Influence of the Conformation of Salen Complexes on the Stereochemistry of the Asymmetric Epoxidation of Olefins

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Dedicated to Professor Dr. Dr. h. c. Paul von Ragué Schleyer on the occasion of his 75th birthday

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Compared with Katsuki's or Jacobsen's catalysts (*R*,*R*,*R*,*R*)-**1** or (*R*,*R*)-**2**, the phenomenon of reversed asymmetric induction in the course of the epoxidation of unfunctionalised olefins in the presence of (salen)*manganese* complex (*S*,*S*)-**3** is indirectly explained by means of quantumchemical calculations, as well as by ^{1}H NMR spectra of salen ligand (*S*,*S*)-**10** and diamagnetic low-spin *nickel* complex (*S*,*S*)-**7** and by its X-ray structure analysis. Whereas in (*R*,*R*,*R*,*R*)-**1** and (*R*,*R*)-**2** the phenyl and cyclohexyl substituents occupy *equatorial* positions, the origin for the reversed enantioselection caused by *manganese* catalyst (*S*,*S*)-**3**, is based on an *axial* position of the acyclic heteroalkyl substituents in the diimine backbone of (*S*,*S*)-**3** as exemplarily confirmed by model *nickel* complex (*S*,*S*)-**7**.

Introduction

The development of efficient catalytic asymmetric reactions is one of the most challenging tasks in current synthetic chemistry. Therefore, many novel ligands (dialkyl tartrate,[1] binaphthol,[2] semicorrin,[3] bisoxazoline[3d,3e,4] and BINAP[5]) have been established and their combination with various metal ions has allowed the design of powerful asymmetric catalysts. Chiral salen ligands and their metal complexes at this instant are used as catalysts for a variety of enantioselective reactions, such as oxidation,[6] aziridination,[7] cyclopropanation,[8] Diels–Alder reaction,[9] addition of TMSCN to aldehydes[10] and Strecker reaction.[11] Perhaps, the most important reactions catalysed by these chiral complexes are the epoxidation of unfunctionalised olefins,[12] the kinetic resolution of racemic epoxides,[13] and the asymmetric epoxide ring-opening.[14] Asymmetric transformations are extensively studied, since optically active epoxides and their derivatives are useful intermediates for the synthesis of numerous natural products.[15]

Over the course of our catalysis studies, starting from L-tartaric acid, via vicinal diamines,[16] we prepared and investigated a series of (salen)Mn^{III} complexes (*S*,*S*)-**3** as catalysts for the enantioselective epoxidation of unfunctionalised (*Z*)-alkenes such as chromenes **4**.[12f] Compared to the stereochemistry of (*R*,*R*)-**5** reported with catalysts (*R*,*R*,*R*,*R*)-**1** and (*R*,*R*)-**2**, stereochemically identical (*S*,*S*)-**3**[17] furnished epoxides (*S*,*S*)-**5** with opposite configuration (*ee* up to 69%, Scheme 1).

Most notable, in (*R*,*R*,*R*,*R*)-**1** and (*R*,*R*)-**2**, the phenyl and cyclohexyl substituents occupy *equatorial* positions.[12a,18] Consequently, the origin for the inversed enantioselection caused by our catalyst (*S*,*S*)-**3**, is more likely based on the possible *axial* position of the acyclic heteroalkyl substituents in the diimine backbone.[12g] However, these arguments remained rather speculative, since it was not possible to grow single crystals of (*S*,*S*)-**3**, suitable for an X-ray analysis. In order to clarify this puzzle, we considered nickel compounds as appropriate model systems.

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Results and Discussions

Quantumchemical Calculations

The mechanism of the epoxidation reaction has been established by several recent computational studies,[19] al-

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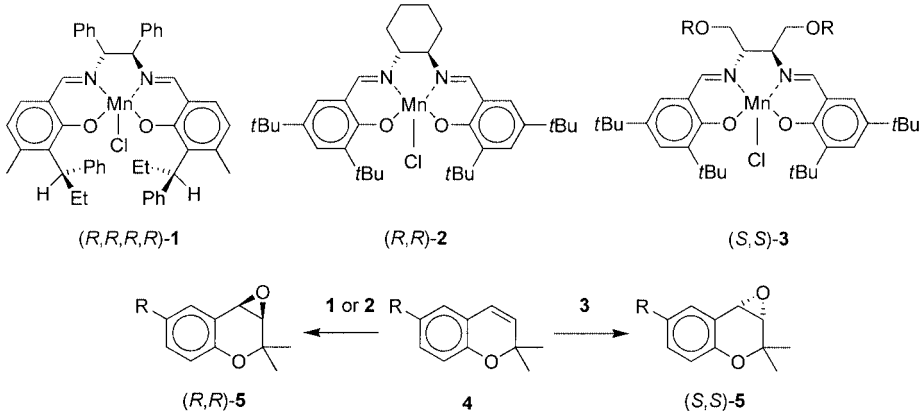


Scheme 1. Influence of the catalysts [(*R*,*R*,*R*,*R*)-**1** or (*R*,*R*)-**2** vs. (*S*,*S*)-**3**)] on the stereochemistry of the asymmetric epoxidation of **4** to give (*R*,*R*)-**5** and (*S*,*S*)-**5**.

though some details are still controversial. In order to support the aforementioned account of the impact of axially substituted salen catalyst (*S*,*S*)-**3** on the stereochemistry of the epoxidation of olefins by DFT calculations, we designed the C_2-symmetric (salen)Ni^{II} model systems **6** and **7** (Figure 1). The energy gap between equatorial *e*-**6** and axial *a*-**6** was calculated by B3LYP/LANL2DZp.[20] The axial conformer *a*-**6** turns out to be 4.3 kcal/mol more stable than equatorial *e*-**6**. Furthermore, when we applied the IPCM solvent model[21] for chloroform on the energy calculation of **6**, the energy gap increased to 12.1 kcal/mol, again in favour of axial *a*-**6**.

In addition, in model system **7a**, the CH_2OMe substituents were also found to take axial positions and the two different rotamers *a*-**7a**′ and *a*-**7a**′′ indicate two or none intramolecular Me*O*–*Ni* contacts (Figure 1). Rotamer *a*-**7a**′′ without any *O*–*Ni* contact was calculated to be the most stable isomer. The relative energy differences and some key structure elements of *a*-**7a**′ and *a*-**7a**′′ are summarised in Table 1.

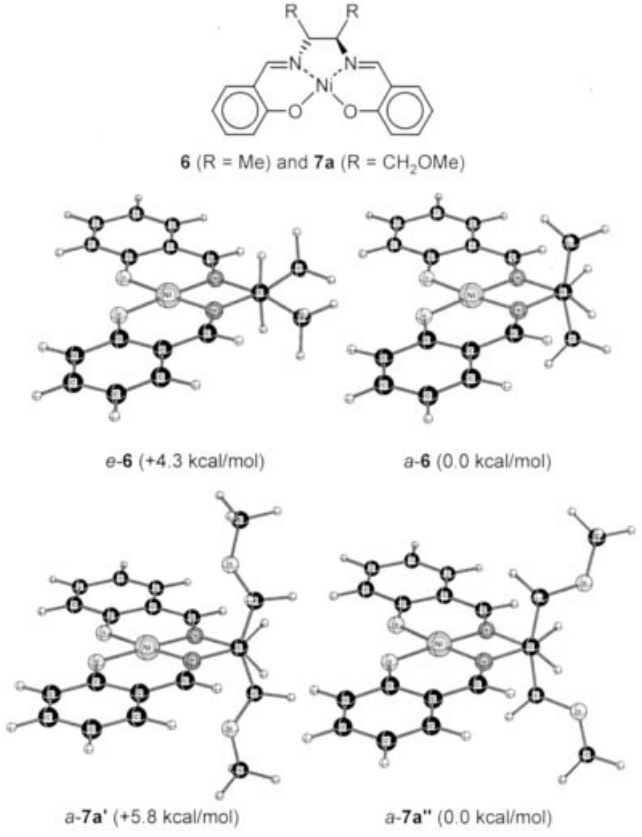


Figure 1. Model systems **6** and **7a**. Molecule plots of calculated structures *a*,*e*-**6** (R = Me) and *a*-**7a** (R = CH_2OMe), view along the C–C bond of the stereogenic centres.

Table 1. Key structure features of the calculated structures **6** and *a*-**7a**.

	e-**6**	*a*-**6**	*a*-**7a**′	*a*-**7a**′′
Relative energy [kcal/mol]	4.3 (12.1)[a]	0	5.8	0
Distance Me–*O*–*Ni* [Å][b]	–	–	3.52	4.69
Distance C–*O*–*Ni* [Å]	1.87	1.87	1.87	1.87
Distance C–*N*–*Ni* [Å]	1.88	1.88	1.87	1.88
Φ CH_2–*C*H–*C*H–CH_2 [°]	65.6	158.9	143.1	162.2
Φ H–C–C–H [°]	173.6	83.3	92.3	79.1
Calculated ^3J [Hz]	10.2	1.4	1.5	1.5

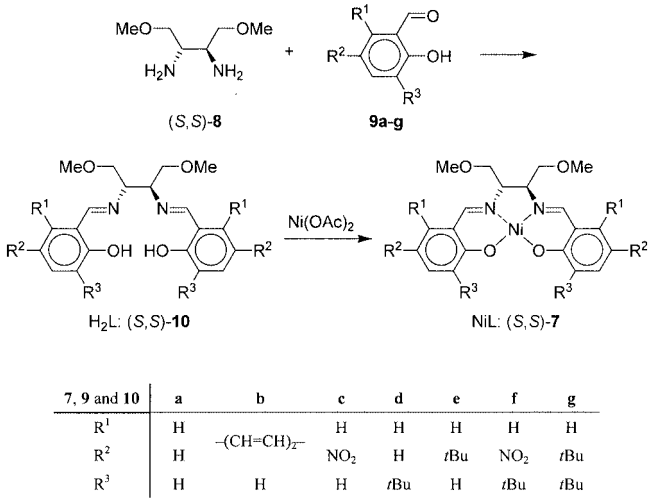
[a] The IPCM solvent model was applied. [b] Intramolecular.

Synthesis of 7

C_2-symmetric vicinal diamine (*S*,*S*)-**8** was treated with a selection of salicylaldehydes **9a**–**g**, yielding the salen derivatives (*S*,*S*)-**10a**–**g**, which with nickel(II) acetate readily afforded the deep red to brown (salen)Ni^{II} compounds (*S*,*S*)-**7a**–**g** (Scheme 2).[12f]

^{1}H NMR Studies of 10 and 7

The salen ligands (*S*,*S*)-**10** and diamagnetic low-spin Ni^{II} complexes (*S*,*S*)-**7** were studied by ^{1}H NMR spectroscopy (Figure 2, Exp. Sect.). Of special interest are the resonances of the hydrogen atoms of the AA′BB′CC′ spin system[12f,16,22] of C_2-symmetric (*S*,*S*)-**10** and (*S*,*S*)-**7**. The analyses of the multiplets observed for the protons H_C/$H_{C'}$



7, 9 and 10	a	b	c	d	e	f	g
R^1	H	–(CH=CH)$_2$–	H	H	H	H	H
R^2	H		NO_2	H	*t*Bu	NO_2	*t*Bu
R^3	H	H	H	*t*Bu	H	*t*Bu	*t*Bu

Scheme 2. Preparation of C_2-symmetric salen ligands (*S*,*S*)-**10**, and Ni^{II} complexes (*S*,*S*)-**7**.

were carried out by means of the simulated ^{1}H NMR spectra of (*S*,*S*)-**10** and revealed coupling constants in the range of $J_{CC'}$ = 3.5–6.0 Hz (Table 2).[12f,22] However, in the case of complexes (*S*,*S*)-**7**, triplets are recorded for $H_C/H_{C'}$, resulting from two doublets with nearly identical coupling constants. Interestingly, for (*S*,*S*)-**7**, the spectroscopic data imply a vicinal coupling constant of $J_{CC'} \approx 0$ Hz. Following the correlation of torsion angle Φ and vicinal coupling constants resulting from the Karplus curve,[23] $J_{CC'} \approx 0$ Hz leads to torsion angles Φ (H_C–C–C–$H_{C'}$) of around 80–100° in complexes (*S*,*S*)-**7**. This piece of spectroscopic evidence implies an arrangement of the alkyl substituents in axial positions as shown in the Newman projections and further supports the calculated structures found for rotamer *a*-**7a**.

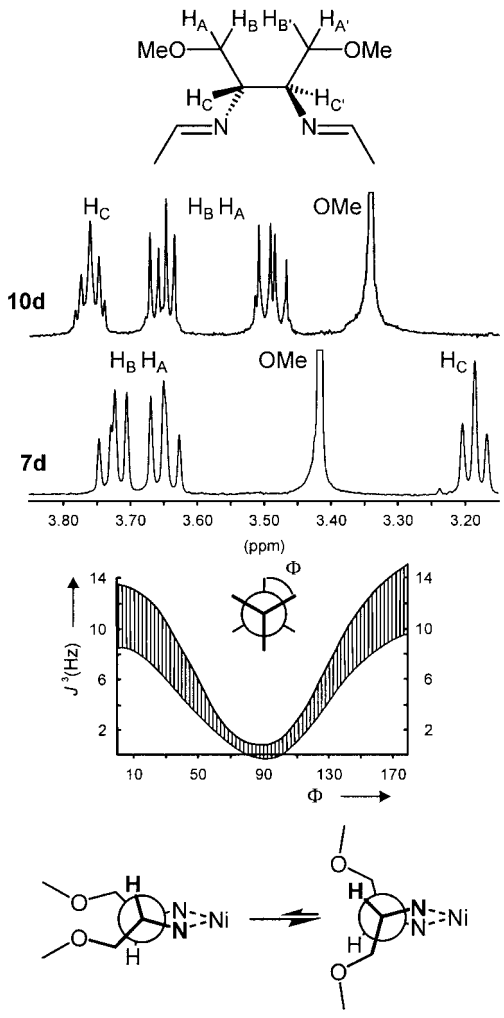


Figure 2. Top: ^{1}H NMR spectra of (*S*,*S*)-**10d** and (*S*,*S*)-**7d**, highlighting the AA′BB′CC′ spin system ($CDCl_3$, 400 MHz, +24 °C, expanded). Center: Presentation of the Karplus curve[23] (Φ defined as dihedral angle H_C–C–C–$H_{C'}$). Bottom: Schematic Newman projection of the equatorial/axial conformers (*S*,*S*)-**7** along the H_CC–$CH_{C'}$ bond.

X-ray Structure Analyses

All the (salen)Ni^{II} complexes (*S*,*S*)-**7a**–**g** were crystallised and crystals suitable for X-ray analyses were obtained for (*S*,*S*)-**7a**–**e**.[24,25] Complexes (*S*,*S*)-**7a**–**c** crystallise in the chiral space group $P2_12_12_1$ (crystal system: orthorhombic), whereas compounds (*S*,*S*)-**7d**,**e** crystallise in the polar space group $P2_1$ (crystal system: monoclinic). An almost perfect square-planar environment for the nickel atoms was observed for complexes (*S*,*S*)-**7a**–**e**. Furthermore, all CH_2OMe groups are in axial position (Figure 3). For example, in (*S*,*S*)-**7a** the torsion angle Φ (CH_2–CH–CH–CH_2) is 161.3°, which is in excellent agreement with 162.2°, calculated for rotamer *a*-**7a**′′ and the *intramolecular* Me*O*–*Ni* distances *d* range from 4.21 to 4.68 Å (Table 3).

Table 2. Chemical shifts and non equal to zero coupling constants of the AA′BB′CC′spin system observed in ^{1}H NMR spectra of compounds **10a**–**g**.

Salen ligand[a]	**10a**	**10b**	**10c**	**10d**	**10e**	**10f**	**10g**[12f]
$\delta_A = \delta_{A'}$ [ppm]	3.442	3.603	3.461	3.489	3.432	3.509	3.482
$\delta_B = \delta_{B'}$ [ppm]	3.606	3.695	3.597	3.652	3.613	3.627	3.665
$\delta_C = \delta_{C'}$ [ppm]	3.748	3.963	3.901	3.760	3.726	3.918	3.746
$J_{AB} = J_{A'B'}$ [Hz]	–9.61	–9.72	–9.66	–9.60	–9.62	–9.68	–9.63
$J_{AC} = J_{A'C'}$ [Hz]	7.23	6.16	7.35	6.94	7.29	7.13	7.01
$J_{BC} = J_{B'C'}$ [Hz]	4.91	5.17	4.96	5.10	4.81	5.31	4.93
$J_{CC'}$ [Hz]	4.16	4.78	4.00	4.54	4.10	3.87	4.51

[a] All spectra were recorded in $CDCl_3$ and processed with a digital resolution of 0.015 Hz.

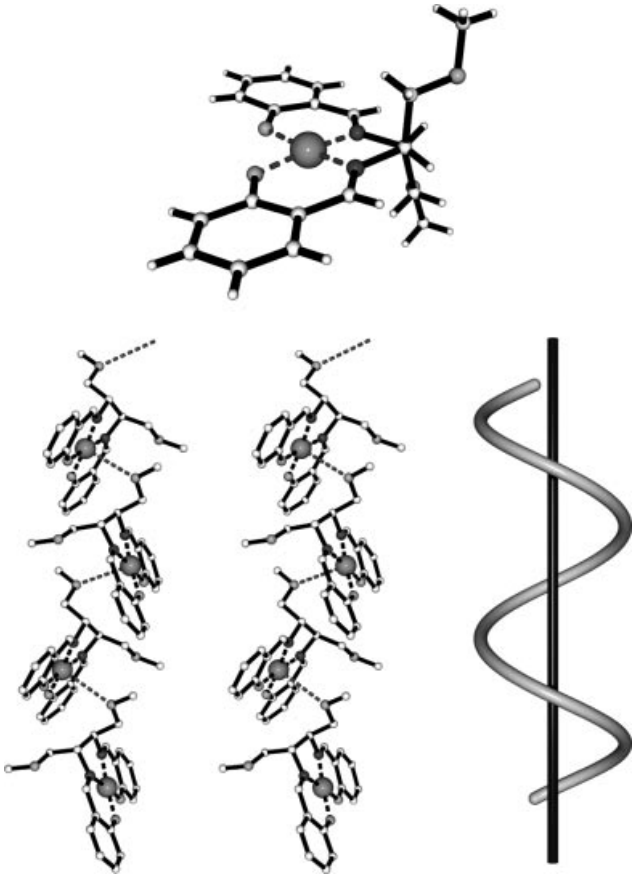


Figure 3. Top: Monomer of **7a**, view along the $H_CC–CH_{C'}$ bond, highlighting the axial positions of the alkyl groups (POVRAY presentation). Bottom left: Stereoview of the X-ray structure of the enantiomerically pure helix (*M*)-1D-$^1{}_\infty$[NiL] **11a**, generated from self-complementary (*S*,*S*)-**7a** (POVRAY presentation, H atoms omitted for clarity). Bottom right: Schematic presentation, highlighting the helical structure of **11a**.

Table 3. Key structure data of rotamer *a*-**7a**′′ (calculated) and complexes (*S*,*S*)-**7a**–**e**.

	a-**7a**′′	**7a**	**7b**	**7c**	**7d**	**7e**
d [Å][a]	4.69	4.27/4.64	4.21/4.68	4.55/4.62	4.27/4.28	4.28/4.63
Φ [°][b]	162.2	161.3	159.5	155.9	156.8	160.9

[a] Intramolecular Me*O*–*Ni* distance. [b] Torsion angle CH_2–*C*H–*C*H–CH_2.

Principally, the complexes **7a**–**e** are self-complementary with respect to their "coordinatively unsaturated" nickel ions and extra CH_2OMe donors and therefore may polymerise. In fact, for (*S*,*S*)-**7a**,**b**, these extra *intermolecular Ni–O*Me contacts of one arm, each, were found to effect the crystal packing. Thus, the monomers (*S*,*S*)-**7a**,**b** give rise to the enantiomerically pure helical one-dimensional coordination polymers (*M*)-1D-$^1{}_\infty$[NiL] **11a**,**b** [*intermolecular Ni–O*Me distances: for (*S*,*S*)-**11a**, *d* = 3.55 Å; for (*S*,*S*)-**11b**, *d* = 3.53 Å].[26] The polymer strand of **11a** together with its schematic presentation, highlighting the helical structure, are presented in Figure 3. The strands of **11a**,**b** are packed parallel in the crystal in two different orientations relative to each other.

Contrary to (*S*,*S*)-**7a**,**b**, in the case of (*S*,*S*)-**7c**, the salen complexes interact intermolecularly through π–π contacts[27] between the nitrophenyl moieties (mean distance between planes, *d* = 3.49 Å) and not via their CH_2OMe donors. In order to avoid steric hindrance of the CH_2OMe side arms, the complexes are alternately rotated by 180° around their complex plane normal, are arranged in parallel and piled in columns along the crystallographic *a* axis, with the nickel centres slightly shifted (Figure 4).

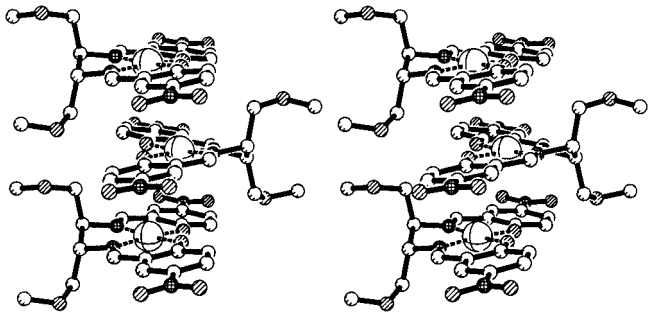


Figure 4. Stereoview of the X-ray structure of complex (*S*,*S*)-**7c**, highlighting the π–π interactions (PLUTON presentation, H atoms omitted for clarity. C: shaded; N: net; O: diagonal; Ni: cross).

In the cases of (*S*,*S*)-**7d**,**e**, there are no special intermolecular interactions in the crystal to be noticed.

Conclusions

The present study substantiates, why, compared with Katsuki's or Jacobsen's catalysts (*R*,*R*,*R*,*R*)-**1** or (*R*,*R*)-**2**, the stereochemistry of the epoxidation of unfunctionalised olefins is inverted, when the (salen)*manganese* complex (*S*,*S*)-**3** is used instead. Whereas in (*R*,*R*,*R*,*R*)-**1** and (*R*,*R*)-**2** the phenyl substituents and the cyclohexyl ring occupy *equatorial* positions, the origin for the reversed enantioselection caused by (*S*,*S*)-**3**, obviously is based on the *axial* position of the acyclic heteroalkyl substituents in the diimine backbone, as confirmed by our model system (*S*,*S*)-**7**. The diamagnetic *nickel* model complexes (*S*,*S*)-**7** were alternatively studied by means of quantumchemical calculations, as well as by ^{1}H NMR and X-ray, establishing the expected axial conformation. Furthermore, in the solid state enantiomerically pure helical one-dimensional coordination polymers (*M*)-1D-$^1{}_\infty$[NiL] **11a**,**b** were observed, generated by the self-complementary monomers (*S*,*S*)-**7a**,**b**.

Experimental Section

General Techniques: All solvents used were purified according to standard procedures. All reagents employed were commercially available, high-grade purity materials and used as supplied (**9a**–**e**,**g**; Fluka, Aldrich). **9f** was prepared by reaction of **9g** with fuming HNO_3, according to a literature procedure.[28] The salen ligand **10g** was prepared as described earlier.[12f] Flash chromatography was carried out using silica gel 60 (70–230 mesh). Melting points were determined with a Wagner–Munz apparatus and are not corrected.

IR spectra were recorded from $CHBr_3$ triturations (NaCl pellets) with a Bruker IFS 25 spectrometer. NMR spectra were obtained in dilute $CDCl_3$ solutions unless stated otherwise, using Me_4Si as an internal standard at 400 MHz for ^1H and 100 MHz for ^{13}C with a Bruker ARX 400 and JEOL EX400 spectrometer; δ values are given in ppm. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), and m (multiplet). FAB-MS spectra were recorded with a Micromass ZAB-Spec spectrometer with *m*NBA as matrix. Optical rotations were determined by using a Perkin Elmer 341 polarimeter. Elemental analyses were performed with an EA 1110 CHNS-Microautomat. Single-crystal X-ray structure analyses: Details for crystal data, data collection and refinement are given in Table 4. The structural (crystallographic) data for **7a** were collected with a Nonius CAD4 diffractometer with graphite-monochromatised Mo-K_α radiation (λ = 0.71073 Å). The cell parameters were obtained by fitting a set of 25 high-θ reflections. The structure was solved with SIR-97[24b] which revealed all non-hydrogen atoms of the compounds. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference. The whole structure was refined with SHELXL-97[24c] by full-matrix least-square techniques on F^2. X-ray data for **7b**–**e** were collected with a Nonius Kappa CCD area detector, using Mo-K_α radiation. The structures were solved by direct methods with SHELXS-97 and refined with full-matrix least squares against F^2 with SHELXL-97.[24c,24d]

General Procedures for the Preparation of the salen Ligands (*S*,*S*)-10a–f: A two-neck round-bottom flask equipped with a reflux condenser and a septum was charged with (2*S*,3*S*)-2,3-diamino-1,4-dimethoxybutane [(*S*,*S*)-**8**] (59 mg, 0.4 mmol) and distilled water (1 mL). The mixture was stirred until dissolution was achieved and then ethanol (3 mL) was added. The resulting mixture was heated at reflux and a solution of a 2-hydroxybenzaldehyde derivative (0.8 mmol) in ethanol (2 mL) was added continuously over 5 min through a microsyringe. The microsyringe was rinsed with ethanol (0.4 mL) and the yellow slurry was stirred at reflux for 2 h before heating was stopped. After evaporation of the solvents, the crude reaction product was redissolved in CH_2Cl_2 (4 mL) and washed with water (2 × 2 mL) and brine (1 mL). After drying with anhydrous Na_2SO_4, the solvent was removed under vacuum. After chromatography on silica gel, the pure salen ligands (*S*,*S*)-**10a**–**f** were isolated.

General Procedures for the Preparation of the (salen)Ni^{II} Complexes (*S*,*S*)-7a–g: A two-neck round-bottom flask equipped with a reflux condenser and a septum was charged with the salen ligand (0.2 mmol) and MeOH (12 mL). After addition of $Ni(OAc)_2{\cdot}4H_2O$ (70 mg, 0.28 mmol) in MeOH (2 mL) via a microsyringe, the solution was refluxed for 3 h. The reaction mixture was cooled to room temperature and kept without stirring for further 16 h. The formed red to brown precipitate was filtered and washed with cold MeOH. Drying under vacuum afforded the deeply red to brown (salen) nickel(II) complexes (*S*,*S*)-**7a**–**g** as a microcrystalline material.

(2*S*,3*S*)-1,4-Dimethoxy-2,3-bis[(salicylidene)amino]butane [(*S*,*S*)-10a]: From **9a** (85 μL, 0.8 mmol). After cooling to room temperature and standing overnight, yellow crystals were isolated (44 mg). Treatment of the mother liquor as mentioned above, afforded the pure salen ligand (*S*,*S*)-**10a** as yellow crystals (solvent gradient from petroleum ether (PE)/EtOAc, 98:2 to PE/EtOAc, 8:2). Yield (overall): 126 mg (88%); m.p. 142–143 °C; R_f = 0.14 (PE/EtOAc, 8:2). IR: $\tilde{\nu}$ = 2990, 2927, 2893, 2830, 1630, 1582, 1495, 1460, 1404, 1277, 1197, 1117, 758 cm^{-1}. ^1H NMR: δ = 13.30 (broad s, 2 H, O*H*), 8.41 (s, 2 H, C*H*=N), 7.32 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 2 H, C*H*-Ph), 7.28 (dd, *J* = 7.7, 1.7 Hz, 2 H, C*H*-Ph), 7.01 (dd, *J* = 8.3, 1.1 Hz, 2 H, C*H*-Ph), 6.88 (ddd, *J* = 7.7, 7.3, 1.1 Hz, 2 H, C*H*-Ph), 3.78–3.71 (m, 2 H, C*H*–N),[22] 3.61 (pseudo dd, *J* = 9.6, 4.9 Hz, 2 H, OCH_2),[22] 3.44 (pseudo dd, *J* = 9.6, 7.2 Hz, 2 H, OCH_2),[22] 3.31 (s, 6 H, OCH_3) ppm. ^{13}C NMR:[29] δ = 166.97 (*C*H=N), 161.30 (C_{ipso} α to OH), 132.58 (*C*H-Ph, correlates with proton signal at δ = 7.32 ppm), 131.66 (*C*H-Ph, correlates with proton signal at δ = 7.28 ppm), 118.61 (4 C, *C*H-Ph, correlates with proton signal at δ = 6.88 ppm, and C_{ipso} α to the imine group), 117.25 (*C*H-Ph, correlates with proton signal at δ = 7.01 ppm), 73.29 (O*C*H_2), 69.33

Table 4. Details of X-ray structure determinations for Ni^{II} salen complexes **7a**–**e**.

	7a	**7b**	**7c**	**7d**	**7e**
Empirical formula	$C_{20}H_{22}N_2NiO_4$	$C_{28}H_{26}N_2NiO_4$	$C_{20}H_{20}N_4NiO_8$	$C_{28}H_{38}N_2NiO_4$	$C_{28}H_{38}N_2NiO_4{\cdot}CHCl_3$
Formula mass	413.11	513.22	503.11	525.31	644.68
Crystal size [mm]	0.45 × 0.25 × 0.22	0.20 × 0.10 × 0.10	0.35 × 0.20 × 0.20	0.40 × 0.30 × 0.30	0.30 × 0.30 × 0.30
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_1$
T [K]	293(2)	173(2)	173(2)	173(2)	173(2)
a [Å]	7.913(3)	7.8495(1)	6.9840(1)	11.7799(2)	11.481(2)
b [Å]	11.573(8)	11.9175(2)	12.0415(2)	9.4477(1)	10.453(2)
c [Å]	21.112(9)	25.1125(3)	24.1397(4)	13.2259(2)	14.026(3)
β [°]				111.894(1)	112.26(3)
V [Å^3]	1933(2)	2349.18(6)	2030.10(6)	1365.79(3)	1557.9(5)
Z	4	4	4	2	2
$\rho_{calcd.}$ [Mg·m^{-3}]	1.419	1.451	1.646	1.277	1.374
θ range [°]	1.93 to 26.96	1.62 to 27.49	2.39 to 27.46	1.66 to 27.48	2.50 to 25.04
Reflections collected	2404	5307	4489	6231	10425
Unique reflections	2404	5307	4489	6231	5443
[R_{int}]	0	0	0	0	0.0182
Refl. observed [$I > 2\sigma(I)$]	1812	4970	4361	5859	4893
Parameters	245	318	298	316	357
Absorption correction method		empirical (scale-pack)	empirical (scale-pack)	empirical (scale-pack)	empirical (scale-pack)
Goodness-of-fit on F^2	0.954	1.100	1.009	1.094	1.742
Final R_1 [$I > 2\sigma(I)$]	0.0361	0.0292	0.0234	0.0262	0.0757
wR_2 (all data)	0.0888	0.0849	0.0632	0.0751	0.2138
Largest residuals [e·Å^{-3}]	0.253/–0.271	0.381/–0.604	0.253/–0.266	0.452/–0.609	0.980/–0.624

(*C*H–N), 59.16 (O*C*H$_3$) ppm. MS: *m/z* (%) = 713 (3) [2 M + H]$^+$, 357 (100) [M + H]$^+$, 235 (6), 206 (8), 178 (12) [M/2]$^+$. $[\alpha]_D^{24}$ = +101.5, $[\alpha]_{578}^{24}$ = +105.7, $[\alpha]_{546}^{24}$ = +122.6 (*c* = 0.88, $CHCl_3$). $C_{20}H_{24}N_2O_4$ (356.42): calcd. C 67.40, H 6.79, N 7.86; found C 66.92, H 6.29, N 7.69.

(2*S*,3*S*)-2,3-Bis{[(2-hydroxynaphth-1-yl)methylene]amino}-1,4-dimethoxybutane [(*S*,*S*)-10b]: From **9b** (172 mg, 1.0 mmol, technical grade ca. 80%). Yellow solid (solvent gradient from CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2). Yield: 139 mg (76%); m.p. 141–142 °C; R_f = 0.22 (CH_2Cl_2/MeOH, 96:4). IR: $\tilde{\nu}$ = 2928, 2893, 2829, 1626, 1587, 1547, 1473, 1406, 1359, 1246, 1188, 971, 827, 750 cm^{-1}. ^{1}H NMR: δ = 14.75 (broad s, 2 H, O*H*), 8.97 (s, 2 H, C*H*=N), 7.92 (d, *J* = 8.2 Hz, 2 H, C*H*-Ar), 7.67 (d, *J* = 9.1 Hz, 2 H, C*H*-Ar), 7.61 (dd, *J* = 7.9, 1.4 Hz, 2 H, C*H*-Ar), 7.43 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 2 H, C*H*-Ar), 7.25 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 2 H, C*H*-Ar), 7.04 (d, *J* = 9.2 Hz, 2 H, C*H*-Ar), 3.99–3.93 (m, 2 H, C*H*–N),[22] 3.70 (pseudo dd, *J* = 9.7, 5.1 Hz, 2 H, OCH_2),[22] 3.60 (pseudo dd, *J* = 9.7, 6.2 Hz, 2 H, OCH_2),[22] 3.38 (s, 6 H, OCH_3) ppm. ^{13}C NMR:[29] δ = 170.86 (C_{ipso} α to OH), 160.94 (*C*H=N), 136.21 (*C*H-Ar, correlates with proton signal at δ = 7.67 ppm), 133.20 (C_{ipso}-Ar), 129.10 (*C*H-Ar, correlates with proton signal at δ = 7.61 ppm), 127.82 (*C*H-Ar, correlates with proton signal at δ = 7.43 ppm), 126.86 (C_{ipso}-Ar), 123.01 (*C*H-Ar, correlates with proton signal at δ = 7.25 ppm), 122.74 (*C*H-Ar, correlates with proton signal at δ = 7.04 ppm), 118.56 (*C*H-Ar, correlates with proton signal at δ = 7.92 ppm), 107.60 (C_{ipso}-Ar), 72.72 (OCH_2), 66.20 (*C*H–N), 59.39 (OCH_3). MS: *m/z* (%) = 913 (2) [2 M + H]$^+$, 457 (100) [M + H]$^+$, 228 (52) [M/2]$^+$. $[\alpha]_D^{26}$ = +127.3, $[\alpha]_{578}^{26}$ = +135.7, $[\alpha]_{546}^{26}$ = +153.4 (*c* = 0.75, $CHCl_3$). $C_{28}H_{28}N_2O_4$ (456.53): calcd. C 73.66, H 6.18, N 6.14; found C 72.96, H 5.96, N 5.92.

(2*S*,3*S*)-1,4-Dimethoxy-2,3-bis[(5-nitrosalicylidene)amino]butane [(*S*,*S*)-10c]: From **9c** (134 mg, 0.8 mmol). After cooling to room temperature and standing overnight, yellow crystals were isolated (97 mg). Treatment of the mother liquor as mentioned above, afforded the pure salen ligand (*S*,*S*)-**10c** as yellow crystals (solvent gradient from CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2). Yield (overall): 166 mg (93%); m.p. 201–203 °C; R_f = 0.22 (CH_2Cl_2/MeOH, 96:4). IR: $\tilde{\nu}$ = 3071, 2949, 2883 (broad), 2830, 1633, 1583, 1526, 1489, 1389, 1340, 1292, 1196, 1096, 922, 837, 794, 741 cm^{-1}. ^{1}H NMR: δ = 14.37 (broad s, 2 H, O*H*), 8.50 (s, 2 H, C*H*=N), 8.30 (d, *J* = 2.7 Hz 2 H, C*H*-Ph), 8.23 (dd, *J* = 9.2, 2.7 Hz, 2 H, C*H*-Ph), 7.09 (d, *J* = 9.2 Hz, 2 H, C*H*-Ph), 3.94–3.87 (m, 2 H, C*H*–N),[22] 3.60 (pseudo dd, *J* = 9.7, 4.9 Hz, 2 H, OCH_2),[22] 3.47 (pseudo dd, *J* = 9.7, 7.3 Hz, 2 H, OCH_2),[22] 3.34 (s, 6 H, OCH_3) ppm. ^{13}C NMR:[29] δ = 167.56 (C_{ipso} α to OH), 166.21 (*C*H=N), 139.59 (C_{ipso} α to NO_2), 128.38 (*C*H-Ph, correlates with proton signal at δ = 8.23 ppm), 128.22 (*C*H-Ph, correlates with proton signal at δ = 8.30 ppm), 118.65 (*C*H-Ph, correlates with proton signal at δ = 7.09 ppm), 117.18 (C_{ipso} α to imino group), 72.69 (OCH_2), 68.19 (*C*H–N), 59.28 (OCH_3) ppm. MS: *m/z* (%) = 893 (2) [2 M + H]$^+$, 447 (100) [M + H]$^+$, 223 (9) [M/2]$^+$. $[\alpha]_D^{26}$ = +77.4, $[\alpha]_{578}^{26}$ = +83.9, $[\alpha]_{546}^{26}$ = +97.1 (*c* = 1.00, $CHCl_3$). $C_{20}H_{22}N_4O_8$ (446.41): calcd. C 53.81, H 4.97, N 12.55; found C 53.73, H 5.08, N 12.42.

(2*S*,3*S*)-2,3-Bis[(3-*tert*-butylsalicylidene)amino]-1,4-dimethoxybutane [(*S*,*S*)-10d]: From **9d** (137 μL, 0.8 mmol). Yellow crystals after storage in the refrigerator (solvent gradient from PE/EtOAc, 98:2 to PE/EtOAc, 8:2). Yield: 163 mg (87%); m.p. 90–91 °C; R_f = 0.22 (PE/EtOAc, 8:2). IR: $\tilde{\nu}$ = 2956, 2896, 1629, 1607, 1482, 1458, 1432, 1390, 1361, 1308, 1268, 1232, 1199, 1088, 1024, 960, 931, 854, 798, 754 cm^{-1}. ^{1}H NMR: δ = 13.77 (broad s, 2 H, O*H*), 8.42 (s, 2 H, C*H*=N), 7.32 (dd, *J* = 7.7, 1.6 Hz, 2 H, C*H*-Ph), 7.13 (dd, *J* = 7.6, 1.6 Hz, 2 H, C*H*-Ph), 6.80 (dd, *J* = 7.7, 7.6 Hz, 2 H, C*H*-Ph), 3.80–3.73 (m, 2 H, C*H*–N),[22] 3.65 (pseudo dd, *J* = 9.6, 5.1 Hz, 2 H, OCH_2),[22] 3.49 (pseudo dd, *J* = 9.6, 7.0 Hz, 2 H, OCH_2),[22] 3.34 (s, 6 H, OCH_3), 1.44 (s, 18 H, C(CH_3)$_3$). ^{13}C NMR:[29] δ = 167.46 (*C*H=N), 160.71 (C_{ipso} α to OH), 137.53 [C_{ipso} α to C$(CH_3)_3$], 129.97 (*C*H-Ph, correlates with proton signal at δ = 7.13 ppm), 129.60 (*C*H-Ph, correlates with proton signal at δ = 7.32 ppm), 118.49 (C_{ipso} α to imino group), 117.66 (*C*H-Ph, correlates with proton signal at δ = 6.80 ppm), 73.27 (OCH_2), 69.17 (*C*H–N), 59.12 (OCH_3), 34.88 [*C*$(CH_3)_3$], 29.31 [6 C, C(*C*H_3)$_3$]. MS: *m/z* (%) = 937 (1) [2 M + H]$^+$, 469 (100) [M + H]$^+$, 234 (31) [M/2]$^+$. $[\alpha]_D^{24}$ = +63.8, $[\alpha]_{578}^{24}$ = +71.4, $[\alpha]_{546}^{24}$ = +76.3 (*c* = 0.75, $CHCl_3$). $C_{28}H_{40}N_2O_4$ (468.63): calcd. C 71.76, H 8.60, N 5.98; found C 71.47, H 8.63, N 5.89.

(2*S*,3*S*)-2,3-Bis[(5-*tert*-butylsalicylidene)amino]-1,4-dimethoxybutane [(*S*,*S*)-10e]: From **9e** (137 μL, 0.8 mmol). Yellow, resin-like residue (solvent gradient from PE/EtOAc, 99:1 to PE/EtOAc, 9:1). Yield: 157 mg (84%); R_f = 0.29 (PE/EtOAc, 8:2). IR: $\tilde{\nu}$ = 2962, 2896, 2870, 1633, 1590, 1491, 1463, 1386, 1288, 1188, 1119, 1059, 963, 933, 793, 731 cm^{-1}. ^{1}H NMR: δ = 13.05 (broad s, 2 H, O*H*), 8.40 (s, 2 H, C*H*=N), 7.36 (dd, *J* = 8.7, 2.5 Hz, 2 H, C*H*-Ph), 7.25 (d, *J* = 2.5 Hz, 2 H, C*H*-Ph), 6.96 (d, *J* = 8.7 Hz, 2 H, C*H*-Ph), 3.75–3.69 (m, 2 H, C*H*–N),[22] 3.61 (pseudo dd, *J* = 9.6, 4.8 Hz, 2 H, OCH_2),[22] 3.43 (pseudo dd, *J* = 9.6, 7.3 Hz, 2 H, OCH_2),[22] 3.32 (s, 6 H, OCH_3), 1.30 (s, 18 H, C(CH_3)$_3$). ^{13}C NMR:[29] δ = 167.22 (*C*H=N), 159.02 (C_{ipso} α to OH), 141.21 (C_{ipso} α to C$(CH_3)_3$), 129.95 (*C*H-Ph, correlates with proton signal at δ = 7.36 ppm), 128.02 (*C*H-Ph, correlates with proton signal at δ = 7.25 ppm), 117.86 (C_{ipso} α to imino group), 116.78 (*C*H-Ph, correlates with proton signal at δ = 6.96 ppm), 73.46 (OCH_2), 69.60 (*C*H–N), 59.19 (OCH_3), 33.96 [*C*$(CH_3)_3$], 31.42 [6 C, C(*C*H_3)$_3$] ppm. MS: *m/z* (%) = 936 (2) [2 M + H]$^+$, 469 (100) [M + H]$^+$, 234 (18) [M/2]$^+$. $[\alpha]_D^{24}$ = +43.2, $[\alpha]_{578}^{24}$ = +44.8, $[\alpha]_{546}^{24}$ = +47.1 (*c* = 0.52, $CHCl_3$). $C_{28}H_{40}N_2O_4$ (468.63): calcd. C 71.76, H 8.60, N 5.98; found C 71.44, H 9.17, N 5.94.

(2*S*,3*S*)-2,3-Bis[(3-*tert*-butyl-5-nitrosalicylidene)amino]-1,4-dimethoxybutane [(*S*,*S*)-10f]: From **9f**[28] (176 mg, 0.8 mmol). Yellow foam (solvent gradient from PE/EtOAc, 95:5 to PE/EtOAc, 7:3). Yield: 203 mg (91%); m.p. 73–75 °C; R_f = 0.27 (PE/EtOAc, 6:4). IR: $\tilde{\nu}$ = 2958, 2876, 2830, 1634, 1614, 1525, 1479, 1438, 1392, 1327, 1285, 1200, 1111, 976, 912, 748 cm^{-1}. ^{1}H NMR: δ = 13.57 (broad s, 2 H, O*H*), 8.50 (s, 2 H, C*H*=N), 8.24 (d, *J* = 2.8 Hz, 2 H, C*H*-Ph), 8.16 (d, *J* = 2.8 Hz, 2 H, C*H*-Ph), 3.95–3.89 (m, 2 H, C*H*–N),[22] 3.63 (pseudo dd, *J* = 9.7, 5.3 Hz, 2 H, OCH_2),[22] 3.51 (pseudo dd, *J* = 9.7, 7.1 Hz, 2 H, OCH_2),[22] 3.38 (s, 6 H, OCH_3), 1.46 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR:[29] δ = 167.18 (C_{ipso} α to OH), 166.77 (*C*H=N), 139.83 and 138.82 (4 C, C_{ipso} α to C$(CH_3)_3$ and to NO_2), 126.46 (*C*H-Ph, correlates with proton signal at δ = 8.24 ppm), 125.27 (*C*H-Ph, correlates with proton signal at δ = 8.24 ppm), 117.00 (C_{ipso} α to imino group), 72.76 (OCH_2), 67.85 (*C*H–N), 59.25 (OCH_3), 35.35 [*C*$(CH_3)_3$], 28.93 [6 C, C(*C*H_3)$_3$] ppm. MS: *m/z* (%) = 1118 (1) [2 M + H]$^+$, 559 (100) [M + H]$^+$, 279 (10) [M/2]$^+$. $[\alpha]_D^{24}$ = +94.7, $[\alpha]_{578}^{24}$ = +111.2, $[\alpha]_{546}^{24}$ = +131.8 (*c* = 0.61, $CHCl_3$).

{(2*S*,3*S*)-1,4-Dimethoxy-2,3-bis[(salicylidene)amino]butane}-nickel(II) [(*S*,*S*)-7a]: From (*S*,*S*)-**10a** (71 mg, 0.2 mmol). After slow cooling to room temperature and standing for 60 h, deep violet crystals were isolated, suitable for X-ray structure analysis. Yield: 67 mg (81%); m.p. 325–327 °C (decomp.); R_f = 0.35 (CH_2Cl_2/MeOH, 96:4). IR: $\tilde{\nu}$ = 2929, 2870, 2812, 1614, 1532, 1448, 1390, 1354, 1319, 1246, 1201, 1104, 1025, 965, 903, 888, 851, 809, 773, 757, 738 cm^{-1}. ^{1}H NMR: δ = 7.50 (s, 2 H, C*H*=N), 7.22 (ddd, *J* = 8.6, 6.8, 1.8 Hz, 2 H, C*H*-Ph), 7.13 (dd, *J* = 7.9, 1.8 Hz, 2 H, C*H*-

Ph), 7.05 (broad d, J = 8.6 Hz, 2 H, C*H*-Ph), 6.56 (tm, J = 7.9 Hz, 2 H, C*H*-Ph), 3.70 (dd, J = 9.5, 6.7 Hz, 2 H, OCH_2), 3.64 (dd, J = 9.5, 8.0 Hz, 2 H, OCH_2), 3.39 (s, 6 H, OCH_3), 3.23 (dd, J = 8.0, 6.7 Hz, 2 H, C*H*–N) ppm. ^{13}C NMR:[29] δ = 165.24 (C_{ipso} α to OH), 163.51 (*C*H=N), 134.22 (*C*H-Ph, correlates with proton signal at δ = 7.22 ppm), 132.38 (*C*H-Ph, correlates with proton signal at δ = 7.13 ppm), 122.01 (*C*H-Ph, correlates with proton signal at δ = 7.05 ppm), 119.83 (C_{ipso} α to imino group), 115.20 (*C*H-Ph, correlates with proton signal at δ = 6.56 ppm), 74.34 (O*C*H$_2$), 69.47 (*C*H–N), 59.40 (O*C*H$_3$) ppm. MS: *m*/*z* (%) = 825 (2) [2 M + H]$^+$, 413 (100) [M + H]$^+$, 323 (24). $C_{20}H_{22}N_2NiO_4$ (413.09): calcd. C 58.15, H 5.37, N 6.78; found C 58.02, H 5.32, N 6.53.

[(2*S*,3*S*)-2,3-Bis{[(2-hydroxynaphth-1-yl)methylene]amino}-1,4-dimethoxybutane]nickel(II) [(*S*,*S*)-7b]: From (*S*,*S*)-**10b** (91 mg, 0.2 mmol). A brown microcrystalline material was isolated (63 mg). Chromatography on silica gel of the extraction residue afforded the pure (salen)Ni^{II} complex (*S*,*S*)-**7b** as brown crystals (solvent gradient from PE/EtOAc, 95:5 to PE/EtOAc, 7:3). Crystals suitable for X-ray analysis were obtained from acetone by vapour diffusion of *n*-pentane. Yield (overall): 89 mg (87%); m.p. 350–352 °C (decomp.); R_f = 0.19 (PE/EtOAc, 6:4). IR: $\tilde{\nu}$ = 2929, 2828, 1617, 1603, 1540, 1506, 1454, 1433, 1361, 1342, 1309, 1254, 1194, 990, 829, 749 cm^{-1}. ^{1}H NMR: δ = 8.35 (s, 2 H, C*H*=N), 7.85 (broad d, J = 8.3 Hz, 2 H, C*H*-Ar), 7.66 (dd, J = 7.9, 1.4 Hz, 2 H, C*H*-Ar), 7.62 (d, J = 9.2 Hz, 2 H, C*H*-Ar), 7.45 (ddd, J = 8.3, 7.0, 1.4 Hz, 2 H, C*H*-Ar), 7.25 (ddd, J = 7.9, 7.0, 0.9 Hz, 2 H, C*H*-Ar), 7.21 (d, J = 9.2 Hz, 2 H, C*H*-Ar), 3.79 (dd, J = 9.6, 6.7 Hz, 2 H, OCH_2), 3.70 (dd, J = 9.6, 7.8 Hz, 2 H, OCH_2), 3.41 (dd, J = 7.8, 6.7 Hz, 2 H, C*H*–N), 3.40 (s, 6 H, OCH_3). ^{13}C NMR:[29] δ = 166.52 (C_{ipso} α to OH), 157.63 (*C*H=N), 134.47 (*C*H-Ar, correlates with proton signal at δ = 7.62 ppm), 133.25 (C_{ipso}-Ar), 129.00 (*C*H-Ar, correlates with proton signal at δ = 7.66 ppm), 127.44 (*C*H-Ar, correlates with proton signal at δ = 7.45 ppm), 126.71 (C_{ipso}-Ar), 124.44 (*C*H-Ar, correlates with proton signal at δ = 7.21 ppm), 122.49 (*C*H-Ar, correlates with proton signal at δ = 7.25 ppm), 118.74 (*C*H-Ar, correlates with proton signal at δ = 7.85 ppm), 110.59 (C_{ipso}-Ar), 74.72 (O*C*H$_2$), 70.22 (*C*H–N), 59.41 (O*C*H$_3$) ppm. MS: *m*/*z* (%) = 1025 (1) [2 M + H]$^+$, 513 (100) [M + H]$^+$, 422 (18). $C_{28}H_{26}N_2NiO_4$ (513.21): calcd. C 65.53, H 5.11, N 5.46; found C 65.11, H 5.19, N 5.39.

{(2*S*,3*S*)-1,4-Dimethoxy-2,3-bis[(5-nitrosalicylidene)amino]butane}-nickel(II) [(*S*,*S*)-7c]: From (*S*,*S*)-**10c** (89 mg, 0.2 mmol). Instead of MeOH a warm mixture of EtOH/*i*PrOH (1:1, 15 mL) was used to solubilise the salen ligand (*S*,*S*)-**10c**. A violet microcrystalline material of pure salen complex (*S*,*S*)-**7c** was isolated. Crystals suitable for X-ray analysis were obtained from $CHCl_3$, layered successively with CH_2Cl_2 and *n*-pentane. Yield: 84 mg (83%); m.p. 353–354 °C (decomp.); R_f = 0.28 (CH_2Cl_2/MeOH, 96:4). IR: $\tilde{\nu}$ = 2972, 2931, 2818, 1614, 1600, 1553, 1496, 1466, 1391, 1319, 1191, 1119, 1103, 1087, 1031, 954, 905, 837, 813, 754, 731 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 12.49 (broad s, 2 H, C*H*=N), 8.42 (d, J = 2.9 Hz, 2 H, C*H*-Ph), 8.17 (dd, J = 9.3, 2.9 Hz, 2 H, C*H*-Ph), 6.77 (d, J = 9.3 Hz, 2 H, C*H*-Ph), 5.12 (broad s, 2 H, C*H*–N), 3.64 (broad s, 4 H, OCH_2), 3.35 (s, 6 H, OCH_3). ^{13}C NMR ([D$_6$]DMSO):[29] δ = 169.91 (*C*H=N), 165.77 (C_{ipso} α to OH), 135.68 (C_{ipso} α to NO_2), 130.40 (4 C, *C*H-Ph, correlates with protons at δ = 8.42 and 6.77 ppm), 129.09 (*C*H-Ph, correlates with proton signal at δ = 8.17 ppm), 121.15 (C_{ipso} α to imino group), 73.65 (O*C*H$_2$), 66.80 (*C*H–N), 58.53 (O*C*H$_3$) ppm. MS: *m*/*z* (%) = 1005 (1) [2 M + H]$^+$, 503 (100) [M + H]$^+$. $C_{20}H_{20}N_4NiO_8$ (503.09): calcd. C 47.75, H 4.01, N 11.14; found C 47.42, H 4.05, N 10.97.

{(2*S*,3*S*)-1,4-Dimethoxy-2,3-bis[(5-nitrosalicylidene)amino]butane}-nickel(II) [(*S*,*S*)-7d]: From (*S*,*S*)-**10d** (94 mg, 0.2 mmol). Brown-violet microcrystalline plates were isolated (55 mg). Chromatography on silica gel of the extraction residue afforded the pure (salen)Ni^{II} complex (*S*,*S*)-**7d** as violet crystals (solvent gradient from PE/EtOAc, 98:2 to PE/EtOAc, 7:3). Crystals suitable for X-ray analysis were obtained from $CHCl_3$ by layering with *n*-pentane. Yield (overall): 100 mg (95%); m.p. 241–242 °C; R_f = 0.23 (PE/EtOAc, 6:4). IR: $\tilde{\nu}$ = 2949, 2868, 2829, 2812, 1612, 1599, 1537, 1468, 1415, 1387, 1338, 1321, 1237, 1196, 964, 867, 756 cm^{-1}. ^{1}H NMR: δ = 7.44 (s, 2 H, C*H*=N), 7.23 (dd, J = 7.3, 1.4 Hz, 2 H, C*H*-Ph), 7.00 (dd, J = 7.7, 1.4 Hz, 2 H, C*H*-Ph), 6.49 (dd, J = 7.7, 7.3 Hz, 2 H, C*H*-Ph), 3.70 (dd, J = 9.4, 7.1 Hz, 2 H, OCH_2), 3.62 (dd, J = 9.4, 7.8 Hz, 2 H, OCH_2), 3.39 (s, 6 H, OCH_3), 3.15 (dd, J = 7.8, 7.1 Hz, 2 H, C*H*–N), 1.40 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR:[29] δ = 164.90 (C_{ipso} α to OH), 163.83 (*C*H=N), 140.95 [C_{ipso} α to C(CH$_3$)$_3$], 131.20 (*C*H-Ph, correlates with proton signal at δ = 7.00 ppm), 130.76 (*C*H-Ph, correlates with proton signal at δ = 7.23 ppm), 120.39 (C_{ipso} α to imino group), 114.22 (*C*H-Ph, correlates with proton signal at δ = 6.49 ppm), 74.39 (O*C*H$_2$), 69.37 (*C*H–N), 59.21 (O*C*H$_3$), 35.59 (*C*(CH$_3$)$_3$), 29.58 (6 C, C(*C*H$_3$)$_3$). MS: *m*/*z* (%) = 525 (100) [M + H]$^+$, 509 (25) [M – CH$_3$]$^+$. $C_{28}H_{38}N_2NiO_4$ (525.31): calcd. C 64.02, H 7.29, N 5.33; found C 63.79, H 7.25, N 5.35.

{(2*S*,3*S*)-2,3-Bis[(5-*tert*-butylsalicylidene)amino]-1,4-dimethoxybutane}nickel(II) [(*S*,*S*)-7e]: From (*S*,*S*)-**10e** (94 mg, 0.2 mmol). A brown microcrystalline material was isolated (51 mg). Chromatography on silica gel of the extraction residue afforded the pure (salen)Ni^{II} complex (*S*,*S*)-**7e** as brown crystals (solvent gradient from CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2). Crystals suitable for X-ray analysis were obtained from $CHCl_3$ by layering with *n*-pentane. Yield (overall): 96 mg (91%); m.p. 248–251 °C (decomp.); R_f = 0.32 (CH_2Cl_2/MeOH, 96:4). IR: $\tilde{\nu}$ = 2961, 2866, 2829, 1619, 1605, 1528, 1470, 1422, 1387, 1364, 1318, 1256, 1216, 1188, 964, 880, 836, 740 cm^{-1}. ^{1}H NMR: δ = 7.48 (s, 2 H, C*H*=N), 7.29 (dd, J = 9.0, 2.6 Hz, 2 H, C*H*-Ph), 7.03 (d, J = 2.6 Hz, 2 H, C*H*-Ph), 7.00 (d, J = 9.0 Hz, 2 H, C*H*-Ph), 3.69 (dd, J = 9.5, 6.9 Hz, 2 H, OCH_2), 3.62 (dd, J = 9.5, 7.7 Hz, 2 H, OCH_2), 3.39 (s, 6 H, OCH_3), 3.22 (dd, J = 7.7, 6.9 Hz, 2 H, C*H*–N), 1.25 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR:[29] δ = 163.54 (C_{ipso} α to OH), 163.53 (*C*H=N), 137.43 (C_{ipso} α to C(CH$_3$)$_3$), 132.67 (*C*H-Ph, correlates with proton signal at δ = 7.29 ppm), 127.45 (*C*H-Ph, correlates with proton signal at δ = 7.03 ppm), 121.61 (*C*H-Ph, correlates with proton signal at δ = 7.00 ppm), 118.85 (C_{ipso} α to imino group), 74.45 (O*C*H$_2$), 69.36 (*C*H–N), 59.39 (O*C*H$_3$), 33.62 [*C*(CH$_3$)$_3$], 31.25 [6 C, C(*C*H$_3$)$_3$] ppm. MS: *m*/*z* (%) = 525 (100) [M]$^+$, 509 (33) [M – CH$_3$]$^+$. $C_{28}H_{38}N_2NiO_4$ (525.31): calcd. C 64.02, H 7.29, N 5.33; found C 64.19, H 7.58, N 5.00.

{(2*S*,3*S*)-2,3-Bis[(3-*tert*-butyl-5-nitrosalicylidene)amino]-1,4-dimethoxybutane}nickel(II) [(*S*,*S*)-7f]: From (*S*,*S*)-**10f** (112 mg, 0.2 mmol). A red microcrystalline material was isolated (74 mg). Chromatography on silica gel of the extraction residue afforded the pure (salen)Ni^{II} complex (*S*,*S*)-**7f** as red crystals (solvent gradient from CH_2Cl_2 to CH_2Cl_2/MeOH, 98:2). Yield (overall): 107 mg (87%); m.p. 310–312 °C (decomp.); R_f = 0.11 (CH_2Cl_2/MeOH, 98:2). IR: $\tilde{\nu}$ = 2956, 1709, 1623, 1595, 1558, 1496, 1424, 1393, 1308, 1231, 1187, 1117, 994, 960, 912, 839, 813, 794, 775, 748, 729 cm^{-1}. ^{1}H NMR: δ = 8.11 (d, J = 3.0 Hz, 2 H, C*H*-Ph), 8.10 (d, J = 3.0 Hz, 2 H, C*H*-Ph), 7.55 (s, 2 H, C*H*=N), 3.76 (dd, J = 9.6, 8.7 Hz, 2 H, OCH_2), 3.66 (dd, J = 9.6, 5.7 Hz, 2 H, OCH_2), 3.44 (s, 6 H, OCH_3), 3.26 (dd, J = 8.7, 5.7 Hz, 2 H, C*H*–N), 1.39 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR:[29] δ = 169.01 (C_{ipso} α to OH), 164.84 (*C*H=N), 142.14 and 136.09 [4 C, C_{ipso} α to C(CH$_3$)$_3$ and to NO_2], 129.22 and 125.50 (4 C, *C*H-Ph, correlates with protons at δ = 8.11 and 8.10 ppm), 119.30 (C_{ipso} α to imino group), 73.72 (O*C*H$_2$), 69.96 (*C*H–N), 59.35 (O*C*H$_3$), 35.92 [*C*(CH$_3$)$_3$], 29.22 [6 C,

C(CH_3)$_3$]. MS: *m*/*z* (%) = 1229 (1) [2 M + H]$^+$, 615 (100) [M + H]$^+$, 599 (33) [M – CH_3]$^+$. $C_{28}H_{36}N_4NiO_8$ (615.30): calcd. C 54.66, H 5.90, N 9.11; found C 54.30, H 5.97, N 8.97.

{(2*S*,3*S*)-2,3-Bis[(3,5-di-*tert*-butylsalicylidene)amino]-1,4-dimethoxybutane}nickel(II) [(*S*,*S*)-7g]: From (*S*,*S*)-**10g** (116 mg, 0.2 mmol).[12f] A brown microcrystalline material was isolated (55 mg). Chromatography on silica gel of the extraction residue afforded the pure (salen)Ni^{II} complex (*S*,*S*)-**7g** as brown crystals (solvent gradient from PE/EtOAc, 99:1 to PE/EtOAc, 9:1). Yield (overall): 115 mg (90%); m.p. 142–144 °C; R_f = 0.18 (PE/EtOAc, 8:2). IR: $\tilde{\nu}$ = 2957, 2866, 1737, 1610, 1527, 1461, 1431, 1413, 1389, 1360, 1324, 1256, 1236, 1202, 1174, 965, 873, 839, 787, 716 cm^{-1}. ^{1}H NMR: δ = 7.44 (s, 2 H, C*H*=N), 7.31 (d, *J* = 2.5 Hz, 2 H, C*H*-Ph), 6.89 (d, *J* = 2.5 Hz, 2 H, C*H*-Ph), 3.71 (dd, *J* = 9.4, 7.3 Hz, 2 H, OCH_2), 3.59 (dd, *J* = 9.4, 7.5 Hz, 2 H, OCH_2), 3.38 (s, 6 H, OCH_3), 3.16 (dd, *J* = 7.5, 7.3 Hz, 2 H, C*H*–N), 1.40 [s, 18 H, C(CH_3)$_3$], 1.26 [s, 18 H, C(CH_3)$_3$] ppm. ^{13}C NMR:[29] δ = 163.73 (*C*H=N), 163.32 (C_{ipso} α to OH), 140.26 [C_{ipso} α to C(CH$_3$)$_3$], 135.95 [C_{ipso} α to C(CH$_3$)$_3$], 129.28 (*C*H-Ph, correlates with proton signal at δ = 7.31 ppm), 126.00 (*C*H-Ph, correlates with proton signal at δ = 6.89 ppm), 119.37 (C_{ipso} α to imino group), 74.54 (O*C*H$_2$), 69.27 (*C*H–N), 59.24 (O*C*H$_3$), 35.81 [*C*(CH$_3$)$_3$], 33.78 [*C*(CH$_3$)$_3$], 31.27 [6 C, C(*C*H$_3$)$_3$, correlates with protons at δ = 1.26 ppm], 29.62 [6 C, C(*C*H$_3$)$_3$, correlates with protons at δ = 1.40 ppm]. MS: *m*/*z* (%) = 1215 (1) [2 M – C(CH$_3$)$_3$]$^+$, 636 (100) [M]$^+$, 621 (44) [M – CH_3]$^+$. $C_{36}H_{54}N_2NiO_4$ (637.52): calcd. C 67.82, H 8.54, N 4.39; found C 68.25, H 8.82, N 4.14.

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