Light-Mediated Iodoperfluoroalkylation of Alkenes/Alkynes Catalyzed by Chloride Ions: Role of Halogen Bonding

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I. General experimental details

All reagents were obtained from commercial sources and used as received. Commercial anhydrous methanol (Sure/Seal, stored on molecular sieves) was used for the ATRA reactions. NMR analyses were carried out on a Bruker avanceII-400 and avanceII-300 (400 MHz and 300 MHz for proton, 101 MHz and 75 MHz for $^{13}$C, 282 MHz for $^{19}$F) in deuterated chloroform as solvent. The chemical shifts ($\delta$) for carbon and proton resonances are given compared to the residual solvent peak and are expressed in ppm. Mass spectra were recorded by the CESAMO (Bordeaux, France) using electrospray ionisation (ESI) or electron impact ionization (EI). HRMS ESI spectra were obtained on a QStar Elite mass spectrometer (Applied Biosystems) using positive polarity electrospray ionization mode, electron impact ionization (EI) mass spectra were obtained on an ISQ mass spectrometer (Thermo Scientific) and HRMS EI spectra were obtained on a Accutof GCv mass spectrometer (JEOL). Absorption spectra were recorded on a Varian Cary 5000 spectrophotometer in 1 cm pathlength quartz cells. Photoirradiations (320-390 nm) were performed using a portable Fisher Bioblock mercury lamp (type Thin Layer Chromatography “TLC”, 6W) set at 365 nm. The transmission spectrum in the UVA region of commercial borosilicate glass of 1 mm thickness can be found at: https://www.sinclairmfg.com/datasheets/optical3.html
Table S1. Optimization of the Reaction Conditions\textsuperscript{a}

\[
\text{\( \overset{7}{\text{C}_8 \text{F}_{17}} \)} + \text{\( \overset{17}{\text{C}_8 \text{F}_{17}} \)} \xrightarrow{\text{Additive, Light}} \text{\( \overset{7}{\text{C}_8 \text{F}_{17}} \)}
\]

\begin{tabular}{|c|c|c|c|}
\hline
entry & additive & conversion (\%)\textsuperscript{b} & yield (\%)\textsuperscript{c} \\
\hline
1 & - & 6 & 4 \\
2 & \(\text{Bu}_4\text{NCl} \) (100 mol\%) & 100 & >95 \\
3 & \(\text{Bu}_4\text{NCl} \) (10 mol\%) & 100 & >95 \\
4 & \(\text{Bu}_4\text{NCl} \) (5 mol\%) & 83 & 80 \\
5 & \(\text{Bu}_4\text{NCl} \) (1 mol\%) & 45 & 41 \\
6 & \(\text{Bu}_4\text{NCl} \) (10 mol\%)\textsuperscript{d} & 0 & - \\
7 & \(\text{Bu}_4\text{NCl} \) (10 mol\%)\textsuperscript{e} & 0 & - \\
8 & \(\text{Bu}_4\text{NCl} \) (10 mol\%)\textsuperscript{f} & 0 & - \\
9 & \(\text{Bu}_4\text{NF} \) (10 mol\%) & 37 & 32 \\
10 & \(\text{Bu}_4\text{NBr} \) (10 mol\%) & 0 & - \\
11 & \(\text{Bu}_4\text{NI} \) (10 mol\%) & 0 & - \\
12 & \(\text{NaCl} \) (10 mol\%) & 100 & >95 \\
\hline
\end{tabular}

\textsuperscript{a} Standard conditions unless otherwise noted: Reactions conducted in NMR tubes in \(\text{CD}_3\text{OD} \) (0.7 mL) on 0.1 mmol of alkene and 0.12 mmol of \(\text{C}_8\text{F}_{17}\text{I} \), degassing by Ar bubbling for 20 min, irradiation for 25 min by placing the low pressure Hg Lamp type TLC (set at 365 nm: emitted light ~ 320-390 nm) at ~ 1 cm from the tube. \textsuperscript{b} Converted alkene. \textsuperscript{c} Isolated yield. \textsuperscript{d} Reaction in the dark. \textsuperscript{e} Reaction in air. \textsuperscript{f} Irradiation with a household CFL bulb (23W).
II. Emission, UV-Vis and NMR spectra.

Figure S1: Emission spectrum of the low-pressure Hg lamp used in this study.

Figure S2: UV light absorption spectrum of a solution of C₈F₁₇I in MeOH (0.15 M, quartz cuvette, path length 10 mm, 3 mL).
Figure S3: $^{19}$F (282 MHz) and $^1$H (300 MHz) NMR spectra in CDCl$_3$ of an aliquot of the reaction mixture obtained after irradiation for 2 h of a deaerated MeOH solution (freeze-pump-thaw cycles, flame-sealed glassware) containing C$_8$F$_{17}$I (0.15 M) and Bu$_4$NCl (10 mol%). Addition of an aliquot of an authentic sample of CH$_2$(OCH$_3$)$_2$ confirmed the proposed assignment.
Figure S4. $^{19}$F (282 MHz) NMR spectrum in CDCl$_3$ of an aliquot of the reaction mixture obtained after irradiation for 2 h of a deaerated MeOH solution (freeze-pump-thaw cycles, flame-sealed glassware) containing C$_8$F$_{17}$I (0.15 M).
III. Determination of the binding stoichiometry of C₈F₁₇I with Cl⁻ (Bu₄N⁺Cl⁻) in CDCl₃

The binding stoichiometry of C₈F₁₇I with Cl⁻ (Bu₄N⁺Cl⁻) was determined by Job’s plot analysis using ¹⁹F NMR and the conditions employed by Chen and coworkers i.e. : CDCl₃ (0.5 mL); total amount of C₈F₁₇I and Bu₄N⁺Cl⁻ kept constant at 0.25 mmol (0.5 M); molar ratios [C₈F₁₇I]/[C₈F₁₇I + Cl⁻] were 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. Analysis of the NMR spectra afforded the results presented below.

<table>
<thead>
<tr>
<th>[C₈F₁₇I] (M)</th>
<th>δ CF₄I (ppm)</th>
<th>Δδ (ppm)</th>
<th>[C₈F₁₇I]/[C₈F₁₇I + Cl⁻]</th>
<th>[C₈F₁₇I]xΔδ (M, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>0.937</td>
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<tr>
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<td>8.649</td>
<td>0.3</td>
<td>1.296</td>
</tr>
<tr>
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<td>7.655</td>
<td>0.4</td>
<td>1.534</td>
</tr>
<tr>
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<td>65.832</td>
<td>6.581</td>
<td>0.5</td>
<td>1.647</td>
</tr>
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<td>59.251</td>
<td>0</td>
<td>1.0</td>
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</table>

y = -6.611x² + 6.7536x - 0.0835
R² = 0.9925

IV. Determination of the association constant (Kₐ) between C₈F₁₇I and Cl⁻ (Bu₄N⁺Cl⁻) in CDCl₃

The association constant between C₈F₁₇I and Cl⁻ (Bu₄N⁺Cl⁻) was determined with Hanna and Ashbaugh’s graphical method using ¹⁹F NMR and the conditions employed by Chen and coworkers i.e. : CDCl₃ (0.6mL); amount of C₈F₁₇I kept constant at 0.03 mmol; amount of
Bu₄N⁺Cl⁻ varied from 0.06 to 1.2 mmol. Analysis of the NMR spectra afforded the results presented below.

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻ (M)</td>
<td>Cl⁻ (M)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>0.5</td>
</tr>
<tr>
<td>0.33</td>
<td>0.34</td>
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<tr>
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<td>0.25</td>
</tr>
<tr>
<td>0.15</td>
<td>0.147</td>
</tr>
<tr>
<td>0.1</td>
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<tr>
<td>Δδ (ppm)</td>
<td>Δδ (ppm)</td>
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<td>1/Δδ</td>
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<td>0.0765</td>
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<tr>
<td>0.1585</td>
<td>0.1798</td>
</tr>
<tr>
<td>0.2070</td>
<td>0.2077</td>
</tr>
</tbody>
</table>

V. General procedure for the ATRAs of R₄I to alkenes and alkynes conducted on 1 mmol scale (scheme 1)

In a test tube (borosilicate glass, wall thickness 0.7 mm, diameter 1.6 cm, height 10 cm), or a Schlenk tube (wall thickness 1.8 mm, diameter 2 cm), was introduced a magnetic stir bar and a solution of anhydrous CH₃OH (7 mL) containing Bu₄NCl A or NaCl B (10 or 20 mol%), R₄I and the alkene or alkyne. Degassing was rapidly initiated (to avoid I₂ formation due to possible oxidation of adventitious HI) by gentle argon bubbling for 30 minutes (test tube) or, even better, by freeze-pump-thaw cycles and filling the tube with argon after the last vacuum pumping (the reaction mixture must remain colorless). It should be noted that a special attention should be taken in the deoxygenation procedure. The reaction was initiated by irradiating at 320-390 nm using a TLC lamp placed at ~ 1 cm from the test tube (irradiation times given in schemes 1-3).
Once the reaction was completed, the CH$_3$OH solvent was evaporated and the residue was purified by flash chromatography over silica gel (pentane/EtOAc).

**Compound 1:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dodec-1-ene (221 µL, 1 mmol) and C$_8$F$_{17}$I (573.2 mg, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 1 as yellow oil in 87% yield (622 mg) with A and 85% yield (608 mg) with B.

\[
\begin{align*}
\text{C}_8\text{F}_{17} & \quad \text{1} \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 4.40-4.26 (m, 1H), 3.06-2.63 (m, 2H), 1.94-1.67 (m, 2H), 1.62-1.17 (m, 16H), 0.88 (t, $J = 6.3$ Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) $\delta$ (ppm) = 41.7 (t, $J = 20.7$ Hz), 40.3, 31.9, 29.7, 29.54, 29.51, 29.4, 29.3, 28.5, 22.7, 20.9, 14.1; $^{19}$F-NMR (CDCl$_3$, 282 MHz) $\delta$ (ppm) = -80.8, -111.1 to -115.3 (m), -121.60, -121.62, -121.9, -122.8, -123.6, -126.1; EI-MS (m/z, relative intensity): 714 (M–H, 2), 587 (M–I, 4), 531 (M–C$_4$H$_9$I, 5), 517 (M–CF$_3$HI, 5), 489 (M–C$_3$H$_7$F$_3$I, 5), 85 (C$_6$H$_{13}$, 40), 71 (C$_2$H$_{11}$, 66), 57 (C$_4$H$_9$, 100), 43 (C$_3$H$_7$, 70).

**Compound 2:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dodec-1-ene (221 µL, 1 mmol) and C$_4$F$_9$I (180 µL, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 2 as yellow oil in 80% yield (412 mg) with A and 78% yield (401 mg) with B.

\[
\begin{align*}
\text{C}_4\text{F}_{9} & \quad \text{2} \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 4.40-4.27 (m, 1H), 3.08-2.63 (m, 2H), 1.95-1.72 (m, 2H), 1.59-1.17 (m, 16H), 0.88 (t, $J = 6.3$ Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) $\delta$ (ppm) = 41.8 (t, $J = 20.6$ Hz), 40.5, 32.1, 29.8, 29.72, 29.69, 29.4, 28.7, 22.8, 21.0, 14.2; $^{19}$F-NMR (CDCl$_3$, 282 MHz) $\delta$ (ppm) = -81.1, -111.3 to -115.6 (m), -124.6, -125.9; HRMS (FI+): Calcd. for C$_{16}$H$_{23}$F$_9$I : 514.0779, Found: 514.0801.

**Compound 3:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dodec-1-ene (221 µL, 1 mmol) and C$_5$F$_{11}$I (204 µL, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 3 as yellow oil in 85% yield (479.4 mg) with A and 82% yield (462.5 mg) with B.

\[
\begin{align*}
\text{C}_5\text{F}_{11} & \quad \text{3} \\
\end{align*}
\]

$^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 4.41-4.25 (m, 1H), 3.07-2.64 (m, 2H), 1.92-1.67 (m, 2H), 1.59-1.12 (m, 16H), 0.88 (t, $J = 6.6$ Hz,
3H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 75 MHz) δ (ppm) = 41.9 (t, J = 20.9 Hz), 40.5, 32.1, 29.8, 29.73, 29.71, 29.55, 29.49, 28.7, 22.9, 21.1, 14.2; \textsuperscript{19}F-NMR (CDCl\textsubscript{3}, 282 MHz) δ (ppm) = -72.1, -111.0 to -116.5 (m), -116.6, -185.9; EI-MS (m/z, relative intensity): 563 (M-H, 5), 437 (M-I, 5), 395 (M-C\textsubscript{3}H\textsubscript{5}I\textsuperscript{+}, 4), 339 (M-C\textsubscript{3}H\textsubscript{4}I\textsuperscript{+}, 4), 85 (C\textsubscript{5}H\textsubscript{3}I\textsuperscript{+}, 40), 71 (C\textsubscript{3}H\textsubscript{2}I\textsuperscript{+}, 66), 57 (C\textsubscript{4}H\textsubscript{3}I\textsuperscript{+}, 100), 43 (C\textsubscript{3}H\textsubscript{2}I\textsuperscript{+}, 80).

\textbf{Compound 4}: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), pent-4-en-1-ol (102 µL, 1 mmol) and C\textsubscript{8}F\textsubscript{17}I (573.2 mg, 1.05 mmol) in CH\textsubscript{3}OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc : 80/20) to afford 4 as yellow oil in 65% yield (411 mg) with A and 81% yield (510 mg) with B.

![](image1)

\textbf{Compound 5}: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), pent-4-en-1-ol (102 µL, 1 mmol) and C\textsubscript{8}F\textsubscript{17}I (573.2 mg, 1.05 mmol) in CH\textsubscript{3}OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc : 80/20) to afford 4 as yellow oil in 65% yield (411 mg) with A and 81% yield (510 mg) with B.

\textbf{Compound 5}: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), pent-4-en-1-ol (102 µL, 1 mmol) and C\textsubscript{8}F\textsubscript{17}I (573.2 mg, 1.05 mmol) in CH\textsubscript{3}OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc : 80/20) to afford 4 as yellow oil in 65% yield (411 mg) with A and 81% yield (510 mg) with B.

\textbf{Compound 5}: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), pent-4-en-1-ol (102 µL, 1 mmol) and C\textsubscript{8}F\textsubscript{17}I (573.2 mg, 1.05 mmol) in CH\textsubscript{3}OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc : 80/20) to afford 4 as yellow oil in 65% yield (411 mg) with A and 81% yield (510 mg) with B.
**Compound 7:** Synthesized from B (5.8 mg, 0.1 mmol), undec-10-en-1-ol (200 µL, 1 mmol) and C₅F₁₁I (204 µL, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 85/15) to afford 7 as yellow oil in 80% yield (450 mg).

**Compound 8:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), tert-butyl allylcarbamate (157 mg, 1 mmol) and C₈F₁₇I (573.2 mg, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 95/5), to afford 8 as a yellow solid in 71% yield (500 mg) with A and 67% yield (473 mg) with B.

**Compound 9:** Synthesized from A (28 mg, 0.1 mmol), tert-butyl allylcarbamate (157 mg, 1 mmol) and C₄F₉I (180 µL, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 95/5), to afford 9 as a yellow solid in 71% yield (500 mg) with A and 67% yield (473 mg) with B.
chromatography over silica gel (pentane/EtOAc, 95/5), to afford 9 as a yellow solid in 61% yield (307 mg).

Mp = 68-70 °C; $^1$H-NMR (CDCl$_3$, 300 MHz) δ (ppm) = 5.04 (brs, 1H), 4.93-4.30 (m, 1H), 3.65-3.33 (m, 2H), 2.98-2.64 (m, 2H), 1.44 (s, 9H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) δ (ppm) = 155.7, 80.4, 49.1, 38.6 (t, J = 21.1 Hz), 28.4, 18.7; $^{19}$F-NMR (CDCl$_3$, 282 MHz) δ (ppm) = -81.1, -111.5 to -115.2 (m), -124.7, -126.0; HRMS (FI+): Calcd. for C$_{12}$H$_{15}$NO$_2$F$_9$I : 503.0003; Found: 503.0010.

**Compound 10:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), 10-bromodec-1-ene (201 µL, 1 mmol) and C$_8$F$_{17}$I (573.2 mg, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 10 as yellow oil in 89% yield (681 mg) with A and 80% yield (610 mg) with B.

$^1$H-NMR (CDCl$_3$, 300 MHz) δ (ppm) = 4.40-4.25 (m, 1H), 3.40 (t, J = 6.9 Hz, 2H), 3.06-2.62 (m, 2H), 1.94-1.66 (m, 4H), 1.59-1.19 (m, 10H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) δ (ppm) = 41.7 (t, J = 20.8 Hz), 40.4, 34.0, 32.9, 29.7, 29.3, 28.8, 28.5, 28.2, 21.0; $^{19}$F-NMR (CDCl$_3$, 282 MHz) δ (ppm) = -80.9, -111.0 to -115.5 (m), -121.64, -121.67, -122.0, -122.8, -123.7, -126.2; CI-MS (m/z, relative intensity): 765 (M–H, 5), 685 (M–Br, 100), 637 (M–I, 90), 557 (C$_{18}$H$_{18}$F$_{17}$+, 80), 503 (C$_{14}$H$_{10}$F$_{17}$+, 30).

**Compound 11:** Synthesized from B (5.8 mg, 0.1 mmol), 10-bromodec-1-ene (201 µL, 1 mmol) and C$_5$F$_{11}$I (204 µL, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 11 as colorless oil in 83% yield (513 mg).

$^1$H-NMR (CDCl$_3$, 300 MHz) δ (ppm) = 4.39-4.25 (m, 1H), 3.40 (t, J = 6.9 Hz, 2H), 3.04-2.68 (m, 2H), 1.92-1.69 (m, 4H), 1.56-1.19 (m, 10H); $^{13}$C-NMR (CDCl$_3$, 75 MHz) δ (ppm) = 41.9 (t, J = 20.8 Hz), 40.4, 34.0, 32.9, 29.7, 29.3, 28.8, 28.5, 28.2, 21.0; $^{19}$F-NMR (CDCl$_3$, 282 MHz) δ (ppm) = -72.0, -110.8 to -115.4 (m), -116.5, -185.8; HRMS (CI+): Calcd. for C$_{15}$H$_{10}$BrF$_{11}$ (M-I) : 487.0494; Found: 487.0507.

**Compound 12:** Synthesized from B (5.8 mg, 0.1 mmol), but-3-en-1-ylbenzene (150 µL, 1 mmol) and C$_8$F$_{17}$I (573 mg, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash
chromatography over silica gel (100% pentane) to afford 12 as pink solid in 88% yield (600 mg).

**M.p.** = 44-46 °C; **^1H-NMR** (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 7.44-7.33 (m, 2H), 7.29-7.18 (m, 3H), 4.41-4.25 (m, 1H), 3.10-2.67 (m, 4H), 2.29-2.06 (m, 2H); **^13C-NMR** (CDCl$_3$, 75 MHz) $\delta$ (ppm) = 140.1, 128.8, 128.7, 126.6, 42.0 (t, $J = 16.5$ Hz), 41.9, 35.9, 20.2; **^19F-NMR** (CDCl$_3$, 282 MHz) $\delta$ (ppm) = -81.1, -110.0 to -115.1 (m), -121.70, -121.73, -122.1, -122.9, -123.7, -126.4; **HRMS** (FI+): Calcd. for C$_{18}$H$_{12}$F$_{17}$: 677.9712; Found: 677.9731.

**Compound 13:** Synthesized from A (28 mg, 0.1 mmol), but-3-en-1-ylbenzene (150 µL, 1 mmol) and C$_5$F$_{11}$I (204 µL, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 13 as yellow oil in 68% yield (460 mg).

**^1H-NMR** (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 7.40-7.31 (m, 2H), 7.27-7.19 (m, 3H), 4.30 (ddd, $J = 5.1$ Hz, $J = 8.4$ Hz and $J = 13.3$ Hz, 1H), 3.12-2.66 (m, 4H), 2.27-2.03 (m, 2H); **^13C-NMR** (CDCl$_3$, 75 MHz) $\delta$ (ppm) = 140.0, 128.8, 128.6, 126.5, 42.0 (t, $J = 16.5$ Hz), 41.9, 35.9, 20.3; **^19F-NMR** (CDCl$_3$, 282 MHz) $\delta$ (ppm) = -72.0, -110.4 to -115.1 (m), -116.5, -185.9; **EI-MS** ($m/z$, relative intensity): 528 (M, 5), 401 (M-I, 5), 91 (C$_7$H$_7^+$, 100).

**Compound 14:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol) and C$_8$F$_{17}$I (573.2 mg, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 14 as colorless oil in 76% yield (535 mg) with A and 76% yield (535 mg) with B.

**^1H-NMR** (CDCl$_3$, 300 MHz) $\delta$ (ppm) = 7.59-7.52 (m, 2H), 7.46-7.37 (m, 3H), 3.38 (dd, $J = 2.7$ Hz and $J = 10.5$ Hz, 1H), 2.79-2.37 (m, 2H), 0.53 (s, 3H), 0.52 (s, 3H); **^13C-NMR** (CDCl$_3$, 75 MHz) $\delta$ (ppm) = 134.5, 134.1, 130.3, 128.3, 38.4 (t, $J = 21.5$ Hz), -0.6, -3.0, -4.4; **^19F-NMR** (CDCl$_3$, 282 MHz) $\delta$ (ppm) = -80.9, -112.9 to -116.7 (m), -121.7, -122.60, -122.4, -122.8, -123.7, -126.2; **HRMS** (FI+): Calcd. for C$_{18}$H$_{14}$F$_{17}$Si: 707.9638, Found: 707.9628.
Compound 15: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol) and C₄F₉I (180 µL, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 15 as colorless oil in 80% yield (408 mg) with A and 79% yield (400 mg) with B.

\[ \begin{align*} \text{C}_4\text{F}_9 & \quad \text{SiMe}_2\text{Ph} \\ -15 \end{align*} \] ¹H-NMR (CDCl₃, 300 MHz) \( \delta \) (ppm) = 7.57-7.51 (m, 2H), 7.47-7.35 (m, 3H), 3.37 (dd, \( J = 2.7 \) Hz and \( J = 10.2 \) Hz, 1H), 2.78-2.37 (m, 2H), 0.53 (s, 3H), 0.51 (s, 3H); ¹³C-NMR (CDCl₃, 75 MHz) \( \delta \) (ppm) = 134.5, 134.1, 130.3, 128.3, 35.1 (t, \( J = 21.8 \) Hz), -0.6, -3.0, -4.4; ¹⁹F-NMR (CDCl₃, 282 MHz) \( \delta \) (ppm) = -81.1, -113.0 to -116.8 (m), -124.7, -126.0; HRMS (FI⁺): Calcd. for C₁₄H₁₄F₉Si: 507.9765; Found: 507.9772.

Compound 16: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dimethyl(phenyl)(vinyl)silane (192 µL, 1 mmol) and C₅F₁₁I (204 µL, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 16 as colorless oil in 82% yield (458 mg) with A and 85% yield (474 mg) with B.

\[ \begin{align*} \text{C}_5\text{F}_{11} & \quad \text{SiMe}_2\text{Ph} \\ -16 \end{align*} \] ¹H-NMR (CDCl₃, 300 MHz) \( \delta \) (ppm) = 7.58-7.51 (m, 2H), 7.47-7.37 (m, 3H), 3.37 (dd, \( J = 2.7 \) Hz and \( J = 10.5 \) Hz, 1H), 2.80-2.38 (m, 2H), 0.53 (s, 3H), 0.52 (s, 3H); ¹³C-NMR (CDCl₃, 75 MHz) \( \delta \) (ppm) = 134.5, 134.1, 130.3, 128.3, 35.3 (t, \( J = 21.8 \) Hz), -0.4, -3.1, -4.4; ¹⁹F-NMR (CDCl₃, 282 MHz) \( \delta \) (ppm) = -72.0, -112.7 to -116.9 (m), -185.8; HRMS (FI⁺): Calcd. for C₁₅H₁₄F₁₁ISi: 557.9734; Found: 557.9746.

Compound 17: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), (Z)-cyclooctene (130 µL, 1 mmol) and C₈F₁₇I (573.2 mg, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane 100%) to afford 17 (d.r = 1:1) as yellow oil in 89% yield (584 mg) with A and 77% yield (505 mg) with B.

\[ \begin{align*} \text{C}_8\text{F}_{17} & \quad \text{SiMe}_2\text{Ph} \\ -17 \end{align*} \] ¹H-NMR (CDCl₃, 300 MHz) \( \delta \) (ppm) = 4.67-4.56 (m, 0.5H, d1 or d2), 4.55-4.48 (m, 0.5H, d1 or d2), 2.52-2.23 (m, 3H, d1 and d2), 2.18-1.96 (m, 3H, d1 and d2), 1.93-1.34 (m, 7H, d1 and d2); ¹³C-NMR (CDCl₃, 75 MHz) \( \delta \) (ppm) = 41.1 (t, \( J = 20.0 \) Hz, d1 or d2), 40.7 (t, \( J = 20.2 \) Hz, d1 or d2), 36.1 (d1 or d2), 35.0 (d1 or d2), 34.7 (d1 or d2), 34.0 (d1 or d2), 27.3 (d1 or d2), 27.2 (d1 or d2), 26.6 (d1 and d2), 25.5 (d1 or d2), 25.1 (d1 or d2), 25.0 (d1 or d2), 23.8 (d1 or d2), 23.6 (d1 or d2); ¹⁹F-NMR (CDCl₃, 282 MHz) \( \delta \) (ppm) = -81.0 (d1
Compound 18: Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), (Z)-cyclooctene (130 µL, 1 mmol) and C₄F₉I (180 µL, 1.05 mmol) in CH₃OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 18 (d.r = 1:1) as yellow oil in 63% yield (289 mg) with A and 79% yield (360 mg) with B.

Compound 19: Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), dodec-1-ene (221 µL, 1 mmol), CF₃I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH₃OH), and CH₃OH (1 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 19 as yellow oil in 76% yield (277 mg) with A and 69% yield (250 mg) with B.

Compound 20: Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), pent-4-en-1-ol (102 µL, 1 mmol), CF₃I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH₃OH), and CH₃OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc:...
85/15) to afford 20 as yellow oil in 79% yield (223 mg) with A and 71% yield (200 mg) with B.

![Image of compound 20](image)

**1H-NMR** (CDCl₃, 300 MHz) δ (ppm) = 4.29-4.15 (m, 1H), 3.69 (t, J = 6.0 Hz, 2H), 2.98 (s, 1H), 2.97-2.70 (m, 2H), 1.93-1.57 (m, 4H); 13C-NMR (CDCl₃, 75 MHz) δ (ppm) = 125.7 (q, J = 276.9 Hz), 61.7, 45.0 (q, J = 28.1 Hz), 36.2, 32.5, 21.3; 19F-NMR (CDCl₃, 282 MHz) δ (ppm) = -63.9 (t, J = 10.2 Hz); CI-MS (m/z, relative intensity): 265 (M-H₂O, 100), 155 (M-I, 50), 137 (C₆H₈F₃⁺, 55).

**Compound 21:** Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), undec-10-en-1-ol (200 µL, 1 mmol), CF₃I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH₃OH), and CH₃OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 85/15) to afford 21 as yellow oil in 81% yield (296 mg) with A and 88% yield (321 mg) with B.

![Image of compound 21](image)

**1H-NMR** (CDCl₃, 300 MHz) δ (ppm) = 4.24-4.10 (m, 1H), 3.63 (t, J = 6.6 Hz, 2H), 2.99-2.63 (m, 2H), 1.82-1.64 (m, 3H), 1.56-1.44 (m, 3H), 1.35-1.23 (m, 10H); 13C-NMR (CDCl₃, 75 MHz) δ (ppm) = 125.7 (q, J = 277.0 Hz), 63.0, 45.0 (q, J = 28.0 Hz), 39.8, 32.8, 29.6, 29.5, 29.4, 29.3, 28.6, 25.8, 22.0; 19F-NMR (CDCl₃, 282 MHz) δ (ppm) = -63.9 (t, J = 10.4 Hz); HRMS (ESI): Calcd. for C₁₂H₂₂F₃NaI : 389.0559; Found: 389.0551.

**Compound 22:** Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), tert-butyl allylcarbamate (157 mg, 1 mmol), CF₃I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH₃OH), and CH₃OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc: 95/5) to afford 22 as white solid in 65% yield (229 mg) with A and 59% yield (207 mg) with B.

![Image of compound 22](image)

**M.p.** = 67-69 °C; **1H-NMR** (CDCl₃, 300 MHz) δ (ppm) = 5.05 (brs, 1H), 4.32-4.16 (m, 1H), 3.62-3.31 (m, 2H), 2.89-2.62 (m, 2H), 1.44 (s, 9H); 13C-NMR (CDCl₃, 75 MHz) δ (ppm) = 155.7, 125.5 (q, J = 276 Hz), 80.3, 48.7, 41.9 (q, J = 28.0 Hz), 28.4, 20.1; 19F-NMR (CDCl₃, 282 MHz) δ (ppm) = -63.9 (t, J = 9.9 Hz); HRMS (FI+): Calcd. for C₉H₁₅O₂F₃NI : 353.0099; Found: 353.0104.
Compound 23: Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), but-3-en-1-ylbenzene (150 µL, 1 mmol), CF$_3$I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH$_3$OH), and CH$_3$OH (1 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 23 as yellow oil in 84% yield (283 mg) with B.

\[
\text{1H-NMR (CDCl}_3, 400 MHz) \delta (ppm) = 7.30-7.19 (m, 2H), 7.14-7.07 (m, 3H), 4.14-3.95 (m, 1H), 2.98-2.76 (m, 2H), 2.75-2.52 (m, 2H), 2.14-1.87 (m, 2H); \text{13C-NMR (CDCl}_3, 101 MHz) \delta (ppm) = 140.1, 128.7, 128.6, 126.5, 125.7 (q, J = 278 Hz), 45.1 (q, J = 29.2 Hz), 41.3, 35.6, 21.1; \text{19F-NMR (CDCl}_3, 376 MHz) \delta (ppm) = -63.7 (t, J = 11.3 Hz); \text{Cl-MS (m/z, relative intensity): 327 (M, 25), 201 (M-I, 30), 91 (C}_7\text{H}_7^+, 100); \text{HRMS (Cl+): Calcd. for C}_{11}\text{H}_{12}\text{F}_3\text{I: 327.9935; Found: 327.9947.}
\]

Compound 24: Synthesized from B (11.6 mg, 0.2 mmol), (-)-Quinine (324 mg, 1 mmol), CF$_3$I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH$_3$OH), and CH$_3$OH (1 mL). The residue was purified by flash chromatography over silica gel (EtOAc 100%) to afford 24 (d.r = 2:1) as yellow solid in 73% yield (380 mg).

M.p. = 203-205 °C; \text{1H-NMR (CDCl}_3, 300 MHz) \delta (ppm) = 8.69-8.57 (m, 1H, d1 and d2), 7.81-7.60 (m, 2H, d1 and d2), 7.13-7.00 (m, 2H, d1 and d2), 6.58-6.52 (m, 0.66H, d1), 6.49-6.44 (m, 0.33H, d2), 5.92 (brs, 1H, d1 and d2), 4.44-4.26 (m, 1H, d1 and d2), 3.82-3.52 (m, 5H, d1 and d2), 3.48-3.34 (m, 1H, d1 and d2), 3.28-3.05 (m, 1H, d1 and d2), 2.90-2.47 (m, 4H, d1 and d2), 2.41-2.05 (m, 3H, d1 and d2), 1.99-1.80 (m, 1H, d1 and d2), 1.45-1.27 (m, 1H, d1 and d2); \text{13C-NMR (CDCl}_3, 75 MHz) \delta (ppm) (d1) = 158.71, 146.85, 144.2, 143.2, 130.8, 126.88, 125.58, 123.20, 119.3, 100.5, 65.7, 60.2, 59.3, 58.7, 44.3, 42.2-41.8 (m), 41.7, 25.4, 24.2, 21.1, 17.8; (d2) = 158.74, 146.81, 144.0, 143.3, 130.9, 126.91, 125.55, 123.22, 122.9, 100.4, 65.9, 60.0, 58.5, 54.5, 44.1, 42.2-41.8 (m), 39.6, 28.3, 24.4, 20.1, 17.6; \text{19F-NMR (CDCl}_3, 282 MHz) \delta (ppm) = -62.8 (t, J = 9.6 Hz, d1), -63.1 (t, J = 9.6 Hz, d2); \text{HRMS (ESI): [M+H] C}_{21}\text{H}_{25}\text{N}_2\text{O}_2\text{F}_3\text{I} : 521.0907; Found: 521.0914.}

Compound 25: Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), 2-allylbenzoic acid (162 mg, 1 mmol), CF$_3$I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH$_3$OH), and CH$_3$OH (1 mL). The residue was purified by flash chromatography over silica
gel (pentane/EtOAc, 90/10) to afford 25 as yellow oil in 73% yield (263 mg) with A and 56% yield (100 mg) with B.

![Image of compound 25]

**Compound 25:** 3H-NMR (CDCl₃, 300 MHz) δ (ppm) = 8.18 (dd, J = 1.2 Hz and J = 7.8 Hz, 1H), 7.58 (td, J = 1.2 Hz and J = 7.5 Hz, 1H), 7.44 (td, J = 0.9 Hz and J = 7.8 Hz, 1H), 4.61-4.43 (m, 1H), 3.85 (dd, J = 4.8 Hz and J = 13.8 Hz, 1H), 3.38 (dd, J = 9.6 Hz and J = 13.8 Hz, 1H), 3.13-2.78 (m, 2H); 13C-NMR (CDCl₃, 75 MHz) δ (ppm) = 172.4, 141.7, 133.4, 133.1, 132.6, 130.0, 127.9, 125.8 (q, J = 276.8 Hz), 45.5, 44.9 (q, J = 29.2 Hz), 21.5 (q, J = 3.0 Hz); 19F-NMR (CDCl₃, 282 MHz) δ (ppm) = -63.5 (t, J = 10.2 Hz); HRMS (ESI): Calcd. for [M-I] C₁₁H₁₀O₂F₃: 231.0638; Found: 231.0642.

Compound 26: Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), dimethyl(phenyl)(vinyl)silane (192 μL, 1 mmol), CF₃I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH₃OH), and CH₃OH (1 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 26 as colorless oil in 77% yield (270 mg) with A and 81% yield (290 mg) with B.

![Image of compound 26]

**Compound 26:** 1H-NMR (CDCl₃, 300 MHz) δ (ppm) = 7.58-7.52 (m, 2H), 7.47-7.36 (m, 3H), 3.28 (dd, J = 2.7 Hz and J = 11.1 Hz, 1H), 2.71-2.40 (m, 2H), 0.53 (s, 3H), 0.51 (s, 3H); 13C-NMR (CDCl₃, 75 MHz) δ (ppm) = 134.6, 134.1, 130.2, 128.3, 126.2 (q, J = 277.0 Hz), 38.4 (q, J = 28.9 Hz), 2.1 (q, J = 2.3 Hz), -2.9, -4.5; 19F-NMR (CDCl₃, 282 MHz) δ (ppm) = -65.0 (t, J = 11.3 Hz); HRMS (FI+): Calcd. for C₁₁H₁₄F₃Si: 357.9861; Found: 357.9850.

Compound 27: Synthesized from A (56 mg, 0.2 mmol) or B (11.6 mg, 0.2 mmol), (Z)-cyclooctene (130 μL, 1 mmol), CF₃I (3 mmol, i.e. 6 mL of a 2 M stock solution in CH₃OH), and CH₃OH (1 mL). The residue was purified by flash chromatography over silica gel (pentane 100%) to afford 27 (d.r = 1:1) as yellow oil in 71% yield (218 mg) with A and 64% yield (196 mg) with B.

![Image of compound 27]

**Compound 27:** 1H-NMR (CDCl₃, 300 MHz) δ (ppm) = 4.64-4.44 (m, 1H, d1 and d2), 2.53-2.20 (m, 3H, d1 and d2), 2.17-2.02 (m, 3H, d1 and d2), 1.99-1.75 (m, 3H, d1 and d2), 2.53-2.20 (m, 5H, d1 and d2); 13C-NMR (CDCl₃, 75 MHz) δ (ppm) = 128.5 (q, J = 277.8 Hz, d1 or d2), 128.4 (q, J = 277.7
Hz, d1 or d2), 42.5 (q, \( J = 24.5 \) Hz, d1 or d2), 42.3 (q, \( J = 24.6 \) Hz, d1 or d2), 38.7 (d1 or d2), 38.1 (d1 or d2), 35.4 (d1 or d2), 35.2 (d1 or d2), 34.1 (d1 and d2), 26.92 (d1 or d2), 26.89 (d1 or d2), 26.1 (d1 or d2), 25.8 (d1 or d2), 25.5-25.2 (m, d1 or d2), 24.5-24.1 (m, d1 or d2); \(^{19}\text{F-NMR} \) (CDCl\(_3\), 282 MHz) \( \delta \) (ppm) = -73.3 (d, \( J = 9.3 \) Hz, d1 or d2), -73.4 (d, \( J = 9.3 \) Hz, d1 or d2);

HRMS (EI): Calcd. for \([M-I]\) C\(_9\)H\(_{14}\)F\(_3\): 179.1047; Found: 179.1049.

**Compound 28:** Synthesized from A (28 mg, 0.1 mmol) or B (5.8 mg, 0.1 mmol), dodec-1-yne (130 \( \mu \)L, 1 mmol) and C\(_8\)F\(_{17}\)I (573.2 mg, 1.05 mmol) in CH\(_3\)OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane 100%) to afford 28 (d.r = 3:1) as yellow oil in 81% yield (577 mg) with A and 69% yield (489 mg) with B.

\(^1\text{H-NMR} \) (CDCl\(_3\), 300 MHz) \( \delta \) (ppm) = 6.34 (t, \( J = 14.4 \) Hz, 1H, d1), 6.39 (t, \( J = 13.2 \) Hz, 0.25H, d2), 2.77-2.57 (m, 2.5H, d1+d2), 1.67-1.52 (m, 2.5H, d1+d2), 1.31-1.19 (m, 17.5H, d1+d2), 0.88 (t, \( J = 6.4 \) Hz, 3.75H, d1+d2); \(^{13}\text{C-NMR} \) (CDCl\(_3\), 75 MHz): d1: \( \delta \) (ppm) = 126.7 (t, \( J = 24.03 \) Hz), 123.3, 41.3, 32.1, 29.7, 29.5, 29.4, 28.6, 22.9, 14.2; d2: \( \delta \) (ppm) = 123.2, 121.8 (t, \( J = 23.93 \) Hz), 48.6, 32.1, 29.7, 29.5, 29.2, 28.2, 22.9, 14.2; \(^1\text{EI-MS} \) (m/z, relative intensity): 712 (M, 2), 585 (M-I, 2), 529 (M-C\(_4\)H\(_8\)I\(^+\), 10), 97 (C\(_7\)H\(_{13}\)\(^+\), 50), 83 (C\(_8\)H\(_{11}\)\(^+\), 60), 57 (C\(_4\)H\(_9\)\(^+\), 90), 43 (C\(_3\)H\(_7\)\(^+\), 100); HRMS (CI\(^+\)): Calcd. for [M-H] C\(_{20}\)H\(_{21}\)F\(_{17}\)I: 711.0416; Found: 711.0426.

**Compound 29:** Synthesized from A (56 mg, 0.1 mmol), but-3-yn-1-ol (77 \( \mu \)L, 1 mmol) and C\(_8\)F\(_{17}\)I (573 mg, 1.05 mmol) in CH\(_3\)OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 90/10) to afford 29 (d.r = 2.3:1) as yellow solid in 71% yield (438 mg).

\(^1\text{H-NMR} \) (CDCl\(_3\), 400 MHz) \( \delta \) (ppm) = 6.48 (t, \( J = 14.0 \) Hz, 0.65H, d1), 6.40 (t, \( J = 13.2 \) Hz, 0.31H, d2), 3.90-3.80 (m, 2H, d1+d2), 3.02-2.87 (m, 2H, d1+d2), 1.69 (brs, 1H, d1), 1.25 (brs, 0.4H, d2); \(^{13}\text{C-NMR} \) (CDCl\(_3\), 101 MHz): d1: \( \delta \) (ppm) = 129.2 (t, \( J = 23.8 \) Hz), 117.2, 62.0, 43.8; d2: \( \delta \) (ppm) = 124.5 (t, \( J = 23.8 \) Hz), 118.7, 60.7, 51.1; HRMS (EI): Calcd. for C\(_{12}\)H\(_3\)F\(_{17}\)IO: 614.9108; Found: 614.9105.

**Compound 30:** Synthesized from B (5.8 mg, 0.1 mmol), but-3-yn-1-ol (77 \( \mu \)L, 1 mmol) and C\(_5\)F\(_{11}\)I (204 \( \mu \)L, 1.05 mmol) in CH\(_3\)OH (7 mL). The residue was purified by flash

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chromatography over silica gel (pentane/EtOAc, 90/10) to afford 30 (d.r = 3:1) as yellow oil in 91% yield (422 mg).

\[
\text{H-NMR (CDCl}_3, 400 MHz) \delta (ppm) = 6.48 (t, J = 14.4 Hz, 1H, d1), 6.39 (t, J = 13.2 Hz, 0.4H, d2), 3.89-3.78 (m, 2.8H, d1+d2), 3.04-2.84 (m, 2.8H, d1+d2), 1.89 (brs, 1.4H, d1+d2); \]

\[
\text{C-NMR (CDCl}_3, 101 MHz) : d1: \delta (ppm) = 129.3 (t, J = 24.03 Hz), 117.2, 62.0, 43.7; d2 : \delta (ppm) = 142.6 (t, J = 23.9 Hz), 120.3, 60.7, 51.0; \]

\[
\text{CI-MS (m/z, relative intensity): 466 (M, 5), 449 (C}_9\text{H}_5\text{F}_{11}\text{I}^+, 45), 437 (C}_8\text{H}_5\text{F}_{11}\text{I}^+, 75), 417 (C}_8\text{H}_4\text{F}_{10}\text{I}^+, 100), 338 (C}_9\text{H}_5\text{F}_{11}\text{O}^+, 82); \]

\[
\text{HRMS (CI+): Calcd. for C}_9\text{H}_5\text{F}_{11}\text{I}(M-H}_2\text{O): 448.9260; Found: 448.9273. \]

**Compound 31:** Synthesized from B (5.8 mg, 0.1 mmol), but-3-yn-1-ol (77 µL, 1 mmol) and C$_4$F$_9$I (180 µL, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 90/10) to afford 31 (d.r = 4:1) as yellow oil in 53% yield (219 mg).

\[
\text{C-NMR (CDCl}_3, 75 MHz): d1: \delta (ppm) = 129.0 (t, J = 23.5 Hz), 117.2, 62.0, 43.8; d2 : \delta (ppm) = 124.3 (t, J = 23.5 Hz), 114.3, 60.7, 51.0; \]

\[
\text{HRMS (CI+): Calcd. for C}_8\text{H}_6\text{F}_9\text{IO: 415.99319; Found: 415.9323.} \]

**Compound 32:** Synthesized from A (56 mg, 0.1 mmol), 6-chlorohex-1-yne (122 µL, 1 mmol) and C$_8$F$_{17}$I (573 mg, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 32 (d.r = 3:1) as yellow oil in 57% yield (188 mg).

\[
\text{C-NMR (CDCl}_3, 101 MHz) : \delta (ppm) = 127.3 (t, J = 23.7 Hz), 121.8, 44.5, 40.3, 31.2, 27.4. \]

**Compound 33:** Synthesized from A (56 mg, 0.1 mmol), prop-2-ynylbenzene (124 µL, 1 mmol) and C$_8$F$_{17}$I (573 mg, 1.05 mmol) in CH$_3$OH (7 mL). The residue was purified by flash chromatography over silica gel (100% pentane) to afford 33 (d.r = 2.1:1) as yellow solid in 82% yield (543 mg).
**Compound 34:** Synthesized from B (5.8 mg, 0.1 mmol), N-allyl-4-methylbenzenesulfonamide (106 mg, 0.5 mmol) and IC₄F₈I (309 mg, 0.68 mmol) in CH₃OH (1.5 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 90/10) to afford 34 as a solid in 79% yield (260 mg).

**Compound 35:** Synthesized from B (3.4 mg, 0.06 mmol), pent-4-en-1-ol (25.8 mg, 0.3 mmol) and 34 (190 mg, 0.29 mmol) in CH₃OH (3 mL). The residue was purified by flash chromatography over silica gel (pentane/EtOAc, 80/20) to afford 35 as yellow oil in 64% yield (139 mg).

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**Mp = 49-51 °C;** **¹H-NMR (CDCl₃, 400 MHz) δ (ppm) = 7.46-7.29 (m, 4.5H, d1+d2), 7.24-7.15 (m, 3H, d1+d2), 6.51 (t, J = 14.0 Hz, 1H, d1), 6.39 (t, J = 13.2 Hz, 0.5H, d2), 4.06 (s, 2H, d1), 4.03 (s, 1H, d2); **¹³C-NMR (CDCl₃, 101 MHz): **d1: δ (ppm) = 136.9, 129.1, 128.9, 127.7 (t, J = 23.8 Hz), 127.6, 46.8; **d2: δ (ppm) = 136.4, 129.3, 129.0, 127.8, 123.4 (t, J = 24.0 Hz), 51.8; **EI-MS (m/z, relative intensity): 662 (M, 10), 535 (M-I, 15), 243 (C₉H₈⁺, 20), 166 (C₁₀H₈F₂⁺, 70), 146 (C₁₀H₇F⁺, 100), 115 (C₉H₈⁺, 70), 69 (CF₃⁺, 10).

**Compound 34:**

**¹H-NMR (CDCl₃, 300 MHz) δ (ppm) = 7.80-7.73 (m, 2H), 7.37-7.28 (m, 2H), 5.09 (t, J = 6.6 Hz, 1H), 4.30-4.18 (m, 2H), 4.30-4.18 (m, 2H), 3.42-3.23 (m, 2H), 2.93-2.61 (m, 2H), 2.42 (s, 3H); **¹³C-NMR (CDCl₃, 75 MHz) δ (ppm) = 144.2, 136.7, 130.1, 127.2, 51.0, 38.5 (t, J = 21.0 Hz), 21.7, 17.0; **¹⁹F-NMR (CDCl₃, 282 MHz) δ (ppm) = -58.7, -111.7 to -114.7 (m), -112.7, -122.6; **HRMS (ESI): Calcd. for C₁₄H₁₃NO₂F₈NaSI₂: 687.8521; Found: 687.8522.

**Compound 35:**

**¹H-NMR (CDCl₃, 300 MHz) δ (ppm) = 7.78-7.69 (m, 2H), 7.36-7.30 (m, 2H), 5.35-5.20 (m, 1H), 4.44-4.29 (m, 1H), 4.27-4.15 (m, 1H), 3.69 (t, J = 6.3 Hz, 2H), 3.38-3.23 (m, 2H), 3.03-2.57 (m, 4H), 2.42 (s, 3H), 1.97-1.63 (m, 5H); **¹³C-NMR (CDCl₃, 75 MHz) δ (ppm) = 144.2, 136.7, 130.1, 127.1, 61.7, 51.0, 41.8 (t, J = 20.5 Hz), 38.5 (t, J = 21.1 Hz), 37.0, 32.7, 21.6, 20.8, 17.0; **¹⁹F-NMR (CDCl₃, 282 MHz) δ (ppm) = -110.3, -115.6, -122.7, -123.9; **HRMS (ESI): Calcd. for C₁₉H₂₃O₃F₈NaSI₂: 773.9252; Found: 773.9273.
VI. $^1$H-, $^{13}$C- and $^{19}$F-NMR spectra

$^1$H-NMR

Compound 1, CDCl₃, 300 MHz

$^{13}$C-NMR

Compound 1, CDCl₃, 75 MHz
**19F-NMR**

Composed 1, CDCl₃, 282 MHz

**1H-NMR**

Compound 2, CDCl₃, 300 MHz
**$^{13}$C-NMR**

Compound 2, CDCl$_3$, 75 MHz

**$^{19}$F-NMR**

Compound 2, CDCl$_3$, 282 MHz
$^1$H-NMR

Compound 3, CDCl$_3$, 300 MHz

$^{13}$C-NMR

Compound 3, CDCl$_3$, 75 MHz
**19F-NMR**

\[ C_6F_{11} \]

Compound 3, CDCl₃, 282 MHz

**1H-NMR**

\[ C_{6}F_{17} \]

Compound 4, CDCl₃, 300 MHz
\textbf{\textsuperscript{13}C-NMR}

\begin{align*}
\text{Compound 4, CDCl}_3, 7.5 \text{ MHz}
\end{align*}

\textbf{\textsuperscript{19}F-NMR}

\begin{align*}
\text{Compound 4, CDCl}_3, 282 \text{ MHz}
\end{align*}
$^1$H-NMR

$^{13}$C-NMR

$C_{6}F_{11}OH$

Compound 5, CDCl$_3$, 300 MHz

$C_{6}F_{11}OH$

Compound 5, CDCl$_3$, 75 MHz
$^{13}$C-NMR

$C_{17}F_{17}$ OH

Compound 6, CDCl$_3$, 75 MHz

$^{19}$F-NMR

$C_{17}F_{17}$ OH

Compound 6, CDCl$_3$, 282 MHz
$^{1}H$-NMR

![NMR spectrum image]

$^{13}C$-NMR

![NMR spectrum image]
$^{19}\text{F-NMR}$

![$^{19}\text{F-NMR}$ spectrum of C$_2$F$_{11}$OH compound 7, CDCl$_3$, 282 MHz](image)

$^2\text{H-NMR}$

![$^2\text{H-NMR}$ spectrum of C$_9$F$_{17}$-NHBoc compound 8, CDCl$_3$, 300 MHz](image)
**13C-NMR**

$\text{C}_8\text{F}_{17} - \text{NHBOC}$

Compound 8, CDCl$_3$, 75 MHz

---

**19F-NMR**

$\text{C}_8\text{F}_{17} - \text{NHBOC}$

Compound 8, CDCl$_3$, 282 MHz
$^{1} \text{H-NMR}$

$\text{C}_9\text{F}_3\text{NHBoc}$

Compound 9, CDCl$_3$, 300 MHz

$^{13} \text{C-NMR}$

$\text{C}_9\text{F}_3\text{NHBoc}$

Compound 9, CDCl$_3$, 75 MHz
**13C-NMR**

\[ \text{Compound 10, CDCl}_3, 75 \text{ MHz} \]

\[ \text{C}_8\text{F}_{17} -\begin{array}\text{I} \end{array} -\begin{array}\text{H} \end{array} -\begin{array}\text{H} \end{array} -\begin{array}\text{Br} \end{array} \]

**19F-NMR**

\[ \text{Compound 10, CDCl}_3, 282 \text{ MHz} \]

\[ \text{C}_8\text{F}_{17} -\begin{array}\text{I} \end{array} -\begin{array}\text{H} \end{array} -\begin{array}\text{H} \end{array} -\begin{array}\text{Br} \end{array} \]
**$^{1}$H-NMR**

![H-NMR Spectrum]

Compound 11, CDCl$_3$, 300 MHz

**$^{13}$C-NMR**

![C-NMR Spectrum]

Compound 11, CDCl$_3$, 75 MHz
**$^{19}$F-NMR**

Compound 13, CDCl$_3$, 262 MHz

**$^1$H-NMR**

Compound 14, CDCl$_3$, 300 MHz
13C-NMR

Compound 14, CDCl₃, 75 MHz

19F-NMR

Compound 14, CDCl₃, 282 MHz
Compound 15. CDCl₃, 300 MHz

$^1$H-NMR

$^{13}$C-NMR
\textbf{\textsuperscript{19}F-NMR}

\begin{center}
\includegraphics[width=\textwidth]{19F-NMR.png}
\end{center}

Compounds 15, CDCl\textsubscript{3}, 282 MHz

\textbf{\textsuperscript{1}H-NMR}

\begin{center}
\includegraphics[width=\textwidth]{1H-NMR.png}
\end{center}

Compounds 16, CDCl\textsubscript{3}, 300 MHz
\textbf{\textsuperscript{13}C-NMR}

\begin{center}
\includegraphics[width=\textwidth]{13C_NMR.png}
\end{center}

\textit{Compound 16, CDCl\textsubscript{3}, 75 MHz}

\textbf{\textsuperscript{19}F-NMR}

\begin{center}
\includegraphics[width=\textwidth]{19F_NMR.png}
\end{center}

\textit{Compound 16, CDCl\textsubscript{3}, 282 MHz}
**1H-NMR**

![1H-NMR](image)

Compound 1, CDCl₃, 300 MHz

**13C-NMR**

![13C-NMR](image)

Compound 1, CDCl₃, 75 MHz
**¹⁹F-NMR**

Compound 17, CDCl₃, 282 MHz

---

**¹³C-NMR**

Compound 18, CDCl₃, 300 MHz

---
**13C-NMR**

Compound 18, CDCl₃, 75 MHz

**19F-NMR**

Compound 18, CDCl₃, 282 MHz
**1H-NMR**

$\text{F}_3\text{C}$

Compound 19, CDCl$_3$, 300 MHz

![1H-NMR spectrum](image)

**13C-NMR**

$\text{F}_3\text{C}$

Compound 19, CDCl$_3$, 75 MHz

![13C-NMR spectrum](image)
\textbf{\textsuperscript{15}F-NMR}

\[
F_3C - \begin{array}{c}
\text{Compound 19, CDCl}_3, 282 \text{ MHz}
\end{array}
\]

\textbf{\textsuperscript{1}H-NMR}

\[
\text{Compound 20, CDCl}_3, 300 \text{ MHz}
\]
**$^{13}$C-NMR**

Compound 20, CDCl$_3$, 75 MHz

**$^{19}$F-NMR**

Compound 20, CDCl$_3$, 282 MHz
**$^1$H-NMR**

![H-NMR spectrum of Compound 21, CDCl$_3$, 300 MHz](image)

**$^{13}$C-NMR**

![C-NMR spectrum of Compound 21, CDCl$_3$, 75 MHz](image)
\textbf{\textsuperscript{19}F-NMR}

\begin{center}
\includegraphics[width=\textwidth]{f1c.png}
\end{center}

Compound 21, CDCl$_3$, 282 MHz

\textbf{\textsuperscript{1}H-NMR}

\begin{center}
\includegraphics[width=\textwidth]{h1c.png}
\end{center}

Compound 22, CDCl$_3$, 300 MHz
$^{13}\text{C-NMR}$

$$\text{F}_2\text{C}\_\text{NHBoc}$$

Compound 22, CDCl$_3$, 75 MHz

$^{19}\text{F-NMR}$

$$\text{F}_2\text{C}\_\text{NHBoc}$$

Compound 22, CDCl$_3$, 282 MHz
**$^{19}$F-NMR**

![$^{19}$F-NMR spectrum](image)

Compound 23, CDCl$_3$, 37.6 MHz

**$^1$H-NMR**

![$^1$H-NMR spectrum](image)

Compound 24, CDCl$_3$, 300 MHz
**13C-NMR**

![13C-NMR Spectrum](image)

Compound 24, CDCl₃, 75 MHz

**19F-NMR**

![19F-NMR Spectrum](image)

Compound 24, CDCl₃, 282 MHz
**$^1$H-NMR**

\[
\begin{align*}
&\text{Compound 25, CDCl}_3, 300 \text{ MHz} \\
&\text{C-NMR}
\end{align*}
\]

**$^{13}$C-NMR**

\[
\begin{align*}
&\text{Compound 25, CDCl}_3, 75 \text{ MHz} \\
&\text{C-NMR}
\end{align*}
\]
\[ {^1}\text{H-NMR} \]

\[ \text{Compound 26, CDCl}_3, 300 \text{ MHz} \]

\[ {^{19}}\text{F-NMR} \]

\[ \text{Compound 25, CDCl}_3, 282 \text{ MHz} \]
Compound 27, CDCl₃, 300 MHz

1H-NMR

Compound 27, CDCl₃, 75 MHz

13C-NMR
$^{13}\text{C-NMR}$

C$_6$F$_{17}$

Compound 28. CDCl$_3$, 75 MHz

$^\text{1H-NMR}$

C$_6$F$_{17}$

Compound 29. CDCl$_3$, 400 MHz
**$^{13}$C-NMR**

\[ \text{C}_{18}F_{17} \] 

Compound 29, CDCl$_3$, 101 MHz

**$^2$H-NMR**

Compound 30, CDCl$_3$, 400 MHz
$^{13}$C-NMR

Compound 30, CDCl$_3$, 101 MHz

$^2$H-NMR

Compound 31, CDCl$_3$, 300 MHz
Compound 32, CDCl₃, 75 MHz

Compound 33, CDCl₃, 400 MHz
Compound 33, CDCl₃, 101 MHz

Compound 34, CDCl₃, 300 MHz
Compound 34, CDCl₃, 75 MHz

Compound 34, CDCl₃, 282 MHz
Compound 35, CDCl₃, 300 MHz

Compound 35, CDCl₃, 75 MHz