DOI: 10.1002/ejic.201((will be filled in by the editorial staff**))**

Exploring the Building Block Potential of Readily Accessible Chiral Zn(salen) Complexes

Eddy Martin,[a] Marta Martínez Belmonte,[a] Eduardo C. Escudero-Adán,[a] and Arjan W. Kleij*[a,b]

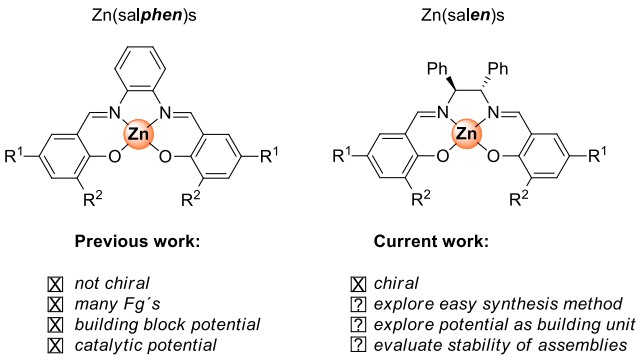
Keywords: Chiral / Salen ligands / Self-assembly / Synthesis / Zinc

The synthesis and full characterization of a series of chiral Zn(salen) complexes comprising a 1,2-diphenyl-ethane backbone is reported. The preparation method here reported simplifies the previously communicated methodology for these types of Zn complexes that utilized air-sensitive $ZnEt_2$ (or alike) as metalating reagent. X-ray molecular structures are also reported for representative examples of this family of Zn(salen)s. A wide range of functionality is shown to be accessible via the present route, amplifying the potential use of these (Lewis acidic) Zn complexes as molecular building blocks. Examples in this work include the formation of supramolecular assemblies having built-in bifunctionality using versatile Zn–N and Zn–O coordination motifs as guiding tools.

Introduction

Metallosalens, i.e. complexes derived from salen type ligands have emerged as privileged catalysts in organic synthesis.[1] More recently, they have also shown great potential as molecular synthons[2] in the preparation of various structures including those incorporating unusual self-assembly behaviour,[3] porous materials for efficient gas sorption,[4] systems able to mediate chirality transfer or expression,[5] supramolecular catalysts[6] among others.[7] One of the building blocks that has been studied intensively over the last ten years is based on the simple "salphen" motif. The *salphen* structure is part of the versatile family of salen ligands having a typical aromatic bridging group usually being a substituted phenyl. We and others have studied the reactivity and synthesis of these salphen systems,[8] in particular when ligated to Zn(II) ions. Notably, these Zn(salphen)s have been applied as efficient catalyst systems in the context of CO_2 conversion,[9] making using of the high Lewis acidic nature of the metal ions embedded in the salphen ligand pocket.

Though much is currently known about the potential of Zn(salphen)s in materials science[2] and homogeneous catalysis,[6, 9] very little synthetic effort has been devoted to the development of chiral Zn(salen)s as possible alternatives for Zn(salphen)s in the aforementioned application areas.[9a,10] The introduction of chirality in the Zn(salen) complex may hold promise to develop new materials and catalysts with the advantage that chiral information could be transduced and new reactivity patterns may become available. Though the synthesis of Zn-based salphen complexes has been developed to a sophisticated level, in the case of other salen based Zn complexes much less synthetic methodology has been reported (Scheme 1). Of relevant note is the synthesis of salen complexes having a built-in chiral 1,2-diphenylethane bridge; both Cozzi[10] and Roesky[11] reported on the use of ZnR_2 (R = Me, Et) to metalate these kind of salen ligands, a procedure that is reminiscent of the one used by Nguyen and Hupp to obtain similar type of (supramolecular) Zn(salen)s.[12]



Scheme 1. Comparison between Zn(salphen)s and chiral Zn(salen)s. Note that only one of the two possible chiral conformations in the Zn(salen) drawing is shown for simplicity.

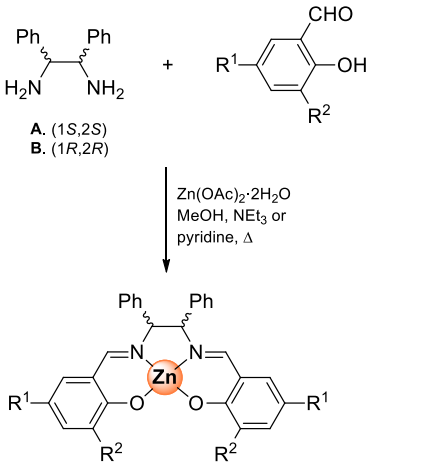
Here we report and detail on a more practical type and general preparation method for a series of Zn(salen)s equipped with a chiral 1,2-diphenylethane bridging fragment. Their building block potential has also been investigated by proper combination with suitable (nucleophilic) reagents affording stable, assembled multinuclear structures, a result that supports that such chiral Zn(salen)s may also function as supramolecular synthons.

[a] Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 – Tarragona, Spain.
Fax: + 34 – 977 920 828
E-mail: akleij@iciq.es
[b] Catalan Institute for Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 – Barcelona, Spain.
Supporting information for this article is available on the WWW under http://www.eurjic.org/ or from the author.

Results and Discussion

Synthesis

As a starting point for the synthesis of chiral, 1,2-bis-phenylethane bridged Zn(salen) complexes, we considered the conditions we employed previously for the Zn(salphen) family of complexes.[13] Thus, we first tried to combine the diamine reagent [i.e., (1*S*,2*S*)-(−)-1,2-diphenylethanediamine] and 3,5-di-*tert*-butylsalicyladehyde in the presence of $Zn(OAc)_2 \cdot 2H_2O$ in MeOH to provide, through a two-step condensation/metalation, the desired complex **1** (Scheme 2). During the course of the reaction a yellow precipitate was formed which was, however, identified by ^{1}H NMR as the non-metalated salen ligand. Apparently, the metalation under these conditions is comparatively slow and selective isolation of the ligand precursor to **1** occurs. However, we found that heating this precursor in its mother liquor dissolves the ligand again, and addition of NEt_3 gave fast precipitation of a product which after filtration was analysed as the targeted Zn(salen) **1** (78% yield). The other enantiomer (cf., complex **2** based on (1*R*,2*R*)-(+)-1,2-diphenylethanediamine) was prepared similarly in 84% isolated yield. Both these complexes retain MeOH as an axially ligating ligand (even after prolonged drying) as supported by ^{1}H NMR and elemental analyses, a result that seems to suggest that the Zn(II) centres in these systems have a fair degree of Lewis acid character. Recrystallization of **2** from hot acetonitrile provided crystals suitable for X-ray analysis (Figure 1).



1. $R^1 = R^2 = t$Bu; (1*S*,2*S*). Yield: 78%
2. $R^1 = R^2 = t$Bu; (1*R*,2*R*). Yield: 84%
3. $R^1 = R^2 =$ H; (1*R*,2*R*). Yield: 83%
4. $R^1 =$ H; $R^2 =$ Me; (1*S*,2*S*). Yield: 81%
5. $R^1 =$ H; $R^2 = t$Bu; (1*S*,2*S*). Yield: 76%
6. $R^1 =$ allyl; $R^2 =$ OMe; (1*S*,2*S*). Yield: 77%
7. $R^1 = R^2 =$ F; (1*S*,2*S*). Yield: 85%
8. $R^1 = C{\equiv}CSiMe_3$; $R^2 =$ H; (1*S*,2*S*). Yield: 92%
9. $R^1 = R^2 =$ Cl; (1*S*,2*S*). Yield: 96%
10. $R^1 = NO_2$; $R^2 =$ H; (1*S*,2*S*). Yield: 91%
11. $R^1 =$ H; $R^2 =$ allyl; (1*S*,2*S*). Yield: 44%
12. $R^1 =$ Me; $R^2 =$ H; (1*S*,2*S*). Yield: 80%
13. $R^1 =$  ; $R^2 = t$Bu; (1*R*,2*R*). Yield: 56%

Scheme 2. Synthesis of chiral Zn(salen) complexes **1-13**; for each complex the absolute configuration is also indicated together with the isolated yield.

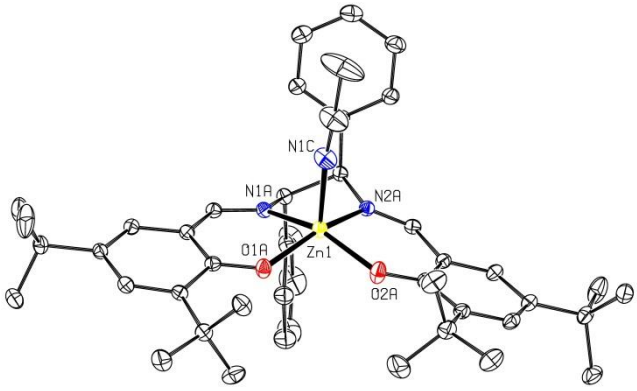


Figure 1. X-ray molecular structure determined for complex **2**·CH_3CN. H-atoms, co-crystallized solvent molecules and most of the numbering scheme are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)-O(1A) = 1.9719(12), Zn(1)-O(2A) = 1.9589(11), Zn(1)-N(1A) = 2.0985(13), Zn(1)-N(2A) = 2.0889(13), Zn(1)-N(1C) = 2.1355(14); N(1A)-Z(1)-N(2A) = 77.60(5), O(1A)-Zn(1)-O(2A) = 96.42(5), N(1A)-Zn(1)-O(2A) = 150.94(5), N(2A)-Zn(1)-O(1A) = 155.08(5).

The presence of CH_3CN (cf., Zn1-N1C bond) in the coordination sphere of **2** further testifies that these Zn(salen)s **1** and **2** show similar Lewis acid properties to Zn(salphen)s. The structure reported here for **2**·CH_3CN is *iso*-structural to the one reported by Roesky[11] where the same complex has an axially ligated Et_2O ligand.

The non-substituted Zn(salen) complex **3** could be prepared using the same methodology, however, the product did not precipitate during the reaction as was observed in the case of **1** and **2**. Concentration of the reaction mixture did also not lead to precipitation and therefore another isolation procedure was used. Addition of water caused precipitation of the product which was then subsequently filtered and dried to give **3** in 83% isolated yield which is significantly higher than previously reported (55%).[11] It should also be noted that no air-sensitive metal reagent (cf., $ZnEt_2$ or $ZnMe_2$) or dry solvents were required making the present method more attractive from a practical point of view. We then explored the preparation of a series of Zn(salen)s (Scheme 2, **4-13**) with different functionalities to evaluate further the usefulness of the preparative method. In general high isolated yields could be obtained (up to 92%) except for complexes **11** (44%) and **13** (56%) whose isolation proved to be more challenging. Of particular note are the syntheses of Zn(salen) complexes **6**, **8**, **11** and **13** incorporating potentially useful allyl, protected alkyne and pyridyl groups. Such functionalities have already proven to be highly useful in the construction of multimetallic Zn(salen) assemblies via olefin metathesis chemistry[14] or Zn–N_{pyr} coordination patterns.[13a,15] Whereas in the majority of the cases the product simply precipitates out during the course of the reaction, the isolation of complexes **5** and **11** required significant concentration of the reaction mixture and extensive sonication periods and/or addition of pyridine (see Experimental Section). Complex **5** was isolated as its pyridine adduct in line with the observed Lewis acid behaviour observed for Zn(salen)s **1** and **2**.

The synthesis of complex **13** requires a more detailed explanation. We first attempted to prepare **13** using the standard procedure used for the other complexes (see Experimental Section). Shortly after addition of the Zn reagent, a yellow solid precipitated out and after isolation the ^{1}H NMR spectrum recorded in

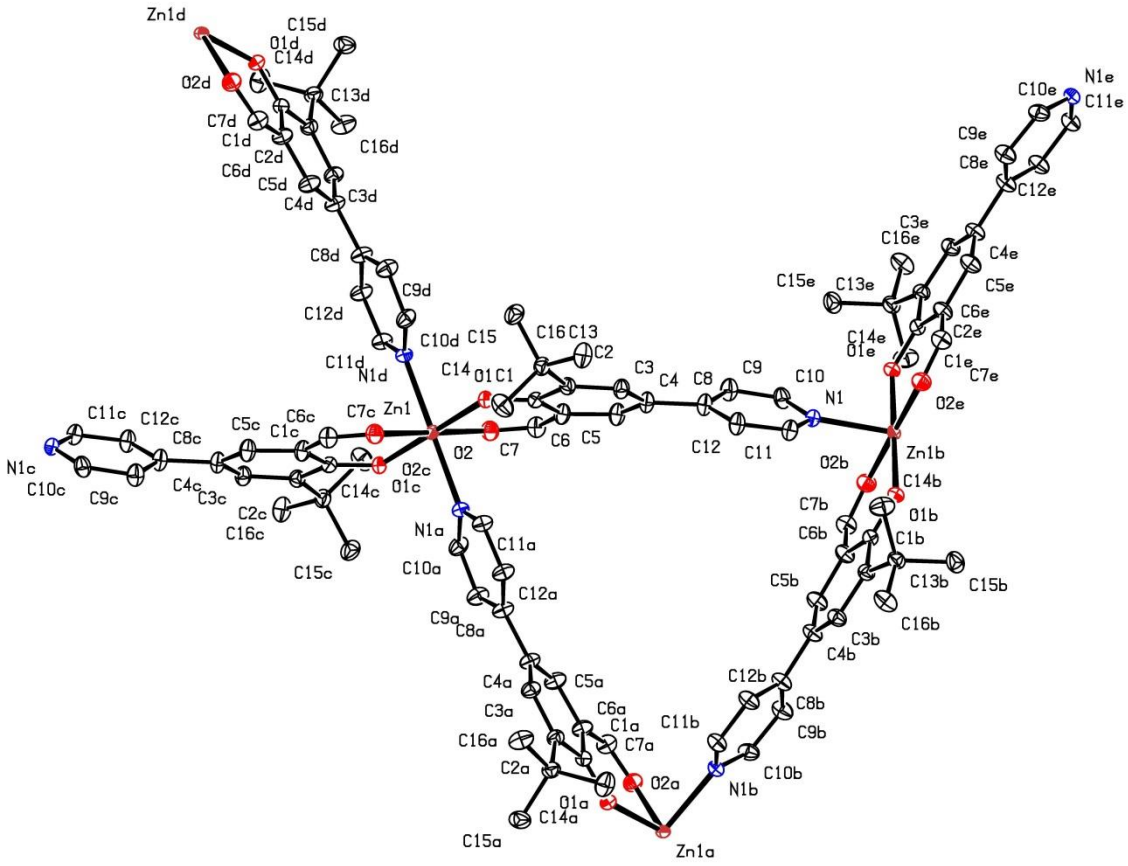


Figure 2. Part of the X-ray molecular structure determined for the polymeric side-product during the synthesis of **13**. H-atoms are omitted are omitted for clarity. Selected bond lengths (Å) and angles (°) around one of the metal ions: Zn(1)-O(1) = 2.0416(13), Zn(1)-O(1C) = 2.0416(13), Zn(1)-O(2) = 2.1024(14), Zn(1)-O(2C) = 2.1024(14), Zn(1)-N(1A) = 2.1595(15), Zn(1)-N(1D) = 2.1595(15); N(1A)-Zn(1)-N(1D) = 180.0, O(1)-Zn(1)-O(1C) = 180.0, O(2)-Zn(1)-O(2C) = 180.00(8), O(1)-Zn(1)-O(2) = 88.45(5), O(1C)-Zn(1)-O(2C) = 88.45(5), O(1)-Zn(1)-N(1A) = 89.62(6), O(1)-Zn(1)-N(1D) = 90.38(6).

[D_6]DMSO clearly displayed a mixture of two principal components. Recrystallization of the crude product from DMSO afforded fortunately, crystals suitable for X-ray analysis providing crucial information about the identity of non-desired component in the isolated mixture (see Figure 2). The structure shows the presence of the 3–*tert*-butyl-5-(4-pyridyl)-salicylaldehyde reagent forming a polymeric, porous structure combined with Zn^{II} ions. Each Zn centre is ligated by two anionic salicylaldehyde fragments and the octahedral coordination geometry around the ion is completed by two pyridine donors originating from distinct salicylaldehyde groups. Unusual triangular shaped pores are formed from three Zn centres and three salicylaldehyde units. This feature shows periodicity in the solid state to afford a polymer with porous channels along one of the crystallographic axes (see the Supporting Information for details).

Realizing that the formation of this stable metal-organic framework efficiently competes with the formation of targeted Zn(salen) complex **13**, we then performed the reaction in the presence of pyridine as co-solvent to prevent early precipitation of the aforementioned side-product and this proved to be helpful; complex **13** could be isolated in fair yield (56%) and purity. All complexes were fully characterized by $^{1}H/^{13}C\{^{1}H\}$ NMR (for **7** also by $^{19}F\{^{1}H\}$ NMR), MALDI-TOF mass spectrometry and elemental analyses. Complex **10** was also characterized by single crystal X-ray crystallography (Figure 3).

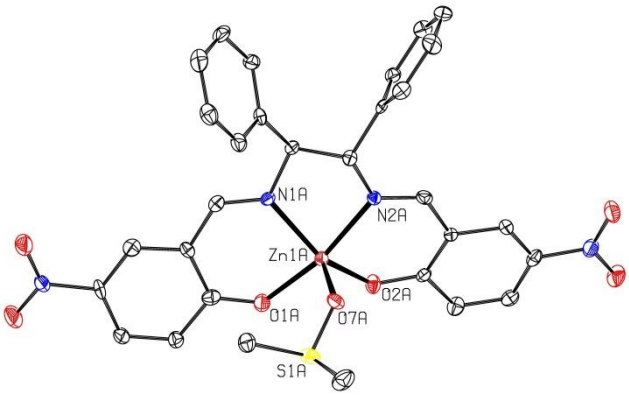


Figure 3. X-ray molecular structure determined for complex **10**·DMSO. H-atoms, co-crystallized solvent molecules and most of the numbering scheme are omitted for clarity. Only one of the crystallographically independent molecules is shown. Selected bond lengths (Å) and angles (°): Zn(1A)-O(1A) = 1.989(3), Zn(1A)-O(2A) = 1.983(3), Zn(1A)-N(1A) = 2.079(3), Zn(1A)-N(2A) = 2.077(3), Zn(1A)-O(7A) = 2.039(3); O(2A)-Zn(1A)-O(1A) = 93.29(12), N(2A)-Zn(1A)-N(1A) = 79.46(12), O(2A)-Zn(1A)-N(1A) = 146.00(11), N(2A)-Zn(1A)-O(1A) = 166.39(11), O(2A)-Zn(1A)-O(7A) = 107.18(11), N(2A)-Zn(1A)-O(7A) = 93.48(11).

Assembly formation with chiral Zn(salen)s

The chiral Zn(salen)s were probed for their ability to form larger multinuclear assemblies. As a role model, Zn(salphen)s have previously demonstrated to readily form such ensembles using a variety of ditopic ligands including DABCO (= 1,4-diazabicyclo[2.2.2]octane),[16] bipyridines,[13a] carboxylates[5c,17] and hydroxo ligands.[18] Thus, such ligands may serve as good probes to determine the building block potential of the chiral Zn(salen) complexes reported in this work. Previous work on chiral Zn(salen)s has shown potential in this respect by evaluation of their binding affinity with pyridine;[19] Zn(salen)s with chiral 1,2-diphenylethane bridging fragment show stability constants K_s in the range 10^4–10^5 M^{-1}, just slightly lower than reported for their Zn(salphen) analogues.[13a] We thus first investigated the use of a ditopic ligand (dabco) to enforce the formation of a 2:1 assembly where both dabco-*N* atoms would be involved in binding to the Zn ions. This assembly (**14**) was easily prepared by combination of Zn(salen) complex **1** with dabco in hot acetonitrile. Cooling of the solution resulted in the formation of needle-shaped crystals which were isolated by filtration (46%) and analysed by ^{1}H NMR (both [D_6]acetone as well as [D_2]DCM were used). In both aforementioned solvents, by comparison with "free" dabco, a relatively small upfield displacement is noted for the dabco hydrogens ($\Delta\delta$ = 0.06 and 0.11 ppm, respectively). Both species integrate such that a 2:1 ratio is supported in the isolated crystalline solid. In both solvents, one singlet peak for the dabco-*H* is noted and only one pattern for the Zn(salen) complex in line with fast exchange between 1:1 and 2:1 assemblies and/or a low energetic barrier for rotation around the Zn–N_{dabco} bonds. As a definite proof of the 2:1 stoichiometry X-ray analysis of crystalline **14** (from CH_3CN) was carried out (Figure 4); in the solid-state arrangement both Zn(salen) units are in a parallel arrangement and it may be assumed that there is ample room for free rotation around both Zn–N_{dabco} axes in solution.

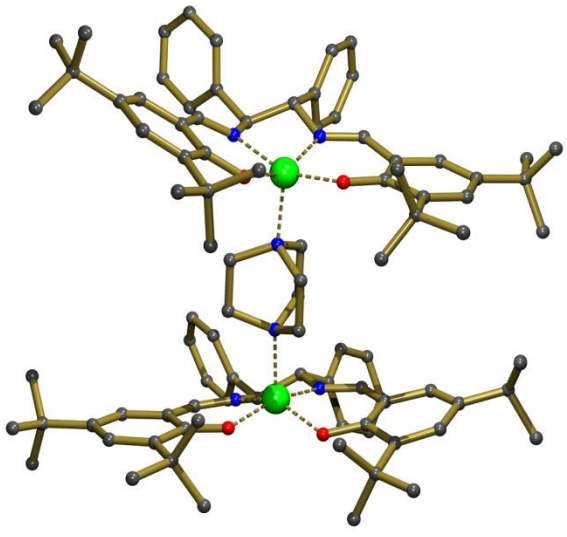


Figure 4. X-ray molecular structure (POV-Ray image) determined for assembly **14**. H-atoms, co-crystallized solvent molecules are omitted for clarity. Colour coding: Zn = Green, O = red, N = blue, C = grey.

Next, we examined a potentially ditopic ligand with a much smaller interconnecting spanning range, i.e. a hydroxide. To this end, complex **2** was combined with NBu_4OH in CH_3CN. After isolation (see Experimental Section) the envisioned assembly (**2**)$_2$·NBu_4OH (**15**) could be obtained as single crystalline material from a saturated solution in acetone. The structure that was determined (see Figure 5) shows the presence of two units of Zn(salen) **2** connected through an OH anion (NBu_4 cation not shown here). Since the two Zn(salen) fragments are bridged by one of the smallest ligands possible, anisotropic effects may be expected if the structure is retained in solution. Therefore, in order to evaluate the stability of assembly **15** in solution analysis by ^{1}H NMR ([D_6]acetone) was carried out and its NMR spectrum compared to the one from free, non-assembled Zn(salen) **2**. Significant changes were noted between the assembly **15** (containing two, OH–bridged Zn(salen) complexes **2**) and free Zn(salen) **2** (Figure 6).

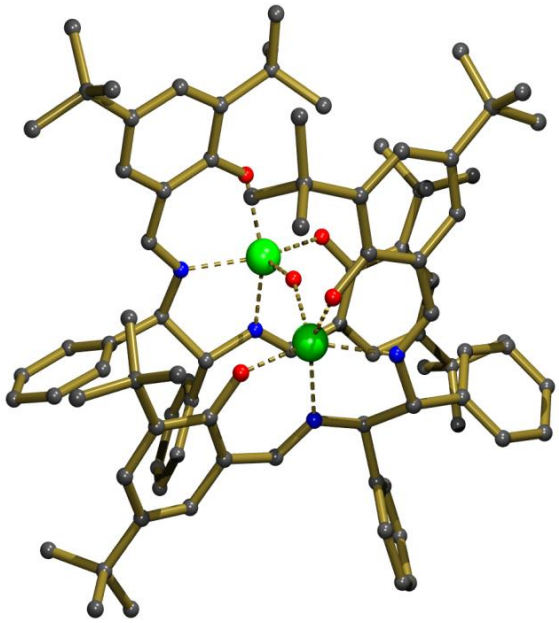


Figure 5. X-ray molecular structure (POV-Ray image) determined for assembly **15**. H-atoms, co-crystallized solvent molecules are omitted for clarity. Colour coding: Zn = Green, O = red, N = blue, C = grey.

For each of the salen units in assembly **15** a dissymmetry is apparent as supported by the presence of multiple signals for the aryl-hydrogens, the imine-H and the bridging Ph(*H*)C–C(*H*)Ph unit. The latter split up and give rise to an AB–pattern with a typical ^2J of around 11 Hz. These doublets also show a hyperfine coupling with both the imine-H (^4J = 1.2–1.4 Hz) located at 7.80 and 7.39 ppm, respectively. The position of these two imine-H is significantly different from the one observed for free, unbound **2** (δ = 8.18 ppm) suggesting the close mutual presence of both salen units. This causes a shielding effect of the aromatic groups exerted by their π-electron ring currents, and displaces all nearby groups to higher field as is indeed observed for the imine-H, the CH–CH fragment, aromatic protons and to a lesser extend the *t*Bu groups. These data are in line with a stable character of the assembly **15** under these conditions. It should be noted that the ^{1}H NMR spectrum of **15** also shows indications of a 1:1 assembly (i.e., **2**·NBu_4OH, see Supporting Information); when a competitive ligand is added in small amount (i.e., [D_6]DMSO), the amount of the 1:1 assembly increases and thus shows that binding of **2** to the OH donor ligand is reversible.

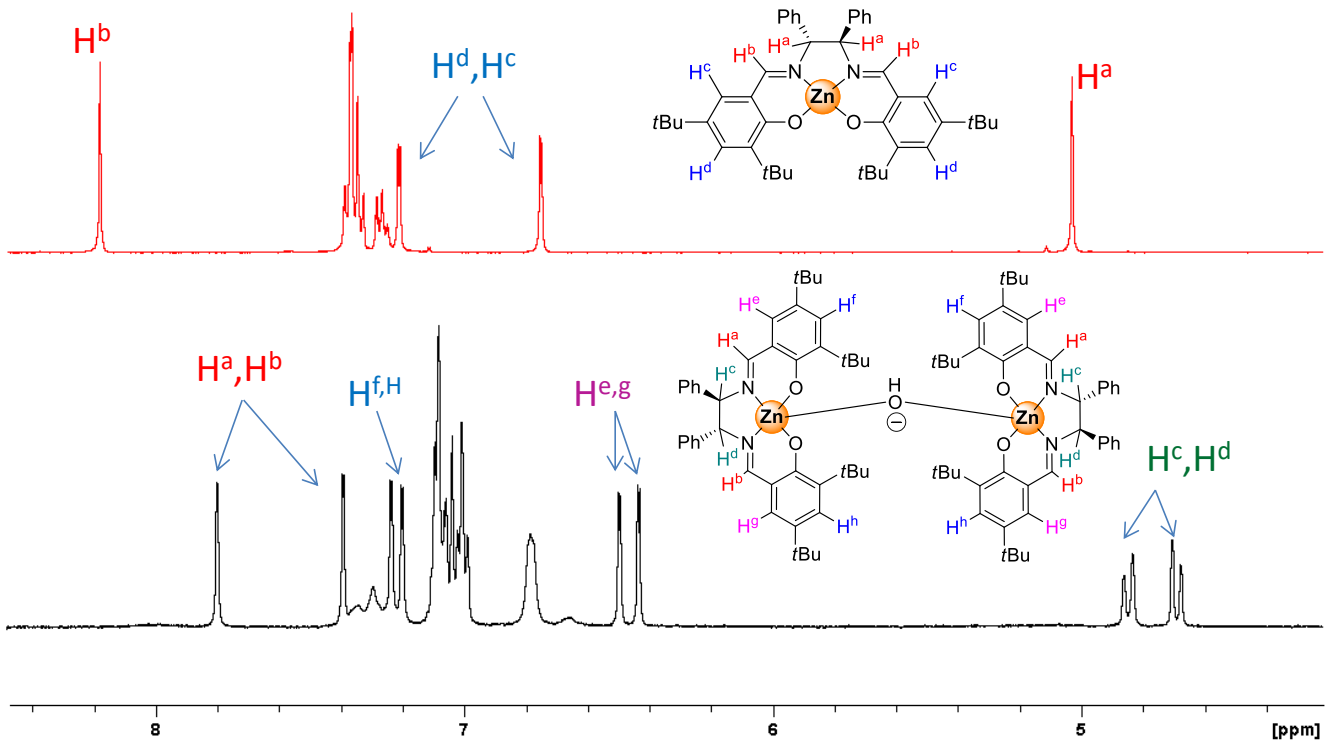


Figure 6. Selected ^{1}H NMR region ([D$_6$]acetone) for Zn(salen) complex **2** (top) and assembly **15** (NBu$_4$ cation not shown for clarity).

Mass spectrometric analysis carried out for **15** indirectly supported the stability of the assembled species; since MeOH was used for the electrospray ionization mass analyses, the OH anion was easily replaced by a methoxy anion through acid-base chemistry and both the 1:1 as well as the 2:1 assembly having a MeO anion associated were observed. Together with these characteristic anionic assemblies also those based on EtO, PrO and even BuO were generated *in situ* as a likely result of the MeOH containing higher alcohol impurities. This result nonetheless demonstrates that such anionic assemblies are sufficiently stable to be formed and analysed by soft MS methods.

Conclusions

In this work we have presented a more facile, general route towards chiral Zn(salen)s based on a 1,2-diphenyl-ethanediamine bridging unit. This method uses simple precursors and can be applied in air and moisture-containing solvent producing the desired Zn(salen)s in fair to high isolated yields. This method tolerates the introduction of synthetically useful acetylenic, allylic and pyridine groups that can be used for post-modification or direct self-assembly (in the case of **13**). The potential of these chiral Zn(salen)s has been demonstrated by the easy formation of two types of assemblies based on either dabco or NBu$_4$OH donors. Thus, these chiral Zn(salen)s may hold promise as steric spectators (after complexation to suitable O– or N–donors of the host) in supramolecular catalyst design providing a chiral environment around the reactive centre[20] and leading to possible asymmetric induction.

Experimental Section

General: NMR measurements were done on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. Elemental analysis was performed by the Unidád de Análisis Elemental at the Universidad de Santiago de Compostela. Mass spectrometric analysis and X-ray diffraction studies were performed by the Research Support Group at the ICIQ. The chiral diamine precursors **A** and **B** (Scheme 2) were commercially purchased, the salicylaldehyde precursors used for the synthesis of complexes **8**[21] and **13**[22] were prepared according to previously reported procedures while the others were purchased from commercial suppliers. Copies of NMR spectra of all isolated Zn(salen) complexes **1-13** are provided in the Supporting Information.

Zn(salen) complex (1): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (172.8 mg, 0.814 mmol), 3,5-di-*tert*-butyl-salicylaldehyde (426.6 mg, 1.82 mmol) and Zn(OAc)$_2$·2H$_2$O (322.2 mg, 1.47 mmol) in MeOH (40 ml) and NEt$_3$ (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 18 h. The desired compound was then isolated by filtration and dried in vacuo to yield a yellow solid. Yield: 469.5 mg (0.634 mmol, 78%; yield of mono–MeOH solvate). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.18 (s, 2H; CH=N), 7.32-7.39 (m, 8H; ArH), 7.24-7.29 (m, 2H; ArH), 7.21 (d, $^{4}J_{H,H}$ = 2.6 Hz, 2H; ArH), 6.75 (d, $^{4}J_{H,H}$ = 2.6 Hz, 2H; ArH), 5.03 (s, 2H, CH–CH), 4.11 (q, $^{3}J_{HH}$ = 5.3 Hz, 1H; CH$_3$O*H*), 3.18 (d, $^{3}J_{HH}$ = 5.2 Hz, 3H; C*H*$_3$OH), 1.47 (s, 18H; C(CH$_3$)$_3$), 1.19 (s, 18H; C(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 170.01, 169.69, 141.93, 140.88, 132.86, 129.00, 128.88, 128.60, 127.97, 127.64, 118.34, 72.47, 49.07, 35.66, 33.84, 31.86, 30.06; MS (MALDI+, pyrene): *m/z* = 706.2 [M]$^+$ (calcd 706.3), 694.1 (M – CH$_3$ + 2H)$^+$ (calcd 694.3); elemental analysis calcd for C$_{44}$H$_{54}$N$_2$O$_2$Zn·MeOH·2½H$_2$O: C 68.82, H 8.09, N, 3.57; found: C 69.02, H 7.68, N 3.33. The presence of 1 equiv of MeOH was supported by ^{1}H NMR analysis, see the Supporting Information.

This MeOH could not be removed by heating the compound for longer periods of time.

Zn(salen) complex (2): A solution of (1*R*,2*R*)-(–)-1,2-diphenylethylenediamine (169.4 mg, 0.798 mmol), 3,5-di-*tert*-butylsalicylaldehyde (488.0 mg, 2.08 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (308.9 mg, 1.40 mmol) in MeOH (35 ml) and NEt_3 (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 18 h. The desired compound was then isolated by filtration and dried in vacuo to yield a yellow solid. Yield: 497.9 mg (0.673 mmol, 84%; yield of mono–MeOH solvate). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.18 (s, 2H; CH=N), 7.33-7.39 (m, 8H; ArH), 7.25-7.29 (m, 2H; ArH), 7.21 (d, $^4J_{H,H}$ = 2.6 Hz, 2H; ArH), 6.75 (d, $^4J_{H,H}$ = 2.6 Hz, 2H; ArH), 5.03 (s, 2H, CH–CH), 4.10 (q, $^3J_{HH}$ = 5.3 Hz, 1H; $CH_3O\mathit{H}$), 3.17 (d, $^3J_{HH}$ = 5.3 Hz, 3H; $C\mathit{H}_3OH$), 1.47 (s, 18H; $C(CH_3)_3$), 1.19 (s, 18H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO): δ = 170.00, 169.69, 141.93, 140.88, 132.84, 128.99, 128.88, 128.57, 127.96, 127.63, 118.34, 72.46, 49.07, 35.66, 33.84, 31.85, 30.05; MS (MALDI+, pyrene): *m/z* = 706.3 $[M]^+$ (calcd 706.3), 694.3 $(M - CH_3 + 2H)^+$ (calcd 694.3); elemental analysis calcd for $C_{44}H_{54}N_2O_2Zn{\cdot}$MeOH: C 73.01, H 7.90, N, 3.78; found: C 73.11, H 7.48, N 3.73. As for complex **1**, the presence of 1 equiv of MeOH was supported by ^{1}H NMR analysis, see the Supporting Information. This MeOH could not be removed by heating the compound for longer periods of time.

Zn(salen) complex (3): A solution of (1*R*,2*R*)-(–)-1,2-diphenylethylenediamine (136.7 mg, 0.644 mmol), salicylaldehyde (213.4 mg, 1.75 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (223.6 mg, 1.02 mmol) in MeOH (30 ml) and NEt_3 (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 22 h. At this stage the yellow solution was concentrated to around 20 mL and water was added to initiate precipitation of the product. The product (a white solid) was then collected by filtration and dried. Yield: 259.9 mg (0.537 mmol, 83%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.22 (s, 2H; CH=N), 7.40 (d, $^3J_{H,H}$ = 7.9 Hz, 4H; ArH), 7.34 (t, $^3J_{H,H}$ = 7.5 Hz, 4H; ArH), 7.26 (t, $^3J_{H,H}$ = 6.9 Hz, 2H; ArH), 7.15 (t, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.7 Hz, 2H; ArH), 7.00 (d, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H; ArH), 6.65 (d, $^3J_{H,H}$ = 8.0 Hz, 2H; ArH), 6.38 (t, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 1.0 Hz, 2H; ArH), 5.10 (s, 2H, CH–CH); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO): δ = 171.80, 170.18, 141.52, 135.58, 133.85, 128.96, 128.22, 127.97, 123.23, 119.70, 112.81, 72.82; MS (MALDI+, dctb): *m/z* = 482.3 $[M]^+$ (calcd 482.1), 968.4 $(2M)^+$ (calcd 968.2); elemental analysis calcd for $C_{28}H_{22}N_2O_2Zn{\cdot}1.33H_2O$: C 66.22, H 4.90, N, 5.52; found: C 66.50, H 5.04, N 5.56.

Zn(salen) complex (4): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (141.0 mg, 0.664 mmol), 3-methylsalicylaldehyde (241.1 mg, 1.77 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (247.0 mg, 1.13 mmol) in MeOH (25 ml) and NEt_3 (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 5 h. The product (a yellow solid) was then collected by filtration and dried. Yield: 276.9 mg (0.541 mmol, 81%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.16 (s, 2H; CH=N), 7.45 (d, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.5 Hz, 4H; ArH), 7.34 (t, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 0.9 Hz, 4H; ArH), 7.26 (t, $^3J_{H,H}$ = 7.3 Hz, $^4J_{H,H}$ = 2.4 Hz, 2H; ArH), 7.12 (t, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 0.9 Hz, 2H; ArH), 6.83 (d, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H; ArH), 6.30 (dd, $^3J_{H,H}$ = 7.4 Hz, 2H; ArH), 5.06 (s, 2H, CH–CH), 2.26 (Ar-CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]DMSO): δ = 170.40, 170.38, 141.96, 133.72, 133.37, 130.42, 128.92, 128.11, 127.88, 118.53, 112.25, 73.41, 17.65; MS (MALDI+, pyrene): *m/z* = 510.1 $[M]^+$ (calcd 510.1); elemental analysis calcd for $C_{30}H_{26}N_2O_2Zn{\cdot}$ 1/3H_2O: C 69.57, H 5.19, N 5.41; found: C 69.81, H 4.90, N 5.40.

Zn(salen) complex (5): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (210.3 mg, 0.991 mmol), 3-*tert*-butylsalicylaldehyde (415.9 mg, 2.33 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (337.8 mg, 1.54 mmol) in MeOH (30 ml) and pyridine (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 18 h. The product (a yellow solid) was then collected by filtration and dried. Yield: 511.4 mg (0.757 mmol, 76%; isolated as mono–pyridine adduct). ^{1}H NMR (400 MHz, [D$_6$]Acetone): δ = 8.27-8.29 (m, 2H; Pyr-H), 8.25 (s, 2H; CH=N), 7.86 (t, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H; Pyr-H), 7.36-7.38 (m, 2H; Pyr-H), 7.34 (d, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.5 Hz, 4H; ArH), 7.34 (t, $^3J_{H,H}$ = 6.8 Hz, 4H; ArH), 7.18-7.26 (m, 8H; ArH), 6.86 (d, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H; ArH), 6.35 (t, $^3J_{H,H}$ = 7.6 Hz, 2H; ArH), 5.15 (s, 2H, CH–CH), 1.45 ($C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]Acetone): δ = 171.99, 170.11, 148.33, 141.78, 140.60, 138.72, 133.53, 129.73, 128.45, 128.26, 127.54, 124.66, 119.45, 111.65, 72.62, 35.04, 29.12; MS (MALDI+, pyrene): *m/z* = 594.1 $[M]^+$ (calcd 594.2); elemental analysis calcd for $C_{41}H_{43}N_3O_2Zn$ (mono-pyridine complex): C 72.93, H 6.42, N 6.22; found: C 72.70, H 6.14, N 6.13.

Zn(salen) complex (6): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (164.1 mg, 0.773 mmol), 3-methoxy-5-allylsalicylaldehyde (359.2 mg, 1.87 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (313.8 mg, 1.43 mmol) in MeOH (30 ml) and NEt_3 (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 16 h. The product (a yellow solid) was then collected by filtration and dried. Yield: 370.8 mg (0.594 mmol, 77%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.18 (s, 2H; CH=N), 7.39 (d, $^3J_{H,H}$ = 7.5 Hz, 4H; ArH), 7.33 (t, $^3J_{H,H}$ = 7.8 Hz, 4H; ArH), 7.25 (t, $^3J_{H,H}$ = 7.3 Hz, 2H; ArH), 6.34 (d, $^4J_{H,H}$ = 1.9 Hz, 2H; ArH), 6.40 (d, $^4J_{H,H}$ = 1.4 Hz, 2H; ArH), 5.86-5.94 (m, 2H, allyl), 5.08 (s, 2H, CH–CH), 5.04 (d, $^2J_{H,H}$ = 17.0 Hz, $^4J_{H,H}$ = 1.6 Hz, 2H; allyl), 4.98 (d, $^2J_{H,H}$ = 10.0 Hz, 2H; ArH), 3.73 (s, 6H; ArOMe), 3.17 (d, $^3J_{H,H}$ = 6.7 Hz, 4H; allyl); $^{13}C\{^1H\}$ NMR (126 MHz, [D$_6$]DMSO): δ = 170.03, 161.47, 152.77, 141.65, 138.84, 128.92, 128.19, 127.90, 125.35, 122.34, 118.07, 115.53, 114.64, 72.87, 55.58, 39.39; MS (MALDI+, pyrene): *m/z* = 622.1 $[M]^+$ (calcd 622.2); elemental analysis calcd for $C_{36}H_{34}N_2O_2Zn{\cdot}1.5H_2O$: C 66.41, H 5.73, N 4.30; found: C 66.52, H 5.35, N 4.23.

Zn(salen) complex (7): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (136.6 mg, 0.643 mmol), 3,5-difluorosalicylaldehyde (298.6 mg, 1.89 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (340.1 mg, 1.55 mmol) in MeOH (35 ml) and NEt_3 (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 45 min. The product (a yellow solid) was then collected by filtration and dried. Yield: 303.2 mg (0.545 mmol, 85%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.31 (s, 2H; CH=N), 7.41 (d, $^3J_{H,H}$ = 8.0 Hz, 4H; ArH), 7.36 (t, $^3J_{H,H}$ = 7.9 Hz, 4H; ArH), 7.28 (t, $^3J_{H,H}$ = 7.2 Hz, 2H; ArH), 7.17-7.27 (m, 2H; ArH), 6.80-6.82 (m, 2H; ArH), 5.19 (s, 2H, CH–CH); $^{19}F\{^1H\}$ NMR (376 MHz, [D$_6$]DMSO): δ = –130.45, –131.43; $^{13}C\{^1H\}$ NMR (126 MHz, [D$_6$]DMSO): δ = 169.66, 157.17, 155.73, 153.79, 149.85, 148.02, 140.86, 129.07, 128.10, 119.02, 113.76, 108.20, 73.02; MS (MALDI+, pyrene): *m/z* = 554.1 $[M]^+$ (calcd 554.1), 1110.1 $(2M)^+$ (calcd 1110.1); elemental analysis calcd for $C_{28}H_{18}F_4N_2O_2Zn{\cdot}H_2O$: C 58.60, H 3.51, N 4.88; found: C 58.40, H 3.36, N 4.88.

Zn(salen) complex (8): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (133.6 mg, 0.629 mmol), 5-trimethylsilylacetylylsalicylaldehyde[21] (341.5 mg, 1.56 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (436.3 mg, 1.98 mmol) in MeOH (30 ml) and NEt_3 (1 mL) was shortly stirred at reflux temperature and then allowed to cool to r.t. and stirred for another 18 h. The product (a light yellow/brown solid) was then collected by filtration and dried. Yield: 390.4 mg (0.577 mmol, 92%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.21 (s, 2H; CH=N), 7.33-7.36 (m, 8H; ArH), 7.26-7.31 (m, 2H; ArH), 7.20-

7.24 (m, 4H; ArH), 6.62 (d, $^3J_{H,H}$ = 8.8 Hz, 2H; ArH), 5.12 (s, 2H, CH–CH), 0.17 (s, 18H; $SiMe_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ = 172.14, 169.61, 140.55, 139.97, 136.52, 129.04, 128.37, 128.16, 123.80, 119.65, 106.99, 106.11, 90.73, 72.57, 0.65; MS (MALDI+, pyrene): *m/z* = 674.2 $[M]^+$ (calcd 674.2); elemental analysis calcd for $C_{38}H_{38}Si_2N_2O_2Zn{\cdot}2H_2O$: C 64.07, H 5.94, N 3.93; found: C 63.72, H 5.49, N 3.79.

Zn(salen) complex (9): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (160.8 mg, 0.757 mmol), 3,5-dichloro-salicylaldehyde (365.3 mg, 1.91 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (256.1 mg, 1.17 mmol) in MeOH (40 ml) was stirred at r.t. for 20 min. The product (a yellow solid) was then collected by filtration and dried. Yield: 406.7 mg (0.654 mmol, 96%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 8.33 (s, 2H; CH=N), 7.48 (d, $^4J_{H,H}$ = 2.9 Hz, 2H; ArH), 7.40 (d, $^3J_{H,H}$ = 7.9 Hz, 4H; ArH), 7.35 (t, $^3J_{H,H}$ = 7.5 Hz, 4H; ArH), 7.28 (t, $^3J_{H,H}$ = 7.2 Hz, 2H; ArH), 7.18 (d, $^4J_{H,H}$ = 2.8 Hz, 2H; ArH), 5.16 (s, 2H, CH–CH); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ = 169.88, 164.43, 140.81, 133.10, 132.54, 129.07, 128.17, 127.97, 127.06, 120.66, 115.11, 73.28; MS (MALDI+, pyrene): *m/z* = 620.0 $[M]^+$ (calcd 619.9), ; elemental analysis calcd for $C_{28}H_{18}Cl_4N_2O_2Zn{\cdot}H_2O$: C 52.57, H 3.15, N, 4.38; found: C 52.48, H 2.96, N 4.30.

Zn(salen) complex (10): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (101.2 mg, 0.477 mmol), 5-nitro-salicylaldehyde (187.9 mg, 1.12 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (270.6 mg, 1.17 mmol) in MeOH (40 ml) was stirred at r.t. for 60 min. The product (a yellow solid) was then collected by filtration and dried. Yield: 248.2 mg (0.433 mmol, 91%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 8.45 (s, 2H; CH=N), 8.20 (d, $^4J_{H,H}$ = 3.1 Hz, 2H; ArH), 8.04 (d, $^3J_{H,H}$ = 9.5 Hz, $^4J_{H,H}$ = 3.1 Hz, 2H; ArH), 7.36-7.38 (m, 8H; ArH), 7.27-7.33 (m, 2H; ArH), 6.76 (d, $^3J_{H,H}$ = 9.5 Hz, 2H; ArH), 5.24 (s, 2H, CH–CH), 4.10 (q, $^3J_{HH}$ = 5.2 Hz, 1H; $CH_3O\mathit{H}$), 3.18 (d, $^3J_{HH}$ = 5.3 Hz, 3H; $C\mathit{H}_3OH$); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ = 176.76, 169.90, 139.92, 134.41, 133.66, 129.18, 128.76, 128.43, 128.37, 123.89, 118.53, 72.38, 49.07; MS (MALDI–, DCTB): *m/z* = 572 $[M]^-$ (calcd 572), 822 $(M+DCTB)^-$ (calcd 822), 1118 (with dctb being *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, M_w = 250.34; elemental analysis calcd for $C_{28}H_{20}N_4O_6Zn{\cdot}½MeOH{\cdot}3H_2O$: C 55.49, H 4.08, N 9.08; found: C 55.07, H 3.97, N 8.78. As for complex **1**, the presence of 0.5 equiv of MeOH was supported by ^1H NMR analysis, see the Supporting Information. This MeOH could not be removed by heating the compound for longer periods of time.

Zn(salen) complex (11): A solution of (1*S*,2*S*)-(–)-1,2-diphenylethylenediamine (171.1 mg, 0.806 mmol), 3-allyl-salicylaldehyde (329.3 mg, 2.03 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (395.0 mg, 1.80 mmol) in MeOH (25 ml) and NEt_3 (1 mL) was stirred at r.t. for 18 h. Then the solution was concentrated to 10 mL and sonicated briefly. In due course, a yellow solid started to preciptate and the product collected by filtration and dried. Yield: 200.2 mg (0.355 mmol, 44%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 8.16 (s, 2H; CH=N), 7.40 (d, $^3J_{H,H}$ = 7.8 Hz, 4H; ArH), 7.34 (t, $^3J_{H,H}$ = 7.7 Hz, 4H; ArH), 7.26 (t, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,H}$ = 1.4 Hz, 2H; ArH), 7.06 (d, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,H}$ = 1.7 Hz, 2H; ArH), 6.87 (d, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz, 2H; ArH), 6.33 (t, $^3J_{H,H}$ = 7.4 Hz, 2H; ArH), 6.08-6.16 (m, 2H; allyl-H), 5.13 (d, $^2J_{H,H}$ = 17.3 Hz, $^4J_{H,H}$ = 1.4 Hz, 2H; allyl-H), 5.07 (s, 2H, CH–CH), 5.00 (d, $^2J_{H,H}$ = 10.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 2H; allyl-H), 3.40 (dd, $^3J_{H,H}$ = 5.4 Hz, 4H; allyl-H); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ = 169.96, 169.66, 141.45, 138.74, 133.73, 132.82, 132.61, 128.97, 128.42, 128.00, 118.88, 115.29, 112.32, 72.87, 35.10; MS (MALDI+, pyrene): *m/z* = 563.1 $[M+H]^+$ (calcd 563.2); elemental analysis calcd for $C_{34}H_{30}N_2O_2Zn{\cdot}½H_2O$: C 71.27, H 5.45, N 4.89; found: C 71.63, H 5.73, N 4.99.

Zn(salen) complex (12): A solution of (1*R*,2*R*)-(–)-1,2-diphenylethylenediamine (162.6 mg, 0.766 mmol), 5-methyl-salicylaldehyde (236.3 mg, 1.74 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (225.8 mg, 1.03 mmol) in MeOH (35 ml) and NEt_3 (1 mL) was stirred at r.t. for 2 days. Then the product (a yellow solid) was collected by filtration and dried. Yield: 313.3 mg (0.612 mmol, 80%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 8.12 (s, 2H; CH=N), 7.38 (d, $^3J_{H,H}$ = 7.8 Hz, 4H; ArH), 7.33 (t, $^3J_{H,H}$ = 7.7 Hz, 4H; ArH), 7.26 (t, $^3J_{H,H}$ = 7.2 Hz, $^4J_{H,H}$ = 1.3 Hz, 2H; ArH), 6.98 (d, $^3J_{H,H}$ = 8.6 Hz, $^4J_{H,H}$ = 2.4 Hz, 2H; ArH), 6.76 (d, $^4J_{H,H}$ = 2.1 Hz, 2H; ArH), 6.58 (d, $^3J_{H,H}$ = 8.6 Hz, 2H; ArH), 5.07 (s, 2H, CH–CH), 2.09 (s, 6H, ArMe); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ = 169.91, 169.74, 141.28, 135.18, 134.84, 128.95, 128.39, 127.97, 123.10, 120.68, 118.93, 72.72, 20.14; MS (MALDI+, dctb): *m/z* = 510.3 $[M]^+$ (calcd 510.1), 1025.3 $(2M+H)^+$ (calcd. 1025.3); elemental analysis calcd for $C_{30}H_{26}N_2O_2Zn{\cdot}½H_2O$: C 69.17, H 5.22, N 5.38; found: C 69.47, H 5.27, N 5.41.

Zn(salen) complex (13): A solution of (1*R*,2*R*)-(–)-1,2-diphenylethylenediamine (66.0 mg, 0.311 mmol), 3-*tert*-butyl-5-(4-pyridyl)-salicylaldehyde[22] (166.9 mg, 0.654 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (81.0 mg, 0.369 mmol) in MeOH (20 ml) and pyridine (0.5 mL) was stirred at r.t. for 65 h and then filtered to give the product as a yellow solid. Yield: 129.5 mg (0.0173 mmol, 56%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 8.39-8.41 (m, 4H; pyr-H), 8.29 (s, 2H; CH=N), 7.56-7.58 (m, 4H; pyr-H), 7.4 (d, $^4J_{H,H}$ = 2.4 Hz, 2H; ArH), 7.31-7.37 (m, 8H; ArH), 7.24-7.28 (m, 2H; ArH), 5.16 (s, 2H, CH–CH), 1.51 (s, 18H, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6]DMSO): δ = 172.86, 170.61, 148.02, 140.64, 132.80, 128.95, 128.45, 128.10, 128.07, 124.08, 119.91, 119.87, 72.21, 35.67, 29.70; MS (MALDI+, pyrene): *m/z* = 749.4 $[M+H]^+$ (calcd 749.3); elemental analysis calcd for $C_{30}H_{26}N_2O_2Zn{\cdot}2½H_2O$: C 69.47, H 6.21, N 7.04; found: C 69.38, H 5.82, N 6.99.

Assembly $(1)_2$·dabco (14): A hot solution of Zn(salen) complex **1** (110.5 mg, 0.149 mmol) in CH_3CN (25 mL) was added to dabco (9.8 mg, 0.0874 mmol) and the mixture was shortly heated to reflux and then allowed to cool to r.t. In due course the product crystallized out as yellow needles which were collected by filtration and dried. Yield: 64.7 mg (0.0406 mmol, 46%). ^1H NMR (400 MHz, [D_6]Acetone): δ = 8.02 (s, 4H; CH=N), 7.21-7.37 (m, 24H; ArH), 6.67 (d, $^4J_{H,H}$ = 2.7 Hz, 4H; ArH), 5.15 (s, 4H, CH–CH), 2.96 (s, 12H; dabco-H), 1.50 (s, 36H; $C(CH_3)_3$), 1.22 (s, 36H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (100 MHz, [D_6] Acetone): δ = 169.84, 169.68, 140.91, 138.80, 132.89, 129.59, 129.00, 128.58, 128.23, 128.21, 128.01, 127.90, 118.12, 72.15, 46.41, 35.30, 33.34, 30.91 (one C-signal is overlapping with solvent residual peaks); MS (ESI+, MeOH): *m/z* = 707.3 (**1**+H)$^+$ (calcd. 707.4), 729.3 (**1**+Na)$^+$ (calcd. 729.3), 819.4 (**1**·dabco+H)$^+$ (calcd. 819.5), 1417.6 $(2M+H)^+$ (calcd. 1417.7), 1439.6 $(2M+Na)^+$ (calcd. 1439.7): elemental analysis calcd for $C_{94}H_{120}N_6O_4Zn_2{\cdot}2H_2O$: C 72.15, H 7.99, N 5.37; found: C 72.31, H 7.96, N 5.50.

Assembly $(1)_2$/NBu_4OH (15): A solution of (1*R*,2*R*)-configured Zn(salen) complex **2** (286.9 mg, 0.405 mmol) in CH_3CN (10 mL) was added NBu_4OH (0.5 mL of a 1 M solution in MeOH). Soon after the addition of the later the mixture was concentrated to about 3 mL and cooled to –30ºC. A few drops of water were added to induce precipitation of the product (light orange/yellow solid), which was collected by filtration and dried. Yield: 203.3 mg (0.210 mmol, 52%). Crystals were obtained from a saturated solution in [D_6]acetone. ^1H NMR (400 MHz, [D_6]Acetone): δ = 7.80 (d, $^4J_{H,H}$ = 1.4 Hz, 2H; CH=N), 7.39 (d, $^4J_{H,H}$ = 1.8 Hz, 2H; CH=N), 7.24 (d, $^4J_{H,H}$ = 2.6 Hz, 2H; ArH), 7.20 (d, $^4J_{H,H}$ = 2.6 Hz, 2H; ArH), 6.99-7.11 (m, 16H; ArH), 6.79 (m, 4H; ArH), 6.50 (d, $^4J_{H,H}$ = 2.6 Hz, 2H; ArH), 6.44 (d, $^4J_{H,H}$ = 2.6 Hz, 2H; ArH), 4.85 (d, $^2J_{H,H}$ = 11.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 2H; C$\boldsymbol{H}_A$–CH_B), 4.69 (d, $^2J_{H,H}$ = 11.3 Hz, $^4J_{H,H}$ = 1.4 Hz, 2H; CH_A–C$\boldsymbol{H}_B$), 3.44-3.48 (m, 8H; NCH_2),

1.80-1.88 (m, 8H; NBu-H), 1.40-1.50 (m, 8H; NBu-H), 1.47 (s, 18H; $C(CH_3)_3$), 1.44 (s, 18H; $C(CH_3)_3$), 1.18 (s, 18H; $C(CH_3)_3$), 1.16 (s, 18H; $C(CH_3)_3$), 0.99 (t, $^3J_{H,H}$ = 7.4 Hz, 12H; NBu-H); assignments supported by ^{1}H-COSY and competition experiments, O-*H* not located; $^{13}C\{^1H\}$ NMR (126 MHz, [D$_6$]Acetone): δ = 170.30, 170.28, 168.36, 165.76, 140.79, 140.46, 140.03, 138.24, 130.43, 130.31, 130.22, 128.61, 128.21, 127.75, 126.86, 126.62, 126.39, 125.95, 118.57, 118.26, 72.59, 71.57, 58.48, 35.50, 35.44, 33.21, 31.32, 31.19, 29.60, 23.51, 19.47, 12.97; MS (ESI–, MeOH): *m/z* = 737.4 [**15**–OH+OMe]$^-$ (calcd 737.4), 751.4 [**15**–OH+OEt]$^-$ (calcd 751.4), 765.4 [**15**–OH+OPr]$^-$ (calcd 765.4), 1461.8 [M–OH+OEt]$^-$ (calcd 1462), 1491.8 [M–OH+OBu]$^-$ (calcd 1490); elemental analysis calcd for $C_{104}H_{145}N_5O_5Zn_2{\cdot}2H_2O$: C 72.96, H 8.77, N 4.09; found: C 72.92, H 8.23, N 4.13.

X-ray crystallographic studies: The measured crystals of were stable under atmospheric conditions; nevertheless they were treated under inert conditions immersed in perfluoropoly-ether as protecting oil for manipulation. Data Collection: Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoKα radiation, Montel mirrors and a Kryoflex low temperature device (T = –173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint + Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008-1 (2008). Structure Solution: SHELXTL Version 6.10 (Sheldrick, 2000)[23] was used. Structure Refinement: SHELXTL-97-UNIX VERSION.

Crystallographic details for (**2**)·$(CH_3CN)_4$: Formula $C_{96}H_{120}N_8O_4Zn_2$; M_w = 1580.74; crystal size 0.60 × 0.60 × 0.50 mm^3; monoclinic; space group *P*2(1); *a* = 14.0779(5) Å, *b* = 21.8466(9) Å, *c* = 14.7791(6) Å; α = 90, β = 105.179(2), γ = 90º; *V* = 4386.8(3) Å^3; *Z* = 2; ρ_{calcd} = 1.197 mg/M^3; μ(MoKα) = 0.601 mm^{-1}; *T* = 100(2) K; θ(min/max) = 1.43/36.35º; *F*(000) = 1688; 38894 reflections collected; 30785 unique reflections (R_{int} = 0.0370); absorption correction empirical; refinement method: full-matrix least-squares on F^2; data/restraints/ parameters: 38894/1/1019; GoF on F^2 = 0.994; R_1 = 0.0443 and wR_2 = 0.1007 [I>2σ(I)]; R_1 = 0.0630 and wR_2 = 0.1072 (all data); largest diff. peak and hole: 1.124 and –0.583 e^3·Å^{-3}; completeness (θ = 36.35º) = 98.1%; Flack parameter: x = 0.003(4).

Crystallographic details for **10**·$(DMSO)_2$: Formula $C_{32}H_{32}N_4O_8S_2Zn$; M_w = 730.11; crystal size 0.30 × 0.12 × 0.12 mm^3; triclinic; space group *P*1; *a* = 9.6549(5) Å, *b* = 11.6525(6) Å, *c* = 14.7054(8) Å; α = 80.141(2), β = 83.968(2), γ = 89.208(2)º; *V* = 1620.94(15) Å^3; *Z* = 2; ρ_{calcd} = 1.496 mg/M^3; μ(MoKα) = 0.944 mm^{-1}; *T* = 100(2) K; θ(min/max) = 1.41/27.27º; *F*(000) = 756; 21345 reflections collected; 8527 unique reflections (R_{int} = 0.0203); absorption correction empirical; refinement method: full-matrix least-squares on F^2; data/restraints/ parameters: 8527/3/862; GoF on F^2 = 1.042; R_1 = 0.0274 and wR_2 = 0.0719 [I>2σ(I)]; R_1 = 0.0281 and wR_2 = 0.0725 (all data); largest diff. peak and hole: 1.097 and –0.447 e^3·Å^{-3}; completeness (θ = 27.27º) = 83.9%; Flack parameter: x = -0.005(8).

Crystallographic details for the polymeric side-product during the synthesis of **13**: Formula $C_{35}H_{38}N_3O_5Zn$; M_w = 646.05; crystal size 0.07 × 0.04 × 0.03 mm^3; rhombohedral; space group *R*-3; *a* = 23.5495(15) Å, *b* = 23.5495(15) Å, *c* = 14.821(3) Å; α = 90, β = 90, γ = 120º; *V* = 7118.3(15) Å^3; *Z* = 9; ρ_{calcd} = 1.356 mg/M^3; μ(MoKα) = 0.823 mm^{-1}; *T* = 100(2) K; θ(min/max) = 1.698/28.686º; *F*(000) = 3051; 12119 reflections collected; 4073 unique reflections (R_{int} = 0.0436); absorption correction empirical; refinement method: full-matrix least-squares on F^2; data/restraints/ parameters: 4073/80/271; GoF on F^2 = 1.146; R_1 = 0.0430 and wR_2 = 0.0992 [I>2σ(I)]; R_1 = 0.0473 and wR_2 = 0.1014 (all data); largest diff. peak and hole: 0.510 and –0.367 e^3·Å^{-3}; completeness (θ = 28.686º) = 99.4%; The absorption correction for this structure was done using the program TWINABS[24] as the sample consisted of two crystalline domains.

Crystallographic details for assembly **14**·$(CH_3CN)_2$: Formula $C_{98}H_{126}N_8O_4Zn_2$; M_w = 1610.80; crystal size 0.35 × 0.02 × 0.02 mm^3; orthorhombic; space group *P*2(1)2(1)2(1); *a* = 11.284(4) Å, *b* = 24.382(9) Å, *c* = 33.548(12) Å; α = β = γ = 90º; *V* = 9230(6) Å^3; *Z* = 4; ρ_{calcd} = 1.159 mg/M^3; μ(MoKα) = 0.573 mm^{-1}; *T* = 100(2) K; θ(min/max) = 1.670/23.416º; *F*(000) = 3448; 166995 reflections collected; 13323 unique reflections (R_{int} = 0.2452); absorption correction empirical; refinement method: full-matrix least-squares on F^2; data/restraints/ parameters: 13323/24/1035; GoF on F^2 = 1.034; R_1 = 0.0906 and wR_2 = 0.2108 [I>2σ(I)]; R_1 = 0.1393 and wR_2 = 0.2462 (all data); largest diff. peak and hole: 1.702 and –1.465 e^3·Å^{-3}; completeness (θ = 23.416º) = 98.6%; Flack parameter: x = -0.033(18).

Crystallographic details for assembly **15**·(acetone): Formula $C_{56.69}H_{81.88}N_{2.5}O_{4.06}Zn$; M_w = 928.74; crystal size 0.30 × 0.15 × 0.15 mm^3; triclinic; space group *P*1; *a* = 13.6739(4) Å, *b* = 16.9639(5) Å, *c* = 25.4140(8) Å; α = 85.441(2), β = 77.685(2), γ = 71.526(2)º; *V* = 5462.2(3) Å^3; *Z* = 4; ρ_{calcd} = 1.129 mg/M^3; μ(MoKα) = 0.494 mm^{-1}; *T* = 100(2) K; θ(min/max) = 1.517/33.081º; *F*(000) = 2008; 120861 reflections collected; 64350 unique reflections (R_{int} = 0.0465); absorption correction empirical; refinement method: full-matrix least-squares on F^2; data/restraints/ parameters: 64350/1003/2622; GoF on F^2 = 0.986; R_1 = 0.0549 and wR_2 = 0.1315 [I>2σ(I)]; R_1 = 0.0888 and wR_2 = 0.1502 (all data); largest diff. peak and hole: 1.017 and –0.985 e^3·Å^{-3}; completeness (θ = 33.081º) = 92.6%; Flack parameter: x = 0.009(5).

Supporting Information (see footnote on the first page of this article): Copies of relevant MS and NMR spectra of known and new compounds. CCDCs 988530-988534 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Spanish Ministry of Science and Innovation (MICINN) through project CTQ2011-27385, ICREA and ICIQ. We thank Dr N. Cabello, A. Gonzalez and S. Arnal for the mass spectrometric analyses. Dr Daniele Anselmo is thanked for experimental assistance concerning complex **2**.

[1] a) T. Katsuki, *Coord. Chem. Rev*. **1995**, *140*, 189-214; b) E.N. Jacobsen, *Acc. Chem. Res*. **2000**, *33*, 421 – 431; c) P. G. Cozzi, *Chem. Soc. Rev*. **2004**, *33*, 410–421; d) E. M. McGarrigle, D. G. Gilheany, *Chem. Rev*. **2005**, *105*, 1563–1602; e) R. M. Haak, S. J. Wezenberg, A. W. Kleij, *Chem. Commun*. **2010**, *46*, 2713; f) A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed*. **2010**, *49*, 9822-9838.

[2] For a review: C. J. Whiteoak, G. Salassa, A. W. Kleij, *Chem. Soc. Rev*. **2012**, *41*, 622-631.

[3] a) J. K.-H. Hui, Z. Yu, M. J. MacLachlan, *Angew. Chem. Int. Ed*. **2007**, *46*, 7980-7983; b) M. V. Escárcega-Bobadilla, G. A. Zelada-Guillén, S. V. Pyrlin, M. Wegrzyn, M. M. D. Ramos, E. Giménez, A. Stewart, G. Maier, A. W. Kleij, *Nat. Comm*. **2013**, *4*, 2648; c) G. Salassa, M. J. J. Coenen, S. J. Wezenberg, B. L. M. Hendriksen, S. Speller, J. A. A.W. Elemans, A.W. Kleij, *J. Am. Chem. Soc*. **2012**, *134*, 7186-7192.

[4] a) A. K. Crane, M. J. MacLachlan, *Eur. J. Inorg. Chem*. **2012**, 17-30; b) G. Li, W. Yu, J. Ni, T. Liu, Y. Liu, E. Sheng, Y. Cui, *Angew. Chem. Int. Ed*. **2008**, *47*, 1245-1247; c) J. H. Chong, S. J. Ardakani, K. J. Smith, M. J. MacLachlan, *Chem. Eur. J*. **2009**, *15*, 11824–11828; d)

F. Song, C. Wang, J. M. Falkowski, L. Ma, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 15390–15398; e) M. Mastalerz, H.-J. S. Hauswald, R. Stoll, *Chem. Commun.* **2012,** *48*, 130-132.

[5] a) S. Akine, S. Sairenji, T. Taniguchi, T. Nabeshima, *J. Am. Chem. Soc.* **2013**, *135*, 12948–12951; b) S. Akine, S. Hotate, T. Nabeshima, *J. Am. Chem. Soc.* **2011**, *133*, 13868–13871; c) S. J. Wezenberg, G. Salassa, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Angew. Chem. Int. Ed.* **2011**, *50*, 713-716; d) M. V. Escárcega-Bobadilla, G. Salassa, M. Martínez Belmonte, E. C. Escudero-Adán, A. W. Kleij, *Chem. Eur. J.* **2012**, *18*, 6805-6810.

[6] Some examples include: a) J. Meeuwissen, J. N. H. Reek, *Nat. Chem.* **2010**, *2*, 615–621; b) J. Flapper, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2007**, *46*, 8590-8592; c) A. W. Kleij, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Commun*. **2005**, 3661-3663.

[7] a) I. Pietro Olivero, S. Failla, A. Colombo, C. Dragonetti, S. Righetto, S. Di Bella, *Dalton Trans.* **2014**, *43*, 2168-2175; b) G. Consiglio, S. Failla, P. Finocchiaro, I. Pietro Oliveri, S. Di Bella, *Dalton Trans.* **2012**, *41*, 387-395; c) C. T. L. Ma, M. J. MacLachlan, *Angew. Chem. Int. Ed.* **2005**, *44*, 4178-4182; d) G. Salassa, J. W. Ryan, E. C. Escudero-Adán, A. W. Kleij, *Dalton Trans*. **2014**, *43*, 210-221.

[8] For a selection: a) J. K.-H. Hui, M. J. MacLachlan, *Chem. Commun*. **2006**, 2480-2481; b) P. D. Frischmann, J. Jiang, J. K.-H. Hui, J. J. Grzybowski, M. J. MacLachlan, *Org. Lett.* **2008**, *10*, 1255-1258; c) E. C. Escudero-Adán, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2010**, *12*, 4592-4595; d) A. M. Castilla, S. Curreli, M. Martínez Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Org. Lett*. **2009**, *11*, 5218-5221.

[9] a) A. Decortes, M. Martínez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Chem. Commun*. **2010**, *46*, 4580-4582; b) A. Decortes, A. W. Kleij, *ChemCatChem* **2011**, *3*, 831-834.

[10] Chiral Zn(salen)s have been applied in asymmetric alkynylation of ketones: a) P. G. Cozzi, *Angew. Chem. Int. Ed*. **2003**, *42*, 2895-2898; other examples reporting on chiral Zn(salen) synthesis: b) A. Patti, S. Pedotti, F. Paolo Ballistreri, G. Trusso Sfrazzetto, *Molecules* **2009**, *14*, 4312-4325; c) W.-Y. Bi, X.-Q. Lü, W.-L. Chai, J.-R. Song, W.-Y. Wong, W.-K. Wong, R. A. Jones, *J. Mol. Struct*. **2008**, *891*, 450-455.

[11] N. Meyer, P. W. Roesky, *Z. Anorg. Allg. Chem*. **2007**, *633*, 229-2295.

[12] S.-S. Sun, C. L. Stern, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc*. **2004**, *126*, 6314-6326.

[13] a) A. W. Kleij, D. M. Tooke, M. Kuil, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem. Eur. J.* **2005**, *11*, 4743-4750; b) A. W. Kleij, D. M. Tooke, M. Lutz, A. L. Spek, J. N.H. Reek, *Eur. J. Inorg. Chem*. **2005**, 4626-4634; A. W. Kleij, *Eur. J. Inorg. Chem*. **2009**, 193-205.

[14] a) R. M. Haak, M. Martínez Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans*. **2010**, *39*, 593-602; b) R. M. Haak, A. M. Castilla, M. Martínez Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans*. **2011**, *40*, 3352-3364.

[15] a) S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem*. **2008**, *47*, 2925-2927; b) S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A.W. Kleij, *Org. Lett*. **2008**, *10*, 3311-3314.

[16] A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Inorg. Chim. Acta* **2006**, *359*, 1807-1814.

[17] S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Chem. Eur. J*. **2009**, *15*, 5695-5700.

[18] D. Anselmo, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans*. **2010**, *39*, 8733-8740.

[19] M. Kuil, PhD thesis "*Supramolecular Ligands in Transition Metal Catalysis*", University of Amsterdam, The Netherlands **2006** (OCLC: 150284917).

[20] R. Bellini, S. H. Chikkali, G. Berthon-Gelloz, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2011**, *50*, 7342-7345.

[21] K.-H. Chang, C.-C. Huang, Y.-H. Liu, Y.-H. Hu, P.-T. Chou, Y.-C. Lin, *Dalton Trans*. **2004**, 1731-1738.

[22] G. A. Morris, S. T. Nguyen, *Tetrahedron Lett*. **2001**, *42*, 2093-2096.

[23] G. M. Sheldrick, *SHELXTL Crystallographic System*, version 6.10, Bruker AXS, Inc., Madison, Wisconsin, **2000**.

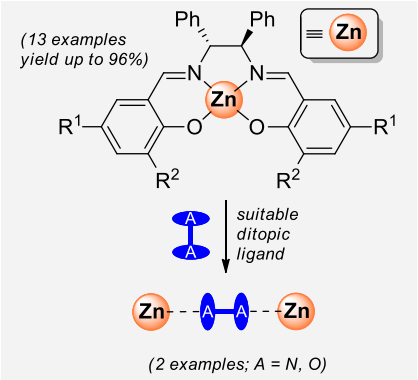
[24] TWINABS, version 2008/4, Bruker AXS; R. H. Blessing, *Acta Crystallogr*. Sect. A **1995**, *51*, 33 –38.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Entry for the Table of Contents:

Key Topic

A convenient method for the synthesis of a series of chiral Zn(salen)s based on a 1,2-diphenylethanediamine backbone has been developed. These complexes have been used to assemble multinuclear supramolecular assemblies of which the solid state and solution properties were determined. These chiral Zn(salen)s hold promise as molecular building blocks with modular characteristics.



Eddy Martin, Marta Martínez Belmonte, Eduardo C. Escudero-Adán, and Arjan W. Kleij*[a,b]……..
Page No. – Page No.

Exploring the Building Block Potential of Readily Accessible Chiral Zn(salen) Complexes

Keywords: Chiral / salen ligands / Self-Assembly / Synthesis / Zinc