Supplementary Information

(2-Fluoroallyl)pyridinium tetrafluoroborates: novel fluorinated electrophiles for Pd-catalyzed allylic substitution

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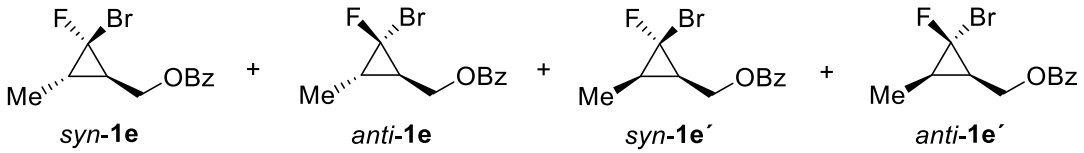
1. General information

All reagents were purchased from Acros, Aldrich or ABCR and used without further purification. THF was distilled over Na-benzophenone ketyl anion-radical and stored over 4A Linde type molecular sieves. DMSO was distilled over CaH_2 under reduced pressure and stored over 4A Linde type molecular sieves. All reactions were carried out under argon atmosphere using standard Schlenk technique. Silica gel 60 (40–63 μm, Macherey-Nagel) 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 5000.2 gas chromatographer (column J&W Scientific DB-5+, 30 m x 0.245 mm, 5%-phenyl-95%-dimethylpolysiloxane 0.25 μm, carrier gas – He, detector – FID). ^{1}H, ^{19}F and ^{13}C NMR were recorded on Varian Inova 400 (400.1, 376.4 and 100.6 MHz, respectively) or Bruker AVANCE II 300 (300.1, 282.3 and 75.4 MHz, respectively) in $CDCl_3$ containing TMS and C_6F_6 as internal standards or in DMSO-d_6. Chemical shifts in $CDCl_3$ were measured relative to TMS (δ = 0 ppm) for ^{1}H, $CDCl_3$ (δ = 77.1 ppm) for ^{13}C, or C_6F_6 (δ = –162.2 ppm) for ^{19}F. Chemical shifts in DMSO-d_6 were measured relative to residual DMSO-d_5 (δ = 2.50 ppm) for ^{1}H, DMSO-d_6 (δ = 39.5 ppm) for ^{13}C, or relative to $CFCl_3$ (δ = 0.0 ppm) used as an external standard. GC/MS analysis was performed on Chromatec Crystal 5000.2 gas chromatographer equipped with Chromatec Quadrupole mass-detector (EI, 70 eV, 200°C) and Chromatec CR-5MS chromatographic column (30 m x 0.25 mm, 5%-phenyl-95%-dimethylpolysiloxane 0.25 μm). For non-volatile compounds, MS data were registered on Finnigan MAT INCOS-50 (EI, 70 eV) using direct probe injections. HRMS were recorded on Bruker micrOTOF equipment using electro-spray ionization (ESI). Melting points were determined on Stuart SMP10 and reported uncorrected. Elemental analyses were made in Laboratory of microanalysis IOC RAS on Perkin-Elmer Series II 2400 CHN Analyzer.

2. Synthesis of *gem*-bromofluorocyclopropanes

gem-Bromofluorocyclopropanes **1** were synthesized by cyclopropanation of alkenes according to previously published procedures using either $CHBr_2F$ under PTC conditions (**1a**, **1b**, **1c**, **1h**, **1j**, see ref. [1]), or CBr_2FCO_2Na under (IPr)AgCl catalysis (**1d**, **1e**, **1f**, **1g**, **1i**, **1k**, see ref. [2]). Cyclopropanes **1e** and **1i** were not previously published, detailed procedures and characterization data for them are listed below.

(2-Bromo-2-fluoro-3-methylcyclopropyl)methyl benzoate 1e



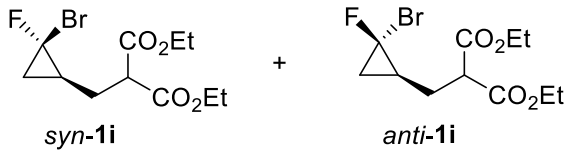
syn-**1e** *anti*-**1e** *syn*-**1e´** *anti*-**1e´**

Obtained by the standard procedure (see ref. [2]) from crotyl benzoate (8.825g, 50 mmol, *E/Z* = 80/20), $CFBr_2CO_2Na$ (29.433 g, 144 mmol), (IPr)AgCl (556 mg, 1.0 mmol, 2 mol.%) and anhydrous DCE (100 mL).

A mixture of $CFBr_2CO_2Na$ and (IPr)AgCl was loaded into three-neck round-bottom flask and dried under high vacuum on a Schlenk line with stirring for 2 h (at this point, if $CFBr_2CO_2Na$ is dried alone, then activation period of 1–2 h was noted previously on model cyclopropanation of styrene). Next, the flask was filled with argon, DCE was added, and the reaction was stirred at 80°C (oil bath) under argon atmosphere while being opened to a Schlenk line for 7 h in the first day plus 9 h in the second day. The reaction progress was monitored by GC. [NOTE: reflux conditions must be avoided. Presumably, if CO_2 is removed from reaction mixture due to reflux, it results in too fast decomposition of $CFBr_2CO_2Na$, and low yield of cyclopropane is observed]. After the reaction complete, it was transferred to a round bottom flask with CH_2Cl_2 and evaporated with Celite (18 g) on a rotary evaporator. The residue was dry loaded on a short silica column (80 g) and eluted with *n*-hexane/EtOAc 10/1 affording **1e** as a yellow oil (12.467 g, 87% yield, *syn*-**1e**/*anti*-**1e**/*syn*-**1e´**/*anti*-**1e´** = 49/33/12/6).

(For the mixture of isomers): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 8.21 – 8.00 (m, 2H), 7.70 – 7.37 (m, 3H), 4.61 – 4.17 (m, 2H), 2.10 – 1.97 and 1.85 – 1.71 and 1.70 – 1.55 and 1.54 – 1.41 (m, 2H total, isomers could not be assigned), 1.33 – 1.18 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –122.7 (t, *J* = 19.5 Hz, *syn*-**1e´**), –141.6 (d, *J* = 21.6 Hz, *anti*-**1e**), –143.6 (d, *J* = 18.9 Hz, *syn*-**1e**), –160.9 (s, *anti*-**1e´**). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** (isomers could not be assigned, some signals of minor isomers were lost due to low intensity or overlapped with other peaks) 166.5 – 166.2 (m, C=O), 133.2 – 133.0 (m), 133.1, 130.6, 123.0 – 129.8 (m), 129.7, 129.7, 128.9, 128.4 (aromatic C and CH), 91.4 (d, *J* = 300.7 Hz, CF), 88.8 (d, *J* = 301.1 Hz, CF), 86.8 (d, *J* = 301.9 Hz, CF), 65.4 (s, CH_2), 62.1 (s, CH_2), 61.9 (d, *J* = 7.7 Hz, CH_2), 58.7 (d, *J* = 7.1 Hz, CH_2), 33.5 (d, *J* = 10.5 Hz, CH), 30.1 (d, *J* = 10.0 Hz, CH), 28.1 (d, *J* = 10.6 Hz, CH), 26.4 (d, *J* = 11.2 Hz, CH), 26.1 (d, *J* = 10.9 Hz, CH), 25.0 (d, *J* = 9.5 Hz, CH), 23.5 (d, *J* = 10.0 Hz, CH), 15.8 (s, CH_3), 11.2 (d, *J* = 6.4 Hz, CH_3), 10.8 (s, CH_3). **MS (EI) *m/z*** 286, 288 ([*M*]$^+$, 2, 3), 148 (6), 105 (100), 85 (5), 77 (17). **HRMS (ESI), *m/z*:** [*M*+Na]$^+$, Calcd. for $C_{12}H_{12}BrFO_2Na^+$ 308.9897 and 310.9877. Found 308.9892 and 310.9872.

Diethyl 2-((2-bromo-2-fluorocyclopropyl)methyl)malonate 1i



syn-**1i** *anti*-**1i**

Obtained by the standard procedure (see ref. [2]) from diethyl allylmalonate (5.00 g, 25 mmol), $CFBr_2CO_2Na$ (32.25 g, 125 mmol), (IPr)AgCl (279 mg, 0.52 mmol, 2 mol.%) and anhydrous DCE (100 mL) at 80°C (oil bath) for 46 h total. The procedure was similar to the described above, but $CFBr_2CO_2Na$ was added in 4 portions — 50 mmol were added first, then the reaction was heated for 7 h, after that 25 mmol were added followed by 10 h of heating, then 25 mmol more and 9 h of heating, then again 25 mmol and 20 h of heating. Work-up as above using *n*-hexane/EtOAc 7/1 for chromatography afforded **1i** as an orange oil (6.621 g, ca. 70% yield, *syn*-**1i**/*anti*-**1i** = 49/51, contained ca. 15 w/w % of side products, presumably, resulted from radial addition of $CFBr_2$ and Br to the C=C bond similar to previously published[2]).

(For the mixture of isomers): **^{1}H NMR (300.0 MHz, $CDCl_3$) δ:** 4.30 – 4.17 (m, 4H), 3.57 – 3.45 (m, 1H), 2.18 – 2.07 and 2.06 – 1.93 (m, 2H total), 1.75 – 1.38 and 1.35 – 1.15 and 1.04 – 0.93 (m, 2H total), 1.32–1.25 (m, 6H). **^{19}F NMR (282.4 MHz, $CDCl_3$) δ:** –128.0 (dddd, *J* = 19.4, 17.1, 7.2, 2.5 Hz, *syn*-**1i**), –149.6 (br. dd, *J* = 17.6, 7.5 Hz, *anti*-**1i**). **^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ:** 168.9 (s, C=O), 168.8 (s, C=O), 168.7 (s, C=O), 168.7 (s, C=O), 86.1 (d, *J* = 298.3 Hz, CF), 81.2 (d, *J* = 300.7 Hz, CF), 61.7 (s, CH_2), 61.7 (s, CH_2), 51.2 (s, CH), 50.7 (s, CH), 30.6 (s, CH_2), 26.6 (d, *J* = 5.8 Hz, CH_2), 26.4 (d, *J* = 10.6 Hz, CH), 23.3 (d, *J* = 10.4 Hz, CH), 22.7 (d, *J* = 10.9 Hz, CH_2), 22.4 (d, *J* = 10.4 Hz, CH_2), 14.1 (s, CH_3), 14.1 (s, CH_3). **MS (EI) *m/z*** 310, 312 ([M^+], 4, 4), 284 (40), 282 (44), 267 (10), 265 (11), 256 (45), 254 (46), 240 (30), 239 (23), 238 (61), 237 (23), 236 (34), 221 (29), 219 (34), 210 (10), 191 (18), 185 (21), 160 (52), 157 (100), 152 (70), 150 (74), 139 (27), 133 (38), 129 (59), 113 (56), 111 (64), 104 (42), 101 (48), 85 (56). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{11}H_{17}BrFO_4^+$ 311.0289 and 313.0269. Found 311.0284 and 313.0268. [*M*+NH_4]$^+$, Calcd. for $C_{11}H_{20}BrFNO_4^+$ 328.0554 and 330.0534. Found 328.0547 and 330.0527. [*M*+Na]$^+$, Calcd. for $C_{11}H_{16}BrFO_4Na^+$ 333.0108 and 335.0088. Found 333.0097 and 335.0079.

3. Synthesis of (2-fluoroallyl)pyridinium salts

General procedure (NMR tube experiment)

NMR tube was charged with a cyclopropane (0.50 mmol) and CuBr (0.10 mmol, 20 mol.%) and filled with argon on a Schlenk line. Next, 4-fluoroanisole or 4-fluorobenzotrifluoride (5.0 μl,

0.044 mmol, an internal standard), followed by pyridine (0.50 mL) were added [for solvent screening, pyridine (1.5 mmol) and a Solvent (0.50 mL) were used]. The tube was sealed with a Teflon cap [Norell TC-5-PTFE caps were used] and heated at 100°C (oil bath) for 5–48 hours. The reaction progress was monitored by ^{19}F NMR. The reaction time determined in these experiments were used for large scale syntheses.

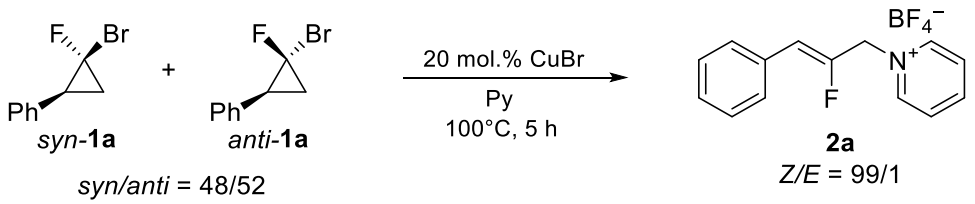
General procedure (large scale synthesis)

A round-bottom flask was charged with a cyclopropane (5.0–50 mmol) and CuBr (20 mol.%) and filled with argon. In a stream of argon, either pyridine (1.0 mL/mmol) or pyridine (3.0 equiv.) and MeCN (1.0 mL/mmol) were added. The reaction flask was sealed with a glass stopper well-fixed with stainless steel springs and heated at 100°C (oil bath) for 5–48 hours [the appropriate reaction time was determined in NMR tube experiments]. After cooling to r.t., the reaction progress can be checked by ^{1}H and ^{19}F NMR of an aliquot (0.10 mL) diluted with DMSO-d_6 (0.50 mL).

For work-up (except benzoate-containing salts **2d** and **2e**, see below), the reaction mixture was evaporated on a rotary evaporator and dried under high vacuum using oil pump connected to the rotary evaporator. The residue was dissolved in MeOH, diluted with *n*-heptane, evaporated and dried on a rotary evaporator again (*n*-heptane is used to completely remove pyridine as an azeotrope). This was repeated two times more. [At this point, usage of an electronic vacuum gauge in not recommended as pyridine vapors can be strongly adsorbed by the pressure sensor making the measured vacuum value erratic. However, this adsorption was found to be reversible and damaged pressure sensor can be recovered by prolonged evacuation under high vacuum.]

The black residue was next extracted with water 5 times using ultrasonic bath. The combined extracts were filtered through a short pad of Celite, and then washed with Et_2O. Next, saturated solution of NH_4BF_4 (2.5 equiv.) was added and the resulted solution was concentrated on a rotary evaporator until precipitation of pyridinium salt was observed, and then extracted 5 times with CH_2Cl_2. The organic extracts were dried over $MgSO_4$, concentrated on a rotary evaporator, and the residue was dried under high vacuum.

(2-Fluoro-3-phenylallyl)pyridinium tetrafluoroborate (2a)



syn-**1a** *anti*-**1a**

syn/anti = 48/52

2a

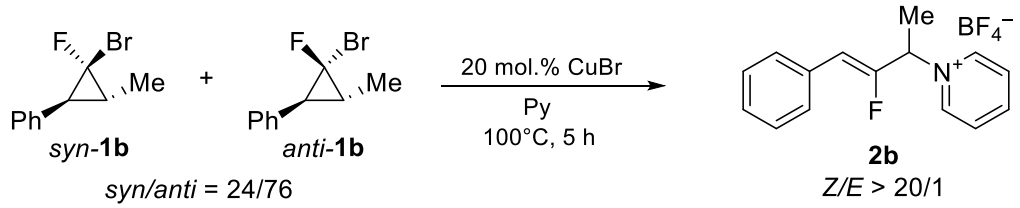
Z/E = 99/1

Obtained by the General procedure on 101 mmol scale using pyridine as the solvent after 5 h at 100°C as a brown glassy solid (25.74 g, 85% yield, *Z/E* = 99/1).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.19 (d, *J* = 6.0 Hz, 2H), 8.71 (t, *J* = 7.8 Hz, 1H), 8.25 (t, *J* = 7.0 Hz, 2H), 7.57–7.50 (m, 2H), 7.48–7.32 (m, 3H), 6.51 (d, *J* = 39.7 Hz, 1H), 5.68 (d, *J* = 18.8 Hz, 2H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –112.2 (dt, *J* = 38.7, 18.8 Hz, 1F), –148.1 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 151.6 (d, *J* = 265.3 Hz, CF), 146.8 (s, CH), 145.0 (s, CH), 131.3 (d, *J* = 3.0 Hz, C), 129.1 (d, *J* = 7.1 Hz, CH), 128.9 (s, CH), 128.7 (d, *J* = 2.2 Hz, CH), 128.6 (s, CH), 113.1 (d, *J* = 4.1 Hz, CH), 61.1 (d, *J* = 27.6 Hz, CH_2). HRMS (ESI), *m/z*: $[M]^+$, Calcd. for $C_{14}H_{13}FN^+$ 214.1027. Found 214.1024.

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.02 (d, *J* = 6.1 Hz, 2H), 8.76–8.67 (m, 1H, overlapped with *Z*-isomer), 8.20 (t, *J* = 7.0 Hz, 2H), 7.57–7.50 (m, 2H, overlapped with *Z*-isomer), 7.48–7.32 (m, 3H, overlapped with *Z*-isomer), 6.99 (d, *J* = 21.2 Hz, 1H), 5.83 (d, *J* = 17.5 Hz, 2H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –109.9 (dt, *J* = 21.2, 17.8 Hz, 1F).

(3-Fluoro-4-Phenylbut-3-en-2-yl)pyridinium tetrafluoroborate (2b)



syn-**1b** *anti*-**1b**

syn/anti = 24/76

2b

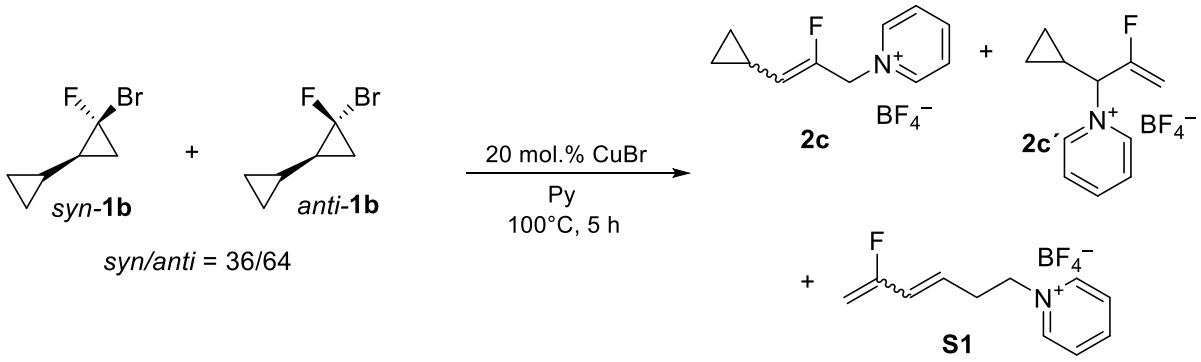
Z/E > 20/1

Obtained by the General procedure on 25 mmol scale using pyridine as the solvent after 5 h at 100°C as a brown oil which slowly solidifies upon storage (6.953 g, 88% yield, *Z/E* > 20/1).

^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ: 9.27 (d, *J* = 6.1 Hz, 2H), 8.71 (t, *J* = 7.7 Hz, 1H), 8.25 (t, *J* = 7.0 Hz, 2H), 7.59–7.53 (m, 2H), 7.46–7.32 (m, 3H), 6.54 (d, *J* = 40.8 Hz, 1H), 6.00 (dq, *J* = 13.8, 7.0 Hz, 1H), 1.94 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** -114.1 (dd,

J = 40.8, 13.1 Hz, 1F), –148.1 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d$_6$) δ:** 154.0 (d, *J* = 265.1 Hz, CF), 147.0 (s, CH), 143.6 (s, CH), 131.2 (d, *J* = 2.7 Hz, C), 129.2 (d, *J* = 7.1 Hz, CH), 128.9–128.6 (m, CH groups), 111.4 (d, *J* = 4.7 Hz, CH), 67.5 (d, *J* = 26.9 Hz, CH), 17.3 (d, *J* = 4.0 Hz, CH_3). HRMS (ESI), *m/z*: $[M]^+$, Calcd. for $C_{15}H_{15}FN^+$ 228.1183. Found 228.1185.

(2-Fluoro-3-cyclopropylallyl)pyridinium tetrafluoroborate (2c) and (2-fluoro-1-cyclopropylallyl)pyridinium tetrafluoroborate (2c´)



Obtained by the General procedure on 25 mmol scale using pyridine as the solvent after 5 h at 100°C as a brown oil (6.124 g, 87% yield, *Z*-**2c**/*E*-**2c**/**2c´** = 67/18/15, contained 4% of impurity preliminary assigned to **S1**).

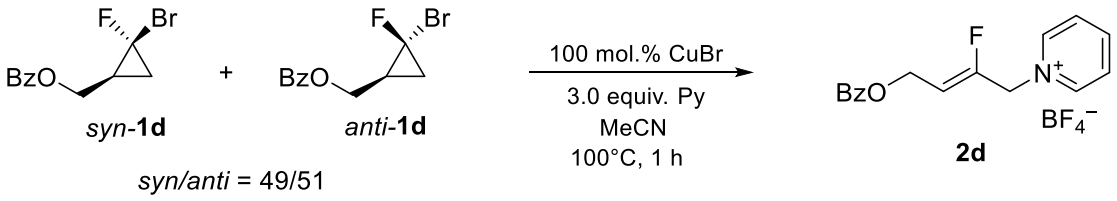
(For *Z*-**2c**): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.10 – 9.03 (m, 2H), 8.76 – 8.64 (m, 1H), 8.30 – 8.18 (m, 2H), 5.46 (d, *J* = 19.2 Hz, 2H), 5.07 (dd, *J* = 36.5, 10.2 Hz, 1H), 1.66 – 1.55 (m, 1H), 0.88 – 0.77 (m, 2H), 0.54 – 0.45 (m, 2H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –124.0 (dt, *J* = 37.5, 19.2 Hz), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d$_6$) δ:** (aromatic C and CH are overlapped with other isomers and could not be resolved: 147.2, 146.8, 146.7, 145.7, 144.8, 144.7, 143.5, 129.0, 128.7, 128.6), 150.9 (d, *J* = 249.8 Hz, CF), 119.2 (d, *J* = 10.0 Hz, CH), 60.4 (d, *J* = 27.8 Hz, CH_2), 6.8 (s, CH_2), 6.8 (d, *J* = 6.0 Hz, CH). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_{11}H_{13}FN^+$ 178.1027. Found 178.1027.

(For *E*-**2c**, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** (aromatic signals are overlapped with other isomers), 5.74 (d, *J* = 20.7 Hz, 2H), 5.29 – 5.19 (m, 1H), 1.88 – 1.77 (m, 1H, overlapped with **2c´**), 1.01 – 0.45 (m, 4H, overlapped with other isomers). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –116.0 (q, *J* = 20.3 Hz). **$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d$_6$) δ:** (aromatic C and CH are overlapped with other isomers), 145.0 (d, *J* = 241.1 Hz, CF), 120.0 (d, *J* = 20.6 Hz, CH), 57.1 (d, *J* = 28.0 Hz, CH_2), 7.1 (d, *J* = 9.9 Hz, CH), 6.8 (s, CH_2).

(For **2c´**, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** (aromatic signals are overlapped with other isomers), 5.41 – 5.25 (m, 2H), 5.15 – 5.05 (m, 1H), 1.88 – 1.77 (m, 1H, overlapped with *E*-**2c**), 1.01 – 0.45 (m, 4H, overlapped with other isomers). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –106.7 (ddd, *J* = 49.7, 17.9, 11.3 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** (aromatic C and CH are overlapped with other isomers), 159.2 (d, *J* = 258.7 Hz, CF), 97.9 (d, *J* = 15.2 Hz, CH_2), 74.5 (d, *J* = 27.1 Hz, CH), 12.5 (d, *J* = 4.6 Hz, CH), 6.1 (s, CH_2), 4.1 (s, CH_2).

(For **S1**, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** (aromatic signals are overlapped with other isomers), 6.05 – 5.91 (m, 2H), 4.73 (t, *J* = 7.0 Hz, 2H), 4.69 (dd, *J* = 16.9, 3.0 Hz, 1H), 4.57 (dd, *J* = 50.7, 2.9 Hz, 1H), 2.81 (q, *J* = 6.5 Hz, 2H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –111.3 (m). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** (CF is missed due to low intensity, aromatic C and CH are overlapped with other isomers), 127.0 (d, *J* = 3.8 Hz, CH), 125.1 (d, *J* = 24.0 Hz, CH), 94.0 (d, *J* = 19.0 Hz, CH_2), 59.6 (s, CH_2), 33.3 (s, CH_2).

(4-Benzoyloxy-2-fluorobut-2-en-1-yl)pyridinium tetrafluoroborate (2d)



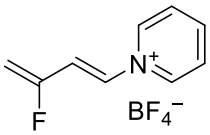
Prepared according to the General procedure on 2.1 mmol scale using 1.0 equiv. of CuBr in MeCN after 1 h of heating at 100°C. Column chromatography on NaBr-saturated silica was required to isolate pure **2d**: after evaporation of the reaction mixture and azeotropic removal of pyridine with *n*-heptane, the residue was dissolved in MeCN and evaporated with Celite (2 g per 1 g of the crude product). The residue was loaded on a column with NaBr-saturated silica[3] (20 g per 1 g of the crude product) and eluted first with CH_2Cl_2/MeOH 10/1 to remove deep-brown copper-containing impurities, then with small amount of CH_2Cl_2/MeOH 7/1, followed by CH_2Cl_2/MeOH 5/1 (R_f on NaBr-saturated TLC plates in CH_2Cl_2/MeOH 7/1 was 0.28 for *E*-isomer and 0.21 for *Z*-isomer). The fractions containing **2d** were combined and evaporated. The most of NaBr was removed by extraction of **2d** from the residue with minimal amount of CH_2Cl_2/MeOH 10/1. After evaporation, crude **2d** as bromide salt was obtained. Next, it was dissolved in minimal amount of water, followed by addition of saturated solution of NH_4BF_4 in water and the resulted solution was extracted with CH_2Cl_2 5 times. The organics were dried over $MgSO_4$, evaporated on a rotary evaporator and the residue was dried under high vacuum affording **2d** as a brown oil (391.8 mg, 47% yield, *Z*/*E* = 86/14, contained ca. 15% of fluorinated impurities and could not be

purified more, contained ca. 9 w/w. % of CH_2Cl_2 that could not be removed by 3 h of drying under high vacuum).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.16 – 9.10 (m, 2H), 8.74 – 8.67 (m, 1H), 8.29 – 8.21 (m, 2H), 8.03 – 7.93 (m, 2H), 7.71 – 7.64 (m, 1H), 7.59 – 7.49 (m, 2H), 5.91 (dt, *J* = 36.5, 6.9 Hz, 1H), 5.61 (d, *J* = 18.1 Hz, 2H), 4.92 (d, *J* = 6.2 Hz, 2H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –112.5 (dt, *J* = 36.2, 18.1 Hz), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 165.4 (s, C), 153.7 (d, *J* = 260.8 Hz), (C from phenyl group is overlapped with the signals of *E*-isomer and impurities), 146.9 (s, CH), 145.0 (s, CH), 133.6 (s, CH), 129.2 (s, CH), 128.8 (s, CH), 128.6 (s, CH), 109.0 (d, *J* = 8.5 Hz, CH), 59.7 (d, *J* = 27.6 Hz, CH_2), 57.1 (d, *J* = 6.0 Hz, CH_2). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_{16}H_{15}FNO_2^+$ 272.1081. Found 272.1089.

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** (aromatic signals are overlapped with *Z*-isomer), 6.02 (d, *J* = 18.9 Hz, 1H), 5.87 (d, *J* = 19.3 Hz, 1H), 5.11 (d, *J* = 7.8 Hz, 2H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –107.1 (q, *J* = 19.4 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** (CF and aromatic C signals lost due too low intensity), (aromatic CH are overlapped with the signals of *Z*-isomer and impurities), 109.4 (d, *J* = 22.0 Hz, CH), 58.9 (d, *J* = 13.2 Hz, CH_2), 56.4 (d, *J* = 26.5 Hz, CH_2).

(3-Fluorobuta-1,3-dien-1-yl)pyridinium tetrafluoroborate (S2)



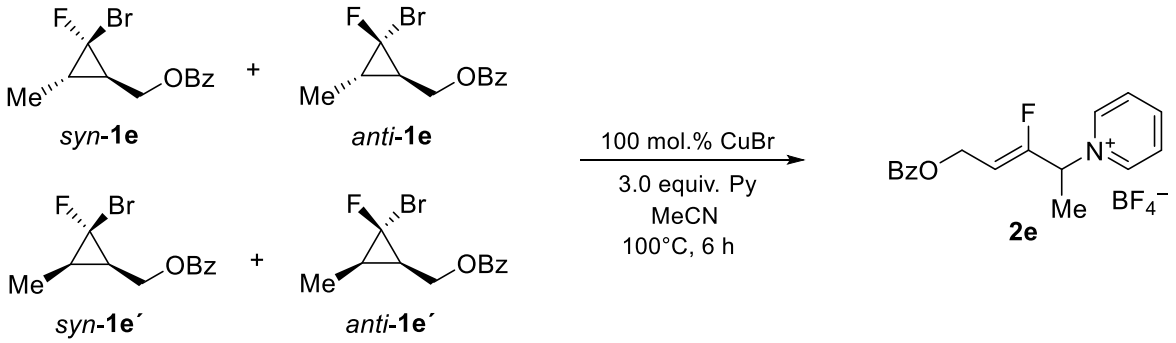
Side product **S2** was isolated in the above experiment during column chromatography (34.6 mg, 7% yield, a brown oil, contained ca. 5% of **2d** and ca. 5% of other fluorinated impurities, R_f on NaBr-saturated TLC plates in CH_2Cl_2/MeOH 7/1 was 0.13).

It should be noted that substantial amounts of side product **S2** were formed (as detected by ^{19}F NMR) when ring-opening of **1d** was heated for longer time. Besides that, it seems that **S2** could forms even during work-up procedure. **S2** was found to be rather soluble in water resulting in substantial loses during conversion to tetrafluoroborate salt.

^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ: 9.28 (d, *J* = 6.2 Hz, 2H), 8.68 (t, *J* = 7.8 Hz, 1H), 8.25 (t, *J* = 7.1 Hz, 2H), 7.90 (d, *J* = 14.0 Hz, 1H), 7.47 (dd, *J* = 25.4, 14.1 Hz, 1H), 5.30 (dd, *J* = 16.3, 3.5 Hz, 1H), 5.16 (dd, *J* = 49.6, 3.4 Hz, 1H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –111.3 (ddd, *J* = 49.6, 25.4, 16.4 Hz), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H}**

NMR (100.6 MHz, DMSO-d$_6$) δ: 158.1 (d, *J* = 251.0 Hz, CF), 147.1 (s, CH), 142.3 (s, CH), 131.7 (d, *J* = 4.5 Hz, CH), 128.0 (s, CH), 121.2 (d, *J* = 22.0 Hz, CH), 101.7 (d, *J* = 17.5 Hz, CH_2). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_9H_9FN^+$ 150.0714. Found 150.0712.

(5-Benzoyloxy-3-fluoropent-3-en-2-yl)pyridinium tetrafluoroborate (2e)



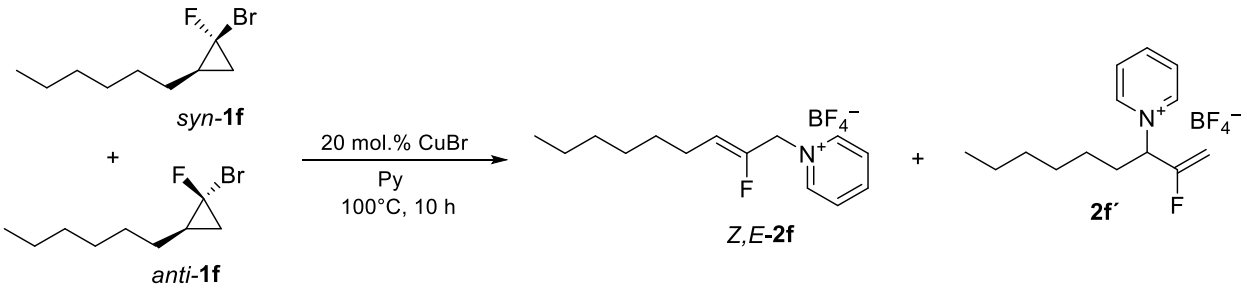
syn-**1e**/*anti*-**1e**/*syn*-**1e´**/*anti*-**1e´** = 49/33/12/6

Prepared according to the General procedure on 0.60 mmol scale using 1.0 equiv. of CuBr in MeCN after 6 h of heating at 100°C. Column chromatography on NaBr-saturated silica was required to isolate pure **2e** similar as described above for **2d** but eluting with CH_2Cl_2/MeOH 7/1 (118.7 mg, 49% yield, *Z*/*E* = 94/6, contained 9 w/w % of CH_2Cl_2 that could not be removed by 3 h of drying under high vacuum, R_f on NaBr-saturated TLC plates in CH_2Cl_2/MeOH 7/1 was 0.31 for *E*-isomer and 0.24 for *Z*-isomer).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.25 – 9.20 (m, 2H), 8.74 – 8.67 (m, 1H), 8.29 – 8.22 (m, 2H), 8.01 – 7.96 (m, 2H), 7.72 – 7.65 (m, 1H), 7.58 – 7.51 (m, 2H), 6.01 – 5.84 (m, 2H), 4.95 (d, *J* = 6.4 Hz, 2H), 1.86 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –114.1 (dd, *J* = 37.0, 12.4 Hz), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 165.5 (s, C), 156.0 (d, *J* = 260.7 Hz, CF), (C from phenyl group is overlapped with the other signals), 147.1 (s, CH), 143.6 (s, CH), 133.6 (s, CH), 129.3 (s, CH), 128.8 (s, CH), 128.8 (s, CH), 107.7 (d, *J* = 9.2 Hz, CH), 66.1 (d, *J* = 26.7 Hz, CH), 57.3 (d, *J* = 6.7 Hz, CH_2), 16.9 (d, *J* = 3.9 Hz, CH_3). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_{17}H_{17}FNO_2^+$ 286.1238. Found 286.1235.

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** (aromatic signals are overlapped with *Z*-isomer), 6.42 (dq, *J* = 27.2, 7.0 Hz, 1H), 5.15 – 5.02 (m, 1H), ($BzOCH_2$ signals are overlapped with *Z*-isomer), 1.94 (d, *J* = 6.9 Hz, 3H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –115.8 (dd, *J* = 27.2, 19.2 Hz).

(2-Fluoronon-2-en-1-yl)pyridinium tetrafluoroborate (2f) and (2-fluoronon-1-en-3-yl)-pyridinium tetrafluoroborate (2f´)



syn/*anti* = 46/54

Obtained by the General procedure on 25.8 mmol scale using pyridine as the solvent after 10 h at 100°C as a beige oil (6.309 g, 79% yield, *Z*-**2f**/*E*-**2f**/**2f´** = 53/34/13).

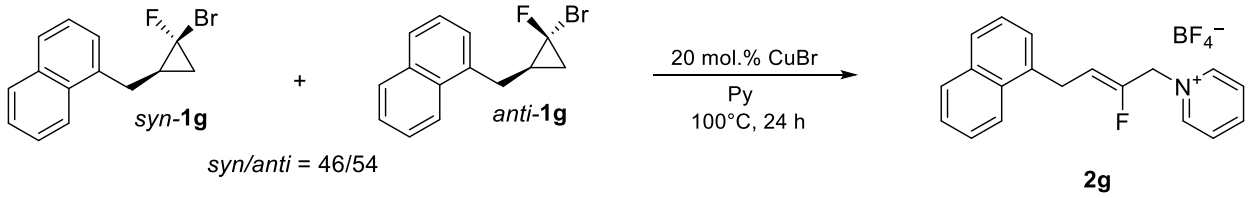
(*Z*-isomer): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.08 (d, *J* = 6.0 Hz, 2H), 8.78 – 8.62 (m, 1H, overlapped with other isomers), 8.38 – 8.17 (m, 2H, overlapped with other isomers), 5.78 – 5.43 (m, 1H, overlapped with other isomers), 5.49 (d, *J* = 18.8 Hz, 2H), 2.13 – 2.02 (m, 2H), 1.56 – 1.00 (m, 8H, overlapped with other isomers), 0.96 – 0.75 (m, 3H, overlapped with other isomers). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –119.1 (dt, *J* = 37.5, 18.7 Hz, 1F), -148.2 (br. s, 4F, $^{10}BF_4^-$), –148.3 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 151.3 (d, *J* = 252.1 Hz, CF),146.7 (s, CH), 144.7 (s, CH), 128.5 (s, CH), 114.4 (d, *J* = 11.4 Hz, CH), 60.3 (d, *J* = 28.6 Hz, CH_2), 30.9 (s, CH_2), 28.1 (s, CH_2), 28.0 (d, *J* = 1.6 Hz, CH_2), 23.1 (d, *J* = 3.4 Hz, CH_2), 22.0 (s, CH_2), 13.9 (s, CH_3). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_{14}H_{21}FN^+$ 222.1653. Found 222.1653.

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.03 (d, *J* = 6.1 Hz, 2H), 8.78 – 8.62 (m, 1H, overlapped with other isomers), 8.38 – 8.17 (m, 2H, overlapped with other isomers), 5.65 (d, *J* = 20.3 Hz, 2H), 5.78 – 5.43 (m, 1H, overlapped with other isomers), 2.37 – 2.14 (m, 2H, overlapped with other isomers), 1.56 – 1.00 (m, 8H, overlapped with other isomers), 0.96 – 0.75 (m, 3H, overlapped with other isomers). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –112.9 (dt, *J* = 20.4, 20.4 Hz, 1F). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 150.7 (d, *J* = 244.4 Hz, CF),146.7 (s, CH), 144.9 (s, CH), 128.6 (s, CH), 115.1 (d, *J* = 16.9 Hz, CH), 56.4 (d, *J* = 28.2 Hz, CH_2), 31.0 (s, CH_2), 28.9 (d, *J* = 2.2 Hz, CH_2), 28.2 (s, CH_2), 24.5 (d, *J* = 7.1 Hz, CH_2), 22.1 (s, CH_2), 13.9 (s, CH_3).

(Branched isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.19 (d, *J* = 6.2 Hz, 2H), 8.78 – 8.62 (m, 1H, overlapped with other isomers), 8.38 – 8.17 (m, 2H, overlapped with other isomers), 5.78 – 5.43 (m, 1H, overlapped with other isomers), 5.35 – 5.18 (m, 2H), 2.37

– 2.14 (m, 2H, overlapped with other isomers), 1.56 – 1.00 (m, 8H, overlapped with other isomers), 0.96 – 0.75 (m, 3H, overlapped with other isomers). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –107.4 (ddd, *J* = 52.1, 15.5, 15.5 Hz, 1F). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 159.2 (d, *J* = 258.6 Hz, CF), 147.2 (s, CH), 143.6 (s, CH), 129.0 (s, CH), 98.1 (d, *J* = 15.5 Hz, CH_2), 70.3 (d, *J* = 26.8 Hz, CH_2), 30.8 (s, CH_2), 29.9 (d, *J* = 2.6 Hz, CH_2), 27.8 (s, CH_2), 24.8 (s, CH_2), 21.9 (s, CH_2), 13.8 (s, CH_3).

[2-Fluoro-4-(naphth-1-yl)but-2-en-1-yl]pyridinium tetrafluoroborate (2g)

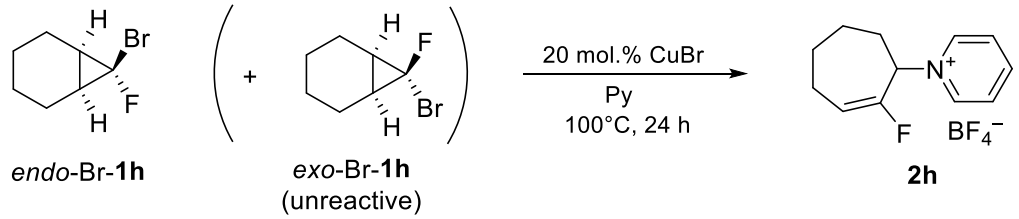


Obtained by the General procedure on 5 mmol scale using pyridine as the solvent after 24 h at 100°C as a brown amorphous solid (1.2185 g, 67% yield, *Z*/*E* = 55/45).

(Z-isomer): **^{1}H NMR (400.0 MHz, DMSO-d$_6$):** 9.14–9.07 (m, 2H), 8.76–8.67 (m, 1H), 8.29–8.20 (m, 2H), 8.16–8.12 (m, 1H), 8.03–7.94 and 7.89–7.82 and 7.65–7.39 (m, 7H total, overlapped with *E*-isomer), 5.85 (dt, *J* = 36.6, 7.4 Hz, 1H, CH), 5.55 (d, *J* = 18.7 Hz, 2H, CH_2), 3.91 (d, *J* = 7.5 Hz, 2H, CH_2). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –117.7 (dt, *J* = 37.2, 18.8 Hz, 1F), –148.1 (br. s, 4F, $^{10}BF_4^-$), –148.2 (br. s, 4F, $^{11}BF_4^-$). **^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ:** 151.5 (d, *J* = 254.5 Hz, CF), {aromatic C and CH signals are overlapped for both isomers and could not be resolved: 146.9 (s, CH), 146.8 (s, CH), 145.1 (s, CH), 144.9 (s, CH), 135.1 (s, C), 134.7 (s, C), 133.5 (s, C), 133.5 (s, C), 131.3 (s, C), 131.2 (s, C), 128.7 (s, CH), 128.7 (s, CH), 128.6 (s, CH), 128.6 (s, CH), 127.3 (s, CH), 127.2 (s, CH), 126.4 (s, CH), 126.3 (s, CH), 126.2 (s, CH), 126.0 (s, CH), 125.9 (s, CH), 125.8 (s, CH), 125.8 (s, CH), 125.5 (s, CH), 123.7 (s, CH), 123.5 (s, CH)}, 113.5 (d, *J* = 19.2 Hz, CH), 56.5 (d, *J* = 27.7 Hz, CH_2), 27.4 (d, *J* = 8.0 Hz, CH_2). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_{19}H_{17}FN^+$ 278.1340. Found 278.1336.

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$):** (aromatic signals are overlapped with *Z*-isomer), 6.05 (dt, *J* = 20.5, 8.1 Hz, 1H, CH), 5.86 (d, *J* = 20.1 Hz, 2H, CH_2), 4.13 (d, *J* = 8.0 Hz, 2H, CH_2). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –110.9 (dt, *J* = 20.2, 20.1 Hz, 1F). **^{13}C NMR (100.6 MHz, DMSO-d$_6$) δ:** 151.7 (d, *J* = 246.5 Hz, CF), (aromatic C and CH are overlapped with *Z*-isomer), 113.5 (d, *J* = 19.2 Hz, CH), 56.5 (d, *J* = 27.7 Hz, CH_2), 27.4 (d, *J* = 8.0 Hz, CH_2-Naphthyl).

(2-Fluorocyclohept-2-en-1-yl)pyridinium tetrafluoroborate (2h)



endo-Br-**1h** *exo*-Br-**1h** (unreactive) **2h**

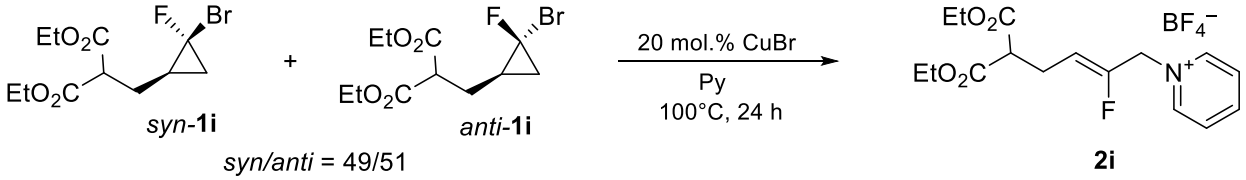
endo-Br/*exo*-Br = 62/38

Obtained by the General procedure from 33 mmol of *endo*-Br-isomer (54 mmol of *endo*-Br/*exo*-Br mixture) using pyridine as the solvent after 24 h at 100°C as a beige amorphous solid (8.254 g, 88% yield on *endo*-Br-**1h**).

(NOTE: *exo*-Br-**1h** is completely unreactive in this reaction).

^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ: 9.16 (d, *J* = 6.0 Hz, 2H), 8.70 (t, *J* = 7.8 Hz, 1H), 8.24 (t, *J* = 7.0 Hz, 2H), 6.07 (ddd, *J* = 24.1, 7.6, 5.5 Hz, 1H), 5.92 (ddd, *J* = 6.4, 6.4, 6.3 Hz, 1H), 2.54–2.38 (m, 1H), 2.37–2.24 (m, 2H), 2.25–2.12 (m, 1H), 1.83–1.55 (m, 4H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –106.5 (dddd, *J* = 24.1, 3.8, 3.7, 3.7 Hz, 1F), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.3 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 152.9 (d, *J* = 244.3 Hz, CF), 146.9 (s, CH), 143.7 (s, CH), 128.8 (s, CH), 115.5 (d, *J* = 19.2 Hz, CH), 71.1 (d, *J* = 26.7 Hz, CH), 30.5 (d, *J* = 6.5 Hz, CH_2), 25.1 (s, CH_2), 21.6 (s, CH_2), 20.5 (d, *J* = 9.2 Hz, CH_2). **HRMS (ESI), *m/z*:** [*M*]$^+$, Calcd. for $C_{12}H_{15}FN^+$ 192.1183. Found 192.1189.

[4,4-Bis(ethoxycarbonyl)-2-fluorobut-2-en-1-yl)pyridinium tetrafluoroborate (2i)



syn-**1i** *anti*-**1i** **2i**

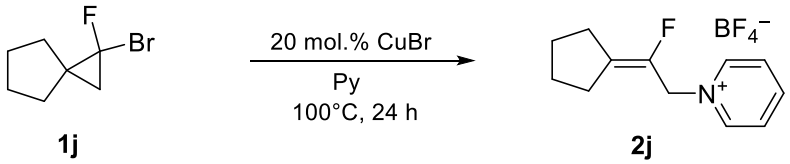
syn/*anti* = 49/51

Obtained by the General procedure on 5 mmol scale using pyridine as the solvent after 24 h at 100°C as a brown oil (1.202 g, 61% yield, *Z*/*E* = 56/44, contained ca. 5% of fluorinated impurities).

(For the mixture of isomers): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.10 – 9.03 (m, 4H), 8.74 – 8.65 (m, 2H), 8.28 – 8.19 (m, 4H), 5.69 (d, *J* = 19.7 Hz, 2H), 5.73 – 5.46 (m, 2H), 5.51 (d, *J* = 19.0 Hz, 2H), 4.21 – 4.03 (m, 8H), 3.78 (t, *J* = 7.2 Hz, 1H), 3.67 (t, *J* = 7.2 Hz, 1H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 6H), 1.14 (t, *J* = 7.1 Hz, 6H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –110.4 (q, *J* = 20.1 Hz, *E*-**2i**), –116.2 (dt, *J* = 37.0, 18.9 Hz,

Z-**2i**), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.3 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 168.4 (s, C), 168.3 (s, C), 152.6 (d, *J* = 256.0 Hz, CF), 152.4 (d, *J* = 246.8 Hz, CF), 146.8 (s, CH), 145.2 (s, CH), 144.8 (s, CH), 128.6 (s, CH), 128.5 (s, CH), 111.2 (d, *J* = 20.8 Hz, CH), 110.6 (d, *J* = 10.3 Hz, CH), 61.3 (s, CH_2), 61.2 (s, CH_2), 60.0 (d, *J* = 27.7 Hz, CH_2), 56.2 (d, *J* = 27.1 Hz, CH_2), 50.3 (d, *J* = 2.6 Hz, CH), 49.9 (s, CH), 24.4 (d, *J* = 8.6 Hz, CH_2), 22.8 (d, *J* = 4.3 Hz, CH_2), 13.9 (s, CH_3), 13.9 (s, CH_3). **HRMS (ESI), *m/z*:** [*M*]$^+$, Calcd. for $C_{16}H_{21}FNO_4^+$ 310.1449. Found 310.1449.

1-(2-Cyclopentylidene-2-fluoroethyl)pyridinium tetrafluoroborate (2j)

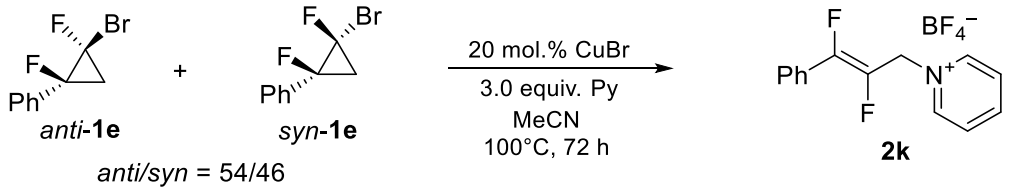


1j **2j**

Obtained by the General procedure on 3.3 mmol scale using pyridine as the solvent after 48 h at 100°C as a beige oil (580.4 mg, 63%).

^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ: 9.05 (d, *J* = 6.1 Hz, 2H), 8.67 (t, *J* = 7.8 Hz, 1H), 8.20 (t, *J* = 7.0 Hz, 2H), 5.56 (d, *J* = 20.1 Hz, 2H, CH_2), 2.70–2.50 (m, 2H), 2.40–2.31 (m, 2H), 1.77–1.61 (m, 4H). **^{19}F NMR (376.4 MHz, DMSO-d$_6$) δ:** –117.0 (t, *J* = 20.2 Hz, 1F), –148.2 (br. s, 4F, $^{10}BF_4^-$), –148.3 (br. s, 4F, $^{11}BF_4^-$). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d$_6$) δ:** 146.6 (s, CH), 144.8 (s, CH), 143.6 (d, *J* = 240.2 Hz, CF), 129.6 (d, *J* = 14.4 Hz, C), 128.5 (s, CH), 58.9 (d, *J* = 28.8 Hz, CH_2), 28.1 (d, *J* = 3.5 Hz, CH_2), 27.9 (d, *J* = 1.9 Hz, CH_2), 26.3 (s, CH_2), 25.7 (s, CH_2). **HRMS (ESI), *m/z*:** [*M*]$^+$, Calcd. for $C_{12}H_{15}FN^+$ 192.1183. Found 192.1188.

(2,3-Difluoro-3-phenylallyl)pyridinium tetrafluoroborate (2k)



anti-**1e** *syn*-**1e** **2k**

anti/syn = 54/46

Obtained by the General procedure on 5 mmol scale using 3 equiv. of pyridine and MeCN as the solvent after 72 h at 100°C as a brown amorphous solid (986.0 mg, 62% yield, *E*/*Z* = 83/17, contained ca. 5% of unidentified non-fluorinated impurity by ^{1}H NMR).

(*E*-isomer): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** 9.19 – 9.13 (m, 2H), 8.75 – 8.66 (m, 1H), 8.30 – 8.17 (m, 2H), 7.70 – 7.45 (m, 5H), 5.96 (dd, *J* = 20.9, 4.8 Hz, 2H). **^{19}F NMR (282.4**

MHz, DMSO-d$_6$) δ: –148.1 (dt, *J* = 125.5, 4.9 Hz, 1F), –153.0 (dt, *J* = 125.5, 20.7 Hz, 1F), –148.3 (br. s, 4F, $^{10}BF_4^-$), –148.4 (br. s, 4F, $^{11}BF_4^-$). **$^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d$_6$) δ:** 149.7 (dd, *J* = 237.2, 40.2 Hz, CF), 146.7 (s, CH), 145.0 (s, CH), 143.8 (dd, *J* = 246.0, 55.4 Hz, CF), 130.6 (s, CH), 128.8 (s, CH), 128.5 (s, CH), 126.9 (dd, *J* = 23.9, 6.0 Hz, C), 125.8 (t, *J* = 7.6 Hz, CH), 56.0 (d, *J* = 24.4 Hz, CH_2). **HRMS (ESI), *m/z*:** $[M]^+$, Calcd. for $C_{14}H_{12}F_2N^+$ 232.0932. Found 232.0932.

(*Z*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, DMSO-d$_6$) δ:** (aromatic signal are overlapped with *E*-isomer), 5.77 (dd, *J* = 19.6, 2.2 Hz, 2H). **^{19}F NMR (282.4 MHz, DMSO-d$_6$) δ:** –117.7 (d, *J* = 13.3 Hz, 1F), –141.5 (td, *J* = 19.6, 13.2 Hz, 1F).

4. Scope of amination

General procedure A

A 25-mL Schlenk flask was charged with pyridinium salt (1.0 mmol), $C_{19}H_{40}$ (20–30 mg, an internal standard) and Na_3PO_4 (3.0 mmol), then connected to a Schlenk line, and evacuated/backfilled with argon three times. Next, freshly prepared solution of $Pd(OAc)_2$ (0.050 mmol) and XantPhos (0.050 mmol) in 5.0 mL of THF was added, the mixture was stirred for 5 min, followed by addition of a solution of a nucleophile (3.0 mmol) in 5.0 mL of THF. The resulted mixture was stirred at 60°C (oil bath) for 4 h. Then, it was diluted with EtOAc and 10% aqueous NaOH. Organic layer was separated, dried over Na_2SO_4, concentrated on a rotary evaporator. The residue was triturated with *n*-heptane, concentrated on a rotary evaporator once again to remove formed pyridine as azeotrope with *n*-heptane and dried under high vacuum. The residue was subjected to column chromatography using 50/1 g/g of silica passivated with NEt_3 (5 μL on 1 g of silica, added to a suspension of silica in an eluent prior to column packing).

General procedure B

The same as the General procedure A, except no Na_3PO_4 was used and the reaction was carried out at r.t. for 5 days.

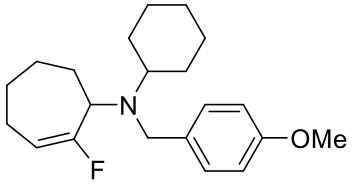
General procedure C

The same as the General procedure A, except DMSO was used as the reaction medium instead of THF.

General procedure D

The same as the General procedure A, except the reaction was carried out at r.t. for 5 days.

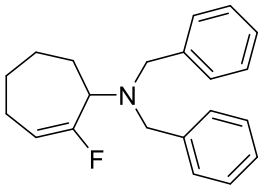
***N*-Cyclohexyl-*N*-(4-methoxybenzyl)-2-fluorocyclohept-2-en-1-amine (4a)**



Obtained by the General procedure A as a colorless oil (268.5 mg, 81%). Eluent — *n*-hexane/benzene/EtOAc 50/50/1 (R_f = 0.27).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.31 – 7.26 (m, 2H), 6.87 – 6.79 (m, 2H), 5.34 (ddd, *J* = 23.6, 8.6, 5.6 Hz, 1H), 3.86 – 3.73 (m, 5H), 3.52 – 3.42 (m, 1H), 2.63 – 2.52 (m, 1H), 2.24 – 2.11 (m, 1H), 1.95 – 1.82 (m, 2H), 1.82 – 1.63 (m, 6H), 1.64 – 1.51 (m, 3H), 1.42 – 0.94 (m, 6H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –99.7 (dd, *J* = 23.7, 9.0 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 163.0 (d, *J* = 252.2 Hz, CF), 158.2 (s, C), 134.6 (s, C), 129.1 (s, CH), 113.4 (s, CH), 106.4 (d, *J* = 22.0 Hz, CH), 59.8 (d, *J* = 24.4 Hz, CH), 58.5 (s, CH), 55.3 (s, CH), 50.8 (d, *J* = 1.4 Hz, CH_2), 32.6 (s, CH_2), 30.7 (d, *J* = 2.4 Hz, CH_2), 29.0 (d, *J* = 11.1 Hz, CH_2), 26.7 (s, CH_2), 26.5 (s, CH_2), 26.3 (s, CH_2), 25.6 (s, CH_2), 22.5 (s, CH_2), 20.3 (d, *J* = 11.3 Hz, CH_2). **MS (EI) *m/z*** 331 ([*M*]$^+$, 9), 288 (4), 274 (3), 219 (2), 210 (3), 122 (24), 121 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{21}H_{31}FNO^+$ 332.2384; Found 332.2381.

***N*,*N*-Dibenzyl-2-fluorocyclohept-2-en-1-amine (4b)**

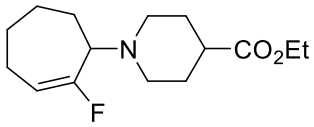


Obtained by the General procedure A as a colorless oil (129.8 mg, 41%). Eluent — *n*-hexane/EtOAc 25/1 (R_f = 0.30).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.43 – 7.37 (m, 4H), 7.33 – 7.26 (m, 4H), 7.24 – 7.18 (m, 2H), 5.44 (ddd, *J* = 24.3, 8.5, 5.6 Hz, 1H), 3.81 – 3.69 (m, 4H), 3.49 – 3.40 (m, 1H), 2.28 – 2.14 (m, 1H), 1.93 – 1.69 (m, 4H), 1.64 – 1.53 (m, 2H), 1.38 – 1.24 (m, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –102.2 (d, *J* = 23.6 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 162.5 (d, *J* = 253.7 Hz, CF), 140.5 (s, C), 128.7 (s, CH), 128.2 (s, CH), 126.8 (s, CH), 107.2 (d, *J* = 21.3 Hz, CH), 59.9 (d, *J* = 23.0 Hz, CH), 55.0 (d, *J* = 1.5 Hz, CH_2), 26.0 (d, *J* = 10.5 Hz, CH_2), 25.6 (d, *J* = 1.6 Hz, CH_2), 22.7 (s, CH_2), 20.4 (d, *J* = 11.1 Hz, CH_2). **MS (EI) *m/z*** 309 ([*M*]$^+$, 36), 280 (6),

218 (12), 197 (7), 106 (9), 91 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{21}H_{25}FN^+$ 310.1966; Found 310.1971.

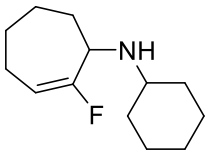
Ethyl 1-(2-fluorocyclohept-2-en-1-yl)piperidine-4-carboxylate (4c)



Obtained by the General procedure A as a yellow-orange oil (247.3 mg, 88%). Eluent — *n*-benzene/EtOAc 8/1 (R_f = 0.33).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 5.43 (ddd, *J* = 22.0, 8.1, 5.6 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.06 – 2.89 (m, 3H), 2.34 – 2.05 (m, 4H), 1.98 – 1.80 (m, 5H), 1.79 – 1.64 (m, 4H), 1.59 – 1.43 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –94.5 (t, *J* = 19.6 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 175.4 (s, C), 162.6 (d, *J* = 251.8 Hz, CF), 108.2 (d, *J* = 21.1 Hz, CH), 65.6 (d, *J* = 26.5 Hz, CH), 60.3 (s, CH_2), 50.4 (s, CH_2), 49.9 (s, CH_2), 41.5 (s, CH), 28.8 (s. CH_2), 28.8 (s, CH_2), 26.6 (d, *J* = 9.6 Hz), 26.4 (d, *J* = 1.4 Hz), 23.4 (s, CH_2), 21.4 (d, *J* = 11.1 Hz, CH_2), 14.3 (s, CH_3). **MS (EI) *m/z*** 269 ([*M*]$^+$, 54), 240 (86), 224 (25), 212 (15), 196 (23), 194 (14), 182 (12), 166 (29), 156 (59), 140 (15), 128 (43), 113 (19), 97 (16), 84 (53), 82 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{15}H_{25}FNO_2^+$ 270.1864; Found 270.1866.

***N*-Cyclohexyl-2-fluorocyclohept-2-en-1-amine (5a)**

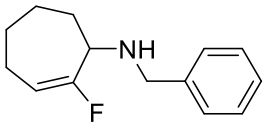


Obtained by the General procedure A as a yellowish oil (130.8 mg, 62%). Eluent — benzene/EtOAc 1/1 + 1 v/v% of NEt_3 (R_f = 0.48).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 5.37 (dt, *J* = 22.7, 6.6 Hz, 1H), 3.60 – 3.48 (m, 1H), 2.58 – 2.49 (m, 1H), 2.14 – 1.88 (m, 3H), 1.87 – 1.45 (m, 10H), 1.40 – 0.99 (m, 6H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –98.6 (dd, *J* = 22.5, 14.4 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 164.7 (d, *J* = 253.2 Hz, CF), 106.7 (d, *J* = 22.1 Hz, CH), 54.9 (d, *J* = 27.9 Hz, CH), 54.3 (s, CH), 34.1 (s, CH_2), 33.6 (s, CH_2), 30.2 (d, *J* = 9.0 Hz, CH_2), 27.3 (s, CH_2), 26.2 (s, CH_2), 25.2 (s, CH_2), 25.1 (s, CH_2), 24.1 (s, CH_2), 22.4 (d, *J* = 11.4 Hz, CH_2). **MS (EI) *m/z*** 211 ([*M*]$^+$, 43), 182 (23),

168 (100), 154 (9), 113 (9), 100 (19), 93 (10). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{13}H_{23}FN^+$ 212.1809; Found 212.1812.

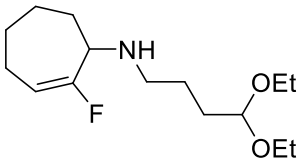
***N*-Benzyl-2-fluorocyclohept-2-en-1-amine (5b)**



Obtained by the General procedure A as a yellow oil (183.4 mg, 84%). Eluent — benzene/EtOAc 10/1 (R_f = 0.30).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.40 – 7.20 (m, 5H), 5.44 (ddd, *J* = 22.8, 7.4, 5.6 Hz, 1H), 3.88 – 3.76 (m, 2H), 3.51 – 3.42 (m, 1H), 2.18 – 2.07 (m, 1H), 2.05 – 1.93 (m, 1H), 1.92 – 1.60 (m, 6H), 1.60 – 1.49 (m, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –99.1 (dd, *J* = 22.8, 13.7 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 163.9 (d, *J* = 251.9 Hz, CF), 140.4 (s, C), 128.4 (s, CH), 128.3 (s, CH), 127.0 (s, CH), 107.5 (d, *J* = 22.1 Hz, CH), 57.8 (d, *J* = 27.8 Hz, CH), 51.6 (s, CH_2), 29.6 (d, *J* = 8.7 Hz, CH_2), 27.3 (s, CH_2), 24.1 (s, CH_2), 22.4 (d, *J* = 11.3 Hz, CH_2). **MS (EI) *m/z*** 219 ([*M*]$^+$, 41), 190 (14), 91 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{14}H_{19}FN^+$ 220.1496; Found 220.1496.

***N*-(4,4-Diethoxybutyl)-2-fluorocyclohept-2-en-1-amine (5c)**

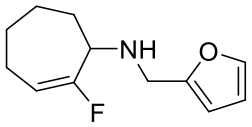


Obtained by the General procedure A as a yellow oil (226.6 mg, 83%). Eluent — benzene/EtOAc 1/1 + 1 v/v % of NEt_3 (R_f = 0.25).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 5.39 (ddd, *J* = 22.9, 7.4, 5.7 Hz, 1H), 4.50 (t, *J* = 5.6 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.54 – 3.44 (m, 2H), 3.43 – 3.35 (m, 1H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.15 – 2.03 (m, 1H), 2.03 – 1.92 (m, 1H), 1.88 – 1.73 (m, 3H), 1.72 – 1.61 (m, 4H), 1.61 – 1.48 (m, 3H), 1.32 (br. s, 1H), 1.20 (t, *J* = 7.1 Hz, 6H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –99.4 (dd, *J* = 23.0, 13.5 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 164.0 (d, *J* = 252.2 Hz, CF), 107.0 (d, *J* = 22.2 Hz, CH), 102.9 (s, CH), 61.0 (s, CH_2), 61.0 (s, CH_2), 58.5 (d, *J* = 27.5 Hz, CH), 47.4 (s, CH_2), 31.5 (s, CH_2), 29.6 (d, *J* = 8.7 Hz, CH_2), 27.2 (s, CH_2), 25.7 (s, CH_2), 24.0 (s, CH_2), 22.3 (d, *J* = 11.4 Hz, CH_2), 15.4 (s, CH_3). **MS (EI) *m/z*** 273 ([*M*]$^+$, 2), 224 (13), 227 (19),

198 (10), 182 (83), 155 (9), 142 (100), 128 (12), 113 (25), 93 (14), 86 (15), 70 (52). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{15}H_{29}FNO_2^+$ 274.2177; Found 274.2171.

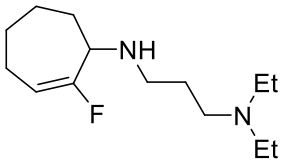
***N*-(Furan-2-ylmethyl)-2-fluorocyclohept-2-en-1-amine (5d)**



Obtained by the General procedure A as an orange oil (158.6 mg, 76%). Eluent — benzene/EtOAc 8/1 (R_f = 0.29).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.38 – 7.35 (m, 1H), 6.33 – 6.29 (m, 1H), 6.22 – 6.18 (m, 1H), 5.44 (ddd, *J* = 22.9, 7.3, 5.7 Hz, 1H), 3.90 – 3.77 (m, 2H), 3.48 – 3.40 (m, 1H), 2.18 – 2.06 (m, 1H), 2.05 – 1.93 (m, 1H), 1.89 – 1.60 (m, 6H), 1.59 – 1.48 (m, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –99.1 (dd, *J* = 23.0, 13.6 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 163.6 (d, *J* = 251.7 Hz, CF), 153.8 (s, C), 141.9 (s, CH), 110.2 (s, CH), 107.6 (d, *J* = 21.9 Hz, CH), 107.1 (s, CH), 57.5 (d, *J* = 27.9 Hz, CH), 44.2 (s, CH_2), 29.6 (d, *J* = 8.6 Hz, CH_2), 27.2 (s, CH_2), 24.0 (s, CH_2), 22.3 (d, *J* = 11.3 Hz, CH_2). **MS (EI) *m/z*** 209 ([*M*]$^+$, 14), 81 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{12}H_{17}FNO^+$ 210.1289; Found 210.1295.

***N*-(3-Diethylaminopropyl)-2-fluorocyclohept-2-en-1-amine (5e)**

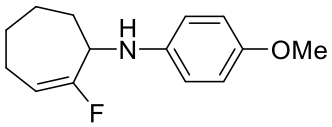


Obtained by the General procedure A. Eluent — CH_2Cl_2/MeOH 1/1 + 1 v/v % of NEt_3 (R_f = 0.30). After column chromatography additional purification of **5e** was necessary. It was performed by conversion of **5e** into hydrochloride with HCl solution in dioxane, dissolving in water, washing with Et_2O, followed by conversion back into base form adding aqueous NaOH to pH 14, extraction with CH_2Cl_2, drying over K_2CO_3 and rotary evaporation. The title compound was obtained as a brown oil (202.4 mg, 84%).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 5.39 (ddd, *J* = 22.9, 7.4, 5.6 Hz, 1H), 3.43 – 3.32 (m, 1H), 2.67 (t, *J* = 6.7 Hz, 2H), 2.58 – 2.44 (m, 6H), 2.15 – 2.04 (m, 1H), 2.03 – 1.93 (m, 1H), 1.89 – 1.60 (m, 8H), 1.59 – 1.48 (m, 1H), 1.01 (t, *J* = 7.1 Hz, 6H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –98.8 (dd, *J* = 22.8, 13.7 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 164.1 (d, *J* = 252.7 Hz, CF), 106.8 (d, *J* = 22.0 Hz, CH), 58.5 (d, *J* = 27.3 Hz, CH), 51.4 (s, CH_2), 46.8 (s, CH_2), 46.7

(s, CH_2), 29.6 (d, *J* = 8.8 Hz, CH_2), 27.5 (s, CH_2), 27.2 (s, CH_2), 24.0 (s, CH_2), 22.2 (d, *J* = 11.4 Hz, CH_2), 11.7 (s, CH_3). **MS (EI)** ***m/z*** 242 ([*M*]$^+$, 0.4), 222 (1), 169 (2), 154 (5), 140 (4), 129 (17), 113 (5), 100 (18), 98 (22), 86 (100), 72 (18), 58 (19). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{14}H_{28}FNO_2^+$ 243.2231; Found 243.2230.

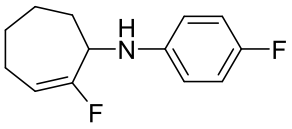
***N*-(4-Methoxyphenyl)-2-fluorocyclohept-2-en-1-amine (6a)**



Obtained by the General procedure A as an orange oil (198.5 mg, 84%). Eluent — benzene/EtOAc 25/1 (R_f = 0.32).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 6.80 – 6.75 (m, 2H), 6.65 – 6.60 (m, 2H), 5.46 (dt, *J* = 22.1, 6.6 Hz, 1H), 4.20 – 4.12 (m, 1H), 3.74 (s, 2H), 3.64 (br. s, 1H), 2.18 – 1.99 (m, 2H), 1.98 – 1.76 (m, 3H), 1.75 – 1.58 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –102.7 (dd, *J* = 22.4, 11.9 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 162.8 (d, *J* = 253.6 Hz, CF), 152.5 (s, C), 141.2 (s, C), 115.1 (s, CH), 114.9 (s, CH), 107.8 (d, *J* = 21.6 Hz, CH), 55.8 (s, CH_3), 55.4 (d, *J* = 27.4 Hz, CH), 29.6 (d, *J* = 6.9 Hz, CH_2), 27.1 (s, CH_2), 24.4 (s, CH_2), 22.5 (d, *J* = 10.8 Hz, CH_2). **MS (EI)** ***m/z*** 235 ([*M*]$^+$, 100), 220 (19), 206 (31), 123 (52), 122 (60), 108 (62), 95 (20). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{14}H_{19}FNO^+$ 236.1445; Found 236.1449.

***N*-(4-Fluorophenyl)-2-fluorocyclohept-2-en-1-amine (6b)**

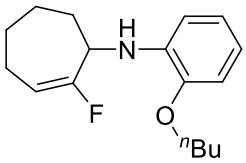


Obtained by the General procedure A as a yellow oil (198.7 mg, 88%). Eluent — *n*-hexane/benzene/EtOAc 30/50/1 (R_f = 0.36).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 6.92 – 6.85 (m, 2H), 6.62 – 6.55 (m, 2H), 5.48 (dt, *J* = 22.0, 6.6 Hz, 1H), 4.21 – 4.13 (m, 1H), 3.79 (br. s, 1H), 2.19 – 2.00 (m, 2H), 1.97 – 1.75 (m, 3H), 1.75 – 1.60 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –103.1 (dd, *J* = 22.0, 11.3 Hz), –128.0 (tt, *J* = 8.6, 4.4 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 162.5 (d, *J* = 253.5 Hz, CF), 156.1 (d, *J* = 235.6 Hz, CF), 143.4 (s, C), 115.8 (d, *J* = 22.4 Hz, CH), 114.4 (d, *J* = 7.5 Hz, CH), 108.0 (d, *J* = 21.7 Hz, CH), 55.0 (d, *J* = 27.8 Hz, CH), 29.7 (d, *J* = 6.6 Hz, CH_2), 27.1 (s, CH_2), 24.5 (s, CH_2), 22.5 (d, *J* = 10.7 Hz, CH_2). **MS (EI)** ***m/z*** 223 ([*M*]$^+$, 42), 202 (9), 194 (46), 174 (17),

111 (100), 93 (17), 83 (15). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{13}H_{16}F_2N^+$ 224.1245; Found 224.1256.

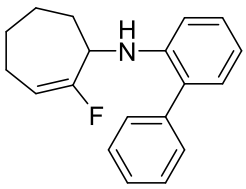
***N*-(2-Butoxyphenyl)-2-fluorocyclohept-2-en-1-amine (6c)**



Obtained by the General procedure A as a yellowish oil (206.3 mg, 72%). Eluent — *n*-hexane/benzene/EtOAc 50/50/1 (R_f = 0.35).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 6.87 – 6.81 (m, 1H), 6.79 – 6.75 (m, 1H), 6.70 – 6.63 (m, 2H), 5.47 (dt, *J* = 21.7, 6.6 Hz, 1H), 4.62 (br. s, 1H), 4.29 – 4.22 (m, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.20 – 1.91 (m, 3H), 1.90 – 1.75 (m, 4H), 1.75 – 1.59 (m, 3H), 1.56 – 1.45 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –101.9 (dd, *J* = 21.7, 12.5 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 163.0 (d, *J* = 254.1 Hz, CF), 146.5 (s, C), 137.2 (s, C), 121.2 (s, CH), 117.0 (s, CH), 110.9 (s, CH), 110.8 (d, *J* = 1.6 Hz, CH), 107.9 (d, *J* = 21.5 Hz, CH), 68.1 (s, CH_2), 54.0 (d, *J* = 28.1 Hz, CH), 31.5 (s, CH_2), 29.4 (d, *J* = 7.0 Hz, CH_2), 27.2 (d, *J* = 1.2 Hz, CH_2), 24.4 (s, CH_2), 22.5 (d, *J* = 10.8 Hz, CH_2), 19.4 (s, CH_2), 13.9 (s, CH_3). **MS (EI) *m/z*** 277 ([*M*]$^+$, 100), 248 (9), 221 (13), 200 (17), 192 (12), 165 (15), 120 (16), 109 (40), 108 (17), 93 (8), 80 (16), 65 (8). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{17}H_{25}FNO^+$ 278.1915; Found 278.1920.

***N*-(2-Fluorocyclohept-2-en-1-yl)-[1,1'-biphenyl]-2-amine (6d)**

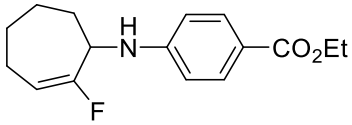


Obtained by the General procedure A as a colorless solid (206.6 mg, 73%, mp = 38–39°C). Eluent — *n*-hexane/EtOAc 25/1 (R_f = 0.27).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.48 – 7.39 (m, 4H), 7.38 – 7.32 (m, 1H), 7.27 – 7.20 (m, 1H), 7.13 – 7.08 (m, 1H), 6.82 – 6.73 (m, 2H), 5.40 (dt, *J* = 21.7, 6.6 Hz, 1H), 4.34 – 4.15 (m, 2H), 2.03 – 1.85 (m, 3H), 1.84 – 1.73 (m, 1H), 1.68 – 1.44 (m, 4H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –101.8 (dd, *J* = 21.6, 12.5 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 162.8 (d, *J* = 254.2 Hz, CF), 143.9 (s, C), 139.4 (s, C), 130.4 (s, CH), 129.4 (s, CH), 129.0 (s, CH), 128.8

(s, CH), 128.3 (s, C), 127.3 (s, CH), 117.5 (s, CH), 111.3 (d, *J* = 1.7 Hz, CH), 108.0 (d, *J* = 21.3 Hz, CH), 54.2 (d, *J* = 28.3 Hz, CH), 29.4 (d, *J* = 6.9 Hz, CH_2), 27.0 (d, *J* = 1.3 Hz, CH_2), 24.5 (s, CH_2), 22.4 (d, *J* = 10.7 Hz, CH_2). **MS (EI) *m/z*** 281 ([*M*]$^+$, 100), 252 (24), 232 (12), 217 (10), 180 (37), 169 (88), 168 (68), 167 (47), 152 (15), 139 (7), 128 (11), 115 (6), 77 (10). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{19}H_{21}FN^+$ 282.1653; Found 282.1650.

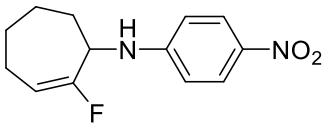
Ethyl 4-((2-fluorocyclohept-2-en-1-yl)amino)benzoate (6e)



Obtained by the General procedure A as a yellow solid (225.9 mg, 75%, mp = 60–61°C). Eluent — benzene/EtOAc 50/1 (R_f = 0.26).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.90 – 7.85 (m, 2H), 6.66 – 6.53 (m, 2H), 5.51 (dt, *J* = 22.0, 6.6 Hz, 1H), 4.41 – 4.17 (m, 4H), 2.20 – 2.01 (m, 2H), 2.00 – 1.77 (m, 3H), 1.76 – 1.61 (m, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –103.8 (m). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 166.9 (s, C), 161.6 (d, *J* = 253.3 Hz, CF), 150.8 (s, C), 131.6 (s, CH), 119.2 (s, C), 111.9 (s, CH), 108.5 (d, *J* = 21.2 Hz, CH), 60.3 (s, CH_2), 53.7 (d, *J* = 27.6 Hz, CH), 29.6 (d, *J* = 6.4 Hz, CH_2), 27.0 (s, CH_2), 24.4 (s, CH_2), 22.4 (d, *J* = 10.5 Hz, CH_2), 14.5 (s, CH_3). **MS (EI) *m/z*** 277 ([*M*]$^+$, 100), 248 (46), 232 (25), 204 (10), 165 (36), 148 (15), 137 (40), 120 (83), 93 (34), 85 (16), 77 (21). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{16}H_{21}FNO_2^+$ 278.1551; Found 278.1549.

***N*-(4-Nitrophenyl)-2-fluorocyclohept-2-en-1-amine (6f)**

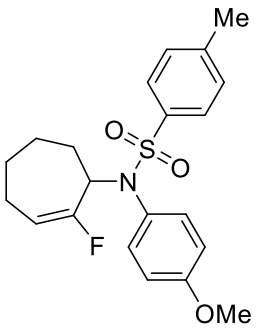


Obtained by the General procedure A as an orange solid (78.5 mg, 28%, mp = 99–100°C). Eluent — benzene/EtOAc 100/1 (R_f = 0.28).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 8.12 – 8.05 (m, 2H), 6.63 – 6.55 (m, 2H), 5.56 (dt, *J* = 22.0, 6.6 Hz, 1H), 4.77 (br. d, *J* = 7.6 Hz, 1H), 4.42 – 4.30 (m, 1H), 2.22 – 2.04 (m, 2H), 2.01 – 1.80 (m, 3H), 1.80 – 1.62 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –104.2 (dd, *J* = 22.1, 10.0 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 160.7 (d, *J* = 253.1 Hz, CF), 152.3 (s, C), 138.4 (s, C), 126.5 (s, CH), 111.6 (s, CH), 109.1 (d, *J* = 20.9 Hz, CH), 53.8 (d, *J* = 27.6 Hz, CH), 29.7

(d, J = 6.2 Hz, CH_2), 26.8 (d, J = 1.2 Hz, CH_2), 24.5 (s, CH_2), 22.4 (d, J = 10.4 Hz, CH_2). **MS (EI)** ***m/z*** 250 ([M]$^+$, 95), 221 (97), 148 (32), 138 (50), 113 (63), 97 (54), 93 (100), 91 (64), 77 (45). **HRMS (ESI),** ***m/z*****:** [M+H]$^+$, Calcd. for $C_{13}H_{16}FN_2O_2^+$ 251.1190; Found 251.1192.

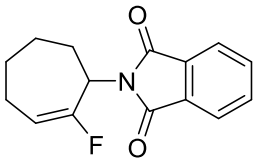
***N*-(2-fluorocyclohept-2-en-1-yl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (7)**



Obtained by the General procedure A as a beige solid which solidified upon storage (341.0 mg, 88%, mp 97–98°C). Eluent — *n*-hexane/benzene/EtOAc 5/5/1 (R_f = 0.39).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.55 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.03 – 6.97 (m, 2H), 6.82 – 6.75 (m, 2H), 5.31 (ddd, J = 22.5, 8.6, 5.4 Hz, 1H), 5.12 – 5.00 (m, 1H), 3.79 (s, 3H), 2.40 (s, 3H), 2.11 – 1.99 (m, 1H), 1.90 – 1.78 (m, 1H), 1.78 – 1.54 (m, 3H), 1.53 – 1.34 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –101.5 (d, J = 21.6 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 159.6 (s, C), 157.2 (d, J = 248.2 Hz, CF), 142.9 (s, C), 137.5 (s, C), 133.4 (d, J = 1.6 Hz, CH), 129.1 (s, CH), 128.2 (s, C), 127.8 (d, J = 1.6 Hz, CH), 113.9 (s, CH), 109.8 (d, J = 20.9 Hz, CH), 61.2 (d, J = 27.3 Hz, CH), 55.4 (s, CH_3), 29.1 (d, J = 9.7 Hz, CH_2), 24.8 (s, CH_2), 21.6 (s, CH_3), 21.3 (s, CH_2), 19.3 (d, J = 10.0 Hz, CH_2). **MS (EI)** ***m/z*** 389 ([M]$^+$, 15), 277 (41), 234 (8), 122 (100), 91 (27). **HRMS (ESI),** ***m/z*****:** [M+H]$^+$, Calcd. for $C_{21}H_{25}FNO_3S^+$ 390.1534; Found 390.1529. [M+NH_4]$^+$, Calcd. for $C_{21}H_{28}FN_2O_3S^+$ 407.1799; Found 407.1798. [M+Na]$^+$, Calcd. for $C_{21}H_{24}FNO_3SNa^+$ 412.1353; Found 412.1354. [M+K]$^+$, Calcd. for $C_{21}H_{24}FNO_3SK^+$ 428.1093; Found 428.1091.

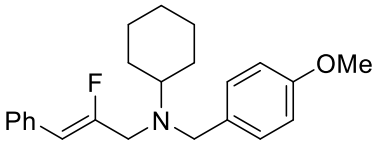
***N*-(2-fluorocyclohept-2-en-1-yl)phthalimide (8)**



Obtained by the General procedure A as a colorless solid (175.7 mg, 67%, mp = 107–108°C). Eluent —benzene (R_f = 0.30).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.89 – 7.81 (m, 2H), 7.76 – 7.69 (m, 2H), 5.60 (dt, *J* = 23.5, 6.5 Hz, 1H), 5.12 – 4.99 (m, 1H), 2.51 – 2.36 (m, 2H), 2.14 – 2.02 (m, 1H), 2.01 – 1.66 (m, 4H), 1.65 – 1.53 (m, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –107.9 (d, *J* = 23.9 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 167.7 (s, C), 156.3 (d, *J* = 249.4 Hz, CF), 134.1 (s, CH), 132.0 (s, C), 123.4 (s, CH), 108.4 (d, *J* = 21.3 Hz, CH), 50.7 (d, *J* = 25.0 Hz, CH), 29.0 (d, *J* = 5.5 Hz, CH_2), 26.2 (d, *J* = 1.2 Hz, CH_2), 24.5 (s, CH_2), 21.7 (d, *J* = 10.1 Hz, CH_2). **MS (EI) *m/z*** 259 ([*M*]$^+$, 5), 239 (8), 211 (8), 196 (4), 148 (100), 130 (38), 112 (16), 97 (29), 76 (17). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{15}H_{15}FNO_2^+$ 260.1081; Found 260.1090. [*M*+Na]$^+$, Calcd. for $C_{15}H_{14}FNO_2Na^+$ 282.0901; Found 282.0908.

***N*-((*Z*)-2-Fluoro-3-phenylallyl)-*N*-(4-methoxybenzyl)cyclohexylamine (10a)**



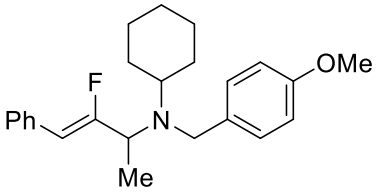
Obtained by the General procedure A as a yellow oil which solidified upon storage in a freezer (302.6 mg, 83%, *Z*/*E* = 98/2, mp = 44–45°C). Eluent — benzene/EtOAc 50/1 (R_f = 0.35).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.49 – 7.44 (m, 2H), 7.34 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 6.87 – 6.81 (m, 2H), 5.71 (d, *J* = 39.4 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 2H), 3.28 (d, *J* = 12.7 Hz, 2H), 2.66 – 2.55 (m, 1H), 1.92 – 1.83 (m, 2H), 1.82 – 1.73 (m, 2H), 1.65 – 1.57 (m, 1H), 1.35 – 0.99 (m, 5H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –105.6 (dt, *J* = 39.5, 12.7 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 159.6 (d, *J* = 268.8 Hz, CF), 158.6 (s, C), 133.8 (d, *J* = 2.4 Hz, C), 132.6 (s, C), 129.5 (s, CH), 128.5 (d, *J* = 7.3 Hz, CH), 128.4 (s, CH), 126.9 (d, *J* = 2.3 Hz, CH), 113.7 (s, CH), 107.1 (d, *J* = 6.9 Hz, CH), 59.0 (s, CH), 55.3 (s, CH_3), 53.4 (s, CH_2), 51.2 (d, *J* = 29.5 Hz, CH_2), 29.1 (s, CH_2), 26.4 (s, CH_2), 26.2 (s, CH_2). **MS (EI) *m/z*** 353 ([*M*]$^+$, 7), 262 (8), 206 (12), 135 (4), 121 (100), 115 (5).

HRMS (ESI), *m/z*: [*M*+H]$^+$, Calcd. for $C_{23}H_{29}FNO^+$ 354.2228; Found 354.2232.

(*E*-isomer): **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –98.5 (q, *J* = 22.0 Hz). **MS (EI) *m/z*** 353 ([*M*]$^+$, 8), 262 (8), 206 (13), 135 (5), 121 (100), 115 (5).

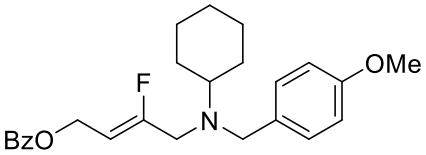
***N*-((*Z*)-3-Fluoro-4-phenylbut-3-en-2-yl)-*N*-(4-methoxybenzyl)cyclohexylamine (10b)**



Obtained by the General procedure B as a colorless oil (286.2 mg, 78%, *Z*/*E* > 20/1). Eluent — *n*-hexane/EtOAc 20/1 (R_f = 0.28).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.52 – 7.44 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.16 (m, 1H), 6.89 – 6.80 (m, 2H), 5.56 (d, *J* = 39.8 Hz, 1H), 3.85 – 3.70 (m, 5H), 3.54 (dq, *J* = 17.2, 7.0 Hz, 1H), 2.77 – 2.65 (m, 1H), 1.87 – 1.67 (m, 4H), 1.62 – 1.54 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.41 – 1.11 (m, 4H), 1.10 – 0.96 (m, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –106.9 (dd, *J* = 39.8, 17.2 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 162.4 (d, *J* = 273.4 Hz, CF), 158.4 (s, C, 133.9 (s, C), 133.8 (d, *J* = 1.9 Hz, C), 129.2 (s, CH), 128.6 (d, *J* = 7.4 Hz, CH), 128.5 (s, CH), 126.9 (d, *J* = 1.8 Hz, CH), 113.6 (s, CH), 106.3 (d, *J* = 8.0 Hz, CH), 56.8 (s, CH), 55.3 (s, CH_3), 54.1 (d, *J* = 24.8 Hz, CH), 49.4 (s, CH_2), 32.4 (s, CH_2), 31.0 (s, CH_2), 26.6 (s, CH_2), 26.5 (s, CH_2), 26.3 (s, CH_2), 16.4 (d, *J* = 4.5 Hz, CH_3). **MS (EI) *m/z*** 271 (100), 256 (17), 149 (66), 129 (83), 123 (69), 122 (81), 108 (28), 95 (15), 77 (10). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{24}H_{31}FNO^+$ 368.2384; Found 368.2387.

(*Z*)-4-(Cyclohexyl(4-methoxybenzyl)amino)-3-fluorobut-2-en-1-yl benzoate (10d)



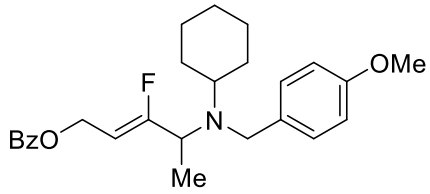
Obtained by the General procedure B as a yellow oil (183.2 mg, 44%, *Z*/*E* = 98/2). Eluent — benzene/EtOAc 30/1 (R_f = 0.20).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 8.07 – 7.97 (m, 2H), 7.60 – 7.50 (m, 1H), 7.47 – 7.38 (m, 2H), 7.29 – 7.21 (m, 2H), 6.87 – 6.78 (m, 2H), 5.20 (dt, *J* = 35.2, 7.4 Hz, 1H), 4.88 (d, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.63 (s, 2H), 3.19 (d, *J* = 12.2 Hz, 2H), 2.59 – 2.48 (m, 1H), 1.88 – 1.72 (m, 4H), 1.65 – 1.54 (m, 1H), 1.30 – 1.00 (m, 5H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –107.4 (dt, *J* = 35.4, 12.2 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 166.5 (s, C), 162.3 (d, *J* = 264.8 Hz), 158.5 (s, C), 133.0 (s, CH), 132.4 (s, C), 130.3 (s, C), 129.7 (s, CH), 129.6 (s, CH), 128.4 (s, CH), 113.6 (s, CH), 101.7 (d, *J* = 11.1 Hz, CH), 59.2 (s, CH), 58.0 (d, *J* = 7.9

Hz, CH_2), 55.3 (s, CH_3), 53.6 (s, CH_2), 50.2 (d, *J* = 29.5 Hz, CH_2), 29.1 (s, CH_2), 26.4 (s, CH_2), 26.1 (s, CH_2). **MS (EI) *m/z*** 411 ([*M*]$^+$, 66), 368 (6), 355 (10), 290 (24), 121 (100), 105 (13), 77 (9). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{25}H_{31}FNO_3^+$ 412.2282; Found 412.2286.

(*E*-isomer): **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –96.3 (q, *J* = 19.8 Hz).

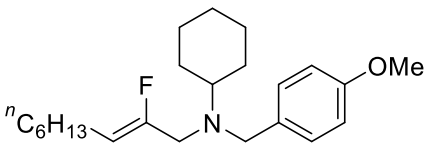
(*Z*)-4-(Cyclohexyl(4-methoxybenzyl)amino)-3-fluoropent-2-en-1-yl benzoate (10e)



Obtained by the General procedure B as a yellowish oil (237.3 mg, 56%, *Z*/*E* > 20/1). Eluent — benzene/EtOAc 40/1 (R_f = 0.37).

^{1}H NMR (400.0 MHz, DMSO-d_6) δ: 7.98 – 7.90 (m, 2H), 7.69 – 7.60 (m, 1H), 7.55 – 7.46 (m, 2H), 7.24 – 7.16 (m, 2H), 6.86 – 6.78 (m, 2H), 5.20 (dt, *J* = 37.2, 7.3 Hz, 1H), 4.82 (d, *J* = 7.2 Hz, 2H), 3.70 (s, 3H), 3.70 – 3.58 (m, 2H), 3.47 (dq, *J* = 14.0, 6.7 Hz, 1H), 2.57 – 2.47 (m, 1H), 1.75 – 1.55 (m, 4H), 1.51 – 1.41 (m, 1H), 1.32 – 0.89 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 5H). **^{19}F NMR (376.4 MHz, DMSO-d_6) δ:** –106.7 (dd, *J* = 37.3, 14.9 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6) δ:** 165.5 (s, C), 164.7 (d, *J* = 267.6 Hz), 158.0 (s, C), 133.4 (s, CH), 133.2 (s, C), 129.6 (s, C), 129.1 (s, CH), 128.8 (s, CH), 128.7 (s, CH), 113.5 (s, CH), 100.8 (d, *J* = 11.6 Hz, CH), 57.4 (d, *J* = 8.5 Hz, CH_2), 56.5 (s, CH), 54.9 (s, CH_3), 52.6 (d, *J* = 24.5 Hz, CH), 48.7 (s, CH_2), 31.1 (s, CH_2), 30.5 (s, CH_2), 25.9 (s, CH_2), 25.6 (s, CH_2), 15.5 (d, *J* = 5.0 Hz). **MS (EI) *m/z*** 425 ([*M*]$^+$, 11), 410 (3), 382 (5), 369 (11), 304 (18), 121 (100), 105 (14), 77 (8). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{26}H_{33}FNO_3^+$ 426.2439; Found 426.2431.

***N*-((*Z*)-2-Fluorononon-2-en-1-yl)-*N*-(4-methoxybenzyl)cyclohexylamine (10f)**



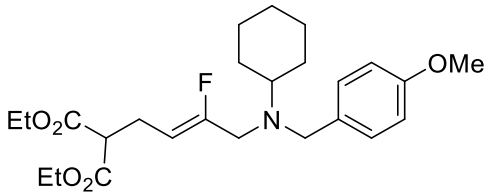
Obtained by the General procedure B as a colorless oil (315.5 mg, 87%, *Z*/*E* = 91/9). Eluent — benzene/EtOAc 50/1 (R_f = 0.33 (*E*-isomer) and 0.26 (*Z*-isomer)).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.30 – 7.22 (m, 2H), 6.87 – 6.79 (m, 2H), 4.68 (dt, *J* = 37.6, 7.5 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 2H), 3.11 (d, *J* = 14.8 Hz, 2H), 2.60 – 2.48 (m, 1H), 2.09 – 1.99 (m, 2H), 1.87 – 1.72 (m, 4H), 1.65 – 1.56 (m, 1H), 1.37 – 0.98 (m, 13H), 0.92

– 0.83 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –114.8 (dt, *J* = 37.6, 14.7 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 158.4 (s, C), 157.7 (d, *J* = 255.3 Hz, CF), 132.9 (s, C), 129.5 (s, CH), 113.5 (s, CH), 107.6 (d, *J* = 14.4 Hz, CH), 58.8 (s, CH), 55.3 (s, CH_3), 53.0 (s, CH_2), 50.6 (d, *J* = 29.7 Hz, CH_2), 31.7 (s, CH_2), 29.5 (d, *J* = 1.6 Hz), 29.1 (s, CH_2), 28.9 (s, CH_2), 26.5 (s, CH_2), 26.2 (s, CH_2), 23.5 (d, *J* = 4.7 Hz, CH_2), 22.7 (s, CH_2), 14.2 (s, CH_3). **MS (EI) *m/z*** 361 ([*M*]$^+$, 15), 318 (13), 305 (4), 290 (3), 276 (2), 262 (3), 240 (3), 218 (3), 121 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{23}H_{37}FNO^+$ 362.2854; Found 362.2866.

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** (aromatic signal are overlapped with the signals of *Z*-isomer), 5.11 (dt, *J* = 21.8, 8.0 Hz, 1H), 3.79 (s, 3H), 3.59 (s, 2H), 3.20 (d, *J* = 21.7 Hz, 2H), (alkyl signals are overlapped with the signals of *Z*-isomer). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –105.6 (q, *J* = 21.7 Hz).

Diethyl (*Z*)-2-[4-(cyclohexyl(4-methoxybenzyl)amino)-3-fluorobut-2-en-1-yl]malonate (10i)

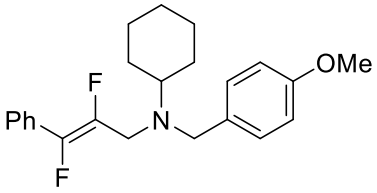


Obtained by the General procedure B as a yellow oil (312.9 mg, 70%, *Z*/*E* = 93/7). Eluent — benzene/EtOAc 20/1 (R_f = 0.26).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.27 – 7.19 (m, 2H), 6.87 – 6.80 (m, 2H), 4.80 (dt, *J* = 36.4, 7.6 Hz, 1H), 4.25 – 4.07 (m, 4H), 3.79 (s, 3H), 3.58 (s, 2H), 3.35 (t, *J* = 7.6 Hz, 1H), 3.10 (d, *J* = 13.1 Hz, 2H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.43 (m, 1H), 1.88 – 1.69 (m, 4H), 1.66 – 1.55 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 6H), 1.29 – 1.00 (m, 5H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –110.8 (dt, *J* = 36.2, 13.1 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 168.9 (s, C), 159.9 (d, *J* = 259.8 Hz, CF), 158.5 (s, C), 132.6 (s, C), 129.4 (s, CH), 113.6 (s, CH), 102.6 (d, *J* = 13.1 Hz, CH), 61.4 (s, CH_2), 58.8 (s, CH), 55.3 (s, CH_3), 53.1 (s, CH_2), 51.8 (d, *J* = 1.9 Hz, CH), 50.2 (d, *J* = 29.7 Hz, CH_2), 29.0 (s, CH_2), 26.4 (s, CH_2), 26.1 (s, CH_2), 23.1 (d, *J* = 5.7 Hz, CH_2), 14.1 (s, CH_3). **MS (EI) *m/z*** 449 ([*M*]$^+$, 9), 406 (5), 404 (6), 393 (4), 290 (23), 218 (3), 121 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{25}H_{37}FNO_5^+$ 450.2650; Found 450.2657.

(*E*-isomer): **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –101.0 (q, *J* = 20.8 Hz).

***N*-((*E*)-2,3-Difluoro-3-phenylallyl)-*N*-(4-methoxybenzyl)cyclohexylamine (10k)**

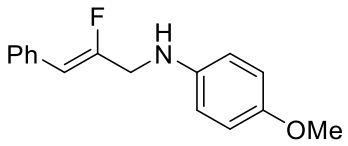


Obtained by the General procedure B as a yellow oil which solidified upon storage in a freezer (132.5 mg, 36%, *E/Z* = 74/26, mp = 67–69°C). Eluent — benzene/EtOAc 100/1 (R_f = 0.34 (*E*-isomer) and 0.26 (*Z*-isomer)).

(*E*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.61 – 7.55 (m, 2H), 7.44 – 7.26 (m, 5H), 6.85 – 6.79 (m, 2H), 3.76 (s, 3H), 3.69 (s, 2H), 3.55 (dd, *J* = 22.7, 5.8 Hz, 2H), 2.66 – 2.54 (m, 1H), 1.96 – 1.86 (m, 2H), 1.83 – 1.74 (m, 2H), 1.66 – 1.56 (m, 1H), 1.38 – 0.98 (m, 5H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –147.3 (dt, *J* = 122.2, 22.8 Hz), –158.2 (dt, *J* = 122.4, 5.8 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 158.5 (s, C), 150.6 (dd, *J* = 250.9, 53.8 Hz, CF), 148.2 (dd, *J* = 227.0, 43.0 Hz, CF), 132.8 (s, C), 129.8 – 127.8 (other aromatic signals are overlapped with the signals of *Z*-isomer), 125.5 (dd, *J* = 8.9, 7.4 Hz, CH), 113.6 (s, CH), 59.8 (s, CH), 55.3 (s, CH_3), 53.6 (s, CH_2), 46.3 (d, *J* = 22.3 Hz, CH_2), 29.3 (s, CH_2), 26.5 (s, CH_2), 26.2 (s, CH_2). **MS (EI) *m/z*** 371 ([*M*]$^+$, 9), 262 (8), 206 (10), 153 (6), 133 (8), 121 (100). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{23}H_{28}F_2NO^+$ 372.2133; Found 372.2138.

(*Z*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** (aromatic signals are overlapped with the signals of *E*-isomer), 3.78 (s, 3H), 3.56 (s, 2H), 3.37 (dd, *J* = 23.6, 2.9 Hz, 2H), (cyclohexyl signals are overlapped with the signals of *E*-isomer). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –130.7 (d, *J* = 11.2 Hz, 1F), –131.9 (td, *J* = 23.6, 11.3 Hz, 1F). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 158.6 (s, C), 146.8 (dd, *J* = 245.4, 18.3 Hz, CF), 145.8 (dd, *J* = 253.5, 16.3 Hz, CF), 132.2 (s, C), 130.0 – 128.2 (other aromatic signals are overlapped with the signals of *E*-isomer), 127.8 (dd, *J* = 4.3, 3.0 Hz, CH), 113.6 (s, CH), 59.2 (s, CH), 55.3 (s, CH_3), 53.1 (s, CH_2), 47.5 (d, *J* = 22.3 Hz, CH_2), 29.0 (s, CH_2), 26.4 (s, CH_2), 26.2 (s, CH_2). **MS (EI) *m/z*** 371 ([*M*]$^+$, 6), 262 (7), 206 (6), 153 (6), 133 (9), 121 (100).

***N*-((*Z*)-2-Fluoro-3-phenylallyl)-4-methoxyaniline (11a)**

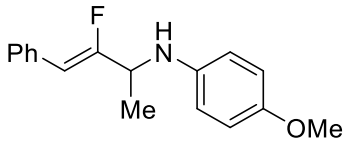


Obtained by the General procedure A as an orange oil which solidified upon storage (187.4 mg, 73%, *Z*/*E* = 99/1, mp = 71–72°C). Eluent — benzene/EtOAc 50/1 (R_f = 0.24).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.49 – 7.44 (m, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.82 – 6.76 (m, 2H), 6.68 – 6.61 (m, 2H), 5.73 (d, *J* = 39.6 Hz, 1H), 3.94 (d, *J* = 10.2 Hz, 2H), 3.79 (br. s, 1H), 3.73 (s, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –109.9 (dt, *J* = 39.6, 10.3 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 157.5 (d, *J* = 267.7 Hz, CF), 152.7 (s, C), 141.3 (s, C), 133.1 (d, *J* = 2.6 Hz, C), 128.6 (d, *J* = 7.2 Hz, CH), 128.5 (s, CH), 127.2 (d, *J* = 2.3 Hz, CH), 115.0 (s, CH), 114.6 (s, CH), 106.9 (d, *J* = 6.6 Hz, CH), 55.8 (s, CH_3), 46.5 (d, *J* = 33.1 Hz, CH_2). **MS (EI) *m/z*** 257 ([*M*]$^+$, 51), 135 (16), 122 (100), 115 (17), 95 (10). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{16}H_{17}FNO^+$ 258.1289; Found 258.1290.

(*E*-isomer): **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –107.2 (q, *J* = 19.9 Hz). **MS (EI) *m/z*** 257 ([*M*]$^+$, 50), 135 (18), 122 (100), 115 (16), 95 (13).

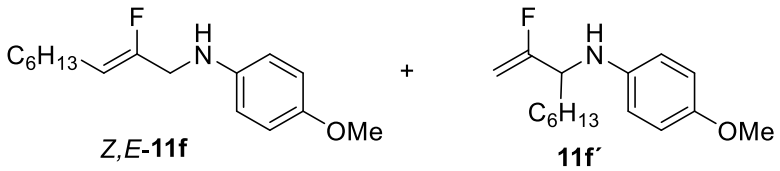
***N*-((*Z*)-3-Fluoro-4-phenylbut-3-en-2-yl)-4-methoxyaniline (11b)**



Obtained by the General procedure C as an orange oil (219.1 mg, 59%, *Z*/*E* > 20/1). Eluent — benzene/EtOAc 40/1 (R_f = 0.16).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.48 – 7.42 (m, 2H), 7.33 – 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 6.79 – 6.74 (m, 2H), 6.66 – 6.60 (m, 2H), 5.73 (d, *J* = 40.0 Hz, 1H), 4.02 (dq, *J* = 13.4, 6.7 Hz, 1H), 3.72 (s, 3H), 3.54 (br. s, 1H), 1.49 (d, *J* = 6.7 Hz, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –116.4 (dd, *J* = 40.0, 13.0 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 160.9 (d, *J* = 270.5 Hz, CF), 152.6 (s, C), 140.7 (s, C), 133.3 (s, C), 128.6 (d, *J* = 7.3 Hz, CH), 128.5 (s, CH), 127.1 (d, *J* = 2.3 Hz, CH), 115.1 (s, CH), 114.9 (s, CH), 105.4 (d, *J* = 6.9 Hz, CH), 55.8 (s, CH_3), 52.1 (d, *J* = 31.3 Hz, CH), 20.0 (s, CH_3). **MS (EI) *m/z*** 271 ([*M*]$^+$, 100), 256 (17), 149 (66), 133 (11), 129 (83), 123 (69), 122 (81), 108 (28), 95 (15), 77 (10). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{17}H_{19}FNO^+$ 272.1445; Found 272.1441.

***N*-((*Z*)-2-Fluoronon-2-en-1-yl)-4-methoxyaniline (11f)**



Z,E-**11f** **11f´**

Obtained by the General procedure D as a brown oil (237.9 mg, 90%, *Z*-**11f**/*E*-**11f**/**11f´** = 61/14/25). Eluent — benzene/EtOAc 40/1 (R_f = 0.39 (**11f´**), 0.30 (*E*-**11f**), 0.27 (*Z*-**11f**)).

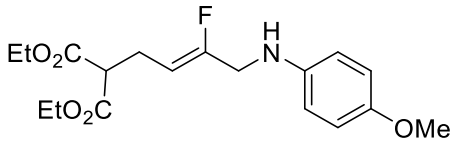
(For *Z*-**11f**): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 6.81 – 6.74 (m, 2H), 6.65 – 6.55 (m, 2H), 4.76 (dt, *J* = 37.9, 7.6 Hz, 1H), 3.80 – 3.70 (m, 5H), 3.64 (br. s, 1H), 2.11 – 1.97 (m, 2H), 1.48 – 1.18 (m, 8H), 0.93 – 0.81 (m, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –118.7 (dt, *J* = 37.8, 12.3 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 156. (d, *J* = 253.8 Hz, CF), 152.6 (s, C), 141.6 (s, C), 115.2 – 114.6 (aromatic CH are overlapped for all isomers), 107.5 (d, *J* = 14.1 Hz, CH), 55.8 (s, CH_3, overlapped with the other isomers), 45.9 (d, *J* = 33.0 Hz, CH_2), (following signals of alkyl CH_2 are overlapped for all isomers and could not be resolved): {33.3, 31.8 – 31.6 (m), 30.0 (d, *J* = 2.2 Hz), 29.3 (d, *J* = 1.7 Hz), 29.1, 28.8 (d, *J* = 1.4 Hz), 26.0, 25.5 (d, *J* = 8.5 Hz), 23.5 (d, *J* = 4.5 Hz), 22.7 – 22.6 (m),} 14.1 (s, CH_3, overlapped with the other isomers). **MS (EI) *m/z*** 265 ([*M*]$^+$, 56), 250 (4), 180 (5), 136 (5), 123 (43), 122 (100), 108 (18), 95 (10), 81 (5), 55 (6). **HRMS (ESI), *m/z*:** [*M*+H]$^+$, Calcd. for $C_{16}H_{25}FNO^+$ 266.1915; Found 266.1920.

(For *E*-**11f**, selected signals): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 5.19 (dt, *J* = 21.7, 8.1 Hz, 1H), 3.84 (d, *J* = 19.6 Hz, 2H), (other signals are overlapped with the signals of *Z*-**11f** and **11f'**). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –112.4 (q, *J* = 20.1 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 156.2 (d, *J* = 247.1 Hz, CF), 152.8 (s, C), 141.6 (s, C), (aromatic CH are overlapped with the other isomers), 108.9 (d, *J* = 19.7 Hz, CH), 55.8 (s, CH_3, overlapped with the other isomers), 42.3 (d, *J* = 29.2 Hz, CH_2), (alkyl CH_2 are overlapped with the other isomers), 14.1 (s, CH_3, overlapped with the other isomers). **MS (EI) *m/z*** 265 ([*M*]$^+$, 42), 250 (2), 180 (3), 136 (5), 123 (100), 122 (68), 108 (27), 95 (11), 81 (4), 55 (5).

(For **11f'**, selected signals): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 4.62 (dd, *J* = 17.4, 3.0 Hz, 1H), 4.43 (dd, *J* = 50.1, 3.0 Hz, 1H), 1.83 – 1.58 (m, 2H), (other signals are overlapped with the signals of *Z*-**11f** and *E*-**11f**). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –111.6 (dt, *J* = 50.0, 16.4 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 165.6 (d, *J* = 262.6 Hz, CF), 152.5 (s, C), 141.0 (s, C), (aromatic CH are overlapped with the other isomers), 90.9 (d, *J* = 18.5 Hz, CH_2), 55.9 (d, *J* = 30.0 Hz, CH), (alkyl CH_2 are overlapped with the other isomers), 14.1 (s, CH_3, overlapped with

the other isomers). **MS (EI)** ***m/z*** 265 ([*M*]$^+$, 28), 180 (100), 160 (19), 148 (4), 136 (3), 123 (6), 122 (13), 108 (8), 95 (4), 77 (3).

Diethyl (Z)-2-[3-fluoro-4-((4-methoxyphenyl)amino)but-2-en-1-yl]malonate (11i)

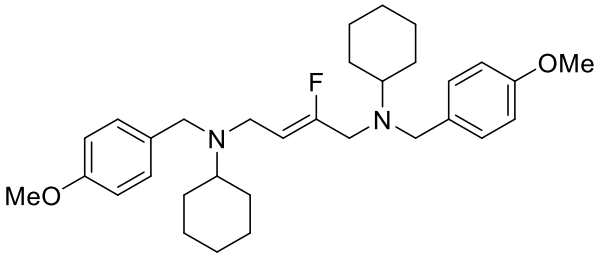


Obtained by the General procedure D as a brown oil (235.7 mg, 67%, *Z*/*E* = 87/13). Eluent — benzene/EtOAc 9/1 (R_f = 0.29).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, CDCl$_3$) δ:** 6.79 – 6.75 (m, 2H), 6.59 – 6.55 (m, 2H), 4.85 (dt, *J* = 36.4, 7.6 Hz, 1H), 4.24 – 4.09 (m, 4H), 3.77 (d, *J* = 11.3 Hz, 2H), 3.74 (s, 3H), 3.69 (br. s, 1H), 3.36 (t, *J* = 7.5 Hz, 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR (376.4 MHz, CDCl$_3$) δ:** –114.5 (dt, *J* = 36.2, 11.2 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$) δ:** 168.8 (s, C), 158.1 (d, *J* = 259.0 Hz, CF), 152.6 (s, C), 141.3 (s, C), 114.9 (s, CH), 114.6 (s, CH), 102.7 (d, *J* = 12.7 Hz, CH), 61.5 (s, CH_2), 55.8 (s, CH_3), 51.6 (d, *J* = 1.9 Hz, CH), 45.6 (d, *J* = 32.7 Hz, CH_2), 23.0 (d, *J* = 5.4 Hz, CH_2), 14.1 (s, CH_3). **MS (EI)** ***m/z*** 353 ([*M*]$^+$, 73), 308 (4), 262 (5), 193 (21), 180 (14), 157 (13), 123 (38), 122 (100), 108 (10), 95 (12), 85 (8), 77 (4), 65 (5). **HRMS (ESI),** ***m/z*****:** [*M*+H]$^+$, Calcd. for $C_{18}H_{25}FNO_5^+$ 354.1711; Found 354.1716.

(*E*-isomer): **^{1}H NMR (400.0 MHz, CDCl$_3$) δ:** 6.80 – 6.75 (m, 2H, overlapped with *Z*-isomer), 6.67 – 6.63 (m, 2H), 5.16 (dt, *J* = 20.5, 8.3 Hz, 1H), 4.23 – 4.11 (m, 4H, overlapped with *Z*-isomer), 3.89 (d, *J* = 19.8 Hz, 2H), 3.75 (s, 3H), 3.69 (br. s, 1H), 3.34 (t, *J* = 7.4 Hz, 1H), 2.63 (t, *J* = 7.8 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{19}F NMR (376.4 MHz, CDCl$_3$) δ:** –106.5 (q, *J* = 19.9 Hz). **MS (EI)** ***m/z*** 353 ([*M*]$^+$, 53), 193 (82), 180 (50), 123 (100), 122 (71), 108 (30), 95 (18).

(*Z*)-*N*^{1},*N*^{4}-Dicyclohexyl-2-fluoro-*N*^{1},*N*^{4}-bis(4-methoxybenzyl)but-2-ene-1,4-diamine (12)



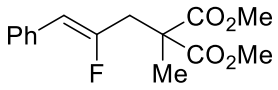
Isolated from the reaction of pyridinium salt **2d** with *N*-(4-methoxybenzyl)cyclohexylamine **3a** as a brown oil (69.7 mg, 13%, *Z*/*E* = 96/4). Eluent — benzene/EtOAc 30/1 (R_f = 0).

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.28 – 7.19 (m, 4H), 6.86 – 6.77 (m, 4H), 4.83 (dt, *J* = 37.7, 7.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.59 (s, 2H), 3.51 (s, 2H), 3.16 (d, *J* = 6.6 Hz, 2H), 3.10 (d, *J* = 13.9 Hz, 2H), 2.59 – 2.41 (m, 2H), 1.87 – 1.70 (m, 8H), 1.63 – 1.54 (m, 2H), 1.31 – 0.98 (m, 10H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –112.8 (dt, *J* = 37.7, 14.0 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 159.2 (d, *J* = 257.6 Hz, CF), 158.4 (s, C), 158.3 (s, C), 133.3 (s, C), 132.7 (s, C), 129.6 (s, CH), 129.4 (s, CH), 113.5 (s, CH), 113.5 (s, CH), 106.3 (d, *J* = 11.5 Hz, CH), 59.1 (s, CH), 58.8 (s, CH), 55.3 (s, CH_3), 53.2 (s, CH_2), 53.0 (s, CH_2), 50.4 (d, *J* = 29.7 Hz, CH_2), 43.3 (d, *J* = 4.3 Hz, CH_2), 29.2 (s, CH_2), 29.0 (s, CH_2), 26.5 (s, CH_2), 26.4 (s, CH_2), 26.2 (s, CH_2), 26.2 (s, CH_2). **MS (EI) *m/z*** 508 ([*M*]$^{+}$, 9), 488 (3), 425 (4), 405 (5), 387 (10), 367 (7), 332 (7), 289 (81), 269 (7), 219 (9), 121 (100), 77 (6). **HRMS (ESI), *m/z*:** [*M*+H]$^{+}$, Calcd. for $C_{32}H_{46}FN_2O_2^{+}$ 509.3538; Found 509.3522.

(*E*-isomer): **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –101.9 (q, *J* = 21.8 Hz).

5. Reactions with other nucleophiles

Dimethyl 2-((*Z*)-2-fluoro-3-phenylallyl)-2-methylmalonate (13)



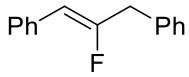
A 10-ml Schlenk tube was charged with **2a** (151.6 mg, 0.50 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol.%) and XantPhos (14.9 mg, 5 mol.%), and filled with argon on a Schlenk line. THF (2.5 mL) was added, and the mixture was stirred at r.t. for 5 min. Next, freshly prepared solution of sodium dimethyl methylmalonate (1.6 equiv.) in 2.5 mL of THF was added [prepared from dimethyl methylmalonate (146.9 mg, 1.0 mmol) and NaH (60% dispersion in mineral oil, 32.3 mg, 0.81 mmol) at 0°C]. The reaction mixture was stirred at r.t. for 5 h. Then, it was diluted with EtOAc and satd. NH_4Cl; the organic phase was separated, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica (50/1) eluting with *n*-hexane/benzene/EtOAc (20/80/1). The title compound was obtained as a colorless oil (120.9 mg, 86% yield, *Z*/*E* > 20/1, R_f = 0.17, contained ca. 3% of probable branched isomer).

NMR data are in agreement with previously published.[4]

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.46 – 7.42 (m, 2H), 7.34 – 7.28 (m, 2H), 7.25 – 7.19 (m, 1H), 5.57 (d, *J* = 38.7 Hz, 1H), 3.75 (s, 6H), 2.99 (d, *J* = 21.9 Hz, 2H), 1.53 (s, 3H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –100.4 (dt, *J* = 38.7, 21.9 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 171.8 (s, C), 156.4 (d, *J* = 266.3 Hz, CF), 133.1 (d, *J* = 2.8 Hz, C), 128.5 (d, *J* = 7.4 Hz, CH),

128.5 (s, CH), 127.3 (d, *J* = 2.3 Hz, CH), 110.1 (d, *J* = 8.3 Hz, CH), 52.9 (s, CH_3), 39.5 (d, *J* = 25.2 Hz, CH_2), 19.7 (s, CH_3).

((*Z*)-2-fluoro-3-phenylallyl)benzene (14)



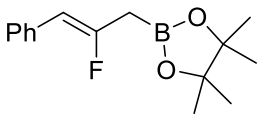
A 25-ml Schlenk tube was charged with $Pd(OAc)_2$ (5.9 mg, 5 mol.%), $PCy_3 \cdot HBF_4$ (18.6 mg, 10 mol.%), Cs_2CO_3 (544.8 mg, 1.7 mmol), and filled with argon on a Schlenk line. Pyridinium salt **2a** (150.6 mg, 0.50 mmol) was added, followed by PhBpin (221.6 mg, 1.1 mmol) as a solution in degassed THF (2.5 mL), and then degassed water (2.5 mL). The Schlenk tube was sealed with a glass stopper fixed with stainless steel springs (silicone grease was used). The reaction was stirred at 80°C (oil bath) for 4 h. After cooling to r.t., it was diluted with Et_2O, washed with satd. NH_4Cl, dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica (100/1) eluting with *n*-hexane/benzene 99/1 [at this stage, side biphenyl was eluted first (R_f = 0.32)]. The title compound was obtained as a colorless oil (62.9 mg, 59% yield, *Z*/*E* = 96/4, R_f = 0.17).

NMR data are in agreement with previously published.[5]

(*Z*-isomer): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** 7.48 – 7.43 (m, 2H), 7.36 – 7.24 (m, 7H), 7.22 – 7.16 (m, 1H), 5.50 (d, *J* = 38.8 Hz, 1H), 3.63 (d, *J* = 17.0 Hz, 2H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –100.6 (dt, *J* = 38.8, 17.0 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 159.6 (d, *J* = 267.4 Hz, CF), 136.2 (d, *J* = 1.4 Hz, C), 133.6 (d, *J* = 2.6 Hz, C), 129.0 (s, CH), 128.7 (s, CH), 128.5 (s, CH), 128.4 (s, CH), 127.0 (s, CH), 127.0 (d, *J* = 2.3 Hz, CH), 107.4 (d, *J* = 8.2 Hz, CH), 39.7 (d, *J* = 27.9 Hz, CH_2).

(*E*-isomer, selected peaks): **^{1}H NMR (400.0 MHz, $CDCl_3$) δ:** (aromatic signals are overlapped with *Z*-isomer), 6.39 (d, *J* = 21.0 Hz, 1H), 3.79 (d, *J* = 24.5 Hz, 2H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –97.3 (td, *J* = 24.3, 20.9 Hz).

((*Z*)-2-fluoro-3-phenylallyl)pinacolboronate (15)



A 10-mL Schlenk tube was charged with **2a** (150.5 mg, 0.50 mmol), B_2pin_2 (217.3 mg, 0.86 mmol) and filled with argon on a Schlenk line. Next, DCE (0.50 mL) was added followed by freshly prepared solution of $[(2\text{-MeAll})PdCl]_2$ (5.0 mg, 0.0125 mml, 5 mol.% of Pd) and tmeda (4

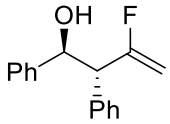
μL, 0.025 mmol, 5 mol.%) in DCE (0.50 mL). The reaction mixture was stirred at 60°C (oil bath) for 3 h. After cooling to r.t., it was concentrated on a rotary evaporator and subjected to column chromatography on silica (10/1) eluting with *n*-hexane/Et_2O 10/1. The title compound was obtained as a colorless oil (69.0 mg, 53% yield, *Z*/*E* = 98/2).

NMR data are in agreement with previously published.[6]

(*Z*-isomer): **^{1}H NMR (300.2 MHz, $CDCl_3$) δ:** 7.51 – 7.46 (m, 2H), 7.36 – 7.29 (m, 2H), 7.24 – 7.17 (m, 1H), 5.54 (d, *J* = 39.3 Hz, 1H), 2.09 (d, *J* = 19.8 Hz, 2H), 1.32 (s, 12H). **^{19}F NMR (282.5 MHz, $CDCl_3$) δ:** –91.2 (dt, *J* = 39.5, 19.8 Hz). **^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$) δ:** 158.5 (d, *J* = 265.3 Hz, CF), 134.4 (s, C), 128.3 (s, CH), 128.2 (d, *J* = 7.4 Hz, CH), 126.3 (d, *J* = 2.2 Hz, CH), 105.9 (d, *J* = 9.3 Hz, CH), 83.9 (s, C), 24.8 (s, CH_3), (signal of CH_2Bpin was lost due to low intensity caused by broadening by quadrupole boron near it).

(*E*-isomer, selected peaks): **^{1}H NMR (300.2 MHz, $CDCl_3$) δ:** (aromatic signals are overlapped with *Z*-isomer), 6.22 (d, *J* = 21.6 Hz, 1H), 2.20 (d, *J* = 28.0 Hz, 2H), (Me-groups in Bpin are overlapped with *Z*-isomer). **^{19}F NMR (282.5 MHz, $CDCl_3$) δ:** –87.6 (td, *J* = 25.8, 21.6 Hz).

3-Fluoro-1,2-diphenylbut-3-en-1-ol (16)



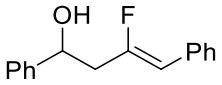
A 12-mL screw-neck vial was charged with boronate **15** (35.3 mg, 0.135 mmol). In a stream of argon, DCE (0.50 mL) was added followed by PhCHO (16 μL, 0.16 mmol). The vial was sealed and the solution was left for 24 h at r.t. After this period, GC indicated complete convertion of *Z*-**15**. The reaction mixture was diluted with Et_2O and vigorously stirred with 10% aq. NaOH for 10 min. The organic layer was separated and stirred with aq. $NaHSO_3$ for 15 min (to remove an excess of PhCHO). The organic layer was separated, washed with water and brine, and dried over Na_2SO_4. After solvent removal, the residue was purified by column chromatography on silica (50/1) eluting with benzene/EtOAc 97/3 (R_f = 0.23). The title compound was obtained as a colorless oil (26.5 mg, 81% yield, *anti*/*syn* > 20/1).

NMR data are in agreement with previously published.[6]

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.22 – 7.03 (m, 10H), 5.07 (dd, *J* = 9.5, 2.8 Hz, 1H), 4.80 (dd, *J* = 17.8, 3.1 Hz, 1H), 4.63 (dd, *J* = 50.2, 3.1 Hz, 1H), 3.71 (dd, *J* = 24.9, 9.4 Hz, 1H), 2.38 (br. d, *J* = 2.8 Hz, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –101.5 (ddd, *J* = 50.1, 24.9, 17.7 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 165.1 (d, *J* = 261.7 Hz, CF), 141.3 (s, C), 137.4

(s, C), 128.6 (d, *J* = 1.9 Hz, CH), 128.4 (s, CH), 128.2 (s, CH), 127.9 (s, CH), 127.3 (s, CH), 126.8 (s, CH), 93.2 (d, *J* = 19.7 Hz, CH_2), 75.1 (d, *J* = 3.0 Hz, CH), 57.8 (d, *J* = 23.6 Hz, CH).

(*Z*)-3-Fluoro-1,4-diphenylbut-3-en-1-ol (17)



Similarly to the synthesis of boronate **15**, pyridinium salt **2a** (151.8 mg, 0.50 mmol) and B_2pin_2 (192.7 mg, 0.76 mmol) were heated in the presence of 2.5 mol.% of $[(2\text{-MeAll})PdCl]_2$ and 5 mol.% of tmeda in DCE (1.0 mL) at 60°C for 3 h. After cooling to r.t., benzaldehyde (61 μL, 0.60 mmol) was added, and the reaction mixture was stirred for 24 h at r.t. Next, it was diluted with Et_2O and stirred with aqueous $NaHSO_3$ for 15 min. Organic layer was separated, washed with water, brine, dried over Na_2SO_4, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica (50/1) eluting with benzene/EtOAc 97/3 (R_f = 0.27). The title compound was obtained as a colorless solid (66.7 mg, 55% yield, *Z*/*E* > 20/1, mp = 88–89°C, contained ca. 2% of **16**).

^{1}H NMR (400.0 MHz, $CDCl_3$) δ: 7.48 – 7.44 (m, 2H), 7.41 – 7.26 (m, 7H), 7.24 – 7.18 (m, 1H), 5.54 (d, *J* = 39.5 Hz, 1H), 5.05 – 4.97 (m, 1H), 2.76 – 2.64 (m, 2H), 2.28 (br. d, *J* = 2.4 Hz, 1H). **^{19}F NMR (376.4 MHz, $CDCl_3$) δ:** –102.6 (dt, *J* = 40.1, 20.2 Hz). **^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ:** 157.3 (d, *J* = 266.0 Hz, CF), 143.2 (s, C), 133.3 (d, *J* = 2.5 Hz, C), 128.6 (s, CH), 128.6 (s, CH), 128.5 (s, CH), 128.0 (s, CH), 127.1 (d, *J* = 2.3 Hz, CH), 125.7 (s, CH), 108.9 (d, *J* = 7.9 Hz, CH), 71.2 (s, CH), 43.7 (d, *J* = 25.5 Hz, CH_2). **MS (EI) *m/z*** 242 ($[M]^+$, 1), 136 (100), 133 (16), 115 (23), 107 (88), 79 (58), 77 (32). **Anal. calcd for $C_{16}H_{15}FO$:** C, 79.32%; H, 6.24%. Found: C, 79.34%; H, 6.16%.

6. References

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