A Convenient Synthetic Route for the Preparation of Nonsymmetric Metallo-salphen Complexes

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New nonsymmetric metallo(II)-salphen complexes **1**–**6** [salphen = *N*,*N*′-bis(salicylidene)-1,2-diaminobenzene, M = Zn, Ni] have been prepared in high yield by a templated, one-pot two-step procedure starting from substituted *ortho*-phenylenediamines, salicylaldehydes and metal acetates in MeOH under mild conditions. The procedure allows the introduction of functional groups in the bridging phenyl fragment, whereas the use of the substituted monoimine intermediates **7**–**10** results in complexes with two structurally different phenyl side groups with various functionalities (complexes **11**–**21**) upon reaction with a second, different, salicylaldehyde reagent. A range of analytical tools confirmed the structures of these nonsymmetric salphen derivatives and the X-ray molecular structure of one of these nonsymmetric Zn^{II}-salphen complexes (i.e., **4**) is also reported.

Introduction

Salen ligands[1] are interesting tetradentate ligands with a rich coordination chemistry. Since the discovery of the effective use of salen-type ligands in the epoxidation of olefins,[2] asymmetric homogeneous catalysis with these systems has been subject of widespread investigations.[3] In order to achieve a constructive transformation of chiral information to a substrate molecule, an effective use of the steric and electronic information of the applied ligand is needed. However, such a desired variation of an asymmetrical ligand is often troublesome and synthetic methods in most cases give rise to a limited number of ligands. Our interest in the salen ligand was recently aroused as the salphen structure [salphen = *N*,*N*′-(phenylene)salicylidene] proved to be a highly useful building block for the construction of supramolecular architectures such as molecular boxes.[4] In these Zn^{II}-salphen complexes the metal ion is located in a nearly planar, rigid N_2O_2 coordination geometry with a vacant axial coordination site. We, and others, have used these planar structures in supramolecular synthesis, where the axial coordination site provides a binding site for suitable N donor systems that allows the construction of multicomponent tailored materials.[5] Beside their use in supramolecular technology, Zn^{II}-salen complexes have also recently gained renewed interest as a result of their scope in a number of catalytic conversions.[6] The blend of these two complementing aspects could launch new opportunities for the construction of catalytically active, functional assemblies.[7] Here, we disclose new, attractive templated methods for nonsymmetrical M^{II}-salphen building blocks, that circumvent the isolation of the salphen ligand prior to metalation.[8] The variation of the steric and electronic features using these flexible procedures will be demonstrated by the introduction of different (functional) groups that ultimately can be used to fine-tune the (donor) properties of the nonsymmetric ligand backbone.

Results and Discussion

The synthetic approach towards nonsymmetric Zn^{II}-salphen complexes **1**–**6** is outlined in Scheme 1. Commercially available, mono-substituted *ortho*-phenylene diamines or diamino-pyridines were used as starting materials.[4] Generally, the aldehyde and phenylene diamine precursors combined with a metal precursor $M(OAc)_2 \cdot nH_2O$ (M = Zn: $n = 2$; M = Ni: $n = 4$) were mixed in the appropriate stoichiometry to afford in a one-pot two step protocol complexes **1**–**6**. In most cases, the product could be simply isolated by one filtration step and isolation of the ligands prior to metalation is thus not necessary. This procedure therefore allows the introduction of functional groups in the phenyl bridge of the salphen structure and also different metal ions can be incorporated concomitantly (cf. complex **6**).

The molecular structure for Zn^{II}-salphen complex **4** was determined by X-ray crystallography (Figure 1). Interestingly, complex **4** is, unlike **1**–**3**, only moderately soluble in

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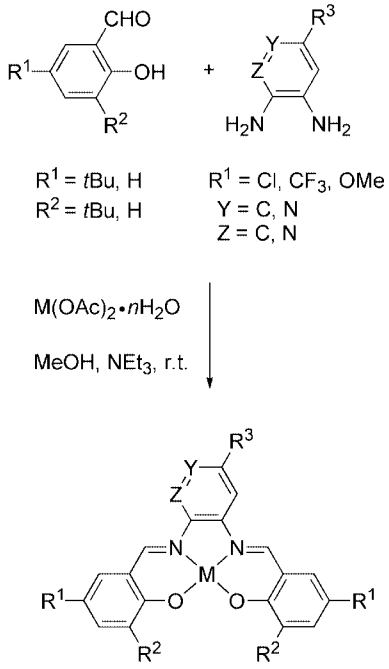


1 $R^1 = R^2 = t$Bu; R^3 = Cl; Y = Z = C; M = Zn
2 $R^1 = R^2 = t$Bu; $R^3 = CF_3$; Y = Z = C; M = Zn
3 $R^1 = R^2 = t$Bu; R^3 = OMe; Y = Z = C; M = Zn
4 $R^1 = R^2 = t$Bu; R^3 = H; Y = C; Z = N; M = Zn
5 $R^1 = R^2$ = H; R^3 = H; Y = N; Z = C; M = Zn
6 $R^1 = R^2$ = H; $R^3 = CF_3$; Y = Z = C; M = Ni

Scheme 1. Synthesis of nonsymmetric M^{II}-salphen complexes **1**–**6** starting from nonsymmetric *ortho*-phenylenediamine precursors.

toluene and CH_2Cl_2 and re-crystallization was achieved from hot toluene. X-ray quality crystals were, however, only obtained from a mixture of hot acetone/pyridine.[9] As expected from our previous studies using the Zn^{II}-salphen structure as a supramolecular building block through axial pyridine ligation,[4,5] complex **4** was analysed as its pyridine adduct under these conditions. Obviously, the presence of an internal pyridine donor in both **4** and **5** could provoke intermolecular association through supramolecular Zn–N_{pyr} interactions, which could account for their low solubility in the common organic solvents. In the presence of an excess of an external pyridine donor the intermolecular association is broken and monomeric **4**·pyridine was obtained exclusively this way. The LC-MS analysis for **5** also revealed the presence of an intensive peak for the dimeric species $[2M^+ + H]$, whereas for other Zn^{II}-salphen species in this work with small 3- and/or 3′-substituents present in the salphen backbone these species were not observed or with very low intensity. These dimeric species observed under the mass spectrometric conditions are generally associated to a dimerization process involving the O atoms of the individual monomers.[10] Obviously, this dimerization process is not only dependent on the size of the salphen substituents, but will also be influenced by the presence of nitrogen donor atoms such as in pyridines (vide supra, Figure 1) and the presence of donor solvents such as acetonitrile (cf. LC-MS studies, Exp. Sect.). The lower solubility features found for **4** and **5** are thus accountable for the presence of larger, associated species. It should be noted that their respective NMR spectra were recorded in the presence of solvent(s) combinations able to compete with this association behav-

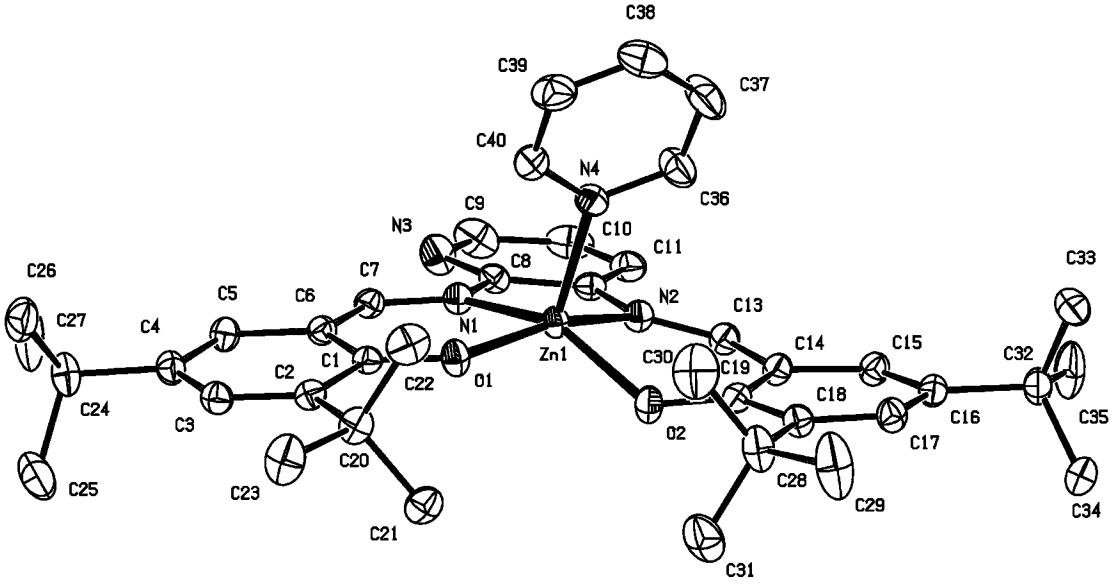


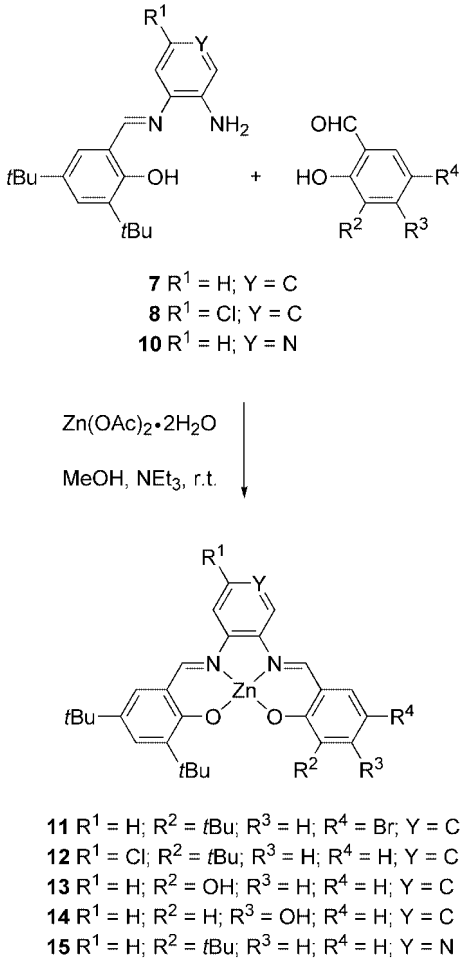
Figure 1. Displacement ellipsoid plot at the 50% probability level of the molecular structure for **4** in the crystal. H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] with esd's in parentheses: Zn(1)–N(1) = 2.0620(11), Zn(1)–N(2) = 2.1168(11), Zn(1)–O(1) = 1.9755(9), Zn(1)–O(2) = 1.9617(10), Zn(1)–N(4) = 2.1164(12), O(1)–Zn(1)–N(2) = 160.49(4), O(2)–Zn(1)–N(2) = 87.00(4), O(1)–Zn(1)–N(1) = 88.72(4), O(2)–Zn(1)–N(1) = 148.27(4), O(1)–Zn(1)–O(2) = 96.30(4), N(1)–Zn(1)–N(2) = 78.77(4), O(1)–Zn(1)–N(4) = 95.66(4), O(2)–Zn(1)–N(4) = 98.54(4), N(1)–Zn(1)–N(4) = 112.16(5), N(2)–Zn(1)–N(4) = 102.88(4).

iour (for, **4**: [D_5]pyridine and for **5**: [D_6]dmso) leading to the predominant observation of monomeric Zn^{II}-salphen complexes.[11]

The coordination geometry around the central zinc atom (Figure 1) is best described as distorted square pyramidal. Interestingly, the distances Zn(1)–N(2) and Zn(1)–N(4) are identical within experimental limits [2.1168(11) Å vs. 2.1164(12) Å], while the remaining Zn(1)–N(1) bond length is significantly shorter [2.0620(11) Å]. This leads to a non-symmetrical positioning of the Zn^{II} center above the N_2O_2 plane since both the Zn–O distances are rather similar [1.9755(9) and 1.9617(10) Å]. The bond length of the axial Zn–N interaction corresponds well with earlier reports on similar Zn^{II}salphen–pyridine interactions in the solid state (Zn–N distance in the range 2.10–2.14 Å),[4,12a] but is somewhat longer than communicated for Zn–pyridine interactions based on cyclohexyl-bridging salen ligands [Zn–N = 2.089(3) Å].[12b]

The introduction of functional entities in the aromatic bridge of the salphen structure was achieved by using a step-wise approach starting with the pre-isolation of the monoimine reagents **7**–**10**.[13] The monoimines **8**–**10** were isolated as mixture of regioisomers.[14] Particularly important in the selective isolation of monoimine products is the choice for an excess of the phenylene diamine reagent, and mono Schiff bases **7**–**10** were isolated as yellow to orange crystalline materials in moderate to good yield (26–84%, Scheme 2).[15]

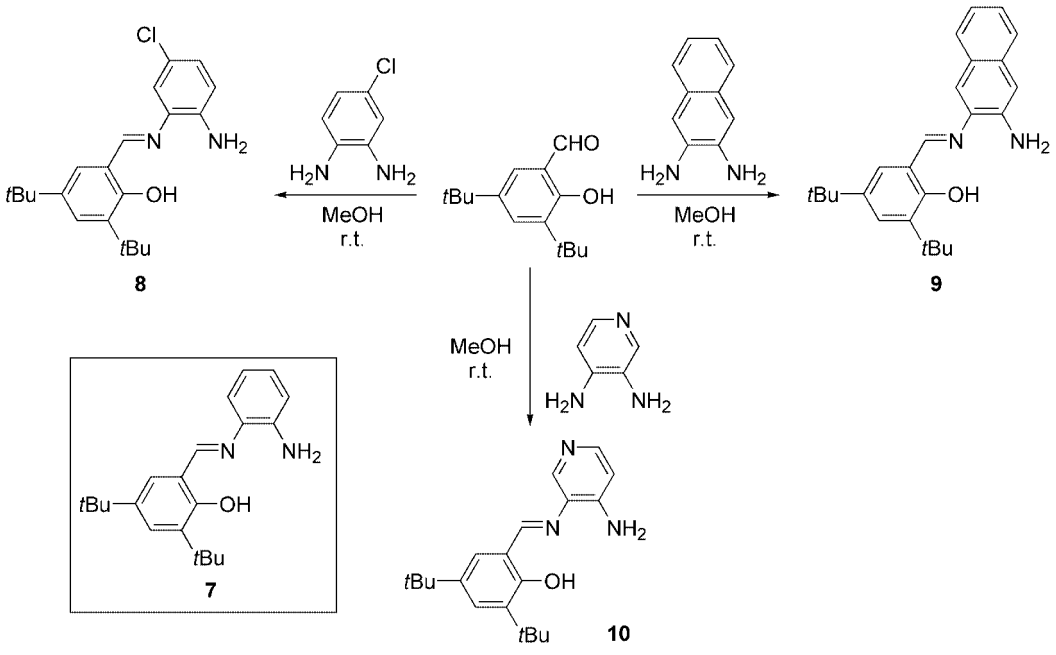
Synthesis of complexes **11**–**15** was carried out with monoimine precursors **7**–**10** and a second aldehyde reagent in the presence of $Zn(OAc)_2{\cdot}2H_2O$ and NEt_3 (see Scheme 3). Complexes **11**–**14** were isolated in high yield (60–94%) while the yield of **15** was low (25%). Interestingly,



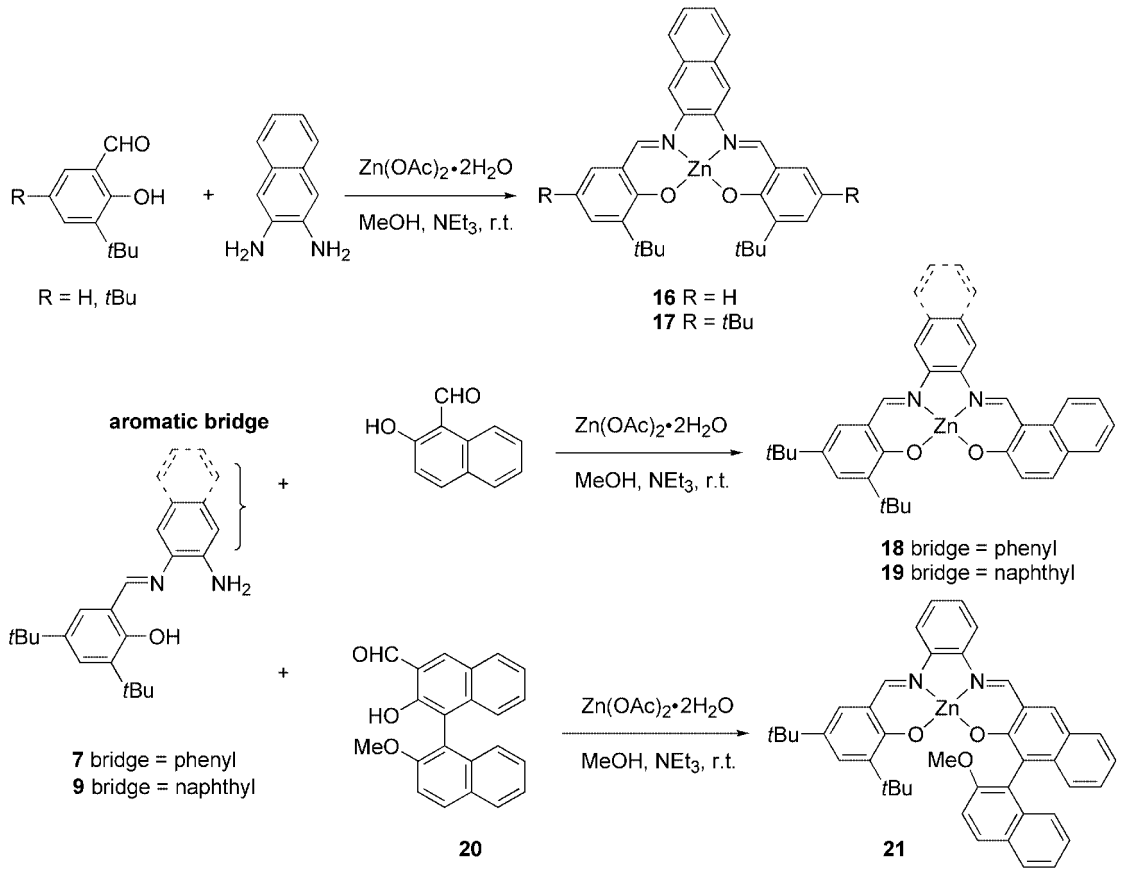
7 R^1 = H; Y = C
8 R^1 = Cl; Y = C
10 R^1 = H; Y = N

11 R^1 = H; R^2 = *t*Bu; R^3 = H; R^4 = Br; Y = C
12 R^1 = Cl; R^2 = *t*Bu; R^3 = H; R^4 = H; Y = C
13 R^1 = H; R^2 = OH; R^3 = H; R^4 = H; Y = C
14 R^1 = H; R^2 = H; R^3 = OH; R^4 = H; Y = C
15 R^1 = H; R^2 = *t*Bu; R^3 = H; R^4 = H; Y = N

Scheme 3. Synthesis of Zn^{II}-salphen complexes **11**–**15** via monoimine precursors **7**–**9**.



Scheme 2. Synthesis of monoimine precursors **8**–**10**.



Scheme 4. Synthesis of (bi)naphthyl-based Zn^{II}-salphen complexes **16**–**19** and **21**.

the use of dihydroxybenzaldehydes allows the easy introduction of synthetically powerful phenol groups (cf. complexes **13**–**14**). We have previously shown that *meso*-phenol-substituted Zn^{II}porphyrins can be readily converted into their respective tri-phosphite derivatives by treatment with PCl_3 and applied in homogeneously catalysed hydroformylation.[16] One important drawback in these cases, however, is the synthetic accessibility of these Zn^{II}porphyrin complexes and the labour-intensive purification procedures. Thus, Zn^{II}-salphen complexes **13**–**14** represent excellent alternatives and their phenol positions could be used for the preparation of new phosphite/phosphinite ligands and their subsequent application in homogeneous catalysis.

We were also interested in the introduction of larger aromatic groups than phenyl in the salphen structure. Obviously, like in conjugated systems such as porphyrin rings, this could lead to interesting photophysical phenomena.[17] Therefore, we first prepared symmetrical Zn^{II}-salphen complex **16** and **17** as model derivatives and these were isolated in high yield (84% and 96%, respectively) (Scheme 4. The use of monoimine reagents **7** and **9** allows the presence of both phenyl as well as naphthyl groups in the final product (cf. complexes **18**, **19** and **21**) and therefore the photochemical properties can be fine-tuned by simple variation of the polyaromatic reagents and/or monoimine precursor.

Please note that complex **21** represents an interesting chiral Zn^{II}-salphen building block with the chiral information located in (only) one of the aromatic side groups. In principle, this procedure can be extended using different chiral aldehyde/ketone reagents and enables simple variation in the salphen structure. This could open up possibilities for the construction of a new combinatorial libraries of chiral (Zn^{II})salphen-based catalysts, a field which has attracted much recent interest.[6] Additionally, such chiral building blocks could also be used for the construction of optically active, multi-component supramolecular assemblies.[4,5]

In summary, this contribution shows that the salphen structure is a versatile building unit that can be functionalised both at the bridging phenyl unit as well as the aromatic side groups with relative ease. Such new complexes will find their way in further synthesis (e. g. cross-coupling procedures and preparation of phosphite ligands) or can be simply used to fine-tune the electronic/steric properties of the salphen building block. This makes the salphen structure extremely useful for the creation of supramolecular materials and salphen-based homogeneous catalysts.[18] Studies along these lines are currently in progress in our laboratory.

Experimental Section

General: All reactions were carried out in air using commercial solvents, and reagent grade starting materials were purchased and used without purification. Compounds **20**,[19] 5-bromo-3-(*tert*-bu-

tyl)salicylaldehyde[20] and complexes **1** and **2**[4] were prepared according to literature procedures. All NMR spectra were recorded at ambient temperature with a Mercury/Inova (Varian) 300 or 500 MHz spectrometer; chemical shift values (δ) are given in ppm. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. MS measurements were carried out in CH_3CN with a Shimadzu LCMS 2010-A spectrometer using atmospheric pressure chemical ionization.

Zn^{II}-salphen Complex 3: A mixture of 4-methoxy-*o*-phenylenediamine (0.51 g, 2.42 mmol), 3,5-bis(*tert*-butyl)salicylaldehyde (1.22 g, 5.21 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.56 g, 2.55 mmol) and neat NEt_3 (2 mL) in MeOH (40 mL) was stirred at room temp. for 24 h. Then the product was isolated as reported for complexes **1** and **2** to furnish, after trituration with pentane, a yellow-orange solid (1.17 g, 76%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.31 [s, 18 H, $C(CH_3)_3$], 1.53 [s, 18 H, $C(CH_3)_3$], 3.90 (s, 3 H, OCH_3), 6.93 [d, ^3J(H,H) = 8.9, $^3J_{H,H}$ = 2.7 Hz, 1 H, ArH], 7.21 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, ArH), 7.23 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.40 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.43 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.47 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.86 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, ArH), 9.01 [s, 1 H, C(H)=N], 9.10 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 31.86, 31.93, 34.42, 36.29, 55.96, 101.43, 113.97, 117.59, 119.29, 119.41, 124.03, 124.37, 124.71, 129.32, 130.16, 130.44, 134.37, 134.56, 136.97, 137.26, 142.13, 142.39, 149.44, 149.82, 150.19, 159.91, 162.11, 171.56, 172.35 ppm. UV/Vis (toluene, c = 0.844 mg/50 mL): λ_{max} (ε) = 428 nm (22400 $mol^{-1}\,dm^3\,cm^{-1}$). MS (LC-MS, direct inlet, CH_3CN, APCI): m/z = 632 [M^+ + H], 674 [M^+ + H + CH_3CN]. $C_{37}H_{48}N_2O_3Zn$ (632.30): calcd. C 70.07, H 7.63, N 4.42; found C 69.92, H 7.74, N 4.32.

Zn^{II}-salphen Complex 4: A mixture of 2,3-diaminopyridine (0.47 g, 4.31 mmol), 3,5-bis(*tert*-butyl)salicylaldehyde (2.09 g, 8.92 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (1.13 g, 5.15 mmol) in MeOH (40 mL) was stirred at room temp. for 18 h. Then the product was collected by filtration to furnish a deep orange solid (2.19 g, 84%). ^{1}H NMR (300 MHz, [D$_6$]acetone/5% [D$_5$]pyridine): δ = 1.31 [s, 9 H, $C(CH_3)_3$], 1.33 [s, 9 H, $C(CH_3)_3$], 1.55 [s, 9 H, $C(CH_3)_3$], 1.56 [s, 9 H, $C(CH_3)_3$], 7.24 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.26 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.31 (dd, $^3J_{H,H}$ = 4.8 Hz, 1 H, pyr-H), 7.49 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.51 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 8.27 (d, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.4 Hz, 1 H, pyr-H), 8.33 (d, $^3J_{H,H}$ = 4.7, $^4J_{H,H}$ = 1.4 Hz, 1 H, pyr-H), 9.15 [s, 1 H, C(H)=N], 9.61 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_2$]dichloromethane/5% [D$_5$]pyridine): δ = 29.90, 31.63, 31.66, 34.30, 36.16, 118.72, 118.64, 122.23, 123.23, 129.57, 130.43, 130.71, 131.00, 135.01, 135.09, 135.51, 142.81, 142.85, 146.03, 151.54, 163.71, 164.56, 172.20, 173.33 ppm. UV/Vis (DMF, c = 0.928 mg/50 mL): λ_{max} (ε) = 433 nm (25900 $mol^{-1}\,dm^3\,cm^{-1}$). MS (LC-MS, direct inlet, CH_3CN, APCI): m/z = 603 [M^+ + H], 644 [M^+ + H + CH_3CN], 683 [M^+ + H + 2CH_3CN]. $C_{35}H_{45}N_3O_2Zn$ (603.28): calcd. C 69.47, H 7.50, N 6.94; found C 69.27, H 7.40, N 7.06.

Zn^{II}-salphen Complex 5: A yellow solution of 3,4-diaminopyridine (0.42 g, 3.85 mmol), salicylaldehyde (0.98 g, 8.02 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.84 g, 3.83 mmol) and NEt_3 (1 mL) in MeOH (40 mL) was stirred at room temp. for 18 h. In due course, an orange suspension was obtained, which was filtered to furnish the product as an orange solid. Yield: 1.32 g (90%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.52–6.56 (m, 2 H, ArH), 6.73 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.25–7.32 (m, 2 H, ArH), 7.42 (dd, $^3J_{H,H}$ = 8.5 Hz, 2 H, ArH), 7.86 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, pyr-H$_{meta}$), 8.49 (d, $^3J_{H,H}$ = 5.3, $^4J_{H,H}$ = 1.5 Hz, 1 H, pyr-H$_{ortho}$), 9.12, 9.14, 9.16 [3×s, 3 H, 2×C(H)=N and other pyr-H$_{ortho}$] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO): δ = 110.88, 113.43, 113.68, 119.34, 119.56, 123.43, 123.74, 135.00, 135.34, 135.87, 136.50, 137.00, 139.19, 145.74, 147.48, 163.89, 165.91, 172.69, 173.79 ppm. UV/Vis (DMF, c = 1.648 mg/50 mL): λ_{max} (ε) = 410 nm (21600 $mol^{-1}\,dm^3\,cm^{-1}$). MS (LC-MS, direct inlet, CH_3CN, APCI): m/z = 377 [M^+ + H], 418 [M^+ + H + CH_3CN], 457 [M^+ + H + 2CH_3CN], 763 [2M^+ + H]. $C_{28}H_{30}N_2O_3Zn$ (379.03): calcd. C 59.94, H 3.44, N 11.04; found C 60.08, H 3.51, N 10.84.

Ni^{II}-salphen Complex 6: To a solution of salicylaldehyde (1.22 g, 10.0 mmol) and 4-trifluoromethyl-*o*-phenylenediamine (0.76 g, 4.31 mmol) in MeOH (50 mL) was added a solution of $Ni(OAc)_2{\cdot}4H_2O$ (1.07 g, 4.30 mmol) in MeOH (15 mL). Slowly a red solid started to precipitate that was collected after 3 h in different fractions. All fractions were combined and dried in vacuo to yield 1.62 g (85%) of **6**. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 6.67 (dt, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.0 Hz, 2 H, ArH), 6.95 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.32–7.39 (m, 2 H, ArH), 7.58 (dt, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.8 Hz, 2 H, ArH), 7.65 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 8.31 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 8.46 (s, 1 H, ArH), 8.90 [s, 1 H, C(H)=N], 8.99 [s, 1 H, C(H)=N] ppm. ^{19}F NMR (282 MHz, [D$_6$]-acetone): δ = –57.1 ppm. The product was too insoluble for a proper ^{13}C{^{1}H} NMR analysis. UV/Vis (DMF, c = 1.193 mg/50 mL): λ_{max} (ε) = 382 nm (26300 $mol^{-1}\,dm^3\,cm^{-1}$), 485 nm (8750 $mol^{-1}\,dm^3\,cm^{-1}$). MS (LC-MS, direct inlet, CH_3CN, APCI): m/z = 441 [M^+ + H]. $C_{21}H_{13}F_3N_2NiO_2$ (440.03): calcd. C 57.19, H 2.97, N 6.35; found C 56.93, H 3.08, N 6.22.

Monoimine 8: A mixture of 4-chloro-*o*-phenylenediamine (4.31 g, 30.23 mmol) and 3,5-di(*tert*-butyl)salicylaldehyde (2.02 g, 8.62 mmol) in MeOH (100 mL) was stirred at room temp. for 16 h. Then the solution was slowly concentrated upon which the title compound separated as a yellow solid. The product was collected by filtration and dried. Yield: 0.79 g (26%). ^{1}H NMR (300 MHz, [D$_6$]acetone, major isomer): δ = 1.33 [s, 9 H, $C(CH_3)_3$], 1.45 [s, 9 H, $C(CH_3)_3$], 5.05 (br. s, 2 H, NH_2), 6.67 (d, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 2.1 Hz, 1 H, ArH), 6.90 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 7.17 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 7.47–7.50 (m, 2 H, ArH), 8.84 [s, 1 H, C(H)=N], 13.44 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$] acetone, major isomer): δ = 31.70, 34.79, 35.64, 115.42, 117.75, 119.83, 120.57, 128.32, 128.51, 133.29, 134.60, 137.11, 141.53, 144.47, 158.67, 164.87 ppm. UV/Vis (toluene, c = 1.163 mg/50 mL): λ_{max} (ε) = 382 nm (11200 $mol^{-1}\,dm^3\,cm^{-1}$). MS (LC-MS, direct inlet, CH_3CN, APCI): m/z = 359 [M^+ + H]. $C_{21}H_{27}ClN_2O$ (358.18): calcd. C 70.28, H 7.58, N 7.81; found C 70.21, H 7.64, N 7.73.

Monoimine 9: A mixture of 2,3-diaminonaphthalene (0.78 g, 4.93 mmol) and 3,5-di(*tert*-butyl)salicylaldehyde (1.10 g, 4.69 mmol) in MeOH (40 mL) was stirred at room temp. for 3 d. Then the mixture was filtered and the product collected by filtration and dried. Yield: 0.78 g (44%). ^{1}H NMR (300 MHz, [D$_6$]-acetone): δ = 1.36 [s, 9 H, $C(CH_3)_3$], 1.48 [s, 9 H, $C(CH_3)_3$], 5.00 (br. s, 2 H, NH_2), 7.14–7.20 (m, 2 H, ArH), 7.30 (t, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.5 Hz, 1 H, ArH), 7.53–7.60 (m, 4 H, ArH), 7.73 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, ArH), 8.97 [s, 1 H, C(H)=N], 13.52 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 29.87, 31.85, 34.92, 35.76, 109.21, 116.93, 119.99, 123.08, 126.12, 126.62, 128.61, 128.67, 128.80, 128.85, 135.26, 137.22, 139.80, 141.81, 142.10, 158.60, 166.35 ppm. UV/Vis (toluene, c = 0.945 mg/50 mL): λ_{max} (ε) = 366 nm (12500 $mol^{-1}\,dm^3\,cm^{-1}$). MS (LC-MS, direct inlet, CH_3CN, APCI): m/z = 375 [M^+ + H]. $C_{25}H_{30}N_2O$ (374.24): calcd. C 80.17, H 8.07, N 7.48; found C 79.97, H 8.10, N 7.36.

Monoimine 10: A mixture of 3,4-diaminopyridine (2.48 g, 22.73 mmol) and 3,5-di(*tert*-butyl)salicylaldehyde (1.84 g, 7.85 mmol) in MeOH (40 mL) was stirred at room temp. for 24 h. Then the mixture was filtered and the product collected by filtration and dried. Concentration of the mother liquor yielded a second fraction of a yellow solid. Total yield: 1.73 g (68%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.34 [s, 9 H, C(CH$_3$)$_3$], 1.46 [s, 9 H, C(CH$_3$)$_3$], 5.60 (br. s, 2 H, NH$_2$), 6.75 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, pyr-H), 7.51 (pseudo s, 2 H, ArH), 8.01 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, pyr-H), 8.11 (s, 1 H, pyr-H), 8.86 [s, 1 H, C(H)=N], 13.30 (s, 1 H, OH) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 29.84, 31.81, 34.84, 35.68, 110.12, 119.83, 128.50, 128.71, 132.99, 137.15, 140.24, 141.60, 148.76, 148.94, 158.73, 165.85 ppm. UV/Vis (toluene, *c* = 1.753 mg/50 mL): λ_{max} (ε) = 365 nm (9400 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): *m*/*z* = 322 [M$^+$ + H]. C$_{20}$H$_{27}$N$_3$O (325.22): calcd. C 73.65, H 8.42, N 12.78; found C 73.81, H 8.36, N 12.91.

Zn^{II}-salphen Complex 11: A mixture of monoimine **1** (0.44 g, 1.36 mmol), 5-bromo-3-(*tert*-butyl)salicylaldehyde[20] (0.35 g, 1.36 mmol), Zn(OAc)$_2$·2H$_2$O (0.33 g, 1.50 mmol) and neat NEt$_3$ (2 mL) in MeOH (40 mL) was stirred at room temp. for 68 h. Then two volumes of H$_2$O were added and the product collected by filtration, dried and triturated with pentane to furnish an orange-yellow solid. Yield: 0.50 g (60%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.31 [s, 9 H, C(CH$_3$)$_3$], 1.51 [s, 9 H, C(CH$_3$)$_3$], 1.53 [s, 9 H, C(CH$_3$)$_3$], 7.26 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.29 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.37–7.40 (m, 2 H, ArH), 7.45 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.93–7.96 (m, 2 H, ArH), 9.05 [s, 1 H, C(H)=N], 9.12 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 30.00, 30.15, 34.40, 36.23, 103.74, 116.53, 116.70, 119.25, 121.89, 127.38, 128.11, 129.94, 130.35, 133.67, 134.79, 136.09, 140.23, 141.04, 142.25, 145.86, 162.13, 163.65, 171.92, 172.08 ppm. UV/Vis (toluene, *c* = 0.814 mg/50 mL): λ_{max} (ε) = 427 nm (17000 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): *m*/*z* = 627 [M$^+$ + H], 668 [M$^+$ + H + CH$_3$CN], 707 [M$^+$ + H + 2CH$_3$CN]. C$_{32}$H$_{37}$BrN$_2$O$_2$Zn (624.13): calcd. C 61.30, H 5.95, N 4.47; found C 61.39, H 6.05, N 4.55.

Zn^{II}-salphen Complex 12: A mixture of monoimine **2** (0.65 g, 1.81 mmol), 3-(*tert*-butyl)salicylaldehyde (0.33 g, 1.85 mmol), Zn(OAc)$_2$·2H$_2$O (0.42 g, 1.91 mmol) and neat NEt$_3$ (1 mL) in MeOH (40 mL) was stirred at room temp. for 41 h. Then the product was collected by filtration and dried to furnish a yellow solid. Yield: 0.99 g (94%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.31 [s, 9 H, C(CH$_3$)$_3$], 1.51 [s, 9 H, C(CH$_3$)$_3$], 1.53 [s, 9 H, C(CH$_3$)$_3$], 6.49 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, ArH), 7.24 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.29–7.33 (m, 2 H, ArH), 7.36 (d, $^4J_{H,H}$ = 2.1 Hz, 1 H, ArH), 7.45 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.93 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, ArH), 7.95 (s, 1 H, ArH), 9.10 [s, 1 H, C(H)=N], 9.11 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_2$]dichloromethane/5% [D$_5$]pyridine): δ = 29.80, 29.90, 31.65, 34.30, 35.87, 36.11, 113.41, 116.50, 117.35, 118.56, 119.80, 127.02, 129.72, 130.42, 131.90, 132.47, 134.80, 135.04, 139.57, 141.58, 142.64, 143.42, 163.24, 163.38, 172.02, 173.90 ppm. UV/Vis (toluene, *c* = 0.728 mg/50 mL): λ_{max} (ε) = 429 nm (20700 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): *m*/*z* = 583 [M$^+$ + H], 622 [M$^+$ + H + CH$_3$CN], 661 [M$^+$ + H + 2CH$_3$CN]. C$_{32}$H$_{37}$ClN$_2$O$_2$Zn·H$_2$O (580.18 for complex without H$_2$O): calcd. C 64.00, H 6.55, N 4.66; found C 63.85, H 6.78, N 4.51.

Zn^{II}-salphen Complex 13: A green suspension of 2,3-dihydroxybenzaldehyde (0.30 g, 2.17 mmol), monoimine **1** (0.71 g, 2.19 mmol) and Zn(OAc)$_2$·2H$_2$O (0.48 g, 2.19 mmol) in MeOH (40 mL) was stirred at room temp. for 24 h. In due course, a yellow-ish suspension was obtained, which was filtered to furnish the product as a yellow-orange solid. Yield: 0.89 g (81%). ^{1}H NMR (300 MHz, [D$_6$]acetone/5% [D$_5$]pyridine): δ = 1.30 [s, 9 H, C(CH$_3$)$_3$], 1.53 [s, 9 H, C(CH$_3$)$_3$], 6.45 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, ArH), 6.82 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, ArH), 6.94 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, Ar-H), 7.23 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.36 (t, $^3J_{H,H}$ = 6.3, $^4J_{H,H}$ = 2.1 Hz, 2 H, ArH), 7.44 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, pyr-H), 7.46 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.84 (t, $^3J_{H,H}$ = 8.7 Hz, 1 H, pyr-H), 9.00 [s, 1 H, C(H)=N], 9.05 [s, 1 H, C(H)=N] ppm. The OH proton was in exchange with residual water in the solvent. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO/5% [D$_5$]pyridine): δ = 29.40, 31.29, 33.53, 35.18, 113.16, 113.47, 116.75, 117.28, 118.21, 125.27, 126.81, 127.73, 128.80, 129.74, 133.61, 139.19, 140.16, 140.71, 148.88, 159.24, 163.13, 164.11, 170.53 ppm. UV/Vis (DMF, *c* = 1.746 mg/50 mL): λ_{max} (ε) = 414 nm (15500 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): *m*/*z* = 507 [M$^+$ + H], 548 [M$^+$ + H + CH$_3$CN], 1017 [2M$^+$ + H]. C$_{28}$H$_{30}$N$_2$O$_3$Zn (506.15): calcd. C 66.21, H 5.95, N 5.52; found C 66.07, H 6.10, N 5.38.

Zn^{II}-salphen Complex 14: A yellow suspension of 2,4-dihydroxybenzaldehyde (0.22 g, 1.59 mmol), monoimine **1** (0.47 g, 1.45 mmol) and Zn(OAc)$_2$·2H$_2$O (0.35 g, 1.59 mmol) in MeOH (40 mL) was stirred at room temp. for 18 h. Hereafter, water was added to precipitate the product, which was washed with pentane and isolated by filtration. Drying in vacuo afforded a yellow solid. Yield: 0.51 g (69%). ^{1}H NMR (300 MHz, [D$_6$]acetone/5% [D$_5$]pyridine): δ = 1.30 [s, 9 H, C(CH$_3$)$_3$], 1.49 [s, 9 H, C(CH$_3$)$_3$], 6.13 (d, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 8.7 Hz, 1 H, ArH), 6.26 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ArH), 7.21–7.30 (m, 4 H, Ar-H), 7.42 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.72–7.76 (m, 2 H, ArH), 8.85 [s, 1 H, C(H)=N], 8.96 [s, 1 H, C(H)=N] ppm. The OH proton was in exchange with residual water in the solvent which appeared as a broad signal at δ = 3.01 ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO/10% [D$_5$]pyridine): δ = 29.63, 30.69, 31.41, 33.61, 35.29, 105.12, 107.06, 113.89, 115.92, 116.39, 118.37, 123.48, 123.80, 124.13, 126.25, 126.80, 128.49, 129.66, 133.34, 136.58, 138.20, 139.74, 140.01, 140.76, 148.44, 148.81, 149.15, 161.15, 164.11, 170.50, 174.77 ppm. UV/Vis (toluene, *c* = 1.888 mg/50 mL): λ_{max} (ε) = 398 nm (15800 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): *m*/*z* = 505 [M$^+$ + H], 546 [M$^+$ + H + CH$_3$CN], 1017 [2M$^+$ + H]. C$_{28}$H$_{30}$N$_2$O$_3$Zn·3.5H$_2$O (506.15 for complex without H$_2$O): calcd. C 58.90, H 6.53, N 4.91; found C 58.73, H 6.51, N 4.83.

Zn^{II}-salphen Complex 15: A mixture of monoimine **4** (0.42 g, 1.29 mmol), 3-(*tert*-butyl)salicylaldehyde (0.24 g, 1.35 mmol) and Zn(OAc)$_2$·2H$_2$O (0.33 g, 1.50 mmol) in MeOH (40 mL) was stirred at room temp. for 3 d. Then the product was collected by filtration to furnish an orange-red solid (178.6 mg, 25%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.33 [s, 9 H, C(CH$_3$)$_3$], 1.53 [s, 9 H, C(CH$_3$)$_3$], 1.58 [s, 9 H, C(CH$_3$)$_3$], 6.53 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, ArH), 7.31–7.37 (m, 3 H, ArH), 7.52 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, ArH), 7.75 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, pyr-H$_{meta}$), 8.46 (d, $^3J_{H,H}$ = 5.7 Hz, 1 H, pyr-H$_{ortho}$), 8.61 (s, 1 H, pyr-H$_{ortho}$), 9.16 [s, 1 H, C(H)=N], 9.28 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_2$]dichloromethane/30% [D$_5$]pyridine): δ = 29.72, 29.85, 31.52, 34.12, 35.74, 36.01, 109.84, 113.67, 118.69, 119.66, 129.74, 130.40, 132.52, 135.06, 139.10, 142.55, 143.52, 146.19, 147.69, 163.71, 164.89, 172.08, 174.90 ppm. UV/Vis (DMF, *c* = 1.294 mg/50 mL): λ_{max} (ε) = 426 nm (20900 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): *m*/*z* = 547 [M$^+$ + H], 588 [M$^+$ + H + CH$_3$CN], 626 [M$^+$ + H + 2CH$_3$CN]. C$_{31}$H$_{37}$N$_3$O$_2$Zn (547.22): calcd. C 67.82, H 6.79, N 7.65; found C 68.64, H 6.66, N 7.72.

Zn^{II}-salphen Complex 16: A mixture of 2,3-diaminonaphthalene (0.42 g, 2.65 mmol), 3-(*tert*-butyl)salicylaldehyde (1.10 g,

6.17 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.66 g, 3.01 mmol) and neat NEt_3 (2 mL) in MeOH (65 mL) was stirred at room temp. for 17 h. Then the product was collected by filtration and dried to furnish an orange solid (1.21 g, 84%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.55 [s, 18 H, C(CH$_3$)$_3$], 6.50 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, ArH), 7.31 (d, $^3J_{H,H}$ = 7.8 Hz, 4 H, ArH), 7.47–7.50 (m, 2 H, ArH), 7.92–7.95 (m, 2 H, ArH), 8.32 (s, 2 H, ArH), 9.22 [s, 2 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone/5% [D$_5$]pyridine): δ = 30.18, 36.03, 113.57, 114.27, 120.72, 126.89, 128.69, 131.89, 133.25, 135.47, 140.56, 143.02, 165.18, 174.13 ppm. UV/Vis (toluene, c = 0.751 mg/50 mL): λ_{max} (ε) = 431 nm (25400 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): m/z = 539 [M$^+$ + H], 581 [M$^+$ + H + CH$_3$CN]. $C_{32}H_{32}N_2O_2Zn{\cdot}H_2O$ (540.18 for complex without H_2O): calcd. C 68.63, H 6.12, N 5.00; found C 68.24, H 6.65, N 4.59.

Zn^{II}-salphen Complex 17: A mixture of 2,3-diaminonaphthalene (0.37 g, 2.34 mmol), 3,5-di(*tert*-butyl)salicylaldehyde (1.24 g, 5.29 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.54 g, 2.46 mmol) and neat NEt_3 (2 mL) in MeOH (40 mL) was stirred at room temp. for 17 h. Then the product was collected by filtration and dried to furnish an orange solid (1.47 g, 96%). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 1.34 [s, 18 H, C(CH$_3$)$_3$], 1.55 [s, 18 H, C(CH$_3$)$_3$], 7.25 (d, $^4J_{H,H}$ = 3.0 Hz, 2 H, ArH), 7.44 (d, $^4J_{H,H}$ = 2.7 Hz, 2 H, ArH), 7.45–7.48 (m, 2 H, ArH), 7.92–7.95 (m, 2 H, ArH), 8.30 (s, 2 H, ArH), 9.21 [s, 2 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone/5% [D$_5$]pyridine): δ = 30.30, 31.86, 34.48, 36.33, 113.63, 114.01, 114.35, 119.55, 126.76, 128.64, 130.47, 133.30, 134.76, 140.95, 142.47, 165.47, 172.61 ppm. UV/Vis (toluene, c = 1.013 mg/50 mL): λ_{max} (ε) = 443 nm (25800 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): m/z = 652 [M$^+$ + H], 694 [M$^+$ + H + CH$_3$CN]. $C_{40}H_{48}N_2O_2Zn$ (652.30): calcd. C 73.44, H 7.40, N 4.28; found C 73.24, H 7.29, N 4.18.

Zn^{II}-salphen Complex 18: A mixture of monoimine **1** (0.66 g, 2.03 mmol), 2-hydroxy-1-naphthalenecarbaldehyde (0.35 g, 2.03 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.52 g, 2.37 mmol) and neat NEt_3 (2 mL) in MeOH (40 mL) was stirred at room temp. for 16 h. Then the product was collected by filtration and dried to furnish an orange/brown solid (0.60 g, 55%). Analytically pure **18** was obtained by crystallization from hot CH$_3$CN. ^{1}H NMR (300 MHz, [D$_6$]acetone/10% [D$_5$]pyridine): δ = 1.32 [s, 9 H, C(CH$_3$)$_3$], 1.56 [s, 9 H, C(CH$_3$)$_3$], 7.00 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, ArH), 7.17–7.47 (m, 6 H, ArH), 7.66–7.82 (m, 3 H, ArH), 8.01 (d, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.8 Hz, 1 H ArH), 8.38 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 9.02 [s, 1 H, C(H)=N], 9.91 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone/10% [D$_5$]pyridine): δ = 31.85, 34.44, 36.26, 110.17, 116.96, 117.55, 119.44, 120.04, 122.41, 127.04, 127.36, 127.77, 128.24, 128.61, 129.74, 129.95, 130.49, 134.74, 136.57, 141.06, 142.23, 142.44, 157.66, 164.34, 172.15, 175.50 ppm. UV/Vis (toluene, c = 0.734 mg/50 mL): λ_{max} (ε) = 423 nm (23000 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): m/z = 539 [M$^+$ + H], 581 [M$^+$ + H + CH$_3$CN], 1088 [2M$^+$ + H]. $C_{32}H_{32}N_2O_2Zn$ (540.18): calcd. C 70.91, H 5.95, N 5.17; found C 70.81, H 6.04, N 5.35.

Zn^{II}-salphen Complex 19: A mixture of monoimine **3** (0.50 g, 1.34 mmol), 2-hydroxy-1-naphthalenecarbaldehyde (0.26 g, 1.51 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.37 g, 1.69 mmol) and neat NEt_3 (2 mL) in MeOH/acetone (40:20 mL) was stirred at room temp. for 18 h. Then, extra MeOH (40 mL) was added and the precipitated product was collected by filtration and dried to furnish an orange solid (0.52 g, 66%). Analytically pure **19** was obtained by crystallization from hot CH_3CN/CH_2Cl_2. ^{1}H NMR (300 MHz, [D$_6$]acetone/10% [D$_5$]pyridine): δ = 1.36 [s, 9 H, C(CH$_3$)$_3$], 1.62 [s, 9 H, C(CH$_3$)$_3$], 7.07 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, ArH), 7.24 (t, $^3J_{H,H}$ = 7.8 Hz, 1 H, ArH), 7.33 (s, 1 H, ArH), 7.44–7.55 (m, 4 H, ArH), 7.69–7.79 (m, 2 H, ArH), 7.93 (m, 1 H, ArH), 8.00 (m, 1 H, ArH), 8.47 (m, 2 H, ArH), 9.18 [s, 1 H, C(H)=N], 10.09 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_2$]dichloromethane/10% [D$_5$]pyridine): δ = 29.90, 31.68, 34.27, 36.06, 109.94, 113.62, 113.87, 119.01, 119.29, 122.26, 126.42, 126.70, 127.90, 128.20, 129.51, 129.88, 130.25, 132.63, 132.91, 135.04, 136.55, 140.62, 142.00, 142.24, 158.19, 164.55, 171.99, 175.38 ppm. UV/Vis (toluene, c = 1.188 mg/50 mL): λ_{max} (ε) = 434 nm (28200 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): m/z = 590 [M$^+$ + H], 631 [M$^+$ + H + CH$_3$CN]. $C_{36}H_{34}N_2O_2Zn{\cdot}1/3CH_2Cl_2{\cdot}1/3CH_3CN$. (590.19 for complex without solvent): calcd. C 70.09, H 5.67, N 5.15; found C 70.29, H 5.24, N 5.30.

Zn^{II}-salphen Complex 21: A mixture of **1** (166.0 mg, 0.512 mmol), (*S*)-2-hydroxy-2′-methoxy-1,1′-binaphthalene-3-carboxaldehyde (168.1 mg, 0.512 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (115.3 mg, 0.525 mmol) and neat NEt_3 (0.5 mL) in hot MeOH (50 mL). The initial dark-red colored solution gradually turned into a suspension, which was filtered after 17 h to give, after drying, an orange to red solid (180.4 mg, 0.258 mmol, 50%). Analytically pure **21** was obtained by crystallization from CH_3CN/CH_2Cl_2. ^{1}H NMR ([D$_6$]acetone): δ = 1.06 [s, 9 H, C(CH$_3$)$_3$], 1.24 [s, 9 H, C(CH$_3$)$_3$], 3.74 (s, 3 H, OCH$_3$), 6.83 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 7.29–6.97 (m, 7 H, ArH), 7.48–7.41 (m, 2 H, ArH), 7.53 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, ArH), 7.77 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, ArH), 7.87 (t, $^3J_{H,H}$ = 8.7 Hz, 2 H, ArH), 7.98 (t, $^3J_{H,H}$ = 7.2 Hz, 2 H, ArH), 8.20 (s, 1 H, ArH), 8.94 [s, 1 H, C(H)=N], 9.36 [s, 1 H, C(H)=N] ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2/d$_5$-pyridine, 95:5): δ = 29.41, 31.55, 34.17, 35.51, 114.90, 116.42, 116.49, 118.20, 120.65, 121.15, 122.99, 123.25, 123.36, 124.17, 124.90, 125.87, 126.06, 126.94, 128.41, 128.46, 128.72, 128.86, 129.36, 129.62, 130.08, 130.21, 134.51, 135.01, 138.03, 138.24, 139.68, 142.00, 142.52, 155.73, 162.91, 163.75, 165.82, 172.00 ppm. UV/Vis (toluene, c = 1.087 mg/50 mL): λ_{max} (ε) = 357, 453 nm (27200, 12800 mol^{-1} dm^3 cm^{-1}). MS (LC-MS, direct inlet, CH$_3$CN, APCI): m/z = 697 [M$^+$ + H]. $C_{44}H_{42}N_2O_3Zn$ (696.23): calcd. C 74.20, H 5.71, N 3.93; found: C 74.05, H 5.94, N 4.01.

Crystal Structure Determination of Zn^{II}-salphen Complex 4: $C_{40}H_{50}N_4O_2Zn$, Fw = 684.21, orange block, 0.34×0.26×0.23 mm. Monoclinic crystal system, space group $P2_1/c$. Cell parameters: a = 12.8185(14) Å, b = 15.3860(12) Å, c = 18.6414(15) Å, β = 91.442(9)°, V = 3675.4(6) Å^3, Z = 4, $D_{calcd.}$ = 1.237 gcm^{-3}. 110831 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and Mo-K_α radiation (graphite monochromator, λ = 0.71073 Å) at a temperature of 150(2) K, using Collect,[21] DIRAX[22] and EvalCCD.[23] A multi-scan absorption correction was applied using SADABS[24] (μ = 0.707 mm^{-1}, 0.74–0.85 transmission). 8401 unique reflections (R_{int} = 0.0306), of which 7376 were observed [$I > 2\sigma(I)$]. The structure was solved with the program DIRDIF,[25] and refined using the program SHELXL-97[26] against F^2 of all reflections up to a resolution of sinθ/λ = 0.65. Non-hydrogen atoms were freely refined with anisotropic displacement parameters. H atoms were placed in geometrically idealized positions [d(C–H) = 0.98 for methyl H atoms and 0.95 for other H atoms] and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and U_{iso}(H) = 1.2U_{eq}(C) for all other H atoms. 436 refined parameters, 0 restraints. R(obsd. refl.): R_1 = 0.0269, wR_2 = 0.0681. R (all data): R_1 = 0.0342, wR_2 = 0.0722. Weighting Scheme $w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.1877P]$, where $P = (F_o^2 + 2F_c^2)/3$. GoF = 1.056. Residual electron density between –0.307 and 0.384 e/Å^3. The drawings, structure calculations, and checking for additional symmetry were performed with the program PLATON.[27]

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[9] CCDC-278364 contains 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.

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