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Efficient one-step synthesis of chiral bidentate oxazoline-alcohol ligands via a cyclic imidate ester rearrangement

Timothy Noël [a], Koen Robeyns [b], Luc Van Meervelt [b], Erik Van der Eycken [c], Johan Van der Eycken [a,*]

[a] *Laboratory for Organic and Bioorganic Synthesis, Department of Organic Chemistry, Ghent University, Krijgslaan 281 (S.4), B-9000 Ghent, Belgium*
[b] *Biomolecular Architecture, Department of Chemistry, K.U. Leuven, Celestijnenlaan 200 F, B-3001 Leuven (Heverlee), Belgium*
[c] *Laboratory for Organic & Microwave-Assisted Chemistry (LOMAC), Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

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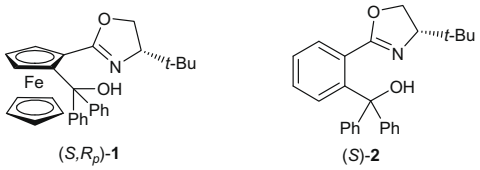
ABSTRACT

Various chiral bidentate oxazoline-alcohol ligands were obtained in a straightforward one-step synthesis via a cyclic imidate ester rearrangement. These chiral ligands were tested and compared in asymmetric diethylzinc additions to aldehydes resulting in selectivities of up to 87% ee. An interesting chirality switch was observed when a CPh_2-tether instead of a CH_2 was present, offering the opportunity for dual stereocontrol.

1. Introduction

The key to successful asymmetric catalysis lies in the careful combination of a suitable ligand with an appropriate metal.[1] The factors determining the success of a ligand are the availability and price of the starting materials, the ease of synthesis, and the possibility to obtain structural variation.[2] A large variety of chiral amino acids are readily available in sufficient quantities from the chiral pool and have been used for the synthesis of chiral oxazoline ligands.[3]

Chiral oxazolines bearing a hydroxyl substituent show excellent catalytic activity in the asymmetric addition of diethylzinc to aldehydes.[4] Bolm et al. studied the role of planar chirality versus central chirality in ferrocene ligands (Fig. 1).[5] The combination of the proper planar chirality and central chirality resulted in a highly active ligand **1**. Remarkably, ligand **2** containing only the central chirality also displays high enantioselectivity and catalytic activity.[5a]



(S,R_p)-**1** (S)-**2**

Figure 1. Examples of bidentate oxazoline-alcohol ligands.

It is known that the synthesis of oxazolines can be efficiently performed via reaction of an aminoalcohol and an imidate. As a result, substituents at C-2 of the oxazoline moiety can be readily incorporated.[6] Very recently, we discovered a method to synthesize chiral imidate ligands starting from cyclic imidate ester 3A.[7] In the present paper, we describe the use of this imidate in an efficient one-step reaction to synthesize analogues of **2** bearing a CH_2– instead of a CPh_2-tether. The newly synthesized ligands were tested and compared in the asymmetric diethylzinc addition to benzaldehydes.

2. Results and discussion

Condensation of imidate esters **3A–C** with several aminoalcohols **4a–f** resulted in the corresponding oxazoline ligands **6** or imidate ligands **5** (Table 1) (Fig. 2). No formation of the imidate alcohols was observed for (1*S*,2*R*)-*cis*-1-amino-2-indanol **4a**, (*S*)-*tert*-leucinol **4b,** and (*S*)-valinol **4c**: the oxazoline-alcohol was obtained in quantitative yield (Table 1, entries 1–3). However, with (*S*)-phenylglycinol **4d** and (*S*)-phenylalaninol **4e** a mixture of imidate alcohol and oxazoline-alcohol was formed, indicating only a small free energy difference between both products (entries 4 and 5).[8] Separation of the two components via preparative HPLC was not possible, suggesting a rapid equilibration. With (1*R*,2*R*)-*trans*-1-amino-2-indanol **4f**, it was possible to selectively form the imidate alcohol (entry 6).[7] The condensation of the substituted imidate esters **3B–C** with aminoalcohol **4a** similarly resulted in the corresponding oxazoline ligands **6aB–6aC** in good yield (entries 7 and 8).

Introduction of substituents on the imidate ester starts from the commercially available substituted 2-methylbenzonitriles (Scheme 1). A Wohl–Ziegler reaction with NBS (1.1 equiv) afforded the desired monobromide **8B–C**. However, formation of a certain amount (up to 24%) of dibromide **9B–C** could not be prevented. This

* Corresponding author. Tel.: +32 9 264 44 80; fax: +32 9 264 49 98.
E-mail address: Johan.Vandereycken@UGent.be (J.V.d. Eycken).

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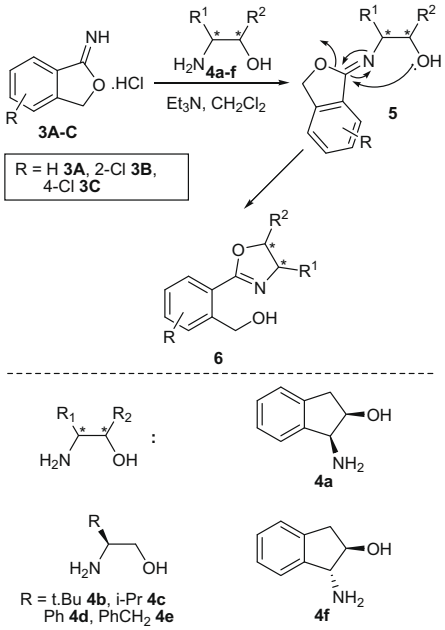
Table 1
Synthesis of imidates **5** and oxazolines **6**



Entry	Imidate ester	Aminoalcohol **4**	Yield oxazoline **6**[a] (%)	Yield imidate **5**[a] (%)
1	**3A**	(1*S*,2*R*)-*cis*-1-Amino-2-indanol **4a**	Quant. **6aA**	[b]
2	**3A**	(*S*)-*tert*-Leucinol **4b**	Quant. **6bA**	[b]
3	**3A**	(*S*)-Valinol **4c**	Quant. **6cA**	[b]
4[c]	**3A**	(*S*)-2-Phenylglycinol **4d**	51.7 **6dA**	48.3 **5dA**
5[c]	**3A**	(*S*)-Phenylalaninol **4e**	69.1 **6eA**	30.9 **5eA**
6	**3A**	(1*R*,2*R*)-*trans*-1-Amino-2-indanol **4f**	[b]	91 **5fA**
7	**3B**	**4a**	83 **6aB**	[b]
8	**3C**	**4a**	66 **6aC**	[b]

[a] Isolated yield.
[b] n.d.: not detected.
[c] An inseparable mixture of imidate and oxazoline is formed.

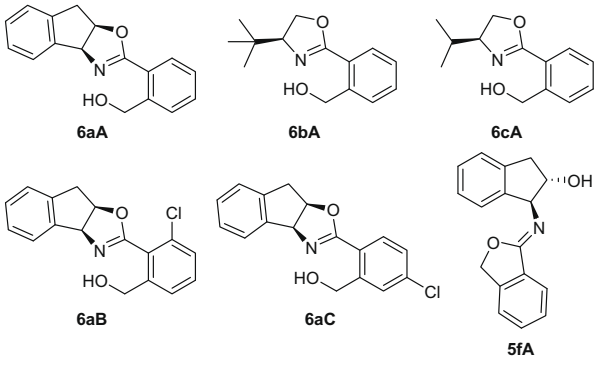
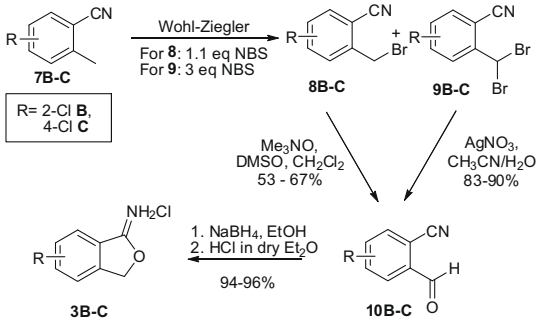


Figure 2. Oxazoline and imidate ligands synthesized.

resulted in lower yields (57–82%) and a difficult separation. Moreover, low yields were obtained in the oxidation of the monobromide with Me_3NO. In contrast, reaction of **7** with 3 equiv of NBS resulted selectively in the dibrominated product **9** in excellent yield (94–98%). Hydrolysis of **9** with $AgNO_3$ in CH_3CN/H_2O afforded **10** in very high yields. The formation of imidate ester **3B–C** occurred nicely via our recently optimized method:[7] treatment of aldehyde **10** with

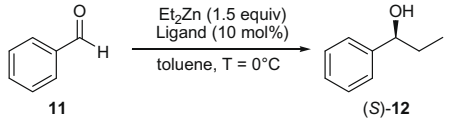


Scheme 1. Synthesis of substituted imidate esters **3B–C**.

$NaBH_4$ resulted in immediate formation of the imidate which was isolated as a crystalline HCl salt.

The synthesized ligands were tested and compared in the asymmetric diethylzinc addition to benzaldehyde **11** (Table 2).[9]

Table 2
Asymmetric addition of diethylzinc to benzaldehyde in the presence of N,O-ligands



Entry	Ligand	Time (h)	Yield[a] (%)	% ee[b]	Configuration[c]
1	**6aA**	48	69	85	*S*-(−)
2	**6bA**	48	31	55	*S*-(−)
3	**6cA**	48	60	44	*S*-(−)
4[d]	**5fA**	24	14	36	*S*-(−)
5	**6aB**	48	25	15	*S*-(−)
6	**6aC**	48	66	79	*S*-(−)

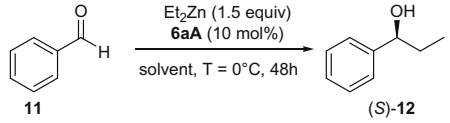
[a] Isolated yield.
[b] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel OD–H).
[c] Assigned by the sign of the specific rotation.
[d] Reaction performed at room temperature.

The best result was obtained with **6aA** as a chiral ligand (69% yield, 85% ee) (Table 2, entry 1). Less bulky groups on the oxazoline ring result in a lower selectivity (Table 2, entries 2 and 3). When performed with the imidate alcohol **5fA** as a chiral ligand, the reaction was sluggish and a low enantioselectivity was observed (Table 2, entry 4). Surprisingly, when the reaction was performed with ligand **6aB**, containing a chlorine substituent in the *ortho*-position, **12** was obtained in a low yield and an enantioselectivity (Table 2, entry 5). In contrast, ligand **6aC**, bearing a chlorine in the *para*-position of the oxazoline substituent, afforded a yield and a selectivity which were only slightly lower than those with **6aA** (Table 2, entry 6).

With **6aA** as our best ligand, we tried to optimize the reaction parameters (Table 3). Addition of $Ti(^iOPr)_4$ resulted in a higher yield but a lower selectivity (Table 3, entry 1). In the presence of $Ti(^iOPr)_4$ and *n*-BuLi, the reaction was rather unselective (Table 3, entry 2). When the reaction was performed with only *n*-BuLi to deprotonate the ligand, the yield and the selectivity did not improve (Table 3, entry 3). Varying the solvent had no beneficial effect as compared to our initial experiment (Table 3, entries 4–7).

Next, a variety of substituted arylaldehydes were submitted (Table 4) to the optimized conditions of Table 2 (entry 1). In general, lower yields and selectivities were obtained in comparison

Table 3
Asymmetric addition of diethylzinc to benzaldehyde in the presence of **6aA** as a chiral ligand



Entry	Solvent	Additive[a]	Yield[b] (%)	% ee[c]
1	Toluene	$Ti(^iOPr)_4$	82	55
2	Toluene	$Ti(^iOPr)_4$/*n*-BuLi	57	9
3	Toluene	*n*-BuLi	46	63
4	*n*-Hexane	/	13	29
5	CH_2Cl_2	/	36	73
6	THF	/	9	81
7	Et_2O	/	58	84

[a] The additives were added in an equimolar amount relative to the ligand.
[b] Isolated yield.
[c] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel OD–H).

with those of unsubstituted benzaldehyde. The best result was obtained with 2-naphthaldehyde (Table 4, entry 4).

Table 4
Asymmetric addition of diethylzinc to several arylaldehydes in the presence of **6aA** as chiral ligand

Entry	Arylaldehyde	Yield[a] (%)	% ee[b]	Configuration[c]
1	2-Cl-Benzaldehyde	57	55	(*S*)-(−)
2	3-Cl-Benzaldehyde	46	74	(*S*)-(−)
3	4-Cl-Benzaldehyde	24	62	(*S*)-(−)
4	2-Naphthaldehyde	52	87	(*S*)-(−)
5	*trans*-Cinnamaldehyde	32	61	(*S*)-(−)

[a] Isolated yield.
[b] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel AD–H, OB–H, and OD–H), see Section 4.
[c] Assigned by the sign of the specific rotations.

Suitable crystals for X-ray diffraction analysis were grown from a solution of **6aA** in isooctane/Et_2O. An X-ray structure was obtained, and is shown in Figure 3. The hydroxyl proton forms a hydrogen bond with the nitrogen of the oxazoline moiety. As a result, a stable seven-membered ring chelate is formed.

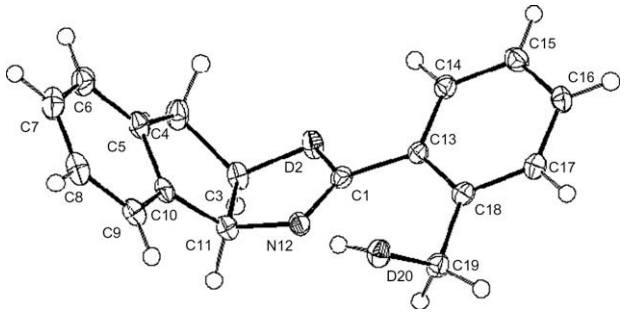
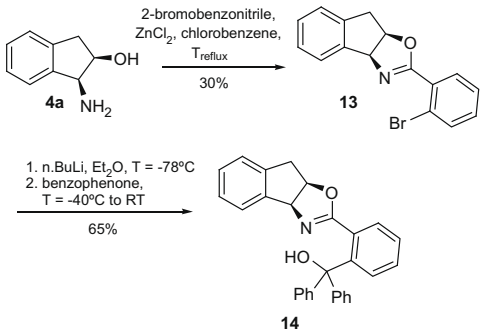


Figure 3. X-ray structure of **6aA**.

Remarkably, with (*S*)-**6bA** as the ligand we obtained (*S*)-**12** with an ee of 55% (Table 2, entry 2), with the related (*S*)-**2** as a ligand. Bolm et al. reported formation of the opposite enantiomer (*R*)-**12** with 92% ee.[5a] In order to verify if this chirality switch also holds for other ligands, we synthesized (1*S*,2*R*)-**14** as an analogue of (1*S*,2*R*)-**6aA** with a CPh_2-tether (Scheme 2). When the diethylzinc addition was performed in the presence of **14**, indeed the opposite enantiomer (*R*)-(**12**) was obtained in 86% yield, but with only 22% ee.

Clearly, this chirality switch is caused by the presence of the two phenyl substituents, as the absolute configuration of the ligand remained unchanged. Similar effects have been reported in other papers and are known as 'dual stereocontrol'.[10,11] Furthermore, in the case of the indane-fused oxazolines **6aA** and **14**, increasing the steric bulk of the tether resulted in a lower enantioselectivity. In contrast, when the chiral substituent on the oxazoline moiety was a *t*-butyl-substituent, higher enantioselectivities were obtained with a bulky phenyl-substituted tether.[5a] This effect, together with the dual stereocontrol, suggests that the introduction of the phenyl substituents modifies the catalytic mechanism or the structure of the catalytic site.[10,11]



Scheme 2. Synthesis of the analogue **14** of **6aA** with a CPh_2-tether.

3. Conclusion

In conclusion, we have successfully developed a one-step synthesis of chiral bidentate CH_2-tethered oxazoline-alcohol ligands via a cyclic imidate ester rearrangement. Application of the ligands in the diethylzinc addition to arylaldehydes resulted in good enantioselectivities (up to 87% ee). We have also shown that the presence of a CPh_2-tether causes a chirality switch, offering the opportunity for tuning the enantioselectivity via dual stereocontrol.

4. Experimental

4.1. General

All reactions were carried out under argon atmosphere in dry solvents under anhydrous conditions, unless otherwise stated. Benzaldehyde was passed through basic alumina. All other reagents were purchased and used without purification, unless otherwise noted. Analytical TLC was performed using Machery-Nagel SIL G-25 UV_{254} plates. Flash chromatography was carried out with Rocc silicagel (0.040–0.063 mm). ^1H NMR and ^{13}C NMR were recorded on a Bruker Avance 300 or a Bruker AM 500 spectrometer as indicated, with chemical shifts reported in ppm relative to TMS, using the residual solvent signal as a standard. ^{13}C NMR spectra were recorded using the attached proton test. IR-spectra were recorded on a Perkin–Elmer spectrum 1000 FT-IR spectrometer with a Pike Miracle HATR module. EI Mass spectra were recorded with a Hewlett–Packard 5988A mass spectrometer. LC–MS analysis was performed on an Agilent 1100 series HPLC with quaternary pump, DAD, and single quadrupole MS detector type VL with an API-ES source, using a Phenomenex Luna C18(2) column (250 × 4.6 mm, particle size 5 μm). Analytical chiral HPLC separations were performed on an Agilent 1100 series HPLC system with DAD detection. Exact molecular masses were measured on a Kratos MS50TC mass spectrometer. Melting points were measured with a Kofler melting point apparatus.

4.2. A typical procedure for the preparation of the substituted 2-(bromomethyl)benzonitriles

4.2.1. Synthesis of 2-chloro-6-(bromomethyl)benzonitrile 8B

A solution of 2-chloro-6-methylbenzonitrile **7B** (4.83 g, 31.9 mmol), NBS (6.24 g, 35.1 mmol), and benzoylperoxide (232.0 mg, 0.96 mmol) in CCl_4 (100 mL) was refluxed for 7 h. Afterwards, the solids are filtered off and the filtrate was concentrated in vacuo. The crude product was purified by flash chromatography over silicagel (pentane/Et_2O, 90/10) resulting in pure **8B**, 4.35 g (82%). No formation of the dibromo product **9B** was observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.60 (s, 2H), 7.43–7.54 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.9 (CH_2), 113.4 (C), 113.9 (C), 128.5 (CH), 129.7 (CH), 133.7 (CH), 137.7 (C), 143.4 (C). IR (HATR): 3070, 3025, 2227, 1588, 1567, 1455, 1443, 1264, 1219, 1203, 1180, 1155, 1117, 988, 905, 796, 780, 737, 628, 609 cm^{-1}. EI-MS *m*/*z* (rel. intensity%): 231 (M^+, 10), 229 (M^+, 8), 152 (33), 150 (100), 123 (27), 114 (22), 81 (18), 79 (18), 63 (21), 50 (14). Mp: 83 °C. HRMS (EI) calcd for $C_8H_5N^{35}Cl^{79}Br$: 228.9294; found 228.9307.

4.2.2. Synthesis of 2-(bromomethyl)-4-chlorobenzonitrile 8C

The reaction was performed on 4-chloro-2-methylbenzonitrile **7C** (2.0 g, 13.2 mmol) according to the typical procedure. The crude product was purified by flash chromatography over silicagel (pentane/Et_2O, 96/4) resulting in pure **8C**, 1.74 g (57%). Formation of the dibromo product **9C** was also observed, 0.97 g (24%). For **8C**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.57 (s, 2H), 7.39 (dd, J = 2.0, 8.3 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.2 (CH_2), 110.8 (C), 116.0 (C), 129.4 (CH), 130.8 (CH), 134.2 (CH), 139.7 (C), 142.8 (C). IR (HATR): 3080, 3035, 2224, 1592, 1564, 1480, 1438, 1404, 1284, 1230, 1222, 1180, 1105, 1080, 900, 882, 827, 742, 726, 630, 618 cm^{-1}. EI-MS *m*/*z* (rel. intensity%): 233 (M^+, 25), 231 (M^+, 100), 229 (M^+, 77), 203 (9), 152 (6), 150 (18), 114 (66), 87 (31), 63 (35). Mp: 78 °C. HRMS (EI) calcd for $C_8H_5N^{35}Cl^{79}Br$: 228.9294; found 228.9287.

4.3. A typical procedure for the preparation of the substituted 2-(dibromomethyl)benzonitriles

Compounds **9B** and **9C** were synthesized according to a literature procedure.[12]

4.3.1. Synthesis of 2-chloro-6-(dibromomethyl)benzonitrile 9B

A solution of 2-chloro-6-methylbenzonitrile **7B** (9.91 g, 65.4 mmol), NBS (35.22 g, 197.9 mmol), and benzoylperoxide (534.0 mg, 2.2 mmol) in CCl_4 (100 mL) was refluxed overnight. Afterwards, the solids were filtered off and the filtrate was concentrated in vacuo. The crude product was purified by flash chromatography over silicagel (hexane/EtOAc, 95/5) resulting in pure **9B**, 19.04 g (94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96 (s, 1H), 7.49 (dd, J = 0.8, 8.1 Hz, 1H), 7.62 (t, J = 8.1 Hz, 1H), 7.94 (dd, J = 0.8, 8.1 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 35.0 (CH), 109.5 (C), 113.1 (C), 128.0 (CH), 130.6 (CH), 134.1 (CH), 136.9 (C), 146.3 (C). IR (HATR): 3076, 3008, 2232, 1589, 1567, 1454, 1439, 1292, 1251, 1238, 1174, 1140, 1134, 891, 796, 779, 735, 651, 633 cm^{-1}. EI-MS *m*/*z* (rel. intensity%): 309 (M^+, 2), 232 (25), 230 (100), 228 (74), 149 (14), 114 (39), 87 (17), 74 (9), 63 (16), 50 (13). Mp: 120 °C. HRMS (EI) calcd for $C_8H_4N^{35}Cl^{79}Br_2$: 306.8399; found 306.8386.

4.3.2. Synthesis of 4-chloro-2-(dibromomethyl)-benzonitrile 9C

The reaction was performed on 4-chloro-2-methylbenzonitrile (9.80 g, 64.6 mmol) according to the typical procedure. The crude product was purified by flash chromatography over silicagel (hexane/EtOAc, 95/5) resulting in pure **9B**, 19.55 g (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (s, 1H), 7.41 (dd, J = 2.0, 8.4 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 2.0, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 34.3 (CH), 106.9 (C), 115.2 (C), 130.4 (CH), 130.6 (CH), 133.5 (CH), 140.5 (C), 145.9 (C). IR (HATR): 3080, 3058, 3028, 3004, 2359, 2227, 1589, 1556, 1481, 1462, 1404, 1304, 1279, 1206, 1170, 1138, 1114, 1081, 902, 820, 742, 689, 649, 622 cm^{-1}. EI-MS *m*/*z* (rel. intensity%): 309 (M^+, 2), 232 (25), 230 (100), 228 (73), 149 (16), 114 (47), 87 (20), 74 (10), 63 (20), 50 (15). Mp: 120 °C. HRMS (EI) calcd for $C_8H_4N^{35}Cl^{79}Br_2$: 306.8399; found 306.8386.

4.4. A typical procedure for the preparation of the substituted 2-formylbenzonitriles

Compounds **10B** and **10C** were synthesized according to a literature procedure.[12]

4.4.1. Synthesis of 2-chloro-6-formylbenzonitrile 10B

To a solution of **9B** (18.0 g, 58.2 mmol) in CH_3CN (60 mL) was added a solution of $AgNO_3$ (39.5 g, 233 mmol) in H_2O (32 mL). The resulting yellow suspension was refluxed for 20 min. The solids were filtered off and washed with CH_2Cl_2 (150 mL). The combined filtrate was washed with H_2O (25 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash chromatography over silicagel (hexane/EtOAc, 2/1) resulting in pure **10B**, 8.67 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (t, J = 7.9 Hz, 1H), 7.79 (dd, J = 1.2, 7.9 Hz, 1H), 7.94 (dd, J = 1.2, 7.9 Hz, 1H), 10.31 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 112.9 (C), 114.4 (C), 127.5 (CH), 133.8 (CH), 134.9 (CH), 138.5 (C), 139.0 (C), 187.6 (CH). IR (HATR): 3069, 2865, 2221, 1697, 1584, 1566, 1443, 1395, 1291, 1224, 1195, 1182, 1155, 922, 798, 781, 726, 675 cm^{-1}. EI-MS *m*/*z* (rel. intensity%): 167 (5); 165 (15), 139 (33), 137 (100), 110 (24), 101 (44), 84 (13), 75 (79), 61 (23), 50 (45). Mp: 140 °C. HRMS (EI) calcd for $C_8H_4NO^{35}Cl$: 164.9981; found 164.9969.

4.4.2. Synthesis of 4-chloro-2-formyl-benzonitrile 10C

The reaction was performed on **9C** (18.07 g, 58.4 mmol) according to the typical procedure. The crude product was purified by flash chromatography over silicagel (hexane/EtOAc, 9/1) resulting in pure **10C**, 8.04 g (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (dd, J = 2.0, 8.3 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 8.00 (d, J = 2.0 Hz, 1H), 10.31 (s, 1H). ^{13}C NMR (75.4 MHz, C_6D_6): δ 111.9 (C), 115.2 (C), 129.2 (CH), 133.3 (CH), 134.6 (CH), 138.0 (C), 139.3 (C), 186.2 (CH). IR (HATR): 3101, 3069, 2871, 2226, 1698, 1584, 1558, 1485, 1376, 1294, 1203, 1119, 1099, 897, 839, 744, 702, 620 cm^{-1}. EI-MS *m*/*z* (rel. intensity%): 167 (10); 165 (29), 139 (33), 137 (100), 110 (26), 102 (44), 100 (33), 75 (55), 61 (16), 50 (39). Mp: 119 °C. HRMS (EI) calcd for $C_8H_4NO^{35}Cl$: 164.9981; found 164.9988.

4.5. A typical procedure for the preparation of imidate esters

4.5.1. Synthesis of 1,3-dihydro-iminoisobenzofuran hydrochloride 3A

2-Formylbenzonitrile (7.0 g, 53.4 mmol) was dissolved in absolute ethanol (420 mL) and cooled to −78 °C. $NaBH_4$ (2.02 g, 53.4 mmol) was added and the reaction mixture was allowed to warm to 0 °C over 30 min. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2 (3 × 1000 mL). The organic phases were dried over Na_2SO_4 and concentrated in vacuo. The resulting orange oil was dissolved in dry CH_2Cl_2 (165 mL) and dry HCl in Et_2O (65 mL) was added. The resulting suspension was filtrated and the white crystals were washed with dry THF. This resulted in 8.3 g (92%) of imidate ester hydrochloride **3A**. ^{1}H NMR (300 MHz, CD_3OD) δ 5.99 (s, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.84 (d,

J = 7.8 Hz, 1H), 7.98 (t, J = 7.8 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H). ^{13}C NMR (75.4 MHz, CD_3OD): δ 81.0 (CH_2), 123.9 (CH), 124.6 (C), 126.5 (CH), 131.1 (CH), 138.1 (CH), 148.9 (C), 178.4 (C). IR (HATR): 3422, 3357, 3062, 3036, 2924, 2806, 2717, 2628, 1676, 1617, 1592, 1560, 1486, 1446, 1330, 1318, 1222, 1080, 938, 794, 739 cm^{-1}. EI-MS m/z (rel. intensity%): 133 ((M$^+$−HCl), 50), 104 (100), 89 (15), 77 (44), 63 (14), 51 (20), 43 (7). ES-MS: 134 [M−Cl$^-$]$^+$. Mp: decomposition. HRMS (EI) calcd for C_8H_7NO: 133.0528; found 133.0533.

4.5.2. Synthesis of 7-chloro-1,3-dihydro-imino-isobenzofuran hydrochloride 3B

The reaction was performed on 2-chloro-6-formylbenzonitrile **10B** (2.0 g, 12.1 mmol) according to the typical procedure resulting in 2.32 g (94%) of imidate ester hydrochloride **3B**. ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.93 (s, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.94 (t, J = 7.8 Hz, 1H). ^{13}C NMR (75.4 MHz, DMSO-d_6): δ 78.0 (CH_2), 121.1 (C), 121.8 (CH), 130.3 (CH), 130.5 (C), 137.9 (CH), 150.3 (C), 173.6 (C). IR (HATR): 3053, 2936, 2861, 2706, 2628, 2545, 2436, 1662, 1610, 1582, 1524, 1474, 1430, 1408, 1322, 1306, 1228, 1196, 1156, 1132, 1060, 1042, 919, 857, 792, 763, 727, 654 cm^{-1}. EI-MS m/z (rel. intensity%): 169 (M$^+$,11), 167 (M$^+$, 33), 140 (33), 138 (100), 111 (10), 102 (47), 89 (74), 75 (69), 63 (42), 50 (50), 43 (19). ES-MS: 168 [M−Cl$^-$]$^+$. Mp: decomposition. HRMS (EI) calcd for $C_8H_6NO^{35}Cl$: 167.0138; found 167.0153.

4.5.3. Synthesis of 5-chloro-1,3-dihydro-imino-isobenzofuran hydrochloride 3C

The reaction was performed on 2-formyl-5-chlorobenzonitrile **10C** (2.0 g, 12.1 mmol) according to the typical procedure resulting in 2.38 g (96%) of imidate ester hydrochloride **3C**. ^{1}H NMR (300 MHz, CD_3OD) δ 5.94 (s, 2H), 7.79 (dd, J = 0.9, 8.5 Hz, 1H), 7.88 (d, J = 0.9 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H). ^{13}C NMR (75.4 MHz, CD_3OD): δ 80.5 (CH_2), 123.7 (C), 124.4 (CH), 127.8 (CH), 131.8 (CH), 144.7 (C), 150.7 (C), 177.6 (C). IR (HATR): 2801, 1671, 1643, 1613, 1586, 1545, 1464, 1447, 1417, 1310, 1290, 1212, 1173, 1119, 1082, 1067, 943, 894, 864, 855, 834, 790, 774, 752, 660 cm^{-1}. EI-MS m/z (rel. intensity%): 169 (M$^+$, 16), 167 (M$^+$, 48), 140 (33), 138 (100), 132 (20), 111 (20), 102 (44), 89 (21), 75 (60), 63 (36), 50 (86), 43 (21). ES-MS: 168 [M−Cl$^-$]$^+$. Mp: decomposition. HRMS (EI) calcd for $C_8H_6NO^{35}Cl$: 167.0138; found 167.0143.

4.6. A typical procedure for the preparation of oxazoline-alcohol ligands 6

4.6.1. Synthesis of 2-(2′-hydroxymethyl)phenyl-(3a*S*,8a*R*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazoline 6aA

A suspension of (1*S*,2*R*)-(−)-*cis*-1-amino-2-indanol (788.0 mg, 5.28 mmol) and imidate ester **3A** (1.0 g, 5.90 mmol) in CH_2Cl_2 (40 mL) was cooled in an ice bath. Et_3N (2.24 mL, 16.1 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. Evaporation in vacuo, purification by flash chromatography over silicagel (hexane/EtOAc, 2/1), and finally recrystallization from hexane/CH_2Cl_2 resulted in **6aA** as a white solid, 1.40 g (quant.). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.42 (d, J = 17.8 Hz, 1H), 3.56 (dd, J = 6.6, 17.8 Hz, 1H), 4.61 (d, J = 5.0 Hz, 1H), 4.64 (d, J = 5.0 Hz, 1H), 5.52 (m, 1H), 5.83 (d, J = 7.8 Hz, 1H), 6.56 (m, 1H), 7.27–7.47 (m, 6H), 7.51–7.57 (m, 1H), 7.86–7.92 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 39.6 (CH_2), 64.6 (CH_2) 76.6 (CH), 83.0 (CH), 125.3 (CH), 125.4 (CH), 126.5 (C), 127.6 (CH), 127.7 (CH), 128.7 (CH), 130.2 (CH), 130.5 (CH), 131.6 (CH), 139.4 (C), 141.7 (C), 142.2 (C), 164.2 (C). IR (HATR): 3202, 2931, 1633, 1599, 1577, 1461, 1445, 1421, 1353, 1293, 1237, 1205, 1169, 1137, 1061, 1018, 998, 968, 956, 858, 785, 778, 755, 709, 691 cm^{-1}. EI-MS m/z (rel. intensity%): 265 (M$^+$, 11), 133 (27), 116 (100), 115 (46), 89 (13), 77 (36), 51 (12). ES-MS: 266 [M+H]$^+$. $[\alpha]_D^{20} = -178.5$ (c 1.02, $CHCl_3$). Mp: 162 °C. HRMS (EI) calcd for $C_{17}H_{15}NO_2$: 265.1103; found 265.1104.

4.6.2. Synthesis of (*S*)-2-(2′-hydroxymethyl)phenyl-4-*tert*-butyloxazoline 6bA

The reaction was performed on (*S*)-*tert*-leucinol (95.0 mg, 0.81 mmol) according to the typical procedure. The crude product was purified by flash chromatography over silicagel (CH_2Cl_2/MeOH, 98/2) resulting in pure **6bA**, 189.0 mg (quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (s, 9H), 4.15 (dd, J = 8.0, 10.1 Hz, 1H), 4.25 (dd, J = 8.0, 8.5 Hz, 1H), 4.39 (dd, J = 8.5, 10.1 Hz, 1H), 4.60 (d, J = 12.3 Hz, 1H), 4.73 (d, J = 12.3 Hz, 1H), 6.82 (br s, 1H), 7.32–7.47 (m, 3H), 7.85 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 25.8 (CH_3), 33.7 (C), 64.7 (CH_2), 68.4 (CH_2), 76.1 (CH), 126.6 (C), 127.6 (CH), 130.0 (CH), 130.3 (CH), 131.4 (CH), 142.2 (C), 163.7 (C). IR (HATR): 3236, 2960, 2905, 2868, 1638, 1573, 1478, 1449, 1396, 1364, 1342, 1312, 1304, 1262, 1214, 1201, 1138, 1076, 1050, 1024, 971, 948, 785, 746, 700 cm^{-1}. EI-MS m/z (rel. intensity%): 233 (M$^+$, 44), 204 (12), 176 (72), 158 (50), 146 (15), 133 (100), 130 (20), 119 (32), 105 (58), 91 (36), 77 (62), 69 (26), 57 (41), 41 (80). ES-MS: 234 [M+H]$^+$. $[\alpha]_D^{20} = -26.6$ (c 0.94, $CHCl_3$). Mp: <50 °C. HRMS (EI) calcd for $C_{14}H_{19}N_2O_2$: 233.1416; found 233.1414.

4.6.3. Synthesis of (*S*)-2-(2′-hydroxymethyl)phenyl-4-*i*-propyloxazoline 6cA

The reaction was performed on L-valinol (116.8 mg, 1.13 mmol) according to the typical procedure. The crude product was purified by flash chromatography over silicagel (hexane/EtOAc, 70/30) resulting in pure **6cA**, 248.0 mg (quant.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (d, J = 6.7 Hz, 3H), 1.03 (d, J = 6.7 Hz, 3H), 1.83 (sept, J = 6.7 Hz, 1H), 4.11–4.21 (m, 2H), 4.41–4.50 (m, 1H), 4.62 (dd, J = 6.0, 12.3 Hz, 1H), 4.69 (dd, J = 4.8, 12.3 Hz, 1H), 6.78 (dd, J = 4.8, 6.0 Hz, 1H), 7.32–7.46 (m, 3H), 7.86 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 18.6 (CH_3), 18.7 (CH_3), 33.0 (CH), 64.7 (CH_2), 70.2 (CH_2), 72.6 (CH), 126.7 (C), 127.7 (CH), 130.1 (CH), 130.4 (CH), 131.5 (CH), 142.2 (C), 163.8 (C). IR (HATR): 3221, 2960, 2900, 2868, 1637, 1598, 1573, 1466, 1446, 1349, 1322, 1310, 1254, 1198, 1061, 1047, 1024, 963, 946, 781, 750, 711 cm^{-1}. EI-MS m/z (rel. intensity%): 219 (M$^+$, 40), 190 (10), 188 (6), 176 (32), 158 (21), 146 (9), 133 (100), 119 (19), 105 (54), 91 (26), 77 (47), 65 (6), 51 (16), 41 (39). ES-MS: 220 [M+H]$^+$. $[\alpha]_D^{20} = -42.9$ (c 0.99, $CHCl_3$). Mp: <50 °C. HRMS (EI) calcd for $C_{13}H_{17}NO_2$: 219.1259; found 219.1259.

4.6.4. Synthesis of 2-(2′-hydroxymethyl-6′-chloro)phenyl-(3a*S*,8a*R*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazoline 6aB

A suspension of (1*S*,2*R*)-(−)-*cis*-1-amino-2-indanol (100.0 mg, 0.67 mmol) and imidate ester **3B** (150.0 mg, 0.74 mmol) in CH_2Cl_2 (5 mL) was cooled in an ice bath. Et_3N (0.28 mL, 2.0 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. Evaporation in vacuo, purification by flash chromatography over silicagel (CH_2Cl_2/MeOH, 98/2), and finally recrystallization from hexane/CH_2Cl_2 resulted in **6aB** as a white solid, 165.1 mg (83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41–3.49 (dd, J = 1.8, 17.9 Hz, 1H), 3.50–3.60 (dd, J = 6.1, 17.9 Hz, 1H), 4.14–4.20 (dd, J = 6.2, 12.5 Hz, 1H), 4.25–4.33 (dd, J = 8.1, 12.5 Hz, 1H), 4.69 (dd, J = 6.2, 8.1 Hz, 1H), 5.60 (ddd, J = 1.8, 6.1, 7.7 Hz, 1H), 5.77 (d, J = 7.7 Hz, 1H), 7.23–7.37 (m, 6H), 7.52–7.57 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 39.3 (CH_2), 63.5 (CH_2), 76.1 (CH), 84.2 (CH), 125.2 (CH), 125.3 (CH), 127.3 (C), 127.7 (CH), 128.7 (CH), 129.4 (CH), 131.4 (CH), 133.8 (C), 139.3 (C), 141.3 (C), 143.3 (C), 163.1 (C). IR (HATR): 3179, 1652, 1478, 1458, 1444, 1420, 1358, 1328, 1292, 1240, 1176, 1150, 1098, 1078, 1049, 991, 853, 777, 758, 730, 714, 642 cm^{-1}. EI-MS m/z (rel. intensity%): 301 (M$^+$, 2), 299 (M$^+$, 7), 167 (12), 131 (10), 116 (100), 104 (19), 77 (32), 63 (11).

ES-MS: 300 [M+H]$^+$. $[\alpha]_D^{20} = -209.5$ (c 0.93, $CHCl_3$). Mp: 158 °C. HRMS (EI) calcd for $C_{17}H_{14}NO_2{}^{35}Cl$: 299.0713; found 299.0719.

4.6.5. Synthesis of 2-(2′-hydroxymethyl-4′-chloro)phenyl-(3a*S*,8a*R*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazoline 6aC

A suspension of (1*S*,2*R*)-(−)-*cis*-1-amino-2-indanol (100.0 mg, 0.67 mmol) and imidate ester **3C** (150.0 mg, 0.74 mmol) in CH_2Cl_2 (5 mL) was cooled in an ice bath. Et_3N (0.28 mL, 2.0 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. Evaporation in vacuo, purification by flash chromatography over silicagel (CH_2Cl_2/MeOH, 99/1), and finally recrystallization from hexane/CH_2Cl_2 resulted in **6aB** as white needles, 131.2 mg (66%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (dd, J = 1.3, 17.9 Hz, 1H), 3.53 (dd, J = 6.5, 17.9 Hz, 1H), 4.53 (dd, J = 7.3, 12.5 Hz, 1H), 4.58 (dd, J = 7.4, 12.5 Hz, 1H), 5.49 (ddd, J = 1.3, 6.5, 7.9 Hz, 1H), 5.79 (d, J = 7.9 Hz, 1H), 6.47 (dd, J = 7.3, 7.5 Hz, 1H), 7.27–7.33 (m, 5H), 7.47–7.51 (m, 1H), 7.79 (d, J = 8.3 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 39.6 (CH_2), 64.2 (CH_2), 76.6 (CH), 83.1 (CH), 124.9 (C), 125.4 (2x CH), 127.7 (CH), 127.8 (CH), 128.8 (CH), 130.5 (CH), 131.6 (CH), 137.5 (C), 139.4 (C), 141.5 (C), 143.9 (C), 163.5 (C). IR (HATR): 3340, 1621, 1595, 1564, 1482, 1456, 1444, 1428, 1400, 1348, 1306, 1292, 1278, 1246, 1229, 1199, 1142, 1103, 1040, 1031, 992, 895, 862, 824, 764, 754, 742, 712, 677 cm^{-1}. EI-MS m/z (rel. intensity%): 301 (M$^+$, 2), 299 (M$^+$, 6), 167 (8), 139 (9), 116 (100), 103 (11), 89 (8), 77 (20), 63 (4). ES-MS: 300 [M+H]$^+$. $[\alpha]_D^{20} = -156.4$ (c 0.98, $CHCl_3$). Mp: 147 °C. HRMS (EI) calcd for $C_{17}H_{14}NO_2{}^{35}Cl$: 299.0713; found 299.0717.

4.7. Synthesis of (1*R*, 2*R*)-*trans*-1-(3*H*-isobenzofuran-1-ylideneamino)-indan-2-ol 5fA

A suspension of (1*R*,2*R*)-(−)-*trans*-1-amino-2-indanol (100.0 mg, 0.67 mmol) and imidate ester **3A** (125.0 mg, 0.74 mmol) in CH_2Cl_2 was cooled in an ice bath. Et_3N (0.28 mL, 2.0 mmol) was added and the reaction mixture was stirred for 48 h at room temperature. Evaporation in vacuo and recrystallization from CH_2Cl_2 resulted in **5fA** as a white solid, 161 mg (91%). ^{1}H NMR (300 MHz, DMSO) δ 2.74 (dd, J = 7.0, 15.6 Hz, 1H), 3.18 (dd, J = 7.0, 15.6 Hz, 1H), 4.33 (m, J = 5.6, 7.0 Hz, 1H), 5.12 (d, J = 5.6 Hz, 1H), 5.16 (d, J = 5.2 Hz, 1H), 5.44 (d, J = 14.9 Hz, 1H), 5.50 (d, J = 14.9 Hz, 1H), 7.05–7.20 (m, 4H), 7.44–7.49 (m, 1H), 7.56–7.63 (m, 2H), 7.70 (d, J = 7.6 Hz, 1H). ^{13}C NMR + HSQC (75.4 MHz, DMSO): 39.3 (CH_2), 68.3 (CH), 72.1 (CH_2), 79.5 (CH), 122.2 (CH), 122.8 (CH), 124.3 (CH), 124.5 (CH), 126.4 (CH), 127.1 (CH), 128.4 (CH), 129.7 (C), 131.5 (CH), 140.2 (C), 143.2 (C), 143.8 (C), 160.1 (C). IR (HATR): 3189, 1680, 1467, 1419, 1369, 1298, 1225, 1200, 1084, 1028, 998, 777, 747, 730, 703, 675 cm^{-1}. EI-MS m/z (rel. intensity%): 265 (M$^+$, 20), 247 (4), 237 (17), 218 (5), 146 (15), 134 (23), 118 (100), 104 (50), 90 (97), 63 (19), 49 (43). ES-MS: 266 [M+H]$^+$. $[\alpha]_D^{20} = -304.8$ (c 0.81, DMSO). Mp: 236 °C. HRMS (EI) calcd for $C_{17}H_{15}NO_2$: 265.1103; found 265.1107.

4.8. Synthesis of 2-(2′-bromophenyl)-(3a*S*,8a*R*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazoline 13

Compound **13** was synthesized according to a literature procedure.[13] A mixture of (1*S*,2*R*)-(−)-*cis*-1-amino-2-indanol (500.0 mg, 3.35 mmol), 2-bromobenzonitrile (610.0 mg, 3.35 mmol), and anhydrous $ZnCl_2$ (23.0 mg, 0.17 mmol) in anhydrous chlorobenzene (2 mL) was refluxed for 24 h. After removal of the solvent in vacuo, the crude product was purified via flash chromatography over silicagel (hexane/EtOAc, 8/2) giving **13** as a colorless oil, 314.2 mg (30%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41 (dd, J = 1.9, 17.9 Hz, 1H), 3.51 (dd, J = 6.4, 17.9 Hz, 1H), 5.52 (ddd, J = 1.9, 6.4, 8.0 Hz, 1H), 5.77 (d, J = 8.0 Hz, 1H), 7.21–7.31 (m, 5H), 7.54–7.64 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 39.7 (CH_2), 77.2 (CH), 83.6 (CH), 121.8 (C), 125.3 (CH), 125.7 (CH), 127.0 (CH), 127.5 (CH), 128.5 (CH), 129.8 (C), 131.5 (CH), 131.6 (CH), 133.7 (CH), 139.7 (C), 141.7 (C), 163.5 (C). IR (HATR): 3065, 3024, 2951, 2918, 2851, 1630, 1619, 1588, 1476, 1458, 1425, 1353, 1316, 1295, 1234, 1212, 1166, 1097, 1081, 1023, 992, 749, 726, 707, 684, 676, 641 cm^{-1}. EI-MS m/z (rel. intensity%): 315 (M$^+$,7), 313 (M$^+$,7), 183 (6), 155 (4), 131 (12), 115 (26), 104 (100), 89 (14), 77 (40), 63 (14), 50 (25). ES-MS: 314 and 316 [M+H]$^+$. $[\alpha]_D^{20} = -164.7$ (c 1.09, $CHCl_3$). HRMS (EI) calcd for $C_{16}H_{12}NO^{79}Br$: 313.0102; found 313.0117.

4.9. Synthesis of 2-(2′-diphenylhydroxymethyl)phenyl-(3a*S*,8a*R*)-3a,8a-dihydro-8*H*-indeno[1,2-*d*]oxazoline 14

Compound **14** was synthesized according to a literature procedure.[5a] A solution of **13** (101.7 mg, 0.33 mmol) in freshly distilled Et_2O (2.5 mL) was cooled to −78 °C and treated dropwise with n-BuLi (0.150 mL, 0.37 mmol, 2.5 M in n-hexane). After being stirred for 1 h at −40 °C, benzophenone (71.0 mg, 0.38 mmol) was added in one portion and stirred overnight at room temperature. The reaction mixture was poured into H_2O (25 mL) and extracted with EtOAc (3 × 25 mL). The organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash chromatography over silicagel (hexane/EtOAc, 8/2) resulting in **14** as a white solid, 88.0 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.17 (d, J = 3.8 Hz, 2H), 4.10 (br s, 1H), 4.63 (m, 1H), 5.51 (d, J = 4.9 Hz, 1H), 6.95–7.05 (m, 2H), 7.16–7.62 (m, 15H), 7.90–7.93 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 39.7 (CH_2), 63.8 (CH), 73.6 (CH), 94.2 (C), 123.8 (CH), 124.1 (CH), 125.2 (2 × CH), 126.4 (CH), 126.8 (2 × CH), 127.5 (CH), 127.6 (2 × CH), 128.2 (CH), 128.3 (2 × CH), 128.4 (3 × CH), 129.0 (CH), 130.0 (C), 131.9 (CH), 141.4 (C), 141.6 (C), 142.0 (C), 142.1 (C), 148.6 (C), 159.9 (C). IR (HATR): 3460, 3070, 3021, 2948, 2914, 1690, 1600, 1492, 1466, 1448, 1428, 1379, 1336, 1313, 1298, 1288, 1257, 1218, 1184, 1157, 1120, 1054, 1043, 984, 959, 944, 930, 866, 760, 754, 746, 718, 695, 679, 656, 632 cm^{-1}. EI-MS m/z (rel. intensity%): 417 (M$^+$, 4), 270 (100), 241 (36), 239 (47), 209 (21), 193 (16), 165 (51), 148 (23), 130 (66), 118 (51), 91 (50), 77 (93), 51 (41), 41 (9). ES-MS: 418 [M+H]$^+$. $[\alpha]_D^{20} = +268.4$ (c 0.94, $CHCl_3$). Mp: 210 °C. HRMS (EI) calcd for $C_{29}H_{23}O_2N$: 417.1729; found 417.1729.

4.10. Typical procedure for the asymmetric Et_2Zn addition to benzaldehyde

Ligand **6aA** (13.1 mg, 0.049 mmol) was dissolved in toluene (2 mL). Then Et_2Zn (0.75 mL, 0.75 mmol, 1 M in hexane) was added and the resulting yellow solution was stirred for 20 min at room temperature under an argon atmosphere. Next, the reaction was cooled to 0 °C and benzaldehyde was added (50 μL, 0.49 mmol). The reaction was stirred for another 48 h. After quenching with 1 mL saturated NH_4Cl solution, the reaction mixture was added to 25 mL H_2O and extracted with EtOAc (3 × 25 mL). The combined organic phases were dried on Na_2SO_4 and evaporated in vacuo. Purification by flash chromatography over silicagel (pentane/EtOAc, 90/10) resulted in **12**, 46.3 mg (69%, 85% ee).

The adducts were fully characterized by comparison of their spectral data with those reported in the literature.[6b] The enantiomeric excess of the product was determined by HPLC analysis with a chiral stationary phase column and the absolute configuration was assigned via correlation of its specific rotation with the values reported in the literature.[14]

Conditions for chiral HPLC:

For 1-phenylpropanol **12**: Chiralcel OD–H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/EtOH (97/3), flow rate = 1 mL/min, T = 35 °C, retention times: 7.8 min for (*R*)-(+)-**12** and 9.0 min for (*S*)-(−)-**12.**

For 1-(2-chlorophenyl)propanol: Chiralcel AD–H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/EtOH (97/3), flow rate = 1 mL/min, T = 35 °C, retention times: 7.7 min for (*R*)-(+) and 8.5 min for (*S*)-(−).

For 1-(3-chlorophenyl)propanol: Chiralcel AD–H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/EtOH (97/3), flow rate = 1 mL/min, T = 35 °C, retention times: 8.9 min for (*R*)-(+) and 10.5 min for (*S*)-(−).

For 1-(4-chlorophenyl)propanol: Chiralcel OB–H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/EtOH (97/3), flow rate = 1 mL/min, T = 35 °C, retention times: 6.5 min for (*S*)-(−) and 7.8 min for (*R*)-(+).

For (*E*)-1-phenyl-1-penten-3-ol: Chiralcel OD–H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/EtOH (90/10), flow rate = 1 mL/min, T = 35 °C, retention times: 5.75 min for (*R*)-(+) and 7.36 min for (*S*)-(−).

For 1-naphthalen-2-yl-1-propanol: Chiralcel OD–H column (250 × 4.6 mm, particle size 10 μm), solvent: *n*-hexane/EtOH (97/3), flow rate = 1 mL/min, T = 35 °C, retention times: 14.68 min for (*S*)-(−) and 16.00 min for (*R*)-(+).

4.11. Crystallographic data

Crystallographic data (excluding structure factors) for ligand **6aA** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 733211. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 lEZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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