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Synthesis of fluorinated dipyrazolyl sulfones from bis(2-fluoro-2-polyfluoroalkylalkenyl) sulfones and diazomethane

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SUPPLEMENTARY INFORMATION

The structures of all compounds were solved by the direct method and refined by the least-squares technique using the Bruker SHELXTL software package.[1]

Crystals of compound **3b** $C_{14}H_{10}F_{12}N_4O_2S$, M= 526.32 are rhombic, of spatial symmetry group *Pbca*, *a*= 14.222(2), *b* = 11.1665(15), *c* = 24.083(3) Å, , V = 3824.7(9)Å^3, Z = 8, d_c = 1.828, μ 0.306 mm^{-1}, F(000) 2096. Crystals of compound **by958 –4a-** $C_{10}H_{10}F_4N_4O_2S$, M= 326.28 are monoclinic, of spatial symmetry group *C2/c*, *a*= 25.046(4), *b* = 8.5574(14), *c* = 14.150(2) Å, β = 122.697(5)°, V = 2552.2(7)Å^3, Z = 8, d_c = 1.698, μ 0.314 mm^{-1}, F(000) 1328. Crystals of compound **by1254 -3a-** $C_{10}H_{10}F_4N_4O_2S$, M= 326.28 are monoclinic, of spatial symmetry group *C2/c*, *a*= 17.3482(15), *b* = 4.8080(4), *c* = 16.1171(13) Å, β = 107.156(5)°, V = 1284.51(19)Å^3, Z = 4, d_c = 1.687, μ 0.312 mm^{-1}, F(000) 664. Crystals of compound **by1352 -8-** $C_{10}H_{10}Cl_4N_4O_2S$, M= 392.08 are triclinic, of spatial symmetry group P-1, *a*= 8.5883(2), *b* = 8.8513(2), *c* = 11.4519(3) Å, α = 70.1874(15), β = 87.1908(16), γ = 78.0373(16)°, V = 801.02(3)Å^3, Z = 2, d_c = 1.626, μ 0.876 mm^{-1}, F(000) 396.

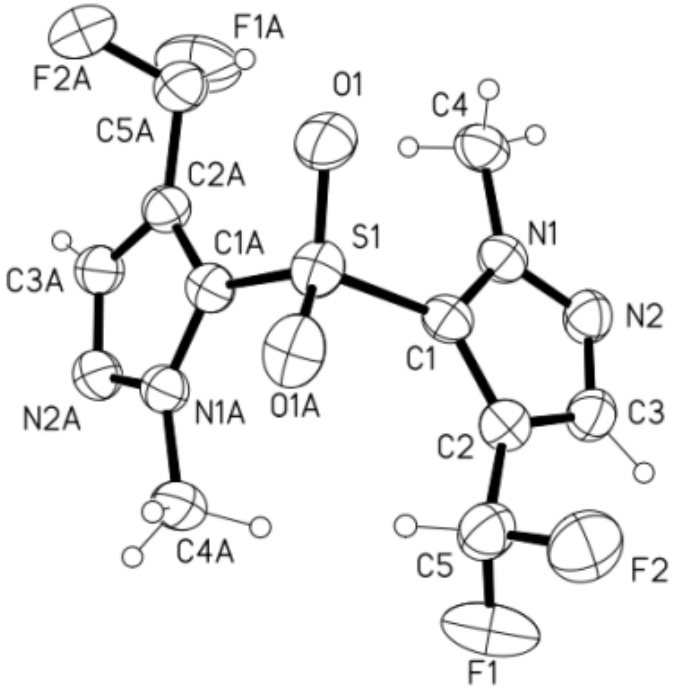

Fig. 1. The molecular structure of compound **3a** $C_{10}H_{10}F_4N_4O_2S$, M= 326.28 are monoclinic, of spatial symmetry group *C2/c*, *a*= 17.3482(15), *b* = 4.8080(4), *c* = 16.1171(13) Å, β = 107.156(5)°, V = 1284.51(19)Å^3, Z = 4, d_c = 1.687, μ 0.312 mm^{-1}, F(000) 664.

Crystals of compound **3a** $C_{10}H_{10}F_4N_4O_2S$, M= 326.28 are monoclinic, of spatial symmetry group *C2/c*, *a*= 17.3482(15), *b* = 4.8080(4), *c* = 16.1171(13) Å, β = 107.156(5)°, V = 1284.51(19)Å^3, Z = 4, d_c = 1.687, μ 0.312 mm^{-1}, F(000) 664. X-ray structural studies of a single crystal of the compound with linear dimensions 0.08 x 0.11 x 0.50 mm were conducted at 173K on a Bruker Smart Apex II diffractometer (λMoK_α - beam, graphite monochromator, θ_{max} 26.29°, sphere segment $-20 \le h \le 21$ $-5 \le k \le 5$, $-19 \le l \le 20$). A total of 6586 reflections were collected, of which 1292 were independent (Averaging R-factor 0.044). All non-hydrogen atoms were refined anisotropically. All CH hydrogen atoms in the compound molecule were planted geometrically ("riders"), and their positions and thermal parameters were refined along with the positions and thermal parameters of the accompanying carbon atoms. 954 reflections were used in the refinement with $I > 2\sigma(I)$, (97 refined parameters, weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (0.0549P)^2 + 1.4137P]$, where $P = (Fo^2 + 2Fc^2)/3$. The final values of the divergence factors R1(F) 0.0498 , wR2(F^2) 0.1131 for reflections with $I > 2\sigma(I)$ and R1(F) 0.0710, wR2(F^2) 0.1247, GOF 1.053 for all independent reflections. Residual electron density from the Fourier differential series after the last refinement cycle was 0.29 and -0.26 e/Å^3. The structure is deposited at the Cambridge Crystallographic Data Center with the registration number CCDC 1905703.

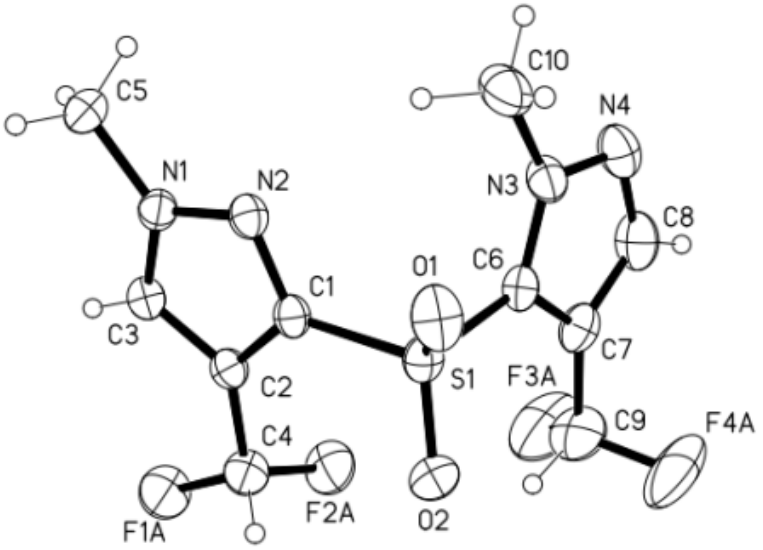

Fig. 2. The molecular structure of compound **4a** $C_{10}H_{10}F_4N_4O_2S$, M= 326.28 are monoclinic, of spatial symmetry group *C2/c*, *a*= 25.046(4), *b* = 8.5574(14), *c* = 14.150(2) Å, β = 122.697(5)°, V = 2552.2(7)Å^3, Z = 8, d_c = 1.698, μ 0.314 mm^{-1}, F(000) 1328

X-ray structural studies of a single crystal of compound **4a** with linear dimensions 0.26 x 0.34 x 0.48 mm were conducted at 173K on a Bruker Smart Apex II diffractometer (λMoK_α - beam, graphite monochromator, θ_{max} 27.6°, sphere segment $-32 \le h \le 32$, $-11 \le k \le 9$, $-18 \le l \le 17$). A total of 14213 reflections were collected, of which 2860 were independent (Averaging R-factor 0.0315). In the solid state, the fluorine atoms of the CHF_2 groups are disordered over two positions A and B with populations of 0.917 and 0.083, respectively, and all non-hydrogen atoms were refined anisotropically (apart from disordered fluorine atoms of position B, which were refined isotropically due to low population). All CH hydrogen atoms in the compound molecule were planted geometrically ("riders"), and their positions and thermal parameters were refined along with the positions and thermal parameters of the accompanying carbon atoms. 2367 reflections were used in the refinement with $I > 2\sigma(I)$, (209 refined parameters, weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (0.0742P)^2 + 5.7301P]$ was used, where $P = (Fo^2 + 2Fc^2)/3$. The final values of the divergence factors R1(F) 0.0478 , wR2(F^2) 0.1296 for reflections with $I > 2\sigma(I)$ and R1(F) 0.0595, wR2(F^2) 0.1395, GOF 1.02 for all independent reflections. Residual electron density from the Fourier differential series after the last refinement cycle was 0.61 and -0.52 e/Å^3. The structure is deposited at the Cambridge Crystallographic Data Center with the registration number CCDC 1905702.

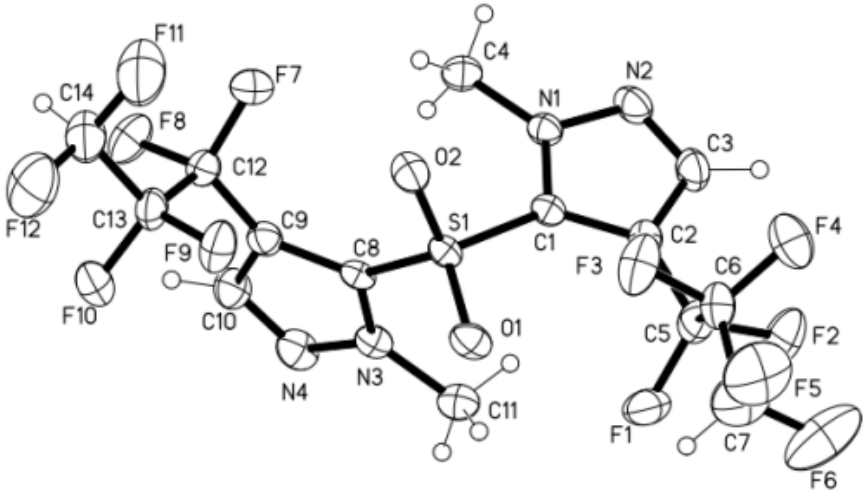

Fig. 3. The molecular structure of compound **3b** $C_{14}H_{10}F_{12}N_4O_2S$, M= 526.32 are rhombic, of spatial symmetry group *Pbca*, *a*= 14.222(2), *b* = 11.1665(15), *c* = 24.083(3) Å, , V = 3824.7(9)Å^3, Z = 8, d_c = 1.828, μ 0.306 mm^{-1}, F(000) 2096

X-ray structural studies of a single crystal of compound **3b** with linear dimensions 0.18 x 0.27 x 0.49 mm were conducted at room temperature on a Bruker Smart Apex II diffractometer (λMoK_α - beam, graphite monochromator, θ_{max} 26.7°, sphere segment $-14 \le h \le 17$, $-11 \le k \le 14$, $-28 \le l \le 29$). A total of 38255 reflections were collected, of which 3998 were independent (Averaging R-factor 0.054). All non-hydrogen atoms were refined anisotropically. All CH hydrogen atoms in the compound molecule were planted geometrically ("riders"), and their positions and thermal parameters were refined together with the positions and thermal parameters of the accompanying carbon atoms. 2611 reflections were used in the refinement with $I > 2\sigma(I)$, (300 refined parameters, weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (0.048P)^2 + 3.314P]$, where $P = (Fo^2 + 2Fc^2)/3$. The final values of the divergence factors R1(F) 0.0467, wR2(F^2) 0.1045 for reflections with $I > 2\sigma(I)$ and R1(F) 0.087, wR2(F^2) 0.1246, GOF 1.031 for all independent reflections. Residual electron density from the Fourier differential series after the last refinement cycle was 0.41 and -0.28 e/Å^3. The structure is deposited at the Cambridge Crystallographic Data Center with the registration number CCDC 1905701.

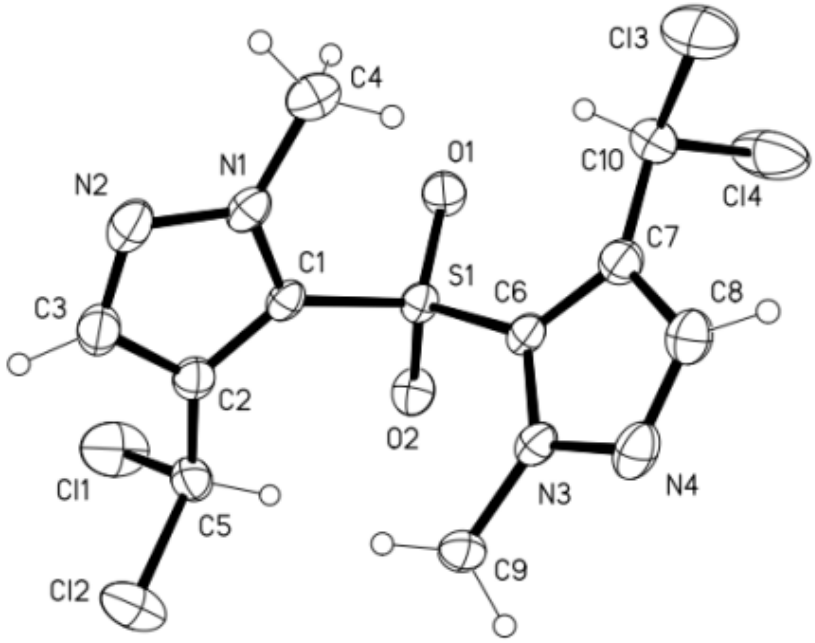

Fig. 4. The molecular structure of compound **8** $C_{10}H_{10}Cl_4N_4O_2S$, M= 392.08 are triclinic, of spatial symmetry group P-1, *a*= 8.5883(2), *b* = 8.8513(2), *c* = 11.4519(3) Å, α = 70.1874(15), β = 87.1908(16), γ = 78.0373(16)°, V = 801.02(3)Å^3, Z = 2, d_c = 1.626, μ 0.876 mm^{-1}, F(000) 396.

Crystals of compound **8** $C_{10}H_{10}Cl_4N_4O_2S$, M= 392.08 are triclinic, of spatial symmetry group P-1, *a*= 8.5883(2), *b* = 8.8513(2), *c* = 11.4519(3) Å, α = 70.1874(15), β = 87.1908(16), γ = 78.0373(16)°, V = 801.02(3)Å^3, Z = 2, d_c = 1.626, μ 0.876 mm^{-1}, F(000) 396. X-ray structural studies of a single crystal of the compound with linear dimensions 0.08 x 0.21 x 0.46 mm were conducted at 173K on a Bruker Smart Apex II diffractometer (λMoK_α - beam, graphite monochromator, θ_{max} 26.58°, sphere segment $-10 \le h \le 10$, $-11 \le k \le 11$, $-14 \le l \le 12$). A total of 12699 reflections were collected, of which 3332 were independent (averaging R-factor 0.0316). All non-hydrogen atoms were refined anisotropically. All CH hydrogen atoms in the compound molecule were planted geometrically ("riders"), and their positions and thermal parameters were refined together with the positions and thermal parameters of the accompanying carbon atoms. 2754 reflections were used in the refinement with $I > 2\sigma(I)$, (192 refined parameters, weighting scheme $\omega = 1/[\sigma^2(Fo^2) + (0.0526P)^2 + 0.5312P]$, where $P = (Fo^2 + 2Fc^2)/3$. The final values of the divergence factors R1(F) 0.0400 , wR2(F^2) 0.0991 for reflections with $I > 2\sigma(I)$ and R1(F) 0.0509, wR2(F^2) 0.1061, GOF 1.038 for all independent reflections. Residual electron density from the Fourier differential series after the last refinement cycle was 0.46 and -0.44 e/Å^3. The structure is deposited at the Cambridge Crystallographic Data Center with the registration number CCDC 1916209

1.Sheldrick, G. *Acta Crystallogr.*, *Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.