Synthesis of a Novel Unsymmetrical Bisoxazoline Ligand with sp^2 Bridging Carbon

Ruslan Yuryev, Andreas Liese*

Institute of Technical Biocatalysis, Hamburg University of Technology, Denickestr. 15, Hamburg 21073, Germany
Fax +49(40)428782127; E-mail: liese@tuhh.de

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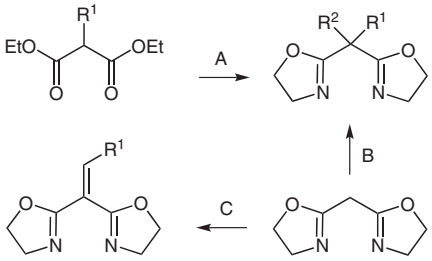
Abstract: A novel unsymmetrical bisoxazoline ligand was synthesized in one step by the Knoevenagel condensation of aldehydes with a C_2-symmetric indane-derived bisoxazoline having two acidic hydrogens connected to the bridging carbon. The electronic properties of incorporated bridge substituent due to π–π conjugation with oxazoline rings can affect the catalytic performance of the ligand in asymmetric syntheses, as was shown for the Henry reaction between benzaldehyde and nitromethane.

Key words: bisoxazoline ligands, asymmetric catalysis, asymmetric synthesis, transition-metal complexes, Henry reaction

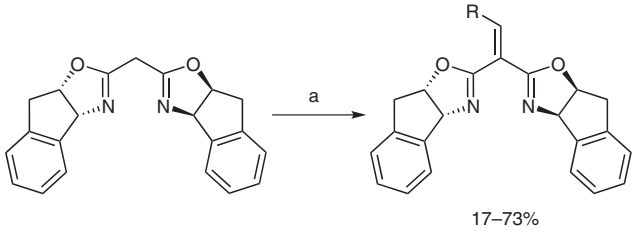
Bisoxazoline (BOX) ligands belong to the class of 'privileged' chiral catalysts, which have been extensively applied in asymmetric organic synthesis in the last decade.[1] The major area of their competence are enantioselective C–C bond formations (e.g., cyclopropanation, aldol- or Michael-type condensation, Diels–Alder cycloaddition) where these ligands show excellent selectivities.[2] Methods for the synthesis of BOX ligands from commercially available precursors are well established and quite versatile allowing 'fine tuning' of the ligand's structure to suit the particular application. Most of the reported synthetic approaches end up with C_2-symmetric structures bearing identical substituents *R* on the bridge carbon. Such symmetrical ligands are the dominant class of BOX-based catalysts used in the chiral transformations. Unsymmetrical BOX catalysts with two different substituents R^1 and R^2 (Scheme 1) are rather rare, but have proved to be very useful for the immobilization of the ligands on polymeric carriers utilizing one of the substituents as a linker.[3]



Scheme 1 Synthetic routes to unsymmetrical BOX ligands

Currently there are two distinct approaches to obtain unsymmetrical BOX ligands. In the first one a monosubstituted malonic acid ester is used as a precursor, which is converted into the desired product by substitution of the bridge hydrogen with a second group and transformation of the ester groups into oxazolines (Scheme 1, route A).[4] This synthetic route is, however, quite long (up to nine intermediate steps) and suffers from low overall yield. An alternative approach utilizes an unsubstituted C_2-symmetrical BOX as a starting material (Scheme 1, route B). In this case the substituents are introduced in two steps by consequent substitution of the two acidic hydrogens connected to the bridge carbon.[5] Although this reaction sequence is significantly shorter, the overall yield of the target compound is also low, because it is difficult to avoid the formation of the C_2-symmetric disubstituted BOX derivative as a byproduct. In order to overcome this problem we decided to remove both bridge hydrogens simultaneously in one step by the Knoevenagel condensation with aldehydes yielding unsymmetrical BOX ligands with an sp^2 bridge carbon (Scheme 1, route C). In principle, such unsymmetrical ligands can be also synthesized by other methods, for example, starting from malonic acid derivatives already having a C=C double bond in the bridge,[6] but the synthetic route proposed herein could have an advantage in the cases when the respective aldehydes and unsubstituted C_2-symmetrical BOX substrates are more accessible than other starting materials.

The new approach was tested in the synthesis of unsymmetrical indane-derived bisoxazoline (IndaBOX) ligands bearing aromatic as well as aliphatic substituents (Scheme 2).[7,8]



Scheme 2 Synthesis of novel unsymmetrical IndaBOX ligands

The isolated yield of the synthesized ligands depended on the nature of the aldehyde (Table 1). The reaction proceeded neatly with benzaldehydes **4** and **5** bearing strong electron-withdrawing substituents, as depicted by their

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Hammet constants.[9] In contrast, for benzaldehydes **2** and **3** the reaction mixtures after 24 hours still contained some unreacted starting material. A similar reactivity order was also observed by Heitler in his study of the Knoevenagel condensation between substituted benzaldehydes and ethyl cyanoacetate.[10]

The condensation of IndaBOX with 4-hydroxybenzaldehyde (entry 6) gave somewhat anomalous results. The product yield was much higher than expected from the Hammet constant for the OH group. Moreover, contrary to other products the ligand **6** obtained was practically insoluble in lower polarity solvents such as dichloromethane or even ethyl acetate. Probably, it reveals that this ligand exists in the form of a zwitterion (Figure 1).

Table 1 Synthesis of Unsymmetrical IndaBOX Ligands

Entry	RCHO	η (%)[a]	σ_p[b]
1	*c*-$C_6H_{11}CHO$	48	–
2	4-$MeOC_6H_4CHO$	24	–0.27
3	4-ClC_6H_4CHO	17	0.23
4	4-NCC_6H_4CHO	60	0.66
5	4-$O_2NC_6H_4CHO$	73	0.78
6	4-HOC_6H_4CHO	62	–0.37
7	4-$OHCC_6H_4CHO$[c]	30	–

[a] Isolated yield.
[b] Hammet constant for *para*-substituent in R.[9]
[c] The condensation product contains two BOX moieties (Figure 2).

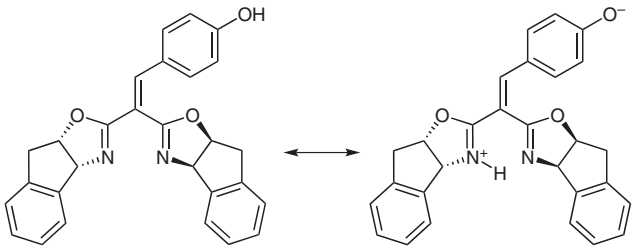


Figure 1 Plausible zwitterionic form of ligand **6**

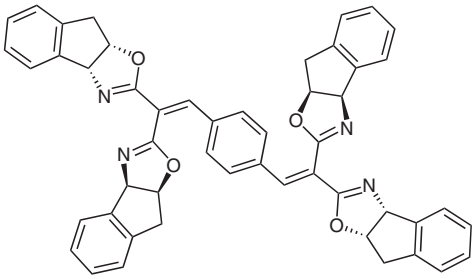


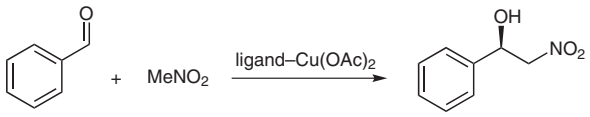
Figure 2 Ligand **7** containing two bisoxazoline moieties

Albeit a simple phenolic OH group ($pK_a = 10$)[9a] is a much weaker acid than the protonated oxazoline ring ($pK_a = 5.5$),[11] militating against formation of such a zwitterion; the gap between the respective pK_a values should be decreased due to π–π conjugation between the electron-releasing *p*-hydroxyphenyl moiety and the two electron-withdrawing oxazoline rings. This rationale is supported by the fact, that other BOX derivatives, which have *p*-hydroxyphenyl groups not conjugated to oxazoline rings, are well soluble in low polarity solvents, such as ethyl acetate or toluene.[4d,12]

The ligand **7** contains two bisoxazoline moieties conjugated with each other via the phenyl ring (Figure 2). This molecule is attractive, not only because of the unusual topology, but also due to its potential application as a recyclable catalyst for asymmetric syntheses, since its bulkiness can facilitate its recovery from reaction mixtures, for instance by means of solvent resistant nanofiltration.[13]

In order to check whether the electronic effects of *p*-substituents on the phenyl group have any influence on catalytic performance of the ligands, the synthesized IndaBOX ligands were complexed with copper(II) acetate[14] and tested as catalysts in the asymmetric nitroaldol (Henry) reaction, in which C_2-symmetric bisoxazolines have been already successfully applied.[15] The condensation between benzaldehyde and nitromethane was chosen as a model system (Table 2). The reactions were carried out either in ethanol or 2-propanol using THF as a co-solvent, because the complexes had limited solubility in these alcohols. The formation of the condensation product (*R*)-2-nitro-1-phenylethanol as well as the ee was followed by HPLC.[16]

Table 2 Condensation of Benzaldehyde and Nitromethane in the Presence of IndaBOX–$Cu(OAc)_2$ Complexes



Ligand	*i*-PrOH–THF (3:2)		EtOH–THF (3:2)	
	ν (mM/h)[a]	ee (%)	ν (mM/h)	ee (%)
1	0.57	54	0.66	34
2	0.27	69	0.29	47
3	0.29	79	0.42	58
4	0.43	82	0.46	73
5	0.46	82	0.50	65
7	0.24	66	0.42	53

[a] Initial reaction rates determined by HPLC analysis; [cat.] = 4 mM, [PhCHO] = 40 mM; [$MeNO_2$] = 3.0 M; 25 °C.

For ligands **2–5** the observed initial reaction rates as well as enantiomeric excess of the resulting β-nitroalcohol were mutually related to the electron-withdrawing power of *p*-substituents. This indicates that these groups, thanks to π–π conjugation, do affect perceptibly the remote cata-

lytic center of the respective BOX ligand. The enhancement of the Henry reaction by electron-withdrawing substituents was expected a priori as a consequence of stabilization of the negatively charged transition structure occurring after the attack on the benzaldehyde carbonyl group by nitromethane anion.[15a,b] The performance of ligand **7** was similar to ligands **2** and **3** pointing out that the bisoxazoline moiety is a weaker electron acceptor compared to CN or NO_2 groups. In 2-propanol all catalysts showed better enantioselectivity, although the reaction rates were practically the same as in ethanol. The analogous solvent effect has been also noticed in the asymmetric Henry reaction catalyzed by C_2-symmetric bisoxazolines.[15a] Contrary to catalysts **2**–**5** the ligand **1**, which had a cyclohexyl group instead of phenyl, showed relative low enantioselectivity exhibiting a comparatively high reaction rate at the same time. It seems probable that the complex between ligand **1** and copper(II) ion has lower stability compared to the others, leading to higher concentration in the reaction mixture of uncomplexed ligand, which promotes parallel unselective reaction and thus decreases the ee value of the condensation product.

In conclusion, the synthesized series of unsymmetrical ligands extends the toolbox of BOX-based chiral catalysts. Due to π–π conjugation such ligands are interesting model systems to study the influence of electronic effects on their catalytic activity. Moreover, thanks to the sp^2 configuration of the bridge carbon they have a ligand bite angle larger than the other known bisoxazolines. This can be an advantage in certain reactions, such as Diels–Alder cycloaddition, where ligands with larger bite angle exhibit higher stereoselectivity.[17] Beside this the synthesis of such unsymmetrical BOX ligands is attractive for immobilization purposes, because it permits a convenient one step procedure to incorporate a linker into the ligand structure. Further studies about application of this type of bisoxazolines in other reactions are under way and will be reported in due course.

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(7) **Representative Procedure for the Synthesis of Ligands 1–7**
IndaBOX (1 mmol), aldehyde (1 mmol), and piperidinium acetate (0.2 mmol) were dissolved in pyridine (5 mL) at 65 °C while stirring. The obtained solution was maintained at the same temperature for 24 h. At the end the solvent is evaporated in vacuo and the solid residue purified by column chromatography on silica using EtOAc as an eluent. For the synthesis of ligand **7** only 0.05 mmol of aldehyde was added, and a EtOAc–MeOH mixture (10:1) was used as an eluent. Ligand **6** was isolated by pouring the reaction mixture into H_2O (50 mL), filtering the precipitate, and washing it on the filter with *i*-PrOH (25 mL) and CH_2Cl_2 (25 mL).

(8) **Characterization Data for Ligands 1–7**
2,2′-(2-Cyclohexylethene-1,1-diyl)bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole) (1)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.37 (m, 2 H), 7.21–7.11 (m, 6 H), 6.43 (d, *J* = 10.0 Hz, 1 H), 5.65 (d, *J* = 7.6 Hz, 1 H), 5.59 (d, *J* = 7.9 Hz, 1 H), 5.32 (ddd, *J* = 7.6, 6.5, 1.2 Hz, 1 H), 5.24 (ddd, *J* = 7.9, 6.7, 1.6 Hz, 1 H), 3.35 (dd, *J* = 18.0, 6.5 Hz, 1 H), 3.32 (dd, *J* = 18.3, 6.7 Hz, 1 H), 3.23–3.13 (m, 2 H), 1.89–1.74 (m, 1 H), 1.47–1.24 (m, 5 H), 0.99–0.58 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 161.1, 151.9, 142.1, 141.8, 139.8, 139.5, 128.4, 128.3, 127.4, 127.3, 125.8, 125.6, 125.2, 125.1, 118.4, 83.2, 83.0, 77.1, 76.7, 39.7, 39.5, 38.6, 31.9, 31.6, 25.6, 25.3, 25.1. MS (EI): *m/z* = 424 [M].
2,2′-[2-(4-Methoxyphenyl)ethene-1,1-diyl]bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole) (2)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.07 (m, 9 H), 6.83–6.67 (m, 2 H), 6.28–6.22 (m, 2 H), 5.75 (d, *J* = 7.7 Hz, 1 H), 5.64 (d, *J* = 7.8 Hz, 1 H), 5.40–5.30 (m, 2 H), 3.63 (s, 3 H), 3.39 (dd, *J* = 18.1, 6.7 Hz, 1 H), 3.36 (dd, *J* = 18.1, 6.7 Hz, 1 H), 3.25 (d, *J* = 17.9 Hz, 1 H), 3.16 (d, *J* = 18.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.2, 160.4, 159.7, 141.0, 139.9, 139.2, 138.8, 130.4, 127.6, 126.8, 126.4, 124.9, 124.8, 124.4, 114.5, 112.6, 82.5, 82.2, 76.3, 76.0, 54.3, 38.6, 38.3. MS (EI): *m/z* = 447 [M – H].
2,2′-[2-(4-Chlorophenyl)ethene-1,1-diyl]bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole) (3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.16 (m, 9 H), 6.80–6.65 (m, 4 H), 5.75 (d, *J* = 7.6 Hz, 1 H), 5.68 (d, *J* = 7.8 Hz, 1 H), 5.36 (ddd, *J* = 7.2, 6.4, 0.9 Hz, 1 H), 5.33 (ddd, *J* = 7.2, 6.4, 1.7 Hz, 1 H), 3.38 (dd, *J* = 17.9, 6.7 Hz, 1 H), 3.32 (dd, *J* = 17.0, 6.1 Hz, 1 H), 3.26 (dd, *J* = 17.4, 1.0 Hz, 1 H), 3.10 (d, *J* = 18.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 160.9, 141.6, 140.7, 140.0, 139.9, 139.7, 135.2, 132.0, 130.5, 128.7, 128.5, 128.3, 127.8, 127.5, 125.9, 125.2, 125.1, 118.9, 83.7, 83.4, 77.3, 76.9, 39.5, 39.1. MS (EI): *m/z* = 451 [M – H].
4-{2,2-Bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazol-2-yl)vinyl}benzonitrile (4)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.16 (m, 9 H), 6.98–6.87 (m, 4 H), 5.72 (d, *J* = 7.6 Hz, 1 H), 5.70 (d, *J* = 7.9 Hz, 1 H), 5.38–5.31 (m, 2 H), 3.39 (dd, *J* = 18.0, 6.7 Hz, 1 H), 3.31 (dd, *J* = 16.6, 6.5 Hz, 1 H), 3.26 (dd, *J* = 17.0, 1.1 Hz, 1 H), 3.05 (d, *J* = 18.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 160.4, 141.4, 140.4, 139.9, 139.6, 139.0, 137.9, 131.7, 129.4, 128.9, 128.6, 127.9, 127.5, 125.9, 125.3, 125.2, 121.8, 118.5, 112.2, 84.0, 83.6, 77.4, 76.9, 39.5, 39.1. MS (EI): *m/z* = 442 [M – H].
2,2′-[2-(4-Nitrophenyl)ethene-1,1-diyl]bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole) (5)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.15 (m, 11 H), 6.98–

6.92 (m, 2 H), 5.72 (d, *J* = 6.4 Hz, 1 H), 5.70 (d, *J* = 6.4 Hz, 1 H), 5.38–5.32 (m, 2 H), 3.39 (dd, *J* = 18.0, 6.7 Hz, 1 H), 3.31 (dd, *J* = 17.9, 6.5 Hz, 1 H), 3.27 (dd, *J* = 18.0, 1.0 Hz, 1 H), 3.06 (d, *J* = 18.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 160.3, 147.4, 141.4, 140.4, 139.9, 139.8, 139.6, 138.7, 129.6, 129.0, 128.7, 127.9, 127.5, 125.9, 125.8, 125.3, 125.2, 123.2, 122.4, 84.1, 83.6, 77.5, 76.9, 39.5, 39.1. MS (EI): *m/z* = 462 [M – H].

4-{2,2-Bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazol-2-yl)vinyl}phenol (6)

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.7 (s, 1 H), 7.38–7.16 (m, 9 H), 6.82–6.75 (m, 2 H), 6.40–6.33 (m, 2 H), 5.65 (d, *J* = 7.7 Hz, 1 H), 5.56 (d, *J* = 7.9 Hz, 1 H), 5.43–5.31 (m, 2 H), 3.40 (dd, *J* = 18.1, 7.0 Hz, 1 H), 3.37 (dd, *J* = 18.0, 6.7 Hz, 1 H), 3.09 (d, *J* = 17.4 Hz, 1 H), 3.05 (d, *J* = 17.8 Hz, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 161.6, 160.1, 159.8, 141.8, 140.6, 140.1, 139.8, 139.6, 131.4, 128.4, 128.2, 127.2, 127.1, 125.4, 125.3, 125.2, 125.1, 123.3, 115.2, 113.5, 82.8, 82.5, 76.3, 76.2, 39.1, 38.8. MS (EI): *m/z* = 433 [M – H].

1,4-Bis{2,2-bis(8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazol-2-yl)vinyl}benzene (7)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.14 (m, 18 H), 6.35 (s, 4 H), 5.71 (d, *J* = 7.7 Hz, 2 H), 5.68 (d, *J* = 7.9 Hz, 2 H), 5.36–5.28 (m, 4 H), 3.39 (dd, *J* = 18.0, 6.6 Hz, 2 H), 3.32–3.22 (m, 4 H), 3.03 (d, *J* = 18.1 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 160.8, 141.7, 140.7, 140.4, 139.9, 139.7, 134.4, 129.0, 128.6, 128.5, 127.7, 127.5, 125.9, 125.8, 125.2, 125.0, 119.0, 83.6, 83.4, 77.3, 76.9, 39.6, 39.1. MS–FAB: *m/z* = 759 [M + H].

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(14) The ligands (1 equiv) were mixed with $Cu(OAc)_2$ (1.5 equiv) in CH_2Cl_2 at r.t. overnight. The uncomplexed salt was removed from the resulting solutions by extraction with H_2O (3×). The organic phases were dried over anhyd Na_2SO_4, the solvent was evaporated in vacuo yielding the complexes as dark solids.

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(16) HPLC conditions used (a) for quantification of 2-nitro-1-phenylethanol and benzaldehyde: RP-8 column (Merck), 30 °C, 67 mM KH_2PO_4–MeOH (65:35), 2 mL/min, 225 nm; (b) for determination of ee of 2-nitro-1-phenylethanol: OD-RH column (Chiralcel), 5 °C, MeOH–H_2O (65:35), 0.2 mL/min, 225 nm.

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