Synthesis of novel non-proteinogenic α-amino acids with charged imidazolium fragment in the side chain

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Zwitterionic imidazolium and benzimidazolium salts bearing chiral amino acid moiety were synthesized using chiral Ni^{II} complexes. Different N-derivatives of the synthesized enantiomerically pure amino acids were prepared; their zwitterionic structures were confirmed by X-ray analysis.

Key words: zwitterionic compounds, imidazolium salts, amino acids, nickel complexes, ionic liquids.

In recent years, the interest in imidazolium salts, precursors for N-heterocyclic carbenes (NHC) increased dramatically; now NHC are popular stable nucleophilic carbenes. In the pioneering work,[1] isolation of the stable carbene in individual state has been reported. The complexation properties of NHC resembled that of phosphines,[2—4] which are widely used in the modern metal complex catalysis. However, in contrast to the latter, N-heterocyclic carbenes possess greater stability and lower toxicity. It should be emphasized that they can be generated *in situ* from even more stable imidazolium salts. In the last years, the use of N-heterocyclic carbenes in organocatalysis[5] is on the way. However, to the present date, the progress in this field is modest due to scarce examples of the reactions catalyzed by stable carbenes.

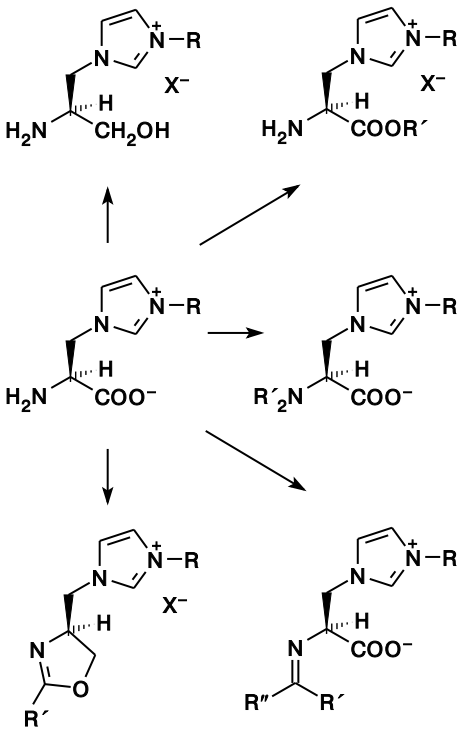
It is particularly noteworthy that great number of organic ionic liquids, which are very popular now as the reaction media, contains imidazolium fragment as the cation.[6]

The present work is devoted to the synthesis of novel non-proteinogenic zwitterionic α-amino acids bearing charged imidazolium or benzimidazolium moieties. Further, these compounds can be used for generation of the corresponding NHC, which, in turn, can be applied as organocatalysts or excellent ligands in the metal complex catalysis.

Significant advantage of the carbene precursors suggested by us is that they are not only polydentate compounds but also polyfunctional ones. Moreover, the modification of the functional groups allows fundamental changes in their chemical properties (Scheme 1).

Six different directions for modification of the abovementioned amino acids, which give rise to the novel organocatalysts and ligands for the metal catalysis, can be distinguished. At first, the stereodifferentiating ability of the

Scheme 1



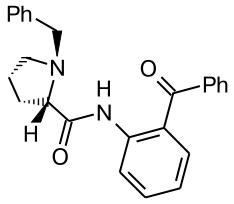
catalyst can be "tuned" by changing the substituent R at the nitrogen atom of the imidazole ring. At second, there is no need in the outer counterion in the synthesis of metal complexes in the positive oxidation degree because the ligand contains the carboxyl group, which can ionize; besides, the metal—ligand bond in this case becomes stronger. At third, the carboxyl group can be converted into the ester group, thus allowing preparation of the labile complex

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1245—1254, June, 2010.

with metal; the alkoxycarbonyl group of the latter can be easily replaced during reactions. At fourth, the carboxyl group can be reduced to the hydroxymethyl group. This transformation will significantly decrease the OH-acidity of the ligand and increase the basicity (and the hardness as well) of the conjugated base affecting positively the stability of the complexes with hard Lewis acids, such as alkali or alkaline earth metals. At fifth, transformation of the amino acid moiety into oxazoline or oxazolidine cycle can be regarded as the promising direction of further modification of the ligand. This modification will reduce the conformational mobility of the ligand. At sixth, the amino group can easily be alkylated, acylated or converted into the Schiff base, which will undoubtedly affect the strength of the ligand bonding with the central atom.

Recently[7] we synthesized N-heterocyclic carbene precursor, non-proteinogenic amino acid bearing imidazolium fragment, and successfully prepared the silver(I) carbene complex on the base of this compound as a ligand. In the present work with the aim at expanding the number of available NHC with amino acid moiety, we developed the procedure for the synthesis of zwitterionic amino acids bearing different imidazolium and benzimidazolium fragments.

Asymmetric synthesis of amino acids suggested by us is based on the application of the chiral reagent (*S*)-BBP (**1**) (see Ref. 8); after completion of the synthesis, ligand **1** can be recovered and reused.

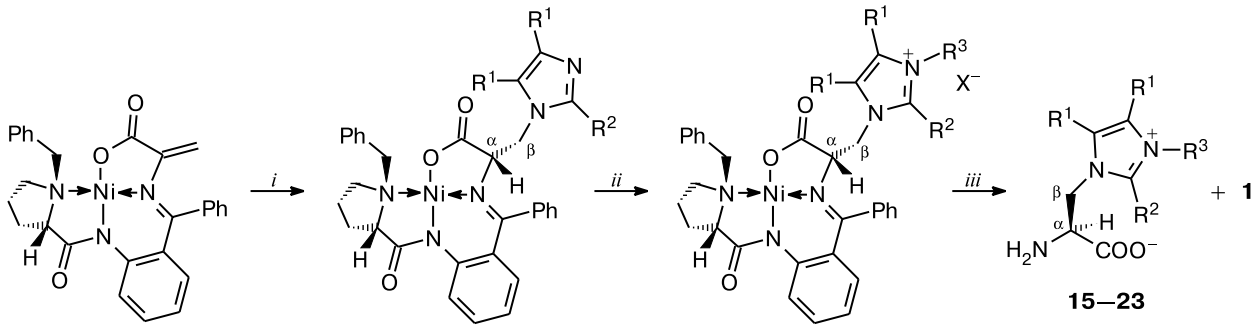


1

Dehydroalanine complex **2** was synthesized from the ligand **1** according to the known procedure.[9] The addition of the azole to the C=C bond of the complex **2** resulted in a mixture of diastereomers **3—6** with noticeable preference for the (*S*,*S*)-diastereomer (Scheme 2). Diastereomers can be separated by column chromatography on silica gel or by crystallization. Diastereomeric purity of thus separated complexes is >99%.

The rate of the addition of the heterocycle to the nickel complex **2** decreases in the series: imidazole > benzimidazole ≈ 2-methylbenzimidazole > 4,5-diphenylimidazole, *i.e.* with increase in the size of the introduced substituent due mainly to the considerable steric hindrances. It should be noted that the diastereoselectivity decreased also in these series. This instance can be explained by the fact that under kinetic control, protonation of the carbanion occurs preferably from the *si*-side, while with the increase in the size of the introduced group the protonation from the *si*-side becomes difficult leading to the decrease in the diastereoselectivity of whole process (Fig.1).

Scheme 2



2 **3—6** **7—14** **15—23**

i. HN(R¹)=C(R¹)N(R²), MeCN, 50—80 °C. *ii*. R^3X. *iii*. 1) HCl, MeOH; 2) Dowex 50W×8 (H^+), 25% aqueous NH_3—EtOH—H_2O (1 : 2 : 2).

Compound	R^1	R^2	R^3	X^-	Compound	R^1	R^2	R^3	X^-
3, **15**	H	H	—	—	**9**, **18**	$(CH)_4$	H	Bn	Br
4	$(CH)_4$	H	—	—	**10**, **23**	$(CH)_4$	H	Ph_2CH	Br
5	Ph	H	—	—	**11**, **20**	H	H	2,4,6-$Me_3C_6H_2$	Cl
6	$(CH)_4$	Me	—	—	**12**, **19**	$(CH)_4$	H	2,4,6-$Me_3C_6H_2$	Cl
7, **16**	H	H	Me	BF_4	**13**, **22**	Ph	H	Bn	Br
8, **17**	H	H	Bn	BF_4	**14**, **21**	$(CH)_4$	Me	Me	I

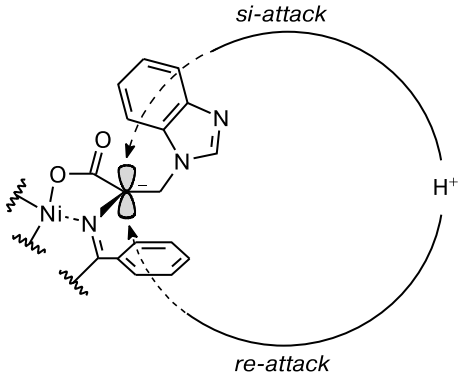


Fig. 1. Schematic representation of *si*- and *re*-protonation of compounds **3**—**6**.

Even greater content of the (*S*,*S*)-diastereomer was achieved, when the reaction mixture was kept in the presence of bases, which are azoles employed in the reaction, until thermodynamic equilibrium.

Alkylation of the resulting complexes **3—6** with different alkyl halides in the absence of base proceeded exclusively at the nitrogen atom (in the presence of base, the destruction of complexes **3—6** to give the starting complex **2** was observed). When iodomethane and benzyl bromide were used as alkylating reagents, the reaction proceeded readily even in dichloromethane; whereas in the case of 2,4,6-trimethylbenzyl chloride and benzhydryl bromide, it is preferable to carry out the reaction under heating in acetonitrile. The products **7—14** were isolated and purified by column chromatography on HW-55 resin, which is hydroxylated methacrylic polymer. The use of HW-55 resin is dictated by the fact that the charged complexes **7—14** cannot be quantitatively eluted from silica gel or aluminum oxide.

We were able to obtain the single crystals of the Ni^{II} complexes **9** and **10** differing in the substituent at the nitrogen atom of the benzimidazolium ring. The X-ray data show that in both cases the benzene rings of the substituents at the nitrogen atom of the heterocycle are located above the plane of the benzimidazolium system and orthogonal to it (Figs 2 and 3). At the same time, the hydrogen atom at the position 2 of benzimidazole ring and the hydrogen atom of benzylic or benzhydrylic groups located in the same plane and aligned in the same direction.

Decomposition of the Ni^{II} complexes and isolation of amino acids **15—23** was carried out according to the known procedure;[9] hydrophobic amino acids **17—23** were eluted from ion exchange resin with a 25% aqueous NH_3—EtOH—H_2O (1 : 2 : 2) mixture instead of 5% aqueous ammonia.

Characterization of the synthesized amino acids was difficult because these compounds are extremely hygroscopic glassy substances. However, their derivatives are mainly crystalline compounds.

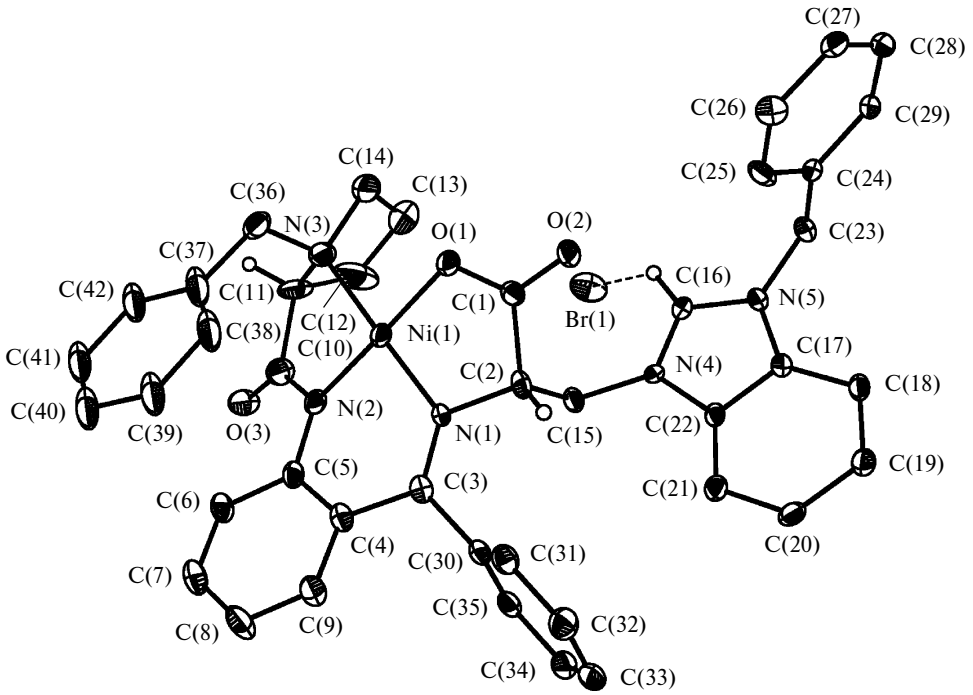


Fig. 2. Crystal structure of compound **9**. Alternative position of the disordered benzyl substituent is not shown. The disordered dichloromethane solvate molecule is omitted. Only the hydrogen atoms at asymmetric centers and the hydrogen atom of the C—H...Br hydrogen bond are shown. The hydrogen bond is shown by dashed line.

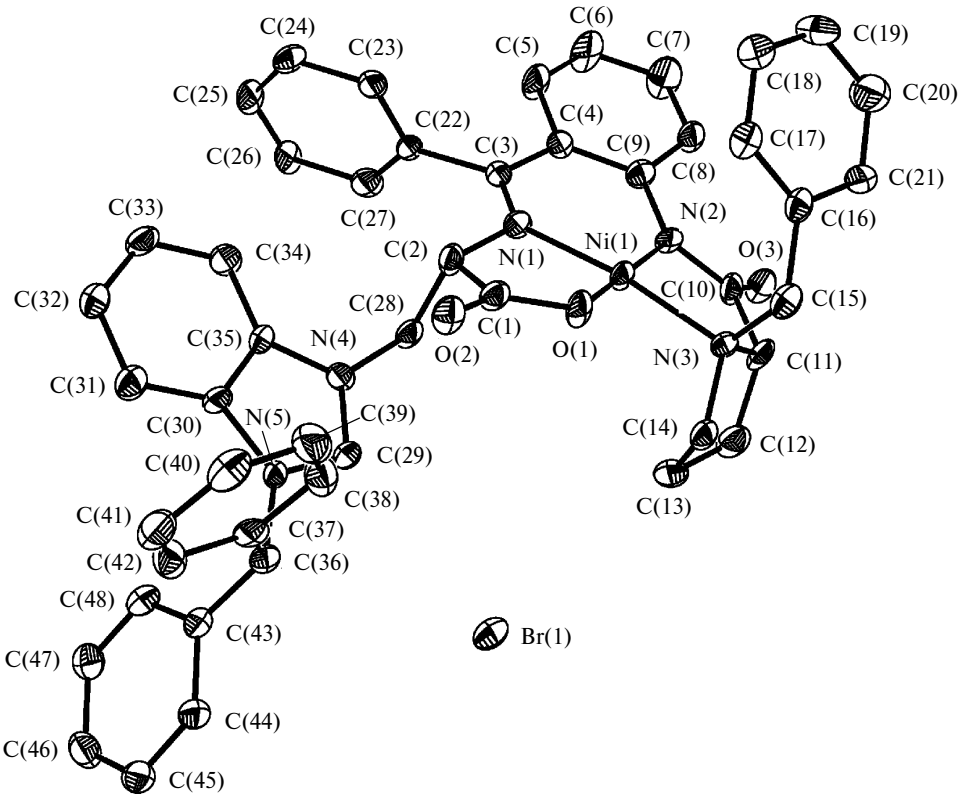
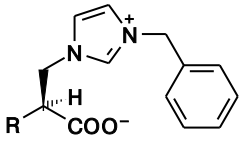


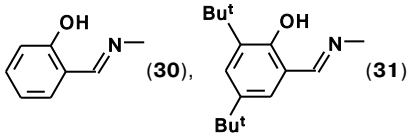
Fig. 3. Geometry of salt **10**. The dichloromethane and water solvate molecules are not shown. Short contact C(29)—H(29A)...Br(1) distances: Br(1)...C(29) is 3.485 Å, Br(1)...H(29A) is 2.60 Å, C(29)—H(29A) is 0.95 Å; angle Br(1)...H(29A)—C(29) is 156°.

To study the effect of the amino group modification on the efficiency and stereoselectivity of the catalysis, potential organocatalysts, compounds **24—31**, were derived from amino acid **17**.



24—31

R = BocNH (**24**), BzNH (**25**), PivNH (**26**), TsNH (**27**), BnNH (**28**),



Me_2N (**29**), (**30**), (**31**)

Primary amino group of compound **17** was converted into secondary and tertiary amino groups by reductive amination with the corresponding aldehydes in the presence of $NaBH_3CN$ to give *N*-benzylamino (**28**) and *N*,*N*-dimethylamino (**29**) derivatives. Rigid amido (**25**, **26**) and sulfamido (**27**) derivatives were synthesized in the presence of Et_3N in methanol. Structure of the tosyl derivative **27** was confirmed by the X-ray analysis (Fig. 4). It is of note that in the crystal of compound **27**, the molecules form the rows due to the π—π-stacking interaction and the H-bonding between the hydrogen atom of the sulfamide group of one molecule with the oxygen atom of the sulfamide group of another. The rows connected to each other by the intermolecular hydrogen bonds between the carboxylate group and the hydrogen atom at the position 2 of the imidazole ring.

N-Boc-derivative **24** characterized by greater conformational mobility was synthesized by treatment of amino acid **17** with Boc_2O.

Reactions of amino acid **17** with salicylic and 3,5-di-*tert*-butylsalicylic aldehydes afforded the Schiff bases **30** and **31**, respectively, which could be used as the tetradentate ligands. The X-ray diffraction study of compounds **31**

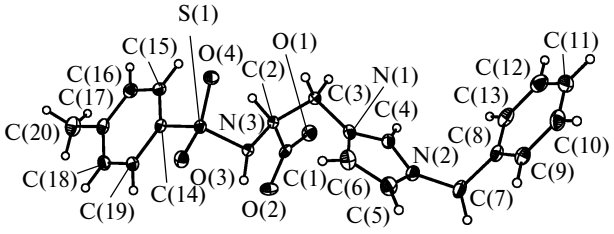
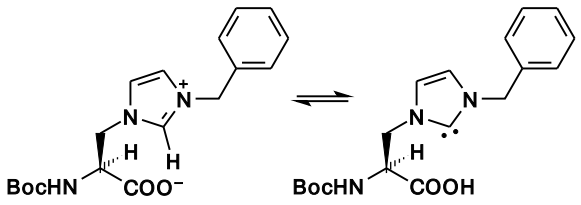


Fig. 4. Geometry of compound **27**.

shows that the Schiff base is also zwitterionic compound with free carboxylate group forming the hydrogen bond with the imidazole hydrogen of the neighboring molecule (Fig. 5). In Fig. 5, the characteristic intramolecular hydrogen bond between the phenyl hydrogen and the imine nitrogen atoms is also shown.

It has previously been shown by the X-ray analysis[7] that *N*-Boc-derivatives have also similar zwitterionic structure. It is known that in the aprotic medium, the carboxylate anion is a rather strong base and, therefore, the proton transfer from the position 2 of the imidazole ring to the carboxylate group to give carbene with the acid function is possible (Scheme 3).

Scheme 3



24

Further, we plan to study the catalytic activity of the synthesized compounds as organocatalysts in the reactions catalyzed traditionally by N-heterocyclic carbenes, namely in the benzoin condensation and trimethylsilylcyanation of the carbonyl compounds.

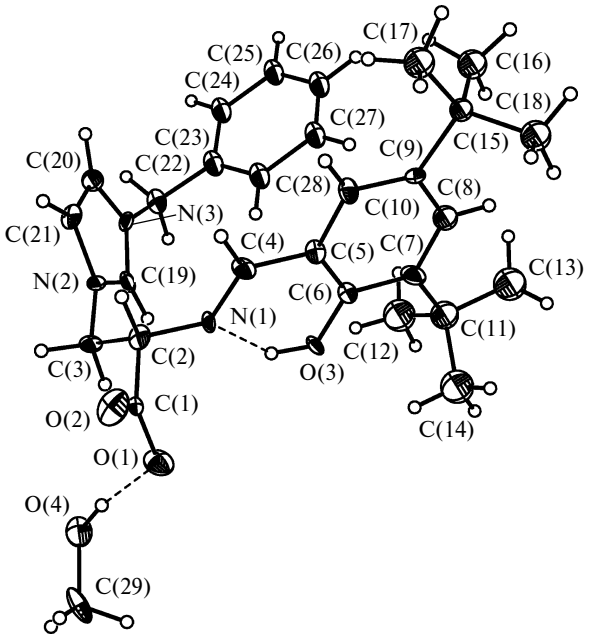


Fig. 5. Geometry of the Schiff base **31**. The alternative position of the disordered *tert*-butyl substituent is not shown. The disordered dichloromethane solvate molecule is omitted. Dashed lines show the hydrogen bonds.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz), and Bruker Avance 600 (600 MHz) spectrometers in $CDCl_3$, D_2O, and CD_3OD. Chemical shifts are given in the δ scale relative to the residual solvent signals. Optical rotation was measured on a Perkin—Elmer 341 polarimeter in a temperature-maintained cell at 25 °C. The solvent and concentration in grams per 100 mL are given for all compounds. Elemental analysis was performed at the Laboratory of Elemental Analysis of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

All reactions were carried out in the solvents, which were purified prior to use by the standard procedures.[10] The reactions were monitored by TLC with $CHCl_3$—acetone (5 : 1) (compounds **3**—**6**), $CHCl_3$—MeOH (95 : 5) (compounds **7**—**14**), and MeOH (compounds **24**—**29**) as the eluents.

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylidenamino)-3-(1*H*-imidazol-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) (3) was prepared from nickel complex **2** (10 g, 0.0196 mol) and imidazole (2.1 g, 0.0309 mol) in MeCN (100 mL) by the known procedure.[11] Reaction mixture was filtered through glass filter, the solvent was removed to dryness, the residue was re-dissolved in $CHCl_3$ (100 mL), and the resulting solution was washed with 10% aqueous AcOH solution (30 mL). The organic layer was separated, washed with water, and the solvent was removed *in vacuo*. The residue was recrystallized from a benzene—acetone mixture. According to the ^{1}H NMR data, the product *de* is > 99%. Yield 9.4 g (83%), m.p. 204—207 °C; $[\alpha]_D^{25}$ +2356 (*c* 0.05, MeOH). Found (%): C, 67.91; H, 5.68; N, 10.81. $C_{31}H_{29}N_5NiO_3 \cdot C_6H_6$. Calculated (%): C, 67.70; H, 5.37; N, 10.67. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.83 (m, 1 H, H(δ), Pro); 2.03 (m, 1 H, H(γ), Pro); 2.39 (m, 1 H, H(γ), Pro); 2.57 (m, 2 H, H(β), Pro); 3.18 (dd, 1 H, H(δ), Pro, $^3J_1$ = 7.3 Hz, $^3J_2$ = 9.4 Hz); 3.48 (d, 1 H, CH_2Ph, ^3J = 12.8 Hz); 3.81 (dd, 1 H, CH_2(β), ^2J = 16.3 Hz, ^3J = 4.6 Hz); 4.26 (m, 3 H, CH_2Ph, CH_2(β), CH(α)); 6.67 (d, 2 H, Ar, J = 4.1 Hz); 6.95 (d, 1 H, Ar, J = 7.1 Hz); 6.67 (s, 1 H, CH_{imid}); 7.18 (m, 2 H, Ar); 7.20—7.35 (m, 5 H, Ar); 7.50—7.60 (m, 4 H, Ar); 8.01 (d, 2 H, Ar, J = 7.3 Hz); 8.28 (d, 1 H, Ar, J = 8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.24 (C(13)); 30.80 (C(12)); 49.03 (C(15)); 57.55 (C(14)); 63.68 (C(26)); 70.36 (C(2)); 70.63 (C(11)); 120.75 (C(8), C(17) or C(18)); 123.63 (C(9)); 125.55 (C(4)); 126.87 (C(30)); 127.40 (C(21) or C(25)); 128.86 (C(29), C(31)); 128.93 (C(22), C(24)); 129.45 (C(23)); 129.66 (C(7)); 130.08 (C(17) or C(18)); 130.34 (C(6)); 131.52 (C(28), C(32)); 133.14 (C(22), C(24)); 133.29 (C(27)); 133.67 (C(21) or C(25)); 134.07 (C(20)); 138.39 (C(16)); 143.50 (C(5)); 172.73 (C(10)); 176.86 (C(3)); 180.61 (C(1)).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(1*H*-benzimidazol-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) (4) was prepared analogously to compound **3** from nickel complex **2** (6 g, 0.0118 mol) and benzimidazole (2 g, 0.017 mol) in MeCN (30 mL). Reaction time was 13 h. The product was recrystallized form CCl_4—CH_2Cl_2 mixture. According to the ^{1}H NMR data, the product *de* is > 99%. Yield 5.9 g (80%), m.p. 170—175 °C; $[\alpha]_D^{25}$ +1971 (*c* 0.1, MeOH). Found (%): C, 66.61; H, 4.95; N, 11.09. $C_{35}H_{31}N_5NiO_3$. Calculated (%): C, 66.90; H, 4.97; N, 11.15. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.45 (m, 1 H, H(δ), Pro); 1.60 (m, 1 H, H(γ), Pro);

1.79 (m, 2 H, H(γ), Pro, H(β), Pro); 2.05 (m, 1 H, H(β), Pro); 2.73 (m, 1 H, H(δ), Pro); 3.14 (dd, 1 H, H(α), Pro, $^3J_1$ = 7.2 Hz, $^3J_2$ = 10.2 Hz); 3.25 (d, 1 H, CH_2Ph, ^3J = 12.8 Hz); 4.12 (d, 1 H, CH_2Ph, ^3J = 12.8 Hz); 4.14 (dd, 1 H, CH_2(β), ^2J = 15.0 Hz, ^3J = 3.3 Hz); 4.40 (t, 1 H, CH(α), ^3J = 3.6 Hz); 4.56 (dd, 1 H, CH_2(β), ^2J = 15.0 Hz, ^3J = 3.3 Hz); 6.67—8.30 (m, 19 H, Ar).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(1*H*-4,5-diphenylimidazol-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) (5). To a solution of nickel complex **2** (1 g, 1.73 mmol) in MeCN (10 mL), 4,5-diphenylimidazole (0.76 g, 3.45 mmol) was added. The reaction mixture was refluxed for 24 h, then cooled to room temperature and filtered through glass filter. The solvent was removed to dryness, the product was purified by column chromatography (silica gel, elution with chloroform—acetone (5 : 1), then MeOH). According to the ^{1}H NMR data, the product *de* is > 99%. Yield 1.1 g (87%), m.p. 142—150 °C; $[\alpha]_D^{25}$ +2012 (*c* 0.05, MeOH). Found (%): C, 70.64; H, 5.05; N, 9.59. $C_{43}H_{37}N_5NiO_3$. Calculated (%): C, 70.70; H, 5.11; N, 9.59. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.75 (m, 1 H, H(δ), Pro); 2.02 (m, 1 H, H(γ), Pro); 2.29 (m, 1 H, H(γ), Pro); 2.47(m, 1 H, H(β), Pro); 2.83 (m, 1 H, H(β), Pro); 3.27 (dd, 1 H, H(α), Pro, $^3J_1$ = 7.5 Hz, $^3J_2$ = 9.9 Hz); 3.37 (m, 1 H, H(δ), Pro); 3.45 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 3.76 (dd, 1 H, CH_2(β), ^2J = 14.7 Hz, ^3J = 3.6 Hz); 4.40 (t, 1 H, CH(α), ^3J = 3.6 Hz); 4.56 (dd, 1 H, CH_2(β), ^2J = 14.7 Hz, ^3J = 3.6 Hz); 4.27 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 5.19 (d, 1 H, Ar); 6.40 (d, 1 H, Ar, ^3J = 8.4 Hz); 6.56 (t, 1 H, Ar, ^3J = 8.4 Hz); 7.0—7.55 (m, 17 H, Ar); 7.81 (s, 1 H, NCHN); 8.0 (d, 2 H, Ar, J = 7.2 Hz); 8.54 (d, 1 H, Ar, ^2J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.20; 31.16; 46.79; 57.62; 63.52; 70.88; 71.24; 120.60; 123.33; 125.41; 126.23; 126.50; 126.56; 126.96; 127.22; 127.83; 128.25; 128.53; 128.83; 128.88; 128.97; 129.17; 129.28; 129.32; 128.79; 130.38; 131.47; 131.87; 133.13; 133.41; 133.71; 133.76; 134.23; 138.37; 143.14; 173.50; 177.12; 180.81.

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(2-methylbenzimidazol-1-yl)propoinato-*N*,*N*′,*N*″,*O*]nickel(II) (6) was prepared as described above for compound **4** from nickel complex **2** (1 g, 1.73 mmol) and 2-methylbenzimidazole (0.32 g, 2.42 mmol) in MeCN (5 mL). Reaction time was 20 h. The product was purified by column chromatography (silica gel, elution with chloroform—acetone (5 : 1), then MeOH). According to the ^{1}H NMR spectroscopy data, the product *de* is > 99%. Yield 0.7 g (63%), m.p. 170—175 °C; $[\alpha]_D^{25}$ +1971 (*c* 0.1, MeOH). Found (%): C, 57.24; H, 4.49; N, 8.76. $C_{36}H_{33}N_5NiO_3 \cdot 0.85CCl_4$. Calculated (%): C, 57.25; H, 4.30; N, 9.06. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.93 (m, 2 H, H(δ), Pro, H(γ), Pro); 2.24 (m, 1 H, H(γ), Pro); 2.37 (m, 1 H, H(β), Pro); 2.50 (s, 3 H, CH_3); 2.79 (m, 1 H, H(β), Pro); 3.11 (m, 1 H, H(δ), Pro); 3.34 (dd, 1 H, H(α), Pro, $^3J_1$ = 6.6 Hz, $^3J_2$ = 10.5 Hz); 3.44 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 4.25 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 4.45 (m, 2 H, CH_2(β), CH(α)); 4.92 (m, 1 H, CH_2(β)); 6.29 (d, 1 H, Ar, ^3J = 8.2 Hz); 6.56 (d, 1 H, Ar, ^3J = 8.1 Hz); 6.56 (t, 1 H, Ar, ^3J = 7.5 Hz); 6.9—7.5 (m, 11 H, Ar); 7.66 (d, 1 H, Ar, ^3J = 8.1 Hz); 8.01 (d, 2 H, Ar, ^3J = 6.9 Hz); 8.18 (d, 1 H, Ar, ^3J = 8.7 Hz).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(3-methylimidazol-3-ium-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) tetrafluoroborate (7). To a solution of complex **3** (8 g, 0.0138 mol) in CH_2Cl_2 (50 mL), iodomethane (19.7 g, 8.65 mL, 0.138 mol) was added. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed *in vacuo*, the residue was dissolved in methanol—water (2 : 1) mixture and passed through a column with ion-exchange resin ARA-20p in BF_4^- form (100 g). Removal of the solvent and recrystallization of the residue from MeOH afforded compound **7**. According to the ^{1}H NMR data, the product *de* is > 99%. Yield 6.5 g, 69%, m.p. 203—204 °C; $[\alpha]_D^{25}$ +2386 (*c* 0.056, MeOH). Found (%): C, 54.91; H, 4.60; N, 9.95. $C_{32}H_{22}BF_4N_5NiO_3 \cdot H_2O$. Calculated (%): C, 55.05; H, 4.91; N, 10.03. ^{1}H NMR (600 MHz, $CDCl_3$—CD_3OD (1 : 1)), δ: 2.16 (m, 1 H, H(δ), Pro); 2.21 (m, 1 H, H(γ), Pro); 2.57 (m, 2 H, H(β), Pro); 3.21 (m, 1 H, H(γ), Pro); 3.35 (dd, 1 H, H(δ), Pro, $^3J_1$ = 7.0 Hz, $^3J_2$ = 10.0 Hz); 3.48 (d, 1 H, CH_2Ph, ^3J = 12.0 Hz); 3.54 (dd, 1 H, H(α), Pro, $^3J_1$ = 8.0 Hz, $^3J_2$ = 10.0 Hz); 3.91 (s, 3 H, CH_3N); 4.15 (dd, 1 H, CH(α), $^3J_1$ = 4.0 Hz, $^3J_2$ = 8.0 Hz); 4.18 (d, 1 H, CH_2Ph, ^3J = 12.0 Hz); 4.27 (dd, 1 H, CH_2(β), ^2J = 15.0 Hz, ^3J = 4.0 Hz); 4.68 (dd, 1 H, CH_2(β), ^2J = 15.0 Hz, ^3J = 4.0 Hz); 6.68 (s, 1 H, CH_{imid}); 6.69 (d, 1 H, Ar, J = 5.0 Hz); 6.72 (dd, 1 H, Ar, $^3J_1$ = 8.0 Hz, $^3J_2$ = 15.0 Hz); 7.16 (m, 2 H, Ar); 7.20 (m, 1 H, Ar); 7.35 (t, 2 H, Ar, J = 8.0 Hz); 7.40 (m, 1 H, Ar); 7.52 (d, 1 H, CH_{imid}, J = 2.0 Hz); 7.61—7.70 (m, 3 H, Ar); 7.99 (d, 1 H, Ar, J = 9.0 Hz); 8.21 (d, 2 H, Ar, J = 8.0 Hz); 8.73 (s, 1 H, CH_{imid}). ^{13}C NMR (150 MHz, $CDCl_3$—CD_3OD (1 : 1)), δ: 24.32 (C(13)); 31.21 (C(12)); 36.54 (C(19)); 51.97 (C(15)); 58.65 (C(14)); 64.65 (C(26)); 68.94 (C(2)); 71.55 (C(11)); 121.38 (C(8)); 122.44 (C(17)); 123.75 (C(9)); 124.14 (C(18)); 125.80 (C(4)); 126.90 (C(30)); 127.58 (C(21) or C(25)); 128.96 (C(29), C(31)); 128.98 (C(22), C(24)); 129.81 (C(23), C(7)); 130.67 (C(6)); 131.25 (C(28), C(32)); 133.21 (C(22), C(24)); 133.25 (C(27)); 133.79 (C(21) or C(25)); 134.11 (C(20)); 138.31 (C(16)); 143.15 (C(5)); 174.97 (C(10)); 177.49 (C(3)); 181.90 (C(1)).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(3-benzylimidazol-3-ium-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) tetrafluoroborate (8) was prepared as described for compound **7** from complex **3** (0.2 g, 0.346 mmol) and benzyl bromide (freshly distilled, 0.089 g, 62 μL, 0.519 mmol) in CH_2Cl_2 (1 mL). The product was additionally purified on a column with Sephadex LH-20 using benzene—ethanol (3 : 1) as eluent. According to the ^{1}H NMR data, the product *de* is > 99%. Yield 0.15 g (60%), m.p. 208—209 °C; $[\alpha]_D^{25}$ +2186 (*c* 0.05, MeOH). Found (%): C, 58.91; H, 7.60; N, 8.95. $C_{38}H_{36}BF_4N_5NiO_3 \cdot H_2O$. Calculated (%): C, 58.79; H, 7.27; N, 9.02. ^{1}H NMR (300 MHz, $CDCl_3$—CD_3OD (1 : 1)), δ: 2.11 (m, 2 H, H(δ), Pro, H(γ), Pro); 2.52 (m, 2 H, H(β), Pro); 3.21 (m, 1 H, H(γ), Pro); 3.35 (m, 1 H, H(δ), Pro); 3.46 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 3.54 (m, 1 H, H(α), Pro); 4.11 (m, 1 H, CH(α)); 4.16 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 4.26 (m, 1 H, CH_2(β)); 4.73 (dd, 1 H, CH_2N); 5.32 (m, 2 H, CH_2Ph); 6.66—8.22 (m, 21 H, Ar); 8.80 (s, 1 H, NCHN).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(3-benzylimidazol-3-ium-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) bromide (9). To a solution of complex **4** (1 g, 1.6 mmol) in CH_2Cl_2 (5 mL), benzyl bromide (0.36 g, 0.25 mL, 2.1 mmol) was added. After been stirred for 5 days at room temperature, the reaction mixture was concentrated to 1—1.5 mL, petroleum ether (10 mL) was added, the precipitate that formed was filtered off and dried on the filter. The precipitate was dissolved in CH_2Cl_2 with addition of MeOH (2—3 drops) followed by addition of acetone (1 mL) to the resulting solution. The precipitate that formed was filtered off. The treatment of the mother liquor was repeated. According to

the ^{1}H NMR data, the product *de* is > 99%. Yield 1.1 g (86%), m.p. 191—193 °C; $[\alpha]_D^{25}$ +1888 (*c* 0.1, MeOH). Found (%): C, 59.57; H, 4.62; N, 8.15. $C_{42}H_{38}BrN_5NiO_3 \cdot 0.7CH_2Cl_3$. Calculated (%): C, 59.72; H, 4.62; N, 8.15. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.16 (m, 2 H, H(δ); Pro, H(γ), Pro); 2.42 (m, 1 H, H(β), Pro); 2.70 (m, 1 H, H(β), Pro); 3.45 (m, 2 H, H(δ), Pro, H(γ), Pro); 3.49 (d, 1 H, CH_2Ph, ^3J = 12.3 Hz); 3.81 (m, 1 H, H(α), Pro); 4.30 (m, 1 H, CH(α)); 4.35 (d, 1 H, CH_2Ph, ^3J = 12.3 Hz); 4.51 (dd, 1 H, CH_2(β), ^2J = 14.1 Hz, ^3J = 4.8 Hz); 5.50 (d, 1 H, NCH_2, ^2J = 15.3 Hz); 5.77 (dd, 1 H, NCH_2, ^2J = 15.3 Hz); 5.87 (d, 1 H, Ar, ^2J = 8.5 Hz); 6.13 (dd, 1 H, CH_2N, ^2J = 14.1 Hz, ^3J = 4.8 Hz); 6.56 (d, 1 H, Ar, ^3J = 6.9 Hz); 6.66 (t, 1 H, Ar, ^3J = 6.9 Hz); 7.1—7.5 (m, 14 H, Ar); 7.7 (m, 3 H, Ar); 8.07 (d, 2 H, Ar, ^3J = 7.2 Hz); 8.20 (d, 1 H, Ar, ^3J = 8.7 Hz); 10.94 (s, 1 H, NCHN). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 24.88; 31.17; 48.35; 51.88; 58.76; 63.70; 66.61; 70.79; 112.04; 114.00; 120.82; 124.07; 125.50; 126.83; 126.98; 127.74; 127.97; 128.66; 128.91; 128.95; 129.20; 129.40; 129.79; 130.16; 130.29; 130.67; 131.22; 131.55; 132.04; 133.33; 133.52; 133.55; 133.71; 143.52; 144.50; 172.84; 175.78; 180.94.

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(3-benzhydrylbenzimidazol-3-ium-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) bromide (10). To a solution of complex **4** (0.63 g, 1 mmol) in MeCN (3 mL), benzhydryl bromide (0.3 g, 1.2 mmol) was added and the reaction mixture was refluxed for 4 h under argon. The reaction mixture was cooled to room temperature and the precipitate that formed was filtered off, washed with diethyl ether, and dried on the filter. According to the ^{1}H NMR data, the product *de* is > 99%. Yield 0.6 g (69%), m.p. 205—208 °C; $[\alpha]_D^{25}$ +2156 (*c* 0.05, MeOH—$CHCl_3$ (1 : 1)). Found (%): C, 65.69; H, 4.77; N, 8.17. $C_{48}H_{42}BrN_5NiO_3$. Calculated (%): C, 65.85; H, 4.84; N, 8.00. ^{1}H NMR (300 MHz, $CDCl_3$—CD_3OD (1 : 1)), δ: 1.91 (m, 1 H, H(δ), Pro); 2.00 (m, 1 H, H(γ), Pro); 2.09 (m, 1 H, H(γ), Pro); 2.46 (m, 2 H, H(β), Pro); 2.98 (m, 1 H, H(δ), Pro); 3.43 (d, 1 H, CH_2Ph, ^3J = 12.3 Hz); 3.45 (m, 1 H, H(α), Pro); 4.20 (d, 1 H, CH_2Ph, ^3J = 12.3 Hz); 4.57 (dd, 1 H, CH_2(β), ^2J = 15.2 Hz, ^3J = 4.8 Hz); 5.29 (m, 1 H, CH(α)); 6.07 (m, 1 H, CH_2N); 6.56 (m, 1 H, Ar); 6.71 (t, 1 H, Ar, ^3J = = 7.2 Hz); 7.1—7.5 (m, 20 H, Ar); 7.7 (m, 3 H, Ar); 8.01 (d, 1 H, Ar, ^3J = 8.7 Hz); 8.13 (d, 2 H, Ar, ^3J = 7.2 Hz); 8.93 (s, 1 H, NCHN).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-[3-(2,4,6-trimethylbenzyl)imidazol-3-ium-1-yl]propionato-*N*,*N*′,*N*″,*O*]nickel(II) chloride (11). To a solution of complex **3** (0.95 g, 1.64 mmol) in MeCN (5 mL), 2,4,6-trimethylbenzyl chloride (0.415 g, 2.46 mmol) was added. The reaction mixture was stirred at 40—50 °C for 24 h. The solvent was removed *in vacuo*, the product was purified by column chromatography (HW-55 resin, elution with $CDCl_3$—acetone (3 : 2)). According to the ^{1}H NMR data, the product *de* is > 99%. Yield 1.05 g (86%), m.p. 145 °C; $[\alpha]_D^{25}$ +2056 (*c* 0.05, MeOH). Found (%): C, 61.37; H, 5.31; N, 8.34. $C_{41}H_{42}ClN_5NiO_3 \cdot 0.6CHCl_3$. Calculated (%): C, 61.04; H, 5.25; N, 8.56. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.08 (m, 2 H, H(δ), Pro, H(γ), Pro); 2.18 (s, 6 H, CH_3); 2,21(s, 3 H, CH_3); 2.40 (m, 1 H, H(β), Pro); 2.62 (m, 1 H, H(β), Pro); 3.41 (dd, 1 H, H(α), Pro, $^3J_1$ = 6.0 Hz, $^3J_2$ = 10.5 Hz); 3.48 (m, 1 H, H(γ), Pro); 3.50 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 3.60 (m, 1 H, H(δ), Pro); 3.98 (m, 1 H, CH(α)); 4.17 (m, 1 H, CH_2(β)); 4.32 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 5.40 (d, 1 H, NCH_2, ^2J = 15.0 Hz); 5.50 (m, 1 H, CH_2(β)); 5.51 (d, 1 H, NCH_2, ^2J = 15.0 Hz); 6.46 (s, 1 H, CH_{imid}); 6.66 (m, 2 H, Ar); 6.87 (s, 2 H, Ar); 7.16 (m, 2 H, Ar); 7.24 (m, 1 H, Ar); 7.33 (t, 2 H, Ar, ^3J = 8.4 Hz); 7.45 (m, 1 H, Ar); 7.53 (m, 2 H, Ar); 7.66 (m, 1 H, Ar); 7.73 (m, 2 H, Ar); 8.02 (d, 2 H, Ar, ^3J = 7.2 Hz); 8.22 (d, 1 H, Ar, ^3J = 8.4 Hz); 10.21 (s, 1 H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 19.71; 21.06; 24.22; 30.79; 47.88; 51.35; 57.80; 63.44; 68.13; 70.37; 70.42; 120.66; 120.90; 121.30; 123.83; 124.00; 125.14; 126.63; 128.33; 128.91; 129.02; 129.33; 129.93; 130.21; 130.30; 131.51; 133.36; 133.40; 133.46; 133.72; 138.18; 139.02; 139.92; 143.33; 173.58; 176.37; 180.86.

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-[3-(2,4,6-trimethylbenzyl)benzimidazol-3-uim-1-yl]propionato-*N*,*N*′,*N*″,*O*]nickel(II) chloride (12) was prepared from complex **4** (0.63 g, 1 mmol) and 2,4,6-trimethylbenzyl chloride (0.25 g, 1.5 mmol) in MeCN (3 mL) as described above for compound **11**. According to the ^{1}H NMR data, the product *de* is > 99%. Yield 0.55 g (69%), m.p. 155 °C; $[\alpha]_D^{25}$ −1628 (*c* 0.05, MeOH). Found (%): C, 62.01; H, 5.15; N, 7.49. $C_{45}H_{44}ClN_5NiO_3 \cdot 3/4CHCl_3$. Calculated (%): C, 61.98; H, 5.09; N, 7.61. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.14 (m, 2 H, H(δ), Pro, H(γ), Pro); 2.27 (s, 3 H, CH_3); 2.29 (s, 6 H, CH_3); 2.42 (m, 1 H, H(β), Pro); 2.74 (m, 1 H, H(β), Pro); 3.44 (m, 2 H, H(α), Pro, H(γ), Pro); 3.46 (d, 1 H, CH_2Ph, ^2J = 12.6 Hz); 3.98 (m, 1 H, CH(α)); 4.26 and 4.42 (both AB part of ABX system, 1 H, CH_2(β), ^3J = 4.5 Hz, ^2J = 10.8 Hz); 4.35 (d, 1 H, CH_2Ph, ^3J = 12.6 Hz); 5.68 (AB system, 2 H, NCH_2, ^2J = 14.7 Hz); 5.80 (d, 1 H, NCH_2, ^2J = 8.1 Hz); 6.25 (m, 1 H, CH(α)); 6.55 (d, 1 H, Ar, ^3J = 6.9 Hz); 6.63 (t, 1 H, Ar, ^2J = 6.9 Hz); 6.90 (s, 2 H, Ar); 6.95 (d, 1 H, Ar, ^3J = 11.4 Hz); 7.18 (m, 3 H, Ar); 7.39 (m, 5 H, Ar); 7.69 (m, 3 H, Ar); 8.06 (d, 2 H, Ar, ^3J = 7.5 Hz); 8.20 (d, 1 H, Ar, ^3J = 11.7 Hz), 10.79 (s, 1 H, NCHN). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 20.25; 21.17; 24.65; 31.19; 47.84; 48.40; 58.70; 63.59; 66.67; 70.70; 112.02; 113.89; 120.78; 124.10; 124.56; 125.48; 126.52; 126.87; 126.91; 127.73; 128.80; 128.91; 128.95; 129.71; 130.08; 130.21; 130.23; 131.09; 131.38; 131.59; 133.26; 133.49; 133.54; 133.78; 137.89; 138.46; 139.82; 143.47; 172.72; 175.83; 180.97.

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(3-benzyl-4,5-diphenylimidazol-3-uim-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) bromide (13). To a solution of complex **5** (1.2 g, 1.6 mmol) in CH_2Cl_2 (2 mL), benzyl bromide (0.51 g, 0.35 mL, 3 mmol) was added and the reaction mixture was stirred for 5 days at room temperature. The solvent was removed *in vacuo*, the product was purified by column chromatography (HW-55 resin, elution with $CHCl_3$—acetone (3 : 2)). According to the ^{1}H NMR data, the product *de* is > 99%. Yield 0.9 g (62%), m.p. 191—193 °C; $[\alpha]_D^{25}$ +1988 (*c* 0.1, MeOH). Found (%): C, 63.57; H, 4.62; N, 7.15. $C_{50}H_{44}BrN_5NiO_3 \cdot 0.7CH_2Cl_2$. Calculated (%): C, 63.37; H, 4.76; N, 7.29. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.79 (m, 1 H, H(δ), Pro); 2.01 (m, 1 H, H(γ), Pro); 2.40 (m, 1 H, H(β), Pro); 2.63 (m, 2 H, H(δ), Pro, H(γ), Pro); 3.05 (m, 1 H, H(β), Pro); 3.33 (m, 1 H, H(α), Pro); 3.42 (d, 1 H, CH_2Ph, ^2J = 12.6 Hz); 3.91 (m, 1 H, CH(α)); 4.25 (d, 1 H, CH_2Ph, ^2J = 12.6 Hz); 4.43 (dd, 1 H, CH_2(β), ^2J = 14.4 Hz, ^3J = 6.0 Hz); 4.94 (dd, 1 H, CH_2(β), ^2J = 14.4 Hz, ^3J = 6.0 Hz); 5.17 (d, 1 H, CH_2Ph, ^2J = 14.7 Hz); 5.35 (d, 1 H, CH_2Ph, ^2J = 14.7 Hz); 6.42 (d, 1 H, Ar, ^3J = 8.1 Hz); 6.56 (t, 1 H, Ar, ^3J = 7.5 Hz); 7.0—7.5 (m, 24 H, Ar); 8.02 (d, 2 H, Ar, ^3J = 7.5 Hz); 8.18 (d, 1 H, Ar, ^3J = 8.7 Hz); 8.95 (s, 1 H, NCHN).

[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]-phenyl}(phenyl)methylideneamino)-3-(2,3-dimethylbenzimidazol-3-ium-1-yl)propionato-*N*,*N*′,*N*″,*O*]nickel(II) iodide (14). To a solution of complex **6** (0.8 g, 1.25 mmol) in CH_2Cl_2 (2 mL), iodomethane (1 mL, 15 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was removed *in vacuo*, the residue was recrystallized from MeOH. Yield 0.73 g (74%). According to the ^{1}H NMR data, *de* > 99%, m.p. 216—218 °C; $[\alpha]_D^{25}$ +1928 (*c* 0.05, MeOH). Found (%): C, 56.84; H, 4.54; N, 8.71. $C_{37}H_{36}IN_5NiO_3$. Calculated (%): C, 56.66; H, 4.63; N, 8.93. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.12 (m, 1 H, H(δ), Pro); 2.28 (m, 1 H, H(γ), Pro); 2.55 (m, 1 H, H(β), Pro); 2.74 (m, 1 H, H(β), Pro); 3.07 (s, 3 H, CH_3); 3.41 (m, 1 H, H(δ), Pro); 3.47 (m, 1 H, H(α), Pro); 3.49 (d, 1 H, CH_2Ph, ^3J = 12.3 Hz); 3.65 (m, 1 H, H(γ), Pro); 3.97 (s, 3 H, CH_3); 4.19 (m, 1 H, CH(α)); 4.26 (d, 1 H, CH_2Ph, ^3J = 12.3 Hz); 4.56 (dd, 1 H, CH_2(β), ^2J = 15.0 Hz, ^3J = 5.4 Hz); 5.56 (dd, 1 H, CH_2(β), ^2J = 15.0 Hz, ^3J = 5.4 Hz); 5.90 (m, 1 H, Ar); 6.59 (d, 1 H, Ar, ^2J = 8.4 Hz); 6.66 (t, 1 H, Ar, ^3J = 7.2 Hz); 7.1—7.8 (m, 12 H, Ar); 8.07 (d, 2 H, Ar, ^3J = 7.5 Hz); 8.20 (d, 1 H, Ar, ^3J = 8.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 12.31; 24.26; 29.43; 30.39; 32.25; 47.69; 57.56; 63.49; 65.86; 70.22; 111.18; 112.28; 121.09; 123.87; 125.48; 126.28; 126.46; 127.39; 128.43; 128.86; 129.49; 130.22; 130.49; 131.17; 131.18; 132.94; 133.15; 133.44; 142.50; 152.01; 173.02; 176.13; 180.58.

Isolation of amino acids 15—23 from the Ni^{II} complexes (general procedure). To a solution of the Ni^{II} complex in MeOH (1 mL of MeOH per 1 g of the Ni^{II} complex), 6 *M* HCl (2 mL per 1 g of the Ni^{II} complex) was added, the reaction mixture was refluxed for 10 min, and cooled to room temperature. The solvent was removed *in vacuo* and water (5—10 mL) was added to the residue. The resulting precipitate of (*S*)-BBP hydrochloride was filtered off and washed with water. The mother liquor was neutralized with aqueous ammonia to pH 6—7 and the remaining (*S*)-BBP was extracted with chloroform (3×30 mL). The aqueous layer was separated, filtered through a paper filter and placed on a top of a column with ion exchange resin Dowex 50W×8 (acidic form, 100 g). The column was carefully washed with water until the washings became neutral. Amino acids **15** and **16** were washed off with 5% aqueous ammonia, amino acids **17—23** were eluted with NH_3 (25% in water)—EtOH—H_2O (1 : 2 : 2). The obtained solutions were concentrated, the target products were purified by column chromatography (silica gel), the impurities were washed off with MeOH, the target products were eluted with MeOH—H_2O (1 : 1).

(*S*)-2-Amino-3-(1*H*-imidazol-1-yl)propionic acid (15). The product was recrystallized form EtOH with addition of a few drops of aqueous ammonia. Yield 53%, m.p. 195—197 °C; $[\alpha]_D^{25}$ −11.25 (*c* 1.0, H_2O). Found (%): C, 41.21; H, 6.32; N, 24.24. $C_6H_7N_3O_2 \cdot H_2O$. Calculated (%): C, 41.61; H, 6.40; N, 24.27. ^{1}H NMR (300 MHz, D_2O), δ: 4.03 (t, 1 H, $CHCO_2$, J = 5.4 Hz); 4.49 (d, 2 H, CH(β), J = 5.4 Hz); 7.05 (s, 1 H, =C<u>H</u>NCH_3); 7.15 (s, 1 H, =C<u>H</u>NCH_2); 7.78 (s, 1 H, NCHN).

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-methyl-1*H*-imidazol-3-ium (16). Yield 73%; $[\alpha]_D^{25}$ −18.4 (*c* 1.4, H_2O). ^{1}H NMR (400 MHz, D_2O), δ: 3.57 (t, 1 H, $CHCO_2$, J = 5.8 Hz); 3.74 (s, 3 H, CH_3); 4.24 (d, 2 H, CH(β), J = 5.8 Hz); 7.28 (d, 1 H, =C<u>H</u>NCH_3, J = 2.0 Hz); 7.29 (d, 1 H, =C<u>H</u>NCH_2, J = 2.0 Hz). ^{13}C NMR (150 MHz, D_2O), δ: 35.7 (CH_3); 53.04 (CH_2); 55.88 (<u>C</u>HCO_2); 122.63 (=<u>C</u>$HN_{imid}CH_2$); 123.62 (=<u>C</u>$HN_{imid}CH_3$); 136.28 (t, NCDN, ^1J = 25.0 Hz); 177.69 (COO^-).

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-benzyl-1*H*-imidazol-3-ium (17). Yield 81%; $[\alpha]_D^{25}$ −7.0 (*c* 1.54, H_2O). ^{1}H NMR (300 MHz, D_2O), δ: 3.67 (t, 1 H, $CHCO_2$, J = 5.4 Hz); 4.33 (d, 2 H, CH(β), J = 5.7 Hz); 5.34 (s, 2 H, CH_2Ph); 7.30—7.50 (m, 7 H, Ar). ^{13}C NMR (150 MHz, D_2O), δ: 53.58 (CH_2); 53.86 (CH_2); 56.50 (<u>C</u>HCO_2); 123.07 (=CHN_{imid}); 123.70 (=CHN_{imid}); 129.27; 129.96; 129.99; 134.00 (C(Ph)); 178.23 (COO^-).

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-benzyl-1*H*-benzimidazol-3-ium (18). Yield 71%; $[\alpha]_D^{25}$ −7.3 (*c* 1.00, H_2O). ^{1}H NMR (300 MHz, CD_3OD), δ: 3.81 (dd, 1 H, $CHCO_2$, $^3J_1$ = 5.1 Hz, $^3J_1$ = 6.9 Hz); 4.64 (dd, 1 H, CH(β), ^2J = 13.8 Hz, ^3J = 6.9 Hz); 4.81 (dd, 1 H, CH(β), ^2J = 13.8 Hz, ^3J = 5.1 Hz); 5.80 (s, 2 H, CH_2Ph); 7.40—7.75 (m, 7 H, Ar); 7.84 (d, 1 H, Ar, ^3J = 8.4 Hz); 8.16 (d, 1 H, Ar, ^3J = 7.8 Hz). ^{13}C NMR (75 MHz, CD_3OD), δ: 50.46 (CH_2); 51.27 (CH_2); 55.14 (<u>C</u>HCO_2); 126.64; 126.76; 127.94; 128.78; 129.01; 131.22; 132.06; 133.28; 176.39 (COO^-).

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-(2,4,6-trimethylbenzyl)-1*H*-benzimidazol-3-ium (19). Yield 78%; $[\alpha]_D^{25}$ −1.4 (*c* 1.0, MeOH). ^{1}H NMR (300 MHz, CD_3OD), δ: 2.29 (s, 6 H, CH_3); 2.31 (s, 1 H, CH_3); 3.70 (m, 1 H, $CHCO_2$); 4.47 (m, 1 H, CH(β)); 4.72 (m, 1 H, CH(β)); 5.67 (s, 2 H, CH_2Ph); 7.04 (s, 2 H, Ar); 7.72 (m, 2 H, Ar); 7.85 (d, 1 H, Ar, ^3J = 8.1 Hz); 8.16 (d, 1 H, Ar, ^3J = 7.8 Hz). ^{13}C NMR (75 MHz, CD_3OD), δ: 19.78; 21.21; 46.74; 52.04; 56.28; 114.33; 114.80; 126.11; 128.27; 128.49; 130.47; 130.85; 132.71; 133.11; 139.71; 141.21; 178.09.

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-(2,4,6-trimethylbenzyl)-1*H*-imidazol-3-ium (20). Yield 73%; $[\alpha]_D^{25}$ +14.7 (*c* 1.06, MeOH). ^{1}H NMR (400 MHz, CD_3OD), δ: 2.25 (s, 6 H, CH_3); 2.28 (s, 1 H, CH_3); 3.68 (t, 1 H, $CHCO_2$, ^3J = 5.6 Hz); 4.34 (d, 2 H, CH(β), ^3J = 5.6 Hz); 5.40 (s, 2 H, CH_2Ph); 7.05 (s, 2 H, Ar); 7.31 (s, 2 H, CH_{imid}); 7.47 (d, 1 H, CH_{imid}, J = 2.0 Hz). ^{13}C NMR (100 MHz, CD_3OD), δ: 19.50; 21.07; 48.31; 54.04; 56.75; 122.98; 123.98; 126.66; 128.27; 130.39; 139.73; 141.26; 151.67; 178.09.

(*S*)-1-(2-Amino-2-carboxylatoethyl)-2,3-dimethyl-1*H*-benzimidazol-3-ium (21). Highly hygroscopic glassy compound. Yield 79%; $[\alpha]_D^{25}$ +19 (*c* 1.0, MeOH). ^{1}H NMR (300 MHz, CD_3OD), δ: 2.92 (s, 3 H, CH_3); 3.72 (dd, X part of ABX system, 1 H, CH(α), J = 6.9 Hz, J = 14.4 Hz); 4.02 (s, 1 H, CH_3); 4.52 and 4.68 (both AB part of ABX system, 1 H, CH(β), J = 6.9 Hz, J = 14.4 Hz); 7.66 (m, 2 H, Ar); 7.84 (m, 1 H, Ar); 7.93 (m, 1 H, Ar).

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-benzyl-4,5-diphenyl-1*H*-imidazol-3-ium (22). Yield 61%; $[\alpha]_D^{25}$ −7.4 (*c* 1.06, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$), δ: 3.63 (m, 1 H, $CHCO_2$); 4.54 (m, 2 H, CH(β)); 5.41 (m, 2 H, CH_2Ph); 6.9—7.5 (m, 15 H, Ar); 10.23 (br. s, 1 H, NCHN).

(*S*)-1-(2-Amino-2-carboxylatoethyl)-3-benzhydryl-1*H*-benzimidazol-3-ium (23). Yield 63%; $[\alpha]_D^{25}$ +1.8 (*c* 1.0, MeOH). ^{1}H NMR (300 MHz, CD_3OD—$CDCl_3$ (1 : 1)), δ: 3.7 (m, 1 H, $CHCO_2$); 4.48 (m, 1 H, CH(β)); 4.61 (m, 1 H, CH(β)); 6.99 (s, 1 H, $CHPh_2$); 7.1—7.5 (m, 11 H, Ar); 7.60 (t, 1 H, Ar, ^3J = 7.8 Hz); 8.05 (d, 1 H, Ar, ^3J = 8.7 Hz); 8.96 (s, 1 H, NCHN).

(*S*)-3-Benzyl-1-(2-*tert*-butoxycarbonylamino-2-carboxylatoethyl)-1*H*-imidazol-3-ium (24). To an emulsion of amino acid **17** (0.93 g, 3.8 mmol) in THF (3 mL), Boc_2O (1.25 g, 1.34 mL, 5.7 mmol) was added and the reaction mixture was stirred at room temperature for 48 h. Removal of the solvent *in vacuo* and purification by column chromatography (silica gel, elution with MeOH) afforded compound **24** in a yield of 1.03 g (79%), m.p. 98—105 °C; $[\alpha]_D^{25}$ +140.1 (*c* 1.0, $CHCl_3$). Found (%): C, 61.41; H, 7.04; N, 11.78. $C_{18}H_{23}N_3O_4 \cdot 0.4H_2O$. Calculated (%):

C, 61.31; H, 6.80; N, 11.92. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.38 (s, 9 H, Bu^t); 4.19 (m, 1 H, $CHCO_2$); 4.63—4.87 (m, 2 H, CH(β)); 5,37 (d, 1 H, CH_2Ph, J = 14.4 Hz); 5.76 (d, 1 H, CH_2Ph, J = 14.4 Hz); 6.02 (s, 1 H, NH); 6.97 (s, 1 H, =C<u>H</u>NCH$_3$); 7.12 (s, 1 H, =C<u>H</u>NCH$_2$); 7.33 (m, 5 H, Ph); 10.27 (s, 1 H, NCHN).

Synthesis of *N*-acyl derivatives of zwitterionic amino acids 25 and 26 (general procedure). To a solution of amino acid **17** (0.2 mmol) in MeOH (1 mL), acylating reagent (0.3 mmol) and Et_3N (0.3 mmol) were added and the reaction mixture was stirred at room temperature for 2 h. Then the solvent was evaporated to dryness, and the product was purified by column chromatography (silica gel, elution with MeOH).

(*S*)-1-(2-Benzoylamino-2-carboxylatoethyl)-3-benzyl-1*H*-imidazol-3-ium (25). White crystals. Yield 91%, m.p. 84—89 °C; $[\alpha]_D^{25}$ +10.0 (*c* 1.0, MeOH). Found (%): C, 65.41; H, 5.57; N, 10.99. $C_{20}H_{19}N_3O_3 \cdot 0.5H_2O \cdot 0.6$MeOH. Calculated (%): C, 65.52; H, 5.98; N, 11.13. ^{1}H NMR (300 MHz $CDCl_3$), δ: 4.75 (m, 1 H, CH(α)); 4.79 (m, 1 H, CH(β)); 4.81 (m, 1 H, CH(β)); 5.29 and 5.32 (both AB system, 1 H, CH_2Ph, J = 13.8 Hz); 7.02 (s, 1 H, CH_{imid}); 7.30 (s, 1 H, CH_{imid}); 7.19—7.80 (m, 10 H, Ar); 8.25 (s, 1 H, NH); 9.31 (s, 1 H, CH_{imid}).

(*S*)-3-Benzyl-1-(2-carboxylato-2-pivaloylaminoethyl)-1*H*-imidazol-3-ium (26). White crystals. Yield 78%, m.p. 80—85 °C; $[\alpha]_D^{25}$ +22.8 (*c* 0.91, MeOH). Found (%): C, 60.36; H, 7.10; N, 11.00. $C_{18}H_{23}N_3O_3 \cdot H_2O \cdot CH_3OH$. Calculated (%): C, 60.14; H, 7.37; N, 11.07. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.15 (s, 9 H, Bu^t); 4.34 (m, 1 H, CH(α)); 4.85 (m, 2 H, CH(β)); 5.48 and 5.62 (both AB system, 1 H, CH_2Ph, J = 14.4 Hz); 7.09 (s, 1 H, CH_{imid}); 7.16 (s, 1 H, CH_{imid}); 7.37 (m, 5 H, Ar); 10.08 (s, 1 H, CH_{imid}). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 27.48; 38.72; 50.93; 53.40; 55.19; 120.53; 123.46; 128.82; 129.48; 133.21; 138.37; 171.17; 179.35.

(*S*)-3-Benzyl-1-(2-carboxylato-2-tosylaminoethyl)-1*H*-imidazol-3-ium (27). To a solution of amino acid **17** (21.5 mg, 0.09 mmol) in MeOH (1 mL), tosyl chloride (36 mg, 0.36 mmol) and Et_3N (20 μL, 14.5 mg, 0.2 mmol) were added and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated to dryness and the residue was purified by column chromatography (silica gel, elution with MeOH) to give compound **27** as a white solid. Yield 30 mg (86%), m.p. 160—162 °C; $[\alpha]_D^{25}$ +60.0 (*c* 1.0, MeOH). Found (%): C, 57.55; H, 5.38; N, 9.39. $C_{20}H_{21}N_3O_4S \cdot 1H_2O$. Calculated (%): C, 57.54; H, 5.55; N, 10.07. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.36 (s, 3 H, CH_3); 3.63 (m, 1 H, CH(α); 4.54 (dd, 1 H, CH(β), J = 3.3 Hz, J = 13.2 Hz); 4.94 (dd, 1 H, CH(β), J = 1.8 Hz, J = 13.2 Hz); 5.48 (d, 1 H, CH_2Ph, J = 14.7 Hz); 6.50 (br. s, 1 H, NH); 7.01 (s, 1 H, CH_{imid}); 7.22—7.40 (m, 8 H, Ar); 7.53 (s, 1 H, CH_{imid}); 7.70 (d, 2 H, Ar, J = 8.1 Hz); 9.71 (s, 1 H, CH_{imid}).

(*S*)-13-Benzyl-(2-benzylamino-2-carboxylatoethyl)-1*H*-imidazol-3-ium (28) was synthesized according to the known procedure.[11] The product was purified by column chromatography (silica gel, elution with MeOH). Hygroscopic glassy compound. Yield 65%, m.p. 56—57 °C; $[\alpha]_D^{25}$ –2.6 (*c* 1.0, MeOH). Found (%): C, 65.90; H, 6.51; N, 11.44. $C_{20}H_{21}N_3O_2 \cdot 1.6H_2O$. Calculated (%): C, 65.95; H, 6.70; N, 11.54. ^{1}H NMR (300 MHz, CD_3OD), δ: 3.37 (m, 1 H, CH(α)); 3.70, 3.87 (both AB system, for 2 H, CH_2Ph, J = 12.9 Hz); 4.39 (m, 2 H, CH(β)); 5.44 (s, 2 H, PhC<u>H</u>$_2$NH); 7.27 (m, 5 H, Ar); 7.70 (m, 5 H, Ar); 7.55 (d, 1 H, CH_{imid}, J = 2.1 Hz); 7.58 (d, 1 H, CH_{imid}, J = 2.1 Hz). No signal for the proton of the NCHN fragment was observed due to complete exchange of the hydrogen on deuterium.

(*S*)-3-Benzyl-1-(2-carboxylato-2-dimethylaminoethyl)-1*H*-imidazol-3-ium (29) was synthesized according to the known procedure.[11] The product was purified by column chromatography (silica gel, elution with MeOH). Highly hygroscopic glassy compound. Yield 65%. ^{1}H NMR (300 MHz, CD_3OD), δ: 2.36 (s, 6 H, CH_3); 3.24 (t, 1 H, CH(α), J = 7.5 Hz); 4.23, 4.42 (both AB system, 1 H, CH(β), J = 7.5 Hz, J = 13.5 Hz); 5.37 (s, 2 H, PhCH_2); 7.42 (m, 6 H, Ar, CH_{imid}); 7.57 (m, 1 H, CH_{imid}). No signal for the proton of the NCHN fragment was observed due to complete exchange of the hydrogen on deuterium.

Synthesis of the Schiff bases 30 and 31 (general procedure). To an emulsion of amino acid **17** (1 mmol) in dichloromethane (5 mL), salicylic or 3,5-di-*tert*-butylsalicylic aldehyde (1 mmol) was added and the reaction mixture was vigorously stirred at room temperature for 24 h. The precipitate that formed was filtered off and washed with small amount of dichloromethane.

(*S*)-3-Benzyl-1-[2-(2-carboxylato)-2-hydroxybenzylideneaminoethyl]-1*H*-imidazol-3-ium (30). Yield 95%, m.p. 102—104 °C; $[\alpha]_D^{25}$ –95.6 (*c* 1.0, MeOH). Found (%): C, 68.48; H, 5.51; N, 12.05. $C_{20}H_{19}N_3O_3$. Calculated (%): C, 68.75; H, 5.48; N, 12.03. ^{1}H NMR (400 MHz, CD_3OD), δ: 4.25 (dd, 1 H, CH(α), J = 4.8 Hz, J = 7.2 Hz); 4.73 (m, 2 H, CH(β)); 5.35 (m, 2 H, CH_2Ph); 6.90 (t, 2 H, Ar, J = 8.1 Hz); 7.20—7.40 (m, 7 H, Ar); 7.54 (d, 1 H, =CHN, J = 1.8 Hz); 7.66 (d, 1 H, =CHN, J = 1.8 Hz); 8.36 (s, 1 H, CH=N); 9.07 (s, 0.3 H, NCHN). ^{13}C NMR (150 MHz, CD_3OD), δ: 53.81; 54.03; 74.49; 117.76; 120.05; 120.22; 123.68; 124.58; 128.60; 129.32; 129.93; 130.18; 130.34; 133.32; 133.90; 135.02; 137.73 (t, NCDN, ^1J = 34.5 Hz); 161.93; 169.52; 173.89.

(*S*)-3-Benzyl-1-[2-carboxylato-2-(3,5-di-*tert*-butyl-2-hydroxybenzylidenamino)ethyl]-1*H*-imidazol-3-ium (31). Yield 95%, m.p. 116—118 °C; $[\alpha]_D^{25}$ –79.3 (*c* 1.0, MeOH). Found (%): C, 67.54; H, 7.70; N, 8.43. $C_{28}H_{35}N_3O_3 \cdot 2H_2O$. Calculated (%): C, 67.58; H, 7.90; N, 8.44. ^{1}H NMR (600 MHz, CD_3OD), δ: 1.31 (s, 9 H, Bu^t); 1.41 (s, 9 H, Bu^t); 4.23 (dd, 1 H, CH(α), J = 5.1 Hz, J = 7.5 Hz); 4.74 (m, 2 H, CH(β)); 5.36 (m, 2 H, CH_2Ph); 6.90 (t, 2 H, Ar, J = 8.1 Hz); 7.10—7.40 (m, 6 H, Ar); 7.43 (d, 1 H, =CHN, J = 2.4 Hz); 7.55 (d, 1 H, =CHN, J = 2.4 Hz); 7.69 (s, 1 H, Ar); 8.37 (s, 1 H, CH=N); 9.10 (s, 0.3 H, NCHN). ^{13}C NMR (150 MHz, CD_3OD), δ: 28.40; 30.07; 33.98; 34.49; 52.81; 53.03; 73.49; 118.22; 122.41; 123.35; 126.75; 127.22; 127.90; 128.82; 129.11; 133.75; 136.24; 140.08; 156.30; 168.52; 173.89.

X-ray diffraction analysis. The X-ray diffraction data of compounds **9**, **10**, **27**, and **31** were collected on an automated Bruker SMART APEX-II CCD diffractometer (T = 100 K, λ(Mo-K_α) radiation, graphite monochromator, θ and ω scan modes). Correction for the absorption were done using the SADABS program.[12] The main crystallographic characteristics are given in Table 1. All structures were solved by direct method and refined by a full-matrix least squares technique in anisotropic approximation for nonhydrogen atoms. The crystal of molecule **10** contains chloroform and water solvate molecules with populations of 0.67 and 0.33, respectively. Crystal of **9** contains dichloromethane solvate molecule, crystal of **31** contains one methanol solvate molecule and one dichloromethane solvate molecule. The dichloromethane solvate molecules in the crystal structures of **9** and **31** are significantly disordered and it was not possible to clarify correctly their positions in the framework of our experiments, therefore, the contribution of these molecules in the total scattering of the X-ray radiation by the crystals of

Table 1. Main crystallographic data and refining parameters for compounds **9**, **10**, **27**, and **31**

Compound	**9** · CH_2Cl_2	**10** · 2/3($CHCl_3$) · 1/3(H_2O)	**27**	**31** · CH_3OH · 1/2CH_2Cl_2
Molecular formula	$C_{43}H_{40}N_5O_3Cl_2NiBr$	$C_{48.67}H_{43.33}O_{3.33}N_5BrCl_2Ni$	$C_{20}H_{21}N_3O_4S$	$C_{29.5}H_{40}N_3O_4Cl$
Molecular weight	884.32	961.07	399.46	536.10
T/K	100	100	100	100
Crystal size/mm^3	0.30×0.20×0.03	0.24×0.10×0.08	0.30×0.20×0.03	0.30×0.10×0.10
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	11.0569(7)	12.695(2)	5.1284(4)	9.532(2)
b/Å	11.7593(7)	16.918(2)	16.3848(12)	10.476(2)
c/Å	16.5736(10)	20.119(3)	22.4329(17)	31.526(7)
α/deg	90	90	90	90
β/deg	91.192(1)	90	90	90
γ/deg	90	90	90	90
V/Å^3	2154.5(2)	4321(1)	1885.0(2)	3148.1(13)
Z	2	4	4	4
d_{calc}/g cm^{-3}	1.363	1.477	1.408	1.131
F(000)	908	1976	840	1148
μmm^{-1}	1.545	1.548	0.205	0.156
$2\theta_{max}$/deg	56	52	61	50
Number of measured reflections	32112	40796	25869	27098
Number of independent reflections	10280	8474	5807	5518
Number of reflections with $I > 2\sigma(I)$	7073	6011	5086	4520
Number of refined parameters	457	568	254	292
R_1 ($I > 2\sigma(I)$)	0.052	0.047	0.034	0.142
wR_2 for all parameters	0.097	0.103	0.083	0.323
GOOF	1.010	1.020	1.000	1.038
T_{max}(T_{min})	0.955 (0.654)	0.886 (0.697)	0.994 (0.943)	0.9859 (0.955)
Flack parameter	0.046(8)	0.00(1)	0.05(5)	0.5(5)

compounds **9** and **31** was accounted using the program SQUEEZE (part of the PLATON-98 program package).[13] The total number of dichloromethane solvate molecules per molecule of the basic compound was defined roughly based on the analysis of the thermal vibrations of the atoms in the positions with maximum population. One of the two benzyl fragments of the molecule **9** is disordered over two positions with equal population, which characterized by the rotation angle around the N(3)—C(36) bond of ~16.7°. One of the two *tert*-butyl group in molecule **31** disordered also over to positions due to free rotation around the C(7)—C(11) bond with the population ratio of 0.6 : 0.4. The hydrogen atoms of the amino group of **27** and the hydroxyl groups of **31** as well as methanol solvate molecules were localized objectively by the difference Fourier synthesis and refined with fixed positional and thermal parameters. The positions of the remaining hydrogen atoms were calculated geometrically and refined in isotropic approximation with fixed positional (riding model) and thermal parameters (U_{iso}(H) = 1.5U_{equiv}(C) for the Me groups and U_{iso}(H) = 1.2U_{equiv}(C) for all other groups). It should be noted that crystal of **31** is a fine needle with a noticeable contribution of the twin component, therefore, the quality of the experiment was quite low. Unfortunately, no crystal of **31** of better quality was obtained. Nevertheless, the model of compound **31** was provided clearly and undoubtedly. The absolute structures of compounds **9**, **10**, and **27** were defined objectively by refinement of the Flack parameter (Table 1). Due to the above-mentioned disordering of the dichloromethane solvate molecule, no absolute structure of compound **31** can be given. All calculations were done using the SHELXTL program package.[14] Atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters of complexes **9** · CH_2Cl_2, **10** · 2/3($CHCl_3$) · 1/3(H_2O), **27**, and **31** · CH_3OH · 1/2CH_2Cl_2 were deposited in the Cambridge Structural Database.

This work was financially supported by the International Science and Technology Center (Grant G-1361) and the Russian Foundation for Basic Research (Project No. 08-03-00466a).

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Received February 24, 2010;
in revised form April 13, 2010