Electronic Supplementary Information for

Supramolecular synthons in fluorinated benzyl nitrophenyl sulfides.

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Figure S1. ORTEP plot of 4-nitrobenzyl pentafluorophenyl sulfide 1

Figure S2. ORTEP plot of 4-nitrophenyl pentafluorobenzyl sulfide 2
Summary of main intermolecular interactions in sulfides (1) and (2)

4-Nitrobenzyl 2,3,4,5,6-pentafluorophenyl sulfide (1)

Hydrogen bondings and similar.
(*) One nitro oxygen atom with both one ortho-hydrogen atom (distance O···H_{ortho} 2.58 Å) and with one methylene hydrogen atom (distance O···H 2.76 Å).
(*) One nitro oxygen atom with one of the phenyl meta-hydrogen (distance O···H 2.74 Å).
(*) One nitro oxygen atom with one ortho-fluorine (distance F_{ortho}···H_{ortho} 2.51 Å).

CF···FC short contacts
(*) CF_{ortho}···F_{meta}C (distance 2.82 Å; C_{ortho}·F_{ortho}·F_{meta} angle = 150° e C_{meta}·F_{meta}·F_{ortho} angle =151°).
(*) CF_{meta}···F_{para} (distance F_{meta}···F_{para} 2.89 Å; C_{para}·F_{para}·F_{meta} angle =168°; C_{meta}·F_{meta}·F_{para} =135°).

4-Nitrophenyl pentafluorobenzyl sulfide (2)

Hydrogen bondings and similar.
(*) One nitro oxygen atom with one methylene hydrogen atom (distance O···H 2.54 Å).
(*) One nitro oxygen atom with one methylene hydrogen atom of a different molecule (distance O···H 2.73 Å).
(*) One ortho-hydrogen atom with one meta-fluorine (distance F_{meta}···H_{ortho} 2.65 Å).
(*) One meta-hydrogen atom with one para-fluorine (distance F_{para}···H_{meta} 2.50 Å).

CF···π short contacts
(*) One meta-fluorine atom with the plane of the pentafluorophenyl group (the distance from the plane is 3.15 Å).
(*) One para-fluorine atom with the plane of the nitrophenyl group (the distance from the plane is 3.18 Å).
CH···F interactions in Sulfides (1) and (2).

Figure S3. CH···F interactions in 4-nitrobenzyl pentafluorophenyl sulfide 1

Figure S4. CH···F interactions in 4-nitrophenyl pentafluorobenzyl sulfide 2
Crystal Explorer Fingerprint Analysis

**Figure S5.** Fingerprint analysis of 4-nitrobenzyl pentafluorophenyl sulfide 1. On the left, O···H contributions to the surface. On the right, F···H contributions.

**Figure S6.** Fingerprint analysis of 4-nitrophenyl pentafluorobenzyl sulfide 2. On the left, O···H contributions to the surface. On the right, F···H contributions.
Figure S7. F···F short contacts in 4-nitrobenzyl pentafluorophenyl sulfide 1