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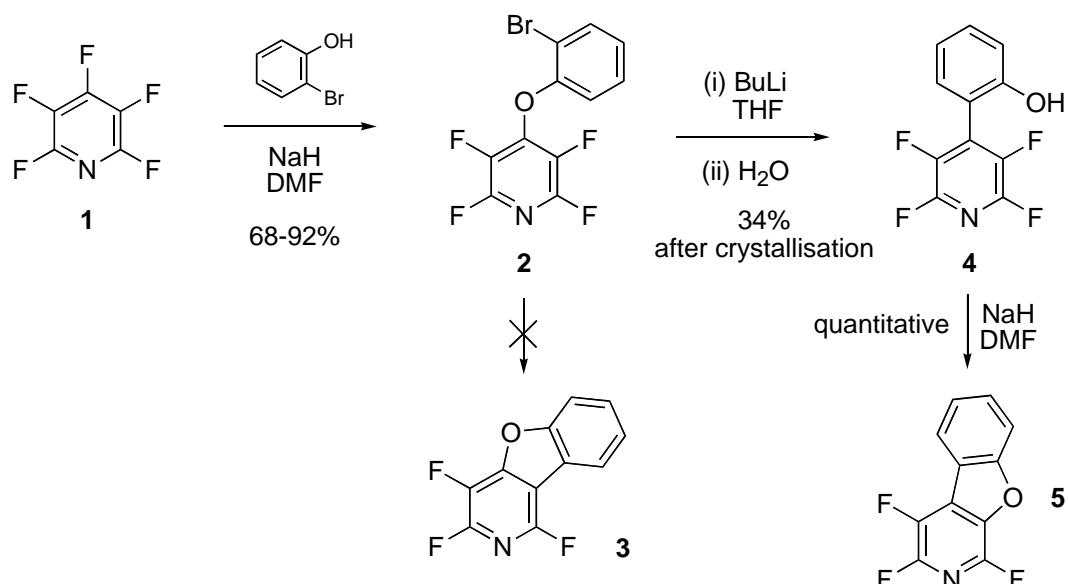
Synthesis of Fluorinated Fused Benzofurans and Benzothiophenes: Smiles-type Rearrangement and Cyclisation of Perfluoro(het)aryl Ethers and Sulfides

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Abstract

Lithium-bromine exchange in 2-bromophenyl perfluoroaryl ethers or sulfides affords fused fluorinated benzofurans or benzothiophenes respectively by S_NAr substitution of the adjacent fluorine in the perfluoroaryl substituent. The structures of the new compounds were confirmed by NMR spectroscopy and single crystal X-ray diffraction analysis. In the case of 2-bromophenyl tetrafluoropyrid-4-yl ether, lithiation promoted a Smiles-type rearrangement which led to formation of 4-(2-hydroxyphenyl)tetrafluoropyridine, the structure of which confirmed by X-ray crystallography.

Aromatic nucleophilic substitution in per- and poly-fluorinated arenes^{1,2} is a valuable method for constructing highly functionalised heterocycles and aromatics.³ Such compounds have been widely investigated by Chambers⁴ and Sandford⁵ and have been used as scaffolds for drug discovery.⁶ The mechanistic and synthetic potential of fluorinated arenes has been reviewed.⁷ There is considerable interest in ring closing reactions of substituted polyfluoroarenes as a way of rapidly generating usefully functionalised polycyclic compounds.^{8,9} As part of our investigations in this area we have studied ring closure by lithiation of bromoaryl ethers and sulfides containing a perfluoroarene ring. Reaction of a lithiated binaphthyl with hexafluorobenzene has recently been used in an elegant synthesis of a fluorinated helicene by Piers.¹⁰ In our study lithiation of the easily prepared 2-bromophenyl tetrafluoropyrid-4-yl ether **2** (Scheme 1) was expected to form the pyrido-fused benzofuran derivative **3** by



Scheme 1 Formation and Smiles-type rearrangement of ether **2**

lithium-bromine exchange and then intramolecular substitution of the fluorine at C-3 of the pyridine ring to close the furan ring. However treatment of the tetrafluoropyridyl ether **2** with *n*-butyllithium in THF at low temperature afforded a compound which was not the expected tricyclic furan **3**. IR and ^1H NMR spectroscopy indicated the presence of an alcohol group (δ_{H} 5.01, exchangeable with D_2O) while the ^{19}F NMR spectrum showed signals for two pairs of fluorine atoms indicating that the tetrafluoropyridine ring was intact. The product was identified as the 2-(tetrafluoropyrid-4-yl)phenol **4** and the structure was confirmed by X-ray crystallography (Figure 1, Table 1) indicating that the reaction had proceeded by a Smiles type^{11,12} rearrangement rather than $\text{S}_{\text{N}}\text{Ar}$ reaction at the 3-position of the pyridine ring. The structure of the biaryl **4** showed a unique hydrogen bond between the phenolic OH group and the weakly basic tetrafluoropyridine nitrogen, resulting in zig-zag chains of molecules. The torsion angle between the two aryl rings is 56.05(3) $^\circ$. Molecules $\pi \cdots \pi$ stack with centroid-centroid separations of 3.864 and 4.021 Å and a shortest contact of 3.620 Å for N(4)···C(12'). Treatment of the phenol **4** with sodium hydride in DMF gave the fused benzofuran **5** quantitatively with the phenoxide oxygen effecting nucleophilic substitution of the fluorine atom at 3-position of the pyridine ring.

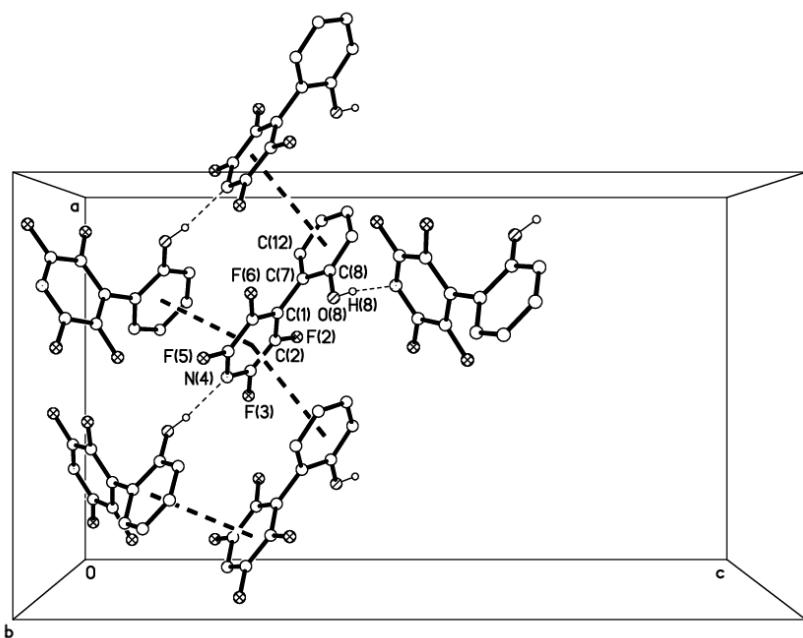
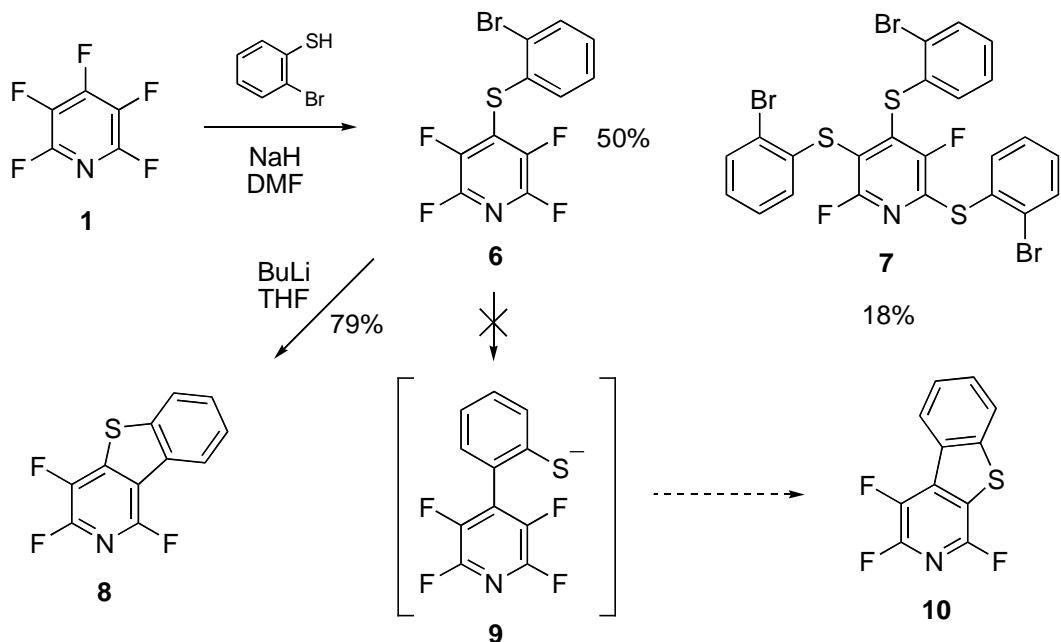


Figure 1. Crystal structure of **4** showing $\pi\cdots\pi$ stacking and H-bond intermolecular interactions. $O(8)-H(8)\cdots N(4') = 2.846 \text{ \AA}$, angle at $H(8) = 168^\circ$.

Reaction of pentafluoropyridine and sodium 2-bromobenzenethiolate in DMF (Scheme 2) gave the corresponding sulfide **6** (50%) together with a small amount (17%) of the product of trisubstitution **7**. The latter was identified as the 2,4,5-tri(2-bromophenylthio)-3,6-difluoropyridine, and the substitution pattern, which differs¹³



Scheme 2 Formation and cyclisation of sulfide **6**

from that usually found¹⁴ for pentafluoropyridine, was shown by the ¹⁹F NMR spectrum (δ_F 45.6 and 99.0), and was confirmed by X-ray crystallography (Figure 2, Table 1). Compound **7** crystallised as the hemi-toluene solvate and exhibits no $\pi\cdots\pi$ stacking but two types of halogen···halogen interactions ($F(3)\cdots Br(3') = 3.248$; $Br(3)\cdots Br(3'') = 3.880 \text{ \AA}$). None of the 2,4-disubstituted product was isolated. Lithiation of sulfide **6** (Scheme 2) gave a pyrido-fused benzothiophene in 79% yield, which was shown by X-ray crystallography (Figure 3, Table 1) to be compound **8** rather than the alternatively fused tricycle **10**. In this case direct intramolecular substitution of the C-3 fluorine in the pyridine ring occurred rather than Smiles rearrangement, which would have formed thiolate **9** that could have undergone ring closure to form isomer **10**.

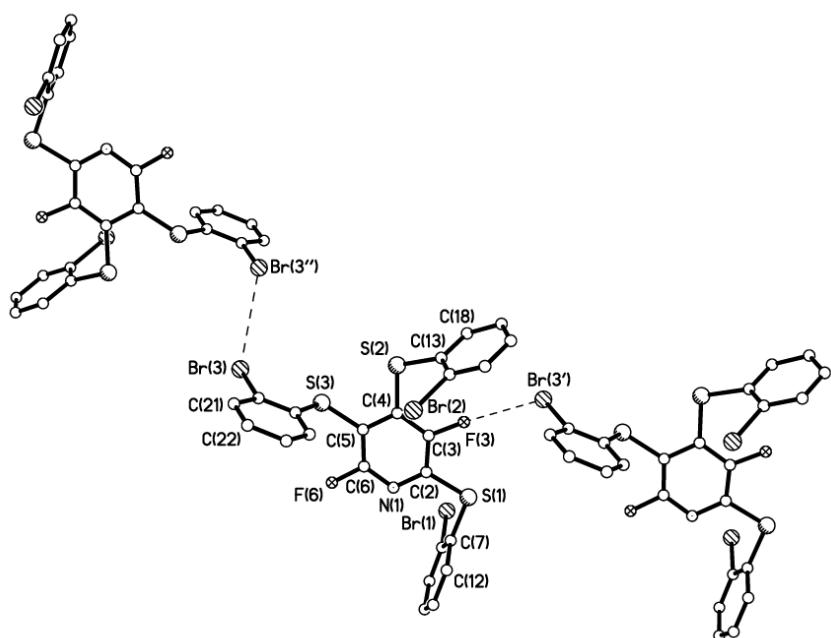


Figure 2. Crystal structure of **7** showing halogen···halogen interactions. Toluene of crystallisation omitted for clarity.

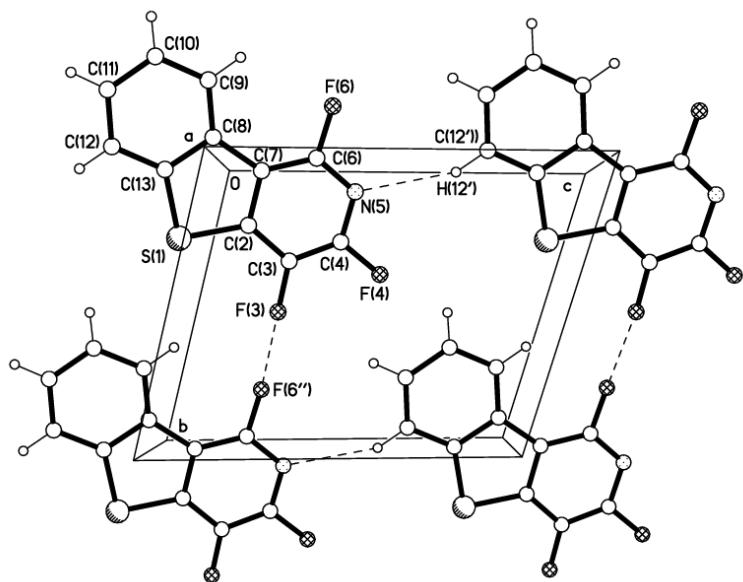
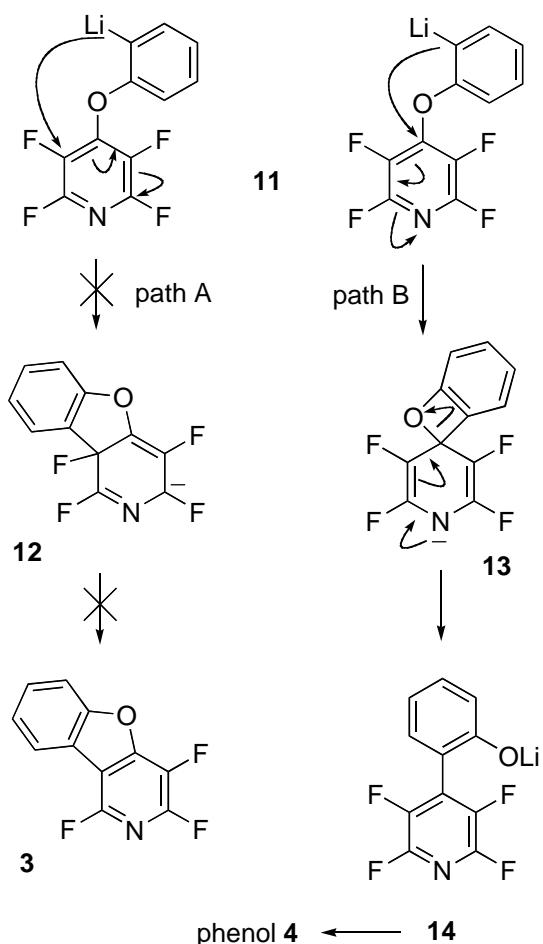


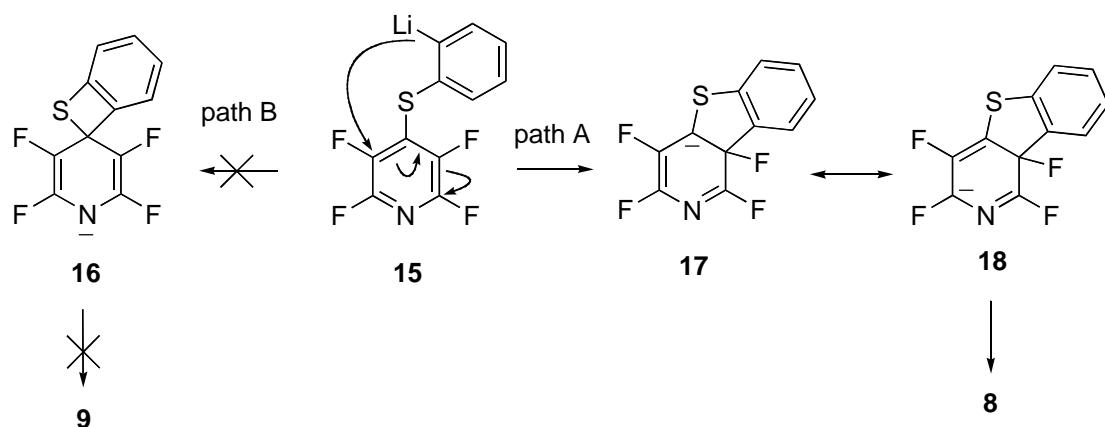
Figure 3. Crystal structure of **8** showing fluorine···fluorine $\{F(3)\cdots F(6'') = 2.800 \text{ \AA}\}$ and H-bond $\{C(12')-\text{H}(12')\cdots N(5) = 2.54 \text{ \AA}; \text{angle at H}(12') = 157^\circ\}$ intermolecular interactions. Not shown: $\pi\cdots\pi$ stacking interactions parallel to a with a spacing of $a/2 = 3.61 \text{ \AA}$.

In the case of the ether **2**, reaction of the lithiated intermediate **11** (Scheme 3) must have proceeded with a Smiles-type rearrangement (path B) with attack at the ipso position occurring, even though this would involve the strained four-membered intermediate **13**. Smiles rearrangements involving five-membered intermediates have been reported for perfluoroarene derivatives,¹⁵ and a radical Smiles rearrangement has



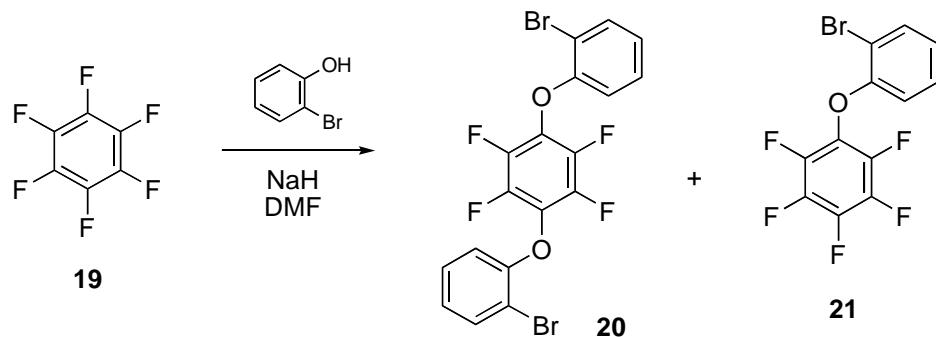
Scheme 3 Possible reaction pathways for lithiated ether **11**

been described by Zard¹⁶ which proceeds through a four-membered cyclic intermediate. Dudley¹⁷ has recently reported a rearrangement of 2-benzyloxypyridines to 2-pyridyl carbinols on treatment with LDA which involves a 3-membered intermediate. Attack at the ipso position in **11** must occur to avoid the unfavourable repulsion effect^{18,19,20} the 6-fluoro substituent would have on the pyridyl anion **12** if attack at C-3 occurred (path A). In the case of the lithiated thioether **15** (Scheme 4), the stabilising effect²¹ of the sulfur atom at C-4 must outweigh the destabilising influence of the fluorine at C-6 allowing attack at C-3 through a less strained five-membered intermediate (**17** \leftrightarrow **18**), rather than attack at C-4 forming **16**. The longer C–S bonds in **15** may also make it harder to close the four-membered ring in **16**. It is not clear why the initially formed phenoxide **14** (Scheme 3), generated in the lithiation promoted Smiles rearrangement of **2**, did not cyclise to **5** under the reaction conditions, but complexation of the alkoxide by lithium in the relatively non-polar THF may have diminished its reactivity.



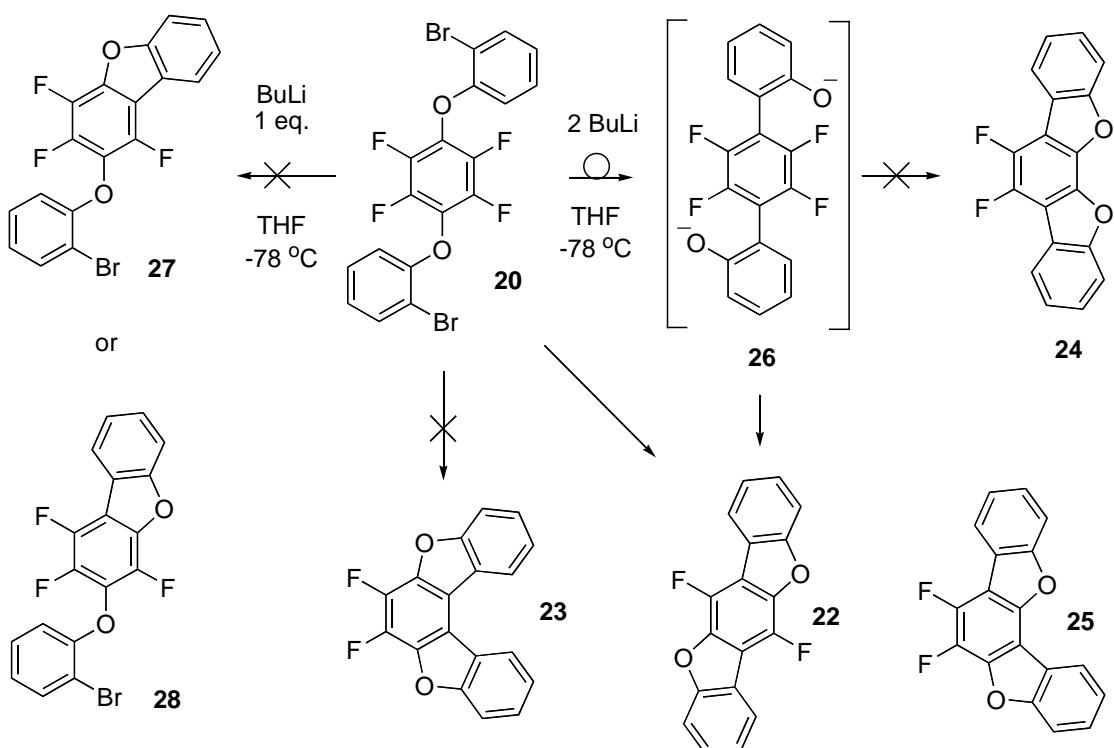
Scheme 4 Mechanism of formation of **8**

We then investigated reaction of hexafluorobenzene **19** with 2-bromophenol or 2-bromobenzenethiol in the presence of sodium hydride. With the phenol it proved difficult to isolate the mono-substitution product **21** (Scheme 5). Replacement of the



Scheme 5 Reaction of hexafluorobenzene with 2-bromophenol

4-fluorine atom in the first-formed product occurred, and the major product formed was the 1,4-bis ether **20**. Only by using ten equivalents of hexafluorobenzene could we isolate the mono-ether **21** in a moderate 58% yield, and **20** was still formed in trace amount. Since bis-ether **20** could be readily formed in quantity, we decide to investigate lithiation of this substrate (Scheme 6). Treatment of **20** with two



Scheme 6 Cyclisation of bis-ether **20** to benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzofuran **22**

equivalents of *n*-butyllithium in THF at -78 °C followed by warming to room temperature gave, after aqueous work-up and crystallisation, a non-phenolic, high melting (279-280 °C) crystalline product in low yield (19%). ¹H and ¹⁹F NMR spectroscopy showed the compound to be a symmetrical molecule with four proton resonances and a single fluorine signal (δ_F 14.7 ppm). X-ray crystallography showed the product to be the centro-symmetric pentacyclic fused bis furan **22** (Figure 4, Table 1). The small, thin, weakly diffracting crystals required synchrotron radiation for data collection. The molecules pack in a herring-bone fashion exhibiting both halogen···halogen and π ··· π stacking interactions.

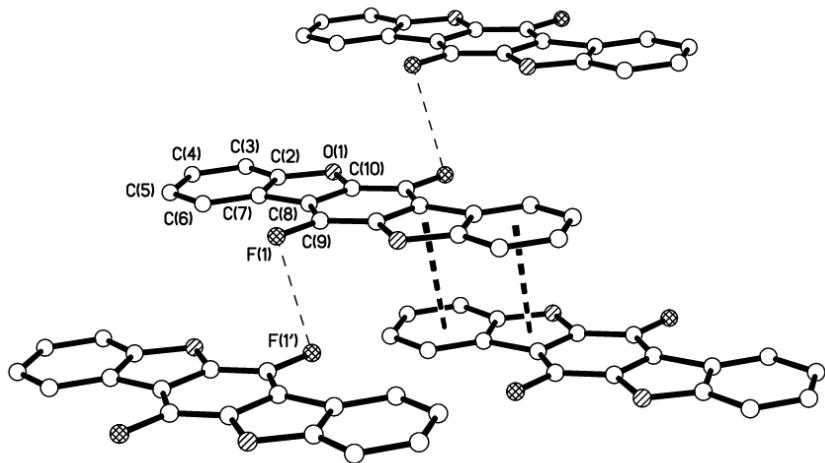
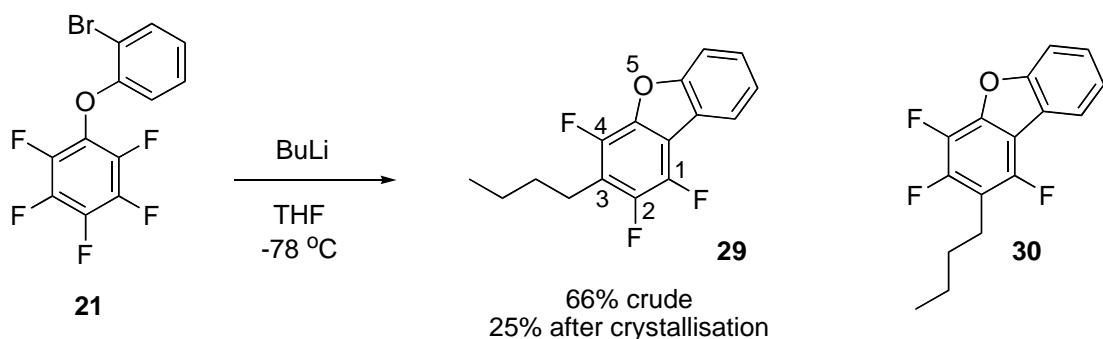


Figure 4. Crystal structure of **22** showing stepped chains via fluorine···fluorine {F(1)···F(1') = 2.833 Å} interactions and head-to-tail $\pi\cdots\pi$ interactions {centroid···centroid = 3.902 Å, closest atom···atom separations ca. 3.42 Å}.

It is not clear if this compound is formed by direct S_NAr substitution of the adjacent fluorine atoms (**20** → **22**), or if Smiles rearrangement has taken place first at both ether linkages, forming the bis-phenoxide **26** which could have undergone ring closure to **22**. None of the other possible products of cyclisation which could have shed light on to whether cyclisation occurred directly **23**, with rearrangement **24**, or with a combination of both **25**, were isolated. An experiment to determine if rearrangement occurred during this reaction was carried out by treating bis-ether **20** with a single equivalent of *n*-butyllithium with the expectation that isolation of **27** would demonstrate direct cyclisation occurred, whereas formation of **28** would show that Smiles rearrangement had preceded cyclisation. Unfortunately this experiment was inconclusive with a complex mixture forming from which no identifiable products could be obtained. Treatment of the pentafluorophenyl ether **21** (Scheme 7) with *n*-butyllithium gave a fluorinated benzofuran in moderate yield (66% crude, 25% after crystallisation). Since excess *n*-butyllithium was employed in this reaction addition

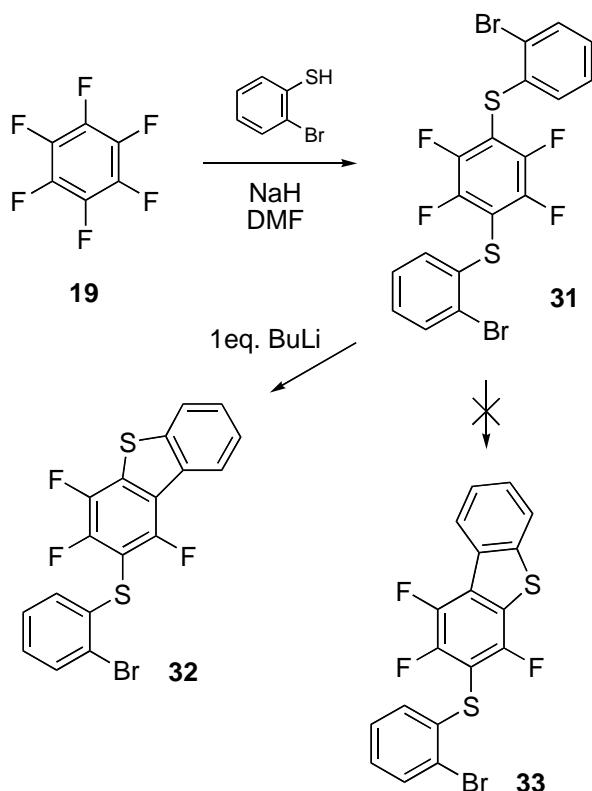


Scheme 7 Reaction of bromophenyl pentafluorophenyl ether **21** with *n*-BuLi

of an *n*-butyl group to the fluorinated ring also occurred. The structure of the product was assigned as the 3-butyl derivative **29** (numbering shown) with the butyl group adding most likely *para* to carbon rather than oxygen (giving **30**) assuming the addition occurred after ring closure. The low melting point (48 °C) of this compound precluded formation of suitable crystals for X-ray diffraction analysis, but detailed analysis of the long range carbon-fluorine coupling constants²² in the ¹³C NMR spectrum supported the assignment of the structure as **29**. Calculation of the Mulliken charges in 1,2,3,4-tetrafluorodibenzofuran (structure optimised using Gaussian 03 at the B3LYP/6-31G* level)²³ indicated C-3 (+0.261) to be more slightly electrophilic than C-4 (+0.258) also supporting assignment as **29**. The values for C-1 and C-4 were +0.250 and +0.255 respectively.

Reaction of 2-bromobenzenethiol (two equivalents), sodium hydride and hexafluorobenzene in DMF gave the 1,4-disubstitution product **31** (Scheme 8) in 81% crude yield (70% after crystallisation). The monosubstitution product could not be formed even when a large excess of hexafluorobenzene was employed. Treatment of **31** with a single equivalent of *n*-butyllithium afforded the 2-(bromophenylthio)-1,3,4-

trifluorodibenzothiophene **32** showing that cyclisation had occurred without initial



Scheme 8 Direct cyclisation of bis-sulfide **31** with 1 equivalent of *n*-BuLi

Smiles rearrangement as was observed for the pyridyl ether. None of the isomer **33** was detected. The structure of the dibenzothiophene **32** was confirmed by X-ray crystallography which showed that the sulfur atoms retained their original 1,4-relationship. The compound crystallised as two monoclinic polymorphs (**32A** – rod-shaped crystals and **32B** – plate-shaped) (Figures 5 and 6, Table 1). Both polymorphs have 3D supramolecular structures, but the balance of $\pi \cdots \pi$ and halogen \cdots halogen interactions differs. In **32A** there are both types: $\text{Br}(1) \cdots \text{Br}(1'') = 3.268$, $\text{F}(3) \cdots \text{F}(3'') = 2.879$ Å and centroid \cdots centroid separations of 3.688 and 3.547 Å for ring C(15)–C(20) with its symmetry equivalent and ring C(8)–C(13) with ring C(2')–C(7') respectively. In **32B** there are no halogen \cdots halogen interactions, although there is an $\text{F}(6) \cdots \text{S}(1') = 3.260$ Å short contact; however there are more $\pi \cdots \pi$ interactions: ring C(15)–C(20) with its symmetry equivalent (centroid \cdots centroid = 3.716 Å) and head-to-tail interactions between the three fused rings and their symmetry equivalents (centroid \cdots centroid = 3.586 Å).

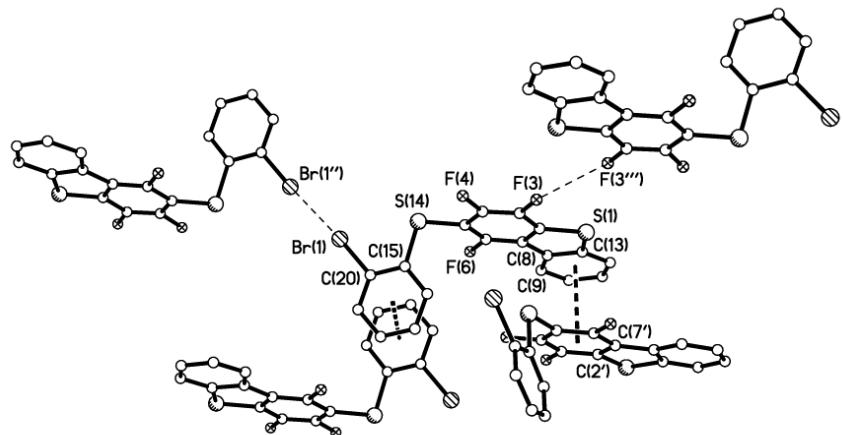


Figure 5 Crystal structure of **32A** showing $\pi\cdots\pi$ and halogen \cdots halogen interactions.

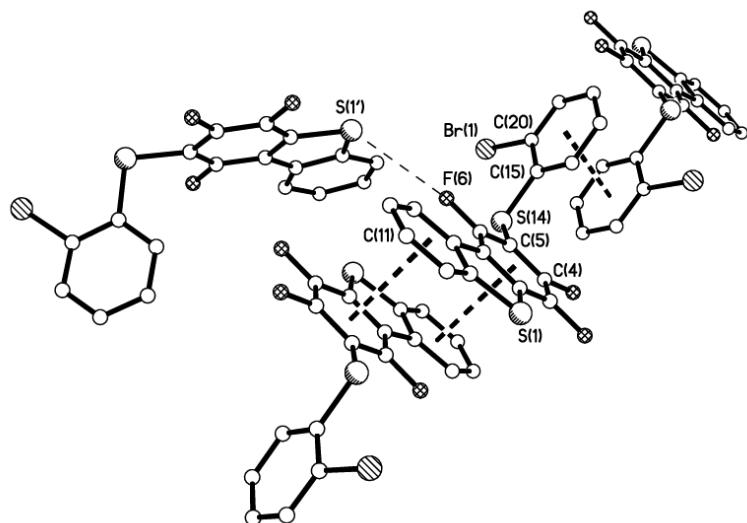


Figure 6 Crystal structure of **32B** showing $\pi\cdots\pi$ and fluorine \cdots sulfur interactions.

When the bis-sulfide **31** was treated with two equivalents of *n*-butyllithium (Scheme 9) cyclisation occurred between both bromophenyl groups and the central fluorinated benzene ring to give the pentacyclic 6,12-difluorobenzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene **34** in high yield (95%). No evidence for formation of any of the other possible cyclisation products (**35**, **36** or **37**) was obtained. The benzo[1,2-*b*:4,5-*b'*]bis[*b*]benzothiophene ring system has recently been synthesised by acid catalysed ring closure of a methylsulfinyl group onto an adjacent benzene ring.²⁴ The structure of **34** was confirmed by X-ray crystallography (Figure 7, Table 1) supporting ring closure by direct S_NAr reaction at C-2 and C-5 without initial

rearrangement. The crystals of **34** were very thin and flexible and the crystal structure showed $\pi \cdots \pi$ stacking parallel to *b* with the closest atom \cdots atom contact being 3.50 Å.

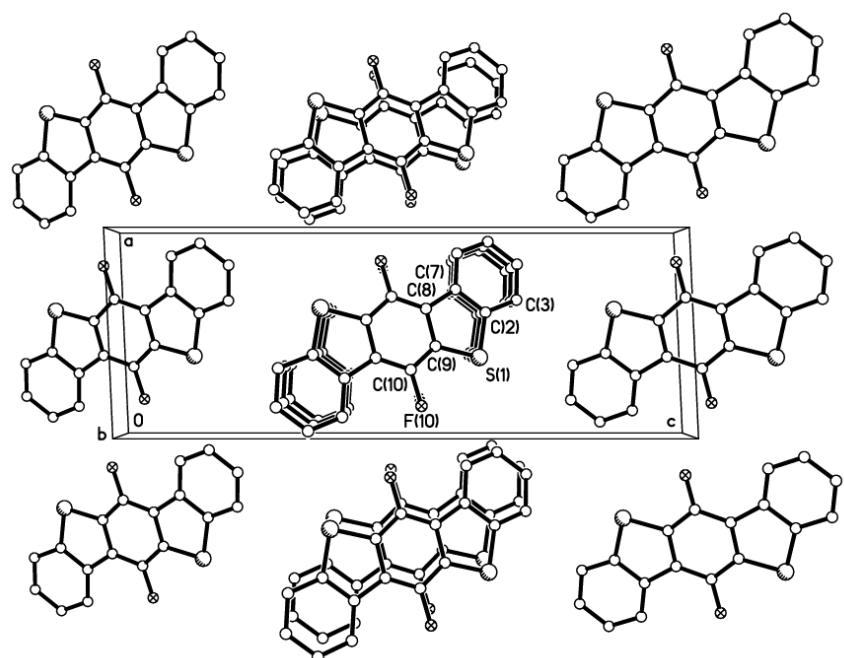
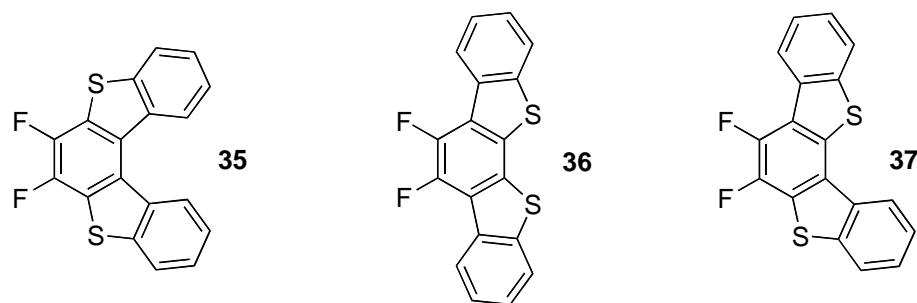
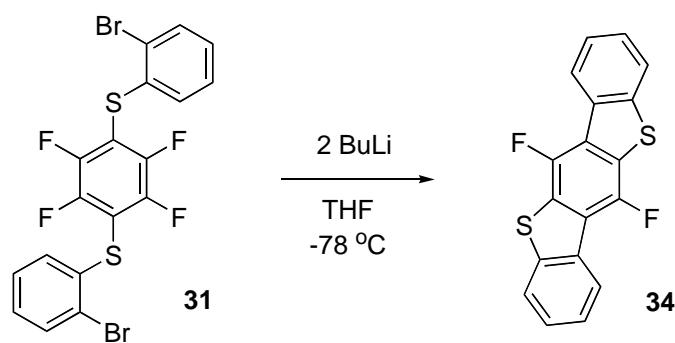


Figure 7 Crystal structure of **7** showing $\pi \cdots \pi$ stacking parallel to *b*.



Scheme 9 Cyclisation of **31** to benzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene **34**

In conclusion we have shown that lithiation of aryloxy- or arylthio-substituents on perfluorinated arenes can be used to rapidly build up usefully functionalised polycyclic structures. Cyclisation can occur by direct attack of the initially formed carbanion on the neighbouring position by S_NAr reaction, and this seems to be the norm for groups attached through a sulfur atom. In the case of fluoroaryl ethers Smiles-type rearrangement of the initially formed carbanion can occur, although the scope of this process needs to be investigated further. The crystal structures of key examples reveal a fine balance between halogen···halogen and $\pi\cdots\pi$ stacking interactions and polymorphism in one case. Further work on the mechanistic aspects of these reactions, and results on the cyclisation of corresponding perfluoroaryl amines will be reported in due course.

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Experimental

General

Commercial dry solvents were used in all reactions except for light petroleum and ethyl acetate which were distilled from $CaCl_2$, dichloromethane which was distilled from CaH_2 , and THF which was distilled from sodium and benzophenone. Light petroleum refers to the fraction boiling between 40-60 °C fraction. Sodium hydride was a 60% dispersion in mineral oil. A 1.6 or 2.5 M solution of *n*-butyllithium in hexane was used. Melting points were determined on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Infrared spectra

were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer on NaCl plates. ^1H (400 MHz), ^{13}C (100 Hz) and ^{19}F (376 MHz) NMR spectra were recorded on a Bruker DPX-400 instrument. ^{19}F NMR spectra are referenced to hexafluorobenzene as internal standard. Spectra were obtained from solutions in CDCl_3 unless otherwise specified. Chemical shifts are given in parts per million (ppm) and J values in hertz (Hz). Assignments were made using a combination of COSY, HMQC and HMBC analysis. Mass spectra were recorded on a Jeol SX102 high resolution mass spectrometer, a ThermoFisher ExactiveTM Orbitrap instrument equipped with an Advion TriVersa NanoMate[®], or were run by the EPSRC MS Service at the University of Wales, Swansea. TLC using silica as absorbent was carried out with aluminium backed plates coated with silica gel (Merck Kieselgel 60 F₂₅₄), and TLC using alumina as absorbent was carried out with aluminium backed plates coated with neutral aluminium oxide (Merck 150 F₂₅₄, TypeT). Silica gel (Merck Kieselgel 60 H silica) was used for column chromatography.

4-(2-Bromophenoxy)tetrafluoropyridine **2**

2-Bromophenol (3.46 g, 0.02 mol) was added dropwise to a stirred suspension of sodium hydride (1.0 g, 0.025 mol) in DMF (40 mL) at ice-bath temperature. When gas evolution had stopped pentafluoropyridine (3.38 g, 0.02 mol) was added dropwise and the resulting turbid yellow solution stirred at room temperature overnight for 19 h. Water (100 mL) was added and the mixture extracted with ether (250 mL). The organic layer was dried over MgSO_4 , filtered and evaporated to give the title compound as a yellow oil (5.96 g, 92%).

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3069, 2925, 2853, 2565, 2033, 1842, 1641, 1576, 1473, 1443, 1259, 1214, 1073.

δ_{H} (400 MHz, CDCl_3) 6.99 (1H, dd, J 1.2 and 8), 7.08, (1H, dt, J 1.2 and 7.6), 7.26 (1H, dt, J 1.6 and 7.6), 7.58 (1H, dd, J 1.6 and 8)

δ_{F} (376 MHz, CDCl_3) 6.5-6.9 (2F, m), 73.5-73.7 (2F, m)

m/z (FAB) 321/323 (MH^+)
Found 320.9420, $\text{C}_{11}\text{H}_5^{79}\text{BrF}_4\text{NO}$ requires 320.9412

4-(2-Hydroxyphenyl)tetrafluoropyridine **4**

A solution of 4-(2-bromophenoxy)tetrafluoropyridine **2** (1.05 g, 0.0033 mol) in anhydrous THF (7 mL) was stirred at -78 °C and treated dropwise with a solution of *n*-butyllithium in hexanes (2.5 M, 1.5 mL, 0.0037 mol). The solution turned orange and then faded to yellow over 50 min. The mixture was stirred and allowed to warm to room temperature overnight. Water (10 mL) was added and the mixture extracted with ether (3 x 20 mL). Brine was added to break up the emulsion which formed during extraction. The combined ether layers were dried over MgSO₄, filtered and evaporated to give a yellow oil (0.9 g) which crystallised on standing. Recrystallisation from dichloromethane and light petroleum gave off-white crystals of the title compound (0.25 g, 31%).

m.p. 138-141 °C

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3380 br. (OH), 3070, 2957, 2927, 2567, 1915, 1842, 1790, 1642, 1590, 1472, 1291, 1263, 1214, 1073, 888, 752.

δ_{H} (400 MHz, CDCl₃) 5.02 (1H, bs, exch., OH) 6.90 (1H, dd, *J* 0.8 and 8.4), 7.12, (1H, dt, *J* 0.8 and 7.6), 7.22 (1H, d, *J* 7.6), 7.35 (1H, dt, *J* 1.6 and 8.4)

δ_{F} (376 MHz, CDCl₃) 20.7-20.9 (2F, m), 70.7-70.9 (2F, m)

m/z (FAB) 244 (MH⁺)

Found 244.0328, C₁₁H₆F₄NO requires 244.0307

1,3,4-Trifluorobenzo[*b*]furo[2,3-*c*]pyridine **5**

4-(2-Hydroxyphenyl)tetrafluoropyridine **4** (0.23 g, 0.95 mmol) was added to a stirred suspension of sodium hydride (0.04 g, 1.0 mmol) in anhydrous DMF (10 mL). The mixture was heated at 100 °C for 3 h. After cooling water (25 mL) was added, and the mixture was extracted with ether (50 mL). The organic extract was dried over MgSO₄, filtered and evaporated to give **5** as a pale yellow solid (0.2 g, quant.), m.p. 136-137 °C (from dichloromethane/light petroleum).

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 1657, 1492, 1474, 1444, 1415, 1252, 1165, 1098, 973.

δ_{H} (400 MHz, CDCl₃) 7.45 (1H, m), 7.62-7.68, (2H, m), 8.07 (1H, d, *J* 8)

δ_F (376 MHz, $CDCl_3$) 6.7 (1F, dd, J 21.6 and 33.5), 60.1 (1F, dd, J 12.4 and 19.9), 69.0 (1F, dd, J 12.8 and 33.5).

m/z (EI) 223 (M^+)
Found 223.0242, $C_{11}H_4F_3NO$ requires 223.0245

Reaction of pentafluoropyridine with 2-bromobzenethiol

2-Bromobzenethiol (0.27 g, 2.1 mmol) was added dropwise to a stirred suspension of sodium hydride (0.1 g, 2.5 mmol) in DMF (4 mL) at ice-bath temperature. When gas evolution had stopped pentafluoropyridine (0.34 g, 2 mmol) was added dropwise. The mixture turned momentarily bright yellow and then faded to colourless. The solution was stirred at room temperature for 24 h. Water (15 mL) was added and the mixture extracted with ether (3 x 15 mL). The organic layers were dried over $MgSO_4$, filtered and evaporated to give a pale yellow malodorous oil (0.76 g). The oil was dissolved in dichloromethane and the solution washed with saturated Na_2CO_3 (aq) and then 5% HCl(aq). Evaporation of the organic layer gave a less odorous brown oil (0.62 g) which was chromatographed over silica. Elution with light petroleum-dichloromethane (5:1) gave 4-(2-bromobzenethio)tetrafluoropyridine **6** as a colourless crystalline solid (0.34 g, 50%).

m.p. 47-48 °C

ν_{max}/cm^{-1} 1699, 1682, 1652, 1627, 1558, 1463, 1235.

δ_H (400 MHz, $CDCl_3$) 7.23 (2H, m), 7.47 (1H, dd, J 1.5, 7.6), 7.59 (1H, dd, J 1.5, 7.6).

δ_F (376 MHz, $CDCl_3$) 25.4-25.6 (2F, m), 71.9-72.0 (2F, m).

m/z (EI) 337/339 (M^+)
Found 339.9177, $C_{11}H_4^{79}BrF_4NS$ requires 336.9184

Further elution gave 2,4,5-tri(2-bromobzenethio)difluoropyridine **7** as a pale yellow solid (0.24 g, 17%)

m.p. 97-98 °C

ν_{max}/cm^{-1} 1652, 1635, 1557, 1505, 1471, 1387.

δ_H (400 MHz, $CDCl_3$) 6.77 (1H, dd, J 0.8, 8.0), 6.97 (1H, dt, J 1.6, 7.2), 7.09 (2H, m), 7.17 (1H, m), 7.23 (1H, dt, J 2.0, 8.0), 7.31 (2H, m), 7.45 (1H, dd, J 1.2, 8.0), 7.51 (1H, dd, J 1.2, 7.6), 7.58 (1H, dd, J 1.6, 7.6), 7.63 (1H, dd, J 1.2, 8.0).

δ_F (376 MHz, $CDCl_3$) 45.6 (1F, d, J 21.1 Hz), 99.0 (1F, d, J 21.1 Hz).

m/z (FAB) (MNa^+) 696-703

Found 697.7512, $C_{23}H_{12}^{79}Br_2^{81}Br F_2NNa^{32}S_3$ requires 697.7522

1,3,4-trifluorobenzo[*b*]thieno[3,2-*c*]pyridine **8**

A stirred solution of 4-(2-bromobenzenethio)tetrafluoropyridine **6** (0.31 g, 0.9 mmol) in anhydrous THF (3 mL) was cooled to -78 °C and treated dropwise with *n*-butyllithium in hexanes (2.5 M, 0.4 mL, 1.0 mmol). The solution turned maroon in colour and then brown. The mixture was allowed to warm to room temperature overnight with stirring during which time it changed to yellow in colour. Water was added, precipitating a solid, and the mixture exhaustively extracted with ether re-dissolving the solid material. Evaporation of the ether afforded a solid (0.2 g) which was dissolved in dichloromethane, and the solution washed with saturated aqueous sodium carbonate to remove acidic material. Evaporation of the organic phase gave the benzothienopyridine **8** as a yellow solid (0.17 g, 79%).

m.p. 151-153 °C (from dichloromethane-light petroleum)

ν_{max}/cm^{-1} 1656, 1618, 1547, 1479, 1439, 1253, 1026, 913.

δ_H (400 MHz, $CDCl_3$) 7.52-7.56 (2H, m), 7.883-7.85 (1H, m) 8.26-8.28 (1H, m)

δ_F (376 MHz, $CDCl_3$) 8.0 (1F, dd, J 20.3 and 29.0), 62.4 (1F, dd, J 11.3 and 20.3), 84.8 (1F, dd, J 11.3 and 29.0)

m/z (EI) 239 (M^+)

Found 239.0017, $C_{11}H_4F_3NS$ requires 239.0016

Reaction of 2-bromophenol with hexafluorobenzene

2-Bromophenol (0.75 g, 4.3 mmol) was added dropwise to a suspension of sodium hydride (0.20 g, 5 mmol) in anhydrous DMF (8 mL) at 0 °C. Hexafluorobenzene (0.040 g, 2.2 mmol) was added dropwise and the resulting mixture stirred at 50 °C

overnight. The cooled mixture was diluted with water (20 mL) and extracted with ether (3 x 40 mL). Evaporation of the organic extracts gave a yellow oil (1.2 g) which was treated with light petroleum. On cooling afforded colourless crystals of 1,4-di(2-bromophenoxy)tetrafluorobenzene **20** (0.3 g, 31%) were formed.

m.p. 113-115 °C

$\nu_{\text{max}}/\text{cm}^{-1}$ 1576, 1510, 1471, 1444, 1313, 1264, 1218.

δ_{H} (400 MHz, CDCl_3) 6.75 (2H, dd, J 1.4, 8.0), 6.97 (2H, dt, J 1.4, 7.6), 7.19 (2H, dt, J 1.6, 7.6), and 7.58 (2H, dd, J 1.6, 8.0).

δ_{F} (376 MHz, CDCl_3) 8.3 (4F, apparent t)

m/z (FAB) 490/492/494 (M^+)

Found 489.8834, $\text{C}_{18}\text{H}_8^{79}\text{Br}_2\text{F}_4\text{O}_2$ requires 489.8827

When the above reaction was conducted using 10 equivalents of hexafluorobenzene 2-bromophenyl pentafluorophenyl ether **21** was obtained in 58% yield as a colourless oil (0.40 g from a 2 mmol scale reaction) after chromatography over silica using light petroleum as eluent.

$\nu_{\text{max}}/\text{cm}^{-1}$ 1733, 1717, 1699, 1683, 1653, 1576, 1558, 1516, 1474, 1319, 1265, 1221.

δ_{H} (400 MHz, CDCl_3) 6.74 (1H, dd, J 1.2, 8.0), 7.05 (1H, dt, J 1.2, 8.0), 7.26 (1H, dt, J 1.6, 8.0), and 7.66 (1H, dd, J 1.6, 8.0).

δ_{F} (376 MHz, CDCl_3) 0.42-0.56 (2F, m), 2.83 (1F, tt, J 1.5, 22.2), 8.37-8.46 (2F, m).

m/z (EI) 338/340 (M^+)

Found 337.9370, $\text{C}_{12}\text{H}_4^{79}\text{BrF}_5\text{O}$ requires 337.9366

The disubstituted product **20** was also isolated (0.005 g, 1%) on further elution.

6,12-difluorobenzo[1,2-*b*:4,5-*b'*]bis[*b*]benzofuran **22**

A solution of the bis ether **20** (0.3 g, 0.6 mmol) in anhydrous THF (2 mL) was stirred at -84 °C and treated with *n*-butyllithium in hexanes (2.5 M, 0.5 mL, 1.25 mmol). The solution turned brown in colour and then faded to yellow after 1 h. After 2 h the

mixture was warmed to room temperature and treated with water (2 mL). Extraction with dichloromethane (x 3) and evaporation of the organic phases gave a pale brown solid (0.2 g). Recrystallisation from dichloromethane - light petroleum gave colourless needles of the benzo-bis-benzofuran **22** (0.033 g, 19%).

m.p. 279-280 °C

$\nu_{\text{max}}/\text{cm}^{-1}$ 1652, 1557, 1539, 1436, 1418, 1306, 1246.

δ_{H} (400 MHz, CD_2Cl_2) 7.39 (1H, dt, J 0.8, 8.0), 7.51 (1H, dt, J 1.2, 8.4), 7.59 (1H, d, J 8.4), and 8.09 (1H, dd, J 0.8, 8.0).

δ_{C} (100 MHz, CD_2Cl_2) 111.81 (C-4,10), 114.48 (dd, J 8, 12, C-6a,12a), 121.86 (C-6b,12b), 122.86 (t, J 2, C-1,7), 123.71 (C-2,8), 128.39 (C-3,9), 137.90 (dd, J 7, 251 Hz, C-6,12), 138.81 (dd, J 8, 10, C-5a,11a), 156.69 (C-4a,10a)

δ_{F} (376 MHz, DMSO-d_6) 14.7 (2F, s)

m/z (EI) 294 (M^+)

Found 294.0495, $\text{C}_{18}\text{H}_8\text{F}_2\text{O}_2$ requires 294.0492

Reaction of 2-bromophenyl pentafluorophenyl ether **21** with *n*-butyllithium

A solution of 2-bromophenyl pentafluorophenyl ether **21** (1.1 g, 3 mmol) in dry THF (15 mL) was stirred at -78 °C and treated with *n*-butyllithium in hexanes (2.5 M, 3.1 mL, 7.8 mmol). The solution turned dark red in colour and then faded to orange after 30 min. The mixture was allowed to warm to room temperature over night and was then treated with water (10 mL). Extraction with ether (3 x 40 mL) and evaporation of the organic phases gave a yellow oil (0.52 g) which was chromatographed over silica. Elution with light petroleum gave colourless crystals of 3-*n*-butyl-1,2,4-trifluorodibenzofuran **29** (0.20 g, 24%).

m.p. 48-49 °C

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3739, 3628, 2958, 2928, 2863, 1708, 1690, 1676, 1648, 1551, 1534, 1479, 1449, 1300, 1262.

δ_{H} (400 MHz, CDCl_3) 0.98 (3H, t, J 7.6, CH_3), 1.44 (2H, sext., J 7.6, CH_2), 1.68 (2H, quin., J 7.6, CH_2), 2.89 (2H, tt, J 2.0, 7.6, CH_2), 7.41 (1H, dt, J 0.8, 7.6), 7.53 (1H, dt, J 1.2, 8.4), 7.60 (1H, td, J 1.0, 8.4), and 8.03 (1H, ddd, J 0.8, 1.2, 7.6).

δ_{C} (100 MHz, CDCl_3) 13.76 (CH_3), 22.34 (CH_2 -3), 22.96 (CH_2 -1), 31.82 (CH_2 -2), 111.87 (C-6), 113.46 (td, J 3.5, 6.3, C-9b), 118.54 (dd, J 18.2, 19.6, C-3), 121.67 (td, J 2.3, 4.6, C-9a), 122.65 (C-9), 123.64 (C-8), 128.13 (C-7), 139.18 (ddd, J 2.0, 7.8,

14.1, C-4a), 140.96 (ddd, J 4.0, 16.1, 248.7, C-1), 141.57 (ddd, J 3.7, 7.1, 244.7, C-4), 144.19 (ddd, J 6.3, 12.0, 240.3, C-2), 156.22 (C-5a).

δ_F (376 MHz, DMSO-d₆) 13.6 (1F, t, J 19.5), 14.5 (1F, d, J 21.1), 18.6 (1F, d, J 19.2).

m/z (EI) 278 (M⁺)

Found 278.0915, C₁₆H₁₃F₃O requires 278.0919

1,4-di(2-bromobzenethio)tetrafluorobenzene **31**

2-Bromobzenethiol (0.78 g, 4 mmol) was added dropwise to a stirred suspension of sodium hydride (0.20 g, 5 mmol) in anhydrous DMF (8 mL). Hexafluorobenzene (0.38 g, 2 mmol) was added dropwise and the resulting yellow mixture stirred at room temperature overnight. The cooled mixture was diluted with water (25 mL) and extracted with ether (3 x 50 mL). Evaporation of the organic extracts gave a yellow solid (0.85 g) with a pungent odour. Crystallisation from dichloromethane - light petroleum afforded pale yellow crystals of the title compound **31** (0.74 g, 70%).

m.p. 138 °C

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 1686, 1652, 1639, 1558, 1464, 1446, 1259.

δ_H (400 MHz, CDCl₃) 7.15-7.19 (2H, m), 7.24-7.27 (1H, m), 7.62 (1H, dd, J 1.2, 8.4).

δ_F (376 MHz, CDCl₃) 31.1 (4F, s)

m/z (EI) 522/524/526 (M⁺)

m/z (FAB) 523 (MH⁺) Found 523.8343, C₁₈H₈⁷⁹Br₂F₄S₂ requires 523.8350

Reactions of bis-sulfide **31** with *n*-butyllithium

A solution of bis-sulfide **31** (1.18 g, 2.2 mmol) in dry THF (6 mL) was stirred at -78 °C and treated dropwise with *n*-butyllithium in hexanes (2.5 M, 1.8 mL, 2.5 mmol). The solution turned dark brown in colour. The mixture was allowed to warm to room temperature over 48 h and was then treated with water (10 mL). Extraction with ether (x 3) and evaporation of the organic phases gave a brown solid (0.91 g) which was crystallised from dichloromethane - light petroleum to give colourless crystals of 2-(2-bromobzenethio)-1,3,4-trifluorodibenzothiophene **32** (0.17 g, 23%).

m.p. 172-173 °C

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 1558, 1481, 1440, 1250.

δ_{H} (400 MHz, CDCl_3) 6.83 (1H, d, J 8.0), 7.05 (1H, dt, J 1.2, 8.0), 7.14 (1H, dt, J 1.2, 8.0), 7.52-7.60 (3H, m), 7.89-7.92 (1H, m), 8.34-8.38 (1H, m).

δ_{F} (376 MHz, CDCl_3) 17.6 (1F, dd, J 17.6, 24, F-3), 27.3 (1F, d, J 24, F-4), 45.8 (1F, d, J 17.6, F-1),

m/z (EI) 424/426 (M^+)

Found 423.9211, $\text{C}_{18}\text{H}_8^{79}\text{BrF}_3\text{S}_2$ requires 423.9203

Reaction with 2.2 equivalents of *n*-butyllithium

The above reaction using bis-sulfide (0.957 g, 0.0018 mmol) and 2.2 equivalents of *n*-butyllithium (2.5 M, 1.6 mL), and extraction with dichloromethane instead of ether afforded 6,12-difluorobenzo[1,2-*b*:4,5-*b*']bis[*b*]benzothiophene **34** as an orange brown solid (0.6 g, 95%). Recrystallisation from dichloromethane - light petroleum gave fine pale yellow needles m.p. 287 °C.

$\nu_{\text{max}}/\text{cm}^{-1}$ (film) 3318, 3105, 3039, 1649, 1608, 1560, 1503, 1433, 1468, 1325, 1252, 1222.

δ_{H} (400 MHz, CDCl_3) 7.46-7.51 (2H, m), 7.82-7.84 (1H, m), 8.40-8.43 (1H, m).

δ_{F} (376 MHz, CDCl_3) 37.9 (2F, s).

m/z (EI) 326 (M^+)

Found 326.0036, $\text{C}_{18}\text{H}_8\text{F}_2\text{S}_2$ requires 326.0036

Crystallography

For each sample, a crystal was mounted in oil on a glass fibre and fixed in the cold nitrogen stream on a Bruker APEX 2 CCD diffractometer equipped with MoK α radiation and a graphite monochromator, except for **22** which was measured at Daresbury Laboratory SRS, Station 9.8 due to tiny crystal size and weak diffraction²⁵. Intensity data were measured by thin-slice ω -scans and corrected for Lp and absorption effects. Data were reduced using the SAINT²⁵ program. The structures were determined by the direct methods routine in the SHELXS-97 program and refined by full-matrix least-squares methods, on F^2 , in SHELXL-97²⁶. The non-

hydrogen atoms were refined with anisotropic thermal parameters. H atoms were constrained.

For **4** the absolute structure could not be reliably determined due to the lack of anomalous scatters, so Friedel pairs were merged. Crystals of **7** were non-merohedrally twinned into two domains related by a 180° rotation about real axis [1 0 0]²⁷. The occupancies of the two domains refined to 0.8744:0.1256(6). Crystals of **8** were non-merohedrally twinned into two domains related by a 180° rotation about reciprocal axis [0 0 1]²⁷. The occupancies of the two domains refined to 0.6215:0.3785(8). Compound **32** grows as either rods (**32A**) or plates (**32B**) which are polymorphic. Although both crystallise in space group $P2_1/c$, the unit cell shapes are entirely different and the $\pi \cdots \pi$ and halogen-halogen interactions are also different (see discussion). Crystals of **34** were extremely thin and flexible which led to some absorption correction difficulties and less than ideal anisotropic displacement parameters. Crystal data and refinement results are collated in Table 1.

Table 1. Crystallographic data for compounds **4**, **7**·½C₇H₈, **8**, **22**, **32A**, **32B**, and **34**.

Compound	4	7 ·½C ₇ H ₈	8	22
Formula	C ₁₁ H ₅ F ₄ NO	C ₂₃ H ₁₂ Br ₃ F ₂ NS ₃ ·½C ₇ H ₈	C ₁₁ H ₄ F ₃ NS	C ₁₈ H ₈ F ₂ O ₂
Formula weight	243.16	722.31	239.21	294.24
Crystal system	Tetragonal	Triclinic	Triclinic	Monoclinic
Space group	<i>I</i> 4 ₁ cd	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 2 ₁ /n
Unit cell dimensions				
<i>a</i> (Å)	13.0912(7)	7.0016(12)	7.2230(8)	6.198(2)
<i>b</i> (Å)	13.0912(7)	10.9436(19)	7.9584(9)	6.525(2)
<i>c</i> (Å)	23.1759(12)	17.466(3)	9.1866(10)	15.416(5)
α (°)	90	92.675(3)	100.979(2)	90
β (°)	90	99.643(3)	97.143(2)	97.211(4)
γ (°)	90	90.003(3)	113.863(2)	90
<i>V</i> (Å ³)	3971.9(4)	1317.9(4)	462.01(9)	618.5(3)
<i>Z</i>	16	2	2	2
Temp. (K)	150(2)	150(2)	150(2)	150(2)
Radiation, <i>λ</i> (Å)	0.71073	0.71073	0.71073	0.6942
<i>D</i> _{calcd} (g cm ⁻³)	1.627	1.820	1.720	1.580
Absorption coefficient (mm ⁻¹)	0.156	4.861	0.362	0.123
Crystal size (mm)	0.59 × 0.22 × 0.20	0.62 × 0.23 × 0.05	0.47 × 0.15 × 0.03	0.07 × 0.01 × 0.01
2θ _{max} (°)	56.66	57.74	54.16	45.98
Reflections measured	12777	14248	7449	2656
Unique reflections, <i>R</i> _{int}	1268, 0.0208	8971, 0.0439	3593, 0.0249	907, 0.0501
Reflections with <i>F</i> ² > 2σ(<i>F</i> ²)	1158	6373	3172	588
Transmission factors	0.914 to 0.969	0.153 to 0.793	0.849 to 0.989	0.992 to 0.999
Number of parameters	155	354	146	101
<i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0305	0.0547	0.0343	0.0949
<i>wR</i> ₂ (all data)	0.0849	0.1632	0.0881	0.2902
Largest difference peak and hole (e Å ⁻³)	0.16 and -0.16	1.03 and -0.88	0.37 and -0.19	0.97 and -0.32

Table 1 Continued.

Compound	32A	32B	34
Formula	$\text{C}_{18}\text{H}_8\text{BrF}_3\text{S}_2$	$\text{C}_{18}\text{H}_8\text{BrF}_3\text{S}_2$	$\text{C}_{18}\text{H}_8\text{F}_2\text{S}_2$
Formula weight	425.27	425.27	326.36
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
<i>a</i> (Å)	9.8845(5)	15.1514(9)	7.823(2)
<i>b</i> (Å)	15.6680(8)	12.9717(8)	3.9110(12)
<i>c</i> (Å)	10.3729(5)	8.1916(5)	21.623(7)
α (°)	90	90	90
β (°)	92.2845	103.5221(9)	92.499(4)
γ (°)	90	90	90
<i>V</i> (Å ³)	1605.18(14)	1565.34(16)	660.9(3)
<i>Z</i>	4	4	2
Temp. (K)	150(2)	150(2)	150(2)
Radiation, λ (Å)	0.71073	0.71073	0.71073
<i>D</i> _{calcd} (g cm ⁻³)	1.760	1.805	1.640
Absorption coefficient (mm ⁻¹)	2.848	2.921	0.417
Crystal size (mm)	0.84 × 0.13 × 0.10	0.70 × 0.29 × 0.03	0.56 × 0.12 × 0.02
$2\theta_{\text{max}}$ (°)	56.66	61.14	52.86
Reflections measured	16379	18058	4059
Unique reflections, <i>R</i> _{int}	3987, 0.0336	4770, 0.0410	1347, 0.0623
Reflections with $F^2 > 2\sigma(F^2)$	3119	3675	1022
Transmission factors	0.196 to 0.756	0.234 to 0.918	0.800 to 0.992
Number of parameters	217	217	100
<i>R</i> ₁ [$F^2 > 2\sigma(F^2)$]	0.0378	0.0355	0.0559
<i>wR</i> ₂ (all data)	0.0976	0.1012	0.1366
Largest difference peak and hole (e Å ⁻³)	1.02 and -0.68	0.56 and -0.40	0.50 and -0.31

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