Novel modified chiral Ni^{II} complexes with the Schiff bases of (*E*)- and (*Z*)-2-aminobut-2-enoic acids: synthesis and study

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Ni^{II} complexes with the Schiff bases of (*E*)- and (*Z*)-2-aminobut-2-enoic acids were obtained with (*S*)-*N*-(2-benzoylphenyl)-1-(2-chlorobenzyl)pyrrolidine-2-carboxamide and (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dimethylbenzyl)pyrrolidine-2-carboxamide as new chiral auxiliaries. Asymmetric addition of nucleophiles to the C=C bond of these complexes was studied.

Key words: 2-aminobut-2-enoic acid, asymmetric synthesis, diastereoselectivity, stereoisomers.

Many physiologically active peptides, antibiotics, and various pharmaceutical drugs contain enantiomerically pure non-proteinogenic amino acids,[1—4] including β-substituted derivatives of α-aminobutyric acid.[5,6] In addition, isotope-labelled amino acids are of considerable current interest: they are successfully used in positron emission tomography for early diagnostics of cancer diseases.[7] For this reason, a search for novel chiral auxiliaries and catalysts that ensure highly selective and rapid asymmetric synthesis of amino acids remains of topical interest.[8—10]

Sufficiently well known studies on asymmetric synthesis of α- and β-substituted α-amino acids are based on increased reactivities of amino acid and dehydroamino acid fragments in square planar Ni^{II} complexes with Schiff bases with the chiral auxiliary reagent (*S*)-*N*-(2-benzoylphenyl)-1-benzylpyrrolidine-2-carboxamide ((*S*)-BPB).[11—15]

Earlier, to enhance the enantioselectivity by increasing the steric strain in complexes, their structures have been modified *via* replacement of the benzyl group in the chiral reagent by naphthylmethyl,[16] 2,4,6-trimethylbenzyl,[17] and 3,4-dichlorobenzyl groups.[18] The enantioselectivity has increased when passing from benzylproline derivatives to naphthylmethylproline ones;[16] however, these reagents have found no use. In the case of 2,4,6-trimethylbenzylproline complexes, the stereoselectivity of the synthesis of amino acids has been low (41—66%).[17] The high reaction stereoselectivity and rate have been observed with complexes with another chiral reagent, namely, (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dichlorobenzyl)pyrrolidine-2-carboxamide ((*S*)-3,4-DCBPB) (*ee* of the resulting amino acids were 90—99%).[18—20]

Previous[19,20] studies of Ni^{II} complexes with the Schiff bases of (*E*)- and (*Z*)-2-aminobut-2-enoic acids in asymmetric addition reactions with nucleophiles (alcohols, thiols, and amines) in the presence of the chiral auxiliary reagents (*S*)-BPB and (*S*)-3,4-DCBPB have given birth to methods for the asymmetric synthesis of β-substituted α-aminobutyric acids of the absolute configuration ((*S*)-*anti* (or *L-allo*)).

Thus, introduction of electron-withdrawing Cl atoms into the aromatic ring of the *N*-benzylproline residue increases the diastereoselectivity and rate of nucleophilic addition. However, this is the only example; because of the foregoing demand for a rapid and highly stereoselective route to amino acids, it was expedient to check this trend.

Results and Discussion

Here we present the synthesis from proline derivatives **1a,b** of the novel chiral auxiliaries (*S*)-*N*-(2-benzoylphenyl)-1-(2-chlorobenzyl)pyrrolidine-2-carboxamide (**2a**) and (*S*)-*N*-(2-benzoylphenyl)-1-(3,4-dimethylbenzyl)pyrrolidine-2-carboxamide (**2b**), as well as of Ni^{II} complexes with their Schiff bases with the amino acids glycine, alanine, and threonine (**3a,b—6a,b**) and (*E*)- and

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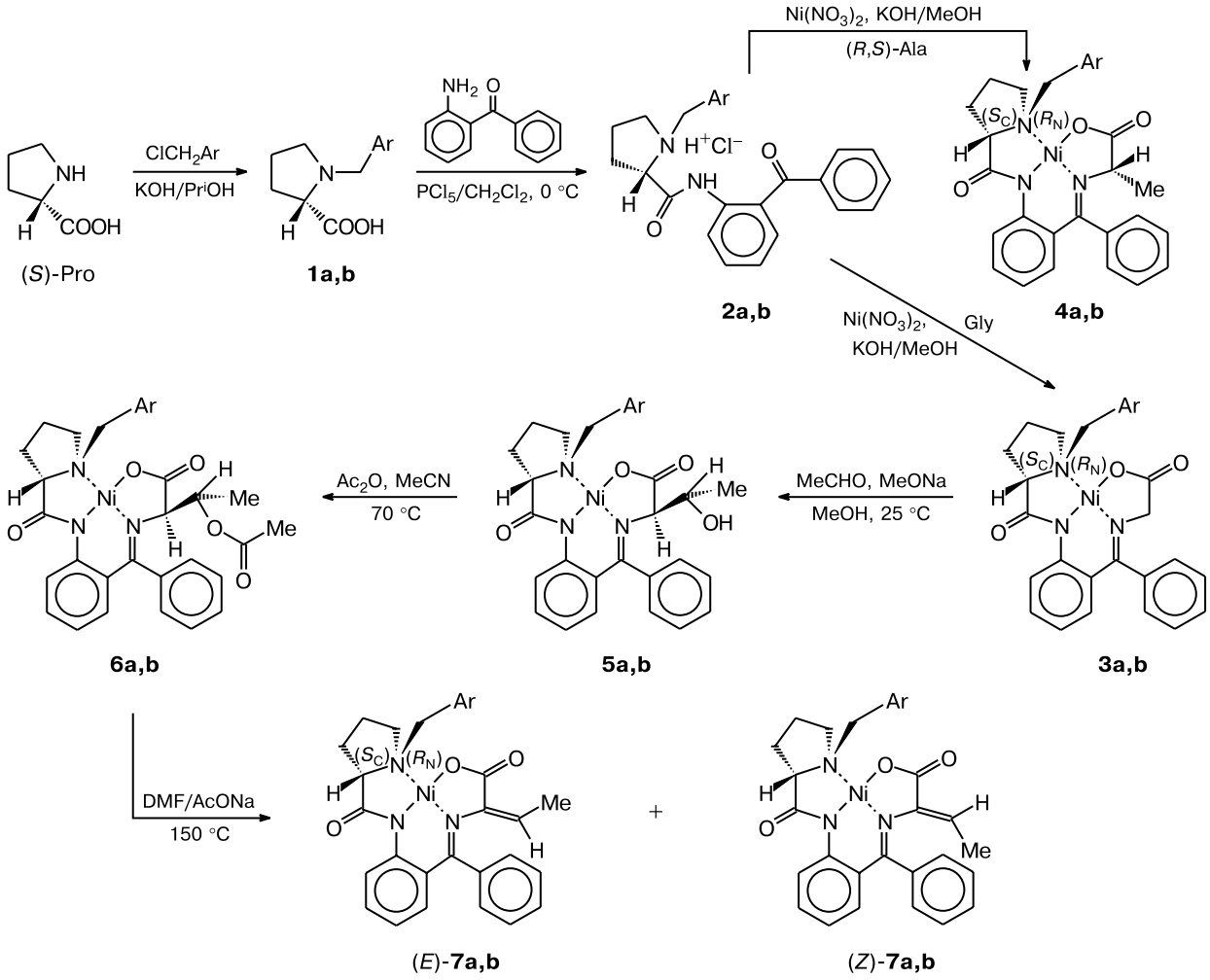
Scheme 1



Ar = 2-ClC_6H_4 (**a**), 3,4-$Me_2C_6H_3$ (**b**)

(*Z*)-2-aminobut-2-enoic acids (**7a,b**) (Scheme 1). Complexes **7a,b** were studied in reactions with nucleophiles (asymmetric addition to the C=C bond).

Novel chiral auxiliaries and their Ni^{II} complexes of Schiff bases with amino acids were synthesized as described earlier[18,19,21,22] (see Scheme 1). The thermodynamic stereoselectivities of formation of complexes of (*S*)-alanine **4a,b*** and (*R*)-threonine **5a,b** were determined by chiral GLC analysis of a mixture of amino acids isolated upon decomposition of the equilibrium mixture of the diastereomeric complexes. The stereoselectivity was 96% for complex **4a** and 92.5% for complex **4b** (the (*S*)-alanine-containing complex is dominant). In the case of the threonine complexes, the *de* value was 96.5% (**5a**) and 91% (**5b**), the diastereomer containing (*R*)-threonine being major.

The configurations of complexes **4a,b** were determined by X-ray diffraction analysis. The molecular structures of complexes **4a,b** are shown in Fig. 1. The X-ray diffraction data unambiguously confirm the (*S*)-configuration of the alanine residue.

The ratio of the (*E*)- to (*Z*)-isomers obtained in the synthesis of complexes **7a,b** was determined by ^1H NMR spectroscopy from the relative intensities of the signals for the Me protons in the dehydroaminobutyric fragment: the ratio was 2 : 1 and 3 : 1 for **7a** and **7b**, respectively. These (*E*)/(*Z*) values are lower than those for complexes based on the chiral reagent (*S*)-BPB.[19] Such a phenomenon has been noted in the preparation of complexes of 2-aminobut-2-enoic acid with (*S*)-3,4-DCBPB.[20]

* For the synthesis of the complexes, racemic alanine was used in a double excess with respect to the chiral reagent. As shown earlier,[12,13,20] the stereoselectivity of the process does not depend on whether racemic or optically pure (*S*)- or (*R*)-alanine is used.

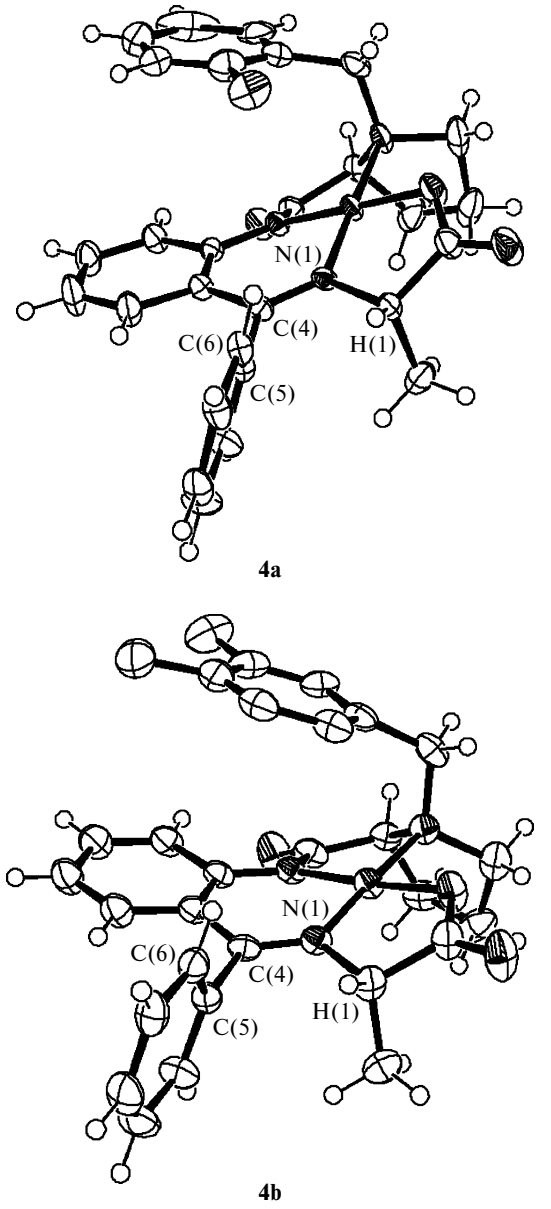
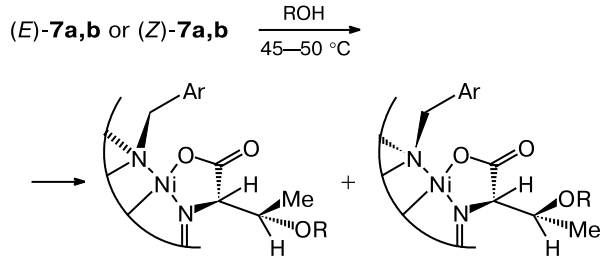


Fig. 1. Structures **4a,b** according to the X-ray diffraction data.

The (*E*)- and (*Z*)-configurations of isomers **7a,b** were assigned from ^{1}H NMR data for the individual complexes by analogy with the (*S*)-BPB-based complex.[19] The spectra of the isomers with the higher R_f values show relatively low-field signals (δ 1.62 and 1.64 for **7a** and **7b**, respectively), which is characteristic of the (*E*)-configuration.[19] Analogous signals for the isomers with the lower R_f values appear in higher fields (δ 0.88 and 0.92 for **7a** and **7b**, respectively). This indicates considerable shielding of the Me protons due to the magnetic anisotropy of the phenyl substituent at the C=N bond, which is characteristic of the (*Z*)-configuration of the dehydroaminobutyric fragment.

Addition of alkoxide ions to the C=C bond of complexes **7a,b** was carried out according to an earlier developed procedure[19,20] (Scheme 2). For this purpose, both the pure (*E*)- and (*Z*)-isomers of complexes **7a,b** and their synthetic mixture were used. In all cases, the addition gave a mixture of diastereomeric complexes with a large excess of the (*S*,*S*,*S*)-diastereomer. The major diastereomeric complexes **8a,b** and **9a,b** were isolated by column chromatography and characterized by spectroscopic methods.

Scheme 2



8a,b, **9a,b**

	Ar	R		Ar	R
8a	2-ClC$_6$H$_4$	Me	**9a**	2-ClC$_6$H$_4$	Et
8b	3,4-Me$_2$C$_6$H$_3$	Me	**9b**	3,4-Me$_2$C$_6$H$_3$	Et

The configuration of the α-C atom of the amino acid residue was determined from the sign of the optical rotation at a wavelength of 589 nm, as had been done earlier[19,20] for complexes of these amino acids with the chiral reagents (*S*)-BPB and (*S*)-3,4-DCBPB.

The configuration of the β-C atom of the amino acid residue was determined by ^{1}H NMR spectroscopy. Earlier, it has been shown that in the spectra of *anti*-isomers ((*S*,*S*,*S*)-diastereomers), the signals for the β-Me protons of the amino acid residue appear in the higher fields than the relatively low-field signals for the *syn*-isomers ((*S*,*S*,*R*)-diastereomers).[19,20] The data obtained suggest that the major adducts are complexes **8a,b** and **9a,b** with the (*S*,*S*,*S*)-configuration. According to the sign of the optical rotation and ^{1}H NMR data, the sole accompanying minor diastereomer in the case of complexes **8a** and **9a** is the complex with (*S*,*S*,*R*)-configuration. In the case of complexes **8b** and **9b**, no accompanying minor diastereomers* were isolated in the individual state.

The (*S*,*S*,*S*)/(*S*,*S*,*R*) ratio for complexes **8a,b** and **9a,b** was determined from the integral intensity ratio of the signals for the β-Me group of the amino acid residue when analyzing the ^{1}H NMR spectra of a mixture of the diastereomers (Table 1). In addition, the ratio of the amino acid diastereomers determined for complexes **8a,b** by

* In this case, two accompanying diastereomeric complexes were detected (^{1}H NMR data).

Table 1. Addition of alkoxide ions to complexes (*E*)-**7a,b** and (*Z*)-**7a,b** at 55—60 °C

Entry	Starting complex	Nucleophile[a]	*t*[b]/h	Product	Yield (%)	*de*[c] (%)
1	(*E*)-**7a**	MeO^-	1	**8a**	92	>98 (99.5)
2	(*Z*)-**7a**	MeO^-	4	**8a**	88	93 (92.5)
3	(*E*,*Z*)-**7a**[d]	MeO^-	4	**8a**	90	96 (96)
4	(*E*)-**7a**	EtO^-	1.5	**9a**	92	>98
5	(*Z*)-**7a**	EtO^-	20	**9a**	88	95
6	(*E*,*Z*)-**7a**[d]	EtO^-	20	**9a**	90	>98
7	(*E*)-**7b**	MeO^-	2	**8b**	86	90 (91[e])
8	(*Z*)-**7b**	MeO^-	3	**8b**	83	80 (71.8[e])
9	(*E*,*Z*)-**7b**[f]	MeO^-	3	**8b**	85	85 (85.3[e])
10	(*E*)-**7b**	EtO^-	5	**9b**	88	89
11	(*Z*)-**7b**	EtO^-	2	**9b**	85	56
12	(*E*,*Z*)-**7b**[f]	EtO^-	3	**9b**	87	76

[a] 0.2 *M* MeONa in MeOH and 0.04 *M* EtONa in EtOH were used.
[b] The reaction duration.
[c] The ratio of the diastereomers according to data from ^{1}H NMR spectroscopy and chiral GLC analysis (in parentheses).
[d] The mixture of the (*E*)- and (*Z*)-isomers in the ratio (*E*)-**7a**/(*Z*)-**7a** = 2 : 1.
[e] A third diastereomer (<3%) with an unidentified configuration was detected.
[f] The mixture of the (*E*)- and (*Z*)-isomers in the ratio (*E*)-**7b**/(*Z*)-**7b** = 3 : 1.

chiral GLC analysis of their mixture obtained upon decomposition of the reaction mixture fully agrees with that from the ^{1}H NMR data. Unfortunately, in the case of addition of ethanol to complexes **7a,b**, we failed to determine the ratio of the amino acid stereoisomers by chiral GLC analysis upon the decomposition of the reaction mixture (complexes **9a,b**).

Thus, the addition of the Me^- and EtO^- ions to the C=C bond of complexes **7a,b** mainly gives complexes of (2*S*,3*S*)-2-amino-3-methoxybutyric acid **8a,b** and (2*S*,3*S*)-2-amino-3-ethoxybutyric acid **9a,b**. A comparison of our data (see Table 1, entries *1*—*12*) with previous results (obtained with complexes based on other chiral derivatives of (*S*)-proline[19,20]) reveals increasing *de* values in the following order of the chiral auxiliaries: BPB (*de* 86%)[19] < 3,4-DCBPB (*de* 90%)[20] < **2b** (*de* 91%) < **2a** (*de* 97%).

The highest *de* values were obtained in the addition of alkoxide ions to complex (*E*)-**7a** (see Table 1, entries *1*, *4*). In addition, in agreement with previous data,[19,20] an increase in *de* and a reduction in the reaction time of the nucleophilic addition were observed when passing from the (*Z*)-isomers of 2-aminobut-2-enoic acid complexes to the (*E*)-isomers (see Table 1; *cf.* entries *2*, *5*, *8*, and *11* with *1*, *4*, *7*, and *10*).

It is evident from the data in Table 1 that the highest diastereoselectivity and nucleophilic addition rate were reached with complexes based on the modified chiral reagent **2a**. This can be explained by analyzing the structures of complexes **4a,b** (see Fig. 1)*. According to X-ray diffraction data, the presence of substituents in the aromatic ring of the *N*-benzylproline fragment causes its benzyl group to change position above the nickel coordination plane. In structure **4a**, the electron-withdrawing substituent of the benzylproline residue is directly above the Ni^{II} ion and its apical coordination to the nickel ion seems to be quite probable. This substantially changes the electron density distribution in the complex and we assume that the increase in the reaction rate can be mainly associated with such a coordination. In addition, because the 2-chlorobenzyl fragment comes closer to the nickel ion (Ni...Cl 3.149 Å), the angle between the Ph group of the benzophenone residue and the nickel coordination plane in the complexes changes (the deviation of the dihedral N(1)—C(4)—C(5)—C(6) angle from 90°, see Fig. 1). This angle for complexes of the type **4** based on the chiral reagents (*S*)-3,4-DCBPB, **2b**, and **2a** was 6°, 8°, and 20°, respectively. With an increase in this angle, steric interactions between the Ph group at the azomethine bond and the α-H(1) atom of the (*S*)-amino acid fragment become stronger; as the result, the (*S*)-amino acid chelate ring is distorted and the H(1) atom occupies an unfavorable equatorial position. In the case of the complexes of (*R*)-amino acid, the Ph group at the azomethine bond interacts with the bulky alkyl radical rather than the H_α atom, which makes the system more strained. Thus, the complex of the (*R*)-amino acid should become substantially less favorable in the order (*S*)-BPB, (*S*)-3,4-DCBPB, **2b**, and **2a**, while this effect for complexes of the (*S*)-amino acid is not so pronounced. Therefore, the energy difference between the diastereomeric complexes with the (*S*)- and (*R*)-amino acids increases, which means that under thermodynamic control (note that addition of nucleophiles to the C=C bond of complexes **7a,b** is thermodynamically controlled) the content of the complex with the (*R*)-amino acid in an equilibrium diastereomeric mixture will progressively decrease.

On decomposition of the complexes and isolation of the amino acids, the starting reagents **2a,b** were easily recovered in >90% yields, their original optical activities being completely retained.

Thus, we obtained the novel and very promising chiral reagent **2a**, which is suitable for highly stereoselective asymmetric synthesis of a wide range of amino acids.

Experimental

Commercial reagents were used: amino acids (Reanal, Hungary); L 40/100 silica gel (Chemapol, Praha); $CHCl_3$, Ac_2O,

* Earlier,[23] it has been shown that the conformations of the complexes are identical in the crystal and in solution.

AcOH, Me_2CO, MeCN, and Pr^iOH (Reakhim); 2-chlorobenzyl chloride, 3,4-dimethylbenzyl chloride, and 2-aminobenzophenone (Aldrich). All solvents were used freshly distilled. Enantiomeric GLC analysis of amino acids as their isopropyl *N*-trifluoroacetates was carried out on the ChirasilVal chiral phase[24] (capillary quartz column 40 m × 0.23 mm, film thickness 0.12 μm, column temperature 125 °C, helium as a carrier gas). ^{1}H NMR spectra were recorded on a Mercury-300 Varian instrument (300 MHz) in DMSO-d_6—CCl_4 (1 : 3) (unless otherwise specified). The signals in the ^{1}H NMR spectra were assigned from double resonance and 2D COSY experiments. Optical rotation was measured on a Perkin—Elmer-341 polarimeter. Column chromatography was carried out on a glass column (2×20 cm) packed with L 40/100 silica gel; Merck glass plates (5×10 cm) were used for TLC.

***N*-Benzylation of proline** was carried out as described earlier.[18] 2-Chlorobenzyl chloride or 3,4-dimethylbenzyl chloride was added to the reaction mixture at 0 °C.

(*S*)-*N*-(2-Chlorobenzyl)proline (1a). The yield was 95%, m.p. 160—162 °C, $[\alpha]_D^{20}$ −21.0, $[\alpha]_{578}^{20}$ −22.1, $[\alpha]_{546}^{20}$ −24.9, $[\alpha]_{436}^{20}$ −40.5, $[\alpha]_{365}^{20}$ −60.4 (*c* 1.0, EtOH). Found (%): C, 60.35; H, 5.56; N, 5.92. $C_{12}H_{14}ClNO_2$. Calculated (%): C, 60.12; H, 5.85; N, 5.85. ^{1}H NMR, δ: 1.90—2.14 (m, 3 H, β-H Pro, γ-H Pro); 2.33 (m, 1 H, β-H Pro); 2.91 (dt, 1 H, δ-H Pro, ^2J = 9.8 Hz, ^3J = 8.1 Hz); 3.26 (dt, 1 H, δ-H Pro, ^2J = 9.8 Hz, ^3J = 6.0 Hz); 3.91 (dd, 1 H, α-H Pro, ^3J = 8.8 Hz, ^3J = 6.4 Hz); 4.22, 4.40 (both d, 1 H each, NC$\underline{H}_2$Ar, ^2J = 13.9 Hz); 7.26—7.39 (m, 3 H, H arom.); 7.78 (dd, 1 H, H arom., ^3J = 6.8 Hz, ^4J = 2.6 Hz).

(*S*)-*N*-(3,4-Dimethylbenzyl)proline (1b). The yield was 74%, m.p. 182—185 °C, $[\alpha]_D^{20}$ −25.6 (*c* 1.0, EtOH). Found (%): C, 72.10; H, 8.26; N, 6.04. $C_{14}H_{19}NO_2$. Calculated (%): C, 72.10; H, 8.15; N, 6.01. ^{1}H NMR, δ: 1.70—2.15 (m, 4 H, β-H Pro, γ-H Pro); 2.23, 2.24 (both s, 3 H each, Me); 2.40 (m, 1 H, δ-H Pro); 2.95 (ddd, 1 H, δ-H Pro, ^2J = 9.1 Hz, ^3J = 7.0 Hz, ^3J = 4.1 Hz); 3.21 (dd, 1 H, α-H Pro, ^3J = 8.7 Hz, ^3J = 5.6 Hz); 3.45, 3.94 (both d, 1 H each, NC$\underline{H}_2$Ar, ^2J = 12.8 Hz); 6.99 (s, 2 H, H arom.); 7.05 (s, 1 H, H arom.).

Synthesis of chiral amides as hydrochlorides was carried out as described earlier.[18] After all the components were added, the reaction mixture was stirred at ~20 °C for 15 h.

(*S*)-*N*-(2-Benzoylphenyl)-1-(2-chlorobenzyl)pyrrolidine-2-carboxamide hydrochloride (2a). The yield was 72%, m.p. 203—205 °C, $[\alpha]_D^{20}$ −40.17 (*c* 1.0, MeOH). Found (%): C, 65.91; H, 3.15; N, 6.14. $C_{25}H_{23}ClN_2O_2 \cdot HCl$. Calculated (%): C, 65.93; H, 3.07; N, 6.15. ^{1}H NMR, δ: 1.60 (m, 1 H, β-H Pro); 1.84, 2.03 (both m, 1 H each, γ-H Pro); 2.43 (m, 1 H, β-H Pro); 4.27—4.90 (br.m, 5 H, α-H Pro, δ-H Pro, NC$\underline{H}_2$Ar); 7.20—7.59 (m, 9 H, H arom.); 7.46 (br.t, 2 H, H arom., ^3J = 7.5 Hz); 7.78 (br.d, 2 H, H arom., ^3J = 7.5 Hz); 9.78 (br, 1 H, NH^+); 12.15 (br.s, 1 H, HCl).

(*S*)-*N*-(2-Benzoylphenyl)-1-(3,4-dimethylbenzyl)pyrrolidine-2-carboxamide hydrochloride (2b). The yield was 40%, m.p. 230—235 °C, $[\alpha]_D^{20}$ −38.46 (*c* 1.0, MeOH). Found (%): C, 72.10; H, 6.28; N, 6.19. $C_{27}H_{28}N_2O_2 \cdot HCl$. Calculated (%): C, 72.24; H, 6.24; N, 6.24. ^{1}H NMR, δ: 1.76, 2.00 (both m, 1 H each, β-H Pro); 2.21, 2.24 (both s, 3 H each, Me); 3.20—3.38 (m, 2 H, γ-H Pro); 4.14—4.5 (br.m, 4 H, δ-H Pro, NC$\underline{H}_2$Ar); 4.72 (m, 1 H, α-H Pro); 7.02—7.56 (m, 10 H, H arom.); 7.77 (d, 2 H, H arom., ^3J = 7.6 Hz); 9.72 (br, 1 H, NH^+); 12.11 (br.s, 1 H, HCl).

Complexes **3a,b** and **4a,b** were obtained according to known procedures.[19,21,22]

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)glycinato-*N*,*N*′,*N*″,*O*]nickel(II) (3a). The yield was 85%, R_f 0.41 (SiO_2, $CHCl_3$—acetone (5 : 1)), m.p. 186—188 °C, $[\alpha]_D^{25}$ +2364 (*c* 0.05, $CHCl_3$). Found (%): C, 60.85; H, 4.58; N, 7.88. $C_{27}H_{24}ClN_3NiO_3$. Calculated (%): C, 60.88; H, 4.54; N, 7.89. ^{1}H NMR, δ: 2.09—2.19 (m, 2 H, β-H Pro, γ-H Pro); 2.54 (m, 1 H, γ-H Pro); 2.77 (m, 1 H, β-H Pro); 3.43 (m, 1 H, δ-H Pro); 3.52 (dd, 1 H, α-H Pro, ^3J = 10.9 Hz, ^3J = 6.1 Hz); 3.64 (m, 1 H, δ-H Pro); 3.69, 3.77 (both d, 1 H each, CH_2 Gly, ^2J = 20.0 Hz); 4.00, 4.56 (both d, 1 H each, NC$\underline{H}_2$Ar, ^2J = 12.9 Hz); 6.73 (br.t, 1 H, H arom., ^3J = 7.6 Hz); 6.83 (dd, 1 H, H arom., ^3J = 8.2 Hz, ^4J = 1.8 Hz); 6.98 (br.m, 1 H, H arom.); 7.15 (br.d, 1 H, H arom., ^3J = 7.2 Hz); 7.21 (ddd, 1 H, H arom., ^3J = 8.6 Hz, ^3J = 6.8 Hz, ^4J = 2.0 Hz); 7.27 (dd, 1 H, H arom., ^3J = 7.6 Hz, ^4J = 1.8 Hz); 7.36 (td, 1 H, H arom., ^3J = 7.5 Hz, ^4J = 1.4 Hz); 7.43 (dd, 1 H, H arom., ^3J = 8.1 Hz, ^4J = 1.4 Hz); 7.48—7.56 (m, 3 H, H arom.); 8.18 (dd, 1 H, H arom., ^3J = 8.8 Hz, ^4J = 1.0 Hz); 8.29 (dd, 1 H, H arom., ^3J = 7.6 Hz, ^4J = 1.8 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)glycinato-*N*,*N*′,*N*″,*O*]nickel(II) (3b). The yield was 75%, R_f 0.66 (SiO_2, $CHCl_3$—acetone (5 : 1)), m.p. 176—178 °C, $[\alpha]_D^{25}$ +1513 (*c* 0.05, $CHCl_3$). Found (%): C, 66.25; H, 5.44; N, 8.00. $C_{29}H_{29}N_3NiO_3$. Calculated (%): C, 66.20; H, 5.52; N, 7.99. ^{1}H NMR, δ: 2.05—2.24 (m, 2 H, β-H Pro); 2.10, 2.18 (both s, 3 H each, Me); 2.36—2.47 (m, 2 H, γ-H Pro); 3.25—3.41 (m, 2 H, α-H Pro, δ-H Pro); 3.50 (d, 1 H, CH_2 Gly, ^2J = 20.0 Hz); 3.51 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 12.3 Hz); 3.57 (m, 1 H, δ-H Pro); 3.63 (d, 1 H, CH_2 Gly, ^2J = 20.0 Hz); 4.32 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 12.9 Hz); 6.60 (ddd, 1 H, H arom., ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz); 6.69 (dd, 1 H, H arom., ^3J = 8.2 Hz, ^4J = 1.8 Hz); 7.05—7.11 (m, 2 H, H arom.); 7.11 (d, 1 H, H arom., ^3J = 7.5 Hz); 7.23 (br.d, 1 H, H arom., ^3J = 7.5 Hz); 7.50—7.62 (m, 3 H, H arom.); 7.76 (dd, 1 H, H arom., ^3J = 7.5 Hz, ^4J = 1.9 Hz); 8.13 (dd, 1 H, H arom., ^3J = 8.9 Hz, ^4J = 1.3 Hz); 8.31 (d, 1 H, H arom., ^4J = 1.9 Hz).

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*S*)-alaninato-*N*,*N*′,*N*″,*O*]nickel(II) (4a). The yield was 92%, R_f 0.64 (SiO_2, $CHCl_3$—acetone (5 : 1)), m.p. 324—326 °C, $[\alpha]_D^{25}$ +2574 (*c* 0.05, $CHCl_3$). Found (%): C, 61.59; H, 4.81; N, 7.61. $C_{28}H_{26}ClN_3NiO_3$. Calculated (%): C, 61.52; H, 4.76; N, 7.69. ^{1}H NMR ($CDCl_3$), δ: 1.58 (d, 3 H, Me Ala, ^3J = 7.0 Hz); 2.09 (m, 1 H, γ-H Pro); 2.26, 2.64 (both m, 1 H each, β-H Pro); 2.94 (m, 1 H, γ-H Pro); 3.51 (dd, 1 H, δ-H Pro, ^3J = 10.4 Hz, ^3J = 6.1 Hz); 3.57 (dd, 1 H, α-H Pro, ^3J = 11.0 Hz, ^3J = 6.1 Hz); 3.72 (m, 1 H, δ-H Pro); 3.90 (q, 1 H, α-H Ala, ^3J = 7.0 Hz); 3.85, 4.50 (both d, 1 H each, NC$\underline{H}_2$Ar, ^2J = 12.9 Hz); 6.64—6.72 (m, 2 H, H arom.); 6.96 (br.d, 1 H, H arom., ^3J = 7.3 Hz); 7.25—7.38 (m, 3 H, H arom.); 7.11—7.22 (m, 2 H, H arom.); 7.43—7.54 (m, 3 H, H arom.); 8.00 (d, 1 H, H arom., ^3J = 8.6 Hz); 8.22 (br.d, 1 H, H arom., ^3J = 7.5 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*S*)-alaninato-*N*,*N*′,*N*″,*O*]nickel(II) (4b). The yield was 80%, R_f 0.70 (SiO_2, $CHCl_3$—acetone (5 : 1)), m.p. 315—317 °C (decomp.), $[\alpha]_D^{25}$ +2562 (*c* 0.05, $CHCl_3$). Found (%): C, 66.76; H, 5.79;

N, 7.71. $C_{30}H_{31}N_3NiO_3$. Calculated (%): C, 66.70; H, 5.74; N, 7.78. ^{1}H NMR, δ: 1.50 (d, 3 H, Me Ala, ^3J = 7.1 Hz); 1.90, 2.00 (both s, 3 H each, Me); 2.01 (m, 1 H, γ-H Pro); 2.17, 2.51 (both m, 1 H each, β-H Pro); 2.97 (m, 1 H, γ-H Pro); 3.21 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 12.3 Hz); 3.37 (dd, 1 H, α-H Pro, ^3J = 11.1 Hz, ^3J = 5.8 Hz); 3.38, 3.63 (both m, 1 H each, δ-H Pro); 3.74 (q, 1 H, α-H Ala, ^3J = 7.1 Hz); 4.19 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 12.3 Hz); 6.49—6.59 (m, 2 H, H arom.); 6.86—7.02 (m, 3 H, H arom.); 7.18 (dt, 1 H, H arom., ^3J = 6.8 Hz, ^4J = 2.0 Hz); 7.36—7.52 (m, 3 H, H arom.); 7.59 (dd, 1 H, H arom., ^3J = 7.1 Hz, ^4J = 1.9 Hz); 7.81 (d, 1 H, H arom., ^3J = 8.6 Hz); 8.40 (d, 1 H, H arom., ^4J = 1.5 Hz).

Aldol condensation of complexes 3a,b was carried out according to known procedures.[19,22] Complexes of (*R*)-threonine were crystallized from heptane—acetone—methanol (1 : 1 : 1).

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*R*)-threoninato-*N*,*N*′,*N*″,*O*]nickel(II) (5a). The yield was 65%, R_f 0.54 (SiO_2, $CHCl_3$—acetone (5 : 1)), m.p. 89—91 °C, $[\alpha]_D^{25}$ −679.3 (*c* 0.05, $CHCl_3$). Found (%): C, 60.60; H, 4.78; N, 7.21. $C_{29}H_{28}ClN_3NiO_4$. Calculated (%): C, 60.40; H, 4.85; N, 7.28. ^{1}H NMR, δ: 1.13 (d, 3 H, β-Me Thr, ^3J = 6.2 Hz); 1.93 (m, 1 H, β-H Pro); 2.05—2.23 (m, 2 H, β-H Pro, γ-H Pro); 2.48 (m, 1 H, γ-H Pro); 2.74 (ddd, 1 H, δ-H Pro, ^2J = 11.5 Hz, ^3J = 8.5 Hz, ^3J = 6.4 Hz); 3.42 (d, 1 H, α-H Thr, ^3J = 7.2 Hz); 3.47 (dd, 1 H, α-H Pro, ^3J = 9.1 Hz, ^3J = 4.6 Hz); 4.06 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 14.1 Hz); 4.10—4.21 (m, 2 H, δ-H Pro, β-H Thr); 4.67 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 14.1 Hz); 5.14 (d, 1 H, OH, ^3J = 6.4 Hz); 6.68 (ddd, 1 H, H arom., ^3J = 8.3 Hz, ^3J = 6.9 Hz, ^4J = 1.3 Hz); 6.78 (dd, 1 H, H arom., ^3J = 8.3 Hz, ^4J = 1.8 Hz); 7.19 (ddd, 1 H, H arom., ^3J = 8.8 Hz, ^3J = 6.9 Hz, ^4J = 1.8 Hz); 7.27, 7.33 (both m, 1 H each, H arom.); 7.41—7.64 (m, 6 H, H arom.); 8.52 (dd, 1 H, H arom., ^3J = 8.8 Hz, ^4J = 1.0 Hz); 9.25 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.6 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*R*)-threoninato-*N*,*N*′,*N*″,*O*]nickel(II) (5b). The yield was 47%, R_f 0.81 (SiO_2, $CHCl_3$—acetone (5 : 1)), m.p. 165—167 °C, $[\alpha]_D^{25}$ −1104.0 (*c* 0.05, $CHCl_3$). Found (%): C, 65.60; H, 5.85; N, 8.00. $C_{31}H_{33}N_3NiO_4$. Calculated (%): C, 65.30; H, 5.91; N, 7.89. ^{1}H NMR, δ: 1.20 (d, 3 H, β-Me Thr, ^3J = 6.2 Hz); 1.86 (m, 1 H, β-H Pro); 1.97—2.15 (m, 2 H, β-H Pro, γ-H Pro); 2.41 (m, 1 H, γ-H Pro); 2.32, 2.34 (both s, 3 H each, Me); 2.68 (m, 1 H, δ-H Pro); 3.42 (d, 1 H, α-H Thr, ^3J = 7.2 Hz); 3.55 (dd, 1 H, δ-H Pro, ^3J = 9.1 Hz, ^3J = 4.0 Hz); 3.63 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 13.0 Hz); 4.15 (ddq, 1 H, β-H Thr, ^3J = 7.2 Hz, ^3J = 6.4 Hz, ^3J = 6.2 Hz); 4.26 (m, 1 H, α-H Pro); 4.49 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 13.0 Hz); 5.05 (d, 1 H, OH); 6.66 (br.t, 1 H, H arom., ^3J = 7.5 Hz); 6.74 (dd, 1 H, H arom., ^3J = 8.3 Hz, ^4J = 1.8 Hz); 7.16 (ddd, 1 H, H arom., ^3J = 8.7 Hz, ^3J = 6.8 Hz, ^4J = 1.8 Hz); 7.21—7.32, 7.46—7.53 (both m, 3 H each, H arom.); 7.60 (m, 1 H, H arom.); 7.75 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.8 Hz); 8.51 (d, 1 H, H arom., ^3J = 8.7 Hz).

***O*-Acetylation and deacetylation of complexes 5a,b** were carried out as described earlier.[19,20] After the deacetylation was completed, the reaction mixture was diluted with a fivefold excess of water and the precipitate of 2-aminobut-2-enoic acid complexes that formed was filtered off. The product was obtained as a mixture of the (*E*)- and (*Z*)-isomers of complexes **7a,b**, which were separated by column chromatography on silica gel with AcOEt—$CHCl_3$ (3 : 1) as an eluent.

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*R*)-*O*-acetylthreoninato-*N*,*N*′,*N*″,*O*]nickel(II) (6a). The yield was 95%, R_f 0.66 (SiO_2, AcOEt—$CHCl_3$ (3 : 1)), m.p. 120—122 °C, $[\alpha]_D^{25}$ −448.1 (*c* 0.05, $CHCl_3$). Found (%): C, 60.10; H, 4.78; N, 6.78. $C_{31}H_{30}ClN_3NiO_5$. Calculated (%): C, 60.17; H, 4.85; N, 6.79. ^{1}H NMR, δ: 1.33 (d, 3 H, β-Me Thr, ^3J = 6.4 Hz); 1.80 (s, 3 H, Me Ac-Thr); 1.94 (m, 1 H, γ-H Pro); 2.15 (m, 2 H, β-H, γ-H Pro); 2.54 (m, 1 H, β-H Pro); 2.68 (ddd, 1 H, δ-H Pro, ^2J = 11.3 Hz, ^3J = 8.7 Hz, ^3J = 6.4 Hz); 3.45 (dd, 1 H, α-H Pro, ^3J = 9.6 Hz, ^3J = 4.4 Hz); 3.61 (d, 1 H, α-H Thr, ^3J = 7.6 Hz); 4.04 (ddd, 1 H, δ-H Pro, ^2J = 11.3 Hz, ^3J = 6.6 Hz, ^3J = 4.4 Hz); 4.20, 4.83 (both d, 1 H each, NC$\underline{H}_2$Ar, ^2J = 13.8 Hz); 5.34 (dq, 1 H, β-H Thr, ^3J = 7.6 Hz, ^3J = 6.3 Hz); 6.70 (ddd, 1 H, H arom., ^3J = 8.3 Hz, ^3J = 6.8 Hz, ^4J = 1.2 Hz); 6.81 (dd, 1 H, H arom., ^3J = 8.3 Hz, ^4J = 1.8 Hz); 7.22 (ddd, 1 H, H arom., ^3J = 8.7 Hz, ^3J = 6.9 Hz, ^4J = 1.8 Hz); 7.26 (m, 1 H, H arom.); 7.34 (br.d, 1 H, H arom., ^3J = 6.8 Hz); 7.42 (ddd, 1 H, H arom., ^3J = 7.9 Hz, ^3J = 7.3 Hz, ^4J = 1.7 Hz); 7.49—7.67 (m, 5 H, H arom.); 8.47 (dd, 1 H, H arom., ^3J = 8.8 Hz, ^4J = 1.2 Hz); 8.84 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.7 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*R*)-*O*-acetylthreoninato-*N*,*N*′,*N*″,*O*]nickel(II) (6b). The yield was 80%, R_f 0.92 (SiO_2, AcOEt—$CHCl_3$ (3 : 1)), m.p. 193—195 °C, $[\alpha]_D^{25}$ −1092.5 (*c* 0.05, $CHCl_3$). Found (%): C, 64.98; H, 5.64; N, 6.92. $C_{33}H_{35}N_3NiO_5$. Calculated (%): C, 64.73; H, 5.72; N, 6.86. ^{1}H NMR, δ: 1.40 (d, 3 H, β-Me Thr, ^3J = 6.4 Hz); 1.81 (s, 3 H, Me Ac-Thr); 2.07 (m, 2 H, β-H Pro, γ-H Pro); 2.30, 2.32 (both s, 3 H each, Me); 2.40 (m, 1 H, γ-H Pro); 2.64 (m, 1 H, β-H Pro); 3.55 (dd, 1 H, α-H Pro, ^3J = 9.5 Hz, ^3J = 4.0 Hz); 3.63 (d, 1 H, α-H Thr, ^3J = 7.4 Hz); 3.84 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 13.2 Hz); 3.92 (ddd, 1 H, δ-H Pro, ^2J = 11.5 Hz, ^3J = 7.3 Hz, ^3J = 4.2 Hz); 4.13 (dd, 1 H, δ-H Pro, ^3J = 5.8 Hz, ^3J = 3.6 Hz); 4.73 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 13.2 Hz); 5.37 (dq, 1 H, β-H Thr, ^3J = 7.4 Hz, ^3J = 6.4 Hz); 6.68 (ddd, 1 H, H arom., ^3J = 8.4 Hz, ^3J = 6.7 Hz, ^4J = 1.1 Hz); 6.77 (dd, 1 H, H arom., ^3J = 8.2 Hz, ^4J = 1.9 Hz); 7.18—7.24 (m, 3 H, H arom.); 7.32 (br.d, 1 H, H arom., ^3J = 7.1 Hz); 7.42 (d, 1 H, H arom., ^4J = 1.9 Hz); 7.50—7.59 (m, 3 H, H arom.); 7.66 (m, 1 H, H arom.); 8.50 (dd, 1 H, H arom., ^3J = 8.8 Hz, ^4J = 1.0 Hz).

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*E*)-2-aminobut-2-enoato-*N*,*N*′,*N*″,*O*]nickel(II) ((*E*)-7a). The yield was 67.4%, R_f 0.55 (SiO_2, AcOEt—$CHCl_3$ (3 : 1)), m.p. 218—220 °C, $[\alpha]_D^{25}$ +3031.8 (*c* 0.022, $CHCl_3$). Found (%): C, 62.42; H, 4.75; N, 7.45. $C_{29}H_{26}ClN_3NiO_3$. Calculated (%): C, 62.34; H, 4.65; N, 7.52. ^{1}H NMR, δ: 1.62 (d, 3 H, >C=CH(Me), ^3J = 7.4 Hz); 2.14—2.31 (m, 2 H, β-H Pro, γ-H Pro); 2.60 (m, 1 H, γ-H Pro); 2.78 (m, 1 H, β-H Pro); 3.28 (dd, 1 H, δ-H Pro, ^3J = 9.1 Hz, ^3J = 6.2 Hz); 3.55 (dd, 1 H, α-H Pro, ^3J = 11.0 Hz, ^3J = 6.2 Hz); 3.67 (m, 1 H, δ-H Pro); 3.78, 4.22 (both d, 1 H each, NC$\underline{H}_2$Ar, ^2J = 12.6 Hz); 5.05 (q, 1 H, >C=C$\underline{H}$(Me), ^3J = 7.4 Hz); 6.65 (ddd, 1 H, H arom., ^3J = 8.3 Hz, ^3J = 6.8 Hz, ^4J = 1.3 Hz); 6.82 (dd, 1 H, H arom., ^3J = 8.3 Hz, ^4J = 1.8 Hz); 7.04 (ddd, 1 H, H arom., ^3J = 8.7 Hz, ^3J = 6.9 Hz, ^4J = 1.8 Hz); 7.12—7.38 (m, 5 H, H arom.); 7.46 (m, 3 H, H arom.); 7.98 (dd, 1 H, H arom., ^3J = 8.7 Hz, ^4J = 1.1 Hz); 8.21 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.8 Hz).

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*Z*)-2-aminobut-2-enoato-

***N*,*N*′,*N*″,*O*]nickel(II) ((*Z*)-7a).** The yield was 32.6%, R_f 0.44 (SiO_2, AcOEt—$CHCl_3$ (3 : 1)), m.p. 243—244 °C, $[\alpha]_D^{25}$ +2645.0 (*c* 0.02, $CHCl_3$). Found (%): C, 62.38; H, 4.75; N, 7.58. $C_{29}H_{26}ClN_3NiO_3$. Calculated (%): C, 62.34; H, 4.65; N, 7.52. ^{1}H NMR, δ: 0.88 (d, 3 H, >C=CH(Me), ^3J = 7.6 Hz); 2.18 (m, 1 H, β-H Pro); 2.29, 2.64 (both m, 1 H each, γ-H Pro); 3.24 (m, 1 H, β-H Pro); 3.56 (dd, 1 H, α-H Pro, ^3J = 10.9 Hz, ^3J = 6.2 Hz); 3.73 (d, 1 H, NCH_2Ar, ^2J = 12.6 Hz); 3.75 (m, 1 H, δ-H Pro); 4.13 (d, 1 H, NCH_2Ar, ^2J = 12.6 Hz); 4.13 (dd, 1 H, δ-H Pro, ^3J = 5.6 Hz, ^3J = 3.5 Hz); 5.55 (q, 1 H, >C=CH(Me), ^3J = 7.6 Hz); 6.69 (ddd, 1 H, H arom., ^3J = 8.2 Hz, ^3J = 6.8 Hz, ^4J = 1.0 Hz); 6.98 (dd, 1 H, H arom., ^3J = 8.2 Hz, ^4J = 1.8 Hz); 7.2 (ddd, 1 H, H arom., ^3J = 8.6 Hz, ^3J = 6.8 Hz, ^4J = 1.8 Hz); 7.22—7.42 (m, 5 H, H arom.); 7.56 (m, 3 H, H arom.); 7.98 (dd, 1 H, H arom., ^3J = 8.6 Hz, ^4J = 1.1 Hz); 8.19 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.8 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*E*)-2-aminobut-2-enoato-*N*,*N*′,*N*″,*O*]nickel(II) ((*E*)-7b). The yield was 60%, R_f 0.82 (SiO_2, AcOEt—$CHCl_3$ (3 : 1)), m.p. 188—190 °C, $[\alpha]_D^{25}$ +2084.7 (*c* 0.05, $CHCl_3$). Found (%): C, 67.73; H, 5.72; N, 7.74. $C_{31}H_{31}N_3NiO_3$. Calculated (%): C, 67.42; H, 5.62; N, 7.61. ^{1}H NMR, δ: 1.64 (d, 3 H, >C=CH(Me), ^3J = 7.4 Hz); 1.97, 2.04 (both s, 3 H each, Me); 2.14 (m, 1 H, β-H Pro); 2.34, 2.65 (both m, 1 H each, γ-H Pro); 2.74 (m, 1 H, β-H Pro); 2.83 (dd, 1 H, δ-H Pro, ^3J = 9.2 Hz, ^3J = 6.4 Hz); 3.42 (dd, 1 H, α-H Pro, ^3J = 11.0 Hz, ^3J = 6.4 Hz); 3.65 (m, 1 H, δ-H Pro); 3.98, 4.10 (both d, 1 H each, NCH_2Ar, ^2J = 12.6 Hz); 5.02 (q, 1 H, >C=CH(Me), ^3J = 7.4 Hz); 6.60 (ddd, 1 H, H arom., ^3J = 8.4 Hz, ^3J = 6.8 Hz, ^4J = 1.1 Hz); 6.78 (dd, 1 H, H arom., ^3J = 8.4 Hz, ^4J = 1.8 Hz); 7.02 (ddd, 1 H, H arom., ^3J = 8.9 Hz, ^3J = 6.8 Hz, ^4J = 1.8 Hz); 7.20—7.42 (m, 4 H, H arom.); 7.56 (m, 3 H, H arom.); 7.64 (dd, 1 H, H arom., ^3J = 8.9 Hz, ^4J = 1.1 Hz); 8.23 (dd, 1 H, H arom., ^3J = 7.6 Hz, ^4J = 1.7 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(*Z*)-2-aminobut-2-enoato-*N*,*N*′,*N*″,*O*]nickel(II) (*Z*-7b). The yield was 40%, R_f 0.64 (SiO_2, AcOEt—$CHCl_3$ (3 : 1)), m.p. >250 °C, $[\alpha]_D^{25}$ +3141.3 (*c* 0.025, $CHCl_3$). Found (%): C, 67.48; H, 5.68; N, 7.74. $C_{31}H_{31}N_3NiO_3$. Calculated (%): C, 67.42; H, 5.62; N, 7.61. ^{1}H NMR, δ: 0.92 (d, 3 H, >C=CH(Me), *J* = 7.6 Hz); 1.99, 2.05 (both s, 3 H each, Me); 2.18 (m, 1 H, β-H Pro); 2.22, 2.63 (both m, 1 H each, γ-H Pro); 2.78 (m, 1 H, β-H Pro); 2.92 (dd, 1 H, δ-H Pro, ^3J = 9.4 Hz, ^3J = 6.4 Hz); 3.22 (dd, 1 H, α-H Pro, ^3J = 11.0 Hz, ^3J = 6.4 Hz); 3.63 (m, 1 H, δ-H Pro); 3.96, 4.23 (both d, 1 H each, NCH_2Ar, ^2J = 12.6 Hz); 5.56 (q, 1 H, >C=CH(Me), ^3J = 7.6 Hz); 6.62 (ddd, 1 H, H arom., ^3J = 8.4 Hz, ^3J = 6.6 Hz, ^4J = 1.3 Hz); 6.80 (dd, 1 H, H arom., ^3J = 8.4 Hz, ^4J = 1.8 Hz); 6.96 (ddd, 1 H, H arom., ^3J = 8.7 Hz, ^3J = 6.9 Hz, ^4J = 1.8 Hz); 7.02—7.46 (m, 4 H, H arom.); 7.62 (m, 3 H, H arom.); 7.98 (dd, 1 H, H arom., ^3J = 8.7 Hz, ^4J = 1.1 Hz); 8.42 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.8 Hz).

Addition of the alkoxide ions to complexes 7a,b was carried out as described earlier.[19,20] Both the individual (*E*)- and (*Z*)-isomers and their mixtures (2 : 1 for **7a** and 3 : 2 for **7b**) obtained in the synthesis were used. The base : complex ratio was 3 : 1.

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(2*S*,3*S*)-*O*-methylthreoninato-*N*,*N*′,*N*″,*O*]nickel(II) (8a). The yield was 90%, m.p. 188—190 °C, $[\alpha]_D^{25}$ +2935 (*c* 0.05, $CHCl_3$). Found (%): C, 61.15; H, 5.22; N, 7.08. $C_{30}H_{30}ClN_3NiO_4$. Calculated (%): C, 61.00; H, 5.12; N, 7.11. ^{1}H NMR, δ: 1.05 (d, 3 H, >CH—CH(Me), ^3J = 6.4 Hz); 2.05—2.21 (m, 2 H, γ-H Pro); 2.60, 2.84 (both m, 1 H each, β-H Pro); 3.26 (m, 1 H, δ-H Pro); 3.29 (qd, 1 H, >CH—CH(Me), ^3J = 6.4 Hz, ^3J = 2.2 Hz); 3.46 (dd, 1 H, α-H Pro, ^3J = 10.7 Hz, ^3J = 6.7 Hz); 3.56 (s, 3 H, OMe); 3.57 (d, 1 H, >CH—CH(Me), ^3J = 2.2 Hz); 3.81 (m, 1 H, δ-H Pro); 3.87, 4.29 (both d, 1 H each, NCH_2Ar, ^2J = 12.7 Hz); 6.59—6.62, 7.01—7.12 (both m, 2 H each, H arom.); 7.17 (td, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.7 Hz); 7.29—7.39, 7.45—7.68 (both m, 3 H each, H arom.); 8.05 (d, 1 H, H arom., ^3J = 8.6 Hz); 8.26 (dd, 1 H, H arom., ^3J = 7.7 Hz, ^4J = 1.6 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(2*S*,3*S*)-*O*-methylthreoninato-*N*,*N*′,*N*″,*O*]nickel(II) (8b). The yield was 85%, m.p. 220—222 °C, $[\alpha]_D^{25}$ +2932 (*c* 0.05, $CHCl_3$). Found (%): C, 65.63; H, 6.02; N, 7.22. $C_{32}H_{35}N_3NiO_4$. Calculated (%): C, 65.77; H, 6.04; N, 7.19. ^{1}H NMR, δ: 1.07 (d, 3 H, >CH—CH(Me), ^3J = 6.4 Hz); 1.98, 2.09 (both s, 3 H each, Me); 2.03—2.17 (m, 3 H, β-H Pro, γ-H Pro); 2.55 (m, 1 H, β-H Pro); 3.28 (qd, 1 H, >CH—CH(Me), ^3J = 6.4 Hz, ^3J = 2.2 Hz); 3.33 (d, 1 H, NCH_2Ar, ^2J = 12.3 Hz); 3.66 (dd, 1 H, α-H Pro, ^3J = 10.4 Hz, ^3J = 6.4 Hz); 3.36 (m, 1 H, δ-H Pro); 3.56 (s, 3 H, OMe); 3.61 (d, 1 H, CH—CH(Me), ^3J = 2.2 Hz); 3.79 (m, 1 H, δ-H Pro); 4.17 (d, 1 H, NCH_2Ar, ^2J = 12.3 Hz); 6.54—6.60 (m, 2 H, H arom.); 6.98—7.08 (m, 3 H, H arom.); 7.38 (br.d, 1 H, H arom., ^3J = 7.5 Hz); 7.43—7.68 (m, 4 H, H arom.); 8.00 (d, 1 H, H arom., ^3J = 8.6 Hz); 8.49 (d, 1 H, H arom., ^4J = 1.9 Hz).

(*S*)-[({2-[1-(2-Chlorobenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(2*S*,3*S*)-*O*-ethylthreoninato-*N*,*N*′,*N*″,*O*]nickel(II) (9a). The yield was 90%, m.p. 166—168 °C, $[\alpha]_D^{25}$ +2409 (*c* 0.05, $CHCl_3$). Found (%): C, 61.61; H, 5.38; N, 6.91. $C_{31}H_{32}ClN_3NiO_4$. Calculated (%): C, 61.57; H, 5.33; N, 6.95. ^{1}H NMR, δ: 0.98 (d, 3 H, >CH—CH(Me), ^3J = 6.4 Hz); 1.37 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 2.04—2.20 (m, 2 H, γ-H Pro, β-H Pro); 2.51 (m, 1 H, β-H Pro); 2.86 (m, 1 H, γ-H Pro); 3.28 (m, 1 H, δ-H Pro); 3.46 (qd, 1 H, >CH—CH(Me), ^3J = 6.4 Hz, ^3J = 2.2 Hz); 3.48 (dd, 1 H, α-H Pro, ^3J = 10.6 Hz, ^3J = 6.6 Hz); 3.65 (d, 1 H, >CH—CH(Me), ^3J = 2.2 Hz); 3.81 (m, 1 H, δ-H Pro); 3.72 (q, 2 H, OCH_2Me, ^2J = 7.0 Hz); 3.33 (d, 1 H, NCH_2Ar, ^2J = 12.2 Hz); 4.19 (d, 1 H, NCH_2Ar, ^2J = 12.7 Hz); 6.59—6.63, 7.01—7.12 (both m, 2 H each, H arom.); 7.18 (td, 1 H, H arom., ^3J = 7.6 Hz, ^4J = 1.7 Hz); 7.31—7.39, 7.45—7.68 (both m, 3 H each, H arom.); 8.06 (d, 1 H, H arom., ^3J = 8.6 Hz); 8.26 (dd, 1 H, H arom., ^3J = 7.6 Hz, ^4J = 1.6 Hz).

(*S*)-[({2-[1-(3,4-Dimethylbenzyl)pyrrolidine-2-carboxamido]phenyl}{phenyl}methylidene)-(2*S*,3*S*)-*O*-ethylthreoninato-*N*,*N*′,*N*″,*O*]nickel(II) (9b). The yield was 87%, m.p. 235—237 °C, $[\alpha]_D^{25}$ +3129 (*c* 0.05, $CHCl_3$). Found (%): C, 66.38; H, 6.27; N, 6.99. $C_{33}H_{37}N_3NiO_4$. Calculated (%): C, 66.24; H, 6.23; N, 7.02. ^{1}H NMR, δ: 1.08 (d, 3 H, >CH—CH(Me), ^3J = 6.4 Hz); 1.37 (t, 3 H, OCH_2Me, ^3J = 7.0 Hz); 1.97 (s, 3 H, Me); 2.04—2.14 (m, 3 H, γ-H Pro, β-H Pro); 2.09 (s, 3 H, Me); 2.51 (m, 1 H, β-H Pro); 3.31—3.44 (m, 2 H, α-H Pro, δ-H Pro); 3.33 (d, 1 H, NCH_2Ar, ^2J = 12.2 Hz); 3.34 (qd, 1 H, >CH—CH(Me), ^3J = 6.4 Hz, ^3J = 2.2 Hz); 3.65 (d, 1 H, >CH—CH(Me), ^3J = 2.2 Hz); 3.72 (q, 2 H, OCH_2Me, ^2J = 7.0 Hz); 3.73 (m, 1 H,

Table 2. Selected crystallographic parameters and a summary of data collection for complexes **4a,b**

Parameter	**4a**	**4b**
Molecular formula	$C_{28}H_{26}ClN_3NiO_3$	$C_{30}H_{31}N_3NiO_3$
Molecular mass	546.68	540.29
T/K	173	105
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	9.3354(19)	9.3420(7)
b/Å	10.033(2)	10.5929(8)
c/Å	25.919(5)	26.297(2)
V/Å^3	2427.6(8)	2602.3(3)
Z	4	4
d_{calc}/g cm^{-3}	1.496	1.379
F(000)	1136	1136
μ/mm^{-1}	0.946	0.782
$2\theta_{max}$/deg	58	56
Number of measured reflections	3632	26535
Number of independent reflections	3632	6269
Number of reflections with $I > 2\sigma(I)$	3265	5581
Number of parameters refined	325	406
R_1 ($I > 2\sigma(I)$)	0.0604	0.0319
wR_2 (all data)	0.1678	0.0690
GOOF	1.027	1.038
Flack parameter	0.00(3)	0.00(1)
T_{min}/T_{max}	—	0.799/0.853

δ-H Pro); 4.19 (d, 1 H, NC$\underline{H}_2$Ar, ^2J = 12.7 Hz); 6.53—6.59 (m, 2 H, H arom.); 6.98—7.04 (m, 3 H, H arom.); 7.39—7.65 (m, 5 H, H arom.); 8.03 (d, 1 H, H arom., ^3J = 8.6 Hz); 8.49 (d, 1 H, H arom., ^4J = 2.0 Hz).

X-ray diffraction analysis of complexes 4a,b. The unit cell parameters and reflection intensities were measured on Syntex $P2_1$ (T = 173 K, Mo-Kα radiation, graphite monochromator, θ/2θ scan mode) and Bruker SMART 1000 CCD automatic diffractometers (T = 105 K, Mo-Kα radiation, graphite monochromator, φ and ω scan modes) for complexes **4a** and **4b**, respectively. In the case of complex **4b**, an absorption correction was applied with the SADABS program.[25] Selected crystallographic parameters and a summary of data collection are given in Table 2. The structures of both the complexes were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. In complex **4b**, the dimethylphenyl fragment was found to be randomly disordered over two positions with the occupancy factors 0.7 and 0.3; these positions are superimposed when rotated about the C(22)—C(23) bond through 180°. The hydrogen atoms were located geometrically and refined isotropically with fixed coordinates ("rider" model) and thermal parameters (U_i(H) = 1.5U_{eq}(C) for the Me group and U_i(H) = 1.2U_{eq}(C) for the other groups). All calculations were performed with the SHELXTL PLUS program package (Version 5.10).[26] The atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for complexes **4a,b** have been deposited with the Cambridge Crystallographic Data Center.

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