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New chiral phosphorus-containing dendrimers with ferrocenes on the periphery

Cédric-Olivier Turrin, Jérome Chiffre, Jean-Claude Daran, Dominique de Montauzon, Anne-Marie Caminade,* Eric Manoury,* Gilbert Balavoine* and Jean-Pierre Majoral*

Laboratoire de Chimie de Coordination, CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

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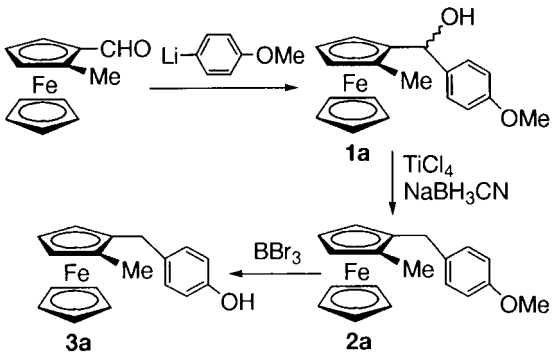
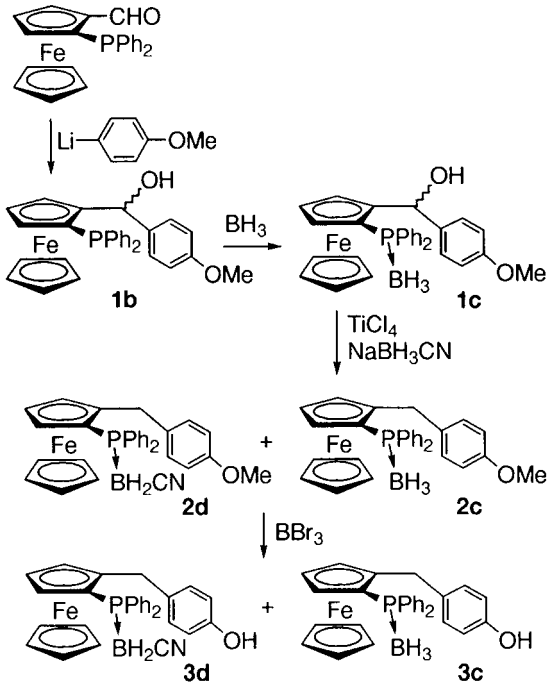
Abstract—Four series of new chiral ferrocenyl dendrimers (up to the 11th generation) have been synthesised and fully characterised. Electrochemical studies have been carried out on these dendrimers. In every case, one single oxidation wave has been observed, corresponding to the independent oxidation of all the ferrocene groups to ferrocenium. The chiroptical properties of the different dendrimers have been studied: the molar rotation depends only on the number of stereogenic units, independently of the generation in all series of dendrimers.

1. Introduction

In the last decade, dendrimers[1] have generated tremendous interest in various fields of science and technology owing to their precisely defined nanoscale molecular structure. Amongst them, the enantiomerically pure chiral dendrimers[2] are of a particular interest, not only for fundamental stereochemistry but also for their various potential applications (clathration,[3] asymmetric catalysis,[4] etc). The chiroptical properties of many chiral dendrimers, with elements of chirality in the core, in the branches or in the periphery, have been extensively studied[5–16] because they give a unique insight on the existence of conformational substructures. In most cases, the specific rotation is roughly proportional to the number of stereogenic units indicating independent and conformationally free branches within the dendrimer.[5–12] However, during studies of various chiral triol built-up dendrimers, Seebach et al. observed a reversal of the sign of the specific rotation on going from the first to the second generation in one series, or from the second to the third in another series, which might be due to



Scheme 1. Synthesis of the ferrocene derivative **3a**.



Scheme 2. Synthesis of the mixture of ferrocene derivatives **3c** and **3d**.

Keywords: dendrimer; ferrocene; chirality; phosphorus.
* Corresponding authors. Present address for G. B.: CNRS/CLORA, 47 rue Montoyer, 1000 Brussels, Belgium. Tel.: +25068842; fax: +25058845; e-mail: caminade@lcc-toulouse.fr; manoury@lcc-toulouse.fr; balavoin@lcc-toulouse.fr; majoral@lcc-toulouse.fr

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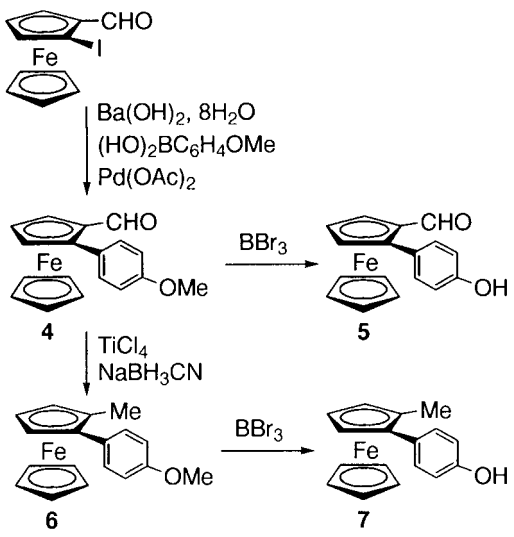


Scheme 3. Synthesis of the ferrocene derivatives **5** and **7**.

conformational secondary structures within the branches.[13] Furthermore, Meijer et al. disclosed that all the aminoacid terminated dendrimers they studied showed a dramatic decrease of their rotatory power down to almost zero going from the first to the fifth generation.[14] This behaviour is probably due to frozen-in conformations because of H-bonds network within the densely packed surface. Recently, Brandi et al. disclosed that in a series of enantiomerically pure dendrimers based on 3,4-dihydroxypyrrolidine, the contribution of each stereogenic subunit to the overall specific rotation decreased significantly from generation zero to generation one, suggesting again a conformational organisation of the branches.[15] A highly congested dendrimer with a stereogenic core shows also a decrease by a factor 2 of the molar rotation from generation zero to generation two.[16]

Recently, we disclosed an efficient synthesis of phosphorus dendrimers bearing a layer of ferrocenes on the periphery.[17] In order to test the possibility of secondary structure for densely packed dendrimers, especially the biggest ones, we synthesised and studied phosphorus dendrimers in which each ferrocenyl unit introduced in the periphery bears a controlled planar chirality.

2. Results and discussion

In order to graft them on the surface of phosphorus dendrimers, a series of enantiomerically pure ferrocenyl compounds bearing a phenol group has been synthesised. The required planar chirality is introduced using Kagan's method.[18] The phenol part and the ferrocenyl part are bound either directly or through a methylene link. The methylene links are obtained by action of 4-lithioanisole on various ferrocenecarboxaldehydes to yield the corresponding

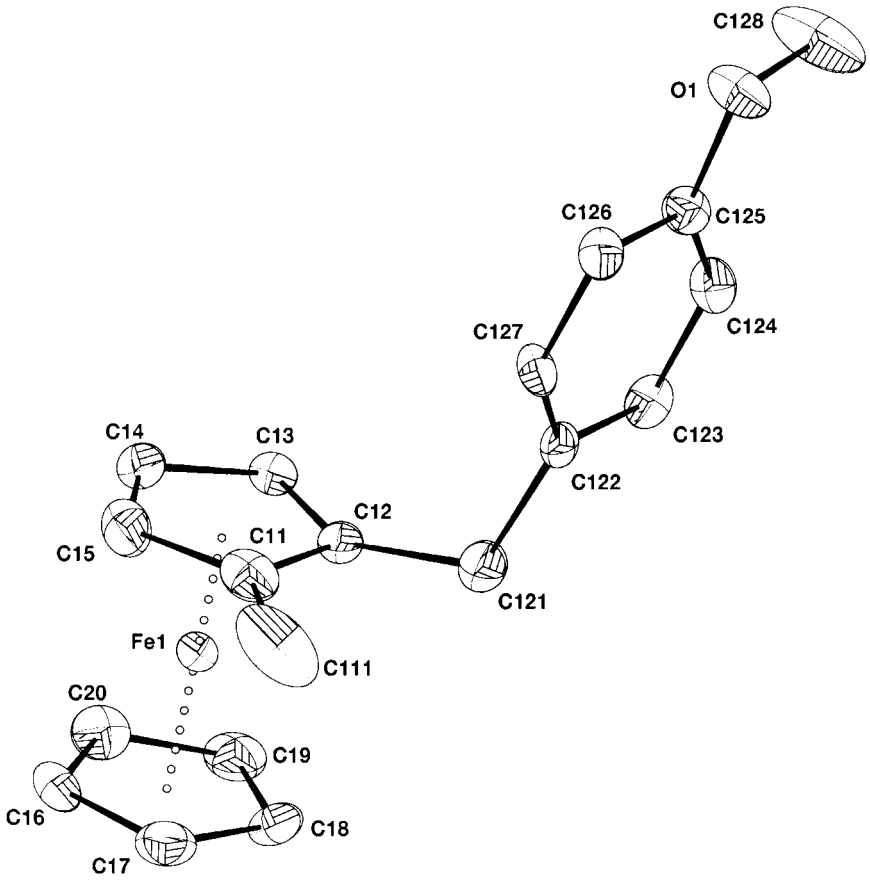


Figure 1. Molecular view of compound **2a** (Molecule **A**). Ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): C(11)–C(111) 1.507(6), C(12)–C(121) 1.501(5), C(121)–C(122) 1.513(4), C(125)–O(1) 1.369(4), O(1)–C(128) 1.415(5), C(12)–C(121)–C(122) 112.4(3), C(125)–O(1)–C(128) 116.1(3).

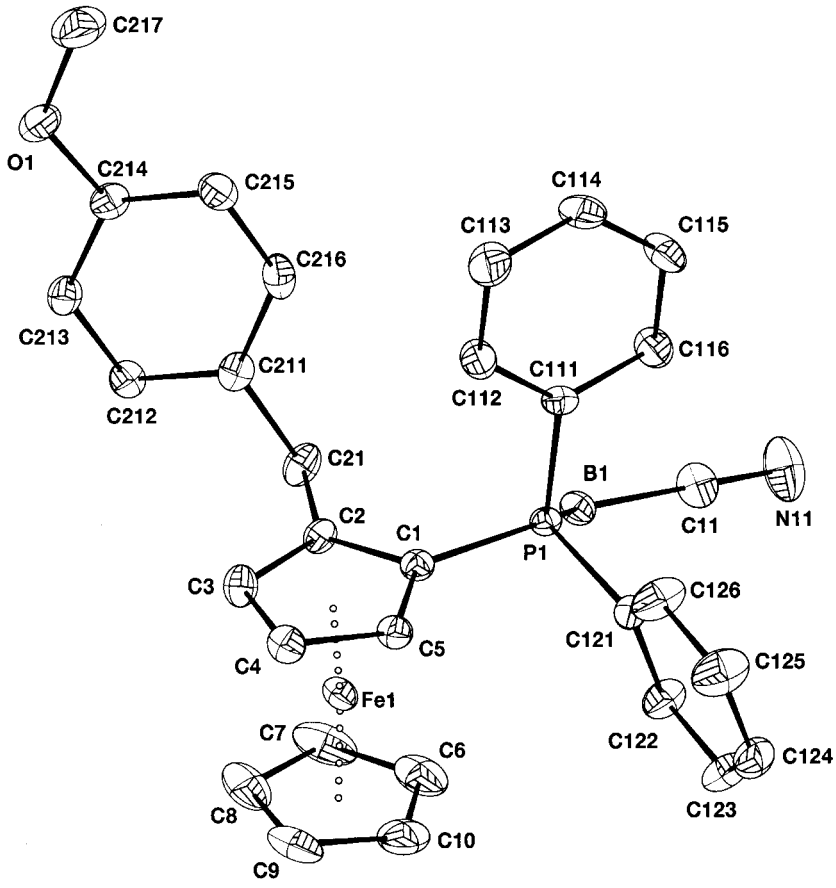


Figure 2. Molecular view of compound **2d**. Ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–P(1) 1.788(2), P(1)–B(1) 1.946(2), P(1)–C(111) 1.810(1), P(1)–C(121) 1.808(2), B(1)–C(11) 1.576(2), C(11)–N(11) 1.144(2), C(2)–C(211) 1.511(2), C(21)–C(211) 1.517(2), C(214)–O(1) 1.368(2), O(1)–C(217) 1.414(2); C(1)–P(1)–B(1) 114.87(7), C(1)–P(1)–C(111) 105.62(7), C(1)–P(1)–C(121) 105.22(7), B(1)–P(1)–C(111) 112.27(7), B(1)–P(1)–C(121) 112.20(7), P(1)–B(1)–C(11) 110.2(1), B(1)–C(11)–N(11) 177.3(2), C(2)–C(21)–C(211) 113.4(1), C(214)–O(1)–C(217) 118.4(1).

secondary alcohols. These alcohols **1** are reduced by $TiCl_4/NaBH_3CN$ to obtain ferrocenylarylmethane in high yields.[19] Finally, the free phenol function can be obtained by action of BBr_3 on the methoxy group (see Schemes 1 and 2).[20]

A Suzuki coupling reaction of 4-methoxyphenylboronic acid on (*S*)-2-iodoferrocenecarboxaldehyde yields enantiomerically pure **4** with a direct connection of a 4-methoxyphenyl group on the 2 position of ferrocenecarboxaldehyde (see Scheme 3). The deprotection of the phenol group (BBr_3) furnishes **5**. The formyl group of **4** can be reduced into a methyl group by action of $TiCl_4/NaBH_3CN$ before deprotection of the phenol function to yield finally **7** bearing a methyl and a 4-hydroxy group.

Crystals of compounds **2a**, **2d**, **4** and **7** suitable for X-ray structure analyses have been obtained by slow diffusion of hexane into a dichloromethane solution of the ferrocenyl derivatives. The molecular views with the atom labelling scheme are shown in Figs. 1–4. In the four compounds, the geometry of the ferrocene framework is as expected and the Fe–C and C–C distances are within the usual range found for such molecules. The absolute configuration for the four molecules was confirmed by refining the Flack's enantiopole parameter.[21]

The asymmetric unit of **2a** contains two independent molecules, which are roughly identical. Only one of these molecules is presented in Fig. 1. Compound **2d** (Fig. 2) presents a rare structural example of a PBH_2CN fragment. Indeed, to the best of our knowledge, only the structure of Ph_3PBH_2CN has been reported so far.[22] As expected, the B–C–N group is linear. In compound **4** (Fig. 3), the phenyl and the Cp ring are not coplanar, they make a dihedral angle of 53.1°. This feature may be retained in the corresponding dendrimers **13**-G_n. In compound **7**, the asymmetric unit is built from two molecules connected through a O–H···O hydrogen bonding as shown in Fig. 4. Moreover, these hydrogen bonds develop along the *b* axis making an infinite helicoidal chain.

The sodium salts of all the phenol ferrocene derivatives **3a**, **3c**–**3d**, **5**, and **7** are easily obtained by reaction with sodium hydride. The reaction of 6 equiv. of the sodium salt **3a**-Na with the first generation dendrimer **8**-G_1 proceeds at room temperature to afford dendrimer **9**-G_1 in nearly quantitative yield (Scheme 4). The reaction is monitored by ^{31}P NMR, which shows first a deshielding of the signal corresponding to the phosphorus atoms that undergo the reaction, from δ=62.8 ppm for **8**-G_1 to δ=66 ppm, indicating the intermediate formation of P(S)Cl(O–Ar) end groups. The substitution of the remaining Cl atoms by **3a**-Na induces the shielding of this signal to δ=63 ppm for **9**-G_1. The same

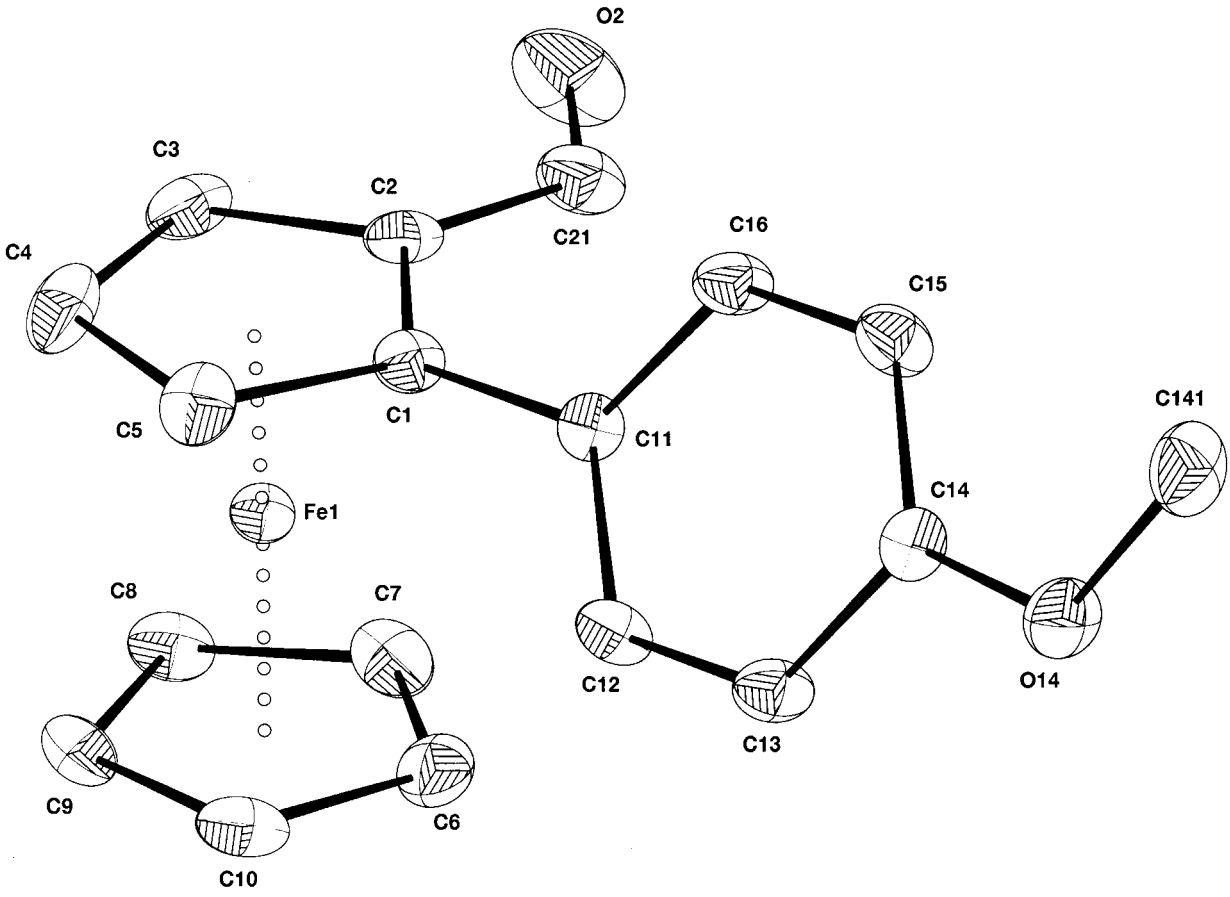


Figure 3. Molecular view of compound **4**. Ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): C(1)–C(11) 1.485(2), C(2)–C(21) 1.457(2), C(21)–O(2) 1.215(2), C(14)–O(14) 1.369(2), O(14)–C(141) 1.430(2); C(2)–C(21)–O(2) 124.0(2), C(14)–O(14)–C(141) 117.0(1).

type of reaction carried out with the third, fifth, and ninth generations of the dendrimers **8**-G_n (n=3, 5, 9) affords dendrimers **9**-G_n (n=3, 5, 9), possessing theoretically 24 (Fig. 5), 96, and 1536 ferrocenyl derivatives, respectively.

The nucleophilic substitution of the chlorine atoms of dendrimers **8**-G_n (n=3, 5, 9) also easily occurs with a mixture of the sodium salt of the phosphinoborane ferrocenes **3c**-Na and **3d**-Na (Scheme 5). However, we observe a partial decomplexation of the phosphine during the reaction. Indeed, ^{31}P NMR spectra of the crude products show the appearance of a small and thin signal at −23 ppm for the free phosphine, beside the broad signal at 8 ppm corresponding to the complexes. Furthermore, this free phosphine is easily oxidised during work-up, as shown by the appearance of a small singlet in ^{31}P NMR at δ=29 ppm. The presence of three types of end groups (Ph_2P or $Ph_2P(O)$, Ph_2PBH_3, Ph_2PBH_2CN) renders the characterisation of the expected compounds **10**-G_n (n=3, 5, 9) difficult, thus, we decided to deprotect all the phosphino groups. The deprotection occurs with an excess of DABCO, but the free phosphine appears very sensitive to air, and we could not avoid a partial oxidation during work up, characterised again by the presence of a small signal at 29 ppm in ^{31}P NMR. The presence of a small amount of this oxide did not preclude the characterisation of compounds **11**-G_n (n=3, 5, 9) by ^{31}P NMR, but we decided not to use this series of dendrimers for further characterisations or experiments.

The third series of ferrocene-containing dendrimers **12**-G_n (n=3, 5, 9) is obtained using the nucleophilic substitution of the chlorine atoms of **8**-G_n (n=3, 5, 9) by the sodium salt **5**-Na. This reaction affords dendrimers functionalised by aldehyde groups on the periphery (Scheme 5).

Finally, the reaction of the sodium salt **7**-Na with dendrimer **8**-G_n (n=5, 9, 11) affords dendrimers **13**-G_n (n=5, 9, 11) (Scheme 5). The substitution occurs without any problem, even for the 11th generation. No phenomenon of overcrowding is observed for this very high generation, as could be anticipated in view of the synthesis of the 12th generation **8**-G_{12}.[23] Even if the MALDI-Tof technique is unusable to check the purity of these dendrimers, due to the presence of hydrazone bonds,[24] the completion of all the reactions reported in this paper has been shown by multinucleus NMR, and particularly by ^{31}P NMR, whose precision is at least 1%.[25] Indeed, the signal corresponding to the phosphorus of the core (P_0) is clearly distinguishable for all fifth generations, and in several cases for the sixth generations. The ratio phosphorus of the core/phosphorus of the surface is 1/96 (fifth generation) and 1/192 (sixth generation), giving the precision of the technique. Furthermore, the purity of these dendrimers (**9**-G_n, **12**-G_n, **13**-G_n) has been checked also by size exclusion chromatography, which shows a narrow size distribution in all cases.

The electrochemical behaviour of series **9**-G_n, **12**-G_n, **13**-G_n has been studied by cyclic voltamperometry in a mixture

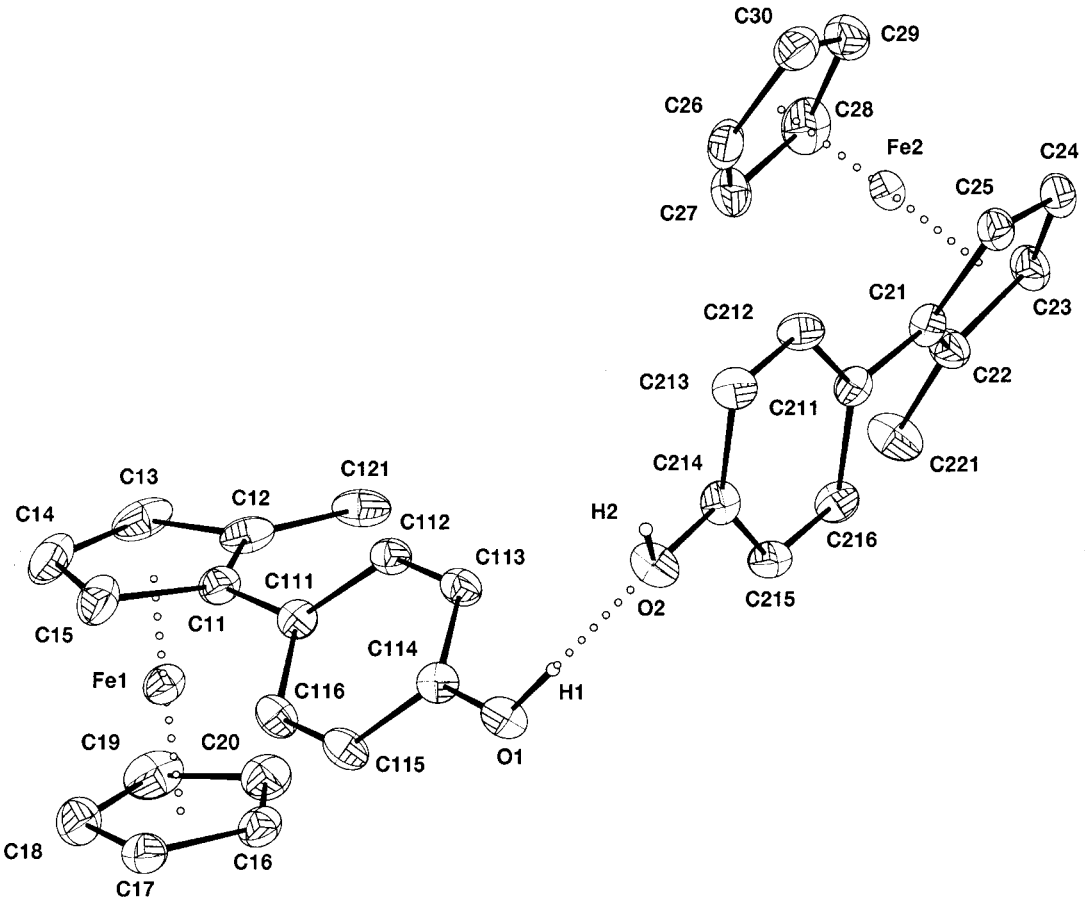
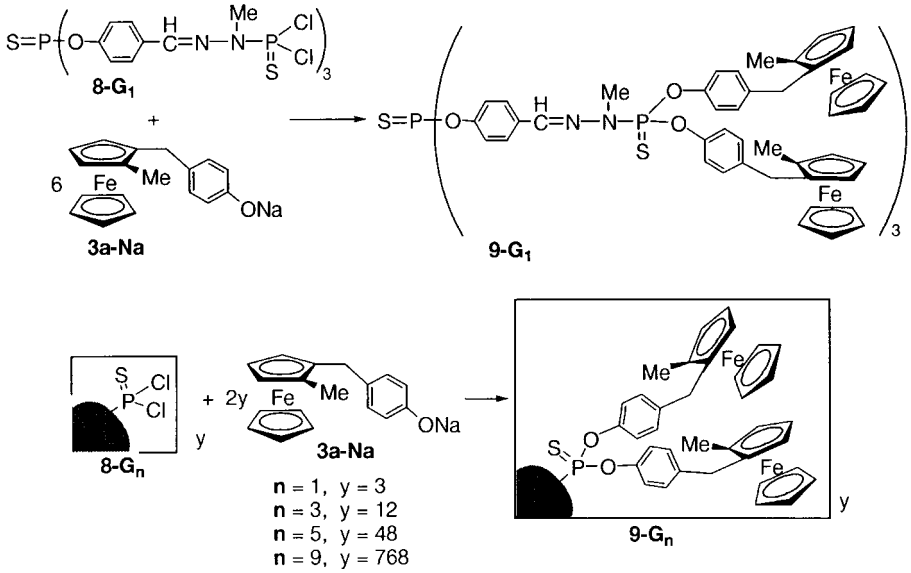


Figure 4. Molecular view of the two molecules linked by hydrogen bonding for compound **7**. Ellipsoids are shown at 50% probability level. Selected bond lengths (Å) and angles (°): C(11)–C(111) 1.473(3), C(21)–C(211) 1.471(3), C(12)–C(121) 1.486(4), C(22)–C(221) 1.497(4), C(114)–O(1) 1.380(3), C(214)–O(2) 1.389(3), O(1)–H(1) 0.85(4), H(1)···O(2) 1.84(4); O(1)–H(1)···O(2) 175(4); O(2)–H(2) 0.81(4), H(2)···O(1, $-x$, 1/2+y, 1−z) 1.88(4); O(2)–H(2)···O(1, $-x$, 1/2+y, 1−z) 169(4).

acetone/THF (1:4) as solvent, using a Pt gauze electrode. All data concerning the electrochemical behaviour of dendrimers are gathered in Table 1. In all cases, we observe the deposition of a blue conducting film onto the platinum electrode after the completion of electrolysis. These changes in solubility properties are detected on cyclic voltamperograms by the presence of a redissolution peak ($I_{pc}/I_{pa}>1$) (Table 1). It is obvious from this table that the



Scheme 4. Synthesis of the series of dendrimers **9**-G$_n$.

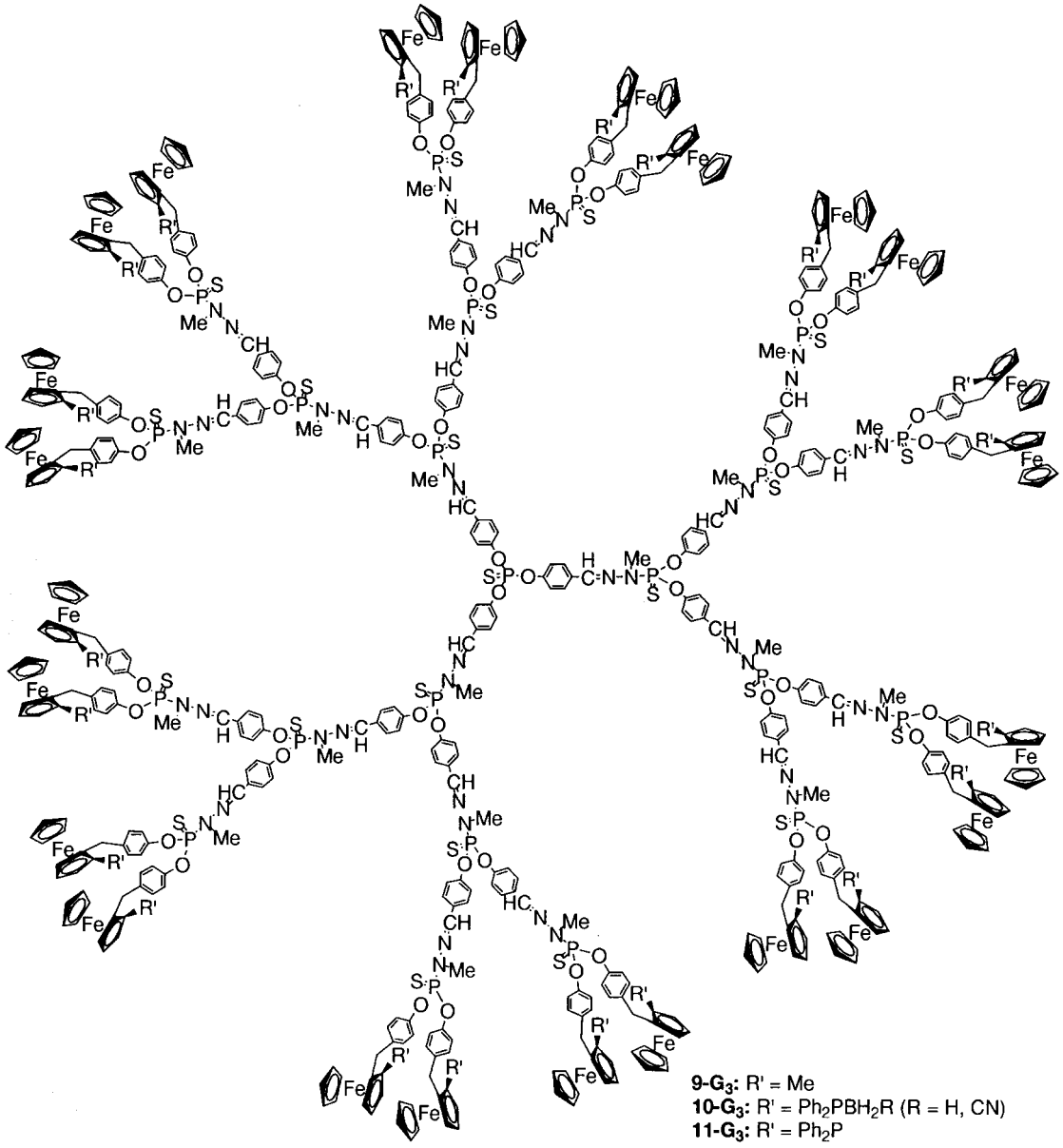
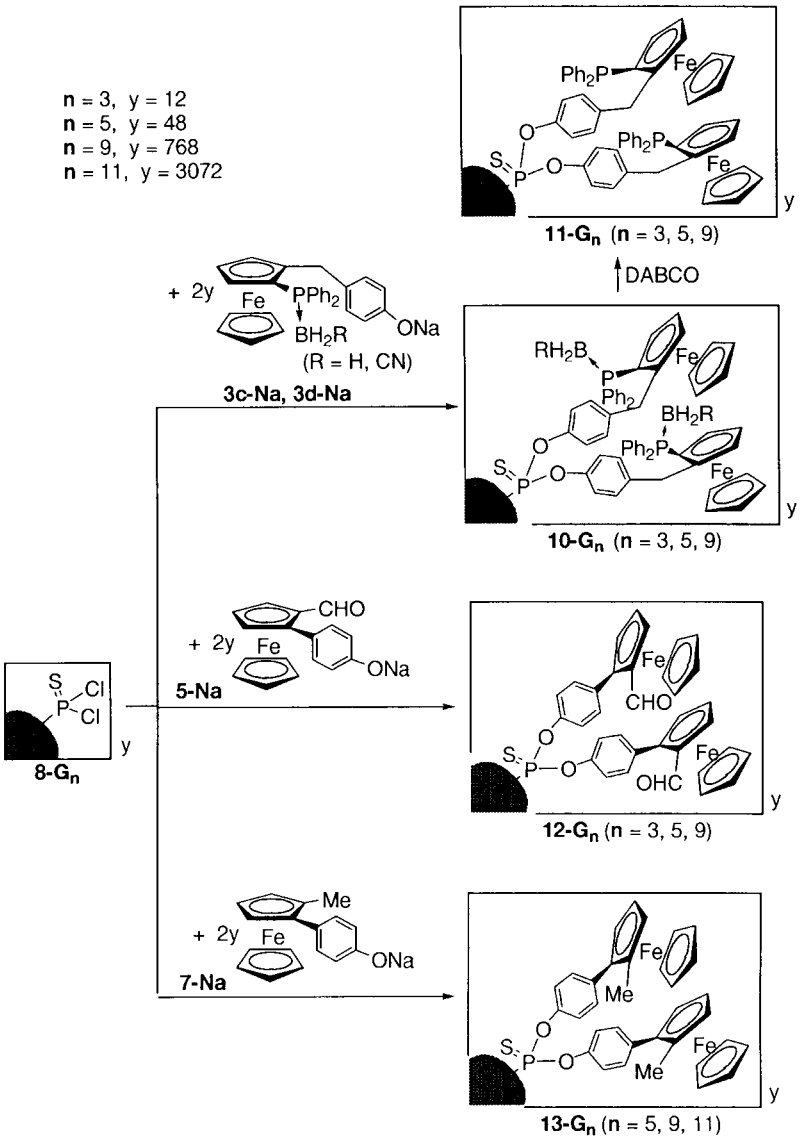


Figure 5. Various ferrocene derivatives linked to a third generation dendrimer.

generation has almost no influence on the electrochemical behaviour of each series of compounds. This trend can be emphasised with series **13**-G_n, which shows practically no difference in the values of E_{pc}, E_{pa}, and I_{pc}/I_{pa} between generations 5 and 11. Even if various ferrocene derivatives have already been linked to high generations of dendrimers, no study had been conducted previously for a generation at the limit of the dense packing. Dendrimer **13**-G_{11} is at this limit, but no overcrowding can be detected when comparing the cyclic voltamperogram of **13**-G_{11} with that of **13**-G_5, which are absolutely identical at the same concentration in ferrocene units (2.5×10^{-3} mol L^{-1}) (Fig. 6). It means that no electronic interactions between the redox centres, which could be caused by the steric hindrance, are detectable. As expected, the theoretical number of transferred electrons is never completed when measured by coulometry during exhaustive electrolysis, but the percentage of ferrocene sites oxidised is similar for **13**-G_5 (88%) and **13**-G_{11} (87%), and compares well with those found for small ferrocene derivatives such as **9**-G_1.

On the contrary to the absence of influence of the generation and consequently the number of end groups, the nature of the direct substituents of the ferrocene has a large influence on the electrochemical properties, as expected. This is obvious when comparing the data for **9**-G_5, **12**-G_5, and **13**-G_5 at the same concentration (0.24 M) (Fig. 6). The suppression of the CH_2 linkage between the ferrocene and the phenoxy group induces an increase of the oxidation potential from E_{pa}=0.49 vs SCE for **9**-G_5 to E_{pa}=0.58 vs SCE for **13**-G_5. The replacement of the methyl group by a formyl group induces a larger increase, from E_{pa}=0.58 vs SCE for **13**-G_5 to E_{pa}=0.88 vs SCE for **12**-G_5 (Table 1), a behaviour related to changes in the electronic density of the metallic centre.



Scheme 5. Synthesis of the series of dendrimers **10**-G_n, **11**-G_n, **12**-G_n, and **13**-G_n.

The chiroptical properties of dendrimers **9**-G_n, **12**-G_n, and **13**-G_n are studied in solution in THF at 20°C. The specific rotation $[\alpha]_D$ is practically constant for each series of dendrimers, even if a slight decrease is observed for the smallest generations (1–3) (Fig. 7). This decrease is only due to the diminution of the relative weight of the stereogenic part of the dendrimer, as reported previously for other stereogenic entities linked to the surface of dendrimers.[10] For instance, the relative weight of the stereogenic ferrocene moieties corresponds to 50.6% for dendrimer **9**-G_1, and only to 41.3% for dendrimer **9**-G_9. However, the main point is the constancy of the specific rotation for high generations, even for the 11th generation **13**-G_{11}. Thus, no overcrowding can be detected for this generation at the limit of the dense packing, in accordance with the remark inferred from electrochemical data (see above). On the other hand, the molar rotation $[\alpha]_{mol}$ vs generations gives an exponential curve for each three families **9**-G_n, **12**-G_n, and **13**-G_n (Fig. 8). This

Table 1.

Compound	Theoretical number of e^-	E_{pc}	E_{pa}	$E^{1/2}$	ΔE_p	I_{pc}/I_{pa}	Electrolysis (%)
9-G_1	6	0.46	0.51	0.48	0.05	1.9	90
9-G_3	24	0.44	0.49	0.47	0.05	1.9	82
9-G_5	96	0.44	0.49	0.47	0.05	1.8	83
9-G_9	1536	0.44	0.49	0.47	0.05	2.2	84
12-G_3	24	0.81	0.87	0.84	0.06	2	99
12-G_5	96	0.82	0.88	0.85	0.06	2	97
12-G_9	1536	0.82	0.88	0.85	0.06	2	85
13-G_5	96	0.52	0.58	0.54	0.06	1.7	88
13-G_9	1536	0.52	0.58	0.54	0.06	1.7	90
13-G_{11}	6144	0.52	0.57	0.53	0.05	1.7	87

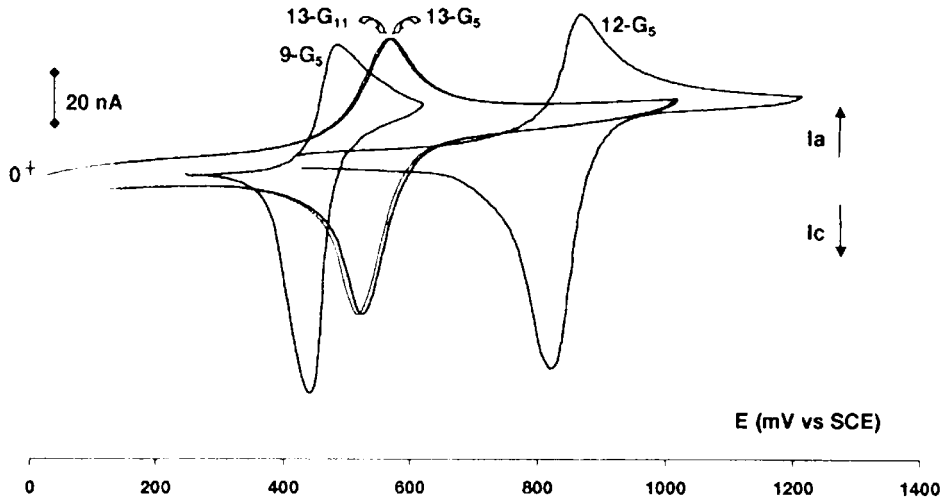


Figure 6. Cyclic voltammograms of dendrimers **9**-G_5, **12**-G_5, **13**-G_5, and **13**-G_{11}.

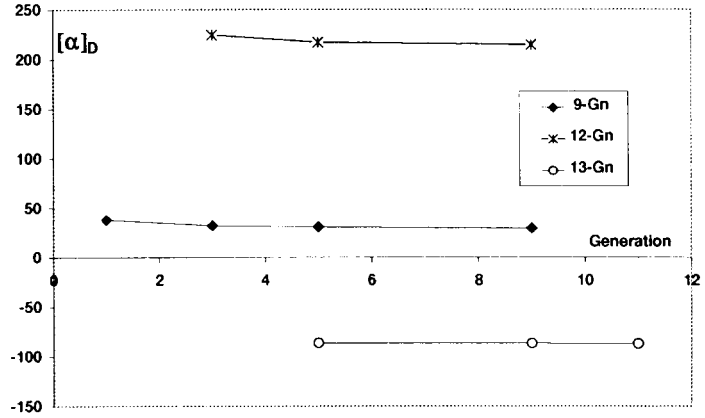


Figure 7. Specific rotation vs generation for series **9**-G_n, **12**-G_n, and **13**-G_n.

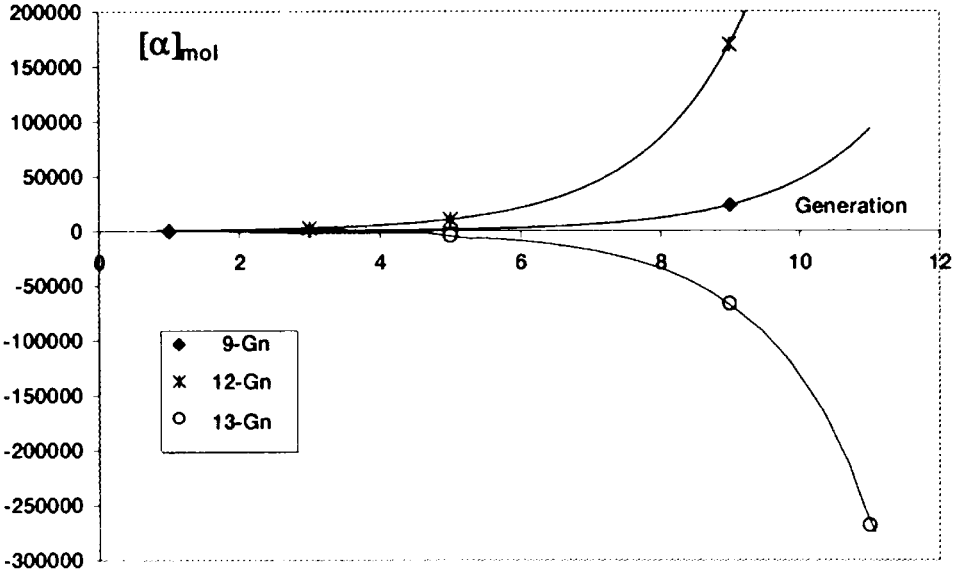


Figure 8. Molar rotation vs generation for series **9**-G_n, **12**-G_n, and **13**-G_n.

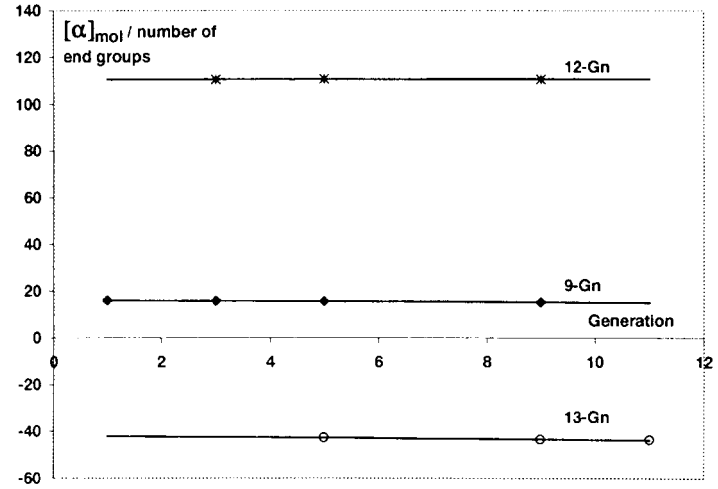


Figure 9. Molar rotation divided by the number of end groups vs generation for series **9**-G_n, **12**-G_n, and **13**-G_n.

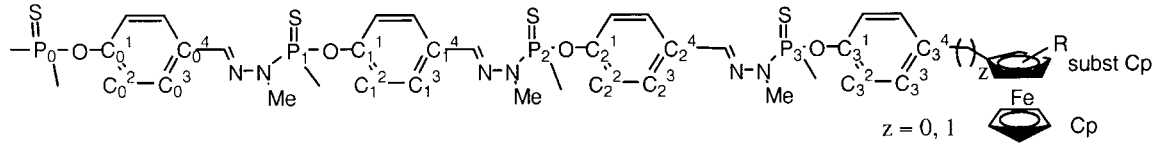


Figure 10. Numbering scheme used for NMR.

tendency reflects the exponential increase of the number of end groups. Consequently, plotting the molar rotation divided by the number of end groups vs generations gives straight lines for each series of dendrimers, corresponding to a constant value (15.8 for **9**-G_n, 110.7 for **12**-G_n, and −43.5 for **13**-G_n) (Fig. 9).

3. Conclusion

The grafting of various chiral ferrocene derivatives on phosphorus-containing dendrimers allowed us to obtain the largest dendrimers with elements of chirality on the surface described so far.[26] Electrochemical measurements carried out with three series of these dendrimers show that there is no influence of the generation on the redox properties. The analysis of the chiroptical properties of the same series of dendrimers indicates that the specific rotation slightly decreases for the small generations, but remains almost constant for the larger dendrimers. It has been shown that this behaviour is due to the diminution of the relative weight of the stereogenic moieties compared to the molecular weight. The molar rotation increases with the generation in an exponential way, as the number of end groups. Consequently, the value of the molar rotation divided by the number of end groups is a constant for each series of dendrimers; there is absolutely no influence of the generation, even for the 11th generation. Thus, no conformational secondary structure could be detected, even for this generation at the limit of the dense-packing.

4. Experimental

4.1. General

All reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried before use. Thin layer chromatography was carried out on Merck Kieselgel $60F_{254}$ precoated silica gel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 (^1H, ^{11}B, ^{13}C and ^{31}P NMR), and Stoe IPDS diffractometer (X-ray). Elemental analyses were performed by the Service d'Analyse du Laboratoire de Chimie de Coordination, Toulouse (France). $[\alpha]_D$ were measured on a PE 241 Perkin–Elmer polarimeter. The numbering used for NMR data of dendrimers is depicted Fig. 10. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR, $SiMe_4$ for ^1H and ^{13}C NMR. The assignment of ^{13}C NMR signals was carried out using J_{mod}, two-dimensional HMBC, and HMQC, Broad-Band or CW ^{31}P-decoupling experiments when necessary. Dendrimers **8**-G_n[23] were prepared according to published procedures.

4.2. Electrochemical measurements

Voltammetric and electrolytic measurements were carried out with a home-made potentiostat[27] using the interrupt method to minimise the uncompensated resistance (*Ri*) drop. Experiments were performed at room temperature in an airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted in a saturated

calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a spiral of ca. 1 cm^2 apparent surface, made of a platinum wire, 8 cm in length and 0.5 cm in diameter. The working electrode was a Pt electrode (1 mm diameter) for cycling voltammetry and a Pt gauze electrode for bulk electrolysis. $E^{1/2}$ values were determined as the average of the cathodic and the anodic peak potentials. The supporting electrolyte [nBu$_4$N][BF_4] (Fluka, electrochemical grade) was used as received.

4.3. Synthesis of alcohols and aldehydes

(*R*)-2-(methyl)ferrocenecarboxaldehyde, (*S*)-2-(diphenylphosphino)-ferrocene-carboxaldehyde and (*S*)-2-(iodo)-ferrocenecarboxaldehyde have been synthesised according to Ref. 18.

4.3.1. (*R*)-2-(methyl)-1-((4-methoxyphenyl)hydroxymethyl)-ferrocene 1a. In a Schlenk tube under argon, 4.4 mL of *p*-bromoanisole (35 mmol) were dissolved in 100 mL of anhydrous THF. After cooling down to −64°C were added 20 mL of a 1.6 M solution of *n*-BuLi in pentane (32 mmol). A white solid precipitated steadily. After 1 h stirring at −64°C, was added a solution of 2.14 g of (*R*)-2-(methyl)ferrocenecarboxaldehyde (10 mmol) in 80 mL of anhydrous THF. After 15 min at −64°C, the yellow–orange solution was allowed to come back to rt and kept 2 h at this temperature. The solution was then diluted by 100 mL of dichloromethane, washed by three 50 mL portions of water and dried on sodium sulfate. After evaporation, impure **3** was obtained as an orange oil which was purified by flash chromatography on silica gel with a pentane/ether mixture as eluent. 2.50 g of **1a** (yield=88%) as a single diastereoisomer was then isolated as a yellow–orange foam.

^{1}H NMR ($CDCl_3$) δ 7.35 (d, J=8.7 Hz, 2H, Ar), 6.93 (d, J=8.7 Hz, 2H, Ar), 5.74 (d, J=4.0 Hz, 1H, CH–O), 4.42 (m, 1H, subst Cp), 4.30 (s, 5H, Cp), 4.17 (m, 1H, subst Cp), 4.10 (t, J=2.4 Hz, 1H, subst Cp), 4.00 (d, J=4.0 Hz, 1H, OH), 3.85 (s, 3H, OCH_3), 2.02 (s, 3H, CH_3);^{13}C {^{1}H} NMR ($CDCl_3$) δ 159.0 (s, quat Ar), 137.6 (s, quat Ar), 127.9 (s, Ar), 113.4 (s, Ar), 93.1 (s, CH–O), 81.6 (s, quat Cp), 70.5 (s, quat Cp), 69.6 (s, subst Cp), 69.3 (s, Cp), 65.1 (s, subst Cp), 64.8 (s, subst Cp), 54.8 (s, OCH_3), 13.1 (s, CH_3). Anal. Calcd for $C_{19}H_{20}FeO_2$: C, 67.88; H, 6.00. Found: C, 67.70; H, 5.96. MS (DCI, NH_3) m/z 336 (M, 5%), 319 (M−17, 100%).

1b has been synthesised by a similar way starting from (*S*)-2-(diphenylphosphino)ferrocenecarboxaldehyde.

4.3.2. (*S*)-2-(diphenylphosphino)-1-((4-methoxyphenyl)-hydroxymethyl)ferrocene 1b. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent (yield=80%).

Major diastereoisomer (69%). ^{1}H NMR ($CDCl_3$) δ 7.60–7.08 (m, 10H, PPh_2), 7.33 (d, J=8.7 Hz, 2H, Ar), 6.74 (d, J=8.7 Hz, 2H, Ar), 5.77 (dd, J=4.9 Hz, J_{HP}=1.7 Hz, 1H, CH–O), 4.33 (m, 1H, subst Cp), 4.31 (t, J=2.4 Hz, 1H, subst Cp), 3.98 (s, 5H, Cp), 3.85 (dd, J=2.4 Hz, J_{HP}=1.4 Hz, 1H, subst Cp), 3.76 (s, 3H, OCH_3), 2.68 (dd, J=4.9 Hz, 1H, OH); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.5 (s, quat Ar), 139.2 (d, J_{CP}=7.3 Hz, quat PPh_2), 136.8 (d, J_{CP}=6.8 Hz, quat PPh_2), 135.4 (s, quat Ar), 135.1 (d, J_{CP}=21.1 Hz, PPh_2), 132.3 (d, J_{CP}=30.7 Hz, PPh_2), 129.3 (s, PPh_2), 128.2 (d, J_{CP}=8.1 Hz, PPh_2), 128.1 (d, J_{CP}=6.2 Hz, PPh_2), 127.9 (s, PPh_2), 127.5 (s, Ar), 113.1 (s, Ar), 97.6 (d, J_{CP}=22.3 Hz, CH–OH), 73.9 (d, J_{CP}=8.4 Hz, quat Cp), 72.1 (d, J_{CP}=6.2 Hz, subst Cp), 71.9 (d, J_{CP}=3.8 Hz, subst Cp), 71.2 (d, J_{CP}=4.4 Hz, subst Cp), 69.8 (s, Cp), 69.7 (s, quat Cp), 55.2 (s, OCH_3); ^{31}P {^{1}H} NMR ($CDCl_3$) δ −22.7. Anal. Calcd for $C_{30}H_{27}FeO_2P$: C, 71.16; H, 5.37. Found: C, 69.82; H, 5.35. MS (DCI/NH_3) m/z 507 (M+1, 100%). $[\alpha]_D$=−238 ($CHCl_3$, c=0.1).

Minor diastereoisomer (31%). ^{1}H NMR ($CDCl_3$) δ 7.70–6.70 (m, 10H, PPh_2), 7.05 (d, J=8.7 Hz, 2H, Ar), 6.51 (d, J=8.7 Hz, 2H, Ar), 5.78 (d, J=1.4 Hz, 1H, CH–O), 4.66 (m, 1H, subst Cp), 4.30 (m, 1H, subst Cp), 4.16 (s, 5H, Cp), 3.77 (m, 1H, subst Cp), 3.67 (s, 3H, OCH_3), 2.55 (t, J=1.4 Hz, 1H, OH); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.6 (s, quat Ar), 138.4 (d, J_{CP}=8.0 Hz, quat PPh_2), 136.8 (d, J_{CP}=8.0 Hz, quat PPh_2), 135.1 (d, J_{CP}=21.0 Hz, PPh_2), 134.8 (s, quat Ar), 132.2 (d, J_{CP}=18.2 Hz, PPh_2), 129.2 (s, PPh_2), 128.1 (d, J_{CP}=7.9 Hz, PPh_2), 128.0 (s, Ar), 127.7 (d, J_{CP}=6.3 Hz, PPh_2), 127.4 (s, PPh_2), 113.2 (s, Ar), 99.9 (d, J_{CP}=22.6 Hz, CH–OH), 74.6 (d, J_{CP}=8.8 Hz, quat Cp), 71.4 (d, J_{CP}=4.5 Hz, subst Cp), 70.8 (d, J_{CP}=10.5 Hz, subst Cp), 69.6 (s, Cp), 69.2 (s, subst Cp), 67.9 (d, J_{CP}=3.9 Hz, quat Cp), 55.1 (s, OCH_3); ^{31}P {^{1}H} NMR ($CDCl_3$) δ −23.0. Anal. Calcd for $C_{30}H_{27}FeO_2P$: C, 71.16; H, 5.37. Found: C, 70.78; H, 5.07. MS (DCI/NH_3) m/z 507 (M+1, 100%). $[\alpha]_D$=−112 ($CHCl_3$, c=0.1).

4.3.3. (*S*)-2-(diphenylphosphino)-1-((4-methoxyphenyl)-hydroxymethyl)ferrocene–borane adduct 1c. The two diastereoisomers of **1c** were obtained by action of 2 equiv. of BH_3·THF in THF at RT during 15 h on each diastereoisomer of **1b**. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent.

Major diastereoisomer (yield=95%). ^{1}H NMR ($CDCl_3$) δ 7.80–7.00 (m, 10H, PPh_2), 7.47 (d, J=8.7 Hz, 2H, Ar), 6.91 (d, J=8.7 Hz, 2H, Ar), 6.05 (d, J=4.5 Hz, 1H, CH–O), 4.36 (m, 1H, subst Cp), 4.31 (m, 1H, subst Cp), 4.06 (s, 5H, Cp), 3.94 (dd, J=3.8 Hz and 2.5 Hz, 1H, subst Cp), 3.84 (s, 3H, OCH_3), 3.23 (d, J=4.5 Hz, 1H, OH); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 158.9 (s, quat Ar), 134.8 (s, quat Ar), 133.4 (d, J_{CP}=9.4 Hz, quat PPh_2), 132.6 (d, J_{CP}=9.5 Hz, quat PPh_2), 131.3 (d, J_{CP}=58.1 Hz, PPh_2), 131.1 (d, J_{CP}=2.2 Hz, 2C PPh_2), 130.9 (d, J_{CP}=78.5 Hz, PPh_2), 128.5 (d, J_{CP}=10.1 Hz, PPh_2), 128.3 (d, J_{CP}=10.2 Hz, PPh_2), 127.9 (s, Ar), 113.2 (s, Ar), 96.2 (d, J_{CP}=13.8 Hz, CH–OH), 73.2 (d, J_{CP}=4.8 Hz, quat Cp), 72.4 (d, J_{CP}=7.4 Hz, subst Cp), 70.4 (d, J_{CP}=6.6 Hz, subst Cp), 70.1 (s, subst Cp), 69.7 (s, Cp), 68.0 (d, J_{CP}=64.1 Hz, quat Cp), 55.3 (s, OCH_3); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 15.3; ^{11}B {^{1}H} NMR ($CDCl_3$) δ −36.3. Anal. Calcd for $C_{30}H_{30}BFeO_2P$: C, 69.27; H, 5.81. Found: C, 69.28; H, 5.41. MS (DCI/NH_3) m/z 491 (M−29, 100%). $[\alpha]_D$=−134 ($CHCl_3$, c=0.1).

Minor diastereoisomer (yield=79%). ^{1}H NMR ($CDCl_3$) δ 7.70–7.00 (m, 10H, PPh_2), 7.04 (d, J=8.7 Hz, 2H, Ar), 6.47 (d, J=8.7 Hz, 2H, Ar), 5.99 (1H, d, J=1.9 Hz, CH–O), 4.85 (m, 1H, subst Cp), 4.41 (1H, t, J=2.6 Hz, subst Cp), 4.40 (s, 5H, Cp), 3.72 (dd, J=3.8 Hz and 2.2 Hz, 1H, subst Cp), 3.67

(s, 3H, OCH_3), 3.39 (d, J=1.9 Hz, 1H, OH). ^{13}C {^1H} NMR ($CDCl_3$) δ 158.6 (s, quat Ar), 134.5 (s, quat Ar), 133.2 (d, J_{CP}=9.5 Hz, quat PPh_2), 132.4 (d, J_{CP}=9.5 Hz, quat PPh_2), 131.0 (d, J_{CP}=2.2 Hz, PPh_2), 130.3 (d, J_{CP}=2.3 Hz, PPh_2), 130.2 (d, J_{CP}=61.0 Hz, PPh_2), 129.6 (d, J_{CP}=57.6 Hz, PPh_2), 128.3 (d, J_{CP}=10.7 Hz, PPh_2), 128.2 (s, Ar), 128.0 (d, J_{CP}=10.1 Hz, PPh_2), 113.1 (s, Ar), 98.6 (d, J_{CP}=14.0 Hz, CH–OH), 73.6 (d, J_{CP}=3.9 Hz, quat Cp), 70.4 (s, Cp), 69.9 (d, J_{CP}=6.8 Hz, subst Cp), 69.8 (d, J_{CP}=5.9 Hz, subst Cp), 69.1 (s, subst Cp), 68.0 (d, J_{CP}=64.0 Hz, quat Cp), 55.1 (s, OCH_3); ^{31}P {^1H} NMR ($CDCl_3$) δ 15.0; ^{11}B {^1H} NMR ($CDCl_3$) δ −36.5. Anal. Calcd for $C_{30}H_{30}BFeO_2P$: C, 69.27; H, 5.81. Found: C, 69.06; H, 5.16. MS (DCI/NH_3) m/z 491 (M−29, 100%). $[\alpha]_D$=−36 ($CHCl_3$, c=0.1).

4.3.4. (*R*)-2-(4-methoxyphenyl)ferrocenecarboxaldehyde 4. In a 250 mL three-necked round-bottom flask, 590 mg of (*S*)-2-iodoferrocenecarboxaldehyde (1.73 mmol) were dissolved in 20 mL of dry THF. 1.50 g of barium hydroxyde octahydrate (4.74 mmol), 370 mg of 4-methoxyphenylboric acid (5.14 mmol), 16 mL of distilled water and 5 mol% of palladium acetate were successively added. The mixture was heated up to 100°C and kept 4 h at this temperature. After cooling back to rt, the solution was diluted by 50 mL of ether, washed by 3×50 mL of brine, dried on sodium sulfate and finally evaporated. The crude material was chromatographied on silica gel with a pentane/ether mixture. 461 mg of an orange solid was obtained (yield=83%).

^1H NMR ($CDCl_3$) δ 10.17 (s, 1H, CHO), 7.57 (d, J=8.9 Hz, 2H, Ar), 6.96 (d, J=8.9 Hz, 2H, Ar), 4.90 (dd, J=1.5 and 2.6 Hz, 1H, subst Cp), 4.88 (dd, J=1.5 and 2.6 Hz, 1H, subst Cp), 4.74 (t, J=2.6 Hz, 2H, subst Cp), 4.26 (s, 5H, Cp), 3.84 (s, 3H, OCH_3); ^{13}C {^1H} NMR ($CDCl_3$) δ 192.2 (s, CHO), 159.5 (s, quat Ar), 131.2 (s, quat Ar), 128.4 (s, Ar), 114.1 (s, Ar), 92.7 (s, quat Cp), 77.3 (s, quat Cp), 74.6 (s, subst Cp), 71.3 (s, Cp), 68.6 (s, subst Cp), 55.1 (s, OCH_3). Anal. Calcd for $C_{18}H_{16}FeO_2$: C, 67.52; H, 5.04. Found: C, 67.68; H, 4.94. MS (DCI, NH_3) m/z 321 (M+1, 100%). $[\alpha]_D$=+419 ($CHCl_3$, c=0.1).

4.4. Reduction of alcohols and aldehydes

The alcohols **1a** and **1c** and the aldehyde **4** have been deoxygenated by action of sodium cyanoborohydride in presence of titanium tetrachloride.[19]

4.4.1. (*R*)-2-(methyl)-1-((4-methoxyphenyl) methyl)-ferro-cene 2a. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **2a** as an orange oil (yield=88%).

^1H NMR ($CDCl_3$) δ 7.21 (d, J=8.6 Hz, 2H, Ar), 6.93 (d, J=8.6 Hz, 2H, Ar), 4.17 (s, 5H, Cp), 4.16 (m, 1H, subst Cp), 4.13 (m, 1H, subst Cp), 4.04 (m, 1H, subst Cp), 3.85 (s, 3H, OCH_3), 3.83 (d, AB syst, J=15.1 Hz, 1H, CH_2), 3.81 (d, AB syst, J=15.1 Hz, 1H, CH_2), 2.10 (s, 3H, CH_3); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.1 (s, quat Ar), 134.1 (s, quat Ar), 129.3 (s, Ar), 113.9 (s, Ar), 87.2 (s, quat Cp), 82.3 (s, quat Cp), 69.1 (s, Cp), 68.3 (s, subst Cp), 65.1 (s, 2C subst Cp), 54.7 (s, OCH_3), 33.4 (s, CH_2), 13.0 (s, CH_3). Anal. Calcd for $C_{19}H_{20}FeO$: C, 71.27; H, 6.30. Found: C, 71.23; H, 6.38. MS (EI) m/z 320 (M, 100%). $[\alpha]_D$=+60 ($CHCl_3$, c=0.5).

After, the reduction of **1c** by $NaBH_3CN/TiCl_4$, two products have been isolated from the crude materials by flash chromatography on silica gel with a pentane/ether mixture as eluent: **2c** (48%) and **2d** (40%).

4.4.2. (*S*)-2-(diphenylphosphino)-1-((4-methoxyphenyl) methyl)ferrocene–borane adduct 2c. ^1H NMR ($CDCl_3$) δ 7.70–7.20 (m, 10H, PPh_2), 6.94 (d, J=8.6 Hz, 2H, Ar), 6.59 (d, J=8.6 Hz, 2H, Ar), 4.38 (m, 1H, subst Cp), 4.31 (t, J=2.5 Hz, 1H, subst Cp), 4.26 (s, 5H, Cp), 3.87 (d, AB syst, J=15.4 Hz, 1H, CH_2), 3.75 (d, AB syst, J=15.4 Hz, 1H, CH_2), 3.74 (m, 1H, subst Cp), 3.72 (s, 3H, OCH_3); ^{13}C {^1H} NMR ($CDCl_3$) δ 157.4 (s, quat Ar), 133.2 (d, J_{CP}=9.4 Hz, quat PPh_2), 132.6 (d, J_{CP}=9.4 Hz, quat PPh_2), 132.5 (s, quat Ar), 130.9 (d, J_{CP}=2.3 Hz, PPh_2), 130.6 (d, J_{CP}=60.6 Hz, PPh_2), 130.5 (d, J_{CP}=2.3 Hz, PPh_2), 130.4 (d, J_{CP}=57.0 Hz, PPh_2), 129.7 (s, Ar), 128.3 (d, J_{CP}=10.0 Hz, PPh_2), 128.2 (d, J_{CP}=10.0 Hz, PPh_2), 113.2 (s, Ar), 93.5 (d, J_{CP}=14.2 Hz, quat Cp), 73.5 (d, J_{CP}=7.7 Hz, subst Cp), 73.2 (d, J_{CP}=5.1 Hz, subst Cp), 70.4 (s, Cp), 69.7 (d, J_{CP}=6.5 Hz, subst Cp), 68.2 (d, J_{CP}=65.2 Hz, quat Cp), 55.1 (s, OCH_3), 33.4 (s, CH_2); ^{31}P {^1H} NMR ($CDCl_3$) δ 15.8; ^{11}B {^1H} NMR ($CDCl_3$) δ −36.5. Anal. Calcd for $C_{30}H_{30}BFeOP$: C, 71.47; H, 6.00. Found: C, 69.63; H, 6.38. MS (DCI/NH_3) m/z 522 (M+18, 100%). $[\alpha]_D$=−44 ($CHCl_3$, c=0.1).

4.4.3. (*S*)-2-(diphenylphosphino)-1-((4-methoxyphenyl) methyl)ferrocene–cyanoborane adduct 2d. ^1H NMR ($CDCl_3$) δ 7.60–7.30 (m, 10H, PPh_2), 6.94 (d, J=8.8 Hz, 2H, Ar), 6.67 (d, J=8.8 Hz, 2H, Ar), 4.42 (dd, J=2.4 and 1.9 Hz, 1H, subst Cp), 4.39 (m, 1H, subst Cp), 4.26 (s, 5H, Cp), 4.00 (dd, J=2.4 and 1.9 Hz, 1H, subst Cp), 3.75 (s, 3H, OCH_3), 3.66 (d, AB syst, J=15.7 Hz, 1H, CH_2), 3.56 (d, AB syst, J=15.7 Hz, 1H, CH_2); ^{13}C {^1H} NMR ($CDCl_3$) δ 157.8 (s, quat Ar), 133.1 (d, J_{CP}=9.4 Hz, quat PPh_2), 132.9 (d, J_{CP}=9.3 Hz, quat PPh_2), 131.9 (d, J_{CP}=2.5 Hz, PPh_2), 131.7 (d, J_{CP}=2.4 Hz, PPh_2), 131.6 (s, Ar), 129.7 (s, quat Ar), 128.8 (d, J_{CP}=8.7 Hz, PPh_2), 128.7 (d, J_{CP}=8.7 Hz, PPh_2), 127.4 (d, J_{CP}=14.6 Hz, PPh_2), 126.8 (d, J_{CP}=16.5 Hz, PPh_2), 113.4 (s, Ar), 93.0 (d, J_{CP}=12.0 Hz, quat Cp), 74.1 (d, J_{CP}=8.2 Hz, subst Cp), 73.7 (d, J_{CP}=8.8 Hz, subst Cp), 70.8 (s, Cp), 70.6 (d, J_{CP}=8.0 Hz, subst Cp), 65.4 (d, J_{CP}=72.6 Hz, quat Cp), 55.3 (s, OCH_3), 33.6 (s, CH_2); ^{31}P {^1H} NMR ($CDCl_3$) δ 10.0; ^{11}B {^1H} NMR ($CDCl_3$) δ −35.6. Anal. Calcd for $C_{31}H_{29}BFeNOP$: C, 70.36; H, 5.52; N, 2.65. Found: C, 69.29; H, 6.46; N, 2.60. MS (DCI/NH_3) m/z 547 (M+18, 57%), 530 (M+1, 8%), 491 (M−38, 100%). $[\alpha]_D$=+46 ($CHCl_3$, c=0.1).

4.4.4. (*S*)-2-methyl(4-methoxyphenyl)ferrocene 6. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **6** as an orange oil (yield=93%).

^1H NMR ($CDCl_3$) δ 7.47 (d, J=8.8 Hz, 2H, Ar), 6.88 (d, J=8.8 Hz, 2H, Ar), 4.32 (dd, J=1.5 and 2.4 Hz, 1H, subst Cp), 4.17 (t, J=2.4 Hz, 1H, subst Cp), 4.10 (m, 1H, subst Cp), 4.03 (s, 5H, Cp), 3.83 (s, 3H, OCH_3), 2.16 (s, 3H, CH_3); ^{13}C {^1H} NMR ($CDCl_3$) δ 158.1 (s, quat Ar), 131.1 (s, quat Ar), 129.9 (s, Ar), 113.6 (s, Ar), 87.0 (s, quat Cp), 81.8 (s,

quat Cp), 70.4 (s, subst Cp), 70.2 (s, Cp), 68.8 (s, subst Cp), 66.0 (s, subst Cp), 55.3 (s, OCH_3), 15.0 (s, CH_3). Anal. Calcd for $C_{18}H_{18}FeO$: C, 70.61, H, 5.93. Found: C, 71.21, H, 5.47. MS (DCI, NH_3) *m/z* 307 (M+1, 100%). $[\alpha]_D$= −524 ($CHCl_3$, *c*=0.15).

4.5. Deprotection of the phenol functions

The methoxy groups of **2a**, **2c**, **2d**, **4** and **6** have been transformed to hydroxy groups by action of boron bromide.[20]

4.5.1. (*R*)-2-(methyl)-1-((4-hydroxyphenyl) methyl)ferrocene 3a. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **3a** as a yellow oil (yield=66%).

^{1}H NMR ($CDCl_3$) δ 8.12 (s, 1H, OH), 6.99 (d, *J*=8.5 Hz, 2H, Ar), 6.71 (d, *J*=8.5 Hz, 2H, Ar), 4.04 (s, 5H, Cp), 4.01–3.99 (m, 2H, subst Cp), 3.90 (t, *J*=2.4 Hz, 1H, subst Cp), 3.70 (d, AB syst, *J*=15.2 Hz, 1H, CH_2), 3.62 (d, AB syst, *J*=15.2 Hz, 1H, CH_2), 1.97 (s, 3H, CH_3); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 155.6 (s, quat Ar), 132.9 (s, quat Ar), 129.3 (s, Ar), 115.1 (s, Ar), 87.6 (s, quat Cp), 82.5 (s, quat Cp), 69.2 (s, Cp), 68.5 (s, 2 subst Cp), 65.0 (s, subst Cp), 35.5 (s, CH_2), 13.0 (s, CH_3). Anal. Calcd for $C_{18}H_{18}FeO$: C, 70.61; H, 5.93. Found: C, 69.76; H, 6.06. MS (DCI/NH_3) *m/z* 307 (M+1, 100%).

4.5.2. (*S*)-2-(diphenylphosphino)-1-((4-hydroxyphenyl) methyl)ferrocene–borane adduct 3c. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **3c** as a yellow oil (yield=72%).

^{1}H NMR (CD_3OCD_3) δ 7.70–7.40 (m, 10H, PPh_2), 6.87 (d, *J*=8.6 Hz, 2H, Ar), 6.65 (d, *J*=8.6 Hz, 2H, Ar), 4.53 (t, *J*=2.4 Hz, 1H, subst Cp), 4.48 (m, 1H, subst Cp), 4.26 (s, 5H, Cp), 4.09 (dd, *J*=2.4 and 4.0 Hz, 1H, subst Cp), 3.68 (d, AB syst, *J*=15.6 Hz, 1H, CH_2), 3.53 (d, AB syst, *J*=15.6 Hz, 1H, CH_2), 3.20 (s, 1H, OH); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 153.9 (s, quat Ar), 134.7 (d, J_{CP}=8.7 Hz, quat PPh_2), 133.8 (d, J_{CP}=8.7 Hz, quat PPh_2), 131.8 (s, quat Ar), 131.7 (d, J_{CP}=2.4 Hz, PPh_2), 131.6 (d, J_{CP}=2.4 Hz, PPh_2), 129.9 (s, Ar), 128.51 (d, J_{CP}=3.9 Hz, PPh_2), 128.48 (d, J_{CP}=3.7 Hz, PPh_2), 126.8 (d, J_{CP}=55.9 Hz, PPh_2), 126.2 (d, J_{CP}=59.8 Hz, PPh_2), 114.9 (s, Ar), 93.7 (d, J_{CP}=11.8 Hz, quat Cp), 73.8 (d, J_{CP}=4.9 Hz, subst Cp), 73.7 (d, J_{CP}=4.7 Hz, subst Cp), 70.7 (s, Cp), 70.5 (d, J_{CP}=7.5 Hz, subst Cp), 66.2 (d, J_{CP}=68.8 Hz, quat Cp), 34.8 (s, CH_2); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 8.8; ^{11}B {^{1}H} NMR ($CDCl_3$) δ −16.1. Anal. Calcd for $C_{29}H_{28}BFeOP$: C, 71.06; H, 5.76. Found: C, 70.56; H, 5.38. MS (DCI/NH_3) *m/z* 489 (M−1, 74%), 477(M−13, 41%). $[\alpha]_D$=−55 ($CHCl_3$, *c*=0.04).

4.5.3. (*S*)-2-(diphenylphosphino)-1-((4-hydroxyphenyl) methyl)ferrocene–cyanoborane adduct 3d. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **3d** as a yellow oil (yield=59%).

^{1}H NMR ($CDCl_3$) δ 8.17 (s, 1H, OH), 7.70–7.45 (m, 10H, PPh_2), 6.89 (d, *J*=8.5 Hz, 2H, Ar), 6.64 (d, *J*=8.5 Hz, 2H, Ar), 4.58 (td, *J*=2.6 and 0.8 Hz, 1H, subst Cp), 4.52 (m, 1H, subst Cp), 4.30 (s, 5H, Cp), 4.10 (m, 1H, subst Cp), 3.69 (d, AB syst, *J*=15.6 Hz, 1H, CH_2), 3.53 (d, AB syst, *J*=15.6 Hz, 1H, CH_2); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 155.9 (s, quat Ar), 133.4 (d, J_{CP}=9.3 Hz, quat PPh_2), 133.2 (d, J_{CP}=9.3 Hz, quat PPh_2), 132.3 (d, J_{CP}=2.4 Hz, PPh_2), 132.2 (d, J_{CP}=2.5 Hz, PPh_2), 130.9 (s, Ar), 130.0 (s, quat Ar), 129.2 (d, J_{CP}=10.7 Hz, PPh_2), 129.1 (d, J_{CP}=10.7 Hz, PPh_2), 127.8 (d, J_{CP}=64.1 Hz, PPh_2), 127.6 (d, J_{CP}=65.9 Hz, PPh_2), 115.1 (s, Ar), 93.6 (d, J_{CP}=12.0 Hz, quat Cp), 74.6 (d, J_{CP}=8.2 Hz, subst Cp), 73.8 (d, J_{CP}=9.3 Hz, subst Cp), 71.2 (d, J_{CP}=8.3 Hz, subst Cp), 71.0 (s, Cp), 65.8 (d, J_{CP}=72.0 Hz, quat Cp), 33.6 (s, CH_2); ^{31}P {^{1}H} NMR ($CDCl_3$) δ 10.0; ^{11}B {^{1}H} NMR ($CDCl_3$) δ −35.6. Anal. Calcd for $C_{30}H_{27}BFeNOP$: C, 69.94; H, 5.28; N, 2.72. Found: C, 70.25; H, 5.67; N, 2.34. MS (DCI/NH_3) *m/z* 533 (M+18, 57%), 477 (M−38, 100%). $[\alpha]_D$=+16 ($CHCl_3$, *c*=0.1).

4.5.4. (*R*)-2-(4-hydroxyphenyl)ferrocenecarboxaldehyde 5. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **5** as an orange foam (yield=93%).

^{1}H NMR ($CDCl_3$) δ 10.17 (s, 1H, CHO), 8.51 (s, 1H, OH), 7.48 (d, *J*=8.7 Hz, 2H, Ar), 6.87 (d, *J*=8.7 Hz, 2H, Ar), 4.88 (dd, *J*=1.5 and 2.7 Hz, 1H, subst Cp), 4.85 (dd, *J*=2.7 and 1.5 Hz, 1H, subst Cp), 4.73 (t, *J*=2.7 Hz, 1H, subst Cp), 4.27 (s, 5H, Cp); ^{13}C {^{1}H} NMR (CD_3COCD_3) δ 192.3 (s, CHO), 157.2 (s, quat Ar), 131.2 (s, quat Ar), 127.2 (s, Ar), 115.5 (s, Ar), 93.3 (s, quat Cp), 77.3 (s, quat Cp), 74.4 (s, subst Cp), 71.8 (s, subst Cp), 71.2 (s, Cp), 68.3 (s, subst Cp). Anal. Calcd for $C_{17}H_{14}FeO_2$: C, 66.70; H, 4.60. Found: C, 66.14; H, 4.13. MS (DCI, NH_3) *m/z* 307 (M+1, 100%). $[\alpha]_D$=+431 ($CHCl_3$, *c*=0.2).

4.5.5. (*S*)-2-methyl(4-hydroxyphenyl)ferrocene 7. Purification by flash chromatography on silica gel with a pentane/ether mixture as eluent to yield **7** as a yellow oil (yield=72%).

^{1}H NMR ($CDCl_3$) δ 7.41 (d, *J*=8.7 Hz, 2H, Ar), 6.79 (d, *J*=8.7 Hz, 2H, Ar), 4.73 (s, 1H, OH), 4.30 (dd, *J*=1.5 and 2.4 Hz, 1H, subst Cp), 4.16 (m, 1H, subst Cp), 4.09 (m, 1H, subst Cp), 4.01 (s, 5H, Cp), 2.14 (s, 3H, CH_3); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 153.8 (s, quat Ar), 131.2 (s, quat Ar), 130.0 (s, Ar), 114.8 (s, Ar), 86.9 (s, quat Cp), 81.8 (s, quat Cp), 70.2 (s, subst Cp), 70.0 (s, Cp), 68.7 (s, subst Cp), 65.8 (s, subst Cp), 14.7 (s, CH_3). Anal. Calcd for $C_{17}H_{16}FeO$: C, 69.89; H, 5.52. Found: C, 69.59; H, 5.42. MS (DCI, NH_3) *m/z* 293 (M+1, 100%). $[\alpha]_D$=−133 ($CHCl_3$, *c*=0.15).

4.6. Synthesis of 9-G_n

To a solution of 250 mg of dendrimer **8**-G_n (*n*=1, 0.275 mmol; *n*=3, 0.047 mmol; *n*=5, 0.011 mmol; *n*=9, 6.6×10^{-4} mmol) in THF (10–20 mL) was added dropwise a fresh solution of sodium salt **3a**-Na (*n*=1, 590 mg (1.799 mmol); *n*=3, 405 mg (1.234 mmol); *n*=5, 374 mg (1.140 mmol); *n*=9, 366 mg (1.116 mmol)) in THF (10–20 mL). The mixture was stirred at room temperature overnight. After centrifugation, the solvent was removed in vacuum and the crude material was washed twice with 20 mL of diethylether to afford dendrimers **9**-G_n as yellow powders.

9-G_1: 92% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 53.1 (s, P_0), 63.0 (s, P_1); ^1H NMR ($CDCl_3$) δ 1.90 (s, 18H, Cp-*CH*$_3$), 3.30 (d, $^3J_{HP1}$=10.2 Hz, 9H, P_1–N–CH_3), 3.62 (d, AB syst, 1H, ^2J=15.2 Hz, CH*H*), 3.70 (d, AB syst, 1H, ^2J=15.2 Hz, C*H*H), 3.90 (br s, 12H, Cp-H), 4.00 (br s, 36H, Cp-H), 7.04–7.72 (m, 39H, Ar, CH=N); ^{13}C {^1H} NMR ($CDCl_3$) δ 13.3 (s, Cp-*CH*$_3$), 33.4 (d, $^2J_{CP1}$=13.2 Hz, P_1–N–CH_3), 33.7 (s, CH_2), 65.0 (s, subst Cp), 68.4 (s, 2 subst Cp), 69.2 (s, Cp), 82.8 (s, quat Cp), 86.1 (s, quat Cp), 121.1 (d, $^3J_{CP1}$=5.0 Hz, C_1^2), 121.5 (d, $^3J_{CP0}$=5.0 Hz, C_0^2), 128.4 (s, C_0^3), 129.1 (s, C_1^3), 132.8 (s, C_0^4), 138.0 (d, $^3J_{CP1}$=13.1 Hz, CH=N), 138.6 (s, C_1^4), 148.7 (d, $^2J_{CP1}$=7.6 Hz, C_1^1), 151.1 (d, $^2J_{CP0}$=5.2 Hz, C_0^1). Anal. Calcd for $C_{132}H_{126}Fe_6N_6O_9P_4S_4$ (2528): C, 62.72; H, 5.02; N, 3.32. Found: C, 62.68; H, 5.08; N, 3.25. $[\alpha]_D$=+38.2 (THF, *c*=1).

9-G_3. 93% yield ^{31}P {^1H} NMR ($CDCl_3$) δ 53.1 (s, P_0), 62.2 (s, P_2), 62.6 (s, P_1), 63.0 (s, P_3); ^1H NMR ($CDCl_3$) δ 1.89 (s, 72H, Cp-*CH*$_3$), 3.28 (d, $^3J_{HP1\text{-}2\text{-}3}$=10.2 Hz, 63H, $P_{1\text{-}2\text{-}3}$–N–CH_3), 3.65 (br s, 48H, CH_2), 3.91 (br s, 48H, Cp-H), 4.02 (br s, 144H, Cp-H), 7.04–7.66 (m, 201H, Ar, CH=N); ^{13}C {^1H} NMR ($CDCl_3$) δ 13.2 (s, Cp-*CH*$_3$), 32.9 (d, $^2J_{CP1\text{-}2\text{-}3}$= 12.8 Hz, $P_{1\text{-}2\text{-}3}$–N–CH_3), 33.6 (s, CH_2), 65.0 (s, subst Cp), 68.4 (s, 2 subst Cp), 69.2 (s, Cp), 82.8 (s, quat Cp), 86.1 (s, quat Cp), 120.9 (d, $^3J_{CP3}$=4.2 Hz, C_3^2), 121.7 (br s, $C_{0\text{-}1\text{-}2}^2$), 128.1 (s, $C_{0\text{-}1\text{-}2}^3$), 129.0 (s, C_3^3), 132.6 (s, $C_{0\text{-}1\text{-}2}^4$), 138.0 (br s, CH=N), 138.5 (s, C_3^4), 148.7 (d, $^2J_{CP3}$=7.1 Hz, C_3^1), 151.0 (d, $^2J_{CP0\text{-}1\text{-}2}$=7.0 Hz, $C_{0\text{-}1\text{-}2}^1$). Anal. Calcd for $C_{600}H_{576}Fe_{24}N_{42}O_{45}P_{22}S_{22}$ (11823): C, 60.96; H, 4.91; N, 4.98. Found: C, 60.79; H, 4.82; N, 5.04. $[\alpha]_D$=+32.3 (THF, *c*=0.7).

9-G_5. 96% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 52.9 (s, P_0), 62.5 (br s, $P_{1\text{-}2\text{-}3\text{-}4}$), 63.0 (br s, P_5); ^1H NMR ($CDCl_3$) δ 1.82 (s, 288H, Cp-*CH*$_3$), 3.25 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 3.62 (br s, 192H, CH_2), 3.90 (br s, 192H, Cp-H), 3.99 (br s, 576H, Cp-H), 6.89–7.65 (m, 849H, Ar, CH=N); ^{13}C {^1H} NMR ($CDCl_3$) δ 13.2 (s, Cp-*CH*$_3$), 32.9 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5}$=12.7 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 33.6 (s, CH_2), 65.0 (s, subst Cp), 68.4 (s, 2 subst Cp), 69.2 (s, Cp), 82.8 (s, quat Cp), 86.1 (s, quat Cp), 120.8 (d, $^3J_{CP5}$=4.0 Hz, C_5^2), 121.6 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}^2$), 128.1 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}^3$), 129.0 (s, C_5^3), 132.5 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}^4$), 138.1 (br s, CH=N), 138.6 (s, C_5^4), 148.7 (d, $^2J_{CP5}$=7.0 Hz, C_5^1), 151.0 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3\text{-}4}$=6.9 Hz, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}^1$). Anal. Calcd for $C_{2472}H_{2376}Fe_{96}N_{186}O_{189}P_{94}S_{94}$ (49002): C, 60.59; H, 4.89; N, 5.32. Found: C, 60.63; H, 5.00; N, 5.25. $[\alpha]_D$=+30.8 (THF, *c*=0.6).

9-G_9. 90% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 62.6 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$), 63.0 (br s, P_9), P_0 undetectable; ^1H NMR ($CDCl_3$) δ 1.81 (s, 4608H, Cp-*CH*$_3$), 3.23 (br s, 4599H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 3.63 (br s, 3072H, CH_2), 3.92 (br s, 3072H, Cp-H), 4.02 (br s, 9216H, Cp-H), 6.86–7.69 (m, 13809H, Ar, CH=N); ^{13}C {^1H} NMR ($CDCl_3$) δ 13.4 (s, Cp-*CH*$_3$), 33.1 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$=12.8 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 33.7 (s, CH_2), 65.0 (s, subst Cp), 68.4 (s, 2 subst Cp), 69.2 (s, Cp), 82.8 (s, quat Cp), 86.1 (s, quat Cp), 120.8 (bd, $^3J_{CP9}$=3.8 Hz, C_9^2), 121.6 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}^2$), 128.1 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}^3$), 129.0 (s, C_9^3), 132.5 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}^4$), 138.1 (br s, CH=N), 138.6 (s, C_9^4), 148.7 (d, $^2J_{CP9}$=7.1 Hz, C_9^1), 151.0 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$= 6.8 Hz, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}^1$). Anal. Calcd for $C_{39912}H_{38376}Fe_{1536}N_{3066}O_{3069}P_{1534}S_{1534}$ (792590): C, 60.48; H, 4.88; N, 5.42. Found: C, 60.33; H, 4.32; N, 5.44. $[\alpha]_D$= +29.7 (THF, *c*=0.7).

4.7. Synthesis of 10-G_n

To a solution of 250 mg of dendrimer **8**-G_n (*n*=5, 0.011 mmol; *n*=9, 6.6×10^{-4} mmol, *n*=11, 1.65×10^{-4} mmol) in THF (10–20 mL) was added dropwise a fresh solution of a mixture of sodium salts **3c**-Na and **3d**-Na (*n*=5.358 mg (1.140 mmol); *n*=9, 350 mg (1.116 mmol); *n*=11, 350 mg (1.116 mmol)) in THF (10–20 mL). The mixture was stirred overnight at room temperature. After centrifugation, the solvent was removed under vacuum and the crude material was washed twice with 20 mL of diethylether to afford dendrimers **10**-G_n as yellow–orange powders. A partial decomplexation of the phosphine (P_{ext}) occurred during the reaction, inducing a partial oxidation of the phosphine during the work-up (ca. 5%).

10-G_3 (impure). 91% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 9.0 (br s, P_{ext}), 29.3 (s, P_{ext} partially oxidised), 52.5 (s, P_0), 62.2 (br s, $P_{1\text{-}2\text{-}3}$); ^1H NMR ($CDCl_3$) δ 3.31 (br s, 63H, $P_{1\text{-}2\text{-}3}$–N–CH_3), 3.55 (br s, 48H, CH_2), 3.80 (s, 24H, Cp-H), 3.95 (s, 120H, Cp-H), 4.20 (s, 24H, Cp-H), 4.34 (s, 24H, Cp-H), 6.66-7.66 (m, 441H, Ar, CH=N), BH_3 undetectable.

10-G_5 (impure). 92% yield. ^{31}P {^1H} NMR ($CDCl_3$) δ 9.1 (br s, P_{ext}), 29.2 (s, P_{ext} partially oxidised), 52.9 (s, P_0), 62.5 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$); ^1H NMR ($CDCl_3$) δ 3.32 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 3.55 (br s, 192H, CH_2), 3.80 (s, 96H, Cp-H), 3.95 (s, 480H, Cp-H), 4.19 (s, 96H, Cp-H), 4.35 (s, 96H, Cp-H), 6.71–7.62 (m, 1809H, Ar, CH=N), BH_3 undetectable.

10-G_9 (impure). 92% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 9.1 (br s, P_{ext}), 29.1 (s, P_{ext} partially oxidised), 62.4 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$), P_0 undetectable; ^1H NMR ($CDCl_3$) δ 3.30 (br s, 4599H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 3.55 (br s, 3072H, CH_2), 3.82 (s, 1536H, Cp-H), 3.97 (s, 7680H, Cp-H), 4.19 (s, 1536H, Cp-H), 4.32 (s, 1536H, Cp-H), 6.73–7.65 (m, 29169H, Ar, CH=N), BH_3 undetectable.

4.8. Synthesis of 11-G_n

To a solution of 200 mg of crude dendrimer **10**-G_n (*n*=3, 0.012 mmol; *n*=5, 0.003 mmol; *n*=9, 1.85×10^{-4} mmol) in THF (15–25 mL) was added dropwise a large excess (>100%) of DABCO in THF (10–20 mL). The mixture was stirred overnight at room temperature. After filtration and centrifugation, the solvent was removed in vacuum and the crude material was washed twice with 30 mL of acetonitrile to afford dendrimers **11**-G_n as pale orange powders. In this case also, a partial oxidation of the phosphine during work-up is observed (ca. 5%).

11-G_3 (impure). 91% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ −23.1 (br s, P_{ext}), 29.3 (s, P_{ext} partially oxidised), 52.4 (s, P_0), 62.3 (br s, $P_{1\text{-}2\text{-}3}$); ^1H NMR ($CDCl_3$) δ 3.30 (br s, 63H, $P_{1\text{-}2\text{-}3}$–N–CH_3), 3.62 (br s, 48H, CH_2), 3.76 (s, 24H, Cp-H), 3.90 (s, 120H, Cp-H), 4.13 (s, 24H, Cp-H), 4.24 (s, 24H, Cp-H), 6.65–7.67 (m, 441H, Ar, CH=N).

11-G_5 (impure). 92% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ −23.1 (br s, P_{ext}), 29.1 (s, P_{ext} partially oxidised), 52.9 (s, P_0), 62.6 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$); ^1H NMR ($CDCl_3$) δ 3.30 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 3.61 (br s, 192H, CH_2), 3.76 (s, 96H, Cp-H), 3.89 (s, 480H, Cp-H), 4.11 (s, 96H, Cp-H), 4.21 (s, 96H, Cp-H), 6.70–7.65 (m, 1809H, Ar, CH=N).

11-G_9 (impure). 92% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ −23.1 (br s, P_{ext}), 29.1 (s, P_{ext} partially oxidised), 62.5 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$), P_0 undetectable; ^1H NMR ($CDCl_3$) δ 3.30 (br s, 4599H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 3.61 (br s, 3072H, CH_2), 3.78 (s, 1536H, Cp-H), 3.92 (s, 7680H, Cp-H), 4.13 (s, 1536H, Cp-H), 4.20 (s, 1536H, Cp-H), 6.73–7.65 (m, 29169H, Ar, CH=N).

4.9. Synthesis of 12-G_n

To a solution of 250 mg of dendrimer **8**-G_n (n=3, 0.047 mmol; n=5, 0.011 mmol; n=9, 6.6×10^{-4} mmol) in THF (10–20 mL) was added dropwise a fresh solution of sodium salt **5**-Na (n=3, 405 mg (1.234 mmol); n=5, 374 mg (1.140 mmol); n=9, 366 mg (1.116 mmol)) in THF (10–20 mL). The mixture was kept under stirring at room temperature overnight. After centrifugation, the solvent was removed and the crude material was washed twice with 20 mL of diethylether to afford dendrimers **12**-G_n as reddish powders.

12-G_3. 93% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 52.6 (s, P_0), 62.0 (s, P_3), 62.6 (s, P_2), 62.8 (s, P_1); ^1H NMR ($CDCl_3$) δ 3.34 (d, $^3J_{HP1\text{-}2\text{-}3}$=10.1 Hz, 63H, $P_{1\text{-}2\text{-}3}$–N–CH_3), 4.15 (s, 120H, Cp-H), 4.62 (s, 24H, Cp-H), 4.72 (s, 24H, Cp-H), 4.90 (s, 24H, Cp-H), 7.12–7.68 (m, 201H, Ar, CH=N), 10.04 (s, 24H, CHO); ^{13}C {^1H} NMR ($CDCl_3$) δ 32.9 (d, $^2J_{CP1\text{-}2\text{-}3}$=12.4 Hz, $P_{1\text{-}2\text{-}3}$–N–CH_3), 68.6 (s, subst Cp), 71.0 (s, Cp), 72.0 (s, subst Cp), 75.0 (s, subst Cp), 77.2 (s, quat Cp), 91.3 (s, quat Cp), 121.1 (d, $^3J_{CP3}$=3.0 Hz, $C_3{}^2$), 121.7 (br s, $C_{0\text{-}1\text{-}2}{}^2$), 128.2 (s, $C_{0\text{-}1\text{-}2}{}^3$), 130.6 (s, $C_3{}^3$), 132.0 (s, $C_{0\text{-}1\text{-}2}{}^4$), 133.1 (s, $C_3{}^4$), 138.8 (d, $^3J_{CP1\text{-}2\text{-}3}$=13.3 Hz, CH=N), 149.6 (d, $^2J_{CP3}$=7.0 Hz, $C_3{}^1$), 151.0 (d, $^2J_{CP0\text{-}1\text{-}2}$=6.0 Hz, $C_{0\text{-}1\text{-}2}{}^1$), 192.0 (s, CHO). IR (KBr) 1699 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{576}H_{480}Fe_{24}N_{42}O_{69}P_{22}S_{22}$ (11821): C, 58.52; H, 4.09; N, 4.98; Fe, 11.33. Found: C, 58.40; H, 4.00; N, 5.11; Fe, 11.24. $[\alpha]_D$=+224.5 (THF, c=0.1).

12-G_5. 96% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 52.6 (s, P_0), 62.0 (br s, P_5), 62.5 (br s, $P_{3\text{-}4}$), 62.7 (br s, $P_{1\text{-}2}$); ^1H NMR ($CDCl_3$) δ 3.34 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 4.13 (s, 480H, Cp-H), 4.60 (s, 96H, Cp-H), 4.71 (s, 96H, Cp-H), 4.87 (s, 96H, Cp-H), 7.12–7.65 (m, 849H, Ar, CH=N), 10.03 (s, 96H, CHO); ^{13}C {^1H} NMR ($CDCl_3$) δ 33.1 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5}$=12.8 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 68.6 (s, subst Cp), 71.0 (s, Cp), 72.0 (s, subst Cp), 75.0 (s, subst Cp), 77.2 (s, quat Cp), 91.3 (s, quat Cp), 121.1 (d, $^3J_{CP5}$=3.1 Hz, $C_5{}^2$), 121.9 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^2$), 128.3 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^3$), 130.7 (s, $C_5{}^3$), 132.2 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^4$), 133.3 (s, $C_5{}^4$), 138.9 (br s, CH=N), 149.7 (d, $^2J_{CP5}$=7.3 Hz, $C_5{}^1$), 151.3 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3\text{-}4}$=7.0 Hz, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^1$), 192.0 (s, CHO). IR (KBr) 1699 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{2376}H_{1992}Fe_{96}N_{186}O_{285}P_{94}S_{94}$ (48998): C, 58.24; H, 4.10; N, 5.32; Fe, 10.94. Found: C, 58.10; H, 3.99; N, 5.29; Fe, 1083. $[\alpha]_D$=+217.1 (THF, c=0.1).

12-G_9. 91% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 62.1 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$), 62.7 (br s, P_9), P_0 undetectable; ^1H NMR ($CDCl_3$) δ 3.35 (br s, 4599H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 3.90–4.95 (m, 12288H, Cp-H), 7.09–7.62 (m, 13809H, Ar, CH=N), 10.01 (s, 1536H, CHO); ^{13}C {^1H} NMR ($CDCl_3$) δ 33.1 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$=12.1 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 68.6 (s, subst Cp), 71.0 (s, Cp), 72.0 (s, subst Cp), 75.0 (s, subst Cp), 77.2 (s, quat Cp), 91.3 (s, quat Cp), 121.2 (br s, $C_9{}^2$), 121.9 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^2$), 128.3 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^3$), 130.7 (s, $C_9{}^3$), 132.1 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^4$), 133.3 (s, $C_9{}^4$), 139.0 (br s, CH=N), 149.0 (br s, $C_9{}^1$), 151.2 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^1$), 192.9 (s, CHO). IR (KBr) 1699 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{38376}H_{32232}Fe_{1536}N_{3066}O_{4605}P_{1534}S_{1534}$ (792524): C, 58.16; H, 4.10; N, 5.42; Fe, 10.82. Found: C, 58.09; H, 4.15; N, 5.49; Fe, 10.77. $[\alpha]_D$=+214.5 (THF, c=0.7).

4.10. Synthesis of 13-G_n

To a solution of 250 mg of dendrimer **8**-G_n (n=5, 0.011 mmol; n=9, 6.6×10^{-4} mmol, n=11, 1.65×10^{-4} mmol) in THF (10–20 mL) was added dropwise a fresh solution of sodium salt **7**-Na (n=5, 358 mg (1.140 mmol); n=9, 350 mg (1.116 mmol); n=11, 350 mg (1.116 mmol)) in THF (10–20 mL). The mixture was stirred overnight at room temperature. After centrifugation, the solvent was removed under vacuum and the crude material was washed twice with 20 mL of diethylether to afford dendrimers **13**-G_n as yellow powders.

13-G_5. 90% yield; ^{31}P {^1H} ($CDCl_3$) δ 52.9 (s, P_0), 62.2 (br s, $P_{1\text{-}2\text{-}3\text{-}4}$), 62.6 (br s, P_5); ^1H NMR ($CDCl_3$) δ 2.07 (s, 288H, Cp-CH_3), 3.32 (br s, 279H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 3.92–4.28 (m, 768H, Cp-H), 7.12–7.65 (m, 849H, Ar, CH=N); ^{13}C {^1H} NMR ($CDCl_3$) δ 14.8 (s, Cp-CH_3), 33.1 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5}$=12.3 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5}$–N–$CH_3$), 66.3 (s, subst Cp), 69.0 (s, subst Cp), 70.1 (s, Cp), 70.6 (s, subst Cp), 81.8 (s, quat Cp), 85.6 (s, quat Cp), 120.8 (d, $^3J_{CP5}$=3.7 Hz, $C_5{}^2$), 121.9 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^2$), 128.3 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^3$), 129.7 (s, $C_5{}^3$), 132.3 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^4$), 136.3 (s, $C_5{}^4$), 138.4 (br s, CH=N), 148.8 (d, $^2J_{CP5}$=7.8 Hz, $C_5{}^1$), 151.3 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3\text{-}4}$=6.0 Hz, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4}{}^1$). Anal. Calcd for $C_{2376}H_{2184}Fe_{96}N_{186}O_{189}P_{94}S_{94}$ (47655): C, 59.88; H, 4.62; N, 5.47; Fe, 11.25. Found: C, 60.01; H, 4.50; N, 5.34; Fe, 11.20. $[\alpha]_D$=−86.4 (THF, c=0.06).

13-G_9. 90% yield; ^{31}P {^1H} NMR ($CDCl_3$) δ 62.3 (br s, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$), 62.7 (br s, P_9), P_0 undetectable; ^1H NMR ($CDCl_3$) δ 2.08 (s, 4608H, Cp-CH_3), 3.35 (br s, 4599H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 3.90–4.29 (m, 12288H, Cp-H), 7.09–7.72 (m, 13809H, Ar, CH=N); ^{13}C {^1H} NMR ($CDCl_3$) δ 14.7 (s, Cp-CH_3), 33.2 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$=12.3 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9}$–N–$CH_3$), 66.3 (s, subst Cp), 69.1 (s, subst Cp), 70.2 (s, Cp), 70.5 (s, subst Cp), 81.8 (s, quat Cp), 85.6 (s, quat Cp), 120.1 (d, $^3J_{CP9}$=3.6 Hz, $C_9{}^2$), 121.9 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^2$), 128.2 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^3$), 129.8 (s, $C_9{}^3$), 132.3 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^4$), 136.2 (s, $C_9{}^4$), 138.4 (br s, CH=N), 148.8 (d, $^2J_{CP9}$=7.7 Hz, $C_9{}^1$), 151.3 (d, $^2J_{CP0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}$=6.1 Hz, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8}{}^1$). Anal. Calcd for $C_{38376}H_{35304}Fe_{1536}N_{3066}O_{3069}P_{1534}S_{1534}$ (771045): C, 59.78; H, 4.61; N, 5.57; Fe, 11.12. Found: C, 59.97; H, 5.46; N, 5.54; Fe, 11.01. $[\alpha]_D$=−86.7 (THF, c=0.03).

13-G_{11}. 92% yield, ^{31}P {^1H} NMR ($CDCl_3$) δ 62.3 (br s,

$P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10}$), 62.7 (br s, P_{11}), P_0 undetectable; ^{1}H ($CDCl_3$) NMR δ 2.08 (s, 18432H, Cp-CH_3), 3.35 (br s, 18423H, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10\text{-}11}$–N–$CH_3$), 3.90–4.29 (m, 49152H, Cp-H), 7.08–7.71 (m, 55281H, Ar, CH=N); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 14.6 (s, Cp-CH_3), 33.2 (d, $^2J_{CP1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10\text{-}11}$=12.1 Hz, $P_{1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10\text{-}11}$–N–$CH_3$), 66.2 (s, subst Cp), 69.1 (s, subst Cp), 70.2 (s, Cp), 70.6 (s, subst Cp), 81.7 (s, quat Cp), 85.6 (s, quat Cp), 120.1 (d, $^3J_{CP11}$=3.5 Hz, $C_{11}{}^2$), 122.0 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10}{}^2$), 128.3 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10}{}^3$), 129.8 (s, $C_{11}{}^3$), 132.2 (s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10}{}^4$), 136.2 (s, $C_{11}{}^4$), 138.5 (br s, CH=N), 148.7 (d, $^2J_{CP11}$=7.6 Hz, $C_{11}{}^1$), 151.3 (br s, $C_{0\text{-}1\text{-}2\text{-}3\text{-}4\text{-}5\text{-}6\text{-}7\text{-}8\text{-}9\text{-}10}{}^1$). Anal. Calcd for $C_{153576}H_{141288}Fe_{6144}N_{12282}O_{12285}P_{6142}S_{6142}$ (3085891): C, 59.77; H, 4.61; N, 5.57; Fe, 11.11. Found: C, 59.99; H, 4.58; N, 5.61; Fe, 10.98. $[\alpha]_D$=−86.9 (THF, c=0.01).

4.11. X-Ray analyses

4.11.1. Crystal data for 2a. $C_{19}H_{20}FeO$, M=320.21, monoclinic, space group $P2_1$, a=11.158(2), b=10.534(1), c=14.185(2) Å, β=112.14(2)°, Z=4, V=1544.4(4) Å^3, D_c=1.377 g cm^{-3}, Mo Kα radiation (λ=71073 Å), μ=0.970 mm^{-1}, crystal dimensions 0.58×0.15×0.05 mm^3, F(000)=673, T=160(2) K. From 15,245 reflections, 5756 were unique (R_{int}=0.0494). 4356 with $I>2\sigma$(I) were used in refinement. Data/parameters ratio 4356/381, R=0.0323, Rw=0.0335, Flack's parameter=0.00(1), S=1.074.

4.11.2. Crystal data for 2d. $C_{31}H_{29}BFeNOP$, M=529.21, monoclinic, space group $P2_1$, a=10.650(2), b=8.8219(2), c=14.436(2) Å, β=104.15(2)°, Z=2, V=1315.1(3) Å^3, D_c=1.336 g cm^{-3}, Mo Kα radiation (λ=71073 Å), μ=0.655 mm^{-1}, crystal dimensions 0.64×0.38×0.25 mm^3, F(000)=553, T=160(2) K. From 12,962 reflections, 5093 were unique (R_{int}=0.0314). 4942 with $I>2\sigma$ (I) were used in refinement. Data/parameters ratio 4942/415, R=0.0236, Rw=0.0280, Flack's parameter=0.00(1), S=1.067.

4.11.3. Crystal data for 4. $C_{18}H_{16}FeO_2$, M=320.17, orthorhombic, space group $P2_12_12_1$, a=9.357(1), b=9.700(1), c=15.568(2) Å, Z=4, V=1413.1(5) Å^3, D_c=1.504 g cm^{-3}, Mo Kα radiation (λ=71073 Å), μ=1.065 mm^{-1}, crystal dimensions 0.75×0.23×0.23 mm^3, F(000)=665, T=180(2) K. From 17,060 reflections, 3426 were unique (R_{int}=0.035). 3317 with $I>2\sigma$ (I) were used in refinement. Data/parameters ratio 3317/241, R=0.0206, Rw=0.0238, *Flack*'s *parameter*=0.00(9), S=1.023.

4.11.4. Crystal data for 7. $C_{17}H_{16}FeO$, M=292.16, monoclinic, space group $P2_1$, a=11.717(2), b=7.4206(8), c=15.452(3) Å, β=95.30(2)°, Z=4, V=1337.8(6) Å^3, D_c=1.450 g cm^{-3}, Mo Kα radiation (λ=71073 Å), μ=1.113 mm^{-1}, crystal dimensions 1.28×0.44×0.06 mm^3, F(000)=609, T=160(2) K. From 13,060 reflections, 5173 were unique (R_{int}=0.0481). 4622 with $I>2\sigma$ (I) were used in refinement. Data/parameters ratio 4622/370, R=0.0276, Rw=0.0309, Flack's parameter=0.00(1), S=1.052.

For the four compounds, the data were collected on a Stoe IPDS diffractometer. The structures were solved by direct methods (SIR97)[28] and refined by full matrix least-squares on F (CRYSTALS).[29] The molecular views were realised using CAMERON.[30]

Crystal and data collection parameters, relevant structure refinement parameters, atomic coordinates for the non-hydrogen atoms, positional and isotropic displacement coefficients for hydrogen atoms, a list of anisotropic displacement coefficients for the non-hydrogen atoms and a full list of bond distances and bond angles have been deposited with the Cambridge Crystallographic Data Centre.

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