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Synthesis of planar chiral ferrocenyl cyclopentadienyl chelate ligand precursors

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ABSTRACT

Two families of planar chiral ferrocenyl cyclopentadienyl chelate ligands for use in *ansa*-half sandwich metallocene complexes of catalytically active transition metals are described. The first family was derived in 4–5 steps from an enzymatic resolution of 1-iodo-2-(methylalcohol)ferrocene and possesses a cyclopentadiene derivative [Cp(H) = 1-indenyl, 2-indenyl or $Ph_4Cp(H)$] directly attached to the ferrocene ring with an adjacent vicinal tether CH_2Z donor group (Z = OH, OMe, NHMe, NMe_2 or PPh_2). The second family was derived from a chiral auxiliary approach and has the donor group ($Z = PPh_2$ or NMe_2) attached directly to the ferrocene ring with an adjacent tether vicinal $CH_2Cp(H)$ group [Cp(H) = Cp(H), fluorenyl, 1-indenyl, $Me_4Cp(H)$ or $Ph_4Cp(H)$].

1. Introduction

The development of ligand architecture has had a huge effect on the catalytic activity of some metals. Chelation of cyclopentadienyl ligands with a pendant donor atom to certain transition metals leads to *ansa*-half sandwich metallocene complexes (Fig. 1). This

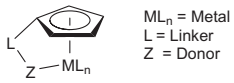

Figure 1. *ansa*-half sandwich metallocene.

unusual ligand may confer enhanced catalytic activity, due in part to the inertness of the cyclopentadienyl ligand and the tuning available from the donor atom, the first example of which was documented for α-olefin polymerisation.[1] There are a number of reviews on the many examples of cyclopentadienyl metal complexes bearing pendant phosphorus/sulfur/arsenic,[2] oxygen[3] and amine[4] donors. A wide variety of metals have been used and the number of *ansa*-half sandwich metallocenes in the literature is ever increasing. However, there are relatively few examples of chiral *ansa*-half sandwich metallocene complexes being used in asymmetric catalysis.[5–10] Chirality is most often conferred on the complex by centres of chirality present between the chelating cyclopentadienyl and donor atom groups that help to create a chiral pocket around the metal centre. The success of these approaches has been limited and we postulate that a planar chiral ferrocene linker could project a more effective chiral environment around a catalytically active *ansa*-half sandwich metallocene.

The superiority of the planar chiral element in ferrocenyl derived ligands, above that of centres of chirality, for the transmission of asymmetry in chemical reactions has been well documented.[11–15] Purely planar chiral ferrocenes have been less well investigated,[16–22] possibly due to the challenges associated with their enantioselective syntheses compared to the multitude of diastereoselective approaches that start, for example, with the ubiquitous Ugi *N,N*-dimethyl-1-ferrocenylethylamine that lead to bidentate Josiphos type ligands.[23–25] In our own work, we have used the Snieckus approach of sparteine mediated enantioselective directed *ortho* metallation of *N,N*-diisopropyl ferrocenecarboxamide[26] to access a series of N–P, N–N, N–O and N–S planar chiral ferrocene chelate ligands (Fig. 2).[27,28] In addition we have also synthesised asymmetric chelate ligands via the sparteine mediated lithiation of the C-2 position of 1,2,3,4,5-pentamethylazaferrocene (Fig. 2).[29]

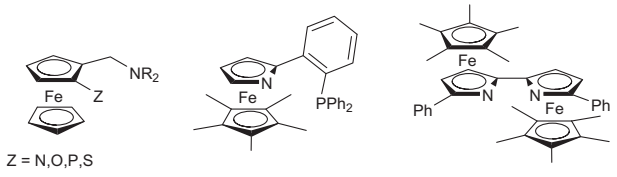

Figure 2. Planar chiral bidentate ligands based on ferrocene.

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In extending these studies we wished to use a planar chiral ferrocene unit to control the asymmetry of a potential chelate *ansa*-half sandwich metallocene. We were aware of only one example of this type of asymmetric scaffold in the literature, but the two complexes were not catalytically active (Fig. 3).[30]

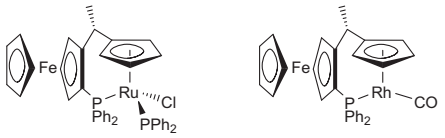


Figure 3. Planar chiral ferrocene *ansa*-half sandwich metallocene.

Conceptually, in order to design catalysts for the stereocontrolled formation of new σ-bonds to a pro-chiral molecule, we require a chiral metal possessing 4 quadrants of differing size (**1**, Scheme 1), with only one side of the metal available for binding. Upon coordination of a prochiral substrate to the available face of the metal, the least sterically congested complex **2** should result. With the prochiral face of the unsaturated system differentiated, addition of H–Nu (Nu = NR_2, SiR_3, BR_2, CN), will form new stereocentres **3** in a controlled fashion. To harness the high configurational metal–ligand stability of the cyclopentadienyl ligand, and open up the metal centres coordination sphere, we set out to synthesise a new class of planar chiral ferrocenyl chelate ligands **4** containing a cyclopentadienyl group tethered to a donor ligand with the planar chiral ferrocene controlling the desired topology **5**. The planar chiral ferrocene ligand links three quadrants, making the metal M chiral and differentiates which face of the metal is available for further coordination. The stabilising effect of the cyclopentadienyl (Cp) ring and donor atoms Z on the catalytically active metal centre M and any coordinated reactive intermediates or products may enhance catalytic transformations at the metal centre M. A variant of this ligand system **6** can also be envisaged.

Herein we report the syntheses of some enantiomerically pure chelate ligands **4**, which rely upon an enzymatic resolution to produce either enantiomer of the desired ligands. We also report the synthesis of an example of ligand **6** which uses directed *ortho*-metallation methodology from a chiral acetal attached to ferrocene.

2. Results and discussion

Initially both the inden-1-yl and inden-2-yl groups were examined as it was thought that when the inden-1-yl group is bonded to a metal, the bulky ferrocene group should dictate that only one isomer is formed (isomers due to the axis of chirality in the inden-1-yl group) (Fig. 4). The atropisomerism associated with the inden-1-yl group may aid the selectivity of the metal catalyst. The symmetrical nature of the inden-2-yl functionality in metal complexes would allow this effect to be investigated.

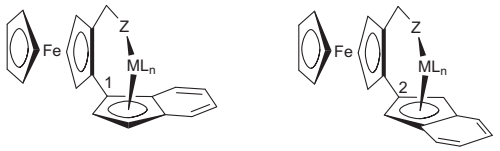
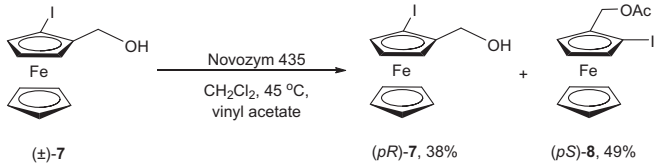


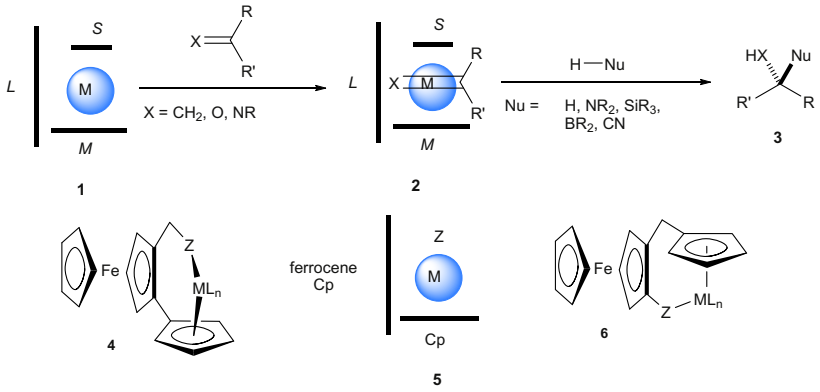
Figure 4. Potential coordination of indenyl ligands to a metal centre.

2.1. Introduction of chirality

Our attempts to incorporate a cyclopentadienyl type ligand directly to one of the ferrocene rings using Snieckus' approach of directed *ortho*-metallation of ferrocenecarboxamides,[26] could be employed to synthesise the racemic ligands (using TMEDA and direct reaction with 1-indanone) but the asymmetric reaction using (−)-sparteine was unsuccessful. The synthesis of the corresponding iodide, and subsequent halogen–lithium exchange and reaction with 1-indanone allowed the incorporation of a Cp group. However, chemical manipulation of the resultant tertiary amide to useful functional groups proved problematic. This, coupled with the fact that the (−)-sparteine methodology formally delivers only one enantiomer[31] led us to consider an alternative approach that relied on halogen lithium exchange of an enatiomerically pure ferrocenyl halide. It was known that (±)-alcohol **7** can be resolved using a lipase enzyme (from Candida Antarctica) and vinyl acetate to give (*pS*)-acetate **8** (98% ee) and remaining (*pR*)-alcohol **7** (95% ee, >99% after recrystallisation from pet. ether).[32] In our hands the immobilised enzyme could be reused (at least 3 times) with no noticeable decrease in enantioselectivity and the reaction could be performed on at least a 50 g scale (Scheme 2). It was found that the quantity of enzyme and amount of DCM used could be greatly reduced from the procedure reported in the literature.



Scheme 2. Resolution of (±)-**7**.

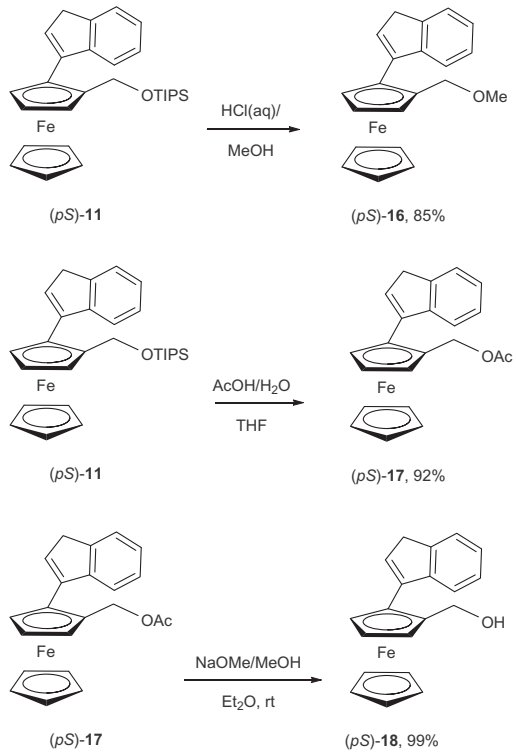


Scheme 1. Design concept.

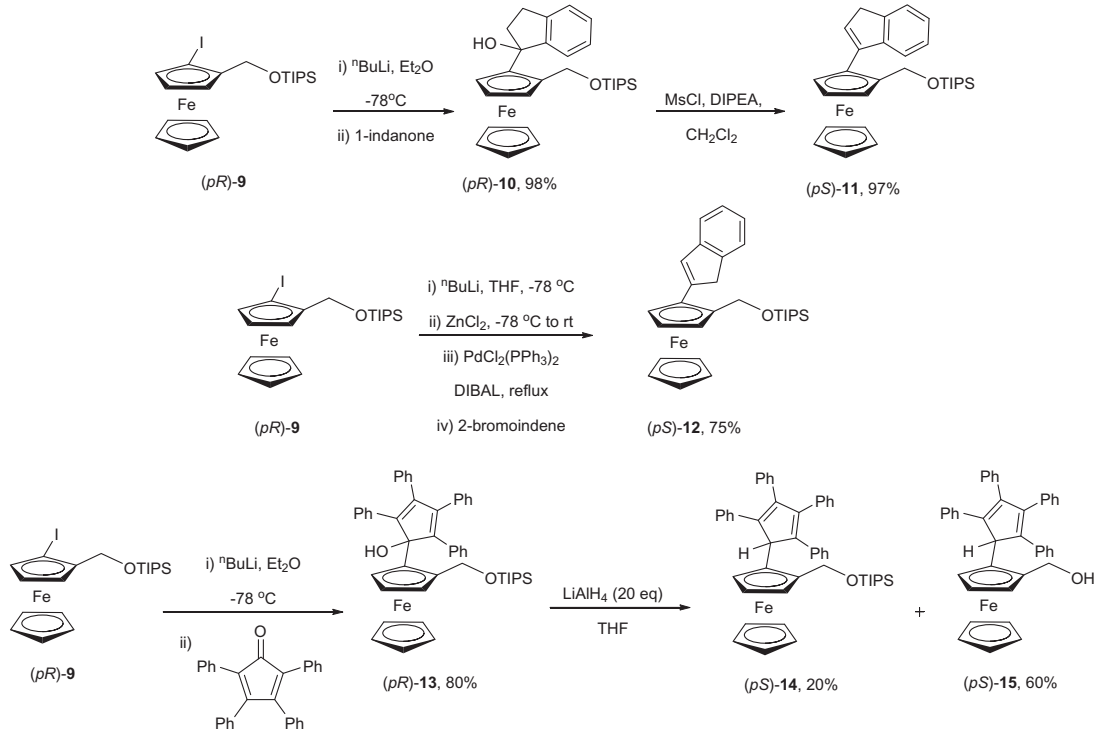
2.2. Cyclopentadiene type compounds with an oxygen donor group

The addition of both the 1-indenyl group (by halogen–lithium exchange followed by addition of 1-indanone) and the 2-indenyl groups (by Negishi cross coupling of 2-bromoindene) was found to give the highest yields when a non-coordinating substituent was present on the pseudo-benzylic position ($Cp(H)CH_2$–) of the donor side chain. An array of compounds were synthesised where the hydroxyl/acetate group of **7**/**8** was converted into a range of donor substituents (N, O or P). The highest yields of the addition were seen when using TIPS ether **9** (Scheme 3). This may be because the less bulky groups are able to coordinate to lithium and make it less reactive and/or are too basic to react with ketones as well as inhibiting the lithium–zinc transmetallation needed for Negishi cross-coupling reactions. This was supported by the fact that no starting material remained at the end of the halogen lithium exchange reactions, with only the proton quenched material isolated in optimisation experiments. The addition of 1-indanone to (*pR*)-**9**, after halogen–lithium exchange of the iodide, gave the resultant alcohol (*pR*)-**10** in 98% yield. Dehydration of the alcohol was achieved by conversion to the mesylate and addition of DIPEA to give (*pS*)-**11** in 97% yield. The hindered TIPS silyl ether also proved to be the best substrate for the Negishi cross-coupling of 2-bromoindene to give (*pS*)-**12** in 75% yield (Scheme 3). The 2-indenyl substituted TIPS ether **12** proved to be much more stable than the corresponding 1-indenyl compound **11** under acidic conditions. This added stability may be due to the fact that in the 1-indenyl ligands there is a doubly benzylic position between the aromatic ring of the indenyl group and the ferrocene Cp ring which may stabilise any incipient carbocation character. The tetraphenylcyclopentadiene group could be introduced by the reaction of tetraphenylcyclopentadienone with **9**, after halogen–lithium exchange, to give alcohol **13** in 80% yield. Reduction using $LiAlH_4$ (2 equiv) gave (*pS*)-**14**, albeit in low yield (20%). A range of other reducing conditions were investigated but all led to degradation of the substrate. However, increasing the amount of $LiAlH_4$ used to 20 equiv surprisingly gave alcohol (*pS*)-**15** in 60% along with (*pS*)-**14** in 20% isolated yield.

All standard conditions for the removal of the TIPS group from the 1-indenyl compound, to give the alcohol, resulted in degradation or, under acidic conditions, substitution of the OTIPS group.[33]



Scheme 4. Synthesis of 1-indenyl oxygen chelate ligands.

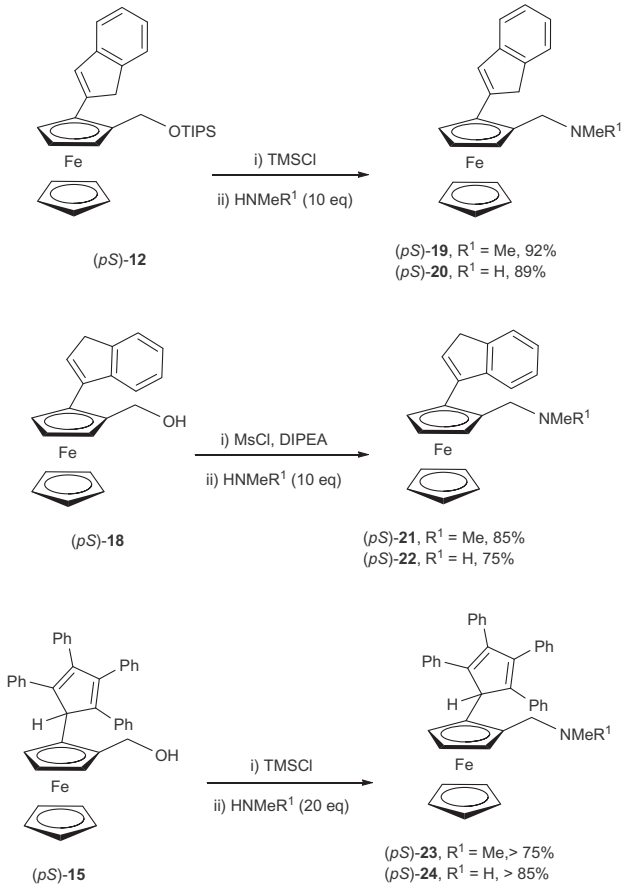


Scheme 3. Addition of cyclopentadiene type groups.

No examples of this deprotection reaction for OTIPS ether at the α-position of a ferrocene compound exist in the literature. Both the methyl ether (*pS*)-**16** (85% yield) using aqueous HCl and MeOH, and acetate, (*pS*)-**17** (92% yield) using aqueous acetic acid in THF, were synthesised presumably by substitution of the –OTIPS group (Scheme 4). Subsequent basic hydrolysis of acetate **17** gave alcohol (*pS*)-**18** (99%).

2.3. Cyclopentadiene type compounds with a nitrogen donor group

It was found that the 2-indenyl amine compounds could be directly synthesised by the addition of TMSCl to TIPS ethers and subsequent transfer of the reaction mixture onto an excess of the amine (Scheme 5). Both the dimethylamine **19** and methylamine **20** compounds were synthesised by this route. The direct addition of the amine to the reaction mixture led to the formation of dimers. The use of these conditions with the 1-indenyl TIPS ether **11** led to degradation, presumably due to the sensitivity of the 1-indenyl compounds to the formation of a doubly benzylic stabilised carbocation in the presence of an acid. Conversion of the alcohol into the mesylate and subsequent reaction with an excess of the amine gave the desired dimethylamino **21** and methylamino **22** compounds. The use of a hindered base such as DIPEA was essential as when less hindered bases such as triethylamine were used the corresponding quaternary amine salt was produced. Amine nucleophiles added in situ did not displace the triethylamine. The tetraphenylcyclopentadiene amine compounds **23** and **24** were synthesised in a similar manner from the alcohol **15**, although these compounds could not be separated from small amounts of remaining starting material.



Scheme 5. Synthesis of Cp(H) type nitrogen chelate ligands.

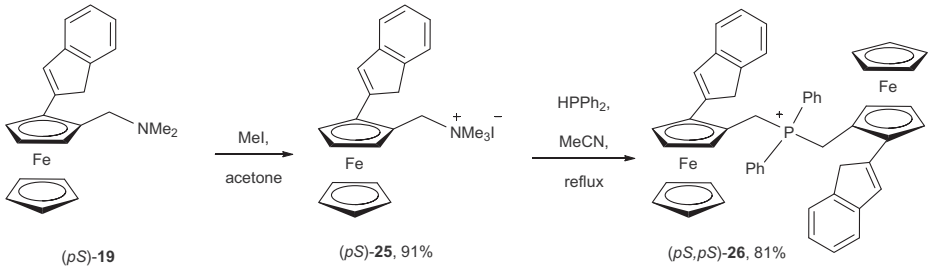
2.4. Cyclopentadiene type compounds with a phosphorus donor group

The most common phosphino *ansa* half sandwich metallocenes in the literature, with a similar tether length to our compounds, utilise a diphenylphosphine group to coordinate to the metal (Fig. 3).[2] The synthesis of the 1-indenyl phosphine compound was unsuccessful despite attempting a range of conditions previously employed for the synthesis of α-substituted ferrocene compounds including the conditions employed for the amino compounds; refluxing the acetate **17** in acetic acid with diphenylphosphine,[23] the use of $BH_3{\cdot}PPh_2H$ as a nucleophile,[34] via a quaternised amine[35] or via an α-carbocation.[36] Complete degradation or recovery of the starting material was observed in these cases. Similar results were seen in the attempted synthesis of the 2-indenyl phosphine compound; however, when diphenylphosphine was added to the quaternary amine salt **25**, an unusual phosphine bridged ferrocene dimer **26** was observed (Scheme 6). It is unclear why the phosphonium cation forms in preference to the 3-coordinate diphenylphosphine. Only a handful of examples exist where a phosphonium cationic species is synthesised from diphenylphosphine and 2 equiv of an electrophile but these require the presence of a base and in our case an excess of phosphine was used.[37,38]

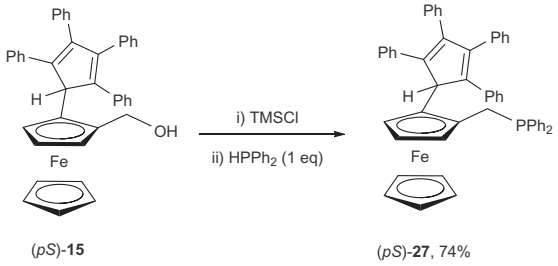
The synthesis of the tetraphenylcyclopentadiene compound proved much more straightforward and could be synthesised from the alcohol **15** using analogous conditions similar to the synthesis of the amine ligands (Scheme 7).

2.5. Donor group directly attached to the ferrocene Cp ring

In addition to the compounds above the donor group and Cp(H) group could be reversed, that is, the Cp(H) group is tethered to the ferrocene Cp ring with a CH_2 linker and the donor group is attached directly onto the ferrocene Cp ring (see **6**, Scheme 1). There is only one example of a similar ligand in the literature (Fig. 3) where in addition to the planar chirality of the molecule, there is also a stereogenic centre at the α-position adjacent to the ferrocene Cp ring.[30] This ligand has been complexed to rhodium or ruthenium and used in a reconstitutive condensation reaction. The synthesis of an analogous compound without this stereogenic centre would



Scheme 6. Formation of the phosphonium dimer.



(*pS*)-**15** (*pS*)-**27**, 74%

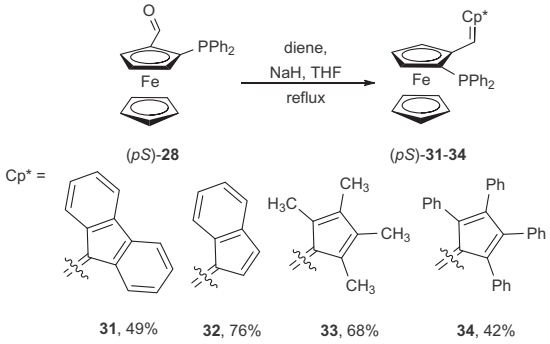
Scheme 7. Synthesis of phosphino tetraphenylcyclopentadiene ligand.

potentially allow us to probe the effect of each stereochemical element.

Phosphinoferrocenyl aldehyde **28** is a known compound and can be accessed in either enantiopure form using Kagan's chiral auxiliary approach from ferrocene carboxaldehyde and 1,2,4-butanetriol.[39,40] It was envisaged that our desired ligands, with a tethered Cp(H) group and donor group directly attached to the ferrocene ring, could be synthesised from **28**. Bildstein et al. have previously shown that a Cp(H) group can be introduced at the α-ferrocenyl position using a condensation reaction between ferrocene carboxaldehyde and cyclopentadiene in the presence of pyrrolidine.[41] Utilisation of the Bildstein conditions to give **29** followed by a subsequent reduction of the fulvene using $LiAlH_4$ gave the desired diphenylphosphino ligand **30** as a mixture of Cp(H) alkene isomers (Scheme 8).

The use of this methodology for other Cp(H) derivatives needed extended reaction times and resulted in poor yields for the condensation reaction. It was thought that this may be due to the poor solubility of **28** in MeOH, the additional steric hindrance of other Cp(H) derivatives and the additional stability and hence the lower reactivity of the deprotonated Cp type anions. We developed an alternative procedure whereby the Cp(H) derivative was deprotonated using sodium hydride and the resultant anion heated at reflux with **28**; reaction times varied for different analogues from 24 h to 3 d (Scheme 9). This allowed for the synthesis of fluorene **31**, indene **32**, tetramethylcyclopentadiene (TMCp(H)) **33** and tetraphenylcyclopentadiene (TPCp(H)) **34** type ligands.

In order to investigate the dimethylamino family of ligands, 2-dimethylaminoferrocenyl aldehyde **37** was required. This compound was synthesised from Kagan's aminoacetal intermediate **35**[40] using a reductive amination to give **36**, prior to removal of the auxiliary (Scheme 10). As with phosphino aldehyde **28**, the Cp(H) group could be installed by using a condensation between **37** and cyclopentadiene in the presence of pyrrolidine to give **38**. Subsequent reduction of the fulvene using $LiAlH_4$ gave the desired dimethylamino ligand **39** as a mixture of Cp(H) alkene isomers (Scheme 10). Ligand **39** was synthesised in racemic form in order to demonstrate the applicability of our methodology to amino ligands in addition to the phosphino ligands. The use of enantiopure 1,2,4-butanetriol should allow for the synthesis of dimethylamino compounds in enantiopure form.[40]



(*pS*)-**28** (*pS*)-**31-34**

31, 49% **32**, 76% **33**, 68% **34**, 42%

Scheme 9. Synthesis of phosphorus Cp(H) type chelate ligands.

3. Conclusion

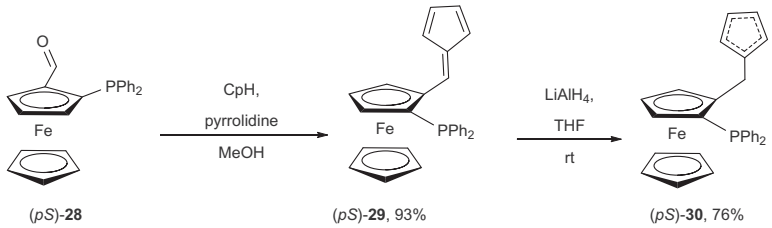
A number of potential ligands have been synthesised with a cyclopentadienyl group (1-indenyl, 2-indenyl and tetraphenylcyclopentadiene) and an additional tethered donor atom (O, N and P). The opposite ligands with a donor group (N, P) and tethered cyclopentadiene group (cyclopentadiene, 1-indenyl, TMCp(H), TPCp(H) and flourene) were also synthesised. Work is underway to complex these compounds to metals and screen them in an array of asymmetric reactions. It is hoped that the large ferrocene group and planar chirality of the complexes will provide great improvements to the current *ansa*-half sandwich metallocene type complexes used in catalysis.

4. Experimental

4.1. General

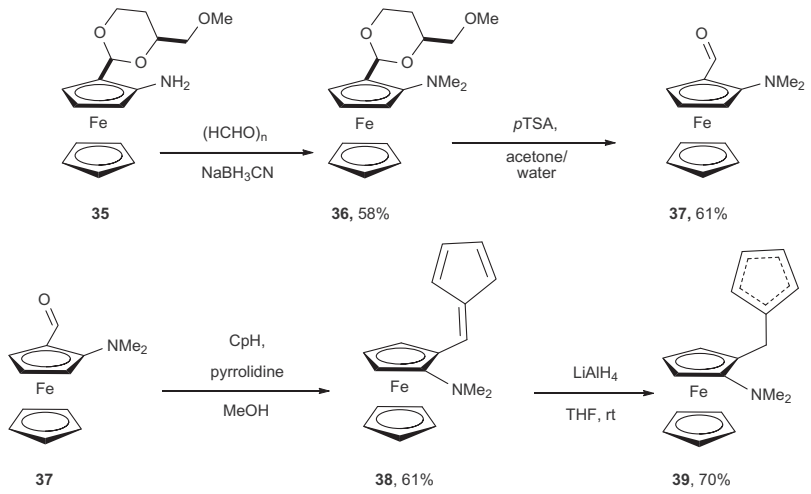
Melting points were recorded on a Stuart Scientific SMP3 apparatus and are uncorrected. Optical rotations were recorded on a Jasco DIP370 Digital Polorimeter. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR instrument as solutions in chloroform unless otherwise stated. The NMR spectra were recorded on Bruker AM/Bruker AMX/Bruker AVANCE III spectrometers at 600, 500, 400 and 300 MHz in a solution in $CDCl_3$ unless otherwise stated. Chemical shifts are reported in ppm relative to $CHCl_3$ (^1H: 7.27), (^{13}C: 77.2). Coupling constants are reported in Hz and rounded to the nearest 0.1 Hz. Signal assignments are as follows: b (broad), s (singlet), d (doublet, t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), etc. Mass spectra were recorded using Thermo Finnigan Mat900xp (EI/CI) VG-70se (FAB) and Waters LCT Premier XE (ES) instruments. Elemental analysis was performed on an Exeter Analytical Inc. EA440 horizontal load analyser or Hewlett Packard 1100 series. HPLC analysis was acquired on a Hewlett Packard Capillary HP4890A GC analyser.

For all non-aqueous chemistry, glassware was rigorously flame dried and an inert (N_2) atmosphere maintained throughout. All solvents and chemicals were used as received unless stated



(*pS*)-**28** (*pS*)-**29**, 93% (*pS*)-**30**, 76%

Scheme 8. Synthesis of a phosphorus cyclopentadiene chelate ligand.



Scheme 10. Synthesis of nitrogen cyclopentadiene chelate ligand.

otherwise. 2-Bromoindene,[42] 4-(methoxymethyl)-2-(α-aminoferrocenyl)-1,3-dioxane **35**,[40] (*pS*)-α-(diphenylphosphino)ferrocenecarboxaldehyde **28**,[40] tetramethylcyclopentadiene (TMCp)[43] and tetraphenylcyclopentadiene (TPCp)[44] were synthesised according to known literature procedures. Chromatographic separations were performed using Flourochem silica gel 60, 35–70 μm. Petroleum ether with a boiling range 40–60 °C was used.

4.2. Synthesis of ferrocene ligands

4.2.1. (*pR*)-1-Iodo-2-(methylalcohol)ferrocene 7[32]

The title compound was resolved from (±)-**7** following a modified literature procedure.[32]

(i) *Small scale*: A solution of (±)-**7** (0.45 g, 1.3 mmol) in DCM (90 mL) was treated with Novozym 435 (0.90 g) and vinyl acetate (1.3 mL). The suspension was heated to 45 °C with shaking (shaker bed, 150 rpm). ^{1}H NMR indicated that after 4 h, the reaction had reached 50% conversion. The solution was filtered to remove the immobilised enzyme and the solvent removed in vacuo. CSP HPLC analysis (Chiracel OD-H, eluent: hexane: ^{i}PrOH, 91:9, flow 0.4 mL/min) determined (*pS*)-**8** (98% ee), (*pR*)-**7** (95% ee) [t_R (minor) = 19.41 min, t_R (major) = 21.42 min]. Compounds **7** and **8** were separated using flash column chromatography (33% EtOAc/pet. ether) to give (*pS*)-**8** (0.24 g, 49%) and (*pR*)-**7** (0.17 g, 38%). ^{1}H NMR was in agreement with the literature data.[45] Recrystallisation of (*pR*)-**7** increased the enantiopurity to >99% ee, 90% recovery.

(ii) *Large scale*: A solution of (±)-**7** (51.3 g, 0.150 mol) in DCM (2.57 L) was treated with Novozym 435 (15.4 g) and vinyl acetate (28.7 mL). The suspension was heated to 34 °C with overhead stirring. LCMS indicated that the reaction had reached 50% conversion after 4 d. The solution was filtered to remove the immobilised enzyme and the solvent was removed in vacuo. Purification and determination of enantiopurity were performed as for the small scale reaction.

4.2.2. (*pR*)-1-Iodo-2-(triisopropylsilylethermethyl)ferrocene 9

A solution of alcohol **7** (5.77 g, 16.7 mmol) in DMF (60 mL) was treated with imidazole (2.91 g, 41.8 mmol) and TIPSCl (4.24 mL, 20.1 mmol) and stirred at rt for 14 h. The reaction was quenched with $NH_4Cl_{(aq)}$ (10 mL), taken up in diethyl ether (100 mL), washed with water (2 × 50 mL), brine (50 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (10% diethyl ether/pet. ether, silica) to give the title compound as an orange oil (8.28 g, 99%). R_f = 0.34 (pet. ether); $[\alpha]_D^{25} = -31.2$ (*c* 1.00, $CHCl_3$); IR ν_{max} 2943, 2891, 2866, 1462, 1383, 1106, 1070, 1058, 999, 883 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.12–1.21 (21H, m, Si(^{i}*Pr*)$_3$), 4.16 (5H, s, Cp_{unsub}), 4.17 (1H, app t, *J* = 2.2, Cp_{sub}), 4.36 (1H, m, Cp_{sub}), 4.42 (1H, dd, *J* = 2.2, 1.2, Cp_{sub}), 4.58 (2H, s, CpC*H*$_2$); ^{13}C NMR (100 MHz) δ 12.1 (CH), 18.2 (CH_3), 42.9 (C), 62.2 (CH_2), 67.2 (CH), 68.3 (CH), 71.5 (CH), 74.3 (CH), 89.0 (C); *m*/*z* (EI+) 521 (10%, M^++Na), 326 (10%, M^++H−OTIPS), 325 (80%, M^+−OTIPS), 229 (42%), 228 (11%), 227 (100%); HRMS $C_{20}H_{31}FeIOSi$ calcd 498.0533, found 498.0536; Anal. Calcd for $C_{20}H_{31}FeIOSi$: C, 48.21; H, 6.27. Found: C, 48.70; H, 6.29.

4.2.3. (*pS*)-1-(Triisopropylsilylethermethyl)-2-(inden-1-yl)-ferrocene 11

A solution of iodide **9** (2.00 g, 4.04 mmol) in diethyl ether (100 mL) was cooled to −78 °C and treated with ^{n}BuLi (1.6 M in hexanes, 5.05 mL, 8.08 mmol), after which the solution was stirred at −78 °C for 30 min. After this time a solution of 1-indanone (1.59 g, 12.1 mmol) in THF (12 mL) was added dropwise, the solution was stirred for 2 h at −78 °C and allowed to warm to rt overnight. The solution was quenched with $NH_4Cl_{(aq)}$, washed with water (2 × 60 mL), brine (60 mL), dried over $MgSO_4$ and concentrated in vacuo to give crude **10**. A solution of crude **10** (3.54 g) in DCM (30 mL) was cooled to −78 °C and treated with MsCl (0.340 mL, 4.87 mmol) followed by DIPEA (1.71 mL, 10.2 mmol) and stirred at −78 °C for 1.5 h. The reaction was quenched with water (10 mL), washed with water (2 × 10 mL), brine (5 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (10% diethyl ether/pet. ether) to give the title compound as an orange oil (2.01 g, 97%). R_f = 0.25 (pet. ether); $[\alpha]_D^{25} = +75.7$ (*c* 0.93, $CHCl_3$); IR ν_{max} 2943, 2891, 2866, 1604, 1462, 1392, 1125, 1094, 1050, 999, 908, 882 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.11–1.19 (21H, m, Si(^{i}*Pr*)$_3$), 3.41 (1H, dd, *J* = 23.6, 2.0, IndC*H*$_2$), 3.49 (1H, dd, *J* = 23.6, 2.0, IndC*H*$_2$), 4.13 (5H, s, Cp_{unsub}), 4.28 (1H, app t, *J* = 2.3, Cp_{sub}), 4.47 (1H, dd, *J* = 2.3, 1.2, Cp_{sub}), 4.61 (1H, dd, *J* = 2.3, 1.2, Cp_{sub}), 4.68 (1H, d, *J* = 11.4, CpC*H*$_2$), 4.78 (1H, d, *J* = 11.4, CpC*H*$_2$), 6.83 (1H, t, *J* = 2.0, IndC*H*), 7.26 (1H, app t, *J* = 7.4, Ar*H*), 7.40 (1H, app t, *J* = 7.6, Ar*H*), 7.52 (1H, d, *J* = 7.4, Ar*H*), 7.96 (1H, d, *J* = 7.6, Ar*H*); ^{13}C NMR (100 MHz) δ 12.2 (CH),

18.2 (CH_3), 38.4 (CH_2), 60.9 (CH_2), 67.4 (CH), 69.1 (CH), 69.6 (CH), 69.7 (CH), 81.2 (C), 85.1 (C), 121.2 (CH), 123.8 (CH), 124.5 (CH), 125.9 (CH), 131.6 (CH), 139.9 (C), 144.8 (C), 144.9 (C); *m*/*z* (EI+) 509 (12%, M^++Na), 314 (23%, M^++H−OTIPS), 313 (100%, M^+−OTIPS), 152 (10%), 150 (16%); HRMS $C_{29}H_{38}FeNaOSi$ calcd 509.1934, found 509.1925.

4.2.4. (*pS*)-1-(Triisopropylsilylethermethyl)-2-(inden-2-yl)ferrocene 12

A solution of (*pS*)-**9** (2.00 g, 4.04 mmol) in THF (70 mL) was cooled to −78 °C, treated with ^{n}BuLi (1.6 M in hexanes, 3.03 mL, 4.85 mmol) and stirred at −78 °C for 30 min. A solution of $ZnCl_2$ (0.5 M in THF, 9.70 mL, 4.85 mmol) was added dropwise, the solution warmed to rt over 30 min and stirred at rt for 1 h. Next, $Pd(PPh_3)_2Cl_2$ (0.140 g, 0.200 mmol) in THF (5 mL) was treated with DIBAL (1 M in THF, 0.400 mL, 0.440 mmol), stirred for 5 min and added dropwise via cannula to the reaction. The resultant solution was heated at reflux and a solution of 2-bromoindene[42] (1.56 g, 8.08 mmol) in THF (5 mL) added dropwise over 30 min. After refluxing for 4 d the solution was cooled to rt, quenched with $NH_4Cl_{(aq)}$ (10 mL), washed with water (2 × 40 mL), brine (40 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (pet. ether) to give the title compound as an orange oil (1.47 g, 75%). R_f = 0.31 (pet. ether); $[\alpha]_D^{25}$ = +235.3 (*c* 1.02, $CHCl_3$); IR ν_{max} 2943, 2866, 1461, 1391, 1130, 1105, 1057, 999, 908, 882 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.18–1.70 (21H, m, Si(^{i}*Pr*)$_3$), 3.72 (1H, d, *J* = 22.8, IndC*H*$_2$), 3.79 (1H, d, *J* = 22.8, IndC*H*$_2$), 4.07 (5H, s, Cp_{unsub}), 4.26 (1H, app t, *J* = 2.5, Cp_{sub}), 4.42 (1H, dd, *J* = 2.5, 1.5, Cp_{sub}), 4.48 (1H, dd, *J* = 2.5, 1.5, Cp_{sub}), 4.74 (1H, d, *J* = 11.6, CpC*H*$_2$), 4.95 (1H, d, *J* = 11.6, CpC*H*$_2$), 7.08 (1H, s, IndC*H*), 7.16 (1H, app dt, *J* = 7.2, 0.8, Ar*H*), 7.25 (1H, app t, *J* = 7.2, Ar*H*), 7.31 (1H, d, *J* = 7.2, Ar*H*), 7.45 (1H, d, *J* = 7.2, Ar*H*); ^{13}C NMR (100 MHz) δ 12.2 (CH), 18.2 (CH_3), 41.0 (CH_2), 61.4 (CH_2), 67.3 (CH), 69.0 (CH), 69.7 (CH), 70.9 (CH), 81.4 (C), 85.0 (C), 120.1 (CH), 123.4 (CH), 123.8 (CH), 126.4 (CH), 126.6 (CH), 142.7 (C), 145.5 (C), 146.2 (C); *m*/*z* (EI+) 510 (10%, M^++HNa), 509 (26%, M^++Na), 314 (23%, M^++H−OTIPS), 313 (100%, M^+−OTIPS), 301 (15%, M^+−COTIPS), 269 (7%); HRMS $C_{29}H_{38}FeNaOSi$ calcd 509.1934, found 509.1903; Anal. Calcd for $C_{29}H_{38}FeOSi$: C, 71.59; H, 7.87. Found: C, 71.10; H, 7.81.

4.2.5. (*pR*)-1-(1-Hydroxy-tetraphenylcyclopentadienyl)-2-(triisopropylsilylether methyl)ferrocene 13

A solution of iodide **9** (0.50 g, 1.0 mmol) in diethyl ether (30 mL) was cooled to −78 °C and treated with ^{n}BuLi (2.5 M in hexanes, 0.80 mL, 2.0 mmol), and stirred at −78 °C for 10 min. After this time the solution was warmed to −40 °C, stirred for 10 min and treated with a solution of tetraphenylcyclopentadienone (0.60 g, 1.5 mmol) in THF (25 mL) until the purple colour remained (15 mL of the solution). The reaction mixture was stirred at −40 °C for 1 h, quenched with water (5 mL), washed with water (2 × 30 mL), brine (30 mL), dried over $MgSO_4$ and concentrated in vacuo. The resultant brown foam was purified using flash column chromatography (5% diethyl ether/pet. ether) to give the title compound as an orange solid (0.60 g, 80%). R_f = 0.34 (5% diethyl ether/pet. ether); mp 82–84 °C; $[\alpha]_D^{25}$ = +413.0 (*c* 1.20, $CHCl_3$); IR ν_{max} 3684, 3016, 2868, 2400, 1550, 1420, 1202, 1109, 928, 802 cm^{-1}; ^{1}H NMR (400 MHz) δ 1.07–1.08 (21H, m, Si(^{i}*Pr*)$_3$), 3.50 (1H, d, *J* = 11.9, CpC*H*$_2$), 3.54 (1H, d, *J* = 11.9, CpC*H*$_2$), 3.64 (5H, s, Cp_{unsub}), 4.10 (1H, m, Cp_{sub}), 4.14 (1H, m, Cp_{sub}), 4.18 (1H, m, Cp_{sub}), 5.15 (1H, s, O*H*), 6.74–6.79 (2H, m, Ar*H*), 6.82–6.97 (7H, m, Ar*H*), 7.01–7.15 (6H, m, Ar*H*), 7.19–7.32 (3H, m, Ar*H*), 7.58–7.64 (2H, m, Ar*H*); ^{13}C NMR (100 MHz) δ 11.8 (CH), 18.1 (CH_3), 60.8 (CH_2), 65.6 (CH), 66.8 (CH), 69.1 (CH), 69.2 (CH), 85.6 (C), 88.8 (C), 89.6 (C), 126.2 (CH), 126.4 (CH), 126.8 (CH), 127.0 (CH), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.8 (CH), 129.7 (CH), 130.1 (CH), 130.8 (CH), 131.1 (CH), 134.7 (C), 135.4 (C), 135.5 (C), 137.1 (C), 138.4 (C), 143.2 (C), 145.9 (C), 151.3 (C); *m*/*z* (EI+) 779 (100%, M^++Na), 757 (22%, M^++H), 757 (38%, M^+), 584 (15%, M^++H−OTIPS); HRMS $C_{49}H_{52}FeNaO_2Si$ calcd 779.2984, found 779.2973; Anal. Calcd for $C_{49}H_{52}FeO_2Si$: C, 77.75; H, 6.92. Found: C, 77.83; H, 6.92.

4.2.6. (*pS*)-1-(Triisopropylsilylethermethyl)-2-(tetraphenylcyclopentadienyl)ferrocene 14 and (*pS*)-1-(methylalcohol)-2-(tetraphenylcyclopentadienyl)ferrocene 15

A solution of **13** (1.00 g, 1.40 mmol) in THF (30 mL) was treated with $LiAlH_4$ (1.08 g, 28.0 mmol), which caused a gas to evolve exothermically and stirred at rt for 10 h. After this time, additional $LiAlH_4$ (0.500 g, 13.8 mmol) was added and the resultant solution was stirred at rt for 5 h. The reaction mixture was cooled to 0 °C, quenched with water (10 mL), washed with water (2 × 20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (10% EtOAc/pet. ether) to give **14** as an orange oil (0.207 g, 20%) and **15** as a yellow oil (0.510 g, 60%).

Compound **14** R_f = 0.62 (10% diethyl ether/pet. ether); $[\alpha]_D^{25}$ = +184.3 (*c* 0.89, $CHCl_3$); IR ν_{max} 2942, 2885, 1600, 1492, 1452, 1105, 1089, 1069, 999, 908, 883 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.85–0.98 (21H, m, Si(^{i}*Pr*)$_3$), 2.53 (1H, d, *J* = 12.7, CpC*H*$_2$), 3.25 (1H, dd, *J* = 2.4, 1.6, Cp_{sub}), 3.88 (1H, d, *J* = 12.7, CpC*H*$_2$), 3.95 (1H, app t, *J* = 2.4, Cp_{sub}), 4.16 (1H, m, Cp_{sub}), 4.22 (5H, s, Cp_{unsub}), 5.29 (1H, s, O*H*), 6.70–6.72 (2H, m, Ar*H*), 6.82–6.97 (7H, m, Ar*H*), 6.95–7.11 (10H, m, Ar*H*), 7.14–7.35 (8H, m, Ar*H*); ^{13}C NMR (100 MHz) δ 11.8 (CH), 18.1 (CH_3), 60.9 (CH_2), 65.1 (CH), 65.8 (CH), 66.6 (CH), 69.0 (CH), 70.0 (CH), 82.4 (C), 87.9 (C), 126.2 (CH), 126.5 (CH), 126.7 (CH), 127.7 (CH), 127.7 (CH), 127.9 (CH), 128.4 (CH), 129.3 (CH), 130.1 (CH), 130.2 (CH), 135.9 (C), 136.0 (C), 138.2 (C), 139.7 (C), 142.0 (C), 143.8 (C), 145.3 (C), 147.0 (C); *m*/*z* (EI+) 741 (38%, M^++H), 740 (71%, M^+); HRMS $C_{49}H_{52}FeOSi$ calcd 740.3131, found 740.3127.

Compound **15** R_f = 0.45 (10% diethyl ether/pet. ether); $[\alpha]_D^{25}$ = +344.7 (*c* 0.64, $CHCl_3$); IR ν_{max} 3572, 2928, 1600, 1492, 1452, 1376, 1106, 1073, 1041, 999, 977 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.39 (1H, t, *J* = 6.0, O*H*), 3.28 (1H, dd, *J* = 12.6, 6.0, CpC*H*$_2$), 3.34 (1H, dd, *J* = 2.4, 1.1, Cp_{sub}), 3.87 (1H, dd, *J* = 12.6, 6.0, CpC*H*$_2$), 4.06 (1H, m, Cp_{sub}), 4.19 (5H, s, Cp_{unsub}), 4.23 (1H, m, Cp_{sub}), 5.24 (1H, s, C*H*), 6.76–6.80 (2H, m, Ar*H*), 6.94–6.97 (2H, m, Ar*H*), 7.00–7.34 (16H, m, Ar*H*); ^{13}C NMR (100 MHz) δ 60.0 (CH_2), 65.3 (CH), 67.6 (CH), 68.0 (CH), 69.4 (CH), 69.8 (CH), 84.2 (C), 86.2 (C), 126.4 (CH), 126.9 (CH), 127.0 (CH), 127.7 (CH), 128.0 (CH), 128.5 (CH), 129.3 (CH), 130.1 (CH), 130.3 (CH), 135.1 (C), 135.1 (C), 135.5 (C), 137.7 (C), 141.8 (C), 142.7 (C), 145.9 (C), 147.4 (C); *m*/*z* (EI+) 607 (100%, M^++Na), 584 (52%, M^+), 567 (15%, M^+−OH); HRMS $C_{40}H_{32}FeNaO$ calcd 607.1695, found 607.1709.

4.2.7. (*pS*)-1-(Methylethermethyl)-2-(inden-1-yl)ferrocene 16

A solution of TIPS ether **11** (50 mg, 0.100 mmol) in MeOH (8.6 mL) was cooled to 5 °C and treated with 2 M HCl (1.7 mL) and stirred at 5 °C for 16 h. The solution was concentrated in vacuo and taken up in DCM (5 mL), washed with $NaHCO_{3(aq)}$ (2 × 4 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (50% diethyl ether/pet. ether) to give the title compound as a yellow/orange oil (29 mg, 85%). R_f = 0.33 (5% diethyl ether/pet. ether); $[\alpha]_D^{25}$ = +110.6 (*c* 1.08, $CHCl_3$); IR ν_{max} 2930, 2891, 2399, 1469, 1389, 1081, 1096, 1025, 998 cm^{-1}; ^{1}H NMR (400 MHz) δ 3.42 (3H, s, OC*H*$_3$), 3.43 (1H, dd, *J* = 23.6, 2.1, IndC*H*$_2$), 3.48 (1H, dd, *J* = 23.6, 2.1, IndC*H*$_2$), 4.13 (5H, s, Cp_{unsub}), 4.27 (1H, d, *J* = 10.8, CpC*H*$_2$), 4.35 (1H, app t, *J* = 2.5, Cp_{sub}), 4.47 (1H, dd, *J* = 2.5, 1.4, Cp_{sub}), 4.55 (1H, d, *J* = 10.8, CpC*H*$_2$), 4.66 (1H, dd, *J* = 2.5, 1.4, Cp_{sub}), 6.76 (1H, app t, *J* = 2.1, IndC*H*), 7.28 (1H, app dt, *J* = 7.4, 1.0, Ar*H*), 7.41 (1H, dt, *J* = 7.8, 1.0, Ar*H*), 7.55 (1H, d, *J* = 7.4, Ar*H*), 7.96 (1H,

d, J = 7.8, Ar*H*); ^{13}C NMR (100 MHz) δ 38.5 (CH_3), 57.7 (CH_2), 68.0 (CH), 69.5 (CH), 69.5 (CH), 69.9 (CH_2), 71.0 (CH), 80.4 (C), 82.0 (C), 121.2 (CH), 123.8 (CH), 124.5 (CH), 125.9 (CH), 131.7 (CH), 139.5 (C), 144.8 (C); m/z (EI+) 367 (12%, M^++Na), 345 (9%, M^++H), 314 (23%, M^++H−OMe), 313 (100%, M^+−OMe), 311 (6%, M^+−H_2-OMe); HRMS $C_{21}H_{21}FeO$ calcd 345.0936, found 345.0943.

4.2.8. (*pS*)-1-(Methylacetate)-2-(inden-1-yl)ferrocene 17

A solution of TIPS ether **11** (2.00 g, 4.01 mmol) in THF (45 mL) was treated with AcOH/water (4:1 solution, 80 mL) and stirred at 5 °C for 3 d. The reaction was quenched with $NaHCO_{3(aq)}$ (100 mL), washed with $NaHCO_{3(aq)}$ (3 × 50 mL), water (2 × 50 mL), brine (50 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (20% EtOAc/pet. ether) to give the title compound as an orange/yellow solid (1.37 g, 92%). Mp 123–125 °C; R_f = 0.21 (5% diethyl ether/pet. ether); $[\alpha]_D^{25} = +141.2$ (c 0.96, $CHCl_3$); IR ν_{max} 2924, 1731, 1459, 1376, 1256, 1106, 1046, 1020, 975, 905 cm^{-1}; ^{1}H NMR (500 MHz) δ 2.10 (3H, s, COCH_3), 3.43 (1H, dd, J = 23.2, 2.1, IndCH_2), 3.49 (1H, dd, J = 23.2, 2.1, IndCH_2), 4.12 (5H, s, Cp_{unsub}), 4.38 (1H, app t, J = 2.6, Cp_{sub}), 4.54 (1H, dd, J = 2.6, 1.4, Cp_{sub}), 4.68 (1H, dd, J = 2.6, 1.4, Cp_{sub}), 4.95 (1H, d, J = 11.9, CpCH_2), 5.28 (1H, d, J = 11.9, CpCH_2), 6.62 (1H, t, J = 2.1, IndC*H*), 7.28 (1H, app dt, J = 7.4, 0.8, Ar*H*), 7.41 (1H, app t, J = 7.6, Ar*H*), 7.54 (1H, d, J = 7.4, Ar*H*), 7.92 (1H, d, J = 7.6, Ar*H*); ^{13}C NMR (100 MHz) δ 21.2 (CH_3), 38.5 (CH_2), 62.2 (CH_2), 68.5 (CH), 69.7 (CH), 69.8 (CH), 71.1 (CH), 77.3 (C), 78.4 (C), 121.1 (CH), 123.9 (CH), 124.8 (CH), 125.8 (C), 126.0 (CH), 131.4 (CH), 139.3 (C), 144.6 (C), 171.0 (C); m/z (EI+) 395 (9%, M^++Na), 373 (7%, M^++H), 372 (25%, M^+), 314 (24%, M^++H−OAc), 313 (100%, M^+−OAc), 282 (14%), 239 (11%), 227 (14%), 202 (18%), 150 (13%); HRMS $C_{22}H_{20}FeO_2$ calcd 372.0812, found 372.1626; Anal. Calcd for $C_{22}H_{20}FeO_2$: C, 70.99; H, 5.42. Found: C, 71.34, H, 5.60.

4.2.9. (*pS*)-1-(Methylalcohol)-2-(inden-1-yl)ferrocene 18

A solution of acetate **17** (1.65 g, 4.62 mmol) in methanol (80 mL)/diethyl ether (20 mL) was treated with NaOMe (1.25 g, 23.1 mmol) and stirred at rt for 2 h. After this time the reaction was concentrated in vacuo, taken up in diethyl ether (30 mL), washed with water (2 × 20 mL), brine (20 mL), dried over $MgSO_4$ and concentrated in vacuo to give the title compound as an orange solid (1.45 g, 99%). Mp 68–70 °C; R_f = 0.35 (30% EtOAc/pet. ether); $[\alpha]_D^{25} = +100.6$ (c 0.68, $CHCl_3$); IR ν_{max} 3684, 3606, 2951, 2891, 2879, 2400, 1465, 1380, 1106, 984 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.62 (1H, dd, J = 6.5, 4.7, O*H*), 3.42 (1H, dd, J = 24.1, 2.2, IndCH_2), 3.51 (1H, dd, J = 24.1, 2.2, IndCH_2), 4.18 (5H, s, Cp_{unsub}), 4.35 (1H, app t, J = 2.5, Cp_{sub}), 4.47 (1H, dd, J = 2.5, 1.4, Cp_{sub}), 4.59 (2H, m, CpCH_2), 4.66 (1H, dd, J = 2.5, 1.4, Cp_{sub}), 6.75 (1H, t, J = 2.2, IndC*H*), 7.28 (1H, app dt, J = 7.4, 1.0, Ar*H*), 7.38 (1H, app t, J = 7.6, Ar*H*), 7.53 (1H, d, J = 7.4, Ar*H*), 7.88 (1H, d, J = 7.6, Ar*H*); ^{13}C NMR (100 MHz) δ 38.5 (CH_2), 60.1 (CH_2), 67.9 (CH), 69.4 (CH), 69.5 (CH), 69.6 (CH), 81.3 (C), 84.9 (C), 121.0 (CH), 123.9 (CH), 124.7 (CH), 126.0 (CH), 131.7 (CH), 139.6 (C), 144.7 (C), 144.8 (C); m/z (EI+) 353 (100%, M^++Na), 331 (25%, M^++H), 330 (68%, M^+), 314 (20%, M^+−O), 313 (84%, M^+−OH), 301 (14%); HRMS $C_{20}H_{18}FeNO$ calcd 353.0605, found 353.0599.

4.2.10. (*pS*)-1-(*N*,*N*-Dimethylaminomethyl)-2-(inden-2-yl)ferrocene 19

A solution of TIPS ether **13** (0.950 g, 1.95 mmol) in MeCN/acetone (1:1, 20 mL) was cooled to 0 °C and treated with TMSCl (0.617 mL, 4.88 mmol) and stirred for 10 min. After this time the resultant solution was transferred dropwise via cannula onto $HNMe_2$ (2 M solution in THF, 19.5 mL, 39.0 mmol) at 0 °C and stirred for 1 h. The reaction mixture was quenched with water (5 mL), washed with water (2 × 10 mL), brine (10 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (10% EtOAc/2% Et_3N/pet. ether, basic alumina) to give the title compound as a dark orange oil (0.640 g, 92%). R_f = 0.35 (10% EtOAc/2% Et_3N/pet. ether, basic alumina); $[\alpha]_D^{25} = +335.9$ (c 0.93, $CHCl_3$); IR ν_{max} 2942, 2857, 2817, 2771, 1460, 1393, 1353, 1105, 1043, 1000, 908 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.30 (6H, s, N(CH_3)$_2$), 3.09 (1H, d, J = 12.6, CpCH_2), 3.72 (1H, d, J = 22.0, IndCH_2), 3.85 (1H, d, J = 22.0, IndCH_2), 3.95 (1H, d, J = 12.6, CpCH_2), 4.07 (5H, s, Cp_{unsub}), 4.27 (1H, app t, J = 2.5, Cp_{sub}), 4.34 (1H, m, Cp_{sub}), 4.51 (1H, m, Cp_{sub}), 7.07 (1H, s, IndC*H*), 7.17 (1H, app dt, J = 7.3, 0.7, Ar*H*), 7.26 (1H, m, Ar*H*), 7.35 (1H, d, J = 7.4, Ar*H*), 7.45 (1H, d, J = 7.3, Ar*H*); ^{13}C NMR (100 MHz) δ 40.1 (CH_2), 44.2 (CH_3), 58.0 (CH_2), 66.4 (CH), 67.9 (CH), 68.8 (CH), 71.9 (CH), 80.5 (C), 81.3 (C), 119.2 (CH), 122.3 (CH), 122.8 (CH), 125.4 (CH), 125.5 (CH), 141.6 (C), 144.7 (C), 145.2 (C); m/z (EI+) 358 (75%, M^++H), 357 (100%, M^+), 314 (8%, M^++H−NMe_2), 313 (48%, M^+−NMe_2); HRMS $C_{22}H_{23}FeN$ calcd 357.1174, found 357.1175; Anal. Calcd for $C_{22}H_{23}NFe$: C, 73.96; H, 6.49; N, 3.42. Found: C, 73.83; H, 6.78; N, 3.74.

4.2.11. (*pS*)-1-(*N*-Methylaminomethyl)-2-(inden-2-yl)ferrocene 20

A solution of TIPS ether **13** (71 mg, 0.14 mmol) in MeCN/acetone (1:1, 2 mL) was cooled to 0 °C and treated with TMSCl (45 μL, 0.36 mmol) and stirred for 10 min. After this time the resultant solution was transferred dropwise via cannula onto H_2NMe (2 M solution in THF, 1.45 mL, 2.89 mmol) at 0 °C and stirred for 1 h. The reaction mixture was quenched with water (1 mL), washed with water (2 × 1 mL), brine (1 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved by acid extraction (8% H_3PO_4), basified by 2 M NaOH, taken up in DCM, separated, dried over $MgSO_4$ and concentrated in vacuo to give the title compound as an orange oil (42 mg, 89%). $[\alpha]_D^{25} = +233.5$ (c 0.40, $CHCl_3$); IR ν_{max} 3755, 2930, 1605, 1460, 1106, 1001, 828 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.53 (3H, s, NCH_3), 3.67 (1H, d, J = 22.0, IndCH_2), 3.73 (1H, d, J = 22.0, IndCH_2), 4.10 (5H, s, Cp_{unsub}), 4.14 (1H, d, J = 13.6, CpCH_2), 4.21 (1H, d, J = 13.6, CpCH_2), 4.36 (1H, app t, J = 2.5, Cp_{sub}), 4.53 (1H, dd, J = 2.5, 1.4, Cp_{sub}), 4.71 (1H, dd, J = 2.5, 1.4, Cp_{sub}), 6.95 (1H, s, IndC*H*), 7.18 (1H, app dt, J = 7.4, 0.7, Ar*H*), 7.25 (1H, app t, J = 7.4, Ar*H*), 7.36 (1H, d, J = 7.5, Ar*H*), 7.44 (1H, d, J = 7.3, Ar*H*); ^{13}C NMR (100 MHz) δ 36.6 (CH_3), 41.3 (CH_2), 51.0 (CH_2), 67.5 (CH), 68.9 (CH), 69.9 (CH), 71.2 (CH), 80.3 (C), 84.5 (C), 120.2 (CH), 123.4 (CH), 124.0 (CH), 125.5 (CH), 126.7 (CH), 142.4 (C), 145.9 (C), 146.1 (C); m/z (EI+) 364 (10%, M^++Na), 343 (41%, M^++Na), 314 (23%, M^++H−NHMe), 313 (100%, M^+−NHMe); HRMS $C_{21}H_{21}FeN$ calcd 343.0167, found 343.0160.

4.2.12. (*pS*)-1-(*N*,*N*-Dimethylaminomethyl)-2-(inden-1-yl)ferrocene 21

A solution of alcohol **18** (0.34 g, 0.97 mmol) in THF (20 mL) was cooled to 0 °C and treated with MsCl (0.12 mL, 0.97 mmol) followed by DIPEA (0.34 mL, 1.9 mmol) and stirred at 0 °C for 1 h. The resultant solution was transferred dropwise via cannula onto $HNMe_2$ (2 M in THF, 4.8 mL, 9.6 mmol) and stirred at 0 °C for 1 h. After this time the solution was quenched with water (10 mL), washed water (2 × 10 mL), brine (5 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved by acid extraction (8% H_3PO_4), basified by 2 M NaOH, taken up in DCM, separated, dried over $MgSO_4$ and concentrated in vacuo to give the title compound as a brown oil (0.34 g, 82%). $[\alpha]_D^{25} = -15.5$ (c 1.10, $CHCl_3$); IR ν_{max} 2943, 2858, 2816, 1693, 1603, 1456, 1368, 1106, 1001, 907 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.21 (6H, s, N(CH_3)$_2$), 3.10 (1H, d, J = 12.6, CpCH_2), 3.42 (1H, dd, J = 24.4, 2.2, IndCH_2), 3.50 (1H, dd, J = 24.4, 2.2, IndCH_2), 3.68 (1H, J = 12.6, CpCH_2), 4.11 (5H, s, Cp_{unsub}), 4.30 (1H, app t, J = 2.4, Cp_{sub}), 4.37 (1H, dd, J = 2.4, 1.4, Cp_{sub}), 4.61 (1H, dd, J = 2.4, 1.4, Cp_{sub}), 6.95 (1H, t, J = 2.2, IndC*H*),

7.26 (1H, app dt, J = 7.4, 0.9, Ar*H*), 7.38 (1H, app t, J = 7.5, Ar*H*), 7.52 (1H, d, J = 7.4, Ar*H*), 7.89 (1H, d, J = 7.7, Ar*H*); ^{13}C NMR (100 MHz) δ 36.5 (CH_2), 43.1 (CH_3), 56.2 (CH_2), 65.4 (CH), 67.0 (CH), 67.7 (CH), 69.3 (CH), 79.2 (C), 81.1 (C), 119.2 (CH), 121.8 (CH), 122.4 (CH), 123.9 (CH), 130.3 (CH), 138.2 (C), 142.8 (C), 143.2 (C); m/z (EI+) 430 (8%), 390 (10%, M^++O_2H), 358 (100%, M^++H), 313 (92%, M^+−NMe_2); HRMS $C_{22}H_{24}FeN$ calcd 358.1253, found 358.1253; Anal. Calcd for $C_{22}H_{23}FeN$: C, 73.96; H, 6.49; N, 3.92. Found: C, 73.98; H, 6.68; N, 3.56.

4.2.13. (*pS*)-1-(*N*-Methylaminomethyl)-2-(inden-1-yl)ferrocene 22

A solution of alcohol **18** (50 mg, 0.150 mmol) in THF (2 mL) was cooled to 0 °C and treated with MsCl (18 μL, 0.150 mmol) followed by DIPEA (50 μL, 0.300 mmol) and stirred at 0 °C for 1 h. The resultant solution was transferred dropwise via cannula onto $MeNH_2$ (2 M in THF, 0.750 mL, 1.50 mmol) and stirred at 0 °C for 1 h. Purification was achieved by acid extraction (8% H_3PO_4) then basified by 2 M NaOH, taken up in DCM, separated, dried over $MgSO_4$ and concentrated in vacuo to give the title compound as an orange oil (39 mg, 75%). R_f = 0.22 (EtOAc/Et_3N); $[\alpha]_D^{25} = -87.5$[†] (c 0.92, $CHCl_3$); IR ν_{max} 2935, 1666, 1459, 1394, 1106, 1000, 905 cm^{-1}; ^{1}H NMR (C_6D_6, 500 MHz) δ 0.6 (1H, b, N*H*), 2.35 (3H, s, NCH_3), 3.15 (1H, dd, J = 23.7, 2.2, IndCH_2), 3.24 (1H, dd, J = 23.7, 2.2, IndCH_2), 3.48 (1H, d, J = 12.4, CpCH_2), 3.70 (1H, d, J = 12.4, CpCH_2), 4.06 (5H, s, Cp_{unsub}), 4.10 (1H, app t, J = 2.5, Cp_{sub}), 4.30 (1H, dd, J = 2.5, 1.5, Cp_{sub}), 4.52 (1H, dd, J = 2.5, 1.5, Cp_{sub}), 6.88 (1H, t, J = 2.2, IndC*H*), 7.23 (1H, app dt, J = 7.3, 1.0, Ar*H*), 7.34–7.39 (2H, m, Ar*H*), 7.98 (1H, m, Ar*H*); ^{13}C NMR (C_6D_6, 125 MHz) δ 35.0 (CH_3), 38.6 (CH_2), 49.4 (CH_2), 68.0 (CH), 69.4 (CH), 70.1 (C), 70.2 (CH), 70.3 (CH), 81.6 (C), 121.4 (CH), 124.2 (CH), 125.1 (CH), 126.4 (CH), 132.1 (CH), 140.5 (C), 144.9 (C), 145.5 (C); m/z (EI+) 344 (48%, M^+), 313 (100%, M−NHMe); HRMS $C_{21}H_{22}NFe$ calcd 344.1096, found 344.1085.

4.2.14. (*pR*)-1-(*N*,*N*-Dimethylaminomethyl)-2-(tetraphenylcyclopentadienyl)ferrocene 23

A solution of **15** (0.20 g, 0.34 mmol) in MeCN/acetone (1:1, 5 mL) was cooled to 0 °C and treated with TMSCl (0.10 mL, 0.86 mmol) and stirred at 0 °C for 10 min. After this time, the resultant solution was transferred dropwise via cannula onto a solution of $HNMe_2$ (2 M, THF, 3.5 mL, 6.8 mmol) at 0 °C, and stirred for 1 h. The reaction mixture was quenched with water (3 mL), washed with water (2 × 5 mL), brine (5 mL), dried over $MgSO_4$ and concentrated in vacuo. ^{1}H NMR analysis indicated 75% conversion to the title compound (based upon integration of the unsubstituted Cp ring). ^{1}H NMR (400 MHz) δ 2.01 (6H, s, N(CH_3)$_2$), 2.63 (1H, d, J = 14.5, CpCH_2), 3.23 (1H, d, J = 14.5, CpCH_2), 3.98 (5H, s, Cp_{unsub}), 3.52–3.56 (2H, m, 2 × Cp_{sub}), 4.30 (1H, m, Cp_{sub}), 5.37 (1H, s, CpCH), 6.88–7.40 (4H, m, Ar*H*), 6.81–7.36 (20H, m, Ar*H*); HRMS $C_{42}H_{37}FeN$ calcd 611.1436, found 611.1442.

4.2.15. (*pR*)-1-(*N*-Methylaminomethyl)-2-(tetraphenylcyclopentadienyl)ferrocene 24

A solution of **15** (79 mg, 0.11 mmol) in MeCN/acetone (1:1, 2 mL) was cooled to 0 °C and treated with TMSCl (31 μL, 0.27 mmol) and stirred at 0 °C for 10 min. After this time the resultant solution was transferred dropwise via cannula onto a solution of H_2NMe (2 M, THF, 1.1 mL, 2.1 mmol) at 0 °C, and stirred for 1 h. The reaction mixture was quenched with water (1 mL), washed with water (2 × 1 mL), brine (1 mL), dried over $MgSO_4$ and concentrated in vacuo. ^{1}H NMR analysis indicated 85% conversion to the title compound (based upon integration of the unsubstituted Cp ring). ^{1}H NMR (400 MHz) δ 2.07 (3H, s, NCH_3), 2.52 (1H, d, J = 13.0, CpCH_2), 3.21 (1H, d, J = 13.0, CpCH_2), 3.36 (1H, dd, J = 4.5, 2.0, Cp_{sub}), 4.06 (1H, dd, J = 4.5, 2.0, Cp_{sub}), 4.18 (5H, s, Cp_{unsub}), 4.32 (1H, m, Cp_{sub}), 5.32 (1H, s, CpCH), 6.72–7.82 (4H, m, Ar*H*), 6.81–7.36 (20H, m, Ar*H*); HRMS $C_{41}H_{35}FeN$ calcd 597.1277, found 597.1300.

4.2.16. [(*pS*)-1-(*N*,*N*,*N*-Trimethylammoniummethyl)-2-(inden-2-yl)ferrocene][iodide] 25

A solution of **19** (57 mg, 0.160 mmol) in acetone (2 mL) was cooled to 0 °C and treated with MeI (45 μL, 0.172 mmol). The reaction was warmed to rt and stirred for 16 h. After this time the reaction was concentrated in vacuo. The resultant brown oil was dissolved in DCM (2 mL), after which diethyl ether (2 mL) was added dropwise and the solution filtered to give the title compound as a bright orange solid (70 mg, 91%). Mp 118–120 °C; $[\alpha]_D^{25} = +100.9$ (c 0.94, $CHCl_3$); IR ν_{max} 2944, 1604, 1485, 1456, 1370, 1108, 1002, 973, 870 cm^{-1}; ^{1}H NMR (500 MHz) δ 3.30 (9H, s, N(CH_3)$_3$), 3.53 (1H, d, J = 22.4, IndCH_2), 3.91 (1H, d, J = 22.4, IndCH_2), 4.26 (5H, s, Cp_{unsub}), 4.51 (1H, app t, J = 2.4, Cp_{sub}), 4.60 (1H, dd, J = 2.4, 1.5, Cp_{sub}), 4.94 (1H, dd, J = 2.4, 1.5, Cp_{sub}), 5.09 (1H, d, J = 13.5, CpCH_2), 5.50 (1H, d, J = 13.5, CpCH_2), 7.19 (1H, app dt, J = 7.4, 0.9, Ar*H*), 7.25–7.29 (2H, m, IndCH, Ar*H*), 7.49 (1H, d, J = 7.4, Ar*H*), 7.52 (1H, d, J = 7.5, Ar*H*); ^{13}C NMR (100 MHz) δ 42.6 (CH_2), 53.0 (CH_3), 65.9 (CH_2), 70.5 (CH), 70.7 (CH), 71.3 (CH), 71.5 (C), 74.7 (CH), 83.0 (C), 121.2 (CH), 123.7 (CH), 124.9 (CH), 127.0 (CH), 128.9 (CH), 142.1 (C), 143.4 (C), 144.9 (C); m/z (EI+) 372 (100%, M^+−I), 313 (85%, M^+−NMe_3I); HRMS $C_{23}H_{26}FeN$ calcd 372.1409, found 372.1393.

4.2.17. (*pS*)-Bis-(2-inden-2-yl-1-ferrocenyl methyl)diphenylphosphonium iodide 26

A solution of **25** (20 mg, 0.040 mmol) in MeCN (1 mL) was treated with $HPPh_2$ (6 μL, 0.032 mmol) and heated at reflux for 16 h. The reaction was quenched with water (0.5 mL), washed with water (2 × 1 mL), brine (1 mL), dried over $MgSO_4$ and concentrated in vacuo. The resultant orange oil was dissolved in DCM (2 mL), pet. ether. (2 mL) was added dropwise and the solution filtered to give the title compound as a pale brown solid (13 mg, 81%); mp 150–152 °C; $[\alpha]_D^{25} = +87.7$ (c 0.35, $CHCl_3$); IR ν_{max} 3548, 3529, 2942, 2310, 1602, 1480, 1398, 1350, 1107, 1020, 999, 908 cm^{-1}; ^{1}H NMR (400 MHz) δ 2.90 (2H, d, J = 22.4, 2 × IndCH_2), 3.46 (2H, d, J = 22.4, 2 × IndCH_2), 4.25 (14H, m, 2 × Cp_{unsub}, 4 × Cp_{sub}), 4.40 (2H, m, 2 × CpCH_2), 4.44 (2H, m, 2 × Cp_{sub}), 5.65 (2H, app t, J = 14.2, 2 × CpCH_2), 6.68 (2H, s, 2 × IndCH), 7.13–7.20 (6H, m, Ar*H*), 7.23–7.36 (6H, m, Ar*H*), 7.41–7.55 (6H, m, Ar*H*); ^{13}C NMR (100 MHz) δ 25.2 (CH_2), 25.2 (CH_2), 42.1 (CH_2) 68.1 (CH), 68.9 (CH), 71.3 (CH), 71.4 (CH), 73.9 (C), 81.3 (C), 116.4 (C), 117.1 (C), 120.6 (CH), 123.4 (CH), 124.5 (CH), 126.7 (CH), 127.7 (CH), 129.3 (CH), 129.4 (CH), 134.0 (CH), 134.1 (CH), 134.3 (CH), 134.3 (CH), 142.1 (C), 144.4 (C), 145.1 (C); ^{31}P NMR δ 20.0, 20.5; m/z (EI+) 812 (62%, M^++H−I), 811 (100%, M^+−I), 500 (16%, M^++H−I$C_{20}H_{17}Fe$), 444 (25%, M^++Na−IPh$C_{20}H_{17}Fe$), 400 (14%), 313 (21%, M^+−IPPh_2-$C_{20}H_{17}Fe$); HRMS $C_{52}H_{44}Fe_2P$ calcd 811.1876, found 811.1871.

4.2.18. (*pS*)-1-(Diphenylphosphinomethyl)-2-(tetraphenylcyclopentadienyl)ferrocene 27

A solution of **15** (58 mg, 0.081 mmol) in MeCN (2 mL) was cooled to 0 °C and treated with TMSCl (23 μL, 0.20 mmol) and stirred at 0 °C for 10 min. After this time, the resultant solution was treated with $HPPh_2$ (1.4 μL, 0.081 mmol) at 0 °C and stirred for 1 h. The reaction mixture was quenched with water (1 mL), washed with water (2 × 1 mL), brine (1 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash

[†] The specific rotation of this compound increased significantly with each successive reading (−142.5 after 10 readings). The temperature was seen to increase slightly upon each reading (by ~0.1 °C) so the value is quoted at 25 °C. The sample was not degrading, upon cooling the sample back to 25 °C the specific rotation returned to −87.5.

column chromatography (10% EtOAc/pet. ether) to give the title compound as an orange oil (45 mg, 74%). R_f = 0.24 (pet. ether); $[\alpha]_D^{25}$ = +216.1 (*c* 0.77, $CHCl_3$); IR υ_{max} 3002, 1711, 1492, 1452, 1106, 1073, 1041, 999, 908 cm^{-1}; ^1H NMR (400 MHz) δ 1.80 (1H, dd, *J* = 16.2, 5.0, CpC*H*$_2$), 2.54 (1H, d, *J* = 16.2, CpC*H*$_2$), 3.36 (1H, m, Cp_{sub}), 3.79 (1H, m, Cp_{sub}), 3.91 (1H, m, Cp_{sub}), 4.27 (5H, s, Cp_{unsub}), 5.32 (1H, s, C*H*), 6.77–6.81 (2H, m, Ar*H*), 6.99–7.41 (28H, m, Ar*H*); ^{13}C NMR (100 MHz) δ 28.2 (CH_2), 65.5 (CH), 66.7 (CH), 68.9 (CH), 70.4.8 (CH), 77.1 (CH), 83.4 (C), 84.7 (C), 126.3 (CH), 126.7 (CH), 126.7 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.1 (CH), 128.2 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 128.8 (CH), 129.3 (CH), 130.2 (CH), 130.3 (CH), 132.2 (CH), 132.3 (CH), 133.0 (CH), 133.2 (CH), 135.3 (C), 135.9 (C), 136.7 (C), 137.9 (C), 139.5 (C), 140.8 (C), 141.9 (C), 143.4 (C), 145.9 (C), 147.4 (C); ^{31}P NMR δ −19.0; *m*/*z* (EI+) 754 (54%, M^++H), 753 (100%, M^+), 752 (100%, M^+−H); HRMS $C_{52}H_{34}FeP$ calcd 753.2392, found 753.2369.

4.2.19. (*pS*)-1-(Diphenylphosphino)-2-[(cyclopenta-2,4-dienylidene)methyl]-ferrocene 29

Freshly cracked cyclopentadiene (0.08 mL, 1.00 mmol), 2-(diphenylphosphino)-ferrocenecarboxaldehyde **28**[40] (100 mg, 0.25 mmol) and pyrrolidine (0.04 mL, 0.50 mmol) were stirred in degassed MeOH (10 mL) at rt for 3.5 h. The reaction was concentrated in vacuo, dried for 2 h under vacuum and purified using flash column chromatography (10% EtOAc/pet. ether) to give the title compound as a red-purple solid (105 mg, 93%). Mp 147–149 °C; R_f = 0.64 (10% EtOAc/pet. ether); $[\alpha]_D^{25}$ = +821.7 (*c* 0.14, $CHCl_3$); IR υ_{max} 3068, 1615, 1606, 1420 cm^{-1}; ^1H NMR (400 MHz) δ 4.07 (1H, m, Cp_{sub}), 4.11 (5H, s, Cp_{unsub}), 4.69 (1H, t, *J* = 2.6, Cp_{sub}), 5.14 (1H, m, Cp_{sub}), 6.31 (1H, dt, *J* = 5.0, 1.7, Fulv), 6.45 (1H, dm, *J* = 5.0, Fulv), 6.63 (1H, ddt, *J* = 5.1, 1.6, 1.9, Fulv), 6.72 (1H, dm, *J* = 5.3, Fulv), 7.13–7.27 (5H, m, PPh_2), 7.43–7.47 (3H, m, PPh_2), 7.48 (1H, d, *J* = 3.1, CpC*H*), 7.60–7.67 (2H, m, PPh_2); ^{13}C NMR (100 MHz) δ 71.0 (CH), 71.1 (CH), 73.0 (CH), 74.3 (CH), 80.6 (C), 85.5 (C), 119.8 (CH), 126.9 (CH), 128.0 (CH), 128.3 (CH), 128.4 (CH), 128.9 (CH), 129.5 (*CH*), 132.0 (CH), 133.4 (CH-Fulv.), 132.0 (CH), 137.0 (C), 138.1 (CH), 139.4 (C), 142.4 (C); ^{31}P NMR (162 MHz) δ -23.0; *m*/*z* (EI+) 447 (28%, M+H), 446 (100%, M), 121 (4%, Cp+Fe); HRMS $C_{28}H_{23}FeP$ calcd 446.08813, found 446.08852.

4.2.20. (*pS*)-1-(Diphenylphosphino)-2-[(cyclopenta-1,3-dienyl) methyl]-ferrocene 30

To a solution of **29** (50.0 mg, 0.11 mmol) in THF (5.0 mL), $LiAlH_4$ was added (0.08 mL, 0.17 mmol, 2 M in THF) and the resulting solution was stirred at rt overnight. Water (4 mL) was added and the mixture was extracted with DCM (2 × 3 mL), washed with water (1 × 2 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (10% EtOAc/pet. ether) to give the title compound as a yellow solid (38.0 mg, 76%) which consisted of 2 inseparable isomers in a 3/2 ratio. Mp 114–116 °C); R_f = 0.66 (10% EtOAc/pet. ether); $[\alpha]_D^{25}$ = −203.9 (*c* 0.98, $CHCl_3$); IR υ_{max} 3062, 3046, 2898, 2872, 1609, 1583, 1475, 1430, 1362, 1172, 1105 cm^{-1}.

Major isomer: ^1H NMR (600 MHz) δ 2.48 (1H, dm, *J* = 24.2, Cp′C*H*$_2$), 2.69 (1H, dm, *J* = 24.3, Cp′C*H*$_2$), 3.54 (1H, dm, *J* = 15.6, CpC*H*$_2$Cp′), 3.71 (1H, m, Cp_{sub}), 3.72 (1H, dm, *J* = 15.2, CpC*H*$_2$Cp′), 4.03 (5H, s, Cp_{unsub}), 4.24 (1H, m, Cp_{sub}), 4.42 (1H, m, Cp_{sub}), 5.77 (1H, m, Cp′C*H*), 6.25 (1H, m, Cp′C*H*), 6.33 (1H, m, Cp′C*H*), 7.03–7.60 (10H, PPh_2); ^{13}C NMR (150 MHz) δ 29.5 (CH_2), 41.1 (CH_2), 69.0 (CH), 69.8 (CH), 71.0 (CH), 71.9 (CH), 75.3 (C), 92.9 (C), 127.4 (CH), 127. 8 (CH), 128.0 (CH), 128. 2 (CH), 129.1 (CH), 132.5 (CH), 133.6 (CH), 134.5 (CH), 135.2 (CH), 137.8 (C), 139.7 (C), 145.3 (C); ^{31}P NMR (162 MHz; $CDCl_3$) δ −23.1.

Minor isomer: ^1H NMR (600 MHz) δ 2.63 (1H, dm, *J* = 22.1, Cp′C*H*$_2$), 2.69 (1H, dm, *J* = 22.3, Cp′C*H*$_2$), 3.61 (1H, dm, *J* = 15.8, CpC*H*$_2$Cp′), 3.73 (1H, m, Cp_{sub}), 3.75 (1H, dm, *J* = 15.0, CpC*H*$_2$Cp′), 4.03 (5H, s, Cp_{unsub}., 4.24 (1H, m, Cp_{sub}), 4.39 (1H, m, Cp_{sub}), 5.94 (1H, m, Cp′C*H*), 6.08 (1H, m, Cp′C*H*), 6.18 (1H, m, Cp′C*H*), 7.03–7.60 (10H, PPh_2); ^{13}C NMR (150 MHz) δ 29.9 (CH_2), 43.3 (CH_2), 69.1 (CH), 69.9 (CH), 70.9 (CH), 71.7 (CH), 75.4 (C), 93.7 (C), 127.4 (CH), 127.8 (CH), 128.0 (d, CH), 128.2 (CH), 129.1 (CH), 130.7 (CH), 132.2 (CH), 132.5 (CH), 135.1 (CH), 137.8 (C), 139.6 (C), 148.1 (C); ^{31}P NMR (162 MHz; $CDCl_3$) δ −23.4; HH; *m*/*z* (EI+) 449 (3%, M+H), 448 (11%, M); HRMS $C_{28}H_{25}FeP$ calcd 448.10378, found 448.10252.

4.2.21. (*pS*)-1-(Diphenylphosphino)-2-[(9*H*-fluoren-9-ylidene) methyl]-ferrocene 31

A solution of fluorene (83 mg, 0.50 mmol) in degassed THF (5 mL) was treated with sodium hydride (12 mg, 0.50 mmol) followed by **28**[40] (200 mg, 0.50 mmol) at rt. The resultant red solution was heated at reflux for 18 h. The reaction was concentrated onto silica and purification was achieved using flash column chromatography (5% EtOAc/Pet. ether) to give the title compound as a red solid (138 mg, 49%). Mp 174–176 °C; R_f = 0.57 (10% EtOAc/Pet. ether); $[\alpha]_D^{25}$ = +2580 (*c* 0.10, $CHCl_3$); IR υ_{max} 3056, 1625, 1602, 1432, 1258, 1170 cm^{-1}; ^1H NMR (600 MHz) δ 4.04 (1H, bs, Cp_{sub}), 4.13 (5H, s, Cp_{unsub}), 4.55 (1H, t, *J* = 2.4, Cp_{sub}), 5.05 (1H, bs, Cp_{sub}), 7.09–7.22 (12H, m, PPh_2 and Flu.C*H*), 7.61–7.65 (2H, m, PPh_2), 7.68 (1H, d, *J* = 6.9, Flu.C*H*), 7.71 (1H, d, *J* = 7.5, Flu.C*H*), 7.72 (1H, s, CpC*H*), 7.80 (1H, d, *J* = 7.3, Flu.C*H*), 8.14 (1H, d, *J* = 7.8, Flu.C*H*); ^{13}C NMR (150 MHz) δ 70.6 (CH), 70.7 (CH), 72.4 (CH), 73.4 (CH), 80.2 (C), 87.3 (C), 119.6 (CH), 119.8 (CH), 120.3 (CH), 124.3 (CH), 125.1 (CH), 126.6 (CH), 126.9 (CH), 127.6 (CH), 127.9 (CH), 127.9 (CH), 128.2 (CH), 128.4 (CH), 129.5 (CH), 132.1 (CH), 135.2 (C), 135.2 (CH), 137.1 (C), 137.4 (C), 138.3 (C), 139.4 (C), 139.9 (C), 140.9 (C); ^{31}P NMR (162 MHz) δ -21.0; *m*/*z* (EI) 547 (2%, M+H), 546 (11%, M), 426 (31%, M−Fe−Cp), 425 (100%, M−Fe−Cp−H); HRMS $C_{36}H_{27}FeP$ calcd 546.11943, found 546.11936.

4.2.22. (*pS*)-1-(Diphenylphosphino)-2-(1*H*-inden-1-ylidene)-methyl)-ferrocene 32

Starting from indene (58 mg, 0.50 mmol) and following the same procedure as reported for **31** (reflux for 3 h) the title compound was obtained as a dark red solid (189 mg, 76%) which consisted of two inseparable isomers in an 8/2 ratio. Mp 70–72 °C; R_f = 0.63 (10% EtOAc/Pet. ether); $[\alpha]_D^{25}$ = +1543 (*c* 0.03, $CHCl_3$); IR υ_{max} 2922, 2852, 1619, 1458, 1258, 1016 cm^{-1}; *m*/*z* (EI) 497 (35%, M+H), 496 (100%, M), 431 (3%, M−Cp); HRMS $C_{32}H_{25}FeP$ calcd 496.10378, found 496.10335.

Major isomer: ^1H NMR (600 MHz) δ 4.02 (1H, m, Cp_{sub}), 4.10 (5H, s, Cp_{unsub}), 4.64 (1H, t, *J* = 2.5, Cp_{sub}), 5.10 (1H, m, Cp_{sub}), 6.97 (1H, dd, *J* = 5.5, 1.0, IndC*H*), 7.04 (1H, d, *J* = 5.5, IndC*H*), 7.12–7.70 (17H, m, PPh_2 and IndC*H* and CpC*H*); ^{13}C NMR (150 MHz) δ 70.9 (CH), 71.0 (CH), 72.4 (CH), 73.9 (CH), 79.9 (C), 86.2 (C), aromatic region is ambiguous, therefore could not be assigned; ^{31}P NMR (162 MHz) δ −22.6.

Minor isomer: ^1H NMR (600 MHz) δ 4.04 (1H, m, Cp_{sub}), 4.11 (5H, s, Cp_{unsub}), 4.59 (1H, t, *J* = 2.5, Cp_{sub}), 5.11 (1H, m, Cp_{sub}), 6.53 (1H, d, *J* = 5.3, IndC*H*), 6.74 (1H, d, *J* = 5.3, IndC*H*), 7.12–7.70 (17H, m, PPh_2 and IndC*H* and CpC*H*); ^{13}C NMR (150 MHz) δ 70.9 (CH), 71.1 (CH), 72.0 (CH), 73.6 (CH), 80.5 (C), 86.8 (C), aromatic region is ambiguous, therefore could not be assigned; ^{31}P NMR (162 MHz) δ −21.6.

4.2.23. (*pS*)-1-(Diphenylphosphino)-2-((2,3,4,5-tetramethylcyclopenta-2,4-dienylidene)methyl)-ferrocene 33

Starting from TMCp (61 mg, 0.50 mmol) and following the same procedure as reported for **31** (reflux for 16 h) the title compound was obtained as an orange solid (170 mg, 68%). Mp 95–97 °C; R_f = 0.70 (5% EtOAc/Pet. ether); $[\alpha]_D^{25}$ = +1891 (*c* 0.10, $CHCl_3$); IR υ_{max} 2912, 1615, 1432, 1200, 1165, 1106 cm^{-1}; ^1H NMR

(600 MHz) δ 1.82 (3H, s, CH_3), 1.84 (3H, s, CH_3), 1.92 (3H, s, CH_3), 2.01 (3H, s, CH_3), 3.92 (1H, m, Cp_{sub}), 4.08 (5H, s, Cp_{unsub}), 4.45 (1H, t, J = 2.4, Cp_{sub}), 4.80 (1H, m, Cp_{sub}), 7.12 (2H, m, PPh_2), 7.19 (3H, m, PPh_2), 7.21 (1H, s, CpC*H*), 7.41 (3H, m, PPh_2), 7.58 (2H, m, PPh_2); ^{13}C NMR (150 MHz) δ 10.1 (CH_3), 11.4 (CH_3), 11.5 (CH_3), 13.9 (CH_3), 70.3 (CH), 70.6 (CH), 73.2 (CH), 73.2 (CH), 80.0 (C), 87.7 (C), 122.0 (C), 126.0 (C), 127.9 (CH), 128.2 (CH), 128.2 (CH), 128.3 (CH), 129.3 (CH), 132.2 (CH), 135.2 (CH), 135.6 (C), 137.6 (C), 139.6 (C), 141.3 (C), 145.5 (C); ^{31}P NMR (162 MHz) δ −23.0; m/z (EI) 503 (5%, M+H), 502 (11%, M); HRMS $C_{32}H_{31}FeP$ calcd 502.15071, found 502.15011.

4.2.24. (*pS*)-1-(Diphenylphosphino)-2-((2,3,4,5-tetraphenylcyclopenta-2,4-dienylidene)methyl)-ferrocene 34

Starting from TPCp[44] (185 mg, 0.50 mmol) and following the same procedure as reported for **31** (reflux for 72 h) the title compound was obtained as a red solid (159 mg, 42%). Mp 124–126 °C; R_f = 0.52 (10% EtOAc/Pet. ether); $[\alpha]_D^{25} = +2625$ (c 0.02, $CHCl_3$); IR υ_{max} 3055, 1592, 1484, 1434, 1235, 1216, 1165, 1106 cm^{-1}; ^{1}H NMR (600 MHz) δ 3.79 (1H, br, Cp_{sub}), 3.86 (1H, br, Cp_{sub}), 4.03 (1H, br, Cp_{sub}), 4.04 (5H, s, Cp_{unsub}), 6.79–7.05 (15H, m, Ar*H*), 7.22–7.25 (4H, m, Ar*H*), 7.31–7.36 (9H, m, Ar*H*), 7.46–7.48 (2H, m, ArH), 7.58 (1H, s, CpC*H*); ^{13}C NMR (150 MHz) δ 70.6 (CH), 71.3 (CH), 72.8 (CH), 74.1 (CH), 82.0 (C), 86.3 (C), 125.8 (CH), 126.0 (CH), 126.1 (CH), 126.5 (CH), 127.2 (CH), 127.3 (CH), 127.5 (CH), 127.7 (CH), 127.9 (CH), 128.2 (CH), 128.2 (CH), 128.5 (CH), 129.2 (CH), 130.4 (CH), 130.6 (CH), 131.1 (C), 131.8 (CH), 132.9 (CH), 134.8 (CH), 135.8 (C), 135.9 (C), 135.9 (C), 136.2 (C), 137.3 (C), 137.6 (C), 139.4 (C), 139.8 (C), 141.0 (CH), 141.1 (CH), 142.1 (C), 144.3 (C); ^{31}P NMR (121 MHz) δ −23.7; m/z (EI) 503 (5%, M+H), 502 (11%, M); HRMS $C_{32}H_{31}FeP$ calcd 446.08813, found 446.08852.

4.2.25. (±)-4-(Methoxymethyl)-2-[α-(*N*,*N*-dimethyl)-ferrocenyl]-1,3-dioxane 36

To a suspension of **35**[40] (300 mg, 0.91 mmol) and paraformaldehyde (272 mg, 9.06 mmol) in MeCN (15 mL), $NaBH_3CN$ (85.0 mg, 1.36 mmol) was added and the mixture was stirred for 10 min at rt while the colour changed from orange to yellow. The suspension was concentrated in vacuo and purified by column chromatography (80% EtOAc/pet. ether) to give the title compound as a yellow solid (190 mg, 58%). Mp 81–83 °C; R_f = 0.41 (80% EtOAc/pet. ether); IR υ_{max} 3094, 2946, 2871, 2843, 2816, 2771, 1483, 1453, 1421, 1319, 1115, 1100 cm^{-1}; ^{1}H NMR (600 MHz) δ 1.51 (1H, d, J = 13.0, CH_2CH_2CH), 1.79 (1H, dd, J = 13.0, 5.0, CH_2CH_2CH), 2.64 (6H, s, N(CH_3)$_2$), 3.34 (3H, s, OCH_3), 3.35 (1H, m, CH_2OMe), 3.47 (1H, dd, J = 9.5, 6.3, CH_2OMe), 3.92 (1H, s, Cp_{sub}), 3.95 (1H, s, Cp_{sub}), 4.00 (2H, m, OC*H* and OCH_2), 4.18 (5H, s, Cp_{unsub}), 4.25 (1H, s, Cp_{sub}), 4.30 (1H, dd, J = 10.9, 4.3, OCH_2), 5.59 (1H, s, CpC*H*); ^{13}C NMR (150 MHz) δ 28.2 (CH_2), 45.6 (CH_3), 56.5 (CH), 59.3 (CH_3), 63.2 (CH), 64.0 (CH), 67.1 (CH_2), 69.3 (CH), 75.6 (CH_2), 76.0 (CH), 79.6 (C), 99.8 (CH), 112.8 (C); m/z (EI+) 360 (4%, M+H), 359 (18%, M); HRMS $C_{18}H_{25}FeNO_3$ calcd 359.11784, found 359.11792.

4.2.26. (±)-2-(*N*,*N*-Dimethyl)-formylferrocene 37

A solution of **36** (405 mg, 1.13 mmol) and pTSA.H_2O (10.0 mg, 0.06 mmol) in acetone/water (4.0 mL/4.0 mL) was refluxed for 3.5 h. Next, DCM (5 mL) was added and the mixture was washed with $NaHCO_{3(aq)}$ (1 × 2 mL), and brine (1 × 2 mL), dried over $MgSO_4$ and concentrated in vacuo. Purification was achieved using flash column chromatography (10% EtOAc/pet. ether) to give the title compound as a red oil (178 mg, 61%). R_f = 0.32 (30% EtOAc/pet. ether); IR υ_{max} 3094, 2950, 2846, 2786, 1666, 1501, 1423, 1106 cm^{-1}; ^{1}H NMR (600 MHz) δ 2.71 (6H, s, N(CH_3)$_2$), 4.29 (6H, s, Cp_{sub} and Cp_{unsub}), 4.42 (1H, app s, Cp_{sub}), 4.63 (1H, app s, Cp_{sub}), 10.15 (1H, s, C*H*O); ^{13}C NMR (150 MHz) δ 45.8 (CH_3), 60.4 (CH), 66.4 (CH), 68.0 (CH), 69.7 (CH), 72.0 (C), 117.7 (C), 193.0 (C); m/z (EI+) 258 (14%, M+H), 257 (100%, M), 186 (22%, M–CHO–NMe_2), 121 (M–CHO–NMe_2–Cp); HRMS $C_{13}H_{15}FeNO$ calcd 257.04976, found 257.04910.

4.2.27. (±)-1-(*N*,*N*-Dimethyl)-2-[(cyclopenta-2,4-dienylidene)-methyl]-ferrocene 38

A solution of **37** (120 mg, 0.47 mmol) in MeOH (20 mL) was treated with pyrrolidine (0.08 mL, 0.93 mmol) and freshly cracked cyclopentadiene (0.02 mL, 1.86 mmol) and the reaction was stirred for 30 min. The mixture was concentrated in vacuo and purified by flash column chromatography (DCM) to give the title compound as a deep-purple-red oil (86.0 mg, 61%). R_f = 0.31 (DCM); IR υ_{max} 3096, 2943, 2821, 2778, 1621, 1609, 1484, 1451, 1431, 1106 cm^{-1}; ^{1}H NMR (600 MHz) δ 2.65 (6H, s, N(CH_3)$_2$), 4.18 (5H, s, Cp_{unsub}), 4.26 (1H, dd, J = 2.6, 1.3, Cp_{sub}), 4.38 (1H, t, J = 2.7, Cp_{sub}), 4.66 (1H, dd, J = 2.5, 1.1, Cp_{sub}), 6.36 (1H, dt, J = 5.0, 1.7, Fulv), 6.50 (1H, dt, J = 5.0, 1.5, Fulv), 6.61 (1H, ddd, J = 5.1, 1.7, 1.5, Fulv), 6.65 (1H, dm, J = 5.2, Fulv), 7.37 (1H, s, CpC*H*); ^{13}C NMR (150 MHz) δ 46.2 (CH_3), 58.0 (CH), 65.4 (CH), 66.7 (CH), 70.4 (CH), 76.0 (C), 117.4 (C), 120.0 (CH), 126.7 (CH), 128.7 (CH), 132.8 (CH), 138.4 (CH), 141.1(C); m/z (EI+) 306 (4%, M+H), 305 (15%, M); HRMS $C_{18}H_{19}FeN$ calcd 305.08614, found 305.08703.

4.2.28. (±)-1-(Dimethylamino)-2-[(cyclopenta-1,3-dienyl)methyl]-ferrocene 39

A solution of **38** (70.0 mg, 0.23 mmol) in THF (15 mL) was treated with $LiAlH_4$ (0.14 mL, 0.28 mmol, 2 M in THF) and the reaction was stirred for 3 h. Water (10 mL) was then added to the mixture at 0 °C and the mixture was extracted with diethyl ether (2 × 15 mL). The combined organics were dried over $MgSO_4$, concentrated in vacuo and purified by flash column chromatography (1% EtOAc/DCM) to give the title compound as a yellow solid (49.0 mg, 70%) which consisted of 2 inseparable isomers in a 55/45 ratio. Mp 52–54 °C, R_f = 0.17 (1% EtOAc/DCM); IR (solid) υ_{max} 3093, 2890, 2826, 2785, 1604, 1490, 1417, 1101 cm^{-1};

Major isomer: ^{1}H NMR (600 MHz) δ 2.57 (6H, s, N(CH_3)$_2$), 2.92 (2H, s, Cp′CH_2), 3.51 (1H, d, J = 16.5, CpCH_2Cp′), 3.70 (1H, d, J = 16.7, CpCH_2Cp′), 3.89 (1H, m, Cp_{sub}), 3.92 (1H, m, Cp_{sub}), 3.96 (1H, m, Cp_{sub}), 4.14 (5H, m, Cp_{unsub}), 6.09 (1H, s, Cp′C*H*), 6.25 (1H, d, J = 4.7, Cp′C*H*), 6.39 (1H, d, J = 3.8, Cp′C*H*); ^{13}C NMR (150 MHz) δ 30.0 (CH_2), 43.7 (CH_2), 45.4 (CH_3), 56.0 (CH), 62.2 (CH), 66.9 (CH), 69.0 (Cp_{unsub}), 80.3 (C), 112.6 (C), 127.4 (CH), 130.9 (CH), 132.4 (CH), 149.1 (C).

Minor isomer: ^{1}H NMR (600 MHz) δ 2.58 (6H, s, N(CH_3)$_2$), 2.95 (2H, s, Cp′CH_2), 3.49 (1H, d, J = 16.1, CpCH_2Cp′), 3.62 (1H, d, J = 16.4, CpCH_2Cp′), 3.89 (1H, m, Cp_{sub}), 3.92 (1H, m, Cp_{sub}), 3.96 (1H, m, Cp_{sub}), 4.14 (5H, m, Cp_{unsub}), 5.96 (1H, s, Cp′C*H*), 6.42 (1H, d, J = 4.4, Cp′C*H*), 6.50 (1H, d, J = 4.2, Cp′C*H*); ^{13}C NMR (150 MHz) δ 29.1 (CH_2), 41.3 (CH_2), 45.4 (CH_3), 56.1 (CH), 62.1 (CH), 66.8 (CH), 68.9 (CH), 79.8 (C), 112.6 (C), 127.0 (CH), 133.8 (CH), 134.9 (CH), 146.4 (C); m/z (EI+) 308 (23%, M+H), 307 (100%, M), 242 (M−Cp), 199 (M−Cp−NMe_2); HRMS $C_{18}H_{21}FeN$ calcd 307.10179, found 307.10158; Anal. Calcd For $C_{18}H_{21}FeN$: C, 70.34; H, 6.89; N, 4.56. Found: C, 70.21; H, 6.88; N, 4.49%.

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