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Asymmetric copper-catalyzed Diels-Alder reaction revisited: control of the structure of bis(oxazoline) ligands.

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Abstract

Synthesis of 1,4-bis(oxazoline) ligands bearing a bicyclo[2,2,2]backbone derived from 9,10-dihydro-9,10-ethanoanthracene *trans*-dicarboxylic acid was revisited. Starting from L- or D-amino alcohols and either (S,S) or (R,R)-dihydroethano *trans*-dicarboxylic acid, a complete series of ligands was evaluated in the copper-catalyzed Diels-Alder reaction. The most efficient ligands with a phenyl substituent on the oxazoline ring afforded enantiomeric excess up to 98%. This is different from previous results indicating that the best enantioselectivity involved a diastereomeric ligand with the meso-backbone.

Keywords: Chiral bis(oxazoline) synthesis; Bicyclo[2.2.2] backbone; Diels-Alder catalysis; Copper; Enantioselectivity.

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1. Introduction

Chiral bis(oxazoline) ligands have emerged as one class of important and efficient C_2 -symmetric ligands in numerous metal-catalyzed asymmetric transformations.¹⁻⁹ Among them, a novel class of oxazoline ligands with multiple elements of chirality has been synthesized from readily available chiral diacid and chiral amino alcohol (Fig. 1). Besides the central chirality element in the oxazoline moiety, these ligands possess an additional chirality element in the backbone such as 1,3-dioxolane **I**,¹⁰⁻¹² bicyclo [2,2,1] **II**, [2,2,2] **III**,¹³ cyclohexane **IV**,^{14,15} and cyclopentane **V**.¹⁶

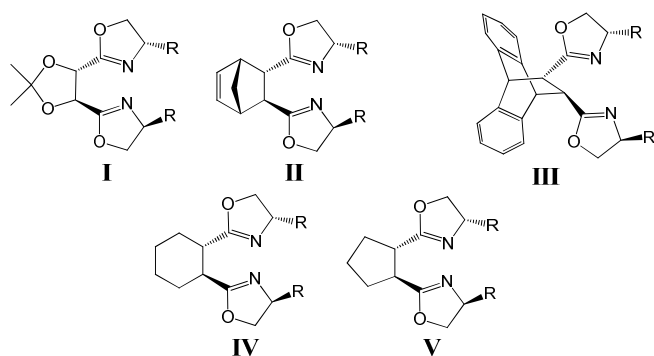


Fig. 1.

Although the Diels-Alder reaction between acrylimide dienophiles and cyclopentadiene was the most successful application of the Cu(II)-bis(oxazoline) catalytic system with enantiomeric excess up to 99%,¹⁷⁻³¹ its application with the ligands **I**, **II**, **III**, **IV** and **V** was less effective in enantioselectivity. In particular, the ligand **III**, previously introduced by Takacs et al.,¹³ has particularly focused our attention since the best enantioselectivity (75%) in the Diels-Alder reaction surprisingly involves the meso-backbone and poor results were obtained with the other chiral configurations. Moreover, the authors¹³ indicated that a phenomenon of epimerization was observed during the synthesis of these ligands. These results inspired us to reinvestigate the synthesis of these ligands with more convenient routes to better control the stability of their relative configuration.

In the present work we revisit this class of bis(oxazoline) ligands in which the two oxazolines are separated by a dihydroethanoanthracene backbone (Figure 1, **III**). With the goal to rationalize and optimize the results obtained in catalysis, a more convenient preparation of the ligand was first described and the four diastereomers were prepared in pure form. The effect of structure change of the ligands on the stereochemical outcome of the asymmetric copper-catalyzed Diels-Alder reaction between N-acryloyloxazolidinone or N-crotonyloxazolidinone and cyclopentadiene was then fully investigated yielding high enantiomeric excess (up to 98%). As expected, the best ees were obtained with pure R,R and S,S bis(oxazoline), provided that the chirality of the backbone matched correctly the chirality of the bis(oxazoline).

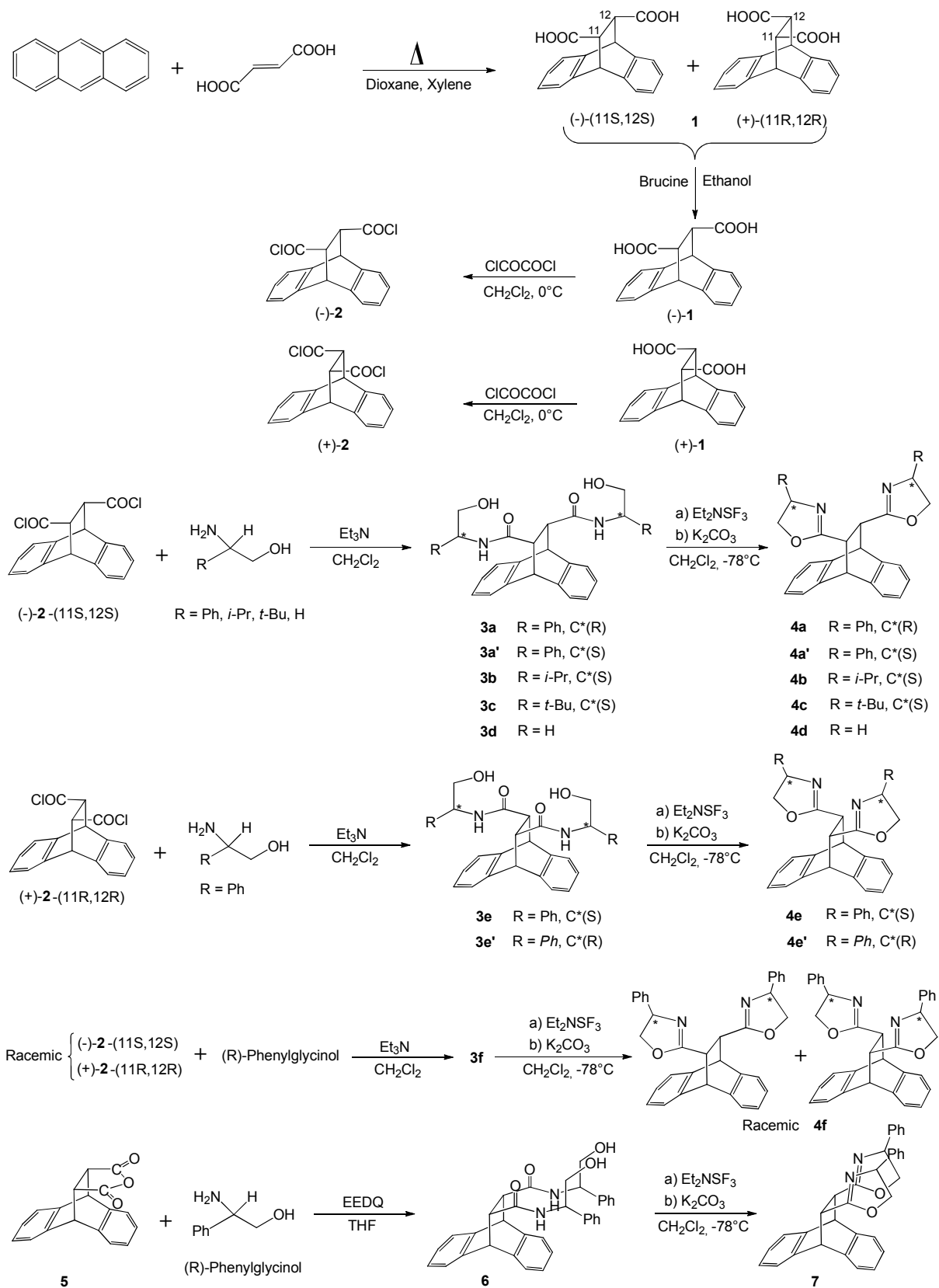
2. Results and Discussion

The bis(oxazoline) ligands were synthesized from the corresponding 9,10-dihydro-9,10-ethanoanthracene *trans*-(11S,12S) and *trans*-(11R,12R) dicarboxylic acid (**1**) as shown in Scheme 1. After chiral separation with brucine,³² conversion of the diacid into the corresponding acid dichloride by reaction with the oxalyl chloride¹⁶ was accomplished within 1 h. After removing the solvent and excess oxalyl chloride, the product was used in the next step without purification. Overnight reaction with 2.2 equiv of the amino alcohol in the presence of triethylamine afforded the expected bis-hydroxyamide **3** as a white solid in 60-85% yield. The ¹H NMR analysis confirmed the presence of the desired product as a single diastereomer. It should be noted that some epimerization occurs with the previously requisited procedure¹³ in forming the diamide intermediate.

Conversion of bis(hydroxyamide) **3** to the corresponding bis(oxazoline) **4** was carried out in one step by reaction with diethylaminosulfur trifluoride in CH₂Cl₂ at -78°C followed by

base induced cyclisation^{16,9} in 50-80% yield. For the ligand **4d**, the bis(hydroxyamide) **3d** was first converted into the bis(amide) dichloride with SOCl₂ and then the cyclization was achieved with aqueous NaOH in 73% yield. The dihydroxyamide **6** with the meso-backbone was synthesized from the anhydride **5** (not the acid)³³ and the (R)-phenylglycinol in the presence of the coupling reagent N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) in 77% yield.^{34,16}

The corresponding meso-bis(oxazoline) ligand **7** was prepared using a similar route with diethylaminosulfur trifluoride in CH₂Cl₂ at -78°C. After purification on column chromatography, the ¹H NMR spectrum shows peaks corresponding to ligands **4a** and **4e'**(15%) due to epimerization (Fig. 2(A)). The ¹H NMR analysis confirms the progressive disappearance of **7** after 24h (50%, Fig. 2(B)) and after 48 hours, there is total conversion into the ligands **4a** and **4e'** in a ratio 53/47 (Fig. 2(C)).



Scheme 1.

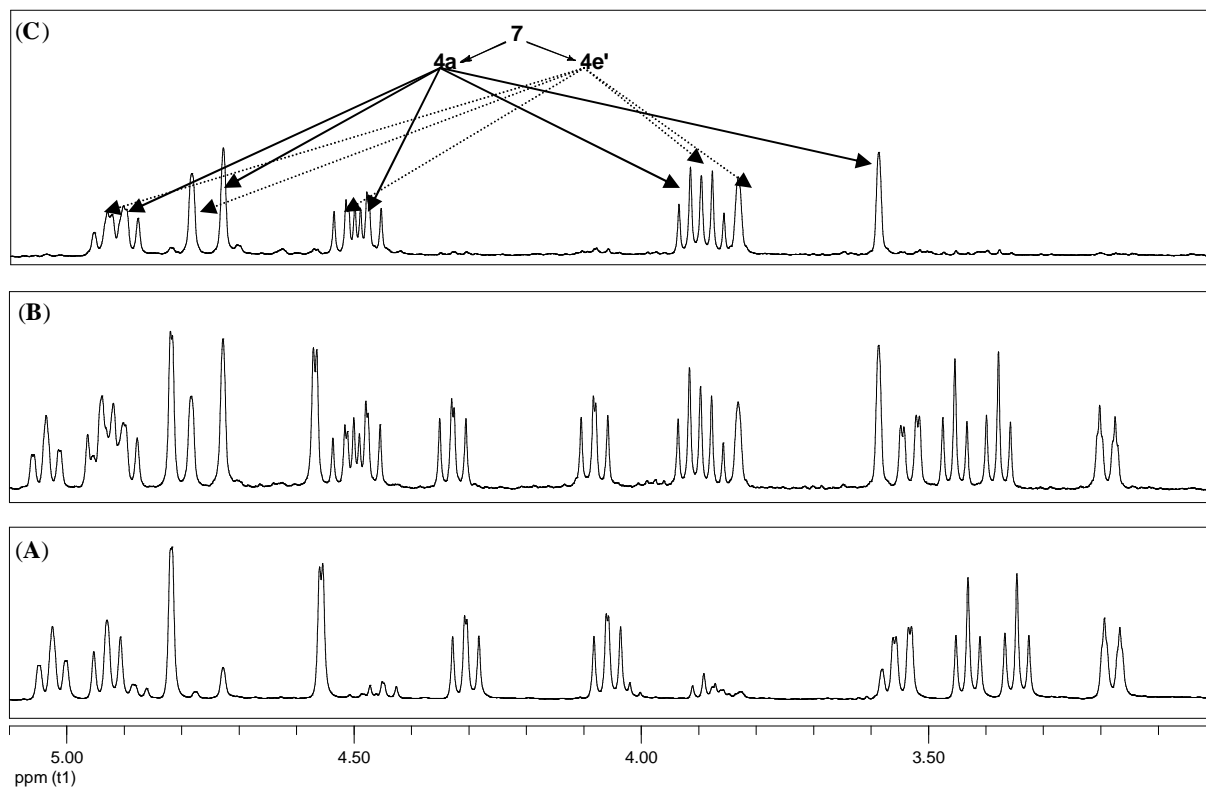


Fig. 2

An X-ray structure of the bis(oxazoline) ligand **4a** has been solved (Fig. 3).³⁵ X-ray diffraction analysis shows that the two chiral oxazoline rings are slightly twisted pushing the two oxazoliny phenyl towards the metal centre. In contrast, X-ray structure of the other diastereomer ligand **4e'** (using the (R)-phenyl glycinol and *trans*-(11R,12R)-dicarboxylic acid **1**),¹³ showed that the two oxazoliny phenyl are far away from the metal centre in the complex.

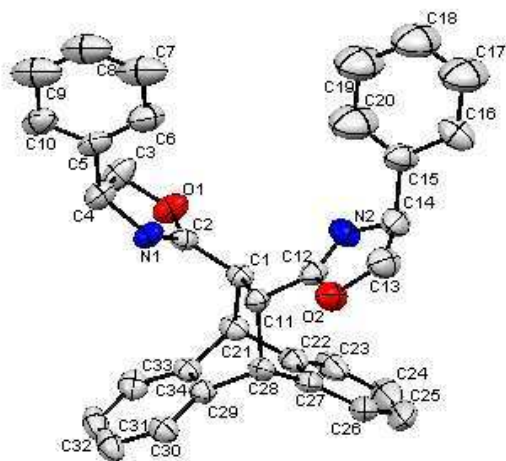
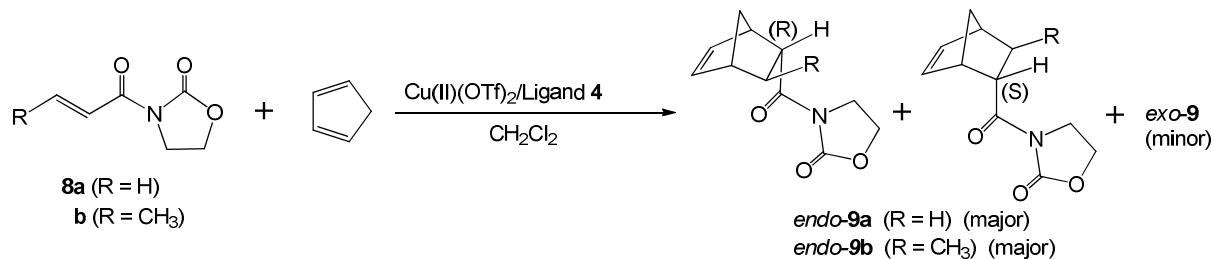


Fig. 3.

The Diels-Alder reaction of N-acryloyloxazolidinone **8a** or N-crotonyloxazolidinone **8b**¹⁹ and cyclopentadiene in the presence of various chiral catalysts derived from the ligands **4** and Cu(II) triflate was then investigated. The catalytic results are summarized in Table 1.

Table 1.

Diels-Alder reaction of **8** with cyclopentadiene catalyzed by Cu(II)(OTf)₂/bis(oxazoline) complexes^a



Entry	Ligand	Time (min)	Temp (°C)	Yield ^b (%)	<i>endo/exo</i> ^c (%)	<i>ee</i> _{<i>endo</i>} ^d (%) (config.)
1	4a	5	20	95	94/6	93 (R)
2	4a'	10	20	80	75/25	21 (R)
3	4b	30	20	80	85/15	16 (R)
4	4c	240	20	50	88/12	10 (S)
5	4d	10	20	80	88/12	20 (R)
6	4e	5	20	95	94/6	94 (S)
7	4e'	15	20	82	76/24	22 (S)
8	4f ^e	10	20	80	90/10	76 (R)
9	7	5	20	82	88/12	77 (R)
10 ^f	4a ^f	240	20	85	93/7	89 (R)
11	4a	5	0	95	96/4	95 (R)
12	4a	30	-40	93	98/2	98 (R)
13	4e	5	0	95	96/4	96 (S)
14	4e	45	-40	92	98/2	98 (S)

^aMolar ratio of metal/ligand/diene/dienophile: 1/1.2/150/50.

^bIsolated yield of cycloadducts after silica gel chromatography.

^cDetermined by ¹H NMR and HPLC.

^dDetermined by chiral HPLC (Chiralcel OD-H column) and comparison of known optical rotation.

^eLigand prepared from the racemic *trans*-dicarboxylic acid **1** and (-)-(R)- phenylglycinol.

^fN-crotonyloxazolidinone as dienophile.

From the results of Table 1, it is shown that the ligands **4a** and **4e** with the phenyl substituted oxazoline gave the best *ee* (93-94%) and *endo/exo* diastereoselectivity (94/6) (entries 1 and 6). With the ligand **4a'** or **4e'**, in which the chirality of the oxazoline ring has

been inverted, the ee was decreased (21%), as well as the diastereoselectivity (75/25) (entries 2 and 7). The ligands with *i*-Pr **4b** and *t*-Bu **4c** gave low ee (< 20%) (entries 3 and 4). The high reactivity of the catalyst leads to short reaction times (5-10mn) with yields in the range 80-95%, excepted for the bulky *t*-Bu group (50% yield) in which a longer reaction time was necessary (4 hours). We also decided to test N-crotonyloxazolidinone **8b** as a substrate to compare our results with those previously reported.¹³ In our hands, the *endo*-cycloadduct **9** was obtained with 89% ee and R configuration, using **4a** as ligand (entry 10), whereas it was previously reported¹³ an enantiomeric excess of 28% with S configuration in a similar situation.

The effect of temperature was studied with ligands **4a** and **4e**. The highest ee and diastereoselectivity was obtained at -40°C (98% and 98/2 respectively) (entries 12 and 14).

The influence of substitution both on the oxazoline ring and on the backbone moiety has been investigated with the goal of better understanding the stereocontrol of the Cu(II)-catalyzed reaction. According to the structure (Fig. 3), we have prepared and tested the four diastereomeric ligands **4** with the phenyl group on the oxazoline ring (as represented in Fig. 4). By changing combination of the enantiomers derived from (+) or (-)-*trans*-dicarboxylic acid and aminoalcohol, the stereochemistry of the four asymmetric centres can be adjustable. There are two sets of enantiomer pairs corresponding to the ligands **4a**, **4e** and **4a'**, **4e'**. The two phenyl groups on the oxazoline ring of ligand **4a** and **4e** are placed nearer to the reaction centre than those of **4a'** and **4e'**, and consequently, have a larger effect on the enantioselectivity (93% versus 21%). These results show that the degree of asymmetric induction depends of the chirality on the oxazoline ring in **4a** and **4a'** or **4e** and **4e'**. Furthermore, with the ligands **4a** and **4a'** or **4e** and **4e'**, the same *endo*-**9**(R) or **9**(S) - cycloadduct was obtained. The sense of asymmetric induction was logically inverted with the

enantiomeric ligands **4a** and **4e** or **4a'** and **4e'** but also with the ligands **4a** and **4e'** or **4a'** and **4e**. These results demonstrate that the chiral sense of enantioselection was determined by the chirality of the backbone. To complete the study, it was also noted that ligand **4d** with no substituent on the oxazoline ring gave an enantioselectivity of 20% (entry 5). This value was similar to the enantioselectivity obtained with ligand **4a'** (entry 2).

In our hands, the ligand **7** gave an ee = 77% for *endo*-**9** (R)-cycloadduct (entry 9). Actually, this value is very close to that obtained with the ligand **4f** derived from the racemic *trans*-dicarboxylic acid **1** and (-)-(R)-phenylglycinol, ee = 76% *endo*-**9**(R)-cycloadduct (entry 8). Taking into account the epimerization observed in the NMR study, an epimerization of the ligand **7** may also occur in the catalytic conditions. Since the epimerization is time dependent, a study of the ee obtained using ligand **7** over the time course of the catalytic reaction might be necessary. However, the short time of the catalytic reaction (<5 min) makes this study too difficult. It should be noted that previous results¹³ gave an ee of 75% for *endo*-**9**(R)-cycloadduct, quite similar to our results (77% ee).

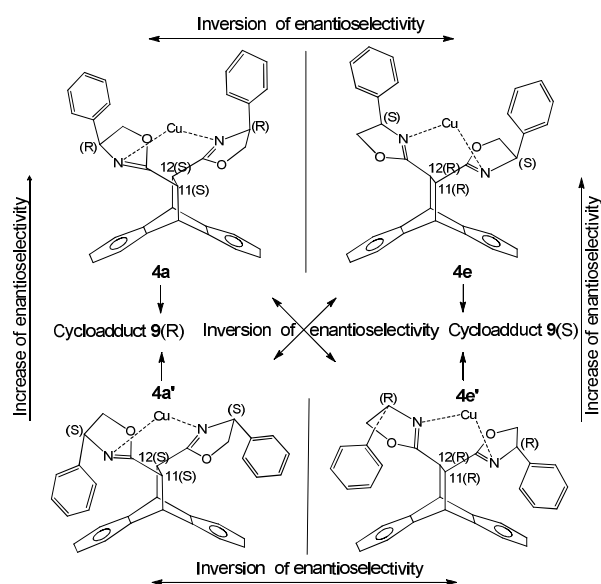


Fig. 4.

3. Conclusion

In conclusion, the synthesis of bis(oxazoline) ligands with four asymmetric centres by combination of the two chiral sources derived from the dihydroethanoanthracene diacid and aminoacids are revisited, and well-structured chiral ligands have been isolated and characterized. The copper-catalyzed asymmetric Diels-Alder reaction between N-acryloyloxazolidinone and N-crotonyloxazolidinone with cyclopentadiene was carried out with these chiral ligands. The best adapted combination for the ligands **4a** and **4e** gave ees up to 98% at -40°C. Studies on the potential of these ligands for other metal-catalyzed asymmetric reactions are now in progress.

4. Experimental

4.1. General

All reactions were performed under argon. Solvent was distilled from appropriate drying agent, CH₂Cl₂ from CaH₂. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck precoated aluminium foil sheets (silica gel 60 with fluorescent indicator UV₂₅₄). Column chromatographies were carried out using silica gel from Acros (0.063-0.200 mm). Melting points were measured on a banc Kofler. ¹H NMR and ¹³C NMR in CDCl₃ were recorded using Bruker (Advance 400dpx) spectrometer at 400 and 100 MHz respectively. The following abbreviations are used in connexion with NMR; s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet. Chiral HPLC analysis was performed on a Varian Prostar 218 system equipped with a Chiralcel OD-H column. Optical rotations were recorded with a Perkin-Elmer 341 polarimeter. High resolution mass spectra were performed by the Centre Regional de Mesures Physiques de l'Ouest (CRMPO) at Rennes, France, on a Q-Tof2 spectrometer in ESI positif mode.

4.2. General procedure of preparation of bis-hydroxyamides **3a**, **3a'**, **3b**, **3c**, **3d**, **3e**, **3e'**, **3f** and **6**

Oxalyl chloride (3 equiv) was added dropwise to a cooled suspension (0°C) of the *trans*-diacide (-)-**1** or (+)-**1** and dimethylformamide (15 mol %) in CH₂Cl₂ (5 mL/mmol) under argon. The reaction mixture was stirred at room temperature for 2 h to give a yellow solution of the *trans*-diacide chloride (-)-**2** or (+)-**2**. The solvent and excess oxalyl chloride were removed in high vacuum, the residue was taken up in CH₂Cl₂ (4 mL/mmol) and added slowly to a cold solution (0°C) of the corresponding amino alcohol (2.2 equiv) and Et₃N (5 equiv) in CH₂Cl₂ (2 mL/mmol) under argon. Stirring was continued for 16 h at room temperature. After evaporation, the crude product was purified by column chromatography (Hexane-EtOAc-MeOH).

4.2.1. (11S,12S)-Bis[(2'-hydroxy-1'-(R)-phenylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene **3a**

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11S,12S)-dicarboxylic acid **1** (0.5 g, 1.7 mmol) and (-)-(R)-phenylglycinol (0.65 g, 3.74 mmol). Purification by column chromatography (hexane-EtOAc, 1:9) yielded a white solid (840 mg, 93%): m.p.= 147-148 °C; [α]_D²⁰ = -34 (*c* 1.44, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 2.91 (s, 2H), 3.66 (br s, 4H), 4.59 (s, 2H), 4.90 (br s, 2H), 7.06-7.32 (m, 18H); ¹³C NMR (100 MHz, CDCl₃): δ = 46.8, 49.6, 55.8, 66.07, 123.4, 125.4, 126.3, 126.7, 127.6, 128.6, 138.8, 140.1, 143.0, 173.5; HRMS [ESI]: *m/z* calcd for C₃₄H₃₂N₂O₄Na: 555.2259 (M+Na)⁺, found: 555.2255.

4.2.2. (11S,12S)-Bis[(2'-hydroxy-1'-(S)-phenylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene **3a'**

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11S,12S)-dicarboxylic acid **1** (0.5 g, 1.7 mmol) and (+)-(S)-phenylglycinol (0.65 g, 3.74 mmol). Purification by column chromatography (EtOAc-MeOH, 0:1) yielded a white solid (720 mg, 80%): m.p.= 174 °C; $[\alpha]_D^{20} = +32$ (*c* 0.84, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 2.96 (s, 2H), 3.68 (dd, *J* = 6.4, 11.6 Hz, 2H), 3.73 (dd, *J* = 3.6, 11.4 Hz, 2H), 4.59 (s, 2H), 4.90 (dd, *J* = 7.2, 11.2 Hz, 2H), 7.00-7.04 (m, 6H), 7.16-7.22 (m, 8H), 7.28, 7.58 (2d, *J* = 8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 45.9, 48.9, 56.2, 65.6, 123.4, 125.3, 125.9, 126.7, 127.3, 128.4, 139.6, 140.4, 143.3, 173.5; HRMS [ESI]: *m/z* calcd for C₃₄H₃₂N₂O₄Na: 555.2259 (M+Na)⁺, found: 555.2255.

4.2.3. (11S,12S)-Bis[(2'-hydroxy-1'-(S)-isopropylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene 3b

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11S,12S)-dicarboxylic acid **1** (0.5 g, 1.7 mmol) and (+)-L-Leucinol (0.438 g, 3.74 mmol). Purification by column chromatography (hexane-EtOAc, 9:1) yielded a white solid (635 mg, 80%): m.p.= 134-135 °C; $[\alpha]_D^{20} = -18$ (*c* 0.55, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 0.78, 0.80 (2d, *J* = 6.4 Hz, 12H), 1.09-1.16, 1.22-1.29 (2m, 4H), 1.39-1.47 (m, 2H), 2.88 (s, 2H), 3.23 (dd, *J* = 6.8, 11.4 Hz, 2H), 3.46 (dd, *J* = 3.6, 11.6 Hz, 2H), 3.85 (br s, 2H), 4.46 (s, 2H), 7.00-7.06 (m, 4H), 7.21, 7.24 (2d, *J* = 6.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 22.0, 23.2, 24.8, 40.2, 46.9, 49.6, 65.4, , 123.2, 125.4, 126.21, 140.3, 143.2, 173.8; HRMS [ESI]: *m/z* calcd for C₃₀H₄₀N₂O₄Na: 515.2885 (M+Na)⁺, found: 515.2883.

4.2.4. (11S,12S)-Bis[(2'-hydroxy-1'-(S)-tert-butylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene 3c

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11S,12S)-dicarboxylic acid **1** (1.0 g, 3.4 mmol) and (+)-(S)-*tert*-Leucinol (0.876 g, 7.48 mmol). Purification by column chromatography (EtOAc:MeOH, 4:1) yielded a white solid (1.27 g, 77%): m.p.= 220 °C; $[\alpha]_{365}^{20} = +57$ (*c* 0.95, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 2.90$ (s, 2H), 2.92 (t, *J* = 6.8 Hz, 2H), 3.36-3.43 (m, 2H), 3.73-3.79 (m, 4H), 4.62 (s, 2H), 7.10-7.17 (m, 4H), 7.28, 7.42 (2d, *J* = 6.4 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 26.8, 33.5, 46.3, 50.5, 59.6, 62.4, , 123.2, 125.7, 126.3, 126.4, 140.2, 143.4, 174.7$; HRMS [ESI]: *m/z* calcd for C₃₀H₄₀N₂O₄Na: 515.2885 (M+Na)⁺, found: 515.2887.

4.2.5. (11S,12S)-Bis[(2'-hydroxy-ethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene **3d**

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11S,12S)-dicarboxylic acid **1** (1 g, 3.40 mmol), and ethanolamine (0.457 g, 7.48 mmol) in THF (5 ml/mmol). Recrystallization from methanol yielded a white solid (578 mg, 45%): m.p.= 262 °C; $[\alpha]_{\text{D}}^{20} = +40$ (*c* 2.25, CH₃OH); ¹H NMR (400 MHz, CD₃OD): $\delta = 3.28$ -3.33 (m, 6H), 3.56 (t, *J* = 6 Hz, 4H), 4.60 (s, 2H), 7.09 (quintuplet, *J* = 7.2 Hz, 4H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.35 (d, *J* = 6.4 Hz, 2H); ¹³C NMR (100 MHz, CD₃OD): $\delta = 40.9, 46.5, 59.7, 122.0, 123.8, 124.9, 139.1, 141.7, 172.6$; HRMS [ESI]: *m/z* calcd for C₂₂H₂₄N₂O₄Na: 403.1633 (M+Na)⁺, found: 403.1633.

4.2.6. (11R,12R)-Bis[(2'-hydroxy-1'-(S)-phenylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene **3e**

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11R,12R)-dicarboxylic acid **1** (0.5 g, 1.7 mmol) and (+)-(S)-phenylglycinol (0.65 g, 3.74 mmol). Purification by column chromatography (hexane-EtOAc, 1:9) yielded a white solid (820 mg, 91%): m.p.= 137-138 °C; $[\alpha]_{\text{D}}^{20} = +30$ (*c* 0.51,

CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 2.92 (s, 2H), 3.64 (m, 4H), 4.58 (s, 2H), 4.89 (dd, J = 5.0, 11.8 Hz, 2H), 7.04-7.30 (m, 18H); ¹³C NMR (100 MHz, CDCl₃): δ = 46.1, 50.1, 55.8, 66.7, 123.5, 125.5, 126.5, 126.6, 127.8, 128.8, 138.5, 140.0, 143.0, 173.6; HRMS [ESI]: *m/z* calcd for C₃₄H₃₂N₂O₄Na: 555.2259 (M+Na)⁺, found: 555.2255.

4.2.7. (11R,12R)-Bis[(2'-hydroxy-1'-(R)-phenylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene 3e'

The product was synthesized according to the general procedure described above from 9,10-dihydro-9,10-ethanoanthracene *trans*-(11R,12R)-dicarboxylic acid **1** (0.5 g, 1.7 mmol) and (-)-(R)-phenylglycinol (0.65 g, 3.74 mmol). A white precipitate was formed in the solution and it was filtered, washed with CH₂Cl₂ and dried in vacuum to provide the corresponding bis(hydroxyamide) (768 mg, 85%): m.p. = 148-150 °C; [α]_D²⁰ = -31 (c 0.71, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 3.19 (s, 2H), 3.75 (br s, 4H), 4.69 (s, 2H), 4.95 (br d, 2H), 7.02 (dd, J = 4.0, 8.4 Hz, 2H), 7.19-7.31 (m, 14H), 7.90 (d, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 46.7, 49.3, 56.1, 65.7, 123.4, 125.4, 126.0, 126.0, 126.7, 128.5, 139.4, 140.4, 143.3, 173.5; HRMS [ESI]: *m/z* calcd for C₃₄H₃₂N₂O₄Na: 555.2259 (M+Na)⁺, found: 555.2255.

4.2.8. (11S,12S+11R,12R)-Bis[(2'-hydroxy-1'-(R)-phenylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene 3f

The product was synthesized according to the general procedure described above from racemic-9,10-dihydro-9,10-ethanoanthracene *trans*-dicarboxylic acid **1** (0.5 g, 1.7 mmol) and (-)-(R)-phenylglycinol (0.65 g, 3.74 mmol). Purification by column chromatography (EtOAc), yielded a white solid (690 mg, 76%): m.p. = 150 °C; [α]₅₈₉²⁰ = -33 (c 1.94, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 3.08 (s, 2H), 3.66 (br s, 4H), 4.60 (s, 2H), 4.87 (br s, 2H), 6.93-7.22 (m, 16H), 7.77 (d, J = 7.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 45.9, 49.3,

56.1, 65.8, 123.4, 125.4, 126.0, 126.7, 127.4, 128.5, 139.4, 140.4, 143.3, 173.58; HRMS [ESI]: m/z calcd for $C_{34}H_{32}N_2O_4Na$: 555.2259 ($M+Na$)⁺, found: 555.2255

4.2.9. Bis[(2'-hydroxy-1'-(R)-phenylethyl)]-amido-9,10-dihydro-9,10-ethanoanthracene 6

The product was synthesized from the *cis*-9,10-dihydro-9,10-ethanoanthracene dicarboxylic anhydride **5** (225mg, 0.9 mmol), (-)-(R)- phenylglycinol (156mg, 0.9 mmol) and N-Ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (247 mg, 1.0 mmol) in 10 ml of THF at ambient temperature for 48 h. Purification by column chromatography (EtOAc-MeOH, 9:1) yielded a white solid (185 mg, 77%): m.p.= 125-127 °C; $[\alpha]_{589}^{20} = -73$ (c 0.82, $CHCl_3$); ¹H NMR (400 MHz, $CDCl_3$): δ = 3.12 (dd, J = 12.0, 22.8 Hz, 2H), 3.23, 3.26 (2d, J = 6.8 Hz, 1H), 3.57-3.63 (m 2H), 3.73, 3.75 (2d, J = 3.6 Hz, 1H), 4.040 (dd, J = 7.2, 14.4 Hz, 1H), 4.41 (br s, 1H), 4.80 (m, 1H), 4.90 (m, 1H), 7.02-7.36 (m, 18H); ¹³C NMR (100 MHz, $CDCl_3$): δ = 46.2, 47.0, 49.4, 50.6, 55.5, 56.2, 65.2, 65.6, 123.5, 123.6, 124.5, 126.3, 126.4, 126.9, 127.0, 127.1, 127.2, 127.7, 127.8, 128.7, 128.7, 138.8, 139.3, 139.5, 141.9, 142.4, 142.8, 172.4, 173.1; HRMS [ESI]: m/z calcd for $C_{34}H_{32}N_2O_4Na$: 555.22598 ($M+Na$)⁺, found: 555.2257.

4.3. General procedure of preparation of bis(oxazoline) 4a, 4a', 4b, 4c, 4d, 4e, 4e', 4f, and 7

Diethylaminosulfur trifluoride (2.2 equiv) was added dropwise to a cooled suspension (-78°C) of the corresponding bis-hydroxyamide in dry CH_2Cl_2 (10 mL/mmol) under argon. After stirring for 3-5 h at the indicated temperature, anhydrous K_2CO_3 (3 equiv) was added and the reaction mixture was allowed to warm to room temperature. A saturated aqueous $NaHCO_3$ solution was added and after phase separation the aqueous layer was extracted with CH_2Cl_2 . After drying over $MgSO_4$ and evaporation, the crude product was purified by column chromatography (Hexane-EtOAc).

4.3.1. (11S,12S)-Bis[(4'R)-phenyloxazoline]-9,10-dihydro-9,10-ethanoanthracene 4a

The product was synthesized from **3a** (0.7 g, 1.31 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:2) yielded a white solid (513 mg, 78%): m.p.= 85-86 °C; $[\alpha]_D^{20} = +83$ (*c* 0.96, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 3.68$ (s, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 4.57 (t, *J* = 9.2 Hz, 2H), 4.82 (s, 2H), 5.01 (t, *J* = 8.4 Hz, 2H), 7.08-7.27 (m, 14H), 7.34, 7.38 (2d, *J* = 6.4 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 42.9, 47.0, 69.3, 75.3, 123.9, 125.1, 126.1, 126.3, 126.6, 127.4, 128.6, 140.5, 142.4, 142.5, 168.8$; HRMS [ESI]: *m/z* calcd for C₃₄H₂₉N₂O₂: 497.2229 (M+H)⁺, found: 497.2229.

4.3.2. (11S,12S)-bis[(4'S)-phenyloxazoline]-9,10-dihydro-9,10-ethanoanthracene 4a'

The product was synthesized from **3a'** (0.50 g, 0.94 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:2) yielded a white solid (300 mg, 68%): m.p.= 177 °C; $[\alpha]_D^{20} = +31$ (*c* 0.87, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 3.83$ (s, 2H), 3.86 (t, *J* = 8.0 Hz, 2H), 4.50 (dd, *J* = 8.4, 10.0 Hz, 2H), 4.78 (s, 2H), 4.92 (t, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 8.4 Hz, 4H), 7.05-7.18 (m, 12H), 7.23, 7.36 (2d, *J* = 6.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 43.1, 46.5, 69.1, 75.9, 124.5, 124.9, 126.3, 126.3, 126.4, 127.2, 128.4, 140.9, 142.0, 142.1, 169.2$; HRMS [ESI]: *m/z* calcd for C₃₄H₂₉N₂O₂: 497.2229 (M+H)⁺, found: 497.2229

4.3.3. (11S,12S)-Bis[(4'S)-isopropyloxazoline]-9,10-dihydro-9,10-ethanoanthracene 4b

The product was synthesized from **3b** (0.5 g, 1.0 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 2:3) yielded a white solid (295 mg, 63%): m.p.= 67-69 °C; $[\alpha]_D^{20} = -11$ (*c* 0.52, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 0.65, 0.71$ (2d, *J* = 6.8 Hz, 12H), 0.78, 0.92 (2 quintuplets, *J* = 7.2 Hz, 4H), 1.30 (septuplet, *J* = 6.8 Hz, 2H), 3.46 (s, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 3.80 (quintuplet, *J* = 7.6 Hz,

2H), 4.13 (t, J = 8.0 Hz, 2H), 4.60 (s, 2H), 6.97-7.05 (m, 4H); 7.13, 7.27 (2d, J = 6.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 22.6, 22.7, 24.9, 42.3, 45.8, 46.9, 64.0, 73.4, 124.0, 124.6, 125.8, 126.1, 140.6, 141.8, 166.9; HRMS [ESI]: *m/z* calcd for C₃₀H₃₇N₂O₂: 457.2855, (M+H)⁺, found: 457.2857.

4.3.4. (11S,12S)-Bis[(4'S)-*tert*-butyloxazoline]-9,10-dihydro-9,10-ethanoanthracene 4c

The product was synthesized from **3c** (0.5 g, 1.02 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:1) yielded a white solid (404 mg, 86%): m.p.= 84-86 °C; [α]_D²⁰ = -19 (c 0.51, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 3.56 (s, 2H), 3.59 (t, J = 9.2 Hz, 2H), 3.86 (t, J = 8.4 Hz, 2H), 4.07 (t, J = 8.4 Hz, 2H), 4.60 (s, 2H), 6.92, 6.98 (2t, J = 7.2 Hz, 4H), 7.10, 7.23 (2d, J = 7.2 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 25.6, 32.9, 43.0, 46.5, 69.1, 75.3, 123.7, 124.9, 125.97, 126.0, 140.8, 142.3, 167.2; HRMS [ESI]: *m/z* calcd for C₃₀H₃₇N₂O₂: 457.2855 (M+H)⁺, found: 457.2855.

4.3.5. (11S,12S)-Bis(oxazoline)-9,10-dihydro-9,10-ethanoanthracene 4d

The bis(hydroxyamide) **3d** (250 mg, 0.66 mmol) in CH₂Cl₂ (5 ml) was treated with SOCl₂ (1.56 g, 13.1 mmol). After 15 min, the solution was heated at reflux for 3 h, then recooled to room temperature and washed sequentially with cold water (10 ml), 0.1 M K₂CO₃ (2 x 10 ml), and saturated aqueous NaCl (10ml). After drying over MgSO₄ and evaporation, the crude bisamide dichloride was obtained as a white solid (175 mg, 93%): ¹H NMR (400 MHz, CDCl₃): δ = 2.84 (s, 2H), 3.45 (m, 8H), 4.55 (s, 2H), 7.04-7.11 (m, 4H), 7.24, 7.29 (2d, J = 6.4 Hz, 4H). HRMS [ESI]: *m/z* calcd for C₂₂H₂₂N₂O₂Cl₂Na: 439.0956 (M+Na)⁺, found: 439.0957.

A mixture of the crude bisamide dichloride, 170mg (0.41 mmol), and NaOH (500 mg, 30 mmol) in 50% aqueous MeOH (5 ml) was heated under reflux for 4 hours. After cooling, the

mixture was extracted with CH_2Cl_2 and washed with saturated aqueous NaCl. Column chromatography on silica (EtOAc/MeOH, 9:1) yielded the ligand **4d** as a white solid (102 mg, 73%): m.p.= 95-98 °C; 0.102g (73%). $[\alpha]_{\text{D}}^{20} = +34$ (*c* 1.23, CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.38$ (s, 2H), 3.44-3.64 (m, 4H), 4.06-4.16 (m, 4H), 4.62 (s, 2H), 6.99-7.05 (m, 4H), 7.15, 7.25 (2d, *J* = 6.4 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 42.7, 46.9, 54.1, 67.8, 123.8, 124.7, 126.0, 126.2, 140.4, 142.3, 168.4$; HRMS [ESI]: *m/z* calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_2$: 345.1603 (M+H)⁺, found: 345.1611.

4.3.6. (11R,12R)-Bis[(4'S)-phenyloxazoline]-9,10-dihydro-9,10-ethanoanthracene **4e**

The product was synthesized from **3e** (0.5 g, 0.94 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:2) yielded a white solid (440 mg, 68%): m.p.= 81-82 °C; $[\alpha]_{\text{D}}^{20} = -82$ (*c* 0.65, CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.58$ (s, 2H), 3.92 (t, *J* = 8.0 Hz, 2H), 4.48 (t, *J* = 8.4 Hz, 2H), 4.72 (s, 2H), 54.90 (t, *J* = 8.0 Hz, 2H), 6.96-7.18 (m, 14H), 7.24, 7.28 (2d, *J* = 6.4 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 43.1, 46.5, 69.1, 75.9, 124.5, 124.9, 126.3, 126.3, 126.4, 127.2, 128.4, 140.9, 142.0, 142.1, 169.2$; HRMS [ESI]: *m/z* calcd for $\text{C}_{34}\text{H}_{29}\text{N}_2\text{O}_2$: 497.2229 (M+H)⁺, found: 497.2229.

4.3.7. (11R,12R)-Bis[(4'R)-phenyloxazoline]-9,10-dihydro-9,10-ethanoanthracene **4e'**

The product was synthesized from **3e'** (0.5 g, 0.94 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:2) yielded a white solid (407 mg, 63%): m.p.= 178 °C; $[\alpha]_{\text{D}}^{20} = -33$ (*c* 0.87, CHCl_3); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.83$ (s, 2H), 3.87 (t, *J* = 8.0 Hz, 2H), 4.50 (dd, *J* = 8.4, 10.0 Hz, 2H), 4.78 (s, 2H), 4.92 (t, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 7.2 Hz, 4H), 7.05-7.18 (m, 10H), 7.23, 7.36 (2d, *J* = 6.8 Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 43.1, 46.5, 69.1, 75.9, 124.5, 124.9, 126.3,$

126.3, 126.4, 127.2, 128.4, 140.9, 142.0, 142.1, 169.2; HRMS [ESI]: m/z calcd for $C_{34}H_{29}N_2O_2$: 497.2229 (M+H)⁺, found: 497.2229.

4.3.8.(11S,12S+11R,12R)-Bis[(4'R)-phenyloxazoline]-9,10-dihydro-9,10-ethanoanthacene 4f

The product was synthesized from **3f** (0.5 g, 0.94 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:2) yielded a white solid (230 mg, 52%): m.p.= 91-95 °C; $[\alpha]_D^{20} = +13$ (c 10, $CHCl_3$); ¹H NMR (400 MHz, $CDCl_3$): δ = 3.58 (s, 2H), 3.83 (s, 2H), 3.87, 3.91 (2t, J = 8.0 Hz, 4H), 4.45-4.53 (m, 4H), 4.72 (s, 2H), 4.78 (s, 2H), 4.87-4.95 (m, 4H), 6.41 (d, J = 6.0 Hz, 4H), 6.96-7.37 (m, 32H); ¹³C NMR (100 MHz, $CDCl_3$): δ = 42.8, 43.1, 46.5, 47.0, 69.1, 69.2, 75.3, 75.9, 123.8, 124.5, 124.8, 125.1, 126.1, 126.2, 126.3, 126.3, 126.4, 126.5, 127.2, 127.4, 128.4, 128.5, 140.4, 140.9, 142.1, 142.3, 142.5, 168.8, 169.2; HRMS [ESI]: calcd for $C_{34}H_{29}N_2O_2$: 497.2229 (M+H)⁺, found: 497.2229.

4.3.9. Bis[(4'R)-phenyloxazoline]-9,10-dihydro-9,10-ethanoanthacene 7

The product was synthesized from **6** (0.3 g, 0.56 mmol) according to the general procedure described above. Purification by column chromatography (hexane-EtOAc, 3:2) yielded a white solid (90 mg, 54%): m.p.= 60-62 °C; $[\alpha]_D^{20} = +43$, c 0.58, $CHCl_3$); ¹H NMR (400 MHz, $CDCl_3$): δ = 3.18 (d, J = 10.8 Hz, 1H), 3.35 (t, J = 8.4 Hz, 1H), 3.43 (d, J = 8.4 Hz, 1H), 3.54 (dd, J = 2.0, 10.8 Hz, 1H), 4.04, 4.07 (2d, J = 8.4 Hz, 1H), 4.29, 4.31 (2d, J = 8.4 Hz, 1H), 4.56 (d, J = 2Hz, 1H), 4.81 (s, 1H), 4.93 (t, J = 9.2 Hz, 2H), 5.03 (t, J = 9.4 Hz, 1H), 6.84-7.25 (m, 17 H), 7.42-7.44 (m, 1H). ¹³C NMR (100 MHz, $CDCl_3$): δ = 41.6, 41.7, 46.5, 48.8, 69.0, 69.1, 74.6, 74.8, 123.5, 124.0, 124.6, 125.7, 126.3, 126.4, 126.5, 126.7, 126.9, 127.1, 127.3, 128.4, 128.6, 140.7, 141.2, 142.3, 142.4, 142.6, 143.7, 168.0, 168.2. HRMS [ESI]: m/z calcd for $C_{34}H_{29}N_2O_2$: 497.2229 (M+H)⁺, found: 497.2229.

4.4. General procedure for asymmetric Diels-Alder reaction

A mixture of Cu(II)(OTf)₂ (5 μmol, 10 mol %) and the ligand **4** (6 μmol,) in dry CH₂Cl₂ (0.2 ml) was stirred for 0.5 h at room temperature under argon. The dienophile (50 μmol in 50 μl CH₂Cl₂) and freshly distilled cyclopentadiene (150 μmol) were then respectively added. The reaction was monitored by TLC and stopped after consumption of the starting substrate. The reaction mixture was purified on silica gel with hexane-ethyl acetate (3:1) to give a mixture of *endo* and *exo* isomers of cycloadducts **9**. The yield was calculated on the basis of the isolated products. The *endo/exo* ratio was determined by ¹H NMR analysis and confirmed by HPLC analysis. The enantiomeric excess of the cycloadduct was determined by chiral HPLC analysis: Daicel Chiralcel OD-H column, hexane-*i*-PrOH, 95:5, flow rate = 1 ml/min, detection: 220 nm. The absolute configuration of the cycloadduct *endo*-**9** product was assigned based upon the comparison of the sign of optical rotation with the literature values: (+) for (R)-**9** and (-) for (S)-**9**.

Supplementary data

Copies of ¹H and ¹³C NMR spectra of bis(hydroxyamide) **3a**, **3a'**, **3b**, **3c**, **3d**, **3e**, **3e'**, **3f** and **6**, copies of ¹H and ¹³C NMR spectra of bis(oxazoline) **4a**, **4a'**, **4b**, **4c**, **4d**, **4e**, **4e'**, **4f** and **7**, HPLC chromatograms of selected Diels-alder reactions, X-ray crystallographic data of ligand **4a**.

Legends

Fig. 1. Structure of various chiral bis(oxazoline) ligands linked with a rigid backbone.

Fig. 2. ¹H NMR study of the epimerization of ligand **7** in CDCl₃

(A) After purification; Time: 1h

(B) Time: 24h

(C) Time: 48h

Fig. 3. ORTEP drawing and atom labeling of ligand **4a**

Fig. 4. Cu(II)-complexes of the four diastereomeric ligands **4** and the correlation between structure of the ligand and configuration of the cycloadduct

Scheme 1. Synthesis of different chiral bis(oxazoline) with a dihydroethanoanthracene backbone.

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