Palladium catalyzed cross- and homo-coupling reactions of 4-Halo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanes with various organometallic reagents

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ABSTRACT

An investigation of palladium catalyzed Kumada type reactions between various Grignard reagents and mono-substituted octafluoroparacyclophane derivatives revealed that by varying the reaction temperature, and mode of addition of the Grignard reagent, it was possible to influence whether the major product was the cross-coupled, or the homo-coupled (reductive dimer) paracyclophane product. This provides an improved methodology to prepare aryl substituted paracyclophanes, and additionally an alternative route to the unusual and rare di-cyclophane skeleton. Analogous reactions with alkyl lithium reagents were also explored, resulting in the generation of some previously unreported octafluoroparacyclophane products.

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1. Introduction

Molecules that have aromatic rings connected by multiple aliphatic bridges are broadly classified as Cyclophanes [1], and comprise a structurally diverse and well studied class of compounds. The paradigm of cyclophane chemistry is [2.2]para-cyclophane (PCP) since it best exemplifies the numerous interesting and unusual characteristics of these highly strained systems with proximate aromatic rings [2,3]. Even now, there is renewed interest in this area due to recent advances in the use of the paracyclophane motif in material science applications, and also the utilization of such molecules as ligands, reagents and catalysts in enantioselective reactions [4].

Over the last two decades, the area of fluorinated paracyclophanes has continued to evolve. Initially this was driven by the industrial application of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (OFP, **1**) [5] as the monomer for the Parylene VIP AF4 polymer, which combines high thermal and chemical stabilities, with low dielectric constant and moisture absorption [6,7] (Scheme 1). There are now viable large scale syntheses of bridge fluorinated **1** [8–10], and more recently the per-fluorinated paracyclophane (PFP) [11] available in the literature [12]. Such

syntheses have permitted fundamental studies on the reactivity of both OFP [13,14] and PFP [15]. The majority of reports are concerned with OFP, and early OFP derivatives have since been used as building blocks in a wide spectrum of synthetic [16–21] and spectroscopic [22–26] endeavors.

Bi-aryl molecules are a family of compounds that are prevalent in nature, and are important as pharmaceuticals, agrochemicals and chiral ligands and catalysts [27]. The preparation of several OFP derivatives with one or more new aryl–aryl linkages have been reported, almost all of which have employed Palladium catalyzed reactions, such as reductive homo-couplings [20], and Suzuki [19], Kumada [13,14] and Negishi cross-coupling reactions [28].

2. Results and discussion

Based on experience, such reported Palladium catalyzed OFP reactions whilst being successful and always completely reproducible, are somewhat sensitive to the reaction conditions. Herein is an investigation into the optimization of some cross-coupling Kumada type reactions, where varying the reaction conditions (e.g. temperature, rate of addition) generated different, and in some cases, unexpected, products. As shown in Table 1, the initial focus was on the reaction of PhMgBr with OFP-Halides and PdCl₂ in THF. As anticipated, it was quickly established (entries 1–3) that OFP-I **2** was the preferred starting material for such reactions, always generating the highest yield. OFP-Cl **3** did not react under the

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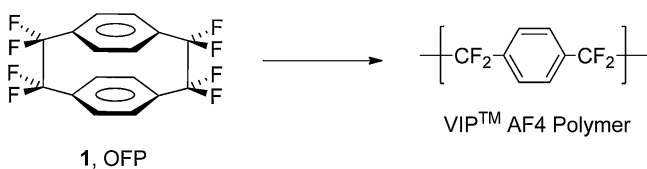
Scheme 1. Polymerization of OFP producing the VIP AF4 Polymer.
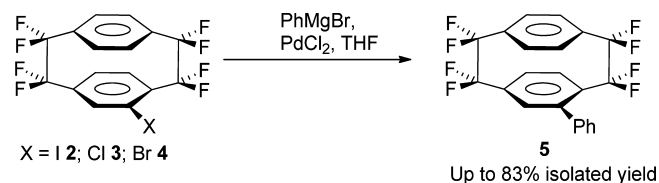
Scheme 2. Kumada aryl cross coupling reactions employing OFP-Halides.

typical reaction conditions, whereas OFP-Br 4 did react, but always with lower isolated yields of desired product, due to an increase in the amount of reduction product, and lower conversion (Scheme 2).

Next the reaction of PhMgBr with 2 was further explored. Running this reaction in the presence of PdCl$_2$, in refluxing THF lead to the desired OFP-Ph 5 cross-coupled product in 49% isolated yield, and as shown in entry 4, reaction in the absence of any PdCl$_2$ catalyst, only resulted in the generation of reduction product 1 in high yield. It was found that the yield was influenced by the speed of addition of the phenyl magnesium bromide. By adding the organometallic reagent slowly (via syringe pump) into the refluxing THF solution, the yield of the cross-coupled product was increased up to 83% (entry 5).

However more surprisingly, it was found that when the reaction was performed at room temperature (entries 6 and 7), in addition to the expected cross-coupled and reduction products, another product was generated. The new unexpected product was identified as bis(OFP) 6 (Scheme 3). Fortunately, the preparation of di-cyclophane 6 has been previously reported [20], including the crystal structures of both diastereomers (since the starting material 2 is planar chiral [29] and racemic), but most importantly also their remarkable ^{19}F NMR spectra, which at room temperature shows significant line broadening caused by restricted molecular rotation observable on the NMR time scale (see Supporting information). Therefore, this distinguishing ^{19}F NMR behaviour immediately prompted the product identification as 6. As shown in entry 7, a yield of 44% for bis(OFP) 6 was obtained at room temperature, whereas no traces of this homo-coupled product were detected at the higher temperatures. The ratio of diastereomers of 6 produced in this reaction was determined by ^{19}F NMR and GC to be 1.9:1. (meso:dl). (The previous deliberate synthesis of 6 using OFP-I/Cu/PdCl$_2$.dppf/DMF/70 °C gave a yield of 74%, with a diastereomeric ratio of meso:dl of 3:2 [20]). In this room temperature reaction, it appears that the Grignard reagent is not acting as a nucleophile (necessary for transmetalation at the

palladium), but rather acting as a reductant, thus promoting reductive homo-coupling rather than the intended cross-coupling.

Most commonly, homo-coupled products in these types of reaction arise from oxidative dimerization of the nucleophilic species [30–32]. In this case it is reductive dimerization of the paracyclophane halide. Usually such couplings are achieved using metals or other reductants [33]. It is possible that in these reactions it is the known single electron transfer (SET) character of the aryl Grignard reagent [34] coming into effect, promoting reductive homo-coupling of the OFP-I. Alternatively, PhMgBr rather than transmetalating the intermediate palladium species, is reacting with OFP-I to produce "OFP-MgBr", which in turn transmetalates with the palladium species, ultimately leading to homo-coupled products.

Having established that in these reactions, the PhMgBr can act as a reductant, as well as a nucleophile, it was investigated whether the nucleophilic (transmetalation) behaviour of the Grignard could be minimized, in order to maximize the homo-coupling process. In this regard, the reaction of more sterically hindered aryl Grignard reagents was explored. As shown in entries 8 and 9, when mesityl magnesium bromide was used, no cross-coupled or homo-coupled products were observed. However, when PCP-MgBr [35] was used (prepared via PCP-Br/^{t}BuLi/MgBr$_2$·Et$_2$O), it was observed that the homo-coupled product 6 was again generated, in 30% isolated yield (entry 10). Disappointingly, no evidence of the cross-coupled "mixed" di-cyclophane (OFP-PCP) was detected, nor was any di-PCP [36] observed.

Encouraged by these productive aryl Grignard reagent reactions, a brief investigation of alkyl organometallics was explored (entries 11–14). Addition of 0.4 equivalents of tert-Butyl Lithium to OFP-I 2 and PdCl$_2$ in THF only yielded reduction product 1, whereas Methyl Lithium (complex with LiBr) gave successful products of cross-coupling, with higher yields being generated at lower temperatures (entries 12–14). The production of OFP-CH$_3$ 7 then permitted the subsequent facile generation of two more previously

Table 1
Organometallic reactions with OFP-Halides.

| Entry	OFP-X	R–M (3 equiv.)	Addn.	Temp.	Time	OFP 1	OFP-R 5 or 7	Bis(OFP) 6
1	–I	PhMgBr	A	Reflux	2 h	44	49	
2	–Br	PhMgBr	A	Reflux	2 h	50[a]	19	
3	–Cl	PhMgBr	A	Reflux	o/n	NR		
4	–I	PhMgBr[b]	A	Reflux	1 h	98		
5	–I	PhMgBr	D	Reflux	o/n	8	83	
6	–I	PhMgBr	D	RT	2 h	20	35	40
7	–I	PhMgBr	D	RT	o/n	15	38	44
8	–I	MesMgBr	D	RT	o/n	93		
9	–I	MesMgBr	A	0 °C	1 h	NR		
10	–I	PCPMgBr	D	RT	o/n	60		30
11	–I	^{t}BuLi[c]	A	RT	2 h	30[d]		
12	–I	CH$_3$Li	D	Reflux	2 h	66	31	
13	–I	CH$_3$Li	D	RT	o/n	40	55	
14	–I	CH$_3$Li	D	0 °C	5 h	17	81	

D = slow addition (either dropwise or via syringe pump); A = added in a single aliquot.
[a] 20% starting material left.
[b] zero PdCl$_2$ added.
[c] 0.4 equivalents used.
[d] 65% starting material left.
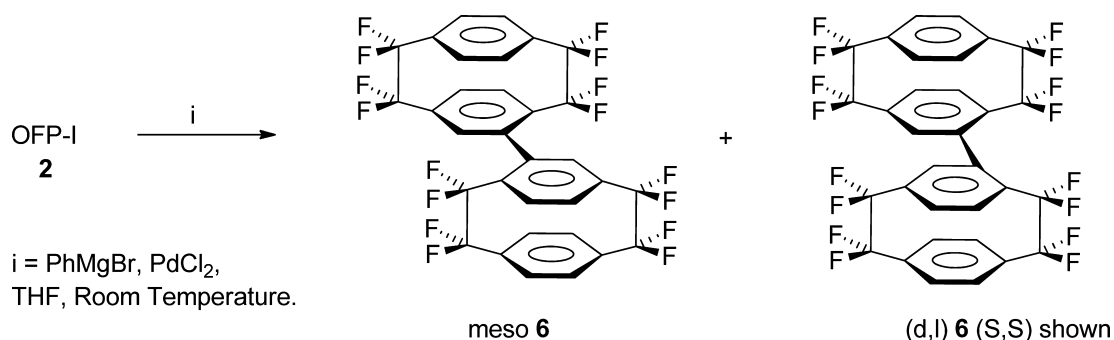
Scheme 3. Production of bis(OFP) diastereomers **6** via reductive homo-coupling.

unreported OFP derivatives, namely OFP-CO_2H **8** and OFP-$CO_2CH_2CH_3$ **9**, via standard oxidation, and esterification processes (Scheme 4).

Compounds **7**–**9** displayed NMR and mass spectrometry characterization data typical for mono-substituted OFP derivatives [13]. For example in the ^{19}F NMR spectra, they exhibited the characteristic four AB patterns with typical doublets $^2J_{FF}$ ~240 Hz, due to the eight chemically different fluorines. Under electron-ionization MS, they showed the characteristic paracyclophane fragmentation of molecular ion into the two xylylene "halves", with the dominant MS peak always arising from the more electron rich deck.

It is noteworthy that OFP-CH_3 **7** exhibits a $^5J_{FH}$ through space coupling of 4.59 Hz between the syn Fluorine on C-2, and the Hydrogens of the methyl group at position 4, (Fig. 1), causing the methyl resonance ($\delta_H = 2.35$ ppm) to appear as a doublet in the ^1H NMR spectrum. The ^{19}F NMR signal of the corresponding Fluorine atom did appear correspondingly broadened, but the coupling was masked within the existing other couplings (e.g. $^3J_{FF}$ ~5–10 Hz) characteristic for such OFP derivatives [26]. A similar through space coupling in the trifluoromethyl-substituted OFP derivative displays $^5J_{FF}$ around 29 Hz [13], whereas the hydrocarbon PCP-CH_3

does not reveal any observable couplings between the methyl group and the bridge hydrogens [37,38]. Since such spectroscopic effects are an insightful probe into the stereochemical and structural peculiarities of these strained and rigid systems [39], it highlights the benefit of the presence of the NMR active fluorine nuclei in such molecules.

The two most widely reported NMR features of substituted paracyclophanes are the ^1H NMR ortho and gem shifts, which are used to investigate homo- and hetero-annular interactions, respectively [39,40]. The ^1H NMR ortho and gem shifts for **7**–**9** are reported in Table 2, and such values are in keeping with the general trends reported for OFP versus PCP values [13].
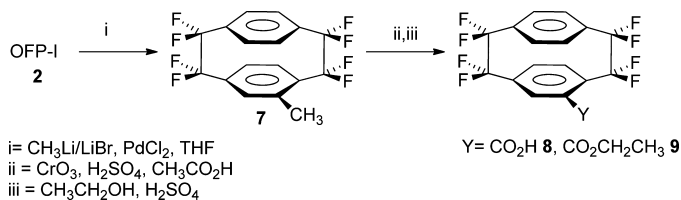
The preparation of these three new derivatives of OFP not only allows the development of new useful starting materials, but also the acquisition of spectral data to help provide insight into the bonding and geometries of these strained systems. Further investigations into organometallic coupling reactions with OFP derivatives are ongoing, including the use of aryl substituted OFP derivatives in material science applications and as enantioselective probes.

3. Conclusions

Herein an investigation of palladium catalyzed Kumada type reactions between various Grignard reagents and mono-substituted octafluoroparacyclophane derivatives is described. It was discovered that by varying the reaction temperature, and mode of addition of the Grignard reagent, it was possible to influence whether the major product was the cross-coupled, or the homo-coupled paracyclophane product. It was found that PhMgBr was especially good at promoting reductive homo-coupling of OFP-I **2**, which provides an alternative method to produce the unusual di-cyclophane **6**. Analogous reactions with alkyl lithium reagents were also explored, resulting in the generation of some previously unreported octafluoroparacyclophane products.

Scheme 4. Preparation of OFP-CH_3 **7** and its subsequent oxidation and esterification.

4. Experimental

All NMR spectra were obtained on a Varian Mercury Plus 300 MHz spectrometer with 5 mm ATB probe. All ^{19}F and ^1H NMR
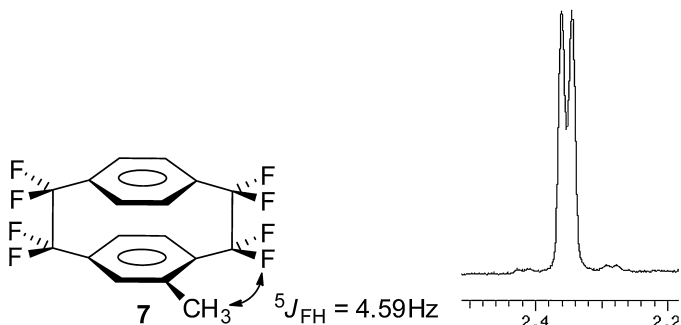

Fig. 1. Expanded ^1H NMR spectrum showing the Methyl resonance of **7** displaying a $^5J_{FH}$ through space coupling of 4.59 Hz with the syn Fluorine on C-2.

Table 2
Ortho and gem shifts for compounds **7**–**9**.

	–CH₃[a] (ppm)	–CO₂H[b] (ppm)	–CO₂CH₂CH₃[b] (ppm)
Ortho shift	−0.55	+0.14	+0.12
Gem shift	+0.09	+0.24	+0.23

[a] Value in $CDCl_3$.
[b] Value in d-6 acetone.

spectra were performed at ambient temperature in deuterated acetone at 282 MHz and 300 MHz, respectively, except where indicated in the text. Chemical shifts for ^{19}F and ^{1}H spectra were determined relative to CFCl$_3$ (0.0 ppm) and TMS (0.0 ppm), respectively. All products were colourless solids, except where specified otherwise. All reagents, unless otherwise specified, were used as purchased from Aldrich or Fisher. Column chromatography was performed using chromatographic silica gel 200–425 mesh, as supplied by Fisher. Low-resolution mass spectrometry was performed at the Center for Advanced Food Technology, New Brunswick, NJ, the University of Pennsylvania, Philadelphia, PA, and at Rutgers University-Camden. High-resolution mass spectrometry was performed at the University of Pennsylvania, Philadelphia, PA. The starting materials (OFP-I 2, OFP-Br 4, OFP-Cl 3 and PCP-Br) were prepared according to their published literature procedures [13,41].

4.1. Synthesis of 4-phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 5

A degassed THF solution (4 ml) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 2 (640 mg, 1.34 mmol) and palladium dichloride (8 mg, 0.04 mmol) was stirred and brought to reflux under a nitrogen atmosphere. A THF solution of phenyl magnesium bromide (1 M, 4 ml, 4.0 mmol) was added via syringe and syringe pump, with completion taking 4 h, and the black solution was refluxed overnight. Evaporation of the solvent was followed by the addition of ice water (75 ml), and the precipitated solids were chromatographed on silica gel (hexane/dichloromethane 8.5/1.5) to give (R_f = 0.49) octafluoro[2.2]paracyclophane 1 (38 mg, 8%) and (R_f = 0.39) 4-phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 5 (476 mg, 83%). Products 1 and 5 were identified by comparison of their ^{19}F and ^{1}H NMR spectra, and GCMS analyses, with published literature data [8,13], and additionally were found to be identical to authentic samples previously prepared. See Supporting information for spectra and data.

4.2. Synthesis of 4,4′-bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane) 6

4.2.1. Method A
A degassed THF solution (10 ml) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 2 (1.60 g, 3.35 mmol) and palladium dichloride (20 mg, 0.10 mmol) was stirred at room temperature under a nitrogen atmosphere for 1 h. A THF solution of phenyl magnesium bromide (1 M, 10 ml, 10.0 mmol) was added via syringe and syringe pump, so that complete addition took 5 h. The resulting black solution was stirred for another 6 h. After that time, evaporation of the solvent was followed by the addition of ice water (250 ml), and the precipitated solids were chromatographed on silica gel (hexane/dichloromethane 8.5/1.5) to give (Rf = 0.49) octafluoro[2.2]paracyclophane 1 (177 mg, 15%), (R_f = 0.39) 4-phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 5 (545 mg, 38%), and (R_f = 0.30) 4,4′-bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane) 6 (517 mg, 44%). The ratio of diastereomers of 6 was 29:15 (meso:dl) as established by ^{19}F NMR and GC analysis using a J&W DB-5ms column (Retention times of 24.0 and 26.5 min. for dl and meso, respectively). Products 6 were identified by comparison of their ^{19}F and ^{1}H NMR spectra, and GCMS analyses, with published literature data [15]. See Supporting information for spectra and data.

4.2.2. Method B
A degassed THF solution (20 ml) containing 4-bromo[2.2]paracyclophane (3.67 g, 12.80 mmol) and magnesium bromide etherate (3.30 g, 12.80 mmol) was stirred at room temperature under a nitrogen atmosphere for 1 h. Then a hexane solution of tert-butyl lithium (1.7 M, 6.6 ml, 11.22 mmol) was added dropwise, and the mixture was stirred for 2 h at room temperature. The resulting pale brown solution was then used in the following reaction: a degassed THF solution (20 ml) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 2 (1.53 g, 3.320 mmol) and palladium dichloride (110 mg, 0.62 mmol) was stirred at room temperature under a nitrogen atmosphere for 1 h. The pre-formed PCP-MgBr solution (27 ml, 11.22 mmol) was slowly added dropwise so that complete addition took 2 h. The resulting black solution was stirred for another 6 h. After that time, evaporation of the solvent was followed by the addition of ice water (200 ml), and the precipitated solids were chromatographed on silica gel (hexane/dichloromethane 8.5/1.5) to give (Rf = 0.49) octafluoro[2.2]paracyclophane 1 (701 mg, 60%), and (Rf = 0.30) 4,4′-bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane) 6 (350 mg, 30%). The ratio of diastereomers of 6 was 1.5:1 (meso:dl) as established by ^{19}F NMR, and GC analysis.

4.3. Synthesis of 4-methyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 7

A degassed THF solution (100 ml) containing 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 2 (10.5 g, 21.87 mmol) and palladium dichloride (0.216 g, 1.22 mmol) was stirred under an atmosphere of nitrogen, and cooled to 0 °C in an ice bath. Over a period of 2 h, an ether solution of methyl lithium/lithium bromide complex (1.5 M, 44 ml, 66.9 mmol) was added dropwise. The solution was maintained at 0 °C for 3 h, and then allowed to warm to room temperature. Analysis of the crude mixture by ^{19}F NMR against an internal standard of trifluorotoluene showed the mixture to comprise of 4-methyl-1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane 7 (17.71 mmol, 81%) and octafluoroparacyclophane 1 (3.72 mmol, 17%). Moist acetone (100 ml) was carefully added to the reaction mixture, and this mixture was filtered, and evaporated under reduced pressure. The resulting solid was suitable for further reactions.

An analytically pure sample was obtained by chromatography on silica gel (hexane/dichloromethane 19/1) to give (R_f = 0.45) 4-methyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 7; mp = 126–131 °C. (NMR spectra obtained in CDCl$_3$ due to superior solubility of OFP-CH$_3$). ^{1}H NMR δ 7.39 (d, ^3J = 8.70 Hz, 1H); 7.41 (d, ^3J = 8.70 Hz, 1H); 7.26–7.04 (m, 4H); 6.98 (d, ^3J = 8.70 Hz, 1H); 6.75 (s, 1H); 2.35 (d, ^5J = 4.59 Hz, 3H); ^{19}F NMR δ −110.21 (dm, ^2J = 243.3 Hz, 1F); −111.97 (d, ^2J = 245.3 Hz, 1F); −113.02 (d, ^2J = 239.1 Hz, 1F); −113.61 (d, ^2J = 239.1 Hz, 1F); −116.41 (d, ^2J = 239.1 Hz, 1F); −116.91 (d, ^2J = 237.1 Hz, 1F); −116.52 (d, ^2J = 237.1 Hz, 1F); −117.03 (d, ^2J = 239.1 Hz, 1F); MS m/z 366 (M+, 20%), 190 (100), 176 (21). Anal. Calcd for C$_{17}$H$_{10}$F$_8$: C, 55.70.46; H, 2.73. Found: C, 55.42; H, 2.55.

4.4. Synthesis of 4-carboxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 8

Sulphuric acid (12 ml, 98% conc.) was carefully added to a solution of glacial acetic acid (400 ml) containing 4-methyl-1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophane 7 (6.64 g, 18.14 mmol). This mixture was immersed in a cool water bath, and with vigorous stirring, chromium trioxide (40.00 g, 44 mmol) was added over a period of 2 h, and left to stir for a further 2 h. Then the mixture was poured into ice water (1000 ml), and left to stir overnight. The resulting solids were filtered, and analysis by ^{19}F NMR against an internal standard of trifluorotoluene showed the mixture to comprise of 4-carboxyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane 8 (15.42 mmol,

85%) and octafluoroparacyclophane **1** (0.91 mmol, 5%). Compound **8** was not stable to the typical column chromatography conditions, and so the crude product was recrystallized from CH_2Cl_2/hexane (2:1), then characterized without further purification, and used "as is" for the subsequent esterification. 4-Carboxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **8**; ^1H NMR δ 7.54 (d, ^3J = 8.10 Hz, 1H); 7.48 (s, 2H); 7.74–7.40 (m, 3H); 7.29 (d, ^3J = 8.10 Hz, 1H); ^{19}F NMR δ −112.46 (d, ^2J = 241.3 Hz, 1F); −112.65 (d, ^2J = 241.3 Hz, 1F); −115.80 (d, ^2J = 237.1 Hz, 1F); −116.43 (d, ^2J = 237.1 Hz, 1F); −116.65 (d, ^2J = 241.0 Hz, 1F); −117.70 (d, ^2J = 241.0 Hz, 1F); −116.42 (d, ^2J = 239.1 Hz, 1F); −117.42 (d, ^2J = 239.1 Hz, 1F); MS m/z 396 (M+, 22%), 348 (25), 200 (24) 176 (100). HRMS calcd. for $C_{17}H_8F_8O_2$ 396.0397, found 396.0381.

4.5. 4-Ethoxycarbonyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **9**

4-Carboxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **8** (1.02 g, 2.57 mmol) was dissolved in ethanol (15 ml) and sulphuric acid (3 ml, 98% conc.) was carefully added dropwise with stirring. The mixture was refluxed overnight. Evaporation of the solvent under reduced pressure gave a pale yellow oil, which crystallized on addition of several drops of water. The solids thus produced were chromatographed on silica gel (hexane/ether 9/1) to give (Rf = 0.47) 4-Ethoxycarbonyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane **9** (1.07 g, 98%); mp = 106–109 °C. ^1H NMR δ 7.51 (d, ^3J = 8.10 Hz, 1H); 7.46 (m, 2H); 7.46–7.38 (m, 3H); 7.30 (d, ^3J = 8.10 Hz, 1H); 4.40 (q, ^3J = 7.20 Hz, 2H); 1.40 (t, ^3J = 7.20 Hz, 3H); ^{19}F NMR δ −114.04 (d, ^2J = 239.3 Hz, 1F); −114.06 (d, ^2J = 239.3 Hz, 1F); −117.35 (d, ^2J = 239.1 Hz, 1F); −117.76 (d, ^2J = 239.1 Hz, 1F); −117.69 (d, ^2J = 236.8 Hz, 1F); −118.97 (d, ^2J = 236.8 Hz, 1F); −118.01 (d, ^2J = 239.3 Hz, 1F); −119.10 (d, ^2J = 239.3 Hz, 1F); MS m/z 424 (M+, 14%), 200 (25), 176 (100). HRMS calcd. for $C_{19}H_{12}F_8O_2$ 424.0710, found 424.0694.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015.02.016.

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