Journal of Fluorine Chemistry 131 (2010) 621–626

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Thermomorphic metal scavengers: A synthetic and multinuclear NMR study of highly fluorinated ketones and their application in heavy metal removal

Robert J. Baker [a,b,*], Thomas McCabe [a], John E. O'Brien [a], Helen V. Ogilvie [b]

[a] School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland
[b] School of Science & Technology, Nottingham Trent University, Clifton Lane, Nottingham, NG11 6NS, UK

ARTICLE INFO

Article history:
Received 2 November 2009
Received in revised form 3 February 2010
Accepted 6 February 2010
Available online 18 February 2010

Keywords:
Fluorinated ligands
NMR spectroscopy
X-ray crystal structure

ABSTRACT

The preparation of a ketone with two long chain perfluoroalkyl groups is reported via the coupling reaction of a perfluorinated alkylzinc reagent and a perfluoro-acid chloride. This ketone has been investigated in the heterogeneous removal of heavy metals M^{2+} (M = Sn, Cd, Pb, Hg) and As^{5+} from aqueous solutions and removal of these metals from organic solvents using the unique thermomorphic properties of the fluorous ketone. In addition, a comprehensive ^{13}C NMR study of one of the intermediates in the synthesis, 2H,2H,3H,3H-perfluoronanoic acid, has allowed the determination of all $^{1}J_{C-F}$ and $^{2}J_{C-F}$ coupling constants. Also reported is the crystal structure of the acid $CF_3(CF_2)_5CH_2CH_2CO_2H$.

1. Introduction

Synthesis and catalysis in biphasic fluorous solvent systems are a now well-established methodology for catalyst immobilisation [1]. In particular, phosphine ligands with fluorous 'pony-tails,' Rf_3P, have become popular since the first report by Horváth and Rábai [2] and there are now a plethora of aryl phosphine ligands with one or more long chain fluorous group substituted onto the aryl ring with a suitable spacer to modulate the electronic effects of the perfluoroalkyl chain, or perfluoroalkylated diarylphosphines $RfPAr_2$ [3]. One observation is that by increasing the amount of fluorine atoms the solubility of the resulting compound decreases substantially in both organic solvents and fluorous solvents. In particular, suitably designed fluorous molecules are insoluble at low temperatures but significantly soluble at elevated temperatures. This thermomorphic property has allowed homogeneous catalysis to function at high-temperatures, with subsequent catalyst recovery by simple liquid/solid-phase separation at lower temperature [4]. Recently the use of Teflon tape to facilitate catalyst recovery has been reported [5].

We have an interest in the use of fluorinated compounds as methods for extracting toxic metals from solid and aqueous phase. We have recently disclosed [6] the utility of the perfluorinated phosphine oxide and sulphide $(RfCH_2CH_2)_3P{=}E$ and $(RfCH_2CH_2)_2P(E)CH_2CH_2P(E)(CH_2CH_2Rf)_2$ ($Rf = CF_3(CF_2)_n$; n = 5, 7, 9; E = O, S) for the extraction of toxic metals such as As, Cr, Co, Cd, Hg, Pb and Sn, as well as radionuclides ^{90}Sr, ^{133}Ba and U, from aqueous solutions into perfluorohexane. As part of this study we wished to extend the scope to take advantage of the insolubility of fluorous substituted ligands so that a heterogeneous metal scavenging compound could be used to remove typical heavy metal contaminants from aqueous waste streams. We have targeted ketones of the type $\{CF_3(CF_2)_n(CH_2)_2\}_2C{=}O$ (n = 5, 7) and herein report the synthesis of symmetric and asymmetric ketones via a coupling reaction of a perfluoroalkyl zinc reagent with an acid chloride, and their subsequent utility in metal removal under heterogeneous and thermomorphic conditions. In addition we include a comprehensive multinuclear NMR study of one of these long chain perfluoroalkyl groups.

2. Results and discussion

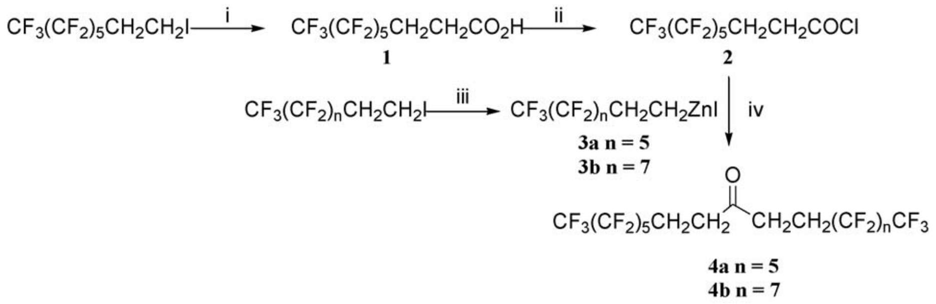
The synthesis of the perfluorinated ketone $\{CF_3(CF_2)_5CH_2CH_2\}_2C{=}O$ is shown in Scheme 1, and the key step involves the coupling of an acid chloride with an alkyl zinc reagent catalysed by CuCN.

The starting point for our synthesis was the preparation of a series of carboxylic acids $CF_3(CF_2)_nCH_2CH_2CO_2H$, which have been reported in the literature by a number of methods [7]. We chose the formation of the Grignard reagent from the corresponding perfluoroalkyl iodide and subsequent quenching with CO_2 followed by an acidic workup to form **1** in excellent yield. This worked efficiently for n = 5, but for n = 7 and 10 we found that the Grignard reaction failed. Other methods for the formation of a carbanion, such as treatment with ^{n}BuLi or MeLi also failed to generate the carboxylic acid after quenching with CO_2, whilst using

---

* Corresponding author at: School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland. Tel.: +353 01 896 3501; fax: +353 01 671 2826.
E-mail address: bakerrj@tcd.ie (R.J. Baker).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.02.004



Scheme 1. Reagents and conditions: (i) Mg, CO_2/H^+, Et_2O; (ii) $SOCl_2$; (iii) Zn, THF; (iv) CuCN.

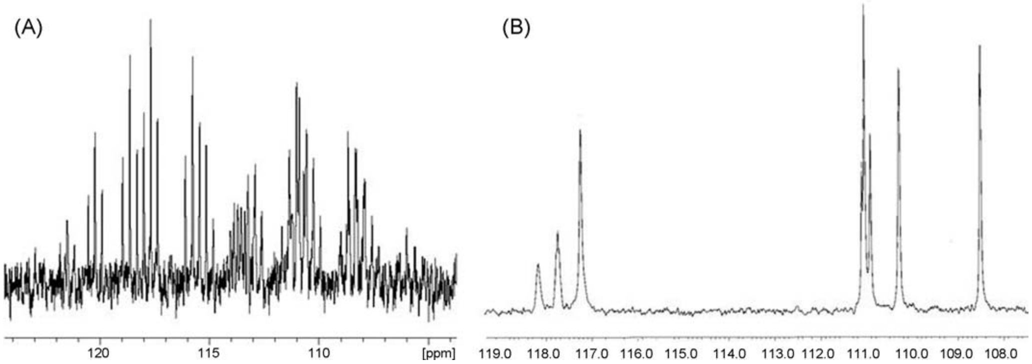


Fig. 1. $^{13}C\{^1H\}$ (A) and $^{13}C\{^{19}F\}$ (B) NMR spectrum of the C–F region of **1** in $CDCl_3$ measured at 100 MHz.

^{t}BuLi a complicated ^{19}F NMR spectrum was obtained, indicating some degradation of the perfluoroalkyl chain presumably accompanied by the formation of LiF. We also note that a small amount of the Wurtz coupled by-product $RfCH_2CH_2CH_2CH_2Rf$ was formed [7(c)], which could be readily separated by fractional recrystallisation from dichloromethane.

Previous publications report only the ^1H and ^{19}F NMR spectra of the acid. We have recorded a ^{19}F–^{19}F COSY to confirm out fluorine NMR assignments, and these compare very well with the values reported for $CF_3(CF_2)_5CH_2CH_2OH$, which is one of few perflouro-organic compounds to be rigorously studied using multinuclear and 2D NMR spectroscopy [8]. We have recorded the ^{13}C NMR spectrum under ^1H and ^{19}F decoupling conditions (Fig. 1) in order to fully assign the perfluorinated chain. The C–H and C–F coupling constants for the CH_2 carbons have been fully determined ($\mathbf{C}H_2CO_2H$: $\delta_C = 25.30$ ppm, $^1J_{C-H} = 130$ Hz, $^3J_{C-F} = 4$ Hz; $CF_2\mathbf{C}H_2CH_2$: $\delta_C = 26.23$ ppm, $^1J_{C-H} = 132$ Hz, $^2J_{C-F} = 22$ Hz). The CF_3 and CF_2 carbons give rise to ~42 resolved lines in a 15 ppm range in the $^{13}C\{^1H\}$ NMR spectrum (Fig. 1a), which collapse into the expected 6 singlets in the $^{13}C\{^{19}F\}$ NMR spectrum (Fig. 1b). As the range of the ^{19}F resonances is quite large (~50 ppm), the broadband decoupling pulse sequence used does not fully decouple the signals in the $^{13}C\{^{19}F\}$ NMR spectrum, so that the peak at 111 ppm has not been fully decoupled. Because of this we have been unable to record high quality $^{13}C\{^{19}F\}$–^{19}F correlation spectra, but a $^{13}C\{^1H\}$–^{19}F hector spectrum did allow us to determine the coupling constant for the CF_3 group which shows a cross peak to the ^{19}F resonance at −80 ppm ($^1J_{C-F} = 280$ Hz), but not the ^{13}C chemical shift (Fig. S1, Supplemental Information). However, with this coupling constant we were able to extract the required data by close examination of the $^{13}C\{^1H\}$ NMR spectrum run on a higher field instrument, and a 1:2:2:1 quartet of triplets can be seen centred at 117.2 ppm; the smaller $^2J_{C-F}$ couplings are also resolvable ($^2J_{C-F} = 33$ Hz). Using a similar approach, and with the $^{13}C\{^{19}F\}$ data in mind, we can give a good estimate to all coupling constants (Fig. 2 and Table 1). In particular the CF_2 group adjacent to the CF_3 can be clearly seen as the upfield multiplet is split into a quartet ($^2J_{C-F} = 38$ Hz). Moreover, using a HMBC experiment we can observe strong correlations of the protons on the methyl groups into the downfield region of the multiplet (Fig. 3), indicating that the ^{13}C resonances at 117.7 and 118.1 ppm are due to the CF_2 groups closest to the methyl groups, although using the techniques available to us it is not possible to distinguish between them. In turn this suggests that the CF_2 groups in the perfluoroalkyl chain are at 110.2 and 111.0 ppm, and in comparison to the reported data for the perfluoroalcohol we can tentatively assign the downfield peak to the $CF_3CF_2\mathbf{C}F_2$ carbon.

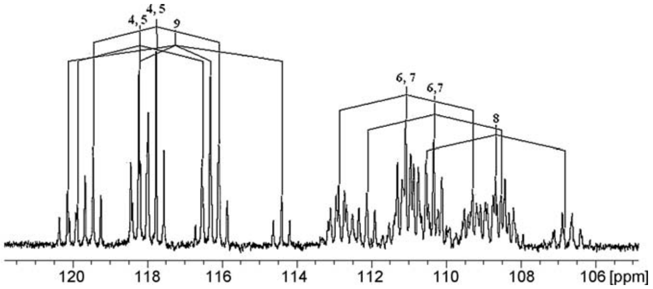


Fig. 2. Multiplet analysis of $^{13}C\{^1H\}$ NMR spectrum of the C–F region of **1** in $CDCl_3$ measured at 150 MHz.

Table 1
Measured 1- and 2-bond C–F coupling constants for **1**.

δ_C	$^1J_{C-F}$ (Hz)	$^2J_{C-F}$ (Hz)	Assignment
108.5	270	38	$CF_3\mathbf{C}F_2$
110.2	270	31	$CF_3CF_2\mathbf{C}F_2$
111.0	271	31	$CF_2\mathbf{C}F_2$
117.2	287	33	$\mathbf{C}F_3$
117.7	255	32	$CF_2CF_2CH_2$
118.1	255	42	$CF_2CF_2CH_2$

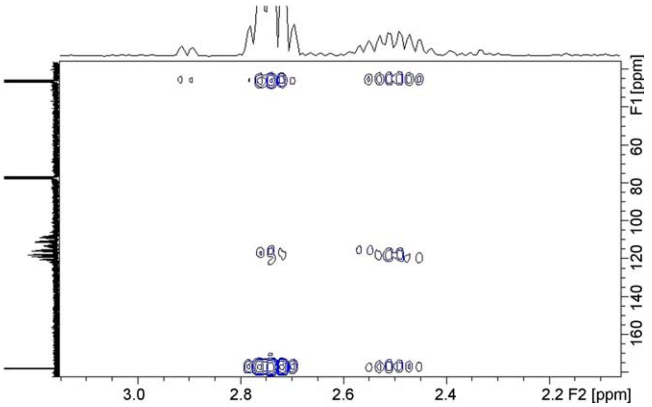


Fig. 3. $^{13}C\{^1H\}$–^1H HMBC spectrum of **1** in $CDCl_3$.

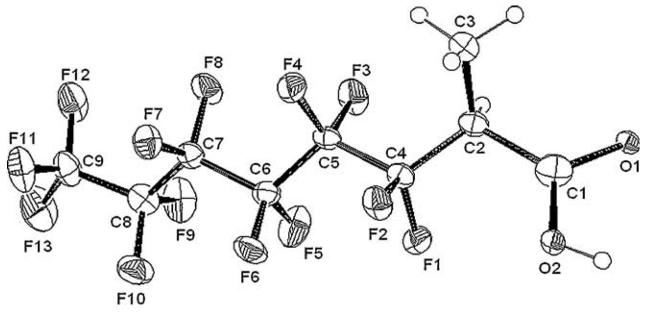


Fig. 4. Solid state structure of **5** (ellipsoids at 40% probability). Selected bond lengths (Å) and angles (°): C(1)–O(1) = 1.380(5), C(1)–O(2) = 1.379(5), C(1)–C(2) = 1.595(6), C(2)–C(4) = 1.500(5), C(4)–C(5) = 1.550(5), O(1)–C(1)–O(2) = 117.9(4), O(1)–C(1)–C(2) = 120.5(4), O(2)–C(1)–C(2) = 121.6(4), C(1)–C(2)–C(3) = 109.2(3), C(1)–C(2)–C(4) = 113.8(3), C(4)–C(2)–C(3) = 114.0(3).

On one attempt at recrystallisation of the acid $CF_3(CF_2)_5CH_2CH_2CO_2H$, a few small crystals were obtained and characterised by X-ray diffraction. Somewhat surprisingly the structure was not disordered and a satisfactory refinement was obtained. The molecular structure of this branched acid, **5**, is shown in Fig. 4. The metric parameters are as would be expected whilst the C–O bond lengths are 1.380(5) Å and 1.379(5) Å for the C–O and C=O bonds respectively, possibly as a consequence of the extensive hydrogen bonding. It has been noted in other examples that the lowest energy conformation of the perfluoroalkyl chains has torsion angles much lower than observed in alkyl chains (ca. 180°) [9], and the C–C–C–C angles in **5** averages at 166.6°. There are also numerous contacts between the fluorine atoms on one molecule to those on adjacent molecules (2.669–2.917 Å) which are close to the van-der-Waals radius of fluorine (1.40 Å) [10], so that the crystal lattice is divided into fluorous and non-fluorous domains.

5 has been characterised by ^1H and ^{19}F NMR and IR spectroscopy. The methyl group appears as a doublet at 1.30 ppm ($^3J_{H-H} = 7.4$ Hz) whilst the methylene moiety is a multiplet at 2.01 ppm in the ^1H NMR spectrum. In the ^{19}F NMR spectrum, all 6 resonances appear in approximately the same position as for the straight chain acid, **1**. The IR spectrum shows the C=O stretch at 1772 cm^{-1}, whilst for **1** the C=O stretch is at 1709 cm^{-1}. This is presumably due to the closer proximity of the carbonyl group to the electron withdrawing perfluoroalkyl chain (*cf.* $\nu(C{=}O) = 1712$ cm^{-1} for $CH_3(CH_2)_7CO_2H$ [11]).

The formation of **5** presumably arises from quenching of the Grignard reagent. We have examined the starting 1H,1H,2H,2H-perfluorooctyl iodide by NMR spectroscopy but could not find any evidence of any isomeric iodides. The most likely explanation therefore stems from the mechanism of the Grignard reaction. It is now well accepted that the reaction goes via formation of radical species $R^\bullet$ which can isomerise during the reaction [12]. We can speculate that due to the electron withdrawing fluorine chain, a hydrogen shift occurs from the primary radical to form a secondary radical. Regardless of the mechanism, this compound represents one of few perfluoro organics that has been characterised by X-ray diffraction.

The carboxylic acid **1** can be readily converted to the acid chloride, **2** [7(b),(c)]. Other methods in the literature have used PCl_5, but in our hands treatment with $SOCl_2$ afforded the pure acid chlorides after simply removing excess thionyl chloride under vacuum. The ^1H, ^{19}F and IR data are consistent with those reported in the literature. The $^{13}C\{^1H\}$ NMR spectrum has been recorded, but the C–F region is not as well resolved as for **1**. The COCl carbon resonance is observed at 172.1 ppm, whilst the CH_2 carbons are at 26.23 (t, $^2J_{CF} = 21$ Hz, $\mathbf{C}H_2CF_2$) and 20.1 (s, $\mathbf{C}H_2CO_2H$); in this case the $^3J_{C-F}$ coupling is unresolved.

In order to form the ketone, we have modified the procedure of Knochel and co-workers, via the CuCN catalysed coupling of an acid chloride and an alkyl zinc reagent [13]. Thus, the zinc compound $CF_3(CF_2)_5CH_2CH_2ZnI$, **3a**, was prepared by the reaction of the perfluoroalkyl iodide and activated zinc powder, to yield a solution of the air and moisture sensitive zinc reagent. This has been characterised spectroscopically and shows a distinctive upfield shift of the CH_2 group bound to the zinc in both the proton ($\delta_H = -0.15$ ppm) and carbon ($\delta_C = -11.1$ ppm) NMR spectra. Coupling of this reagent with the acid chloride using a CuCN catalyst proceeds in good yield to give the ketone $\{CF_3(CF_2)_nCH_2CH_2\}_2C{=}O$, **4a** after recrystallisation from chloroform/DMF. The compound is poorly soluble in most organic solvents and fluorous solvents which precluded the determination of the partition coefficient between organic and fluorous solvents. Spectroscopic data were recorded in Me_2SO-d_6 at 60 °C in which the ketone has reasonable solubility. The carbonyl carbon appears at $\delta_C = 169.9$ ppm and the C=O stretch is at 1724 cm^{-1} in the infrared spectrum. This stretching frequency can be compared to 3-pentanone [14] and 3-perfluoropentanone [15] at 1695 and 1790 cm^{-1} respectfully, and suggests that the electron withdrawing nature of the fluorous chain is not fully removed using an ethylene bridge. This is consistent with previous reports on the comparisons between fluorous and non-fluorous phosphines [16]. In order to explore the generality of this CuCN catalysed coupling methodology, and we have also prepared the unsymmetrical ketone $CF_3(CF_2)_5CH_2CH_2C({=}O)CH_2CH_2(CF_2)_7CF_3$, **4b** from the acid chloride **2** and the zinc reagent **3b**. However, poor solubility of this compound precluded satisfactory purification. The spectroscopic data are similar to the symmetrical ketone. The carbonyl carbon appears at 170.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum and 1744 cm^{-1} in the infrared spectrum, and the ^{19}F NMR spectrum shows two resonances assigned to the $\mathbf{CF}_2CH_2$ at −116.8 and −117.2 ppm, however the remaining resonances in the $^{13}C\{^1H\}$ and ^{19}F NMR spectra could not be unambiguously assigned.

With these ketones in hand we have carried out studies on the effectiveness of these towards the removal of the heavy metals M^{2+} (M = Sn, Cd, Pb and Hg) and arsenic(V). In a typical procedure, the ketone **4a** was added to a solution of known concentration of the metal(oid) in water and the mixture heated to 80 °C for 5 h, with a concomitant colour change of the ketone from pale brown to dark brown. After this time, the solution was cooled to room temperature and the ketone complex(es) removed by filtration. The aqueous solution was re-analysed using ICP-MS in order to determine the concentration of the remaining metal (Table 2). For all metals studied the ketone **4a** effectively removes them from water. These results compare well to conventional heavy metal extractants such as trioctylphosphine oxide [17] and our recently investigated perfluorooctyl phosphine oxide [6].

Table 2
Extraction of selected metals using ketone **4a**.

Metal	Initial concentration (μg/l)	Concentration after reaction (μg/l)
Cadmium	1198.10	698.44
Mercury	5000.0	0.39
Lead	5000.0	946
Arsenic	5000.0	2388.4
Tin	241.10	<1

We have examined the extraction of tin(II) from organic solvents by multinuclear NMR spectroscopy. At room temperature the NMR spectra (^{1}H, ^{19}F and ^{119}Sn) show only a small amount of **4a** in solution, but upon heating the position of the peaks change. Whilst for the ^{1}H and ^{19}F spectra the change is small, ^{119}Sn NMR spectroscopy conclusively shows that the tin has dissolved and formed a complex. The resonance at −452.6 ppm can be compared to $SnCl_2$ in Me_2SO (δ_{119Sn} = −363.4 ppm at similar concentrations) [18], and in line with the expected increase in shielding of the tin nucleus due to an increase in coordination number [19]. Upon addition of more than two equivalents of **4a**, the tin resonance does not change, which suggests a 2:1 complex formation and is consistent with literature data of other ketone complexes of Sn(II) [20]. Upon cooling the solution, no tin resonance is observed in the ^{119}Sn NMR spectrum but the precipitate shows a large shift in the carbonyl stretch in the infrared spectrum to 1599 cm^{-1}, again indicative of coordination.

Finally, we have explored the reactivity of ketone **4**, and found it to be inert towards Wittig reagents $Ph_3P{=}CH_2$ and even common carbanions such as RLi, in which the ketone was fully recovered after quenching with water. We ascribe this apparent lack of reactivity to the insoluble nature of the ketones.

3. Conclusions

In conclusion, we have shown that a symmetric and unsymmetrical ketone with long chain perfluoroalkyl groups can be prepared in good yields and show good ability to extract selected metals from aqueous solutions. Moreover, using the thermomorphic properties of these highly fluorous ketones we have demonstrated for the first time that these class of compounds could have use in the removal of heavy metals from solution. In addition, a comprehensive NMR study of one of these compounds has been undertaken and a rare example of a crystal structure of a perfluoro-organic compound reported.

4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity nitrogen. Toluene and THF were distilled over potassium, whilst diethyl ether was distilled over Na/K. ^{1}H, ^{13}C, ^{19}F and ^{119}Sn NMR spectra were recorded on either a Bruker AV400 spectrometer operating at 400.13 (^{1}H), 376.55 (^{19}F), 100.65 (^{13}C) and 149.24 MHz (^{119}Sn), a Bruker Avance II 600 NMR with a TCI cryoprobe operating at 150.92 MHz (^{13}C) or a JEOL ECX-400 at 399.7 (^{1}H), 376.11 (^{19}F) and 100.51 MHz (^{13}C), and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used or external $CFCl_3$ (^{19}F) or $SnMe_4$ (^{119}Sn). ^{19}F assignments were confirmed using ^{19}F–^{19}F COSY spectra. Infrared spectra were recorded on a PerkinElmer Spectrum 100 with ATR. Metal analysis was carried out on an Agilent 7500a Inductively Coupled Plasma Mass Spectrometer and calibrated using commercial standards before use. DSC spectra were recorded on a PerkinElmer Diamond DSC. Mass spectra were obtained from the EPSRC National Mass Spectrometry Service at Swansea University (ESI). Melting points were determined in sealed glass capillaries under nitrogen and are uncorrected. Fluorinated solvents and reagents were acquired from Apollo or Fluorochem and all other reagents from commercial sources and used as received.

4.1. $CF_3(CF_2)_5CH_2CH_2CO_2H$, 1

To a suspension of Mg turnings (2.43 g, 0.1 moles) in Et_2O was added $CF_3(CF_2)_5CH_2CH_2I$ (24.5 cm^{3}, 0.1 moles) in Et_2O drop-wise over 2 h and then stirred for a further 2 h. The mixture was cooled to 0 °C and dry CO_2 (10 g) added slowly. The mixture was stirred for 15 min before a solution of 10% H_2SO_4 added. The organic layer was separated, dried over $MgSO_4$ and the solvent removed under vacuum. The residue was recrystallised from dichloromethane to yield a free flowing white powder (21.21 g, 54%). MPt (DSC): 63.57 °C; ^{1}H NMR (399.71 MHz, $CDCl_3$): δ 2.42 (2H, m, $C\mathbf{H}_2CF_2$), 2.62 (2H, t, $^{3}J_{HH}$ = 3.6 Hz, $C\mathbf{H}_2CO_2H$), 9.70 (1H, s, $O\mathbf{H}$); ^{13}C NMR (100.51 Hz, $CDCl_3$): δ 25.3 (t, $^{3}J_{CF}$ = 4 Hz, $\mathbf{C}H_2CO_2H$), 26.23 (t, $^{2}J_{CF}$ = 22 Hz, $\mathbf{C}H_2CF_2$), 108–118 (m, $\mathbf{C}F_2$), 177.2 (s, $\mathbf{C}O_2H$); ^{19}F NMR (376.11 MHz, $CDCl_3$): δ – 80.88 (t, $^{4}J_{FF}$ = 10 Hz, $C\mathbf{F}_3$), −114.8 (s, $C\mathbf{F}_2CH_2$), −121.9 (s, $CF_3CF_2C\mathbf{F}_2$), −122.9 (s, $CF_3CF_2CF_2C\mathbf{F}_2$), −123.5 (s, $CH_2CF_2C\mathbf{F}_2$), −126.2 ($CF_3C\mathbf{F}_2$); IR (cm^{-1}) ν: 2965 (w, OH), 1709 (m, C=O), 1473 (w), 1444 (w), 1366 (w), 1318 (w), 1183 (s, C–F), 1138 (s, C–F), 1083 (m), 1062 (m), 984 (m), 911 (w), 793 (w), 696 (m), 641 (m), 566 (m), 527 (m); MS (ES−) *m*/*z*: 391.1 [M−H, 100%]; HRMS (ES−) calculated for $C_9H_4F_{13}O_2$: 391.0009, found: 391.0012.

4.2. $CF_3(CF_2)_5CH(CH_3)CO_2H$, 5

Small crystals of **5** (~0.2 g) were obtained by slow evaporation of solutions of **1** in CH_2Cl_2. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.01 (1H, m, $C\mathbf{H}CF_2$), 2.51 (d, $^{3}J_{HH}$ = 7.4 Hz, 3H, $C\mathbf{H}_3$); ^{19}F NMR (376.55 MHz, Me_2SO-d$_6$, 60 °C): δ −80.83 (s, $C\mathbf{F}_3$), −114.44 (s, $C\mathbf{F}_2CH_2$), −122.40 (s, $CF_3CF_2C\mathbf{F}_2$), −123.32 (s, $CF_3CF_2CF_2C\mathbf{F}_2$), −123.86 (s, $CH_2CF_2C\mathbf{F}_2$), −126.42 ($CF_3C\mathbf{F}_2$); IR (cm^{-1}) ν: 2978 (w, OH), 1772 (m, C=O), 1478 (w), 1454 (w), 1372 (w), 1319 (w), 1185 (s, C–F), 1142 (s, C–F), 1086 (m), 1071 (m), 989 (m), 909 (w), 796 (w), 699 (m), 638 (m), 571 (m), 522 (m).

4.3. $CF_3(CF_2)_5CH_2CH_2COCl$, 2

Excess freshly distilled $SOCl_2$ (7 cm^{3}) was added to $CF_3(CF_2)_5CH_2CH_2CO_2H$ (3.00 g, 7.65 mmol) and this was stirred for 12 h under an atmosphere of N_2. The excess thionyl chloride was removed *in vacuo* and toluene added to the oil. This was stirred for 10 min then the solvent removed *in vacuo* to yield an air sensitive yellow oil. ^{1}H NMR (399.71 MHz, $CDCl_3$): δ 2.70 (2H, m, $C\mathbf{H}_2CF_2$), 3.40 (2H, t, $^{3}J_{HH}$ = 7.6 Hz, $C\mathbf{H}_2COCl$); ^{13}C NMR (100.51 Hz, $CDCl_3$): δ 20.1 (s, $\mathbf{C}H_2CO_2H$), 26.23 (t, $^{2}J_{CF}$ = 21 Hz, $\mathbf{C}H_2CF_2$), 108.5–117 (m, $\mathbf{C}F_2$), 172.1 (s, $\mathbf{C}OCl$); ^{19}F NMR (376.11 MHz, $CDCl_3$): δ – 80.72 (s, $C\mathbf{F}_3$), −114.2 (s, $C\mathbf{F}_2CH_2$), −121.7 (s, $CF_3CF_2C\mathbf{F}_2$), −122.7 (s, $CF_3CF_2CF_2C\mathbf{F}_2$), −123.3 (s, $CH_2CF_2C\mathbf{F}_2$), −126.0 ($CF_3C\mathbf{F}_2$).

4.4. $\{CF_3(CF_2)_5CH_2CH_2\}ZnI$, 3a

LiCl (0.324 g, 7.65 mmol) was heating under vacuum for 30 min at 150 °C and after cooling, zinc powder (0.915 g, 1.40 mmol) added and the mixture heated to 130 °C under vacuum for 30 min. This was allowed to cool and THF (20 cm^{3}) added followed by $BrCH_2CH_2Br$ (0.10 cm^{3}) and Me_3SiCl (0.10 cm^{3}). After stirring for 10 min $CF_3(CF_2)_5CH_2CH_2I$ (0.38 cm^{3}, 1.42 mmol) was added and the mixture heated to 50 °C for 1 h to form RZnI. This was filtered and the solvent removed *in vacuo* to yield a very air and moisture sensitive oil that was characterised by NMR spectroscopy and used immediately. ^{1}H NMR (399.71 MHz, C_6D_6): δ −0.15 (4H, m, $ZnC\mathbf{H}_2$), 0.93 (4H, m, $C\mathbf{H}_2CF_2$); ^{13}C NMR (100.51 Hz, C_6D_6): δ −11.1 (s, $Zn\mathbf{C}H_2$), 4.1 (m, $\mathbf{C}H_2CF_2$), 110–121 (m, $\mathbf{C}F_2$); ^{19}F NMR (376.11 MHz,

$\mathrm{C_6D_6}$): δ −80.19 (s, $\mathrm{C\mathbf{F}_3}$), −113.0 (s, $\mathrm{C\mathbf{F}_2CH_2}$), −121.21 (s, $\mathrm{CF_3CF_2C\mathbf{F}_2}$), −122.13 (s, $\mathrm{CF_3CF_2CF_2C\mathbf{F}_2}$), −122.73 (s, $\mathrm{CH_2CF_2C\mathbf{F}_2}$), −125.24 ($\mathrm{CF_3C\mathbf{F}_2}$).

4.5. *{$\mathrm{CF_3(CF_2)_7CH_2CH_2}$}ZnI, **3b***

This was prepared analogously to **3a**. ^{1}H NMR (399.71 MHz, $\mathrm{C_6D_6}$): δ −0.14 (4H, m, $\mathrm{ZnC\mathbf{H}_2}$), 0.94 (4H, m, $\mathrm{C\mathbf{H}_2CF_2}$); ^{13}C NMR (100.51 Hz, $\mathrm{C_6D_6}$): δ −11.9 (s, $\mathrm{Zn\mathbf{C}H_2}$), 3.7 (m, $\mathrm{\mathbf{C}H_2CF_2}$), 110–121 (m, $\mathrm{\mathbf{C}F_2}$); ^{19}F NMR (376.11 MHz, $\mathrm{C_6D_6}$): δ −81.09 (s, $\mathrm{C\mathbf{F}_3}$), −116.62 (s, $\mathrm{C\mathbf{F}_2CH_2}$), −122.23 (s, $\mathrm{CF_3CF_2C\mathbf{F}_2}$ and $\mathrm{CF_3CF_2CF_2C\mathbf{F}_2}$), −123.02 (s, $\mathrm{CF_3CF_2CF_2CF_2C\mathbf{F}_2}$), −123.82 (s, $\mathrm{CH_2CF_2CF_2C\mathbf{F}_2}$), −126. 43 ($\mathrm{CF_3C\mathbf{F}_2}$).

4.6. *{$\mathrm{CF_3(CF_2)_5CH_2CH_2}$}$_2$C=O, **4***

A solution of {$\mathrm{CF_3(CF_2)_5CH_2CH_2}$}ZnI was cooled to −30 °C and a solution of CuCN·2LiCl (0.333 g, 1.91 mmol) in THF (20 cm^3) was then added and this mixture stirred for 30 min at this temperature. A solution of $\mathrm{CF_3(CF_2)_5CH_2CH_2COCl}$ (7.65 mmol) in THF (10 cm^3) was added and stirring continued for 1 h at −30 °C and then 14 h at room temperature. The mixture was quenched with aqueous $\mathrm{NH_4Cl}$ and the organic layer separated. The aqueous phase was washed with EtOAc, the organic extracts combined, dried over $\mathrm{MgSO_4}$ and the solvent removed *in vacuo* to yield a brown oily solid. Recrystallisation from $\mathrm{CHCl_3}$/DMF afforded a crystalline brown solid (2.62 g, 50%) MPt: 137–141 °C; Anal. Calcd for $\mathrm{C_{17}H_8F_{26}O}$: C, 28.27; H, 1.11. Found: C, 28.19; H, 1.18; ^{1}H NMR (399.71 MHz, $\mathrm{Me_2SO\text{-}d_6}$, 333 K): δ 1.74 (4H, m, $\mathrm{C\mathbf{H}_2CF_2}$), 2.50 (4H, m, $\mathrm{C\mathbf{H}_2CO}$); ^{13}C NMR (100.51 Hz, $\mathrm{Me_2SO\text{-}d_6}$, 333 K): δ 24.8 (s, $\mathrm{\mathbf{C}H_2CO}$), 59.5 (t, $^2J_{CF}$ = 21 Hz, $\mathrm{\mathbf{C}H_2CF_2}$), 110–121 (m, $\mathrm{\mathbf{C}F_2}$), 169.9 (s, $\mathrm{\mathbf{C}{=}O}$); ^{19}F NMR (376.11 MHz, $\mathrm{Me_2SO\text{-}d_6}$, 333 K): δ −80.19 (s, $\mathrm{C\mathbf{F}_3}$), −113.0 (s, $\mathrm{C\mathbf{F}_2CH_2}$), −121.21 (s, $\mathrm{CF_3CF_2C\mathbf{F}_2}$), −122.13 (s, $\mathrm{CF_3CF_2CF_2C\mathbf{F}_2}$), −122.73 (s, $\mathrm{CH_2CF_2C\mathbf{F}_2}$), −125.24 ($\mathrm{CF_3C\mathbf{F}_2}$); IR (cm^{-1}) ν: 1724 (m, C=O), 1442 (w), 1364 (w), 1317 (w), 1231 (s, C–F), 1186 (s, C–F), 1121 (m), 1064 (m), 985 (m), 910 (w), 793 (w), 697 (m), 651 (m), 566 (m), 529 (m); MS (EI$^+$) *m*/*z*: 736.11 [M+$\mathrm{NH_4}$, 100%].

4.7. *$\mathrm{CF_3(CF_2)_5CH_2CH_2C({=}O)CH_2CH_2(CF_2)_7CF_3}$*

This was prepared analogously but could not be satisfactorily purified.

4.8. *[{$\mathrm{CF_3(CF_2)_5CH_2CH_2}$}$_2$C=O]$_2$$\mathrm{SnCl_2}$*

To a solution of {$\mathrm{CF_3(CF_2)_5CH_2CH_2}$}$_2$C=O (0.15 g, 0.21 mmol) in $\mathrm{Me_2SO\text{-}d_6}$ was added $\mathrm{SnCl_2}$ (0.02 g, 0.10 mmol) and the mixture heated to 60 °C for 20 min to form a homogeneous solution. This was transferred to an NMR tube and the spectra acquired at 60 °C and at room temperature. ^{1}H NMR (400.13 MHz, $\mathrm{Me_2SO\text{-}d_6}$, 333 K): δ 2.00 (4H, m, $\mathrm{C\mathbf{H}_2CF_2}$), 2.51 (4H, m, $\mathrm{C\mathbf{H}_2CO}$), 3.71 (br, $\mathrm{H_2O}$); ^{19}F NMR (376.55 MHz, $\mathrm{Me_2SO\text{-}d_6}$, 333 K): δ −80.83 (s, $\mathrm{C\mathbf{F}_3}$), −114.44 (s, $\mathrm{C\mathbf{F}_2CH_2}$), −122.40 (s, $\mathrm{CF_3CF_2C\mathbf{F}_2}$), −123.32 (s, $\mathrm{CF_3CF_2CF_2C\mathbf{F}_2}$), −123.86 (s, $\mathrm{CH_2CF_2C\mathbf{F}_2}$), −126.42 ($\mathrm{CF_3C\mathbf{F}_2}$); ^{119}Sn NMR (149.21 MHz, $\mathrm{Me_2SO\text{-}d_6}$, 333 K): δ −452.6 ppm IR (cm^{-1}) ν: 1599 (m, C=O), 1477 (w), 1258 (s, C–F), 1198 (s, C–F), 1137 (m), 1084 (m), 1017 (m), 797 (w), 697 (m).

4.9. *Crystallographic studies*

Crystals of **5** suitable for X-ray structural determination were mounted on a glass fiber tip and placed on the goniometer head in a 123 K $\mathrm{N_2}$ gas stream. The crystal data was collected on a Rigaku Saturn 724 CCD Diffractometer. The data set was collected using Crystalclear-SM 1.4.0 software and 528 diffraction images, of 0.5° per image, were recorded. Data integration, reduction and correction for absorption and polarization effects were all performed using Crystalclear-SM 1.4.0 software. Space group determination, structure solution and refinement were obtained using Crystalstructure ver. 3.8 and Bruker Shelxtl Ver. 6.14 software [21]. Crystal data: $\mathrm{C_{36}H_{20}F_{52}O_8}$, M = 1568.52, Monoclinic, a = 23.03(3), b = 5.925(7), c = 9.741(12) Å, $\alpha = \gamma = 90^\circ$ $\beta = 94.47^\circ(16)$, U = 1325(3) Å^3, T = 123 K, space group P21/c, Z = 1, μ (Mo Kα) = 0.25 mm^{-1}, ρ = 1.966 g/cm^3, 15,857 reflections collected, 2326 unique, (R_{int} = 0.0868), $^aR_1$ = 0.0597, wR_2 $[I > 2\sigma(I)]$ = 0.1469, *Gof* = 0.990, $\{^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|,\ wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}\}$.

Supplementary material

The ^{13}C{^{1}H}–^{19}F HETCOR spectrum of **1** is included as supplementary information. Crystallographic data (excluding structure factors) for the structure of **5** has been deposited with the Cambridge Crystallographic Data Centre CCDC no. 752695. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We wish to thank The Lachesis Fund and Trinity College, Dublin for financial Support. The EPSRC National Mass Spectrometry Service at Swansea University and the Centre for Microscopy and Analysis at Trinity College, Dublin are also gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.02.004.

References

[1] J.A. Gladysz, D.P. Curran, I.T. Horváth (Eds.), Handbook of Fluorous Chemistry, Wiley VCH, Weinheim, 2004.
[2] I.T. Horváth, J. Rábai, Science 266 (1994) 72–75.
[3] D. Gudmunsena, E.G. Hope, D.R. Paigea, A.M. Stuart, J. Fluorine Chem. 130 (2009) 942–950, and references therein.
[4] (a) M. Wende, R. Meier, J.A. Gladysz, J. Am. Chem. Soc. 123 (2001) 11490–11491;
(b) M. Wende, J.A. Gladysz, J. Am. Chem. Soc. 125 (2003) 5861–5872;
(c) K. Ishihara, S. Kondo, H. Yamamoto, Synlett. (2001) 1371–1374;
(d) K. Ishihara, A. Hasegawa, H. Yamamoto, Synlett. (2002) 1299–1301;
(e) K. Mikami, Y. Mikami, H. Matsuzawa, Y. Matsumoto, J. Nishikido, F. Yamamoto, H. Nakajima, Tetrahedron 58 (2002) 4015–4021;
(f) J. Otera, Acc. Chem. Res. 37 (2004) 288–296;
(g) G. Maayan, R.H. Fish, R. Neumann, Org. Lett. 5 (2003) 3547–3550;
(h) J.A. Gladysz, V. Tesevic, Top. Organomet. Chem. 23 (2008) 67–89;
(i) D. Mandal, M. Jurisch, C. Consorti, J.A. Gladysz, Chem. Asian J. 3 (2008) 1772–1782;
(j) F.O. Seidel, J.A. Gladysz, Adv. Synth. Catal. 350 (2008) 2443–2449.
[5] (a) I.T. Horváth, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rábai, E.J. Mozeleski, J. Am. Chem. Soc. 120 (1998) 3133–3143;
(b) L.J. Alvey, R. Meier, T. Soós, P. Bernatis, J.A. Gladysz, Eur. J. Inorg. Chem. (2000) 1975–1983.
[6] R.J. Baker, H.V. Ogilvie, WO2009109754A1.
[7] (a) P. Thebault, E. Taffin de Givenchy, M. Starita-Geribaldi, F. Guittard, S. Geribaldi, J. Fluorine Chem. 128 (2007) 211–218;
(b) D. Hazafya, M. Sobociková, P. Štěpničkab, J. Ludvíkc, M. Kotora, J. Fluorine Chem. 124 (2003) 177–181;
(c) A.M. Jouani, F. Sziinyi, A. Cambon, J. Fluorine Chem. 56 (1992) 85–92;
(d) K. von Werner, H. Blank, A. Gisser, E. Manhart, J. Fluorine Chem. 16 (1980) 193–197.
[8] (a) A.A. Ribeiro, Mag. Res. Chem. 35 (1997) 215–221;
(b) A.A. Ribeiro, J. Mag. Res. A 117 (1995) 257–261;
(c) A.A. Ribeiro, J. Fluorine Chem 83 (1997) 61–66.
[9] (a) C.S. Consorti, F. Hampel, J.A. Gladysz, Inorg. Chim. Acta 359 (2006) 4874–4884;
(b) B. Albinsson, J. Michl, J. Phys. Chem. 100 (1996) 3418–3429;
(c) E.K. Watkins, W.L. Jorgensen, J. Phys. Chem. A 105 (2001) 4118–4125;
(d) J.D. Dunitz, A. Gavezzotti, W.B. Schweizer, Helv. Chim. Acta 86 (2003) 4073–4092;

(e) K. Monde, N. Miura, M. Hashimoto, T. Taniguchi, T. Inabe, J. Am. Chem. Soc. 128 (2006) 6000–6001;
(f) A. Casnati, R. Liantonio, P. Metrangolo, G. Resnati, R. Ungaro, F. Ugozzoli, Angew. Chem., Int. Ed. 45 (2006) 1915–1918.
[10] A. Bondi, J. Phys. Chem. 68 (1964) 441–445.
[11] F. Zimmermann, E. Meux, J.-L. Mieloszynski, J.-M. Lecuireb, N. Oget, Tetrahedron Lett. 46 (2005) 3201–3203.
[12] J.F. Garst, M.P. Soriaga, Coord. Chem. Rev. 248 (2004) 623–652.
[13] D. Soorukram, N. Boudet, V. Malakhov, P. Knochel, Synthesis (2007) 3915–3922.
[14] E.J. Hartwell, R.E. Richards, H.W. Thompson, J. Chem. Soc. (1948) 1436–1441.
[15] A.Y. Zapevalov, T.I. Filyakova, I.P. Kolenko, M.I. Kodess, Zh. Org. Khim. 22 (1986) 93–99.
[16] (a) I.T. Horváth, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rábai, E.J. Mozeleski, J. Am. Chem. Soc 120 (1998) 3133–3143;
(b) L.J. Alvey, R. Meier, T. Soós, P. Bernatis, J.A. Gladysz, Eur. J. Inorg. Chem (2000) 1975–1983;
(c) D.J. Adams, J.A. Bennett, D. Duncan, E.G. Hope, J. Hopewell, A.M. Stuart, A.J. West, Polyhedron 26 (2007) 1505–1513.
[17] D.S. Flett, J. Organomet. Chem. 690 (2005) 2426–2438.
[18] H.-M.M. Yeh, R.A. Geanangel, Inorg. Chim. Acta 52 (1981) 113–118.
[19] J.D. Kennedy, W. McFarlane, in: J. Mason (Ed.), Multinuclear NMR, Plenum Press, New York, 1987, pp. 305–333.
[20] J.D. Donaldson, D.G. Nicholson, J. Chem. Soc. A (1970) 145–150.
[21] Manual, version 5.625; Bruker Analytical X-Ray Systems Inc.: Madison, WI, 2001. G.M. Sheldrick, SHELXTL, An Integrated System for Data Collection, Processing, Structure Solution and Refinement; Bruker Analytical X-Ray Systems Inc.: Madison, WI, 2001.