Novel Synthesis of 2,2,2-Trifluoroethyl Compounds from Homoallylic Alcohols: A Copper(I) Iodide-initiated Trifluoromethyl–Dehydroxylation Process

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Benzyl, prop-2-ynyl and allyl chlorodifluoroacetates **3a**, bromodifluoroacetates **3b** or fluorosulfonyldifluoroacetates **3c**, when decomposed in the presence of 1 equivalent of copper(I) iodide at an appropriate temperature in dimethylformamide, gave the corresponding trifluoromethyl derivatives in good to excellent yields. The products can also be obtained directly by ester exchange of XCF_2CO_2Et (X = FSO_2, Cl, Br) **6** and the corresponding alcohols in the presence of KF and CuI. A trifluoromethylation–dehydroxylation mechanism, initiated by CuI, is proposed.

The unique properties of the trifluoromethyl group,[1] e.g. high electronegativity,[2] stability[3] and lipophilicity,[4] have ensured it an increasingly important role in organic synthesis.[5-7] Although many methods have been reported for the synthesis of trifluoromethyl compounds, most of them are based on the replacement of the halogen atom of alkyl (or aryl) halides by the CF_3 group.[8] Carboxy[9] and amino[10] groups apart few reports for the conversion of other groups (e.g. hydroxy) into CF_3 have appeared. Thus, the displacement of OH by CF_3 in benzyl alcohols with CF_2Br_2–Cu–DMF,[11] gives low yields of products. In our previous study on the trifluoromethylation of organic halides with methyl halogenodifluoroacetates[12] and fluorosulfonyldifluoroacetate[13] in the presence of potassium fluoride and copper(I) iodide, we proposed that the reaction occurred by initial attack of iodide ion on the methyl carbon of the methyl esters to yield methyl iodide. Thus, we envisaged that the hydroxy groups in the benzyl and allyl alcohols might be displaced by trifluoromethyl groups via the corresponding esters **3** (XCF_2CO_2R, X = Cl **a**, Br **b**, FSO_2 **c**, R = benzyl, allyl) in good yields. Here we describe these results in detail.

Results and Discussion

Benzyl and allyl esters (XCF_2CO_2R, X = Cl **a**, Br **b**, FSO_2 **c**, R = benzyl, allyl) **3** were found to be easily prepared from the corresponding acid fluorides and alcohols. For example, chlorodifluoroacetyl **1a**, bromodifluoroacetyl **1b**, fluorosulfonyldifluoroacetyl **1c** fluorides, prepared by treatment of $ClCF_2CF_2I$ (for **1a**),[14] $BrCF_2CFClBr$ (for **1b**)[14] and $CF_2=CF_2$ (for **1c**)[15] with SO_3 at appropriate temperatures, reacted with various benzyl alcohols smoothly in CH_2Cl_2 in the presence of pyridine to give the esters **3** in high yields (Scheme 1). The

$$XCF_2COF + ROH + Py \longrightarrow XCF_2CO_2R + Py \cdot HF$$
$$\quad\quad 1 \quad\quad\quad 2 \quad\quad\quad\quad\quad\quad\quad 3$$
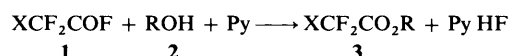
X		ROH		
1a	Cl	**a**	$PhCH_2OH$	
1b	Br	**b**	$p\text{-}ClC_6H_4CH_2OH$	
1c	FSO_2	**c**	$m\text{-}ClC_6H_4CH_2OH$	
		d	$o\text{-}Cl\text{-}C_6H_4CH_2OH$	
		e	$p\text{-}MeC_6H_4CH_2OH$	
		f	$m\text{-}MeC_6H_4CH_2OH$	

g	$m\text{-}NO_2C_6H_4CH_2OH$	
h	$p\text{-}NO_2C_6H_4CH_2OH$	
i	$CH_2=CHCH_2OH$	
j	$PhCH=CHCH_2OH$	
k	$CH\equiv CCH_2OH$	
l	$p\text{-}BrC_6H_4CH_2OH$	

Scheme 1

results are listed in Table 1. For p- and m-methylbenzyl alcohols (**2e** and **2f**) it was necessary to employ a lower reaction temperature ($-10\,°C$), as it was for allyl alcohols **2i** and **2j** ($-20\,°C$).

Table 1 Reaction of the alcohol 2 with 1 [2:1 = 1:1 (molar ratio)] in CH_2Cl_2 in the presence of pyridine for 20 min
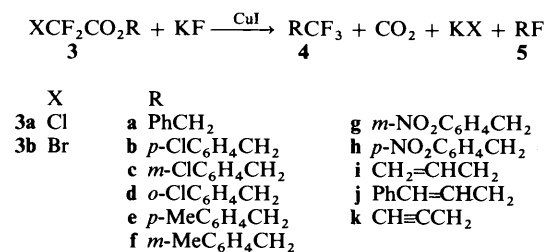
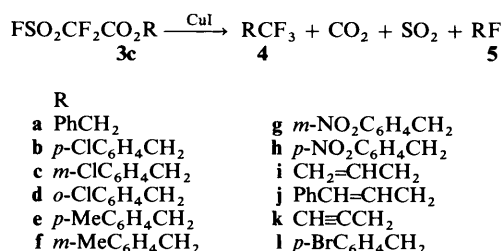| Entry	1	2	$T/°C$	Yield 3(%)^a
1	**1a**	**2a**	0–10	91
2	**1a**	**2b**	0–10	93
3	**1a**	**2c**	0–10	92
4	**1a**	**2d**	0–10	94
5	**1a**	**2e**	−10	88
6	**1a**	**2f**	−10	93
7	**1a**	**2g**	0–10	83
8	**1a**	**2h**	0–10	77
9	**1a**	**2i**	−20	73
10	**1a**	**2j**	−20	74
11	**1a**	**2k**	0–10	88
12	**1b**	**2a**	0–10	94
13	**1b**	**2b**	0–10	92
14	**1b**	**2c**	0–10	95
15	**1b**	**2d**	0–10	93
16	**1b**	**2e**	−10	94
17	**1b**	**2f**	−10	92
18	**1b**	**2g**	0–10	82
19	**1b**	**2h**	0–10	79
20	**1b**	**2i**	−20	75
21	**1b**	**2j**	−20	77
22	**1c**	**2a**	0–10	87
23	**1c**	**2b**	0–10	85
24	**1c**	**2c**	0–10	83
25	**1c**	**2d**	0–10	78
26	**1c**	**2e**	−10	83
27	**1c**	**2f**	−10	75
28	**1c**	**2g**	0–10	73
29	**1c**	**2h**	0–10	75
30	**1c**	**2i**	−20	74
31	**1c**	**2j**	−20	76
32	**1c**	**2l**	0–10	82

^{a} Isolated yield based on 2.

Unlike the reaction of saturated alcohols with **1c**,[15] unless 1 equivalent of pyridine was present to neutralize the hydrogen fluoride produced, unidentified white solids were obtained.

Treatment of the esters **3a** and **3b** with copper(I) iodide in the presence of anhydrous potassium fluoride in N,N-dimethylformamide (DMF) at 75–110 °C for 4–12 h gave upon work-up, the corresponding trifluoromethylated compounds in good yields together with a little alkyl fluoride RF (Scheme 2). The results are listed in Table 2.

Treatment of the ester **3c** with copper(I) iodide in DMF at 50–70 °C for 4–9 h, afforded the corresponding trifluoromethylated compounds **4** in good yields (Scheme 3, Table 3) together with a little (typically 0–3%) alkyl fluoride.

$$XCF_2CO_2R + KF \xrightarrow{CuI} RCF_3 + CO_2 + KX + RF$$
$$3\phantom{+ KF \xrightarrow{CuI} R} 4 5$$

	X		R		
3a	Cl	a	$PhCH_2$	g	$m\text{-}NO_2C_6H_4CH_2$
3b	Br	b	$p\text{-}ClC_6H_4CH_2$	h	$p\text{-}NO_2C_6H_4CH_2$
		c	$m\text{-}ClC_6H_4CH_2$	i	$CH_2\text{=}CHCH_2$
		d	$o\text{-}ClC_6H_4CH_2$	j	$PhCH\text{=}CHCH_2$
		e	$p\text{-}MeC_6H_4CH_2$	k	$CH\text{≡}CCH_2$
		f	$m\text{-}MeC_6H_4CH_2$		

Scheme 2

$$FSO_2CF_2CO_2R \xrightarrow{CuI} RCF_3 + CO_2 + SO_2 + RF$$
$$3c \phantom{\xrightarrow{CuI} R} 4 5$$

	R		
a	$PhCH_2$	g	$m\text{-}NO_2C_6H_4CH_2$
b	$p\text{-}ClC_6H_4CH_2$	h	$p\text{-}NO_2C_6H_4CH_2$
c	$m\text{-}ClC_6H_4CH_2$	i	$CH_2\text{=}CHCH_2$
d	$o\text{-}ClC_6H_4CH_2$	j	$PhCH\text{=}CHCH_2$
e	$p\text{-}MeC_6H_4CH_2$	k	$CH\text{≡}CCH_2$
f	$m\text{-}MeC_6H_4CH_2$	l	$p\text{-}BrC_6H_4CH_2$

Scheme 3

Table 2 Reaction of **3a** and **3b** with potassium fluoride in the presence of copper(I) iodide (3:KF:CuI = 1:1:1) in DMF

Entry	3	t/h	$T/°C$	Yield 4(%)[a]	Yield 5(%)[a]
1	3aa	10	100	59	4
2	3ab	10	100	62[b]	4
3	3ac	10	100	53[b]	4
4	3ad	12	100	48[b]	4
5	3ae	10	100	65	3
6	3af	10	100	68	3
7	3ag	12	110	47	6
8	3ah	12	110	51	4
9	3ai	5	100	78	2[c]
10	3aj	5	100	81[d]	2[c]
11	3ak	4	100	71[e]	3[c]
12	3ba	8	80	68	2[c]
13	3bb	8	80	64[b]	4[c]
14	3bc	8	80	65[b]	3[c]
15	3bd	10	80	58[b]	2[c]
16	3be	7	80	71	4[c]
17	3bf	8	80	69	3[c]
18	3bg	8	85	58	4[c]
19	3bh	9	85	53	4[c]
20	3bi	8	70	89	0
21	3bj	4	70	87[d]	2[c]
22	3aa	10	100	0[f]	12[c]

[a] Isolated yields based on **3**. [b] Only monotrifluoromethylated product was obtained. [c] Determined by ^{19}F NMR based on **3**. [d] Only PhCH=CHCH$_2$CF$_3$ was isolated. [e] Only CH$_2$=C=CHCF$_3$ was isolated. [f] In the absence of copper iodide.

Table 3 Reaction of **3c** in the presence of copper(I) iodide [3c:CuI = 1:1 (molar ratio)] in DMF

Entry	3	t/h	$T/°C$	Yield 4(%)[a]
1	3ca	7	60	71
2	3cb	8	60	75[b]
3	3cc	8	60	69[b]
4	3cd	9	65	63[b]
5	3ce	6	60	75
6	3cf	6	60	73
7	3cg	7	70	60
8	3ch	8	70	58
9	3ci	4	50	85
10	3cj	4	50	90[c]
11	3cl	8	70	72[b]
12	3ca	7	60	0[d]

[a] Isolated yields based on **3c**, in addition a small amount of **5** was formed. [b] Only monotrifluoromethylated product was obtained. [c] Only PhCH=CHCH$_2$CF$_3$ was detected. [d] In the absence of CuI.

As expected, only monotrifluoromethylated products were obtained when chloro- and bromo-benzyl esters **3** were used, since chlorine and bromine were inert to the reaction conditions (entries 2, 3, 4, 12, 13 and 14 in Table 2 and entries 2, 3 and 4 in Table 3). Cinnamyl esters **3aj**, **3bj** and **3cj** underwent CuI-initiated decomposition to give the normal trifluoromethyl-dehydroxylated products, whereas the prop-2-ynyl ester **3k** afforded a rearranged product CH$_2$=C=CHCF$_3$[17] (entry 11 in Table 2).

The data in Tables 2 and 3 indicate that allylic esters were more reactive and, consequently, gave higher yields of product than benzyl esters. For example, cinnamyl bromodifluoro-acetate gave the corresponding trifluoromethylated product in 87% yield in 4 h, whilst the benzyl ester, under similar conditions, afforded 2,2,2-trifluoroethylbenzene in only 68% yield after 8 h (entries 21 and 12 in Table 2). Such results demonstrate that steric hindrance influenced the reactivity of the substrates. For example, 2-chlorobenzyl esters, **3ad**, **3bd** and **3cd**, decomposed more slowly than 4-chlorobenzyl esters, **3ab**, **3bb** and **3cb**, affording lower yields of product (entries 2, 4, 13 and 15 in Table 2 and entries 2 and 4 in Table 3).

We propose a mechanism similar to that reported earlier for the trifluoromethylation of organic halides with methyl esters (XCF$_2$CO$_2$Me).[12,13] Thus, initially, copper(I) iodide attack on the ester yields alkyl iodide and XCF$_2$CO$_2$Cu, although since no HCF$_2$X was detected, the carbanion XCF$_2$⁻ may not be produced but, rather, the copper salt formed may decompose in a concerted manner to give difluorocarbene; this then combines with the fluoride ion added (for **3a** and **b**) or generated in situ (for **3c**) to form the trifluoromethide ion. In the presence of copper(I) iodide, the equilibrium readily shifts to the right forming trifluoromethylcopper or its complex, which then reacts with the alkyl iodide formed initially to afford the final product, Scheme 4.

$$XCF_2CO_2R + CuI \longrightarrow RI + XCF_2CO_2Cu$$

$$XCF_2CO_2Cu \longrightarrow X^- \text{ (or } F^- + SO_2) + CO_2 + CF_2:$$

$$CF_2: + F^- \rightleftharpoons CF_3^-$$

$$CF_3^- + CuI \longrightarrow CF_3Cu \text{ (or } CF_3CuI^-)$$

$$CF_3Cu \text{ (or } CF_3CuI^-) + RI \longrightarrow RCF_3 + CuI + I^-$$

Scheme 4

Although the fluoride ion could be generated from di-fluorocarbene and DMF[16] in the case of **3a** and **3b**, the presence of potassium fluoride was necessary in order to obtain higher yields of the products; in its absence only very low yields (e.g. 10% for **3ba**) of the trifluoromethylated derivatives were obtained. For **3c**, the addition of potassium fluoride had no influence on the yields. As evidenced by the lack of reaction when hexamethylphosphoric triamide (HMPA) replaced DMF, the solvent employed also played an important role in the reaction.

The gases evolved from the reaction mixture were identified as CO$_2$, SO$_2$ (for FSO$_2$CF$_2$CO$_2$R) and a small amount of HCF$_3$ by GC–MS. Also benzyl and allylic fluoride **5** (0–10%) were separated. No XCF$_2$H[X = Cl (for **3a**), Br (for **3b**), and FSO$_2$ (for **3c**)] were detected.

The steric effect may be explained in terms hindrance by the ortho substituent on decomposition of **3** in the first step.

Table 4 Reaction of **2** with **6** in the presence of KF and CuI in DMF
(2:6 = 1:2)

Entry	2	6	Time (h)	$T/^\circ C$	Yield 4(%)^a
1	2a	6a	10	100	43
2	2i	6a	6	100	71
3	2j	6a	7	100	64
4^b	2l	6a	10	100	40
5	2a	6b	8	90	39
6	2j	6b	10	90	72
7	2a	6c	9	70	47
8	2j	6c	7	65	63

^{a} Isolated yield based on **2**. ^{b} Only p-$BrC_6H_4CH_2CF_3$ was obtained.

The formation of RF as a by-product may result from nucleophilic attack of the fluoride ion on the esters:

$$XCF_2CO_2R + F^- \longrightarrow RF + CO_2 + CF_2: + X^-$$
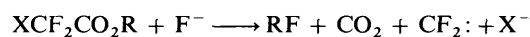
Based on the mechanism proposed, it seemed possible that in the presence of some base catalysts ester exchange could take place *in situ* and hence a direct displacement of the hydroxy groups in benzyl and allylic alcohols by the trifluoromethyl moiety would occur. Interestingly, it was found that potassium fluoride serves well the dual purpose of being a base catalyst and a fluoride ion source in the reaction. Ethyl halogeno- and fluorosulfonyl-difluoroacetates (XCF_2CO_2Et, X = FSO_2, Br, Cl) **6*** were found to be suitable for the ester exchange.

Treatment of benzyl and allyl alcohols with **6** in the presence of potassium fluoride and copper(ı) iodide in DMF at appropriate temperatures for 6–10 h gave the corresponding trifluoromethylated products in moderate to good yields (Scheme 5), although slightly lower than those by the indirect methods mentioned above. The results are listed in Table 4.

$$ROH + XCF_2CO_2Et + KF \xrightarrow{CuI} RCF_3 + CO_2 + EtOH$$
$$\quad 2 \qquad\qquad 6 \qquad\qquad\qquad 4$$

	R		X
2a	$PhCH_2$	6a	Cl
2i	$CH_2=CHCH_2$	6b	Br
2j	$PhCH=CHCH_2$	6c	FSO_2
2l	4-$BrC_6H_4CH_2$		
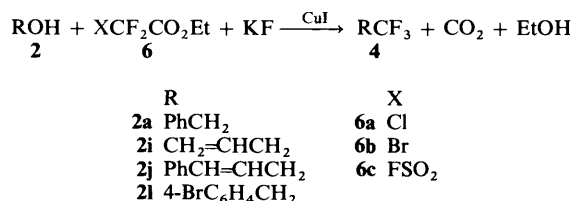
Scheme 5

The presence of potassium fluoride was essential to the reaction since in its absence ester exchange failed to occur, although **6** decomposed completely during 5–10 h; the expected products were not, however, detected. Copper(ı) iodide also played an important role in the reaction. Although ester exchange was detected without CuI (by TLC), no decarboxylation of the ester formed took place.
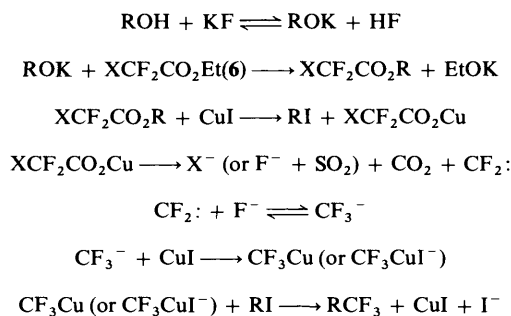
The formation of **3** *via* ester exchange may be ascribed to nucleophilic attack on the ethyl ester **6** by RO^- which results from the interaction of KF with the alcohols (Scheme 6). The benzyl, allyl and prop-2-ynyl esters **3** then decomposed in the presence of copper(ı) iodide to give the final products following the mechanism described earlier.

Possibly, because of incomplete ester exchange, the yields of the 'one-pot' reaction are not as high as those of the indirect procedure.

Experimental

All b.p.s are uncorrected. IR spectra were obtained on a Shimadzu—440 model instrument as KBr pellets for solid

* Use of methyl esters gave the methyl alkyl ethers as the main products.

$$ROH + KF \rightleftharpoons ROK + HF$$

$$ROK + XCF_2CO_2Et(6) \longrightarrow XCF_2CO_2R + EtOK$$

$$XCF_2CO_2R + CuI \longrightarrow RI + XCF_2CO_2Cu$$

$$XCF_2CO_2Cu \longrightarrow X^- (or\ F^- + SO_2) + CO_2 + CF_2:$$

$$CF_2: + F^- \rightleftharpoons CF_3^-$$

$$CF_3^- + CuI \longrightarrow CF_3Cu\ (or\ CF_3CuI^-)$$

$$CF_3Cu\ (or\ CF_3CuI^-) + RI \longrightarrow RCF_3 + CuI + I^-$$

Scheme 6

samples and as films for liquid samples. ^1H NMR spectra were obtained on EM-360A (60 MHz) and XL-200 (200 MHz) NMR spectrometers. [^2H]Chloroform was used as solvent with tetramethylsilane as external reference. ^{19}F NMR spectra were obtained on an EM-360L (60 MHz) NMR spectrometer with $CFCl_3$ as external reference and chemical shifts in ppm were positive upfield. *J* Values are given in Hz. Mass spectra were recorded with a GC-MS-4021 mass spectrometer. Silica gel (40 μm) was used for column chromatography. All reagents were purified prior to use. CH_2Cl_2 was dried with molecular sieves and DMF with CaH_2.

Fluorosulfonyldifluoroacetyl fluoride was prepared according to ref. 15; bromodifluoroacetyl fluoride and chlorodifluoroacetyl fluoride were synthesized according to ref. 14. The ethyl esters **6** were prepared based on ref. 15.

Typical Procedure for the Preparation of Compound **3aa**.—To a 50 cm^3 three-necked round-bottomed flask equipped with a stirrer at 0–10 °C, freshly distilled CH_2Cl_2 (30 cm^3), pyridine (0.8 g 10 mmol) and benzyl alcohol (1.1 g, 10 mmol) were added. $ClCF_2COF$ (1.3 g, 10 mmol) was then added through a gas inlet over 10 min to the reaction mixture which was then stirred for a further 10 min at 10 °C. After completion of the reaction, the solution was washed with water until neutral (pH 7). The organic layer was then dried (Na_2SO_4) and the CH_2Cl_2 was distilled off to afford a crude product which was subjected to chromatography using light petroleum–diethyl ether (10:1) as eluent to give benzyl chlorodifluoroacetate **3aa** (2.0 g, 91%).

Without the addition of pyridine, **1a** reacted with **2a** under the conditions described above to give a white solid, which was insoluble in acetone and had a molecular weight of 800–1000. The product was not studied further.

Benzyl chlorodifluoroacetate **3aa**. B.p. 147–149.5 °C/20 mmHg (Found: C,48.7; H, 3.2: F, 17.1. Calc. for $C_9H_7ClF_2O_2$: C, 48.98; H, 3.17; F, 17.23%); ν_{max}/cm^{-1} 1772, 1600, 1351, 1272 and 1150; δ_H 4.9 (s, 2 H) and 6.8 (s, 5 H); δ_F −66 (s, 2 F); m/z 220 [M(^{35}Cl)]$^+$, 23%], 222 [M(^{37}Cl)$^+$, 6.1], 85 ($CF_2{}^{35}Cl^+$, 4.3), 87 ($CF_2{}^{37}Cl^+$, 1.1) and 91 ($C_6H_5CH_2{}^+$, 100).

4-Chlorobenzyl chlorodifluoroacetate **3ab**. Oil (Found: C, 42.1; H, 2.3. Calc. for $C_9H_6Cl_2F_2O_2$: C, 42.35; H, 2.35%); ν_{max}/cm^{-1} 1778, 1490, 1230, 1087, 1018, 802 and 630; δ_H 5.15 (s, 2 H) and 7.1 (s, 4 H); δ_F −66.3 (s, 2 F); m/z 254 [M(^{35}Cl)$^+$, 27.2%)], 256 [M(^{37}Cl, ^{35}Cl)$^+$, 17.7], 258 [M(2^{37}Cl)$^+$, 2.1], 85 [$^{35}ClCF_2{}^+$, 5.4], 87 [$^{37}ClCF_2{}^+$, 1.6], 125 ($^{35}ClC_6H_4CH_2{}^+$, 100) and 127 ($^{37}ClC_6H_4CH_2{}^+$, 30.4).

3-Chlorobenzyl chlorodifluoroacetate **3ac**. Oil (Found: C, 42.2; H, 2.5. Calc. for $C_9H_6Cl_2F_2O_2$: C, 42.35; H, 2.35%); ν_{max}/cm^{-1} 1772, 1564, 1472, 1235, 1108, 1043, 1010, 857, 775 and 647; δ_H 5.12 (s, 2 H) and 7.12 (m, 4 H); δ_F −66 (s, 2 F); m/z 254 [H($^{35}Cl_2$)$^+$, 36.8%], 256 [M(^{37}Cl, ^{35}Cl)$^+$, 23.8], 258 [M(2^{37}Cl)$^+$, 2.1], 85 ($^{35}ClCF_2{}^+$, 2.9), 125 ($^{35}ClC_6H_4CH_2{}^+$, 100) and 127 ($^{37}ClC_6H_4CH_2{}^+$, 32.8).

2-Chlorobenzyl chlorodifluoroacetate **3ad**. Oil (Found: C,

42.2; H, 2.25. Calc. for $C_9H_6Cl_2F_2O_2$: C, 42.35; H, 2.35%); v_{max}/cm^{-1} 1774, 1567, 1480, 1260, 1238, 1168, 1011 and 746; δ_H 5.2 (s, 2 H) and 6.83–7.3 (m, 4 H); δ_F −66.3 (s, 2 F); m/z 254 [M($^{35}Cl_2$)]$^+$, 29.7%], 256 [M(^{37}Cl, ^{35}Cl)$^+$, 19.3], 258 [M ($2^{37}Cl$)$^+$, 3.1], 125 ($^{35}ClC_6H_4CH_2^+$, 100), 127 ($^{37}ClC_6H_4$-CH_2^+, 31.8), 113 ($^{35}ClCF_2CO^+$, 5.7) and 115 ($^{37}ClCF_2CO^+$, 1.4).

4-Methylbenzyl chlorodifluoroacetate **3ae**. Oil (Found: C, 51.3, H, 3.9. Calc. for $C_{10}H_9ClF_2O_2$: C, 51.17; H, 3.84%); v_{max}/cm^{-1} 1768, 1272, 1253 and 1150; δ_H 2.29 (s, 3 H), 5.18 (s, 2 H) and 6.92 (s, 4 H); δ_F −66 (s, 2 F); m/z 234 [M(^{35}Cl)$^+$ 43.1%], 236 [M(^{37}Cl)$^+$, 12.8] and 105 ($CH_3C_6H_4CH_2^+$, 100).

3-Methylbenzyl chlorodifluoroacetate **3af**. Oil (Found: C, 51.3; H, 3.8. Calc. for $C_{10}H_9ClF_2O_2$: C, 51.7; H, 3.84%) v_{max}/cm^{-1} 1771, 1272, 1251 and 1150; δ_H 2.31 (s, 3 H), 5.15 (s, 2 H) and 6.89 (s, 4 H); −66.1 (s, 2 F); m/z 234 [M(^{35}Cl)$^+$ 32.7%], 236 [M(^{37}Cl)$^+$, 9.2] and 105 ($CH_3C_6H_4CH_2^+$, 100).

3-Nitrobenzyl chlorodifluoroacetate **3ag**. Oil (Found: C, 40.5; H, 2.3; F, 14.1. Calc. for $C_9H_6ClF_2NO_4$: C, 40.68. H, 2.26; F, 14.31%); v_{max}/cm^{-1} 1775, 1600, 1277, 1252, 1147 and 1082; δ_H 5.15 (s, 2 H) and 7.38–8.0 (m, 4 H); δ_F −66.8 (s, 2 F); m/z 265 [M(^{35}Cl)$^+$, 31.9%], 267 [M(^{37}Cl)$^+$, 8.9], 136 ($NO_2C_6H_4CH_2^+$, 100) and 46 (NO_2^+, 1.3).

4-Nitrobenzyl chlorodifluoroacetate **3ah**. Oil (Found: C, 40.5; H, 2.2. Calc. for $C_9H_6ClF_2NO_4$: C, 40.68; H, 2.26%); v_{max}/cm^{-1} 1778, 1603, 1271, 1254, 1147 and 1023; δ_H 5.28 (s, 2 H), 7.6 (d, J 8.3, 2 H) and 8.24 (d, J 8.3, 2 H); δ_F −66.1 (s, 2 F); m/z 265 [M(^{35}Cl)$^+$, 29.2%], 267 [M(^{37}Cl)$^+$, 8.2] and 136 ($NO_2C_6H_4CH_2^+$, 100).

Allyl chlorodifluoroacetate **3ai**. B.p. 109–112 °C/760 mmHg (Found: C, 35.4; H, 3.2; F, 22.1. Calc. for $C_5H_5ClF_2O_2$: C, 35.19; H, 3.04; F, 22.28%); v_{max}/cm^{-1} 1780, 1273, 1252 and 1153; δ_H 4.9 (d, J 7.3, 2 H), 5.43 (dd, J 7.1, 5.6, 1 H), 5.71 (m, 1 H) and 6.02 (m, 1 H); δ_F −66 (s, 2 F); m/z 170 [M(^{35}Cl)$^+$, 21%], 172 [M(^{37}Cl)$^+$, 5.9] and 41 ($C_3H_5^+$, 100).

Cinnamyl chlorodifluoroacetate **3aj**. Oil (Found: C, 53.8; H, 3.71. Calc. for $C_{11}H_9ClF_2O_2$: C, 53.55; H, 3.65%); v_{max}/cm^{-1} 1769, 1250, 1187 and 1084; δ_H 5.1 (d, J 7.1, 2 H), 6.3 (dt, J 14.7, 7.1, 1 H), 6.7 (d, J 14.7, 1 H) and 7.21 (s, 5 H); δ_F −66.3 (s, 2 F); m/z 246 [M(^{35}Cl)$^+$, 36.7%], 248 [M(^{37}Cl)$^+$, 10.8] and 117 ($C_6H_5CH=CHCH_2^+$, 100).

Prop-2-ynyl chlorodifluoroacetate **3ak**. B.p. 80–82.5 °C/100 mmHg (Found: M$^+$, 168.5284. Calc. for $C_5H_3ClF_2O_2$: M, 168.5275); v_{max}/cm^{-1} 1772, 1270, 1109 and 1087; δ_H 2.28 (s, 1 H) and 4.87 (s, 2 H); δ_F −66 (s, 2 F); m/z 168 [M(^{35}Cl)$^+$, 21.6%), 170 [M(^{37}Cl)$^+$, 5.9] and 39 ($C_3H_3^+$, 100).

Benzyl bromodifluoroacetate **3ba**. Oil (Found: C, 40.9; H, 2.6. Calc. for $C_9H_7BrF_2O_2$: C, 40.76; H, 2.64%); v_{max}/cm^{-1} 3030, 1764, 1600, 1350, 1280 and 1150; δ_H 4.9 (s, 2 H) and 6.8 (s, 5 H); δ_F −62 (s, 2 F); m/z 264 [M(^{79}Br)$^+$, 53.1%], 266 [M(^{81}Br)$^+$, 52.9], 129 ($CF_2^{79}Br^+$, 3.2), 131 ($CF_2^{81}Br^+$, 3.2) and 91 ($C_6H_5CH_2^+$, 100).

4-Chlorobenzyl bromodifluoroacetate **3bb**. Oil (Found: C, 35.9; H, 1.9. Calc. for $C_9H_6BrClF_2O_2$: C, 36.06; H, 2.00%); v_{max}/cm^{-1} 1760, 1490, 1230, 1092, 1011, 802 and 630; δ_H 5.2 (s, 2 H) and 7.1 (m, 4 H); δ_F −62.1 (s, 2 F); m/z 298 [M(^{35}Cl, ^{79}Br)$^+$, 34.2%], 300 [M(^{37}Cl + ^{79}Br or ^{35}Cl + ^{81}Br)$^+$, 45.6], 258 [M(^{37}Cl, ^{81}Br)$^+$, 11.2], 157 ($^{79}BrCF_2CO^+$, 7.4), 159 ($^{81}BrCF_2$-CO^+, 7.4), 125 ($^{35}ClC_6H_4CH_2^+$, 100) and 127 ($^{37}ClC_6H_4$-CH_2^+, 33.1).

3-Chlorobenzyl Bromodifluoroacetate **3bc**. Oil (Found: C, 35.9; H, 2.1; F, 12.8. Calc. for $C_9H_6BrClF_2O_2$: C, 30.06; H, 2.00; F, 12.69%); v_{max}/cm^{-1} 1763, 1568, 1470, 1235, 1092, 1010, 1080, 857, 773 and 642; δ_H 5.1 (s, 2 H) and 7.08 (s, 4 H); δ_F −62 (s, 2 F); m/z 298 [M(^{35}Cl, ^{79}Br)$^+$, 36.7%], 300 [M(^{37}Cl + ^{79}Br, ^{35}Br)$^+$, 49.1], 302 [M(^{37}Cl, ^{81}Br)$^+$, 11.4], 157 ($^{79}BrCF_2CO^+$, 6.9), 159 ($^{81}BrCF_2CO^+$, 6.9), 125 ($^{35}ClC_6H_4CH_2^+$, 100) and 127 ($^{37}ClC_6H_4CH_2^+$, 31.1).

2-Chlorobenzyl bromodifluoroacetate **3bd**. Oil (Found: C, 36.2; H, 1.9; F, 12.7. Calc. for $C_9H_6BrClF_2O_2$: C, 36.06; H, 2.00; F, 36.23%) v_{max}/cm^{-1} 1771, 1571, 1480, 1260, 1238, 1171, 1011 and 750; δ_H 5.2 (s, 2 H) and 6.9–7.3 (m, 4 H); δ_F −62.5 (s, 2 F); m/z 298 [M(^{35}Cl, ^{79}Br)$^+$, 32.7%], 300 [M(^{37}Cl + ^{79}Br and ^{35}Cl + ^{81}Br)$^+$, 43.7], 302 [M(^{37}Cl, ^{81}Br)$^+$ 10.4], 157 ($^{79}BrCF_2CO^+$, 6.3), 159 ($^{81}BrCF_2CO^+$, 6.3), 125 ($^{35}ClC_6$-$H_4CH_2^+$, 100) and 127 ($^{37}ClC_6H_4CH_2^+$, 31.8).

4-Methylbenzyl bromodifluoroacetate **3be**. Oil (Found: M$^+$, 279.0816. Calc. for $C_{10}H_9BrF_2O_2$: M, 279.0809); v_{max}/cm^{-1} 1763, 1272, 1250 and 1153; δ_H 2.29 (s, 3 H), 5.1 (s, 2 H) and 6.9 (s, 4 H); δ_F −62 (s, 2 F); m/z 278 [M(^{79}Br)$^+$ 58.2%], 280 [M(^{81}Br)$^+$, 58.1] and 105 ($CH_3C_6H_4CH_2^+$, 100).

3-Methylbenzyl bromodifluoroacetate **3bf**. Oil (Found: C, 43.1; H, 3.2. Calc. for $C_{10}H_9BrF_2O_2$: C, 40.1; H, 3.22%); v_{max}/cm^{-1} 1771, 1272, 1250 and 1155; δ_H 2.29 (s, 3 H), 5.1 (s, 2 H) and 6.9 (s, 4 H); δ_F −62 (s, 2 F); m/z 278 [M(^{79}Br)$^+$, 49.2], 280 [M(^{81}Br)$^+$, 49.0] and 105 ($CH_3C_6H_4CH_2^+$, 100).

3-Nitrobenzyl bromodifluoroacetate **3bg**. Oil (Found: H, 1.9; F, 12.0. Calc. for $C_9H_6BrF_2NO_4$: H, 1.94; F, 12.26%); v_{max}/cm^{-1} 1773, 1600, 1275, 1257 and 1147; δ_H 5.15 (s, 2 H) and 7.38–8.0 (m, 4 H); δ_F −62 (s, 2 F); m/z 209 [M(^{79}Br)$^+$, 32%], 311 [M(^{81}Br)$^+$, 32.2] and 136 ($NO_2C_6H_4CH_2^+$, 100).

4-Nitrobenzyl bromodifluoroacetate **3bh**. Oil (Found: H, 2.0; F, 12.5. Calc. for $C_9H_6BrF_2NO_4$: H, 1.94; F, 12.26%); v_{max}/cm^{-1} 1773, 1600, 1275, 1257 and 1147; δ_H 5.23 (s, 2 H), 7.60 (d, J 8, 2 H) and 8.21 (d, J 8, 2 H); δ_F −62.1 (s, 2 F); m/z 309 [M(^{79}Br)$^+$, 32%), 311 [M(^{81}Br)$^+$, 32.2] and 136 ($NO_2C_6H_4CH_2^+$, 100).

Allyl bromodifluoroacetate **3bi**. B.p. 122–124 °C/760 mmHg (Found: M$^+$, 214.9953, Calc. for $C_5H_5BrF_2O_2$: M, 214.9941); v_{max}/cm^{-1} 1780, 1273, 1252 and 1153; δ_H 4.94 (d, J 7.1, 2 H), 5.42 (dd, J 7.3, 5.4, 1 H), 5.72 (dd, J 14.1, 5.4, 1 H) and 6.02 (m, 1 H); δ_F −62 (s, 2 F); m/z 214 [M(^{79}Br)$^+$, 21%], 216 [M(^{81}Br)$^+$, 21.3] and 41 ($C_3H_5^+$, 100).

Cinnamyl bromodifluoroacetate **3bj**. Oil (Found: C, 45.17; H, 3.14. Calc. for $C_{11}H_9BrF_2O_2$: C, 45.36; H, 3.09%); v_{max}/cm^{-1} 1772, 1250, 1187 and 1063; δ_H 5.1 (d, J 7.1, 2 H), 6.3 (dt, J 14.7, 7.1, 1 H), 6.7 (d, J 14.7, 1 H) and 7.21 (s, 5 H); δ_F −62.3 (s, 2 F); m/z 290 [M(^{79}Br)$^+$, 23.6%], 292 [M(^{81}Br)$^+$, 23.6] and 117 ($C_6H_5CH=CHCH_2^+$, 100).

Benzyl fluorosulfonyldifluoroacetate **3ca**. Oil (Found: M$^+$, 268.2078. Calc. for $C_9H_7F_3O_4S$: M$^+$, 268.2071) v_{max}/cm^{-1} 1764, 1600, 1468, 1278, 1150 and 1063; δ_H 5.0 (s, 2 H) and 6.8 (s, 5 H); δ_F 40 (s, 1 F) and −107.1 (s, 2 F); m/z 268 (M$^+$, 23.1%) and 91 ($C_6H_5CH_2^+$, 100).

4-Chlorobenzyl fluorosulfonyldifluoroacetate **3cb**. Oil (Found: M$^+$, 302.6531. Calc. for $C_9H_6ClF_3SO_4$: M, 302.6522); v_{max}/cm^{-1} 1760, 1490, 1468, 1230, 1092, 1011, 802 and 630; δ_H 5.2 (s, 2 H) and 7.1 (s, 4 H); δ_F 40.1 (s, 1 F) and −107.1 (s, 2 F); m/z 302 [M(^{35}Cl)$^+$, 17.2%], 256 [M(^{37}Cl)$^+$, 5.3], 125 [M($^{35}ClC_6H_4CH_2^+$, 100] and 127 ($^{37}ClC_6H_4CH_2^+$, 32.8).

3-Chlorobenzyl fluorosulfonyldifluoroacetate **3cc**. Oil: (Found: M$^+$, 302.6516. Calc. for $C_9H_6ClF_3SO_4$: M, 302.6522); v_{max}/cm^{-1} 1778, 1571, 1480, 1471, 1260, 1238, 1171, 1011 and 750; δ_H 5.1 (s, 2 H) and 7.1 (s, 4 H); δ_F 40.4 (s, 1 F) and −106.4 (s, 2 F); m/z 302 [M(^{35}Cl)$^+$, 19.7%], 304 [M(^{37}Cl)$^+$, 6.2], 125 ($^{35}ClC_6H_4$-CH_2^+, 100) and 127 ($^{37}ClC_6H_4CH_2^+$, 32.7).

2-Chlorobenzyl fluorosulfonyldifluoroacetate **3cd**. Oil (Found: M$^+$, 302.6534. Calc. for $C_9H_6ClF_3SO_4$: M, 302.6522); v_{max}/cm^{-1} 1778, 1571, 1480, 1471, 1260, 1238, 1172, 1011 and 750; δ_H 5.2 (s, 2 H) and 6.9–7.3 (m, 4 H); δ_F 40.2 (s, 1 F) and −106.3 (s, 2 F); m/z 302 [M(^{35}Cl)$^+$, 21.5%], 304 [M(^{37}Cl)$^+$, 6.8], 125 ($^{35}ClC_6$-$H_4CH_2^+$, 100) and 127 ($^{37}ClC_6H_4CH_2^+$, 32.7).

4-Methylbenzyl fluorosulfonyldifluoroacetate **3ce**. Oil (Found: M$^+$, 282.2343. Calc. for $C_{10}H_9F_3SO_4$: M, 282.2339); v_{max}/cm^{-1} 1763, 1273, 1250, 1153 and 1082; δ_H 2.30 (s, 3 H), 5.1 (s, 2 H) and 6.9 (s, 4 H); δ_F 40.2 (s, 1 F) and −106.4 (s, 2 F); m/z 282 (M$^+$, 58.1%) and 105 ($CH_3C_6H_4CH_2^+$, 100).

3-*Methylbenzyl fluorosulfonyldifluoroacetate* **3cf**. Oil (Found: M⁺, 282.2331. Calc. for $C_{10}H_9F_3SO_4$: M, 282.2339); ν_{max}/cm^{-1} 1763, 1468, 1272, 1250 and 1153; δ_H 2.29 (s, 3 H), 5.04 (s, 2 H) and 6.58 (s, 4 H); δ_F 40.3 (s, 1 F) and −106.3 (s, 2 F); m/z 282 (M⁺, 58.1%) and 105 ($CH_3C_6H_4CH_2^+$, 100).

3-*Nitrobenzyl fluorosulfonyldifluoroacetate* **3cg**. Oil (Found: M⁺, 313.2053. Calc. for $C_9H_6F_3NSO_6$: M^+ 313.2047); ν_{max}/cm^{-1} 1773, 1600, 1469, 1275, 1257, 1147 and 1082; δ_H 5.15 (s, 2 H) and 7.36–8.0 (s, 4 H); δ_F 40.1 (s, 1 F) and −106.8 (s, 2 F); m/z 313 (M⁺, 43.7%) and 136 ($NO_2C_6H_4CH_2^+$, 100).

4-*Nitrobenzyl fluorosulfonyldifluoroacetate* **3ch**. Oil (Found: M⁺, 313.2042. Calc. for $C_9H_6F_3NSO_6$: M, 313.2047); ν_{max}/cm^{-1} 1775, 1600, 1468, 1269, 1254, 1147 and 1023; δ_H 5.25 (s, 2 H), 7.6 (d, J 6.3, 2 H) and 8.24 (d, J 6.3, 2 H); δ_F 40.5 (s, (s, 1 F) and − 106.2 (s, 2 F); m/z 313 (M⁺, 27.4%) and 136 ($NO_2C_6H_4CH_2^+$, 100).

Allyl fluorosulfonyldifluoroacetate **3ci**. B.p. (decomp.) 80 °C/ 100 mmHg (Found: M⁺, 218.1482. Calc. for $C_5H_5F_3O_4S$: M, 218.1473); ν_{max}/cm^{-1} 1780, 1467, 1273, 1252 and 1153; δ_H 4.9 (d, J 7.1, 2 H), 5.38 (dd, J 7.1, 4.8, 1 H), 5.7 (dd, J 4.5, 4.8, 1 H) and 6.0 (m, 1 H); δ_F 40.1 (s, 1 F) and −107.1 (s, 2 F); m/z 218 (M⁺, 27.3%) and 41 ($C_3H_5^+$, 100).

Cinnamyl fluorosulfonyldifluoroacetate **3cj**. Oil (Found: M⁺, 294.2453. Calc. for $C_{11}H_9F_3O_4S$: M, 294.2449); ν_{max}/cm^{-1} 1771, 1473, 1250, 1180 and 1010; δ_H 5.2 (d, J 7.2, 2 H), 6.3 (dt, J 14.7, 7.2, 1 H), 6.7 (m, 1 H) and 7.21 (s, 5 H); δ_F 40.3 (s, 1 F) and −106.2 (s, 2 F); m/z 294 (M⁺, 47.1) and 117 ($C_6H_5CH= CHCH_2^+$, 6.8).

4-*Bromobenzyl fluorosulfonyldifluoroacetate* **3cl**. Oil (Found: M^+, 347.1038. Calc. for $C_9H_6BrF_3SO_4$: M^+ 347.1032); ν_{max}/cm^{-1} 1768, 1490, 1468, 1230, 1092, 1011, 802 and 630; δ_H 5.25 (s, 2 H) and 7.1 (s, 4 H); δ_F 40.1 (s, 1 F) and −107.3 (s, 2 F); m/z 346 [M(⁷⁹Br)⁺, 19.2%], 348 [M(⁸¹Br)⁺, 19.2], 169 (⁷⁹BrC₆H₄-CH₂⁺, 100) and 171 (⁸¹BrC₆H₄CH₂⁺, 100).

Typical Procedure for the Preparation of Compounds **4**.—To a 50 cm³ three-necked round-bottomed flask, equipped with a stirrer, freshly distilled DMF (30 cm³), dry KF (0.58 g, 10 mmol) and CuI (2.0 g, 10 mmol) were added under nitrogen. The mixture was then heated to 100 °C and $PhCH_2OCOCF_2Cl$ (2.2 g, 10 mmol) was added dropwise to it over 2 h. The solution was heated for a further 6 h. On completion of the reaction, the solution was poured into ice–water (100 cm³) and the mixture was filtered. The residue was separated and the aqueous layer was extracted with diethyl ether (3 × 30 cm³). The combined extracts were then dried (Na_2SO_4) and after removal of the ether, the crude product was subjected to column chromatography using light petroleum as eluent to give 2,2,2-trifluoro-ethylbenzene **4** (0.94 g, 59%).

2,2,2-*Trifluoroethylbenzene* **4a**. B.p. 116–118 °C/760 mmHg (lit.,[18] 124–126 °C); ν_{max}/cm^{-1} 1278 and 1150; δ_H 3.32 (q, J 11.2, 2 H) and 6.8 (s, 5 H); δ_F −65.7 (t, J 11.2); m/z 160 (M⁺, 23.1%), 91 ($C_6H_5CH_2^+$, 100) and 69 (CF_3^+, 2.3).

4-(2,2,2-*Trifluoroethyl)chlorobenzene* **4b**.[11] B.p. 80–82 °C/20 mmHg; ν_{max}/cm^{-1} 1260 and 1092; δ_H 3.52 (q, J 10.8, 2 H) and 7.1 (m, 4 H); δ_F −65.6 (t, J 10.8); m/z 194 [M(³⁵Cl)⁺, 30.8%], 196 [M(³⁷Cl)⁺, 8.3], 125 (³⁵ClC₆H₄CH₂⁺, 100) and 127 (³⁷ClC₆H₄CH₂⁺, 32.1).

3-(2,2,2-*Trifluoroethyl)chlorobenzene* **4c**.[11] B.p. 92–93.5 °C/ 25 mmHg; ν_{max}/cm^{-1} 1568, 1235 and 1102; δ_H 3.58 (q, J 10.6, 2 H) and 7.06 (s, 4 H); δ_F −65.2 (t, J 10.6); m/z 194 [M(³⁵Cl)⁺, 45.3%], 196 [M(³⁷Cl)⁺, 12.8], 125 (³⁵ClC₆H₄CH₂⁺, 100), 127 (³⁷ClC₆H₄CH₂⁺, 32.5) and 69 (CF_3^+, 3.5).

2-(2,2,2-*Trifluoroethyl)chlorobenzene* **4d**.[11] B.p. 73–75 °C/18 mmHg; ν_{max}/cm^{-1} 1571, 1260, 1238, 1172 and 750; δ_H 3.6 (q, J 10.8, 2 H) and 6.9–7.3 (m, 4 H); δ_F −65.2 (t, J 10.8); m/z 194 [M(³⁵Cl)⁺, 31.5%], 196 [M(³⁷Cl)⁺, 8.7], 125 (³⁵ClC₆H₄CH₂⁺, 100), 127 (³⁷ClC₆H₄CH₂⁺, 32.7) and 69 (5.8).

4-(2,2,2-*Trifluoroethyl)toluene* **4e**.[18] B.p. 128–131 °C/760 mmHg; ν_{max}/cm^{-1} 1273, 1250, 1153 and 1082; δ_H 2.3 (s, 3 H), 3.31 (q, J 10.8, 2 H) and 6.9 (s, 4 H); δ_F −65.7 (t, J 10.8); m/z 174 (M⁺, 47.1%), 105 ($CH_3C_6H_4CH_2^+$, 100) and 69 (CF_3^+, 12.6).

3-(2,2,2-*Trifluoroethyl)toluene* **4f**. B.p. 87–90 °C/90 mmHg (lit.,[18] 37–39 °C/8 mmHg); ν_{max}/cm^{-1} 1272, 1275, 1257 and 1147; δ_H 2.29 (s, 3 H), 3.27 (q, J 11.0, 2 H) and 6.9 (s, 4 H); δ_F −65.3 (t, J 11.0); m/z 174 (M⁺, 38.6%), 105 ($CH_3C_6H_4CH_2^+$, 100) and 69 (CF_3^+, 4.3).

3-(2,2,2-*Trifluoroethyl)nitrobenzene* **4g**.[19] M.p. 41–42.5 °C; ν_{max}/cm^{-1} 1538, 1275, 1257 and 1147; δ_H 3.42 (q, J 10.2, 2 H), 7.6 (m, 2 H) and 8.12 (m, 2 H); δ_F −65.2 (t, J 10.8); m/z 205 (M⁺, 27.7%) and 136 ($NO_2C_6H_4CH_2^+$, 100).

4-(2,2,2-*Trifluoroethyl)nitrobenzene* **4h**.[19] M.p. 64.5–66 °C; ν_{max}/cm^{-1} 1528, 1269, 1254 and 1147; δ_H 3.50 (q, J 10.3, 2 H), 7.52 (d, J 8.7, 2 H) and 8.21 (d, J 8.7, 2 H); δ_F −65.0 (t, J 10.3); m/z 205 (M⁺, 27.4%) and 136 ($NO_2C_6H_4CH_2^+$, 100).

4,4,4-*Trifluorobut-1-ene* **4i**.[13] B.p. 10–12 °C/760 mmHg; δ_H 3.21 (m, 2 H), 5.3 (dd, J 7.3, 4.8, 1 H), 5.68 (dd, J 14.5, 4.8, 1 H) and 6.0 (m, 1 H); δ_F −65.1 (t, J 10.3); m/z 110 (M⁺, 16.4%), 91 (M⁺ −F, 6.38), 90 (M⁺ − HF, 2.90), 71 (M⁺ − HF − F, 3.96), 69 (CF_3^+, 17.04) and 41 (M⁺ − CF_3, 100).

1-4,4,4-*Trifluoro-1-phenyl-but-1-ene* **4j**.[11] M.p. 35–37 °C; ν_{max}/cm^{-1} 1250 and 1180; δ_H 3.2 (m, 2 H), 6.3 (dt, J 14.7, 7.1, 1 H), 6.7 (d, J 14.7, 1 H) and 7.18 (s, 5 H); δ_F −65.1 (t, J 10.7); m/z 186 (M⁺, 52.1%), 117 (M⁺ − CF_3, 100) and 77 ($C_6H_5^+$, 6.8).

4,4,4-*Trifluorobuta-1,2-diene* **4k**.[17] B.p. 8–10 °C/760 mmHg; δ_H 5.2 (m, 2 H) and 5.36 (m, 1 H); δ_F −63.7 (d, J 10); m/z 108 (M⁺,100%) and 69 (CF_3^+, 23).

4-(2,2,2-*Trifluoroethyl)bromobenzene* **4l**. B.p. 120–123 °C/25 mmHg; (Found: M⁺, 239.0353. Calc. for $C_8H_6BrCF_3$: M, 239.0346); ν_{max}/cm^{-1} 1266 and 1103; δ_H 3.42 (q, J 10.3, 2 H) and 7.16 (m, 4 H); δ_F −65.6 (t, J 10.3); m/z 238 [M(⁷⁹Br)⁺, 36.8%], 240 [M(⁸¹Br)⁺, 35.9], 169 (⁷⁹BrC₆H₄CH₂⁺, 100) and 171 (⁸¹BrC₆H₄CH₂⁺, 100).

Typical Procedure for the Direct Trifluoromethylation–dehydroxylation of Alcohols.—To a 50 cm³ three-necked round-bottomed flask, equipped with a stirrer, DMF (30 cm³), KF (0.5 g, 10 mmol), CuI (2.0 g, 10 mmol), **2a** (1.08 g, 10 mmol) and **6a** (3.2 g, 20 mmol) were added under nitrogen. The mixture was then heated to 100 °C for 10 h. On completion of the reaction, the solution was poured into ice–water (100 cm³) and the mixture was filtered and the residue was washed with diethyl ether (3 × 10 cm³). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 30 cm³). The combined organic extracts were then dried (Na_2SO_4) and after removal of the ether, the crude product was subjected to column chromatography using light petroleum as eluent to give **4a** (0.7 g, 43%).

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