SUPPORTING INFORMATION

General

^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a Bruker AV300M (300 MHz) spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million down field from tetramethylsilane as an internal standard ($\delta = 0$) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million in $CDCl_3$ as an internal standard ($\delta = 77.0$). Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from BTF as an external standard ($\delta = -63.24$) in $CDCl_3$. Important NMR data were tabulated in following order: multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sext: sextet, sept: septet, m: multiplet, brs: broad singlet, brm: broad multiplet) and coupling constant (*J* (Hz)).

IR spectra were measured on a JASCO FT/IR-4200 spectrometer.

Mass spectra were measured on a JEOL JMS-T100CS.

Analytical thin layer chromatography (TLC) was performed on a glass plates pre-coated with silica-gel (Merck Kieselgal 60 F_{254}, layer thickness 0.25 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$ and phosphomolybdic acid.

Column chromatography was performed on KANTO Silica Gel 60N (spherical, neutral).

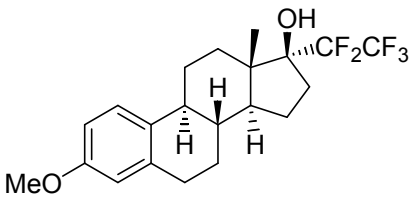
Anhydrous diethyl ether, tetrahydrofuran, dichloromethane and 1,4-dioxane were purchased from Kanto Chemical Co., Inc. Anhydrous dimethylsulfoxide was purchased from Sigma-Aldrich Co., Inc.

All experiments were carried out under argon atmosphere otherwise noted.

General procedure for the perfluoroalkylation of aldehydes, ketones and esters

To a solution of Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) in Et_2O (2.4 mL) was added ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol), 1,4-dioxane (23 μL, 0.27 mmol) and perfluorohexyl iodide (78 μL, 0.36 mmol) (and methylaluminoxane (10 wt% in toluene, 0.16 mL, 0.24 mmol)) at -78 °C. After stirring at -78 °C for 1 h, benzaldehyde (**1b**) (20 μL, 0.20 mmol) was added. The reaction mixture was then stirred at room temperature for 1 h, quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to give 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenylheptan-1-ol (**2b**) (85.2 mg, >99%).

(8*R*, 9*S*, 13*S*, 14*S*, 17*S*)-3-Methoxy-13-methyl-17-(pentafluoroethyl)-7,8,9,11,12,13, 14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-ol (2a)[S1]



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.28-1.60 (m, 4H), 1.71-1.96 (m, 6H), 2.09 (brs, 1H), 2.26 (td, *J* = 11.1 and 4.2, 1H), 2.33-2.49 (m, 2H), 2.86-2.91 (m, 2H), 3.79 (s, 3H), 6.65 (d, *J* = 2.7 Hz, 1H), 6.73 (dd, *J* = 8.4 and 7.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H).

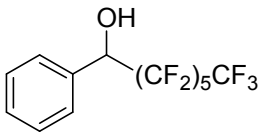
^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 24.5, 26.7, 27.6, 29.7, 33.2 (dd, J_{CF} = 6.8 and 2.3 Hz), 33.5 (t, J_{CF} = 3.0 Hz), 39.5, 43.1, 50.4, 51.2, 55.2, 84.5 (t, J_{CF} = 22.5 Hz), 111.5, 112.7-126.6 (m, CF_2CF_3), 113.8, 126.3, 132.2, 137.8, 157.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -77.1 (s, 3F), -118.5 (d, J_{FF} = 272.7 Hz, 1F), -119.9 (d, J_{FF} = 272.7 Hz, 1F).

HRMS (APCI-TOF) Calcd for $C_{21}H_{24}F_5O_2$ $[M-H]^-$: 403.1697, Found: 403.1693.

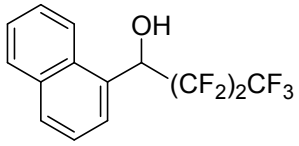
IR (KBr) 737, 908, 1218, 1506, 1609, 1719, 1871, 2069, 2928, 3629 cm^{-1}

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-phenylheptan-1-ol (2b)[S1]



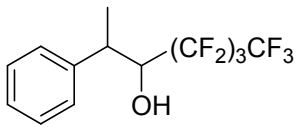
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.54 (d, J = 5.1 Hz, 1H), 5.21 (ddd, J_{HF} = 17.7 and 5.4 Hz, J = 5.4 Hz, 1H), 7.41-7.49 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 72.3 (dd, J_{CF} = 28.5 and 22.5 Hz), 104.6-122.9 (m, $(CF_2)_5CF_3$), 128.0, 128.6, 129.7, 133.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.3 Hz, 3F), -117.4-(-127.3) (m, 10F).
HRMS(APCI-TOF) Calcd for $C_{13}H_6F_{13}O$ $[M-H]^-$: 425.0211, Found: 425.0198.
IR (KBr) 702, 819, 1060, 1203, 1355, 1451, 1458, 1959, 3038, 3416 cm^{-1}.

2,2,3,3,4,4,4-Heptafluoro-1-(naphthalen-1-yl)butan-1-ol (2c)[S1]



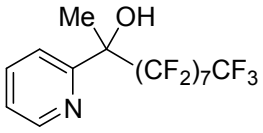
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.70 (d, J = 5.1 Hz, 1H), 6.12 (ddd, J_{HF} = 19.8 and 3.9 Hz, J = 3.9 Hz, 1H), 7.51-7.61 (m, 3H), 7.83-8.03 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 67.5 (dd, J_{CF} = 30.0 and 21.8 Hz), 106.4-128.5 (m, $(CF_2)_2CF_3$), 122.7, 124.8, 125.2, 126.6, 126.9, 129.0, 130.2, 130.3, 131.4, 133.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.7 (t, J_{FF} = 10.2 Hz, 3F), -115.9-(-117.0) (m, 1F), -124.4-(-127.9) (m, 3F).
HRMS (APCI-TOF) Calcd for $C_{14}H_8F_7O$ $[M-H]^-$: 325.0463, Found: 325.0454.
IR (KBr) 785, 963, 1231, 1348, 1513, 1698, 1932, 3052, 3513 cm^{-1}.

4,4,5,5,6,6,7,7,7-Nonafluoro-2-phenylheptan-3-ol (2d)[S1]



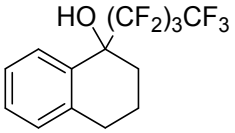
Physical data of mixture of the two isomers (67:33)
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (dd, J = 6.9 and 1.2 Hz, 3H, major), 1.47 (dd, J = 7.5 and 2.1 Hz, 3H, minor), 1.85 (d, J = 8.4 Hz, 1H, minor), 2.11 (d, J = 7.5 Hz, 1H, major), 3.29-3.37 (m, 1H), 4.18-4.34 (brm, 1H), 7.28-7.40 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 18.9, 39.1, 39.8, 72.5 (dd, J_{CF} = 26.3 and 20.3 Hz), 73.1 (dd, J_{CF} = 27.8 and 21.8 Hz), 104.9-123.6 (m, $(CF_2)_3CF_3$), 127.2, 127.6, 128.5, 128.8, 128.8, 128.9, 140.0, 143.1.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.0 (s, 3F), -116.0-(-127.8) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{13}H_{10}F_9O$ $[M-H]^-$: 353.0588, Found: 353.0583.
IR (neat) 706, 1025, 1134, 1235, 1358, 1453, 1603, 1717, 2940, 3341 cm^{-1}

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-2-(pyridin-2-yl)decan-2-ol (2e)[S1]



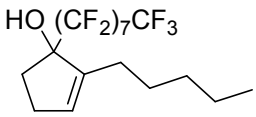
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 (s, 3H), 6.51 (s, 1H), 7.36 (dd, J = 7.8 and 4.8 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.80 (td, J = 7.8 and 1.5 Hz, 1H), 8.58 (d, J = 4.8 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 75.4 (t, J_{CF} = 24.0 Hz), 104.5-124.1 (m, $(CF_2)_7CF_3$), 121.6 (t, J_{CF} = 3.0 Hz), 123.8, 137.5, 147.1, 155.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.9 Hz, 3F), -115.9-(-119.0) (m, 4F), -121.8-(-122.0) (m, 6F), -122.8 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{15}H_7F_{17}NO$ $[M-H]^-$: 540.0256, Found: 540.0270.
IR (KBr) 661, 764, 963, 1142, 1203, 1410, 1596, 1719, 2963, 3285 cm^{-1}

1-Nonafluorobutyl-1,2,3,4-tetrahydronaphthalen-1-ol (2f)[S1]



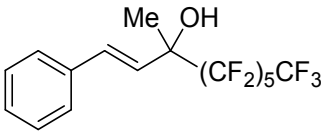
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89-2.16 (m, 3H), 2.36-2.43 (m, 1H), 2.51 (s, 1H), 2.83-2.87 (m, 2H), 7.19 (d, J = 6.9 Hz, 1H), 7.20-7.34 (m, 2H), 7.71 (d, J = 7.2 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 29.5, 33.0 (dd, J_{CF} = 7.5 and 3.8 Hz), 74.8 (dd, J_{CF} = 22.5 and 21.0 Hz), 104.2-123.8 (m, $(CF_2)_3CF_3$), 126.6, 127.6 (t, J_{CF} = 3.8 Hz), 129.1, 129.5, 134.0, 138.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.8 (t, J_{FF} = 7.9 Hz, 3F), -110.4 (d, J_{FF} = 286.5 Hz, 1F), -116.8-(-118.8) (m, 2F), -120.3-(-121.4) (m, 1F), -124.2-(-125.4) (m, 1F), -126.5-(-127.7) (m, 1F).
HRMS (APCI-TOF) Calcd for $C_{14}H_{10}F_9O$ $[M-H]^-$: 365.0588, Found: 365.0597.
IR (neat) 692, 733, 1025, 1134, 1235, 1358, 1446, 1487, 2954, 3484 cm^{-1}

2-Pentyl-1-(haptadecafluorooctyl)cyclopent-2-enol (2g)[S1]



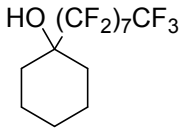
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 6.9 Hz, 3H), 1.31-1.36 (m, 3H), 1.46-1.63 (m, 2H), 1.99-2.17 (m, 3H), 2.25 (s,1H), 2.30-2.58 (m, 3H), 5.83 (s,1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.5, 26.8, 27.8, 29.2, 31.8, 34.5, 87.7 (dd, J_{CF} = 25.5 and 20.3 Hz), 104.1-122.9 (m, $(CF_2)_7CF_3$), 132.5, 142.6.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.0 (t, J_{FF} = 9.6 Hz, 3F), -116.8-(-119.7) (m, 4F), -121.8 (brm, 6F), -122.8 (s, 2F), -126.3 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{18}H_{16}F_{17}O$ $[M-H]^-$: 571.0930, Found: 571.0937.
IR (neat) 1072, 1147, 1208, 1242, 1371, 1467, 1609, 2859, 2933, 3464 cm^{-1}

(*E*)-4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-3-methyl-1-phenylnon-1-en-3-ol (2h)[S1]



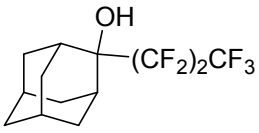
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3H), 2.39 (s, 1H), 6.34 (d, J = 16.2 Hz, 1H), 6.87 (d, J = 16.2 Hz, 1H), 7.26-7.44 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 76.1 (t, J_{CF} = 24.0 Hz), 104.8-123.6 (m, $(CF_2)_5CF_3$), 126.7, 127.0, 128.5, 128.9, 131.5, 136.0.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.9 Hz, 3F),-117.8-(-121.9) (m, 6F), -122.8 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{16}H_{10}F_{13}O$ $[M-H]^-$: 465.0524, Found: 465.0504.
IR (KBr) 565, 743, 977, 1238, 1368, 1493, 1706, 1953, 3025, 3636 cm^{-1}

1-Heptadecafluorooctyl-cyclohexanol (2i)[S1]



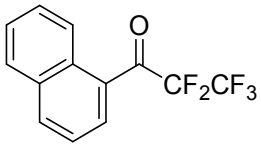
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18-1.25 (m, 1H), 1.63-1.74 (m, 7H), 1.83-1.92 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 25.0, 29.9 (t, J_{CF} = 2.3 Hz), 75.3 (t, J_{CF} = 22.5 Hz), 105.1-123.3 (m, $(CF_2)_7CF_3$).
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.0 (t, J_{FF} = 9.9 Hz, 3F), -119.1 (s, 2F), -121.6-(-126.2) (m, 6F), -122.9 (s, 2F), -122.9 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{14}H_{10}F_{17}O$ $[M-H]^-$: 517.0460, Found: 517.0456.
IR (KBr) 644, 909, 991, 1052, 1228, 1464, 1717, 2947, 3457, 3606 cm^{-1}

(1*r*,3*r*,5*r*,7*r*)2-(Perfluoropropyl)adamantan-2-ol (2j)[S1]



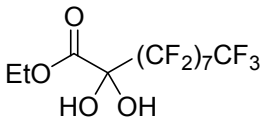
^{1}H NMR (300 MHz, C_6D_6) δ 1.21-1.26 (m, 3H), 1.43-1.58 (m, 6H), 1.95-2.04 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 26.3, 27.0, 33.0, 33.2 (t, J_{CF} = 3.8 Hz), 33.5, 38.4, 76.7 (t, J_{CF} = 21.8 Hz), 107.1-125.0 (m, $(CF_2)_2CF_3$).
^{19}F NMR (282 MHz, C_6D_6) δ -80.3 (t, J_{FF} = 10.2 Hz, 3F), -113.0 (brm, 2F), -122.9 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{13}H_{14}F_7O$ $[M-H]^-$: 319.0933, Found: 319.0928.
IR (KBr) 558, 730, 881, 943, 1225, 1335, 1458, 1719, 2928, 3478 cm^{-1}

2,2,3,3,3-Pentafluoro-1-(naphthalen-1-yl)propan-1-one (2k)[S1]



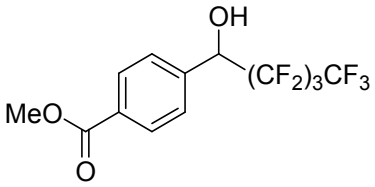
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.71 (m, 3H), 7.92-7.95 (m, 1H), 8.13-8.17 (m, 2H), 8.56 (d, J = 8.7 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 104.2-129.8 (m, CF_2CF_3), 124.2, 125.0, 127.3, 128.2, 129.1, 129.4, 130.6 (t, J_{CF} = 6.0 Hz), 131.0, 134.1, 135.7, 186.0 (t, J_{CF} = 25.5 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.1 (s, 3F), -114.3 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{13}H_7F_5O$ $[M]^-$: 274.0417, Found: 274.0410.
IR (neat) 719, 773, 889, 1005, 1228, 1344, 1507, 1576, 1704, 3056 cm^{-1}

Ethyl 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-2,2-dihydroxydecanoate (2l)[S1]



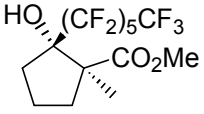
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (t, J = 7.2 Hz, 3H), 4.41 (q, J = 7.2 Hz, 2H), 4.62 (brs, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 65.0, 92.0 (t, J_{CF} = 19.5 Hz), 107.8-123.5 (m, $(CF_2)_7CF_3$), 167.1.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.0 (t, J_{FF} = 9.9 Hz, 3F), -120.4 (s, 2F), -121.2 (s, 2F), -122.0 (s, 2F), -122.9 (s, 2F), -126.3 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{12}H_6F_{17}O_4$ $[M-H]^-$: 536.9995, Found: 537.0012.
IR (neat) 658, 726, 855, 1018, 1147, 1235, 1371, 1745, 2995, 3450 cm^{-1}

Methyl 4-(2,2,3,3,4,4,5,5,5-nonafluoro-1-hydroxypentyl)-benzoate (2m)



^{1}H NMR (300 MHz, $CDCl_3$) δ 3.09 (brs, 1H), 3.92 (s, 3H), 5.28 (dd, J_{HF} = 17.1 and 6.0 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 72.0 (dd, J_{CF} = 28.5 and 22.5 Hz), 104.6-130.6 (m, $(CF_2)_3CF_3$), 128.2, 129.9, 131.3, 138.9, 166.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 8.3 Hz, 3F), -117.3-(-127.5) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{13}H_8F_9O_3$ $[M-H]^-$: 383.0330, Found: 383.0329.
IR (KBr) 537, 723, 888, 1211, 1307, 1444, 1706, 1953, 2970, 3458 cm^{-1}

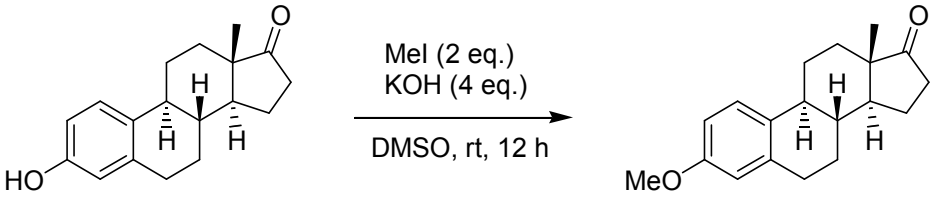
Methyl 2-hydroxy-1-methyl-2-(perfluorohexyl)cyclopentanecarboxylate (2n)



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 3H), 1.71-1.81 (m, 1H), 1.84-2.20 (m, 4H), 2.42- 2.52 (m, 1H), 2.45 (s, 1H), 3.69 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 20.6, 33.2 (t, J_{CF} = 5.3 Hz), 52.3, 56.8, 85.6 (dd, J_{CF} = 26.3 and 21.0 Hz), 106.5-123.1 (m, $(CF_2)_5CF_3$), 175.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.2 Hz, 3F), -114.7-(-115.9) (m, 1F), -117.5-(-118.6) (m, 1F), -119.5-(-121.4) (m, 2F), -121.7-(-121.8) (brm, 2F), -122.8 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{14}H_{12}F_{13}O_3$ $[M-H]^-$: 475.0579, Found: 475.0590.
IR (KBr) 644, 855, 1005, 1141, 1235, 1364, 1467, 1717, 2968, 3477 cm^{-1}

Synthesis of non-commercially available ketones

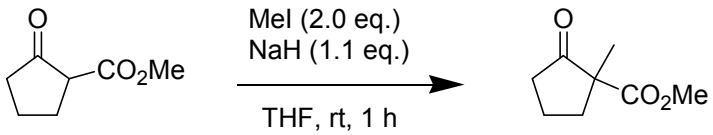
3-*O*-Methylestrone[S1] (1a)



SI-1 **1a**

Estrone (**SI-1**) (1.35 g, 5.00 mmol) was added to a suspention of KOH (1.12 g, 20.0 mmol) in DMSO (30 mL). After adding MeI (0.62 mL, 10.0 mmol), the resulting mixture was stirred at room temperature for 12 h. Then the crude was quenched with water and extracted three times with CH_2Cl_2. The combined organic layers were washed three times with water, dried over Na_2SO_4 and concentrated *in vacuo*. Silica gel column chromatography (Hexane/AcOEt = 9/1) of the crude afforded **1a** (1.16 g, 82%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 3H), 1.37-1.69 (m, 6H), 1.91-2.28 (m, 5H), 2.38-2.43 (m, 1H), 2.51 (dd, *J* = 18.3 and 8.7 Hz, 1H), 2.89-2.94 (m, 2H), 3.78 (s, 3H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 8.4 and 2.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 21.6, 26.0, 26.6, 29.7, 31.6, 35.9, 38.4, 44.0, 48.0, 50.4, 55.2, 111.6, 113.9, 126.3, 132.0, 137.7, 157.6, 220.8.

Methyl 1-methyl-2-oxocyclopentanecarboxylate[S2] (1n)



SI-2 **1n**

To a suspension of NaH (60% in mineral oil, 0.44 g, 11 mmol) in THF, methyl cyclopentan-one-2-carboxylate (**SI-2**) (1.35 mL, 10.0 mmol) and MeI (1.25 mL, 20.0 mmol) was added at 0 °C. After stirring at room temperature for 1 h, the reaction was quenched with saturated aq. NH_4Cl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 10/1) to furnish **1n** (1.37 g, 88%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.72-1.87 (m, 2H), 1.90-2.02 (m, 1H), 2.15- 2.33 (m, 2H), 2.36-2.46 (m, 1H), 3.59 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 19.5, 36.0, 37.5, 52.3, 55.8, 172.7, 215.6.

HRMS (APCI-TOF) Calcd for $C_8H_{13}O_3$ $[M+H]^+$: 157.0865, Found: 157.0859.
IR (neat) 844, 940, 1063, 1158, 1275, 1452, 1732, 1752, 2887, 2962 cm^{-1}

Procedure for Scheme 4 (Perfluoroalkyl Grignard reagent)

To a solution of ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol) in Et_2O (2.4 mL) was added perfluorohexyl iodide (78 μL, 0.36 mmol) at -78 °C . After stirring at -78 °C for 1 h, Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) and 1,4-dioxane (0.23 μL, 0.27 mmol) was added and the reaction mixture was stirred at -20 °C for 2 h before benzaldehyde (**1b**) (20 μL, 0.20 mmol) was added. After stirring at room temperature for 1 h, the reaction was quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The yield of 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenylheptan-1-ol (**2b**) (56%) was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Procedure for Scheme 4 (Perfluoroalkyl lithium reagent)

To a solution of MeLi (1.6 M in Et_2O, 0.15 mL, 0.24 mmol) in Et_2O (2.4 mL) was added perfluorohexyl iodide (78 μL, 0.36 mmol) at -78 °C. After stirring at -78 °C for 15 min, Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) was added and the reaction mixture was stirred at -20 °C for 2 h before benzaldehyde (**1b**) (20 μL, 0.20 mmol) was added. After stirring at room temperature for 1 h, the reaction was quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude mixture was analyzed by ^{1}H NMR.

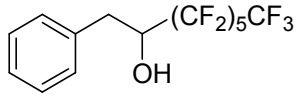
Procedure for Scheme 5

To a solution of Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) in Et_2O (2.4 mL) was added ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol), 1,4-dioxane (23 μL, 0.27 mmol) and perfluorohexyl iodide (78 μL, 0.36 mmol) in this order at -78 °C. After stirring at -78 °C for 1 h, styrene oxide (**3a**) (23 μL, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and removed solvent *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to give 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloctan- 2-ol (**4a**) (37.9 mg, 43%) and 2-chloro-2-phenylethanol[S3] (**6**) (3.1 mg, 10%).

General procedure for the perfluoroalkylation of epoxides

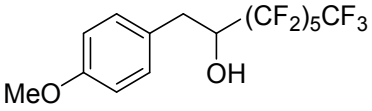
To a solution of Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) in Et_2O (2.4 mL) was added ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol) and perfluorohexyl iodide (78 μL, 0.36 mmol). After stirring at -78 °C for 1 h, 1,4-dioxane (23 μL, 0.27 mmol) and methylaluminoxane (10 wt% in toluene, 0.16 mL, 0.24 mmol) were added. After the mixture was stirred at 0 °C for 2 min, styrene oxide (**3a**) (23 μL, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and condensed *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to give 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloctan- 2-ol (**4a**) (77.5 mg, 88%).

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



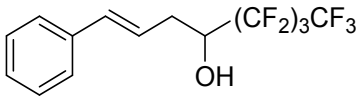
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (d, J = 6.3 Hz, 1H), 2.87 (dd, J = 14.1 and 10.5 Hz, 1H), 3.15 (d, J = 14.1 Hz, 1H), 4.26-4.38 (m, 1H), 7.27-7.42 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5, 71.1 (dd, J_{CF} = 28.5 and 21.8 Hz), 104.2-123.4 (m, $(CF_2)_5CF_3$), 127.2, 128.8, 129.5, 135.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.1 (t, J_{FF} = 9.9 Hz, 3F), -119.9-(-127.6) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{14}H_8F_{13}O$ [M-H]$^-$: 439.0368, Found: 439.0353.
IR (neat) 651, 706, 1147, 1201, 1249, 1358, 1460, 1500, 3035, 3531 cm^{-1}

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecaflioro-1-(4-methoxy-phenyl)octan-2-ol (4b)



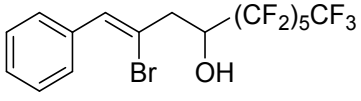
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (d, J = 6.3 Hz, 1H), 2.82 (dd, J = 14.1 and 10.2 Hz, 1H), 3.07 (d, J = 14.1 Hz, 1H), 3.80 (s, 3H), 4.28-4.31 (m, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6, 55.3, 71.1 (dd, J_{CF} = 28.5 and 23.3 Hz), 100.2-123.4 (m, $(CF_2)_5CF_3$), 114.3, 127.3, 130.6, 158.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.6 Hz, 3F), -119.8-(-127.3) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{15}H_{10}F_{13}O_2$ [M-H]$^-$: 469.0473, Found: 469.0488.
IR (neat) 748, 885, 967, 1124, 1131, 1240, 1357, 2921, 3030, 3454 cm^{-1}

(*E*)-5,5,6,6,7,7,8,8,8-Nonafluoro-1-phenyl-oct-1-en-4-ol (4c)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (d, J = 7.2 Hz, 1H), 2.58-2.68 (m, 1H), 2.72-2.79 (m, 1H), 4.21-4.35 (m, 1H), 6.18-6.28 (m, 1H), 6.61(d, J = 15.6 Hz, 1H), 7.26-7.42 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 33.2, 93.2 (dd, J_{CF} = 27.8 and 22.5 Hz), 107.1-119.8 (m, $(CF_2)_3CF_3$), 122.7, 126.3, 127.9, 128.7, 135.3, 136.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.0 Hz, 3F), -120.1-(-127.6) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{14}H_{10}F_9O$ [M-H]$^-$: 365.0588, Found: 365.0584.
IR (KBr) 748, 885, 967, 1124, 1131, 1240, 1357, 2921, 3030, 3454 cm^{-1}

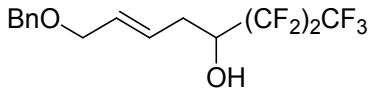
(*Z*)-2-Bromo-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-1-phenyldec-1-en-4-ol (4d)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (d, J = 6.3 Hz, 1H), 2.92-3.07 (m, 2H), 4.57-4.71 (m, 1H), 6.95 (s, 1H), 7.30-7.41 (m, 3H), 7.60 (d, J = 6.9 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 43.5, 68.2 (dd, J_{CF} = 28.9 and 23.3 Hz), 107.0-123.2 (m, $(CF_2)_5CF_3$), 119.5,

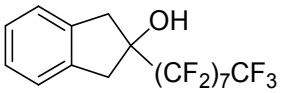
128.4, 128.5, 129.1, 132.9, 135.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.8 (t, J_{FF} = 9.6 Hz, 3F), -119.7-(-127.3) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{16}H_9BrF_{13}O$ $[M-H]^-$: 542.9629, Found: 545.9630.
IR (neat) 692, 753, 916, 1147, 1242, 1317, 1371, 1446, 3056, 3410 cm^{-1}

(*E*)-8-(Benzyloxy)-1,1,1,2,2,3,3-heptafluorooct-6-en-4-ol (4e)



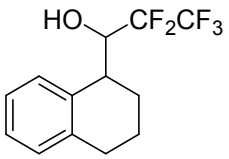
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35-2.45 (m, 1H), 2.50-2.57 (m, 1H), 2.78 (d, *J* = 6.6 Hz, 1H), 4.01-4.11 (m, 3H), 4.53 (s, 2H), 5.68-5.86 (m, 2H), 7.28-7.39 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 68.9 (dd, J_{CF} = 28.5 and 23.3 Hz), 72.5, 106.1-123.5 (m, $(CF_2)_2CF_3$), 127.1, 127.8, 127.8, 128.5, 131.7, 137.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 10.2 Hz, 3F), -121.0 (dd, J_{FF} = 282.4 Hz and J_{FH} = 5.5 Hz, 1F), -124.7-(-128.3) (m, 3F).
HRMS (APCI-TOF) Calcd for $C_{15}H_{14}F_7O_2$ $[M-H]^-$: 359.0882, Found: 359.0871.
IR (neat) 733, 916, 978, 1114, 1228, 1351, 1460, 2859, 2933, 3395 cm^{-1}

2-(Perfluorooctyl)-2,3-dihydro-1*H*-inden-2-ol (4f)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 1H), 3.10 (d, *J* = 16.8 Hz, 1H), 3.58 (d, *J* = 16.8 Hz, 1H), 7.24-7.31 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 42.8, 84.0 (t, J_{CF} = 25.5 Hz), 104.8-120.7 (m, $(CF_2)_7CF_3$), 125.2, 127.5, 138.4.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.6 Hz, 3F), -118.4 (s, 2F), -119.4 (s, 2F), -121.8-(-121.8) (brm, 6F), -122.8 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{17}H_8F_{17}O$ $[M-H]^-$: 551.0304, Found: 551.0300.
IR (KBr) 659, 753, 1072, 1208, 1480, 1725, 1935, 3035, 3579 cm^{-1}

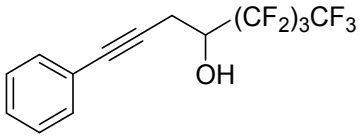
2,2,3,3,3-Pentafluoro-1-(1,2,3,4-tetrahydronaphthalen-1-yl)propan-1-ol (4g)



Physical data of mixture of the two isomers (52:48)
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59-1.71 (m, 1H), 1.87-2.09 (m, 4H), 2.68-2.92 (m, 2H), 3.38-3.43 (brm, 1H), 4.02-4.15 (m, 1H, major), 4.57-4.69 (m, 1H, minor), 7.12-7.24 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 21.8, 22.6 (d, J_{CF} = 3.8 Hz), 28.1 (d, J_{CF} = 3.0 Hz), 28.5, 29.9, 37.5, 38.2, 71.7 (dd, J_{CF} = 28.5 and 22.5 Hz), 72.3 (dd, J_{CF} = 27.0 and 19.5 Hz), 110.4-125.0 (m, CF_2CF_3), 126.0, 126.6, 126.7, 127.5, 127.9, 129.9, 130.2, 130.9 (d, J_{CF} = 3.8 Hz), 132.3, 135.1, 139.1, 140.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.8 (s, 3F, minor), -82.8 (s, 3F, major), -120.1 (d, J_{FF} = 276.0 Hz, 1F,

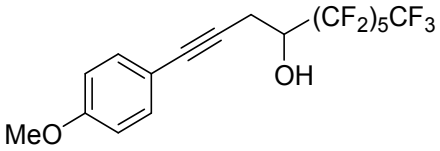
major), -123.0 (d, J_{FF} = 276.1 Hz, 1F, minor), -127.9 (dd, J_{FF} = 276.1 Hz and J_{FH} = 22.3 Hz, 1F, minor), -131.6 (dd, J_{FF} = 276.0 Hz and J_{FH} = 22.4 Hz, 1F, major).
HRMS (APCI-TOF) Calcd for $C_{13}H_{12}F_5O$ $[M-H]^-$: 279.0808, Found: 279.0806.
IR (neat) 740, 1038, 1120, 1195, 1244, 1453, 1493, 2872, 2947, 3538 cm^{-1}

5,5,6,6,7,7,8,8,8-Nonafluoro-1-phenyloct-1-yn-4-ol (4h)



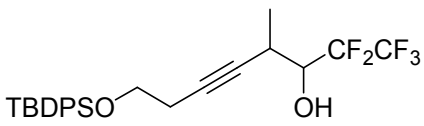
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 (d, J = 6.9 Hz, 1H), 2.86-3.02 (m, 2H), 4.38-4.44 (m, 1H), 7.29-7.45 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8 (t, J_{CF} = 0.4 Hz), 68.3 (dd, J_{CF} = 29.3 and 22.5 Hz), 82.5, 84.4, 99.8-129.5 (m, $(CF_2)_3CF_3$), 122.6, 128.5, 128.7, 131.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 8.3 Hz, 3F), -119.6-(-128.5) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{14}H_8F_9O$ $[M-H]^-$: 363.0431, Found: 363.0433.
IR (neat) 755, 885, 1131, 1233, 1350, 1493, 1678, 2927, 3064, 3488 cm^{-1}

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-1-(4-methoxyphenyl)dec-1-yn-4-ol (4i)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.70 (d, J = 7.2 Hz, 1H), 2.84-3.00 (m, 2H), 3.91 (s, 3H), 4.34-4.46 (m, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 55.4, 68.3 (dd, J_{CF} = 29.3 and 22.5 Hz), 81.0, 84.4, 106.4-129.0 (m, $(CF_2)_5CF_3$), 114.1, 114.7, 133.3, 159.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.8 (t, J_{FF} = 9.3 Hz, 3F),-119.8-(-128.3) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{17}H_{10}F_{13}O_2$ $[M-H]^-$: 493.0473, Found: 493.0459.
IR (KBr) 695, 826, 1032, 1245, 1506, 1603, 1719, 2852, 2970, 3313 cm^{-1}

8-((*tert*-Butyldiphenylsilyl)oxy)-1,1,1,2,2-pentafluoro-4-methyloct-5-yn-3-ol (4j)

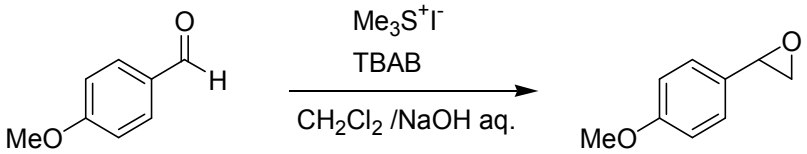


Major
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.28 (d, J = 7.2 Hz, 3H), 2.38-2.46 (m, 3H), 2.98-3.01 (brm, 1H), 3.76 (t, J = 6.9 Hz, 2H), 4.07-4.19 (m, 1H), 7.37-7.47 (m, 6H), 7.67-7.70 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 19.2, 22.8, 26.7, 28.0, 62.5, 70.5 (dd, J_{CF} = 27.0 and 20.3 Hz), 80.6, 80.7, 109.5-124.6 (m, CF_2CF_3), 127.7, 129.7, 133.6, 135.6.
^{19}F NMR (282 MHz, $CDCl_3$) δ -82.7 (s, 3F), -121.4 (d, J_{FF} = 276.9 Hz, 1F), -130.0 (dd, J_{FF} = 276.9 Hz and J_{FH} = 20.9 Hz, 1F).
HRMS (APCI-TOF) Calcd for $C_{25}H_{28}F_5O_2Si$ $[M-H]^-$: 483.1779, Found: 483.1764.

IR (neat) 699, 733, 822, 1059, 1106, 1195, 1426, 2859, 2933, 3524 cm^{-1}
Minor
^1H NMR (300 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.33 (d, J = 6.9 Hz, 3H), 2.44 (td, J = 6.6 and 2.1 Hz, 2H), 2.69 (d, J = 10.5 Hz, 1H), 3.03-3.06 (m, 1H), 3.75 (t, J = 6.6 Hz, 2H), 3.79-3.84 (m, 1H), 7.36-7.47 (m, 6H), 7.66-7.69 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 19.4, 22.8, 26.7, 27.3, 62.4, 70.8 (dd, J_{CF} = 28.5 and 21.8 Hz), 77.9, 83.5, 112.7-126.3 (m, CF_2CF_3), 127.7, 129.7, 133.5, 135.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -82.3 (s, 3F), -122.0 (d, J_{FF} = 276.1 Hz, 1F), -132.6 (dd, J_{FF} = 276.1 Hz and J_{FH} = 19.9 Hz, 1F).
HRMS (APCI-TOF) Calcd for $C_{25}H_{28}F_5O_2Si$ $[M-H]^{\cdot-}$: 483.1779, Found: 483.1761.
IR (neat) 699, 733, 1018, 1106, 1201, 1426, 1589, 2859, 2933, 3491 cm^{-1}

Synthesis of non-commercially available epoxides

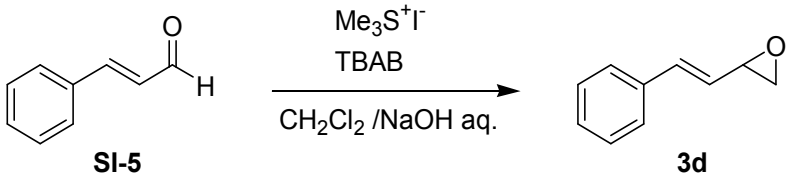
p-Methoxystyrene oxide[S4] (3b)



SI-3 **3b**

In a round-bottom flask was placed *p*-anisaldehyde (**SI-3**) (3.04 mL, 25.0 mmol), CH_2Cl_2 (100 mL), 50 wt% aq. NaOH (100 mL), tetrabutylammonium bromide (0.11 g, 3.80 mmol) and trimethylsulphonium iodide (10.0 g, 50.0 mmol). The mixture was stirred at 50 °C for 4 days. Water was slowly added at 0 °C, the organic layer was removed and the aqueous solution was extracted three times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was removed. The crude product was purified by Kugelrohr distillation to give **3b** (1.99 g, 53%).
^1H NMR (300 MHz, $CDCl_3$) δ 2.80 (dd, J = 5.4 and 2.7 Hz, 1H), 3.12 (dd, J = 5.4 and 4.2 Hz, 1H), 3.80 (s, 3H), 3.82 (dd, J = 4.2 and 2.7 Hz, 1H), 6.86-6.91 (m, 2H), 7.18- 7.23 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 51.0, 52.2, 55.3, 114.0, 126.9, 129.5, 159.7.

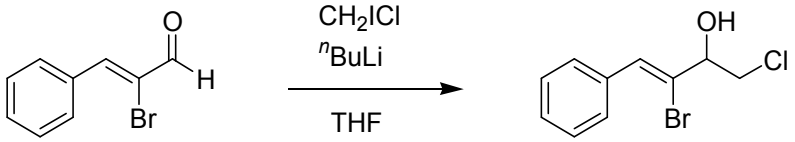
2-Styryloxirane[S6] (3d)



SI-5 **3d**

3d was prepared from *trans*-cinnamaldehyde (**SI-5**) (1.25 mL, 10.0 mmol) in a similar to a manner as **3b** (1.01 g, 69%).
^1H NMR (300 MHz, $CDCl_3$) δ 2.80 (dd, J = 5.1 and 2.4 Hz, 1H), 3.09 (dd, J = 5.1 and 4.2 Hz, 1H), 3.52-3.57 (m, 1H), 5.91 (dd, J = 15.9 and 8.1 Hz, 1H), 6.84 (d, J = 15.9 Hz, 1H), 7.26-7.43 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.3, 52.6, 126.5, 127.0, 128.1, 128.7, 134.6, 136.1.

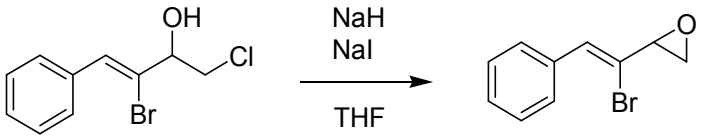
(*Z*)-3-Bromo-1-chloro-4-phenylbut-3-en-2-ol[S6] (SI-7)



SI-6 **SI-7**

A round bottom flask was charged with α-bromocinnamaldehyde (**SI-6**) (2.11 g, 10.0 mmol) and THF (20 mL). The resulting solution was cooled to -78 °C and chloroiodomethane (2.05 g, 11.6 mmol) was added followed by the slow addition of ^{n}BuLi (1.65 M in hexane, 7.0 mL, 11.6 mmol) over 30 minutes. After 1 h, the reaction was quenched with saturated aq. NH_4Cl and warmed to room temperature. The organic layer was removed and the aqueous solution was extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography to give **SI-7** (1.82 g, 69%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (brs, 1H), 3.78 (dd, J = 11.4 and 6.6 Hz, 1H), 3.86 (dd, J = 11.4 and 4.8 Hz, 1H), 4.55 (dd, J = 11.4 and 5.7 Hz, 1H), 7.23 (s, 1H), 7.32-7.41 (m, 3H), 7.64 (d, J = 7.2 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 47.5, 77.0, 124.1, 128.3, 128.6, 129.2, 130.5, 134.6.

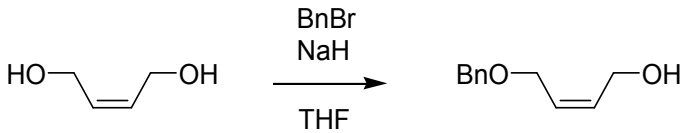
(*Z*)-2-(1-Bromo-2-phenylvinyl)oxirane[S6] (3e)



SI-7 **3e**

To a solution of NaH (60% in mineral oil, 0.30 g, 7.6 mmol) and NaI (0.10 g, 0.70 mmol) in THF (7.0 mL), **SI-7** (1.8 g, 6.9 mmol) in THF (7.0 mL) was added at 0 °C. After 1 h, the reaction was quenched with saturated aq. NH_4Cl, the organic layer was removed and the aqueous solution was extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (5% NEt_3 in Hexane/AcOEt = 20/1) to give **3e** (1.36 g, 87%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.96-3.02 (m, 2H), 3.65-3.67 (m, 2H), 7.19 (s, 1H), 7.31-7.42 (m, 3H), 7.66 (d, J = 4.5 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 48.8, 55.4, 121.7, 128.3, 128.5, 129.1, 129.6, 134.7.

(*Z*)-4-(Benzyloxy)but-2-en-1-ol[S7] (SI-9)

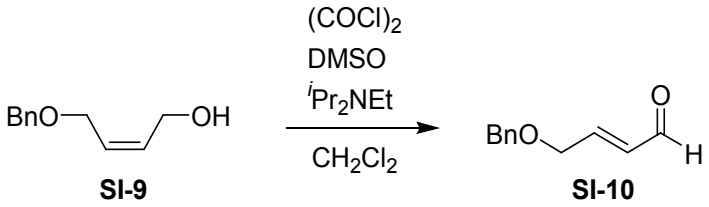


SI-8 **SI-9**

NaH (60% in mineral oil, 1.26 g, 31.5 mmol) was added very carefully to a solution of *cis*-2-butene-1,4-diol (**SI-8**) (7.29 mL, 89.4 mmol) in THF (32 mL) at 0 °C. The resulting mixture was stirred at room temperature for 1.5 h and then benzyl bromide (3.56 mL, 30.0 mmol) was added. The reaction mixture was refluxed for 1 h and then cooled to ambient temperature. The reaction was acidified with 1 *N* HCl carefully and the resulting two phases were separated. The aqueous phase was extracted three times with CH_2Cl_2 and the combined organic phases were dried over $MgSO_4$. After removal of solvent under reduced pressure the residue was purified by silica gel column chromatography (Hexane/AcOEt = 10/1 ~ 5/1) to give **SI-9** (5.27 g, 98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.82 (brs, 1H), 4.08 (d, *J* = 5.7 Hz, 2H), 4.11 (d, *J* = 6.3 Hz, 2H), 4.51 (s, 2H), 5.67-5.83 (m, 2H), 7.27-7.40 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 58.2, 65.7, 72.4, 127.6, 127.8, 127.9, 128.5, 132.6, 138.0.

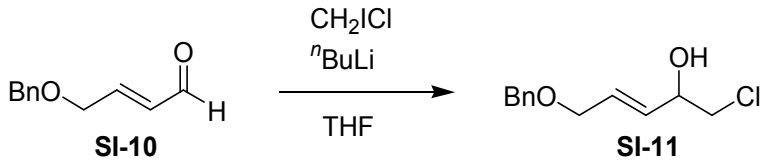
(*E*)-4-(Benzyloxy)but-2-enal[S8] (SI-10)



To a solution oxalyl chloride (3.8 mL, 44 mmol) in CH_2Cl_2, DMSO (6.3 mL, 89 mmol) was added dropwise at -78 °C. The mixture was stirred for 20 min and then was added a solution of **SI-9** (5.3 g, 30 mmol, in 5.0 mL of CH_2Cl_2) dropwise and then stirred for 1 h. After that, diisopropylethylamine (31 mL, 177 mmol) was added slowly and stirred for 20 min and then allowed to warm up to room temperature by itself. The reaction mixture was washed with ice-cold 1 *N* HCl and then dried over Na_2SO_4. The solution of crude product was directly used in the next step.

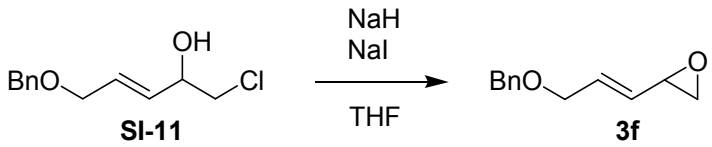
To the solution obtained in the proceeding step was added catalytic amount of conc. HCl. The solution was stirred at room temperature for 30 min and quenched with saturated aq. $NaHCO_3$. The organic layer was washed again with water until pH 7, and then dried over Na_2SO_4. The solution then filtered and concentrated *in vacuo*. Silica gel column chromatography afforded **SI-10** (3.30 g, 73%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.25 (dd, *J* = 3.9 and 1.8 Hz, 2H), 4.56 (s, 2H), 6.39 (ddt, *J* = 15.6, 8.1 and 1.8 Hz, 1H), 6.81 (dt, *J* = 15.6 and 3.9 Hz, 1H), 7.26-7.39 (m, 5H), 9.55 (d, *J* = 8.1 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 68.6, 72.9, 127.7, 127.9, 128.5, 131.6, 137.6, 153.3, 193.3.

(*E*)-5-(Benzyloxy)-1-chloropent-3-en-2-ol (SI-11)



SI-11 was prepared from **SI-10** (1.76 g, 10.0 mmol) in a similar to a manner as **SI-7** (1.87 g, 82%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.74 (brs, 1H), 3.49 (dd, *J* = 11.1 and 7.2 Hz, 1H), 3.60 (dd, *J* = 11.1 and 4.2 Hz, 1H), 4.05 (d, *J* = 5.4 Hz, 2H), 4.35 (dd, *J* = 9.9 and 5.7 Hz, 1H), 4.53 (s, 2H), 5.77 (dd, *J* = 15.6 and 5.7 Hz, 1H), 5.90-5.99 (m, 1H), 7.28-7.39 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.4, 69.7, 71.6, 72.4, 127.7, 127.8, 128.5, 129.9, 130.8, 138.0.

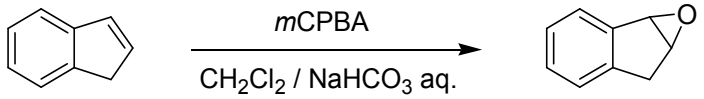
(*E*)-2-(3-(Benzyloxy)prop-1-en-1-yl)oxirane (3f)



3f was prepared from **SI-11** (1.87 g, 8.25 mmol) in a similar to a manner as **3e** (1.46 g, 93%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64-2.67 (m, 1H), 2.94-2.97 (m, 1H), 3.35-3.40 (m, 1H), 4.05 (dd, *J* = 5.4 and 1.2 Hz, 2H), 4.53 (s, 2H), 5.44-5.52 (m, 1H), 6.08 (dt, *J* = 15.6 and 5.4 Hz, 1H), 7.27-7.36 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 48.8, 51.8, 69.7, 72.3, 127.6, 127.7, 128.4, 130.4, 132.1, 138.1.
HRMS (APCI-TOF) Calcd for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072, Found: 191.1065.
IR (neat) 699, 733, 842, 964, 1106, 1249, 1358, 1453, 2852, 3029 cm^{-1}

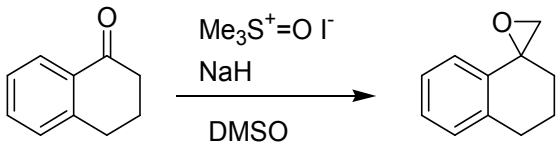
6,6a-Dihydro-1a*H*-indeno[1,2-*b*]oxirene[S9] (3g)



SI-12 **3g**

To a stirred solution of indene (**SI-12**) (1.16 mL, 10.0 mmol) in CH_2Cl_2-saturated aq. $NaHCO_3$ (200 mL, 1:1) was added *m*-CPBA (2.47 g, 10.0 mmol) in small portions over a 10-min period at 0 °C. After stirring for 5 h at room temperature, *m*-CPBA (2.47 g, 10.0 mmol) was added in small portions to the mixture at 0 °C over second 10-min period. The mixture was stirred at ambient temperature for 5 h and the organic layer was separated, washed with saturated aq. $Na_2S_2O_3$ and water, and dried over Na_2SO_4. The crude product was purified by Kugelrohr distillation to give **3g** (0.50 g, 38%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.00 (dd, *J* = 18.0 and 3.0 Hz, 1H), 3.30 (d, *J* = 18.0 Hz, 1H), 4.16 (t, *J* = 3.0 Hz, 1H), 4.31 (t, *J* = 1.2 Hz, 1H), 7.23-7.35 (m, 3H), 7.55 (d, *J* = 6.9 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 34.7, 57.7, 59.1, 125.2, 126.1, 126.3, 128.6, 141.0, 143.6.

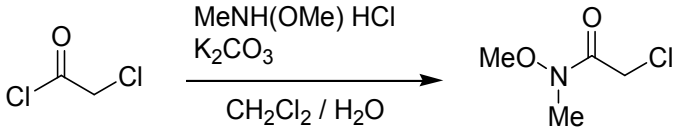
3,4-Dihydro-2H-spiro[naphthalene-1,2'-oxirane][S10] (3h)



SI-13 **3h**

Trimethylsulphoxonium iodide (4.4 g, 20 mmol) was added rapidly to a well stirred suspension of NaH (60% in mineral oil, 0.80 g, 20 mmol) in DMSO (10 mL) at 0 °C. After the addition, stirring continued for a further 15 min and α-tetralone (**SI-13**) (1.3 mL, 10 mmol) was then introduced. The reaction mixture was allowed to warm to room temperature and it was then heated to refluxed for 1 h and finally set aside to cool overnight. The next day water was added and the product extracted three times with Et_2O. The combined organic layers were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (5% NEt_3 in Hexane/AcOEt = 20/1) to give **3h** (1.00 g, 63%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84-1.91 (m, 1H), 1.97-2.23 (m, 3H), 2.91-2.97 (m, 2H), 3.03 (d, *J* = 12.3 Hz, 1H), 3.05 (d, *J* = 12.3 Hz, 1H), 7.13-7.28 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 29.7, 32.0, 56.6, 59.0, 123.5, 126.4, 127.6, 128.7, 135.7, 139.5.
HRMS (APCI-TOF) Calcd for $C_{11}H_{11}O$ $[M-H]^-$: 159.0810, Found: 159.0805.
IR (neat) 753, 916, 1038, 1453, 1487, 1603, 1725, 2866, 3035 cm^{-1}

2-Chloro-*N*-methoxy-*N*-methylacetamide[S11] (SI-15)



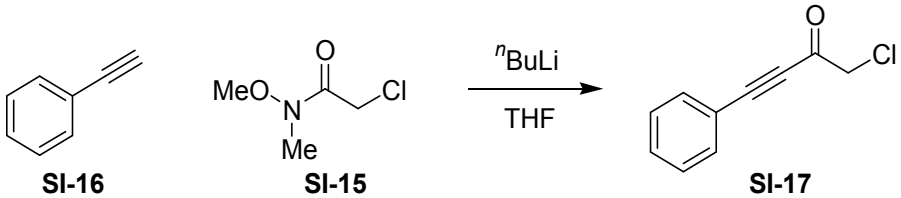
SI-14 **SI-15**

Chloroacetyl chloride (**SI-14**) (2.86 g, 36.0 mmol) was dissolved in CH_2Cl_2 (20 mL) and this solution was added to a solution of the hydrochloride salt of *N,O*-dimethylhydroxyl- amine (2.93 g, 30.0 mmol) in water (20 mL). To the resulting biphasic solution was slowly added K_2CO_3 (4.97 g, 30.0 mmol) and the reaction mixture was allowed to stir for 12 h. The solution was then extracted three times with CH_2Cl_2, and the combined organic extracts were dried over Ns_2SO_4 and concentrated to furnish **SI-15** (4.13 g, >99%). The product was used without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (s, 3H), 3.65 (s, 3H), 4.15 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 32.5, 40.9, 61.6, 167.3.

1-Chloro-4-phenylbut-3-yn-2-one[S12] (SI-17)



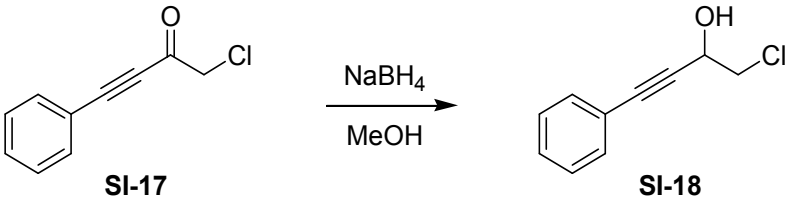
SI-16 **SI-15** **SI-17**

To a stirred solution of phenyl acetylene (**SI-16**) (1.94 mL, 15 mmol) in THF (30 mL) cooled at 0 °C was added dropwise ^{n}BuLi (1.65 M in hexane, 9.1 mL, 15 mmol) and stirred for 30 min. To the so generated lithium acetylide, the solution of Weinreb amide **SI-15** (1.38 g, 10 mmol) in THF (20 mL) was added dropwise at the same temperature and the reaction mixture stirred for another 30 min. The reaction mixture was quenched 1 *N* HCl. The solution was then extracted three times with Et_2O and the combined organic extracts were dried over Ns_2SO_4. The solvent was removed under reduced pressure and the crude material was purified by silica gel column chromatography (Hexane/AcOEt = 20/1 ~ 10/1) to furnish **SI-17** (1.53 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31(s, 3H), 7.37-7.42 (m, 2H), 7.46-7.52 (m, 1H), 7.58-7.62 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 49.6, 85.6, 95.4, 119.2, 128.8, 131.5, 133.4, 178.9.

1-Chloro-4-phenylbut-3-yn-2-ol (SI-18)



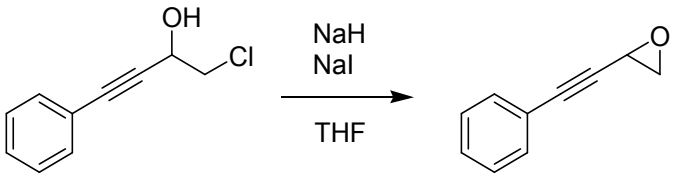
SI-17 **SI-18**

To a stirred solution of **SI-17** (1.53 g, 8.5 mmol) in MeOH(50 mL), $NaBH_4$ (0.48 g, 12.8 mmol) was added at 0 °C. The resulting solution was stirred at room temperature for 2 h. The reaction was quenched with water and the solution was extracted three times with Et_2O. The combined organic extracts were washed with water and brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (hexane/AcOEt = 10/1 ~ 5/1) to furnish **SI-18** (1.49 g, 97%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.00 (brs, 1H), 3.71-3.83 (m, 2H), 4.83 (dd, J = 6.3 and 4.5 Hz, 1H), 7.31-

7.35 (m, 3H), 7.44-7.47 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.0, 63.1, 86.1, 86.3, 121.8, 128.4, 128.9, 131.9.

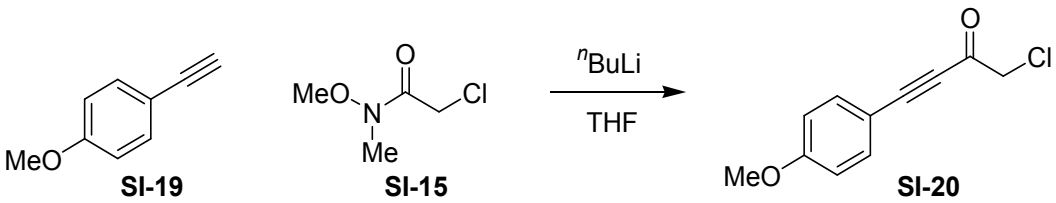
2-(Phenylethynyl)oxirane (3i)



SI-18 **3i**

3i was prepared from **SI-18** (0.84 g, 4.7 mmol) in a similar to a manner as **3e** (0.51 g, 76%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (d, *J* = 3.3 Hz, 2H), 3.57 (t, *J* = 3.3 Hz, 1H), 7.28-7.34 (m, 3H), 7.44-7.47 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 40.2, 49.1, 83.4, 85.9, 122.0, 128.4, 128.8, 131.9.
HRMS (APCI-TOF) Calcd for $C_{10}H_9O$ $[M+H]^+$: 145.0653, Found: 145.0647.
IR (neat) 755, 830, 926, 1227, 1370, 1486, 1964, 2230, 2996, 3058 cm^{-1}

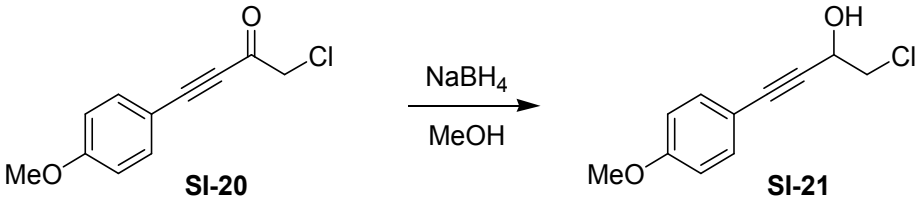
1-Chloro-4-(4-methoxyphenyl)but-3-yn-2-one (SI-20)



SI-19 **SI-15** **SI-20**

SI-20 was prepared from *p*-methoxyphenyl acetylene (**SI-19**) (0.66 g, 5.0 mmol) in a similar to a manner as **SI-17** (0.53 g, 51%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.25 (s, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.6, 55.5, 85.6, 96.7, 110.7, 114.5, 135.5, 162.2, 178.6.

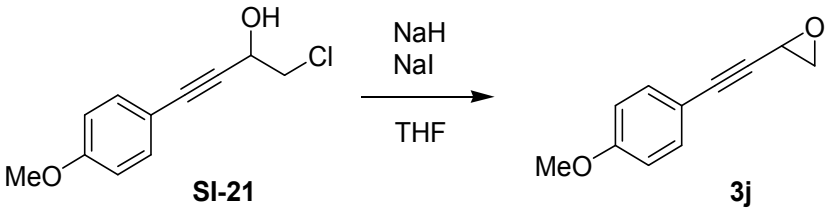
1-Chloro-4-(4-methoxyphenyl)but-3-yn-2-ol (SI-21)



SI-20 **SI-21**

SI-21 was prepared from **SI-20** (0.53 g, 2.6 mmol) in a similar to a manner as **SI-18** (0.54 g, >99%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67 (brs, 1H), 3.69-3.83 (m, 2H), 3.81 (s, 3H), 4.77-4.84 (m, 1H), 6.81-6.85 (m, 2H), 7.36-7.40 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.2, 55.3, 63.1, 84.7, 86.4, 113.9, 114.0, 133.4, 160.0.

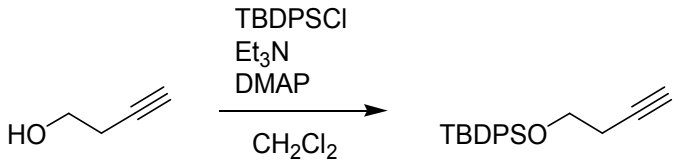
2-((4-Methoxyphenyl)ethynyl)oxirane (3j)



SI-21 **3j**

3j was prepared from **SI-21** (0.54 g, 2.6 mmol) in a similar to a manner as **3e** (0.37 g, 83%).
^{1}H NMR (300 MHz, C_6D_6) δ 2.35 (ddd, *J* = 6.3, 3.9 and 0.6 Hz, 1H), 2.63 (dd, *J* = 6.3 and 2.4 Hz, 1H), 3.17 (s, 3H), 3.21 (dd, *J* = 3.9 and 2.4 Hz, 1H), 6.52-6.56 (m, 2H), 7.30-7.35 (m, 2H).
^{13}C NMR (75 MHz, C_6D_6) δ 40.2, 48.5, 54.8, 83.7, 85.7, 114.4, 114.7, 133.7, 160.4.
HRMS (APCI-TOF) Calcd for $C_{11}H_{11}O_2$ $[M+H]^+$: 175.0759, Found: 175.0761.
IR (neat) 837, 1247, 1507, 1609, 2046, 2230, 2545, 2839, 2996 cm^{-1}

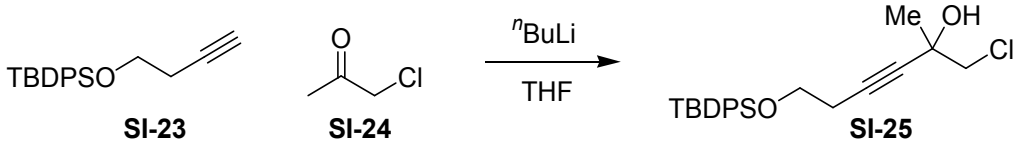
(But-3-yn-1-yloxy)(*tert*-butyl)diphenylsilane (SI-23)



SI-22 **SI-23**

To a stirred solution of 3-butyn-1-ol (**SI-22**) (0.23 mL, 3.0 mmol) in CH_2Cl_2 (12 mL), triethylamine (0.83 mL), DMAP (0.11 g, 0.9 mmol) and TBDPSCl (0.92 mL, 3.6 mmol) was added at 0 °C and stirred for 12 h. The reaction mixture was quenched with saturated aq. $NaHCO_3$ and the solution was extracted three times with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to furnish **SI-23** (0.93 g, .99%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.97 (t, *J* = 2.7 Hz, 1H), 2.49 (td, *J* = 7.2 and 2.7 Hz, 2H), 3.83 (t, *J* =7.2 Hz, 2H), 7.39-7.49 (m, 6H), 7.71-7.75 (m, 4H).

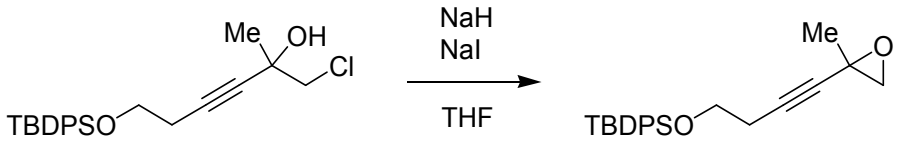
6-((*tert*-Butyldiphenylsilyl)oxy)-1-chloro-2-methylhex-3-yn-2-ol (SI-25)



SI-23 **SI-24** **SI-25**

SI-25 was prepared from **SI-23** (0.98 g, 3.2 mmol) and chloroacetone (**SI-24**) (0.28 mL, 3.5 mmol) in a similar to a manner as **SI-17** (0.71 g, 56%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.55 (s, 3H), 2.51 (t, *J* = 6.9 Hz, 2H), 2.51 (brs, 1H), 3.55 (d, *J* = 10.8 Hz, 1 H), 3.64 (d, *J* = 10.8 Hz, 1H), 3.79 (t, *J* = 6.9 Hz, 2H), 7.38-7.48 (m, 6H), 7.71 (dd, *J* = 7.5 and 1.8 Hz, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 22.8, 26.8, 27.1, 54.3, 62.2, 67.5, 82.0, 82.5, 127.7, 129.8, 133.6, 135.6.

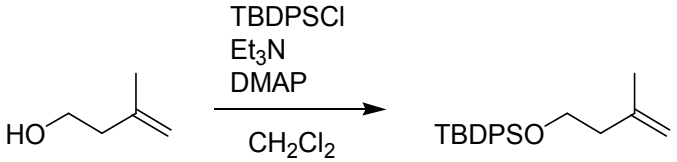
***tert*-Butyl((4-(2-methyloxiran-2-yl)but-3-yn-1-yl)oxy)diphenylsilane (3k)**



SI-25 **3k**

3k was prepared from **SI-25** (0.71 g, 1.8 mmol) in a similar to a manner as **3e** (0.65 g, >99%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.52 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 2.71 (d, *J* = 5.7 Hz, 1H), 2.95 (d, *J* = 5.7 Hz, 1H), 3.76 (t, *J* = 6.9 Hz, 2H), 7.37-7.47 (m, 6H), 7.69 (dd, *J* = 7.5 and 1.8 Hz, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 22.8, 23.2, 26.8, 47.4, 55.5, 62.2, 80.0, 80.6, 127.7, 129.7, 133.5, 135.6.
HRMS (APCI-TOF) Calcd for $C_{23}H_{28}NaO_2Si$ $[M+Na]^+$: 387.1756, Found: 387.1766.
IR (neat) 701, 912, 1111, 1432, 1896, 1958, 2245, 2852, 2948, 3051 cm^{-1}

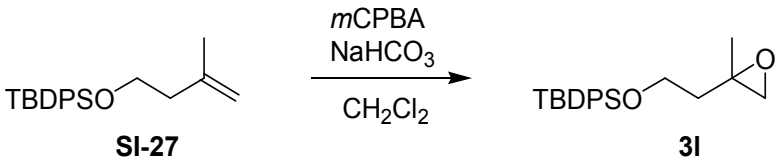
***tert*-Butyl((3-methylbut-3-en-1-yl)oxy)diphenylsilane (SI-27)**



SI-26 **SI-27**

SI-27 was prepared from 3-methyl-3-buten-1-ol (**SI-26**) (0.38 mL, 3.9 mmol) in a similar to a manner as **SI-23** (1.40 g, >99%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.81 (s, 3H), 2.42 (t, *J* = 6.9 Hz, 2H), 3.91 (t, *J* = 6.9 Hz, 2H), 4.83 (s, 1H), 4.89 (s, 1H), 7.47-7.56 (m, 6H), 7.83 (dd, *J* = 7.5 and 2.1 Hz, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 22.9, 27.0, 41.0, 62.9, 111.9, 127.8, 129.7, 134.1, 135.7, 143.0.

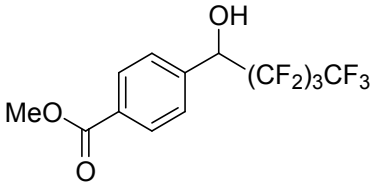
***tert*-Butyl((2-(2-methyloxiran-2-yl)ethoxy)diphenylsilane (3l)**



SI-27 **3l**

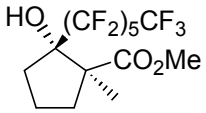
To a heterogeneous solution of $NaHCO_3$ (0.98 g, 11.7 mmol) and **SI-27** (1.27 g, 3.9 mmol) in CH_2Cl_2 (13 mL), *m*-CPBA (0.40 g, 4.7 mmol) was added at 0 °C. After stirring at room temperature for 12 h, the reaction was quenched with saturated aq. $Na_2S_2O_3$ at 0 °C. The organic layer was separated, washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to furnish **3l** (0.40 g, 30%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.35 (s, 3H), 1.70-1.79 (m, 1H), 1.91-2.00 (m, 1H), 3.82 (t, *J* = 6.3 Hz, 2H), 7.39-7.49 (m, 6H), 7.70-7.73 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 21.5, 26.9, 39.7, 54.2, 55.5, 60.7, 127.7, 1289.7, 133.7, 135.6.
HRMS (APCI-TOF) Calcd for $C_{21}H_{28}NaO_2Si$ $[M+Na]^+$: 363.1756, Found: 363.1751.
IR (KBr) 702, 936, 1101, 1383, 1581, 1829, 2852, 2935, 3072 cm^{-1}

Methyl 4-(2,2,3,3,4,4,5,5,5-nonafluoro-1-hydroxypentyl)-benzoate (2m)



^{1}H NMR (300 MHz, $CDCl_3$) δ 3.09 (brs, 1H), 3.92 (s, 3H), 5.28 (dd, J_{HF} = 17.1 and 6.0 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 52.5, 72.0 (dd, J_{CF} = 28.5 and 22.5 Hz), 104.6-130.6 (m, $(CF_2)_3CF_3$), 128.2, 129.9, 131.3, 138.9, 166.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 8.3 Hz, 3F), -117.3-(-127.5) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{13}H_8F_9O_3$ $[M-H]^-$: 383.0330, Found: 383.0329.
IR (KBr) 537, 723, 888, 1211, 1307, 1444, 1706, 1953, 2970, 3458 cm^{-1}

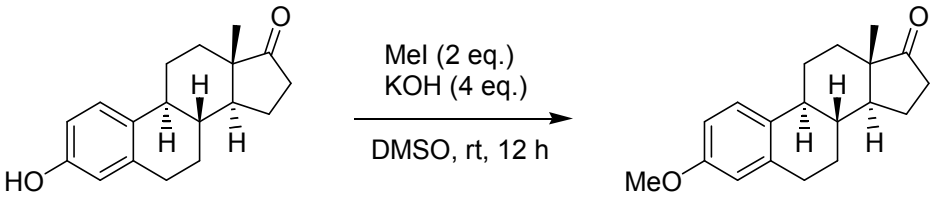
Methyl 2-hydroxy-1-methyl-2-(perfluorohexyl)cyclopentanecarboxylate (2n)



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (s, 3H), 1.71-1.81 (m, 1H), 1.84-2.20 (m, 4H), 2.42- 2.52 (m, 1H), 2.45 (s, 1H), 3.69 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 20.6, 33.2 (t, J_{CF} = 5.3 Hz), 52.3, 56.8, 85.6 (dd, J_{CF} = 26.3 and 21.0 Hz), 106.5-123.1 (m, $(CF_2)_5CF_3$), 175.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.2 Hz, 3F), -114.7-(-115.9) (m, 1F), -117.5-(-118.6) (m, 1F), -119.5-(-121.4) (m, 2F), -121.7-(-121.8) (brm, 2F), -122.8 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{14}H_{12}F_{13}O_3$ $[M-H]^-$: 475.0579, Found: 475.0590.
IR (KBr) 644, 855, 1005, 1141, 1235, 1364, 1467, 1717, 2968, 3477 cm^{-1}

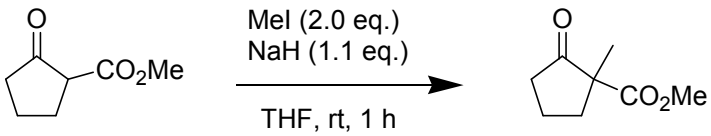
Synthesis of non-commercially available ketones

3-*O*-Methylestrone (1a)[S2]



SI-1 **1a**

Methyl 1-methyl-2-oxocyclopentanecarboxylate (1n)[S3]



SI-2 **1n**

Procedure for Scheme 4 (Perfluoroalkyl Grignard reagent)

To a solution of ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol) in Et_2O (2.4 mL) was added perfluorohexyl iodide (78 μL, 0.36 mmol) at -78 °C . After stirring at -78 °C for 1 h, Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) and 1,4-dioxane (0.23 μL, 0.27 mmol) was added and the reaction mixture was stirred at -20 °C for 2 h before benzaldehyde (**1b**) (20 μL, 0.20 mmol) was added. After stirring at room temperature for 1 h, the reaction was quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The yield of 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenylheptan-1-ol (**2b**) (56%) was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Procedure for Scheme 4 (Perfluoroalkyl lithium reagent)

To a solution of MeLi (1.6 M in Et_2O, 0.15 mL, 0.24 mmol) in Et_2O (2.4 mL) was added perfluorohexyl iodide (78 μL, 0.36 mmol) at -78 °C. After stirring at -78 °C for 15 min, Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) was added and the reaction mixture was stirred at -20 °C for 2 h before benzaldehyde (**1b**) (20 μL, 0.20 mmol) was added. After stirring at room temperature for 1 h, the reaction was quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and the solvent was removed *in vacuo*. The crude mixture was analyzed by ^{1}H NMR.

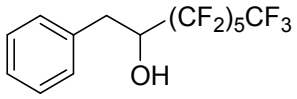
Procedure for Scheme 6

To a solution of Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) in Et_2O (2.4 mL) was added ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol), 1,4-dioxane (23 μL, 0.27 mmol) and perfluorohexyl iodide (78 μL, 0.36 mmol) in this order at -78 °C. After stirring at -78 °C for 1 h, styrene oxide (**3a**) (23 μL, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and removed solvent *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to give 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloctan- 2-ol (**4a**) (37.9 mg, 43%) and 2-chloro-2-phenylethanol[S4] (**6**) (3.1 mg, 10%).

General procedure for the perfluoroalkylation of epoxides

To a solution of Cp_2ZrCl_2 (70.2 mg, 0.24 mmol) in Et_2O (2.4 mL) was added ^{n}BuMgCl (2.0 M in Et_2O, 0.12 mL, 0.24 mmol) and perfluorohexyl iodide (78 μL, 0.36 mmol). After stirring at -78 °C for 1 h, 1,4-dioxane (23 μL, 0.27 mmol) and methylaluminoxane (10 wt% in toluene, 0.16 mL, 0.24 mmol) were added. After the mixture was stirred at 0 °C for 2 min, styrene oxide (**3a**) (23 μL, 0.20 mmol) was added. The reaction mixture was stirred at room temperature for 1 h, quenched by 1 *N* HCl and extracted three times with Et_2O. Combined organic layer was dried over Na_2SO_4 and condensed *in vacuo*. The crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to give 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-phenyloctan- 2-ol (**4a**) (77.5 mg, 88%).

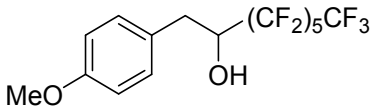
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-phenyloctan-2-ol (4a)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (d, *J* = 6.3 Hz, 1H), 2.87 (dd, *J* = 14.1 and 10.5 Hz, 1H), 3.15 (d, *J* = 14.1 Hz, 1H), 4.26-4.38 (m, 1H), 7.27-7.42 (m, 5H).

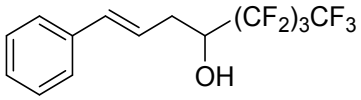
^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5, 71.1 (dd, J_{CF} = 28.5 and 21.8 Hz), 104.2-123.4 (m, $(CF_2)_5CF_3$), 127.2, 128.8, 129.5, 135.7.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.1 (t, J_{FF} = 9.9 Hz, 3F), -119.9-(-127.6) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{14}H_8F_{13}O$ $[M-H]^-$: 439.0368, Found: 439.0353.
IR (neat) 651, 706, 1147, 1201, 1249, 1358, 1460, 1500, 3035, 3531 cm^{-1}

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecaflioro-1-(4-methoxy-phenyl)octan-2-ol (4b)



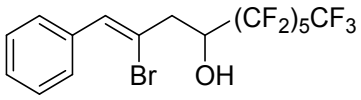
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (d, J = 6.3 Hz, 1H), 2.82 (dd, J = 14.1 and 10.2 Hz, 1H), 3.07 (d, J = 14.1 Hz, 1H), 3.80 (s, 3H), 4.28-4.31 (m, 1H), 6.88 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6, 55.3, 71.1 (dd, J_{CF} = 28.5 and 23.3 Hz), 100.2-123.4 (m, $(CF_2)_5CF_3$), 114.3, 127.3, 130.6, 158.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.6 Hz, 3F), -119.8-(-127.3) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{15}H_{10}F_{13}O_2$ $[M-H]^-$: 469.0473, Found: 469.0488.
IR (neat) 748, 885, 967, 1124, 1131, 1240, 1357, 2921, 3030, 3454 cm^{-1}

(*E*)-5,5,6,6,7,7,8,8,8-Nonafluoro-1-phenyl-oct-1-en-4-ol (4c)



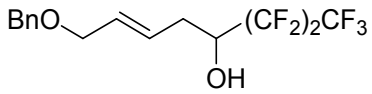
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (d, J = 7.2 Hz, 1H), 2.58-2.68 (m, 1H), 2.72-2.79 (m, 1H), 4.21-4.35 (m, 1H), 6.18-6.28 (m, 1H), 6.61(d, J = 15.6 Hz, 1H), 7.26-7.42 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 33.2, 93.2 (dd, J_{CF} = 27.8 and 22.5 Hz), 107.1-119.8 (m, $(CF_2)_3CF_3$), 122.7, 126.3, 127.9, 128.7, 135.3, 136.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.0 Hz, 3F), -120.1-(-127.6) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{14}H_{10}F_9O$ $[M-H]^-$: 365.0588, Found: 365.0584.
IR (KBr) 748, 885, 967, 1124, 1131, 1240, 1357, 2921, 3030, 3454 cm^{-1}

(*Z*)-2-Bromo-5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-1-phenyldec-1-en-4-ol (4d)



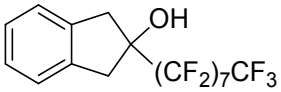
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (d, J = 6.3 Hz, 1H), 2.92-3.07 (m, 2H), 4.57-4.71 (m, 1H), 6.95 (s, 1H), 7.30-7.41 (m, 3H), 7.60 (d, J = 6.9 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 43.5, 68.2 (dd, J_{CF} = 28.9 and 23.3 Hz), 107.0-123.2 (m, $(CF_2)_5CF_3$), 119.5, 128.4, 128.5, 129.1, 132.9, 135.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.8 (t, J_{FF} = 9.6 Hz, 3F), -119.7-(-127.3) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{16}H_9BrF_{13}O$ $[M-H]^-$: 542.9629, Found: 545.9630.
IR (neat) 692, 753, 916, 1147, 1242, 1317, 1371, 1446, 3056, 3410 cm^{-1}

(*E*)-8-(Benzyloxy)-1,1,1,2,2,3,3-heptafluorooct-6-en-4-ol (4e)



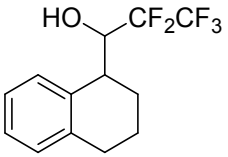
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35-2.45 (m, 1H), 2.50-2.57 (m, 1H), 2.78 (d, J = 6.6 Hz, 1H), 4.53 (s, 3H), 5.68-5.86 (m, 2H), 7.28-7.39 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 32.4, 68.9 (dd, J_{CF} = 28.5 and 23.3 Hz), 72.5, 106.1-123.5 (m, $(CF_2)_2CF_3$), 127.1, 127.8, 127.8, 128.5, 131.7, 137.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 10.2 Hz, 3F), -121.0 (dd, J_{FF} = 282.4 Hz and J_{FH} = 5.5 Hz, 1F), -124.7-(-128.3) (m, 3F).
HRMS (APCI-TOF) Calcd for $C_{15}H_{14}F_7O_2$ $[M-H]^-$: 359.0882, Found: 359.0871.
IR (neat) 733, 916, 978, 1114, 1228, 1351, 1460, 2859, 2933, 3395 cm^{-1}

2-(Perfluorooctyl)-2,3-dihydro-1*H*-inden-2-ol (4f)



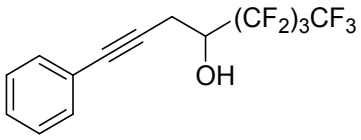
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (s, 1H), 3.10 (d, J = 16.8 Hz, 1H), 3.58 (d, J = 16.8 Hz, 1H), 7.24-7.31 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 42.8, 84.0 (t, J_{CF} = 25.5 Hz), 104.8-120.7 (m, $(CF_2)_7CF_3$), 125.2, 127.5, 138.4.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 9.6 Hz, 3F), -118.4 (s, 2F), -119.4 (s, 2F), -121.8-(-121.8) (brm, 6F), -122.8 (s, 2F), -126.2 (s, 2F).
HRMS (APCI-TOF) Calcd for $C_{17}H_8F_{17}O$ $[M-H]^-$: 551.0304, Found: 551.0300.
IR (KBr) 659, 753, 1072, 1208, 1480, 1725, 1935, 3035, 3579 cm^{-1}

2,2,3,3,3-Pentafluoro-1-(1,2,3,4-tetrahydronaphthalen-1-yl)propan-1-ol (4g)



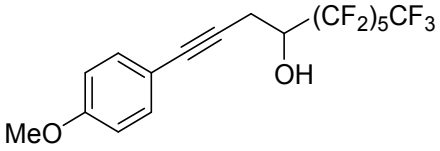
Physical data of mixture of the two isomers (52:48)
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59-1.71 (m, 1H), 1.87-2.09 (m, 4H), 2.68-2.92 (m, 2H), 3.38-3.43 (brm, 1H), 4.02-4.15 (m, 1H, major), 4.57-4.69 (m, 1H, minor), 7.12-7.24 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 21.8, 22.6 (d, J_{CF} = 3.8 Hz), 28.1 (d, J_{CF} = 3.0 Hz), 28.5, 29.9, 37.5, 38.2, 71.7 (dd, J_{CF} = 28.5 and 22.5 Hz), 72.3 (dd, J_{CF} = 27.0 and 19.5 Hz), 110.4-125.0 (m, CF_2CF_3), 126.0, 126.6, 126.7, 127.5, 127.9, 129.9, 130.2, 130.9 (d, J_{CF} = 3.8 Hz), 132.3, 135.1, 139.1, 140.2.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.8 (s, 3F, minor), -82.8 (s, 3F, major), -120.1 (d, J_{FF} = 276.0 Hz, 1F, major), -123.0 (d, J_{FF} = 276.1 Hz, 1F, minor), -127.9 (dd, J_{FF} = 276.1 Hz and J_{FH} = 22.3 Hz, 1F, minor), -131.6 (dd, J_{FF} = 276.0 Hz and J_{FH} = 22.4 Hz, 1F, major).
HRMS (APCI-TOF) Calcd for $C_{13}H_{12}F_5O$ $[M-H]^-$: 279.0808, Found: 279.0806.
IR (neat) 740, 1038, 1120, 1195, 1244, 1453, 1493, 2872, 2947, 3538 cm^{-1}

5,5,6,6,7,7,8,8,8-Nonafluoro-1-phenyloct-1-yn-4-ol (4h)



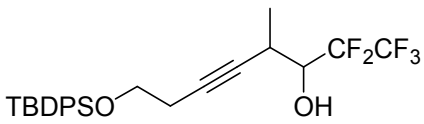
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.69 (d, J = 6.9 Hz, 1H), 2.86-3.02 (m, 2H), 4.38-4.44 (m, 1H), 7.29-7.45 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8 (t, J_{CF} = 0.4 Hz), 68.3 (dd, J_{CF} = 29.3 and 22.5 Hz), 82.5, 84.4, 99.8-129.5 (m, $(CF_2)_3CF_3$), 122.6, 128.5, 128.7, 131.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.9 (t, J_{FF} = 8.3 Hz, 3F), -119.6-(-128.5) (m, 6F).
HRMS (APCI-TOF) Calcd for $C_{14}H_8F_9O$ $[M-H]^-$: 363.0431, Found: 363.0433.
IR (neat) 755, 885, 1131, 1233, 1350, 1493, 1678, 2927, 3064, 3488 cm^{-1}

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-1-(4-methoxyphenyl)dec-1-yn-4-ol (4i)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.70 (d, J = 7.2 Hz, 1H), 2.84-3.00 (m, 2H), 3.91 (s, 3H), 4.34-4.46 (m, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 55.4, 68.3 (dd, J_{CF} = 29.3 and 22.5 Hz), 81.0, 84.4, 106.4-129.0 (m, $(CF_2)_5CF_3$), 114.1, 114.7, 133.3, 159.9.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.8 (t, J_{FF} = 9.3 Hz, 3F),-119.8-(-128.3) (m, 10F).
HRMS (APCI-TOF) Calcd for $C_{17}H_{10}F_{13}O_2$ $[M-H]^-$: 493.0473, Found: 493.0459.
IR (KBr) 695, 826, 1032, 1245, 1506, 1603, 1719, 2852, 2970, 3313 cm^{-1}

8-((*tert*-Butyldiphenylsilyl)oxy)-1,1,1,2,2-pentafluoro-4-methyloct-5-yn-3-ol (4j)

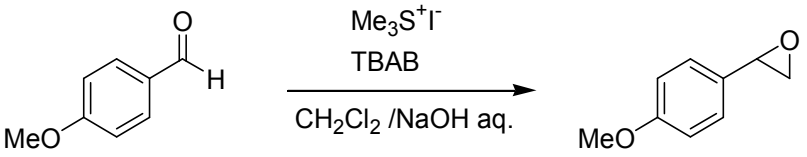


Major
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.28 (d, J = 7.2 Hz, 3H), 2.38-2.46 (m, 3H), 2.98-3.01 (brm, 1H), 3.76 (t, J = 6.9 Hz, 2H), 4.07-4.19 (m, 1H), 7.37-7.47 (m, 6H), 7.67-7.70 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 19.2, 22.8, 26.7, 28.0, 62.5, 70.5 (dd, J_{CF} = 27.0 and 20.3 Hz), 80.6, 80.7, 109.5-124.6 (m, CF_2CF_3), 127.7, 129.7, 133.6, 135.6.
^{19}F NMR (282 MHz, $CDCl_3$) δ -82.7 (s, 3F), -121.4 (d, J_{FF} = 276.9 Hz, 1F), -130.0 (dd, J_{FF} = 276.9 Hz and J_{FH} = 20.9 Hz, 1F).
HRMS (APCI-TOF) Calcd for $C_{25}H_{28}F_5O_2Si$ $[M-H]^-$: 483.1779, Found: 483.1764.
IR (neat) 699, 733, 822, 1059, 1106, 1195, 1426, 2859, 2933, 3524 cm^{-1}
Minor
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.33 (d, J = 6.9 Hz, 3H), 2.44 (td, J = 6.6 and 2.1 Hz, 2H), 2.69 (d, J = 10.5 Hz, 1H), 3.03-3.06 (m, 1H), 3.75 (t, J = 6.6 Hz, 2H), 3.79-3.84 (m, 1H), 7.36-7.47 (m, 6H), 7.66-7.69 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 19.4, 22.8, 26.7, 27.3, 62.4, 70.8 (dd, J_{CF} = 28.5 and 21.8 Hz), 77.9,

83.5, 112.7-126.3 (m, CF_2CF_3), 127.7, 129.7, 133.5, 135.5.
^{19}F NMR (282 MHz, $CDCl_3$) δ -82.3 (s, 3F), -122.0 (d, J_{FF} = 276.1 Hz, 1F), -132.6 (dd, J_{FF} = 276.1 Hz and J_{FH} = 19.9 Hz, 1F).
HRMS (APCI-TOF) Calcd for $C_{25}H_{28}F_5O_2Si$ $[M-H]^-$: 483.1779, Found: 483.1761.
IR (neat) 699, 733, 1018, 1106, 1201, 1426, 1589, 2859, 2933, 3491 cm^{-1}

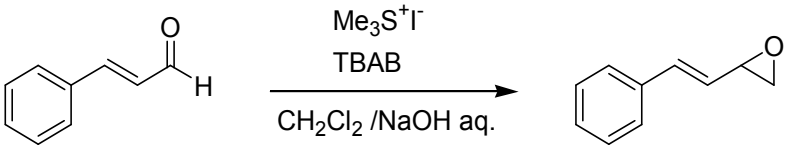
Synthesis of non-commercially available epoxides

_p_-Methoxystyrene oxide (3b)[S5]



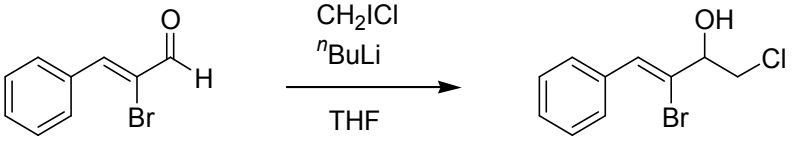
SI-3 **3b**

2-Styryloxirane (3d)[S7]



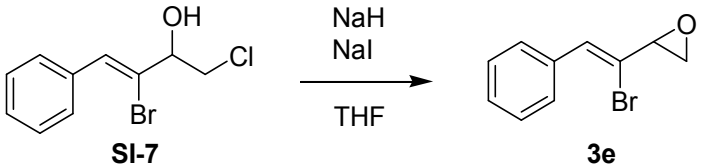
SI-5 **3d**

(*Z*)-3-Bromo-1-chloro-4-phenylbut-3-en-2-ol (SI-7)[S7]



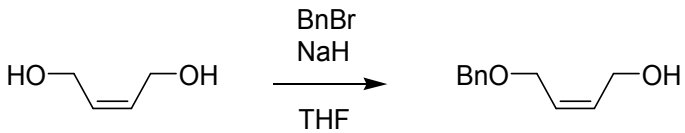
SI-6 **SI-7**

(*Z*)-2-(1-Bromo-2-phenylvinyl)oxirane (3e)[S7]



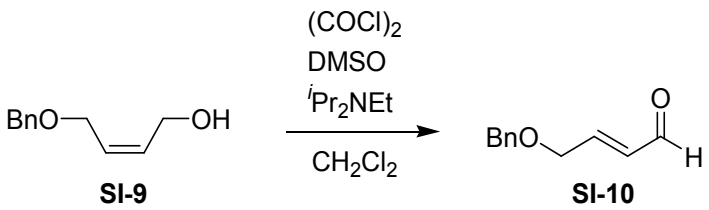
SI-7 **3e**

(*Z*)-4-(Benzyloxy)but-2-en-1-ol (SI-9)[S8]



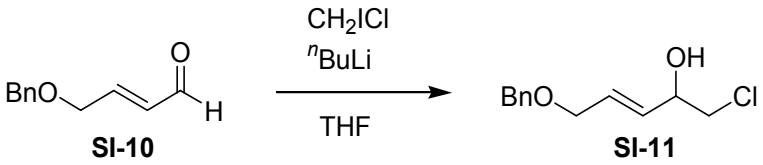
SI-8 **SI-9**

(*E*)-4-(Benzyloxy)but-2-enal (SI-10)[S9]



SI-9 **SI-10**

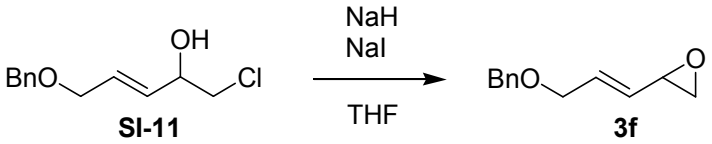
(*E*)-5-(Benzyloxy)-1-chloropent-3-en-2-ol (SI-11)



SI-10 **SI-11**

SI-11 was prepared from **SI-10** (1.76 g, 10.0 mmol) in a similar to a manner as **SI-7** (1.87 g, 82%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.74 (brs, 1H), 3.49 (dd, *J* = 11.1 and 7.2 Hz, 1H), 3.60 (dd, *J* = 11.1 and 4.2 Hz, 1H), 4.05 (d, *J* = 5.4 Hz, 2H), 4.35 (dd, *J* = 9.9 and 5.7 Hz, 1H), 4.53 (s, 2H), 5.77 (dd, *J* = 15.6 and 5.7 Hz, 1H), 5.90-5.99 (m, 1H), 7.28-7.39 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.4, 69.7, 71.6, 72.4, 127.7, 127.8, 128.5, 129.9, 130.8, 138.0.

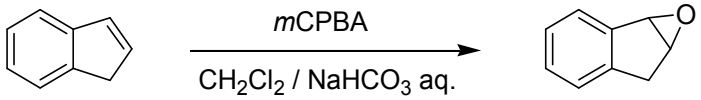
(*E*)-2-(3-(Benzyloxy)prop-1-en-1-yl)oxirane (3f)



SI-11 **3f**

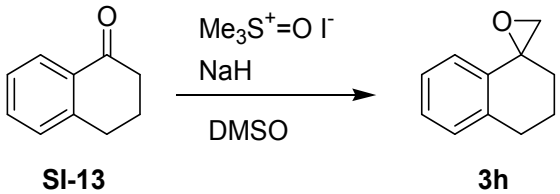
3f was prepared from **SI-11** (1.87 g, 8.25 mmol) in a similar to a manner as **3e** (1.46 g, 93%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64-2.67 (m, 1H), 2.94-2.97 (m, 1H), 3.35-3.40 (m, 1H), 4.05 (dd, *J* = 5.4 and 1.2 Hz, 2H), 4.53 (s, 2H), 5.44-5.52 (m, 1H), 6.08 (dt, *J* = 15.6 and 5.4 Hz, 1H), 7.27-7.36 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 48.8, 51.8, 69.7, 72.3, 127.6, 127.7, 128.4, 130.4, 132.1, 138.1.
HRMS (APCI-TOF) Calcd for $C_{12}H_{15}O_2$ $[M+H]^+$: 191.1072, Found: 191.1065.
IR (neat) 699, 733, 842, 964, 1106, 1249, 1358, 1453, 2852, 3029 cm^{-1}

6,6a-Dihydro-1a*H*-indeno[1,2-*b*]oxirene (3g)[S10]



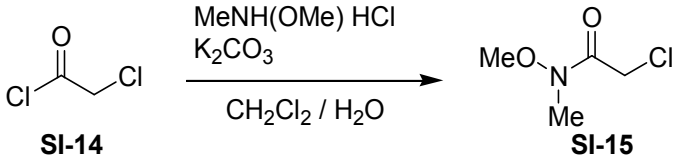
SI-12 **3g**

3,4-Dihydro-2H-spiro[naphthalene-1,2'-oxirane] (3h)[S11]



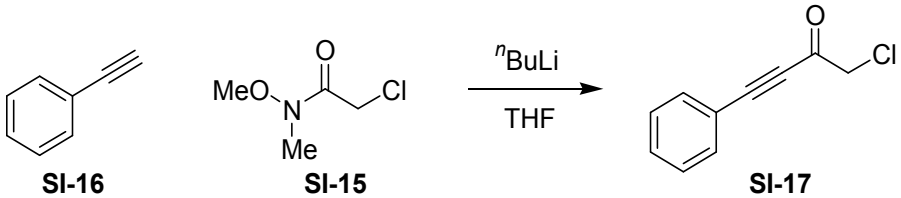
SI-13 **3h**

2-Chloro-*N*-methoxy-*N*-methylacetamide (SI-15)[S12]



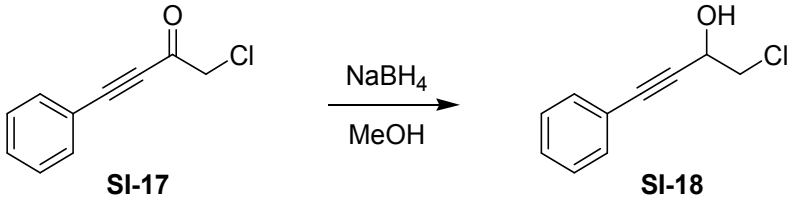
SI-14 **SI-15**

1-Chloro-4-phenylbut-3-yn-2-one (SI-17)[S13]



SI-16 **SI-15** **SI-17**

1-Chloro-4-phenylbut-3-yn-2-ol (SI-18)



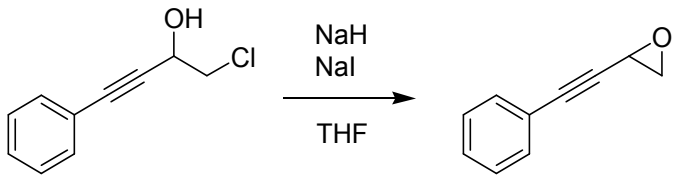
SI-17 **SI-18**

To a stirred solution of **SI-17** (1.53 g, 8.5 mmol) in MeOH(50 mL), $NaBH_4$ (0.48 g, 12.8 mmol) was added at 0 °C. The resulting solution was stirred at room temperature for 2 h. The reaction was quenched with water and the solution was extracted three times with Et_2O. The combined organic extracts were washed with water and brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (hexane/AcOEt = 10/1 ~ 5/1) to furnish **SI-18** (1.49 g, 97%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.00 (brs, 1H), 3.71-3.83 (m, 2H), 4.83 (dd, *J* = 6.3 and 4.5 Hz, 1H), 7.31-7.35 (m, 3H), 7.44-7.47 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 49.0, 63.1, 86.1, 86.3, 121.8, 128.4, 128.9, 131.9.

2-(Phenylethynyl)oxirane (3i)



SI-18 **3i**

3i was prepared from **SI-18** (0.84 g, 4.7 mmol) in a similar to a manner as **3e** (0.51 g, 76%).

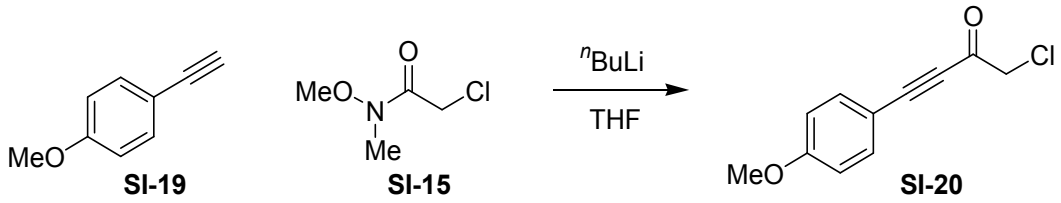
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (d, *J* = 3.3 Hz, 2H), 3.57 (t, *J* = 3.3 Hz, 1H), 7.28-7.34 (m, 3H), 7.44-7.47 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 40.2, 49.1, 83.4, 85.9, 122.0, 128.4, 128.8, 131.9.

HRMS (APCI-TOF) Calcd for $C_{10}H_9O$ $[M+H]^+$: 145.0653, Found: 145.0647.

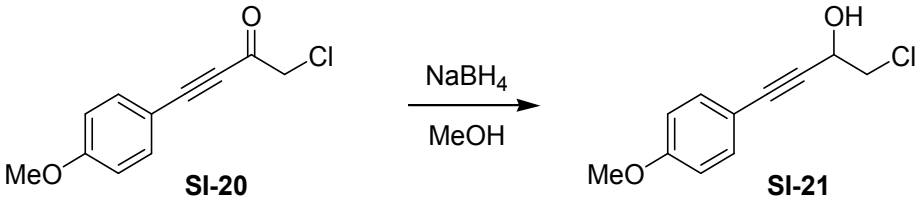
IR (neat) 755, 830, 926, 1227, 1370, 1486, 1964, 2230, 2996, 3058 cm^{-1}

1-Chloro-4-(4-methoxyphenyl)but-3-yn-2-one (SI-20)



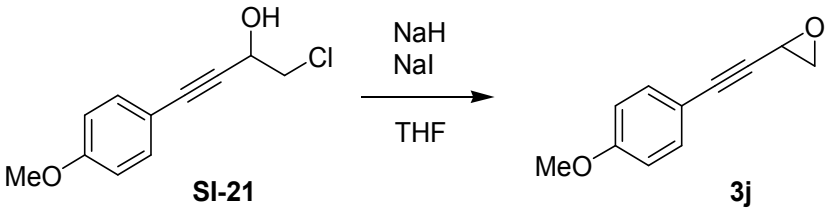
SI-20 was prepared from *p*-methoxyphenyl acetylene (**SI-19**) (0.66 g, 5.0 mmol) in a similar to a manner as **SI-17** (0.53 g, 51%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.25 (s, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.6, 55.5, 85.6, 96.7, 110.7, 114.5, 135.5, 162.2, 178.6.

1-Chloro-4-(4-methoxyphenyl)but-3-yn-2-ol (SI-21)



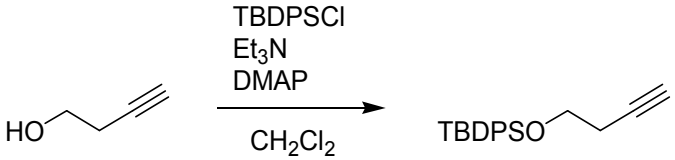
SI-21 was prepared from **SI-20** (0.53 g, 2.6 mmol) in a similar to a manner as **SI-18** (0.54 g, >99%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67 (brs, 1H), 3.69-3.83 (m, 2H), 3.81 (s, 3H), 4.77-4.84 (m, 1H), 6.81-6.85 (m, 2H), 7.36-7.40 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 49.2, 55.3, 63.1, 84.7, 86.4, 113.9, 114.0, 133.4, 160.0.

2-((4-Methoxyphenyl)ethynyl)oxirane (3j)



3j was prepared from **SI-21** (0.54 g, 2.6 mmol) in a similar to a manner as **3e** (0.37 g, 83%).
^{1}H NMR (300 MHz, C_6D_6) δ 2.35 (ddd, *J* = 6.3, 3.9 and 0.6 Hz, 1H), 2.63 (dd, *J* = 6.3 and 2.4 Hz, 1H), 3.17 (s, 3H), 3.21 (dd, *J* = 3.9 and 2.4 Hz, 1H), 6.52-6.56 (m, 2H), 7.30-7.35 (m, 2H).
^{13}C NMR (75 MHz, C_6D_6) δ 40.2, 48.5, 54.8, 83.7, 85.7, 114.4, 114.7, 133.7, 160.4.
HRMS (APCI-TOF) Calcd for $C_{11}H_{11}O_2$ $[M+H]^+$: 175.0759, Found: 175.0761.
IR (neat) 837, 1247, 1507, 1609, 2046, 2230, 2545, 2839, 2996 cm^{-1}

(But-3-yn-1-yloxy)(*tert*-butyl)diphenylsilane (SI-23)

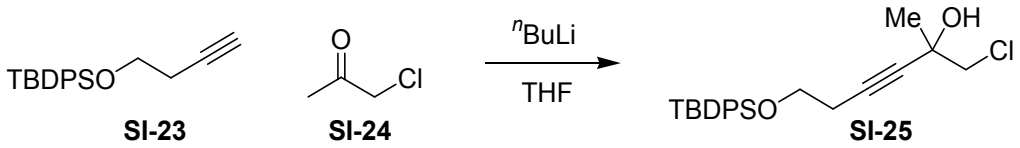


SI-22 **SI-23**

To a stirred solution of 3-butyn-1-ol (**SI-22**) (0.23 mL, 3.0 mmol) in CH_2Cl_2 (12 mL), triethylamine (0.83 mL), DMAP (0.11 g, 0.9 mmol) and TBDPSCl (0.92 mL, 3.6 mmol) was added at 0 °C and stirred for 12 h. The reaction mixture was quenched with saturated aq. $NaHCO_3$ and the solution was extracted three times with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to furnish **SI-23** (0.93 g, .99%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.97 (t, *J* = 2.7 Hz, 1H), 2.49 (td, *J* = 7.2 and 2.7 Hz, 2H), 3.83 (t, *J* =7.2 Hz, 2H), 7.39-7.49 (m, 6H), 7.71-7.75 (m, 4H).

6-((*tert*-Butyldiphenylsilyl)oxy)-1-chloro-2-methylhex-3-yn-2-ol (SI-25)



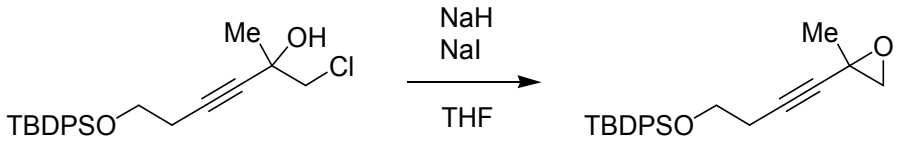
SI-23 **SI-24** **SI-25**

SI-25 was prepared from **SI-23** (0.98 g, 3.2 mmol) and chloroacetone (**SI-24**) (0.28 mL, 3.5 mmol) in a similar to a manner as **SI-17** (0.71 g, 56%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.55 (s, 3H), 2.51 (t, *J* = 6.9 Hz, 2H), 2.51 (brs, 1H), 3.55 (d, *J* = 10.8 Hz, 1 H), 3.64 (d, *J* = 10.8 Hz, 1H), 3.79 (t, *J* = 6.9 Hz, 2H), 7.38-7.48 (m, 6H), 7.71 (dd, *J* = 7.5 and 1.8 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 22.8, 26.8, 27.1, 54.3, 62.2, 67.5, 82.0, 82.5, 127.7, 129.8, 133.6, 135.6.

***tert*-Butyl((4-(2-methyloxiran-2-yl)but-3-yn-1-yl)oxy)diphenylsilane (3k)**



SI-25 **3k**

3k was prepared from **SI-25** (0.71 g, 1.8 mmol) in a similar to a manner as **3e** (0.65 g, >99%).

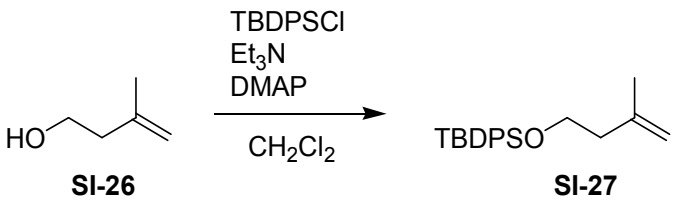
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (s, 9H), 1.52 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 2.71 (d, *J* = 5.7 Hz, 1H), 2.95 (d, *J* = 5.7 Hz, 1H), 3.76 (t, *J* = 6.9 Hz, 2H), 7.37-7.47 (m, 6H), 7.69 (dd, *J* = 7.5 and 1.8 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 22.8, 23.2, 26.8, 47.4, 55.5, 62.2, 80.0, 80.6, 127.7, 129.7, 133.5, 135.6.

HRMS (APCI-TOF) Calcd for $C_{23}H_{28}NaO_2Si$ $[M+Na]^+$: 387.1756, Found: 387.1766.

IR (neat) 701, 912, 1111, 1432, 1896, 1958, 2245, 2852, 2948, 3051 cm^{-1}

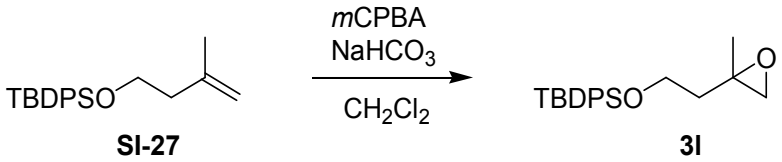
***tert*-Butyl((3-methylbut-3-en-1-yl)oxy)diphenylsilane (SI-27)**



SI-26 **SI-27**

SI-27 was prepared from 3-methyl-3-buten-1-ol (**SI-26**) (0.38 mL, 3.9 mmol) in a similar to a manner as **SI-23** (1.40 g, >99%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.81 (s, 3H), 2.42 (t, *J* = 6.9 Hz, 2H), 3.91 (t, *J* = 6.9 Hz, 2H), 4.83 (s, 1H), 4.89 (s, 1H), 7.47-7.56 (m, 6H), 7.83 (dd, *J* = 7.5 and 2.1 Hz, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 22.9, 27.0, 41.0, 62.9, 111.9, 127.8, 129.7, 134.1, 135.7, 143.0.

***tert*-Butyl((2-(2-methyloxiran-2-yl)ethoxy)diphenylsilane (3l)**



SI-27 **3l**

To a heterogeneous solution of $NaHCO_3$ (0.98 g, 11.7 mmol) and **SI-27** (1.27 g, 3.9 mmol) in CH_2Cl_2 (13 mL), *m*-CPBA (0.40 g, 4.7 mmol) was added at 0 °C. After stirring at room temperature for 12 h, the reaction was quenched with saturated aq. $Na_2S_2O_3$ at 0 °C. The organic layer was separated, washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (Hexane/AcOEt = 20/1) to furnish **3l** (0.40 g, 30%).
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10 (s, 9H), 1.35 (s, 3H), 1.70-1.79 (m, 1H), 1.91-2.00 (m, 1H), 3.82 (t, *J* = 6.3 Hz, 2H), 7.39-7.49 (m, 6H), 7.70-7.73 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 21.5, 26.9, 39.7, 54.2, 55.5, 60.7, 127.7, 1289.7, 133.7, 135.6.
HRMS (APCI-TOF) Calcd for $C_{21}H_{28}NaO_2Si$ $[M+Na]^+$: 363.1756, Found: 363.1751.
IR (KBr) 702, 936, 1101, 1383, 1581, 1829, 2852, 2935, 3072 cm^{-1}

Referenced ^{1}H Diffusion Ordered NMR (^{1}H DOSY)

Internal references: benzene (BEN, 78.1 g/mol, 7.16ppm), cyclooctene (COE, 110 g/mol, 5.48ppm), 1-tetradecene (TDE, 196 g/mol, 5.60ppm/4.79ppm) and squalene (SQU, 410 g/mol, 4.97ppm/1.52ppm). NMR experiments were taken at -70 °C in diethyl ether.

Table S1. D-FW analysis of ^{1}H DOSY data of Cp_2ZrCl_2 in diethyl ether

Entry	Compound	FW g/mol	D m^2/s	Predicted FW g/mol	% Error
1	BEN	78.1	1.171E-9	77	-1
2	COD	110	9.220E-10	115	5
3	TDE	196	7.000E-10	184	-6
4	SQU	410	4.286E-10	421	3
5	Cp_2ZrCl_2		6.587E-10	**204***	

* The solid density of Cp_2ZrCl_2 is 1.70 g/cm^3. However, our reference system is optimized to test complexes with density 0.9 g/cm^3 (liquid density) ~ 1.0 g/cm^3 (solid density). Therefore, the predicted FWs of Cp_2ZrCl_2 here are on the base of assumption that the density of Cp_2ZrCl_2 particle is around 1.0g/cm^3.

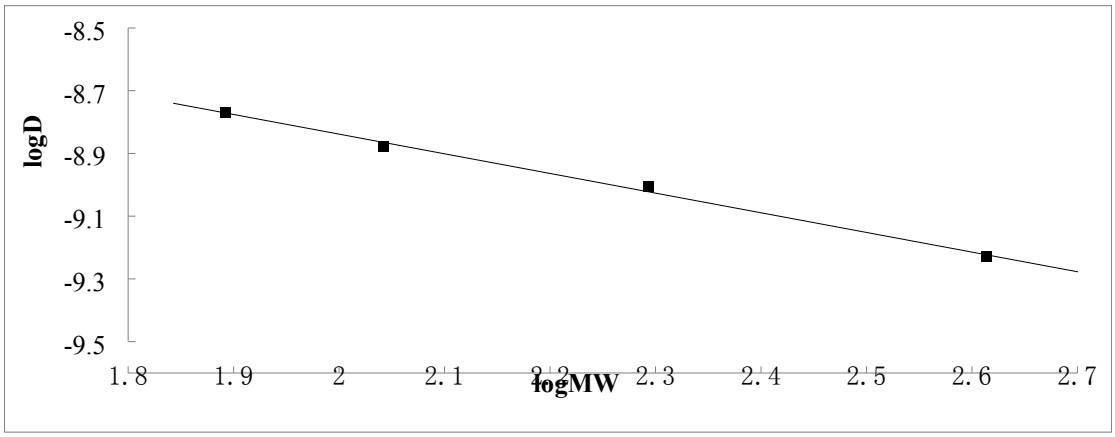


Figure S1. D-FW analysis of ^{1}H DOSY data of Cp_2ZrCl_2 in diethyl ether.

Table S2. D-FW analysis of ^{1}H DOSY data of Cp_2ZrCl_2 with 20eq dioxane

Entry	Compound	FW g/mol	D m^2/s	Predicted FW g/mol	% Error
1	BEN	78.1	1.281E-9	81	3
2	COD	110	1.104E-9	110	0
3	TDE	196	8.724E-10	181	-8
4	SQU	410	5.791E-10	429	4
5	Cp_2ZrCl_2		7.047E-10	**284***	

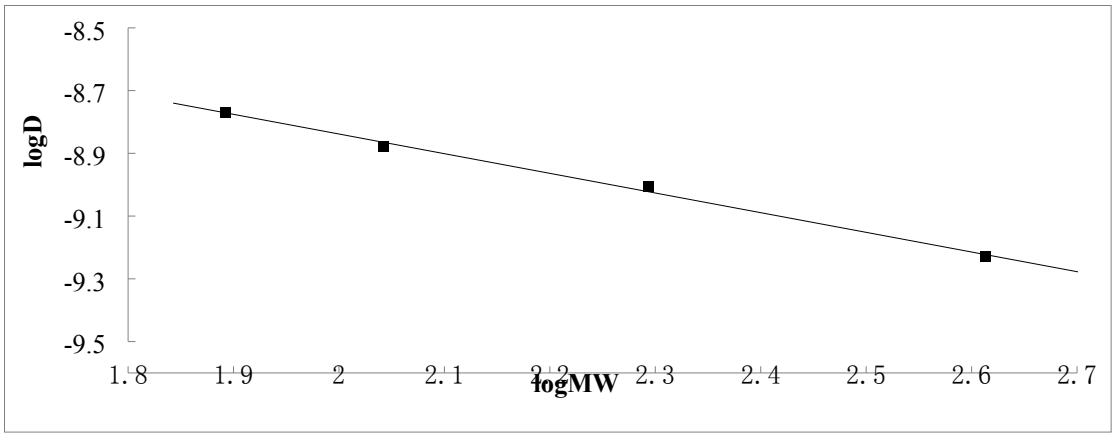


Figure S2. D-FW analysis of ^{1}H DOSY data of Cp_2ZrCl_2 with 20eq dioxane

Table S3. D-FW analysis of ^{1}H DOSY data of Cp_2ZrCl_2 with (1eq *n*-C_4F_9MgCl+1eq dioxane+1eq MAO)

Entry	Compound	FW g/mol	D m^2/s	Predicted FW g/mol	% Error
1	BEN*	78.1	--	--	--
2	COD	110	6.402E-10	113	2
3	TDE	196	4.282E-10	189	-4
4	SQU	410	2.324E-10	417	2
5	Cp_2ZrCl_2		3.875E-10	215	

* Benzene peak overlaps with toluene peak (from MAO)

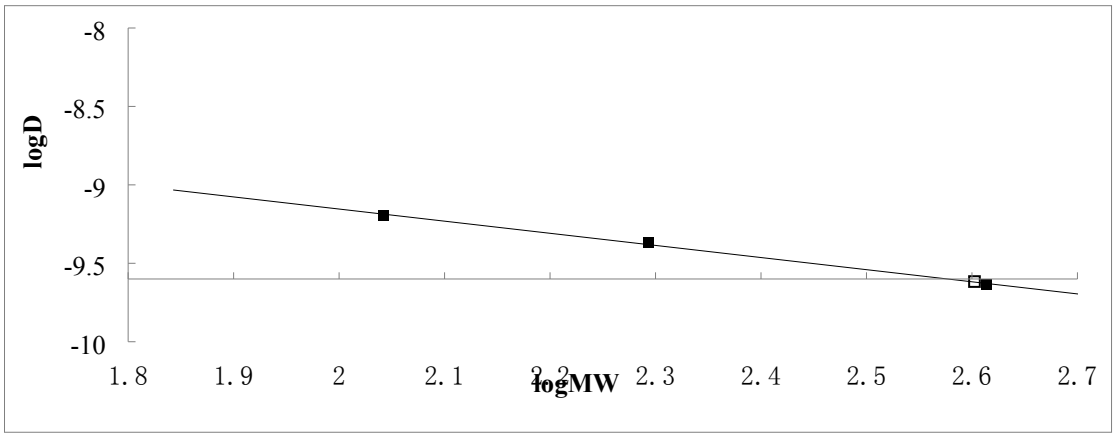


Figure S3. D-FW analysis of ^{1}H DOSY data of Cp_2ZrCl_2 with (1eq *n*-C_4F_9MgCl+1eq dioxane+1eq MAO).

Referenced ^{19}F Diffusion Ordered NMR (^{19}F DOSY)

Internal references: 1-perfluorobutene (C_4F_8, 200 g/mol, -86.3ppm, -97.9ppm, -105.4ppm, -122.9ppm, -193.6ppm), 1*H*-nonafluorobutane (C_4F_9H, 220 g/mol, -82.7ppm, -129.4ppm, -132.0ppm, -140.2ppm), 1,3,5-tris(trifluoromethyl)benzene (tTFB, 282 g/mol, -64.9). NMR experiments were taken at -70 ˚C in diethyl ether.

Table S4. D-FW analysis of ^{19}F DOSY data of *n*-C_4F_9MgCl in diethyl ether

Entry	Compound	FW g/mol	D m^2/s	Predicted FW g/mol	% Error
1	C_4F_8	200	2.247E-9	197	-1
2	C_4F_9H	220	2.029E-9	224	2
3	tTFB	282	1.698E-9	281	0
4	*n*-C_4F_9Mg		1.637E-9	**294**	

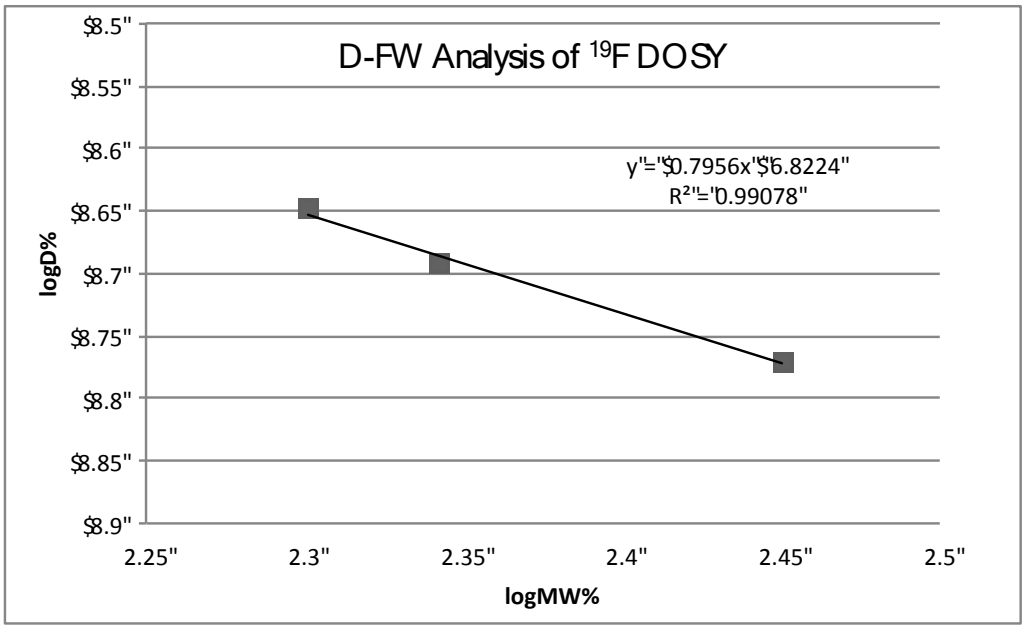


Figure S4. D-FW analysis of ^{19}F DOSY data of *n*-C_4F_9MgCl in diethyl ether

Table S5. D-FW analysis of ^{19}F DOSY data of *n*-C_4F_9MgCl with 1eq MAO

Entry	Compound	FW g/mol	D m^2/s	Predicted FW g/mol	% Error
1	C_4F_8	200	1.742E-9	199	-1
2	C_4F_9H	220	1.597E-9	222	1
3	tTFB	282	1.322E-9	281	0
4	*n*-C_4F_9Mg		1.121E-9	**346**	

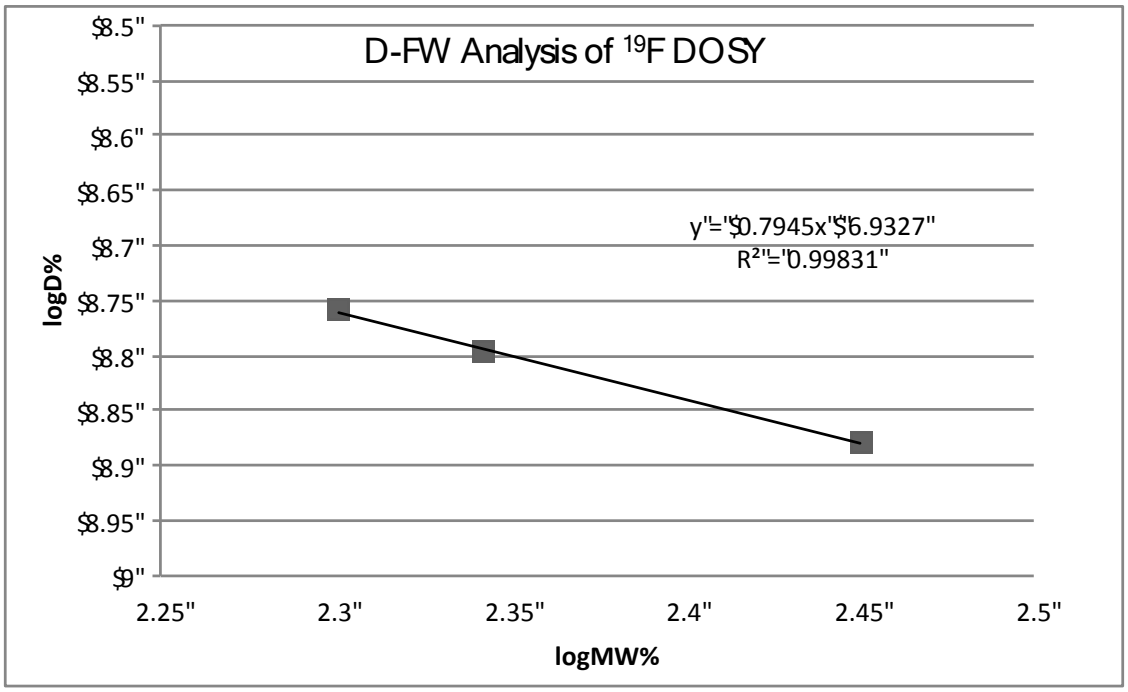


Figure S5. D-FW analysis of ^{19}F DOSY data of *n*-C_4F_9MgCl with 1eq MAO

Table S6. D-FW analysis of ^{19}F DOSY data of *n*-C_4F_9MgCl with (1eq dioxane + 1eq MAO)

Entry	Compound	FW g/mol	D m^2/s	Predicted FW g/mol	% Error
1	C_4F_8	200	1.912E-9	202	1
2	C_4F_9H	220	1.841E-9	217	-1
3	tTFB	282	1.604E-9	283	0
4	*n*-C_4F_9Mg		1.408E-9	**364**	

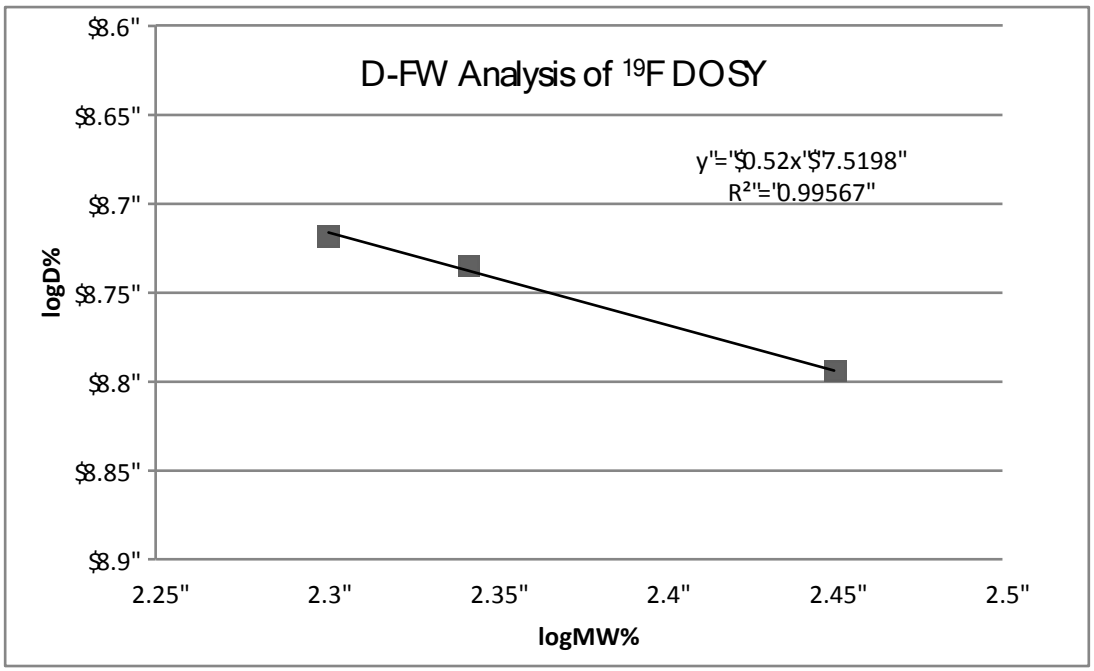


Figure S6. D-FW analysis of ^{19}F DOSY data of *n*-C_4F_9MgCl with (1eq dioxane + 1eq MAO)

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