Reactions involving fluoride ion. Part 44.[1] Synthesis and chemistry of aromatics with bulky perfluoroalkyl substituents

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The observable perfluoroalkyl carbanion **1a**, generated by addition of fluoride ion to perfluoroalkene **1**, reacts efficiently with benzyl bromide and a range of related derivatives **3a**–**g** and this provides methodology for the preparation of aromatic rings with large perfluoroalkyl substituents. Purification of the perfluoroalkylated products **4a**–**g** was accomplished by selective extraction from the reaction medium by a perfluorocarbon fluid. Products obtained upon nitration and bromination of **4a** demonstrate that the orientation of electrophilic substitution in **4a** is controlled predominantly by the steric rather than electronic effects of the polyfluoroalkyl group. The methodology was applied to the preparation of azo-dyes **15a**–**c** that are completely soluble in perfluorocarbon fluids.

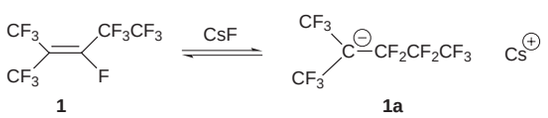
Introduction

The development of efficient methodology for the preparation of organic molecules bearing perfluoroalkyl substituents is an important target because of the profound changes in physical, chemical and biological properties that can occur upon incorporation of a perfluoroalkyl group into an organic substrate.[2] For example, there are many pharmaceuticals and plant protection agents[3] which owe their enhanced biological activity to the presence of a trifluoromethyl group in their structures. Furthermore, long, highly lipophilic perfluoroalkyl chains can impart valuable properties of *oil* (unique) and water repellency to surfaces, leading to soil resistance, and this effect has been exploited by the surfactant and textile treatment industries.[4]

Perfluoroalkyl substituents can also markedly enhance the solubility of a substrate in perfluorocarbon fluids and this unusual property has been used to great effect recently in the growing field of biphasic fluorous catalysis[5,6] and fluorous synthesis.[7]

Although current methodology for the introduction of perfluoroalkyl substituents into organic molecules includes free radical[8] (*e.g.* derived from perfluoroalkyl iodides), electrophilic[9] (*e.g.* 'FITS' reagents) and nucleophilic[10] (*e.g.* CF_3SiMe_3) perfluoroalkylating reagents, many established methodologies are concerned with the preparation of trifluoromethyl derivatives,[11–13] while processes for the incorporation of longer chain perfluoroalkyl groups into aromatic systems remain less developed.

In this series,[1] we have been pursuing a 'mirror image' relationship between the role of fluoride ion in fluorocarbon chemistry with that of the proton in hydrocarbon chemistry. For example, we established that addition of fluoride ion to some perfluoroalkenes *e.g.* **1**, can result in the preparation of stable, observable perfluorinated carbanions[14] **1a** (Scheme 1), and this



Scheme 1

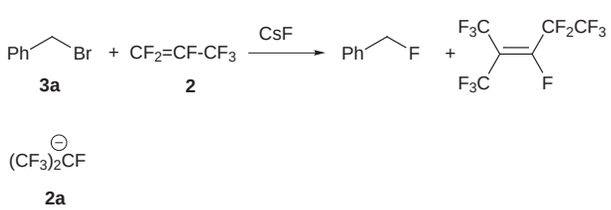
chemistry can be considered to mirror the now classic developments by Olah and co-workers in carbocation chemistry.[15]

Several perfluoroalkyl carbanion species can be prepared by the addition of fluoride ion to a fluoroalkene and the intermediate perfluoroalkyl carbanions, *e.g.* **2a**, can react with a variety of electrophilic reagents leading to an extensive chemistry, which includes oligomerisations, negative Friedel–Crafts reactions and rearrangements.[16,17]

In this paper, we describe the synthesis of a variety of perfluoroalkylated benzyl systems using this methodology, in which the electrophilic species are benzyl bromide or derivatives, as a general route to the preparation of aromatic systems containing bulky perfluoroalkyl substituents. Application of these procedures to the synthesis of novel azo-dyes that are completely soluble in perfluorocarbon fluids is described.

Results and discussion

We have established previously that perfluoroisopropyl anions **2a**, derived from the addition of fluoride ion to hexafluoropropene **2**, can be trapped by a variety of electrophiles including perfluoroalkenes[16,17] and perfluoroheterocycles.[18] However, our initial attempts at reaction between benzyl bromide **3a**, hexafluoropropene **2** and fluoride ion, under a variety of conditions, were unsuccessful in that no perfluoroalkylated aromatic derivatives were obtained. Benzyl fluoride, derived from displacement of bromide by fluoride ion, and hexafluoropropene dimer were obtained as the major products (Scheme 2).

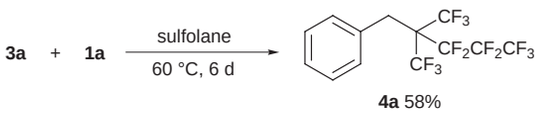


Scheme 2

We deduced that these reactions were unsuccessful due to the low concentration of perfluorocarbanion **2a** in the reaction mixture and, consequently, we explored the possibility of increasing the concentration of perfluoroalkyl carbanions by reacting preformed solutions of stable perfluorocarbanions with benzyl bromide.

Solutions of perfluorocarbanion **1a** were prepared by stirring fluoroalkene **1** with dry caesium fluoride in sulfolane for 2 days at room temperature, after which ^{19}F NMR analysis[14] of the reaction mixture indicated complete conversion to carb-

anion **1a**. Addition of **3a** and heating at 60 °C for 6 days resulted in the disappearance of carbanion **1a** (as revealed by ^{19}F NMR analysis of a sample of the reaction mixture) and the appearance of benzyl fluoride together with the perfluoroalkylated product **4a** (Scheme 3).



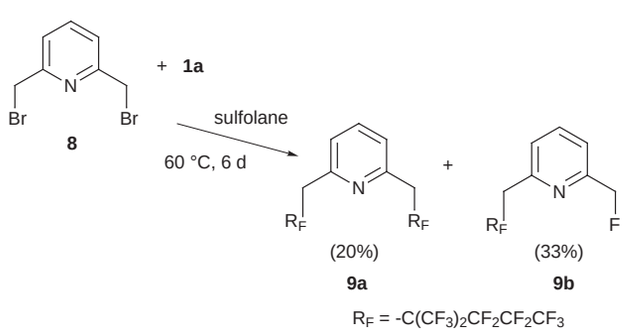
Scheme 3

Isolation of perfluoroalkylated aromatic derivatives from polar aprotic solvents such as sulfolane has, in the past, presented major practical difficulties.[19,20] However, in this case, we found that **4a** could be selectively and completely extracted from the sulfolane and benzyl fluoride impurity by a perfluorocarbon fluid, such as Fluorinert® (3M Co.), because the large perfluoroalkyl substituent renders the aromatic substrate **4a** preferentially soluble in such media while sulfolane is completely insoluble in the perfluorocarbon. This was established by examination of the sulfolane layer by ^{19}F NMR spectroscopy; only a residual fluorine signal corresponding to benzyl fluoride could be detected. Removal of the perfluorocarbon fluid by distillation gave crude perfluoroalkylated product **4a** which could be further purified by column chromatography.

A range of functionalised perfluoroalkylated benzyl derivatives were prepared in a similar manner and 3-bromo-, 4-bromo-, 3-nitro- and 4-nitro-benzyl bromides **3c**–**f** were perfluoroalkylated efficiently (Table 1). However, perfluoroalkylation of 2-bromobenzyl bromide **3b** gave lower yields of product **4b**, presumably due to steric hindrance by the bromine atom *ortho* to the bromomethyl group.

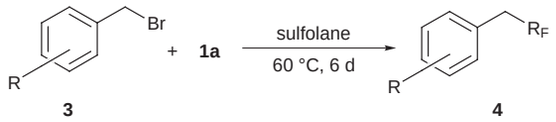
The possibility of incorporating two bulky perfluoroalkyl chains into an aromatic substrate using this methodology was demonstrated in reactions involving xylylene dibromides **5a**–**c**. By a similar process to that described above, reaction of **5a**–**c** with excess of carbanion **1a** gave mixtures of the corresponding bis-perfluoroalkylated products **6a**–**c** and perfluoroalkyl fluoride derivatives **7a**–**c** (Table 2). 1,2-Xylylene dibromide **5a** gave predominantly the fluoride derivative **7a** due to the steric hindrance of the large perfluoroalkyl group preventing attack by a second carbanion **1a**, whereas 1,3- and 1,4-xylylene dibromides **5b**–**c** gave mainly the di-perfluoroalkylated derivatives **6b**, **c**.

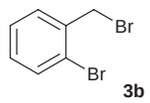
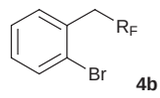
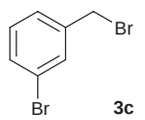
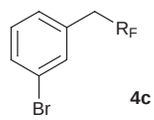
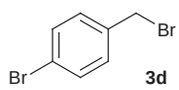
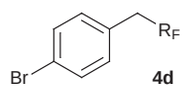
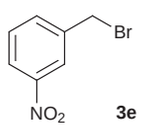
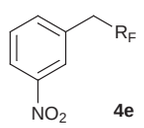
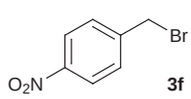
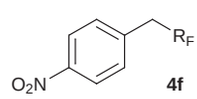
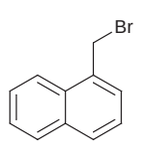
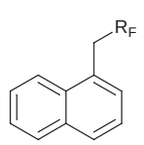
Similarly, the pyridyl system **8** gave a mixture of two products **9a**,**b** upon reaction with carbanion **1a** (Scheme 4).



Scheme 4

Table 1 Perfluoroalkylation of benzyl bromide derivatives



ArCH$_2$Br **3**	Product **4**	Yield (%)
 **3b**	 **4b**	34
 **3c**	 **4c**	64
 **3d**	 **4d**	62
 **3e**	 **4e**	64
 **3f**	 **4f**	60
 **3g**	 **4g**	58

ppm, a shift of about 1 ppm from the CH_2 group in the appropriate starting benzyl bromide derivative. Full assignments of the ^{1}H NMR spectra were accomplished with the aid of NOE and ^{1}H–^{1}H COSY experiments. For example, in an NOE experiment on a sample of **4b**, irradiation of the methylene resonance showed an enhancement of the signal at 7.43 ppm which must, therefore, be attributed to the hydrogen atom on the aromatic ring *ortho* to the -CH_2R_F group (H-3). The unambiguous assignment of H-3, combined with information derived from a ^{1}H–^{1}H COSY experiment, which shows the coupling between H-3 and the other ring hydrogen atoms, allowed a full interpretation of the ^{1}H NMR spectrum and interpretation of the ^{13}C NMR spectrum followed simply from a subsequent ^{1}H–^{13}C HETCOR experiment. Spectral data for all products **4,6,7,9** synthesised by the present methodology could be interpreted similarly.

Characterisation of the products

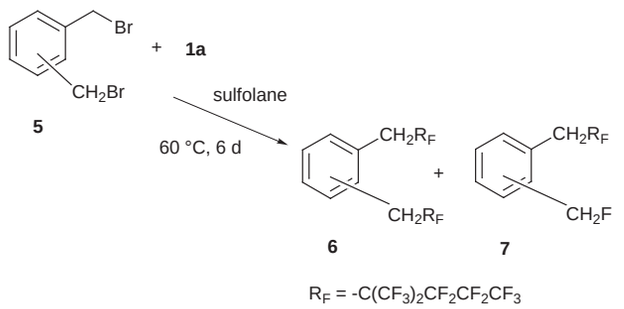
All products were fully characterised by elemental analysis, mass spectrometry and NMR spectroscopy. The ^{19}F NMR spectra of all products consisted of four resonances at around −62, −80, −106 and −125 ppm, with relative intensities of 6:3:2:2 respectively, consistent with the presence of the -$C(CF_3)_2CF_2CF_2CF_3$ group. In the ^{1}H NMR spectra, the methylene groups appear as characteristic singlets at around 3.5

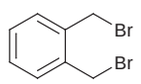
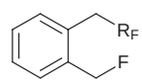
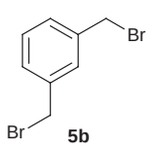
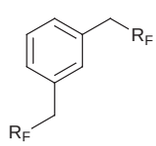
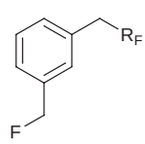
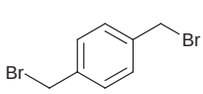
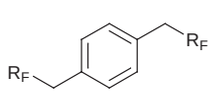
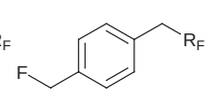
Chemistry of perfluoroalkylated derivatives

We were interested in evaluating the effect of the -CH_2R_F group on the reactivity of the aromatic ring in electrophilic substitution reactions.

Nitration of **4a** by nitronium tetrafluoroborate in sulfolane[21] gave a mixture of the *ortho*, *meta* and *para* nitro derivatives in the ratio 1:3.8:3.8 (Scheme 5). Since both the *meta*-**4e** and *para*-**4f** nitro derivatives had been prepared unambiguously

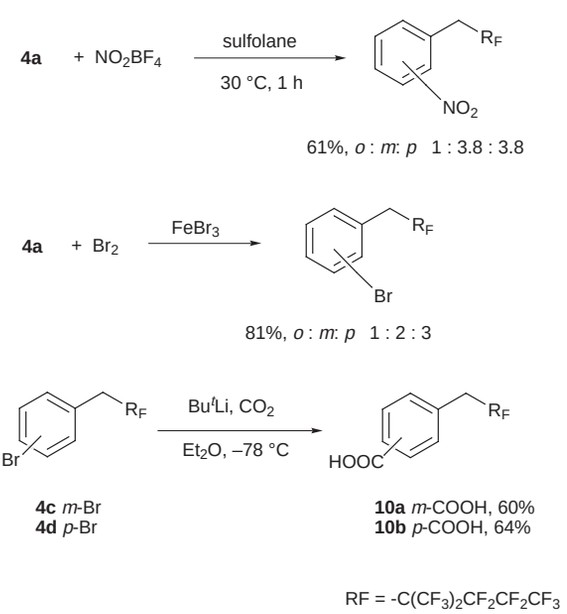
Table 2 Polyperfluoroalkylation of xylylene dibromides



$ArCH_2Br$	Products (% yield)	
 **5a**	 (12%) **6a**	 (66%) **7a**
 **5b**	 (56%) **6b**	 (21%) **7b**
 **5c**	 (59%) **6c**	 (22%) **7c**

previously (Table 1), the identity of the products and the ratio of isomers obtained were simple to deduce by GC–MS.

Also, bromination of **4a** by bromine catalysed by ferric bromide[22] gave *ortho*-, *meta*- and *para*-bromobenzene derivatives in the ratio 1 : 2 : 3 (Scheme 5).

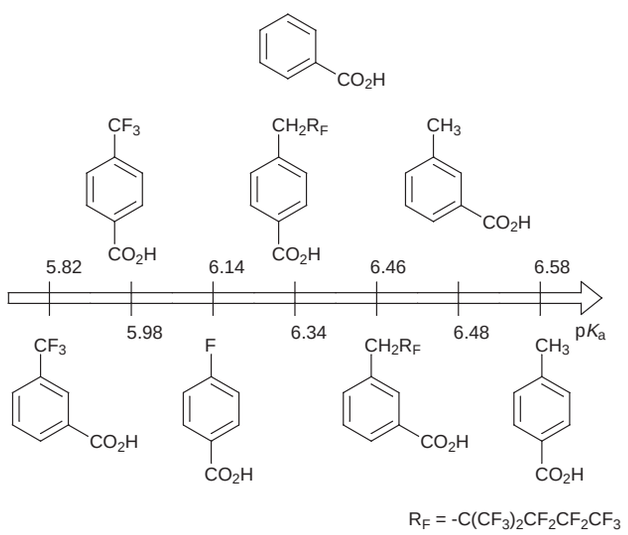


Scheme 5

Of course, we would expect an electron-withdrawing substituent attached to an aromatic ring to give mainly *meta* derivatives and an electron-donating substituent to give predominantly *ortho* and *para* products, but in this case, electrophilic substitution occurs at all three possible sites and gives similar amounts of the *meta* and *para* derivatives. Thus, it appears that the R_FCH_2- group imparts little net electron-donating or electron-withdrawing effect on the aromatic ring, (also, see pK_a measurements below) and the ratio of isomers obtained must be largely governed by steric control, the least hindered sites, *meta* and *para*, being most reactive. It is well known that the steric demand of a substituent can have a great effect on the ratios of isomers produced upon electrophilic substitution; for example compare ratios of isomers obtained in the nitration of toluene and *tert*-butylbenzene.[23]

To confirm the lack of an overall electronic influence of the R_FCH_2- group on the aromatic ring, we compared the pK_a values of the benzoic acid derivatives **10** with other related acids. The acids **10** were prepared (Scheme 5) by selective debromometallation of the bromobenzene derivatives **4c,d** using *tert*-butyllithium and reaction with solid carbon dioxide.[24] Surprisingly, deprotonation at the benzylic sites did not occur, as observed in attempted deuterium exchange reactions.

The pK_a values of acids **10** and a series of related substituted benzoic acid derivatives were measured, following literature methods,[25] in a dioxane–water solvent system at 24 °C, and the results are depicted in Scheme 6. These measurements confirm

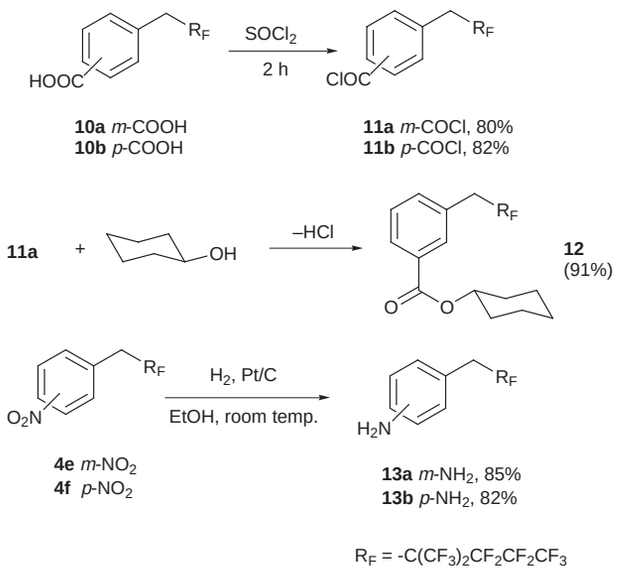


Scheme 6

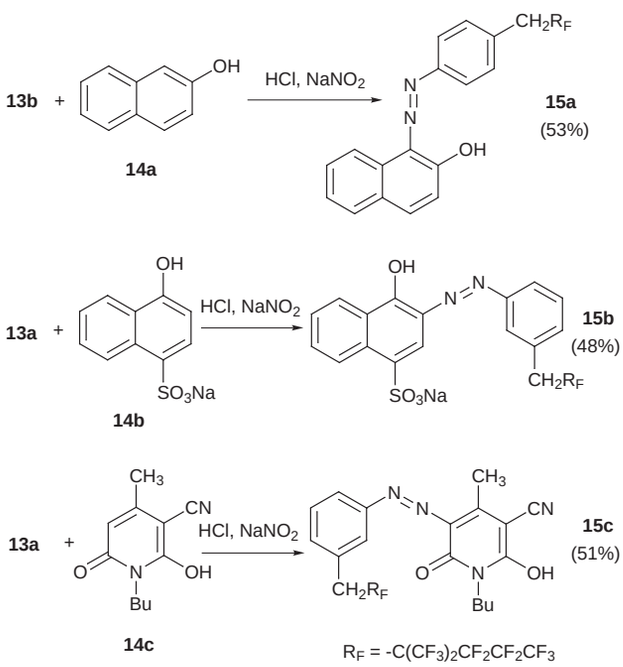
that the -CH_2R_F group imparts little overall electronic influence on the aromatic ring, as the pK_a of **10b** is identical with benzoic acid itself, and is a result consistent with the observed orientation of the electrophilic substitution reactions discussed above.

The perfluoroalkylated acids **10** could be converted to the corresponding acid chlorides **11** upon reaction with thionyl chloride[26] and esterification of **11a** with cyclohexanol also proceeded very efficiently to give **12** (Scheme 7). Cyclohexanol can be considered as a model for cellulose and, therefore, we consider that this series of reactions demonstrates that the present methodology could be applied to the introduction of perfluoroalkyl groups onto surfaces which can be rendered nucleophilic for use in textile treatment.

Perfluoroalkylated anilines **13** were prepared (Scheme 7) by reduction of the nitrobenzene derivatives **4e**, **f** using hydrogen and a platinum on carbon catalyst.[27] The corresponding diazonium salts formed efficiently upon reaction of the anilines with nitrous acid and were coupled with several activated aromatic substrates **14a–c** to form three azo-dye derivatives (Scheme 8) **15a–c** respectively.[26] The azo-dyes were all shades of orange in colour (extinction coefficients included in Experimental



Scheme 7



Scheme 8

section) and the presence of the large perfluoroalkyl group in the structure of each azo-dye **15a**–**c**, renders the dyes *completely soluble in perfluorocarbon fluids*, such as Fluorinert® (3M Co). To the best of our knowledge, **15a**–**c** represent the first azo-dyes that are completely soluble in perfluorocarbon media.

Experimental

All starting materials were either obtained commercially (Aldrich) or prepared by literature procedures, and all solvents were dried before use. Sulfolane was distilled under vacuum from sodium and stored over 4 Å molecular sieves under a nitrogen atmosphere. NMR spectra were recorded in deuteriochloroform unless otherwise stated on either a Varian Gemini 200, a Varian VXR 400S or a Bruker AC250 NMR spectrometer with tetramethylsilane and trichlorofluoromethane as internal standards. In ^{19}F NMR spectra, upfield shifts are quoted as negative. Coupling constants (J) are given in Hz. Mass spectra were recorded on either a VG 7070E spectrometer or a Fissons VG Trio 1000 spectrometer coupled with a Hewlett Packard 5890 series II gas chromatograph. Accurate mass measurements were performed by the EPSRC Mass Spectrometry Service, Swansea, UK. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer while elemental analyses were obtained on either a Perkin-Elmer 240 or a Carlo Erba Elemental Analyser. Melting points and boiling points were recorded at atmospheric pressure and are uncorrected. Column chromatography was performed using silica gel (Merck No. 9385) and silica plates (Merck) were used for TLC analysis. The pK_a values of acids **10** were measured using a Beckman research pH meter in 1,4-dioxane–water (1:1 v/v) solution at 24 °C according to literature methods.[25]

Perfluoroalkylation reactions

General procedure. A flask was charged with perfluoro-2-methylpent-2-ene **1**, dry caesium fluoride and sulfolane. The solution was stirred continuously at 30–35 °C for 40 h and monitored by ^{19}F NMR until quantitative conversion of **1** to the perfluoroalkyl-carbanion **1a** was observed;[14] δ_F (sulfolane) −41.2 [6F, s, $(CF_3)_2C$], −79.7 (3F, s, CF_3CF_2), −92.0 (2F, s, $CF_2CF_2CF_3$), −125.4 (2F, s, CF_2CF_3). The aromatic bromide (**3a**–**g**, **5a**–**c**, **8**) was added slowly under nitrogen to the mixture which was then heated with stirring at 65 °C for 6 days. The mixture was filtered and extracted by a perfluorocarbon fluid such as Fluorinert® FC-84 (3M Co.) (2 × 30 ml). The solvent was cautiously removed by distillation under reduced pressure to afford perfluoroalkylated product which could be further purified by column chromatography on silica gel if required.

[(Perfluoro-2-methylpentan-2-yl)methyl]benzene 4a. Compound **1** (16.8 g, 56 mmol), caesium fluoride (7.9 g, 52 mmol) and benzyl bromide **3a** (5.6 g, 33 mmol) in sulfolane (40 ml) gave, after column chromatography using *n*-hexane–light petroleum (1:1) as eluant, *[(perfluoro-2-methylpentan-2-yl)-methyl]benzene* **4a**[14,28] (7.5 g, 58%) as a pale yellow liquid; ν_{max}/cm^{-1} 3041 (Ar-H), 2964 (C-H), 1263 (C-F); δ_H 3.36 (2H, s, CH_2), 7.11 (5H, s, Ph); δ_F −62.7 [6F, s, $C(CF_3)_2$], −80.5 (3F, s, CF_2CF_3), −106.4 (2F, s, $CF_2CF_2CF_3$), −123.4 (2F, s, CF_2CF_3); m/z (EI$^+$) 410 (M$^+$, 4%), 91 (100), 69 (12).

2-[(Perfluoro-2-methylpentan-2-yl)methyl]bromobenzene 4b. Compound **1** (16.2 g, 54 mmol), caesium fluoride (7.9 g, 52 mmol) and 2-bromobenzyl bromide **3b** (8.6 g, 34.6 mmol) in sulfolane (40 ml) gave *2-[(perfluoro-2-methylpentan-2-yl)-methyl]bromobenzene* **4b** (5.6 g, 34%) as a pale yellow liquid; bp 230–233 °C (Siwoloboff) (Found: C, 31.7; H, 1.2. $C_{13}H_6BrF_{13}$ requires C, 31.9; H, 1.2%); ν_{max}/cm^{-1} 1220–1272 (C-F); δ_H 3.84 (2H, s, CH_2), 7.13 (1H, t, ^3J 7.9, H-5), 7.25 (1H, t, ^3J 7.6, H-4), 7.43 (1H, d, ^3J 7.9, H-3), 7.59 (1H, d, ^3J 7.9, H-6); δ_F −61.5 [6F, s, $C(CF_3)_2$], −80.6 (3F, s, CF_2CF_3), −107.9 (2F, s, $CF_2CF_2CF_3$), −122.7 (2F, s, CF_2CF_3); δ_C {H} 31.7 (s, CH_2), 61.9 [sept, $^2J_{CF}$ 25, $C(CF_3)_2$], 109.8 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 37, CF_2CF_3), 115.1 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.9 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 34, CF_2CF_3), 122.2 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 127.1 (s, C-1), 127.2 (s, C-4), 129.7 (s, C-5), 131.6 (s, C-2), 132.6 (s, C-3), 133.7 (s, C-6); m/z (EI$^+$) 490 (M$^+$, 12%), 488 (M$^+$, 13%), 171 (94), 169 (100), 109 (15), 90 (21), 69 (14).

3-[(Perfluoro-2-methylpentan-2-yl)methyl]bromobenzene 4c. Compound **1** (16.2 g, 54 mmol), caesium fluoride (7.9 g, 52 mmol) and 3-bromobenzyl bromide **3c** (8.5 g, 34.2 mmol) in sulfolane (40 ml) gave *3-[(perfluoro-2-methylpentan-2-yl)methyl]bromobenzene* **4c** (13.2 g, 64%) as a pale yellow liquid; bp 234–236 °C (Siwoloboff) (Found: C, 31.8; H, 1.2. $C_{13}H_6BrF_{13}$ requires C, 31.9; H, 1.2%); ν_{max}/cm^{-1} 1220–1268 (C-F); δ_H 3.49 (2H, s, CH_2), 7.16 (1H, t, ^3J 7.6, H-5), 7.22 (1H, d, ^3J 7.2, H-4), 7.44 (1H, d, ^3J 8.4, H-6), 7.45 (1H, s, H-2); δ_F −62.5 [6F, s, $C(CF_3)_2$], −80.4 (3F, s, CF_2CF_3), −106.1 (2F, s, $CF_2CF_2CF_3$), −123.1 (2F, s, CF_2CF_3); δ_C {H} 32.1 (s, CH_2), 61.7

[sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 109.8 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 37, CF_2CF_3), 114.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.7 (qt, $^1J_{CF}$ 290, $^2J_{CF}$ 34, CF_2CF_3), 122.0 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 122.3 (s, C-1), 129.7 (s, C-5), 130.2 (s, C-4), 131.5 (s, C-6), 133.3 (s, C-3), 134.7 (s, C-2); *m/z* (EI$^+$) 490 (M^+, 11%), 488 (M^+, 10), 171 (92), 169 (100), 109 (23), 90 (35), 69 (17).

4-[(Perfluoro-2-methylpentan-2-yl)methyl]bromobenzene 4d. Compound **1** (16.2 g, 54 mmol), caesium fluoride (7.9 g, 52 mmol) and 4-bromobenzyl bromide **3d** (8.9 g, 36 mmol) in sulfolane (40 ml) gave *4-[(perfluoro-2-methylpentan-2-yl)methyl]-bromobenzene* **4d** (10.8 g, 62%) as a pale yellow liquid; bp 244 °C (Siwoloboff) (Found: C, 31.9; H, 1.2. $C_{13}H_6BrF_{13}$ requires C, 31.9; H, 1.2%); ν_{max}/cm^{-1} 1269 (C-F), 1220 (C-F), 700 (C-Br); δ_H 3.49 (2H, s, CH_2), 7.16 (2H, AX, J_{AX} 8.4, H-2), 7.44 (2H, AX, J_{AX} 8.4, H-3); δ_F −62.9 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.6 (2F, s, $CF_2CF_2CF_3$), −123.6 (2F, s, CF_2CF_3); δ_C {H} 32.1 (s, CH_2), 62.4 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 109.6 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 38, CF_2CF_3), 114.8 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 32, $CF_2CF_2CF_3$), 117.5 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 121.9 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 122.5 (s, C-1), 129.9 (s, C-4), 131.4 (s, C-3), 133.1 (s, C-2); *m/z* (EI$^+$) 488 (M^+, 3%), 490 (M^+, 3), 201 (11), 181 (15), 169 (100), 151 (15), 109 (21), 69 (85).

3-[(Perfluoro-2-methylpentan-2-yl)methyl]nitrobenzene 4e. Compound **1** (31.0 g, 107 mmol), caesium fluoride (15.0 g, 99 mmol) and 3-nitrobenzyl bromide **3e** (13.5 g, 62.6 mmol) in sulfolane (40 ml) gave *3-[(perfluoro-2-methylpentan-2-yl)-methyl]nitrobenzene* **4e** (18.2 g, 64%) as a pale yellow liquid; bp >250 °C (decomp., Siwoloboff) (Found: C, 34.5; H, 1.3; N, 3.0. $C_{13}H_6F_{13}NO_2$ requires C, 34.3; H, 1.3; N, 3.0%); ν_{max}/cm^{-1} 1537 (N=O), 1353 (N=O), 1243 (br, C-F); δ_H (CD_3CN) 3.80 (2H, s, CH_2), 7.58 (1H, t, ^3J 8.0, H-5), 7.75 (1H, d, ^3J 7.6, H-4), 8.19 (1H, d, ^3J 8.8, H-6), 8.2 (1H, s, H-2); δ_F (CD_3CN) −62.8 [6F, s, $C(CF_3)_2$], −81.0 (3F, s, CF_2CF_3), −106.4 (2F, s, $CF_2CF_2CF_3$), −123.3 (2F, s, CF_2CF_3); δ_C {H} (CD_3CN) 32.6 (s, CH_2), 61.7 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 110.6 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 37, CF_2CF_3), 115.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 118.6 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 34, CF_2CF_3), 123.0 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 124.3 (s, C-6), 127.4 (s, C-2), 130.5 (s, C-5), 134.1 (s, C-3), 139.0 (s, C-4), 149.0 (s, C-1); *m/z* (EI$^+$) 455 (M^+, 14%), 169 (17), 151 (25), 136 (62), 109 (100), 90 (20), 78 (38), 69 (77).

4-[(Perfluoro-2-methylpentan-2-yl)methyl]nitrobenzene 4f. Compound **1** (41 g, 141 mmol), caesium fluoride (20 g, 133 mmol) and 4-nitrobenzyl bromide **3f** (18.6 g, 86 mmol) in sulfolane (40 ml) gave *4-[(perfluoro-2-methylpentan-2-yl)methyl]-nitrobenzene* **4f** (23.4 g, 60%) as a pale yellow liquid; bp >250 °C (decomp., Siwoloboff) (Found: C, 34.6; H, 1.2; N, 3.2. $C_{13}H_6F_{13}NO_2$ requires C, 34.3; H, 1.3; N, 3.1%); ν_{max}/cm^{-1} 1609 (C=C), 1530 (N=O), 1351 (N=O), 1242 (br, C-F); δ_H (CD_3CN) 3.78 (2H, s, CH_2), 7.58 (2H, AX, J_{AX} 8.8, H-3), 8.16 (2H, AX, J_{AX} 8.8, H-2); δ_F (CD_3CN) −62.8 [6F, s, $C(CF_3)_2$], −81.0 (3F, s, CF_2CF_3), −106.4 (2F, s, $CF_2CF_2CF_3$), −123.3 (2F, s, CF_2CF_3); δ_C {H} (CD_3CN) 32.7 (s, CH_2), 62.4 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 109.6 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 38, CF_2CF_3), 114.7 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 32, $CF_2CF_2CF_3$), 117.5 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 121.9 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 124.1 (s, C-2), 133.9 (s, C-3), 139.6 (s, C-4), 148.8 (s, C-1); *m/z* (EI$^+$) 455 (M^+, 27%), 151 (16), 136 (100), 109 (96), 89 (29), 78 (34), 69 (34).

2-[(Perfluoro-2-methylpentan-2-yl)methyl]naphthalene 4g. Compound **1** (7.3 g, 24.3 mmol), caesium fluoride (3.8 g, 25 mmol) and 2-bromomethylnaphthalene **3g** (3.0 g, 13.5 mmol) in sulfolane (40 ml) gave *2-[(perfluoro-2-methylpentan-2-yl)-methyl]naphthalene* **4g** (3.6 g, 58%) as a pale yellow liquid; bp 284 °C (Siwoloboff) (Found: C, 44.3; H, 2.0. $C_{17}H_9F_{13}$ requires C, 44.3; H, 1.9%); λ_{max}(*n*-hexane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 224 (19145), 276 (5744); ν_{max}/cm^{-1} 3064 (br, C-H), 1263–1218 (C-F), 739 and 701 (C-H); δ_H 3.67 (2H, s, CH_2), 7.34–7.48 (3H, m, Ar-H), 7.73–7.80 (4H, m, Ar-H); δ_F −62.2 [6F, s, $C(CF_3)_2$], −80.1 (3F, s, CF_2CF_3), −105.9 (2F, s, $CF_2CF_2CF_3$), −122.8 (2F, s, CF_2CF_3); δ_C {H} 32.8 (s, CH_2), 61.6 [sept, $^2J_{CF}$ 25, $C(CF_3)_2$], 109.7 (tsex, $^1J_{CF}$ 270, $^2J_{CF}$ 37, CF_2CF_3), 114.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.7 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 34, CF_2CF_3), 122.1 [q, $^1J_{CF}$ 291, $C(CF_3)_2$], 126.3, 126.5, 127.5, 127.8, 127.9, 128.3, 128.8, 131.2, 132.8, 133.0 (all s, all Ar-C); *m/z* (EI$^+$) 460 (M^+, 12%), 141 (100), 115 (15), 71 (10).

1,2-Bis[(perfluoro-2-methylpentan-2-yl)methyl]benzene 6a and 1-fluoromethyl-2-[(perfluoro-2-methylpentan-2-yl)methyl]-benzene 7a. Compound **1** (12.3 g, 41 mmol), caesium fluoride (6.0 g, 39.4 mmol) and 1,2-xylylene dibromide **5a** (3.23 g, 12.3 mmol) in sulfolane (30 ml) gave, after column chromatography on silica gel using *n*-hexane–light petroleum (bp 40–60 °C) (1 : 1) as eluant, *1,2-bis[(perfluoro-2-methylpentan-2-yl)methyl]-benzene* **6a** (1.1 g, 12%) as a pale yellow liquid; bp 264 °C (Siwoloboff); R_F 0.4 (Found: M^+, 742.021000. $C_{20}H_8F_{29}$ requires M^+, 742.021084); δ_H 3.65 (2H, s, CH_2), 7.2–7.4 (4H, m, Ar-H); δ_F −61.7 [6F, s, $C(CF_3)_2$], −80.4 (3F, s, CF_2CF_3), −107.6 (2F, s, $CF_2CF_2CF_3$), −123.0 (2F, s, CF_2CF_3); δ_C 27.3 (s, CH_2), 60.5 [m, $C(CF_3)_2$], 108.4 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 33, CF_2CF_3), 113.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 34, $CF_2CF_2CF_3$), 116.5 (qt, $^1J_{CF}$ 290, $^2J_{CF}$ 34, CF_2CF_3), 120.9 [q, $^1J_{CF}$ 291, $(CF_3)_2C$], 127.1 (s, C-4), 130.5 (s, C-1), 131.3 (s, C-3); *m/z* (EI$^+$) 423 ($M^+ - C_6F_{13}$, 42%), 181 (27), 123 (86), 104 (42), 93 (17), 69 (100), and *1-fluoromethyl-2-(perfluoro-2-methylpentan-2-yl)benzene* **7a** (3.6 g, 66%) as a pale yellow liquid; bp 180 °C (Siwoloboff); R_F 0.2 (Found: C, 38.2; H, 1.9. $C_{14}H_8F_{14}$ requires C, 38.0; H, 1.8%); λ_{max}(*n*-hexane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 221 (1331), 267 (285); ν_{max}/cm^{-1} 3038 (Ar-H), 2924 (C-H), 1275–1220 (C-F), 734 (C-H); δ_H 3.75 (2H, s, CH_2), 5.48 (2H, d, $^2J_{HF}$ 47, CH_2F), 7.3–7.4 (4H, m, Ar-H); δ_F −61.5 [6F, s, $C(CF_3)_2$], −80.6 (3F, s, CF_2CF_3), −107.6 (2F, s, $CF_2CF_2CF_3$), −122.8 (2F, s, CF_2CF_3), −205.3 (1F, t, $^2J_{HF}$ 47, CH_2F); δ_C {H} 28 (s, CH_2), 62.0 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 82.7 (d, $^1J_{CF}$ 164, CH_2F), 109.8 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 38, CF_2CF_3), 115.1 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.8 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 34, CF_2CF_3), 122.2 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 128.2 (s, C-2), 128.7 (s, C-4), 129.1 (d, $^4J_{CF}$ 3, C-5), 130.4 (d, $^3J_{CF}$ 7, C-6), 132.3 (s, C-3), 136.5 (d, $^2J_{CF}$ 15, C-1); *m/z* (EI$^+$) 442 (M^+, 1%), 123 (100, $M^+ - C_6F_{13}$).

1,3-Bis[(perfluoro-2-methylpentan-2-yl)methyl]benzene 6b and 1-fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]-benzene 7b. Compound **1** (16.0 g, 53 mmol), caesium fluoride (7.98 g, 53 mmol) and 1,3-xylylene dibromide **5b** (4.25 g, 16 mmol) in sulfolane (40 ml) gave, after column chromatography on silica gel using *n*-hexane–light petroleum (bp 40–60 °C) (1 : 1) as eluant, *1,3-bis[(perfluoro-2-methylpentan-2-yl)methyl]-benzene* **6b** (6.8 g, 56%) as a pale yellow liquid; bp 286 °C (Siwoloboff); R_F 0.4 (Found: C, 32.0; H, 0.8. $C_{20}H_8F_{26}$ requires C, 32.3; H, 1.1%); λ_{max}(*n*-hexane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 220 (1039), 261 (209); ν_{max}/cm^{-1} 3030 (br, Ar-H), 1264–1218 (C-F), 736 and 708 (C-H); δ_H 3.50 (4H, s, CH_2), 7.2 (4H, m, Ar-H); δ_F −62.9 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.5 (2F, s, $CF_2CF_2CF_3$), −123.5 (2F, s, CF_2CF_3); δ_C {H} 32.8 (s, CH_2), 61.8 [sept, $^2J_{CF}$ 25, $C(CF_3)_2$], 110.0 (tsex, $^1J_{CF}$ 271, $^2J_{CF}$ 38, CF_2CF_3), 115.1 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.9 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 34, CF_2CF_3), 122.3 [q, $^1J_{CF}$ 289, $C(CF_3)_2$], 128.3 (s, C-2), 131.5 (s, C-6), 131.7 (s, C-1), 135.1 (s, C-5); *m/z* (EI$^+$) 742 (M^+, 1%), 423 (100), 253 (12), 235 (26), 185 (36), 165 (11), 104 (39), and *1-fluoromethyl-3-[(perfluoro-2-methylpentan-2-yl)methyl]benzene* **7b** (1.5 g, 21%) as a pale yellow liquid; bp 207 °C (Siwoloboff); R_F 0.2 (Found: C, 37.7; H, 1.6. $C_{14}H_8F_{14}$ requires C, 38.0; H, 1.8%); λ_{max}(*n*-hexane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 222 (1245), 267 (296); ν_{max}/cm^{-1} 3030br (Ar-H), 1263–1218 (C-F), 734 and 707 (C-H); δ_H 3.56 (2H, s, CH_2), 5.35 (2H, d, $^2J_{HF}$ 48, CH_2F), 7.3 (4H, m, Ar-H); δ_F −62.7 [6F, s, $C(CF_3)_2$], −80.5 (3F, s, CF_2CF_3), −106.3 (2F, s, $CF_2CF_2CF_3$), −123.3 (2F,

s, CF_2CF_3), −208.8 (1F, t, $^2J_{HF}$ 48, CH_2F); δ_C {H} 32.6 (s, CH_2), 61.6 [sept, $^2J_{CF}$ 21, $C(CF_3)_2$], 84.2 (d, $^1J_{CF}$ 167, CH_2F), 109.7 (tsex, $^1J_{CF}$ 271, $^2J_{CF}$ 37, CF_2CF_3), 114.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.7 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 122.1 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 127.3 (d, $^3J_{CF}$ 6, C-2), 128.6 (d, $^4J_{CF}$ 1, C-5), 130.6 (d, $^3J_{CF}$ 6, C-6), 131.5 (s, C-3), 131.9 (s, C-4), 136.5 (d, $^2J_{CF}$ 17, C-1); *m/z* (EI^+) 442 (M^+, 5%), 123 (100).

1,4-Bis[(perfluoro-2-methylpentan-2-yl)methyl]benzene 6c and 1-fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]-benzene 7c. Compound **1** (16.2 g, 54 mmol), dry caesium fluoride (8.1 g, 53 mmol) and 1,4-xylylene dibromide **5c** (4.25 g, 16 mmol) in sulfolane (45 ml) gave, after column chromatography on silica gel using *n*-hexane–light petroleum (bp 40–60 °C) (1 : 1) as eluant, *1,4-bis[(perfluoro-2-methylpentan-2-yl)methyl]-benzene* **6c** (7.1 g, 59%) as a pale yellow liquid; bp 294 °C (Siwoloboff); R_F 0.4 (Found: C, 32.3; H, 0.9. $C_{20}H_8F_{26}$ requires C, 32.3; H, 1.1%); λ_{max}(*n*-hexane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 222 (1064), 266 (326); ν_{max}/cm^{-1} 1263–1220 (C-F), 732 and 701 (C-H); δ_H 3.54 (4H, s, CH_2), 7.26 (4H, s, Ar-H); δ_F −62.8 [6F, s, $C(CF_3)_2$], −80.7 (3F, s, CF_2CF_3), −106.3 (2F, s, $CF_2CF_2CF_3$), −123.3 (2F, s, CF_2CF_3); δ_C {H} 32.3 (s, CH_2), 61.6 [sept, $^2J_{CF}$ 25, $C(CF_3)_2$], 109.8 (tsex, $^1J_{CF}$ 271, $^2J_{CF}$ 38, CF_2CF_3), 114.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 117.7 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 122.1 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 131.1 (s, C-1), 131.4 (s, C-2); *m/z* (EI^+) 423 ($M^+ - C_6F_{13}$, 64%), 181 (12), 104 (100), 93 (15), 69 (74), and *1-fluoromethyl-4-[(perfluoro-2-methylpentan-2-yl)methyl]-benzene* **7c** (1.5 g, 22%) as a pale yellow liquid; bp 212 °C (Siwoloboff); R_F 0.2 (Found: C, 37.7; H, 1.6. $C_{14}H_8F_{14}$ requires C, 38.0; H, 1.8%); ν_{max}/cm^{-1} 3038 (Ar-H), 2964 (C-H), 1263–1220 (C-F), 732 and 701 (C-H); δ_H 3.49 (2H, s, CH_2), 5.30 (2H, d, $^2J_{HF}$ 48, CH_2F), 7.26 (4H, s, Ar-H); δ_F −62.7 [6F, s, $C(CF_3)_2$], −80.4 (3F, s, CF_2CF_3), −106.4 (2F, s, $CF_2CF_2CF_3$), −123.4 (2F, s, CF_2CF_3), −209.4 (1F, t, $^2J_{HF}$ 48, CH_2F); *m/z* (EI^+) 442 (M^+, 1%), 123 (100, $M^+ - C_6F_{13}$), 103 (12).

2,6-Bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine 9a and 2-fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]-pyridine 9b. Compound **1** (13.2 g, 44 mmol), caesium fluoride (6.5 g, 42.7 mmol) and 2,6-bis-(bromomethyl)pyridine **8** (3.6 g, 13.5 mmol) in sulfolane (40 ml) gave, after column chromatography on silica gel using light petroleum (bp 40–60 °C) as eluant, *2,6-bis[(perfluoro-2-methylpentan-2-yl)methyl]pyridine* **9a** (1.9 g, 20%) as a pale yellow liquid; bp 277 °C (Siwoloboff); R_F 0.36 (Found: C, 30.6; H, 0.9; N, 2.0. $C_{19}H_7F_{26}N$ requires C, 30.7; H, 0.9; N, 1.9%); δ_H 3.67 (4H, s, CH_2), 7.22 (2H, d, ^3J 7.6, H-3), 7.61 (1H, t, ^3J 7.9, H-4); δ_F −62.6 [6F, s, $C(CF_3)_2$], −80.3 (3F, s, CF_2CF_3), −106.0 (2F, s, $CF_2CF_2CF_3$), −123.0 (2F, s, CF_2CF_3); δ_C {H} 34.9 (s, CH_2), 61.1 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 109.5 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 38, CF_2CF_3), 114.7 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 32, $CF_2CF_2CF_3$), 117.5 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 121.9 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 124.6 (s, C-3), 136.5 (s, C-4), 151.6 (s, C-2); *m/z* (EI^+) 743 (M^+, 2%), 574 (11), 424 (24), 255 (13), 235 (18), 181 (16), 119 (10), 105 (12), 69 (100), and *2-fluoromethyl-6-[(perfluoro-2-methylpentan-2-yl)methyl]pyridine* **9b** (1.7 g, 33%) as a pale yellow liquid; bp 230 °C (Siwoloboff); R_F 0.16 (Found: C, 35.2; H, 1.6; N 3.2. $C_{13}H_7F_{14}N$ requires C, 35.2; H, 1.6; N, 3.1%); ν_{max}/cm^{-1} 2960 (C-H), 1596 (C=C), 1581 (C=N), 1461 (C=C), 1268–1214 (C-F); δ_H 3.71 (2H, s, CH_2), 5.43 (2H, d, $^2J_{HF}$ 46, CH_2F), 7.25 (1H, dd, $^3J_{HH}$ 7.6, $^4J_{HF}$ 4.0, H-2), 7.40 (1H, d, $^3J_{HH}$ 7.6, H-4), 7.70 (1H, t, $^3J_{HH}$ 7.6, H-3); δ_F −62.8 [6F, s, $C(CF_3)_2$], −80.6 (3F, s, CF_2CF_3), −106.2 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3), −222.9 (1F, t, $^2J_{HF}$ 46, CH_2F); δ_C {H} 34.9 (s, CH_2), 62.4 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 84.1 (d, $^1J_{CF}$ 169, CH_2F), 109.6 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 38, CF_2CF_3), 114.7 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 32, $CF_2CF_2CF_3$), 117.6 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 119.3 (d, $^3J_{CF}$ 5, C-3), 121.9 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 124.7 (s, C-5), 137.0 (s, C-4), 151.3 (s, C-6), 156.2 (d, $^2J_{CF}$ 22, C-2); *m/z* (EI^+) 443 (M^+, 24%), 274 (24), 254 (37), 235 (11), 186 (16), 181 (14), 124 (94), 69 (100).

Electrophilic substitution reactions

Nitration. A mixture consisting of **4a** (2.1 g, 5 mmol) and nitronium tetrafluoroborate (0.7 g, 5 mmol) in sulfolane (40 ml) was stirred for 2 h at 30 °C. The mixture was extracted with Fluorinert® FC-84 (2 × 30 ml). The solvent was removed by distillation under reduced pressure to afford crude product (2.2 g). GC–MS analysis showed that the product consisted of three isomers, 2-[(perfluoro-2-methylpentan-2-yl)methyl]nitrobenzene **4h**, **4e** and **4f**, in the ratio 1 : 3.8 : 3.8. Column chromatography on alumina using hexane as eluant gave a mixture of nitrobenzene derivatives **4e**,**f**,**h** (1.42 g, 61%) as a pale yellow liquid; spectral data were consistent with those obtained above and no further separation and purification was attempted.

Bromination. Bromine (0.3 g, 2.3 mmol) was added slowly to a hot (80 °C), stirred mixture of **4a** (1 g, 2.4 mmol) and ferric bromide. The solution was heated at reflux temperature until evolution of hydrogen bromide had ceased and then the reaction mixture was cooled, filtered and dissolved in pentane. The pentane solution was washed successively with 6 M hydrochloric acid (20 ml), 10% sodium bisulfite (20 ml), and saturated sodium chloride (20 ml). After drying ($MgSO_4$), the solvent was cautiously distilled under reduced pressure to afford a mixture of **4b**, **4c** and **4d** (0.97 g, 81%) in the ratio 1 : 2 : 3 by GC–MS analysis; spectral data were consistent with those obtained above and no further separation and purification was attempted.

Preparation of benzoic acid derivatives 10

General procedure. *tert*-Butyllithium (1.7 M in hexanes) was added to a solution of **4** in cold (−78 °C) diethyl ether under dry nitrogen. After stirring for 1 h, solid carbon dioxide was added and the mixture was allowed to warm to room temperature. The reaction mixture was extracted with 2 M NaOH (2 × 30 ml) and then the aqueous phase was acidified with 2 M HCl. A white solid precipitated which was isolated by filtration. Recrystallization from hexane gave pure samples of benzoic acid derivatives **10**.

3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid 10a. *tert*-Butyllithium (2.6 ml, 4.5 mmol) and **4c** (1.1 g, 2 mmol) in diethyl ether (30 ml) gave *3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid* **10a** (0.62 g, 60%) as white crystals; mp 81–83 °C (Found: C, 36.8; H, 1.4. $C_{14}H_7F_{13}O_2$ requires C, 37.0; H, 1.5%); δ_H 3.84 (2H, s, CH_2), 7.50 (1H, t, $^3J_{HH}$ 7.6, H-5), 7.60 (1H, d, $^3J_{HH}$ 8.0, H-4), 8.00 (1H, dd, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.2, H-6), 8.07 (1H, s, H-2); δ_F −62.7 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.2 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); *m/z* (EI^+) 454 (M^+, 63%), 437 (27), 201 (11), 181 (11), 151 (15), 135 (100), 109 (41).

4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoic acid 10b. *tert*-Butyllithium (2.4 ml, 4.5 mmol) and **4d** (1.0 g, 2 mmol) in diethyl ether (40 ml) gave *4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoic acid* **10b** (0.6 g, 64%) as white crystals; mp 135–138 °C (Found: C, 37.0; H, 1.5. $C_{14}H_7F_{13}O_2$ requires C, 37.0; H, 1.5%); ν_{max}/cm^{-1} 3100 (br, OH), 1683 (C=O), 1176–1326 (C-F and C–O); δ_H 3.86 (2H, s, CH_2), 7.56 (2H, AX, J_{AX} 7.9, H-3), 8.03 (2H, AX, J_{AX} 8.4, H-2); δ_F −62.6 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.3 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); *m/z* (EI^+) 454 (M^+, 8%), 151 (11), 135 (100), 109 (22), 107 (65), 90 (22), 69 (56).

Preparation of benzoyl chloride derivatives 11

General procedure. A mixture containing **10** and thionyl chloride was heated at reflux temperature for 2 h or until the evolution of hydrogen chloride and sulfur dioxide had ceased. Distillation of the crude reaction mixture under reduced pressure gave the benzoyl chloride derivative **11**.

3-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride 11a. Compound **10a** (0.51 g, 1.2 mmol) and thionyl chloride (30 ml) gave *3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride* **11a** (0.42 g, 80%) as a colourless liquid; bp 60 °C (4 mmHg) (Found: C, 35.4; H, 1.4. $C_{14}H_6ClF_{13}O$ requires: C, 35.5; H, 1.3%); ν_{max}/cm^{-1} 1775 (C=O), 1242 (br C-F); δ_H 3.97 (2H, s, CH_2), 7.69 (1H, t, $^3J_{HH}$ 7.9, H-5), 7.80 (1H, d, $^3J_{HH}$ 7.6, H-4), 8.16 (1H, dd, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.2, H-6), 8.20 (1H, br s, H-2); δ_F −62.7 [6F, s, $C(CF_3)_2$], −80.5 (3F, s, CF_2CF_3), −106.4 (2F, s, $CF_2CF_2CF_3$), −123.4 (2F, s, CF_2CF_3); *m/z* (EI$^+$) 437 (M^+ − Cl, 100%), 181 (15), 153 (21), 118 (11), 109 (35), 90 (21).

4-[(Perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride 11b. Compound **10b** (0.54 g, 1.2 mmol) and thionyl chloride (30 ml) gave *4-[(perfluoro-2-methylpentan-2-yl)methyl]benzoyl chloride* **11b** (0.46 g, 82%) as a colourless liquid; bp 70 °C (4 mmHg) (Found: C, 35.3; H, 1.3. $C_{14}H_6ClF_{13}O$ requires: C, 35.5; H, 1.3%); δ_H 3.93 (2H, s, CH_2), 8.15 (2H, AX, J_{AX} 8.0, H-3), 7.70 (2H, AX, J_{AX} 8.0, H-2); δ_F −62.6 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.2 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); *m/z* (EI$^+$) 437 (M^+ − Cl, 76%), 181 (25), 153 (13), 137 (43), 125 (16), 118 (44), 109 (70).

Esterification

Cyclohexyl 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoate 12. A mixture consisting of **11a** (0.50 g, 1.2 mmol), cyclohexanol (25 ml) and conc. hydrochloric acid (2 ml) was heated at reflux temperature for 14 h. Distillation of the reaction mixture gave *cyclohexyl 3-[(perfluoro-2-methylpentan-2-yl)methyl]benzoate* **12** (0.58 g, 91%) as a viscous, colourless liquid; bp 200 °C (Found: C, 45.1; H, 3.4. $C_{20}H_{17}F_{13}O_2$ requires C, 44.8; H, 3.2%); ν_{max}/cm^{-1} 2938 (br C-H), 1721 (C=O), 1591 (C=C), 1338–1200 (br C-O and C-F); δ_H (CD_3CN) 1.2–1.9 (10H, m, cyclohexyl CH_2), 3.74 (2H, s, CH_2R_F), 4.98 (1H, m, CH-O), 7.46 (1H, t, $^3J_{HH}$ 7.9, H-5), 7.58 (1H, d, $^3J_{HH}$ 7.0, H-4), 7.97 (1H, d, $^3J_{HH}$ 6.4, H-6), 8.02 (1H, s, H-2); δ_F (CD_3CN) −62.8 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.2 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); δ_C (CD_3CN) 24.2, 26.2 and 32.1 (all s, all cyclohexyl CH_2), 32.9 (s, CH_2R_F), 61.3 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 74.0 (s, CH–O), 110.6 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 37, CF_2CF_3), 115.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 118.6 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 34, CF_3), 123.1 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 129.5 (s, C-5), 130.0 (s, C-4), 132.1 (s, C-6), 132.5 (s, C-3), 133.6 (s, C-2), 137.0 (s, C-1), 166.0 (s, C=O); *m/z* (EI$^+$) 456 (M^+, 55%), 438 (70), 217 (33), 135 (32), 118 (49), 109 (31), 99 (20), 82 (100).

Preparation of aniline derivatives 13

General procedure. A mixture consisting of the nitrobenzene derivative **4e**,**f**, 10% Pt on activated carbon and ethanol was stirred under a positive pressure (3 bar) of hydrogen gas at room temperature overnight. The solution was cautiously filtered to remove the catalyst and evaporation of ethanol afforded the desired aniline derivative **13** which did not require further purification.

3-[(Perfluoro-2-methylpentan-2-yl)methyl]aniline 13a. Compound **4e** (5.1 g, 11.2 mmol), 10% Pt on activated carbon (0.5 g) and ethanol (50 ml) gave *3-[(perfluoro-2-methylpentan-2-yl)methyl]aniline* **13a** (4.0 g, 85%) as a yellow liquid; bp 238 °C (Found: C, 36.8; H, 2.0; N, 3.3. $C_{13}H_8F_{13}N$ requires C, 36.7; H, 1.9; N, 3.3%); ν_{max}/cm^{-1} 3373 (N-H), 1624 (C=C), 1497 (N–H), 1243 (br C-F); δ_H 3.56 (2H, s, CH_2), 6.57 (1H, d, $^3J_{HH}$ 7.2, H-4), 6.66 (1H, d, $^3J_{HH}$ 7.6, H-6), 6.69 (1H, br s, H-2), 7.02 (1H, t, $^3J_{HH}$ 7.9, H-5); δ_F −62.7 [6F, s, $C(CF_3)_2$], −80.9 (3F, s, CF_2CF_3), −106.3 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); δ_C 33.3 (s, CH_2), 62.5 [sept, $^2J_{CF}$ 24, $C(CF_3)_2$], 109.1 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 37, CF_2CF_3), 114.9 (s, C-6), 115.2 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 33, $CF_2CF_2CF_3$), 118.0 (qt, $^1J_{CF}$ 285, $^2J_{CF}$ 34, CF_2CF_3), 118.4 (s, C-2), 120.7 (s, C-4), 123.1 [q, $^1J_{CF}$ 290, $C(CF_3)_2$], 129.6 (s, C-5), 149.2 (s, C-2), 152.9 (s, C-NH_2); *m/z* (EI$^+$) 425 (M^+, 2%), 106 (100), 69 (11).

4-[(Perfluoro-2-methylpentan-2-yl)methyl]aniline 13b. Compound **4f** (5.1 g, 11 mmol), 10% Pt on activated carbon (0.5 g) and ethanol (50 ml) gave *4-[(perfluoro-2-methylpentan-2-yl)methyl]aniline* **13b** (3.9 g, 82%) as a yellow liquid; bp 230 °C (Found: C, 37.0; H, 2.1; N, 3.6. $C_{13}H_8F_{13}N$ requires C, 36.7; H, 1.9; N, 3.3%); ν_{max}/cm^{-1} 3370 (N–H), 1626 (C=C), 1520 (N–H), 1241 (br C-F); δ_H (acetone-d_6) 3.56 (2H, s, CH_2), 6.63 (2H, AX, J_{AX} 8.4, H-2), 7.03 (2H, AX, J_{AX} 7.9, H-3); δ_F (acetone-d_6) −62.7 [6F, s, $C(CF_3)_2$], −80.9 (3F, s, CF_2CF_3), −106.3 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); δ_C (acetone-d_6) 32.8 (s, CH_2), 62.0 [m, $C(CF_3)_2$], 110.4 (tsex, $^1J_{CF}$ 272, $^2J_{CF}$ 38, CF_2CF_3), 114.7 (s, C-2), 115.9 (tt, $^1J_{CF}$ 270, $^2J_{CF}$ 25, $CF_2CF_2CF_3$), 118.6 (qt, $^1J_{CF}$ 289, $^2J_{CF}$ 33, CF_2CF_3), 123.1 [q, $^1J_{CF}$ 291, $C(CF_3)_2$], 133.1 (s, C-4), 149.2 (s, C-3), 152.7 (s, C-NH_2); *m/z* (EI$^+$) 425 (M^+, 6%), 106 (100).

Preparation of azo-dyes 15

General procedure. The aniline derivative **13** was dissolved in a mixture consisting of hot water (7 ml) and 10% HCl (1.5 ml). Sodium nitrite (0.16 g) in water (2 ml) was added to the cold (0 °C), stirred solution at a rate that ensured that the temperature of the mixture remained below 5 °C and then a solution of the coupling agent in 10% aq. NaOH (2 ml) was added slowly. Coupling occurred rapidly and a dark orange solid precipitated within a few minutes. The mixture was cooled in ice and the azo-dye **15** was collected by filtration and purified by column chromatography on silica gel.

Azo-dye 15a. Compound **13b** (1.0 g, 2.3 mmol) and β-naphthol **14a** (0.31 g, 2.2 mmol) gave, after purification by column chromatography using methanol–water as the eluant, dye **15a** (0.7 g, 53%) as a bright orange solid; mp 110–115 °C (M^+, 580.08200. $C_{26}H_{13}F_{13}N_2O$ requires M^+, 580.08203); λ_{max}(CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 199 (120359), 250 (16249), sh 420 (7999), sh 500 (7999); ν_{max}/cm^{-1} 3412 (O–H), 3062 (C-H), 2968 (C-H), 1622 (C=C), 1517–1454 (br N=N), 1330–1145 (N–C and C-F); δ_H 3.8 (2H, s, CH_2), 6.6–8.6 (10H, m, Ar-H); δ_F −62.6 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.2 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); *m/z* (EI$^+$) 444 (20), 425 (25), 385 (11), 265 (23), 169 (11), 124 (100).

Azo-dye 15b. Compound **13a** (0.5 g, 1.17 mmol) and 4-hydroxynaphthalene-1-sulfonic acid sodium salt hydrate **14b** (0.27 g, 1.1 mmol) gave, after column chromatography using methanol–water as the eluant, dye **15b** (0.7 g, 48%) as a bright orange solid; mp 195–200 °C; λ_{max}(CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 198 (184812), sh 235 (11331), 350 (2331), 490 (3716); ν_{max}/cm^{-1} 3470 (br O–H), 3084 (br C-H), 1620 (br C=C), 1593–1577 (br N=N), 1270–1158 (N–C and C-F); δ_H 3.8 (2H, s, CH_2), 7.0–8.6 (8H, m, Ar-H); δ_F −62.6 [6F, s, $C(CF_3)_2$], −80.7 (3F, s, CF_2CF_3), −106.3 (2F, s, $CF_2CF_2CF_3$), −123.0 (2F, s, CF_2CF_3); *m/z* (ES, EI$^+$) 660 (M^+, 20%), 659 (100), 425 (48), 223 (40).

Azo-dye 15c. Compound **13a** (0.5 g, 1.17 mmol) and 1-*n*-butyl-6-hydroxy-5-cyano-4-methyl-2-pyridone **14c** (0.27 g, 1.1 mmol) gave, after column chromatography using methanol–water as the eluant, dye **15c** (0.7 g, 51%) as an orange solid; mp 75–80 °C (M^+, 642.130000. $C_{24}H_{19}F_{13}N_4O_2$ requires M^+, 642.130043); λ_{max}(CH_3CN)/nm (ε/dm^3 mol^{-1} cm^{-1}) 199 (1369732), sh 263 (55401), 420 (7035); ν_{max}/cm^{-1} 3450 (br O–H), 2959 (C-H), 2235 (C≡N), 1698–1640 (C=O and C=C), 1525 (br N=N), 1280–1145 (N–C and C-F); δ_F −62.6 [6F, s, $C(CF_3)_2$], −80.8 (3F, s, CF_2CF_3), −106.2 (2F, s, $CF_2CF_2CF_3$), −123.2 (2F, s, CF_2CF_3); *m/z* (CI$^+$) 643 (M^+ + 1, 4%), 253 (17), 237 (15), 220 (9).

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