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Novel Chiral Oxazoline Ligands for Potential Charge-Transfer Effects in the Rh(I)-Catalysed Enantioselective Hydrosilylation☆

Henri Brunner*[a], Reinhard Störiko[a], and Frank Rominger[b]

Institut für Anorganische Chemie der Universität Regensburg[a],
D-93040 Regensburg, Germany
Fax: (internat.) +49 (0)941 9434439

Organisch-Chemisches Institut der Universität Heidelberg[b],
D-69120 Heidelberg, Germany
E-mail: henri.brunner@chemie.uni-regensburg.de

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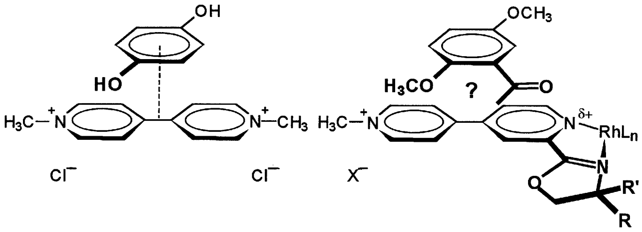
Novel 2-(4,4′-bipyridin-2-yl)oxazolines, bearing a chiral oxazoline moiety, were synthesised starting from 4,4′-bipyridine and selectively monomethylated in the *N*′-position. After coordination to rhodium these electron-poor ligands are supposed to exhibit charge-transfer effects with electron-donating substrates in the Rh(I)-catalysed enantioselective hydrosilylation (see next publication). Similar effects were expected from 4,4′-bipyridine- and pyrazine-bisoxazolines after complexation with rhodium. For comparison 2-(4-phenylpyridin-2-yl)oxazoline ligands were synthesised. Rh(I)-complexes of selected ligands were prepared and characterised, including an X-ray structure analysis.

Introduction

A well-known example in asymmetric catalysis is the Rh(I)-catalysed enantioselective hydrosilylation of prochiral ketones, which after hydrolysis gives chiral secondary alcohols[2][3][4]. Asymmetric induction is brought about by *in situ* Rh(I)-catalysts consisting of $[Rh(cod)Cl]_2$ and preferably nitrogen ligands[5][6][7]. In particular, ligands containing chiral oxazolines proved to be effective[8][9][10][11].

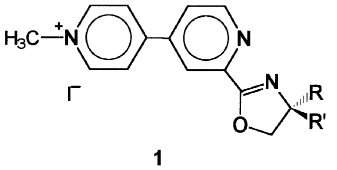
Our point of interest was a possible pre-orientation of the substrate to be hydrosilylated with respect to the catalytic centre. Such a pre-orientation of the metal bound prochiral ketone might result in a higher enantiodiscrimination. We propose charge-transfer interactions for this pre-orientation. Charge-transfer interactions usually appear in systems consisting of electron-donating and electron-accepting compounds[12][13][14][15]. In addition to the isolation of stable charge-transfer complexes, e.g. the paraquat-hydroquinone adduct[16][17] (Scheme 1), charge-transfer interactions were used as a template effect for ring closure reactions[18].

Scheme 1



We tried to introduce charge-transfer interactions in the Rh(I)-catalysed hydrosilylation using the electron-rich 2,5-dimethoxyacetophenone as the substrate. The acceptor had to be a chiral ligand whose electron-accepting properties should be amplified by coordination to Rh(I). *N*′-Methylated 2-(4,4′-bipyridin-2-yl)oxazolines **1**, which resemble paraquat after coordination to Rh, promised to be a suitable system (Scheme 1). The ligands of type **1** contain the same chelating unit as the ligands of type **2**, which were among the first successful chiral nitrogen ligands in enantioselective catalysis[11][19]. Since the formation of oxazoline rings is straightforward and the necessary enantiopure amino alcohols are accessible by reduction of amino acids, chirality should be easily introduced into 4,4′-bipyridine-oxazolines, provided a synthesis of the 2-cyano precursor is found. Another task is the selective methylation of the *N*′-position, which is necessary to increase the electron accepting properties of the 4,4′-bipyridine system.

Scheme 2



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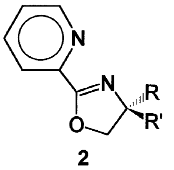

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[◇] Part 116: See ref.[1].

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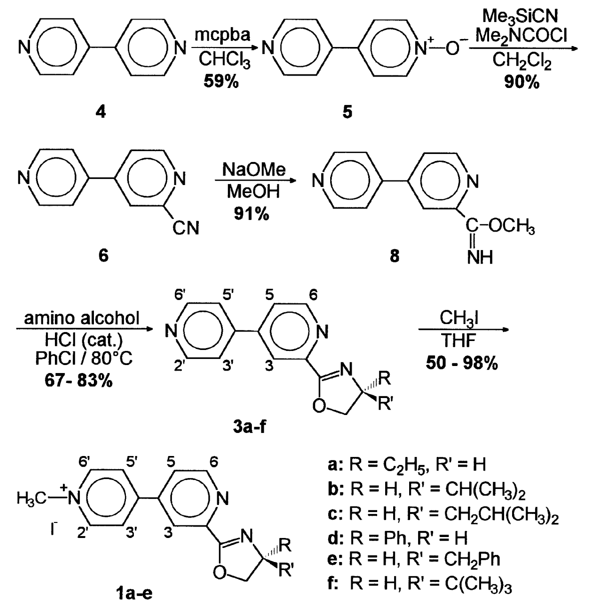
In this paper we describe the synthesis and characterisation of 2-(4,4′-bipyridin-2-yl)oxazolines and their *N*′-methylated derivatives, 2-(4-phenylpyridin-2-yl)oxazolines, 4,4′-bipyridine- and pyrazine-bisoxazolines as well as some Rh(I)-complexes[20]. The next paper reports on the catalytic results.

The 2-(4,4′-Bipyridin-2-yl)oxazolines 3a-f

Six novel 2-(4,4′-bipyridin-2-yl)oxazolines **3a-f** were prepared from 4,4′-bipyridine via the four-step synthesis shown in Scheme 3.

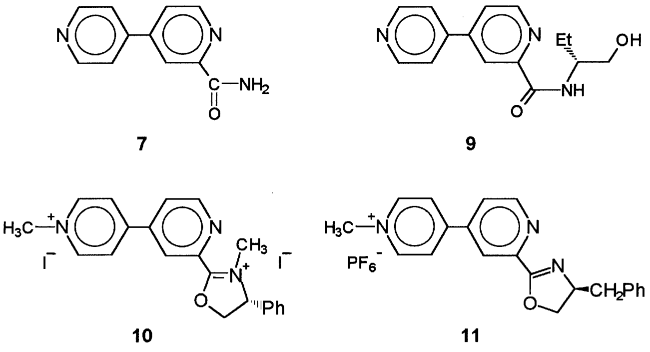
Scheme 3



In a variation of known procedures[21][22][23], 4,4′-bipyridine (**4**) was oxidised to the *N*-oxide **5** with *m*-chloroperbenzoic acid (mcpba) in $CHCl_3$. Chromatography on SiO_2 using an acetone/methanol gradient was necessary to separate the desired **5** from unreacted 4,4′-bipyridine and 4,4′-bipyridine *N*,*N*′-dioxide. α-Cyanation of the *N*-oxide **5** with trimethylsilyl cyanide and dimethylcarbamoyl chloride in CH_2Cl_2[24] yielded the nitrile **6** in 90% (Scheme 3) which had been only prepared as *N*,*N*′-bisquarternised salts[25]. A small amount of a side-product was obtained, characterised as the previously unknown 4,4′-bipyridine-2-carboxamide **7** (Scheme 4), probably resulting from partially hydrolysed **6**. Conversion of **6** into the carboximidate **8** (91% yield) was accomplished by stirring **6** for 2 d in dry methanol containing catalytic amounts of methanolate[26], according to Scheme 3. The resulting iminoether **8** was air-stable and could be stored for months if kept dry. The acid-catalysed condensation of **8** and enantiopure amino alcohols gave the corresponding oxazolines **3a-f** (Scheme 3). After flash chromatography and recrystallisation all six new ligands were obtained analytically pure in good yields (67−83%). By $^{13}C/^{1}H$ correlation experiments for **3c** all its protons and carbon atoms could be assigned. Comparison of their chemical shifts with those of the other ligands allowed almost complete assignment of their signals, too.

The oxazolines were unstable towards acids. Crude **3a** in chlorobenzene was almost completely transferred into the aqueous layer while shaking with 2 N HCl, thereby hydrolysing to the hydroxyalkylamide **9** (Scheme 4). After treatment of **9** with *p*-tosyl chloride and triethylamine in $CHCl_3$ according to ref.[27] the original oxazoline **3a** was restored.

Scheme 4



The *N*′-Methylated 2-(4,4′-Bipyridin-2-yl)oxazolines 1a−e and 11

The 2-(4,4′-bipyridin-2-yl)oxazolines **3a-e** were treated with excess methyl iodide in absolute THF at room temperature according to Scheme 3. A comparable selective *N*′′-methylation of 2,2′;4,4′′-terpyridine was reported by Persaud and Barbiero[28]. For **3e** nearly quantitative quarternisation of the *N*′-position occurred selectively and the product **1e** was isolated as an orange solid. The location of the methyl group was determined unequivocally by NMR spectroscopy. The AA′BB′ system of the Py′ ring in the ^{1}H NMR spectrum was shifted downfield compared to the non-methylated ligand **3e** and the CH_3 group showed a cross-peak with H-2′ and H-6′ in the NOESY spectrum. In the ^{13}C NMR spectrum the signals of C-2′ and C-6′ are broader than the other peaks due to the quadrupol momentum of the quarternised nitrogen.

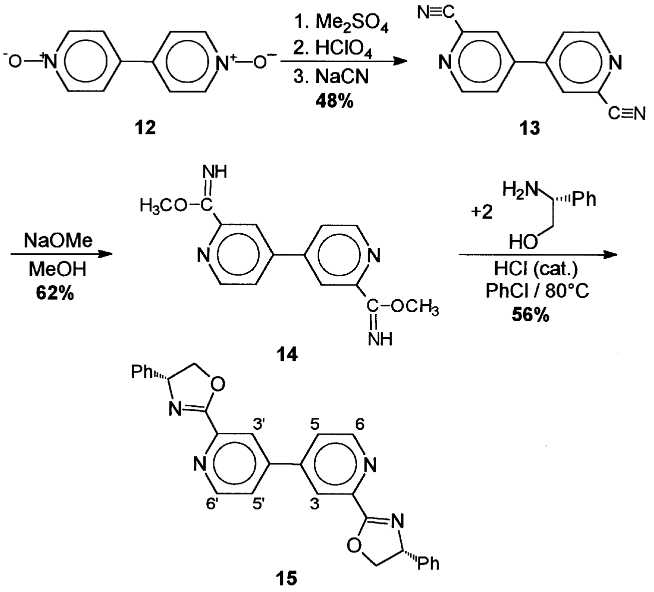
For **3a-d** the analogous reactions gave the corresponding *N*′-methylated ligands **1a-d** (Scheme 3) in satisfying yields (50−63%). Here, the formation of a red side-product was observed. It could be removed by fractional crystallisation from methanol/ether solutions at −20°C. For **3d** the side-product was recrystallised from aqueous acetone/methanol yielding dark red tetrahedra, which were characterised as the dimethylated compound **10** (Scheme 4). 2D NMR experiments (NOESY and $^{13}C/^{1}H$ correlations) showed that the second methyl group is attached to the oxazoline-nitrogen. The methylated ligands **1a-e** are orange solids, which are hygroscopic and have to be stored under dry nitrogen. Spectroscopic characterisation including a $^{13}C/^{1}H$ NMR correlation spectrum for **1c** allowed almost complete assignment of all carbon and hydrogen atoms.

By treating **1e** (dissolved in water) with saturated aqueous NH_4PF_6 the iodide was substituted by hexafluorophosphate to yield **11** in 88% (Scheme 4), which was sparingly soluble in methanol and could be recrystallised from boiling water.

The 2,2′-Bis(oxazolin-2-yl)-4,4′-bipyridine 15, the 2,5-Bis(oxazolin-2-yl)-3,6-dimethylpyrazine 19 and the 2-(4-Phenylpyridin-2-yl)oxazolines 23a,b

Since the *N*-oxidation of 4,4′-bipyridine **4** always yielded ca. 30% *N*,*N*′-dioxide **12**, the novel bisoxazoline **15** could be prepared via the dinitrile **13**[29] and the biscarboximidate **14**[30] (Scheme 5).

Scheme 5

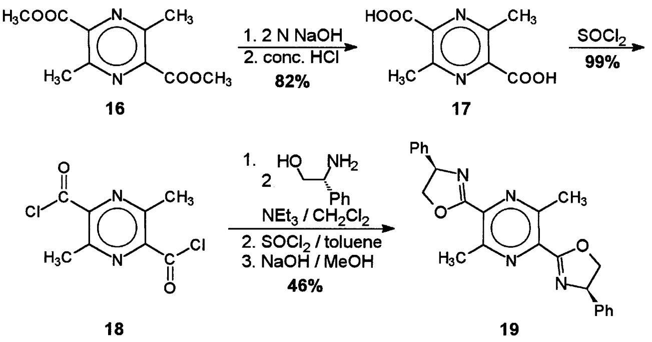


4,4′-Bipyridine *N*,*N*′-dioxide **12** as a single product was obtained in excellent yield (95%) by oxidation of 4,4′-bipyridine **4** with excess H_2O_2/urea adduct and phthalic anhydride in CH_2Cl_2 (80% yield were reported by using smaller amounts of oxidising agent[31]). Condensation of **14** with 2 equivalents of *(R)*-α-phenylglycinol yielded **15** as the first example of a chiral C_2-symmetrical 4,4′-bipyridine derivative, which is able to coordinate to two metal centres. The corresponding 2,2′-bipyridine-bisoxazoline was synthesised by Nishiyama et al.[32]. In the ^1H NMR spectra **15** and its mono-oxazoline counterpart **3d** display nearly identical chemical shifts for the oxazoline protons and the ABX system of the pyridine ring.

Since pyrazine is a "shortened" 4,4′-bipyridine, a Rh(I)-coordinated pyrazoline-bisoxazoline could also exhibit charge-transfer properties. Such a bisoxazoline was synthesised starting from dimethyl 3,6-dimethylpyrazine-2,5-dicarboxylate **16**[33]. After hydrolysis of **16** to **17**, the diacid chloride **18** was prepared using $SOCl_2$. Without isolation of intermediates the two oxazoline rings were condensed via a three-step reaction (Scheme 6). The pyrazine-bisoxazoline **19** was obtained in 46% yield.

For comparison two 2-(4-phenylpyridin-2-yl)oxazolines **23a,b** were synthesised from commercially available 4-phenylpyridine *N*-oxide **20** using the same reactions as for **3a-f** via the intermediates **21** and **22** (Scheme 7). **23a,b** differ from **3c** and **3e**, respectively, only in the nature of the 4-substituent (phenyl vs. 4′-pyridine). Thus, the spectroscopic data of **23a,b** are very similar to their 4,4′-bipyridine counterparts.

Scheme 6



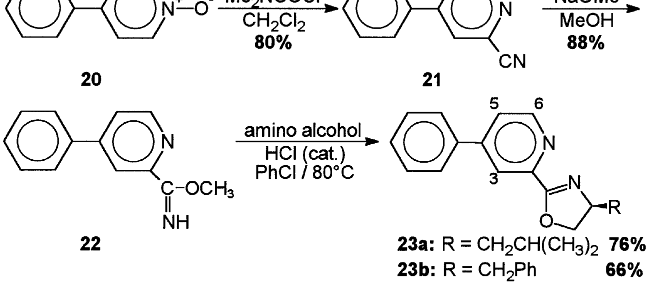
The Rh(I) Complexes 24−28

To ascertain that the 4,4′-bipyridine-oxazolines **3** prefer chelate coordination via pyridine- and oxazoline-*N* with regard to a monodentate coordination via *N*′, a series of Rh(I)-complexes was synthesised. All complexes were prepared by adding a solution of $[Rh(cod)Cl]_2$ in CH_2Cl_2 to the dissolved ligand. Exchange of chloride by PF_6^- (**24**, **25**) or BF_4^- (**26**) gave the corresponding red complexes in 82−92% yields (Scheme 8).

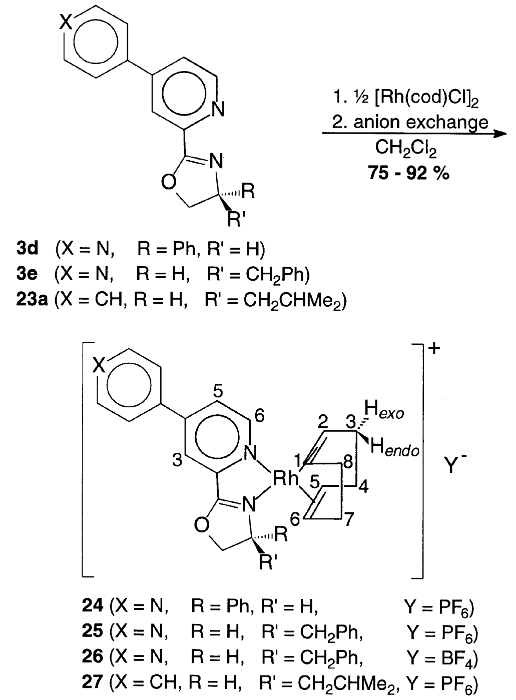
The ^1H NMR data (including COSY) proved the chelate coordination, because for **24** H-6 exhibited a strong downfield shift (0.87 ppm) compared to the free ligand **3d** due to the proximity of the rhodium. On the other hand H-2′/H-6′ did not shift at all. The [Rh(cod)**3e**]$^+$-complexes were synthesised with two different anions (**25** = PF_6^-, **26** = BF_4^-). Interestingly, both the ^1H and ^{13}C NMR spectra showed significant differences especially for the pyridine signals. All three pyridine protons H-3, H-5 and H-6 and the carbon atoms C-5 and C-6 of **26** were shifted downfield compared to **25**. The olefinic ^{13}C atoms of 1,5-cyclooctadiene coupled with ^{103}Rh giving rise to doublets ($^1J_{C,Rh}$ = 12.6−12.9 Hz) in both ^{13}C NMR spectra.

The Rh(I)-complex **27** (Scheme 8) derived from the oxazoline **23a** (75% yield) showed broad signals for all 1,5-cyclooctadiene carbons in the ^{13}C NMR spectrum, but long-range couplings between ^{103}Rh and ^{13}C atoms of the ligand were identified. The carboxylic and the methine carbons of the oxazoline ring gave rise to doublets ($^2J_{C,Rh}$ =

Scheme 7



Scheme 8



3d (X = N, R = Ph, R' = H)
3e (X = N, R = H, R' = CH$_2$Ph)
23a (X = CH, R = H, R' = CH$_2$CHMe$_2$)

24 (X = N, R = Ph, R' = H, Y = PF$_6$)
25 (X = N, R = H, R' = CH$_2$Ph, Y = PF$_6$)
26 (X = N, R = H, R' = CH$_2$Ph, Y = BF$_4$)
27 (X = CH, R = H, R' = CH$_2$CHMe$_2$, Y = PF$_6$)

1.4 Hz and 2.1 Hz, respectively). Similarly, the pyridine carbons C-6, C-5 and C-3 appeared as doublets ($^2J_{C,Rh}$ = 0.6 Hz and $^3J_{C,Rh}$ = 0.9 Hz). Analogous couplings were not found for **25** and **26**.

By slow diffusion of ether into a CHCl$_3$ solution of **27** red needles suitable for an X-ray structure analysis were obtained. There are two independent species in the unit cell (Figure 1).

Figure 1. Molecular structure of the two different species in the unit cell of **27**

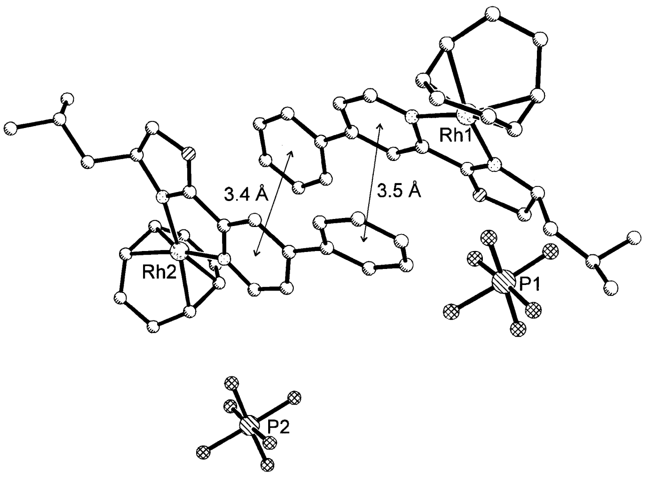
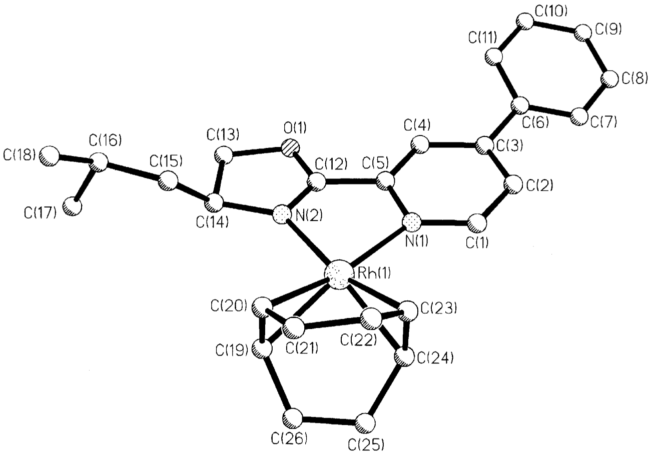


Figure 2. Molecular structure of one of the cations of **27**[a]



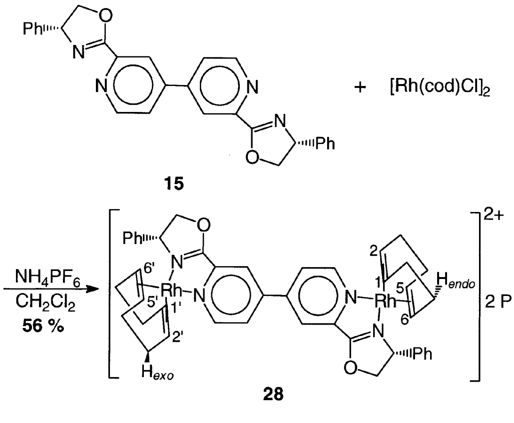
[a] Selected bond lengths [Å] and angles [°]: Rh1–N1 2.119, Rh1–N2 2.102, Rh1–(C23=C24)[b] 1.995, Rh1–(C19=C20)[b] 2.025, C23–C24 1.366, C19–C20 1.353, N2–C14 1.498, C14–C13 1.526, C13–O1 1.458, O1–C12 1.328 C12–C5 1.461, C12–N2 1.269; (C23=C24)-Rh1–(C19=C20)[b] 87.3, N1–Rh1–N2 79.4, Rh1–N1–C5 112.5, N1–C5–C12 113.8, C5–C12–N2 122.3, Rh1–N2–C12 111.8, N2–C12–O1 120.0, C12–O1–C13 104.7, O1–C13–C14 106.0, C13–C14–N2 102.2, C14–N2–C12 106.8, phenyl/pyridine (same cation) 20.7 and 27.1. – [b] C19=C20/C23=C24: statistical middle of the olefinic double bond.

Both cations differ to some extent in the arrangement of the cod-ligands. The most interesting feature is the orientation of the two aromatic rings of both complexes. Each phenyl ring is oriented in a plane above the pyridine ring of the other cation and vice versa (arrows in Figure 1). The angles phenyl plane versus pyridine plane of the other cation are very small (2.7° and 6.7°, respectively). With 3.4–3.5 Å the distances of the aromatic rings are similar to that between graphite layers (3.35 Å). This π-stacking is probably amplified by charge-transfer interactions between the electron-rich phenyl and the electron-accepting pyridine ring.

Figure 2 shows the molecular structure of one of the cations of **27**, establishing the expected square planar coordination of rhodium by the two nitrogen atoms of ligand **23a** and the two double bonds of 1,5-cyclooctadiene. The (*S*)-configuration of the chiral carbon atom in the oxazoline ring was unequivocally proven. Selected bond lengths and angles are summarised in Table 1. For further details and the CSD number see Experimental Section.

Reaction of bisoxazoline **15** with [Rh(cod)Cl]$_2$ (2 equivalents of Rh) yielded the dinuclear complex **28** in 56% yield

Scheme 9



15

28

(Scheme 9). The symmetry introduced by the bridging of **15** between two Rh(cod) units showed up in the ^{1}H NMR spectrum of **28**, the signals of which were somewhat broadened (no sharpening even at −80°C, 250 MHz, CD_2Cl_2).

We thank the *Fonds der Chemischen Industrie* for providing a *Kekulé* scholarship for R.S. and for financial support.

Experimental Section

General: Chromatography: Merck silica gel 60 (63−200 mesh). − Melting points (not corrected): Büchi SMP 20 (open capillaries). − Elemental analyses: Microanalytical Laboratory, University of Regensburg. − ^{1}H/^{13}C NMR: Bruker AW-80 (80 MHz, T = 31°C), AC-250 (250/62.9 MHz, T = 24°C) and ARX-400 (400/100.6 MHz, T = 21°C), TMS or the solvent itself as internal standard. For optimal resolution some spectra were altered after acquisition using Bruker WIN NMR 5.0/5.1 software. The protons H-2′/H-6′ and H-3′/H-5′ in all 4,4′-bipyridine derivatives form AA′BB′ spin systems and were assigned as centred multiplets (AA′BB′). The two diastereotopic protons of the oxazoline CH_2 group are differentiated as H_Z and H_E (*cis* and *trans*, respectively, with regard to the methine proton). The abbreviations *qC* in the ^{13}C NMR data represent quarternary carbon atoms. − MS: Finnigan MAT 95 (FAB and FD), Finnigan MAT 311 A (EI, 70 eV). High-resolution mass spectra were recorded at the Max-Planck-Institut für medizinische Forschung in Heidelberg: VG Analytic ZAB 2E/70SE (FAB) and Joel JMS-SX102A (EI, 70 eV); the abbreviation K^+ represents the cationic species of salt like compounds. − IR: Beckman IR 4240 (solids as KBr pellets, liquids as films between NaCl plates); only characteristic bands are listed. − Optical rotation: Perkin-Elmer Polarimeter 241 (0.1 or 0.2 dm cuvettes).

Materials: Commercially available reagents were used without further purification. All anhydrous solvents were stored under nitrogen.

Abbreviations: cod = η^4-1,5-cyclooctadiene, *m*-NBA = *m*-nitrobenzyl alcohol, Ox = oxazoline, PE = petroleum ether (b.p. 40−60°C), TFA = trifluoroacetic acid.

4,4′-Bipyridine N-Oxide Hemihydrate (**5**): To a stirred solution of 10.0 g (64.0 mmol) of 4,4′-bipyridine (**4**) in $CHCl_3$ (200 ml) was added during 6 h a solution of 57−86% mcpba (12.9 g, max. 64.0 mmol) in $CHCl_3$ (500 ml). After 3 d four portions of mcpba (2.0 g each) in $CHCl_3$ (150 ml each) were added every 24 h. Stirring at r. t. was continued for a total of 17 d. The solution was reduced to ca. 30 ml and the mixture was separated by column chromatography (SiO_2, 20 × 5 cm). Elution with acetone yielded unreacted **4** (R_f = 0.5 [methanol]) and *m*-chlorobenzoic acid. After removing the acid by extracting a $CHCl_3$ solution with 2 N NaOH, 1.05 g (6.7 mmol, 10.5%) of 4,4′-bipyridine were reisolated. With an acetone/methanol gradient (4:1 → 3:1) the desired product **5** (R_f = 0.31 [methanol]) was obtained. Recrystallisation from acetone afforded 6.07 g (33.5 mmol, 55%) of **5**. Cream-coloured crystals, mp. 170°C (ref.[21]: 180°C, ref.[22]: 174−176°C). − ^{1}H NMR (250 MHz, D_2O): δ = 7.50 (AA′BB′, 2 H, H-3′, H-5′), 7.70 (AA′BB′, 2 H, H-3, H-5), 8.20 (AA′BB′, 2 H, H-2, H-6), 8.42 (AA′BB′, 2 H, H-2′, H-6′). − MS (EI): *m*/*z* (%) = 172 (100) [M$^+$], 156 (38) [M$^+$ $^-$ O], 155 (18), 116 (16), 90 (14), 89 (15), 63 (14), 51(14). − IR (KBr): ṽ (cm^{-1}) = 1250/1225 s (NO). − $C_{10}H_8N_2O$ Γ 1/2 H_2O (181.20): calcd. C 66.29, H 5.01, N 15.46; found C 66.11, H 5.22, N 15.15. With pure methanol as liquid phase 4.41 g (19.7 mmol, 31%) of 4,4′-bipyridine *N*,*N*′-dioxide **12** as the dihydrate were eluted (R_f = 0.1 [methanol]).

4,4′-Bipyridine-2-carbonitrile (**6**): 6.0 g (33.1 mmol) of **5** were dissolved under nitrogen in dry CH_2Cl_2 (70 ml). After adding 4.8 ml (38.4 mmol) of trimethylsilyl cyanide the solution was stirred for 5 min and then treated with 3.1 ml (33.7 mmol) of dimethylcarbamoyl chloride. Stirring at r. t. was continued for 2 d. The solvent was evaporated and the yellow residue treated with 10% aqueous K_2CO_3 (70 ml). The solid was sucked off and dried. Recrystallisation from acetone yielded 5.4 g (29.8 mmol, 90%) of **6**. White solid, m.p. 238−240°C. − ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.93 (AA′BB′, 2 H, H-3′, H-5′), 8.21 (dd, ^3J = 5.2 Hz, ^4J = 1.9 Hz, 1 H, H-5), 8.57 (dd, ^4J = 1.9 Hz, ^5J = 0.9 Hz, 1 H, H-3), 8.78 (AA′BB′, 2 H, H-2′, H-6′), 8.90 (dd, ^3J = 5.2 Hz, ^5J = 0.9 Hz, 1 H, H-6). − ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 117.6 (*C*N), 121.6 (C-3′, C-5′), 125.4/126.8 (C-3 and C-5), 133.8 (C-2), 142.6 (C-4), 146.2 (C-4′), 150.9 (C-2′, C-6′), 152.3 (C-6). − MS (EI): *m*/*z* (%) = 181 (100) [M$^+$], 180 (21), 57 (21). − IR (KBr): ṽ (cm^{-1}) = 2240 w (C≡N). − $C_{11}H_7N_3$ (181.20): calcd. C 72.92, H 3.89, N 23.19; found C 72.84, H 4.15, N 22.87.

If the crude product was purified by flash chromatography (SiO_2, 15 × 4.5 cm) with PE/acetone (1:1) 300 mg (1.5 mmol, 4.5%) of a side-product (R_f = 0.31 [acetone]) were obtained. It crystallised from ether and was characterised as *4,4′-bipyridine-2-carboxamide* (**7**). Colourless needles, m.p. 176−178°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.00 (br s, 1 H, N*H*H′), 7.61 (AA′BB′, 2 H, H-3′, H-5′), 7.71 (dd, ^3J = 5.1 Hz, ^4J = 1.9 Hz, 1 H, H-5), 7.92 (br s, 1 H, NH*H*′), 8.50 (dd, ^4J = 1.9 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.71 (dd, ^3J = 5.1 Hz, ^5J = 0.8 Hz, 1 H, H-6), 8.78 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 120.3 (C-3 or C-5), 121.4 (C-3′, C-5′), 123.9 (C-5 or C-3), 144.7/147.2 (qC), 149.2 (C-6), 150.7 (qC), 150.8 (C-2′, C-6′), 166.3 (*C*=O). − MS (EI): *m*/*z* (%) = 199 (53) [M$^+$], calcd. for $C_{11}H_9N_3O$ 199.07456, found 199.07442, diff. −0.14 mmu/0.7 ppm, 157 (12), 156 (100) [M$^+$ − HNCO], 155 (41) [M$^+$ − CONH$_2$], 129 (16), 128 (14), 102 (11), 101 (11). − IR (KBr): ṽ (cm^{-1}) = 3415/3380/3290/3200 m (NH), 1795/1775/1690 s (C=O).

Methyl 4,4′-Bipyridine-2-carboximidate (**8**): 50 mg (2.2 mmol) of sodium were dissolved in dry methanol (35 ml) under nitrogen. Then 1.63 g (9.0 mmol) of **6** were added and allowed to react for 2 d at r. t. The suspension became finally a clear solution. After adding 0.1 ml (1.6 mmol) of acetic acid the solvent was evaporated. The residue was treated with warm ether (ca. 400 ml). Insoluble inorganic salts were removed by hot filtration. Cooling of the filtrate to −20°C afforded 1.74 g (8.2 mmol, 91%) of white crystals, m.p. 134−136°C. **8** is easily hydrolysed but can be stored for months if kept dry. − ^{1}H NMR (250 MHz, C_6D_6): δ = 3.94 (s, 3 H, C*H*$_3$), 6.76 (dd, ^3J = 5.1 Hz, ^4J = 1.9 Hz, 1 H, H-5), 6.78 (AA′BB′, 2 H, H-3′, H-5′), 7.86 (dd, ^4J = 1.9 Hz, ^5J = 0.9 Hz, 1 H, H-3), 8.33 (dd, ^3J = 5.1 Hz, ^5J = 0.9 Hz, 1 H, H-6), 8.53 (AA′BB′, 2 H, H-2′, H-6′), 9.98 (br s, 1 H, N*H*). − ^{13}C NMR (62.9 MHz, C_6D_6): δ = 53.7 (*C*H$_3$), 118.8 (C-3), 121.2 (C-3′, C-5′), 122.6 (C-5), 144.6/147.1/149.1 (qC), 150.1 (C-6), 151.1 (C-2′, C-6′), 166.2 (*C*=N). − MS (EI): *m*/*z* (%) = 213 (87) [M$^+$], 183 (15), 182 (83) [M$^+$ $^-$ OCH$_3$], 170 (17) [M$^+$ − CH$_3$ − CO], 157 (10), 156 (100) [M$^+$ − OCH$_3$ − CN], 155 (39) [M$^+$ $^-$ OCH$_3$ − HCN], 101 (13), 51 (11). − IR (KBr): ṽ (cm^{-1}) = 3310 w (NH), 1655 s (C=N), 1370 vs (CO). − $C_{12}H_{11}N_3O$ (213.24): calcd. C 67.59, H 5.67, N 19.71; found C 67.44, H 5.48, N 19.32.

General Procedure I (Preparation of Oxazolines): To a solution of **8** (2.3 g, 10.8 mmol) and 10.8 mmol of the amino alcohol in dry chlorobenzene (20 ml) one drop of conc. HCl was added and the solution was stirred at 80°C with a gentle stream of nitrogen bubbling through. After 47−68 h the cooled solution was directly purified by flash chromatography.

(+)-2-[4-(R)-Ethyloxazolin-2-yl]-4,4′-bipyridine (**3a**): Amino alcohol: 2-*(R)*-aminobutan-1-ol. 14 × 3.5 cm SiO$_2$ with PE/acetone (1:1) as eluent (R_f = 0.32 [acetone]). Recrystallisation from ether/PE yielded 1.83 g (7.2 mmol, 67%) of colourless crystals, m.p. 73–76°C. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.05 (t, ^3J = 7.4 Hz, 3 H, C*H*$_3$), 1.69 ("oct", ^3J ≈ 7.0 Hz, 1 H, C*H*$_A$H$_B$CH$_3$), 1.84 (m, 1 H, CH$_A$*H*$_B$CH$_3$), 4.18 ("t", ^2J = ^3J = 8.1 Hz, 1 H, Ox-C*H*$_Z$H$_E$), 4.35 (m, 1 H, Ox-C*H*), 4.62 (dd, ^2J = 8.1 Hz, ^3J = 9.3 Hz, 1 H, Ox-CH$_Z$*H*$_E$), 7.60 (AA′BB′, 2 H, *H-3′, H-5′*), 7.64 (dd, ^3J = 5.1 Hz, ^4J = 1.8 Hz, 1 H, H-5), 8.32 (d, ^4J = 1.8 Hz, 1 H, H-3), 8.76 (AA′BB′, 2 H, H-2′, H-6′), 8.82 (d, ^3J = 5.1 Hz, 1 H, *H-6*). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 10.0 (*C*H$_3$), 28.5 (*C*H$_2$CH$_3$), 68.4 (Ox-*C*H), 72.9 (Ox-*C*H$_2$), 121.4 (C-3′, C-5′), 121.6 (C-3), 122.9 (C-5), 144.8/146.4/148.0 (qC), 150.5 (*C*-6), 150.8 (C-2′, C-6′), 162.4 (*C*=N). – MS (EI): *m/z* (%) = 253 (11) [M$^+$], 225 (28), 224 (100) [M$^+$ – C$_2$H$_5$], 208 (13), 196 (20), 182 (13), 169 (25), 155 (26). – IR (KBr): ṽ (cm^{-1}) = 3030 w, 2965/2930 m, 2870/2860 w (CH), 1640 s (C=N). – C$_{15}$H$_{15}$N$_3$O (253.30): calcd. C 71.13, H 5.97, N 16.59; found C 70.76, H 6.06, N 16.40. – Optical rotation (c = 1.27, CHCl$_3$): $[\alpha]^{21}_{D}$ = +36, $[\alpha]^{21}_{578}$ = +38, $[\alpha]^{21}_{546}$ = +45, $[\alpha]^{21}_{436}$ = +94, $[\alpha]^{21}_{365}$ = +197.

(–)-2-[4-(S)-Isopropyloxazolin-2-yl]-4,4′-bipyridine (**3b**): Amino alcohol: *(S)*-valinol. 12 × 3.5 cm SiO$_2$ with acetone as eluent (R_f = 0.32). Recrystallisation from ether/PE yielded a light yellow solid (70%), m.p. 76–78°C. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.98 (d, ^3J = 6.7 Hz, 3 H, C*H*$_3$), 1.08 (d, ^3J = 6.7 Hz, 3 H, C*H*$_3$′), 1.93 ("sept", ^3J ≈ 6.7 Hz, 1 H, C*H*Me$_2$), 4.16–4.30 (m, 2 H, Ox-C*H*$_Z$H$_E$ and Ox-C*H*?), 4.56 (m, 1 H, Ox-CH$_Z$*H*$_E$?), 7.60 (AA′BB′, 2 H, H-3′, H-5′), 7.64 (dd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, 1 H, H-5), 8.33 (d, ^4J = 1.7 Hz, 1 H, *H-3*), 8.76 (AA′BB′, 2 H, H-2′, H-6′), 8.82 (d, ^3J = 5.1 Hz, 1 H, H-6). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 18.2 (*C*H$_3$), 19.0 (*C*H$_3$′), 32.8 (*C*HMe$_2$), 70.9 (Ox-*C*H$_2$), 73.2 (Ox-*C*H), 121.4 (C-3′, C-5′), 121.7 (C-3), 123.0 (C-5), 144.9/146.4/148.1 (qC), 150.6 (C-6), 150.8 (C-2′, C-6′), 162.4 (*C*=N). – MS (EI): *m/z* (%) = 267 (7) [M$^+$], 225 (21), 224 (100) [M$^+$-C$_3$H$_7$], 223 (23), 196 (17), 169 (21), 156 (11), 155 (22), 43 (10) [C$_3$H$_7^+$]. – IR (KBr): ṽ (cm^{-1}) = 3040 w, 2980 m, 2960 s, 2930/2910/2870 m (CH), 1645 s (C=N). – C$_{16}$H$_{17}$N$_3$O (267.33): calcd. C 71.89, H 6.41, N 15.72; found C 71.78, H 6.63, N 15.55. – Optical rotation (c = 1.24, CHCl$_3$): $[\alpha]^{20}_{D}$ = –29, $[\alpha]^{20}_{578}$ = –30, $[\alpha]^{20}_{546}$ = –34, $[\alpha]^{20}_{436}$ = –73, $[\alpha]^{20}_{365}$ = –155.

(–)-2-[4-(S)-(2-Methylpropyl)oxazolin-2-yl]-4,4′-bipyridine (**3c**): Amino alcohol: *(S)*-leucinol. Flash chromatography on SiO$_2$ (15 × 3.5 cm) with PE/acetone (1:1) as eluent (R_f = 0.32 [acetone]) yielded a yellow oil (73%), which neither crystallised nor could be distilled without decomposition. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.99 (d, ^3J ≈ 6.0 Hz, 3 H, C*H*$_3$), 1.01 (d, ^3J = 6.5 Hz, 3 H, C*H*$_3$′), 1.44 ("dt", ^2J = 13.3 Hz, ^3J ≈ 7.1 Hz, 1 H, C*H*$_A$H$_B$CHMe$_2$), 1.78 ("dt", ^2J = 13.3 Hz, ^3J ≈ 6.6 Hz, 1 H, CH$_A$*H*$_B$CHMe$_2$), 1.90 ("sept", ^3J ≈ 6.6 Hz, 1 H, C*H*Me$_2$), 4.12 ("t", ^2J = ^3J = 8.1 Hz, 1 H, Ox-C*H*$_Z$H$_E$), 4.44 (m, 1 H, Ox-C*H*), 4.65 (dd, ^2J = 8.1 Hz, ^3J = 9.4 Hz, 1 H, Ox-CH$_Z$*H*$_E$), 7.60 (AA′BB′, 2 H, H-3′, H-5′), 7.65 (dd, ^3J = 5.2 Hz, ^4J = 1.7 Hz, 1 H, H-5), 8.32 (d, ^4J = 1.7 Hz, 1 H, H-3), 8.76 (AA′BB′, 2 H, H-2′, H-6′), 8.82 (d, ^3J = 5.2 Hz, 1 H, H-6). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 22.69 (*C*H$_3$), 22.71 (*C*H$_3$′), 25.4 (*C*HMe$_2$), 45.5 (*C*H$_2$CHMe$_2$), 65.6 (Ox-*C*H), 73.8 (Ox-*C*H$_2$), 121.4 (C-3′, C-5′), 121.6 (C-3), 122.9 (C-5), 144.8/146.4/148.1 (qC), 150.5 (C-6), 150.7 (C-2′, C-6′), 162.2 (*C*=N). – MS (EI): *m/z* (%) = 281 (35) [M$^+$], 238 (24) [M$^+$ – C$_3$H$_7$], 225 (27), 224 (79) [M$^+$ – C$_4$H$_9$], 196 (26), 183 (21), 182 (33), 181 (46), 180 (60), 170 (36), 169 (25), 165 (45), 156 (54), 155 (62), 98 (26), 84 (68), 71 (28), 57 (100) [C$_4$H$_9^+$], 56 (22), 55 (26), 43 (45), 42 (30), 41 (57). – IR (film): ṽ (cm^{-1}) = 3030 w, 2975/2930 m, 2870 w (CH), 1645 m (C=N). – C$_{17}$H$_{19}$N$_3$O (281.36): calcd. C 72.57, H 6.81, N 14.93; found C 71.89, H 7.06, N 14.86. – Optical rotation (c = 1.6, CHCl$_3$): $[\alpha]^{20}_{D}$ = –39, $[\alpha]^{20}_{578}$ = –40, $[\alpha]^{20}_{546}$ = –48, $[\alpha]^{20}_{436}$ = –100, $[\alpha]^{20}_{365}$ = –208.

(–)-2-[4-(R)-Phenyloxazolin-2-yl]-4,4′-bipyridine (**3d**): Amino alcohol: *(R)*-α-phenylglycinol. 15 × 3.5 cm SiO$_2$ with PE/acetone (1:1) as eluent (R_f = 0.35 [acetone]). Recrystallisation from ether yielded a white foam (80%), m.p. 52–55°C. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 4.44 ("t", ^2J = ^3J ≈ 8.6 Hz, 1 H, Ox-C*H*$_Z$H$_E$), 4.94 (dd, ^2J = 8.7 Hz, ^3J = 10.2 Hz, 1 H, Ox-CH$_Z$*H*$_E$), 5.50 (dd, ^3J = 8.5 Hz, ^3J = 10.2 Hz, 1 H, Ox-C*H*), 7.27–7.41 (m, 5 H, Ph-*H*), 7.59 (AA′BB′, 2 H, H-3′, H-5′), 7.67 (dd, ^3J = 5.1 Hz, ^4J = 1.8 Hz, 1 H, H-5), 8.45 (dd, ^4J = 1.8 Hz, ^5J = 0.7 Hz, 1 H, H-3), 8.75 (AA′BB′, 2 H, H-2′, H-6′), 8.85 (dd, ^3J = 5.1 Hz, ^5J = 0.7 Hz, 1 H, H-6). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 70.5 (Ox-*C*H), 75.4 (Ox-*C*H$_2$), 121.4 (*C-3′*, *C-5′*), 122.0 (*C-3*), 123.2 (*C-5*), 126.8 (*o*- or *m*-Ph-*C*), 127.8 (*p*-Ph-*C*), 128.8 (*m*- or *o*-Ph-*C*), 141.6 (qC of Ph), 144.7/146.5/147.8 (qC), 150.6 (C-6), 150.8 (C-2′, C-6′), 163.7 (*C*=N). – MS (EI): *m/z* (%) = 301 (100) [M$^+$], 272 (25), 271 (96) [M$^+$ – CH$_2$O], 156 (44), 155 (36), 118 (36), 91 (22), 90 (31), 89 (32). – IR (KBr): ṽ (cm^{-1}) = 3055/3025/2980/2890 w (CH), 1650 s (C=N). – C$_{19}$H$_{15}$N$_3$O (301.35): calcd. C 75.73, H 5.02, N 13.94; found C 75.28, H 5.24, N 13.81. – Optical rotation (c = 1.27, CHCl$_3$): $[\alpha]^{22}_{D}$ = –52, $[\alpha]^{22}_{578}$ = –54, $[\alpha]^{22}_{546}$ = –63, $[\alpha]^{22}_{436}$ = –107, $[\alpha]^{22}_{365}$ = –156.

(+)-2-[4-(S)-Benzyloxazolin-2-yl]-4,4′-bipyridine (**3e**): Amino alcohol: *(S)*-phenylalaninol. 8 × 3.5 cm SiO$_2$ with ethyl acetate/acetone (1:1) as eluent (R_f = 0.39 [acetone]). Recrystallisation from ether yielded a white solid (83%), m.p. 95–98°C. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.79 (dd, ^2J = 13.8 Hz, ^3J = 9.0 Hz, 1 H, C*H*$_A$H$_B$Ph), 3.32 (dd, ^2J = 13.8 Hz, ^3J = 4.9 Hz, 1 H, CH$_A$*H*$_B$Ph), 4.27 (dd, ^2J = 8.6 Hz, ^3J = 7.8 Hz, 1 H, Ox-C*H*$_Z$H$_E$), 4.49 (dd, ^2J = 8.6, ^3J = 9.4 Hz, 1 H, Ox-CH$_Z$*H*$_E$), 4.71 (dddd, ^3J = 9.4 Hz, ^3J = 9.0 Hz, ^3J = 7.8 Hz, ^3J = 4.9 Hz, 1 H, Ox-C*H*), 7.21–7.35 (m, 5 H, Ph-*H*), 7.59 (AA′BB′, 2 H, H-3′, H-5′), 7.64 (dd, ^3J = 5.1 Hz, ^4J = 1.8 Hz, 1 H, H-5), 8.33 (d, ^4J = 1.8 Hz, 1 H, H-3), 8.76 (AA′BB′, 2 H, H-2′, H-6′), 8.83 (d, ^3J = 5.1 Hz, 1 H, H-6). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 41.7 (*C*H$_2$Ph), 68.2 (Ox-*C*H), 72.7 (Ox-*C*H$_2$), 121.4 (C-3′, C-5′), 121.7 (C-3), 123.1 (C-5), 126.6 (*p*-Ph-*C*), 128.6/129.2 (*o*- and *m*-Ph-*C*), 137.7 (qC of Ph), 144.8/146.5/147.9 (qC), 150.6 (C-6), 150.8 (C-2′, C-6′), 162.9 (*C*=N). – MS (EI): *m/z* (%) = 315 (10) [M$^+$], 225 (16), 224 (100) [M$^+$ – CH$_2$Ph], 196 (16), 169 (19), 155 (18), 91 (12) [PhCH$_2^+$]. – IR (KBr): ṽ (cm^{-1}) = 3030 m, 2985/2920/2880 w (CH), 1635 s (C=N). – C$_{20}$H$_{17}$N$_3$O (315.37): calcd. C 76.17, H 5.43, N 13.32; found C 76.13, H 5.75, N 13.24. – Optical rotation (c = 1.26, CHCl$_3$): $[\alpha]^{20}_{D}$ = +30, $[\alpha]^{20}_{578}$ = +33, $[\alpha]^{20}_{546}$ = +36, $[\alpha]^{20}_{436}$ = +69, $[\alpha]^{20}_{365}$ = +132.

(–)-2-[4-(S)-tert-Butyloxazolin-2-yl]-4,4′-bipyridine (**3f**): Amino alcohol: *(S)*-*tert*-leucinol. 11.5 × 2.5 cm SiO$_2$ with PE/acetone (3:2) as eluent (R_f = 0.09). Stirring in PE/ether and filtration gave a white solid (76%), m.p. 98–99°C. – ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = 0.90 (s, 9 H, C*H*$_3$), 3.90 (dd, ^2J = 7.8 Hz, ^3J = 10.8 Hz, 1 H, Ox-C*H*$_E$H$_Z$?), 4.041 (d, ^2J = 7.8 Hz, 1 H, Ox-CH$_E$*H*$_Z$?), 4.044 (d, ^3J = 10.8 Hz, 1 H, Ox-C*H*?), 6.73 (AA′BB′, 2 H, H-3′, H-5′), 6.77 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.42 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.48 (AA′BB′, 2 H, H-2′, H-6′), 8.50 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6). – ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 26.0 (*C*H$_3$), 34.0 (*C*Me$_3$), 69.4 (Ox-*C*H$_2$), 76.7 (Ox-*C*H), 121.4 (C-3′, C-5′), 121.7 (C-3), 122.9 (C-5), 144.9/146.4/148.1 (qC), 150.5 (C-6), 150.7 (C-2′, C-6′), 162.2 (*C*=N). – MS (EI): *m/z* (%) = 281 (3) [M$^+$], 225 (100) [M$^+$ – C$_4$H$_8$], 224 (78) [M$^+$ –

C_4H_9], 223 (35), 196 (33), 170 (10), 169 (25), 156 (44), 155 (61), 57 (20) [$C_4H_9^+$], 41 (17). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3060 w, 2960/2950 m, 2905/2865 w (CH), 1665/1645 m (C=N). − $C_{17}H_{19}N_3O$ (281.36): calcd. C 72.57, H 6.81, N 14.93; found C 72.22, H 6.42, N 14.44. − Optical rotation (c = 1.1, $CHCl_3$): $[\alpha]^{20}_D = -30$, $[\alpha]^{20}_{578} = -32$, $[\alpha]^{20}_{546} = -38$, $[\alpha]^{20}_{436} = -79$, $[\alpha]^{20}_{365} = -156$.

(+)-N-[2-(R)-(1-Hydroxybutyl)]-4,4′-bipyridine-2-carboxamide (**9**): 2.03 g (9.5 mmol) of **8** and 0.9 ml (9.5 mmol) of 2-*(R)*-aminobutan-1-ol were heated to 80°C in dry chlorobenzene (15 ml) for 66 h. After cooling the solvent was removed. The residue was treated with ether (30 ml) and extracted with 2 N HCl (2× 5 ml). Almost all the substance was transferred into the aqueous layer, which then was alkalised with 2 N NaOH. After extraction with $CHCl_3$ (3× 20 ml) the organic layer was dried over $MgSO_4$ and the solvent evaporated. Recrystallisation from cyclohexane/acetone afforded 910 mg (3.4 mmol, 35%) of **9**. Colourless crystals, m.p. 117−119°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.55−1.86 (m, 2 H, CH_2CH_3), 3.69−3.86 (br s, 1 H, O*H*), 3.73 (dd, ^2J = 11.1 Hz, ^3J = 5.5 Hz, 1 H, CH_AH_B), 4.01−4.15 (m, 1 H, C*H*), 3.82 (dd, ^2J = 11.1 Hz, ^3J = 4.0 Hz, 1 H, CH_AH_B), 7.53 (AA′BB′, 2 H, H-3′, H-5′), 7.60 (dd, ^3J = 5.1 Hz, ^4J = 1.7 Hz, 1 H, H-5), 8.18 (d, ^3J = 8.2 Hz, 1 H, N*H*), 8.38 (d, ^4J = 1.7 Hz, 1 H, H-3), 8.60 (d, ^3J = 5.1 Hz, 1 H, H-6), 8.69 (AA′BB′, 2 H, *H-2′*, *H-6′*). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 10.6 (CH_3), 24.3 (CH_2CH_3), 53.7 (*C*H), 65.0 (CH_2OH), 120.0 (C-3), 121.3 (C-3′, C-5′), 123.5 (C-5), 144.8/147.0 (qC), 149.0 (C-6), 150.7 (C-2′, C-6′), 151.0 (qC), 164.4 (*C*=O). − MS (EI): *m/z* (%) = 271 (1) [M^+], 241 (32) [$M^+ - CH_2O$], 240 (100) [$M^+ - CH_2OH$], 183 (12), 156 (26), 155 (86). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3450/3390/3345/3270 m (OH, NH), 2960/2930 m, 2880 w (CH), 1670 s (C=O). − $C_{15}H_{17}N_3O_2$ (271.32): calcd. C 66.40, H 6.32, N 15.49; found C 65.87, H 6.36, N 15.19. − Optical rotation (c = 0.16, $CHCl_3$): $[\alpha]^{22}_D = +45$, $[\alpha]^{26}_{578} = +53$, $[\alpha]^{26}_{546} = +64$, $[\alpha]^{26}_{436} = +103$, $[\alpha]^{26}_{365} = +138$.

General Procedure II (N′-Methylation): 2.6 mmol of 2-(4,4′-bipyridin-2-yl)oxazoline (**3**) were dissolved in dry THF (30 ml) under nitrogen. After adding 3.0 ml (48.0 mmol) of methyl iodide the light-protected solution was stirred for 63−90 h at r. t. The resulting reddish precipitate was collected and washed with dry ether (3 × 5 ml). The red side-product was removed by dissolving the precipitate in dry methanol and adding dry ether till an appearing cloudiness just faded. After cooling (−20°C) only the side-product crystallised and was filtered off. Dry ether (5−15 ml) was added to the resulting filtrate and after cooling to −20°C the pure, hygroscopic product **1** was obtained.

(+)-N′-Methyl-2-[4-(R)-ethyloxazolin-2-yl]-4,4′-bipyridinium Iodide (**1a**): From oxazoline **3a**. Orange solid (51%), m.p. > 68°C (dec.). − ^{1}H NMR (250 MHz, CD_3OD): δ = 1.04 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.61−1.88 (m, 2 H, CH_2CH_3), 4.27 ("t", ^2J = ^3J = 7.9 Hz, 1 H, Ox-CH_ZH_E), 4.29−4.44 (m, 1 H, Ox-C*H*), 4.51 (s, 3 H, N-CH_3), 4.69 (dd, ^2J = 7.9 Hz, ^3J = 9.2 Hz, 1 H, Ox-CH_ZH_E), 8.13 (dd, ^3J = 5.2 Hz, ^4J = 1.9 Hz, 1 H, H-5), 8.53 (dd, ^4J = 1.9 Hz, ^5J = 0.9 Hz, 1 H, H-3), 8.55 (AA′BB′, 2 H, H-3′, H-5′), 8.91 (dd, ^3J = 5.2 Hz, ^5J = 0.9 Hz, 1 H, H-6), 9.10 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CD_3OD): δ = 10.1 (CH_2CH_3), 29.4 (CH_2CH_3), 49.0 (N-CH_3), 69.3 (Ox-*C*H), 74.4 (Ox-CH_2), 123.3 (C-3), 125.5 (C-5), 127.1 (C-3′, C-5′), 144.4 (qC), 147.6 (C-2′, C-6′), 149.1 (qC), 152.2 (C-6), 154.2 (qC), 164.1 (*C*=N). − MS (FAB, MeOH/glycerol): *m/z* = 663 [2 K^+ + I^-], 268 [K^+]. − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3030/2960/2930 m, 2875 w (CH), 1645 s (C=N). − $C_{16}H_{18}IN_3O \bullet 1/2\ H_2O$ (404.25): calcd. C 47.54, H 4.74, N 10.39; found C 47.79, H 5.12, N 9.97. Optical rotation (c = 2.2, MeOH): $[\alpha]^{22}_D = +25$, $[\alpha]^{22}_{578} = +26$, $[\alpha]^{22}_{546} = +31$.

(−)-N′-Methyl-2-[4-(S)-isopropyloxazolin-2-yl]-4,4′-bipyridinium Iodide (**1b**): From oxazoline **3b**. Orange solid (53%), m.p. > 130°C (dec.). − ^{1}H NMR (250 MHz, CD_3OD): δ = 0.99 (d, ^3J = 6.7 Hz, 3 H, CH_3), 1.08 (d, ^3J = 6.7 Hz, 3 H, CH_3'), 1.92 (m, 1 H, C*H*Me_2), 4.22−4.33 (m, 1 H, Ox-C*H*), 4.37 ("t", ^2J = ^3J = 8.3 Hz, 1 H, Ox-CH_ZH_E), 4.51 (s, 3 H, N-CH_3), 4.63 (dd, ^2J = 8.3 Hz, ^3J = 9.6 Hz, 1 H, Ox-CH_ZH_E), 8.14 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.53 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.55 (AA′BB′, 2 H, H-3′, H-5′), 8.91 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6), 9.11 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CD_3OD): δ = 18.5 (CH_3), 19.0 (CH_3'), 33.9 (*C*HMe_2), 49.0 (N-CH_3), 72.4 (Ox-CH_2), 73.9 (Ox-*C*H), 123.3 (C-3), 125.5 (C-5), 127.1 (C-3′, C-5′), 144.4 (qC), 147.6 (C-2′, C-6′), 149.1 (qC), 152.2 (C-6), 154.2 (qC), 164.1 (*C*=N). − MS (FAB, MeOH/glycerol): *m/z* = 282 [K^+]. − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3020/2960 m, 2870 w (CH), 1645 s (C=N). − $C_{17}H_{20}IN_3O \bullet 2\ H_2O$ (445.30): calcd. C 45.85, H 5.43, N 9.44; found C 45.98, H 5.12, N 8.91. − Optical rotation (c = 2.2, MeOH): $[\alpha]^{22}_D = -23$, $[\alpha]^{22}_{578} = -24$, $[\alpha]^{22}_{546} = -28$.

(−)-N′-Methyl-2-[4-(S)-(2-methylpropyl)oxazolin-2-yl]-4,4′-bipyridinium Iodide (**1c**): From oxazoline **3c**. Orange solid (50%), m.p. > 85°C (dec.). − ^{1}H NMR (250 MHz, CD_3OD): δ = 1.00 (d, ^3J = 6.6 Hz, 3 H, CH_3), 1.02 (d, ^3J = 6.6 Hz, 3 H, CH_3'), 1.48 ("dt", ^2J = 13.3 Hz, ^3J = 7.3 Hz, 1 H, $CH_AH_BCHMe_2$), 1.78 ("dt", ^2J = 13.3 Hz, ^3J = 6.6 Hz, 1 H, $CH_AH_BCHMe_2$), 1.89 ("sept", ^3J = 6.6 Hz, 1 H, C*H*Me_2), 4.19 ("t", ^2J = ^3J = 8.1 Hz, 1 H, Ox-CH_ZH_E), 4.41−4.56 (m, 1 H, Ox-C*H*), 4.51 (s, 3 H, N-CH_3), 4.73 (dd, ^2J = 8.1 Hz, ^3J = 9.5 Hz, 1 H, Ox-CH_ZH_E), 8.13 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.53 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.55 (AA′BB′, 2 H, H-3′, H-5′), 8.90 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6), 9.10 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CD_3OD): δ = 23.1 (CH_3), 23.2 (CH_3'), 26.5 (*C*HMe_2), 46.5 (CH_2CHMe_2), 49.0 (N-CH_3), 66.5 (Ox-*C*H), 75.4 (Ox-CH_2), 123.3 (C-3), 125.5 (C-5), 127.1 (C-3′, C-5′), 144.4 (qC), 147.6 (C-2′, C-6′), 149.1 (qC), 152.2 (C-6), 154.2 (qC), 163.9 (*C*=N). − MS (FAB, MeOH/glycerol): *m/z* = 719 [2K$^+$ + I^-], 424 [MH^+], 268 [K^+]. − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3020 m, 2950 s, 2865 m (CH), 1645 s (C=N). − $C_{18}H_{22}IN_3O \bullet H_2O$ (441.32): calcd. C 48.98, H 5.48, N 9.52; found C 49.24, H 5.46, N 9.61. − Optical rotation (c = 2.2, MeOH): $[\alpha]^{22}_D = -31$, $[\alpha]^{22}_{578} = -32$, $[\alpha]^{22}_{546} = -36$.

(−)-N′-Methyl-2-[4-(R)-phenyloxazolin-2-yl]-4,4′-bipyridinium Iodide (**1d**): From oxazoline **3d**. Orange solid (63%), m.p. > 135°C (dec.). − ^{1}H NMR (250 MHz, CD_3OD): δ = 4.40 ("t", ^2J = ^3J ≈ 8.5 Hz, 1 H, Ox-CH_ZH_E), 4.50 (s, 3 H, N-CH_3), 5.03 (dd, ^2J = 8.7 Hz, ^3J = 10.3 Hz, 1 H, Ox-CH_ZH_E), 5.54 (dd, ^3J = 8.3 Hz, ^3J = 10.3 Hz, 1 H, Ox-C*H*), 7.29−7.38 (m, 5 H, Ph-*H*), 8.15 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.54 (AA′BB′, 2 H, H-3′, H-5′), 8.58 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, *H-3*), 8.93 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6), 9.09 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CD_3OD): δ = 49.1 (N-CH_3), 71.3 (Ox-*C*H), 77.1 (Ox-CH_2), 123.6 (C-3), 125.8 (C-5), 127.1 (C-3′, C-5′), 128.0 (*o*- or *m*-Ph-*C*), 129.0 (*p*-Ph-*C*), 130.0 (*m*- or *o*-Ph-*C*), 143.0 (qC of Ph), 144.4 (qC), 147.6 (C-2′, C-6′), 148.9 (qC), 152.4 (C-6), 154.1 (qC), 165.2 (*C*=N). − MS (FAB, MeOH/glycerol): *m/z* = 316 [K^+]. − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3020 m (CH), 1645 s (C=N). − $C_{20}H_{18}IN_3O \bullet H_2O$ (461.31): calcd. C 52.07, H 4.37, N 9.11; found C 52.08, H 4.55, N 8.96. − Optical rotation (c = 2.2, MeOH): $[\alpha]^{22}_D = -15$, $[\alpha]^{22}_{578} = -17$, $[\alpha]^{22}_{546} = -19$.

In this case the red side-product was recrystallised from aqueous acetone/methanol to give dark-red tetrahedra, m.p. > 215°C (dec.), which were characterised as *N′,N′′-dimethyl-2-[4-(R)-phenylox-*

azolinium-2-yl]-4,4′-bipyridinium Diiodide (**10**). − ^{1}H NMR (400 MHz, D_2O): δ = 3.14 (s, 3 H, Ox-N-CH_3), 4.40 (s, 3 H, N′-CH_3), 5.16 (dd, ^2J = 14.4 Hz, ^3J = 3.9 Hz, 1 H, Ox-CH_ZH$_E$), 5.40 (dd, ^2J = 14.4 Hz, ^3J = 4.7 Hz, 1 H, Ox-CH$_Z$$H_E$), 5.48 ("t", ^3J ≈ 4.3 Hz, 1 H, Ox-C*H*), 7.19−7.22 (m, 2 H, *o*-Ph-*H*), 7.30−7.36 (m, 3 H, *m*- and *p*-Ph-*H*), 8.47 (AA′BB′, 2 H, H-3′, H-5′), 8.55 (dd, ^3J = 6.3 Hz, ^4J = 2.4 Hz, 1 H, H-5), 8.90 (d, ^3J = 5.2 Hz, 1 H, H-6), 8.97 (AA′BB′, 2 H, H-2′, H-6′), 9.09 (d, ^4J = 2.4 Hz, 1 H, H-3). − ^{13}C NMR (100.6 MHz, D_2O): δ = 34.5 (Ox-N-*C*H$_3$), 48.7 (N′-*C*H$_3$), 58.8 (Ox-*C*H), 59.1 (Ox-*C*H$_2$), 126.7 (*o*-Ph-*C*), 126.9 (C-3), 127.0 (C-3′, C-5′), 129.2 (C-5), 129.6 (*p*-Ph-*C*), 129.7 (*m*-Ph-*C*), 133.7/141.9 (qC), 146.3 (C-6), 146.6 (C-2′, C-6′), 149.2/152.3 (qC), 156.7 (*C*=N). − MS (FAB, H_2O/glycerol)[34]: *m/z* = 332 (weak) [KH$^+$], 331 [K$^+$], 165.5 = 331/2 (very weak) [K^{++}]. − IR (KBr): ṽ (cm^{-1}) = 3060/2990 w (CH), 1675 s (C=N). − $C_{21}H_{21}I_2N_3O$ • $2H_2O$ (621.26): calcd. C 40.60, H 4.06, N 6.76; found C 40.71, H 4.32, N 6.53.

(+)-N′-Methyl-2-[4-(S)-benzyloxazolin-2-yl]-4,4′-bipyridinium Iodide (**1e**): 1.3 g (4.1 mmol) of **3e** and 5.0 ml (80.0 mmol) of methyl iodide in dry THF (50 ml) were stirred at r. t. for 40 h under nitrogen. The precipitated orange solid was filtered off and washed with dry ether (2× 10 ml). After recrystallisation from methanol/ether at −20°C 1.84 g (4.0 mmol, 98%) of pure **1e** were obtained. Light orange solid, m.p. > 165°C (dec.). − ^{1}H NMR (250 MHz, CD_3OD): δ = 2.92 (dd, ^2J = 13.7 Hz, ^3J = 7.1 Hz, 1 H, CH_AH$_B$Ph), 3.11 (dd, ^2J = 13.7 Hz, ^3J = 5.9 Hz, 1 H, CH$_A$$H_B$Ph), 4.33 (dd, ^2J = 8.5 Hz, ^3J = 7.5 Hz, 1 H, Ox-CH_ZH$_E$), 4.48 (s, 3 H, N-CH_3), 4.58 (dd, ^2J = 8.5 Hz, ^3J = 9.5 Hz, 1 H, Ox-CH$_Z$$H_E$), 4.75 (m, 1 H, Ox-C*H*), 7.15−7.33 (m, 5 H, Ph-*H*), 8.11 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.48 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.51 (AA′BB′, 2 H, H-3′, H-5′), 8.89 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6), 9.08 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CD_3OD): δ = 42.2 (*C*H$_2$Ph), 49.0 (N-*C*H$_3$), 69.0 (Ox-*C*H), 74.0 (Ox-*C*H$_2$), 123.3 (C-3), 125.6 (C-5), 127.1 (C-3′, C-5′), 127.7 (*p*-Ph-*C*), 129.6/130.6 (*o*- and *m*-Ph-*C*), 138.9 (qC of Ph), 144.3 (qC), 147.6 (C-2′, C-6′), 149.0 (qC), 152.2 (C-6), 154.2 (qC), 164.4 (*C*=N). − MS (FAB, H_2O/glycerol): *m/z* = 787 [2K$^+$ + I$^-$], 330 [K$^+$]. − IR (KBr): ṽ (cm^{-1}) = 3020 m (CH), 1645 s (C=N). − $C_{21}H_{20}IN_3O$ • 1/2 H_2O (466.32): calcd. C 54.09, H 4.54, N 9.01; found C 54.21, H 4.66, N 8.69. − Optical rotation (*c* = 2.2, MeOH): $[\alpha]^{22}_{D}$ = +11, $[\alpha]^{22}_{578}$ = +12, $[\alpha]^{22}_{546}$ = +15, $[\alpha]^{22}_{436}$ = +27.

(+)-N′-Methyl-2-[4-(S)-benzyloxazolin-2-yl]-4,4′-bipyridinium Hexafluorophosphate (**11**): 460 mg (1.0 mmol) of **1e** were dissolved in water (15 ml) and treated with 1 ml of saturated aqueous NH_4PF_6. The precipitated yellow solid was collected after 30 min and washed with little water. After recrystallisation from boiling water 420 mg (0.9 mmol, 88%) of **11** were isolated. Light yellow, hygroscopic solid, m.p. > 120°C (dec.). − ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 2.90 (dd, ^2J = 13.9 Hz, ^3J = 7.5 Hz, 1 H, CH_AH$_B$Ph), 3.11 (dd, ^2J = 13.9 Hz, ^3J = 6.3 Hz, 1 H, CH$_A$$H_B$Ph), 4.24 (dd, ^2J = 8.3 Hz, ^3J = 7.5 Hz, 1 H, Ox-CH_ZH$_E$), 4.55 (dd, ^2J = 8.3 Hz, ^3J = 9.5 Hz, 1 H, Ox-CH$_Z$$H_E$), 4.69 (s, 3 H, N-C$H_3$), 4.67−4.86 (m, 1 H, Ox-C*H*), 7.13−7.38 (m, 5 H, Ph-*H*), 8.12 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.53 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.71 (AA′BB′, 2 H, H-3′, H-5′), 8.92 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6), 9.25 (AA′BB′, 2 H, H-2′, H-6′). − MS (FAB, MeOH/glycerol): *m/z* = 476 (weak) [MH$^+$], 330 [K$^+$]. − IR (KBr): ṽ (cm^{-1}) = 3150/3060/3030/2970/2910 w (CH), 1650 s (C=N), 840 vs, 555 s (PF). $C_{21}H_{20}F_6N_3OP$ • H_2O (493.39): calcd. C 51.12, H 4.49, N 8.52; found C 51.12, H 4.44, N 8.36. − Optical rotation (*c* = 2.2, acetone): $[\alpha]^{22}_{D}$ = +7.7, $[\alpha]^{22}_{578}$ = +8.6, $[\alpha]^{22}_{546}$ = +10, $[\alpha]^{22}_{436}$ = +20.

4,4′-Bipyridine N,N′-Dioxide Dihydrate (**12**): 5.4 g (57.4 mmol) of commercially available H_2O_2/urea adduct and 8.5 g (57.4 mmol) of phthalic anhydride were suspended in CH_2Cl_2 (60 ml). After 15 min 2.0 g (12.8 mmol) of 4,4′-bipyridine (**4**) were added and stirred for 3 d. Then the resulting suspension was poured into a saturated solution of aqueous $NaHCO_3$ (200 ml) and continuously extracted with $CHCl_3$ for 3 d. Removing the solvent and recrystallisation from water afforded 2.72 g (12.1 mmol, 95% [ref.[31]: 80%]) of 4,4′-bipyridine *N,N*′-dioxide as the yellow dihydrate, m.p. > 250°C (ref.: 305°C[31], 305−306°C[36], 335°C[21]). − ^{1}H NMR (250 MHz, D_2O): δ = 7.84 (AA′BB′, 4 H, H-3,3′, H-5,5′), 8.30 (AA′BB′, 4 H, H-2,2′, H-6,6′). − MS (FD, MeOH): *m/z* = 188 [M$^+$]. − IR (KBr): ṽ (cm^{-1}) = 1255 s, 1245 vs (NO). $C_{10}H_8N_2O_2$ • 2 H_2O (224.22): calcd. C 53.57, H 5.39, N 12.49; found C 53.98, H 5.42, N 12.26.

4,4′-Bipyridine-2,2′-dicarbonitrile (**13**): **12** (1.7 g, 7.6 mmol) and dimethyl sulfate (15 ml, 157.7 mmol) were heated at 140°C for 30 min. The cooled solution was treated with ethanol (30 ml) and 70% $HClO_4$ (10 ml). The precipitated solid was collected, dried, dissolved in water (90 ml), weakly alkalised with Na_2CO_3 and cooled on ice. A solution of 2.6 g (59 mmol) of NaCN in water (25 ml) was added and the precipitation completed by stirring for 1 h. After washing the filtered precipitate with ice water it was dried in vacuo over P_4O_{10}. Recrystallisation from ethanol yielded 760 mg (3.7 mmol, 48%) of the white dinitrile **13**. − ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 8.29 (dd, ^3J = 5.2 Hz, ^4J = 1.9 Hz, 2 H, H-5, H-5′), 8.66 (dd, ^4J = 1.9 Hz, ^5J = 0.9 Hz, 2 H, H-3, H-3′), 8.95 (dd, ^3J = 5.2 Hz, ^5J = 0.9 Hz, 2 H, H-6, H-6′). − MS (EI): *m/z* (%) = 206 (100) [M$^+$]. − IR (KBr): ṽ (cm^{-1}) = 2230 m (C≡N).

Dimethyl 4,4′-Bipyridine-2,2′-dicarboximidate (**14**): 50 mg (2.2 mmol) of sodium were dissolved in dry methanol (40 ml) under nitrogen. 750 mg (3.6 mmol) of **13** were added and stirring at r. t. was continued for 4 d. After addition of acetic acid (0.1 ml, 1.6 mmol) the solvent was evaporated and the residue treated with warm ether (300 ml). Inorganic salts were removed by hot filtration. Cooling the filtrate to −20°C lead to 600 mg (2.2 mmol, 62%) of **14**. Colourless crystals, m.p. 211−214°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.07 (s, 6 H, CH_3), 7.66 (dd, ^3J = 5.1 Hz, ^4J = 1.8 Hz, 2 H, H-5, H-5′), 7.86 (dd, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 2 H, H-3, H-3′), 8.79 (dd, ^3J = 5.1 Hz, ^5J = 0.8 Hz, 2 H, H-6, H-6′), 9.31 (br s, 2 H, N*H*). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 54.0 (*C*H$_3$), 118.8 (C-3, C-3′), 123.0 (C-5, C-5′), 146.7/148.8 (qC), 150.1 (C-6, C-6′), 166.2 (*C*=N). − MS (EI): *m/z* (%) = 270 (100) [M$^+$], 240 (15), 239 (63) [M$^+$ − OCH$_3$], 227 (20), 214 (14), 213 (83) [M$^+$ − OCH$_3$ − CH$_3$OH], 182 (13), 181 (15), 180 (23), 156 (12), 155 (18), 153 (13), 58 (17). − IR (KBr): ṽ (cm^{-1}) = 3300/3265 m (NH), 1645 s (C=N), 1365 vs (CO). − $C_{14}H_{14}N_4O_2$ (270.29): calcd. C 62.21, H 5.22, N 20.73; found C 62.21, H 5.18, N 20.32.

(−)-2,2′-Bis[4-(R)-phenyloxazolin-2-yl]-4,4′-bipyridine (**15**): Following general procedure I 580 mg (2.1 mmol) of **14** and 590 mg (4.3 mmol) of *(R)*-α-phenylglycinol were heated at 80°C in dry chlorobenzene (20 ml) for 6 d. Flash chromatography (SiO_2, 9.5 × 2.5 cm) with PE/acetone (1:1) as eluent (R_f = 0.37 [acetone]) followed by recrystallisation from PE/ether afforded 520 mg (1.2 mmol, 56%) of **15**. Light yellow foam, m.p. 102−105°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.44 ("t", ^2J = ^3J = 8.6 Hz, 2 H, Ox-CH_ZH$_E$), 4.94 (dd, ^2J = 8.6 Hz, ^3J = 10.2 Hz, 2 H, Ox-CH$_Z$$H_E$), 5.50 (dd, ^3J = 8.6 Hz, ^3J = 10.2 Hz, 2 H, Ox-C*H*), 7.30−7.41 (m, 10 H, Ph-*H*), 7.74 (dd, ^3J = 5.0 Hz, ^4J = 1.9 Hz, 2 H, H-5, H5′), 8.50 (dd, ^4J = 1.9 Hz, ^5J = 0.9 Hz, 2 H, H-3, H-3′), 8.86 (dd, ^3J = 5.0 Hz, ^5J = 0.9 Hz, 2 H, H-6, H-6′). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 70.5 (Ox-*C*H), 75.5 (Ox-*C*H$_2$),

122.1/123.4 (C-3, C-3′ and C-5, C-5′), 126.9 (*o*- or *m*-Ph-*C*), 127.9 (*p*-Ph-*C*), 128.9 (*m*- or *o*-Ph-*C*), 141.6 (qC of Ph), 145.8/148.0 (qC), 150.7 (C-6, C-6′), 163.6 (*C*=N). − MS (EI): *m/z* (%) = 446 (100) [M$^+$], calcd. for $C_{28}H_{22}N_4O_2$ 446.1743, found 446.1737, diff. −0.5 mmu/1.2 ppm, 416 (28) [M$^+$ − CH_2O], 315 (20), 301 (20), 296 (21), 269 (31), 91 (44), 90 (42), 89 (24). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3055/3025/2890 w (CH), 1640 s (C=N). − Optical rotation (*c* = 1.27, $CHCl_3$): $[\alpha]^{22}_D = -78$, $[\alpha]^{22}_{578} = -82$, $[\alpha]^{22}_{546} = -95$, $[\alpha]^{22}_{436} = -168$, $[\alpha]^{22}_{365} = -271$.

3,6-Dimethylpyrazine-2,5-dicarboxylic Acid (**17**): 1.4 g (6.2 mmol) of dimethyl 3,6-dimethylpyrazine-2,5-dicarboxylate (**16**)[133] were refluxed in 2 N NaOH (50 ml) for 30 min. The cooled solution was acidified with conc. HCl and the precipitate filtered off. After recrystallisation from ethyl acetate 1.0 g (5.1 mmol, 82%) of **17** were obtained. Colourless crystals, m.p 195°C (ref. 194−195°C[37], 200−201°C[38]). − ^{1}H NMR (80 MHz, [D_6]acetone): δ = 2.78 (s, C*H*$_3$). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3465 s (OH), 1705 s (C=O).

3,6-Dimethylpyrazine-2,5-dicarboxylic Acid Chloride (**18**): 970 mg (5.1 mmol) of **17** and 1.1 ml of $SOCl_2$ were refluxed for 2 h. Excess $SOCl_2$ was removed in vacuo and the residue (1.18 g, 5.1 mmol, 99%), m.p. 98°C, was directly used in the next reaction. − ^{1}H NMR (80 MHz, $CDCl_3$): δ = 2.85 (s, C*H*$_3$). − MS (EI): *m/z* (%) = 234 (14)/232 (21) [M$^+$], 199 (33)/197 (100) [M$^+$ − Cl], 171 (24)/169 (74) [M$^+$ − Cl − CO], 143 (13)/141 (41) [M$^+$ − Cl − 2 CO], 106 (17) [M$^+$ − 2 Cl − 2 CO]. − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 1755 vs (C=O), 880/865 s (CCl).

(+)-2,5-Bis[4-(R)-phenyloxazolin-2-yl]-3,6-dimethylpyrazine (**19**): To a solution of (*R*)-α-phenylglycinol (1.36 g, 9.9 mmol) and dry triethylamine (1.4 ml) in CH_2Cl_2 (15 ml) was added during 15 min a solution of **18** (1.15 g, 4.9 mmol) in CH_2Cl_2 (12 ml) at 0°C under nitrogen. The mixture was stirred for 16 h at r. t. The solvent was removed and the residue treated with toluene (30 ml) and $SOCl_2$ (2.2 ml). After refluxing for 1 h the cooled solution was evaporated. A solution of NaOH (800 mg, 20.0 mmol) in methanol (40 ml) was added and refluxing continued for 3.5 h. To the cooled solution ether (100 ml) and brine (30 ml) were added. The organic layer was collected and the aqueous layer extracted with acetone (3× 30 ml). After washing with brine (20 ml) the combined organic layers were dried over $MgSO_4$ and evaporated. The oily residue was purified by flash chromatography (SiO_2, 10 × 3 cm) with PE/ethyl acetate (1:1) as eluent (R_f = 0.65 [ethyl acetate]). Recrystallisation from ether/acetone yielded 900 mg (2.3 mmol, 46%) of **19**. Light yellow solid, m.p. 143°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.99 (s, 6 H, C*H*$_3$), 4.35 ("t", $^2J = {^3J} \approx$ 8.6 Hz, 2 H, Ox-CH_ZH$_E$), 4.90 (dd, ^2J = 8.7 Hz, ^3J = 10.2 Hz, 2 H, Ox-CH$_Z$$H_E$), 5.56 (dd, ^3J = 8.5 Hz, ^3J = 10.2 Hz, 2 H, Ox-C*H*), 7.31 (m, 2 H, *p*-Ph-*H*), 7.34 (m, 4 H, *o*- or *m*-Ph-*H*), 7.38 (m, 4 H, *m*- or *o*-Ph-*H*). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.4 (*C*H$_3$), 71.1 (Ox-*C*H), 74.6 (Ox-*C*H$_2$), 126.7 (*o*- or *m*-Ph-*C*), 127.8 (*p*-Ph-*C*), 128.9 (*m*- or *o*-Ph-*C*), 141.0/141.7/151.6 (qC), 162.4 (*C*=N). − MS (EI): *m/z* (%) = 398 (100) [M$^+$], 307 (32), 121 (24), 118 (39), 104 (73), 103 (27), 91 (57), 89 (24). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3050/3020/2950/2920/2890 w (CH), 1645 s (C=N). − $C_{24}H_{22}N_4O_2$ (398.46): calcd. C 72.34, H 5.56, N 14.06; found C 72.21, H 5.57, N 13.90. − Optical rotation (*c* = 1.29, $CHCl_3$): $[\alpha]^{22}_D = +53$, $[\alpha]^{22}_{578} = +57$, $[\alpha]^{22}_{546} = +68$, $[\alpha]^{22}_{436} = +171$.

4-Phenylpyridine-2-carbonitrile (**21**): 5.0 g (29.2 mmol) of commercially available 4-phenylpyridine *N*-oxide (**20**) and 4.0 ml (32.0 mmol) of trimethylsilyl cyanide were dissolved in CH_2Cl_2 (50 ml) and stirred for 5 min under nitrogen. After adding 2.7 ml (29.3 mmol) of dimethylcarbamoyl chloride the resulting solution was stirred at r. t. for 2 d. A solution of 10% aqueous K_2CO_3 (50 ml) was added and stirring continued for 10 min. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (2× 25 ml). The combined organic layers were washed with 25 ml of brine and dried over $MgSO_4$. Recrystallisation from PE (750 ml) yielded 4.2 g (23.3 mmol, 80%) of **21**. Colourless needles, m.p. 99°C (ref.: 99−100°C[39], 99°C[40][41], 98−99°C[42]). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.49−7.66 (m, 5 H, Ph-*H*), 7.72 (dd, ^3J = 5.2 Hz, ^4J = 1.6 Hz, 1 H, H-5), 7.90 (dd, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.75 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 117.4 (*C*N), 124.6/126.4 (C-3 and C-5), 127.0/129.5 (*o*- and *m*-Ph-*C*), 130.2 (*p*-Ph-*C*), 134.6/136.0/149.9 (qC), 151.5 (C-6). − MS (EI): *m/z* (%) = 180 (100) [M$^+$], 179 (18), 153 (11). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 2220 w (C≡N). − $C_{12}H_8N_2$ (180.21): calcd. C 79.98, H 4.47, N 15.54; found C 79.77, H 4.65, N 15.40.

Methyl 4-Phenylpyridine-2-carboximidate (**22**): 20 mg (0.9 mmol) of sodium were dissolved in dry methanol (8 ml) under nitrogen. 1.26 g (7.0 mmol) of **21** were added and stirring at r. t. was continued for 90 h. After addition of a few drops of acetic acid the solvent was evaporated and the residue treated with warm ether (70 ml). Inorganic salts were removed by hot filtration. After evaporation of the solvent and recrystallisation from PE 1.31 g (6.2 mmol, 88%) of the imino ether **22** were obtained as a light yellow solid, m.p. 81−83°C. − ^{1}H NMR (250 MHz, C_6D_6): δ = 3.93 (s, 3 H, C*H*$_3$), 6.95 (dd, ^3J = 5.1 Hz, ^4J = 1.8 Hz, 1 H, H-5), 6.99−7.28 (m, 5 H, Ph-*H*), 8.05 (dd, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.36 (dd, ^3J = 5.0 Hz, ^5J = 0.8 Hz, 1 H, H-6), 10.02 (br s, 1 H, N*H*). − ^{13}C NMR (62.9 MHz, C_6D_6): δ = 53.7 (*C*H$_3$), 119.0/122.9 (C-3 and C-5), 127.3/129.26 (*o*- and *m*-Ph-*C*), 129.27 (*p*-Ph-*C*), 138.2 (qC of Ph), 148.8/149.8 (qC), 149.9 (C-6), 166.7 (*C*=N). − MS (EI): *m/z* (%) = 212 (79) [M$^+$], 182 (17), 181 (83) [M$^+$ − OCH_3], 156 (13), 155 (100) [M$^+$ − CH_3 − CN], 154 (29) [M$^+$ − CH_3 − HCN], 153 (11), 128 (17), 127 (27), 77 (17), 43 (17). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3290 m (NH), 1655 s (C=N), 1365 vs (CO). − $C_{13}H_{12}N_2O$ (212.25): calcd. C 73.57, H 5.70, N 13.20; found C 73.57, H 5.90, N 12.61.

(−)-4-(S)-(2-Methylpropyl)-2-(4-phenylpyridin-2-yl)oxazoline (**23a**): Following general procedure I 1.35 g (6.3 mmol) of **22** and 750 mg (6.4 mmol) of *(S)*-leucinol were heated at 80°C in dry chlorobenzene (25 ml) for 64 h. Flash-chromatography (SiO_2, 9 × 3 cm) with PE/acetone (2:1) as eluent (R_f = 0.26) followed by recrystallisation from PE/ether afforded 1.35 g (4.8 mmol, 76%) of **23a**. Colourless needles, m.p. 43−44°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.98 (d, ^3J = 6.7 Hz, 3 H, C*H*$_3$), 1.00 (d, ^3J = 6.3 Hz, 3 H, C*H*$_3$′), 1.43 ("dt", ^2J = 13.5 Hz, ^3J = 7.1 Hz, 1 H, CH_AH$_B$CHMe$_2$), 1.78 ("dt", ^2J = 13.5 Hz, $^3J \approx$ 6.7 Hz, 1 H, CH$_A$$H_B$CHMe$_2$), 1.89 ("sept", $^3J \approx$ 6.3 and 6.7 Hz, 1 H, C*H*Me$_2$), 4.10 ("t", $^2J = {^3J}$ = 8.0 Hz, 1 H, Ox-CH_ZH$_E$), 4.43 (m, 1 H, Ox-C*H*), 4.65 (dd, ^2J = 8.0 Hz, ^3J = 9.5 Hz, 1 H, Ox-CH$_Z$$H_E$), 7.41−7.55 (m, 3 H, Ph-*H*), 7.59 (dd, ^3J = 5.2 Hz, ^4J = 1.6 Hz, 1 H, H-5), 7.66−7.72 (m, 2 H, Ph-*H*), 8.29 (dd, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.74 (dd, ^3J = 5.2 Hz, ^5J = 1.2 Hz, 1 H, H-6). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.7 (*C*H$_3$ and *C*H$_3$′), 25.5 (*C*HMe$_2$), 45.5 (*C*H$_2$CHMe$_2$), 65.5 (Ox-*C*H), 73.7 (Ox-*C*H$_2$), 121.8 (C-3), 123.1 (C-5), 127.1/129.1 (*o*- and *m*-Ph-*C*), 129.3 (*p*-Ph-*C*), 137.5 (qC of Ph), 147.6/149.1 (qC), 150.1 (C-6), 162.6 (*C*=N). − MS (EI): *m/z* (%) = 280 (21) [M$^+$], 224 (40), 223 (80) [M$^+$ − C_4H_9], 196 (21), 195 (35), 181 (42), 169 (100), 168 (30), 155 (47), 154 (63), 127 (34), 84 (30). − IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3055/3025 w, 2955 s, 2925/2875 m (CH), 1645 s (C=N). − $C_{18}H_{20}N_2O$ (280.37): calcd. C 77.11, H 7.19, N 9.99; found C 76.94, H 7.18, N 9.95. Optical rotation (*c* = 1.27, $CHCl_3$): $[\alpha]^{22}_D = -30$, $[\alpha]^{22}_{578} = -33$, $[\alpha]^{22}_{546} = -39$, $[\alpha]^{22}_{436} = -78$, $[\alpha]^{22}_{365} = -160$.

(+)-4-(S)-Benzyl-2-(4-phenylpyridin-2-yl)oxazoline (**23b**): Following general procedure I 580 mg (2.7 mmol) of **22** and 415 mg (2.7 mmol) of *(S)*-phenylalaninol were heated at 80°C in dry chlorobenzene (20 ml) for 64 h. Flash-chromatography (SiO$_2$, 10 × 3 cm) with PE/acetone (2:1) as eluent (R_f = 0.17) followed by recrystallisation from PE/ether afforded 560 mg (1.8 mmol, 66%) of **23b**. Ivory coloured needles, m.p. 156−157°C. − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.78 (dd, ^2J = 13.8 Hz, ^3J = 9.1 Hz, 1 H, C*H*$_A$H$_B$Ph), 3.33 (dd, ^2J = 13.8 Hz, ^3J = 5.0 Hz, 1 H, CH$_A$*H*$_B$Ph), 4.25 (dd, ^2J = 8.6 Hz, ^3J = 7.7 Hz, 1 H, Ox-C*H*$_Z$H$_E$), 4.47 (dd, ^2J = 8.6 Hz, ^3J = 9.4 Hz, 1 H, Ox-CH$_Z$*H*$_E$), 4.69 (dddd, ^3J = 9.4 Hz, ^3J = 9.1 Hz, ^3J = 7.7 Hz, ^3J = 5.0 Hz, 1 H, Ox-C*H*), 7.19−7.35 (m, 5 H, Ox-Ph-*H*), 7.41−7.53 (m, 3 H, Py-Ph-*H*), 7.60 (dd, ^3J = 5.2 Hz, ^4J = 2.0 Hz, 1 H, H-5), 7.67−7.72 (m, 2 H, Py-Ph-*H*), 8.31 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1 H, H-3), 8.74 (dd, ^3J = 5.2 Hz, ^5J = 0.8 Hz, 1 H, H-6). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 41.7 (*C*H$_2$Ph), 68.2 (Ox-*C*H), 72.6 (Ox-*C*H$_2$), 121.9 (C-3), 123.4 (C-5), 126.6 (Ox-*p*-Ph-*C*), 127.1 (Ox-*o*- or *m*-Ph-*C*), 128.6 (Py-*o*- or *m*-Ph-*C*), 129.17/129.23 (Ox- and Py-*m*- or *o*-Ph-*C*), 129.4 (Py-*p*-Ph-*C*), 137.4 (qC of Py-Ph), 137.9 (qC of Ox-Ph), 147.4/149.2 (qC), 150.2 (*C-6*), 163.3 (*C*=N). − MS (EI): *m/z* (%) = 314 (5) [M$^+$], 224 (17), 223 (100) [M$^+$ − CH$_2$Ph], 195 (21), 168 (24), 167 (12), 154 (14), 127 (12). − IR (KBr): ṽ (cm^{-1}) = 3050/3030/2970/2955/2920/2890 w (CH), 1650 s (C=N). − C$_{21}$H$_{18}$N$_2$O (314.39): calcd. C 80.23, H 5.77, N 8.91; found C 80.30, H 5.82, N 8.91. − Optical rotation (*c* = 1.26, CHCl$_3$): $[\alpha]^{20}_{D}$ = +33, $[\alpha]^{20}_{578}$ = +35, $[\alpha]^{20}_{546}$ = +40, $[\alpha]^{20}_{436}$ = +79, $[\alpha]^{20}_{365}$ = +148.

General Procedure III [(η^4-1,5-Cyclooctadiene)oxazoline-rhodium(I) Complexes]: To a stirred solution of 1.0 mmol of oxazoline in dry CH$_2$Cl$_2$ (6 ml) were added 247 mg (0.5 mmol) of [Rh(cod)Cl]$_2$ in dry CH$_2$Cl$_2$ (6 ml) under nitrogen. The resulting dark red solution was stirred for 2 h, then excess (ca. 1.4 mmol) of solid NH$_4$PF$_6$ or NaBF$_4$ (for **26**) was added. After stirring for another 1−2 h, the inorganic salts were filtered off and rinsed with 2 ml of dry CH$_2$Cl$_2$. The filtrate containing the complex was treated as described for the individual compounds.

(−)-(η^4-1,5-Cyclooctadiene){2-[4-(R)-phenyloxazolin-2-yl]-4,4′-bipyridine-N,N′′}rhodium(I) Hexafluorophosphate (**24**): From oxazoline **3d**. By adding 6 ml of dry PE to the filtrate and cooling to −20°C 607 mg (0.9 mmol, 92%) of **24** were obtained. Red microcrystalline solid, m.p. > 245°C (dec.). − ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.72−1.80 (m, 2 H, cod-H$_{endo}$-3, H$_{endo}$-8), 1.89−1.94 (m, 2 H, cod-H$_{endo}$-4, H$_{endo}$-7), 2.19−2.28 (m, 2 H, cod-H$_{exo}$-3, *H*$_{exo}$-8), 2.43−2.52 (m, 2 H, cod-H$_{exo}$-4, H$_{exo}$-7), 3.93−4.00 (m, 2 H, cod-H-1, H-2), 4.41−4.48 (m, 2 H, cod-H-5, H-6), 4.67 (m, 1 H, Ox-C*H*?), 5.33 (m, 2 H, Ox-C*H*$_2$?), 7.31−7.33 (m, 2 H, *m*-Ph-*H*), 7.41−7.47 (m, 3 H, *o*- and *p*-Ph-*H*), 7.65 (AA′BB′, 2 H, H-3′, H-5′), 7.98 ("d", ^3J = 5.6 Hz, 1 H, H-6), 8.06 (dd, ^3J = 5.6 Hz, ^4J = 2.0 Hz, 1 H, H-5), 8.17 (dd, ^4J = 2.0 Hz, ^5J = 0.5 Hz, 1 H, H-3), 8.75 (AA′BB′, 2 H, H-2′, H-6′). − MS (FD, CH$_2$Cl$_2$): *m/z* = 512 [K$^+$]. HR-MS (FAB, *m*-NBA + 1% TFA): *m/z* (%) = 512 (100%) [K$^+$], calcd. for C$_{27}$H$_{27}$N$_3$ORh 512.1209, found 512.1215, diff. +0.6 mmu/1.2 ppm. − IR (KBr): ṽ (cm^{-1}) = 2985/2950/2885/2840 w (CH), 1645 w (C=N), 840 vs, 555 s (PF). − Optical rotation (*c* = 0.38, MeOH): $[\alpha]^{22}_{D}$ = −6.6, $[\alpha]^{22}_{578}$ = −6.6, $[\alpha]^{22}_{546}$ = −15.

(+)-(η^4-1,5-Cyclooctadiene){2-[4-(S)-benzyloxazolin-2-yl]-4,4′-bipyridine-N,N′′}rhodium(I) Hexafluorophosphate (**25**): From oxazoline **3e**. The filtrate was evaporated, the residue was dissolved in dry acetone (5 ml) and dry ether (10 ml) was added. Crystallisation at −20°C yielded 550 mg (0.8 mmol, 82%) of **25**. Red needles, m.p. > 205°C (dec.). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.82−2.02 (m, 2 H, cod-H$_{endo}$-3, H$_{endo}$-8), 2.09−2.16 (m, 2 H, cod-H$_{endo}$-4, H$_{endo}$-7), 2.35−2.44 (m, 2 H, cod-H$_{exo}$-3, H$_{exo}$-8), 2.58−2.74 (m, 2 H, cod-H$_{exo}$-4, H$_{exo}$-7), 2.84 (dd, ^2J = 13.9 Hz, ^3J = 8.1 Hz, 1 H, C*H*$_A$H$_B$Ph), 3.03 (dd, ^2J = 13.9 Hz, ^3J = 4.4 Hz, 1 H, CH$_A$*H*$_B$Ph), 4.36−4.46 (m, 3 H, Ox-C*H*? and cod-H-1, H-2), 4.64−4.81 (m, 4 H, Ox-C*H*$_2$? and cod-H-5, H-6), 7.22−7.35 (m, 5 H, Ph-*H*), 7.60 (AA′BB′, 2 H, H-3′, H-5′), 7.98 ("s", 1 H, H-3), 8.02 ("d", ^3J ≈ 5.4 Hz, 1 H, H-6), 8.08 ("d", ^3J ≈ 5.4 Hz, 1 H, H-5), 8.76 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 29.7 (cod-C-3, C-8), 31.3 (cod-C-4, C-7), 40.5 (*C*H$_2$Ph), 63.9 (Ox-*C*H), 76.4 (Ox-*C*H$_2$), 82.6 (d, $^1J_{\mathrm{Rh,C}}$ = 12.9 Hz, cod-C-1, C-2), 85.0 (d, $^1J_{\mathrm{Rh,C}}$ = 12.6 Hz, cod-C-5, C-6), 121.5 (C-3′, C-5′), 123.3 (C-3), 127.5 (*p*-Ph-*C*), 127.9 (C-5), 129.0/129.6 (*o*- and *m*-Ph-*C*), 134.8 (qC of Ph), 142.2/145.6/150.1 (qC), 150.2 (C-6), 151.2 (C-2′, C-6′), 171.1 (*C*=N). − MS (FAB, CH$_2$Cl$_2$/*m*-NBA): *m/z* = 526 [K$^+$], 418 [K$^+$ − cod]. − IR (KBr): ṽ (cm^{-1}) = 2950/2925/2890/2840 w (CH), 1650 w (C=N), 845 vs, 565 s (PF). − C$_{28}$H$_{29}$F$_6$N$_3$OPRh (671.43): calcd. C 50.09, H 4.35, N 6.26; found C 49.84, H 4.47, N 6.03. − Optical rotation (*c* = 0.29, MeOH): $[\alpha]^{26}_{D}$ = +63, $[\alpha]^{26}_{578}$ = +52, $[\alpha]^{26}_{546}$ = +66.

(+)-(η^4-1,5-Cyclooctadiene){2-[4-(S)-benzyloxazolin-2-yl]-4,4′-bipyridine-N,N′′}rhodium(I) Tetrafluoroborate (**26**): From oxazoline **3e**. The filtrate was evaporated, the residue was dissolved in dry acetone (5 ml) and dry ether (5 ml) was added. Crystallisation at −20°C yielded 540 mg (0.9 mmol, 88%) of **26**. Red microcrystalline solid, m.p. > 150°C (dec.). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.79−1.93 (m, 2 H, cod-H$_{endo}$-3, H$_{endo}$-8), 2.04−2.17 (m, 2 H, cod-H$_{endo}$-4, H$_{endo}$-7), 2.30−2.44 (m, 2 H, cod-H$_{exo}$-3, H$_{exo}$-8), 2.59−2.74 (m, 2 H, cod-H$_{exo}$-4, H$_{exo}$-7), 2.87 (dd, ^2J = 13.9 Hz, ^3J = 7.6 Hz, 1 H, C*H*$_A$H$_B$Ph), 3.03 (dd, ^2J = 13.9 Hz, ^3J = 4.5 Hz, 1 H, CH$_A$*H*$_B$Ph), 4.40−4.51 (m, 3 H, Ox-C*H*? and cod-H-1, H-2), 4.59−4.86 (m, 4 H, Ox-C*H*$_2$? and cod-H-5, H-6), 7.21−7.35 (m, 5 H, Ph-*H*), 7.65 (AA′BB′, 2 H, H-3′, H-5′), 7.99 ("s", 1 H, *H*-3), 8.14 ("d", ^3J ≈ 5.5 Hz, 1 H, H-6), 8.23 ("d", ^3J ≈ 4.0 Hz, 1 H, H-5), 8.77 (AA′BB′, 2 H, H-2′, H-6′). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 29.7 (cod-C-3, C-8), 31.3 (cod-C-4, C-7), 40.5 (*C*H$_2$Ph), 63.9 (Ox-*C*H), 76.5 (Ox-*C*H$_2$), 82.6 (d, $^1J_{\mathrm{Rh,C}}$ = 12.7 Hz, cod-C-1, C-2), 85.1 (d, $^1J_{\mathrm{Rh,C}}$ = 12.6 Hz, cod-C-5, C-6), 121.5 (C-3′, C-5′), 123.1 (C-3), 127.5 (*p*-Ph-*C*), 128.2 (C-5), 129.0/129.6 (*o*- and *m*-Ph-*C*), 134.8 (*qC* of Ph), 142.1/145.4/150.0 (qC), 150.7 (C-6), 151.2 (C-2′, C-6′), 171.2 (*C*=N). − MS (FD, CH$_2$Cl$_2$): *m/z* = 526 [K$^+$]. − IR (KBr): ṽ (cm^{-1}) = 2945/2915/2880/2835 w (CH), 1645 w (C=N), 1085/1060 vs (BF). − C$_{28}$H$_{29}$BF$_4$N$_3$ORh • H$_2$O (631.29): calcd. C 53.27, H 4.95, N 6.65; found C 53.36, H 4.79, N 6.43. Optical rotation (*c* = 0.58, MeOH): $[\alpha]^{23}_{D}$ = +73°, $[\alpha]^{23}_{578}$ = +70°, $[\alpha]^{23}_{546}$ = +83°.

(+)-(η^4-1,5-Cyclooctadiene){4-(S)-(2-methylpropyl)-2-(4-phenylpyridin-2-yl)oxazoline-N,N′}rhodium(I) Hexafluorophosphate (**27**): From oxazoline **23a**. By adding 12 ml of dry ether to the filtrate and cooling to −20°C a bright orange solid (475 mg, 0.7 mmol, 75%) was obtained. Slow diffusion of ether into a CHCl$_3$ solution yielded **27** as red needles, m.p. > 185°C (dec.). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.93 (d, ^3J = 6.5 Hz, 3 H, C*H*$_3$), 0.98 (d, ^3J = 6.5 Hz, 3 H, C*H*$_3$′), 1.40−1.70 (m, 3 H, C*H*$_2$C*H*Me$_2$), 1.89 (m, 2 H, cod-H$_{endo}$-3, H$_{endo}$-8), 2.05−2.20 (m, 2 H, cod-H$_{endo}$-4, H$_{endo}$-7), 2.43 (m, 2 H, cod-H$_{exo}$-3, H$_{exo}$-8), 2.58−2.82 (m, 2 H, cod-H$_{exo}$-4, H$_{exo}$-7), 4.16−4.27 (m, 1 H, Ox-C*H*?), 4.30−4.80 (m, 4 H, cod-olefinic-*H*), 4.58 (dd, ^2J ≈ 9.0 Hz, ^3J = 5.9 Hz, 1 H, Ox-C*H*$_E$H$_Z$?), 4.96 ("t", ^2J = ^3J = 9.0 Hz, 1 H, Ox-CH$_E$*H*$_Z$?), 7.48−7.56 (m, 3 H, Ph-*H*), 7.66−7.73 (m, 2 H, Ph-*H*), 7.89−7.94 (m, 1 H, Py-*H*), 7.99−8.02 (m, 2 H, Py-*H*). − ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 21.5 (*C*H$_3$), 23.7 (*C*H$_3$′), 25.3 (*C*HMe$_2$), 29.3/30.4/31.2 (br, cod-*C*H$_2$), 44.1 (*C*H$_2$CHMe$_2$), 62.1 (d, $^2J_{\mathrm{Rh,C}}$ = 2.1 Hz, Ox-*C*H), 77.3 (Ox-*C*H$_2$), 82.5/83.1/85.9 (br, cod-*C*H), 123.0 (d,

$^3J_{Rh,C}$ = 0.9 Hz, C-3), 127.2 (d, $^3J_{Rh,C}$ = 0.9 Hz, C-5), 127.4/129.7 (*o*- and *m*-Ph-*C*), 131.3 (*p*-Ph-*C*), 134.6 (qC of Ph), 145.2 (qC), 149.6 (d, $^2J_{Rh,C}$ = 0.6 Hz, *C*-*6*), 153.0 (qC), 170.9 (d, $^2J_{Rh,C}$ = 1.4 Hz, *C*=N). − MS (FAB, CH_2Cl_2/*m*-NBA): *m*/*z* = 491 [K^+]. − IR (KBr): ṽ (cm^{-1}) = 2965/2885 w (CH), 1645 w (C=N), 840 vs, 555 s (PF). − $C_{26}H_{32}F_6N_2OPRh$ (636.42): calcd. C 49.07, H 5.07, N 4.40; found C 49.07, H 5.25, N 4.43. − Optical rotation (*c* = 0.46, MeOH): $[\alpha]^{22}_D$ = +83, $[\alpha]^{22}_{578}$ = +88, $[\alpha]^{22}_{546}$ = +87.

X-ray Structure Analysis of **27**: $C_{26}H_{32}F_6N_2OPRh$ (636.42); crystal dimensions 0.32 × 0.13 × 0.13 mm^3; crystal system tetragonal; space group $I4_1$ (80); unit cell dimensions: $a = b = 38.1211(1)$, $c = 7.5213(1)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 10930.1(2)$ Å^3, $Z = 16$; density $d_{calcd.}$ = 1.55 g/cm^3, μ(Mo-K_α) = 0.75 mm^{-1}, T = 293(2) K; θ range for data collection 1.5−25.6°; total no. of reflections 41381, independent reflections 9353 (R_{int} = 0.0523), observed reflections with $I > 2\sigma(I)$ 7346; data/restraints/parameters: 9349/29/691; goodness-of-fit on F^2 = 1.11; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.044, $wR2$ = 0.092; absolute structure parameter: −0.05(3). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-407778.

(+)-Di(η^4-1,5-cyclooctadiene){2,2'-bis[4-(R)-phenyloxazolin-2-yl]-4,4'-bipyridine-N,N'',N',N'''}dirhodium(I) Bis(hexafluorophosphate) (**26**): To a stirred solution of 150 mg (0.33 mmol) of **15** in dry CH_2Cl_2 (4 ml) were added 163 mg (0.33 mmol) of $[Rh(cod)Cl]_2$ in CH_2Cl_2 (5 ml) under nitrogen. The resulting dark red solution was stirred for 1.5 h, then solid NH_4PF_6 (165 mg, 1.0 mmol) was added. After stirring for another 1.5 h, the inorganic salts were filtered off and rinsed with 2 ml of CH_2Cl_2. The filtrate was evaporated and the residue was dissolved in dry acetone (5 ml). Adding dry ether (5 ml) and subsequent cooling to −20°C yielded 215 mg (0.2 mmol, 56%) of **26**. Dark red solid, m.p. > 110°C (dec.). − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.60−2.00 (m, 8 H, cod-H_{endo}), 2.10−2.60 (m, 8 H, cod-H_{exo}), 3.96 (m, 4 H, cod-H-1, H-2, H-1', H-2'), 4.42 (m, 4 H, cod-H-5, H-6, H-5', H-6'), 4.62 (m, 2 H, Ox-C*H*?), 5.10−5.50 (m, 4 H, Ox-CH_2?), 7.10−7.50 (m, 10 H, Ph-*H*), 8.26 and 8.51 (m, 6 H, Py-*H*). − MS (FD, CH_2Cl_2): *m*/*z* = 1013 [M^+ − PF_6], 657 [Rh(cod)**15**$^+$], 434 = 868/2 [K^{++}]. − HR-MS (FAB, *m*-NBA + 1% TFA): *m*/*z* (%) = 657 (100%) [Rh(cod)**15**$^+$], calcd. for $C_{36}H_{34}N_4O_2Rh$ 657.1737, found 657.1713, diff. −2.4 mmu/3.7 ppm. − IR (KBr): ṽ (cm^{-1}) = 3060/3030/2940/2915/2875/2830 w (CH), 1645 w (C=N), 840 vs, 555 s (PF). − Optical rotation (*c* = 0.45, acetone): $[\alpha]^{23}_D$ = +16, $[\alpha]^{23}_{578}$ = +12, $[\alpha]^{23}_{546}$ = −3.3.

☆ Dedicated to Professor *H. Nöth* on the occasion of his 70th birthday.

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