Reinventing Phenanthroline Ligands − Chiral Derivatives for Asymmetric Catalysis?

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Over the last three decades, the rational design of chiral ligands for asymmetric catalysis has increasingly replaced the trial-and-error approach. A well-known analytical reagent, 1,10-phenanthroline, is now being employed as a template for the development of chiral ligands. In most cases these heterocyclic ligands have been functionalized in the peripheral region utilizing three prevailing ligand templates. Chiral groups are either introduced in the 2-, 3-, 8- and/or 9-position (**I**, **II**) or are incorporated by ring fusion to phenanthroline (**III**).

Introduction

It has been recognized that catalysis will play a crucial role in the 21st century in the environmentally benign synthesis of new and existing chemicals.[1−3] Asymmetric catalysis, in particular, will continue to play an integral part in future applications due to a strong emphasis on the production of single stereoisomers for the marketing of new drugs. With industry adjusting to a changing regulatory climate mandated in the United States by the FDA, the control of stereochemistry and the design of new methodologies for asymmetric catalysis has become essential. The preparation of enantiomerically pure compounds has become an important aspect of organic synthesis and, thus, has received extensive attention from academic and industrial chemists alike.[4−9] This trend has fostered the development of numerous reactions in which chirality information is communicated to a substrate, and an important focus of this research is asymmetric catalysis.

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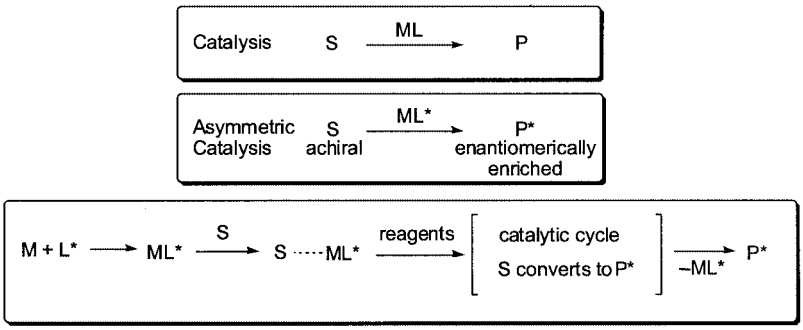
The conversion of an achiral substrate (S) into an enantiomerically enriched product (P*) can be viewed as the offspring of many disciplines, including organic, inorganic, and organometallic chemistry.[10,11] Scheme 1 illustrates the concept of transition-metal-mediated asymmetric catalysis. In most cases, asymmetric catalysis employs nonracemic ligands (L*) that bind to transition metals (M) with vacant coordination sites to produce a catalyst (ML*) according to the principles of coordination chemistry. Virtually any functional group in an organic substrate (S) can interact with metals or metal−ligand complexes, which direct functional group transformations by stabilizing or activating the substrate and by controlling chemo-, regio-, and stereoselectivities in unconventional ways.[12,13] Therefore, it is not surprising that a great number of man-made chiral catalysts have contributed to successful applications in synthetic organic chemistry, such as hydrogenation, epoxidation, dihydroxylation, carbonylation, allylic substitution, aldol and Grignard reactions. Each synthetic transformation requires its own reagent(s) that facilitate(s) the ligand substitution necessary for catalytic activity. Each component in a reaction mixture (precatalyst, ligand, base, solvent, salts, etc.) may engage in a number of equilibria that are involved in

Elke Schoffers was born in Bad Kreuznach, Germany, in 1967. She received her undergraduate chemistry degree at the Johannes Gutenberg Universität in Mainz in 1986 and continued her graduate and postgraduate education in the United States. Working under the supervision of Prof. I. Ojima at SUNY Stony Brook, she investigated asymmetric reactions of chiral β-lactam esters and received her Masters degree in 1991. She continued her graduate studies at Wayne State University under the supervision of Prof. C. R. Johnson with whom she completed her Ph.D. work in chemoenzymatic synthesis (1996). After studying (π-allyl)molybdenum complexes as a postdoctoral associate at Case Western Reserve University with Prof. A. J. Pearson (1996−98), she started her independent career as an Assistant Professor at Western Michigan University in Kalamazoo, Michigan. She is interested in the development of new synthetic methods, the synthesis of bioactive molecules and the design of ligands for catalysis.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.



Scheme 1. Concept of asymmetric catalysis; chiral species are labeled with an asterisk[17]

a catalytic cycle,[14] which generally consists of oxidative addition, migration/isomerization, and reductive elimination steps. The initial metal−ligand complex is returned to its original state at the end of one cycle, thus only sub-stoichiometric amounts are required. The conversion of substrate to product always involves changes in metal oxidation state or coordination number that ultimately determine the success of a catalytic process. During *asymmetric* catalysis, chirality information of the ligand (L*) is generally transferred to an achiral substrate (S), yielding an enantiomerically enriched product (P*).[15] One or more asymmetric catalysis steps enable asymmetric synthesis, which has been widely used in natural product syntheses and in the industrial preparation of pharmaceuticals, agrochemicals, and food ingredients.[4−6,8,16,17] Therefore, the success of *asymmetric* catalysis is based on developing suitable *nonracemic* ligands.

Chiral phosphane ligands have received much attention due to their successful application in Rh^I complexes for asymmetric hydrogenation[18,19] in the pioneering work of Kagan,[20,21] Knowles,[22] and Horner[23] between 1968 and 1972. Since then, P-containing ligands have been recruited for many other asymmetric reactions.[24] However, the early success of phosphorus ligands has apparently set a trend that may have delayed the design of nitrogen-containing ligands in asymmetric catalysis. Nitrogen donors are also recognized to be useful in organometallic chemistry and homogenous catalysis.[25,26] Many successful chiral N-containing ligands have been derived from natural sources, such as terpenes, carbohydrates, and amino acids, and have been employed in asymmetric allylation, hydrosilylation, and transfer hydrogenation reactions. This review will focus on recent advances of a somewhat neglected ligand template, 1,10-phenanthroline.

Since the first reported synthesis of 1,10-phenanthroline[27−33] in 1898 by Blau,[34] this bidentate ligand has had a profound impact on the development of analytical reagents. It is amazing that the discovery of the first 1,10-phenanthroline[35] actually precedes the concept of coordination chemistry, put forward by Alfred Werner in 1893.[36] The well-known complexes of 1,10-phenanthroline[37,38] with metals and nonmetals have been exploited for the determination of metals by analytical chemists since the 1930s.[27,39,40] The formation, stability and reactivity of ligand complexes are governed by the rules of coordination and organometallic chemistry. Therefore, it is surprising that despite the well-known coordination properties of 1,10-phenanthroline, there have been very few reports on the application of phenanthrolines as chiral ligand templates for asymmetric catalysis. Yet, several reports indicate that these ligands might become increasingly important in future catalytic methods.[41]

Chiral 1,10-Phenanthroline Ligands

In an attempt to design chiral phenanthrolines for asymmetric catalysis, most researchers have focused on functionalizing the peripheral region of these heterocyclic ligands, leaving the aromaticity and, thus, the planarity of all three rings intact (Figure 1). To date, there are two prevailing approaches for the design of new, optically active phenanthroline ligands: (1) the introduction of chiral groups in the 2-, 3-, 8- and/or 9-position (**I**, **II**), and (2) the annulation of phenanthroline with one or two chiral units (**III**). Following is an overview of chiral phenanthroline derivatives that have been described in the literature thus far, including catalysis data wherever available. Among others, Gladiali, Chelucci, Thummel, Brunner, Åkermark, and Helquist have made seminal contributions to the development of N-donor ligands based on 1,10-phenanthroline for asymmetric catalysis.

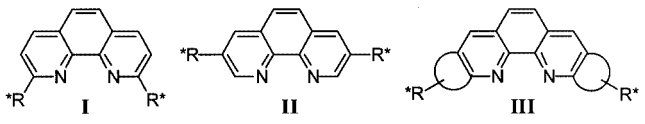


Figure 1. Ligand templates

Initial reports of optically active phenanthrolines appeared in 1986/87 by Gladiali and co-workers, who studied catalytic activities and stereoselectivities of 3-substituted phenanthrolines (Figure 2) in rhodium-catalyzed hydrogenation[42−45] and hydrosilylation[46] reactions [Equation (1)].

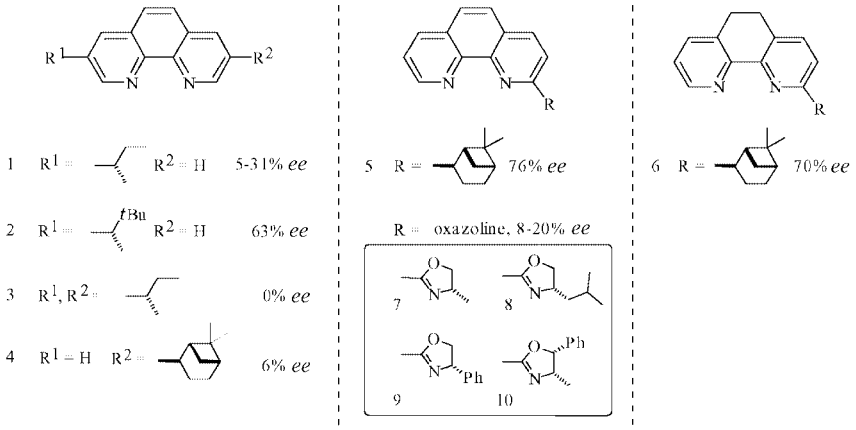
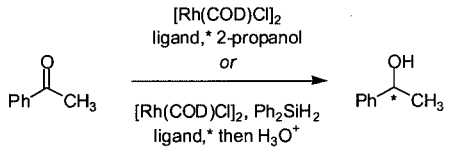


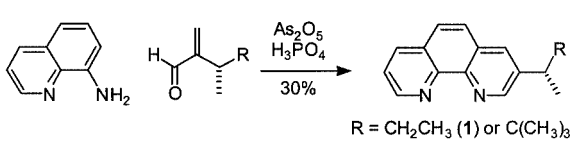
Figure 2. Enantioselsectivities of transfer hydrogenation (**1**−**3**) and hydrosilylation (**4**−**10**) with Gladiali/Chelucci ligands [Equation (1)][41,43−46]



(1)

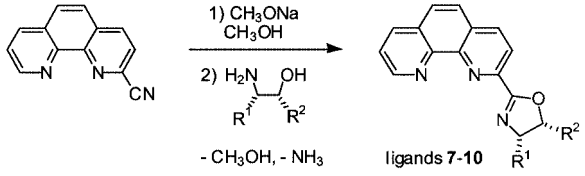
Several ligands were prepared by modified Doebner−Miller reactions with 8-aminoquinoline [Equation (2)] and applied to asymmetric transfer hydrogenation reactions.[43] The optical yields of the reactions with ligand **1** were very sensitive to experimental conditions and ranged from 5 to 31% *ee*. Surprisingly, this low to moderate degree of asymmetric induction was achieved even though the stereogenic center of the substituent in the 3-position is removed from the metal center by four bonds.

In subsequent work,[45,46] additional 3-substituted phenanthrolines were prepared, and their catalytic activities were assessed. Asymmetric induction improved when the *sec*-butyl substituent in ligand **1** was replaced with the 1,2,2-trimethylpropyl moiety (**2**, 63% *ee*). Conversely, the C_2-symmetrical ligand **3**, bearing *sec*-butyl groups in the 3- and the 8-positions, showed poor catalytic activity and no enantioselectivity. The authors speculated that the bulky 3,8-disubstituted phenanthroline ligand decreases the stability of the catalytically active species, $[Rh(Phen)(ROH)_2]^+Cl^-$.



(2)

Additional nitrogen ligands (**4**−**10**), such as norbornyl-substituted derivatives[44] **4**−**6** (Figure 2) and oxazolines **7**−**10**,[46] were prepared from 5,6-dihydro-8(7*H*)-quinolinone[47] and methoxyimidate intermediates, respectively [Equation (3)].

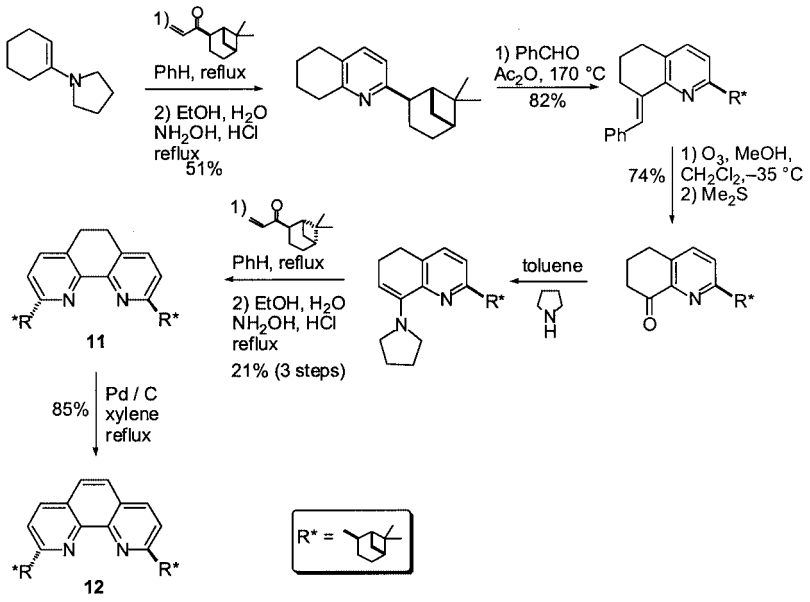


(3)

Ligands **4**−**10** were employed in the Rh-catalyzed enantioselective hydrosilylation reactions of acetophenone;[46] their enantioselectivities are included in Figure 2. Potentially terdentate ligands **7**−**10** with chiral oxazolinyl groups in the 2-position provided low stereoselectivities (8−20%). Asymmetric induction greatly improved with the introduction of norbornyl substituents in the 2-position (70% *ee* for **5**, 76% *ee* for **6**). Both norbornyl derivatives gave low selectivities during transfer hydrogenation reactions (≤ 15% *ee*).[44] Ligands **4**−**10** show large structural variations and, therefore, do not provide sufficient information to allow a rationalization of catalytic activities and selectivities. Moreover, this work illustrates that many successful ligands have been identified by a trial-and-error approach.

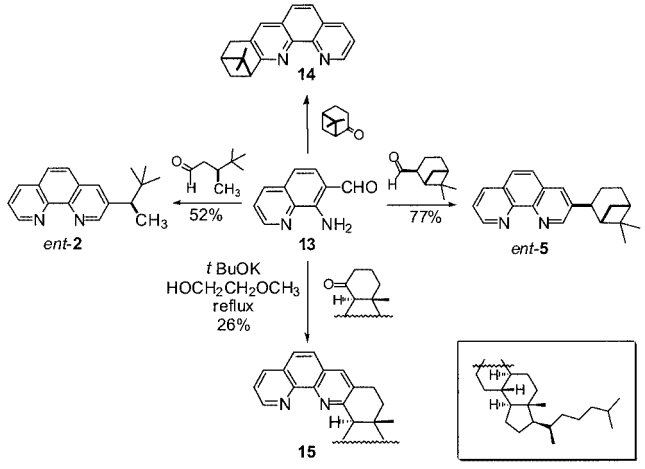
Chelucci and co-workers prepared 2,9-disubstituted phenanthroline derivatives with two 6,6-dimethylnorpinan-2-yl groups.[48] Sequential condensation of enamines and enones allowed for the preparation of heterocyclic ligands **11** and **12**, as depicted in Scheme 2; overall yields were 6.5% and 5.5%, respectively. Many ligand syntheses have involved the construction of the heterocyclic template to introduce chiral substituents. However, these approaches lengthen the ligand syntheses and often diminish overall yields substantially.

Thummel and co-workers developed an efficient Friedländer methodology to prepare 2-aryl-1,10-phenanthrolines.[49] This method was applied to condense 8-amino-7-quinolinecarbaldehyde (**13**) with either enantiomer of nopinone in 40−58% yield (Scheme 3).[50] The corresponding pineno-1,10-phenanthroline products **14** and *ent*-**14** (the



Scheme 2. Sequential pyridine construction from enamines and enones[48]

enantiomer of **14**) were converted into chiral copper(I) complexes and their photophysical behavior was studied.



Scheme 3. Ligands prepared by Friedländer methodology[50,51]

A recent joint publication by Gladiali, Chelucci, Thummel, and others[51] disclosed an improved synthesis for stereoisomers of ligands **2** and **5** from (+)-3,4,4-trimethylpentanal and (−)-pinenecarbaldehyde (Scheme 3). The phenanthroline derivative *ent*-**5** gave low selectivities during cyclopropanation (21% *ee*)[52] and substitution (14% *ee*)[53] reactions. Condensation reactions of aminoaldehyde **13** with cholestanone, cholestan-3-one, 5α-androst-2-en-17-one and chiral hexanone derivatives [(+)-3-methylcyclohexanone, (+)-camphor, (−)-3-pinanone], afforded the corresponding phenanthroline derivatives in variable yields (5−97%).

The catalytic activity of ligands derived from naturally occurring ketones was assessed in palladium-mediated allylic substitutions.[54] Enantioselectivities of up to 96% *ee* were observed with the cholestanone-based ligand **15**. However, the latter was synthesized in only 26% yield from intermediate **13**.

The Friedländer reaction of compound **13** with the hindered ketone (+)-camphor proceeded with only 5% yield. An alternative method starting from 8-nitro-7-quinolinecarbaldehyde provided chiral 1,7,7-trimethylbicyclo[2.2.1]heptano[2,3-*b*]-1,10-phenanthroline in three steps and 51% overall yield (Figure 3).[55]

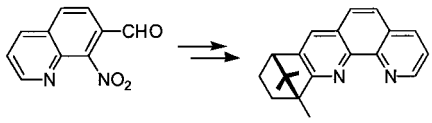


Figure 3. Synthesis of a chiral phenanthroline ligand from camphor[55]

A more direct route for the introduction of optically active substituents was employed by Engbersen et al.[56] who incorporated a combination of chiral amines, such as ephedrine and (2-pyrrolidinyl)methanol, in the 2- and 2,9-positions of phenanthroline from the corresponding halomethyl precursors. The new phenanthroline ligands were tested for activities of metal-ion complexes in enantioselective hydrolyses of *N*-protected amino acid esters (Figure 4).

Steckhan and co-workers[57] employed readily available halogenated phenanthroline precursors for the preparation of 2,9-disubstituted camphor sultam based ligands (**16** and **17**, Scheme 4). The copper-mediated aromatic nucleophilic substitution of 2,9-dichlorophenanthroline proceeded in moderate yield (30%) while substitution of 2,9-bis(bromomethyl)phenanthroline provided the corresponding C_2-symmetrical ligand in 60% yield. Applications of these ligands in transition-metal-mediated catalysis were not reported.

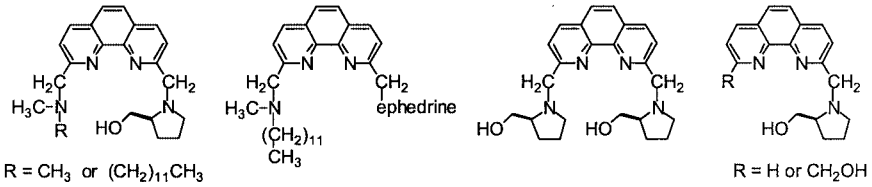
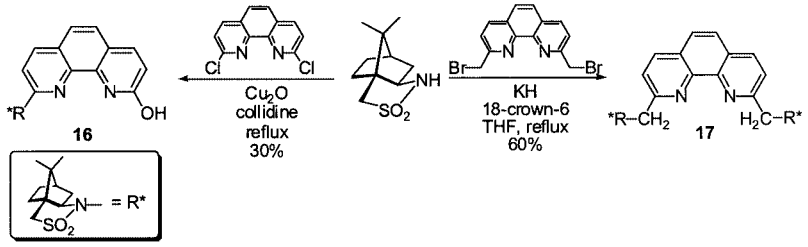


Figure 4. Phenanthroline ligands from halomethyl precursors[56]



Scheme 4. Camphor sultam based ligands[57]

Early work by Chelucci and co-workers focused on (+)-(*R*)-5-methyl-5,6-dihydro-1,10-phenanthroline (**18**) as a novel heterocyclic ligand, which was prepared in a laborious fashion in 13 steps and 0.9% overall yield.[58] The detailed synthesis starting with (+)-pulegone is shown in Scheme 5. The heterocyclic template was built in a stepwise fashion via a 2-(2′-bromoethyl)-1,3-dioxolane intermediate. This is the only example of a chiral, optically active 5,6-dihydro-1,10-phenanthroline ligand described in the literature bearing a stereogenic center in the B-ring. Unfortunately, the lengthy synthesis limits the availability of this ligand, and its catalytic performance has not yet been tested.

Ligand **18** was characterized by NMR spectroscopy and circular dichroism. The spectroscopic data suggest that a conformation with the 5-methyl group in a pseudo-axial orientation prevails in solution in order to avoid allylic strain between the methyl group and 4-H (Figure 5). The use of this chiral phenanthroline ligand in metal-catalyzed reactions has not been reported.

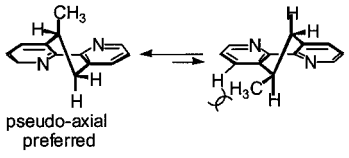
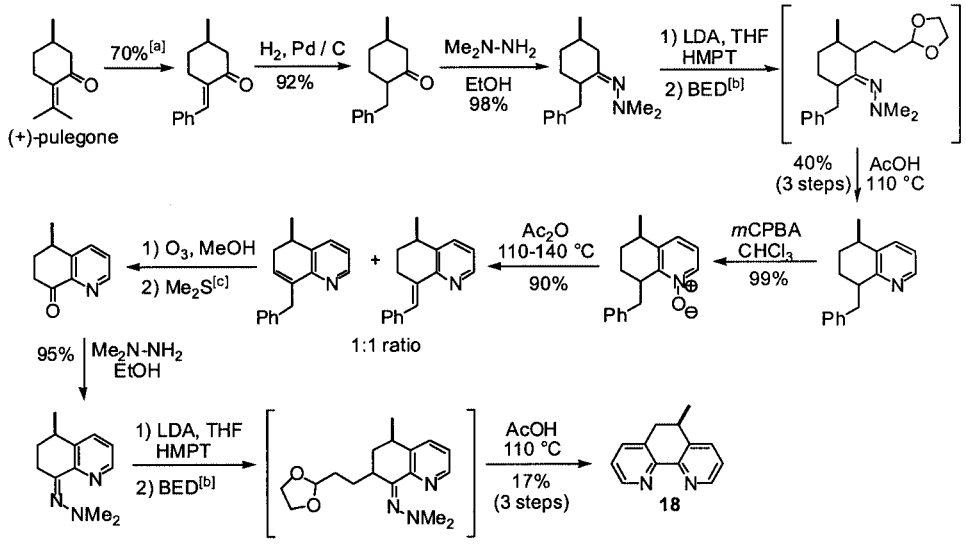
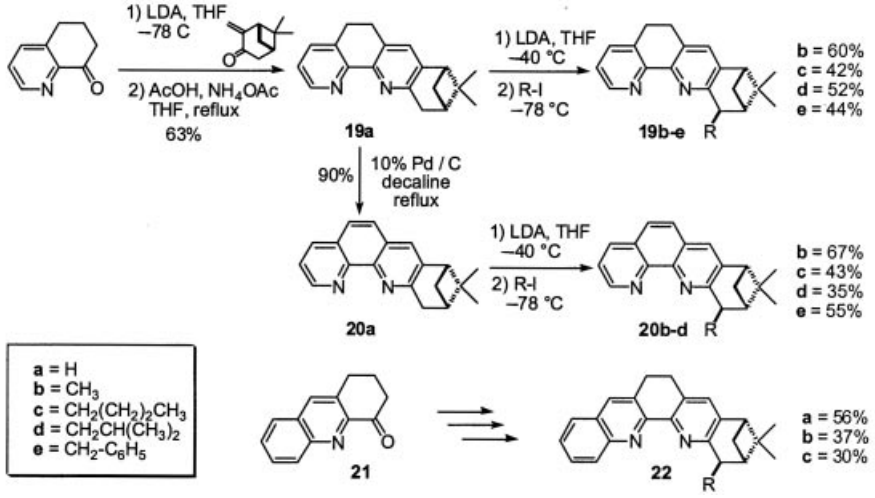


Figure 5. Conformational preference of ligand **18**[58]

Chelucci and Saba studied a series of alkyl-substituted phenanthroline, bipyridine, and terpyridine ligands, bearing the same substituent on the heterocycle, and reported that phenanthroline gave the more reactive catalyst with higher enantioselectivity.[53] This supports the hypothesis that rigidity in phenanthroline derivatives favors pre-organized structures and translates into higher stereogenicity during

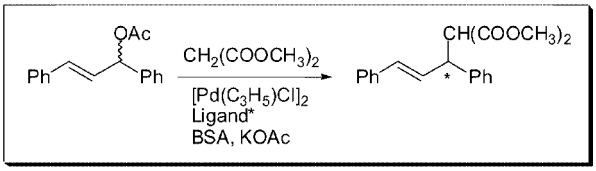


Scheme 5. Chiral ligand with B-ring modification;[58] [a] *J. Org. Chem.* **1974**, *39*, 1535; [b] 2-(2′-bromoethyl)-1,3-dioxolane; [c] 51% based on benzylidene



Scheme 6. Ligands prepared from tetrahydroquinolones;[59,60] stereoselectivities of allylic alkylation reactions for ligands **19**, **20**, and **22** are summarized in Scheme 7

catalysis. Chelucci and Saba also prepared a series of 2,3-disubstituted phenanthroline ligands with fused 2,2-dimethylnorpin-2-yl rings.[59,60] Ligands **19** and **20** were obtained from tetrahydroquinolone in 26−63% and 20−57% overall yields (Scheme 6), respectively, and were applied to allylic alkylation reactions of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate (Scheme 7). The corresponding benzo-fused phenanthroline derivatives were prepared in analogous fashion from acridine **21** in 30−56% overall yields. Additional introduction of alkyl groups in the 11-position was critical for improving stereoselectivities of all ligands. Ligands without substitutions at this position gave low optical yields (**19a**, **20a**, **22a**, 2−4% *ee*), which improved drastically with a methyl group on C-11, (70 and 78% *ee* for **19b** and **20b**, respectively). Optical yields improved even further with an *n*-butyl substituent (84% *ee* for **19c**), but decreased with the isobutyl group (70% *ee* for **19d**). A similar trend was reported for ligand **20**. Significant differences were observed with the sterically more demanding benzo-fused ligands **22**. Even though substitution reactions proceeded in good yields (87−93%), the asymmetric induction stayed below 23% *ee* (**22c**).



Ligand **19**	Ligand **20**	Ligand **22**
a = 87%y, 3% *ee*	**a** = 93%y, 4% *ee*	**a** = 93%y, 2% *ee*
b = 92%y, 70% *ee*	**b** = 95%y, 78% *ee*	**b** = 87%y, 6% *ee*
c = 96%y, 72% *ee*	**c** = 93%y, 84% *ee*	**c** = 89%y, 23% *ee*
d = 95%y, 40% *ee*	**d** = 88%y, 34% *ee*	
e = 98%y, 81% *ee*	**e** = 91%, 70% *ee*	

Scheme 7. Catalytic performance during allylic alkylation reactions[59,60]

The performance of ligands **19** and **20** was also examined in transition-metal-catalyzed cyclopropanation and hydrosilylation reactions.[61] Enantioselectivities of up to 68% *ee* were observed during Cu^{I}-mediated cyclopropanation of styrene with diazoacetates, although the *cis*/*trans* product ratio did not improve beyond 78:22. Hydrosilylation reactions of acetophenone with rhodium(I) complexes gave low stereoselectivities (< 33% *ee*). The difference in catalytic performance illustrates that ligand properties are transmitted differently to the substrate in reactions involving different metal complexes.

Åkermark, Helquist and co-workers have extensively investigated several substituted phenanthrolines for use in asymmetric Pd-catalyzed reactions of allylic acetates.[62−65] Moreover, specially parameterized molecular mechanics tools have been developed to guide the rational design of asymmetric catalysts.[66] Calculation-based predictions were in good agreement with experimental results of phenanthroline and other previously reported ligands. Molecular mechanics calculations serve as useful tools for assisting the rational design of asymmetric catalysis. Figure 6 shows a bornyl-substituted phenanthroline that was predicted to have high *ee* values. This work emphasizes the utility of a combined calculational/experimental approach for ligand design.

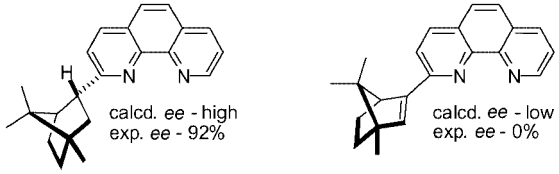
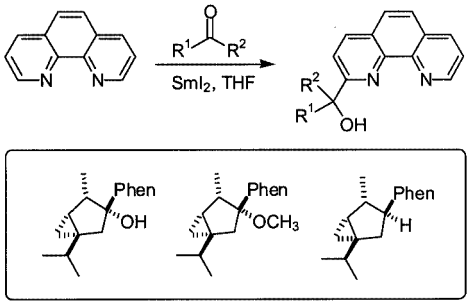


Figure 6. Computer-assisted ligand assessment[66]

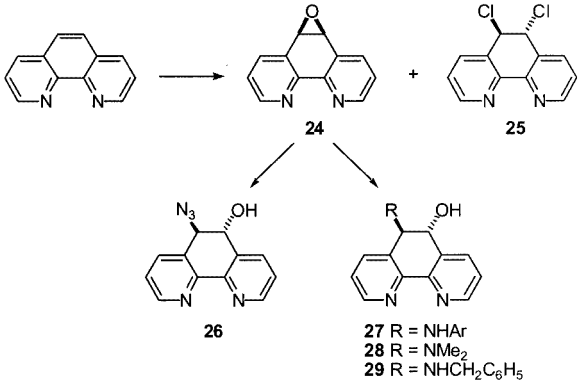
Recently, Helquist et al. published the samarium(II) iodide mediated coupling of phenanthroline with ketones, producing 2-(1-hydroxalkyl)-1,10-phenanthrolines (Scheme 8).[67] Subsequent *O*-methylation and demethoxylation with SmI_2

afforded the corresponding 2-alkylphenanthrolines. Coupling reactions with chiral ketones such as thujone and pulegone were also reported, giving rise to nonracemic products; no applications to asymmetric catalysis were reported.



Scheme 8. Samarium(II)-promoted coupling reactions[67]

Lastly, it should be mentioned that several reports include the preparation of racemic phenanthroline intermediates (Scheme 9). For example, phenanthroline was converted into dichloride **25**,[68] and ring-opening of epoxide **24**[68−70] furnished alcohols **26**−**29**.[69,71−73] Derivatives **24**−**29** have not been tested as ligands in asymmetric catalysis.



Scheme 9. Racemic ligands[68−73]

Outlook

Analyzing the examples above, several successful ligand applications can be identified for asymmetric catalysis. However, it appears that the development of chiral ligands from 1,10-phenanthroline is still in its infancy and that, despite the well-known chelation properties, this bidentate heterocyclic template has been largely neglected for transition-metal-catalyzed enantioselective reactions. Yet, 1,10-phenanthroline complexes with numerous metals have been known since the 1930s. Therefore, it can be anticipated that chiral phenanthroline ligands will have many applications in the future as synthetic methods for their preparation emerge.

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[14] Each catalytic cycle represents a turnover that produces a molecule of product. A stoichiometric reaction undergoes only one turnover per molecule of product generated.
[15] Usually the substrate is prochiral but the substrate may also be chiral, either racemic, as in a kinetic resolution, or nonracemic, as in a diastereoselective transformation.
[16] The Royal Swedish Academy of Sciences awarded the 2001 Nobel Prize in Chemistry to W. S. Knowles, R. Noyori, and K. B. Sharpless for their development of catalytic asymmetric synthesis.
[17] Due to significant economic advantages, many catalytic methods have been commercialized for the production of enantiopure compounds. Following are examples of asymmetric processes in the 1970s: hydrogenation (BINAP, Monsanto); 1980s: Sharpless epoxidation (tartrate, Arco Co. USA), isomerization (BINAP, Takasago International Corp.), cyclopropanation (chiral Schiff bases, Sumitomo Chemical Co. Ltd., Merck & Co. Inc.); 1990s: Jacobsen epoxidation (salen, Sepracor Inc.), Sharpless dihydroxylation (cinchona alkaloid, Sepracor Inc.), hydroboration (oxazoborolidine, Merck & Co. Inc.).
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