A Novel "one-pot" Conversion of Aldehydes to Trifluoromethylated Bromoallylic Alcohols

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Supporting Information

3,3,3-Tribromo-1,1,1-trifluoroacetone

It was prepared according to the method reported in literature. (Mcbee, E. T.; Burton, T. M. *J. Am. Chem. Soc.* **1952**, *74*, 3902.)

5a. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-fluorophenyl)-but-1-ene

Yield: 81%, O.T.= 72 ° C/0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δ ppm): 7.66-7.63(m, 2H), 7.22(s, 1H), 7.08(t, J=6.5Hz, 2H), 4.70(q, J=6.1Hz, 1H), 2.74(s, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.3(d, J=6.1Hz, 3F), +33.0(m, 1F).

NOESY spectrum shows that the CH(OH)-CF_3 group was *cis* with respect to vinyl proton. Therefore, the double bond in compounds **5a** is in the Z configuration

IR(film, cm^{-1}): 3420(s), 1640(w), 1600(s), 1510(s), 1270(s), 1240(s), 1180(s), 1130(s), 840(s).

MS(m/z): 299(M^++1, 5), 297(M^+-1, 7), 229(21), 203(43), 183(22), 149(34), 71(51), 57(100), 43(61).

Analysis: $C_{10}H_7BrF_4O$(299.06) Calcd: C, 40.16; H, 2.36.
Found: C, 40.40; H, 2.51.

5b. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-chlorophenyl)-but-1-ene

Yield: 61%; O.T.= 70° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δ ppm): 7.58(d, J=8.6Hz, 2H), 7.41(d, J=8.6Hz, 2H), 7.22(s, 1H), 4.69(dq, J_1=8.4Hz, J_2=6.1Hz, 1H), 2.88(d, J=8.4Hz, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δ ppm): -1.0(d, J=6.1Hz, 3F).

IR(film, cm^{-1}): 3430(s), 1640(w), 1590(m), 1490(s), 1270(s), 1180(s), 1130(s), 1090(s), 1020(s).

MS(m/z): 315(M^++1, 86), 313(M^+-1, 62), 247(100), 165(59), 131(76), 102(65), 75(47).

Analysis: $C_{10}H_7BrClF_3O$(315.51) Calcd: C, 38.07; H, 2.24.
Found: C, 38.49; H, 2.43.

5c. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-bromophenyl)-but-1-ene

Yield: 54%; O.T. =85° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δ ppm): 7.48-7.61(m, 4H), 7.31(s, 1H), 4.70(q, J=6.1Hz, 1H), 2.98(s, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.2(d, J=6.1Hz, 3F).

IR(film, cm^{-1}): 3420(s), 1640(w), 1590(s), 1490(s), 1400(s), 1270(s), 1180(s), 1130(s), 1080(s), 1010(s).

MS(m/z): 361(M^++3, 11), 359(M^++1, 20), 357(M^+-1, 11), 290(37), 211(19), 131(100), 102(57), 75(32), 51(34).

Analysis: $C_{10}H_7Br_2F_3O$(359.96) Calcd: C, 33.37; H, 1.96.
Found: C, 33.27; H, 2.03.

5d. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-methylphenyl)-but-1-ene

Yield: 88%; O.T. =90° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δppm): 7.58(d, J=8.2Hz, 2H), 7.35-7.15(m, 3H), 4.70(q, J=6.1Hz, 1H), 2.90(s, 1H), 2.39(s, 3H).

^{19}F-NMR ($CDCl_3$/TFA, δ ppm): -0.8(d, J=6.1Hz, 3F).

IR(film, cm^{-1}): 3340(s), 3030(w), 2930(w), 1640(m), 1610(m), 1510(s), 1270(s), 1180(s), 1130(s).

MS(m/z): 296(M^++2, 53), 294(M^+, 54), 227(74), 209(28), 145(100), 115(93), 91(53).

Analysis: $C_{11}H_{10}BrF_3O$(295.09) Calcd: C, 44.77; H, 3.42.
Found: C, 44.30; H, 3.21.

5e. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-ethylphenyl)-but-1-ene

Yield: 85%; O.T. =65° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δppm): 7.61(d, J=8.2Hz, 2H), 7.40-7.10(m, 3H), 4.70(dq, J_1=8.5Hz, J_2=6.2Hz, 1H), 3.01(d, J=8.5Hz, 1H), 2.67(q, J=7.6Hz, 2H), 1.25(t, J=7.6Hz, 3H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.3(d, J=6.2Hz, 3F).

IR(film, cm^{-1}): 3430(s), 2970(s), 1640(m), 1610(m), 1510(s), 1270(s), 1180(s), 1130(s).

MS(m/z): 309(M^++1, 94), 307(M^+-1, 86), 241(86), 159(93), 131(100), 115(85), 103(46), 91(46).

Analysis: $C_{12}H_{12}BrF_3O$(309.12) Calcd: C, 46.63; H, 3.91.
Found: C, 46.53; H, 3.86.

5f. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-methoxyphenyl)-but-1-ene

Yield: 84%; O.T. =90° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δppm): 7.71(d, J=7.5Hz, 2H), 7.18(s, 1H), 6.99(d, J=7.5Hz, 2H), 4.69(q, J=6.1Hz, 1H), 3.84(s, 3H), 3.00(s, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.3(d, J=6.1Hz, 3F).

IR(film, cm^{-1}): 3440(s), 2840(s), 1610(s), 1510(s), 1260(s), 1180(s), 1130(s), 1030(s).

MS(m/z): 311(M^++1, 100), 309(M^+-1, 93), 243(85), 223(27), 162(46), 147(32), 133(35), 89(34).

Analysis: $C_{11}H_{10}BrF_3O_2$(311.09) Calcd: C, 42.47; H, 3.24.
Found: C, 42.40 H, 3.16.

5g. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(4-trifluoromethoxyphenyl)-but-1-ene

Yield: 50%; O.T. =110° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δ ppm): 7.80-7.52(m, 2H), 7.48-7.20(m, 3H), 4.85-4.65(m, 1H), 3.00(d, J=7.5Hz, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δ ppm): -20.3(s, 3F), -1.5(d, J=6.0Hz, 3F).

IR(film, cm^{-1}): 3420(m), 1610(m), 1590(m), 1450(m), 1490(m), 1260(s), 1220(s), 1180(s), 1130(s).

MS(m/z): 365(M^++1, 62), 363(M^+-1, 63), 296(76), 215(67), 189(54), 175(75), 103(57), 69(73), 43(100).

Analysis: $C_{11}H_7BrF_6O_2$(365.06) Calcd: C, 36.19; H, 1.93.
Found: C, 36.34; H, 1.87.

5h. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(2,4-dichlorophenyl)-but-1-ene

Yield: 68%; O.T. =85° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δppm): 7.65(d, J=8.4Hz, 1H), 7.45(s, 1H), 7.35-7.10(m, 2H), 4.78(q, J=6.0Hz, 1H), 3.15(s, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.3(d, J=6.0Hz, 3F).

IR(film, cm^{-1}): 3420(s), 1590(s), 1550(w), 1470(s), 1270(s), 1180(s), 1140(s), 1050(s).

MS(m/z): 351(M^++3, 37), 349(M^++1, 77), 347(M^+-1, 46), 280(100), 262(21), 201(33), 165(43), 136(43), 99(39).

Analysis: $C_{10}H_6BrCl_2F_3O$(349.96) Calcd: C, 34.32; H, 1.73.
Found: C, 34.36; H, 1.75.

5i. *Z*-4,4,4-Trifluoro-3-hydroxy-2-bromo-1-(phenyl)-but-1-ene

Yield: 62%; O.T. =65° C /0.5mmHg;

^{1}H-NMR ($CDCl_3$/TMS, δ ppm): 7.80-7.60(m, 2H), 7.45-7.30(m, 3H), 7.24(s, 1H), 4.70(dq, J_1=8.4Hz, J_2=6.1Hz, 1H), 3.10(d, J=8.4Hz, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.3(d, J=6.1Hz, 3F).

IR(film, cm^{-1}): 3260(s), 1640(m), 1490(m), 1450(m), 1260(s), 1180(s), 1130(s).

MS(m/z): 282(M^++2, 13), 280(M^+, 15), 211(30), 193(12), 131(52), 103(48), 77(47), 44(100).

Analysis: $C_{10}H_8BrF_3O$(281.07) Calcd: C, 42.73; H, 2.87.
Found: C, 42.65 H, 2.87.

5j. 6,6,6-Trifluoro-5-hydroxy-4-bromo-1-(phenyl)-hex-1*E*,3*Z*-diene

Yield: 70%; O.T. =65° C /0.5mmHg; B.P. 60℃;

^{1}H-NMR ($CDCl_3$/TMS, δppm): 7.80-7.20(m, 5H), 7.18-6.80(m, 3H), 4.64(q, J=6.1Hz, 1H), 2.91(s, 1H).

^{19}F-NMR ($CDCl_3$/TFA, δppm): -1.1(d, J=6.1Hz, 3F).

IR(film, cm^{-1}): 3450(s), 1630(m), 1450(m), 1350(m), 1260(s), 1200(s), 1130(s), 1110(s), 970(s).

MS(m/z): 307(M^++1, 57), 305(M^+-1, 53), 237(27), 209(28), 158(47), 129(78), 91(100), 77(21).

Analysis: $C_{12}H_{10}BrF_3O$(307.11) Calcd: C, 46.93; H, 3.28.
Found: C, 46.72; H, 3.21.