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Synthesis of novel chiral 6,6′-bis(oxazolyl)-1,1′-biphenyls and their application as ligands in copper(I)-catalyzed asymmetric cyclopropanation

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Abstract—The synthesis of a number of novel chiral bis(oxazolyl) ligands with a biphenyl backbone from ellagic acid **1** and their application in the copper(I)-catalyzed asymmetric cyclopropanation was described.

1. Introduction

Optically active cyclopropane derivatives, especially 2-substituted cyclopropane carboxylates are present in many biologically important substances.[1] 2-Phenyl-1-cyclopropane carboxylates are very useful intermediates in the synthesis of these chiral compounds.[2] Up until now, several strategies have been developed for enantioselective cyclopropanation.[3] In this context, axially chiral binaphthyl ligands (BINAP) with a C_2-symmetry axis have also been applied in the copper(I)-catalyzed asymmetric cyclopropanation.[4]

Herein, we report on the synthesis of a number of optically active bis(oxazolyl) derivatives with a biphenyl backbone and their use as chiral ligands in the copper(I)-catalyzed asymmetric cyclopropanation of styrene **18** with ethyl diazoacetate **19**.

2. Results and discussion

Bis-lactone **2** was prepared by the reaction of ellagic acid **1** with benzyl chloride in the presence of potassium carbonate in water. The opening of the lactone rings of bis-lactone **2** under strongly basic conditions with potassium hydroxide in the presence of benzyl chloride gave *rac*-**3** as a racemic mixture (Scheme 1), which was further characterized by X-ray analysis (Fig. 1). Hydrolysis of ester *rac*-**3** under basic conditions led to the formation of the corresponding biaryldicarboxylic acid *rac*-**4** in a quantitative yield.

At this stage, attempts to separate the racemic mixture *rac*-**4** into its enantiomerically pure atropisomers (a*R*)-**4** and (a*S*)-**4** by using cinchonin, was only effective for (a*R*)-**4**, but unfortunately not for (a*S*)-**4** (Scheme 1).

Enantiomerically pure (a*R*)-**4** was treated with achiral amine **5** to give β-hydroxylamide (a*R*)-**8** (Scheme 2). All attempts to crystallize (a*R*)-**8** failed. However, we were able to obtain crystals from *rac*-**8**, which was further characterized by X-ray analysis (Fig. 2).

β-Hydroxamide (a*R*)-**8** was then converted into the novel chiral ligand (a*R*)-**9** by mesylation and spontaneous cyclization (Scheme 2).

However, *rac*-**4** was treated with the enantiomerically pure amines **6** and **7** to give two diastereomeric pairs of β-hydroxylamides **10/11** and **12/13** (Scheme 3), respectively, which could be separated by chromatography on silica gel. For the synthesis of stereochemically pure β-hydroxylamides **10**–**13**, prior activation of the carboxylic groups of dicarboxylic acid **4** was necessary, which could be achieved upon its treatment with thionyl chloride. The resulting dichlorides (not shown) from these reactions were

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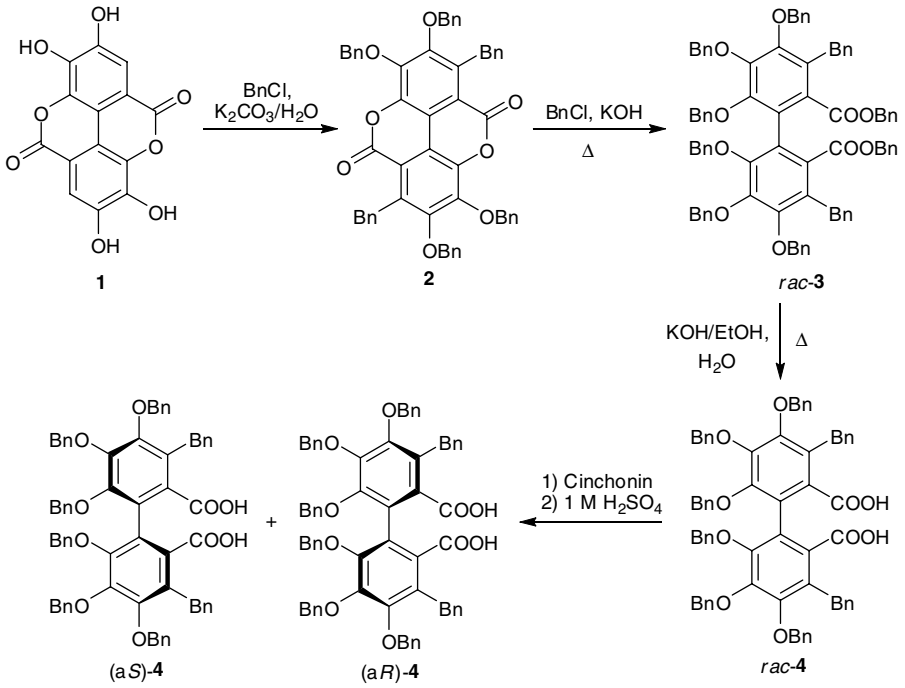


Scheme 1. Synthesis and the separation of *rac*-**4** into its enantiomerically pure atropisomers (a*R*)-**4** and (a*S*)-**4**.

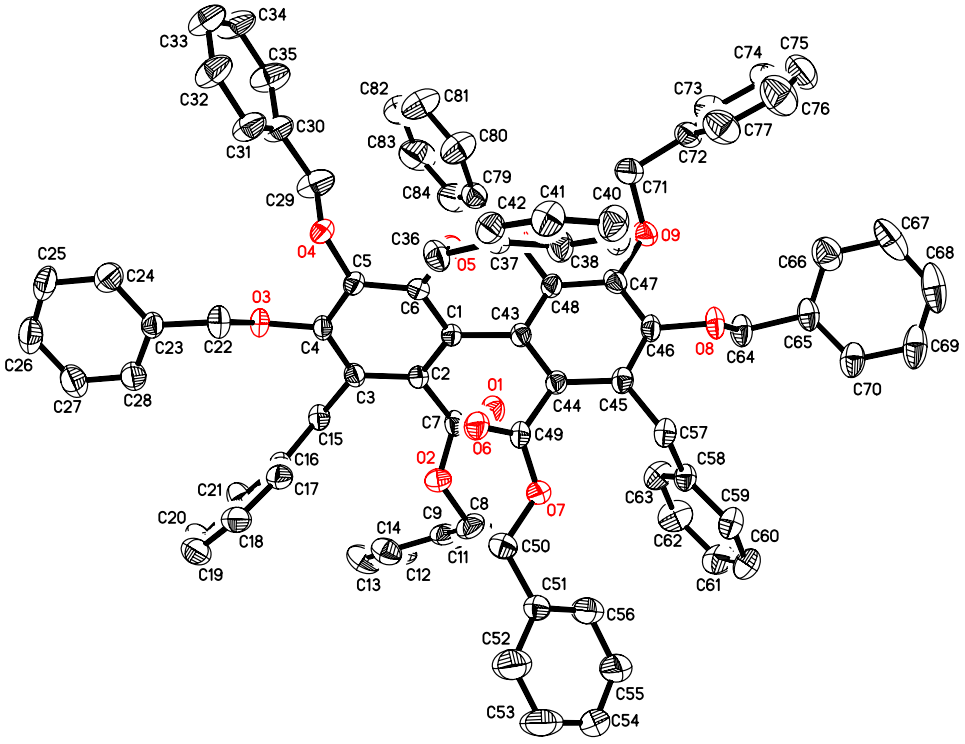
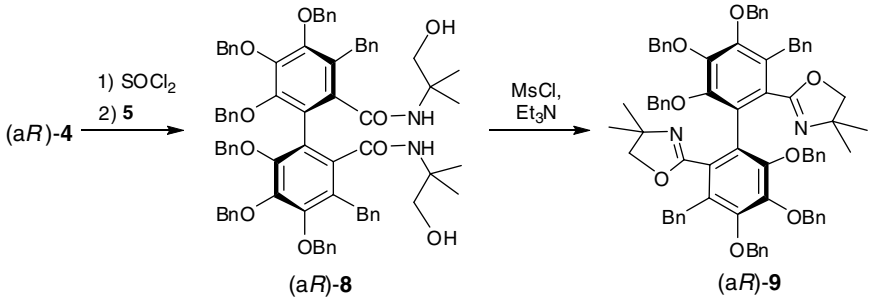


Figure 1. Molecular structure of *rac*-**3** by X-ray analysis. The hydrogen atoms are omitted for clarity.

then condensed with one of the commercially available amines **6** or **7** in situ to furnish the corresponding β-hydroxylamides **10**–**13**. With these compounds in hand, we now were able to synthesize four novel chiral ligands **14**–**17** by mesylation of their hydroxyl groups and spontaneous cyclization (Scheme 3).

To investigate the catalytic potential of these chiral ligands, we decided to run a series of copper(I)-catalyzed stereoselective cyclopropanations of styrene **18** with ethyl diazoacetate **19** (Scheme 4). As a result, freshly prepared chiral copper complex **II** was applied to the stereoselective process (Scheme 4). Principally, four stereoisomers [two pairs



Scheme 2. Synthesis of the chiral ligand (a*R*)-**9**.

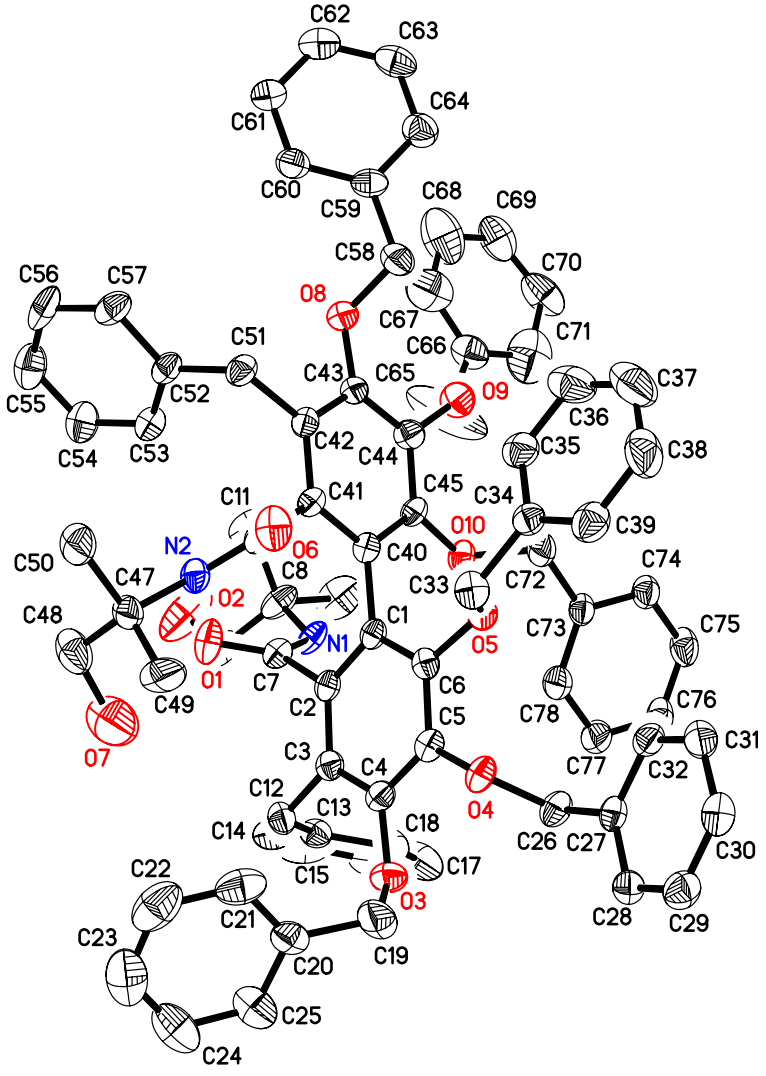
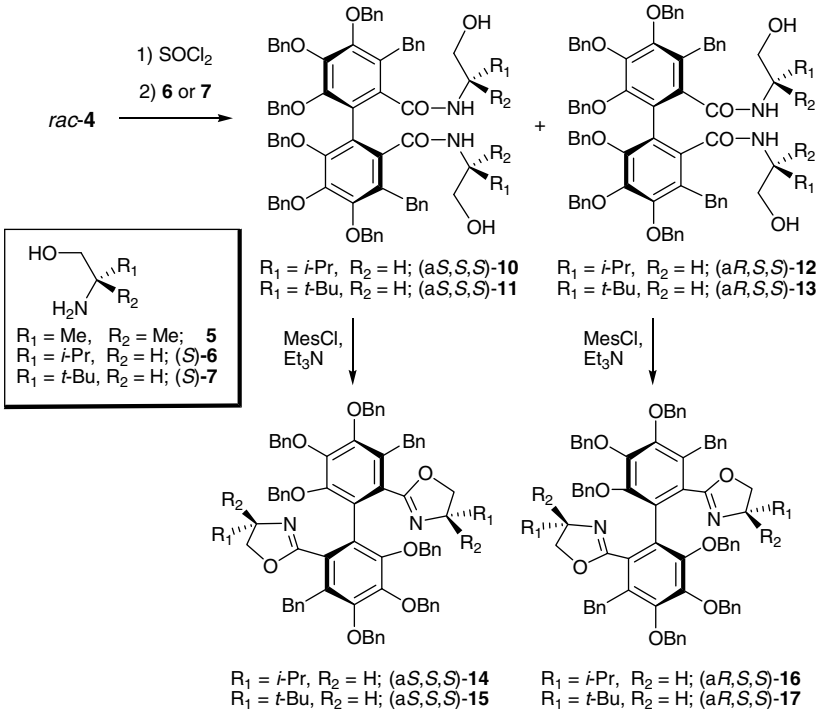


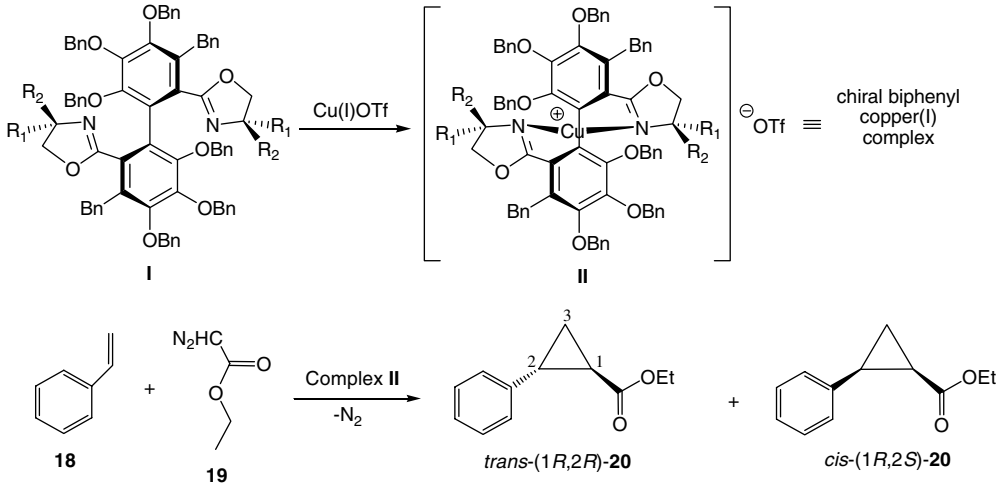
Figure 2. Molecular structure of *rac*-**8** by X-ray analysis.

of enantiomers *trans*-(1*S*,2*S*)-**20**/*trans*-(1*R*,2*R*)-**20** and *cis*-(1*S*,2*R*)-**20**/*cis*-(1*R*,2*S*)-**20**] could be formed from this reaction.

We expected that the application of enantiomeric ligands **I** in this reaction would lead favourably to the enantioselective formation of one of the two possible diastereomeric pairs from this reaction, either *trans*-(1*S*,2*S*)-**20**/*cis*-(1*S*,2*R*)-**20** or *trans*-(1*R*,2*R*)-**20**/*cis*-(1*R*,2*S*)-**20** (Scheme 4). In this context, we ran the cyclopropanation reaction of stryrene **18** with ethyl diazoacetate **19** in the presence of our new chiral ligands **9**, **14**–**17** and analyzed the products obtained by gas chromatography (GC) on a chiral column. It should be noted, that we used 4–10 mol %



Scheme 3. Synthesis of β-hydroxylamides **10**–**13** and chiral ligands **14**–**17**.



Scheme 4. Enantioselective cyclopropanation by using a chiral biphenyl copper(I)-complex.

chiral ligand in each run. To ensure a complete consumption of ethyl diazoacetate **19**, stryrene **18** was generally used in excess (2.5 equiv). Before the product composition was analyzed by GC, the metal components were separated by flash chromatography on silica gel. The results of these reactions are listed in Table 1, which shows that most of the ligands have an influence on the stereochemical course of the reaction. As expected, ligands (a*S*,*S*,*S*)-**14** preferentially gave rise to the formation of a mixture of the diastereomeric compounds *trans*-(1*R*,2*R*)-**20**/*cis*-(1*R*,2*S*)-**20**. The highest enantioselectivity [83% ee, *cis*-(1*R*,2*S*)-**20**] was provided by the chiral ligand (a*S*,*S*,*S*)-**15**, having bulky *tert*-butyl groups in the neighbourhood of the N-atoms of the catalyst, whereas its diastereomeric counterpart (a*R*,*S*,*S*)-**17** was inactive in the same process at room temperature. This result is similar to the result in the same asymmetric process [for cyclopropane *cis*-(1*R*,2*S*)-**20**, 86% ee] by using a chiral BINAP ligand.[4]

To study the ability of axially chiral ligands without a carbon centred chirality, we next synthesized ligand (a*R*)-**9** with two methyl groups in the neighbourhood of the N-atoms of the ligands ($R_1 = R_2 = Me$). The application of ligand (a*R*)-**9** in the same catalytic process preferentially led to the stereoselective formation of *cis*-(1*S*,2*R*)-**20** with 61% ee. It should also be noted that not only ligand

Table 1. Enantioselective cyclopropanation of styrene **18** with ethyl diazoacetate **19** catalyzed by transition-metal complexes **II**[a]

Ligand	Yield (%)[b]	Ratio[c] of *trans*/*cis*	% ee[c] (config)[d]	
			trans	*cis*
(a*R*)-**9**	43	38/62	56 (1*S*,2*S*)	61 (1*S*,2*R*)
(a*S*,*S*,*S*)-**14**	44	45/55	10 (1*R*,2*R*)	56 (1*R*,2*S*)
(a*S*,*S*,*S*)-**15**	44	49/51	60 (1*R*,2*R*)	83 (1*R*,2*S*)
(a*R*,*S*,*S*)-**16**	42	54/46	54 (1*R*,2*R*)	28 (1*R*,2*S*)
(a*R*,*S*,*S*)-**17**	41	—	—	—

[a] Styrene (4.7 mmol), ethyl diazoacetate (1.9 mmol), [Cu(I)OTf(C_6H_6)$_{0.5}$] (1 mol %), ligand (4–10 mol %) in chloroform (4 ml) at room temperature for 24 h.

[b] Isolated yield of a mixture of *trans*- and *cis*-**20**.

[c] Determined by GC with FS-Hydrodex-β-3P.

[d] By comparison of their specific rotation with the one reported for *trans*- and *cis*-**20**.

(a*R*)-**9**, but also ligands (a*S*,*S*,*S*)-**14** and (a*S*,*S*,*S*)-**15** in the same catalytic process led preferentially to the stereoselective formation of *cis*- rather than *trans*-cyclopropanes, although with different absolute stereochemistry (Table 1).

The specific rotations for the two stereoisomers **20** are reported as follows: *cis*-(1*S*,2*R*)-**20** (99% ee): $[\alpha]_D = +18.6$ (*c* 1.01 g/100 ml, $CHCl_3$), *trans*-(1*S*,2*S*)-**20** (99% ee): $[\alpha]_D = +296$ (*c* 0.88 g/100 ml, $CHCl_3$).[5]

3. Experimental

3.1. General remarks

All solvents were dried and purified by standard literature methods prior to use. Melting points were determined on a BÜCHI SMP-20 apparatus. IR spectra (film or KBr) were measured with a FT-IR-Spectrometer NICOLET 510 P instrument. Mass spectra were recorded with a FINNIGAN MAT 8200 apparatus. Elemental analysis was carried out by the Perkin–Elmer Elemental Analyser 2400, Reactions were monitored with Merck TLC aluminium sheets (Kieselgel 60 F_{254}) and preparative chromatography was carried out with silica gel 60 (70–230 mesh ASTM). ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were acquired on a Bruker AMX 500 spectrometer in $CDCl_3$, with TMS as the internal standard.

3.1.1. 3,3′,4,4′-Tetra-*O*-benzyl-5,5′-di-*C*-benzylellagic acid 2. A stirred suspension of ellagic acid (10 g, 0.033 mol), potassium carbonate (150 g, 1.125 mol) and benzyl chloride (250 ml, 2.14 mol) in water (430 ml) were refluxed for 15 h. The reaction mixture was then cooled down to room temperature. The organic layer were separated and the products extracted from the organic layer with dichloromethane and dried over Na_2SO_4. After filtration of Na_2SO_4, the solvent was evaporated and the crude product was obtained as a dark red oil. Overnight, colourless needles were formed from this oil, which were separated and washed with acetone and dried in vacuum to give colourless needles (8.36 g, 30%), mp 239 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 4.78 (s, 4H, RCH_2Ph), 5.02 (s, 4H, OCH_2Ph), 5.5 (s, 4H, OCH_2Ph), 7.16–7.53 (m, 30Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 32.18 (t, R*C*H$_2$Ph), 76.06, 76.17 (t, O*C*H$_2$Ph), 111.67 (s, biaryl-*C*-1, biaryl-*C*-1′), 116.28 (s, biaryl-*C*-6, biaryl-*C*-6′), 125.85, 127.69, 128.21, 128.39, 128.48, 128.51, 128.53, 128.65, 128.76, 128.85 (d, Ar–*C*), 135.96 (s, biaryl-*C*-5, biaryl-*C*-5′), 136.35, 136.69, 140.33, 141.16 (s, biaryl-*C*-3, biaryl-*C*-3′), 144.27 (s, biaryl-*C*-2, biaryl-*C*-2′), 152.64 (s, biaryl-*C*-4, biaryl-*C*-4′), 157.21 (s, *C*–lactone). IR (KBr): ν (cm^{-1}): 3064, 3032, 2934, 2874, 1748, 1253, 1096. $C_{56}H_{42}O_8$ (842.928): calcd C, 79.79; H, 5.02; found C, 79.39; H, 4.90.

3.1.2. Dibenzyl 2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-1,1′-diphenyl-6,6′-dicarboxylate *rac*-3. A stirred suspension of 3,3′,4,4′-tetra-*O*-benzyl-5,5′-di-*C*-benzylellagic acid **2** (5.0 g, 5.93 mmol), potassium carbonate (10 g, 0.075 mol) and benzyl chloride (50 ml, 0.43 mol) were refluxed for 1 h. At ca. 100 °C, the reaction mixture suddenly became red. The crude product was extracted with dichloromethane and dried over Na_2SO_4. After filtration of Na_2SO_4, the solvent was first evaporated. After the evaporation of excess BnCl under a high vacuum, the crude product was obtained, which was recrystallized from ethanol to give the racemic mixture *rac*-**3** as colourless crystals (5.1 g, 70%), mp 108 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 4.18–4.25 (dd, 4H, J = 15.4 Hz, J = 20.7 Hz, CH_2Ph, ester), 4.73–4.99 (m, 14H, OCH_2Ph, RCH_2Ph), 5.01 (d, 2H, J = 10.4 Hz, OCH_2Ph), 6.92–7.35 (m, 50 Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 32.98 (t, R*C*H$_2$Ph), 67.12 (t, *C*H$_2$Ph), 73.82, 75.45, 75.49 (t, O*C*H$_2$Ph), 125.72 (d, Ar–*C*), 126.8 (s, biaryl-*C*-1, biaryl-*C*-1′), 127.05, 127.23, 127.97, 128.0, 128.04, 128.07, 128.26, 128.28, 128.32, 128.36, 128.4, 128.71, 128.76 (d, Ar–*C*), 129.16 (s, biaryl-*C*-6, biaryl-*C*-6′), 129.68 (s, biaryl-*C*-5, biaryl-*C*-5′), 135.18, 137.2, 137.25, 138.16, 141.02 (s, Ar–*C*), 147.6 (s, biaryl-*C*-3, biaryl-*C*-3′), 150.32 (s, biaryl-*C*-2, biaryl-*C*-2′), 151.51 (s, biaryl-*C*-4, biaryl-*C*-4′), 167.37 (s, *C*OOBn). IR (KBr): ν (cm^{-1}): 3065, 3035, 2945, 2884, 1752, 1255, 1195. MS (FAB/NBA): m/z (%) = 1240.4 (3) [M]$^+$. $C_{84}H_{70}O_{10}$ (1239.5): calcd C, 81.4; H, 5.69; found C, 81.35; H, 5.29.

3.1.3. *rac*-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-diphenic acid 4. Dibenzylester **3** (5.0 g, 4.0 mmol) was dissolved in ethanol under heating and treated with a saturated solution of potassium hydroxide in water (60 ml). The reaction mixture was then stirred at reflux for 15 h. Approximately 2/3 of the solvent was removed and the residue was treated with 3 N HCl at 0 °C. The reaction mixture was then diluted with water and the product was extracted with dichloromethane, dried over Na_2SO_4. After filtration of Na_2SO_4, the solvent was evaporated to give racemic mixture *rac*-**4** as a yellow solid (4.2 g, 98%), mp 109 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) = 4.06 (s, 4H, RCH_2Ph), 4.62–5.04 (m, 12H, OCH_2Ph), 6.85–7.34 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 33.66 (t, R*C*H$_2$Ph), 74.54, 75.04, 75.27 (t, O*C*H$_2$Ph), 124.5 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.62, 126.62, 126.98 (d, Ar–*C*), 127.14 (s, biaryl-*C*-6, biaryl-*C*-6′), 127.58, 127.81, 127.98, 128.09, 128.14, 128.22, 128.26, 128.34, 128.54, 128.67 (d, Ar–*C*), 137.14, 137.34, 137.87, 141.66 (s, Ar–*C*), 145.95 (s, biaryl-*C*-3, biaryl-*C*-3′), 149.26 (s, biaryl-*C*-2, biaryl-*C*-

2′), 151.4 (s, biaryl-*C*-4, biaryl-*C*-4′), 174.08 (s, *C*OOH). IR (KBr): ν (cm^{-1}): 3607, 3431, 3059, 3025, 2938, 2873, 1686, 1561, 1364, 1093. MS (FAB/NBA): m/z (%) = 1059.8 (27) [M^+]. $C_{70}H_{58}O_{10}$ (1059.204): calcd C, 79.38; H, 5.52; found C, 75.43; H, 5.23.

3.1.4. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-diphenic acid 4. A suspension of *rac*-**4** (5.0 g, 4.0 mmol) and cinchonin (2.95 g, 10.0 mmol) in dried ethanol (150 ml) were stirred at reflux, until a clear solution were formed. After cooling down the reaction mixture to room temperature, colourless needles were obtained after 12 h, which were then separated by filtration. After recrystallization of the separated crystals from dry ethanol, the (a*R*)-diastereomeric salt was obtained in a stereochemically pure form. The hydrolysis of the obtained (a*R*)-diastereomeric salt with 1 M H_2SO_4 at 0 °C followed by the extraction of the resulting product with dichloromethane gave (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-diphenic acid **4** as a yellow solid (2 g, 47%). $[\alpha]_D = -66$ (*c* 1 g/100 ml, $CHCl_3$).

3.2. General procedure I for the preparation of β-hydroxylamides

A solution of biaryldicarboxylic acid and Et_3N in dried dichloromethane was treated with thionyl chloride at 0 °C and the solution was then stirred for 3 h at room temperature. Both, the solvent and the excess of thionyl chloride evaporated at room temperature, first dichloromethane on a rotary evaporator and then the excess of thionyl chloride on an oil pump at a high vacuum. The resulting dichloride was resolved in dried dichloromethane and treated dropwise with a solution of the chiral amine in dried dichloromethane at 0 °C.

After adding Et_3N in dried dichloromethane, the reaction mixture was stirred for 5 h at room temperature. The reaction mixture was diluted with water and the product was extracted three times with dichloromethane. The organic phases were then washed once with a saturated solution of NaCl in water, dried over Na_2SO_4. After filtration, the solvent was evaporated and the resulting product was purified by chromatography on silica gel.

3.2.1. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1,1-dimethyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl 8. This compound was prepared by general procedure I from (a*R*)-**4** (0.5 g, 0.47 mmol) and thionyl chloride (300 μl, 4.14 mmol) and amine **5** to give after chromatographic purification, (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1,1-dimethyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl **8** as a yellow solid (0.51 g, 90%), mp 53 °C. $[\alpha]_D = -19.6$ (*c* 1 g/100 ml, $CHCl_3$). ^1H NMR ($CDCl_3$): δ (ppm) = 0.82 (s, 9H, CH_3), 0.86 (s, 3H, CH_3), 3.17–3.24 (dd, 4H, $J = 11.6$ Hz, $J = 18.2$ Hz, *H*-2), 4.1 (d, 2H, $J = 15.7$ Hz, RCH_2Ph), 4.32 (d, 2H, $J = 15.7$ Hz, RCH_2Ph), 4.95–5.19 (m, 12H, OCH_2Ph), 7.01–7.38 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 23.31, 23.51 (q, *C*H_3), 32.69 (t, R*C*H_2Ph), 56.64 (s, *C*-1), 70.38 (*C*-2), 75.05, 75.48, 75.66 (t, O*C*H_2Ph), 124.08 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.89, 127.52, 127.71 (d, Ar–*C*), 127.79 (s, biaryl-*C*-6, biaryl-*C*-6′), 128.06 (s, biaryl-*C*-5, biaryl-*C*-5′), 128.15, 128.22, 128.27, 128.34, 128.39, 128.46, 128.48 (d, Ar–*C*), 135.11, 136.91, 136.98, 137.88 (s, Ar–*C*), 140.69 (s, biaryl-*C*-3, biaryl-*C*-3′), 146.82 (s, biaryl-*C*-2, biaryl-*C*-2′), 152.34 (s, biaryl-*C*-4, biaryl-*C*-4′), 169.32 (s, *C*ONR). IR (KBr): ν (cm^{-1}): 3405, 3215, 3053, 2960, 1645, 1253. MS (FAB/NBA): m/z (%) = 1202.2 (50) [M^+]. $C_{78}H_{76}N_2O_{10}$ (1201.445): calcd C, 77.98; H, 6.38; N, 2.33; found C, 77.99; H, 6.24; N, 2.19.

3.2.2. (a*S*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*iso*-propyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl 10. This compound was prepared by general procedure I from *rac*-**4** (0.5 g, 0.47 mmol), thionyl chloride (300 μl, 4.14 mmol) and chiral amine (*S*)-**6** to give, after chromatographic purification, (a*S*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*iso*-propyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl **10** as a yellow solid (0.26 g, 45%), mp 51 °C. $[\alpha]_D = +1.5$ (*c* 1 g/100 ml, $CHCl_3$). ^1H NMR ($CDCl_3$): δ (ppm) = 0.58–0.69 (dd, 12H, $J = 16$ Hz, $J = 6.7$ Hz, CH_3), 1.49–1.66 (m, 2H, *i*-Pr), 2.46 (2H, RO*H*), 3.28–3.39 (m, 4H, *H*-2), 3.45–3.57 (m, 2H, *H*-1), 4.21 (d, 2H, $J = 15.8$ Hz, RCH_2Ph), 4.35 (d, 2H, $J = 15.8$ Hz, RCH_2Ph), 4.96–5.28 (m, 12H, OCH_2Ph), 7.11–7.55 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 19.17, 19.43 (q, *C*H_3), 29.21 (d, *C*–*i*-Pr), 33.8 (t, R*C*H_2Ph), 58.68 (d, *C*-1), 63.98 (t, *C*-2), 75.55, 75.58 (t, O*C*H_2Ph), 124.57 (s, biaryl-*C*-1, biaryl-*C*-1′), 126.42, 128.17, 128.28, 128.47, 128.67, 128.8, 128.87, 128.96 (d, Ar–*C*), 137.34, 137.47, 138.1, 141.23 (s, Ar–*C*), 147.28 (s, biaryl-*C*-3, biaryl-*C*-3′), 149.63 (s, biaryl-*C*-2, biaryl-*C*-2′), 152.69 (s, biaryl-*C*-4, biaryl-*C*-4′), 169.98 (*C*ONR). $C_{80}H_{80}N_2O_{10}$ (1229.499): calcd C, 78.15; H, 6.56; N, 2.28; found C, 77.62; H, 6.25; N, 2.14.

3.2.3. (a*S*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*tert*-butyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl 11. This compound was prepared by general procedure I from *rac*-**4** (1.0 g, 0.94 mmol), thionyl chloride (300 μl, 4.14 mmol) and chiral amine (*S*)-**7** to give, after chromatographic purification, (a*S*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*tert*-butyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl **11** as a yellow solid (0.53 g, 45%), mp 58 °C. $[\alpha]_D = +16.5$ (*c* 1 g/100 ml, $CHCl_3$). ^1H NMR ($CDCl_3$): δ (ppm) = 0.59 (s, 18H, CH_3), 3.34–3.37 (dd, 2H, $J = 6.3$ Hz, $J = 11.8$ Hz, *H*-2), 3.44–3.47 (dd, 2H, $J = 3.1$ Hz, $J = 11.8$ Hz, *H*-2), 3.63–3.67 (m, 2H, *H*-1), 4.12 (d, 2H, $J = 16.1$ Hz, RCH_2Ph), 4.31 (d, 2H, $J = 16.1$ Hz, RCH_2Ph), 4.93–4.99 (m, 6H, OCH_2Ph), 5.12–5.17 (m, 6H, OCH_2Ph), 7.1–7.36 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 26.7 (q, *C*H_3), 33.61 (t, R*C*H_2Ph), 60.92 (d, *C*-1), 62.95 (t, *C*-2), 74.83, 75.17, 75.32 (t, O*C*H_2Ph), 124.11 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.96, 127.78, 127.94, 127.98, 128.02, 128.18, 128.32, 128.34, 128.48 (d, Ar–*C*), 136.04, 136.92, 137.07, 137.66 (s, Ar–*C*), 140.81 (s, biaryl-*C*-3, biaryl-*C*-3′), 146.8 (s, biaryl-*C*-2, biaryl-*C*-2′), 152.27 (s, biaryl-*C*-4, biaryl-*C*-4′), 169.66 (s, *C*ONR). IR (KBr): ν (cm^{-1}): 3405, 3215, 3053, 2960, 1645, 1253. MS (FAB/NBA): m/z (%) = 1258.5 (5) [M^+]. $C_{82}H_{84}N_2O_{10}$ (1257.552): calcd C, 78.32; H, 6.73; N, 2.23; found C, 77.99; H, 6.73; N, 2.16.

3.2.4. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*iso*-propyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl 12. This compound was prepared by general procedure I from *rac*-**4** (0.5 g, 0.47 mmol), thionyl chloride (300 μl, 4.14 mmol) and chiral amine (*S*)-**6** to give after chromatographic purification (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*iso*-propyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl **12** as a yellow oil (0.26 g, 45%). $[\alpha]_D = -45.8$ (*c* 1 g/100 ml, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.58–0.69 (dd, 12H, $J = 16$ Hz, $J = 6.7$ Hz, C*H*$_3$), 1.49–1.66 (m, 2H, *i*-Pr), 2.46 (2H, RO*H*), 3.28–3.39 (m, 4H, *H*-2), 3.45–3.57 (m, 2H, *H*-1), 4.21 (d, 2H, $J = 15.8$ Hz, RC*H*$_2$Ph), 4.35 (d, 2H, $J = 15.8$ Hz, RC*H*$_2$Ph), 4.96–5.28 (m, 12H, OC*H*$_2$Ph), 7.11–7.55 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 19.17, 19.43 (q, *C*H$_3$), 29.21 (d, *C*–*i*-Pr), 33.8 (t, R*C*H$_2$Ph), 58.68 (d, *C*-1), 63.98 (t, *C*-2), 75.55, 75.58 (t, O*C*H$_2$Ph), 124.57 (s, biaryl-*C*-1, biaryl-*C*-1′), 126.42, 128.17, 128.28, 128.47, 128.67, 128.8, 128.87, 128.96 (d, Ar–*C*), 137.34, 137.47, 138.1, 141.23 (s, Ar–*C*), 147.28 (s, biaryl-*C*-3, biaryl-*C*-3′), 149.63 (s, biaryl-*C*-2, biaryl-*C*-2′), 152.69 (s, biaryl-*C*-4, biaryl-*C*-4′), 169.98 (*C*ONR). $C_{80}H_{80}N_2O_{10}$ (1229.499): calcd C, 78.15; H, 6.56; N, 2.28; found C, 77.62; H, 6.25; N, 2.14.

3.2.5. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*tert*-butyl-2-hydroxyethyl)carboxamido]-1,1′-biphenyl 13. This compound was prepared by general procedure I from *rac*-**4** (1.0 g, 0.94 mmol), thionyl chloride (300 μl, 4.14 mmol) and chiral amine (*S*)-**7** to give after chromatographic purification (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[*N*-(1*S*)-(1-*tert*-butyl-2-hydroxy-ethyl)carboxamido]-1,1′-biphenyl **13** as a yellow solid (0.53 g, 45%), mp 57 °C. $[\alpha]_D = -57$ (*c* 1 g/100 ml, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.59 (s, 18H, C*H*$_3$), 3.34–3.37 (dd, 2H, $J = 6.3$ Hz, $J = 11.8$ Hz, *H*-2), 3.44–3.47 (dd, 2H, $J = 3.1$ Hz, $J = 11.8$ Hz, *H*-2), 3.63–3.67 (m, 2H, *H*-1), 4.12 (d, 2H, $J = 16.1$ Hz, RC*H*$_2$Ph), 4.31 (d, 2H, $J = 16.1$ Hz, RC*H*$_2$Ph), 4.93–4.99 (m, 6H, OC*H*$_2$Ph), 5.12–5.17 (m, 6H, OC*H*$_2$Ph), 7.1–7.36 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 26.7 (q, *C*H$_3$), 33.61 (t, R*C*H$_2$Ph), 60.92 (d, *C*-1), 62.95 (t, *C*-2), 74.83, 75.17, 75.32 (t, O*C*H$_2$Ph), 124.11 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.96, 127.78, 127.94, 127.98, 128.02, 128.18, 128.32, 128.34, 128.48 (d, Ar–*C*), 136.04, 136.92, 137.07, 137.66 (s, Ar–*C*), 140.81 (s, biaryl-*C*-3, biaryl-*C*-3′), 146.8 (s, biaryl-*C*-2, biaryl-*C*-2′), 152.27 (s, biaryl-*C*-4, biaryl-*C*-4′), 169.66 (s, *C*ONR). IR (KBr): ν (cm^{-1}): 3405, 3215, 3053, 2960, 1645, 1253. MS (FAB/NBA): *m*/*z* (%) = 1258.5 (5) [M$^+$]. $C_{82}H_{84}N_2O_{10}$ (1257.552): calcd C, 78.32; H, 6.73; N, 2.23; found C, 77.72; H, 6.63; N, 2.09.

3.3. General procedure II for the preparation of chiral ligands

A solution of carboxamido-1,1′-biphenyl and Et_3N in dried dichloromethane was treated with mesyl chloride at 0 °C. The reaction mixture was then warmed up to room temperature and stirred for 3 h. After dilution of the reaction mixture with water, the products were extracted three times with dichloromethane. The organic phases were then dried over Na_2SO_4. After filtration, the solvent was evaporated and the resulting products were purified by chromatography on silica gel.

3.3.1. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis(4,4-dimethyloxazolin-2-yl)-1,1′-biphenyl 9. This compound was prepared by general procedure II from (a*R*)-**8** (0.1 g, 0.083 mmol) and mesyl chloride (200 ml, 2.1 mmol) and Et_3N (3 ml). After chromatographic purification, the (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis(4,4-dimethyloxazolin-2-yl)-1,1′-biphenyl **9** was obtained as a yellow oil (0.087 g, 90%). $[\alpha]_D = +21.7$ (*c* 1 g/100 ml, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.92 (s, 6H, C*H*$_3$), 1.04 (s, 6H, C*H*$_3$), 3.58 (d, 2H, $J = 7.7$ Hz, *H*-5), 3.79 (d, 2H, $J = 7.7$ Hz, *H*-5), 4.28 (2H, $J = 15.4$ Hz, RC*H*$_2$Ph), 4.41 (d, 2H, $J = 15.4$ Hz, RC*H*$_2$Ph), 4.94–5.01 (m, 6H, OC*H*$_2$Ph), 5.05 (d, 2H, $J = 10.7$ Hz, OC*H*$_2$Ph), 5.22 (d, 2H, $J = 11.2$ Hz, OC*H*$_2$Ph), 5.42 (d, 2H, $J = 11.2$ Hz, OC*H*$_2$Ph), 7.06–7.42 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 27.71, 27.88 (q, *C*H$_3$), 33.09 (t, R*C*H$_2$Ph), 67.52 (s, *C*-4), 73.72, 75.52, 75.69 (t, O*C*H$_2$Ph), 78.07 (t, *C*-5), 125.58 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.43, 127.08, 127.38, 127.95, 127.96, 128.1, 128.31, 128.36, 128.55, 128.6, 128.67, 128.89, 129.42 (d, Ar–*C*), 137.45, 137.52, 138.86, 141.29 (s, Ar–*C*), 147.15 (s, biaryl-*C*-3, biaryl-*C*-3′), 150.73 (s, biaryl-*C*-2, biaryl-*C*-2′), 151.42 (s, biaryl-*C*-4, biaryl-*C*-4′), 160.11 (s, *C*NO). IR (KBr): ν (cm^{-1}): 3058, 2975, 1650, 1356, 1098. $C_{78}H_{72}N_2O_8$ (1165.415): calcd C, 80.39; H, 6.23; N, 2.40; found C, 79.66; H, 6.12; N, 2.26.

3.3.2. (a*S*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*iso*-propyloxazolin-2-yl)]-1,1′-biphenyl 14. This compound was prepared by general procedure II from (a*S*,*S*,*S*)-**10** (0.15 g, 0.122 mmol), mesyl chloride (250 μl, 2.6 mmol) and Et_3N (4 ml). After chromatographic purification, the (a*S*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*iso*-propyloxazolin-2-yl)]-1,1′-biphenyl **14** was obtained as a yellow oil (0.138 g, 95%). $[\alpha]_D = -51$ (*c* 1 g/100 ml, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.77 (d, 6H, $J = 6.6$ Hz, C*H*$_3$), 0.86 (d, 6H, $J = 6.6$ Hz, C*H*$_3$), 1.44–1.46 (m, 2H, *i*-Pr), 3.55–3.62 (m, 4H, *H*-5), 4.04–4.09 (m, 2H, *H*-4), 4.21 (d, 2H, $J = 15.3$ Hz, RC*H*$_2$Ph), 4.31 (d, 2H, $J = 15.3$ Hz, RC*H*$_2$Ph), 4.9 (d, 2H, $J = 10.6$ Hz, OC*H*$_2$Ph), 4.96–4.99 (dd, 4H, $J = 4$ Hz, $J = 10.6$ Hz, OC*H*$_2$Ph), 5.1 (d, 2H, $J = 10.8$ Hz, OC*H*$_2$Ph), 5.2 (d, 2H, $J = 11.3$ Hz, OC*H*$_2$Ph), 5.35 (d, 2H, $J = 11.3$ Hz, OC*H*$_2$Ph), 7.08–7.43 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 18.93, 19.53 (q, *C*H$_3$), 32.75 (d, *C*–*i*-Pr), 33.54 (t, R*C*H$_2$Ph), 69.89 (t, *C*-5), 73.65 (d, *C*-4), 73.78, 75.39, 75.52 (t, O*C*H$_2$Ph), 125.67 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.39, 127.12, 127.41, 127.84, 127.91, 127.96, 128.06, 128.18, 128.31, 128.35, 128.52, 128.57, 128.7 (d, Ar–*C*), 129.4, 129.68, 137.49, 137.55, 138.83, 141.69 (s, Ar–*C*), 147.14 (s, biaryl-*C*-3, biaryl-*C*-3′), 150.62 (s, biaryl-*C*-2, biaryl-*C*-2′), 151.09 (s, biaryl-*C*-4, biaryl-*C*-4′), 161.62 (s, *C*NO). MS (FAB/NBA): *m*/*z* (%) = 1194.3 (55) [M$^+$]. $C_{80}H_{76}N_2O_8$ (1193.468): calcd C, 80.51; H, 6.42; N, 2.35; found C, 79.33; H, 5.47; N, 2.27.

3.3.3. (a*S*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*tert*-butyloxazolin-2-yl)]-1,1′-biphenyl 15. This compound was prepared by general procedure II from (a*S*,*S*,*S*)-**11** (0.21 g, 0.17 mmol), mesyl chloride (250 μl,

2.6 mmol) and Et_3N (4 ml). After chromatographic purification, the (a*S*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*tert*-butyloxazolin-2-yl)]-1,1′-biphenyl **15** was obtained as a colourless solid (0.2 g, 98%), mp 105 °C. $[\alpha]_D = -58$ (*c* 1 g/100 ml, $CHCl_3$). ^1H NMR ($CDCl_3$): δ (ppm) = 0.7 (s, 18H, C*H*$_3$), 3.62 (t, 2H, *J* = 9.8 Hz, *H*-5), 3.69 (t, 2H, *J* = 9.6 Hz, *H*-5), 3.96–3.99 (dd, 2H, *J* = 8.1 Hz, *J* = 9.9 Hz, *H*-4), 4.15 (d, 2H, *J* = 15.4 Hz, RC*H*$_2$Ph), 4.27 (d, 2H, *J* = 15.4 Hz, RC*H*$_2$Ph), 4.82 (d, 2H, *J* = 10.6 Hz, OC*H*$_2$Ph), 4.92–4.95 (dd, 4H, *J* = 2.4 Hz, *J* = 10.7 Hz, OC*H*$_2$Ph), 5.07 (d, 2H, *J* = 10.7 Hz, OC*H*$_2$Ph), 5.19 (d, 2H, *J* = 11.3 Hz, OC*H*$_2$Ph), 5.35 (d, 2H, *J* = 11.3 Hz, OC*H*$_2$Ph), 6.99–7.38 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 25.99 (q, *C*H$_3$), 33.04 (s, *C*–*t*-Bu), 33.54 (t, R*C*H$_2$Ph), 67.56 (t, *C*-5), 73.72, 75.37, 75.59 (t, O*C*H$_2$Ph), 76.93 (d, *C*-4), 125.74 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.37, 127.05, 127.33, 127.85, 127.93, 128.26, 128.29, 128.32, 128.58 (d, Ar–*C*), 129.47, 129.54, 137.46, 137.56, 138.86, 141.59 (s, Ar–*C*), 147.15 (s, biaryl-*C*-3, biaryl-*C*-3′), 150.72 (s, biaryl-*C*-2, biaryl-*C*-2′), 151.15 (s, biaryl-*C*-4, biaryl-*C*-4′), 161.66 (s, *C*NO). MS (FAB/NBA): *m*/*z* (%) = 1222.6 (70) [M^+]. $C_{82}H_{80}N_2O_8$ (1221.521): calcd C, 80.63; H, 6.60; N, 2.29; found C, 80.13; H, 6.06; N, 1.79.

3.3.4. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*iso*-propyloxazolin-2-yl)]-1,1′-biphenyl 16. This compound was prepared by general procedure II from (a*R*,*S*,*S*)-**12** (0.15 g, 0.122 mmol), mesyl chloride (250 μl, 2.6 mmol) and Et_3N (4 ml). After chromatographic purification, (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*iso*-propyloxazolin-2-yl)]-1,1′-biphenyl **16** was obtained as a yellow oil (0.138 g, 95%). $[\alpha]_D = +35.5$ (*c* 1 g/100 ml, $CHCl_3$). ^1H NMR ($CDCl_3$): δ (ppm) = 0.78–0.81 (t, 12H, C*H*$_3$), 1.38–1.53 (m, 2H, *i*-Pr), 3.68–3.93 (m, 4H, *H*-5), 4.12–4.21 (m, 2H, *H*-4), 4.24–4.44 (dd, 4H, *J* = 15 Hz, *J* = 23.7 Hz, RC*H*$_2$Ph), 4.87–5.15 (m, 8H, OC*H*$_2$Ph), 5.22 (d, 2H, *J* = 10.9 Hz, OC*H*$_2$Ph), 5.45 (d, 2H, *J* = 10.9 Hz, OC*H*$_2$Ph), 7.04–7.48 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 19.57, 20.2 (q, *C*H$_3$), 33.6 (d, *C*–*i*-Pr), 34.07 (t, R*C*H$_2$Ph), 70.43 (t, *C*-5), 73.87 (d, *C*-4), 74.25, 75.92, 76.05 (t, O*C*H$_2$Ph), 126.21 (s, biaryl-*C*-1, biaryl-*C*-1′), 125.98, 127.62, 128.06, 128.4, 128.68, 128.81, 129.09, 129.24 (d, Ar–*C*), 129.68, 130.19, 137.91, 138.01, 139.04, 141.82 (s, Ar–*C*), 147.87 (s, biaryl-*C*-3, biaryl-*C*-3′), 151.21 (s, biaryl-*C*-2, biaryl-*C*-2′), 151.94 (s, biaryl-*C*-4, biaryl-*C*-4′), 162.13 (s, *C*NO). MS (FAB/NBA): *m*/*z* (%) = 1194.3 (55) [M^+]. $C_{80}H_{76}N_2O_8$ (1193.468): calcd C, 80.51; H, 6.42; N, 2.35; found C, 79.33; H, 5.47; N, 2.27.

3.3.5. (a*R*)-2,2′,3,3′,4,4′-Hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*tert*-butyloxazolin-2-yl)]-1,1′-biphenyl 17. This compound was prepared by general procedure II from (a*R*,*S*,*S*)-**13** (0.21 g, 0.17 mmol), mesyl chloride (250 μl, 2.6 mmol) and Et_3N (4 ml). After chromatographic purification, (a*R*)-2,2′,3,3′,4,4′-hexabenzyloxy-5,5′-dibenzyl-6,6′-bis[(4*S*)-(*tert*-butyloxazolin-2-yl)]-1,1′-biphenyl **17** was obtained as a yellow solid (0.2 g, 98%), mp 49 °C. $[\alpha]_D = +36.5$ (*c* 1 g/100 ml, $CHCl_3$). ^1H NMR ($CDCl_3$): δ (ppm) = 0.7 (s, 18H, C*H*$_3$), 3.7 (t, 2H, *J* = 10.3 Hz, *H*-5), 3.88 (t, 2H, *J* = 9.1 Hz, *H*-5), 4.02–4.06 (dd, 2H, *J* = 8.3 Hz, *J* = 10.1 Hz, *H*-4), 4.22 (d, 2H, *J* = 15.2 Hz, RC*H*$_2$Ph), 4.28 (d, 2H, *J* = 15.2 Hz, RC*H*$_2$Ph), 4.84 (d, 2H, *J* = 10.6 Hz, OC*H*$_2$Ph), 4.91 (d, 2H, *J* = 10.7 Hz, OC*H*$_2$Ph), 4.99 (d, 2H, *J* = 10.6 Hz, OC*H*$_2$Ph), 5.05 (d, 2H, *J* = 10.7 Hz, OC*H*$_2$Ph), 5.15 (d, 2H, *J* = 11 Hz, OC*H*$_2$Ph), 5.41 (d, 2H, *J* = 11 Hz, OC*H*$_2$Ph), 6.99–7.38 (m, 40H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 26.26 (q, *C*H$_3$), 33.05 (s, *C*–*t*-Bu), 33.57 (t, R*C*H$_2$Ph), 67.82 (t, *C*-5), 73.75, 75.33, 75.65 (t, O*C*H$_2$Ph), 76.71 (d, *C*-4), 125.43, 127.09, 127.52, 127.86, 127.91, 127.93, 128.2, 128.31, 128.65, 128.81 (d, Ar–*C*), 129.81, 137.45, 137.63, 138.64 (s, Ar–*C*), 141.23 (s, biaryl-*C*-3, biaryl-*C*-3′), 150.78 (s, biaryl-*C*-2, biaryl-*C*-2′), 151.53 (s, biaryl-*C*-4, biaryl-*C*-4′), 161.66 (s, *C*NO). MS (FAB/NBA): *m*/*z* (%) = 1222.5 (40) [M^+]. $C_{82}H_{80}N_2O_8$ (1221.521): calcd C, 80.63; H, 6.60; N, 2.29; found C, 79.86; H, 6.49; N, 2.21.

3.4. General procedure III for the preparation of the *cis*- and the *trans*-cyclopropanes

Cyclopropanes were prepared from styrene **18** (4.7 mmol), ethyl diazoacetate **19** (1.9 mmol), [Cu(I)OTf(C_6H_6)$_{0.5}$] (1 mol %) and chiral biarylligand (4–10 mol %) in chloroform (4 ml) at room temperature. The reaction mixture was then stirred for 24 h at room temperature to give a mixture of *trans*- and *cis*-**20** as a yellow oil after purification of the crude products on silica gel. The composition of the obtained products was analyzed by GC on a chiral column with FS-Hydrodex-β-3P.

3.4.1. Compound *trans*-20. ^1H NMR ($CDCl_3$): δ (ppm) = 1.34 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 1.3–1.38 (m, 1H, *H*-3), 1.61–1.7 (m, 1H, *H*-3), 1.92–2.0 (m, 1H, *H*-1), 2.53–2.63 (m, 1H, *H*-2), 4.15–4.28 (dd, 2H, *J* = 7.1 Hz, *J* = 14.3 Hz, C*H*$_2$), 7.13–7.38 (m, 5H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 14.71 (q, *C*H$_3$), 17.51 (t, *C*-3), 24.63, 26.61 (d, *C*-1, *C*-2), 61.14 (t, *C*H$_2$), 126.59, 126.9, 128.9 (d, Ar–*C*), 140.56 (s, Ar–*C*), 173.85 (s, *C*OOEt).

3.4.2. Compound *cis*-20. ^1H NMR ($CDCl_3$): δ (ppm) = 1.01 (t, *J* = 7.1 Hz, 3H, C*H*$_3$), 1.31–1.42 (m, 1H, *H*-3), 1.71–1.81 (m, 1H, *H*-3), 2.06–2.18 (m, 1H, *H*-1), 2.56–2.69 (m, 1H, *H*-2), 3.86–3.97 (dd, 2H, *J* = 7.1 Hz, *J* = 14.3 Hz, C*H*$_2$), 7.18–7.34 (m, 5H, Ar–*H*). ^{13}C NMR ($CDCl_3$): δ (ppm) = 11.5 (t, *C*H$_3$), 14.42 (q, *C*-3), 22.22, 25.86 (d, *C*-1, *C*-2), 60.56 (t, *C*H$_2$), 127.04, 128.28, 129.72 (d, Ar–*C*), 136.99 (s, Ar–*C*), 171.37 (s, *C*OOEt).

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