Asymmetric Synthesis of [3](1,1′)- and [3](1,1′)[3](3,3′)-Ferrocenophanes

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(*R*)-α-Ferrocenyl alcohols underwent conversion to their corresponding methyl ethers on treatment with MeOH/AcOH, which were in turn converted to ethyl 3-ferrocenylpropanoates when combined with 1-ethoxy-1-(trimethylsilyloxy)ethene and $BF_3{\cdot}OEt_2$. After ester hydrolysis, the resulting acids (92−96% ee) underwent heteroannular Friedel−Crafts cyclization to give singly bridged ferrocenophanes of high enantiomeric purity. The methanolysis and silyl ketene acetal addition sequence was also applied to (*R*,*R*)-1,1′-bis(phenylhydroxymethyl)-ferrocene, and to (*R*,*R*)-1,1′-bis((4-bromophenyl)hydroxymethyl)ferrocene, to give the corresponding diacids (94% ee) after ester hydrolysis. On Friedel−Crafts cyclization, the first of these diacids gave a 7:37:56 ratio of singly bridged ferrocenophanes after conversion of the remaining acid functionalities to methyl esters. The least abundant product was identified as ($_p$*R*)-1,1′-(*R*)-(1-oxo-3-phenyl-1,3-propanediyl)-2-(*R*)-(3-methoxy-3-oxo-1-phenylpropyl)ferrocene by an X-ray crystal structure analysis. After separation, the most abundant isomer was converted in four steps to the novel doubly bridged C_2-symmetric ferrocenophane (*R*,*R*,$_p$*S*,$_p$*S*)-1,1′-(1-phenyl-1,3-propanediyl)-3,3′-(3-phenyl-1,3-propanediyl)ferrocene, characterized by an X-ray crystal structure analysis. The remaining isomer was converted to the corresponding 1,1′,3,3′-(*R*,*R*,$_p$*R*,$_p$*R*)-ferrocenophane. Also synthesized by this method was (*R*,*R*,$_p$*S*,$_p$*S*)-1,1′-(1-(4-bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)-ferrocene, which after bromine−lithium exchange was converted to the corresponding dicarboxylic acid. (*R*,*R*,$_p$*S*,$_p$*S*)-1,1′-(1-Phenyl-1,3-propanediyl)-3,3′-(3-phenyl-1,3-propanediyl)-ferrocenium tetrafluoroborate catalyzed the reaction between methacrolein and cyclopentadiene, although no enantioselectivity was observed in the resulting Diels−Alder adducts.

Introduction

The concept of ferrocene acting as a three-dimensional metal-containing equivalent of benzene has prompted the synthesis of novel air-stable structures that have found many applications in catalysis and materials science.[1] This has recently been extended with the development of several methods for the asymmetric generation of ferrocene derivatives containing both planar and central elements of chirality.[2] However, this activity has been barely applied to the asymmetric synthesis of bridged ferrocenophanes,[3] which are comparatively rigid ferrocene derivatives due to linkage of the two cyclopentadienyl rings. We are interested in the possibilities offered by chiral, metal-containing, and conformationally restricted building blocks for the synthesis of new catalysts and materials, as could be explored following the development of methodology for the rapid asymmetric synthesis of ferrocenophanes. To this end we noted that [3]-ferrocenophanes are generated in high yield on heteroannular Friedel−Crafts cyclization of ferrocenepropanoic acids,[4] a reaction extended to α-substituted and thus chiral ferrocenepropanoic acids[5] that have been resolved prior to cyclization.[6] Resolution has also been utilized during the synthesis of nonracemic planar chiral [3]-ferrocenophanes.[7]

We recently reported that ferrocenepropanoates can be rapidly accessed by addition of silyl ketene acetals to ferrocenylmethyl ethers promoted by $BF_3{\cdot}OEt_2$.[8] With the aim of applying this reaction to the synthesis of ferrocenophanes, and specifically the C_2-symmetric ferrocenophane **1**, we also reported that the racemic diester

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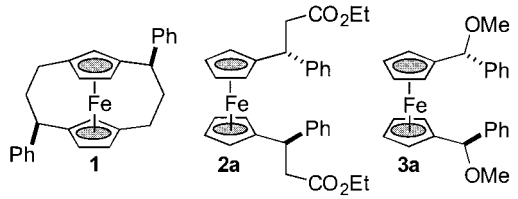
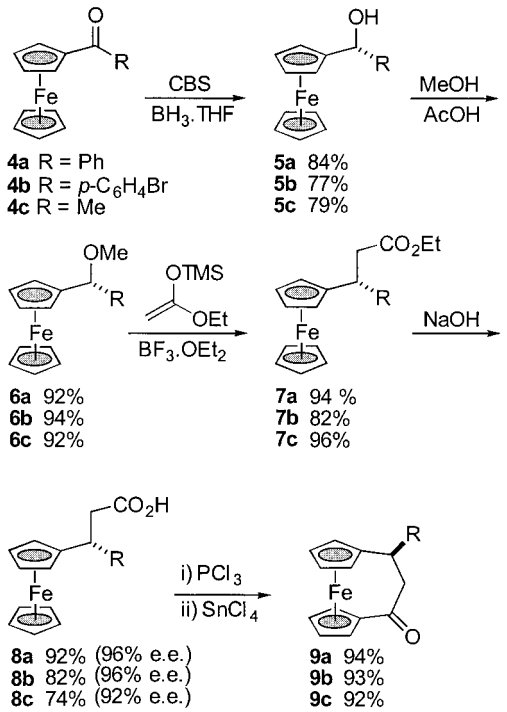
2a can be readily prepared from the racemic diether **3a** with complete control of relative stereochemistry. This reaction occurs with the addition of 2 equiv of 1-ethoxy-1-(trimethylsilyloxy)ethene to intermediate α-ferrocenylcarbenium ions formed by Lewis acid-promoted methoxide removal. We now wish to give a full account of this reaction for the asymmetric synthesis of ferrocenophanes, as exemplified by **1**, the stereoselectivity of the heteroannular cyclization required for this structure, and the use of these processes for the synthesis of functionalized ferrocenophanes.[9]



Results and Discussion

The generation of **2a** proceeds via the in situ generation and trapping of α-ferrocenylcarbenium ions obtained when **3a** is treated with $BF_3{\cdot}OEt_2$ in the presence of 1-ethoxy-1-(trimethylsilyloxy)ethene. It was anticipated that the known configurational stability of α-ferrocenylcarbenium ions[10] would permit application of this general reaction to the asymmetric synthesis of ethyl 3-ferrocenylpropanoates. To test this theory, we began by carrying out the previously reported oxazaborolidine-catalyzed reduction of ferrocenyl ketones[11] **4a**−**c** to give known alcohols **5a**/**c** and the new alcohol **5b**. For **5a**/**c** this reaction had been reported to proceed in >95% ee, and the rotations we obtained for these two compounds were very close to those previously reported. Subsequent methanolysis was achieved by treatment with 10% acetic acid in methanol[12] to give excellent yields of ethers **6a**−**c**. The absolute configuration of **6c** was determined by comparison of its rotation to that previously reported for (*R*)-**6c**,[13] confirming that methanolysis proceeds with retention of configuration. On treatment with 1-ethoxy-1-(trimethylsilyloxy)ethene and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 at −78 °C, followed by warming of the reaction mixture to room temperature, each of the ethers was cleanly converted to ethyl 3-ferrocenylpropanoates **7a**−**c**. Following hydrolysis to their corresponding acids **8a**−**c**, their enantiomeric excesses were determined by DCC-mediated coupling with (*S*)-methyl mandelate and examination of the resulting mixture by NMR on completion of the reaction. The high enantiomeric excesses measured (Scheme 1) reveal that both methanolysis and silyl ketene acetal addition proceed with excellent stereochemical integrity. The absolute configurations assigned to **8a**−**c** assume that C−C bond formation also proceeds with retention of configuation,

Scheme 1



as has been reported for the addition of organozincs[14] and heteroatom nucleophiles to ferrocenyl acetates.[15,16] The first series of enantiomerically enriched ferrocenophanes were completed by intramolecular Friedel−Crafts cyclization. Although the best yields for this reaction had previously been obtained by direct cyclization of acids with TFAA in CCl_4,[4] we found that $SnCl_4$-promoted cyclization of the preformed 3-ferrocenylpropanoyl chlorides gave excellent yields of ferrocenophanes **9a**−**c**.

This methodology was then extended to the 1,1′-ferrocenyldiketones **10a**/**b**. Again use of the previously reported oxazaborolidine-catalyzed reduction methodology[17] gave an excellent yield of known (from **10a**) and new (from **10b**) diols, both obtained as 92:8 mixtures of diastereoisomers. Attempted purification of these diols led to significant formation of oxaferrocenophanes formed by dehydration. As contamination by the oxazaborolidine catalyst residues could not be removed by recrystallization, the crude diols were treated directly with acetic acid in methanol to give ethers **3a**/**3b**, from which the minor *meso* diastereoisomers were readily removed on recrystallization. Treatment with 1-ethoxy-1-(trimethylsilyloxy)ethene and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 as before gave clean conversion to diesters **2a**/**b** with complete control of relative stereochemistry, only a single diastereoisomer being observed in the crude product mixture

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(12) Nesmeyanov, A. N.; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, *11*, 1972.

(13) The previous synthesis of nonracemic **6c** used resolved (*R*)-*N*,*N*,-dimethyl-1-ferrocenylethylamine followed by quaternization and treatment with 1:1 methanol/acetonitrile: Gokel, G. W.; Marquarding, D.; Ugi, I. K. *J. Org. Chem.* **1972**, *37*, 3052.

(14) Perea, J. J. A.; Ireland, T.; Knochel, P. *Tetrahedron Lett.* **1997**, *38*, 5961.

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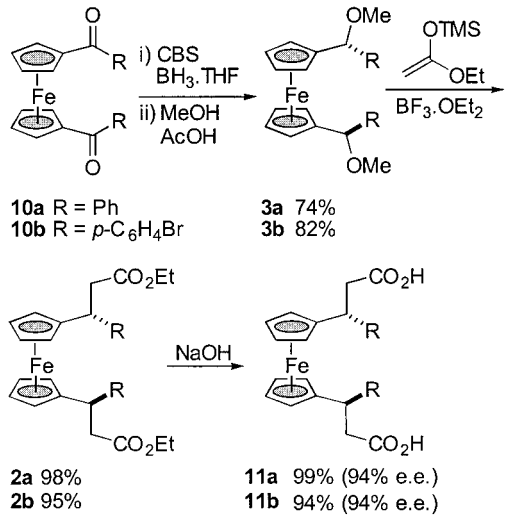
(16) For an exception to this general rule see: Taniguchi, N.; Uemura, M. *Tetrahedron Lett.* **1998**, *30*, 5385.

(17) (a) Schwink, L.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 25. (b) Schwink, L.; Knochel, P. *Chem. Eur. J.* **1998**, *4*, 950.

Scheme 2



of each reaction. To determine the control of absolute stereochemistry in these reactions, the diacids **11a**/**b** obtained on hydrolysis were coupled with (*S*)-methyl mandalate, revealing both to be of high enantiomeric purity (Scheme 2). We had been concerned that methanolysis and/or silyl ketene acetal addition might have proceeded via intermediate *meso* oxoniumferrocenophanes, which can now be ruled out, as these would have led to racemic products.

The synthesis of **1** requires a double intramolecular Friedel−Crafts cyclization of **11a** and reduction of the resulting α-keto groups. Our expectation was that only heteroannular cyclization would occur and that this would lead predominantly to bond formation at diastereomeric β-positions 3′ and 4′ in preference to diastereomeric α-positions 2′ and 5′, these being adjacent to a bulky alkyl substituent. This was supported by the previously reported cyclization of 1,1′-bis(2-carboxyethyl)ferrocene, which ultimately gave an isolated ratio of 1,1′,3,3′- over 1,1′,2,2′-(1,3-propanediyl)ferrocenophanes of 43:1.[18] Treatment of the (*R*,*R*)-diacid **11a** with PCl_3 gave the corresponding diacid chloride, which was added to 2.2 equiv of $SnCl_4$ at 0 °C. After quenching, the reaction mixture gave a mixture of acids, revealing that only a single Friedel−Crafts cyclization had occurred. As the acids proved unstable, decomposing during attempted chromatography or recrystallization, they were directly converted to their corresponding methyl esters obtained as a 7:37:56 ratio of isomers. Column chromatography permitted isolation of the least abundant product (R_f = 0.23, 10% EtOAc/petroleum ether) identified as **12** by an X-ray crystal structure determination (Figure 1). The remaining two products eluted simultaneously (R_f = 0.13, 10% EtOAc/petroleum ether) in a good overall yield, and a single recrystallization from a mixture of these two solvents gave a pure sample of the major diastereoisomer. Subsequent ionic hydrogenation and ester hydrolysis was followed by TFAA-mediated intramolecular Friedel−Crafts cyclization. This proceeded with excellent selectivity due to the rigidity imposed by the first formed bridge. Further ionic hydrogenation gave a ferrocenophane for which the

(18) Rinehart, K. L.; Bublitz, D. E.; Gustafson, D. H. *J. Am. Chem. Soc.* **1963**, *85*, 970.

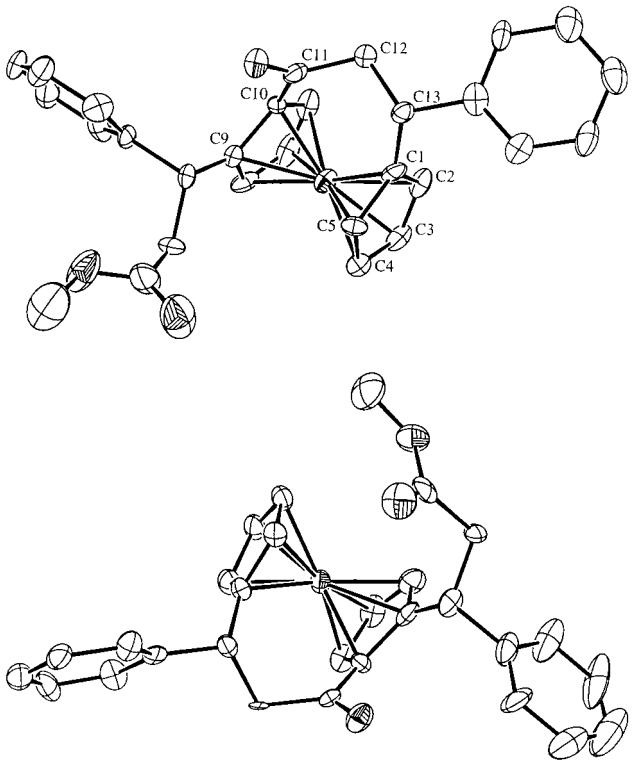


Figure 1. Two independent crystal structures of **12**. Selected bond distances (Å) and angles (deg) with corresponding values for the second structure given in parentheses: C(1)−Fe 2.026(8) [2.004(7)], C(3)−Fe 2.051(7) [2.031(7)], C(1)−C(13) 1.549(10) [1.532(9)], C(10)−C(11) 1.464(10) [1.456(10)], C(1)−C(13)−C(12) 110.7(6) [110.6(6)], C(13)−C(12)-C(11) 109.0(6) [106.6(6)], C(10)−C(11)−C(12) 118.0(6) [117.3(7)].

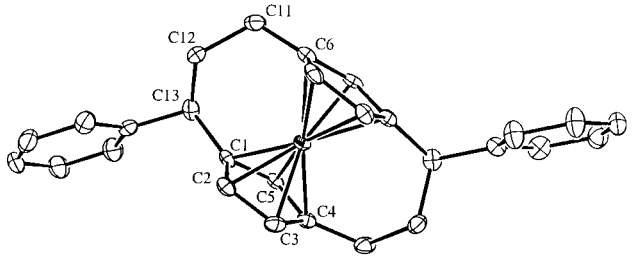
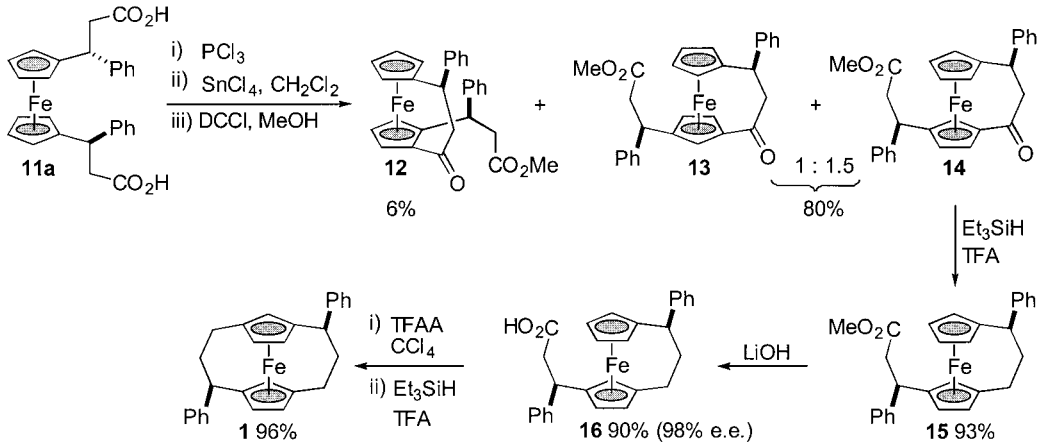


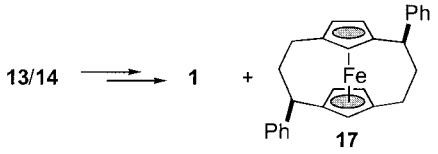
Figure 2. Crystal structures of **1**. Selected bond distances (Å) and angles (deg): C(1)−Fe 2.002(3), C(2)−Fe 2.027(4), C(5)−Fe 2.005(4), C(1)−C(13) 1.514(5), C(6)−C(11) 1.522, C(1)−C(13)−C(12) 113.3(3), C(13)−C(12)−C(11) 117.2, C(6)−C(11)−C(12) 114.0(3).

simplicity of the $^1H/^{13}C$ NMR spectra was consistent with a doubly bridged C_2-symmetric structure, and a complete stereochemical assignment was made by an X-ray crystal structure analysis (Figure 2). This revealed the ferrocenophane to be (*R*,*R*,$_p$*S*,$_p$*S*)-**1**, thus proving the structures of **14**, **15**, and **16**, and also the absolute configuration of these intermediates (Scheme 3). The enantiomeric excess of **16** was determined as 98% using ^1H NMR analysis after coupling to (*S*)-methyl mandelate as before. The mother liquors from the isolation of pure **14** were evaporated and found to contain a 1:1.5 ratio of **14** and **13**. As further recrystallization proved unsuccessful in providing a pure sample of either diastereoisomer, this mixture was carried through the same series of reactions to give a 1:1.5 mixture of **1** and a new ferrocenophane. This also gave

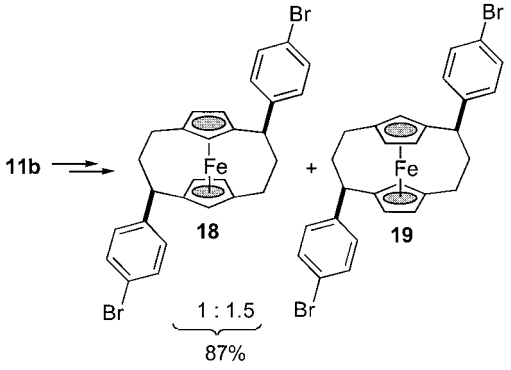
Scheme 3



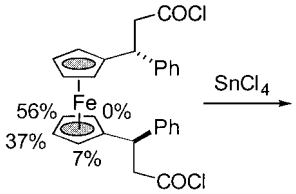
Scheme 4



Scheme 5



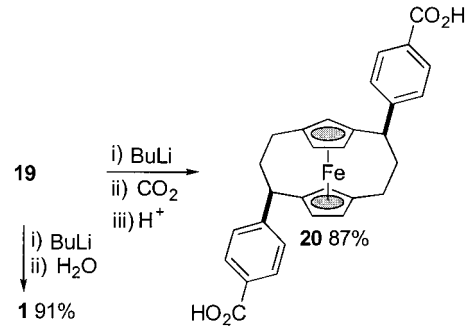
$^1H/^{13}C$ spectra consistent with a C_2-symmetric structure which was determined to contain the 1,1′,3,3′-substitution pattern of **17** by the absence of an NOE between the hydrogens at positions 2 and 2′ with those at the remaining cyclopentadienyl ring positions (Scheme 4). Repeated recrystallization of a mixture of **1** and **17** consistently led to the isolation of pure samples of **1** even when present as less than 17% of the mixture. As a consequence, a pure sample of **17** could not be obtained. These structural determinations enable the following assignments of selectivity to be made for intramolecular heteroannular Friedel−Crafts cyclization of **11a**.



As predicted, this process is regioselective (93:7), although only poorly diastereoselective (1.5:1) for the two β-substituted regioisomers. In contrast, the minor α-substituted regioisomer is formed with good diastereoselectivity. No evidence for homoannular cyclization was observed. Other Lewis acids including $AlCl_3$, $BF_3{\cdot}OEt_2$, $TiCl_4$, and methylaluminum bis(2,6-di-*tert*-butylphenoxide)[19] all failed to promote significant levels of cyclization, and Et_2AlCl led to a 1:1 mixture of **13** and **14**.

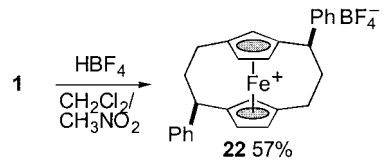
This ferrocenophane synthesis methodology was also applied to the diacid **11b**, except that the monobridged acids resulting from the first $SnCl_4$-promoted Friedel−Crafts cyclization were not converted into their methyl esters, but were instead directly reduced with $HSiEt_3$ in TFA. The inseparable products were further cyclized with TFAA and reduced as before to give an excellent overall yield of only two ferrocenophanes in a 1:1.5 ratio. Due to the similarities of their ^1H NMR spectra to those of **17** and **1**, they were assigned structures **18** and **19**, respectively, and from this mixture pure **19** was readily isolated on recrystallization from EtOAc/petroleum ether (Scheme 5). Further recrystallization of the evaporated mother liquors consistently gave smaller pure samples of this same isomer. Its structure was assigned unequivocally by bromine−lithium exchange and addition of water, which gave the parent ferrocenophane **1**. When instead CO_2 was passed through the reaction mixture following bromine−lithium exchange, an excellent yield of the diacid **20** was obtained after an acidic workup, a further building block for the synthesis of functionalized ferrocenophane derivatives (Scheme 6). As a direct application of ferrocenophane **1**, we sought to investigate the use of its ferrocenium ion as a potential chiral Lewis acid in the Diels−Alder reaction.

Scheme 6



(19) Maruoka, K.; Itoh, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 4573.

Scheme 7



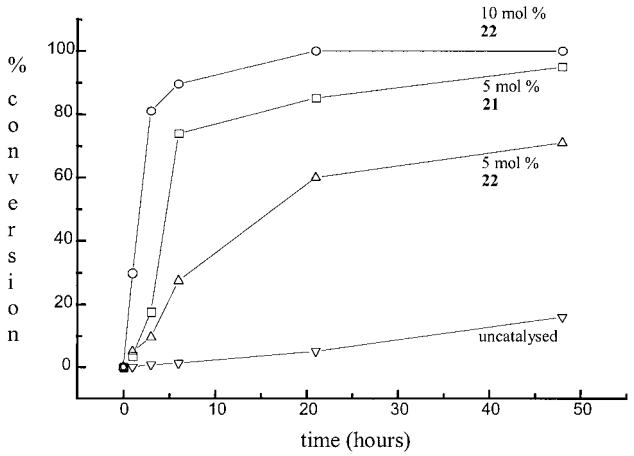


Figure 3.

Ferrocenium hexafluorophosphate **21** has been reported to act in this capacity,[20] and the ferrocenium ion of a singly bridged C_2-symmetric [4]-ferrocenophane has also been shown to catalyze the Diels−Alder reaction between methacrolein and cyclopentadiene, the product being obtained in a modest 10% enantiomeric excess.[3a] Treatment of **1** with HBF_4 gave dark blue crystals of the ferrocenium salt **22** after a basic workup to ensure removal of trace acid (Scheme 7). Both this and commercially available ferrocenium hexafluorophosphate **21** were employed as catalysts for this same Diels−Alder reaction, the results of which are shown in Figure 3.

Compared to the uncatalyzed background reaction, use of 5 mol % of both **21** and **22** gave a comparable modest enhancement of rate, although 10 mol % of **22** was required to ensure completion of the reaction within a reasonable time scale. Unfortunately, for both the resulting *exo*:*endo* (84:16) diastereoisomers, no enantioselectivity was observed as determined by examination by GC and ^{1}H NMR of their acetals derived from (*R*,*R*)-2,4-pentanediol.[21]

Examination of the X-ray structure of **1** reveals a cyclopentadienyl ring−ring tilt angle of 6.5°, further opening up exposure to the metal at the side of the molecule containing the 4/4′ and 5/5′ positions. In attempting to use the ferrocenium ion of **1** as a chiral Lewis acid, it was reasoned that association of a dienophile to this *exo* face would place it within the C_2-symmetric environment defined by the two phenyl substituents. However, the equatorial orientation of these groups in **1** is maintained in solution, as shown by the coupling constant of 9.8 Hz to the benzylic methine protons, thus reducing their influence and possibly explaining the lack of enantioselectivity observed with **22**.

In conclusion, this work has described the asymmetric synthesis of singly bridged ferrocenophanes from α-ferrocenyl alcohols, utilizing enantiospecific methanolysis and further enantiospecific C−C bond forming addition of a silyl ketene acetal. This methodology is equally applicable to 1,1′-disubstituted ferrocenes, and the resulting diacids undergo a highly regioselective and partially diastereoselective heteroannular Friedel−Crafts cyclization. Further high-yielding steps have provided both unfunctionalized **1**/**17** and functionalized **18**/**19**/**20** doubly bridged C_2-symmetric ferrocenophanes of high enantiomeric purity. Although these structures are not suited for use as a ferrocenium chiral Lewis acids, the X-ray structure of **1** reveals their potential as frameworks for novel ligands and materials, on which we aim to report in due course.

Experimental Section

Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl. Toluene, dichloromethane, hexane, and ethyl acetate were distilled from calcium hydride. Diisopropylamine was distilled from sodium hydroxide. Petroleum ether refers to that fraction boiling in the range 40−60 °C and hexane to the fraction boiling in the range 65.5−70 °C. Column chromatography was performed on Matrix silica 60 (35−70 μm) in 10% EtOAc/40−60 petroleum ether unless otherwise stated. The reagents BH_3·THF and BH_3·SMe_2 were used as 2 M solutions in THF.

Asymmetric Reduction of Ferrocenyl Ketones. The oxazaborolidine catalyst was prepared as previously described.[22] The reductions of **4a**−**c** followed the procedure previously described for the reduction of 1,1′-disubstituted ferrocenyl ketones.[17]

Synthesis of (*R*)-Phenylhydroxymethylferrocene 5a. Benzoylferrocene **4a** (0.20 g, 0.69 mmol), (*S*)-α,α-diphenyl *B*-methyloxazaborolidine (0.06 g, 0.22 mmol), BH_3·THF (0.14 mL, 0.14 mmol), and BH_3·Me_2S (0.28 mL, 0.56 mmol) were used in the synthesis. Chromatography gave an orange crystalline solid (0.17 g, 84%): mp 89−91 °C (EtOAc/petroleum ether); $[\alpha]_D^{23} = -129$ (*c* 0.09 in C_6H_6) (lit.[11] $[\alpha]_D^{20} = -85$ (*c* 3.4 in C_6H_6)].

Synthesis of (*R*)−(4-Bromophenyl)hydroxymethylferrocene 5b. 4-Bromobenzoylferrocene[23] **4b** (0.46 g, 1.25 mmol), (*S*)-α,α-diphenyl *B*-methyloxazaborolidine (0.11 g, 0.40 mmol), BH_3·THF (0.27 mL, 0.27 mmol), and BH_3·Me_2S (0.55 mL, 1.10 mmol) were used in the synthesis. Chromatography gave an orange crystalline solid (0.36 g, 77%): mp 105−107 °C (EtOAc/petroleum ether); $[\alpha]_D^{25} = +73$ (*c* 0.055 in C_6H_6); (found C, 54.86; H, 4.20; $C_{17}H_{15}FeBrO$ requires C, 55.02; H, 4.08); ν_{max} (Nujol)/cm^{-1} 3362 and 1108; δ_H (400 MHz, $CDCl_3$) 2.38 (1 H, d, *J* 3.0, −O*H*), 4.08−4.14 (4 H, m, Fc × 4), 4.16 (5 H, s, C_5H_5), 5.34 (1 H, d, *J* 3.0, FcC*H*Ar−), 7.19 (2H, d, *J* 8.4, Ar), 7.37 (2H, d, *J* 8.4, Ar); δ_C (100 MHz, $CDCl_3$) 66.13 (Fc), 67.80 (Fc), 68.67 (Fc), 68.70 (Fc), 68.89 (C_5H_5), 71.70 (Fc*C*HAr−), 94.42 (Fc − *ipso*), 121.58 (Ar − *ipso*), 128.29 (Ar), 131.67 (Ar), 142.66 (Ar − *ipso*); *m*/*z* (ES) 372.2 (M^+, 92), 370.2 (M^+, 100).

Synthesis of (*R*)-1-Hydroxyethylferrocene 5c. Acetylferrocene **4c** (1.07 g, 4.69 mmol), (*S*)-α,α-diphenyl *B*-methyloxazaborolidine (0.39 g, 1.41 mmol), BH_3·THF (0.94 mL, 0.94 mmol), and BH_3·Me_2S (1.90 mL, 3.80 mmol) were used in the synthesis. Chromatography gave a yellow crystalline solid

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(0.85 g, 79%): mp 70−72 °C (EtOAc/petroleum ether); $[\alpha]_D^{21} = -34$ (*c* 0.07 in C_6H_6) [lit.[11] $[\alpha]_D^{20} = -31$ (*c* 3.4 in C_6H_6)].

General Method for the Methanolysis of α-Ferrocenyl Alcohols. The appropriate α-ferrocenyl alcohol (1.0 mmol) was dissolved in methanol (4.5 mL). To the yellow solution was added glacial acetic acid (0.5 mL) and the reaction stirred at room temperature for 24 h. The yellow reaction mixture was then quenched slowly with saturated $NaHCO_3$(aq) (5 mL) and extracted with Et_2O (5 mL + 1 mL), and the combined organic phases were washed with NaCl(aq) (5 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo.

Synthesis of (*R*)-Phenylmethoxymethylferrocene 6a. (*R*)-Phenylhydroxymethylferrocene **5a** (1.04 g, 3.56 mmol) was used in the synthesis. Chromatography gave a yellow crystalline solid (1.00 g, 92%): mp 92−94 °C (EtOAc/petroleum ether); $[\alpha]_D^{22} = +52$ (*c* 0.185 in EtOH).

Synthesis of (*R*)−(4-Bromophenyl)methoxymethylferrocene 6b. (*R*)−(4-Bromophenyl)hydroxymethylferrocene **5b** (0.36 g, 0.97 mmol) was used in the synthesis. Chromatography gave a yellow crystalline solid (0.35 g, 94%): mp 148−149 °C (EtOAc/petroleum ether); $[\alpha]_D^{18} = +48$ (*c* 0.05 in EtOH); (found C, 56.36; H, 4.64; $C_{18}H_{17}BrFeO$ requires C, 56.13; H, 4.46**);** ν_{max} (Nujol)/cm^{-1} 1073 and 1108; δ_H (400 MHz, $CDCl_3$) 3.29 (3 H, s, −OC*H*$_3$), 3.90 (1 H, s, Fc), 4.06 (5 H, s, C_5H_5), 4.09 (1 H, s, Fc), 4.14 (1 H, s, Fc), 4.28 (1 H, s, Fc), 4.97 (1 H, s, FcC*H*Ar−), 7.30 (2 H, d, *J* 8.4, Ar), 7.50 (2 H, d, *J* 8.4, Ar); δ_C (100 MHz, $CDCl_3$) 57.42 (−O*C*H$_3$), 67.31(Fc), 68.08 (Fc), 68.47 (2 × Fc), 69.20 (C_5H_5), 82.45 (Fc*C*HAr-), 90.10 (Fc − *ipso*), 128.85 (Ar − *ipso*), 129.41 (Ar), 131.79 (Ar), 132.92 (Ar − *ipso*); *m*/*z* (ES) 387.5 (MH^+, 14), 386.4 (M^+, 60), 385.7 (MH^+, 74), 384.1 (M^+, 100), 153.3 (58), 152.0 (100), 150.0 (64), 121.5 (100) 55.9 (45).

Synthesis of (*R*)-1-methoxyethylferrocene 6c. (*R*)-1-Hydroxyethylferrocene **5c** (0.85 g, 3.69 mmol) was used in the synthesis. Chromatography gave an orange oil (0.83 g, 92%); $[\alpha]_D^{23} = +29.6$ (*c* 0.093 in EtOH) [lit.[13] $[\alpha]_D^{25} = +27.5$ (*c* 2.0 in EtOH)].

Synthesis of (*R*)-3-Ethoxy-3-oxo-1-phenylpropylferrocene 7a. Following the previously reported procedure,[8] (*R*)-phenylmethoxymethylferrocene **6a** (0.09 g, 0.29 mmol), 1-ethoxy-1-(trimethylsiloxy)ethene (0.18 g, 1.12 mmol), and BF_3·OEt_2 (0.05 g, 0.35 mmol) gave, after chromatography, an orange oil (0.10 g, 94%); $[\alpha]_D^{23} = +53$ (*c* 0.155 in $CHCl_3$).

Synthesis of (*R*)-1-(4-Bromophenyl)-3-ethoxy-3-oxopropylferrocene 7b. (*R*)−(4-Bromophenyl)methoxymethylferrocene **6b** (0.32 g, 0.83 mmol), 1-ethoxy-1-(trimethylsiloxy)-ethene (0.54 g, 3.37 mmol), and BF_3·OEt_2 (0.13 g, 0.92 mmol) were used in the synthesis. Chromatography gave a yellow crystalline solid (0.30 g, 82%): mp 111−113 °C (EtOAc/petroleum ether); $[\alpha]_D^{18} = +78$ (*c* 0.125 in $CHCl_3$); (found C, 57.37; H, 4.99; $C_{21}H_{21}FeBrO_2$ requires C, 57.17; H, 4.81); ν_{max} (Nujol)/cm^{-1} 1718 and 1108; δ_H (400 MHz, $CDCl_3$) 1.11 (3 H, t, *J* 7.2, −C*H*$_3$), 2.73 (1 H, dd, *J* 10.7, 15.3, −C*H*HCO$_2$Et), 3.04 (1 H, dd, *J* 4.6, 15.3, −CH*H*CO$_2$Et), 3.87−3.88 (1 H, m, Fc), 4.04 (5 H, s, C_5H_5), 3.97−4.05 (5 H, m, Fc × 3 and −OCH_2-CH$_3$), 4.12 (1 H, dd, *J* 4.6, 10.7, FcC*H*Ar−), 7.01 (2 H, d, *J* 8.4, Ar), 7.31 (2 H, d, *J* 8.4, Ar); δ_C (100 MHz, $CDCl_3$) 14.52 (−*C*H$_3$), 41.94 (−*C*H$_2$CO$_2$Et), 42.26 (Fc*C*HAr−), 60.92 (−O*C*H$_2$CH$_3$), 66.75 (Fc), 67.80 (Fc), 68.06 (Fc), 68.33 (Fc), 69.09 (C_5H_5), 92.44 (Fc − *ipso*), 120.68 (Ar − *ipso*), 129.81 (Ar), 131.74 (Ar), 143.53 (Ar − *ipso*), 172.15 (*C*═O); *m*/*z* (ES) 442.3 (M^+, 85%), 440.2 (M^+, 93), 142.0 (93), 100.8 (100).

Synthesis of (*S*)-3-Ethoxy-1-methyl-3-oxopropylferrocene 7c. (*R*)-1-Methoxyethylferrocene **6c** (0.11 g, 0.45 mmol), 1-ethoxy-1-(trimethylsiloxy)ethene (0.29 g, 1.81 mmol), and BF_3·OEt_2 (0.07 g, 0.49 mmol) were used in the synthesis. Chromatography gave an orange oil (0.13 g, 96%): $[\alpha]_D^{19} = +19$ (*c* 0.105 in $CHCl_3$).

General Method for the Hydrolysis of Ethyl 3-Ferrocenylpropanoates. The appropriate ester (1 mmol) was suspended in 1:1 MeOH/H_2O (2 mL) containing NaOH (1.5 mmol) and heated at reflux overnight. After cooling to room temperature, the resultant yellow solution was acidified with dilute hydrochloric acid and the product extracted into CH_2Cl_2 (5 mL + 5 mL). The organic phases were combined, dried (Na_2SO_4), filtered, and evaporated in vacuo, and the residue was purified by column chromatography.

Synthesis of (*R*)-2-Carboxy-1-phenylethylferrocene 8a. (*R*)-3-Ethoxy-3-oxo-1-phenylpropylferrocene **7a** (0.33 g, 0.91 mmol) was used in the synthesis. Chromatography gave a yellow crystalline solid (0.28 g, 92%): mp 99−101 °C (EtOAc/petroleum ether); $[\alpha]_D^{20} = +97$ (*c* 0.095 in EtOH).

Synthesis of (*R*)-1-(4-Bromophenyl)-2-carboxyethylferrocene 8b. (*R*)-1-(4-Bromophenyl)-3-ethoxy-3-oxopropylferrocene **7b** (0.30 g, 0.68 mmol) was used in the synthesis. Chromatography gave an orange crystalline solid (0.23 g, 82%): mp 130−132 °C (EtOAc/petroleum ether); $[\alpha]_D^{21} = +56$ (*c* 0.100 in EtOH); (found C, 55.51; H, 4.40; $C_{19}H_{17}BrFeO_2$ requires C, 55.24; H, 4.16); ν_{max} (Nujol)/cm^{-1} 3420, 1698 and 1106; δ_H (400 MHz, $CDCl_3$) 2.77 (1 H, dd, *J* 10.4, 15.8, −C*H*HCO$_2$H), 3.10 (1 H, dd, *J* 4.5, 15.7, −CH*H*CO$_2$H), 3.88 (1 H, s, Fc), 4.04 (7 H, s, C_5H_5 and Fc × 2), 4.06 (1 H, s, Fc), 4.10 (1 H, dd, *J* 4.6, 10.5, FcC*H*Ar−), 7.01 (2 H, d, *J* 8.4, Ar), 7.31 (2 H, d, *J* 8.3, Ar); δ_C (100 MHz, $CDCl_3$) 41.68 (−*C*H$_2$CO$_2$H), 41.82 (Fc*C*HAr−), 66.75 (Fc), 67.92 (Fc), 68.12 (Fc), 68.48 (Fc), 69.20 (C_5H_5), 92.29 (Fc − *ipso*), 120.86 (Ar − *ipso*), 129.71 (Ar), 131.89 (Ar), 143.29 (Ar − *ipso*), *C*═O signal not observed; *m*/*z* (ES) 414.3 (M^+, 43), 412.3 (M^+, 43), 59.7 (100).

Synthesis of (*S*)-2-Carboxy-1-methylethylferrocene 8c. (*S*)-3-Ethoxy-1-methyl-3-oxopropylferrocene **7c** (0.84 g, 2.80 mmol) was used in the synthesis. Chromatography gave an orange oil (0.56 g, 74%): $[\alpha]_D^{20} = +34$ (*c* 0.11 in EtOH).

General Method for the Synthesis of (*S*)-Methyl Mandelate Esters. The appropriate ferrocenylpropanoic acid (0.06 mmol) was dissolved in dry CH_2Cl_2 (3 mL) and cooled to 0 °C under an atmosphere of nitrogen. Dicyclohexylcarbodiimide (0.14 mmol), (dimethylamino)pyridine (0.05 mol), and (*S*)-methyl mandelate (0.11 mmol) were added to the resultant yellow solution, which was allowed to stir overnight. The reaction was quenched with saturated $NaHCO_3$(aq) (3 mL), and after separation, the organic phase was washed with saturated NaCl(aq) (3 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo. The resultant yellow semisolids were examined by ^{1}H NMR spectroscopy to determine the ratio of diastereoisomers.

Data for **8a**: Major diastereoisomer, δ_H (400 MHz, $CDCl_3$) 5.76 (1 H, s, −OC*H*(CO$_2$CH$_3$)Ph). Corresponding peak for minor diastereoisomer, 5.80, 96% ee.

Data for **8b**: Major diasteroisomer, δ_H (400 MHz, $CDCl_3$) 3.64 (3 H, s, −CO$_2$C*H*$_3$), 5.78 (1 H, s, −OC*H*(CO$_2$CH$_3$)Ph). Corresponding peaks for minor diastereoisomer, 3.57, 5.82, 96% ee.

Data for **8c**: Major diastereoisomer, δ_H (400 MHz, $CDCl_3$) 2.77 (1 H, dd, *J* 15.2, 4.6, −C*H*HCO$_2$−), 5.89 (1 H, s, −OC*H*(CO$_2$CH$_3$)Ph). Corresponding peaks for minor diastereoisomer, 2.69 (dd, *J* 15.1, 4.7), 5.87, 92% ee.

General Method for the Friedel−Crafts Cyclization of Ferrocenylpropanoic Acids. The appropriate ferrocenylpropanoic acid (1 mmol) was suspended in neat PCl_3 (4 mmol) under an atmosphere of nitrogen and stirred for 30 min. After this time the ferrocenylpropanoic acid had dissolved to give a yellow solution of the acid chloride. The excess PCl_3 was removed in vacuo to yield a yellow gum, which was subsequently dissolved in dry CH_2Cl_2 (2 mL). In a separate vessel, $SnCl_4$ (1.2 mmol) was added to dry CH_2Cl_2 (2 mL) under an atmosphere of nitrogen and cooled to 0 °C. The acid chloride solution was added dropwise to this $SnCl_4$ solution over 5 min. The resultant red solution was allowed to stir at 0 °C for 15 min, after which the cooling bath was removed and the solution allowed to stir for a further 5 min before quenching with saturated $NaHCO_3$(aq) (4 mL). The two phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 mL). The organic phases were combined, washed with saturated NaCl-

(aq) (5 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo, and the residue was column chromatographed.

Synthesis of (*R*)-1,1′-(1-Oxo-3-phenyl-1,3-propanediyl)-ferrocene 9a. (*R*)-2-Carboxy-1-phenylethylferrocene **8a** (0.36 g, 1.08 mmol), PCl_3 (0.59 g, 4.29 mmol), and $SnCl_4$ (0.31 g, 1.19 mmol) were used in the synthesis. Chromatography gave an orange crystalline solid (0.32 g, 94%): mp 202−204 °C (EtOAc/petroleum ether); $[\alpha]_D^{23} = +1375$ (*c* 0.095 in $CHCl_3$).

Synthesis of (*R*)-1,1′-(1-(4-Bromophenyl)-3-oxo-1,3-propanediyl)ferrocene 9b. (*R*)-1-(4-Bromophenyl)-2-carboxyethylferrocene **8b** (0.37 g, 0.90 mmol), PCl_3 (0.49 g, 3.57 mmol), and $SnCl_4$ (0.25 g, 0.96 mmol) were used in the synthesis. Chromatography gave an orange crystalline solid (0.33 g, 93%): mp 239−240 °C (EtOAc/petroleum ether); $[\alpha]_D^{24} = +967$ (*c* 0.115 in $CHCl_3$); (found: C, 57.96; H, 4.06; $C_{19}H_{15}FeBrO$ requires C, 57.75; H, 3.83); ν_{max} (Nujol)/cm^{-1} 1652; δ_H (400 MHz, $CDCl_3$) 2.61 (1 H, dd, *J* 3.3, 10.3, FcC*H*ArCH$_2$−), 3.88 (1 H, dd, *J* 10.2, 12.9, FcCHArC*H*H−), 3.93−3.95 (1 H, m, Fc), 4.10−4.09 (1 H, m, Fc), 4.27 (1 H, dd, *J* 3.2, 12.9 FcCHArCH*H*−), 4.32−4.34 (1 H, m, Fc), 4.38−4.39 (1 H, m, Fc), 4.50−4.51 (1 H, m, Fc), 4.58−4.59 (1 H, m, Fc), 4.66−4.67 (1 H, m, Fc), 5.01−5.02 (1 H, m, Fc), 7.07 (2 H, d, *J* 8.4, Ar), 7.34 (2 H, d, *J* 8.4, Ar); δ_C (100 MHz, $CDCl_3$) 49.03 (Fc*C*HAr−), 50.14 (FcCHAr*C*H$_2$−), 68.31 (Fc), 68.38 (Fc), 68.74 (Fc), 71.57 (Fc), 72.69 (Fc), 73.41 (Fc), 73.48 (Fc), 73.12 (Fc), 76.79 (Fc − *ipso*), 91.62 (Fc − *ipso*), 120.95 (Ar - *ipso*), 128.63 (Ar), 131.99 (Ar), 142.49 (Ar − *ipso*), 208.25 (*C*═O); *m*/*z* (ES) 397.3 (MH^+, 100), 396.2 (M^+, 29), 395.2 (MH^+, 74), 394.2 (M^+, 13).

Synthesis of (*S*)-1,1′-(1-Methyl-3-oxo-1,3-propanediyl)-ferrocene 9c. (*S*)-2-Carboxy-1-methylethylferrocene **8c** (0.29 g, 1.07 mmol), PCl_3 (0.59 g, 4.30 mmol), and $SnCl_4$ (0.31 g, 1.19 mmol) were used in the synthesis. Chromatography gave an orange crystalline solid (0.25 g, 92%): mp 136−137.5 °C (EtOAc/petroleum ether); $[\alpha]_D^{20} = +833$ (*c* 0.17 in $CHCl_3$).

Synthesis of 1,1′-Bis(4-bromobenzoyl)ferrocene 10b. Following the procedure previously described for the synthesis of dibenzoylferrocene,[24] ferrocene (10.00 g, 53.8 mmol), 4-bromobenzoyl chloride (25.95 g, 118.2 mmol), and $AlCl_3$ (15.77 g, 118.3 mmol) gave dark purple fibrous crystals after recrystallization from THF/petroleum ether (25.81 g, 87%): mp 193−194 °C; (found C, 51.98; H, 2.68; $C_{24}H_{16}Br_2FeO_2$ requires C, 52.21; H, 2.93); ν_{max} (Nujol)/cm^{-1} 1630; δ_H (400 MHz, $CDCl_3$) 4.52 (4 H, s, Fc × 4), 4.78 (4 H, s, Fc × 4), 7.48 (4 H, d, *J* 7.5, Ar), 7.53 (4 H, d, *J* 7.2, Ar); δ_C (100 MHz $CDCl_3$) 73.66 (Fc), 74.90 (Fc), 79.69 (Fc − *ipso*), 127.33 (Ar − *ipso*), 129.98 (Ar), 131.98 (Ar), 137.97 (Ar − *ipso*), 197.01 (*C*═O); *m*/*z* (ES) 553.8 (M^+, 45), 551.7 (M^+, 94), 549.8 (M^+, 50), 184.7 (43), 182.7 (45), 156.6 (37), 154.6 (35), 138.7 (100), 93.5 (63).

Synthesis of (*R*,*R*)-1,1′-Bis(phenylmethoxymethyl)ferrocene 3a. 1,1′-Bis(benzoyl)ferrocene **10a** (6.03 g, 15.3 mmol), (*S*)-α,α-diphenyl *B*-methyloxazaborolidine (2.54 g, 9.17 mmol), BH_3·THF (6.13 mL, 6.13 mmol), and BH_3·Me_2S (6.11 mL, 12.22 mmol) gave, as previously reported,[17] the crude diol as a yellow solid (5.79 g). Due to the tendency of these diols to form cyclic ethers during column chromatography, this was instead subjected directly to methanolysis which, after recrystallization from EtOAc/petroleum ether, gave **3a** as a yellow crystalline solid (4.82 g, 74% from **10a**): mp 104−106 °C (EtOAc/petroleum ether); $[\alpha]_D^{19} = +87$ (*c* 0.11 in EtOH).

Synthesis of (*R*,*R*)-1,1′-Bis((4-bromophenyl)methoxymethyl)ferrocene 3b. 1,1′-Bis(4-bromobenzoyl)ferrocene **10b** (15.00 g, 27.2 mmol), (*S*)-α,α-diphenyl *B*-methyl-oxazaborolidine (4.52 g, 16.32 mmol), BH_3·THF (10.87 mL, 10.87 mmol), and BH_3·Me_2S (21.73 mL, 43.46 mmol) gave the crude diol as a yellow solid (14.56 g). Methanolysis and recrystallization from EtOAc/petroleum ether gave **3b** as a yellow crystalline solid (13.06 g, 82% from **10b**): mp 115−117 °C; $[\alpha]_D^{19} = +80$ (*c* 0.08 in EtOH); (found C, 53.21; H, 4.14; $C_{26}H_{24}Br_2FeO_2$ requires C, 53.45, H, 4.15); ν_{max} (Nujol)/cm^{-1} 1083; δ_H (400 MHz, $CDCl_3$) 3.17 (6 H, s, −OC*H*$_3$), 3.64 (2 H, s, Fc), 3.91 (2 H, s, Fc), 3.97 (2 H, s, Fc), 4.13 (2 H, s, Fc), 4.75 (2 H, s, FcC*H*Ar−), 7.15 (4 H, d, *J* 8.4, Ar), 7.43 (4 H, d, *J* 8.3, Ar); δ_C (100 MHz, $CDCl_3$) 55.84 (−O*C*H$_3$), 66.76 (Fc), 67.36 (Fc), 67.91 (Fc), 67.96 (Fc), 80.73 (Fc*C*HAr−), 88.82 (Fc − *ipso*), 120.43 (Ar − *ipso*), 127.93 (Ar), 130.35 (Ar), 139.38 (Ar − *ipso*); *m*/*z* (ES) 586.3 (47), 585.4 (60), 584.3 (100), 583.4 (60), 581.6 (49).

Synthesis of (*R*,*R*)-1,1′-Bis(3-ethoxy-3-oxo-1-phenylpropyl)ferrocene 2a. Following the previously reported procedure,[8] (*R*,*R*)-1,1′-bis(phenylmethoxymethyl)ferrocene **3a** (0.33 g, 0.77 mmol), 1-ethoxy-1-(trimethylsiloxy)ethene (0.49 g, 3.06 mmol), and BF_3·OEt_2 (0.24 g, 1.69 mmol) gave, after chromatography, an orange crystalline solid (0.41 g, 98%): mp 83−84 °C (EtOAc/petroleum); $[\alpha]_D^{21} = +95$ (*c* 0.08 in $CHCl_3$).

Synthesis of (*R*,*R*)-1,1′-Bis(1-(4-bromophenyl)-3-ethoxy-3-oxopropyl)ferrocene 2b. Using the same method as that for **2a**, (*R*,*R*)-1,1′-bis((4-bromophenyl)methoxymethyl)ferrocene **3b** (1.32 g, 2.26 mmol), 1-ethoxy-1-(trimethylsiloxy)ethene (1.45 g, 9.06 mmol), and BF_3·OEt_2 (0.71 g, 5.00 mmol) gave, after chromatography, an orange oil (1.50 g, 95%): $[\alpha]_D^{22} = +75°$ (*c* 0.57 in $CHCl_3$); (found C, 54.93; H, 4.77; $C_{32}H_{32}Br_2FeO_4$ requires C, 55.19, H, 4.64); ν_{max} (liquid)/cm^{-1} 1738; δ_H (400 MHz, $CDCl_3$) 1.02 (6 H, t, *J* 7.1, −C*H*$_3$), 2.63 (2 H, dd, *J* 10.4, 15.2, −C*H*HCO$_2$Et), 2.85 (2 H, dd, *J* 8.0, 15.2, −CH*H*CO$_2$Et), 3.66−3.67 (2 H, m, Fc × 2), 3.88−4.00 (12 H, m, Fc × 6, FcC*H*ArCH$_2$CO$_2$C*H*$_2$CH$_3$), 6.93 (4 H, d, *J* 8.4, Ar), 7.27 (4 H, d, *J* 8.4, Ar); δ_C (100 MHz, $CDCl_3$) 15.53 (−*C*H$_3$), 42.87 (Fc*C*HAr−), 43.48 (−*C*H$_2$CO$_2$Et), 61.96 (−O*C*H$_2$CH$_3$), 68.31 (Fc) 69.66 (Fc), 69.97 (Fc), 70.39 (Fc), 93.59 (Fc − *ipso*), 121.79 (Ar − *ipso*), 130.86 (Ar), 132.81 (Ar), 144.22 (Ar − *ipso*), 172.98 (C═O); *m*/*z* (ES) 699.3 (MH^+, 22), 698.4 (M^+, 52), 697.5 (MH^+, 68), 696.4 (M^+, 100), 695.5 (MH^+, 97), 694.3 (M^+, 73).

Synthesis of (*R*,*R*)-1,1′-Bis(2-carboxy-1-phenylethyl)-ferrocene 11a. As previously reported for the racemic series,[8] (*R*,*R*)-1,1′-bis(3-ethoxy-3-oxo-1-phenylpropyl)ferrocene **2a** (6.56 g, 12.19 mmol) gave a yellow crystalline solid after workup and evaporation of the solvent (5.82 g, 99%): mp 191−193 °C (EtOAc/petroleum ether); $[\alpha]_D^{18} = +122$ (*c* 0.095 in EtOH).

Synthesis of (*R*,*R*)-1,1′-Bis(1-(4-bromophenyl)-2-carboxyethylferrocene 11b. Using the same method as that for **11a** (*R*,*R*)-1,1′-bis(1-(4-bromophenyl)-3-ethoxy-3-oxopropyl)ferrocene **2b** (2.47 g, 3.55 mmol) gave a yellow crystalline solid (2.14 g, 94%): mp 179−184 °C (EtOAc/petroleum ether); $[\alpha]_D^{19} = +152$ (*c* 0.05 in EtOH); (found C, 52.79; H, 3.99; $C_{28}H_{24}Br_2FeO_4$ requires C, 52.53, H, 3.79); ν_{max} (Nujol)/cm^{-1} 1710; δ_H (400 MHz, DMSO-d_6) 2.58 (2 H, dd, *J* 10.8, 15.6, −C*H*HCO$_2$H), 3.78 (2 H, dd, *J* 4.5, 15.6, −CH*H*CO$_2$H), 3.65 (2 H, d, *J* 1.36, Fc × 2), 3.76 (2 H, dd, *J* 4.5, 10.6, FcC*H*Ar−), 3.81 (4 H, t, *J* 1.33, Fc × 4), 4.00 (2 H, d, *J* 1.32, Fc), 6.95 (4 H, d, *J* 8.4, Ar), 7.22 (4 H, d, *J* 8.3, Ar), 12.12 (2 H, s, −CO$_2$*H*); δ_C (100 MHz, DMSO-d_6) 42.29 (−*C*H$_2$CO$_2$H), 42.42 (Fc*C*HAr−), 68.16 (Fc), 69.48 (Fc) 69.85 (Fc), 69.99 (Fc), 94.27 (Fc − *ipso*), 120.76 (Ar − *ipso*), 131.34 (Ar), 132.48 (Ar), 145.57 (Ar − *ipso*), 174.22 (*C*═O); *m*/*z* (ES) 643.6 (MH^+, 0.21), 642.6 (M^+, 0.50), 641.6 (MH^+, 1.33), 640.6 (M^+, 0.58), 60.9 (100).

From the diacids (0.06 mmol), dry CH_2Cl_2 (4 mL), dicyclohexylcarbodiimide (0.28 mmol), (dimethylamino)pyridine (0.10 mmol), and (*S*)-methyl mandelate (0.22 mmol), the methyl mandalate diesters were synthesized as described above.

Data for **11a**: Major diastereoisomer, δ_H (400 MHz, $CDCl_3$) 3.61 (6 H, s, −CO$_2$C*H*$_3$). Corresponding peak for minor diastereoisomer, 3.54, 94% ee.

Data for **11b**: Major diastereoisomer, δ_H (400 MHz, $CDCl_3$) 5.76 (2 H, s, −OC*H*(CO$_2$CH$_3$)Ar). Corresponding peak for minor diastereoisomer, 5.81, 94% ee.

The Friedel−Crafts Cyclization of 11a. (*R*,*R*)-1,1′-Bis-(2-carboxy-1-phenylethyl)ferrocene **11a** (0.96 g, 2.0 mmol) was suspended in neat PCl_3 (20 mL) under an atmosphere of nitrogen and warmed to 70 °C for 60 min. After this time, the diacid had dissolved to give a yellow solution of the corre-

(24) Rausch, M.; Vogel, M.; Rosenberg, H. *J. Org. Chem.* **1957**, *22*, 903.

sponding diacid chloride. The excess PCl_3 was removed in vacuo to yield a yellow gum, which was subsequently dissolved in dry CH_2Cl_2 (35 mL). In a separate vessel, $SnCl_4$ (1.15 g, 4.4 mmol) was added to dry CH_2Cl_2 (30 mL) under an atmosphere of nitrogen and cooled to 0 °C. The acid chloride solution was added dropwise to this $SnCl_4$ solution over 5 min. The resultant red solution was allowed to stir at 0 °C for 15 min, after which the cooling bath was removed and the solution allowed to stir for a further 5 min before quenching with dilute HCl(aq) (65 mL). The two resulting phases were separated, and the aqueous phase was extracted with additional CH_2Cl_2 (5 mL). The organic phases were combined, washed with dilute HCl(aq) (2 × 30 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo to yield the semicyclized acids as a dark orange residue (0.81 g). These were dissolved in dry CH_2Cl_2 (20 mL) under a nitrogen atmosphere, and the resulting solution was cooled to 0 °C. To this was added DCC (0.76 g, 3.68 mmol), DMAP (0.09 g, 0.74 mmol), and dry MeOH (0.15 mL, 3.7 mmol), and the resulting solution was stirred at room temperature overnight. After addition of saturated $NaHCO_3$(aq) (20 mL), the two resulting phases were separated and the aqueous phase was washed with additional CH_2Cl_2 (4 mL). The organic components were combined, washed with NaCl(aq) (20 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo to give a dark orange/brown solid.

($_p$*R*)-1,1′-((*R*)-1-Oxo-3-phenyl-1,3-propanediyl)-2-((*R*)-3-methoxy-3-oxo-1-phenylpropyl)-ferrocene 12. Chromatography gave an orange solid (0.057 g, 6% from **11a**): mp 151−154 °C (EtOAc/petroleum ether); $[\alpha]_D^{22} = -573$ (*c* 0.13 in $CHCl_3$); (found C, 72.76; H, 5.59; $C_{29}H_{26}FeO_3$ requires C, 72.80; H, 5.49); ν_{max} (Nujol)/cm^{-1} 1731 and 1661; δ_H (400 MHz, $CDCl_3$) 2.55 (1 H, dd, *J* 3.1, 10.4, FcC*H*PhCH$_2$CO−), 2.89 (1 H, dd, *J* 11.4, 14.9, FcCHPhC*H*HCO$_2$CH$_3$), 3.29 (1 H, dd, *J* 3.7, 14.9, FcCHPhCH*H*CO$_2$CH$_3$), 3.57 (3 H, s, −OC*H*$_3$), 3.88 (1 H, dd, *J* 10.4, 13.2 FcCHPhC*H*HCO-), 4.00−4.01 (1 H, m, Fc), 4.09−4.10 (1 H, m, Fc), 4.31−4.32 (1 H, m, Fc), 4.36−4.37 (1 H, m, FcCHPhCH*H*CO−), 4.41−4.42 (2 H, m, Fc), 4.59 (1 H, dd, *J* 3.7, 11.3, FcC*H*PhCH$_2$CO$_2$CH$_3$), 4.63−4.64 (1 H, m, Fc), 4.97−4.98 (1 H, m, Fc), 7.06 (1 H, t, *J* 7.3, Ph − *para*), 7.11−7.27 (9 H, m, Ph); δ_C (100 MHz $CDCl_3$) 40.55 (Fc*C*H-PhCH$_2$CO$_2$CH$_3$), 42.27 (FcCHPh*C*H$_2$CO$_2$CH$_3$), 49.28 (Fc*C*HPh−), 51.08 (FcCHPh*C*H$_2$−), 52.12 (−O*C*H$_3$), 68.27 (Fc), 68.75 (Fc), 71.08 (Fc), 71.31 (Fc), 71.46 (Fc), 73.78 (Fc − *ipso*), 75.13 (Fc), 75.34 (Fc), 92.97 (Fc − *ipso*), 93.48 (Fc − *ipso*), 126.80 (Ph), 126.86 (Ph), 127.17 (Ph), 128.05 (Ph), 128.58 (Ph), 128.99 (Ph), 143.98 (Ph − *ipso*), 144.68 (Ph − *ipso*), 172.65 (−*C*O$_2$CH$_3$), 207.46 (*C*═O); *m*/*z* (ES) 479.6 (MH$^+$, 34), 478.8 (M$^+$, 18), 42.1 (100).

($_p$*R*)-1,1′-((*R*)-1-Oxo-3-phenyl-1,3-propanediyl)-3-((*R*)-3-methoxy-3-oxo-1-phenylpropyl)ferrocene 14. Chromatography gave an orange solid (0.76 g, 80% from **11a**) isolated as a 1.0:1.5 mixture of diastereoisomers **13** and **14**. Recrystallization from EtOAc/petroleum ether gave the major diastereoisomer **14**: mp 144−148 °C; $[\alpha]_D^{20} = -693$ (*c* 0.105 in $CHCl_3$); (found C, 72.59; H, 5.77; $C_{29}H_{26}FeO_3$ requires C, 72.80; H, 5.49); ν_{max} (Nujol)/cm^{-1} 1731 and 1652; δ_H (400 MHz, $CDCl_3$) 2.57 (1 H, dd, *J* 3.2, 10.3, FcC*H*PhCH$_2$CO−), 2.81 (1 H, dd, *J* 9.4, 15.5, FcCHPhC*H*HCO$_2$CH$_3$), 2.91 (1 H, dd, *J* 5.9, 15.5, FcCHPhCH*H*CO$_2$CH$_3$), 3.52 (3 H, s, −OC*H*$_3$), 3.67 (1 H, s, Fc), 3.87 (1 H, dd, *J* 10.3, 12.9, FcCHPhC*H*HCO−), 4.05−4.09 (2 H, dd and s, *J* 5.9, 9.4, FcC*H*PhCH$_2$CO$_2$CH$_3$ and Fc), 4.24 (1 H, dd, *J* 3.1, 13.0, FcCHPhCH*H*CO−), 4.29 (1 H, s, Fc), 4.44 (1 H, s, Fc), 4.55 (1 H, s, Fc), 4.59 (1 H, s, Fc), 4.97 (1 H, s, Fc), 7.10−7.23 (10 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 41.44 (Fc*C*H-PhCH$_2$CO$_2$CH$_3$), 42.28 (FcCHPh*C*H$_2$CO$_2$CH$_3$), 49.51 (Fc*C*HPh), 50.28 (FcCHPh*C*H$_2$−), 52.11 (−O*C*H$_3$), 67.20 (Fc), 68.25 (Fc), 70.80 (Fc), 71.53 (Fc), 72.29 (Fc), 73.21 (Fc), 73.46 (Fc), 76.21 (Fc − *ipso*), 92.30 (Fc − *ipso*), 98.63 (Fc − *ipso*), 126.82 (Ph), 127.16 (Ph − *para*), 127.31 (Ph − *para*), 127.94 (Ph), 128.84 (Ph), 128.95 (Ph), 143.44 (Ph − *ipso*), 143.88 (Ph − *ipso*), 172.44 (−*C*O$_2$CH$_3$), 208.64 (*C*═O); *m*/*z* (ES) 479.4 (MH$^+$, 100), 478.5 (M$^+$, 7). (**13**: δ_H (400 MHz, $CDCl_3$) 3.05 (1 H, dd, *J* 5.7, 15.4), 3.55 (3 H, s), 4.14 (1 H, s), 4.63 (1 H, s), 4.93 (1 H, s) − other peaks obscured by **14** in mixture).

($_p$*S*)-1,1′-((*R*)-3-Phenyl-1,3-propanediyl)-3-((*R*)-3-methoxy-3-oxo-1-phenylpropyl)ferrocene 15. ($_p$*R*)-1,1′-((*R*)-1-Oxo-3-phenyl-1,3-propanediyl)-3-((*R*)-3-methoxy-3-oxo-1- phenylpropyl)ferrocene **14** (0.096 g, 0.20 mmol) was dissolved in 1:1 TFA/CH_2Cl_2 (2 mL) under an atmosphere of nitrogen to give a red solution. Triethylsilane (0.05 g, 0.43 mmol) was added quickly to the reaction mixture, which was stirred for 5 min. The resultant dark blue solution was quenched slowly by the dropwise addition of saturated $NaHCO_3$(aq) (2 mL) and followed by the addition of CH_2Cl_2 (2 mL). The organic phase was separated, washed with saturated NaCl(aq), dried (Na_2SO_4), filtered, and evaporated in vacuo to yield an orange solid. Recrystallization from EtOAc/petroleum ether gave an orange crystalline solid (0.087 g, 93%): mp 121.5−123 °C; $[\alpha]_D^{21} = +9$ (*c* 0.115 in $CHCl_3$); (found C, 74.78; H, 6.09; $C_{29}H_{28}FeO_2$ requires C, 74.99; H, 6.09); ν_{max} (Nujol)/cm^{-1} 1728; δ_H (400 MHz, $CDCl_3$) 1.75 (1 H, td, *J* 3.9, 13.1, FcCHPhCH$_2$C*H*H−), 2.21−2.24 (2 H, m, FcCHPhC*H*$_2$−), 2.42 (1 H, dt, *J* 3.2, 14.4, FcCHPhCH$_2$CH*H*−), 2.81 (1 H, dd, *J* 10.1, 15.3, FcCHPhC*H*-HCO$_2$CH$_3$), 3.01 (1 H, dd, *J* 3.2, 10.9, FcC*H*PhCH$_2$CH$_2$−), 3.08 (1 H, dd, *J* 5.1, 15.4, FcCHPhCH*H*CO$_2$CH$_3$), 3.53 (3 H, s, −OC*H*$_3$), 3.80 (1 H, m, Fc), 3.95−3.97 (3 H, m, Fc × 3), 4.03 (1 H, dd, *J* 5.1, 10.1, FcC*H*PhCH$_2$CO$_2$CH$_3$), 4.07 (3 H, s, Fc × 3), 7.05−7.23 (10 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 26.61 (FcCH-PhC*H*$_2$−), 41.84 (Fc*C*HPh−), 42.73 and 43.35 (Fc*C*H$_2$− and FcCHPhC*H*$_2$CO$_2$CH$_3$), 44.17 (Fc*C*HPhCH$_2$CO$_2$CH$_3$), 52.01 (−O*C*H$_3$), 66.54 (Fc), 67.05 (Fc), 68.22 (Fc), 69.76 (Fc), 70.77 (Fc), 71.80 (Fc), 71.89 (Fc), 87.10 (Fc − *ipso*), 88.63 (Fc − *ipso*), 92.94 (Fc − *ipso*), 126.42 (Ph − *para*), 126.93 (Ph − *para*), 127.63 (Ph), 127.96 (Ph), 128.68 (Ph), 128.72 (Ph), 144.54 (Ph − *ipso*), 145.79 (Ph − *ipso*), 172.98 (*C*═O); *m*/*z* (ES) 465.4 (MH$^+$, 34), 464.4 (M$^+$, 100).

($_p$*S*)-1,1′-((*R*)-3-Phenyl-1,3-propanediyl)-3-((*R*)-3-carboxy-1-phenylethyl)ferrocene 16. ($_p$*S*)-1,1′-((*R*)-3-Phenyl-1,3-propanediyl)-3-((*R*)-3-methoxy-3-oxo-1-phenylpropyl)ferrocene **15** (0.31 g, 0.67 mmol) was suspended in 1:1 THF/H_2O (12 mL) containing LiOH (0.16 g, 6.7 mmol) and stirred at room temperature for 64 h. The resultant yellow solution was acidified with dilute HCl(aq) and the product extracted with CH_2Cl_2 (24 mL + 2 mL). The organic phases were combined, dried (Na_2SO_4), filtered, and evaporated in vacuo to yield a yellow solid. Recrystallization from hexane/methanol gave a yellow crystalline solid (0.27 g, 90%): mp 179−181 °C; $[\alpha]_D^{24} = -76$ (*c* 0.100 in EtOH); (found C, 74.67; H, 5.80; $C_{28}H_{26}FeO_2$ requires C, 74.66; H, 5.83); ν_{max} (Nujol)/cm^{-1} 1692; δ_H (400 MHz, $CDCl_3$) 1.74 (1 H, td, *J* 3.9, 13.1, FcCHPhCH$_2$C*H*H−), 2.14−2.26 (2 H, m, FcCHPhC*H*$_2$−), 2.38 (1 H, d, *J* 14.4, FcCHPhCH$_2$CH*H*−), 2.83 (1 H, dd, *J* 9.7, 15.7, FcCHPhC*H*-HCO$_2$H), 3.00 (1 H, dd, *J* 3.0, 11.0, FcC*H*PhCH$_2$CH$_2$−), 3.11 (1 H, dd, *J* 5.2, 15.6, FcCHPhCH*H*CO$_2$H), 3.80 (1 H, m, Fc), 3.96−3.97 (3 H, m, Fc × 3), 4.02 (1 H, dd, *J* 5.3, 9.7, FcC*H*PhCHHCO$_2$H), 4.05−4.07 (3 H, m, Fc × 3), 7.02−7.23 (10 H, m, Ph); δ_C (100 MHz, $CDCl_3$) 26.57, (FcCHPhC*H*$_2$−), 41.59 (FcCHPh−), 42.48 and 43.28 (Fc*C*H$_2$− and FcCHPhC*H*$_2$-CO$_2$H), 44.12 (Fc*C*HPhCH$_2$CO$_2$H), 66.58 (Fc), 67.08 (Fc), 68.19 (Fc), 69.91 (Fc), 70.87 (Fc), 71.71 (Fc), 71.89 (Fc), 87.17 (Fc − *ipso*), 88.65 (Fc − *ipso*), 92.77 (Fc − *ipso*), 126.42 (Ph − *para*), 127.01 (Ph − *para*), 127.61 (Ph), 127.90 (Ph), 128.71 (Ph), 128.74 (Ph), 144.37 (Ph − *ipso*), 145.72 (Ph − *ipso*), 177.96 (*C*═O); *m*/*z* (ES) 450.0 (M$^+$, 100), 391.1 (93).

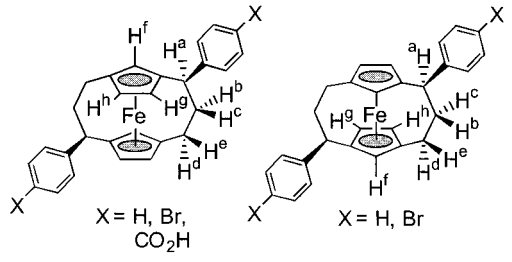
The methyl mandalate ester of **16** was synthesized as described for **8a**−**c**.

Data for **16**: Major diastereoisomer; δ_H (400 MHz, $CDCl_3$) 5.75 (1 H, s, −OC*H*(CO$_2$CH$_3$)Ph). Corresponding peak for minor diastereoisomer, 5.80, 98% ee.

Synthesis of (*R*,*R*,$_p$*S*,$_p$*S*)-1,1′-(1-Phenyl-1,3-propanediyl)-3,3′-(3-phenyl-1,3-propanediyl)ferrocene 1. ($_p$*S*)-1,1′-((*R*)-3-Phenyl-1,3-propanediyl)-3-((*R*)-3-carboxy-1-phenylethyl)fer-

rocene **16** (0.36 g, 0.80 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under an atmosphere of nitrogen at room temperature. TFAA (0.34 g, 1.62 mmol) was added to the resultant dark orange solution, which was allowed to stir overnight to yield a dark green solution. The reaction mixture was quenched slowly by the dropwise addition of saturated $NaHCO_3$(aq) (10 mL). The organic phase was separated, washed with saturated NaCl(aq) (10 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo to yield a yellow/green semisolid (0.35 g). This α-keto-ferrocenophane was dissolved in 1:1 TFA/CH_2Cl_2 (10 mL) under an atmosphere of nitrogen. Triethylsilane (0.19 g, 1.63 mmol) was added quickly to the resultant solution, which was further stirred for 10 min. The resultant dark blue solution was quenched slowly by the dropwise addition of saturated $NaHCO_3$(aq) (10 mL). The organic phase was separated, washed with saturated NaCl(aq) (10 mL), dried (Na_2SO_4), filtered, and evaporated in vacuo to yield a yellow solid. Chromatography with 3:97 EtOAc/petroleum ether gave a yellow crystalline solid (0.32 g, 96% from **16**): mp 254−256 °C (EtOAc/petroleum ether); $[\alpha]_D^{24} = -99$ (*c* 0.185 in $CHCl_3$); (found C, 80.65; H, 6.02; $C_{28}H_{26}Fe$ requires C, 80.37; H, 6.28); δ_H (400 MHz, $CDCl_3$) 1.79 (2 H, td, *J* 3.5, 11.5, H^d), 2.15−2.26 (4 H, m, H^b and H^c), 2.38 (2 H, brd d, *J* 14.4, H^e), 3.04 (2 H, d, *J* 9.9, H^a), 4.03 (2 H, s, H^g or H^h), 4.09 (2 H, s, H^g or H^h), 4.25 (2 H, s, H^f), 7.09 (2 H, t, *J* 7.3, Ph − *para*), 7.20 (4 H, t, *J* 7.6, Ph − *meta*), 7.28 (4 H, d, *J* 7.5, Ph − *ortho*); δ_C (100 MHz, $CDCl_3$) 25.98 (FcCHPh*C*H_2−), 43.87 (Fc*C*HPh−), 46.40 (Fc*C*H_2−), 69.32 (Fc), 70.41 (Fc × 2), 86.14 (Fc − *ipso*), 86.99 (Fc − *ipso*), 125.88 (Ph − *para*), 127.33 (Ph), 128.24 (Ph), 145.40 (Ph − *ipso*); *m*/*z* (ES) 419.5 (MH^+, 40), 418.3 (M^+, 88), 102.0 (66), 59.9 (100).

Synthesis of (*R*,*R*$_p$,*R*$_p$,*R*)-1,1′-(1-Phenyl-1,3-propanediyl)-3,3′-(3-phenyl-1,3-propanediyl)ferrocene 17. A mixture of **13**/**14** was carried through the above procedure to give a mixture of ferrocenophanes from which **1** could be isolated on recrystallization from EtOAc/petroleum ether. Repeated recrystallization of the mother liquors gave a yellow solid enriched in the minor ferrocenophane **17**: (found C, 80.15; H, 6.40; $C_{28}H_{26}Fe$ requires C, 80.37; H, 6.28); δ_H (400 MHz, $CDCl_3$) 1.80 (2 H, td, *J* 3.0, 12.9, H^d), 2.11−2.27 (4 H, m, H^b and H^c), 2.50 (2 H, dt, *J* 3.2, 14.6, H^e), 2.99 (2 H, dd, *J* 2.2, 11.6, H^a), 3.98 (2 H, s, H^g or H^h), 4.01 (2 H, s, H^g or H^h), 4.15 (2 H, s, H^f), 7.09 (2 H, t, *J* 7.3, Ph − *para*), 7.20 (4 H, t, *J* 7.5, Ph − *meta*), 7.28 (4 H, d, *J* 7.3, Ph − *ortho*); δ_C (100 MHz, $CDCl_3$) 25.80 (FcCHPh*C*H_2−), 42.78 (Fc*C*H_2−), 43.38 (Fc*C*HPh−), 67.33 (Fc), 70.24 (Fc), 71.52 (Fc), 85.68 (Fc − *ipso*), 86.67 (Fc − *ipso*), 124.94 (Ph − *para*), 126.18 (Ph), 127.29 (Ph), 144.74 (Ph − *ipso*).



Synthesis of (*R*,*R*$_p$,*R*$_p$,*R*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)-ferrocene 18 and (*R*,*R*$_p$,*S*$_p$,*S*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)-ferrocene 19. Using the methods described for the synthesis of **1**, (*R*,*R*)-1,1′-bis(1-(4-bromophenyl)-2-carboxyethylferrocene **11b** (5.15 g, 8.04 mmol), PCl_3 (80 mL), and $SnCl_4$ (4.61 g, 17.70 mmol) gave 4.93 g of the intermediate semicyclized acids. Direct reduction with triethylsilane (2.02 g, 17.37 mmol) in 1:1 TFA/CH_2Cl_2 (80 mL) gave the trimethylene acids as a yellow solid (4.65 g, 95% from **11b**): ν_{max} (Nujol)/cm^{-1} 1708; *m*/*z* (ES) 610.6 (35), 609.7 (41), 608.5 (86), 607.4 (61), 605.9 (90), 165.1 (97), 151.9 (100). Subsequent cyclization with TFAA (3.49 g, 16.62 mmol) gave two α-keto ferrocenophanes as a yellow/green impure solid (4.75 g), that was reduced with triethylsilane (1.91 g, 16.43 mmol) in 1:1 TFA/CH_2Cl_2 (100 mL) to give a 1:1.5 ratio of **18** and **19** as a yellow solid (4.05 g, 92% from the two intermediate trimethylene acids).

Isolation of (*R*,*R*$_p$,*S*$_p$,*S*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)-ferrocene 19. Recrystallization from EtOAc/petroleum ether gave pure **19** as a yellow crystalline solid: mp 228−229 °C; $[\alpha]_D^{20} = -71$ (*c* 0.205 in $CHCl_3$); (found C, 58.27; H, 4.21; $C_{28}H_{24}Br_2Fe$ requires C, 58.36; H, 4.21); δ_H (400 MHz, $CDCl_3$) 1.78 (2 H, td, *J* 3.3, 13.0, H^d), 2.10−2.24 (4 H, m, H^b and H^c), 2.38 (2 H, brd, *J* 14.3, H^e), 2.99 (2 H, brd, *J* 9.9, H^a), 4.03 (4 H, s, H^g and H^h), 4.23 (2 H, s, H^f), 7.14 (4 H, d, *J* 8.4, Ar), 7.30 (4 H, d, *J* 8.4, Ar); δ_C (100 MHz; $CDCl_3$) 26.31 (FcCHAr*C*H_2−), 43.69 (Fc*C*HAr−), 46.61 (Fc*C*H_2−), 69.67 (Fc), 70.96 (Fc × 2), 86.55 (Fc − *ipso*), 86.98 (Fc − *ipso*), 120.05 (Ar − *ipso*), 129.50 (Ar), 131.67 (Ar), 144.76 (Ar − *ipso*); *m*/*z* (ES) 578.2 (M^+, 56), 575.9 (M^+, 100), 574.2 (M^+, 43).

Isolation of (*R*,*R*$_p$,*R*$_p$,*R*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)-ferrocene 18. Repeated recrystallization of the mother liquors gave a yellow solid enriched in the minor ferrocenophane **18**, which was characterized as a mixture of diastereoisomers. (found C, 58.49; H, 4.39; $C_{28}H_{24}FeBr_2$ requires C, 58.36; H, 4.21); δ_H (400 MHz, $CDCl_3$) 1.79 (2 H, td, *J* 2.9, 12.8, H^d), 2.05−2.23 (4 H, m, H^b and H^c), 2.50 (2 H, dt, *J* 3.3, 14.6, H^e), 2.93 (2 H, dd, *J* 2.3, 11.8, H^a), 3.97 (2 H, m, H^g or H^h), 4.01 (2 H, m, H^g or H^h), 4.09 (2 H, s, H^f), 7.15 (4 H, d, *J* 8.4, Ar), 7.31 (4 H, d, *J* 8.4, Ar); δ_C (100 MHz, $CDCl_3$) 25.66 (FcCHAr*C*H_2−), 42.58 (Fc*C*H_2−), 42.78 (Fc*C*HAr−), 67.13 (Fc), 70.29 (Fc), 71.73 (Fc), 85.68 (Fc − *ipso*), 86.25 (Fc − *ipso*), 118.66 (Ar − *ipso*), 127.94 (Ar), 130.28 (Ar), 143.66 (Ar − *ipso*).

Proof of the Structure of (*R*,*R*$_p$,*S*$_p$,*S*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)ferrocene 19. (*R*,*R*$_p$,*S*$_p$,*S*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)ferrocene **19** (0.050 g, 0.087 mmol) was dissolved in dry THF (2 mL) under an atmosphere of nitrogen and cooled to −78 °C. Butyllithium in hexane (0.347 mmol) was added to the resultant yellow solution, which was stirred at −78 °C for 60 min. The cooling bath was removed and the yellow solution allowed to warm to room temperature for 15 min. The resultant dark orange/red solution was quenched with H_2O (2 mL). Standard workup and chromatography with 3:97 EtOAc/petroleum ether gave a yellow crystalline solid (0.033 g, 91%): mp 253−255 °C. The ^1H NMR spectroscopic data obtained were identical to that previously reported for **1**.

Synthesis of (*R*,*R*$_p$,*S*$_p$,*S*)-1,1′-(1-(4-Carboxyphenyl)-1,3-propanediyl)-3,3′-(3-(4-carboxyphenyl)-1,3-propanediyl)-ferrocene 20. (*R*,*R*$_p$,*S*$_p$,*S*)-1,1′-(1-(4-Bromophenyl)-1,3-propanediyl)-3,3′-(3-(4-bromophenyl)-1,3-propanediyl)ferrocene **19** (0.216 g, 0.375 mmol) was dissolved in dry THF (7 mL) under an atmosphere of nitrogen and cooled to −78 °C. Butyllithium in hexane (0.94 mmol) was added to the resultant yellow solution, which was stirred at −78 °C for 60 min. Dry CO_2 was bubbled through the yellow solution for 5 min to give a yellow suspension. The cooling bath was removed and the reaction mixture allowed to warm to room temperature before it was quenched with dilute HCl(aq) (10 mL). Further addition of Et_2O (5 mL) gave a yellow emulsion, which was separated and filtered in vacuo to yield **20** as a yellow solid (0.183 g, 87%): mp > 300 °C; (found C, 64.07; H, 5.12; $C_{30}H_{26}FeO_4 \cdot 3H_2O$ requires C, 64.29; H, 5.77); ν_{max} (Nujol)/cm^{-1} 1680; δ_H (400 MHz, DMSO-d_6) 1.78 (2 H, t, *J* 12.4, H^d), 2.08−2.27 (6 H, m, H^b, H^c, H^e), 3.13 (2 H, d, *J* 10.5, H^a), 4.04 (2 H, s, H^g or H^h), 4.13 (2 H, s, H^g or H^h), 4.39 (2 H, s, H^f), 7.29 (4 H, d, *J* 8.3, Ar), 7.41 (4 H, d, *J* 8.3, Ar), 12.75 (brs, 2 H, $-CO_2H$); δ_C (100 MHz, DMSO-d_6) 26.16 (FcCHAr*C*H_2−), 43.93 (Fc*C*HAr−),

46.50 (FcCH_2−), 69.86 (Fc), 71.14 (Fc × 2), 86.66 (Fc − *ipso*), 87.51 (Fc − *ipso*), 126.29 (Ar), 128.26 (Ar), 130.14 (Ar), 151.81 (Ar), 168.07 (−*C*═O); *m*/*z* (LSIMS) 506.0 (M^+, 4%), 505.0 (M − H^+, 4), 153 (65), 107 (100).

Preparation of (*R*,*R*$_p$*S*,$_p$*S*)-1,1′-(1-Phenyl-1,3-propanediyl)-3,3′-(3-phenyl-1,3-propanediyl)ferrocenium Tetrafluoroborate 22. (*R*,*R*$_p$*S*,$_p$*S*)-1,1′-(1-Phenyl-1,3-propanediyl)-3,3′-(3-phenyl-1,3-propanediyl)ferrocene **1** (0.19 g, 0.045 mmol) was dissolved in CH_2Cl_2 (5 mL) and CH_3NO_2 (2 mL) to yield a yellow solution. To this was added HBF_4 (54% in ether, 0.006 mL, 0.044 mmol), and the resultant dark blue mixture was stirred for 90 min. The solvent was evaporated in vacuo to yield a dark blue oil, which was triturated with hexane (2 × 3 mL). The resultant dark blue semisolid was stirred with Et_2O (5 mL) for 120 min, after which the solvent was decanted to yield a dark blue semisolid. The oil was dissolved in nitromethane (1 mL) and filtered through Na_2SO_4 into a vessel containing Et_2O (3 mL), which was cooled at −10 °C overnight. The resultant blue solid was removed by filtration, dissolved in CH_2Cl_2 (5 mL), and quenched with saturated $NaHCO_3$(aq) (5 mL) (to remove any remaining HBF_4). The organic phase was evaporated in vacuo, and the resultant dark blue solid was dissolved in CH_2Cl_2 (1 mL), covered with a layer of hexane (3 mL), and cooled at −10 °C overnight. The resultant blue crystals were contaminated with yellow crystals of **1**, which were removed manually. Recrystallization from CH_2Cl_2/hexane gave a blue crystalline solid (0.13 g, 57%): mp 218−221 °C; $[\alpha]_D^{21}$ = +400 (*c* 0.01 in CH_2Cl_2); (found C, 66.85; H, 5.39; $C_{28}H_{26}FeBF_4$ requires C, 66.56; H, 5.20); *m*/*z* (APCI) 418 ($C_{28}H_{26}Fe^+$, 100).

General Method for the Diels−Alder Reaction between Methacrolein and Cyclopentadiene. Methacrolein (0.021 g, 0.30 mmol) and cyclopentadiene (0.040 g, 0.61 mmol) were dissolved in dry CH_2CH_2 (2 mL) under an atmosphere of nitrogen at room temperature. Either no catalyst, ferrocinium hexafluorophosphate **21** (0.005 g, 0.015 mmol), or **22** (0.0076 g, 0.015 mmol, 5 mol %, or 0.0152 g, 0.030 mmol, 10 mol %) was added to the reaction mixture. Samples were taken from the reaction mixture using a microsyringe, at 1, 3, 6, 21, and 48 h intervals, filtered through an alumina plug (to remove ferrocinium salts), dissolved in $CDCl_3$ (≅1 mL), and examined by ^{1}H NMR spectroscopy. Then 1.1 equiv (with respect to methacrolein) of (*R*, *R*)-2,4-pentanediol (0.034 g, 0.33 mmol) and a catalytic quantity of *p*-TsOH were added to the Diels−Alder reaction. The resultant solutions were allowed to stir overnight, after which the solutions were filtered through alumina plugs to remove any ferricinium salts and *p*-TsOH. The resultant solutions were examined directly by both ^{1}H NMR spectroscopy and gas chromatography.

Crystal Structure Determinations. Crystals of complexes **1** and **12** were selected for full structural X-ray analysis. They had dimensions of 0.12 × 0.10 × 0.10 and 0.3 × 0.4 × 0.2, respectively, and were mounted with Areldite on glass fibers. Cell dimensions and intensity data for both crystals were recorded at 150 K, as previously described,[25] using a FAST TV area detector diffractometer mounted at the window of a rotating anode. The generator was operated at 50 kV, 50 mA with a graphite monochromated molybdenum anode (λ-(Mo Kα) = 0.71069 Å). The crystal-to-detector distance was 50 mm, and the detector 2θ swing angle was 20°. Slightly more than one hemisphere of data were recorded. Following normal data processing, the space groups were determined as $P2_1$ (**1**) and $P2_12_12_1$ (**12**) from analysis of the systematically absent reflections and progression to a smooth refinement. The structures were solved via direct methods[26] and refined by full-matrix least squares.[27] Corrections for absorption were made using the program DIFABS,[28] and the maximum, minimum, and average correlation factors were 1.048, 0.927, 0.994 (**1**) and 1.201, 0.818, 1.002 (**12**). Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated ideal positions. Refinement was based on F^2 and involved a total of 262 (**1**) and 598 (**12**) parameters. Crystal data, details of data collection, and refinement are given in Table 1.

Table 1. Crystallographic Data for Complexes 1 and 12

	1	**12**
formula	$C_{28}H_{26}Fe$	$C_{58}H_{50}Fe_2O_6$
fw	418.34	954.68
temp, K	150(2)	150(2)
wavelength, Å	0.71069	0.71069
cryst syst	monoclinic	orthorhombic
space group	*P*2(1)	*P*2(1)2(1)2(1)
a, Å	12.911(3)	9.5070(9)
b, Å	5.8400(10)	19.9830(16)
c, Å	13.436(3)	23.830(5)
β, deg	103.72(3)	
V, Å^3	984.2(4)	4527.2(10)
Z	4	4
d_{calcd}, g cm^{-3}	1.412	1.401
μ, mm^{-1}	0.778	0.696
F(000)	440	1992
cryst size, mm	0.12 × 0.10 × 0.10	0.3 × 0.4 × 0.2
θ range, deg	1.97−25.03	1.99−25.11
no. of reflns coll	4412	18598
no. of indep reflns	2468 (R_{int} = 0.0694)	6799 (R_{int} = 0.1414)
no. of data/restraints/params	2468/1/262	6799/6/598
GOF on F^2	1.008	0.384
final *R* indices [$I > 2\sigma I$]	R1 = 0.0321, wR2 = 0.0826	R1 = 0.0419, wR2 = 0.0908
R indices (all data)	R1 = 0.0339, wR2 = 0.0831	R1 = 0.1164, wR2 = 0.1249

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Supporting Information Available: Text giving full characterization for **2a**, **3a**, **5a**−**9a**, **5c**−**9c**, and **11a** and details of the X-ray structure determinations of **1** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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