Supplementary Information

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

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Contents

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 (δ 0) or $CHCl_3$ (δ 7.26) and chemical shifts in ^{13}C NMR spectra were recorded relative to $CDCl_3$ (δ 77.16). ^{19}F NMR chemical shifts were recorded relative to $CFCl_3$ (δ 0). Data were recorded as follows: chemical shifts in ppm (δ), 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 SHIMDZU 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, λ = 254 nm) and Phenomenex Luna® Silica (5 μm, 210 × 21.2 mm). Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (40–63 μm)).

2. Materials

1,4-Dioxane (super dehydrated) [CAS: 123-91-1] was purchased from FUJIFILM Wako Pure Chemichal 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

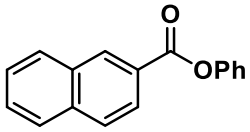
(1) Procedure A: Synthesis of Esters from Acid Chlorides

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_2CO_3, and brine. After drying over Na_2SO_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

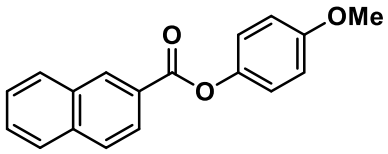
To a round-bottom flask with a magnetic stirring bar, carboxylic acid (1.1 equiv), phenol (1 equiv), DMAP (5 mol %) and EDC·HCl (1.1 equiv) were added, and the resulting mixture was stirred in THF (0.2 M) overnight at room temperature. After the reaction reached completion, saturated aq. $NaHCO_3$ was 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 Na_2SO_4, 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].



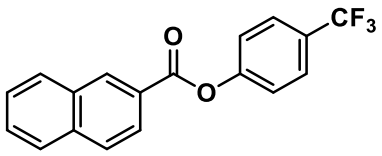
Procedure A (1 M aq. NaOH was used for washing instead of sat. aq. K_2CO_3). The product was obtained by recrystallization from hexane/EtOAc in 66% (2.1952 g, 8.8 mmol) as a colorless crystal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.20 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{17}H_{13}O_2$ 249.09101; Found 249.09143.

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



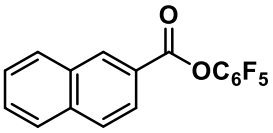
Procedure A. The product was obtained by recrystallization from hexane/EtOAc in 56% (907.7 mg, 3.3 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.19 (dd, *J* = 8.6, 1.6 Hz, 1H), 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{18}H_{15}O_3$ 279.10157; Found 279.10145.

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



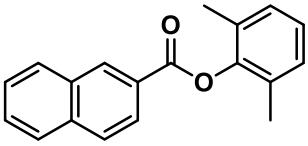
Procedure A. The product was obtained by recrystallization from hexane/EtOAc in 66% (1.0927 g, 3.5 mmol) as a colorless crystal. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.19 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.68-7.58 (c, 2H), 7.41 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ –62.7. HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{12}F_3O_2$ 317.07839; Found 317.07931.

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



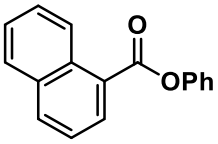
Procedure A. The product was obtained by flash column chromatography on NH_2-modified silica gel (eluent: $CHCl_3$, R_f = 0.57 in hexane/EtOAc = 5/1) in 95% yield (5.0393 g, 14.9 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.16 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.02 (d, *J* = 8.0 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, $CDCl_3$): δ 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, $CDCl_3$): δ –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. Calcd for $C_{17}H_7F_5O_2$: 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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*: $[M + H]^+$ Calcd for $C_{19}H_{17}O_2$ 277.12231; Found 277.12360.

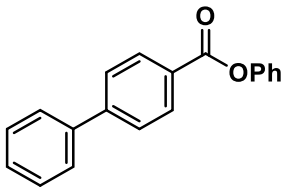
Phenyl 1-naphthoate (1b) [CAS: 36773-67-8].



Procedure A (1 M aq. NaOH was used for washing instead of sat. aq. K_2CO_3). The product was obtained by

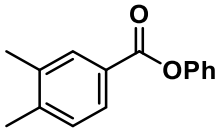
recrystallization from hexane/EtOAc in 82% (10.7637 g, 43.4 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (d, J = 8.7 Hz, 1H), 8.49 (dd, J = 7.3, 1.2 Hz, 1H), 8.12 (d, J = 8.2, 1H), 7.94 (dt, 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). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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]



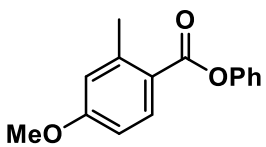
Procedure A (1 M aq. NaOH was used for washing instead of sat. aq. K_2CO_3). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1 to 1/1, R_f = 0.51 in hexane/EtOAc = 5/1) in 40% yield (1.8704 g, 6.8 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (dt, J = 8.5, 1.5 Hz, 2H), 7.74 (dt, J = 8.6, 1.9, 2H), 7.68-7.65 (m, 2H), 7.52-7.40 (c, 5H), 7.31-7.22 (c, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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].



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, $CDCl_3$): δ 7.96 (s, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.43-7.39 (m, 2H), 7.27-7.19 (c, 4H). 2.334 (s, 3H), 2.328 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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 $C_{15}H_{15}O_2$ 227.10666; Found 227.10778.

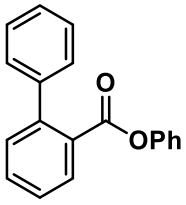
Phenyl 4-methoxy-2-methylbenzoate (1e).



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

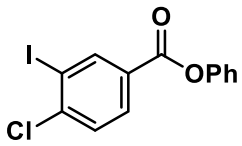
recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. Mp = 80.2-81.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.17 (m, 1H), 7.44-7.40 (m, 2H), 7.26 (tt, *J* = 7.4, 1.1Hz, 1H), 7.20-7.17 (m, 2H), 6.83-6.81 (m, 2H), 3.87 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 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].



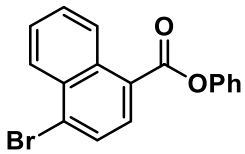
Procedure B (1 M aq. NaOH was used for washing instead of sat. aq. K_2CO_3). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 30/1, R_f = 0.43 in hexane/EtOAc = 5/1) in 59% yield (2.441 g, 8.9 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (ddd, *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).



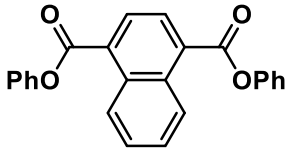
Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1, R_f = 0.57 in hexane/EtOAc = 5/1) in 87% yield (2.5136g, 7 mmol) as a white solid. Further purification from hexane/EtOAc was performed to obtain an analytically pure sample. Mp = 85.3-86.5 °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, 129.7, 129.5, 129.3, 126.4, 121.7, 98.2. IR (ATR, cm^{-1}): 3075 w, 1735 s, 1491 m, 1231 s, 1189 s. MS (EI, relative intensity, %) *m/z*: 360 (3, $[M + 2]^+$), 358 (9, M^+), 267 (32), 265 (100), 237 (17), 110 (25). HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_9ClIO_2$ 358.93303; Found 358.93476.

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



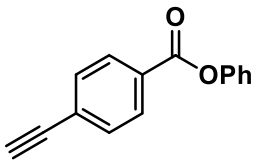
Procedure B (sat. aq. K_2CO_3 was used for washing instead of 1 M aq. NaOH). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1 to 30/1 to 20/1, R_f = 0.43 in hexane/EtOAc = 5/1) in 72% yield (1.8267 g, 5.6 mmol) as a white solid. Mp = 101.4-102.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{17}H_{12}BrO_2$ 327.00152; Found 327.00188.

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



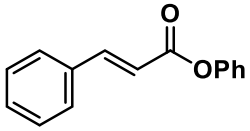
Procedure B. The product was obtained by recrystallization from hexane/EtOAc in 33% (2.8625 g, 7.8 mmol). ^{1}H NMR ($CDCl_3$): δ 9.02-8.98 (m, 2H), 8.44 (s, 2H), 7.74-7.69 (m, 2H), 7.53-7.47 (m, 4H), 7.35-7.31 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 165.5, 150.9, 131.9, 131.4, 129.8, 128.9, 128.5, 126.4, 126.1, 121.9. HRMS (DART) *m*/*z*: $[M + H]^+$ Calcd for $C_{24}H_{17}O_4$ 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, R_f = 0.49 in hexane/EtOAc = 5/1) and GPC in 35% yield (459.5 mg, 2.1 mmol) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 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, 1H), 7.24-7.20 (m, 2H), 3.28 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{15}H_{11}O_2$ 223.07536; Found 223.07640.

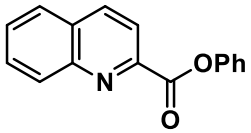
Phenyl *trans*-cinnamate (1k) [CAS: 25695-77-6].



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. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 150.9, 146.7, 134.3, 130.8, 129.6, 129.1, 128.4, 125.9, 121.8,

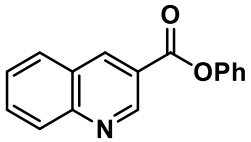
117.4. HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}O_2$ 225.09101; Found 225.09151.

Phenyl quinoline 2-carboxylate (1l) [CAS: 145133-85-3].



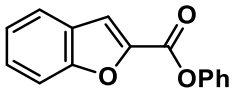
Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1 to 1/1, R_f = 0.20 in hexane/EtOAc = 5/1) in 71% yield (3.0586 g, 12.3 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{16}H_{12}NO_2$ 250.08626; Found 250.08675.

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



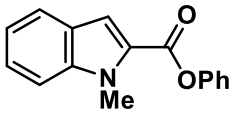
Procedure B (washing with 1 M aq. HCl was skipped). The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1 to 1/1, R_f = 0.20 in hexane/EtOAc = 5/1) in 20% yield (2.9036 g, 11.6 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 150.7, 150.23, 150.17, 139.6, 132.4, 129.71, 129.65, 129.3, 127.7, 126.9, 126.3, 122.5, 121.7. HRMS (DART) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{12}NO_2$ 250.08626; Found 250.08722.

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



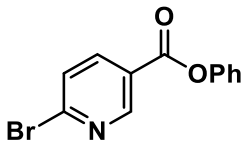
Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1 to 0/1, R_f = 0.49 in hexane/EtOAc = 5/1) in 59% yield (840.1 mg, 3.5 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{15}H_{11}O_3$ 239.07027; Found 239.07145.

Phenyl 1-methyl-1*H*-indole-2-carboxylate (1o) [CAS: 1997317-94-8].



Procedure B (sat. aq. NH_4Cl 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}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$): δ 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 $C_{16}H_{14}NO_2$ 252.10191; Found 252.10265.

Phenyl 6-bromonicotinate (1p).

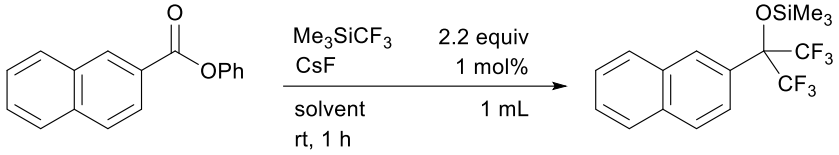


Procedure B. The product was isolated by flash column chromatography on silica gel (eluent: hexane/EtOAc = 5/1 to 3/1, R_f = 0.34 in hexane/EtOAc = 5/1) in 73% yield (1.8072 g, 6.5 mmol) as a white solid. Further recrystallization from hexane/EtOAc was performed to obtain an analytically pure sample. Mp = 93.5-94.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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}C NMR (100 MHz, $CDCl_3$): δ 163.4, 152.0, 150.4, 147.7, 139.8, 129.8, 128.4, 126.6, 125.0, 121.6. IR (ATR, cm^{-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 $C_{12}H_9BrNO_2$ 277.98112; Found 277.98164.

4. General Procedure for Preparing *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_3SiCF_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

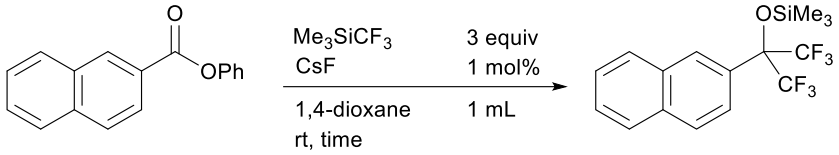


1a 0.3 mmol **2a**

Entry	Solvent	NMR Yields (%)	
		2a	**1a**
1	1,4-dioxane	64[a]	19[a]
2	THF	64	36
3	Et_2O	39	53
4	DMF	9[a]	88[a]
5	CH_2Cl_2	5	83
6	toluene	trace	quant

[a] Isolated yield.

Table S1 Screening of solvents.



1a 0.3 mmol **2a**

Entry	Time	Isolated Yields (%)	
		2a	**1a**
1	1 h	62	33
2	3 h	79	12
3	6 h	98	1

Table S2 Screening of reaction time.

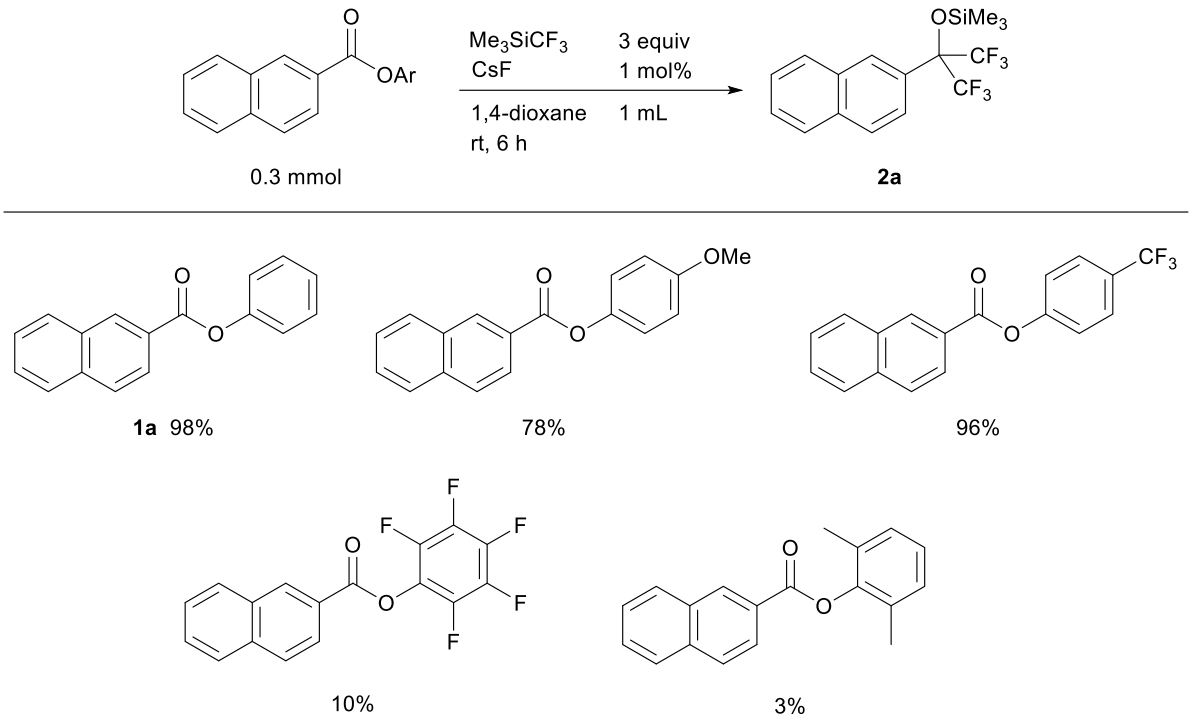
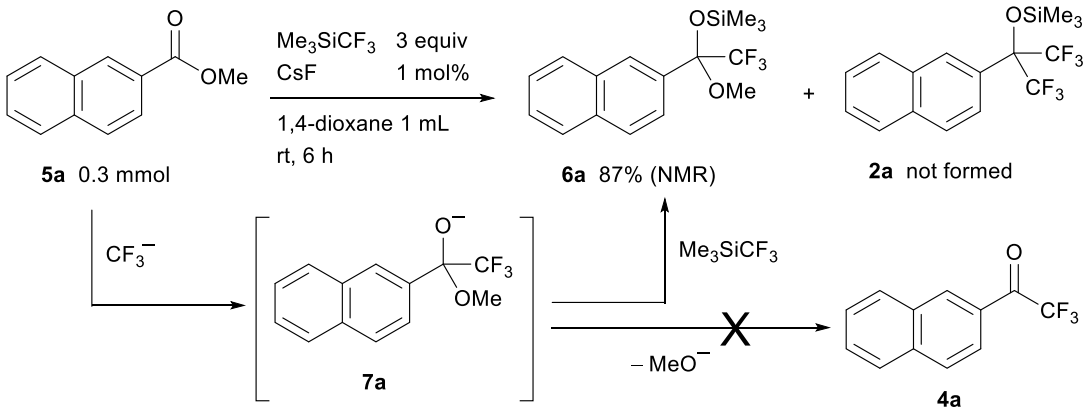


Table S3 Screening of leaving groups.

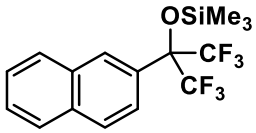


Scheme S1 Bis-trifluromethylation of methyl 2-naphthoate under the optimized condition.

When the reaction of methyl 2-naphthoate (**5a**) with Me_3SiCF_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_3SiCF_3 to give **6a**, rather than elimination of MeO^- to give **4a**.

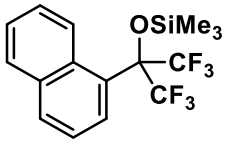
6. Characterization of Products

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



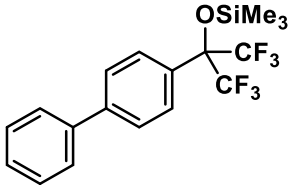
The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, R_f = 0.60 in hexane/EtOAc = 5/1) in 98% yield (107.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.90-7.85 (m, 3H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.58-7.51 (m, 2H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 132.7, 129.4, 128.9, 128.2, 127.75, 127.67, 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, $CDCl_3$): δ –73.9. IR (ATR, cm^{-1}): 3064 w, 2962 w, 1291 s, 1256 s, 1192 s, 1147 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 $C_{13}H_7F_6O$ 293.04066; Found 293.03937.

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



The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, R_f = 0.51 in hexane/EtOAc = 5/1) in 82% yield (94.8 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ –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 $C_{13}H_7F_6O$ 293.04066; Found 293.04039.

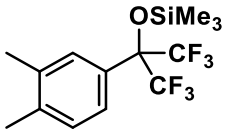
{2-[(1,1'-Biphenyl-4-yl)-1,1,1,3,3,3-hexafluoropropan-2-yl]oxy}trimethylsilane (2c).



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 98% yield (114.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ –74.1. IR (ATR, cm^{-1}): 3034 w, 2962 w, 1257 m, 1194 s. MS (EI, relative

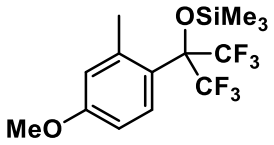
intensity, %) *m*/*z*: 392 (4, M^+), 284 (10), 283 (63), 233 (53), 215 (15), 214 (100), 183 (29), 165 (11). HRMS (DART (–)) *m*/*z*: $[M - SiMe_3]^-$ Calcd for $C_{15}H_9F_6O$ 319.05631; Found 319.05735.

{[2-(3,4-Dimethylphenyl)-1,1,1,3,3,3-hexafluoropropan-2-yl]oxy}trimethylsilane (2d).



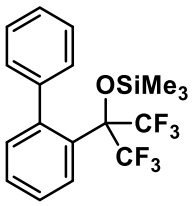
The reaction was performed for 24 h. The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, R_f = 0.69 in hexane/EtOAc = 5/1) in 89% yield (91.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 3H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ –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 $C_{11}H_9F_6O$ 271.05631; Found 271.05637.

{[1,1,1,3,3,3-Hexafluoro-2-(4-methoxy-2-methylphenyl)propan-2-yl]oxy}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, R_f = 0.54 in hexane/EtOAc = 5/1) in 71% yield (76.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ –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 $C_{11}H_9F_6O_2$ 287.05122; Found 287.05074.

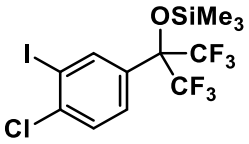
({2-[(1,1'-Biphenyl)-2-yl]-1,1,1,3,3,3-hexafluoropropan-2-yl}oxy)trimethylsilane (2f).



The reaction was performed for 24 h. The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc =80/1, R_f = 0.66 in hexane/EtOAc = 5/1) in 45% yield (52.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 144.4, 143.1, 135.0, 129.1, 128.9, 128.6, 128.3 (brt, *J* = 3.4 Hz), 127.7,

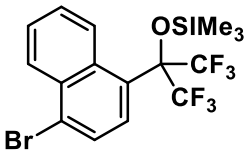
127.0, 126.5, 123.0 (q, J = 290.3 Hz), 81.9 (sept, J = 29.9 Hz), 1.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –71.5. IR (ATR, cm^{-1}): 3062 w, 2961 s, 1252 m, 1193 s, 1148 m. MS (EI, relative intensity, %) *m*/*z*: 392 (2, M^+), 284 (10), 283 (65), 233 (52), 215 (16), 214 (100), 183 (29). HRMS (DART (–)) *m*/*z*: $[M - SiMe_3]^-$ Calcd for $C_{15}H_9F_6O$ 319.05631; Found 319.05664.

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



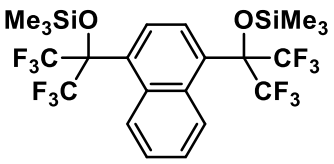
The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, R_f = 0.71 in hexane/EtOAc = 5/1) in 78% yield (113.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 2.1 Hz, 1H), 7.58-7.52 (m, 1H), 7.49 (d, J = 8.7 Hz, 1H), 0.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ –74.2. IR (ATR, cm^{-1}): 2961 w, 1296 m, 1257 s, 1197 s, 1150 s. MS (EI, relative intensity, %) *m*/*z*: 478 (5, $[M + 2]^+$), 476 (12, M^+), 365 (27), 240 (32), 238 (100). HRMS (DART (–)) *m*/*z*: $[M - SiMe_3]^-$ Calcd for $C_9H_3ClF_6IO$ 402.88268; Found 402.88351.

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



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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ –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 $C_{13}H_6BrF_6O$ 370.95117; Found 370.09297.

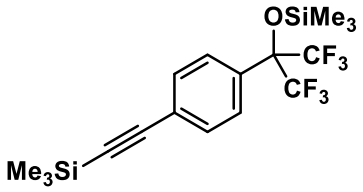
1,4-Bis{1,1,1,3,3,3-hexafluoro-2-[(trimethylsilyl)oxy]propan-2-yl}naphthalene (2i).



The reaction was performed with Me_3SiCF_3 (256 mg, 1.8 mmol, 6 equiv) for 24 h. The title compound was obtained

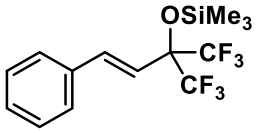
by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, R_f = 0.69 in hexane/EtOAc = 5/1) in 90% yield (163.8 mg) as a white solid. Mp = 110.0-112.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90-8.85 (m, 2H), 7.80 (s, 2H), 7.59-7.55 (m, 2H), –0.02 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 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. ^{19}F NMR (376 MHz, $CDCl_3$): 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*: $[M – SiMe_3]^-$ Calcd for $C_{19}H_{15}F_{12}O_2Si$ 531.06552; Found 531.06555.

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



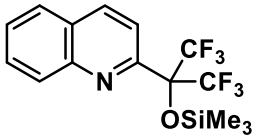
The reaction was performed with Me_3SiCF_3 (220 mg, 1.5 mmol, 5 equiv). The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 80/1, R_f = 0.71 in hexane/EtOAc = 5/1) in 90% yield (110.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.7 Hz, 2H), 7.52-7.49 (m, 2H), 0.26 (s, 9H), 0.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 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. ^{19}F NMR (376 MHz, $CDCl_3$): 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*: $[M – SiMe_3]^-$ Calcd for $C_{14}H_{13}F_6OSi$ 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, R_f = 0.60 in hexane/EtOAc = 5/1) in 85% yield (91.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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. ^{19}F NMR (376 MHz, $CDCl_3$): 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*: $[M – SiMe_3]^-$ Calcd for $C_{11}H_7F_6O$ 269.04066; Found 269.04000.

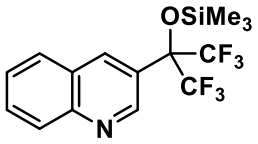
2-{1,1,1,3,3,3-Hexafluoro-2-[(trimethylsilyl)oxy]propan-2-yl}quinolone (2l).



The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 10/1, R_f =

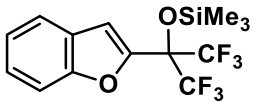
0.49 in hexane/EtOAc = 5/1) in 83% yield (92.3 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.9 Hz, 1H), 8.20 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.79 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.64 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 0.3 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ –74.6. IR (ATR, cm^{-1}): 2960 w, 1505 w, 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 $C_{12}H_6F_6NO$ 294.03591; Found 294.03679.

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



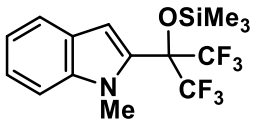
The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 20/1, R_f = 0.49 in hexane/EtOAc = 5/1) in 89% yield (96.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (d, *J* = 2.1 Hz, 1H), 8.42 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.90 (dd, *J* = 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, $CDCl_3$): δ 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, $CDCl_3$): δ –73.5. IR (ATR, cm^{-1}): 2963 w, 1494 w, 1294 m, 1259 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 $C_{12}H_6F_6NO$ 294.03591; Found 294.03596.

{[2-(Benzofuran-2-yl)-1,1,1,3,3,3-hexafluoropropan-2-yl]oxy}trimethylsilane (2n).



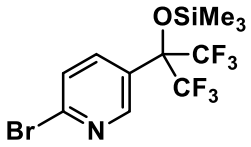
The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 50/1, R_f = 0.60 in hexane/EtOAc = 5/1) in 86% yield (92.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.55 (ddd, *J* = 8.3, 1.7, 0.8 Hz, 1H), 7.40 (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, $CDCl_3$): δ 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, $CDCl_3$): δ –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 $C_{11}H_5F_6O_2$ 283.01992; Found 283.02014.

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



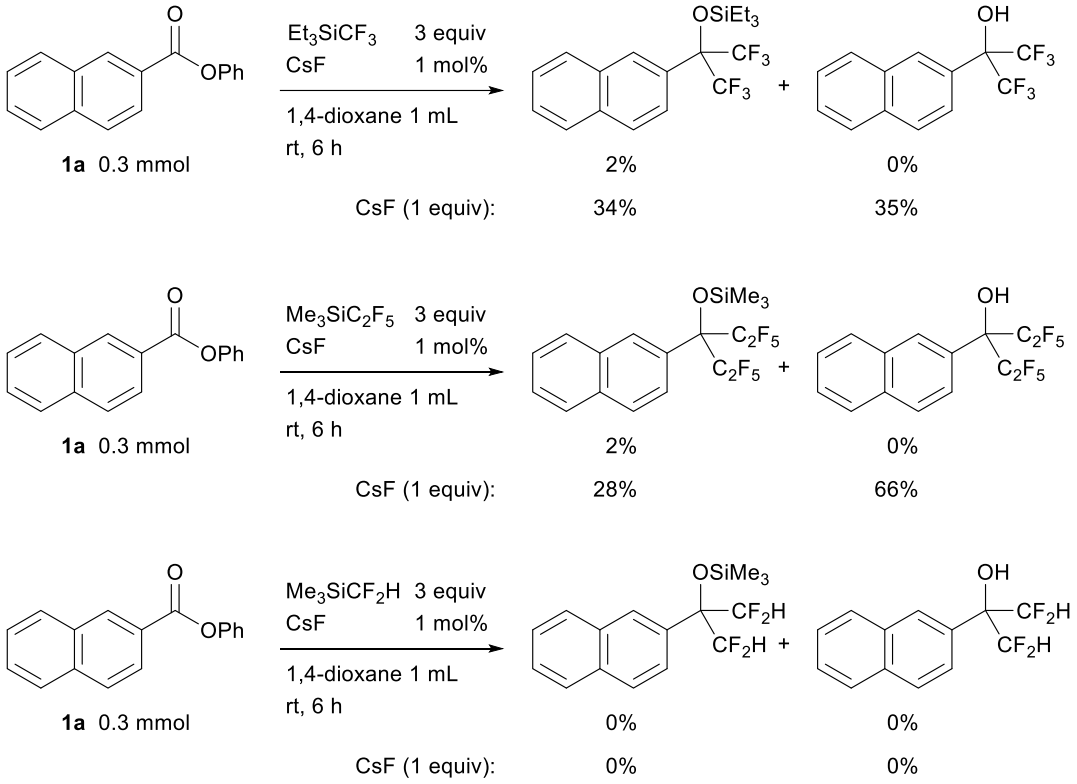
The title compound was obtained by flash column chromatography on silica gel (eluent: hexane/EtOAc = 100/1 , R_f = 0.63 in hexane/EtOAc = 5/1) in 67% yield (73.7 mg) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.34-7.29 (m, 1H), 7.18-7.14 (m, 1H), 6.81 (s, 1H), 3.94 (s, 3H), 0.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 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. ^{19}F NMR (376 MHz, $CDCl_3$): 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*: $[M - SiMe_3]^-$ Calcd for $C_{12}H_8F_6NO$ 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, R_f = 0.54 in hexane/EtOAc = 5/1) in 81% yield (97.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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. ^{19}F NMR (376 MHz, $CDCl_3$): 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 $C_{11}H_{13}BrF_6NOSi$ 395.98485; Found 395.98574.

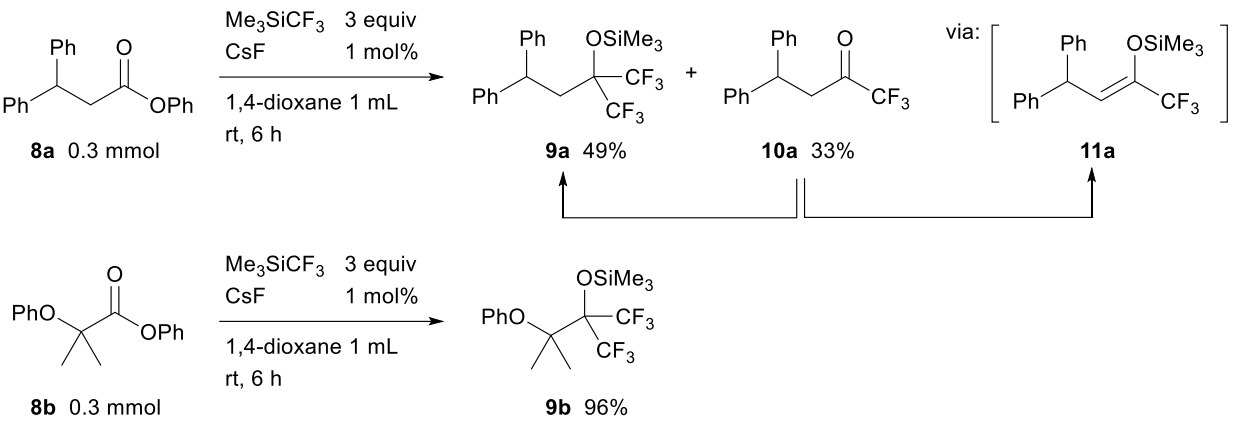
7. Perfluoroalkylation of 1a Using Other (Perfluoroalkyl)trialkylsilanes



Scheme S2 The reaction of phenyl 2-naphthoate **1a** with other (perfluoroalkyl)trialkylsilanes.

When the reaction of **1a** with Et_3SiCF_3 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 Me_3SiCF_2H occurred even in the presence of the stoichiometric amount of CsF (Scheme S2c), because of the low reactivity of Me_3SiCF_2H (Fuchikami reported that the difluoromethylation of aldehydes with Me_3CF_2H can be performed at 100 °C,[2] whereas the trifluoromethylation of aldehydes with Me_3SiCF_3 took place at room temperature[3]).

8. Examination of Phenyl Esters of Aliphatic Carboxylic Acids under the Optimized Conditions



Scheme S3 Bis-trifluoromethylation of phenyl esters of aliphatic carboxylic acids under the optimized conditions.

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 ^{1}H NMR. This result indicates that a competition between the nucleophilic addition of CF_3^- to **10a** and deprotonation of an α-proton in **10a** takes place, which decreases the yield of the desired product **9a**. In contrast, the reaction of a phenyl ester without α-proton, such as phenyl 2-methyl-2-phenoxypropanoate (**8b**), exclusively afforded the desired *O*-silyl-protected hexafluoroisopropanol **9b**.

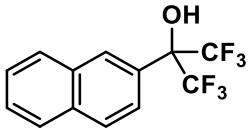
9. Large-Scale Preparation of 2a

In a glovebox filled with nitrogen, dried CsF (6.0 mg, 3.9 mmol, 1 mol%), Me_3SiCF_3 (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 1,1,1,3,3,3-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].



Mp: 82.0-82.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ –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 $C_{13}H_7OF_6$ 293.04066; Found 293.04085.

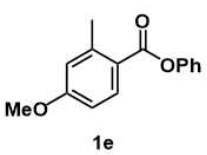
11. References

1 R. P. Singh, G. Cao, R. L. Kirchmeier and J. M. Shreeve, *J. Org. Chem.*, **1999**, *64*, 2873.

2 T. Hagiwara and T. Fuchikami, *Synlett*, **1995**, 717.

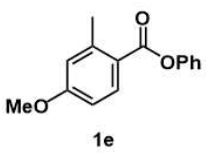
3 G. K. S. Prakash, R. Krishnamurti and G. A. Olah, *J. Am. Chem. Soc.*, **1989**, *111*, 393.

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



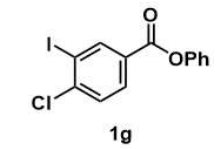
1e

X : parts per Million : Proton



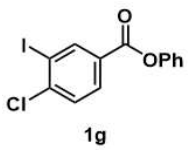
1e

X : parts per Million : Carbon13



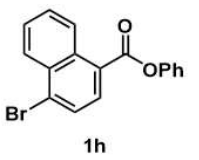
1g

X : parts per Million : Proton



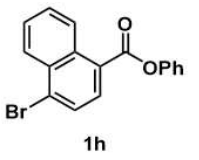
1g

X : parts per Million : Carbon13



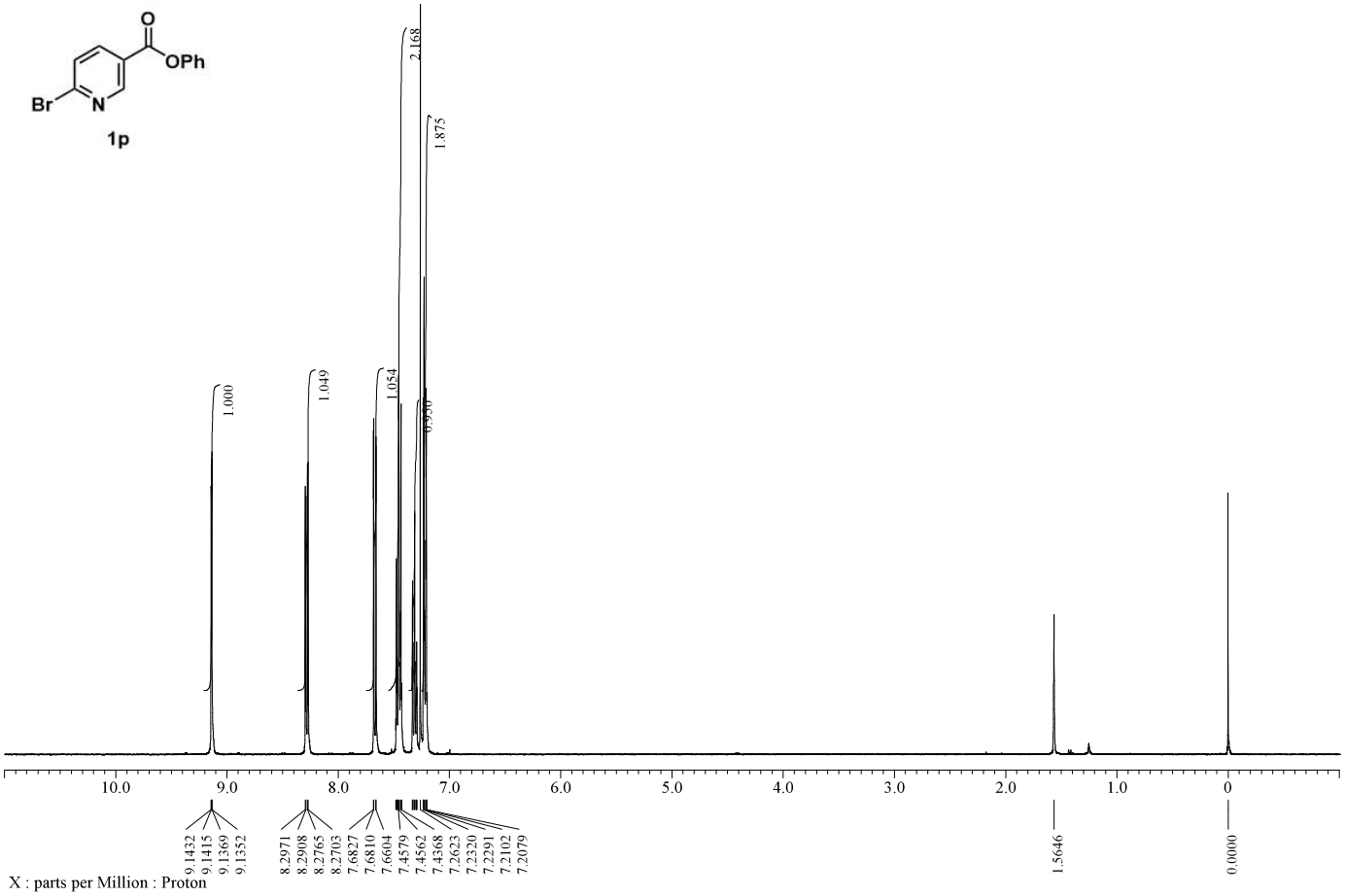
1h

X : parts per Million : Proton

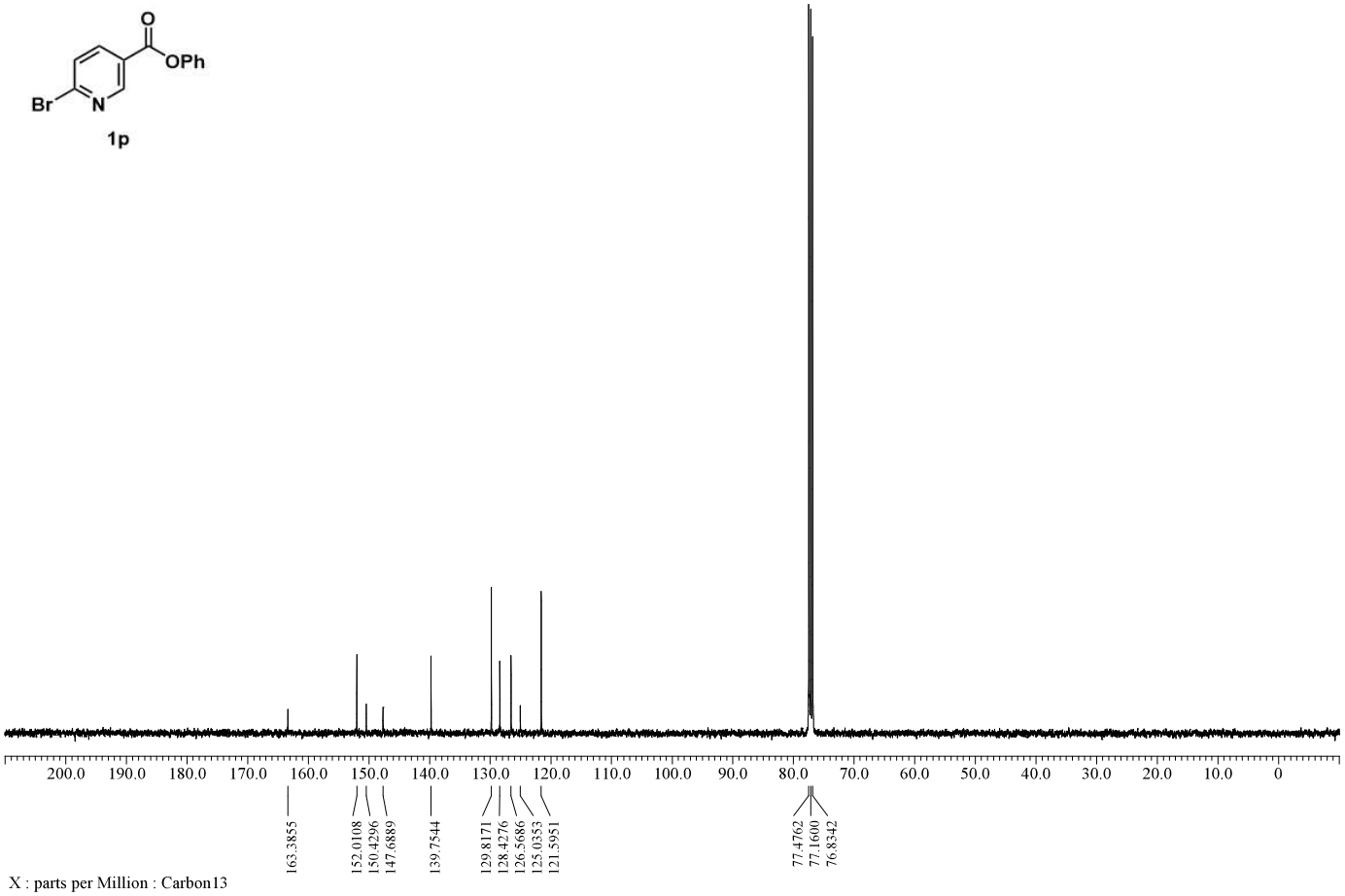


1h

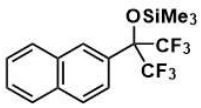
X : parts per Million : Carbon13



X : parts per Million : Proton

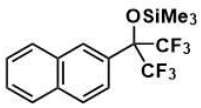


X : parts per Million : Carbon13



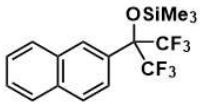
2a

X : parts per Million : Proton



2a

X : parts per Million : Carbon13



2a

X : parts per Million : Fluorine19

2b

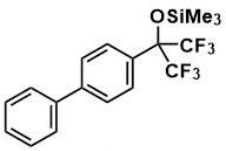
X : parts per Million : Proton

2b

X : parts per Million : Carbon13

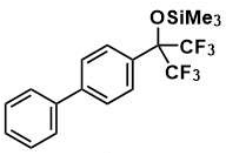
2b

X : parts per Million : Fluorine19



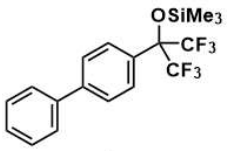
2c

X : parts per Million : Proton



2c

X : parts per Million : Carbon13

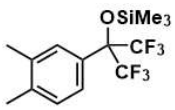


2c

X : parts per Million : Fluorine19

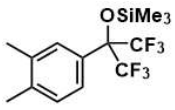
2d

X : parts per Million : Proton



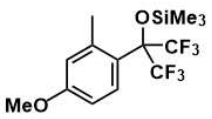
2d

X : parts per Million : Carbon13



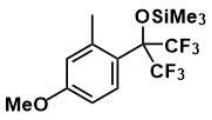
2d

X : parts per Million : Fluorine19



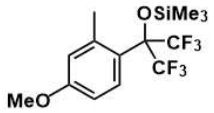
2e

X : parts per Million : Proton



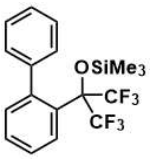
2e

X : parts per Million : Carbon13



2e

X : parts per Million : Fluorine19



2f

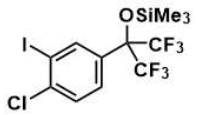
X : parts per Million : Proton

2f

X : parts per Million : Carbon13

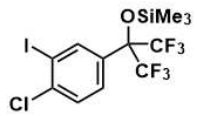
2f

X : parts per Million : Fluorine19



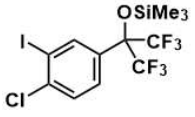
2g

X : parts per Million : Proton



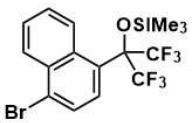
2g

X : parts per Million : Carbon13



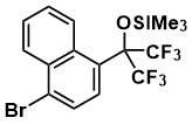
2g

X : parts per Million : Fluorine19



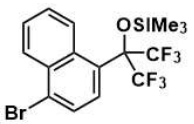
2h

X : parts per Million : Proton



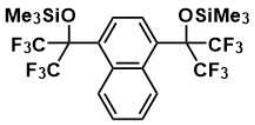
2h

X : parts per Million : Carbon13



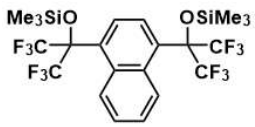
2h

X : parts per Million : Fluorine19



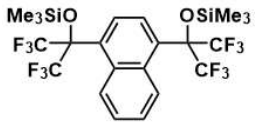
2i

X : parts per Million : Proton



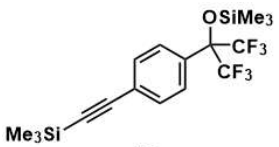
2i

X : parts per Million : Carbon13



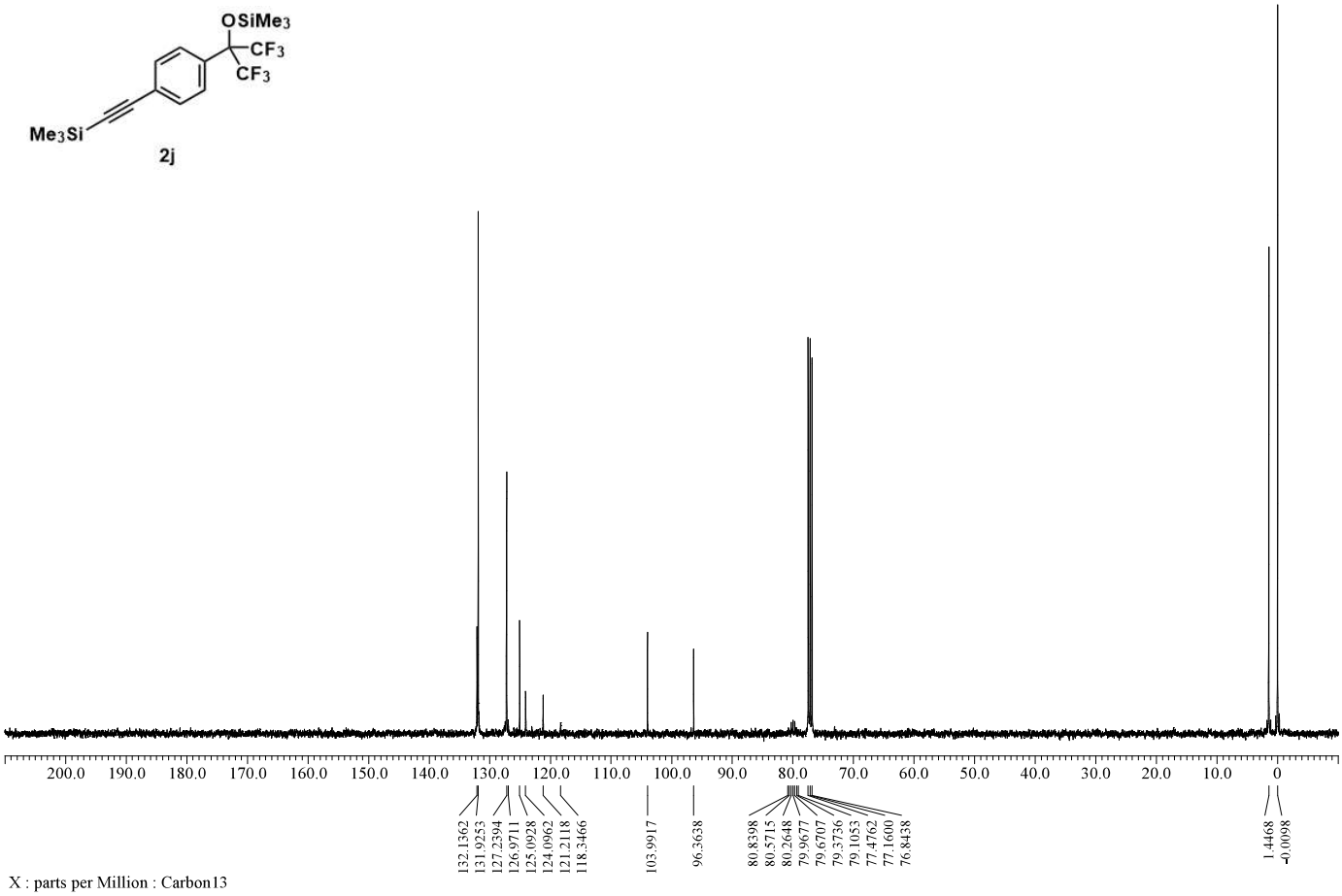
2i

X : parts per Million : Fluorine19

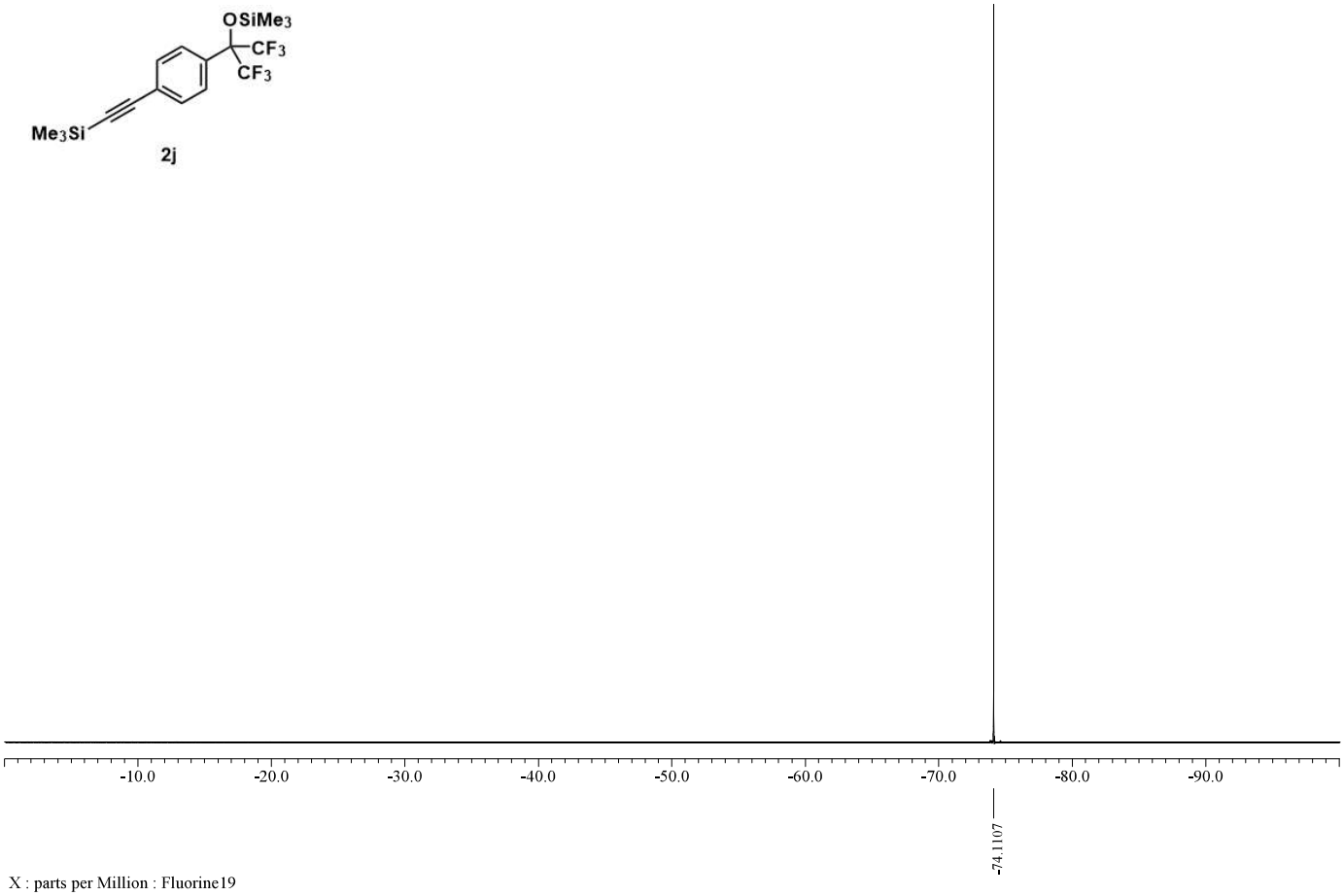


2j

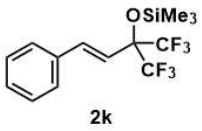
X : parts per Million : Proton



X : parts per Million : Carbon13

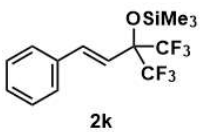


X : parts per Million : Fluorine19



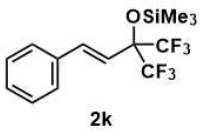
2k

X : parts per Million : Proton



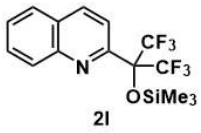
2k

X : parts per Million : Carbon13



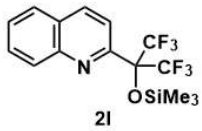
2k

X : parts per Million : Fluorine19



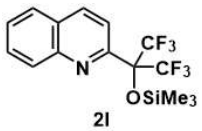
2l

X : parts per Million : Proton



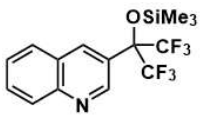
2l

X : parts per Million : Carbon13



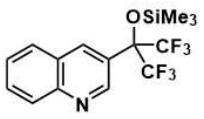
2l

X : parts per Million : Fluorine19



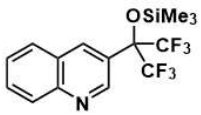
2m

X : parts per Million : Proton



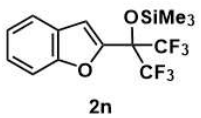
2m

X : parts per Million : Carbon13



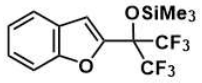
2m

X : parts per Million : Fluorine19



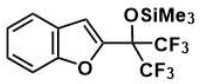
2n

X : parts per Million : Proton



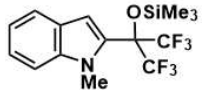
2n

X : parts per Million : Carbon13



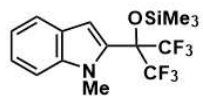
2n

X : parts per Million : Fluorine19



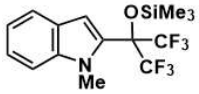
2o

X : parts per Million : Proton



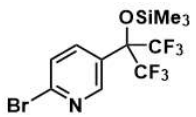
2o

X : parts per Million : Carbon13



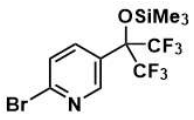
2o

X : parts per Million : Fluorine19



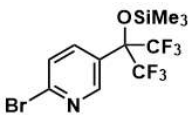
2p

X : parts per Million : Proton



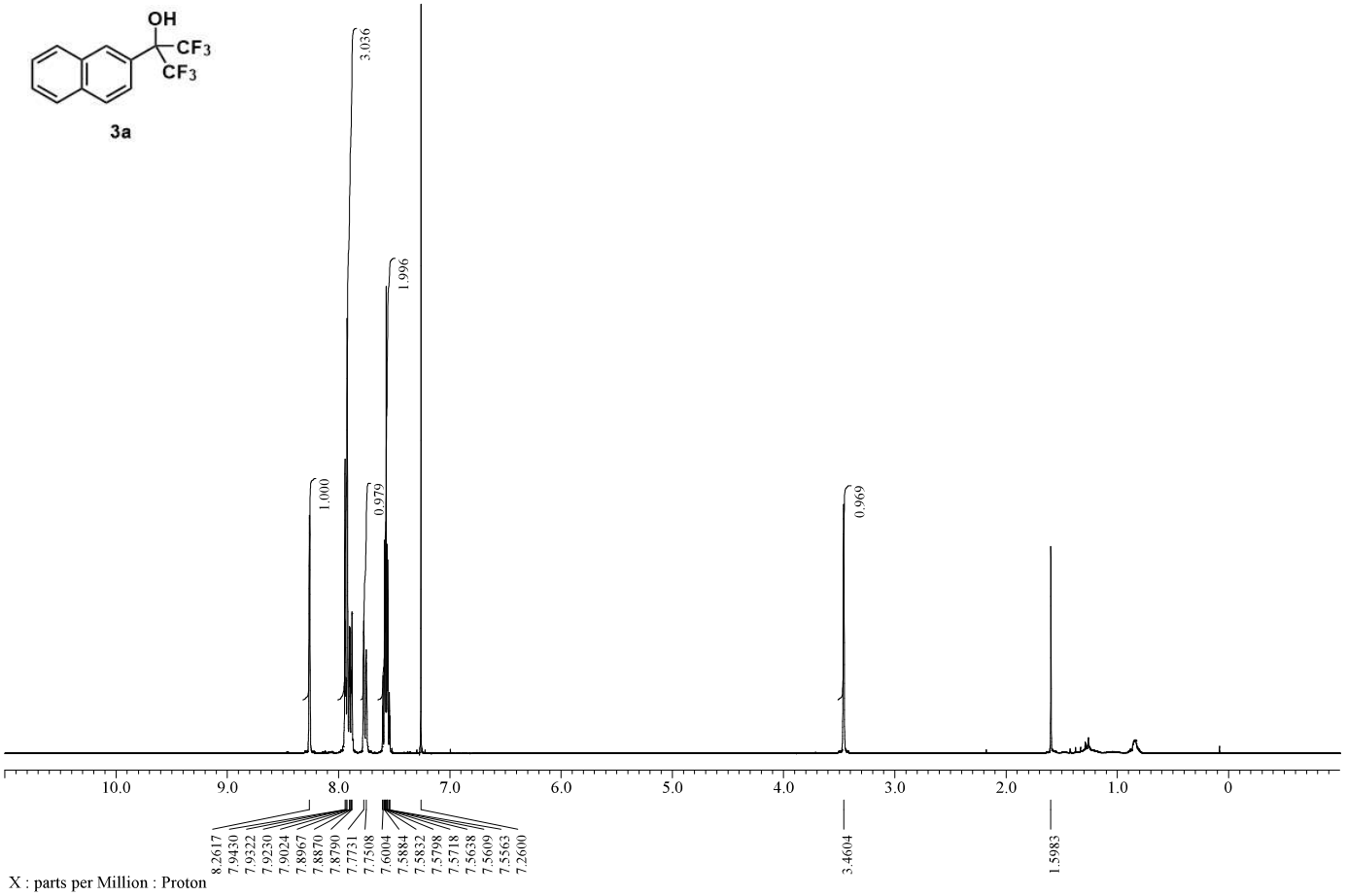
2p

X : parts per Million : Carbon13

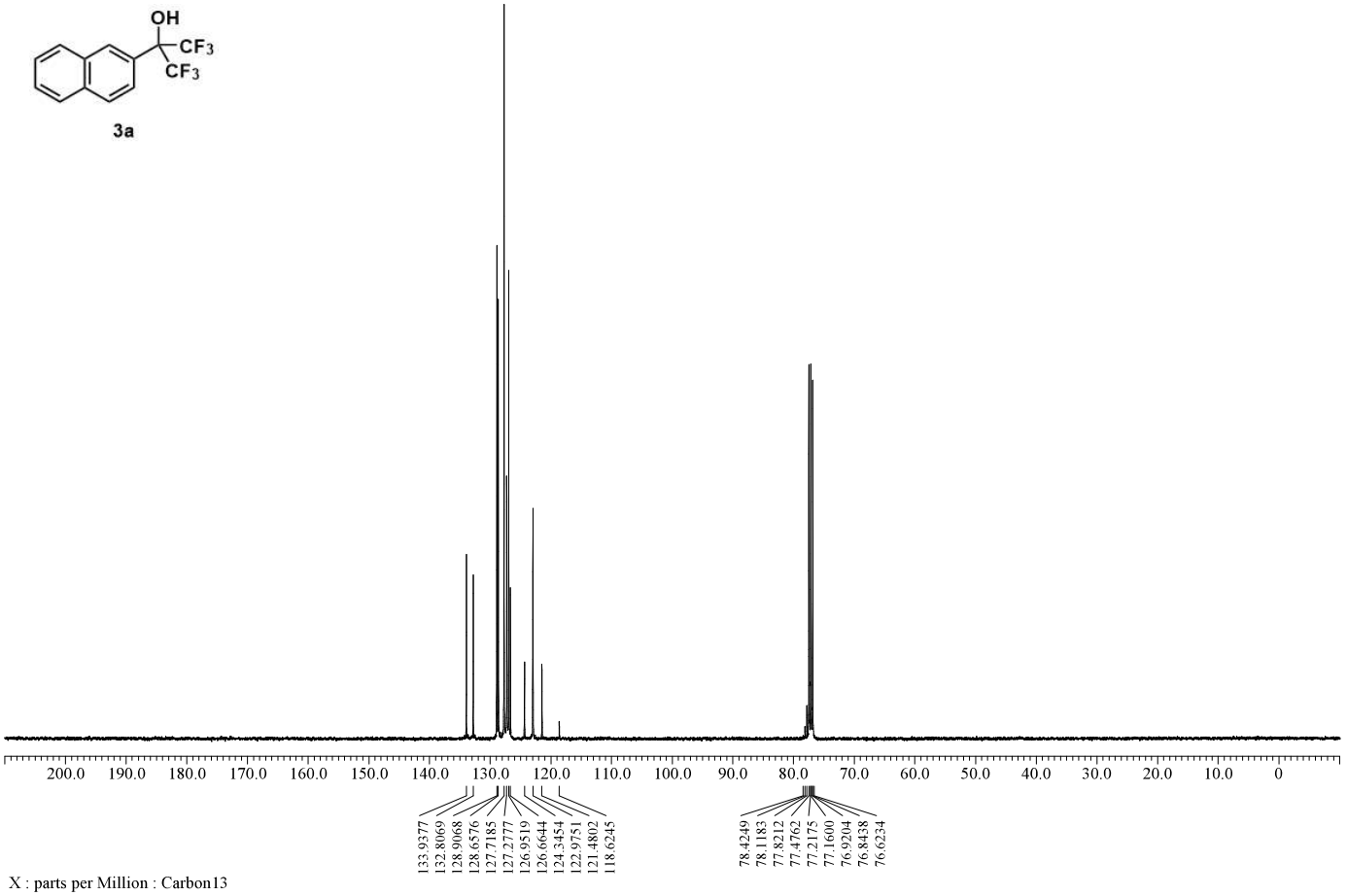


2p

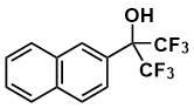
X : parts per Million : Fluorine19



X : parts per Million : Proton



X : parts per Million : Carbon13



3a

X : parts per Million : Fluorine19