Supplementary Information

Fluoride anion-initiated bis-trifluoromethylation of phenyl aromatic carboxylates with (trifluoromethyl)trimethylsilane

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1. General Information

$^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a JEOL ECZ-400 spectrometer. $^1$H NMR chemical shifts were recorded relative to tetramethylsilane ($\delta$ 0) or CHCl$_3$ ($\delta$ 7.26) and chemical shifts in $^{13}$C NMR spectra were recorded relative to CDCl$_3$ ($\delta$ 77.16). $^{19}$F NMR chemical shifts were recorded relative to CFCl$_3$ ($\delta$ 0). Data were recorded as follows: chemical shifts in ppm ($\delta$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, br = broad, m = multiplet, c = complex), coupling constant (Hz), and integration. Infrared spectra (IR) were recorded on a JASCO FT/IR-4000 spectrometer using the ATR method. Absorption data are reported in reciprocal centimeters from 800 to 3500 cm$^{-1}$ with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a SHIMADZU QP-2010 spectrometer with a quadrupole mass analyzer at 70 eV. Data were recorded as follows: mass/charge ratio and relative intensity to base peak at 100 %. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-T100LP spectrometer with a time-of-flight mass analyzer. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. Melting points were determined on a Stanford Research Systems MPA100 apparatus equipped with a digital thermometer and are uncorrected. Analytical gas chromatography (GC) was carried out on a SHIMADZU GC-2014 chromatograph equipped with a flame ionization detector. Preparative gel permeation chromatography (GPC) was carried out on a JAI LC-5060 equipped with two JAIGEL-2HR columns connected in series or two JAIGEL-2HR-40 columns connected in series. High-pressure liquid chromatography (HPLC) was performed with a SHIMADZU LC-20AR equipped with a SHIMADZU SPD-20A (UV Detector, $\lambda$ = 254 nm) and Phenomenex Luna$^\text{®}$ Silica (5 $\mu$m, 210 $\times$ 21.2 mm). Column chromatography was performed with SiO$_2$ (Silicycle Siliaflash F60 (40–63 $\mu$m)).

2. Materials

1,4-Dioxane (super dehydrated) [CAS: 123-91-1] was purchased from FUJIFILM Wako Pure Chemical Co. (Trifluoromethyl)trimethylsilane [CAS: 81290-20-2] and cesium fluoride [CAS: 13400-13-0] were purchased from Tokyo Chemical Industry Co., Ltd. Other starting materials were prepared as described below.

3. Preparation of Starting Esters

(1) Procedure A: Synthesis of Esters from Acid Chlorides

A three necked flask with a magnetic stirring bar was dried with a heat gun and purged with N$_2$. After allowing the flask to cool to room temperature, the acid chloride (1 equiv), phenol (1.1 equiv), DMAP (5 mol%), and toluene (0.3 M) were added to the flask, after which trimethylamine (1.1 equiv) was added dropwise to the mixture. After stirring overnight at room temperature, saturated aq. NaHCO$_3$ was added, the mixture was filtered through a pad of Celite. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times. The combined organic layer was successively washed with 1M aq. HCl, saturated aq. K$_2$CO$_3$, and brine. After drying over Na$_2$SO$_4$, the mixture was concentrated under reduced pressure and the resulting crude mixture was purified by recrystallization or column chromatography.
(2) Procedure B: Synthesis of Esters from Carboxylic Acids
To a round-bottom flask with a magnetic stirring bar, carboxylic acid (1.1 equiv), phenol (1 equiv), DMAP (5 mol %) and EDC·HCl (1.1 equiv) were added, and the resulting mixture was stirred in THF (0.2 M) overnight at room temperature. After the reaction reached completion, saturated aq. NaHCO₃ was added, and the mixture was filtered through a pad of Celite. The organic layer was then separated, and the aqueous layer was extracted with EtOAc three times. The organic layer was successively washed with 1 M aq. HCl, 1 M aq. NaOH, and brine. After drying over Na₂SO₄, the resulting solution was concentrated under the reduced pressure. The resulting crude mixture was purified by recrystallization or column chromatography.

Phenyl 2-naphthoate (1a) [CAS: 82408-29-5].

Procedure A (1 M aq. NaOH was used for washing instead of sat. aq. K₂CO₃). The product was obtained by recrystallization from hexane/EtOAc in 66% (2.1952 g, 8.8 mmol) as a colorless crystal. ¹H NMR (400 MHz, CDCl₃): δ 8.80 (s, 1H), 8.20 (dd, J = 8.7, 1.8 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.66-7.57 (m, 2H), 7.49-7.44 (c, 2H), 7.32-7.26 (c, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 151.2, 135.9, 132.6, 132.1, 129.7, 129.6, 128.8, 128.5, 128.0, 127.0, 126.9, 126.1, 125.6, 121.9. HRMS (DART) m/z: [M + H]⁺ Calcd for C₁₇H₁₃O₂ 249.09101; Found 249.09143.

4-Methoxyphenyl 2-naphthoate [CAS: 444112-92-9].

Procedure A. The product was obtained by recrystallization from hexane/EtOAc in 56% (907.7 mg, 3.3 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ¹H NMR (400 MHz, CDCl₃): δ 8.78 (s, 1H), 8.19 (dd, J = 8.6, 1.6 Hz, 1H), 8.00 (dd, J = 8.2, 0.8 Hz, 1H), 7.96-7.91 (c, 2H), 7.65-7.56 (c, 2H), 7.21-7.17 (m, 2H), 6.99-6.95 (m, 2H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.9, 157.5, 144.6, 135.9, 132.6, 132.0, 129.6, 128.7, 128.5, 128.0, 127.0, 125.6, 122.6, 114.7, 55.8 (one signal is obscured by overlap with another signal). HRMS (DART) m/z: [M + H]⁺ Calcd for C₁₈H₁₅O₃ 279.10157; Found 279.10145.

4-(Trifluoromethyl)phenyl 2-naphthoate [CAS: 1393716-91-0].

S3
Procedure A. The product was obtained by recrystallization from hexane/EtOAc in 66% (1.0927 g, 3.5 mmol) as a colorless crystal. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.80 (s, 1H), 8.19 (dd, \(J = 8.6, 1.7\) Hz, 1H), 8.02 (d, \(J = 8.0\) Hz, 1H), 7.97 (d, \(J = 8.6\) Hz, 1H), 7.93 (d, \(J = 8.2\) Hz, 1H), 7.73 (d, \(J = 8.5\) Hz, 2H), 7.68-7.58 (c, 2H), 7.41 (d, \(J = 8.4\) Hz, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 165.0, 153.7, 136.1, 132.6, 132.3, 129.6, 129.0, 128.7, 128.3 (q, \(J = 32.8\) Hz), 128.0, 127.1, 127.0 (q, \(J = 2.9\) Hz), 126.2, 125.4, 123.9 (q, \(J = 262.0\) Hz), 122.5. 

\[^{19}\]F NMR (376 MHz, CDCl\(_3\)): \(\delta\) –62.7. HRMS (DART) \(m/z\): [M + H]\(^+\) Caled for C\(_{18}\)H\(_{12}\)F\(_3\)O\(_2\): 317.07839; Found 317.07931.

2,3,4,5,6-Pentafluorophenyl 2-naphthoate [CAS: 158407-26-2].

Procedure A. The product was obtained by flash column chromatography on NH\(_2\)-modified silica gel (eluent: CHCl\(_3\), \(R_f = 0.57\) in hexane/EtOAc = 5/1) in 95% yield (5.0393 g, 14.9 mmol) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.81 (s, 1H), 8.16 (dd, \(J = 8.6, 1.8\) Hz, 1H), 8.02 (d, \(J = 8.0\) Hz, 1H), 7.98 (d, \(J = 8.7\) Hz, 1H), 7.94 (d, \(J = 8.2\) Hz, 1H), 7.70-7.66 (m, 1H), 7.64-7.59 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 162.9, 142.9-140.2 (m), 141.1-138.2 (m), 139.5-136.6 (m), 136.3, 133.1, 132.5, 129.7, 129.5, 128.9, 128.0, 127.3, 125.7-125.3 (m), 125.4, 124.1. 

\[^{19}\]F NMR (376 MHz, CDCl\(_3\)): \(\delta\) –152.8 (dt, \(J = 26.4, 4.9\) Hz, 2F), –158.4 (t, \(J = 22.2\) Hz, 1F), –162.8- –162.6 (m, 2F). MS (EI, relative intensity, \%) \(m/z\): 338 (M\(^+\), 1), 155 (100), 127 (81), 126 (12). Anal. Caled for C\(_{17}\)H\(_{17}\)F\(_5\)O\(_2\): C, 60.37; H, 2.09; F, 28.08. Found: C, 60.32; H, 2.14; F, 28.21.

2,6-Dimethylphenyl 2-naphthoate [CAS: 1338458-35-7].

Procedure A. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1 to 5/1, \(R_f = 0.49\) in hexane/EtOAc = 5/1) in 66% yield (1.0749 g, 3.9 mmol) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.84 (s, 1H), 8.24 (dd, \(J = 8.6, 1.7\) Hz, 1H), 8.02 (dd, \(J = 8.0, 0.9\) Hz, 1H), 7.97 (d, \(J = 8.7\) Hz, 1H), 7.93 (d, \(J = 8.2\) Hz, 1H), 7.66-7.57 (c, 2H), 7.15-7.09 (c, 3H), 2.23 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 164.6, 148.5, 135.9, 132.6, 132.0, 130.5, 129.5, 128.74, 128.72, 128.6, 127.9, 127.0, 126.5, 126.0, 125.6, 16.5. HRMS (DART) \(m/z\): [M + H]\(^+\) Caled for C\(_{19}\)H\(_{17}\)O\(_2\): 277.12231; Found 277.12360.

Phenyl 1-naphthoate (1b) [CAS: 36773-67-8].

Procedure A (1 M aq. NaOH was used for washing instead of sat. aq. K\(_2\)CO\(_3\)). The product was obtained by
recrystallization from hexane/EtOAc in 82% (10.7637 g, 43.4 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.04 (d, \(J = 8.7\) Hz, 1H), 8.49 (dd, \(J = 7.3, 1.2\) Hz, 1H), 8.12 (d, \(J = 8.2\) Hz, 1H), 7.94 (dt, \(J = 8.1, 1.2\) Hz, 1H), 7.67-7.63 (m, 1H), 7.60-7.56 (c, 2H), 7.52-7.46 (c, 2H), 7.34-7.28 (c, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.0, 151.1, 134.5, 134.0, 131.8, 131.4, 129.7, 128.8, 128.3, 126.5, 126.1, 126.0, 125.9, 124.7, 122.0. HRMS (DART) \(m/z\): [M + H]\(^+\) Calcd for C\(_{17}\)H\(_{13}\)O\(_2\) 249.09101; Found 249.09171.

Phenyl biphenyl-4-carboxylate (1c) [CAS: 78322-97-1]

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{Ph}
\end{array}
\]

Procedure A (1 M aq. NaOH was used for washing instead of sat. aq. K\(_2\)CO\(_3\)). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1 to 1/1, \(R_f = 0.51\) in hexane/EtOAc = 5/1) in 40% yield (1.8704 g, 6.8 mmol) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.28 (dt, \(J = 8.5, 1.5\) Hz, 2H), 7.74 (dt, \(J = 8.6, 1.9\) Hz, 2H), 7.68-7.65 (m, 2H), 7.52-7.40 (c, 5H), 7.31-7.22 (c, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 165.2, 151.1, 146.4, 140.0, 130.8, 129.7, 129.1, 128.5, 128.4, 127.5, 127.4, 126.0, 121.9. HRMS (DART) \(m/z\): [M + H]\(^+\) Calcd for C\(_{19}\)H\(_{15}\)O\(_2\) 275.10666; Found 275.10760.

Phenyl 3,4-dimethylbenzoate (1d) [CAS: 723256-69-7].

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{Ph}
\end{array}
\]

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1, \(R_f = 0.54\) in hexane/EtOAc = 5/1) in 80% yield (1.1539 g, 5.1 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.28 (dt, \(J = 8.5, 1.5\) Hz, 2H), 7.74 (dt, \(J = 8.6, 1.9\) Hz, 2H), 7.68-7.65 (m, 2H), 7.52-7.40 (c, 5H), 7.31-7.22 (c, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 165.5, 151.2, 143.2, 137.1, 131.2, 130.0, 129.5, 127.9, 127.2, 125.8, 121.9, 20.2, 19.8. HRMS (DART) \(m/z\): [M + H]\(^+\) Calcd for C\(_{15}\)H\(_{13}\)O\(_2\) 227.10666; Found 227.10778.

Phenyl 4-methoxy-2-methylbenzoate (1e).

\[
\begin{array}{c}
\text{MeO} \\
\text{Ph} \\
\text{O}
\end{array}
\]

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1 to 20/1, \(R_f = 0.43\) in hexane/EtOAc = 5/1) in 61% yield (893.8 mg, 3.7 mmol) as a white solid. Further
recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. Mp = 80.2-81.3 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.19-8.17 (m, 1H), 7.44-7.40 (m, 2H), 7.26 (tt, $J = 7.4$, 1.1 Hz, 1H), 7.20-7.17 (m, 2H), 6.83-6.81 (m, 2H), 3.87 (s, 3H), 2.67 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 165.5, 163.0, 151.1, 144.5, 133.8, 129.6, 125.8, 122.1, 120.7, 117.3, 111.3, 55.5, 22.7. IR (ATR, cm$^{-1}$): 3069 w, 1714 m, 1608 s, 1567 m, 1499 m, 1249 s. MS (EI, relative intensity, %) m/z: 242 (0.4, M$^+$), 150 (10), 149 (100), 121 (16), 91 (10). HRMS (DART) m/z: [M + H]$^+$ Calcd for C$_{15}$H$_{15}$O$_3$ 243.10157; Found 243.10247.

Phenyl biphenyl-2-carboxylate (1f) [CAS: 13811-19-3].

![Phenyl biphenyl-2-carboxylate](image)

Procedure B (1 M aq. NaOH was used for washing instead of sat. aq. K$_2$CO$_3$). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1, $R_f$ = 0.43 in hexane/EtOAc = 5/1) in 59% yield (2.441 g, 8.9 mmol) as a white solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.99 (ddd, $J = 7.7$, 1.4, 0.5 Hz, 1H), 7.60 (td, $J = 7.6$, 1.4 Hz, 1H), 7.51-7.36 (c, 7H), 7.32-7.27 (c, 2H), 7.16 (tt, $J = 7.4$, 1.1 Hz, 1H), 6.85-6.83 (c, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 167.4, 150.8, 142.9, 141.4, 131.9, 131.0, 130.6, 130.4, 129.4, 128.7, 128.4, 127.6, 127.5, 125.9, 121.4. HRMS (DART) m/z: [M + H]$^+$ Calcd for C$_{19}$H$_{15}$O$_2$ 275.10666; Found 275.10760.

Phenyl 4-chloro-3-iodobenzoate (1g).

![Phenyl 4-chloro-3-iodobenzoate](image)

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1, $R_f$ = 0.57 in hexane/EtOAc = 5/1) in 87% yield (2.5136 g, 7 mmol) as a white solid. Further purification from hexane/EtOAc was performed to obtain an analytically pure sample. Mp = 85.3-86.5 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.67 (d, $J = 2.0$ Hz, 1H), 8.10 (dd, $J = 8.4$, 2.1 Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.47-7.42 (m, 2H), 7.29 (tt, $J = 7.4$, 1.3 Hz, 1H), 7.22-7.18 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 163.1, 150.7, 144.4, 141.9, 131.0, 130.6, 130.4, 129.4, 128.7, 128.4, 127.6, 127.5, 125.9, 121.4. HRMS (DART) m/z: [M + H]$^+$ Calcd for C$_{13}$H$_9$ClIO$_2$ 275.10666; Found 275.10760.

Phenyl 4-bromo-1-naphthoate (1h).

![Phenyl 4-bromo-1-naphthoate](image)
Procedure B (sat. aq. K₂CO₃ was used for washing instead of 1 M aq. NaOH). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1 to 30/1 to 20/1, Rf = 0.43 in hexane/EtOAc = 5/1) in 72% yield (1.8267 g, 5.6 mmol) as a white solid. Mp = 101.4-102.1 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.09-9.03 (m, 1H), 8.41-8.36 (m, 1H), 8.29 (d, J = 7.9 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.72-7.66 (c, 2H), 7.50-7.45 (m, 2H), 7.34-7.26 (c, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 150.9, 132.8, 132.5, 131.1, 130.1, 129.8, 129.1, 129.0, 128.01, 127.97, 126.3, 126.2, 125.9, 121.9. IR (ATR, cm⁻¹): 3073 w, 1730 s, 1491 m, 1237 s, 1126 s. MS (EI, relative intensity, %) m/z: 328 (2, [M + 2]⁺), 326 (6, M⁺), 236 (12), 235 (94) 234 (13), 233 (100), 207 (23), 205 (24), 127 (12), 126 (90). HRMS (DART) m/z: [M + H]⁺ Calcd for C₁₇H₁₂BrO₃ 327.00152; Found 327.00188.

Diphenyl naphthalene-1,4-dicarboxylate (1i) [CAS: 50863-17-7].

Procedure B. The product was obtained by recrystallization from hexane/EtOAc in 33% (2.8625 g, 7.8 mmol). ¹H NMR (CDCl₃): δ 9.02-8.98 (m, 2H), 8.44 (s, 2H), 7.74-7.69 (m, 2H), 7.53-7.47 (m, 4H), 7.31-7.26 (m, 1H), 7.24-7.20 (m, 2H), 3.28 (s, 1H). ¹³C NMR (CDCl₃): δ 165.5, 150.9, 131.9, 131.4, 129.8, 128.9, 128.5, 126.4, 126.1, 121.9. HRMS (DART) m/z: [M + H]⁺ Calcd for C₂₄H₁₇O₄ 369.11214; Found 369.11273.

Phenyl 4-ethynylbenzoate (1j) [CAS: 144003-07-6].

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1 to 20/1, Rf = 0.49 in hexane/EtOAc = 5/1) and GPC in 35% yield (459.5 mg, 2.1 mmol) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.18-8.15 (m, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.47-7.42 (m, 2H), 7.31-7.26 (m, 4H), 7.24-7.20 (m, 2H), 3.28 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 164.6, 150.9, 132.3, 130.1, 129.7, 129.6, 127.5, 126.1, 121.7, 82.8, 80.7. HRMS (DART) m/z: [M + H]⁺ Calcd for C₁₅H₁₁O₂ 223.07536; Found 223.07640.

Phenyl trans-cinnamate (1k) [CAS: 25695-77-6].

Procedure A (washing with 1 M aq. HCl was skipped). The product was obtained by recrystallization from hexane/EtOAc and GPC in 82% yield (1.9313 g, 8.6 mmol) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.87 (d, J = 16.0 Hz, 1H), 7.62-7.57 (m, 2H), 7.45-7.39 (c, 5H), 7.25 (tt, J = 7.4, 1.1 Hz, 1H), 7.19-7.16 (m, 2H), 6.64 (d, J = 16.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 165.5, 150.9, 146.7, 134.3, 130.8, 129.6, 129.1, 128.4, 125.9, 121.8,
Phenyl quinoline 2-carboxylate (I) [CAS: 145133-85-3].

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1 to 1/1, R_f = 0.20 in hexane/EtOAc = 5/1) in 71% yield (3.0586 g, 12.3 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^1^H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.38 (d, J = 8.5 Hz, 2H), 8.32 (d, J = 8.5 Hz, 1H), 7.93 (dd, J = 8.2, 1.4 Hz, 1H), 7.84 (ddd, J = 8.4, 7.0, 1.4 Hz, 1H), 7.70 (ddd, J = 8.3, 6.7, 1.0 Hz, 1H), 7.50-7.44 (m, 2H), 7.34-7.29 (c, 3H). ^1^C NMR (100 MHz, CDCl\textsubscript{3}): δ 164.3, 151.2, 147.9, 147.5, 137.6, 131.0, 130.6, 129.7, 129.1, 127.7, 126.3, 121.9, 121.6 (one signal is obscured by overlap with another signal). HRMS (DART) m/z: [M + H]^+ Calcd for C\textsubscript{16}H\textsubscript{12}NO\textsubscript{2} 250.08675; Found 250.08722.

Phenyl quinoline 3-carboxylate (1m) [CAS: 1380573-03-4].

Procedure B (washing with 1 M aq. HCl was skipped). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1 to 1/1, R_f = 0.20 in hexane/EtOAc = 5/1) in 20% yield (2.9036 g, 11.6 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^1^H NMR (400 MHz, CDCl\textsubscript{3}): δ 9.60 (d, J = 2.2 Hz, 1H), 9.03 (d, J = 1.7 Hz, 1H), 8.21 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.91-7.87 (m, 1H), 7.70-7.65 (m, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.34-7.27 (c, 3H). ^1^C NMR (100 MHz, CDCl\textsubscript{3}): δ 164.1, 150.7, 150.23, 150.17, 139.6, 132.4, 129.71, 129.65, 129.1, 127.7, 126.3, 121.9, 121.6. HRMS (DART) m/z: [M + H]^+ Calcd for C\textsubscript{16}H\textsubscript{12}NO\textsubscript{2} 250.08626; Found 250.08675.

Phenyl benzofuran-2-carboxylate (1n) [CAS: 92439-07-1].

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1 to 0/1, R_f = 0.49 in hexane/EtOAc = 5/1) in 59% yield (840.1 mg, 3.5 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^1^H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.75-7.73 (c, 2H), 7.65 (dd, J = 8.5, 0.8 Hz, 1H), 7.52-7.43 (c, 3H), 7.37-7.25 (c, 4H). ^1^C NMR (100 MHz, CDCl\textsubscript{3}): δ 158.0, 156.2, 150.3, 144.9, 129.7, 128.2, 127.0, 126.4, 124.1, 123.2, 121.7, 115.6, 112.6. HRMS (DART) m/z: [M + H]^+ Calcd for C\textsubscript{15}H\textsubscript{11}O\textsubscript{3} 239.07027; Found 239.07145.
Phenyl 1-methyl-1\textit{H}-indole-2-carboxylate (1o) [CAS: 1997317-94-8].

![Phenyl 1-methyl-1\textit{H}-indole-2-carboxylate](image)

Procedure B (sat. aq. NH\textsubscript{4}Cl was used for washing instead of 1 M aq. HCl). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1 to 5/1, \( R_f = 0.37 \) in hexane/EtOAc = 5/1) in 87% yield (1.1931 g, 4.7 mmol) as a white solid. \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.74 (d, \( J = 8.0 \) Hz, 1H), 7.56 (s, 1H), 7.47-7.38 (c, 4H), 7.30-7.17 (c, 4H), 4.12 (s, 3H).

\( ^{13}\text{C} \) NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 160.8, 150.7, 140.3, 129.7, 126.9, 126.1, 126.0, 125.7, 123.0, 122.0, 121.0, 111.8, 110.5, 31.8.

HRMS (DART) \( m/z: \) [M + H]\(^+\) Calcd for C\textsubscript{16}H\textsubscript{14}NO\textsubscript{2} 252.10191; Found 252.10265.

Phenyl 6-bromonicotinate (1p).

![Phenyl 6-bromonicotinate](image)

Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1 to 3/1, \( R_f = 0.34 \) in hexane/EtOAc = 5/1) in 73% yield (1.8072 g, 6.5 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. \( \text{Mp} = 93.5-94.5 \) °C. \( ^1\text{H} \) NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 9.14 (dd, \( J = 2.5, 0.7 \) Hz, 1H), 8.28 (dd, \( J = 8.2, 2.5 \) Hz, 1H), 7.67 (dd, \( J = 8.2, 0.7 \) Hz, 1H), 7.48-7.43 (m, 2H), 7.31 (tt, \( J = 7.4, 1.3 \) Hz, 1H), 7.24-7.20 (m, 2H). \( ^{13}\text{C} \) NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 163.4, 152.0, 150.4, 147.7, 139.8, 129.8, 128.4, 126.6, 125.0, 121.6. IR (ATR, cm\textsuperscript{-1}): 3069 w, 1728 s, 1577 m, 1302 s, 1271 s, 1243 s, 1092 s. MS (EI, relative intensity, %) \( m/z: \) 279 (10, [M + 2]\(^+\)), 277 (10, M\(^+\)), 186 (97), 184 (100), 158 (25), 156 (26), 77 (19), 76 (19). HRMS (DART) \( m/z: \) [M + H]\(^+\) Calcd for C\textsubscript{12}H\textsubscript{9}BrNO\textsubscript{2} 277.98112; Found 277.98164.

4. General Procedure for Preparing \textit{O}-Silyl-Protected 2-Aryl-1,1,1,3,3,3-hexafluoroisopropanols

In a glovebox filled with nitrogen, dried CsF (0.5 mg, 0.003 mmol, 1 mol%), Me\textsubscript{3}SiCF\textsubscript{3} (128 mg, 0.9 mmol, 3 equiv), phenyl carboxylate (0.3 mmol, 1 equiv) and 1,4-dioxane (1 mL) were added to a 10 mL-sample vial equipped with a Teflon-sealed screwcap. After stirring the mixture at room temperature for 6 h, the resulting solution was filtered through a pad of silica gel and further eluted with EtOAc. The filtrate was analyzed by GC. The crude mixture was concentrated under reduced pressure, and the resulting mixture was purified by flash column chromatography over silica gel or preparative HPLC.
5. Screening of Reaction Conditions

Table S1  Screening of solvents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>NMR Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,4-dioxane</td>
<td>64* 19*</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>64 36</td>
</tr>
<tr>
<td>3</td>
<td>Et2O</td>
<td>39 53</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>9* 88*</td>
</tr>
<tr>
<td>5</td>
<td>CH2Cl2</td>
<td>5 83</td>
</tr>
<tr>
<td>6</td>
<td>toluene</td>
<td>trace quant</td>
</tr>
</tbody>
</table>

* Isolated yield.

Table S2  Screening of reaction time.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Time</th>
<th>Isolated Yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 h</td>
<td>62 33</td>
</tr>
<tr>
<td>2</td>
<td>3 h</td>
<td>79 12</td>
</tr>
<tr>
<td>3</td>
<td>6 h</td>
<td>98 1</td>
</tr>
</tbody>
</table>
When the reaction of methyl 2-naphthoate (5a) with Me$_3$SiCF$_3$ (3 equiv) was conducted under the optimized condition, methyl silyl ketal derivative 6a was obtained in 87% NMR yield. However, the expected bis-trifluoromethylated alcohol derivative 2a was not formed. This result is consistent with Shreeve’s report,$^1$ in which methyl silyl ketal derivative (e.g. 6a) was initially formed and it was then converted to a trifluoromethyl ketone (e.g. 4a) on the treatment with aqueous acid during the workup. Therefore, we propose that the initial addition of CF$_3^-$ to 5a gave 7a which reacts with Me$_3$SiCF$_3$ to give 6a, rather than elimination of MeO$^-$ to give 4a.
6. Characterization of Products

\{[1,1,3,3,3-Hexafluoro-2-(naphthalen-2-yl)propan-2-yl]oxy\}trimethylsilane (2a).

![Structure diagram for 2a](image)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, Rf = 0.60 in hexane/EtOAc = 5/1) in 98% yield (107.3 mg) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.14 (s, 1H), 7.90-7.85 (m, 3H), 7.71 (d, \(J = 8.8\) Hz, 1H), 7.58-7.51 (m, 2H), 0.26 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 133.8, 132.7, 129.4, 128.9, 128.2, 127.75, 127.5, 126.8, 124.0, 122.9 (q, \(J = 290.0\) Hz), 80.4 (sept, \(J = 29.9\) Hz), 1.5. \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) –73.9. IR (ATR, cm\(^{-1}\)): 3064 w, 2962 w, 1291 s, 1256 s, 1194 s, 1123 s. MS (EI, relative intensity, %) \(m/z\): 367 (11, \([M + 1]^+\)), 366 (50, \(M^+\)), 297 (39), 227 (31), 207 (16), 155 (100), 127 (23). HRMS (DART (−)) \(m/z\): [M – SiMe\(_3\)]\(^+\) Calcd for C\(_{13}\)H\(_{23}\)F\(_3\)O 293.04066; Found 293.03937.

\{[1,1,3,3,3-Hexafluoro-2-(naphthalen-1-yl)propan-2-yl]oxy\}trimethylsilane (2b) [CAS: 848347-41-1].

![Structure diagram for 2b](image)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, Rf = 0.51 in hexane/EtOAc = 5/1) in 82% yield (94.8 mg) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.72 (d, \(J = 8.2\) Hz, 1H), 7.93 (d, \(J = 8.2\) Hz, 1H), 7.89-7.85 (m, 1H), 7.80 (d, \(J = 7.8\) Hz, 1H), 7.55-7.49 (m, 2H), 7.46 (t, \(J = 7.8\) Hz, 1H), 0.03 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 134.9, 132.1, 131.8, 129.4, 127.7, 127.2, 126.3, 125.9, 124.4, 123.5 (q, \(J = 291.6\) Hz), 83.4 (sept, \(J = 29.9\) Hz), 0.9 (one signal is obscured by overlap with another signal). \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) –71.0. MS (EI, relative intensity, %) \(m/z\): 366 (32, \(M^+\)), 297 (23), 257 (27), 255 (16), 235 (26), 227 (16), 207 (26), 188 (16), 177 (26), 156 (12), 155 (100), 127 (20). HRMS (DART (−)) \(m/z\): [M – SiMe\(_3\)]\(^+\) Calcd for C\(_{13}\)H\(_{23}\)F\(_3\)O 293.04066; Found 293.04039.

\{2-[(1,1'-Biphenyl-4-yl)-1,1,3,3,3-hexafluoropropan-2-yl]oxy\}trimethylsilane (2c).

![Structure diagram for 2c](image)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, Rf = 0.60 in hexane/EtOAc = 5/1) in 98% yield (114.0 mg) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.70 (d, \(J = 8.7\) Hz, 2H), 7.66-7.60 (m, 4H), 7.48-7.43 (m, 2H), 7.37 (tt, \(J = 7.3\), 1.4 Hz, 1H), 0.26 (s, 9H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.8, 140.1, 131.0, 129.0, 128.0, 127.8, 127.3, 127.1, 122.9 (q, \(J = 290.0\) Hz), 80.1 (sept, \(J = 30.1\) Hz), 1.5. \(^19\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) –74.1. IR (ATR, cm\(^{-1}\)): 3034 w, 2962 w, 1257 m, 1194 s. MS (EI, relative
The reaction was performed for 24 h. The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, Rf = 0.69 in hexane/EtOAc = 5/1) in 89% yield (91.5 mg) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.37 (s, 1H), 7.35 (d, $J$ = 8.6 Hz, 1H), 7.18 (d, $J$ = 8.0 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 0.22 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.7, 136.7, 129.7, 129.4, 128.3, 124.7, 122.9 (q, $J$ = 289.3 Hz), 80.0 (sept, $J$ = 29.5 Hz), 20.3, 19.6, 1.5. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –74.3. IR (ATR, cm$^{-1}$): 2963 w, 1257 m, 1200 s, 1149 m. MS (EI, relative intensity, %) $m/z$: 344 (6, M$^+$), 275 (31), 233 (100), 234 (12), 205 (47), 185 (38), 133 (91), 105 (13). HRMS (DART (−)) $m/z$: [M – SiMe$_3$]$^+$ Calcd for C$_{17}$H$_{36}$F$_6$O 271.05631; Found 271.05637.

$\{2\text{-}(3,4\text{-Dimethylphenyl})\text{-}1,1,1,3,3,3\text{-hexafluoropropan-2-yl} \text{oxy}\} \text{trimethylsilane (2d).}$

$\{1,1,1,3,3,3\text{-Hexafluoro-2-(4-methoxy-2-methylphenyl)propan-2-yl} \text{oxy}\} \text{trimethylsilane (2e).}$

The reaction was performed for 24 h. The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, Rf = 0.54 in hexane/EtOAc = 5/1) in 71% yield (76.3 mg) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 (d, $J$ = 8.9 Hz, 1H), 6.74-6.71 (m, 2H), 3.81 (s, 3H), 2.54 (s, 3H), 0.20 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.9, 141.0, 129.5 (brt, $J$ = 2.9 Hz), 123.4 (q, $J$ = 291.2 Hz), 122.0, 119.0, 110.8, 82.3 (sept, $J$ = 29.7 Hz), 55.2, 23.1, 1.5. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –72.1. IR (ATR, cm$^{-1}$): 2962 w, 1611 w, 1256 s, 1191 s, 1142 m. MS (EI, relative intensity, %) $m/z$: 360 (8, M$^+$), 291 (35), 149 (100). HRMS (DART (−)) $m/z$: [M – SiMe$_3$]$^+$ Calcd for C$_{17}$H$_{36}$F$_6$O 287.05122; Found 287.05074.

$\{2\text{-}[1,1^\prime\text{-Biphenyl}-2\text{-yl}]\text{-}1,1,1,3,3,3\text{-hexafluoropropan-2-yl} \text{oxy}\} \text{trimethylsilane (2f).}$

The reaction was performed for 24 h. The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc =80/1, Rf = 0.66 in hexane/EtOAc = 5/1) in 45% yield (52.7 mg) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (dd, $J$ = 7.9, 1.3 Hz, 1H), 7.39-7.26 (c, 5H), 7.19-7.16 (m, 2H), 7.03-7.00 (m, 1H), –0.15 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.4, 143.1, 135.0, 129.1, 128.9, 128.6, 128.3 (brt, $J$ = 3.4 Hz), 127.7,
127.0, 126.5, 123.0 (q, \( J = 290.3 \) Hz), 81.9 (sept, \( J = 29.9 \) Hz), 1.3. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta = 71.5 \). IR (ATR, cm\(^{-1}\)): 3062 w, 2961 s, 1252 m, 1193 s, 1148 m. MS (EI, relative intensity, %) \( m/z \): 392 (2, \( M^+ \)), 284 (10), 283 (65), 233 (52), 215 (16), 214 (100), 183 (29). HRMS (DART (−)) \( m/z \): [M − SiMe\(_3\)]\(^{−}\) Calcd for C\(_{15}\)H\(_9\)F\(_6\)O\(_3\) 319.05631; Found 319.05664.

\([\{2-\text{(4-Chloro-3-iodophenyl)}-1,1,3,3,3\text{-hexafluoropropan-2-yl}]\text{oxy}\}\text{trimethylsilane (2g).}\)

![](image1)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, \( R_f = 0.71 \) in hexane/EtOAc = 5/1) in 78% yield (113.7 mg) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.10 \) (d, \( J = 2.1 \) Hz, 1H), 7.58-7.52 (m, 1H), 7.49 (d, \( J = 8.7 \) Hz, 1H), 0.26 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 140.8, 139.4, 132.1, 129.2, 128.2, 122.4 \) (q, \( J = 289.0 \) Hz), 98.1, 79.2 (sept, \( J = 30.6 \) Hz), 1.5. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta = -74.2 \).

\([\{2-\text{(4-Bromonaphthalen-1-yl)}-1,1,3,3,3\text{-hexafluoropropan-2-yl}]\text{oxy}\}\text{trimethylsilane (2h).}\)

![](image2)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, \( R_f = 0.69 \) in hexane/EtOAc = 5/1) in 86% yield (116.3 mg) as a colorless crystal. Mp = 112.5-114.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 8.79 \) (d, \( J = 8.5 \) Hz, 1H), 8.38 (dd, \( J = 8.3, 1.3 \) Hz, 1H), 7.81 (d, \( J = 8.2 \) Hz, 1H), 7.66-7.57 (m, 3H), 0.00 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 133.4, 132.9, 128.8, 128.4, 128.0, 127.4, 127.34, 127.29, 127.1, 123.2 \) (q, \( J = 293.5 \) Hz), 83.2 (sept, \( J = 29.7 \) Hz), 0.9 (one signal is obscured by overlap with another signal). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta = -70.9 \). IR (ATR, cm\(^{-1}\)): 2967 w, 1224 s, 1205 s, 1144 s. MS (EI, relative intensity, %) \( m/z \): 446 (28, [M + 2]^+), 444 (27, M^+), 377 (34), 375 (34), 337 (15), 335 (18), 236 (12), 235 (93), 234 (17), 233 (94), 207 (30), 206 (21), 73 (100). HRMS (DART (−)) \( m/z \): [M − SiMe\(_3\)]\(^{−}\) Calcd for C\(_{13}\)H\(_6\)BrF\(_6\)O 402.88268; Found 402.88351.

1,4-Bis\([\{\text{(trimethylsilyl)}\text{oxy}\}\text{propan-2-yl}]\)naphthalene (2i).

![](image3)

The reaction was performed with Me\(_3\)SiCF\(_3\) (256 mg, 1.8 mmol, 6 equiv) for 24 h. The title compound was obtained
by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, Rf = 0.69 in hexane/EtOAc = 5/1) in 90% yield (163.8 mg) as a white solid. Mp = 110.0-112.1 °C. 1H NMR (400 MHz, CDCl3): δ 8.90-8.85 (m, 2H), 7.80 (s, 2H), 7.59-7.55 (m, 2H), −0.02 (s, 18H). 13C NMR (100 MHz, CDCl3): δ 133.4, 130.2, 128.1, 126.0, 125.8, 123.3 (q, J = 290.6 Hz), 83.4 (sept, J = 29.9 Hz), 0.94. 19F NMR (376 MHz, CDCl3): δ −70.7. IR (ATR, cm⁻¹): 2978 w, 1235 m, 1199 s, 1147 m. MS (EI, relative intensity, %) m/z: 604 (10, M⁺), 499 (24), 403 (14), 401 (10), 394 (12), 393 (50), 77 (32), 73 (100). HRMS (DART (−)) m/z: [M – SiMe₃]⁺ Calcd for C₁₉H₁₉F₁₂O₂Si 531.06552; Found 531.06555.

\[
[(4\{1,1,3,3,3-Hexafluoro-2\}-(trimethylsilyl)oxy\}propan-2-yl)phenyl]ethynyl(trimethylsilane (2j)).
\]

The reaction was performed with Me₃SiCF₃ (220 mg, 1.5 mmol, 5 equiv). The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, Rf = 0.71 in hexane/EtOAc = 5/1) in 90% yield (110.1 mg) as a colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.56 (d, J = 8.7 Hz, 2H), 7.52-7.49 (m, 2H), 0.26 (s, 9H), 0.22 (s, 9H). 13C NMR (100 MHz, CDCl3): δ 132.1, 131.9, 127.2, 125.1, 122.7 (q, J = 289.0 Hz), 104.0, 96.4, 80.0 (sept, J = 29.9 Hz), 1.4, −0.01. 19F NMR (376 MHz, CDCl3): δ −74.1. IR (ATR, cm⁻¹): 2962 w, 1254 m, 1201 s, 1154 m. MS (EI, relative intensity, %) m/z: 412 (22, M⁺), 398 (24), 397 (88), 344 (11), 343 (37), 255 (10), 201 (45), 73 (100). HRMS (DART (−)) m/z: [M – SiMe₃]⁺ Calcd for C₁₉H₁₉F₁₂O₂Si 339.06453; Found 339.06315.

\[(E)-Trimethyl[1,1,1-trifluoro-4-phenyl-2-(trifluoromethyl)but-3-en-2-yl]oxy]silane (2k) [CAS: 247912-50-1].
\]

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 100/1, Rf = 0.60 in hexane/EtOAc = 5/1) in 85% yield (91.1 mg) as a colorless oil. 1H NMR (400 MHz, CDCl3): δ 7.45-7.42 (m, 2H), 7.40-7.31 (c, 3H), 7.01 (d, J = 16.0 Hz, 1H), 6.21 (d, J = 16.0 Hz, 1H), 0.26 (9H). 13C NMR (100 MHz, CDCl3): δ 137.4, 135.0, 129.3, 129.0, 127.3, 122.6 (q, J = 288.5 Hz), 118.3, 78.6 (sept, J = 31.1 Hz), 1.6. 19F NMR (376 MHz, CDCl3): δ −76.2. IR (ATR, cm⁻¹): 2964 w, 1255 m, 1194 s. MS (EI, relative intensity, %) m/z: 342 (7, M⁺), 274 (13), 273 (64), 183 (47), 182 (33), 133 (29), 131 (100), 104 (17), 103 (17). HRMS (DART (−)) m/z: [M – SiMe₃]⁺ Calcd for C₁₉H₁₉F₁₂O 269.04066; Found 269.04000.

\[2\{1,1,3,3,3-Hexafluoro-2\}-(trimethylsilyl)oxy\}propan-2-yl]quinolone (2l).
\]

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1, Rf =
0.49 in hexane/EtOAc = 5/1) in 83% yield (92.3 mg) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.25 (d, $J$ = 8.9 Hz, 1H), 8.20 (dd, $J$ = 8.5, 0.7 Hz, 1H), 7.89 (dd, $J$ = 8.1, 1.3 Hz, 1H), 7.79 (ddd, $J$ = 8.5, 7.0, 1.5 Hz, 1H), 7.75 (d, $J$ = 8.7 Hz, 1H), 7.64 (ddd, $J$ = 8.2, 6.9, 1.2 Hz, 1H), 0.3 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.8, 146.5, 137.3, 130.4, 129.3, 128.2, 128.1, 127.8, 122.7 (q, $J$ = 288.7 Hz), 119.3, 81.5 (brt, $J$ = 2.4 Hz), 2.8. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −74.6. IR (ATR, cm$^{-1}$): 2960 w, 1505 s, 1250 s, 1198 s, 1167 m. MS (EI, relative intensity, %) m/z: 367 (8, M$^+$), 366 (10), 353 (21), 352 (100), 283 (13), 228 (26), 178 (22), 128 (43). HRMS (DART (−)) m/z: [M − SiMe$_3$]$^+$ Calcd for C$_{12}$H$_8$F$_6$NO 294.03591; Found 294.03679.

3-[1,1,1,3,3,3-Hexafluoro-2-[(trimethylsilyl)oxy]propan-2-yl]quinolone (2m).

![Chemical Structure](image)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1, $R_f$ = 0.49 in hexane/EtOAc = 5/1) in 89% yield (96.6 mg) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.16 (d, $J$ = 2.1 Hz, 1H), 8.42 (s, 1H), 8.16 (d, $J$ = 8.5 Hz, 1H), 7.90 (ddd, $J$ = 8.2, 1.1 Hz, 1H), 7.82 (ddd, $J$ = 8.5, 6.9, 1.5 Hz, 1H), 7.63 (ddd, $J$ = 8.1, 7.0, 1.1 Hz, 1H), 0.3 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.5, 148.4, 135.6, 131.2, 129.3, 128.7, 127.6, 126.7, 125.2, 122.6 (q, $J$ = 289.0 Hz), 79.5 (sept, $J$ = 30.8 Hz), 1.4. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −73.5. IR (ATR, cm$^{-1}$): 2963 w, 1494 w, 1294 m, 1194 s, 1152 s. MS (EI, relative intensity, %) m/z: 367 (22, M$^+$), 298 (19), 257 (14), 256 (100), 228 (17), 156 (25), 128 (14). HRMS (DART (−)) m/z: [M − SiMe$_3$]$^+$ Calcd for C$_{12}$H$_8$F$_6$NO 294.03591; Found 294.03596.

2-[1,1,1,3,3,3-Hexafluoro-2-[(trimethylsilyl)oxy]propan-2-yl]-1-methyl-1H-indole (2o).

![Chemical Structure](image)

The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, $R_f$ = 0.60 in hexane/EtOAc = 5/1) in 86% yield (92.0 mg) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.64 (ddd, $J$ = 7.8, 1.3, 0.7 Hz, 1H), 7.55 (ddd, $J$ = 8.3, 1.7, 0.8 Hz, 1H), 7.40 (ddd, $J$ = 8.4, 7.2, 1.3 Hz, 1H), 7.33-7.28 (m, 1H), 7.04 (d, $J$ = 0.4 Hz, 1H), 0.12 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.7, 146.0, 127.2, 126.2, 123.9, 122.16, 122.15 (q, $J$ = 289.3 Hz), 111.8, 109.4, 77.3 (sept, $J$ = 31.4 Hz), 0.9. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ −75.5. IR (ATR, cm$^{-1}$): 2964 w, 1453 w, 1255 s, 1218 s, 1185 s. MS (EI, relative intensity, %) m/z: 356 (24, M$^+$), 341 (21), 287 (37), 246 (12), 245 (100), 217 (33), 145 (73). HRMS (DART (−)) m/z: [M − SiMe$_3$]$^+$ Calcd for C$_{11}$H$_5$F$_6$O$_2$ 283.01992; Found 283.02014.
The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 100/1, Rf = 0.63 in hexane/EtOAc = 5/1) in 67% yield (73.7 mg) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.63 (dd, J = 7.9, 0.7 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.34-7.29 (m, 1H), 7.18-7.14 (m, 1H), 6.81 (s, 1H), 3.94 (s, 3H), 0.16 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 138.9, 127.4, 126.5, 123.6, 122.6 (q, J = 289.8 Hz), 121.6, 120.6, 109.8, 105.5, 79.3 (sept, J = 30.8 Hz), 33.0, 0.9. ¹⁹F NMR (376 MHz, CDCl₃): δ –73.0. IR (ATR, cm⁻¹): 2962 w, 1469 w, 1289 m, 1220 s, 1191 s, 1172 s. MS (EI, relative intensity, %) m/z: 369 (43, M⁺), 300 (32), 258 (13), 159 (11), 158 (100). HRMS (DART) m/z: [M – SiMe₃⁺] Calcd for C₁₂H₈F₆NO 296.05156; Found 296.05169.

2-Bromo-5-{1,1,1,3,3,3-hexafluoro-2-[(trimethylsilyl)oxy]propan-2-yl}pyridine (2p).

The reaction was performed for 24 h. The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1, Rf = 0.54 in hexane/EtOAc = 5/1) in 81% yield (97.1 mg) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 8.64 (d, J = 2.5 Hz, 1H), 7.79-7.75 (m, 1H), 7.57 (dd, J = 8.6, 0.6 Hz, 1H), 0.27 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 144.3, 137.3, 127.84, 127.77, 122.1 (q, J = 297.3 Hz), 79.0 (sept, J = 30.8 Hz) 1.4. ¹⁹F NMR (376 MHz, CDCl₃): δ –74.4. IR (ATR, cm⁻¹): 2964 w, 1459 w, 1256 m, 1201 s, 1154 m, 1092 m. MS (EI, relative intensity, %) m/z: 397 (0.4, [M + 2]⁺), 395 (0.4, M⁺), 286 (58), 284 (62), 258 (10), 256 (10), 208 (12), 206 (14), 205 (28), 77 (100), 73 (30). HRMS (DART) m/z: [M + H]⁺ Calcd for C₁₂H₁₃BrF₆NOSi 395.98485; Found 395.98574.
7. Perfluoroalkylation of 1a Using Other (Perfluoroalkyl)trialkylsilanes

When the reaction of 1a with Et₃SiCF₃ was conducted, a trace amount of the corresponding O-silyl-protected alcohol was obtained along with the recovery of a large amount of starting materials (Scheme S2a). However, the use of 1 equiv of CsF led to the successful trifluoromethylation of 1a to give the O-silyl-protected alcohol and the free alcohol in 34% and 35% isolated yields, respectively. Pentafluoroethylation of 1a was also took place when the stoichiometric amount of CsF was used, though the catalytic condition was ineffective (Scheme S2b). On the other hand, no difluoromethylation of 1a using Me₃SiCF₂H occurred even in the presence of the stoichiometric amount of CsF (Scheme S2c), because of the low reactivity of Me₃SiCF₂H (Fuchikami reported that the difluoromethylation of aldehydes with Me₃CF₂H can be performed at 100 °C, whereas the trifluoromethylation of aldehydes with Me₃SiCF₃ took place at room temperature).
8. Examination of Phenyl Esters of Aliphatic Carboxylic Acids under the Optimized Conditions

![Scheme S3]

The reaction of phenyl 3,3-diphenylpropionate (8a) under the optimized conditions gave the desired O-silyl-protected 2-alkyl-1,1,1,3,3,3-hexafluoroisopropanol 9a and trifluoromethyl ketone 10a in 49% and 33% isolated yields, respectively. We also observed the formation of a silyl enol ether of the trifluoromethyl ketone 11a in the crude mixture by 1H NMR. This result indicates that a competition between the nucleophilic addition of CF\(_3^-\) to 10a and deprotonation of an \(\alpha\)-proton in 10a takes place, which decreases the yield of the desired product 9a. In contrast, the reaction of a phenyl ester without \(\alpha\)-proton, such as phenyl 2-methyl-2-phenoxypropanoate (8b), exclusively afforded the desired O-silyl-protected hexafluoroisopropanol 9b.

9. Large-Scale Preparation of 2a

In a glovebox filled with nitrogen, dried CsF (6.0 mg, 3.9 mmol, 1 mol%), Me₃SiCF₃ (1.3266 g, 9.3 mmol, 2.9 equiv), phenyl 2-naphthoate 1a (803.6 mg, 3.2 mmol, 1 equiv) and 1,4-dioxane (10 mL) were added to a 20 mL two necked flask. After stirring the mixture for 6 h, the crude mixture was filtered through silica gel, further eluted with EtOAc and the resulting solution was concentrated under reduced pressure. The resulting mixture was purified by flash column chromatography over silica gel (eluent: hexane/EtOAc = 80/1). The product was obtained (1.1395 g, 96%) as a colorless oil.

10. Synthesis of 1,1,3,3,3-Hexafluoro-2-(naphthalen-2-yl)propan-2-ol (3a)

The product obtained above, 1,4-dioxane (5 mL) and 1 M NaOH (5 mL) were added to a 200 mL round bottom flask and stirred for 30 min at room temperature. The resulting crude mixture was filtered through silica gel, further eluted with EtOAc and concentrated under reduced pressure. The resulting mixture was purified by flash column chromatography over silica gel (eluent: hexane/EtOAc = 20/1, \(R_f = 0.37\) in hexane/EtOAc = 5/1), followed by bulb-to-bulb distillation (1.4 mmHg, 120 °C). The product 3a (840.2 mg, 88% from 1a) was obtained as a white solid.
1,1,1,3,3,3-Hexafluoro-2-(naphthalen-2-yl)propan-2-ol (3a) [CAS: 4288-11-3]

![Chemical Structure](image)

Mp: 82.0-82.4 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.26 (s, 1H), 7.95-7.88 (c, 3H), 7.76 (d, $J$ = 8.9 Hz, 1H), 7.61-7.54 (m, 2H), 3.46 (s, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 133.9, 132.8, 128.9, 128.7, 127.7, 127.3, 127.0, 126.7, 123.0, 122.9 (q, $J$ = 287.5 Hz), 77.5 (sept, $J$ = 30.2 Hz) (one signal is obscured by overlap with another signal). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –75.8. IR (ATR, cm$^{-1}$): 3312 w, 2924 w, 2853 w, 1263 s, 1202 s, 1156 s. MS (EI, relative intensity, %) $m/z$: 295 (11, [M + 1]$^+$), 294 (74, M$^+$), 226 (11), 225 (84), 155 (57), 128 (100), 127 (37). HRMS (DART (–)) $m/z$: [M – H]$^-$. Calcd for C$_{13}$H$_7$OF$_6$ 293.04066; Found 293.04085.

11. References
12. Copies of $^1$H, $^{13}$C, and $^{19}$F NMR Spectra

$\text{MeO}$

$\text{OPh}$

$\text{1e}$

$X$: parts per Million: Proton

$\text{MeO}$

$\text{OPh}$

$\text{1e}$

$X$: parts per Million: Carbon13
X: parts per Million: Fluorine19

X: parts per Million: Proton
S27

2b

X: parts per Million: Carbon-13

2b

X: parts per Million: Fluorine-19

S27
X: parts per Million: Fluorine

X: parts per Million: Proton
2d

X: parts per Million: Carbon-13

2d

X: parts per Million: Fluorine-19

S30
X: parts per Million: Fluorine 19

X: parts per Million: Proton
X: parts per Million: Fluorine

X: parts per Million: Proton
X: parts per Million: Fluorine19

X: parts per Million: Proton
X: parts per Million: Fluorine

X: parts per Million: Proton

S44
X: parts per Million: Fluorine 19

X: parts per Million: Proton
X: parts per Million: Fluorine 19