SYNTHESIS OF 2,2′-BIPYRIDINES WITH AXIALLY CHIRAL 1,1′-BINAPHTHALENE UNITS

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Dedicated to Professor Milan Kratochvíl on the occasion of his 75th birthday.

Synthesis of a series of novel 2,2′-bipyridine-based ligands bearing the axially chiral 2,2′-dialkoxy-1,1′-binaphthalene units is presented. The oxydimethylene, amidomethylene and amido spacers have been utilised to link the 3 or 3,3′ positions of the binaphthalene skeleton with the 6 or 6,6′ positions of the 2,2′-bipyridine moieties. The ligands have been synthesised in both racemic and enantiomerically pure *R* forms.

Key words: N-Ligands; Chiral ligands; Axial chirality; Bipyridines; Biaryls; Binaphthalenes; Copper complexes.

2,2′-Bipyridines have been known for a long time as excellent ligands for cation complexation. Coordination chemistry of their complexes has been thoroughly studied. Thanks to well defined geometry of the coordination sphere of the metal and unique spectroscopic and electrochemical properties of the complexes, 2,2′-bipyridines became very popular structural units in supramolecular chemistry and molecular architecture[1]. The 2,2′-bipyridine motif has been incorporated many times into the ligands that in the presence of the metal ions assemble into helical supermolecules[2]. If the 2,2′-bipyridine-based ligand is chiral, then one of its stereoisomers could form only one stereoisomer of the superstructure (*e.g.* right-handed helix), provided that the latter is also chiral. In general, the chirality of the assembled superstructure is the result of the chirality within the molecular units and also the specific orientations of intermolecular interactions. Stereochemistry of the self-assembly processes is a challenging area of current chemistry.

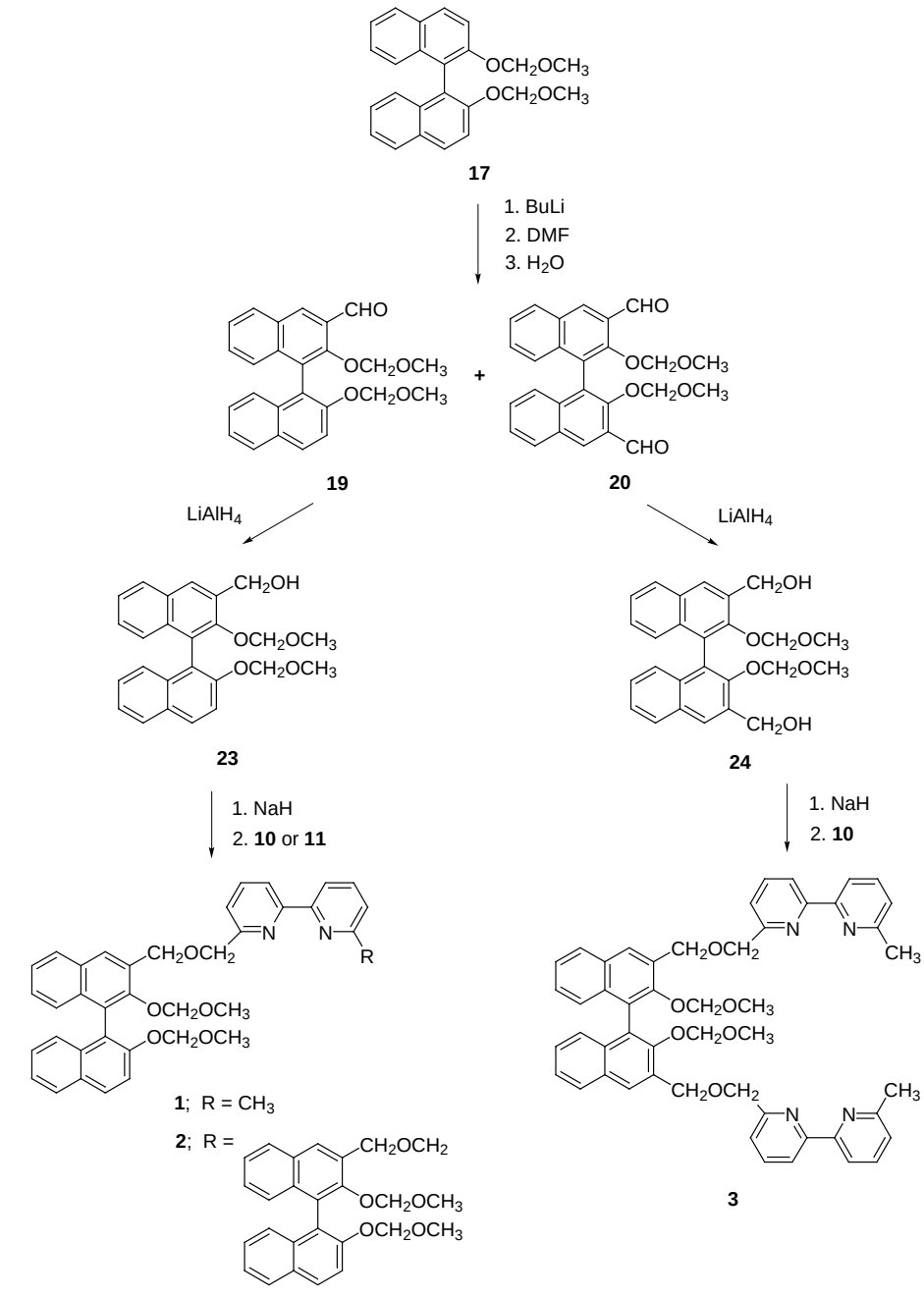
In this paper we report on the synthesis of novel 2,2′-bipyridine ligands with the axially chiral 2,2′-disubstituted 1,1′-binaphthalene units appended to the 6 or 6,6′ positions of the bipyridine moiety. The atropisomeric binaphthalene unit has been chosen because of its highly stable chiral configuration. 2,2′-Disubstituted 1,1′-binaphthalenes have been extensively used to control many asymmetric processes and have demonstrated outstanding chiral discrimination properties[3]. Our new ligands can be utilised not only in the supramolecular stereochemical studies but also as ligands in catalytic asymmetric reactions. Several 2,2′-bipyridine-based chiral ligands have been successfully used in enantioselective hydrosilylation of aromatic ketones[4], alkylation of aldehydes with diethylzinc[5], cyclopropanation[6] or palladium-catalysed allylic substitution[7].

RESULTS AND DISCUSSION

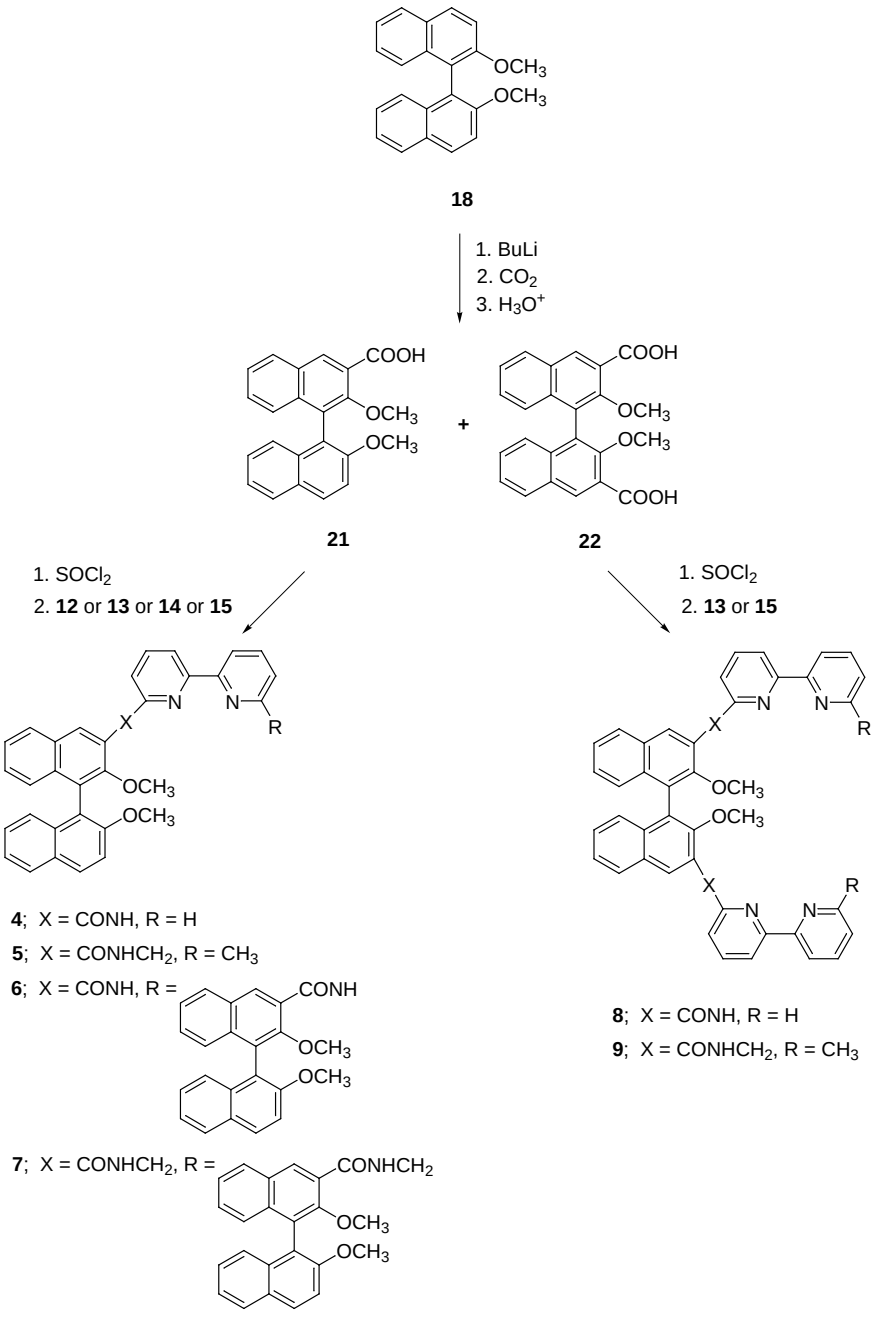
A series of novel 2,2′-bipyridine-based ligands **1**–**9** has been synthesised (Schemes 1 and 2). The ligands were prepared in both racemic and enantiomerically pure *R* forms. The ligands containing the oxydimethylene spacer between the bipyridine and binaphthol units (**1**–**3**) were prepared by the Williamson reaction from the hydroxymethyl derivatives of 1,1′-binaphthalene-2,2′-diol and the bromomethyl derivatives of 2,2′-bipyridine. The compounds with the amide spacer were synthesised from the 1,1′-binaphthalene-2,2′-diol-based acids and the amino (ligands **4**, **6** and **8**) or aminomethyl derivatives (ligands **5**, **7** and **9**) of 2,2′-bipyridine.

The 2,2′-bipyridine-based building blocks, *i.e.* 6-bromomethyl-6′-methyl-2,2′-bipyridine[8] (**10**), 6,6′-bis(bromomethyl)-2,2′-bipyridine[8] (**11**), 6,6′-bis-(aminomethyl)-2,2′-bipyridine[9] (**12**), 6-amino-2,2′-bipyridine[10] (**13**) and 6,6′-diamino-2,2′-bipyridine[11] (**14**), were prepared according to the literature procedures. Analogously to the synthesis of **12** (ref.[9]), 6-aminomethyl-6′-methyl-2,2′-bipyridine (**15**) was prepared from **10** using the Delépine reaction.

Synthetic methodology for the preparation of optically active binaphthol-based precursors started from 1,1′-binaphthalene-2,2′-diol[12] (**16**) whose resolution to enantiomers was described several times[13]. We have chosen the resolution method[13a] that utilises enantioselective formation of solid clathrate of (*R*)-**16** with *N*-benzylcinchonidinium chloride. Major advantage of this method is its simplicity, however, only the *R* isomer is produced in sufficient optical purity. Later, at the final stages of our work, the improved version of this resolution method has been published[13b] allowing to produce both *R* and *S* enantiomers of **16**.

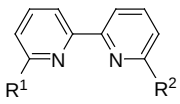

OCH2OCH3
OCH2OCH3
17
1. BuLi
2. DMF
3. H2O
CHO
OCH2OCH3
OCH2OCH3
+
CHO
OCH2OCH3
OCH2OCH3
CHO
19
20
LiAlH4
LiAlH4
CH2OH
OCH2OCH3
OCH2OCH3
CH2OH
OCH2OCH3
OCH2OCH3
CH2OH
23
24
1. NaH
2. 10 or 11
1. NaH
2. 10
N
N
R
CH2OCH2
OCH2OCH3
OCH2OCH3
1; R = CH3
2; R =
CH2OCH2
OCH2OCH3
OCH2OCH3
N
N
CH3
CH2OCH2
OCH2OCH3
OCH2OCH3
CH2OCH2
CH3
N
N
3

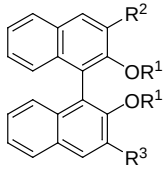
SCHEME 1


OCH3
OCH3
18
1. BuLi
2. CO2
3. H3O+
COOH
OCH3
OCH3
+
COOH
OCH3
OCH3
COOH
21
22
1. SOCl2
2. 12 or 13 or 14 or 15
1. SOCl2
2. 13 or 15
X
N
N
R
OCH3
OCH3
4; X = CONH, R = H
5; X = CONHCH2, R = CH3
6; X = CONH, R =
CONH
OCH3
OCH3
7; X = CONHCH2, R =
CONHCH2
OCH3
OCH3
8; X = CONH, R = H
9; X = CONHCH2, R = CH3

SCHEME 2

Our synthetic strategy towards the optically active binaphthalene precursors utilised *ortho* lithiation of 2,2′-bis(methoxymethoxy)- or 2,2′-dimethoxy-1,1′-binaphthalene (**17** or **18**) as a method of introduction of a functional group into the 3 and 3,3′ positions of the binaphthalene skeleton[14]. Lithiation was carried out using one equivalent of butyllithium followed by the reaction with dimethylformamide or carbon dioxide to give a





	R^1	R^2
10	CH_2Br	CH_3
11	CH_2Br	CH_2Br
12	CH_2NH_2	CH_2NH_2
13	H	NH_2
14	NH_2	NH_2
15	CH_2NH_2	CH_3

	R^1	R^2	R^3
16	H	H	H
25	H	COOH	COOH
26	H	$COOCH_3$	H
27	H	$COOCH_3$	$COOCH_3$
28	CH_3	$COOCH_3$	H
29	CH_3	$COOCH_3$	$COOCH_3$
30	CH_2OCH_3	$COOCH_3$	H
31	CH_2OCH_3	$COOCH_3$	$COOCH_3$

statistical mixture of aldehydes **19** and **20**, or acids **21** and **22**, respectively. The individual compounds were isolated from the mixtures by column chromatography. Aldehydes **19** and **20** were further reduced to alcohols **23** and **24** using lithium aluminium hydride. Alternatively, alcohols **23** and **24** could be prepared from 3-lithio intermediates by reaction with formaldehyde[15]. However, this method proved to be irreproducible in our hands giving alcohols in significantly lower yields. The methoxymethyl (MOM) group was chosen to protect the phenolic hydroxyl groups since its oxygen atom participates in chelation of lithium and in this way facilitates the *ortho* lithiation step. However, the MOM group is not stable under acidic conditions. At the attempt to prepare 3-carboxylic acid from **17**, the deprotection of phenolic hydroxyles occurred even under careful acidification of the reaction mixture using a solution of citric acid. For this reason, the methyl group was used as a protecting group in the acid preparations despite its lower reactivity in the *ortho* lithiation reaction. We did not in-

tend to remove the protecting groups at the final stages of the syntheses in order that the final ligands would contain only the bipyridine nitrogens as ligating sites for metal complexations. Column chromatography isolation of highly polar diacid **22** proved to be time-consuming and ineffective. Thus, the optically pure (*R*)-**22** was also prepared by a known synthetic procedure[16] starting from (*R*)-2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylic acid[17] (**25**).

The synthetic route was tested first on racemic compounds, then the optimised reaction conditions were used in preparation of optically active compounds possessing the *R* enantiomer of the binaphthalene moiety. Simultaneously, racemic binaphthalene building blocks were synthesised starting from esters **26** and **27** (ref.[18]). First, the phenolic hydroxyl groups were protected giving esters **28** (ref.[16b]), **29** (refs[16b,19]), **30** and **31**, then the ester groups were transformed either to carboxyl groups by alkaline hydrolysis[16a,20] or to hydroxymethyl groups by lithium aluminium hydride reduction. In this way, racemic compounds **21** (ref.[16b]) and **22** (ref.[16a]), and **23** and **24**, respectively, were obtained in high yields.

At the later stages of our experimental work, a paper presenting the preparation of *S* enantiomers of dialdehyde **20** and diol **24** *via ortho* lithiation was published[21]. The synthetic procedure slightly differs from ours as the published work aimed at obtaining of the 3,3′-disubstituted products only. However, the published analytical data of (*S*)-**20** and (*S*)-**24** (ref.[21]) differ from those of (*R*)-**20** and (*R*)-**24** obtained by us. We believe that we were able to obtain the compounds, in particular **20**, in higher purity. It is noteworthy that the compounds are not entirely stable: colourless aldehydes **19** and **20** gradually changed colour to yellow upon standing. Simultaneously, we observed significant changes in optical rotation values upon standing of samples, *e.g.* for (*R*)-**20**, $[\alpha]_D$ varied from +6.8 (measured immediately after purification) to +24.5. The instability was also observed in the case of alcohol **23**. At the attempt to crystallise it from boiling toluene and after a long-term standing, the formation of three by-products arising from the deprotection of the phenolic OH groups as well as of the migration of MOM group from the phenolic hydroxyl to the benzylic one was observed. On the other hand, the final bipyridine-based ligands bearing the MOM groups are sufficiently stable as they do not contain the acidic hydrogens.

The final ligands possessing the oxydimethylene spacer units (**1**–**3**) were prepared by the Williamson reaction. Sodium salts of 3- or 3,3′-hydroxymethyl substituted binaphthalenes (**23**, **24**) prepared using sodium hydride were immediately reacted with bromomethyl derivatives of bipyridine (**10**, **11**) to give the desired products **1**, **2** or **3** in high yields. For the preparation

of the ligands having the amide spacer, a standard procedure utilising acid chloride as an intermediate was used. The binaphthalene acids were transformed to their chlorides by reaction with thionyl chloride. The acid chlorides were not purified but used immediately in the next steps. In the case of ligand **5**, three synthetic procedures were tried. In the first one, acid chloride was used as an intermediate; in the second one, activated ester was prepared from acid **21** by reaction with *N*-hydroxy- succinimide in the presence of *N*,*N*′-dicyclohexylcarbodiimide and then reacted with amine **15**; the third one utilised direct coupling of acid **21** with amine **15** in the presence of *N*,*N*′-dicyclohexylcarbodiimide. All three methods gave ligand **5** in comparable yields (76, 63 and 68%, respectively). Since purification of the product obtained by the first method was less demanding and the yield of the product was slightly higher, we have decided to use the acid chloride method for the preparations of all ligands having the amide spacer.

Compound (*R*,*R*)-**7** forms a crystalline toluene clathrate (stoichiometry ligand : toluene = 1 : 2) whose structure was determined by X-ray diffraction[22]. The crystal consists of asymmetric units containing two independent molecules of (*R*,*R*)-**7**, which are mainly associated *via* π–π interactions, and four toluene molecules.

Preliminary cation complexation studies (using known procedures[23]) have revealed that novel ligands **1**, **4** and **5** form $Cu^{I}(ligand)_2$ complexes possessing the tetrahedral arrangements of the ligands around a metal centre. Whilst the copper(I) complexes of **1** and **5** proved to be sufficiently stable, that of **4** exhibited a strong tendency to oxidation to the copper(II) complex. This is likely due to the close proximity of the amide groups, which could contribute to the cation binding preferring the planar copper(II) complex. As the ligands **1**, **4** and **5** are unsymmetrically substituted 2,2′-bipyridines, the copper atom becomes a new chiral centre in the tetrahedral complexes. In NMR spectra of the $Cu^{I}(ligand)_2$ complexes of (*R*)-**1** and (*R*)-**5** the presence of both possible diastereomers of the complexes was observed in the ratios approximately 4 : 5 indicating that asymmetric induction occurs only to a low extent during the complexation step. Complexation behaviour of the other novel ligands is a more complex problem which will be a subject of future research.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. NMR spectra were measured on a Varian Gemini 300HC spectrometer (^1H at 300.07 Hz and ^{13}C at 75.46 Hz) with tetramethylsilane as an internal standard. Coupling constants, *J*, are given in Hz. Mass spectra were recorded on a ZAB-EQ (VG Analytical) instrument using the EI (70 eV) or FAB

(Xe, 8 kV) techniques. IR spectra (ν in cm^{-1}) were obtained on a Nicolet 750 FT IR spectrometer. Optical rotations were determined on a JASCO DIP370 digital polarimeter or a Perkin–Elmer 241 polarimeter. Specific optical rotations, $[\alpha]_D$, are given in deg cm^3 g^{-1} dm^{-1} and concentrations, *c*, in g/100 ml. Thin-layer chromatography (TLC) was carried out on Silufol-UV 254 (Kavalier), Polygram SIL-G/UV254 (Macherey–Nagel) or Polygram ALOX-N/UV_{254} (Macherey–Nagel) plates. HPLC analyses were performed on a ECOM chromatograph with a UV detector operating at 254 nm. Enantiomeric purity was tested on a column with chiral stationary phase Chiralpak OP+ (Daicel) using methanol as a mobile phase; retention times, t_R, are given in minutes. Preliminary complexation studies were carried out with $Cu[CH_3CN]_4ClO_4$ in acetonitrile and chloroform using a standard UV or NMR spectrometric titration protocol[23].

6-Aminomethyl-6′-methyl-2,2′-bipyridine (**15**)

Hexamethylenetetramine (1.37 g, 9.77 mmol) was dissolved in CH_2Cl_2 (25 ml) and the mixture heated to reflux. Solution of **10** (ref.[8]; 2.31 g, 8.78 mmol) in CH_2Cl_2 (25 ml) was added dropwise and the resulting mixture was refluxed for 3 h. The reaction mixture was left standing overnight at room temperature. The white crystalline salt was isolated, washed with CH_2Cl_2 and dried. Then it was suspended in a mixture of ethanol (46 ml) and concentrated HCl (7 ml), heated until the salt dissolved and then left standing overnight at room temperature. The white crystals of hexamethylenetetramine hydrochloride were filtered off and the mother liquor was evaporated to dryness. The residue was suspended in CH_2Cl_2 (50 ml) and water (30 ml); the mixture was alkalinised to pH 13 using 10 M NaOH, thoroughly shaken for 5 min and then the layers were separated. The water layer was additionally extracted with CH_2Cl_2 (2 × 10 ml). The combined CH_2Cl_2 extracts were dried over $MgSO_4$ and evaporated to dryness. Amine **15** was obtained in 73.1% yield (1.28 g, 6.42 mmol) as a colourless oil, that solidified upon standing. For $C_{12}H_{13}N_3$ (199.3) calculated: 72.34% C, 6.58% H, 21.09% N; found: 72.41% C, 6.54% H, 20.83% N. ^{1}H NMR ($CDCl_3$): 8.27 d, 1 H, *J* = 7.8 (ArH); 8.23 d, 1 H, *J* = 7.8 (ArH); 7.75 t, 1 H, *J* = 7.8 (ArH); 7.72 t, 1 H, *J* = 7.8 (ArH); 7.24 d, 1 H, *J* = 7.3 (ArH); 7.16 d, 1 H, *J* = 7.7 (ArH); 4.03 s, 2 H (CH_2); 2.63 s, 3 H (CH_3); 2.01 br s, 2 H (NH_2). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 137.63, 123.86, 121.71, 119.89, 118.78, 25.32; CH_2 and C: 161.49, 158.55 156.56, 156.32, 48.30. FAB-MS (matrix: glycerol–thioglycerol), *m/z*: 200 ($[M + H]^+$).

(*R*)-(+)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthalene [(*R*)-**17**]

Compound (*R*)-**17** was obtained in 88% yield using the literature procedure for the preparation of racemic **17** (ref.[24]). HPLC analysis on a Chiralpak OP+ column showed only a single peak with t_R = 22 (racemate: t_{R1} = 22, t_{R2} = 34). M.p. 101–102 °C (CH_2Cl_2–hexane); (ref.[25]: 99–100 °C, ref.[21]: *S* enantiomer 95.1–96.6 °C). $[\alpha]_D^{20}$ +98.2 (*c* 0.994, THF); (ref.[25]: $[\alpha]_D^{23}$ +94.0 (*c* 1.0, $CHCl_3$), ref.[21]: *S* enantiomer $[\alpha]_D$ –79.0 (*c* 0.990, THF)). ^{1}H NMR ($CDCl_3$): 7.85–8.00 m, 4 H (ArH); 7.59 d, 2 H, *J* = 9.0 (ArH); 7.14–7.39 m, 6 H (ArH); 4.99 and 5.09 AB-system, 4 H, J_{AB} = 6.8 (CH_2); 3.15 s, 6 H (CH_3).

(*R*)-(+)-2,2′-Dimethoxy-1,1′-binaphthalene [(*R*)-**18**]

Optically pure (*R*)-**18** was prepared according to a literature procedure[26] in 91% yield. HPLC analysis on a Chiralpak OP+ column showed only a single peak with t_R = 24 (racemate: t_{R1} =

24, t_{R2} = 46). M.p. 230–231 °C (CH_2Cl_2); (ref.[26]: 224–225 °C, ref.[20]: 184–185 °C, ref.[27]: 230–232 °C). $[\alpha]_D^{20}$ +70.7 (*c* 1.032, THF), $[\alpha]_D^{20}$ +162.2 (*c* 1.080, anisole); (ref.[26]: $[\alpha]_D^{25}$ +72.8 (*c* 1.2, THF), ref.[20]: $[\alpha]_D^{21}$ +79.5 (*c* 1.0, THF), ref.[27]: $[\alpha]_D$ +151 (*c* 1, anisole)). For $C_{22}H_{18}O_2$ (314.4) calculated: 84.05% C, 5.77% H; found: 83.98% C, 5.77% H. ^{1}H NMR ($CDCl_3$): 7.99 d, 2 H, *J* = 9.0 (ArH); 7.88 d, 2 H, *J* = 8.2 (ArH); 7.48 d, 2 H, *J* = 9.0 (ArH); 7.33 m, 2 H (ArH); 7.23 m, 2 H (ArH); 7.13 d, 2 H, *J* = 8.2 (ArH); 3.78 s, 6 H (CH_3O).

(*R*)-(+)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthalene-3-carbaldehyde [(*R*)-**19**] and
(*R*)-(+)-2,2′-Bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-dicarbaldehyde [(*R*)-**20**]

A solution of (*R*)-**17** (2.0 g, 5.34mmol) in dry THF (40 ml) was placed into a carefully dried flask. The flask was repeatedly evacuated and purged with nitrogen. A solution of butyllithium in hexanes (1.8 mol l^{-1}, 3 ml, 5.40 mmol) was added through a septum using a syringe. The reaction mixture was stirred at room temperature for 1 h. Then dry dimethylformamide was added (2 ml) and stirring continued for 8 h. Water (5 ml) was carefully added, the mixture was stirred for another 10 min and then partitioned between $CHCl_3$ (100 ml) and water (50 ml). The layers were separated and the water layer was extracted with another portion of $CHCl_3$ (25 ml). The combined $CHCl_3$ extracts were washed with water (2 × 25 ml) and dried over $MgSO_4$. After solvent removal, the residue was subjected to column chromatography (silica gel; toluene–acetone from 99 : 1 to 97 : 3) to yield 50.2% of (*R*)-**19** (1.08 g, 2.68 mmol) and 22.6% of (*R*)-**20** (0.52 g, 1.21 mmol).

(*R*)-**19**: M.p. 129–131 °C (toluene–hexane). $[\alpha]_D^{20}$ +102.2 (*c* 1.020, THF), $[\alpha]_D^{20}$ +104 (*c* 0.114, THF). For $C_{25}H_{22}O_5$ (402.4) calculated: 74.60% C, 5.51% H; found: 74.98% C, 5.42% H. ^{1}H NMR ($CDCl_3$): 10.60 s, 1 H (CHO); 8.58 s, 1 H (ArH); 7.10–8.10 m, 10 H (ArH); 5.06 and 5.17 AB-system, 2 H, J_{AB} = 7.0 (OCH_2O); 4.65 and 4.77 AB-system, 2 H, J_{AB} = 5.8 (OCH_2O); 3.17 s, 3 H (OCH_3); 3.01 s, 3 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 56.72, 57.84, 116.98, 124.90, 125.79, 126.48, 126.59, 127.53, 128.62, 129.89, 130.75, 130.88, 131.60, 191.62; CH_2 and C: 95.59, 100.80, 120.10, 127.40, 129.65, 130.27, 134.33, 137.58, 153.47, 154.39. EI-MS, *m/z* (rel.%): 402 ($M^{+\bullet}$, 28), 326 (21), 296 (42), 239 (17), 226 (8), 183 (2), 69 (2), 57 (3), 45 (100). IR (CCl_4): ν(C=O) 1 693.

(*R*)-**20**: M.p. 114–115 °C (toluene–hexane). $[\alpha]_D^{20}$ +6.8 (*c* 1.069, THF); (ref.[21]: *S* enantiomer $[\alpha]_D$ –43.9 (*c* 0.440, THF)). For $C_{26}H_{22}O_6$ (430.5) calculated: 72.55% C, 5.15% H; found: 72.84% C, 5.18% H. ^{1}H NMR ($CDCl_3$): 10.55 s, 2 H (CHO); 8.62 s, 2 H (ArH); 8,09 d, 2 H, *J* = 8.3 (ArH); 7.53 m, 2 H (ArH); 7.43 m, 2 H (ArH); 7.23 d, 2 H, *J* = 8.3 (ArH); 4.74 and 4.70 AB-system, 4 H, J_{AB} = 6.5 (OCH_2O); 2.89 s, 6 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 191.04, 132.85, 130.85, 130.16, 126.83, 126.67, 57.69; CH_2 and C: 154.55, 137.26, 130.65, 129.51, 126.48, 101.20. EI-MS, *m/z* (rel.%): 430 ($M^{+\bullet}$, 2), 386 (2), 354 (37), 339 (5), 324 (100), 309 (5), 297 (21), 283 (8), 269 (9), 239 (12), 226 (10), 183 (8). IR (CCl_4): ν(C=O) 1 695.

(*R*)-(+)-2,2′-Dimethoxy-1,1′-binaphthalene-3-carboxylic Acid [(*R*)-**21**] and
(*R*)-(+)-2,2′-Dimethoxy-1,1′-binaphthalene-3,3′-dicarboxylic Acid [(*R*)-**22**]

A solution of (*R*)-**18** (1.25 g, 3.98 mmol) in dry THF (50 ml) was placed into a carefully dried three-necked flask equipped with a magnetic stirrer, nitrogen inlet/outlet and septum. The flask was repeatedly evacuated and purged with nitrogen. A solution of butyllithium in hexanes (1.6 mol l^{-1}, 2.5 ml, 4.00 mmol) was added through a septum using a syringe. The reaction mixture was heated to 50 °C for 1 h and then cooled to –78 °C. A large excess of dry

CO_2 was bubbled through the reaction mixture. It was left to heat to room temperature spontaneously and stirred for another 1 h at this temperature. THF was distilled off and 0.5 M HCl (40 ml) and CH_2Cl_2 (40 ml) were added. The mixture was vigorously stirred for 30 min and the layers were separated. The water layer was extracted with CH_2Cl_2 (2 × 20 ml). The CH_2Cl_2 extracts were combined and dried over $MgSO_4$. The residue obtained upon CH_2Cl_2 removal was subjected to flash chromatography (silica gel; toluene–acetone 9 : 1). Unreacted (*R*)-**18** (28.0%, 0.35 g) eluted first, then (*R*)-**21** was obtained in 39.2% yield (0.56 g, 1.56 mmol). Futher elution using acetone gave (*R*)-**22** (19.9% yield, 0.32 g, 0.80 mmol).

(*R*)-**21**: $[\alpha]_D^{20}$ +89.2 (*c* 0.993, THF). For $C_{23}H_{18}O_4$ (358.4) calculated: 77.08% C, 5.06% H; found: 76.83% C, 4.96% H. ^{1}H NMR ($CDCl_3$): 8.93 s, 1 H (ArH); 8.07 m, 2 H (ArH); 7.92 d, 1 H, *J* = 7.7 (ArH); 7.51 m, 2 H (ArH); 7.39 m, 2 H (ArH); 7.30 m, 1 H (ArH); 7.19 d, 1 H, *J* = 8.8 (ArH); 7.09 d, 1 H, *J* = 8.7 (ArH); 3.83 s, 3 H (OCH_3); 3.50 s, 3 H (OCH_3). ^{13}C NMR, APT (DMSO-d_6): CH_3 and CH: 131.49, 129.93, 128.95, 128.08, 128.03, 126.57, 125.36, 124.69, 124.26, 123.41, 113.71, 61.01, 55.98; CH_2 and C: 167.52, 154.57, 153.57, 134.73, 133.22, 129.32, 128.52, 126.39, 126.19, 117.46. EI-MS, *m/z* (rel.%): 358 ($M^{+\bullet}$, 100), 312 (38), 239 (18), 28 (25). IR ($CHCl_3$): ν(C=O) 1 738, ν(OH) 3 200.

(*R*)-**22**: Analytical data were in accordance with those previously published[16].

(*R*)-(+)-3-Hydroxymethyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene [(*R*)-**23**]

To a stirred suspension of $LiAlH_4$ (0.10 g, 2.64 mmol) in dry THF (10 ml) a solution of (*R*)-**19** (0.61 g, 1.52 mmol) in dry THF (20 ml) was added dropwise at room temperature under nitrogen atmosphere. The mixture was stirred for another 15 min and the excess of hydride was decomposed by gradual addition of $MgSO_4 \cdot 7\ H_2O$. After the evolution of hydrogen ceased, small amount of water was added to complete the hydride decomposition. The solid was removed by filtration through a Celite pad, the solvent was evaporated and the residue was taken up to toluene (50 ml) and water (50 ml). The organic layer was separated, washed with water (2 × 20 ml) and dried over $MgSO_4$. The solvent was evaporated and the product dried *in vacuo*. The product (*R*)-**23** was obtained as a colourless oil in 96% yield (0.59 g, 1.46 mmol). $[\alpha]_D^{20}$ +91.6 (*c* 1.059, THF). For $C_{25}H_{24}O_5$ (404.5) calculated: 74.24% C, 5.98% H; found: 74.09% C, 5.89% H. ^{1}H NMR ($CDCl_3$): 8.01–7.98 m, 2 H (ArH); 7.93–7.85 m, 2 H (ArH); 7.60 d, 1 H, *J* = 9.1 (ArH); 7.45–7.34 m, 2 H (ArH); 7.31–7.21 m, 2 H (ArH); 7.19–7.11 m, 2 H (ArH); 5.13 and 5.05 AB-system, 2 H, J_{AB} = 7.0 (CH_2); 4.70 and 4.49 AB-system, 2 H, J_{AB} = 6.1 (CH_2); 3.46 br t, 1 H, *J* = 6.9 (OH); 3.26 s, 3 H (CH_3); 3.16 s, 3 H (CH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 130.55, 129.61, 128.53, 128.48, 127.37, 126.76, 126.18, 125.88, 125.70, 124.78, 117.03, 57.60, 56.52; CH_2 and C: 153.65, 153.27, 134.84, 134.31, 134.27, 131.58, 130.23, 126.02, 121.01, 99.83, 95.44, 62.64. EI-MS, *m/z* (rel.%): 404 ($M^{+\bullet}$, 22), 269 (100), 298 (84), 239 (82), 253 (62), 282 (60), 226 (35), 328 (21), 310 (18). IR ($CHCl_3$): ν(OH) 3 457.

(*R*)-(-)-3,3′-Bis(hydroxymethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene [(*R*)-**24**]

Analogously to the preparation of (*R*)-**23**, compound (*R*)-**24** was synthesised in 97% yield as a colourless oil. The only difference was that CH_2Cl_2 was used instead of toluene in the extraction step. $[\alpha]_D^{20}$ –81.7 (*c* 0.121, THF); (ref.[21]: *S* enantiomer $[\alpha]_D$ +66.4 (*c* 0.256, THF)). For $C_{26}H_{26}O_6$ (434.5) calculated: 71.78% C, 6.03% H; found: 71.93% C, 5.98% H. ^{1}H NMR

($CDCl_3$): 8.03 s, 2 H (ArH); 7.92 d, 2 H, J = 8.2 (ArH); 7.44 m, 2 H (ArH); 7.27 m, 2 H (ArH); 7.18 m, 2 H (ArH); 5.00 and 4.86 AB-system, 4 H, J_{AB} = 12.6 (OCH_2O); 4.49 and 4.46 AB-system, 4 H, J_{AB} = 6.3 (CH_2); 3.50 br s, 2 H (OH); 3.20 s, 3 H (CH_3O). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 153.71, 135.18, 134.38, 131.56, 130.29, 128.80, 127.42, 126.37, 126.03, 57.70; CH_2 and C: 153.71, 135.18, 134.38, 131.56, 125.77, 99.93, 62.46. EI-MS, *m/z* (rel.%): 434 ($M^{+\bullet}$, 32), 372 (43), 358 (40), 340 (45), 328 (100), 310 (43), 269 (27), 253 (71), 239 (40), 226 (13).

Methyl 2,2′-Bis(methoxymethoxy)-1,1′-binaphthalene-3-carboxylate (**30**)

A three-necked 500 ml flask equipped with a dropping funnel, reflux condenser, nitrogen inlet and magnetic stirrer was charged with NaH (94%, 1.9 g, 79 mmol) and dry THF (150 ml). To the stirred suspension a solution of methyl ester **26** (ref.[28]; 10 g, 29 mmol) in dry THF (100 ml) was added dropwise at room temperature under nitrogen. The reaction mixture was stirred at room temperature for 1 h, refluxed for 30 min and then cooled to room temperature. A solution of chloromethyl methyl ether (5.1 g, 63 mmol) in dry THF (30 ml) was added dropwise and then the reaction mixture was heated to reflux for 1 h. Second portion of MOM chloride was added and the reaction mixture was refluxed for another 30 min. Progress of the reaction was monitored by TLC (silica gel; toluene–acetone 9 : 1). After cooling to room temperature, THF was evaporated and the residue was partitioned between $CHCl_3$ (500 ml) and water (150 ml). The $CHCl_3$ layer was separated, washed with 5% aqueous $NaHCO_3$ (100 ml), water (2 × 100 ml) and dried over $MgSO_4$. After solvent removal, **30** was obtained in 97.9% yield as a pale yellow oil. It was used in the next step without further purification. M.p. 105–106 °C (toluene). For $C_{26}H_{24}O_6$ (432.5) calculated: 72.21% C, 5.59% H; found: 71.89% C, 5.64% H. ^{1}H NMR ($CDCl_3$): 8.54 s, 1 H (ArH); 8.02–7.93 m, 2 H (ArH); 7.88 d, 1 H, J = 8.1 (ArH); 7.61 d, 1 H, J = 9.0 (ArH); 7.50–7.15 m, 6 H (ArH); 5.17 and 5.03 AB-system, 2 H, J_{AB} = 6.9 (CH_2); 4.82 and 4.79 AB-system, 2 H, J_{AB} = 5.6 (CH_2); 4.00 s, 3 H (CH_3); 3.19 s, 3 H (CH_3); 2.65 s, 3 H (CH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 133.35, 130.53, 129.57, 128.85, 128.44, 127.31, 126.60, 126.26, 126.16, 124.74, 117.02, 56.83, 56.53, 52.99; CH_2 and C: 167.57, 153.65, 151.72, 136.27, 134.64, 130.50, 130.22, 128.34, 126.00, 120.85, 100.58, 95.57. EI-MS; *m/z* (rel. %): 432 ($M^{+\bullet}$, 24), 239 (100), 226 (88), 268 (82), 237 (48), 356 (45), 224 (40), 255 (37), 283 (36), 325 (27). IR ($CHCl_3$): ν(C=O) 1 725.

3-Hydroxymethyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (**23**)

To a stirred suspension of $LiAlH_4$ (1.80 g, 47 mmol) in dry THF (100 ml), a solution of **30** (11.78 g, 27.2 mmol) in dry THF (100 ml) was added dropwise at room temperature under nitrogen. The mixture was stirred for another 15 min and the excess of hydride was decomposed by gradual addition of $MgSO_4 \cdot 7\ H_2O$. After the evolution of hydrogen ceased, small amount of water was added to complete the hydride decomposition. The solid was removed by filtration through a Celite pad, the solvent was evaporated and the residue was taken up into $CHCl_3$ (300 ml) and water (200 ml). The organic layer was separated, washed with water (100 ml) and dried over $MgSO_4$. The solvent was evaporated and the product dried *in vacuo*. Alcohol **23** was obtained in 97% (10.7 g, 26.5 mmol) yield as a colourless oil, which was crystallised from either toluene or ethanol. M.p. 116–118 °C (toluene). For $C_{25}H_{24}O_5$ (404.5) calculated: 74.24% C, 5.98% H; found: 74.13% C, 5.90% H. Spectral data were identical with those of (*R*)-**23**.

Dimethyl 2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3,3′-dicarboxylate (**31**)

To a stirred suspension of NaH (94%, 0.13 g, 5.09 mmol) in dry THF (15 ml) was added dropwise a solution of **27** (ref.[18]; 0.463 g, 1.15 mmol) in dry THF (5 ml) under nitrogen atmosphere. The reaction mixture was heated to 35 °C and stirred for 30 min at this temperature. Chloromethyl methyl ether (0.41 g, 5.09 mmol) was added and the mixture was stirred for 5 h at 35–40 °C. The reaction was monitored by TLC (silica gel; toluene–acetone 9 : 1). Excess of NaH was decomposed by careful addition of water and the product was extracted into $CHCl_3$ (50 ml). The $CHCl_3$ layer was washed with 5% aqueous $NaHCO_3$ (20 ml) and water (2 × 20 ml), and dried over $MgSO_4$. ^{1}H NMR ($CDCl_3$): 8.53 s, 4 H (ArH); 8.05–7.80 m, 4 H (ArH); 7.30–7.10 m, 6 H (ArH); 4.84 and 4.80 AB-system, 4 H, J_{AB} = 6.4 (CH_2); 3.97 s, 6 H (CH_3); 2.53 s, 6 H (CH_3).

3,3′-Bis(hydroxymethyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthalene (**24**)

Analogously to the procedure for the synthesis of **23**, diol **24** was prepared by $LiAlH_4$ reduction of **31** (0.548 g, 1.12 mmol) in 95% yield (0.460 g, 1.06 mmol) as a colourless oil. Analytical data were in accordance with those of published previously[29].

General Procedure for Preparations of Ligands **1**–**3**

To a stirred suspension of NaH (1.5 or 3.0 molar equivalents) in dry THF a solution of hydroxymethyl derivative **23** or **24** (1.0 molar equivalent) in dry THF was added dropwise at room temperature. The reaction mixture was heated to reflux for 1 h. After cooling to room temperature, a solution of bromomethyl derivative **10** or **11** (2.0 or 1.0 molar equivalents) in dry THF was added dropwise. The mixture was then refluxed for 4 h. Progress of the reaction was monitored using TLC (Al_2O_3; toluene–acetone 9 : 1). After cooling, the excess of NaH was carefully decomposed by dropwise addition of water. THF was distilled off and the residue was partitioned between $CHCl_3$ and water. The organic layer was separated, washed twice with water and dried over $MgSO_4$. The product was purified by chromatography on a short column (neutral Al_2O_3, $CHCl_3$).

6-{[2,2′-Bis(methoxymethoxy)-1,1′-binaphthalene-3-yl]methoxymethyl}-6′-methyl-2,2′-bipyridine (**1**). Yield 86.1% (oil). For $C_{37}H_{34}N_2O_5$ (586.7) calculated: 75.75% C, 5.84% H, 4.77% N; found: 75.93% C, 5.87% H, 4.67% N. ^{1}H NMR ($CDCl_3$): 8.36 d, 1 H, *J* = 7.7 (ArH); 8.26–8.19 m, 2 H (ArH); 8.03–7.85 m, 4 H (ArH); 7.75–7.59 m, 3 H (ArH); 7.47–7.36 m, 2 H (ArH); 7.34–7.17 m, 5 H (ArH); 5.06 s, 2 H (CH_2); 5.13 and 5.04 AB-system, 2 H, J_{AB} = 6.9 (OCH_2O); 7.97 s, 2 H (CH_2); 4.67 and 4.59 AB-system, 2 H, J_{AB} = 5.5 (OCH_2O); 3.17 s, 3 H (OCH_3); 2.87 s, 3 H (OCH_3); 2.65 s, 3 H (CH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 138.05, 137.58, 130.43, 129.10, 128.60, 128.45, 127.31, 126.67, 126.32, 126.20, 125.58, 124.74, 123.80, 121.82, 120.40, 118.84, 117.17, 57.29, 56.67, 25.43; CH_2 and C: 158.67, 158.42, 156.39, 156.20, 153.47, 152.48, 134.63, 134.15, 132.25, 131.50, 130.27, 125.96, 121.39, 100.00, 95.60, 74.57, 69.62. EI-MS, *m/z* (rel.%): 586 ($M^{+\bullet}$, 4), 541 (2), 525 (2), 342 (3), 310 (6), 297 (6), 281 (12), 243 (15), 199 (10), 184 (100), 111 (9), 97(12), 83 (12), 71 (18), 57 (27), 45 (25).

(*R*)-**1**: Yield 87.2%. The product was crystallised from either toluene or ethyl acetate. M.p. 132–134 °C (toluene). $[\alpha]_D^{20}$ +70.2 (*c* 1.078, THF), $[\alpha]_D^{20}$ +69.7 (*c* 0.178, THF). For $C_{37}H_{34}N_2O_5$ (586.7) calculated: 75.75% C, 5.84% H, 4.77% N; found: 75.59% C, 5.83% H, 4.71% N.

6,6′-Bis{[2,2′-bis(methoxymethoxy)-1,1′-binaphthalene-3-yl]methoxymethyl}-2,2′-bipyridine (**2**). Yield 89.2%. For $C_{62}H_{56}N_2O_{10}$ (989.1) calculated: 75.28% C, 5.71% H, 2.83% N; found:

74.92% C, 5.69% H, 2.78% N. ^{1}H NMR ($CDCl_3$): 8.36 d, 2 H, *J* = 7.8 (ArH); 8.17 s, 2 H (ArH); 8.00–7.82 m, 8 H (ArH); 7.63 d, 2 H, *J* = 7.7 (ArH); 7.59 d, 2 H, *J* = 9.0 (ArH); 7.44–7.33 m, 4 H (ArH); 7.30–7.16 m, 8 H (ArH); 5.06 s, 4 H (CH_2); 5.13 and 5.03 AB-system, 4 H, J_{AB} = 6.9 (OCH_2O); 4.97 s, 4 H (CH_2); 4.67 and 4.58 AB-system, 4 H, J_{AB} = 5.5 (OCH_2O); 3.16 s, 6 H (OCH_3); 2.86 s, 6 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 138.15, 130.51, 129.19, 128.68, 128.54, 127.38, 126.75, 126.40, 126.26, 125.67, 124.82, 122.05, 120.51, 117.23, 57.24, 56.62; CH_2 and C: 158.83, 156.23, 153.59, 152.61, 134.71, 134.24, 132.32, 131.59, 130.35, 126.05, 121.44, 100.00, 95.61, 74.54, 69.61. FAB-MS (matrix: thioglycerol–glycerol), *m/z*: 989 ([M + H]$^+$).

(*R,R*)-**2**: Yield 94.0%. $[\alpha]_D^{20}$ +79.1 (*c* 1.025, THF). For $C_{62}H_{56}N_2O_{10}$ (989.1) calculated: 75.28% C, 5.71% H, 2.83% N; found: 75.20% C, 5.73% H, 2.80% N.

2,2′-Bis(methoxymethoxy)-3,3′-bis[(6′-methyl-2,2′-bipyridine-6-yl)methoxymethyl]-1,1′-binaphthalene (**3**). Chromatographic purification using a toluene–acetone (95 : 5) mixture gave **3** in 72.8% yield. For $C_{50}H_{46}N_4O_6$ (798.9) calculated: 75.17% C, 5.80% H, 7.01% N; found: 74.92% C, 5.80% H, 6.95% N. ^{1}H NMR ($CDCl_3$): 8.34 d, 2 H, *J* = 7.2 (ArH); 8.25–8.19 m, 4 H (ArH); 7.93 d, 2 H, *J* = 7.9 (ArH); 7.86 t, 2 H, *J* = 7.8 (ArH); 7.69 t, 2 H, *J* = 7.8 (ArH); 7.61 d, 2 H, *J* = 7.7 (ArH); 7.43 m, 2 H (ArH); 7.31–7.20 m, 4 H (ArH); 7.17 d, 2 H, *J* = 7.7 (ArH); 5.03 br s, 4 H (CH_2); 4.96 s, 4 H (CH_2); 4.63 and 4.52 AB-system, 4 H, J_{AB} = 5.9 (OCH_2O); 2.82 s, 6 H (CH_3); 2.64 s, 6 H (CH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 138.13, 137.63, 129.53, 128.72, 127.12, 126.78, 125.80, 123.85, 121.86, 120.48, 118.86, 57.25, 25.33; CH_2 and C: 158.61, 158.54, 156.55, 156.28, 152.85, 134.44, 132.46, 131.45, 126.00, 100.08, 74.62, 69.47. FAB-MS (matrix: 3-nitrobenzyl alcohol), *m/z*: 799 ([M + H]$^+$).

(*R*)-**3**: Yield 71.3%. $[\alpha]_D^{20}$ –37.3 (*c* 0.922, THF). For $C_{50}H_{46}N_4O_6$ (798.9) calculated: 75.17% C, 5.80% H, 7.01% N; found: 75.35% C, 5.71% H, 6.99% N.

General Procedure for Preparations of Ligands **5**, **7** and **9**

Acid **21** or **22** (2.0 or 1.0 molar equivalents) was refluxed in a large excess of thionyl chloride for 3 h. The reagent was distilled off and the crude acid chloride was thoroughly dried. It was dissolved in dry CH_2Cl_2 and a solution of aminomethyl derivative **15** or **12** (1.0 or 2.0 molar equivalents) and triethylamine (2.0 or 4.0 molar equivalents) in dry CH_2Cl_2 was added dropwise and the mixture was stirred at room temperature for another 1 h. After solvent removal, the residue was subjected to a column chromatography (neutral Al_2O_3).

N-[(6′-Methyl-2,2′-bipyridine-6-yl)methyl]-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxamide (**5**). Chromatographic isolation using a toluene–acetone (95 : 5) mixture gave **5** in 75.7% yield. For $C_{35}H_{29}N_3O_3$ (539.6) calculated: 77.90% C, 5.42% H, 7.79% N; found: 77.81% C, 5.38% H, 7.73% N. ^{1}H NMR ($CDCl_3$): 9.84 br t, 1 H (CONH); 8.93 s, 1 H (ArH); 8.34 d, 1 H, *J* = 7.8 (ArH); 8.16–8.03 m, 3 H (ArH); 7.95 d, 1 H, *J* = 8.2 (ArH); 7.79 t, 1 H, *J* = 7.7 (ArH); 7.54–7.16 m, 8 H (ArH); 7.02 d, 1 H, *J* = 7.4 (ArH); 6.87 t, 1 H, *J* = 7.7 (ArH); 4.95 d, 2 H, *J* = 4.4 (CH_2); 3.79 s, 3 H (CH_3); 3.35 s, 3 H (CH_3); 2.57 s, 3 H (CH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 138.24, 137.60, 133. 87, 130.78, 130.15, 128.59, 128.56, 127.54, 126.16, 126.05, 125.90, 124.45, 123.88, 122.41, 120.06, 118.77, 114.04, 62.00, 57.08, 25.19; CH_2 and C: 166.13, 158.28, 156.14, 155.98, 155.64, 154.36, 136.16, 134.64, 131.15, 129.77, 127.13, 126.36, 119.36, 45.77.

(*R*)-**5**: Yield 72.6%. $[\alpha]_D^{20}$ +153.8 (*c* 0.980, THF). For $C_{35}H_{29}N_3O_3$ (539.6) calculated: 77.90% C, 5.42% H, 7.79% N; found: 77.61% C, 5.60% H, 7.45% N.

N,N′-[(2,2′-Bipyridine-6,6′-diyl)dimethyl]-bis(2,2′-dimethoxy-1,1′-binaphthalene-3-carboxamide) (**7**). The product was obtained after chromatographic isolation using a toluene–acetone (9 : 1) mixture and crystallisation from toluene in 79.7% yield. M.p. 186–188 and 244–246 °C (toluene; two types of crystals). For $C_{58}H_{46}N_4O_6$ (895.0) calculated: 77.82% C, 5.18% H, 6.26% N; found: 77.62% C, 5.16% H, 6.19% N. ^{1}H NMR ($CDCl_3$): 9.84 br t, 2 H (CONH); 8.91 s, 2 H (ArH); 8.21 d, 2 H, *J* = 8.0 (ArH); 8.07 m, 4 H (ArH); 7.95 d, 2 H, *J* = 8.2 (ArH); 7.52–7.15 m, 16 H (ArH); 6.86 t, 2 H, *J* = 7.8 (ArH); 4.88 d, 4 H, *J* = 3.9 (CH_2); 3.77 s, 6 H (OCH_3); 3.31 s, 6 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 138.19, 133.86, 130.83, 130.15, 128.61 (overlap of two signals), 127.54, 126.21, 126.06, 125.86, 124.49, 122.51, 120.00, 114.00, 61.97, 57.06; CH_2 and C: 166.07, 155.69, 155.60, 155.30, 154.28, 136.15, 134.61, 131.16, 129.76, 127.19, 126.26, 119.29, 45.65. FAB-MS (matrix: bis(2-hydroxyethyl) disulfide), *m/z*: 895 ($[M + H]^+$).

(*R,R*)-**7**: Yield 74.6%. The product crystallises from toluene as a clathrate (stoichiometry 1 : 2). M.p.: decomp. $[\alpha]_D^{20}$ +189.1 (*c* 0.214, THF).

N,N′-Bis[(6′-methyl-2,2′-bipyridine-6-yl)methyl]-2,2′-dimethoxy-1,1′-binaphthalene-3,3′-dicarboxamide (**9**). Chromatographic isolation using a toluene–acetone (98 : 2) mixture gave **9** in 79.9% yield. For $C_{48}H_{40}N_6O_4$ (764.9) calculated: 75.37% C, 5.27% H, 10.99% N; found: 75.42% C, 5.21% H, 10.89% N. ^{1}H NMR ($CDCl_3$): 9.90 br t, 2 H (CONH); 9.04 s, 2 H (ArH); 8.20 d, 2 H, *J* = 7.8 (ArH); 8.14-8.05 m, 4 H (ArH); 7.71 t, 2 H, *J* = 7.8 (ArH); 7.51 t, 2 H, *J* = 7.7 (ArH); 7.37 t, 2 H, *J* = 7.7 (ArH); 7.28–7.18 m, 4 H (ArH); 7.03 t, 2 H, *J* = 7.8 (ArH); 6.89 d, 2 H, *J* = 7.4 (ArH); 4.91 d, 4 H, *J* = 1.8 (CH_2); 3.36 s, 6 H (OCH_3); 2.45 s, 6 H (CH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 137.94, 137.22, 134.54, 130.27, 129.09, 126.43, 126.19, 123.63, 122.06, 119.99, 118.33, 62.53, 25.24; CH_2 and C: 165.66, 158.01, 156.02, 155.19, 154.96, 154.63, 136.03, 131.00, 126.46, 126.29, 45.73. FAB-MS (matrix: bis(2-hydroxyethyl) disulfide), *m/z*: 765 ($[M + H]^+$).

(*R*)-**9**: Yield 66.8%. M.p. 128–130 °C (toluene–hexane). $[\alpha]_D^{20}$ –55.1 (*c* 1.018, THF). For $C_{48}H_{40}N_6O_4$ (764.9) calculated: 75.37% C, 5.27% H, 10.99% N; found: 75.12% C, 5.22% H, 10.81% N.

General Procedure for Preparations of Ligands **4**, **6** and **8**

Acid **21** or **22** (2.0 or 1.0 molar equivalents) was refluxed in a large excess of thionyl chloride for 3 h. The reagent was distilled off and the crude acid chloride was thoroughly dried. It was dissolved in dry toluene and a solution of amino derivative **13** or **14** (1.0 or 2.0 molar equivalents) and 4-(dimethylamino)pyridine (1.2 or 2.4 molar equivalents) in dry toluene was added dropwise under nitrogen atmosphere. The mixture was refluxed for 2 h. After solvent removal, the residue was subjected to a column chromatography (neutral Al_2O_3).

N-(2,2′-Bipyridine-6-yl)-2,2′-dimethoxy-1,1′-binaphthalene-3-carboxamide (**4**). Chromatographic isolation using toluene gave **4** in 65.8% yield. For $C_{33}H_{25}N_3O_3$ (511.6) calculated: 77.48% C, 4.93% H, 8.21% N; found: 77.16% C, 4.89% H, 8.18% N. ^{1}H NMR ($CDCl_3$): 10.72 br s, 1 H (CONH); 8.97 s, 1 H (ArH); 8.66 m, 1 H (ArH); 8.54 d, 1 H, *J* = 8.2 (ArH); 8.30 d, 1 H, *J* = 8.1 (ArH); 8.20 d, 1 H, *J* = 7.7 (ArH); 8.08 d, 2 H, *J* = 8.9 (ArH); 7.92 m, 2 H (ArH); 7.73 m, 1 H (ArH); 7.6–7.1 m, 8 H (ArH); 3.84 s, 3 H (OCH_3); 3.62 s, 3 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 149.75, 139.86, 137.37, 134.56, 131.00, 130.24, 129.10, 128.78, 127.67, 126.46, 126.13, 125.67, 124.53, 124.33, 121.63, 117.64, 115.53, 114.09, 62.57, 57.12; CH_2 and C: 164.57, 156.30, 155.62, 155.15, 153.91, 152.03, 136.61, 131.13, 129.78, 127.41, 126.02, 118.87. FAB-MS (matrix: glycerol–thioglycerol), *m/z*: 512 ($[M + H]^+$).

(*R*)-**4**: Yield 56.5%. $[\alpha]_D^{20}$ +141.1 (*c* 0.596, THF). For $C_{33}H_{25}N_3O_3$ (511.6) calculated: 77.48% C, 4.93% H, 8.21% N; found: 77.25% C, 4.97% H, 8.09% N.

N,N′-(2,2′-Bipyridine-6,6′-diyl)-bis(2,2′-dimethoxy-1,1′-binaphthalene-3-carboxamide) (**6**). Chromatographic isolation using a toluene–acetone (98 : 2) mixture gave **6** in 76.3% yield. For $C_{56}H_{42}N_4O_6$ (867.0) calculated: 77.58% C, 4.88% H, 6.46% N; found: 77.36% C, 4.85% H, 6.39% N. ^{1}H NMR ($CDCl_3$): 10.72 s, 2 H (CONH); 8.96 s, 2 H (ArH); 8.50 d, 2 H, *J* = 8.2 (ArH); 8.13–8.04 m, 6 H (ArH); 7.94 d, 2 H, *J* = 8.0 (ArH); 7.82 t, 2 H, *J* = 8.0 (ArH); 7.55–7.43 m, 4 H (ArH); 7.42–7.25 m, 6 H (ArH); 7.21–7.13 m, 4 H (ArH); 3.84 s, 6 H (OCH_3); 3.61 s, 6 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 139.68, 134.57, 131.03, 130.26, 129.11, 128.81, 127.69, 126.46, 126.17, 125.68, 124.56, 117.52, 115.55, 114.11, 62.58, 57.16; CH_2 and C: 164.58, 155.65, 154.64, 153.96, 151.97, 136.64, 134.60, 131.14, 129.82, 127.43, 125.99, 118.88. FAB-MS (matrix: glycerol–thioglycerol), *m/z*: 867 ($[M + H]^+$).

(*R,R*)-**6**: Yield 81.9%. $[\alpha]_D^{20}$ +162.2 (*c* 1.092, THF), $[\alpha]_D^{20}$ +164 (*c* 0.109, THF). For $C_{56}H_{42}N_4O_6$ (867.0) calculated: 77.58% C, 4.88% H, 6.46% N; found: 77.54% C, 4.82% H, 6.45% N.

N,N′-Bis(2,2′-bipyridine-6-yl)-2,2′-dimethoxy-1,1′-binaphthalene-3,3′-dicarboxamide (**8**). Chromatographic isolation using a toluene–acetone (98 : 2) mixture gave **8** in 41.4% yield. M.p. >300 °C (acetone). For $C_{44}H_{32}N_6O_4$ (708.8) calculated: 74.56% C, 4.55% H, 11.86% N; found: 74.49% C, 4.57% H, 11.70% N. ^{1}H NMR ($CDCl_3$): 10.61 s, 2 H (CONH); 9.04 s, 2 H (ArH); 8.64 m, 2 H (ArH); 8.54 d, 2 H, *J* = 8.1 (ArH); 8.32 d, 2 H, *J* = 8.2 (ArH); 8.22 d, 2 H, *J* = 7.6 (ArH); 8.14 d, 2 H, *J* = 8.2 (ArH); 7.94 t, 2 H, *J* = 8.0 (ArH); 7.68 m, 2 H (ArH); 7.55 m, 2 H (ArH); 7.43 m, 2 H (ArH); 7.28–7.16 m, 4 H (ArH); 3.60 s, 3 H (OCH_3). ^{13}C NMR, APT ($CDCl_3$): CH_3 and CH: 149.80, 140.00, 137.47, 135.35, 130.53, 126.86, 126.20, 124.41, 121.61, 117.89, 115.51, 63.00; CH_2 and C: 164.28, 156.17, 155.31, 154.14, 151.85, 136.48, 131.08, 126.52, 126.26. FAB-MS (matrix: glycerol–thioglycerol), *m/z*: 709 ($[M + H]^+$).

(*R*)-**8**: Yield 46.7%. $[\alpha]_D^{20}$ –135.7 (*c* 0.112, THF). For $C_{44}H_{32}N_6O_4$ (708.8) calculated: 74.56% C, 4.55% H, 11.86% N; found: 74.58% C, 4.51% H, 11.78% N.

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