# Iron(II) and zinc(II) monohelical binaphthyl-salen complexes with overlapping benz[*a*]anthryl sidearms†

**Alexander V. Wiznycia, John Desper and Christopher J. Levy***

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The synthesis of the polyaromatic aldehyde 1-hydroxybenz[*a*]anthracene-2-carboxaldehyde is reported *via* a seven step protocol from 9,10-dihydroanthracene, with an overall yield of 30%. Two equivalents of the aldehyde are condensed with (*R*)-1,1′-binaphthyl-2,2′-diamine to produce a new binaphthyl-salen ligand, which is subsequently complexed to iron(II) and zinc(II) ions. The ligand and complexes are characterized by single-crystal X-ray crystallography. The complexes have distinct helical structures with overlapping benz[*a*]anthryl sidearms, and only *M*-helices are observed. The ligand and complexes are further characterized by solution $^{1}$H and $^{13}$C NMR spectroscopy as well as UV-visible and ECD spectroscopies. These studies indicate that there is a single component in solution, consistent with the solid state characterization.

## Introduction

The helix is one of the most important chiral motifs in natural systems and there is an increasing interest in the development of helical transition metal complexes and related supramolecular helical structures.[1] There is an extensive literature concerning complexes with two or more metal centers, but mononuclear helical complexes (monohelices) have received considerably less attention. We are particularly interested in monohelices formed by wrapping a single multidentate chiral ligand around a metal center. The high asymmetry of monohelical complexes make them attractive candidates as asymmetric catalysts, as has been explored in several studies.[2]

Monohelices can be difficult to prepare, since multidentate ligands often prefer to bridge metal centers and produce helicates. The preference derives from the exact geometric relationship between the donor atoms and the flexibility of the spacers between them.[3] If the donors can orient themselves to form strong binding interactions with a single metal and if the ligand is pliable enough to allow for wrapping without strong steric repulsions, then a monohelical complex is likely.

This contribution focuses on employing chiral ligands to produce monohelices of only one helical form (*M* or *P*). We recently reported monohelical salen complexes constructed from rigid phenathryl sidearms attached to a helix-directing (*R*)-binaphthyl backbone (Fig. 1).[4] In addition we have shown that monohelical salen complexes with significantly overlapping sidearms can be generated using the (1*R*,2*R*)-cyclohexyl backbone and benz[*a*]anthracene sidearms (Fig. 1).[5] Herein we detail a new system that combines the rigid 1,1′-binaphthyl backbone and the extended benz[*a*]anthryl sidearms.

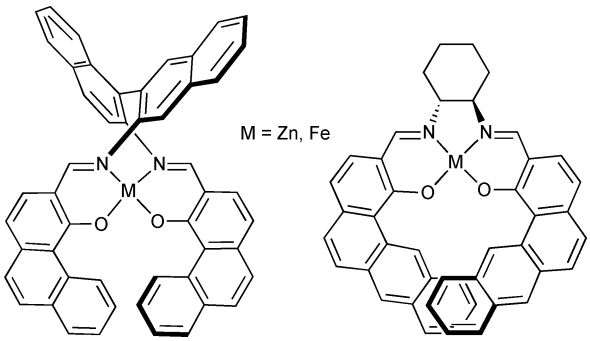
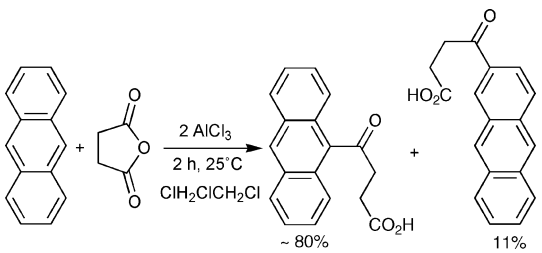



**Fig. 1** Monohelical systems from previous studies.

## Results and discussion

### Synthesis

In a previous study,[4] we synthesized a phenanthryl aldehyde precursor by a five step procedure that started with Friedel–Crafts acylation of naphthalene. The analogous route to the benz[*a*]anthryl precursor *via* the initial alkylation of anthracene is not feasible, since reaction occurs predominantly at the 9-position: only 11% of the desired 2-substituted product could be obtained by this route (eqn (1)).




In order to circumvent this problem, 9,10-dihydroanthracene, **1**, was used as an entry point into the four-ring system (Scheme 1). Now, substitution is directed to the 2-position, giving **2**, while the 9-position is inert to electrophilic attack. The alkylation is accompanied by a 3–5% oxidation to give the fully-aromatized

*Department of Chemistry, Kansas State University, 111 Willard Hall, Manhattan, KS, USA 66506. E-mail: clevy@ksu.edu; Fax: (785) 532-6666; Tel: (785) 532-6688*

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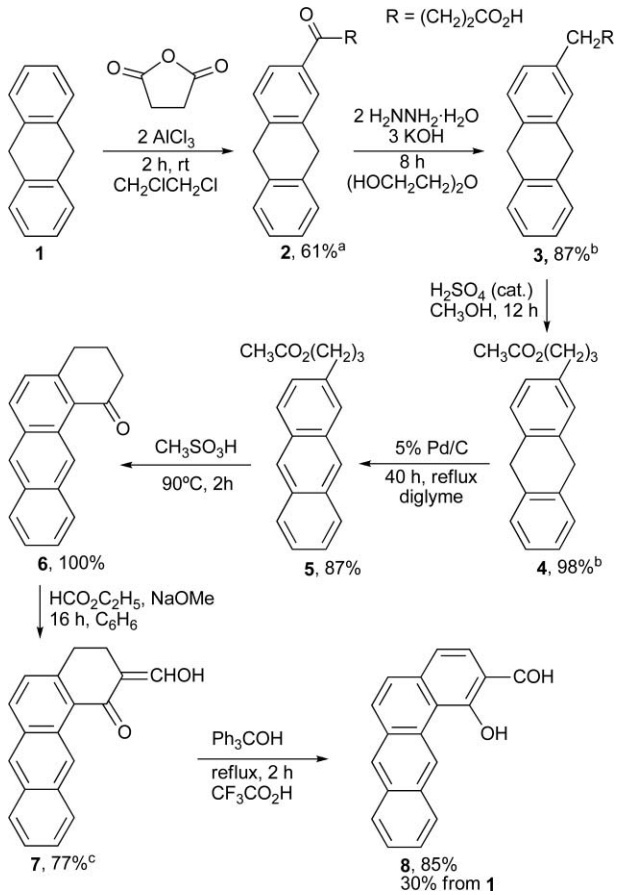
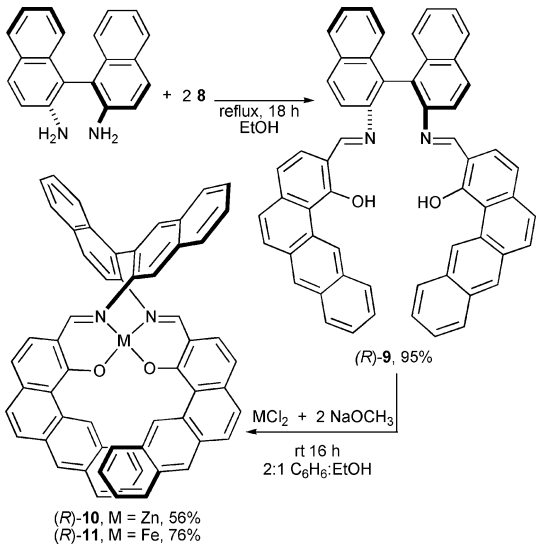



**Scheme 1** Synthesis of the key precursor **8**. [a]Includes 3–5% of the fully aromatized analogue.[b]Includes 10% of the fully aromatized analogue. [c]Includes 15% of the aldehyde **8**.

anthracene analog. No attempt was made to separate this side product since it will ultimately converge with the main product in a subsequent dehydrogenation step.

With the sidechain installed on the anthracene framework, it must now be reduced and cyclized. Reduction of the ketone was accomplished using standard Wolf–Kishner conditions,[6] affording **3**. At this point, all attempts at cyclization to form the fourth ring gave primarily the linear ketone due to unfavorable regioselectivity.[7] This necessitated the aromatization of **3** prior to cyclization. Prior to this step **3** was converted to its methyl ester, **4**, by acid catalyzed condensation. This prevents catalyst deactivation[8] in the subsequent dehydrogenation by refluxing in a high boiling solvent over Pd/C to give **5**. Treatment of this product in hot methanesulfonic acid produces the cyclized ketone, **6**, in quantitative yield. Condensation of **6** with ethyl formate gives predominantly **7**, but also 15% of the final product, **8**. The remainder of **7** can be readily oxidized using triphenylmethanol in TFA[9] to give the desired aldehyde, **8**, in a respectable 30% yield over seven steps.

With aldehyde **8** prepared, the ligand (*R*)-**9** could be synthesized by condensation of **8** with (*R*)-1,1′-binaphthyl-2,2′-diamine (Scheme 2). The ligand was metallated with $FeCl_2$ and $ZnCl_2$, employing sodium methoxide as the requisite base (Scheme 2). For the solvent system, a mixture benzene and ethanol was chosen: the combination was necessary in order to sufficiently solubilize




**Scheme 2** Synthesis of (*R*)-**9** and its complexes.

both the ligand and its sodium salt, which is formed *in situ*. The iron(II) complex, (*R*)-**11**, was highly sensitive to air and water, while the zinc(II) complex, (*R*)-**10**, was air stable but hydrolyzed in wet solvents.

## Structural characterization

Crystal data for the structures presented in this article are provided in Table 1. Selected bond lengths, bond angles and torsion angles are presented in Table 2.

Single crystals of the ligand were grown by diffusion of hexanes into a methylene chloride solution of (*R*)-**9**. The structure consists of a single, approximately $C_2$ symmetric, molecule (Fig. 2).[10] The naphthyl and benz[*a*]anthryl groups, which comprise each half of the structure, are extensively π-delocalized and show near co-planarity as indicated by the interplanar angles of 7.0° and 7.6°. Further stabilizing this arrangement are hydrogen-bonding contacts, which occur between the hydroxyl moieties and imine nitrogen atoms. For each of these interactions the O–H···N distance is 2.497(5) Å and the N···H contact is calculated to be 1.75 Å. The angle between the naphthyl planes is 108.1°, well within the broad ~60–130° low energy well for binaphthyl torsion angles.[11]

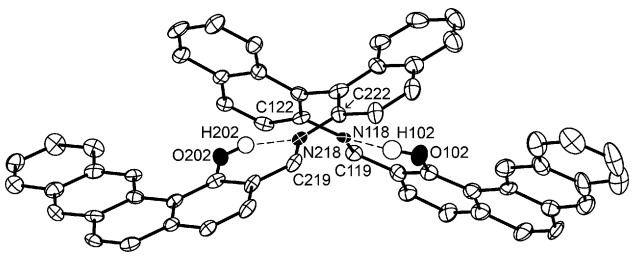



**Fig. 2** Thermal ellipsoid (50%) plot of (*R*)-**9**.

Bright yellow single crystals of [(*R*)-**10**]$_2$·2$CH_2Cl_2$·$Et_2O$ were grown by diffusion of diethyl ether into a methylene chloride solution of the complex. There are two distinct molecules of (*R*)-**10** in the asymmetric unit (Fig. 3), with the methylene chlorides of crystallization sandwiched between them. The two molecules are

**Table 1** Crystal data for the ligand (*R*)-**9** and its metal complexes, (*R*)-**10** and (*R*)-**11**

| Compound | (*R*)-**9**·$CH_2Cl_2$ | [(*R*)-**10**]$_2$·$2CH_2Cl_2$·$Et_2O$ | (*R*)-**11**·$Et_2O$ |
|---|---|---|---|
| Formula | $C_{59}H_{38}Cl_2N_2O_2$ | $C_{122}H_{82}Cl_4N_4O_5Zn_2$ | $C_{62}H_{44}FeN_2O_3$ |
| *M* | 877.81 | 1956.46 | 920.84 |
| Crystal system | Orthorhombic | Monoclinic | Trigonal |
| *a*/Å | 8.8321(14) | 12.5693(17) | 12.6954(3) |
| *b*/Å | 11.5748(18) | 32.926(4) | 12.6954(3) |
| *c*/Å | 42.316(7) | 12.6967(17) | 24.3493(10) |
| *α*/° | 90 | 90 | 90 |
| *β*/° | 90 | 119.512(2) | 90 |
| *γ*/° | 90 | 90 | 120 |
| Unit cell vol./Å$^3$ | 4325.9(12) | 4572.9(11) | 3398.68(18) |
| Space group | $P2_12_12_1$ | $P2_1$ | $P3_2$ |
| *Z* | 4 | 2 | 3 |
| *T*/K | 100(2) | 100(2) | 100(2) |
| *μ*/mm$^{-1}$ | 0.200 | 0.705 | 0.385 |
| *N* | 24399 | 29596 | 39455 |
| $N_{ind}$ | 7579 | 15636 | 13200 |
| $R_{int}$ | 0.0467 | 0.0270 | 0.0447 |
| $R_1{}^a$ ($I > 2\sigma(I)$) | 0.0928 | 0.0547 | 0.0524 |
| $wR_2{}^a$ ($I > 2\sigma(I)$) | 0.1882 | 0.1475 | 0.1178 |
| $R_1$ (all data) | 0.0957 | 0.0572 | 0.0622 |
| $wR_2$ (all data) | 0.1896 | 0.1504 | 0.1231 |
| GoF | 1.353 | 1.335 | 1.017 |
| Flack parameter | 0.04(17) | 0.029(11) | 0.004(14) |

$^a$ $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ for $F_o > 2\sigma(F_o)$ and $wR_2 = \{\sum[w(F^2_o - F^2_c)^2]/\sum[w(F^2_c)]\}^{1/2}$.

very similar, both having *M* helicity and four coordinate zinc in a distorted tetrahedral environment. The molecules are stacked and are rotated by *ca.* 55° with respect to each other. Fig. 3 shows the thermal ellipsoid plot of the arrangement and Fig. 4 shows a space-filling representations of the molecule containing Zn1. There is clearly a helical structure with overlapping ligand sidearms. The interplanar angle between the naphthyl fragments is 78.5°, significantly smaller than in the free ligand, but still

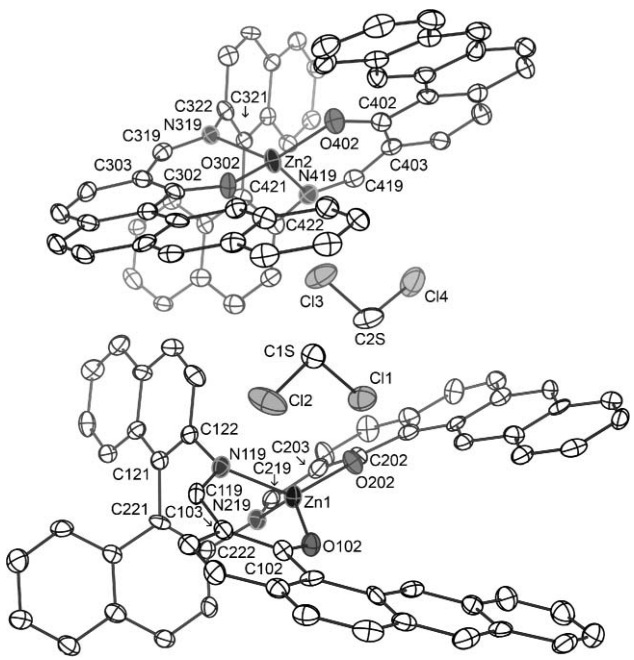



**Fig. 3** Thermal ellipsoid plot (50%) of [(*R*)-**10**]$_2$·$2CH_2Cl_2$·$Et_2O$ showing the two independent complexes in the unit cell.

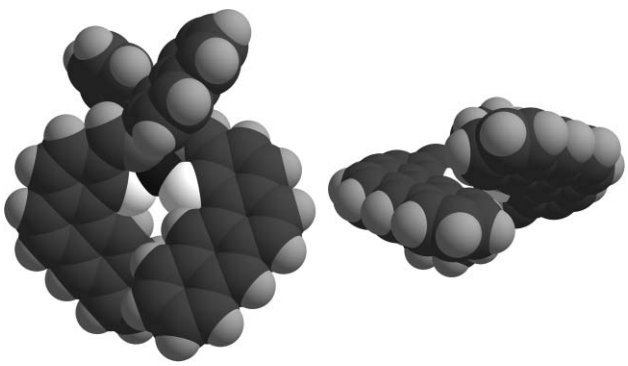


**Fig. 4** Two views of the space-filling model (50%) of (*R*)-**10**.

within the region where binaphthyl-based steric repulsions are relatively low.[11] The interplanar angles between the sidearms are 34.0° and 35.2° for the two molecules, somewhat smaller that the 47.3° angle seen for the complex with phenanthryl sidearms (and a five coordinate zinc center).[4]

The $Fe^{II}$ complex, (*R*)-**11**, was isolated as an air and moisture sensitive paramagnetic dark brown powder. Diffusion of diethyl ether into a methylene chloride solution of (*R*)-**11** gave single crystals of (*R*)-**11**·$Et_2O$ suitable for X-ray analysis. The crystal structure reveals an *M* helix (Fig. 5) with a structure very similar to that of (*R*)-**10**: the interplanar angle between the naphthyl groups is 82.7° and the angle between the sidearm planes is 34.7°. This latter angle is significantly smaller that the 74.5° seen for the analogous $Fe^{II}$ complex with phenanthrene-based sidearms.[4] This can be explained by the added steric requirements of the extended sidearms in (*R*)-**11**: in order to avoid edge-to-face repulsions the planar fragments cannot be severely twisted with respect to one another and must adopt a more stacked arrangement.

**Table 2** Selected bond lengths (Å), bond angles (°) and torsion angles (°) from crystal data

| Compound | (*R*)-**9** | (*R*)-**10**, M = Zn | (*R*)-**11**, M = Fe |
|---|---|---|---|
| H102–O102 | 0.84[a] | — | — |
| H102–N119 | 1.75[a] | — | — |
| H202–O202 | 0.84[a] | — | — |
| H202–N219 | 1.75[a] | — | — |
| O102–C102 | 1.318(5) | 1.292(7) | 1.308(4) |
| O202–C202 | 1.343(5) | 1.288(7) | 1.316(4) |
| N119–C119 | 1.289(6) | 1.304(8) | 1.289(4) |
| N119–C122 | 1.432(6) | 1.421(8) | 1.426(4) |
| N219–C219 | 1.292(6) | 1.262(8) | 1.292(4) |
| N219–C222 | 1.412(6) | 1.439(7) | 1.441(4) |
| M1–O102 | — | 1.896(4) | 1.897(2) |
| M1–O202 | — | 1.894(4) | 1.895(2) |
| M1–N119 | — | 2.001(5) | 2.030(3) |
| M1–N219 | — | 2.038(5) | 2.040(3) |
| O102–H102–N119 | 147.0[a] | — | — |
| O202–H202–N219 | 147.0[a] | — | — |
| C119–N119–C122 | 123.5(4) | 121.8(5) | 121.2(3) |
| C219–N219–C222 | 124.9(4) | 124.0(5) | 121.3(3) |
| N119–M1–N219 | — | 93.45(19) | 94.54(10) |
| N119–M1–O102 | — | 95.21(19) | 90.21(11) |
| N119–M1–O202 | — | 133.4(2) | 131.62(12) |
| N219–M1–O102 | — | 126.38(19) | 132.23(11) |
| N219–M1–O202 | — | 93.31(18) | 89.78(11) |
| O102–M1–O202 | — | 116.78(18) | 121.03(10) |
| C122–C121–C221–C222 | −106.5(5) | −69.5(7) | −72.6(4) |
| C102–C103–C119–N119 | −3.1(7) | −11.1(10) | −4.2(5) |
| C202–C203–C219–N219 | 2.7(7) | 0.9(9) | −3.0(5) |
| C103–C119–N119–C122 | −179.9(4) | 178.7(6) | −178.4(3) |
| C203–C219–N219–C222 | 175.5(4) | 178.2(5) | 179.0(3) |
| Nap–Nap[b] | 108.1 | 78.4 | 82.7 |
| Arm–Arm[c] | 63.2 | 36.8 | 35.8 |
| Nap1–Arm1[d] | 7.6 | 87.9 | 88.5 |
| Nap2–Arm2[e] | 7.0 | 80.3 | 84.1 |

[a] Hydrogen at calculated position. [b] Absolute value of the angle between the naphthyl planes. [c] Absolute value of the angle between the benz[*a*]anthryl planes. [d] Absolute value of the angle between the naphthyl plane C120–C129 and the benz[*a*]anthryl plane C101–C118. [e] Absolute value of the angle between the naphthyl plane C220–C229 and the benz[*a*]anthryl plane C201–C218.

In both complexes there is significant rotation of the sidearms relative to the naphthyl units (dihedral angles range from 80.6° to 88.6°) indicating that there is little delocalization of π electrons between these aromatic segments. A roughly perpendicular relationship between the naphthyl units and the aromatic sidearms has been observed in other binaphthyl Schiff base complexes,[12] and is necessary for effective coordination of the four donors to a single metal center. Neither complex has axial ligands in the solid state, consistent with sterically-congested metal centers and limited conformational flexibility due to sidearm interactions (*vide supra*). The metal centers are best described as having a distorted tetrahedral geometry. Chelate pairs of donors have bond angles close to 90° with the metal: 90–95° for N–M–O units and 93–95° for N–M–N. The bond angles between non-adjacent donors is

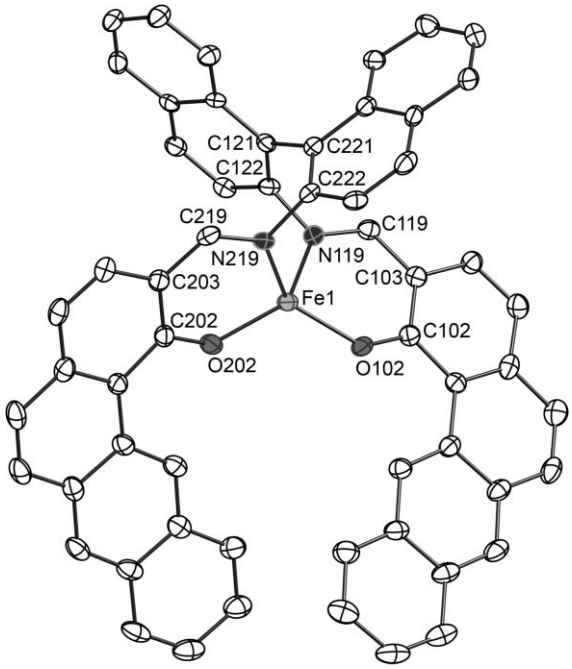



**Fig. 5** Thermal ellipsoid plot (50%) of (*R*)-**11**.

significantly opened up from ideal tetrahedral: 116–121° for O–M–O and 126–133° for N–M–O.

## NMR Characterization

The ligand (*R*)-**9** and its $Zn^{II}$ complex (*R*)-**10** have well resolved $^{1}H$ and $^{13}C$ spectra. In each case, spectra are consistent with a single $C_2$ symmetric compound in solution. The $^{1}H$ NMR of the $Fe^{II}$ complex, (*R*)-**11**, has broad signals and a wide chemical shift range, consistent with a paramagnetic metal center and an extensively conjugated ligand system. Seventeen resonances are expected for a $C_2$ complex, and 15 of these are readily identified. It is likely that the remaining two resonances are not observed due to strong paramagnetic broadening of protons near the metal center. For all three compounds, the $C_2$ symmetry indicated by the NMR studies is consistent with the X-ray structural data, which show a symmetric ligand and only *M* helical complexes for (*R*)-**10** and (*R*)-**11**.

In the $^{1}H$ spectrum of the ligand, (*R*)-**9**, the intramolecularly bonded O–H · · · N protons appear at 15.17 ppm. While tautomerization may be present for this complex, only an averaged spectrum would be observed due to rapid proton transfer. Other notable signals in the $^{1}H$ spectrum are the imine protons at 8.93 ppm and the signal at 9.96 ppm which is due to the bay region hydrogens at the 5-positions of the benz[*a*]anthryl rings. These latter protons are effected by edge position aromatic deshielding and anisotropic deshielding from the hydroxyl group at the nearby 4-position.[13]

The spectrum of the $Zn^{II}$ complex, (*R*)-**10**, is similar to that of the uncomplexed ligand. The most notable differences are the absence of the phenolic resonance and the significant downfield shift of the bay region proton to 12.15 ppm. This dramatic shift is mainly the result of increased anisotropic deshielding by the phenoxide donor at the 4-position. Previous studies on phenanthrenes have shown that the heteroatom at the 4-position can have a dramatic effect on the chemical shift of the proton at the 5-position.[14]

### Electronic and ECD spectroscopy

The electronic spectrum of the ligand precursor **8** (Fig. 6) shows a number of overlapping signals: there is an envelope of absorptions from 225 to 300 nm, an absorption at 338 nm, and a lower intensity envelope from 340–430 nm. The low energy envelope matches up well with the vibronic series of the first electronic transition ($L_b$ band), centered at 385 nm, reported for benz[*a*]anthracene.[15] The UV spectral features of **8** are similar to those seen for 4-hydroxybenz[*a*]anthracene.[16] The high energy envelope is believed to result primarily from two strongly overlapping electronic transitions, which are centered at 256 nm for benz[*a*]anthracene.[15] For **8** $\lambda_{max}$ is shifted to 270 nm, consistent with the conjugation effect of the aldehyde, as was noted for benz[*a*]anthryl systems.[17]

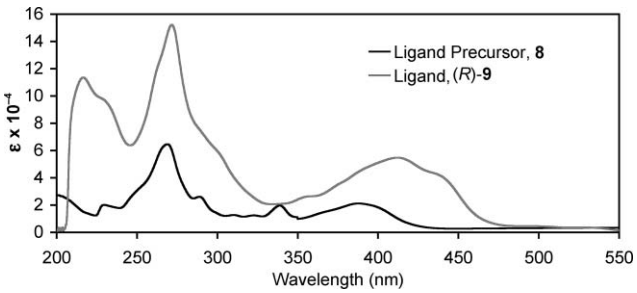



**Fig. 6** Electronic spectra of **8** ($2.5 \times 10^{-5}$ M) and (*R*)-**9** ($1.5 \times 10^{-5}$ M) in THF.

The electronic spectrum of the free ligand, (*R*)-**9**, in THF (Fig. 6) contains signals for π to π* transitions from three major chromophores: the imine π-bonds, the benz[*a*]anthryl sidearms, and the binaphthyl backbone. The low energy envelope for 500 to 350 nm results from imine π–π* absorption[18] as well as the sidearm $L_b$ band. The strong signal with $\lambda_{max}$ at 271 nm has not shifted significantly compared to the aldehyde **8**. The ligand shows a high energy absorption in the UV that is not present in **8**. This strong signal, with $\lambda_{max}$ at 216 nm and a low energy shoulder, is due to the binaphthyl backbone.[11] The electronic spectrum of the free ligand does not display distinct signals for the keto-amine tautomer, as were observed for the phenanthryl analog.[4]

Complexes (*R*)-**10** and (*R*)-**11** have similar electronic spectra (Fig. 7), both of which have the same general features as the spectrum of the free ligand, with additional absorption in the low energy 450–500 nm range. The shift to low energy is consistent with the shift in the imine π–π* transition upon metallation.[18] The ECD spectra of the two complexes (Fig. 8) have a general similarity, with the most notable differences being significant

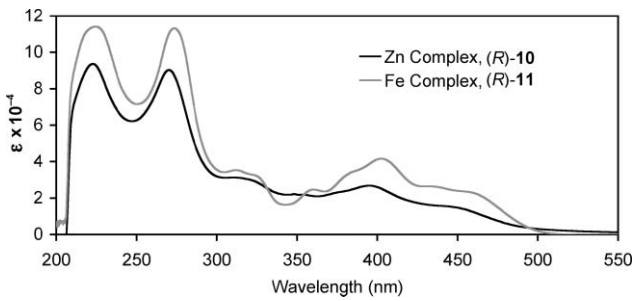



**Fig. 7** Electronic spectra of (*R*)-**10** ($2.5 \times 10^{-5}$ M) and (*R*)-**11** ($1.5 \times 10^{-5}$ M) in THF.

broadening and intensity reduction for the paramagnetic iron complex compared to the dimagnetic zinc complex, especially at energies below 240 nm. The ECD spectra of the complexes have pronounced differences to that of the ligand, consistent with the wrapping of the extended ligand into conformationally fixed helical complexes. The signs of signals are generally reversed through the 240–340 nm range and the low energy signal due to the imine π–π* transition is prominent in the spectra of the complexes. The low energy signals from 340 to 480 nm show a negative Cotton effect at long wavelengths, consistent with the *R* configuration of the binaphthyl backbone.[11,18a]

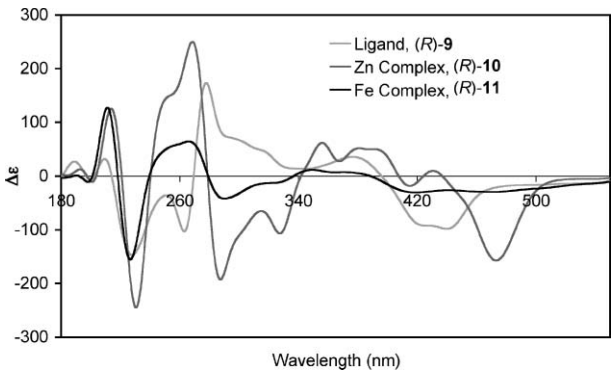



**Fig. 8** ECD spectra of (*R*)-**9** ($2.5 \times 10^{-5}$ M) (*R*)-**10** ($2.5 \times 10^{-5}$ M) and (*R*)-**11** ($1.5 \times 10^{-5}$ M) in THF.

## Conclusions

The binaphthyl-salen ligand with extend polyaromatic benz[*a*]-anthryl sidearms produces helical complexes with *M* helicity and overlapping sidearms. The twisted binaphthyl backbone directs the rigid sidearms and causes a strong preference for the *M* helix. The preference is not as strong when the more flexible cyclohexyl backbone is used, and *M* and *P* helices are observed in most cases, even with the extended benz[*a*]anthryl sidearms.[5] Thus, the binaphthyl backbone appears to have a high fidelity for generating helices of a predetermined handedness in salen systems. Despite the overlapping sidearms, there is no significant face-to-face π–π stacking of the benz[*a*]anthryl units within a complex. The geometric constraints of the binaphthyl backbone are transmitted to the sidearms, and they are directed away from one another, instead of stacking. On the other hand, the more flexible cyclohexyl backbone can allow significant π–π staking interactions of the benz[*a*]anthryl sidearms.[5]

Helical complexes have great potential as asymmetric catalysts, and we are currently examining their utility for the asymmetric oxidation of alkenes and sulfides.

## Experimental

### General methods

All reactions were carried out under inert atmospheres unless otherwise noted. All air and/or moisture sensitive compounds were manipulated using standard high-vacuum line, Schlenk, or cannula techniques, or in a glove box under a nitrogen atmosphere as described previously.[19] All solvents were stored

under vacuum over sodium benzophenone ketyl, titanocene, or calcium hydride prior to use. Solvents used in metallation reactions were degassed before use and inert gas was purified by passing through 4 Å molecular sieves and Engelhard Q5 catalyst. Magnetic susceptibilities were measured at 296 K using a Magway Mk1 magnetic susceptibility balance. The instrument was calibrated with $Hg[Co(NCS)_4]$ standard. Magnetic susceptibilities of the iron salen complexes were corrected for metal core electrons and the diamagnetism of the free ligands. Effective magnetic moments were calculated from the corrected susceptibilities as $\mu_{eff} = (8\chi_M T)^{1/2}$. NMR data were collected on a Varian Unity 400 MHz spectrometer using the residual solvent protons as an internal standard. Electronic spectra were collected on a Cary 500 spectrometer with a 1 cm quartz cell. ECD spectra were collected using a Jasco 720 spectropolarimeter with a 1 cm quartz cell in a nitrogen-purged cavity. Spectroscopic grade THF was used for these studies. The concentrations of ligands and complexes ranged from 1.5 to $2.5 \times 10^{-5}$ M. All the preparations that follow are new, although some of the procedures follow general methods we have previously reported.[4]

### Synthesis of the aldehyde precursor, 8

**3-(9,10-Dihydro-2-anthroyl)propionic acid (2).** To a solution of 9,10-dihydroanthracene (**1**, 74.23 g, 412 mmol) in 1,2-dichloroethane (325 mL) at 0 °C was added a mixture of succinic anhydride (37.50 g, 374 mmol) and aluminium chloride (99.83 g, 749 mmol) in small portions over 80 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 2 h. It was then quenched *via* the addition of $H_2O$ (1.25 L), and diluted with hexanes (1.5 L). The resulting precipitate was collected, washed with $H_2O$ (500 mL), and suspended into 5 M NaOH (1 L). After stirring for 30 min it was recollected, washed with 5 M NaOH (3 × 300 mL), and dissolved into 4 : 1 $H_2O$–ethanol (1 L). The solution was filtered to remove trace insoluble solids, and acidified to pH 1 with 5 M HCl. The resulting light yellow solid was collected and washed with $H_2O$ (500 mL) to afford **2** (63.61 g, 61% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.83 (t, 2 H, $J$ = 6.5 Hz, $CH_2$), 3.33 (t, 2 H, $J$ = 6.5 Hz, $CH_2$), 4.01 (s, 4 H, $CH_2$), 7.20–7.26 (m, 2 H, CH), 7.29–7.35 (m, 2 H, CH), 7.40 (d, 1 H, $J$ = 7.8 Hz, CH), 7.83 (dd, 1 H, $J$ = 1.8, 7.8, CH), 7.93 (d, 1 H, $J$ = 1.8 Hz, CH), 10.65 (br, s, 1 H, OH). $^1$H NMR analysis indicated the presence of 3–5% of the fully aromatized analogue of the product. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 28.33, 33.35, 36.26, 36.51, 126.29, 126.59, 126.63, 127.29, 127.62, 127.65, 127.87, 134.84, 135.74, 136.16, 137.44, 142.92, 178.98, 197.83. Anal. calc. for $C_{18}H_{16}O_3$: C 77.12, H 5.75. Found: C 76.87, H 5.50%.

**4-(9,10-Dihydro-2-anthryl)butanoic acid (3).** To a solution of **2** (63.07 g, 225 mmol) in diethylene glycol (600 mL) at 100 °C was added hydrazine monohydrate (33 mL, 679 mmol). The reaction mixture was stirred for 1 h, then potassium hydroxide was added (37.89 g, 675 mmol) and the temperature was raised to 200 °C. After stirring for 8 h the reaction mixture was allowed to cool, and diluted with $H_2O$ (2.4 L). The solution was filtered twice through a Celite plug to remove insoluble solids, and the clear filtrate acidified to pH 1 with 5 M HCl. The resulting precipitate was collected, washed with $H_2O$ (750 mL), and dissolved into methylene chloride (700 mL). The aqueous layer was separated and discarded, and the organic solution dried over anhydrous $MgSO_4$, then filtered. The solvent was removed *in vacuo* to give **3** (52.02 g, 87% yield) as a light tan solid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.99 (quin, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.40 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.69 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), 3.95 (s, 4 H, $CH_2$), 7.05 (dd, 1 H, $J$ = 1.8, 7.6, Hz, CH), 7.15 (d, 1 H, $J$ = 1.8 Hz, CH), 7.19–7.26 (m, 3 H, CH), 7.29–7.35 (m, 2 H, CH), 11.54 (br, s, 1 H, OH). $^1$H NMR analysis indicated the presence of approximately 10% of the fully aromatized analogue of the product. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 26.56, 33.52, 34.87, 35.97, 36.37, 126.27, 126.27, 126.45, 127.60, 127.62, 127.64, 127.73, 134.61, 136.89, 136.96, 137.02, 139.22, 179.93. Anal. calc. for $C_{18}H_{18}O_2$: C 81.17, H 6.81. Found: C 80.63, H 6.71%.

**Methyl 4-(9,10-dihydro-2-anthryl)butanoate (4).** A mixture of **3** (51.79 g, 194 mmol) and sulfuric acid (5.2 mL) in methanol (520 mL) was refluxed for 18 h. After cooling, the reaction mixture was diluted with diethyl ether (800 mL) and consecutively washed with 1 M $NaHCO_3$ (800 mL) and $H_2O$ (500 mL). The organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford **4** (53.37 g, 98% yield) as a red-brown oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.97 (quin, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.35 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.65 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), 3.68 (s, 3 H, $CH_3$), 3.93 (s, 4 H, $CH_2$), 7.03 (dd, 1 H, $J$ = 1.4, 7.6, Hz, CH), 7.14 (d, 1 H, $J$ = 1.4 Hz, CH), 7.18–7.25 (m, 3 H, CH), 7.28–7.34 (m, 2 H, CH). $^1$H NMR analysis indicated the presence of approximately 10% of the fully aromatized analogue of the product. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 26.85, 33.62, 35.00, 35.98, 36.39, 51.67, 126.26, 126.26, 126.45, 127.59, 127.59, 127.59, 127.73, 134.54, 136.91, 136.91, 137.05, 139.41, 174.17. Anal. calc. for $C_{19}H_{20}O_2$: C 81.40, H 7.19. Found: C 81.60, H 7.02%.

**Methyl 4-(2-anthryl)butanoate (5).** A solution of **4** (53.18 g, 190 mmol) in 2-ethoxyethyl ether (200 mL) was refluxed in the presence of 5% Pd/C catalyst (5.32 g) for 40 h. After cooling, the reaction mixture was poured into acetone (300 mL), and the solution filtered to remove palladium catalyst. Dilution of the filtrate with $H_2O$ (750 mL) gave a precipitate that was collected, and washed with a further portion of $H_2O$ (200 mL). The precipitate was dissolved into methylene chloride (250 mL), and the aqueous layer separated and discarded. The organic solution was dried over anhydrous $MgSO_4$, filtered, and diluted with hexanes (1.25 L). Upon concentration to 1/2 volume a cream colored precipitate formed, and this was collected and washed with hexanes (200 mL) to yield **5** (45.90 g, 87% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.12 (quin, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.42 (t, 2 H, $J$ = 7.5 Hz, $CH_2$), 2.87 (t, 2 H, $J$ = 7.6 Hz, $CH_2$), 3.68 (s, 3 H, $CH_3$), 7.33 (dd, 1 H, $J$ = 1.5, 8.7, Hz, CH), 7.42–7.49 (m, 2 H, CH), 7.77 (s, 1 H, CH), 7.93–8.02 (m, 3 H, CH), 8.35 (s, 1 H, CH), 8.40 (s, 1 H, CH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 26.18, 33.64, 35.65, 51.70, 125.25, 125.51, 125.70, 126.17, 126.40, 127.43, 128.28, 128.38, 128.52, 130.84, 131.61, 132.10, 132.10, 138.44, 174.11. Anal. calc. for $C_{19}H_{18}O_2$: C 81.99, H 6.52. Found: C 81.51, H 6.76%.

**3,4-Dihydrobenz[*a*]anthracen-1(2*H*)-one (6).** A solution of **5** (45.70 g, 164 mmol) in methanesulfonic acid (450 mL) was heated to 90 °C and stirred for 2 h. The reaction mixture was poured into $H_2O$ (900 mL) and allowed to cool. The resulting aqueous mixture was extracted with methylene chloride (1 × 300 mL, 4 × 100 mL), and the extracts combined and washed consecutively with 1 M

$NaHCO_3$ (300 mL) and $H_2O$ (300 mL). The organic solution was dried over anhydrous $MgSO_4$, filtered, and concentrated to afford **6** (40.31 g, 100% yield) as a yellow-brown solid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.23 (quin, 2 H, $J$ = 6.4 Hz, $CH_2$), 2.84 (t, 2 H, $J$ = 6.6 Hz, $CH_2$), 3.13 (t, 2 H, $J$ = 6.1 Hz, $CH_2$), 7.25 (d, 1 H, $J$ = 8.6, Hz, CH), 7.47–7.55 (m, 2 H, CH), 7.95–8.00 (m, 1 H, CH), 8.06 (d, 1 H, $J$ = 8.6, Hz, CH), 8.11–8.16 (m, 1 H, CH), 8.34 (s, 1 H, CH), 10.11 (s, 1 H, CH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 23.13, 32.09, 41.24, 126.11, 126.16, 126.61, 126.95, 127.01, 127.87, 128.63, 129.69, 131.27, 131.27, 133.89, 135.11, 148.01, 200.38 (one signal not observed). Anal. calc. for $C_{18}H_{14}O$: C 87.78, H 5.73. Found: C 87.75, H 5.72%.

**3,4-Dihydro-2-(hydroxymethylene)benz[*a*]anthracen-1(2*H*)-one (7).** To a solution of ethyl formate (23.49 g, 317 mmol) in benzene (500 mL) was added sodium methoxide (12.85 g, 238 mmol). To this vigorous stirring mixture was added a solution of **6** (39.05 g, 158 mmol) in benzene (500 ml) and the reaction mixture then stirred for 16 h. This was diluted with hexanes (1 L), filtered, and the collected solid was washed with a further portion of hexanes (500 mL). The solid was redissolved into methanol (300 mL), acidified with 2.5 M HCl (700 mL), and the precipitate extracted into methylene chloride (3 × 300 mL). The extracts were combined, dried over anhydrous $MgSO_4$, filtered, and the solvent removed *in vacuo*. Purification of the crude material was accomplished by filtration through a silica gel plug (1 : 1 hexanes–methylene chloride) to give **7** (33.35 g, 77% yield) as a bright orange solid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 2.57 (t, 2 H, $J$ = 6.8 Hz, $CH_2$), 3.04 (t, 2 H, $J$ = 6.8 Hz, $CH_2$), 7.27 (d, 1 H, $J$ = 8.6 Hz, CH), 7.48–7.56 (m, 2 H, CH), 7.79 (d, 1 H, $J$ = 8.4, Hz, CH), 7.96–8.01 (m, 1 H, CH), 8.06 (d, 1 H, $J$ = 8.6 Hz, CH), 8.09–8.14 (m, 1 H, CH), 8.38 (s, 1 H, CH), 9.91 (s, 1 H, CH), 15.11 (d, 1 H, $J$ = 8.8 Hz, OH). $^1$H NMR analysis indicated the presence of approximately 15% of the fully aromatized analogue of the product. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 23.43, 31.44, 110.75, 126.17, 126.23, 126.29, 126.50, 127.28, 127.32, 127.93, 128.33, 129.54, 131.36, 131.55, 133.47, 134.94, 145.66, 168.04, 190.45. Anal. calc. for $C_{19}H_{14}O_2$: C 83.19, H 5.14. Found: C 82.97, H 4.76%.

**1-Hydroxybenz[*a*]anthracene-2-carboxaldehyde (8).** A mixture of **7** (33.08 g, 121 mmol) and triphenylmethanol (62.78 g, 241 mmol) in trifluoroacetic acid (500 mL) was refluxed for 2 h. The solution was cooled and diluted with $H_2O$ (1 L). The resulting precipitate was collected, washed with $H_2O$ (200 mL), and suspended into 2 : 1 1 M NaOH–ethanol (600 mL). The mixture was stirred for 15 min, filtered, and the insoluble material washed with a further portion of 2 : 1 1 M NaOH–ethanol (100 mL). The filtrates were combined, acidified to pH 1 with 5 M HCl, and extracted with methylene chloride (1 × 700 mL, 2 × 200 mL). The organic extracts were combined, dried over anhydrous $MgSO_4$, filtered, and the solvent removed *in vacuo*. The resulting solid was recrystallized from ethyl acetate–ethanol to afford **8** (27.85 g, 85% yield) as a yellow-green powder. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.38 (d, 1 H, $J$ = 8.1 Hz, CH), 7.51 (d, 1 H, $J$ = 8.9 Hz, CH), 7.57–7.63 (m, 3 H, CH), 7.92 (d, 1 H, $J$ = 8.9 Hz, CH), 8.00–8.06 (m, 1 H, CH), 8.15–8.21 (m, 1 H, CH), 8.33 (s, 1 H, CH), 9.98 (s, 1 H, CH), 10.28 (s, 1 H, CH), 13.44 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 117.86, 119.52, 120.54, 126.16, 126.51, 126.64, 127.25, 127.60, 128.38, 128.68, 129.66, 130.57, 130.99, 131.58, 132.97, 133.13, 139.97, 163.50, 196.74. Anal. calc. for $C_{19}H_{12}O_2$: C 83.81, H 4.44. Found: C 83.52, H 4.53%.

## Synthesis of the ligand and its complexes

**2,2′-[(1*R*)-[1,1′-Binaphthalene]-2,2′-diylbis(nitrilomethylidyne)]-bisbenz[*a*]anthracen-1-ol, [(*R*)-9].** A mixture of **8** (3.009 g, 11.1 mmol) and (*R*)-1,1′-binaphthyl-2,2′-diamine (1.571 g, 5.5 mmol) in ethanol (150 mL) was brought to reflux. After 18 h the resultant suspension was hot filtered, and the precipitate washed with boiling ethanol (100 mL) to give (*R*)-**9** (4.149 g, 95% yield) as a bright red solid. $^1$H NMR (TFA-*d*, 400 MHz): $\delta$ 7.47 (d, 2 H, $J$ = 8.8 Hz, CH), 7.57 (d, 2 H, $J$ = 8.3 Hz, CH), 7.74–7.82 (m, 6 H, CH), 7.87–7.94 (m, 4 H, CH), 7.99 (d, 2 H, $J$ = 8.8 Hz, CH), 8.08 (t, 2 H, $J$ = 7.5 Hz, CH), 8.12 (d, 2 H, $J$ = 8.4 Hz, CH), 8.21 (d, 2 H, $J$ = 8.2 Hz, CH), 8.39 (s, 2 H, CH), 8.49 (d, 2 H, $J$ = 9.1 Hz, CH), 8.61 (d, 2 H, $J$ = 8.3 Hz, CH), 8.69 (s, 2 H, CH), 8.84 (d, 2 H, $J$ = 9.1 Hz, CH), 9.37 (s, 2 H, CH). The phenolic hydrogen was not observed due to deuterium exchange. In $CDCl_3$ the phenolic hydrogen is observed at 15.17 ppm. $^{13}$C NMR (TFA-*d*, 100 MHz): $\delta$ 115.68, 117.13, 122.26, 125.97, 126.10, 126.32, 127.27, 127.32, 127.56, 129.57, 129.89, 129.95, 130.05, 131.40, 131.59, 131.83, 132.47, 132.74, 134.50, 134.73, 135.37, 135.51, 136.09, 136.64, 138.48, 146.25, 161.43, 163.26 (one signal not observed). Anal. calc. for $C_{58}H_{36}N_2O_2$: C 87.86, H 4.58, N 3.53. Found: C 87.84, H 4.62, N 3.56%. Single crystals suitable for X-ray analysis were grown by slow diffusion of hexanes into a solution of (*R*)-**9** in methylene chloride.

**Zn(II) complex of (*R*)-9, [(*R*)-10].** Anhydrous zinc chloride (0.048 g, 0.35 mmol), sodium methoxide (0.052 g, 0.96 mmol) and (*R*)-**9** (0.252 g, 0.32 mmol) were suspended into a 2 : 1 mixture of benzene–ethanol (15 mL) and stirred for 12 h. The reaction mixture was concentrated to a yellow solid that was dissolved into THF (10 mL), and filtered to remove fine insoluble solids. The clear filtrate was diluted with ethanol (20 mL), and concentrated to 2/3 volume resulting in formation of a yellow precipitate. The precipitate was collected to afford (*R*)-**10** (0.153 g, 56% yield). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 6.70 (t, 2 H, $J$ = 7.5 Hz, CH), 6.99 (d, 2 H, $J$ = 8.6 Hz, CH), 7.09 (d, 2 H, $J$ = 8.2 Hz, CH), 7.19 (t, 2 H, $J$ = 7.5 Hz, CH), 7.23–7.29 (m, 4 H, CH), 7.44 (t, 2 H, $J$ = 7.6 Hz, CH), 7.48 (d, 2 H, $J$ = 8.5 Hz, CH), 7.51–7.55 (m, 4 H, CH), 7.84 (d, 2 H, $J$ = 8.3 Hz, CH), 7.91 (d, 2 H, $J$ = 8.2 Hz, CH), 7.95 (d, 2 H, $J$ = 8.8 Hz, CH), 8.02 (d, 2 H, $J$ = 8.6 Hz, CH), 8.32 (s, 2 H, CH), 8.58 (s, 2 H, CH), 11.30 (s, 2 H, CH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 116.30, 116.47, 122.37, 123.79, 124.94, 125.54, 125.89, 126.48, 126.59, 126.87, 126.87, 127.10, 127.31, 128.36, 128.61, 129.76, 130.32, 131.02, 131.07, 131.40, 132.31, 132.35, 133.13, 133.99, 134.20, 139.55, 145.53, 170.59, 173.65. Anal. calc. for $C_{58}H_{34}N_2O_2Zn$: C 81.35, H 4.00, N 3.27. Found: C 80.53, H 4.35, N 3.05%. Single crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a solution of (*R*)-**10** in methylene chloride.

**Fe(II) complex of (*R*)-9, [(*R*)-11].** Iron(II) chloride (0.053 g, 0.42 mmol), sodium methoxide (0.061 g, 1.14 mmol) and (*R*)-**9** (0.300 g, 0.38 mmol) were suspended into a 2 : 1 mixture of benzene–ethanol (15 mL) and stirred for 12 h. The reaction mixture was concentrated to a brown-black residue that was dissolved into THF (15 mL), and filtered to remove fine insoluble

solids. The clear filtrate was diluted with ethanol (45 mL), and stirred for 30 min. A brown precipitate of (*R*)-**11** formed gradually, and this was collected and dried *in vacuo* (0.244 g, 76% yield). $^1$H NMR ($CD_2Cl_2$, 400 MHz): $\delta$ −38.86 (br, s, 2 H, CH), −13.43 (s, 2 H, CH), −8.90 (s, 2 H, CH), −7.52 (s, 4 H, CH), 2.25 (s, 2 H, CH), 5.02 (s, 2 H, CH), 8.18 (s, 2 H, CH), 10.33 (s, 2 H, CH), 11.90 (s, 2 H, CH), 13.05 (s, 2 H, CH), 13.60–14.40 (m, 4 H, CH), 24.12 (s, 2 H, CH), 62.02 (br, s, 2 H, CH). Anal. calc. for $C_{58}H_{34}N_2O_2Fe$: C 82.27, H 4.05, N 3.31. Found: C 82.38, H 4.29, N 3.22%. Single crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a solution of (*R*)-**11** in methylene chloride.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700001d

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