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The Influence of Different Spacer Lengths on the Selectivity of Self-Assembly Processes of Bis(bipyridine)-BINOL Helicates

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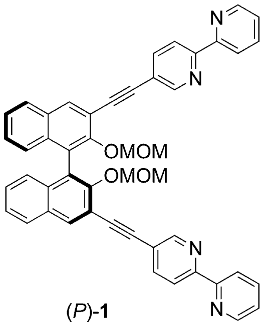
In memoriam of Professor Dr. Peter Köll

Keywords: Diastereoselectivity / Helical structures / Circular dichroism / Self-assembly / Heterocycles

The synthesis and self-assembly behaviour of a series of enantiomerically pure bis(chelating) ligands is reported. The ligands differ in the spacer unit between a BINOL core and two bipyridyl groups as the chelating entities and were found to undergo completely diastereoselective self-assembly to dinuclear double-stranded helicates with silver(I) salts, as demonstrated by NMR and CD spectroscopy and ESI mass spectrometry. Upon coordination to iron(II) or zinc(II) ions, however, a dramatic loss in the diastereoselectivity of the self-assembly of dinuclear triple-stranded helicates was observed as a result of increasing spacer length. In the case of zinc(II), the self-assembly processes were even found to be nonselective with regard to the composition of the helicates.

Introduction

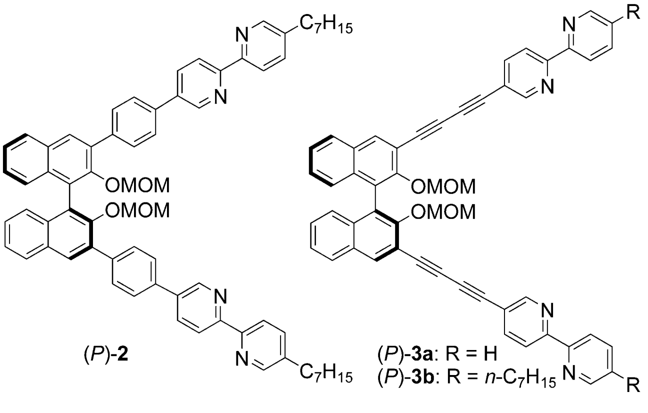
Self-assembly has been proven to be an elegant method for generating supramolecular aggregates[1] with well-defined composition and stereochemistry.[2] Helicates are among the best-studied examples in this context.[3] However, it is still very difficult to predict the degree of stereoselectivity and the resulting relative configuration of the newly formed stereogenic metal centres just by looking at a given ligand structure. Some time ago we reported the bis(bipyridyl) ligand **1** (Scheme 1), which undergoes completely diastereoselective self-assembly to dinuclear double- and triple-stranded helicates upon coordination to late-transition-metal ions.[4]



(*P*)-**1**

Scheme 1.

Since then we have been able to show that other dissymmetric building blocks, for example, differently substituted BINOLs,[5] Tröger's base derivatives[6] or D-isomannide,[7] can also be used in this way. In this account we want to address the question, how far does chirality transfer from the central stereochemical axis of the BINOL core to the metal centres work? Therefore, we prepared two ligands **2** and **3** (Scheme 2), which differ from **1** in the length of the rigid spacer unit. In our initial ligand the BINOL unit and the bipyridyl groups were connected through an ethynylene spacer, whereas in **2** we used a *p*-phenylene and in **3** a butadiynylene.



Scheme 2. Extended bis(bipyridyl) ligands **2** and **3**.

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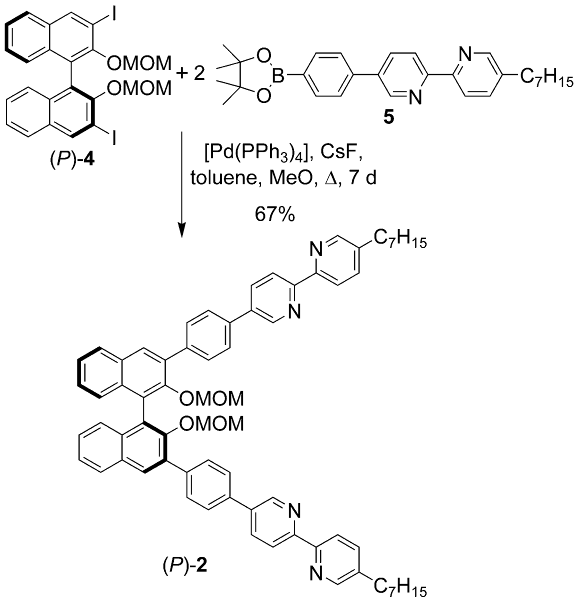
Results and Discussion

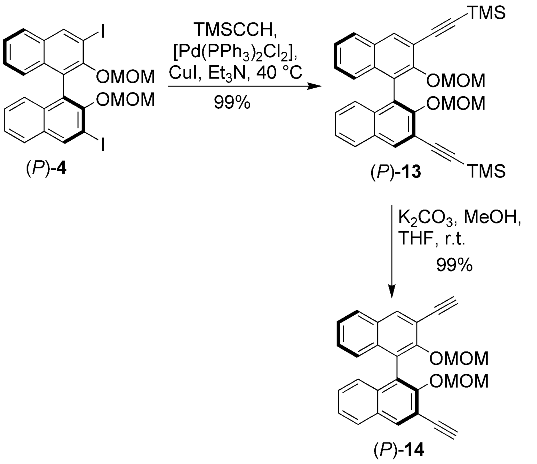
Synthesis

The known 2,2′-bis(methoxymethoxy)-3,3′-diiodo-1,1′-binaphthyl (**4**), which can be prepared in an optically pure form in four steps from 2-naphthol,[8–11] was identified as the core building block for the synthesis of ligands **2** and **3**. Binaphthyl **4** could be coupled directly with boronic acid ester **5** (Scheme 3) in a two-fold Suzuki reaction to give **2** in 67% yield. Note that this reaction requires a very long reaction time (7 d) and a very high, almost stoichiometric, catalyst loading (50 mol-%). Bipyridyl-boronic acid ester **5**[12] was prepared in six steps starting from 2-chloro-5-iodopyridine (**6**), which included our Negishi-type cross-coupling procedure[13] for the synthesis of the 2,2′-bipyridine as the key step (Scheme 4).



Scheme 3. Synthesis of ligand **2**.

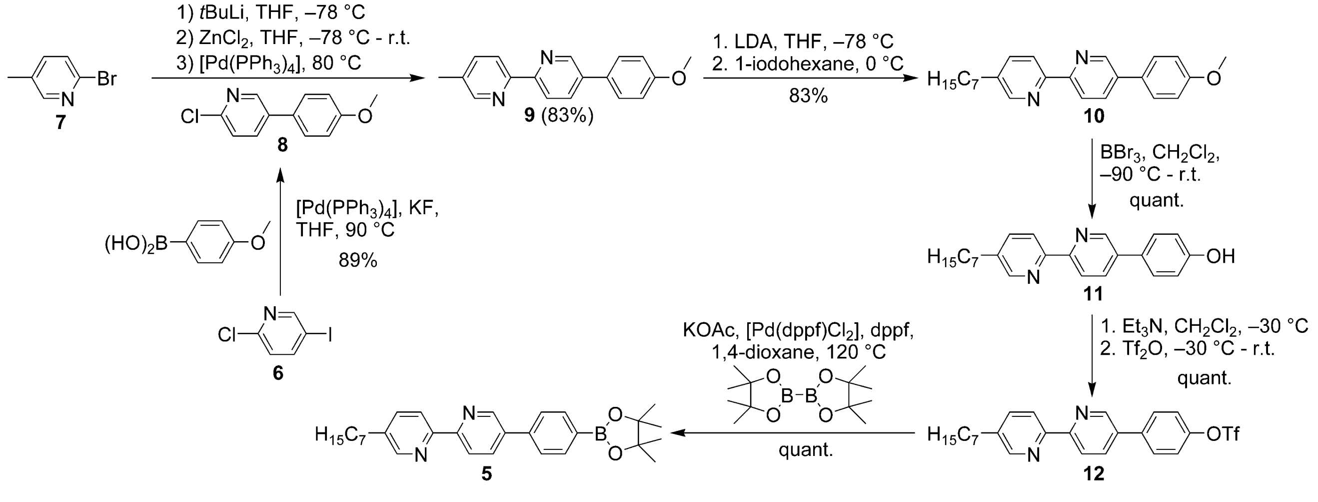
However, BINOL derivative **4** can also be converted into diethynylated **14** by Sonogashira cross-coupling[12] with TMS-protected acetylene and subsequent cleavage of the silyl groups[11] (Scheme 5) to give the first building block for the synthesis of **3**.



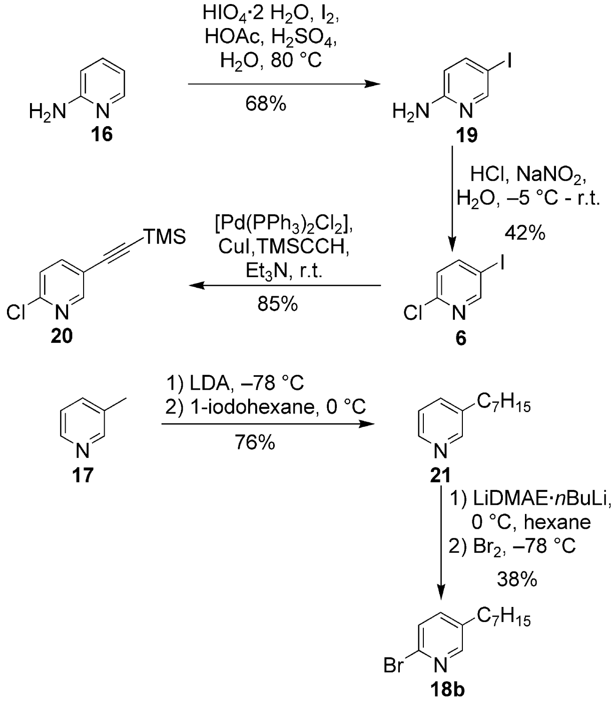
Scheme 5. Synthesis of 3,3′-diethynylated 1,1′-binaphthyl **14**.

The other substrates for the final coupling reaction are the bromoacetylenes **15a** and **15b**, which were prepared in six and eight steps, respectively, starting from commercially available 2-aminopyridine (**16**), picoline (**17**) and 2-bromopyridine (**18**; see Schemes 6 and 7).[6a,13,14]

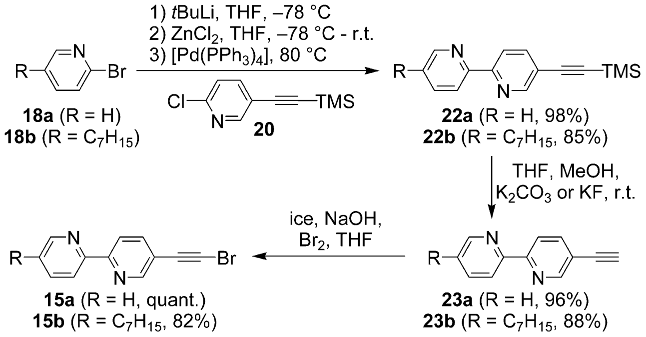
Finally, two-fold Cadiot–Chodkiewicz coupling of the bromoacetylenes **15a** and **15b** with BINOL derivative **14** gave ligands **3a** and **3b**, respectively. Whereas this reaction gave **3a** in a good yield of 63%, it yielded **3b** in only a moderate yield of 29% (Scheme 8).



Scheme 4. Synthesis of boronic acid ester **5**.



Scheme 6. Synthesis of the pyridine building blocks **18b** and **20**.



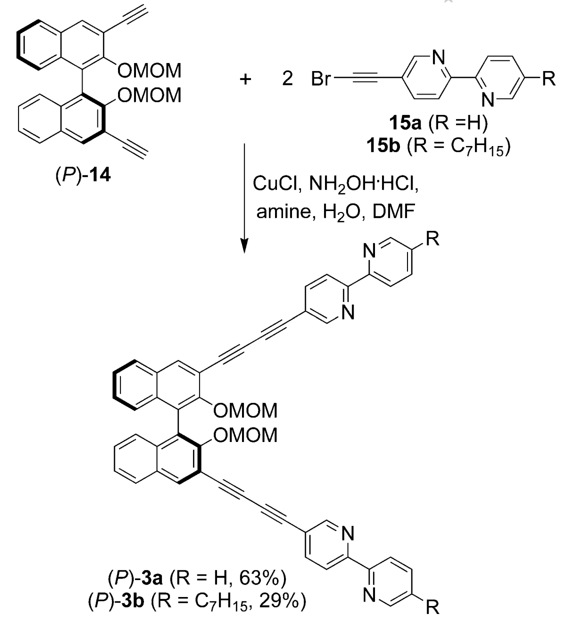
Scheme 7. Synthesis of bipyridyl(bromo)acetylenes **15**.

Complexation Behaviour

After the successful synthesis of both enantiomers of ligands **2** and **3** we studied their complexation behaviour towards late-transition-metal ions to compare these results with those previously published for ligand **1**.

For this purpose we generated solutions of the ligands in dichloromethane and $[Ag(CH_3CN)_4]BF_4$, $[Zn(BF_4)_2{\cdot}7H_2O]$ and $[Fe(BF_4)_2{\cdot}6H_2O]$ in acetonitrile. Upon mixing the ligand and salt solutions immediate colour changes occurred, which indicated the successful formation of bipyridine complexes: pale yellow for silver(I), yellow for zinc(II) and deep red for iron(II). To analyse the stoichiometric composition of the complexes we performed ESI-MS measurements.

An exemplary spectrum obtained from the analysis of the silver(I) complex solutions is shown in Figure 1. The spectrum of the silver(I) complex of ligand **2** shows a peak at *m*/*z* = 1139.4 that results from the dinuclear double-stranded $[Ag_2\mathbf{2}_2]^{2+}$. However, not unexpectedly on the basis of our previous results,[4–7] the silver complexes generally turned out to be the least stable of the coordination compounds under ESI conditions and show a high tendency to fragment. This is also true for the silver complex of ligand **2**; thus, the spectrum also shows signals for $[Ag\mathbf{2}]^+$ and $[\mathbf{2}+H]^+$ and some other protonated fragments. As we will see later in the discussion of the NMR spectra, these fragments result from the ESI process rather than species present in solution.



Scheme 8. Synthesis of ligand **3**.

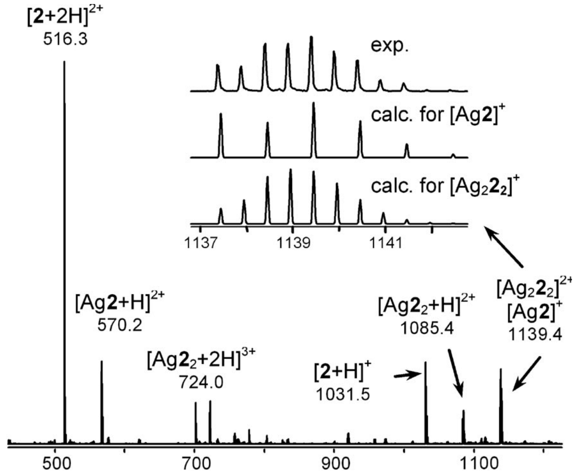


Figure 1. Positive ESI-MS of the silver(I) complex of ligand **2** (5×10^{-5} mol/L in CH_2Cl_2/CH_3CN, 1:1).

In contrast, zinc(II) and iron(II) complexes usually give very clear ESI mass spectra that hardly contain any fragments. However, the zinc(II) solution of ligand **3** behaves differently and gives the most interesting spectrum: first of all the spectrum contains an unusual amount of fragmentation signals (e.g., $[Zn\mathbf{3a}]^{2+}$ and $[Zn\mathbf{3a}_2]^{2+}$) and signals arising from non-specific aggregates ($[Zn_2\mathbf{3a}_4]^{2+}$). Also the base peak can be assigned to the singly protonated ligand at *m*/*z* = 779.3 $[\mathbf{3a}+H]^+$ (Figure 2). Furthermore, two discrete species can be observed at *m*/*z* = 616.7 and 421.1 and assigned as $[Zn_2\mathbf{3a}_3]^{4+}$ and $[Zn_2\mathbf{3a}_2]^{4+}$, respectively (the last one accompanied by a $[Zn\mathbf{3a}]^{2+}$ fragment, see inset in Figure 2). From MS/MS studies we know that the $[Zn_2\mathbf{3a}_2]^{4+}$ ion is not a fragment of the expected $[Zn_2\mathbf{3a}_3]^{4+}$ ion. Although zinc(II) is known to form coordination compounds with tetrahedrally as well as octahedrally coordinated metal centres,[15] this behaviour is still surprising because ligand **1**, which has only a slightly shorter spacer between the bipyridyl units and the BINOL core, exclusively forms triple-stranded species.[4] Clearly, the self-assembly is no longer selective in terms of the resulting complex composition when the spacer gets too long.

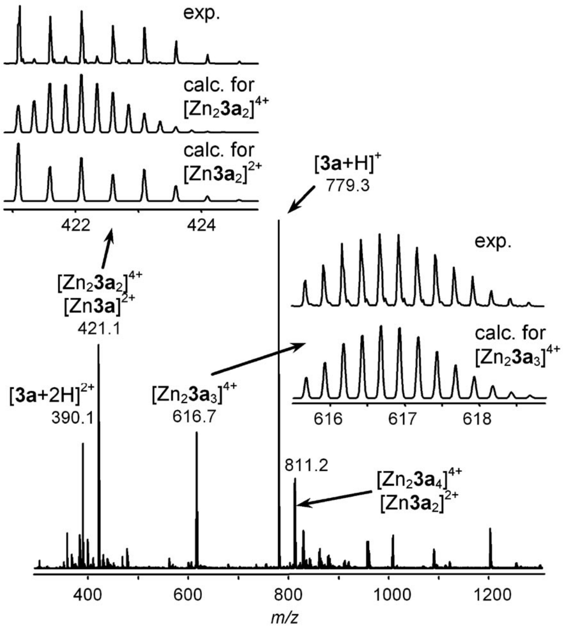


Figure 2. Positive ESI-MS of the zinc(II) complexes of ligand **3a** (5×10^{-5} mol/L in CH_2Cl_2/CH_3CN, 1:1).

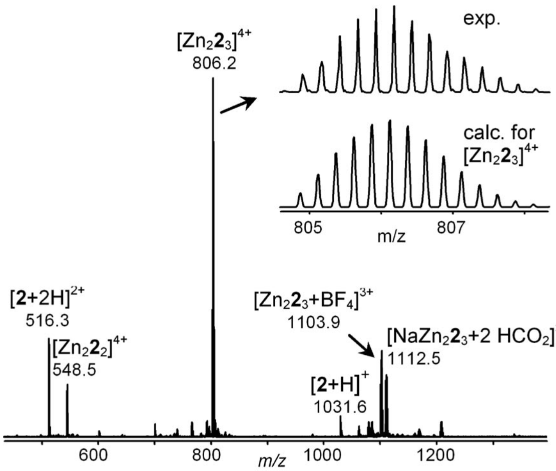


Figure 3. Positive ESI-MS of the zinc(II) complexes of ligand **2** (5×10^{-5} mol/L in CH_2Cl_2/CH_3CN, 1:1).

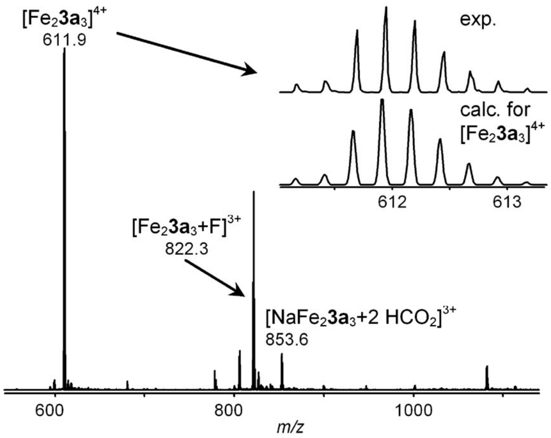


Figure 4. Positive ESI-MS of the iron(II) complexes of ligand **3a** (5×10^{-5} mol/L in CH_2Cl_2/CH_3CN, 1:1; note that the fluoride ion of the ion giving rise to the signal at *m*/*z* = 822.3 results from fragmention of the tetrafluoroborate ion).

A similar result was obtained for the zinc(II) complexes of ligand **2** (Figure 3). Again, signals arising from both quadruply charged triple- ($[Zn_2\mathbf{2}_3]^{4+}$ at *m*/*z* = 806.2) and double-stranded dinuclear zinc(II) complexes ($[Zn_2\mathbf{2}_2]^{4+}$ at *m*/*z* = 548.5) could be observed, although the triple-stranded complex seems to be more dominant in this case and the complexes show a lower tendency to fragment.

All the iron complexes, however, gave rise to the expected clean spectra that contain only signals of triple-stranded dinuclear complexes (some of them still carrying counterions), as demonstrated in Figure 4 for the iron(II) complexes of **3a**.

We then investigated the coordination behaviour by NMR spectroscopy. Figure 5 and Figure 6 show the spectra that were obtained for the silver(I) and zinc(II) complexes of ligands **2** and **3a** (ligand **3b** behaves like **3a**). Together with the results of the MS analysis these spectra reveal that coordination to silver(I) exclusively yields D_2-symmetric double-stranded dinuclear helicates in a completely diastereoselective manner as only one set of sharp signals was obtained and these were shifted as expected relative to the free ligands. Zinc(II), however, forms at least two species in a non-selective fashion although the spectra are more or less dominated by a D_3-symmetric triple-stranded dinuclear species, again corroborating the result obtained by MS (besides the formation of double- and triple-stranded species the formation of different stereoisomers seems to be very likely).

Unfortunately, the spectra of the iron complexes were found to be very broad in mixtures of [D$_2$]dichloromethane and [D$_3$]acetonitrile. In principle, this could a) indicate the formation of oligomeric or polymeric coordination compounds, b) be a result of paramagnetic impurities of iron(III) or c) indicate a highly dynamic behaviour in terms of ligand exchange and/or intramolecular movements. The formation of oligomeric and polymeric species could be

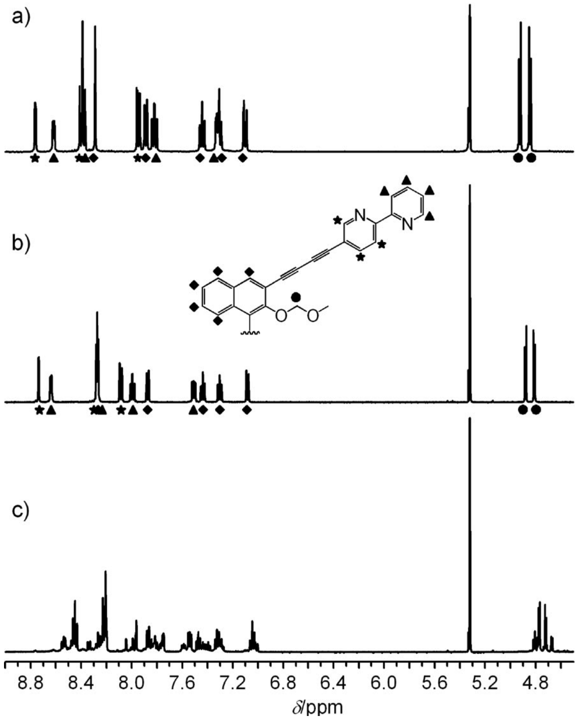


Figure 5. ^{1}H NMR spectra (1×10^{-3} mol/L in CD_2Cl_2/CD_3CN, 5:3) of a) (*P*)-**3a**, b) the silver helicate $[Ag_2\{(P)\text{-}\mathbf{3a}\}_2](BF_4)_2$ and c) a 3:2 mixture of (*P*)-**3a** and $[Zn(BF_4)_2{\cdot}7H_2O]$.

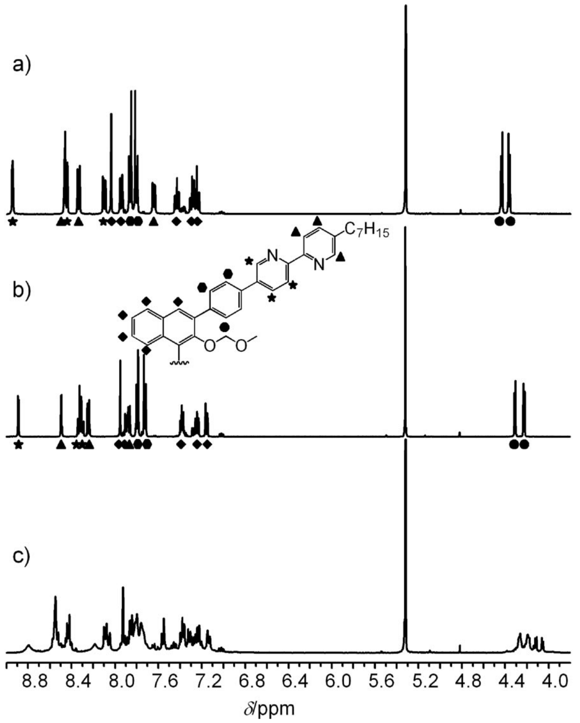


Figure 6. ^{1}H NMR spectra (1×10^{-3} mol/L in CD_2Cl_2/CD_3CN, 3:1) of a) (*P*)-**2**, b) the silver helicate $[Ag_2\{(P)\text{-}\mathbf{2}\}_2](BF_4)_2$ and c) a 3:2 mixture of (*P*)-**2** and $[Zn(BF_4)_2{\cdot}7H_2O]$.

ruled out as dilution experiments down to concentrations close to those used for the ESI-MS experiments, in which we only observed discrete triple-stranded dinuclear complexes, did not lead to a change in the spectra. Unfortunately, cooling the samples to slow the dynamics was not possible below 0 °C because the complexes tend to precipitate from solutions at this temperature. However, changing the solvent to a mixture of $[D_2]$dichloromethane and $[D_6]$-DMSO was found to slow the dynamics considerably (without changing the composition of the coordination compounds, as demonstrated by MS).

In fact it was found to be so slow that we were able to follow the self-assembly process. This can best be seen with ligand **1** (Figure 7): whereas initially a complex mixture of coordination compounds is formed the self-assembly process ultimately leads to the most stable complex in a completely diastereoselective manner.

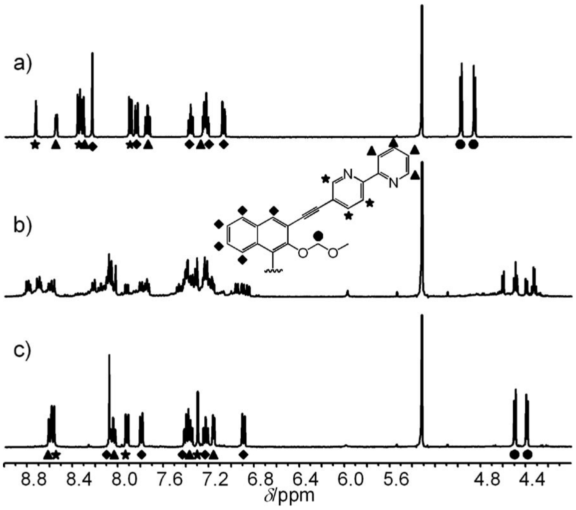


Figure 7. ^{1}H NMR spectra (1×10^{-3} mol/L in $CD_2Cl_2/[D_6]DMSO$, 3:1) of a) (*P*)-**1**, b) a 3:2 mixture of (*P*)-**1** and $[Fe(BF_4)_2{\cdot}6H_2O]$ 45 min after mixing and c) the same mixture after 72 h.

We then studied the behaviour of the iron complexes of **2** and **3**. Again it took about one day for the mixtures to reach their equilibrium composition at room temperature (Figure 8 and Figure 9). In contrast to **1**, these spectra reveal that the self-assembly of the triple-stranded dinuclear iron complexes of **2** is still highly but not completely diastereoselective.

This tendency grows when the length of the spacer is further increased by about 1 Å (distances between the BINOL and the bipyridyls: ethynylene ca. 4.1 Å, phenylene ca. 5.8 Å and butadiynylene ca. 6.8 Å) resulting in an almost complete loss of diastereoselectivity in the case of **3**.

After scrutinizing the selectivity of the self-assembly process in terms of aggregate composition and diastereoselective formation, we tried to identify which of the three possible diastereomeric silver(I) complexes are generated by the ligands. Because the metal centres become stereogenic centres upon complexation with the ligands, the possible diastereomers that can form when employing enantiomerically pure ligands are the (Δ,Δ), (Δ,Λ) and (Λ,Λ) diastereomers (Figure 10). Of these, the C_2-symmetric (Δ,Λ) isomers can be ruled out for symmetry reasons because we

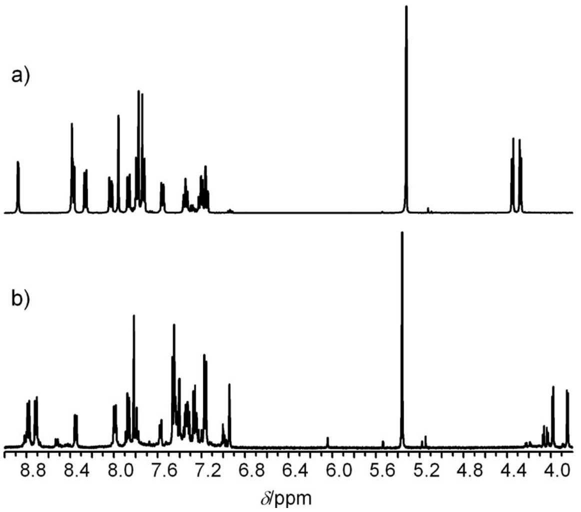


Figure 8. ^{1}H NMR spectra (1×10^{-3} mol/L in CD_2Cl_2/[D$_6$]DMSO, 3:1) of a) (*P*)-**2** and b) a 3:2 mixture of (*P*)-**2** and [Fe(BF$_4$)$_2$·6H$_2$O] 24 h after mixing.

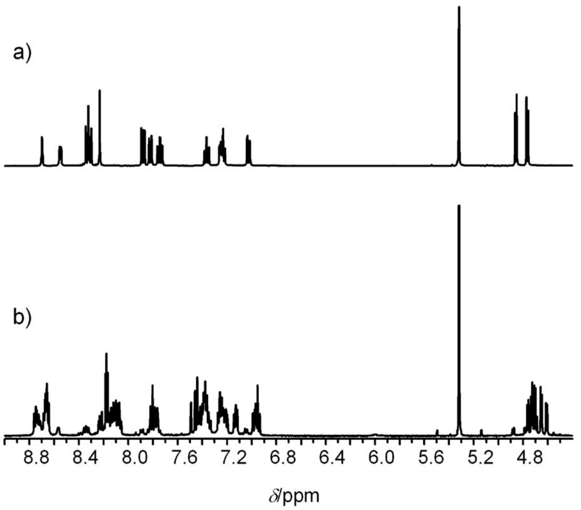


Figure 9. ^{1}H NMR spectra (1×10^{-3} mol/L in CD_2Cl_2/[D$_6$]DMSO, 3:1) of a) (*P*)-**3a** and b) a 3:2 mixture of (*P*)-**3a** and [Fe(BF$_4$)$_2$·6H$_2$O] 24 h after mixing.

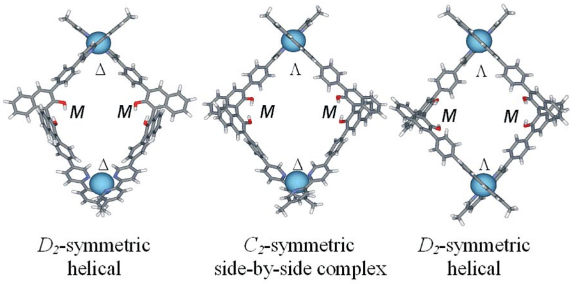


Figure 10. PM3-TM-minimized structures of the three possible double-stranded silver(I) complexes of ligand (*M*)-**2** (hydroxy protecting groups have been omitted and the heptyl chains shortened to methyl groups for clarity).

already know from the ^{1}H NMR spectra that the assemblies have to be *D*-symmetric.

Unfortunately, we were neither able to crystallize one of the complexes nor could ROESY NMR experiments be used to reveal the relative orientation of the bipyridine units to the BINOL core due to the long distance (**3**) or the ambiguous results obtained with **2** because of the rotation of the phenylene unit around the aryl–aryl bonds. Therefore, we used electron circular dichroism (ECD) spectroscopy to study the diastereomers.[16]

Figure 11 depicts the ECD spectra of solutions of the silver(I) complexes of ligands **1**, **2** and **3a**. All of them show the same negative Cotton effect at around 350 nm, which would give rise to a (Δ,Δ) configuration at the metal centres when using (*M*)-configured ligands after the Exiton theory.[16] However, this would be in contrast to our previous assignment based on ROESY experiments for ligand **1**. Indeed, one has to be careful with this assignment because if the metal centres are coordinated by the two bipyridyl groups in an ideally tetrahedral geometry, the peak and trough of the Cotton effect would cancel each other to zero owing to the loss of the Davijdov split. In this case the measured spectrum of the complex solution would be the same as the spectrum of the free ligand for lack of complex-specific CD activity.[17]

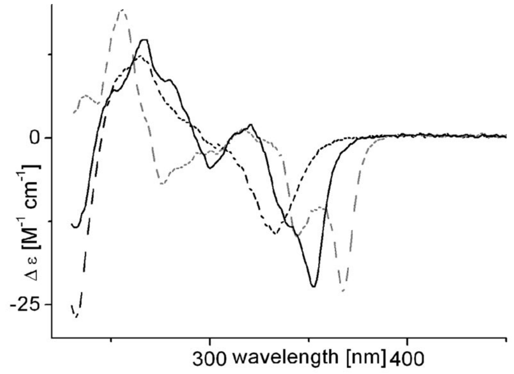


Figure 11. ECD spectra (CH_2Cl_2/CH_3CN, 1:1; 5×10^{-5} mol/L) of solutions of the silver(I) complexes of (*M*)-configured ligands **1** (black), **2** (black dashed) and **3a** (grey dashed).

As Figure 12 shows for ligand **2**, this is the case for all ligands. This might be a coincidence, but because we lack an alternative appropriate analytical method, we do not dare to make a definite assignment.

Octahedrally coordinated stereogenic metal centres, however, usually give rise to very distinct complex-specific CD signals that allow an unambiguous assignment of the stereochemistry of the metal centres. Unfortunately, only three triple-stranded dinuclear complexes with octahedral coordination of the metal centres are formed in a totally [zinc(II) and iron(II) with ligand **1**] or highly diastereoselective manner [iron(II) with ligand **2**]. The CD spectra of these complexes obtained from the (*M*)-configured ligands are shown in Figure 13. For the iron(II) complex of **2** the CD effects of the dominating species should dominate the spectrum. That is why this method is applicable even to mixed complex solutions.

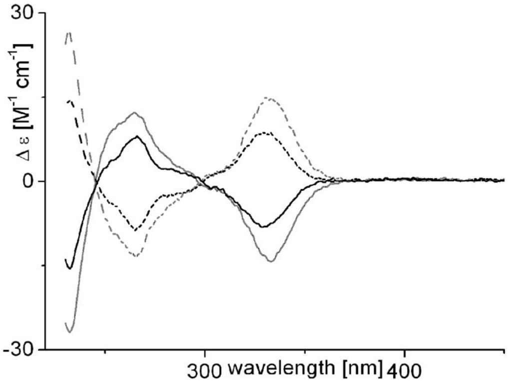


Figure 12. ECD spectra (CH_2Cl_2/CH_3CN, 1:1; 5×10^{-5} mol/L) of the solutions of free ligand **2**: (*M*)-**2** (black), (*P*)-**2** (black dashed) and solutions of silver(I) complexes with (*M*)-**2** (grey) and (*P*)-**2** (grey dashed).

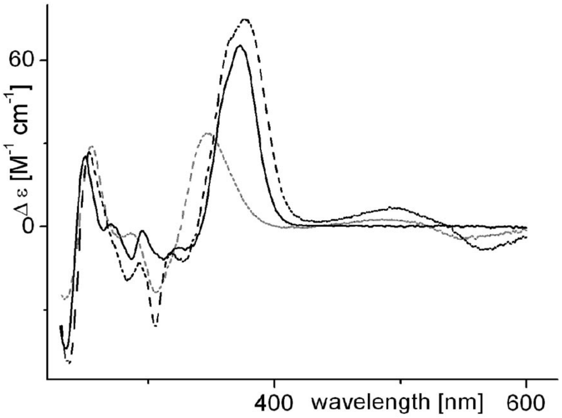


Figure 13. ECD spectra (CH_2Cl_2/CH_3CN, 1:1; 5×10^{-5} mol/L) of the zinc(II) complex formed by ligand (*M*)-**1** (black) and the iron(II) complexes formed by (*M*)-configured ligands **1** (black dashed) and **2** (grey dashed).

In fact, all three complexes exhibit strong positive cotton effects at about 380 nm, thus revealing a (Λ,Λ) configuration of the metal centres of the (*M*)-configured ligands, in accord with the Exiton theory.[16] This is in full agreement with the assignment of the (Δ,Δ) configuration to the $[Zn_2\{(P)\text{-}\mathbf{1}\}_3](BF_4)_4$ helicate on the basis of ROESY NMR studies and an X-ray crystal structure analysis.[4]

Conclusions

We have established a concise and effective synthesis of the enantiomerically pure bis(bipyridyl)-BINOL ligands **2** and **3** by 13–15-step reaction sequences. The self-assembly of dinuclear metal coordination compounds from ligands **2** and **3** and the late-transition-metal ions silver(I), zinc(II) and iron(II) was studied by ESI mass spectrometry and NMR spectroscopy to investigate the influence of different spacer lengths on the selectivity of these processes in terms of aggregate composition and diastereoselectivity in comparison with the previously published ligand **1**. Both ligands as well as **1** form double-stranded D_2-symmetric helicates upon coordination to silver(I) in a totally diastereoselective fashion. Unfortunately, neither ROESY NMR nor CD spectroscopy allowed an unambiguous assignment of the stereochemistry of the newly formed stereogenic metal centres.

With zinc(II), however, the elongated ligands **2** and **3** form mixtures of double- and triple-stranded ligands, thus lacking the selective formation of a single triple-stranded species as observed for ligand **1** earlier. In addition, the self-assembly of **1** with zinc(II) ions was found to be completely diastereoselective and the assignment of (Δ,Δ) stereochemistry to the metal centres formed with (*P*)-configured **1** was proven by CD spectroscopy.

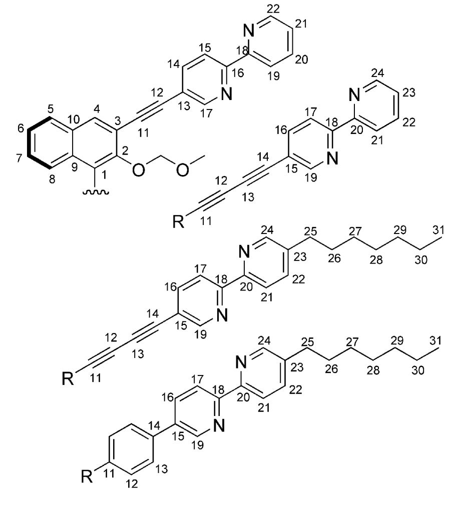
The same behaviour was previously found for ligand **1** upon complexation with iron(II). However, elongating the spacer again resulted in a different behaviour of ligands **2** and **3**. Although only triple-stranded species were formed with iron, the diastereoselectivity was found to drop with increasing spacer length: whereas intermediate ligand **2** was found to undergo highly diastereoselective self-assembly, ligand **3** was found to be totally unselective.

Thus, self-assembly processes yielding triple-stranded coordination compounds were found to be much more sensitive to subtle changes in the ligand structure, like an increase in spacer length, and react (either) with a growing loss of selectivity in terms of stoichiometric composition and/or diastereoselectivity of the assembly.

Experimental Section

General Remarks: All solvents were distilled and thoroughly dried prior to use according to standard procedures. All syntheses with air- and moisture-sensitive compounds were performed under Schlenk conditions with argon as the inert gas. For purification purposes column chromatography on silica gel and preparative thin-layer chromatography with silica gel layers were applied. Solvents for mobile phases were distilled prior to use. Detection was performed under UV light (254 and 366 nm). ^1H and ^{13}C NMR spectra were recorded at 298 K at 500.1 or 400.1 MHz and 125.8 or 100.6 MHz, respectively. ^1H NMR chemical shifts are reported on the δ scale (ppm) relative to residual non-deuterated solvent as the internal standard. ^{13}C NMR chemical shifts are given in δ values (ppm) relative to deuterated solvent as the internal standard. Signals were assigned on the basis of ^1H, ^{13}C, HMQC, HMBC and ROESY NMR experiments. The numbering of the ^1H and ^{13}C nuclei is shown in Scheme 9. Melting points are uncorrected.

Chemicals and reagents (except for the solvents) obtained from commercial sources were used as received. The following compounds were prepared according to published procedures: (*M*)- and (*P*)-2,2′-dihydroxy-1,1′-binaphthyl,[8,9] (*M*)- and (*P*)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl,[11] (*M*)- and (*P*)-3,3′-diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl [(*M*)- and (*P*)-**4**],[11] 4-(5′-heptyl-2,2′-bipyridyl-5-yl)phenylboronic acid pinalcolato ester (**5**),[13] 2-chloro-5-iodopyridine (**6**),[18] 2-chloro-5-(4-methoxyphenyl)pyridine (**8**),[14b] 5-methyl-5′-(4-methoxyphenyl)-2,2′-bipyridine (**9**),[13] 5-heptyl-5′-(4-methoxyphenyl)-2,2′-bipyridine (**10**),[13] 5-heptyl-5′-(4-hydroxyphenyl)-2,2′-bipyridine (**11**),[13] 4-(5′-heptyl-2,2′-bipyridyl-5-ylphenyl triflate (**12**),[13] (*M*)- and (*P*)-3,3′-bis[(trimethylsilyl)ethynyl]-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl [(*M*)- and (*P*)-**13**],[12] (*M*)- and (*P*)-3,3′-diethynyl-2,2′-bis-



Scheme 9. Numbering of nuclei.

(methoxymethoxy)-1,1′-binaphthyl [(*M*)- and (*P*)-**14**],[11] 5-bromoethynyl-2,2′-bipyridine (**15a**),[13] 2-bromo-5-heptylpyridine (**18b**),[13] 2-amino-5-iodopyridine (**19**),[19] 2-chloro-5-[(trimethylsilyl)ethynyl]pyridine (**20**),[20] 3-heptylpyridine (**21**),[13] 5-[(trimethylsilyl)ethynyl]-2,2′-bipyridine (**22a**),[13,14a] 5-heptyl-5′-[(trimethylsilyl)ethynyl]-2,2′-bipyridine (**22b**),[13] 5-ethynyl-2,2′-bipyridine (**23a**)[13,14a] and 5-ethynyl-5′-heptyl-2,2′-bipyridine (**23b**).[13]

(*M*)- and (*P*)-2,2′-Bis(methoxymethoxy)-3,3′-bis[4-(5′-heptyl-2,2′-bipyridyl-5-yl)phenyl]-1,1′-binaphthyl (2): (*M*)- or (*P*)-3,3′-Diiodo-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (**4**; 100 mg, 0.16 mmol, 1 equiv.), 5-heptyl-5′-[4-(pinacolatoboronyl)phenyl]-2,2′-bipyridine (**5**; 182 mg, 0.4 mmol, 2.5 equiv.), caesium fluoride (73 mg, 0.48 mmol, 3 equiv.) and [Pd(PPh$_3$)$_4$] (92 mg, 80 µmol, 0.5 equiv.) were dissolved in dry toluene (7 mL) and dry methanol (3 mL). The reaction mixture was heated at reflux for 7 d. The mixture was cooled to room temperature and water was added to dissolve inorganic byproducts. The layers were separated and the polar layer was extracted thoroughly with ethyl acetate. The combined organic layers were dried with Na$_2$SO$_4$. After removal of the solvents the crude product was purified by repeated flash column chromatography [1. petroleum ether (40–60 °C)/EtOAc/Et$_3$N (6:1:1) on silica gel; 2. petroleum ether (40–60 °C)/EtOAc/Et$_3$N (3:1:1) on alumina (neutral, activated); 3. petroleum ether (40–60 °C)/EtOAc/Et$_3$N (3:1:1) on alumina (basic, activated); 4. *n*-hexane/EtOAc/Et$_3$N (3:2:1) on silica gel; 5. preparative TLC (silica gel) with petroleum ether (40–60 °C)/EtOAc/Et$_3$N (6:1:1) as eluent]. Yield 110 mg (67%); m.p. 182 °C. Specific rotation: (*M*)-**2**: $[\alpha]_D^{23.8} = -193.3\times10^{-1}$ (c = 0.465, CH$_2$Cl$_2$); (*P*)-**2**: $[\alpha]_D^{22.1} = +197.9\times10^{-1}$ (c = 0.4725, CH$_2$Cl$_2$). CD (CH$_2$Cl$_2$/CH$_3$CN, 1:1, $c = 5\times10^{-5}$ mol/L): (*M*)-**2**: λ ($\Delta\varepsilon$) = 232 (–15.5), 266 (8.2), 329 (–8.2 L/mol cm) nm; (*P*)-**2**: λ ($\Delta\varepsilon$) = 232 (14.3), 265 (–8.7), 329 (8.7 L/mol cm) nm. R_f = 0.94 [petroleum ether (40–60 °C)/EtOAc/Et$_3$N (4:2:1) silica gel], 0.45 [petroleum ether (40–60 °C)/EtOAc/Et$_3$N (6:1:1) silica gel]. MS (ESI, pos.): *m*/*z* (%) = 1031.54 (100) [M + H]$^+$. HRMS (ESI, pos.): calcd. for [C$_{70}$H$_{71}$N$_4$O$_4$]$^+$ 1031.547; found 1031.5471. ^{1}H NMR (CDCl$_3$, 298.0 K, 400.1 MHz): δ = 0.83–0.93 (m, 6 H, 31-H), 1.20–1.43 (m, 16 H, 27-H, 28-H, 29-H, 30-H), 1.63–1.74 (m, 4 H, 26-H), 2.42 (s, 6 H, OCH$_3$), 2.69 (t, $^3J_{25,26}$ = 7.6 Hz, 4 H, 25-H), 4.46 (d, ^2J = 5.7 Hz, 2 H, OCH$_2$O), 4.51 (d, ^2J = 5.7 Hz, 2 H, OCH$_2$O), 7.31–7.38 (m, 4 H, 7-H, 8-H), 7.45 (ddd, $^3J_{6,5}$ = 6.2, $^3J_{6,7}$ = 6.3, $^4J_{6,8}$ = 1.8 Hz, 2 H, 6-H), 7.66 (dd, $^3J_{22,21}$ = 8.3, $^4J_{22,24}$ = 2.1 Hz, 2 H, 22-H), 7.79 (d, $^3J_{13,12}$ = 8.4 Hz, 4 H, 13-H), 7.92–7.95 (m, 6 H, 5-H, 12-H), 8.04 (s, 2 H, 4-H), 9.09 (dd, $^3J_{16,17}$ = 8.3, $^4J_{16,19}$ = 2.4 Hz, 2 H, 16-H), 8.38 (d, $^3J_{21,22}$ = 8.3 Hz, 2 H, 21-H), 8.49 (d, $^3J_{17,16}$ = 8.3 Hz, 2 H, 17-H), 8.54 (d, $^4J_{24,22}$ = 2.1 Hz, 2 H, 24-H), 9.00 (d, $^4J_{19,16}$ = 2.4 Hz, 2 H, 19-H) ppm. ^{13}C NMR (CDCl$_3$, 298.0 K, 100.6 MHz): δ = 14.0 (C-31), 22.6 (C-30), 29.1 (C-29)*, 29.1 (C-28)*, 31.1 (C-26), 31.7 (C-27)*, 32.9 (C-25), 55.9 (OCH$_3$), 98.6 (OCH$_2$O), 120.6 (C-21)*, 120.7 (C-17)*, 125.3 (C-6), 126.4 (C-8)*, 126.5 (C-1)*, 126.6 (C-7)*, 126.9 (C-13), 127.9 (C-5), 130.3 (C-12), 130.6 (C-10)*, 130.9 (C-4), 133.7 (C-9)*, 134.7 (C-3)*, 135.0 (C-16), 135.6 (C-15), 136.5 (C-14), 136.8 (C-22), 138.3 (C-23), 138.9 (C-11), 147.5 (C-19), 149.4 (C-24), 151.3 (C-2), 153.5 (C-20), 155.2 (C-18) ppm; * assignments may be interchanged.

(*M*)- and (*P*)-3,3′-Bis(2,2′-bipyridyl-5-ylbutadiynyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (3a): A solution of CuI (34 mg, 0.343 mmol, 1 equiv.) and NH$_2$OH·HCl (53 mg, 0.755 mmol, 2.2 equiv.) in EtNH$_2$ solution (2 mL, 70% in water) was added to a solution of (*M*)- or (*P*)-3,3′-diethynyl-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (**14**; 145 mg, 0.343 mmol, 1 equiv.) in dry DMF (2 mL). The mixture was stirred for 3 min. Then a solution of 5-bromoethynyl-2,2′-bipyridine (**15a**; 249 mg, 0.96 mmol, 2.8 equiv.) in dry DMF (3 mL) was slowly added over a period of 30 min. After 2 h the solution was quenched with satd. aq. EDTA followed by satd. aq. Na$_2$CO$_3$. The aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layers were dried with Na$_2$SO$_4$. The solvents were removed and the crude product was purified by flash column chromatography on silica gel [petroleum ether (40–60 °C)/EtOAc (2:1) + 5% Et$_3$N]. Yield 168 mg (63%); m.p. 108 °C. Specific rotation: (*M*)-**3a**: $[\alpha]_D^{23.5} = -525.5\times10^{-1}$ (c = 0.4725, CH$_2$Cl$_2$); (*P*)-**3a**: $[\alpha]_D^{23.8} = +512.3\times10^{-1}$ (c = 0.29, CH$_2$Cl$_2$). CD [CH$_2$Cl$_2$/CH$_3$CN (1:1) $c = 5\times10^{-5}$ mol/L]: (*M*)-**3a**: λ ($\Delta\varepsilon$) = 237 (3.5), 255 (9.7), 276 (–3.3), 345 (–7.5), 368 (–11.6 L/mol cm) nm; (*P*)-**3a**: λ ($\Delta\varepsilon$) = 235 (–4.1), 255 (–10.3), 276 (3.6), 344 (9.1), 367 (13.1 L/mol cm) nm; R_f = 0.3 [petroleum ether (40–60 °C)/EtOAc (2:1) + 5% Et$_3$N]. MS (ESI, pos.): *m*/*z* (%) = 801.2 (100) [M + Na]$^+$ + [(M + Na)$_2$]$^{2+}$, 779.3 (50) [M + H]$^+$. HRMS (ESI, pos.): calcd. for [C$_{52}$H$_{34}$N$_4$O$_4$Na]$^+$ 801.2472; found 801.2433. ^{1}H NMR (CDCl$_3$, 298.0 K, 400.1 MHz): δ = 2.66 (s, 6 H, OCH$_3$), 4.92 (d, ^2J = 6.1 Hz, 2 H, OCH$_2$O), 5.09 (d, ^2J = 6.1 Hz, 2 H, OCH$_2$O), 7.22 (d, $^3J_{8,7}$ = 8.4 Hz, 2 H, 8-H), 7.29–7.36 (m, 4 H, 7-H, 23-H), 7.45 (ddd, $^3J_{6,7}$ = 6.8, $^3J_{6,5}$ = 8.1, $^4J_{6,8}$ = 1.1 Hz, 2 H, 6-H), 7.81 (ddd, $^3J_{22,21}$ = 7.7, $^3J_{22,23}$ = 7.8, $^4J_{22,24}$ = 1.8 Hz, 2 H, 22-H), 7.86 (d, $^3J_{5,6}$ = 8.1 Hz, 2 H, 5-H), 7.93 (dd, $^3J_{16,17}$ = 8.3, $^4J_{16,19}$ = 2.2 Hz, 2 H, 16-H), 8.26 (s, 2 H, 4-H), 8.40–8.43 (m, 4 H, 17-H, 21-H), 8.68 (ddd, $^3J_{24,23}$ = 4.8, $^4J_{24,22}$ = 1.8, $^5J_{24,21}$ = 0.9 Hz, 2 H, 24-H), 8.81 (dd, $^4J_{19,16}$ = 2.2, $^5J_{19,17}$ = 0.8 Hz, 2 H, 19-H) ppm. ^{13}C NMR (CDCl$_3$, 298.0 K, 100.6 MHz): δ = 56.4 (OCH$_3$), 77.8, 78.2 (C-12, C-13)*, 79.6 (C-14), 80.3 (C-11), 99.3 (OCH$_2$O), 115.9 (C-3), 119.0 (C-15), 120.4 (C-17), 121.7 (C-21), 124.2 (C-23), 125.9, 126.0 (C-1, C-6)*, 126.6 (C-8), 127.9 (C-5), 128.2 (C-7), 130.3 (C-10), 134.3 (C-9), 136.2 (C-4), 137.1 (C-22), 140.4 (C-16), 149.4 (C-24), 152.7 (C-19), 153.7 (C-2), 155.3 (C-20), 155.6 (C-18) ppm; * assignments may be interchanged.

(*P*)-3,3′-Bis(5′-heptyl-2,2′-bipyridyl-5-ylbutadiyndiyl)-2,2′-bis(methoxymethoxy)-1,1′-binaphthyl (3b): (*P*)-3,3′-Bis(ethynyl)-2,2′-bis-(methoxymethoxy)-1,1′-binaphthyl (**13**; 42 mg, 0.1 mmol, 1 equiv.) was dissolved in THF (1 mL) and water (0.5 mL). Then *n*BuNH$_2$ (120 µL, 88 mg, 1.2 mmol, 98%, 12 equiv.) was slowly added. After that CuCl (3 mg, 0.03 mmol, 30 mol-%) and NH$_2$OH·HCl (4.2 mg, 0.06 mmol, 60 mol-%) were consecutively added. The mixture was stirred for 15 min. Then a solution of 5-bromoethynyl-5′-heptyl-2,2′-bipyridine (**15b**; 107 mg, 0.3 mmol, 3 equiv.) in THF (1 mL) was added dropwise and the solution was stirred for 20 h at room temperature. The mixture was quenched with water and diethyl ether was added. The layers were separated and the organic layer was washed three times with satd. aq. EDTA, water and brine. The organic layer was dried with Na_2SO_4 and the solvents were removed. The crude product was purified by flash column chromatography on silica gel [*n*-hexane/EtOAc (3:1) + 5% Et_3N]. Yield 28 mg (29%); m.p. 138–140 °C. Specific rotation: (*P*)-**3b**: $[\alpha]_D^{27}$ = +122.0 × 10^{-1} (*c* = 0.395, CH_2Cl_2); R_f = 0.67 [*n*-hexane/EtOAc (3:1) + 5% Et_3N]. MS (ESI, pos.): *m*/*z* (%) = 975.5 (70) $[M + H]^+$, 488.2 (100) $[M + 2H]^+$. HRMS (ESI, pos.): calcd. for $[C_{66}H_{63}N_4O_4]^+$ 975.4844; found 975.4835. ^1H NMR ($CDCl_3$, 300.0 K, 500.1 MHz): δ = 0.88 (t, $^3J_{31,30}$ = 7.1 Hz, 6 H, 31-H), 1.23–1.39 (m, 16 H, 27-H, 28-H, 29-H, 30-H), 1.63–1.70 (m, 4 H, 26-H), 2.64–2.71 (m, 4 H, 25-H), 2.67 (s, 6 H, OCH_3), 4.93 (d, ^2J = 6.2 Hz, 2 H, OCH_2O), 5.09 (d, ^2J = 6.2 Hz, 2 H, OCH_2O), 7.22 (d, $^3J_{8,7}$ = 8.1 Hz, 2 H, 8-H), 7.34 (dd, $^3J_{7,6}$ = 7.4, $^3J_{7,8}$ = 8.1 Hz, 2 H, 7-H), 7.45 (dd, $^3J_{6,7}$ = 7.4, $^3J_{6,5}$ = 7.4 Hz, 2 H, 6-H), 7.66 (dd, $^3J_{22,21}$ = 8.1, $^4J_{22,24}$ = 1.4 Hz, 2 H, 22-H), 7.86 (d, $^3J_{5,6}$ = 7.4 Hz, 2 H, 5-H), 7.92 (dd, $^3J_{16,17}$ = 8.2, $^4J_{16,19}$ = 2.1 Hz, 2 H, 16-H), 8.27 (s, 2 H, 4-H), 8.34 (d, $^3J_{21,22}$ = 8.1 Hz, 2 H, 21-H), 8.41 (d, $^3J_{17,16}$ = 8.2 Hz, 2 H, 17-H), 8.52 (s, 2 H, 24-H), 8.80 (s, 2 H, 19-H) ppm. ^{13}C NMR ($CDCl_3$, 300.0 K, 125.8 MHz): δ = 14.0 (C-31), 22.6 (C-30), 29.05, 29.08 (C-28, C-29)*, 31.0 (C-26), 31.7 (C-27), 32.9 (C-25), 56.3 (OCH_3), 77.7, 77.9 (C-12, C-13)*, 79.6 (C-14), 80.1 (C-11), 99.2 (OCH_2O), 115.9 (C-3), 118.6 (C-15), 120.1 (C-17), 121.3 (C-21), 125.7 (C-1), 125.9 (C-6), 126.4 (C-8), 127.8 (C-5), 128.0 (C-7), 130.1 (C-10), 134.2 (C-9), 136.1 (C-4), 137.1 (C-22), 139.0 (C-23), 140.2 (C-16), 149.3 (C-24), 152.6 (C-19), 152.7 (C-20), 153.6 (C-2), 155.4 (C-18) ppm; * assignment may be interchanged.

5-(Bromoethynyl)-5′-heptyl-2,2′-bipyridine (15b): Br_2 (22 µL) was added to a solution of ice (320 mg) and aq. NaOH (130 µL, 10 mol/L) in an open flask to form a light-yellow solution of sodium hypobromite. A satd. solution of 5-ethynyl-5′-heptyl-2,2′-bipyridine (**23b**; 100 mg, 0.432 mmol) in THF was slowly added dropwise (it is crucial to keep the amount of THF as small as possible). The reaction was monitored by TLC [*n*-hexane/EtOAC (5:1) + 0.5% Et_3N]. After about 24 h the reaction was quenched by addition of satd. aq. NH_4Cl. The product was extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4 and the solvent was removed. The crude product was purified by chromatography on silica gel [*n*-hexane/EtOAc (10:1) + 5% Et_3N]. Yield 127 mg (82%); m.p. 73 °C. R_f = 0.67 [*n*-hexane/EtOAc (10:1) + 5% Et_3N]. $C_{19}H_{21}BrN_2\cdot 1/9C_6H_{14}$ (357.29+9.57): calcd. C 64.39, H 6.20, N 7.64; found C 64.55, H 6.21, N 7.67. MS (EI): *m*/*z* (%) = 356.1 (100) $[M(^{79}Br)]^+$, 358.1 (99) $[M(^{81}Br)]^+$, 285.0 (38) $[M(^{79}Br) - C_5H_{11}]^+$, 285.0 (38) $[M(^{81}Br) - C_5H_{11}]^+$, 271.0 (98) $[M(^{79}Br) - C_6H_{13}]^+$, 273.0 (98) $[M(^{81}Br) - C_6H_{13}]^+$. HRMS (EI): calcd. for $[C_{19}H_{21}{}^{79}BrN_2]^+$ 356.0888; found 356.0896. ^1H NMR ($CDCl_3$, 298.0 K, 400.1 MHz): δ = 0.87 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.22–1.38 (m, 8 H, 4 CH_2), 1.60–1.69 (m, 2 H, CH_2), 2.65 (t, ^3J = 7.6 Hz, 2 H, CH_2-bipy), 7.62 (dd, ^3J = 8.1, ^4J = 2.2 Hz, 1 H, bipy), 7.83 (dd, ^3J = 8.3, ^4J = 2.1 Hz, 1 H, bipy), 8.29 (d, ^3J = 8.1 Hz, 1 H, bipy), 8.34 (dd, ^3J = 8.3, ^5J = 0.7 Hz, 1 H, bipy), 8.49 (d, ^4J = 2.2 Hz, 1 H, bipy), 8.49 (dd, ^4J = 2.1, ^5J = 0.7 Hz, 1 H, bipy) ppm. ^{13}C NMR ($CDCl_3$, 298.0 K, 100.6 MHz): δ = 14.2 (CH_3), 22.8 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 31.2 (CH_2), 31.9 (CH_2), 33.0 (CH_2-bipy), 52.3 (Br-*C*≡C-bipy), 77.5 (Br-C≡*C*-bipy), 119.5 (bipy), 120.1 (bipy), 121.2 (bipy), 136.9 (bipy), 138.9 (bipy), 139.9 (bipy), 149.6 (bipy), 152.2 (bipy), 153.1 (bipy), 155.6 (bipy) ppm.

Preparation of Metal Complexes as Exemplified for the Synthesis of $[Ag_2\{(M)\text{-}\mathbf{2}\}_2](BF_4)_2$: Compound (*M*)-**2** (3.00 mg, 2.91 µmol) and $[Ag(CH_3CN)_2]BF_4$ (1.065 mg, 2.91 µmol) were dissolved in CD_2Cl_2 (0.6 mL) and CD_3CN (0.3 mL), respectively. The two solutions were combined and mixed. The resulting light-yellow solution was transferred into an NMR tube. Likewise solutions for ESI-MS and CD were generated. For ESI-MS and CD studies 5×10^{-5} mol/L solutions were prepared (CH_2Cl_2/CH_3CN, 1:1).

$[Ag_2\{(M)\text{-}\mathbf{2}\}_2](BF_4)_2/[Ag_2\{(P)\text{-}\mathbf{2}\}_2](BF_4)_2$: CD: (*M*): λ ($\Delta\varepsilon$): = 232 (–26.9), 265 (12.3), 333 (–14.3 L/mol cm) nm; (*P*): = 232 (26.5), 266 (–13.2), 330 (14.8 L/mol cm) nm. MS (ESI, pos., CD_2Cl_2/CD_3CN): *m*/*z* (%) = 1139.4 (25) $[Ag_2\mathbf{2}_2]^{2+}$, $[Ag\mathbf{2}]^+$, 1085.5 (10) $[Ag\mathbf{2} + H]^{2+}$, 1031.6 (10) $[\mathbf{2} + H]^+$, 724.0 (15) $[Ag\mathbf{2} + 2H]^{3+}$, 570.2 (25) $[Ag\mathbf{2} + H]^{2+}$, 516.3 (100) $[\mathbf{2} + 2H]^{2+}$. ^1H NMR [CD_2Cl_2/CD_3CN (2:1), 298.0 K, 500.1 MHz]: δ = 0.87 (t, $^3J_{31,30}$ = 7.1 Hz, 12 H, 31-H), 1.23–1.40 (m, 32 H, 27-H, 28-H, 29-H, 30-H), 1.64–1.72 (m, 8 H, 26-H), 2.27 (s, 12 H, OCH_3), 2.73 (t, $^3J_{25,26}$ = 7.8 Hz, 8 H, 25-H), 4.27 (d, ^2J = 5.5 Hz, 4 H, OCH_2O), 4.35 (d, ^2J = 5.5 Hz, 4 H, OCH_2O), 7.20 (d, $^3J_{8,7}$ = 8.5 Hz, 4 H, 8-H), 7.28 (ddd, $^3J_{7,8}$ = 8.5, $^3J_{7,6}$ = 6.8, $^4J_{7,5}$ = 1.2 Hz, 4 H, 7-H), 7.42 (ddd, $^3J_{6,5}$ = 8.4, $^3J_{6,7}$ = 6.8, $^4J_{6,8}$ = 1.2 Hz, 4 H, 6-H), 7.76 (d, $^3J_{13,12}$ = 8.4 Hz, 8 H, 13-H), 7.83 (d, $^3J_{12,13}$ = 8.4 Hz, 8 H, 12-H), 7.91 (d, $^3J_{5,6}$ = 8.4 Hz, 4 H, 5-H), 7.94 (dd, $^3J_{22,21}$ = 8.3, $^4J_{22,24}$ = 2.1 Hz, 4 H, 22-H), 7.99 (s, 4 H, 4-H), 8.28 (d, $^3J_{21,22}$ = 8.3 Hz, 4 H, 21-H), 8.34 (dd, $^3J_{16,17}$ = 8.5, $^4J_{16,19}$ = 2.2 Hz, 4 H, 16-H), 8.37 (dd, $^3J_{17,16}$ = 8.5, $^5J_{17,19}$ = 0.6 Hz, 4 H, 17-H), 8.53 (d, $^4J_{24,22}$ = 2.1 Hz, 4 H, 24-H), 8.93 (dd, $^4J_{19,16}$ = 2.2, $^5J_{19,17}$ = 0.6 Hz, 4 H, 19-H) ppm. ^{13}C NMR [CD_2Cl_2/CD_3CN (2:1), 298.0 K, 125.8 MHz]: δ = 13.6 (C-31), 22.5 (C-30), 28.9 (C-28/C-29), 30.8 (C-26), 31.6 (C-27), 32.4 (C-25), 55.6 (OCH_3), 98.4 (OCH_2O), 122.3 (C-17/C-21), 125.4 (C-6), 126.0 (C-8), 126.4 (C-1), 126.5 (C-7), 126.9 (C-13), 128.0 (C-5), 130.4 (C-12), 130.6 (C-4), 130.9 (C-10), 133.6 (C-9), 134.4 (C-3), 134.9 (C-14), 136.8 (C-16), 137.4 (C-15), 139.0 (C-22), 139.6 (C-11), 140.9 (C-23), 148.7 (C-19), 149.5 (C-20), 150.8 (C-24), 150.9 (C-2/C-18) ppm.

$[Ag_2\{(M)\text{-}\mathbf{3a}\}_2](BF_4)_2/[Ag\{(P)\text{-}\mathbf{3a}\}_2](BF_4)_2$: CD: (*M*): λ ($\Delta\varepsilon$) = 237 (6.4), 256 (19.3), 275 (–6.8), 344 (–14.8), 367 (–22.9 L/mol cm) nm; (*P*) = 236 (–7.7), 256 (–19.9), 277 (6.9), 345 (16.3), 368 (24.2 L/mol cm) nm. MS (ESI, pos., CD_2Cl_2/CD_3CN): *m*/*z* (%) = 887.2 (90) $[Ag_2\mathbf{3a}_2]^{2+}$, $[Ag\mathbf{3a}]^+$, 779.3 (100) $[\mathbf{3a} + H]^+$, 390.1 (50) $[\mathbf{3a} + 2H]^{2+}$. ^1H NMR [CD_2Cl_2/CD_3CN (5:32), 298.0 K, 500.1 MHz]: δ = 2.61 (s, 12 H, OCH_3), 4.81 (d, ^2J = 5.9 Hz, 4 H, OCH_2O), 4.88 (d, ^2J = 5.9 Hz, 4 H, OCH_2O), 7.08 (d, $^3J_{8,7}$ = 8.5 Hz, 4 H, 8-H), 7.30 (ddd, $^3J_{7,8}$ = 8.5, $^3J_{7,6}$ = 6.8, $^4J_{7,5}$ = 2.2 Hz, 4 H, 7-H), 7.44 (ddd, $^3J_{6,7}$ = 6.8, $^3J_{6,5}$ = 8.2, $^4J_{6,8}$ = 1.1 Hz, 4 H, 6-H), 7.51 (ddd, $^3J_{23,24}$ = 4.9, $^3J_{23,22}$ = 7.9, $^4J_{23,21}$ = 1.1 Hz, 4 H, 23-H), 7.87 (d, $^3J_{5,6}$ = 8.2 Hz, 4 H, 5-H), 7.99 (ddd, $^3J_{22,23}$ = 7.9, $^3J_{22,21}$ = 7.9, $^4J_{22,24}$ = 1.7 Hz, 4 H, 22-H), 8.09 (dd, $^3J_{16,17}$ = 8.4, $^4J_{16,19}$ = 2.1 Hz, 4 H, 16-H), 8.25–8.30 (m, 12 H, 4-H, 17-H, 21-H), 8.64 (ddd, $^3J_{24,23}$ = 4.9, $^4J_{24,22}$ = 1.7, $^5J_{24,21}$ = 0.8 Hz, 4 H, 24-H), 8.74 (dd, $^4J_{19,16}$ = 2.1, $^5J_{19,17}$ = 0.6 Hz, 4 H, 19-H) ppm. ^{13}C NMR [CD_2Cl_2/CD_3CN (5:3), 298.0 K, 125.8 MHz]: δ = 56.6 (OCH_3), 77.3 (C-13)*, 78.8 (C-14), 79.2 (C-12)*, 81.4 (C-11), 99.6 (OCH_2O), 115.9 (C-3), 120.6 (C-15), 122.2 (C-17), 123.3 (C-21), 126.10, 126.12 (C-1/C-23), 126.58, 126.61 (C-6/C-8), 128.6 (C-5), 128.8 (C-7), 130.7 (C-10), 134.8 (C-9), 136.9 (C-4), 139.3 (C-22), 142.2 (C-16), 151.2 (C-24), 152.6 (C-20), 152.9 (C-18), 153.75 (C-2), 153.81 (C-19) ppm; * assignments may be interchanged.

Supporting Information (see also the footnote on the first page of this article): MS spectra of the complexes $[Ag_2\mathbf{3a}_2](BF_4)_2$ and $[Fe_2\mathbf{2}_3](BF_4)_4$, CD spectra of both enantiomers of **3a** and their silver(I) helicates.

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[1] For general reviews, see: a) J. S. Lindsey, *New J. Chem.* **1991**, *15*, 153–180; b) D. S. Lawrence, T. Jiang, M. Levett, *Chem. Rev.* **1995**, *95*, 2229–2260; c) M. C. T. Fyfe, J. F. Stoddart, *Acc. Chem. Res.* **1997**, *30*, 393–401; d) L. M. Greig, D. Philp, *Chem. Soc. Rev.* **2001**, *30*, 287–302.

[2] For recent reviews on stereoselective self-assembly, see: a) M. S. Spector, J. V. Selinger, J. M. Schnur, *Top. Stereochem.* **2003**, *24*, 281–372; b) T. D. Hamilton, L. R. MacGillivray, *Cryst. Growth Des.* **2004**, *4*, 419–430; c) M. A. Mateos-Timoneda, M. Crego-Calama, D. N. Reinhoudt, *Chem. Soc. Rev.* **2004**, *33*, 363–372; d) *Supramolecular Chirality* (Eds.: M. Crego-Calama, D. N. Reinhoudt), *Topics in Current Chemistry* **2006**, vol. 265; e) C. He, Y. Zhao, D. Guo, Z. Lin, C. Duan, *Eur. J. Inorg. Chem.* **2007**, 3451–3463; f) S. L. Lee, W. Lin, *Acc. Chem. Res.* **2008**, *41*, 521–537.

[3] a) E. C. Constable, *Tetrahedron* **1992**, *48*, 10013–10059; b) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062; c) M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–287; d) A. von Zelewsky, *Coord. Chem. Rev.* **1999**, *190–192*, 811–825; e) U. Knof, A. von Zelewsky, *Angew. Chem.* **1999**, *111*, 312–333; *Angew. Chem. Int. Ed.* **1999**, *38*, 302–322; f) A. von Zelewsky, O. Mamula, *J. Chem. Soc., Dalton Trans.* **2000**, 219–231; g) M. Albrecht, *Chem. Eur. J.* **2000**, *6*, 3485–3489; h) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; i) O. Mamula, A. von Zelewsky, *Coord. Chem. Rev.* **2003**, *242*, 87–95; for a more comprehensive list of references on the diastereoselective self-assembly of helicates, see references listed in ref.[5].

[4] A. Lützen, M. Hapke, J. Griep-Raming, D. Haase, W. Saak, *Angew. Chem.* **2002**, *114*, 2190–2194; *Angew. Chem. Int. Ed.* **2002**, *41*, 2086–2089.

[5] J. Bunzen, T. Bruhn, G. Bringmann, A. Lützen, *J. Am. Chem. Soc.* **2009**, *131*, 3621–3630.

[6] a) U. Kiehne, T. Weilandt, A. Lützen, *Org. Lett.* **2007**, *9*, 1283–1286; b) U. Kiehne, T. Weilandt, A. Lützen, *Eur. J. Org. Chem.* **2008**, 2056–2064.

[7] U. Kiehne, A. Lützen, *Org. Lett.* **2007**, *9*, 5333–5336.

[8] L. F. Tietze, T. Eicher in *Reaktionen und Synthesen im organisch-chemischen Praktikum und Forschungslaboratorium*, 2nd ed., Thieme, Stuttgart, **1991**, p. 446.

[9] Q.-S. Hu, D. Vitharana, L. Pu, *Tetrahedron: Asymmetry* **1995**, *6*, 2123–2126.

[10] X.-W. Yang, J.-H. Sheng, C.-S. Da, H.-S. Wang, W. Su, R. Wang, A. S. C. Chan, *J. Org. Chem.* **2000**, *65*, 295–296.

[11] A. Bähr, A. S. Droz, M. Puentener, U. Neidlein, S. Anderson, P. Seiler, F. Diederich, *Helv. Chim. Acta* **1998**, *81*, 1931–1963.

[12] O. Dangles, F. Guibe, G. Balavoine, S. Lavielle, A. Marquet, *J. Org. Chem.* **1987**, *52*, 4984–4993.

[13] U. Kiehne, J. Bunzen, H. Staats, A. Lützen, *Synthesis* **2007**, 1061–1069.

[14] a) A. Lützen, M. Hapke, *Eur. J. Org. Chem.* **2002**, 2292–2297; b) A. Lützen, M. Hapke, H. Staats, J. Bunzen, *Eur. J. Org. Chem.* **2003**, 3948–3957; c) M. Hapke, H. Staats, I. Wallmann, A. Lützen, *Synthesis* **2007**, 2711–2719; d) M. Hapke, L. Brandt, A. Lützen, *Chem. Soc. Rev.* **2008**, *37*, 2782–2797.

[15] H. Sigel, R. B. Martin, *Chem. Soc. Rev.* **1994**, *23*, 83–91.

[16] N. Berova, K. Nakanishi, R. W. Woody (Eds.), *Circular Dichroism: Principles and Applications*, Wiley-VCH, Weinheim, **2000**.

[17] M. Ziegler, A. von Zelewsky, *Coord. Chem. Rev.* **1998**, *177*, 257–300.

[18] O. Magidson, G. Menschikov, *Ber. Dtsch. Chem. Ges. B* **1925**, *58*, 113–118.

[19] a) Y. Hama, Y. Nobuhara, Y. Aso, T. Otsubo, F. Ogura, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1683–1686; b) L. Dolci, F. Dolle, H. Valette, F. Vaufrey, C. Fuseau, M. Bottlaender, C. Crouzel, *Bioorg. Med. Chem.* **1999**, *7*, 467–479.

[20] P. N. W. Baxter, *J. Org. Chem.* **2000**, *65*, 1257–1272.

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