *Z*-**1h**, *J* = 4.4 Hz), 28.8 (d, Naphth-CH_2, *E*-**1h**, *J* = 8.1 Hz), 37.7 (d, CH_2Cl, *E*-**1h**, *J* = 32.7 Hz), 38.6 (d, Naphth-CH_2, **1'h**, *J* = 1.0 Hz), 42.0 (d, CH_2Cl, *Z*-**1h**, *J* = 32.2 Hz), 57.9 (d, CHCl, **1'h**, *J* = 29.3 Hz), 93.8 (d, =CH_2, *E*-**1h**, *J* = 18.9 Hz), 109.8 (d, =CH–, *Z*-**1h**, *J* = 14.1 Hz), 109.9 (d, =CH–, *E*-**1h**, *J* = 21.7 Hz), 123.0 (s), 123.3 (s), 123.6 (d, *J* = 1.1 Hz), 125.5 (s), 125.7 (s), 125.7 (s), 125.8 (s), 125.8 (s), 125.8 (s), 125.9 (s), 126.1 (s), 126.2 (s), 126.3 (s), 126.5 (s), 127.4 (s), 127.6 (s), 128.2 (s), 128.3 (s), 128.9 (s), 129.0 (s), 129.2 (s), 131.7 (s), 131.7 (s), 131.8 (s), 132.4 (s), 133.9 (s), 134.0 (s), 134.0 (s), 134.8 (d, *J* = 2.1 Hz), 135.3 (d, *J* = 1.8 Hz), 154.2 (d, =CF–, *Z*-**1h**, *J* = 254 Hz), 155.3 (d, =CF–, *E*-**1h**, *J* = 248 Hz), 162.2 (d, =CF–, *E*-**1h**, *J* = 259 Hz). **Anal.:** calcd. for $C_{14}H_{12}ClF$: C, 71.65%; H, 5.15%. Found: C, 71.42%; H, 5.36%.

Diethyl 2-(4-chloro-3-fluorobut-2-en-1-yl)malonate (1i) and diethyl 2-(2-chloro-3-fluorobut-3-en-1-yl)malonate (1'i)



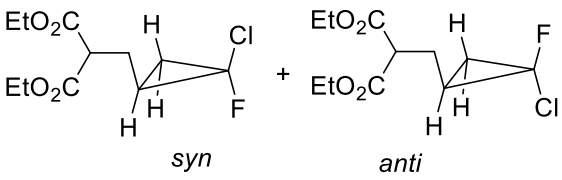
To a solution of (2-chloro-2-fluorocyclopropyl)methanol (3.74 g, 30 mmol), PPh_3 (13.74 g, 52.5 mmol) and imidazole (3.78 g, 55 mmol) in 150 mL of Et_2O/MeCN (3/2), I_2 (15.24 g, 60 mmol) was added in one portion at –4°C (NaCl/ice bath). The reaction mixture was stirred for 30 min at –4°C and 6 hours at room temperature. Then it was poured slowly under stirring into 300 mL of *n*-hexane. The obtained suspension was washed with a solution of $Na_2S_2O_3 \cdot 5H_2O$ (60 g in 300 mL of water). Organic layer was separated and water phase was washed twice with *n*-hexane. Combined extracts were washed with $Na_2S_2O_3$ solution, then water and brine. Residual Ph_3PO was filtered off through a short plug of silica. The filtrate was dried over $MgSO_4$ and concentrated on a rotary evaporator (100 mmHg, 25°C). The residue was purified by 'bulb-to-bulb' distillation (8 mmHg, bath temperature 70–75°C) affording of (2-chloro-2-fluorocyclopropyl)methyl iodide (2.95 g, 42% yield, *syn/anti* = 59/41).



^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 0.98 (td, 1H, *syn*, *J* = 7.7, 6.4 Hz), 1.22 (dt, 1H, *anti*, *J* = 16.9, 7.7 Hz), 1.54 (m, 1H, *anti*, *J* = 10.2, 7.6 Hz), 1.77 (ddd, 1H, *syn*, *J* = 15.4, 11.1, 7.7 Hz), 1.92–2.31 (m, 1H, both isomers), 3.10–3.41 (m, 2H, CH_2I, both isomers). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –129.8 (ddd, *syn*, *J* = 16.0, 16.0, 6.4 Hz), –153.1 (dd, *anti*, *J* = 16.9, 7.4 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** –0.4 (d, CH_2I, *anti*, *J* = 6.5 Hz), 2.0 (d, CH_2I, *syn*, *J* = 1.5 Hz), 24.9 (d, CH_2-cycloprop., *syn*, *J* = 11.1 Hz), 25.2 (d, CH_2-cycloprop., *anti*, *J* = 11.1 Hz), 28.5 (d, CH-cycloprop., *syn*, *J* = 12.1 Hz), 31.1 (d, CH-cycloprop., *anti*, *J* = 10.8 Hz), 95.2 (d, CFCl, *anti*, *J* = 288.0 Hz), 97.5 (d, CFCl, *syn*, *J* = 289.0 Hz). **Anal.:** calcd. for C_4H_5ClFI: C, 20.49%; H, 2.15%. Found: C, 20.62%; H, 2.06%.

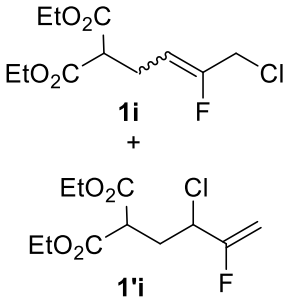
To a suspension of NaH (376 mg, 10 mmol, 63 w/w % in mineral oil) in abs. DMF (20 mL), diethyl malonate (1.55 mL, 10 mmol) was added dropwise under argon atmosphere and

cooling on an ice bath. The mixture was stirred at room temperature for 1 hour. Then a solution of (2-chloro-2-fluorocyclopropyl)methyl iodide (936 mg, 4.0 mmol) in abs. DMF (2 mL) was added at 0°C, and the reaction mixture was stirred for additional 3 hours, then diluted with Et_2O, washed with water and brine, dried over $MgSO_4$, and concentrated. The residue was dried under high vacuum and purified by column chromatography on silica eluting with *n*-hexane/EtOAc (7/1). Diethyl [(2-chloro-2-fluorocyclopropyl)methyl]malonate was obtained as a colorless liquid (811 mg, 76% yield, *syn/anti* = 59/41).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 0.82–1.80 (m, 9H, 3H-cycloprop. + $2CH_3$), 1.92–2.22 (m, 2H, CH_2), 3.42–3.57 (m, 1H, -C*H*$(CO_2Et)_2$), 4.14–4.33 (m, 4H, $2OCH_2CH_3$). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –131.6 (m, *syn*-isomer), –151.9 (m, *anti*-isomer). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 14.0 (s, 2 CH_3, *syn*), 14.0 (s, 2 CH_3, *anti*), 21.2 (d, CH_2-cycloprop., *anti*, *J* = 10.9 Hz), 21.3 (d, CH_2-cycloprop., *syn*, *J* = 11.4 Hz), 23.0 (d, CH-cycloprop., *syn*, *J* = 11.1 Hz), 25.3 (d, CH-cycloprop., *anti*, *J* = 11.1 Hz), 26.6 (d, CH_2, *anti*, *J* = 5.5 Hz), 28.7 (d, CH_2, *syn*, *J* = 0.8 Hz), 50.8 (d, -*C*H$(CO_2Et)_2$, *syn*, *J* = 1.3 Hz), 51.2 (s, -*C*H$(CO_2Et)_2$, *anti*), 61.6 (s, 2 OCH_2, *anti*), 61.6 (s, 2 OCH_2, *syn*), 92.7 (d, CFCl, *anti*, *J* = 286.5 Hz), 95.1 (d, CFCl, *syn*, *J* = 285.2 Hz), 168.6 (s, CO_2Et, *syn*), 168.7 (s, CO_2Et, *anti*), 168.8 (s, CO_2Et, *syn*), 168.8 (s, CO_2Et, *anti*). **MS (EI) *m/z*** 267/269 ([M+H$^+$], 4/1), 266/268 ([M$^+$], 3/1), 238/240 (53/16), 210/212 (54/17), 194 (52), 192 (63), 185 (14), 177 (17), 175 (59), 160 (49), 157 (80), 147 (23), 133 (42), 129 (58), 114 (43), 106 (100), 101 (33), 93 (24), 85 (89), 83 (64), 73 (48), 68 (81), 65 (45), 55 (70). **Anal.:** calcd. for $C_{11}H_{16}ClFO_4$: C, 49.54%; H, 6.05%. Found: C, 49.39%; H, 6.21%.

According to the general procedure, a mixture of **S1i** (521.9 mg, 2.0 mmol), CuCl (41.1 mg, 0.42 mmol) and 2.0 mL of MeCN was heated at 100°C for 80 hours. After column chromatography (25 : 1, *n*-hexane/EtOAc = 4/1), **1i,1'i** was obtained as a colorless oil (439.4 mg, 84% yield, *Z*-**1i**/*E*-**1i**/**1'i** = 64/23/13).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 1.23–1.32 (m, 6H, $2CH_3CH_2O$, all isomers), 2.43 (ddd, 1H, **1'i**, $(EtO_2C)_2CHCH_2$, *J* = 14.4, 9.2, 6.2 Hz), 2.55 (ddd, 1H, **1'i**, $(EtO_2C)_2CHCH_2$, *J* = 14.2, 8.5, 5.6 Hz), 2.62 (ddd, 2H, *E*-**1i**, $(EtO_2C)_2CHCH_2$, *J* = 8.3, 7.3, 0.9 Hz), 2.70 (td, 2H, *Z*-**1i**, $(EtO_2C)_2CHCH_2$, *J* = 7.5, 1.8 Hz), 3.39 (t, 1H, *E*-**1i**, $(EtO_2C)_2CH$, *J* = 7.3 Hz), 3.41 (t, 1H, *Z*-**1i**, $(EtO_2C)_2CH$, *J* = 7.4 Hz), 3.63 (dd, 1H, **1'i**, $(EtO_2C)_2CH$, *J* = 8.5, 6.2 Hz), 4.02 (d, 2H, *Z*-**1i**, CH_2Cl, *J* = 17.9 Hz), 4.18 (d, 2H, *E*-**1i**,

CH_2Cl, *J* = 21.0 Hz), 4.16–4.25 (m, 4H, $2CH_3C\underline{H_2}O$, all isomers), 4.49 (ddd, 1H, **1'i**, CHCl, *J* = 18.9, 9.1, 5.6 Hz), 4.66 (dd, 1H, **1'i**, $=CH_2$, *J* = 46.6, 3.5 Hz), 4.78 (dd, 1H, **1'i**, $=CH_2$, *J* = 15.4, 3.5 Hz, 1H), 5.04 (dt, 1H, *Z*-**1i**, –CH=, *J* = 33.5, 7.6 Hz, 1H), 5.26 (dt, 1H, *E*-**1i**, –CH=, *J* = 18.3, 8.4 Hz, 1H). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –106.5 (tdt, *E*-**1i**, *J* = 21.3, 18.4, 1.0 Hz), –109.8 (ddd, **1'i**, *J* = 46.6, 18.9, 15.4 Hz), –113.8 (dtt, *Z*-**1i**, *J* = 33.5, 17.8, 1.8 Hz). **^{13}C NMR (75 MHz, $CDCl_3$) δ:** 14.0 ($\underline{C}H_3CH_2O$, all isomers), 23.2 (d, *Z*-**1i,** $(EtO_2C)_2CH\underline{C}H_2$, *J* = 4.4 Hz), 25.2 (d, *E*-**1i**, $(EtO_2C)_2CH\underline{C}H_2$, *J* = 8.8 Hz), 33.7 (d, **1'i**, $(EtO_2C)_2CH\underline{C}H_2$, *J* = 1.5 Hz), 37.2 (d, *E*-**1i**, CH_2Cl, *J* = 31.9 Hz), 41.6 (d, *Z*-**1i,** CH_2Cl, *J* = 32.1 Hz), 49.0 (s, **1'i**, $(EtO_2C)_2\underline{C}H$), 51.1 (d, *E*-**1i**, $(EtO_2C)_2\underline{C}H$, *J* = 2.0 Hz), 51.5 (d, *Z*-**1i**, $(EtO_2C)_2\underline{C}H$, *J* = 2.9 Hz), 55.5 (d, **1'i**, CHCl, *J* = 29.8 Hz), 61.6 (s, *Z*-**1i**, $CH_3\underline{C}H_2O$), 61.8 (s, *E*-**1i**, $CH_3\underline{C}H_2O$), 61.9 (s, **1'i**, $CH_3\underline{C}H_2O$), 61.9 (s, **1'i**, $CH_3\underline{C}H_2O$), 93.6 (d, **1'i**, $=CH_2$, *J* = 18.7 Hz), 106.5 (d, *Z*-**1i**, –CH=, *J* = 13.6 Hz), 107.0 (d, *E*-**1i**, –CH=, *J* = 23.3 Hz), 155.7 (d, *Z*-**1i**, –CF=, *J* = 256 Hz), 156.7 (d, *E*-**1i**, –CF=, *J* = 250 Hz), 162.1 (d, **1'i**, –CF=, *J* = 260 Hz), 168.3 (s, **1'i**, C=O), 168.4 (s, *E*-**1i**, C=O), 168.5 (s, **1'i**, C=O), 168.6 (s, *Z*-**1i**, C=O). **MS (EI, 70 eV) *m/z*** 267/269 ($[M+H^+]$, 0.9/0.3), 231 (100), 221 (17), 203 (12), 185 (16), 175 (8), 160 (14), 157 (84), 129 (34), 115 (54), 113 (26), 107 (13), 85 (39), 65 (23). **Anal.:** calcd. for $C_{11}H_{16}ClFO_4$: C, 49.54%; H, 6.05%. Found: C, 49.29%; H, 6.26%.

3. Silylation and borylation of 2-fluoro-3-phenylallyl chloride (1a)

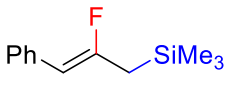
Silylation/borylation with Mg and TMSCl/TBSCl/HBpin

Modified reaction procedure was used [4]:

A round-bottom flask was charged with 37 mg of Mg-turnings (1.5 mmol) and dried under high vacuum (less than 0.1 mmHg) with heating by heatgun for 15 min. After cooling to room temperature, a magnetic stirring bar and small crystal of I_2 were added, the flask was sealed with rubber septum and filled with argon on a Schlenk line. Then the flask was heated with heatgun and cooled back to r.t. THF (2.0 mL) and TMSCl/TBSCl (3.0 mmol) or HBpin (2.0 mmol) were added, then *Z*-**1a** (*Z*/*E* > 99.9) (0.15 mL, 1.0 mmol) was added dropwise, and the reaction mixture was stirred at r.t. for 5 hours. 4-Fluoroanisol (10.0 μL, 0.088 mmol, an internal standard) was added and an aliquot was analyzed by ^{19}F NMR. The data are presented in Table 1 of the main article (entries 1, 4, 5).

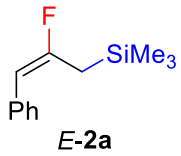
Multigram scale synthesis of *Z*-2a

To a stirred mixture of 3.65 g (150 mmol) of Mg-turnings, 38 mL (300 mmol) of TMSCl in 100 mL of abs. THF a solution of 17.1 g (100 mmol) of **1a** (*Z*/*E* >99.9) in 10 mL of abs. THF was added dropwise over 5 min at room temperature under cooling with water bath. The reaction mixture was stirred for 1 hour, and the reaction progress was checked by GC. If complete conversion of **1a** was not achieved, then additional 3.65 g (150 mmol) of Mg were added, and the mixture was stirred for 1 hour more. After the reaction complete, it was diluted with hexane, washed with water and dried over Na_2SO_4. All volatiles were removed, and the residue was fractionally distilled under reduced pressure on a 200 mm Vigreux column. The fraction with bp 74.5–75.0°C / 2 mmHg was collected affording 9.30 g of *Z*-**2a** as a colorless oil (45% yield, *Z*/*E* = 99/1). NMR data are fully consistent with previously published.[5]



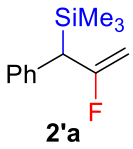
Z-**2a**

^{1}H NMR (200.1 MHz, $CDCl_3$) δ: 0.12 (d, 9H, $Si(CH_3)_3$, *J* = 0.6 Hz), 1.79 (d, 2H, CH_2TMS, *J* = 25.5 Hz), 5.29 (d, 1H, =CH–, *J* = 39.4 Hz), 7.09-7.20 (m, 1H, arom.), 7.22-7.34 (m, 2H, arom.), 7.37-7.47 (m, 2H, arom.). **^{19}F NMR (188.3 MHz, $CDCl_3$) δ:** –89.9 (dt, *J* = 39.4, 25.5 Hz). **^{13}C NMR (50.3 MHz, $CDCl_3$) δ:** –1.5 (s, $Si(CH_3)_3$), 24.0 (d, CH_2TMS, *J* = 29.8 Hz), 103.9 (d, =CH–, *J* = 10.2 Hz), 126.1 (d, CH-arom., *J* = 2.2 Hz), 127.9 (d, CH-arom., *J* = 7.4 Hz), 128.4 (s, CH-arom.), 134.7 (d, C-arom., *J* = 2.5 Hz), 160.8 (d, =CF–, *J* = 263 Hz). **MS (EI) *m/z*** 208 ($[M]^+$, 19), 116 ($[M–SiMe_3–H]^+$, 100), 77 ($[Ph]^+$, 21), 73 ($[SiMe_3]^+$, 49).



E-**2a**

^{1}H NMR (200.1 MHz, CDCl$_3$) δ: 0.09 (d, 9H, Si(CH$_3$)$_3$, *J* = 0.5 Hz), 1.99 (d, 2H, CH$_2$TMS, *J* = 28.1 Hz), 6.07 (d, 1H, =CH–, *J* = 22.8 Hz), 7.09-7.35 (m, 5H, arom.). **^{19}F NMR (188.3 MHz, CDCl$_3$) δ:** –85.4 (td, *J* = 28.1, 22.8 Hz). **^{13}C NMR (50.3 MHz, CDCl$_3$) δ:** –1.1 (s, Si(CH$_3$)$_3$), 20.2 (d, CH$_2$TMS, *J* = 32.1 Hz), 105.7 (d, =CH–, *J* = 30.5 Hz), 126.2 (s, CH-arom.), 128.3 (d, CH-arom., *J* = 2.6 Hz), 128.5 (s, CH-arom.), 135.2 (d, C-arom., *J* = 14.7 Hz), 162.1 (d, =CF–, *J* = 247 Hz). **MS (EI) *m/z*** 208 ([M]$^+$, 16), 193 ([M–CH$_3$]$^+$, 2), 116 ([M–SiMe$_3$–H]$^+$, 100), 77 ([Ph]$^+$, 18), 73 ([SiMe$_3$]$^+$, 42).



2'a

^{1}H NMR (200.1 MHz, CDCl$_3$) δ: 0.06 (d, 9H, Si(CH$_3$)$_3$, *J* = 0.7 Hz), 3.07 (d, 1H, CH(TMS), *J* = 28.9 Hz), 4.24 (dd, 1H, =CH$_2$ (*trans* to F), *J* = 50.1, 2.7 Hz), 4.54 (ddd, 1H, =CH$_2$ (*cis* to F), *J* = 17.5, 2.7, 0.4 Hz), 7.09-7.35 (m, 5H, arom.). **^{19}F NMR (188.3 MHz, CDCl$_3$) δ:** –86.6 (ddd, *J* = 50.1, 28.9, 17.5 Hz). **^{13}C NMR (50.3 MHz, CDCl$_3$) δ:** –2.1 (s, Si(CH$_3$)$_3$), 43.0 (d, CH(TMS), *J* = 29.2 Hz), 89.6 (d, =CH$_2$, *J* = 23.6 Hz), 125.6 (s, CH-arom.), 128.0 (s, CH-arom.), 128.5 (s, CH-arom.), 139.5 (s, C-arom.), 167.6 (d, =CF–, *J* = 256 Hz). **MS (EI) *m/z*** 208 ([M]$^+$, 5), 193 ([M–CH$_3$]$^+$, 1), 116 ([M–SiMe$_3$–H]$^+$, 100), 77 ([Ph]$^+$, 24), 73 ([SiMe$_3$]$^+$, 36).

Silylation with Me$_3$SiSiMe$_3$

General procedure 1:

(Pd source = Pd$_2$(dba)$_3$, Pd(dppf)Cl$_2$·CH$_2$Cl$_2$, Pd(OAc)$_2$, PdCl$_2$)

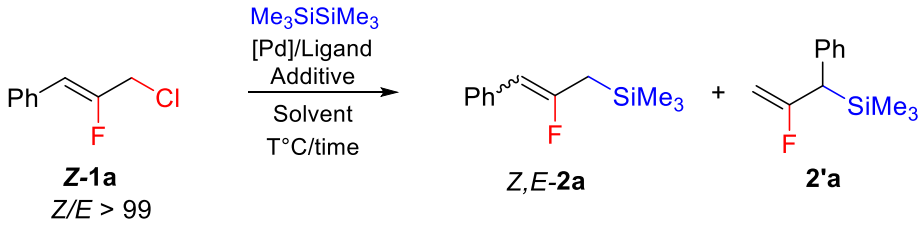
An NMR tube was charged with Pd source, Ligand and Additive; then filled with argon on a Schlenk line (by evacuation/backfilling with argon 3 times). In a stream of argon, 0.50 mL of a solution of *Z*-**1a** (C = 0.50 M, 0.50 mmol), Me$_3$SiSiMe$_3$ (C = 1.0 M, 1.0 mmol) and 4-fluoroanisole (C = 0.11 M, 0.055 mmol) in abs. dioxane were added. The reaction mixture was sonicated on ultrasonic bath for 15 min, and then heated on an oil bath at 80°C for 4 hours. After cooling to room temperature, it was analyzed by ^{19}F NMR (see table S1).

General procedure 2:

(Pd source = [(2-MeAll)PdCl]$_2$/TMEDA)

An NMR tube was charged with *Z*-**1a** (43.1 mg, 0.25 mmol) and filled with argon on a Schlenk line. Then, in a steam of argon, Me$_3$SiSiMe$_3$ (102 μL, 0.50 mmol), 4-fluoroanisole (5.0 μL, 0.044 mmol, an internal standard) 0.25 mL of dry DCE and 0.25 mL of a solution of [(2-MeAll)PdCl]$_2$ (C = 0.025 M, 2.5 mol %) and TMEDA (C = 0.050 M, 5 mol %) in dry DCE were added. The reaction mixture was heated at 60°C for 24 hours. The reaction progress was controlled by ^{19}F NMR (see table S1).

Table S1. Pd-catalyzed silylation of *Z*-**1a** (Z/E >99) with $Me_3SiSiMe_3$



	[Pd]	Ligand	Additive	Solvent	T/time (°C/hours)	Recovery of **1a** (%)	Yield (%)		
							2a	*Z/E*	**2'a**
1	$Pd_2(dba)_3$ (2.5 mol %)	—	—	dioxane	80°C/4 h	29	49	84/16	17
2	$Pd_2(dba)_3$ (2.5 mol %)	—	LiCl (50 mol %)	dioxane	80°C/4 h	53	29	85/15	11
3	$Pd_2(dba)_3$ (2.5 mol %)	PPh_3 (20 mol %)	—	dioxane	80°C/4 h	81	0	—	0
4	$Pd_2(dba)_3$ (2.5 mol %)	PPh_3 (20 mol %)	LiCl (50 mol %)	dioxane	80°C/4 h	86	0	—	0
5	$Pd_2(dba)_3$ (2.5 mol %)	dppe (10 mol %)	—	dioxane	80°C/4 h	92	0	—	0
6	$Pd_2(dba)_3$ (2.5 mol %)	dppe (10 mol %)	LiCl (50 mol %)	dioxane	80°C/4 h	95	0	—	0
7	$Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (5 mol %)	—	—	dioxane	80°C/4 h	99	0	—	0
8	$Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (5 mol %)	—	LiCl (50 mol %)	dioxane	80°C/4 h	100	0	—	0
9	$Pd(OAc)_2$ (5 mol %)	—	—	dioxane	80°C/4 h	0	64	84/16	18
10	$Pd(OAc)_2$ (5 mol %)	—	LiCl (50 mol %)	dioxane	80°C/4 h	58	26	85/15	9

11	$Pd(OAc)_2$ (5 mol %)	PPh_3 (20 mol %)	—	dioxane	80°C/4 h	98	0	—	0
12	$Pd(OAc)_2$ (5 mol %)	PPh_3 (20 mol %)	LiCl (50 mol %)	dioxane	80°C/4 h	96	0	—	0
13	$Pd(OAc)_2$ (5 mol %)	dppe (10 mol %)	—	dioxane	80°C/4 h	82	10	86/14	3
14	$Pd(OAc)_2$ (5 mol %)	dppe (10 mol %)	LiCl (50 mol %)	dioxane	80°C/4 h	92	4	91/9	1
15	$PdCl_2$ (5 mol %)	—	—	dioxane	80°C/4 h	54	29	82/18	12
16	$PdCl_2$ (5 mol %)	—	LiCl (50 mol %)	dioxane	80°C/4 h	93	4	86/14	1
17	$PdCl_2$ (5 mol %)	PPh_3 (20 mol %)	—	dioxane	80°C/4 h	99	0	—	0
18	$PdCl_2$ (5 mol %)	PPh_3 (20 mol %)	LiCl (50 mol %)	dioxane	80°C/4 h	99	0	—	0
19	$PdCl_2$ (5 mol %)	dppe (10 mol %)	—	dioxane	80°C/4 h	100	0	—	0
20	$PdCl_2$ (5 mol %)	dppe (10 mol %)	LiCl (50 mol %)	dioxane	80°C/4 h	100	0	—	0
21	$[(2\text{-MeAll})PdCl]_2$ (2.5 mol %)	TMEDA (5 mol %)	—	DCE	60°C/3 h	90	< 1	—	0
22					60°C/24 h	48	36	88/12	6

Borylation with B_2pin_2

General procedure:

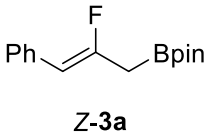
An NMR tube was charged with $[(2\text{-MeAll})PdCl]_2$ (0.0031 mmol) and a Ligand (0.063 mmol) (TMEDA and COD were added after filling with argon), and then evacuated and backfilled with argon on a Schlenk line 3 times. In a stream of argon 0.25 mL of dry degassed Solvent were added, and the tube was sonicated for 10 min. After that in a steam of argon, 4-fluoroanisole (5.0 μL, 0.044 mmol, an internal standard) and 0.25 mL of a solution of *Z*-**1a** (C = 1.0 M) and B_2pin_2 (C = 1.2 M) in Solvent were added. The reaction mixture was kept at r.t. for 20 hours or heated on an oil bath at 60°C for 5 hours. The yields were determined by ^{19}F NMR (see table S2).

Isolation of (2-fluorocinnamyl)boronate 3a

A 10-mL Schlenk tube was charged with 49.6 mg of $[(2\text{-MeAll})PdCl]_2$ (0.25 mmol) and filled with argon an a Schlenk line. First, 2.0 mL of dry degassed DCE were added, then — 37.5 μL of TMEDA (0.25 mmol). The yellow solution was stirred at r.t. for 5 min.

A 25-mL Schlenk tube was charged with 853 mg of *Z*-**1a** (5.0 mmol) and 1.547 g of B_2pin_2 (6.0 mmol) and filled with argon on a Schlenk line. Next, 8.0 mL of dry degassed DCE were added followed by the solution of $[(2\text{-MeAll})PdCl]_2$/TMEDA in DCE. The reaction mixture was stirred for 2 hours at 60°C and concentrated on a rotary evaporator. Residual black oil (ca. 2 g) was subjected to a column chromatography (30 g of silica gel 40–63 μm, *n*-hexane/Et_2O 20/1) affording 968.6 mg of **3a** as a colorless oil (*Z*/*E* = 96/4, 74% yield).

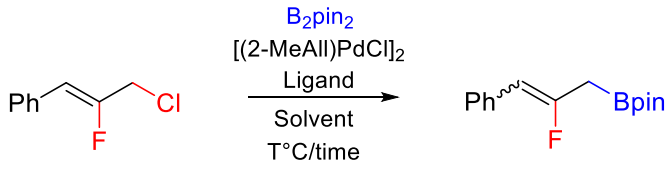
Boronate **3a** decomposes readily forming a complex mixture upon storage at room temperature for several hours or overnight in a freezer (–18°C), therefore it should be used immediately.



Z-**3a**

^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 1.26 (s, 12H, Bpin, *E*-**3a**), 1.28 (s, 12H, Bpin, *Z*-**3a**), 2.05 (d, 2H, CH_2B, *Z*-**3a**, *J* = 19.7 Hz), 2.16 (d, 2H, CH_2B, *E*-**3a**, *J* = 25.8 Hz), 5.50 (d, 1H, –CH=, *Z*-**3a**, *J* = 39.3 Hz), 6.18 (d, 1H, –CH=, *E*-**3a**, *J* = 21.6 Hz, 1H), 7.11–7.20 (m, 1H, arom.), 7.20–7.33 (m, 2H, arom.), 7.40–7.48 (m, 2H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –87.5 (td, *E*-**3a**, *J* = 25.8, 21.6 Hz), –91.1 (dt, *Z*-**3a**, *J* = 39.3, 19.7 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** (only for *Z*-**3a**) 18.2 (broad, CH_2B), 24.8 (s, $4CH_3$), 84.0 (s, $2\underline{C}(Me)_2$), 106.0 (d, =CH–, *J* = 9.4 Hz), 126.4 (d, CH-arom., *J* = 2.3 Hz), 128.3 (d, 2CH-arom., *J* = 7.4 Hz), 128.3 (s, 2CH-arom.,), 134.4 (d, C-arom., *J* = 2.6 Hz), 158.5 (d, =CF–, *J* = 265 Hz). ^{11}B NMR (96.3 MHz, $CDCl_3$) δ: 32.3 (s). **MS (EI, 70 eV) *m/z*** 262 ([M^+], 10), 189 (19), 162 (9), 146 (13), 143 (25), 135 (11), 131 (24), 116 (45), 115 (100), 105 (13), 89 (10), 83 (16), 59 (17). **HRMS (ESI)**, calcd. for $C_{15}H_{20}BFO_2$: *m/z* 263.1616 [M+H^+], 280.1881 [M+NH_4^+], 285.1435 [M+Na^+]. Found: *m/z* 263.1612 [M+H^+], 280.1877 [M+NH_4^+], 285.1433 [M+Na^+].

Table S2. Pd-catalyzed borylation of *Z*-**1a** (*Z*/*E* >99) with B_2pin_2



***Z*-1a**
Z/*E* > 99

***Z*,*E*-3a**

	[(2-MeAll)PdCl]$_2$	Ligand	Solvent	T/time (°C/hours)	Recovery of **1a** (%)	Yield (%) **3a**	Yield (%) *Z*/*E*
1	1.25 mol %	—	THF	r.t. / 20 h	53	41	98/2
				60°C/5 h	36	56	97/3
2		PPh_3 (2.5 mol %)	THF	r.t. / 20 h	58	38	98/2
				60°C/5 h	13	76	97/3
3		PPh_3 (5 mol %)	THF	r.t. / 20 h	100	0	—
				60°C/5 h	99	0	—
4		TMEDA (2.5 mol %)	THF	r.t. / 20 h	26	66	98/2
				60°C/5 h	4	86	97/3
5		phen (2.5 mol %)	THF	r.t. / 20 h	100	0	—
				60°C/5 h	100	0	—
6		bipy (2.5 mol %)	THF	r.t. / 20 h	96	3	>10/1
				60°C/5 h	95	4	>10/1
7		dppe (2.5 mol %)	THF	r.t. / 20 h	100	0	—
				60°C/5 h	75	22	97/3
8		cod (2.5 mol %)	THF	r.t. / 20 h	78	19	96/4
				60°C/5 h	64	31	98/2
9	1.25 mol %	—	toluene	r.t. / 20 h	88	10	>10/1
				60°C/5 h	58	37	98/2
10		PPh_3 (2.5 mol %)	toluene	r.t. / 20 h	87	5	>10/1
				60°C/5 h	25	72	94/6
11		PPh_3 (5 mol %)	toluene	r.t. / 20 h	100	0	—

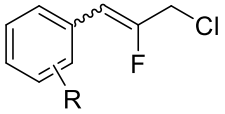
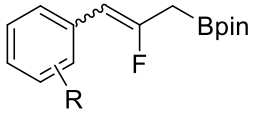
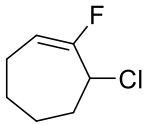
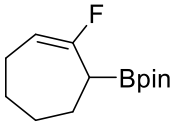
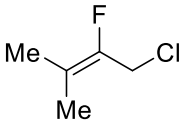
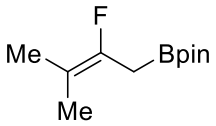
				60°C/5 h	99	0	—
12		TMEDA (2.5 mol %)	toluene	r.t. / 20 h	24	75	97/3
				60°C/5 h	0	99	97/3
13		phen (2.5 mol %)	toluene	r.t. / 20 h	100	0	—
				60°C/5 h	81	17	95/5
14		bipy (2.5 mol %)	toluene	r.t. / 20 h	96	3	>10/1
				60°C/5 h	96	3	>10/1
15		dppe (2.5 mol %)	toluene	r.t. / 20 h	100	0	—
				60°C/5 h	100	0	—
16		cod (2.5 mol %)	toluene	r.t. / 20 h	85	15	>10/1
				60°C/5 h	72	27	97/3
17	1.25 mol %	—	DCE	r.t. / 20 h	80	19	>10/1
				60°C/5 h	8	80	98/2
18		PPh_3 (2.5 mol %)	DCE	r.t. / 20 h	43	56	99/1
				60°C/5 h	5	90	98/2
19		PPh_3 (5 mol %)	DCE	r.t. / 20 h	100	0	—
				60°C/5 h	100	0	—
20		TMEDA (2.5 mol %)	DCE	r.t. / 20 h	0	99	98/2
				60°C/5 h	0	99	98/2
21		phen (2.5 mol %)	DCE	r.t. / 20 h	100	0	—
				60°C/5 h	100	0	—
22		bipy (2.5 mol %)	DCE	r.t. / 20 h	100	0	—
				60°C/5 h	98	1	>10/1
23		dppe (2.5 mol %)	DCE	r.t. / 20 h	100	0	—
				60°C/5 h	100	0	—
24		cod (2.5 mol %)	DCE	r.t. / 20 h	53	46	98/2
				60°C/5 h	17	82	98/2
25	[(2-MeAll)Pd(IPr)Cl] (5 mol %)		DCE	60°C/5 h	0	100	98/2

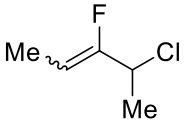
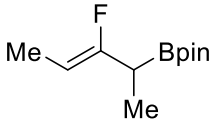
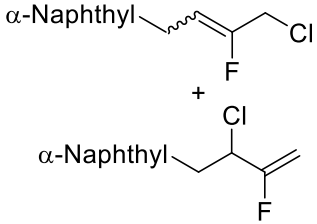
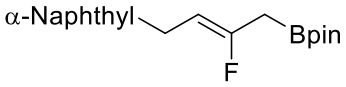
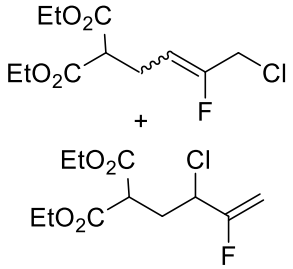
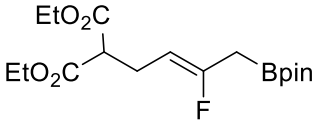
4. Borylation of 2-fluoroallyl chlorides 1b-1i

General procedure

An NMR tube was charged with 2-fluoroallyl chloride (0.25 mmol), B_2pin_2 (0.30 mmol), and then evacuated and backfilled with argon on a Schleck line 3 times (low boiling 2-fluoroallyl chlorides **1e,f,g** were added by volume after filling with argon). In a stream of argon 4-fluoroanisole (5.0 μL, 0.044 mmol, internal standard), 0.25 mmol of dry degassed DCE and 0.25 mL of a freshly prepared solution of $[(2\text{-MeAll})PdCl]_2$ (C = 0.025 M, 2.5 mol %) and TMEDA (C = 0.050 M, 5.0 mol %) in DCE were added. The reaction mixture was heated on an oil bath at 50–60°C for 4–24 hours. The yields were determined by ^{19}F NMR (see table S3).

Table S3. Borylation of 2-fluoroallyl chlorides **1b-1i**

Entry	2-Fluoroallyl chloride	T°C/time, h	2-Fluoroallyl boronate	^{19}F NMR (188.3 MHz, DCE)		MS (EI, 70eV)
				Z-isomer	*E*-isomer	
1	 R = 4-F: **1b** (*Z*/*E* 78/22)	50°C / 4 h	 **3b** (97%, *Z*/*E* 98/2)	–92.3 (dt, *J* = 39.6, 20.0 Hz), –116.4 (m, FC_6H_4-)	–87.6 (tdd, *J* = 26.3, 21.3, 2.8 Hz) (signal of FC_6H_4- missed due to low intensity)	280 ([M^+], 100), 207 (75), 180 (15), 161 (58), 134 (69), 133 (90), 131 (61), 115 (21), 105 (36), 83 (33), 59 (24)
2	R = 4-NO_2: **1c** (*Z*/*E* 87/13)	50°C / 4 h	**3c** (100%, *Z*/*E* 98/2)	–84.5 (dt, *J* = 38.4, 20.4 Hz)	–80.1 (td, *J* = 26.5, 21.4 Hz)	307 ([M^+], 100), 234 (54), 201 (6), 184 (16), 156 (32), 141 (32), 131 (72), 115 (50), 105 (61), 83 (59), 59 (39), 55 (28)
3	R = 2-NO_2: **1d** (*Z*/*E* 86/14)	50°C / 4 h	**3d** (99%, *Z*/*E* 97/3)	–88.8 (dt, *J* =36.7, 18.9 Hz)	–85.3 (td, *J* = 25.9, 19.9 Hz)	161 (13), 145 (30), 131 (38), 117 (100), 104 (30), 90 (38), 89 (36), 63 (12), 58 (8)
4	 **1e**	60°C / 3 h	 **3e** (76%) (21% of **1e** were recovered; further heating lowered the yield)	–88.4 (t, *J* = 20.2 Hz)	—	240 ([M^+], 0.5), 147 (3), 131 (12), 91 (25), 84 (100), 79 (37), 69 (25), 59 (48), 55 (48)
5	 **1f**	60°C / 3 h	 **3f** (80%) (6% of **1f** were recovered; further heating lowered the yield)	–102.0 (t, *J* = 24.0 Hz)	—	214 ([M^+], 18), 157 (11), 147 (30), 141 (24), 131 (86), 113 (18), 104 (52), 95 (42), 84 (100), 83 (96), 67 (69), 59 (58), 55 (54)

6	 **1g** (*Z*/*E* 92/8)	60°C / 24 h	 **3g** (88%, *Z*/*E* >20/1)	–106.4 (dd, *J* = 38.2, 18.3 Hz)	—	214 ([M$^+$], 6), 157 (5), 147 (9), 141 (32), 131 (55), 127 (20), 113 (12), 104 (38), 95 (41), 84 (72), 83 (66), 67 (71), 59 (100), 5 (59)
7	 **1h,1h'** (*Z*/*E*/**1'** 47/37/16)	50°C / 4 h	 **3h** (98%, *Z*/*E* 97/3)	–98.7 (dt, *J* = 36.9, 19.4 Hz)	–93.0 (td, *J* = 25.3, 20.9 Hz)	326 ([M$^+$], 45), 249 (8), 226 (23), 198 (66), 179 (54), 165 (100), 141 (39), 131 (26), 115 (21), 104 (7), 84 (51), 83 (25), 69 (12), 59 (7), 55 (10)
8	 **1i,1i'** (*Z*/*E*/**1'** 64/23/13)	50°C / 4 h	 **3i** (88%, *Z*/*E* 95/5)	–96.7 (dt, *J* = 36.9, 18.6 Hz)	–91.1 (td, *J* = 24.9, 20.8 Hz)	358 ([M$^+$], 7), 313 (15), 284 (10), 258 (26), 228 (35), 213 (11), 199 (28), 187 (50), 184 (51), 160 (30), 140 (19), 131 (40), 112 (39), 93 (26), 84 (100), 83 (98), 69 (27), 59 (17), 55 (37)

5. *One-pot* 2-fluoroallylboration of aldehydes

Preparation of a batch solution of 3a

A 10-mL Schlenk tube was charged with 49.6 mg of $[(2\text{-MeAll})PdCl]_2$ (0.25 mmol) and filled with argon an a Schlenk line. First, 2.0 mL of dry degassed DCE were added, then — 37.5 μL of TMEDA (0.25 mmol). The yellow solution was stirred at r.t. for 5 min.

A 25-mL Schlenk tube was charged with 853 mg of *Z*-**1a** (5.0 mmol) and 1.547 g of B_2pin_2 (6.0 mmol) and filled with argon on a Schlenk line. Next, 8.0 mL of dry degassed DCE were added followed by the solution of $[(2\text{-MeAll})PdCl]_2$/TMEDA in DCE. The reaction mixture was stirred for 2 hours at 60°C. After cooling to r.t., an aliquot was analyzed by ^{19}F NMR using (*Z*)-2-fluorocinnamyl acetate (*Z/E* > 99) as an internal standard. The concentration of **3a** (*Z/E* = 98/2) was estimated to be 0.44–0.47 M. This solution is stable for more than 2 months at r.t. under argon atmosphere.

General procedure A (using a batch solution of *Z*-3a)

A 4 mL screw-cap vial was charged with 0.60 mmol of an aldehyde. In a stream of argon 1.1 mL (0.50 mmol) of a batch solution of *Z*-**3a** in DCE prepared as above (C = 0.44–0.47 M) were added. In cases of aliphatic aldehydes, additionally 49 mg of $Sc(OTf)_3$ (0.10 mmol) were added. The reaction was stirred at room temperature for 1–3 days (5–10 hours in the presence of $Sc(OTf)_3$) until disappearance of *Z*-**3a** monitored by GC. Then, the reaction mixture was diluted with CH_2Cl_2 and 1 M NaOH and stirred for 10 min. The organic layer was washed with $NaHSO_3$ solution, then with water and brine, dried over $MgSO_4$. The residue after evaporation of a solvent was purified by column chromatography on silica (50 g per 1 g of the crude product).

Anti-selectivity of the reaction was proved on compound *anti*-**5aa**. Thus, *syn*-isomer *syn*-**5aa** was previously published[5] and its' configuration was unambiguously determined by X-Ray. Moreover, it is well known that allylboration of aldehydes proceeds with *anti*-selectivity; therefore, configuration of other 3-fluorohomoallylic alcohols was not checked and assigned as "*anti*".

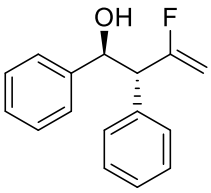
General procedure B (*one pot* borylation/allylation)

A Schlenk tube was charged with 0.50 mmol of 2-fluoroallyl chloride and 0.525 mmol of B_2pin_2. In a steam of argon 0.50 mL of dry DCE were quickly added and the solution was degassed by evacuation/backfilling with argon three times. Then, a degassed solution of 0.0125

mmol of [(2-MeAll)PdCl]$_2$ and 0.025 mmol of TMEDA in 0.50 mL of dry DCE was added and the reaction mixture was heated to 60°C for 3–24 hours. The reaction progress was monitored by GC. After completion of the borylation step the reaction mixture was cooled to room temperature and 0.60 mmol of an aldehyde were added. The reaction was stirred at room temperature for 1–3 days until disappearance of 2-fluoroallylboronate monitored by GC. Work-up as above followed by chromatographic purification gave target 3-fluorohomoallylic alcohol.

2-Fluoro-3,4-diphenylbut-1-en-4-ol (5aa)

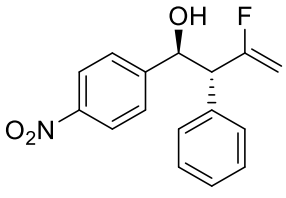
Obtained by the procedure **A** after column chromatography (*n*-hexane/EtOAc, 10/1) as a colorless solid (91.3 mg, 75%, *anti/syn* = 96/4, mp 67–68°C). NMR data of the minor isomer *syn*-**5aa** are fully consistent with previously published.[5]



^{1}H NMR (300.1 MHz, CDCl$_3$) δ: 2.36 (br. d, 1H, -OH, *J* = 2.7 Hz), 3.71 (dd, 1H, C*H*(Ph), *J* = 24.6, 9.3 Hz), 4.62 (dd, 1H, =CH$_2$ (*trans*- to F), *J* = 50.1, 3.1 Hz), 4.78 (ddd, 1H, =CH$_2$ (*cis*- to F), *J* = 17.8, 3.1, 0.6 Hz), 5.07 (dd, 1H, C*H*(OH), *J* = 9.3, 2.7 Hz, 1H), 6.73–7.48 (m, 10H, 2Ph). **^{19}F NMR (282.4 MHz, CDCl$_3$) δ:** –101.0 (ddd, *J* = 50.1, 24.6, 17.8 Hz). **^{13}C NMR (75.5 MHz, CDCl$_3$) δ:** 57.7 (d, *C*H(Ph), *J* = 23.7 Hz), 75.1 (d, CH(OH), *J* = 3.0 Hz), 93.1 (d, =CH$_2$, *J* = 19.7 Hz), 126.7 (s, CH-arom.), 127.2 (s, CH-arom.), 127.8 (s, CH-arom.), 128.1 (s, CH-arom.), 128.4 (s, CH-arom.), 128.5 (d, CH-arom., *J* = 1.9 Hz), 137.4 (d, C-arom., *J* = 2.3 Hz), 141.3 (s, C-arom.), 165.1 (d, –CF=, *J* = 261.7 Hz). **MS (EI) *m/z*** 136 (60), 133 (68), 115 (100), 107 (98), 89 (17), 77 (76), 51 (48). **Anal.:** calcd. for C$_{16}$H$_{15}$FO: C, 79.32%; H, 6.24%. Found: C, 79.12%; H, 6.33%.

2-Fluoro-3-phenyl-4-(4-nitrophenyl)but-1-en-4-ol (5ab)

Obtained by the procedure **B** using 5 mol % of [(2-MeAll)Pd(IPr)Cl] as a catalyst after column chromatography (*n*-hexane/EtOAc, 4/1) as a colorless oil which solidified upon storage (125.2 mg, 87%, *anti/syn* > 20/1, mp 61–63°C).



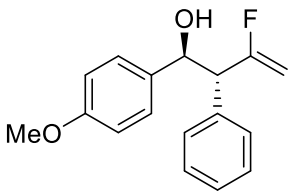
^{1}H NMR (300.1 MHz, CDCl$_3$) δ: 2.65 (br. d, 1H, OH, *J* = 3.0 Hz), 3.66 (dd, 1H, C*H*(Ph), *J* = 24.3, 9.2 Hz), 4.63 (dd, 1H, =CH$_2$ (*trans*- to F), *J* = 50.0, 3.2 Hz), 4.83 (ddd, 1H, =CH$_2$ (*cis*- to F), *J* = 17.8, 3.2, 0.6 Hz), 5.19 (dd, *J* = 9.2, 3.0 Hz), 7.04–7.10 (m, 2H, Ph), 7.16–7.23 (m, 3H, Ph), 7.24–7.30 (m, 2H, -C$_6$H$_4$(NO$_2$)), 8.04 – 7.98 (m, 2H, -C$_6$H$_4$(NO$_2$)). **^{19}F NMR (282.4 MHz, CDCl$_3$) δ:** –101.3 (ddd, *J* = 50.0, 24.3, 17.8 Hz). **^{13}C NMR (75.5 MHz, CDCl$_3$)**

δ: 57.9 (d, *C*H(Ph), *J* = 23.7 Hz), 74.3 (d, CH(OH), *J* = 2.9 Hz), 94.0 (d, =CH_2, *J* = 19.5 Hz), 123.3 (s, CH-arom.), 127.6 (s, CH-arom.), 127.9 (s, CH-arom.), 128.5 (d, CH-arom., *J* = 1.9 Hz), 128.8 (s, CH-arom.), 136.4 (d, C-arom., *J* = 2.1 Hz), 147.4 (s, C-arom.), 148.6 (s, C-arom.), 164.2 (d, –CF=, *J* = 261.8 Hz). **MS (EI)** ***m/z*** 207 (8), 151 (100), 135 (9), 120 (13), 104 (22), 92 (12), 77 (52), 65 (14), 51 (91). **HRMS (ESI)**, calcd. for $C_{16}H_{14}FNO_3$: *m/z* 305.1296 [*M*+NH_4^+], 310.0850 [*M*+Na^+]. Found: *m/z* 305.1296 [*M*+NH_4^+], 310.0852 [*M*+Na^+].

2-Fluoro-3-phenyl-4-(4-methoxyphenyl)but-1-en-4-ol (5ac)

The procedure **B** resulted in substantial chlorination of alcohol **5ac** forming 1-(1-chloro-3-fluoro-2-phenylbut-3-en-1-yl)-4-methoxybenzene **6** in 74% yield (for all details see page S36).

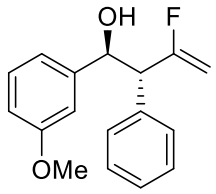
Therefore, the procedure **B** on 1.0 mmol scale was modified in the following way: After completion of the borylation step, 2.0 mmol of NaOAc were added, and the reaction mixture was stirred for additional 1 hour at 60°C in order to convert ClBpin (a stoichiometric by-product of the borylation) into less acidic AcOBpin. Anisaldehyde was further added in the same way as in the procedure B. Chromatographic purification (*n*-hexane/EtOAc, 3/1) gave **5ac** as a colorless oil (251.3 mg, 92%, *anti/syn* = 98/2).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 2.31 (br. s, 1H, OH), 3.69 (dd, 1H, C*H*Ph, *J* = 24.7, 9.5 Hz), 3.71 (s, 3H, OCH_3), 4.61 (dd, 1H, =CH_2, *J* = 50.1, 3.0 Hz), 4.77 (ddd, 1H, =CH_2, *J* = 17.8, 3.0, 0.5 Hz), 5.03 (d, 1H, C*H*(OH), *J* = 9.4 Hz), 6.67–6.73 (m, 2H, arom.), 7.00–7.21 (m, 7H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –101.2 (ddd, *J* = 50.1, 24.7, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 55.2 (s, OCH_3), 57.8 (d, *C*H(Ph), *J* = 23.6 Hz), 74.7 (d, CH(OH), *J* = 3.1 Hz), 93.0 (d, =CH_2, *J* = 19.8 Hz), 127.2 (s, CH-arom.), 128.0 (s, CH-arom.), 128.4 (s, CH-arom.), 128.6 (d, CH-arom., *J* = 1.9 Hz), 133.6 (s, C-arom.), 137.6 (d, C-arom., *J* = 2.3 Hz), 159.2 (s, C-arom.), 165.4 (d, =CF–, *J* = 262 Hz). **MS (EI)** ***m/z*** 137 (100), 135 (12), 133 (14), 115 (24), 109 (28), 94 (22), 77 (25), 66 (11). **Anal.:** calcd. for $C_{17}H_{17}FO_2$: C, 74.98%; H, 6.29%. Found: C, 74.62%; H, 6.28%.

2-Fluoro-3-phenyl-4-(3-methoxyphenyl)but-1-en-4-ol (5ad)

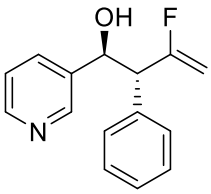
Obtained by the procedure **B** on 1.0 mmol scale after column chromatography (*n*-hexane/EtOAc, 4/1) as a colorless oil (242.4 mg, 89%, *anti/syn* = 99/1).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 2.36 (br. d, 1H, OH, *J* = 2.7 Hz), 3.66 (s, 3H, OCH_3), 3.70 (dd, 1H, C*H*Ph, *J* = 24.7, 9.2 Hz), 4.61 (dd, 1H, =CH_2, *J* = 50.1, 3.1 Hz), 4.78 (dd, 1H, =CH_2, *J* = 17.8, 3.1 Hz), 5.05 (dd, 1H, C*H*(OH), *J* = 9.3, 2.7 Hz), 6.65–6.72 (m, 3H, arom.), 7.04–7.22 (m, 6H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –101.0 (ddd, *J* = 50.1, 24.6, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 55.2 (s, OCH_3), 57.7 (d, *C*H(Ph), *J* = 23.6 Hz), 75.0 (d, CH(OH), *J* = 3.0 Hz), 93.1 (d, =CH_2, *J* = 19.7 Hz), 112.1 (s, CH-arom.), 113.7 (s, CH-arom.), 119.1 (s, CH-arom.), 127.3 (s, CH-arom.), 128.4 (s, CH-arom.), 128.6 (d, CH-arom., *J* = 1.9 Hz), 129.1 (s, CH-arom.), 137.5 (d, C-arom., *J* = 2.3 Hz), 143.0 (s, C-arom.), 159.4 (s, C-arom.), 165.1 (d, =CF–, *J* = 262 Hz). **MS (EI) *m/z*** 272 ([M^+], 2), 137 (71), 136 (100), 133 (25), 115 (34), 109 (94), 94 (27), 77 (22), 66 (9), 65 (8). **Anal.:** calcd. for $C_{17}H_{17}FO_2$: C, 74.98%; H, 6.29%. Found: C, 74.65%; H, 6.40%.

2-Fluoro-3-phenyl-4-(3-pyridyl)but-1-en-4-ol (5ae)

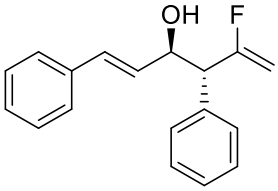
Obtained by the procedure **A** after column chromatography (gradient from CH_2Cl_2 to CH_2Cl_2/MeOH 25/1) as a colorless solid (106.4 mg, 88%, *anti/syn* = 97/3, mp 78–79°C).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 3.67 (dd, 1H, C*H*(Ph), *J* = 24.4, 9.4 Hz), 4.24 (br. s, 1H, OH), 4.62 (dd, 1H, =CH_2 (*trans*- to F), *J* = 50.0, 3.1 Hz), 4.79 (dd, 1H, =CH_2 (*cis*- to F), *J* = 17.8, 3.1 Hz), 5.07 (d, 1H, C*H*(OH), *J* = 9.4 Hz), 7.00–7.12 (m, 3H, Ph + Py), 7.21 – 7.12 (m, 3H, Ph), 7.47 (dt, 1H, Py, *J* = 7.9, 2.0 Hz), 8.16 (d, 1H, Py *J* = 2.2 Hz), 8.26 (dd, 1H, Py, *J* = 4.8, 1.7 Hz). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –101.7 (ddd, *J* = 50.0, 24.4, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 57.8 (d, *C*H(Ph), *J* = 23.8 Hz), 72.6 (d, CH(OH), *J* = 3.0 Hz), 93.4 (d, =CH_2, *J* = 19.6 Hz), 123.1 (s, CH-arom.), 127.6 (s, CH-arom.), 128.5 (d, CH-arom., *J* = 2.0 Hz), 128.7 (s, CH-arom.), 134.5 (s, CH-arom.), 136.9 (d, C-arom., *J* = 2.3 Hz), 137.6 (s, C-arom.), 148.3 (s, CH-arom.), 148.6 (s, CH-arom.), 164.7 (d, –CF=, *J* = 261.7 Hz). **MS (EI) *m/z*** 136 (100), 115 (60), 108 (80), 89 (8), 80 (59), 78 (24), 63 (9), 53 (37), 51 (23). **HRMS (ESI)**, calcd. for $C_{15}H_{14}FNO$: *m/z* 244.1132 [*M*+H^+]. Found: *m/z* 244.1139 [*M*+H^+].

2-Fluoro-3,6-diphenylhexa-1,5-dien-4-ol (5af)

Obtained by the procedure **A** after column chromatography (*n*-hexane/EtOAc, gradient from 10/1 to 5/1) as a light brown oil (93.8 mg, 70%, *anti/syn* = 93/7).

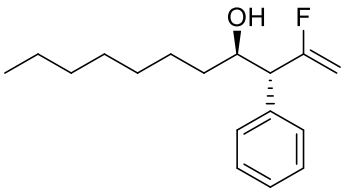


^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 2.12 (br. s, 1H, OH), 3.59 (dd, 1H, C*H*(Ph), *J* = 23.0, 8.4 Hz), 4.58 (dd, 1H,=CH_2 (*trans*- to F), *J* = 50.3,

3.1 Hz), 4.77 (dd, 1H, =CH_2 (*cis*- to F), *J* = 17.9, 3.1 Hz), 4.77 (m, 1H, C*H*(OH)), 6.06 (dd, 1H, =C*H*–CH(OH), *J* = 15.9, 6.2 Hz), 6.53 (dd, 1H, Ph–C*H*=, *J* = 15.9, 1.3 Hz), 7.15–7.43 (m, 10H, 2Ph). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –100.5 (ddd, *J* = 50.3, 23.0, 17.9 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 56.3 (d, *C*H(Ph), *J* = 23.8 Hz), 72.8 (d, CH(OH), *J* = 3.1 Hz), 93.1 (d, =CH_2, *J* = 19.6 Hz), 126.5 (s, CH-arom.), 127.6 (s, CH-arom.), 127.8 (s, CH-arom.), 128.5 (s, CH-arom.), 128.7 (d, CH-arom., *J* = 1.4 Hz), 128.7 (s, CH-arom.), 129.3 (s, =*C*H–CH(OH)), 131.8 (s, Ph–*C*H=), 136.6 (s, C-arom.), 137.3 (d, C-arom., *J* = 1.3 Hz), 165.0 (d, –CF=, *J* = 261.3 Hz). **MS (EI) *m/z*** 268 ([M^+], 1), 224 (7), 164 (4), 146 (8), 133 (71), 115 (100), 109 (11), 105 (90), 91 (23), 83 (7), 77 (59), 65 (6), 51 (10). **Anal.:** calcd. for $C_{18}H_{17}FO$: C, 80.57%; H, 6.39%. Found: C, 80.20%; H, 6.45%.

2-Fluoro-3-phenylundec-1-en-4-ol (5ag)

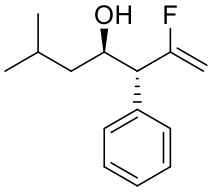
Obtained by the procedure **A** in the presence of additional 10 mol % of $Sc(OTf)_3$ after column chromatography (*n*-hexane/EtOAc, 10/1) as a colorless oil which solidified upon storage (97.2 mg, 74%, *anti/syn* = 96/4, mp 43–44°C).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 0.85 (m, 3H, CH_3, *J* = 6.7 Hz), 1.11–1.55 (m, 12H, 6CH_2), 1.94 (br. s, 1H, OH), 3.39 (dd, 1H, C*H*(Ph), *J* = 25.1, 8.6 Hz), 4.06 (m, 1H, C*H*(OH), *J* = 6.3 Hz), 4.53 (dd, 1H, =CH_2 (*trans*- to F), *J* = 50.2, 3.0 Hz), 4.71 (dd, 1H, =CH_2 (*cis*- to F), *J* = 17.8, 3.0 Hz), 7.20–7.40 (m, 5H, Ph). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –100.5 (ddd, *J* = 50.2, 25.1, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 14.1 (s, CH_3), 22.7 (s, CH_2), 25.6 (s, CH_2), 29.2 (s, CH_2), 29.4 (s, CH_2), 31.8 (s, CH_2), 34.6 (s, CH_2), 56.4 (d, *C*H(Ph), *J* = 23.4 Hz), 71.9 (d, CH(OH), *J* = 2.4 Hz), 92.7 (d, =CH_2, *J* = 19.9 Hz), 127.4 (s, CH-arom.), 128.4 (d, CH-arom., *J* = 1.5 Hz), 128.8 (s, CH-arom.), 138.3 (d, CH-arom., *J* = 1.7 Hz), 165.6 (d, -CF=, *J* = 261.6 Hz). **MS (EI) *m/z*** 136 (100), 133 (27), 115 (91), 109 (12), 91 (8), 83 (4), 77 (4), 69 (24), 57 (17), 55 (21). **Anal.:** calcd. for $C_{17}H_{25}FO$: C, 77.23%; H, 9.53%. Found: C, 76.98%; H, 9.71%.

2-Fluoro-3-phenyl-6-methylhept-1-en-4-ol (5ah)

Obtained by the procedure **B** on 1.0 mmol scale in the presence of additional 10 mol % of $Sc(OTf)_3$ after column chromatography (*n*-hexane/EtOAc, 10/1) as a light brown oil which solidified upon storage (119.6 mg, 54%, *anti/syn* = 98/2, mp 44–45°C).

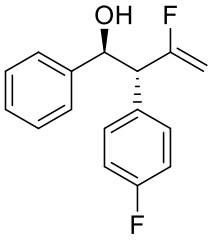


^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 0.79–0.89 (m, 6H, 2CH_3), 1.06 (ddd, 1H in CH_2, *J* = 14.0, 10.0, 2.5 Hz), 1.33 (ddd, 1H in CH_2, *J* = 14.0, 10.0, 4.1

Hz), 1.83 (m, 1H, C*H*$(CH_3)_2$), 1.91 (br. s, 1H, OH), 3.36 (dd, 1H, C*H*(Ph), *J* = 25.4, 8.5 Hz), 4.14 (m, 1H, C*H*(OH)), 4.53 (dd, 1H, =CH_2 (*trans*- to F), *J* = 50.3, 3.0 Hz), 4.71 (ddd, 1H, =CH_2 (*cis*- to F), *J* = 17.8, 3.0, 0.8 Hz), 7.22–7.37 (m, 5H, Ph). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –100.8 (ddd, *J* = 50.3, 25.4, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 21.4 (s, CH_3), 23.8 (s, CH_3), 24.6 (s, CH_2), 43.9 (s, *C*H$(CH_3)_2$), 57.0 (d, *C*H(Ph), *J* = 23.4 Hz), 70.0 (d, CH(OH), *J* = 2.3 Hz), 92.9 (d, =CH_2, *J* = 19.9 Hz), 127.4 (s, CH-arom.), 128.4 (d, CH-arom., *J* = 1.5 Hz), 128.8 (s, CH-arom.), 138.3 (d, C-arom., *J* = 1.6 Hz), 165.5 (d, –CF=, *J* = 261.6 Hz). **MS (EI) *m/z*** 136 ($[M - (CH_3)_2CHCH_2CH=O]^+$, 100), 135 (34), 115 (40), 109 (6), 91 (6), 69 (25). **Anal.:** calcd. for $C_{14}H_{19}FO$: C, 75.64%; H, 8.62%. Found: C, 75.46%; H, 8.80%.

2-Fluoro-3-(4-fluorophenyl)-4-phenylbut-1-en-4-ol (5ba)

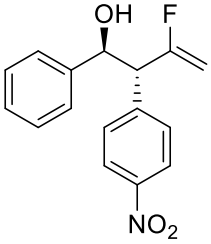
Obtained by the procedure **B** after column chromatography (*n*-hexane/EtOAc, 5/1) as a yellowish oil (101.7 mg, 78%, *anti/syn* > 20/1).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 2.43 (br. d, 1H, OH, *J* = 2.8 Hz), 3.69 (dd, 1H, C*H*(Ar), *J* = 24.5, 9.5 Hz), 4.62 (dd, 1H, =CH_2 (*trans*- to F), *J* = 50.1, 3.1 Hz), 4.79 (dd, 1H, =CH_2 (*cis*- to F), *J* = 17.8, 3.1 Hz), 5.00 (dd, 1H, C*H*(OH), *J* = 9.5, 2.8 Hz), 6.78–6.88 (m, 2H, arom.), 6.97–7.05 (m, 2H, arom.), 7.06–7.14 (m, 2H, arom.), 7.15–7.22 (m, 3H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –101.9 (ddd, 1F, –CF=, *J* = 50.1, 24.5, 17.8 Hz), –115.70 (m, 1F, arom.). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 57.0 (d, *C*H(Ar), *J* = 23.9 Hz), 75.1 (d, CH(OH), *J* = 2.1 Hz), 93.2 (d, =CH_2, *J* = 19.7 Hz), 115.2 (d, CH-arom., *J* = 21.3 Hz), 126.8 (s, CH-arom.), 128.0 (s, CH-arom.), 128.3 (s, CH-arom.), 130.1 (dd, CH-arom., *J* = 8.0, 2.1 Hz), 133.2 (dd, C-arom., *J* = 3.4, 2.4 Hz), 141.2 (s, C-arom.), 162.0 (d, CF-arom., *J* = 245.8 Hz), 164.9 (d, –CF=, *J* = 261.4 Hz). **MS (EI) *m/z*** 154 ($[M - Ph\text{-}CH=O]^+$, 66), 133 (35), 107 (89), 79 (100), 77 (80). **Anal.:** calcd. for $C_{16}H_{14}F_2O$: C, 73.83%; H, 5.42%. Found: C, 73.72%; H, 5.61%.

2-Fluoro-3-(4-nitrophenyl)-4-phenylbut-1-en-4-ol (5ca)

Obtained by the procedure **B** after column chromatography (*n*-hexane/EtOAc, 3/1) as a yellowish oil (102.1 mg, 71%, *anti/syn* > 20/1).

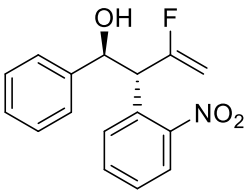


^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 2.53 (br. d, 1H, OH, *J* = 3.0 Hz), 3.85 (dd, 1H, C*H*(Ar), *J* = 24.1, 9.4 Hz), 4.70 (dd, 1H, =CH_2 (*trans*- to F), *J* = 49.9, 3.3 Hz), 4.86 (dd, 1H, =CH_2 (*cis*- to F), *J* = 17.7, 3.4 Hz), 5.07 (dd,

1H, C*H*(OH), *J* = 9.4, 2.9 Hz), 7.07–7.15 (m, 2H, arom.), 7.15–7.25 (m, 5H, arom.), 7.96–8.03 (m, 2H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –102.2 (ddd, *J* = 49.9, 24.1, 17.7 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 57.5 (d, *C*H(Ar), *J* = 24.0 Hz), 74.8 (d, CH(OH), *J* = 3.0 Hz), 94.2 (d, $=CH_2$, *J* = 19.3 Hz), 123.5 (s, CH-arom.), 126.7 (s, CH-arom.), 128.4 (s, CH-arom.), 128.5 (s, CH-arom.), 129.5 (d, CH-arom., *J* = 2.2 Hz), 140.5 (s, C-arom.), 144.9 (d, C-arom., *J* = 2.6 Hz), 147.1 (s, C-arom.), 163.6 (d, –CF=, *J* = 261.6 Hz). **MS (EI) *m/z*** 181 ([M – Ph-CH=O]$^+$, 48), 151 (37), 133 (39), 115 (59), 109 (38), 106 (42), 105 (43), 103 (37), 89 (10), 83 (19), 77 (100), 74 (23), 63 (26), 51 (67), 50 (48). **HRMS (ESI)**, calcd. for $C_{16}H_{14}FNO_3$: *m/z* 310.0850 [*M*+Na$^+$]. Found: *m/z* 310.0854 [*M*+Na$^+$].

2-Fluoro-3-(2-nitrophenyl)-4-phenylbut-1-en-4-ol (5da)

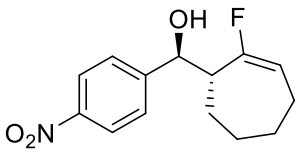
Obtained by the procedure **B** after column chromatography (*n*-hexane/EtOAc, gradient from 5/1 to 3/1) as a light brown oil (72.9 mg, 51%, *anti/syn* > 20/1).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: (spin system was simulated in Bruker TopSpin 3.5pl7) 2.41 (br. s, 1H, OH), 4.71 (dd, 1H, CH(Ar), *J* = 24.2, 8.6 Hz), 4.79 (dd, 1H, $=CH_2$, *J* = 49.6, 2.7 Hz), 4.85 (dd, $=CH_2$, *J* = 18.8, 2.7 Hz), 5.14 (d, 1H, CH(OH), *J* = 8.6 Hz), 7.10–7.22 (m, 5H, Ph), 7.30 (m, 1H, Ar(NO_2)), 7.52 (m, 1H, Ar(NO_2)), 7.60 (m, 1H, Ar(NO_2)), 7.72 (m, 1H, Ar(NO_2)). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –102.70 (dddd, *J* = 49.8, 24.0, 18.1, 1.6 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 50.2 (d, CH(Ar), *J* = 23.7 Hz), 74.9 (d, CH(OH), *J* = 3.0 Hz), 95.0 (d, $=CH_2$, *J* = 19.2 Hz), 124.6 (s, Ar), 126.5 (s, Ar), 128.1 (s, Ar), 128.3 (s, Ar), 128.6 (s, Ar), 130.3 (d, Ar, *J* = 4.0 Hz), 131.9 (d, Ar, *J* = 2.8 Hz), 132.5 (s, Ar), 149.8 (s, Ar), 163.0 (d, -CF=, *J* = 262 Hz). MS (EI) *m/z* 181 ([M – Ph-CH=O]$^+$, 5), 133 (22), 115 (16), 109 (16), 106 (39), 105 (41), 89 (10), 83 (15), 77 (100), 74 (25), 64 (50), 51 (66), 50 (49). **HRMS (ESI)**, calcd. for for $C_{16}H_{14}FNO_3$: *m/z* 310.0850 [*M*+Na$^+$]. Found: *m/z* 310.0846 [*M*+Na$^+$].

(2-Fluorocyclohept-2-enyl)(4-nitrophenyl)methanol (5eb)

Obtained by the procedure **B** after column chromatography (*n*-hexane/EtOAc, 5/1) as a yellowish oil which solidified upon storage (91.7 mg, 69%, *anti/syn* > 20/1, mp 112–114°C).

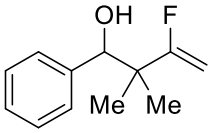


^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 1.39–2.27 (m, 8H, 4CH_2), 2.29 (br. d, 1H, OH), 2.74 (m, 1H, CH-cyclohept.), 5.20 (m, 1H, C*H*(OH)), 5.49 (ddd, 1H, =CH–, *J* = 23.7, 7.9, 5.4 Hz, 1H), 7.52–7.57 (m, 2H, arom.), 8.16–8.21 (m, 2H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –97.9 (dd, *J* = 23.7, 13.2 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 22.0 (d, CH_2, *J* = 11.4 Hz), 23.7 (d, CH_2,

J = 7.3 Hz), 25.3 (s, CH_2), 26.9 (s, CH_2), 49.8 (d, CH-cyclohept., *J* = 24.0 Hz), 72.2 (d, CH(OH), *J* = 1.4 Hz), 109.0 (d, =CH–, *J* = 22.3 Hz), 123.5 (s, CH-arom.), 127.1 (s, CH-arom.), 147.3 (s, C-arom.), 149.9 (s, C-arom.), 161.2 (d, –CF=, *J* = 249.0 Hz). **MS (EI) *m/z*** 266 ($[M+H]^+$, 0.4), 152 (100), 136 (33), 122 (19), 114 (98), 106 (39), 99 (29), 94 (43), 77 (52), 72 (13), 65 (17), 51 (17). **HRMS (ESI)**, calcd. for $C_{14}H_{16}FNO_3$: *m/z* 288.1006 [*M*+Na^+]. Found: *m/z* 288.0997 [*M*+Na^+].

2-Fluoro-3,3-dimethyl-4-phenylbut-1-en-4-ol (5fa)

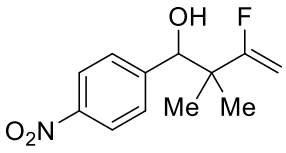
Obtained by the procedure **B** on 5.0 mmol scale after column chromatography (*n*-hexane/EtOAc, 7/1) as a yellow oil (513 mg, 53%).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 1.01 (s, 3H, CH_3), 1.11 (br. s, 3H, CH_3), 2.12 (br. d, 1H, OH, *J* = 2.6 Hz), 4.30 (dd, =CH_2 (*trans*- to F), *J* = 52.1, 3.1 Hz), 4.61 (dd, 1H, =CH_2 (*cis*- to F), *J* = 19.8, 3.1 Hz), 4.78 (d, 1H, C*H*(OH), *J* = 2.3 Hz), 7.22–7.34 (m, 5H, Ph). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –103.7 (dd, *J* = 52.1, 19.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 20.1 (d, CH_3, *J* = 3.9 Hz), 21.7 (d, CH_3, *J* = 2.9 Hz), 44.0 (d, *C*$(CH_3)_2$, *J* = 21.5 Hz), 77.3 (s, CH(OH)), 90.6 (d, =CH_2, *J* = 21.4 Hz), 127.63–127.73 (m, 3CH-arom.), 140.2 (s, C-arom.), 171.0 (d, –CF=, *J* = 260.5 Hz). **MS (EI) *m/z*** 107 (82), 88 (56), 79 (100), 77 (62), 73 (21). **Anal.:** calcd. for $C_{12}H_{15}FO$: C, 74.20%; H, 7.78%. Found: C, 74.13%; H, 7.91%.

2-Fluoro-3,3-dimethyl-4-(4-nitrophenyl)but-1-en-4-ol (5fb)

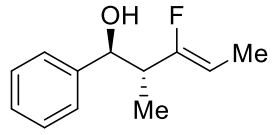
Obtained by the procedure **B** after column chromatography (*n*-hexane/EtOAc, 5/1) as a colorless solid (78.6 mg, 61%, mp 79–80°C).



^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 1.02 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.34 (br. s, 1H, OH), 4.30 (dd, 1H, =CH_2 (*trans*- to F), *J* = 51.9, 3.3 Hz), 4.64 (dd, 1H, =CH_2 (*cis*- to F), *J* = 19.8, 3.3 Hz), 4.90 (s, 1H, C*H*(OH)), 7.48–7.53 (m, 2H, arom.), 8.13–8.18 (m, 2H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –103.4 (dd, *J* = 51.9, 19.8 Hz). **^{13}C NMR (100.6 MHz, $CDCl_3$) δ:** 20.8 (d, CH_3, *J* = 3.5 Hz), 20.8 (d, CH_3, *J* = 3.3 Hz), 44.2 (d, *C*$(CH_3)_2$, *J* = 21.7 Hz), 76.5 (s, CH(OH)), 91.4 (d, =CH_2, *J* = 21.0 Hz), 122.8 (s, CH-arom.), 128.5 (s, CH-arom.), 147.5 (s, C(NO_2)-arom.), 147.7 (s, C-arom.), 170.0 (d, –CF=, *J* = 260.1 Hz). **MS (EI) *m/z*** 152 (39), 136 (9), 122 (10), 106 (23), 94 (20), 88 (100), 77 (34), 73 (19), 67 (16), 59 (12), 51 (17). **HRMS (ESI)**, calcd. for $C_{12}H_{14}FNO_3$: *m/z* 262.0850 [*M*+Na^+]. Found: *m/z* 262.0847 [*M*+Na^+].

3-Fluoro-2-methyl-1-(4-phenyl)pent-3-en-1-ol (5ga)

Obtained by the modified procedure **B**: a solution of **3g** in DCE, prepared as above from 1.0 mmol of **1g** (*Z*/*E* = 92/8), was added to freshly activated powdered Linde type molecular sieves 4A (100 mg). At –30°C $BF_3{\cdot}Et_2O$ (25 μL, 0.20 equiv.) was added and the mixture was stirred for 5 min. Then, PhCHO (122 μL, 1.2 equiv.) were added and the reaction mixture was stirred for 5 hours maintaining the temperature from –35 to –30°C. After aqueous work-up and column chromatography (*n*-hexane/EtOAc, 10/1), **5ga** was obtained as a colorless solid (111.3 mg, 57%, *anti*/*syn* > 20/1, *Z*/*E* > 20/1, mp 63–64°).

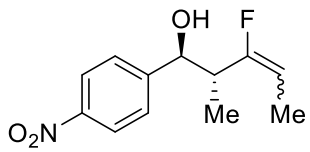


^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 0.86 (d, 3H, CH_3, *J* = 7.1 Hz), 1.63 (dd, 3H, CH_3, *J* = 6.9, 2.3 Hz), 2.26 (br. s, 1H, OH), 2.53 (ddq, 1H, C*H*(Me), *J* = 25.3, 8.7, 7.1 Hz), 4.57 (br. d, C*H*(OH), *J* = 8.5 Hz), 4.70 (dq, =C*H*Me, *J* = 38.1, 6.9 Hz), 7.23–7.38 (m, 5H, Ph). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –120.9 (ddq, *J* = 38.1, 25.2, 2.3 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 8.9 (d, CH_3, *J* = 6.9 Hz), 14.2 (d, CH_3, *J* = 2.0 Hz), 45.4 (d, *C*H(Me), *J* = 24.9 Hz), 75.5 (s, CH(OH)), 102.0 (d, =*C*HMe, *J* = 15.9 Hz), 126.9 (s, CH-arom.), 128.0 (s, CH-arom.), 128.4 (s, CH-arom.), 141.9 (s, C-arom.), 160.4 (d, -CF=, *J* = 256 Hz). MS (EI) *m*/*z* 194 ([M^+], 0.1), 107 (100), 79 (44), 77 (22), 51 (3). **Anal.:** calcd. for $C_{12}H_{15}FO$: C, 74.20%; H, 7.78%. Found: C, 74.10%; H, 7.87%.

3-Fluoro-2-methyl-1-(4-nitrophenyl)pent-3-en-1-ol (5gb)

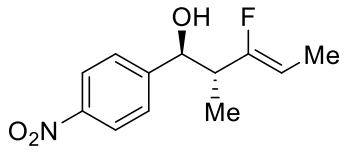
Obtained by the procedure **B** after column chromatography (*n*-hexane/EtOAc, 5/1) as a yellowish oil (81.6 mg, 68%, *anti*/*syn* > 20/1, *Z*/*E* = 39/61).

Using the procedure described for **5ga** (e.g. the reaction with aldehyde was carried out in the presence of 20 mol % of $BF_3{\cdot}Et_2O$ at –35 — –30°C for 5 hours) on 1.0 mmol scale, **5gb** was obtained as almost pure *Z*-isomer (a yellow oil, 177.5 mg, 74%, *anti*/*syn* > 20/1, *Z*/*E* = 98/2).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 0.93 (d, 3H, CH_3, *Z*-**5gb**, *J* = 7.1 Hz), 0.98 (d, 3H, CH_3, *E*-**5gb**, *J* = 7.0 Hz), 1.53 (dd, 3H, CH_3, *E*-**5gb**, *J* = 7.2, 2.3 Hz), 1.62 (dd, 3H, CH_3, *Z*-**5gb**, *J* = 6.9, 2.4 Hz), 2.50 (br. d, 1H, OH, both isomers, *J* = 2.5 Hz), 2.57 (ddq, 1H, *C*H(CH_3), *Z*-**5gb**, *J* = 23.0, 7.1, 7.1 Hz), 2.90 (ddq, 1H, *C*H(CH_3), *E*-**5gb**, *J* = 30.9, 8.3, 7.0 Hz), 4.68 (dq, 1H, =CH–, *Z*-**5gb**, *J* = 38.1, 6.9 Hz), 4.70–4.80 (m, 1H, CH(OH), both isomers), 5.27 (dq, 1H, =CH–, *E*-**5gb**, *J* = 22.4, 7.2 Hz), 7.45–7.58 (m, 2H, arom., both isomers), 8.15–8.24 (m, 2H, arom., both isomers). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –118.4 (dd, *E*-**5gb**, *J* = 30.9, 22.4 Hz), –119.3 (dd, *Z*-**5gb**, *J* = 38.1, 23.0). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ: (*Z*-5gb):** 8.8 (d, CH_3, *J* = 6.8 Hz), 13.6 (d, CH_3, *J* = 2.7 Hz), 45.2 (d, *C*H(CH_3), *J* = 24.8 Hz), 74.5 (s, CH(OH)), 102.9 (d, –

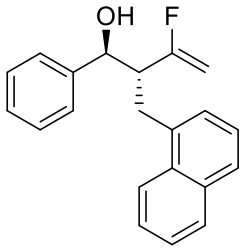
CH=, *J* = 15.6 Hz), 123.4 (s, CH-arom.), 127.7 (s, CH-arom.), 147.6 (s, C-arom.), 149.2 (s, CH-arom.), 159.3 (d, –CF=, *J* = 255.2 Hz); **(*E*-5gb):** 10.2 (d, CH_3, *J* = 9.8 Hz), 13.8 (d, CH_3, *J* = 1.6 Hz), 40.6 (d, *C*H(CH_3), *J* = 25.5 Hz), 75.1 (s, CH(OH)), 103.5 (d, –CH=, *J* = 23.4 Hz), 123.6 (s, CH-arom.), 127.7 (s, CH-arom.), 147.7 (s, C-arom.), 149.6 (s, C-arom.), 159.2 (d, –CF=, *J* = 247.3 Hz). **MS (EI) *m/z*** (for both isomers) 152 (93), 136 (10), 122 (18), 106 (24), 94 (30), 88 (100), 77 (31), 67 (32), 59 (18), 51 (15). **HRMS (ESI)**, calcd. for $C_{12}H_{14}FNO_3$: *m/z* 262.0850 [*M*+Na^+]. Found: *m/z* 262.0861 [*M*+Na^+].



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 0.93 (d, 3H, CH_3, *Z*-**5gb**, *J* = 7.1 Hz), 1.62 (dd, 3H, CH_3, *Z*-**5gb**, *J* = 6.9, 2.4 Hz), 2.43 (br. d, 1H, OH, *J* = 2.7 Hz), 2.57 (ddq, 1H, *C*H(CH_3), *Z*-**5gb**, *J* = 23.0, 7.1, 7.1 Hz), 4.68 (dq, 1H, =CH–, *Z*-**5gb**, *J* = 38.1, 6.9 Hz), 4.70–4.80 (m, 1H, CH(OH)), 7.45–7.53 (m, 2H, arom.), 8.15–8.23 (m, 2H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –119.3 (dd, *Z*-**5gb**, *J* = 38.1, 23.0). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 8.8 (d, CH_3, *J* = 6.8 Hz), 13.6 (d, CH_3, *J* = 2.7 Hz), 45.2 (d, *C*H(CH_3), *J* = 24.8 Hz), 74.5 (s, CH(OH)), 102.9 (d, –CH=, *J* = 15.6 Hz), 123.4 (s, CH-arom.), 127.7 (s, CH-arom.), 147.6 (s, C-arom.), 149.2 (s, CH-arom.), 159.3 (d, –CF=, *J* = 255.2 Hz).

3-Fluoro-2-(naphthalene-1-ylmethyl)-1-phenylbut-3-en-1-ol (5ha)

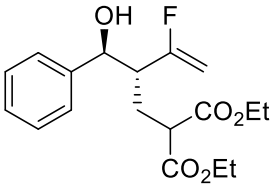
Obtained by procedure **B** after column chromatography (*n*-hexane/EtOAc, 5/1) as a light brown solid (81.6 mg, 68%, *anti/syn* = 96/4). This compound could be additionally purified by crystallization from *n*-hexane affording 40.0 mg of **5ha** as colorless needles (*anti/syn* > 20/1).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 2.29 (br. d, 1H, OH, *J* = 3.1 Hz), 2.77–2.99 (m, 1H, C*H*CH_2Naphth), 2.98–3.07 (m, 2H, CH_2Naphth), 3.99 (dd, 1H, =CH_2, *J* = 50.7, 2.9 Hz), 4.55 (dd, 1H, =CH_2, *J* = 17.7, 2.7 Hz), 4.80 (dd, 1H, CH(OH), *J* = 8.3, 3.0 Hz), 7.23 (d, 1H, arom., *J* = 6.6 Hz), 7.27–7.52 (m, 9H, arom.), 7.67 (d, 1H, arom., *J* = 8.1 Hz), 7.79 (d, 1H, arom., *J* = 8.0 Hz). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –108.0 (ddd, *J* = 50.7, 27.3, 17.8 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 31.4 (s, CH_2Naphth), 53.0 (d, *C*HCH_2Naphth, *J* = 23.9 Hz), 74.5 (s, CH(OH),), 94.9 (d, =CH_2, *J* = 19.3 Hz), 123.4 (s, arom.), 125.4 (s, arom.), 125.4 (s, arom.), 125.9 (s, arom.), 127.1 (s, arom.), 127.2 (s, arom.), 127.6 (s, arom.), 128.5 (s, arom.), 128.8 (s, arom.), 128.9 (s, arom.), 131.7 (s, arom.), 134.0 (s, arom.), 135.1 (s, arom.), 142.0 (s, arom.), 163.9 (d, -CF=, *J* = 260 Hz). **MS (EI) *m/z*** 200 ([M – Ph-CH=O]$^+$, 68), 185 (33), 179 (31), 165 (100), 153 (59), 139 (10), 127 (15), 106 (38), 77 (66), 63 (19), 51 (58). **Anal.:** calcd. for $C_{21}H_{19}FO$: C, 82.33%; H, 6.25%. Found: C, 82.20%; H, 6.41%.

Diethyl 2-[3-fluoro-2-(hydroxy(phenyl)methyl)but-3-en-1-yl]malonate (5ia)

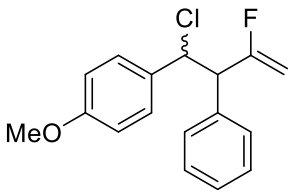
Obtained by procedure **B** after column chromatography (*n*-hexane/EtOAc, 3/1) as a light brown oil (114.0 mg, 65%, *anti/syn* = 97/3).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 1.18 (t, 3H, CH_3, *J* = 7.3 Hz), 1.21 (t, 3H, CH_3, *J* = 7.3 Hz), 1.66–1.83 (m, 1H, CH_2), 1.88–1.98 (m, 1H, CH_2), 2.36 (br. s, 1H, OH), 2.52–2.76 (m, 1H, C*H*-CF=CH_2), 3.37 (dd, 1H, C*H*$(CO_2Et)_2$, *J* = 10.9, 4.3 Hz), 4.11 (q, 2H, C*H*$_2$$CH_3$, *J* = 7.3 Hz), 4.12 (q, 2H, C*H*$_2$$CH_3$, *J* = 7.3 Hz), 4.41 (dd, 1H, =CH_2, *J* = 50.2, 2.9 Hz), 4.65 (d, 1H, CH(OH), *J* = 8.4 Hz), 4.78 (dd, 1H, =CH_2, *J* = 17.5, 2.9 Hz), 7.18–7.42 (m, 5H, arom.). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ**: –107.3 (ddd, *J* = 50.2, 27.6, 17.6 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ**: 14.0 (s, CH_3), 14.0 (s, CH_3), 26.9 (s, *C*H_2CH$(CO_2Et)_2$), 48.7 (d, *C*H-CF=CH_2, *J* = 24.1 Hz), 49.7 (s, *C*H$(CO_2Et)_2$), 61.4 (s, *C*$H_2$$CH_3$), 61.6 (s, *C*$H_2$$CH_3$), 74.5 (s, CH(OH)), 95.0 (d, =CH_2, *J* = 19.1 Hz), 126.9 (s, arom.), 128.3 (s, arom.), 128.6 (s, arom.), 141.2 (s, arom.), 163.55 (d, -CF=, *J* = 261 Hz), 168.7 (s, C=O), 169.1 (s, C=O). **MS (EI) *m/z*** 232 ([M – Ph-CH=O]$^+$, 31), 187 (5), 160 (100), 141 (8), 133 (25), 113 (19), 107 (33), 105 (18), 88 (13), 86 (16), 82 (15), 79 (44), 77 (51), 72 (34). **Anal.:** calcd. for $C_{18}H_{23}FO_5$: C, 63.89%; H, 6.85%. Found: C, 63.67%; H, 7.01%.

1-(1-Chloro-3-fluoro-2-phenylbut-3-en-1-yl)-4-methoxybenzene (6)

Obtained by the non-modified procedure **B** on 1.0 mmol scale after column chromatography (*n*-hexane/EtOAc, 7/1) as a colorless waxy solid (188.5 mg, 74%, d.r. 54/46).



^{1}H NMR (300.1 MHz, $CDCl_3$) δ: 3.69 (s, 3H, OMe, major), 3.79 (s, 3H, OMe, minor), 3.98 (dd, 1H, C*H*Ph, minor, *J* = 25.0, 10.3 Hz), 4.00 (dd, 1H, C*H*Ph, major, *J* = 25.9, 11.0 Hz), 4.21 (dd, 1H, =CH_2, minor, *J* = 49.5, 3.3 Hz), 4.37 (dd, 1H, =CH_2, minor, *J* = 17.6, 3.3 Hz), 4.63 (dd, 1H, =CH_2, major, *J* = 49.4, 3.3 Hz), 4.75 (dd, 1H, =CH_2, major, *J* = 17.7, 3.5 Hz), 5.28 (d, 1H, CHCl, major, *J* = 11.0 Hz), 5.33 (d, 1H, CHCl, minor, *J* = 10.3 Hz), 6.62–6.73 (m, 2H, arom., major), 6.82–6.92 (m, 2H, arom., minor), 7.00–7.19 (m, 7H, arom., major), 7.26–7.46 (m, 7H, arom., minor). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –103.7 (ddd, minor, *J* = 49.5, 25.0, 17.6 Hz), –105.9 (ddd, major, *J* = 49.4, 25.9, 17.4 Hz). **^{13}C NMR (75.5 MHz, $CDCl_3$) δ:** 55.2 (s, OCH_3, major), 55.3 (s, OCH_3, minor), 58.3 (d, *C*HPh, major, *J* = 24.4 Hz), 58.4 (d, *C*HPh, minor, *J* = 23.1 Hz), 62.0 (d, CH(OH), major, *J* = 2.8 Hz), 63.1 (s, CH(OH), minor), 93.0 (d, =CH_2, major, *J* = 19.6 Hz), 93.1 (d, =CH_2, minor, *J* = 19.3 Hz), 113.8 (s, CH-arom., major), 114.0 (s, CH-arom., minor), 127.5 (s, CH-arom.), 127.9 (s, CH-

arom.), 128.3 (s, CH-arom.), 128.3 (s, CH-arom.), 128.6 (m, CH-arom.), 128.8 (s, CH-arom.), 129.0 (s, CH-arom.), 131.3 (s, C-arom., major), 131.9 (s, C-arom., minor), 137.6 (d, C-arom., major, J = 2.9 Hz), 137.9 (d, C-arom., minor, J = 1.6 Hz), 159.4 (s, C-arom., major), 159.8 (s C-arom., minor), 163.8 (d, =CF–, minor, J = 261 Hz), 164.6 (d, =CF–, major, J = 262 Hz). **MS (EI)** ***m/z*** 290/292 ([M^+], 3/1), 254 (1), 157 (33), 155 (100), 133 (6), 115 (9), 91 (5), 77 (4). **Anal.:** calcd. for $C_{17}H_{16}ClFO$: C, 70.22%; H, 5.55%. Found: C, 70.22%; H, 5.47%.

6. References

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