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Regioselective functionalization of *gem*-bis(trifluoromethylated) alkanols

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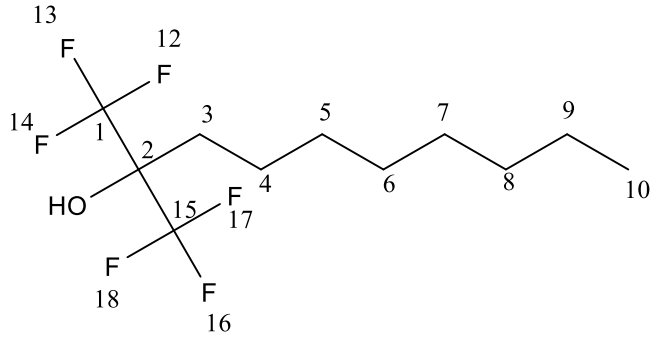
ATTENTION! Atom numbering in structures in some cases does not correspond to systematic one and is given for MNR assignment.

1,1,1-Trifluoro-2-(trifluoromethyl)decan-2-ol (1).

At (-65) ÷ (-60) °C, *n*-$C_8H_{17}MgCl$ (1 M, 180 ml, 0.18 mol) was added dropwise to a stirred solution of CF_3COCF_3 (30 g, 0.18 mol) in absolute diethyl ether (75 ml). The mixture was stirred at 20-25 °C for 1 h. At 5 ÷ 10 °C, the mixture was treated with 10% HCl, the organic layer was separated, washed with H_2O and dried with $MgSO_4$. The solvent was removed and the residue was distilled at 0.3 Torr, b.p. 65-67 °C (0.3 Torr). Yield 15.8 g (31%). The product was purified by repeated distillation *in vacuo*.



^{1}H NMR: 0.92 (t., $^3J_{HH}$ = 6.4, 3H, $^{10}C\mathbf{H}_3$); 1.31–1.34 (m, 10H, $^{5–9}C\mathbf{H}_2$); 1.50 –1.60 (m, 2H, $^4C\mathbf{H}_2$); 1.95 (t., $^3J_{HH}$ = 8.10, 2H, $^3\mathbf{C}H_2$); 2.76 (bs., 1H, O**H**).^{19}F NMR: -- 76.91 (s., 6H, $\mathbf{CF_3}$). ^{13}C NMR: 13.82 ($^{10}\mathbf{C}H_3$); 21.80 ($^9\mathbf{C}H_2$); 22.65 ($^{\mathbf{4}}\mathbf{C}H_2$); 29.22 ($^{8,9}\mathbf{C}H_2$); 29.95 ($^5\mathbf{C}H_2$); 30.53 ($^7\mathbf{C}H_2$); 31.87 ($^3\mathbf{C}H_2$); 76.48 (sept, $^2J_{CF}$ = 28.8, $^2\mathbf{C}$); 123.26. (q., $^1J_{CF}$ = 286.83, $\mathbf{C}F_3$). MS: 280, M^+ (1.4), 279, M^+ -H (11); 237, $HOC(CF_3)_2(CH_2)_5^+$ (61); 223, $HOC(CF_3)_2(CH_2)_4^+$ (18); 209, $HOC(CF_3)_2(CH_2)_3^+$ (30); 203 (5); 185 (3); 171 (4); 151 (4; 145 (6); 141 (18); 121 (5); 115 (3); 91 (5); 85 (8); 83 (7); 73 (6); 71 (22); 70 (8); 69, CF_3^+,(11); 67 (5); 65 (6); 61 (4); 59 (5); 57 (100)..

*Prodicts **2a**-e (typical procedure):*

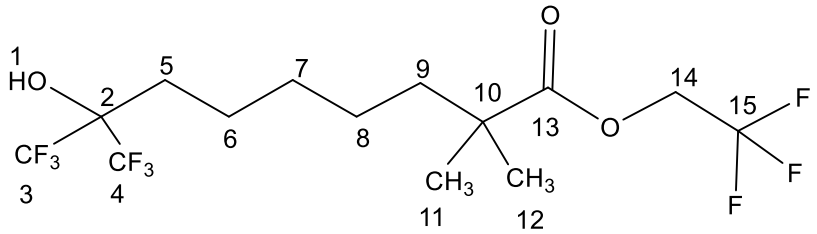
At - 20 °C under CO atmosphere (1 atm), substrate **1** (0.82–1.36 mmol) was added to a stirred solution of $CBr_4 \cdot 2AlBr_3$ (1.62–2.72 mmol) freshly prepared from CBr_4 and $AlBr_3$ in the molar ratio 1:2 in anhydrous CH_2Br_2 (2–3 ml) at room temperature. After stirring for 2 h at the same temperature under a CO atmosphere, the appropriate nucleophile was added to the *in situ*

prepared carbonylation intermediate strictly under CO. The mixture was stirred for 10-20 min at -20 °C and then warmed to 0 °C within 20-30 min. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral pH, and dried over Na_2SO_4. The structures of the products were established by ^1H, ^{13}C, and ^{19}F NMR spectroscopy, and from GC-MS spectra; conversions and isomeric ratios were determined by GC. To perform NMR measurements, all the solvents and highly volatile compounds were removed under reduced pressure. In some cases, in order to remove by-products, the crude product was washed with pentane or purified by column chromatography (silica gel) using hexane-acetone (5:1) as an eluent. The yields of the products were determined by ^1H NMR spectroscopy with mesitylene as an internal standard. All NMR spectra were recorded on a Bruker Avance in $CDCl_3$ (^1H NMR 400.13 MHz; ^{13}C NMR 100.61 MHz in δ from Me_4Si; ^{19}F 376.49 MHz, δ from $CFCl_3$, *J*, Hz). ^{19}F NMR spectra were recorded with full ^1H–^{19}F decoupling. The GC–MS spectra were recorded on a Finnigan Polaris GCO Plus.

The numbering of atoms in all structures refers to NMR spectra and is not related to nomenclature of compounds.

2,2,2-Trifluoroethyl 9,9,9-trifluoro-8-hydroxy-2,2-dimethyl-8-(trifluoromethyl)nonanoate (2a).

Reagent quantities used: substrate **1** (0.32 g, 1.14 mmol), electrophile (1.97 g, 2.28 mmol) prepared from CBr_4 (0.76 g., 2.28 mmol) and $AlBr_3$ (1,21 g. 4,55 mmol), CH_2Br_2 (3 ml), $HOCH_2CF_3$ (0.39 g, 3.90 mmol), -20 ^{O}C, 2 h. The liquid product remaining after removal the volatiles in a vacuum was mixed with dry pentane. Then pentane was removed and the pentane washing was repeated. The product was dried from the pentane. Yield 0.39 g (84%).

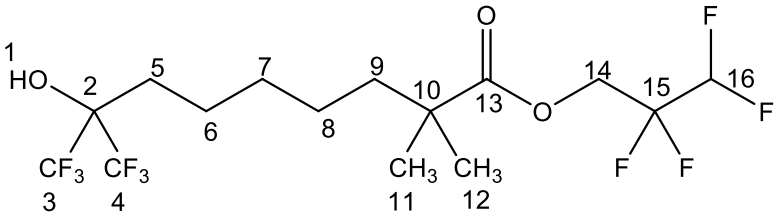


^1H NMR: 1.23 (s, 6H, $^{11,12}C\mathbf{H}_3$); 1.30–1.81 (m, 8H, $^{5–8}C\mathbf{H}_2$); 1.91 (t., $^3J_{HH}$ = 7.90, 2H, $^9C\mathbf{H}_2$), 3.60–4.0 (bs., 1H, $^1\mathbf{H}O$); 4.48 (q., $^3J_{HF}$ = 8.40, 2H, $^{14}C\mathbf{H}_2$); ^{19}F NMR: -74.05 ($^{15}C\mathbf{F}_3$); -76.64 ($^{3,4}C\mathbf{F}_3$). ^{13}C NMR: 20.34 ($^8\mathbf{C}H_2$); 24.24 ($^6\mathbf{C}H_2$); 24.77 ($^{\mathbf{11,12}}\mathbf{C}H_3$); 29.92 ($^7\mathbf{C}H_2$); 30.20 ($^5\mathbf{C}H_2$); 39.95 ($^9\mathbf{C}H_2$); 42.42 ($^{10}\mathbf{C}$); 60.29 (q., $^3J_{CF}$ = 36.3, $^{14}\mathbf{C}H_2$), 76.06 (sept, $^2J_{CF}$ = 29.0, $^2\mathbf{C}$); 122.9. (q., $^1J_{CF}$ = 261.5, $^3J_{CF}$ = 37.0, $^{15}\mathbf{C}F_3$); 123.3 (q., $^1J_{CF}$ = 282.4, $^{3,4}CF_3$); 176.53 ($^{13}\mathbf{C}O$). MS: 407, M^+ + H (15), 279, M^+ - $COOCH_2CF_3$ (2); 237, $HOC(CF_3)_2(CH_2)_5^+$ (21); 217 (3); 207 (6); 203 (4); 189

(3); 185 (3); 184 (8); 183 (5); 171 (5); 170 (47); 169 (12); 165 (3); 163 (3); 155 (12); 153 (3); 150 (6); 149 (8); 145 (5); 141 (7); 139 (3); 135 (23); 127 (5); 123 (5); 115 (4); 97 (8); 95 (3); 91 (5); 87 (4); 83 (13); 79 (4); 77 (4): 75 (3); 73 (4); 71 (14); 70 (4); 69 (21); 67 (5); 65 (10); 61 (6); 59 (7); 57 (100); 55 (23).

2,2,3,3-Tetrafluoropropyl 9,9,9-trifluoro-8-hydroxy-2,2-dimethyl-8-(trifluoromethyl)-nonanoate (2b).

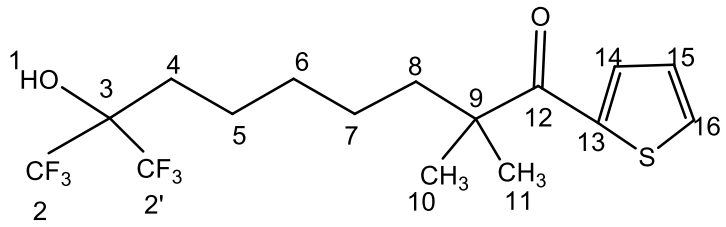
Reagent quantities used: substrate **1** (0.27 g, 0.96 mmol), electrophile (1.66 g, 1.92 mmol), prepared from CBr_4 (0.64 g., 1.92 mmol) and $AlBr_3$ (1,02 g. 3.84 mmol), CH_2Br_2 (2.4 ml), $HOCH_2(CF_2)_2H$ (0.23 g, 1.74 mmol), -20 °C, 2 h. The liquid product remaining after removing the volatiles in a vacuum was mixed with dry pentane. After that, pentane was removed and the operation of purifying the product from impurities with pentane was repeated. The product was dried from the pentane. Yield 0.31 g (74%).



^{1}H NMR: 1.20 (s, 6H, ^{11,12}C**H**$_3$); 1.20 – 1.68 (m, 8.3 H, $^{5–8}$C**H**$_2$); 1.89 (t., $^3J_{HH}$ = 7.90, 2H, ^{9}C**H**$_2$); 3.75 (bs, I.1 H, ^{1}**H**O); 3.45 (t, $^3J_{HF}$= 12.7, 2H, ^{14}C**H**$_2$); 5,84 (t, $^1J_{HF}$= 53.1, 1H, ^{16}**C**F$_2$H). ^{19}F NMR: -76.76 (^{3,4}C**F**$_3$); -65.10 (^{15}C**F**$_2$); -78.79 (^{16}C**F**$_2$H). ^{13}C NMR: 24.24 (^{6}**C**H$_2$); : 21.34 (^{8}**C**H$_2$); :24.71 (^{11,12}**C**H$_3$); 29.93 (^{7}**C**H$_2$); 30.24 (^{5}**C**H$_2$); 40.03 (^{9}**C**H); 42.48 (^{10}**C**); 59.50 (t., $^3J_{CF}$ = 29.0, ^{14}**C**H$_2$), 76.08 (sept, $^2J_{CF}$ = 29.0, ^{2}**C)** 109.30 (tt., $^1J_{CF}$ = 250.8, $^3J_{CF}$ = 37.0,^{16}**C**F$_2$H); 114.07 (tt., $^1J_{CF}$ = 249.1, $^3J_{CF}$ = 28.2, ^{15}CF$_2$); 123.10 (q, $^1J_{CF}$ = 287.2, ^{3,4}**C**F$_3$); 176.92 (^{13}**C**O). MS: M^+ + H, 439 (100); 401 (3); 279 (4); 277 (10); 237 (10); 217 (3); 216 (3); 215 (3); 207 (3); 203 (7); 202 (34); 201 (4); 187 (6); 173 (4); 167 (4); 159 (4); 149 (4); 145 (4); 91 (3); 87 (3); 83 (7); 73 (3); 71 (13); 70 (5); 69 (15); 67 (3); 65 (6); 59 (6); 58 (4); 55 (13).

9,9,9-Trifluoro-8-hydroxy-2,2-dimethyl-1-(2-thienyl)-8-(trifluoromethyl)nonan-1-one (2c).

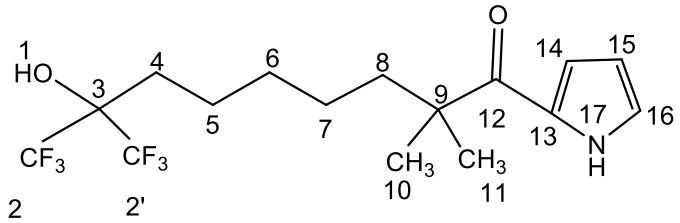
Reagent quantities used: substrate **1** (0.24 g., 0.86 mmol), electrophile (1.46 g., 1.69 mmol), prepared from CBr_4 (0.56 g., 1.69 mmol) and $AlBr_3$ (0.90 g. 3.38 mmol), CH_2Br_2 (2.5 ml), thiophene (0.23 g, 2.55 mmol), -20 °C, 2 h. The product was purified by column chromatography (silica gel) using hexane-acetone (5:1) as an eluent. Yield 0.22g (64%).



^{1}H NMR: 1.38 (s, 6H, ^{10,11}C**H**$_3$); 1.10–2.0 (m, 6.2 H, $^{5–7}$C**H**$_2$); 1.82 (t., $^{3}J_{HH}$ = 6.90, 2H, ^{4}C**H**$_2$); 1.89 (t., $^{3}J_{HH}$ = 7.79, 2H, ^{8}C**H**$_2$**);** 3.2–3.8 (bs., 0.9 H, ^{1}**H**O); 7.13 (t., $^{3}J_{HH}$ = 3.85; 1H, ^{15}C**H**); 7.59 (d, $^{3}J_{HH}$ = 4.95, 1H, ^{16}C**H**); 7.81 (d, $^{3}J_{HH}$ = 4.85, 1H, ^{14}C**H**). ^{13}C NMR: 21.22 (^{7}**C**H$_2$); 24.10 (^{5}**C**H$_2$); 26.16 (s., ^{10,11}**C**H$_3$); 30.06 (^{6}**C**H$_2$); 30.24 (^{4}**C**H$_2$); 41.15 (^{8}**C**H$_2$); 47.41 (^{9}**C**); 76.10 (sept, $^{2}J_{CF}$ = 29.0, ^{2}**C**); 123.12 (q, $^{1}J_{CF}$ = 288.7, ^{2}CF$_3$); 127.78 (^{15}**C**H); 131.83 (^{14}**C**H); 132.60 (^{16}**C**H); 142.40 (^{13}**C**); 198.09 (^{12}**C**O). ^{19}F:-76.52 ($^{2,2'}$ C**F**$_3$). MS: 391, M$^+$ + H (19); 273, M$^+$ - HOC(CF$_3$)$_2$(CH$_2$)$_5$ (3); 167 (2); 158 (2); 154 (2); 153 (2); 149 (2); 145 (2); 139 (2); 125 (2); 112 (7); 111, COC$_4$H$_3$S (100); 97 (3); 86 (2); 84 (2); 83 (5); 71 (3); 69 (6); 65 (3); 59 (2); 57 (20); 56 (7); 55 (6).

9,9,9-Trifluoro-8-hydroxy-2,2-dimethyl-1-(1*H*-pyrrol-2-yl)-8-(trifluoromethyl)nonan-1-one (2d).

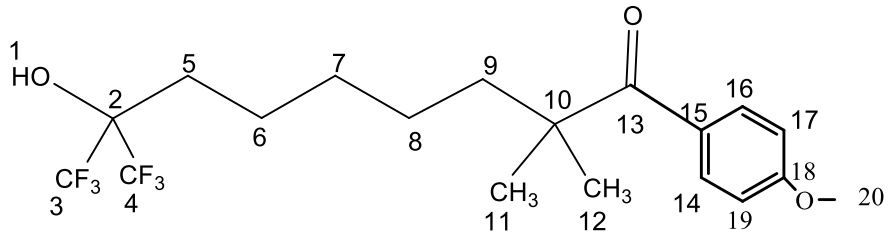
Reagent quantities used: substrate **1** (0.23 g, 0.82 mmol), electrophile (1.42 g.,1.64 mmol), prepared from CBr$_4$ (0.54 g., 1.64 mmol) and AlBr$_3$ (0.90 g. 3.38 mmol), CH$_2$Br$_2$ (2 ml), pyrrole (0.16 g, 2.40 mmol), -20 °C, 2 h. The product was purified by column chromatography (silica gel) using hexane-acetone (5:1) as an eluent. Yield 0.12 g., 40%.



^{1}H NMR: 1.34 (s, 6.2H, ^{10,11}C**H**$_3$); 1.29–1.53 (m, 6.7 H, $^{5–7}$C**H**$_{2)}$; 1.77 ($^{3}J_{HH}$ = 7.92, 2H, ^{4}C**H**$_2$); 1.88 (t., $^{3}J_{HH}$ = 8.00, 2H, ^{8}C**H**$_2$**);** 2.35 (bs., 0.9 H, ^{1}**H**O) 6.31 (d, $^{1}J_{HH}$ = 2.8, 1H, ^{16}C**H**), 6.99 (m., 2H,^{14,15}C**H**); 9.69 (bs., 0.85, ^{17}NH);. ^{19}F NMR:-76.49 ($^{2,2'}$C**F**$_3$). ^{13}C NMR: 21.18 (^{7}**C**H$_2$); 24.04 (^{5}**C**H$_2$); 26.34 ($^{10,\ 11}$CH$_3$); 30.03 (^{6}CH$_2$); 30.29 (^{4}CH$_2$); 41.57 (^{8}CH$_2$); 46.19 (^{9}C); 76.10 (hept, $^{2}J_{CF}$ = 29.0, ^{3}**C**); 110.45 (^{15}CH); 116.05 (^{14}**C**H); 123.4 (q, $^{1}J_{CF}$ = 288.2, $^{2,2'}$**C**F$_3$); 129.41 (^{16}**C**H); 134.29 (^{13}**C**); 196.86 (^{12}**C**O). MS: 374, M$^+$ + H (2), 317 (3); 137 (25); 122 (6); 109 (3); 96 (3); 95 (10); 94, C$_4$H$_3$NHCO$^+$ (100); 69 (3); 68 (3); 67 (6); 66, C$_4$H$_3$NH$^+$ (10); 57 (4); 55 (3).

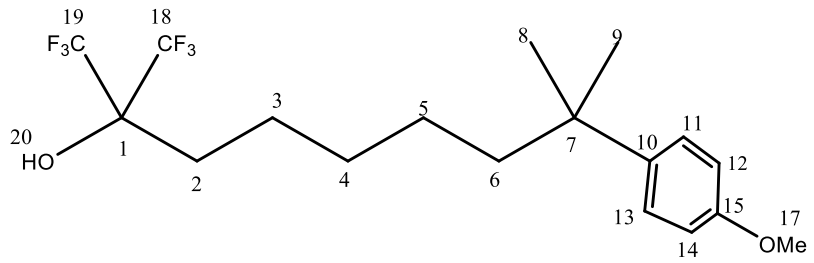
9,9,9-Trifluoro-8-hydroxy-1-(4-methoxyphenyl)-2,2-dimethyl-8-(trifluoromethyl)nonan-1-one (2e).

Reagent quantities used: substrate **1** (0.25 g, 0.89 mmol), electrophile (1.54 g, 1.79 mmol), prepared from CBr_4 (0.59 g., 1.79 mmol) and $AlBr_3$ (0.95 g. 3.58 mmol), CH_2Br_2 (2.5 ml), anisole (0.29 g, 2.69 mmol), -20 °C, 2 h. The product was purified by column chromatography (silica gel) using hexane-acetone (5:1) as an eluent. Yield 0.22 g., 60%.



(**2e**).[1] H NMR: 1.35 (s.,6.1H, $^{10,11}C\mathbf{H}_3$); 1.18- 1.28, 1.51 (m, 6.4 H, $^{6-8}C\mathbf{H}_2$); 1.78 (t., $^3J_{HH}$ = 9,0, 2H, $^5C\mathbf{H}_2$); 1,89 (t., $^3J_{HH}$ = 9,0, 2H**,** $^9C\mathbf{H}_2$); 2.31 (bs , 1H, bs, $^1\mathbf{H}O$); 3.87 (s., 3H,$^{20}C\mathbf{H}_3$); 6.91 (d, 2H,$^3J_{HH}$ = 9,0, $^{17,19}C\mathbf{H}$**),** 7.84 **(**1.9H**,** d, $^3J_{HH}$ = 9.0, $^{14,16}C\mathbf{H}$. ^{19}F NMR:-18.31 ($^{3,4}C\mathbf{F}_3$). ^{13}C NMR: 21.09 ($^6\mathbf{C}H_2$); 24.07 ($^8\mathbf{C}H_2$); 26.50 ($^{11,12}\mathbf{C}H_3$); 30.01 ($^7\mathbf{C}H_2$); 30.14 ($^5\mathbf{C}H_2$); 40.99 ($^9\mathbf{C}H_2$); 47.45 ($^{10}\mathbf{C}$); 55.24 ($^{20}\mathbf{C}H_3$); 76.08 (sept, $^2J_{CF}$ = 28.0, $^2\mathbf{C}$); 113.07 ($^{17,19}\mathbf{C}H$); 123.10 (q, $^1J_{CF}$ = 287.6, $^{3,4}\mathbf{C}F_3$); 130.39 ($^{15}\mathbf{C}$); 130.58 ($^{14,16}\mathbf{C}H$); 162.04 ($^{18}\mathbf{C}$); 206.55 ($^{13}\mathbf{C}O$). MS: 415, M^+ + H (0.6), 136 (10); 135 (100); 107 (8); 92 (4); 78 (2); 77 (12); 64 (2).

NMR–and GC-MS spectra of **3** were determined in the mixture of **2e** and **3**



1,1,1-trifluoro-8-(4-methoxyphenyl)-8-methyl-2-(trifluoromethyl)nonan-2-ol (**3**)

(**3**) [1] H NMR: 1.29 (s, 7H,$^{8,9}C\mathbf{H}_3$); 2.30 (bs, $^1\mathbf{H}O$); 1.34–1.83 (m, $^{2\text{-}6}\mathbf{C}H_2$);.3.81 (s.,3H, $^{17}C\mathbf{H}_3$); 6.87 (d, $^3J_{HH}$ = 8.82, 2H$^{12,14}C\mathbf{H}$**),** 7.26 (d, $^3J_{HH}$ = 8.90, 2H,$^{11,13}C\mathbf{H}$) ^{19}F NMR:-18.31 ($^{18,19,4}C\mathbf{F}_3$). ^{13}C NMR: 21.64 ($^3\mathbf{C}H_2$); 24.82 ($^5\mathbf{C}H_2$); 29.04 ($^{8,9}\mathbf{C}H_3{}^{8.9}$); 29.30 ($^4\mathbf{C}H_2$); 32.80 ($^2\mathbf{C}H_2$); 37.20 ($^7\mathbf{C}$); 42.22 ($^6\mathbf{C}H_2$); 55.18 ($^{17}\mathbf{C}H_3$); 113.36 ($^{12,14}\mathbf{C}H$); 119.11($^{18,19}\mathbf{C}H_2$); 126.48 ($^{11,13,}\mathbf{C}H$); 141.69 ($^{10}\mathbf{C}$); 157.13 ($^{15}\mathbf{C}H_2$); MS: M^+, 386 (1.4), 150, $HC(CH_3)_2C_6H_4O^+Me$ (11); 149, $^+C(CH_3)_2C_6H_4OMe$ (100); 135 (7); 122 (6); 122 (28); 100 (6); 94 (2); 91 (6); 79 (2); 77 (4)/.

Ethyl 9,9,9-trifluoro-8-hydroxy-2,2-dimethyl-8-(trifluoromethyl)nonanoate.

Reagent quantities used: substrate **1** (0.38 g, 1.36 mmol), electrophile (2.35 g., 2.71 mmol, prepared from CBr_4 (0.90 g., 2.71 mmol) and $AlBr_3$ (1.44 g. 5.40 mmol), CH_2Br_2 (3 ml), EtOH (2 ml), -20 °C, 2 h. Conversion of $HOC(CF_3)_2C_8H_{17}$ was 79%

(**2f**) MS: 353, M^+ + 1 (100), 351 (3), 279 (3): 277 (3); 237 (11); 217 (2); 209 (2); 207 (2); 203 (3); 153 (2); 149 (4); 145 (4); 141 (3); 135 (2); 130 (3); 129 (5); 121 (2); 117 (6); 116 (56); 115 (9); 111 (2); 109 (2); 101 (6); 97 (5); 95 (2); 91 (3); 89 (3); 88 (47); 87 (7); 83 (5); 77 (2) 73 (23); 71 (13); 70 (7); 69 (15); 67 (3); 65 (7); 61 (3); 59 (8); 58 (4); 57 (85); 56 (13); 55 (15).

***S*-Octyl 9,9,9-trifluoro-8-hydroxy-2,2-dimethyl-8-(trifluoromethyl)nonanthioate.**

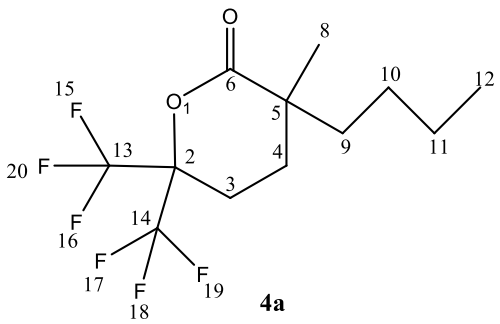
Reagent quantities used: substrate **1** (0.30 g, 1.07 mmol), electrophile (1.85 g., 2.14 mmol), prepared from CBr_4 (0.71 g., 2.14 mmol) and $AlBr_3$ (1,14 g. 4.28 mmol), CH_2Br_2 (2.4 ml), $C_8H_{17}SH$ (0.48 g, 3.29 mmol), -20 °C, 2 h.

(**2g**) MS: 453, M^+ + 1 (19), 279 (6): 237 (17); 223 (3); 145 (2); 71 (14); 69 (6); 65 (3); 61 (3); 58 (4); 57 (100); 56 (5); 55 (6).

By-product: $C_8H_{17}SSC_8H_{17}$. MS: 291, M^+ + 1 (40), 290, M^+, 290 (26), 289 (4); 237 (3); 178 (19); 147 (5); 146 (11); 145 (100); 144 (3); 143 (8); 115 (10); 111 (4); 101 (10); 87 (17); 82 (4); 81 (7); 79 (4); 72 (4); 71 (66); 70 (3); 69 (22); 67 (8); 65 (7); 61 (3); 59 (4); 57 (87), which was identical with authentic dioctyl disulfide, $C_8H_{17}SSC_8H_{17}$.

Reaction of $HOC(CF_3)_2C_8H_{17}$ 1 with CO at 0 °C

Reagent quantities used: substrate **1** (0.30 g, 1.07 mmol), electrophile (1.83 g., 2.12 mmol) prepared from CBr_4 (0.71 g., 2.13 mmol) and $AlBr_3$ (1,13 g. 4.24 mmol)), CH_2Br_2 (2.4 ml), 0 °C, 2 h. Conversion 92%. Products are four isomeric lactones with M^+ 306. Based on the NMR and MS spectra**,** the main isomers were assigned to structures **4a** and **4b.**

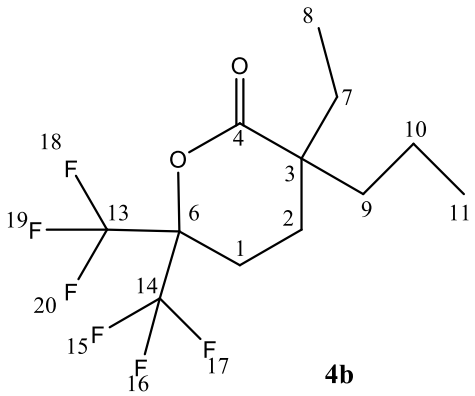


4a

3-Butyl-3-methyl-6,6-bis(trifluoromethyl)oxan-2-one **4a**

^{1}H NMR: 0.89 (t., $^3J_{HH}$ =7.3, $^{12}C\mathbf{H}_3$); 1.27 (s, $^8C\mathbf{H}_3$); 1.50–2.29 (m, $^{3,4,9,10}C\mathbf{H}_2$). ^{13}C NMR: 13.92 ($^{12}\mathbf{C}H_3$); 24.72 ($^8\mathbf{C}H_3$,); 22.92 ($^{11}\mathbf{C}H_2$); 25.73 ($^{10}\mathbf{C}H_3$); 27.40 ($^3\mathbf{C}H_2$); 29.48 ($^4\mathbf{C}H_2$); 38.56 ($^9\mathbf{C}H_2$);

40.74 (^{5}**C**); 80.89 (sept, $^{3}J_{CF}$ = 27.0, ^{2}**C**); 123.19 (q, $^{1}J_{CF}$ = 287.0, ^{13,14}**C**); 171.55 (^{6}**C**O); MS: 307, M^+ + H (89), 291, M^+ - Me (6); 277, M^+ - Et (6); 264, M^+ - C_3H_6 (4); 263, M^+ - Pr (11); 251, M^+ - C_4H_7 (10) 250, M^+- C_4H_8 (100); 249, M^+ - C_4H_9 (15); 236 (5); 235, M^+- C_4H_8 -Me (76); 221 (12); 207 (3); 203 (3); 191 (3); 181 (4); 153 (4); 149 (8); 145 (3); 139 (3); 135 (3); 127 (3); 154 (4); 109 (3); 97 (3); 95 (5); 86 (3); 85 (5); 77 (3); 71 (4); 69 (9); 68 (14); 67 (5); 57 (7); 55 (12).



4b

3-Ethyl-3-propyl-6,6-bis(trifluoromethyl)oxan-2-one **4b**

^{13}C NMR: 8.09 (^{8}**C**H_3); 14.77 (^{11}**C**H_3); 18.28 (^{10}**C**H_2); 24.36 (^{1}**C**H_2); 27.56 (^{7}**C**H_2); 32.52 (^{2}**C**H_2); 38.45 (^{9}**C**H_2); 76.02 (sept, $^{3}J_{CF}$ = 30.0, ^{6}**C**); 121.63 (q, $^{1}J_{CF}$ = 284.0, ^{13,14}**C**); 170.54. (^{4}**C**O); MS: 307, M^+ + H (32), 291, M^+ - Me (0.4); 278, M^+ - C_2H_4 (6), 277, M^+ - Et (10); 265 (3); 264, M^+ - C_3H_6 (29); 263, M^+ - Pr (6); 250 (9); 249, M^+ - Pr –CH_4 (100); 235 (10); 207 (5); 181 (7); 161 (3); 153 (3); 149 (5); 133 (3); 95 (5); 85 (8); 77 (2); 69 (4); 67 (5); 57 (2); 56 (9).