Supplementary Information

TMSCFX₂ (X = Cl, Br) as halofluorocarbene sources for the synthesis of halofluorocyclopropanes

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1. General Information

Commercially available reagents were used without further purification. The solvent toluene was distilled from CaH$_2$. CFBr$_3$ was synthesized according to the literature.$^{[1]}$ Column chromatography was performed with 300-400 mesh silica gel. All melting points are uncorrected. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on a 400 MHz NMR spectrometer. $^1$H NMR chemical shifts were determined relative to internal (CH$_3$)$_4$Si at $\delta$ 0.00 ppm. $^{19}$F NMR chemical shifts were reported relative to CFCl$_3$ at $\delta$ 0.00 ppm. $^{13}$C NMR chemical shifts were determined relative to the signal of internal (CH$_3$)$_4$Si at $\delta$ 0.00 ppm. TLC was carried out with 0.2-mm-thick silica gel plates (GF254). Visualization was accomplished by UV light. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode.

2. Experimental Procedures

2.1 General procedures for the synthesis of chlorofluorocyclopropanes with TMSCFCI$_2$

Under argon atmosphere, $n$-Bu$_4$NBr (8.0 mg, 0.025 mmol, 5 mol%), alkene 1 (0.5 mmol, 1.0 equiv), TMSCFCI$_2$ (130.0 mg, 0.75 mmol, 1.5 equiv) and toluene (2.0 mL) were added into an oven-dried pressure tube. The tube was sealed and the mixture was heated at 110 °C for 4 h. Then it was cooled to room temperature and poured into water (5 mL), followed by extraction with methyl tert-butyl ether (3 × 15 mL). The organic layers were combined and dried over anhydrous MgSO$_4$. After filtration and evaporation under vacuum, the residue was subjected to silica gel column chromatography using hexane as eluent to give product 2.

2.2 General procedures for the synthesis of bromofluorocyclopropanes with TMSCFBr$_2$

Alkene 1 (0.25 mmol, 1.0 equiv.), benzyl triethylammonium chloride (5.5 mg, 10
mol%), TMSCFBr₂ (141 mg, 0.5 mmol, 2.0 equiv.) and dichloromethane (2.0 mL) were added into a reaction tube. NaOH (120 mg, 3.0 mmol, 12.0 equiv.) formulated into 50 wt% aqueous NaOH solution (about 0.4 mL) was slowly dripped into the reaction tube, and then the mixture was stirred for 4 h at room temperature. After the reaction was finished, the water (10.0 mL) was added, followed by extraction with dichloromethane (3 × 15 mL). The organic layers were combined and dried over anhydrous Na₂SO₄. After filtration and evaporation under vacuum, the residue was subjected to silica gel column chromatography using hexane as eluent to give product 3.

2.3 Experimental procedures for the synthesis of TMSCFCl₂ and TMSCFBr₂

Under argon atmosphere, chlorotrimethylsilane (100.0 mmol), CFCl₃ (13.6 g, 100.0 mmol) or CFBr₃ (26.8 g, 100.0 mmol) in CH₂Cl₂ (50.0 mL) were added to a dry three-necked flask. Then tris(N,N-diethylamino)phosphine ((Et₂N)₃P, 24.7g, 100.0 mmol) in CH₂Cl₂ (50.0 mL) was slowly injected into the flask by a syringe pump in three hours at –70 °C. The reaction was gradually warmed to room temperature and stirred overnight. The product and the solvent CH₂Cl₂ were directly pumped into a cold trap by an oil pump, followed by distillation to remove dichloromethane and vacuum distillation (water pump) to obtain TMSCFCl₂ (10.9 g, 63% yield) or TMSCFBr₂ (22.3 g, 85% yield) in 60–80 °C.

3. Screening of Reaction Conditions Using TMSCFBr₂ and 1,1-Diphenylethylene in A Non-aqueous Medium

Table S1 Screening of reaction conditions using TMSCFBr₂ and 1,1-diphenylethylene 1,1-diphenylethylene (1a) in a non-aqueous medium"
Proposed Mechanism of the [2+1] Cycloaddition Reactions between TMSCFX₂ and Alkenes in Non-aqueous or Aqueous Medium

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator ( ^b )</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield( ^c ) (%)</th>
</tr>
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<tr>
<td>1</td>
<td>( n\text{-Bu}_4\text{NBr} )</td>
<td>110</td>
<td>4</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>( n\text{-Bu}_4\text{NBr} )</td>
<td>110</td>
<td>8</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>( n\text{-Bu}_4\text{NBr} )</td>
<td>80</td>
<td>8</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>( n\text{-Bu}_4\text{NCl} )</td>
<td>110</td>
<td>8</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>( n\text{-Bu}_4\text{NF} )</td>
<td>110</td>
<td>8</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>None</td>
<td>110</td>
<td>8</td>
<td>0</td>
</tr>
</tbody>
</table>

\( ^a \) TMSCFBr₂ (0.3 mmol, 1.5 equiv) and 1a (0.2 mmol, 1.0 equiv) were used. \( ^b \) The amount of initiator was calculated on the basis of the amount of reagent 1a used. \( ^c \) All yields were determined using \(^1\text{H}\)NMR spectroscopy with PhCF₃ as an internal standard.

**Scheme S1** The proposed mechanism of the [2+1] cycloaddition reaction between TMSCFX₂ and alkene in a non-aqueous medium
The proposed mechanism of the [2+1] cycloaddition reactions between TMSCFBr$_2$ and alkene in an aqueous medium.

**Further discussion:** In the non-aqueous medium, TBAB (as a Lewis base initiator) attacks the silicon atom of TMSCFX$_2$ to produce a pentacoordinate silicate species, which releases a halofluoromethanide anion. The halofluoromethanide anion undergoes alpha-elimination of a halide anion to give halofluorocarbene under heating, which reacts with alkenes to give halofluorocyclopropanes. The activity of three different carbene reagents (towards the reaction with Lewis base TBAB) is different, as their Lewis acidities are different. Indeed, we found that TMSCFBr$_2$ (with the lowest Lewis acidity among three carbene precursors) could not be fully consumed after heating in toluene for 4 hours in the presence of catalytic amount of TBAB, and 28% of unreacted TMSCFBr$_2$ remained. However, in aqueous medium, NaOH (as a strong nucleophile) can attack all three halofluorocarbene reagents (TMSCF$_2$Br, TMSCFCl$_2$, and TMSCFBr$_2$) readily to produce halofluorocarbene species. Because the intrinsic reactivity of chlorofluorocarbene and bromofluorocarbene towards alkenes are higher than that of difluorocarbene, as evidenced by the fact that the [2+1] cyclopropanations can be achieved in aqueous solution with TMSCFCl$_2$ and TMSCFBr$_2$. Note that such [2+1] reaction with difluorocarbene (from TMSCF$_2$Br) could not be efficiently accomplished in aqueous NaOH solution because NaOH competes with alkene to react with difluorocarbene. These results are indeed consistent with the previous literature.$^{18}$
5. Synthesis of Chlorofluorocyclopropane-Containing Hypolipemic Agent A

\[
\begin{align*}
\text{HO-CH} & + \text{Br-COOEt} \xrightarrow{\text{K}_2\text{CO}_3, \text{MeCN, reflux}} \text{HO-CH} \xrightarrow{1q, 58\%} \\
\text{HO-CH} & + \text{TMSCFCl}_2 \xrightarrow{n\text{-Bu}_3\text{SnH (5 mol\%) \text{PhMe, 110 }^\circ\text{C}}} \text{HO-CH} \xrightarrow{A, 70\%}
\end{align*}
\]

4-Vinylphenol (1.2 g, 10.0 mmol), ethyl 2-bromo-2-methylpropanoate (2.34 g, 12.0 mmol) and K$_2$CO$_3$ (2.76 g, 20.0 mmol) in MeCN (30 mL) was stirred at reflux for 5 hours. Then the mixture was filtered and the filtrate was evaporated under vacuum. The residue was subjected to silica gel column chromatography using ethyl acetate and n-hexane as eluent to give ethyl 2-methyl-2-(4-vinylphenoxy)propanoate (1q) (1.35 g, 58\% yield).

The hypolipemic agent A was synthesized from 1q and TMSCFCl$_2$ according to the general procedures for the synthesis of chlorofluorocyclopropane products 2. The yield of A was 70\%.

6. Debromination of Fluorobromocyclopropane 3a with \(n\text{-Bu}_3\text{SnH}\)

\[
\begin{align*}
\text{F-Br-CH} & \xrightarrow{n\text{-Bu}_3\text{SnH} \text{PhMe, 70 }^\circ\text{C}} \text{F-CH} \xrightarrow{75\%}
\end{align*}
\]

To a stirred solution of fluorobromocyclopropane 3a (291.0 mg, 1.0 mmol) and AIBN (16.4 mg, 0.1 mmol) in benzene (5.0 mL) at 70 \(^\circ\)C under argon atmosphere was
slowly added (ca. 0.5 h) a solution of tributyltin hydride (1.0 mL, 3.7 mmol) in benzene (3.0 mL). The reaction mixture was further stirred at 70 °C for 4 h. After the removal of benzene under reduced pressure, acetonitrile (10.0 mL) was added, and the mixture was washed with n-hexane (3 × 5.0 mL). Acetonitrile was removed under reduced pressure, and the residue was subject to flash chromatography to give the pure product in 75% yield (159.0 mg).

7. Characterization Data of Isolated Products

(2-Chloro-2-fluorocyclopropane-1,1-diyl) dibenzene (2a)[3]

Yield: 119 mg (97%), Yellow solid. M.p.: 76 – 77 °C. \( ^1H \text{NMR} \) (400 MHz, CDCl₃): \( \delta 7.46 – 7.42 \) (m, 4H, CH, Ar), \( 7.35 – 7.27 \) (m, 4H, CH, Ar), \( 7.26 – 7.18 \) (m, 2H, CH, Ar), 2.23 [dd, \( J = 16.4, 7.6 \) Hz, 1H, CH₂ (cis- to F)], 2.09 [t, \( J = 7.2 \) Hz, 1H, CH₂ (trans- to F)]. \( ^19F \text{NMR} \) (376 MHz, CDCl₃): \( \delta -131.59 \) (ddd, \( J = 16.3, 6.7, 3.3 \) Hz, 1F). \( ^13C \text{NMR} \) (101 MHz, CDCl₃): \( \delta 140.2 \) (d, \( J_{CF} = 2.5 \) Hz) (C, Ar), 139.3 (d, \( J = 2.5 \) Hz) (C, Ar), 129.2 (CH, Ar), 128.8 (CH, Ar), 128.9 (CH, Ar), 128.6 (CH, Ar), 128.5 (CH, Ar), 127.4 (CH, Ar), 95.5 (d, \( J_{CF} = 291.1 \) Hz) (CF), 43.0 (d, \( J_{CF} = 10.6 \) Hz) (CAr), 28.0 (d, \( J_{CF} = 10.4 \) Hz) (CH₂). \( \text{MS (EI, } m/z, \%) \): 246 (M⁺, 24.63), 211 (100.00). \( \text{HRMS (EI): } m/z \text{ calcd. for C}_{15}H_{12}ClF (M⁺), 246.0612; \text{ found, 246.0607.} \)

1-Chloro-4-(2-chloro-2-fluorocyclopropyl) benzene (2b)
Yield: 97 mg (95%, syn/anti = 77/23). Light yellow liquid. **1H NMR** (400 MHz, CDCl₃): \( \delta \) 7.39 – 7.27 (m, 2H, CH, Ar), 7.16 (ddd, \( J = 10.9, 8.5 \) Hz, 2H, CH, Ar), 2.84 (ddd, \( J = 16.8, 11.5, 8.6 \) Hz, 0.77×1H, CHAr, syn-isomer), 2.72 – 2.59 (m, 0.23×1H, CHAr, anti-isomer), 2.00 (ddd, \( J = 15.6, 11.6, 7.8 \) Hz, 0.77×1H, CH₂ (cis- to F), syn-isomer), 1.87 – 1.73 (m, 0.46H, CH₂ (cis- and trans- to F), anti-isomer), 1.63 – 1.56 (m, 0.77×1H, CH₂ (trans- to F), syn-isomer). **19F NMR** (377 MHz, CDCl₃): \( \delta \) -128.76 (dt, \( J = 13.9, 4.9 \) Hz, 0.77×1F, syn-isomer), -148.71 (dd, \( J = 14.0, 8.6 \) Hz, 0.23×1F, anti-isomer). **13C NMR** (101 MHz, CDCl₃): \( \delta \) 133.4/133.3 (C, Ar), 133.0/132.1 (d, \( J_{CF} = 1.2 \) Hz) (CH, Ar), 129.8 (d, \( J_{CF} = 2.0 \) Hz)/129.6(CH, Ar), 128.6/128.5 (C, Ar), 94.3 (d, \( J_{CF} = 288.2 \) Hz)/91.6 (d, \( J_{CF} = 286.9 \) Hz) (CF), 31.6 (d, \( J = 11.1 \) Hz)/29.7 (d, \( J_{CF} = 11.9 \) Hz) (CHAr), 21.7 (d, \( J_{CF} = 11.0 \) Hz), 21.0 (d, \( J_{CF} = 11.3 \) Hz) (CH₂). **HRMS (EI):** m/z calcd. for C₉H₇Cl₂F (M⁺), 203.9909; found, 203.9907.

**1-Bromo-4-(2-chloro-2-fluorocyclopropyl)benzene (2c)**

Yield: 88 mg (71%, syn/anti = 54/46). Light yellow liquid. **1H NMR** (400 MHz, CDCl₃): \( \delta \) 7.53 – 7.42 (m, 2H, CH, Ar), 7.11 (ddd, \( J = 11.0, 8.4 \) Hz, 2H, CH, Ar), 2.83 (ddd, \( J = 16.8, 11.6, 8.5 \) Hz, 0.54×1H, CHAr, syn-isomer), 2.72 – 2.57 (m, 0.46×1H, CHAr, anti-isomer), 2.01 [ddd, \( J = 15.6, 11.6, 7.8 \) Hz, 0.54×1H, CH₂ (cis- to F), syn-isomer], 1.88 – 1.74 [m, 0.92H, CH₂ (cis- and trans- to F), anti-isomer], 1.66 –
1.54 [m, 0.54×1H, CH$_2$ (trans- to F), syn-isomer]. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$
-127.14 (d, $J = 13.6$ Hz, 0.54×1F, syn-isomer), -133.63 (dd, $J = 15.3$, 7.7 Hz, 0.46×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 133.5/132.7 (d, $J_{CF} = 1.5$ Hz) (C, Ar), 131.6/131.5 (CH, Ar), 130.2 (d, $J_{CF} = 2.0$ Hz)/130.0 (d, $J_{CF} = 1.1$ Hz) (CH, Ar), 121.4/121.3 (C, Ar), 94.3 (d, $J_{CF} = 288.3$ Hz)/91.6 (d, $J_{CF} = 287.4$ Hz) (CF), 31.7 (d, $J_{CF} = 11.2$ Hz)/29.8 (d, $J_{CF} = 12.0$ Hz) (CHAr), 21.7 (d, $J_{CF} = 10.9$ Hz)/21.0 (d, $J_{CF} = 11.2$ Hz) (CH$_2$). HRMS (EI): m/z calcd. for C$_9$H$_7$BrClF (M$^+$), 247.9404; found, 247.9403.

1-(2-Chloro-2-fluorocyclopropyl)-4-methoxybenzene (2d) [4]

Yield: 96 mg (96%, syn/anti = 55/45). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.17 – 7.11 (m, 2H, CH, Ar), 6.88 – 6.85 (m, 2H, CH, Ar), 3.79 (s, 0.55×3H, CH$_3$), 3.78 (s, 0.45×3H, CH$_3$), 2.81 (ddd, $J = 17.0$, 11.6, 8.5 Hz, 0.55×1H, CHAr, syn-isomer), 2.73 – 2.58 (m, 0.45×1H, CHAr, anti-isomer), 1.93 [ddd, $J = 15.9$, 11.6, 7.7 Hz, 0.55×1H, CH$_2$ (cis- to F), syn-isomer], 1.82 – 1.65 [m, 0.90H, CH$_2$ (cis- and trans- to F), anti-isomer], 1.54 [ddd, $J = 8.4$, 7.7, 6.2 Hz, 0.55×1H, CH$_2$ (trans- to F), syn-isomer]. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$
-127.3 – -130.3 (m, 0.55×1F, syn-isomer), -147.6 – -150.9 (m, 0.45×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.9 (MeOC, Ar), 129.6 (d, $J_{CF} = 2.0$ Hz)/129.4 (CH, Ar), 126.6/125.5 (C, Ar), 113.9/113.8 (CH, Ar), 95.0 (d, $J_{CF} = 287.7$ Hz)/92.0 (d, $J_{CF} = 287.1$ Hz) (CF), 55.30/55.27 (CH$_3$), 31.6 (d, $J_{CF} = 11.3$ Hz)/29.6 (d, $J_{CF} = 11.7$ Hz) (CHAr), 21.4 (d, $J_{CF} = 10.9$ Hz)/20.8 (d, $J_{CF} = 11.2$ Hz) (CH$_2$). MS (ESI) m/z: 201 ([M+H]$^+$). HRMS (ESI): m/z calcd. for C$_{10}$H$_9$ClFO ([M-H]$^+$), 199.0326; found,
1-Tert-butyl-4-(2-chloro-2-fluorocyclopropyl)benzene (2e)

Yield: 100 mg (88%, syn/anti = 57/43). Light yellow liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, J = 7.2 Hz, 2H, CH, Ar), 7.17 (dd, J = 12.5, 8.3 Hz, 2H CH, Ar), 2.85 (ddd, J = 17.2, 11.6, 8.6 Hz, 0.57×1H, CHAr, syn-isomer), 2.74 – 2.61 (m, 1H, 0.43×1H, CHAr, anti-isomer), 1.97 [ddd, J = 15.9, 11.6, 7.7 Hz, 0.57×1H, CH₂ (cis-to F), syn-isomer], 1.79 [ddd, J = 26.5, 11.1, 7.8 Hz, 0.86H, CH₂ (cis- and trans- to F), anti-isomer], 1.66 – 1.55 [m, 1H, 0.57×1H, CH₂ (trans- to F), syn-isomer], 1.33 (s, 0.57×9H, CH₃, syn-isomer), 1.32 (s, 0.43×9H, CH₃, anti-isomer). ¹⁹F NMR (376 MHz, CDCl₃): δ -127.88 - -128.86 (m, 0.57×1F, syn-isomer), -148.8 (ddd, J = 15.9, 7.5, 1.2 Hz, 0.43×1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 150.3 (C, Ar), 131.5/130.6 (d, J₉C = 1.4 Hz) (C, Ar), 128.1 (d, J₉C = 1.9 Hz)/127.9 (d, J₉C = 1.9 Hz) (CH, Ar), 125.4/125.3 (CH, Ar), 94.9 (d, J₉C = 287.7 Hz)/92.1 (d, J₉C = 288.0 Hz) (CF), 34.55 /34.54 [C(CH₃)₃], 32.0 (d, J₉C = 11.2 Hz)/30.0 (d, J₉C = 11.7 Hz) (CHAr), 31.4/31.3 (CH₃), 21.6 (d, J₉C = 10.9 Hz)/20.9 (d, J₉C = 11.1 Hz) (CH₂). MS (EI, m/z, %): 211 (100), 226 (M⁺, 7.31). HRMS (EI): m/z calcd. for C₁₃H₁₆ClF (M⁺), 226.0925; found, 226.0919.

(2-Chloro-2-fluorocyclopropyl)benzene (2f)[⁵]
Yield: 47 mg (94%, syn/anti = 52/48). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 (dddd, $J = 27.9, 9.1, 9.3, 4.4$ Hz, 5H, CH, Ar), 2.89 (ddd, $J = 17.2, 11.5, 8.6$ Hz, 0.52×1H, CHAr, syn-isomer), 2.81 – 2.55 (m, 0.48×1H, CHAr, anti-isomer), 1.99 [ddd, $J = 15.8, 11.6, 7.7$ Hz, 0.52×1H, CH$_2$ (cis- to F), syn-isomer], 1.92 – 1.72 [m, 0.96H, CH$_2$ (cis- and trans- to F), anti-isomer]. 1.63 [dt, $J = 7.7, 7.0$ Hz, 0.52×1H, CH$_2$ (trans- to F), syn-isomer]. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -128.39 (td, $J = 16.6, 5.8$ Hz, 0.52×1F, syn-isomer), -148.79 (dd, $J = 16.1, 7.6$ Hz, 0.48×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 134.5/133.6 (C, Ar), 128.5 (d, $J_{CF} = 2.0$ Hz)/128.47 (CH, Ar), 128.4/128.3 (CH, Ar), 127.4/127.3 (C, Ar), 94.8 (d, $J_{CF} = 287.8$ Hz)/91.9 (d, $J_{CF} = 287.6$ Hz) (CF), 32.4 (d, $J_{CF} = 11.2$ Hz)/30.4 (d, $J_{CF} = 11.6$ Hz) (CHAr), 21.5 (d, $J_{CF} = 11.0$ Hz)/20.8 (d, $J_{CF} = 11.1$ Hz) (CH$_2$). MS (EI, m/z, %): 115 (59.58), 135 (100), 170 (M$^+$, 21.83). HRMS (EI): m/z calcd. for C$_9$H$_8$ClF (M$^+$), 170.0299; found, 170.0292.

2-(4-(2-Chloro-2-fluorocyclopropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g)

Yield: 88 mg (89%, syn/anti = 60/40). Yellow solid. M.p.: 55–56 °C. $^1$H NMR (400
MHz, CDCl$_3$): $\delta$ 7.78 (dd, $J = 7.5, 5.3$ Hz, 2H, CH, Ar), 7.23 (dd, $J = 11.5, 8.0$ Hz, 2H, CH, Ar), 2.88 (ddd, $J = 17.1, 11.5, 8.7$ Hz, 0.60×1H, CHAr, syn-isomer), 2.76 – 2.56 (m, 0.40×1H, CHAr, anti-isomer), 1.98 [ddd, $J = 15.7, 11.6, 7.8$ Hz, 0.60×1H, CH$_2$ (cis- to F), syn-isomer], 1.92 – 1.74 [m, 0.80H, CH$_2$ (cis- and trans- to F), anti-isomer], 1.65 [dd, $J = 14.4, 8.1$ Hz, 0.60×1H, CH$_2$ (trans- to F), syn-isomer], 1.33 (s, 12H, CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -128.15 (ddd, $J = 15.9, 11.5, 4.5$ Hz, 0.60×1F, syn-isomer), -148.64 (dd, $J = 16.1, 7.6$ Hz, 0.40×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 137.5/136.70 (d, $J_{CF} = 1.4$ Hz) (C, Ar), 134.9 (CH, Ar), 134.80 (CH, Ar), 127.8 (d, $J_{CF} = 1.9$ Hz)/127.6, 94.7 (d, $J_{CF} = 288.1$ Hz)/91.9 (d, $J_{CF} = 288.0$ Hz) (CF), 83.85/83.84 (C-O), 32.4 (d, $J_{CF} = 11.2$ Hz)/30.54 (d, $J_{CF} = 11.7$ Hz) (CHAr), 24.88/24.86 (CH$_3$), 21.59 (d, $J_{CF} = 10.9$ Hz)/20.81 (d, $J_{CF} = 11.1$ Hz) (CH$_2$). MS (EI, m/z, %): 161(89.34), 197(100), 261(84.62), 296 (M$^+$, 10.58). HRMS (EI): m/z calcd. for C$_{15}$H$_{18}$BClF$_2$ ($^{10}$B[M-H]$^+$), 294.1109; found, 294.1098.

4-(2-Chloro-2-fluorocyclopropyl)-N,N-dimethylaniline (2h)

Yield: 53 mg (50%, syn/anti = 69/31). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.10 (dd, $J = 13.7, 8.7$ Hz, 2H, CH, Ar), 6.71 (d, $J = 8.7$ Hz, 2H, CH, Ar), 2.94 (s, 0.69×6H, CH$_3$, syn-isomer), 2.93 (s, 0.31×6H, CH$_3$, anti-isomer), 2.78 (ddd, $J = 17.2, 11.6, 8.6$ Hz, 0.69×1H, CHAr, syn-isomer), 2.69 – 2.47 (m, 0.31×1H, CHAr, anti-isomer), 1.90 (ddd, $J = 16.0, 11.7, 7.6$ Hz, 0.69×1H, CH$_2$ (cis- to F), syn-isomer), 1.81 – 1.63 (m, 0.62×1H, CH$_2$ (cis- and trans- to F), anti-isomer), 1.59 – 1.47 (m, 0.69×1H, CH$_2$ (trans- to F), syn-isomer). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -128.76 (td, $J = 16.9, 5.5$ Hz, 0.69×1F, syn-isomer), -148.91 (dd, $J = 15.8, 7.2$ Hz, 0.31×1F,
\textit{anti}-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): \(\delta\) 149.8/149.7 (Me$_2$NC, Ar), 129.2 (d, \(J_{CF}=1.9\) Hz)/129.0 (CH, Ar), 122.2/122.1 (C, Ar), 112.6/112.4 (CH, Ar), 95.5 (d, \(J_{CF}=287.8\) Hz)/92.3 (d, \(J_{CF}=287.2\) Hz) (CF), 40.7/40.6 (s, CH$_3$), 31.6 (d, \(J_{CF}=11.2\) Hz)/29.6 (d, \(J_{CF}=11.4\) Hz) (CHAr), 21.2 (d, \(J_{CF}=10.7\) Hz)/20.7 (d, \(J_{CF}=11.1\) Hz) (CH$_2$). \textbf{HRMS (ESI)}: \(m/z\) calcd. for C$_{11}$H$_{14}$ClF$_2$N \([\text{M+H}]^+\), 214.0799; found, 214.0795.

\textit{Methyl 4-(2-chloro-2-fluorocyclopropyl)benzoate (2i)}

Yield: 82 mg (72\%, \textit{syn/anti} = 50/50). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): \(\delta\) 8.31 – 7.73 (m, 2H, CH, Ar), 7.29 (dd, \(J = 16.2, 7.6\) Hz, 2H, CH, Ar), 3.92 (s, 0.50×3H, CH$_3$, \textit{syn}-isomer), 3.91 (s, 0.50×3H, CH$_3$, \textit{anti}-isomer), 2.92 (ddd, \(J = 16.8, 11.5, 8.7\) Hz, 0.50×1H, CHAr, \textit{syn}-isomer), 2.75 (dd, \(J = 14.2, 5.1\) Hz, 0.50×1H, CHAr, \textit{anti}-isomer), 2.05 (ddd, \(J = 15.6, 11.5, 7.9\) Hz, 0.50×1H, CH$_2$ (\textit{cis-} to F), \textit{syn}-isomer), 1.94 – 1.79 (m, 1H, CH$_2$ (\textit{cis-} and \textit{trans-} to F), \textit{anti}-isomer), 1.69 (td, \(J = 8.2, 6.3\) Hz, 0.50×1H, CH$_2$ (\textit{trans-} to F), \textit{syn}-isomer). $^{19}$F NMR (377 MHz, CDCl$_3$): \(\delta\) -128.15 (td, \(J = 16.9, 7.5\) Hz, 0.50×1F, \textit{syn}-isomer), -148.58 (dd, \(J = 15.7, 7.6\) Hz, 0.50×1F, \textit{anti}-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): \(\delta\) 165.7 (COOMe), 138.6/137.8 (d, \(J_{CF}=1.1\) Hz) (C, Ar), 128.7/128.6 (CH, Ar), 128.3/128.2 (C, Ar), 127.5 (d, \(J_{CF}=2.0\) Hz)/127.2 (d, \(J_{CF}=1.2\) Hz) (CH, Ar), 93.2 (d, \(J_{CF}=288.8\) Hz)/90.7 (d, \(J_{CF}=287.7\) Hz) (CF), 51.1 (s, CH$_3$), 31.2 (d, \(J_{CF}=11.1\) Hz)/29.3 (d, \(J_{CF}=12.0\) Hz) (CHAr), 21.0 (d, \(J_{CF}=11.0\) Hz)/ 20.1 (d, \(J_{CF}=11.1\) Hz) (CH$_2$). \textbf{HRMS (ESI)}: \(m/z\) calcd. for C$_{11}$H$_9$ClFO$_2$ \([\text{M-H}]^+\), 227.0275; found, 227.0257.
(2-Chloro-2-fluoro-1-methylcyclopropyl)benzene (2j) \[^5\]

Yield: 89 mg (96%, syn/anti = 50/50). Light yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.58 – 6.78 (m, 5H, CH, Ar), 1.91 [dd, \(J = 17.4, 7.5\) Hz, 0.50×1H, CH\(_2\) (cis- to F), syn-isomer], 1.72 – 1.61 [m, 1H, CH\(_2\) (cis- and trans- to F), anti-isomer], 1.60 (d, \(J = 2.2\) Hz, 0.5×3H, CH\(_3\), syn-isomer), 1.58 (d, \(J = 2.2\) Hz, 0.5×3H, CH\(_3\), anti-isomer), 1.36 [t, \(J = 7.6\) Hz, 0.5×1H, CH\(_2\) (cis- to F), syn-isomer]. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) -133.36 (dd, \(J = 17.3, 6.6\) Hz, 0.5×1F, syn-isomer), -140.94 (dd, \(J = 15.8, 3.2\) Hz, 0.5×1F, anti-isomer). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 140.9 (d, \(J_{CF} = 1.8\) Hz)/139.2 (d, \(J_{CF} = 3.9\) Hz) (C, Ar), 128.58/128.55 (CH, Ar), 128.48 (CH, Ar), 128.42 (d, \(J_{CF} = 1.8\) Hz)/127.27 (d, \(J_{CF} = 4.7\) Hz) (CH, Ar), 97.1 (d, \(J_{CF} = 286.9\) Hz)/96.9 (d, \(J_{CF} = 291.7\) Hz) (CF), 34.3 (d, \(J_{CF} = 10.8\) Hz)/33.7 (d, \(J_{CF} = 9.8\) Hz) (CAr), 27.1 (d, \(J_{CF} = 10.5\) Hz)/26.9 (d, \(J_{CF} = 10.3\) Hz) (CH\(_2\)), 25.1 (d, \(J_{CF} = 2.3\) Hz)/21.8 (d, \(J_{CF} = 8.1\) Hz) (CH\(_3\)). MS (EI, m/z, %): 149 (100), 179 (39.13), 184 (M\(^+\), 21.04). HRMS (EI): m/z calcd. for C\(_{10}\)H\(_{10}\)ClF (M\(^+\)), 184.0455; found, 184.0456.

2-(2-Chloro-2-fluoro-1-methylcyclopropyl)benzofuran (2k)

Yield: 90 mg (80%, syn/anti = 52/48). Light yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.53 (dd, \(J = 7.5, 4.2\) Hz, 1H, CH, Ar), 7.45 (dd, \(J = 8.0, 4.5\) Hz, 1H, CH, Ar), 7.34 – 7.17 (m, 2H, CH, Ar), 6.59 (s, 0.52×1H, CH=CH, syn-isomer), 6.57 (s,
0.48×1H, anti-isomer), 2.27 [dd, J = 17.2, 7.8 Hz, 0.52×1H, CH₂ (cis- to F), syn-isomer], 2.05 [t, J = 7.6 Hz, 0.48×1H, CH₂ (cis- to F), anti-isomer], 1.70 (s, 0.52×3H, CH₃, syn-isomer), 1.69 (s, 0.48×3H, CH₃, anti-isomer), 1.71 – 1.65 [m, 0.48×1H, CH₂ (trans- to F), anti-isomer], 1.45 [t, J = 7.9 Hz, 0.52×1H, CH₂ (trans- to F), syn-isomer]. ¹⁹F NMR (376 MHz, CDCl₃): δ -138.42 (dd, J = 17.1, 7.7 Hz, 0.52×1F, syn-isomer), -140.03 (dd, J = 15.8, 5.8 Hz, 0.48×1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 156.35 (d, J = 2.5 Hz)/154.82 (d, J = 3.9 Hz) (O-C=), 154.7/154.6 (O-C, Ar), 128.4/128.3 (C, Ar), 124.1/124.0 (CH, Ar), 122.9/122.8 (CH, Ar), 120.8/120.7 (CH, Ar), 111.1/111.0 (CH, Ar), 104.15 (d, JCF = 1.6 Hz)/104.08 (d, JCF = 0.9 Hz) (HC=), 96.4 (d, JCF = 289.8 Hz)/95.8 (d, JCF = 294.2 Hz) (CF), 28.6 (d, JCF = 12.5 Hz)/27.8 (d, JCF = 9.6 Hz) (CAr), 27.1 (d, J = 11.1 Hz)/26.6 (d, JCF = 9.9 Hz) (CH₂), 20.21 (d, JCF = 2.0 Hz)/17.03 (d, JCF = 6.5 Hz) (CH₃). MS (EI, m/z, %): 189 (100), 224 (M⁺, 31.84). HRMS (EI): m/z calcd. for C₁₂H₁₀ClFO (M⁺), 224.0404; found, 224.0397.

2-(2-Chloro-2-fluoro-1-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2I)

Yield: 118mg (80%, syn/anti = 52/48). Colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.14 (m, 5H, CH, Ar), 2.25 [dd, J = 13.9, 6.6 Hz, 0.52×1H, CH₂ (cis- to F), syn-isomer], 1.98 – 1.84 [m, 0.96×H, CH₂ (cis- and trans- to F), anti-isomer], 1.70 – 1.67 [m, 0.52×1H, CH₂ (trans- to F), syn-isomer], 1.24 – 1.23 (m, 0.52×12H, CH₃, syn-isomer), 1.18 (s, 0.48×12H, CH₃, anti-isomer). ¹⁹F NMR (376 MHz, CDCl₃): δ -127.14 (d, J = 13.6 Hz, 0.52×1F, syn-isomer), -133.63 (dd, J = 15.3, 7.7 Hz, 0.48×1F,
anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 137.8/136.2 (d, $J_{CF} = 3.8$ Hz) (C, Ar), 129.4/129.3 (d, $J_{CF} = 2.3$ Hz) (CH, Ar), 128.2/128.1 (CH, Ar), 126.7/126.6 (CH, Ar) 97.48 (d, $J_{CF} = 286.2$ Hz)/94.46 (d, $J = 289.6$ Hz) (CF), 84.6/84.5 (C-O), 24.77/24.74 (CH$_3$), 24.7/24.6 (d, $J_{CF} = 2.3$ Hz) (CH$_2$), 24.5/24.4 (CH$_3$). MS (ESI, m/z, %): 319 ([M+Na]$^+$). HRMS (ESI): m/z calcd. for C$_{15}$H$_{19}$BClFNaO$_2$ [M+Na]$^+$, 319.1048; found, 319.1039.

$I$-(2-Chloro-2-fluoro-3-methylcyclopropyl)-4-methoxybenzene (2m)

Yield: 84 mg (78%, syn/anti = 58/42). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.10 – 6.93 (m, 2H, CH, Ar), 6.75 (dd, $J = 8.8$, 3.0 Hz, 2H, CH, Ar), 3.68 (s, 0.42×3H, CH$_3$, anti-isomer), 3.67 (s, 0.58×3H, CH$_3$, syn-isomer), 2.24 (dd, $J = 18.1$, 8.1 Hz, 0.42×1H, CHAr, anti-isomer), 2.05 (d, $J = 8.0$ Hz, 0.58×1H, CHAr, syn-isomer), 1.85 – 1.70 (m, 1H, 0.57×1H, CHMe, syn-isomer), 1.70 – 1.58 (m, 0.42×1H, CHMe, anti-isomer), 1.28 (d, $J = 6.3$ Hz, 0.42×3H, CH$_3$, anti-isomer), 1.24 (dd, $J = 6.3$, 1.9 Hz, 0.58×3H, CH$_3$, syn-isomer). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -142.03 (d, $J = 19.7$ Hz, 0.58×1F, syn-isomer), -142.64 (d, $J = 18.1$ Hz, 0.42×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.7 (MeOC, Ar), 129.4 (d, $J = 1.8$ Hz)/129.2 ((d, $J = 0.6$ Hz) (CH, Ar), 127.0/126.1 (d, $J = 1.8$ Hz) (C, Ar), 113.9/113.7 (CH, Ar), 97.57 (d, $J_{CF} = 292.1$ Hz)/97.48 (d, $J = 289.1$ Hz) (CF), 55.31/55.28 (CH$_3$), 38.18 (d, $J_{CF} = 11.3$ Hz)/36.04 (d, $J_{CF} = 10.6$ Hz) (CHAr), 27.66 (d, $J_{CF} = 11.1$ Hz)/26.02 (d, $J_{CF} = 9.6$ Hz) (CHMe), 14.5/11.8 (d, $J_{CF} = 6.4$ Hz) (CH$_3$). HRMS (EI): m/z calcd. for C$_{11}$H$_{11}$ClFO ([M-H]$^+$), 213.0483; found, 213.0482.
1-((2-Chloro-2-fluorocyclopropyl)methyl)-4-methoxybenzene (2n)

Yield: 78 mg (73%, syn/anti = 52/48). Yellow liquid. **\(^1\)H NMR** (400 MHz, CDCl\(_3\)): \(\delta\) 7.19 (t, \(J = 8.4\) Hz, 2H, CH, Ar), 6.90 – 6.86 (m, 2H, CH, Ar), 3.81 (s, 3H, CH\(_3\)), 2.87 – 2.63 (m, 2H, syn-isomer and anti-isomer, CH\(_2\)Ar), 1.95 – 1.76 (m, 1H, 0.52\(\times\)1H, CHCH\(_2\)Ar, syn-isomer), 1.75 – 1.69 (m, 0.48\(\times\)1H, CHCH\(_2\)Ar, anti-isomer), 1.68 – 1.62 [m, 0.52\(\times\)1H, CH\(_2\) (cis- to F), syn-isomer], 1.49 – 1.38 [m, 0.48\(\times\)1H, CH\(_2\) (cis- to F), anti-isomer], 1.35 – 1.20 [m, 0.48\(\times\)1H, CH\(_2\) (trans- to F), anti-isomer], 1.01 [td, \(J = 7.6, 6.1\) Hz, 0.52\(\times\)1H, CH\(_2\) (trans- to F), syn-isomer]. **\(^1\)F NMR** (376 MHz, CDCl\(_3\)): \(\delta\) -129.77 – -131.77 (m, 0.52\(\times\)1F, syn-isomer), -149.39 – -150.59 (m, 0.48\(\times\)1F, anti-isomer). **\(^{13}\)C NMR** (101 MHz, CDCl\(_3\)): \(\delta\) 158.27/158.26 (MeOC, Ar), 131.7/131.4 (d, \(J_{CF} = 1.3\) Hz) (C, Ar), 129.22/129.18 (CH, Ar), 114.03/114.01 (CH, Ar), 96.0 (d, \(J_{CF} = 285.4\) Hz)/93.4 (d, \(J_{CF} = 287.0\) Hz) (CF), 55.3 (CH\(_3\)), 34.6/32.4 (d, \(J_{CF} = 5.2\) Hz) (ArCH\(_2\)), 28.9 (d, \(J_{CF} = 11.2\) Hz)/26.4 (d, \(J_{CF} = 10.2\) Hz) (CHCH\(_2\)Ar), 21.4 (d, \(J_{CF} = 7.1\) Hz)/21.3 (d, \(J_{CF} = 6.6\) Hz) (CHCH\(_2\)CFCl). **MS** (EI, m/z, %): 179 (100), 214 (M\(^+\), 67.82). **HRMS (EI)**: m/z calcd. for C\(_{11}\)H\(_{12}\)ClFO (M\(^+\)), 214.0561; found, 214.0559.

(2-(2-Chloro-2-fluorocyclopropyl)ethyl)benzene (2o)
Yield: 84 mg (85%, syn/anti = 51/49). Light yellow liquid.  

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 – 6.95 (m, 5H, CH, Ar), 2.90 – 2.63 (m, 2H, CH$_2$Ar, syn-isomer and anti-isomer), 1.96 – 1.67 (m, 2H, CH$_2$CH$_2$Ar, syn-isomer and anti-isomer), 1.65 – 1.50 (m, 1H, CFClCH$_2$, syn-isomer and anti-isomer), 1.45 [dd, $J = 16.3, 8.6$ Hz, 1H, 0.51×1H, CH$_2$ (cis- to F), syn-isomer], 1.32 [dt, $J = 17.8, 9.1$ Hz, 0.49×1H, CH$_2$ (cis- to F), anti-isomer], 1.11 [dt, $J = 15.3, 7.5$ Hz, 0.49×1H, CH$_2$ (trans- to F), syn-isomer], 0.85 [d, $J = 5.7$ Hz, 0.51×1H, CH$_2$ (trans- to F), syn-isomer]. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -130.50 (td, $J = 17.7, 2.8$ Hz, 0.51×1F, syn-isomer), -151.63 (dd, $J = 16.3, 5.6$ Hz, 0.49×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.3 (C, Ar), 128.52/128.50 (CH, Ar), 128.48/128.47 (CH, Ar), 126.11/126.10 (CH, Ar), 96.2 (d, $J_{CF} = 284.7$ Hz)/93.5 (d, $J_{CF} = 287.0$ Hz) (CF), 35.2/34.8 (d, $J_{CF} = 1.3$ Hz) (CH$_2$Ar), 31.8 (d, $J = 0.8$ Hz)/29.3 (d, $J_{CF} = 4.5$ Hz) (CH$_2$CH$_2$Ar), 27.4 (d, $J_{CF} = 11.2$ Hz)/24.9 (d, $J_{CF} = 10.1$ Hz) (CFClCH$_2$), 21.4 (d, $J_{CF} = 6.6$ Hz)/21.3 (d, $J_{CF} = 5.9$ Hz) (CHCH$_2$CFCl). HRMS (EI): $m/z$ calcd. for C$_{11}$H$_{12}$ClF (M$^+$), 198.0612; found, 198.0612.

(2-chloro-2-fluorocyclopropoxy)benzene (2p)

Yield: 87 mg (94%, syn/anti = 40/60). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 – 7.28 (m, 2H, CH, Ar), 7.11 – 6.92 (m, 3H, CH, Ar), 4.09 (ddd, $J = 12.0, 8.8, 5.0$ Hz, 0.40×1H, CHOAr, syn-isomer), 3.94 – 3.72 (m, 0.60×1H, CHOAr, anti-isomer), 2.10 – 1.90 (m, 0.40×1H, CH$_2$ (cis- to F), syn-isomer), 1.84 (ddd, $J = 18.7, 9.2, 4.6$ Hz, 0.60×1H, CH$_2$ (cis to F), anti-isomer), 1.72 (dd, $J = 17.6, 9.2$ Hz,
0.60×1H, CH$_2$ (trans- to F), anti-isomer), 1.56 (ddd, $J = 8.9, 7.4, 5.2$ Hz, 0.40×1H, CH$_2$ (trans- to F), syn-isomer). $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -137.44 – -140.63 (m, 0.40×1F, syn-isomer), -155.75 – -160.20 (m, 0.60×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 157.8/157.3 (C, Ar), 129.8/129.7 (CH, Ar), 122.4 (C, Ar), 115.0/114.9 (CH, Ar), 92.1 (d, $J_{CF} = 290.4$ Hz)/89.6 (d, $J_{CF} = 292.4$ Hz) (CF), 58.2 (d, $J_{CF} = 9.6$ Hz)/56.3 (d, $J_{CF} = 14.2$ Hz) (CHOAr), 23.31 (d, $J_{CF} = 11.9$ Hz), 22.54 (d, $J_{CF} = 10.9$ Hz) (CH$_2$). HRMS (ESI): $m/z$ calcd. for C$_9$H$_7$ClFO ([M-H]$^+$), 185.0170; found, 185.0163.

**(Dichlorofluoromethyl)trimethylsilane**[7]

![Dichlorofluoromethyltrimethylsilane](image)

White solid. M.p.: 42–43 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.32 (s, 9H, CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -75.73 (1F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 123.65 (d, $J = 321.7$ Hz) (CF), -4.29 (CH$_3$).

**(Dibromofluoromethyl)trimethylsilane**[8]

![Dibromofluoromethyltrimethylsilane](image)

Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.31 (s, 9H, CH$_3$). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -76.29 (1F). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 103.93 (d, $J = 339.6$ Hz) (CF), -4.74 (CH$_3$). MS (ESI, $m/z$, %): 264 (M$^+$), 266 ([M+2]$^+$).

**(2-Bromo-2-fluorocyclopropane-1,1-diyl)dibenzene (3a)**[9]
Yield: 139 mg (96%), Light yellow solid. M.p.: 78 - 79 °C. **\(^1\)H NMR** (400 MHz, CDCl\(_3\)): δ 7.44 (dd, \(J = 12.7, 7.6\) Hz, 4H, CH, Ar), 7.31 (dd, \(J = 4.4, 1.8\) Hz, 4H, CH, Ar), 7.26 – 7.19 (m, 2H, CH, Ar), 2.27 [dd, \(J = 17.6, 7.7\) Hz, 1H, CH\(_2\) (cis- to F)], 2.16 [dd, \(J = 10.7, 4.9\) Hz, 1H, CH\(_2\) (trans- to F)]. **\(^{19}\)F NMR** (376 MHz, CDCl\(_3\)): δ -123.51 (dd, \(J = 16.7, 7.6\) Hz, 1F). **\(^{13}\)C NMR** (101 MHz, CDCl\(_3\)): δ 141.3 (d, \(J_{CF} = 2.6\) Hz) (C, Ar), 139.1 (d, \(J_{CF} = 2.8\) Hz) (C, Ar), 129.3 (CH, Ar), 128.8 (CH, Ar), 128.79 (CH, Ar), 128.6 (CH, Ar), 128.5 (CH, Ar), 127.4 (CH, Ar), 86.6 (d, \(J_{CF} = 305.0\) Hz) (CF), 43.08 (d, \(J_{CF} = 10.1\) Hz) (CAr), 29.11 (d, \(J_{CF} = 9.8\) Hz) (CH\(_2\)). **MS** (EI, \(m/\zeta\), %): 290 (M\(^+\), 3.32), 211 (100.00). **HRMS** (EI): \(m/\zeta\) calcd for C\(_{15}\)H\(_{12}\)FBr (M\(^+\)), 290.0106; found, 290.0115.

*1-Bromo-4-(2-bromo-2-fluorocyclopropyl)benzene (3b)*\(^{[10]}\)

Yield: 112 mg (76%, *symlanti* = 38/62). Light yellow oil. **\(^1\)H NMR** (400 MHz, CDCl\(_3\)): δ 7.47 (dd, \(J = 8.3, 6.6\) Hz, 2H, CH, Ar), 7.10 (dd, \(J = 14.6, 8.3\) Hz, 2H, CH, Ar), 2.98 – 2.55 (m, 1H, syn-isomer and anti-isomer), 2.06 [ddd, \(J = 17.0, 11.6, 8.0\) Hz, 0.38×1H, CH\(_2\) (cis- to F), syn-isomer], 1.95 – 1.74 [m, 1H, 1.24H, CH\(_2\) (cis- and trans- to F), anti-isomer], 1.64 [dd, \(J = 15.9, 8.0\) Hz, 0.38×1H, CH\(_2\) (trans- to F), syn-isomer]. **\(^{19}\)F NMR** (376 MHz, CDCl\(_3\)): δ -125.45 (td, \(J = 17.4, 7.3\) Hz, 0.38×1F,
syn-isomer), -145.77 – -147.48 (m, 0.62×1F, anti-isomer). \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)): \(\delta\) 134.5/132.6 (d, \(J_{\text{CF}} = 1.8\) Hz) (C, Ar), 131.6/131.5 (CH, Ar), 130.3 (d, \(J_{\text{CF}} = 2.0\) Hz)/130.1 (d, \(J_{\text{CF}} = 1.1\) Hz) (CH, Ar), 121.5/121.4 (C, Ar), 85.5 (d, \(J_{\text{CF}} = 302.0\) Hz)/79.9 (d, \(J_{\text{CF}} = 301.7\) Hz) (CHAr), 22.8 (d, \(J_{\text{CF}} = 10.4\) Hz)/22.2 (d, \(J_{\text{CF}} = 10.6\) Hz) (CH\(_2\)). **MS (EI, m/z, %):** 292 (M\(^+\), 0.21), 134 (100.00). **HRMS (EI):** m/z calcd for C\(_9\)H\(_7\)FBr\(_2\) (M\(^+\)): 291.8899; found: 291.8912.

\(1-(2\text{-Bromo-2-fluorocyclopropyl})-4\text{-fluorobenzene (3c)}\)\(^{[11]}\)

Yield: 81 mg (70%, syn/anti = 42/58), Light yellow oil. \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.20 (ddd, \(J = 8.4, 7.0, 3.7\) Hz, 2H, CH, Ar), 7.09 – 6.98 (m, 2H, CH, Ar), 2.81 – 2.69 (m, 1H, syn-isomer and anti-isomer), 2.05 [ddd, \(J = 17.0, 11.6, 7.9\) Hz, 0.42×1H, CH\(_2\) (cis- to F), syn-isomer], 1.86 – 1.80 [m, 1H, 1.16H, CH\(_2\) (cis- and trans- to F), anti-isomer], 1.63 [dd, \(J = 15.7, 8.0\) Hz, 0.42×1H, CH\(_2\) (trans- to F), syn-isomer]. \(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)): \(\delta\) -114.84 – -115.1 (m, F-Ar), -125.67 (td, \(J = 17.4, 7.1\) Hz, 0.42×1F, syn-isomer), -146.46 – -146.61 (m, 0.58×1F, anti-isomer). \(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)): \(\delta\) 162.3 (d, \(J_{\text{CF}} = 246.2\) Hz)/162.1 (d, \(J_{\text{CF}} = 246.0\) Hz), 131.2 (d, \(J_{\text{CF}} = 3.3\) Hz)/129.3, 130.2 (d, \(J_{\text{CF}} = 8.2\) Hz)/129.9 (d, \(J_{\text{CF}} = 8.1\) Hz), 115.4 (d, \(J_{\text{CF}} = 21.6\) Hz)/115.3 (d, \(J_{\text{CF}} = 21.5\) Hz), 85.9 (d, \(J_{\text{CF}} = 301.4\) Hz)/80.1 (d, \(J_{\text{CF}} = 301.5\) Hz), 32.5 (d, \(J_{\text{CF}} = 10.8\) Hz)/29.8 (d, \(J_{\text{CF}} = 11.2\) Hz), 22.8 (d, \(J_{\text{CF}} = 10.3\) Hz)/22.1 (d, \(J_{\text{CF}} = 10.6\) Hz). **MS (EI, m/z, %):** 232 (M\(^+\), 0.19), 153(100.00). **HRMS (EI):** m/z calcd for C\(_9\)H\(_7\)FBr (M\(^+\)), 231.9699; found, 231.9693.
Yield: 112 mg (90%, syn/anti = 43/57). Light yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta$ 7.31 (t, $J$ = 6.8 Hz, 2H, CH, Ar), 7.16 (dd, $J$ = 14.3, 8.1 Hz, 2H, CH, Ar), 2.75 (t, $J$ = 18.1 Hz, 1H, syn-isomer and anti-isomer), 2.19 – 1.92 [m, 0.43×1H, CH$_2$ (cis- to F), syn-isomer ], 1.84 [t, $J$ = 11.3 Hz, 1H, 1.14H, CH$_2$ (cis- and trans- to F), anti-isomer], 1.65 [dd, $J$ = 15.7, 7.8 Hz, 0.43×1H, CH$_2$ (trans- to F), syn-isomer]. $^{19}\text{F NMR}$ (376 MHz, CDCl$_3$): $\delta$ -125.50 (dd, $J$ = 16.5, 7.5 Hz, 0.43×1F, syn-isomer), -146.47 (d, $J$ = 7.6 Hz, 0.57×1F, anti-isomer). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$): $\delta$ 134.0/133.4 (C, Ar), 133.3/132.1 (d, $J_{\text{CF}}$ = 1.7 Hz), 129.9 (d, $J_{\text{CF}}$ = 1.9 Hz) (CH, Ar)/129.7 (d, $J_{\text{CF}}$ = 0.8 Hz) (CH, Ar), 128.7/128.6 (s) (CH, Ar), 85.6 (d, $J$ = 301.5 Hz)/79.9 (d, $J_{\text{CF}}$ = 301.2 Hz) (CF), 32.6 (d, $J_{\text{CF}}$ = 10.8 Hz)/29.9 (d, $J_{\text{CF}}$ = 11.3 Hz) (CHAr), 22.82 (d, $J_{\text{CF}}$ = 10.3 Hz)/22.08 (d, $J_{\text{CF}}$ = 10.7 Hz) (CH$_2$). MS (EI, m/z, %): 248 (M$^+$, 1.3), 169 (100.00); HRMS (EI): m/z calcd for C$_9$H$_7$FClBr (M$^+$); 247.9404, found, 247.9411.

Yield: 97 mg (90%, syn/anti = 43/57). Light yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl$_3$): $\delta$ 7.35 – 7.20 (m, 5H, CH, Ar), 2.83-2.75 (m, 1H, CHAr, syn-isomer and anti-isomer),
2.07 – 1.98 [m, 0.43 × 1H, CH₂ (cis- to F), syn-isomer], 1.93 – 1.78 [m, 1.14H, CH₂ (cis- and trans- to F), anti-isomer], 1.70 – 1.65 [m, 0.43 × 1H, CH₂ (trans- to F), syn-isomer]. ¹⁹F NMR (376 MHz, CDCl₃/TMS): δ -124.98 (td, J = 17.6, 7.3 Hz, 0.43 × 1F, syn-isomer), δ -146.33 (dd, J = 17.1, 8.8 Hz, 0.57 × 1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 135.4/133.5 (d, JCF = 1.7 Hz) (C, Ar), 128.52 (d, JCF = 2.1 Hz)/128.48 (CH, Ar), 128.36/128.34 (d, JCF = 1.4 Hz) (CH, Ar), 127.5/127.4 (CH, Ar), 86.13 (d, JCF = 301.4 Hz)/80.41 (d, JCF = 302.1 Hz) (CF), 33.23 (d, JCF = 10.8 Hz)/30.57 (d, JCF = 11.0 Hz) (CH₂). MS (EI, m/z, %): 248 (M⁺, 1.3), 169 (100.00), HRMS (EI): m/z calcd for C₉H₈FBr (M⁺), 213.9793; found, 213.9797.

4-(2-Bromo-2-fluorocyclopropyl)-N,N-dimethylaniline (3f)

Yield: 103 mg (80%, syn/anti = 61/39), White solid, M.p. 72-73 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.09 (dd, J = 18.3, 8.4 Hz, 2H, CH, Ar), 6.71 (d, J = 8.5 Hz, 2H, CH, Ar), 2.94 (s, 0.61 × 6H, CH₃, syn-isomer), 2.93 (s, 0.39 × 6H, CH₃, anti-isomer), 2.76 – 2.56 (m, 1H, CHAr, syn-isomer and anti-isomer), 2.03 – 1.87 [m, 0.61 × 1H, CH₂ (cis- to F), syn-isomer], 1.78 [dt, J = 17.5, 9.2 Hz, 0.78H, CH₂ (cis- and trans- to F), anti-isomer], 1.59 [dd, J = 15.8, 7.7 Hz, 0.61 × 1H, CH₂ (trans- to F), syn-isomer]. ¹⁹F NMR (376 MHz, CDCl₃): δ -145.50 (0.61 × 1F, syn-isomer), δ -125.29 (0.39 × 1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 149.4 (C, Ar), 129.3 (C, Ar), 129.2/129.1 (CH, Ar), 113.0/112.7 (CH, Ar), 87.3 (d, JCF = 301.7 Hz)/81.0 (d, JCF = 301.7 Hz) (CF), 41.0/40.9 (CH₃), 32.6 (d, JCF = 10.8 Hz)/29.9 (d, JCF = 10.9 Hz) (CHAr), 22.4 (d, JCF = 10.3 Hz)/21.8 (d, JCF = 10.5 Hz) (CH₂). MS (EI, m/z, %): 257
(M⁺, 0.5), 178(100.00). **HRMS (ESI):** m/z calcd for C₁₁H₁₄BrFN ([M+H]⁺), 258.0294; found, 258.0301.

1-(2-Bromo-2-fluorocyclopropyl)-4-methoxybenzene(3g)\[^{[13]}\]

Yield: 119 mg (97%, syn/anti = 48/52), Light yellow oil. **¹H NMR** (400 MHz, CDCl₃): δ 7.15 (dd, J = 16.8, 8.2 Hz, 2H, CH, Ar), 6.87 (dd, J = 4.5, 1.9 Hz, 2H, CH, Ar), 3.79 (s, 3H, CH₃), 2.71 (dd, J = 19.5, 9.9 Hz, 1H, CHAr, syn-isomer and anti-isomer), 2.07 – 1.89 [m, 0.48×1H, CH₂ (cis- to F), syn-isomer], 1.80 [dd, J = 18.1, 9.2 Hz, 1.04×1H, CH₂ (cis- and trans- to F), anti-isomer], 1.61 [dd, J = 17.4, 9.8 Hz, 0.48×1H, CH₂ (trans- to F), syn-isomer]. **¹⁹F NMR** (376 MHz, CDCl₃/TMS): δ -125.43 (td, J = 17.7, 7.3 Hz, 0.48×1F, syn-isomer), -146.47 (dd, J = 15.3, 10.1 Hz, 0.52×1F, anti-isomer). **¹³C NMR** (101 MHz, CDCl₃): δ 158.9 (MeOC, Ar), 129.6 (d, J CF = 2.0 Hz)/129.4 (d, J CF = 0.8 Hz) (CH, Ar), 127.6/125.5 (d, J CF = 2.0 Hz) (C, Ar), 113.93/113.75 (CH, Ar), 86.7 (d, J CF = 301.7 Hz)/ 80.6 (d, J CF = 301.7 Hz) (CF), 55.3/55.3 (CH₃), 32.6 (d, J CF = 10.8 Hz)/29.9 (d, J CF = 11.0 Hz) (CHAr), 22.5 (d, J CF = 10.3 Hz)/21.9 (d, J CF = 10.6 Hz) (CH₂). **MS (EI, m/z, %):** 244 (M⁺, 1.09), 165 (100.00); HRMS(EI): m/z calcd for C₁₆H₁₀OFBr(M⁺), 243.9899; found, 243.9904.

1-(2-Bromo-2-fluorocyclopropyl)-4-tert-butylbenzene(3h)
Yield: 95 mg (70%, syn/anti = 22/78), Light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.36 (dd, $J = 8.3, 1.6$ Hz, 2H, CH, Ar), 7.16 (dd, $J = 16.6, 8.3$ Hz, 2H, CH, Ar), 2.83 – 2.66 (m, 1H, CHAr, syn-isomer and anti-isomer), 2.01 [ddd, $J = 17.2, 11.7, 7.8$ Hz, 0.22×1H, CH$_2$ (cis- to F), syn-isomer], 1.92 – 1.72 [m, 1.56 H, CH$_2$ (cis- and trans- to F), anti-isomer], 1.65 [dd, $J = 16.2, 7.7$ Hz, 0.22×1H, CH$_2$ (trans- to F), syn-isomer], 1.32 (s, 0.22×9H), 1.31 (s, 0.78×9H). $^{19}$F NMR (376 MHz, CDCl$_3$): δ -124.79 (td, $J = 17.5, 7.5$ Hz), -145.82 – -147.35 (0.78×1F, anti-isomer). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 150.35/150.33 (C, Ar), 132.4/130.5 (d, $J_{CF} = 1.7$ Hz) (C, Ar), 128.1 (d, $J_{CF} = 2.0$ Hz)/127.9 (d, $J_{CF} = 1.1$ Hz) (CH, Ar), 125.4/125.2 (CH, Ar), 86.4 (d, $J_{CF} = 301.3$ Hz)/80.6 (d, $J_{CF} = 302.2$ Hz) (CF), 34.54/34.52 (C(CH$_3$)$_3$), 32.9 (d, $J_{CF} = 10.8$ Hz)/30.2 (d, $J_{CF} = 11.0$ Hz) (CHAr), 31.33/31.31 [C(CH$_3$)$_3$], 22.7 (d, $J_{CF} = 10.3$ Hz)/22.0 (d, $J_{CF} = 10.5$ Hz) (CH$_2$). MS (EI, m/z, %): 270 (M$^+$, 0.13), 57 (100.00). HRMS (EI): m/z calcd for C$_{10}$H$_{16}$FBr (M$^+$), 270.0419; found, 270.0406.

Methyl 4-(2-bromo-2-fluorocyclopropyl)benzoate (3i)

Yield: 60 mg (44%, syn/anti = 46/54). Light yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.01 (t, $J = 8.3$ Hz, 2H, CH, Ar ), 7.48 – 7.06 (m, 2H, CH, Ar), 3.92 (s, 0.46×3H, CH$_3$, syn-isomer), 3.91 (s, 0.54×3H, CH$_3$, anti-isomer), 2.91 – 2.73 (m, 1H,
CHAr, syn-isomer and anti-isomer), 2.10 (ddd, J = 16.9, 11.5, 8.0 Hz, 0.46×1H, CH₂ (cis- to F), syn-isomer), 2.00 – 1.81 (m, 1.08H, CH₂ (cis- and trans- to F), anti-isomer), 1.74 (dd, J = 16.0, 8.1 Hz, 0.46×1H, CH₂ (trans- to F), syn-isomer). ¹⁹F NMR (377 MHz, CDCl₃): δ -124.84 (dd, J = 17.1, 11.2 Hz, 0.46×1F, syn-isomer), -146.28 (dd, J = 16.9, 8.7 Hz, 0.54×1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 166.8 (COOMe), 140.6/138.8 (C, Ar), 129.7/129.6 (CH, Ar), 129.3/129.2 (C, Ar), 128.5 (d, J = 1.9 Hz)/128.3 (CH, Ar), 85.23 (d, J = 302.2 Hz/79.91 (d, J = 302.2 Hz) (CF), 52.2 (CH₃), 33.2 (d, J = 10.7 Hz)/30.5 (d, J = 11.4 Hz) (CHAr), 23.2 (d, J = 10.4 Hz)/22.2 (d, J = 10.4 Hz) (CH₂). HRMS (ESI): m/z calcd. for C₁₁H₁₀FBr ([M+H]+), 272.9926; found, 272.9946.

1-(2-Bromo-2-fluorocyclopropyl)-2-methylbenzene (3j) [¹³]

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\text{\begin{align*}
\text{syn-3j} & \quad + \quad \text{anti-3j} \\
\end{align*}}
\]

Yield: 83 mg (73%, syn/anti = 52/48), Light yellow oil. ¹H NMR (376 MHz, CDCl₃): δ 7.25-6.96 (m, 4H, CH, Ar), 2.74 (ddd, J = 17.4, 11.2, 8.8 Hz, 1H, CHAr, syn-isomer and anti-isomer), 2.46 (s, 0.52×3H, CH₃, syn-isomer), 2.44 (s, 0.48×3H, CH₃, anti-isomer), 2.04 [ddd, J = 16.6, 11.5, 7.8 Hz, 0.52×1H, CH₂ (cis- to F), syn-isomer], 1.98 – 1.78 [m, 0.96 H, CH₂ (cis- and trans- to F), anti-isomer]. ¹⁹F NMR (376 MHz, CDCl₃): δ -127.75 (t, J = 17.3 Hz, 0.52×1F, syn-isomer), -145.79 (dd, J = 17.2, 7.8 Hz, 0.48×1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 139.0/138.6 (C, Ar), 134.27/132.23 (d, J_CF = 2.3 Hz) (C, Ar), 129.9/129.8 (CH, Ar), 127.9/127.7 (CH, Ar), 127.7/127.3 (d, J = 4.3 Hz) (CH, Ar), 125.9 (CH, Ar), 86.2 (d, J_CF = 302.4 Hz)/80.8 (d, J_CF = 300.2 Hz) (CF), 32.3 (d, J_CF = 11.3 Hz)/29.7 (d, J_CF = 10.6 Hz) (CHAr), 21.4 (d, J_CF = 4.4 Hz)/21.3 (d, J_CF = 4.7 Hz) (CH₂), 20.1/19.8 (CH₃). MS (EI, m/z, %): 228 (M⁺, 0.44), 189 (100.00).
HRMS (EI): m/z calcd for C_{10}H_{10}FBr(M^+), 227.9950; found, 227.9948.

1-Bromo-1-fluoro-1,1a,6,6a-tetrahydro-cycloprop[a]indene (3k)\textsuperscript{[14]}

Yield: 79.5 mg (70%), White solid, M.p.: 70-71 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.36 (dd, J = 5.1, 3.5 Hz, 1H, CH, Ar), 7.21 – 7.12 (m, 3H, CH, Ar), 3.26 – 3.17 (m, 3H), 2.58 – 2.51 (m, 1H).

\textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}): δ -160.1.

\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 143.53 (d, J_{CF} = 2.2 Hz) (C, Ar), 137.10 (d, J_{CF} = 2.6 Hz) (C, Ar), 127.32 (CH, Ar), 126.71 32 (CH, Ar), 125.30 32 (CH, Ar), 124.38 32 (CH, Ar), 82.57 (d, J_{CF} = 315.1 Hz) (CF), 41.30 (d, J_{CF} = 12.3 Hz) (CH), 34.04 (d, J_{CF} = 13.0 Hz) (CH), 32.26 (d, J_{CF} = 3.8 Hz) (CH\textsubscript{2}). MS (EI, m/z, %): 226 (M^+, 0.27), 147(100.00).

HRMS (EI): m/z calcd for C_{10}H_{7}FBr ([M-H]^+), 224.9715; found, 224.9722.

(2-(2-Bromo-2-fluorocyclopropyl)ethyl)benzene (3l)

Yield: 49 mg (40\%, syn/anti = 42/58), Light yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.31-7.27 (m, 2H, CH, Ar), 7.23 – 7.16 (m, 3H, CH, Ar), 2.90 – 2.64 (m, 2H, CH\textsubscript{2}Ar, syn-isomer and anti-isomer), 1.96 – 1.67 (m, 2H, syn-isomer and anti-isomer), 1.66-1.53 (m, 1H, CHCFBr, syn-isomer and anti-isomer), 1.53 – 1.44 [m, 0.42×1H, CH\textsubscript{2} (cis- to F), syn-isomer], 1.47 – 1.30 [m, 0.58×1H, CH\textsubscript{2} (cis- to F), anti-isomer], 1.12 [dt, J = 17.6, 7.6 Hz, 0.58×1H, CH\textsubscript{2} (trans- to F), anti-isomer], 0.90 [dd, J = 15.0,
7.4 Hz, 0.42×1H, CH₂ (trans- to F), syn-isomer. ¹⁹F NMR (376 MHz, CDCl₃): δ -122.99 (ddd, J = 17.4, 12.0, 3.9 Hz, 0.42×1F, syn-isomer), -145.20 (dd, J = 17.6, 7.0 Hz, 0.58×1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 141.23/141.22 (C, Ar), 128.51/128.49 (CH, Ar), 128.47/128.46 (CH, Ar), 126.10/126.09 (CH, Ar), 87.5 (d, JCF = 298.0 Hz)/82.3 (d, JCF = 301.3 Hz) (CF), 35.1/34.5 (d, JCF = 0.7 Hz) (ArCH₂), 33.6 (d, JCF = 0.8 Hz)/29.3 (d, JCF = 4.7 Hz) (ArCH₂CH₂), 28.4 (d, JCF = 10.7 Hz)/25.1 (d, JCF = 9.3 Hz) (CHCFBr), 22.6 (d, JCF = 10.8 Hz)/22.3 (d, JCF = 10.1 Hz) (CH₂CFBr). HRMS (EI): m/z calcd for C₁₁H₁₂BrF (M⁺), 242.0106; found, 242.0103.

((2-Bromo-2-fluorocyclopropyl)methyl)benzene (3m) [¹⁵]

Yield: 46 mg (40%, syn/anti = 40/60), Light yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.57 – 6.93 (m, 5H, CH, Ar), 2.97 – 2.64 (m, 1H, ArCH₂), 2.79 (dd, J = 15.1, 6.8 Hz, 0.6×1H, ArCH₂), 2.68 (ddd, J = 15.2, 6.5, 2.9 Hz, 0.4×1H, ArCH₂), 1.89 – 1.73 (m, 1H, CHCFBr, syn-isomer and anti-isomer), 1.72 – 1.67 [m, 0.40×1H, CFBrCH₂ (cis- to F), syn-isomer], 1.52 – 1.42 [m, 0.6×1H, CFBrCH₂ (cis- to F), anti-isomer], 1.31 [dt, J = 17.5, 7.7 Hz, 0.6×1H, CH₂ (trans- to F), anti-isomer], 1.15 – 1.00 [m, 1H, 0.40×1H, CH₂ (trans- to F), syn-isomer]. ¹⁹F NMR (376 MHz, CDCl₃): δ -127.12 (d, J = 11.5 Hz, 0.40×1F, syn-isomer), -147.53 (s, 0.60×1F, anti-isomer). ¹³C NMR (101 MHz, CDCl₃): δ 139.6/139.2 (d, JCF = 1.1 Hz) (C, Ar), 128.64/128.62 (CH, Ar), 128.34/128.29 (CH, Ar), 126.53/126.49 (CH, Ar), 87.2 (d, JCF = 298.6 Hz)/82.0 (d, JCF = 301.4 Hz) (CF), 37.2 (d, JCF = 0.7 Hz)/33.2 (d, JCF = 5.4 Hz) (ArCH₂), 29.6 (d, JCF = 10.7 Hz)/26.4 (d, JCF = 9.6 Hz) (CHCFBr), 22.8 (d, JCF = 10.8 Hz)/22.5 (d, JCF = 10.3 Hz) (CH₂CFBr). HRMS (EI): m/z calcd for C₁₀H₁₀FBr (M⁺), 227.9950; found, 227.9941.

S28
(2-bromo-2-fluorocyclopropoxy)benzene (3n)

Yield: 110 mg (96%, syn/anti = 32/68). Light yellow liquid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.34 (td, \( J = 7.6, 1.0 \) Hz, 2H, CH, Ar), 7.10 – 6.98 (m, 3H, CH, Ar), 4.10 – 3.90 (m, 1H, CHOAr, syn-isomer and anti-isomer), 2.03 (dt, \( J = 19.4, 9.2 \) Hz, 0.32\( \times \)1H, CH\(_2\) (cis to F), syn-isomer), 1.90 (ddddd, \( J = 20.3, 9.5, 4.9, 0.5 \) Hz, 0.68\( \times \)1H, CH\(_2\) (cis to F), anti-isomer), 1.80 (dt, \( J = 18.1, 9.2 \) Hz, 0.68\( \times \)1H, CH\(_2\) (trans to F), anti-isomer), 1.67 – 1.57 (m, 0.32\( \times \)1H, CH\(_2\) (trans to F), syn-isomer). \( ^19F \) NMR (377 MHz, CDCl\(_3\)): \( \delta \) -136.41 – -138.15 (m, 0.32\( \times \)1F, syn-isomer), -155.90 – -157.50 (m, 0.68\( \times \)1F, anti-isomer). \( ^13C \) NMR (101 MHz, CDCl\(_3\)): \( \delta \) 157.8/157.1 (C, Ar), 129.7/129.6 (CH, Ar), 122.3 (C, Ar), 115.1/114.9 (CH, Ar), 82.4 (d, \( J_{CF} = 303.7 \) Hz)/78.4 (d, \( J_{CF} = 306.6 \) Hz) (CF), 58.9 (d, \( J_{CF} = 9.4 \) Hz)/56.3 (d, \( J_{CF} = 13.8 \) Hz) (CHOAr), 24.8 (d, \( J_{CF} = 11.4 \) Hz)/23.5 (d, \( J_{CF} = 10.5 \) Hz) (CH\(_2\)). HRMS (ESI): m/z calcd. for C\(_9\)H\(_7\)BrFO ([M-H]\(^+\)), 228.9665; found, 228.9670.

Ethyl 2-methyl-2-(4-vinylphenoxy)propanoate (6a)\(^6\)

Light yellow liquid. \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.29 (d, \( J = 8.6 \) Hz, 2H, CH, Ar), 6.80 (d, \( J = 8.7 \) Hz, 2H, CH, Ar), 6.64 (dd, \( J = 17.6, 10.9 \) Hz, 1H, CH\(_2\)=CH\(_2\)), 5.62 (dd, \( J = 17.6, 0.8 \) Hz, 1H, CH\(_2\)=CH\(_2\)), 5.14 (dd, \( J = 10.9, 0.7 \) Hz, 1H, CH\(_2\)=CH\(_2\)), 4.23 (q, \( J \)
= 7.1 Hz, 2H, OCH₂), 1.60 (s, 6H, 2CH₃), 1.25 (t, J = 7.1 Hz, 3H, CH₂CH₃). \(^{13}\)C NMR (101 MHz, CDCl₃): \(\delta\) 174.3 (C=O), 155.2 (ArC-O), 136.1 (CH=CH₂), 131.7 (C, Ar), 127.0 (CH, Ar), 119.0 (CH, Ar), 112.2 (CH=CH₂), 79.2 (C(CH₃)₂), 61.5 (OCH₂CH₃), 25.4 (C(CH₃)₂), 14.1 (OCH₂CH₃). HRMS (ESI): m/z calcd. for C₁₃H₁₉NaO₃ [M+Na]^⁺, 257.1154; found, 257.1156.

**Ethyl 2-(4-(2-chloro-2-fluorocyclopropyl)phenoxy)-2-methylpropanoate (A)**

Yield: 92 mg (60%, synlanti = 1:1). Yellow liquid. \(^{1}\)H NMR (400 MHz, CDCl₃): \(\delta\) 7.09 (dd, J = 12.2, 8.6 Hz, 2H, CH, Ar), 6.81 (dd, J = 8.7, 2.0 Hz, 2H, CH, Ar), 4.22 (tt, J = 7.1, 3.6 Hz, 2H, OCH₂CH₃), 2.80 (ddd, J = 17.1, 11.6, 8.6 Hz, 0.52×1H, CHAr, syn-isomer), 2.63 (t, J = 9.7 Hz, 1H, 0.48×1H, CHAr, anti-isomer), 1.94 [ddd, J = 15.9, 11.6, 7.7 Hz, 0.52×1H, CH₂ (cis- to F), syn-isomer], 1.80 – 1.72 [m, 0.96H, CH₂ (cis- and trans- to F), anti-isomer], 1.59 (s, 0.52×6H, 2CH₃, syn-isomer), 1.58 (s, 0.48×6H, 2CH₃, anti-isomer), 1.55 – 1.50 [m, 0.52×1H, CH₂ (trans- to F), syn-isomer], 1.23 (td, J = 7.1, 4.5 Hz, 3H, OCH₂CH₃). \(^{19}\)F NMR (376 MHz, CDCl₃): \(\delta\) -128.71 (td, J = 16.4, 5.9 Hz, 0.52×1F, syn-isomer), -148.95 (dd, J = 15.7, 8.0 Hz,0.48×1F, anti-isomer). \(^{13}\)C NMR (101 MHz, CDCl₃): \(\delta\) 174.2 (C=O), 154.8/154.7 (ArC-O), 129.2 (d, J_{CF} = 2.0 Hz)/129.0 (d, J_{CF} = 0.6 Hz) (CH, Ar), 128.0/127.1 (d, J_{CF} = 1.6 Hz) (C, Ar), 119.0/118.8 (CH, Ar), 94.8 (d, J_{CF} = 293.6 Hz)/92.0 (d, J_{CF} = 293.4 Hz) (CF), 79.2 [O(=CH₂)₂], 61.4 (OCH₂CH₃), 31.6 (d, J_{CF} = 11.3 Hz)/29.7 (d, J_{CF} = 11.7 Hz) (CHAr), 25.39/25.36 (C(CH₃)₂), 21.5 (d, J_{CF} = 10.9 Hz)/20.9 (d, J_{CF} = 11.1 Hz) (FCICCH₂), 14.1(OCH₂CH₃). HRMS (ESI): m/z calcd. for C₁₅H₁₈ClFNaO₃ [M+Na]^⁺, 323.0826; found, 323.0827.
(2-Fluorocyclopropane-1,1-diyl)dibenzene

Yield: 76 mg (72%), Light yellow viscous oil. $^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.42 (d, $J = 7.4$ Hz, 2H, CH, Ar), 7.33 (t, $J = 7.4$ Hz, 2H, CH, Ar), 7.25 (d, $J = 5.7$ Hz, 3H, CH, Ar), 7.17 (d, $J = 7.3$ Hz, 3H, CH, Ar), 5.00 (dd, $J = 65.0$, 3.3 Hz, 1H, CFH), 1.87 – 1.72 (m, 1H, CH₂), 1.63 – 1.47 (m, 1H, CH₂). $^{19}$F NMR (376 MHz, CDCl₃): $\delta$ -207.04 (ddd, $J = 65.1$, 22.7, 11.3 Hz, 1F). $^{13}$C NMR (101 MHz, CDCl₃) $\delta$: 143.4 (d, $J_{CF} = 2.0$ Hz), 139.0 (d, $J_{CF} = 3.1$ Hz), 130.4, 128.6, 128.4, 127.6 (d, $J_{CF} = 1.4$ Hz), 127.0, 126.6, 77.0 (d, $J_{CF} = 229.5$ Hz) (CF), 35.1 (d, $J_{CF} = 10.5$ Hz) (C(Ph)₂), 20.7 (d, $J_{CF} = 9.6$ Hz) (CH₂). MS (EI, m/z, %): 212 (M⁺, 88.93), 165 (100.00). HRMS (EI): m/z calcd for C₁₀H₁₃F (M⁺), 212.0101; found, 212.0995.

(Z)-(3-Bromo-2-fluoroprop-1-en-1-yl)benzene

$^1$H NMR (400 MHz, CDCl₃): $\delta$ 7.50 (d, $J = 7.3$ Hz, 2H), 7.29 (ddd, $J = 11.1$, 9.4, 6.1 Hz, 3H), 5.85 (d, $J = 36.0$ Hz, 1H), 4.10 (d, $J = 20.1$ Hz, 2H). $^{19}$F NMR (376 MHz, CDCl₃): $\delta$ -107.73 (dt, $J = 36.1$, 20.1 Hz). $^{13}$C NMR (101 MHz, CDCl₃): $\delta$ 154.5 (d, $J = 262.8$ Hz), 132.4, 129.0 (d, $J = 7.6$ Hz), 128.7, 128.2, 110.5 (d, $J = 8.2$ Hz), 29.7 (d, $J = 31.3$ Hz). MS (EI, m/z, %): 214 (M⁺, 7.44), 216 ([M+2]⁺, 7.70), 135 (100.00), 115 (54.04).

2-(p-Tolyl)cycloprop-2-en-1-one
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.42 (s, 1H), 7.76 (d, $J = 8.1$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 2.45 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.6, 155.4, 144.7, 139.1, 131.3, 130.1, 120.5, 22.0. HRMS (ESI): $m/z$ calcd. for C$_{10}$H$_9$O [M+H]$^+$, 145.0653; found, 146.0654.

8. Full List of Ref. 6(b)

FSO$_2$CF$_2$CO$_2$R (R = SiMe$_3$, Me)

BrCF$_2$CO$_2$Na

TMSCF$_2$X (X = F, Cl, Br)

Ph$_3$P*CF$_2$CO$_2$–

9. References


Chem. Soc. 1968, 90, 6717.


10. $^1$H, $^{13}$C and $^{19}$F NMR Spectra
$^{19}$F NMR

Br

2c

Br

Cl

F

Cl

F

S41
$^{13}$C NMR
$^{1}H$ NMR

\begin{align*}
t-	ext{Bu} & \begin{array}{c}
\text{Cl} \quad \text{F} \\
\end{array} \\
\text{2e} & + \\
t-	ext{Bu} & \begin{array}{c}
\text{F} \quad \text{Cl} \\
\end{array}
\end{align*}
$^{19}$F NMR

$t$-Bu

$2e$

$t$-Bu

Cl

F

F

Cl
$^{19}$F NMR

\[ \text{MeO}_2C \quad 2i \quad \text{MeO}_2C \]

+ 

$\text{Cl}_2\text{F}$

$\text{F}_2\text{Cl}$
$^1$H NMR

![Chemical Structure Diagram]

2h
$^{19}$F NMR

\[
\begin{array}{c}
\text{Cl} \quad \text{F} \\
\text{Me} \\
\end{array}
\quad + 
\quad 
\begin{array}{c}
\text{F} \quad \text{Cl} \\
\text{Me} \\
\end{array}
\]

2h
$^{19}\text{F NMR}$

\[ \begin{align*}
\text{Cl} & \quad \text{F} \\
\text{Me} & \\
\text{O} & \\
\end{align*} \] $+ \quad \begin{align*}
\text{F}_2 \quad \text{Cl} \\
\text{Me} & \\
\text{O} & \\
\end{align*} \] 

2i

\[ \begin{array}{c}
-145.0 & -142.0 & -140.0 & -138.0 & -136.0 & -134.0 & -132.0 \\
1.50 & 1.50 & 1.50 & 1.50 & 1.50 & 1.50 & 1.50 \\
\end{array} \]
$^{13}$C NMR

\[ \text{Compound } 2i \]

\[ \text{Structural formula of compound } 2i \]

\[ \text{NMR spectrum of compound } 2i \]
\[ ^1\text{H NMR} \]

\[ \text{Si-CFCI}_2 \]
$^{19}$F NMR

$\text{Si} - \text{CFCl}_2$
$^{13}\text{C NMR}$

$\text{Si} - \text{CFCl}_2$
$^{19}\text{F NMR}$

$\text{Si-}\text{CFBr}_2$
$^{13}$C NMR

$\text{Si-CFBr}_2$
$^{19}\text{F NMR}$

![Chemical Structure](image)

![NMR Spectrum](image)

S90
$^1$H NMR

\[ \text{Br} \quad \text{F} \quad + \quad \text{F} \quad \text{Br} \]

3e
$^{19}$F NMR

\[ \text{Br}_2F + \text{F}_2\text{Br} \]

3f
$^{13}$C NMR

$\text{Br}_2 \text{F}$

$3i$

$\text{Br}_2 \text{F}$

$\text{F}_2 \text{Br}$
$^{19}$F NMR
$^{13}$C NMR

\[ \text{F} \quad \text{Br} \quad + \quad \text{F} \quad \text{Br} \]

3k
$^{13}$C NMR

\[ \text{Br} \quad \text{F} \quad + \quad \text{F} \quad \text{Br} \]

3I
$^{13}$C NMR

\[ \text{O} \quad \text{Br} \quad \text{F} \quad \text{O} \]

\[ + \]

\[ \text{F} \quad \text{Br} \]

3n
$^{13}$C NMR

![NMR Spectrogram](image)
$^{13}$C NMR

![Chemical Structures](image)

![NMR Spectrum](image)