# The use of a modified Suzuki reaction for the synthesis of monoarylferrocenes

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A modification of the Suzuki cross-coupling reaction proved to be a clean and useful method for the preparation of monosubstituted arylferrocenes. Iodoferrocene was reacted with a series of substituted arylboronic acids in the presence of sodium carbonate and palladium acetate in aqueous ethanol at room temperature to produce a range of substituted monoarylferrocenes. A systematic investigation undertaken to determine optimal reaction conditions indicated that scrupulous deoxygenation of the solvent is critical. The use of stronger bases such as barium hydroxide and potassium carbonate is favourable and gives rise to better yields of monoarylferrocenes. The reactions also proceed efficiently in aqueous DMF, broadening the scope of the reaction allowing efficient reactions with boronic acids that show low solubility in organic solvents.

## Introduction

The biphenyl unit is useful in molecules where some degree of structural rigidity is required, such as in liquid crystals. The replacement of one of its phenyl rings with a ferrocenyl unit would be expected to result in a structural unit with a similar rigidity. The significance of using a phenyl ring to link the large organic (mesogenic) substituent to the ferrocenyl unit in ferrocenyl-containing liquid crystals (ferrocenomesogens)[1] was recently demonstrated by us[1h] (Fig. 1). Our initial efforts to synthesize the monoarylferrocene unit were frustrated by the poor yields and selectivities of existing methods. In view of these problems, we undertook a systematic investigation of the synthesis of monoarylferrocenes using a modification of the Suzuki cross-coupling reaction and the results are presented in this paper.

A summary of the methods previously used in the preparation of monoarylferrocenes is shown in Scheme 1. The most
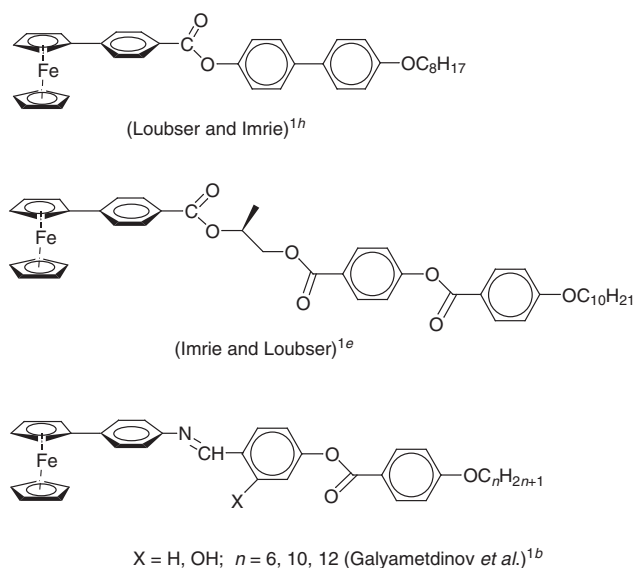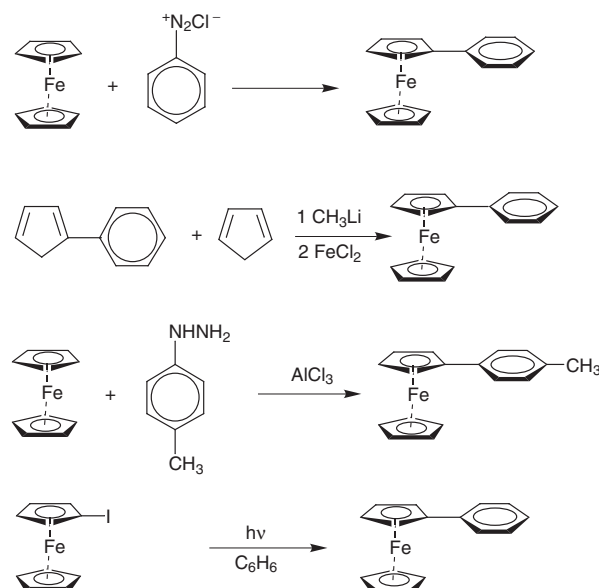


(Loubser and Imrie)[1h]

(Imrie and Loubser)[1e]

X = H, OH;  n = 6, 10, 12 (Galyametdinov et al.)[1b]

**Fig. 1**  Examples of liquid crystals containing a ferrocenyl-phenyl group.



**Scheme 1**  Methods available for the synthesis of monoarylferrocenes.

frequently used method is an arylation process involving the reaction of ferrocene with aryldiazonium salts.[2] However, the yields of monoarylferrocenes obtained in these reactions seldom exceeded 40% and were in many cases appreciably lower (Table 1). Furthermore, these reactions are seldom specific, also producing 1,1'-, 1,2- and 1,3-diarylferrocenes which are normally difficult to separate. The yields of monoarylferrocenes in these reactions have been improved by employing diethyl ether[3] as solvent in place of either acetone or glacial acetic acid as described in all the early literature. The poor selectivity and low yields indicate that the aryl intermediates responsible for the arylations are indiscriminate. It is now generally accepted that this arylation reaction takes place in a two-step mechanism,[2h] the first of which involves electron-transfer from ferrocene to the aryldiazonium cation, giving ferrocenium ions and aryldiazonium radicals. The latter readily lose nitrogen to form aryl radicals which then react with ferrocenium ions to give the products.

**Table 1** Yields of arylferrocenes obtained from the reaction of aryl-diazonium salts with ferrocene
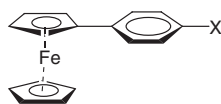
| Substituent X | Yield (%)[a] |
| --- | --- |
| OCH$_3$ | 43 |
| CH$_3$ | 24 |
| H | 17 |
| COCH$_3$ | 23 |
| CF$_3$ | 5 |
| Br | 19 |

[a] Yields are based on the amount of ferrocene starting material.

The second equation in Scheme 1 for the preparation of monoarylferrocenes relies on the reaction of arylcyclopentadienes with iron(II) chloride in the presence of cyclopentadiene; the yields of monoarylferrocene are generally low and this method is more effective for the preparation of multisubstituted arylferrocenes with at least one substituent on each ring.[4]

The third procedure in Scheme 1 for the preparation of monoarylferrocenes involves the reaction of arylhydrazines with ferrocene catalysed by aluminium chloride.[5] This was the first example of the arylation of ferrocene by an ionic mechanism and also the first arylation of neutral ferrocene. A range of arylferrocenes were synthesized by this method including 2-tolyl-, 4-tolyl-, 4-bromophenyl- and α-naphthyl-ferrocene. Only the monoarylated product formed, but conversions (<50%) and yields (<30%) were generally poor.[5] The final reaction in Scheme 1 involves free radical ferrocenylation of benzene as described by Imrie et al.[6] For substituted arenes, regioselectivity was poor and resulted in the formation of all three isomers of the appropriate monoarylferrocenes.

Several other methodologies for the preparation of monoarylferrocenes have been reported involving the use of diferrocenylmercury and diarylmercury compounds,[7] the interaction of ferroceneboronic acid with copper salts[8] and, finally, the interaction of tetraarylborocopper salts with bromoferrocene.[9]

In view of the poor yields and selectivities generally associated with the syntheses of monoarylferrocenes by the reactions just described, we set out to develop improved methods of synthesizing monoarylferrocenes; this paper describes our efforts in applying a modification of the Suzuki reaction to that end.

## Results and discussion

Transition metal-catalysed cross-coupling reactions have proved their value in synthetic and materials chemistry as tools for C–C bond formation (Scheme 2) and may be applied to the synthesis of diaryls containing virtually any functional group.[10]

$$R\text{-}m + X\text{-}R' \xrightarrow{ML} R\text{-}R + m\text{-}X$$

M = Ni, Pd, Rh, Ru

m = Li, Mg, Zn, B, Al, Zr, Hg, Sn

L = Ligand

R' = Aryl, vinyl, allyl, benzyl, alkyl

R = Aryl, vinyl, allyl, benzyl, alkyl

X = Cl, Br, I, OSO$_2$CF$_3$

**Scheme 2** Generalized reaction for a transition metal-catalyzed cross-coupling.

The Suzuki reaction (where M = Pd, and m = B) is an important member of this class of reactions. The variables in the Suzuki reaction as applied to the synthesis of arylferrocenes are numerous. Firstly, either R or R$^1$ can represent the ferrocenyl group leading to a choice of either ferroceneboronic acid or a haloferrocene (usually iodo or bromo) as the starting material. Since there is little difference between ferroceneboronic acid and the haloferrocenes in terms of their availability or stability, the choice of route is determined more by the availability and stability of the reaction partners.

Arylboronic acids are readily synthesized by lithiation of bromoarenes, followed by reaction with trialkylborates and hydrochloric acid; they are reasonably stable solids. Iodoarenes on the other hand are less readily available than bromoarenes and are in many cases light sensitive. For our work, we used the combination of haloferrocene (iodoferrocene) and arylboronic acid. Other variables in the Suzuki reaction include the choice of the palladium catalyst, the base and the solvent. The first reported[11] Suzuki coupling reactions between arylboronic acids and haloarenes employed tetrakis(triphenylphosphino)-palladium(0) as catalyst and required 2 equivalents of aqueous sodium carbonate as base and benzene as solvent. Two factors discouraged us from using the phosphine catalyst. Firstly, it is oxidatively sensitive and hence difficult to handle and, secondly, Wallow and Novak have shown[12] that phosphine inhibition plays a key role in limiting catalytic efficiency. Pd[(Ph$_3$P)$_4$] in fact proved to be the least active in a series of palladium catalytic species investigated. We were attracted rather to a modification of the original Suzuki reaction reported recently by Campi et al.[13] where unsymmetrical biaryls were obtained in high yields from the cross-coupling of arylboronic acids with haloarenes using palladium acetate as the catalyst, solid sodium carbonate or barium hydroxide as base and 95% aqueous ethanol as solvent. Our strategy has been to use the modified Suzuki reaction in Scheme 3 as our starting point for the synthesis of arylferrocenes.
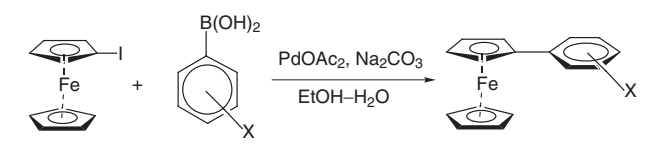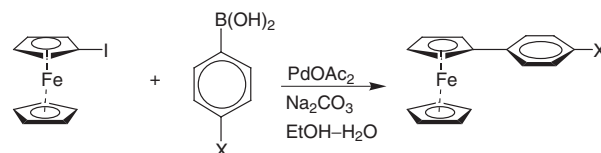
X = OCH$_3$, CH$_3$, H, C$_6$H$_5$, F, Br, COCH$_3$, CHO, CF$_3$

**Scheme 3** The use of a modified Suzuki reaction for the synthesis of monoarylferrocenes.

In our initial reactions, equimolar quantities of iodoferrocene and a series of arylboronic acids were allowed to react together under exactly the same reaction conditions as described by Campi et al.[13] In all cases, the reactions proved to be clean and easy to work-up, in contrast to those involving the reaction of diazonium salts with ferrocene. The results of these reactions are given in Table 2 and show a distinctive trend with respect to the electronic character of the substituent on the arylboronic acid. When the substituent is electron-donating or neutral (Table 2, entries 1–6 and 12–16), conversions and overall yields are higher than when substituents are electron-withdrawing in nature (Table 2, entries 7–11).

The crux of the observed substituent effect may lie in the transmetallation step of the catalytic cycle. In cases where the substituent is electron-donating, the nucleophilic nature of the organoboronic acid is increased thereby facilitating the transfer of the organic group to the adjacent positive centre. In most of the reactions, small quantities of self-coupling side-products were also obtained; these types of products have been observed before by Song and Wong.[14] Since we did not determine the yields of the self-coupling product, it is not possible at this stage to comment on the observation of Moreno–Mañas et

**Table 2** Yields of monoarylferrocenes obtained in the modified Suzuki reaction of iodoferrocene and a series of arylboronic acids



| Entry | X | Recovered iodoferrocene (%) | Yield (%)[a] | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 4-OMe[c] | 57 | 100 | 43 |
| 2 | 3-OMe[d] | 55 | 100 | 45 |
| 3 | 2-OMe[d] | 40 | 48 | 29 |
| 4 | 4-Me[c] | 66 | 50 | 17 |
| 5 | 4-H[c] | 61 | 87 | 36 |
| 6 | 4-F[c] | 54 | 41 | 19 |
| 7 | 4-CF$_3$[c] | 0 | — | 5 |
| 8 | 4-CF$_3$[d] | 80 | 75 | 16 |
| 9 | 4-CHO[c] | 60 | 13 | 5 |
| 10 | 4-CHO[d] | 84 | 79 | 13 |
| 11 | 4-Br[d] | 61 | 61 | 24 |
| 12 | 4-C$_6$H$_5$[d] | 54 | 41 | 19 |
| 13 | 4-OC$_8$H$_{17}$[c] | — | — | 67 |
| 14 | 4-OC$_{10}$H$_{21}$[d] | 33 | 42 | 28 |
| 15 | 4-COCH$_3$[e] | 49 | 70 | 37 |
| 16 | 4-OCH$_2$C$_6$H$_5$[f] | 54 | 93 | 43 |

[a] Yield is based on the amount of reacted iodoferrocene. [b] Yield is based on the amount of iodoferrocene as starting material. [c] Typical procedure. To ethanol (95%) under nitrogen was added the arylboronic acid (1 eq.), iodoferrocene (1 eq.), sodium carbonate (1.4 eq.) and palladium acetate (0.04 eq.). The reaction mixture was stirred under nitrogen for 24 h. [d] Same procedure as for c with the exception that the amount of palladium acetate (0.2 eq.) was increased and the reaction mixture was shaken for 30 min prior to stirring. [e] Same procedure as for d with the exception that the amount of arylboronic acid (5 eq.) was increased and the reaction mixture was allowed to stir for 120 h. [f] Same procedure as for e with the exception that ethanol (90%) was used as solvent and was deaerated more extensively by freeze–thawing and nitrogen bubbling; the base was barium hydroxide and the reaction was allowed to stir for 24 h.

*al.* that more electron-withdrawing substituents result in lower self-coupling yields than with electron-donating substituents.[15]

The modified Suzuki reaction was then applied to the synthesis of more elaborate arylferrocenes such as 1-ferrocenylnaphthalene, 2-ferrocenylthiophene and 4-octyloxyphenylferrocene (Fig. 2). The relatively good conversions and yields (see Experimental section) indicate that the reaction is relatively insensitive to steric repulsion effects. Miyaura and Suzuki[16] reported that the reaction of hindered bromoarenes (*e.g.*, mesityl bromide and 1-bromonaphthalene) with arylboronic acids occurred slowly in refluxing benzene; yields were improved at higher temperatures.

Although the initial yields in the modified Suzuki reaction proved to be somewhat better than those obtained by the diazonium method and the reactions were considerably cleaner, an investigation was next undertaken in order to establish ways of improving the conversions reported in Table 2. In order to determine more optimum conditions for the Suzuki reaction to synthesize monoarylferrocenes, the reaction of iodoferrocene and 4-methylbenzeneboronic acid was used as a model in which the effect of varying the concentrations of the reaction components, the base, the nature and purity of the solvent and the effect of using heat or ultrasonic radiation were investigated (Table 3).

Using the initial conditions, the result obtained was a 34% conversion of iodoferrocene to give 4-methylphenylferrocene (yield 50% based on reacted iodoferrocene and 17% overall). Increasing the concentration of either the catalyst (palladium acetate) or base (sodium carbonate) with respect to iodoferrocene and the boronic acid had a negligible effect on either the

yields or conversions (compare entries 2, 3 and 4 with entry 1). Due to the awkwardness of working with such a small amount of catalyst (3 mg in initial reaction) and as increasing the amount of catalyst was having no significant effect on the course of the reaction, the concentration of catalyst was increased for all subsequent reactions (Table 3, entries 5–16). Heating the reaction mixture at 80 °C prior to stirring (Table 3, entry 5) or carrying out the reaction in an ultrasonic bath (Table 3, entry 6) had no significant effect on either the conversions or overall yields. Mounting the reaction flask on a flask shaker (Table 3, entry 7) resulted in a small increase in the efficiency of the reaction and a more significant increase in the overall yield of 4-methylphenylferrocene. Reaction mixtures for all subsequent reactions were shaken for 30 min prior to stirring under nitrogen (Table 3, entries 7–16). Addition of second batches of catalyst (0.2 eq.) and arylboronic acid (0.5 eq.) seven hours into the reaction resulted in a significant increase in the conversion and yield (Table 3, entry 8). This was not unexpected since deboronation would be expected to occur with a rate constant independent of the rate of aryl coupling due to the mild hydrolytic instability of arylboronic acids. It has been shown that in the majority of Suzuki reactions, addition of 10% excess of boronic acid ensures quantitative consumption of the aryl halide.[12] The next reaction performed in this study was one in which the solvent was purged more extensively by nitrogen bubbling (3 h) and in which the amount of arylboronic acid was increased five-fold with respect to iodoferrocene. This manipulation increased the conversion to 62% and resulted in an overall yield of 44% (Table 3, entry 9). To eliminate oxygen as far as possible, the solvent was degassed using a freeze–thaw cycle before being purged by nitrogen bubbling. The result was a small increase in the overall yield (Table 3, entry 10). This reaction was repeated using only 1.2 eq. of the arylboronic acid instead of 5 eq. (Table 3, entry 11), but little change in either the conversion or overall yield was observed. Comparisons of the results in entries 1–7 with 9–11 and entry 9 with entry 11 suggests that scrupulous deoxygenation of the solvent is critical, probably preventing undue removal of the arylboronic acid in a self-coupling reaction, which is a reaction known to be accelerated by oxygen. The efficacy of these modifications were confirmed when applied to 4-methoxybenzeneboronic acid which afforded 4-methoxyphenylferrocene with a significantly improved yield of 69% (*vs.* 46%; Table 1, entry 1) and conversion (68 *vs.* 43%).

The effect of changing the base from sodium carbonate (Na$_2$CO$_3$) which is a relatively weak base to stronger bases such as potassium carbonate (K$_2$CO$_3$) and barium hydroxide was investigated next. Since both of these bases are less soluble than sodium carbonate in 95% ethanol, the solvent system was changed to 90% ethanol. Utilising Ba(OH)$_2$ as base resulted in a 62% conversion of iodoferrocene after 280 h of which 95% afforded the desired product (overall yield of 57%) (Table 3, entry 12). The reaction utilising Ba(OH)$_2$ as base was repeated, except that the solvent was degassed more stringently and the reaction time reduced to 5 h. In this case, no unreacted iodoferrocene was observed (*i.e.*, 100% conversion) whilst 4-methylphenylferrocene was isolated in an excellent yield of 84% (Table 3, entry 13). Use of Ba(OH)$_2$ clearly dramatically improves conversions and accelerates the reaction. This finding is consistent with those of Suzuki and Campi and their collaborators. Use of potassium carbonate instead of sodium carbonate also led to an improved yield and conversion (Table 3, entry 14). It is clear that with our reaction systems, relatively strong bases such as Ba(OH)$_2$ and K$_2$CO$_3$ are more efficient bases than Na$_2$CO$_3$ for the Suzuki cross-coupling reaction. The use of silver carbonate as base proved to be less efficient (see Experimental section).

Reactions were also carried out in two alternative solvents to aqueous ethanol. When 95% acetonitrile was used as solvent, the conversion dropped to 57% with an overall yield of 20%

**Table 3** Optimization results. Yield of 4-methylphenylferrocene from the Suzuki reaction of iodoferrocene and 4-methylbenzeneboronic acid under different conditions
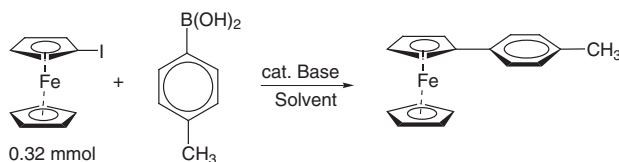


| Entry | 4-Methylbenzene boronic acid/ mmol | PdOAc$_2$/mmol | Base/mmol | Solvent | Time/h | Iodoferrocene recovered(%) | Yield (%)[n] | Yield (%)[o] |
|---|---|---|---|---|---|---|---|---|
| 1[a] | 0.32 | 0.013 | Na$_2$CO$_3$ (0.45) | EtOH (95%) | 24 | 66 | 50 | 17 |
| 2[b] | 0.32 | 0.044 | Na$_2$CO$_3$ (0.45) | EtOH (95%) | 24 | 60 | 42 | 17 |
| 3[b] | 0.32 | 0.089 | Na$_2$CO$_3$ (0.45) | EtOH (95%) | 24 | 65 | 48 | 17 |
| 4[c] | 0.32 | 0.013 | Na$_2$CO$_3$ (0.94) | EtOH (95%) | 24 | 65 | 55 | 19 |
| 5[d] | 0.32 | 0.067 | Na$_2$CO$_3$ (0.45) | EtOH (95%) | 24 | 59 | 55 | 23 |
| 6[e] | 0.34 | 0.075 | Na$_2$CO$_3$ (0.47) | EtOH (95%) | 24 | 59 | 59 | 25 |
| 7[f] | 0.32 | 0.067 | Na$_2$CO$_3$ (0.45) | EtOH (95%) | 24 | 60 | 73 | 29 |
| 8[g] | 0.32 + 0.16 | 0.067 + 0.067 | Na$_2$CO$_3$ (0.46) | EtOH (95%) | 72 | 53 | 78 | 36 |
| 9[h] | 1.61 | 0.072 | Na$_2$CO$_3$ (0.46) | EtOH (95%) | 45 | 38 | 70 | 44 |
| 10[i] | 1.62 | 0.070 | Na$_2$CO$_3$ (0.46) | EtOH (95%) | 90 | 38 | 79 | 49 |
| 11[j] | 0.38 | 0.067 | Na$_2$CO$_3$ (0.46) | EtOH (95%) | 108 | 32 | 62 | 42 |
| 12[k] | 1.61 | 0.067 | Ba(OH)$_2$ (0.45) | EtOH (90%) | 280 | 38 | 95 | 57 |
| 13[k] | 1.61 | 0.069 | Ba(OH)$_2$ (0.45) | EtOH (90%) | 5 | 0 | 84 | 84 |
| 14[l] | 1.61 | 0.070 | K$_2$CO$_3$ (0.46) | EtOH (90%) | 256 | 16 | 80 | 67 |
| 15[m] | 1.62 | 0.068 | Na$_2$CO$_3$ (0.45) | CH$_3$CN (95%) | 39 | 43 | 35 | 20 |
| 16[m] | 1.60 | 0.070 | Na$_2$CO$_3$ (0.46) | DMF (95%) | 82 | — | — | 57 |

[a] Results obtained using standard conditions as described by Campi *et al.* [b] Effect of the amount of catalyst on the reaction. [c] Effect of the amount of base on reaction. [d] Effect of heating the reaction prior to stirring. [e] Carrying out the reaction in an ultrasonic bath. [f] Shaking the reaction using an electronic shaker prior to stirring. [g] Batchwise addition of catalyst and boronic acid. [h] Increased concentration of boronic acid and improved degassing. [i] Freeze–thawing solvent and degassing (5 eq. boronic acid). [j] Freeze–thawing solvent and degassing (1.2 eq. boronic acid). [k] Base effect using Ba(OH)$_2$ as base. [l] Base effect using K$_2$CO$_3$ as base. [m] Solvent effect. [n] Yield is based on the amount of reacted iodoferrocene. [o] Yield is based on the amount of iodoferrocene as starting material.
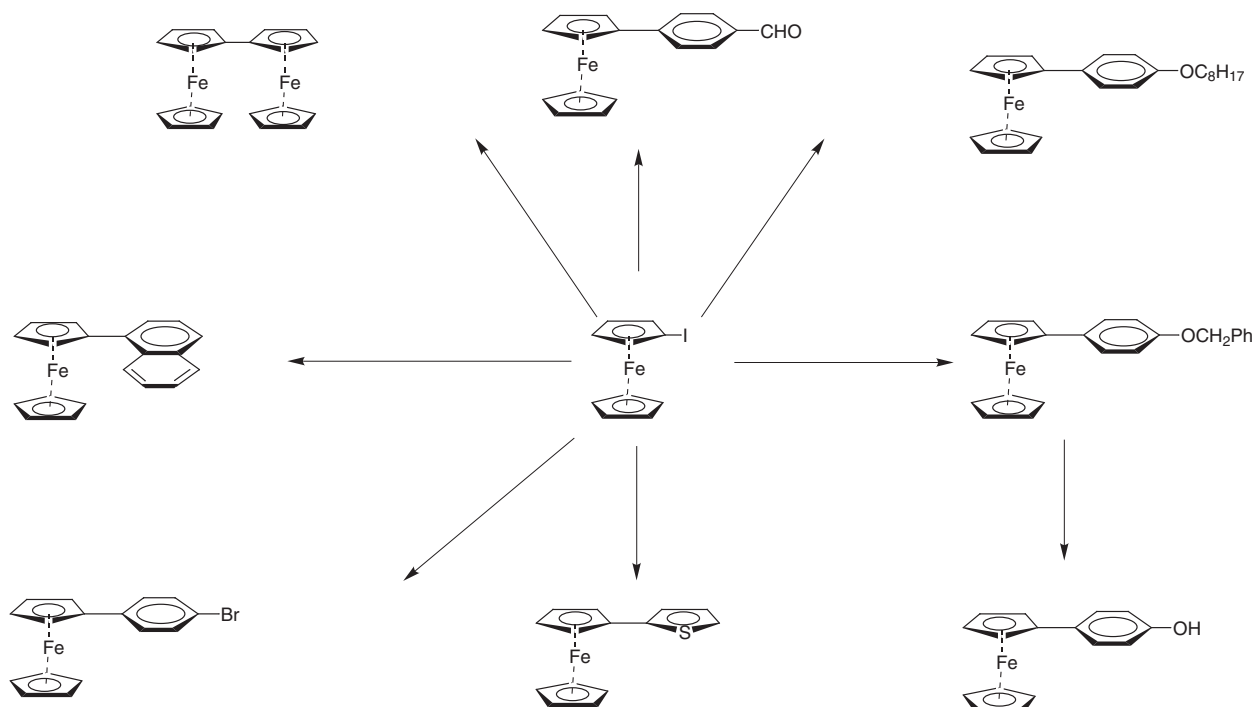


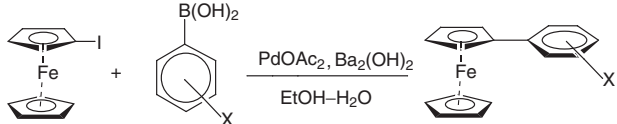**Fig. 2** Ferrocene derivatives synthesized by the modified Suzuki reaction.

(Table 3, entry 15), while 95% DMF gave rise to 4-methylphenylferrocene in an overall yield of 57% (Table 3 entry 16). A drawback to the use of DMF is its high boiling point which makes its removal at the end of the reaction more difficult.

The reaction of iodoferrocene and substituted arylboronic acids was carried out on a larger scale (10×) under optimum conditions and the results are shown in Table 4. When the substituent on the benzene ring of the boronic acid is electron donating, the conversions are good and the overall yields are acceptable. Under the same reaction conditions and reaction time, boronic acids containing electron-withdrawing substituents provided significantly lower conversions and yields. It was decided therefore to monitor the effect of reaction time and heat and so the reaction between iodoferrocene and 4-formyl-benzeneboronic acid was carried out for 72, 336 and 772 h, and in one case 72 h with heat. A comparison of entries 9, 10, 11 and

**Table 4** Scale-up reactions. Yield of arylferrocenes from the Suzuki reaction of iodoferrocene and arylboronic acids



| Entry | X | Recovered iodoferrocene (%) | Reaction time/h | Yield (%)[a] | Yield (%)[b] |
|---|---|---|---|---|---|
| 1[c] | 4-OMe | 16 | 72 | 58 | 49 |
| 2[d] | 4-OMe | 4 | 72 | 62 | 60 |
| 3[c] | 3-OMe | 25 | 72 | 51 | 38 |
| 4[c] | 2-OMe | 17 | 72 | 68 | 56 |
| 5[c] | 4-Me | 12 | 72 | 65 | 57 |
| 6[c] | 4-F | 15 | 336 | 61 | 51 |
| 7[c] | 3-F | 42 | 336 | 97 | 56 |
| 8[c] | 4-CF$_3$ | 0 | 336 | | 26 |
| 9[c] | 4-CHO | 50 | 72 | 28 | 14 |
| 10[d] | 4-CHO | 42 | 72 | 63 | 36 |
| 11[c] | 4-CHO | 40 | 336 | 42 | 25 |
| 12[c] | 4-CHO | 10 | 772 | 48 | 43 |
| 13[c] | 4-OC$_8$H$_{17}$ | 41 | 72 | 31 | 18 |
| 14[c] | 4-OCH$_2$C$_6$H$_5$ | 41 | 72 | 60 | 35 |

[a] Yield is based on the amount of reacted iodoferrocene. [b] Yield is based on the amount of iodoferrocene as starting material. [c] Typical procedure (see general method in Experimental section for full details). To ethanol (90%) under nitrogen was added the arylboronic acid (6.48 mmol), iodoferrocene (1.0 g, 3.21 mmol), barium hydroxide (1.43 g, 4.50 mmol) and palladium acetate (0.16 g, 0.72 mmol). The reaction mixture was stirred under nitrogen. [d] Procedure as for c except solution heated under reflux during the day (3 × 8 h) over three days.

12 in Table 4 shows that conversions and yields improve significantly with time of reaction without heating, and with heating the reaction. The application of heat to the Suzuki reactions under optimized conditions results in faster reaction times and improved yields but the formation of biferrocenyl (self-coupling product) becomes significant and makes purification of the monoarylferrocene more difficult. Starting with just over 3 g of iodoferrocene, more than 1 g of 4-formylphenylferrocene was isolated and this compound is not easy to synthesize by the traditional diazonium reaction. In these Suzuki reactions involving ferrocenes, some decomposition of the ferrocenyl system is evident and is most clearly highlighted by the reaction between iodoferrocene and 4-trifluoromethylbenzeneboronic acid. The yield of monoarylferrocene is low (entry 8, Table 4) and no other ferrocenyl-containing molecule was obtained which suggests that some species in the solution can oxidize the ferrocenyl moiety to ferrocenium which leads to decomposition.

4-Formylphenylferrocene is one of the monoarylferrocenes that is of particular interest to us for our current work on ferrocenomesogens, the others being 4-hydroxy- and 4-carboxyphenylferrocenes. Attempts to prepare the latter two compounds directly by the modified Suzuki reaction using either, 4-hydroxy- or 4-carboxy-benzeneboronic acid failed, and this may in-part be due to the low solubility of the arylboronic acids. The modified Suzuki reaction was used to prepare 4-hydroxyphenylferrocene in two steps from iodoferrocene. Reaction of iodoferrocene with 4-benzyloxybenzeneboronic acid gave 4-benzyloxyphenylferrocene which upon hydrogenation provided 4-hydroxyphenylferrocene. A full report on the synthesis of a new series of ferrocenomesogens derived from monoarylferrocenes will appear at a later stage.

## Conclusion

A new synthesis of monoarylferrocenes has been developed based on a modification of the Suzuki cross-coupling reaction and this offers several advantages over alternative methods; it is cleaner, more selective and more efficient. The optimum reaction conditions were investigated by a systematic study into the effect of changing various parameters on the conversion of the iodoferrocene starting material into product. Optimal conditions were found to involve deoxygenated 90% ethanol as solvent, palladium acetate as catalyst and either potassium carbonate or barium hydroxide as base. Scrupulous deoxygenation of the solvent was found to be most critical.

## Experimental

All reactions were performed under an atmosphere of dry nitrogen. Silica gel 50 or aluminium oxide (active, neutral, Brockmann Grade I) were used for column chromatography. Plate chromatography was performed on a model 7924T Harrison chromatotron utilising silica gel 60PF-254 as adsorbent with calcium sulfate as binder. Melting points were recorded on an Electrothermal IA 900 series digital melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 series Fourier Transform IR spectrometer as KBr discs. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Gemini 200 spectrometer as solutions in CDCl$_3$ using tetramethylsilane (TMS) as internal standard. Coupling constants are measured in Hz. Mass spectra were recorded on a VG70-SEQ/MSSMS2 spectrometer at the Cape Technikon. Microanalyses were performed on a Carlo-Erba MOD 1160 elemental analyser by the Council for Scientific and Industrial Research, Pretoria. Reaction mixtures were shaken on a Griffin flask shaker (896331/2). The majority of the arylboronic acids were purchased from Lancaster Synthesis (UK) and were used without further purification. The other arylboronic acids were synthesized by a standard method given later in the Experimental section. Petroleum ether was a fraction with bp 40–60 °C.

### Chloromercurioferrocene

A solution of mercuric acetate (105.84 g, 0.33 mol) in absolute methanol (850 cm³) was added dropwise to a stirred solution of ferrocene (124.95 g, 0.67 mol) in dry benzene (500 cm³). The reaction was continued under a nitrogen atmosphere at room temperature for 10 h, and then lithium chloride (29.52 g, 0.70 mol) in a 1:1 ethanol–water (200 cm³) mixture was added dropwise. The resulting orange suspension was stirred at room temperature for 2 h, then heated under reflux for 1 h, and was finally collected, placed in a Soxhlet, and extracted with dichloromethane. The dichloromethane extract was washed thoroughly with water and dried over sodium sulfate. After removal of the solvent, the solid residue was sublimed *in vacuo* to remove unchanged ferrocene. In this manner ferrocene (63.45 g) was recovered. The unsublimed portion gave on recrystallisation from dichloromethane–petroleum ether, chloromercuriferrocene (60.12 g, 43%) as golden platelets, mp 195 °C decomp. (lit.,[17] 194–198 °C decomp.); $\nu_{max}$(KBr)/cm$^{-1}$ 1600, 1400, 1140, 1100, 820; $\delta_H$(CDCl$_3$) 4.67 (2 H, t, J 1.9, C$_5$H$_4$), 4.45 (5 H, s, C$_5$H$_5$), 4.35 (2 H, t, J 1.9, C$_5$H$_4$); *m/z* 423 (26%), 422 (59), 421 (30), 186 (21), 185 (37), 184 (100) (Found: C, 28.4; H, 2.2%. C$_{10}$H$_9$ClFeHg requires C, 28.5; H, 2.2%).

### Iodoferrocene

**Method 1.** Chloromercurioferrocene (10.00 g, 0.024 mol) was stirred with iodine (15.00 g, 0.059 mol) in anhydrous dichloromethane for 1 h. A spatula tip of ascorbic acid was then added and the mixture allowed to stir for a further hour. After this, the mixture was thoroughly washed with water. The organic layer was washed successively with a 10% aqueous sodium thiosulfate solution and water prior to drying over anhydrous sodium sulfate. The solvent was removed and the organic residue subjected to column chromatography on aluminium oxide using petroleum ether as the eluent. A single

yellow fraction was eluted from the column and after evaporation of the solvent gave an orange solid. Upon recrystallisation from hexane, iodoferrocene (5.25 g, 72%) was recovered, mp 48 °C (lit.,[18] 49–49.5 °C); $v_{max}$(KBr)/cm$^{-1}$ 3090, 1600–1700, 1410, 1100, 1020, 1000, 820; $\delta_H$(CDCl$_3$) 4.33 (2 H, t, $J$ 1.9, C$_5$H$_4$), 4.10 (5 H, s, C$_5$H$_5$), 4.00 (2 H, t, $J$ 1.9, C$_5$H$_4$); $m/z$ 312 (12%), 311 (M$^+$, 100), 310 (7), 186 (23), 185 (16), 184 (40) (Found: C, 38.7; H, 2.7%. C$_{10}$H$_9$FeI requires C, 38.5; H, 2.9%).

**Method 2.** A solution of iodine (6.00 g, 0.025 mol) in anhydrous dichloromethane (200 cm$^3$) was added dropwise to a cold, stirred solution of chloromercurioferrocene (10.00 g, 0.024 mol) in anhydrous dichloromethane (500 cm$^3$). The reaction was continued at room temperature under a nitrogen atmosphere for 8 h, after which time an aqueous solution of sodium thiosulfate was added to destroy excess iodine. The organic material was extracted with diethyl ether (3 × 500 cm$^3$) and then dried over sodium sulfate. After evaporation of the solvent, the residue was dissolved in petroleum ether, passed through a column of alumina and concentrated. A single yellow fraction was eluted from the column, which gave iodoferrocene (4.82 g, 60%) as an orange solid after evaporation of the solvent.

The spectral characteristics were identical to those observed before.

## Preparation of arylboronic acids

**General method.** A solution of the appropriate bromoaromatic compound (1 eq.) in anhydrous tetrahydrofuran (THF) was cooled to −78 °C. $n$-Butyllithium (1.5 eq.) was added dropwise. The reaction mixture was maintained under these conditions for 3 h, and then a solution of trimethylborate (6 eq.) in dry tetrahydrofuran was added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature overnight, and then stirred for 1 h with 10% HCl. The product was extracted into diethyl ether and the combined ethereal extracts were washed with water, dried and finally the solvent was removed *in vacuo* to leave in most cases off-white solids.

## Suzuki reactions—small scale non-optimised reactions

**General method.** To 95% ethanol, which had been purged for 30 min with nitrogen, was added the substituted arylboronic acid (0.32 mmol), iodoferrocene (0.32 mmol), sodium carbonate (0.45 mmol) and palladium acetate (0.013 mmol) under nitrogen. The reaction was allowed to stir under nitrogen for 24 h at room temperature. The reaction mixture was then filtered and poured into diethyl ether (100 cm$^3$). The ethereal solution was washed with water and dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was passed through a column of silica gel. Recovered iodoferrocene was eluted with petroleum ether. A mixture of petroleum ether–diethyl ether (9:1) eluted the monoarylferrocene. Yields of monoarylferrocenes are quoted with respect to the amount of reacted iodoferrocene.

**4-Methoxyphenylferrocene.** Quantities: 4-methylbenzeneboronic acid (49 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol) and palladium acetate (3 mg, 0.013 mmol). Workup gave recovered iodoferrocene (57 mg, 43% conversion) and 4-methoxyphenylferrocene (43 mg, 100%) as orange crystals (from hexane), mp 113 °C (lit.,[2d] 112–114 °C); $v_{max}$(KBr)/cm$^{-1}$ 2955, 2924, 2854, 1607, 1524, 1501, 1458, 1436, 1276, 1248, 1180, 1104, 1035, 811; $\delta_H$(CDCl$_3$) 7.42 (2 H, d, $J$ 8.8, ArH), 6.86 (2 H, d, $J$ 8.8, ArH), 4.58 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.28 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.05 (5 H, s, C$_5$H$_5$), 3.83 (3 H, s, OCH$_3$); $m/z$ 292 (M$^+$, 100%), 277 (23), 249 (14), 214 (9), 199 (7), 128 (7), 122 (27).

**4-Methylphenylferrocene.** Quantities: 4-methylbenzeneboronic acid (44 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32

mmol), sodium carbonate (48 mg, 0.45 mmol), palladium acetate (3 mg, 0.013 mmol). Workup gave recovered iodoferrocene (66 mg, 34% conversion) and 4-methylphenylferrocene (15 mg, 50%) as orange crystals (from hexane) mp 141 °C (lit.,[19] 140–142 °C); $v_{max}$(KBr)/cm$^{-1}$ 3086, 3017, 2361, 1525, 1455, 1405, 1386, 1280, 1104, 1082, 1027, 999, 886, 817; $\delta_H$(CDCl$_3$) 7.38 (2 H, d, $J$ 8.1, ArH), 7.10 (2 H, d, $J$ 8.1, ArH), 4.62 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.29 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.04 (5 H, s, C$_5$H$_5$), 2.33 (3 H, s, CH$_3$); $\delta_C$ (CDCl$_3$) 138.05, 137.51, 131.05, 128.09, 87.78, 71.54, 70.65, 68.36, 23.18; $m/z$ 227 (34%), 276 (M$^+$, 100), 211 (7), 121 (18).

**4-Phenylferrocene.** Quantities: 4-phenylboronic acid (70 mg, 0.48 mmol), iodoferrocene (0.150 g, 0.48 mmol), sodium carbonate (0.100 g, 0.94 mmol), palladium acetate (10 mg, 0.044 mmol). Workup gave recovered iodoferrocene (92 mg, 39% conversion) and 4-phenylferrocene (45 mg, 87%) as orange crystals (from hexane) mp 110–111 °C (lit.,[20] 114–115 °C); $v_{max}$(KBr)/cm$^{-1}$ 3100, 3056, 1512, 1450, 1404, 1278, 1102, 1025, 996, 817; $\delta_H$(CDCl$_3$) 7.50 (2 H, d, $J$ 8.8, ArH), 7.28 (3 H, m, ArH), 4.66 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.33 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.06 (5 H, s, C$_5$H$_5$); $m/z$ 263 (20%), 262 (M$^+$, 100), 167 (14), 149 (34), 121 (9) (Found: M$^+$, 262.0450. C$_{16}$H$_{14}$Fe requires $M$, 262.0441).

**4-Octyloxyphenylferrocene.** Quantities: 4-Octyloxybenzeneboronic acid (80 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol), palladium acetate (3 mg, 0.013 mmol). Workup gave 4-octyloxyphenylferrocene (84 mg, 67%) as orange crystals (from hexane) mp 81–82 °C); $v_{max}$(KBr)/cm$^{-1}$ 2954, 2916, 2848, 1609, 1525, 1457, 1281, 1246, 1180, 1105, 1048, 1034, 1000, 886, 820; $\delta_H$(CDCl$_3$) 7.40 (2 H, d, $J$ 8.7, ArH), 6.84 (2 H, d, $J$ 8.7, ArH), 4.57 (2 H, t, $J$ 1.9, C$_5$H$_4$), 4.27 (2 H, t, $J$ 1.9, C$_5$H$_4$), 4.04 (5 H, s, C$_5$H$_5$), 3.97 (2 H, t, $J$ 6.6, OCH$_2$), 1.80 (2 H, m, CH$_2$), 1.32 (10 H, m, CH$_2$ × 5), 0.91 (3 H, t, CH$_3$); $m/z$ 391 (29%), 390 (M$^+$, 100), 278 (22), 277 (9), 186 (29) (Found: C, 73.8; H, 8.0%; M$^+$, 390.1646. C$_{24}$H$_{30}$FeO requires C, 73.9; H, 7.7%; $M$, 390.1644).

**4-Fluorophenylferrocene.** Quantities: 4-fluorobenzeneboronic acid (45 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol), palladium acetate (3 mg, 0.013 mmol). Workup gave recovered iodoferrocene (54 mg, 46% conversion) and 4-fluorophenylferrocene (17 mg, 41%) obtained as orange crystals (from hexane) mp 104 °C (lit.,[21] 101–104 °C); $v_{max}$(KBr)/cm$^{-1}$ 3079, 2962, 2361, 2337, 1522, 1452, 1408, 1382, 1260, 1226, 1159, 1102, 1032, 887, 832, 806. $\delta_H$(CDCl$_3$) 7.44 (2 H, m, ArH), 6.99 (2 H, m, ArH), 4.60 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.30 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.05 (5 H, s, C$_5$H$_5$); $m/z$ 280 (M$^+$, 100%), 215 (3), 159 (6) (Found: C, 68.4; H, 4.7%; M$^+$, 280.0336. C$_{16}$H$_{13}$FeF requires C, 68.6; H, 4.7%; $M$, 280.0347).

**3-Methoxyphenylferrocene.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 3-methoxybenzeneboronic acid (49 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol) and palladium acetate (15 mg, 0.067 mmol), under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir at room temperature for 24 h under a nitrogen atmosphere. The solvent was removed, the residue taken up in diethyl ether (100 cm$^3$) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was chromatographed on a chromatotron. Recovered iodoferrocene (55 mg, 45% conversion) was eluted with petroleum ether. A mixture of petroleum ether and diethyl ether (9:1) eluted 3-methoxyphenylferrocene (42 mg, 100%) as orange crystals (from hexane) mp 45 °C (lit.,[22] 43–45 °C); $v_{max}$(KBr)/cm$^{-1}$ 2928, 1713, 1605, 1578, 1466, 1288, 1220, 1179, 1103, 1049, 871, 811; $\delta_H$(CDCl$_3$) 7.08 (2 H, m, ArH), 6.76 (2 H, m, ArH), 4.64 (2 H, t, $J$ 1.9, C$_5$H$_4$), 4.31 (2 H,

t, $J$ 1.9, $C_5H_4$), 4.04 (5 H, s, $C_5H_5$), 3.86 (3 H, s, $OCH_3$); $m/z$ 292 ($M^+$, 100%), 277 (2), 249 (12), 214 (18), 128 (5), 122 (1).

**2-Methoxyphenylferrocene.** Quantities: 2-methoxybenzeneboronic acid (50 mg, 0.33 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol), palladium acetate (15 mg, 0.067 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (40 mg, 60% conversion) and 2-methoxyphenylferrocene (27 mg, 48%) obtained as an orange solid, mp 57–58 °C (lit.,[23] 58 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 2928, 1713, 1605, 1578, 1466, 1288, 1220, 1179, 1103, 1049, 871, 811; $\delta_H$(CDCl$_3$) 7.46 (1H, dd, $J$ 1.7 ArH), 7.13 (1H, m, ArH), 6.85 (2H, m, ArH), 4.75 (2 H, t, $J$ 1.8, $C_5H_4$), 4.25 (2 H, t, $J$ 1.8, $C_5H_4$) 4.01 (5 H, s, $C_5H_5$), 3.90 (3 H, s, $CH_3$); $m/z$ 293 (21%), 292 ($M^+$, 100), 277 (18), 212 (15), 149 (14), 121 (8), 56 (9), 43 (4) (Found: C, 69.9; H, 5.5%; $M^+$, 292.0546. $C_{17}H_{16}FeO$ requires C, 69.9; H, 5.5%; $M$, 292.0549).

**Biphenyl-4-ylferrocene.** Quantities: biphenyl-4-ylboronic acid (63 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (50 mg, 0.47 mmol), palladium acetate (17 mg, 0.077 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (54 mg, 46% conversion) and biphenyl-4-ylferrocene (20 mg, 41%) as orange crystals (from hexane) mp 160 °C (lit.,[24] 164–165 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3097, 3028, 2962, 1714, 1597, 1535, 1492, 1451, 1409, 1262, 1206, 1103, 1085, 1029, 1001, 885, 841, 807; $\delta_H$(CDCl$_3$) 7.64 (2 H, m, $J$ 1.3, ArH), 7.55 (3 H, s, ArH), 7.42 (4 H, m, $J$ 1.6, ArH), 4.69 (2 H, t, $J$ 1.9, $C_5H_4$), 4.35 (2 H, t, $J$ 1.9, $C_5H_4$), 4.08 (5 H, s, $C_5H_5$); $m/z$ 339 (26%), 338 ($M^+$, 100), 336 (8), 306 (12), 305 (10), 273 (22), 215 (18).

**1-Ferrocenylnaphthalene.** Quantities: naphthalene-1-boronic acid (55 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (49 mg, 0.46 mmol), palladium acetate (15 mg, 0.067 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (47 mg, 53% conversion) and 1-ferrocenylnaphthalene (38 mg, 72%) as orange crystals (from hexane) mp 87 °C (lit.,[26] 92.5–93.5 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3096, 3054, 2927, 1590, 1392, 1106, 1022, 1002, 823, 803; $\delta_H$(CDCl$_3$) 8.54 (1 H, m, ArH), 7.87 (2 H, m, ArH), 7.77 (1 H, m, ArH), 7.47 (3 H, m, ArH), 4.66 (2 H, t, $J$ 1.8, $C_5H_4$), 4.41 (2 H, t, $J$ 1.8, $C_5H_4$), 4.20 (5 H, s, $C_5H_5$); $m/z$ 313 (28%), 312 ($M^+$, 100), 310 (13), 191 (6), 190 (16), 189 (22).

**2-Ferrocenylthiophene.** Quantities: thiophene-2-boronic acid (42 mg, 0.33 mmol), iodoferrocene (0.103 g, 0.33 mmol), sodium carbonate (50 mg, 0.47 mmol), palladium acetate (16 mg, 0.070 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (54 mg, 47% conversion) and 2-ferrocenylthiophene (27 mg, 65%) as orange crystals (from hexane), mp 113 °C (lit.,[8] 116.5–117.5 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 2924, 2853, 1460, 1408, 1260, 1230, 1102, 1043, 1021, 1000, 816; $\delta_H$(CDCl$_3$) 7.16 (1 H, m, ArH), 7.01 (1 H, m, ArH), 6.93 (1 H, m, ArH), 4.58 (2 H, t, $J$ 1.8, $C_5H_4$), 4.28 (2 H, t, $J$ 1.9, $C_5H_4$), 4.10 (5 H, s, $C_5H_5$); $m/z$ 269 (41%), 268 ($M^+$, 100), 266 (24) (Found: C, 63.3; H, 4.5%; $M^+$, 268.1630. $C_{14}H_{12}FeS$ requires C, 62.7; H, 4.5%; $M$, 268.1623).

**4-Formylphenylferrocene.** Quantities: 4-formylbenzeneboronic acid (48 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (49 mg, 0.46 mmol), palladium acetate (16 mg, 0.070 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (81 mg, 16% conversion) and 4-formylphenylferrocene (12 mg, 79%) as red crystals (from

hexane) mp 133–136 °C (lit.,[27] 133–136 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 2924, 2730, 1699, 1600, 1565, 1520, 1422, 1385, 1304, 1280, 1261, 1213, 1172, 1103, 1081, 1028, 999, 885, 827; $\delta_H$(CDCl$_3$) 9.98 (1 H, s, CHO), 7.81 (2 H, d, $J$ 8.5, ArH), 7.61 (2 H, d, $J$ 8.5, ArH), 4.75 (2 H, t, $J$ 1.8, $C_5H_4$), 4.45 (2 H, t, $J$ 1.8, $C_5H_4$), 4.06 (5 H, s, $C_5H_5$); $m/z$ 291 (21%), 290 ($M^+$, 100), 261 (5), 225 (2), 202 (3), 169 (2), 145 (9), 141 (8), 139 (5), 121 (23), 115 (5) (Found: C, 69.9; H, 4.8%; $M^+$, 290.0384. $C_{17}H_{14}FeO$ requires C, 70.5; H, 4.9%; $M$, 290.0393).

**4-Bromophenylferrocene.** Quantities: 4-bromobenzeneboronic acid (65 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (49 mg, 0.46 mmol), palladium acetate (16 mg, 0.073 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (61 mg, 39% conversion) and 4-bromophenylferrocene (26 mg, 61%) as red crystals (from hexane) mp 122–123 °C (lit.,[28] 125 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3086, 3053, 2925, 2853, 1588, 1509, 1446, 1406, 1383, 1278, 1103, 1088, 1066, 1050, 1030, 1001, 884, 819; $\delta_H$(CDCl$_3$) 7.41 (2 H, d, $J$ 8.5, ArH), 7.34 (2 H, d, $J$ 8.5, ArH), 4.62 (2 H, t, $J$ 1.8, $C_5H_4$), 4.34 (2H, t, $J$ 1.8, $C_5H_4$), 4.04 (5 H, s, $C_5H_5$); $m/z$ 343 (18%), 342 (96), 341 (22), 340 ($M^+$, 100), 260 (3), 205 (23), 203 (10), 202 (9) (Found: C, 56.4; H, 3.8%; $M^+$, 339.9551. $C_{16}H_{13}BrFe$ requires C, 56.6; H, 3.9%; $M$, 339.9550).

**4-Trifluoromethylphenylferrocene.** Quantities: 4-trifluoromethylbenzeneboronic acid (61 mg, 0.32 mmol), iodoferrocene (0.101 g, 0.32 mmol), sodium carbonate (49 mg, 0.46 mmol), palladium acetate (16 mg, 0.072 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (80 mg, 20% conversion) and 4-trifluoromethylphenylferrocene (17 mg, 75%) obtained as red crystals (from hexane) mp 137–138 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 2916, 2849, 1613, 1420, 1330, 1281, 1191, 1158, 1425, 1107, 1088, 1063, 1036, 1013, 887, 841, 820; $\delta_H$(CDCl$_3$) 7.54 (4 H, s, ArH), 4.69 (2 H, t, $J$ 1.9, $C_5H_4$), 4.39 (2 H, t, $J$ 1.9, $C_5H_4$), 4.06 (5 H, s, $C_5H_5$); $m/z$ 331 (23%), 330 ($M^+$, 100), 311 (3), 265 (5), 209 (3), 190 (63), 170 (11), 164 (15), 151 (7), 139 (5), 121 (5) (Found: C, 61.5; H, 4.0%; $M^+$, 330.0302. $C_{17}H_{13}FeF_3$ requires C, 61.9; H, 4.0%; $M$, 330.0315).

**4-Decyloxyphenylferrocene.** Quantities: 4-decyloxybenzeneboronic acid (90 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol), palladium acetate (15 mg, 0.067 mmol). The experimental procedure was as described for the preparation of 3-methoxyphenylferrocene. Workup gave recovered iodoferrocene (33 mg, 67% conversion) and 4-decyloxyphenylferrocene (38 mg, 42%) as orange crystals (from hexane) mp 84–85 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 2954, 2915, 2847, 1607, 1525, 1457, 1282, 1248, 1180, 1105, 1033, 819; $\delta_H$(CDCl$_3$) 7.42 (2 H, d, $J$ 8.8, ArH), 6.84 (2 H, d, $J$ 8.8, ArH), 4.57 (2 H, t, $J$ 1.8, $C_5H_4$), 4.27 (2 H, t, $J$ 1.8, $C_5H_4$), 4.04 (5 H, s, $C_5H_5$), 3.97 (2 H, t, $J$ 6.6, $OCH_2$), 1.80 (2 H, m, $CH_2$), 1.35 (14 H, m, $CH_2 \times 7$), 0.89 (3 H, t, $CH_3$); $m/z$ 419 (29%), 418 ($M^+$, 100), 278 (20), 277 (8), 149 (14), 121 (5) (Found: C, 74.5; H, 8.3%; $M^+$, 418.1948. $C_{26}H_{34}FeO$ requires C, 74.7; H, 8.2%; $M$, 418.1950).

**4-Acetylphenylferrocene.** To 95% ethanol, which was purged with nitrogen for 3 h, was added 4-acetylbenzeneboronic acid (0.264 g, 1.61 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.46 mmol) and palladium acetate (16 mg, 0.073 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir at room temperature for 120 h under nitrogen. The solvent was removed, the residue taken up in diethyl ether (100 cm$^3$) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with

petroleum ether so as to remove the residual arylboronic acid. The solvent was removed again *in vacuo* and the residue chromatographed on a chromatotron. Recovered iodoferrocene (49 mg, 51% conversion) was eluted with petroleum ether. A mixture of petroleum ether and diethyl ether (9:1) eluted 4-acetylphenylferrocene (36 mg, 70%), mp 173–174 °C (lit.,[2f] 176–178 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3100, 2924, 2854, 1668, 1600, 1560, 1450, 1412, 1357, 1303, 1273, 1186, 1105, 1088, 1067, 1027, 1000, 958, 886, 833, 804; $\delta_H$(CDCl$_3$) 7.90 (2H, d, *J* 8.7, ArH), 7.54 (2H, d, *J* 8.7, ArH), 4.73 (2H, t, *J* 1.9, C$_5$H$_4$), 4.42 (2H, t, *J* 1.9, C$_5$H$_4$), 4.05 (5H, s, C$_5$H$_5$), 2.61 (3H, s, CH$_3$); *m/z* 304 (M$^+$, 100%), 261 (15), 152 (2), 144 (11), 121 (9) (Found: C, 71.1; H, 5.3%. C$_{18}$H$_{16}$FeO requires C, 71.2; H, 5.3%).

**4-Hydroxyphenylferrocene.** *(a) 4-Benzyloxyphenylferrocene.* To 90% ethanol, which was deaerated *via* three freeze–thawing cycles and then purged with nitrogen for 15 h was added 4-benzyloxybenzeneboronic acid (0.169 g, 74 mmol), iodoferrocene (0.150 g, 48 mmol), barium hydroxide (0.215 g, 68 mmol) and palladium acetate (23 mg, 10 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir at room temperature for 24 h under nitrogen. The solvent was removed, the residue taken up in diethyl ether (100 cm$^3$) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was again removed *in vacuo* and the residue chromatographed on a chromatotron. Recovered iodoferrocene (82 mg, 46% conversion) was eluted with petroleum ether. A mixture of petroleum ether and diethyl ether (9:1) eluted 4-benzyloxyphenylferrocene (76 mg, 93%) as orange crystals (from hexane), mp 176–177 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3426, 3086, 3032, 2962, 2924, 2854, 1712, 1605, 1523, 1499, 1454, 1381, 1261, 1243, 1177, 1102, 1018, 918, 806; $\delta_H$(CDCl$_3$) 7.45 (3 H, m, ArH), 7.42 (2 H, m, ArH), 7.39 (2 H, m, ArH), 6.95 (2 H, d, *J* 8.8, ArH), 5.08 (2 H, s, OCH$_2$), 4.57 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.27 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.04 (5 H, s, C$_5$H$_5$); *m/z* 369 (24%), 368 (M$^+$), 278 (25), 277 (100), 121 (29) (Found: C, 74.9; H, 5.4%; M$^+$, 368.0869. C$_{23}$H$_{20}$FeO requires C, 75.0; H, 5.5%; *M*, 368.0862).

*(b) 4-Hydroxyphenylferrocene.* 4-Benzyloxyphenylferrocene (55 mg, 0.15 mmol) was hydrogenated with palladium over carbon in deaerated ethanol for 96 h. The residual palladium was filtered off and the solvent removed *in vacuo*. The residue was then subjected to column chromatography on silica gel. The solvent combination petroleum ether–diethyl ether 9:1 eluted recovered 4-benzyloxyphenylferrocene (28 mg, 0.076 mmol)—characterization as before. The solvent system petroleum ether–diethyl ether 1:1 eluted 4-hydroxyphenylferrocene (26 mg, 62%) as yellow crystals (from hexane), mp 162 °C (lit.,[2c] 165 °C); $\nu_{max}$(KBr)/cm$^{-1}$ 3515, 1607, 1525, 1454, 1434, 1264, 1210, 1176, 1102, 1027, 998, 885, 839, 816; $\delta_H$(CDCl$_3$) 7.38 (2 H, d, *J* 8.5, ArH), 6.79 (2 H, d, *J* 8.1, ArH), 4.87 (1 H, s, OH), 4.58 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.28 (2 H, t, *J* 1.9, C$_5$H$_4$), 4.05 (5 H, s, C$_5$H$_5$); *m/z* 280 (39%), 277 (M$^+$, 81), 276 (100), 220 (10), 213 (39).

## Optimization of Suzuki reaction conditions. Reaction of iodoferrocene and 4-methylbenzeneboronic acid

**(a) Effect of increasing the amount of catalyst.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 4-methylbenzeneboronic acid (44 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol) and palladium acetate (10 mg, 0.045 mmol) under nitrogen. The reaction mixture was then allowed to stir under nitrogen for 24 h at room temperature. The reaction mixture was filtered and then poured into diethyl ether (100 cm$^3$). The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was passed through a column of silica gel. Recovered iodoferrocene (60 mg, 40% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (15 mg, 42%).

(ii) The same procedure as described in (i) was used except palladium acetate (20 mg, 0.089 mmol) was used. After removing the solvent *in vacuo*, the residue was passed through a column of silica gel. Recovered iodoferrocene (65 mg, 35% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–ether (9:1) eluted 4-methylphenylferrocene (15 mg, 48%).

**(b) Effect of increasing the amount of base.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 4-methylbenzeneboronic acid (44 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (0.100 g, 0.94 mmol) and palladium acetate (3 mg, 0.013 mmol) under nitrogen. The reaction mixture was allowed to stir under nitrogen for 24 h at room temperature. The reaction mixture was filtered and then poured into diethyl ether (100 cm$^3$). The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was passed through a column of silica gel. Recovered iodoferrocene (65 mg, 35% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (17 mg, 55%).

**(c) Effect of shaking the reaction mixture prior to stirring.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 4-methylbenzeneboronic acid (44 mg, 0.32 mmol), iodoferrocene (0.100 mg, 0.32 mmol) sodium carbonate (48 mg, 0.45 mmol) and palladium acetate (15 mg, 0.067 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min, and then allowed to stir at room temperature for 24 h under nitrogen. The reaction mixture was filtered and then poured into diethyl ether (100 cm$^3$). The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was passed through a column of silica gel. Recovered iodoferrocene (60 mg, 40% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (26 mg, 73%).

**(d) Effect of ultrasonic agitation.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 4-methylbenzeneboronic acid (46 mg, 0.34 mmol), iodoferrocene (0.102 g, 0.33 mmol), sodium carbonate (50 mg, 0.47 mmol) and palladium acetate (17 mg, 0.075 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min, and then allowed to stir for 24 h in an ultrasonic bath under nitrogen. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm$^3$) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. The solvent was then removed *in vacuo* and the residue chromatographed on a chromatotron. Recovered iodoferrocene (60 mg, 41% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (22 mg, 59%).

**(e) Effect of temperature.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 4-methylbenzeneboronic acid (44 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol) and palladium acetate (15 mg, 0.067 mmol), under nitrogen. The reaction mixture was vigorously shaken for 30 min, and then heated under reflux for 2 h at 80 °C (under nitrogen) before being allowed to stir for 24 h under nitrogen at room temperature. The solvent was removed *in vacuo*, the residue taken up in diethyl ether (100 cm$^3$) and filtered. The ethereal solution was washed with water

and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*, and the residue chromatographed on a chromatotron. Recovered iodoferrocene (59 mg, 41% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (20 mg, 55%).

**(f) Effect of adding additional catalyst and arylboronic acid after 7 h.** To 95% ethanol, which was purged with nitrogen for 30 min, was added 4-methylbenzeneboronic acid (44 mg, 0.32 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.46 mmol) and palladium acetate (15 mg, 0.069 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min, and then allowed to stir for 7 h under nitrogen at room temperature. A further batch of 4-methylbenzeneboronic acid (22 mg, 0.16 mmol) and palladium acetate (15 mg, 0.067 mmol) was then added and the reaction mixture allowed to stir for a further 65 h under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was chromatographed on a chromatotron. Recovered iodoferrocene (53 mg, 47% conversion) was eluted with petroleum ether. The solvent system petroleum ether:ether (9:1) eluted 4-methylphenylferrocene (32 mg, 78%).

**(g) Effect of improving the deaeration of the solvent.** To 95% ethanol, which was purged with nitrogen for 3 h, and then further deaerated by the freeze–thaw method, was added 4-methylbenzeneboronic acid (52 mg, 0.38 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (48 mg, 0.46 mmol) and palladium acetate (15 mg, 0.068 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 108 h under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was removed again and the residue chromatographed on a chromatotron. Recovered iodoferrocene (32 mg, 68% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (37 mg, 62%).

**(h) Combined effect of increasing the amount of arylboronic acid and improved solvent deaeration.** (i) To 95% ethanol, which was purged with nitrogen for 3 h, was added 4-methylbenzeneboronic acid (0.219 g, 1.61 mmol), iodoferrocene (0.101 g, 0.32 mmol), sodium carbonate (48 mg, 0.46 mmol) and palladium acetate (16 mg, 0.072 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 45 h under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was again removed *in vacuo* and the residue chromatographed on a chromatotron. Recovered iodoferrocene (38 mg, 62% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (39 mg, 70%).
(ii) To 95% ethanol, which was purged with nitrogen for 3 h, and then further deaerated by the freeze–thaw method, was added 4-methylbenzeneboronic acid (0.220 g, 1.62 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (49 mg, 0.46 mmol) and palladium acetate (16 mg, 0.070 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min

and then allowed to stir for 90 h under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with petroleum ether (40–60 °C), so as to remove the residual arylboronic acid. The solvent was again removed and the residue chromatographed on a chromatotron. Recovered iodoferrocene, (38 mg, 62% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (43 mg, 79%).

**(i) Base effect.** *(i) Barium hydroxide.* To 90% ethanol, which was purged with nitrogen for 3 h, and then further deaerated by the freeze–thaw method, was added 4-methylbenzeneboronic acid (0.219 g, 1.61 mmol), iodoferrocene (0.100 g, 0.32 mmol) barium hydroxide (0.142 g, 0.45 mmol) and palladium acetate (15 mg, 0.067 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 280 h under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was removed again *in vacuo* and the residue chromatographed on a chromatotron. Recovered iodoferrocene (38 mg, 62% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (50 mg, 95%).
In a repeat reaction, 4-methylbenzeneboronic acid (0.218 g, 1.61 mmol), iodoferrocene (0.101 g, 0.32 mmol), barium hydroxide (0.143 g, 0.45 mmol) and palladium acetate (16 mg, 0.069 mmol) were allowed to react together as described above with the exception that the solvent was initially freeze–thawed and then purged with nitrogen for 10 h. The reaction mixture was also stirred for only 5 h. Yield of 4-methylphenylferrocene 75 mg (84%).
*(ii) Potassium carbonate.* To 90% ethanol, which was purged with nitrogen for 3 h, and then further deaerated by the freeze–thaw method, was added 4-methylbenzeneboronic acid (0.219 g, 1.61 mmol), iodoferrocene (0.100 g, 0.32 mmol), potassium carbonate (64 mg, 0.46 mmol) and palladium acetate (16 mg, 0.070 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 256 h under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo* the residue was filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was removed again *in vacuo* and the residue chromatographed on a chromatotron. Recovered iodoferrocene (16 mg, 84% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (59 mg, 80%).
In a repeat reaction, 4-methylbenzeneboronic acid (0.218 g, 1.61 mmol), iodoferrocene (0.101 g, 0.32 mmol), potassium carbonate (62 mg, 0.45 mmol) and palladium acetate (15 mg, 0.067 mmol) were allowed to react together. The experimental procedure was as described for the above reaction, except that the reaction mixture was allowed to stir for only 48 h. Workup gave recovered iodoferrocene (17 mg, 84% conversion) and 4-methylphenylferrocene (59 mg, 80%).

**(j) Effect of solvent.** *(i) Acetonitrile.* To 95% acetonitrile, which was purged with nitrogen for 3 h, and then further deaerated by the freeze–thaw method, was added 4-methylbenzeneboronic acid (0.220 g, 1.62 mmol), iodoferrocene

(0.101 g, 0.32 mmol), sodium carbonate (48 mg, 0.45 mmol) and palladium acetate (15 mg, 0.068 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 39 h under nitrogen at room temperature. The solvent was removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was again removed and the residue chromatographed on a chromatotron. Recovered iodoferrocene (43 mg, 57% conversion) was eluted with petroleum ether. The solvent combination petroleum ether–diethyl ether (9:1) eluted 4-methylphenylferrocene (18 mg, 35%).

*(ii) Dimethylformamide.* To 95% dimethylformamide, which was purged with nitrogen for 3 h, and then further deaerated by the freeze–thaw method, was added 4-methylbenzeneboronic acid (0.218 g, 1.60 mmol), iodoferrocene (0.100 g, 0.32 mmol), sodium carbonate (49 mg, 0.46 mmol) and palladium acetate (16 mg, 0.071 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 82 h under nitrogen at room temperature. The solvent was then distilled off, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. After removing the solvent *in vacuo*, the residue was filtered through silica gel with petroleum ether so as to remove the residual arylboronic acid. The solvent was again removed *in vacuo* and the residue chromatographed on a chromatotron. 4-Methylphenylferrocene (50 mg, 57%) was eluted with petroleum ether–diethyl ether (9:1).

### Suzuki reactions—larger scale reactions under optimized conditions

**General method.** To 90% ethanol, which was degassed by nitrogen bubbling for 48 h, deaerated by the freeze-thaw method (3 cycles) and degassed by nitrogen bubbling for another 24 h was added the substituted arylboronic acid (6.48 mmol), iodoferrocene (1.0 g, 3.21 mmol), barium hydroxide (1.43 g, 4.50 mmol) and palladium acetate (0.16 g, 0.72 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for either 72, 336 or 772 h (see Table 4) under nitrogen at room temperature. The solvent was then removed *in vacuo*, the residue taken up in diethyl ether (100 cm³) and filtered. The ethereal solution was washed with water and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and the residue passed through a silica gel column. Hexane eluted recovered iodoferrocene and the solvent system hexane–dichloromethane (8:2) eluted the monoaryl-ferrocene (see Table 4 for yields and conversions).

**4-Formylphenylferrocene.** General procedure as above except for the quantities of reagents: iodoferrocene (3.10 g, 9.95 mmol), 4-formylbenzeneboronic acid (2.97 g, 19.85 mmol), barium hydroxide (4.40 g, 13.96 mmol), palladium acetate (0.46 g, 2.07 mmol) and reaction time 772 h. Reaction gave recovered iodoferrocene (0.31 g, 90% conversion) and 4-formylphenyl-ferrocene (1.25 g, yield wrt conversion 48%, overall 43%)—characterization as before.

**1-Ferrocenylnaphthalene.** General procedure as above except for the quantities of reagents: iodoferrocene (0.80 g, 2.56 mmol), naphthalene-1-boronic acid (0.87 g, 5.06 mmol), barium hydroxide (1.12 g, 3.55 mmol), and palladium acetate (0.12 g, 0.53 mmol). Reaction gave recovered iodoferrocene (0.104 g, 87% conversion) and 1-ferrocenylnaphthalene (0.55 g, yield wrt conversion 79%, overall 69%)—characterization as before.

**3-Fluorophenylferrocene.** General procedure as above except for the quantities of reagents: iodoferrocene (1.008 g, 3.23 mmol), 3-fluorobenzeneboronic acid (0.902 g, 6.45 mmol), barium hydroxide (1.447 g, 4.59 mmol) and palladium acetate (0.144 g, 0.641 mmol). The reaction time was 336 h. Reaction gave recovered iodoferrocene (0.422 g, 58% conversion) and 3-fluorophenylferrocene (0.509 g, yield wrt conversion 97%, overall 56%). The product was removed from a column of silica gel using hexane–dichloromethane and recrystallized from hexane–ethanol in the cold, mp 58–59 °C (lit.,[29] 62–63 °C); $v_{max}$(KBr)/cm$^{-1}$ 3106, 2932, 2854, 1613, 1582, 1508, 1463, 1408, 1386, 1289, 1266, 1193, 1161, 1104, 1068, 1027, 1000, 924, 868, 824, 780, 692, 518, 504, 488; $\delta_H$(CDCl$_3$) 7.00 (4 H, m, ArH), 4.56 (2 H, t, $J$ 1.8, C$_5$H$_4$), 4.26 (2 H, t, $J$ 1.8, C$_5$H$_4$), 3.98 (5 H, s, C$_5$H$_5$); $m/z$ 281 (19%), 280 (M$^+$, 100), 215 (3), 159 (10) (Found: M$^+$, 280.0348. C$_{16}$H$_{13}$FeF requires $M$, 280.0353).

**Biferrocenyl.** General procedure as above except for the quantities of reagents: iodoferrocene (1.062 g, 3.41 mmol), ferroceneboronic acid (1.473 g, 6.41 mmol), barium hydroxide (1.433 g, 4.54 mmol) and palladium acetate (0.144 g, 0.641 mmol). The reaction time was 336 h. Reaction gave recovered iodoferrocene (0.489 g, 54% conversion) and biferrocenyl (0.0562 g, yield wrt conversion 17%, overall 9%). The product was removed from a column of silica gel using dichloromethane–hexane (7:3) and recrystallized from dichloromethane–hexane in the cold, mp 242 °C decomp. (lit.,[18] 239–240 °C decomp.); $v_{max}$(KBr)/cm$^{-1}$ 1685 (br), 1411, 1384, 1261, 1109, 1035, 1003, 819, 487; $\delta_H$(CDCl$_3$) 4.28 (4 H, t, $J$ 1.8, C$_5$H$_4$ × 2), 4.10 (4 H, t, $J$ 1.8, C$_5$H$_4$ × 2), 3.92 (10 H, s, C$_5$H$_5$ × 2); $\delta_C$(CDCl$_3$) 69.01, 67.59, 66.36, 65.30; $m/z$ 371 (27%), 370 (M$^+$, 100), 305 (26), 304 (15), 249 (9), 186 (5), 185 (7), 121 (25) (Found: M$^+$, 370.01068. C$_{20}$H$_{18}$Fe$_2$ requires $M$, 370.01057).

**4-Methylphenylferrocene using silver carbonate as base.** General procedure as above except for the quantities of reagents: iodoferrocene (1.062 g, 3.40 mmol), 4-methylbenzeneboronic acid (0.878 g, 6.45 mmol), silver carbonate (1.317 g, 4.76 mmol) and palladium acetate (0.145 g, 0.646 mmol). The reaction time was 336 h. Reaction gave recovered iodoferrocene (0.526 g, 50% conversion) and 4-methylphenylferrocene (0.151 g, yield wrt conversion 32%, overall 16%). The product has been characterized previously.

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