Supporting Information
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New Electrophilic Bromodifluoromethylation and Pentafluoroethylolation Reagents

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Supporting information

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General

Unless otherwise stated, NMR spectra were recorded in deuterated chloroform at 300 MHz (1H NMR) and 282 MHz (19F NMR). 13C NMR spectra were recorded at 100 MHz in CDCl3. All chemical shifts were reported in ppm relative to TMS and CFCl3 (positive for downfield shifts) as external standards. Benzene and dichloromethane were distilled from CaH2 before use. All starting fluoroalkylsulfinate salts were prepared by using the known procedures.14

Typical procedure for the preparation of 1a-d

Under nitrogen atmosphere, benzene (7.5 mL, 84.0 mmol) and trifluoromethanesulfonic anhydride (6.0 mL, 35.5 mmol) were added into a suspension of sodium pentafluoroethanesulfinate14 (3.18 g, 15.4 mmol) in dichloromethane (5 mL), which was well cooled by ice-bath. After vigorously stirring at 0 °C for 2 h, the reaction mixture was warmed to room temperature and continued to react for 4 days. Then the reaction mixture was diluted with CH2Cl2 (60 mL) and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane / acetonitrile (4:1) as the eluent. After recrystallization from pentane/ethyl acetate, 1.40 g of 1b (20%) was obtained as a white solid. 1H NMR (300 MHz, CDCl3): δ 7.84 (t, J = 7.7 Hz, 2H), 7.95 (t, J = 8.2 Hz, 1H), 8.34 (d, J = 8.2 Hz, 2H). 19F NMR (282 MHz, CDCl3): δ -94.5 (s, 2F), -75.7 (s, 3F), -76.8 (s, 3F). 13C NMR (100 MHz, CDCl3): δ 137.4, 133.9, 132.3. IR (KBr): 3067, 1477, 1455, 1311, 1288, 1254, 1234, 1160, 1128, 1031, 938, 757, 639, 517, 504 cm-1. Anal. Calcd for C15H10F8O3S2: C, 39.65; H, 2.22. Found: C, 39.64; H, 2.51.

(Bromodifluoromethyl)diphenylsulfonium trifluoromethanesulfonate (1a): white solid. 44%. 1H NMR (300 MHz, CDCl3): δ 7.82 (t, J = 7.8 Hz, 2H), 7.94 (t, J = 8.2 Hz, 1H), 8.25 (d, J = 8.2 Hz, 2H). 19F NMR (282 MHz, CDCl3): δ -77.8 (s, 3F), -34.9 (s, 2F). 13C NMR (100 MHz, CDCl3): δ 137.0, 133.2, 132.1, 119.0. ESI-MS: m/z = 315.0 [M+], 317.0 [M+2]. IR (KBr): 3067, 1478, 1450, 1276, 1259, 1224, 1158, 1141, 1097, 1029, 828, 755, 685, 634, 517, 509, 494 cm-1. Anal. Calcd for C15H10BrF2O3S2: C, 36.14; H, 2.17. Found: C, 36.13; H, 1.95.

(2-Chloro-1,1,2,2-tetrafluoroethoxy)diphenylsulfonium 2-chloro-1,1,2,2-tetrafluoroethene-1-sulfonate and trifluoromethanesulfonate (1c): white solid. 8%. 1H NMR (300 MHz, CDCl3): δ 7.82 (t, J = 7.7 Hz, 2H), 7.93 (t, J = 8.2 Hz, 1H), 8.34 (d, J = 8.2 Hz, 2H). 19F NMR (282 MHz, CDCl3): δ -112.0 (s, 1.8F), -91.1 (t, J = 6.2 Hz, 2F), -77.8 (s, 0.3F), -65.0 (s, 1.8F), -64.6 (t, J = 6.2 Hz, 2F). 13C NMR (100 MHz, CDCl3): δ 137.2, 133.9, 132.2, 117.1. ESI-MS: m/z = 321.0 [M+], 323.0 [M+2], 214.9 [M-1], 216.9 [M+2], 149.0 [M-1]. IR (KBr): 3057, 1476, 1454, 1282, 1258, 1201, 1160, 1124, 1089, 1025, 835, 808, 759, 694, 684, 632, 505 cm-1. Anal. Calcd for [C15H10ClF4S][Cl2F2SO3][CF3SO3]0.9[CF3SO3]0.1: C, 35.99; H, 1.90. Found: C, 35.63; H, 2.37.

(4-Chloro-1,1,2,2,3,3,4,4-octafluorobutyl)diphenylsulfonium 4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonate (1d): white solid. 4.5%. 1H NMR (300 MHz, CDCl3): δ 7.83 (t, J = 7.7 Hz, 2H), 7.94 (t, J = 8.2 Hz, 1H), 8.34 (d, J = 8.2 Hz, 2H). 19F NMR (282 MHz, CDCl3): δ -119.2 (m, 4F), -118.7 (t, J = 13.4 Hz, 2F), -114.4 (m, 2F), -113.8 (t, J = 14.4 Hz, 2F), -89.1 (t, J = 14.5 Hz, 2F), -67.4 (t, J = 12.4 Hz, 2F), -66.9 (t, J = 13.4 Hz, 2F). 13C NMR (100 MHz, CDCl3): δ 137.3, 134.0, 132.3, 116.9. ESI-MS: m/z = 421.0 [M+], 423.0 [M+2], 315.0 [M-], 317.0 [M+2]. IR (KBr): 3100, 1475, 1451, 1280, 1256,
To a 25 mL round-bottomed flask, 1-ethynylbenzene (50 mg, 0.49 mmol) and anhydrous THF (4 mL) were added and maintained under a N₂ atmosphere at −78 °C. n-BuLi (0.22 mL of a 2.5 mol L⁻¹ solution in hexane, 0.55 mmol) was added and the reaction mixture was stirred at −78 °C for 30 min. Then 1b (226 mg in 2 mL of anhydrous THF, 0.50 mmol) was added. After 1 hour, the cooling bath was removed and the reaction was warmed naturally to room temperature. Then the reaction mixture was poured into water (30 mL), extracted with diethyl ether (30 mL), washed by brine (3 x 20 mL) and dried over anhydrous Na₂SO₄. The ether was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using pentane as the eluent. 28 mg of 2g (25%) was obtained as a colorless liquid. ¹H NMR: δ 7.57 (d, J = 7.7 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 19F NMR: δ -101.2 (q, J = 4.2 Hz, 2F), -85.3 (t, J = 4.2 Hz, 3F).

1-(3-Bromo-3,3-difluoroprop-1-ynyl)benzene (2a): colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.22-7.49 (m, 5H), 19F NMR (282 MHz, CDCl₃): δ -31.2 (s, 2F).

1-(3-Bromo-3,3-difluoroprop-1-ynyl)-4-methoxybenzene (2b): colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.41 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ -30.3 (s, 2F).

1-Bromo-4-(3-bromo-3,3-difluoroprop-1-ynyl)benzene (2c): colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.44-7.58 (m, 2H), 7.28-7.35 (m, 2H); ¹⁹F NMR (282 MHz, CDCl₃): δ -31.9 (s, 2F).

1-Bromo-1,1-difluoro-oct-2-yn (2d): colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 2.34-2.41 (m, 1H), 2.22 (t, J = 6.9Hz, 1H), 1.51-1.64 (m, 2H), 1.27-1.45 (m, 4H), 0.90-0.96 (m, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ -29.8 (t, J = 4.5 Hz, 2F).

Typical procedure for the fluoroalkylation of 2e-f, 2h

To a 25 mL round-bottomed flask, ethyl 2-methyl-3-oxobutanoate (70 mg, 0.49 mmol) was dissolved into anhydrous DMF (4 mL). NaH (24 mg, 56%, 0.56 mmol) was added under a N₂ atmosphere. The reaction mixture was stirred at room temperature for 30 min then cooled to −50 °C. 1b (226 mg in 2 mL of anhydrous DMF, 0.50 mmol) was added and the cooling bath was removed. After warming naturally to room temperature, the reaction mixture was poured into water (30 mL), extracted with diethyl ether (30 mL), washed by brine (3 x 20 mL) and dried over anhydrous Na₂SO₄. The ether layer was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether / ethyl acetate (10:1) as the eluent. 42 mg of 2h (33 %) was obtained as a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 4.29 (q, J = 7.3 Hz, 2H), 2.34 (s, 3H), 1.61 (s, 3H), 1.30 (t, J = 7.3 Hz, 3H). ¹⁹F NMR (282 MHz, CDCl₃): δ -113.5 (dd, AB, J_FF = 282.5 Hz, 2F), -78.8 (s, 3F). ¹³C NMR (100 MHz, CDCl₃): δ 197.1, 166.1, 63.3 (t, J = 19.5 Hz), 62.8, 27.9, 15.6, 13.7. Ei-MS: m/z = 43 (100), 44 (5.3), 73 (3.0), 77 (2.9), 105 (7.3), 123 (6.1), 192 (3.4), 220 (7.3). IR (KBr): 2988, 2942, 1734, 1466, 1389, 1365, 1338, 1260, 1209, 1107, 1044, 745 cm⁻¹. HRMS for C₉H₁₁O₃F₅: 262.0628. Found: 262.0625

Ethyl 2-(bromodifluoromethyl)-2-methyl-3-oxobutanoate (2e): colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 4.30 (q, J = 7.0 Hz, 2H), 2.46 (s, 3H), 2.00 (s, 3H), 1.33 (t, J = 7.0 Hz, 3H).
$^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -47.9 (dd, AB, $J = 164.0$ Hz, 2F). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.5, 167.5, 62.4, 61.9, 25.0, 24.5, 13.1. EI-MS: m/z = 43 (100), 44 (26.9), 87 (12.9), 105 (13.3), 151 (10.3), 154 (9.6), 180 (11.3), 182 (13.2). IR (KBr): 2987, 2937, 1729, 1446, 1377, 1359, 1254, 1122, 1096, 1073, 1017, 940, 862, 551 cm$^{-1}$. HRMS for C$_8$H$_{11}$O$_2$F$_2$Br: 271.9860. Found: 271.9847. HRMS for [C$_8$H$_{11}$O$_2$F$_2$]: 193.0679. 

3-(Difluoromethoxy)-2-methylcyclopent-2-enone (2f): white solid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.70 (t, $J = 72.1$ Hz, 1H), 2.80-2.83 (m, 2H), 2.54-2.58 (m, 2H), 1.72 (t, $J = 2.0$ Hz, 3H). $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta$ -81.2 (d, $J = 72.1$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 204.7, 174.3, 122.5, 114.3 (t, $J = 265.6$ Hz, CF$_2$H), 33.8, 25.9, 6.11. EI-MS: m/z = 43 (44.7), 44 (47.9), 51 (45.4), 55 (87.6), 67 (53.4), 83 (100.00), 111 (40.4), 162 (77.9). IR (KBr): 2931, 2869, 1708, 1666, 1448, 1414, 1383, 1330, 1220, 1114, 894, 628 cm$^{-1}$; HRMS for C$_7$H$_8$O$_2$F$_2$: 162.0492. Found: 162.0496.
The $^1$H, $^{19}$F and $^{13}$C NMR spectra of compounds 1a-d, 2a-h
$\text{1c} \quad \text{CF}_3\text{CF}_2\text{Cl} \quad 0.1\text{CF}_3\text{SO}_3^- \quad 0.5\text{CF}_2\text{CF}_2\text{SO}_3^-$

$\text{1d} \quad \text{CF}_2\text{CF}_2\text{CF}_2\text{Cl} \quad \text{Cl}\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_3^-$
$\text{CIF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{SO}_3^-$

1d