Fluorination of α-phenylsulfanyl esters using difluoroiodotoluene

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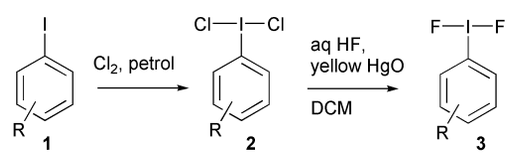
Treatment of α-phenylsulfanyl esters **11**–**14** with one equivalent of difluoroiodotoluene **3a** produced the α-fluoro sulfides **17**–**20** in good overall yield through a Fluoro-Pummerer reaction. A second equivalent of reagent produced α,α-difluoro sulfides and a third led to α,α-difluoro sulfoxides. An identical pattern of reactivity was observed with the α-phenylsulfanyl lactone **26**. This sequential fluorination–oxidation behaviour was exploited in the one-pot synthesis of 3-fluoro-2(5*H*)-furanone **33** starting from α-phenylsulfanylbutyrolactone **32**.

Introduction

The importance of selectively fluorinated compounds in medicinal chemistry has provided a strong incentive for the discovery of new fluorinating reagents which can operate in an efficient, safe and mild manner. In consequence, the controlled introduction of one or more fluorine atoms into organic molecules continues to present a worthwhile challenge for modern synthetic methods.[1] Within this area, our own interest has centred around an exploration of fluorinating agents based on the hypervalent iodoarene difluoride structure **3**. These venerable compounds have seen only sporadic[2] use in fluorination until recently, when we,[3–9] and others,[10–16] have examined them in the context of mild and convenient reagents for the formation of the carbon–fluorine bond.

Hypervalent iodine(III) difluorides were first synthesised by Stille in 1901,[17] and several procedures have since been described for their preparation.[18] For our own studies, we have found that the best method is that of Carpenter, involving halogen exchange of the congeneric iodine(III) dichloride. This protocol provides a safe, reproducible and experimentally convenient procedure for laboratory use and the simple two-step operation is readily adapted to a multi-gram scale (Scheme 1).[19]



R = *p*-Me (**a**), *p*-Bu^t (**b**), *p*-Cl (**c**), H (**d**)

Scheme 1

Thus, the iodoarene **1** is first treated with chlorine gas to form the aryliodine dichloride **2**, and then transhalogenated with aqueous hydrofluoric acid in the presence of mercuric oxide to yield the iodine difluoride **3**. We were initially concerned over the stability of **3**, as previous workers had used these compounds as DCM solutions, being concerned about possible decomposition in the solid state.[2e,f,19] However, we have found that the crystalline *p*-Me (difluoroiodotoluene, DFIT, **3a**) and *p*-Bu^t (**3b**) derivatives could be easily manipulated and stored as solids, consequently these two reagents have subsequently been used in all of our fluorination work.

Our earlier studies established that the electrophilic hypervalent iodine difluorides have a particular affinity for nucleophilic sulfur-containing compounds, and this observation has been exploited in the fluorination of dithioketals,[4] arylthioglycosides,[5] xanthate esters[6] and, most recently a variety of α-acylsulfides.[7–9] Two principal mechanisms can be considered for the introduction of fluorine into sulfides using **3** (Scheme 2). Firstly, substrates preferably possessing a geminal heteroatom such as **4** are fluorinated with cleavage of the carbon–sulfur bond. The electrophilic iodine reagent is first attacked by nucleophilic sulfur to give an adduct such as **5**, the ligand exchange at iodine resulting in the displacement of fluoride. The activated sulfur-species is then displaced by nucleophilic fluoride, often with participation from the neighbouring heteroatom, to produce fluorides **6**.

By way of contrast, the second pathway which can operate does not involve cleavage of the carbon–sulfur bond, and is analogous to the classical Pummerer reaction. In this instance, sulfides such as **7** containing an electron-withdrawing group in the α-position are activated by **3** to form adducts **8**, which are sufficiently acidic to undergo deprotonation with basic fluoride. The resulting sulfonium species **9** may then be trapped with fluoride to produce the α-substituted products **10**. In mechanistic terms, the hypervalent iodoarene difluorides do bear some similarity to the widely used fluorinating agent DAST,[20] inasmuch as both are inherently electrophilic in character and function in the first instance to create both an activated leaving group and also to provide a source of nucleophilic fluoride for nucleophilic displacement. The significant difference however is that whilst DAST is primarily oxophilic, reagents **3** exhibit thiophilic character.

In this and the following paper we discuss, in full detail, the fluorination of a range of sulfides which illustrate both of the Type 1 and 2 pathways. The present paper focuses on α-phenylsulfanyl esters, a class of substrates that effectively undergo Fluoro-Pummerer (Type 2) reaction with DFIT **3a** to give α-fluoro sulfides.

Results and discussion

The α-fluorination of sulfoxides or sulfides through the Fluoro-Pummerer reaction is known as an effective strategy for the synthesis of α-fluoro sulfides and a number of reagents have been shown to effect this transformation.[21] The α-fluoro sulfides

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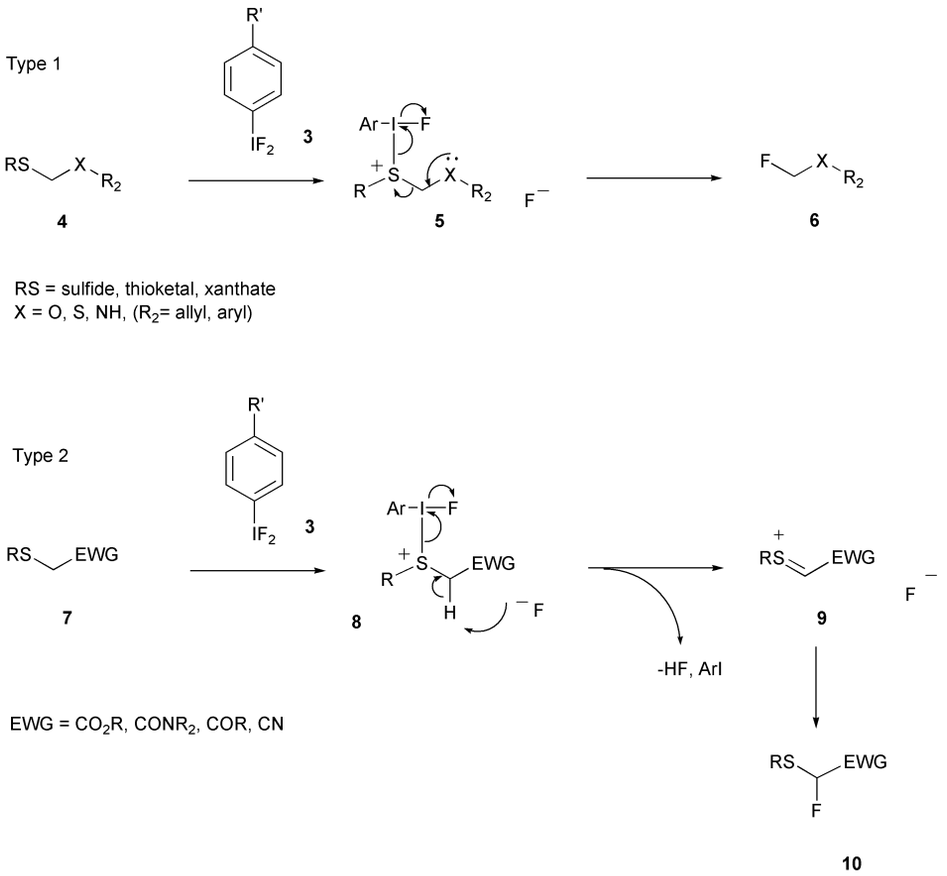


Scheme 2

synthesised in this manner have found application as enzyme inhibitors,[22] as ^{19}F NMR structural probes in proteins[23] and as synthons for vinyl fluorides.[24] We were particularly interested in examining the fluorination of α-phenylsulfanyl esters in light of a report by Fuchigami on the fluorination of ethyl (arylsulfanyl)-acetates with electrogenerated difluoroiodoarenes in the presence of $Et_3N{\cdot}3HF$.[16] In that system reactions were found to be incomplete, necessitating two equivalents of fluorinating agent and the product fluorides were isolated in moderate yields (<50%). Our results using difluoroiodotoluene (DFIT, **3a**) in the Fluoro-Pummerer reaction of some α-phenylsulfanyl-acetates are shown in Table 1.

Examination of the results (Entries 1–4) shows that the expected α-fluoro sulfides were formed cleanly and in good overall yields upon treatment with only one single equivalent of DFIT in DCM. It was also of interest to note (Entries 2 and 3) that capture of the Pummerer intermediate by fluoride anion was faster than cyclisation to give a γ-lactone by π-participation, even when a tertiary or benzylic carbocation could be formed. It is therefore interesting to speculate that capture of fluoride from the Pummerer intermediate might possibly occur *via* a "reductive elimination" or S_{Ni} sequence as shown in Fig. 1.

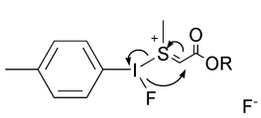
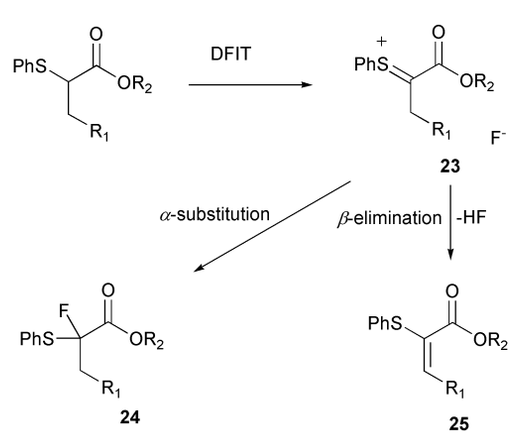


Fig. 1

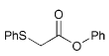
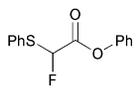
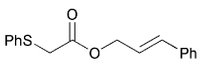
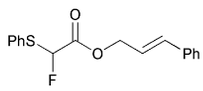
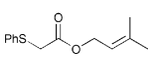
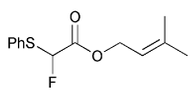
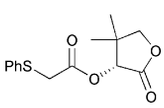
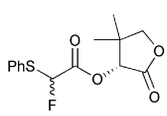
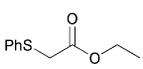
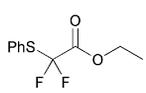
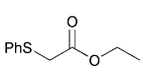
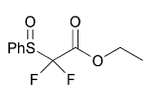
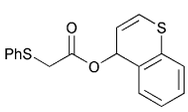
Most significantly, and in contrast to DAST, a second fluorination was also possible with the α,α-difluorosulfide **21** (Entry 5) being formed on treatment of the ethyl derivative **15** with two equivalents of DFIT. Two sequential Fluoro-Pummerer reactions have been found to be problematic with the widely-employed fluorinating agent DAST.[21b] The finding that addition of a third equivalent (Entry 6) led to the α,α-difluorosulfoxide **22** was also worthy of note and suggested possible applications to the synthesis of vinyl fluorides (*vide infra*). The thiochromanyl derivative **16** (Entry 7) was exceptional in being unproductive in the Fluoro-Pummerer reaction, decomposing to a number of unidentified products when treated with DFIT. The presence of an additional sulfur atom in the substrate may be important in this regard, offering an extra coordination site to the reagent.

In order to gain further insight into the nature of the surrounding environment when ester functionality is used as the electron withdrawing group we were therefore interested in extending the Fluoro-Pummerer chemistry of aryl iodine difluorides to more complex systems. The Pummerer reaction is of broad scope, especially when applied to sulfoxides having both α and β hydrogens.[25] In such systems the formation of the α,β-unsaturated sulfide **25**, arising from β-elimination in the acylsulfonium intermediate **23** is frequently competitive with the α-substitution product **24** (Scheme 3).[26]



Scheme 3

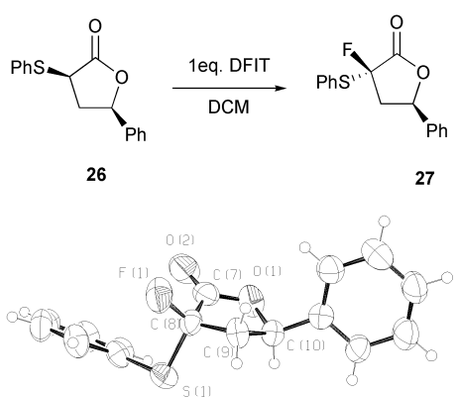
Table 1 Fluorination of α-phenylsulfanyl acetates with DFIT [a]

Entry		Ester		Product	Yield (%) [b]
1	**11**		**17**		**72**
2	**12**		**18**		**67**
3	**13**		**19**		**64**
4	**14**		**20** [c]		**53**
5	**15** [d]		**21**		**80**
6	**15** [e]		**22**		**38**
7	**16**		–		**0**

[a] Method: DFIT (1 eq.), DCM, 0 °C, stirring overnight. [b] Isolated yields. [c] Isolated as a 1:1 mixture of diastereoisomers. [d] 2 eq. DFIT. [e] 3 eq. DFIT, 19% of **21** also isolated

The racemic lactone **26** was accordingly prepared with a view to examining whether the presence of β hydrogens would lead to alternative products in the Fluoro-Pummerer reaction with DFIT.

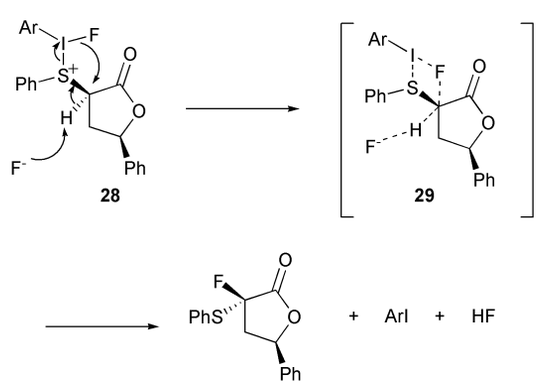
In the event, treatment of **26** with one equivalent of DFIT gave the α-fluoro sulfide **27** as a single diastereoisomer in 62% yield as the only isolated product. The X-ray structure of **27** shows the fluoride to have been introduced *syn* to the bulky phenyl group in the 5-position. The phenylsulfanyl group occupies a pseudoaxial position and the phenyl group is disposed pseudoequatorially, a consequence of the longer C–S bond relative to the C–C bond (Scheme 4).



X-Ray structure of **27**

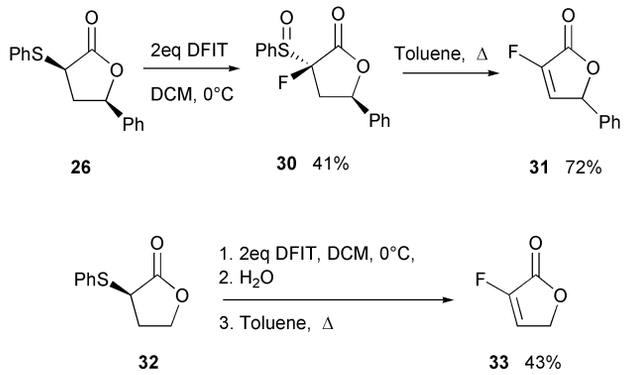
Scheme 4

Introduction of fluorine *syn* to the bulky phenyl group was unexpected, given that electrophilic addition of methyl iodide to the lithium enolate of **26** is known to give the *anti* product.[27] Nucleophilic addition of acetate to the more hindered face in classical Pummerer reactions has been reported, and is believed to be due to a highly concerted transition state involving simultaneous deprotonation and nucleophilic attack.[28] Although detailed mechanistic studies have yet to be carried out, a similar mechanism may be operating here. Scheme 5 shows the Pummerer adduct **28**, formed from DFIT addition to **27**, being deprotonated by fluoride from the α-face necessitating intramolecular delivery of fluoride from the β-face through the highly synchronous transition state **29**.



Scheme 5

As expected, the use of a second equivalent of DFIT produced the fluoro-sulfoxide **30**, in analogy to the fluorination of the acyclic ester **15** (Scheme 6). We recognised this result to have a significant bearing on our interest in the synthesis of vinyl fluorides as α-fluoro sulfoxides may be converted to these compounds through pyrolytic elimination of sulfenic acid. Accordingly, heating **30** in toluene for 20 min provided the expected 3-fluoro-2(5*H*)-furanone derivative **31** in 72% yield. It was found that isolation of the intermediate α-fluoro sulfoxide was



Scheme 6

unnecessary. Thus, treatment of **32** with DFIT followed by aqueous work-up and thermolysis of the crude product in refluxing toluene gave the 2-fluorobut-2-en-4-olide **33** directly in 43% yield.

Previous syntheses of these fluorinated synthons have required an (*E*)-selective Wittig–Horner reaction of an aldehyde with a fluorophosphonate followed by hydrolytic ring-closure.[29] Sulfanylation of an appropriate lactone followed by DFIT treatment, hydrolysis and *syn* elimination thus represents a versatile alternative.

Conclusions

We have demonstrated that difluoroiodotoluene **3a** is an effective reagent for the α-fluorination of α-phenylsulfanylesters. The systems investigated fall squarely within the Type 2 reaction mechanism manifold we have defined, reliably producing the simple Fluoro-Pummerer products under mild reaction conditions, without the necessity for any further additions of external fluoride sources or catalysts.

Experimental

Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. DCM and chloroform were distilled from either phosphorus pentoxide or calcium hydride. Toluene and benzene were distilled over sodium. Methanol was distilled from magnesium turnings. Triethylamine, pyridine, isopropylamine and acetonitrile were distilled over calcium hydride.

Melting points were determined using a Reichert hot stage and are uncorrected. Boiling points for Kugelröhr distillations refer to uncorrected air temperatures. Microanalyses were performed by Mr Alan Stone and Mrs Jill Maxwell, Christopher Ingold Building, University College London. Infrared spectra were recorded as thin films or Nujol mulls on KBr plates, as KBr discs, or as CCl_4 solutions on a Perkin-Elmer FT-IR 1605 instrument. Major features of each spectrum are reported. The abbreviations used to denote peak intensity are w, weak; m, medium; s, strong; br, broad. ^{1}H NMR spectra were recorded at 500 MHz on a Bruker Avance 500, at 400 MHz on a Varian VXR-400 or a Bruker AMX-400 and at 300 MHz on a Bruker AMX-300 spectrometer. ^{13}C NMR Spectra were recorded at 125 MHz, 100 MHz or 75 MHz on the instruments above. ^{13}C NMR spectra assignments are supported by DEPT editing. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak. (2C) Indicates that the quoted chemical shift refers to two signals separated by less than 0.05 ppm. ^{19}F NMR Spectra were recorded at 471 MHz, 376 MHz or 282 MHz on the instruments above. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to $CFCl_3$. Coupling constants are measured in Hertz and quoted to the nearest Hertz for all spectra. The abbreviations used to indicate multiplicity are s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; dt, double triplet; m, multiplet; br, broad. Low resolution mass spectra were recorded under either electron impact, atmospheric pressure chemical ionisation, or fast atom bombardment conditions on a VG 305 or a VG ZAB SE mass spectrometer at the School of Pharmacy, University of London. Only molecular ions, fragments from molecular ions and other major peaks are reported. High resolution mass spectra were recorded using a VG 7070b mass spectrometer at the School of Pharmacy, University of London.

Difluoroiodotoluene 3a [19]

Dry chlorine gas was blown over the surface of a stirred solution of iodotoluene (7.50 g, 35 mmol) in dry PE 40–60 (65 mL) at 0 °C in the dark for 1.5 h. After flushing with nitrogen for 1 h the mixture was filtered to give dichloroiodotoluene (9.64 g, 95%) as a yellow solid; mp 62–65 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.48 (3H, s, CH_3), 7.28 (2H, AA′BB′ d *J* 9 Hz, 3-H, 5-H), 8.05 (2H, AA′BB′ d *J* 9 Hz, 2-H, 6-H); MS (APCI): *m*/*z* 255 ([M − ^{35}Cl]$^+$, 30%), 253 ([M − ^{37}Cl]$^+$, 100), 218 ([C_7H_7I]$^+$, 65). Dichloroiodotoluene (9.64 g) was dissolved in DCM (60 mL) in a polypropylene erlenmeyer flask. Yellow mercuric oxide (9.50 g, 44 mmol) and 48% aq. hydrofluoric acid (13 mL, 410 mmol) were then added. The slurry was vigorously shaken periodically over 2 h, then filtered and the organic layer separated. After swirling with MgO the solution was decanted and concentrated *in vacuo* to yield the title compound **3a** (5.87 g, 66%) as a white solid; mp 110 °C (decomp., DCM); IR (thin film/cm^{-1}): ν_{max} 1636m, 1395w, 1278w, 1116w, 800s; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.48 (3H, s, CH3), 7.40 (2H, AA′BB d *J* 8 Hz, 3-H, 5-H), 7.84 (2H, AA′BB′ d *J* 8 Hz, 2-H, 6-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 21.2 (CH_3), 130.3, 132.2, 137.3, 142.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ_F −177.1; MS (EI): *m*/*z* 256 ($M^{\bullet+}$, 15%), 218 ([C_7H_7I]$^+$, 80), 127 (I^+, 7), 91 ([C_7H_7]$^+$, 100); HRMS (EI) calcd. for $C_7H_7F_2I$: 255.9561. Found: 255.9570. In some runs the DFIT was contaminated with unreacted iodotoluene. The extent of reaction could be quantified by ^{1}H NMR, and is indicated as a percentage where appropriate. No percentage figure indicates pure (^{1}H NMR) difluoroiodotoluene.

General procedure for the synthesis of α-phenylsulfanyl acetates. Triethylamine or pyridine (1 eq.) was added to a stirred solution of alcohol (1 eq.) in DCM (*ca.* 3 mL mmol^{-1}). The mixture was cooled in an ice-salt bath (<0 °C) and phenylsulfanylacetyl chloride was added dropwise. Consumption of starting alcohol was monitored by TLC and the reaction was quenched with water upon completion. The aqueous phase was extracted with DCM (×2), the combined extracts dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography afforded pure products.

Phenyl (phenylsulfanyl)acetate 11. Colourless oil; R_f 0.65 (SiO_2, PE 30–40:ether 80:20); IR (thin film/cm^{-1}): ν_{max} 3062m (CH), 1763s (C=O), 1590m, 1488s, 1440w, 1405w, 1252s, 1193s, 1116s, 1024w, 934m, 894m, 742s, 689s; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 3.88 (2H, s, SCH_2), 7.02 (2H, dd *J* 7, 1 Hz), 7.25–7.54 (6H, m), 7.55 (2H, dd *J* 7, 1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 37.4 (SCH_2), 121.7, 126.5, 127.8, 129.6, 129.8, 131.1, 134.8 (SC_{ipso}), 151.0 (OC_{ipso}), 168.7 (C=O); MS (FAB): *m*/*z* 244 (M^+, 100%); HRMS (FAB) calcd. for $C_{14}H_{12}O_2S$: 244.0558. Found 244.0567.

(*E*)-Cinnamyl (phenylsulfanyl)acetate 12. Green oil; R_f 0.58 (SiO_2, PE 30–40:ether 85:15); IR (thin film/cm^{-1}): ν_{max} 3058m, 2945m (CH), 1732 (C=O), 1583m, 1440s, 1265s, 1141s, 965s, 742s, 691s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.71 (2H, s, SCH_2), 4.79 (2H, d *J* 7 Hz, 1-H), 6.23 (1H, dt $^{trans}J_{AB}$ 16 Hz, $^3J_{2,1}$ 7 Hz 2-H), 6.65 (1H, d $^{trans}J_{AB}$ 16 Hz, 3-H), 7.19–7.47 (10H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 36.7 (SCH_2), 66.0

(1-C), 122.5 (2-C), 126.6 (2C), 127.1, 128.1, 128.6, 129.0, 130.1, 134.6, 136.0, 169.5 (C=O); MS (FAB): *m*/*z* 417 (MCs^+, 30%), 284 (M^+, 100); HRMS (FAB) calcd. for $C_{17}H_{16}O_2S$: 284.0871. Found: 284.0866.

Prenyl (phenylsulfanyl)acetate 13. Colourless oil; bp 175 °C/0.5 mBar; R_f 0.43 (SiO_2, PE 30–40:ether 90:10); IR (thin film/cm^{-1}): ν_{max} 2924m (CH), 1734s (C=O), 1440w, 1276m, 1130m, 959w, 740m, 688m; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.69 (3H, s, CH_3), 1.76 (3H, s, CH_3), 3.66 (2H, s, SCH_2), 4.62 (2H, d *J* 8 Hz, 1-H), 5.30 (1H, m, 2-H), 7.23–7.43 (5H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 18.1 (CH_3), 25.8 (CH_3), 36.8 (SCH_2), 62.4 (1-C), 118.1 (2-C), 126.9, 129.0, 130.0, 135.0, 139.9, 169.7 (C=O); MS (FAB): *m*/*z* 236 (M^+, 35%), 123 ([M − $PhSCH_2$]$^+$, 100); Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82%. Found: C, 65.80; H, 6.58%.

(3*R*)-4,5-Dihydro-4,4-dimethyl-3-(phenylsulfanyl)acetoxy-2(3*H*)-furanone 14. Yellow oil; R_f 0.32 (SiO_2, PE 30–40:ether 50:50); IR (thin film/cm^{-1}): ν_{max} 2967m (CH), 1790s (C=O lactone), 1747s (C=O ester), 1584m, 1470m, 1378m, 1263s, 1128s, 1079s, 1013m, 743s, 690s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.01 (3H, s, CH_3), 1.18 (3H, s, CH_3), 3.60–3.77 (2H, m, 5-H), 4.02 (2H, s, SCH_2), 5.36 (1H, s, 3-H), 7.26–7.48 (5H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 19.6 (CH_3), 22.7 (CH_3), 36.2, 40.2, 75.7, 76.1, 127.2, 129.1, 130.1, 134.3, 168.8, 171.9; MS (FAB): *m*/*z* 413 (MCs^+, 100%), 303 (MNa^+, 25), 281 (MH^+, 75); HRMS (FAB) calcd. for $C_{14}H_{16}O_4S$ (MH^+): 281.0848. Found: 281.0830.

Ethyl (phenylsulfanyl)acetate 15. Colourless oil; R_f 0.65 (SiO_2, PE 30–40:ether 80:20); IR (thin film/cm^{-1}): ν_{max} 2982s (CH), 1736s (C=O), 1582m, 1273s, 1135s, 1028s, 743s, 691s; ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.20 (3H, t *J* 9 Hz, CH_3), 3.61 (2H, s, SCH_2) 4.14 (2H, q *J* 9 Hz, OCH_2), 7.20–7.40 (5H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 14.0 (CH_3), 36.8 (SCH_2), 61.5 (OCH_2), 126.9, 129.0, 129.9, 135.0 (C_{ipso}), 169.8 (C=O); MS (FAB): *m*/*z* 196 (M^+, 65%), 123 (M^+, 100); HRMS (FAB) calcd. for $C_{10}H_{12}O_2S$: 196.0558. Found: 196.0550.

4-Thiochromanyl (phenylsulfanyl)acetate 16. Yellow oil; R_f 0.55 (SiO_2, PE 30–40:ether 85:15); IR (thin film/cm^{-1}): ν_{max} 3058w, 2925w (CH), 1725s (C=O), 1586m, 1477m, 1438m, 1264s, 1126s, 1002m, 962m, 746s, 691s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.03–2.13 (1H, m, 3-H), 2.29–2.35 (1H, m, 3-H), 2.75–2.82 (1H, m, 2-H), 3.09–3.19 (1H, m, 2-H), 3.67 (2H, s, SCH_2), 6.05 (1H, t *J* 3 Hz, 4-H), 7.01–7.54 (9H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 22.4, 28.7, 37.8, 70.1 (4-C), 125.1, 127.6, 128.0, 130.0, 130.8, 131.1, 132.7, 135.0, 135.5, 169.9 (C=O); MS (FAB): *m*/*z* 316 (M^+, 75%), 219 (35); HRMS (FAB) calcd. for $C_{17}H_{16}O_2S_2$ (MH^+): 316.0598. Found: 316.0592.

General procedure for the fluorination of substrates using DFIT. A solution of DFIT in DCM was prepared in a 25 mL polypropylene flask protected from light by aluminium foil. The solution was cooled to 0 °C in an ice–salt bath and a solution of the substrate in DCM was then added *via* cannula. The mixture was left to stir at this temperature. Upon completion (TLC) the reaction was quenched with water and extracted with DCM. The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography yielded pure materials.

Phenyl (2-fluoro-2-phenylsulfanyl)acetate 17. A solution of DFIT (185 mg, 0.73 mmol) and sulfide **11** (163 mg, 0.67 mmol) in DCM (5 mL) was stirred overnight. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 95:5) gave the fluoride **17** (126 mg, 72%) as a white solid; R_f 0.52 (SiO_2, PE 30–40:ether 85:15); IR (thin film/cm^{-1}): ν_{max} 3049w, 2951w, 1742s (C=O), 1588m, 1483m, 1434m, 1309w, 1246s, 1190s, 1015s, 931m, 840w, 742w, 686m; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 6.28 (1H, d $^2J_{HF}$ 51 Hz, 2-H), 6.84–7.64 (10H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 93.8 (d $^2J_{CF}$ 234 Hz, 2-C) 120.9, 126.4, 129.0 (SC_{ipso}), 129.3, 129.5, 129.7, 134.5, 149.8 (OC_{ipso}), 163.8 (d $^2J_{CF}$ 31 Hz, C=O); ^{19}F NMR (282 MHz, $CDCl_3$): δ_F −158.5 (d $^2J_{FH}$ 51 Hz); MS (FAB): *m*/*z* 285 (MNa^+, 35%), 262 (M^+, 100); HRMS (FAB) calcd. for $C_{14}H_{11}FO_2S$: 262.0464. Found: 262.0459; plus unreacted starting material (12%).

Cinnamyl (2-fluoro-2-phenylsulfanyl)acetate 18. A solution of DFIT (80%, 328 mg, 1.1 mmol) and sulfide **12** (300 mg, 1.1 mmol) in DCM (6 mL) was stirred for 2.5 h. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 95:5) yielded the fluoride **18** (221 mg, 67%) as a colourless oil; R_f 0.18 (SiO_2; PE 30–40:ether 90:10); IR (thin film/cm^{-1}): ν_{max} 3028s, 2953s (CH), 1756s (C=O), 1441s, 1322s, 1297s, 1175s, 1037s, 967s, 747s, 691s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.72–4.76 (2H, m, 1-H), 6.12 (1H, d $^2J_{HF}$ 52 Hz, SCHF), 6.13 (1H, *dt* $^{trans}J_{2,3}$ 16 Hz, $^3J_{2,1}$ 7 Hz, 2-H), 6.63 (1H, d $^{trans}J_{3,2}$ 16 Hz, 3-H), 7.27–7.57 (10H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 66.7 (1-C), 94.11 (d $^1J_{CF}$ 232 Hz, SCHF), 121.6 (2-C), 126.7, 128.3, 128.6, 129.2, 129.5, 134.3 (2C), 135.6, 135.8, 165.1 (d $^2J_{CF}$ 29 Hz, C=O); ^{19}F NMR (376 MHz, $CDCl_3$): δ_F −158.7 (d $^1J_{HF}$ 52 Hz); MS (FAB): *m*/*z* 302 (M^+, 100%); HRMS (FAB) calcd. for $C_{17}H_{15}FO_2S$: 302.0777. Found: 302.0762.

Prenyl (2-fluoro-2-phenylsulfanyl)acetate 19. A solution of DFIT (87%, 350 mg, 1.2 mmol) and sulfide **13** (257 mg, 1.10 mmol) in DCM (6 mL) was stirred for 2 h. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 90:10) yielded the fluoride **19** (178 mg, 64%) as a colourless oil; R_f 0.40 (SiO_2, PE 30–40:ether 90:10); IR (thin film/cm^{-1}): ν_{max} 2975m, 2936m (CH), 1752s (C=O), 1275s, 1177s, 1034s, 957s, 748s, 693s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.68 (3H, s, CH_3), 1.75 (3H, s, CH_3) 4.58 (2H, d *J* 8 Hz, 1-H), 5.21–5.25 (1H, m, 2-H), 6.07 (1H, d $^2J_{HF}$ 52 Hz, SCHF), 7.33–7.57 (5H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 17.9 (CH_3), 25.7 (CH_3), 63.0 (1-C), 94.2 (d $^1J_{CF}$ 234 Hz, SCHF), 117.3 (2-C), 128.9, 129.0, 129.3, 134.0, 140.4, 165.3 (d $^2J_{CF}$ 29 Hz, C=O); ^{19}F NMR (470 MHz, $CDCl_3$): δ_F −158.6 (d, $^2J_{FH}$ 53 Hz); MS (FAB): *m*/*z* 387 (MCs^+, 100%), 293 (MK^+, 60), 277 (MNa^+, 80), 255 (MH^+, 85); HRMS (FAB) calcd. for $C_{13}H_{15}FO_2S$: 255.0855. Found: 255.0861.

(3*R*,2′*R*/2′*S*)-4,5-Dihydro-3-(2′-fluoro-2′-phenylsulfanyl)-acetoxy-4,4-dimethyl-2(3*H*)-furanone 20. A solution of DFIT (83%, 219 mg, 0.71 mmol) and sulfide **14** (186 mg, 0.62 mmol) in DCM (5 mL) was stirred overnight. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 60:40) afforded the fluoride **20** (103 mg, 53%) as a colourless oil (*3R,2′R*:*3R,2′S* 1:1); R_f 0.37 (SiO_2, PE 30–40: ether 60:40); IR (thin film/cm^{-1}): ν_{max} 2969s (CH), 1770s (C=O), 1476m, 1378m, 1260s, 1157s, 1077s, 1013s, 754s, 692s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.02, 1.06, 1.07, 1.10 (12H, 4 × s, 4 × CH_3), 3.97–4.04 (4H, m, 5-H), 5.25 (1H, s, 3-H), 5.32 (1H, s, 3-H), 6.18 (1H, d $^2J_{HF}$ 51 Hz, 2′-H), 6.23 (1H, d $^2J_{HF}$ 51 Hz, 2′-H), 7.49–7.67 (5H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 19.7 (CH_3), 19.8 (CH_3), 22.6 (CH_3), 22.8 (CH_3), 40.3 (4-C), 40.4 (4-C), 76.1 (3-H), 76.1 (3-H), 76.4 (4-H), 76.5 (4-H), 93.4 (d $^1J_{CF}$ 230 Hz, 2′-H), 94.1 (d $^1J_{CF}$ 233 Hz, 2′-H), 129.4, 129.4, 129.9, 130.2, 133.2, 133.2, 135.0, 135.0, 164.4 (d $^2J_{CF}$ 13 Hz, 1′-C), 164.7 (d $^2J_{CF}$ 13 Hz, 1′-C); ^{19}F NMR (376 MHz, $CDCl_3$): δ_F −160.2 (d $^2J_{FH}$ 51 Hz), −156.3 (d $^2J_{FH}$ 51 Hz); MS (FAB): *m*/*z* 298 (M^+ 55%), 279 ([M − F]$^+$, 100); HRMS (FAB) calcd. for $C_{14}H_{15}O_4FS$: 298.0675. Found 298.0670.

Ethyl (2,2-difluoro-2-phenylsulfanyl)acetate 21. A solution of DFIT (75%, 671 mg, 2 mmol) and sulfide **15** (200 mg, 1.00 mmol) in DCM (7 mL) was stirred overnight. The crude

material was absorbed onto silica gel and washed with PE 30–40. A second wash with PE 30–40:ether 80:20 afforded the difluoride **21** (188 mg, 80%) as a colourless oil; R_f 0.48 (SiO_2, PE 30–40:ether 90:10); IR (thin film/cm^{-1}): ν_{max} 3063m, 2986s, 2940m (CH), 1767 (C=O), 1476s, 1442s, 1371s, 1234s, 1106s, 1017s, 978s, 753s, 691s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.24 (3H, t J 4 Hz, CH_3), 4.23 (2H, q J 4 Hz, CH_2), 7.36–7.61 (5H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.76 (CH_3), 63.5 (CH_2), 120.0 (t $^1J_{CF}$ 287 Hz), 124.9 (C_{ipso}), 129.3, 130.6, 136.7, 161.6 (t $^2J_{CF}$ 32 Hz, C=O); ^{19}F NMR (282 MHz, $CDCl_3$): δ_F −82.7; MS (FAB): m/z 232 (M^+ 100%), 213 ([M − F]$^+$, 20), 159 (90); HRMS (FAB) calcd. for $C_{10}H_{10}F_2O_2S$: 232.0370. Found: 232.0362.

Ethyl (2,2-difluoro-2-phenylsulfinyl)acetate 22. A solution of DFIT (75%, 754 mg, 2.28 mmol) and sulfide **15** (150 mg, 0.76 mmol) in DCM (10 mL) was stirred overnight. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 95:5) afforded the difluoro-sulfoxide **22** (71 mg, 38%) as a colourless oil; R_f 0.11 (PE 30–40:ether 90:10); IR (thin film/cm^{-1}): ν_{max} 3064m, 2988s, 2942m (CH), 1760s (C=O), 1475s, 1447s, 1373s, 1306s, 1132s, 1062s, 1031s, 964s, 854m, 833m, 752m, 689s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.18 (3H, t J 7 Hz, CH_3), 4.19 (2H, q J 7 Hz, CH_2), 7.49–7.67 (5H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 14.2 (CH_3), 64.6 (CH_2), 118.4 (t $^1J_{CF}$ 302 Hz, 2-C), 126.4, 129.8, 133.6, 136.44 (C_{ipso}), 159.7 (t $^2J_{CF}$ 28 Hz, C=O); ^{19}F NMR (282 MHz, $CDCl_3$): δ_F −110.3 (ABq $^2J_{FH}$ 578, 228 Hz); MS (FAB): m/z 271 (MNa^+ 10%), 249 (MH^+, 100); HRMS (FAB) calcd. for $C_{10}H_{11}F_2O_3S$ (MH^+): 249.0397. Found: 249.0388; plus **21** (34 mg, 19%).

3-Fluoro-4,5-dihydro-3-phenylsulfanyl-*anti*-5-phenyl-2(3*H*)-furanone 27. A solution of DFIT (75%, 365 mg, 1.1 mmol) and lactone **26**[27] (300 mg, 1.1 mmol) in DCM (5 mL) was stirred for 7 h. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 90:10) afforded the fluoride **27** (197 mg, 62%) as colourless crystals; mp 98–100 °C (PE 30–40:ether); R_f 0.29 (SiO_2, PE 30–40:ether 80:20); IR (thin film/cm^{-1}): ν_{max} 3062w, 1789s (C=O), 1598w, 1474w, 1442w, 1328w, 1279w, 1203m, 1180m, 1041m, 1014m, 938w, 847w, 749m, 697s; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.66–2.74 (1H, m, 4-H), 2.89 (1H, dd J 11, 4 Hz, 4-H), 5.51 (1H, dd J 8, 4 Hz, 5-H), 7.33–7.65 (10H, m, Ar–H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 43.7 (d $^2J_{CF}$ 21 Hz, 4-C), 77.1 (d $^3J_{CF}$ 4 Hz, 5-C), 99.8 (d $^1J_{CF}$ 246 Hz, 3-C), 125.8, 127.3, 128.9, 129.1, 129.3, 130.4, 135.7, 136.6, 167.3 (d $^2J_{CF}$ 31 Hz, C=O); ^{19}F NMR (471 MHz, $CDCl_3$): δ_F −132.4 (d $^3J_{FH}$ 16 Hz); MS (FAB): m/z 288 (M^+, 23%), 269 ([M − F]$^+$, 100), 223 (100); Anal: calcd. for $C_{16}H_{13}FO_2S$: C, 66.65; H, 4.54; S, 11.12%. Found: C, 66.63; H, 4.45; S, 10.96%.

3-Fluoro-4,5-dihydro-3-phenylsulfinyl-*anti*-5-phenyl-2(3*H*)-furanone 30. A solution of DFIT (75%, 731 mg, 2.2 mmol) and lactone **26**[27] (300 mg, 1.1 mmol) in DCM (8 mL) was stirred overnight. Work-up according to the general procedure followed by flash chromatography (SiO_2, PE 30–40:ether 90:10) afforded the fluoro-sulfoxide **30** (136 mg, 41%) (sulfoxide diastereomeric ratio 5:2, unassigned) as colourless crystals; R_f 0.27 (SiO_2, PE 30–40:ether 50:50); IR (thin film/cm^{-1}): ν_{max} 3061w, 1785s (C=O), 1444w, 1332w, 1201m, 1086m, 1056m, 940w, 750m, 697m; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.23–2.40 (1H, m, 4-H major), 2.65–2.73 (1H, m, 4-H minor), 3.24–3.29 (1H, m, 4-H major), 3.63–3.68 (1H, m, 4-H minor), 4.76–4.79 (1H, m, 5-H minor), 5.60–5.66 (1H, m, 5-H major), 7.24–7.86 (10H, m, Ar–H); ^{19}F NMR (471 MHz, $CDCl_3$): δ_F −152.7 (dd $^3J_{FH}$ 24, 5 Hz, major), −151.1 (d $^3J_{FH}$ 24 Hz, minor); MS (FAB): m/z 327 (MNa^+, 30%), 305 (MH^+, 85), 179 ([M − PhSO]$^+$, 100); Anal. calcd. for $C_{16}H_{13}FO_3S$: C, 63.14; H, 4.31; S, 10.54%. Found: C, 63.09; H, 4.19; S, 10.26%.

3-Fluoro-5-phenyl-2(5*H*)-furanone 31. A solution of fluoro-sulfoxide **30** (94 mg, 0.31 mmol) in toluene (5 mL) was refluxed for 20 min. Concentration *in vacuo* followed by flash chromatography (SiO_2, PE 30–40:ether 95:5) afforded the fluoride **31** (43 mg, 72%) as a colourless oil; R_f 0.16 (SiO_2, PE 30–40:ether 85:15); IR (thin film/cm^{-1}): ν_{max} 3108w (CH), 1783s (C=O), 1678m, 1288w, 1108m; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 5.88 (1H, dd $^3J_{HF}$ 6 Hz, $^3J_{HH}$ 2 Hz, 4-H), 6.76 (1H, t $^3J_{HH}$ 2 Hz, $^4J_{HF}$ 2 Hz, 5-H), 7.18–7.38 (5H, m, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 79.0 (d $^3J_{CF}$ 8 Hz, 5-C), 126.1 (d $^2J_{CF}$ 6 Hz, 4-C), 127.2, 129.6, 130.3, 134.0 (d $^4J_{CF}$ 2 Hz, C_{ipso}), 148.6 (d $^1J_{CF}$ 281 Hz, 3-C), 165.0 (d $^2J_{CF}$ 32 Hz, C=O); ^{19}F NMR (282 MHz, $CDCl_3$): δ_F −142.1 (d $^3J_{FH}$ 6 Hz); MS (FAB): m/z 179 (MH^+, 65%), 159 ([M − F]$^+$, 100); HRMS (FAB) calcd. for $C_{10}H_8FO_2$ (MH^+): 179.0508. Found: 179.0502.

3-Fluoro-2(5*H*)-furanone 33[29b]**.** A solution of DFIT (91%, 1.25 g, 4.2 mmol) and sulfide **32**[30] (400 mg, 2.1 mmol) in DCM (15 mL) was stirred overnight. The reaction was worked-up as usual and the crude product taken into toluene (10 mL) and stirred at reflux for 30 min. After cooling to room temperature the solution was concentrated *in vacuo* then chromatographed (SiO_2, PE 30–40:ether 70:30) to afford the fluoride **33** (92 mg, 43%) as a yellow oil; R_f 0.27 (SiO_2, DCM); IR (thin film/cm^{-1}): ν_{max} 2929m (CH), 1777s (C=O), 1680s, 1450s, 1332m, 1107s, 1040s, 824m, 760s; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.81 (2H, dd $^2J_{HH}$ 6 Hz, $^3J_{HH}$ 2 Hz, 5-H), 6.79 (1H, dd $^3J_{HF}$ 4 Hz, $^3J_{HH}$ 2 Hz, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 66.6 (d $^3J_{CF}$ 8 Hz, 5-C), 123.3 (d $^2J_{CF}$ 8 Hz, 4-C), 148.5 (d $^1J_{CF}$ 275 Hz, 3-C), 165.5 (d $^2J_{CF}$ 32 Hz, C=O); ^{19}F NMR (282 MHz, $CDCl_3$): δ_F −146.8 (t J 6 Hz).

Crystal data for 27. $C_{16}H_{13}FO_2S$, M = 288.32, monoclinic, a = 6.2010(10), b = 7.933(2), c = 14.948(3) Å, β = 92.11(3)°, U = 734.8(3) Å^3, T = 293(2) K, space group P_c, Z = 2, μ(Mo-Kα) = 0.229 mm^{-1}, 1367 reflections measured, 1367 unique (R_{int} = 0.0000) which were used in all calculations. The final $wR(F^2)$ was 0.1842 (all data). Absolute configuration not determined by X-ray determination, Flack parameter 0.26(25). CCDC 193940. See http://www.rsc.org/suppdata/p1/b2/b209079a/ for crystallographic files in CIF or other electronic format.

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References

1 V. A. Soloshonok, Enantiocontrolled Synthesis of Fluoro-Organic Compounds. Stereochemical Challenges and Biomedicinal Targets, Wiley, New York, 1999.
2 (*a*) W. Bockemüller, *Chem. Ber.*, 1931, **64B**, 522; (*b*) B. S. Garvey, Jr, L. F. Halley and C. F. H. Allen, *J. Am. Chem. Soc.*, 1937, **59**, 1827; (*c*) G. M. Badger and J. F. Stephens, *J. Chem. Soc.*, 1956, 3637; (*d*) J. Bornstein, M. R. Borden, F. Nunes and H. I. Tarlin, *J. Am. Chem. Soc.*, 1963, **85**, 1609; (*e*) A. Gregorčič and M. Zupan, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 517; (*f*) T. B. Patrick, J. J. Scheibel, W. E. Hall and Y. H. Lee, *J. Org. Chem.*, 1980, **45**, 4492; (*g*) T. Tsushima, K. Kawada and T. Tsuji, *Tetrahedron Lett.*, 1982, **23**, 1165.
3 J. J. Edmunds and W. B. Motherwell, *Chem. Commun.*, 1989, 1348.
4 W. B. Motherwell and J. A. Wilkinson, *Synlett*, 1991, 191.
5 S. Caddick, L. Gazzard, W. B. Motherwell and J. A. Wilkinson, *Tetrahedron*, 1996, **52**, 149.
6 M. J. Koen, F. Le Guyader and W. B. Motherwell, *Chem. Commun.*, 1995, 1241.
7 M. F. Greaney and W. B. Motherwell, *Tetrahedron Lett.*, 2000, **41**, 4463.
8 M. F. Greaney and W. B. Motherwell, *Tetrahedron Lett.*, 2000, **41**, 4467.

9 M. F. Greaney, W. B. Motherwell and D. A. Tocher, *Tetrahedron Lett.*, 2001, **42**, 8523.
10 M. Yoshida, D. Ota, T. Fukuhara, N. Yoneda and S. Hara, *J. Chem. Soc., Perkin Trans. 1*, 2002, 384 and references therein.
11 S. Hara, J. Nakahigashi, K. Ishi-i, T. Fukuhara and N. Yoneda, *Tetrahedron Lett.*, 1998, **39**, 2589.
12 S. Hara, J. Nakahigashi, K. Ishi-i, M. Sawaguchi, H. Sakai, T. Fukuhara and N. Yoneda, *Synlett*, 1998, 495.
13 M. Sawaguchi, S. Hara, T. Fukuhara and N. Yoneda, *J. Fluorine Chem.*, 2000, **104**, 277.
14 M. Sawaguchi, S. Hara and N. Yoneda, *J. Fluorine Chem.*, 2000, **105**, 313.
15 S. Hara, M. Sekiguchi, A. Ohmori, T. Fukuhara and N. Yoneda, *Chem. Commun.*, 1996, 1899.
16 T. Fuchigami, T. Fujita, S. Higashiya and A. Konno, *J. Chin. Chem. Soc.*, 1998, **45**, 131.
17 R. F. Weinland and W. Stille, *Chem. Ber.*, 1901, **34**, 2631.
18 (*a*) O. D. Dimroth and W. Bockemuller, *Ber.*, 1931, **64B**, 516; (*b*) D. Naumann and G. Rüther, *J. Fluorine Chem.*, 1980, **15**, 213; (*c*) N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 1963, 4103; (*d*) H. Schmidt and H. Meinert, *Angew. Chem.*, 1960, **72**, 109; (*e*) M. Sawaguchi, S. Ayuba and S. Hara, *Synthesis*, 2002, 1802.
19 W. Carpenter, *J. Org. Chem.*, 1966, **31**, 2688.
20 M. Hudlický, *Org. React.*, 1988, **35**, 513.
21 DAST: (*a*) J. R. McCarthy, N. P. Peet, M. E. LeTourneau and M. Inbasekaran, *J. Am. Chem. Soc.*, 1985, **107**, 735; (*b*) M. J. Robins and S. F. Wnuk, *J. Org. Chem.*, 1993, **58**, 3800; XeF_2: (*c*) M. J. Zupan, *J. Fluorine Chem.*, 1976, **8**, 305; (*d*) R. K. Marat and A. F. Janzen, *Can. J. Chem.*, 1977, **55**, 3031; $Bu_4NH_2F_3$: (*e*) S. Furuta, M. Kuroboshi and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2687; N-F reagents: (*f*) T. Umemoto and G. Tomizawa, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3625; $Et_3N{\cdot}n$HF: (*g*) T. Brigaud and E. Laurent, *Tetrahedron Lett.*, 1990, **31**, 2287; (*h*) T. Fuchigami, T. Higashiya, Y. Hou and K. M. Dawood, *Rev. Heteroatom Chem.*, 1999, **19**, 67 and references cited therein.
22 (*a*) J. R. Sufrin, A. J. Spiess, D. L. Kramer, P. R. Libby and C. W. Porter, *J. Med. Chem.*, 1989, **32**, 997; (*b*) D. Lesuisse, J.-F. Gourvest, O. Benslimane, F. Canu, C. Delaisi, B. Doucet, C. Hartmann, J.-M. Lefrançois, B. Tric, D. Mansuy, D. Philibert and G. Teutsch, *J. Med. Chem.*, 1996, **39**, 757; (*c*) S. F. Wnuk, C.-S. Yuan, R. T. Borchardt, J. Balzarini, E. De Clercq and M. J. Robins, *J. Med. Chem.*, 1997, **40**, 1608.
23 M. D. Vaughn, P. Cleve, V. Robinson, H. S. Duewel and J. F. Honek, *J. Am. Chem. Soc.*, 1999, **121**, 8475.
24 J. R. McCarthy, D. P. Matthews, M. L. Edwards, D. M. Stemerick and E. T. Jarvi, *Tetrahedron Lett.*, 1990, **31**, 5449 and references cited therein.
25 O. De Lucchi, U. Miotti and G. Modena, *Org. React.*, 1991, **40**, 157.
26 H. Monteiro and A. L. Gemal, *Synthesis*, 1975, 437.
27 A. Flores-Parra, D. M. Gutiérrez-Avella, Y. J. Guzmán-Vázquez, A. Ariza-Castolo and R. Contreras, *J. Org. Chem.*, 1992, **57**, 6067.
28 T. Masuda, T. Numata, N. Furukawa and S. Oae, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1302.
29 (*a*) T. B. Patrick, M. V. Lanahan, C. Yang, J. K. Walker, C. L. Hutchinson and B. E. Neal, *J. Org. Chem.*, 1994, **59**, 1210; (*b*) J. Kvícala, J. Plocar, R. Vlasáková, O. Paleta and A. Pelter, *Synlett*, 1997, 986.
30 G. J. Hollingworth, G. Perkins and J. Sweeney, *J. Chem. Soc., Perkin Trans. 1*, 1996, 1913.