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4-Naphthyl-Substituted Bis(Oxazoline): a New, Easily Recoverable and Efficient Chiral Ligand in Asymmetric Catalysis of the Diels-Alder Reaction

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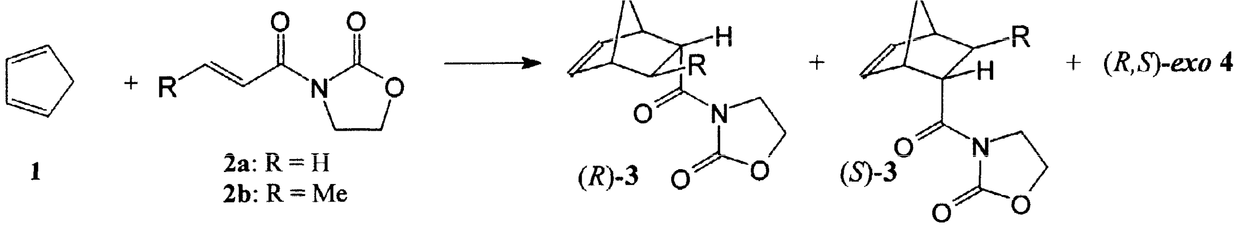
Abstract - 2,2-Bis{2-[(4*R*)-(2'-naphthyl)-1,3-oxazolinyl]}propane and its (4*S*) enantiomer were prepared starting from 2-vinylnaphthalene, following the Sharpless protocol, and were found to be optically pure (*ee* ≥ 99.5%) by hplc analysis. These new bis(oxazolines) are efficient chiral ligands in the asymmetric catalysis of the Diels-Alder reaction of *N*-alkenoyl-oxazolidin-2-one derivatives since *endo* cycloadducts are obtained with up to 94% *ee*. Different Lewis acids were tested, the best one being the Mg(II) cation derived from the corresponding triflate. A remarkable feature of such new chiral ligands is the low solubility in polar solvents, so that the chiral ligand can be easily recovered by a simple filtration. The recovered ligand can be directly reused in other asymmetric syntheses, without any further purification and, overall, without any drop in the induced enantioselectivities.

Introduction

The C_2-symmetric chiral bis(oxazolines) are very useful ligands in the catalysis of many reactions.[1] This kind of ligand has found extensive applications in the preparation of chiral complexes which give excellent results in the asymmetric catalysis of Diels-Alder (DA) cycloadditions.[1-19] The Lewis acid cores of such supramolecular catalysts were: Fe(II),[3,4] Cu(II),[5,14] Zn(II),[9-13] Ni(II),[11] Co(II),[11] Mn(II),[11] and Mg(II).[4,9,12,13,17-19]

In the previous papers of this series,[17-19] the effect of Mg(II)-bis(oxazoline) complexes as chiral catalysts in the DA reaction between cyclopentadiene (**1**) and *N*-alkenoyl-oxazolidin-2-ones (**2a,b**) was investigated, the magnesium cation being derived from the corresponding perchlorate (MP) or triflate (MT), Scheme 1.



Scheme 1

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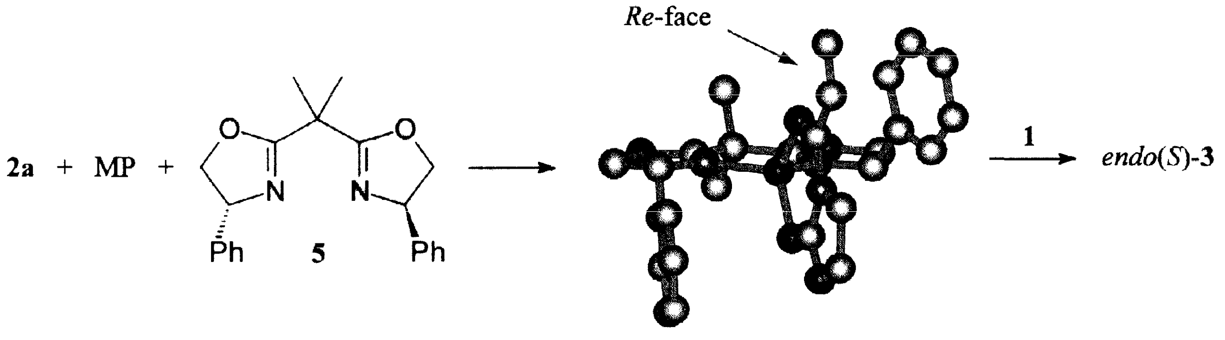
The structure of the reacting complexes can be either tetrahedral or octahedral, depending on the specific anion and, in the case of MP, on the eventually present auxiliary ligand.[19] The complex between **2a**, MP, and (4*R*)-phenyl-bis(oxazoline) (**5**) has a tetrahedral structure,[18] and the preferential attack of cyclopentadiene is from the less hindered *Re*-face of the coordinated dienophile, Scheme 2.



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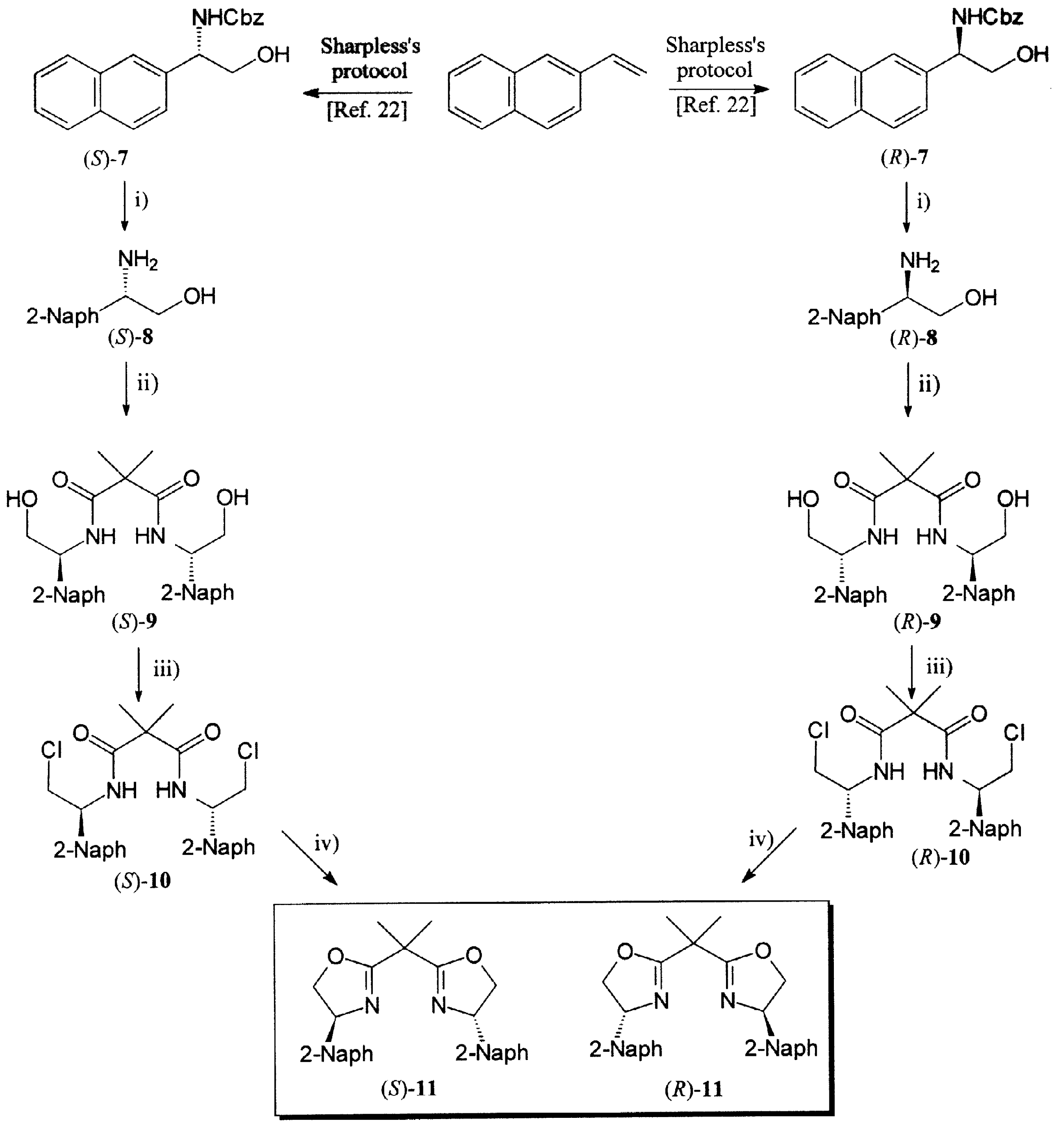
Scheme 2

In order to increase enantioselectivitiy, modifications of the chiral ligand **5** are required. The increase of the shielding of the *Si*-face by introducing hindering alkyl substituents is worthless.[18] An alternative possible modification is the substitution of the simple phenyl group on the C-4 of **5** with a more extended aromatic system.

Results

Synthesis of 4-(2-naphthyl)bis(oxazoline) chiral ligand 11. The starting idea was offered by a series of interesting papers by Sharpless on the catalytic asymmetric aminohydroxylation of olefins.[20-23] Among several examples, both enantiomers of *N*-benzyloxycarbonyl-2-amino-2-(2'-naphthyl)-ethanol (**7**) were prepared in good yields and excellent *ee* starting from 2-vinylnaphthalene.[22,24]

The complete reaction sequence to obtain the chiral bis(oxazolines) (*S*)-**11** and (*R*)-**11** is depicted in Scheme 3. The protected chiral amino ethanols (**7**) were prepared following the Sharpless protocol.[22] Deprotection by catalytic hydrogenation gave the chiral amino alcohols **8**; the reaction proceeds under standard conditions with quantitative yields affording **8** as white crystals. The amino alcohol was made to react with 2,2-dimethyl-malonic acid dichloride under usual conditions[25] to give in good yields the corresponding bis(hydroxy)amide **9**. The reaction of **9** with $SOCl_2$ (CH_2Cl_2, reflux) afforded with quantitative yield the corresponding bis(chloride) derivatives **10**, which, upon exposure to base, furnished the bis(oxazolines) **11** in good yields.



i) H_2, Pd-C, ethanol, quant.; ii) 2,2-dimethyl-malonic acid dichloride, CH_2Cl_2, Et_3N, 70%; iii) $SOCl_2$, CH_2Cl_2, Δ, quant.; iv) NaOH, EtOH/THF, Δ, 55%.

Scheme 3

The optical purity of each chiral bis(oxazoline) was determined by hplc analysis on a Chiralpak AD column® (*n*-hexane-*i*-propanol 8:2 as eluent; flow = 1.0 mL/min). This column discriminates the two enantiomeric ligands, the retention times being 8.4 and 55.4 min for the (*S*)- and (*R*)-enantiomers respectively. In each case the enantiomeric purity of **11** was found to be higher than 99.5%.

DA reaction between 1 and 2a,b catalyzed by (R)-11 - Lewis acid chiral complexes. The efficiency of **11** as a chiral ligand in the asymmetric catalysis of the DA reaction was tested on the cycloaddition between cyclopentadiene **1** and **2a,b** (Scheme 1). Mg(II) (from MP or MT) and Cu(II) triflate (CT) were tested as Lewis acid.

Dienophile **2a,b**, bis(oxazoline) **11**, and the inorganic salt in the ratio 10 : 1 : 1 were stirred in dichloromethane at ambient temperature for about 1 hour in a rubber septum sealed vial. The mixture was then cooled to the required temperature and, after 30 minutes, cyclopentadiene **1** was added. The typical experiment reported in this paper was run on 0.3 mmol of **2a,b**, and **1** was added in excess (about 1.5 mmol). After completion of the cycloaddition, the reaction mixture was decomposed in water, extracted with dichloromethane, and briefly dried. The organic layer was evaporated to dryness and the residue, dissolved in ethyl acetate, was then analyzed by hplc analysis (see experimental section for details).

During the dissolution of the residue in ethyl acetate, quite surprisingly **11** crystallized out as nice white crystals. The precipitate was filtered off and found to be pure enough (hplc analysis) to be re-used in further catalytic processes. Even if the chiral ligand is one of the minor components of the reaction mixture, the low solubility of **11** in ethyl acetate or in diisopropyl ether allowed its recovery in about 75% yield using this simple methodology. The results of the catalyzed cycloadditions (all reactions proceeded with quantitative yields) are reported in Table 1.

The tetrahedral reactive complex derived from MP, (*R*)-**11**, and **2a,b**, gives moderate levels of enantioselection. The preferential attack on the less hindered *Re*-face of the coordinated dienophile allows preparation of (*S*)-**4a** and (*S*)-**4b** with up to 77 and 42% *ee* respectively (Table 1, entries 1,8).

When two equivalents of auxiliary achiral ligand [H_2O or tetramethylurea (TMU)] were added, the enantioselectivity was reversed, and (*R*)-**4a,b** were obtained with up to 90% *ee* (Table 1, entries 2,3 and 9,10). In the reaction of **2b**, a small decrease in the reactivity was evident, since 90 hours were required to bring the reaction to completion.

The change of the anion of Mg(II) from perchlorate to triflate, beside a small decrease in the reactivity of **2b**, resulted in the formation of *the (R)-enantiomer with an excellent level of stereoselectivity in the presence of (R)-11: the ee of **4a,b** were 94 and 92% respectively* (Table 1, entries 4,11). Obviously, by using bis(oxazoline) (*S*)-**11** as chiral ligand the opposite enantiomeric adducts were obtained with the same selectivities (Table 1, entries 5,12).

The change of the cation of triflate from Mg(II) to Cu(II) resulted in an increased reactivity (particularly evident for **2b**), but the stereoselection was strongly lowered, since (*R*)-**4a,b** were obtained in only 20-34% *ee* (Table 1, entries 7,13).

Table 1. Enantioselectivity of the DA reaction between **1** and **2a,b** with the catalysts from (*R*)-**11**, inorganic salt, and the eventual auxiliary ligands, run in dichloromethane (quantitative yields).

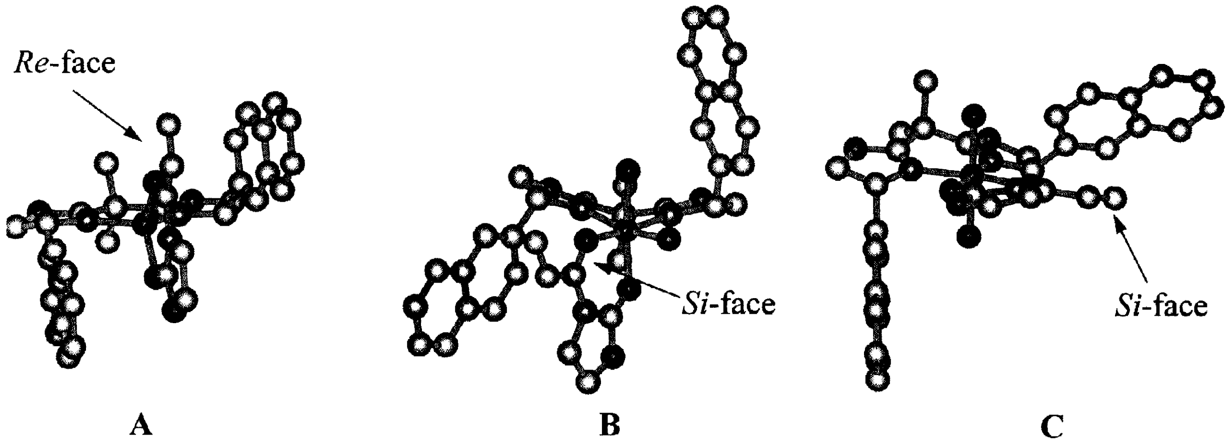
n	Dienophile	Salt	Auxiliary Ligand	T/°C	t/h	*endo* : *exo*	% *ee endo*-**3**	e.r. *exo*-**4**[a]
1	**2a**	MP	---	-50	16	91 : 9	77 (*S*)[b]	---
2	**2a**	MP	H_2O	-50	16	90 : 10	84 (*R*)	---
3	**2a**	MP	TMU	-50	16	94 : 6	80 (*R*)	---
4	**2a**	MT	---	-50	16	89 : 11	94 (*R*)	---
5[c]	**2a**	MT	---	-50	16	90 : 10	94 (*S*)	
6[d]	**2a**	MT	---	-50	16	90 : 10	94 (*R*)	---
6bis[c]	**2a**	MT	---	-50	16	90 : 10	94 (*R*)	---
6ter[f]	**2a**	MT	---	-50	16	90 : 10	94 (*R*)	---
7	**2a**	CT	---	-50	16	87 : 13	20 (*R*)	---
8	**2b**	MP	---	-15	16	80 : 20	42 (*S*)[b]	55 : 45
9	**2b**	MP	H_2O	-15	90	87 : 13	83 (*R*)	12 : 88
10	**2b**	MP	TMU	-15	90	88 : 12	90 (*R*)	15 : 85
11	**2b**	MT	---	-15	40	80 : 20	92 (*R*)	7 : 93
12[c]	**2b**	MT	---	-15	40	80 : 20	93 (*S*)	n.d.
13	**2b**	CT	---	-15	16	85 : 15	34 (*R*)	68 : 32

[a] The absolute configuration of *exo*-**4b** is unknown, the ratio refers to the order of elution. [b] Reaction run in the presence of powdered MS 4Å (50 mg). [c] Reaction run by using (*S*)-**11** as chiral ligand. [d] Reaction performed on 1.4 mmol scale. [e] Reaction performed on 1.0 mmol scale using as chiral ligand the bis(oxazoline) recovered from the reaction in entry 6. [f] Reaction performed on 0.7 mmol scale using as chiral ligand the bis(oxazoline) recovered from the reaction in entry 6bis.

Discussion and Conclusions

The stereoselectivity observed in the reaction between **1** and **2a,b** in the presence of the chiral ligand **11** and the Lewis acid can be rationalized by considering the reactive complexes **A**-**C**, Scheme 4.

In the MP-based complex, the Mg(II) cation is tetrahedrally coordinated (structure **A**). Compared to the use of (*R*)-phenyl oxazoline **5** as chiral ligand, small increases in the enantioselectivity are observed (from 70 to 77% *ee* in the cycloaddition of **2a**, and from 28 to 42% *ee* in that of **2b**).[17,19] Hence the use of a more extended aromatic system as substituent on the chiral ligand has a small, but positive effect on the stereoselectivity of a tetrahedrally organised chiral catalyst.



Scheme 4

When two equivalents of auxiliary ligands are added to the tetrahedral complex, the *cis* octahedral complex (**B**) is formed and the enantioface selectivity is reversed. As found with the previously investigated chiral bis(oxazolines), water is the best auxiliary ligand for **2a** [(*R*)-**4a** is obtained with up to 84% *ee*], while TMU works better than water in the cycloaddition of **2b** [(*R*)-**4b** is obtained with up to 90% *ee*].[18-19]

When the catalyst is built from MT, the octahedral complex **C** is obtained, with the triflate anions behaving as auxiliary ligands in the axial *trans* positions. Both cycloadditions of **2a,b** gave high degrees of enantioselection, and the *endo* adducts were obtained with up to 92-94% *ee*.

The starting target of this research, the optimisation of the chiral ligand structure, has been achieved by changing the phenyl group on the C-4 of the oxazoline ring to a naphthyl substituent. The comparison between the data reported in Table 1 with those obtained using (*R*)-**5** as chiral ligand,[17-19] clearly show the increased enantioselectivity obtainable with **11**, since all the cycloadditions catalysed by the Mg(II) cation gave cycloadducts with *ee* whose values are comparable with those obtained with *cis*-4,5-diphenyl-bis(oxazoline).

When the cationic core of the chiral catalyst was Cu(II), low levels of stereoselectivity were observed, and this result confirms the inefficiency of bis(oxazolines) with aromatic substituents to behave as chiral ligands in Cu(II)-based processes.[5,12]

A remarkable feature of **11** is represented by its low solubility in polar solvents, allowing an easy recovery of the chiral ligand. When the cycloaddition was performed on a 1.4 mmol scale (Table 1 - entry 6) the enantioselectivity was again excellent and **11** was recovered, after quenching of the reaction mixture and dissolution of the residue in diisopropyl ether, by a simple filtration, in 75% yield. The ligand was reused, without any further purification, in a second cycloaddition (Table 1 - entry 6bis) giving the same enantioselectivity. The recovery and reuse of the chiral ligand was repeated in a third reaction (Table 1 - entry 6ter) giving the same reproducible results.

In conclusion, starting from 2-vinylnaphthalene a new chiral bis(oxazoline) was synthesised in both enantiomerically pure forms, fully characterised, and found to be an excellent ligand in the asymmetric catalysis of the DA reaction. The low solubility of such bis(oxazolines) in polar aprotic solvents allows an easy recovery and the reuse in further catalytic processes, without any change in the induced enantioselectivities.

Experimental Section

Melting points were determined by the capillary method and are uncorrected. Elemental analyses were made on C. Erba CHN analyzer mod. 1106. ^{1}H NMR (TMS as standard) spectra were recorded on a Bruker AC 300 spectrometer, ir spectra (Nujol mulls) were recorded on a Perkin Elmer 881 spectrophotometer; optical rotations were mausered at room temperature on a Perkin Elmer 241 polarimeter with a 1 dm cell. Column chromatography was carried out on silica gel 230-400 mesh.

Materials. Dichloromethane was the hydrocarbon-stabilized Aldrich ACS grade, distilled from calcium hydride and used immediately. Inorganic salts were anhydrous Aldrich ACS reagents. 2-Vinylnaphathalene was a commercial Aldrich grade reagent. 3-Acryloyl-1,3-oxazolidin-2-one (**2a**) and (*Z*)-3-crotonyl-1,3-oxazolidin-2-one (**2b**) were prepared following the literature method.[19,26] The *endo* : *exo* ratios were measured by HPLC and confirmed by ^{1}H NMR spectroscopy; the enantiomer ratios were determined by HPLC [Daicel Chiralcel OD (**2a**) and Chiralpak AD column (**2b**)].

(2R)-N-Benzyloxycarbonyl-2-amino-2-(2'-naphthyl) ethanol (7). The two protected enantiomeric chiral amino ethanols were prepared as decribed in literature starting from 2-vinyl naphthalene.[22] (*R*)-**7**: mp, 134-135 °C (lit.[22] 133-134 °C); $[\alpha]_D^{20}$ = -50.0 (c, 0.38; 95% ethanol). (*S*)-**7**: $[\alpha]_D^{20}$ = +50.2 (c, 0.36, 95% ethanol) [lit.[22] +50.9 (c, 0.32; 95% ethanol)].

(2R)-2-Amino-2-(2'-naphthyl) ethanol (8). To the protected amino alcohol **7** (1.30 g - 4.05 mmol), 0.45 g of 5% C-Pd and 50 mL of 95% ethanol were added. Hydrogenation was run under standard conditions. After removal of the catalyst by filtration, the solvent was evaporated to dryness to give 0.75 g of **8** as white crystals (quantitative yield). (*R*)-**8**; mp = 88-89 °C (lit.[27] 98-99 °C); IR: 3368, 3302, and 3188 cm^{-1}. ^{1}H NMR (acetone-d_6), δ: 8.1-7.8 (4H, m, aromatic protons), 7.7-7.4 (3H, m, aromatic protons), 4.70 (1H, t, J = 7.5 Hz, H-2), 4.30 (1H, t, J = 7.5 Hz, *H*-1), 3.65 (1H, t, J = 7.5 Hz, *H*-1), 3.07 (2H, bs, -NH_2), 1.41 (1H, bs, O*H*). Elem. anal.: calc. for $C_{12}H_{13}NO$: C, 77.0; H, 7.0; N, 7.5. Found: C, 77.2; H, 7.1; N, 7.4%. (*R*)-**8**: $[\alpha]_D^{20}$ = -33.8 (c, 1.41; chloroform); (*S*)-**8**: $[\alpha]_D^{20}$ = +33.9 (c, 1.39; chloroform) [lit.[27] +31.0 (c, 1.41; chloroform)].

N,N'-Bis[(1R)-(2'-naphthyl)-2-hydroxyethyl]-2,2-dimethylpropane-1,3-diamide (9). (*R*)-**8** (1.20 g - 6.4 mmol) was suspended in dichloromethane (3 mL) and triethylamine (0.77 g - 7.6 mmol) was added under stirring. Dimethyl malonyl dichloride[28] (0.54 g - 3.2 mmol) was added dropwise under stirring keeping the temperature below -10 °C. Stirring was continued at room temperature for 7 h, then the reaction mixture was decomposed with water. A white solid separated that was filtered and crystallized from ethyl acetate to give 1.05 g (70% yield) of (*R*)-**9**; mp = 169-170 °C; IR: 3380 and 1641 cm^{-1}. ^{1}H NMR (CD_3OH), δ: 8.15 (1H, d, *J* = 8.5 Hz, -N*H*), 7.75-7.60 (4H, m, aromatic protons), 7.45-7.30 (3H, m, aromatic protons), 5.22 (1H, m, -C*H*-N), 3.94-3.80 (2H, m, -CH_2-O), 3.35 (1H, s, -O*H*), 1.68 (3H, s, -*Me*). Elem. anal.: calc. for $C_{29}H_{30}N_2O_4$: C, 74.0; H, 6.4; N, 5.95. Found: C, 73.8; H, 6.2; N, 5.8%. $[\alpha]_D^{20}$ = -84.9 (c = 0.20; 95% ethanol); (*S*)-**9**: $[\alpha]_D^{20}$ = +85.0 (c = 0.20; 95% ethanol).

N,N'-Bis[(1R)-(2'-naphthyl)-2-chloroethyl]-2,2-dimethylpropane-1,3-diamide (10). (*R*)-**9** (1.10 g - 2.34 mmol) was suspended in 28 mL of dichloromethane, and then 9.2 mL of $SOCl_2$ were added dropwise under stirring at room temperature. The solution was refluxed for 4 h and then the reaction mixture was evaporated under vacuum to give 1.17 g (quantitative yield) of a solid which was used in the last step of the synthesis without any purification. ^{1}H NMR (CD_3OH), δ: 8.28 (1H, d, *J* = 7.5 Hz, -N*H*), 7.69 (2H, m, aromatic protons), 7.61 (1H, d, aromatic proton), 7.53 (1H, d, aromatic proton), 7.43-7.25 (3H, m, aromatic protons), 5.39 (1H, q, *J* = 7.5 Hz, -C*H*-N), 3.95 (2H, d, *J* = 7.5 Hz, -CH_2-Cl), 1.60 (3H, s, -*Me*).

2,2-Bis{2-[(4R)(2'-naphthyl)-1,3-oxazolinyl]}propane (11). (*R*)-**10** (1.17 g - 2.31 mmol) was dissolved in 30 mL of THF, and the solution was cooled at 0 °C. 0.24 g of NaOH dissolved in 16 mL of EtOH were added dropwise under stirring within 15 min. The green solution was heated under reflux, and, after 1.5 h, the colour was pale yellow. The solvent was removed under vacuum, *ca.* 50 mL of water were added, and then the mixture was extracted with dichloromethane (3 × 30 mL). The organic layer was dried over Na_2SO_4, and then evaporated. The residue was column chromatographed (cyclohexane:ethyl acetate 60:40) to give 0.55 g of bis(oxazoline) (*R*)-**11** (55% yield); mp = 173-174 °C from ethyl acetate; IR: 1665 and 1100 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ: 7.80-7.65 (4H, m, aromatic protons), 7.58-7.45 (3H, m, aromatic protons), 5.41 (1H, dd, *J* = 7.5 and 10.0 Hz, -*H*4), 4.76 (1H, dd, *J* = 7.5 and 10.0 Hz, -H_5), 4.26 (1H, t, *J* = 7.5 Hz, -$H_{5'}$), 1.76 (3H, s, -*Me*). ^{13}C NMR ($CDCl_3$), δ: 170.4, 139.6, 133.3, 132.8, 128.6, 127.8, 127.5, 126.0, 125.7, 125.5, 124.5, 75.3, 69.7, 39.0, 24.5. Elem. anal.: calc. for $C_{29}H_{26}N_2O_2$: C, 80.2; H, 6.0; N, 6.45. Found: C, 80.0; H, 6.1; N, 6.4%. $[\alpha]_D^{20}$ =+231.3 (c = 0.55; chloroform); (*S*)-**11**: $[\alpha]_D^{20}$ = -232.5 (c = 0.55; chloroform). The enantiomeric purity was checked by hplc analyses on a Water mod. 515 and found to be higher than 99.5%. Column: Chiralpak AD column; eluent: *n*-hexane-*i*-propanol 80:20; flow: 1.0 mL/min; retention times: (*S*)-**11** 8.4 min, (*R*)-**11** 55.4 min.

*DA Reaction of cyclopentadiene **(1)** and 3-alkenoyl-1,3-oxazolidin-2-one **(2a,b)** catalyzed by inorganic perchlorate or triflate and bis(oxazoline) **11**.* The cycloadditions were performed as previously described.[19] The standard analysis of the reaction mixture was performed by hplc analysis: **3a**: Daicel OD column with 10% 2-propanol in hexane as eluent [1 mL/min; average retention times: 19.9 and 20.7 min for *exo* enantiomers, 21.9 min for (*S*)-**3a** and 24.6 min for (*R*)-**3a**]. The *exo* : *endo* ratio, determined by HPLC, was identical to that determined by ^{1}H NMR. **3b**: Chiralpak AD column with 5% 2-propanol in hexane as eluant [0.5 mL/min; average retention times: 24.8 and 27.0 min for *exo* enantiomers, 25.8 min for (*S*)-**3b** and 29.6 min for (*R*)-**3b**].

*DA Reaction between **2a** and **1** and recovery of the chiral ligand **11** (Table 1 - entries 5).* Anhydrous magnesium triflate (40 mg - 0.13 mmol), bis(oxazoline) **11** (60 mg - 0.14 mmol) and 3-acryloyl-1,3-oxazolidin-2-one (**2a**) (200 mg -1.4 mmol) were added to anhydrous CH_2Cl_2 (1.2 mL) under stirring at ambient temperature in a rubber septum sealed vial. Within one hour the inorganic salt dissolved. The vial was chilled at -50 °C and after 30 minutes cyclopentadiene (0.3 mL - about 4.5 mmol) was added. Stirring was continued overnight, then the reaction was decomposed in water, extracted with CH_2Cl_2 and dried . A portion of the crude mixture was monitored by ^{1}H NMR spectroscopy and the *endo* : *exo* ratio was determined. The solvent was evaporated and the solid dissolved in hot diisopropyl ether. The solution was concentrated to about 8 mL and the chiral ligand **11** precipitated in a few minutes. Filtration gave 45 mg of **11** (75% yield) pure by HPLC analisys and ^{1}H NMR spectroscopy. The recovered chiral ligand was reused in a second cycloaddition on 1.0 mmol scale. The bis(oxazoline) was again recovered in 70% yield, and tested in a further experiment on 0.7 mmol scale. In all the cycloadditions reaction yields, *endo*-selectivity and *ee* of (*R*)-**3a** were almost identical to the results obtained for the 0.35 mmol scale cycloadditions.

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