Supporting information

Metal-free visible-light-induced hydroxy-perfluoroalkylation of conjugated olefins using enamine catalyst

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1. General information

Unless otherwise noted, all reactions were performed under argon atmosphere. \(^1\)H, \(^13\)C and \(^19\)F NMR spectra were recorded on a JEOL GSX-400 spectrometer (400 MHz for \(^1\)H, 126 MHz for \(^13\)C, and 376 MHz for \(^19\)F), a JEOL ECX-500 spectrometer (500 MHz for \(^1\)H and 471 MHz for \(^19\)F), or a BRUKER AVANCE 600 spectrometer (600 MHz for \(^1\)H and 151 MHz for \(^13\)C) with CDCl\(_3\) as solvent, tetramethylsilane (TMS: \(\delta\) 0 ppm for \(^1\)H), chloroform-d (CDCl\(_3\): \(\delta\) 76.9 ppm for \(^13\)C) and hexafluorobenzene (C\(_6\)F\(_6\): \(-162.2\) ppm for \(^19\)F) as an internal standard. IR spectra were taken on SHIMADZU IRSpirt-T, and HRMS were obtained with a JEOL JMS-T100TD (DART-TOF), JEOL JMS-700 (EI), or BRUKER Compact (ESI). Precoated Merck Kieselgel 60 F254 and Kanto silica gel 60 (spherical neutral) were used for thin layer chromatography and flash chromatography, respectively. Visualization was accomplished by UV light (254 nm). All commercially available reagents and solvents were used as received, without further purification. Starting materials 1\(^{j1}\), 1\(^{k1}\), 1\(^{l2}\) and 1\(^{s3}\) were synthesized according to the previous literature.

2. General procedures

Scheme S1. General procedures for hydroxy-perfluoroalkylation.

To an oven-dried 20 ml two-necked flask equipped with a magnetic stirrer bar was fitted with a septum and degassed through alternating vacuum evacuation/argon backfill (\(\times 10\)) before dry 1,2-dichloroethane (2.5 ml) was added. Then oxygen (5.0 mL, 0.8 eq.), diphenylacetaldehyde (3, 4.4\(\mu\)L, 10 mmol), pyrrolidine (4, 8.4 \(\mu\)L, 40 mol%), DIPEA (88 \(\mu\)L, 2.0 eq.), electron-deficient olefin 1 or styrene 6 (0.25 mmol), and perfluoroalkyl iodide 2 (3.0 eq.) were added respectively. The mixture was stirred for 24 hours at 25\(^\circ\)C under white LED irradiation. The resulting mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give 5 or 7 as a yellow oil or white solid.
3. Optimization studies

3-1. Evaluation of oxygen equivalents

Table S1. Evaluation of oxygen equivalents

| Entry | O₂     | yield⁸ |
|-------|--------|--------|
| 1     | -      | trace  |
| 2     | 0.5 eq. (3.1 mL) | 58%    |
| 3     | 0.6 eq. (3.7 mL)  | 61%    |
| 4     | 0.7 eq. (4.3 mL)  | 68%    |
| 5     | 0.8 eq. (5.0 mL)  | 75%    |
| 6     | 0.9 eq. (5.5 mL)  | 68%    |
| 7     | 1.0 eq. (6.1 mL)  | 53%    |
| 8     | 2.0 eq. (12.3 mL) | 30%    |
| 9     | excess (50 mL)    | 9%     |

⁸Yields based on ¹⁹F NMR spectroscopy using benzotrifluoride as an internal standard.

The reaction does not proceed without oxygen (entry 1). With low amount of oxygen, oligomerization of 1a was observed (entries 2-4). However, with high amount of oxygen, by-product derived from 4, 2a, and oxygen were obtained (Scheme S1), and only 9% of 5aa were produced in the oxygen atmosphere (entry 9).⁴

Scheme S2. Side reaction from 4, 2a, and oxygen.⁴
3-2. Evaluation of 3 and 4 equivalents

Table S2. Evaluation of adding quantity of 3 and 4

| Entry | 3            | 4            | yield* |
|-------|--------------|--------------|--------|
| 1     | 10 mol% (4.9 mg) | 10 mol% (2.1 µL) | 50%    |
| 2     | 10 mol% (4.9 mg) | 40 mol% (8.4 µL) | 75%    |
| 3     | 1 mol% (0.5 mg)  | 1 mol% (0.2 µL)  | 53%    |
| 4     | 1 mol% (0.5 mg)  | 40 mol% (8.4 µL) | 73%    |

*Yields based on $^{19}$F NMR spectroscopy using benzo trifluoride as an internal standard.

3-3. Reactions with pre-synthesized enamine

Enamine was synthesized according to the previous literature.\(^5\)

Table S3. Reaction with pre-synthesized enamine.

| Entry | enamine | pyrrolidine (4) | yield* |
|-------|---------|----------------|--------|
| 1     | 10 mol% (6.2 mg) | -              | 60%    |
| 2     | 40 mol% (24.9 mg) | -              | 72%    |
| 3     | 10 mol% (6.2 mg)  | 30 mol% (6.3 µL) | 74%    |

*Yields based on $^{19}$F NMR spectroscopy using benzo trifluoride as an internal standard.
### 3–4. Evaluation of tertiary amine

**Table S4.** Evaluation of tertiary amine.

| entry | tertiary amine      | yield\(^a\) |
|-------|---------------------|-------------|
| 1     | N-methyl pyrroldine | 51%         |
| 2     | TEA                 | 49%         |
| 3     | DIPEA               | 75%         |
| 4     | DIPEA\(^b\)        | 74%         |
| 5     | TBA                 | 73%         |
| 6     | TMEDA               | 63%         |
| 7     | TEEDA               | 55%         |
| 8     | PMDETA              | 48%         |

\(^a\)Yields based on \(^{19}\)F NMR spectroscopy using benzotrifluoride as an internal standard. \(^b\)3.0 eq. of DIPEA.

### 3–5. Evaluation of photocatalyst

**Table S5.** Evaluation of photocatalyst.

| entry | Photocatalyst            | yield\(^a\) |
|-------|--------------------------|-------------|
| 1     | pyrrolidine, diphenylacetaldehyde 10 mol%, 40 mol% | 75%         |
| 2     | Eosin Y-2Na              | 10 mol%     | 36%         |
| 3     | Phloxine B-2Na           | 10 mol%     | 40%         |
| 4     | Methylene Blue-3H\(_2\)O | 10 mol%     | 37%         |
| 5     | [Ir(dtbbpy)(ppy)$_2$]PF$_6$ | 1 mol%     | 65%         |
| 6     | Ru(bpy)$_2$Cl$_2$-6H$_2$O | 1 mol%     | 63%         |

\(^a\)Yields based on \(^{19}\)F NMR spectroscopy using benzotrifluoride as an internal standard.
3–6. Limitation of the substrate scope

Table S6. Limitation of the substrate scope.

![Chemical reactions and structures](image)

Yields based on $^{19}$F NMR spectroscopy using benzotrifluoride as an internal standard.

3–7. Evaluation of 2 for 1a

Table S7. Evaluation of 2 for 1a.

![Chemical reactions and structures](image)

Yields based on $^{19}$F NMR spectroscopy using benzotrifluoride as an internal standard; isolated yields are given in parentheses.

Owing to their low boiling point, the isolated yields were lower than the $^{19}$F NMR yields.
3–8. Reaction using XCF₂CO₂Et

Table S8. Reaction using XCF₂CO₂Et.

| Entry | 2          | yield (%)<sup>a</sup> |
|-------|------------|-----------------------|
| 1     | 2α: ICF₂CO₂Et | 9                     |
| 2     | 2α': BrCF₂CO₂Et | n.r.                 |

<sup>a</sup>based on <sup>19</sup>F NMR spectroscopy using benzotrifluoride as an internal standard.

4. Stereochemistry

4–1. Determination of diastereoselectivity of compound 5la by HPLC

HPLC: GL Science Inc. Inertsil<sup>®</sup> Diol column; detected at 294 nm; hexane/ethanol, 95/5; flow = 1.0 mL/min; retention times: 6.40 min, 6.92 min.

![Graphical representation of the reaction and product](image)

| No. | Rt  | Peak Name | Area  | Area(%) | Height | NTP   | Tf   | Resolution |
|-----|-----|-----------|-------|---------|--------|-------|------|------------|
| 1   | 6.4 |           | 366987.5 | 4.5187 | 36970 | 9392.6 | 0.975 | 1.894      |
| 2   | 6.92|           | 7754629 | 95.4813 | 714956 | 9207.3 | 1.033 | ----       |
| Total|     |           | 8121617 | 100     | 751926 |        |      |            |

d.r. = 95:5.

Figure S1. Determination of diastereoselectivity of compound 5la by HPLC
4-2. Determination of stereochemistry (compounds 5la).\textsuperscript{6}  
Stereochemistry of 5la was determined by comparing the optical rotation of compound 5lf\textsuperscript{*} with known compound.\textsuperscript{6}

Scheme S3. Determination of stereochemistry of compound 5lf\textsuperscript{*}

Yields based on \textsuperscript{19}F NMR spectroscopy using benzotriﬂuoride as an internal standard.
5. Gram scale reaction

Scheme S4. Gram scale reaction.

Figure S2. Gram scale reaction apparatus.
6. Mechanistic studies
6-1. Labelled experiments

Scheme S5. Labelled experiments with H$_2^{18}$O or $^{18}$O$_2$.

Figure S3. MS spectra of labelled experiments with or $^{18}$O$_2$.  

S11
6–2. Titration experiment

6–2–1. Titration experiment of C₆F₁₃I with enamine

¹⁹F NMR spectra of seven samples of the mixtures of C₆F₁₃I (2a), diphenylacetaldehyde (3) and pyrrolidine (4) (3:4 = 1:1) in CDCl₃ were recorded (hexafluorobenzene (C₆F₆: -162.2 ppm for ¹⁹F) was used as an internal standard). The amount of 2a was kept constant at 0.025 mmol while that of 3 and 4 was varied from 0 to 0.125 mmol, respectively. The molar ratio of 2a: (3+4) were 1:0, 1:1, 1:2, 1:3, 1:4, 1:7, and 1:10.

Figure S4–1. ¹⁹F Titration experiment of C₆F₁₃I with enamine.

Figure S4–2. ¹⁹F Titration experiment of C₆F₁₃I with enamine.

S12
6-2-2. Titration experiment of C\textsubscript{6}F\textsubscript{13}I with DIPEA

\textsuperscript{19}F NMR spectra of seven samples of the mixtures of C\textsubscript{6}F\textsubscript{13}I (2a) and DIPEA in CDCl\textsubscript{3} were recorded (hexafluorobenzene (C\textsubscript{6}F\textsubscript{6}: -162.2 ppm for \textsuperscript{19}F) was used as an internal standard). The amount of 2a was kept constant at 0.025 mmol while that of DIPEA was varied from 0 to 0.25 mmol. The molar ratio of 2a: DIPEA were 1:0, 1:1, 1:2, 1:3, 1:4, 1:5, and 1:10.

**Figure S5–1.** \textsuperscript{19}F Titration experiment of C\textsubscript{6}F\textsubscript{13}I with DIPEA.

**Figure S5–2.** \textsuperscript{19}F Titration experiment of C\textsubscript{6}F\textsubscript{13}I with DIPEA.
The -CF₂I upfield-shift of the ¹⁹F NMR was observed with the addition of enamine or DIPEA into 2a. It indicated the formation of halogen-bonding between 2a and enamine or DIPEA. Figure S4 shows a clearer upfield-shift than Figure S5, indicating that the interaction between 2a and enamine was stronger than that of DIPEA.

6–3. Determination of binding stoichiometry
Determination of binding stoichiometry experiments were conducted by Job’s plot analysis according to the previous literature.⁷

6–3–1. Determination of binding stoichiometry between C₆F₁₃I and enamine
¹⁹F NMR spectra of eleven samples of the mixtures of C₆F₁₃I (2a), diphenylacetaldehyde (3) and pyrrolidine (4) (3:4 = 1:1) in CDCl₃ were recorded (hexafluorobenzene (C₆F₆): -162.2 ppm for ¹⁹F) was used as an internal standard). The total amount of 2a, 3, and 4 were kept constant at 0.25 mmol (0.5 M), while the amount of 2a was varied from 0 to 0.25 mmol (0–0.5 M). The molar ratio of 2a: {2a+3+4} were 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. ¹⁹F NMR for each sample was recorded to measure the change in chemical shift for the F of CF₂I. The stoichiometry was determined by plotting ratios of [2a]×Δδ against ratios of [2a]/ [2a+3+4]. Figure S6 show the maximum at ratio [2a]/ [2a+3+4] = 0.5, which meant a 1:1 complex ratio between 2a and enamine.

| [2a] (M) | ∆δ (ppm) | [2a]/[2a+3+4] | [2a]×Δδ (M ppm) |
|----------|----------|----------------|-----------------|
| 0        | 0.000    | 0.0            | 0               |
| 0.05     | 2.550    | 0.1            | 0.255           |
| 0.1      | 2.181    | 0.2            | 0.4362          |
| 0.15     | 1.905    | 0.3            | 0.5715          |
| 0.2      | 1.567    | 0.4            | 0.6268          |
| 0.25     | 1.352    | 0.5            | 0.676           |
| 0.3      | 1.106    | 0.6            | 0.6636          |
| 0.35     | 0.922    | 0.7            | 0.6454          |
| 0.4      | 0.676    | 0.8            | 0.5408          |
| 0.45     | 0.368    | 0.9            | 0.3312          |
| 0.5      | 0.000    | 1.0            | 0               |

Figure S6. Job’s plot between C₆F₁₃I and enamine.
Determination of binding stoichiometry between C₆F₁₃I and DIPEA

¹⁹F NMR spectra of eleven samples of the mixtures of C₆F₁₃I (2a), DIPEA in CDCl₃ were recorded (hexafluorobenzene (C₆F₆): -162.2 ppm for ¹⁹F) was used as an internal standard). The total amount of 2a and DIPEA were kept constant at 0.25 mmol (0.5 M), while the amount of 2a was varied from 0 to 0.25 mmol (0–0.5 M). The molar ratio of 2a: [2a+DIPEA] were 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. ¹⁹F NMR for each sample was recorded to measure the change in chemical shift for the F of CF₂I. The stoichiometry was determined by plotting ratios of [2a] × Δδ against ratios of [2a]/[2a+DIPEA]. Figure S7 show the maximum at ratio [2a]/[2a+DIPEA] = 0.5, which meant a 1:1 complex ratio between 2a and DIPEA.

| [2a] (M) | Δδ(ppm) | [2a]/[2a+DIPEA] | [2a] × Δδ(M ppm) |
|----------|---------|-----------------|-----------------|
| 0        | 0.000   | 0.0             | 0               |
| 0.05     | 0.491   | 0.1             | 0.0491          |
| 0.1      | 0.461   | 0.2             | 0.0922          |
| 0.15     | 0.399   | 0.3             | 0.1197          |
| 0.2      | 0.338   | 0.4             | 0.1352          |
| 0.25     | 0.276   | 0.5             | 0.138           |
| 0.3      | 0.245   | 0.6             | 0.147           |
| 0.35     | 0.184   | 0.7             | 0.1288          |
| 0.4      | 0.123   | 0.8             | 0.0984          |
| 0.45     | 0.061   | 0.9             | 0.0549          |
| 0.5      | 0.000   | 1.0             | 0               |

Figure S7. Job’s plot between C₆F₁₃I and DIPEA.
6–4. Determination of the association constant ($K_a$)

The association constant ($K_a$) was calculated using Hanna and Ashbaugh’s method, according to the previous literature.

6–4–1. Determination of the association constant ($K_a$) between C$_6$F$_{13}$I and enamine

$^{19}$F NMR spectra of six samples of the mixtures of C$_6$F$_{13}$I (2a), diphenylacetaldehyde (3) and pyrrolidine (4) (3:4 = 1:1) in CDCl$_3$ were recorded (hexafluorobenzene (C$_6$F$_6$: -162.2 ppm for $^{19}$F) was used as an internal standard). The amount of 2a was kept constant at 0.025 mmol while that of 3 and 4 was varied from 0.0125 to 0.125 mmol, respectively. The molar ratio of 2a: (3+4) were 1:1, 1:2, 1:3, 1:4, 1:7, and 1:10. $^{19}$F NMR for each sample was recorded to measure the change in chemical shift for the F of CF$_2$I.

| 3 + 4 (mmol) | 3 + 4 (mol/L) | 1/3 + 4 (L/mol) | $\Delta \delta$ (ppm) | $1/\Delta \delta$ (ppm$^{-1}$) |
|--------------|---------------|-----------------|-----------------------|--------------------------|
| 0.25         | 0.42          | 2.4             | 1.844                 | 0.5423                   |
| 0.175        | 0.29          | 3.4             | 1.476                 | 0.6775                   |
| 0.1          | 0.17          | 6.0             | 1.045                 | 0.9569                   |
| 0.075        | 0.13          | 8.0             | 0.799                 | 1.2516                   |
| 0.05         | 0.08          | 12.0            | 0.584                 | 1.7123                   |
| 0.025        | 0.04          | 24.0            | 0.277                 | 3.6101                   |

$K = \frac{0.1377}{1.1419} = 0.97$

**Figure S8.** association constant ($K_a$) between C$_6$F$_{13}$I and enamine

The association constant of 2a and enamine ($K_{enamine}$) was calculated to be 0.97 ($K_{enamine} = 0.97$ M$^{-1}$).
6-4-2. Determination of the association constant \( (K_a) \) between \( C_6F_{13}I \) and DIPEA

\(^{19}\text{F} \) NMR spectra of six samples of the mixtures of \( C_6F_{13}I \) (2a) and DIPEA in CDCl\(_3\) were recorded (hexafluorobenzene \( (C_6F_6; -162.2 \) ppm for \( ^{19}\text{F} \)) was used as an internal standard). The amount of 2a was kept constant at 0.025 mmol while that of DIPEA was varied from 0.025 to 0.25 mmol. The molar ratio of 2a:DIPEA were 1:1, 1:2, 1:3, 1:4, 1:7, and 1:10. \(^{19}\text{F} \) NMR for each sample was recorded to measure the change in chemical shift for the F of CF\(_2\)I.

| DIPEA (mmol) | DIPEA (mol/L) | 1/DIPEA (l/mol) | \( \Delta\delta \) (ppm) | 1/\( \Delta\delta \) (ppm\(^{-1}\)) |
|-------------|---------------|-----------------|------------------|------------------|
| 0.25        | 0.42          | 2.4             | 0.277            | 3.6101           |
| 0.175       | 0.29          | 3.4             | 0.216            | 4.6296           |
| 0.1         | 0.17          | 6.0             | 0.154            | 6.4935           |
| 0.075       | 0.13          | 8.0             | 0.093            | 10.7527          |
| 0.05        | 0.08          | 12.0            | 0.062            | 16.1290          |
| 0.025       | 0.04          | 24.0            | 0.031            | 32.2581          |

\[
K = \frac{0.2648}{1.3517} = 0.20
\]

Figure S9. Association constant \( (K_a) \) between \( C_6F_{13}I \) and DIPEA

The association constant of 2a and DIPEA \( (K_{\text{DIPEA}}) \) was calculated to be 0.20 \( (K_{\text{DIPEA}} = 0.20 \text{ M}^{-1} ) \).

A comparison of the association constant \( (K_a) \) in Figure S8 and S9 suggested that enamine interacted with \( C_6F_{13}I \) more effectively that DIPEA.
6–5. UV-Vis absorption spectra

Optical absorption spectra were recorded 1,2-dichloroethane solution (0.1 M) in 1 mm path quartz cuvettes using a JASCO V-650 UV-visible Spectrophotometer.

![UV-Vis absorption spectra and visual appearance of EDA complexation](image)

**Figure S10.** UV-Vis absorption spectra and visual appearance of EDA complexation.

The biggest long-wavelength shifted peak was observed for the solution G and H (with both 3 and 4; enamine), as well as a visual appearance (yellow colour). It indicated that EDA complex was formed between 2a and enamine. One the other hand, there are no colour change and little peak shift for solution B–F (with only DIPEA, 3, or 4) compared to solution A. This result exclude the possibility of the EDA complexation between DIPEA, 3, or 4 with 2a, respectively.
6–6. Crude $^1$H NMR

6–6–1. Crude $^1$H NMR compared with 3, 4 and enamine.

Figure S11. Crude $^1$H NMR compared with 3, 4 and enamine.

Crude $^1$H NMR (top row) shows that aldehyde 3 remained after the reaction (the red circled part).
6–6–2. Crude $^1$H NMR compared with DIPEA.

**Figure S12.** DIPEA after the reaction.

In Crude $^1$H NMR, remaining free DIPEA was not observed. A comparison with previous studies\textsuperscript{10} suggests that the red circled peak is the DIPEA and HI salt.
7. Characterization of the products

Ethyl 4,4',5,5',6,6',7,7',8,8',9,9'-tridecafluoro-2-hydroxy-2-methylnonanoate (5aa)

Yellow oil, 90.2 mg, yield: 80%. $^1$H NMR (400 MHz, CDCl$_3$) δ: 4.37–4.22 (2H, m), 3.50 (1H, s), 2.81–2.68 (1H, m), 2.58–2.44 (1H, m), 1.52 (3H, s), 1.31 (3H, t, $J = 7.3$ Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) δ: 175.3, 120.4–106.6 (6C, m), 71.4 (d, $J = 1.5$ Hz), 62.8, 39.4 (t, $J = 20.4$ Hz), 28.0. $^{19}$F NMR (376 MHz, CDCl$_3$) δ: -81.3 (3F, s), -110.3 (1F, d, $J = 288.9$ Hz), -114.7 (1F, d, $J = 288.9$ Hz), -122.2 (2F, s), -123.4 (2F, s), -124.5 (2F, s), -126.7 (2F, s). IR (neat, cm$^{-1}$) 3389, 3061, 3028, 2922, 1780, 1279, 1236, 1186, 1142. HRMS (ESI$^+$) calcd for C$_2_1$H$_1_1$F$_1_3$O$_3$ [M+Na]$^+$: 473.0393, found 473.0406.

Methyl 4,4',5,5',6,6',7,7',8,8',9,9'-tridecafluoro-2-hydroxy-2-methylnonanoate (5ba)

Yellow oil, 79.0 mg, yield: 73%. $^1$H NMR (500 MHz, CDCl$_3$) δ: 3.84 (3H, s), 3.46 (1H, s), 2.76–2.66 (1H, m), 2.57–2.46 (1H, m), 1.52 (3H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ: 175.7, 118.2–108.9 (6C, m), 71.4 (d, $J = 1.5$ Hz), 53.6, 39.5 (t, $J = 19.6$ Hz), 27.9. $^{19}$F NMR (471 MHz, CDCl$_3$) δ: -81.3 (3F, s), -111.3 (1F, d, $J = 277.9$ Hz), -115.1 (1F, d, $J = 277.9$ Hz), -122.3 (2F, s), -123.4 (2F, s), -124.5 (2F, s), -126.7 (2F, s). IR (neat, cm$^{-1}$) 3059, 2924, 2855, 1719, 1317, 1238, 1177. HRMS (DART$^+$) calcd for C$_{1_1}$H$_{9_1}$F$_{1_3}$O$_{3_1}$ [M+H]$^+$: 437.0422, found 437.0442.

tert-Butyl 4,4',5,5',6,6',7,7',8,8',9,9'-tridecafluoro-2-hydroxy-2-methylnonanoate (5ca)

White solid, 95.9 mg, yield: 80%. $^1$H NMR (500 MHz, CDCl$_3$) δ: 3.53 (1H, s), 2.77–2.67 (1H, m), 2.51–2.41 (1H, m), 1.49 (9H, s), 1.46 (3H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ: 174.4, 120.2–108.1 (6C, m), 83.7, 71.4 (d, $J = 3.0$ Hz), 39.3 (t, $J = 19.6$ Hz), 31.1, 28.2, 27.7 (2C). $^{19}$F NMR (471 MHz, CDCl$_3$) δ: -81.3 (3F, s), -109.3 (1F, d, $J = 272.5$ Hz), -114.5 (1F, d, $J = 272.5$ Hz), -122.3 (2F, s), -126.7 (2F, s). IR (neat, cm$^{-1}$) 3482, 3092, 3063, 3036, 1653, 1279, 1233, 1188, 1142, 1121. HRMS (ESI$^+$) calcd for C$_{1_4_1}$H$_{1_5_1}$F$_{1_3_1}$O$_{3_1}$ [M+Na]$^+$: 501.0706, found 501.0707.

Benzyl 4,4',5,5',6,6',7,7',8,8',9,9'-tridecafluoro-2-hydroxy-2-methylnonanoate (5da)

Yellow solid, 101.57 mg, yield: 79%. $^1$H NMR (500 MHz, CDCl$_3$) δ: 7.40–7.26 (5H, m), 5.23 (2H, dd, $J = 16.0$, 12.0 Hz), 3.46 (1H, s), 2.79–2.68 (1H, m), 2.56–2.48 (1H, m), 1.51 (3H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) δ: 175.1, 134.6, 129.0, 128.8 (2C), 128.7, 119.5–108.3 (6C, m), 71.5 (d, $J = 3.0$ Hz), 68.7, 39.4 (t, $J = 21.1$ Hz), 28.0. $^{19}$F NMR (471 MHz, CDCl$_3$) δ: -81.3 (3F, s), -110.8 (1F, d, $J = 272.5$ Hz), -114.8 (1F, d, $J = 272.5$ Hz), -122.3 (2F, s), -123.4 (2F, s), -124.4 (2F, s), -126.7 (2F, s). IR (neat, cm$^{-1}$) 3503,
Phenyl 4,4,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5ea)

White solid, 85.9 mg, yield: 69%. 1H NMR (400 MHz, CDCl₃) δ: 7.45–7.40 (2H, m), 7.31–7.26 (1H, m), 7.08 (2H, d, J = 7.8 Hz), 3.47 (1H, s), 3.01–2.88 (1H, m), 2.73–2.59 (1H, m), 1.71 (3H, s). 13C NMR (151 MHz, CDCl₃) δ: 174.1, 150.3, 129.9 (2C), 126.8, 121.1, 120.3–108.2 (6C, m), 71.7 (d, J = 3.0 Hz), 39.6 (t, J = 20.4 Hz), 28.2. 19F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -110.3 (1F, d, J = 283.2 Hz), -113.9 (1F, d, J = 283.2 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.4 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3466, 2580, 1762, 1366, 1237, 1189, 1144, 1121, 749, 700. HRMS (ESI⁺) calcd for C₁₆H₁₁F₁₃O₃ [M+Na]⁺: 521.0393, found 521.0407.

Cyclohexyl 4,4,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5fa)

Yellow oil, 101.89 mg, yield: 81%. 1H NMR (500 MHz, CDCl₃) δ: 4.92 (1H, m), 3.52 (1H, s), 2.80–2.69 (1H, m), 2.55–2.44 (1H, m), 1.86 (2H, m), 1.73 (2H, m), 1.56 (2H, m), 1.51–1.35 (6H, m), 1.50 (3H, s). 13C NMR (151 MHz, CDCl₃) δ: 174.8, 119.5–107.6 (6C, m), 75.6, 71.4 (d, J = 3.0 Hz), 39.3 (t, J = 21.1 Hz), 31.5, 31.1, 28.2, 25.3, 23.7, 23.6. 19F NMR (471 MHz, CDCl₃) δ: -81.3 (3F, s), -110.3 (1F, d, J = 272.5 Hz), -114.7 (1F, d, J = 272.5 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.5 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3509, 2942, 2864, 1732, 1451, 1235, 1180, 1144, 1123. HRMS (DART⁺) calcd for C₁₆H₁₁F₁₃O₃ [M+H]⁺: 505.1048, found 505.1016.

Oxiran-2-ylmethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5ga)

Yellow oil, 84.1 mg, yield: 70%. 1H NMR (400 MHz, CDCl₃) δ: 4.37–4.28 (1H, m), 3.92–3.86 (1H, m), 3.61 (1H, s), 3.41–3.23 (2H, m), 2.85–2.70 (1H, m), 2.64–2.48 (2H, m), 1.56 (3H, s). 13C NMR (151 MHz, CDCl₃) δ: 175.1 (d, J = 4.5 Hz), 119.4–106.4 (6C, m), 71.7, 68.9 (d, J = 1.5 Hz), 68.7, 39.5 (t, J = 19.6 Hz), 28.1 8.6 (d, J = 15.1 Hz). 19F NMR (376 MHz, CDCl₃) δ: 81.3 (3F, s), -110.7 (1F, d, J = 277.4 Hz), -114.4 (1F, d, J = 277.4 Hz), -122.2 (2F, s), -123.4 (2F, s), -124.4 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3415, 2958, 1743, 1317, 1232, 1187, 1139, 799, 707. HRMS (ESI⁺) calcd for C₁₃H₁₁F₁₄O₄ [M+Na]⁺: 501.0342, found 501.0340.
2,2,2-Trifluoroethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5Ha)

Yellow oil, 83.7 mg, yield: 68%. ¹H NMR (400 MHz, CDCl₃) δ: 4.67–4.51 (2H, m), 3.30 (1H, s), 2.86–2.72 (1H, m), 2.64–2.50 (1H, m), 1.58 (3H, s).

¹³C NMR (151 MHz, CDCl₃) δ: 173.9, 128.5–108.3, (7C, m), 71.7 (d, J = 3.0 Hz), 61.9 (dd, J = 74.7, 37.0 Hz), 39.5 (t, J = 20.4 Hz), 27.9. ¹⁹F NMR (376 MHz, CDCl₃) δ: -74.5 (3F, s), -81.3 (3F, s), -110.5 (1F, d, J = 266.96 Hz), -114.6 (1F, d, J = 266.96 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.5 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3519, 2987, 1763, 1364, 1287, 1235, 1136, 814, 700, 654. HRMS (ESI⁺) calcd for C₁₂H₉F₁₅O₃ [M+Na]+: 527.0110, found 527.0126

(1R,2R,4R)-1,7-trimethyl-2-bicyclo[2.2.1]heptanyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5ia)

Yellow oil, 98.5 mg, yield: 71%. ¹H NMR (400 MHz, CDCl₃) δ: 4.80 (minor, 1H, dd, J = 6.9, 2.7 Hz), 4.64 (major, 1H, dd, J = 7.8, 3.2 Hz), 3.56 (minor, 1H, s), 3.53 (major, 1H, s), 2.73–2.60 (major and minor, 1H, m), 2.57–2.43 (major and minor, 1H, m), 1.92 (major, 1H, dd, J = 13.7, 7.8 Hz), 1.85–1.79 (minor, 1H, m), 1.85–1.68 (major and minor, 3H, m), 1.63–1.56 (major and minor, 1H, m), 1.49 (major and minor, 3H, d, J = 6.4 Hz), 1.23–1.08 (major and minor, 2H, m), 0.96 (major and minor, 3H, s), 0.87 (major and minor, 3H, s), 0.86 (major and minor, 3H, s). ¹³C NMR (151 MHz, CDCl₃) δ: 174.9 (minor), 174.8 (major), 129.0–106.6 (major and minor, 6C, m), 84.5 (major), 83.9 (minor), 71.4 (major, d, J = 1.5 Hz), 71.2 (minor, d, J = 1.5 Hz), 49.2 (major), 48.7 (minor), 47.2 (major), 47.1 (minor), 45.1 (major), 45.0 (minor), 39.2 (major and minor, m), 38.0 (major and minor), 33.9 (major), 33.7 (minor), 28.2 (minor), 27.9 (major), 27.0 (major and minor), 20.1 (major and minor), 19.9 (major), 19.7 (minor), 11.5 (major), 11.3 (minor). ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.4 (3F, s), -110.9 (1F, dd, J = 267.1, 67.7 Hz), -114.6 (1F, dd, J = 312.2, 45.1 Hz), -122.4 (2F, s), -123.5 (2F, s), -124.3 (2F, d, J = 69.4 Hz), -126.8 (2F, s). IR (neat, cm⁻¹) 3518, 2958, 1736, 1458, 1232, 1144, 814, 773, 732, 700. HRMS (ESI⁺) calcd for C₁₂H₉F₁₅O₃ [M+Na]+: 581.1332, found 581.1350. HPLC: GL Science Inc. Inertsil® Diol column; detected at 294 nm; hexanes/ethanol, 95/5; flow = 1.0 mL/min; retention times: 5.50 min, 7.04 min.

S23
(1R,2S,5R)-5-Methyl-2-(1-methylethyl)cyclohexyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5ja)

Yellow oil, 115.9 mg, yield: 82%. 1H NMR (400 MHz, CDCl3) δ: 4.83–4.73 (major and minor, 1H, m), 3.55 (major, 1H, s), 3.54 (minor, 1H, s), 2.82–2.70 (major and minor, 1H, m), 2.56–2.42 (major and minor, 1H, m), 2.04–1.98 (major and minor, 1H, m), 1.90–1.79 (major and minor, 1H, m), 1.71 (major and minor, 2H, d, J = 11.9 Hz), 1.55–1.40 (major and minor, 5H, m), 1.12–0.96 (major and minor, 2H, m), 0.94–0.83 (major and minor, 7H, m), 0.74 (major and minor, 3H, dd, J = 15.1, 7.1 Hz). 13C NMR (151 MHz, CDCl3) δ: 175.0 (major and minor), 119.5–108.7 (major and minor, 6C, m), 77.5 (major and minor), 71.5 (minor, m), 71.4 (major, m), 47.1 (minor), 47.0 (major), 40.4 (major), 40.0 (minor), 39.3 (major, t, J = 20.4 Hz), 38.7 (minor, t, J = 20.4 Hz), 34.2 (major and minor), 31.5 (major and minor), 28.4 (major). 28.2 (minor), 26.2 (major), 25.6 (minor), 23.1 (minor), 22.8 (major), 22.1 (major), 22.0 (minor), 21.0 (minor), 20.9 (major), 15.8 (major), 15.4 (minor). 19F NMR (376 MHz, CDCl3) δ: -81.3 (3F, s), -109.7 (1F, dd, J = 278.4, 184.3 Hz), -114.6 (1F, t, J = 289.6 Hz), -122.3 (2F, d, J = 34.7 Hz), -123.4 (2F, s), -124.4 (2F, d, J = 57.8 Hz), -126.7 (2F, s). IR (neat, cm⁻¹)3453, 2960, 1748, 1458, 1232, 1187, 1144, 1009, 814, 748, 699. HRMS (ESI⁺) calcd for C29H25F13O3 [M+Na⁺]: 583.1488, found 583.1501. HPLC: GL Science Inc. Inertsil® Diol column; detected at 294 nm; hexane/ethanol, 95/5; flow = 1.0 mL/min; retention times: 3.09 min, 3.86 min.

(1R,2S,5R)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-methylnonanoate (5ka)

Yellow oil, 111.9 mg, yield: 70%. 1H NMR (400 MHz, CDCl3) δ: 7.37–7.28 (major and minor, 4H, m), 7.22–7.16 (major and minor, 1H, m), 4.90–4.79 (major and minor, 1H, m), 2.54–2.38 (major and minor, 1H, m), 2.30–2.14 (major and minor, 2H, m), 2.04–1.95 (major and minor, 1H, m), 1.83–1.79 (major and minor, 1H, m), 1.73–1.66 (major and minor, 1H, m), 1.55–1.47 (major and minor, 1H, m), 1.34 (major and minor, 3H, s), 1.27 (major and minor, 3H, s), 1.22–1.17 (major and minor, 5H, m), 1.16–0.99 (major and minor, 2H, m), 0.96–0.86 (major and minor, 3H, m). 13C NMR (151 MHz, CDCl3) δ: 171.4 (minor), 173.1 (major), 152.2 (major), 151.6 (minor), 128.5 (major, 2C), 128.4 (minor, 2C), 125.7 (major), 125.6 (minor), 125.4 (minor), 125.3 (major), 121.9–106.8 (major and minor, 6C, m), 78.5 (minor), 78.0 (major), 72.3 (major), 71.8 (minor), 49.5 (major), 49.4 (minor), 40.7 (minor), 40.5 (major), 39.7 (minor), 39.6 (major), 39.0 (major, t, J = 19.6 Hz), 38.5 (minor, t, J = 19.6 Hz), 34.6 (major and minor), 31.4 (major and minor), 29.5 (major), 28.7 (minor), 27.3 (major and minor), 26.9 (minor), 26.7 (major), 25.3 (minor), 24.0 (major), 21.8 (major and minor).
4.4.5.6,6,7,7,8,8,9,9,9-Tridecafluoro-2-hydroxy-2-methyl-1-(10,10-dimethyl-3,3-dioxo-3\textsuperscript{\alpha}-thia-4-azatricyclo[5.2.1.0\textsuperscript{3,4}]decan-4-yl)nonan-1-one (5\textit{la})

(95: 5 diastereomer mixture, dr was measured by HPLC.)

Yellow oil, 37.1 mg, yield: 24%. \(^1\text{H} \text{NMR (500 MHz, CDCl}_3, \text{major}) \delta: \)
4.04 (1H, dd, J = 7.7, 4.6 Hz), 3.75 (1H, s), 3.58 (1H, d, J = 13.5 Hz), 3.47 (1H, d, J = 13.5 Hz), 3.09–3.04 (1H, m), 2.46–2.42 (1H, m), 2.04–1.87 (5H, m), 1.63 (3H, s), 1.46–1.41 (1H, m), 1.36–1.34 (1H, m), 1.18 (3H, s), 0.99 (3H, s). \(^{13}\text{C} \text{NMR (151 MHz, CDCl}_3, \text{major}) \delta: 175.8, 143.2–97.9 (6C, m), 75.7, 67.7, 53.9, 48.7, 47.9, 44.9, 41.2 (t, J = 19.6 Hz), 38.2, 33.4, 26.9, 26.5, 21.0, 20.1. \(^{19}\text{F} \text{NMR (471 MHz, CDCl}_3, \text{major}) \delta: \)
-81.0 (3F, s), -107.7 (1F, d, J = 289.0 Hz), -102.5 (1F, d, J = 289.0 Hz), -121.9 (2F, s), -123.1 (2F, s), -124.1 (2F, s), -126.4 (2F, s). IR (neat, cm\textsuperscript{-1}) 3495, 2984, 2976, 2959, 2889, 1699, 1314, 1236, 1173, 1159, 1142, 1123. [\(\alpha\)]\text{D}^{21} = 22.3 (c 1, CHCl\textsubscript{3}). HRMS (DART\textsuperscript{+}) calcd for C\textsubscript{29}H\textsubscript{29}F\textsubscript{13}NO\textsubscript{5}S [M+H]: 620.1140, found 620.1134. HPLC: GL Science Inc. Inertsil\textsuperscript{®} Diol column; detected at 294 nm; hexane/IPA, 90/10; flow = 0.25 mL/min; retention times: 18.09 min, 19.06 min.

4.4.5.6,6,7,7,8,8,9,9,9-Tridecafluoro-2-hydroxy-N,N2-trimethylnonanamide (5\textit{ma})

Yellow oil, 21.0 mg, yield: 18%. \(^1\text{H} \text{NMR (500 MHz, CDCl}_3) \delta: 4.84 (1H, s), 3.11 (6H, s), 2.76–2.59 (2H, m), 1.61 (3H, s). \(^{13}\text{C} \text{NMR (151 MHz, CDCl}_3) \delta: 173.5, 132.6–108.5 (6C, m), 71.4, 39.7 (t, J = 21.1 Hz), 38.6, 27.2 (2C). \(^{19}\text{F} \text{NMR (471 MHz, CDCl}_3) \delta: -81.3 (3F, s), -112.3 (1F, d, J = 267.0 Hz), -114.3 (1F, d, J = 267.0 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.2 (2F, s), -126.6 (2F, s). IR (neat, cm\textsuperscript{-1}) 3268, 2982, 2955, 2934, 1616, 1233, 1184, 1165, 1140, 1123. HRMS (DART\textsuperscript{+}) calcd for C\textsubscript{12}H\textsubscript{12}F\textsubscript{13}NO\textsubscript{2} [M+H]: 450.0739, found 450.0699.

4.4.5.6,6,7,7,8,8,9,9,9-Tridecafluoro-2-hydroxy-N,N-dimethylnonanamide (5\textit{na})

Yellow oil, 20.6 mg, yield: 20%. \(^1\text{H} \text{NMR (400 MHz, CDCl}_3) \delta: 4.85–4.80 (1H, m), 3.90 (1H, d, J = 7.8 Hz), 3.05 (3H, s), 3.02 (3H, s), 2.43–2.29 (2H, m). \(^{13}\text{C} \text{NMR (151 MHz, CDCl}_3) \delta: 172.2, 119.6–105.8 (6C, m), 61.9, 36.8 (t, J = 23.4 Hz), 36.4 (2C). \(^{19}\text{F} \text{NMR (376 MHz, CDCl}_3) \delta: -81.3 (3F, s), -113.5 (1F, d, J = 277.4 Hz), -114.4 (1F, d, J = 277.4 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.0 (2F, s), -
126.6 (2F, s). IR (neat, cm⁻¹) 3347, 1634, 1228, 1185, 1141, 1121, 1086, 716, 656. HRMS (ESI⁺) calec for C₁₁H₁₀NO₂[M+Na⁺]: 458.0396, found 458.0414.

**Methyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonanoate (5oa)**

Yellow oil, 17.9 mg, yield: 17%. ¹H NMR (400 MHz, CDCl₃) δ: 4.62–4.58 (1H, m), 3.87 (3H, s), 3.02 (1H, d, J = 5.0 Hz), 2.76–2.62 (1H, m), 2.54–2.39 (1H, m).

¹³C NMR (151 MHz, CDCl₃) δ: 173.5, 119.3–110.3 (6C, m), 64.9, 53.5, 35.4 (t, J = 21.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -113.2 (1F, d, J = 277.4 Hz), -114.2 (1F, d, J = 277.4 Hz), -121.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3459, 2963, 1748, 1565, 1442, 1230, 1191, 1142, 815, 705. HRMS (ESI⁺) calec for C₁₀H₁₂F₁₃O₃ [M+Na⁺]: 445.0080, found 445.0078.

**Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonanoate (5pa)**

Yellow oil, 25.2 mg, yield: 23%. ¹H NMR (400 MHz, CDCl₃) δ: 4.59–4.56 (1H, m), 4.32 (2H, dd, J = 14.4, 7.6 Hz), 3.06 (1H, d, J = 5.0 Hz), 2.75–2.61 (1H, m), 2.54–2.39 (1H, m), 1.33 (3H, t, J = 7.1 Hz). ¹³C NMR (151 MHz, CDCl₃) δ 170.5, 122.1–106.8 (6C, m), 65.0, 63.0, 35.3 (t, J = 20.4 Hz), 14.2. ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -113.5 (2F, t, J = 294.8 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3461, 2989, 1743, 1565, 1531, 1231, 1122, 779, 707. HRMS (ESI⁺) calec for C₁₁H₁₃F₁₃O₃ [M+Na⁺]: 459.0236, found 459.0236.

**tert-Butyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonanoate (5qa)**

Yellow oil, 37.3 mg, yield: 32%. ¹H NMR (400 MHz, CDCl₃) δ: 4.45–4.41 (1H, m), 3.11 (1H, d, J = 4.6 Hz), 2.69–2.55 (1H, m), 2.51–2.36 (1H, m), 1.51 (9H, s).

¹³C NMR (151 MHz, CDCl₃) δ: 172.2, 119.5–108.5 (6C, m), 84.2, 65.3, 35.3 (t, J = 21.1 Hz), 28.0 (3C). ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.1 (3F, s), -112.9 (2F, s), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.5 (2F, s). IR (neat, cm⁻¹) 3433, 2981, 1727, 1166, 1139, 1086, 829, 752, 703. HRMS (ESI⁺) calec for C₁₃H₁₅F₁₃O₃ [M+Na⁺]: 487.0549, found 487.0549.

**Benzyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxynonanoate (5ra)**

Yellow oil, 21.9 mg, yield: 18%. ¹H NMR (400 MHz, CDCl₃) δ: 7.42–7.34 (5H, m), 5.26 (2H, dd, J = 17.9, 12.4 Hz), 4.63–4.59 (1H, m), 3.03 (1H, d, J = 5.0 Hz), 2.75–2.61 (1H, m), 2.54–2.39 (1H, m). ¹³C NMR (151 MHz, CDCl₃) δ: 172.9, 134.5, 129.1, 128.9 (2C), 128.8, 119.3–108.4 (6C, m), 68.6, 65.1, 35.2 (t, J = 21.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -113.4 (2F, t, J = 295.2 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3464, 2969, 1743, 1529, 1232, 1142, 812, 732,
HRMS (ESI⁺) cale for C₁₆H₁₁F₁₃O₃ [M+Na⁺]: 521.0393, found 521.0392.

Ethyl 4,4,5,6,7,7,8,8,9,9,9-tridecafluoro-2-hydroxy-2-phenylethynonanoate (5sa)

Yellow oil, 89.4 mg, yield: 66%. ¹H NMR (500 MHz, CDCl₃) δ: 7.30–7.15 (5H, m), 4.30 (1H, dq, J = 10.9, 7.2 Hz), 4.22 (1H, dq, J = 10.9, 7.2 Hz), 3.62 (1H, s), 2.83–2.80 (1H, m), 2.79–2.66 (1H, m), 2.58–2.52 (1H, m), 2.43 (1H, m), 2.06 (2H, dt, J = 11.5, 5.2 Hz), 1.31 (3H, t, J = 7.2 Hz). ¹³C NMR (151 MHz, CDCl₃) δ: 174.5, 140.8, 128.7, 128.5 (2C), 126.3, 120.2–110.5 (6C, m), 73.7, 63.0, 42.2, 39.0 (t, J = 21.1 Hz), 29.3, 14.1. ¹⁹F NMR (471 MHz, CDCl₃) δ: -81.3 (3F, s), -110.5 (1F, d, J = 279.3 Hz), -114.1 (1F, d, J = 279.3 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.5 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3528, 3067, 2996, 2951, 1732, 1362, 1229, 1184, 1138, 1121, 745, 696. HRMS (DART⁺) cale for C₁₉H₁₇F₁₃O₅ [M+H⁺]: 541.1048, found 541.1083.

Dimethyl 2-hydroxy-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluorohexyloxy)-butanedioate (5ta)

Yellow oil, 44.3 mg, yield: 36%. ¹H NMR (400 MHz, CDCl₃) δ: 4.01 (1H, s), 3.87 (1H, s), 3.72 (1H, s), 2.90 (2H, dd, J = 60.2, 15.8 Hz), 2.72–2.55 (2H, m). ¹³C NMR (151 MHz, CDCl₃) δ: 173.5, 170.2, 122.5–106.6 (6C, m), 72.3, 53.8, 52.4, 43.8, 38.6 (t, J = 34.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -112.0 (1F, d, J = 265.9 Hz), -113.8 (1F, d, J = 265.9 Hz), -122.2 (2F, s), -123.4 (2F, s), -124.2 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3532, 1732, 1568, 1364, 1270, 1182, 1159, 1138, 694, 660. HRMS (ESI⁺) cale for C₁₃H₁₁F₁₃O₅ [M+Na⁺]: 517.0291, found 517.0306.

Diethyl 2-hydroxy-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluorohexyloxy)-butanedioate (5ua)

Yellow oil, 50.6 mg, yield: 39%. ¹H NMR (400 MHz, CDCl₃) δ: 4.37–4.26 (2H, m), 4.17 (2H, dd, J = 7.0, 3.5 Hz), 4.05 (1H, s), 2.87 (2H, dd, J = 63.0, 15.8 Hz), 2.69–2.58 (2H, m), 1.32 (3H, t, J = 7.1 Hz), 1.26 (3H, t, J = 7.1 Hz). ¹³C NMR (151 MHz, CDCl₃) δ: 173.0, 169.7, 120.6–105.9 (6C, m), 72.3, 63.1, 61.4, 44.0, 38.6 (t, J = 20.2 Hz), 14.2, 14.0. ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -111.5 (1F, d, J = 277.4 Hz), -113.5 (1F, d, J = 277.4 Hz), -122.2 (2F, s), -123.4 (2F, s), -124.2 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3498, 2989, 1743, 1231, 1189, 1122, 814, 745, 697. HRMS (ESI⁺) cale for C₁₅H₁₃F₁₃O₅ [M+Na⁺]: 523.0785, found 523.0784.
Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-2-hydroxy-2-methyldecanoate (5ab)

Yellow oil, 100.29 mg, yield: 80%. 1H NMR (400 MHz, CDCl3) δ: 4.37–4.22 (2H, m), 3.49 (1H, s), 2.81–2.68 (1H, m), 2.57–2.44 (1H, m), 1.51 (3H, s), 1.31 (3H, t, J = 7.1 Hz). 13C NMR (151 MHz, CDCl3) δ 175.3, 120.2–106.6 (7C, m), 71.4 (d, J = 1.5 Hz), 62.9, 39.4 (t, J = 20.4 Hz), 28.0, 14.0. 19F NMR (376 MHz, CDCl3) δ: -81.3 (3F, s), -110.3 (1F, d, J = 283.2 Hz), -114.7 (1F, d, J = 283.2 Hz), -122.1 (2F, s), -122.6 (2F, s), -123.2 (2F, s), -124.5 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3511, 2990, 1739, 1452, 1237, 1141, 1014, 721, 702. HRMS (ESI⁺) calcd for C13H11F13O3 [M+Na⁺]: 523.0361, found 523.0372.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-heptadecafluoro-2-hydroxy-2-methylundecanoate (5ac)

Yellow solid, 103.0 mg, yield: 76%. 1H NMR (400 MHz, CDCl3) δ: 4.37–4.21 (2H, m), 3.50 (1H, s), 2.80–2.68 (1H, m), 2.57–2.44 (1H, m), 1.52 (3H, s), 1.31 (3H, t, J = 7.3 Hz). 13C NMR (151 MHz, CDCl3) δ 175.3, 120.4–106.4 (8C, m), 71.4 (d, J = 1.5 Hz), 62.9, 39.4 (t, J = 19.6 Hz), 28.0, 14.0. 19F NMR (376 MHz, CDCl3) δ: -81.2 (3F, s), -110.3 (1F, d, J = 283.2 Hz), -114.6 (1F, d, J = 283.2 Hz), -122.0 (2F, s), -122.4 (4F, s), -123.2 (2F, s), -124.5 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3504, 1725, 1370, 1326, 1198, 1144, 885, 703, 660. HRMS (ESI⁺) calcd for C14H12F13O3 [M+Na⁺]: 573.0329, found 573.0333.

Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-2-hydroxy-2-methyltridecanoate (5ad)

White solid, 122.6 mg, yield: 76%. 1H NMR (400 MHz, CDCl3) δ: 4.37–4.21 (2H, m), 3.51 (1H, s), 2.80–2.68 (1H, m), 2.57–2.44 (1H, m), 1.51 (3H, s), 1.31 (3H, t, J = 7.1 Hz). 13C NMR (151 MHz, CDCl3) δ 175.3, 120.3–106.5 (10C, m), 71.4 (d, J = 1.5 Hz), 62.9, 39.4 (t, J = 19.6 Hz), 28.0, 14.0. 19F NMR (376 MHz, CDCl3) δ: -81.2 (3F, s), -110.2 (1F, d, J = 277.4 Hz), -114.6 (1F, d, J = 277.4 Hz), -122.0 (2F, s), -122.3 (8F, s), -123.2 (2F, s), -124.5 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3505, 1726, 1343, 1214, 1184, 1149, 875, 799, 666. HRMS (ESI⁺) calcd for C15H12F21O3 [M+Na⁺]: 673.0265, found 673.0264.

Ethyl 4,4-difluoro-4-(2,3,4,5,6-pentafluorophenyl)-2-hydroxy-2-methylbutanoate (5ae)

Yellow oil, 61.5 mg, yield: 71%. 1H NMR (400 MHz, CDCl3) δ: 4.35–4.23 (2H, m), 3.32 (1H, d, J = 0.9 Hz), 2.94–2.84 (1H, m), 2.80–2.68 (1H, m), 1.44 (3H, s), 1.34 (3H, t, J = 7.1 Hz). 13C NMR (151 MHz, CDCl3) δ 175.7, 145.4–117.9 (7C, m), 71.5 (dd, J = 7.6, 1.5 Hz), 62.9, 46.4 (t, J = 25.7 Hz), 28.0, 14.1. 19F NMR (376 MHz, CDCl3) δ: -81.9 (1F, d, J = 260.7 Hz), -92.9 (1F, dd, J = 268.0, 36.7 Hz), -140.7–140.9 (2F, m), -151.7 (1F, d, J = 23.1 Hz), -161.7 (2F, t, J = 23.1 Hz). IR (neat, cm⁻¹) 3497, 2942, 1732, 1656, 1528, 1336, 1178, 1047, 990, 852, 684. HRMS (ESI⁺) calcd for C13H11F3O3
[M+Ma]$: 371.0489, found 371.0489.

**Benzy1 4.4.4-trifluoro-2-hydroxy-2-methylbutanoate (5df)**

Colorless oil, 50.0 mg, yield: 76%. ¹H NMR (400 MHz, CDCl₃) δ: 7.42–7.34 (5H, m), 5.23 (2H, dd, J = 29.8, 11.9 Hz), 3.43 (1H, s), 2.76–2.65 (m), 2.61–2.50 (1H, m), 1.49 (3H, s). ¹³C NMR (151 MHz, CDCl₃) δ 175.0, 134.7, 128.9 (2C), 128.6 (2C), 128.0–122.5 (1C, m), 71.3 (d, J = 3.0 Hz), 68.6, 43.0 (dd, J = 55.9, 27.9 Hz), 27.2. ¹⁹F NMR (376 MHz, CDCl₃) δ: -62.1 (3F, s). IR (neat, cm⁻¹) 3511, 2987, 1739, 1369, 1268, 1182, 1144, 1075, 966, 911, 750. HRMS (ESI⁺) calc'd for C₁₂H₁₃F₃O₃ [M+Na]⁺: 285.0709, found 285.0708.

**Benzy1 4.4.5.5,5-pentafluoro-2-hydroxy-2-methylpentanoate (5dg)**

Yellow oil, 56.0 mg, yield: 72%. ¹H NMR (400 MHz, CDCl₃) δ: 7.41–7.33 (5H, m), 5.22 (2H, dd, J = 11.6, 5.8 Hz), 3.47 (1H, s), 2.74–2.61 (1H, m), 2.54–2.41 (1H, m), 1.51 (3H, s). ¹³C NMR (151 MHz, CDCl₃) δ 175.1, 134.7, 129.0, 128.9, 128.7 (2C), 121.6–113.1 (2C, m), 71.4 (d, J = 1.5 Hz), 68.7, 39.3 (t, J = 19.6 Hz), 27.8. ¹⁹F NMR (376 MHz, CDCl₃) δ: -86.9 (3F, s), -115.2 (1F, dd, J = 268.8, 26.0 Hz), -118.6 (1F, dd, J = 268.8, 26.0 Hz). IR (neat, cm⁻¹) 3511, 2987, 1739, 1333, 1197, 1144, 1020, 961, 910, 752, 697. HRMS (ESI⁺) calc'd for C₁₃H₁₃F₅O₃ [M+Na]⁺: 335.0677, found 335.0672.

**Benzy1 4.4.5.5,6,6,6-heptafluoro-2-hydroxy-2-methylhexanoate (5dh)**

Yellow oil, 64.0 mg, yield: 71%. ¹H NMR (400 MHz, CDCl₃) δ: 7.40–7.33 (5H, m), 5.22 (2H, dd, J = 18.2, 12.1 Hz), 3.46 (1H, s), 2.78–2.66 (1H, m), 2.56–2.43 (1H, m), 1.52 (3H, s). ¹³C NMR (151 MHz, CDCl₃) δ 175.1, 134.6, 129.0, 128.8 (2C), 128.7, 118.8–108.3 (3C, m), 71.5 (d, J = 1.5 Hz), 68.7, 39.1 (t, J = 19.6 Hz), 28.0. ¹⁹F NMR (376 MHz, CDCl₃) δ: -80.8 (3F, s), -111.6 (1F, dd, J = 277.4, 23.1 Hz), -115.8 (1F, dd, J = 277.4, 23.1 Hz), -128.7 (2F, s). IR (neat, cm⁻¹) 3511, 2987, 1736, 1353, 1277, 1221, 1121, 971, 911, 726, 697. HRMS (ESI⁺) calc'd for C₁₄H₁₃F₆O₃ [M+Na]⁺: 385.0645, found 385.0646.

**Benzy1 4.4.5.5,6,6,6,7,7-nonafluoro-2-hydroxy-2-methylheptanoate (5di)**

Yellow oil, 75.5 mg, yield: 73%. ¹H NMR (400 MHz, CDCl₃) δ: 7.39–7.33 (5H, m), 5.23 (2H, dd, J = 15.1, 11.9 Hz), 3.47 (1H, s), 2.80–2.67 (1H, m), 2.57–2.43 (1H, m), 1.52 (3H, s). ¹³C NMR (151 MHz, CDCl₃) δ 175.1, 134.7, 129.0, 128.8 (2C), 128.7, 119.5–108.6 (4C, m), 71.5 (d, J = 3.0 Hz), 68.7, 39.3 (t, J = 20.4 Hz), 28.0. ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.6 (3F, s), -110.7 (1F, d, J = 265.9 Hz), -114.9 (1F, d, J = 265.9 Hz), -125.3 (2F, s), 126.4 (2F, s). IR (neat, cm⁻¹) 3518, 2987, 1739, 1353, 1301, 1217,
Benzy1 4.4.5.5.6.6.7.7.8.8.8-undecafluoro-2-hydroxy-2-methyltoctanoate (5dj)

Yellow oil, 85.4 mg; yield: 74%. 1H NMR (400 MHz, CDCl3) δ: 7.41–7.33 (5H, m), 5.23 (2H, dd, J = 14.2, 11.9 Hz), 3.47 (1H, s), 2.80–2.67 (1H, m), 2.57–2.44 (1H, m), 1.52 (3H, s). 13C NMR (151 MHz, CDCl3) δ: 175.1, 134.6, 129.0, 128.8 (2C), 128.7, 119.4–108.6 (5C, m), 71.5 (d, J = 3.0 Hz), 68.7, 39.4 (t, J = 20.4 Hz), 28.0. 19F NMR (376 MHz, CDCl3) δ: -81.2 (3F, s), -110.5 (1F, d, J = 289.0 Hz), -114.7 (1F, d, J = 289.0 Hz), -123.0 (2F, s), -124.6 (2F, s), 126.8 (2F, s). IR (neat, cm⁻¹) 3508, 2987, 1740, 1458, 1232, 1185, 1139, 874, 824, 697. HRMS (ESI⁺) calcd for C₃₉H₃₁F₁₄O₃ [M+Na⁺]: 485.0581, found 485.0581.

Benzy1 4.5.5.5-tetrafluoro-2-hydroxy-2-methyl-(trifluoromethyl)pentanoate (5dk)

Yellow oil, 57.9 mg; yield: 64%. 1H NMR (400 MHz, CDCl3) δ: 7.41–7.33 (5H, m), 5.21 (2H, dd, J = 75.6, 11.9 Hz), 3.47 (1H, s), 2.78–2.72 (1H, m), 2.55–2.46 (1H, m), 1.51 (3H, s). 13C NMR (151 MHz, CDCl3) δ: 175.0, 134.6, 129.0, 128.8, 128.7 (2C), 126.0–90.2 (3C, m), 71.6 (d, J = 4.5 Hz), 68.7, 37.0 (d, J = 18.1 Hz), 28.8. 19F NMR (376 MHz, CDCl3) δ: -76.0 (3F, s), -78.2 (3F, m), -187.4 (1F, s). IR (neat, cm⁻¹) 3518, 2987, 1739, 1277, 1224, 1155, 1129, 996, 960, 908, 696. HRMS (ESI⁺) calcd for C₃₉H₃₁F₁₄O₃ [M+Na⁺]: 385.0645, found 385.0639.

Benzy1 3-(1.2,2.3.3.4.4.5.5.6.6-undecafluorocyclohexyl)-2-hydroxy-2-methylpropanoate (5dl)

Yellow oil, 31.6 mg; yield: 27%. 1H NMR (400 MHz, CDCl3) δ: 7.41–7.33 (5H, m), 5.22 (2H, dd, J = 67.8, 12.4 Hz), 3.49 (1H, s), 2.85–2.79 (1H, m), 2.65–2.56 (1H, m), 1.54 (3H, s). 13C NMR (151 MHz, CDCl3) δ: 175.0, 134.6, 129.0, 128.8 (3C), 119.1–90.5 (6C, m), 71.3 (d, J = 4.5 Hz), 68.7, 34.7 (d, J = 19.6 Hz), 28.9. 19F NMR (376 MHz, CDCl3) δ: -117.6 (1F, d, J = 300.06 Hz), -119.4 (1F, d, J = 300.06 Hz), -122.9 (2F, dd, J = 277.4, 173.4 Hz), -124.6 (1F, d, J = 277.4 Hz), -131.3 (1F, d, J = 300.06 Hz), -134.5 (1F, d, J = 300.06 Hz), -139.5 (2F, dd, J = 289.0, 57.8 Hz), -142.7 (1F, d, J = 289.0 Hz), -187.2 (1F, s). IR (neat, cm⁻¹) 3517, 2987, 1739, 1458, 1316, 1221, 1142, 983, 967, 904, 697. HRMS (ESI⁺) calcd for C₃₇H₃₁F₁₄O₃ [M+Na⁺]: 497.0571, found 497.0573.
Benzyl 5,5,5-trifluoro-2-hydroxy-2-methylpentanoate (5dm)

Yellow oil, 18.0 mg, yield: 26%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.42–7.34 (5H, m), 5.23 (2H, dd, $J = 20.6$, 12.4 Hz), 3.20 (1H, d, $J = 0.9$ Hz), 2.32–2.18 (1H, m), 2.06–1.99 (1H, m), 1.95–1.87 (1H, m), 1.86–1.76 (1H, m), 1.45 (3H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 176.3, 135.0, 128.9 (2C), 128.5 (2C), 109.7–99.9 (m), 73.3, 68.2, 31.9 (q, $J = 3.0$ Hz), 28.7 (dd, $J = 58.1$, 29.4 Hz), 26.4. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -67.0 (3F, s). IR (neat, cm$^{-1}$) 3507, 2958, 1729, 1456, 1320, 1221, 1144, 1078, 981, 750, 697. HRMS (ESI$^+$) calcd for C$_{13}$H$_{15}$F$_3$O$_3$ [M+Na]$^+$: 299.0865, found 299.0859.

Benzyl 5,5,6,6,7,7,7-heptafluoro-2-hydroxy-2-methylheptanoate (5dn)

Colorless oil, 20.0 mg, yield: 21%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.41–7.34 (5H, m), 5.24 (2H, dd, $J = 40.3$, 12.4 Hz), 3.21 (1H, d, $J = 0.9$ Hz), 2.32–2.16 (1H, m), 2.10–2.03 (1H, m), 1.98–1.90 (1H, m), 1.85–1.68 (1H, m), 1.47 (3H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 176.3, 135.0, 129.0, 128.9, 128.5 (2C), 119.4–108.7 (3C, m), 73.4, 68.2, 30.1 (t, $J = 3.0$ Hz), 26.5, 25.5 (t, $J = 21.9$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -80.6 (3F, s), -115.5 (2F, s), -127.8 (2F, s). IR (neat, cm$^{-1}$) 3502, 2953, 1732, 1458, 1354, 1217, 1171, 1076, 956, 908, 697. HRMS (ESI$^+$) calcd for C$_{15}$H$_{15}$F$_3$O$_3$ [M+Na]$^+$: 399.0802, found 399.0797.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-phenyloctan-1-ol (7aa)

Yellow oil, 99.1 mg, yield: 89%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.42–7.32 (4H, m), 5.23 (1H, dd, $J = 9.0$, 3.5 Hz), 2.69–2.57 (1H, m), 2.48–2.37 (1H, m). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 141.7, 128.1 (2C), 127.6, 124.8 (2C), 118.7–105.4 (6C, m), 67.1, 39.0 (t, $J = 21.1$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$: -81.3 (3F, s), -112.9 (1F, d, $J = 286.1$ Hz), -114.3 (1F, d, $J = 286.1$ Hz), -122.3 (2F, s), -123.4 (2F, s), -124.2 (2F, s), -126.7 (2F, s). IR (neat, cm$^{-1}$) 3397, 1319, 1233, 1142, 1121, 727, 698. HRMS (EI$^+$) calcd for C$_{14}$H$_{18}$F$_{13}$O [M$^+$]: 440.0446, found 440.0452.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(4-tolyloctan-1-ol (7ba)

Yellow oil, 93.1 mg, yield: 82%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.29 (2H, d, $J = 8.2$ Hz), 7.20 (2H, d, $J = 7.8$ Hz), 5.20 (1H, dd, $J = 8.7$, 3.2 Hz), 2.70–2.55 (1H, m), 2.47–2.32 (1H, m), 2.36 (3H, s), 2.11 (1H, s). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$: 139.8, 138.4, 130.2, 129.7, 125.7, 122.8, 122.8–108.7 (6C, m), 68.0, 39.9 (d, $J = 20.4$ Hz), 21.3. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$: -81.3 (3F, s), -112.9 (1F, d, $J = 138.7$ Hz), -114.4 (1F, d, $J = 138.7$ Hz), -122.3 (2F, s).
-123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3385, 1517, 1364, 1228, 1121, 1073, 921, 746, 704. HRMS (El⁺) calc for C₁₃H₁₁F₁₃O [M]⁺: 454, 0602, found 454.0602.

3,3,4,4,5,5,6,6,7,7,8,8,8-Trimodecafluoro-1-(4-methoxyphenyl)octan-1-ol (7ca)

Yellow oil, 102.1 mg, yield: 87%. ¹H NMR (400 MHz, CDCl₃) δ:

7.31 (2H, d, J = 6.4 Hz), 6.91 (2H, d, J = 6.4 Hz), 5.17 (1H, dd, J = 8.7, 3.7 Hz), 3.81 (3H, s), 2.70–2.54 (1H, m), 2.47–2.32 (1H, m). ¹³C NMR (126 MHz, CDCl₃) δ: 159.8, 135.0, 132.9–108.8 (6C, m), 127.1 (2C), 114.4 (2C), 67.7, 55.5, 39.9 (t, J = 21.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -113.0 (1F, d, J = 288.9 Hz), -114.4 (1F, d, J = 288.9 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3436, 2842, 1660, 1614, 1515, 1235, 1144, 1036, 834, 731. HRMS (El⁺) calc for C₁₃H₁₁F₁₃O [M⁺]: 470.0551, found 470.0591.

1-(3-Butylphenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-trimodecafluorooctan-1-ol (7da)

Yellow oil, 96.7 mg, yield: 78%. ¹H NMR (400 MHz, CDCl₃) δ: 7.43–7.40 (2H, m), 7.33–7.25 (2H, m), 5.20 (1H, dd, J = 10.0, 5.0 Hz), 2.69–2.56 (1H, m), 2.47–2.36 (1H, m), 2.18 (1H, s), 1.32 (9H, s). ¹³C NMR (126 MHz, CDCl₃) δ: 151.7, 139.8, 130.2, 128.4, 126.0, 125.5, 119.7–109.4 (6C, m), 67.9, 39.9 (t, J = 20.4 Hz), 34.7, 31.4 (3C). ¹⁹F NMR (471 MHz, CDCl₃) δ: -81.3 (3F, s), -112.9 (1F, d, J = 270.8 Hz), -114.5 (1F, d, J = 270.8 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3408, 2967, 2874, 1364, 1235, 1144, 1073, 836, 731, 702. HRMS (El⁺) calc for C₁₃H₁₇F₁₃O [M⁺]: 496.1071, found 496.1085.

1-(Biphenyl-4-yl)-3,3,4,4,5,5,6,6,7,7,8,8,8-trimodecafluoroctan-1-ol (7ea)

White solid, 104.9 mg, yield: 81%. ¹H NMR (400 MHz, CDCl₃) δ: 7.62–7.57 (4H, m), 7.50–7.43 (4H, m), 7.38–7.34 (1H, m), 5.29–5.25 (1H, m), 2.74–2.56 (1H, m), 2.53–2.39 (1H, m), 2.29 (1H, d, J = 1.8 Hz). ¹³C NMR (151 MHz, CDCl₃) δ: 141.7, 141.6, 140.6, 132.6, 130.2, 129.0, 128.4, 127.8, 127.7, 127.3, 126.2, 120.2–108.4, 67.9, 40.0 (t, J = 20.4 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ: -81.2 (3F, s), -112.8 (1F, d, J = 134.9 Hz), -114.2 (1F, d, J = 134.9 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3299, 1234, 1189, 1144, 1007, 839, 766, 692, 651. HRMS (ESI⁺) calc for C₂₀H₁₃F₁₃O [M+Na⁺]: 539.0651, found 539.0644.
1-(4-Chlorophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-ol (7fa)

Yellow oil, 105.0 mg, yield: 88%. 1H NMR (500 MHz, CDCl3) δ: 7.36–7.34 (4H, m), 5.22 (1H, dt, J = 5.9, 2.8 Hz), 2.63–2.57 (1H, m), 2.44–2.33 (1H, m), 2.20 (1H, s). 13C NMR (151 MHz, CDCl3) δ: 141.1, 134.3, 129.3–106.9 (6C, m), 129.2 (2C), 127.4 (2C), 125.5–106.9 (6C, m), 67.5, 40.0 (t, J = 21.1 Hz). 19F NMR (471 MHz, CDCl3) δ: -81.3 (3F, s), -113.2 (1F, d, J = 136.2 Hz), -114.4 (1F, d, J = 136.2 Hz), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3385, 3069, 2984, 2903, 1323, 1190, 1142, 1121, 1092, 812, 700. HRMS (EI⁺) calcd for C14H8ClF12O [M⁺]: 474.0056, found 474.0043.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(4-fluorophenyl)octan-1-ol (7ga)

Yellow oil, 100.0 mg, yield: 87%. 1H NMR (500 MHz, CDCl3) δ: 7.38 (2H, m), 7.10–7.06 (2H, m), 5.22 (1H, dd, J = 8.7, 3.3 Hz), 2.67–2.55 (1H, m), 2.45–2.34 (1H, m). 13C NMR (151 MHz, CDCl3) δ: 162.7 (d, J = 247.5 Hz), 138.5 (d, J = 3.0 Hz), 127.2 (2C, d, J = 9.0 Hz), 119.6–110.3 (6C, m), 115.9 (2C, d, J = 22.6 Hz), 67.5, 40.1 (t, J = 21.1 Hz). 19F NMR (471 MHz, CDCl3) δ: -81.3 (3F, s), -113.2 (1F, d, J = 286.1 Hz), -114.4 (1F, d, J = 286.1 Hz), -114.0 (1F, s), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3405, 2357, 1670, 1607, 1229, 1188, 1142, 1121, 837, 704. HRMS (EI⁺) calcd for C14H8F14O [M⁺]: 458.0352, found 458.0394.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(4-(trifluoromethyl)phenyl)octan-1-ol (7ha)

Yellow oil, 94.0 mg, yield: 74%. 1H NMR (500 MHz, CDCl3) δ: 7.66 (2H, d, J = 8.0 Hz), 7.54 (2H, d, J = 8.0 Hz), 5.31 (1H, d, J = 8.6 Hz), 2.68–2.56 (1H, m), 2.48–2.36 (1H, m), 2.28 (1H, s). 13C NMR (151 MHz, CDCl3) δ: 146.3, 132.6, 130.8 (dd, J = 64.9, 33.2 Hz), 130.2, 128.3, 126.2, 126.0 (q, J = 3.0 Hz), 121.3–106.4 (6C, m), 67.5, 40.1 (t, J = 21.1 Hz). 19F NMR (471 MHz, CDCl3) δ: -63.2 (3F, s), -81.3 (3F, s), -112.9 (1F, d, J = 277.9 Hz), -114.0 (1F, d, J = 277.9 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3374, 3038, 1669, 1622, 1325, 1235, 1167, 1123, 1069, 845, 696. HRMS (EI⁺) calcd for C15H8F16O [M⁺]: 508.0320, found 508.0271.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(4-nitrophenyl)octan-1-ol (7ia)

Yellow oil, 47.9 mg, yield: 39%. 1H NMR (500 MHz, CDCl3) δ: 8.28–8.24 (2H, m), 7.60 (2H, d, J = 9.2 Hz), 5.39–5.35 (1H, m), 2.71–2.56 (1H, m), 2.49–2.36 (2H, m). 13C NMR (151 MHz, CDCl3) δ: 149.6, 147.9, 126.8 (2C), 124.3 (2C), 120.1–108.4 (6C, m), 67.2, 40.1 (t, J =
21.1 Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$: -81.3 (3F, s), -112.8 (1F, d, $J = 272.5$ Hz), -113.7 (1F, d, $J = 272.5$ Hz), -122.2 (2F, s), -123.3 (2F, s), -124.0 (2F, s), -126.6 (2F, s). IR (neat, cm$^{-1}$) 3424, 2899, 1601, 1518, 1352, 1233, 1188, 1142, 1123, 855, 694. HRMS (El$^+$) calcd for C$_{14}$H$_8$F$_{13}$NO$_5$ [M$^+$]: 485.0297, found 485.0250.

1-(2-Chlorophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (7ja)

Yellow oil, 86.4 mg, yield: 73%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.66 (1H, dd, $J = 7.7, 1.7$ Hz), 7.36 (2H, ddd, $J = 15.8, 7.7, 1.4$ Hz), 7.27 (1H, td, $J = 7.7, 1.7$ Hz), 5.65 (1H, dd, $J = 9.2, 1.4$ Hz), 2.59-2.39 (2H, m), 2.31 (1H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 139.9, 131.3, 129.8, 129.5, 127.6, 127.1, 120.0-106.6 (6C, m), 64.8 (d, $J = 4.5$ Hz), 38.4 (t, $J = 21.1$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$: -81.3 (3F, s), -112.8 (1F, d, $J = 272.5$ Hz), -115.1 (1F, d, $J = 272.5$ Hz), -122.3 (2F, s), -123.4 (2F, s), -124.2 (2F, s), -126.6 (2F, s). IR (neat, cm$^{-1}$) 3462, 3065, 3003, 2971, 2947, 1231, 1204, 1142, 1074, 754, 702. HRMS (El$^+$) calcd for C$_{14}$H$_8$ClF$_{13}$O [M$^+$]: 474.0056, found 474.0029.

1-(3-Chlorophenyl)-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (7ka)

Yellow oil, 95.0 mg, yield: 80%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 7.42 (1H, t, $J = 1.7$ Hz), 7.36–7.27 (3H, m), 5.22 (1H, dd, $J = 8.9, 4.4$ Hz), 2.63–2.57 (1H, m), 2.42–2.38 (1H, m), 2.24 (1H, s). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 144.5, 135.0, 130.4, 128.7, 126.0, 123.9, 120.2–108.5 (6C, m), 67.5, 40.1 (t, $J = 21.1$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$: -81.3 (3F, s), -113.2 (1F, d, $J = 140.8$ Hz), -114.4 (1F, d, $J = 140.8$ Hz), -122.3 (2F, s), -123.4 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm$^{-1}$) 3401, 3065, 2978, 2895, 1669, 1233, 1188, 1142, 1074, 812, 694. HRMS (El$^+$) calcd for C$_{14}$H$_8$ClF$_{13}$O [M$^+$]: 474.0056, found 474.0011.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(2,3,4,5,6-pentafluorophenyl)octan-1-ol (7la)

Yellow oil, 83.3 mg, yield: 63%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$: 5.60 (1H, dd, $J = 12.9, 6.6$ Hz), 3.01–2.89 (1H, m), 2.73–2.61 (1H, m), 2.44 (1H, d, $J = 6.6$ Hz). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$: 145.8–135.1 (5C, m), 132.6, 118.2–110.3 (6C, m), 59.5, 37.3 (t, $J = 21.1$ Hz). $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$: -81.5 (3F, s), -113.8 (1F, d, $J = 272.5$ Hz), -114.6 (1F, d, $J = 272.5$ Hz), -122.5 (2F, s), -123.6 (2F, s), -124.3 (2F, s), -126.9 (2F, s), -143.9 (2F, s), -153.3 (1F, t, $J = 21.6$ Hz), -161.4 (2F, t, $J = 21.6$ Hz). IR (neat, cm$^{-1}$) 3495, 1505, 1233, 1190, 1142, 1121. HRMS (El$^+$) calcd for C$_{14}$H$_8$F$_{13}$O [M$^+$]: 529.9975, found 529.9951.
4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-2-phenylnonan-2-ol (7ma)

Yellow oil, 102.3 mg, yield: 90%. $^1$H NMR (400 MHz, CDCl₃) δ: 7.50–7.25 (5H, m), 2.74–2.43 (2H, m), 1.76 (3H, d, J = 4.0 Hz). $^{13}$C NMR (126 MHz, CDCl₃) δ: 146.6, 128.5 (2C), 127.5, 124.4 (2C), 118.7–105.7 (6C, m), 72.9, 42.6 (t, J = 19.8 Hz), 30.2. $^{19}$F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -110.9 (1F, d, J = 274.6 Hz), -113.5 (1F, d, J = 274.6 Hz). -122.2 (2F, s), -123.4 (2F, s), -124.2 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 2953, 2918, 2851, 1235, 1190, 1167, 1145, 1121, 698. HRMS (EI⁺) calcd for C₁₅H₁₁F₁₃O [M⁺]: 454.0602, found 454.0595.

2-(4-Chlorophenyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononan-2-ol (7na)

Yellow oil, 98.0 mg, yield: 80%. $^1$H NMR (500 MHz, CDCl₃) δ: 7.42 (2H, d, J = 8.7 Hz), 7.34 (2H, d, J = 8.7 Hz), 2.71–2.48 (2H, m), 2.28 (1H, s), 1.75 (3H, s). $^{13}$C NMR (151 MHz, CDCl₃) δ: 145.0, 133.4, 132.6, 130.2, 128.7, 128.4, 126.1, 120.3–108.4 (6C, m), 72.7, 42.6 (t, J = 19.6 Hz), 30.5. $^{19}$F NMR (471 MHz, CDCl₃) δ: -81.3 (6F, s), -110.9 (1F, d, J = 271.7 Hz), -113.4 (1F, d, J = 271.7 Hz), -122.2 (2F, s), -123.4 (2F, s), -124.2 (2F, s), -126.7 (2F, s). IR (neat, cm⁻¹) 3464, 2984, 1491, 1233, 1190, 1165, 1142, 1119, 1013, 831. HRMS (EI⁺) calcd for C₁₅H₁₀ClF₁₃O [M⁺]: 488.0213, found 488.0188.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1,1-diphenyloctan-1-ol (7oa)

Yellow oil, 89.3 mg, yield: 69%. $^1$H NMR (400 MHz, CDCl₃) δ: 7.45–7.42 (4H, m), 7.36–7.31 (4H, m), 7.28–7.24 (2H, m), 3.17 (2H, t, J = 18.3 Hz), 2.74 (1H, t, J = 2.1 Hz). $^{13}$C NMR (151 MHz, CDCl₃) δ: 145.5 (2C), 137.7, 132.6, 130.2, 128.6 (2C), 128.4, 127.7 (2C), 125.5 (2C), 120.1–108.4 (6C, m), 76.6, 41.0 (t, J = 19.6 Hz). $^{19}$F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -109.5 (2F, s), -122.1 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3470, 3088, 3061, 2971, 3028, 1655, 1495, 1233, 1188, 1142, 1121, 812, 696. HRMS (ESI⁺) calcd for C₂₀H₁₃F₁₃O [M-H]⁻: 515.0681, found 515.0641.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-(naphthalen-2-yl)octan-1-ol (7pa)

White solid, 69.6 mg, yield: 56%. $^1$H NMR (400 MHz, CDCl₃) δ: 7.89–7.79 (4H, m), 7.53–7.25 (3H, m), 5.41–5.37 (1H, m), 2.79–2.63 (1H, m), 2.57–2.44 (1H, m), 2.34 (1H, d, J = 11.8 Hz). $^{13}$C NMR (151 MHz, CDCl₃) δ: 140.1, 133.3 (d, J = 3.0 Hz), 130.2, 129.1, 128.4, 128.2, 127.9, 126.6 (d, J = 24.2 Hz), 124.8, 123.4, 119.7–108.4 (6C, m), 68.2, 40.0 (t, J = 21.1 Hz). $^{19}$F NMR (376 MHz, CDCl₃) δ: -81.3 (3F, s), -112.8 (1F, d, J = 129.1 Hz), -
114.2 (1F, d, J = 129.1 Hz), -122.2 (2F, s), -123.3 (2F, s), -124.1 (2F, s), -126.6 (2F, s). IR (neat, cm⁻¹) 3321, 1364, 1234, 1194, 1144, 1073, 1017, 826, 745, 692. HRMS (El⁺) calcd for C₁₈H₁₁F₁₃O [M⁺]: 490.0602, found 490.0620.

2-(1,1,2,2,3,3,4,4,5,5,6,6,6-Tridecafluorohexyl)-1,2,3,4-tetrahydronaphthalen-1-ol (7qa)

(84: 16 diastereomer mixture, dr was measured by HPLC)

Yellow oil, 75.2 mg, yield: 55%. ¹H NMR (500 MHz, CDCl₃) δ: 7.51–7.12 (major and minor, 4H, m), 5.14 (major, 1H, d, J = 6.5 Hz), 5.11 (minor, 1H, s), 2.92–2.75 (major and minor, 3H, m), 2.33–2.01 (major and minor, 2H, m), 1.92–1.84 (major and minor, 1H, m). ¹³C NMR (151 MHz, CDCl₃) δ: 136.7 (minor), 136.4 (major), 132.6 (minor), 130.2 (major), 129.3 (minor), 129.0 (minor), 128.8 (major), 128.5 (major), 128.4 (minor), 128.2 (major), 127.0 (major), 126.8 (minor), 121.0–106.9 (major and minor, 6C, m), 66.9 (major), 66.1 (minor), 45.6 (major, t, J = 19.6 Hz), 42.4 (minor, t, J = 19.6 Hz), 28.5 (minor), 27.5 (major), 20.6 (major), 16.2 (minor). ¹⁹F NMR (471 MHz, CDCl₃) δ: -81.3 (3F, s), -113.8 (major, 1F, d, J = 283.3 Hz), -114.7 (minor, 1F, d, J = 283.3 Hz), -116.2 (minor, 1F, d, J = 283.3 Hz), -117.3 (major, 1F, d, J = 283.3 Hz), -120.6–1234.0 (6F, m), -125.8–127.3 (2F, m). IR (neat, cm⁻¹) 3447, 3063, 3013, 2986, 2936, 2884, 1491, 1451, 1227, 1190, 1179, 1142, 1121, 1045, 743. HRMS (EI⁺) calcd for C₂₆H₁₈F₁₃O [M⁺]: 466.0602, found 466.0565. HPLC: GL Science Inc. Inertsil® Diol column; detected at 294 nm; hexane/ethanol, 95/5; flow = 1.0 mL/min; retention times: 6.20 min, 8.65 min.

3,3,4,4,5,5,6,7,7,8,8,8-Tridecafluoro-2-methyl-1-phenyloctan-1-ol (7ra)

(76: 24 diastereomer mixture, dr was measured by HPLC.)

Yellow oil, 21.9 mg, yield: 19%. ¹H NMR (500 MHz, CDCl₃) δ: 7.47–7.27 (major and minor, 5H, m), 5.44 (major, 1H, s), 5.04 (minor, 1H, dd, J = 6.7, 1.0 Hz), 2.88–2.79 (minor, 1H, m), 2.62–2.51 (major, 1H, m), 2.15 (minor, 1H, s), 1.95 (major, 1H, d, J = 3.2 Hz), 1.08 (major, 3H, dd, J = 7.0, 1.0 Hz), 0.91 (minor, 3H, d, J = 6.9 Hz). ¹³C NMR (151 MHz, CDCl₃) δ: 141.6 (major), 140.9 (minor), 128.7 (minor, 2C), 128.6 (major, 2C), 127.8 (major), 127.2 (minor), 125.6 (major, 2C), 125.5 (minor, 2C), 119.5–109.2 (major and minor, 6C, m), 73.1 (minor, d, J = 4.5 Hz), 69.7 (major, d, J = 4.5 Hz), 43.4 (major and minor, t, J = 19.6 Hz), 10.1 (minor), 5.3 (major). ¹⁹F NMR (471 MHz, CDCl₃) δ: -81.3 (3F, s), -112.1 (minor, 1F, d, J = 286.1 Hz), -114.9 (major, 1F, d, J = 272.5 Hz), -116.8 (major, 1F, d, J = 272.5 Hz), -117.3 (minor, 1F, d, J = 286.1 Hz), -120.1–123.3 (6F, m), -124.1–127.3 (2F, m). IR (neat, cm⁻¹) 3464, 3065, 3028, 2998, 2970, 1670, 1233, 1194, 1142, 1123, 746, 698. HRMS (EI⁺) calcd for C₂₆H₁₁F₁₃O [M⁺]: 454.0602, found 454.0560. HPLC: GL Science Inc. Inertsil® Diol column; detected at 294 nm; hexane/ethanol, 95/5; flow = 1.0 mL/min; retention times: 4.44 min, 4.77 min.
8. References

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9. $^1$H, $^{13}$C and $^{19}$F NMR spectra

**5aa: $^1$H NMR (CDCl$_3$, 400 MHz)**

**5aa: $^{13}$C NMR (CDCl$_3$, 151 MHz)**
5aa: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5ba: $^1$H NMR (CDCl$_3$, 500 MHz)
5ba: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5ba: $^{19}$F NMR (CDCl$_3$, 471 MHz)
**5ca.** $^1$H NMR (CDCl$_3$, 500 MHz)

**5ca.** $^{13}$C NMR (CDCl$_3$, 151 MHz)
5ca. $^{19}$F NMR (CDCl$_3$, 471 MHz)

5da. $^1$H NMR (CDCl$_3$, 500 MHz)
5da: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5da: $^{19}$F NMR (CDCl$_3$, 471 MHz)
5ea: $^1$H NMR (CDCl$_3$, 400 MHz)

5ea: $^{13}$C NMR (CDCl$_3$, 151 MHz)
5ea: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5fa: $^1$H NMR (CDCl$_3$, 500 MHz)
5fa: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5fa: $^{19}$F NMR (CDCl$_3$, 471 MHz)
5ga: $^1$H NMR (CDCl$_3$, 400 MHz)

5ga: $^{13}$C NMR (CDCl$_3$, 151 MHz)
5ga: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5ha: $^1$H NMR (CDCl$_3$, 400 MHz)
Sha: $^{13}$C NMR (CDCl$_3$, 151 MHz)

Sha: $^{19}$F NMR (CDCl$_3$, 376 MHz)
Sia: $^1$H NMR (CDCl$_3$, 400 MHz)

Sia: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**5ia.** $^{19}$F NMR (CDCl$_3$, 376 MHz)

**5ja.** $^1$H NMR (CDCl$_3$, 400 MHz)
5ja: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5ja: $^{19}$F NMR (CDCl$_3$, 376 MHz)
5ka: $^1$H NMR (CDCl$_3$, 400 MHz)

5ka: $^{13}$C NMR (CDCl$_3$, 151 MHz)
$5\text{ka}$: $^{19}$F NMR (CDCl$_3$, 376 MHz)

$5\text{la}$: $^1$H NMR (CDCl$_3$, 500 MHz)
5la: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5la: $^{19}$F NMR (CDCl$_3$, 376 MHz)
5ma: $^1$H NMR (CDCl$_3$, 500 MHz)

5ma: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**5ma**: $^{19}$F NMR (CDCl$_3$, 471 MHz)

**5na**: $^1$H NMR (CDCl$_3$, 400 MHz)
**5na**: $^{13}$C NMR (CDCl$_3$, 151 MHz)

![13C NMR spectrum](image)

**5na**: $^{19}$F NMR (CDCl$_3$, 376 MHz)

![19F NMR spectrum](image)
50a: $^1$H NMR (CDCl$_3$, 400 MHz)

50a: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**5oa: $^{19}$F NMR (CDCl$_3$, 376 MHz)**

![Chemical structure and NMR spectrum for 5oa](image)

**5pa: $^1$H NMR (CDCl$_3$, 400 MHz)**

![Chemical structure and NMR spectrum for 5pa](image)
$^{13}$C NMR (CDCl$_3$, 151 MHz)

$^{19}$F NMR (CDCl$_3$, 376 MHz)
5qa: $^1$H NMR (CDCl$_3$, 400 MHz)

$^1$H NMR (CDCl$_3$, 400 MHz)

5qa: $^{13}$C NMR (CDCl$_3$, 151 MHz)

$^{13}$C NMR (CDCl$_3$, 151 MHz)
5qa: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5ra: $^1$H NMR (CDCl$_3$, 400 MHz)
5ra: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5ra: $^{19}$F NMR (CDCl$_3$, 376 MHz)
**5sa: **$^1$H NMR (CDCl$_3$, 500 MHz)

**5sa: **$^{13}$C NMR (CDCl$_3$, 151 MHz)
5sa: $^{19}$F NMR (CDCl$_3$, 471 MHz)

5ta: $^1$H NMR (CDCl$_3$, 400 MHz)
5ta: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5ta: $^{19}$F NMR (CDCl$_3$, 376 MHz)
**Sua:** $^1$H NMR (CDCl$_3$, 400 MHz)

**Sua:** $^{13}$C NMR (CDCl$_3$, 151 MHz)
**5ua:** $^{19}$F NMR (CDCl$_3$, 376 MHz)

**5ab:** $^1$H NMR (CDCl$_3$, 400 MHz)
5ab: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5ab: $^{19}$F NMR (CDCl$_3$, 376 MHz)

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5ac: $^1$H NMR (CDCl$_3$, 400 MHz)

5ac: $^{13}$C NMR (CDCl$_3$, 151 MHz)
5ac: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5ad: $^1$H NMR (CDCl$_3$, 400 MHz)
**5ad:** $^{13}$C NMR (CDCl$_3$, 151 MHz)

**5ad:** $^{19}$F NMR (CDCl$_3$, 376 MHz)
5ae: $^1$H NMR (CDCl$_3$, 400 MHz)

5ae: $^{13}$C NMR (CDCl$_3$, 151 MHz)
5ae: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5df: $^1$H NMR (CDCl$_3$, 400 MHz)
5df: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5df: $^{19}$F NMR (CDCl$_3$, 376 MHz)
5dg: $^1$H NMR (CDCl$_3$, 400 MHz)

5dg: $^{13}$C NMR (CDCl$_3$, 151 MHz)
5dg: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5dh: $^1$H NMR (CDCl$_3$, 400 MHz)
5dh: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5dh: $^{19}$F NMR (CDCl$_3$, 376 MHz)
5di: $^1$H NMR (CDCl$_3$, 400 MHz)

5di: $^{13}$C NMR (CDCl$_3$, 151 MHz)
5di: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5dj: $^1$H NMR (CDCl$_3$, 400 MHz)
**5dj: **$^{13}$C NMR (CDCl$_3$, 151 MHz)

![13C NMR spectrum](image)

**5dj: **$^{19}$F NMR (CDCl$_3$, 376 MHz)

![19F NMR spectrum](image)
5dk: $^1$H NMR (CDCl$_3$, 400 MHz)

5dk: $^{13}$C NMR (CDCl$_3$, 151 MHz)

S83
5dk: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5dl: $^1$H NMR (CDCl$_3$, 400 MHz)
5dI: $^{13}$C NMR (CDCl$_3$, 151 MHz)

5dI: $^{19}$F NMR (CDCl$_3$, 376 MHz)
5dm: $^1$H NMR (CDCl$_3$, 400 MHz)

![NMR spectrum](image)

5dm: $^{13}$C NMR (CDCl$_3$, 151 MHz)

![NMR spectrum](image)
5dn: $^{19}$F NMR (CDCl$_3$, 376 MHz)

5dm: $^1$H NMR (CDCl$_3$, 400 MHz)
5dn: $^{13}$C NMR (CDCl$_3$, 151 MHz)

![13C NMR spectrum of 5dn](image)

5dn: $^{19}$F NMR (CDCl$_3$, 376 MHz)

![19F NMR spectrum of 5dn](image)
7aa: $^1$H NMR (CDCl$_3$, 500 MHz)

7aa: $^{13}$C NMR (CDCl$_3$, 151 MHz)
7aa: $^{19}$F NMR (CDCl$_3$, 471 MHz)

7ba: $^1$H NMR (CDCl$_3$, 400 MHz)
7ba: $^{13}$C NMR (CDCl$_3$, 151 MHz)

7ba: $^{19}$F NMR (CDCl$_3$, 376 MHz)
7ca: $^1$H NMR (CDCl$_3$, 400 MHz)

7ca: $^{13}$C NMR (CDCl$_3$, 126 MHz)
7ca: \(^{19}\text{F} \) NMR (CDCl\(_3\), 376 MHz)

7da: \(^{1}\text{H} \) NMR (CDCl\(_3\), 500 MHz)
7da: $^{13}$C NMR (CDCl$_3$, 151 MHz)

7da: $^{19}$F NMR (CDCl$_3$, 471 MHz)
7ea: $^1$H NMR (CDCl$_3$, 400 MHz)

7ea: $^{13}$C NMR (CDCl$_3$, 151 MHz)
7ea: $^{19}$F NMR (CDCl$_3$, 376 MHz)

7fa: $^1$H NMR (CDCl$_3$, 500 MHz)
7fa. $^{13}$C NMR (CDCl$_3$, 151 MHz)

7fa. $^{19}$F NMR (CDCl$_3$, 471 MHz)
7ga: $^1$H NMR (CDCl$_3$, 500 MHz)

7ga: $^{13}$C NMR (CDCl$_3$, 151 MHz)
7ga: $^{19}$F NMR (CDCl$_3$, 471 MHz)

7ha: $^1$H NMR (CDCl$_3$, 500 MHz)
7ha: $^{13}$C NMR (CDCl$_3$, 151 MHz)

7ha: $^{19}$F NMR (CDCl$_3$, 471 MHz)
7ia: $^1$H NMR (CDCl$_3$, 400 MHz)

7ia: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**7ia:** $^{19}$F NMR (CDCl$_3$, 471 MHz)

**7ja:** $^1$H NMR (CDCl$_3$, 500 MHz)
7ja. $^{13}$C NMR (CDCl$_3$, 151 MHz)

7ja. $^{19}$F NMR (CDCl$_3$, 471 MHz)
7ka: $^1$H NMR (CDCl$_3$, 500 MHz)

7ka: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**7ka:** $^{19}$F NMR (CDCl$_3$, 471 MHz)

**7la:** $^1$H NMR (CDCl$_3$, 500 MHz)
**7la**: $^{13}$C NMR (CDCl$_3$, 151 MHz)

**7la**: $^{19}$F NMR (CDCl$_3$, 471 MHz)
7ma: $^1$H NMR (CDCl$_3$, 400 MHz)

7ma: $^{13}$C NMR (CDCl$_3$, 126 MHz)
7ma: $^{19}$F NMR (CDCl$_3$, 376 MHz)

7ma: $^1$H NMR (CDCl$_3$, 400 MHz)
**7na: \(^{13}\)C NMR (CDCl\(_3\), 151 MHz)**

- **ObsNuc**: 13C
- **Date**: 26/Feb/2022 15:53:34
- **EditMode**: ZGP4230
- **ObsFreq**: 150.86 MHz
- **ObsSet**: 0.0 kHz
- **ObsFine**: 9899.09 Hz
- **Point**: 32769
- **Scan**: 1024
- **AcqTime**: 9.9988 s
- **PD**: 2.0 s
- **Prw/Width**: 10.0 μs
- **Solvent**: CDCl3
- **Reference**: 77.16 ppm
- **Broad Factor**: 0.0052 Hz
- **Gain**: 2.03

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**7na: \(^{19}\)F NMR (CDCl\(_3\), 376 MHz)**

- **ObsNuc**: 19F
- **Date**: 22/Feb/2022 17:57:06
- **EditMode**: single pulse 200
- **ObsFreq**: 376.17 MHz
- **ObsSet**: 1.05 kHz
- **ObsFine**: 30.251 Hz
- **Point**: 13107
- **Scan**: 15151.2 Hz
- **AcqTime**: 5.0 s
- **Prw/Width1**: 6.405 μs
- **Temperature**: 19.0 °C
- **Solvent**: CDCl3
- **Reference**: -182.2 ppm
- **Broad Factor**: 5.7759 Hz
- **Gain**: 42
7oa: $^1$H NMR (CDCl$_3$, 400 MHz)

7oa: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**7oa: $^{19}$F NMR (CDCl$_3$, 376 MHz)**

![19F NMR spectrum of 7oa]

**7pa: $^1$H NMR (CDCl$_3$, 400 MHz)**

![1H NMR spectrum of 7pa]
7pa: $^{13}$C NMR (CDCl$_3$, 151 MHz)

7pa: $^{19}$F NMR (CDCl$_3$, 376 MHz)
7qa: $^1$H NMR (CDCl$_3$, 500 MHz)

7qa: $^{13}$C NMR (CDCl$_3$, 151 MHz)
**7qa**: $^{19}$F NMR (CDCl$_3$, 471 MHz)

**7ra**: $^1$H NMR (CDCl$_3$, 500 MHz)

S114
**7ra:** $^{13}$C NMR (CDCl$_3$, 151 MHz)

![Carbon-13 NMR spectrum of 7ra](image)

**7ra:** $^{19}$F NMR (CDCl$_3$, 471 MHz)

![Fluorine-19 NMR spectrum of 7ra](image)