ELSEVIER

Journal of Organometallic Chemistry 645 (2002) 65–81

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis of ferrocenylphenyl derivatives including biphenylferrocenes, arylferrocenylphenyl ethers and arylferrocenylphenyl amines

Christopher Imrie [a,*], Pieter Engelbrecht [a], Christa Loubser, Cedric W. McCleland [a], Vincent O. Nyamori [a], Robert Bogardi [b], Demetrius C. Levendis [b], Nomfuneko Tolom [a], Jason van Rooyen [a], Nadia Williams [a]

[a] *Department of Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth 6000, South Africa*
[b] *Department of Chemistry, Centre for Molecular Design, University of the Witwatersrand, Johannesburg, South Africa*

Received 18 June 2001; received in revised form 27 September 2001; accepted 8 October 2001

Abstract

The preparation of a series of substituted biphenylferrocenes via a modified Suzuki reaction between 4-bromophenylferrocene and substituted phenylboronic acids is described. The X-ray crystal structure of 4′-formyl-4-biphenylferrocene is reported and this compound is then incorporated into the first series of ferrocenomesogens containing the ferrocenylbiphenyl unit. The synthesis of a series of arylferrocenylphenyl ethers and arylferrocenylphenyl amines is also described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Biphenylferrocenes; Arylferrocenylphenyl ethers; Arylferrocenylphenyl amines

1. Introduction

Following the publication in 1993 by Loubser et al. [1] of the first X-ray crystal structure of a monosubstituted ferrocenomesogen (ferrocenyl-containing liquid crystal), in which it was shown that a bulky terminal ferrocenyl group could be readily incorporated into the supramolecular architecture, there has been a significant interest in these compounds amongst chemists [2]. A question that has been at the forefront of our research methodology from the start is: what are the structural limits within which the liquid-crystalline state can be generated and retained in these molecules? In 1997, we reported on the liquid crystal properties of a series of compounds represented by the general structure shown in Fig. 1[3].

The compounds in this series were readily synthesized by reacting a 4-substituted phenylferrocene (in these examples 4-ferrocenylbenzoic acid, $j = 1$) with a functionalized phenyl or biphenyl compound. It was established that a minimum of three aromatic rings in the substituent core, *Z*, are necessary for stabilizing a nematic liquid crystal phase, and that four rings substantially enhance the nematic behavior. It was also established that it is advantageous to insert at least one phenyl ring between the ferrocenyl group and the linker (the group which connects the rigid conjugated sections of liquid crystals). With a view to extending the range of monosubstituted ferrocenomesogens, it was decided

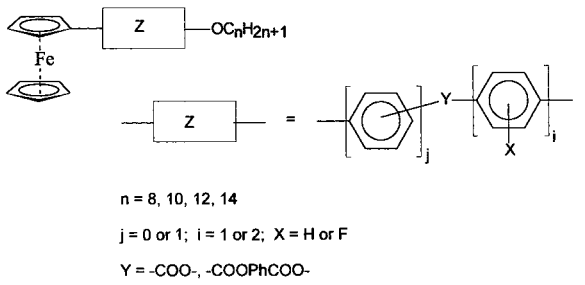
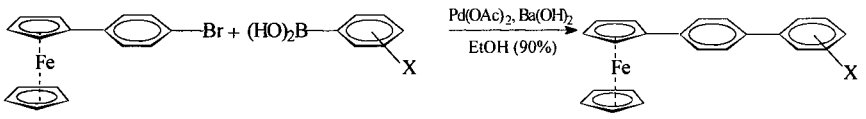


Fig. 1. General structure representing the compounds prepared by Loubser and Imrie.

* Corresponding author. Fax: +27-41-504-2573.
E-mail address: chacci@upe.ac.za (C. Imrie).

PII: S0022-328X(01)01410-3

Table 1
Yields of biphenylferrocenes from the reaction of 4-bromophenylferrocene with substituted phenylboronic acids



Entry	X	4-Bromophenylferrocene (mmol)	Time (days)	Yield (%) [a]
1	4-OCH_3 [b]	1.5	14	93
2	4-CH_3 [b]	1.5	14	88
3	4-OC_8H_{17} [b]	1.5	14	65
4	4-Ph [b]	1.5	14	79
5	4-CHO [c]	3.0	21	50
6	4-CHO [b]	3.0	32	13
7	4-CHO [b]	3.0	1	10
8	4-F [b]	3.0	14	89
9	4-$COCH_3$ [c]	3.0	14	14
10	4-CH_2Ph [c]	1.5	14	70
11	3-NO_2 [b]	1.5	14	38

[a] Yields are based on 4-bromophenylferrocene.

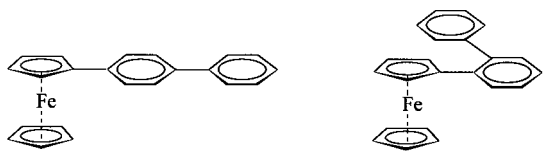
[b] Typical procedure: to 90% ethanol, which was degassed by purging with nitrogen for 48 h, deaerated by the freeze-thaw method (3 cycles) and finally purged with nitrogen for another 24 h was added the subsitituted phenylboronic acid (two equivalents), 4-bromophenylferrocene (one equivalent), barium hydroxide (1.4 equivalents) and palladium(II) acetate (0.3 equivalents) under nitrogen. The reaction mixture was then vigorously shaken for 30 min prior to stirring under nitrogen.

[c] The same procedure as described for (b) with the exception that the reaction mixture was intermittently heated under reflux (7×7 h).

to synthesize molecules where $j = 2$ (Fig. 1) and for this, it was necessary to synthesize 4-substituted biphenylferrocenes. It was also decided to introduce new linking units into the general structure, namely the ether (Y=O) and the amine linkage (Y=NH). For this, a synthesis of arylferrocenylphenyl ethers and arylferrocenylphenyl amines was required.

There are few references to ferrocenylbiphenyl compounds in the literature. The crystal structures of 4-biphenylylferrocene **1** [4] and 2-biphenylylferrocene **2** [5] have been determined. The two compounds are also mentioned in the context of several other papers in the early literature of ferrocene chemistry concerned with the arylation of ferrocene via the reaction of ferrocene with diazonium ions [6].

We have recently reported the use of a modified Suzuki cross-coupling procedure for the synthesis of 4-substituted phenylferrocenes [7]. Iodoferrocene was reacted with a series of 4-substituted phenylboronic acids in the presence of a base and catalyst to provide a range of 4-substituted phenylferrocenes. One of the products from the initial work was 4-bromophenylferrocene **3**. This article discusses the use of **3** in the efficient synthesis of 4-substituted biphenylferrocenes by a modified Suzuki cross-coupling reaction. It also discusses the first synthesis of arylferrocenylphenyl ethers and arylferrocenylphenyl amines by the reaction of phenylboronic acids with 4-ferrocenylphenol and 4-ferrocenylaniline, respectively.



1 **2**

2. Results and discussion

2.1. Synthesis of substituted biphenylferrocenes

The optimum reaction conditions that were determined in earlier work by us for modified Suzuki cross-coupling reactions of iodoferrocene with arylboronic acids were employed for the reactions of 4-bromophenylferrocene and phenylboronic acids. The reactions were performed using palladium(II) acetate as catalyst, barium hydroxide as base and 90% EtOH as solvent. The reactions were carried out at either room temperature (in the cases where the phenylboronic acid contained an electron-donating group) or under reflux (in the cases where the phenylboronic acid contained an electron-withdrawing group). Thorough degassing of the solvent is crucial and was carried out by nitrogen purging and the freeze-thaw technique. The isolated yields of the products ranged from good-to-excellent in most cases (Table 1). A summary of the reactions is

shown in Fig. 2. In comparison to the reactions using iodoferrocene, it was found that the current reactions gave significantly higher overall yields and were generally more efficient. The starting material was recovered in only trace quantities in most of the reactions as compared to reactions with iodoferrocene in which considerable amounts of starting material was recovered. Of particular interest for the synthesis of liquid crystals were 4-substituted biphenylferrocenes in which the substituent could be further derivatized. For example, 4′-formyl-4-biphenylferrocene **4** was prepared in one step. In the initial attempts to synthesize **4** (entries 6 and 7, in Table 1), the reactions were performed at room temperature and the overall yields of product were very low. For entry 5, the reaction was heated intermittently and this resulted in a significant improvement in the yield of **4**. 4′-Hydroxy-4-biphenylferrocene **5** was synthesized in either a one or two step reaction from 4-bromophenylferrocene (Fig. 2). Reduction of 4′-formyl-4-biphenylferrocene using lithium aluminium hydride provided 4′-hydroxymethyl-4-biphenylferrocene in excellent yield. Another useful functional group that was introduced to the ferrocenylbiphenyl group was the NH_2 group. Commercially available 3-nitrobenzeneboronic acid was coupled with 4-bromophenylferrocene and the resulting 3′-nitro-4-biphenylferrocene **6** was reduced by catalytic hydrogenation using a palladium on charcoal catalyst.

2.2. Synthesis of arylferrocenylphenyl ethers

The next stage of our study involved the synthesis of arylferrocenylphenyl ethers and arylferrocenylphenyl amines since we wanted to investigate the effect of the ether and amine linkage on the thermal properties of elongated ferrocene molecules. Reports have recently appeared on the synthesis of diaryl ethers by the copper acetate promoted coupling of arylboronic acids and phenols [8]. Evans et al. reported good yields of diaryl ethers by this reaction and it was found to be tolerant of a wide range of substituents on both coupling partners [8b]. Chan et al. extended the reaction to the arylation of N–H containing compounds providing a useful route to diarylamines [8c]. Simon et al. have recently reported on the regioselective conversion of arylboronic acids to phenols and subsequent coupling to symmetrical diaryl ethers [8d].

In our first series of reactions, 4-ferrocenylphenol was reacted with a range of substituted phenylboronic acids in the presence of triethylamine, crushed 4 Å molecular sieves and copper(II) acetate catalyst. The copper(II) acetate initially used was a hydrated form which had been dried in a vacuum oven at ca. 200 °C for 48 h prior to use. The isolated yields of the ethers varied according to the nature of the substituent on the phenylboronic acid (Table 2). Yields were generally lower when the substituents were electron-withdrawing.

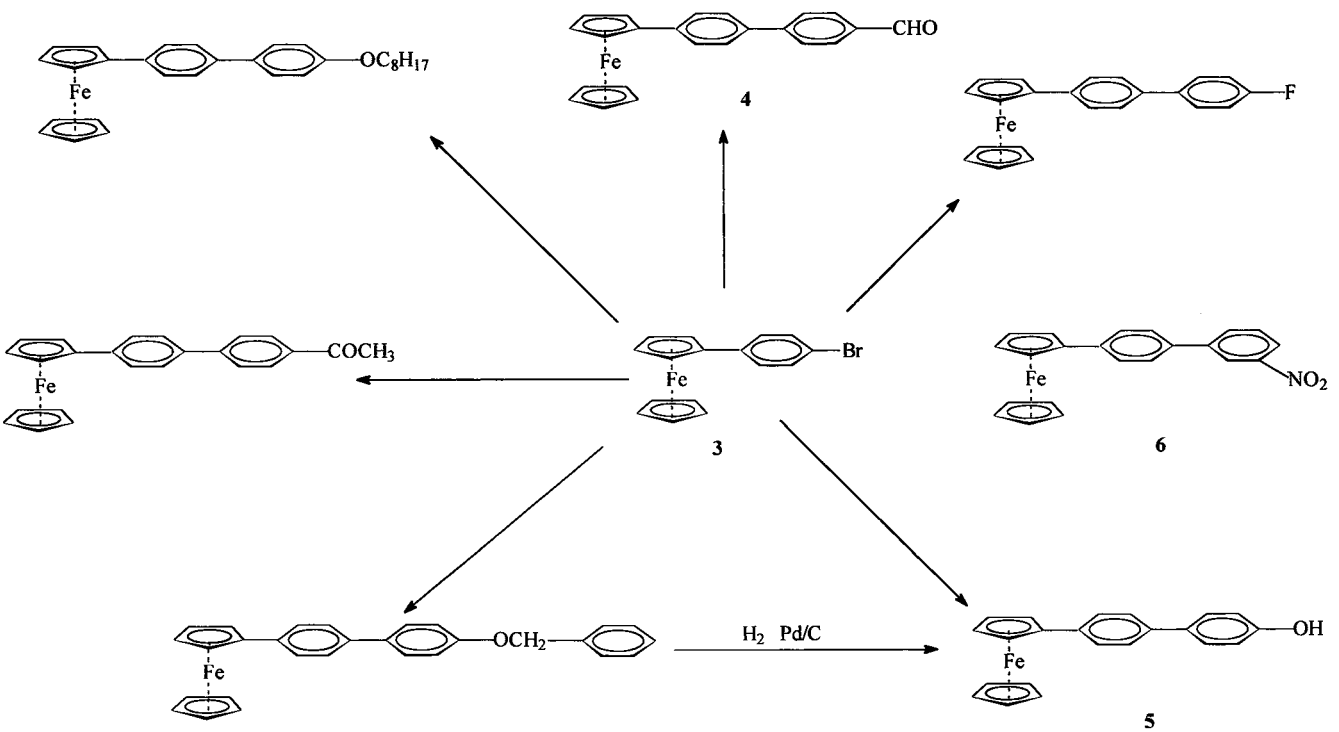
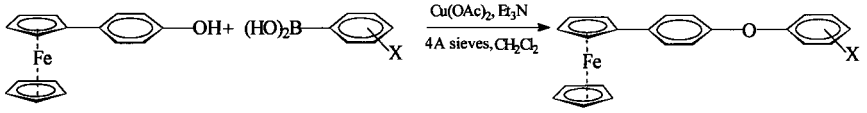


Fig. 2. Bophenylferrocene derivatives synthesized by the modified Suzuki method.

Table 2
Yield of arylferrocenylphenyl ethers from the reaction of 4-ferrocenylphenol and substituted phenylboronic acids



Entry	Substituent X	Yield (%) [a]
1	4-CH_3 [b,d]	49
2	4-CH_3 [c]	70
3	4-OCH_3 [b,d]	41
4	4-OCH_3 [c]	56
5	3,4,5-$(OCH_3)_3$ [b,d]	42
6	4-OCH_2Ph [b,d]	44
7	4-H [b,d]	51
8	4-H [c]	93
9	4-OC_8H_{17} [b,d]	21
10	4-F [b,d]	34
11	4-F [c]	67
12	3-F [b,d]	27
13	4-Br [b,d]	19
14	4-$COCH_3$ [b,d]	32
15	4-CHO [b,d]	26
16	4-CHO [b,e]	34
17	4-CHO [c]	64
18	4-OCF_3 [b,d]	28
19	4-CF_3 [b,d]	2
20	3-NO_2 [b,e]	10

[a] Yields are based on 4-ferrocenylphenol.
[b] Typical procedure: 4-ferrocenylphenol (one equivalent), anhydrous copper(II) acetate (one equivalent), the substituted phenylboronic acid (1.2 equivalents), powdered 4 Å molecular sieves, and distilled triethylamine (five equivalents) were added to anhydrous dichloromethane. The reaction mixture was allowed to stir at room temperature for 168 h.
[c] The procedure was as in b except that 98% copper(II) acetate was used (Aldrich Chemical Company).
[d] Reactions were carried out using 200 mg 4-ferrocenylphenol.
[e] Reactions were carried out using ca. 1 g 4-ferrocenylphenol.

The compounds of particular interest to us were those with the potential for further functionalization at the terminal position. 4-(4-Formylphenoxy)phenylferrocene was prepared in a 26% isolated yield in the small scale reaction. A 34% yield was obtained in a five fold larger scale reaction.

In the second series of reactions, a different grade of copper(II) acetate catalyst was used. It was a 98% commercially available grade (Aldrich Chemical Company) and this catalyst led to a significant improvement in the overall yields of the ether products (see entries 2, 8, 11 and 17 in Table 2).

Since by-products were generally observed, one reaction, namely that between 4-ferrocenylphenol and 4-methylbenzeneboronic acid was subjected to closer scrutiny. The reaction mixture was analyzed by GC–MS after filtration through a silica gel column to remove any inorganic components. The major components were shown to be 4-(4-methylphenoxy)phenylferrocene and unreacted 4-ferrocenylphenol. Minor components included *p*-cresol, 4,4′-dimethylbiphenyl ether, 4,4′-dimethylbiphenyl and 4-acetoxytoluene.

2.3. Synthesis of arylferrocenylphenyl amines

Replacement of 4-ferrocenylphenol by 4-ferrocenylaniline in the etherification reactions provided low yields of arylferrocenylphenyl amines (Table 3). There was evidence in these reactions for significant decomposition of the ferrocenyl compounds which probably accounts for the low overall yields and poor material balances. Ferrocenes have previously been observed to decompose in the presence of amines and other electron-donor molecules especially under oxidative conditions where ferrocenium ions can be generated [9]. Attempts to synthesize the 4-formyl substituted derivative failed presumably due to the reactivity of the formyl substituent to further attack by amine.

2.4. Crystal structure of 4′-formyl-4-biphenylferrocene

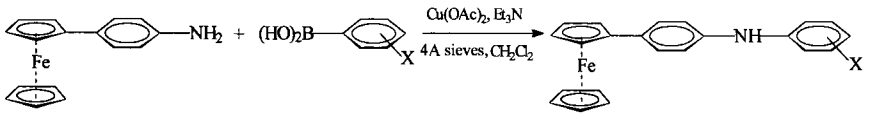
Crystals of 4′-formyl-4-biphenylferrocene **4** suitable for X-ray crystallography were obtained from dichloromethane–hexane. The molecular structure of **4** together with numbering scheme is shown in Fig. 3. The unit cell

is orthorhombic and the molecular geometry is extended and linear. The two cyclopentadienyl rings in the ferrocenyl group are slightly staggered. Looking at the cyclopentadienyl ring with the attached phenyl chain from above, the unsubstituted cyclopentadienyl ring is rotated clockwise by 13.5° with respect to the substituted ring. This means that the conformation is almost midway between the fully eclipsed (angle of rotation 0°) and fully staggered (angle of rotation 36°). With the long chain directed towards the viewer, the first phenyl plane is rotated anticlockwise by 10.8° with respect to the cyclopentadienyl plane. The second phenyl plane is rotated anticlockwise by 27.8° with respect to the first phenyl plane. Also, the chain is not quite linear. The angle extending from the centroid of the cyclopentadienyl ring to the centroids of the first and second phenyl rings is 176.6°. The mean bond distances are normal for this type of molecule, Fe–C = 2.03 Å, C–C (five-membered rings) = 1.40 Å, C–C (six-membered rings) = 1.39 Å, C–C (between rings) = 1.48 Å. The molecular packing of **4** emphasizes the arrangement between molecules within a layer and between layers. The molecules are arranged parallel to each other in an extended fashion in a head-to-tail/tail-to-head format. The only significantly short intermolecular bond distance is between H(2) and O(1) and is 2.6054 Å. All other intermolecular bond distances are well beyond the range for hydrogen bonding (Table 4). H(2) is in close contact with the ferrocenyl group and the results suggest that there may be a considerable electrostatic interaction between the ferrocenyl group and the aldehydic oxygen atom of another molecule. A similar interaction has been reported by Sato et al. for ferrocenecarboxaldehyde in an investigation of the plastic crystal phase of that molecule by X-ray diffraction [10]. This type of interaction has also been reported by Ferguson et al. [11] in α-hydroxyferrocene derivatives.

2.5. Thermal properties of elongated biphenylferrocenes

A series of imines based on structures **7** and **8** were synthesized. The compounds of series **7** were synthesized

Table 3
Yield of arylferrocenylphenyl amines from the reaction of 4-ferrocenylaniline and substituted phenylboronic acids



Entry	Substituent X	Yield (%) [a]
1	4-CH_3 [b]	14
2	4-CH_3 [c]	21
3	4-OCH_3 [b]	3
4	4-Br [b]	28

[a] Yields are based on 4-ferrocenylaniline.

[b] Typical procedure: 4-ferrocenylaniline (one equivalent), anhydrous copper(II) acetate (one equivalent), the substituted phenylboronic acid (1.2 equivalents), powdered 4 Å molecular sieves (300 mg) and distilled triethylamine (five equivalents) was added to anhydrous dichloromethane. The reaction was allowed to stir at room temperature for 168 h.

[c] Duplicate experiment.

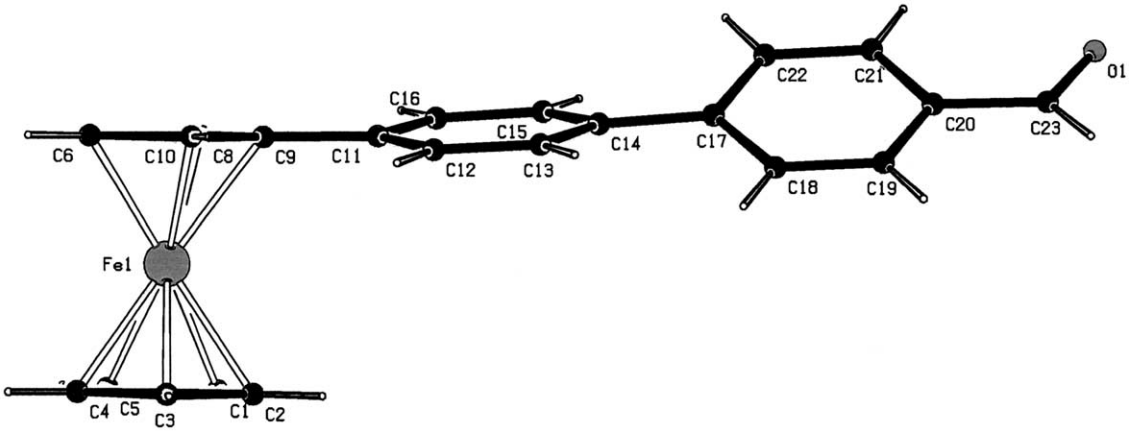


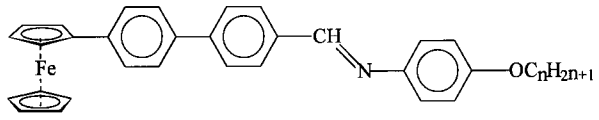
Fig. 3. Molecular structure of 4′-formyl-4-biphenylferrocene with numbering scheme.

Table 4
Selected bond lengths (Å) and selected bond angles (°) for compound **4**

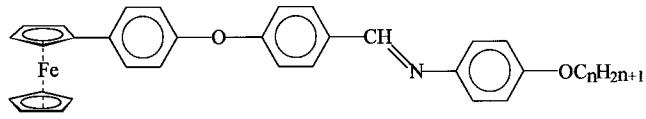
Bond lengths			
C(2)–C(3)	1.394(6)	C(3)–C(4)	1.381(6)
C(4)–C(5)	1.410(7)	C(6)–C(7)	1.388(6)
C(6)–C(10)	1.398(5)	C(7)–C(8)	1.415(5)
C(8)–C(9)	1.418(5)	C(9)–C(10)	1.431(4)
C(9)–C(11)	1.475(4)	C(11)–C(16)	1.389(4)
C(11)–C(12)	1.392(4)	C(12)–C(13)	1.376(4)
C(13)–C(14)	1.399(4)	C(14)–C(17)	1.483(4)
C(17)–C(18)	1.391(4)	C(18)–C(19)	1.388(5)
C(20)–C(21)	1.389(4)	C(21)–C(22)	1.371(4)
C(1)–C(2)	1.388(8)	C(1)–C(5)	1.418(7)
C(14)–C(15)	1.393(4)	C(15)–C(16)	1.379(4)
C(17)–C(22)	1.406(4)	C(19)–C(20)	1.386(4)
C(20)–C(23)	1.469(5)	O(1)–C(23)	1.214(5)
Bond angles			
C(8)–C(9)–C(11)	125.9(3)	C(10)–C(9)–C(11)	128.2(3)
C(16)–C(11)–C(12)	116.6(3)	C(16)–C(11)–C(9)	120.8(3)
C(12)–C(11)–C(9)	122.6(3)	C(13)–C(12)–C(11)	122.0(3)
C(12)–C(13)–C(14)	121.4(3)	C(15)–C(14)–C(13)	116.6(3)

by the reaction of 4′-formyl-4-biphenylferrocene **4** with a series of *n*-alkoxyanilines. Series **8** were similarly prepared starting from 4-(4-formylphenoxy)phenylferrocene.

For series **7**, the compounds where $n = 8$ and 14 exhibit enantiotropic smectic and nematic phases, whereas the compound where $n = 5$ exhibits a monotropic nematic phase (Table 5). The liquid crystal domains in all cases are relatively short and the usual effect of chain lengthening in relation to the lowering of clearing temperatures is observed. A DSC curve is shown in Fig. 4 for the compound where $n = 14$ and the enthalpies of transition for the compounds are provided in Table 6. A graphical representation of the phase distribution for series **7** is shown in Fig. 5. Compounds in series **8** ($n = 5$ and 14) were non-liquid crystalline (melting points provided in Section 4).



7

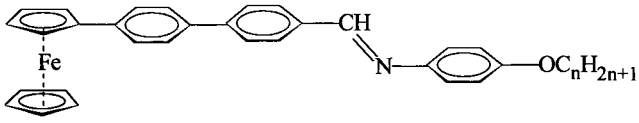


8

2.6. Structure-liquid crystal properties of elongated ferrocenes

A compound requires two important criteria in order to exhibit calamitic mesomorphism. Firstly, it should have a long linear shape and secondly a large enough length–depth (l/d) ratio so that significant intermolecular interactions can be generated. A conformational search on a general structure of series **7** and **8** ($n = 1$)

Table 5
Phase transition temperatures and melting points of new ferrocenomesogens



n	Phase transitions/°C
5	K 215°C I; 148°C N; 208°C
8	K 177°C S_X 183°C N 201°C I; 147°C; 199°C
14	K 146°C S_X 164°C N 182°C I; 137°C; 149°C; 180°C

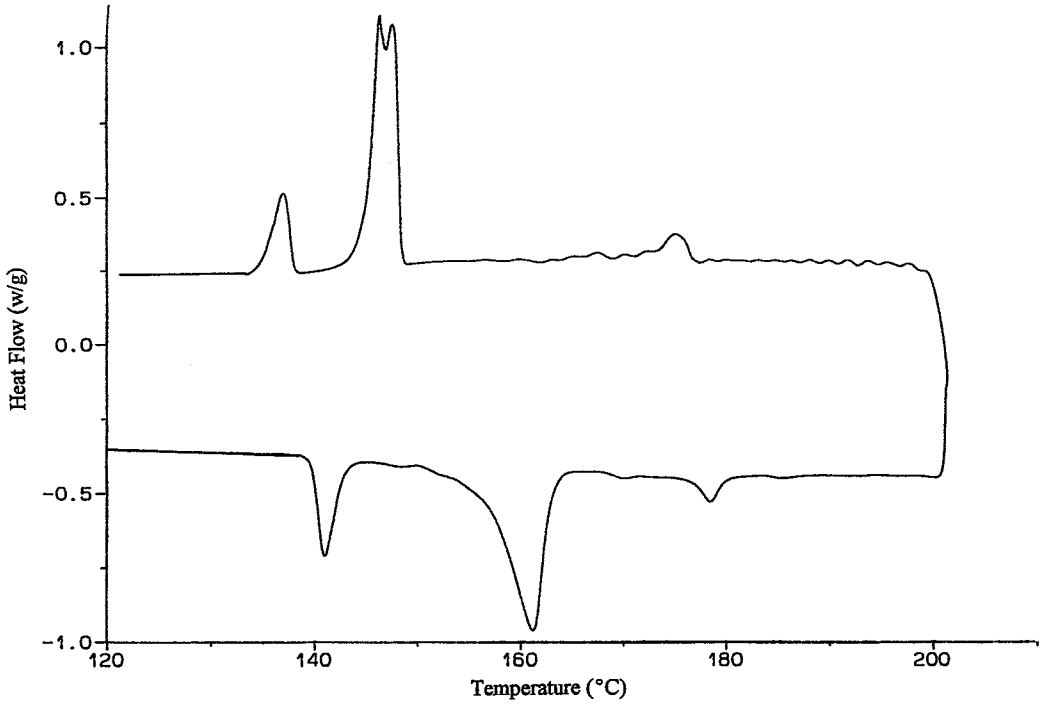


Fig. 4. Dsc curve for a compound of series **7**.

was performed and compared with results for other elongated ferrocenyl molecules prepared by us previously [12] (series **9**, **10**, **11** and **12**) (Fig. 6). In order to minimize computational times, the *n*-alkoxy chains were kept short (we used methoxy- or methoxycarbonyloxy). Calculation of the *l*/*d* ratios however, was carried out for molecules containing an *n*-octyloxy chain since these derivatives are liquid crystalline in series, **7**, **9** and **10** but not in series **11** and **12**. The assumption was made that the *n*-octyloxy chains would adopt relatively linear conformations. The MM^+ calculations were based on the atomic charges in each molecule, as calculated earlier from a ZINDO-1 single-point calculation on the initial structures. The lowest energy geometries of these conformers which resulted were then further optimized at the ZINDO-1 semi-empirical MO level. It is clear from the results in Table 7 that monosubstituted ferrocenomesogens have a much larger *l*/*d* ratio than non-liquid-crystalline elongated ferrocenes.

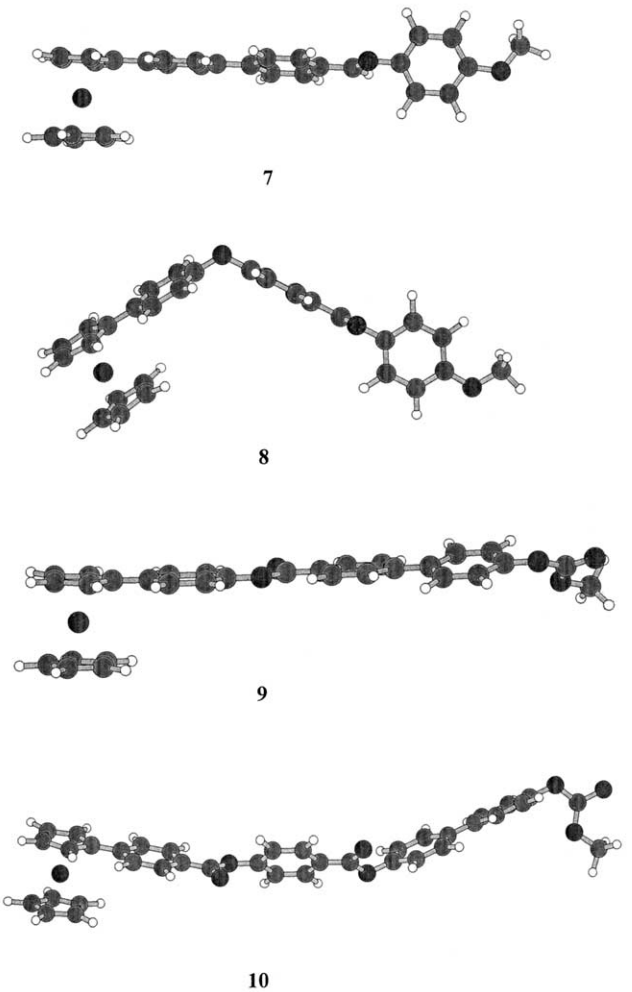


Table 6
The enthalpies of transition (ΔH[J g^{-1}]) for the compounds of series **7**

n	K→S_x	K→I	S_x→N	N→I	I→N	N→S_x	N→K	S_x→K
5		36.7			1.5		22.9	
8	31.5		31.5	1.2	1.3	22.6		NS
14	4.6		15.9	0.97	1.3	18.5		5.0

Abbreviations: K, crystalline; S_x, unidentified smectic phase; N, nematic phase; I, isotropic liquid; NS, observed by optical microscopy only.

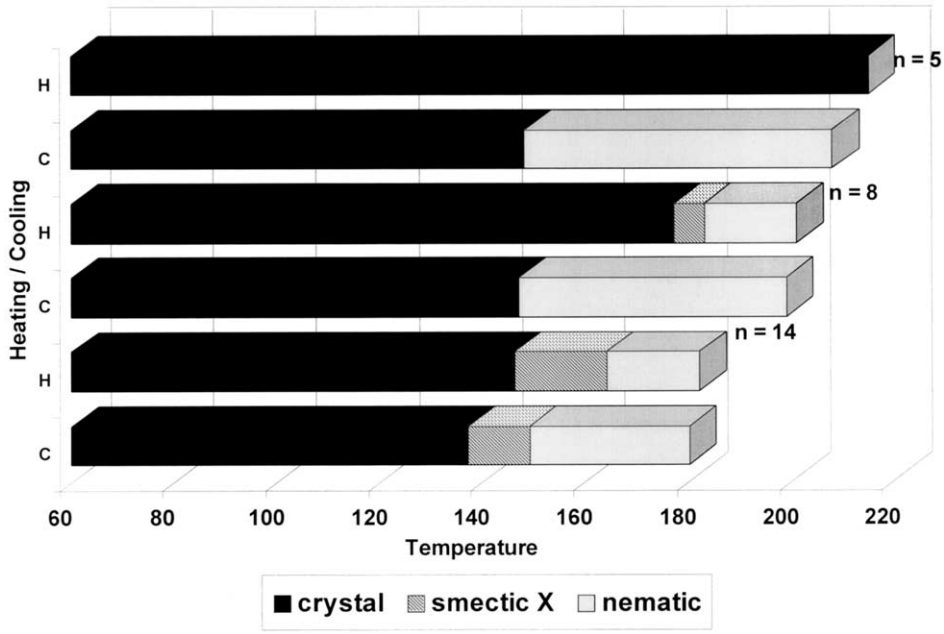


Fig. 5. Phase distribution of compounds in series **7**.

Deschenaux and co-workers reported that 1,3-disubstituted ferrocenomesogens [13] have an l/d ratio greater than 5. The lowest energy conformations of the non-mesogenic **8**, **11** and **12** show pronounced kinks in the molecular structures that result in lower l/d ratios.

3. Conclusion

The synthesis of a series of substituted biphenylferrocenes using a modified Suzuki cross-coupling reaction has been achieved. The biphenylferrocenes were obtained in high yield. The X-ray crystal structure of 4′-formyl-4-biphenylferrocene was obtained and it provided evidence of intermolecular hydrogen bonding between molecules. This molecule was further extended by reaction with *n*-alkoxyanilines to provide the first series of ferrocenomesogens with a terminal biphenylferrocene group. The first synthesis of arylferrocenylphenyl ethers was achieved by the reaction of 4-ferrocenylphenol with substituted phenylboronic acids. The initial yields of these molecules using an oven dried copper(II) acetate catalyst were low but were significantly improved by using 98% copper(II) acetate (Aldrich Chemical Company). The synthesis of arylferrocenylphenyl amines was similarly achieved by the reaction of 4-ferrocenylaniline and substituted phenylboronic acids.

4. Experimental

4.1. Purification and characterization of the materials

All reactions were performed under an atmosphere of dry nitrogen. Silica gel 50 or Al_2O_3 (active, neutral, Brockmann Grade I) were used for column chromatography. Thin layer preparative chromatography was carried out on plates using Merck silica gel 60 F_{254} (1.5 mm) as adsorbent. M.p. were recorded on an Electrothermal IA 900 series digital m.p. apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600 series Fourier Transform IR spec-

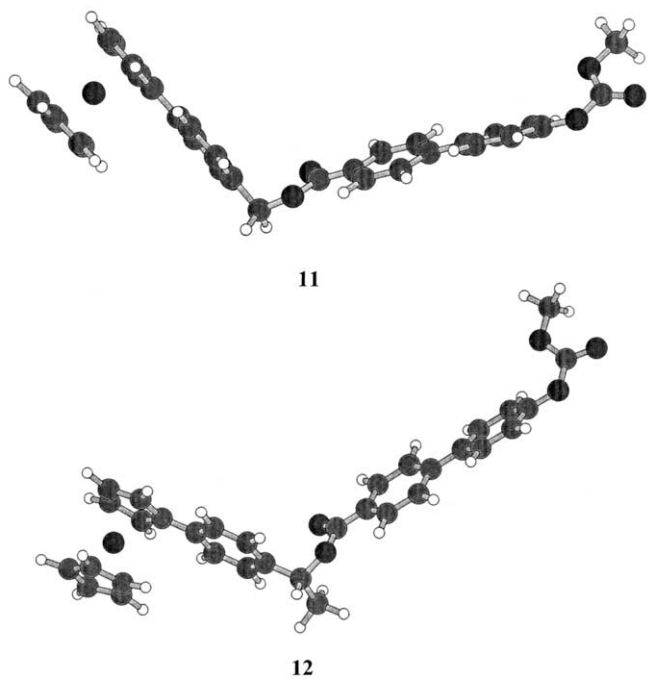


Fig. 6. The optimized geometries of elongated monosubstituted ferrocenyl derivatives.

Table 7
Approximate length–depth ratios of elongated ferrocenyl derivatives

Compound	l/d (Å) [a]
7	8
9	6
10	6
11	2
12	2

[a] l/d ratios calculated for the OC_8H_{17} derivative of each series.

trometer as KBr discs or as solutions in chloroform. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solution in $CDCl_3$ or Me_2SO using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a VG70-SEQ/MSSMS2 spectrometer at the Cape Technikon. Microanalyses were performed on a Carlo-Erba MOD 1160 elemental analyzer by the Council for Scientific and Industrial Research, Pretoria and at the University of Cape Town. Crystal X-ray crystallography was performed on a Bruker/AXS SMART-CCD diffractometer at the Department of Chemistry, University of the Witwatersrand, Johannesburg. Transition temperatures of the liquid crystal molecules were investigated by differential scanning calorimetry (DSC) utilizing a Du Pont 910 DSC cell, connected to a Du Pont 9000 Thermal Analyser. Compounds were studied at various scanning rates (2.5, 5 or 10 °C min^{-1}) for both the heating and cooling cycles, after being encapsulated in aluminium pans. An empty aluminium pan served as the reference. The calorimeter was calibrated with an indium standard. The textures of the mesophases were studied with a standard Zeiss polarizing microscope equipped with a Reichert hot stage at UPE and with a Nikon Eclipse E600 optical polarizing microscope equipped with a Linkam heating–freezing stage linked to a Linkam range TMS 93 precision temperature control at Rhodes University, Grahamstown. Reaction mixtures were shaken on a Griffin flask shaker (896331/2). The GC–MS work was carried out using a HP5972 Series mass selective detector coupled with a HP Series 25890 spectrometer. The column used was a Chrompack HP1 (30 m × 0.32 × 0.25 μm). The majority of the phenylboronic acids and palladium(II) acetate (99%) were purchased from Lancaster Synthesis (UK) and were used without further purification The copper(II) acetate catalyst used in the etherification reactions was either hydrated copper(II) acetate dried in a vacuum oven at 200 °C for 48 h or copper(II) acetate (98%) purchased from the Aldrich Chemical Company (USA). Unless otherwise stated all recrystallizations were performed at room temperature (r.t.). If more than one solvent was used to perform the recrystallization, two different annotations are used, e.g. CH_2Cl_2/EtOH denotes that a mixture of two solvents was used, whereas CH_2Cl_2–EtOH denotes that CH_2Cl_2 was used to dissolve the solid and the slow addition of EtOH resulted in crystallization. All solvents that required distillation, were distilled directly into the reaction flask to be used, under nitrogen.

4.2. Preparation of substituted biphenylferrocenes

4.2.1. 4′-Methoxy-4-biphenylferrocene

To 90% EtOH (150 cm^3), which was purged with nitrogen for 24 h, deaerated by the freeze-thaw method (3 cycles) and purged further with nitrogen for another 24 h, was added 4-methoxybenzeneboronic acid (445 mg, 2.9 mmol), 4-bromophenylferrocene (500 mg, 1.5 mmol), $Ba(OH)_2$ (650 mg, 2.1 mmol) and palladium(II) acetate (110 mg, 0.49 mmol) under nitrogen. The reaction mixture was vigorously shaken for 30 min and then allowed to stir for 2 weeks under nitrogen at r.t. Thereupon, the solvent was removed in vacuo, the residue taken up in CH_2Cl_2 and filtered. The organic extracts were then washed with water prior to drying over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was chromatographed through a flash silica gel column. Elution with C_6H_{14} afforded unreacted 4-bromophenylferrocene (36 mg, 93% conversion) which was characterized as described earlier. Elution with C_6H_{14}–CH_2Cl_2 (1:1) stripped the column, and this residue was subjected to plate chromatography on silica gel. Elution with C_6H_{14}–CH_2Cl_2 (7:3) afforded 4′-methoxy-4-biphenylferrocene (504 mg, 93%) as orange crystals (from CH_2Cl_2–C_6H_{14} in the cold), m.p. 190–192 °C; IR (KBr cm^{-1}) 1605, 1578, 1454, 1440, 1404, 1306, 1289, 1252, 1179, 1104, 1033, 998, 886, 827, 713; ^{1}H-NMR ($CDCl_3$) 7.56 (2H, d, *J* 8.8, ArH), 7.51 (2H, s, ArH), 7.48 (2H, d, *J* 8.8, ArH), 6.98 (2H, d, *J* 8.8, ArH), 4.67 (2H, t, *J* 1.8, C_5H_4), 4.33 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5), 3.86 (3H, s, OCH_3); ^{13}C-NMR ($CDCl_3$) 159.00, 138.24, 137.70, 133.51, 127.78, 126.55, 126.47, 114.22, 85.16, 69.61, 68.92, 66.45, 55.35; *m*/*z* 369 (27%), 368 [M$^+$, 100], 366 (7), 353 (10), 326 (5), 325 (21), 204 (6), 202 (5), 184 (9), 120 (9). Anal. Calc. for $C_{23}H_{20}FeO$: C, 75.0; H, 5.5; [M], 368.08635. Found: C, 74.8, H, 5.7%, [M$^+$], 368.08580.

4.2.2. 4′-Methyl-4-biphenylferrocene

Quantities: 4-methylbenzeneboronic acid (399 mg, 2.9 mmol), 4-bromophenylferrocene (500 mg, 1.5 mmol), $Ba(OH)_2$ (650 mg, 2.1 mmol) and palladium(II) acetate (110 mg, 0.49 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene. 4′-Methyl-4-biphenylferrocene (457 mg, 88%) was obtained as orange crystals (from CH_2Cl_2–C_6H_{14} in the cold), m.p. 184–185 °C; IR (KBr cm^{-1}) 1509, 1452, 1402, 1104, 1087, 1032, 1001, 886, 813, 735; ^{1}H-NMR ($CDCl_3$) 7.52 (6H, m, ArH), 7.26 (2H, d, *J* 7.9, ArH), 4.67 (2H, t, *J* 1.8, C_5H_4), 4.33 (2H, t, *J* 1.8,

C_5H_4), 4.07 (5H, s, C_5H_5), 2.40 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$) 138.54, 138.04, 136.79, 129.49, 126.78, 126.60, 126.45, 85.13, 69.62, 68.95, 66.48, 21.11; *m*/*z* 353 (27%), 352 [M^+, 100], 351 (5), 350 (8), 231 (7), 215 (5), 176 (6), 121 (7). Anal. Calc. for $C_{23}H_{20}Fe$: C, 78.4; H, 5.7; [M], 352.09144. Found: C, 77.9; H, 6.0%; [M^+], 352.09292.

4.2.3. 4′-Octyloxy-4-biphenylferrocene

Quantities: 4-octyloxybenzeneboronic acid (734 mg, 2.9 mmol), 4-bromophenylferrocene (500 mg, 1.5 mmol), $Ba(OH)_2$ (647 mg, 2.01 mmol) and palladium(II) acetate (110 mg, 0.49 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene. 4-Bromophenylferrocene (93 mg, 81% conversion) was obtained which was characterized as described earlier and 4′-octyloxy-4-biphenylferrocene (446 mg, 65%) as orange crystals (from CH_2Cl_2–C_6H_{14} in the cold), m.p. 136 °C; IR (KBr cm^{-1}) 2954–2864 (br.), 1912, 1886, 1606, 1578, 1501, 1474, 1393, 1250, 1178, 1104, 1033, 995, 824, 721; ^{1}H-NMR ($CDCl_3$) 7.57–7.45 (6H, m, ArH), 6.92 (2H, t, *J* 8.4, ArH), 4.63 (2H, t, *J* 1.8, C_5H_4), 4.28 (2H, t, *J* 1.8, C_5H_4), 4.03 (5H, s, C_5H_5), 3.95 (3H, t, *J* 6.6, OCH_2), 1.77 (2H, m, CH_2), 1.44–1.29 (10H, m, 5 × CH_2), 0.89 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$) 158.61, 138.34, 137.61, 133.27, 127.74, 127.66, 126.52, 126.47, 114.81, 114.75, 85.26, 69.64, 68.93, 68.12, 66.47, 31.84, 29.39, 29.33, 29.27, 26.09, 22.68, 14.12; *m*/*z* 467 (35%), 466 [M^+, 100], 464 (7), 411 (8), 354 (9), 353 (7), 323 (8), 186 (12). Anal. Calc. for $C_{30}H_{34}FeO$: C, 77.3; H, 7.3; [M] 466.19591. Found: C, 77.8; H, 8.0%; [M^+], 466.19685.

4.2.4. 4-Biphenylferrocene

Quantities: benzeneboronic acid (357 mg, 2.9 mmol), 4-bromophenylferrocene (500 mg, 1.5 mmol), $Ba(OH)_2$ (647 mg, 2.1 mmol) and palladium(II) acetate (110 mg, 0.49 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene. 4-Bromophenylferrocene (98 mg, 80% conversion) was obtained and 4-biphenylferrocene (391 mg, 79%) as orange crystals (from C_6H_{14}), m.p. 160 °C ([4] 164–165 °C); IR (KBr cm^{-1}) 3097, 3028, 2962, 1714, 1597, 1535, 1492, 1451, 1409, 1262, 1206, 1103, 1085, 1029, 1001, 885, 841, 807; ^{1}H-NMR ($CDCl_3$) 7.64 (2H, m, ArH), 7.55 (3H, s, ArH), 7.42 (4H, m, ArH), 4.69 (2H, t, *J* 1.9, C_5H_4), 4.35 (2H, t, *J* 1.9, C_5H_4), 4.08 (5H, s, C_5H_5); *m*/*z* 339 (26%), 338 [M^+, 100], 336 (8), 306 (12), 305 (10), 273 (22), 215 (18).

4.2.5. 4′-Formyl-4-biphenylferrocene

4.2.5.1. Reaction 1. Quantities: 4-formylbenzeneboronic acid (0.88 g, 5.9 mmol), 4-bromophenylferrocene (1.00 g, 2.9 mmol), $Ba(OH)_2$ (1.30 g, 4.1 mmol) and palladium(II) acetate (0.22 g, 0.98 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene with the exception that the reaction mixture was heated under reflux for 7 × 7 h during the reaction time of 504 h, and that the product was eluted with CH_2Cl_2–C_6H_{14} (3:2). 4-Bromophenylferrocene (175 mg, 83% conversion) was obtained and 4′-formyl-4-biphenylferrocene (537 mg, 50%) as red crystals (from CH_2Cl_2–C_6H_{14} in the cold), m.p. 194–195 °C; IR (KBr cm^{-1}) 1696, 1599, 1531, 1403, 1384, 1306, 1280, 1217, 1189, 1167, 1104, 1085, 1030, 1002, 887, 815, 739; ^{1}H-NMR ($CDCl_3$) 10.06 (1H, s, CHO), 7.96 (2H, d, *J* 8.2, ArH), 7.79 (2H, d, *J* 8.2, ArH), 7.58 (4H, s, ArH), 4.71 (2H, t, *J* 1.8, C_5H_4), 4.37 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 191.90, 146.91, 140.15, 136.88, 135.00, 130.34, 127.27, 127.19, 126.61, 84.40, 69.76, 69.36, 66.63; *m*/*z* 368 (6%), 367 (36), 366 [M^+, 100], 364 (10). Anal. Calc. for $C_{23}H_{18}FeO$: C, 75.4; H, 5.0; [M], 366.07070. Found: C, 75.3; H, 4.9%; [M^+], 366.07002.

4.2.5.2. Reaction 2. Quantities: 4-formylbenzeneboronic acid (0.88 g, 5.9 mmol), 4-bromophenylferrocene (1.00 g, 2.9 mmol), $Ba(OH)_2$ (1.30 g, 4.1 mmol) and palladium(II) acetate (0.22 g, 0.98 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene with the exception that the reaction time was 768 h. Yield of 4′-formyl-4-biphenylferrocene (0.14 g, 13%).

4.2.5.3. Reaction 3. Quantities: 4-formylbenzeneboronic acid (0.88 g, 5.9 mmol), 4-bromophenylferrocene (1.00 g, 2.9 mmol), $Ba(OH)_2$ (1.30 g, 4.1 mmol) and palladium(II) acetate (0.22 g, 0.98 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene with the exception that the reaction time was 24 h. 4-Bromophenylferrocene (0.61 g, 39% conversion) and 4′-formyl-4-biphenylferrocene (0.11 g, 10%) were obtained.

4.2.6. 4′-Hydroxymethyl-4-biphenylferrocene

A round-bottomed flask was charged with lithium aluminium hydride (LAH) (16 mg, 0.41 mmol) in anhydrous Et_2O (50 cm^3). The solution was stirred and treated with an ethereal solution of 4′-formyl-4-biphenylferrocene (150 mg, 0.41 mmol), and then heated under reflux for 2 h. Excess LAH was destroyed by addition of EtOAc, and the reaction mixture was then carefully added to an ice-water slurry. The organic layer was separated and washed twice with water, dried over anhydrous Na_2SO_4, and then evaporated to dryness. The orange residue was then subjected to column chromatography on silica gel. Dichloromethane was used to elute 4′-hydroxymethyl-4-biphenylferrocene which was recrystallized from an EtOH–CH_2Cl_2 mixture in the cold (144 mg, 95%), m.p. 185–187 °C; IR (KBr cm^{-1}) 3564, 3112, 3048, 2952, 2871, 1919, 1610, 1546, 1514, 1457, 1424, 1384, 1286, 1214, 1116, 1091, 1043, 1010, 897, 824, 743, 654, 630; ^{1}H-NMR ($CDCl_3$)

7.63 (2H, d, *J* 8.1, ArH), 7.53 (4H, m, ArH), 7.45 (2H, d, *J* 8.3, ArH), 4.74 (2H, s, CH_2), 4.68 (2H, t, *J* 1.9, C_5H_4), 4.34 (2H, t, *J* 1.9, C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 140.38, 139.66, 138.55, 138.18, 127.52, 126.94, 126.51, 85.11, 69.67, 69.06, 66.54, 65.17; *m*/*z* 369 (26%), 368 [M^+, 100], 367 (6), 366 (19), 231 (7), 230 (35). Anal. Calc. for $C_{23}H_{20}FeO$: C, 75.0; H, 5.5; [M], 368.08635. Found: C, 74.5; H, 5.6%; [M^+], 368.08633.

4.2.7. 4′-Fluoro-4-biphenylferrocene

Quantities: 4-fluorobenzeneboronic acid (0.82 g, 5.9 mmol), 4-bromophenylferrocene (1.00 g, 2.9 mmol), $Ba(OH)_2$ (1.30 g, 4.1 mmol) and palladium(II) acetate (0.22 g, 0.98 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene. Yield of 4′-fluoro-4-biphenylferrocene (0.93 g, 89%) as orange crystals (from CH_2Cl_2–C_6H_{14} in the cold), m.p. 189–190 °C; IR (KBr cm^{-1}) 1595, 1505, 1454, 1398, 1239, 1200, 1163, 1106, 1030, 1001, 890, 821; ^{1}H-NMR ($CDCl_3$) 7.58 (2H, d, *J* 8.7, ArH), 7.54 (2H, d, *J* 8.0, ArH), 7.47 (2H, d, *J* 8.4, ArH), 7.13 (2H, t, *J* 8.7), 4.68 (2H, t, *J* 1.8, C_5H_4), 4.34 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 138.47, 137.60, 128.34, 126.86, 126.51, 115.77, 115.48, 84.86, 69.65, 69.06, 66.51; *m*/*z* 357 (26%), 356 [M^+, 100], 354 (8), 235 (11), 233 (5), 178 (5), 120 (13). Anal. Calc. for $C_{22}H_{17}FFe$: C, 74.2; H, 4.8; [M], 356.06637. Found: C, 74.0; H, 4.8%; [M^+], 356.06579.

4.2.8. 4′-Acetyl-4-biphenylferrocene

Quantities: 4-acetylbenezeneboronic acid (0.95 g, 5.80 mmol), 4-bromophenylferrocene (1.00 g, 2.90 mmol), $Ba(OH)_2$ (1.30 g, 4.1 mmol) and palladium(II) acetate (0.22 g, 0.98 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene except that the reaction mixture was heated under reflux for 3×7 h during the reaction period. 4-Bromophenylferrocene (0.098 g, 90% conversion) was obtained and 4′-acetyl-4-biphenylferrocene (0.160 g, 14%) as red crystals (from C_6H_{14}), m.p. 196–198 °C; IR (KBr cm^{-1}) 1692, 1617, 1412, 1380, 1283, 971, 831, 604; ^{1}H-NMR ($CDCl_3$) 8.04 (2H, d, *J* 8.3, ArH), 7.72 (2H, d, *J* 8.3, ArH), 7.57 (4H, s, ArH), 4.69 (2H, t, *J* 1.8, C_5H_4), 4.36 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5), 2.64 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$) 197.79, 145.49, 139.80, 137.06, 135.60, 128.99, 127.16, 126.74, 126.56, 84.45, 69.84, 69.69, 69.25, 66.58; *m*/*z* 380 [M^+, 5%], 239 (7), 238 (41), 224 (16), 223 (100), 153 (6), 152 (19), 151 (9), 43 (56). Anal. Calc. for $C_{24}H_{20}OFe$: C, 75.8; H, 5.3; [M], 380.08635. Found: C, 76.4; H, 5.6%; [M^+], 380.08550.

4.2.9. 4′-Benzyloxy-4-biphenylferrocene

Quantities: 4-benzyloxybenzeneboronic acid (478 mg, 2.9 mmol), 4-bromophenylferrocene (500 mg, 1.5 mmol), $Ba(OH)_2$ (650 mg, 2.1 mmol) and palladium(II) acetate (110 mg, 0.49 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene. Yield of 4′-benzyloxy-4-biphenylferrocene (600 mg, 70%), m.p. 210–212 °C; IR (KBr cm^{-1}) 3091, 3040, 2911, 1609, 1506, 1471, 1377, 1283, 1180, 1103, 1060, 837, 649, 503; ^{1}H-NMR ($CDCl_3$) 7.44 (11H, m, ArH), 7.04 (2H, dd, *J* 8.8, ArH), 5.12 (2H, s, CH_2), 4.67 (2H, t, *J* 1.8, C_5H_4), 4.33 (2H, t, *J* 1.8, C_5H_4), 4.06 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 158.22, 157.93, 138.19, 137.74, 137.00, 133.76, 128.62, 127.99, 127.80, 127.75, 127.50, 126.56, 126.47, 115.17, 115.11, 85.14, 70.09, 69.61, 68.93, 66.45; *m*/*z* 446 (3), 445 (20), 444 [M^+, 59], 442 (4), 367 (9), 366 (33), 354 (10), 353 (38), 326 (5), 325 (19), 276 (4), 275 (15), 121 (5), 91 (100). Anal. Calc. for $C_{29}H_{24}FeO$: [M], 444.11765. Found: [M^+], 444.11771.

4.2.10. 4′-Hydroxy-4-biphenylferrocene

4-Benzyloxy-4′-biphenylferrocene (250 mg, 0.563 mmol) was placed in a Parr hydrogenation reactor together with deaerated EtOH (200 cm^3), anhydrous THF (200 cm^3), and 10% palladium on charcoal (1.0 g). The reactor was purged with hydrogen and the mixture was allowed to stir under hydrogen for 76 h. The reaction was monitored by tlc which showed that unreacted starting material was still present. A further batch of catalyst and hydrogen was added and the reaction continued for another 48 h. The residual palladium was filtered off and the solvent removed in vacuo. The residue was then subjected to column chromatography on silica gel and the product was isolated as a yellow solid (48 mg, 24%), m.p. 173–174 °C; IR (KBr cm^{-1}) 3590, 3240, 2920, 2840, 1596, 1461, 1410, 1380, 1255, 1175, 1100, 1011, 820, 730, 515, 490; ^{1}H-NMR ($CDCl_3$) 7.48 (6H, m, ArH), 6.95 (2H, d, *J* 8.5, ArH), 4.86 (1H, s, OH), 4.73 (2H, t, *J* 1.8 C_5H_4), 4.39 (2H, t, *J* 1.8 C_5H_4), 4.11 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 155.37, 138.57, 138.14, 134.12, 128.40, 126.92, 126.85, 116.06, 85.53, 69.99, 69.32, 66.84; *m*/*z* 356 (4), 355 (26), 354 [M^+, 100], 353 (4), 352 (7), 121 (7). Anal. Calc. for $C_{22}H_{18}FeO$: [M], 354.07070. Found: [M^+], 354.07079.

4.2.11. 4′-Hydroxy-4-biphenylferrocene from the reaction of 4-bromophenylferrocene and 4-hydroxyphenylboronic acid

Quantities: 4-hydroxybenzeneboronic acid (163 mg, 1.17 mmol), 4-bromophenylferrocene (267 mg, 0.587 mmol), $Ba(OH)_2$ (270 mg, 0.42 mmol), and palladium(II) acetate (47 mg, 0.098 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene. The product was obtained as a yellow solid (72 mg, 33%) and the characterization was the same as described in Section 4.2.10.

4.2.12. 3′-Nitro-4-biphenylferrocene

Quantities: 3-nitrobenzeneboronic acid (1.25 g, 7.5 mmol), 4-bromophenylferrocene (1.0 g, 2.9 mmol), $Ba(OH)_2$ (1.67 g, 5.25 mmol), and palladium(II) acetate (0.28 g, 1.25 mmol). The experimental procedure was as described for 4′-methoxy-4-biphenylferrocene except that the reaction mixture was heated intermittently under reflux during the reaction period (14 × 8 h). The product was obtained as a red–orange solid (0.42 g, 38%), m.p. 163–164 °C; IR (KBr cm^{-1}) 3083, 2853, 1607, 1522, 1348, 1282, 1105, 1083, 999, 887, 835, 818, 772, 726, 679; 501; ^{1}H-NMR ($CDCl_3$) 8.41 (1H, t, *J* 1.9, ArH), 8.12 (1H, m, ArH), 7.87 (1H, m, ArH), 7.51 (5H, m, ArH), 4.63 (2H, t, *J* 1.8, C_5H_4), 4.30 (2H, t, *J* 1.8, C_5H_4), 4.00 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 149.20, 143.03, 140.57, 136.26, 132.98, 130.10, 127.45, 127.09, 122.14, 121.93, 84.57, 70.10, 69.72, 69.40, 66.99; *m*/*z* 384 (32), 383 [M^+, 100], 337 (27), 215 (17), 185 (17), 121 (7). Anal. Calc. for $C_{22}H_{17}FeNO_2$: C, 68.9; H, 4.5; N, 3.6; [M], 383.0620. Found: C, 68.3; H, 4.7; N, 3.3%; [M^+], 383.0609.

4.2.13. 3′-Amino-4-biphenylferrocene

A mixture of 3′-nitro-4-biphenylferrocene (150 mg, 0.46 mmol), 10% Pd/C (500 mg) and THF (500 cm^3) was placed in a Parr hydrogenation reactor. The reactor was purged with hydrogen and then the mixture was allowed to stir under hydrogen for 72 h. The solution was filtered through celite and concentrated to leave a brown oily residue. The residue was passed through a column of silica gel. Unreacted starting material was first removed using C_6H_{14}–CH_2Cl_2 and the product was eluted as an orange band using CH_2Cl_2. Removal of the solvent from the second orange band left yellow crystals identified as 3′-amino-4-biphenylferrocene (121 mg, 89%), m.p. 125–126 °C; IR (KBr cm^{-1}) 3446, 3365, 3089, 2922, 1618, 1530, 1492, 1455, 1406, 1313, 1227, 1104, 1000, 834, 780, 698, 497; ^{1}H-NMR ($CDCl_3$) 7.52–7.43 (4H, m, ArH), 7.22 (1H, d, *J* 7.8, ArH), 7.02 (1H, m, ArH), 6.93 (1H, m, ArH), 6.67 (1H, m, ArH), 4.67 (2H, t, *J* 1.8, C_5H_4), 4.33 (2H, t, *J* 1.8, C_5H_4), 4.06 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 147.10, 142.54, 139.16, 138.74, 130.09, 127.35, 126.76, 117.77, 114.36, 113.94, 85.47, 70.18, 69.37, 66.89; *m*/*z* 353 [M^+, 100], 352 (5), 351 (8), 232 (9), 176 (11). Anal. Calc. for $C_{22}H_{19}FeN$: C, 74.8, H, 5.4; N, 4.0; [M], 353.08669. Found: C, 75.1, H, 6.6; N, 3.5%; [M^+], 353.08572.

4.3. Preparation of arylferrocenylphenyl ethers. General method

To a 100 cm^3 round-bottomed flask was added 4-ferrocenylphenol (200 mg, 0.72 mmol), anhydrous copper(II) acetate (131 mg, 0.72 mmol), the substituted arylboronic acid (0.86 mmol) and dried powdered 4 Å molecular sieves (300 mg). To this mixture was added anhydrous CH_2Cl_2 (20 cm^3) and Et_3N (364 mg, 3.60 mmol). The reaction mixture was allowed to stir at r.t. for 168 h during which time its color darkened. The reaction mixture was then filtered and the filtrate was passed through a column of silica gel eluting with Et_2O and this removed any inorganic materials. The solvent was removed in vacuo and the residue was then subjected to flash chromatography on silica gel. In most cases, the arylferrocenylphenyl ether was eluted from the column using a C_6H_{14}–CH_2Cl_2 (1:1) mixture but in cases where the substituent group was more polar (CHO, $COCH_3$), CH_2Cl_2 was used on its own. Unreacted starting material remained behind on the column. The arylferrocenylphenyl ether was then subjected to further purification on a TLC preparative plate and again elution was carried out using C_6H_{14}–CH_2Cl_2. Extraction from the silica gel material with CH_2Cl_2 and final evaporation of the solvent left in most cases orange solids.

4.3.1. 4-(4-Methylphenoxy)phenylferrocene

The reaction yielded the product as orange crystals (130 mg, 49%), m.p. 76–78 °C; IR (KBr cm^{-1}) 3075, 3019, 2912, 1605, 1504, 1453, 1273, 1239, 1160, 1104, 884, 834, 523, 501; ^{1}H-NMR ($CDCl_3$) 7.41 (2H, d, *J* 8.8 ArH), 7.15 (2H, d, *J* 8.2, ArH), 6.94 (2H, d, *J* 8.1, ArH), 6.91 (2H, d, *J* 8.6, ArH), 4.58 (2H, t, *J* 1.8, C_5H_4), 4.28 (2H, t, *J* 1.8, C_5H_4), 4.05 (5H, s, C_5H_5), 2.34 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$) 155.99, 154.86, 133.76, 132.78, 130.21, 127.29, 118.94, 118.38, 85.37, 69.53, 68.69, 66.31, 20.71; *m*/*z* 370 (4), 369 (27), 368 [M^+, 100], 121 (6). Anal. Calc. for $C_{23}H_{20}FeO$: C, 75.1; H, 5.5; [M], 368.08635. Found: C, 74.9, H, 5.8%; [M^+], 368.08676.

4.3.2. 4-(4-Methoxyphenoxy)phenylferrocene

The reaction yielded the product as orange crystals (113 mg, 41%), m.p. 94–96 °C; IR (KBr cm^{-1}) 3091, 2983, 2954, 1530, 1497, 1451, 1288, 1242, 1105, 1034, 883, 831, 629, 570; ^{1}H-NMR ($CDCl_3$) 7.40 (2H, d, *J* 8.7, ArH), 7.00 (2H, d, *J* 9.1, ArH), 6.89 (2H, d, *J* 9.1, ArH), 6.87 (2H, d, *J* 8.7, ArH), 4.57 (2H, t, *J* 1.8, C_5H_4), 4.28 (2H, t, *J* 1.8, C_5H_4), 4.04 (5H, s, C_5H_5), 3.81 (3H, s, OCH_3); ^{13}C-NMR ($CDCl_3$) 156.73, 155.81, 150.29, 133.35, 127.26, 120.65, 117.62, 114.84, 85.42, 69.51, 68.65, 66.28, 55.67; *m*/*z* 385 (28), 384 [M^+, 100], 262 (4), 261 (18), 192 (6), 121 (6). Anal. Calc. for $C_{23}H_{20}FeO_2$: C, 71.9; H, 5.2; [M], 384.08127. Found: C, 71.9; H, 5.1%; [M^+], 384.08205.

4.3.3. 4-Phenoxyphenylferrocene

The reaction yielded the product as orange crystals (130 mg, 51%), m.p. 129–130 °C; IR (KBr cm^{-1}) 2919, 1590, 1519, 1490, 1449, 1290, 1243, 1167, 1102, 1073, 1002, 885, 850, 814, 761, 691, 520, 497; ^{1}H-NMR ($CDCl_3$) 7.44 (2H, d, *J* 8.7, ArH), 7.35 (2H, t, *J* 7.6,

ArH), 7.10 (1H, t, *J* 7.6, ArH), 7.03 (2H, d, *J* 8.7, ArH), 6.95 (2H, d, *J* 8.7, ArH), 4.59 (2H, t, *J* 1.8, C_5H_4), 4.29 (2H, t, *J* 1.8, C_5H_4), 4.05 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 157.39, 155.37, 134.24, 129.72, 127.34, 123.09, 118.93, 118.69, 85.25, 69.55, 68.75, 66.34; *m*/*z* 355 (26), 354 [M^+, 100], 352 (6), 121 (8). Anal. Calc. for $C_{22}H_{18}FeO$: [M], 354.07070. Found: [M^+], 354.0716.

4.3.4. 4-(4-Fluorophenoxy)phenylferrocene

The reaction yielded the product as orange crystals (90 mg, 34%), m.p. 113–115 °C; IR (KBr cm^{-1}) 3074, 2921, 1530, 1497, 1451, 1295, 1256, 1216, 1105, 1031, 999, 890, 831, 815, 753, 720, 550, 511; ^{1}H-NMR ($CDCl_3$) 7.42 (2H, d, *J* 8.8, ArH), 7.02 (4H, m, ArH), 6.90 (2H, d, *J* 8.8, ArH), 4.59 (2H, t, *J* 1.7, C_5H_4), 4.29 (2H, t, *J* 1.7, C_5H_4), 4.05 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 160.74, 157.54, 156.23, 153.41, 134.58, 127.77, 120.79, 120.68, 118.70, 116.80, 116.50, 85.55, 69.94, 69.17, 66.73; *m*/*z* 373 (26), 372 [M^+, 100], 277 (3), 261 (3), 186 (6), 121 (11). Anal. Calc. for $C_{22}H_{17}FFeO$: C, 71.0; H, 4.6%; [M], 372.06128. Found: C, 71.1; H, 4.8; [M^+], 372.06147.

4.3.5. 4-(4-Octyloxyphenoxy)phenylferrocene

The reaction yielded the product as orange crystals (72 mg, 21%), m.p. 75–76 °C; IR (KBr cm^{-1}) 3108, 2924, 2855, 1598, 1502, 1473, 1449, 1386, 1281, 1229, 1171, 1104, 999, 889, 720, 649, 505; ^{1}H-NMR ($CDCl_3$) 7.39 (2H, d, *J* 8.3, ArH), 6.98 (2H, d, *J* 8.9, ArH), 6.89 (4H, m, ArH), 4.58 (2H, s, C_5H_4), 4.28 (2H, s, C_5H_4), 4.04 (5H, s, C_5H_5), 3.94 (2H, t, *J* 6.5, OCH_2), 1.78 (2H, quintet, CH_2), 1.55–1.25 (10H, m, $CH_2 \times 5$), 0.88 (3H, t, CH_3); ^{13}C-NMR ($CDCl_3$) 157.23, 155.81, 150.49, 133.66, 127.65, 121.03, 117.95, 115.87, 85.94, 69.96, 69.08, 68.92, 66.73, 32.21, 29.77, 29.74, 29.64, 26.46, 23.06, 14.50; *m*/*z* 483 (35), 482 [M^+, 100], 480 (7), 426 (8), 371 (9), 370 (36), 369 (4), 277 (2), 262 (3), 261 (16), 185 (3). Anal. Calc. for $C_{30}H_{34}FeO_2$: [M], 482,19082. Found: [M^+], 482.19104.

4.3.6. 4-(4-Benzyloxyphenoxy)phenylferrocene

The reaction yielded the product as orange crystals (148 mg, 44%), m.p. 157–158 °C; IR (KBr cm^{-1}) 2930, 2864, 1507, 1460, 1381, 1235, 1108, 1019, 888, 860, 818, 752, 710, 644, 527, 494; ^{1}H-NMR ($CDCl_3$) 7.37 (7H, m, ArH), 6.98 (4H, m, ArH), 6.88 (2H, d, *J* 8.5, ArH), 5.06 (2H, s, CH_2), 4.65 (2H, s, C_5H_4), 4.28 (2H, s, C_5H_4), 4.05 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 157.00, 155.38, 150.99, 137.41, 133.84, 129.00, 128.40, 127.90, 127.66, 120.95, 118.14, 116.30, 85.80, 70.95, 69.91, 69.06, 66.68; *m*/*z* 462 (9), 461 (39), 460 [M^+, 100], 458 (7), 370 (15), 369 (47), 262 (11), 261 (56), 260 (8), 205 (10), 203 (6), 139 (5), 121 (6). Anal. Calc. for $C_{29}H_{24}FeO_2$: [M], 460.11257. Found: [M^+], 460.11256.

4.3.7. 4-(4-Formylphenoxy)phenylferrocene

4.3.7.1. Reaction 1. Smaller scale reaction. The reaction yielded the product as red crystals (72 mg, 26%), m.p. 107–109 °C; IR (KBr cm^{-1}) 1702, 1595, 1501, 1453, 1388, 1305, 1252, 1158, 1110, 1009, 856, 820, 542, 471; ^{1}H-NMR ($CDCl_3$) 9.92 (1H, s, CHO), 7.85 (2H, d, *J* 8.8, ArH), 7.50 (2H, d, *J* 8.7, ArH), 7.08 (2H, d, *J* 8.7, ArH), 7.01 (2H, d, *J* 8.7, ArH), 4.62 (2H, t, *J* 1.8, C_5H_4), 4.32 (2H, t, *J* 1.8, C_5H_4), 4.06 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 190.78, 163.33, 153.10, 136.24, 131.97, 131.19, 127.62, 120.39, 117.45, 84.64, 69.61, 69.02, 66.46; *m*/*z* 383 (27), 382 [M^+, 100], 277 (2), 267 (4), 261 (2), 191 (4), 190 (12), 149 (18), 121 (15). Anal. Calc. for $C_{23}H_{18}FeO_2$: C, 72.3; H, 4.7; [M], 382.06562. Found: C, 72.5; H, 5.0%; [M^+], 382.06442.

4.3.7.2. Reaction 2. The reaction procedure was the same as in the general procedure except that the quantities of reagents were as follows. 4-Ferrocenylphenol (972 mg, 3.5 mmol), 4-formylbenzeneboronic acid (630 mg, 4.2 mmol), copper(II) acetate (637 mg, 3.6 mmol), Et_3N (1.82 g, 1.8 mmol), 4 Å molecular sieves (1.5 g) and CH_2Cl_2 (140 cm^3). The product was obtained as red crystals (456 mg, 34%), characterized as in Section 4.3.7.1.

4.3.8. 4-(4-Bromophenoxy)phenylferrocene

The reaction yielded the product as yellow crystals (60 mg, 19%), m.p. 110–111 °C; IR (KBr cm^{-1}) 3099, 2934, 2851, 1579, 1520, 1490, 1449, 1241, 1164, 1105, 1004, 856, 809, 530, 483; ^{1}H-NMR ($CDCl_3$) 7.43 (4H, m, ArH), 6.91 (4H, m, ArH), 4.59 (2H, t, *J* 1.8, C_5H_4), 4.30 (2H, t, *J* 1.8, C_5H_4), 4.05 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 157.09, 155.19, 135.25, 133.04, 127.84, 120.64, 119.46, 115.85, 85.39, 69.96, 69.24, 66.77; *m*/*z* 435 (25), 434 (95), 433 (26), 432 [M^+, 100], 353 (3), 297 (2), 293 (7), 291 (7), 261 (3), 217 (6), 216 (6), 139 (6), 121 (11). Anal. Calc. for $C_{22}H_{17}BrFeO$: C, 61.2; H, 4.0; [M], 431.98122. Found: C, 61.7; H, 4.4%; [M^+], 431.97884.

4.3.9. 4-(4-Trifluoromethylphenoxy)phenylferrocene

The reaction yielded the product as red crystals (7 mg, 2%), m.p. 106–107 °C; IR (KBr cm^{-1}) 3074, 2926, 2849, 1614, 1523, 1510, 1455, 1416, 1324, 1253, 1159, 1116, 1107, 1066, 1033, 888, 853, 838, 817, 625, 588, 528, 490; ^{1}H-NMR ($CDCl_3$) 7.58 (2H, d, *J* 8.5, ArH), 7.48 (2H, d, *J* 8.5, ArH), 7.07 (2H, d, *J* 8.6, ArH), 6.98 (2H, d, *J* 8.5, ArH), 4.62 (2H, t, *J* 1.8, C_5H_4), 4.33 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 161.02, 154.15, 136.13, 127.96, 127.52, 127.47, 120.33, 118.08, 85.17, 69.99, 69.35, 66.82; *m*/*z* 424 (4), 423 (27), 422 [M^+, 100], 420 (7), 283 (2), 282 (12), 211 (4), 140 (15), 139 (18), 126 (6), 121 (4). Anal. Calc. for $C_{23}H_{17}F_3FeO$: [M], 422.05809. Found: [M^+], 422.05925.

4.3.10. 4-(3-Fluorophenoxy)phenylferrocene

The reaction yielded the product as yellow crystals (73 mg, 27%), m.p. 87–89 °C; IR (KBr cm^{-1}) 3071, 3025, 2923, 1595, 1522, 1490, 1444, 1264, 1223, 1103, 961, 841, 685; ^{1}H-NMR ($CDCl_3$) 7.46 (2H, d, *J* 8.6, ArH), 7.25 (1H, m, ArH), 6.97 (2H, d, *J* 8.6, ArH), 6.76 (3H, m, ArH), 4.61 (2H, t, *J* 1.7, C_5H_4), 4.31 (2H, t, *J* 1.7, C_5H_4), 4.06 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 154.73, 130.90, 130.77, 127.85, 119.93, 114.17, 110.22, 109.94, 106.38, 106.06, 85.36, 69.97, 69.25, 66.79; *m/z* 373 (26), 372 [M^+, 100], 370 (7), 277 (2), 261 (3), 186 (5), 121 (10). Anal. Calc. for $C_{22}H_{17}FFeO$: C, 71.0; H, 4.6; [M], 372.06128. Found: C, 71.3; H, 4.8%; [M^+], 372.06200.

4.3.11. 4-(4-Trifluoromethoxyphenoxy)phenylferrocene

The reaction yielded the products as yellow crystals (89 mg, 28%), m.p. 74–76 °C; IR (KBr cm^{-1}) 3088, 2920, 2849, 1520, 1502, 1453, 1276, 1244, 1187, 1169, 1107, 893, 858, 818, 529; ^{1}H-NMR ($CDCl_3$) 7.45 (2H, d, *J* 8.7, ArH), 7.21 (2H, d, *J* 8.4, ArH), 7.01 (2H, d, *J* 9.1, ArH), 6.94 (2H, d, *J* 8.7, ArH), 4.59 (2H, t, *J* 1.8, C_5H_4), 4.30 (2H, t, *J* 1.8, C_5H_4), 4.05 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 156.43, 155.22, 144.72, 135.36, 127.87, 122.97, 122.61, 119.72, 119.55, 119.22, 85.41, 69.99, 69.28, 66.79; *m/z* 439 (36), 438 [M^+, 100%], 436 (7), 261 (2), 232 (2), 219 (8), 139 (3), 121 (5). Anal. Calc. for $C_{23}H_{17}F_3FeO_2$: C, 63.1; H, 3.9; [M], 438.05300. Found: C, 63.3; H, 3.9%; [M], 438.05330.

4.3.12. 4-(4-Acetylphenoxy)phenylferrocene

The reaction yielded the product as orange crystals (92 mg, 32%), m.p. 118–120 °C; IR (KBr cm^{-1}) 3097, 2920, 1674, 1594, 1526, 1503, 1451, 1354, 1269, 1166, 1109, 829, 594, 531, 497; ^{1}H-NMR ($CDCl_3$) 7.95 (2H, d, *J* 8.8 ArH), 7.48 (2H, d, *J* 8.5, ArH), 7.01 (4H, t, *J* 8.8, ArH), 4.64 (2H, t, *J* 1.8, C_5H_4), 4.34 (2H, t, *J* 1.8, C_5H_4) 4.08 (5H, s, C_5H_5), 2.58 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$) 197.11, 162.48, 153.95, 136.25, 132.23, 130.99, 127.95, 120.52, 117.54, 70.12, 69.47, 66.90, 26.84; *m/z* 397 (31), 396 [M^+, 100], 394 (7), 353 (5), 261 (2), 191 (3), 190 (11), 121 (8). Anal. Calc. for $C_{24}H_{20}FeO_2$: C, 72.8; H, 5.1; [M], 396.08127. Found: C, 72.5; H, 5.3%; [M], 396.08036.

4.3.13. 4-(3,4,5-Trimethoxyphenoxy)phenylferrocene

The reaction yielded the product as orange crystals (112 mg, 42%), m.p. 131–133 °C; IR (KBr cm^{-1}) 3084, 2957, 2927, 2830, 1606, 1504, 1467, 1425, 1413, 1226, 1184, 1130, 991, 816, 490; ^{1}H-NMR ($CDCl_3$) 7.44 (2H, d, *J* 8.7, ArH), 6.93 (2H, d, *J* 8.4, ArH), 6.21 (2H, s, ArH), 4.60 (2H, s, C_5H_4), 4.30 (2H, s, C_5H_4), 4.05 (5H, s, C_5H_5), 3.82 (9H, s, 3 × OCH_3); ^{13}C-NMR ($CDCl_3$) 155.74, 153.89, 153.26, 134.14, 134.06, 127.32, 118.27, 96.78, 85.53, 69.76, 68.97, 66.41, 61.03, 56.13; *m/z* 446 (5), 445 (29), 444 [M^+, 100], 442 (6), 414 (3), 386 (3), 363 (4), 278 (3), 261 (4), 222 (3), 185 (4), 121 (4). Anal. Calc. for $C_{25}H_{24}FeO_4$: C, 67.6; H, 5.4; [M], 444.10240. Found: C, 67.9; H, 5.9%; [M^+], 444.10201.

4.3.14. 4-(3-Nitrophenoxy)phenylferrocene

The reaction procedure was the same as in the general procedure except that the reagents were used in the following quantities: 4-ferrocenylphenol (1.0 g, 3.60 mmol), 3-nitrobenzeneboronic acid (516 mg, 3.094 mmol), copper(II) acetate (650 mg, 3.6 mmol), Et_3N (1.82 g, 18 mmol), 4 Å molecular sieves (1.5 g) and CH_2Cl_2 (150 cm^3). The reaction yielded the product as red crystals (145 mg, 10%), m.p. 92–94 °C; IR (KBr cm^{-1}) 3097, 2920, 2849, 1618, 1524, 1471, 1449, 1347, 1276, 1236, 1107, 942, 884, 858, 844, 818, 742, 667, 520; ^{1}H-NMR ($CDCl_3$) 7.93 (1H, dd, *J* 7.8, 1.2, ArH), 7.82 (1H, t, *J* 2.2, ArH), 7.49 (3H, m, ArH), 7.33 (1H, dd, *J* 8.2, 2.4, ArH), 6.98 (2H, d, *J* 8.7, ArH), 4.68 (2H, t, *J* 1.8, C_5H_4), 4.32 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5); ^{13}C-NMR ($CDCl_3$) 159.05, 153.94, 149.70, 136.56, 130.69, 128.15, 124.39, 120.19, 117.92, 113.12, 85.06, 70.02, 69.40, 66.88; *m/z* 401 (4), 400 (26), 399 [M^+, 100], 397 (10), 353 (8), 352 (4), 277 (3), 260 (3), 199 (3), 139 (4), 121 (13). Anal. Calc. for $C_{22}H_{17}FeNO_3$: C, 66.2; H, 4.3; N, 3.5; [M], 399.05578. Found: C, 66.3; H, 4.5; N, 3.4%; [M^+], 399.05582.

4.4. Preparation of arylferrocenylphenyl amines. The reaction of 4-ferrocenylaniline and 4-substituted phenylboronic acids

To a 100 cm^3 RB flask was added 4-ferrocenylaniline (200 mg, 0.72 mmol), copper(II) acetate (131 mg, 0.72 mmol), the 4-substituted phenylboronic acid (0.86 mmol) and powdered 4 Å molecular sieves (300 mg). To this mixture was added anhydrous CH_2Cl_2 (20 cm^3) and Et_3N (364 mg, 3.60 mmol). The reaction mixture was allowed to stir at r.t. for 168 h. The reaction mixture was then filtered through a column of silica gel and Et_2O was used to strip the column of the organic components. The solvent was removed in vacuo and the residue was then subjected to separation and purification by preparative thin layer plate chromatography. The developing solvent used was either C_6H_{14}–CH_2Cl_2 (50/50) (for the methyl derivative) or a solvent system consisting of C_6H_{14}–CH_2Cl_2–ether (60/35/5) (for the methoxy and bromo derivatives). Considerable quantities of dark inorganic materials were removed from the reaction mixtures during the purification steps.

4.4.1. 4-(4-Methylanilino)phenylferrocene

The reaction yielded the product as a yellow solid (38 mg, 14%), m.p., 118–120 °C; IR (KBr cm^{-1}) 3396 (NH), 3098, 2964, 2925, 1615, 1536, 1520, 1456, 1330, 1183, 1104, 1084, 1027, 1003, 888, 820, 498; ^{1}H-NMR ($CDCl_3$) 7.35 (2H, d, *J* 8.5, ArH), 7.09 (2H, d, *J* 8.3, ArH), 7.00 (2H, d, *J* 8.4, ArH), 6.95 (2H, d, *J* 8.5,

ArH), 5.59 (1H, s[br], NH), 4.56 (2H, t, *J* 1.5, C_5H_4), 4.25 (2H, t, *J* 1.5, C_5H_4), 4.04 (5H, s, C_5H_5), 2.30 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$) 142.34, 140.87, 131.39, 131.07, 130.28, 127.48, 118.99, 117.51, 86.57, 69.88, 68.84, 66.39, 21.12; *m*/*z* 369 (3), 368 (20), 367 [M,$^+$ 100], 366 (3), 246 (7), 184 (7), 121 (3). Anal. Calc. for $C_{23}H_{21}FeN$: [M], 367.10234. Found: [M^+], 367.10201.

4.4.2. 4-(4-Methoxyanilino)phenylferrocene

The reaction yielded the product as a brown solid (9 mg, 3%), m.p., 144–147 °C; IR (KBr cm^{-1}) 3392 (NH), 3105, 2964, 2930, 2856, 1614, 1533, 1520, 1460, 1328, 1301, 1254, 1104, 1031, 831, 811, 566, 503; ^{1}H-NMR ($CDCl_3$) 7.34 (2H, d, *J* 8.6, ArH), 7.08 (2H, d, *J* 8.9, ArH), 6.87 (2H, d, *J* 9.0, ArH), 6.86 (2H, d, *J* 8.7, ArH), 5.49 (1H, s[br], NH), 4.55 (2H, t, *J* 1.8, C_5H_4), 4.25 (2H, t, *J* 1.8, C_5H_4), 4.04 (5H, s, C_5H_5), 3.81 (3H, s, OCH_3); ^{13}C-NMR ($CDCl_3$) 155.11, 143.19, 135.93, 130.20, 127.11, 121.81, 115.87, 114.69, 86.31, 69.43, 68.33, 65.91, 55.61; *m*/*z* 385 (4), 384 (27), 383 [M,$^+$ 100], 368 (9), 261 (7), 191 (4), 184 (5), 121 (4). Anal. Calc. for $C_{23}H_{21}FeNO$: [M], 383.09725. Found: [M^+], 383.09706.

4.4.3. 4-(4-Bromoanilino)phenylferrocene

The reaction yielded the product as a yellow solid (87 mg, 28%), m.p., 118–120 °C; IR (KBr cm^{-1}) 3400 (NH), 3088, 2960, 2922, 2853, 2360, 1594, 1529, 1498, 1454, 1384, 1324, 1261, 1174, 1104, 1074, 1031, 1000, 888, 819, 518; ^{1}H-NMR ($CDCl_3$) 7.39 (2H, d, *J* 8.6, ArH), 7.35 (2H, d, *J* 8.8, ArH), 7.00 (2H, d, *J* 8.6, ArH), 6.94 (2H, d, *J* 8.8, ArH), 5.67 (1H, s[br], NH), 4.58 (2H, t, *J* 1.8, C_5H_4), 4.28 (2H, t, *J* 1.8, C_5H_4), 4.05 (5H, s, C_5H_5); *m*/*z* 434 (26), 433 [M,$^+$ 100], 432 (25), 431 (93), 368 (5), 366 (5), 297 (5), 296 (20), 231 (10), 229 (4), 228 (5), 216 (8), 139 (5), 121 (4). Anal. Calc. for $C_{22}H_{18}FeN^{79}Br$: [M], 430.99720. Found: [M^+], 430.99710.

4.5. Preparation of elongated ferrocenes

4.5.1. 4-Pentyloxy-N-[4-(4-ferrocenylphenyl)-benzylidene]aniline

To a solution containing 4′-formyl-4-biphenylferrocene (150 mg, 0.41 mmol) and 4-pentyloxyaniline (73 mg, 0.41 mmol) in anhydrous MeOH (30 cm^3) was added 4 Å molecular sieves (0.40 g), and the mixture was heated under reflux overnight. The reaction mixture was then concentrated in vacuo, and the residue recrystallized from CH_2Cl_2–C_6H_{14} in the cold (213 mg, 99%), m.p. 210–212 °C; IR (KBr cm^{-1}) 3112, 3080, 3048, 2952, 2871, 1919, 1627, 1610, 1505, 1481, 1392, 1295, 1254, 1197, 1181, 1116, 1091, 1059, 1035, 1019, 995, 897, 832; ^{1}H-NMR ($CDCl_3$) 8.53 (1H, s, CH), 7.97 (2H, d, *J* 8.3, ArH), 7.73 (2H, d, *J* 8.3, ArH), 7.58 (4H, m, ArH), 7.26 (2H, d, *J* 8.7, ArH), 6.94 (2H, d, *J* 8.9, ArH), 4.70 (2H, t, *J* 1.8, C_5H_4), 4.36 (2H, t, *J* 1.8, C_5H_4), 4.08 (5H, s, C_5H_5), 3.09 (2H, t, *J* 6.6, OCH_2), 1.81 (2H, m, CH_2), 1.57–1.44 (4H, m, $2 \times CH_2$), 0.95 (3H, m, CH_3) *m*/*z* 529 (39%), 527 [M^+, 100], 525 (9), 457 (8), 456 (11), 228 (12). Anal. Calc. for $C_{34}H_{33}FeNO$: C, 77.4; H, 6.3; N, 2.7; [M], 527.19115. Found: C, 77.0; H, 6.6; N, 2.6%; [M^+], 527.19210.

4.5.2. 4-Octyloxy-N-[4-(4-ferrocenylphenyl)-benzylidene]aniline

Quantities: 4′-formyl-4-biphenylferrocene (150 mg, 0.41 mmol) and 4-octyloxyaniline (91 mg, 0.41 mmol). The experimental procedure was as described for 4-pentyloxy-*N*-[4-(4-ferrocenylphenyl)benzylidene]aniline. The product was isolated as a yellow solid (170 mg, 73%), m.p. (liquid crystal) 177 °C (K/S), 183 °C (S/N), 201 °C (N/I); IR (KBr cm^{-1}) 3112, 3097, 3048, 2968, 2870, 1627, 1610, 1578, 1514, 1481, 1400, 1303, 1270, 1197, 1116, 1043, 1010, 897, 840, 735; ^{1}H-NMR ($CDCl_3$) 8.53 (1H, s, CH), 7.97 (2H, d, *J* 8.3, ArH), 7.73 (2H, d, *J* 8.3, ArH), 7.58 (4H, m, ArH), 7.26 (2H, d, *J* 8.8, ArH), 6.94 (2H, d, *J* 8.8, ArH), 4.70 (2H, t, *J* 1.8, C_5H_4), 4.36 (2H, t, *J* 1.8, C_5H_4), 4.08 (5H, s, C_5H_5), 3.99 (2H, t, *J* 6.6, OCH_2), 1.80 (2H, m, CH_2), 1.56–1.30 (10H, m, $5 \times CH_2$), 0.90 (3H, m, CH_3); ^{13}C-NMR ($CDCl_3$) 158.30, 158.23, 145.15, 143.77, 139.64, 137.99, 135.63, 129.50, 127.43, 127.37, 126.95, 122.63, 115.39, 85.08, 70.10, 69.57, 68.70, 66.96, 32.25, 29.81, 29.74, 29.68, 26.49, 23.10, 14.55; *m*/*z* 570 (43%), 569 [M^+, 100], 567 (7), 457 (9), 456 (10), 228 (10). Anal. Calc. for $C_{37}H_{39}FeNO$: C, 78.0; H, 6.9; N, 2.5; [M], 569.23810. Found: C, 78.1; H, 7.2; N, 2.4%; [M^+], 569.23754.

4.5.3. 4-Tetradecyloxy-N-[4-(4-ferrocenylphenyl)-benzylidene]aniline

Quantities: 4′-formyl-4-biphenylferrocene (150 mg, 0.41 mmol) and 4-tetradecyloxyaniline (125 mg, 0.41 mmol). The experimental procedure was as described for 4-pentyloxy-*N*-[4-(4-ferrocenylphenyl)benzylidene]-aniline. The product was isolated as a yellow solid (214 mg, 75%), m.p. (liquid crystal) 146 °C (K/S), 164 °C (S/N), 182 °C (N/I); IR (KBr cm^{-1}) 3113, 3080, 3048, 2935, 2871, 1910, 1886, 1773, 1627, 1603, 1578, 1513, 1473, 1400, 1303, 1254, 1197, 1157, 1116, 1027, 1010, 897, 840, 824, 735; ^{1}H-NMR ($CDCl_3$) 8.63 (1H, s, CH), 7.96 (2H, d, *J* 8.3, ArH), 7.73 (2H, d, *J* 8.2, ArH), 7.58 (4H, m, ArH), 7.26 (2H, d, *J* 8.7, ArH), 6.94 (2H, d, *J* 8.7, ArH), 4.70 (2H, t, *J* 1.7, C_5H_4), 4.36 (2H, t, *J* 1.7, C_5H_4), 4.07 (5H, s, C_5H_5), 3.98 (2H, t, *J* 6.6, OCH_2), 1.80 (2H, m, CH_2), 1.47–1.27 (22H, m, $11 \times CH_2$), 0.88 (3H, m, CH_3); ^{13}C-NMR ($CDCl_3$) 157.94, 157.81, 143.41, 139.27, 137.63, 135.25, 129.12, 127.04, 126.98, 126.56, 122.23, 115.04, 84.72, 69.70, 69.17, 68.35, 66.57, 31.95, 29.69, 29.63, 29.45, 29.39, 26.09, 22.72, 14.15; *m*/*z* 654 (50%), 653 [M^+, 100], 652 (6), 651 (8), 457 (9), 456 (10), 228 (10). Anal Calc. for $C_{43}H_{51}FeNO$: C, 79.0;

H, 7.9; N, 2.1; [M], 653.33200. Found: C, 79.0; H, 8.2; N, 2.1%; [M^+], 653.33108.

4.5.4. 4-Pentyloxy-N-{1-[4(ferrocenylphenoxy)-phenyl]methylidene}aniline

To a solution containing 4-(4-formylpenoxy)phenylferrocene (200 mg, 0.52 mmol) and 4-pentyloxyaniline (93 mg, 0.52 mmol) in anhydrous MeOH (30 cm^3) was added 4 Å molecular sieves (400 mg) and the mixture was heated under reflux overnight. The reaction mixture was then concentrated in vacuo and the residue recrystallized from CH_2Cl_2–MeOH in the cold (148 mg, 52%), m.p. 151–153 °C; IR (KBr cm^{-1}) 2949, 1601, 1503, 1451, 1249, 1160, 1104, 897, 832, 531; ^{1}H-NMR ($CDCl_3$) 8.44 (1H, s, CH), 7.86 (2H, d, *J* 8.7, ArH), 7.47 (2H, d, *J* 8.6, ArH), 7.21 (2H, d, *J* 8.8, ArH), 7.08 (2H, d, *J* 8.7, ArH), 7.00 (2H, d, *J* 8.6, ArH), 6.92 (2H, d, *J* 8.8, ArH), 4.61 (2H, t, *J* 1.8, C_5H_4), 4.31 (2H, t, *J* 1.8, C_5H_4), 4.07 (5H, s, C_5H_5), 3.97 (2H, t, *J* 6.6, OCH_2), 1.80 (2H, m, CH_2), 1.53–1.33 (4H, m, $2 \times CH_2$), 0.94 (3H, t, CH_3); ^{13}C-NMR ($CDCl_3$) 160.54, 158.14, 157.73, 154.72, 135.58, 131.79, 130.65, 127.86, 122.49, 120.05, 118.57, 115.38, 85.36, 69.97, 69.27, 68.68, 66.79, 29.40, 28.61, 22.87, 14.42; *m*/*z* 545 (9), 544 (39), 543 [M^+, 100], 541 (7), 473 (5), 472 (4), 408 (3), 407 (10), 379 (3), 237 (3), 236 (9), 121 (3). Anal. Calc. for $C_{34}H_{33}FeNO_2$: C, 75.2; H, 6.1; N, 2.6; [M], 543.18607. Found: C, 75.0; H, 6.8; N, 2.4%; [M^+], 543.18565.

4.5.5. 4-Tetradecyloxy-N-{1-[4-(ferrocenylphenoxy)-phenyl]methylidene}aniline

To a solution containing 4-(4-formylphenoxy)-phenylferrocene (200 mg, 0.52 mmol) and 4-tetradecycloxyaniline (159 mg, 0.52 mmol) in anhydrous MeOH (30 cm^3) was added 4 Å molecular sieves (400 mg) and the mixture was heated under reflux overnight. The reaction mixture was then concentrated in vacuo and the residue recrystallized from CH_2Cl_2–MeOH in the cold (151 mg, 43%), m.p. 126–128 °C; IR (KBr cm^{-1}) 3073, 2920, 2849, 1596, 1502, 1461, 1279, 1250, 1156, 1103, 1020, 885, 838, 721, 544, 521; ^{1}H-NMR ($CDCl_3$) 8.44 (1H, s, CH), 7.86 (2H, d, *J* 8.7, ArH), 7.47 (2H, d, *J* 8.6, ArH), 7.21 (2H, d, *J* 8.8, ArH), 7.08 (2H, d, *J* 8.6, ArH), 6.99 (2H, d, *J* 8.6, ArH), 6.92 (2H, d, *J* 8.8, ArH), 4.61 (2H, t, *J* 1.7, C_5H_4), 4.31 (2H, t, *J* 1.7, C_5H_4), 4.06 (5H, s, C_5H_5), 3.97 (2H, t, *J* 6.5, OCH_2), 1.79 (2H, m, CH_2), 1.60–1.26 (22H, m, $11 \times CH_2$), 0.88 (3H, t, CH_3); ^{13}C-NMR ($CDCl_3$) 160.54, 158.16, 157.69, 154.74, 145.21, 135.58, 131.81, 130.64, 127.86, 122.48, 120.04, 118.57, 115.40, 85.37, 69.97, 69.26, 68.72, 66.79, 32.31, 30.05, 29.99, 29.80, 29.74, 29.71, 26.45, 23.07, 14.50; *m*/*z* 672 (8), 671 (32), 670 (83), 669 [M^+, 100], 668 (23) 667 (18), 487 (5), 486 (7), 485 (8), 474 (11), 473 (16), 472 (12), 408 (12), 407 (14), 380 (9), 379 (15), 367 (11), 354 (9), 353 (13), 305 (10), 278 (26), 277 (12), 262 (15), 261 (23), 203 (6). Anal. Calc. for $C_{43}H_{51}FeNO_2$: C, 77.2; H, 7.7; N, 2.1; [M], 669.32692. Found: C, 77.0; H, 8.5; N, 2.0%; [M^+], 669.32537.

4.6. Larger scale reaction for GC–MS analysis. 4-(4-Methylphenoxy)phenylferrocene

The reaction was repeated as in the general procedure except that the quantities of the reactants and reagents were scaled up. The quantities were as follows: 4-Ferrocenylphenol (1.00 g, 3.6 mmol), 4-methylbenzeneboronic acid (585 mg, 4.3 mmol), copper(II) acetate (655 mg, 3.6 mmol), Et_3N (1.82 g, 18 mmol), 4 Å molecular sieves (1.5 g) and CH_2Cl_2 (100 cm^3). The reaction was analyzed by GC–MS. The following compounds were identified as major components; 4-(4-methylphenoxy)phenylferrocene and 4-ferrocenylphenol. Minor components were *p*-cresol, 4,4′-dimethylbiphenyl, 4,4′-dimethylbiphenyl ether and 4-acetoxytoluene.

4.7. Crystal structure determination

Crystal data for **6**: $M_r = 322.19$ g mol^{-1}, size $0.25 \times 0.24 \times 0.08$ mm, orthorhombic, space group *Pbca*, $a = 9.8870(11)$, $b = 10.7315(12)$, $c = 31.933(3)$ Å, $V = 3388.2$ (6) $Å^3$, $T = 296$ K, $Z = 8$, $\rho_{calc} = 1.436$ g cm^{-3}, $\mu(Mo–K_a) = 0.897$ mm^{-1}, $F(000) = 1520$, 35755 reflections in $h(-13/13)$, $k(-14/14)$, $l(-42/38)$, measured in the range $5.65 \leq \Theta \leq 25.00°$, 4180 independent reflections, $R_{int} = 0.1206$, 230 parameters, 0 restraints. $R_{1obs} = 0.0466$, $wR_{2obs} = 0.1167$, $R_{1all} = 0.1286$, $wR_{2all} = 0.1600$, goodness-of-fit = 0.822, largest difference peak and hole: $0.213/-0.429$ e $Å^{-3}$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157093 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors wish to thank the following persons for technical assistance: Mr H. Marchard (UPE) for general technical assistance, Dr P. Boshoff (Cape Technikon, Cape Town) for his mass spectroscopic analyses, Dr R. Sheets (Rhodes University, Grahamstown) for help with use of the Linkam hotstage and polarizing microscope and Dr B. Schoonees (Port Elizabeth Tech-

nikon) for help with GC–MS analyses. The National Research Foundation and the University of Port Elizabeth are thanked for funding. The authors wish to extend a special word of gratitude to Lancaster Synthesis (UK) for the supply of phenylboronic acids.

References

[1] C. Loubser, C. Imrie, P.H. van Rooyen, Adv. Mater. 5 (1993) 45.
[2] (a) N. Nakamura, T. Hanasaki, H. Onoi, Mol. Cryst. Liq. Cryst. 225 (1993) 269;
(b) N. Nakamura, T. Hanasaki, H. Onoi, T. Oida, Chem. Express 8 (1993) 467;
(c) T. Hanasaki, M. Ueda, N. Nakamura, Mol. Cryst. Liq. Cryst. 237 (1993) 329;
(d) N. Nakamura, H. Onoi, T. Oida, T. Hanasaki, Mol. Cryst. Liq. Cryst. 257 (1994) 43;
(e) N. Nakamura, T. Oida, M. Shonago, H. Onoi, T. Hanasaki, Mol. Cryst. Liq. Cryst. 265 (1995) 1;
(f) J. Andersch, S. Diele, C. Tschierske, J. Mater. Chem. 6 (1996) 1465;
(g) M.J. Cook, G. Cooke, A. Jafari-Fini, J. Chem. Soc. Chem. Commun. (1995) 1715;
(h) T. Seshadri, H.-J. Haupt, J. Mater. Chem. 8 (1998) 1345;
(i) T. Seshadri, H.-J. Haupt, Chem. Commun. (1998) 735.
[3] C. Loubser, C. Imrie, J. Chem. Soc. Perkin Trans 2 (1997) 399.
[4] F.H. Allen, J. Trotter, C.S. Williston, J. Chem. Soc. A (1970) 907.
[5] J. Trotter, C.S. Williston, J. Chem. Soc. A (1967) 1379.
[6] (a) M. Rosenblum, W.G. Howells, A.K. Banerjee, C. Bennett, J. Am. Chem. Soc. 84 (1962) 2726;
(b) W.F. Little, C.N. Reilley, J.D. Johnson, K.N. Lynn, A.P. Sanders, J. Am. Chem. Soc. 86 (1964) 1376.
[7] C. Imrie, C. Louber, P. Engelbrecht, C.W. McCleland, J. Chem. Soc. Perkin Trans 1 (1999) 2513.
[8] (a) F. Theil, Angew. Chem. Int. Ed. 38 (1999) 2345;
(b) D.A. Evans, J.L. Katz, T.R. West, Tetrahedron Lett. 39 (1998) 2937;
(c) D.M.T. Chan, K.L. Monaco, R.-P. Wang, M.P. Winters, Tetrahedron Lett. 39 (1998) 2933;
(d) J. Simon, S. Salzbrunn, G.K. Surya Prakash, N.A. Petasis, G.A. Olah, J. Org. Chem. 66 (2001) 633.
[9] R. Prins, A.R. Korswagen, A.G.T.G. Kortbeek, J. Organomet. Chem. 39 (1972) 335.
[10] K. Sato, M. Iwai, H. Sano, M. Konno, Bull. Chem. Soc. Jpn. 57 (1984) 634.
[11] G. Ferguson, J.F. Gallagher, C. Glidewell, C.M. Zakaria, Acta Cryst. C 49 (1993) 967.
[12] C. Imrie, P. Engelbrecht, C. Louber, C.W. McCleland, Appl. Organomet. Chem. 15 (2001) 1.
[13] R. Deschenaux, I. Kosztics, J.-L. Marendaz, H. Stoeckli-Evans, Chimia 47 (1993) 206.