# Phase-transfer enantioselective monoalkylation of prochiral nickel(II) complexes catalyzed by 3,3′-bis[hydroxy(diphenyl)methyl]-1,1′-binaphthyl-2,2′-diol (BIMBOL) as a route to α-amino acids

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An achiral nickel complex with a Schiff base derived from glycine was alkylated with alkyl halides under conditions of asymmetric phase-transfer catalysis. The chiral tetraol (*R*)-BIMBOL was employed as a catalyst. The enantiomeric purity of the alkylation products was up to 88%. Subsequent decomposition of the complexes afforded the corresponding α-amino acids.

**Key words:** phase-transfer asymmetric catalysis, α-amino acids, nickel complexes, alkylation.

Enantiomerically pure α-amino acids, especially non-proteinogenic ones, are frequently used as building blocks for designing important medicines and modern antibiotics[1,2] as well as modified enzymes and peptides.[3,4] In the last few years, they have also served as chiral catalysts for asymmetric synthesis.[5] Catalytic asymmetric synthesis has important advantages over other routes to amino acids[6] such as (1) the possibility of preparing non-proteinogenic and/or *D*-amino acids and (2) formation of large amounts of an enantioenriched product from a racemic or achiral starting material through the use of small amounts of a chiral catalyst.

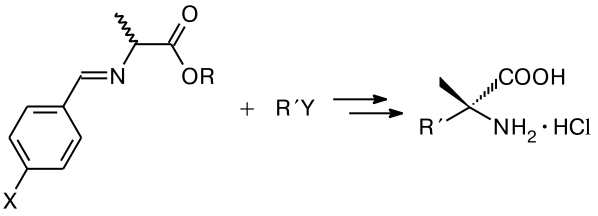
Because of this, it is currently important to develop efficient methods for catalytic asymmetric synthesis of amino acids.[6—11]

Among the merits of phase-transfer asymmetric catalysis are feasible procedures, mild reaction conditions, inexpensive starting reagents and solvents, and the possibility of easily scaling the synthesis.[12]

Phase-transfer asymmetric catalytic α-alkylation of prochiral glycine synthons is a very attractive approach to the synthesis of enantioenriched α-amino acids.[13] Most of the phase-transfer catalysts employed earlier for this purpose belong to the alkaloid cinchonine derivatives.[12] They are difficult to modify rationally and this is a serious drawback precluding "fine tuning" of the catalyst to various substrates needed to achieve reasonable reactivity and selectivity.[14—18]

Earlier, we have demonstrated that α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-diyldimethanol (TADDOL) efficiently catalyzes phase-transfer asymmetric alkylation of Schiff bases derived from alanine esters (Scheme 1) in the presence of solid NaOH. Based on the results obtained, we have developed a method of asymmetric synthesis of quaternary amino acids with considerable asymmetric induction.[19] This catalyst acts by transforming TADDOL into a conjugated alkoxide base that is soluble in the organic phase. The driving force of the process is the reaction of the base with a CH acid (Schiff base of alanine) followed by alkylation of an intermediate carbanion in a complex with TADDOL. Application of this approach to the synthesis of amino acids containing an acidic α-proton failed because the conjugated TADDOL base was very strong and the final product underwent *in situ* racemization.

**Scheme 1**




R = Me, X = H; R = $Pr^i$, X = H; R = $Pr^i$, X = Cl; R = $Pr^i$, X = F; R = $Bu^t$, X = H
R′ = Bn, allyl, α-naphthylmethyl; Y = Br, Cl

Recently, we have found that the use of salts of (*R*)- or (*S*)-3,3′-bis[hydroxy(diphenyl)methyl]-1,1′-binaphthyl-2,2′-diol (BIMBOL) as phase-transfer catalysts for enan-

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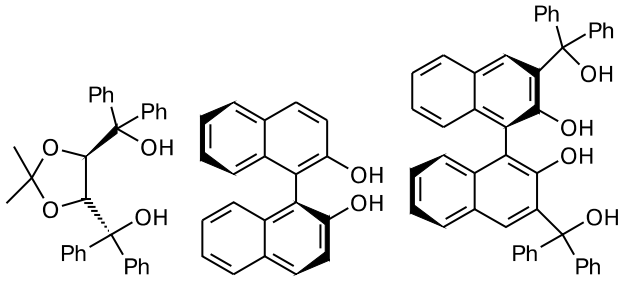
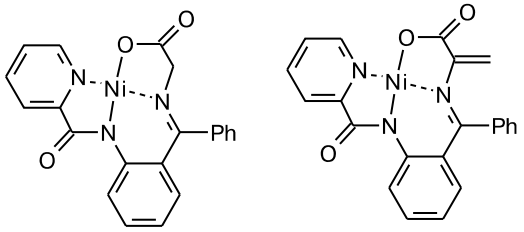


**1** **2**

tioselective Michael addition involving nickel complexes with Schiff bases derived from glycine (**1**) and dehydroalanine (**2**) affords glutamic acid derivatives with no appreciable racemization.[20]

It was interesting to extend the scope of this system by applying it to phase-transfer alkylation for the synthesis of amino acids containing an acidic α-proton. BIMBOL itself can easily be prepared from commercial BINOL.

Here we describe phase-transfer alkylation of achiral nickel complex **1** with BIMBOL as a catalyst.

The use of an achiral nickel complex with a glycine derivative as a substrate provides a number of important advantages. First, this complex can efficiently be coordinated with a chiral catalyst, thus predetermining the direction of an attack of an alkylating agent on the glycine moiety. Second, both the starting complex and the alkylation product are brightly colored, which facilitates handling these substances. Third, all the resulting enantioenriched alkylation products have high specific rotation and hence their enantiomeric purity can be determined much more easily.[21]

**Table 1.** Efficiency—structure relationship for the catalyst in the monoalkylation of complex **1** with benzyl bromide

| Entry | Catalyst | B | *t*/min | Y (%) | *ee*[b] (%) |
|---|---|---|---|---|---|
| *1* | (*R*)-TADDOL | NaOH | 10 | 10 | 12 (*R*) |
| *2* | (*R*)-TADDOL | NaOH | 60 | 30 | 0 |
| *3* | (*S*)-BINOL | NaOH | 60 | 14 | 17 (*R*) |
| *4* | (*R*)-BIMBOL | NaOH | 60 | 65 | 9 (*S*) |
| *5* | (*R*)-TADDOL | KOH | 60 | 75 | 0 |
| *6* | (*R*)-BINOL | KOH | 60 | 85 | 16 (*S*) |
| *7* | (*R*)-BIMBOL | KOH | 60 | 67 | 50 (*S*) |

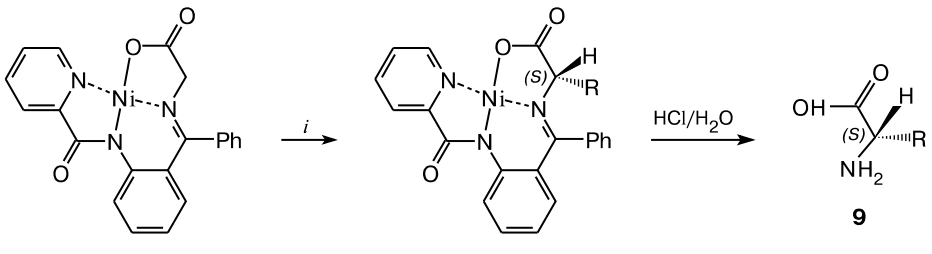
*Note.* B is the base used, *t* is the reaction time, and Y is the yield.
[a] Reaction conditions: ~20 °C, $CH_2Cl_2$, 10 mol.% catalyst, NaOH (10 equiv.) or KOH (2.5 equiv.), benzyl bromide (1.2 equiv. with respect to **1**).
[b] *ee* of the corresponding phenylalanine was determined by GLC on a chiral column.

## Results and Discussion

The catalytic efficiencies of TADDOL, BINOL, and (*R*)-BIMBOL in the alkylation of complex **1** with benzyl bromide as an example (Scheme 2) under conditions of phase-transfer catalysis are compared in Table 1.

It can be seen that (*R*)-TADDOL favors rapid racemization of the alkylation product (see Table 1, entries *1*, *2*, and *5*). BINOL is highly efficient only with KOH as a base; however, the *ee* of the product is 16% only (see Table 1, entries *3* and *6*). (*R*)-BIMBOL actively catalyzes the alkylation reaction in the presence of both KOH and NaOH (see Table 1, entries *4* and *7*). However, the enantiomeric purity of the product was measurable (50%) only when KOH was used (see Table 1, entry *7*). Thus, the

**Scheme 2**



**1** **3—8** **9**

X = Br, I; R = All (**3**), Bn (**4**), 4-F-Bn (**5**), 4-I-Bn (**6**), 4-$NO_2$-Bn (**7**), $C_2H_5$ (**8**), All (**9**)

**Reagents and conditions:** *i.* RX (2 equiv.); (*R*)-BIMBOL (10 mol.%); $CH_2Cl_2$; base; 20 °C.

catalyst containing four OH groups (BIMBOL) is highly active and provides higher enantioselectivity than do the aforementioned diols.

Further, we studied alkylation of complex **1** with alkyl halides in the presence of (*R*)-BIMBOL under various conditions; no dialkylation products were detected. This is due to a lower C—H acidity of the amino acid moiety in the monoalkylated complex and the steric hindrances to an attack of a second alkylating agent.[21]

To optimize the reaction conditions, we alkylated complex **1** with allyl bromide in the presence of a number of alkali metal hydroxides; other variables included the solvent and the concentrations of the starting reagents. The results obtained are summarized in Table 2.

As expected, the reaction does not occur when no base is used (see Table 2, entry *1*). With a strong base, $Bu^nLi$, the alkylation proceeds rapidly, although with no asymmetric induction (see Table 2, entry *2*). With weaker bases (alkali metal hydroxides), the enantioselectivy of the reaction substantially depends on the metal ion used. The enantiomeric purity of the product is unsatisfactory with NaOH as a base (see Table 2, entries *3*, *4*). For other alkali metals, *ee* decreases in the order: K > Cs > Rb (see Table 2, entries *6*, *10*, *11*).

The presence of water in the reaction mixture is also crucial. Alkylation in anhydrous $CH_2Cl_2$ with anhydrous KOH as a base affords a product with *ee* 88% (see Table 2, entry *5*), while addition of water (*e.g.*, the use of 50% aqueous KOH) blocks the reaction so that no alkylation product is formed even in four hours (see Table 2, entry *9*). Even a small amount of water added to the reaction mixture decreases the reaction rate, probably because of hydrolysis of (*R*)-BIMBOL phenolate, an actual catalytic species. A similar effect of water has been noted in the study of phase-transfer alkylation with TADDOL as a catalyst.[19]

An increase in either the amount of the base or the reaction time (see Table 2, entries *7*, *8*) results in the formation of alkylation products with lower enantiomeric purity, which can be attributed to promotion of racemization as a side process.

The choice of solvent is also crucial since the alkylation reaction gives good results only in anhydrous $CH_2Cl_2$ (see Table 2, entries *12*—*14*).

Alkylation with other alkylating agents was carried out under the optimized reaction conditions (see Table 2, entry *6*). The data obtained are given in Table 3.

The use of (*R*)-BIMBOL affords an (*S*)-product. With (*S*)-BIMBOL, as expected, an (*R*)-product is formed (see Table 3, entry *2*). Thus, by employing the catalytic system described above (note that both BIMBOL enantiomers are equally accessible), one can obtain amino acids of both (*R*)- and (*S*)-configurations.

The reaction mechanism is similar to that proposed earlier for the catalysis with TADDOL[19] and involves the

**Table 2.** (*R*)-BIMBOL-catalyzed monoalkylation of complex **1** with allyl bromide[a]

| Entry | B (equiv.) | Solvent | *t*/min | Y (%) | $[\alpha]_D^{25}$ | *ee* (%) |
|---|---|---|---|---|---|---|
| *1* | — | $CH_2Cl_2$ | 120 | 0 | — | - |
| *2* | $Bu^nLi$ (1) | $CH_2Cl_2$ | 20 | 80 | 0 | 0 |
| *3* | NaOH (1) | $CH_2Cl_2$ | 120 | 15 | +64 | 2(*S*) |
| *4* | NaOH (10) | $CH_2Cl_2$ | 60 | 70 | 0 | 0 |
| *5*[b,c] | KOH (1.5) | $CH_2Cl_2$ | 120 | 30 | +2902 | 88(*S*) |
| *6*[c] | KOH (2.5) | $CH_2Cl_2$ | 60 | 60 | +2682 | 81(*S*) |
| *7*[c] | KOH (3) | $CH_2Cl_2$ | 60 | 60 | +2481 | 75(*S*) |
| *8* | KOH (3) | $CH_2Cl_2$ | 120 | 70 | +1909 | 58(*S*) |
| *9* | 50% aqueous KOH | $CH_2Cl_2$ | 240 | 0 | — | — |
| *10* | $CsOH \cdot H_2O$ (2.5) | $CH_2Cl_2$ | 60 | 70 | +1262 | 38(*S*) |
| *11* | RbOH (2.5) | $CH_2Cl_2$ | 60 | 80 | +1134 | 34(*S*) |
| *12* | KOH (1.5) | THF | 120 | 30 | +56 | 2(*S*) |
| *13* | KOH (1.5) | PhMe | 120 | 10 | — | — |
| *14* | KOH (1.5) | MeCN | 120 | 30 | +120 | 4(*S*) |

*Note.* B is the base used, *t* is the reaction time, and Y is the yield.

[a] (*R*)-BIMBOL (10 mol.%) and an excess of allyl bromide (2 equiv.) with respect to complex **1** were used.

[b] An excess of allyl bromide (1.2 equiv.) was used with respect to complex **1**.

[c] In entries *5*—*7*, first the specific rotation angles of the complexes obtained were measured and then the corresponding amino acids were isolated. Their enantiomeric purity was determined by GLC on a chiral phase. The *ee* of the amino acid was plotted versus $[\alpha]_D^{25}$ of the complex and the resulting plot was used to determine the enantiomeric purity of the products obtained in the other entries from $[\alpha]_D^{25}$ without isolating the amino acid. For the enantiomerically pure complex (*S*)-4, $[\alpha]_D^{25}$ ($CHCl_3$/MeOH) is 3306.

**Table 3.** (*R*)-BIMBOL-catalyzed monoalkylation of complex **1**[a]

| Entry | Product | Alkylating agent (equiv.) | *t*/min | Y (%) | $[\alpha]_D^{25}$ | *ee*[b] (%) |
|---|---|---|---|---|---|---|
| *1* | **3** | AllBr (2) | 60 | 70 | +2682 | 81 (*S*) |
| *2* | **4**[c] | BnBr (2) | 60 | 67 | +1703 | 50 (*S*) |
| *3* | **5** | 4-F-BnBr (2) | 60 | 60 | +2128 | 63 (*S*) |
| *4* | **6** | 4-I-BnBr (2) | 60 | 65 | +1349 | 40 (*S*) |
| *5* | **7** | 4-$NO_2$-BnBr (2) | 60 | 82 | +974 | 29 (*S*) |
| *6* | **8** | $C_2H_5I$ (3) | 240 | 20 | +358 | 11 (*S*) |

*Note.* *t* is the reaction time and Y is the yield.

[a] Reaction conditions: ~20 °C, $CH_2Cl_2$, (*R*)-BIMBOL (10 mol.%), KOH (2.5 equiv. with respect to **1**).

[b] The *ee* values of the amino acids obtained were determined by GLC on a chiral phase.

[c] With (*S*)-BIMBOL as a catalyst, the (*R*)-enantiomer of the product was obtained.

formation of BIMBOL phenolate on the surface of a solid base. This chiral phenolate abstracts a proton from complex **1** to form neutral BIMBOL and the carbanion of complex **1**. The $K^+$ ion and both the components are combined into a chiral complex as discussed earlier.[20] The phenyl substituent in the carbanion of complex **1** effects chiral shielding of the glycine moiety. Subsequent alkylation of the chiral carbanion leads to the formation of the target product.

To sum up, BIMBOL is a an efficient catalyst for asymmetric phase-transfer alkylation. Our current investigations pursue the use of this catalyst in various C—C bond making reactions and its structural modification for achieving better efficiency.

## Experimental

$^1$H NMR spectra were recorded on Bruker Avance 300 spectrometers in $CDCl_3$, $CD_3OD$, and $D_2O$; chemical shifts are referenced to the residual signals of the deuterated solvent. Optical rotation was measured on a Perkin—Elmer 341 polarimeter (temperature-controlled cell, $l$ = 5 cm, 25 °C).

Silica gel 60 (Merck) was used as a sorbent.

Analysis of amino acids was carried out by GLC on γ-cyclodextrin as a chiral phase with *n*-propyl trifluoroacetates.

The enantiomeric purity of BINOL was verified by liquid chromatography on a Chiralcel® IB-3 column (hexane—$Pr^iOH$ (90 : 10) as an eluent, flow rate 1.0 mL $min^{-1}$, UV detector, 254 nm).

All alkylation reactions were carried out under dry argon. Solvents were purified according to standard procedures.[22]

Elemental analysis of the compounds obtained was performed at the Elemental Analysis Laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences).

**(*R*)-3,3′-Bis[hydroxy(diphenyl)methyl]-1,1′-binaphthyl-2,2′-diol ((*R*)-BIMBOL)** was prepared from (*R*)-BINOL with *ee* 99.9% (retention time 5.499 min) as described earlier;[23] $[\alpha]_D^{25}$ +109.8 (*c* 1.00, $CHCl_3$) (*cf.* Ref. 23: $[\alpha]_D^{20}$ +113.4 (*c* 1.00, $CHCl_3$)), m.p. 186—188 °C (*cf.* Ref. 24: m.p. 176—179 °C). $^1$H NMR ($CDCl_3$), δ: 4.79 (s, 2 H, OH); 6.70 (s, 2 H, OH); 7.14—7.17 (m, 2 H, Ar); 7.19 (s, 2 H, Ar); 7.28—7.40 (m, 24 H, Ar), 7.65—7.68 (m, 2 H, Ar). Found (%): C, 79.2; H, 5.8. $C_{46}H_{34}O_4 \cdot 2H_2O \cdot Me_2CO$. Calculated (%): C, 78.9; H, 5.9.

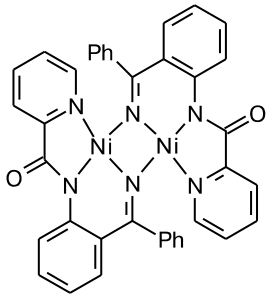
**(*S*)-3,3′-Bis[hydroxy(diphenyl)methyl]-1,1′-binaphthyl-2,2′-diol ((*S*)-BIMBOL)** was prepared from (*S*)-BINOL with *ee* 99.9% (retention time 5.058 min) as described earlier;[23] $[\alpha]_D^{25}$ −107.3 (*c* 1.00, $CHCl_3$) (*cf.* Ref. 23: $[\alpha]_D^{20}$ −109.5 (*c* 1.00, $CHCl_3$)).

The nickel(II) complex used as a substrate was synthesized according to a known procedure.[21] The $^1$H NMR spectra of the complex obtained are identical with the literature data.[21]

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}glycinato-*N*,*N*′,*N*″,*O*)nickel(II) (complex 1)**, m.p. >280 °C (decomp.). $^1$H NMR ($CDCl_3$), δ: 3.89 (s, 2 H, $CH_2$); 6.84—6.89 (m, 1 H, Ar); 6.96—6.99 (m, 1 H, Ar); 7.16—7.18 (m, 2 H, Ar); 7.41—7.53 (m, 2 H, Ar); 7.60—7.62 (m, 3 H, Ar); 7.94—7.96 (m, 1 H, Ar); 8.03—8.08 (m, 1 H, Ar); 8.33—8.35 (m, 1 H, Ar); 9.03—9.06 (m, 1 H, Ar). Found (%): C, 60.58; H, 3.60; N, 10.05. $C_{21}H_{15}N_3O_3Ni$. Calculated (%): C, 60.62; H, 3.63; N, 10.10.

**Monoalkylation of complex 1 under the conditions of phase-transfer catalysis (general procedure with allyl bromide as an example).** (*R*)-BIMBOL (0.0047 g, $7.2 \cdot 10^{-6}$ mol), freshly ground KOH (0.010 g, $1.8 \cdot 10^{-4}$ mol), and the starting complex **1** (0.03 g, $7.2 \cdot 10^{-5}$ mol) were mixed in a round-bottom flask filled with argon. The mixture was dissolved with stirring in anhydrous $CH_2Cl_2$ (1 mL). After 7—8 min, allyl bromide (0.012 mL, $1.44 \cdot 10^{-4}$ mol) was added to the stirred mixture. The course of the reaction was monitored by TLC ($SiO_2$, $CHCl_3$—$Me_2CO$ (5 : 1) as an eluent). For all alkylated products, the $R_f$ values are close (0.45); for the starting complex **1**, $R_f$ is 0.09). After 1 h, glacial AcOH (0.015 mL, $2.6 \cdot 10^{-4}$ mol) was added and the reaction mixture was stirred for an additional 5—10 min and purified by column chromatography on $SiO_2$ with $CHCl_3$—$Me_2CO$ (5 : 1) as an eluent. The yield of product **3** was 70% (0.022 g, $5.04 \cdot 10^{-5}$ mol).

During the alkylation reactions, a small amount of dinuclear complex **10** was detected. This complex[25] is produced by a side reaction involving oxidation of the starting reagent **1** in the presence of oxygen and a base.[25] To avoid the formation of this by-product, the dried solvent was degassed by a freeze—thaw procedure *in vacuo* (this procedure serves to remove oxygen and, accordingly, prevent oxidation into the above by-product).




**10**

**Decomposition of the complexes and isolation of amino acids (with complex 3 as an example).** A 18% aqueous solution of HCl (0.4 mL) was added at 50 °C to a stirred solution of alkylated

complex **3** (0.069 g, $1.5 \cdot 10^{-4}$ mol) in methanol (0.2 mL). Stirring was continued until the red color of the solution characteristic of these complexes disappeared. Then the mixture was cooled to ~20 °C. The precipitate of the achiral ligand *N*-(2-benzoylphenyl)picolinamide that formed as hydrochloride was filtered off. The mother liquor was concentrated *in vacuo*. This was followed by addition of water and 5% aqueous $NH_3$ to reach pH 7—8. The residual amounts of the ligand were extracted with $CHCl_3$.

The amino acid was isolated from an aqueous solution using the DOWEX (50×8) cation-exchange resin ($H^+$) with 5% aqueous $NH_3$ as an eluent. Ammonia was removed from the eluate, which was then concentrated *in vacuo*. The amino acid was analyzed by GLC.

Complexes **3**—**9** were obtained according to the optimized procedure.

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*S*)-2-aminopent-4-enoato-*N*,*N*′,*N*′′,*O*)nickel(II) (3).** Yield 60% (0.020 g, $4.3 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ +2682 (*c* 0.1, $CHCl_3$—MeOH), *ee* 81% (*S*), m.p. 232—235 °C. $^1$H NMR ($CDCl_3$), δ: 2.53—2.58 (m, 2 H, $CH_2$); 4.15—4.18 (m, 1 H, CH); 5.21 (d, 1 H, CH=CH<u>H</u>, *J* = 17.0 Hz); 5.38 (d, 1 H, CH=C<u>H</u>H, *J* = 10.0 Hz); 6.42—6.55 (m, 1 H, C<u>H</u>=$CH_2$); 6.83—6.87 (m, 2 H, Ar); 7.14—7.16 (m, 1 H, Ar); 7.34—7.43 (m, 2 H, Ar); 7.47—7.52 (m, 1 H, Ar); 7.57—7.62 (m, 3 H, Ar); 7.95 (d, 1 H, Ar, *J* = 7.1 Hz); 8.04—8.09 (m, 1 H, Ar); 8.27 (d, 1 H, Ar, *J* = 5.4 Hz); 8.98 (d, 1 H, Ar, *J* = 8.6 Hz). Found (%): C, 63.24; H, 4.34; N, 9.16. $C_{24}H_{19}N_3O_3Ni$. Calculated (%) C, 63.20; H, 4.20; N, 9.21.

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*S*)-phenylalaninato-*N*,*N*′,*N*′′,*O*)nickel(II) (4)** was obtained from complex **1** and benzyl bromide as described above. Yield 67% (0.024 g, $4.8 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ +1703 (*c* 0.12, $CHCl_3$—MeOH), *ee* 50% (*S*), m.p. 276—278 °C. $^1$H NMR ($CDCl_3$), δ: 2.93 and 3.20 (ABX system, 2 H, $CH_2$, $J_{AB}$ = 13.4 Hz, $J_{AX}$ = 2.9 Hz, $J_{BX}$ = 5.5 Hz); 4.43 (ABX system, 1 H, $J_{AX}$ = 2.9 Hz, $J_{BX}$ = 5.5 Hz); 6.86—6.90 (m, 2 H, Ar); 6.92 (t, 1 H, Ar, *J* = 7.4 Hz); 7.20—7.25 (m, 3 H, Ar); 7.34—7.44 (m, 3 H, Ar); 7.47 (d, 2 H, Ar, *J* = 7.3 Hz); 7.58—7.65 (m, 3 H, Ar); 7.75 (d, 1 H, Ar, *J* = 5.3 Hz); 7.83 (d, 1 H, Ar, *J* = 7.1 Hz); 7.97 (t, 1 H, Ar, *J* = 7.7 Hz); 8.78 (d, 1 H, Ar, *J* = 8.6 Hz). Found (%): C, 66.46; H, 4.10; N, 8.22. $C_{28}H_{21}N_3O_3Ni$. Calculated (%): C, 66.40; H, 4.15; N, 8.30.

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*R*)-phenylalaninato-*N*,*N*′,*N*′′,*O*)nickel(II) (*R*-4)** was obtained as described above from complex **1** and benzyl bromide (1.1 equiv. with respect to **1**) in the presence of (*S*)-BIMBOL and KOH (1 equiv.). Yield 40% (0.014 g, $2.9 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ −1273 (*c* 0.093, $CHCl_3$—MeOH), *ee* 37% (*R*).

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*S*)-4-fluorophenylalaninato-*N*,*N*′,*N*′′,*O*)nickel(II) (5)** was obtained from complex **1** and 4-fluorobenzyl bromide as described above. Yield 60% (0.023 g, $4.3 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ +2128 (*c* 0.115, $CHCl_3$—MeOH), *ee* 63% (*S*), m.p. 101—103 °C. $^1$H NMR ($CDCl_3$), δ: 2.91 and 3.16 (ABX system, 2 H, $CH_2$, $J_{AB}$ = 13.6 Hz, $J_{AX}$ = 2.6 Hz, $J_{BX}$ = 5.3 Hz); 4.41 (ABX system, 1 H, $J_{AX}$ = 2.6 Hz, $J_{BX}$ = 5.3 Hz); 6.86—6.94 (m, 4 H, Ar); 7.18—7.25 (m, 1 H, Ar); 7.37—7.45 (m, 5 H, Ar); 7.62—7.66 (m, 3 H, Ar); 7.76 (d, 1 H, Ar, *J* = 5.3 Hz); 7.88 (d, 1 H, Ar, *J* = 7.6 Hz), 8.02 (t, 1 H, Ar, *J* = 7.7 Hz); 8.77 (d, 1 H, Ar, *J* = 8.6 Hz).

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*S*)-4-iodophenylalaninato-*N*,*N*′,*N*′′,*O*)nickel(II) (6)** was obtained from complex **1** and 4-iodobenzyl bromide as described above. Yield 65% (0.029 g, $4.7 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ +1349 (*c* 0.116, $CHCl_3$—MeOH), *ee* 40% (*S*), m.p. 140—142 °C. $^1$H NMR ($CDCl_3$), δ: 2.86 and 3.11 (ABX system, 2 H, $CH_2$, $J_{AB}$ = 13.7 Hz, $J_{AX}$ = 2.6 Hz, $J_{BX}$ = 5.5 Hz); 4.43 (ABX system, 1 H, $J_{AX}$ = 2.6 Hz, $J_{BX}$ = 5.5 Hz); 6.87 (d, 2 H, Ar, *J* = 4.1 Hz); 7.21—7.26 (m, 3 H, Ar); 7.36—7.45 (m, 3 H, Ar); 7.56 (d, 2 H, Ar, *J* = 8.1 Hz); 7.61—7.66 (m, 3 H, Ar); 7.73 (d, 1 H, Ar, *J* = 5.3 Hz); 7.93 (d, 1 H, Ar, *J* = 7.8 Hz), 8.09 (t, 1 H, Ar, *J* = 7.7 Hz); 8.79 (d, 1 H, Ar, *J* = 8.6 Hz).

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*S*)-4-nitrophenylalaninato-*N*,*N*′,*N*′′,*O*)nickel(II) (7)** was obtained from complex **1** and 4-nitrobenzyl bromide as described above. Yield 82% (0.032 g, $5.9 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ +974 (*c* 0.107, $CHCl_3$—MeOH), *ee* 29% (*S*), m.p. 175—177 °C. $^1$H NMR ($CDCl_3$), δ: 3.05 and 3.25 (ABX system, 2 H, $CH_2$, $J_{AB}$ = 13.1 Hz, $J_{AX}$ = 2.7 Hz, $J_{BX}$ = 5.7 Hz); 4.48 (ABX system, 1 H, $J_{AX}$ = 2.7 Hz, $J_{BX}$ = 5.7 Hz); 6.88 (d, 2 H, Ar, *J* = 4.1 Hz); 7.22—7.27 (m, 1 H, Ar); 7.33—7.46 (m, 3 H, Ar); 7.61 (d, 2 H, Ar, *J* = 8.4 Hz); 7.64—7.71 (m, 4 H, Ar); 7.81 (d, 1 H, Ar, *J* = 7.5 Hz); 7.96 (t, 1 H, Ar, *J* = 7.6 Hz); 8.07 (d, 2 H, Ar, *J* = 8.5 Hz); 8.76 (d, 1 H, Ar, *J* = 8.6 Hz).

**(*N*-{Phenyl[2-(pyridine-2-carboxamido)phenyl]methylidene}-(*S*)-2-aminobutanoato-*N*,*N*′,*N*′′,*O*)nickel(II) (8)** was obtained from complex **1** and ethyl iodide as described above. The reaction time was 4 h. Yield 20% (0.0064 g, $1.4 \cdot 10^{-5}$ mol), $[\alpha]_D^{25}$ +358 (*c* 0.128, $CHCl_3$—MeOH), *ee* 11% (*S*), m.p. 274—276 °C. $^1$H NMR ($CDCl_3$), δ: 1.45 (t, 3 H, *J* = 7.5 Hz); 1.80 (m, 1 H, $CH_2$); 2.02 (m, 1 H, $CH_2$); 4.06 (m, 1 H, CH); 6.81—6.87 (m, 2 H, Ar); 7.13 (d, 1 H, Ar, *J* = 6.9 Hz); 7.39—7.44 (m, 2 H, Ar); 7.51 (t, 1 H, Ar, *J* = 6.9 Hz), 7.55—7.61 (m, 3 H, Ar); 7.96 (d, 1 H, Ar, *J* = 7.8 Hz), 8.07 (t, 1 H, Ar, *J* = 7.8 Hz); 8.30 (d, 1 H, Ar, *J* = 5.3 Hz), 9.00 (d, 1 H, Ar, *J* = 8.7 Hz).

**2-Aminopent-4-enoic acid (9)** was obtained by acid hydrolysis of complex **3** (0.069 g, $1.5 \cdot 10^{-4}$ mol) (see above). Yield 62% (0.0107 g, $9.3 \cdot 10^{-5}$ mol), *ee* 81% (*S*), m.p. 250—252 °C. $^1$H NMR ($CDCl_3$), δ: 2.26—2.40 (m, 2 H, $CH_2$); 3.50 (t, 1 H, CH, *J* = 5.8 Hz); 4.97 (m, 2 H, CH=C<u>H</u>$_2$); 5.46 (m, 1 H, C<u>H</u>=$CH_2$). Found (%): C, 52.14; H, 7.9; N, 12.18. $C_5H_9NO_2$. Calculated (%): C, 52.16; H, 7.88; N, 12.17.

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