

# Supporting information

## Unexpected Formation of Tetrasubstituted 2,3-Dihydrofurans from the Reaction of beta-Keto Polyfluoroalkanesulfones with Aldehydes

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## General experimental procedure

Melting points were measured in Temp-Melt apparatus and were uncorrected. NMR spectra were taken at 300 MHz (for  $^1\text{H}$  NMR) or 282 MHz (for  $^{19}\text{F}$  NMR) in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  and  $\text{CFCl}_3$  (with upfield negative) as the internal and external standards, respectively. IR spectra were obtained using an FT IR spectrometer and only major peaks are reported in  $\text{cm}^{-1}$ . Mass spectra were recorded by the EI method. Thin-layer chromatography was performed on pre-coated silica gel 60 F254 analytical plates. All liquid aldehydes were distilled prior to use. Solid aldehydes were used without further purification. Solvents were reagent grade and used directly without drying.

***trans*-2-Benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3,5-diphenyl  
-2,3-dihydrofuran (3aa)**

Silica gel chromatography (eluent: hexane/ethyl ether, 10:1) provided pale yellow solid (213 mg, 84%). mp: 110-111°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.37-8.02(15H, m), 6.00(1H, d, *J*=3.0 Hz), 4.64(1H, d, *J*=3.0 Hz). <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ -68.3(2F, t, *J*=15Hz), -111.8--112.2(2F, AB), -119.9--120.5(4F, m). IR (KBr) cm<sup>-1</sup>: 3064, 3030, 2947, 1704, 1611, 1588, 1574, 1490, 1451, 1360, 1227, 1201, 1145, 1122, 1076, 766, 698. Ms (70eV, EI) *m/z* (%): 605(M<sup>+</sup>F, 2.78), 589(13.28), 519(2.15), 389(23.02), 325(100), 105(100), 77(98.92). Anal. Calcd. for C<sub>27</sub>H<sub>17</sub>F<sub>8</sub>ClO<sub>4</sub>S: C, 51.88; H, 2.72, F, 24.34. Found: C, 51.69; H, 2.57; F, 24.58.

***trans*-2-benzoyl-3-(4-bromophenyl)-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)  
-5-phenyl-2,3-dihydrofuran (3ab)**

Silica gel chromatography (eluent: hexane/ethyl ether 10:1) provided pale yellow solid (247 mg, 87%). mp: 107-109°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.25-8.00(14H, m), 5.96(1H, d, *J*=3.3Hz), 4.63(1H, d, *J*=3.3Hz). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.3(2F, t, *J*=14Hz), -110.9--112.9(2F, AB), -119.8--120.4(4F, m). IR (KBr) cm<sup>-1</sup>: 3065, 1701, 1606, 1585, 1570, 1488, 1361, 1223, 1202, 1168, 1142, 1117, 1075, 722. MS (70eV, EI) *m/z* (%): 667(M<sup>+</sup>Cl, 0.30), 467(1.04), 403(35.81), 105(100), 77(24.89). Anal. Calcd. for C<sub>27</sub>H<sub>16</sub>F<sub>8</sub>ClBrO<sub>4</sub>S: C, 46.06; H, 2.27. Found: C, 46.07; H, 2.31.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3-(4-nitrophenyl)**

**-5-phenyl-2,3-dihydrofuran (3ac)**

Silica gel chromatography (eluent: hexane/ethyl ether 4:1) provided pale yellow solid (244 mg, 90%). mp: 133-135°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.49-8.35(14H, m), 5.99(1H, d, *J*=3.3Hz), 4.84(1H, d, *J*=3.3Hz). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.3(2F, t, *J*=13Hz), -110.9--112.9(2F, AB), -119.7--120.3(4F, m). IR (KBr) cm<sup>-1</sup>: 3081, 1700, 1606, 1585, 1570, 1523, 1361, 1350, 1223, 1204, 1169, 1142, 1074, 775, 692. MS (70eV, EI) *m/z* (%): 669(M<sup>+</sup>, 0.02), 634(0.81), 434(3.50), 370(56.84), 105(100), 77 28.06). Anal. Calcd. for C<sub>27</sub>H<sub>16</sub>F<sub>8</sub>ClNO<sub>6</sub>S: C, 48.39; H, 2.39; N, 2.09. Found: C, 48.53; H, 2.51; N, 1.83.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3-(4-methylphenyl)**

**-5-phenyl-2,3-dihydrofuran (3ad)**

Silica gel chromatography (eluent: hexane/ethyl ether 10:1) provided pale yellow solid (202 mg, 78%). mp: 98-100°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.24-8.01(14H, m), 5.97(1H, d, *J*=3.6Hz), 4.60(1H, d, *J*=3Hz), 2.396(3H, s). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.2(2F, t, *J*=15Hz), -110.9--113.2(2F, AB), -119.7--120.8(4F, m). IR (KBr) cm<sup>-1</sup>: 3025, 2928, 2869, 1705, 1612, 1590, 1576, 1359, 1228, 1199, 1163, 1145, 1124, 1077, 768, 759, 733, 694, 689. MS (70eV, EI) *m/z* (%): 619(M<sup>+</sup>F, 0.20) 603(1.05), 403(1.78), 339(78.73), 105(100), 77(30.95). Anal. Calcd. for C<sub>28</sub>H<sub>19</sub>F<sub>8</sub>ClO<sub>4</sub>S: C, 52.62; H, 2.98. Found: C, 52.95; H, 3.13.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)**

**-3-(4-methoxyphenyl) -5-phenyl-2,3-dihydrofuran (3ae)**

Silica gel chromatography (eluent: hexane/ethyl ether 10:1) provided pale yellow solid (211 mg, 80%). mp: 96-98°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 6.96-8.00(14H, m), 5.97(1H, d, 3.3Hz), 4.59(1H, d, *J*=3.3Hz), 3.84(3H, s). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.2(2F, t, *J*=14Hz), -110.9--112.9(2F, AB), -119.7--120.3(4F, m). IR (KBr) cm<sup>-1</sup>: 3009, 2956, 2838, 1703, 1608, 1585, 1572, 1513, 1361, 1281, 1235, 1226, 1203, 1171, 1141, 1117, 1075, 843, 764, 691. MS (70eV, EI) *m/z* (%): 619(M<sup>+</sup>-Cl, 1.28), 419(0.42), 355(100), 105(84.93), 77(35.96). Anal. Calcd. for C<sub>28</sub>H<sub>19</sub>F<sub>8</sub>ClO<sub>5</sub>S: C, 51.34; H, 2.90. Found: C, 51.45; H, 2.96.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3-(4-chlorophenyl)-5-phenyl-2,3-dihydrofuran (3af)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 15:1) provided pale yellow solid (281 mg, 85%). mp: 103-105°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.30-8.01(14H, m), 5.951(1H, d, *J*=3.3Hz), 4.64(1H, d, *J*=3.3Hz). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.2(2F, t, *J*=14Hz), -110.9--112.9(2F, AB), -119.7--120.4(4F, m). IR (KBr) cm<sup>-1</sup>: 2925, 2868, 1708, 1611, 1589, 1576, 1491, 1360, 1228, 1200, 1171, 1145, 1124, 1078, 768, 688. MS (70eV, EI) *m/z* (%): 623(M<sup>+</sup>-Cl, 0.71), 423(2.75), 359(75.15), 105(100), 77(48.26). Anal. Calcd. for C<sub>27</sub>H<sub>16</sub>F<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub>S: C, 49.17; H, 2.43. Found: C, 49.29; H, 2.49.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3-(3-chlorophenyl)-5-phenyl-2,3-dihydrofuran (3ag)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided pale yellow solid (292 mg,

88%). mp: 102-104°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.26-8.00(14H, m), 5.96(1H, d, *J* = 3Hz), 4.66(1H, d, *J*=3Hz). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.2(2F, t, *J*=13Hz), -110.8--112.9(2F, AB), -119.7--120.3(4F, m). IR (KBr) cm<sup>-1</sup>: 2953, 2925, 2868, 1705, 1611, 1587, 1574, 1452, 1358, 1225, 1202, 1146, 1121, 1076, 771, 690. MS (70eV, EI) *m/z* (%): 623(M<sup>+</sup>-Cl, 0.67), 423(2.66), 359(48.98), 105(100), 77(31.27). Anal. Calcd. for C<sub>27</sub>H<sub>16</sub>F<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub>S: C, 49.17; H, 2.43. Found: C, 49.33; H, 2.48.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3-(2-chlorophenyl)-5-phenyl-2,3-dihydrofuran (3ah)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided pale yellow solid (271 mg, 82%). mp: 98-100°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 7.29-7.93(14H, m), 5.97(1H, d, *J*=3.6Hz), 5.39(1H, d, *J*=3.6Hz). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.2(2F, t, *J*=13Hz), -110.7--112.9(2F, AB), -119.6--120.3(4F, m). IR (KBr) cm<sup>-1</sup>: 2925, 2868, 1709, 1567, 1450, 1227, 1199, 1175, 1143, 1123, 756, 686. MS (70eV, EI) *m/z* (%): 623(M<sup>+</sup>-Cl, 2.26), 423(2.77), 359(34.85), 105(100), 77(33.83). Anal. Calcd. for C<sub>27</sub>H<sub>16</sub>F<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub>S: C, 49.17; H, 2.43. Found: C, 49.38; H, 2.50.

***trans*-2-benzoyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-5-phenyl-3-(4-pyridyl)-2,3-dihydrofuran (3aj)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided yellow solid (274 mg, 85%). mp: 145-147°C. <sup>1</sup>H NMR (300MHz, CDCl<sub>3</sub>): δ 8.70(2H, d, *J* = 4.8Hz), 7.25-7.97(12H, m), 5.93(1H, d, *J*=3Hz), 4.72(1H, d, *J*=3.6Hz). <sup>19</sup>F NMR (282MHz, CDCl<sub>3</sub>): δ -68.2(2F, t, *J*=14Hz),

-110.6--112.6(2F, AB), -119.5--120.3(4F, m). IR (KBr)  $\text{cm}^{-1}$ : 3061, 2925, 1703, 1609, 1587, 1574, 1449, 1369, 1227, 1200, 1163, 1143, 1124, 1074, 945, 770, 702. MS (70eV, EI)  $m/z$  (%): 625( $\text{M}^{\ddagger}$ , 0.06), 590(0.83), 390(4.47), 326(54.85), 105(100), 77(31.06). Anal. Calcd. for  $\text{C}_{26}\text{H}_{16}\text{F}_8\text{ClNO}_4\text{S}$ : C, 49.88; H, 2.56; N, 2.24. Found: C, 50.19; H, 2.63; N, 2.22.

***trans*-2-acetyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-5-methyl-3-phenyl-2,3-dihydrofuran (3ba)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided yellow oil (141 mg, 70%).  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23-7.37(5H, m), 4.96(1H, d,  $J=4.2\text{Hz}$ ), 4.52(1H, d,  $J=4.5\text{Hz}$ ), 2.47(3H, s), 2.26(3H, s).  $^{19}\text{F}$  NMR (282MHz,  $\text{CDCl}_3$ ):  $\delta$  -68.3(2F, t,  $J=17\text{Hz}$ ), -112.3--114.2(2F, AB), -119.4--120.4(4F, m). IR (Film)  $\text{cm}^{-1}$ : 3034, 1732, 1608, 1368, 1200, 1143, 959, 699. MS (70eV, EI)  $m/z$  (%): 500( $\text{M}^{\ddagger}$ , 0.20), 481(1.14), 465(3.31), 457(3.71), 395(0.58), 265(7.58), 201(97.70), 43(100). Anal. Calcd. for  $\text{C}_{17}\text{H}_{13}\text{F}_8\text{ClO}_4\text{S}$ : C, 40.76; H, 2.60. Found: C, 41.02; H, 2.88.

***trans*-2-acetyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-5-methyl-3-(4-nitrophenyl)-2,3-dihydrofuran (3bc)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided yellow solid (253 mg, 92%). mp: 103-105°C.  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  8.22(2H, d,  $J=9.3\text{Hz}$ ), 7.50(2H, d,  $J=9\text{Hz}$ ), 4.95(1H, d,  $J=4.8\text{Hz}$ ), 4.73(1H, d,  $J=4.5\text{Hz}$ ), 2.51(3H, s), 2.33(3H, s).  $^{19}\text{F}$  NMR (282MHz,  $\text{CDCl}_3$ ):  $\delta$  -68.4(2F, t,  $J=13\text{Hz}$ ), -112.1--114.1(2F, AB), -119.9--120.3(4F, m). IR (Film)  $\text{cm}^{-1}$ :

3081, 2917, 2849, 1731, 1609, 1525, 1351, 1201, 1144, 958, 740. MS (70eV, EI)  $m/z$  (%): 545( $M^+$ , 0.07), 526(1.14), 510(3.45), 310(33.18), 246(100), 43(80.34). Anal. Calcd. for  $C_{17}H_{13}F_8ClO_4S$ : C, 37.40; H, 2.20; N, 2.57. Found: C, 37.37; H, 2.44; N, 2.45.

***trans*-2-acetyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-5-methyl-3-(4-methylphenyl)-2,3-dihydrofuran (3bd)**

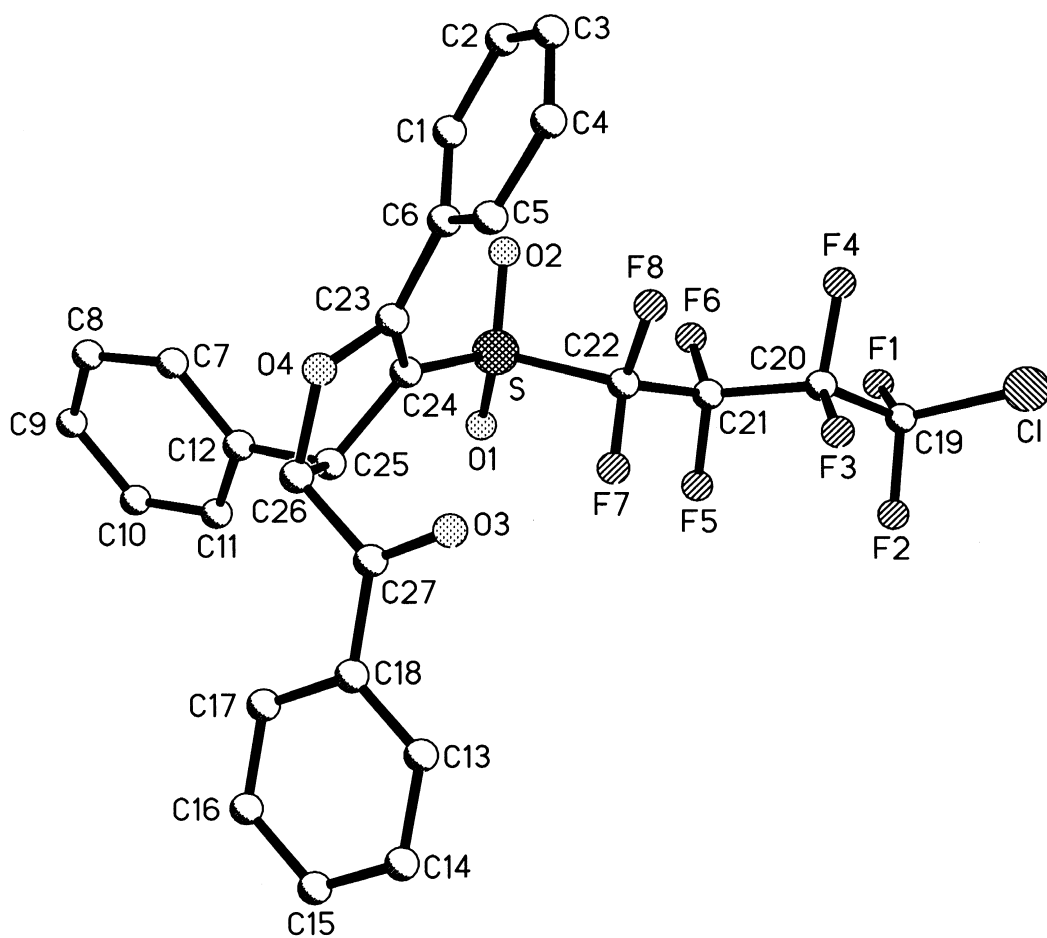
Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided yellow oil (187 mg, 72%).  $^1H$  NMR (300MHz,  $CDCl_3$ ):  $\delta$  7.15(4H, q,  $J=8.1$ Hz), 4.93(1H, d,  $J=4.8$ Hz), 4.47(1H, d,  $J=4.5$ Hz), 2.47(3H, s), 2.34(3H, s), 2.27(3H, s).  $^{19}F$  NMR ( $CDCl_3$ ):  $\delta$  -68.2--68.3(2F, m), -112.2--114.2(2F, AB), -119.7--120.3(4F, m). IR (Film): 3026, 2929, 1731, 1608, 1367, 1200, 1143, 959  $cm^{-1}$ . MS (70eV, EI)  $m/z$  (%): 514( $M^+$ , 0.75), 495(0.54), 479(3.29), 471(3.32), 279(4.44), 215(100), 43(93.07). Anal. Calcd. for  $C_{17}H_{13}F_8ClO_4S$ : C, 41.98; H, 2.92. Found: C, 41.88; H, 3.00.

***trans*-2-acetyl-4-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutane-1-sulfonyl)-3-(2-furyl)-5-methyl-2,3-dihydrofuran (3bi)**

Silica gel chromatography (eluent: hexane/ ethyl acetate 20:1) provided yellow solid (187 mg, 54%). mp: 60-62°C.  $^1H$  NMR (300MHz,  $CDCl_3$ ):  $\delta$  7.38(1H, d,  $J=1.2$ Hz), 6.25-6.34(2H, m), 5.13(1H, d,  $J=5.7$ Hz), 4.72(1H, d,  $J=4.8$ Hz), 2.41(3H, s), 2.27(3H, s).  $^{19}F$  NMR (282MHz,  $CDCl_3$ ):  $\delta$  -68.4(2F, t,  $J=12$ Hz), -112.6--115.0(2F, AB), -118.9--121.5(4F, m). IR (KBr)  $cm^{-1}$ : 2927, 1728, 1606, 1365, 1203, 1175, 1142, 1131, 1011, 741, 608. MS (70eV, EI)  $m/z$  (%): 490( $M^+$ , 1.78), 455(4.51), 447(10.78), 255(4.18), 191(83.57), 43(100). Anal. Calcd. for  $C_{17}H_{13}F_8ClO_4S$ : C,



36.70; H, 2.24. Found: C, 36.62; H, 2.19.



X-ray crystallography of **3aa**