New Axially Chiral Bis(dihydrooxazoles) as Ligands in Stereoselective Transition-Metal Catalysis

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The new, axially chiral bis(4,5-dihydrooxazoles) **4** have been synthesized in a straightforward manner, starting from the substituted, racemic 1,1′-biphenyl-2,2′-dicarboxylic acids **1** and optically active amino alcohols **2**. The adducts were resolved by medium-performance liquid chromatography (MPLC; see *Scheme 1*). Formation of Cu^I complexes of **4** was followed by ^{1}H-NMR spectroscopy. The catalytic behavior of these complexes has been investigated by asymmetric cyclopropanation of styrene with ethyl diazoacetate. Beside the influence of steric factors, a significant electronic effect on asymmetric induction could also be observed (see *Scheme 2* and *Table*).

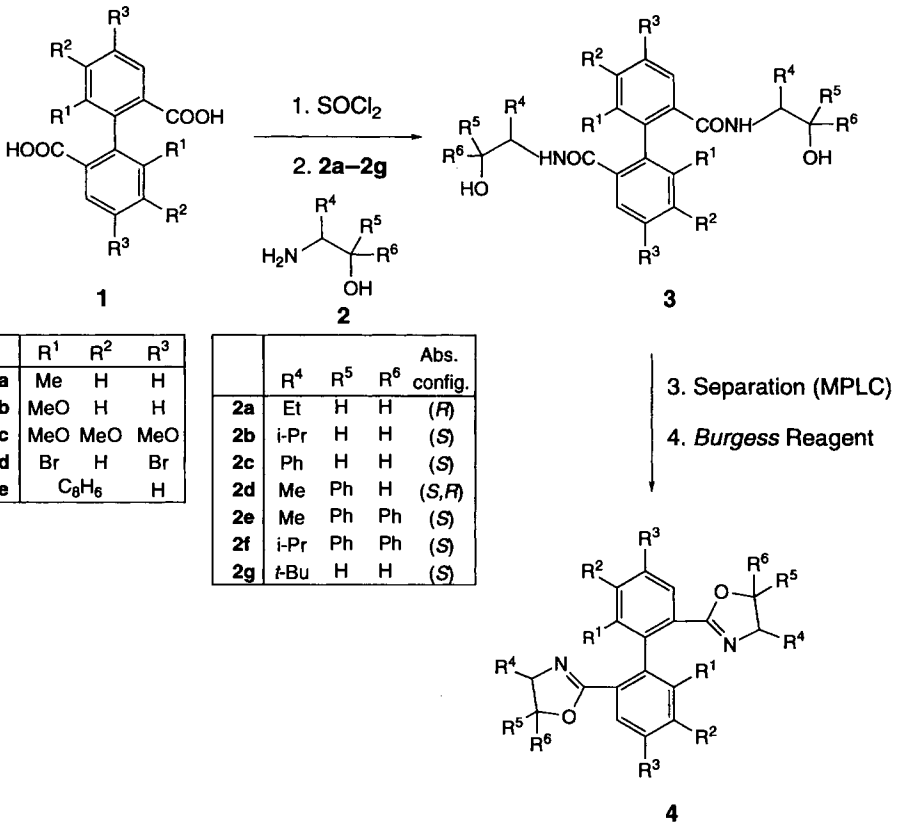
1. Introduction. – In the last decade, chiral dihydrooxazoles have been widely used as powerful nitrogen-donor ligands in transition-metal-catalyzed asymmetric reactions [1–6]. On the other hand, axially chiral biaryl ligands played an important role in developing highly enantioselective transition-metal-catalyzed reactions, *e.g.*, asymmetric hydrogenation of a wide variety of prochiral organic substrates with bidentate phosphorous ligands such as 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthalene (binap) [7] or similar systems [8–10]. These axially chiral biaryl systems can be substituted in order to investigate the donating properties of the heteromonocycles attached to, *e.g.*, dihydrooxazoles. It is known that electronic properties of a ligand can have an influence on the stereoselectivity of transition-metal-catalyzed reactions [9][10]. Several other groups have recently disclosed their results on C_2-symmetric chiral bis(dihydrooxazoles) with axially chiral backbones [11–13] or with backbones which are derived from diethyl D- or L-2,3-*O*-isopropylidenetartrates [14][15]. In this work, the synthesis, resolution, and evalution of several new, C_2-symmetric, axially chiral bis(dihydrooxazole) ligands **4** (see *Scheme 1*) with different substitution-dependent properties is decribed. Their use as potential ligands in asymmetric transformations has been evaluated in Cu^I-catalyzed cyclopropanation of styrene with commercially available ethyl diazoacetate.

2. Results and Discussion. – 2.1. *Synthesis and Resolution.* The bis(dihydrooxazole) ligands **4** can be synthesized from the 1,1′-biphenyl-2,2′-dicarboxylic acids **1** and amino alcohols **2** (see *Scheme 1*). With enantiomerically pure amino alcohols **2**, bis(carboxamides) **3** were obtained as mixtures of two optically pure diastereoisomers, which are easily distinguishable by their ^{1}H- and ^{13}C-NMR spectra. After the separation of **3** by medium-performance liquid chromatography (MPLC[1]); AcOEt as eluant)[2]), the ring closure and

[1]) This method offers better separation factors than in usual flash chromatography and results also in better reproducibility of retention times. Compared to preparative HPLC, larger amounts of mixtures can be seperated in one run (*e.g.*, up to 1 g for **4ab** (size of the column 400 × 30 mm)).

[2]) After chromatographic separation, it has been found that some of the diasteroisomeric mixtures of **3** are also seperable by crystallization from AcOEt. In general, the pure matched forms (*e.g.*, for **4ab**, the (*M*,4*S*)-isomer) show higher tendency for crystallization.

Scheme 1



	R^1	R^2	R^3
1a	Me	H	H
1b	MeO	H	H
1c	MeO	MeO	MeO
1d	Br	H	Br
1e	C_6H_6		H

	R^4	R^5	R^6	Abs. config.
2a	Et	H	H	(*R*)
2b	i-Pr	H	H	(*S*)
2c	Ph	H	H	(*S*)
2d	Me	Ph	H	(*S,R*)
2e	Me	Ph	Ph	(*S*)
2f	i-Pr	Ph	Ph	(*S*)
2g	*t*-Bu	H	H	(*S*)

dehydration with methyl *N*-[(triethylammonio)sulfonyl]carbamate (*Burgess* reagent) led to **4** in yields up to 91%. Other procedures for the ring closure such as $PPh_3/CCl_4/MeCN$ or $MsCl/NEt_3/CH_2Cl_2$ also led to the desired **4**, but required longer reaction times and resulted in lower yields. The diastereoisomers (*M*,4*S*)-**4ac** and (*P*,4*S*)-**4ac** can also be seperated by MPLC with hexane/EtO_2 as eluant (*cf. Exper. Part*). The bis(dihydrooxazoles) **4** are colorless oily compounds that solidify upon standing. They were characterized by their ^{1}H- and ^{13}C-NMR spectra.

In the same manner, other axially chiral 1,1′-biaryl-2,2′-dicarboxylic acids **1b–e** could also be transformed into corresponding bis(dihydrooxazoles) **4bb–eb** (see *Scheme 1*). The sense of axial chirality was determined by their major *Cotton* effects (*CE*) in the CD spectra in the series of bis(carboxamides) with i-Pr substituents in the side chains, *i.e.*, **3ab–3db**. The *CE*s were compared with spectra in the literature of compounds with the same axially chiral backbone [8][16]. The diastereoisomer of **3ab**, which was first eluted from the MPLC column, was deduced to have the (*M*)-configuration at the chiral axis, negative *CE* at 198.6 nm (*cf. Exper. Part* and [8]). The same elution/relative configuration relationship was also determined for the 6,6′-dimethoxy-1,1′-biphenyl and 4,4′,5,5′,6,6′-hexamethoxy-1,1′-biphenyl backbones (*cf. Fig. 2*); but the relationship

was reversed for the 4,4′,6,6′-tetrabromo-1,1′-biphenyl-2,2′-bis(carboxamide) **3db**. However, the determination of the absolute configuration of the axially chiral 4,4′,5,5′,6,6′-hexamethoxy-1,1′-biphenyl backbone could not be fully deduced from the CD spectra. So, the absolute configuration was secured by the $[\alpha]_D$ values of the corresponding bis(dihydrooxazoles) **4cb** ($[\alpha]_D^{25} = +52.1$ ($c = 0.5$, $CHCl_3$)) and **4cg** ($[\alpha]_D^{25} = +59.8$ ($c = 0.5$, $CHCl_3$)). These values were compared with the optical rotation for the diastereoisomer (*M*,*S*)-**4cb** ($[\alpha]_D^{25}$) $= -31.8$ ($c = 3.3$, $CHCl_3$) [17].

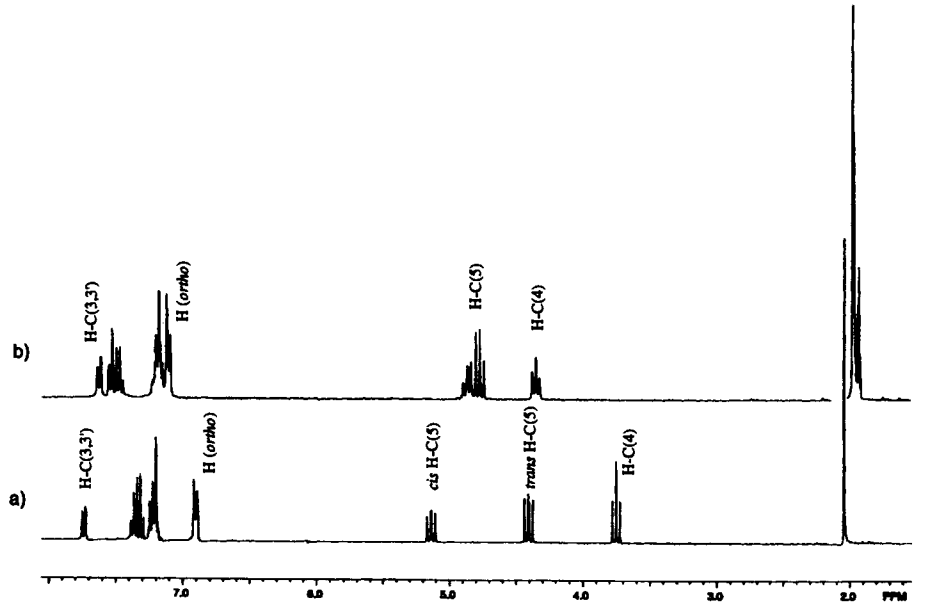


Fig. 1. a) *^{1}H-NMR* ($CDCl_3$)[3]) *Spectrum of* (P,S,S)-**4ac**. b) *^{1}H-NMR* ((D_6)acetone) *Spectrum of [Cu^I((P,S,S)-**4ac**)(MeCN)] [PF_6]*

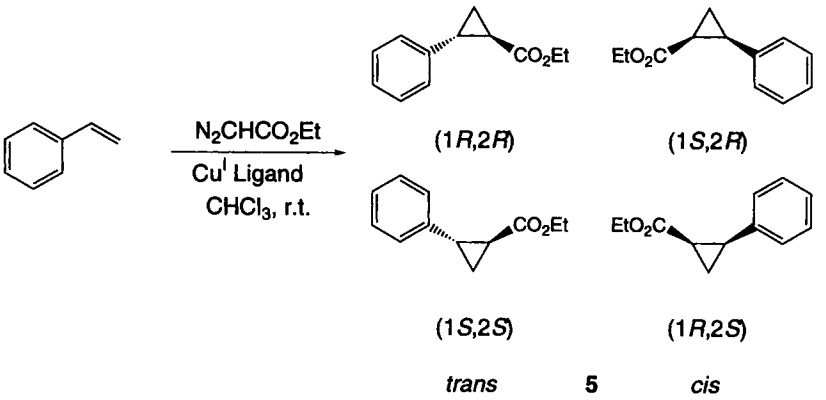
The coordination behavior of Cu^I compounds with **4** as a ligand was studied by ^{1}H-NMR of **4ab** and **4ac**. There is a remarkable change in the chemical shift of the H-atoms of the dihydrooxazole moiety upon coordination with $[Cu^I(MeCN)_4][PF_6]$, especially demonstrated by the complex $[Cu^I((P,S)$-**4ac**$)(MeCN)][PF_6]$ (see *Fig. 1*)[3]).

2.2. *Stereoselectivity in Catalysis.* Cu^I Complexes of all synthesized ligands **4** were tested for their catalytic properties in cyclopropanation of styrene with commercially available ethyl diazoacetate (*cf. Scheme 2*). This reaction has been most often examined with chiral dihydrooxazole-type ligands [1][2][11][12][18] (for recent reviews, see [19][20]).

However, it was of interest to test these new ligands not only with respect to their potency to induce enantioselectivity, but also regarding their potency to cause diastereoselectivity. Several authors have showed that high asymmetric inductions can be attained by chosing sterically demanding groups in the dihydrooxazole moiety and in the alkyl

[3]) The solvent-dependent $\Delta\delta$ for (*P*,4*S*)-**4ac** is only small for $CDCl_3$ and (D_6)acetone (0.01–0.05 ppm; *cf. Exper. Part*), but, for the ligand, $CDCl_3$ was chosen because of same δ for Me–C(6,6′) and (D_6)acetone.

Scheme 2



part of the diazoacetate. Thus, stereoselectivities of up to 99% ee for *trans*-**5** and > 96% ee for *cis*-**5** as well as *trans*/*cis* ratios of 94:6, *i.e.*, diastereoselectivities of up to 88% de, were observed [5] (similar results were reported in [3][4]).

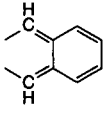
Also [Co^{III}(*N*,*N*′-bis(salicylidene)ethylenediamine)][X] ([Co^{III}(salen)][X]) and [Ru^{II}-(2,6-bis(dihydrooxazol-2-yl)pyridine)][X]$_2$ ([Ru^{II}(pybox)][X]$_2$) are catalyst for cyclopropanation, and the induced stereoselectivity using chiral complexes of the latter ones is influenced by the same properties as in the Cu^I-catalyzed version [21][22]. In this study, cyclopropanation was carried out in $CHCl_3$ at 25° in the presence of 2 mol-% of the Cu^I catalyst, generated *in situ* by mixing [$Cu^I(C_6H_6)_{0.5}$][OTf] (benzenebis(copper(I)-triflate)) and the respective ligand **4**. The results are summarized in the *Table*.

2.2.1. *Configuration of the Formed Cyclopropanes* **5**. The absolute configuration of the major stereoisomer of *trans*-**5** and *cis*-**5**, using (*M*,4*S*)-**4ab** ligand, was assigned on the basis of the sign of optical rotation ($[\alpha]_D^{25} = -152$ ($c = 1.1$, $CHCl_3$) for *trans*-**5** and $[\alpha]_D^{25} = -9.3$ ($c = 0.9$, $CHCl_3$) for *cis*-**5**). These values revealed that the major configuration formed in the Cu^I-catalyzed cyclopropanation with matched ligand (*M*,*S*)-**4ab** to be (1*R*,2*R*) for *trans*-**5** and (1*R*,2*S*) for *cis*-**5** [5][12][14][15]. The other matched ligands generated the same major stereoisomers of *trans*-**5** and *cis*-**5** such as (*M*,*S*)-**4ab**, detectable by the retention times of their chromatographic separation on a chiral HPLC column (*cf. Exper. Part*).

2.2.2. *Enantioselectivities Induced by the New Ligands* **4**. If we compare the two diastereoisomers of **4**, *e.g.*, (*M*,4*S*)-**4ab** and (*P*,4*S*)-**4ab**, both have the same configuration at the heterocycle but different sense of axial chirality, the induced stereoselectivity in the performed cyclopropanation being controlled by the axial chirality (*cf. Entries 2*, *3*, and *4*, *5* in the *Table*). Ligands inducing higher enantioselectivity in this catalytic reaction are called matched. The change of the absolute configuration in the series of the matched ligands is due to a change in priority along the chirality axis (*cf. Entries 2*, *10*, *11*, and *13* in the *Table*; see also *Fig. 2*).

The enantioselectivity can be tuned by two factors, *i.e.*, steric and electronic. *1*) Sterically demanding groups at C(5) of the dihydrooxazole moieties increase the ee values. The influence on the enantioselectivity of substituents at C(4) of the dihydrooxazole moieties is ambiguous. On one hand, Ph substituents at C(4) can increase the

Table. *Enantioselectivity and Diastereoselectivity in the Cu^{I}-Catalyzed Cyclopropanation of Styrene with Ethyl Diazoacetate Using the New Bis(4,5-dihydrooxazol-2-yl)-1,1′-biphenyl Ligands* **4**

Entry	Ligand	R^1	R^2	R^3	R^4	R^5	R^6	Sense of axial chirality	Configuration at C(4) of the dihydrooxazole moieties	Configuration at C(5) of the dihydrooxazole moieties	*trans*/*cis* Ratio of **5** [%]	de [%]	ee *trans* [%]	ee *cis* [%]
1	**4aa**	Me	H	H	Et	H	H	(*P*)	(*R*)	–	69:31	38	14	18
2	**4ab**	Me	H	H	i-Pr	H	H	(*M*)	(*S*)	–	70:30	40	55	59
3	**4ab**	Me	H	H	i-Pr	H	H	(*P*)	(*S*)	–	73:27	46	0	0
4	**4ac**	Me	H	H	Ph	H	H	(*M*)	(*S*)	–	78:22	56	49	53
5	**4ac**	Me	H	H	Ph	H	H	(*P*)	(*S*)	–	80:20	60	0	0
6	**4ad**	Me	H	H	Me	Ph	H	(*M*)	(*S*)	(*R*)	65:35	30	33	34
7	**4ad**	Me	H	H	Me	Ph	H	(*P*)	(*S*)	(*R*)	68:32	36	8	8
8	**4ae**	Me	H	H	Me	Ph	Ph	(*M*)	(*S*)	–	67:33	34	34	13
9	**4af**	Me	H	H	i-Pr	Ph	Ph	(*M*)	(*S*)	–	65:35	30	48	70
10	**4bb**	MeO	H	H	i-Pr	H	H	(*P*)	(*S*)	–	70:30	40	66	70
11	**4cb**	MeO	MeO	MeO	i-Pr	H	H	(*P*)	(*S*)	–	79:21	68	71	74
12	**4cg**	MeO	MeO	MeO	*t*-Bu	H	H	(*P*)	(*S*)	–	67:33	34	88	89
13	**4db**	Br	H	Br	i-Pr	H	H	(*P*)	(*S*)	–	72:28	44	44	49
14	**4db**	Br	H	Br	i-Pr	H	H	(*M*)	(*S*)	–	90:10	80	0	10
15	**4eb**			H	i-Pr	H	H	(*M*)	(*S*)	–	85:15	70	46	49

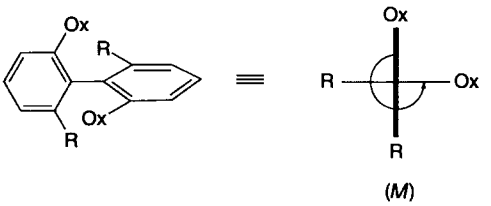


Fig. 2. *Axial chirality is (*M*) as long as the dihydrooxazol-2-yl moieties have higher priority than substituents R. Otherwise, the sense of axial chirality is reversed although the relative configuration of the dihydrooxazoles remaines unchanged*

ee values, if, at C(5), there is a small substituent such as Me (*cf. Entries 1–6*, and *8*); on the other hand, the values decrease slightly for a more demanding group such as i-Pr at C(5) and two Ph groups at C(5) for the *trans*-isomer of **5**, but, for *cis*-**5**, a higher value has been detected compared to the dihydrooxazole moiety, with a i-Pr group at C(4) and no substituents at C(5) (*cf. Entries 2* and *9*). *2*) Electronic properties of the ligand have an influence on the enantioselectivity. Donating groups increase the ee values, electron-withdrawing groups induce the opposite effect (*cf. Entries 2*, *10*, *11*, *13*, and *14*). The best ligand in the i-Pr series, *i.e.*, (*P*)-2,2′-bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-4,4′,5,5′,6,6′-hexamethoxy-1,1′-biphenyl ((*P*,*S*)-**4cb**) was chosen and tested with a *t*-Bu group instead of i-Pr at C(4) of the dihydrooxazole moiety, *i.e.*, (*P*)-2,2′-bis[(*S*)-4,5-dihydro-4-(1,1-dimethylethyl)oxazol-2-yl]-4,4′,5,5′,6,6′-hexamethoxy-1,1′-biphenyl ((*P*,*S*)-**4cg**). The highest ee value for this class of ligands was observed (88% ee for *trans*-**5** and 89% ee for *cis*-**5**; *cf. Entry 12*) using commercially available ethyl diazoacetate.

2.2.3. *Diastereoselectivity Induced by the New Ligands* **4**. In general, the differences in diastereoselectivity are small compared to enantioselectivity. But some general trends can be outlined. The mismatched ligands show better de values (*cf. Entries 2 vs. 3*, *4 vs. 5*, *6 vs. 7*, and *13 vs. 14*). The steric influence reaches a maximum with Ph substituents at C(4) of the dihydrooxazole moiety, smaller and more-demanding groups lower the de values. Additional substituents at C(5) have either no effect or a slightly negative effect (*cf. Entries 6–9*). The electronic properties of the ligands have an effect, but a general trend is not obvious. However, one mismatched ligand with electron-withdrawing groups, (*M*)-2,2′-bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-4,4′,6,6′-tetrabromo-1,1′-biphenyl ((*M*,4*S*)-**4db**), showed a high de value (80%; *cf. Entry 14*) in the cyclopropanation using the described substrates.

3. Conclusion. – For the first time, it could be shown that the enantioselectivity in the asymmetric cyclopropanation, catalyzed by [Cu^{I}(bis(dihydrooxazole))], was improved by electron-donating properties of the ligands of type **4**. The effect of these new, axially chiral ligands on the diastereoselectivity showes some trends, but further experiments will be conducted to control the stereoselectivity (enantio- and diastereoselectivity) in the cyclopropanation. Investigations on the scope and limitation of these potential ligands in other transition-metal-catalyzed organic transformations are in progress.

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Experimental Part

General. All catal. reactions were performed under N_2. All used solvents were distilled under N_2 prior to their use. THF was purified over Al_2O_3 (basic). 3-Methyl-2-nitrobenzoic acid (*Fluka, purum.*), 3-methoxy-2-nitrobenzoic acid (*Lancaster*), and 2-nitro-3,4,5-trimethoxybenzoic acid (*Aldrich*) were reduced with H_2 and Pd/C (*Fluka*) to the corresponding anthranilic acids. 2-Amino-3,5-dibromobenzoic acid (*Lancaster*), thionyl chloride (*Fluka, puriss.*), the amino alcohols (*Fluka*), and styrene (*Fluka, puriss.*) were used without further purification. (*S*)-2-Amino-3-methyl-1,1-diphenylbutan-1-ol was synthesized from (*S*)-valine (*Fluka*) according to [23]. $[Cu^I(MeCN)_4][PF_6]$ and $[Cu^I(C_6H_6)_{0.5}][OTf]$ were synthesized according to [24] and [25], resp. Ethyl diazoacetate (*Fluka*; 90% soln. in CH_2Cl_2) was diluted with $CHCl_3$ to obtain a *ca.* 0.8M soln. GC: *Hewlett-Packard* (model *5890*) with an *Alltech SE-54* column (30 m × 0.25 mm, 0.25 μm). MPLC: Silica gel (15–25 μm, *Lichroprep® Si60, Merck*) with HP pump (*KronLab*, model *Masterkron 4*) and a UV detector (*Dynamax*, model *UV-1*); CV_n: column volumes and α = seperation factor. HPLC: *LichroCart®* (*S,S*)-*Whelk-O1* (*Merck, # 1.50164*) column (24.4 cm × 4 mm, 5 μm) with *LiChrospher® 100 Diol* (*Merck, # 1.50960*) as a precolumn (4 mm × 4 mm, 5 μm) equipped with a UV photodiodearray detector (*Jasco*, model *MD-910*) and a *Milton Roy* pump (model *CM 4000*). M.p.: on an apparatus constructed and assembled by *K. Hochreutener*, University of Zurich; the values are not corrected. Optical rotations: *Perkin-Elmer* (model *MC 241*) polarimeter. CD: *Jasco* (model *J-715*) spectropolarimeter; λ in nm ($\Delta\varepsilon$). ^{1}H- and ^{13}C-NMR: *Bruker AC 300, ARX 300*, and *AMX 600* spectrometers. δ in ppm relative to an internal standard (δ(TMS) = 0 ppm).

1. *General Procedure for the Synthesis of the 1,1'-Biphenyl-2,2'-dicarboxylic Acids* **1a**–**1d**. The corresponding anthranilic acids were diazotized with $NaNO_2$ (*Fluka*), and the coupling to the biphenyls was achieved by Cu^I salt derived from $Cu(SO_4)_2$ (see [26][27]). Yields of the racemic diacids after crystallization (solvent): 74% (acetone) of *(*MP*)-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxylic acid* (**1a**); 79% (acetone) of *(*MP*)-6,6'-dimethoxy-1,1'-biphenyl-2,2'-dicarboxylic acid* (**1b**); 84% (acetone) of *(*MP*)-4,4',5,5',6,6'-hexamethoxy-1,1'-biphenyl-2,2'-dicarboxylic acid* (**1c**); 35% (conc. H_2SO_4) of *(*MP*)-4,4',6,6'-tetrabromo-1,1'-biphenyl-2,2'-dicarboxylic acid* (**1d**).

1.1. *Data of* **1a**. Synthesis according to [26] (*cf.* also [28]). ^{1}H-NMR (300 MHz, (D_6)DMSO): 12.29 (br. *s*, COOH); 7.71 (*dd*, $^3J(3,4) = 7.5$, $^4J(3,5) = 0.7$, H–C(3,3')); 7.44 (*d*, $^3J(4,5) = 7.3$, H–C(5,5')); 7.31 (*t*, $^3J(3,4) = {}^3J(4,5) = 7.6$, H–C(4,4')); 1.81 (*s*, Me). ^{13}C-NMR (75 MHz, (D_6)DMSO): 168.0 (COOH); 140.6 (C(1,1')); 135.9 (C(6,6')); 132.8 (C(5,5')); 130.4 (C(2,2')); 127.2 (C(3,3')); 126.6 (C(4,4')); 19.7 (Me). ^{1}H-NOE (600 MHz, (D_6)DMSO): 1.81 (Me) → 7.44 (*s*, H–C(5,5')). ^{13}C/^{1}H-HSQC (600 MHz, (D_6)DMSO): 132.8 (C(5,5') → 7.44 H–C(5,5')); 127.2 (C(3,3') → 7.71 H–C(3,3')); 126.6 (C(3,3') → 7.31 H–C(4,4')); 19.7 (Me) → 1.81 (Me).

1.2. *Data of* **1b**. Synthesis according to [26] (*cf.* also [29]). ^{1}H-NMR (300 MHz, (D_6)DMSO): 12.10 (br. *s*, COOH); 7.44 (*dd*, $^3J(3,4) = 7.8$, $^4J(3,5) = 1.1$, H–C(3,3')); 7.32 (*t*, $^3J(3,4) = {}^3J(4,5) = 7.9$, H–C(4,4')); 7.14 (*dd*, $^3J(4,5) = 8.2$, $^4J(3,5) = 1.1$, H–C(5,5')); 3.57 (*s*, MeO). ^{13}C-NMR (75 MHz, (D_6)DMSO): 167.7 (COOH); 156.6; 132.0; 127.5; 127.4; 121.4; 114.0; 55.7 (MeO).

1.3. *Data of* **1c**. Synthesis to [26] (*cf.* also [17]). ^{1}H-NMR (300 MHz, (D_6)DMSO): 11.9 (br. *s*, COOH); 7.30 (*s*, H–C(5,5')); 3.87 (*s*, MeO); 3.80 (*s*, MeO); 3.47 (*s*, MeO). ^{13}C-NMR (75 MHz, (D_6)DMSO): 167.1 (COOH); 156.2; 150.6; 144.3; 126.4; 125.6; 108.8; 60.2 (MeO); 59.9 (MeO); 55.6 (MeO).

1.4. *Data of* **1d**. Synthesis according to [27] (*cf.* also [30]). ^{1}H-NMR (300 MHz, (D_6)DMSO): 12.8 (br. *s*, COOH); 8.24 (*d*, $^4J = 2.0$); 8.11 (*d*, $^4J = 2.0$). ^{13}C-NMR (75 MHz, (D_6)DMSO): 164.7 (COOH); 140.7; 137.5; 133.5; 131.9; 125.2; 121.3.

2. *General Procedure for the Synthesis of the Optically Pure* N,N-*Bis(hydroxyalkyl)-1,1'-biphenyl-2,2'-dicarboxamides* **3aa**–**3eb**. The diacids (4 mmol) **1a**–**1e**, in the presence of a three molar excess (24 mmol) of $SOCl_2$, were transformed into the corresponding diacid chlorides. Excess $SOCl_2$ was evaporated, and the diacid chlorides were dissolved in THF (20 ml), Et_3N (8 mmol) was added and the resulting mixture cooled to 0°. Then, a soln. of the amino alcohol (8 mmol) in THF (20 ml) was added dropwise to the soln. After addition, the mixture was stirred for 1 h at 0°, then warmed up to r.t. The white precipitation was filtered off and the solvent removed. The slightly yellow residue was separated by MPLC to afford the optically pure diastereoiomers **3aa**–**3eb** in yields of 40–45% for each diastereoisomer (80–90% total yield).

2.1. *Data of (*P*)-N,N-Bis[(*R*)-1-(hydroxymethyl)propyl]-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxamide* ((*P,R*)-**3aa**). M.p. 175° (AcOEt). MPLC (AcOEt): CV_1: 6.3; CV_2: 8.0; $\alpha = 1.3$. ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.38–7.31 (*m*, H–C(3,3',4,4',5,5')); 7.22 (br. *d*, $^3J \approx 9.5$, NH); 3.78 (*m*, H–C(1'')); 3.44 (*dd*, $J_{AB} = 11.3$, $^3J = 3.4$, 1 H, CH_2OH); 3.31 (*dd*, $J_{AB} = 11.3$, $^3J = 5.6$, 1 H, CH_2OH); 1.99 (*s*, Me–C(6,6')); 1.95 (br. *s*, OH); 1.47

[4]) In the NMR spectra doubly primed numbers correspond to the atoms of the *N*-side chains.

(*m*, J_{AB} = 13.8, ^3J = 7.5, 6.3, 1 H, $CH_2(2'')$); 1.44 (*sept.*, J_{AB} = 13.8, ^3J = 7.4, 1 H, $CH_2(2'')$); 0.84 (*t*, ^3J = 7.4, Me–C(2'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 171.3 (CO); 137.2; 137.0; 136.3; 131.7; 128.0; 124.2; 64.8 (CH_2OH); 53.3 (C(1'')); 23.8 (C(2'')); 20.1 (*Me*–C(6,6')); 10.5 (*Me*–C(2'')). Anal. calc. for $C_{24}H_{32}N_2O_4$ (412.53): C 69.88, H 7.82, N 6.79, O 15.51; found: C 69.59; H 7.57, N 6.80.

2.2. *Data of (*M*)-*N,N*-Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxamide* ((*M*,1*S*)-**3ab**). M.p. 151° (AcOEt). MPLC (AcOEt): CV_1: 3.8; CV_2: 7.2; α = 2.2. CD ($c = 4.72 \times 10^{-5}$ M, EtOH): 198.6 (–45.35), 214.2 (5.63), 223.4 (2.59, sh), 231.0 (0.06), 243.8 (5.09), 272.0 (–1.31). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.40–7.31 (*m*, H–C(3,3',4,4',5,5'), 2 NH); 3.69 (*m*, H–C(1'')); 3.46 (*dd*, J_{AB} = 11.3, ^3J = 3.4, 1 H, CH_2OH); 3.36 (*dd*, J_{AB} = 11.3, ^3J = 6.5, 1 H, CH_2OH); 2.01 (*s*, Me–C(6,6')); 1.92 (br. *s*, OH); 1.77 (*oct.*, ^3J = 6.5, H–C(2'')); 0.86, 0.83 (2*d*, ^3J = 6.8, $Me_2CH(2'')$). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.8 (CO); 137.2; 136.3; 131.7; 128.0; 124.4; 63.7 (CH_2OH); 57.1 (C(1'')); 29.1 (C(2'')); 20.2 (*Me*–C(6,6')); 19.4, 18.8 ($Me_2CH(2'')$). Anal. calc. for $C_{26}H_{36}N_2O_4$ (440.59): C 70.88, H 8.24, N 6.36, O 14.53; found: C 70.99, H 7.95, N 6.44.

*Data of (*P,S*)-***3ab***.* M.p. 178° (AcOEt/Et_2O). CD ($c = 4.45 \times 10^{-5}$ M, EtOH): 200.8 (46.44); 214.4 (–9.61); 223.4 (–0.17, sh); 231.2 (4.25); 243.8 (–7.03); 265.8 (1.65). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.48–7.27 (*m*, H–C(3,3',4,4',5,5'), 2 NH); 3.61 (*m*, H–C(1'')); 3.48 (*d*, ^3J = 4.2, CH_2OH); 2.72 (br. *s*, OH); 1.92 (*s*, Me–C(6,6')); 1.65 (*oct.*, ^3J = 6.8, H–C(2'')); 0.73, 0.71 (*dd*, ^3J = 6.8, $Me_2CH(2'')$). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 171.4 (CO); 136.9; 136.5; 132.2; 128.0; 125.4; 63.8 (CH_2OH); 57.5 (C(1'')); 29.0 (C(2'')); 20.1 (Me–C(6,6')); 19.2, 18.6, (*Me*–C(2'')). Anal. calc. for $C_{26}H_{36}N_2O_4$ (440.59): C 70.88, H 8.24, N 6.36, O 14.53; found: C 70.96, H 8.02, N 6.45.

2.3. *Data of (*M*)-*N,N*-Bis[(*S*)-2-hydroxy-1-phenylethyl]-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxamide* ((*M*,*S*)-**3ac**). M.p. 98°. MPLC (AcOEt): CV_1: 2.6; CV_2: 4.2; α = 2.0. ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.61 (br. *s*, NH); 7.39–7.19 (*m*, H–C(3,3',4,4',5,5'), 6 arom. H); 7.08 (*m*, 4 H_o); 4.97 (*dd*, ^3J = 6.3, ^3J = 4.4, H–C(1'')); 3.60 (*dd*, J_{AB} = 11.5, ^3J = 4.4, 1 H, $CH_2(2'')$); 3.53 (*dd*, J_{AB} = 11.5, ^3J = 6.4, 1 H, $CH_2(2'')$); 2.32 (br. *s*, OH); 1.97 (*s*, Me–C(6,6')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.7 (CO); 138.6; 137.1; 136.8; 136.2; 131.9; 128.6; 128.1; 127.6; 126.8; 124.8; 65.9 (C(2'')); 55.6 (C(1'')); 20.1 (*Me*–C(6,6')). Anal. calc. for $C_{32}H_{32}N_2O_4$ (508.62): C 75.57, H 6.34, N 5.51, O 12.58; found: C 75.63, H 6.18, N 5.54.

*Data of (*P,S*)-***3ac***.* M.p. 111° (AcOEt). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.98 (br. *d*, ^3J = 6.7, NH); 7.32–7.11 (*m*, H–C(3,3',4,4',5,5'), 6 arom. H); 6.87 (*dd*, ^3J = 7.6, ^4J = 1.6, 4 H_o); 4.79 (*dd*, ^3J = 6.5, ^3J = 4.8, H–C(1'')); 3.61 (*dd*, J_{AB} = 11.4, ^3J = 4.6, 1 H, $CH_2(2'')$); 3.56 (*dd*, J_{AB} = 11.5, ^3J = 6.4, 1 H, $CH_2(2'')$); 2.75 (br. *s*, OH); 1.85 (*s*, Me–C(6,6')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.8 (CO); 138.6; 136.5; 136.4; 136.2; 132.2; 128.5; 127.9; 127.4; 126.7; 125.3; 66.1 (C(2'')); 56.3 (C(1'')); 20.0 (*Me*–C(6,6')).

2.4. *Data of (*M*)-*N,N*-Bis[(1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl]-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxamide* ((*M*,1*S*,2*R*)-**3ad**). M.p. 187° (AcOEt). MPLC (AcOEt): CV_1: 2.9; CV_2: 3.8; α = 1.5. ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.38–7.22 (*m*, H–C(3,3',4,4',5,5'), 10 arom. H, 2 NH); 4.61 (*d*, ^3J = 2.4, H–C(2'')); 4.08 (*m*, H–C(1'')); 2.93 (br. *s*, OH); 1.96 (*s*, Me–C(6,6')); 0.77 (*d*, ^3J = 6.9, Me–C(1'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.3 (CO); 140.8; 137.1; 136.7; 136.0; 131.7; 128.1; 127.2; 125.8; 124.4; 74.8 (C(2'')); 51.5 (C(1'')); 19.9 (*Me*–C(6,6')); 12.1 (*Me*–C(1'')). Anal. calc. for $C_{34}H_{36}N_2O_4$ + $(AcOEt)_{0.25}$ (558.69): C 75.24, H 6.80, N 5.01, O 12.95; found: C 75.22, H 6.49, N 5.02.

*Data of (*P,1S,2R*)-***3ad***.* M.p. 196° (AcOEt/Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.42–7.12 (*m*, H–C(3,3',4,4',5,5'), 10 arom. H, 2 NH); 4.68 (*d*, ^3J = 2.9, H–C(2'')); 4.05 (*m*, ^3J = 2.9, ^3J = 6.9, H–C(1'')); 3.08 (br. *s*, OH); 1.94 (*s*, Me–C(6,6')); 0.67 (*d*, ^3J = 6.9, Me–C(1'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.4 (CO); 140.9; 136.6; 136.3; 132.0; 128.1; 128.0; 127.3; 126.1; 125.1; 75.7 (C(2'')); 51.5 (C(1'')); 20.1 (*Me*–C(6,6')); 13.0 (*Me*–C(1'')).

2.5. *Data of (*M*)-*N,N*-Bis[(*S*)-2-hydroxy-1-methyl-2,2-diphenylethyl]-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxamide* ((*M*,*S*)-**3ae**). Separation of the diastereoisomers by crystallization from AcOEt. M.p. 268° (AcOEt). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.70 (br. *d*, ^3J = 9.4, NH); 7.46 (*d* with f.s., ^3J = 7.3, arom. H); 7.39 (*d* with f.s., ^3J = 7.3, arom. H); 7.32–7.19 (*m*, 12 arom. H); 6.98 (*t*, ^3J = 7.4, H–C(4,4')); 6.93 (*dd*, ^3J = 7.4, ^4J = 1.4); 6.82 (*dd*, ^3J = 7.2, ^4J = 1.6); 5.03 (*dq*, ^3J = 9.4, ^3J = 6.6, H–C(1'')); 3.02 (br. *s*, OH); 1.67 (*s*, Me–C(6,6')); 0.87 (*d*, ^3J = 6.6, Me–C(1'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.1 (CO); 145.6; 145.2; 136.3; 136.0; 132.1; 128.3; 128.2; 127.8; 126.9; 126.6; 125.8; 125.3; 124.4; 80.3 (C(2'')); 51.2 (C(1'')); 19.9 (*Me*–C(6,6')); 15.6 (*Me*–C(1'')). Anal. calc. for $C_{46}H_{44}N_2O_4$ + $(AcOEt)_{0.25}$ (710.89): C 79.40, H 6.52, N 3.94, O 9.29; found: C 79.32, H 6.29, N 3.84.

2.6. *Data of (*M*)-*N,N*-Bis[(*S*)-2-hydroxy-1-(1-methylethyl)-2,2-diphenylethyl]-6,6'-dimethyl-1,1'-biphenyl-2,2'-dicarboxamide* ((*M*,*S*)-**3af**). MPLC (hexane/AcOEt 1:2): CV_1: 4.0; CV_2: 4.8; α = 1.3. M.p. 281° (AcOEt/Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.53 (br. *d*, ^3J = 9.6, NH); 7.46–7.40 (*m*, 10 arom. H); 7.30–7.12

(*m*, 12 arom. H); 6.94 (*t*, ^3J = 7.5, H–C(4,4')); 6.85 (*d*, ^3J = 6.9); 6.73 (*d*, ^3J = 6.9); 4.97 (*dd*, ^3J = 9.9, ^3J = 2.1, H–C(1'')); 2.52 (br. *s*, OH); 1.72 (*s*, Me–C(6,6')); 1.67 (*sept.d*, ^3J = 6.9, ^3J = 2.3, Me_2CH); 0.87, 0.66 (2*d*, ^3J = 6.8, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.8 (CO); 146.7; 145.8; 136.9; 136.0; 135.7; 131.8; 128.4; 128.2; 127.7; 126.8; 126.5; 125.6; 125.2; 124.2; 81.9 (C(2'')); 58.0 (C(1'')); 29.1 (Me_2CH); 22.2, 17.1 (Me_2CH); 20.3 (*Me*–C(6,6')).

2.7. *Data of* (P)-N,N-*Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-6,6'-dimethoxy-1,1'-biphenyl-2,2'-dicarboxamide* ((*P*,*S*)-**3bb**). Separation of the diastereoisomers by crystallization from AcOEt. M.p. 162° (AcOEt). CD ($c = 4.23 \times 10^{-5}$ M, EtOH): 202.4 (–39.44); 213.2 (–0.15); 222.6 (–7.62); 232.8 (6.06); 242.0 (–1.16); 254.4 (2.32); 281.0 (–8.82). ^{1}H-NMR (300 MHz, $CDCl_3$)[3]): 7.39 (*t*, ^3J = 8.0, H–C(4,4')); 7.14 (*dd*, ^3J = 7.6, ^4J = 0.6); 7.01 (*d*, ^3J = 8.3); 6.83 (br. *s*, NH); 3.72 (*s*, MeO); 3.64 (*m*, H–C(1'')); 3.36 (*m*, CH_2OH); 2.34 (br. *s*, OH); 1.73 (*oct.*, ^3J = 6.9, H–C(2'')); 0.87, 0.75 (2*d*, ^3J = 6.8, Me_2CH(2'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.7 (CO); 157.1; 139.3; 129.6; 122.6; 112.5; 63.7 (CH_2OH); 57.5 (C(1'')); 56.2 (MeO); 29.0 (C(2'')); 19.3, 18.8 (Me_2CH(2'')). Anal. calc. for $C_{26}H_{36}N_2O_6$ (472.59): C 66.08, H 7.68, N 5.93, O 20.31; found: C 65.88, H 7.38, N 5.66.

2.8. *Data of* (P)-N,N-*Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-4,4',5,5',6,6'-hexamethoxy-1,1'-biphenyl-2,2'-dicarboxamide* ((*P*,*S*)-**3cb**). MPLC (AcOEt/EtOH 9:1): CV_1: 2.2; CV_2: 2.7, α = 1.5. M.p. 175° (AcOEt). $[\alpha]_D^{25}$ = + 52.1 (*c* = 0.5, $CHCl_3$). CD ($c = 4.72 \times 10^{-5}$ M, EtOH): 198.6 (–15.26); 226.8 (31.32); 245.8 (–11.21); 266.2 (2.43). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 6.89 (*s*, H–C(5,5')); 6.88 (br. *s*, NH); 3.92 (*s*, MeO); 3.89 (*s*, MeO); 3.70 (*s*, MeO); 3.62, 3.46 (2 br. *s*, 2 H–C(1''), 2 CH_2OH); 1.82 (*oct.*, ^3J = 6.7, H–C(2'')); 0.85, 0.78 (2*d*, ^3J = 6.7, Me_2CH(2'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.4 (CO); 153.5; 151.5; 143.5; 133.4; 120.5; 106.4; 63.6 (CH_2OH); 61.2 (MeO); 60.7 (MeO); 58.0 (C(1'')); 56.3 (MeO); 29.0 (C(2'')); 19.2, 18.9 (Me_2CH(2'')). Anal. calc. for $C_{30}H_{44}N_2O_{10}$ (592.69): C 60.80, H 7.48, N 4.73, O 26.99; found: C 60.94, H 7.31, N 4.74.

2.9. *Data of* (P)-N,N-*Bis[(*S*)-1-(hydroxymethyl)-2,2-dimethylpropyl]-4,4',5,5',6,6'-hexamethoxy-1,1'-biphenyl-2,2'-dicarboxamide* ((*P*,*S*)-**3cg**). Separation of the diastereoisomers by crystallization from AcOEt. M.p. 188° (AcOEt). $[\alpha]_D^{25}$ = + 59.8 (*c* = 0.48, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 6.89 (*s*, H–C(5,5')); 6.83 (br. *d*, ^3J = 9.7, NH); 3.92 (*s*, MeO); 3.90 (*s*, MeO); 3.79 (*m*, H–C(1'')); 3.72 (*s*, MeO); 3.66 (*dd*, J_{AB} = 11.5, ^3J = 3.1, 1 H, CH_2OH); 3.36 (*dd*, J_{AB} = 11.5, ^3J = 7.9, 1 H, CH_2OH); 2.23 (br. *s*, OH); 0.86 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.8 (CO); 153.4; 151.5; 143.5; 133.3; 120.8; 106.4; 63.1 (CH_2OH); 61.1 (MeO); 60.8 (MeO); 60.3 (C(1'')); 56.3 (MeO); 33.5 (C(2'')); 26.8 (Me_3C(2'')). Anal. calc. for $C_{32}H_{48}N_2O_{10}$ (620.75): C 61.92; H 7.79; N 4.51; O 25.77; found: C 62.05, H 7.55, N 4.61.

2.10. *Data of* (P)-N,N-*Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-4,4',6,6'-tetrabromo-1,1'-biphenyl-2,2'-dicarboxamide* ((*P*,*S*)-**3db**). MPLC: See *2.10*. (*P*,1*S*)-**3db** (matched; see also *Fig. 2*) was the second compound eluted from the column. M.p. 212° (AcOEt/hexane). CD ($c = 4.72 \times 10^{-5}$ M, EtOH): 205.8 (–6.35, sh), 210.0 (–6.96); 213.8 (–6.45); 229.2 (–17.09); 259.2 (4.04); 280.2 (–0.23). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.88 (*d*, ^4J = 1.9); 7.61 (*d*, ^4J = 1.9); 7.28 (br. *d*, ^3J = 9.3, NH); 3.68 (*m*, H–C(1'')); 3.53 (*dd*, J_{AB} = 11.4, ^3J = 3.7, 1 H, CH_2OH); 3.42 (*dd*, J_{AB} = 11.4, ^3J = 6.6, 1 H, CH_2OH); 1.78 (*oct.*, ^3J = 6.8, H–C(2'')); 0.88, 0.85 (2*d*, ^3J = 6.8, Me_2CH(2'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 167.9 (CO); 140.1; 136.4; 129.1; 125.9; 123.2; 63.4 (CH_2OH); 57.3 (C(1'')); 29.1 (C(2'')); 19.5, 18.7 (Me_2CH(2'')).

Data of (M,S)-**3db**. MPLC (AcOEt/hexane 2:1): CV_1: 4.2; CV_2: 4.8; α = 1.2. (*M*,1*S*)-**3db** (mismatched; see also *Fig. 2*) was the first compound eluted from the column. M.p. 233° (AcOEt/hexane). CD ($c = 4.87 \times 10^{-5}$ M, EtOH): 211.0 (7.48); 213.8 (7.01); 229.8 (19.02); 260.1 (–5.89); 273.2 (1.46). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.90 (*d*, ^4J = 1.9); 7.69 (*d*, ^4J = 1.9); 7.42 (br. *d*, ^3J = 8.8, NH); 3.68 (*m*, H–C(1'')); 3.56 (*m*, CH_2OH); 1.74 (*oct.*, ^3J = 6.8, H–C(2'')); 0.79, 0.74 (2*d*, ^3J = 6.8, Me_2CH(2'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 167.6 (CO); 140.1; 136.8; 135.7; 130.1; 124.9; 123.6; 63.3 (CH_2OH); 57.7 (C(1'')); 29.0 (C(2'')); 19.3, 18.6 (Me_2CH(2'')).

2.11. *Data of* (M)-N,N-*Bis[(*S*)-1-(hydroxymethyl)-2-methylpropyl]-1,1'-bianthryl-2,2'-dicarboxamide* ((*M*,*S*)-**3eb**). M.p. 238° (AcOEt). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 8.53 (*s*); 8.22 (*d*, ^3J = 8.7); 7.98 (*d*, ^3J = 8.5); 7.87 (*s*); 7.72 (*d*, ^3J = 8.7); 7.62 (*d*, ^3J = 8.5); 7.43 (*t* with f.s., ^3J = 7.9); 7.29 (*t* with f.s., ^3J = 7.9); 7.22 (br. *d*, ^3J = 9.0, NH); 3.48 (*m*, H–C(1'')); 3.16 (*m*, CH_2OH); 1.43 (*oct.*, ^3J = 6.8, H–C(2'')); 0.49, 0.37 (2*d*, ^3J = 6.8, Me_2CH(2'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 170.1 (CO); 133.2; 130.6; 129.5; 128.7; 127.9; 127.1; 126.8; 124.3; 64.2 (CH_2OH); 57.9 (C(1'')); 29.5 (C(2'')); 19.8, 19.0 (Me_2CH(2'')).

3. *General Procedure for the Synthesis of the Optically Pure Bis(4,5-dihydrooxazol-2-yl)-1,1'-biaryls* **4aa**–**4eb**: The dicarboxamides **3aa**–**3eb** (1 mmol) were disolved in THF (15 ml), and *Burgess* reagent (methyl *N*-[(triethylammonio)sulfonyl]carbamate) was added. After 10 min a white solid precipitated. The mixture was stirred for 1 h at r.t., and the reaction was checked by TLC (hexane/Et_2O 1:1). For the formation of **4af** and **4db**, longer reaction times (4 h) and higher reaction temp. (50°) were necessary. The white precipitate was filtered off and the residue filtered over SiO_2 (1% Et_3N) to yield pure bis(4,5-dihydrooxazol-2-yl)-1,1'-biaryls **4aa**–**4eb** in 85–95% yield, as colorless oils which solidify upon standing.

3.1. *Data of (*P*)-2,2'-Bis[(*R*)-4-ethyl-4,5-dihydrooxazol-2-yl]-6,6'-dimethyl-1,1'-biphenyl* ((*P,R*)-**4aa**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.64 (*d*, ^3J = 7.6); 7.31 (*d*, ^3J = 7.6); 7.22 (*t*, ^3J = 7.5, H–C(4,4')); 3.99–3.87 (*m*, H–C(4''), CH_2(5'')); 3.54 (*dd*, J_{AB} = 7.7, ^3J = 7.7, H–C(5'')); 1.96 (*s*, Me–C(6,6')); 1.37 (*sept.*, J_{AB} = 13.8, ^3J = 7.5, 6.3, 1 H, MeCH_2); 1.34 (*sept.*, J_{AB} = 13.8, ^3J = 7.4, 7.4, 1 H, MeCH_2); 0.84 (*t*, ^3J = 7.4, *Me*CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 164.1 (C(2'')); 139.5; 136.8; 131.5; 127.8; 126.8; 72.0; 67.7; 28.4 (MeCH_2); 20.1 (*Me*–C(6,6')); 9.8 (*Me*CH_2).

3.2. *Data of (*M*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-6,6'-dimethyl-1,1'-biphenyl* ((*M,S*)-**4ab**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.70 (*dd*, ^3J = 7.4, ^4J = 1.3); 7.30 (*d*, ^3J = 7.5); 7.23 (*t*, ^3J = 7.5, H–C(4,4')); 3.95 (*dd*, J_{AB} = 7.7, ^3J = 9.0, 1 H, CH_2(5'')); 3.75 (*sext.*, ^3J = 9.1, 7.7, 6.6, H–C(4'')); 3.67 (*t*, J_{AB} = 7.7, ^3J = 7.7, 1 H, CH_2(5'')); 1.93 (*s*, Me–C(6,6')); 1.55 (*oct.*, ^3J = 6.7, Me_2CH); 0.78, 0.73 (2*d*, ^3J = 6.7, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[3]): 163.8 (C(2'')); 139.9; 136.6; 131.5; 127.7; 126.8; 126.5; 72.4 (C(4'')); 69.8 (C(5'')); 32.7 (Me_2CH); 20.1 (*Me*–C(6,6')); 18.6, 18.1 (Me_2CH).

*Data of (*P,S*)-***4ab***.* ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.61 (*dd*, ^3J = 7.5, ^4J = 1.3); 7.28 (*d*, ^3J = 7.0); 7.25 (*t*, ^3J = 7.5, H–C(4,4')); 4.01 (*dd*, J_{AB} = 7.9, ^3J = 9.5, 1 H, CH_2(5'')); 3.88 (*sext.*, ^3J = 9.4, 7.9, 6.6, H–C(4'')); 3.63 (*t*, J_{AB} = 7.9, ^3J = 7.9, 1 H, CH_2(5'')); 1.97 (*s*, Me–C(6,6')); 1.46 (*oct.*, ^3J = 6.7, Me_2CH); 0.71, 0.69 (2*d*, ^3J = 6.7, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 163.8 (C(2'')); 139.9; 136.6; 131.5; 127.7; 126.8; 126.5; 72.5 (C(4'')); 69.9 (C(5'')); 32.6 (Me_2CH); 20.2 (*Me*–C(6,6')); 18.6, 18.1 (Me_2CH).

3.3. *Data of (*M*)-2,2'-Bis[(*S*)-4,5-dihydro-4-phenyloxazol-2-yl]-6,6'-dimethyl-1,1'-biphenyl* ((*M,S*)-**4ac**). MPLC (hexane/EtO_2 2:1): CV_1: 2.5; CV_2: 3.1; α = 1.4. ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.83 (*dd*, ^3J = 7.6, ^4J = 1.2); 7.37 (*d* with f.s., ^3J = 7.6); 7.29 (*t*, ^3J = 7.6, H–C(4,4')); 7.25–7.16 (*m*, 6 arom. H); 7.04 (*dd* with f.s., ^3J = 7.3, ^4J = 2.4, 1.8, 4 H_o); 5.12 (*dd*, J_{AB} = 10.1, ^3J = 8.3, 1 H, CH_2(5'')); 4.37 (*dd*, J_{AB} = 10.1, ^3J = 8.3, 1 H, CH_2(5'')); 3.53 (*t*, ^3J = 8.3, H–C(4'')); 1.99 (*s*, Me–C(6,6')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 165.5 (C(2'')); 142.7; 140.0; 136.9; 132.1; 128.4; 127.3; 127.1; 126.9; 126.7; 74.5 (C(4'')); 69.8 (C(5'')); 20.3 (*Me*–C(6,6')).

*Data of (*P,S*)-***4ac***.* ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.73 (*dd*, ^3J = 7.4, ^4J = 1.2, H–C(3,3')); 7.36 (*d* with f.s., ^3J = 7.4, H–C(5,5')); 7.31 (*t*, ^3J = 7.5, H–C(4,4')); 7.25–7.18 (*m*, 6 arom. H); 6.90 (*dd* with f.s., ^3J = 7.9, ^4J = 2.1, 1.6, 4 H_o); 5.14 (*dd*, J_{AB} = 10.1, ^3J = 8.6, 1 H, CH_2(5'')); 4.40 (*dd*, J_{AB} = 10.1, ^3J = 8.3, 1 H, CH_2(5'')); 3.75 (*t*, ^3J = 8.4, H–C(4'')); 2.05 (*s*, Me–C(6,6)). ^{1}H-NMR (300 MHz, (D_6)acetone)[4]): 7.72 (*dd*, ^3J = 7.4, ^4J = 1.2, H–C(3,3')); 7.34 (*d* with f.s., ^3J = 7.5, H–C(5,5')); 7.29 (*t*, ^3J = 7.6, H–C(4,4')); 7.21–7.16 (*m*, 6 arom. H); 6.88 (*dd*, ^3J = 7.8, ^4J = 1.8, 4 H_o); 5.13 (*dd*, J_{AB} = 10.9, ^3J = 8.5, 1 H, CH_2(5'')); 4.37 (*dd*, J_{AB} = 10.1, ^3J = 8.3, 1 H, CH_2(5'')); 3.71 (*t*, ^3J = 8.3, H–C(4'')); 2.03 (*s*, Me–C(6,6')). ^{1}H-NOESY (300 MHz, $CDCl_3$): 7.73 → 7.31; 7.36 → 7.31, 2.05; 7.31 → 7.83, 7.36; 7.25–7.18 → 6.90; 6.90 → 7.25–7.18, 5.14, 3.75 (*w*); 5.14 → 7.25–7.18, 4.40, 3.75; 4.40 → 5.14, 3.75 (*s*); 3.75 → 7.25–7.18 (*w*); 5.14, 4.40 (*s*); 2.05 → 7.36. ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 165.6 (C(2'')); 142.5; 139.4; 137.5; 131.9; 128.3; 127.8; 127.0; 126.9; 126.8; 126.5; 74.6 (C(4'')); 69.8 (C(5'')); 20.2 (*Me*–C(6,6')).

3.4. *Data of (*M*)-2,2'-Bis[(4*S*,5*R*)-4,5-dihydro-4-methyl-5-phenyloxazol-2-yl]-6,6'-dimethyl-1,1'-biphenyl* ((*M*,4*S*,5*R*)-**4ad**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.76 (*dd*, ^3J = 7.2, ^4J = 1.7, H–C(3,3')); 7.31 (*dd*, ^3J = 7.6, ^4J = 1.7, H–C(5,5')); 7.26 (*t*, ^3J = 7.4, H–C(4,4')); 7.24–7.20 (*m*, 6 arom. H); 6.93–6.90 (*m*, 4 H_o); 4.66 (*d*, ^3J = 8.1, H–C(5'')); 3.90 (*oct.*, ^3J = 8.1, ^3J = 6.7, H–C(4'')); 1.97 (*s*, Me–C(6,6')); 1.28 (*d*, ^3J = 6.7, Me–C(4'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 163.8 (C(2'')); 140.5; 139.6; 136.9; 131.9; 128.3; 127.8; 127.6; 127.3; 126.9; 125.1; 87.9; 70.1; 21.3; 20.2.

*Data of (*P,4*S*,5*R*)-***4ad***.* ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.71 (*dd*, ^3J = 7.3, ^4J = 1.5, H–C(3,3')); 7.32 (*dd*, ^3J = 7.5, ^4J = 1.6, H–C(5,5')); 7.27 (*t*, ^3J = 7.4, H–C(4,4')); 7.24–7.18 (*m*, 6 arom. H); 7.01–6.98 (*m*, 4 H_o); 4.65 (*d*, ^3J = 7.7, H–C(5'')); 3.90 (*quint.* with f.s., ^3J = 7.7, ^3J = 6.7, H–C(4'')); 2.02 (*s*, Me–C(6,6')); 1.15 (*d*, ^3J = 6.6, Me–C(4'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 164.1 (C(2'')); 140.6, 139.4; 137.4; 131.8; 128.4; 128.1; 127.7; 127.4; 127.0; 125.3; 87.8; 70.3; 21.3; 20.2.

3.5. *Data of (*M*)-2,2'-Bis[(*S*)-4,5-dihydro-4-methyl-5,5-diphenyloxazol-2-yl]-6,6'-dimethyl-1,1'-biphenyl* ((*M,S*)-**4ae**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 8.00 (*dd*, ^3J = 7.2, ^4J = 1.8, H–C(3,3')); 7.25–7.03 (*m*, 20 arom. H); 6.87–6.84 (*m*, 4 H_o); 3.90 (*q*, ^3J = 6.8, H–C(4'')); 1.68 (*s*, Me–C(6,6')); 0.78 (*d*, ^3J = 6.9, Me–C(4'')). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 163.1 (C(2'')); 143.9; 140.7; 136.8; 132.6; 128.1; 128.0; 127.6; 127.5; 127.4; 126.9; 126.8; 126.7; 126.4; 93.7 (C(5'')); 67.7 (HC(4'')); 20.3; 19.5.

3.6. *Data of (*M*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1-methylethyl)-5,5-diphenyloxazol-2-yl]-6,6'-dimethyl-1,1'-biphenyl* ((*M,S*)-**4af**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]): 7.99 (*d*, ^3J = 7.5, H–C(3,3')); 7.22–6.91 (*m*, 24 arom. H); 4.58(*d*, ^3J = 3.8, H–C(4'')); 1.54 (*s*, Me–C(6,6')); 0.84, 0.25 (2*d*, ^3J = 6.8, Me_2CH); 0.80 (*m*, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]): 162.4 (C(2'')); 145.3; 140.7; 140.3; 136.4; 132.6; 127.9; 127.3; 127.2; 127.0; 126.8; 126.6; 126.5; 126.4; 92.7 (C(5'')); 77.8 (C(4'')); 30.2 (Me_2CH); 22.0; 20.2; 16.2.

3.7. *Data of (*P*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-6,6'-dimethoxy-1,1'-biphenyl* ((*P*,*S*)-**4bb**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]: 7.48 (*dd*, ^3J = 7.8, ^4J = 1.1); 7.29 (*t*, ^3J = 8.0, H–C(4,4')); 6.97 (*dd*, ^3J = 8.2, ^4J = 1.0); 4.00 (*m*, 2 H); 3.81–3.67 (*m*, 4 H); 3.67 (*s*, MeO); 1.54 (*oct.*, ^3J = 6.7, Me_2CH); 0.80, 0.74 (2*d*, ^3J = 6.7, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]: 163.6 (C(2")); 156.0; 139.1; 129.4; 122.2; 118.7; 112.8; 72.5 (C(4")); 69.9 (C(5")); 56.1 (MeO); 32.7 (Me_2CH); 18.9, 18.2 (Me_2CH).

3.8. *Data of (*P*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-4,4',5,5',6,6'-hexamethoxy-1,1'-biphenyl* ((*P*,*S*)-**4cb**; *cf.* [17]). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]: 7.23 (*s*, H–C(5,5')); 4.04 (*dd*, J_{AB} = 7.6, ^3J = 9.0, 1 H, CH_2(5")); 3.93 (*s*, MeO); 3.90 (*s*, MeO); 3.77 (*m*, H–C(4")); 3.69 (*t*, J_{AB} = 7.7, ^3J = 7.7, 1 H, CH_2(5")); 3.66 (*s*, MeO); 1.60 (*oct.*, ^3J = 6.7, Me_2CH); 0.84, 0.76 (2*d*, ^3J = 6.7, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]: 163.4 (C(2")); 152.1; 151.6; 143.9; 125.5; 123.6; 108.2; 72.6 (C(4")); 70.1 (C(5")); 60.7 (MeO); 60.5 (MeO); 56.1 (MeO); 32.8 (Me_2CH); 19.0, 18.3 (Me_2CH).

3.9. *Data of (*P*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1,1-dimethylethyl)oxazol-2-yl]-4,4',5,5',6,6'-hexamethoxy-1,1'-biphenyl* ((*P*,*S*)-**4cg**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]: 7.26 (*s*, H–C(5,5')); 4.00 (*dd*, J_{AB} = 7.5, ^3J = 9.0, 1 H, CH_2(5")); 3.93 (*s*, MeO); 3.91 (*s*, MeO); 3.85–3.69 (*m*, 3 H, 2 H–C(4"), CH_2(5")); 3.65 (*s*, MeO); 0.75 (*s*, *t*-Bu). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]: 163.2 (C(2")); 152.1; 151.6; 144.0; 125.5; 123.6; 108.2; 75.9 (C(4")); 68.2 (C(5")); 60.6 (MeO); 60.4 (MeO); 56.0 (MeO); 33.7 (Me_3C); 25.8 (Me_3C).

3.10. *Data of (*P*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-4,4',6,6'-tetrabromo-1,1'-biphenyl* ((*P*,*S*)-**4db**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]: 8.08 (*d*, ^4J = 2.0); 7.86 (*d*, ^4J = 2.0); 4.12 (*m*, 2 H); 3.85–3.79 (*m*, 4 H); 1.53 (*oct.*, ^3J = 6.6, Me_2CH); 0.74 (*d*, ^3J = 6.7, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]: 160.3 (C(2")); 139.7; 136.6; 131.4; 130.6; 125.4; 121.7; 73.0 (C(4")); 70.3 (C(5")); 32.9 (Me_2CH); 18.4 (Me_2CH).

*Data of (*M,*S*)-***4db***). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]: 8.03 (*d*, ^4J = 2.0); 7.87 (*d*, ^4J = 2.0); 4.12 (*m*, 2 H); 3.86–3.74 (*m*, 4 H); 1.49 (*oct.*, ^3J = 6.7, Me_2CH); 0.73, 0.71 (2*d*, ^3J = 6.7, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]: 160.4 (C(2")); 139.5; 136.5; 131.3; 130.3; 126.1; 121.7; 73.0 (C(4")); 70.3 (C(5")); 32.8 (Me_2CH); 18.3 (Me_2CH).

3.11. *Data of (*M*)-2,2'-Bis[(*S*)-4,5-dihydro-4-(1-methylethyl)oxazol-2-yl]-1,1'-bianthryl* ((*M*,*S*)-**4eb**). ^{1}H-NMR (300 MHz, $CDCl_3$)[4]: 8.48 (*s*); 8.19 (*d*, ^3J = 8.6); 8.13 (*d*, ^3J = 8.5); 7.99 (*d*, ^3J = 8.7); 7.80 (*s*); 7.58 (*d*, ^3J = 8.5); 7.41 (*t* with f.s., ^3J = 7.9); 7.26 (*t* with f.s., ^3J = 7.9); 3.72–3.50 (*m*, 6 H); 1.36 (*oct.*, ^3J = 6.8, Me_2CH); 0.62, 0.57 (*d*, ^3J = 6.8, Me_2CH). ^{13}C-NMR (75 MHz, $CDCl_3$)[4]: 164.1 (C(2")); 132.1; 131.8; 131.7; 128.9; 127.9; 127.6; 126.8; 126.0; 125.8; 125.5; 125.1; 72.2 (C(4")); 70.1 (C(5")); 32.6 (Me_2CH); 18.5, 18.0 (Me_2CH).

4. *Synthesis of the Cu^I Complexes.* $[Cu^I(MeCN)_4][PF_6]$ was dissolved in CH_2Cl_2, and an equimolar amount of the ligands **4ab** and **4ac** was added. The mixture was stirred at r.t. for 1 h in a glove box. Precipitation of the complex was achieved by addition of Et_2O. The soln. was filtered and the white microcrystalline complex dried. The yields of the formed complexes were in the range of 65–80%.

4.1. *Data of the Cu^I Complex of (*M,*S*)-***4ab***.* ^{1}H-NMR (300 MHz, (D_6)acetone)[4]: 7.48–7.41 (*m*, 4 H); 7.36 (*t*, ^3J = 7.5, H–C(4,4')); 4.61 (*dd*, J_{AB} = 9.2, ^3J = 10.0, 1 H, CH_2(5")); 4.29 (*dd*, J_{AB} = 9.1, ^3J = 6.8, 1 H, CH_2(5")); 3.95 (*sext.*, ^3J = 10.1, 6.7, 6.7, H–C(4")); 2.11 (*s*, MeCN); 1.86 (*s*, Me–C(6,6')); 1.25 (*oct.*, ^3J = 6.7, Me_2CH); 0.44, 0.42 (2*d*, ^3J = 6.7, Me_2CH).

4.2. *Data of the Cu^I Complex of (*M,*S*)-***4ac***.* ^{1}H-NMR (300 MHz, (D_6)acetone)[4]: 7.65 (*dd*, ^3J = 6.9, ^4J = 2.0); 7.61 (*t*, ^3J = 6.8, H–C(4,4')); 7.50 (*dd*, ^3J = 6.8, ^4J = 2.0); 7.16–7.04 (*m*, 6 H); 6.40–6.33 (*m*, 2 H_o); 5.20 (*dd*, J_{AB} = 10.5, ^3J = 8.4, 1 H, CH_2(5")); 4.99 (*dd*, J_{AB} = 10.6, ^3J = 8.9, 1 H, CH_2(5")); 4.12 (*t*, ^3J = 8.6, H–C(4")); 1.98 (*s*, Me–C(6,6')); 1.94 (*s*, MeCN). ^{13}C-NMR (150 MHz, (D_6)acetone)[4]: 170.8 (MeCN); 141.4; 138.4; 137.6 (C(2")); 134.6; 129.7; 129.4; 128.8; 127.6; 127.1; 77.3; 70.0; 20.1 (*Me*–C(6,6')); 1.2 (*Me*CN).

*Data of the Cu^I Complex of (*P,*S*)-***4ac***.* ^{1}H-NMR (300 MHz, (D_6)acetone)[4]: 7.62 (*dd*, ^3J = 6.7, ^4J = 1.0); 7.53 (*d*, ^3J = 6.8); 7.47 (*t*, ^3J = 7.5, H–C(4,4')); 7.21–7.08 (*m*, 10 H); 4.86 (*dd*, J_{AB} = 10.3, ^3J = 7.5, 1 H, CH_2(5")); 4.77 (*dd*, J_{AB} = 10.3, ^3J = 8.5, 1 H, CH_2(5")); 4.35 (*t*, ^3J = 8.4, 7.6, H–C(4")); 1.96 (*s*, Me–C(6,6')); 1.87 (*s*, MeCN). ^{13}C-NMR (150 MHz, (D_6)acetone): 171.2 (MeCN); 140.7; 138.1; 137.0 (C(2")); 134.2; 129.5; 129.4; 129.3; 129.2; 128.3; 127.1; 77.4; 70.2; 19.9 (*Me*–C(6,6')); 1.5 (*Me*CN).

5. *General Procedure for the Cyclopropanation.* $Cu^IOTf(C_6H_6)_{0.5}$ (0.01 mmol, 2 mol-%) and the corresponding ligand **4aa**–**4eb** (0.011 mmol, 1.1 equiv.) were disolved in $CHCl_3$ (1 ml) and stirred at 25° for 30 min. Then, styrene (0.44 ml, 4 mmol) was added, and the soln. of $N_2CHCOOEt$ in $CHCl_3$ (0.63 ml, 0.5 mmol) was added over 3 h by a syringe pump. After addition, the mixture was stirred for 30 min, then the mixture was filtered over SiO_2 to remove the catalyst, and the stereochemical outcome of the reaction was checked by GC on a *SE-54* column and HPLC on a *(S,S)-Whelk-O1* column (eluant hexane/EtOH 0.2%, flow 1 ml): (1*R*,2*R*)-**5**: t_R 8.0 min; (1*S*,2*S*)-**5**: t_R 10.3 min; (1*S*,2*R*)-**5**: t_R 11.1 min; (1*R*,2*S*)-**5**: t_R 13.8 min; *cf.* [5][12][14][15]. For the determination

of the abs. configuration of the formed cyclopropanes **5**, the reaction mixture with **4ab** was separated by liquid chromatography using SiO_2 and hexane/EtO_2 4:1 to isolate optically enriched *trans*-**5** and *cis*-**5**. *trans*-**5**: $[\alpha]_D^{25} = -152$ ($c = 1.1$, $CHCl_3$) and *cis*-**5**: $[\alpha]_D^{25} = -9.3$ ($c = 0.9$, $CHCl_3$) [5][12][14][15].

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