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On the way to biodegradable poly(hydroxy butyrate) from propylene oxide and carbon monoxide via β-butyrolactone: Multisite catalysis with newly designed chiral indole-imino chromium(III) complexes

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ABSTRACT

Enantioenriched poly(hydroxy butyrate) (PHB) is a biodegradable polyester of significant commercial interest as an environmentally benign substitute of commodity polyolefines. We report on the design and development of new chiral indole-based ligand families and on their chromium(III) complexes as enantioselective catalysts for the conversion of propylene oxide and carbon monoxide to enantioenriched β-butyrolactone, the key monomer for the production of PHB by ring-opening polymerization. The enantioselective carbonylation catalysts are based on new chiral tri- and tetradentate [N_2O] and [N_4] chromium(III) complexes containing chiral indolaldimine ligand scaffolds. The conceptual design of these ligands is inspired by Jacobsen's salicylaldimine lead structure; the key difference is an exchange of the salicyl-O-donor against an indole-N-donor, allowing additional structural diversity and stereoelectronic tuning by the indole substitution pattern. Synthetically, chiral indolealdimines are easily accessible from 7-formylindoles by standard Schiff base condensation with chiral amine building blocks; the 7-formylindoles in turn are synthesized from the corresponding 7-bromoindoles by the Rapoport synthesis, and the starting 7-bromoindoles are accessible from 2-bromoaniline by the classical Fischer indole synthesis. Three generations of chiral [N_2O] and [N_4] chromium(III) catalysts have been developed and evaluated in the enantioselective carbonylation of racemic propylene oxide with carbon monoxide using tetracarbonylcobaltate as the nucleophilic reagent for the insertion of carbon monoxide into the activated propylene oxide/chiral Lewis acid complex. The best catalyst out of 10 candidates showed at a temperature of 80 °C an activity of 37% conversion, 100% chemoselectivity, and 19% stereoselectivity.

1. Introduction

In the past decades, an enormous market for biologically compatible products evolved. In this context, biologically degradable polymers are still rather underdeveloped. Although well known in principle, application of these materials has been limited to only specialized usage in medicine. However, there is without doubt great commercial potential of biodegradable plastics as substitute for polyolefin commodities like polypropylene (PP) and polyethylene (PE), but currently the high costs and the limited availability of these materials stand in the way of a broad introduction to a ready market [1].

One of these promising materials is poly[(*R*)-3-hydroxybutyric acid] (PHB). PHB is naturally produced by various bacteria as a reserve polymer and has found a small and very specialized application as medical sewing and tissue-supporting material. Pure, naturally produced PHB is strictly isotactic has a M_w of 500 000, a M_n of 150 000, shows a glass transition at 4 °C and melts at 180 °C. In its mechanical properties, it is similar to poly(ethylene terephthalate) (PET). Since its melting point is problematically close to its decomposition point, it is imperative to lower it in order to obtain a processible material. Biotechnological strategies involve the change of fermentation conditions to obtain a blended material (e.g. with some percentage of valerianic units in the polymer chain) or to produce copolymers with terephtalic esters. However, all these strategies are too expensive for a marketable, reasonable cheap commodity [2].

Hence a petrochemical approach starting from readily available cheap feedstock is an interesting alternative. Conceptually, the lowering of PHB's melting point can be realized by a controlled decrease of its tacticity. This results in the softening of the polymer as well and so a sheet-material similar to PP can be obtained. Mechanistically, PHB can be conveniently synthesized by ring-opening polymerization (ROP) of β-butyrolactone (BL) (Scheme 1) [3].

This reaction and its catalysis are well known and are extensively treated in the literature [4]. The control of the tacticity of the resulting polymer is achieved by the use of appropriate mix-

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Scheme 1. Ring-opening polymerization of β-butyrolactone to yield PHB.

tures of enantiomers of β-butyrolactone. Doi and co-workers correlated mechanical properties, melting point and tacticity of PHB and found an optimal range to be between 70% and 80% isotacticity for a PP-like material with a melting point between 95 and 130 °C [5]. These findings make enantioenriched β-butyrolactone (BL) the key monomer for an industrial production of environmentally benign PHB. To get access to enantioenriched BL on an industrial scale, the most promising method consists in the enantioselective carbonylation of racemic propylene oxide (PO). The goal of the present work was to develop a catalytic process for this purpose.

In general, the carbonylation of epoxides is a deeply investigated topic and extensive investigations have shown that the most promising catalyst system for such a multisite catalysis is a combination of a suitable Lewis acid for the electrophilic activation of the epoxide and a nucleophilic carbonylating reagent for the insertion of carbon monoxide into the activated epoxide [6]. As shown by Coates, tetracarbonylcobaltate with various counterions [Lewis acid]$^+$[Co(CO)$_4$]$^-$, under application of high carbon monoxide pressures is the best available carbonylating system in that context [7]. By the use of a chiral Lewis acid, it should be possible to achieve the defined goal (Scheme 2).

A multisite catalyst system to produce enantioenriched BL has to fulfil three main tasks: First, the system has to be active: Propylene oxide has to be activated and carbon monoxide has to be consumed by insertion. Second, the system has to be chemoselective: as a side reaction – when the carbonylation is too slow-activated propylene oxide can undergo an undesired rearrangement to form acetone. Therefore a critical balance between the nucleophilicity of the carbonylating reagent and the electrophilic activation by the Lewis acid is mandatory. Third, the system has to be stereoselective: this can be achieved by use of a stereo-inducing Lewis acid which effects a kinetic resolving activation [8].

2. Results and discussion

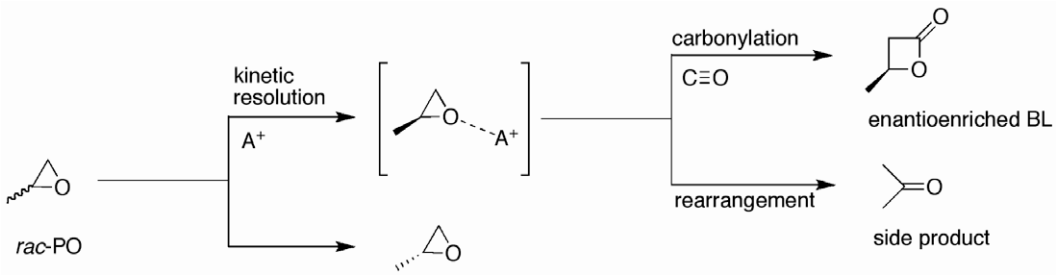
2.1. Proof of principle with Jacobsen catalysts

Seminal work by Jacobsen has shown that chiral salicylimidato transition metal complexes are well capable to activate epoxides in a stereoselective manner [9]. As a starting point for the enantioselective formation of BL from PO and CO according to Scheme 1, we investigated Jacobson's classical tri- and tetradentate chromium(III)-salicylimidato complexes **1–3** (Fig. 1, Table 1).

The results clearly showed that chromium(III) complexes containing a chiral ligand backbone are in principle capable of catalyzing the chemoselective and (in the case of bulky tridentate complexes **2** and **3**) even stereoselective carbonylation of propylene oxide. In addition to their stereoselectivity, the tridentate [NO_2]–chromium(III) salicylimidates are also faster than a classical tetradentate [N_2O_2]-system like **1**. Based on these promising first results we set out to design and develop novel chiral ligand structures aiming at an improvement of the catalytic performance of their chromium(III) complexes.

2.2. Indole-based building blocks for new tridentate [N_2O] and tetradentate [N_4] ligand families

Since salicylaldimines are such extremely versatile ligands for purposes as ROP and activation of epoxides, aziridines, lactones and other cyclic polar substrates, it is of great interest to develop novel ligand families based on this "privileged" structural motif [10]. On the search for such salicyl-analoguos systems we have reported earlier on planar–chiral ferrocene ligands [11]; here we summarize our results on new indole-based [N_2O] and [N_4] ligand families who were designed to be as close-as-possible to Jacobsen's successful [NO_2] and [N_2O_2] motive. Conceptually, these new ligands should be accessible in a straightforward and modular man-



Scheme 2. Illustration of the targeted catalytic reaction.

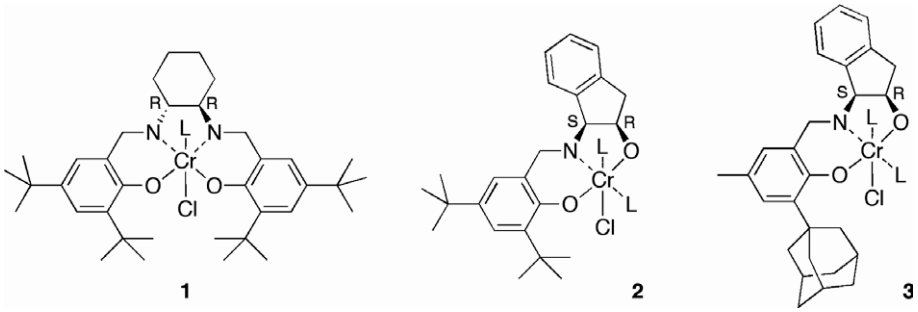


Fig. 1. Jacobsen's salicylaldiminato chromium(III) complexes.

Table 1
Enantioselective carbonylation with Jacobsen's chromium(III) complexes.

Catalyst	T [°C]	t [h]	Δp[a] [bar]	TO_{BL}[b] [%]	TO_{AC}[c] [%]	BL_{rel}[d] [%]	ee[e] [%]
1	80	6	18	19	4	83	–
	40	22	17	11	2	85	–
2	80	6	27	27	2	93	–
	40	22	6	6	1	86	7, *R*
3	80	6	28	27	3	90	13, *R*
	40	22	8	7	1	88	25, *R*

[a] Decrease of carbon monoxide pressure.
[b] Yield of β-butyrolactone (turnover).
[c] Yield of acetone (turnover).
[d] Percentage β-butyrolactone in product mixture (chemoselectivity).
[e] Enantiomeric excess of BL-isomer (stereoselectivity).

ner and they should incorporate the important structural features of the Jacobsen systems. These considerations led to 7-formylindoles as the key building blocks for such new [N_2O] and [N_4] ligand families (Fig. 2).

In medicinal and pharmaceutical chemistry, indoles are very important constituents of physiologically active compounds, therefore many substituted indoles are known, but-unfortunately-not many 7-formylindoles [12]. The parent compound, 7-formylindole, is the main target and first example of Bartoli's indole synthesis. Even though it is commercially available, it is rather expensive. However, by Dobson's variation of the Bartoli synthesis it is easily accessible from cheap starting materials [13]. In contrast, for the synthesis of substituted 7-formylindoles, there are only very few methodologies known. In our context, 2-substituted-7-formylindoles are especially important building blocks, because the steric bulk of the substituent in the vicinity of the indole–N-donor will be beneficial for the catalytic performance of their [N_2O] or [N_4] chromium(III) complexes, in analogy to Jacobsen's systems. In a carefully performed literature search, we came across the work of Black [14] who has already used 7-formylindoles as building blocks for chelating ligands of late transition metal complexes. Their synthesis involves a Vilsmeyer strategy on methoxy-protected indoles, however, for our purposes this reaction sequence is too cumbersome and too limited in scope. In a more useful organometallic approach, Rapoport reported the synthesis of 2-methyl-7-formylindole from the corresponding 7-bromoindole in good yield [15]. This strategy involves the protection of the amine function by its potassium salt, followed by metal–halogen exchange of the bromine by *t*-BuLi in ether at low temperature, and finally conversion of the doubly metalated indole to its 7-formyl derivative by reaction with dimethylformamide (DMF) (Scheme 3).

This method has the great advantage of introducing the rather labile aldehyde functionality in the last step of the reaction sequence, therefore it seemed especially suitable for the synthesis of a library of new 2-substituted 7-formylindole building blocks. The necessary starting materials, 2-substituted 7-bromoindoles, should in principle be accessible by applying the classical Fischer indole synthesis [16] on the corresponding bromo derivatives. This was indeed the case: First, 2-bromophenylhydrazine **4** was prepared in excellent yield by reduction of the diazonium chloride of 2-bromoaniline with tin(II)chloride [17]. Second, **4** was condensed with various methyl ketones to hydrazones **5**–**11** by aceotropic removal of water (Scheme 4).

Third, hydrazones **5**–**11** were transformed to 7-bromoindoles **13**–**16** by refluxing in mesitylene in the presence of an excess of zinc(II)chloride as Lewis acid following the standard conditions of Fischer's indole synthesis [16]. From hydrazones **5**–**8** containing a methyl and a "normal" aromatic substituent at the imino-carbon, the desired 7-bromoindoles **13**–**16** were obtained without difficulties (Fig. 3), but aliphatic *t*-butyl hydrazone **10** failed to react in the anticipated manner, suggesting limitation of this method to methyl/aryl hydrazone substrates. Furthermore, pentafluorohydrazone **11** rearranged to tetrafluorobenzodiazole **12** in a reaction that has precedence in the literature as was found afterwards (Scheme 5) [18], and isopropyl/phenyl hydrazone **9** reacted to isoindole **17** [19].

With these four new 7-bromoindoles in hand, the corresponding 7-formylindoles **20**–**23** as well as the known representatives **18**, **19** were synthesized in good yield by Rapoport's method (Scheme 3) [15] resulting in a library of the desired 7-formylindole key synthons (Fig. 4). The new indole aldehydes **20**–**23** were fully characterized by ^{1}H NMR, ^{13}C NMR and by IR-spectroscopy as well as by mass spectrometry. Characteristic features of the aldehyde group included low-field NMR signals (^{1}H NMR: δ = 10.1–10.2 ppm; ^{13}C NMR: δ = 193.7–193.9 ppm) and strong IR absorptions ($\nu_{C=O}$ = 1668–1675 cm^{-1}), the N–H proton of the indole heterocyclic core was clearly evidenced by observation of low-field, broad ^{1}H NMR signals (δ = 10.0–10.7 ppm) and strong IR absorptions (ν_{N-H} = 3340–3384 cm^{-1}).

Furthermore, isoindole **17** could be transformed to 7-formylindoline **24** by a similar organometallic route: reaction with three equivalents of phenyl lithium effected first nucleophilic addition to the isoindole imine bond followed by bromine–lithium exchange and, after addition of dimethylformamide and aqueous workup, formation of novel 7-formylindoline **24** (Fig. 4). Although in retrospect this reaction looks rather simple, experimentally it was quite difficult to find the proper work-up conditions. In principle, many other organyl lithium compounds than phenyl lithium would also effect this 7-formylindoline formation, allowing thereby further structural diversity, but with the drawback of producing racemic mixtures due to the new chiral center at the 2-indoline position. In comparison to indole aldehydes **18**–**23**, indoline aldehyde **24** showed similar spectral features characteristic of its aldehyde group [δ(^{1}H) = 9.9 ppm, δ(^{13}C) = 193.2 ppm, $\nu_{C=O}$ = 1661 cm^{-1}] and slightly different

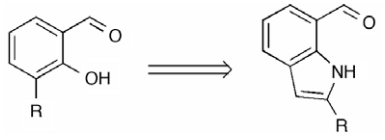
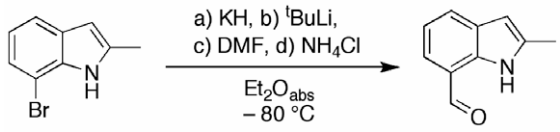
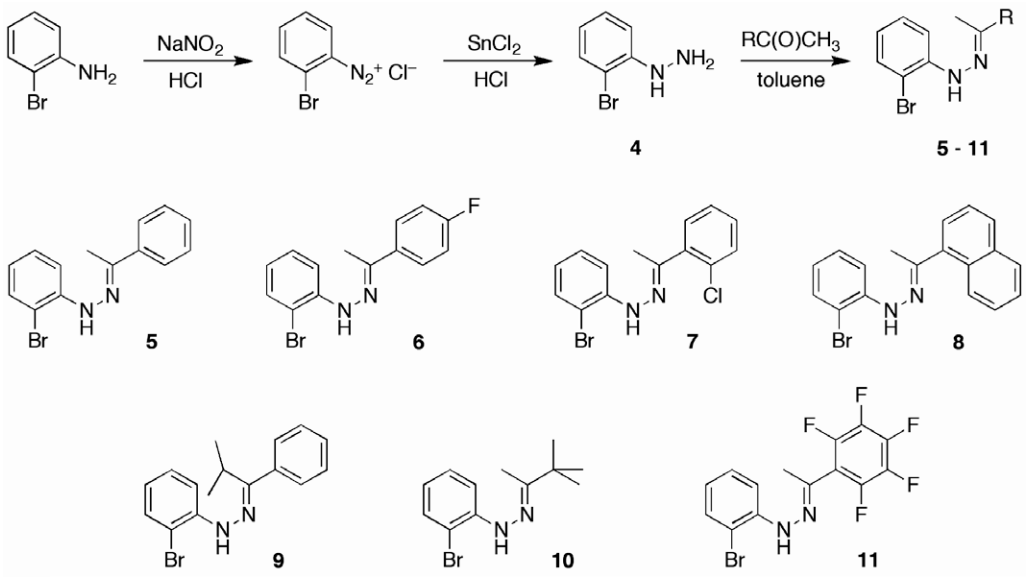


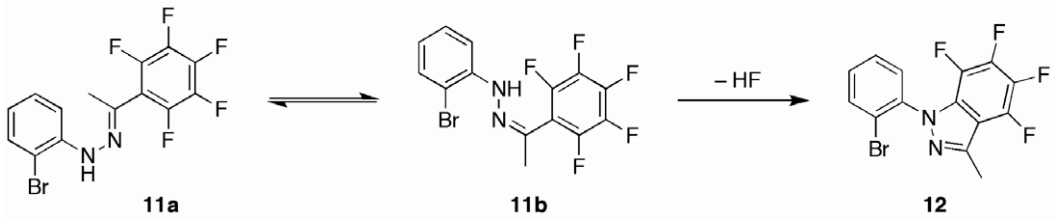
Fig. 2. 7-Formylindole building blocks based on the salicyl aldehyde lead structure.



Scheme 3. Rapoport's 7-formylindole synthesis.



Scheme 4. Modular route to hydrazones **5**–**11**.



Scheme 5. Rearrangement of hydrazone **11** to benzodiazole **12**.

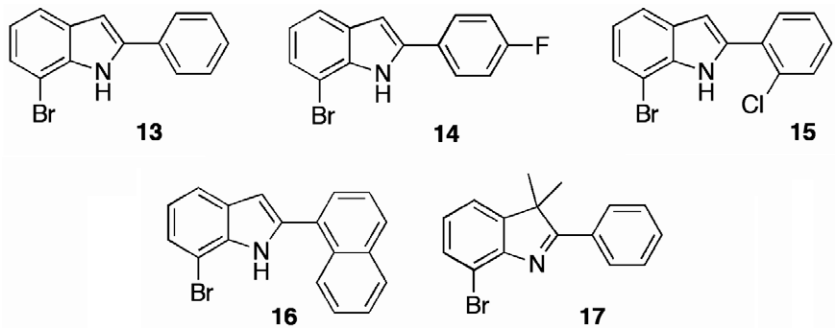


Fig. 3. Library of 2-substituted-7-bromoindoles **13**–**16** and 7-bromoisoindole **17**.

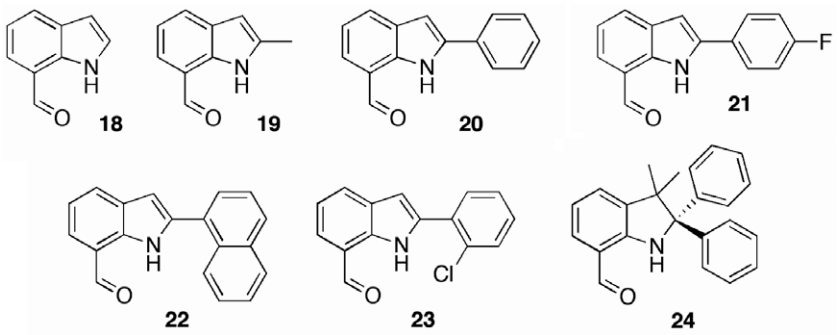


Fig. 4. Library of 2-substituted-7-formyl-indoles **18**–**23** and indoline **24**.

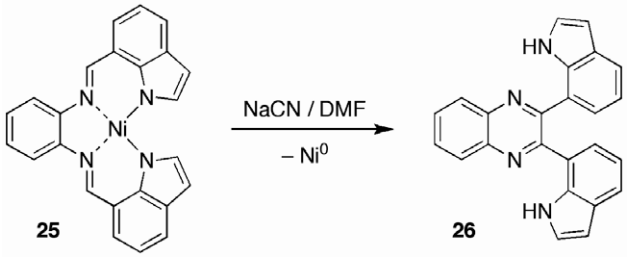
features for its non-aromatic heterocyclic N–H proton [$\delta(^1H)$ = 7.3 ppm, ν_{N-H} = 3380 cm^{-1}].

These indole (**18–23**) and indoline (**24**) aldehydes constituted now the key precursors for novel achiral/chiral salicylaldiminato-analogous [N_2O] and [N_4] ligand libraries and their chromium(III) complexes.

2.3. Achiral indolyl [N_4] Cr(III) catalysts

In general, salicylaldimine ligands are easily synthesized by simple condensation of salicylaldehyde with various amines. In analogy, starting from indol(in)e aldehydes **18–24** the corresponding Schiff bases should be easily accessible. In a first attempt, unsubstituted 7-formylindole **18** was chosen to investigate its applicability as a salicylaldehyde analogue in the condensation with *o*-phenylenediamines. Much to our surprise and against all chemical intuition, this seemingly simple reaction proved quite difficult. First, applying all standard condensation methods failed completely, no reaction was observed. Second, nickel-templated condensation according to Black's procedure [20] did afford the expected indolylimidato-nickel complex **25** as a purple and rather insoluble solid, but all attempts to remove the coordinated Ni^{2+} by hydrochloric acid, sulfide, or cyanide [21] failed to give the free [N_4]H_2 ligand. Interestingly, with cyanide as de-metalating agent an undesired but already reported oxidation to bis(indolyl)quinoxaline **26** with concomitant formation of elemental nickel was observed (Scheme 6) [22].

Third, applying brute force gave finally access to the desired salophen-analogous "indolophen" [N_4]H_2 ligands: heating a stoichiometric mixture of the starting materials at 600 W for 45 min in a microwave reactor [23], followed by extraction of the cooled melt, allowed the isolation of tetradentate ligands **27** and **28** in 47% and 39% yield, respectively (Fig. 5). The spectral properties of these two [N_4]H_2 ligands were in line with their structures, characteristic features included ^{13}C NMR signals of the imine carbons [**27**: $\delta(^{13}C)$ = 161.2 ppm, **28**: $\delta(^{13}C)$ = 160.4 ppm] shifted towards high field in comparison to their aldehyde precursor **18**, and strong IR absorptions of the hydrogen-bridged indole N–H protons [**27**: ν_{N-H} = 3390, 3359 cm^{-1}, **28**: ν_{N-H} = 3388, 3317 cm^{-1}] as well as strong imine bands [**27**: $\nu_{C=N}$ = 1619 cm^{-1}, **28**: $\nu_{C=N}$ = 1621 cm^{-1}].



Scheme 6. Cyanide-induced oxidation of **25**.

The general method for the synthesis of salophen chromium(III) complexes consists in a simple ligand exchange with chromium(II) halide precursors in basic medium, followed by oxidation in air to the desired chromium(III) complexes [9]. The obvious advantage of this procedure is the use of substitution-labile Cr(II) instead of kinetically inert Cr(III), however, the products are usually difficult to purify. Impure metal complexes hamper the accuracy and interpretation of their catalysis data, therefore a more defined complex/catalyst synthesis was desirable. Hence we avoided the oxidation step and used a standard organometallic transmetalation method, consisting in deprotonation of the ligands in dry THF with butyl lithium, followed by slow transmetalation with anhydrous $CrCl_3$ and removal of lithium chloride by filtration. In practice, this method afforded the desired [N_4]Cl(THF)Cr complexes **29** and **30** on a millimolar scale in reaction periods of 24 h as red solids in quantitative yield (Fig. 5). Due to their paramagnetism, no useful NMR data could be obtained and-unfortunately-all attempts to grow suitable single crystals for X-ray structure analysis met so far with failure.

Chromium(III) complexes **29** and **30** are potential catalysts for ring-opening polymerization (ROP) of racemic β-butyrolactone (Scheme 1). To test their applicability in this regard, preliminary tests were performed which showed that these metal Lewis acids are rather poor ROP catalysts, only oligomers instead of polymers were obtained (Table 2).

In summary, tetradentate salophen-analogous "indolophen" [N_4]H_2 ligands are accessible by forced microwave-assisted condensation of 7-formylindole with *o*-phenylenediamines. Their chromium(III) complexes may be prepared without the need of an oxidation step in excellent yield by standard organometallic procedures. Their use as catalysts for ring-opening polymerization of lactones has been tested, however, their catalytic performance is rather poor in comparison to established other metal complex Lewis acids.

2.4. Chiral indolyl [N_2O] and [N_4] Cr(III) catalysts

As has been shown above (Fig. 1, Table 1), Jacobsen's chiral salicylaldiminato [N_2O] and [N_2O_2] chromium(III) complexes **1**, **2** and **3** are capable of catalyzing the stereoselective carbonylation of propylene oxide to enantioenriched β-butyrolactone, the key precursor of biodegradable poly(hydroxy butyrate) (PHB). The enantiomeric excess was rather low and tridentate [NO_2]L_2ClCr complexes **2** and **3** performed better than tetradentate [N_2O_2]LClCr complex **1**.

Table 2
ROP of racemic β-butyrolactone with [N_4]Cl(THF)Cr complexes **29** and **30**.

Catalyst	Turnover [%][a]	Polymerization degree *n*[b]
29	95	13
30	94	15

[a] Calculated from ^1H NMR data.
[b] 1-Crotonyl-endgroup per *n* repetition units.

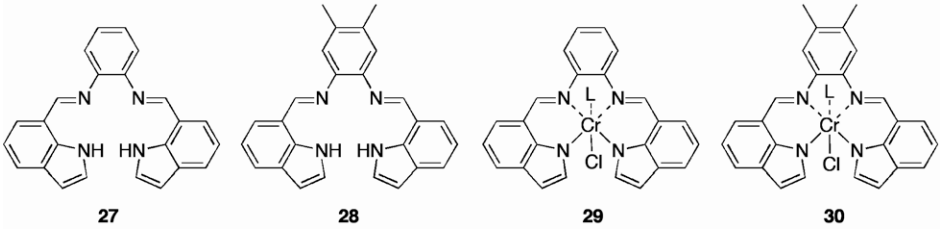


Fig. 5. Indolophen ligands **27**, **28** and their chromium(III) complexes **29**, **30** [L = THF].

Therefore we anticipated that analogous chiral indole-based catalyst systems would be active as well and hoped that their performance would surpass that of Jacobsen's complexes.

Synthesis of a first generation of such chiral indole-based ligands was easily accomplished by standard Schiff base condensation of 7-formylindole **18** with both diastereomers of *cis*-1-aminoindane-2-ol and *R,R*-cyclohexane-1,2-diamine in dry, boiling methanol to give **31**, **32** and **33** in 78%, 69% and 85% yield, respectively (Fig. 6). Gratifyingly, the ease of these condensations with aliphatic aminoalcohols allowed access to the targeted ligands without any problems, whereas severe activation proved necessary for indolophen ligands **27** and **28** (vide supra). The quantitative conversion of **31**, **32** and **33** to their corresponding chromium(III) catalysts **34**, **35**, **36** was achieved by a similar transmetalation route as described above starting from the lithiated ligands and anhydrous chromium(III) chloride.

Spectroscopically, ligands **31**–**33** were fully characterized by ^{1}H, ^{13}C NMR, IR-spectroscopy as well as mass spectrometry and showed the expected features of their aldimine functionalities [**31**: $\delta(^{1}H) = 8.77$ ppm, $\delta(^{13}C) = 164.9$ ppm, $\nu_{C=N} = 1628\ cm^{-1}$; **32**: $\delta(^{1}H) = 8.82$ ppm, $\delta(^{13}C) = 165.8$ ppm, $\nu_{C=N} = 1627\ cm^{-1}$; **33**: $\delta(^{1}H) = 8.48$ ppm, $\delta(^{13}C) = 161.6$ ppm, $\nu_{C=N} = 1631\ cm^{-1}$], indole moieties [**31**: $\delta(^{1}H) = 10.86$ ppm, $\nu_{N-H} = 3416\ cm^{-1}$, **32**: $\delta(^{1}H) = 10.35$ ppm, $\nu_{N-H} = 3419\ cm^{-1}$, **33**: $\delta(^{1}H) = 10.77$ ppm, $\nu_{N-H} = 3328\ cm^{-1}$], and hydroxyl groups [**31**: $\delta(^{1}H) = 3.99$ ppm, $\nu_{O-H} = 3489\ cm^{-1}$, **32**: $\delta(^{1}H) = 2.65$ ppm, $\nu_{O-H} = 3492\ cm^{-1}$]. In addition, for ligand **32** a single crystal structure is available (Fig. 7), giving full structural proof and illustrating the orthogonal steric shielding of the chiral indanyl moiety vs. the principal $[O,N,N]H_2$ coordination plane. In contrast, no informative NMR signals could be measured for the paramagnetic Cr(III) complexes **34**–**36**, and up to now no suitable single crystals for X-ray structure analysis could be obtained.

Of prime interest was the catalytic performance of this first generation of new catalysts in the carbonylation of propylene oxide (Table 3). In general, the results were encouraging: Whereas activity (TO_{BL}) was slightly lower than with Jacobsen's catalysts **1**–**3** (compare Table 1), chemoselectivity (BL_{rel}) was significantly improved with comparable stereoselectivity (ee). The conformations of the catalysts and their products were consistent, *S,R*-catalyst **31** yielded *R*-BL while *R,S*-catalyst **32** gave *S*-BL. Analogously as in the case of Jacobsen's catalysts **1**–**3**, tridentate [N,N,O]-complexes **34** and **35** exhibited better performance as compared to tetradentate [N,N,N,N]-complex **36**.

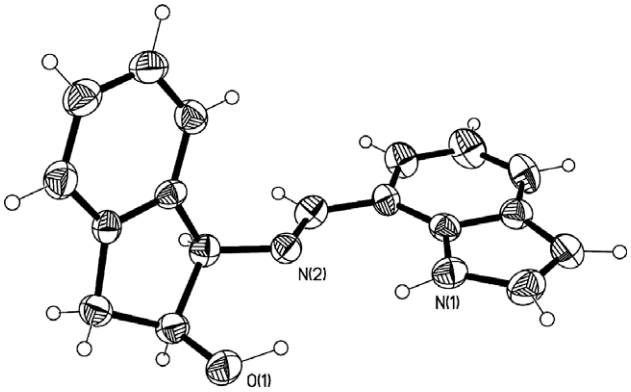


Fig. 7. Molecular structure of **32**.

Based on these first promising results a second generation of catalysts had to be developed. The main guiding principle was to introduce additional steric shielding in the vicinity of the indole-N-donor and to modulate the electronic properties of this substituent as well. To this end, ligands **37**–**39** (Fig. 8), containing either a methyl or a phenyl substituent in the indole-2-position, and their Cr(III) complexes **40**–**42** (Fig. 8) were synthesized starting from the corresponding 2-substituted 7-formylindoles **19** or **20** (Fig. 4).

Spectroscopically, ligands **37**–**39** were fully characterized by ^{1}H, ^{13}C NMR, IR-spectroscopy as well as mass spectrometry and showed the expected features of their aldimine functionalities [**31**: $\delta(^{1}H) = 8.56$ ppm, $\delta(^{13}C) = 161.7$ ppm, $\nu_{C=N} = 1630\ cm^{-1}$; **38**: $\delta(^{1}H) = 8.78$ ppm, $\delta(^{13}C) = 166.0$ ppm, $\nu_{C=N} = 1625\ cm^{-1}$; **39**: $\delta(^{1}H) = 8.82$ ppm, $\delta(^{13}C) = 165.1$ ppm, $\nu_{C=N} = 1626\ cm^{-1}$], indole moieties [**37**: $\delta(^{1}H) = 10.56$ ppm, $\nu_{N-H} = 3351\ cm^{-1}$, **38**: $\delta(^{1}H) = 10.01$ ppm, $\nu_{N-H} = 3427\ cm^{-1}$, **39**: $\delta(^{1}H) = 10.85$ ppm, $\nu_{N-H} = 3381\ cm^{-1}$], and hydroxyl groups [**38**: $\delta(^{1}H) = 2.69$ ppm, $\nu_{O-H} = 3536\ cm^{-1}$, **39**: $\delta(^{1}H) = 2.35$ ppm, $\nu_{O-H} = 3567\ cm^{-1}$]. In addition, for ligands **38** and **39** single crystal structures are available (Figs. 9 and 10), giving full structural proof and once again illustrating the orthogonal steric shielding of the indanyl groups vs. the principal $[O,N,N]H_2$ coordination planes. In comparison to the structure of unsubstituted ligand **32** (vide supra), the additional steric pressure

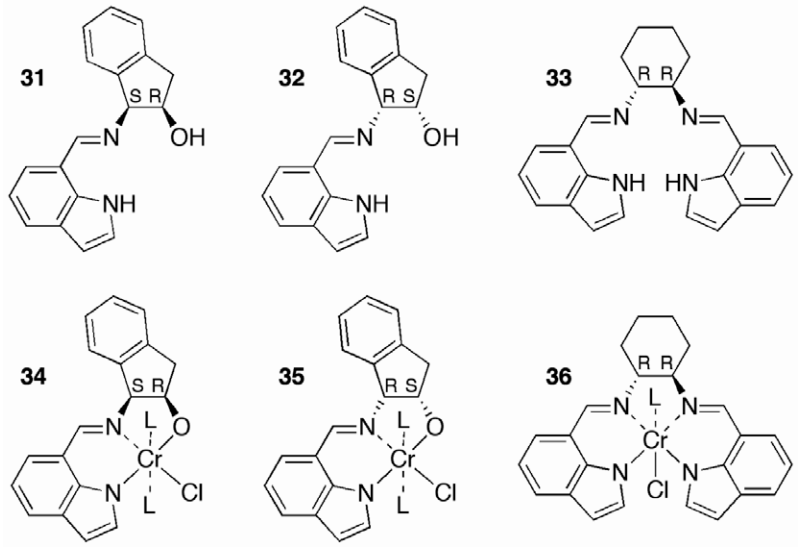


Fig. 6. First generation of chiral indolyl ligands **31**–**33** and their Cr(III) complexes **34**–**36** (L = THF).

Table 3
Enantioselective carbonylation with 1st generation indole-catalysts **34**–**36**.

Catalyst	T [°C]	t [h]	Δp[a] [bar]	TO_{BL}[b] [%]	TO_{AC}[c] [%]	BL_{rel}[d] [%]	ee[e] [%]
34	80	6	10	8	1	89	16, *R*
	40	22	2	4	0	100	19, *R*
35	80	6	18	15	0	100	8, *S*
	40	22	5	5	1	83	11, *S*
36	80	6	10	7	0	100	5, *S*
	40	22	4	3	3	50	–

[a] Decrease of carbon monoxide pressure.
[b] Yield of β-butyrolactone (turnover).
[c] Yield of acetone (turnover).
[d] Percentage β-butyrolactone in product mixture (chemoselectivity).
[e] Enantiomeric excess of BL-isomer (stereoselectivity).

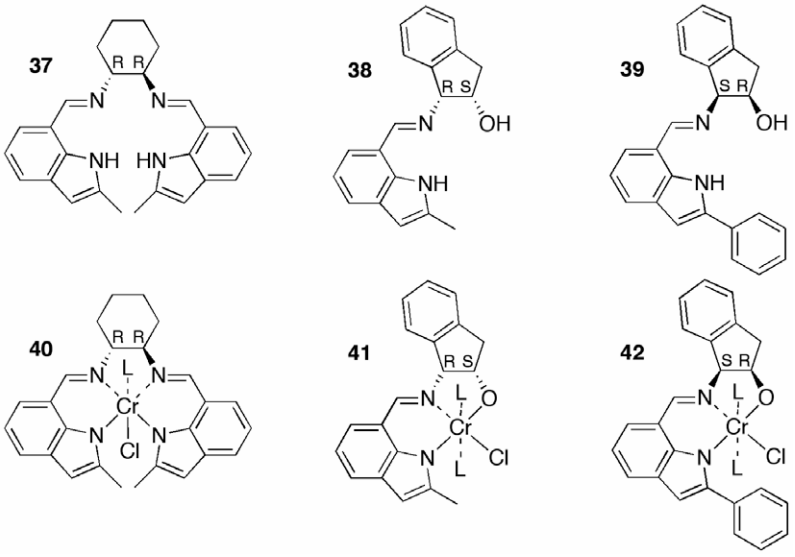


Fig. 8. Second generation of chiral indolyl ligands **37**–**39** and their Cr(III) complexes **40**–**42** (L = THF).

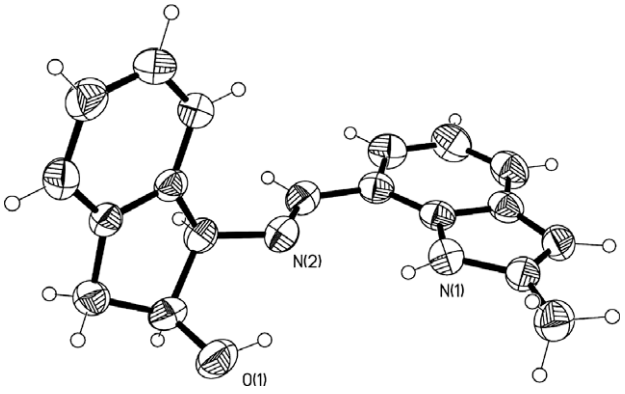


Fig. 9. Molecular structure of ligand **38**.

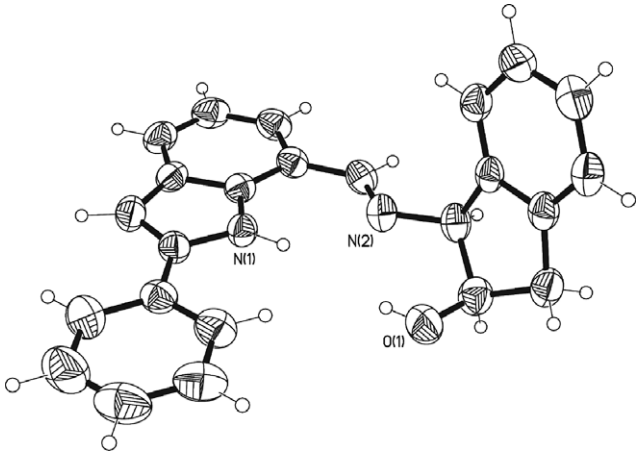


Fig. 10. Molecular structure of ligand **39**.

by the methyl (Fig. 9) or phenyl (Fig. 10) group around the coordination site is clearly evident. In contrast, no informative NMR signals could be measured for the paramagnetic Cr(III) complexes **40**–**42**, and up to now no suitable single crystals for X-ray structure analysis could be obtained.

The catalytic performance of these second generation catalysts (Table 4) was gratifyingly a significant improvement, at least in the case of tridentate [N,N,O] complexes **41** and **42**. Tetradentate [N,N,N,N]-complex **40** gave quite similar results as its non-methylated relative **36** (vide supra, Table 3), indicating that a further modification of this backbone will not serve our purpose. In stark contrast, tridentate *R,S*-aminoindanol-derived catalysts **41** and **42** showed clearly that their additional substituent at the 2-indole-position was very beneficial in comparison to unsubstituted relative **35** (vide supra, Table 3), thereby giving access to catalysts with doubled activity as well as stereoselectivity. In terms of activity, the electron-withdrawing phenyl group (catalyst **42**) is clearly

Table 4
Enantioselective carbonylation with 2nd generation indole-catalysts **40**–**42**.

Catalyst	T [°C]	t [h]	Δp[a] [bar]	TO_{BL}[b] [%]	TO_{AC}[c] [%]	BL_{rel}[d] [%]	ee[e] [%]
40	80	6	11	8	1	89	6, *S*
	40	22	2	0	0	–	–
41	80	6	20	23	1	96	16, *S*
	40	22	12	13	0	100	16, *S*
42	80	6	33	37	0	100	19, *R*
	40	22	16	20	0	100	16, *R*

[a] Decrease of carbon monoxide pressure.
[b] Yield of β-butyrolactone (turnover).
[c] Yield of acetone (turnover).
[d] Percentage β-butyrolactone in product mixture (chemoselectivity).
[e] Enantiomeric excess of BL-isomer (stereoselectivity).

much better than an electron-donating methyl substituent (catalyst **41**). Therefore we anticipated that aryl groups containing electron-accepting moieties will increase the activity of the next generation of catalysts.

Based on these findings and considerations, the third and last generation of catalysts focused on tridentate [N,N,O]H ligands based on chiral aminoindanol and 7-formylindol(in)e building blocks **21**–**24** (vide supra, Fig. 4) containing various aryl substituents in the 2-indol(in)e-position (Fig. 11).

Synthetically, ligands **43**–**46** were easily accessible by standard Schiff base condensation in good to excellent yields of 58–99%. Complexation of the ligands with Cr(III) to the target catalysts **47**–**50** was achieved as described above in quantitative yield by transmetalation from the lithiated ligands.

Spectroscopically, ligands **43**–**46** were fully characterized by ^1H, ^{13}C NMR, IR-spectroscopy as well as mass spectrometry and showed the expected features of their aldimine functionalities [**43**: $\delta(^1H) = 8.85$ ppm, $\delta(^{13}C) = 165.4$ ppm, $\nu_{C=N} = 1628$ cm^{-1}; **44**: $\delta(^1H) = 8.65$ ppm, $\delta(^{13}C) = 165.7$ ppm, $\nu_{C=N} = 1625$ cm^{-1}; **45**: $\delta(^1H) = 8.80$ ppm, $\delta(^{13}C) = 165.3$ ppm, $\nu_{C=N} = 1630$ cm^{-1}; **46**: $\delta(^1H) = 8.82$ ppm, $\delta(^{13}C) = 165.0$ ppm, $\nu_{C=N} = 1628$ cm^{-1}], indole moieties [**43**: $\delta(^1H) = 10.73$ ppm, $\nu_{N-H} = 3374$ cm^{-1}, **45**: $\delta(^1H) = 10.72$ ppm, $\nu_{N-H} = 3342$ cm^{-1}, **46**: $\delta(^1H) = 11.21$ ppm, $\nu_{N-H} = 3384$ cm^{-1}], and hydroxyl groups [**43**: $\delta(^1H) = 2.64$ ppm, $\nu_{O-H} = 3547$ cm^{-1}, **44**: $\delta(^1H) = 2.79$ ppm, $\nu_{O-H} = 3538$ cm^{-1}; **45**: $\delta(^1H) = 2.72$ ppm, $\nu_{O-H} = 3564$ cm^{-1}; **46**: $\delta(^1H) = 2.73$ ppm, $\nu_{O-H} = 3541$ cm^{-1}]. In contrast, no informative NMR signals could be measured for the paramagnetic Cr(III) complexes **47**–**50**, and-unfortunately-up to now no suitable single crystals for X-ray structure analysis could be obtained.

In this last family of catalysts, indoline compound **48** was expected to show the highest stereoselectivity on cost of activity due to the high steric demand by the two geminal phenyl groups. *p*-Fluorophenyl-indole complex **49** was expected to show similar stereoselectivity as **42** but increased activity due to its electronically withdrawing fluoro substituent. The same consideration should hold true for the 2-naphthyl-indole derivative **47**. Finally, *o*-chlorophenyl-indole complex **50** should represent the "best" catalyst due to its balanced stereoelectronic properties by the electronically withdrawing and at the same time slightly sterically active *o*-chloro substituent. These considerations, although somewhat logical, were dramatically proven wrong by the actual catalytic experiments (Table 5).

As can be seen from inspection of Table 5, the performance of the catalysts of the third generation was inferior in comparison to second generation complex **42** containing an unsubstituted phe-

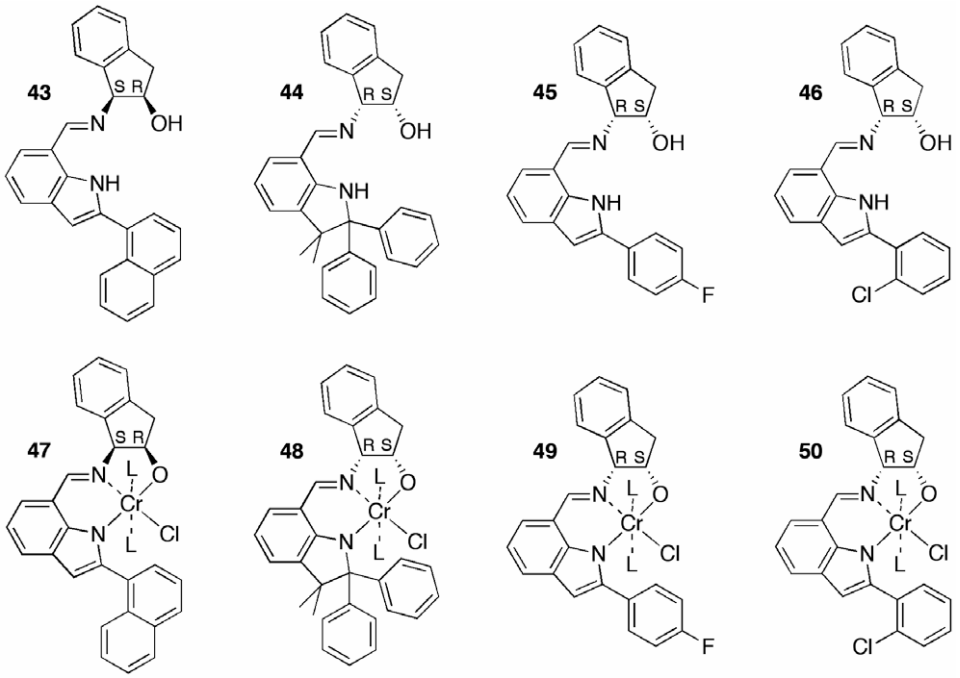


Fig. 11. Third generation of chiral indol(in)yl ligands **43**–**46** and their Cr(III) complexes **47**–**50** (L = THF).

Table 5
Enantioselective carbonylation with 3rd generation indol(in)e-catalysts **47**–**50**.

Catalyst	T [°C]	t [h]	Δp[a] [bar]	TO_{BL}[b] [%]	TO_{AC}[c] [%]	BL_{rel}[d] [%]	ee[e] [%]
47	80	6	30	36	1	97	8, *R*
	40	24	11	11	0	100	16, *R*
48	80	6	7	6	0	100	6, *S*
	40	24	6	5	0	100	6, *S*
49	80	6	21	22	1	96	14, *S*
	40	24	11	13	0	100	16, *S*
50	80	6	24	18	1	95	14, *S*
	40	24	11	11	0	100	16, *S*

[a] Decrease of carbon monoxide pressure.
[b] Yield of β-butyrolactone (turnover).
[c] Yield of acetone (turnover).
[d] Percentage β-butyrolactone in product mixture (chemoselectivity).
[e] Enantiomeric excess of BL-isomer (stereoselectivity).

nyl moiety (vide supra, Table 4), indicating that increasing electron-withdrawal at this substituent is counterproductive. The anticipated lower activity of indoline-catalyst **48** as the bulkiest system was indeed observed, however, without a concomitant increase in stereoselectivity. The activity and stereoselectivity of naphthyl-catalyst **47** was more or less the same as for phenyl-catalyst **42**, suggesting that possible intermolecular π-stacking of the 2-aryl-indole substituent plays no role in this multisite catalytic system.

2.5. Summary and conclusions

The goal of this work was to develop a catalyst system capable of enantioselective conversion of racemic propylene oxide to enantioenriched β-butyrolactone as the key monomer for ring-opening polymerization to give access to poly(hydroxybutyric acid), a biodegradable polymer of significant commercial interest.

Mechanistically, this multisite catalytic system is composed of a chiral Lewis acid for the enantioselective activation of propylene oxide and tetracarbonylcobaltate as the nucleophilic carbonylation reagent responsible for the chemoselective insertion of carbon monoxide.

The catalyst design of the chiral Cr(III) Lewis acid focused on novel indole-based ligand structures inspired by the successful salicylaldimine lead structure of Jacobsen. The key building blocks are new 7-formylindoles which were accessible in a modular and straightforward manner from the corresponding 7-bromo-indoles. By condensing these indole aldehydes with various achiral and chiral amino compounds new $[N,N,N,N]H_2$ and $[O,N,O]H_2$ ligand libraries were realized. Their Cr(III) complexes were synthesized in a clean manner from the lithiated ligands and anhydrous $CrCl_3$ by a standard transmetalation procedure.

The catalytic performance of three successive generations of catalysts was evaluated (Fig. 12); in the end complex **42** turned out to be the best catalyst for the enantioselective carbonylation of propylene oxide. Its performance [**42** (80 °C): TO_{BL} = 37%, TO_{AC} = 0%, BL_{rel} = 100%, ee = 19 *R*] compares favourably with the best of Jacobsen's catalysts [**3** (80 °C): TO_{BL} = 27%, TO_{AC} = 3%, BL_{rel} = 90%, ee = 13 *R*], but our goal of optimizing these catalysts to an enantioselectivity > 70% according to Doi's proposal [5] could unfortunately not be achieved. Hence it will be necessary to design completely new catalyst structures for this purpose in the future.

On the other hand, our newly developed $[N,N,N,N]H_2$ and $[O,N,O]H_2$ ligand systems based on the "privileged" indole scaffold might find use in other chiral Lewis acids for applications in enantioselective homogeneous catalysis.

3. Experimental

3.1. Catalysis: conversion of propylene oxide and carbon monoxide to enantioenriched β-butyrolactone

Carbonylation experiments were performed in a steel autoclave equipped with gas inlet, thermo- and pressure-sensor. The catalyst system was produced in situ by mixing 3 mmol of Lewis acid [**1**, **2**, **3** (Jacobsen complexes); **34**, **35**, **36** (1st generation catalysts); **40**, **41**, **42** (2nd generation catalysts); **47**, **48**, **49**, **50** (3rd generation catalysts] with 3 mmol of sodium tetracarbonylcobaltate followed by addition of 1 ml racemic PO in 1 ml diglyme, corresponding to 2% catalyst loading. The autoclave was closed, heated to the appro-

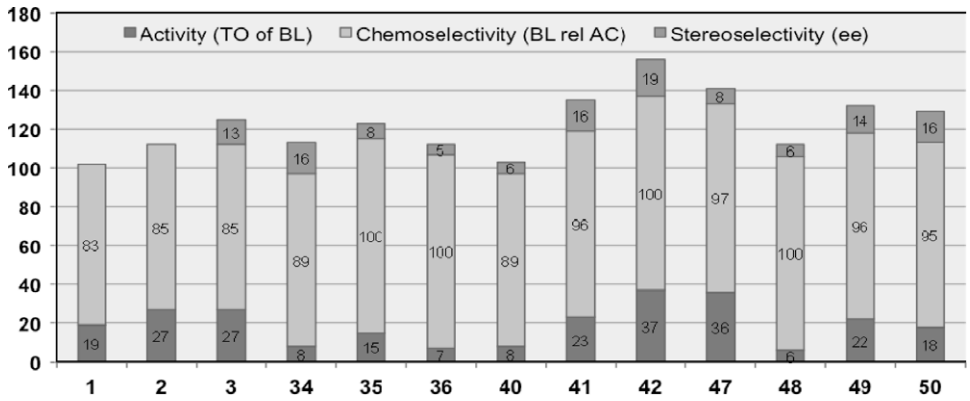


Fig. 12. Catalytic performance at 80 °C of catalysts **1**, **2**, **3** (Jacobsen complexes); **34**, **35**, **36** (1st generation catalysts); **40**, **41**, **42** (2nd generation catalysts); and **47**, **48**, **49**, **50** (3rd generation catalysts).

priate temperature and 60 bar of CO–pressure were applied. This presents the optimized system to have all analytical concentrations reasonable on the one hand, but also to have a sufficient dilution to allow conclusions about the catalytic performance on the other hand. Since reactions are faster at higher temperatures and heating is cheaper than cooling, it is preferable to run the carbonylation at temperatures as high as possible. However, since kinetic resolution is better at lower temperatures, a temperature optimum with balanced turn-over-frequency (TOF) and enantiomeric excess (ee) must exist. The reaction conditions were designed to get reproducible and comparable data. Therefore the reaction of propylene oxide (PO) to β-butyrolactone (BL) was run at two temperatures and for defined periods in order to be able to compare the time-dependent conversion. Reactions performed at 40 °C were stirred for 22 h and those performed at 80 °C were stirred for 6 h. During the reaction the pressure decrease of carbon monoxide was monitored as a functional dimension for the catalyst activity. The yields of β-butyrolactone (BL) and acetone (AC) were determined by ^{1}H NMR spectroscopy and the stereoselectivity of the catalysts was ascertained by chiral gas chromatography.

3.2. General

Commercially available starting materials were used as obtained. Solvents were dried, deoxygenated, and saturated with argon according to standard procedures in organometallic chemistry. Reactions of air-sensitive materials were performed in Schlenk glassware under an atmosphere of argon using techniques common in organometallic chemistry.

3.2.1. 2-Bromophenylhydrazine **4**

A 100 ml three-necked flask was charged with 2-bromoaniline (8.6 g, 50 mmol) and aqueous HCl (21 ml, 6 N, 2.5 eq.). After the stirred suspension was cooled to −15 °C a solution of $NaNO_2$ (3.45 g, 50 mmol) in 20 ml of water was added dropwise keeping the internal temperature below 5 °C. The resulting cold diazonium chloride solution was then added dropwise and under mechanical stirring to a chilled (−30 °C) solution of $SnCl_2$ (33.85 g, 150 mmol) in 35 ml aqueous HCl keeping the internal temperature during addition below −10 °C. The resulting off-white solid was stored overnight at 4 °C, collected by filtration, triturated with aqueous NaOH until basic, and immediately extracted with four portions of diethyl ether. The combined organic layers were washed with water, saturated bicarbonate solution and brine, dried over sodium sulfate, filtered and evaporated. The crude reddish hydrazine was repeatedly extracted with hot petrol ether; on cooling the product crystallized as a colorless cotton–wool-like solid (8.2 g, 44 mmol, 88% yield). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 145.9 (3), 130.7 (5), 126.8 (7), 118.0 (6), 110.5 (8), 106.2 (4). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 7.47 (1H, dd, 5); 7.32 (1H, dt, 7); 7.12 (1H, dd, 8); 6.74 (1H, dt, 6); 3.94 (3H, bs, 1, 2). IR (ATR) ν [cm^{-1}]: 3538s (NH, NH_2), 3265w, 3090w, 2978w, 1670w, 1591s, 1485 m, 1425w, 1391w, 1365w, 1299w, 1235w, 1151w, 1118w, 1079w, 1026s, 938w, 860m, 750s, 656w, 572w, 514w, 472w, 430w (Fig. 13).

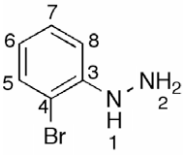


Fig. 13. Numbering of **4** for NMR assignment.

3.3. General procedure for the preparation of hydrazones **5**–**11**

A Dean–Stark apparatus was charged with 1.0 equivalent of **4**, 1.2 equivalent of ketone, 0.1 equivalent of *p*-toluenesulfonic acid monohydrate and 100 ml of toluene. The mixture was refluxed over night, cooled to room temperature, diluted with 50 ml toluene, washed twice with saturated K_2CO_3 solution, dried over Na_2SO_4, filtered and evaporated. The oily residue was dissolved in approximately 5 ml of ether and eluted with a mixture of hexane/ether (v/v = 1/1) through a short column of basic alumina, affording the pure hydrazone as the first fraction. The hydrazone should be used immediately for further reactions.

3.3.1. N-(2-Bromphenyl)-N′-[1-phenyl-ethylidene]-hydrazine **5**

Starting materials: **4** (760 mg, 3.74 mmol), acetophenone (450 mg, 3.74 mmol), *p*-toluenesulfonic acid monohydrate (40 mg, 0.2 mmol). 79% Yield (882 mg, 2.90 mmol, brown oil). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 143.9 (7), 142.3 (9), 139.1 (2), 132.5 (6), 128.9 (12), 128.6 (13, 11), 128.6 (5), 126.0 (14, 10), 120.9 (4), 114.8 (3), 108.0 (1), 12.3 (8). ^{1}H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 7.88 (3H, d, t, 12, 10, 14); 7.74 (1H, dd, 6); 7.55-7.34 (5H, m, NH, 11, 13, 3, 4); 6.81 (1H, dt, 5); 2.29 (3H, s, 8). IR (ATR) ν [cm^{-1}]: 3355w (NH), 3055w, 2923w, 1587s (C=N), 1570m, 1509m, 1490s, 1443s, 1368w, 1333m, 1307w, 1282m, 1239s, 1183w, 1139s, 1105w, 1067m, 1040w, 1020s, 970w, 929w, 911w, 824w, 758s, 741s, 689s, 677m, 634m, 587w, 559w, 533w, 474w, 453w, 433m, 419w, 408w (Fig. 14).

3.3.2. N-(2-Bromphenyl)-N′-[1-(4-fluorophenyl)-ethylidene]-hydrazine **6**

Starting materials: **4** (2.055 g, 11 mmol), *p*-fluoroacetophenone (1.824 g, 13.2 mmol), *p*-toluenesulfonic acid monohydrate (210 mg, 1.1 mmol). 93% Yield (3.146 g, 10.24 mmol, pale yellow oil). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 163.2 (d, 12), 142.5 (7), 142.1 (2), 135.2, 135.2 (9), 132.5 (6), 129.0 (5), 127.8, 127.7 (14, 10), 121.0 (4), 115.7, 114.9 (11, 13), 115.4 (3), 108.1 (1), 12.2, 12.15 (8). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 7.79-7.73 (4H, m, 10, 14, 6, NH); 7.54 (1H, d, 3); 7.39 (1H, t, 4); 7.15 (2H, t, 11, 13); 6.83 (1H, t, 5); 2.17 (3H, s, 8). IR (ATR) ν [cm^{-1}]: 3357w (NH), 3064w, 1590s (C=N), 1497s, 1452m, 1404w, 1368w, 1330m, 1283m, 1224s, 1158w, 1140s, 1100w, 1068w, 1040w, 1019s, 972w, 930w, 831s, 738s, 704w, 664w, 635w, 610w, 579w, 555w, 531w, 496m, 434m (Fig. 15).

3.3.3. N-(2-Bromphenyl)-N′-[1-(2-chlorophenyl)-ethylidene]-hydrazine **7**

Starting materials: **4** (2.167 g, 11.6 mmol), *o*-chloroacetophenone (2.685 g, 17.4 mmol), *p*-toluenesulfonic acid monohydrate

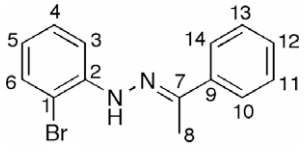


Fig. 14. Numbering of **5** for NMR assignment.

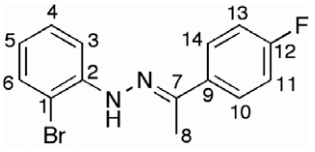


Fig. 15. Numbering of **6** for NMR assignment.

(579 mg, 0.57 mmol). 89% Yield (3.351 g, 10.3 mmol, colorless solid). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: (mixture of two isomers in a 4:6 ratio) 144.8, 144.3 (7), 142.0, 141.9 (9), 139.6, 134.6 (2), 132.7, 131.9 (14), 132.5, 132.4 (10), 130.9, 130.88 (12), 130.7, 130.3 (11), 129.7, 128.8 (6), 129.0, 128.9 (13), 128.3, 127.2 (5), 121.2, 120.4 (4), 115.0, 114.3 (3), 108.0, 107.3 (1), 24.1, 16.8 (8). ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: (mixture of two isomers in a 4:6 ratio) 7.96 (0.6 H, s, NH); 7.65 (1H, d, 6); 7.61–7.27 (6.4 H, m, 4, 3, NH, 10–13); 6.81 (0.6 H, t, 5); 6.73 (0.4 H, t, 5); 2.41, 2.39 (3H, 2s, 8) (Fig. 16).

3.3.4. N-(2-Bromphenyl)-N′-[1-(1-naphth-1-yl)-ethylidene]-hydrazine **8**

Starting materials: **4** (2.000 g, 10.7 mmol), 2-naphthylmethylketone (2.184 g, 12.8 mmol), *p*-toluenesulfonic acid monohydrate (203 mg, 1.08 mmol). 91% Yield (3.290 g, 9.7 mmol, yellow oil). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: (mixture of two isomers; major isomer) 146.4 (7), 142.4 (9), 134.3 (2), 133.9 (14), 132.6 (6), 129.9 (17), 129.4 (12), 129.2 (13), 129.0 (16), 127.9 (15), 127.2 (11), 126.5 (5), 125.6 (18), 125.3 (10), 120.4 (4), 114.4 (3), 107.4 (1), 25.77 (8); (mixture of two isomers; minor isomer) 145.6, 138.5, 134.6, 132.7, 131.4, 129.3, 129.2, 127.0, 126.7, 125.8, 121.2, 115.2, 108.2, 25.7. ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: (mixture of two isomers in a 85:15 ratio) 8.08–8.07 (2H, m, 10, 12); 8.01–7.94 (2H, m, 17, 14); 7.87 (1H, s, NH); 7.74–7.64 (3H, m, 11, 15, 16); 7.55 (1H, dd, 6); 7.50–7.45 (2H, m, 3, 4); 6.92 (0.15 H, dt, 5); 6.81 (0.85 H, dt, 5); 2.70 (2.55 H, s, 8); 2.56 (0.45 H, s, 8). IR (ATR) ν [cm^{-1}]: 3328w (NH), 3057w, 2905w, 1588s (C=N), 1497s, 1452m, 1425w, 1396w, 1369w, 1319w, 1284m, 1241 m, 1194w, 1128s, 1097m, 1063w, 1041w, 1020s, 987w, 951w, 930w, 862w, 846w, 800s, 775s, 742s, 675w, 660w, 634w, 623w, 599w, 563w, 534w, 491w, 469w, 434m (Fig. 17).

3.3.5. N-(2-Bromphenyl)-N′-[1-(2-methyl-1-phenyl-propylidene]-hydrazine **9**

Starting materials: **4** (2.115 g, 11.3 mmol), α-methylpropiophenone (1.840 g, 12.4 mmol), *p*-toluenesulfonic acid monohydrate (105 mg, 0.55 mmol). 76% Yield (2.713 g, 8.6 mmol, yellow oil). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 154.8 (7), 142.6 (1), 134.6 (8), 132.4 (3), 129.7 (12, 10), 129.2 (5), 128.7 (4), 127.9 (9, 13), 120.0 (11), 114.3 (6), 107.3 (2), 36.4 (14), 20.8 (15, 16). ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 7.80 (1H, s, NH); 7.64 (1H, d, 3); 7.59–7.54 (2H, m, 13, 9); 7.48 (1H, d, 6); 7.38–7.29, (4H, m, 5, 10–12); 6.68 (1H, dt, 4); 2.94 (1H, hep, 14); 1.26 (6H, d, 15, 16). IR (ATR) ν [cm^{-1}]: 3332m (NH), 3058w, 2963m, 2926w, 2868w, 1588s (C=N), 1495s, 1452s, 1429w, 1381w, 1362w, 1305m, 1289m, 1241m, 1170w, 1134m, 1066s, 1045w, 1019s, 928w, 883w, 846w, 776s, 741s, 701s, 665w, 617w, 604w, 569w, 551w, 534w, 480w, 436m, 418w (Fig. 18).

3.4. General procedure for the preparation of the 2-aryl-7-bromoindoles **13**–**16**

A Schlenk tube was charged with 1 equivalent of hydrazone **5**–**8**, mesitylene (30 ml) and 5 equivalents of anhydrous $ZnCl_2$. The suspension was heated to reflux under efficient stirring for at least 48 h. After complete conversion was indicated by TLC analysis, the reaction mixture was cooled to ambient temperature, triturated with diluted hydrochloric acid, and extracted with three portions of ether. The combined organic layers were washed with water, saturated Na_2CO_3 solution, water, brine, dried over Na_2SO_4, and filtered. Volatile materials were stripped off in vacuum, first on a rotary evaporator, then in high vacuum to remove most of the high-boiling mesitylene. The resulting oily solid was purified by chromatography (silica, CH_2Cl_2/toluene = 1/2).

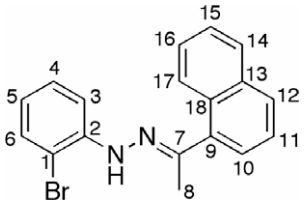


Fig. 17. Numbering of **8** for NMR assignment.

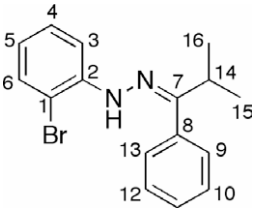


Fig. 18. Numbering of **9** for NMR assignment.

3.4.1. 7-Bromo-2-phenyl-1H-indole **13**

Starting materials: **5** (1.400 g, 4.84 mmol), $ZnCl_2$ (7.000 g, 5 meq.). 67% Yield (882 mg, 3.24 mmol, pale yellow solid, m.p.: 111–113 °C). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 138.9 (9), 135.7 (10), 131.9 (2), 130.6 (4), 129.3 (14, 12), 128.5 (7), 125.5 (11, 15), 124.8 (13), 121.6 (6), 120.0 (5), 104.5 (8), 101.1 (3). ^1H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 8.57 (1H, bs, 1); 7.72 (2H, d, 11, 15); 7.57 (1H, d, 5); 7.48 (2H, t, 12, 14); 7.40–7.33 (2d, 2H, 7, 13); 7.01 (1H, bt, 6); 6.91 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3434s (NH), 2922m, 2852m, 1726w, 1600w, 1566m, 1518w, 1482m, 1451m, 1430w, 1389w, 1350m, 1324m, 1297m, 1274w, 1241w, 1192m, 1160w, 1135s, 1097w, 1074w, 1049w, 1028w, 991w, 965w, 939w, 913w, 872w, 842w, 806s, 766s, 731s, 688s, 583m, 566w, 519s, 485s, 426s. MS (EI pos) *m*/*z*: 270.99 (M−1), 271.99 (M), 272.99 (M+1), 274.0 (M+2). Anal. Calc. for $C_{14}H_{10}BrN$ (272.15): C, 61.79; H, 3.70; N, 5.15. Found: C, 61.57; H, 3.58; N, 5.11% (Fig. 19)

3.4.2. 7-Bromo-2-(4-fluorophenyl)-1H-indole **14**

Starting materials: **6** (3.150 g, 10.24 mmol), $ZnCl_2$ (16.000 g, 5 meq.). 34% Yield (1.000 g, 3.45 mmol, pale yellow solid, m.p.: 64–66 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 164.5, 161.2 (13), 137.9 (9), 135.7 (2), 130.5 (4), 128.3, 128.29 (10), 127.4, 127.3 (11, 15), 124.9 (7), 121.8 (6), 120.0 (5), 116.6, 116.3 (12, 14), 104.6 (8), 101.1 (3). ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 8.37 (1H, bs, 1); 7.67–7.62 (2H, m, 11, 15); 7.56 (1H, d, 5); 7.35 (1H,

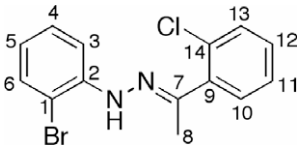


Fig. 16. Numbering of **7** for NMR assignment.

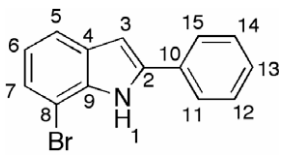


Fig. 19. Numbering of **13** for NMR assignment.

dd, 7); 7.16 (2H, tt, 12, 14); 7.02 (1H, t, 6); 6.81 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3422s (NH), 1601w, 1567w, 1543w, 1498m, 1484m, 1429m, 1422m, 1378w, 1341w, 1322w, 1296m, 1233s, 1190m, 1159m, 1131w, 1099m, 1045w, 1011w, 955w, 937w, 904m, 847w, 836s, 797s, 771m, 734s, 715m, 666w, 654w, 631w, 606w, 550m, 533m, 517m, 497m, 447s. MS (EI pos) m/z: 289.03 (M−1), 290.04 (M), 291.03 (M+1), 292.04 (M+2). Anal. Calc. for $C_{14}H_9BrFN$ (290.14): C, 57.96; H, 3.13; N, 4.83. Found: C, 57.89; H, 3.04; N, 4.77% (Fig. 20).

3.4.3. 7-Bromo-2-(2-chloro-phenyl)-1H-indole **15**

Starting materials: **7** (2.707 g, 8.36 mmol), $ZnCl_2$ (27.000 g, 10 meq.). 50% Yield (1.294 g, 4.2 mmol, yellow oil). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 135.9 (10), 135.4 (9), 131.8 (2), 131.2 (7), 130.9 (12), 130.8 (11), 129.5 (13), 129.4 (4), 127.6 (14), 125.1 (15), 121.6 (6), 120.3 (5), 104.8 (3), 104.8 (8). ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 8.91 (1H, s, 1); 7.67 (1H, dd, 5); 7.63 (1H, dd, 12); 7.52 (1H, dd, 7); 7.41 (1H, dd, 15); 7.37–7.31, (2H, dt 13, 14); 7.05 (1H, t, 6); 6.96 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3450s (NH), 3060w, 2922w, 2845w, 1594w, 1596m, 1492w, 1471w, 1458m, 1428s, 1385w, 1349w, 1341w, 1318w, 1303s, 1254w, 1230m, 1191s, 1161w, 1134m, 1076m, 1034s, 943w, 914s, 863w, 846w, 799s, 752s, 729s, 662m, 589m, 551w, 521w, 494w, 459s. MS (EI pos) m/z: 307.02 (M), 308.03 (M+1), 309.03 (M+2). Anal. Calc. for $C_{14}H_9BrClN$ (306.59): C, 54.85; H, 2.96; N, 4.57. Found: C, 54.78; H, 2.92; N, 4.52% (Fig. 21).

3.4.4. 7-Bromo-2-(2-naphth-1-yl)-1H-indole **16**

Starting materials: **8** (3.577 g, 10 mmol), $ZnCl_2$ (36.000 g, 10 meq.). 23% Yield (740 mg, 2.3 mmol, pale orange oil). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 137.6 (9), 135.4 (2), 134.1 (10), 131.7 (4), 130.7 (14), 130.1 (19), 129.3 (7), 128.8 (12), 127.7 (15), 127.2 (18), 126.5 (13), 125.7 (16), 125.6 (17), 124.7 (6), 121.6 (5), 120.0 (11), 104.9 (3), 104.6 (8). ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 8.51 (1H, s, 1); 8.33–8.30 (1H, m, 13); 7.97–7.93 (2H, m, 15, 18); 7.70–7.65 (2H, 2t, 12, 17); 7.60–7.55 (3H, m, 5, 11, 16); 7.41 (1H, dd, 7); 7.09 (1H, t, 6); 6.89 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3417s (NH), 3047m, 2922m, 1591w, 1564m, 1534w, 1505w, 1488w, 1459w, 1429s, 1385s, 1332s, 1296s, 1260w, 1235w, 1190s, 1159w, 1133m, 1111m, 1046w, 1022w, 10007w, 969w, 952w, 928w, 907m, 864w, 795s, 789s, 729s, 686s, 666s, 637w, 616w, 589m, 572m, 537m, 520w, 476s, 415s. MS (EI pos) m/z: 321.10 (M−1), 322.11 (M), 323.10 (M+1), 324.11 (M+2). Anal. Calc. for $C_{18}H_{12}BrN$ (322.21): C, 67.10; H, 3.75; N, 4.35. Found: C, 67.02; H, 3.68; N, 4.28% (Fig. 22).

3.4.5. 7-Bromo-3,3-dimethyl-2-phenyl-3H-indole **17**

A dry Schlenk tube was charged with hydrazone **9** (3.3 g, 10.4 mmol), anhydrous $ZnCl_2$ (10.5 g, 77 mmol, 7.4 eq.) and dry ethanol (25 ml). The solution was refluxed for three days under an argon atmosphere. After cooling to room temperature, the mixture was poured on 4 N hydrochloric acid and extracted with three portions of ether. The combined organic layers were washed twice with a saturated $NaHCO_3$ solution, once with water and brine, dried over sodium sulfate, filtered and evaporated. The residual orange oil was purified by chromatography (silica; hexanes/ethyl acetate = 95/5) to yield 1.29 g (4.3 mmol, 41%) **17** as a yellow oil.

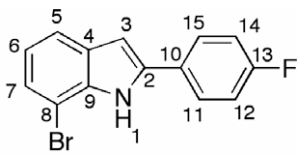


Fig. 20. Numbering of **14** for NMR assignment.

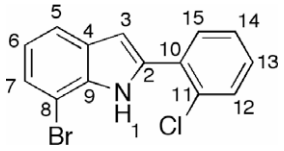


Fig. 21. Numbering of **15** for NMR assignment.

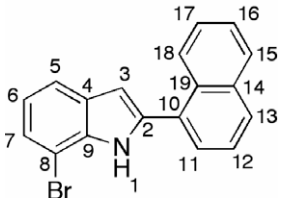


Fig. 22. Numbering of **16** for NMR assignment.

^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 184.4 (8), 151.7 (6), 149.6 (5), 133.1 (9), 131.4 (12), 131.3 (2), 128.9 (10, 11), 127.5 (4), 120.3 (3), 115.3 (1), 55.6 (7), 25.0, 24.97 (13, 14). ^1H NMR (300 MHz, $CDCl_3$) δ [ppm]: 8.23–8.20 (2H, d, 10); 7.52 (1H, d, 2); 7.49–7.47 (3H, m, 11, 12); 7.25 (1H, d, 4); 7.11 (1H, t, 3); 1.56 (6H, s, 13, 14). MS (EI pos) m/z: 299.01 (M−1), 300.01 (M), 301.01 (M+1). Anal. Calc. for $C_{16}H_{14}BrN$ (300.02): C, 64.02; H, 4.70; N, 4.67. Found: C, 63.96; H, 4.65; N, 4.60% (Fig. 23).

3.5. General procedure for the preparation of the 2-alkyl/aryl-7-formylindoles **19–23**

A dry Schlenk tube was charged under an argon atmosphere with 1 equivalent of 7-bromoindole (**13–16**) and dry ether (50 ml). The solution was cooled to −30 °C, 1.2 equivalents of KH was added and the resulting suspension was stirred at room temperature for approximately 1 h until all gas evolution has subsided. After cooling the mixture to −90 °C, 2 equivalents of a *t*-BuLi-solution were added in one portion, stirring at −90 °C was continued for 30 min, the cooling bath was removed, and the stirred mixture was allowed to warm to room temperature during 2 h. After the addition of 3 equivalents of dry dimethylformamide, the mixture was stirred overnight. Workup: the mixture was poured on saturated ammonium chloride solution and extracted with four portions of ether. The combined organic layers were washed with water and brine, dried over sodium sulfate, filtered and evaporated. The crude formylindoles were purified by chromatography (silica; CH_2Cl_2/toluene = 1/1).

3.5.1. 2-Methyl-1H-indole-7-carbaldehyde **19**

Starting materials: 2-methyl-7-bromoindole (575 mg, 2.74 mmol), KH (110 mg, 2.74 mmol), *t*-BuLi (1.7 molar solution in pentane, 3.3 ml, 5.48 mmol), dimethylformamide (406 mg, 0.43 ml, 5.5 mmol). 53% Yield (232 mg, 1.46 mmol, pale yellow solid, m.p.: 62–64 °C). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 193.8 (9), 137.8 (10), 134.1 (2), 130.5 (4), 127.7 (7), 126.9 (5), 120.0 (8),

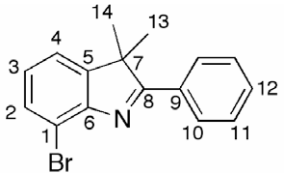


Fig. 23. Numbering of **17** for NMR assignment.

119.4 (6), 100.4 (3), 13.7 (11). ^{1}H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.09 (1H, s, 9); 10.02 (1H, bs, 1); 7.80 (1H, d, 5); 7.56 (1H, dd, 7); 7.21 (1H, t, 6); 6.31 (1H, d, 3); 2.49 (3H, s, 11). IR (ATR) ν [cm^{-1}]: 3384s (NH), 3360s (NH); 2797 m, 2721w, 1668s (C=O), 1605m, 1589m, 1556s, 1487m, 1451m, 1375m, 1346m, 1331m, 1282m, 1233m, 1196m, 1172m, 1146m, 1061w, 1044m, 993w, 975w, 951w, 896w, 874w, 794s, 761m, 738s, 693s, 661s, 610w, 590w, 574w, 550w, 465w, 421m. Anal. Calc. for $C_{10}H_9NO$ (159.19): C, 75.45; H, 5.70; N, 8.80. Found: C, 75.42; H, 5.67; N, 8.74% (Fig. 24).

3.5.2. 2-Phenyl-1H-indole-7-carbaldehyde **20**

Starting materials: **13** (1.437 g, 5.3 mmol), KH (253 mg, 6.34 mmol), *t*-BuLi (1.7 molar solution in pentane, 6.2 ml, 10.6 mmol), dimethylformamide (0.9 ml, 10.6 mmol). 89% Yield (1.035 g, 4.7 mmol, orange solid, m.p.: 127–129 °C). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 193.7 (9); 140.0 (10); 134.9 (2); 131.8 (11); 130.6 (4); 129.3 (13, 15); 128.9 (14); 128.5 (7); 127.8 (5); 125.6 (12, 16); 120.6 (8); 120.1 (6); 99.6 (3). ^{1}H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.39 (1H, bs,1); 10.13 (1H, s, 9); 7.92 (1H, d, 5); 7.76 (2H, dd,12, 16); 7.65 (1H, dd, 7); 7.48 (2H, t,13, 15); 7.37 (1H, tt, 14); 7.27 (1H, t, 6); 6.91 (1H, d,3). IR (ATR) ν [cm^{-1}]: 3349s (NH), 3050w, 2921w, 2835w, 2809w, 2728w, 1675s (C=O), 1605w, 1591m, 1580w, 1545m, 1484m, 1451m, 1384w, 1358m, 13340w, 1303m, 1280w, 1222s, 1194w, 1170w, 1099w, 1047s, 1029s, 955w, 930w, 911m, 897w, 877w, 849w, 805s, 774s, 756s, 738s, 689m, 669m, 607s, 574m, 518m, 474w, 442w. MS (FAB pos, NOBA) *m*/*z*: 221.11 (M), 222.12 (M+1). Anal. Calc. for $C_{15}H_{11}NO$ (221.26): C, 81.43; H, 5.01; N, 6.33. Found: C, 81.37; H, 4.94; N, 6.28% (Fig. 25).

3.5.3. 2-(4-Fluoro-phenyl)-1H-indole-7-carbaldehyde **21**

Starting materials: **14** (900 mg, 3.1 mmol), KH (150 mg, 3.72 mmol), *t*-BuLi (1.7 molar solution in pentane, 3.65 ml, 6.2 mmol), dimethylformamide (453 mg, 0.48 ml, 6.2 mmol). 56% Yield (412 mg, 1.7 mmol, pale yellow solid, m.p.: 141–144 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 193.9 (9), 164.5, 161.3 (14), 139.1 (10), 134.9 (2), 130.5 (4), 128.9 (7), 128.2, 128.1 (11), 128.0 (5), 127.5, 127.4 (12, 16), 120.5 (8), 120.2 (6), 116.5, 116.2 (13, 15), 99.57 (3). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 10.19 (1H, bs, 1); 10.11 (1H, s, 9); 7.89 (1H, d, 5); 7.68 (2H, m, 12, 16); 7.62 (1H, dd, 7); 7.26 (1H, t, 6); 7.15 (2H, m, 13, 15); 6.79 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3344s (NH), 3055w, 2819w, 2742w, 1672s (C=O), 1609w, 1591s, 1549s, 1504s, 1486s, 1427m, 1385w, 1342m, 1304m, 1217s, 1164w, 1102w, 1062m, 1050s, 1014w, 957w, 932w, 902w, 880w, 836s, 799s, 766w, 742s, 728s, 711w, 675w, 655m, 634w, 605m, 575w, 563w, 522m, 491w, 443w, 415m. MS (EI pos) *m*/*z*: 238.09 (M−1), 239.10 (M), 240.10 (M+1). Anal. Calc. for $C_{15}H_{10}FNO$ (239.25): C, 75.30; H, 4.21; N, 5.85. Found: C, 75.32; H, 4.24; N, 5.78% (Fig. 26).

3.5.4. 2-(2-Chloro-phenyl)-1H-indole-7-carbaldehyde **22**

Starting materials: **15** (1.225 g, 4 mmol), KH (200 mg, 4.8 mmol), *t*-BuLi (1.7 molar solution in pentane, 4.7 ml, 8 mmol), dimethylformamide (585 mg, 0.62 ml, 8 mmol). 62% Yield (632 mg, 2.5 mmol, yellow solid, m.p.: 104–106 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 193.7 (9), 137.1 (10), 134.2 (2), 132.1 (4), 131.2 (7), 130.8 (5), 130.76 (11), 129.6 (12), 129.5 (13), 129.4 (15), 128.3 (14), 127.5 (16), 120.6 (8), 120.0 (6), 103.6 (3). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 10.67 (1H, bs, 1); 10.14 (1H, s, 9); 7.95 (1H, d, 5); 7.67 (2H, 2 dd, 13, 16); 7.51 (1H, dd, 7); 7.38–7.26 (3H, m, 6, 14, 15); 6.97 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3340s (NH), 3060w, 2808w, 2729w, 1670s (C=O), 1592m, 1566w, 1551w, 1471m, 1452w, 1435w, 1396w, 1378w, 1351m, 1302w, 1264w, 1242w, 1221m, 1161w, 1127w, 1080w, 1065w, 1047m, 1036m, 943w, 932w, 893w, 860w, 799s, 767w, 745s, 736s, 723s, 699w, 684m, 657w, 618m, 586w, 571w, 551w, 479w, 454w, 445w, 427w. MS (EI pos) *m*/*z*: 255.10 (M), 256.10 (M+1), 257.10 (M+2). Anal. Calc. for $C_{15}H_{10}ClNO$ (255.71): C, 70.46; H, 3.94; N, 5.48. Found: C, 70.44l; H, 3.98; N, 5.45% (Fig. 27).

3.5.5. 2-Naphth-1-yl-1H-indole-7-carbaldehyde **23**

Starting materials: **16** (1.301 g, 4 mmol), KH (200 mg, 4.8 mmol), *t*-BuLi (1.7 molar solution in pentane, 4.7 ml, 8 mmol), dimethylformamide (585 mg, 0.62 ml, 8 mmol). 73% Yield (792 mg, 2.9 mmol, yellow solid, m.p.: 115–117 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 193.8 (9), 138.9 (10), 134.4 (2), 134.2 (11), 131.6 (20), 130.5 (4), 130.3 (8), 129.3 (7), 129.0 (13), 128.8 (16), 128.1 (19), 127.7 (14), 127.2 (17), 126.5 (18), 125.7 (6), 125.6 (12), 120.6 (15), 120.1 (5), 103.7 (3). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 10.41 (1H, bs, 1); 10.15 (1H, s, 9); 8.35 (1H, d, 14); 8.02 (1H, d, 19); 7.97–7.92 (2H, m, 5, 13); 7.61–7.53 (3H, m, 7, 12, 16); 7.35 (1H, t, 6); 6.91 (1H, d, 3). IR (ATR) ν [cm^{-1}]: 3349s (NH), 2981m, 2793w, 2712w, 1673s (C=O), 1604w, 1591m, 1560w, 1539m, 1508w, 1486w, 1449w, 1395w, 1377w, 1345m, 1300m, 1259w, 1245w, 1227w, 1191w, 1169w, 1110m, 1064m, 1050s, 1033m, 1001m, 1001w, 958w, 909w, 887w, 879w, 861w, 818w, 806m, 786s, 769s, 737m, 718m, 698m, 663w, 635w, 621m, 567w, 535w, 499w, 472w, 453w, 440w, 424w, 414w, 401w. MS (EI pos) *m*/*z*: 270.17 (M−1), 271.16 (M), 272.16 (M+1). Anal. Calc. for $C_{19}H_{13}NO$ (271.32): C, 84.11; H, 4.83; N, 5.16. Found: C, 84.06; H, 4.80; N, 5.12% (Fig. 28).

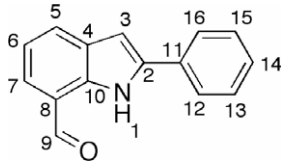


Fig. 25. Numbering of **20** for NMR assignment.

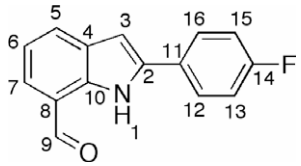


Fig. 26. Numbering of **21** for NMR assignment.

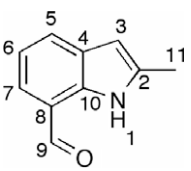


Fig. 24. Numbering of **19** for NMR assignment.

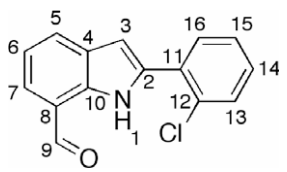


Fig. 27. Numbering of **22** for NMR assignment.

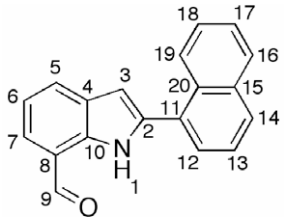


Fig. 28. Numbering of **23** for NMR assignment.

3.5.6. 3,3-Dimethyl-2,2-diphenyl-2,3-dihydro-1H-indole-7-aldehyde **24**

A Schlenk vessel was charged with **17** (1.29 g, 4.3 mmol) and dry ether (50 ml). After the solution was cooled to −100 °C in an ethanol/liquid nitrogen cooling bath, phenyllithium (4 eq., 1.8 M in cyclohexane/ether; 9.6 ml, 17.2 mmol) was added in one portion, the mixture was stirred for one hour at to −100 °C and then allowed to warm to ambient temperature. Dry dimethylformamide (585 mg, 0.62 ml, 8 mmol) was added and the solution was stirred over night. Workup: the mixture was poured on cold, saturated ammonium chloride solution, extracted with three portions of ether, the combined organic layers were washed with water and brine, dried over sodium sulfate, filtered and evaporated. Decaline (30 ml, mixture of *cis*/*trans*-isomers) was added to the residue and volatile materials were evaporated under high vacuum at 70 °C. The residue was purified by chromatography (silica; hexane/ether = 3/1) to yield 895 mg **24** as a pale yellow solid (2.7 mmol; 63%), mp.: 138–141 °C. ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 193.2 (9), 150.2 (10), 142.8 (11), 141.5 (4),131.3 (7), 128.1 (13), 127.7 (12), 127.6 (14), 126.8 (5), 117.8 (6), 117.0 (8), 80.6 (2), 48.9 (3), 27.2 (15). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 9.93 (1H, s, 9); 7.43 (1H, d, 5); 7.38 (4H, dd, 12); 7.29–7.26 (7H, m, 1, 13, 14); 7.20 (1H, d, 7); 6.83 (1H, t, 6); 1.21 (6H, s, 15). IR (ATR) ν [cm^{-1}]: 3380m (NH), 3056w, 2963w, 2926w, 2813w, 2727w, 1702w, 1661s (CHO), 1611m, 1589s, 1517w, 1493w, 1461s, 1443s, 1378m, 1337m, 1263m, 1196s, 1155w, 1127m, 1083w, 1056w, 1033w, 1014w, 1000w, 989m, 931w, 903w, 882w, 786w, 765m, 749m, 723m, 698s, 641w, 631w, 591w, 562w, 516m, 489m. MS (EI pos) *m*/*z*: 327.17 (M), 328.17 (M+1). Anal. Calc. for: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.32; H, 6.42; N, 4.23% (Fig. 29).

3.6. General procedure for the preparation of achiral indolophenligands **27** and **28**

A mixture of 7-formylindole (2 equivalents) and one equivalent of the respective *o*-phenylenediamine was heated for 15 min at 600 W power in an "Anton Paar Synthos 3000" microwave reactor. The resulting cake was dissolved in dichloromethane, dried over sodium sulfate, filtered and evaporated. The crude ligands were purified by chromatography (silica; hexane/ether = 1/1).

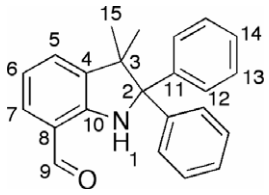


Fig. 29. Numbering of **24** for NMR assignment.

3.6.1. N,N′-Bis-[1-(1H-indol-7-yl)-methylidene]-benzyl-1,2-diamine **27**

Starting materials: 7-formylindole (871 mg, 6 mmol), *o*-phenylenediamine (324 mg, 3 mmol). 47% Yield (514 mg, 1.4 mmol, yellow solid). ^{13}C NMR (75.432 MHz, CDCl3) δ [ppm]: 161.2 (9), 145.3 (11), 134.3 (10), 129.0 (8), 127.3 (13), 126.8 (5), 125.7 (2), 125.1 (6), 120.2 (4), 119.8 (7), 119.1 (12), 102.7 (3). ^{1}H NMR (300 MHz, CDCl3) δ [ppm]: 11.02 (1H, bs, 1); 8.83 (1H, s, 9); 7.83 (1H, d, 5); 7.45 (1H, dd, 7); 7.36 (2H, s, 12, 13); 7.22 (1H, t, 6); 6.81 (1H, t, 2); 6.57 (1H, t, 3). IR (ATR) ν [cm^{-1}]: 3390s (NH), 3359s (NH), 3063w, 2923w, 2887w, 1619s (C=N), 1595s, 1569s, 1506w, 1478m, 1441m, 1405w, 1365s, 1333s, 1277w, 1249w, 1208m, 1172m, 1093s, 1065m, 1034s, 974w, 947w, 932w, 898m, 879w, 853w, 821m, 792s, 760m, 749w, 724s, 692m, 630m, 595s, 575w, 554s, 530m, 502w, 465w. MS (FAB pos, NOBA) *m*/*z*: 362.14 (M), 363.14 (M+1), 364 15 (M+2). Anal. Calc. for $C_{24}H_{18}N_4$ (362.44): C, 79.54; H, 5.01; N, 15.46. Found: C, 79.48; H, 4.97; N, 15.40% (Fig. 30).

3.6.2. N,N′-Bis-[1-(1H-indol-7-yl)-methylidene]-4,5-dimethyl-benzyl-1,2-diamine **28**

Starting materials: 7-formylindole (871 mg, 6 mmol), 4,5-dimethyl-1,2-phenylendiamine (409 mg, 3 mmol). 39% Yield (461 mg, 1.18 mmol, yellow solid, m.p.: 116–118 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 160.4 (9), 143.0 (11), 135.8 (13), 134.3 (10), 129.0 (8), 126.6 (5), 125.6 (2), 124.8 (6), 120.4 (4), 120.2 (7), 119.7 (12), 102.7 (3), 20.0 (14). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 11.07 (1H, bs, 1); 8.83 (1H, s, 9); 7.82 (1H, d, 5); 7.45 (1H, d, 7); 7.22 (1H, t, 6); 7.17 (1H, s, 12); 6.82 (1H, t, 2); 6.58 (1H, t, 3); 2.40 (3H, s, 14). IR (ATR) ν [cm^{-1}]: 3388s (NH), 3317s (NH), 3053w, 2881w, 1621s (C=N), 1584s, 1490m, 1439m, 1394w, 1361m, 1335s, 1278w, 1232m, 1205w, 1191w, 1169m, 1096s, 1063m, 1034s, 1001m, 965w, 884m, 867s, 792s, 725s, 641m, 613w, 603w, 593w, 574w, 560m, 535w, 510w, 491w, 472w, 440w, 425w, 415w. MS (EI pos) *m*/*z*: 390.22 (M), 391.22 (M+1). Anal. Calc. for $C_{26}H_{22}N_4$ (390.49): C, 79.97; H, 5.68; N, 14.35. Found: C, 79.88; H, 5.59; N, 14.28% (Fig. 31).

3.7. (N,N′-Bis-[1-(1H-indolato-7-yl)-meth-(E)-ylidene]-benzyl-1,2-diamino)-chloro-tetrahydrofurano-chromium(III) **29**

A Schlenk tube was charged with **27** (120 mg, 0.33 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.41 ml, 0.66 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (104 mg, 0.66 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with dry dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **29** (175 mg, 0.33 mmol, 99%) as a red,

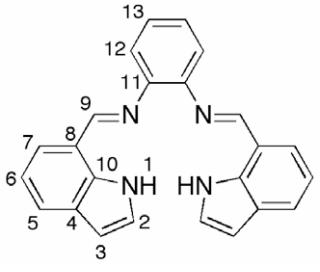


Fig. 30. Numbering of **27** for NMR assignment.

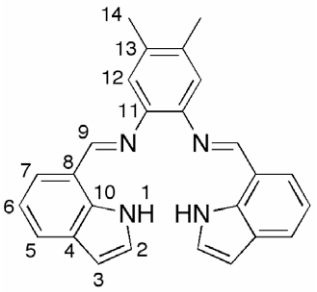


Fig. 31. Numbering of **28** for NMR assignment.

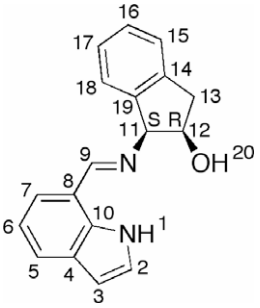


Fig. 32. Numbering of **31** for NMR assignment.

paramagnetic solid. Anal. Calc. for $C_{28}H_{24}ClCrN_4O$ (519.97): C, 64.68; H, 4.65; N, 10.78. Found: C, 64.56; H, 4.53; N, 10.64%.

3.8. (N,N′-Bis-[1-(1H-indolato-7-yl)-meth-(E)-ylidene]-4,5-dimethyl-benzyl-1,2-diamino)-chloro-tetrahydrofurano-chromium(III) **30**

A Schlenk tube was charged with 28 (398 mg, 1 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 1 ml, 2 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (316 mg, 2 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with dry dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording 30 (583 mg, 1 mmol, 99%) as a red, paramagnetic solid. Anal. Calc. for $C_{30}H_{28}ClCrN_4O$ (548.02): C, 65.75; H, 5.15; N, 10.22. Found: C, 65.58; H, 5.01; N, 10.11%.

3.9. (1S,2R)-(−)-cis-1-{[1-(1H-Indol-7-yl)-methylidene]-amino}-indan-2-ol **31**

A Schlenk tube was charged with 7-formylindole (207 mg, 1.4 mmol), (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (209 mg, 1.4 mmol) and dry methanol (5 ml). The mixture was refluxed over night. On cooling to room temperature, the product precipitated as a colorless solid. Workup: the solid was collected, washed three times with small portions of cold methanol, and recrystallized from dichloromethane. Yield: 78% (300 mg, 1.08 mmol, colorless solid, m.p.: 153–157 °C). ^{13}C NMR (75.432 MHz, THF-d8) δ [ppm]: 164.9 (9), 143.9 (19), 142.4 (14), 134.2 (10), 129.6 (8), 128.2 (17), 126.9 (16), 126.3 (15), 126.1 (7), 125.7 (2), 125.2 (18), 124.2 (5), 120.4 (4), 119.3 (6), 102.2 (3), 78.8 (12), 76.2 (11), 40.9 (13). ^{1}H NMR (300 MHz, THF-d8) δ [ppm]: 10.86 (1H, bs,1); 8.77 (1H, s, 9); 7.67 (1H, d, 5); 7.36 (1H, d, 7); 7.28–7.08 (6H, m, 2, 6, 15–18); 6.47 (1H, t, 3); 4.77 (1H, d, 11); 4.56 (1H, t, 12); 3.99 (1H, d, 20); 3.12 (2H, m,13). IR (ATR) ν [cm^{-1}]: 3489 m (OH), 3416s (NH), 3059w, 3023w, 2920w, 2838w, 1628s (C=N), 1599s, 1558w, 1541w, 1508w, 1476m, 1457w, 1443w, 1428w, 1400w, 1387w, 1360m, 1335s, 1288m, 1257m, 1241m, 1208w, 1184m, 1171m, 1157m, 1059s, 1061m, 1039s, 989m, 977m, 956w, 946w, 890m, 874w, 862w, 842w, 829m, 794s, 753s, 747s, 730s, 721m, 669s, 602w, 577m, 564m, 529w, 504w, 473w, 452w, 403m. MS (FAB pos, NOBA) *m*/*z*: 276.1 (M), 277.2 (M+1). Anal. Calc. for $C_{18}H_{16}N_2O$ (276.34): C, 78.24; H, 5.84; N, 10.14. Found: C, 78.15; H, 5.76; N, 10.08% (Fig. 32).

3.10. (1R,2S)-(+)-cis-1-{[1-(1H-Indol-7-yl)-methylidene]-amino}-indan-2-ol **32**

A Schlenk tube was charged with 7-formylindole (145 mg, 1 mmol), (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (150 mg, 1 mmol) and dry methanol (10 ml). The mixture was refluxed over night. On cooling to room temperature, the product precipitated as a colorless solid. Workup: the solid was collected, washed three times with small portions of cold methanol, and recrystallized from methanol. Yield: 69% (190 mg, 0.69 mmol, colorless solid). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 165.8 (9), 142.0 (19), 141.7 (14), 133.9 (10), 128.8 (8), 128.4 (17), 127.0 (16), 126.6 (15), 125.6 (2), 124.9 (93), 124.6 (5), 119.6 (6), 119.2 (23), 102.6 (3), 77.9 (12), 75.7 (11), 40.2 (13). ^{1}H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.35 (1H, bs, 1); 8.82 (1H, s, 9); 7.79 (1H, d, 5); 7.44 (1H, dd, 7); 7.34 (1H, d, 18); 7.28 (1H, d, 15); 7.24–7.15 (4H, m, 17, 16, 6, 2); 6.58 (1H, t, 3); 4.84 (1H, d, 11); 4.47 (1H, q, 12); 3.20 (2H, dq, 13); 2.65 (1H, bs, 20). IR (ATR) ν [cm^{-1}]: 3492m (OH), 3419s (NH), 3022w, 2919w, 2837w, 1627s (C=N), 1599s, 1517w, 1485m, 1467m, 1475w, 1442w, 1428w, 1400w, 1388w, 1360w, 1335m, 1288m, 1259m, 1240m, 1208w, 1187s, 1171s, 1158w, 1120w, 1089s, 1060m, 1039s, 989s, 978m, 956w, 945w, 922w, 890w, 873w, 861w, 842w, 830w, 749s, 754s, 746m, 731s, 721w, 694w, 670s, 602w, 578s, 565m, 529w, 504w, 478w, 452m, 421w, 414w. MS (FAB pos, NOBA) *m*/*z*: 276.2 (M), 277.17 (M+1), 278.17 (M+2). Anal. Calc. for $C_{18}H_{16}N_2O$ (276.34): C, 78.24; H, 5.84; N, 10.14. Found: C, 78.20; H, 5.79; N, 10.07% (Fig. 33).

3.11. (1R,2R)-N,N′-Bis-[1-(1H-indol-7-yl)-methylidene]-cyclohexane-1,2-diamine **33**

A Schlenk tube was charged with 7-formylindole (290.3 mg, 2 mmol), (1*R*,2*R*)-cyclohexane-1,2-diamine (114.2 mg, 1 mmol) and dry methanol (20 ml). The mixture was refluxed over night. On cooling to room temperature, the product precipitated as a colorless powder. Workup: the solid was collected and washed three times with small portions of cold methanol. Yield: 85% (312 mg, 0.85 mmol, colorless powder). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 161.6 (9), 134.2 (10), 128.5 (8), 125.2 (5), 125.1 (2), 123.4 (7), 119.7 (4), 119.3 (6), 102.2 (3), 74.6 (11), 33.7 (12), 25.0 (13). ^{1}H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.77 (1H, bs, 1); 8.48 (1H,

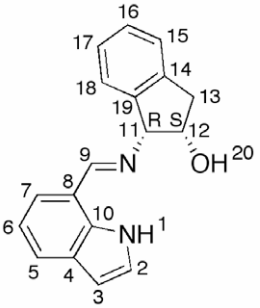


Fig. 33. Numbering of **32** for NMR assignment.

s, 9); 7.66 (1H, d, 5); 7.26 (1H, t, 2); 7.15 (1H, dd, 7); 7.06 (1H, t, 6); 6.55 (1H, t, 3); 3.53 (1H, ddd, 11 diast.); 1.99 (3H, m,13, 12 E); 1.61 (1H, dd, 12 Z). IR (ATR) ν [cm^{-1}]: 3328s (NH), 3055w, 3010w, 2942w, 2905w, 2852w, 1631s (C=N), 1597s, 1520w, 1481m, 1458w, 1444m, 1400w, 1372m, 1338s, 1306m, 1238m, 1202s, 1169s, 1142w, 1097s, 1064s, 1028s, 968w, 938w, 899w, 858s, 846s, 817w, 791s, 754w, 731s, 722s, 667m, 632w, 602m, 572s, 549w, 539s, 495w, 457w, 432w. MS (FAB pos, NOBA) *m*/*z*: 368.21 (M), 369.22 (M+1), 370.22 (M+2). Anal. Calc. for $C_{24}H_{24}N_4$ (368.49): C, 78.23; H, 6.57; N, 15.21. Found: C, 78.14; H, 6.50; N, 15.10% (Fig. 34).

3.12. Bis(tetrahydrofurano)-chloro-(1S,2R)-(−)-cis-1-{[1-(1H-indolato-7-yl)-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) **34**

A Schlenk tube was charged with **31** (97 mg, 0.35 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.35 ml, 0.7 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (112 mg, 0.7 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with dry dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **34** (188 mg, 0.37 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{26}H_{32}ClCrN_2O_3$ (507.99): C, 61.47; H, 6.35; N, 5.51. Found: C, 61.31; H, 6.23; N, 5.42%.

3.13. Bis(tetrahydrofurano)-chloro-(1R,2S)-(+)-cis-1-{[1-(1H-indolato-7-yl)-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) **35**

A Schlenk tube was charged with **32** (118 mg, 0.43 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.43 ml, 0.86 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (138 mg, 0.86 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with dry dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **35** (218 mg, 0.43 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{26}H_{32}ClCrN_2O_3$ (507.99): C, 61.47; H, 6.35; N, 5.51. Found: C, 61.36; H, 6.27; N, 5.45%.

3.14. (1R,2R)-N,N′-Bis-[1-(1H-indolato-7-yl)-methylidene]-cyclohexan-1,2-diamino-chloro-tetrahydrofurano-chromium(III) **36**

A Schlenk tube was charged with **33** (270 mg, 0.73 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.73 ml, 1.46 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (221 mg, 1.4 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with dry dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **36** (394 mg, 0.75 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{28}H_{30}ClCrN_4O$ (526.01): C, 63.93; H, 5.75; N, 10.65. Found: C, 63.80; H, 5.62; N, 10.52%.

3.15. (1R,2R)-N,N′-Bis-[1-(2-methyl-1H-indol-7-yl)-methylidene]-cyclohexane-1,2-diamine **37**

A Schlenk tube was charged with **19** (120 mg, 0.75 mmol), (1*R*,2*R*)-cyclohexane-1,2-diamine (43 mg, 0.38 mmol) and dry methanol (20 ml). The mixture was refluxed over night. On cooling to room temperature, the product precipitated as a pale yellow powder. Workup: the solid was collected and washed three times with small portions of cold methanol. Yield: 97% (148 mg, 0.37 mmol, pale yellow powder). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 161.7 (9), 136.4 (10), 134.5 (2), 129.8 (8), 124.3 (5), 122.4 (7), 119.1 (6), 118.9 (4), 100.2 (3), 74.4 (11), 33.7 (12), 25.1 (13), 13.8 (14). ^1H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.56 (1H, bs,1); 8.56 (1H, s, 9); 7.62 (1H, d, 5); 7.18 (1H, d, 7); 7.12 (1H, t, 6); 6.31 (1H, t, 3); 3.62 (1H, ddd, 11 diast.); 2.48 (3H, s, 14); 2.08 (3H, m, 13, 12 E); 1.68 (1H, dd, 12 Z). IR (ATR) ν [cm^{-1}]: 3351s (NH), 2927s, 2851s, 1630s (C=N), 1604s, 1556m, 1489m, 1443m, 1397w, 1377m, 1345m, 1298m, 1239w, 1190w, 1173m, 1143m, 1090m, 1056s, 1025w, 968w, 934w, 895w, 856w, 846w, 794s, 758m, 743s, 659s, 596w, 572m, 548w, 524w, 494w, 475w, 432w, 416w. MS (FAB pos, NOBA) *m*/*z*: 396.25 (M), 397.26 (M+1), 398.26 (M+2). Anal. Calc. for $C_{26}H_{28}N_4$ (396.54): C, 78.75; H, 7.12; N, 14.13. Found: C, 78.78; H, 7.14; N, 14.07% (Fig. 35).

3.16. (1R,2S)-(+)-cis-1-{[1-(2-Methyl-1H-indol-7-yl)-methylidene]-amino}-indan-2-ol **38**

A Schlenk tube was charged with **19** (159 mg, 1 mmol), (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (150 mg, 1 mmol) and dry methanol (5 ml). The mixture was refluxed over night. Workup: volatile materials were removed in vacuo, the residual oil was triturated with ether, and the solidified product was collected. Yield: 78% (226 mg, 0.78 mmol, colorless solid, m.p.: 122–125 °C). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 166.0 (9), 142.8 (19), 141.6 (14), 136.8 (2), 134.2 (10), 129.9 (8), 128.3 (17), 127.0 (16), 125.6 (7, 15), 124.9 (18), 123.4 (5), 119.3 (6), 118.4 (4), 100.5 (3), 78.0 (12), 75.6 (11), 40.1 (13), 13.9 (21). ^1H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.01 (1H, bs, 1); 8.78 (1H, s, 9); 7.65 (1H, d, 5); 7.37–7.13 (6H, m, 6, 7, 15–18); 6.27 (1H, t, 3); 4.83 (1H, d, 11); 4.67 (1H, dd, 12); 3.20 (2H, dq, 13); 2.69 (1H, bs, 20); 2.41 (3H, s, 21).

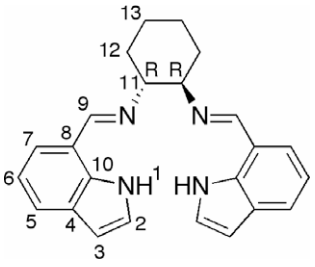


Fig. 34. Numbering of **33** for NMR assignment.

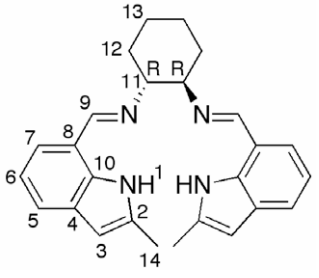


Fig. 35. Numbering of **37** for NMR assignment.

IR (ATR) ν [cm^{-1}]: 3536m (OH), 3427s (NH), 3022w, 2964w, 2920w, 2826w, 1625s (C=N), 1602s, 1561m, 1540w, 1507w, 1488w, 1474m, 1455m, 1445m, 1384m, 1345m, 1317w, 1286m, 1253w, 1239m, 1179m, 1146m, 1099m, 1074m, 1053s, 1024w, 978m, 948w, 920w, 880w, 849w, 831m, 799s, 769s, 746s, 737s, 668m, 646s, 598w, 575s, 550s, 528w, 507w, 468m, 438w. MS (FAB pos, glycerine) *m/z*: 289.10 (M−1), 290.11 (M), 291.11 (M+1), 292.12 (M+2). Anal. Calc. for $C_{19}H_{18}N_2O$ (290.36): C, 78.59; H, 6.25; N, 9.65. Found: C, 78.51; H, 6.17; N, 9.55% (Fig. 36).

3.17. (1S,2R)-(−)-cis-1-{[1-(2-Phenyl-1H-indol-7-yl)-methylidene]-amino}-indan-2-ol **39**

A Schlenk tube was charged with **20** (200 mg, 0.9 mmol), (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (134 mg, 0.9 mmol) and dry methanol (5 ml). The mixture was refluxed over night. Workup: volatile materials were removed in vacuo, the oily residue was recrystallized from ethanol. Yield: 84% (226 mg, 0.75 mmol, pale yellow crystals, m.p.: 106–110 °C). ^{13}C NMR (75.432 MHz, CD_2Cl_2) δ [ppm]: 165.1 (9), 142.5 (19), 141.3 (14), 138.9 (2), 135.2 (10), 132.2 (21), 129.9 (8), 129.3 (23, 26), 128.4 (17), 128.0 (24), 127.1 (16), 126.4 (15), 125.6 (7), 125.2 (22, 25), 124.9 (18), 124.2 (5), 112.0 (6), 119.2 (4), 99.4 (3), 77.2 (12), 75.7 (11), 40.2 (13). ^1H NMR (300 MHz, CD_2Cl_2) δ [ppm]: 10.85 (1H, bs, 1); 8.82 (1H, s, 9); 7.76 (1H, dd, 5); 7.60 (2H, d,7,18); 7.43–7.20, (9H, m, 6, 15–17, 22–26); 6.89 (1H, t, 3); 4.89 (1H, d, 11); 4.74 (1H, dd,12); 4.24 (2H, dq,13); 2.35 (1H, bs, 20). IR (ATR) ν [cm^{-1}]: 3567m (OH), 3381s (NH), 3058w, 3016w, 2919w, 2853w, 1626s (C=N), 1597s, 1545w, 1478s, 1453m, 1425w, 1374m, 1358s, 1336w, 1304m, 1288w, 1239w, 1223w, 1185w, 1167w, 1156w, 1097s, 1081m, 1049s, 1036s, 976m, 899w, 880w, 865w, 843w, 827w, 797s, 774m, 758s, 733s, 683m, 700w, 646w, 595w, 572w, 521w, 504w, 471w, 409w. MS (FAB pos, NOBA) *m/z*: 352.14 (M), 353.15 (M+1), 354.15 (M+2). Anal. Calc. for $C_{24}H_{20}N_2O$ (352.45): C, 81.79; H, 5.72; N, 7.95. Found: C, 81.63; H, 5.66; N, 7.87% (Fig. 37).

3.18. (1R,2R)-N,N′-Bis-[1-(2-methyl-1H-indolato-7-yl)-methylidene]-cyclohexane-1,2-diamino-chloro-tetrahydrofurano-chromium(III) **40**

A Schlenk tube was charged with **37** (100 mg, 0.25 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.25 ml, 0.5 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (80 mg, 0.5 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with dry dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **40** (146 mg, 0.25 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{30}H_{36}ClCrN_4O$ (556.09): C, 64.80; H, 6.53; N, 10.08. Found: C, 64.67; H, 6.41; N, 9.94%.

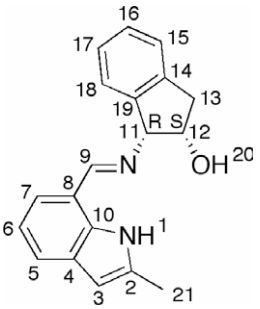


Fig. 36. Numbering of **38** for NMR assignment.

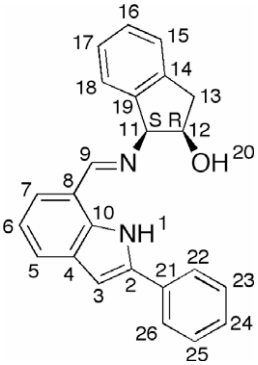


Fig. 37. Numbering of **39** for NMR assignment.

3.19. Bis(tetrahydrofurano)-chloro-(1R,2S)-(+)-cis-1-{[1-(2-methyl-1H-indolato-7-yl)-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) **41**

A Schlenk tube was charged with **38** (235 mg, 0.85 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.85 ml, 0.8 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (267 mg, 1.7 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were stripped off in vacuum, the residue was triturated with toluene (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **41** (415 mg, 0.8 mmol, 94%) as a brown, paramagnetic solid. Anal. Calc. for $C_{27}H_{36}ClCrN_2O_3$ (524.04): C, 61.88; H, 6.92; N, 5.35. Found: C, 61.73; H, 6.80; N, 5.22%.

3.20. Bis(tetrahydrofurano)-chloro-(1S,2R)-(−)-cis-1-{[1-(2-phenyl-1H-indolato-7-yl)-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) **42**

A Schlenk tube was charged with **39** (275 mg, 0.78 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.78 ml, 1.56 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (190 mg, 1.2 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were removed in vacuum, the residue was triturated with dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **42** (437 mg, 0.75 mmol, 96%) as a brown, paramagnetic solid. Anal. Calc. for $C_{32}H_{34}ClCrN_2O_3$ (582.08): C, 66.03; H, 5.89; N, 4.81. Found: C, 65.91; H, 5.76; N, 4.72%.

3.21. (1S,2R)-(−)-cis-1-{[1-(2-Naphthalin-1-yl-1H-indol-7-yl)-methylidene]-amino}-indan-2-ol **43**

A Schlenk tube was charged with **22** (508 mg, 1.87 mmol), (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (284 mg, 1.9 mmol) and dry methanol (5 ml). The mixture was refluxed over night. Workup: volatile materials were removed in vacuo, the oily residue was dissolved in hexane, the solution was filtered through Celite®, hexane was evaporated, affording the solid product. Yield: 88% (660 mg, 1.64 mmol, pale yellow solid, m.p.: 58–60 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 165.4 (9), 142.0 (19), 141.2 (14), 138.3 (2), 134.7 (10), 134.3 (27), 131.5 (22), 130.9 (21), 129.8 (8), 129.0 (29), 128.9 (28), 128.6 (17), 127.5 (25), 127.2 (24), 127.1 (16), 126.6 (30), 126.4 (15), 125.8 (23, 26), 125.5 (7), 124.9 (18), 124.6 (5), 120.0 (6), 119.1 (4), 103.6 (3), 77.5 (12), 75.6 (11), 40.2

(13). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 10.73 (1H, bs, 1); 8.85 (1H, s, 9); 8.39 (1H, d, 28); 7.93 (3H, m,5, 23, 30); 7.66 (1H, d, 7); 7.57–7.21 (9H, m, 6, 15–18, 24–26, 29); 6.93 (1H, s, 3); 4.87 (1H, d, 11); 4.72 (1H, q, 12); 3.17 (2H, dd, 13); 2.64 (1H, bs, 20). IR (ATR) ν [cm^{-1}]: 3547w (OH), 3374s (NH), 3047m, 2910m, 1628m (C=N), 1598s, 1541w, 1508w, 1490w, 1476w, 1458w, 1437m, 1393m, 1376m, 1348m, 1299m, 1262m, 1228w, 1168w, 1109w, 1051m, 1020w, 978w, 947w, 912w, 861w, 798s, 776s, 734s, 693m, 664w, 637w, 595w, 569w, 518w, 484w, 466w, 453w, 423m. MS (EI pos) *m*/*z*: 402.20 (M), 403.20 (M+1). Anal. Calc. for $C_{28}H_{22}N_2O$ (402.49): C, 83.56; H, 5.51; N, 6.96. Found: C, 83.59; H, 5.55; N, 6.89% (Fig. 38).

3.22. (1R,2S)-(+)-cis-1-{[1-(3,3-Dimethyl-2,2-diphenyl-2,3-dihydro-1H-indole-7-yl)-methylidene]-amino}-indan-2-ol **44**

A Schlenk tube was charged with **24** (665 mg, 2 mmol), (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (313 mg, 2 mmol) and dry methanol (5 ml). The mixture was refluxed over night. Workup: volatile materials were removed in vacuo, the residue was dissolved in dichloromethane, the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum. Yield: 98% (900 mg, 1.96 mmol, yellow–green solid). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 165.7 (9); 149.1 (10); 143.9, 143.3 (21); 142.4 (19); 141.1 (14); 140.6 (4); 130.3, 128.3 (24); 128.1, 128.0 (23, 25); 127.6, 127.5 (22, 26); 127.2, 127.1, 127.0 (15, 16, 17); 125.7 (5); 124.7 (18); 123.9 (7); 118.0 (6); 115.4 (8); 80.4 (2); 77.2 (12); 75.3 (11); 49.0 (3); 40.0 (13); 27.8, 26.3 (27). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 8.65 (1H, s, 9); 7.42–7.17 (16 H, m, arom., 1); 6.95 (1H, d, 5); 6.85 (1H, t, 6); 4.76 (1H, d,11); 4.64 (1H, t, 12); 3.12 (2H, dd, 13); 2.79 (1H, bs, 20); 1.30, 1.19 (2x3H, 2s, 27). IR (ATR) ν [cm^{-1}]: 3538w (OH), 3307w (NH), 3054m, 2962m, 2923m, 1625s (C=N), 1588s, 1491m, 1460s, 1443s, 1386m, 1364w, 1330m, 1263m, 1217w, 1201m, 1155w, 1127w, 1097w, 1081w, 1051m, 1033m, 982w, 947w, 912w, 885w, 860w, 825w, 788w, 748s, 699s, 642w, 593w, 530w, 497w, 467w, 454w, 415w. MS (EI pos) *m*/*z*: 458.30 (M), 459.30 (M+1), 460.30 (M+2). Anal. Calc. for $C_{32}H_{30}N_2O$ (458.59): C, 83.81; H, 6.59; N, 6.11. Found: C, 83.78; H, 6.56; N, 6.05% (Fig. 39).

3.23. (1R,2S)-(+)-cis-1-{[1-[2-(4-Fluoro-phenyl)-1H-indol-7-yl]-methylidene]-amino}-indan-2-ol **45**

A Schlenk tube was charged with **21** (350 mg, 1.46 mmol), (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (220 mg, 1.48 mmol) and dry methanol (10 ml). The mixture was refluxed over night. Workup: volatile materials were removed in vacuo, the residue was dissolved in dichloromethane, the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum. Yield: 58% (313 mg, 0.84 mmol, yellow–green solid, m.p.: 136–138 °C). ^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 165.3 (9), 164.3, 161.1 (24), 142.1 (19), 141.0 (14), 138.2 (2), 135.2 (10), 130.0 (8), 128.9, 128.5 (21), 128.6 (17), 127.3 (16), 127.1, 127.0 (22, 26), 126.5 (15), 125.8 (7), 124.9 (18), 124.4 (5), 120.1 (6), 119.0 (4), 116.5, 116.2 (23, 25), 99.5 (3), 77.2 (12), 75.6 (11), 40.2 (13). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 10.72 (1H, bs,1); 8.80 (1H, s, 9); 7.78 (1H, d, 5); 7.75 (2H, 2d, 7, 18); 7.41–7.06 (8H, m, 6, 15–17, 22–25); 6.80 (1H, d, 3); 4.89 (1H, d, 11); 4.76 (1H, dd, 12); 3.26 (2H, dq, 13); 2.72 (1H, bs, 20). IR (ATR) ν [cm^{-1}]: 3564w (OH), 3342m (NH), 3068w, 2918m, 2839m, 1630s (C=N), 1602s, 1592s, 1547m, 1502s, 1484s, 1458m, 1441w, 1425m, 1373m, 1353s, 1305w, 1232s (C–F), 1179w, 1159s, 1098m, 1078w, 1049s, 1033w, 1012w, 974m, 948w, 935w, 913w, 900w, 884w, 836s, 803s, 757s, 742s, 711m, 661m, 634w, 596w, 572m, 515m, 470m, 426w, 404w. MS (EI pos) *m*/*z*: 370.20 (M), 371.20 (M+1), 372.21 (M+2). Anal. Calc. for $C_{24}H_{19}FN_2O$ (370.42): C, 77.82; H, 5.17; N, 7.56. Found: C, 77.76; H, 5.11; N, 7.48% (Fig. 40).

3.24. (1R,2S)-(+)-cis-1-{[1-[2-(2-Chloro-phenyl)-1H-indol-7-yl]-methylidene]-amino}-indan-2-ol **46**

A Schlenk tube was charged with **23** (493 mg, 1.93 mmol), (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (291 mg, 1.93 mmol) and dry methanol (10 ml). The mixture was refluxed over night. Workup: volatile materials were removed in vacuo, the residue was dissolved in dichloromethane, the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum. Yield: 99% (738 mg, 1.91 mmol, colorless solid).

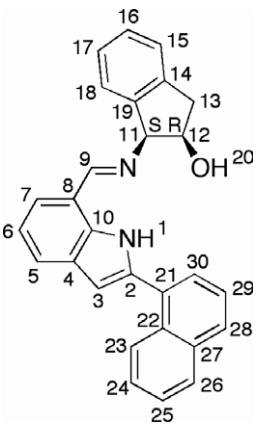


Fig. 38. Numbering of **43** for NMR assignment.

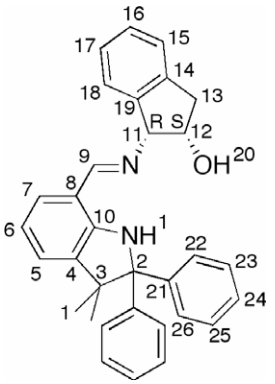


Fig. 39. Numbering of **44** for NMR assignment.

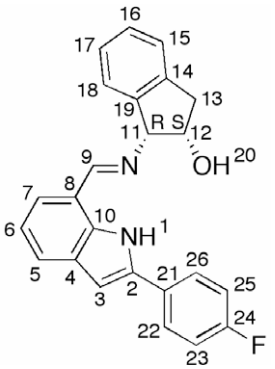


Fig. 40. Numbering of **45** for NMR assignment.

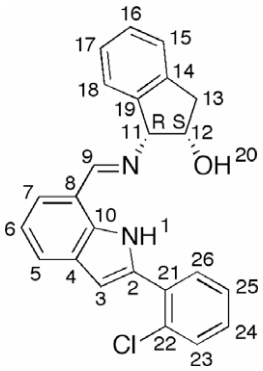


Fig. 41. Numbering of **46** for NMR assignment.

^{13}C NMR (75.432 MHz, $CDCl_3$) δ [ppm]: 165.0 (9), 142.2 (19), 141.3 (14), 136.5 (2), 134.6 (10), 131.3 (22), 131.2 (23), 130.9 (21), 130.8 (26), 129.1 (24), 128.9 (8), 128.6 (17), 127.5 (25), 127.2 (16), 127.0 (15), 125.7 (7), 125.0 (18), 124.7 (5), 120.0 (6), 119.2 (4), 102.1 (3), 77.5 (12), 75.7 (11), 40.2 (13). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm]: 11.21 (1H, bs, 1); 8.82 (1H, s, 9); 7.83 (1H, d, 5); 7.68 (1H, d, 7); 7.47–7.18 (9H, m, 6, 15–18, 23–26); 6.93 (1H, t, 3); 4.86 (1H, d, 11); 4.76 (1H, d, 12); 3.29 (2H, m, 13); 2.73 (1H, bs, 20). IR (ATR) ν [cm^{-1}]: 3541w (OH), 3384s (NH), 3060w, 2910m, 1628s (C=N), 1597s, 1565w, 1533w, 1470m, 1456s, 1439s, 1376m, 1358m, 1304m, 1260w, 1238w, 1215m, 1168w, 1123w, 1098m, 1080s, 1052s, 1032s, 979w, 946w, 858w, 805s, 742s, 698m, 677m, 634w, 590m, 505w, 474w, 448m, 426w, 415w. MS (EI pos) *m*/*z*: 386.14 (M), 388.14 (M+2). Anal. Calc. for $C_{24}H_{19}ClN_2O$ (386.87): C, 74.51; H, 4.95; N, 7.24. Found: C, 74.50; H, 4.91; N, 7.20% (Fig. 41).

3.25. Bis(tetrahydrofurano)-chloro-(1S,2R)-(−)-cis-1-{[1-(2-napht-1-yl-1H-indolato-7-yl)-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) ***47***

A Schlenk tube was charged with **43** (530 mg, 1.3 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 1.3 ml, 2.6 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (417 mg, 2.6 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were removed in vacuum, the residue was triturated with dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **47** (820 mg, 1.3 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{36}H_{36}ClCrN_2O_3$ (632.13): C, 68.40; H, 5.74; N, 4.43. Found: C, 68.32; H, 5.66; N, 4.38%.

3.26. Bis(tetrahydrofurano)-chloro-(1R,2S)-(+)-cis-1-{[1-(3,3-dimethyl-2,2-diphenyl-2,3-dihydro-1H-indolato-7-yl)-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) ***48***

A Schlenk tube was charged with **44** (688 mg, 1.5 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 1.5 ml, 3 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (475 mg, 3 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were removed in vacuum, the residue was triturated with dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **48** (1025 mg, 1.49 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{40}H_{44}ClCrN_2O_3$ (688.24): C, 69.81; H, 6.44; N, 4.07. Found: C, 69.68; H, 6.30; N, 3.92%.

3.27. Bis(tetrahydrofurano)-chloro-(1R,2S)-(+)-cis-1-{[1-[2-(4-fluorophenyl)-1H-indolato-7-yl]-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) ***49***

A Schlenk tube was charged with **45** (265 mg, 0.715 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 0.715 ml, 1.43 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (226 mg, 1.43 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were removed in vacuum, the residue was triturated with dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **49** (449 mg, 0.75 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{32}H_{33}ClCrFN_2O_3$ (600.06): C, 64.05; H, 5.54; N, 4.67. Found: C, 63.91; H, 5.41; N, 4.50%.

3.28. Bis(tetrahydrofurano)-chloro-(1R,2S)-(+)-cis-1-{[1-[2-(2-chlorphenyl)-1H-indolato-7-yl]-meth-(E)-ylidene]-amino}-indan-2-olato-chromium(III) ***50***

A Schlenk tube was charged with **46** (436 mg, 1.15 mmol) and dry THF (20 ml). The solution was cooled to −80 °C, *n*-BuLi (2 M solution in hexane, 1.15 ml, 3.3 mmol) was added in one portion, and the stirred mixture was allowed to warm to room temperature. Anhydrous $CrCl_3$ (365 mg, 2.3 mmol) was added and stirring was continued for 24 h. Workup: solvents and volatile materials were removed in vacuum, the residue was triturated with dichloromethane (20 ml), the resulting suspension was filtered through Celite®, the filtrate was evaporated and the product was dried in vacuum, affording **50** (710 mg, 1.15 mmol, 99%) as a brown, paramagnetic solid. Anal. Calc. for $C_{32}H_{33}Cl_2CrN_2O_3$ (616.52): C, 62.34; H, 5.40; N, 4.54. Found: C, 62.18; H, 5.27; N, 4.44%.

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Appendix A. Supplementary material

CCDC 705051, 705052 and 705053 contain the supplementary crystallographic data for the structures of **32**, **38** and **39**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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