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Chiral salen ligands designed to form polymetallic complexes

Thierry R.J. Achard, William Clegg, Ross W. Harrington, Michael North *

School of Chemistry and University Research Centre in Catalysis and Intensified Processing, Newcastle University, Bedson Building, Newcastle upon Tyne, NE1 7RU, UK

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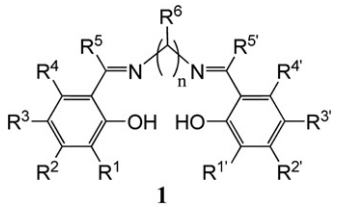
ABSTRACT

Chiral salen ligands capable of forming polymetallic complexes have been designed. The ligands possess substituents in the 4,4′-positions, but have no substituent in the 3,3′-positions to allow a second metal ion access to the salen oxygen atoms. Ligands in which a polyether chain links the 4,4′-positions were prepared and complexed to copper. In addition, acyclic ligands with potential metal coordinating substituents in the 4,4′-positions were prepared and complexed to copper and cobalt. The crystal structure of one of the cobalt complexes shows it to be a trimetallic complex in which a $Co(II)(OAc)_2$ group coordinates to the salen oxygen atoms of two Co(III)(salen)(OAc) units. In contrast, the crystal structure of a Co(salen) complex with *tert*-butyl groups attached to the 3,3′-positions is found to be mononuclear. All of the complexes were tested as asymmetric phase transfer catalysts for the asymmetric alkylation of an alanine methyl ester, forming (*R*)-α-methyl phenylalanine methyl ester with up to 85% ee.

1. Introduction

Salen ligands of general structure **1** are amongst the most versatile ligands available.[1] They are constructed by a modular synthesis from salicylaldehydes and diamines and the structure of both of these components can readily be extensively varied, thus allowing the steric, electronic and physical properties of the ligand to be tuned[2] and facilitating the synthesis of immobilized and recyclable salen complexes.[3] Chiral versions of the ligands are available by a number of methodologies, most commonly by the use of a diamine containing one or more stereocentres[4] or a stereoaxis,[5] though the introduction of axial[6] or planar[7] chirality within the salicylaldehyde unit is also possible. Most commonly, the two salicylaldehyde units are identical and the diamine is C_2-symmetrical so that the ligand is also C_2-symmetrical.[8] However, C_1-symmetrical salen ligands can also be prepared by the use of a C_1-symmetrical diamine[9,10] and/or two different salicylaldehydes.[9]



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Once formed, salen ligands are known to form mononuclear complexes with over 40 metals from lithium[11] to uranium[12] and these complexes can have various geometries[13] including square-planar (with varying degrees of distortion towards tetrahedral),[14] square-based pyramidal[15,16] and octahedral.[16,17] In the latter case, the salen ligand can occupy four coplanar coordination sites (giving a *trans*-geometry), or it can occupy four coordination sites, which are not all coplanar, resulting in the formation of *cis*-α and *cis*-β geometries, which are intrinsically chiral at the metal ion.[18]

The versatility of salen ligands is further enhanced by their ability to form bi- or poly-metallic complexes of various forms. Most simply, this can be achieved by coordination of one[19] or both[20] of the salen oxygen atoms to a second metal, giving complexes of general structure **2a** and **2b**, respectively, a situation, which is most common when M^1 forms a four-coordinate salen complex. In addition, the metals may be coordinated through one or two ancillary ligands giving structures **3a**,**b** depending on whether M^1 and M^2 share one[16,21] or two bridging ligands.[22] It is also possible to use the ancillary ligand to bridge between a metal(salen) unit and a different metal(ligand) unit.[23] Finally, additional functional groups may be introduced onto the salen ligand to coordinate to a second metal. Examples of this include polyether macrocycles **4**[24] and **5**[25] and phenoxy-derivatives in which the *ortho*-oxygen atoms may be alkylated[26] **6a** or deprotonated[27] **6b**. Simultaneous use of more than one of the above coordination modes to form bimetallic complexes is also possible.[28]

Much of the interest in metal(salen) complexes in recent years has focused on their applications as asymmetric catalysts,[2,3,5,6,7a,8,9,11,18,26,27,29] and they display such high levels of

* Corresponding author. Tel.: +44 191 222 7128; fax: +44 191 222 6929; e-mail address: Michael.north@ncl.ac.uk (M. North).

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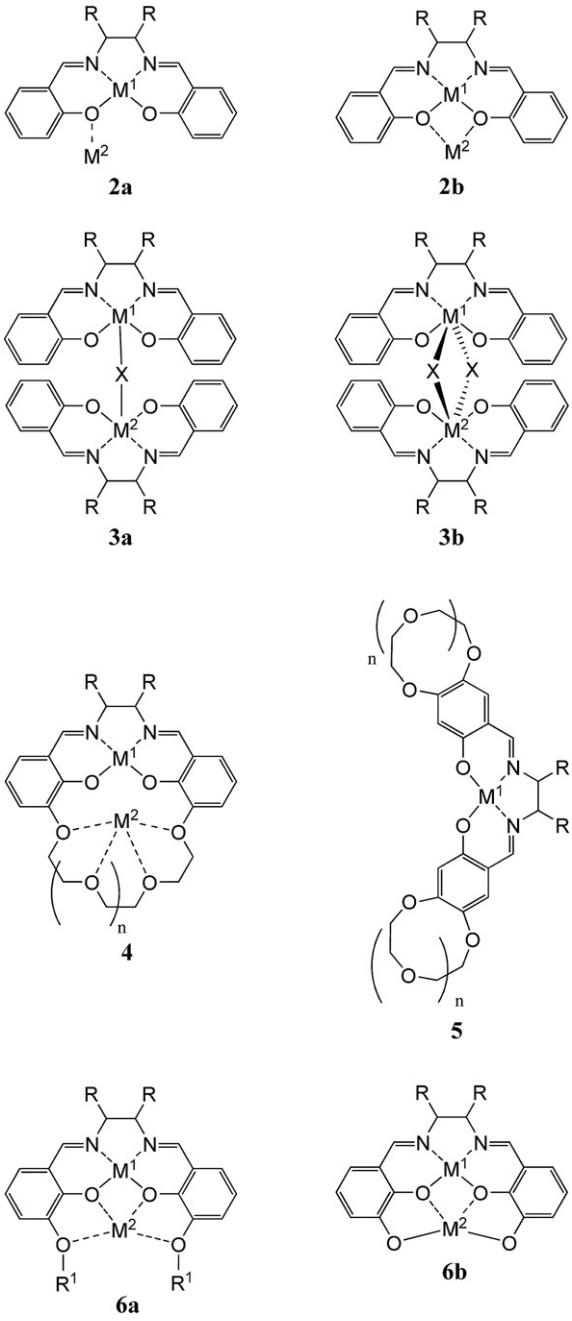
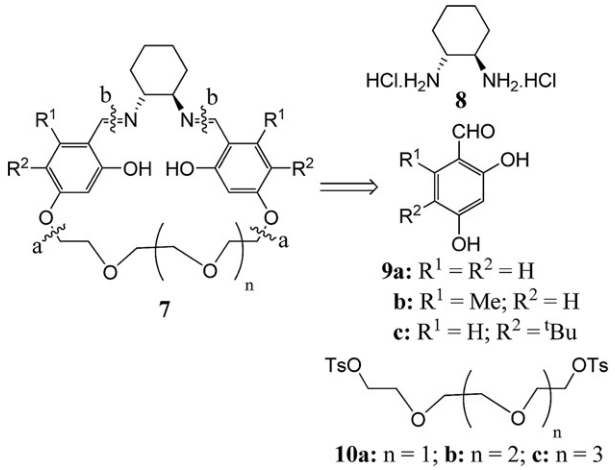
catalytic activity in a wide range of reactions that they are referred to as privileged catalysts.[30] In a number of cases the ability of salen ligands to form bimetallic complexes has been found to be critical to the high level of catalytic activity they display.[26,27,31–38] However, the ability of salen ligands to form polymetallic complexes also gives them other applications in the construction of supramolecular architectures with potential receptor and materials science applications.[39] In view of our previous work on metal salen complexes of type **2b** where the central metal is copper[31,32] or cobalt,[32,33] type **3a** where both metals are aluminium,[34] titanium[16] or vanadium,[35] and type **3b** where both metals are titanium[36] or one is titanium and the other vanadium,[37] we decided to investigate the synthesis of salen ligands designed specifically to bind to two or more metal ions and in this paper we report the results of this study.



2. Results and discussion

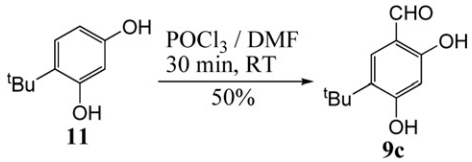
2.1. Macrocyclic salen ligands with a polyether bridge

Our starting point for this project was to develop salen ligands, which also contain polyether macrocycles. Previous work has concentrated on complexes **4** in which the polyether bridges the *ortho*-positions of the salen ligand[24] or **5** in which the polyether linkages do not bridge the salen aromatic rings.[25] However, structure **5** offers limited opportunities for metal–metal interactions and our previous work on copper(salen) and cobalt(salen) complexes has shown that substituents in the *ortho*-positions can prevent bimetallic complex formation.[32,33] Therefore, we decided to target polyether macrocycles **7** in which the polyether linkages are in the *meta*-positions of the salen aromatic rings. Retrosynthetic analysis of structure **7** (Scheme 1) indicated that the macrocyclic structure could be constructed from fragments **8**–**10** by formation of bonds 'a' and 'b'. Since imine formation is a reversible process, it was decided that formation of the salen unit should be the final step of the synthesis to minimize problems due to subsequent hydrolysis and equilibration.



Scheme 1. Retrosynthetic analysis of macrocycles **7**.

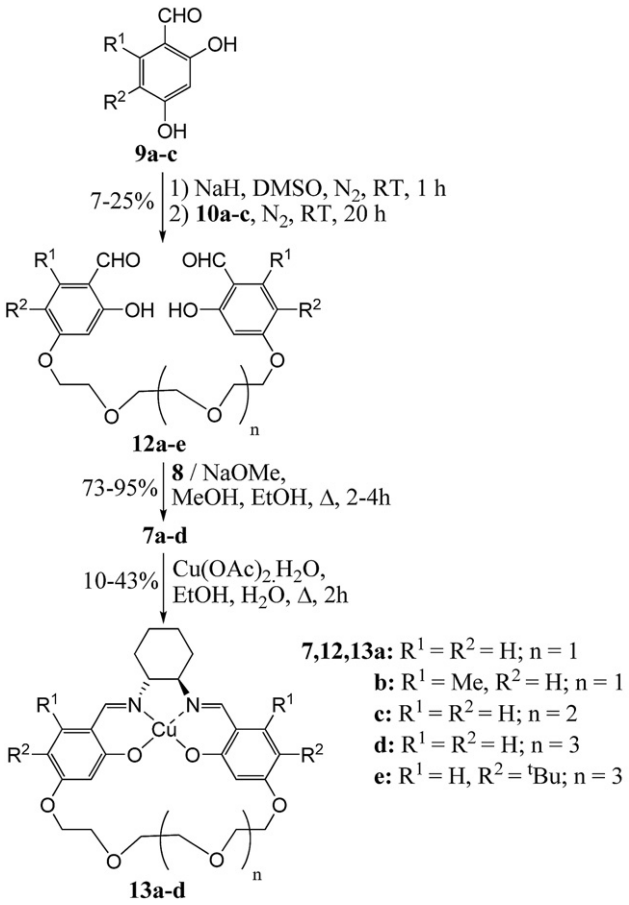
Therefore, the starting point for the synthesis of ligands **7** became aldehydes **9**. Three different aldehydes **9a**–**c** were chosen as starting materials to allow the influence of substituents on the aromatic rings to be investigated. Compound **9a** was commercially available and **9b** was prepared by a literature procedure.[40] Aldehyde **9c** was prepared in 50% yield by the formylation of the known[41] dihydroxybenzene derivative **11** as shown in Scheme 2.



Scheme 2. Synthesis of aldehyde **9c**.

Rather than rely on a lengthy protection/deprotection strategy for the selective alkylation of the 4-phenoxy group in aldehydes **9a**–**c**, it was decided instead to rely on alkylation occurring selectively at the less hindered 4-phenoxy group. Therefore, aldehydes **9a**–**c** were treated with sodium hydride in DMSO followed by the

addition of a bis-tosylate **10a**–**c** to give a set of five bis-aldehydes **12a**–**e** (Scheme 3). In all cases, the yields of bis-aldehydes **12a**–**e** were low (7–25%) due to formation of byproducts in which alkylation had occurred at the 2-phenoxy group, but the desired product could be separated from the regioisomers by column chromatography. Notably, the lowest yield was obtained for compound **12e**, which is probably due to the large *tert*-butyl group in the 5-position hindering the desired alkylation of the 4-phenoxy group in this case. In the case of compounds **12a**,**c**, the regiochemistry of the alkylation was proven by NOESY experiments, which showed cross-peaks between the $ArOCH_2CH_2$ hydrogens and the protons in both positions 3 and 5 of the aromatic ring.



Scheme 3. Synthesis of copper complexes **13a**–**d**.

The low yield obtained for the production of bis-aldehyde **12e** prevented its further manipulation. However, treatment of bis-aldehydes **12a**–**d** with (*R*,*R*)-1,2-diaminocyclohexane dihydrochloride[42] **8** in refluxing methanol and ethanol gave macrocyclic salen ligands **7a**–**d** in 73–95% yield. Salen ligands **7a**–**d** were found to have only low solubility in a range of organic solvents. The solubility was not improved by alkylation of the aromatic ring (**7b**), but did increase as the size of the polyether chain increased. This permitted a study of the stability of ligands **7c** and **7d** in chloroform and in both cases, the ligands were found to be unstable in solution, equilibrating to a mixture of cyclic monomers, dimers and trimers, through reversible hydrolysis of the imine bonds.

Only a preliminary study of the ability of ligands **7a**–**d** to form metal complexes has been carried out. However, each of ligands **7a**–**d** was found to form a paramagnetic copper(II) complex **13a**–**d** when treated with copper(II) acetate. Complexes **13a**–**d** were isolated in 10–43% yield, which probably reflects the poor solubility of both the ligands and the copper complexes. The electrospray mass spectra of complexes **13a**,**c**,**d** all showed M+Na peaks, suggesting that the polyether chain can coordinate to a sodium ion resulting in the formation of a heterobimetallic complex. In addition, the mass spectrum of complex **13c** showed peaks corresponding to 2M+Na and 3M+Na, providing further evidence for the formation of cyclic dimer and trimer from ligand **7c** in solution.

2.2. Salen ligands with potential metal-complexing groups in the 4 and 4′-positions

In view of the poor solubility encountered for ligands **7a**–**d** and their corresponding copper complexes **13a**–**d**, it was decided to investigate a different approach to the synthesis of salen ligands capable of binding two metal ions. This is shown in Fig. 1 and involves the introduction of flexible groups onto the 4-position of the salen aromatic rings, terminated by a donor group capable of coordinating to a metal ion. Five potential metal-complexing groups were selected. Three of these have a methoxy group at the end of a long alkyl chain (containing 8–12 carbon atoms) and are based on the known ability of methoxy groups in complexes of type **6a** to coordinate to a metal ion.[26] The introduction of a benzylic alcohol into the 4-position was also investigated by analogy with complexes **6b**,[27] and the introduction of a polyether chain was felt to mimic macrocycles **4** and **7**.[24]

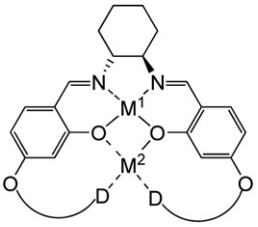
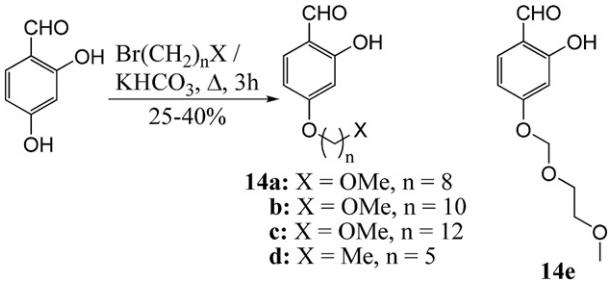
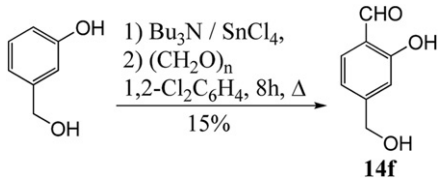


Fig. 1. Design of non-macrocyclic, bimetallic salen complexes.

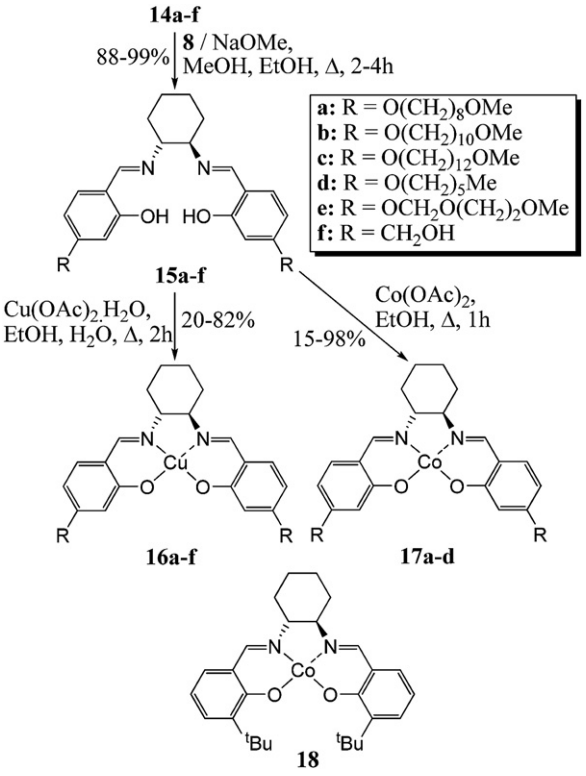
Aldehydes **14a**–**d** were prepared by the alkylation of 2,4-dihydroxybenzaldehyde using potassium hydrogen carbonate as base[43] as shown in Scheme 4. Aldehyde **14d** was included in this study as a control compound lacking a potential metal-coordinating group at the end of the alkyl chain. Known aldehyde **14e** was prepared by the literature procedure[44] and aldehyde **14f** was prepared by the formylation[45] of 3-hydroxymethylphenol in 1,2-dichlorobenzene (Scheme 5). Each of aldehydes **14a**–**f** was then converted into the corresponding salen ligand **15a**–**f** in 88–99% yield by treatment with compound **8** in the presence of sodium methoxide (Scheme 6). Ligands **15a**–**f** were each complexed to copper by treatment with



Scheme 4. Synthesis of aldehydes **14a**–**d**.



Scheme 5. Synthesis of aldehyde **14f**.



Scheme 6. Synthesis of ligands **15a**–**f** and their metal(II) complexes.

copper(II) acetate to give copper complexes **16a**–**f**. The complexes were isolated in good yield (67–82%) except for complex **16f**, which was isolated in only 20% yield due to the high solubility of the copper complex.

Ligands **15a**–**d** were also converted into the corresponding Co(salen) complexes **17a**–**d** by treatment with anhydrous cobalt(II) acetate. For comparison, Co(II)(salen) complex **18** with *tert*-butyl groups in the 3 and 3′-positions of the salen ligand was also prepared by metallation of the known[22f,46] salen ligand using the same methodology. Complexes **17a** and compound **18** were found to form crystals suitable for analysis by X-ray crystallography. **18** is a mononuclear square-planar complex with a structure that is essentially identical to those of other Co(II)(salen) complexes[13b,32a,47] and other square-planar M(II)(salen) complexes previously reported. The structure of one of the four independent molecules of the asymmetric unit is shown in Fig. 2. The four molecules are related in pairs by pseudo-inversion symmetry, the *R* chirality of all the ligand chiral centres leading to conformations of the cyclohexane rings that break this pseudo-symmetry. Two of the molecules show significantly greater twisting and folding deviations from ideal square-planar geometry than the other two, but in other respects the molecules have essentially identical geometry.

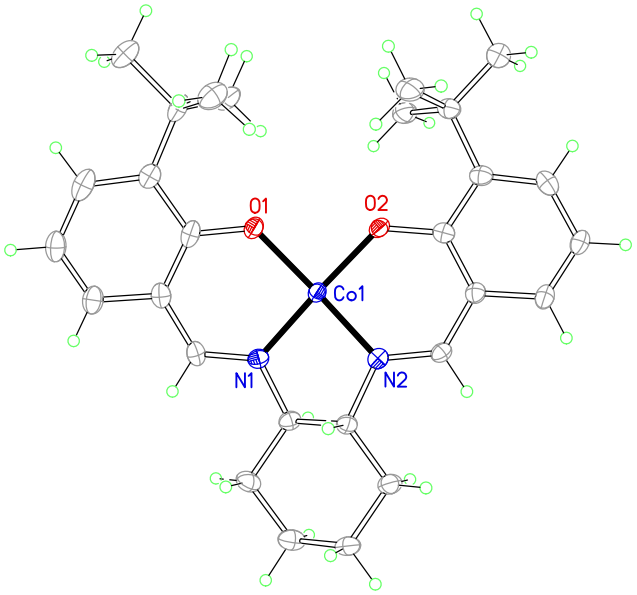


Fig. 2. The structure of one molecule of complex **18**, with 40% probability displacement ellipsoids and selective atom labelling.

In contrast, the structure of complex **17a** is much more complex (Fig. 3). The molecular structure is trimetallic, consisting of two Co(III)(salen)(acetate) units joined by a Co(II)(acetate)$_2$ unit. Each cobalt ion is octahedral and the Co(salen) units adopt the *trans*-geometry. The central cobalt ion is coordinated by the salen oxygen atoms of both salen ligands (cf. **2b**), and two of the acetate units bridge between the central cobalt and the Co(salen) units while the

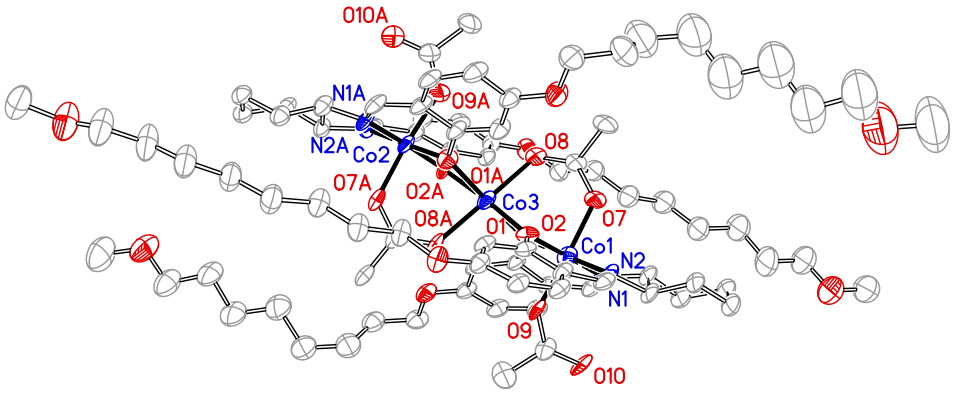


Fig. 3. Molecular structure of complex **17a** from X-ray crystallography, with 40% probability displacement ellipsoids. H atoms are omitted for clarity. The selective atom labelling shown emphasizes the pseudo-inversion symmetry of the molecule, broken principally by the identical rather than opposite absolute configurations of the two cyclohexanediamine units. While the view chosen for Fig. 2 is perpendicular to the salen coordination plane, here it is at right-angles, looking in the salen coordination plane of both the outer cobalt atoms.

other two are bonded terminally as monodentate ligands to the outer cobalt atoms. The acetate units present in the complex come from the cobalt(II) acetate used for its synthesis. The molecule has almost exact inversion symmetry, the *R*,*R* chirality of the two salen ligands being almost the only exception. A simplified representation of the structure is shown in Fig. 4. This type of trimetallic structure for Co(salen) complexes has been reported before, but only for complexes with no substituents in the 3- and 3′-positions of the salen aromatic rings,[48] and can give rise to complexes with urease inhibitory activity.[48e] Complex **17a** is also the only known chiral example of this type of structure. Thus, the contrasting structures of complexes **17a** and **18** clearly illustrate how substituents in the 3- and 3′-position of a salen ligand prevent the coordination of a second metal to the oxygen atoms of an M(salen) complex.

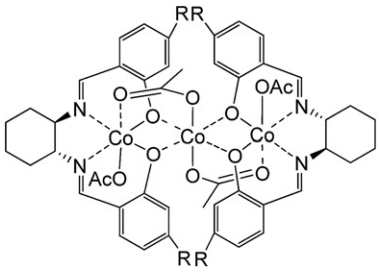
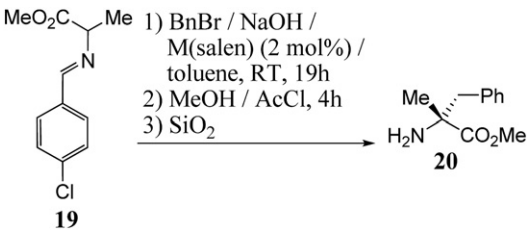


Fig. 4. Representation of the trimetallic molecular structure of complex **17a**. R=O(CH$_2$)$_8$OMe.

2.3. Catalytic activity of the metal(salen) complexes

We have previously reported that Cu(salen) and Co(salen) complexes make highly effective solid–liquid asymmetric phase transfer catalysts for the alkylation of amino acid enolates, using sodium hydroxide as a base and leading to enantiomerically enriched α,α-disubstituted amino acids.[31,32] The highest levels of catalytic activity were displayed by catalysts, which lacked substituents in the 3 and 3′-positions of the salen ring, suggesting that the formation of heterobimetallic complexes of type **2a** or **2b** may be important to the catalytic activity. Therefore, copper complexes **13a**–**d** and **16a**–**f** along with cobalt complexes **17a**–**d** were screened as catalysts for the alkylation of substrate **19**, leading to α-methyl-phenylalanine methyl ester **20** as shown in Scheme 7, and the results are tabulated in Table 1.



Scheme 7. Use of M(salen) complexes as asymmetric phase transfer catalysts.

Macrocyclic complexes **13a**–**d** were all found to show negligible levels of asymmetric induction (Table 1, entries 1–4) and the product that was formed in these reactions probably arises from the uncatalysed background reaction. The lack of catalytic activity displayed by complexes **13a**–**d** is probably due to their poor solubilities. In contrast, copper complexes **16a**–**d** with substituents in the 4 and 4′-positions of the salen rings are highly enantioselective catalysts (Table 1, entries 5–8). Notably, the asymmetric induction

Table 1
Synthesis of α-methyl phenylalanine methyl ester **20**

Entry	Catalyst	Yield	ee[a]
1	**13a**	41	2 (*R*)
2	**13b**	30	7 (*R*)
3	**13c**	30	7 (*R*)
4	**13d**	71	6 (*R*)
5	**16a**	94	85 (*R*)
6	**16b**	73	79 (*R*)
7	**16c**	74	75 (*R*)
8	**16d**	98	79 (*R*)
9	**16e**	62	57 (*R*)
10	**16f**	61	6 (*R*)
11	**17a**	72	53 (*R*)
12	**17b**	42	55 (*R*)
13	**17c**	48	38 (*R*)
14	**17d**	78	74 (*R*)

[a] Determined by ^{1}H NMR analysis of the diastereomeric ureas formed on treatment of product **20** with (*S*)-phenylethylisocyanate.

depends on the length of the methoxyalkyl chain, with complex **16a** bearing the shortest chain giving the highest asymmetric induction (Table 1, entry 5). Lengthening the methoxyalkyl chain (Table 1, entries 6 and 7) or removing the methoxy group (Table 1, entry 8), results in a decrease in the asymmetric induction. These results support the supposition that the methoxy groups can facilitate formation of a heterobimetallic complex as shown in Fig. 1, though the effect on the catalytic activity of the complexes is not dramatic. Complex **16e** with a polyether chain is a less enantioselective catalyst (Table 1, entry 9), and catalyst **16f** with hydroxymethyl substituents displays negligible asymmetric induction.

Cobalt complexes **17a**–**d** all display moderate levels of catalytic activity (Table 1, entries 11–14). Interpretation of these results is complicated since complex **17a** is known to exist as a mixed Co(II)/Co(III) trimetallic complex in the solid state, and how, if at all, this dissociates in situ is not known. The solid state structures of complexes **17b**–**d** have not been determined.

3. Conclusions

A series of macrocyclic and acyclic salen complexes bearing substituents at the 4 and 4′-positions, but with no substituents at the 3 and 3′-positions, have been prepared. The substituents were designed to facilitate the formation of polymetallic complexes and the X-ray crystal structure of a cobalt complex of one of the acyclic complexes confirms the formation of a trimetallic complex. The copper and cobalt complexes of the salen ligands were tested as asymmetric phase transfer catalysts and a copper complex with O(CH$_2$)$_8$OMe substituents in the 4 and 4′-positions was found to display the highest level of asymmetric induction.

4. Experimental

4.1. General

Chromatographic separations were performed with silica gel 60 (230–400 mesh) and thin-layer chromatography was performed on polyester-backed sheets coated with silica gel 60 F_{254}, both supplied by Merck. Melting points were determined with Barnstead Electrothermal apparatus No IA9100. Optical rotations were recorded on a Perkin–Elmer 343 or a PoLARR 2001 polarimeter in a thermostated cell of length 1 dm at 20 °C using the sodium D-line, and a suitable solvent that is reported along with the concentration (in g/100 ml). Infrared spectra were recorded on a Perkin–Elmer FT-IR Paragon 1000 spectrometer from a thin film between NaCl plates in the reported solvent, or from KBr discs. The characteristic absorption is reported as strong (s), medium (m) or weak (w).

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 360 spectrometer, (^{1}H 360 MHz, ^{13}C 90 MHz) or a Jeol-Lambda (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometer. All spectra were recorded at room temperature and the solvent for a particular spectrum is given in parentheses. ^{1}H and ^{13}C NMR spectra were referenced to TMS and chemical shift (δ) values, expressed in parts per million (ppm), are reported downfield of TMS. The multiplicity of signals is reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br) or a combination of any of these. Coupling constant values (J) are given in hertz. Low- and high-resolution mass spectra were recorded at the EPSRC national service at the University of Wales, Swansea, or on a Bruker Apex III FTMS or Jeol AX505 W spectrometer within the Chemistry Department at King's College London. The sample was ionized by electron ionization (EI), chemical ionization (CI), fast atom bombardment (FAB) or electrospray ionization (ESI). The major fragment ions are reported and only the molecular ions are assigned.

X-ray single-crystal diffraction data were collected for complex **18** using a Bruker SMART 1K diffractometer with Mo Kα radiation (λ=0.71073 Å) at 150 K. The small and weakly diffracting crystals of complex **17a** required the use of synchrotron radiation at station 9.8 of the SRS at Daresbury Laboratory (λ=0.6893 Å), measurements being made at 120 K. Standard Bruker control and integration software was used, and the structures were solved and refined with SHELXTL.[49] Data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ (see http://www.ccdc.cam.ac.uk/products/csd/request/) with reference numbers CCDC 835278 and 835279.

4.2. Synthesis of polyethers 12a–e

*4.2.1. 2,4-Dihydroxy-5-tert-butylbenzaldehyde (**9c**).* Phosphorus oxychloride (1.4 mL) was added dropwise to DMF (37 mL) with rapid stirring over 30 min whilst keeping the reaction temperature below 10 °C. A solution of 3-hydroxy-4-*tert*-butylphenol[41] **11** (14.1 g, 85.0 mol) in DMF (38 mL) was then slowly added, keeping the temperature below 10 °C. The reaction was warmed to room temperature and stirred for 1 h. Then ice and 10% aqueous NaOH were added to adjust the pH to 9–10, resulting in formation of a solid. This mixture was heated to reflux for 10 min and then adjusted to pH 3 with 10% aqueous HCl. After cooling to room temperature, the mixture was left overnight. The solid product was collected by filtration, washed with water until neutral, dried and purified by column chromatography using hexane/$CHCl_3$ (70:30) to give compound **9c** (1.495 g, 50%) as a soft orange solid. R_f (11% Et_2O/hexane) 0.22; ν_{max} (KBr) 3330 (br), 2970 (w), 1644 (s) and 1510 cm^{-1} (w); δ_H ($CDCl_3$) 1.32 (9H, s, $(CH_3)_3$), 5.75 (1H, s, OH), 6.23 (1H, s, ArCH), 7.31 (1H, s, ArCH), 9.64 (1H, s, CHO), 11.17 (1H, s, OH); δ_C ($CDCl_3$) 30.0, 34.5, 105.4, 115.1, 130.2, 133.4, 162.7, 163.3, 195.3; m/z (CI, NH_3) 212 ($M+NH_4^+$, 68) 195 (MH^+, 100) 179 (19); HRMS (ES): $M+Na^+$, found 217.0840. $C_{11}H_{14}NaO_3$ requires 217.0835.

*4.2.2. O,O′-(3-Hydroxy-4-formylphenyl) triethylene glycol (**12a**).* To a suspension of NaH (0.47 g, 15.92 mmol) in dry DMSO (10 mL) under nitrogen, a solution of 2,4-dihydroxybenzaldehyde **9a** (1.00 g, 7.24 mmol) in dry DMSO (6 mL) was added dropwise with vigorous stirring whilst keeping the temperature below 25 °C. The resulting brown solution was stirred for 1 h. Then a solution of triethylene glycol ditosylate **10a** (1.65 g, 3.62 mmol) in dry DMSO (5 mL) was added in one portion and the resulting mixture stirred for 20 h. Subsequently, water (200 mL) was added, and the resulting brown solution was acidified with 6 M HCl to pH 1, whereupon the solution became milky yellow. The aqueous mixture was extracted with $CHCl_3$ (5×40 mL). The combined organic layers were washed with a solution of 1 M HCl (200 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product was purified by column chromatography (Et_2O) to give two fractions. The first was compound **12a** obtained as a white solid and the second was a mixture of compound **12a** and the 2,2-dialkylated regioisomer, which could be separated by recrystallization from $CHCl_3$/Et_2O to give compound **12a** (350 mg, 25%) as a white solid. R_f (Et_2O) 0.40; ν_{max} ($CHCl_3$) 1634 (s) and 1505 (m) cm^{-1}; δ_H ($CDCl_3$) 3.68 (4H, s, $ArOCH_2CH_2OCH_2$), 3.81 (4H, t J 4.6 Hz, $ArOCH_2CH_2$), 4.10 (4H, t J 4.6 Hz, $ArOCH_2$), 6.35 (2H, d J 2.3 Hz, ArH), 6.48 (2H, dd J 8.6, 2.3 Hz, ArH), 7.34 (2H, d J 8.6 Hz, ArH), 9.64 (2H, s, CHO), 11.39 (2H, s, OH); δ_C ($CDCl_3$) 66.3, 69.8, 71.3, 101.7, 109.1, 115.7, 135.6, 164.8, 166.3, 194.8; m/z (CI, NH_3) 391 (MH^+, 100), 408 (52), 392 (24); HRMS (ES): $M+Na^+$, found 413.1204. $C_{20}H_{22}NaO_8$ requires 413.1206.

*4.2.3. O,O′-(3-Hydroxy-4-formyl-5-methylphenyl) triethylene glycol (**12b**).* To a suspension of NaH (0.30 g, 7.66 mmol) in dry DMSO (6 mL) under nitrogen, a solution of 2,4-dihydroxy-6-methylbenzaldehyde[40] **9b** (0.53 g, 3.48 mmol) in dry DMSO (5 mL) was added dropwise with vigorous stirring. The temperature was kept under 25 °C and the resulting brown solution was stirred for 1 h. Then a solution of triethylene glycol ditosylate **10a** (0.80 g, 1.74 mmol) in dry DMSO (8 mL) was added in one portion and the resulting mixture was stirred for 20 h. Subsequently, water (150 mL) was added, and the resulting brown solution was acidified with 6 M HCl to pH 1, whereupon the solution became milky yellow. The aqueous mixture was extracted with $CHCl_3$ (5×40 mL). The combined organic layers were washed with a solution of 1 M HCl (150 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by column chromatography (5/1: Et_2O/$CHCl_3$) to give compound **12b** (320 mg, 10%) as a white solid. R_f (17% $CHCl_3$/Et_2O) 0.51; ν_{max} (KBr) 3435 (br), 3019 (s), 2400 (w) and 1630 cm^{-1} (m); δ_H ($CDCl_3$) 2.53 (6H, s, CH_3), 3.76 (4H, s, $ArOCH_2CH_2OCH_2$), 3.87 (4H, t J 4.5 Hz, $ArOCH_2CH_2$), 4.16 (4H, t J 4.5 Hz, $ArOCH_2$), 6.26 (2H, d J 2.3 Hz, ArH), 6.26 (2H, d J 2.3 Hz, ArH), 10.10 (2H, s, CHO), 12.46 (2H, s, OH); δ_C ($CDCl_3$) 18.7, 68.0, 69.8, 71.3, 99.6, 111.3, 113.8, 144.2, 166.3, 166.8, 193.3; m/z (ES) 441 ($M+Na^+$, 100), 353 (19); HRMS (ES): $M+Na^+$, found 441.1517. $C_{22}H_{26}NaO_8$ requires 441.1519.

*4.2.4. O,O′-(3-Hydroxy-4-formylphenyl) tetraethylene glycol (**12c**).* To a suspension of NaH (6.33 g, 159.28 mmol) under nitrogen in dry DMSO (125 mL), a solution of 2,4-dihydroxybenzaldehyde **9a** (10.00 g, 72.40 mmol) in dry DMSO (70 mL) was added dropwise with vigorous stirring. The temperature was kept below 25 °C and the resulting brown solution was stirred for 1 h. Then a solution of tetraethylene glycol ditosylate **10b** (18.19 g, 36.20 mmol) in dry DMSO (40 mL) was added in one portion and the resulting mixture was stirred for 20 h. Subsequently, water (700 mL) was added, and the resulting brown solution was acidified with 6 M HCl to pH 1, whereupon the solution became milky yellow. The aqueous mixture was extracted with $CHCl_3$ (4×200 mL). The combined organic layers were washed with a solution of 1 M HCl (400 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by column chromatography (Et_2O followed by Et_2O/$CHCl_3$ (5:1)) to give compound **12c** (3.70 g, 23%) as an orange oil; R_f (17% $CHCl_3$/Et_2O) 0.23; ν_{max} ($CHCl_3$) 2252 (w), 1635 (m) and 1507 cm^{-1} (m); δ_H ($CDCl_3$) 3.71–3.85 (8H, m, $ArOCH_2CH_2OCH_2CH_2$), 3.88 (4H, t J 4.6 Hz, $ArOCH_2CH_2$), 4.18 (4H, t J 4.6 Hz, $ArOCH_2$), 6.43 (2H, d J 2.3 Hz, ArH), 6.57 (2H, dd J 8.7, 2.3 Hz, ArH), 7.44 (2H, d J 8.7 Hz, ArH), 9.73 (2H, s, CHO), 11.48 (2H, s, OH); δ_C ($CDCl_3$) 68.3, 69.7, 71.1, 71.3, 101.7, 109.1, 115.7, 135.6, 164.8, 166.4, 194.8; m/z (EI) 434 (M^+, 100), 297 (29), 252 (37), 226 (44), 208 (52), 164 (61), 139 (30), 105 (16); HRMS (ES): $M+Na^+$, found 457.1475. $C_{22}H_{26}NaO_9$ requires 457.1469.

*4.2.5. O,O′-(3-Hydroxy-4-formylphenyl) pentaethylene glycol (**12d**).* To a suspension of NaH (6.33 g, 159.28 mmol) under nitrogen in dry DMSO (125 mL), a solution of 2,4-dihydroxybenzaldehyde **9a** (10.00 g, 72.40 mmol) in dry DMSO (70 mL) was added dropwise with

vigorous stirring. The temperature was kept below 25 °C and the resulting brown solution was stirred for 1 h. Then a solution of pentaethylene glycol ditosylate **10c** (19.79 g, 36.20 mmol) in dry DMSO (40 mL) was added in one portion and the resulting mixture was stirred for 20 h. Subsequently, water (700 mL) was added, and the resulting brown solution was acidified with 6 M HCl to pH 1, whereupon the solution became milky yellow. The aqueous mixture was extracted with $CHCl_3$ (4×200 mL). The combined organic layers were washed with a solution of 1 M HCl (400 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by column chromatography ($CHCl_3$/EtOAc, 1:1) to give compound **12d** (3.45 g, 20%) as a soft orange oil; R_f (50% $CHCl_3$/EtOAc) 0.26; ν_{max} ($CHCl_3$) 3019 (w), 2400 (w), 1630 (m) and 1508 cm^{-1} (s); δ_H ($CDCl_3$) 3.62–3.77 (12H, m, $ArOCH_2CH_2OCH_2CH_2OCH_2$), 3.87 (4H, t *J* 4.9 Hz, $ArOCH_2CH_2$), 4.18 (4H, t *J* 4.9 Hz, $ArOCH_2$), 6.43 (2H, d *J* 2.2 Hz, ArH), 6.57 (2H, dd *J* 8.6, 2.2 Hz, ArH), 7.74 (2H, d *J* 8.6 Hz, ArH), 9.72 (2H, s, CHO), 11.47 (2H, s, OH); δ_C ($CDCl_3$) 68.3, 69.7, 71.0, 71.0, 71.3, 101.7, 109.1, 115.6, 135.6, 164.8, 166.4, 194.8; *m*/*z* (CI, NH_3) 496 ($M+NH_4^+$, 100), 376 (28), 358 (12), 332 (7); HRMS (ES): $M+Na^+$, found 501.1674. $C_{24}H_{30}NaO_{10}$ requires 501.1686.

*4.2.6. O,O′-(2-tert-Butyl-4-formyl-5-hydroxy phenyl) pentaethylene glycol (**12e**).* To a suspension of NaH (0.13 g, 3.40 mmol) in dry DMSO (4 mL) under nitrogen, a solution of 2,4-dihydroxy-5-*tert*-butyl-benzaldehyde **9c** (0.30 g, 1.54 mmol) in dry DMSO (1.5 mL) was added dropwise with vigorous stirring. The temperature was kept below 25 °C and the resulting brown solution was stirred for 1 h. Then a solution of pentaethylene glycol ditosylate **10c** (0.42 g, 0.77 mmol, 1 equiv) in dry DMSO (4 mL) was added in one portion and this mixture was stirred for 20 h. Subsequently, water (40 mL) was added, and the resulting brown solution was acidified with 6 M HCl to pH 1, whereupon the solution became milky yellow. The aqueous mixture was extracted with $CHCl_3$ (5×10 mL). The combined organic layers were washed with a solution of 1 M HCl (40 mL) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by column chromatography (Et_2O/hexane: 70/30) to give compound **12e** (20 mg, 7%) as a soft green oil; R_f (30% hexane/Et_2O) 0.51; ν_{max} ($CHCl_3$) 3019 (m), 2963 (w), 2400 (w), 1639 (s) and 1582 cm^{-1} (w); δ_H($CDCl_3$) 1.29 (18H, s, $(CH_3)_3$), 3.51–3.61 (8H, m, $ArOCH_2CH_2OCH_2CH_2OCH_2$), 3.63 (4H, t *J* 2.4 Hz, $ArOCH_2CH_2OCH_2$), 3.83 (4H, t *J* 4.5 Hz, $ArOCH_2CH_2$), 4.09 (4H, t *J* 4.5 Hz, $ArOCH_2$), 6.31 (2H, s, ArH), 7.28 (2H, s, ArH), 9.63 (2H, s, CHO), 11.29 (2H, s, OH); δ_C ($CDCl_3$) 30.1, 34.7, 67.9, 69.7, 71.0, 71.1, 71.1, 100.4, 114.4, 131.5, 131.9, 163.2, 165.4, 195.2; *m*/*z* (CI, NH_3) 608 ($M+NH_4^+$, 100), 413 (11), 69 (15); HRMS (ES): $M+Na^+$, found 613.2987. $C_{32}H_{46}NaO_{10}$ requires 613.2983.

4.3. General procedure for the synthesis of ligands 7a–d

To a stirred mixture of bis-aldehyde **12a–d** (10.0 mmol) and (*R*,*R*)-1,2-diaminocyclohexane dihydrochloride[42] **8** (1.87 g, 10.0 mmol) in MeOH (37 mL) and EtOH (37 mL) was added NaOMe (1.26 g, 23.3 mmol) dissolved in MeOH (5 mL) at room temperature. The resulting bright yellow solution was stirred under reflux overnight. Subsequently, the reaction mixture was allowed to cool to room temperature and then filtered and evaporated in vacuo. The yellow residue was taken up in CH_2Cl_2 (80 mL), filtered and then the organic layers were washed with water (2×30 ml) and brine (1×30 ml). The combined aqueous layers were back-extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated to dryness to leave ligands **7a–d**.

*4.3.1. Compound **7a**.* Obtained as a hard yellow gel in 87% yield. $[\alpha]_D^{20}$ −567 (*c* 0.035, $CHCl_3$); ν_{max} ($CHCl_3$) 3435 (br), 3019 (m), 1627 (s) and 1515 cm^{-1} (w); δ_H ($CDCl_3$) 1.50–2.05 (8H, m, $NCHCH_2CH_2$), 3.20–3.33 (2H, m, NCH), 3.70 (4H, s, $ArOCH_2CH_2OCH_2$), 3.80 (4H, br, $ArOCH_2CH_2$), 4.06 (4H, br, $ArOCH_2$), 6.21–6.32 (4H, m, 2× ArH), 6.97 (2H, d *J* 8.7 Hz, ArH), 8.08 (2H, s, CH=N), 13.81 (2H, s, OH); δ_C ($CDCl_3$) 24.6, 33.1, 67.5, 69.6, 71.0, 71.4, 101.8, 102.4, 106.6, 106.8, 132.9, 133.3, 162.6; *m*/*z* (ES) 469 (MH^+,100), 341 (32), 295 (27), 259 (38), 255 (73); HRMS (ES): MH^+, found 469.2334. $C_{26}H_{33}N_2O_6$ requires 469.2333.

*4.3.2. Compound **7b**.* Obtained as a yellow gel in 73% yield. $[\alpha]_D^{20}$ −578 (*c* 0.1, $CHCl_3$); ν_{max} ($CHCl_3$) 2938 (m), 2360 (m), 2253 (s), 1614 (s) and 1457 cm^{-1} (m); δ_H ($CDCl_3$) 1.54–2.68 (8H, m, $NCHCH_2CH_2$), 2.13 (6H, s, CH_3), 3.21–3.25 (2H, m, NCH), 3.71 (4H, s, $ArOCH_2CH_2OCH_2$), 3.82 (4H, t *J* 4.9 Hz, $ArOCH_2CH_2$), 4.06 (4H, t *J* 4.9 Hz, $ArOCH_2$), 6.09 (2H, s, ArH), 6.17 (2H, s, ArH), 8.27 (2H, s, CH=N), 14.63 (2H, s, OH); δ_C ($CDCl_3$) 19.1, 24.6, 33.2, 67.5, 69.9, 71.1, 71.2, 100.3, 109.2, 110.4, 141.1, 161.9, 163.3, 168.4; *m*/*z* (CI, NH_3) 497 (MH^+, 6); HRMS (ES): MH^+, found 497.2638. $C_{28}H_{37}N_2O_6$ requires 497.2646.

*4.3.3. Compound **7c**.* Obtained as a yellow oil in 95% yield. $[\alpha]_D^{20}$ −320 (*c* 0.017, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (br), 2938 (w), 1627 (s) and 1515 cm^{-1} (w); δ_H ($CDCl_3$) 1.51–2.03 (8H, m, $NCHCH_2CH_2$), 3.21–3.26 (2H, m, NCH), 3.70–3.80 (8H, m, $ArOCH_2CH_2OCH_2CH_2$), 3.80 (4H, t *J* 5.0 Hz, $ArOCH_2CH_2$), 4.07 (4H, t *J* 4.5 Hz, $ArOCH_2$), 6.31–6.40 (4H, m, 2× ArH), 6.98 (2H, d *J* 8.5 Hz, ArH), 8.08 (2H, s, CH=N), 13.81 (2H, s, OH); δ_C ($CDCl_3$) 24.6, 33.6, 67.8, 69.9, 71.0, 71.2, 72.1, 102.1, 107.1, 112.6, 133.1, 162.9, 164.1, 165.1; *m*/*z* (CI, NH_3) 513 (MH^+, 39), 402 (23), 369 (28), 254 (33), 153 (48) 115 (100); HRMS (ES): $M+Na^+$, found 535.2435. $C_{28}H_{36}N_2NaO_7$ requires 535.2414.

*4.3.4. Compound **7d**.* Obtained as a yellow oil in 86% yield. $[\alpha]_D^{20}$ −724 (*c* 0.021, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (br), 2937 (w), 1627 (s) and 1515 cm^{-1} (w); δ_H ($CDCl_3$) 1.33–2.01 (8H, m, $NCHCH_2CH_2$), 3.21–3.27 (2H, m, NCH), 3.60–3.67 (12H, m, $ArOCH_2CH_2OCH_2CH_2OCH_2$), 3.81 (4H, t *J* 4.8 Hz, $ArOCH_2CH_2$), 4.08 (4H, t *J* 4.4 Hz, $ArOCH_2$), 6.31–6.39 (4H, m, 2× ArH), 6.98 (2H, d *J* 8.4 Hz, ArH), 8.09 (2H, s, CH=N), 13.82 (2H, s, OH); *m*/*z* (CI, NH_3), 558 (MH^+, 22), 511 (14), 441 (14), 403 (14), 349 (16), 274 (16), 222 (17),126 (25) and 115 (100); HRMS (ES): $M+Na^+$, found 579.2675. $C_{30}H_{40}N_2NaO_8$ requires 579.2676.

4.4. General procedure for the synthesis of copper complexes 13a–d

Solutions of salen ligand **7a–d** (0.83 mmol) in EtOH (20 mL) and $Cu(OAc)_2 \cdot H_2O$ (0.17 g, 0.83 mmol) in water (2 mL) were mixed and refluxed with vigorous stirring for 2 h. The resulting solution was then cooled to room temperature, filtered and the precipitate washed successively with H_2O, MeOH and Et_2O (3×10 mL) to provide copper complexes **13a–d**.

*4.4.1. Compound **13a**.* Obtained as a black solid in 42% yield. Mp>400 °C; ν_{max} (KBr) 3435 (br), 1605 (s) and 1524 cm^{-1} (m); HRMS (ES): $M+Na^+$, found 552.1294. $C_{26}H_{30}CuN_2NaO_6$ requires 552.1297.

*4.4.2. Compound **13b**.* Obtained as a brown/green solid in 30% yield. Mp>400 °C; ν_{max} (KBr) 2865 (br), 1605 (s) and 1522 cm^{-1} (m); HRMS (ES): $M+Na^+$, found 580.1619. $C_{28}H_{34}CuN_2NaO_6$ requires 580.1611.

*4.4.3. Compound **13c**.* Obtained as a black solid in 23%. Mp>400 °C; $[\alpha]_D^{20}$ −320 (*c* 0.0056, DMSO); ν_{max} (KBr) 2859 (br), 1605 (s), 1525 (s) and 1428 cm^{-1} (m); *m*/*z* (ES) 596 ($M+Na^+$, 48), 367 (100), 301 (57), 242 (50), 177 (82); HRMS (ES): $M+Na^+$, found 596.1592. $C_{28}H_{34}CuN_2NaO_7$ requires 596.1554. $2M+Na^+$, found 1169.3477. $C_{56}H_{68}Cu_2N_4NaO_{14}$ requires 1169.3222. $3M+Na^+$, found 1742.5299. $C_{84}H_{102}Cu_3N_6NaO_{21}$ requires 1742.4884.

*4.4.4. Compound **13d**.* Obtained as a black solid in 10% yield. Mp>400 °C; $[\alpha]_D^{20}$ −263 (*c* 0.0095, DMSO); ν_{max} (KBr) 3436 (br),

2862 (w), 1606 (s), 1527 (s) and 1485 cm^{-1} (w); *m*/*z* (ES) 640 ($M+Na^+$, 95), 337 (100); HRMS (ES): $M+Na^+$, found 640.1780. $C_{30}H_{38}CuN_2NaO_8$ requires 640.1816.

4.5. General procedure for the synthesis of aldehydes 14a–d

2,4-Dihydroxybenzaldehyde (1.99 g, 14.5 mmol) and the appropriate bromoalkane[50] (14.5 mmol) were dissolved in DMF (20 mL) and $KHCO_3$ (1.45 g, 14.5 mmol) was added. The mixture was heated at reflux for 3 h, then cooled to room temperature and poured into an aqueous 6 N HCl solution (200 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether (3×60 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo. The residue was purified by column chromatography (hexane/acetone: 99/1) to give compounds **14a**–**d**.

*4.5.1. Compound **14a**.* Obtained as a colourless oil in 30% yield. R_f (10% acetone/hexane) 0.21; ν_{max} ($CHCl_3$) 3019 (m), 2932 (w), 2860 (w), 2400 (w), 1630 (m), 1575 (w) and 1508 cm^{-1} (w); δ_H ($CDCl_3$) 1.28–1.53 (10H, m, $(CH_2)_5$), 1.68–1.75 (2H, m, $ArOCH_2CH_2$), 3.26 (3H, s, OCH_3), 3.30 (2H, t *J* 6.5 Hz, $MeOCH_2$), 3.92 (2H, t *J* 6.5 Hz, $ArOCH_2$), 6.34 (1H, d *J* 2.2 Hz, ArH), 6.45 (1H, dd *J* 8.7, 2.2 Hz, ArH), 7.34 (1H, d *J* 8.7 Hz, ArH), 9.63 (1H, s, CHO), 11.41 (1H, s, OH); δ_C ($CDCl_3$) 26.2, 26.4, 29.3, 29.6, 29.7, 30.0, 58.4, 69.0, 73.3, 101.4, 109.2, 115.4, 135.6, 164.9, 166.8, 194.7; *m*/*z* (CI, NH_3) 281 (MH^+, 100); HRMS (ES): MH^+, found 281.1745. $C_{16}H_{25}O_4$ requires 281.1747.

*4.5.2. Compound **14b**.* Obtained as a colourless oil in 40% yield. R_f (10% acetone/hexane) 0.33; ν_{max} ($CHCl_3$) 3417 (br), 3155 (w), 2930 (s), 2856 (w), 2253 (w), 1630 (s), 1576 (w), 1506 (w) and 1467 cm^{-1} (w); δ_H ($CDCl_3$) 1.26–1.60 (14H, m, $(CH_2)_7$), 1.76–1.84 (2H, m, $ArOCH_2CH_2$), 3.34 (3H, s, OCH_3), 3.38 (2H, t *J* 6.6 Hz, $MeOCH_2$), 4.01 (2H, t *J* 6.6 Hz, $ArOCH_2$), 6.42 (1H, d *J* 2.3 Hz, ArH), 6.54 (1H, dd *J* 8.7, 2.3 Hz, ArH), 7.43 (1H, d *J* 8.7 Hz, ArH), 9.72 (1H, s, CHO), 11.49 (1H, s, OH); δ_C ($CDCl_3$) 26.3, 26.5, 29.3, 29.7, 29.8, 29.85, 29.9, 30.0, 59.0, 69.0, 73.3, 101.4, 109.2, 115.4, 135.6, 164.9, 166.9, 194.7; *m*/*z* (EI) 308 (M^+, 100); HRMS (ES): MH^+, found 309.2064. $C_{18}H_{29}O_4$ requires 309.2060.

*4.5.3. Compound **14c**.* Obtained as a colourless oil in 25% yield. R_f (10% acetone/hexane) 0.29; ν_{max} ($CHCl_3$) 3019 (s), 2929 (m), 2857 (w), 2400 (w), 1630 (s) and 1508 cm^{-1} (w); δ_H ($CDCl_3$) 1.29–1.60 (18H, m, $(CH_2)_9$), 1.77–1.84 (2H, m, CH_2), 3.35 (3H, s, OCH_3), 3.38 (2H, t *J* 6.6 Hz, $MeOCH_2$), 4.02 (2H, t *J* 6.6 Hz, $ArOCH_2$), 6.42 (1H, d *J* 2.2 Hz, ArH), 6.54 (1H, dd *J* 8.7, 2.2 Hz, ArH), 7.43 (1H, d *J* 8.7 Hz, ArH), 9.72 (1H, s, CHO), 11.50 (1H, s, OH); δ_C ($CDCl_3$) 26.0, 26.2, 26.4, 29.0, 29.1, 29.4, 29.5, 29.6, 29.7, 29.8, 58.9, 69.0, 73.4, 101.4, 109.2, 115.4, 135.6, 164.9, 166.9, 194.7; *m*/*z* (CI, NH_3) 337 (MH^+, 100); HRMS (ES): MH^+, found 337.2377. $C_{20}H_{33}O_4$ requires 337.2373.

*4.5.4. Compound **14d**[43].* Obtained as an orange gel in 38% yield. R_f (10% EtOAc/heptane) 0.44; ν_{max} ($CHCl_3$) 3019 (m), 2932 (w), 2860 (w), 2400 (w), 1630 (m), 1575 (w) and 1508 cm^{-1} (w); δ_H ($CDCl_3$) 0.92 (3H, t *J* 7.0 Hz, CH_3), 1.31–1.50 (6H, m, $(CH_2)_3$), 1.77–1.85 (2H, m, CH_2), 4.00 (2H, t *J* 6.5 Hz, OCH_2), 6.42 (1H, d *J* 2.3 Hz, ArH), 6.54 (1H, dd *J* 8.6, 2.3 Hz, ArH), 7.44 (1H, d *J* 8.6 Hz, ArH), 9.72 (1H, s, CHO), 11.50 (1H, s, OH); δ_C ($CDCl_3$) 14.4, 22.9, 26.0, 29.3, 31.9, 69.0, 101.4, 109.2, 115.4, 135.6, 164.9, 166.9, 194.2; *m*/*z* (ES) 223 (MH^+, 100); HRMS (ES): MH^+, found 223.1326. $C_{13}H_{19}O_3$ requires 223.1329.

*4.5.5. 2-Hydroxy-4-hydroxymethylbenzaldehyde (**14f**).* To a 50 mL four-necked round-bottom flask equipped with a reflux condenser, mechanical stirrer, thermometer and a nitrogen inlet were added 1,2-dichlorobenzene (20 mL), 3-hydroxymethylphenol (3.99 g, 32.2 mmol), tin(IV) chloride (0.37 mL, 3.22 mmol) and tributylamine (3.07 mL, 12.9 mmol). The mixture was stirred for 20 min at room temperature, then paraformaldehyde (2.12 g, 70.9 mmol) was added. The resulting yellowish solution was heated to 100 °C±5 °C for 8 h. After cooling, the reaction mixture was poured into water (10 mL) and the aqueous phase was extracted with $CHCl_3$ (3×30 ml). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography ($CHCl_3/Et_2O$, 1:1) to give compound **14f** (740 mg, 15%) as a white solid. Mp 78–80 °C; R_f (50% $CHCl_3/Et_2O$) 0.21; ν_{max} ($CHCl_3$) 3434 (br), 3020 (s), 2977 (w), 2400 (m), 1655 (s), 1575 (w) and 1508 cm^{-1} (w); δ_H ($CDCl_3$) 4.77 (2H, s, CH_2), 7.02–7.05 (2H, m, 2× ArH), 7.57 (1H, d *J* 7.7 Hz, ArH), 9.90 (1H, s, CHO), 11.10 (1H, s, OH); δ_C ($CDCl_3$) 64.4, 114.9, 117.7, 119.8, 134.0, 151.1, 161.9, 196.1; *m*/*z* (CI) 152 (MH^+, 100), 135 (16), 123 (63), 95 (60), 77 (78); HRMS (ES): M^+, found 152.0469. $C_8H_8O_3$ requires 152.0468.

4.6. General procedure for the synthesis of ligands 15a–f

To a stirred mixture of aldehyde **14a**–**f** (1.24 mmol) in MeOH (10 mL) was added a solution of (*R*,*R*)-1,2-diaminocyclohexane dihydrochloride[42] (0.13 g, 0.69 mmol) and sodium methoxide (0.074 g, 1.37 mmol) in MeOH (10 mL) at room temperature. The resulting bright yellow solution was stirred at reflux for 2 h. Subsequently, the reaction was allowed to cool to room temperature and the solvent evaporated in vacuo. The residue was dissolved in $CHCl_3$ (35 mL) and washed with water (5×8 mL). The combined aqueous phase was extracted with $CHCl_3$ (8 mL). The combined organic layers were washed with brine (8 mL), dried ($MgSO_4$) and the solvent was removed in vacuo to give ligands **15a**–**f**.

*4.6.1. Compound **15a**.* Obtained as a yellow oil in 90% yield. $[\alpha]_D^{20}$ −528 (*c* 0.0125, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2935 (m), 2960 (w), 1626 (s) and 1515 cm^{-1} (w); δ_H ($CDCl_3$) 1.25–1.89 (32H, br, $(CH_2)_6+CHCH_2CH_2$), 3.13–3.16 (2H, m, NCH), 3.25 (6H, s, OCH_3), 3.28 (4H, t *J* 6.6 Hz, $MeOCH_2$), 3.84 (4H, t *J* 6.5 Hz, $ArOCH_2$), 6.22 (2H, dd *J* 8.5, 2.3 Hz, ArH), 6.25 (2H, d *J* 2.3 Hz, ArH), 6.90 (2H, d *J* 8.5 Hz, ArH), 8.00 (2H, s, CH=N), 13.73 (2H, br, OH); δ_C ($CDCl_3$) 24.9, 26.6, 26.7, 29.7, 29.9, 30.0, 30.3, 33.7, 59.2, 68.6, 72.2, 73.5, 102.2, 107.3, 112.7, 133.3, 163.6, 164.3, 165.5; *m*/*z* (CI), 639 (MH^+, 90), 377 (90), 280 (26), 253 (27), 178 (59), 158 (35), 115 (100); HRMS (ES): MH^+, found 639.4376. $C_{38}H_{59}N_2O_6$ requires 639.4368.

*4.6.2. Compound **15b**.* Obtained as a yellow oil in 93% yield. $[\alpha]_D^{20}$ −530 (*c* 0.01, $CHCl_3$); ν_{max} ($CHCl_3$) 3435 (br), 2930 (m), 2856 (w), 1623 (s) and 1512 cm^{-1} (w); δ_H ($CDCl_3$) 1.21–1.89 (40H, br, $(CH_2)_8+CHCH_2CH_2$), 3.12–3.15 (2H, m, NCH), 3.25 (6H, s, OCH_3), 3.28 (4H, t *J* 6.7 Hz, $MeOCH_2$), 3.83 (4H, t *J* 6.6 Hz, $ArOCH_2$), 6.23 (2H, dd *J* 8.5, 2.3 Hz, ArH), 6.25 (2H, d *J* 2.3 Hz, ArH), 6.90 (2H, d *J* 8.5 Hz, ArH), 8.00 (2H, s, CH=N), 13.73 (2H, br, OH); δ_C ($CDCl_3$) 24.4, 26.1, 26.2, 29.2, 29.4, 29.52, 29.58, 29.6, 29.8, 33.2, 58.9, 68.4, 72.0, 73.3, 102.9, 107.0, 112.4, 133.1, 163.4, 164.1, 165.2; *m*/*z* (ES), 695 (MH^+, 100); HRMS (ES): MH^+, found 695.4991. $C_{42}H_{67}N_2O_6$ requires 695.4994.

*4.6.3. Compound **15c**.* Obtained as a yellow oil in 97% yield. $[\alpha]_D^{20}$ −451 (*c* 0.0175, $CHCl_3$); ν_{max} ($CHCl_3$) 3400 (br), 2930 (s), 2855 (m), 2252 (w), 1627 (s) and 1512 cm^{-1} (w); δ_H ($CDCl_3$) 1.19–1.97 (48H, br, $(CH_2)_{10}+CHCH_2CH_2$), 3.13–3.16 (2H, m, NCH), 3.26 (6H, s, OCH_3), 3.29 (4H, t *J* 6.7 Hz, $MeOCH_2$), 3.84 (4H, t *J* 6.5 Hz, $ArOCH_2$), 6.23 (2H, dd *J* 8.5, 2.3 Hz, ArH), 6.26 (2H, d *J* 2.3 Hz, ArH), 6.91 (2H, d *J* 8.5 Hz, ArH), 8.00 (2H, s, CH=N), 13.73 (2H, br, OH); δ_C ($CDCl_3$) 24.3, 26.1, 26.2, 29.2, 29.4, 29.60, 29.65, 29.66, 29.68, 29.75, 29.8, 33.2, 58.9, 68.4, 72.0, 73.4, 102.9, 107.1, 112.4, 133.1, 163.4, 164.1, 165.2; *m*/*z* (ES)

751 (MH^+, 100); HRMS (ES): MH^+, found 751.5627. $C_{46}H_{75}N_2O_6$ requires 751.5620.

*4.6.4. Compound **15d**.* Obtained as a yellow solid in 99% yield. Mp 60–64 °C; $[\alpha]_D^{20}$ −598 (*c* 0.03, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (w), 2225 (m), 1626 (s) and 1513 cm^{-1} (w); δ_H ($CDCl_3$) 0.90 (6H, t *J* 6.7 Hz, CH_3), 1.30–1.98 (24H, m, $(CH_2)_4$+$CHCH_2CH_2$), 3.19–3.24 (2H, m, NCH), 3.93 (4H, t *J* 6.6 Hz, OCH_2), 6.32 (2H, dd *J* 8.6, 2.2 Hz, ArH), 6.35 (2H, d *J* 2.2 Hz, ArH), 6.99 (2H, d *J* 8.6 Hz, ArH), 8.09 (2H, s, CH=N), 13.82 (2H, s, OH); δ_C ($CDCl_3$) 14.4, 23.0, 24.6, 26.0, 29.4, 31.9, 33.5, 68.4, 72.0, 101.9, 107.0, 112.4, 133.1, 163.4, 164.0, 165.2; *m*/*z* (ES) 523 (MH^+, 100); HRMS (ES): MH^+, found 523.3532. $C_{32}H_{47}N_2O_4$ requires 523.3530.

*4.6.5. Compound **15e**.* Obtained as a yellow oil in 96% yield after extraction using EtOAc rather than $CHCl_3$. $[\alpha]_D^{20}$ −533 (*c* 0.046, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2400 (w), 1628 (m) and 1515 cm^{-1} (w); δ_H ($CDCl_3$) 1.43–1.97 (8H, m, $CHCH_2CH_2$), 3.20–3.28 (2H, m, NCH), 3.37 (6H, s, OCH_3), 3.50–3.56 (4H, br, $MeOCH_2$), 3.71–3.82 (4H, br, $MeOCH_2CH_2$), 5.25 (4H, s, OCH_2O), 6.47 (2H, dd *J* 8.5, 2.3 Hz, ArH), 6.54 (2H, d *J* 2.3 Hz, ArH), 7.04 (2H, d *J* 8.5 Hz, ArH), 8.15 (2H, s, CH=N), 13.75 (2H, s, OH); δ_C ($CDCl_3$) 24.6, 33.5, 59.4, 68.2, 71.9, 72.4, 93.4, 104.1, 107.5, 113.7, 133.1, 161.0, 164.13, 164.16; *m*/*z* (CI) 531 (MH^+, 100), 444 (12), 323 (60); HRMS (ES): M+Na^+, found 553.2565. $C_{28}H_{38}N_2NaO_8$ requires 553.2520.

*4.6.6. Compound **15f**.* Obtained as a yellow oil in 88% yield. $[\alpha]_D^{20}$ −125 (*c* 0.02, $CHCl_3$); ν_{max} ($CHCl_3$) 2930 (w), 1629 (m) and 1560 cm^{-1} (s); δ_H (THF-d_8) 1.31–1.90 (8H, m, $CHCH_2CH_2$), 3.11–3.18 (2H, m, NCH), 4.25 (4H, s, CH_2), 6.50 (2H, d *J* 7.8 Hz, ArH), 6.60 (2H, s, ArH), 6.90 (2H, d *J* 7.8 Hz, ArH), 8.10 (2H, s, CH=N), 10.67 (2H, s, OH), 12.80 (2H, s, ArOH); δ_C ($CDCl_3$) 24.2, 33.0, 64.8, 72.6, 114.7, 116.7, 121.0, 131.6, 145.6, 161.3, 164.3; *m*/*z* (ES) 405 (M+Na^+, 27), 383 (MH^+, 100); HRMS (ES): MH^+, found 383.1965. $C_{22}H_{27}N_2O_4$ requires 383.1964.

4.7. General procedure for the synthesis of copper complexes 16a–f

Solutions of salen ligand **15a–f** (0.83 mmol) in EtOH (20 mL) and $Cu(OAc)_2 \cdot H_2O$ (0.17 g, 0.83 mmol) in water (2 mL) were mixed and refluxed with vigorous stirring for 2 h. The resulting solution was then cooled to room temperature, filtered and the precipitate washed successively with H_2O, MeOH and Et_2O (3×10 mL) to provide copper complexes **16a–f**.

*4.7.1. Compound **16a**.* Obtained as a brown solid in 71% yield. Mp 212–213 °C; $[\alpha]_D^{20}$ −837 (*c* 0.0245, $CHCl_3$); ν_{max} (KBr) 3430 (br), 3019 (s), 2936 (m), 2861 (w), 1607 (s) and 1529 cm^{-1} (m); *m*/*z* (FAB) 722 (M+Na^+, 24), 700 (MH^+, 100); HRMS (ES): MH^+, found 700.3512. $C_{38}H_{57}CuN_2O_6$ requires 700.3507.

*4.7.2. Compound **16b**.* Obtained as a dark brown solid in 81% yield. Mp 208–210 °C; $[\alpha]_D^{20}$ −645 (*c* 0.0165, $CHCl_3$); ν_{max} ($CHCl_3$) 3420 (br), 3019 (s), 2932 (m), 2857 (w), 2359 (s), 2341 (s), 1607 (s) and 1528 cm^{-1} (w); *m*/*z* (ES) 756 (MH^+, 100); HRMS (ES): MH^+, found 756.4136. $C_{42}H_{65}CuN_2O_6$ requires 756.4133.

*4.7.3. Compound **16c**.* Obtained as a dark brown solid in 67% yield. Mp 202–204 °C; $[\alpha]_D^{20}$ −587 (*c* 0.015, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2929 (m), 2856 (w), 2359 (s), 2341 (s), 1607 (s) and 1527 cm^{-1} (w); *m*/*z* (ES) 812 (MH^+, 100); HRMS (ES): MH^+, found 812.4758. $C_{46}H_{73}CuN_2O_6$ requires 812.4759.

*4.7.4. Compound **16d**.* Obtained as a brown solid in 82% yield. Mp 261–267 °C; $[\alpha]_D^{20}$ −787 (*c* 0.015, $CHCl_3$); ν_{max} (KBr) 3419 (br), 3019 (s), 2937 (m), 2861 (w), 1607 (s), 1529 (m) and 1429 cm^{-1} (w); *m*/*z* (ES) 606 (M+Na^+, 59), 584 (MH^+, 100); HRMS (ES): MH^+, found 584.2667. $C_{32}H_{45}CuN_2O_4$ requires 584.2670.

*4.7.5. Compound **16e**.* Obtained as a dark purple solid in 68% yield. Mp>400 °C; $[\alpha]_D^{20}$ −320 (*c* 0.0197, $CHCl_3$); ν_{max} (KBr) 2929 (br), 1628 (s), 1535 (s) and 1448 cm^{-1} (m); *m*/*z* (ES) 614 (M+Na^+, 100), 592 (MH^+, 80); HRMS (ES): M+Na^+, found 614.1663. $C_{28}H_{36}CuN_2NaO_8$ requires 614.1665.

*4.7.6. Compound **16f**.* Obtained as a brown solid in 20% yield. Mp>400 °C; $[\alpha]_D^{20}$ −1020 (*c* 0.007, $CHCl_3$); ν_{max} ($CHCl_3$) 3424 (br), 3018 (s), 2398 (w), 1632 (s), 1520 (w) and 1422 cm^{-1} (w); *m*/*z* (ES) 466 (M+Na^+, 31), 444 (MH^+, 100); HRMS (ES): MH^+, found 444.1100. $C_{22}H_{25}CuN_2O_4$ requires 444.1105.

4.8. General procedure for the synthesis of cobalt complexes 17a–d and 18

Salen ligand (5.0 mmol) and anhydrous cobalt(II) acetate (1.25 g, 5.0 mmol) were added to ethanol (16 mL) and the solution stirred at 70 °C for 1 h under an argon atmosphere. During this time an orange solid precipitated. The reaction mixture was allowed to cool to room temperature and then filtered and washed with hexane under a nitrogen atmosphere. The orange precipitate was purified by suspension in refluxing ethanol under an argon atmosphere, followed by filtration and washing with hexane.

*4.8.1. Compound **17a**.* Obtained as a dark brown solid in 98% yield. Crystals suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$/hexane. Mp 160–167 °C; $[\alpha]_D^{20}$ +103 (*c* 0.0258, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2933 (m), 2859 (w), 2400 (w), 1606 (s), 1526 (m) and 1468 cm^{-1} (w); *m*/*z* (FAB) 695 (Co(salen)$^+$, 100); HRMS (ES): Co(salen)$^+$, found 695.3470. $C_{38}H_{56}CoN_2O_6$ requires 695.3465. Selected crystallographic data: $C_{84}H_{124}Co_3N_4O_{20}$, *M*=1686.7, triclinic, space group *P*1, *a*=10.799(4), *b*=13.577(5), *c*=15.613(6) Å, *α*=87.211(4), *β*=73.262(4), *γ*=77.983(4)°, *V*=2144.0(14) $Å^3$, *Z*=1, *T*=120 K, *R* (*F*, $F^2>2\sigma$)=0.081, R_w (F^2, all data)=0.237. The structure of the molecule is close to centrosymmetric, the pseudosymmetry being broken mainly by the *R* chirality of all the chiral centres of the two ligand cyclohexanediamine groups; this absolute configuration is satisfactorily confirmed from anomalous scattering effects,[51] though these are relatively weak because the heavy Co atoms have a centrosymmetric arrangement. Refinement required the use of similarly restraints on the geometry of the ligands and restraints on displacement parameters, and there is undoubtedly unresolved disorder in the side-chains of the ligands, as indicated by high displacement parameters and short intermolecular contacts.

*4.8.2. Compound **17b**.* Obtained as a dark brown solid in 93% yield. Mp 148–156 °C; $[\alpha]_D^{20}$ +380 (*c* 0.0316, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2931 (m), 2858 (w), 2400 (w), 1606 (s), 1606 (m), 1531 (w) and 1430 cm^{-1} (w); *m*/*z* (FAB) 751 (MH^+, 100); HRMS (ES): MH^+, found 752.4166. $C_{42}H_{65}CoN_2O_6$ requires 752.4169.

*4.8.3. Compound **17c**.* Obtained as a dark brown solid in 93% yield. Mp 114–118 °C; $[\alpha]_D^{20}$ +577 (*c* 0.0142, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2929 (w), 2857 (w), 2400 (w), 1607 (m), 1519 (m) and 1428 cm^{-1} (w); *m*/*z* (FAB) 808 (MH^+, 90), 807 (100); HRMS (ES): MH^+, found 808.4801. $C_{46}H_{73}CoN_2O_6$ requires 808.4795.

*4.8.4. Compound **17d**.* Obtained as an orange solid in 15% yield. Mp>350 °C; $[\alpha]_D^{20}$ −823 (*c* 0.011, $CHCl_3$); ν_{max} (KBr) 3019 (s), 2939 (m), 2861 (w), 1599 (m), 1523 (m) and 1431 cm^{-1} (w); *m*/*z* (ES) 579

(MH^+, 100); HRMS (ES): MH^+, found 579.2631. $C_{32}H_{45}CoN_2O_4$ requires 579.2628.

*4.8.5. Compound **18**.* Obtained as a red solid in 53% yield. Crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2. Mp 291–297 °C; $[\alpha]_D^{20}$ −125 (*c* 0.0386, $CHCl_3$); ν_{max} ($CHCl_3$) 3019 (s), 2946 (m), 2400 (m), 1597 (m), 1535 (m) and 1420 cm^{-1} (w); *m*/*z* (ES) 491 (MH^+, 100), 210 (70); HRMS (ES): MH^+, found 491.2112. $C_{28}H_{37}CoN_2O_2$ requires 491.2103. Selected crystallographic data: $C_{28}H_{36}CoN_2O_2 \cdot 0.25CH_2Cl_2$, M=512.8, monoclinic, space group $C2$, a=30.229(3), b=18.755(2), c=19.046(2) Å, β=103.959(2)°, V=10,479.2(19) $Å^3$, Z=16, T=150 K, R (F, $F^2>2\sigma$)=0.047, R_w (F^2, all data)=0.114. The asymmetric unit of the crystal structure contains four crystallographically independent molecules of the complex, together with half each of two dichloromethane solvent molecules, one of which is disordered; further, highly disordered solvent molecules may also be present, as indicated by the identification of small voids in the structure,[52] but these could not be modelled with discrete atoms. The structure overall is close to centrosymmetric, the pseudosymmetry being broken mainly by the *R* chirality of all the chiral centres of the ligand cyclohexanediamine groups; this absolute configuration is confirmed from anomalous scattering effects.[51] The four molecules are related in pairs by pseudo-inversion centres.

4.9. Synthesis of α-methyl-phenylalanine methyl ester[31] (20)

(±)-*N*-*para*-Chlorobenzylidene alanine methyl ester[31] **19** (0.20 g, 1.05 mmol) was dissolved in dry toluene (2.5 mL) under an argon atmosphere. To this solution, catalyst (0.02 mmol), powdered sodium hydroxide (0.15 g, 3.66 mmol) and benzyl bromide (0.15 mL, 1.26 mmol) were added sequentially. The mixture was stirred for 19 h under an argon atmosphere, then MeOH (2 mL) and AcCl (0.5 mL) were added, the latter added dropwise. The reaction was stirred for a further 4 h, then the solvents were removed in vacuo. The residue was purified by column chromatography (EtOAc then EtOH/EtOAc 1:4) to give compound **20** as a colourless oil. δ_H($CDCl_3$) 1.35 (3H, s, CH_3C), 2.12 (2H, br s, NH_2), 2.76 (1H, d *J* 13.2 Hz, CH_2), 3.07 (1H, d *J* 13.2 Hz, CH_2), 3.63 (3H, s, OCH_3), 7.02–7.33 (5H, m, ArCH); δ_C ($CDCl_3$) 28.3, 48.6, 53.7, 60.5, 128.6, 130.0, 131.6, 138.2, 179.2. To determine the enantiomeric excess, (*S*)-phenylethylisocyanate (1 or 2 drops) was added to an NMR sample of compound **20** and allowed to react overnight until there was no unreacted amino ester present. The de of the resulting urea, which corresponds to the ee of compound **20** was determined by integration of the $PhCH_2$ protons of the resulting diastereomeric ureas.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.10.084. This data includes MOL files and InChiKeys of the most important compounds described in this article

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