Synthesis of Optically Active Bis(2-oxazolines): Crystal Structure of a 1,2-Bis(2-oxazolinyl)benzene · $ZnCl_2$ Complex

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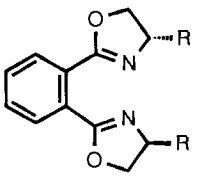
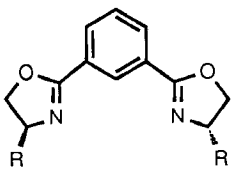
Dinitriles (**5**–**7**, **12**, **13**) react with enantiomerically pure β-amino alcohols (**8**–**11**, **17**) under zinc chloride catalysis to give optically active C_2-symmetric bis(oxazolines). 1,2-Bis(2-oxazolin-2-yl)benzenes **1a**–**e** are obtained under mild reaction conditions. ^{1}H-NMR spectroscopy indicates the formation of 1:1 complexes **23** of these compounds with $ZnCl_2$. The energy required for a conformational interconversion of zinc dichloride complex **23e** was determined by variable-temperature ^{1}H-NMR studies. An X-ray structure analysis was performed with the substituted [1,2-bis(2-oxazolinyl)benzene]zinc dichloride complex **23a**.

Optically active oxazolines have been extensively used as valuable auxiliaries in asymmetric synthesis[2)]. They can effect efficient chirality transfer from the heterocycle to newly formed bonds, thereby generating new centers of chirality with high asymmetric induction. Oxazolines have also been found in many microbial metal chelators such as vibriobactin, mycobactin, and parabactin[3)]. In these cases they are incorporated into extremely strong multidentate metal complexes, illustrating the high chelating ability of this moiety. Based on these properties, optically active oxazolines have been used as chiral ligands for transition metals in asymmetric catalysis[4)].

During our studies of new bidentate ligands for enantioselective transition-metal catalysis[5)], we have envisioned that C_2-symmetric homochiral bis(2-oxazolinyl)benzenes of type **1** and **2** might be effective ligands for affecting asymmetric catalysis.

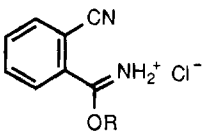


type 1



type 2

Compounds of type **2** have previously been prepared by dehydration of 1,3-bis(benzoylamino)benzenes[4a,6)] with thionyl chloride or by modified Pinner reactions (diimidate formation of 1,3-dinitriles, followed by reaction with amino alcohols)[7)]. However, *ortho*-substituted benzenes of type **1** are not easily accessible by these routes. They have only been synthesized under vigorous reaction conditions. For example, dehydration of 1,2-bis(benzoylamino) derivatives to 1,2-bis(2-oxazolin-2-yl)benzenes (type **1**) requires high temperatures (100–170°C) and strongly acidic conditions (30% SO_3 in 70% sulfuric acid)[8)]. The Pinner method fails because 1,2-dinitriles can only be converted to stable monoimidate salts (**3**). The second cyano group of **3** is inert, and bisimidates are not formed[9)].



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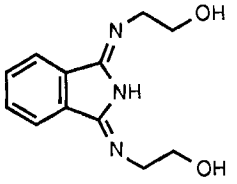

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In 1974 Witte and Seeliger reported on a procedure for the preparation of mono- and bis(2-oxazolines) by direct reaction of nitriles with amino alcohols in the presence of catalytic amounts of metal salts[10a)]. However, attempts to use phthalonitrile and 2-aminoethanol gave exclusively 2,3-dihydro-1,3-bis(2-hydroxyethylimino)-1*H*-isoindol (**4**); no 1,2-bis(2-oxazolinyl) derivatives could be obtained. The stereochemical course of this reaction was not examined.

Synthesis of Bis(2-oxazolines)

By a careful reinvestigation of Witte and Seeliger's metal-catalyzed oxazoline synthesis, we now demonstrate that a variety of substituted optically active bis(2-oxazolinyl) derivatives can readily be prepared under mild reaction conditions. We obtained *ortho*-substituted bis(2-oxazolin-2-yl)-benzenes of type **1** by using a slightly modified procedure. The procedure entails refluxing a solution of an appropriate dinitrile and an excess of the appropriate amino alcohol in chlorobenzene in the presence of a catalytic amount of zinc dichloride (Scheme 1). Aqueous workup followed by column chromatography gives the desired bis(2-oxazolines) in moderate to good yields (Table 1).

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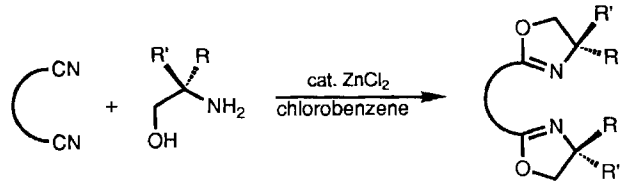
Table 1. Synthesis of bis(2-oxazolines) from dinitriles[a]

Entry	Dinitrile	Amino-alcohol	R	R'	Yield[b] [%]	Product No.
1	5	8	-CH(CH$_3$)$_2$	-H	89	1a
2	5	9	(*S*)-CH(CH$_3$)(C$_2$H$_5$)	-H	69	1b
3	5	10	-C$_6$H$_5$	-H	66	1c
4	5	11	-CH$_2$C$_6$H$_5$	-H	25	1d
5	5	17	-CH$_3$	-CH$_3$	63	1e
6	6	8	-CH(CH$_3$)$_2$	-H	67	2a
7	6	9	(*S*)-CH(CH$_3$)(C$_2$H$_5$)	-H	42	2b
8	7	8	-CH(CH$_3$)$_2$	-H	77	14a
9	7	9	(*S*)-CH(CH$_3$)(C$_2$H$_5$)	-H	63	14b
10	12	8	-CH(CH$_3$)$_2$	-H	59	15a
11	13	8	-CH(CH$_3$)$_2$	-H	42	16a

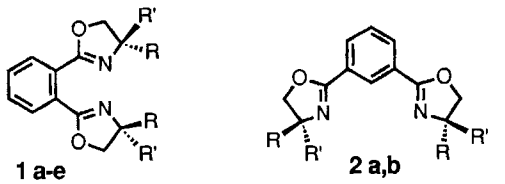
[a] **5** = Phthalonitrile, **6** = isophthalonitrile, **7** = terephthalonitrile, **12** = 1,2-dicyanoethane, **13** = 1,3-dicyanopropane. — [b] Isolated and purified by flash chromatography[11] or by MPLC.

Scheme 1



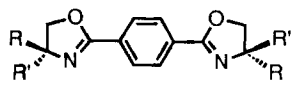
5-7,12,13 **8-11,17** **1a-e**

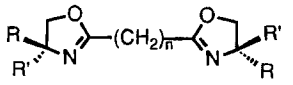
ortho-, *meta-*, and *para*-disubstituted benzenes are obtained starting from phthalo- (**5**), isophthalo- (**6**), and terephthalonitrile (**7**). The yields depend on the amino alcohol employed. Whereas valinol [(*S*)-**8**], isoleucinol [(*S*)-**9**], and phenylglycinol [(*S*)-**10**] give the desired bis(2-oxazolines) of type **1** and **2** in good yields, the reaction of phenylalaninol [(*S*)-**11**] results in the formation of only small amounts of product. 1,2-Dicyanoethane (**12**) and 1,3-dicyanopropane (**13**) are converted into the bis(2-oxazolines) in moderate yield. Malono- and fumaronitrile do not give any of the desired product under these conditions.



1a-e

2a,b



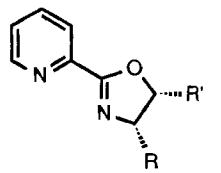


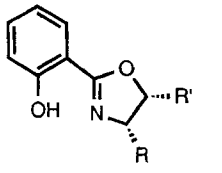
14a,b

	n
15a	2
16a	3

Enantiomerically pure amino alcohols are either commercially available or easily obtained by reduction of the corresponding amino acids[12]. In order to assure that no racemization had occured during the zinc-catalyzed ring formation, we have examined the ^{1}H-NMR spectra of crude mixtures of bis(2-oxazolines) synthesized from enantiomerically pure β-amino alcohols under our modified reaction conditions. No signals derived from diastereomeric compounds have been detected.

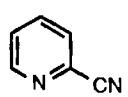
Known monooxazolines **18a–c**[4b] and **19a,b** were synthesized from 2-cyanopyridine (**20**) and 2-hydroxybenzonitrile (**21**), respectively, in high yields (75–84%) under the same conditions used in the synthesis of the bisoxazolines.





	R	R'
18a	CH(CH$_3$)$_2$	H
18b	CH(CH$_3$)(C$_2$H$_5$)	H
18c	CH$_3$	C$_6$H$_5$

	R	R'
19a	CH(CH$_3$)$_2$	H
19b	CH$_3$	C$_6$H$_5$



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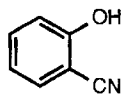

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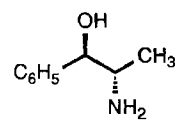

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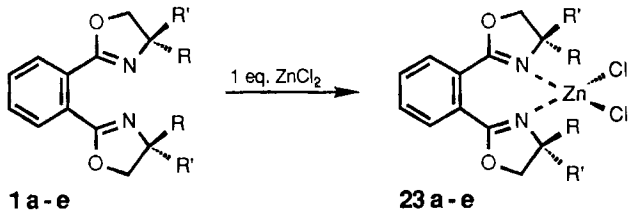
An analysis of optical purity by a comparison of the optical rotation values for compounds **18a–c** with the reported data[4b] indicates the stereochemical integrity of the chiral centers during ring formation[13]. The stereospecificity of the oxazoline formation is demonstrated by the synthesis of **18c** by the reaction of (1*R*,2*S*)-norephedrine (**22**) with 2-cyanopyridine **20**. The reaction proceeds with complete retention of configuration at both chiral centers[14]. Attempts to determine the optical purity of **19a** by its α-methoxy-α-(trifluoromethyl)phenylacetate[15] failed due to decomposition during the derivatization step. The enantiomers of *rac*-**19a** could not be separated by using a chiral HPLC column (CHIRALCEL OD).

Zinc Complex Formation and Crystal Structure of 23a

Treatment of *ortho*-substituted bis(2-oxazolinyl)benzenes (**1a–e**) with one equivalent of zinc dichloride in THF results in the formation of stable 1:1 complexes. These are isolated by crystallization upon slow evaporation of the solvent, and they may be recrystallized from ethanol. A variety of complexes containing mono- and disubstituted oxazolinyl rings are obtained (Scheme 2).

All complexes **23a–e** have been fully characterized both spectroscopically and analytically. The molecular structure of **23a** has been determined by X-ray diffraction analysis (Figure 1). Crystals of **23a** grown in ethanol are orthorhombic with space group $P2_12_12_1$ (No. 19). The zinc atom is tetrahedrally surrounded by two chlorine atoms and two nitrogen atoms of the oxazolinyl groups.

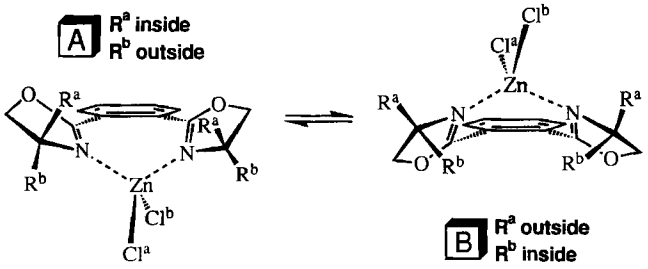
Scheme 2



1/23	a	b	c	d	e
R	$CH(CH_3)_2$	$CH(CH_3)(C_2H_5)$	C_6H_5	$CH_2C_6H_5$	CH_3
R'	H	H	H	H	CH_3

The distances between the metal and the nitrogen atoms are 2.046(8) and 2.049(7) Å, respectively. The proximity of the oxazolines requires a complexation of the zinc atom below the plane of the aromatic ring. The torsion angles C4–C9–C10–N2 of 46.6° and N1–C3–C4–C9 of −46.5° represent the angles between the planes of the benzene ring and the oxazolinyl rings. The latter are symmetrically tilted causing a nonequivalence of the isopropyl substituents. For each oxazoline, one of the isopropyl groups points into the cavity formed by the two oxazoline rings, whereas the other one points out. The ^{1}H-NMR spectrum of **23a** indicates that both isopropyl groups are equivalent in solution with respect to the NMR time scale. This equivalence is caused by a rapid interconversion between **A** [R^a inside the bis(oxazolinyl) cavity; R^b = outside] and **B** (R^a = outside; R^b = inside) (Scheme 3). All zinc dichloride complexes **23a–e** show the same behavior in solution, giving a single set of signals for the diastereomeric oxazoline protons in their ^{1}H-NMR spectra[16].

Scheme 3



The interconversion between **A** and **B** of complex **23e** (R^a = R^b = methyl) in solution has been examined by variable-temperature NMR studies. The methyl protons in the ^{1}H-NMR spectrum of a 0.065 M solution of **23e** give rise to one singlet at room temperature. However, the rapid interconversion between **A** and **B** is slowed down at lower temperatures, and coalescence is reached at −27°C. Further reduction of the temperature results in two separate well-resolved signals for the methyl protons and an AB quadruplet for the methylene protons of the oxazoline rings. An energy barrier of 50.7 kJ · mol^{-1} for the interconversion of **A** and **B** has been calculated by using the Eyring equation[17].

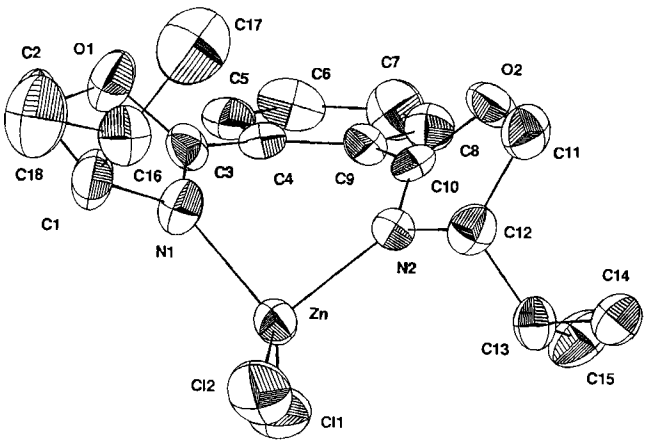


Figure 1. Molecular structure of compound **23a** (ORTEP, 50% probability ellipsoids, with atomic numbering; H atoms omitted for clarity)

NMR Spectroscopy of Complex Formation

In order to investigate the formation of the complexes of bis(2-oxazolinyl)-benzenes of type **1** or **2** with zinc salts in solution, **1a** and **2a** were dissolved in [D_3]acetonitrile and portions of zinc dichloride were added successively. Upon sequential addition of substoichiometric amounts of the zinc salt to **1a**, extensive broadening of the ^{1}H-NMR signals indicated a rapid exchange of the zinc salt between various oxazolines (Figure 2)[18]. Each addition of zinc dichloride caused a downfield shift of all signals, except those associated with the methyl groups of the oxazolinyl substituent, which shifted upfield. After the addition of one equivalent of zinc dichloride, immediate sharpening of the signals was

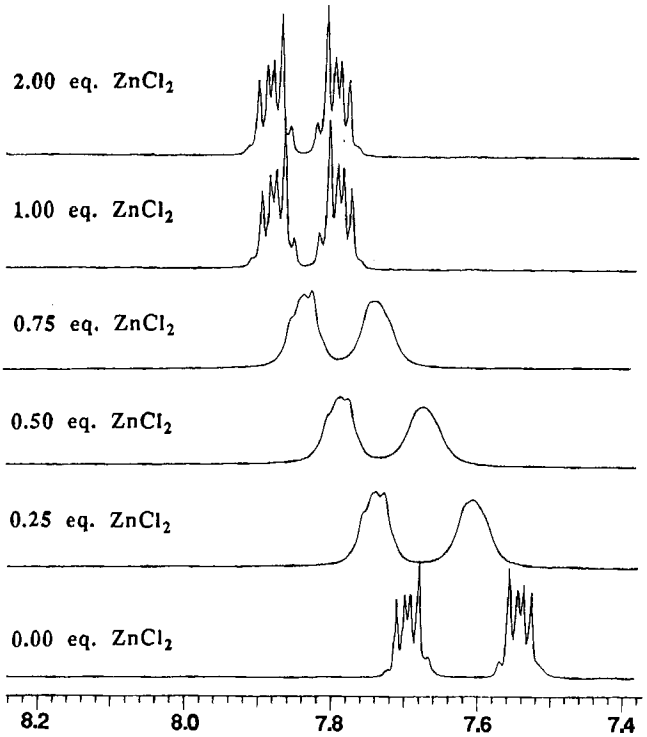


Figure 2. ^{1}H-NMR spectra (300 MHz, [D_3]acetonitrile) of **1a** with various amounts of $ZnCl_2$ (aromatic region)

observed. Line-shape and chemical shift did not change upon further addition of zinc dichloride. These results indicate the formation of a 1:1 complex **23a** in solution.

In contrast, treatment of **2a** with increasing amounts of zinc dichloride resulted in a less defined behavior. No sharpening of the signals was observed. Even after addition of a large excess of the metal salt, the chemical shifts continue to change upon each successive addition of zinc dichloride. In this case, the signals for the aromatic proton at C-2, the methylene protons of the heterocycle, and the protons of the methyl groups moved upfield until the addition of about one equivalent of zinc dichloride. Further addition of the zinc salt caused downfield shifts of these signals. All other signals moved downfield gradually.

Summary

This article describes the synthesis of optically active bis(oxazolines) by the zinc dichloride-catalyzed reaction of dinitriles with enantiomerically pure β-amino alcohols. Substituted 1,2-bis(2-oxazolinyl)benzene derivatives, not easily accessible by other methods, can be synthesized in moderate to good yields under mild reaction conditions. No racemization is observed during oxazoline formation. 1,2-Bis(2-oxazolinyl)benzenes serve as strong bidentate ligands for zinc dichloride. The molecular structure of the neutral 1:1 zinc(II) complex **23a** has been determined by X-ray diffraction analysis. Both oxazoline rings are tilted with respect to the plane of the aromatic ring such that the zinc atom is tetrahedrally surrounded by two oxazoline nitrogens and two chlorine atoms.

The formation of 1:1 complexes of $ZnCl_2$ with substituted 1,2-bis(2-oxazolinyl)benzenes in solution has been detected by ^{1}H-NMR investigations. Addition of successive amounts of zinc dichloride leads to broadening of the signals. After one equivalent is added, sharpening of the signals is observed. Further addition of $ZnCl_2$ does not change the spectrum anymore. 1,3-bis(oxazolines) exhibit a different complexation behavior. Upon treatment with various amounts of zinc dichloride, no indication of a defined complex can be detected.

Variable-temperature NMR studies have been performed with the achiral zinc dichloride complex **23e**. At ambient temperature both methyl groups appear to be equivalent with respect to the NMR time scale. Lowering the temperature allows the diastereotopic methyl groups to become distinguishable. An activation energy of 50.7 kJ · mol^{-1} is calculated for the conformational interconversion.

Zinc dichloride complexes of diamines have been used as catalysts for the enantioselective conjugate additions of organometallic reagents to enones[19]. The use of bis(2-oxazoline)zinc complexes as asymmetric catalysts for these and other stereoselective transformations is currently under investigation.

This work was generously supported by the *Volkswagen-Stiftung* and the *Ciba-Stiftung*. C. B. thanks the *Fonds der Chemischen Industrie* for a Liebig fellowship.

Experimental

^{1}H and ^{13}C NMR: Varian Gemini 300, Varian VXR 400; tetramethylsilane or $CHCl_3$ as internal standard in $CDCl_3$, unless noted otherwise. – IR: Perkin Elmer 781. – MS: VG 70-250. – All experiments were carried out in flame-dried glassware under argon. – The preparation of the amino alcohols has been previously described[12]. Anhydrous zinc dichloride was purchased from Siegfried and Alfa (ultrapure) and dried by melting under high vacuum prior to use.

General Procedure for the Preparation of Bis(2-oxazolines): In a 100-ml two-necked flask, 68 mg of zinc chloride (0.50 mmol) was melted under high vacuum and cooled under argon. After cooling to room temp., 30 ml of chlorobenzene was added followed by 10 mmol of the dinitrile and 30 mmol of the amino alcohol. The mixture was heated under reflux for 24 h. The solvent was removed under reduced pressure to give an oily residue, which was dissolved in 30 ml of dichloromethane. The solution was extracted three times with 20 ml of water and the aqueous phase with 30 ml of dichloromethane. The combined organic phases were dried with sodium sulfate, and the solvent was removed in vacuo. The resulting oil was purified by flash chromatography[11] or MPLC (pentane/ethyl acetate 4:1) to afford a clean product.

1,2-Bis[(4S)-4-isopropyl-2-oxazolin-2-yl]benzene (**1a**): 1.28 g (10 mmol) of **5** and 3.10 g (30 mmol) of (*S*)-valinol gave 2.68 g (89%) of **1a**. Colorless oil, b.p. 175°C/10^{-2} mbar. – IR (neat): $\tilde{\nu}$ = 1655 cm^{-1} (C=N), 1250 (C–O). – ^{1}H NMR: δ = 0.95 [d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$], 1.04 [d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$], 1.88 [sept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$], 4.04–4.13 (m, 4H, OCH$_2$), 4.34–4.42 (m, 2H, CHN), 7.45–7.50 (m, 2H, 4-, 5-H), 7.74–7.77 (m, 2H, 3-, 6-H). – ^{13}C NMR: δ = 17.92 (q), 18.78 (q), 32.39 (d), 70.46 (t, C-5'), 72.87 (d, C-4'), 128.61 (s, C-1, -2), 129.97 (d, C-4, -5), 130.36 (d, C-3, -6), 163.95 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 257 (58), 171 (100), 130 (15), 116 (5).

$C_{18}H_{24}N_2O_2$ (300.4)
Calcd. C 71.97 H 8.05 N 9.33
Found C 72.00 H 8.14 N 9.52

1,2-Bis{(4S)-4-[(1S)-1-methylpropyl]-2-oxazolin-2-yl}benzene (**1b**): 1.28 g (10 mmol) of **5** and 3.52 g (30 mmol) of (2*S*,3*S*)-isoleucinol gave 2.27 g (69%) of **1b**. Colorless oil. – IR (neat): $\tilde{\nu}$ = 1645 cm^{-1} (C=N), 1240 (C–O). – ^{1}H NMR: δ = 0.90–0.99 (m, 12H, CH$_3$), 1.21–1.31 (m, 2H, CH), 1.59–1.76 (m, 4H, CH$_2$), 4.08 (dd, *J* = 7.9, 7.9 Hz, 2H, OCH$_2$), 4.17–4.25 (m, 2H, NCH), 4.36 (dd, *J* = 7.6, 7.6 Hz, 2H, OCH$_2$), 7.46–7.49 (m, 2H, 4-, 5-H), 7.74–7.77 (m, 2H, 3-, 6-H). – ^{13}C NMR: δ = 11.25 (q), 14.16 (q), 26.04 (t), 38.87 (d), 70.09 (t, C-5'), 71.55 (d, C-4'), 128.74 (s, C-1, -2), 130.06 (d, C-4, -5), 130.42 (d, C-3, -6), 163.93 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 328 (2) [M$^+$], 271 (100), 230 (7), 217 (5), 171 (91).

$C_{20}H_{28}N_2O_2$ (328.5)
Calcd. C 73.14 H 8.59 N 8.53
Found C 73.00 H 8.75 N 8.41

1,2-Bis[(4S)-4-phenyl-2-oxazolin-2-yl]benzene (**1c**): 1.28 g (10 mmol) of **5** and 4.12 g (30 mmol) of (*S*)-phenylglycinol gave 2.42 g (66%) of **1c**. Pale yellow wax, b.p. 210°C/10^{-2} mbar. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1650 cm^{-1} (C=N). – ^{1}H NMR: δ = 4.20 (dd, *J* = 8.3, 8.5 Hz, 2H, OCH$_2$), 4.69 (dd, *J* = 8.3, 10 Hz, 2H, OCH$_2$), 5.36 (dd, *J* = 8.5, 10 Hz, 2H, CHN), 7.24–7.38 (m, 10H, CHC$_6$*H*$_5$), 7.53–7.57 (m, 2H, 4-, 5-H), 7.86–7.92 (m, 2H, 3-, 6-H). – ^{13}C NMR: δ = 70.50 (d), 75.26 (t), 127.12 (d), 127.70 (d), 128.49 (s), 128.79 (d), 130.25 (d), 130.85 (d), 142.47 (s), 165.25 (s). – MS (EI,

70 eV): *m/z* (%) = 268 (0.2) [M^+], 264 (100), 250 (12), 233 (14), 205 (4), 130 (24), 117 (8), 104 (48), 91 (17).

$C_{24}H_{20}N_2O_2$ (368.4)
Calcd. C 78.24 H 5.47 N 7.60
Found C 78.48 H 5.68 N 7.43

1,2-Bis[(4S)-4-benzyl-2-oxazolin-2-yl]benzene (**1d**): 1.28 g (10 mmol) of **5** and 4.54 g (30 mmol) of (*S*)-phenylalaninol gave 1.02 g (25%) of **1d**. Pale yellow wax. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1650 cm^{-1} (C=N). – ^1H NMR: δ = 2.77 (dd, *J* = 13.8, 8.9 Hz, 2H, $CH_2C_6H_5$), 3.24 (dd, *J* = 13.8, 5.3 Hz, 2H, $CH_2C_6H_5$), 4.10 (dd, *J* = 7.9, 7.9 Hz, 2H, OCH_2), 4.31 (dd, *J* = 8.9, 8.9 Hz, 2H, OCH_2), 4.55–4.66 (m, 2H, CHN), 7.21–7.35 (m, 10H, $CH_2C_6H_5$), 7.49–7.54 (m, 2H, 4-, 5-H), 7.73–7.78 (m, 2H, 3-, 6-H). – ^{13}C NMR: δ = 41.21 (t), 67.94 (d), 72.25 (t), 126.68 (d), 128.34 (s), 128.72 (d), 129.44 (d), 130.08 (d), 130.72 (d), 138.06 (s), 164.68 (s). – MS (EI, 70 eV): *m/z* (%) = 305 (100), 171 (71), 130 (12), 91 (61).

$C_{26}H_{24}N_2O_2$ (396.5)
Calcd. C 78.76 H 6.10 N 7.07
Found C 78.78 H 6.14 N 7.26

1,2-Bis(4,4-dimethyl-2-oxazolin-2-yl)benzene (**1e**): 1.28 g (10 mmol) of **5** and 2.67 g (30 mmol) of 2-amino-2,2-dimethylethanol gave 1.72 g (63%) of **1e**. Colorless oil, b.p. 140°C/5 · 10^{-2} mbar. – IR (neat): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^1H NMR: δ = 1.39 [s, 12H, $NC(CH_3)_2$], 4.07 (s, 4H, OCH_2), 7.45–7.48 (m, 2H, 4-, 5-H), 7.72–7.76 (m, 2H, 3-, 6-H). – ^{13}C NMR: δ = 27.91 (q), 67.83 (s), 79.45 (t), 128.75 (s), 129.86 (d), 130.34 (d), 162.57 (s). – MS (EI, 70 eV): *m/z* (%) = 272 (1) [M^+], 257 (30), 227 (7), 216 (48), 201 (2), 185 (100), 130 (34).

$C_{16}H_{20}N_2O_2$ (272.35)
Calcd. C 70.56 H 7.40 N 10.29
Found C 70.53 H 7.52 N 10.42

1,3-Bis[(4S)-4-isopropyl-2-oxazolin-2-yl]benzene (**2a**): 1.28 g (10 mmol) of **6** and 3.10 g (30 mmol) of (*S*)-valinol gave 2.00 g (67%) of **2a**. Colorless crystals, m.p. 53°C. – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (C=N), 1270 (C–O). – ^1H NMR: δ = 0.94 [d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$], 1.04 [d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$], 1.87 [sept, *J* = 6.7 Hz, 2H, $CH(CH_3)_2$], 4.09–4.19 (m, 4H, OCH_2), 4.38–4.48 (m, 2H, CHN), 7.46 (t, *J* = 7.8 Hz, 1H, 5-H), 8.08 (d, *J* = 7.8 Hz, 2H, 4-, 6-H), 8.52 (s, 1H, 2-H). – ^{13}C NMR: δ = 17.82 (q), 18.64 (q), 32.60 (d), 70.11 (t, C-5'), 72.63 (d, C-4'), 128.17 (d, C-5), 128.33 (s, C-1, -3), 128.43 (d, C-4, -6), 130.95 (d, C-2), 162.97 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 257 (100), 229 (10), 215 (4), 171 (6), 144 (24), 116 (12).

$C_{18}H_{24}N_2O_2$ (300.4)
Calcd. C 71.97 H 8.05 N 9.33
Found C 71.74 H 8.30 N 9.47

1,3-Bis{(4S)-4-[(1S)-1-methylpropyl]-2-oxazolin-2-yl}benzene (**2b**): 1.28 g (10 mmol) of **6** and 3.52 g (30 mmol) of (2*S*,3*S*)-isoleucinol gave 1.37 g (42%) of **2b**. Colorless oil, b.p. 220°C/10^{-2} mbar. – IR (neat): $\tilde{\nu}$ = 1655 cm^{-1} (C=N), 1250 (C–O). – ^1H NMR: δ = 0.87 (d, *J* = 6.8 Hz, 6H, $CHCH_3$), 0.97 (t, *J* = 7.4 Hz, 6H, CH_2CH_3), 1.18–1.30 [m, 2H, $CH(CH_3)C_2H_5$], 1.56–1.76 (m, 4H, CH_2), 4.14–4.21 (m, 2H, OCH_2), 4.23–4.28 (m, 2H, NCH), 4.41–4.47 (m, 2H, OCH_2), 7.53 (t, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 7.8 Hz, 2H, 4-, 6-H), 8.25 (s, 1H, 2-H). – ^{13}C NMR: δ = 11.24 (q), 14.13 (q), 25.84 (t), 38.96 (d), 70.12 (t, C-5'), 71.37 (d, C-4'), 129.34 (d, C-5), 132.02 (s, C-1, -3), 132.42 (d, C-4, -6), 134.40 (d, C-2), 161.57 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 329 (100) [M^+ + 1], 271 (12), 229 (28), 203 (4), 171 (3), 103 (6).

$C_{20}H_{28}N_2O_2$ (328.5)
Calcd. C 73.14 H 8.59 N 8.53
Found C 73.17 H 7.90 N 8.71

1,4-Bis[(4S)-4-isopropyl-2-oxazolin-2-yl]benzene (**14a**): 1.28 g (10 mmol) of **7** and 3.10 g (30 mmol) of (*S*)-valinol gave 2.31 g (77%) of **14a**. Colorless crystals, m.p. 132°C. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^1H NMR: δ = 0.93 [d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$], 1.04 [d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$], 1.87 [sept, *J* = 6.6 Hz, 2H, $CH(CH_3)_2$], 4.07–4.17 (m, 4H, OCH_2), 4.38–4.45 (m, 2H, CHN), 7.98 (s, 4H, aromatic H). – ^{13}C NMR: δ = 17.88 (q), 18.74 (q), 32.66 (d), 70.19 (t, C-5'), 72.75 (d, C-4'), 128.30 (d), 130.52 (s, C-1, -4), 163.08 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 257 (100), 229 (7), 171 (3), 144 (14), 116 (5), 103 (3).

$C_{18}H_{24}N_2O_2$ (300.4)
Calcd. C 71.97 H 8.05 N 9.33
Found C 71.55 H 8.15 N 9.40

1,4-Bis{(4S)-4-[(1S)-1-methylpropyl]-2-oxazolin-2-yl}benzene (**14b**): 1.28 g (10 mmol) of **7** and 3.52 g (30 mmol) of (2*S*,3*S*)-isoleucinol gave 2.08 g (63%) of **14b**. Colorless crystals, m.p. 119°C. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^1H NMR: δ = 0.87 [d, *J* = 6.8 Hz, 6H, $CH(CH_3)C_2H_5$], 0.96 (dd, *J* = 7.4, 7.4 Hz, 6H, CH_2CH_3), 1.20–1.30 [m, 2H, $CH(CH_3)C_2H_5$], 1.58–1.75 (m, 4H, CH_2CH_3), 4.15 (t, *J* = 7.7 Hz, 2H, OCH_2), 4.20–4.28 (m, 2H, CHN), 4.40 (dd, *J* = 7.7, 7.7 Hz, 2H, OCH_2), 7.99 (s, 4H, aromatic H). – ^{13}C NMR: δ = 11.34 (q), 14.09 (q), 25.97 (t), 39.00 (d), 69.70 (t, C-5'), 71.33 (d, C-4'), 128.29 (d), 130.52 (s, C-1, -4), 163.00 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 271 (100), 243 (8), 223 (11), 215 (4), 182 (10), 171 (4), 144 (14).

$C_{20}H_{28}N_2O_2$ (328.5)
Calcd. C 73.14 H 8.59 N 8.53
Found C 72.92 H 9.30 N 8.42

1,2-Bis[(4S)-4-isopropyl-2-oxazolin-2-yl]ethane (**15a**): 0.80 g (10 mmol) of **12** and 3.10 g (30 mmol) of (*S*)-valinol gave 1.49 g (59%) of **15a**. Colorless oil, b.p. 150°C/2 · 10^{-2} mbar. – IR (neat): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^1H NMR: δ = 0.87 [d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$], 0.95 [d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$], 1.74 [sept, *J* = 6.7 Hz, 2H, $CH(CH_3)_2$], 2.63 [s, 4H, $(CH_2)_2$], 3.84–3.98 (m, 4H, OCH_2), 4.22 (dd, *J* = 8.5, 8.5 Hz, 2H, CHN). – ^{13}C NMR: δ = 17.68 (q), 18.45 (q), 24.40 (t), 32.28 (d), 69.90 (t, C-5'), 71.92 (d, C-4'), 166.21 (s, C-2'). – MS (EI, 70 eV): *m/z* (%) = 209 (100), 140 (4), 123 (73), 96 (13), 69 (16), 55 (12), 41 (24).

$C_{14}H_{24}N_2O_2$ (252.4)
Calcd. C 66.63 H 9.59 N 11.10
Found C 66.71 H 9.78 N 11.05

1,3-Bis[(4S)-4-isopropyl-2-oxazolin-2-yl)propane (**16a**): 0.94 g (10 mmol) of **13** and 3.10 g (30 mmol) of (*S*)-valinol gave 1.12 g (42%) of **16a**. Colorless oil, b.p. 120°C/2 · 10^{-2} mbar. – IR (neat): $\tilde{\nu}$ = 1640 cm^{-1} (C=N). – ^1H NMR: δ = 0.88 [d, *J* = 6.7 Hz, 6H, $CHCH_3$], 0.95 (d, *J* = 6.7 Hz, $CHCH_3$), 1.74 [sept, *J* = 6.7 Hz, 2H, $CH(CH_3)_2$], 2.33–2.61 (m, 6H), 3.85–3.98 (m, 4H, OCH_2CHN), 4.18–4.26 (m, 2H, $NCHCH_2O$). – ^{13}C NMR: δ = 17.77 (q), 18.37 (q), 21.66 (t), 26.21 (t), 32.27 (d), 69.87 (t), 71.94 (d), 165.53 (s). – MS (EI, 70 eV): *m/z* (%) = 266 (0.3) [M^+], 223 (75), 140 (100), 137 (71), 127 (34), 96 (19), 84 (18), 69 (13), 41 (32).

$C_{15}H_{26}N_2O_2$ (266.4)
Calcd. C 67.63 H 9.84 N 10.52
Found C 67.39 H 9.78 N 10.41

(4S)-4-Isopropyl-2-(2-pyridinyl)-2-oxazoline (**18a**)[4b]: 1.04 g (10 mmol) of **20** and 1.55 g (15 mmol) of (*S*)-valinol gave 1.61 g (84%) of **18a**. Colorless crystals, m.p. 52°C. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^1H NMR: δ = 0.97 (d, *J* = 6.8 Hz, 3H, CH_3), 1.08 (d, *J* = 6.8 Hz, 3H, CH_3), 1.87–1.96 (m, 1H, CH), 4.15–4.27 (m, 2H, OCH_2), 4.48–4.56 (m, 1H, NCH), 7.38–7.42 (m, 1H, py-5-H), 7.76–7.82 (m, 1H, py-4-H), 8.07–8.10 (m, 1H, py-3-H), 8.73 (dd,

J = 4.8, 0.9 Hz, 1H, py-6-H). – ^{13}C NMR: δ = 17.89 (q), 18.74 (q), 32.51 (d), 70.63 (t), 72.87 (d), 123.98 (d), 125.51 (d), 136.68 (d), 147.10 (s), 149.89 (d), 162.76 (s). – MS (EI, 70 eV): m/z (%) = 190 (1) [M^+], 147 (100), 146 (16), 119 (17), 105 (11), 92 (39), 78 (26).

$C_{11}H_{14}N_2O$ (190.25)
Calcd. C 69.45 H 7.42 N 14.73
Found C 69.08 H 7.66 N 14.80

(4S)-4-[(1S)-1-Methylpropyl]-2-(2-pyridinyl)-2-oxazoline (**18b**)[4b]: 1.04 g (10 mmol) of **20** and 1.76 g (15 mmol) of (2*S*,3*S*)-isoleucinol gave 1.70 g (83%) of **18b**. Colorless oil. – IR (neat): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^{1}H NMR: δ = 0.91 (d, J = 6.7 Hz, 3H, CHCH_3), 0.98 (t, J = 7.4 Hz, 3H, CH_2CH_3), 1.21–1.36 [m, 1H, CH(CH$_3$)C$_2$H$_5$], 1.63–1.81 (m, 2H, CH_2CH$_3$), 4.21–4.35 (m, 2H, OCH$_2$), 4.49–4.54 (m, 1H, NCH), 7.38–7.42 (m, 1H, py-5-H), 7.76–7.82 (m, 1H, py-4-H), 8.07–8.10 (m, 1H, py-3-H), 8.73 (d, J = 4.8 Hz, 1H, py-6-H). – ^{13}C NMR: δ = 11.03 (q), 13.88 (q), 25.68 (t), 38.63 (d), 69.97 (t), 71.20 (d), 123.80 (d), 125.34 (d), 136.52 (d), 146.88 (s), 149.68 (d), 162.53 (s). – MS (EI, 70 eV): m/z (%) = 204 (1) [M^+], 148 (16), 147 (100), 119 (19), 105 (12), 98 (5), 92 (37), 84 (13), 78 (31).

$C_{12}H_{16}N_2O$ (204.3)
Calcd. C 70.56 H 7.89 N 13.71
Found C 70.39 H 8.11 N 13.80

(4S,5R)-4-Methyl-5-phenyl-2-(2-pyridinyl)oxazoline (**18c**)[4b]: 1.04 g (10 mmol) of **20** and 2.27 g (15 mmol) of (1*R*,2*S*)-norephedrine gave 1.78 g (75%) of **18c**. Colorless crystals, m.p. 126°C. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^{1}H NMR: δ = 0.93 (d, J = 6.9 Hz, 3H, CHCH_3), 4.69–4.79 (m, 1H, NCH), 5.86 (d, J = 9.9 Hz, 1H, OCH), 7.27–7.38 (m, 5H, aromatic H), 7.40–7.45 (m, 1H, py-5-H), 7.79–7.84 (m, 1H, py-4-H), 8.10 (d, J = 7.8 Hz, 1H, py-3-H), 8.78 (d, J = 5.0 Hz, 1H, py-6-H). – ^{13}C NMR: δ = 17.35 (q), 65.61 (d), 84.67 (d), 123.91 (d), 125.69 (d), 126.28 (d), 127.96 (d), 128.33 (d), 136.79 (d), 146.81 (s), 150.17 (d), 162.37 (s). – MS (EI, 70 eV): m/z (%) = 238 (32) [M^+], 194 (3), 132 (100), 105 (25), 91 (4), 79 (74).

$C_{15}H_{14}N_2O$ (238.3)
Calcd. C 75.61 H 5.92 N 11.76
Found C 75.35 H 6.11 N 11.80

(4S)-2-(2-Hydroxyphenyl)-4-isopropyl-2-oxazoline (**19a**): 1.19 g (10 mmol) of **21** and 1.55 g (15 mmol) of (*S*)-valinol gave 1.60 g (78%) of **19a**. Colorless oil, b.p. 130°C/5 · 10^{-3} mbar. – IR (neat): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^{1}H NMR: δ = 0.94 (d, J = 6.7 Hz, 3H, CH$_3$), 1.01 (d, J = 6.7 Hz, 3H, CH$_3$), 1.80 [sept, J = 6.7 Hz, 1H, CH(CH$_3$)$_2$], 4.08–4.15 (m, 2H, OCH$_2$), 4.37–4.44 (m, 1H, NCH), 6.86 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 7.35–7.38 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 12.36 (s, 1H, OH). – ^{13}C NMR: δ = 18.31 (q), 18.42 (q), 32.81 (d), 69.77 (t), 71.45 (d), 110.78 (s), 116.78 (d), 118.63 (d), 128.11 (d), 133.39 (d), 160.23 (s), 165.34 (s). – MS (EI, 70 eV): m/z (%) = 205 (52) [M^+], 162 (100), 134 (36), 121 (11), 120 (13), 107 (28), 92 (10).

$C_{12}H_{15}NO_2$ (205.3)
Calcd. C 70.22 H 7.37 N 6.82
Found C 70.01 H 7.45 N 6.98

(4S,5R)-2-(2-Hydroxyphenyl)-4-methyl-5-phenyl-2-oxazoline (**19b**): 1.19 g (10 mmol) of **21** and 2.27 g (15 mmol) of (1*R*,2*S*)-norephedrine gave 2.01 g (79%) of **19b**. Colorless, air-sensitive crystals, m.p. 43°C. – IR (neat): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^{1}H NMR: δ = 0.88 (d, J = 7.0 Hz, 3H, CH$_3$), 4.66–4.76 (m, 1H, OCHCH$_3$), 5.76 (d, J = 9.6 Hz, 1H, NCHC$_6$H$_5$), 6.91 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.2 Hz, 1H), 7.24–7.26 (m, 2H), 7.33–7.44 (m, 5H, aromatic H), 7.78 (dd, 1H), 12.19 (s, 1H, OH). – ^{13}C NMR: δ = 17.63 (q), 64.27 (d), 83.28 (d), 110.68 (s), 116.91 (d), 118.84 (d), 126.34 (d), 128.31 (d), 128.57 (d), 133.62 (d), 136.42 (s), 160.30 (s), 164.89 (s). – MS (EI, 70 eV): m/z (%) = 253 (86) [M^+], 162 (40), 148 (29), 133 (94), 121 (100), 105 (9), 91 (24).

$C_{16}H_{15}NO_2$ (253.3)
Calcd. C 75.87 H 5.97 N 5.53
Found C 75.86 H 6.20 N 5.81

Table 2. Optical rotations of bis- and monooxazolines[a]

No.	c	$[\alpha]^{25}_{589}$	$[\alpha]^{25}_{578}$	$[\alpha]^{25}_{546}$	$[\alpha]^{25}_{436}$	$[\alpha]^{25}_{365}$
1a	2.13	- 98.8	-103.5	-119.4	-225.6	- 415.2
1b	2.21	- 88.4	- 92.5	-106.8	-201.9	- 371.7
1c	2.80	-119.6	-125.2	-145.3	-287.6	---
1d	1.09	- 57.8	- 60.0	- 69.4	-130.2	---
2a	2.67	- 91.3	- 95.6	-111.0	-216.6	- 408.1
2b	2.21	- 62.9	- 66.0	- 76.7	-148.9	- 282.5
14a	1.62	- 97.7	-102.0	-118.1	-238.1	---
14b	3.24	- 65.7	- 68.8	- 79.6	-158.4	---
15a	2.28	- 93.6	- 97.8	-112.1	-200.7	- 335.5
16a	3.05	- 57.4	- 59.7	- 68.4	-122.2	- 204.0
18a	5.18	-105.4	-110.5	-128.7	-257.5	- 523.6
18b	4.55	- 96.4	-101.2	-118.1	-236.9	- 479.5
18c	2.04	-376.0	-393.6	-454.3	-856.9	-1566.2
19a	4.62	- 64.9	- 67.7	- 77.6	-135.4	- 188.5
19b	2.98	-354.0	-361.6	-408.0	-713.2	-1092.2

[a] **1, 2, 14, 15, 16** in dichloromethane, **18a,b, 19a** in toluene, **18c, 19b** in chloroform.

General Procedure for the Preparation of the $ZnCl_2$-Complexes: A solution of 1 mmol of 1,2-bis(2-oxazolin-2-yl)benzene in 5 ml of dry THF was added to a solution of 136 mg (1 mmol) of $ZnCl_2$ in 10 ml of dry THF. The resulting crystals were isolated by filtration. If no crystals were formed, the solvent was evaporated and the residue crystallized from ethanol.

{1,2-Bis[(4S)-4-isopropyl-2-oxazolin-2-yl]benzene}zinc(II) Chloride (**23a**): 0.30 g (1 mmol) of **1a** gave 0.42 g (98%) of **23a**. Colorless crystals, m.p. 202°C. – IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1} (C=N). – ^{1}H NMR (CD$_3$CN): δ = 0.84 [d, J = 6.9 Hz, 6H, CH(CH_3)$_2$], 0.95 [d, J = 7.1 Hz, 6H, CH(CH_3)$_2$], 2.52–2.62 [m, 2H, CH(CH$_3$)$_2$], 4.50–4.62 (m, 6H, OCH_2CHN), 7.77–7.81 (m, 2H, 4-, 5-H), 7.85–7.89 (m, 2H, 3-, 6-H). – ^{13}C NMR (CD$_3$CN): δ = 14.85 (q), 18.59 (q), 30.92 (d), 71.08 (d), 71.39 (t), 126.57 (s), 132.25 (d), 134.05 (d), 168.99 (s). – MS (FAB): m/z (%) = 837 (9) [M_2^+ – Cl], 399 (100), 357 (3), 301 (33).

$C_{18}H_{24}Cl_2N_2O_2Zn$ (436.7)
Calcd. C 49.51 H 5.54 N 6.42
Found C 49.36 H 5.73 N 6.17

⟨1,2-Bis{(4S)-4-[(1S)-1-methylpropyl]-2-oxazolin-2-yl}benzene⟩zinc(II) Chloride (**23b**): Colorless crystals, m.p. 196°C. – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (C=N). – ^{1}H NMR (CD$_3$CN): δ = 0.82 (d, J = 6.8 Hz, 6H, CHCH_3), 0.98 (t, J = 7.3 Hz, 6H, CH_2CH_3), 1.23–1.38 (m, 4H, CHCH_2CH$_3$), 2.37–2.45 [m, 2H, CH(CH$_3$)-CH$_2$], 4.57–4.70 (m, 6H, NCHCH_2O), 7.78–7.82 (m, 2H, 4-, 5-H), 7.86–7.91 (m, 2H, 3-, 6-H). – ^{13}C NMR (CD$_3$CN): δ = 12.1 (q), 12.2 (q), 26.6 (t), 37.4 (d), 69.8 (d), 70.6 (t), 126.2 (s), 131.8 (d), 133.6 (d), 168.3 (s). – MS (FAB): m/z (%) = 893 (5) [M_2^+ – Cl], 427 (100), 371 (4), 329 (53), 271 (3), 229 (11), 171 (5), 130 (13), 105 (3), 89 (6), 76 (8).

$C_{20}H_{28}Cl_2N_2O_2Zn$ (464.7)
Calcd. C 51.69 H 6.07 N 6.02
Found C 51.56 H 6.33 N 5.71

{1,2-Bis[(4S)-4-phenyl-2-oxazolin-2-yl]benzene}zinc(II) Chloride (**23c**): 0.37 g (1 mmol) of **1c** gave 0.44 g (87%) of **23c**. Colorless

crystals, m.p. 282°C. – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (C=N). – ^1H NMR (CD_3CN): δ = 4.60–4.65 (m, 2H, OCH_2), 4.87 (dd, J = 9.5, 9.5 Hz, 2H, OCH_2), 5.27–5.32 (m, 2H, NCH), 7.27–7.33 (m, 5H, aromatic H), 7.34–7.42 (m, 5H, aromatic H), 7.78–7.81 (m, 2H, 4-, 5-H), 7.94–7.98 (m, 2H, 3-, 6-H). – ^{13}C NMR (CD_3CN): δ = 70.2 (d), 78.7 (t), 127.0 (s), 128.4 (d), 130.0 (d), 130.3 (d), 132.6 (d), 134.4 (d), 141.5 (d), 170.1 (s). – MS (FAB): m/z (%) = 973 (1) [M_2^+ – Cl], 837 (1), 543 (18), 467 (100), 407 (18), 369 (79), 249 (20), 232 (9), 219 (5), 130 (30).

$C_{24}H_{20}Cl_2N_2O_2Zn$ (504.7)
Calcd. C 57.11 H 3.99 N 5.55
Found C 57.12 H 4.14 N 5.32

{1,2-Bis[(4S)-4-benzyl-2-oxazolin-2-yl)benzene}zinc(II) Chloride (**23d**): 0.40 g (1 mmol) of **1d** gave 0.36 g (68%) of **23d**. Pale yellow crystals, m.p. 109°C. – IR (KBr): $\tilde{\nu}$ = 1645 cm^{-1} (C=N). – ^1H NMR (CD_3CN): δ = 3.09 (dd, J = 13.7, 8.0 Hz, 2H, $CH_2C_6H_5$), 3.49 (dd, J = 13.7, 3.4 Hz, 2H, $CH_2C_6H_5$), 4.57–4.69 (m, 4H, OCH_2), 4.91–5.00 (m, 2H, CHN), 7.30–7.47 (m, 10H, $CH_2C_6H_5$), 7.65–7.68 (m, 2H, 4-, 5-H), 7.71–7.78 (m, 2H, 3-, 6-H). – ^{13}C NMR (CD_3CN): δ = 40.13 (t), 67.41 (d), 74.11 (t), 126.10 (s), 128.39 (d), 130.05 (d), 131.19 (d), 132.49 (d), 134.11 (d), 137.46 (d), 168.95 (s). – MS (FAB): m/z (%) = 495 (31), 477 (9), 415 (9), 397 (7), 172 (7), 148 (10), 130 (19), 117 (47), 91 (97), 55 (100). – No correct C,H,N analysis could be obtained.

[1,2-Bis(4,4-dimethyl-2-oxazolin-2-yl)benzene]zinc(II) Chloride (**23e**): 0.27 g (1 mmol) of **1e** gave 0.40 g (98%) of **23e**. Colorless crystals, m.p. 310°C. – IR (KBr): $\tilde{\nu}$ = 1650 cm^{-1} (C=N). – ^1H NMR (CD_3CN): δ = 1.62 [s, 12H, $NC(CH_3)_2$], 4.40 (s, 4H, OCH_2), 7.75–7.79 (m, 2H, 4-, 5-H), 7.87–7.92 (m, 2H, 3-, 6-H). – ^{13}C NMR (CD_3CN): δ = 27.81 (q), 70.79 (t), 81.88 (s), 127.18 (s), 132.40 (d), 133.71 (d), 167.72 (s). – MS (FAB): m/z (%) = 781 (4), [M_2^+ – Cl], 371 (100), 357 (3), 299 (3), 273 (10), 227 (12), 201 (9), 130 (12).

$C_{16}H_{20}Cl_2N_2O_2Zn$ (408.6)
Calcd. C 47.03 H 4.93 N 6.86
Found C 47.26 H 5.11 N 6.70

Table 3. Crystal structure determination data for the compound **23a**

Formula $C_{18}H_{24}Cl_2N_2O_2Zn$, M_r = 436.71
a = 11.929(2), b = 12.007(2), c = 14.578(4) Å; V = 2088.1(8) $Å^3$
Z = 4, $Q_{calc.}$ = 1.389 g · cm^{-3}, orthorhombic system, space group $P2_12_12_1$ (No. 19)
$\mu(Mo\text{-}K_\alpha)$ = 13.75 cm^{-1}, graphite monochromator, T = 20°C, $(\sin\Theta/\lambda)_{max}$ = 28, hkl range
2314 unique reflections, 1945 observed reflections [$F_o > 2\sigma(F_o)$], 239 refined parameters, R = 0.069; R_w = 0.071

Table 4. Selected interatomic distances [Å], angles [°], and torsion angles [°] with standard deviation in units of the last significant figure in parentheses for compound **23a**

Zn - Cl1	2.217(3)	Zn - Cl2	2.216(3)
Zn - N1	2.046(8)	Zn - N2	2.049(7)
Cl1 - Zn - Cl2	120.4(1)	Cl1 - Zn - N1	108.4(2)
Cl1 - Zn - N2	109.0(2)	Cl2 - Zn - N1	114.0(2)
Cl2 - Zn - N2	110.0(2)	N1 - Zn - N2	91.0(3)
Zn - N1 - C1	127.3(6)	Zn - N1 - C3	123.9(6)
Zn - N2 - C10	127.1(7)	Zn - N2 - C12	124.4(6)
Cl1 - Zn - N1 - C3	-53.76	Cl1 - Zn - N2 - C10	61.78
Cl2 - Zn - N1 - C3	169.14	Cl2 - Zn - N2 - C10	-164.17
N1 - C3 - C4 - C9	-46.51	C4 - C9 - C10 - N2	46.64

Crystal Structure Determination[20]: A summary of the data collection and structure refinement parameters are given in Table 3. Selected interatomic distances, angles, and torsion angles are presented in Table 4. Table 5 contains the fractional atomic coordinates for complex **23a**.

Table 5. Fractional atomic coordinates for complex **23a**

Atom	x/a	y/b	z/c	B_{eq}[a]
ZN	0.2374 (1)	-0.1717 (1)	0.5780 (1)	3.49
CL1	0.2641 (3)	-0.1756 (2)	0.4276 (2)	5.44
CL2	0.2635 (3)	-0.3237 (2)	0.6616 (2)	6.15
O1	-0.0416 (5)	0.0395 (6)	0.5902 (5)	4.56
O2	0.3757 (6)	0.1320 (5)	0.6651 (5)	3.86
N1	0.0893 (6)	-0.0918 (7)	0.6039 (5)	3.33
N2	0.3263 (6)	-0.0415 (6)	0.6326 (5)	2.83
C1	-0.0093 (8)	-0.1353 (9)	0.6579 (8)	4.57
C2	-0.1018 (9)	-0.0554(11)	0.6284(10)	5.70
C3	0.0655 (7)	0.0046 (7)	0.5740 (7)	3.08
C4	0.1334 (7)	0.0842 (7)	0.5212 (6)	2.90
C5	0.0803 (9)	0.1419 (8)	0.4526 (6)	3.58
C6	0.1340(11)	0.2245 (9)	0.4030 (7)	4.38
C7	0.2470 (9)	0.2503 (8)	0.4227 (7)	4.71
C8	0.2983 (9)	0.1963 (8)	0.4927 (7)	3.93
C9	0.2450 (8)	0.1124 (7)	0.5428 (6)	3.18
C10	0.3137 (7)	0.0607 (8)	0.6153 (6)	3.14
C11	0.4335 (9)	0.0666 (9)	0.7332 (7)	4.32
C12	0.4172 (7)	-0.0535 (8)	0.7017 (7)	3.36
C13	0.5188 (8)	-0.1095 (9)	0.6571 (6)	3.46
C14	0.5612(10)	-0.0481(11)	0.5721 (8)	5.29
C15	0.6148 (9)	-0.1191 (9)	0.7297 (9)	4.77
C16	0.0183 (9)	-0.1382 (9)	0.7587 (8)	4.41
C17	0.0526(15)	-0.0255(14)	0.7971 (9)	7.51
C18	-0.0786(12)	-0.1943(14)	0.8117(10)	7.39

[a] $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

NMR Experiments: In a NMR tube 20 mg (0.046 mmol) of **1a** was dissolved in 0.75 ml of [D_3]acetonitrile. A ^1H-NMR spectrum was recorded. The sample was added to the appropriate amount of solid zinc dichloride, which had been dried by melting under high vacuum and cooling under argon. A clear solution resulted from which ^1H-NMR spectra were recorded after each addition of zinc dichloride (Figure 2).

CAS Registry Numbers

1a: 131380-80-8 / **1b**: 131380-81-9 / **1c**: 131380-82-0 / **1d**: 131380-83-1 / **1e**: 131380-84-2 / **2a**: 131380-85-3 / **2b**: 131380-86-4 / **5**: 91-15-6 / **6**: 626-17-5 / **7**: 623-26-7 / **8**: 2026-48-4 / **9**: 24629-25-2 / **10**: 20989-17-7 / **11**: 3182-95-4 / **12**: 110-61-2 / **13**: 544-13-8 / **14a**: 131380-87-5 / **14b**: 131380-88-6 / **15a**: 131380-89-7 / **16a**: 131380-90-0 / **17**: 124-68-5 / **18a**: 108915-04-4 / **18b**: 108915-03-3 / **18c**: 108915-10-2 / **19a**: 131380-91-1 / **19b**: 131380-92-2 / **20**: 100-70-9 / **21**: 611-20-1 / **22**: 492-41-1 / **23a**: 131380-93-3 / **23b**: 131406-58-1 / **23c**: 131380-94-4 / **23d**: 131380-95-5 / **23e**: 131380-96-6

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