Pergamon

Tetrahedron, Vol. 53, No. 43, pp. 14749-14762, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00986-1

A Rapid and Convenient Approach to Functionally Diverse Monofluorinated Vinylic Compounds

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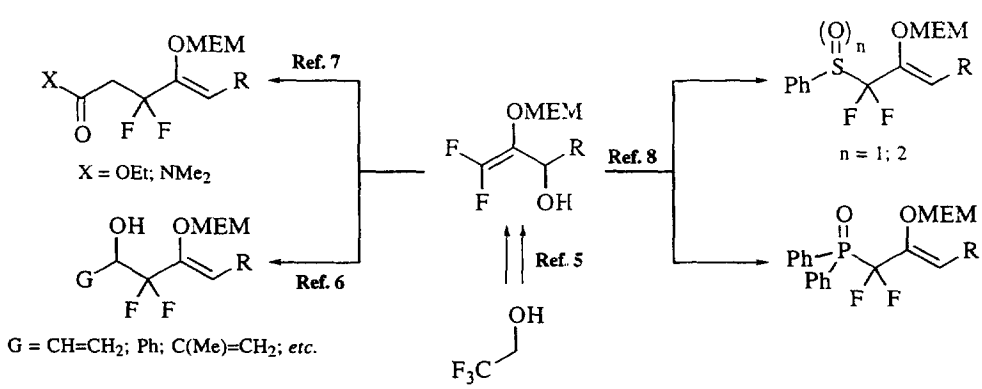
Abstract: Monofluorinated allylic ether **3**, synthesised in 4 steps from trifluoroethanol, underwent metallation at the CF vinylic position upon treatment with strong base. Monofluoro vinyllithium **4** was trapped efficiently with a variety of electrophiles, including Group (IV) halides, methyl iodide and benzaldehyde. Attempts to couple monofluoro vinyl stannane **5d** with aryl iodides and triflates under palladium catalysis proved only moderately successful. Conversion of **4** to the monofluoro vinylzinc reagent allowed access to monofluoro vinyl iodide **5e**, which was successfully coupled with a range of terminal alkynes. © 1997 Elsevier Science Ltd.

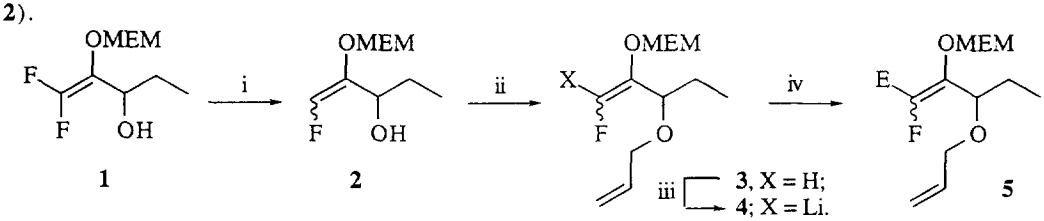
The ability of the fluorine atom to impart enhanced biological and therapeutic activity has led to widespread interest in the selective introduction of either one or two fluorine atoms into organic molecules. Traditionally, such fluorine introduction has involved the direct reaction of either inherent hydroxyl or carbonyl functionality with a fluorinating reagent. Both nucleophilic and electrophilic sources of fluorine have been widely described.[1] An alternative, more rational approach to highly functionalised fluorinated molecules involves the use of simple, easily-derived fluorine-containing *building blocks*.[2] A showcase example of the latter approach has been reported recently by Boger.[3] The synthesis of a CF_2 analogue of the potent Duocarmycin antitumour antibiotic was described: introduction of the CF_2 group was achieved using McCarthy's α-lithio phenyl difluoromethylsulfone building block chemistry.[4]



Scheme 1. Some functionally diverse CF_2-containing molecules available from trifluoroethanol.

Over the past few years, we have developed (**Scheme 1**) a similarly user-friendly approach to highly functionalised fluorinated species, based upon versatile and robust building blocks derived from trifluoroethanol.[5] Manipulation of difluoroallylic alcohols using classical organic reactions, such as sigmatropic rearrangements, has provided an efficient route into a range of functionality-rich difluoromethylene-containing molecules, including α,α-CF_2-alcohols,[6] β,β-CF_2-carbonyl derivatives,[7] α,α-CF_2-sulfoxides and sulfones[8] and α,α-CF_2-phosphine oxides.[8] Monofluorinated compounds have also found specific application in both the pharmaceutical and agrochemical industries, and, in spite of recent progress in the area, still represent a synthetic challenge.[9] Naturally, we sought to extend our methodology to the preparation of densely-functionalised monofluoro-derivatives, and herein we report in full our results to date in this area.[10]

Smooth stereoselective reduction of secondary difluoroallylic alcohol **1** was found to occur upon treatment with Red-Al (SMEAH) in either pentane or hexane.[7,11] A 9:1 *E*:*Z* mixture of monofluoroallylic alcohols **2** was isolated in 79% yield. Under the phase transfer catalysed conditions developed by Schlosser,[12] the mixture of stereoisomeric alcohols **2** was converted readily to the corresponding allylic ethers **3** in 83% yield, in which the 9:1 *E*:*Z* ratio of isomers was retained. It was envisaged that monofluoroallylic ether **3** would represent an ideal substrate for [2,3]-Wittig rearrangement; we had reported the [2,3]-Wittig rearrangement of analogous difluoroallylic ethers previously as a high yielding and general reaction.[6] However, upon treatment of **3** with strong base (either *n*-BuLi or LDA), deprotonation did not occur at the non-fluorinated allylic position to generate a stabilised carbanion capable of [2,3]-Wittig rearrangement. Instead, β-metallation at the vinylic *CF*-centre was found to occur to give fluoro vinyllithium **4**;[13] work-up with deuterated methanol resulted in the isolation of the β-deuterated compound **5a** in 89% yield (**Scheme 2**).



Scheme 2. Reagents and Conditions: i, Red-Al (3.8 eq.), pentane, reflux, 3 hours (*79%*); ii, $H_2C{=}CHCH_2Br$ (1.3 eq.), 50% aq. NaOH, Bu_4NHSO_4 (cat.), 0 °C to r.t., overnight (*83%*); iii, *n*-BuLi (or LDA) (2.0 eq.), THF, -78 °C; iv, electrophile, warm to r.t. overnight, then NH_4Cl(aq).

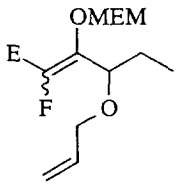
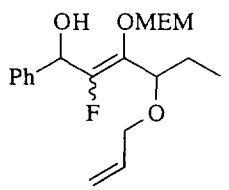
Monofluoro vinyllithium **4** was trapped subsequently with a range of electrophiles, as shown in **Table 1**. Group (IV) halides gave good to excellent yields of products. Methylation of **4** proved to be more problematic; all attempts to alkylate **4** at –78 °C were unsuccessful, even in the presence of a large excess of methyl iodide. However, upon allowing the vinyllithium species **4** to reach –50 °C, subsequent addition of ten equivalents of methyl iodide yielded **5f** in 57% yield. In all cases, separation of the major (*E*) and minor (*Z*) isomeric products of **5**, still present in the original 9:1 ratio established in the stereoselective reduction of

1, could be achieved by careful flash column chromatography of the products. Earlier in the synthetic sequence, separation of the stereoisomers of **2** or **3** proved less convenient.

Successful reaction of β-lithiomonofluoroenol acetal **4** with aldehyde electrophiles would yield formal (didehydro) [2,3]-Wittig rearrangement products, and this was investigated next. However, acceptable yields were only obtained with aromatic aldehydes such as benzaldehyde, in which case, a 1:1 mixture of diastereoisomeric alcohols **5g** were obtained in 83% yield.[14] Yields proved to be particularly poor (*ca.* 20%) for aliphatic aldehydes such as propanal and propenal.

Although the desired [2,3]-Wittig rearrangement of monofluoro allylic ether **3** had failed, due to the enhanced acidity of the vinylic proton, we rationalised that with this vinylic position blocked, as in derivatives **5**, the required allylic deprotonation would take place, leading to the possibility of sigmatropic rearrangement.

Table 1. Quenching **4** with electrophiles.

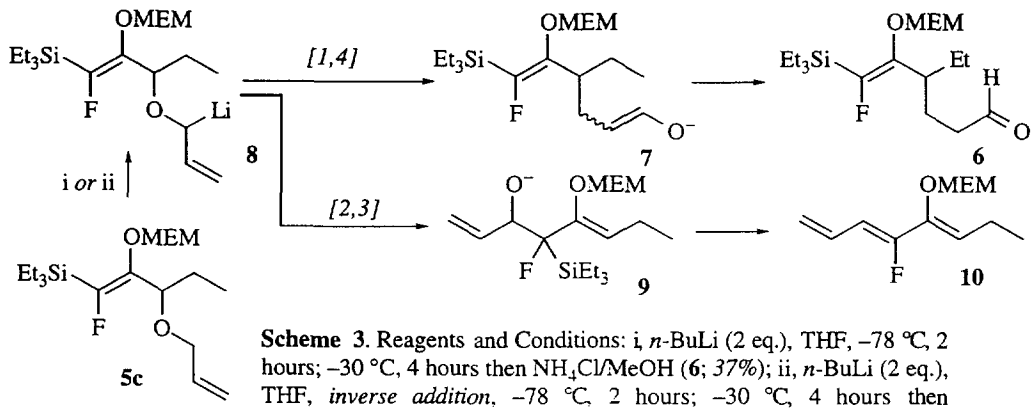
Electrophile	Product		E	% Yield
MeOD		**5a**	D	89
Me_3SiCl		**5b**	Me_3Si	71
Et_3SiCl		**5c**	Et_3Si	60
Bu_3SnCl		**5d**	Bu_3Sn	90
$ZnCl_2$.TMEDA, I_2[a]		**5e**	I	63
CH_3I[b]		**5f**	CH_3	57
Benzaldehyde		**5g**	–	83[c,d]

[a]Zinc salt added at -78 °C, then warmed to 0°C; iodine added then warm to r.t.. [b]Iodomethane (10 equivalents) added at -50 °C. [c]Isolated as a 1:1 mixture of diastereoisomers. [d]For the *E* alkene diastereoisomer.

To test this hypothesis, triethylsilyl derivative **5c** was treated with *n*-butyllithium (2 equivalents) at –78 °C in THF. However, after warming to –30 °C and subsequent work-up, the desired [2,3]-Wittig rearrangement product was not obtained; instead, aldehyde **6** was isolated in 37% yield. The formation of aldehyde **6** was thought to occur from protonation of enolate **7**, itself arising from formal [1,4]-rearrangement of the desired stabilised carbanion **8**. The propensity for such a [1,4]-rearrangement appeared to be related to the slow addition of the base to **5c** because the desired [2,3]-Wittig rearrangement of **5c**, also *via* carbanion **8**, was achieved upon inverse addition of **5c** to a THF solution of *n*-butyllithium (2 equivalents) at –78 °C. However, the immediate product of [2,3]-rearrangement could not be isolated, as under the reaction conditions, rapid Peterson olefination occurred (from **9**), to furnish triene **10** in 55% yield (**Scheme 3**). The ^{19}F NMR spectrum of **10** contained solely a doublet at –110.3 ppm, with a $^3J_{H\text{-}F}$ coupling constant

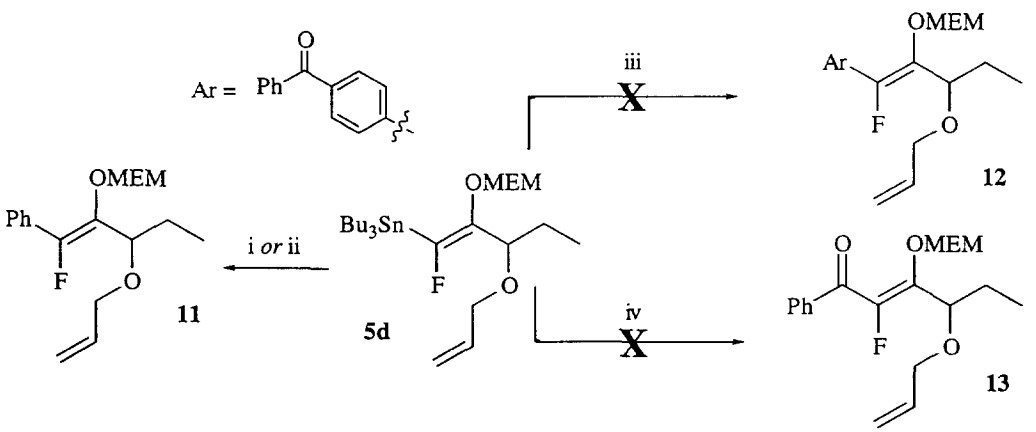
of 20.3 Hz (consistent with either *E* or *Z* configuration). Triene **10** proved to be particularly unstable, and decomposed rapidly, even at lower temperatures.

Vinyl iodide **5e** was prepared in moderate (37%) yield initially by the reaction of **4** with zinc bromide (as a freshly prepared 1M solution in THF) at –78 °C. Warming to 0 °C resulted (presumably) in formation of the vinylzinc species, which was quenched subsequently with a solution of iodine in THF.[5] An improved yield (63%) of **5e** was achieved upon use of non-hygroscopic zinc chloride/TMEDA complex in the transmetallation step.[15]



Scheme 3. Reagents and Conditions: i, *n*-BuLi (2 eq.), THF, –78 °C, 2 hours; –30 °C, 4 hours then NH_4Cl/MeOH (**6**; *37%*); ii, *n*-BuLi (2 eq.), THF, *inverse addition*, –78 °C, 2 hours; –30 °C, 4 hours then NH_4Cl/MeOH (**10**; *55%*).

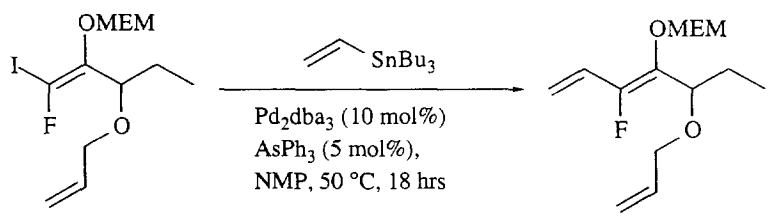
Again, iodide **5e** was obtained as a single fluoroenol diastereoisomer by normal flash column chromatography. It was envisaged that both stannane **5d** and iodide **5e** would prove useful precursors for the further elaboration of our monofluoro systems *via* palladium-catalysed coupling reactions.[16]



Scheme 4. Reagents and Conditions: i, PhI, $PdCl_2(PPh_3)_2$ (5 mol%), THF, Δ, 18 hrs (*20%*); ii, PhI, Pd_2dba_3 (2 mol%), $AsPh_3$ (4 mol%), NMP, r.t., 18 hrs (*40%*); iii, ArOTf, $PdCl_2(PPh_3)_2$ (2 mol%), LiCl (3 eq.), DMF, 60 *or* 100 °C; iv, PhCOCl, $PdCl_2(PPh_3)_2$ (5 mol%), 90 °C, sealed tube.

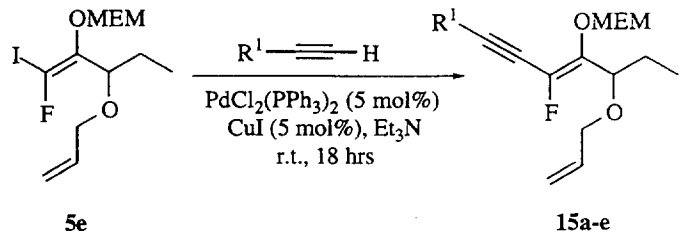
First, we investigated sp^2-sp^2 coupling reactions of *E*-monofluoro vinyl stannane **5d**. Conventional Stille coupling[17] of **5d** with iodobenzene produced the arylated product **11** in poor (20%) yield. Under the more reactive conditions described by Farina,[18] which use triphenylarsine for ligand exchange and *N*-methylpyrrolidinone (NMP) as solvent, an increased but still modest yield (*ca.* 40% by ^{19}F NMR) of **11** was obtained. Attempts to couple an aryl triflate[19] with **5d** to produce **12** proved unsuccessful using Stille conditions at both 60 and 100 °C (**Scheme 4**).Recently, McCarthy has described the high-yielding palladium-catalysed coupling of benzoyl chloride to (*E*)-tributyl-(1-fluoro-2-trimethylsilyl)vinyl stannane, a substrate, similar in structure to **5d**, though less highly functionalised.[20] However, the application of McCarthy's conditions to **5d** resulted in the formation of a complex reaction mixture from which the desired product **13** could not be isolated. Presumably the low reactivity of vinyl stannane **5d** arises from inductive electron withdrawing (*–I*) effects of both the α-fluorine atom and the β- and γ-oxygen functions lowering the nucleophilicity of the stannane. If the fluorinated coupling component was the electrophile instead of the nucleophile, the same *-I* effect might be expected to result in a *higher* level of reactivity. We therefore began to explore the chemistry of iodoalkene **5e**.

We anticipated that iodoalkene **5e** would be an extremely reactive substrate in sp^2-sp coupling reactions.[21] Of the possible methods for the coupling of alkynes with haloalkenes, the method used most frequently is the procedure pioneered by Sonogashira,[22] in which a terminal alkyne reacts with a haloalkene in the presence of a catalytic amount of a Pd(II) complex, copper(I) iodide and a tertiary amine.



5e **Scheme 5** **14**

As a direct precedent to our monofluoro system, Burton[23] has described the direct coupling of substituted fluorinated vinyl iodides with 1-alkynes in excellent yield though the examples reported have a low level of functionalisation and there are very few reports of exploitation of the method for the construction of interesting fluorinated molecules. Coupling of monofluoro vinyl iodide **5e** occurred with a range of terminal alkynes under Sonogashira conditions, including the low-cost ethyne equivalent 2-methyl-3-butyn-2-ol;[24] couplings proceeded in moderate to excellent yield[25] at room temperature (**Scheme 6**). These examples represent the first published couplings to *highly functionalised* fluoroalkenes and set the stage for the stereoselective synthesis of complex molecules containing a single fluorine atom. Towards such a goal, the examination of further transformations of the highly functionalised fluoroenynes **15a-e,** *via* alkyne manipulation and utilisation of the repertoire of asymmetric reactions based on allylic alcohols, is currently ongoing in our laboratories.



5e 15a-e

15	R^1	Yield/%
a	$H_3C(CH_2)_4$-	76
b	Ph-	75
c	Ph_3Si-	37
d	$HO(Me)_2C$-	51
e	HOH_2C-	42

Scheme 6. Sonogashira Couplings of Monofluoro vinyl iodide **5e**.

Acknowledgements

The authors wish to thank the EPSRC (Postdoctoral Fellowship to RDW) for financial support.

EXPERIMENTAL

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AC-300 (300.13 and 75.47 MHz respectively) and Bruker AMX-400 (400.14 and 100.6 MHz respectively) spectrometers. All spectra were recorded relative to tetramethylsilane as the internal standard. ^{19}F-NMR spectra were recorded on a Bruker AC-300 (282.41 MHz) spectrometer relative to chlorotrifluoromethane as the internal standard. ^{13}C NMR spectra were recorded using the pendant pulse sequence. Mass spectra were recorded on a Kratos MS-80 mass spectrometer with a DS-55 data system or a Kratos MS-580 RF mass spectrometer. Chemical ionisation (CI^+) methods used ammonia as the carrier gas. For TLC, precoated aluminium-backed silica gel plates were supplied by E. Merck, A.G. Darmstadt, Germany. (Silica gel 60 F_{254}, thickness 0.2 mm, Art. 5554). Anisaldehyde staining was employed for visualisation. Column chromatography was performed using silica gel (E. Merck A. G. Kieselgel 60, Art. 9385). Column fractions were collected and monitored by thin layer chromatography. Infra red spectra were obtained from a Perkin Elmer 1600 series FTIR spectrophotometer, in the region 4000-625 cm^{-1}. The samples were run as films.

Tetrahydrofuran was dried by refluxing with sodium metal and benzophenone under dry nitrogen, until a deep purple colour persisted. The solvent was then distilled and collected by syringe as required. *n*-Butyllithium was purchased from the Aldrich Chemical Company as a 2.5 M solution in hexanes. The molarity was determined immediately prior to use by titration against a THF solution of 1,3-diphenyl-2-propanone-*p*-toluenesulfonylhydrazone.[26] Chlorotrimethylsilane, chlorotriethylsilane and tributyltin chloride were purchased from the Aldrich Chemical Company and were distilled immediately prior to use. Methanol-*d*, methyl iodide and allyl bromide were also purchased from the Aldrich Chemical Company. Triethylamine was distilled over calcium hydride and stored over potassium hydroxide pellets. *N*-Methylpyrrolidinone was distilled over calcium hydride immediately prior to use. *bis*(Triphenylphosphino)palladium(II) chloride and *tris*(dibenzylideneacetone)dipalladium(0) were purchased from the Aldrich Chemical Company and were used as supplied and stored under argon. Copper(I) iodide was purified prior to use by recrystallisation from a saturated solution of sodium iodide.[27] 1-Heptyne, phenylacetylene, 2-methyl-3-butyn-2-ol, propargyl alcohol and vinyltributyltin were purchased from the Aldrich Chemical Company and were Kugelrohr distilled prior to use. Triphenylsilylacetylene, triphenylarsine and iodobenzene were purchased from the Aldrich Chemical Company and were used as supplied.

(*E*) and (*Z*)-3-(Allyloxy)-1-fluoro-2-([methoxyethoxy]methoxy)pent-1-ene (3).

A 9:1 mixture of (*E*) and (*Z*)-1-fluoro-3-hydroxy-2-([methoxyethoxy]methoxy)pent-1-ene **2** (6.00 g, 28.80 mmol), allyl bromide (3.24 mL, 37.50 mmol), 50% aqueous sodium hydroxide solution (*ca.* 80 mL) and

tetrabutylammonium hydrogen sulfate (0.49 g, 1.44 mmol) was stirred at 0 °C for 30 minutes. The mixture was allowed to warm to room temperature and stirred overnight. Saturated aqueous ammonium chloride solution (50 mL) was added, and the mixture was extracted with diethyl ether (4 x 100 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography, using 30% ethyl acetate/petroleum ether as eluant, gave **3**, which was isolated as a 9:1 *E*:*Z* mixture of isomers, as a pale yellow oil (5.95 g, 83%), (R_f 0.70): (Found: C, 57.77; H, 8.68. $C_{12}H_{21}FO_4$ requires C, 58.05; H, 8.52%); IR (film) 1750, 1687, 1647 and 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) (*major E isomer*) δ 0.87 (t, 3H, $^3J_{H-H}$ = 7.5 Hz), 1.52-1.82 (m, 2H), 3.35 (s, 3H), 3.52 (t, 2H, $^3J_{H-H}$ = 4.6 Hz), 3.63-3.72 (m, 2H), 3.82 (dd, 1H, $^3J_{H-H}$ = 12.0 Hz, $^2J_{H-H}$ = 5.5 Hz), 4.01 (dd, 1H, $^3J_{H-H}$ = 12.5 Hz, $^2J_{H-H}$ = 5.5 Hz), 4.23 (dt, 1H, $^4J_{H-F}$ = 3.8 Hz, $^3J_{H-H}$ = 7.5 Hz), 4.90 (s, 2H), 5.12 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.23 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.76-5.96 (m, 1H), 7.06 (d, 1H, $^2J_{H-F}$ = 81.0 Hz); (*minor Z isomer*) distinct signal at d 6.33 (d, 1H, $^2J_{H-F}$ = 78.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) (*major E isomer*) δ 9.9, 24.8, 59.0, 67.5, 69.6, 71.5, 73.9, 94.8, 116.9, 117.1, 134.7, 143.7 (d, $^2J_{C-F}$ = 25.1 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –171.9 (dd, $^4J_{H-F}$ = 3.4 Hz, $^2J_{H-F}$ = 81.0 Hz); (*minor Z isomer*) δ –155.6 (d, $^2J_{H-F}$ = 78.0 Hz); m/z (CI, NH_3) 266 (34%) ($[M+NH_4]^+$), 249 (6) ($[M+H]^+$), 229 (39), 153 (49), 94 (83), 89 (93), 44 (100).

Reactions of Monofluoro vinyllithium ***4***

In each case given below a 9:1 mixture of *E* and *Z* 3-(allyloxy)-1-fluoro-2-([methoxyethoxy]methoxy)pent-1-ene **3** was used as starting material. Examination of the ^{19}F NMR spectrum of the crude reaction mixture revealed a similar 9:1 *E*:*Z* ratio of products. In most cases the major (*E*) and minor (*Z*) isomers were separated. Yields given below refer to the combined yield of both isolated isomers, however except where stated, data refers to the major (*E*) isomer.

3-(Allyloxy)-1-fluoro-1-deutero-2-([methoxyethoxy]methoxy)pent-1-ene (5a).

n-Butyllithium (0.81 mL of a 2.0 M solution in hexanes, 1.61 mmol) was added slowly to a solution of 3-(allyloxy)-1-fluoro-2-([methoxyethoxy]methoxy)pent-1-ene **3** (0.20 g, 0.81 mmol) in THF (10 mL) at –78 °C. The resultant yellow solution was stirred at –78 °C for 30 minutes, after which time a solution of methanol-*d* (1 mL) was added, and the yellow colour faded. The solution was allowed to warm to room temperature overnight. Saturated aqueous ammonium chloride solution (10 mL) was added, and the mixture was extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography, using 20% ethyl acetate/petroleum ether as eluant, gave **5a** as a colourless oil (0.18 g, 89%), (R_f 0.31): IR (film) 1681, 1646 and 1457 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.87 (t, 3H, $^3J_{H-H}$ = 7.5 Hz), 1.52-1.81 (m, 2H), 3.35 (s, 3H), 3.52 (t, 2H, $^3J_{H-H}$ = 4.8 Hz), 3.63-3.76 (m, 2H), 3.82 (dd, 1H, $^3J_{H-H}$ = 6.3 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.01 (dd, 1H, $^3J_{H-H}$ = 5.1 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.23 (dt, 1H, $^4J_{H-F}$ = 3.7 Hz, $^3J_{H-H}$ = 7.4 Hz), 4.90 (s, 2H), 5.11 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.22 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.78-5.93 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.8, 24.8, 59.0, 67.4, 69.5, 71.5, 73.8, 94.8, 117.1, 134.7, 143.5 (d, $^2J_{C-F}$ = 25.4 Hz), DFC signal not observed; ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –172.4 (dt, $^4J_{H-F}$ = 2.5 Hz, $^2J_{D-F}$ = 12.7 Hz); (*minor Z isomer*) δ –156.2 (t, $^2J_{D-F}$ = 12.1 Hz); m/z (CI, NH_3) 267 (89%) ($[M+NH_4]^+$), 250 (15) ($[M+H]^+$), 230 (75), 89 (100), 59 (64), 44 (44); HRMS calcd. for $C_{12}H_{24}DFNO_4$ ($[M+NH_4]^+$) 267.18304, found 267.18357.

3-(Allyloxy)-1-fluoro-1-trimethylsilyl-2-([methoxyethoxy]methoxy)pent-1-ene (5b)

The silane was prepared as for **5a** except chlorotrimethylsilane was used as the electrophile. Standard work-up and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **5b** as a yellow oil (0.18 g, 71%), (R_f 0.49): IR (film) 2240, 1653 and 1459 cm^{-1}; ^1H NMR ($CDCl_3$, 300

MHz) δ 0.21 (s, 9H), 0.87 (t, 3H, $^3J_{H-H}$ = 7.5 Hz), 1.53-1.84 (m, 2H), 3.36 (s, 3H), 3.54 (t, 2H, $^3J_{H-H}$ = 4.7 Hz), 3.71-3.91 (m, 3H), 4.02 (dd, 1H, $^3J_{H-H}$ = 5.0 Hz, $^2J_{H-H}$ = 12.0 Hz), 4.32 (dt, 1H, $^4J_{H-F}$ = 4.5 Hz, $^3J_{H-H}$ = 7.5 Hz), 4.85 (d, 1H, $^2J_{H-H}$ = 5.0 Hz), 5.05 (d, 1H, $^2J_{H-H}$ = 5.0 Hz), 5.12 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.24 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.78-5.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ –1.8, 10.0, 25.2, 59.0, 68.8, 69.6, 71.7, 75.0, 97.9, 116.7, 134.8, 151.7 (d, $^2J_{C-F}$ = 25.8 Hz), 162.9 (d, $^1J_{C-F}$ = 269.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –149.5 (s); (*minor Z isomer*) d –136.7 (s); m/z (CI, NH_3) 338 (79%) ($[M+NH_4]^+$), 301 (97), 90 (100), 59 (24), 44 (43); HRMS calcd. for $C_{15}H_{33}FNO_4Si$ ($[M+NH_4]^+$) 338.21629, found 338.21581.

3-(Allyloxy)-1-fluoro-1-triethylsilyl-2-([methoxyethoxy]methoxy)pent-1-ene (5c)
The silane was prepared as for **5a** and on the same scale except chlorotriethylsilane was used as electrophile. Standard work-up and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **5c** as a yellow oil (0.18 g, 60%), (R_f 0.29): (Found: C, 59.74; H, 9.67. $C_{18}H_{35}FO_4Si$ requires C, 59.63; H, 9.73%); IR (film) 2249, 1647, 1636 and 1458 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.73 (q, 6H, $^3J_{H-H}$ = 7.6 Hz), 0.88 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 0.96 (t, 9H, $^3J_{H-H}$ = 7.6 Hz), 1.56-1.86 (m, 2H), 3.37 (s, 3H), 3.53 (t, 2H, $^3J_{H-H}$ = 4.8 Hz), 3.66-3.90 (m, 3H), 4.02 (dd, 1H, $^3J_{H-H}$ = 5.2 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.35 (dt, 1H, $^4J_{H-F}$ = 4.4 Hz, $^3J_{H-H}$ = 7.5 Hz), 4.84 (d, 1H, $^2J_{H-H}$ = 5.1 Hz), 5.06 (d, 1H, $^2J_{H-H}$ = 5.1 Hz), 5.12 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.24 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.79-5.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.7, 7.3, 10.0, 25.2, 59.0, 68.7, 69.5, 71.7, 75.0, 97.8, 116.8, 134.7, 152.6 (d, $^2J_{C-F}$ = 25.7 Hz), 161.7 (d, $^1J_{C-F}$ = 269.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –148.6 (s); (*minor Z isomer*) δ –137.2 (s); m/z (CI, NH_3) 380 (46%) ($[M+NH_4]^+$), 343 (63), 229 (97), 191 (65), 89 (100), 59 (55).

3-(Allyloxy)-1-fluoro-1-tributylstannyl-2-([methoxyethoxy]methoxy)pent-1-ene (5d)
The stannane was prepared as for **5a** and on the same scale except tributyltin chloride was used as electrophile. Standard work-up and purification by flash column chromatography, using 20% ethyl acetate/petroleum ether as eluant, gave **5d** as a pale yellow oil (0.39 g, 90%), (R_f 0.64): (Found: C, 53.39; H, 8.87. $C_{24}H_{47}FO_4Sn$ requires C, 53.65; H, 8.82%); IR (film) 1646, 1629 and 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 12H, $^3J_{H-H}$ = 7.2 Hz), 1.04 (t, 6H, $^3J_{H-H}$ = 8.0 Hz), 1.32 (sextet, 6H, $^3J_{H-H}$ = 7.2 Hz), 1.52 (q, 6H, $^3J_{H-H}$ = 8.0 Hz), 1.58-1.82 (m, 2H), 3.37 (s, 3H), 3.54 (t, 2H, $^3J_{H-H}$ = 4.7 Hz), 3.70-3.92 (m, 3H), 4.04 (dd, 1H, $^3J_{H-H}$ = 5.1 Hz, $^2J_{H-H}$ = 12.8 Hz), 4.34 (dt, 1H, $^4J_{H-F}$ = 5.1 Hz, $^3J_{H-H}$ = 12.8 Hz), 4.79 (d, 1H, $^2J_{H-H}$ = 5.0 Hz), 5.01 (d, 1H, $^2J_{H-H}$ = 5.0 Hz), 5.13 (dd, 1H, $^3J_{H-H(cis)}$ = 10.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.24 (dd, 1H, $^3J_{H-H(trans)}$ = 17.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.81-6.00 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.1, 10.2, 13.7, 25.1, 27.2, 29.0, 59.0, 68.6, 69.4, 71.7, 74.7, 98.2, 116.7, 134.9, 151.8 (d, $^2J_{C-F}$ = 18.6 Hz), 167.2 (d, $^1J_{C-F}$ = 309.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –138.4 (t, $^2J_{Sn-F}$ = 104.3 Hz); (*minor Z isomer*) δ –126.6 (s); m/z (CI, NH_3) 481 (32%) ([M-$CH_2CH_2CH_2CH_3$]$^+$), 291 (100), 229 (70), 153 (86), 89 (84), 44 (89).

3-(Allyloxy)-1-fluoro-1-iodo-2-([methoxyethoxy]methoxy)pent-1-ene (5e).
Method A:- n-Butyllithium (1.21 mL of a 2.0 M solution in hexanes, 2.42 mmol) was added slowly to a solution of 3-(allyloxy)-1-fluoro-2-([methoxyethoxy]methoxy)pent-1-ene **3** (0.30 g, 1.21 mmol) in THF (10 mL) at –78 °C. The resultant orange solution was stirred at –78 °C for 30 minutes, then a freshly prepared 1 M solution of zinc bromide in THF (1.33 mL, 1.33 mmol) was added. The orange colour faded, and the solution was allowed to warm to 0 °C slowly over 30 minutes. The solution was stirred for a further 1 hour at 0 °C, then a solution of iodine (0.34 g, 1.33 mmol) in THF (5 mL) was added, and the solution was allowed to warm to room temperature overnight. Saturated aqueous ammonium chloride solution (10 mL) was added,

and the mixture was extracted with diethyl ether (3 x 25 mL). The combined organic extracts were washed with 10% aqueous sodium sulfite solution (10 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **5e** as a colourless oil (0.17 g, 37%), (R_f 0.44): IR (film) 1645 and 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 1.57-1.83 (m, 2H), 3.38 (s, 3H), 3.57 (t, 2H, $^3J_{H-H}$ = 4.8 Hz), 3.78-3.90 (m, 2H), 3.91-4.02 (m, 1H), 4.06 (ddt, 1H, $^4J_{H-H}$ = 1.1 Hz, $^3J_{H-H}$ = 5.2 Hz, $^2J_{H-H}$ = 12.5 Hz), 4.31 (dt, 1H, $^4J_{H-F}$ = 4.3 Hz, $^3J_{H-H}$ = 7.4 Hz), 5.05 (d, 1H, $^2J_{H-H}$ = 5.5 Hz), 5.09 (d, 1H, $^2J_{H-H}$ = 5.5 Hz) 5.15 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.24 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.0 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.79-5.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.0, 25.5, 59.0, 69.4, 69.9, 71.7, 75.5, 97.1, 105.3 (d, $^1J_{C-F}$ = 321.6 Hz), 117.2, 134.3, 145.3 (d, $^2J_{C-F}$ = 27.1 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –103.5 (d, $^4J_{H-F}$ = 5.1 Hz); (*minor Z isomer*) δ –88.9 (d, $^4J_{H-F}$ = 2.5 Hz); m/z (CI, NH_3) 392 (100%) ($[M+NH_4]^+$), 375 (6) ($[M+H]^+$), 94 (40), 44 (52); HRMS calcd. for $C_{12}H_{24}FINO_4$ ($[M+NH4]^+$) 392.07341, found 392.07416.

Method B:- As for *Method A* except anhydrous zinc chloride-TMEDA complex[15] (0.33 g, 1.33 mmol) was added from a solid addition funnel in place of a freshly prepared 1 M solution of zinc bromide in THF. Work-up as described for *Method A* and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **5e** as a colourless oil (0.29 g, 63%): data as recorded above.

4-(Allyloxy)-2-fluoro-3-([methoxyethoxy]methoxy)hex-2-ene (5f).

n-Butyllithium (0.81 mL of a 2.0 M solution in hexanes, 1.61 mmol) was added slowly to a solution of 3-(allyloxy)-1-fluoro-2-([methoxyethoxy]methoxy)pent-1-ene **3** (0.20 g, 0.81 mmol) in THF (10 mL) at –78 °C. The resultant yellow solution was stirred at –78 °C for 30 minutes, then the solution was allowed to warm slowly to –50 °C. After stirring at –50 °C for 1 hour, methyl iodide (0.50 mL, 8.06 mmol) was added, and a fading of the yellow colour was observed. The solution was allowed to warm to room temperature overnight. Usual work-up and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **5f** as a colourless oil (0.12 g, 57%), (R_f 0.15): IR (film) 1701, 1647 and 1457 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.86 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 1.52-1.79 (m, 2H), 2.03 (d, 3H, $^3J_{H-F}$ = 17.8 Hz), 3.37 (s, 3H), 3.54 (t, 2H, $^3J_{H-H}$ = 4.8 Hz), 3.70-3.91 (m, 3H), 4.02 (dd, 1H, $^3J_{H-H}$ = 5.1 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.20 (dt, 1H, $^4J_{H-F}$ = 3.7 Hz, $^3J_{H-H}$ = 7.4 Hz), 4.92 (d, 1H, $^2J_{H-H}$ = 5.9 Hz), 4.95 (d, 1H, $^2J_{H-H}$ = 5.9 Hz), 5.12 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.23 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.79-5.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.1, 13.6, 25.1, 59.1, 68.7, 69.3, 71.7, 75.3, 97.8, 116.8, 134.8, 135.8 (d, $^2J_{C-F}$ = 35.6 Hz), 155.0 (d, $^1J_{C-F}$ = 244.4 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –126.8 (dq, $^4J_{H-F}$ = 5.1 Hz, $^3J_{H-F}$ = 17.8 Hz); m/z (CI, NH_3) 280 (57%) ($[M+NH_4]^+$), 243 (100), 222 (44), 89 (42), 59 (13), 44 (19); HRMS calcd. for $C_{13}H_{27}FNO_4$ ($[M+NH4]^+$) 280.19241, found 280.19321.

1-Phenyl-4-(allyloxy)-2-fluoro-3-([methoxyethoxy]methoxy)hex-2-en-1-ol (5g)

The alcohol was prepared as for **5a** except benzaldehyde was used as the electrophile. Standard work-up and purification by flash column chromatography, using 20% ethyl acetate/petroleum ether as eluant, gave **5g** as a separable 1:1 mixture of diastereoisomeric alcohols (combined yield 0.24 g, 83%).

Diastereoisomer 1 (R_f 0.18):- IR (film) 3422, 1647, 1604 and 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.85 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 1.56-1.83 (m, 2H), 3.40 (s, 3H), 3.58-3.63 (m, 2H), 3.66-3.73 (m, 1H), 3.86-4.01 (m, 2H), 4.14 (dd, 1H, $^3J_{H-H}$ = 5.1 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.20-4.50 (br. s, 1H, *-OH*), 4.22 (dt, 1H, $^4J_{H-H}$ = 3.7 Hz, $^3J_{H-H}$ = 7.4 Hz), 4.91 (dd, 1H, $^4J_{H-H}$ = 1.8 Hz, $^2J_{H-H}$ = 6.3 Hz), 5.14 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.2 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.24 (d, 1H, $^2J_{H-H}$ = 6.3 Hz), 5.26 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.81-5.95 (m, 1H), 5.95 (d, 1H, $^3J_{H-F}$ = 29.3 Hz),

7.21-7.37 (m, 3H), 7.40-7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.9, 25.0, 59.1, 66.0, 68.5, 69.6, 71.8, 75.4, 96.5, 117.1, 126.1, 127.4, 128.2, 134.6, 137.4 (d, $^2J_{C-F}$ = 34.2 Hz), 139.1, 157.9 (d, $^1J_{C-F}$ = 253.8 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −150.2 (d, $^3J_{H-F}$ = 29.3 Hz); m/z (CI, NH_3) 266 (16%) ([M+NH_4–PhCHOH]$^+$), 249 (100) ([M+H–PhCHOH]$^+$), 231 (17), 193 (28), 94 (38), 58 (25), 44 (20).
Diastereoisomer 2 (R_f 0.15):- IR (film) 3422, 1647, 1604 and 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.93 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 1.61-1.88 (m, 2H), 3.35 (s, 3H), 3.44 (br. s, 1H, *-OH*), 3.53 (t, 2H, $^3J_{H-H}$ = 7.4 Hz), 3.72-3.89 (m, 3H), 4.04 (ddt, 1H, $^4J_{H-H}$ = 2.6 Hz, $^3J_{H-H}$ = 5.2 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.25 (dt, 1H, $^4J_{H-H}$ = 4.4 Hz, $^3J_{H-H}$ = 7.3 Hz), 5.02 (dd, 1H, $^4J_{H-H}$ = 0.7 Hz, $^2J_{H-H}$ = 6.3 Hz), 5.13 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.20 (d, 1H, $^2J_{H-H}$ = 6.3 Hz), 5.26 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.80-5.95 (m, 1H), 5.91 (dd, 1H, $^3J_{H-F}$ = 27.6 Hz, $^3J_{H-H}$ = 5.5 Hz), 7.24-7.41 (m, 3H), 7.44-7.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.2, 26.3, 59.0, 67.5, 68.6, 69.9, 71.6, 75.4, 96.7, 117.2, 126.3, 127.7, 128.4, 134.5, 137.4 (d, $^2J_{C-F}$ = 34.2 Hz), 156.0 (d, $^1J_{C-F}$ = 250.8 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −150.5 (dd, $^4J_{H-F}$ = 3.8 Hz, $^3J_{H-F}$ = 27.6 Hz); m/z (CI, NH_3) 266 (7%) ([M+NH_4–PhCHOH]$^+$), 249 (100) ([M+H–PhCHOH]$^+$), 193 (15), 94 (22), 58 (44), 44 (44).

Attempted [2,3]-Wittig Rearrangement of **5c**

1-Fluoro-1-triethylsilyl-2-([methoxyethoxy]methoxy)-3-ethyl-hex-1-en-6-al (6).
n-Butyllithium (0.41 mL of a 2.0 M solution in hexanes, 0.83 mmol) was added dropwise to a solution of **5c** (0.15g, 0.41 mmol) in THF (5 mL) at −78 °C. The resultant orange solution was stirred at −78 °C for 2 hours, then warmed slowly to −30 °C. After stirring at −30 °C for 4 hours, the reaction was quenched with a saturated methanolic solution of ammonium chloride (10 mL). Usual work-up and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **6** as a colourless oil (0.055 g, 37%), (R_f 0.10): IR (film) 1726, 1634 and 1456 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.66 (q, 6H, $^3J_{H-H}$ = 8.0 Hz), 0.88 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 0.94 (t, 9H, $^3J_{H-H}$ = 8.0 Hz), 1.39-1.66 (m, 2H), 1.74-1.90 (m, 2H), 2.42 (t, 2H, $^3J_{H-H}$ = 7.5 Hz), 2.56-2.69 (m, 1H), 3.36 (s, 3H), 3.53 (t, 2H, $^3J_{H-H}$ = 4.6 Hz), 3.72-3.78 (m, 2H), 4.77 (s, 2H), 9.73 (t, 1H, $^3J_{H-H}$ = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 2.8, 7.3, 12.2, 24.2, 25.3, 40.5, 42.3, 59.1, 68.4, 71.6, 98.8, 158.8, 160.8 (d, $^1J_{C-F}$ = 241.5 Hz), 202.6; ^{19}F NMR ($CDCl_3$, 282 MHz) δ −149.4 (s); m/z (CI, NH_3) 380 (16%) ([M+NH_4]$^+$), 363 (7) ([M+H]$^+$), 257 (45), 89 (100), 59 (35), 44 (33); HRMS calcd. for $C_{18}H_{39}FNO_4Si$ ([M+NH_4]$^+$) 380.26324, found 380.26311.

4-Fluoro-5-([methoxyethoxy]methoxy)-octa-1,3,5-triene (10).
A solution of **5c** (0.15g, 0.41 mmol) in THF (2 mL) was added dropwise to a solution of *n*-butyllithium (0.41 mL of a 2.0 M solution in hexanes, 0.83 mmol) in THF (5 mL) at −78 °C. The resultant dark orange solution was stirred at −78 °C for 2 hours, and was then warmed slowly to −30 °C. After stirring at −30 °C for 4 hours, the reaction was quenched with a saturated methanolic solution of ammonium chloride (10 mL). Usual work-up and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **10** as a colourless oil (0.105 g, 55%), (R_f 0.35): IR (film) 1651, 1634, 1456 and 1337 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.03 (t, 3H, $^3J_{H-H}$ = 7.5 Hz), 2.26 (dq, 2H, $^3J_{H-H}$ = 7.5 Hz, $^3J_{H-H}$ = 2.2 Hz), 3.38 (s, 3H), 3.53-3.58 (m, 2H), 3.79-3.83 (m, 2H), 4.91 (s, 2H), 5.08 (d, 1H, $^3J_{H-H}$ = 10.3 Hz), 5.22 (d, 1H, $^3J_{H-H}$ = 16.2 Hz), 5.34 (t, 1H, $^3J_{H-H}$ = 7.5 Hz), 5.96 (dd, 1H, $^3J_{H-F}$ = 20.3 Hz, $^3J_{H-H}$ = 11.4 Hz), 6.61 (ddd, 1H, $^3J_{H-H}$ = 16.2 Hz, $^3J_{H-H}$ = 11.4 Hz, $^3J_{H-H}$ = 10.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.8, 18.8, 59.0, 68.6, 71.7, 95.2, 112.6 (d, $^2J_{C-F}$ = 27.9 Hz), 118.2 (d, $^3J_{C-F}$ = 9.3 Hz), 123.8, 130.4 (d, $^3J_{C-F}$ = 9.1 Hz), 142.6, 154.4 (d, $^1J_{C-F}$ = 248.5 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −110.3 (d, $^3J_{H-F}$ = 20.3 Hz); due to its instability, a satisfactory mass spectrum of **10** could not be obtained.

Palladium-catalysed couplings of stannane 5d

3-(Allyloxy)-1-fluoro-1-phenyl-2-([methoxyethoxy]methoxy)pent-1-ene (11).

3-(Allyloxy)-1-fluoro-1-tributylstannyl-2-([methoxyethoxy]methoxy)pent-1-ene **5d** (0.10 g, 0.19 mmol), iodobenzene (0.021 mL, 0.19 mmol) and *bis*(triphenylphosphine)palladium(II) chloride (5 mol%, 0.007 g, 0.009 mmol) were refluxed in THF (5 mL) overnight. The deep red solution was cooled to room temperature and concentrated *in vacuo*. Purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **11** as a pale yellow oil (0.012 g, 20%), (R_f 0.40): IR (film) 1666, 1649 and 1446 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.97 (t, 3H, $^3J_{H-H}$ = 7.4 Hz), 1.72-1.92 (m, 2H), 3.30 (s, 3H), 3.33-3.40 (m, 2H), 3.58-3.64 (m, 2H), 3.95 (dd, 1H, $^3J_{H-H}$ = 6.1 Hz, $^2J_{H-H}$ = 12.7 Hz), 4.15 (dd, 1H, $^3J_{H-H}$ = 5.2 Hz, $^2J_{H-H}$ = 12.9 Hz), 4.43 (dt, 1H, $^4J_{H-F}$ = 4.4 Hz, $^3J_{H-H}$ = 7.4 Hz), 4.98 (d, 1H, $^2J_{H-H}$ = 5.5 Hz), 5.04 (d, 1H, $^2J_{H-H}$ = 5.5 Hz), 5.18 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.30 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.86-6.03 (m, 1H), 7.28-7.42 (m, 3H), 7.73-7.80 (d, 2H, $^3J_{H-H}$ = 7.0 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –137.1 (s); m/z (CI, NH_3) 342 (72%) ($[M+NH_4]^+$), 284 (76), 264 (81), 247 (100), 188 (45), 94 (36); HRMS calcd. for $C_{18}H_{29}FNO_4$ ($[M+NH_4]^+$) 342.20806, found 342.20763.

Palladium-catalysed couplings of iodide 5e

5-(Allyloxy)-3-fluoro-4-([methoxyethoxy]methoxy)hept-1,3-diene (14).

Triphenylarsine (5 mol%, 0.004 g, 0.013 mmol) and *tris*(dibenzylideneacetone)dipalladium(0) (5 mol%, 0.012 g, 0.013 mmol) were added to a solution of 3-(allyloxy)-1-fluoro-1-iodo-2-([methoxyethoxy]methoxy)pent-1-ene **5e** (0.10 g, 0.27 mmol) and vinyltributyltin (0.086 mL, 0.29 mmol) in *N*-methylpyrrolidinone (NMP) (2 mL). The mixture became black in colour instantaneously. The solution was stirred at room temperature overnight. The resultant black solution was poured onto a 10% aqueous solution of hydrochloric acid (20 mL), and the aqueous layer extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **14** as a yellow oil (0.031 g, 42%), (R_f 0.27): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3H, $^3J_{H-H}$ = 7.5 Hz), 1.56-1.85 (m, 2H), 3.39 (s, 3H), 3.57 (t, 2H, $^3J_{H-H}$ = 4.8 Hz), 3.75-3.93 (m, 3H), 4.06 (dd, 1H, $^3J_{H-H}$ = 5.0 Hz, $^2J_{H-H}$ = 12.7 Hz), 4.29 (dt, 1H, $^4J_{H-F}$ = 3.7 Hz, $^3J_{H-H}$ = 7.4 Hz), 5.03 (s, 2H), 5.16 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(cis)}$ = 10.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.23 (dt, 1H, $^4J_{H-F}$ = 3.1 Hz, $^3J_{H-H(cis)}$ = 11.0 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.26 (dq, 1H, $^4J_{H-H}$ = 1.5 Hz, $^3J_{H-H(trans)}$ = 17.3 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.50 (dd, 1H, $^3J_{H-H(trans)}$ = 17.4 Hz, $^2J_{H-H}$ = 1.5 Hz), 5.82-5.96 (m, 1H), 6.67 (ddd, 1H, $^3J_{H-F}$ = 26.7 Hz, $^3J_{H-H(trans)}$ = 17.4 Hz, $^3J_{H-H(cis)}$ = 11.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.0, 25.4, 59.1, 68.9, 69.7, 71.7, 75.6, 97.9, 114.5, 117.0, 134.7, 143.4, 144.9, 153.5 (d, $^1J_{C-F}$ = 239.9 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ (*major E isomer*) d –149.9 (d, $^3J_{H-F}$ = 26.7 Hz); due to its instability a satisfactory mass spectrum of **14** could not be obtained.

10-(Allyloxy)-8-fluoro-9-([methoxyethoxy]methoxy)dodeca-8-en-6-yne (15a).

A solution of 3-(allyloxy)-1-fluoro-1-iodo-2-([methoxyethoxy] methoxy)pent-1-ene **5e** (0.075 g, 0.20 mmol) in triethylamine (2 mL) was added to a mixture of copper (I) iodide (5 mol%, 0.002 g, 0.01 mmol) and *bis*(triphenylphosphine)palladium(II) chloride (5 mol%, 0.007 g, 0.01 mmol) . 1-Heptyne (0.026 mL, 0.22 mmol) was added to the yellow solution, which instantaneously became dark green in colour. The mixture was stirred at room temperature overnight. The resultant black solution was poured onto a 10% aqueous solution of hydrochloric acid (20 mL), and the aqueous layer extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **15a** as a pale brown oil (0.052 g, 76%), (R_f 0.37): (Found: C, 66.51; H, 9.22. $C_{19}H_{31}FO_4$ requires C, 66.64; H, 9.12%); IR (film) 2222, 1655 and 1459 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, 6H, $^3J_{H-H}$ = 7.0 Hz), 1.24-1.44 (m, 4H), 1.52-1.62 (m, 2H), 1.62-1.81 (m, 2H), 2.41 (q, 2H, $^3J_{H-H}$ = 7.0 Hz, $^2J_{H-H}$ = 12.5 Hz), 3.39 (s, 3H),

3.57 (t, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz), 3.79-3.97 (m, 3H), 4.07 (dd, 1H, $^3J_{H\text{-}H}$ = 5.0 Hz, $^2J_{H\text{-}H}$ = 12.7 Hz), 4.26 (dt, 1H, $^4J_{H\text{-}F}$ = 3.7 Hz, $^3J_{H\text{-}H}$ = 7.4 Hz), 5.12 (d, 1H, $^2J_{H\text{-}H}$ = 5.7 Hz), 5.16 (d, 1H, $^3J_{H\text{-}H(cis)}$ = 10.3 Hz), 5.18 (d, 1H, $^2J_{H\text{-}H}$ = 5.7 Hz), 5.27 (d, 1H, $^3J_{H\text{-}H(trans)}$ = 17.4 Hz), 5.81-5.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.0, 13.9, 19.6, 22.2, 25.2, 27.9, 31.1, 59.0, 68.6, 69.7, 70.1, 71.7, 75.4, 96.9, 100.8, 117.1, 134.6, 138.3 (d, $^1J_{C\text{-}F}$ = 226.3 Hz), 145.2 (d, $^2J_{C\text{-}F}$ = 40.2 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ (*major E isomer*) d –136.2 (q, $^5J_{H\text{-}F}$ = 5.1 Hz, $^4J_{H\text{-}F}$ = 3.7 Hz); (*minor Z isomer*) δ –126.4 (q, $^5J_{H\text{-}F}$ = 5.1 Hz, $^4J_{H\text{-}F}$ = 3.7 Hz); m/z (CI, NH_3) 360 (98%) ($[M+NH_4]^+$), 323 (73), 285 (80), 265 (100), 209 (98), 89 (42), 59 (25), 44 (18).

5-(Allyloxy)-3-fluoro-1-phenyl-4-([methoxyethoxy]methoxy)hept-3-en-1-yne (15b)
The enyne was prepared as for **15a** except a solution of phenylacetylene (0.05 mL, 0.44 mmol) was used as the alkyne component. Usual work-up and purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **15b** as an orange oil (0.104 g, 75%), (R_f 0.19): (Found: C, 69.05; H, 7.08. $C_{20}H_{25}FO_4$ requires C, 68.95; H, 7.23%); IR (film) 2204, 1653, 1595 and 1457 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, 3H, $^3J_{H\text{-}H}$ = 7.5 Hz), 1.63-1.88 (m, 2H), 3.35 (s, 3H), 3.51-3.57 (m, 2H), 3.84-4.02 (m, 3H), 4.12 (dd, 1H, $^3J_{H\text{-}H}$ = 5.0 Hz, $^2J_{H\text{-}H}$ = 12.7 Hz), 4.34 (dt, 1H, $^4J_{H\text{-}F}$ = 3.7 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz), 5.18 (dq, 1H, $^4J_{H\text{-}H}$ = 1.5 Hz, $^3J_{H\text{-}H(cis)}$ = 10.3 Hz, $^2J_{H\text{-}H}$ = 1.5 Hz), 5.21 (d, 1H, $^2J_{H\text{-}H}$ = 5.9 Hz), 5.28 (d, 1H, $^2J_{H\text{-}H}$ = 5.9 Hz), 5.29 (dq, 1H, $^4J_{H\text{-}H}$ = 1.5 Hz, $^3J_{H\text{-}H(trans)}$ = 17.3 Hz, $^2J_{H\text{-}H}$ = 1.5 Hz), 5.84-5.98 (m, 1H), 7.30-7.39 (m, 3H), 7.42-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 10.0, 25.3, 59.0, 68.7, 69.9, 71.6, 75.5, 78.7 (d, $^2J_{C\text{-}F}$ = 38.0 Hz), 97.1, 98.6, 117.2, 121.6, 128.5, 129.3, 131.4, 134.5, 137.9 (d, $^1J_{C\text{-}F}$ = 225.9 Hz), 146.7 (d, $^2J_{C\text{-}F}$ = 38.9 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ (*major E isomer*) d –138.3 (s); (*minor Z isomer*) d –129.1 (s); m/z (CI, NH_3) 366 (53%) ($[M+NH_4]^+$), 291 (67), 271 (35), 215 (100), 89 (22), 59 (11).

5-(Allyloxy)-3-fluoro-1-triphenylsilyl-4-([methoxyethoxy]methoxy)hept-3-en-1-yne (15c)
The enyne was prepared as for **15a** except a solution of triphenylsilylacetylene (0.125 g, 0.44 mmol) in triethylamine (1 mL) was used as the alkyne component. After stirring at room temperature overnight, the resultant beige coloured solution was subjected to the usual work-up. Purification by flash column chromatography, using 10% ethyl acetate/petroleum ether as eluant, gave **15c** as an orange oil (0.08 g, 37%), (R_f 0.13): (Found: C, 71.35; H, 6.82. $C_{32}H_{35}FO_4Si$ requires C, 71.11; H, 6.96%); IR (film) 2149, 1645, 1589 and 1429 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.96 (t, 3H, $^3J_{H\text{-}H}$ = 7.5 Hz), 1.62-1.89 (m, 2H), 3.27 (s, 3H), 3.58 (t, 1H, $^3J_{H\text{-}H}$ = 4.6 Hz), 3.65-3.80 (m, 3H), 3.89 (dd, 1H, $^3J_{H\text{-}H}$ = 6.6 Hz, $^2J_{H\text{-}H}$ = 12.5 Hz), 4.13 (dd, 1H, $^3J_{H\text{-}H}$ = 5.2 Hz, $^2J_{H\text{-}H}$ = 12.5 Hz), 4.34 (dt, 1H, $^4J_{H\text{-}F}$ = 3.8 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz), 5.16-5.23 (m, 3H), 5.30 (dq, 1H, $^4J_{H\text{-}H}$ = 1.5 Hz, $^3J_{H\text{-}H(trans)}$ = 17.3 Hz, $^2J_{H\text{-}H}$ = 1.5 Hz), 5.84-5.99 (m, 1H), 7.36-7.51 (m, 9H), 7.62-7.70 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.9, 25.3, 58.7, 68.5, 69.9, 71.3, 75.3, 96.7, 97.4 (d, $^2J_{C\text{-}F}$ = 36.4 Hz), 100.6, 117.1, 128.0, 130.1, 132.2, 134.3, 135.5, 137.3 (d, $^1J_{C\text{-}F}$ = 225.5 Hz), 148.6 (d, $^2J_{C\text{-}F}$ = 37.9 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ (*major E isomer*) d –140.8 (s); (*minor Z isomer*) d –132.9 (s); m/z (CI, NH_3) 548 (100%) ($[M+NH_4]^+$), 531 (47) ($[M+H]^+$), 276 (61), 218 (54), 94 (35), 44 (19).

7-(Allyloxy)-5-fluoro-1-methyl-1-hydroxy-6-([methoxyethoxy]methoxy)non-5-en-3-yne (15d)
The enyne was prepared as for **15a** except 2-methyl-3-butyn-2-ol (0.043 mL, 0.44 mmol) was used as the alkyne component. Usual work-up and purification by flash column chromatography, using 30% ethyl acetate/petroleum ether as eluant, gave **15d** as a viscous off-white oil (0.068 g, 51%), (R_f 0.40): (Found: C, 61.72; H, 8.35. $C_{17}H_{27}FO_5$ requires C, 61.80; H, 8.24%); IR (Nujol mull) 3205, 2222, 1651 and 1463 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, 3H, $^3J_{H\text{-}H}$ = 7.5 Hz), 1.51 (s, 3H), 1.55 (s, 3H), 1.57-1.81 (m,

2H), 2.30 (br. s, 1H, *OH*), 3.39 (s, 3H), 3.60 (t, 2H, $^{3}J_{H-H}$ = 5.0 Hz), 3.76-3.89 (m, 2H), 3.99-4.10 (m, 2H), 4.26 (dt, 1H, $^{4}J_{H-F}$ = 3.8 Hz, $^{3}J_{H-H}$ = 7.4 Hz), 5.07 (d, 1H, $^{2}J_{H-H}$ = 5.9 Hz), 5.15 (dq, 1H, $^{4}J_{H-H}$ = 1.5 Hz, $^{3}J_{H-H(cis)}$ = 10.3 Hz, $^{2}J_{H-H}$ = 1.5 Hz), 5.18 (d, 1H, $^{2}J_{H-H}$ = 5.9 Hz), 5.25 (dq, 1H, $^{4}J_{H-H}$ = 1.5 Hz, $^{3}J_{H-H(trans)}$ = 17.3 Hz, $^{2}J_{H-H}$ = 1.5 Hz), 5.79-5.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.9, 25.2, 30.9, 31.1, 59.1, 65.1, 68.5, 69.8, 71.7, 75.4, 84.0, 97.1, 103.5, 117.3, 134.4, 137.8 (d, $^{1}J_{C-F}$ = 226.3 Hz), 146.0 (d, $^{2}J_{C-F}$ = 39.1 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) δ (*major E isomer*) d –137.8 (d, $^{4}J_{H-F}$ = 3.8 Hz); (*minor Z isomer*) d –129.5 (s); m/z (CI, NH_3) 348 (37%) ([M+NH_4]$^+$), 255 (21), 225 (33), 166 (43), 149 (55), 131 (100), 94 (17), 59 (9), 44 (9).

6-(Allyloxy)-4-fluoro-1-hydroxy-5-([methoxyethoxy]methoxy)oct-4-en-2-yne (15e)
The enyne was prepared as for **15a** except propargyl alcohol (0.015 mL, 0.25 mmol) was used as the alkyne component. Usual work-up and purification by flash column chromatography, using 30% ethyl acetate/petroleum ether as eluant, gave **15e** as a colourless oil (0.029 g, 42%), (R_f 0.24): IR (Nujol mull) 3416, 2214, 1651 and 1456 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (t, 3H, $^{3}J_{H-H}$ = 7.5 Hz), 1.60-1.84 (m, 2H), 3.00 (t, 1H, *OH*, $^{3}J_{H-H}$ = 5.7 Hz), 3.42 (s, 3H), 3.63 (t, 2H, $^{3}J_{H-H}$ = 5.1 Hz), 3.75-3.91 (m, 2H), 4.02-4.12 (m, 2H), 4.28 (dt, 1H, $^{4}J_{H-F}$ = 3.7 Hz, $^{3}J_{H-H}$ = 7.4 Hz), 4.45 (t, 2H, $^{5}J_{H-F}$ = 3.7 Hz, $^{3}J_{H-H}$ = 5.7 Hz), 5.07 (d, 1H, $^{2}J_{H-H}$ = 6.3 Hz), 5.17 (dq, 1H, $^{4}J_{H-H}$ = 1.5 Hz, $^{3}J_{H-H(cis)}$ = 10.3 Hz, $^{2}J_{H-H}$ = 1.5 Hz), 5.20 (d, 1H, $^{2}J_{H-H}$ = 6.3 Hz), 5.27 (dq, 1H, $^{4}J_{H-H}$ = 1.5 Hz, $^{3}J_{H-H(trans)}$ = 17.3 Hz, $^{2}J_{H-H}$ = 1.5 Hz), 5.81-5.96 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.9, 25.3, 51.2, 59.2, 68.7, 69.9, 71.7, 74.9, 75.5, 97.3, 97.3, 117.4, 134.4, 137.9 (d, $^{1}J_{C-F}$ = 226.6 Hz), 146.7 (d, $^{2}J_{C-F}$ = 37.9 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz) (*major E isomer*) δ –138.1 (q, $^{5}J_{H-F}$ = 5.1 Hz, $^{4}J_{H-F}$ = 3.7 Hz); m/z (CI, NH_3) 320 (100%) ([M+NH_4]$^+$), 215 (15), 122 (14), 94 (39), 59 (11), 44 (12); HRMS calcd. for $C_{15}H_{27}FNO_5$ ([M+NH_4]$^+$) 320.18733, found 320.18793.

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(*Received in UK* 21 *July* 1997; *revised* 19 *August* 1997; *accepted* 21 *August* 1997)