

# The synthesis and liquid crystal behaviour of monosubstituted ferrocenomesogens

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## Abstract

The synthesis and characterization of several new series of monosubstituted ferrocenyl-containing liquid crystals has been achieved. The results indicate that a terminal ferrocenyl group can promote stabilization of a nematic liquid crystal state. At least three phenyl rings are required in the molecular core in order to provide nematic properties and addition of a fourth ring substantially enhances it. Bulky lateral substituents or the introduction of linker groups that introduce kinks inhibit liquid crystal phase formation. Short highly polarising terminal groups or terminal groups that support hydrogen bonding support liquid crystal behaviour.

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## 1. Introduction

Malthête and Billard synthesized the initial series of mesogenic ferrocene derivatives [1]. Compounds of three structural variation were synthesized (Fig. 1, 1–3) and in each case the ferrocenyl group was situated in a terminal position. The compounds of series 1 displayed enantiotropic nematic liquid crystal phases characterized by their Schlieren texture but exhibited relatively short liquid crystalline domains. The compounds of series 2 and 3 were monotropic nematogens.

The results of Malthête and Billard were surprising at the time in that it seemed likely that monosubstituted ferrocenes would be poor candidates for stabilizing liquid crystalline phases owing to disruption of the overall linear shape of the molecule by the bulky ferrocenyl group. It was only in 1993 that a publication by Loubser et al. shed some light on the manner in which a terminal ferrocenyl group can be incorporated and tolerated in a liquid crystal [2]. The article by

Loubser et al. described the X-ray structure of a monosubstituted ferrocenomesogen (4) [a ferrocenyl-containing liquid crystal]. The molecule 4 contained a terminal ferrocenyl group and laterally substituted

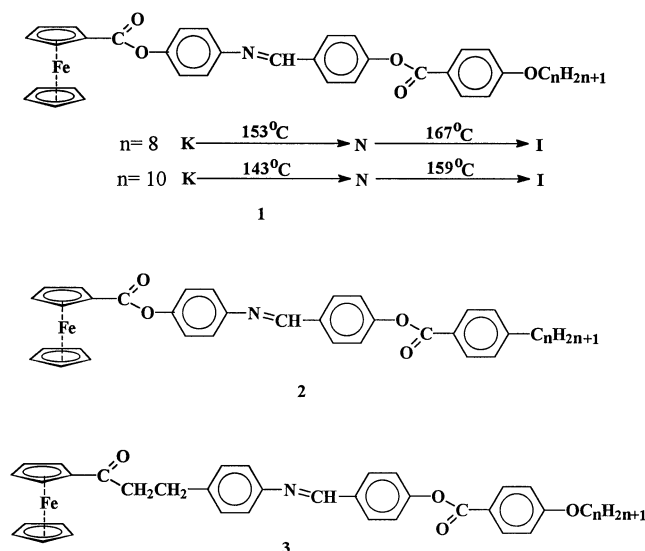
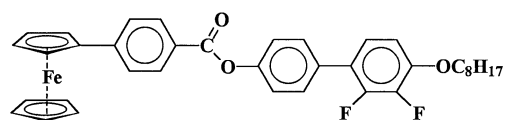


Fig. 1. The first monosubstituted ferrocenomesogens.

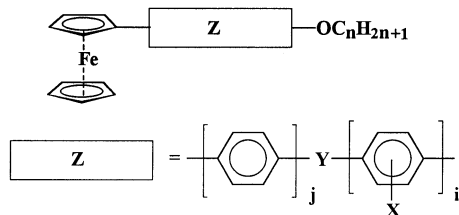
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fluorine atoms and exhibited an enantiotropic nematic phase with a relatively low melting and clearing temperature. Analysis of the molecular structure of **4** by X-ray diffraction indicated that there was an intermolecular association between two molecules in neighbouring layers resulting in an overall extended S-shape with the ferrocenyl–phenyl groups forming the ‘core’ and the remainder of each pair of molecules extending in opposite but parallel directions.



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$n = 8, 10, 12, 14$

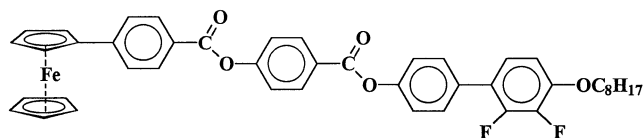
$j = 0 \text{ or } 1; i = 1 \text{ or } 2; X = \text{H or F}$

$Y = -\text{COO}-, -\text{COOPhCOO}-$

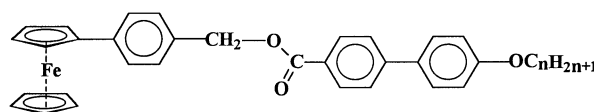
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This stimulated a systematic investigation into the structural limits in which the liquid crystalline state can be generated and retained in monosubstituted ferrocenomesogens, which was undertaken by Loubser and Imrie over the period 1993–1997 [3]. The authors synthesized a series of molecules based on the general structure **5**. The authors determined that a minimum of three benzene rings and a ferrocenyl group in the molecular core could stabilize the nematic phase, but that addition of a fourth benzene ring greatly enhanced nematic behaviour. The nematic phase was destabilized by increasing the length of the terminal alkoxy chain  $n$ , and lateral fluorination reduced the nematic phase range and suppressed smectic phases. It was shown that both the number and position of the fluorine atoms on the core was important. An alteration in the shape of the core by moving the carbonyloxy linker group from the 4- to the 3-position resulted in a suppression of the nematic phase as a result of introducing a kink into the molecular structure.

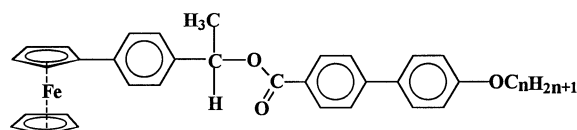
Loubser and Imrie also highlighted the importance of taking into account stability considerations when designing new organometallic liquid crystals. It was shown that the insertion of a benzene ring as a spacer between the ferrocenyl group and carbonyloxy linker resulted in a lowering of clearing temperature and increased both



11



12



13

the thermal and photochemical stabilities. Insertion of the spacer group attenuates the withdrawal of electron density from the ferrocenyl group, which would have resulted in a reduction of Cp–Fe back donation and subsequent weakening of the metal–ligand bonds. Compounds lacking the spacer were also found to be more prone to hydrolysis during the purification procedure.

Several other researchers have reported interesting results in the area of monosubstituted ferrocenomesogens and the field has been the subject of a recent review article [4]. In this current article, we present our latest results on the structure–liquid crystals activity of monosubstituted ferrocenomesogens.

## 2. Results and discussion

### 2.1. Synthesis and properties of elongated ferrocenes

The ferrocenomesogens synthesized in this work were designed according to the initial guidelines of Loubser and Imrie. Hence, a benzene ring was inserted as a spacer between the ferrocenyl group and the linker, and the core of the molecule contained at least three benzene rings (molecules contained a ferrocenyl group and at least three benzene rings). Within this framework, other variables with regard to the general structure **5** were of interest to us. These included, the effect of switching the linker group from  $-\text{COO}-$  to  $-\text{OOC}-$ , the effect of making  $j = 2$ , the effect of introducing different linker groups such as  $-\text{CH}=\text{N}-$ ,  $-\text{CH}_2\text{OOC}-$ ,  $-\text{CH}(\text{CH}_3)\text{OOC}-$ , the effect of lengthening the core

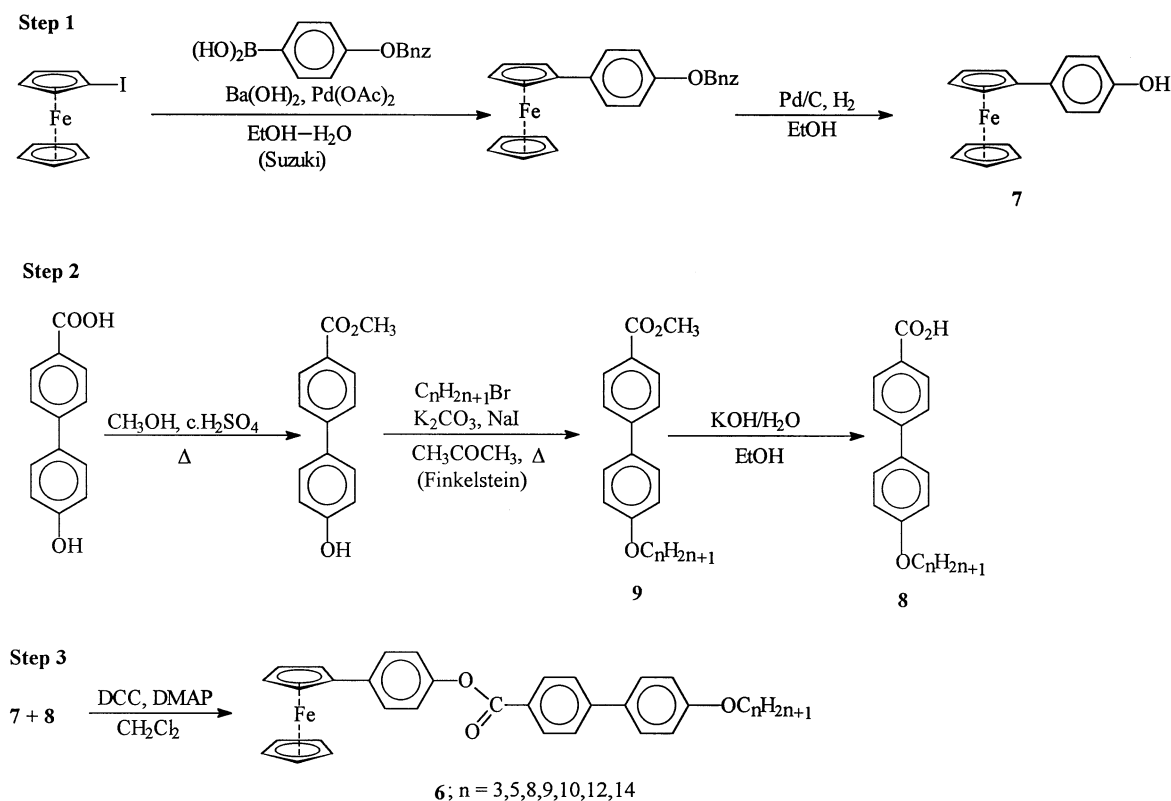
and the effect of using shorter terminal groups (CN and OCOOCH<sub>3</sub>).

The total synthesis of series **6** ( $n = 3, 5, 8, 9, 10, 12, 14$ ) is illustrated in **Scheme 1** and is representative of the types of reaction used in the synthesis of all series. 4-Ferrocenylphenol (**7**), synthesized via the Suzuki cross-coupling reaction of iodoferrocene and 4-benzyloxybenzeneboronic acid or by the diazonium method [5] was reacted with a series of 4'-alkoxy-4-biphenylcarboxylic acids (**8**) ( $n = 3, 5, 8, 9, 10, 12, 14$ ). The acids (**8**) were synthesized in three steps from 4-hydroxy-4'-biphenylcarboxylic acid. The etherification steps were performed using an adaption of the Finkelstein reaction [6] and good-to-excellent yields were achieved (46–98%). The final step in the syntheses of the compounds of series **6** involved the esterification of **8** which was accomplished by treating **8** with **7** in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP).

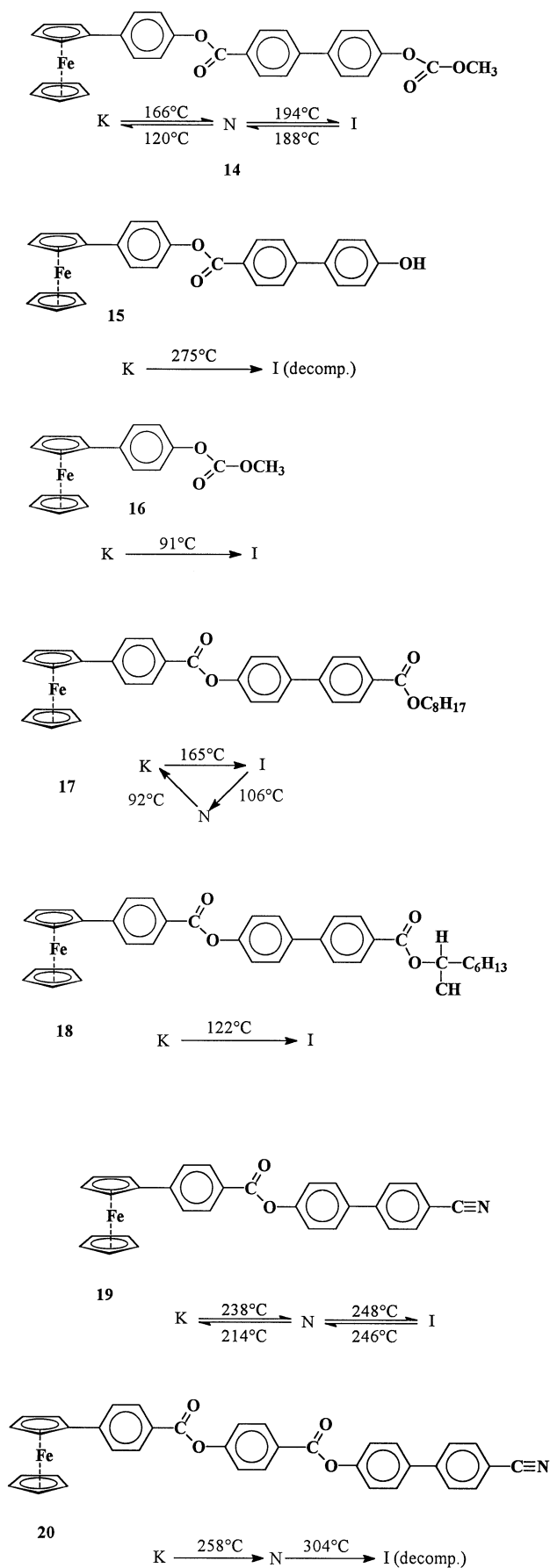
The phase transition temperatures of the compounds of series **6** (and all subsequent series) were determined from optical microscopy and differential scanning calorimetry (DSC). The phase transition temperatures for the series are provided in **Table 1**. All the compounds in series **6** exhibited stable nematic phases with characteristic Schlieren textures (**Fig. 2**) with the exception of the compounds where  $n = 3$  which was non-mesogenic and  $n = 5$  which exhibited a monotropic

nematic phase. As the length of the terminal alkoxy chain increased, smectic behaviour developed and the compounds where  $n = 8–10$  exhibited monotropic smectic A phases (the compound where  $n = 9$  also exhibited a short monotropic smectic C phase), and those with longer chains ( $n = 12, 14$ ) enantiotropic smectic A and monotropic smectic C phases. The texture of the smectic A phase was often observed as homeotropic, but sometimes it was seen as a focal conic as in **Fig. 3**. The smectic C phase was usually observed as a Schlieren texture developing from the homeotropic smectic A phase. The compounds of series **6** showed a reduction in clearing temperature as the length of the terminal alkoxy chain increased (**Fig. 4**); this type of behaviour has been observed previously [3]. The enthalpies of transition for the compounds of series **6** appear in **Table 2**.

Two series of precursors of **6** (**8** and **9**) were also mesogenic (with the exception of **9** where  $n = 3, 5$ ) and the observed phase transition temperatures correlated closely with those reported earlier by Gray et al. [7]. Comparing the phase behaviour of compounds in series **6** with their precursors (series **8**) illustrates the ability of a terminal ferrocenyl-phenyl group to stabilize the nematic liquid crystalline state. For example, in series **8**, the molecules where  $n = 12$  and 14 do not exhibit nematic behaviour and those in the series with shorter terminal chains have very narrow nematic ranges [7].



Scheme 1. The synthesis of 4-ferrocenylphenyl 4'-alkoxy-4-biphenylcarboxylates.



A comparison of the phase behaviour of compounds in series **6** with those of series **5** ( $j = 1$ ,  $i = 2$ ,  $X = \text{H}$ ,  $Y = \text{COO}$ ) synthesized by Loubser and Imrie previously, in which there has been a reversal of the carbonyloxy linkage, shows that aside from the different smectic behaviour, compounds in the two series have remarkably similar nematic behaviour and similar clearing temperatures. This is in contrast to results published by Deschenaux et al. in relation to isomeric 1,3- and 1,1'-disubstituted ferrocene derivatives where the reorientation of the ester functionality provided significantly different liquid crystal properties [8].

Loubser and Imrie previously established that a minimum of three benzene rings in the molecular core (total number of rings in molecule =  $1\text{Fc} + 3\text{Ph}$ ) stabilized the nematic phase and that the addition of a fourth benzene ring greatly enhanced nematic behaviour. However, since the latter conclusion was based on the properties of only two molecules, series **10** was synthesized in which another benzene ring was introduced into the core in relation to the compounds of series **6**, lengthening the linear rod-like shape of the general structure.

The total synthesis of the compounds of series **10** ( $n = 5, 8, 9, 10, 12, 14$ ) is illustrated in Scheme 2. The compounds of this series exhibited very broad and high temperature nematic phases (Table 3) and decomposition was evident for these compounds above  $250^\circ\text{C}$ . Two of the compounds of series **10** ( $n = 5, 8$ ) exhibited crystal-to-crystal transitions. The transitions generally occurred from a fluffy texture to a more structured texture.

A comparison of the phase behaviour of one of the compounds in series **10** ( $n = 8$ ) and a compound made previously by Loubser and Imrie (**11**) highlights the effect of lateral fluorination. Both compounds exhibited enantiotropic nematic phases with very broad liquid crystalline domains,  $84^\circ\text{C}$  for **10** ( $n = 8$ ) and  $100^\circ\text{C}$  for **11**. However, in the latter compound, there is a significant lowering of the clearing and melting points. This trend parallels that observed for organic liquid crystals when the introduction of a highly electronegative fluorine atom is known to be effective at reducing the melting point without disrupting the overall phase behaviour.

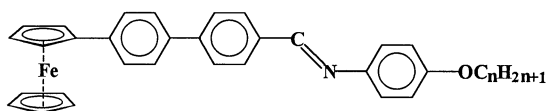
The insertion of additional methylene ( $\text{CH}_2$ ) and methylmethine  $\text{CH}(\text{CH}_3)$  spacers between the benzene ring of the ferrocenylphenyl unit and the carbonyloxy linkage resulted in the non-mesogenic derivatives **12** and **13** (Table 4). The new linker groups  $-\text{CH}_2\text{OOC}-$  and  $-\text{CH}(\text{CH}_3)\text{OOC}-$  would prevent conjugation between the ferrocenyl-phenyl group and the rest of the molecule which in turn would affect the polarity of the molecule. Computer modelling of compounds in series **6**, **12** and **13** (see Section 2.3) indicated that the introduction of the  $-\text{CH}_2-$  and  $-\text{CH}(\text{CH}_3)-$  spacers resulted in significant

Table 1  
The phase transition temperatures of series 6

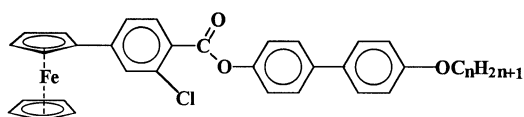
n	Temperature of phase transition (°C <sup>a,b</sup> )
3	$K \xrightleftharpoons[221]{229} I$
5	$\begin{array}{ccc} K & \xrightarrow{187} & I \\ & \searrow & \swarrow \\ & N & \\ & \swarrow & \searrow \\ 170 & & 178 \end{array}$
8	$\begin{array}{ccc} K & \xrightarrow{146} & N \xrightarrow[160]{161} I \\ & \searrow & \swarrow \\ & S_A & \\ 115 & & 126 \end{array}$
9	$\begin{array}{ccc} K & \xrightarrow{127} & N \xrightarrow[156]{157} I \\ & \searrow & \swarrow \\ & S_c & \\ 102 & & 130 \\ & \swarrow & \searrow \\ & S_A & \\ & 104 & \end{array}$
10	$\begin{array}{ccc} K & \xrightarrow{135} & N \xrightarrow[154]{155} I \\ & \searrow & \swarrow \\ & S_A & \\ 104 & & 134 \end{array}$
12	$\begin{array}{ccc} K & \xrightarrow{123} & S_A \xrightarrow[131]{133} N \xrightarrow[148]{149} I \\ & \searrow & \swarrow \\ & 72 & 92 \end{array}$
14	$\begin{array}{ccc} K & \xrightarrow{119} & S_A \xrightarrow[132]{136} N \xrightarrow[140]{143} I \\ & \searrow & \swarrow \\ & 82 & 100 \end{array}$

<sup>a</sup> Phase transition temperatures were calculated from a combination of optical microscopy and DSC.

<sup>b</sup> Abbreviations: K, crystalline; S<sub>A</sub>, smectic A-phase; S<sub>C</sub>, smectic C-phase; N, nematic phase; I, isotropic liquid.



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kinks in the molecular backbone of molecules in series **12** and **13**. The resultant kinks decrease the length/depth ( $l/d$ ) ratio of the molecules and when this drops below a certain value, the molecules become non-mesogenic. The results of the kinking effect are consistent with previous

observations reported by Loubser and Imrie; nematic phase behaviour was suppressed when the shape of the core was altered by moving the carbonyloxy linkage from the 4- to the 3-position with respect to the

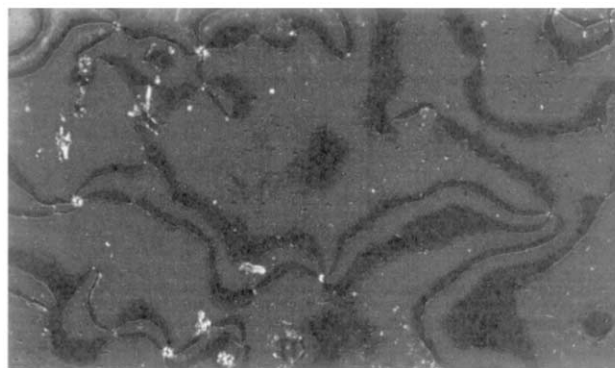


Fig. 2. Photomicrograph of a ferrocenomesogen in series **6** with a nematic phase exhibiting a Schlieren texture.

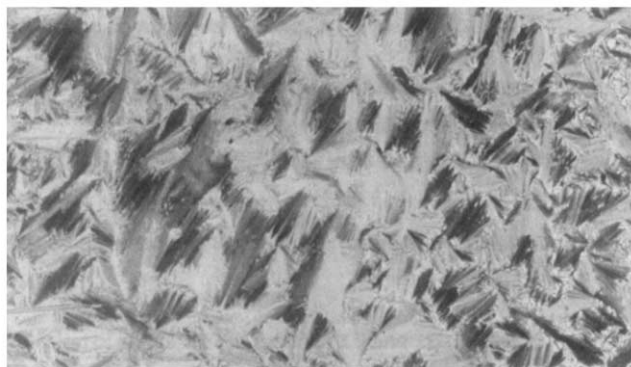


Fig. 3. Photomicrograph of a ferrocenomesogen in series 6 with a smectic A phase exhibiting a focal conic texture.

ferrocenyl group. The compounds of series 12 also exhibited changes in the crystalline form (crystal–crystal modifications) on heating and these modifications proved to be reproducible but were not observed by DSC. The methods used in the synthesis of 12 and 13 were similar to those described previously except that the esterification of compounds in series 13 was achieved by the Mitsunobo reaction instead of the DCC/DMAP protocol.

In an extension of series 6, compounds 14 and 15 were synthesized. Compound 14 exhibited an enantiotropic nematic phase with characteristic Schlieren textures, whilst compound 15 proved to be non-mesogenic. A DSC spectrum for 14 is shown in Fig. 5 and is representative of those obtained for most of the ferrocenomesogens. The solid state to nematic phase and nematic phase to isotropic liquid transitions are clearly observed. The phase behaviour of 14 may seem anomalous when compared to the compounds of series 6 especially those where  $n = 3$  and 5 (Table 1). However, X-ray crystallography of 14 provided evidence for the

involvement of hydrogen bonding in the development of an extended molecular architecture (see Section 2.2). Not surprisingly, 4-methoxycarbonyloxy-4'-phenylferrocene (16) (1Fc+1Ph ring) proved to be non-mesogenic and it does not conform to the guidelines established by Loubser and Imrie even, upon dimerization.

In the next facet of our work, we focused on modification of the  $n$ -alkoxy terminal group and compounds 17–20 were synthesized. In compounds 17 and 18, the terminal group was modified to a benzoate unit by insertion of an additional carbonyl group. Compound 17 exhibited a monotropic nematic phase whereas 18 proved to be non-mesogenic. The reduction of liquid crystalline properties in compounds 17 and 18 in relation to those of 5 ( $j = 1$ ,  $i = 2$ ,  $Y = \text{COO}$ ,  $X = \text{H}$ ,  $n = 8$ ) or 6 ( $n = 8$ ) upon introduction of a carbonyl group could possibly be rationalized in terms of a reversal of mesomerism resulting in an alteration of polarizability and intermolecular interactions. The introduction of an extra carbonyl group in 17 and 18 results in an additional kink in the molecular structure of these compounds with respect to 5 and 6 which would lead to a lower  $l/d$  ratio. Due to the non-mesogenic behaviour of 18 it was decided not to synthesize its chiral analogue (starting from  $S$ -(2)-octanol) as it is highly unlikely that this ferrocene derivative would be mesogenic.

In compounds 19 and 20, the terminal  $n$ -alkoxy chains used in previous series were replaced with terminal cyano groups. The cyano group is frequently used as the terminal group in liquid crystals as it is highly polarizable. Compounds synthesized by Gray et al. [7] which were at the forefront of the commercial exploitation of liquid crystals for electrooptic displays incorporated terminal cyano groups. The cyano group is known to stabilize the nematic phase and so we were most interested in investigating the effect of having a

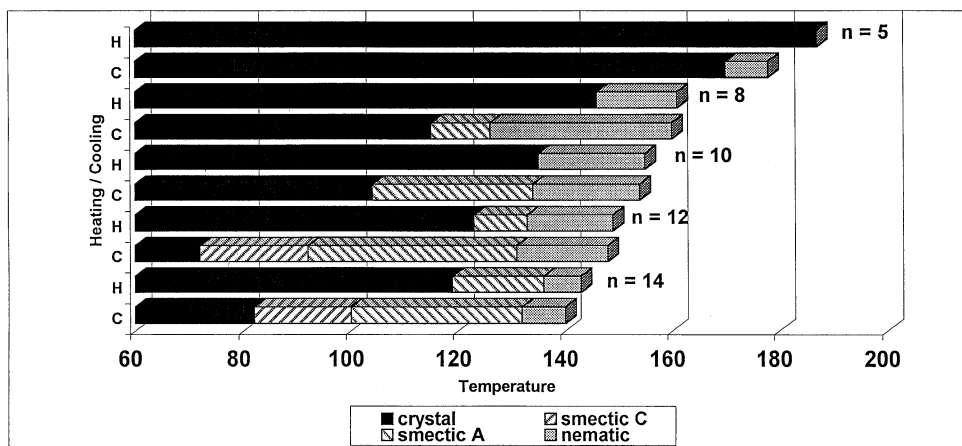
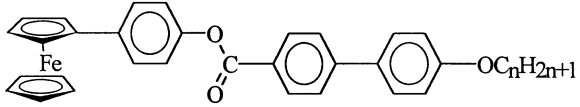


Fig. 4. Phase distribution for the molecules in series 6.



Table 2  
The enthalpies of transition ( $\Delta H/\text{kJ mol}^{-1}$ ) as observed for the compounds of series 6



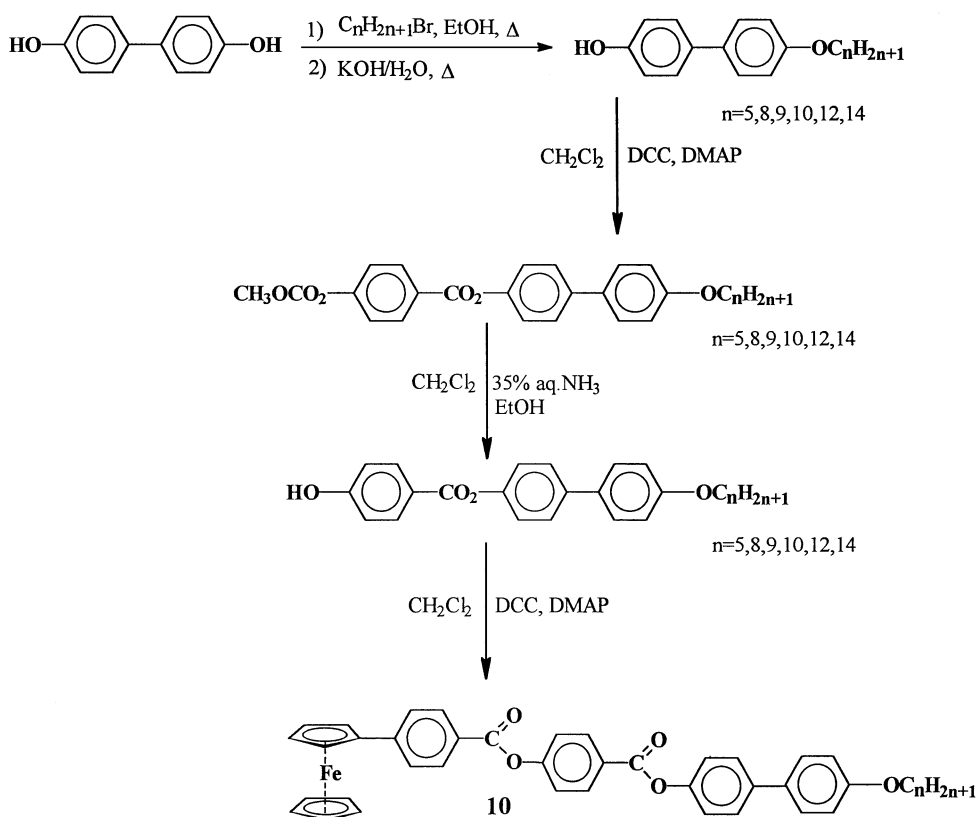
<i>n</i>	K → I	K → S <sub>A</sub>	K → N	S <sub>A</sub> → N	N → I	I → N	N → K	N → S <sub>A</sub>	S <sub>A</sub> → K	S <sub>A</sub> → S <sub>C</sub>	S <sub>C</sub> → K
5	33.3	–	–	–	–	7.52	21.52	–	–	–	–
8	–	–	41.9	–	1.02	1.33	–	25.7*	25.7*	–	–
9	–	–	33.9	–	1.12	1.06	–	NS	–	NS	NS
10	–	–	48.8	–	0.21	0.50	–	NS	36.1	–	–
12	–	28.6	–	0.75	0.85	1.02	–	–	–	NS	26.3
14	–	27.2	–	0.69	0.80	0.98	–	–	–	NS	22.2

Abbreviations: K, crystalline; S<sub>A</sub>, smectic A-phase; S<sub>C</sub>, smectic C-phase; N, nematic phase; I, isotropic liquid; NS, observed by polarized optical microscopy only; \*, only one large unresolved peak was observed for the two transitions.

terminal cyano and ferrocenyl group (a group which also appears to stabilize nematic phases) in the same molecule. Compound **19** exhibited a relatively short- and high-temperature nematic phase. A comparison of compound **19** with its *n*-alkoxy analogues **5** ( $j = 1$ ,  $i = 2$ , Y = COO, X = H,  $n = 8, 10, 12, 14$ ) revealed that the introduction of a terminal cyano group resulted in the complete suppression of smectic behaviour and con-

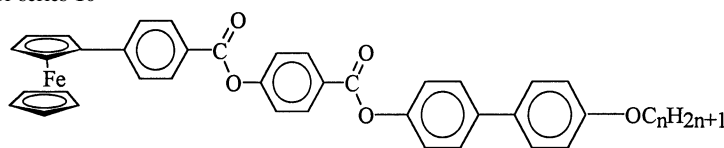
siderably elevates the clearing temperature (an increase of between 70 and 109 °C).

Compound **20** in which an additional benzene ring (1Fc+4Ph) was introduced with respect to **19** exhibited a relatively broad very high temperature nematic phase. Comparing the behaviour of compound **20** with its *n*-alkoxy analogues **10** once more showed the complete suppression of smectic behaviour upon introduction of



Scheme 2. The total synthesis of series 10.

Table 3  
The phase transition temperatures of series **10**



n	Temperature of phase transition (°C) <sup>a</sup>
5	K $\xrightarrow{178}$ K <sub>1</sub> $\xrightarrow{192}$ N $\xrightarrow{291}$ I (dec.)
8	K $\xrightarrow{163}$ K <sub>1</sub> $\xrightarrow{191}$ N $\xrightarrow{275}$ I (dec.)
9	K $\xrightarrow{172}$ N $\xrightarrow{268}$ I (dec.)
10	K $\xrightarrow{200}$ N $\xrightarrow{262}$ I (dec.)
12	K $\xrightarrow{147}$ S <sub>A</sub> $\xrightarrow{154}$ N $\xrightarrow{258}$ I (dec.)
14	K $\xrightarrow{141}$ S <sub>C</sub> $\xrightarrow{150}$ N $\xrightarrow{232}$ I (dec.)

<sup>a</sup> Phase transition temperatures were calculated from a combination of optical microscopy and DSC.

Abbreviations: K, crystalline; S<sub>A</sub>, smectic A-phase; S<sub>C</sub>, smectic C-phase; N, nematic phase; I, isotropic liquid.

the terminal cyano group. It was, however, not feasible to compare the liquid crystal domain size of these compounds (**20** and **10**) since **20** showed evidence of decomposition above 250 °C.

The series of Schiff's bases **21** ( $n = 5, 8, 14$ ) were synthesized, as we were interested in observing the effect of introducing a terminal ferrocenylbiphenyl unit into ferrocenomesogens. The compounds of series **21** were synthesized by the reaction of 4-formyl-4'-biphenylferrocene with a series of  $n$ -alkoxyanilines [9]. The compounds where  $n = 8$  and 14 exhibited enantiotropic smectic and nematic phases, whereas the compound where  $n = 5$  exhibited a monotropic nematic phase. In general, liquid crystal domains were short and once again, the effects of increasing the length of the alkoxy chain with relation to the lowering of clearing temperatures were observed.

Finally, the compounds of series **22** were synthesized in which a lateral chlorine atom was introduced on the benzene ring of the ferrocenylphenyl unit. The compounds of series **22** exhibited low-temperature monotropic nematic phases with characteristic Schlieren textures.

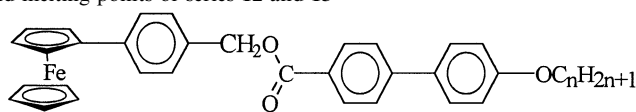
## 2.2. Crystal structure of 4-methoxycarbonyloxy-4'-biphenylcarboxyphenylferrocene

Compound **14** containing a bulky terminal ferrocenyl group and a short terminal methoxycarbonyloxy group

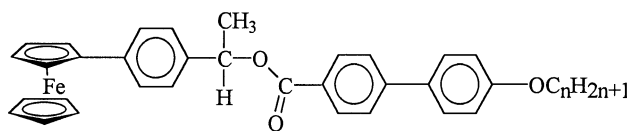
exhibits a short but stable nematic liquid crystal phase. The molecular structure of **14** together with numbering scheme is shown in Fig. 6. The unit cell is triclinic and the bond lengths and angles fall within the expected limits (Table 5). The molecular geometry is extended and linear. The two cyclopentadienyl rings in the ferrocenyl group are eclipsed. The cyclopentadienyl ring and the adjacent phenyl ring are tilted at an angle of 1.3° with respect to one another. The phenyl rings in the biphenyl group are tilted at an angle of 2.2° with respect to one another. The biphenyl unit is approximately orthogonal to the ferrocenylphenyl unit. The molecular packing is depicted in Fig. 7. This emphasizes the interesting arrangement between molecules within a layer and between two layers. The molecules are arranged parallel to each other in an extended fashion in a head-to-tail/tail-to-head format. The position of the formate ester groups allows for hydrogen bonding between O(2) in one molecule and H···C(58) in another molecule. The distance between O(2) and C(58) is 3.129 Å and between O(2)–HC(58) 2.4854 Å. The O(2)–HC(58) distance is well within the range to allow hydrogen bonding.  $\pi$ – $\pi$  Stacking of the aromatic rings enforces the extended molecular arrangement. For example, the average intermolecular distance between the aromatic ring containing C41–C46 to the ring containing C51–C55 is 3.69 Å. Recently, Tse et al. [10] reported  $\pi$  stacking between the aromatic planes of



Table 4  
The phase transition temperatures and melting points of series **12** and **13**



n	Phase transition (°C) <sup>a,b</sup>
8	$K_1 \xrightarrow{66} K_2 \xrightarrow{91} I$
10	$K_1 \xrightarrow{66} K_2 \xrightarrow{97} I$ $\xleftarrow{59}$
14	$K_1 \xrightarrow{76} K_2 \xrightarrow{99} I$ $\xleftarrow{80}$



n	Melting point (°C) <sup>a,b</sup>
8	$K \xrightarrow{89-92} I$
10	$K \xrightarrow{89-92} I$
14	$K \xrightarrow{93-94} I$

<sup>a</sup> Phase transitions are quoted as observed with optical microscopy.

<sup>b</sup> Abbreviations: K, crystalline; I, isotropic liquid.

some cyclometallated platinum(II) polymeric structures with an average distance of 3.68 Å.

### 2.3. Structure–liquid crystal properties of elongated ferrocenes

In order for a molecule to exhibit calamitic mesomorphism, it should normally have a long linear shape and a large enough *l/d* ratio so that significant intermolecular interactions can be generated. We have in one of our previous papers [9] reported on conformational searches on molecules in series **6**, **12**, **13**, and **21**. Calculation of the approximate *l/d* ratios was carried out for molecules in each series (for molecules with an octyloxy terminal group). The clear trend from these results was that monosubstituted ferrocenesomesogens have a much larger *l/d* ratio than non-liquid crystalline elongated ferrocenes. The lowest energy conformation of non-mesogenic molecules in series **12** and **13** show pronounced kinks in the molecular structure that result in lower *l/d* values.

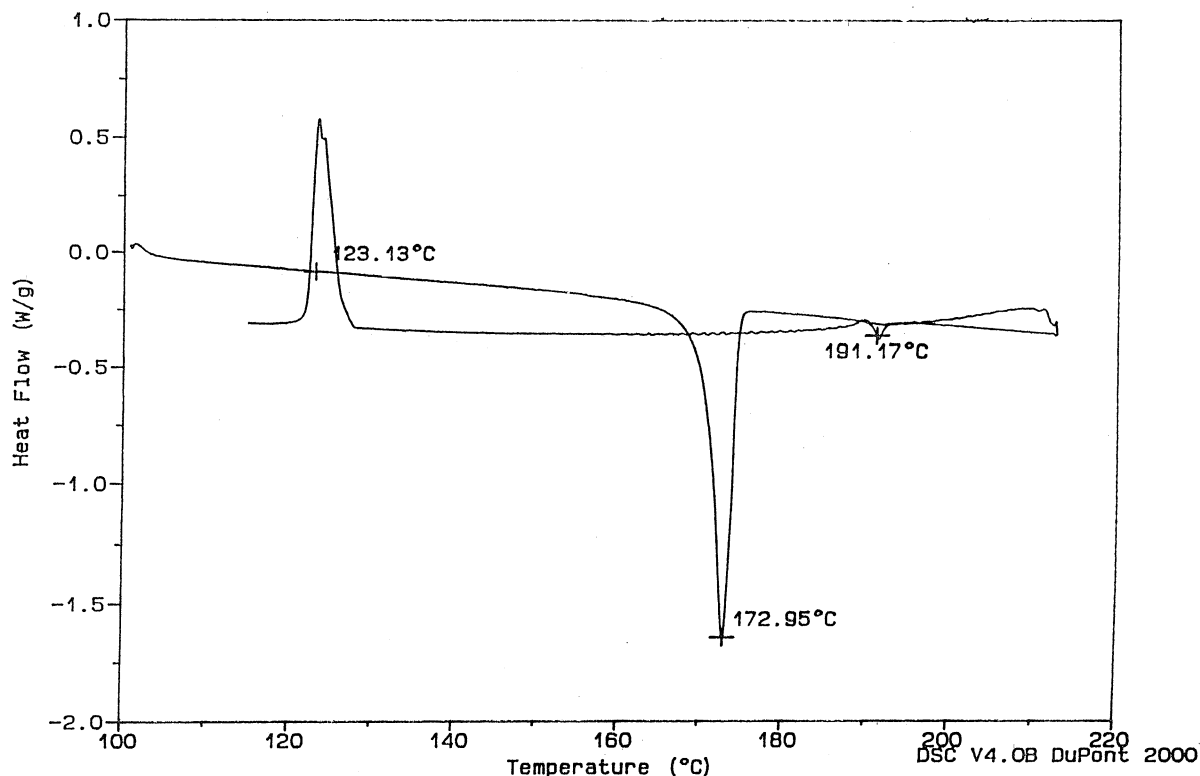
### 3. Conclusion

Monosubstituted ferrocene derivatives with large enough *l/d* ratios can support liquid crystal behaviour. The terminal ferrocenyl group is particularly good at supporting stable nematic phases and phase behaviour is normally observed at temperatures in excess of 100 °C. Large lateral or linker groups that introduce kinks in these molecules inhibit liquid crystal formation.

### 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<sub>2</sub>O<sub>3</sub> (active, neutral, Brockmann Grade I) were used for column chromatography. Plate chromatography was performed on a model 7924T Harrison chromatotron using silica gel 60PF-254 as adsorbent with CaSO<sub>4</sub> as binder or thin layer preparative chromatography plates using Merck silica gel 60 F<sub>254</sub> (1.5 mm). Melting points were recorded

Fig. 5. DSC spectrum of compound **14**.

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 or as solutions in  $\text{CHCl}_3$ .  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer as solutions in  $\text{CDCl}_3$  or  $\text{Me}_2\text{SO}-d_6$  using tetramethylsilane ( $\text{Me}_4\text{Si}$ ) as internal standard;  $^1\text{H}$ -NMR peak frequencies are quoted in ppm and coupling constants in Hz. Mass spectra were recorded on an AEI MS 902/MSS update (70 eV, direct insertion probe) at the Cape Technikon. Microanalyses were performed by the Council for Scientific and Industrial Research, Pretoria and at the University of Cape Town. Crystal X-ray crystallography was performed at the Inorganic Chemistry Laboratory

at Oxford University. Transition temperatures were investigated by 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  $10\text{ }^\circ\text{C min}^{-1}$ ) for both the heating and cooling cycle, 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. Photomicrographs were ta-

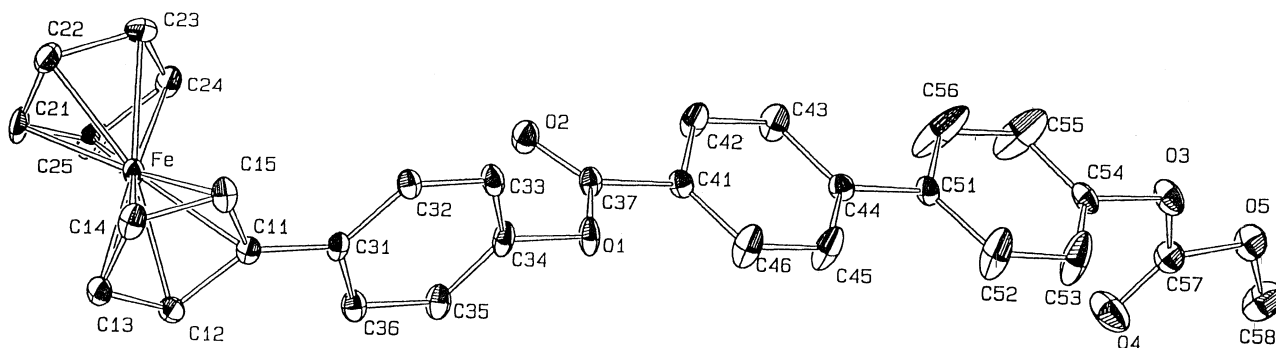
Fig. 6. Molecular structure of **14** with numbering scheme.

Table 5  
Selected bond lengths (Å) and angles (°) for compound **14**

Bond lengths			
Fe–C(11)	2.034(5)	Fe–C(15)	2.037(5)
Fe–C(12)	2.039(4)	Fe–C(23)	2.040(4)
Fe–C(14)	2.042(4)	Fe–C(22)	2.043(5)
Fe–C(13)	2.043(4)	Fe–C(24)	2.046(4)
Fe–C(21)	2.050(5)	Fe–C(25)	2.058(5)
O(1)–C(37)	1.360(5)	O(1)–C(34)	1.423(5)
O(2)–C(37)	1.201(6)	O(3)–C(57)	1.351(6)
O(3)–C(54)	1.417(5)	O(4)–C(57)	1.179(7)
O(5)–C(57)	1.322(6)	O(5)–C(58)	1.443(6)
C(11)–C(12)	1.422(6)	C(11)–C(15)	1.439(6)
C(11)–C(31)	1.485(6)	C(12)–C(13)	1.427(6)
C(13)–C(14)	1.411(7)	C(14)–C(15)	1.429(7)
C(21)–C(22)	1.416(8)	C(21)–C(25)	1.423(7)
C(22)–C(23)	1.427(8)	C(23)–C(24)	1.413(7)
C(24)–C(25)	1.424(8)		
Bond angles			
C(11)–Fe–C(15)	41.41(17)	C(11)–Fe–C(12)	40.85(18)
C(15)–Fe–C(12)	68.95(19)	C(37)–O(1)–C(34)	115.0(4)
C(57)–O(3)–C(54)	115.4(4)		

ken with a Zeiss MC63 photo-micrographic camera mounted on a standard Zeiss polarizing microscope equipped with a Reichert hot stage. 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. Unless otherwise stated all recrystallizations were performed at room temperature (r.t.). If more than one solvent was used to perform the recrystalliza-

tion, two different annotations are used. For example, CH<sub>2</sub>Cl<sub>2</sub>/EtOH denotes that a mixture of two solvents were used, whereas CH<sub>2</sub>Cl<sub>2</sub>–EtOH denotes that CH<sub>2</sub>Cl<sub>2</sub> was used to dissolve the solid and the slow addition of EtOH resulted in crystallization. The X-ray data were collected on an Enraf–Nonius DIP2000 image-plate diffractometer with monochromated Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The images were processed with the DENZO and SCALEPAK programs [11]. The structure was solved via direct methods [12] and refined by full-matrix least-squares [13]. A representative synthesis of one member of each of the series **6**, **10**, **12** and **13** is provided. The full data on other members of each series is provided in the supplementary information.

## 4.2. Synthesis

### 4.2.1. 2-Chloro-4-ferrocenylbenzoic acid

2-Chloro-4-ferrocenylbenzoic acid was synthesized by the diazonium method. Quantities: 4-amino-2-chlorobenzoic acid (5.35 g, 31.2 mmol), ferrocene (5.80 g, 31.2 mmol) and NaNO<sub>2</sub> (2.90 g, 42.0 mmol). 2-Chloro-4-ferrocenylbenzoic acid (0.57 g, 5%) was filtered off as red crystals which were recrystallized from hot C<sub>3</sub>H<sub>6</sub>O, m.p. 180 °C (dec.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3050–2800 (br), 1686, 1598, 1565, 1505, 1427, 1407, 1306, 1257, 1162, 1104, 1089, 1044, 931, 906, 879;  $\delta_{\text{H}}(\text{Me}_2\text{SO}-d_6)$  7.67 (1H, d, *J* 8.2, ArH), 7.58 (1H, s, ArH), 7.51 (1H, d, *J* 8.1, ArH), 4.88 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.38 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 3.99 (5H, s, C<sub>5</sub>H<sub>5</sub>); *m/z* 340 ([M<sup>+</sup>], 11%), 260

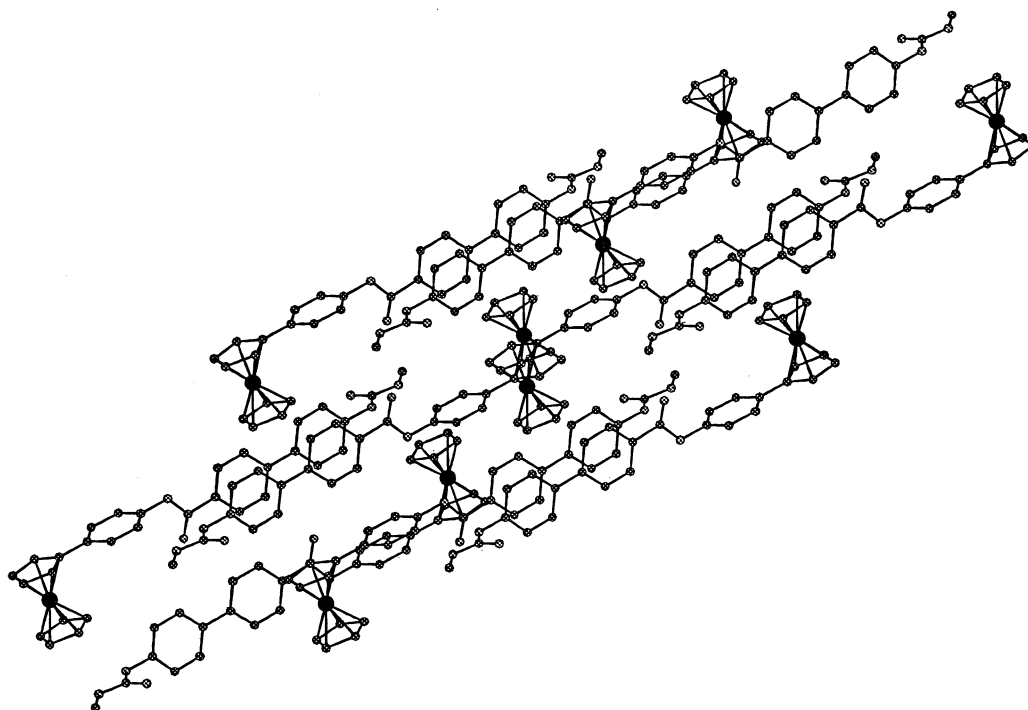


Fig. 7. Molecular packing diagram for compound **14**.

(5), 219 (18), 217 (5), 203 (5), 189 (5), 167 (5), 163 (5), 154 (7), 149 (21), 147 (7), 145 (5), 137 (5), 136 (7), 133 (6), 131 (6), 129 (9), 128 (5), 123 (6), 121 (7), 97 (16), 95 (21), 91 (20), 87 (15), 85 (17), 84 (40), 83 (27), 81 (27), 79 (15), 77 (15), 71 (34), 69 (48), 67 (28), 57 (100), 55 (77). Anal. Found: C, 60.0; H, 4.4%;  $[M^+]$ , 339.9940. Calc. for  $C_{17}H_{13}ClFeO_2$ : C, 60.0; H, 3.8%;  $[M^+]$ , 339.9952.

#### 4.2.2. 4-Methoxycarbonyloxyphenylferrocene

A solution of NaOH (0.12 g, 3.0 mmol) in water (10  $cm^3$ ) was chilled to 0 °C in ice and to this was added 4-ferrocenylphenol (0.30 g, 1.1 mmol). Methyl chloroformate (0.30 g, 3.2 mmol) was added slowly keeping the temperature of the reaction mixture below 5 °C. After stirring the mixture for 3 h at 0 °C, the solution was acidified using dilute HCl. The solution was then extracted with  $Et_2O$  and after removing the solvent, the residue was subjected to column chromatography, elution with  $C_6H_{14}/CH_2Cl_2$  (1:1) afforded the product. Yield of **17** obtained was 0.19 g, 51%, m.p. 91 °C;  $\nu_{max}(KBr)/cm^{-1}$  3109, 3088, 3010, 2961, 2853, 1754, 1525, 1458, 1440, 1267, 1218, 1105, 1087, 1067, 1036, 1020, 1002, 951, 932, 888, 848, 823, 780, 740, 529, 500;  $\delta_H(CDCl_3)$  7.47 (2H, d,  $J$  8.8, ArH), 7.11 (2H, d,  $J$  8.8, ArH), 4.61 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.32 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.05 (5H, s,  $C_5H_5$ ), 3.92 (3H, s,  $CH_3$ );  $m/z$  337 (33%), 336 ( $[M^+]$ , 100), 334 (11), 278 (32), 277 (49), 249 (25), 121 (51). Anal. Found: C, 64.4; H, 4.8%;  $[M^+]$ , 336.0445. Calc. for  $C_{18}H_{16}FeO_3$ : C, 64.4; H, 4.8%;  $[M^+]$ , 336.0444.

#### 4.2.3. 4-Ferrocenylphenyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate (**14**)

A solution of 4'-methoxycarbonyloxy-4-biphenylcarboxylic acid (835 mg, 3.1 mmol), 4-ferrocenylphenol (853 mg, 3.1 mmol) and DMAP (125 mg, 1.0 mmol) in anhydrous  $CH_2Cl_2$  (15  $cm^3$ ) was prepared under an atmosphere of dry nitrogen. A solution of DCC (787 mg, 3.8 mmol) in anhydrous  $CH_2Cl_2$  (40  $cm^3$ ) was then added over 1 min and the solution stirred at r.t. for 5 days. The solution was then filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography over silica gel using a mixture of  $C_6H_{14}-CH_2Cl_2$  (1:1) as the eluent. The solvent was removed from the collected fractions and the yellow solid was recrystallized from  $MeOH-CH_2Cl_2$  (1.18 g, 72%) in the cold, m.p. (liquid crystal) 166, 194 °C;  $\nu_{max}(KBr)/cm^{-1}$  3079, 2960, 2922, 2362, 1769, 1714, 1604, 1519, 1491, 1437, 1396, 1268, 1222, 1183, 1164, 1104, 1072, 1028, 1004, 933, 883, 810;  $\delta_H(CDCl_3)$  8.28 (2H, d,  $J$  8.5, ArH), 7.71 (2H, d,  $J$  8.5, ArH), 7.67 (2H, d,  $J$  8.7, ArH), 7.54 (2H, d,  $J$  8.7, ArH), 7.31 (2H, d,  $J$  8.7, ArH), 7.17 (2H, d,  $J$  8.6, ArH), 4.64 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.33 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.07 (5H, s,  $C_5H_5$ ), 3.94 (3H, s,  $OCH_3$ );  $\delta_C(CDCl_3)$  156.2, 153.3, 151.1, 147.2, 139.9, 139.1, 132.8, 130.5, 129.2, 129.1, 86.8, 71.6,

71.0, 68.6, 57.5;  $m/z$  533 (31%), 532 ( $[M^+]$ , 100), 530 (7), 337 (6), 336 (29), 278 (8), 277 (15), 256 (9), 255 (51), 168 (9), 140 (5), 139 (5). Anal. Found: C, 69.9; H, 4.5%;  $[M^+]$ , 532.09716. Calc. for  $C_{31}H_{24}FeO_5$ : C, 69.9; H, 4.5%;  $[M^+]$ , 532.0973.

#### 4.2.4. 4-Ferrocenylphenyl 4'-hydroxy-4-biphenylcarboxylate (**15**)

4-Ferrocenylphenyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate (920 mg, 1.7 mmol) was suspended in a mixture of  $CH_2Cl_2$  (370  $cm^3$ ), EtOH (75  $cm^3$ ) and  $NH_3$  (35%, 55  $cm^3$ ) and the mixture stirred overnight at r.t. The solvents were removed in vacuo and the residue purified by utilizing the insoluble nature of the compound, impurities were washed out with  $CH_2Cl_2$ . The residue was filtered leaving a yellow solid identified as 4-ferrocenylphenyl 4'-hydroxy-4-biphenylcarboxylate (716 mg, 87%), m.p. 275 °C (dec.);  $\nu_{max}(KBr)/cm^{-1}$  3414, 1712, 1590, 1521, 1497, 1442, 1277, 1187, 1093, 1014, 887, 832;  $\delta_H(Me_2SO-d_6)$  8.17 (2H, d,  $J$  8.3, ArH), 7.84 (2H, d,  $J$  8.3, ArH), 7.64 (4H, m, ArH), 7.23 (2H, d,  $J$  8.5, ArH), 6.92 (2H, d,  $J$  8.5, ArH), 4.81 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.36 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.05 (5H, s,  $C_5H_5$ );  $m/z$  475 (34%), 474 ( $[M^+]$ , 100), 472 (6), 279 (10), 278 (51), 255 (13), 277 (14), 198 (13), 197 (90), 169 (15), 168 (8), 150 (9), 141 (14), 121 (20). Anal. Found:  $[M^+]$ , 474.09225. Calc. for  $C_{29}H_{22}FeO_3$ :  $[M^+]$ , 474.09183.

#### 4.2.5. Representative synthesis of compounds in series **6**

4.2.5.1. 4-Ferrocenylphenyl 4'-propyloxy-4-biphenylcarboxylate (**6**,  $n = 3$ ). Quantities: 4'-propyloxy-4-biphenylcarboxylic acid (227 mg, 0.89 mmol), 4-ferrocenylphenol (255 mg, 0.92 mmol), DCC (244 mg, 1.18 mmol) and DMAP (51 mg, 0.42 mmol). The experimental procedure was as described in Section 4.2.3. The product **6** ( $n = 3$ ) was obtained as yellow crystals and was recrystallized from  $CH_2Cl_2/MeOH$  (85 mg, 18%), m.p. 229 °C;  $\nu_{max}(KBr)/cm^{-1}$  3080, 2968, 2934, 2878, 1723, 1603, 1522, 1497, 1473, 1454, 1403, 1298, 1271, 1200, 1170, 1104, 1072, 1029, 1014, 875, 826, 766, 717, 536;  $\delta_H(CDCl_3)$  8.18 (2H, d,  $J$  8.4, ArH), 7.64 (2H, d,  $J$  8.4, ArH), 7.54 (2H, d,  $J$  8.7, ArH), 7.47 (2H, d,  $J$  8.6, ArH), 7.10 (2H, d,  $J$  8.6, ArH), 6.95 (2H, d,  $J$  8.7, ArH), 4.57 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.26 (2H, t,  $J$  1.8,  $C_5H_4$ ), 4.01 (5H, s,  $C_5H_5$ ), 3.92 (2H, t,  $J$  6.6,  $OCH_2$ ), 1.79 (2H, m,  $CH_2$ ), 1.00 (3H, m,  $CH_3$ );  $m/z$  518 (7%), 517 (38), 516 ( $[M^+]$ , 100), 514 (7), 444 (5), 363 (7), 331 (7), 325 (6), 317 (18), 301 (7), 287 (5), 283 (6), 275 (9), 262 (6), 251 (12), 244 (7), 239 (22), 233 (11), 232 (12), 225 (10), 213 (24), 183 (16), 151 (63), 149 (14), 147 (9), 144 (7), 133 (28), 132 (18), 120 (13), 101 (30), 95 (15), 85 (18), 70 (22), 56 (13), 43 (11). Anal. Found: C, 73.8; H, 5.4%;  $[M^+]$ , 516.1385. Calc. for  $C_{32}H_{28}FeO_3$ : C, 74.4; H, 5.5%;  $[M^+]$ , 516.1388.

#### 4.2.6. 1-(4-Ferrocenylphenyl)ethyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate

Quantities: 4'-methoxycarbonyloxy-4-biphenylcarboxylic acid (433 mg, 1.59 mmol), 4-(1-hydroxyethyl)phenylferrocene (405 mg, 1.32 mmol), DMAP (54 mg, 0.44 mmol), DCC (412 mg, 2.00 mmol). The experimental procedure was as described in Section 4.2.3. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–MeOH in the cold (297 mg, 40%), m.p. 162 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3340, 2928, 1709, 1687, 1603, 1527, 1496, 1448, 1404, 1362, 1321, 1266, 1197, 1110, 1062, 1019, 997, 885, 856, 832, 774;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.24 (2H, d, *J* 8.5, ArH), 7.72 (2H, d, *J* 8.4, ArH), 7.71 (2H, d, *J* 8.6, ArH), 7.56 (2H, d, *J* 8.2, ArH), 7.46 (2H, d, *J* 8.2, ArH), 7.36 (2H, d, *J* 8.7, ArH), 6.24 (1H, q, *J* 6.6, CH), 4.70 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.38 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.12 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.01 (3H, t, *J* 6.6, OCH<sub>3</sub>), 1.78 (3H, d, *J* 6.6, CH<sub>3</sub>); *m/z* 560 ([M<sup>+</sup>], 10%), 290 (8), 289 (22), 288 (100), 286 (9), 272 (19), 228 (23), 214 (5), 213 (14), 185 (12), 168 (6), 167 (10), 165 (7), 152 (5), 139 (9), 121 (9). Anal. Found: [M<sup>+</sup>], 560.1278. Calc. for C<sub>33</sub>H<sub>28</sub>FeO<sub>5</sub>: [M<sup>+</sup>], 560.1285.

#### 4.2.7. Representative synthesis of compound in series 13

4.2.7.1. 1-(4-Ferrocenylphenyl)ethyl 4'-octyloxy-4-biphenylcarboxylate (**13**, *n* = 8). A solution of 4'-octyloxy-4-biphenylcarboxylic acid (533 mg, 1.6 mmol), 4-(1-hydroxyethyl)phenylferrocene (500 mg, 1.6 mmol) and diethylazodicarboxylate (DEAD) (347 mg, 2.0 mmol) in anhydrous tetrahydrofuran (THF) (40 cm<sup>3</sup>) was prepared under an atmosphere of dry Ar. A solution of triphenylphosphine (522 mg, 2.0 mmol) in anhydrous THF (5 cm<sup>3</sup>) was then slowly added and the solution stirred for 2 weeks at r.t. The solvent was then removed on a rotary evaporator, and the product recovered on a short silica gel column using CH<sub>2</sub>Cl<sub>2</sub>–C<sub>6</sub>H<sub>14</sub> (3:1) as the eluent. The initial orange band was collected, the solvent was then removed and the residue recrystallized from CH<sub>2</sub>Cl<sub>2</sub>–MeOH in the cold (240 mg, 24%), m.p. 89–92 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2925, 2853, 1709, 1609, 1524, 1495, 1472, 1395, 1339, 1280, 1246, 1187, 1118, 1102, 1058, 999, 829;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.16 (2H, d, *J* 8.5, ArH), 7.65 (2H, d, *J* 8.5, ArH), 7.58 (2H, d, *J* 8.5, ArH), 7.50 (2H, t, *J* 8.5, ArH), 7.40 (2H, d, *J* 8.5, ArH), 7.01 (2H, d, *J* 8.5, ArH), 6.19 (1H, q, *J* 6.5, CH), 4.64 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.33 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.09 (5H, s, C<sub>5</sub>H<sub>5</sub>), 4.02 (2H, t, *J* 6.6, OCH<sub>2</sub>), 1.82 (2H, m, CH<sub>2</sub>), 1.72 (3H, d, *J* 6.6, CH<sub>3</sub>), 1.31 (10H, m, 5 × CH<sub>2</sub>), 0.90 (3H, t, CH<sub>3</sub>);  $\delta_{\text{C}}(\text{CDCl}_3)$  165.6, 159.2, 145.1, 139.1, 138.8, 132.0, 130.0, 128.1, 126.2, 126.1, 126.0, 114.7, 85.1, 72.5, 69.8, 68.5, 68.0, 66.4, 31.6, 29.2, 29.0, 25.8, 22.5, 22.0, 13.9; *m/z* 614 ([M<sup>+</sup>], 2%), 327 (14), 326 (59), 289 (38), 288 (67), 287 (5), 286 (17), 223 (5), 215 (28), 214 (100), 167 (18), 152 (9), 149 (7), 144 (9), 141 (6), 139 (8), 137 (8), 136 (5), 121 (18), 81 (23), 69 (54), 57 (32), 43

(39). Anal. Found: C, 76.1; H, 6.9%; [M<sup>+</sup>], 614.2471. Calc. for C<sub>39</sub>H<sub>42</sub>FeO<sub>3</sub>: C, 76.3; H, 6.9%; [M<sup>+</sup>], 614.2481.

#### 4.2.8. 4-Hydroxymethylphenylferrocene

4.2.8.1. *Step one. 4-Ferrocenylbenzoyl imidazolide.* A solution of 1,1'-carbonyldiimidazole (13.24 g, 81.7 mmol) in anhydrous THF (500 cm<sup>3</sup>) was added to a solution of 4-ferrocenylbenzoic acid (5.00 g, 16.3 mmol) in anhydrous THF (30 cm<sup>3</sup>) and the mixture stirred for 24 h at r.t. The solvent volume was reduced to ca. 20 cm<sup>3</sup>, and this solution was passed rapidly through a silica gel column. Elution with Et<sub>2</sub>O afforded the product which was obtained as a red solid (4.28 g, 74%), m.p. 157–158 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2923, 2853, 1682, 1601, 1525, 1469, 1419, 1379, 1312, 1284, 1271, 1252, 1198, 1178, 1123, 1105, 1084, 1068, 1036, 1018, 969, 905, 882, 852, 836, 746, 694;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.07 (1H, s, C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>), 7.68 (2H, d, *J* 8.3, ArH), 7.55 (2H, d, *J* 8.3, ArH), 7.51 (1H, s, C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>), 7.12 (1H, s, C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>), 4.68 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.39 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.01 (5H, s, C<sub>5</sub>H<sub>5</sub>); *m/z* 356 ([M<sup>+</sup>], 13%), 307 (2), 306 (11), 261 (7), 168 (3), 140 (4), 139 (5). Anal. Found: [M<sup>+</sup>], 356.0622. Calc. for C<sub>20</sub>H<sub>16</sub>FeN<sub>2</sub>O: [M<sup>+</sup>], 356.0610.

4.2.8.2. *Step two. Reduction of 4-ferrocenylbenzoyl imidazolide.* 4-Ferrocenylbenzoyl imidazolide (3.00 g, 8.4 mmol) was added to a solution of Et<sub>2</sub>O (250 cm<sup>3</sup>) containing lithium aluminium hydride (LAH) (0.64 g, 16.8 mmol). The solution was stirred for 1 h at r.t. prior to heating under reflux for 3 h. Excess LAH was destroyed by the addition of EtOAc, and then by addition of a cold ice–water slurry. The reaction mixture was filtered, extracted with Et<sub>2</sub>O (3 × 100 cm<sup>3</sup>) and the combined ether extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo and the residue passed through a column of silica gel, elution with CH<sub>2</sub>Cl<sub>2</sub>–C<sub>6</sub>H<sub>14</sub> (3:1) afforded the product. 4-Hydroxybenzylferrocene was obtained as yellow crystals (1.10 g, 45%), m.p. 109.5–110 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3287 (br), 2924, 1611, 1526, 1423, 1368, 1279, 1213, 1106, 1081, 1035, 1000, 886, 843, 804, 651, 537, 507, 482;  $\delta_{\text{H}}(\text{CDCl}_3)$  7.47 (2H, d, *J* 8.2, ArH), 7.28 (2H, d, *J* 8.2, ArH), 4.66 (2H, d, *J* 5.5, CH<sub>2</sub>), 4.64 (2H, t, *J* 1.8, C<sub>5</sub>H<sub>4</sub>), 4.31 (2H, t, *J* 1.7, C<sub>5</sub>H<sub>4</sub>), 4.04 (5H, s, C<sub>5</sub>H<sub>5</sub>); *m/z* 293 (21%), 292 ([M<sup>+</sup>], 100), 290 (12), 227 (13), 154 (54), 153 (11), 152 (13), 121 (7). Anal. Found: C, 70.0; H, 5.8%; [M<sup>+</sup>], 292.0546. Calc. for C<sub>17</sub>H<sub>16</sub>FeO: C, 69.9; H, 5.5%; [M<sup>+</sup>], 292.0549.

#### 4.2.9. 4-Ferrocenylbenzyl 4'-methoxycarbonyloxy-4-biphenylcarboxylate

A solution of 4'-methoxycarbonyloxy-4-biphenylcarboxylic acid (189 mg, 0.69 mmol), 4-hydroxybenzylferrocene (200 mg, 0.68 mmol) and DMAP (44 mg, 0.15



mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (40  $\text{cm}^3$ ) was prepared under an atmosphere of dry nitrogen. A solution of DCC (189 mg, 0.92 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) was then added over 1 min and the solution stirred at r.t. for 5 days. The solution was then filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography over silica gel using  $\text{CH}_2\text{Cl}_2$  as the eluent. The solvent was removed from the collected fractions and the yellow solid was recrystallized from  $\text{CH}_2\text{Cl}_2$ –MeOH (270 mg, 72%), m.p. 150 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3934–3150 (br), 2949, 1760, 1709, 1611, 1526, 1497, 1440, 1377, 1269, 1217, 1175, 1103, 1011, 937, 823, 771;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.09 (2H, d, *J* 8.3, ArH), 7.58 (2H, d, *J* 8.3, ArH), 7.55 (2H, d, *J* 8.3 ArH), 7.44 (2H, d, *J* 8.2, ArH), 7.32 (2H, d, *J* 8.1, ArH), 7.23 (2H, d, *J* 8.1, ArH), 5.29 (2H, s,  $\text{CH}_2\text{O}$ ), 4.58 (2H, t, *J* 1.8,  $\text{C}_5\text{H}_4$ ), 4.26 (2H, t, *J* 1.8,  $\text{C}_5\text{H}_4$ ), 3.98 (5H, s,  $\text{C}_5\text{H}_5$ ), 3.87 (3H, s,  $\text{OCH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  166.73, 154.60, 151.53, 145.09, 139.97, 138.40, 133.85, 130.73, 129.51, 128.85, 127.46, 126.70, 121.95, 85.25, 70.03, 69.45, 67.14, 66.99, 55.95; *m/z* 548 (9%), 547 (41), 546 ( $[\text{M}^+]$ , 100), 544 (7), 275 (10), 251 (7), 155 (7), 154 (45), 153 (6). Anal. Found: C, 69.9; H, 5.0%;  $[\text{M}^+]$ , 546.1130. Calc. for  $\text{C}_{32}\text{H}_{26}\text{FeO}_5$ : C, 70.3; H, 4.8%;  $[\text{M}^+]$ , 546.1130.

#### 4.2.10. Representative synthesis of compound in series 12

**4.2.10.1. 4-Ferrocenylbenzyl 4'-octyloxy-4-biphenyl-carboxylate (12, *n* = 8).** Quantities: 4'-octyloxy-4-biphenylcarboxylic acid (224 mg, 0.69 mmol), 4-hydroxybenzylferrocene (200 mg, 0.68 mmol), DMAP (45 mg, 0.37 mmol), DCC (183 mg, 0.89 mmol) and  $\text{CH}_2\text{Cl}_2$  (150  $\text{cm}^3$ ). The experimental procedure was as described in Section 4.2.9. The product was obtained as yellow crystals recrystallized from  $\text{CH}_2\text{Cl}_2$ /MeOH in the cold (224 mg, 54%), m.p. 91 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3409, 3090, 2925, 2852, 1708, 1601, 1527, 1496, 1462, 1376, 1266, 1192, 1100, 1025, 997, 926, 887, 820, 767, 720, 633, 549, 495;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.12 (2H, d, *J* 8.3, ArH), 7.62 (2H, d, *J* 8.3, ArH), 7.55 (2H, d, *J* 8.6, ArH), 7.49 (2H, d, *J* 8.0, ArH), 7.37 (2H, d, *J* 8.1, ArH), 6.98 (2H, d, *J* 8.6, ArH), 5.35 (2H, s,  $\text{CH}_2\text{O}$ ), 4.67 (2H, t, *J* 1.8,  $\text{C}_5\text{H}_4$ ), 4.32 (2H, t, *J* 1.8,  $\text{C}_5\text{H}_4$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.00 (2H, t, *J* 6.6,  $\text{OCH}_2$ ), 1.80 (2H, m,  $\text{CH}_2$ ), 1.47–1.29 (10H, m,  $5 \times \text{CH}_2$ ), 0.88 (3H, s,  $\text{CH}_3$ ); *m/z* 602 (10%), 601 (43), 600 ( $[\text{M}^+]$ , 100), 327 (6), 326 (27), 276 (5), 275 (7), 244 (9), 215 (13), 214 (83), 197 (7), 154 (23). Anal. Found: C, 76.0; H, 6.9%;  $[\text{M}^+]$ , 600.2321. Calc. for  $\text{C}_{38}\text{H}_{40}\text{FeO}_3$ : C, 76.0; H, 6.7%;  $[\text{M}^+]$ , 600.2324.

#### 4.2.11. 4'-Octyloxy-carboxyl-4-biphenyl 4-ferrocenylbenzoate (17)

A catalytic amount of DMAP was added to a solution of 4-ferrocenylbenzoic acid (700 mg, 2.94 mmol) and 1-octyl 4-hydroxy-4-biphenylcarboxylate (756 mg, 2.94 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (300  $\text{cm}^3$ ). To this was added a

solution of DCC (650 mg, 3.15 mmol) in  $\text{CH}_2\text{Cl}_2$  (30  $\text{cm}^3$ ), and the reaction stirred at 25 °C for 16 h. The *N,N*-dicyclohexylurea precipitate was filtered off and the filtrate evaporated to dryness. The crude product was subjected to chromatography on silica gel and elution with  $\text{C}_6\text{H}_{14}$ – $\text{CH}_2\text{Cl}_2$  (1:1) afforded the product. Recrystallization from  $\text{CH}_2\text{Cl}_2$ –MeOH in the cold gave the product as a fluffy orange solid (737 mg, 41%), m.p. 165 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2957, 2924, 2853, 1737, 1709, 1606, 1566, 1526, 1490, 1464, 1419, 1389, 1264, 1214, 1180, 1167, 1114, 1069, 1004, 859, 814, 771;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.14 (2H, d, *J* 8.4, ArH), 8.13 (2H, d, *J* 8.0, ArH), 7.70 (2H, d, *J* 8.5, ArH), 7.68 (2H, d, *J* 8.1, ArH), 7.60 (2H, d, *J* 8.1, ArH), 7.34 (2H, d, *J* 8.1, ArH), 4.77 (2H, t, *J* 1.7,  $\text{C}_5\text{H}_4$ ), 4.44 (2H, t, *J* 1.7,  $\text{C}_5\text{H}_4$ ), 4.35 (2H, t,  $\text{OCH}_2$ ), 4.07 (5H, s,  $\text{C}_5\text{H}_5$ ), 1.82 (2H, m,  $\text{CH}_2$ ), 1.58–1.20 (10H, m,  $5 \times \text{CH}_2$ ), 0.89 (3H, m,  $\text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  166.97, 165.60, 151.53, 146.70, 145.11, 138.16, 138.81, 130.53, 129.76, 128.82, 127.41, 126.74, 126.19, 122.71, 83.39, 70.43, 70.31, 67.40, 65.63, 32.22, 29.69, 29.63, 29.16, 26.48, 23.08, 14.53; *m/z* 616 (11%), 615 (42), 614 ( $[\text{M}^+]$ , 100), 612 (7), 290 (9), 289 (40), 262 (20), 261 (97), 260 (5), 259 (7), 242 (6), 214 (5), 205 (6), 140 (5), 139 (8). Anal. Found: C, 74.0; H, 6.8%;  $[\text{M}^+]$ , 614.2120. Calc. for  $\text{C}_{38}\text{H}_{38}\text{FeO}_4$ : C, 74.3; H, 6.7%;  $[\text{M}^+]$ , 614.2120.

#### 4.2.12. 4'-(2-Octyloxy)carbonyl-4-biphenyl 4-ferrocenylbenzoate (18)

A catalytic amount of DMAP was added to a solution of 4-ferrocenylbenzoic acid (370 mg, 1.21 mmol) and 2-octyl 4'-hydroxy-4-biphenylcarboxylate (355 mg, 1.21 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (150  $\text{cm}^3$ ). To this was added a solution of DCC (304 mg, 1.47 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ). The reaction was stirred at r.t. for 16 h. The *N,N*-dicyclohexylurea was filtered off and the filtrate was then evaporated to dryness. The crude product was subjected to chromatography on silica gel and elution with  $\text{C}_6\text{H}_{14}$ – $\text{CH}_2\text{Cl}_2$  (1:1) afforded the product as an orange solid recrystallized from MeOH (433 mg, 58%), m.p. 119–122 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2926, 2872, 2854, 1738, 1709, 1607, 1528, 1491, 1466, 1267, 1182, 1108, 1066;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.14 (2H, d, *J* 8.5, ArH), 8.13 (2H, d, *J* 8.4, ArH), 7.70 (2H, d, *J* 8.7, ArH), 7.68 (2H, d, *J* 8.0, ArH), 7.61 (2H, d, *J* 8.3, ArH), 7.34 (2H, d, 8.7, ArH), 5.20 (1H, m, CH), 4.76 (2H, t, *J* 1.7,  $\text{C}_5\text{H}_4$ ), 4.43 (2H, t, *J* 1.7,  $\text{C}_5\text{H}_4$ ), 4.07 (5H, s,  $\text{C}_5\text{H}_5$ ), 1.92 (2H, m,  $\text{CH}_2$ ), 1.76–1.20 (11H, m,  $\text{CH}_3$  and  $4 \times \text{CH}_2$ ), 0.89 (3H, t,  $\text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  166.49, 165.60, 151.51, 146.69, 145.02, 138.22, 130.81, 130.51, 130.17, 128.82, 127.38, 126.75, 126.19, 122.70, 83.39, 72.24, 70.43, 70.32, 67.40, 36.51, 32.17, 29.60, 25.85, 23.02, 20.54, 14.50; *m/z* 616 (9%), 615 (39), 614 ( $[\text{M}^+]$ , 100), 612 (6), 366 (9), 328 (5), 316 (10), 290 (10), 289 (43), 287 (5), 266 (14), 262 (19), 261 (89), 260 (7), 259 (6), 250 (6), 243 (12), 214 (7), 205 (5), 139 (7). Anal. Found: C, 74.0; H, 6.2%;  $[\text{M}^+]$ , 614.2115. Calc. for  $\text{C}_{38}\text{H}_{38}\text{FeO}_4$ : C, 74.3; H, 6.2;  $[\text{M}^+]$ , 614.2120.



#### 4.2.13. 4'-Octyloxy-4-biphenyl 2-chloro-4-ferrocenylbenzoate (**22**, $n = 8$ )

A solution of 2-chloro-4-ferrocenylbenzoic acid (286 mg, 0.84 mmol), 4-hydroxy-4'-octyloxybiphenyl (250 mg, 0.84 mmol) and DMAP (34 mg, 0.28 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) was prepared under an atmosphere of dry nitrogen. A solution of DCC (206 mg, 1.00 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (30  $\text{cm}^3$ ) was then added over 1 min and the solution stirred at r.t. for 14 days. The solution was then filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography over silica gel using a mixture of  $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  (1:1) as the eluent. The solvent was removed from the collected fractions and the red solid was recrystallized from  $\text{CH}_2\text{Cl}_2\text{-MeOH}$  (232 mg, 45%), m.p. 141 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2923, 2853, 2362, 1741, 1600, 1548, 1495, 1474, 1408, 1388, 1289, 1249, 1202, 1153, 1092, 1030, 999, 906, 882, 843, 832, 804, 765, 686, 668, 524, 500;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.02 (1H, d,  $J$  8.2, ArH), 7.59 (3H, d,  $J$  8.6, ArH), 7.51 (2H, d,  $J$  8.6, ArH), 7.45 (1H, d,  $J$  8.2, ArH), 7.29 (2H, d,  $J$  8.5, ArH), 6.97 (2H, d,  $J$  8.7, ArH), 4.72 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.44 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.08 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.00 (2H, t,  $J$  6.6,  $\text{OCH}_2$ ), 1.82 (2H, m,  $\text{CH}_2$ ), 1.49–1.25 (10H, m,  $5 \times \text{CH}_2$ ), 0.91 (3H, t,  $\text{CH}_3$ );  $m/z$  622 (16%), 621 ( $[\text{M}^+]$ , 39), 620 (93), 618 (6), 366 (5), 325 (5), 323 (18), 322 (79), 320 (5), 316 (5), 297 (7), 296 (33), 295 (20), 294 (100), 266 (7), 211 (7), 204 (16), 203 (6), 200 (6), 186 (11), 185 (6), 181 (5), 139 (5). Anal. Found: C, 71.6; H, 6.1%;  $[\text{M}^+]$ , 620.17702. Calc. for  $\text{C}_{37}\text{H}_{37}\text{ClFeO}_3$ : C, 71.6; H, 6.0%;  $[\text{M}^+]$  620.17806.

#### 4.2.14. 4'-Decyloxy-4-biphenyl 2-chloro-4-ferrocenylbenzoate (**22**, $n = 10$ )

Quantities: 2-chloro-4-ferrocenylbenzoic acid (233 mg, 0.68 mmol), 4'-decyloxy-4-hydroxybiphenyl (223 mg, 0.68 mmol), DMAP (28 mg, 0.23 mmol) and DCC (183 mg, 0.89 mmol). The experimental procedure was as in Section 4.2.13. The product ( $n = 10$ ) was obtained as red crystals recrystallized from  $\text{CH}_2\text{Cl}_2\text{-MeOH}$  in the cold (216 mg, 49%), m.p. 130 °C;  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  2921, 2865, 2363, 1741, 1599, 1547, 1494, 1474, 1467, 1387, 1289, 1267, 1251, 1202, 1166, 1094, 1032, 1014, 1001, 906, 882, 833, 805, 767, 686, 668, 500;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.03 (1H, d,  $J$  8.2, ArH), 7.60 (3H, d,  $J$  8.7, ArH), 7.51 (2H, d,  $J$  8.7, ArH), 7.45 (1H, d,  $J$  8.2, ArH), 7.30 (2H, d,  $J$  8.6, ArH), 6.97 (2H, d,  $J$  8.7, ArH), 4.72 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.44 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.08 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.00 (2H, t,  $J$  6.6,  $\text{OCH}_2$ ), 1.81 (2H, m,  $\text{CH}_2$ ), 1.45–1.29 (14H, m,  $7 \times \text{CH}_2$ ), 0.89 (3H, m,  $\text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  163.96, 158.82, 149.67, 146.69, 138.86, 135.00, 132.71, 132.34, 128.19, 128.12, 127.74, 125.40, 123.90, 121.87, 114.85, 81.58, 70.28, 69.98, 68.12, 67.02, 31.91, 29.57, 29.42, 29.33, 26.07, 22.69, 14.13;  $m/z$  651 (15%), 650 (41), 649 (44), 648 ( $[\text{M}^+]$ , 100), 646 (7), 614 (5), 326 (5), 325 (27), 324 (17), 323 (76), 321 (5), 298 (7), 297 (31), 296

(19), 295 (95), 261 (5), 204 (13), 203 (6), 202 (6), 186 (12), 185 (7), 139 (5), 43 (8). Anal. Found: C, 71.9; H, 6.6%;  $[\text{M}^+]$ , 648.2087. Calc. for  $\text{C}_{39}\text{H}_{41}\text{ClFeO}_3$ : C, 72.2; H, 6.4%;  $[\text{M}^+]$ , 648.2094.

#### 4.2.15. Representative synthesis of compounds in series **10**

##### 4.2.15.1. 4-(4'-Pentyloxy-4-biphenyloxycarbonyl)phenyl 4-ferrocenylbenzoate (**10**, $n = 5$ )

A solution of 4-ferrocenylbenzoic acid (407 mg, 1.3 mmol), 4'-pentyloxy-4-biphenyl 4-hydroxybenzoate (500 mg, 1.3 mmol) and DMAP (54 mg, 0.44 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (200  $\text{cm}^3$ ) was prepared under an atmosphere of dry nitrogen. A solution of DCC (383 mg, 1.9 mmol) was then added over 1 min, and the solution stirred at r.t. for 72 h. The solution was then filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography over silica gel using  $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  (4:1) as the eluent. The product ( $n = 5$ ) was obtained as orange crystals recrystallized from  $\text{CH}_2\text{Cl}_2\text{-MeOH}$  in the cold (601 mg, 68%), m.p. (liquid crystal) 178, 192, 291 °C (dec.);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3070, 2924, 2856, 2360, 1732, 1604, 1571, 1524, 1500, 1471, 1412, 1388, 1271, 1197, 1181, 1161, 1115, 1104, 1084, 1072, 1032, 1015, 920, 885;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.32 (2H, d,  $J$  8.7, ArH), 8.13 (2H, d,  $J$  8.4, ArH), 7.60 (4H, d,  $J$  8.2, ArH), 7.52 (2H, d,  $J$  8.7, ArH), 7.41 (2H, d,  $J$  8.7, ArH), 7.27 (2H, d,  $J$  9.1, ArH), 6.98 (2H, d,  $J$  8.7, ArH), 4.77 (2H, d,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.44 (2H, d,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.07 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.01 (2H, t,  $J$  6.6,  $\text{OCH}_2$ ), 1.82 (2H, m,  $\text{CH}_2$ ), 1.44 (4H, m,  $2 \times \text{CH}_2$ ), 0.95 (3H, m,  $\text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  165.01, 159.20, 155.73, 150.18, 147.04, 139.24, 133.11, 132.29, 130.87, 128.54, 128.19, 127.43, 126.34, 126.23, 122.51, 122.30, 115.22, 83.25, 70.51, 70.34, 68.50, 67.43, 29.41, 28.64, 22.91, 14.48;  $m/z$  666 (12%), 665 (47), 664 ( $[\text{M}^+]$ , 100), 662 (7), 290 (11), 289 (47), 262 (13), 261 (62), 259 (5), 256 (12), 205 (7), 204 (20), 186 (28), 185 (7), 179 (12), 144 (15), 139 (5), 121 (5). Anal. Found: C, 73.8; H, 5.6%;  $[\text{M}^+]$ , 664.1924. Calc. for  $\text{C}_{41}\text{H}_{36}\text{FeO}_5$ : C, 74.1; H, 5.5%;  $[\text{M}^+]$ , 664.1912.

##### 4.2.16. 4'-Cyano-4-biphenyl 4'-ferrocenylbenzoate (**19**)

A solution of 4-ferrocenylbenzoic acid (513 mg, 1.7 mmol), 4-cyano-4'-hydroxybiphenyl (327 mg, 1.7 mmol) and DMAP (20 mg, 0.17 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (200  $\text{cm}^3$ ) was prepared under an atmosphere of dry nitrogen. A solution of DCC (415 mg, 2.0 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (60  $\text{cm}^3$ ) was then added over 1 min and the solution stirred at r.t. for 24 h. The solution was then filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography over silica gel using a mixture of  $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  (1:1) as the eluent. The solvent was removed from the collected fractions and the red solid was recrystallized from  $\text{CH}_2\text{Cl}_2\text{-MeOH}$  (780 mg, 96%), m.p. (liquid

crystal) 238, 248 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  2940, 2926, 2857, 2366, 2354, 2229, 1720, 1600, 1520, 1491, 1417, 1269, 1229, 1183, 1069, 1006, 886, 851, 822, 800, 771, 703;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.06 (2H, d,  $J$  8.4, ArH), 7.68 (2H, d,  $J$  8.6, ArH), 7.63 (2H, d,  $J$  8.6, ArH), 7.59 (2H, d,  $J$  8.6, ArH), 7.53 (2H, d,  $J$  8.5, ArH), 7.29 (2H, d,  $J$  8.6, ArH), 4.70 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.37 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.00 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  165.12, 151.53, 146.43, 144.85, 136.81, 132.67, 130.40, 128.40, 127.71, 126.18, 125.79, 122.55, 118.90, 111.00, 82.91, 70.06, 69.91, 67.00;  $m/z$  485 (6%), 484 (30), 483 ( $[\text{M}^+]$ , 100), 481 (6), 290 (6), 289 (26), 262 (18), 261 (92), 260 (6), 259 (6), 205 (9), 203 (5), 195 (7), 183 (7), 170 (6), 145 (6), 140 (10), 139 (19), 121 (7). Anal. Found: C, 74.5; H, 4.3; N, 2.9%;  $[\text{M}^+]$ , 483.09301. Calc. for  $\text{C}_{30}\text{H}_{21}\text{FeNO}_2$ : C, 74.5; H, 4.4; N, 2.9%;  $[\text{M}^+]$ , 483.0917.

#### 4.2.17. 4-(4'-Cyano-4-biphenyloxy)carbonylphenyl 4-ferrocenylbenzoate (20)

Quantities: 4-ferrocenylbenzoic acid (200 mg, 0.65 mmol), 4'-cyano-4-biphenyl 4-hydroxyphenylbenzoate (250 mg, 0.65 mmol), DCC (188 mg, 0.91 mmol) and DMAP (26 mg, 0.22 mmol). The experimental procedure as in Section 4.2.16. The product was an orange-red solid (146 mg, 37%), m.p. (liquid crystal) 258, 304 °C (dec.);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3500–3000 (br), 2242, 1935, 1732, 1603, 1530, 1497, 1424, 1392, 1295, 1278, 1205, 1189, 1173, 1092, 1068, 1011, 897, 808, 776, 686;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.32 (2H, d,  $J$  8.7, ArH), 8.13 (2H, d,  $J$  8.5, ArH), 7.67–7.61 (8H, m, ArH), 7.42–7.36 (4H, m, ArH), 4.77 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.45 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.07 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  165.02, 164.81, 155.90, 151.75, 147.12, 145.20, 137.42, 133.10, 132.34, 130.88, 128.87, 128.14, 127.09, 126.24, 122.90, 122.61, 119.30, 111.47, 83.21, 70.53, 70.34, 67.43;  $m/z$  604 (39%), 603 ( $[\text{M}^+]$ , 91), 601 (6), 290 (12), 289 (54), 262 (20), 261 (100), 260 (8), 259 (7), 205 (10), 204 (18), 203 (7), 195 (19), 168 (10), 166 (6), 145 (7), 144 (29), 140 (13), 139 (18), 121 (26). Anal. Found:  $[\text{M}^+]$ , 603.11313. Calc. for  $\text{C}_{37}\text{H}_{25}\text{FeNO}_4$ :  $[\text{M}^+]$ , 603.11330.

#### 4.2.18. 4-[(1)-Chloro-(2)-methylbutyl carboxy]-4'-biphenylcarboxy phenylferrocene

A solution of 4-ferrocenylphenyl 4'-hydroxy-4-biphenylcarboxylate (260 mg, 0.55 mmol), 1-chloro-2-methylbutanecarboxylic acid (74 mg, 0.55 mmol) and DMAP (22 mg, 0.18 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (100  $\text{cm}^3$ ) was prepared under an atmosphere of dry nitrogen. A solution of DCC (158 mg, 0.77 mmol) in anhydrous  $\text{CH}_2\text{Cl}_2$  (50  $\text{cm}^3$ ) was then added over 1 min and the solution stirred at r.t. for 2 weeks. TLC indicated that the reaction was proceeding very slowly and thus the solution was then stirred under reflux for another week. The solution was then filtered and the solvent removed in vacuo. The crude product was purified by flash column chromatography over silica gel using a mixture

of  $\text{C}_6\text{H}_{14}-\text{CH}_2\text{Cl}_2$  (1:1) as the eluent. The solvent was removed from the collected fractions and the orange solid recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (259 mg, 78%), m.p. 167–168 °C;  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3691–3143 (br), 3100, 2980, 2946, 2886, 1780, 1746, 1660, 1617, 1531, 1506, 1471, 1403, 1283, 1206, 1180, 1154, 1086, 1017, 837;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.29 (2H, d,  $J$  8.4, ArH), 7.71 (4H, t,  $J$  8.7, ArH), 7.54 (2H, d,  $J$  8.6, ArH), 7.26 (2H, d,  $J$  8.5, ArH), 7.17 (2H, d,  $J$  8.6, ArH), 4.64 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.42 (1H, d,  $J$  7.1, CH), 4.33 (2H, t,  $J$  1.8,  $\text{C}_5\text{H}_4$ ), 4.08 (5H, s,  $\text{C}_5\text{H}_5$ ), 2.26 (1H, m, CH), 1.47 (2H, m,  $\text{CH}_2$ ), 1.16 (3H, d,  $J$  6.8,  $\text{CH}_3$ ), 1.01 (3H, t,  $J$  7.4,  $\text{CH}_3$ );  $\delta_{\text{C}}(\text{CDCl}_3)$  168.39, 165.42, 150.93, 149.45, 145.60, 138.52, 137.51, 128.96, 128.74, 127.64, 127.47, 122.83, 122.21, 121.93, 85.21, 70.03, 69.38, 66.99, 63.01, 39.47, 25.56, 16.44, 11.31;  $m/z$  608 (40%), 607 (41), 606 ( $[\text{M}^+]$ , 100), 604 (6), 572 (8), 571 (8), 570 (19), 558 (6), 474 (13), 473 (8), 331 (7), 329 (19), 278 (18), 277 (25), 249 (6), 198 (12), 197 (86), 169 (11), 168 (6), 141 (7), 121 (18). Anal. Found: C, 69.9; H, 5.3%;  $[\text{M}^+]$ , 606.12593. Calc. for  $\text{C}_{35}\text{H}_{31}\text{ClFeO}_4$ : C, 69.4, H, 5.2%;  $[\text{M}^+]$ , 606.12603.

### 4.3. Crystal structure determination

#### 4.3.1. Crystal data for 14

$M_r = 532.35 \text{ g mol}^{-1}$ , size  $0.08 \times 0.07 \times 0.05 \text{ mm}^3$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.0750(10)$ ,  $b = 12.0290(10)$ ,  $c = 12.522(2) \text{ \AA}$ ,  $V = 1207.9(3) \text{ \AA}^3$ ,  $T = 296 \text{ K}$ ,  $Z = 2$ ,  $\rho_{\text{calc}} = 1.464 \text{ mg m}^{-3}$ ,  $\mu(\text{Mo}-\text{K}\alpha) = 0.666 \text{ mm}^{-1}$ ,  $F(000) = 552$ , 2756 reflections in  $h$  (0/10),  $k$  (–15/14),  $l$  (–15/14), measured in the range  $2.47 \leq \theta \leq 26.52^\circ$ , 2422 independent reflections,  $R_{\text{int}} = 0.0563$ ,  $R_{1 \text{ obs}} = 0.0466$ ,  $wR_{1 \text{ obs}}^2 = 0.1445$ ,  $R_{1 \text{ all}} = 0.0637$ ,  $wR_{1 \text{ all}}^2 = 0.1508$ , goodness-of-fit = 1.027.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 186235 for compound 14. 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>).

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