Palladium-catalysed Alkynyl-dehydroxylation of Polyfluorophenols

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Treatment of polyfluorophenyl perfluoroalkanesulfonates $R_fSO_3C_6F_4X$-*p* (**1**, X = F, Cl) with alkynes in the presence of $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ and Et_3N in DMF gave polyfluorophenylalkynes in good to high yields. The same products were also prepared in a one-pot reaction from the corresponding perfluoroalkanesulfonyl fluoride and polyfluorophenol in comparable yields.

Perfluoroalkanesulfonate esters are one of the most important derivatives of perfluoroalkanesulfonic acid and they have been extensively studied both in theory and in their synthetic applications.[1] For example, it has been reported that the nucleophilic attack on 1*H*,1*H*-perfluoroalkyl perfluoroalkanesulfonates ($R_fSO_3CH_2R_f$) leads predominantly to carbon–oxygen bond cleavage,[2] whereas on perfluoroalkyl[3] and perfluorophenyl[4] perfluoroalkanesulfonates ($R_fSO_3R_f$, $R_fSO_3C_6F_5$) or perfluorophenyl perfluorobenzenesulfonates ($C_6F_5SO_3C_6F_5$),[5] only sulfur–oxygen bond scission occurs. However, a palladium-catalysed Heck coupling reaction of vinyl, aryl perfluoroalkanesulfonates with alkenes,[6,7] alkynes[7] and a variety of organometallic reagents[8] has been developed as a general method for carbon–carbon bond formation, *i.e.* an exclusive carbon–oxygen bond fragmentation.

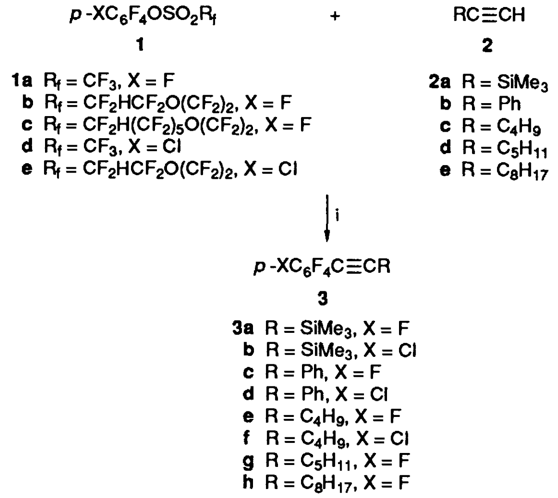
It was of interest to us to investigate where this palladium-catalysed reaction could be applied to the polyfluroaryl perfluoroalkanesulfonates $R_fSO_3C_6F_4X$-*p* (**1**, X = F, Cl) because of the higher acidity of *p*-XC_6F_4OH compared to that of phenols. Furthermore this reaction would also provide a simple method of preparation of substituted polyfluorobenzenes, in particular, polyfluorophenylakynes which are intermediates in the synthesis of potential optical materials.[9]

Perfluorophenylakynes have previously been prepared by the coupling of C_6F_5I with CuC≡CR or C_6F_5Cu with IC≡CR using inconvenient procedures and in some cases low yields.[9,10] A recent modification has been reported *via* fluorinated halides and alkynes in the presence of palladium.[11] This paper describes a novel, convenient method for the preparation of perfluorophenylalkynes from compounds **1** or directly from polyfluorophenols **5**.

Results and Discussion

Polyfluorophenyl perfluoroalkanesulfonates **1** may be easily prepared in excellent yield from the reaction of polyfluorophenoxide (*p*-$CX_6F_4O^-$, X = F, Cl) and perfluoroalkanesulfonyl fluoride.[4]

Heating perfluorophenyl perfluoroalkanesulfonates **1** with alkynes **2** in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ (5 mol%) and NEt_3 in dimethylformamide (DMF) at 80 °C for several hours gave the corresponding polyfluorophenylalkynes **3** in good to high yields (Scheme 1). The results are shown in Table 1.



Scheme 1 *Reagents and conditions:* i, $Pd(PPh_3)_2Cl_2$, Et_3N, DMF, 80 °C

Table 1 $Pd(PPh_3)_2Cl_2$-catalysed coupling reaction of *p*-$C_6F_4OSO_2R_f$ **1** and HC≡CR **2** at 80 °C in DMF

Entry	1	2	*t*/h	Product	Yield[a] (%)
1[b]	**1a**	**2a**	9	**3a**	95
2[b]	**1b**	**2a**	10	**3a**	92
3[b]	**1d**	**2a**	12	**3b**	87
4	**1a**	**2b**	10	**3c**	92
5	**1b**	**2b**	8	**3c**	90
6	**1c**	**2b**	16	**3c**	84
7[c]	**1b**	**2b**	8	**3c**	34
8[d]	**1b**	**2b**	10	**3c**	52
9[e]	**1b**	**2b**	10	**3c**	49
10[f]	**1b**	**2b**	10	**3c**	54
11[g]	**1b**	**2b**	5	**3c**	0
12	**1d**	**2b**	12	**3d**	89
13	**1e**	**2b**	13	**3d**	90
14	**1a**	**2c**	11	**3e**	77
15	**1c**	**2c**	11	**3e**	75
16	**1b**	**2c**	14	**3e**	69
17	**1d**	**2c**	12	**3f**	72
18	**1e**	**2c**	10	**3f**	68
19	**1b**	**2d**	16	**3g**	65
20	**1b**	**2e**	18	**3h**	67

[a] Isolated yield based on **1**. [b] Reaction in a sealed glass tube. [c] *T* = 95 °C. [d] In the presence of *p*-DNB (20 mol%). [e] In the presence of Bu^t_2NO (20 mol%). [f] In the presence of hydroquinone (20 mol%). [g] $NaHCO_3$ instead of NEt_3 as a base.

The palladium catalyst was essential; without it the reactants were recovered completely. The reaction did not occur at room temp. for several hours, whereas a temperature above 95 °C gave mainly polyfluorophenol: *e.g.*, perfluorophenol (57%) and **3c** (34%) were formed when **1a** and **2b** reacted at 95 °C for 8 h. The best results were obtained at 80 °C. NEt_3 is necessary in this reaction, utilization of $NaHCO_3$ instead of NEt_3 in DMF gave only perfluorophenol without the coupling products **3** (see entry 11, Table 1). Variation of the R_f group had little influence on the yield as shown in Table 1. The presence of *p*-dinitrobenzene (*p*-DNB), Bu^t_2NO (known electron scavengers) or

Table 2 Reaction of **1** with **2** (**1**:**2** = 1:3) in the presence of $Pd(PPh_3)_4$ in DMF at 80 °C

Entry	1	2	t/h	Product	Yield[a] (%)
1[b]	**1a**	**2a**	12	**3a**	86
2	**1a**	**2b**	12	**3c**	92
3	**1b**	**2b**	10	**3c**	94
4[c]	**1b**	**2b**	10	**3c**	90
4[d]	**1b**	**2b**	10	**3c**	86
6[e]	**1b**	**2b**	10	**3c**	88
7	**1c**	**2c**	14	**3d**	85
8	**1d**	**2c**	12	**3d**	90
9	**1a**	**2c**	9	**3e**	75
10	**1b**	**2c**	10	**3e**	78
11	**1d**	**2c**	11	**3f**	70
12	**1a**	**2d**	14	**3g**	65
13	**1b**	**2e**	20	**3h**	68

[a] Isolated yield based on **1**. [b] Reaction in a sealed glass tube. [c] In the presence of *p*-DNB (20 mol%). [d] In the presence of Bu^t_2NO (20 mol%). [e] In the presence of hydroquinone (20 mol%).

Table 3 One-pot reaction of R_fSO_2F **4**, p-XC_6H_4OH **5**, alkynes **2** and NEt_3 (**2**:**4**:**5**:NEt_3 = 3:1:1:5) in the presence of $Pd(PPh_3)_2Cl_2$ (5 mol%) in DMF at 80 °C

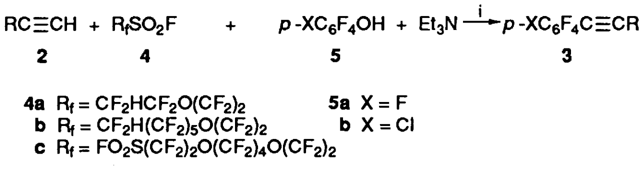
Entry	2	4	5	t/h	Product	Yield[a] (%)
1[b]	**2a**	**4a**	**5a**	11	**3a**	65
2[b]	**2a**	**4a**	**5b**	14	**3b**	67
3	**2b**	**4a**	**5a**	14	**3c**	76
4	**2b**	**4b**	**5a**	10	**3c**	70
5	**2b**	**4c**	**5a**	17	**3c**	80
6	**2b**	**4a**	**5b**	13	**3d**	84
7	**2b**	**4c**	**5b**	15	**3d**	81
8	**2c**	**4a**	**5a**	10	**3e**	75
9	**2c**	**4c**	**5a**	8	**3e**	72
10	**2c**	**4a**	**5b**	10	**3f**	70
11	**2d**	**4c**	**5a**	18	**3g**	60
12	**2e**	**4a**	**5a**	20	**3h**	70
13	**2e**	**4c**	**5a**	20	**3h**	67

[a] Isolated yield based on **4**. [b] Reaction in a sealed glass tube.

hydroquinone (free radical inhibitor) decreased significantly the yields of products **3** (entries 8, 9 and 10 in Table 1).

It was found that palladium(0) also catalysed this reaction with comparable yields. However, adding *p*-DNB, Bu^t_2NO or hydroquinone to the reaction mixture did not affect the product yield (see Table 2).

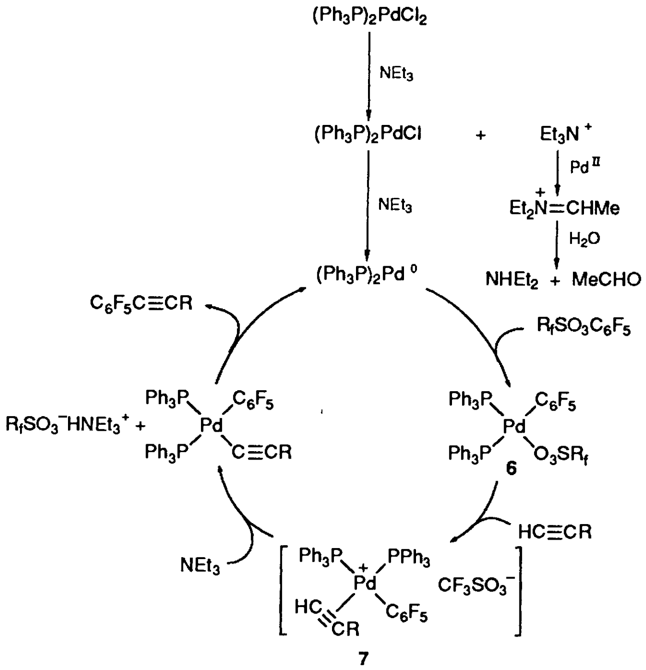
All these products could be also generated directly in good yield in a one-pot reaction of polyfluoroalkanesulfonyl fluoride **4**, polyfluorophenol **5**, alkyne **2** and NEt_3 in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ in DMF at 80 °C for several hours (Scheme 2). The results (see Table 3) may be explained in terms of the currently accepted mechanism involving the initial oxidative addition of **1** to Pd^0 to afford an organopalladium(II) complex **6**. The coordination of the oxidative adduct with alkynes to give a new Pd^{II} species **7** which rapidly undergoes elimination to form the coupled product and regenerates the Pd^0 catalyst is outlined with some modifications in Scheme 3. However, how is the $Pd^{II}Cl_2$ reduced to Pd^0? Previous workers proposed that the reduction occurs *via* the alkynes or alkenes present,[12] but, more recently, it was found that tertiary amines are able to reduce Pd^{II} to active catalytic Pd^0 rapidly.[13] As mentioned above, the presence of *p*-DNB, Bu^t_2NO, or hydroquinone in the $Pd(PPh_3)_2Cl_2$–NEt_3–DMF system suppressed significantly the product yield and we also detected a small amount of $NHEt_2$ which should be the result of the oxidation of NEt_3.[14] The inhibitors did not affect the yields in the $Pd(PPh_3)_4$–NEt_3 system. So, it appears that the Pd^{II}-catalysed reaction may involve a single electron transfer (SET) process, *i.e.* $Pd^{II} \longrightarrow Pd^{I} \longrightarrow Pd^0$. The small influence of the inhibitors in the Pd^0-catalysed reaction, implies that the initial oxidation–addition step does not involve a SET or a radical process.*[,15] On the other hand, because the trifluoromethanesulfonate anion is known to be easily exchanged in the oxidative addition complex **6** by alkynes,[16] it is reasonable to assume that formation of a cationic alkyne-coordination species **7** occurs (see Scheme 3).



$$\underset{\mathbf{2}}{RC{\equiv}CH} + \underset{\mathbf{4}}{R_fSO_2F} + \underset{\mathbf{5}}{p\text{-}XC_6F_4OH} + Et_3N \xrightarrow{i} \underset{\mathbf{3}}{p\text{-}XC_6F_4C{\equiv}CR}$$

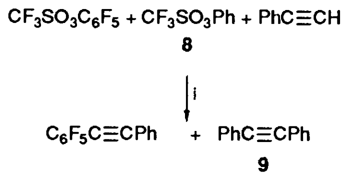
4a $R_f = CF_2HCF_2O(CF_2)_2$ **5a** X = F
b $R_f = CF_2H(CF_2)_5O(CF_2)_2$ **b** X = Cl
c $R_f = FO_2S(CF_2)_2O(CF_2)_4O(CF_2)_2$

Scheme 2 *Reagents and conditions:* i, $Pd(PPh_3)_2Cl_2$, DMF, 80 °C



Scheme 3

In order to compare the relative reactivity of **1** with non-fluorophenyl perfluoroalkanesulfonate $R_fSO_3C_6H_5$, a reaction of equivalents of $CF_3SO_3C_6F_5$ **1a**, CF_3SO_3Ph **8** and $PhC{\equiv}CH$ **2b** in the presence of a catalytic amount of $Pd(PPh_3)_2Cl_2$ was carried out (Scheme 4). It was found that the product ratio of



$$CF_3SO_3C_6F_5 + \underset{\mathbf{8}}{CF_3SO_3Ph} + PhC{\equiv}CH \xrightarrow{i} C_6F_5C{\equiv}CPh + \underset{\mathbf{9}}{PhC{\equiv}CPh}$$

Scheme 4 *Reagents and conditions:* $Pd(PPh_3)_2Cl_2$, NEt_3, DMF, 80 °C

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* Heck coupling reaction of chloroarenes with olefins has been reported in the $NiBr_2$–NaI–Pd^0 system. The reaction was suppressed by *p*-DNB and it was suggested that the initial step is $S_{RN}1$-like. *p*-DNB is effective in this reaction but should not affect the following oxidative step.

$$NiX_4^{2-} + PhCl \rightleftharpoons [PhCl]^{\cdot-} + NiX_4^{\cdot-}$$
$$[PhCl]^{\cdot-} + I^- \rightleftharpoons [PhI]^{\cdot-} + PhCl^-$$
$$PhCl + [PhI]^{\cdot-} \rightleftharpoons [PhCl]^{\cdot-} + PhI \xrightarrow[CH_2{=}CHZ]{Pd^0} PhCH{=}CHZ$$

compounds **9** to **3c** varied from about 1:2 to 2:3. Because it is known that perfluorophenylpalladium bromide is much more stable than the non-fluorophenyl analogue,[17] it is reasonable to infer that the formation of the adduct of **1a** with Pd^0 should be easier than that of compound **8**. This is consistent with the results obtained and at the same time reflects the ionic character of complex **7**.

In conclusion, an indirect and direct alkynyl-dehydroxylation of polyfluorophenols was developed *via* a Heck reaction. In the catalytic PdCl$_2$–NEt$_3$ system, the initial reduction of Pd^{II} to Pd^0 may be a simple SET process. The oxidative addition of **1** to Pd^0 is proposed to be ionic.

Experimental

M.p.s and b.p.s are uncorrected. IR spectra were run on a Shimadzu-440 spectrometer with solid samples as KBr pellets and liquid samples as films. NMR spectra (chemical shifts in ppm from internal SiMe$_4$ for ^{1}H and from external CF$_3$CO$_2$H for ^{19}F, positive for upfield shifts) were recorded on an EM-360 NMR spectrometer at 60 MHz. The mass spectra were obtained on an MS-4201 instrument. DMF was dried over CaH$_2$ and NEt$_3$ over KOH before use. Silica gel (10–40 μ) was used for column chromatography.

Starting Materials.—The compounds H(CF$_2$CF$_2$)$_n$O(CF$_2$)$_2$SO$_2$F (n = 1, 3) were easily synthesized by the reduction of I(CF$_2$CF$_2$)$_n$O(CF$_2$)$_2$SO$_2$F (n = 1, 3) (commercial product), which were prepared according to ref. 18. Compound **4c** was prepared according to ref. 19.

Perfluorophenyl trifluoromethanesulfonate **1a**. (CF$_3$SO$_2$)$_2$O (4.1 g, 50 mmol) was added dropwise during 2 h to a mixture of C$_6$F$_5$OH (9.3 g, 50 mmol), NEt$_3$ (8 cm^3) and bis(2-methoxyethyl) ether (20 cm^3) with stirring at room temperature and the mixture was stirred for a further 6 h. The water (60 cm^3) was added and the organic layer was washed with water until it was neutral; distillation gave the title compound **1a** (11.0 g, 70%); b.p. 72–74 °C/40 mmHg; ν_{max}/cm^{-1} 3000, 2670, 1650, 1445, 1220 and 800; δ_F(CDCl$_3$) –2.6 (3 F, s), 75.8 (2 F, d), 78.9 (1 F, t) and 86.0 (2 F, t); *m/z* (%) 316 (M$^+$, 5), 184 (C$_6$F$_5$OH$^+$, 100), 183 (C$_6$F$_5$O$^+$, 12), 133 (43) and 69 (CF$_3$$^+$, 88).

p-*Chlorotetrafluorophenyl trifluoromethanesulfonate* **1d**. B.p. 80–82 °C/40 mmHg, yield 62% (Found: C, 25.2; Cl, 10.7; F, 39.75. Calc. for C$_7$Cl–F$_7$O$_3$S: C, 25.27; Cl, 10.66; F, 39.99%); ν_{max}/cm^{-1} 3020, 1520, 1450, 1250, 1225 and 800; δ_F(CDCl$_3$) –2.8 (3 F, s), 63.8 (2 F, d) and 75.2 (2 F, d); *m/z* (%) 334 (M$^+$, 2), 332 (M$^+$, 5), 199 (C$_6$F$_4$ClO$^+$, 100), 133 (CF$_3$SO$_2$$^+$, 12) and 69 (CF$_3$$^+$, 9).

Perfluorophenyl 5H-3-*oxaperfluoropentanesulfonate* **1b**. Compound **1b** was prepared according to ref. 4, b.p. 53–55 °C/1.5 mmHg, yield 80% (Found: C, 26.0; F, 53.1; S, 7.3. Calc. for C$_{10}$HF$_{13}$O$_4$S: C, 25.87; F, 53.21; S, 6.91%); ν_{max}/cm^{-1} 3000, 2660, 1655, 1480, 1320 and 775; δ_F(CDCl$_3$) 4.3 (2 F, s), 11.2 (2 F, s), 36.1 (2 F, s), 60.7 (2 F, d), 74.6 (2 F, d), 76.4 (1 F, t) and 83.9 (2 F, t); *m/z* (%) 464 (M$^+$, 5), 400 (26), 231 (43), 184 (100) and 100 (C$_2$F$_4$$^+$, 6).

p-*Chlorotetrafluorophenyl* 5H-3-*oxaperfluoropentanesulfonate* **1e**. B.p. 60–62 °C/1.5 mmHg, yield 78% (Found: C, 24.8; Cl, 7.2; F, 47.2. Calc. for C$_{10}$HClF$_{12}$O$_4$S: C, 24.99; Cl, 7.38; F, 47.44%); ν_{max}/cm^{-1} 3000, 2480, 1660, 1385, 1205 and 780; δ_F(CDCl$_3$) 4.5 (2 F, s), 11.4 (2 F, s), 35.9 (2 F, s), 61.0 (2 F, d), 64.0 (2 F, d) and 75.3 (2 F, d); *m/z* (%) 482 (M$^+$, 2), 480 (M$^+$, 6), 200 (C$_6$ClF$_4$OH$^+$, 100), 100 (CF$_2$CF$_2$$^+$, 4).

Perfluorophenyl 9H-3-*oxaperfluorononanesulfonate* **1c**. B.p. 78–80 °C/0.1 mmHg, yield 70% (Found: C, 23.6; F, 59.7; S, 5.1. Calc. for C$_{14}$HF$_{21}$O$_4$S: C, 23.81; F, 60.06; S, 4.82%); ν_{max}/cm^{-1} 3000, 2650, 1650, 1475, 1310, 1140 and 840; δ_F[(CD$_3$)$_2$CO] 4.5 (2 F, s), 6.0 (2 F, s), 36.2 (2 F, s), 45.8 (2 F, s), 46.9 (2 F, s), 48.9 (2 F, s), 52.8 (2 F, s), 61.0 (2 F, d), 74.8 (2 F, d), 77.0 (1 F, t) and 84.2 (2 F, t); *m/z* (%) 664 (M$^+$, 7), 601 (81), 231 (68) and 183 (100).

Typical Procedure for the Pd(PPh$_3$)$_2$Cl$_2$-*catalysed Reaction of Compounds* **1** *and* **2**.—A mixture of **1a** (1.58 g, 5 mmol), **2b** (1.53 g, 15 mmol), NEt$_3$ (3 cm^3), Pd(PPh$_3$)$_2$Cl$_2$ (175 mg, 0.25 mmol) and DMF (5 cm^3) were stirred at 80 °C for 12 h and then diluted with water (15 cm^3) and extracted with ether (3 × 8 cm^3). The organic layer was washed with water until it was neutral and then dried (MgSO$_4$). After the solvent was removed, the oily residue was purified by column chromatography on silica gel using ether–light petroleum (1:10) as eluent to give **3c** (2.6 g, 90%). In order to detect remaining diethylamine, water (2 cm^3) was added and the mixture was stirred at room temp. for several h and then distilled under reduced pressure. NHEt$_2$ [4% based on Pd(PPh$_3$)$_2$Cl$_2$] was detected by gas phase chromatography.

2-*Perfluorophenyl*-1-*phenylacetylene* **3c**. M.p. 92–93 °C (lit.,[10] 92–93 °C); ν_{max}/cm^{-1} 2925, 2220 (C≡C), 1520 and 1180; δ_H(CDCl$_3$) 7.2 (m); δ_F(CDCl$_3$) 61.6 (2 F, d), 79.0 (1 F, t) and 87.7 (2 F, t); *m/z* (%) 269 (M$^+$ + 1, 22), 268 (M$^+$, 100), 248 (M$^+$ – HF, 9), 202 (12) and 134 (18).

1-*Perfluorophenyl-2-trimethylsilylacetylene* **3a**. ν_{max}/cm^{-1} 2965, 2210 (C≡C), 1510, 1460, 1200 and 970; δ_H[(CD$_3$)$_2$CO] 0.30 (s); δ_F[(CD$_3$)$_2$CO] 61.6 (2 F, d), 78.1 (1 F, t) and 87.5 (2 F, t); *m/z* (%) 264 (M$^+$, 9.22), 249 (M$^+$ – CH$_3$, 100), 191 (C$_8$F$_5$$^+$, 15), 124 (15), 99 (15) and 47 (14).

1-(p-*Chlorotetrafluorophenyl*)-2-*trimethylsilylacetylene* **3b**. ν_{max}/cm^{-1} 2965, 2215 (C≡C), 1500 and 1205; δ_H(CDCl$_3$) 0.35 (s); δ_F(CDCl$_3$) 60.5 (2 F, d) and 66.7 (2 F, d); *m/z* (%) 282 (M$^+$, 6), 280 (M$^+$, 15), 267 (M$^+$ – CH$_3$, 37) and 265 (M$^+$ – CH$_3$, 100).

1-(p-*Chlorotetrafluorophenyl*)-2-*phenylacetylene* **3d**. M.p. 96–97 °C (Found: C, 59.0; H, 1.5; Cl, 12.3; F, 26.9. Calc. for C$_{14}$H$_5$ClF$_4$: C, 59.07; H, 1.77; Cl, 12.45; F, 26.70%); ν_{max}/cm^{-1} 2180 (C≡C), 1470, 1415, 1365, 1225 and 1060; δ_H(CDCl$_3$) 7.57 (m); δ_F(CDCl$_3$) 58.7 (2 F, d) and 63.9 (2 F, d); *m/z* (%) 286 (M$^+$, 36), 284 (M$^+$, 100), 248 (M$^+$ – HCl, 11) and 200 (7).

1-*Perfluorophenylhexyne* **3e**. B.p. 90–92 °C/ mmHg (Found: C, 57.95; H, 3.65; F, 38.2. Calc. for C$_{12}$H$_9$F$_5$: C, 58.06; H, 3.66; F, 38.27%); ν_{max}/cm^{-1} 2955, 2925, 2230 (C≡C), 1520, 1320 and 990; δ_H(CDCl$_3$) 0.86 (3 H, t), 1.47 (4 H, m) and 2.37 (2 H, t); δ_F(CDCl$_3$) 60.0 (2 F, d), 77.6 (1 F, t) and 85.8 (2 F, t); *m/z* (%) 248 (M$^+$, 25), 234 (M$^+$ + 1 – CH$_3$, 14), 233 (M$^+$ – CH$_3$, 100), 219 (M$^+$ – C$_2$H$_5$, 14), 192 (29) and 43 (35).

1-(p-*Chlorotetraflurophenyl*)*hexyne* **3f**. B.p. 94–97 °C/25 mmHg (Found: C, 54.2; H, 3.0; F, 28.7. Calc. for C$_{12}$H$_9$ClF$_4$: C, 54.24; H, 3.02; F, 28.74%); ν_{max}/cm^{-1} 2970, 2940, 2220 (C≡C), 1485, 1285, 1190 and 880; δ_H(CDCl$_3$) 0.90 (3 H, t), 1.40 (2 H, m), 1.46 (2 H, m) and 2.31 (2 H, t); δ_F(CDCl$_3$) 60.2 (2 F, d) and 66.0 (2 F, d); *m/z* (%) 266 (M$^+$, 12), 264 (M$^+$, 36), 263 (M$^+$ – 1, 50), 251 (M$^+$ – CH$_3$, 43), 249 (100) and 200 (17).

1-*Perfluorophenylheptyne* **3g** (Found: C, 59.6; H, 4.5; F, 36.0. Calc. for C$_{13}$H$_{11}$F$_5$: C, 59.54; H, 4.24; F, 36.23%); ν_{max}/cm^{-1} 2990, 2890, 2270 (C≡C) 1520, 1440, 1330, 1000 and 740; δ_H(CDCl$_3$) 1.0 (3 H, t), 1.3 (3 H, m) and 2.4 (2 H, t); δ_F(CDCl$_3$) 60.0 (2 F, d), 78.2 (1 F, t) and 87.1 (2 F, t); *m/z* (%) 262 (M$^+$, 15), 247 (M$^+$ – CH$_3$, 10), 233 (M$^+$ – C$_2$H$_5$, 56), 205 (52), 55 (30) and 42 (100).

1-*Perfluorophenyldecyne* **3h**. (Found: C, 63.2; H, 5.6; F, 31.1. Calc. for C$_{16}$H$_{17}$F$_5$: C, 63.1; H, 5.6; F, 31.2%); ν_{max}/cm^{-1} 2960, 2890, 2270 (C≡C), 1520, 1475, 1385, 1035 and 730; δ_H(CDCl$_3$) 1.0 (3 H, t), 1.2–1.4 (12 H, m) and 2.3 (2 H, t); δ_F(CDCl$_3$) 61.0 (2 F, d), 78.6 (1 F, t) and 87.6 (2 F, t); *m/z* (%) 304 (M$^+$, 2), 303 (M$^+$ – 1, 1), 261 (M$^+$ – C$_3$H$_7$, 19), 233 (61), 81 (41) and 55 (100).

Pd(PPh$_3$)$_4$-*catalysed Reaction of Compounds* **1** *and* **2**.—This reaction was similar to the Pd^{II}-catalysed one, but was carried out under an atmosphere of nitrogen.

Typical Procedure for One-pot Reaction of Compounds **2**, **4** *and* **5** *Catalysed by* $Pd(PPh_3)_2Cl_2$.—A mixture of **2b** (1.53 g, 15 mmol), **4a** (1.50 g, 5 mmol), **5a** (0.98 g, 5 mmol), NEt_3 (3.0 cm^3) and $Pd(PPh_3)_2Cl_2$ (169 mg, 0.25 mmol) in DMF (5 cm^3) was stirred at 80 °C for 14 h. After work-up as above **3c** (1.0 g, 76%) was obtained.

Competing Reaction of **1a** *with Phenyl Trifluoromethanesulfonate* **8**.—Compound **1a** (3.16 g, 10 mmol), $CF_3SO_3C_6H_5$ (2.26 g, 10 mmol), **2b** (1.02 g, 10 mmol), NEt_3 (2 cm^3) and $Pd(PPh_3)_2Cl_2$ (320 mg, 0.5 mmol) were added to DMF (5 cm^3). The mixture was stirred at 80 °C. Five samples (1 cm^3) were taken out every 2 h for a total of 10 h. After work-up as above, the samples were purified by preparative thin layer chromatography using ether–light petroleum (1:10) as eluent.

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References

1 P. I. Stang, M. Hanaka and L. R. Subramanian, *Synthesis*, 1982, 85; W.-Y. Huang and Q.-Y. Chen, in *The Chemistry of Sulphonic Acids, Esters, and their Derivatives*, eds. S. Patai and Z. Rapport, 1991, Wiley, Chichester, p. 917.

2 Q.-Y. Chen, R.-X. Zhu, Z.-Z. Li, S.-D. Wang and W.-Y. Huang, *Acta Chim. Sinica*, 1982, **40**, 337.

3 Q.-Y. Chen and S.-Z. Zhu, *Acta Chim. Sinica*, 1982, **40**, 670; 1983, **41**, 1044.

4 Q.-Y. Chen and S.-Z. Zhu, *Acta Chim. Sinica*, 1983, **41**, 1153; 1984, **42**, 541.

5 Q.-Y. Chen and M.-F. Chen, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1071.

6 S. Cacchi, P. G. Ciattini, E. Morera and G. Ortar, *Tetrahedron Lett.*, 1987, **28**, 3039.

7 Q.-Y. Chen and Z.-Y. Yang, *Tetrahedron Lett.*, 1986, **27**, 1171; A. Arcadi, S. Cacchi and F. Marinelli, *Tetrahedron Lett.*, 1989, **30**, 2581; J. W. Tilley and S. Zawoiski, *J. Org. Chem.*, 1988, **53**, 386.

8 Q.-Y. Chen and Y.-B. He, *Tetrahedron Lett.*, 1987, **28**, 2387; *Youji Huaxue*, 1987, 474 (*Chem. Abstr.*, 1988, **109**, 109940b); *Chin. J. Chem.*, 1990, 451; G. K. Cook, W. J. Hornback, C. J. Jordan, J. H. McDonald I and J. E. Munroe, *J. Org. Chem.*, 1989, **54**, 5828.

9 J. E. Soln, A. F. Garito, K. N. Desai, R. S. Narang, M. Kuzyk, *Makromol. Chem.*, 1979, **180**, 2975; Y. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, 1991, **51**, 229.

10 R. Filler and E. W. Heffern, *J. Org. Chem.*, 1967, **32**, 3249; R. G. Gastinger, E. F. Tokas and M. D. Rausch, *J. Org. Chem.*, 1978, **43**, 159.

11 Y. D. Zhang and J. X. Wen, *J. Fluorine Chem.*, 1990, **47**, 533; B. V. Ngulyn, Z.-Y. Yang and D. J. Burton, *J. Fluorine Chem.*, 1990, **50**, 265.

12 R. F. Heck, in *Palladium-Catalyzed Vinylation of Organic Halide*, Organic Reaction, ed. W. G. Dauben, Wiley, New York, 1982, vol. **27**, p. 345; R. F. Heck and J. P. Nolley, Jr., *J. Org. Chem.*, 1972, **12**, 146.

13 W. Cabri, I. Candini, S. DeBernardinis, F. Fraucalanci and S. Penco, *J. Org. Chem.*, 1991, **56**, 5796; P. P. Nicholas, *J. Org. Chem.*, 1987, **52**, 5266; J. M. Saa, M. Dopico, G. Martoroll, A. Garcia-Raso, *J. Org. Chem.*, 1990, **55**, 991.

14 M. A. Kellett, D. G. Whitten and I. R. Gould, *J. Am. Chem. Soc.*, 1991, **113**, 358.

15 J. J. Bozell and C. E. Vogt, *J. Am. Chem. Soc.*, 1988, **110**, 2655.

16 F. Ozawa, A. Kubo and T. Hayashi, *J. Am. Chem. Soc.*, 1991, **113**, 1417; R. J. Hinkle, P. J. Stang and M. H. Kowalski, *J. Org. Chem.*, 1990, **55**, 5033.

17 J. K. Stille, Oxidative addition and reductive elimination, in *The Chemistry of the Metal–Carbon Bond*, ed. F. R. Hartley and S. Patai, 1985, Wiley, New York, vol. 2, pp. 649–651.

18 Perfluorosulfonic Acid Group, Shanghai Institute of Organic Chemistry, *Acta Chim. Sinica*, 1978, **37**, 315 (*Chem. Abstr.*, 1980, **93**, 113886g); G. A. Bargigia, G. Laporiccio and M. Pianca, *J. Fluorine Chem.*, 1982, **19**, 403.

19 C-Y. Guo, Y.-F. Zhang and Q.-Y. Chen, *Huaxue Xuebao*, 1982, **40**, 828.

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