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Suzuki aryl cross-coupling chemistry using derivatives of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane

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Dedicated to R.D. Chambers on the occasion of his 70th birthday.

Abstract

An exploration into the scope of Suzuki aryl cross-coupling chemistry using derivatives of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane is reported. The coupling of 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane with various aryl boronic acids and boronic acid pinacol esters was successful, with the exception of very sterically demanding systems, such as mesityl. The synthesis of the previously unreported 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanyl-4-boronic acid is described, together with various Suzuki aryl cross-coupling reactions of this new system. Using standard Suzuki methodology, it was possible to prepare dicyclophanes bearing two octafluoro[2.2]paracyclophane units separated by both one and two benzene rings.

Keywords: Octafluoro[2.2]paracyclophane; OFP; Paracyclophane; Dicyclophane; Suzuki aryl cross-coupling

1. Introduction

The recent improved synthetic routes to 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (OFP) [1], and its simple derivatives [2,3], have paved the way for an exploration and elaboration of the chemistry of this cyclophane with its signature octafluorinated bridges. This chemistry is still in its infancy, which explains why even though bi-aryl compounds are ubiquitous in the applied fields of liquid crystals, polymers and advanced materials, including many examples of aryl groups connected to the hydrocarbon [2.2]paracyclophane (PCP) skeleton [4], the literature concerning aryl groups connected to the OFP framework is very scarce. The only reported compounds are the phenyl- [2,3] and thiophenyl-derivatives [3], together with several polycyclic structures derived from Diels–Alder trapping of the OFP-aryne moiety [5].

There is merit in preparing a selection of arene substituted OFP derivatives since OFP is the precursor to the increasingly important commercial polymer Parylene VIP™ AF4 [6], and the presence of bulky arene substituents carrying different functional groups should not only vary the electronic and structural properties of such polymers but also afford routes to prepare more structurally complex monomers. The opportunity to develop the chemistry of this fluorinated cyclophane, and compare it with the behavior of its famous and thoroughly studied hydrocarbon analogue [7] should also not be overlooked, especially since initial reports demonstrate that the fluorines significantly modify the chemistry of this [2.2]paracyclophane [2,3].

Connecting two cyclophane units through an aryl–aryl linkage generates a class of compounds called dicyclophanes. As shown in Fig. 1, various dicyclophanes have been reported previously in the literature. Both the classic diPCP, **1,** (cyclophane units linked via a 4-4′ aryl–aryl bond) [8] and its bridge fluorinated analogue, bisOFP, **2**, [9], have been described, and also several structures where two PCP units are linked by various inorganic, organic [10,11], and transition metal [12] containing ‘‘spacer groups’’. Dicyclophanes are of commercial interest since they lead to cross-linked parylene polymers. Indeed one example is reported to

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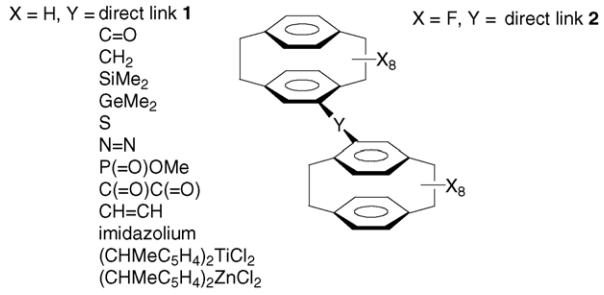


Fig. 1. Dicyclophanes described in the literature (only meso diastereomers shown).

be a promising sensor material for air humidity [13]. Since each cyclophane unit exhibits planar chirality, the diastereoselectivity of dicyclophane formation is of interest. Furthermore, observable spectroscopic differences between diastereomers of this type, and the cause of such differences, have been addressed by Ernst and coworkers [10].

2. Results and discussion

Of the many well established and thoroughly studied aryl–aryl cross-coupling methods available, the Suzuki cross-coupling route [14] was selected due to its convenience and other advantages, including the low toxicity of reagents, no prerequisite of anhydrous conditions and excellent tolerance of various functional groups. Given that Suzuki reactions employ aryl halides reacting with aryl boronic acids/esters, our first line of investigation was to react various aryl boronic acids with the 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (OFP–I), **3**, derivative which has been previously described in [2]. Our investigation showed that under standard Suzuki conditions it was possible to achieve successful aryl cross-coupling reactions with a variety of electronically diverse aryl substituted boronic acids in high yields, as shown in Table 1 (entries 1–4). Whilst the sterically hindered *ortho* toluene boronic acid did couple smoothly, the more sterically hindered mesityl boronic acid did not (Table 1, entry 5). Identical reactions employing the corresponding aryl boronic acid pinacol esters were performed and similar trends were observed (Table 1, entries 6–10). Attempts to substitute **3** with OFP–Br [2] led to severely diminished yields, and OFP–Cl [2] was found to be unreactive under the conditions used (Table 1, entries 11 and 12).

Table 1
Reactions of OFP–halides with aryl boronic acids (esters)

Entry	Z	X	Y	Product	Isolated yield (%)
1	I	$B(OH)_2$	H	**4**	86
2	I	$B(OH)_2$	2-CH_3	**5**	76
3	I	$B(OH)_2$	4-CN	**6**	80
4	I	$B(OH)_2$	3-OH	**7**	85
5	I	$B(OH)_2$	2,4,6-$(CH_3)_3$	**8**	0
6	I	$BO_2C_6H_{12}$	H	**4**	88
7	I	$BO_2C_6H_{12}$	2-CH_3	**5**	78
8	I	$BO_2C_6H_{12}$	4-CN	**6**	83
9	I	$BO_2C_6H_{12}$	3-OH	**7**	89
10	I	$B(OR)_2$[a]	2,4,6-$(CH_3)_3$	**8**	0
11	Br	$B(OH)_2$	4-CN	**6**	29[b]
12	Cl	$B(OH)_2$	4-CN	**6**	0

[a] Dipinacol ester.
[b] Yield based on ^{19}F NMR.

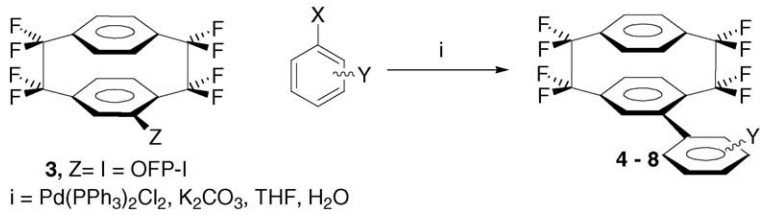
For all of the coupling reactions described in this paper, the same protocol was followed: the reagents/catalyst were added into a flask under a counter current of dry nitrogen, the solvent was syringed in, and then the reaction was warmed to 66 °C for 48 h. ^{19}F NMR and TLC were used to confirm whether reaction had proceeded to completion, and then ether/water workup was followed by column chromatography on silica gel (Scheme 1).

Having demonstrated that Suzuki chemistry was possible using the OFP–I/aryl boronic acid (ester) route, the reverse approach was investigated. This required the preparation of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanyl-4-boronic acid (OFP–$B(OH)_2$), **9**, which had been previously unreported in the literature. Compound **9** was successfully prepared from **3** using *n*-butyllithium for lithium–iodide exchange at −78 °C in ether, followed by reaction with trimethyl borate and subsequent acid hydrolysis. OFP–$B(OH)_2$ was formed in reasonable isolated yield (60%), and was found to be stable in air and could be purified by column chromatography on silica gel. This is in contrast to the corresponding hydrocarbon analogue, PCP–$B(OH)_2$, which is oxidatively unstable and yields PCP–OH and PCP in air or exposure to silica gel [15]. Clearly the electron withdrawing effect of the bridge fluorines in **9** confer extra oxidative stability to this system. Under more forcing conditions, **9** was oxidized to OFP–OH, **10**, via reaction with alkaline hydrogen peroxide (69% conversion after 24 h) (Scheme 2).

Compound **9** could be stored for several days and then used in Suzuki cross-coupling reactions (Table 2, entries 1–5). Furthermore, it was also possible, and generally more convenient, to prepare the corresponding dimethylborate **11** in situ, and then use it immediately for a two step, one pot coupling reaction [16] (Table 2, entries 6–10; Scheme 3).

The fluorinated products all displayed the characteristic ^{19}F NMR spectrum resulting from their eight chemically different fluorines [2], each strongly coupling to its geminal fluorine ($^2J_{F-F} \sim 240$ Hz) which yields 4AB quartets.

Several recurring spectroscopic features pertaining to the OFP skeleton were identified throughout the inspection of the spectra of these related structures. Such observations, combined with the predictability of the ^{13}C NMR chemical shifts of the arene substituents allowed elucidation of the ^{13}C NMR spectra of these systems [15]. Our comprehension of the ^{13}C NMR data was greatly enhanced by running separate ^{13}C NMR experiments in ^1H decoupled and ^{19}F decoupled modes. Recurring features of these arene substituted OFP derivatives included the four CF_2 bridge carbons C-1,2,9,10 ($\delta_C \sim 118$ ppm), which were easy to identify, appearing in the $^{13}C\{^1H\}$ NMR as triplets of triplets ($^1J_{C-F} \sim 270$ Hz,



Scheme 1. Suzuki aryl cross-coupling reactions employing OFP–halides.

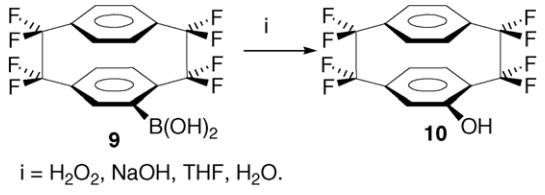
$^{2}J_{C-F} \sim 27$ Hz), but as four singlets in the $^{13}C\{^{19}F\}$ NMR. The four bridgehead carbons of the OFP unit (C-3,6,11,14) appeared as triplets ($^{2}J_{C-F} \sim 26$ Hz) in the $^{13}C\{^{1}H\}$ NMR, but in the $^{13}C\{^{19}F\}$ NMR as three triplets and one doublet (typical $^{3}J_{H-C} \sim 9$ Hz). This doublet could therefore be unambiguously assigned C-6, since it is the only bridgehead with only one *meta* located C–H unit (hence doublet), whereas the other three (C-3,11,14) are flanked by two *meta* C–H units (hence triplets) (Fig. 2).

For the derivatives bearing an *ortho* or *para* substituted phenyl group, it was possible to identify unambiguously the ^{13}C shift of C-8 from the $^{13}C\{^{19}F\}$ NMR spectra. All the arene C–H resonances in these systems should appear as doublets of doublets ($^{1}J_{C-H} \sim 170$ Hz, $^{3}J_{C-H} \sim 7$ Hz) due to the presence of a *meta* located C–H unit, except for C-8, which appears only as a doublet ($^{1}J_{C-H} \sim 170$ Hz). This was most easily confirmed for **6**, due to the convenient resolution of all the signals in the δ_C 126–134 ppm region. However, we observed that for all the aryl substituted OFP derivatives described in this paper, the ^{13}C resonance corresponding to C-8 was always the most downfield of all the arene C–H ^{13}C signals. Moreover, it was observed that C-8 always displayed an unusually strong coupling with the fluorines on C-2, which resulted in C-8 appearing as a doublet of doublets ($^{3}J_{C-F} \sim 13$ and 5 Hz), or a triplet (7 Hz) in some cases. It is tempting to attribute this enhanced coupling to the arene substituent forcing the connected ring to twist into a conformation that changes the alignment of C-8 with the fluorines on C-2.

The electron ionization mass spectrometry of these products provided excellent examples of the characteristic cleavage into ''halves'' associated with cyclophane to xylylene fragmentations [2,7].

Encouraged by the success of these Suzuki reactions, we applied this methodology to the preparation of some new dicyclophane derivatives containing the OFP unit. Our attempts to prepare dicyclophanes connected through a direct aryl–aryl linkage met with frustration. Suzuki reaction of **3** and PCP–$B(OH)_2$ did not yield any dicyclophane product, nor did the alternate strategy of **9** with PCP–Br. The increased steric bulk of PCP seems to be prohibitively large to use these Suzuki conditions to prepare the so-far elusive ''mixed'' dicyclophane, OFP–PCP.

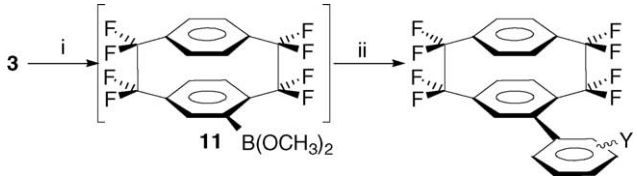
Recognizing this limitation, we turned our attention to the preparation of new dicyclophane derivatives with OFP units separated via ''spacer groups''. Towards this goal, we reacted two equivalents of **3** with *para* phenylenedi-boronic acid under standard Suzuki conditions. The ^{19}F NMR spectrum of the crude reaction showed the presence of two OFP containing products. Initially, we presumed this was an indication of both diastereomers of the desired product, but



Scheme 2. Oxidation of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanyl-4-boronic acid.

Table 2
Suzuki reactions employing OFP boronic acid (ester)

Entry	Boronate	Y	Product	Isolated yield (%)
1	**9**	H	**4**	76
2	**9**	2-CH_3	**5**	86
3	**9**	4-CN	**6**	80
4	**9**	3-OH	**7**	85
5	**9**	2,4,6-$(CH_3)_3$	**8**	0
6	**11**	H	**4**	81
7	**11**	2-CH_3	**5**	79
8	**11**	4-CN	**6**	76
9	**11**	3-OH	**7**	86
10	**11**	2,4,6-$(CH_3)_3$	**8**	0



Scheme 3. In situ Suzuki aryl cross-coupling reactions.

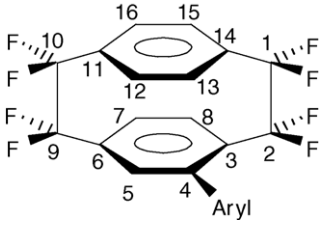


Fig. 2. Cahn–Ingold–Prelog carbon numbering scheme for [2.2]paracyclophanes [17].

Table 3
Dicyclophane formation

Entry	OFP–X	Y–Ph–Y	Ratio	Yield (%)	
				12	**13**
1	OFP–I	$B(OH)_2PhB(OH)_2$	2:1	30	20
2	OFP–I	$B(OH)_2PhB(OH)_2$	4:1	51	–
3	OFP–I	PIN–Ph–PIN	4:1	60	–
4	OFP–$B(OH)_2$	Br–Ph–Br	4:1	53	–
5	OFP–$B(OCH_3)_2$	Br–Ph–Br	4:1	56	–

were surprised to find that the two fluorinated products could be easily separated by column chromatography. Further characterization confirmed the products **12** and **13** as dicyclophanes with two OFP units connected by one and two *para* linked benzene rings in 30% and 20% isolated yields, respectively. Compound **13** appears to arise from a homocoupling of boronic acids, and formation of this product could be suppressed by increasing the stoichiometry of **3** to diboronic acid to 4:1. Similar improved yields of **12** were obtained employing the boronic acid pinacol ester, and also using the reverse approach of OFP–$B(OH)_2$ (and corresponding in situ dimethylborate analogue) with *para*-dibromobenzene (Table 3; Scheme 4).

In the ^{1}H NMR, **12** displayed a singlet (4H) $\delta_H = 7.78$ ppm, further downfield from the 14 OFP hydrogens at $\delta_H = 7.36$–7.66 ppm. Whereas **13** displayed its 14 OFP hydrogens in a similar region, but also exhibited an AB quartet (8H) arising from the non-equivalent hydrogen atoms on the biphenyl spacer group, with one of the doublets further downfield from the other hydrogens at $\delta_H = 7.72$ ppm. The $^{13}C\{^1H\}$ and $\{^{19}F\}$ NMRs of **12** and **13** displayed the same characteristic features as described previously for the aryl substituted derivatives. The ^{19}F NMR spectra of the isolated products **12** and **13** exhibited only one set of eight sharp doublets and did not show any evidence of the significant line broadening due to restricted rotation, as described for **2** and related systems [9].

The preparation of other related dicyclophane systems, and their diastereoselectivity of formation, spectroscopic properties and device application are currently under investigation.

3. Summary

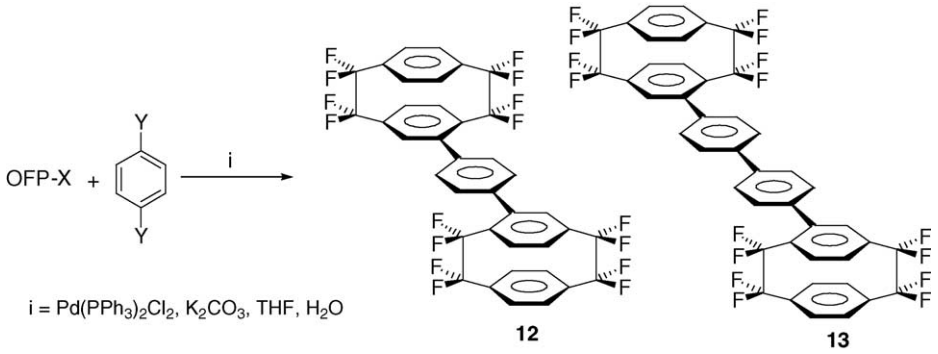
The first examples of Suzuki aryl cross-coupling chemistry using derivatives of 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane are reported. The coupling of 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane with various aryl boronic acids and boronic acid pinacol esters was successful, with the exception of very sterically demanding systems, such as mesityl. The synthesis of the previously unreported 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanyl-4-boronic acid is described, along with various Suzuki aryl cross-coupling reactions of this new system. Using Suzuki methodology, it was possible to prepare dicyclophanes bearing two OFP units separated by both one and two benzene rings.

4. Experimental

All NMR spectra were obtained on a Varian Mercury Plus 300 MHz spectrometer with 5 mm ATB probe at ambient temperature. All ^{19}F, ^{1}H and ^{13}C NMR spectra were performed in deuterated acetone at 282, 300 and 75 MHz, respectively, except where indicated in the text. Chemical shifts for ^{19}F, ^{1}H and ^{13}C spectra were determined relative to $CFCl_3$ (0.0 ppm), TMS (0.0 ppm) and d_6-acetone (29.8 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. Melting points are uncorrected. Low-resolution mass spectrometry was performed at the Center for Advanced Food Technology, New Brunswick, NJ, and high-resolution mass spectrometry was performed at the University of Pennsylvania, Philadelphia, PA.

4.1. Starting materials

The aryl bromides, halides, boronic acids and boronic acid pinacol esters used were purchased from commercial sources except for the following.



Scheme 4. Formation of dicyclophanes with phenyl spacer groups. (Only *meso* diastereomers are shown.)

4.1.1. 2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxaborolane

Based on a published procedure [18], a flask charged with [1,1′-bis(diphenylphosphino)-ferrocenyl]dichloropalladium(II) (0.16 g, 0.19 mmol), potassium acetate (1.87 g, 19.10 mmol), and bis(pinacolato)diboron (1.77 g, 6.99 mmol) was flushed with N_2. DMSO (38 mL) and bromobenzene (0.67 mL, 6.36 mmol) were then added. The reaction mixture was left stirring overnight at 80 °C. Then the mixture was extracted with ethyl acetate (4 × 25 mL) and dried ($MgSO_4$). The crude product was distilled and the fraction with boiling point 118–127 °C was confirmed as phenylboronic acid pinacol ester (0.66 g, 51%) by comparison of ^{1}H NMR with literature values [18,19]. ^{1}H NMR δ 7.81 (d, ^3J = 7.8 Hz, 2H), 7.46 (t, ^3J = 7.3 Hz, 1H), 7.36 (t, ^3J = 7.3 Hz, 2H), 1.35 (s, 12H).

4.1.2. 2-(2-Methylphenyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane

A mixture of 2-methylphenylboronic acid (0.80 g, 5.88 mmol), pinacol (0.69 g, 5.84 mmol) and DCM (9 mL) was stirred at room temperature for 4 h. Water (3 mL) was added, the reaction was extracted with ether (2 × 30 mL) and the organic layer was evaporated under reduced pressure to give 2-(2-methylphenyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane (1.02 g, 80%). ^{1}H NMR δ 7.72 (d, ^3J = 7.5 Hz, 1H), 7.31 (t, ^3J = 7.2 Hz, 1H), 7.07–7.17 (m, 2H), 2.10 (s, 3H), 1.35 (s, 12H), in excellent agreement with previously reported values [19].

4.1.3. 2,2′-(1,4-Phenylene)bis[4,4,5,5-tetramethyl-1,3-dioxaborolane]

A variation on a published method [20] was used. A suspension of phenyl-1,4-diboronic acid (1.00 g, 6.03 mmol), pinacol (1.70 g, 14.47 mmol), and $MgSO_4$ (2.00 g, 16.62 mmol) in DCM (9 mL) was stirred overnight at room temperature. The residue was extracted with ethyl acetate (2 × 30 mL) and the solvent was evaporated under reduced pressure. The crude product was column chromatographed (dichloromethane, R_f = 0.92) to give phenyl-1-4-diboronic acid bis-pinacol ester (1.55 g, 78%), whose ^{1}H NMR δ 7.82 (s, 4H), 1.35 (s, 24H), matched the literature values [19,20].

4.1.4. 4-Iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**3**)

This compound was prepared from 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane [1] by the published procedure [2]. ^{13}C NMR data for this compound have not been previously reported; ^{13}C{^{1}H} NMR δ 141.90, 133.72 (dd, J = 14.2, 3.8 Hz), 130.58, 130.18, 129.96, 129.46, 126.69 (t, J = 6.2 Hz) (aryl C–Hs); 119.16 (tt, J = 269.0, 28.8 Hz), 118.88 (tt, J = 270.8, 27.3 Hz), 118.52 (tt, J = 269.4, 28.0 Hz), 118.15 (tt, J = 271.1, 28.8 Hz) (CF_2s); 94.85 (d, J = 7.0 Hz) (C–I); 136.67 (t, J = 25.9 Hz), 135.93 (t, J = 26.4 Hz), 135.10 (t, J = 26.8 Hz), 134.33 (t, J = 26.2 Hz) (cyclophane bridgeheads); Relevant ^{13}C{^{19}F} NMR data 141.90 (dd, J = 170.6, 6.7 Hz), 133.72 (d, J = 170.6 Hz), 130.58 (dd, J = 167.5, 6.5 Hz), 130.18 (dd, J = 166.9, 6.7 Hz), 129.96 (dd, J = 166.1, 6.7 Hz), 129.46 (dd, J = 168.4, 6.7 Hz), 126.69 (dd, J = 166.8, 6.7 Hz) (aryl C–Hs); 94.85 (d, J = 9.3 Hz) (C–I); 136.67 (t, J = 7.3 Hz), 135.93 (d, J = 8.6 Hz), 135.10 (t, J = 8.1 Hz), 134.33 (t, J = 7.8 Hz) (cyclophane bridgeheads).

4.1.5. 1,1,2,2,9,9,10,10-Octafluoro[2.2]paracyclophanyl-4-boronic acid (**9**)

4-Iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.50 g, 1.05 mmol) and ether (11 mL) were cooled to −78 °C under a N_2 atmosphere. *n*-Butyllithium (1.30 mL of 1.6 M in hexane, 2.08 mmol) was added, and the solution was stirred for 1 h at this temperature. Trimethyl borate (0.25 mL, 2.08 mmol) was syringed into the solution and the solution was left to stir for an additional hour whilst warming to room temperature. Then the reaction mixture was diluted with 10:1 (v/v) H_2O/HCl (110 mL), and the reaction was left stirring overnight at room temperature. The solution was ether extracted (3 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The solid residue was column chromatographed (chloroform, R_f = 0.12) to give 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanyl-4-boronic acid (0.25 g, 60%); mp = 76–80 °C. ^{1}H NMR δ 7.49 (s, 1H), 7.38 (d, ^3J = 8.9 Hz, 1H), 7.15–7.19 (m, 4H); 7.12 (d, ^3J = 9.6 Hz, 1H), 5.55 (s, 2H); ^{13}C NMR δ 136.79 (dd, J = 10.0, 5.6 Hz), 132.32, 130.36, 129.43, 129.35, 129.03, 128.76 (t, J = 6.0 Hz) (aryl C–Hs); 135.17 (t, J = 26.8 Hz), 134.72 (t, J = 26.0 Hz), 133.09 (t, J = 26.4 Hz), 132.87 (t, J = 26.4 Hz) (cyclophane bridgeheads); 119.02 (t, J = 270.8 Hz), 118.47 (t, J = 269.1 Hz), 118.30 (t, J = 269.4 Hz), 118.09 (t, J = 269.1 Hz) (CF_2s); ^{19}F NMR δ −114.5 (d, ^2J = 236.8 Hz, 1F), −115.7 (d, ^2J = 236.8 Hz, 1F), −116.4 (d, ^2J = 237.0 Hz, 1F), −118.8 (d, ^2J = 237.1 Hz, 1F), −118.1 (d, ^2J = 237.1 Hz, 1F), −118.8 (d, ^2J = 237.1 Hz, 1F), −118.2 (d, ^2J = 232.0 Hz, 1F), −119.0 (d, ^2J = 232.0 Hz, 1F); MS m/z 396 (M^+, 30%), 202 (40), 57 (50), 220 (60), 176 (100). HRMS (ESI) calculated for $C_{16}H_9B\,F_8O_2$ $[M + Na]^+$ 419.04655, found 419.0482.

4.2. 4-Hydroxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (**10**)

4-Iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.10 g, 0.21 mmol) and ether (11 mL) were cooled to −78 °C under a N_2 atmosphere. *n*-Butyllithium (0.26 mL of 1.6 M in hexane, 0.42 mmol) was added, and the solution was stirred for 1 h at this temperature. Trimethyl borate (0.05 mL, 0.42 mmol) was syringed into the solution and the solution was left to stir for an additional 1 h as it warmed up to room temperature. To the reaction mixture an aqueous solution of 0.5 M sodium hydroxide (0.86 mL, 0.43 mmol) and 30% hydrogen peroxide (0.74 mL, 6.49 mmol) were added, and then warmed to 40 °C for 24 h. The solution was acidified by dilute HCl and extracted with ether

(3 × 20 mL). The ether layer was shown to contain 4-hydroxy-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane [2] in 69% yield by integration of the ^{19}F NMR spectrum against an internal added standard of bis(trifluoromethyl)-benzene.

4.3. Coupling reactions

4.3.1. 4-(3-Hydroxyphenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (7)

Method A. Under a counter current of nitrogen gas, a round bottomed flask was charged with 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.10 g, 0.21 mmol), 3-hydroxyphenylboronic acid (0.04 g, 0.30 mmol), bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol), potassium carbonate (0.08 g, 0.58 mmol), THF (2 mL), and water (0.5 mL). The vessel was thoroughly flushed with N_2 and refluxed for 48 h. The reaction mixture was then cooled to room temperature, ether extracted (3 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed (hexane/ether 1/1, $R_f = 0.33$) to give 4-(3-hydroxyphenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (79 mg, 85%); mp = 212–215 °C. ^1H NMR δ 8.58 (s, 1H), 7.58–7.50 (m, 4H), 7.39 (d, $^3J = 8.4$ Hz, 1H), 7.32 (d, $^3J = 8.1$ Hz, 1H), 7.31 (d, $^3J = 7.8$ Hz, 1H), 7.20 (s, 1H), 7.04 (d, $^3J = 10.8$ Hz, 2H), 6.96 (dd, $^3J = 7.8$ Hz, $^4J = 2.1$ Hz, 1H); ^{13}C NMR δ 134.08 (dd, $J = 11.0$, 5.3 Hz), 130.45, 130.37, 130.28, 129.61 (dd, $J = 7.0$, 3.1 Hz), 129.40, 129.05, 127.70 (t, $J = 6.3$ Hz), 121.65, 117.44, 115.92 (aryl C–Hs); 132.57 (t, $J = 26.4$ Hz), 132.02 (t, $J = 26.8$ Hz), 131.31 (t, $J = 26.4$ Hz), 130.83 (t, $J = 26.2$ Hz) (Cyclophane bridgeheads); 157.09 (C–OH); 139.71, 137.67 (quaternary); 118.86 (t, $J = 269.0$ Hz), 117.37 (t, $J = 269.0$ Hz), 117.32 (t, $J = 269.0$ Hz), 117.25 (t, $J = 269.0$ Hz) (CF_2s); relevant $^{13}C\{^{19}F\}$ NMR data δ 134.08 (d, $J = 170.6$ Hz), 121.65 (dd, $J = 158.9$, 7.2 Hz), 117.44 (dd, $J = 160.2$, 7.2 Hz), 115.92 (d, $J = 159.4$ Hz); ^{19}F NMR δ −101.6 (d, $^2J = 236.8$ Hz, 1F), −109.7 (d, $^2J = 236.8$ Hz, 1F), −114.5 (d, $^2J = 236.8$ Hz, 1F), −116.9 (d, $^2J = 236.8$ Hz, 1F), −114.3 (s, 2F), −115.8 (d, $^2J = 237.1$ Hz, 1F), −116.9 (d, $^2J = 237.1$ Hz, 1F); MS *m/z* 444 (M^+, 40%), 267 (100). HRMS (CI+) calculated for $C_{22}H_{12}OF_8$ $[MH]^+$ 445.07604, found 445.0855.

Method B. Under a counter current of nitrogen gas, a round bottomed flask was charged with 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.10 g, 0.21 mmol), 4-hydroxyphenylboronic acid pinacol ester (0.07 g, 0.32 mmol), bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol), potassium carbonate (0.08 g, 0.58 mmol), THF (2 mL), and water (0.5 mL). The vessel was thoroughly flushed with N_2 and refluxed for 48 h. The reaction mixture was then cooled to room temperature, ether extracted (3 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was chromatographed (hexane/ether 1/1, $R_f = 0.33$) to give 4-(3-hydroxyphenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (83 mg, 89%) spectroscopically identical the sample prepared above.

Method C. Under a counter current of nitrogen gas, a round bottomed flask was charged with 1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophanyl-4-boronic acid (0.10 g, 0.25 mmol), 3-bromophenol (0.07 g, 0.40 mmol), bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol), potassium carbonate (0.08 g, 0.58 mmol), THF (2 mL), and water (0.5 mL). The vessel was thoroughly flushed with N_2, and refluxed for 48 h. The reaction mixture was then cooled to room temperature, ether extracted (3 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure The crude product was chromatographed (hexane/ether 1/1, $R_f = 0.33$) to give 4-(3-hydroxyphenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (94 mg, 85%) spectroscopically identical the sample prepared above.

Method D. 4-Iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.10 g, 0.21 mmol) and ether (11 mL) were cooled to −78 °C under a N_2 atmosphere. *n*-Butyllithium (0.26 mL of 1.6 M in hexane, 0.42 mmol) was added, and the solution was stirred for 1 h at this temperature. Trimethyl borate (0.05 mL, 0.42 mmol) was syringed into the solution and the solution was left to stir for an additional hour whilst warming to 0 °C. Through a pressure equalizing dropping funnel, a THF (2 mL) solution of 3-bromophenol (73 mg, 0.42 mmol), and bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol), was added followed by an aqueous solution (0.5 mL) of potassium carbonate (0.08 g, 0.58 mmol). The vessel was thoroughly flushed with N_2, and refluxed for 48 h. The reaction mixture was then cooled to room temperature, ether extracted (3 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure The crude product was chromatographed (hexane/ether 1/1, $R_f = 0.33$) to give 4-(3-hydroxyphenyl)-1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophane (80 mg, 86%) spectroscopically identical the sample prepared above.

4.3.2. 4-(2-Methylphenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (5)

Using the same scale and procedure as method A with 2-methylphenylboronic acid, after column chromatography (hexane/chloroform 7/1, $R_f = 0.73$) gave 4-(2-methylphenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (76%); mp = 140–142 °C. ^1H NMR δ 7.83 (d, $^3J = 7.2$ Hz, 1H), 7.62 (d, $^3J = 8.7$ Hz, 1H), 7.27 (d, $^3J = 7.2$ Hz, 1H), 7.37–7.57 (m, 7H), 7.12 (m, 1H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR δ 132.13 (t, $J = 7.5$ Hz), 129.48, 129.40, 129.25, 129.20, 129.11, 128.92, 127.85, 127.42, 127.30, 125.49 (aryl C–Hs); 118.76 (tt, $J = 269.8$, 21.2 Hz), 118.57 (tt, $J = 269.0$, 28.2 Hz), 118.14 (tt, $J = 270.1$, 26.4 Hz), 117.80 (tt, $J = 269.8$, 26.4 Hz) (CF_2s); 138.56 (d, $J = 5.8$ Hz), 138.02, 136.48 (quaternary); 134.44 (t, $J = 24.7$ Hz), 134.11 (t, $J = 25.0$ Hz), 133.77 (t, $J = 24.4$ Hz), 133.62 (t, $J = 25.0$ Hz) (cyclophane bridgeheads); 18.94 (CH_3); relevant $^{13}C\{^{19}F\}$ NMR data δ 132.13 (d, $J = 166.0$ Hz), 127.85 (dd, $J = 158.8$, 7.2 Hz), 127.30 (dd,

J = 159.4, 7.2 Hz), 125.49 (dd, J = 160.0, 9.0 Hz), 18.94 (q, J = 126.2 Hz); ^{19}F NMR δ −109.8 (d, ^2J = 236.8 Hz, 1F), −110.8 (d, ^2J = 236.8 Hz, 1F), −113.3 (d, ^2J = 234.5 Hz, 1F), −115.1 (d, ^2J = 234.5 Hz, 1F), −113.6 (d, ^2J = 237.1 Hz, 1F), −116.8 (d, ^2J = 237.1 Hz, 1F), −115.6 (d, ^2J = 234.5 Hz, 1F), −117.4 (d, ^2J = 234.5 Hz, 1F); MS *m/z* 442 (M^+, 40%), 176 (70), 256 (100). HRMS (CI+) calculated for $C_{23}H_{14}F_8$ $[M]^+$ 442.09677, found 442.0957.

Method B using 2-methylphenylboronic acid pinacol ester gave **5** in 78% isolated yield; method C using 2-bromotoluene gave **5** in 86%; method D using 2-bromotoluene gave **5** in 79%.

4.3.3. 4-Phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (*4*)

Using the same scale and procedure as method A with phenylboronic acid, after column chromatography (hexane/dichloromethane 9/1, R_f = 0.30) gave 4-phenyl-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (86%); ^{1}H NMR δ 7.24 (s, 1H), 7.61–7.33 (m, 11H); ^{19}F NMR δ −102.1 (d, ^2J = 239.9 Hz, 1F), −110.8 (d, ^2J = 239.9 Hz, 1F), −115.3 (m, 2F), −115.4 (d, ^2J = 237.4 Hz, 1F), −117.9 (d, ^2J = 237.4 Hz, 1F), −116.7 (d, ^2J = 239.6 Hz, 1F), −117.8 (d, ^2J = 239.6 Hz, 1F). Such characterization is in excellent agreement with previously reported values [2].

Method B using phenylboronic acid pinacol ester gave **4** in 88% isolated yield; method C using bromobenzene gave **4** in 76%; method D using bromobenzene gave **4** in 81%.

4.3.4. 4-(4-Cyanophenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (*6*)

Using the same scale and procedure as method A with 4-cyanophenylboronic acid, after column chromatography (hexane/ether 5/1, R_f = 0.28) gave 4-(4-cyanophenyl)-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (80%); mp = 160–162 °C. ^{1}H NMR δ 7.93 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 2H), 7.87 (dd, ^3J = 9.0 Hz, ^4J = 2.4 Hz, 2H), 7.63 (d, ^3J = 9.0 Hz, 1H), 7.62 (d, ^3J = 9.3 Hz, 1H), 7.55 (d, ^3J = 6.9 Hz, 1H), 7.53 (d, ^3J = 7.5 Hz, 1H), 7.44 (d, ^3J = 8.4 Hz, 2H), 7.33 (s, 1H); ^{13}C{^{1}H} NMR δ 133.59 (dd, J = 10.0, 6.2 Hz), 131.21, 130.58, 129.63, 129.56, 129.48, 129.41, 128.90 (dd, J = 5.6, 2.5 Hz), 126.88 (t, J = 6.0 Hz) (aryl C–Hs); 118.42 (t, J = 272.6 Hz), 118.27 (t, J = 273.2 Hz), 118.05 (t, J = 270.1 Hz), 117.90 (t, J = 271.0 Hz) (CF_2s); 134.37 (t, J = 26.4 Hz), 134.14 (t, J = 26.8 Hz), 134.02 (t, J = 26.0 Hz), 133.88 (t, J = 26.1 Hz) (cyclophane bridgeheads); 141.58 (d, J = 7.0 Hz), 137.39, 111.75 (quaternary); 117.42 (CN); relevant ^{13}C{^{19}F} NMR data δ 133.59 (d, J = 168.5 Hz), 131.21 (dd, J = 167.6, 6.2 Hz), 130.58 (dd, J = 164.6, 6.0 Hz), 129.63 (dd, J = 168.8, 6.4 Hz), 129.56 (dd, J = 168.3, 6.4 Hz), 129.48 (dd, J = 165.9, 6.2 Hz), 129.41 (dd, J = 168.3, 6.4 Hz), 128.90 (dd, J = 166.4, 6.2 Hz), 126.88 (dd, J = 167.8, 6.6 Hz); ^{19}F NMR δ −102.3 (d, ^2J = 239.3 Hz, 1F), −110.2 (d, ^2J = 239.3 Hz, 1F), −114.5 (d, ^2J = 232.0 Hz, 1F), −114.6 (s, 2F), −115.6 (d, ^2J = 236.8 Hz, 1F), −116.9 (d, ^2J = 236.8 Hz, 2F); MS m/z 453 (M^+, 30%), 276 (74), 177 (80), 277 (40), 176 (100). HRMS (CI+) calculated for $C_{23}H_{11}F_8N$ $[M]^+$ 453.07638, found 453.0759.

Method B using 4-cyanophenylboronic acid pinacol ester gave **6** in 83% isolated yield; method C using 4-bromobenzonitrile gave **6** in 86%; method D using 4-bromobenzonitrile gave **6** in 76%.

4.3.5. 1,4-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophan-4-yl)phenyl (*12*)

Method A. Under a counter current of nitrogen gas, a round bottomed flask was charged with 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.20 g, 0.42 mmol), phenylene-1,4-diboronic acid (17 mg, 0.10 mmol), bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol), potassium carbonate (0.16 g, 1.16 mmol), THF (4 mL), and water (1 mL). The vessel was thoroughly flushed with N_2 and refluxed for 48 h. The reaction mixture was then cooled to room temperature, ether extracted (3 × 20 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was column chromatographed (hexane/chloroform 3/1, R_f = 0.19) to give 1,4-bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophan-4-yl)phenyl (40 mg, 51%); mp = 295–296 °C. ^{1}H NMR δ 7.78 (s, 4H), 7.37–7.44 (m, 6H), 7.54–7.66 (m, 8H); ^{13}C{^{1}H} NMR δ 133.41 (dd, J = 11.5, 6.0 Hz), 129.68, 129.60, 129.51, 129.46, 128.77 (dd. J = 7.2, 3.0 Hz), 128.46 (d, J = 7.4 Hz), 126.72 (t, J = 6.3 Hz) (aryl C–Hs); 118.53 (t, J = 265.3 Hz), 118.14 (t, J = 266.0 Hz), 117.89 (t, J = 262.8 Hz), 117.50 (t, J = 261.1 Hz) (CF_2s); 141.06 (d, J = 6.9 Hz), 137.79 (quaternary); 135.07 (t, J = 25.4 Hz), 134.96 (t, J = 26.5 Hz), 134.65 (t, J = 26.5 Hz), 134.28 (t, J = 26.5 Hz) (cyclophane Bridgeheads); relevant ^{13}C{^{19}F} NMR data δ 133.41 (d, J = 166.9 Hz), 128.77 (dd, J = 166.1, 6.2 Hz), 128.46 (dd, J = 166.1, 6.5 Hz), 126.72 (dd, J = 166.9, 6.8 Hz); ^{19}F NMR δ −101.0 (d, ^2J = 239.0 Hz, 1F), −110.1 (d, ^2J = 239.0 Hz, 1F), −114.4 (d, ^2J = 234.5 Hz, 1F), −116.8 (d, ^2J = 234.5 Hz, 1F), −114.4 (s, 2F), −115.7 (d, ^2J = 236.8 Hz, 1F), −116.8 (d, ^2J = 236.8 Hz, 1F); MS *m/z* 778 (M^+, 60%), 127 (40), 176 (60), 602 (50), 601 (100); HRMS (ESI) calculated for $C_{38}H_{18}F_{16}$ $[M + Na]^+$ 801.10507, found 801.1071.

Method B using phenylene-1,4-diboronic acid bis-pinacol ester gave **12** in 60% isolated yield; method C using 1,4-dibromobenzene gave **12** in 53%; method D using 1,4-dibromobenzene gave **12** in 56%.

4.3.6. 4,4′-Bis(1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophan-4-yl)biphenyl (*13*)

Under a counter current of nitrogen gas, a round bottomed flask was charged with 4-iodo-1,1,2,2,9,9,10,10-octafluoro[2.2]paracyclophane (0.20 g, 0.42 mmol), phenylene-1,4-diboronic acid (35 mg, 0.21 mmol), bis(triphenylphosphine)palladium(II) chloride (7 mg, 0.01 mmol), potassium carbonate (0.16 g, 1.16 mmol), THF (4 mL), and water (1 mL). The vessel was thoroughly flushed with N_2 and refluxed for 48 h. The reaction mixture was then cooled to room temperature, ether extracted (3 × 20 mL), dried

($MgSO_4$), and evaporated under reduced pressure. ^{19}F NMR and TLC analysis showed a mixture of two products. The mixture was column chromatographed (hexane/chloroform 3/1) to give ($R_f = 0.45$) 4,4′-bis(1,1,2,2,9,9,10,10-octafluoro-[2.2]paracyclophan-4-yl)biphenyl (27 mg, 30%); mp = 270–272 °C. ^1H NMR δ 7.72 (d, $^3J = 8.3$ Hz, 4H), 6.96–7.68 (m, 18H); $^{13}C\{^1H\}$ NMR δ 133.47 (dd, $J = 12.1, 5.5$ Hz), 130.36 (d, $J = 4.0$Hz), 129.69, 129.61, 129.52, 129.47, 128.78 (dd, $J = 7.25$, 3.0 Hz), 128.46 (d, $J = 7.0$ Hz), 126.74 (t, $J = 6.3$ Hz), 125.96 (aryl C–Hs); 118.49 (t, $J = 269.2$ Hz), 118.16 (t, $J = 269.6$ Hz), 118.08 (t, $J = 268.9$ Hz), 117.92 (t, $J = 270.6$ Hz) (CF_2s); 141.03 (d, $J = 7.4$ Hz), 139.52, 137.80 (quaternary); 134.23 (t, $J = 27.3$ Hz), 134.18 (t, $J = 26.5$ Hz), 134.12 (t, $J = 27.3$ Hz), 130.10 (t, $J = 27.0$ Hz) (cyclophane bridgeheads); relevant $^{13}C\{^{19}F\}$ NMR data δ 133.47 (d, $J = 168.3$ Hz), 130.36 (dd, $J = 166.0$, 7.0 Hz), 128.78 (dd, $J = 166.7, 6.7$ Hz), 128.46 (dd, $J = 166.0, 5.7$ Hz), 126.74 (dd, $J = 167.0$, 6.8 Hz), 134.23 (d, $J = 7.6$ Hz), 134.18 (t, $J = 7.4$ Hz), 134.12 (d, $J = 8.1$ Hz), 130.10 (d, $J = 7.6$ Hz); ^{19}F NMR δ −101.2 (d, $^2J = 236.8$ Hz, 1F), −109.9 (d, $^2J = 236.8$ Hz, 1F); −114.6 (d, $^2J = 236.8$ Hz, 1F); −116.9 (d, $^2J = 236.8$ Hz, 1F), −114.4 (s, 2F), −115.7 (d, $^2J = 236.8$ Hz, 1F), −116.9 (d, $^2J = 236.8$ Hz, 1F); MS m/z 854 (M^+, 10%), 232 (60), 115 (100). HRMS (ESI) calculated for $C_{44}H_{22}F_{16}$ $[M + Na]^+$ 877.13636, found 877.1395.

A slower running band (hexane/chloroform 3/1, $R_f = 0.19$) gave **12** 1,4-bis(1,1,2,2,9,9,10,10-octafluoro[2.2]-paracyclophan-4-yl)phenyl (33 mg, 20%), spectroscopically identical to the samples prepared above.

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References

[1] W.R. Dolbier Jr., J.-X. Duan, A.J. Roche, US Patent 5,841,005 (1998); W.R. Dolbier Jr., J.-X. Duan, A.J. Roche, Org. Lett. 2 (2000) 1867–1869;
H. Amii, Y. Hatamoto, M. Seo, K. Uneyama, J. Org. Chem. 66 (2001) 7216–7218.
[2] A.J. Roche, W.R. Dolbier Jr., J. Org. Chem. 64 (1999) 9137–9143.
[3] A.J. Roche, W.R. Dolbier Jr., J. Org. Chem. 65 (2000) 5282–5290; L. Guyard, P. Audebert, W.R. Dolbier Jr., J.-X. Duan, J. Electroanal. Chem. 537 (2002) 189–193.
[4] (a) S.C. Dickerman, N. Milstein, J. Org. Chem. 32 (1967) 852–853;
(b) P. Kus, Pol. J. Chem. 68 (1994) 1983–1988;
(c) V.I. Rozenberg, D.Y. Antonov, R.P. Zhuravsky, E.V. Vorontsov, Z.A. Starikova, Tetrahedron Lett. 44 (2003) 3801–3804;
(d) B. Konig, B. Knieriem, A. de Meijere, Chemische Berichte 126 (1993) 1643–1650;
(e) S. Sankararaman, H. Hopf, I. Dix, P.G. Jones, Eur. J. Org. Chem. (2000) 2711–2716.
[5] M.A. Battiste, J.-X. Duan, Y.-A. Zhai, I. Ghiviriga, K.A. Abboud, W.R. Dolbier Jr., J. Org. Chem. 68 (2003) 3078–3083.
[6] W.R. Dolbier Jr., W.F. Beach, J. Fluorine Chem. 122 (2003) 97–104; W.F. Beach, C. Lee, D.R. Bassett, T.M. Austin, R.A. Olson, 2nd ed. Wiley Encyclopedia of Polymer Science and Technology, vol. 17, Wiley, New York, 1989, pp. 990–1025.
[7] F. Vogtle, Cyclophane Chemistry, Wiley, New York, 1993; V. Boekelheide, Cyclophanes. I, Top. Curr. Chem. 113 (1983) 87–143; H. Hopf, C. Marquard, Strain and its Implications in Organic Chemistry, Kluwer, Dordrecht, 1989.
[8] P.G. Jones, P. Kus, Pol. J. Chem. 72 (1998) 1106–1111 (reports the crystal structure from the synthetic work described in Ref. [4b]).
[9] A.J. Roche, J.-X. Duan, W.R. Dolbier Jr., K.A. Abboud, J. Org. Chem. 66 (2001) 7055–7058.
[10] L. Ernst, L. Wittkowski, Eur. J. Org. Chem. 7 (1999) 1653–1663; P.G. Jones, L. Ernst, I. Dix, L. Wittkowski, Acta Crystallogr. C56 (2000) 239–241.
[11] Y. Ma, C. Song, C. Ma, Z. Sun, Q.C. Chai, M.B. Andrus, Angew. Chem. Int. Ed. 42 (2003) 5871–5874;
E.S. Baker, J.W. Hong, J. Gidden, G.P. Bartholomew, G.C. Bazan, M.T. Bowers, J. Am. Chem. Soc. 126 (2004) 6255–6257;
V.I. Rozenberg, D.Y. Antonov, R.P. Zhuravsky, E.V. Vorontsov, V.N. Khrustalev, N.S. Ikonnikov, Y.N. Belokon, Tetrahedron: Asymmetry 11 (2000) 2683–2693;
A.A. Aly, Tetrahedron 59 (2003) 1739–1747.
[12] H. Hopf, S. Sankararaman, I. Dix, P.G. Jones, H.G. Alt, A. Licht, Eur. J. Inorg. Chem. 1 (2002) 123–131.
[13] E. Popova, D. Antonov, E. Sergeeva, E. Vorontsov, A. Stash, V. Rozenberg, H. Hopf, Eur. J. Inorg. Chem. 11 (1998) 1733–1737;
G.N. Gerasimov, E.L. Popova, E.V. Nikolaeva, S.N. Chvalun, E.I. Grigoriev, L.I. Trakhtenberg, V.I. Rozenberg, H. Hopf, Macromol. Chem. Phys. 199 (1998) 2179–2184.
[14] Recent reviews include J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev., 102 (2002) 1359–1470 (section 14);
S. Kotha, K. Lahiri, D. Kashinath, Tetrahedron 58 (2002) 9633–9695;
N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483.
[15] An investigation into the chemistry of [2.2]paracyclophanyl-4-boronic acid and its pinacol ester, including similar Suzuki aryl cross-coupling reactions, will be reported separately; A.J. Roche, B. Canturk, Org. Biomol. Chem., (2004) doi:10.1039/8415764N.
[16] Rozenberg in Ref. [4c] reports a moderate yielding two step one pot Suzuki coupling reaction employing an ortho directed lithiation on a 4-alkoxy[2.2]paracyclophane..
[17] R.S. Cahn, C.K. Ingold, V. Prelog, Experientia 12 (1956) 81–124; R.S. Cahn, C.K. Ingold, V. Prelog, Angew. Chem. Int. Ed. Engl. 5 (1966) 385–415.
[18] T. Ishiyama, M. Murata, N. Miyaura, J. Org. Chem. 60 (1995) 7508–7510.
[19] Y. Ma, C. Song, J. Chun, W. Jiang, G. Xue, J.F. Cannon, X. Wang, M.B. Andrus, Org. Lett. 5 (2003) 4635–4638;
M. Murata, T. Oyama, S. Watanabe, Y. Masuda, J. Org. Chem. 65 (2000) 164–168.
[20] H. Chaumeil, C.L. Drian, A. Defoin, Synthesis 6 (2002) 757–760.