Long-Distance Propagation of Stereochemical Information by Stereoselective Synthesis of Copper(I) Bipyridine Helicates

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Several chiral ligands have been obtained by linking two achiral chains containing up to three bipyridine units to various dissymmetric templates. Addition of copper(I) and silver(I) ions resulted in the highly stereoselective formation of bis(helicates), the absolute configuration of which was dictated by that of the templates, with (*P*) or (*M*) helicates being formed from (*R*) or (*S*) templates, respectively. In the cases of ligands containing three bipyridine units, the stereochemical information was transferred from the templates to the helicates over a distance of about 20 Å.

Introduction

Information technology, the storage and transmission of information, is a dominant issue in present day science. Chemistry deals with information technology at the molecular level, at which stereochemical information represents an important characteristic, capable of being manipulated. A few "molecular devices" capable of performing information-related functions have been synthesized.[1] These include, among others, several helical structures capable of chirality amplification,[1] and a sensor able to "memorize" chirality.[2]

In principle, any stereoselective process generating new stereogenic element(s) under the influence of pre-existing one(s) can be regarded as a transfer of stereochemical information.[3,4] As such, transmission of stereochemical information from one molecule to another, or within the same molecule, may appear an easy task to accomplish. However, even if some examples of this so-called "remote asymmetric induction" are known, the efficiency of these transfers generally decreases sharply when the distance between the "informing" and the "informed" stereogenic elements is increased.[3]

Supramolecular chemistry, allowing the assembly of large, cooperative structures in a relatively simple way, offers new opportunities not only for long-distance propagation of stereochemical information, but also for the stereoselective construction of uncommon stereogenic elements, such as those in a helicate.[5] In the last few years, various examples of stereoselective syntheses of helicates have been reported.[6]

In these, the presence of stereocenters located either within,[6b,6f,6g] or at the end of,[6c−6e,6h,6i] the residues involved in helicate formation have been exploited to control the stereochemistry of the supramolecular structure.

In tackling this problem, we selected a different approach: namely, the use of an auxiliary template that should be able to direct the helicate configuration, and then eventually be removable to deliver a chiral, nonracemic helicate devoid of any other stereogenic element besides the helix itself. Here we report the results of this work.[7]

The C_2-symmetric compounds **1−5** (Scheme 1, see **A** for a general representation) were identified as possible chiral templates. They differed in their conformational flexibility around the bonds connecting the reacting functionalities, and were expected to allow a straightforward attachment of achiral ligands for helicate construction. Oligobipyridines were chosen as these ligands, on the basis of the demonstrated tendency of these derivatives to wrap around metal ions to generate double helical structures.[5,6]

Treatment of the chiral templates **1−5** with the appropriate bipyridine **6** or **7** (Scheme 1, general formula **B**) gave ligands **8−12** (Scheme 1, **C**). In particular, esters **8**, **9**, and **11** were obtained by conversion of **1**, **2**, and **4** into the corresponding acid chlorides (oxalyl chloride, dichloromethane), followed by treatment with alcohol **6** (TEA, dichloromethane, cat. DMAP), in 70, 56, and 65% yields, respectively. Treatment of **3** and **5** with NaH in THF, followed by treatment with bromide **7**, gave ethers **10** (55% yield) and **12** (40% yield).

Addition of 1 mol-equiv. of CuOTf or $CuOCOCF_3$, dissolved in acetonitrile, to a 0.01−0.05 M solution of **8−10** (derived from the chiral templates **1−3**) in chloroform under argon (Scheme 2) resulted in the formation of single complexes **13−15**. The products were isolated in nearly quantitative yield (≥ 95%) by filtration on deactivated alumina (see below for structural determination). On the other hand, ligands **11** and **12** did not afford single copper complexes upon addition of CuOTf, but exclusively gave complexes **16** and **17** as single species upon treatment with AgOTf.[8] The yields of the silver complexes were similarly high

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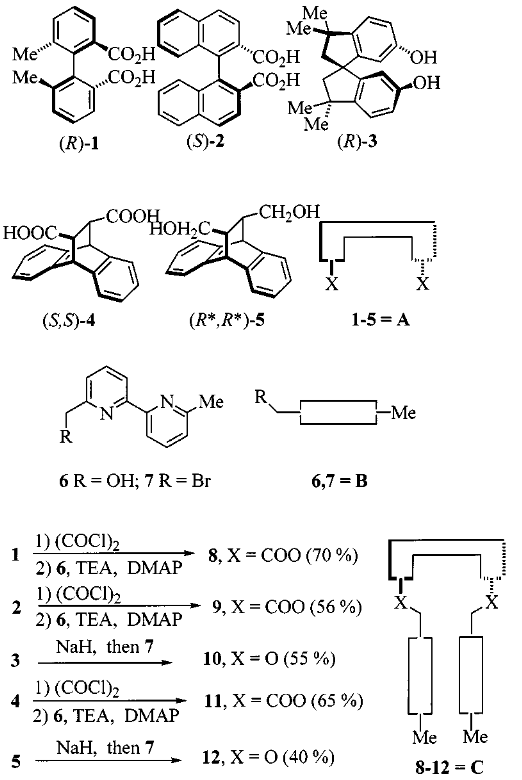
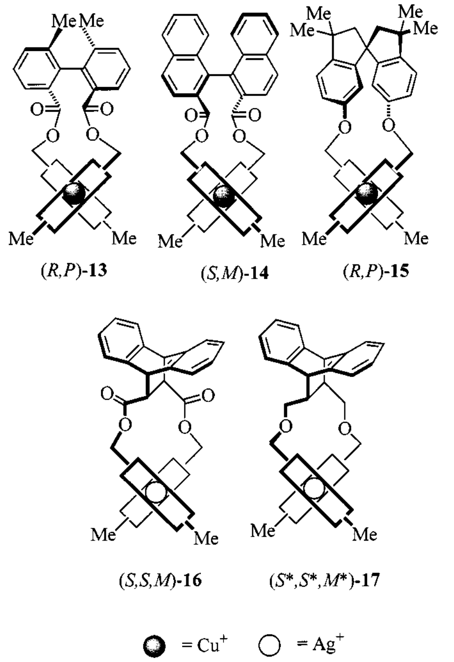


Scheme 1. Structures of templates **1−5** and bipyridines **6−7**, and synthesis of ligands **8−12**

and no purification was required. Thus, the template spacer induced selectivity for a specific metal into the ligand.

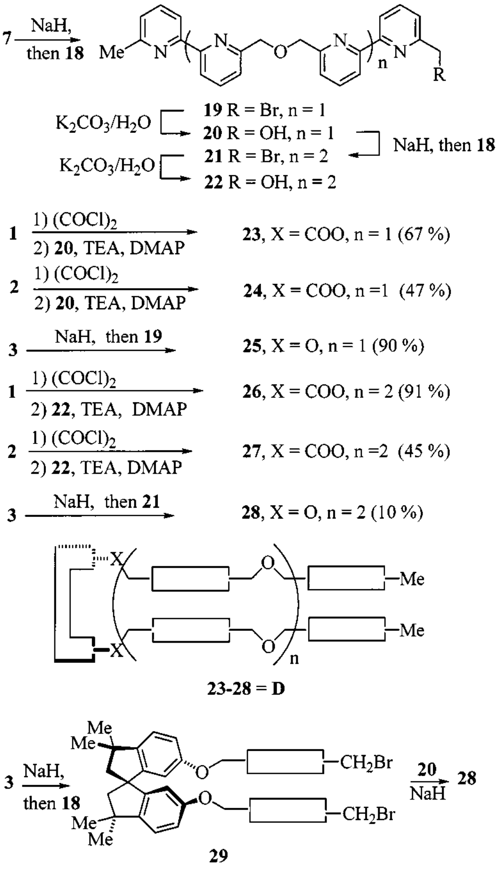


Scheme 2. Synthesis of complexes **13−17**

The different behavior of ligands **8−10** and **11** and **12** toward copper(I) ions can be accounted for by the different conformational rigidity of the chiral templates. When the bipyridine units are bound to templates **4** and **5**, they cannot be brought as close to each other as when bound to templates **1−3**. As a consequence, it is likely that the cavities formed in the cases of ligands **11** and **12** are larger than those in the cases of **8−10**. In these cavities, the smaller copper ion fits loosely, while the bigger[9] silver one can be better accommodated.

It is well known that the formation constant for Ag(bipy)$_2^+$ is much lower than that for Cu(bipy)$_2^+$.[9,10] Since effective metal/ligand complexation was necessary to build metal helicates strong enough to survive the projected removal of the chiral template, it was decided not to develop the ligands derived from templates **4** and **5** further.

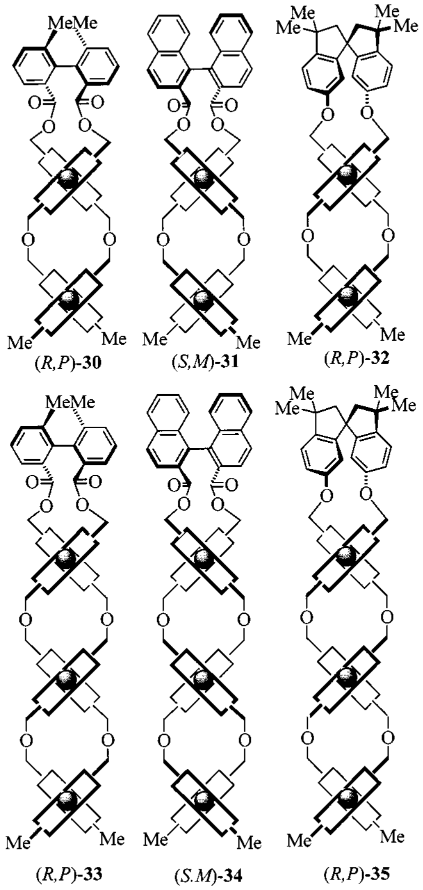
The synthesis of longer bipyridine chains **19−22** was accomplished as described in Scheme 3. Alcohol **6** was first transformed into its sodium salt and then treated with 6,6′-bis(bromomethyl)-2,2′-bipyridine (**18**) to give bromide **19** in 64% yield. K_2CO_3-promoted hydrolysis in dioxane/water gave alcohol **20** in 98% yield. Iteration of this procedure, starting from **20**, gave bromide **21** (61%) and alcohol **22** (63%).



Scheme 3. Synthesis of polybipyridines **19−22** and of ligands **23−28**

Attachment of these strands to templates **1−3** was performed as described above. Although ligands **23−27** (general formula **D**) were isolated in yields ranging from 47 to 90%, condensation of template **3** with bromide **21** gave ether **28** in very low yield.[11] An alternative pathway to this compound was found in treatment of template **3** with dibromide **18** (52%), followed by condensation of the resulting adduct **29** with the sodium salt of alcohol **20**. Compound **28** was thus obtained in 76% yield.

Addition of Cu^I salts to ligands **23−28** (see above) resulted in the formation of deep red solutions, from which the metal complexes **30−35** (Scheme 4) were isolated in ≥ 95% yields by filtration on deactivated alumina.[12]



Scheme 4. Synthesis of complexes **30−35**

The structures of these complexes were established by a combination of NMR spectroscopy and chiroptical studies. The ^{1}H and ^{13}C NMR spectra of the ligands showed discrete regions for each of the respective proton and carbon types. Upon metal complexation, specific signal regions of the ^{1}H NMR spectra experienced dramatic changes that were diagnostic of helicate formation. For instance, the signals of the methylene groups closest to the template in ligands **8**, **23**, and **26** (derived from template **1**) were singlets at $\delta \approx 5.2$, due to accidental isochrony of the diastereotopic protons. Upon formation of helicates **13**, **30**, and **33**, these signals shifted about 1 ppm upfield, and appeared as wide, four-line AB patterns. The signals of the methylene groups of the bridges connecting the bipyridine units showed similar behavior; they were singlets at $\delta \approx 4.9$ in ligands **8**, **23**, and **26**, and AB systems at $\delta = 3.6-3.9$ in complexes **13**, **30**, and **33**. Analogous changes in the ^{1}H NMR spectra were observed on passing from ligands **9**, **24**, and **27** (derived from template **2**) and **10**, **25**, and **28** (derived from template **3**) to the corresponding copper(I) complexes (see Exp. Sect.). The proximity of the methylene groups to the shielding cone of the heterocycles and the regular helix structure are the likely causes of the upfield shift and the strong manifestation of diastereotopism. The signal of the proton *ortho* to the oxygen atom in ligands **10**, **25**, and **28** also underwent a strong upfield shift (about 1.5 ppm) upon complexation.

The changes observed in the ^{1}H NMR spectra on passing from ligands **11** and **12** to their silver(I) complexes **16** and **17** were similar, but less impressive. For instance, the signals of the methylene protons of the bipyridine moieties of **16** and **17** shifted upfield "only" 0.35 and 0.25 ppm with respect to those of **11** and **12**.

Taken as a whole, the spectral changes support helicate formation under the influence of the chiral template. In each case, the collections of signals could be accounted for by a single stereoisomeric species arising from a highly diastereoselective complexation. Although precise evaluation of the diastereoselectivity of the process is not possible, because ^{1}H NMR analysis of the crude complexes is hampered by the presence of paramagnetic species, the very high isolated yields (≥ 95%) of single stereoisomeric products point to highly stereoselective helicate formation. In this process, the stereochemical information present in the chiral template is transferred all the way along the helical structure up to a distance of 20 Å, as in the case of complexes **33−35**.

Chiroptical measurements were also in agreement with this hypothesis (see Table 1). In particular, marked increases in the optical rotations were observed on passing from the ligands to the helicates. In some cases, the complexes showed $[\alpha]_D$ values that were opposite in sign and more than one hundred times stronger than those of the parent ligand. Comparison of the circular dichroism (CD) spectra of ligands **24** and **27** with those of the corresponding complexes **31** and **34** confirmed the helicity of the latter.

Table 1. Optical rotations of ligands **8−10** and **23−28**, and of helicates **13−15** and **30−35**

Ligand[a]	$[\alpha]_D^{23}$	$[M]_D$[b]	Helicate	$[\alpha]_D^{23}$	$[M]_D$[b]
(*R*)-**8**	−27.1	−172	(*R,P*)-**13**	317	2686
(*R*)-**23**	−18.1	−186	(*R,P*)-**30**	472	6723
(*R*)-**26**	−7.3	−104	(*R,P*)-**33**	501	10027
(*S*)-**9**	20.4	144	(*S,M*)-**14**	−660	−6068
(*S*)-**24**	10.4	115	(*S,M*)-**31**	−689	−10531
(*S*)-**27**	6.0	90	(*S,M*)-**34**	−707	−15112
(*R*)-**10**	45.9	308	(*R,P*)-**15**	419	3710
(*R*)-**25**	72.1	771	(*R,P*)-**32**	778	11627
(*R*)-**28**	108.2	1586	(*R,P*)-**35**	516	10851

[a] For ligands: $c = 1.0$, in chloroform; for helicates: $c = 0.1-0.05$, in acetonitrile. − [b] $[M]_D = [\alpha]_D \times MW/100$.

The chiroptical properties of complexes **30−35** also served for tentative assignment of their absolute configuration, by comparison with the data for the helicates prepared by Lehn.[6b] In particular, this comparison suggested the (*P*) configuration for the helicates derived from templates (*R*)-**1** and (*R*)-**3**, and the (*M*) configuration for those obtained starting from template (*S*)-**2**. This was also in agreement with an empirical rule that correlates positive (negative) CD absorptions to (*P*)-configured (*M*-configured) helicates formed from bipyridine ligands and copper(I) and silver(I) ions.[6c]

Removal of the chiral template from the helicates was then attempted. Although the ether linkage of **32** and **35** proved too robust to cleave under conditions mild enough to preserve the copper/bipyridine complexes, esters **30**, **31**, **33**, and **34** seemed more amenable to template removal. This was attempted by different procedures, including Ti(OEt)$_4$-promoted transesterification with methyl propanoate, and basic hydrolysis with KOH on alumina or *t*BuOK in acetonitrile. These reactions, however, led either to recovery of the starting complexes or to their decomposition, depending on the reaction conditions.

Different results were obtained when helicate **31** was treated with 3 mol-equiv. of MeONa in methanol at room temperature. From this reaction, optically inactive 50:50 mixture of complexes was obtained after chromatography. The ^{1}H NMR spectra of the mixtures suggested that these compounds could be the head-to-head (HH) and the head-to-tail (HT) dinuclear Cu^I complexes of alcohol **20**. Support for this hypothesis was found when the same 50:50 mixture was obtained directly from **20** upon complexation with two mol-equiv. of CuOTf. Thus, cleavage of the ester bonds of helicate **31** did occur, with concomitant decomplexation of the helicate, followed by random re-complexation of the bis(bipyridine) chains.

In the hope that a higher number of copper binding sites would contribute to preserve the bis(helicate) structure, the MeONa-promoted hydrolysis was attempted on helicate **33**. From this reaction, an optically active 66:34 mixture of complexes was obtained, with an $[\alpha]_D^{23}$ value of +83.0 (*c* = 0.1, in acetonitrile). This mixture was very similar by ^{1}H NMR to that prepared from alcohol **22** by treatment with 3 mol-equiv. of CuOTf. In this case, a 60:40 mixture of complexes was obtained. The optical activity observed for the mixture of isomers derived from helicate **33** could be considered an indication that the helicate structure had partially survived the removal of the template, and − at least to some extent − preserved its stereochemical integrity.[13]

As a whole, however, the results of attempted template removal strongly suggested that complexes that are more stable, either because they contain a higher number of copper binding sites or because they feature phenanthroline rather than bipyridine ligands, are required in order to perform a template removal compatible with the helicate structure. The synthesis of phenanthroline-containing ligands suitable for attachment to the chiral templates is currently underway in our laboratories.

Experimental Section

General: ^{1}H NMR spectra were recorded at 300 or at 500 MHz and were referenced to tetramethylsilane (TMS) at $\delta = 0.00$. ^{13}C NMR spectra were recorded at 75 or at 125 MHz and were referenced to $\delta = 77.0$ in [D]chloroform (CDCl$_3$) and to tetramethylsilane (TMS) at $\delta = 0.00$ in [D$_3$]acetonitrile (CD$_3$CN) and in [D$_2$]dichloromethane. − UV/Vis spectra were recorded in 1-cm quartz cuvettes. − Optical rotations were measured at the Na D-line in a 1-dm cell at 23 °C. − CD spectra were recorded at 23 °C. − Compounds **1**,[14] **2**,[15] **3**,[16] **4**,[17] **5**,[18] **6**,[19] **7**,[19] and **18−20**,[19] were prepared according to the published procedures.

Bromomethyl Derivative 21: Compound **21** was prepared in 61% yield by treatment of the sodium salt of alcohol **20** with 6,6′-bis(bromomethyl)-2,2′-bipyridine (**18**), by a modification of the published procedure.[19] Sodium hydride (60% dispersion in mineral oil, 1.5 mol-equiv.) was added portionwise to a 0.1 M solution of alcohol **20** (0.5−1.0 mmol) in dry tetrahydrofuran. The reaction mixture was stirred at room temperature for 1 h. Compound **18** (2.0 mol-equiv.) was then added and the reaction mixture was refluxed overnight. The reaction mixture was then cooled, and residual sodium hydride quenched by addition of a small amount of methanol. The solvent was removed under vacuum. The crude product was purified by flash chromatography, with a 99:1 dichloromethane/methanol mixture as eluent, to give a white solid. − M.p. 168 °C (dec.). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.33−8.39 (5 H, m), 8.21 (1 H, d, *J* = 8.0 Hz), 7.80−7.89 (5 H, m), 7.70 (1 H, t, *J* = 8.0 Hz), 7.58−7.61 (4 H, m), 7.47 (1 H, t, *J* = 8.0 Hz), 7.18 (1 H, d, *J* = 8.0 Hz), 4.92 (8 H, s), 4.64 (2 H, s), 2.64 (3 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 158.03, 158.01, 157.98, 157.95, 156.33, 156.30, 156.00, 155.71, 155.65, 155.62, 155.58, 155.17, 137.99, 137.93, 137.91, 137.63, 137.56, 137.09, 123.60, 123.28, 121.60, 121.38, 121.36, 121.18, 120.56, 120.43, 119.96, 119.93, 119.90, 118.27, 73.99, 73.96, 73.94, 73.92, 34.05, 24.58. − MS (FAB); *m*/*z*: 659/661 [MH]$^+$. − UV/Vis (CHCl$_3$, $2.0 \cdot 10^{-4}$ M): λ_{max} (ε_{max}) = 243 ($1.4 \cdot 10^4$), 290 nm ($2.3 \cdot 10^4$).

Alcohol 22 was prepared in 63% yield from **21**. A 0.05 M solution of bromide **21** (0.5−1.0 mmol) and potassium carbonate (3.0 mol-equiv.) in a 7:3 dioxane/water mixture was refluxed overnight. The cooled mixture was then transferred to a separating funnel and extracted three times with dichloromethane. The organic fractions were combined and dried with magnesium sulfate, and the solvent was removed under vacuum. Purification by flash chromatography on neutral alumina (Brockman type II), with a 8:2 dichloromethane/methanol mixture as eluent, gave a white solid. − M.p. 184−186 °C. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.32−8.38 (5 H, m), 8.20 (1 H, d, *J* = 8.0 Hz), 7.80−7.90 (5 H, m), 7.69 (1 H, t, *J* = 8.0 Hz), 7.61 (1 H, d, *J* = 8.0 Hz), 7.58−7.60 (3 H, m), 7.25 (1 H, d, *J* = 8.0 Hz), 7.18 (1 H, d, *J* = 7.0 Hz), 4.92 (8 H, s), 4.84 (2 H, bs), 2.64 (3 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 159.38, 158.18, 158.04, 157.95, 157.90, 156.02, 155.74, 155.70, 155.65, 155.64, 155.13, 155.11, 137.52, 137.48, 137.44, 137.36, 137.30, 136.90, 123.09, 121.54, 121.32, 121.30, 121.14, 120.31, 119.89, 119.83, 119.80, 119.76, 119.63, 118.18, 74.05, 74.01, 73.99, 73.96, 64.02, 24.43. − MS (FAB); *m*/*z*: 597 [MH]$^+$. − UV/Vis (CHCl$_3$, $2.0 \cdot 10^{-4}$ M): λ_{max} (ε_{max}) = 243 ($1.1 \cdot 10^4$), 290 nm ($1.9 \cdot 10^4$).

Synthesis of the Ligands

General Procedure for the Synthesis of Esters 8, 9, 11, 23, 24, 26, and 27: Oxalyl chloride (5 mol-equiv.) was added dropwise to a stirred 0.1 M solution of dicarboxylic acid (0.2−1.0 mmol) in dry dichloromethane under argon. The reaction mixture was stirred for 3 to 5 h, and then the low-boiling materials were removed under vacuum. The solid residue was dissolved in dry dichloromethane to obtain a 0.1 M solution; this was added dropwise to a 0.1 M dichloromethane solution of the alcohol (2.5 mol-equiv.), dry triethylamine (3.0 mol-equiv.), and a catalytic amount of DMAP, cooled to 0 °C and kept under argon. The mixture was allowed to warm up to room temperature, stirred for 20 h, and then poured into water. The organic phase was separated, the aqueous phase extracted twice with chloroform, and the combined organic phases were dried with magnesium sulfate and concentrated under vacuum. The residue was purified by flash chromatography, with 99:1 to 95:5 dichloromethane/methanol mixtures as eluent. The products were white solids. The yields are reported in the text.

Esters Derived from (*R*)-Dicarboxylic Acid 1

Ester 8: M.p. 67−68 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29 (2 H, d, J = 8.0 Hz), 8.15 (2 H, d, J = 8.0 Hz), 7.92 (2 H, d, J = 8.0 Hz), 7.68 (2 H, t, J = 8.0 Hz), 7.67 (2 H, t, J = 8.0 Hz), 7.37 (2 H, d, J = 8.0 Hz), 7.26 (2 H, t, J = 8.0 Hz), 7.16 (2 H, d, J = 8.0 Hz), 7.04 (2 H, d, J = 8.0 Hz), 5.21 (4 H, s), 2.63 (6 H, s), 1.90 (6 H, s). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.91, 157.91, 155.92, 155.45, 155.25, 141.23, 137.36, 137.05, 136.74, 133.86, 129.30, 128.19, 127.11, 123.31, 121.39, 119.96, 118.28, 67.50, 24.56, 19.99. − MS (FAB); *m/z*: 635 $[MH]^+$, 767 $[M + Cs]^+$. − UV/Vis ($CHCl_3$, $3.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 242 ($2.7\cdot10^4$), 290 nm ($3.7\cdot10^4$).

Ester 23: M.p. 110−111 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (2 H, d, J = 8.0 Hz), 8.29 (2 H, d, J = 8.0 Hz), 8.28 (2 H, d, J = 8.0 Hz), 8.20 (2 H, d, J = 8.0 Hz), 7.91 (2 H, d, J = 8.0 Hz), 7.84 (2 H, t, J = 8.0 Hz), 7.81 (2 H, t, J = 8.0 Hz), 7.68 (2 H, t, J = 8.0 Hz), 7.67 (2 H, t, J = 8.0 Hz), 7.56 (4 H, d, J = 8.0 Hz), 7.36 (2 H, d, J = 8.0 Hz), 7.25 (2 H, t, J = 8.0 Hz), 7.16 (2 H, d, J = 8.0 Hz), 7.04 (2 H, d, J = 8.0 Hz), 5.21 (4 H, s), 4.91 (4 H, s), 4.89 (4 H, s), 2.63 (6 H, s), 1.90 (6 H, s). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.80, 158.58, 157.43, 156.70, 155.26, 154.89, 154.82, 141.10, 138.40, 137.96, 137.47, 136.70, 133.84, 129.14, 128.05, 127.05, 125.06, 123.06, 122.27, 121.69, 121.64, 121.25, 120.24, 120.22, 73.64, 73.31, 67.01, 22.06, 19.89. − MS (FAB); *m/z*: 1031 $[MH]^+$, 1163 $[M + Cs]^+$. − UV/Vis ($CHCl_3$, $3.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 242 ($9.9\cdot10^4$), 291 nm ($1.1\cdot10^5$).

Ester 26: M.p. 147−148 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.33 (6 H, d, J = 8.0 Hz), 8.29 (2 H, d, J = 8.0 Hz), 8.28 (2 H, d, J = 8.0 Hz), 8.20 (2 H, d, J = 8.0 Hz), 7.91 (2 H, d, J = 8.0 Hz), 7.80−7.86 (8 H, m), 7.69 (2 H, t, J = 8.0 Hz), 7.68 (2 H, t, J = 8.0 Hz), 7.56−7.59 (8 H, m), 7.36 (2 H, d, J = 8.0 Hz), 7.26 (2 H, t, J = 8.0 Hz), 7.17 (2 H, d, J = 8.0 Hz), 7.05 (2 H, d, J = 8.0 Hz), 5.22 (4 H, s), 4.91 (12 H, bs), 4.90 (4 H, s), 2.64 (6 H, s), 1.90 (6 H, s). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.97, 158.12, 158.07, 158.05, 158.02, 157.98, 156.08, 155.82, 155.76, 155.73, 155.71, 155.49, 155.34, 141.16, 137.45, 137.44, 137.30, 137.01, 136.85, 133.77, 129.62, 128.16, 127.11, 123.18, 121.59, 121.47, 121.41, 121.38, 121.22, 120.05, 119.97, 119.95, 119.93, 119.90, 118.28, 74.13, 74.10, 74.08, 67.34, 24.51, 19.91. − MS (FAB); *m/z*: 1427 $[MH]^+$. − UV/Vis ($CHCl_3$, $3.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 242 ($1.9\cdot10^5$), 290 nm ($2.7\cdot10^5$).

Esters Derived from (*S*)-Dicarboxylic Acid 2

Ester 9: M.p. 130−133 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.22 (2 H, d, J = 7.8 Hz), 8.15 (2 H, d, J = 8.7 Hz), 8.06 (2 H, d, J = 7.8 Hz), 7.85 (2 H, d, J = 8.7 Hz), 7.82 (2 H, dd, J = 8.1, 1.0 Hz), 7.63 (2 H, t, J = 7.8 Hz), 7.51 (2 H, t, J = 7.8 Hz), 7.46 (2 H, dt, J = 8.1 Hz, 1.0 Hz), 7.21 (2 H, dt, J = 8.1, 1.0 Hz), 7.13 (2 H, d, J = 7.8 Hz), 7.09 (2 H, dd, J = 8.1, 1.0 Hz), 6.61 (2 H, d, J = 7.8 Hz), 5.09 (4 H, AB system, J = 13.0 Hz), 2.61 (6 H, s). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 157.7, 155.7, 155.2, 154.7, 140.0, 137.2, 136.9, 134.9, 132.9, 128.0, 127.7, 127.4, 127.2, 126.8, 126.1, 123.2, 121.1, 119.8, 118.3, 67.6, 24.6. − MS (FAB); *m/z*: 707 $[MH]^+$. − UV/Vis ($CHCl_3$, $6.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 245 ($2.9\cdot10^4$), 293 nm ($2.4\cdot10^4$).

Ester 24: M.p. 161−163 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (2 H, d, J = 7.8 Hz), 8.23 (2 H, d, J = 7.8 Hz), 8.18 (4 H, d, J = 7.8 Hz), 8.15 (2 H, d, J = 8.7 Hz), 7.84 (2 H, d, J = 8.7 Hz), 7.82 (2 H, dd, J = 8.1, 1.0 Hz), 7.81 (2 H, t, J = 7.8 Hz), 7.78 (2 H, t, J = 7.8 Hz), 7.67 (2 H, t, J = 7.8 Hz), 7.55 (4 H, d, J = 7.8 Hz), 7.50 (2 H, t, J = 7.8 Hz),7.45 (2 H, dt, J = 8.1, 1.0 Hz), 7.21 (2 H, dt, J = 8.1, 1.0 Hz), 7.15 (2 H, d, J = 7.8 Hz), 7.08 (2 H, dd, J = 8.1,1.0 Hz), 6.61 (2 H, d, J = 7.8 Hz), 5.09 (4 H, AB system, J = 11.0 Hz), 4.89 (8 H, s), 2.63 (6 H, s). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 157.8, 157.7, 155.8, 155.5, 155.3, 155.2, 154.7, 140.0, 137.4, 137.2, 137.0, 134.9, 132.9, 128.0, 127.7, 127.3, 127.2, 126.8, 126.1, 123.2, 121.3, 121.1, 119.8, 118.2, 74.0, 67.5, 24.6. − MS (FAB); *m/z*: 1103 $[MH]^+$. − UV/Vis ($CHCl_3$, $8.4\cdot10^{-6}$ M): λ_{max} (ε_{max}) = 245 ($8.7\cdot10^4$), 293 nm ($6.6\cdot10^4$). − CD (c = $8.4\cdot10^{-6}$ M in $CHCl_3$): θ = $3.9\cdot10^5$, $\Delta\varepsilon$ = 119 (at 246 nm); − θ = $-7.9\cdot10^4$, $\Delta\varepsilon$ = −24 (at 283 nm).

Ester 27: M.p. 182−185 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.31 (6 H, d, J = 7.8 Hz), 8.23 (2 H, d, J = 7.8 Hz), 8.18 (4 H, d, J = 7.8 Hz), 8.15 (2 H, d, J = 8.7 Hz), 7.84 (2 H, d, J = 8.7 Hz), 7.82 (6 H, m), 7.81 (2 H, t, J = 7.8 Hz), 7.78 (2 H, t, J = 7.8 Hz), 7.67 (2 H, t, J = 7.8 Hz), 7.57 (6 H, d, J = 7.8 Hz), 7.56 (2 H, d, J = 7.8 Hz), 7.50 (2 H, t, J = 7.8 Hz), 7.45 (2 H, dt, J = 8.1, 1.0 Hz), 7.21 (2 H, dt, J = 8.1, 1.0 Hz), 7.15 (2 H, d, J = 7.8 Hz), 7.09 (2 H, dd, J = 8.1,1.0 Hz), 6.62 (2 H, d, J = 7.8 Hz), 5.09 (4 H, AB system, J = 11.0 Hz), 4.90 (16 H, s), 2.62 (6 H, s). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 157.8, 157.0, 154.7, 155.5, 155.3, 155.2, 140.0, 137.5, 137.4, 137.2, 137.0, 134.9, 132.9, 128.0, 127.7, 127.4, 127.2, 126.8, 126.1, 123.2, 121.3, 121.1, 119.8, 118.2, 74.0, 67.5, 24.6. − MS (FAB); *m/z*: 1500 $[MH]^+$. − UV/Vis (CH_3CN, $4.78\cdot10^{-6}$ M): λ_{max} (ε_{max}) = 245 ($1.7\cdot10^5$), 302 nm ($1.4\cdot10^5$). − CD (c = $1.3\cdot10^{-5}$ M in $CHCl_3$): θ = $6.0\cdot10^4$, $\Delta\varepsilon$ = 18.2 (at 246 nm); θ = $-6.7\cdot10^3$, $\Delta\varepsilon$ = −2.0 (at 283 nm).

Ester 11, Derived from (*S,S*)-Dicarboxylic Acid 4: M.p. 158−160 °C. − $[\alpha]_D^{23}$ −23.6 (c = 0.2 in CH_3CN). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (2 H, d, J = 7.7 Hz), 8.19 (2 H, d, J = 7.7 Hz), 7.74 (2 H, t, J = 7.7 Hz), 7.68 (2 H, t, J = 7.7 Hz), 7.34 (2 H, dd, J = 8.5, 2.0 Hz), 7.16 (2 H, d, J = 7.7 Hz), 7.14 (2 H, dd, J = 8.5, 2.0 Hz), 7.10 (2 H, dt, J = 8.5, 2.0 Hz), 7.09 (2 H, d, J = 7.7 Hz), 7.01 (2 H, dt, J = 8.5, 2.0 Hz), 5.25 (4 H, s), 4.82 (2 H, s), 3.65 (2 H, s), 2.60 (6 H, s). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.9, 156.1, 155.2, 154.9, 137.5, 137.1, 126.5, 126.4, 124.85, 123.9, 123.4, 121.5, 120.25, 118.3, 67.6, 48.1, 46.7, 24.6. − MS (FAB); *m/z*: 659 $[MH]^+$. − UV/Vis ($CHCl_3$, $6.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 245 ($1.21\cdot10^4$), 290 nm ($2.1\cdot10^4$).

General Procedure for the Synthesis of Ethers 10, 12, 25, and 28: NaH (2.5 mol-equiv.) was added portionwise to a stirred 0.1 M solution of diol (0.2−1.0 mmol) in dry tetrahydrofuran under argon. After gas evolution had subsided, the mixture was stirred at room temperature for 2 h. A 0.05−0.1 M solution of bromomethyl compound (2.1 mol-equiv.) in tetrahydrofuran was then added, and the mixture was stirred at reflux for 15 h (for the synthesis of ligand **12**, the mesylate of alcohol **6** was used). To the cooled mixture were added a few drops of methanol, to quench the excess NaH, and the solvent was evaporated under vacuum. The residue was dissolved in chloroform, washed with water, dried with magnesium sulfate, and concentrated under vacuum to give the crude product, that was purified by flash chromatography with a 99:1 to 95:5 dichloromethane/methanol mixture as eluent. The products were white solids. Yields are reported in the text.

Ethers Derived from Diol (*R*)-3

Ether 10: M.p. 218−222 °C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (2 H, d, J = 8.0 Hz), 8.12 (2 H, d, J = 8.0 Hz), 7.79 (2 H, t, J = 8.0 Hz), 7.67 (2 H, t, J = 8.0 Hz), 7.51 (2 H, d, J = 8.0 Hz), 7.16 (2 H, d, *J*.0 = 8 Hz), 7.06 (2 H, d, *J* = 8.0 Hz), 6.87 (2 H, dd, *J* = 1.0, 8.0 Hz), 6.45 (2 H, d, *J* = 1.0 Hz), 5.15 (2 H, d, *J* = 14.0 Hz), 5.14 (2 H, d, *J* = 14.0 Hz), 2.63 (6 H, s), 2.34 (2 H, d, *J* = 13.0 Hz), 2.25 (2 H, d, *J* = 13.0 Hz), 1.36 (6 H, s), 1.32 (6 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 158.31, 157.97, 157.13, 155.87, 155.60, 152.04, 145.04, 137.57, 137.10, 123.26, 122.55, 121.06, 119.93, 118.29, 114.11, 110.17, 70.97, 59.59, 57.70, 42.83, 31.70, 30.37, 24.54. − MS (FAB); *m*/*z*: 806 [M + Cs]$^+$. − UV/Vis (CH$_2$Cl$_2$, 3.0·10^{-4} M): λ_{max} (ε_{max}) = 233 (1.7·10^4), 285 nm (2.0·10^4).

Ether 25: M.p. 233−234 °C. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.32 (2 H, d, *J* = 8.0 Hz), 8.28 (2 H, d, *J* = 8.0 Hz), 8.25 (2 H, d, *J* = 8.0 Hz), 8.19 (2 H, d, *J* = 8.0 Hz), 7.84 (2 H, t, *J* = 8.0 Hz), 7.83 (2 H, t, *J* = 8.0 Hz), 7.78 (2 H, t, *J* = 8.0 Hz), 7.68 (2 H, t, *J* = 8.0 Hz), 7.58 (2 H, d, *J* = 8.0 Hz), 7.57 (2 H, d, *J* = 8.0 Hz), 7.52 (2 H, d, *J* = 8.0 Hz), 7.17 (2 H, d, *J* = 8.0 Hz), 7.07 (2 H, d, *J* = 8.0 Hz), 6.87 (2 H, dd, *J* = 3.0, 8.0 Hz), 6.44 (2 H, d, *J* = 3.0 Hz), 5.15 (2 H, d, *J* = 14.0 Hz), 5.13 (2 H, d, *J* = 14.0 Hz), 4.91 (4 H, s), 4.90 (4 H, s), 2.63 (6 H, s), 2.34 (2 H, d, *J* = 13.0 Hz), 2.24 (2 H, d, *J* = 13.0 Hz), 1.36 (6 H, s), 1.32 (6 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 158.30, 158.00, 157.95, 157.16, 155.98, 155.69, 155.54, 155.52, 152.05, 145.06, 137.59, 137.57, 137.55, 137.10, 123.28, 122.57, 121.35, 121.25, 121.18, 119.99, 119.92, 119.90, 118.29, 114.13, 110.17, 73.98, 73.94, 70.97, 59.60, 57.72, 42.84, 31.70, 30.37, 24.56. − MS (FAB); *m*/*z*: 1069 [MH]$^+$. − UV/Vis (CH$_2$Cl$_2$, 2.0·10^{-4} M): λ_{max} (ε_{max}) = 235 (4.4·10^4), 289 nm (6.2·10^4).

Ether 28: M.p. 168−169 °C. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.32−8.33 (6 H, m), 8.28 (2 H, d, *J* = 8.0 Hz), 8.26 (2 H, d, *J* = 8.0 Hz), 8.20 (2 H, d, *J* = 8.0 Hz), 7.80−7.86 (8 H, m), 7.78 (2 H, t, *J* = 8.0 Hz), 7.68 (2 H, t, *J* = 8.0 Hz), 7.57−7.58 (8 H, m), 7.52 (2 H, d, *J* = 8.0 Hz), 7.16 (2 H, d, *J* = 8.0 Hz), 7.06 (2 H, d, *J* = 8.0 Hz), 6.87 (2 H, dd, *J* = 2.0, 8.0 Hz), 6.44 (2 H, d, *J* = 2.0 Hz), 5.15 (2 H, d, *J* = 14.0 Hz), 5.13 (2 H, d, *J* = 14.0 Hz), 4.91 (16 H, s), 2.63 (6 H, s), 2.33 (2 H, d, *J* = 14.0 Hz), 2.25 (2 H, d, *J* = 14.0 Hz), 1.36 (6 H, s), 1.34 (6 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 158.32, 158.01, 157.98, 157.96, 157.17, 156.00, 155.71, 155.65, 155.62, 155.54, 155.53, 152.05, 145.07, 137.53, 137.06, 123.25, 122.57, 121.37, 121.35, 121.26, 121.18, 119.97, 119.94, 119.92, 119.88, 118.27, 114.16, 110.18, 74.00, 73.97, 73.95, 70.99, 59.62, 57.72, 42.83, 31.70, 30.38, 24.56. − MS (FAB); *m*/*z*: 1466 [MH]$^+$. − UV/Vis (CH$_2$Cl$_2$, 2.0·10^{-4} M): λ_{max} (ε_{max}) = 236 (8.6·10^4), 289 nm (1.3·10^5).

Ether 12, Derived from Diol (*R,*R**)-5:** M.p. 149−151 °C. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.29 (2 H, d, *J* = 7.8 Hz), 8.15 (2 H, d, *J* = 7.8 Hz), 7.80 (2 H, t, *J* = 7.8 Hz), 7.66 (2 H, t, *J* = 7.8 Hz), 7.46 (2 H, d, *J* = 7.8 Hz), 7.29 (2 H, dd, *J* = 8.5, 2.1 Hz), 7.26 (2 H, dd, *J* = 8.5, 2.1 Hz), 7.14 (2 H, d, *J* = 7.8 Hz), 7.09 (2 H, dt, *J* = 8.5, 2.1 Hz), 7.08 (2 H, dt, *J* = 8.5, 2.1 Hz), 4.65 (4 H, AB system, *J* = 14.0 Hz), 4.44 (2 H, s), 3.38 (2 H, A part of an AB system, *J* = 9.0, 5.0 Hz), 3.03 (2 H, B part of an AB system, *J* = 9.0 Hz), 2.63 (6 H, s), 1.74 (2 H, dd, *J* = 9.0, 5.0 Hz). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 158.15, 157.9, 155.8, 155.7, 143.5, 141.0, 137.4, 137.0, 126.0, 125.65, 125.5, 123.5, 123.2, 121.0, 120.25, 119.7, 118.2, 74.2, 73.75, 45.85, 43.35, 24.7. − MS (FAB); *m*/*z*: 631 [MH]$^+$. − UV/Vis (CHCl$_3$, 3.0·10^{-4} M): λ_{max} (ε_{max}) = 245 (1.1·10^4), 290 nm (2.1·10^4).

Alternative Synthesis of Ligand 28

Synthesis of Bromomethyl Derivative 29: This compound was prepared by treatment of the sodium salt of compound **3** with 6,6′-bis(bromomethyl)-2,2′-bipyridine (**18**) (see above). The product was obtained as a white solid after purification by flash chromatography, with a 99:1 dichloromethane/methanol mixture as eluent. − M.p. 174 °C (dec.). − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.32 (2 H, d, *J* = 8.0 Hz), 8.27 (2 H, d, *J* = 8.0 Hz), 7.81 (2 H, t, *J* = 8.0 Hz), 7.79 (2 H, t, *J* = 8.0 Hz), 7.54 (2 H, d, *J* = 8.0 Hz), 7.46 (2 H, d, *J* = 8.0 Hz), 7.05 (2 H, d, *J* = 8.0 Hz), 6.86 (2 H, dd, *J* = 3.0, 8.5 Hz), 6.41 (2 H, d, *J* = 3.0 Hz), 5.13 (4 H, s), 4.63 (4 H, s), 2.33 (2 H, d, *J* = 14.0 Hz), 2.24 (2 H, d, *J* = 14.0 Hz), 1.35 (6 H, s), 1.32 (6 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 158.25. 157.19, 156.28, 155.88, 155.04, 152.04, 145.05, 137.92, 137.66, 123.40, 122.56, 121.50, 120.41, 120.10, 114.15, 110.12, 70.92, 59.57, 57.69, 42.84, 34.07, 31.70, 30.36. − MS (FAB); *m*/*z*: 829/831/833 [MH]$^+$. − UV/Vis (CH$_2$Cl$_2$, 2.2·10^{-4} M): λ_{max} (ε_{max}) = 232 (4.4·10^4), 282 (4.9·10^4), 288 nm (4.9·10^4). − Treatment of **29** with the sodium salt of alcohol **20** (2.5 mol-equiv.) in refluxing THF gave **28** in 76% yield.

Synthesis of the Complexes 13−17 and 30−35

General Procedure: To a stirred 0.01 M solution of the ligand (0.05−0.1 mmol) in degassed chloroform under argon, were added dropwise either commercially available CuOTf · 0.5 benzene or AgOTf (10% excess of the required amount) in degassed acetonitrile (final solvent ratio 1:1). The mixture (which had a deep red color for copper complexes and a pale yellow color for silver complexes) was stirred at room temperature for 3−5 h in the case of ligands **8−12** and **23−25**, and for 15 h in the case of ligands **26−28**. The solvent was then evaporated under vacuum to give a solid residue that was analyzed as such in the case of the silver complexes **16** and **17**, and purified by filtration on neutral alumina, with a 95:5 dichloromethane/methanol mixture as eluent, in the case of the copper complexes **13−15** and **30−35**. The complexes were isolated in ≥ 95% yield.

Monocopper Complex (*R*,*P*)-13: ^{1}H NMR (500 MHz, CD$_3$CN): δ = 8.39 (2 H, d, *J* = 8.0 Hz), 8.34 (2 H, d, *J* = 8.0 Hz), 8.09 (2 H, t, *J* = 8.0 Hz), 7.99 (2 H, t, *J* = 8.0 Hz), 7.53 (2 H, d, *J* = 8.0 Hz), 7.35 (2 H, d, *J* = 8.0 Hz), 7.09 (2 H, t, *J* = 8.0 Hz), 7.08 (2 H, d, *J* = 8.0 Hz), 7.02 (2 H, d, *J* = 8.0 Hz), 4.56 (2 H, d, *J* = 12.0 Hz), 4.52 (2 H, d, *J* = 12.0 Hz), 2.13 (6 H, s), 1.67 (6 H, s). − ^{13}C NMR (125 MHz, CDCl$_3$): δ = 167.37, 158.80, 153.84, 153.77, 152.62, 141.85, 140.17, 139.74, 137.17, 134.77, 129.93, 128.50, 128.09, 128.06, 127.40, 123.12, 120.83, 68.19, 25.37, 20.20. − MS (ES); *m*/*z*: 697 [M − OTf]$^+$. − UV/Vis (CHCl$_3$, 2.0·10^{-5} M): λ_{max} (ε_{max}) = 242 (3.2·10^4), 300 (3.2·10^4), 450 nm (5.1·10^3).

Dicopper Complex (*R*,*P*)-30: ^{1}H NMR (500 MHz, CD$_3$CN): δ = 8.41 (2 H, d, *J* = 8.0 Hz), 8.32 (2 H, d, *J* = 8.0 Hz), 8.22 (2 H, d, *J* = 8.0 Hz), 8.15 (2 H, d, *J* = 8.0 Hz), 8.08 (4 H, t, *J* = 8.0 Hz), 7.98 (2 H, t, *J* = 8.0 Hz), 7.79 (2 H, t, *J* = 8.0 Hz), 7.50 (2 H, d, *J* = 8.0 Hz), 7.33 (2 H, d, *J* = 8.0 Hz), 7.10 (2 H, d, *J* = 8.0 Hz), 7.05 (2 H, t, *J* = 8.0 Hz), 6.97 (2 H, d, *J* = 8.0 Hz), 6.96 (2 H, d, *J* = 8.0 Hz), 6.75 (2 H, d, *J* = 8.0 Hz), 4.44 (2 H, d, *J* = 12.0 Hz), 4.36 (2 H, d, *J* = 12.0 Hz), 3.83 (4 H, t, *J* = 13.0 Hz), 3.68 (4 H, t, *J* = 13.0 Hz), 2.14 (6 H, s), 1.63 (6 H, s). − ^{13}C NMR (125 MHz, CD$_2$Cl$_2$): δ = 166.52, 157.58, 155.28, 155.15, 152.88, 152.58, 152.25, 151.79, 151.49, 141.37, 140.03, 139.71, 138.99, 136.57, 134.34, 128.92, 128.12, 128.05, 127.30, 126.51, 124.86, 124.12, 123.33, 123.01, 122.45, 120.65, 72.21, 72.14, 67.31, 25.58, 20.05. − MS (ES); *m*/*z*: 1305/1307 [M − 2 OTf]$^{2+}$. − UV/Vis (CHCl$_3$, 2.0·10^{-5} M): λ_{max} (ε_{max}) = 242 (4.5·10^4), 266 (4.4·10^4), 302 (5.7·10^4), 450 nm (9.4·10^3).

Tricopper Complex (*R*,*P*)-33: ^{1}H NMR (500 MHz, CD$_3$CN): δ = 8.45 (2 H, d, *J* = 8.0 Hz), 8.33−8.35 (6 H, m), 8.28 (2 H, d, *J* = 8.0 Hz), 8.19 (2 H, d, *J* = 8.0 Hz), 8.07 (4 H, t, *J* = 8.0 Hz), 7.99 (2 H, t, *J* = 8.0 Hz), 7.87−7.93 (4 H, m), 7.73 (2 H, t, *J* = 8.0 Hz), 7.50 (2 H, d, J = 8.0 Hz), 7.33 (2 H, d, J = 8.0 Hz), 7.09 (2 H, d, J = 8.0 Hz), 7.06 (2 H, t, J = 8.0 Hz), 6.95 (4 H, d, J = 8.0 Hz), 6.82 (2 H, d, J = 8.0 Hz), 6.76 (4 H, t, J = 8.0 Hz), 4.45 (2 H, d, J = 11.0 Hz), 4.33 (2 H, d, J = 11.0 Hz), 3.84 (4 H, t, J = 13.0 Hz), 3.77 (2 H, d, J = 13.0 Hz), 3.66−3.73 (4 H, m), 3.56−3.63 (6 H, m), 2.15 (6 H, s), 1.62 (6 H, s). − ^{13}C NMR (125 MHz, CD_3CN): δ = 166.51 157.53, 155.25, 155.18, 155.12, 155.08, 154.91, 152.71, 152.59, 151.70, 151.52, 151.39, 151.35, 141.42, 140.08, 139.96, 139.87, 139.75, 139.71, 139.05, 136.53, 134.35, 129.01, 128.14, 128.12, 128.02, 127.29, 126.50, 125.18, 124.85, 124.41, 123.66, 123.65, 123.63, 123.61, 123.10, 120.92, 72.51, 72.36, 72.31, 67.36, 25.61, 20.05. − MS (ES); m/z: 539 [one third of M − 3 OTf]$^{3+}$. − UV/Vis ($CHCl_3$, $1.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 246 ($4.7\cdot10^4$), 268 ($5.1\cdot10^4$), 302 ($6.3\cdot10^4$), 450 nm ($1.1\cdot10^4$). − CD (c = $2\cdot10^{-5}$ M in CH_3CN): θ = $-3.16\cdot10^5$, Δε = −96 (at 251.5 nm); θ = $7.96\cdot10^5$, Δε = 233 (at 313.5 nm).

Monocopper Complex (*S,M*)-14: ^{1}H NMR (300 MHz, CD_3CN): δ = 8.45 (2 H, d, J = 7.8 Hz), 8.39 (2 H, d, J = 7.8 Hz), 8.10 (2 H, t, J = 7.8 Hz), 8.02 (2 H, t, J = 7.8 Hz), 7.98 (2 H, dd, J = 8.1, 1.0 Hz), 7.81 (2 H, d, J = 8.7 Hz), 7.54 (2 H, dt, J = 8.1, 1.0 Hz), 7.53 (2 H, d, J = 7.8 Hz), 7.35 (2 H, d, J = 8.7 Hz), 7.19 (2 H, dt, J = 8.1, 1.0 Hz), 6.82 (2 H, d, J = 7.8 Hz), 6.73 (2 H, dd, J = 8.1, 1.0 Hz), 4.60 (2 H, A part of an AB system, J = 13.0 Hz), 4.32 (2 H, B part of an AB system, J = 13.0 Hz), 2.10 (6 H, s). − ^{13}C NMR (75 MHz, CD_3CN): δ 166.8, 158.6, 153.8, 153.5, 152.5, 140.2, 140.1, 135.8, 133.4, 129.0, 128.2, 127.9, 127.8, 127.3, 126.2, 123.2, 120.8, 68.3, 25.4. − MS (ES); m/z: 769 [M − OTf]$^+$. − UV/Vis (CH_3CN, $2.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 242 ($6.5\cdot10^4$), 300 ($4.5\cdot10^4$), 450 nm ($7.0\cdot10^3$).

Dicopper Complex (*S,M*)-31: ^{1}H NMR (300 MHz, CD_3CN): δ = 8.48 (2 H, d, J = 7.8 Hz), 8.38 (2 H, d, J = 7.8 Hz), 8.24 (2 H, d, J = 7.8 Hz), 8.17 (2 H, d, J = 7.8 Hz), 8.11 (2 H, t, J = 7.8 Hz), 8.07 (2 H, t, J = 7.8 Hz), 8.00 (2 H, t, J = 7.8 Hz), 7.99 (2 H, dd, J = 8.1, 1.0 Hz), 7.80 (2 H, t, J = 7.8 Hz), 7.78 (2 H, d, J = 8.7 Hz), 7.51 (2 H, dt, J = 8.1, 1.0 Hz), 7.50 (2 H, d, J = 7.8 Hz), 7.35 (2 H, d, J = 8.7 Hz), 7.18 (2 H, dt, J = 8.1, 1.0 Hz), 6.98 (2 H, d, J = 7.8 Hz), 6.87 (2 H, d, J = 7.8 Hz), 6.75 (2 H, d, J = 7.8 Hz), 6.72 (2 H, dd, J = 8.1, 1.0 Hz), 4.47 (2 H, A part of an AB system, J = 11.0 Hz), 4.15 (2 H, B part of an AB system, J = 11.0 Hz), 3.83 (2 H, A part of an AB system, J = 14.0 Hz), 3.81 (2 H, A part of an AB system, J = 14.0 Hz), 3.68 (2 H, B part of an AB system, J = 14.0 Hz), 3.32 (2 H, B part of an AB system, J = 14.0 Hz), 2.18 (6 H, s). − ^{13}C NMR (75 MHz, CD_3CN): δ = 167.0, 158.6, 156.3, 156.0, 153.8, 152.5, 152.0, 140.5, 140.3, 140.1, 139.6, 139.4, 135.8, 133.5, 129.0, 128.9, 128.5, 127.9, 127.8, 127.5, 127.0, 126.2, 125.4, 124.5, 123.4, 122.7, 122.1, 120.7, 72.4, 72.2, 68.0, 25.6. − MS (FAB); m/z: 1377/1379 [M − OTf]$^+$. − UV/Vis (CH_3CN, $2.6\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 242 ($10.7\cdot10^4$), 289 ($6.2\cdot10^4$), 443 nm ($8.3\cdot10^3$). − CD (c = $1.24\cdot10^{-5}$ M in CH_3CN): θ = $2.3\cdot10^5$, Δε = 68.4 (at 246 nm); θ = − $2.7\cdot10^5$, Δε = −81.4 (at 302 nm).

Tricopper Complex (*S,M*)-34: ^{1}H NMR (300 MHz, CD_3CN): δ = 8.37 (4 H, d, J = 7.8 Hz), 8.50 (2 H, d, J = 7.8 Hz), 8.40 (2 H, d, J = 7.8 Hz), 8.28 (2 H, d, J = 7.8 Hz), 8.20 (2 H, d, J = 7.8 Hz), 8.10 (2 H, t, J = 7.8 Hz), 8.07 (2 H, t, J = 7.8 Hz), 8.00 (2 H, t, J = 7.8 Hz), 7.98 (2 H, dd, J = 8.1, 1.0 Hz), 7.91 (2 H, t, J = 7.8 Hz), 7.90 (2 H, t, J = 7.8 Hz), 7.77 (2 H, d, J = 8.7 Hz), 7.74 (2 H, t, J = 7.8 Hz), 7.52 (2 H, dt, J = 8.1, 1.0 Hz), 7.50 (2 H, d, J = 7.8 Hz), 7.25 (2 H, d, J = 8.7), 7.17 (2 H, dt, J = 8.1, 1.0 Hz), 6.97 (2 H, d, J = 7.8 Hz), 6.84 (2 H, d, J = 7.8 Hz), 6.81 (2 H, d, J = 7.8 Hz), 6.75 (4 H, t, J = 7.8 Hz), 6.68 (2 H, dd, J = 8.1, 1.0 Hz), 4.50 (2 H, A part of an AB system, J = 11.0 Hz), 4.13 (2 H, B part of an AB system, J = 11.0 Hz), 3.87 (2 H, A part of an AB system, J = 14.0 Hz), 3.86 (2 H, A part of an AB system, J = 14.0 Hz), 3.77 (2 H, A part of an AB system, J = 14.0 Hz), 3.76 (2 H, A part of an AB system, J = 14.0 Hz), 3.67 (2 H, B part of an AB system, J = 14.0 Hz), 3.65 (2 H, B part of an AB system, J = 14.0 Hz), 3.54 (2 H, B part of an AB system, J = 14.0 Hz), 3.53 (2 H, B part of an AB system, J = 14.0 Hz), 2.18 (6 H, s). − ^{13}C NMR (75 MHz, CD_3CN): δ = 167.0, 158.2, 156.0, 153.0, 152.0, 140.5, 140.2, 140.1, 139.9, 139.8, 139.6, 139.4, 135.8, 133.3, 129.0, 128.9, 127.8, 128.4, 127.6, 127.0, 126.1, 125.4, 125.1, 125.0, 124.5, 123.5, 122.7, 122.6, 122.3, 122.1, 120.8, 72.4, 68.0, 25.6. − MS (FAB); m/z: 1986/1988 [M − OTf]$^+$. − UV/Vis (CH_3CN, $2.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 242 ($10.5\cdot10^4$), 301 ($6.2\cdot10^4$), 450 nm ($7.5\cdot10^3$). − CD (c = $4.0\cdot10^{-5}$ M in CH_3CN): θ = $3.3\cdot10^5$, Δε = 100 (at 246 nm); θ = $-4.5\cdot10^5$, Δε = −135 (at 305 nm).

Monocopper Complex (*R,P*)-15: ^{1}H NMR (500 MHz, CD_3CN): δ = 8.17 (2 H, d, J = 8.0 Hz), 8.00 (2 H, d, J = 8.0 Hz), 7.87−7.92 (4 H, m), 7.44 (2 H, d, J = 8.0 Hz), 6.85−6.91 (4 H, m), 6.43 (2 H, dd, J = 2.0, 8.0 Hz), 4.98 (2 H, d, J = 2.0 Hz), 4.52 (2 H, AB, J = 11.0 Hz), 4.24 (2 H, AB, J = 11.0 Hz), 2.08−2.11 (8 H, m), 1.53 (2 H, d, J = 13.0 Hz), 1.24 (6 H, s), 1.07 (6 H, s). − ^{13}C NMR (125 MHz, CD_3CN): δ = 158.74, 158.32, 155.20, 153.64, 152.65, 151.91, 145.94, 139.82, 139.49, 127.51, 127.46, 123.89, 122.69, 120.48, 113.57, 109.52, 71.38, 60.74, 58.22, 43.52, 32.23, 30.98, 25.26. − MS (ES); m/z: 735 [M − OTf]$^+$. − UV/Vis (CH_2Cl_2, $2.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 265 ($2.3\cdot10^4$), 299 ($2.7\cdot10^4$), 452 nm ($5.0\cdot10^3$).

Dicopper Complex (*R,P*)-32: ^{1}H NMR (500 MHz, CD_3CN): δ = 8.29 (4 H, d, J = 8.0 Hz), 8.22 (2 H, d, J = 8.0 Hz), 8.08 (2 H, t, J = 8.0 Hz), 7.99−8.04 (4 H, m), 7.84 (2 H, t, J = 8.0 Hz), 7.73 (2 H, t, J = 8.0 Hz), 7.51 (2 H, d, J = 8.0 Hz), 6.80−6.84 (8 H, m), 6.32 (2 H, dd, J = 3.0, 8.0 Hz), 4.87 (2 H, d, J = 3.0 Hz), 4.02 (2 H, AB, J = 11.0 Hz), 4.43 (2 H, AB, J = 11.0 Hz), 3.88−3.93 (4 H, m), 3.67 (4 H, AB, J = 14.0 Hz), 2.13 (6 H, s), 2.08 (2 H, d, J = 13.0 Hz), 1.44 (2 H, d, J = 13.0 Hz), 1.23 (6 H, s), 0.99 (6 H, s). − ^{13}C NMR (125 MHz, CD_3CN): δ = 158.70, 158.07, 155.48, 155.45, 155.06, 152.86, 152.82, 152.54, 151.94, 151.65, 145.92, 140.13, 140.01, 139.89, 139.61, 127.93, 127.29, 125.29, 124.59, 124.14, 123.18, 122.42, 122.20, 120.88, 113.82, 108.78, 72.38, 72.30, 71.46, 60.98, 58.10, 43.52, 32.26, 30.93, 25.58. − MS (ES); m/z: 598 [one half of M − 2 OTf]$^{2+}$. − UV/Vis (CH_2Cl_2, $1.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 265 ($3.1\cdot10^4$), 301 ($3.9\cdot10^4$), 450 nm ($7.5\cdot10^3$).

Tricopper Complex (*R,P*)-35: ^{1}H NMR (500 MHz, CD_3CN): δ = 8.40 (2 H, br. s), 8.32 (2 H, d, J = 8.0 Hz), 8.23 (2 H, d, J = 8.0 Hz), 8.08 (2 H, d, J = 8.0 Hz), 7.94−8.30 (8 H, m), 7.84 (2 H, t, J = 8.0 Hz), 7.72−7.80 (4 H, m), 7.64 (2 H, t, J = 8.0 Hz), 7.50 (2 H, d, J = 8.0 Hz), 6.94 (4 H, br. s), 6.82 (2 H, d, J = 8.0 Hz), 6.77 (2 H, d, J = 8.0 Hz), 6.76 (2 H, d, J = 8.0 Hz), 6.68 (2 H, d, J = 8.0 Hz), 6.28 (2 H, d, J = 8.0 Hz), 4.86 (2 H, br. s), 4.30 (2 H, A part of AB system, J = 11.0 Hz), 4.00 (2 H, B part of AB system, J = 11.0 Hz), 3.82−3.86 (6 H, m), 3.77 (2 H, A part of AB system, J = 13.5 Hz), 3.68 (2 H, B part of AB system, J = 11.0 Hz), 3.50−3.65 (6 H, m), 2.13 (6 H, s), 2.06 (2 H, A part of AB system, J = 14.0 Hz), 1.40 (2 H, B part of AB system, J = 14.0 Hz), 1.21 (6 H,s), 0.97 (6 H, s). − MS (ES); m/z: 552 [one third of M − 3 OTf]$^{3+}$. − UV/Vis (CH_2Cl_2, $1.0\cdot10^{-5}$ M): λ_{max} (ε_{max}) = 227 ($2.8\cdot10^4$), 292 ($3.7\cdot10^4$), 448 nm ($4.6\cdot10^3$).

Silver Complex (*S,S,M*)-16: $[\alpha]_D^{23}$ = −98.6 (c = 0.05 in CH_3CN). − ^{1}H NMR (300 MHz, CD_3CN): δ = 8.26 (2 H, d, J = 7.7 Hz), 8.19 (2 H, d, J = 7.7 Hz), 8.03 (2 H, t, J = 7.7 Hz), 7.99 (2 H, t, J = 7.7 Hz), 7.53 (2 H, d, J = 7.7 Hz), 7.41 (2 H, d, J = 7.7 Hz), 7.16 (2 H, dd, J = 8.5, 2.0 Hz), 7.00−7.06 (4 H, m), 6.97 (2 H, dt, *J* = 8.5, 2.0 Hz), 5.03 (2 H, A part of an AB system, *J* = 13.2 Hz), 4.76 (2 H, B part of an AB system, *J* = 13.2 Hz), 4.49 (2 H, s), 3.04 (2 H, s), 2.43 (6 H, s). − ^{13}C NMR (75 MHz, CD_3CN): δ = 159.5, 156.4, 153.0, 151.8, 137.5, 140.9, 140.6, 127.2, 127.0, 126.5, 125.8, 125.4, 124.4, 123.2, 121.4, 68.5, 48.4, 46.6, 26.8. − MS (FAB); *m*/*z*: 765/767 [M − OTf]$^+$. − UV/Vis (CH_3CN, $2.2 \cdot 10^{-5}$ M): λ_{max} (ε_{max}) = 248 ($12.4 \cdot 10^4$), 298 nm ($16.2 \cdot 10^4$). − CD (*c* = $2.6 \cdot 10^{-5}$ M in CH_3CN): θ = $-5.1 \cdot 10^4$, Δε = −15.4 (at 305 nm).

Silver Complex (*R,*R**,*P**)-17:** ^{1}H NMR (300 MHz, CD_3CN): δ = 8.21 (2 H, d, *J* = 7.8 Hz), 8.12 (2 H, d, *J* = 7.8 Hz), 7.99 (2 H, t, *J* = 7.8 Hz), 7.92 (2 H, t, *J* = 7.8 Hz), 7.52 (2 H, d, *J* = 7.8 Hz), 7.40 (2 H, d, *J* = 7.8 Hz), 7.02−7.04 (8 H, m), 4.46 (2 H, A part of an AB system, *J* = 12.5 Hz), 4.31 (2 H, B part of an AB system, *J* = 12.5 Hz), 3.99 (2 H, s), 2.80 (2 H, A part of an AB system, *J* = 16.0 Hz), 2.66 (2 H, B part of an AB system, *J* = 16.0 Hz), 2.34 (6 H, s), 1.27 (2 H, s). − ^{13}C NMR (75 MHz, CD_3CN): δ = 159.5, 158.9, 153.5, 152.8, 144.3, 141.75, 140.4, 140.0, 126.9, 126.5, 126.0, 125.3, 124.1, 122.5, 120.8, 75.4, 74.95, 46.3, 43.75, 26.2. − MS (FAB); *m*/*z*: 735/737 [M − OTf]$^+$.

Cleavage of the Template from Bis(helicate) 33: To a stirred solution of bis(helicate) **33** (15 mg, 0.007 mmol) in dry methanol (1.0 mL), kept under argon, was added dropwise 0.3 mL of a 0.1 M solution of sodium methoxide in dry methanol (2 mol-equiv.). The mixture was stirred at room temperature for 15 h and then concentrated under vacuum. The resulting residue was purified by filtration through a short column of deactivated alumina, with a 85:15 dichloromethane/ methanol mixture as eluent, to give the product. It had an $[\alpha]_D^{23}$ value of + 83.0 (*c* = 0.1 in acetonitrile). − ^{1}H NMR (500 MHz, CD_3CN): δ = 8.50 (4 H, d, *J* = 8.0 Hz), 8.28−8.45 (6 H, m), 8.15 (2 H, t, *J* = 7.7 Hz), 8.11 (4 H, t, *J* = 7.5 Hz), 7.99 (2 H, t, *J* = 7.5 Hz), 7.74−7.93 (6 H, m), 7.59 (2 H, d, *J* = 7.7 Hz), 7.07 (6 H, d, *J* = 7.5 Hz), 6.88 (4 H, d, *J* = 7.5 Hz), 4.26 (2.6 H, AB system, *J* = 15.0 Hz, major isomer), 4.24 (1.4 H, AB system, *J* = 15.0 Hz, minor isomer), 3.74−4.00 (16 H, m), 2.22 (4 H, s, major isomer), 2.20 (2 H, s, minor isomer).

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