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A New Method for the Synthesis of Aromatic Sulfurpentafluorides and Studies of the Stability of the Sulfurpentafluoride Group in Common Synthetic Transformations

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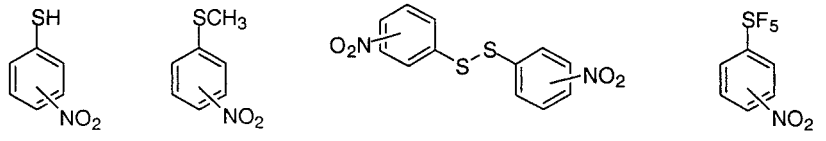
Abstract—A new synthesis of aromatic sulfurpentafluoride compounds is described. Subsequent elaboration of the aromatic rings in the presence of the sulfurpentafluoride group is also discussed for a variety of common synthetic methods. This paper also describes ab initio electronic structure calculations of 3- and 4-aminophenylsulfurpentafluoride, compared with 3- and 4-aminobenzotrifluoride, and presents X-ray crystal structures of two aromatic sulfurpentafluoride derivatives.

Organofluorine compounds, and in particular fluorinated aromatic compounds such as benzotrifluoride and its derivatives, are well established[1–4] in synthetic organic chemistry and have found wide application as dye-stuffs, fluoroplastics, anaesthetics and as chemotherapeutic treatments, amongst others. Less well known in organofluorine chemistry, however, is the use of the sulfurpentafluoride group, and in particular the use of aromatic sulfurpentafluoride compounds. Despite having been first prepared[5,6] forty years ago little development of aromatic sulfurpentafluoride chemistry has been reported. Probably one of the key stumbling blocks to the exploration of aromatic sulfurpentafluoride chemistry has been the lack of good synthetic routes available for the preparation of these materials. The only reported method, described by Sheppard, and subsequently modified[7] by Zeneca, utilises silver fluoride as the fluorinating reagent, but suffers, however, from the disadvantages that silver fluoride is rather expensive and that the yields of the desired sulfurpentafluoride compounds are generally low (<20%). Despite this, some synthetic work utilising aromatic sulfurpentafluorides has been described[8] including reductions, diazotisations and hydrolyses. Other characterisation studies[9–15] and properties[16,17] (such as insecticidal activity) also point to the potential synthetic utility and stability of these materials.

Here, we present a new method for the direct preparation[18] of aromatic sulfurpentafluorides from readily available starting materials. The stability of the sulfurpentafluoride group to several common synthetic transformations is also described, as well as the attempted hydrolysis of the sulfurpentafluoride group under basic and acidic conditions. The first two crystal structures of aromatic sulfurpentafluorides[19] and some ab initio electronic structure calculations on (aminophenyl)sulfurpentafluorides are also reported.

Our strategy for the preparation of aromatic sulfurpentafluorides involved a direct fluorination process using F_2 gas. Three readily available starting materials—the thiophenols **1**, aromatic methyl thioethers **2** and disulfides **3** (Fig. 1)—



1a 3-NO_2 **1b** 4-NO_2 **2a** 3-NO_2 **2b** 4-NO_2 **3a** 3,3'-NO_2 **3b** 4,4'-NO_2 **4a** 3-NO_2 **4b** 4-NO_2

Figure 1. Potential starting materials **1**–**3** for the preparation of nitrophenyl sulfurpentafluorides **4**.

Keywords: sulfur halogen compounds; fluorine and compounds; coupling reactions; X-ray crystallography.
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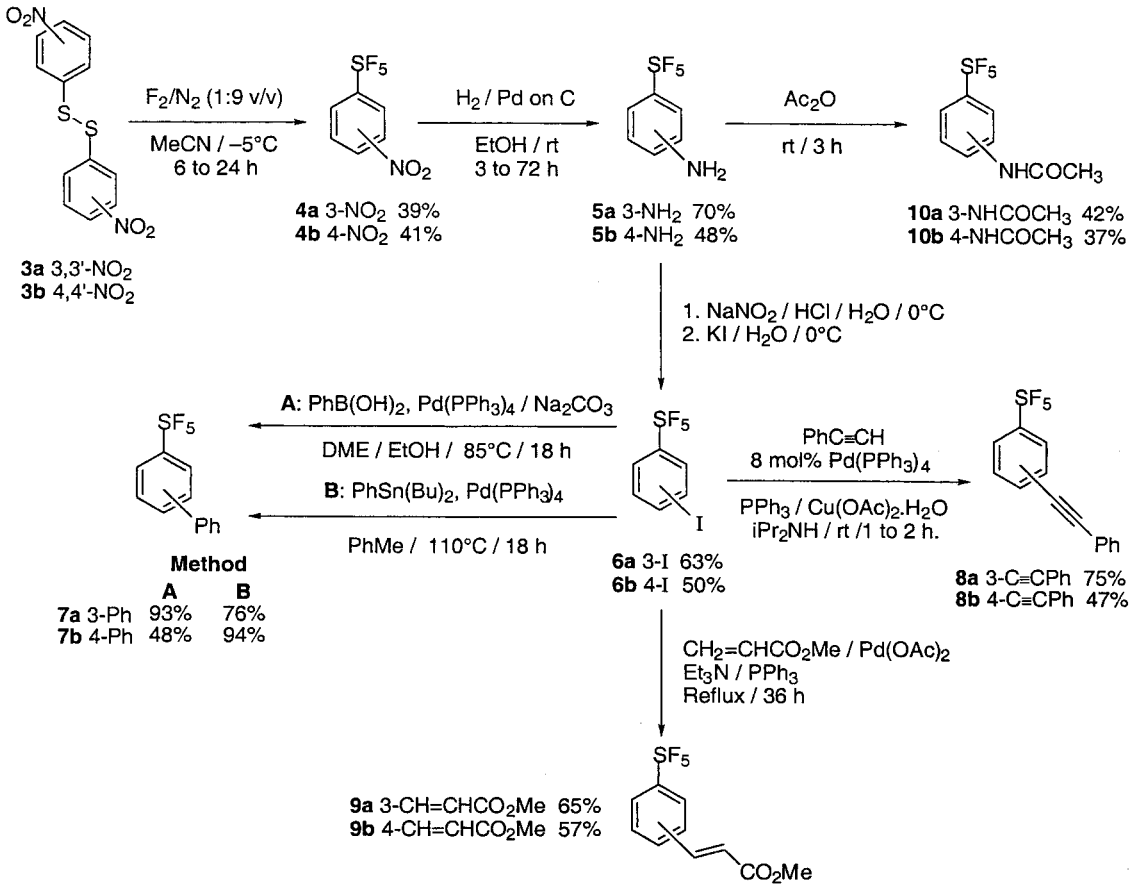


Scheme 1. The synthesis and some reactions of 3-nitrophenylsulfurpentafluoride **4a** and 4-nitrophenylsulfurpentafluoride **4b**.

were identified as being suitable for study and their reactivities were investigated.

In a typical fluorination procedure, the substrate was dissolved in anhydrous acetonitrile at a temperature of between −8 and −4°C. A steady stream of a mixture of F_2 and N_2 gas (10% v/v F_2) was then passed through the reaction mixture. Using this procedure, bis(4-nitrophenyl)-disulfide **3b** gave an isolated yield of (4-nitrophenyl)sulfurpentafluoride **4b** of 41%. The use of chloroform as solvent proved to be less successful, giving significantly lower yields of the desired product. Further improvements in yield could be achieved by allowing the reaction mixture to warm to room temperature after the initial formation of the intermediate sulfurtrifluoride compound. Direct fluorination of 4-nitrothiophenol **1b** or the thioether **2b** in acetonitrile gave lower yields of the desired 4-nitrophenyl sulfurpentafluoride **4b**, despite the fact that the thiol substrate is observed to proceed via the same disulfide **3b** used above. Direct fluorination in acetonitrile could also be carried out successfully starting from bis(3-nitrophenyl)-disulfide **3a**, affording the desired nitrophenyl sulfurpentafluoride **4a** in 39% yield. Again the yields for this reaction were improved by allowing the intermediate trifluoride compound to warm to room temperature before continuing fluorination. Unfortunately, the direct fluorination methodology could not be applied fully to the *ortho* substituted starting materials,[20] which gave only the intermediate trifluorosulfur compounds as the major products. Presumably, the steric hindrance from the *ortho*-nitro substituent prevents complete fluorination at the adjacent SF_3 site. These results are consistent with earlier work by Kharasch who demonstrated[21] that fluorination of bis(2,4-dinitrophenyl)disulfide using F_2 in anhydrous HF afforded only the sulfurtrifluorides in high yield. We have also fluorinated successfully other aromatic disulfides, using the above procedure, to give several substituted aromatic sulfurpentafluorides, such as trifluoromethylphenyl sulfurpentafluoride. The procedure described above (see also Scheme 1) represents a significant improvement on Sheppard's method for the preparation of aromatic sulfurpentafluoride compounds and has also been successfully applied to the preparation of multi-kilogram quantities of aromatic sulfurpentafluoride compounds.

Having established a new method for the preparation of aromatic sulfurpentafluorides, we were keen to demonstrate further the synthetic utility of these materials. As described earlier, Sheppard has reported[8] reduction of nitrophenyl sulfurpentafluorides to the corresponding amines using catalytic hydrogenation methods. Subsequent diazotisation of the resulting amines was also described in the same article. With these methods as a starting point, a variety of new aromatic sulfurpentafluorides were prepared, using some common synthetic, and in particular cross-coupling, methodologies.

In the first instance, reduction of the nitro groups by hydrogenation, as described by Sheppard, using PtO_2 in ethanolic HCl, proved unsuccessful, giving only low yields of the

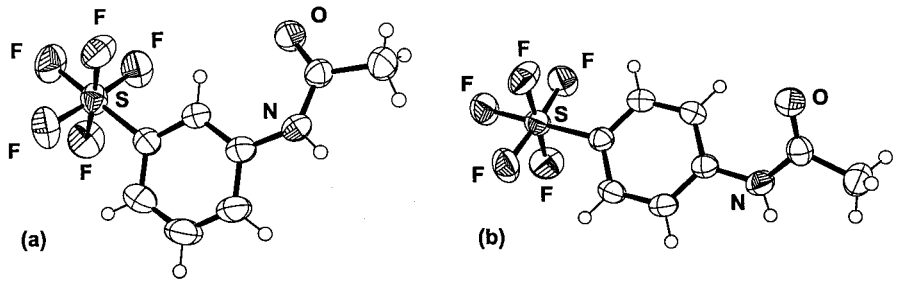


Figure 2. Molecular structures of: (a) **10a**, and (b) **10b** determined by X-ray diffraction.

desired amines **5a** and **5b**, as the corresponding hydrochloride salts. The same reactions carried out in the absence of HCl also failed to give significant quantities of the amines. Successful reduction was achieved readily, however, by employing 10% Pd on charcoal as the catalyst, under an atmosphere of hydrogen in ethanol as solvent. This gave high yields of the desired amines **5a** and **5b**.

Amines **5a** and **5b** were diazotized[16] (Scheme 1) by the addition of an aqueous solution of sodium nitrite to a slurry of the amine hydrochloride in dilute hydrochloric acid. The aromatic diazonium salts were then trapped successfully by pouring the aqueous solution of the salt slowly into an aqueous solution of potassium iodide at 0°C, affording the two aromatic iodides **6a** and **6b**. Reversing the order of addition in this reaction, i.e. addition of the amines to an aqueous solution of sodium nitrite and HCl, followed by addition of aqueous KI solution to the diazonium salt, gave generally lower yields of the iodides.

We wished to test the stability of the sulfurpentafluoride group to reaction conditions employed in common synthetic transformations. In particular, we were interested in metal-catalysed cross-coupling reactions. Therefore, iodides **6a** and **6b** were reacted in a series of Pd(0) catalysed reactions giving generally high yields of cross-coupled products. Thus, **6a** and **6b** were reacted[22] with phenylboronic acid, in the presence of sodium carbonate, using a mixture of dimethoxyethane and ethanol as solvent and $Pd(PPh_3)_4$ as catalyst, to afford the corresponding biphenyls **7a** and **7b** in acceptable yields. Similarly, reaction[22,23] of **6a** and **6b** with phenyltributylstannane using toluene as solvent and $Pd(PPh_3)_4$ as catalyst afforded the biphenyls **7a** and **7b** in good to excellent yields. Disappointingly, reaction[22,24] of **6a** and **6b** with phenylmagnesium bromide in diethyl ether in the presence of $Ni(dppe)Cl_2$—the Kharasch reaction—afforded no significant quantities of **7a** and **7b**. Pd catalysed cross-coupling[25] of **6a** and **6b** with phenylacetylene gave the desired acetylenic products **8a** and **8b** in acceptable yields. Rigorous deoxygenation of the solvent was essential in these reactions to prevent the formation of significant quantities of 1,4-diphenyl-1,3-butadiyne arising from homo-couping of the alkyne starting material. However, small quantities of 1,4-diphenyl-1,3-butadiyne present in the crude products could be removed successfully by flash column chromatography. As a final test of the stability of the aryl sulfurpentafluorides to Pd-mediated chemistry, the iodides **6a** and **6b** were reacted[26] with methyl acrylate under Heck conditions to afford the corresponding acrylates **9a** and **9b** in good yield.

Although there are several reported[27–29] crystal structures of alkyl sulfurpentafluorides, there have been no crystal structures of aromatic sulfurpentafluorides described to date. Therefore, we prepared the acetamides **10a** and **10b** (Scheme 1) in the hope that single crystals of these compounds, suitable for X-ray diffraction studies, could be grown. Slow evaporation of dichloromethane solutions of **10a** and **10b** afforded plate-like single crystals of the acetamides which proved to be suitable for X-ray crystallographic analysis.

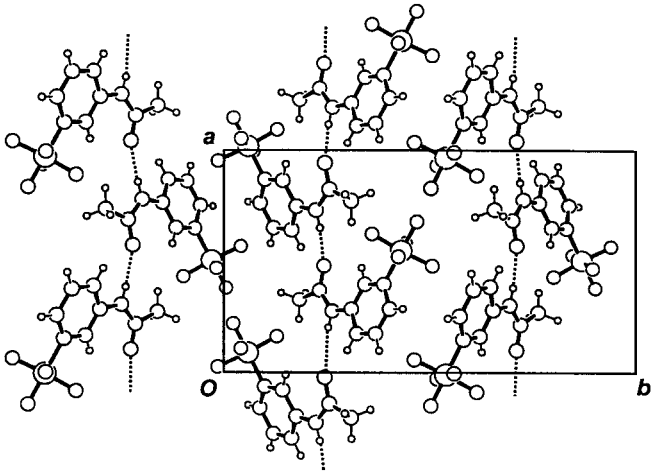


Figure 3. Packing diagram for the solid state structure of **10a** determined by X-ray diffraction. Molecules are shown in ball-and-stick representation and the structure is being viewed along the crystallographic *c* axis. Dashed lines represent N–H···O hydrogen bonds.

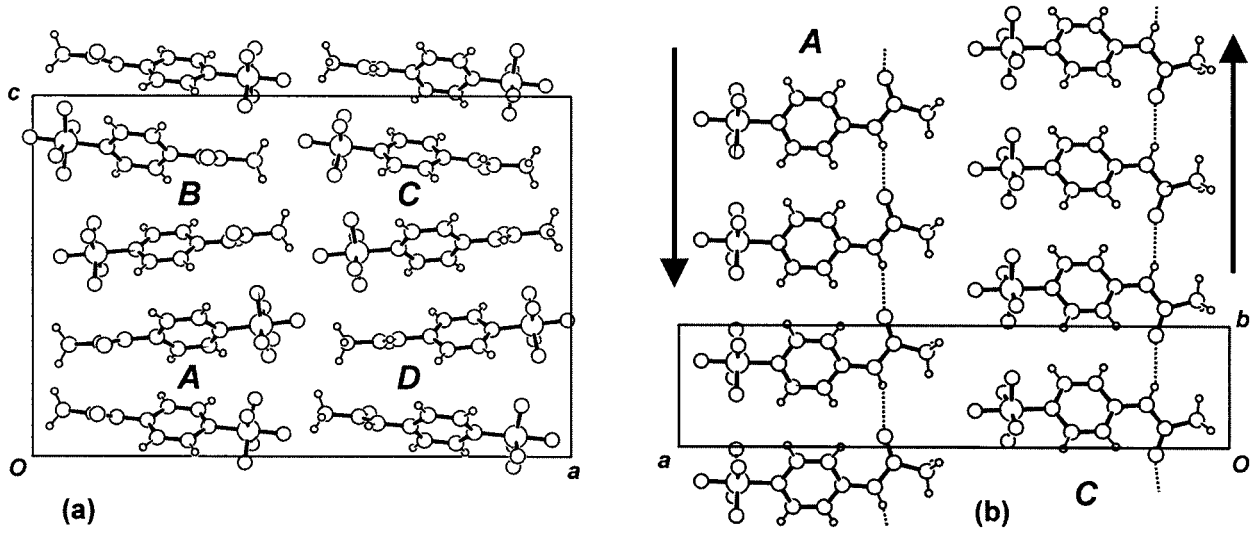


Figure 4. Packing diagram for the solid state structure of **10b** determined by X-ray diffraction. Molecules are shown in ball-and-stick representation and the structure is being viewed: (a) along the crystallographic *b* axis; and (b) along the crystallographic *c* axis. Dashed lines represent N–H···O hydrogen bonds. The bold arrows in (b) represent the directions of hydrogen bonding in the tapes formed by **10b**.

The structures of **10a** and **10b** (Fig. 2) were determined from single crystal X-ray diffraction data and demonstrate that, in both cases, the sulfur atom of the SF_5 group is in an approximately octahedral environment.

Within the SF_5 groups, all S–F bond lengths are approximately 1.58 Å, with the C–S bond length being 1.81 Å. In both **10a** and **10b**, the F–S–F bond angles are 90° between two equatorial F atoms, and 87° between an equatorial F atom and the axial F atom. In both cases, the equatorial F atoms of the SF_5 groups adopt an approximately staggered conformation with respect to the aromatic ring. In **10a**, the F–S–C–C dihedral angles are 50 and 40°, whilst in **10b** they are 60 and 30°. The central plane of the SF_5 group is distorted away from the aromatic ring slightly, as evidenced by the small reduction in the F–S–F bond angles between the equatorial and axial F atoms. This distortion presumably arises as a result of steric interactions with the *ortho* hydrogen atoms of the aromatic ring.

Compound **10a** crystallises[30] in the $P2_12_12_1$ space group with four molecules occupying the unit cell. In the solid state structure of **10a**, molecules of **10a** are oriented (Fig. 3) by N–H···O hydrogen bonds between adjacent acetamido groups such that molecular tapes are formed which run parallel to the crystallographic *a* axis. These tapes pack in an antiparallel fashion to form corrugated sheets which lie approximately in the *ab* plane. The SF_5 groups of molecules in adjacent tapes pack together, although there are no close contacts between the SF_5 group and other surrounding functional groups.

Compound **10b** crystallises[31] in the $Pca2_1$ space group with eight molecules occupying the unit cell. In the solid state structure of **10b**, molecules of **10b** are oriented (Fig. 4) by N–H···O hydrogen bonds between adjacent acetamido groups such that molecular tapes are formed which run parallel to the crystallographic *b* axis. The packing of these tapes is, however, somewhat complex. The unit cell may be divided (Fig. 4a) into four quadrants, **A**–**D**. Each quadrant contains two hydrogen bonded tapes which have the same molecular orientation and direction. Quadrant **A** is related to quadrant **B** by a C_2 axis thus the tapes in quadrant **B** have the same directionality with respect to the *b* axis as **A**, but have reversed molecular orientations. Tapes in quadrant **C** have the same molecular orientations as those in **A**, but reversed directionality (Fig. 4b) with respect to the *b* axis. The same relationship holds between quadrants **B** and **D**.

In order to provide a direct comparison of the stability of the sulfurpentafluoride group with that of the trifluoromethyl group, we attempted to hydrolyse 4-aminophenylsulfurpentafluoride **5b** under acidic and basic conditions. Using concentrated sulfuric acid at elevated temperatures, it has been shown[32,33] that 2- and 4-aminobenzotrifluoride both hydrolyse to give, after aqueous work-up of the intermediate acylfluoride, the corresponding aminobenzoic acids. Sheppard has also shown[8] that phenylsulfurpentafluoride is susceptible to hydrolysis by concentrated sulfuric acid, giving phenylsulfonyl fluoride (40%) and phenylsulfonic acid (not isolated). Using analogous conditions 4-aminophenylsulfurpentafluoride **5b** was treated with concentrated sulfuric acid at approximately 160°C over a period of 18 h. Dilution of the reaction mixture with water and extraction with ethyl acetate gave no isolable materials. Increasing the pH of the aqueous phase with dilute aqueous sodium bicarbonate, and further extraction with ethyl acetate also failed to give identifiable compounds. It would appear that, similarly to Sheppard's work, and in common with aromatic trifluoromethyl compounds, the SF_5 group is unstable to concentrated sulfuric acid at elevated temperatures, and that the resulting sulfonic acids are not isolable. It is also possible that the electron donating amine group activates the ring towards direct electrophilic sulfonation, and that again the resulting sulfonic acids are not isolable.

By way of contrast, **5b** was recovered cleanly and in high yield (91%) when stirred with 2*N* aqueous sodium hydroxide solution at room temperature for 48 h. At first

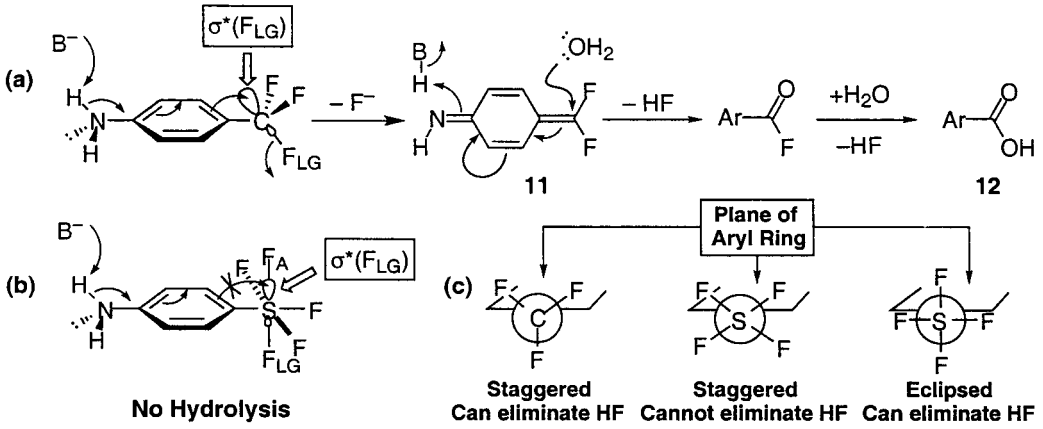


Figure 5. (a) Mechanism for hydrolysis of 4-aminobenzotrifluoride. (b) Required conformation for hydrolysis of 4-aminosulfurpentafluoride. (c) Schematic diagram of staggered conformation for benzotrifluorides and both staggered and eclipsed conformations for aryl sulfurpentafluorides.

glance this result might be considered surprising, given that 4-aminobenzotrifluoride readily hydrolyses[34–36] to 4-aminobenzoic acid in 1*N* sodium hydroxide solution after only 2 h. Presumably, the mechanism for the latter transformation is one involving direct deprotonation of the amine by hydroxide, with the nitrogen anion resonance stabilised by the CF_3 group, with loss of fluoride anion (Fig. 5a). Subsequent addition of water to the intermediate **11**, followed by loss of HF and hydrolysis of the resulting acylfluoride, gives 4-aminobenzoic acid **12**.

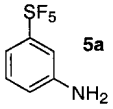
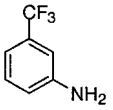
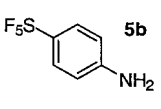
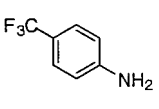
For the analogous SF_5 compound, however, it is more difficult to stabilise the nitrogen anion by loss of fluoride (Fig. 5b). The σ^* orbital of the equatorial S–F_{LG} bond is less able to accept electron density from the aromatic ring due to electron repulsion with the electrons within the S–F_A σ bond and therefore it cannot readily eliminate fluoride in the same manner as for 4-aminobenzotrifluoride. A difference in the assumed conformational preferences for the two systems also allows a rationalisation of the above results. In the benzotrifluoride systems, a staggered conformation of the CF_3 group relative to the aryl ring always leaves one of the F atoms in the correct alignment (i.e. perpendicular to the plane of the aromatic ring) for elimination of HF to occur. In the SF_5 system the SF_5 group must rotate into an eclipsed, and therefore energetically less favourable, conformation for correct orbital alignment (and thus loss of HF) to occur (Fig. 5c). In solution, all four equatorial fluorine atoms are equivalent by ^{19}F NMR, suggesting that the SF_5 group is either rotating freely around the C–S bond, or that the SF_5 group sits in the staggered conformation described above. In either situation the SF_5 group does not reach the required, and sterically unfavoured, conformation.

In order to gain some insight into the electronic effect of the SF_5 group on the aromatic ring, we performed ab initio molecular orbital calculations on **5a** and **5b** and the corresponding benzotrifluorides at the HF/6-31G(d) level of theory.

The calculated structures of **5a** and **b**, and, in particular, the geometry of the SF_5 group, are in close agreement with the geometry anticipated from the solid state structures of **10a** and **10b**. We were particularly interested in the electronic effect of the SF_5 group on amine basicity when compared to the corresponding benzotrifluoride. Therefore, the ab initio wavefunctions were used to derive selected molecular properties and to generate electrostatic potential (ESP) surfaces for **5a** and **5b** and the corresponding benzotrifluorides (the results of these calculations are presented in Table 1). It is clear from the data presented in Table 1 that the SF_5 group, in agreement with work described[9] by Sheppard, is considerably more electron withdrawing than the CF_3 group. The electrostatic potential on nitrogen is diminished significantly and the molecular dipole increased significantly upon exchange of a CF_3 group for an SF_5 group.

In conclusion, this paper describes a new, straightforward method for the preparation of aromatic sulfurpentafluoride compounds in good yields, using readily available starting materials, which is a significant improvement on current methodology. The procedure is amenable to scale-up and can be used to prepare multigram quantities of the desired sulfurpentafluoride compounds without the use of expensive reagents such as silver fluoride. The synthetic utility and stability of the sulfurpentafluoride group has been established for a variety of common synthetic transformations,

Table 1. Calculated (HF/6-31G(d)) properties of aminophenyl sulfurpentafluorides **5a** and **5b** and the corresponding benzotrifluorides

Structure	 **5a**		 **5b**	
ESP_{min} $(NH_2)^a$	−11.1	−33.8	−8.23	−12.5
Dipole (D)	5.22	3.70	6.27	4.87

[a] Minimum value (in kcal) of the electrostatic potential surface centred on the nitrogen atom of the amino group.

giving generally good yields of cross-coupling products when used in palladium-catalysed chemistry. Only when treated under very harsh hydrolysis conditions does the sulfurpentafluoride group undergo decomposition. It should be noted that the yields reported in Scheme 1 are from unoptimised synthetic procedures. We have also reported here the first two crystal structures obtained for aromatic sulfurpentafluorides.

Experimental

General procedures

Thin layer chromatography was carried out using Kieselgel 60 aluminium or glass backed plates containing a UV fluorescent indicator (F 254 nm). Plates were visualised by UV or using $KMnO_4$ or I_2/SiO_2. Flash column chromatography was carried out using Kieselgel 60, particle size 40–63 μm (230–400 mesh). Infra red spectroscopy was performed on a Perkin Elmer Paragon 1000 FTIR spectrometer using 16 scans. Oils were run neat between two sodium chloride plates and solids were run as solutions in dichloromethane. In all cases spectra were compared with background spectra obtained using clean sodium chloride plates or neat dichloromethane as appropriate. Nuclear magnetic resonance (NMR) spectroscopy was performed on Bruker AC300 and DRX500 spectrometers. Solvents and operating frequencies are given for each compound. ^1H spectra were referenced against residual $CHCl_3$ at δ_H=7.26 ppm ($CDCl_3$ solvent) or against the centre line of residual CHD_2COCHD_2 at δ_H=2.04 ppm (CD_3COCD_3 solvent). ^{19}F NMR spectra were referenced against $CFCl_3$ at δ_F=0.0 ppm. ^{13}C NMR spectra were referenced against the centre line of the $CDCl_3$ triplet set to a value of δ_C=77.0 ppm ($CDCl_3$ solvent) or against the centre peak for the solvent CD_3 resonance set to a value of δ_C=29.8 ppm (CD_3COCD_3 solvent) and were run using the PENDANT sequence. Coupling constants are quoted to the nearest 0.5 Hz. Low and high resolution mass spectroscopic data were obtained on either VG Zabspec or VG Prospec mass spectrometers. All spectra were obtained by electron ionisation mass spectroscopy (EIMS) at 70 eV. Melting points were measured using an Electrothermal 9200 melting point apparatus and are uncorrected. UV/visible spectra were recorded on a Hewlett Packard 8450A diode array spectrophotometer at room temperature (ca 25°C). Single crystal X-ray diffraction experiments were carried out using graphite-monochromated MoKα radiation (λ=0.71069 Å,) on a Rigaku R-Axis II diffractometer equipped with an area detector and a rotating anode source. Both structures reported here were solved and refined by standard methods.[37–39] All ab initio molecular orbital calculations were performed using Spartan (Version 5.1.3, Wavefunction Inc., Irvine, CA., 1999). Initial input geometries were generated using the Spartan Builder and all structures were then optimised at the HF/3-21G level of theory. The results of these calculations were then used as starting points for calculations at the HF/6-31G(d) level of theory.

Synthetic procedures

(3-Nitrophenyl)sulfurpentafluoride 4a.[6,8] Bis(3-nitrophenyl)disulfide (25.0 g, 81.1 mmol) was suspended in anhydrous acetonitrile (270 ml) in a refrigerated stirred tubular glass reaction vessel at −10°C. Fluorine (44.7 g, 1176 mmol, 14.5 equiv.), diluted to 10% in nitrogen, was then bubbled through the suspension which was kept between −7.6 and −4.5°C for 6 h. The resulting solution was poured onto water and treated with sodium hydroxide solution until alkaline. The resulting mixture was then extracted with dichloromethane (4×100 ml), the combined extracts were dried ($MgSO_4$) and solvent removed under reduced pressure to give a brown oil. The product was purified by distillation at 106°C, 2 mmHg (lit.[8] 85°C, 2.6 mmHg) to give (3-nitrophenyl)sulfurpentafluoride **4a** as a yellow oil (7.88 g, 39%); R_f 0.50 (20% diethyl ether in hexane); Found 248.987316 (M^+), $C_6H_4F_5NO_2S$ requires 248.988291; ν_{max}(neat)/cm^{-1} 3114, 2879, 1609, 1540, 1356, 893 (S–F/NO_2), 847 (S–F/NO_2), 736, 722, 670, 601; λ_{max} (CH_3CN)/nm (ϵ/$dm^3mol^{-1}cm^{-1}$) 213 (35000), 251 (21000), 361 (2100); δ_H ($CDCl_3$, 300 MHz) 8.65 (1H, dd, J=2 Hz, 2, H_2), 8.42 (1H, d, J=8 Hz, H_4 or H_6), 8.11 (1H, dd, J=8, 1.5 Hz, H_6 or H_4), 7.73 (1H, dd, J=8, 8 Hz, H_5); δ_H (CD_3COCD_3, 300 MHz), 8.64 (1H, dd, J=2, 2 Hz, H_2), 8.55 (1H, dm, J=8.5 Hz, H_4 or H_6), 8.36 (1H, dd, J=8, 1.5 Hz, H_6 or H_4), 7.99 (1H, dd, J=8.5, 8 Hz, H_5, δ_F ($CDCl_3$, 282 MHz) 81.2 (1F, quintet, J=151 Hz, SF_{ax}), 62.9 (4F, d, J=151 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 154.0 (apparent t, J=21 Hz, C–SF_5), 147.8 (C–NO_2), 131.7 (quintet, J=4.5 Hz, CH), 130.1 (CH), 126.4 (CH), 121.8 (bm, CH); δ_C (CD_3COCD_3, 75.5 MHz) 154.0 (apparent t, J=19 Hz, C–SF_5), 148.7 (C–NO_2), 132.5 (quintet, J=4.5, CH), 131.7 (CH), 127.6 (CH), 121.8 (quintet, J=5 Hz, CH); m/z (EI+, 70 eV) 249 (M+, 100%), 230 [$(M-F)^+$, 13], 203 [$(M-NO_2)^+$, 50], 111 (13), 95 (91), 75 (100) and 50 (48).

(4-Nitrophenyl)sulfurpentafluoride 4b.[6,8] Bis(4-nitrophenyl)disulfide (85%, 14.51 g, 40 mmol) was suspended in acetonitrile (200 ml) and cooled to −7°C whilst purging with nitrogen. Fluorine (19.82 g, 521.6 mmol, 13.0 equiv.), diluted to 10% in nitrogen, was then bubbled through the suspension which was kept between −7.6°C and −4.5°C for 24 h. The solvent was removed from the pale yellow solution to give a dark red oily liquid which was dissolved in dichloromethane (200 ml) and washed with 10% aqueous sodium hydroxide solution (2×30 ml) followed by water (2×30 ml). After drying ($MgSO_4$), the solvent was removed to give a dark red liquid. The crude material was purified by vacuum distillation to (4-nitrophenyl) sulfurpentafluoride **4b** as a low melting yellow solid (8.10 g, 41%); mp 38–40°C (lit.[8] 38°C); R_f 0.33 (25% dichloromethane in hexane); Found 248.987910 (M^+), $C_6H_4F_5NO_2S$ requires 248.988291; ν_{max}(neat)/cm^{-1} 3116, 3068, 2989, 2880, 1931, 1793, 1613, 1531, 1487, 1409, 1357, 1101, 853 (S–F/NO_2), 603, 577; δ_H ($CDCl_3$, 300 MHz) 8.33 (2H, d, J=9 Hz), 7.97 (2H, d, J=9 Hz); δ_F ($CDCl_3$, 282 MHz) 81.2 (1F, quintet, J=151 Hz, SF_{ax}), 62.7 (4F, d, J=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 157.7 (m, C–SF_5), 149.1 (C–NO_2), 127.6 (quintet, J=5 Hz, C_2 and C_6), 124.1 (C_3 and C_5); m/z (EI+, 70 eV) 248 (M^+, 85%, 229 [$(M-F)^+$, 14], 203 [$(M-NO_2)^+$, 42], 95 (80), 75 (100) and 50 (51).

(3-Aminophenyl)sulfurpentafluoride 5a.[6,8] Palladium on carbon [10% (w/w) Pd, 0.80 g, 0.75 mmol] was added in

one portion to a solution of (3-nitrophenyl)sulfurpentafluoride (3.75 g, 15.05 mmol) in ethanol (degassed, 47 ml). The mixture was stirred under an atmosphere of hydrogen until complete consumption of starting material (TLC analysis). The mixture was filtered to remove the catalyst, and the solvent removed under reduced pressure. The crude product was purified by column chromatography (25% dichloromethane in hexane) to afford (3-aminophenyl)sulfurpentafluoride **5a** as a yellow oil that slowly crystallised (2.3 g, 70%); mp 35–36°C (lit.[8] 37°C); R_f 0.40 (25% dichloromethane in hexane); Found 219.014196 (M^+), $C_6H_6F_5NS$ requires 219.014112; ν_{max}(neat)/cm^{-1} 3472 (b), 3400 (b), 3219, 3061, 1934, 1852, 1718, 1636, 1494, 1312, 1127, 1093, 920, 853 (S–F); δ_H ($CDCl_3$, 300 MHz) 7.23 (1H, ddm, J=8, 8 Hz, H_5), 7.15 (1H, dd, J=2, 2 Hz, H_2) 7.01, (1H, dd, J=8, 2 Hz, H_4 or H_6), 6.88 (1H, dd, J=8, 2 Hz, H_6 or H_4); δ_F ($CDCl_3$, 282 MHz), 85.5 (1F, quintet, J=150 Hz, SF_{ax}) 62.5 (4F, d, J=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 154.8 (apparent t, J=16 Hz, C–SF_5), 146.6 (C–NH_2), 129.3 (CH), 117.6 (CH), 115.7 (quintet, J=5 Hz, CH), 112.1 (quintet, J=5 Hz, CH); m/z (EI+, 70 eV) 219 (M^+, 100%), 111 (32), 92 (74) and 65 (52).

(4-Aminophenyl)sulfurpentafluoride 5b.[6,8] Prepared according to the above procedure using (4-nitrophenyl)-sulfurpentafluoride (6.00 g, 24.1 mmol) and palladium on carbon (10% w/w Pd, 3.26 g, 1.2 mmol) in ethanol (degassed, 75 ml). The crude product was purified by recrystallisation (diethyl ether/hexane) to give (4-aminophenyl)sulfurpentafluoride **5b** as a pale yellow solid (2.55 g, 48%); mp 57–59°C (lit.[8] 68°C); R_f 0.40 (25% dichloromethane in hexane); Found 219.013347 (M^+), $C_6H_6F_5NS$ requires 219.014112; ν_{max}(neat)/cm^{-1} 3496 (b, N–H), 3403 (b, N–H), 3214, 3054, 2990, 1895, 1764, 1626, 1600, 1507, 1304, 1194, 1099, 858 (S–F), 582; δ_H ($CDCl_3$, 300 MHz) 7.51 (2H, dm, J=9 Hz, 2×aromatic CH), 6.60 (2H, d, J=9 Hz, 2×aromatic CH), 3.85 (2H, bs, NH_2); δ_F ($CDCl_3$, 282 MHz) 88.3 (1F, quintet, J=150 Hz, SF_{ax}), 64.9 (4F, d, J=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 148.9 (C–NH_2), 144.3 (apparent t, J=17 Hz, C–SF_5), 127.4 (quintet, J=4.5, C_2 and C_6), 113.4 (2×CH); m/z (EI+, 70 eV) 219 (M^+, 100%), 200 [$(M-F)^+$, 9], 111 (100), 92 (50), 84 (19), 65 (67), 52 (10), and 39 (30).

(3-Iodophenyl)sulfurpentafluoride 6a. A solution of cold (0°C) $NaNO_2$ (0.5 g, 7.5 mmol) in water (5 ml) was added slowly to a cold (0°C) solution of (3-aminophenyl)sulfurpentafluoride (1.5 g, 6.8 mmol) in HCl (12 *M*, 3 ml, 3.7 mmol) and ice (5 g). The mixture was stirred at 0°C for a further 2 min before being added slowly, over 10 min, to a solution of KI (11.3 g, 6.8 mmol) in water (40 ml), whilst ensuring the temperature was kept below 10°C at all times. The mixture was left for 30 min in ice and then allowed to warm to rt. The product was extracted with dichloromethane (3×180 ml), and the combined extracts were then washed with saturated aqueous $NaHCO_3$ solution (3×100 ml) and dried ($MgSO_4$) and decolorized (activated charcoal). After filtration through Celite® (1 cm depth) the solvent was removed under reduced pressure to give a yellow oil which was purified by column chromatography (12% dichloromethane in hexane) to give (3-iodophenyl)sulfurpentafluoride **6a** as a colourless oil (1.4 g, 63%); R_f 0.60 (20% dichloromethane in hexane); Found 329.899472 (M^+), $C_6H_4F_5IS$ requires 329.899865; ν_{max}(neat)/cm^{-1} 3097, 3068, 2925, 2871, 1953, 1891, 1764, 1700, 1574, 1464, 1416, 1110, 1065, 996, 836 (S–F), 782, 710, 681, 661, 599; δ_H ($CDCl_3$, 300 MHz) 8.07 (1H, dd, J=2, 2 Hz, H_2), 7.85 (1H, d, J=8 Hz, H_4 or H_6), 7.73 (1H, dd, J=8, 2 Hz, H_6 or H_4), 7.20 (1H, dd, J=8, 8 Hz, H_5); δ_F ($CDCl_3$, 282 MHz) 83.2 (1F, quintet, J=150 Hz, SF_{ax}), 62.9 (4F, d, J=151 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 154.4 (apparent t, J=18 Hz, C–SF_5), 140.6 (C_5 or C_4), 134.6 (quintet, J=5 Hz, C_2 or C_6), 130.2 (C_4 or C_5), 125.1 (quintet, J=5 Hz, C_2 or C_6), 93.1 (C–I); m/z (EI+, 70 eV) 330 (M^+, 100%), 311 [$(M-F)^+$, 5] 222 [$(M-SF_4)^+$, 10], 203 [$(M-I)^+$, 60], 127 (15), 95 (63), 76 (14) and 50 (3).

(4-Iodophenyl)sulfurpentafluoride 6b. Prepared according to the above procedure using (4-aminophenyl)sulfurpentafluoride (1.00 g, 4.56 mmol), sodium nitrite (0.35 g, 5.02 mmol), HCl (12 *M*, 18 ml), potassium iodide (7.58 g, 45.6 mmol) and water (31 ml). The crude product was purified by column chromatography (hexane) to give (4-iodophenyl)sulfurpentafluoride **6b** as a white solid (0.75 g, 50%); R_f 0.60 (hexane); mp 38–39°C; Found 329.898704 (M^+), $C_6H_4F_5IS$ requires 329.899865; ν_{max}(neat)/cm^{-1} 2991, 2926, 2855, 1912, 1785, 1643, 1605, 1572, 1485, 1473, 1391, 1102, 1064, 1007, 860 (S–F), 797, 658, 599, 580; δ_H ($CDCl_3$, 300 MHz) 7.80 (2H, d, J=8.5 Hz, 2×aromatic CH), 7.47 (2H, d, J=9 Hz, 2×aromatic CH); δ_F ($CDCl_3$, 282 MHz) 83.6 (1F, quintet, J=150 Hz, SF_{ax}), 62.8 (4F, d, J=151 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 153.5 (apparent t, J=18 Hz, C–SF_5), 137.9 (C_3 and C_5), 127.5 (quintet, J=4.5 Hz, C_2 and C_6); m/z (EI+, 70 eV) 330 (M^+, 100%), 311 [$(M-F)^+$, 3], 222 (26), 203 (25), 127 (14), 95 (86), 76 (66) and 50 (43).

(3-Biphenyl)sulfurpentafluoride 7a.[8] *Suzuki coupling reaction:* 3-(Iodophenyl)sulfurpentafluoride (0.25 g, 0.76 mmol) was added to a suspension of tetrakis(triphenylphosphine)palladium (40 mg, 0.04 mmol) in dimethoxyethane (11 ml) and stirred for 10 min under N_2 at rt. Phenylboronic acid (0.14 g, 1.14 mmol) in ethanol (2 ml) and Na_2CO_3 (0.16 g, 1.52 mmol) in water (~2 ml) were added and the resulting mixture was heated to reflux for 3 h. On cooling, dichloromethane (50 ml) was added, and the organic phase was dried ($MgSO_4$). The resulting solution was filtered through Celite® (1 cm depth) and the solvent removed under reduced pressure. The crude product was purified by column chromatography (hexane) to give (3-biphenyl)sulfurpentafluoride **7a** as a colourless oil (0.20 g, 93%); R_f 0.40 (100% hexane); Found 280.035674 (M^+), $C_{12}H_9F_5S$ requires 280.034513; ν_{max}(neat)/cm^{-1} 3068, 3034, 1953, 1893, 1599, 1568, 1476, 1417, 1114, 1022, 837 (S–F), 796, 756, 697, 648, 596; δ_H ($CDCl_3$, 300 MHz) 7.95 (1H, dd, J=2, 2 Hz, H_2), 7.75–7.70 (2H, m), 7.61–7.40 (6H, m); δ_F ($CDCl_3$, 282 MHz) 84.7 (1F, pentet, J=150 Hz, SF_{ax}), 62.9 (4F, d, J=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 154.5 (m, C–SF_5), 142.3 (quaternary C), 139.4 (quaternary C), 130.2 (CH), 129.1 (3×CH), 128.2 (CH), 127.2 (2×CH), 124.7 (quintet, J=5 Hz, C_2 or C_6), 124.6 (quintet, J=5 Hz, C_6 or C_2); m/z (EI+, 70 eV) 280 (M^+, 100%), 172 (22), 152 (53) and 76 (8).

(3-Biphenyl)sulfurpentafluoride 7a.[8] *Stille coupling reaction:* Toluene (25 ml) and tetrakis(triphenylphosphine)palladium (40 mg, 0.04 mmol) were added to (3-iodophenyl)sulphurpentafluoride (0.25 g, 0.76 mmol) and stirred under N_2 for 10 min. Phenyltributylstannane (0.30 g, 0.90 mmol) was added in one portion and the mixture was heated to reflux for 18 h. On cooling, dichloromethane (30 ml) was added, the organic phase was dried ($MgSO_4$), and the resulting mixture filtered through Celite® (1 cm depth). The solvent was removed under reduced pressure to give a yellow oil that was purified by column chromatography (hexane) to give (3-biphenyl)sulfurpentafluoride **7a** as a colourless oil (0.16 g, 76%) with spectroscopic data as above.

(4-Biphenyl)sulfurpentafluoride 7b. *Suzuki coupling reaction:* Following the Suzuki coupling procedure above, (4-iodophenyl)sulfurpentafluoride (0.25 g, 0.76 mmol), tetrakis(triphenylphospine) palladium (0.04 g, 0.04 mmol), phenyl boronic acid (0.14 g, 1.14 mmol) and sodium carbonate (2*M* in water, 0.16 g, 1.52 mmol) in dimethoxyethane (5 ml) and ethanol (1 ml) were heated at 85°C for 2 h. Work-up gave a crude product which was purified by column chromatography (hexane) to give (4-biphenyl)-sulfurpentafluoride **7b** as a white solid (2.55 g, 48%); mp 64°C; R_f 0.40 (hexane); Found 280.035419 (M^+), $C_{12}H_9F_5S$ requires 280.034513; ν_{max}(neat)/cm^{-1} 2926, 2854, 1598, 1570, 1484, 1401, 1271, 1102, 842 (S–F), 596, 514; δ_H ($CDCl_3$, 300 MHz) 7.82 (2H, dd, *J*=7, 2 Hz, 2×aromatic CH), 7.65 (2H, d, *J*=8.5 Hz, 2×aromatic CH), 7.60–7.57 (2H, m), 7.51–7.44 (3H, m); δ_F ($CDCl_3$, 282 MHz) 84.9 (1F, quintet, *J*=150 Hz, SF_{ax}), 63.3 (4F, d, *J*=151 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 152.8 (apparent t, *J*=17 Hz, C–SF_5), 144.5 (quaternary C), 139.0 (quaternary C), 129.0 (2×CH), 128.4 ($C_{4'}$), 127.3 (2×CH), 127.2 (2×CH), 126.4 (quintet, *J*=4.5 Hz, C_2 and C_6); *m/z* (EI+, 70 eV) 280 (M^+, 65%), 172 (100), 152 (37), 126 (8), 102 (10), 86 (11), 76 (20), 63 (14) and 51 (19).

(4-Biphenyl)sulfurpentafluoride 7b. *Stille coupling reaction*: Following the Stille coupling procedure above, (4-iodophenyl)sulfurpentafluoride (0.25 g, 0.76 mmol), tetrakis(triphenylphosphine) palladium (40 mg, 0.04 mmol) and tris(*n*-butyl)phenylstannane (0.30 g, 0.91 mmol) in toluene (4 ml) were heated to reflux for 18 h. Work up gave a crude product which was purified by column chromatography (hexane) to give (4-biphenyl)sulfurpentafluoride **7b** as a white solid (0.20 g, 94%); mp 67°C with spectroscopic data as above.

(3-(2-Phenylethyn-1-yl)phenyl)sulfurpentafluoride 8a. Copper (II) acetate hydrate (8 mg, 0.04 mmol), triphenylphosphine (34 g, 0.13 mmol) and palladium (II) chloride (12 mg, 0.07 mmol) were added to a degassed mixture of (3-iodophenyl)sulfurpentafluoride (287 mg, 0.87 mmol) in diisopropylamine (3 ml). The mixture was degassed further then warmed to dissolve the solids before cooling to room temperature. Phenylacetylene (107 mg, 1.04 mmol) was added via a syringe, in small portions, to the vigorously stirred mixture, over 20 min. The resulting mixture was stirred at room temperature for 1.25 h before filtering through Celite® (1 cm depth). The solid Celite® cake was washed with dichloromethane (3×50 ml) and the filtrate concentrated under reduced pressure to give a brown solid. Purification of the crude product by column chromatography (hexane) gave (3-(2-phenylethyn-1-yl)phenyl)-sulfurpentafluoride **8a** as a colourless oil (198 mg, 75%); R_f 0.65 (hexane); Found 304.033971 (M^+), $C_{14}H_9F_5S$ requires 304.034513; ν_{max}(neat)/cm^{-1} 3082, 2927, 2359, 2230, 1954, 1896, 1830, 1752, 1708, 1603, 1494, 1477, 1444, 1421, 1106, 800, 820, 791, 755, 725, 684, 649, 599; δ_H ($CDCl_3$, 300 MHz) 7.97 (1H, bs, H_2), 7.72 (1H, dd, *J*=8, 1.5 Hz, H_4 or H_6), 7.66 (1H, d, *J*=8 Hz, CH), 7.61–7.56 (2H, m), 7.46–7.35 (4H, m); δ_F ($CDCl_3$, 282 MHz) 83.8 (1F, quintet, *J*=150 Hz, SF_{ax}), 62.7 (4F, d, *J*=151 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 153.8 (quintet, *J*=18 Hz, C–SF_5), 134.3 (CH), 131.7 (2×CH), 129.1 (quintet, *J*=4.5 Hz, C_2 or C_6), 128.9 (CH), 128.7 (CH), 128.4 (2×CH), 125.4 (quintet, *J*=4.5, C_6 or C_2), 124.4 (aryl quaternary C), 122.4 (aryl quaternary C), 91.3 (alkyne quaternary C), 87.3 (alkyne quaternary C); *m/z* (EI+, 70 eV) 304 (M^+, 100%), 196 (14), 176 (29), 151 (13), 98 (9).

(4-(2-Phenylethyn-1-yl)phenyl)sulfurpentafluoride 8b. Prepared according to the above Heck coupling procedure using (4-iodophenyl)sulfurpentafluoride (0.15 g, 0.45 mmol), triphenylphosphine (0.01 g, 0.05 mmol), palladium (II) chloride (0.004 g, 0.02 mmol), copper (II) acetate mono hydrate (0.004 g, 0.02 mmol) and phenylacetylene (0.06 g, 0.55 mmol) in diisopropylamine (2 ml). After 1.5 h at room temperature work up gave a yellow oil. Attempted purification by sublimation and distillation proved unsuccessful, however, the product was successfully purified by flash column chromatography (hexane) to give (4-(2-phenylethyn-1-yl)phenyl)pentafluorosulfur **8b** as a white solid (0.07 g, 47%); mp 133°C; R_f 0.45 (hexane); Found 304.034792 (M^+), $C_{14}H_9F_5S$ requires 304.034513; ν_{max}(neat)/cm^{-1} 2957, 2925, 2854, 2221, 1665, 1602, 1502, 1401, 1251, 1093, 862 (S–F), 781, 600, 583, 571; δ_H ($CDCl_3$, 300 MHz) 7.73 (2H, d, *J*=9 Hz, 2×aromatic CH), 7.60–7.53 (4H, m), 7.40–7.36 (3H, m); δ_F ($CDCl_3$, 282 MHz) 84.2 (1F, quintet, *J*=150 Hz, SF_{ax}), 62.8 (4F, d, *J*=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 153.0 (apparent t, *J*=18 Hz, C–SF_5), 131.8 (2×CH), 131.6 (2×CH), 129.0 (CH), 128.5 (2×CH) 127.0 (aryl quaternary C), 126.0 (quintet, *J*=4.5 Hz, C_2 or C_6), 122.3 (aryl quaternary C), 92.4 (alkyne quaternary C), 87.3 (alkyne quaternary C); *m/z* (EI+, 70 eV) 304 (M^+, 100%), 285 [$(M-F)^+$, 3], 196 (88), 176 (28), 151 (10), 126 (10) and 89 (17).

Methyl 2-(3-pentafluorosulfurylphenyl)acrylate 9a. Palladium acetate (7 mg, 0.03 mmol) and triphenylphosphine (16 mg, 0.06 mmol) were added to a solution of (3-iodophenyl)sulfurpentafluoride (219 mg, 0.66 mmol) in triethylamine (degassed, 2 ml). The resulting mixture was warmed a little to dissolve all the solids and methyl acrylate (115 mg, 1.3 mmol) was added. The resulting solution was then heated to reflux overnight. Removal of the solvents gave a brown oil that was purified by flash column chromatography (15% ethyl acetate in hexane) to give methyl 2-(3-pentafluorosulfurphenyl)acrylate **9a** as a pale yellow oily solid (113 mg, 65%); R_f 0.75 (25% ethyl acetate in hexane); Found 288.025233 (M^+), $C_{10}H_9F_5SO_2$ requires 288.024343; ν_{max}(CH_2Cl_2)/cm^{-1} 2954, 2848, 1720 (C=O), 1644, 1573, 1482, 1437, 1316, 1281, 1211, 1175, 1113, 979,

894, 841, 738, 681, 641, 599; δ_H ($CDCl_3$, 300 MHz) 7.87 (1H, bs, H_2), 7.74 (1H, dd, J=8, 1.5 Hz, H_4 or H_6), 7.70–7.63 (2H, m, H_6 or H_4 and H_α), 7.48 (1H, t, J=8 Hz, H_5), 6.49 (1H, d, J=16 Hz, H_β), 3.81 (3H, s, OCH_3); δ_F ($CDCl_3$, 282 MHz) 83.7 (1F, quintet, J=150 Hz, SF_{ax}), 62.6 (4F, d, J=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 166.6 (C═O), 154.5 (quintet, J=17.5 Hz, C–SF_5), 142.5 (CH), 135.5 (quaternary C), 130.6 (CH), 129.3 (CH), 127.2 (quintet, J=4.5 Hz, C_2 or C_6), 125.4 (quintet, J=4.5 Hz, C_6 or C_2), 120.4 (CH), 51.9 (OCH_3); m/z (EI+, 70 eV) 288 (M^+, 46%), 257 [$(M-OMe)^+$, 100], 229 (13), 161 (4), 130 (20), 102 (25), 75 (6), 45 (6).

Methyl 2-(4-pentafluorosulfurylphenyl)acrylate 9b. Using the above procedure a mixture of palladium acetate (9 mg, 0.04 mmol), triphenylphosphine (22 mg, 0.08 mmol), (4-iodophenyl)sulfurpentafluoride (300 mg, 0.91 mmol) and methyl acrylate (157 mg, 1.8 mmol) in triethylamine (degassed, 3 ml) was heated to reflux overnight. Removal of the solvents gave a brown oil that was purified by flash column chromatography (25% ethyl acetate in hexane) to give methyl 2-(4-pentafluorosulfurphenyl)acrylate **9b** as a yellow solid (150 mg, 57%); mp 78–80°C; R_f 0.65 (25% ethyl acetate in hexane); Found 288.023954 (M^+), $C_{10}H_9F_5SO_2$ requires 288.024343; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2953, 1919, 1720 (C═O), 1643, 1578, 1504, 1327, 1293, 1198, 1177, 1100, 982, 909, 846, 595, 581; δ_H ($CDCl_3$, 300 MHz) 7.74 (2H, d, J=9 Hz), 7.66 (1H, d, J=16 Hz, H_α), 7.56 (2H, d, J=9 Hz), 6.49 (1H, d, J=16 Hz, H_β), 3.81 (3H, s, OCH_3); δ_F ($CDCl_3$, 282 MHz) 83.8 (1F, quintet, J=151 Hz, SF_{ax}), 62.7 (4F, d, J=149 Hz, 4×SF_{eq}); δ_C ($CDCl_3$, 75.5 MHz) 166.6 (C═O), 154.5 (apparent t, J= 18 Hz, C–SF_5), 142.1 (CH), 137.5 (quaternary C), 128.0 (C_3 and C_5), 126.5 (quintet, J=4.5 Hz, C_2 and C_6), 121.0 (CH), 51.9 (OCH_3); m/z (EI+, 70 eV) 288 (M^+, 53%), 257 (100), 229 (7), 161 (12), 149 (11), 130 (80), 121 (45), 102 (44).

(3-Acetamidophenyl)sulfurpentafluoride 10a. (3-Aminophenyl)sulfurpentafluoride (0.25 g, 1.14 mmol) was added to acetic anhydride (13 ml) and the resulting mixture was left to stir for 1.5 h. Dichloromethane (10 ml) was added and the organic phase was washed with ice cold water (3×50 ml) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a yellow oil which was taken up in diethyl ether (100 ml) and washed with saturated aqueous $NaHCO_3$ solution (3×100 ml). The organic phase was then dried ($MgSO_4$), decolorized (charcoal) and filtered through Celite® (1 cm depth) and the solvent removed under reduced pressure. (3-Acetamidophenyl)sulfurpentafluoride **10a** was isolated as colourless crystals (0.13 g, 42%); mp 146–148°C; R_f 0.17 (100% dichloromethane); Found 261.024824 (M^+), $C_8H_8F_5NOS$ requires 261.024677; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3426 (N–H), 3064, 3049, 1702 (C═O), 1606, 1522, 1490, 1369, 1306, 854 (S–F), 819, 646, 597; δ_H (CD_3COCD_3, 300 MHz) 9.55 (1H, bs, NH), 8.36 (1H, s, H_2), 7.81–7.77 (1H, m, H_5), 7.56–7.49 (2H, m, H_4 or H_6), 2.06 (3H, s, $COCH_3$); δ_F (CD_3COCD_3, 282 MHz) 85.7 (1F, quintet, J=148 Hz, SF_{ax}), 62.9 (4F, d, J=148 Hz, 4×SF_{eq}); δ_C (CD_3COCD_3, 75.5 MHz) 169.6 (C═O), 154.5 (m, C–SF_5), 140.9 (*C*-NHCOCH$_3$), 130.1 (CH), 123.0 (CH), 121.0 (quintet, J=5 Hz, C_2 or C_6), 117.1 (quintet, J=5 Hz, C_6 or C_2); m/z (EI+, 70 eV) 261 (M^+, 30%), 219 (100), 134 (12), 111 (40), 92 (25), 83 (6), 65 (15) and 43 (87).

(4-Acetamidophenyl)sulfurpentafluoride 10b. Prepared according to the above procedure using (4-aminophenyl)-sulfurpentafluoride (0.25 g, 1.14 mmol) and acetic anhydride (13 ml). After 3 hours at room temperature work up gave crude product which was purified by recrystallisation (diethyl ether/hexane) to give (4-acetamidophenyl)sulfurpentafluoride **10b** as a white solid (0.11 g, 37%); mp 131°C; R_f 0.45 (25% dichloromethane in hexane); Found 261.023719 (M^+), $C_8H_8F_5NOS$ requires 261.024677; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3424 (N–H), 3045, 2990, 1705 (C═O), 1598, 1516, 1402, 1316, 1104, 856 (S–F), 820; δ_H ($CDCl_3$, 300 MHz) 7.69 (2H, d, J=9 Hz, 2×aromatic CH), 7.61–7.58 (3H, m, 2×aromatic CH and NH), 2.21 (3H, s, NHCOC*H*$_3$); δ_H (CD_3COCD_3, 300 MHz) 9.58 (1H, s, NH), 7.83 (2H, d, J=9 Hz, 2×aromatic CH), 7.76 (2H, d, J=9 Hz, 2×aromatic CH), 2.13 (3H, s, NHCOC*H*$_3$); δ_F (CD_3COCD_3, 282 MHz) 86.9 (1F, quintet, J=149 Hz, SF_{ax}), 64.1 (4F, d, J=148 Hz, 4×SF_{eq}); δ_C (CD_3COCD_3, 75.5 MHz) 169.5 (CONH), 148.4 (apparent t, J=17 Hz, C–SF_5), 143.2 (*C*–NHCOCH$_3$), 127.3 (quintet, J=4.5 Hz, 2×*C*HCSF$_5$), 119.1 (2×*C*HCNR), 24.0 (CH_3); m/z (EI+, 70 eV) 261 (M^+, 68%), 219 (100), 111 (89) and 43 (83).

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31. Crystal data for (4-acetamidophenyl)sulfurpentafluoride **10b**: $C_8H_8F_5NOS$, M=261.22, orthorhombic, space group $Pca2_1$ (no 29), a=23.706 (2), b=5.2534 (4), c=15.9163 (13) Å, V=1982.2 (3) Å^3, Z=8, D_c=1.751 g cm^{-3}, 10120 reflections measured, 3289 unique, R=0.0335. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre.
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