Michael Addition Reactions between Chiral Ni(II) Complex of Glycine and 3-(*trans*-Enoyl)oxazolidin-2-ones. A Case of Electron Donor−Acceptor Attractive Interaction-Controlled Face Diastereoselectivity[1]

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This study has demonstrated that the readily available and inexpensive 3-(*trans*-3′-alkyl/arylpropenoyl)oxazolidin-2-ones, featuring high electrophilicity and conformational homogeneity, are synthetically superior Michael acceptors over the conventionally used alkyl enoylates, allowing for a remarkable improvement in reactivity and, in most cases, diastereoselectivity of the addition reactions with a Ni(II) complex of the chiral Schiff base of glycine with (*S*)-*o*-[*N*-(*N*-benzylprolyl)-amino]benzophenone. Kinetically controlled diastereoselectivity in the corresponding Michael addition reactions between the Ni(II) complex of glycine and the oxazolidin-2-ones was systematically studied as a function of steric, electronic, and position effects of the substituents on the starting Michael acceptor. In both aliphatic and aromatic series the simple diastereoselectivity was found to be virtually complete, affording the products via the corresponding TSs with the approach geometry *like*. The face diastereoselectivity of the reactions between the Ni(II) complex of glycine and the 3-(*trans*-3′-alkylpropenoyl)oxazolidin-2-ones was found to depend exclusively on the steric bulk of the alkyl group on the starting Michael acceptor. In contrast, the face diastereoselectivity in the reactions of aromatic oxazolidin-2-ones with the Ni(II) complex of glycine was shown to be controlled predominantly by the electronic properties of the aryl ring. In particular, the additions of the Ni(II) complex of glycine with 3-(*trans*-3′-arylpropenoyl)oxazolidin-2-ones, bearing electron-withdrawing substituents on the phenyl ring, afforded the (2*S*,3*R*)-configured products with synthetically useful diastereoselectivity and in quantitative chemical yields, thus allowing for an efficient access to the sterically constrained β-aryl-substituted pyroglutamic and glutamic acids.

Introduction

Recently, we reported asymmetric Michael addition reactions between a Ni(II) complex of the chiral Schiff base of glycine with (*S*)-*o*-[*N*-(*N*-benzylprolyl)amino]-benzophenone (**1**) and a series of the β-trifluoromethyl-substituted alkyl acrylates leading to the corresponding sterically constrained and trifluoromethyl-containing pyroglutamic acids in enantiomerically pure form.[1a,b] Since pyroglutamic acids could serve as key compounds to a whole variety of five-carbon atom amino acids,[2−4] we were interested in generalizing of this method to afford the corresponding β-alkyl- and β-aryl-substituted derivatives, which are extraordinary useful compounds in the de novo design of peptides with rationally modified three-dimensional structures and biological functions.[5] However, our attempts to involve β-alkyl- or β-arylacrylic esters in the reaction with complex **1** encountered unexpected problems of low reactivity of these substrates and poor stereochemical outcome. Apparently, the successful results of the additions between **1** and trifluoromethyl containing acrylates are due to the enhanced electrophilicity and steric demands of these derivatives provided by the trifluoromethyl group.[6] To overcome the problems associated with β-alkyl/arylacrylic esters, we searched for other derivatives of α,β-unsaturated carboxylic acids which would feature higher electrophilicity (issue of reactivity) and conformational homogeneity (issue of diastereoselectivity). Recently, we have found that readily available and inexpensive 3-(*trans*-enoyl)-oxazolidin-2-ones (**2**) perfectly meet the required char-

(1) Stereochemically Defined *C*-Substituted Glutamic Acids and Their Derivatives. 9. For previous papers in this series, see: (a) Soloshonok, V. A.; Cai, C.; Hruby, V. J.; Meervelt, L. V.; Mischenko, N. *Tetrahedron* **1999**, *55*, 12031. (b) Soloshonok, V. A.; Cai, C.; Hruby, V. J.; Meervelt, L. V. *Tetrahedron* **1999**, *55*, 12045. (c) Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Tetrahedron*: *Asymmetry* **1999**, *10*, 4265. (d) Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Tetrahedron Lett.* **2000**, *41*, 135. (e) Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2172. (f) Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Org. Lett.* **2000**, *2*, 747. (g) Soloshonok, V. A.; Cai, C.; Hruby, V. J.; Meervelt, L. V.; Yamazaki, T. *J. Org Chem.* **2000**, *29*, 6688. (h) Soloshonok, V. A.; Cai, C.; Hruby, V. J. *Tetrahedron Lett.* **2000**, *41*, 9645.

(2) For reviews on asymmetric synthesis of α-amino acids in general and the target amino acids in particular, see: (a) Duthaler, R. O. *Tetrahedron* **1994**, *50*, 1539. (b) Williams, R. M. *Synthesis of Optically Active α-Amino Acids*; Pergamon Press: Oxford, 1989.

(3) For papers, see: (a) Kanemasa, S.; Tatsukawa, A.; Wada, E.; *J. Org. Chem.* **1991**, *56*, 2875. (b) Schöllkopf, U.; Pettig, D.; Busse, U. *Synthesis* **1986**, 737.

(4) For recent review on various synthetic transformations of pyroglutamic acid and its derivatives, see: Najera, C.; Yus, M. *Tetrahedron*: *Asymmetry* **1999**, *10*, 2245.

(5) For reviews see: (a) Goodman, M.; Ro, S. In *Burger's Medicinal Chemistry and Drug Discovery*, 5th ed.; Wolff, M. E., Ed.; John Wiley and Sons: New York, 1995; Vol. 1, pp 803−861. (b) Gante, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1699. (c) Giannis, A.; Kolter, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1244. (d) Hruby, V. J.; Al-Obeidi, F.; Kazmierski, W. *Biochem. J.* **1990**, *268*, 249. (e) Hruby, V. J. *Med. Res. Rev.* **1989**, *9*, 343.

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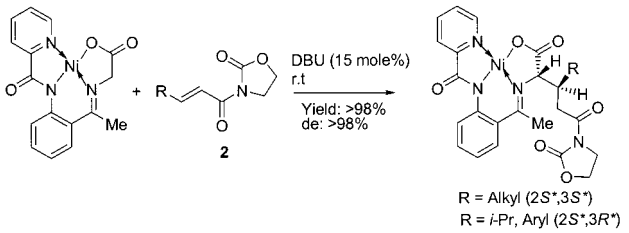
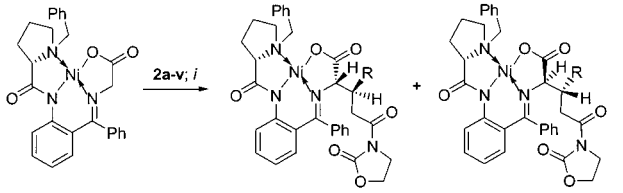
Scheme 1



Scheme 2[a]



R = Me (**a**), Et (**b**), *n*-Pr (**c**), *i*-Pr (**d**), *t*-Bu (**e**), Ph (**f**), α-naphthyl (**g**), β-naphthyl (**h**), 2-MeO-C_6H_4 (**i**), 3-MeO-C_6H_4 (**j**), 4-MeO-C_6H_4 (**k**), 2-CF_3-C_6H_4 (**l**), 3-CF_3-C_6H_4 (**m**), 4-CF_3-C_6H_4 (**n**), *N*-Mts-β-indolyl (**o**), C_6F_5 (**p**), 2,6-F_2-C_6H_3 (**q**), 2-F-C_6H_4 (**r**), 3,4-F_2-C_6H_3 (**s**), 4-MeO-C_6F_4 (**t**), 3,4-Cl_2-C_6H_3 (**u**), 4-NO_2-C_6H_4 (**v**)

acteristics of the ideal Michael acceptors allowing the corresponding additions with achiral Ni(II) complex of glycine Schiff base with *o*-(*N*-α-picolylamino)acetophenone (Scheme 1) to proceed with *virtually complete* simple diastereoselectivity (>98% de) at *room temperature* in the presence of *nonchelating organic base*.[1d,g] In this paper, we describe in full detail[1c] the asymmetric version of the reaction using a Ni(II) complex **1** as a chiral equivalent of nucleophilic glycine in the additions with various 3-(*trans*-enoyl)oxazolidin-2-ones (**2**) to demonstrate the scope and limitations of this method for preparing the target χ-constrained amino acids.[7]

Results and Discussion

Michael Addition Reactions of Glycine Ni(II) Complex 1[8] with 3-(*trans*-3′-Alkylpropenoyl)oxazolidin-2-ones (2a−d). Previously, we have shown that the Michael addition reaction between complex **1** and ethyl crotonate, conducted in DMF in the presence of DBU (50 mol %) for 1 h, gave rise to a mixture of the corresponding (2*R*,3*R*)-, (2*S*,3*S*)-, and (2*S*,3*R*)-diastereomers in a ratio of 19.0/76.2/4.8, respectively, and in 78% chemical yield.[1a] In contrast, we have found that reaction of *N*-*trans*-crotonyl-derived oxazolidin-2-one **2a** with complex **1** in the presence of catalytic amounts of DBU (10−15 mol %) proceeds at a substantially higher reaction rate (15 min), affording quantitatively a mixture of (2*S*,3*S*)- and (2*R*,3*R*)-configured products in a ratio of 2.4/1 (**3a** and **4a**, respectively) (Scheme 2, Table 1, entry 1). Due to the quantitative chemical yield, this outcome is synthetically superior to the previously reported procedure,[1a] as the diastereomerically pure major product (2*S*,3*S*)-**3a** could be isolated in 67% yield simply by crystallizing the resultant mixture from benzene/hexanes. Increasing the steric bulk of the alkyl group on the starting oxazolidin-2-one resulted in a reduced reaction rate of the additions of complex **1** with the ethyl- and *n*-propyl-containing

Table 1. Addition Reactions of Ni(II) Complex (*S*)-1 with *N*-((*E*)-Enoyl)-3-oxazolidin-2-ones 2a−v[a]

			products **3a−v**, **4a−v**	
entry	**2a−v**	time	yield,[b] %	ratio **3**/**4**[c]
1	**a**	15 min	>98	2.4/1
2	**b**	20 min	96	3.1/1
3	**c**	35 min	94	3.1/1
4	**d**	45 min	91	5.2/1
5	**e**		no reaction	
6	**f**	15 min	94	4.0/1
7	**g**	20 min	93	3.5/1
8	**h**	20 min	98	5.3/1
9	**i**	2.5 h	98	2.7/1
10	**j**	25 min	96	4.2/1
11	**k**	40 min	99	4.5/1
12	**l**	20 min	95	8.5/1
13	**m**	2 min	95	5.4/1
14	**n**	2 min	98	8.4/1
15	**o**	1 h	94	4.5/1
16	**p**	<2 min	>98	>26/1
17	**q**	5 min	95	2.6/1
18	**r**	5 min	>98	3.6/1
19	**s**	2 min	98	7.2/1
20	**t**	2 min	96	2.6/1
21	**u**	2 min	98	9.7/1
22	**v**	2 min	>98	7.6/1

[a] All reactions were run in DMF in the presence of 15 mol % of DBU at ambient temperature. Ratio **1**/**2** 1/1.05−1.1. [b] Isolated yield of crude product. [c] Determined by NMR (500 MHz) analysis of the crude reaction mixtures.

oxazolidin-2-ones **2b**,**c**. However, the major products (2*S*,3*S*)-**3b**,**c** were obtained with higher selectivity (entries 2 and 3). Sterically bulky isopropyl-containing oxazolidin-2-one **2d** readily reacted with complex **1** to give quantitatively a mixture of (2*S*,3*R*)-**3d** and (2*R*,3*S*)-diastereomers **4d**[9] with a synthetically useful excess of the major product (entry 4). It is interesting to note that attempts to conduct addition between complex **1** and ethyl 4-methylpentenoylate failed,[11] undoubtedly, due to the sterically congested nature of the ester. On the other hand, these results could serve as a clear example of the synthetic superiority of the oxazolidin-2-one derivatives **2**, as Michael acceptors, over the corresponding esters. However, application of oxazolidin-2-one derivatives **2** in Michael additions with complex **1** was found to have some limitations. Thus, the reaction between **1** and *tert*-butyl-containing derivative **2e** did not occur at all under the standard conditions. Application of equimolar amounts of the base or elevated temperatures resulted in formation of decomposition products.

Considering the kinetically controlled (vide infra) stereochemical outcome of these reactions, we can conclude that oxazolidin-2-ones **2a−d** feature much higher reac-

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(8) For recent papers on asymmetric synthesis of α-amino acids using Ni(II) complex **1**, see: (a) Soloshonok, V. A.; Avilov, D. V.; Kukhar′, V. P. *Tetrahedron*: *Asymmetry* **1996**, *7*, 1547. (b) Soloshonok, V. A.; Avilov, D. V.; Kukhar′, V. P. *Tetrahedron* **1996**, *52*, 12433. (c) Soloshonok, V. A.; Avilov, D. V.; Kukhar′, V. P.; Meervelt, L. V.; Mischenko, N. *Tetrahedron Lett.* **1997**, *38*, 4671. (d) Soloshonok, V. A.; Avilov, D. V.; Kukhar′, V. P.; Meervelt, L. V.; Mischenko, N. *Tetrahedron Lett.* **1997**, *38*, 4903. (e) Qiu, W.; Soloshonok, V. A.; Cai, C.; Tang, X.; Hruby, V. J., *Tetrahedron* **2000**, *56*, 2577. (f) Tang, X.; Soloshonok, V. A.; Hruby, V. J. *Tetrahedron*: *Asymmetry* **2000**, *11*, 2917.

(9) (2*S*,3*R*) or (2*R*,3*S*) absolute stereochemistry for the isopropyl- or aryl-containing (R = *i*-Pr, Ph) derivatives is a consequence of the Cahn−Ingold−Prelog priority (see ref 10) and is stereochemically equivalent to the (2*S*,3*S*) or (2*R*,3*R*) configuration, respectively, in the aliphatic (R = Me, Et, *n*-Pr) series of compounds.

(10) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(11) Soloshonok, V. A.; Cai, C.; Hruby, V. J. Unpublished data.

tivity than the corresponding alkyl esters and provide better diastereoselectivity in the addition reaction with complex **1**. The absolute configuration (vide infra) of the diastereomeric products suggests that the reactions occur with virtually complete simple diastereoselectivity, while the complex **1** derived enolate (2*S*)/(2*R*)-face selectivity is relatively poor.

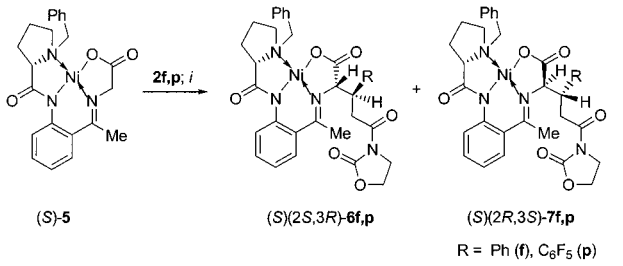
Michael Addition Reactions of Glycine Ni(II) Complex 1 with 3-(*trans*-3′-Arylpropenoyl)oxazolidin-2-ones (2f−w). As in the aliphatic series, all reactions between complex **1** and aryl-containing Michael acceptors **2f**−**w** were conducted under the same, standard reaction conditions: DMF as a solvent, 15 mol % DBU as a base, ambient temperature. The addition of phenyl-containing oxazolidin-2-one **2f** with complex **1** occurred with the same rate and quantitative yield as the reaction of methyl derivative **2a**, but with more appreciable diastereoselectivity (entry 6). The main product (2*S*,3*R*)-**3f**[3] was isolated in 76% chemical yield simply by crystallizing the resulting mixture of diastereomers. The reaction of more sterically bulky[12] α- and *β*-naphthyl-containing oxazolidin-2-ones **2g**,**h**, respectively, proceeded at a slightly lower rate and with noticeably different diastereoselectivities (entries 7 and 8). Thus, the stereochemical outcome in the reaction of the α-naphthyl derivative **2g** with complex **1** was poorer, as compared with the addition of phenyl-containing **2f** (entry 7 vs 6). In contrast, the diastereoselectivity of the reaction between *β*-naphthyl-containing oxazolidin-2-one **2h** and complex **1** was found to be higher than that of phenyl derivative **2f** (entry 8 vs 6). These data suggested that in the addition of complex **1** with aryl-containing oxazolidin-2-ones **2** not only the total steric bulk of the substituent, as observed in the aliphatic series (entries 1−4), but also the pattern of substitution on the aromatic ring might play an important role in determining the stereochemical outcome. Therefore, to investigate systematically electronic and position effects of substituents on the phenyl ring of the starting oxazolidin-2-ones on the stereochemical outcome of the reactions, we prepared a series of *o*-, *m*-, and *p*-methoxy- (**2i**−**k**) and *o*-, *m*-, and *p*-trifluoromethylphenyl derivatives **2l**−**n**. The reaction of *o*-methoxy-substituted **2i** with complex **1** occurred at low reaction rate and with noticeably lower diastereoselectivity as compared with the outcome of unsubstituted phenyl derivative **2f** reaction (entry 9 vs 6). Surprisingly, *m*-methoxyphenyl-containing **2j** reacted with complex **1** at a high rate, furnishing the corresponding diastereomeric products (2*S*,3*R*)-**3j** and (2*R*,3*S*)-**4j** in a ratio comparable with the result obtained in the reaction of **2f** with **1** (entry 10 vs 9, 6). The addition of the *p*-methoxyphenyl derivative **2k** occurred at a relatively low rate but with the highest diastereoselectivity in the series (entry 11 vs 9, 10). Considering the electron-releasing effect of methoxy group decreasing electrophilicity of the C,C double bond in the corresponding derivatives **2i**−**k**, the lowering in the reaction rates of the additions between complex **1** and **2i**−**k** was quite anticipated. However, such a noticeable influence of the position of the methoxy group on the reaction rate (entry 9 vs 10) and the diastereoselectivity (entry 9 vs 11) was rather intriguing. Considering the results obtained for the naphthyl (entries 7, 8) and methoxyphenyl (entries 9−11) series, we can conclude that ortho substitution on the aromatic ring in the starting Michael acceptors is unfavorable for both the reaction rate and diastereoselectivity of the corresponding addition reactions. In agreement with this conclusion, the reaction of *o*-trifluoromethylphenyl-substituted **2l** with complex **1** occurred with the slowest rate (entry 12), as compared with the almost instant additions of the meta- and para-substituted derivatives **2m**,**n**, respectively (entries 13 and 14). However, the diastereoselectivity of the reaction between **2l** and **1** was the highest in a series of trifluoromethylphenyl-containing Michael acceptors **2l**−**n**. This unexpected result could be rationalized assuming that in the corresponding transition state (TS) (vide infra) the *o*-trifluoromethyl group is situated in close proximity with the positively charged Ni(II) cation of the glycine complex **1**, allowing for corresponding electrostatic attractive interactions, which would contribute to the thermodynamic stability of the TS.[13] In general, high reaction rates, even in the case of ortho-substituted **2l** (20 min), observed in the series of trifluoromethylphenyl-containing Michael acceptors, was a pleasant result suggesting that the present method would be of particular use for preparing the target amino acids containing electron-withdrawing substituents.

Next, we studied the reactions of complex (*S*)-**1** with Michael acceptors containing indolyl- (**2o**) and pentafluorophenyl-containing derivatives **2p**, representing electron-excessive and electron-deficient aromatic rings, respectively. As expected, considering the reduced electrophilicity of the C,C double bond in **2o** due to the electron-releasing effect of the indolyl group, the reaction with complex (*S*)-**1** occurred at relatively low rate, but with slightly enhanced diastereoselectivity (ca. 82%) as compared with the addition of **2f** (entry 15 vs 6). In contrast, the exothermic reaction (<2 min) of the pentafluorophenyl derivative **2p** afforded the major product (2*S*,3*R*)-**3p** with at least 96% diastereoselectivity (entry 16). While the reaction rates of these reactions could be readily accounted for by electronic effects, such dramatic differences in the diastereoselectivity were unexpected. We assumed first that the reason behind the phenomenon observed is the fact that pentafluorophenyl ring and C,C double bond in **2p** cannot adopt a coplanar geometry due to the steric demands of the two *o*-fluorine atoms, a property that makes **2p** different from all previously studied Michael acceptors. Therefore, we conducted the addition reactions between complex **1** and a series of bis- and monofluoro-substituted derivatives **2q**−**s**. The reaction of 2,6-difluorophenyl derivative **2q** occurred at high rate, but with disappointedly low diastereoselectivity (entry 17). The addition of mono-2-fluorophenyl-substituted **2r** proceeded at the same rate and with higher diastereoselectivity (entry 18). Surprisingly, the diastereoselectivity of the reaction of 3,4-difluorophenyl derivative **2s** (entry 19) featured the level observed in the series of trifluoromethylphenyl-containing Michael acceptors (entries 12−14). These results allowed us to conclude that the origin of the diastereoselectivity observed in the reaction between complex **1** and pentafluorophenyl-containing **2p** is not the steric or geometric

(12) Attempts to conduct the reactions of complex **1** with the ethyl esters of *trans*-3-(α- or *β*-naphthyl)propenoic acids failed.

(13) Electrostatic attractive interactions between the nickel(II) ion and fluorine atoms, were shown to be a paramount factor controlling virtually complete diastereoselectivity in the aldol addition reaction between trifluoromethyl alkyl/aryl ketones and complex (*S*)-**1**; see refs 8a,b and 14.

Scheme 3[a]



properties of the latter but the extreme electron-deficient nature of the pentafluorophenyl ring. To have a final and straightforward proof to this conclusion, we synthesized *p*-methoxytetrafluorophenyl derivative **2t**, which, possessing the steric and geometric profile of **2p**, lacks its extreme electron-deficient nature,[6] due to the presence of the electron-releasing methoxy group. The result was quite convincing; the addition of **2t** with complex **1** occurred at a high reaction rate and with the same, low diastereoselectivity that was obtained in the reaction of 2,6-difluorophenyl-containing **2q** (entry 20 vs 17). To demonstrate the generality of this electron-deficient aromatic ring-induced diastereoselectivity, and being aware of the unique stereocontrolling ability of fluorine atoms,[6] we investigated the reactions of the Michael acceptors **2u**,**v** bearing electron-withdrawing substituents other than fluorine. To our satisfaction, the exothermic and quantitative additions of complex **1** with 3,4-dichlorophenyl **2u** and 4-nitrophenyl derivatives **2v** featured high diastereoselectivity (entries 21, 22), suggesting that the electron-deficiency of the phenyl ring, rather than the presence of fluorine atoms, is the cause of the results obtained.

With these results in hand, we next examined the origin of this electron-deficient aromatic ring-induced high diastereoselectivity. Considering the structure of glycine complex (*S*)-**1**, one can identify at least four potential sites for nonbonded interactions with the electron-deficient aromatic ring on the starting Michael acceptors: the three aromatic rings of (*S*)-**1** can be involved in the corresponding attractive interactions and the Ni(II) ion in repulsive interactions. Taking into account that the electron-deficient aromatic ring on the starting Michael acceptors favors a (2*S*,3*R*) absolute configuration of the major diastereomeric product, we assumed that the ketimine phenyl of complex (*S*)-**1** might be involved in the corresponding electron donor−acceptor attractive interactions. To prove this, we prepared glycine complex (*S*)-**5** (Scheme 3) in which the ketimine phenyl is substituted by the methyl. Since the methyl group in complex (*S*)-**5** cannot be involved in the interactions under study, we expected that the reaction between complex (*S*)-**5** and pentafluorophenyl-containing **2p** would feature lower diastereoselectivity, as compared with the outcome of the addition of complex (*S*)-**1** with **2p** (entry 16). Indeed, the reaction between complex (*S*)-**5** and **2p** proceeded at a high rate, giving rise to (2*S*,3*R*)-**6p** and (2*R*,3*S*)-diastereomeric products **7p** in a ratio of 3/1, respectively. Most interestingly, the addition between complex (*S*)-**5** and unsubstituted phenyl-containing **2f** gave the diastereomers (2*S*,3*R*)-**6f** and (2*R*,3*S*)-**7f** in exactly the same ratio of 3/1, respectively. These data clearly demonstrate that the ketimine phenyl of complex (*S*)-**1** and the electron-deficient aromatic ring of the Michael acceptor are involved in the electron donor−acceptor attractive interactions that render the (2*S*,3*R*)-configured diastereomers **3** substantially favored over (2*R*,3*S*)-**4**. Accordingly, the stereochemical outcome of the addition reactions under study is governed by the combined effect of steric and electronic/electrostatic[15] interactions which are a function of the substitution pattern on the aromatic ring and the nature of the substituent.

In general, as shown in the aliphatic series, the addition reactions between complex (*S*)-**1** and aromatic Michael acceptors **2f**−**v** proceeded with excellent simple and variable face diastereoselectivity giving rise to a mixture of (2*S*,3*R*)-**3f**−**v** and (2*R*,3*S*)-**4f**−**v** diastereomers. On the other hand, the face diastereoselectivity was found to vary from poor to excellent depending, in contrast to the aliphatic series, on the combined effect of steric and electronic factors, allowing for the efficient asymmetric synthesis of the target *β*-aryl-substituted glutamic/pyroglutamic acids containing electron-withdrawing substituents on the aryl group (vide versa).

Determination of the Absolute Configuration of the Products. Decomposition of the Diastereomerically Pure Complexes 3 and 4: Isolation of Pyroglutamic Acids 8 and Recovery of the Chiral Ligand (*S*)-10. The α-absolute configuration of the glutamic acid residue in the diastereomeric products **3**, **4** and **6**, **7** could be easily determined on the basis of their chiroptical properties and NMR data.[16] The absolute configuration of the *β*-stereogenic carbon in **3**, **4** and **6**, **7** also could be reliably assigned using proton NMR data.[17] Nevertheless, taking advantage of the fact that physicochemical and chiroptical data for *β*-methyl- and *β*-phenyl-substituted pyroglutamic acids were available in the literature,[1a,19,20] we decomposed, under the standard conditions,[1a,b] dia-

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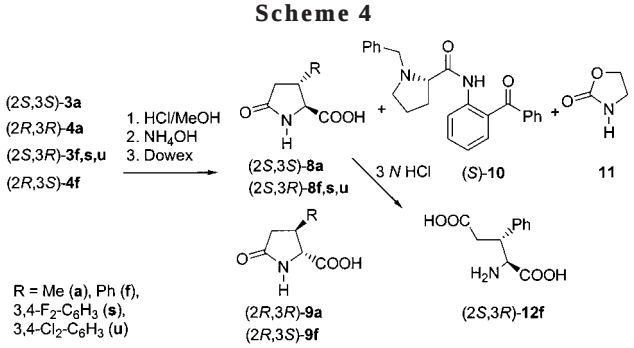
(16) As has been demonstrated (see refs 1 and 8), the CD and ORD spectra of Ni(II) complexes of this type in neutral solutions exhibit two maxima in the region of metal d−d transition (Cotton effects at 450 and 550 nm). In the ORD spectra, the sign of Cotton effects in this region strictly depends on a conformation of the polycyclic system of chelate rings. Thus, in the case of complexes containing α-monosubstituted α-amino acid, the pseudoaxial orientation of the amino acid side chain, corresponding to an α-(*L*) configuration of α-amino acid, causes a Cotton effect with a positive sign at the 500−700 nm region and negative sign at 400−450 nm. On the other hand, a pseudoequatorial orientation of the amino acid side chain brings about opposite signs of the Cotton effects at 400−450 (positive) and at the 500−700 nm (negative) region. As was established in numerous studies, this general trend is not influenced by the structure and nature of the α-amino acid side chain, and the configuration of stereogenic centers within it. ^{1}H NMR spectra of the complexes containing α-L- and α-D-amino acids also are very characteristic, featuring substantial differences in chemical shifts of aromatic and methylene protons of the (*N*-benzyl)proline moiety.

(17) Due to the sterically congested nature and structural sophistication of Ni(II)-complexes **3**, **4** and **6**, **7** free rotation of the glutamic acid residues in the complexes is substantially restricted. As a result of this, the corresponding diastereomeric products differing for the absolute configuration in the *β*-position have characteristic patterns in their proton NMR spectra. For a discussion of the NMR data characteristic for the diastereomeric Ni(II) complexes containing *β*-alkyl- and *β*-aryl-substituted glutamic acid residues, see refs 1a,b and 18, respectively.

(18) Belokon′, Y. N.; Bulychev, A. G.; Ryzhov, M. G.; Vitt, S. V.; Batsanov, A. S.; Struchkov, Y. T.; Bakchmutov, V. I.; Belikov, V. M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1865.

(19) Ezquerra, J.; Pedregal, C.; Merino, I.; Flórez, J.; Barluenga, J.; García-Granda, S.; Llorca, M.-A. *J. Org. Chem.* **1999**, *64*, 6554.

Scheme 4



stereomerically pure complexes **3a**,**f** and **4a**,**f** to afford the corresponding pyroglutamic acids **8a**,**f** and **9a**,**f**, respectively, along with recovery of the chiral ligand (*S*)-**10** and the oxazolidin-2-one (Scheme 4). Comparison of the proton NMR and chiroptical data of **8a**,**f** and **9a**,**f**, with those of the literature revealed (2*S*,3*S*) and (2*R*,3*R*) absolute configurations for **8a** and **9a**, respectively, and (2*S*,3*R*) and (2*R*,3*S*)[9] stereochemistry for **8f** and **9f**, respectively. The absolute configurations of the rest of diastereomeric products **3b**−**d**,**g**−**v** and **4b**−**d**,**g**−**v** were assigned on the basis of a close similarity of their chiroptical and proton NMR data to those of **8a**,**f** and **9a**,**f**.

To demonstrate the synthetic aspects of the method, we performed preparative (3−5 g) synthesis of (2*S*,3*R*)-**8f**,**s**,**u** (Scheme 4). Major products (2*S*,3*R*)-**3f**,**s**,**u** were isolated in diastereomerically pure form by recrystallization of the resulting reaction mixture, and decomposed to afford the target pyroglutamic acids (2*S*,3*R*)-**8f**,**s**,**u** along with quantitative recovery of ligand (*S*)-**10**. Furthermore, phenyl-containing (2*S*,3*R*)-**8f** was hydrolyzed to the corresponding glutamic acid (2*S*,3*R*)-**12f** in high chemical yield.

Mechanistic Considerations. First, we investigated the reversibility of the reactions under study to determine whether the stereochemical outcome is kinetically or thermodynamically controlled. Resubmission of the diastereomerically pure products **3a**,**f** and **4a**,**f** to the original reaction conditions did not give any of the starting compounds in detectable amounts (^{1}H NMR, 500 MHz). These results suggested that the reactions are rather irreversible, and thus, the stereochemical outcome of the addition reactions is most likely kinetically controlled. That is in good agreement with previous results obtained on the DBU-catalyzed Michael addition reactions of Ni(II) complexes with α,*β*-unsaturated carboxylic acid derivatives.[1a,b,h] According to the absolute configurations of diastereomeric products **3** and **4**, the relative topicity[20] of coupling is *like*. Taking into account the mechanistic rationale for the addition reactions between the achiral Ni(II) complex of glycine Schiff base with *o*-(*N*-α-picolylamino)acetophenone and Michael acceptors **2** (Scheme 1),[1h] we can suggest that the formation of the major diastereomeric products **3** in the reaction under study proceeds through TS **A** (Figure 1). As one can see, in TS **A** the aromatic ring of the Michael acceptor and the ketimine phenyl of the Ni(II) complex are in close proximity to each other, and that would allow for nonbonding electron donor−acceptor attractive interactions adding to the stability of TS **A**. The high diastereoselectivity in the addition between complex (*S*)-**1** and *o*-trifluoromethyl-containing **2l** (Table 1, entry 12) also could be easily accounted for considering TS **A′** in which the fluorine atoms are located in close proximity with the Ni(II) and could interact[13] with the latter, adding to the stability of TS **A′**.

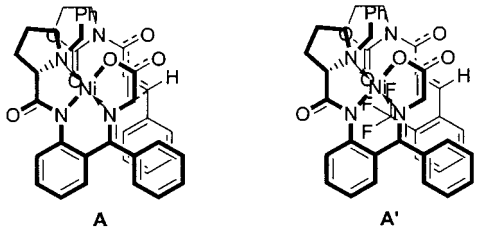


Figure 1. Possible TSs in the addition between **1** and **2**

In conclusion, we have demonstrated that the readily available and inexpensive 3-(*trans*-3′-alkyl/arylpropenoyl)oxazolidin-2-ones (**2a**−**d**,**f**−**v**), featuring high electrophilicity and conformational homogeneity, are synthetically more superior Michael acceptors than the corresponding alkyl enoylates, allowing for a remarkable improvement in reactivity and, in most cases, diastereoselectivity of the addition reactions with a Ni(II) complex of the chiral Schiff base of glycine (*S*)-**1**. The kinetically controlled diastereoselectivity in the Michael addition reactions between (*S*)-**1** and **2a**−**v** was systematically studied as a function of steric, electronic and position effects of the substituents on the starting Michael acceptor. In both the aliphatic and aromatic series, simple diastereoselectivity was found to be virtually complete, affording the products via the corresponding TSs with the approach geometry *like*. The face diastereoselectivity of the reactions between complex (*S*)-**1** and 3-(*trans*-3′-alkylpropenoyl)oxazolidin-2-ones (**2a**−**d**) was found to depend exclusively on the steric bulk of the alkyl group on the starting Michael acceptor. In contrast, the face diastereoselectivity of aromatic oxazolidin-2-ones **2f**−**v** was shown to be controlled predominantly by the electronic properties of the aryl ring. In particular, the additions of complex (*S*)-**1** with 3-(*trans*-3′-arylpropenoyl)-oxazolidin-2-ones bearing electron-withdrawing substituents on the phenyl ring afforded the (2*S*,3*R*)-configured products with synthetically useful diastereoselectivities and in quantitative chemical yields, thus allowing for an efficient access to sterically constrained *β*-aryl-substituted pyroglutamic and glutamic acids.

Experimental Section

General Methods. ^{1}H, ^{13}C, and ^{19}F NMR (299.94 MHz) were recorded using TMS, $CDCl_3$, and CCl_3F as internal standards. High-resolution mass spectra (HRMS) and optical rotations were recorded at facilities available at the Department of Chemistry, University of Arizona. Melting points (mp) are uncorrected and were obtained in open capillaries. All reagents and solvents, unless otherwise stated, are commercially available and were used as received. Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by ^{1}H, ^{13}C, and ^{19}F NMR spectrometry. All new compounds were characterized by ^{1}H, ^{13}C, and ^{19}F NMR and HRMS.

For an updated, improved large-scale preparation of chiral ligand (*S*)-*o*-[*N*-(*N*-benzylprolyl)amino]benzophenone (BPB) (**10**) and the corresponding Ni(II) complex, see ref 21. Michael acceptors **2a**−**v** were prepared according to the general methods A and B described previously.[1h] For properties,

(20) Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.

constants, and NMR data of derivatives **2a**,**c**,**d**,**f**−**h**,**k**,**n**−**p**, see ref 1h. The new Michael acceptors used in this study are listed below.

3-(*trans*-2′-Pentenoyl)oxazolidin-2-one (2b) (method A): yield 52%; oil; ^{1}H NMR ($CDCl_3$) δ 1.11 (3H, t, J = 7.5 Hz), 2.27−2.36 (2H, m), 4.07−4.43 (4H, AB, J = 8.0 Hz), 7.16−7.28 (2H, m); ^{13}C NMR ($CDCl_3$) δ 12.2, 25.8, 42.7, 60.0, 119.1, 153.0, 153.5, 165.4; HRMS(FAB) [M + H]$^+$ calcd for $C_8H_{12}NO_3$ 170.0817, found 170.0817.

3-(4′,4′-Dimethyl-*trans*-2-pentenoyl)oxazolidin-2-one (2e) (method B): yield 79%; mp 73.0−73.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.12 (9H, s), 4.08, 4.43 (4H, AB, J = 8.1 Hz), 7.71 (2H, s); ^{13}C NMR ($CDCl_3$) δ 28.5, 34.2, 42.7, 61.9, 115.4, 153.4, 161.1, 165.8; HRMS(FAB) [M + H]$^+$ calcd for $C_{10}H_{16}NO_3$ 198.1130, found 198.1130.

3-(*trans*-2′-Methoxycinnamoyl)oxazolidin-2-one (2i) (method A): yield 56%; mp 169.0−170.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.91 (3H, s), 4.14, 4.45 (4H, AB, J = 8.0 Hz), 6.91−7.00 (2H, m), 7.34−7.40 (1H, m), 7.64 (1H, dd, J = 1.7, 7.8 Hz), 7.97, 8.21 (2H, AB, J = 15.9 Hz); ^{13}C NMR ($CDCl_3$) δ 42.9, 55.5, 62.0, 111.1, 116.9, 120.7, 123.5, 129.3, 131.9, 141.6, 158.7, 165.9; HRMS(FAB) [M + H]$^+$ calcd for $C_{13}H_{14}NO_4$ 248.0923, found 248.0926.

3-(*trans*-3′-Methoxycinnamoyl)oxazolidin-2-one (2j) (method B): yield 84%; mp 134.0−135.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.84 (3H, s), 4.14, 4.46 (4H, AB, J = 8.0 Hz), 6.94−6.97 (1H, m), 7.12−7.13 (1H, m), 7.29 (2H, m), 7.82, 7.90 (2H, AB, J = 15.7 Hz); ^{13}C NMR ($CDCl_3$) δ 42.8, 55.3, 62.1, 113.4, 116.6, 116.8, 121.3, 129.9, 135.8, 146.2, 153.6, 159.8, 165.3; HRMS(FAB) [M + H]$^+$ calcd for $C_{13}H_{14}NO_4$ 248.0923, found 248.0927.

3-(*trans*-2′-Trifluoromethylcinnamoyl)oxazolidin-2-one (2l) (method B): yield 85%; mp 128.0−129.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.16, 4.49 (4H, AB, J = 8.0 Hz), 7.47−7.52 (1H, m), 7.57−7.62 (1H, m), 7.70−7.73 (1H, m), 7.84−7.86 (1H, m), 7.89, 8.23 (2H, ABX, J = 2.1, 5.6 Hz); ^{19}F NMR ($CDCl_3$) δ −59.9 (3F, s); ^{13}C NMR ($CDCl_3$) δ 42.8, 62.2, 120.7, 123.9 (q, J = 274.0 Hz), 126.1 (q, J = 6.0 Hz), 128.3, 129.1 (q, J = 32.3 Hz), 129.9, 132.1, 133.3, 141.4 (q, J = 2.0 Hz), 153.6, 164.5; HRMS(FAB) [M + H]$^+$ calcd for $C_{13}H_{11}F_3NO_3$ 286.0691, found 286.0681.

3-(*trans*-3′-Trifluoromethylcinnamoyl)oxazolidin-2-one (2m) (method B): yield 79%; mp 141.5−142.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.16, 4.49 (4H, AB, J = 8.0 Hz), 7.51−7.56 (1H, m), 7.64−7.67 (1H, m), 7.80−7.82 (2H, m), 7.86, 7.97 (2H, AB, J = 15.6 Hz); ^{19}F NMR ($CDCl_3$) δ −64.0 (3F, s); ^{13}C NMR ($CDCl_3$) δ 42.8, 62.2, 118.4, 123.7 (q, J = 274.0 Hz), 125.3 (q, J = 4.0 Hz), 127.0 (q, J = 3.0 Hz), 129.4, 131.3, 131.4 (q, J = 32.3 Hz), 135.2, 144.3, 153.6, 164.9; HRMS(FAB) [M + H]$^+$ calcd for $C_{13}H_{11}F_3NO_3$ 286.0691, found 286.0704.

3-(*trans*-2′,6′-Difluorocinnamoyl)oxazolidin-2-one (2q) (method B): yield 73%; mp 164.0−165.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.15, 4.46 (4H, AB, J = 8.0 Hz), 6.91−6.99 (2H, m), 7.27−7.37 (1H, m), 7.94, 8.14 (2H, AB, J = 15.9 Hz); ^{19}F NMR ($CDCl_3$) δ −110.6 (2F, s); ^{13}C NMR ($CDCl_3$) δ 38.6, 57.9, 107.7 (m), 108.4, 118.2 (t, J = 9.1 Hz), 127.2 (t, J = 11.1 Hz), 127.6, 149.1, 155.9 (d, J = 7.0 Hz), 159.3 (d, J = 7.0 Hz), 161.2; HRMS(FAB) [M + H]$^+$ calcd for $C_{12}H_{10}F_2NO_3$ 254.0629, found 254.0621.

3-(*trans*-2′-Fluorocinnamoyl)oxazolidin-2-one (2r) (method B): yield 88%; mp 133.0−134.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.15, 4.47 (4H, AB, J = 8.0 Hz), 7.08−7.21 (2H, m), 7.35−7.40 (1H, m), 7.66−7.71 (1H, m), 7.96, 8.05 (2H, AB, J = 15.9 Hz); ^{19}F NMR ($CDCl_3$) δ −115.5 (1F, m); ^{13}C NMR ($CDCl_3$) δ 42.8, 62.1, 116.2 (d, J = 22.1 Hz), 118.7 (d, J = 5.1 Hz), 122.6 (d, J = 12.4 Hz), 124.4 (d, J = 4.0 Hz), 129.0 (d, J = 2.0 Hz), 132.1 (d, J = 9.1 Hz), 138.4 (d, J = 4.1 Hz), 153.5, 159.8, 163.2, 165.2; HRMS(FAB) [M + H]$^+$ calcd for $C_{12}H_{11}FNO_3$ 236.0723, found 236.0722.

3-(*trans*-3′,4′-Difluorocinnamoyl)oxazolidin-2-one (2s) (method B): yield 72%; mp 156.5−157.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.14, 4.48 (4H, AB, J = 8.0 Hz), 7.15−7.24 (1H, m), 7.33−7.38 (1H, m), 7.41−7.48 (1H, m), 7.75, 7.84 (2H, AB, J = 15.9 Hz); ^{19}F NMR ($CDCl_3$) δ −137.7 (1F, m), −134.6 (1F, m); ^{13}C NMR ($CDCl_3$) δ 42.7, 62.1, 116.8 (m), 117.7 (m), 125.3 (m), 131.7 (m), 143.7, 148.8 (m), 150.0 (m), 152.2 (m), 153.4 (m), 164.9; HRMS(FAB) [M + H]$^+$ calcd for $C_{12}H_{10}F_2NO_3$ 254.0629, found 254.0636.

3-(*trans*-4′-Methoxy-2′,3′,5′,6′-tetrafluorocinnamoyl)-oxazolidin-2-one (2t) (method B): yield 86%; mp 83.0−83.5 °C; ^{1}H NMR ($CDCl_3$) δ 4.15 (3H, s), 4.16, 4.48 (4H, AB, J = 8.0 Hz), 7.81, 8.11 (2H, AB, J = 16.3 Hz); ^{19}F NMR ($CDCl_3$) δ −159.5 (2F, m), −141.6 (2F, m); ^{13}C NMR ($CDCl_3$) δ 42.7, 62.0, 62.1 (t, J = 5.0 Hz), 107.8 (t, J = 13.6 Hz), 122.7 (t, J = 8.6 Hz), 129.9, 139.0 (m), 139.5 (m), 142.2 (m), 144.3 (m), 147.7 (m), 153.3, 164.8; HRMS(FAB) [M + H]$^+$ calcd for $C_{13}H_{10}F_4NO_4$ 320.0546, found 320.0561.

3-(*trans*-3′,4′-Dichlorocinnamoyl)oxazolidin-2-one (2u) (method B): yield 84%; mp 182.0−183.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.14, 4.48 (4H, AB, J = 8.1 Hz), 7.45−7.49 (2H, m), 7.68−7.69 (1H, m), 7.73, 7.88 (2H, AB, J = 15.6 Hz); ^{13}C NMR ($CDCl_3$) δ 42.8, 62.2, 118.3, 127.5, 128.6, 130.1, 130.9, 133.2, 134.5, 143.4, 153.5, 164.8; HRMS(FAB) [M + H]$^+$ calcd for $C_{12}H_{10}Cl_2NO_3$ 286.0038, found 286.0031.

3-(*trans*-4′-Nitrocinnamoyl)oxazolidin-2-one (2v) (method B): yield 75%; mp 235.0−236.0 °C; ^{1}H NMR ($CDCl_3$) δ 4.16, 4.51 (4H, AB, J = 8.0 Hz), 7.76, 8.26 (2H, AB, J = 8.8 Hz), 7.86, 8.04 (2H, AB, J = 15.9 Hz); ^{13}C NMR ($CDCl_3$) δ 42.8, 62.2, 120.7, 124.2, 129.1, 140.5, 142.9, 148.6, 153.5, 164.5; HRMS(FAB) [M + H]$^+$ calcd for $C_{12}H_{11}N_2O_5$ 263.0668, found 263.0669.

General Procedure for the Reactions of Glycine Ni(II) Complex (*S*)-1 with Michael Acceptors 2a−v. To a suspension of Ni(II) complex (*S*)-**1** (0.500 mmol) in DMF (2.0 mL) was added the corresponding Michael acceptor **2** (0.525 mmol). After the mixture was stirred for 10 min at ambient temperature, DBU (0.01 mL, 0.07 mmol) was added. The reaction was monitored by TLC (each sample was quenched with 5% aqueous acetic acid and the products were extracted with chloroform before being applied to the plate). Upon disappearance of the starting (*S*)-**1**, the reaction mixture was poured into icy 5% aqueous acetic acid (80 mL) and stirred with a glass bar to initiate crystallization of the product. The crystalline product was filtered off, thoroughly washed with water, and dried in vacuo to afford addition products **3** and **4**. The major diastereomeric products **3** were obtained in diastereomerically pure form by recrystallization of the reaction mixture from benzene/hexanes or by column chromatography on SiO_2 (eluent: acetone/chloroform 1/4). Minor reaction products **4** were obtained only by column chromatography on SiO_2. Diastereomers **4** always emerged first from the column. Yields and ratios of the diastereomeric products **3** and **4** are given in Table 1; physicochemical and NMR data are listed below.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*S*)-3-methyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3a): mp 241.0−242.0 °C; $[\alpha]^{25}_D$ +2665 (*c* 0.011, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.97 (3H, d, J = 6.6 Hz), 2.02−2.12 (2H, m), 2.41−2.59 (2H, m), 2.78−2.88 (3H, m), 3.34−3.54 (3H, m), 3.60 (1H, part of AB, J = 12.7 Hz), 3.80−3.87 (2H, m), 4.10 (1H, d, J = 5.1 Hz), 4.27−4.34 (2H, m), 4.44 (1H, part of AB, J = 12.7 Hz), 6.59−6.68 (2H, m), 6.98 (1H, d, J = 7.3 Hz), 7.11−7.18 (2H, m), 7.27−7.35 (3H, m), 7.43−7.57 (3H, m), 8.04 (2H, d, J = 7.3 Hz), 8.23 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.6, 23.1, 30.7, 33.7, 38.4, 42.4, 56.7, 61.8, 63.2, 70.4, 72.7, 120.6, 123.2, 126.3, 127.2, 128.1, 128.7, 129.1, 129.5, 131.5, 132.3, 133.2, 133.6, 134.0, 142.4, 153.1, 171.0, 171.3, 177.4, 180.3; HRMS(FAB) [M + H]$^+$ calcd for $C_{34}H_{35}N_4NiO_6$ 653.1910, found 653.1900.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*R*)-3-methyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4a): mp 206.0−207.0 °C; $[\alpha]^{25}_D$ −1277 (*c* 0.021, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.68−1.94 (2H, m), 1.82 (3H, d, J = 6.8 Hz), 2.10−2.20 (1H, m), 2.44−2.64 (3H, m), 2,77, 2.87 (2H, ABX, J = 6.7, 7.3, 17.1 Hz), 3.63−3.67 (1H, m), 3.83−4.09 (5H, m), 4.30−4.35 (2H, m), 4.88 (1H, part of AB, J = 13.4 Hz), 6.71−6.81 (2H, m), 7.12 (1H, d, J = 6.6 Hz), 7.23−7.31 (2H, m), 7.39−7.51 (6H, m), 7.64−7.67 (2H, m), 8.53 (1H, d, J = 8.5

(21) Belokon′, Y. N.; Tararov, V. I.; Maleev, V. I.; Savel′eva, T. F.; Ryzhov, M. G. *Tetrahedron*: *Asymmetry* **1998**, *9*, 4249.

Hz); ^{13}C NMR ($CDCl_3$) δ 16.4, 23.5, 30.9, 34.5, 38.6, 42.4, 56.4, 61.1, 61.9, 68.4, 73.1, 120.7, 123.6, 126.0, 127.0, 128.4, 128.6, 128.9, 129.0, 129.2, 129.5, 131.9, 132.0, 132.5, 133.9, 134.3, 142.9, 153.1, 171.0, 172.1, 177.8, 182.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{34}H_{35}N_4NiO_6$ 653.1910, found 653.1907.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*S*)-3-ethyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3b): mp 194.0−195.0 °C; $[\alpha]^{25}_D$ +2052 (*c* 0.032, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.05 (3H, t, *J* = 7.5 Hz), 1.84−1.94 (1H, m), 2.01−2.18 (2H, m), 2.31−2.42 (1H, m), 2.46−2.60 (1H, m), 2.77−3.01 (3H, m), 3.38−3.59 (4H, m), 3.56, 4.42 (2H, AB, *J* = 12.7 Hz), 3.73−3.87 (2H, m), 4.15−4.33 (3H, m), 6.58−6.68 (2H, m), 6.97−7.01 (1H, m), 7.10−7.17 (2H, m), 7.27−7.34 (3H, m), 7.44−7.58 (3H, m), 8.04 (2H, d, *J* = 7.1 Hz), 8.22 (1H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 11.8, 22.9, 23.3, 30.4, 34.5, 39.8, 42.2, 56.7, 61.8, 63.1, 70.3, 71.5, 120.4, 122.9, 126.2, 127.1, 128.0, 128.5, 128.6, 128.9, 129.2, 131.2, 132.0, 133.2, 133.4, 133.7, 142.1, 153.1, 171.1, 177.5, 180.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{35}H_{37}N_4NiO_6$ 667.2067, found 667.2065.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*R*)-3-ethyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4b): mp 152.0−153.0 °C; $[\alpha]^{25}_D$ −1446 (*c* 0.023, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.01 (3H, t, *J* = 7.3 Hz), 1.66−1.91 (3H, m), 2.05−2.08 (1H, m), 2.36−2.67 (3H, m), 2.87, 3.00 (2H, ABX, *J* = 4.9, 8.8, 17.3 Hz), 3.10−3.22 (1H, m), 3.69 (1H, part of ABX, *J* = 3.7, 9.5 Hz), 3.76−3.91 (2H, m), 3.96−4.36 (4H, m), 4.02, 4.90 (2H, AB, *J* = 13.4 Hz), 6.70−6.80 (2H, m), 7.10−7.31 (3H, m), 7.42−7.66 (8H, m), 8.55 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 12.1, 23.3, 23.5, 30.8, 35.0, 40.5, 42.7, 56.5, 60.8, 61.9, 68.5, 71.9, 120.7, 123.4, 126.0, 127.2, 128.5, 128.8, 129.0, 129.2, 129.4, 132.0, 132.5, 134.0, 134.2, 142.9, 153.4, 171.5, 171.9, 178.1, 182.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{35}H_{37}N_4NiO_6$ 667.2067, found 667.2074.

Ni(II) complex of Schiff base of (*S*)-BPB and (2*S*,3*S*)-3-*n*-propyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3c): mp 255.0−256.0 °C; $[\alpha]^{25}_D$ +2809 (*c* 0.017, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.08 (3H, t, *J* = 7.2 Hz), 1.21−1.42 (1H, m), 1.53−1.63 (1H, m), 1.83−2.14 (3H, m), 2.25−2.38 (1H, m), 2.48−2.61 (1H, m), 2.80−2.92 (1H, m), 2.85, 2.96 (2H, ABX, *J* = 4.4, 9.3, 17.3 Hz), 3.43−3.67 (4H, m), 3.59, 4.44 (2H, AB, *J* = 12.7 Hz), 3.71−3.86 (2H, m), 4.19−4.34 (3H, m), 6.58 (1H, part of ABX, *J* = 1.8, 8.3 Hz), 6.63−6.68 (1H, m), 6.95−6.98 (1H, m), 7.10−7.17 (2H, m), 7.27−7.34 (3H, m), 7.43−7.58 (3H, m), 8.03 (2H, d, *J* = 7.3 Hz), 8.23 (1H, d, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.2, 20.6, 22.9, 30.5, 32.8, 35.0, 38.0, 42.3, 56.6, 61.8, 63.2, 70.4, 71.6, 120.5, 123.0, 126.3, 127.2, 128.0, 128.5, 128.6, 128.9, 129.3, 131.3, 132.1, 133.1, 133.5, 133.9, 142.2, 153.2, 171.1, 171.2, 177.6, 180.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{36}H_{39}N_4NiO_6$ 681.2223, found 681.2239.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*R*)-3-*n*-propyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4c): mp 129.0−130.0 °C; $[\alpha]^{25}_D$ −1190 (*c* 0.032, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.03 (3H, t, *J* = 7.2 Hz), 1.30−1.96 (5H, m), 2.05−2.18 (1H, m), 2.43−2.68 (3H, m), 2.87, 3.02 (2H, ABX, *J* = 4.6, 8.8, 17.3 Hz), 3.20−3.31 (1H, m), 3.68 (1H, part of ABX, *J* = 3.8, 9.6 Hz), 3.75−4.01 (3H, m), 4.08, 4.97 (2H, AB, *J* = 13.3 Hz), 4.22−4.35 (3H, m), 6.70−6.79 (2H, m), 7.10−7.12 (1H, m), 7.20−7.31 (2H, m), 7.39−7.63 (8H, m), 8.53 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 14.3, 20.5, 23.5, 29.2, 30.9, 32.7, 35.5, 42.4, 56.1, 60.9, 61.9, 68.3, 72.0, 120.7, 123.4, 126.1, 127.1, 128.4, 128.6, 128.8, 129.0, 129.2, 129.4, 131.8, 132.1, 132.5, 133.9, 134.2, 142.8, 153.3, 171.4, 171.9, 178.2, 182.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{36}H_{39}N_4NiO_6$ 681.2223, found 681.2228.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*S*)-3-*i*-propyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3d): mp 155.0−156.0 °C; $[\alpha]^{25}_D$ +2699 (*c* 0.029, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.40 (3H, d, *J* = 6.8 Hz), 0.95 (3H, d, *J* = 6.8 Hz), 2.06−2.18 (2H, m), 2.43−2.70 (3H, m), 2.87−2.96 (1H, m), 2.92 (1H, part of ABX, *J* = 9.8, 18.1 Hz), 3.28−3.34 (1H, m), 3.40 (1H, part of AB, *J* = 12.5 Hz), 3.47 (1H, dd, *J* = 6.0, 11.2 Hz), 3.55−2.60 (1H, m), 3.70−3.92 (5H, m), 4.13−4.18 (1H, m), 4.39 (1H, part of AB, *J* = 12.7 Hz), 6.63−6.75 (2H, m), 7.00−7.11 (2H, m), 7.22−7.28 (4H, m), 7.48−7.58 (3H, m), 8.09 (2H, d, *J* = 7.3 Hz), 8.33 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.9, 21.9, 23.5, 27.1, 30.4, 30.7, 42.5, 45.4, 57.6, 62.3, 63.5, 70.7, 71.7, 120.5, 122.1, 125.4, 127.7, 128.4, 128.7, 129.1, 129.3, 129.7, 131.2, 132.5, 133.8, 134.1, 142.4, 153.4, 172.0, 172.4, 178.6, 180.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{36}H_{39}N_4NiO_6$ 681.2223, found 681.2242.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*R*)-3-isopropyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4d): mp 134.0−135.0 °C; $[\alpha]^{25}_D$ −2189 (*c* 0.015, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.38 (3H, d, *J* = 6.8 Hz), 0.96 (3H, d, *J* = 6.8 Hz), 1.44−1.61 (2H, m), 1.91−1.97 (1H, m), 2.18−2.28 (1H, m), 2.55−2.77 (3H, m), 3.10 (1H, part of ABX, *J* = 10.0, 18.3 Hz), 3.40−3.46 (1H, m), 3.76−4.06 (6H, m), 4.16 (1H, part of AB, *J* = 13.7 Hz), 4.22−4.27 (1H, m), 5.47 (1H, part of AB, *J* = 13.7 Hz), 6.73−6.89 (2H, m), 7.21−7.51 (11H, m), 8.62 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 16.0, 21.9, 23.7, 27.2, 31.0, 31.1, 42.7, 45.3, 55.5, 60.3, 62.4, 68.7, 71.9, 120.8, 122.7, 125.6, 127.8, 128.7, 128.8, 129.1, 129.3, 129.4, 129.7, 132.0, 132.2, 132.7, 134.0, 134.4, 142.9, 153.5, 171.9, 172.9, 178.8, 182.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{36}H_{39}N_4NiO_6$ 681.2223, found 681.2220.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-phenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3f): mp 158.0−159.0 °C; $[\alpha]^{25}_D$ +2303 (*c* 0.011, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.47−1.57 (1H, m), 1.94−2.04 (2H, m), 2.14−2.24 (2H, m), 2.89−2.97 (2H, m), 3,25 (1H, t, *J* = 8.6 Hz), 3.42 (1H, part of AB, *J* = 12.7 Hz), 3.46−3.52 (1H, m), 3.64−3.81 (3H, m), 4.22−4.31 (4H, m), 6.67 (2H, d, *J* = 3.9 Hz), 7.11−7.21 (3H, m), 7.25−7.38 (5H, m), 7.45−7.62 (6H, m), 7.98 (2H, d, *J* = 7.3 Hz), 8.27 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.1, 30.7, 37.3, 42.3, 44.9, 57.3, 61.8, 63.6, 70.4, 73.5, 120.5, 123.0, 125.9, 127.2, 127.9, 128.3, 128.7, 128.9, 129.0, 129.3, 129.6, 131.5, 132.5, 133.2, 133.7, 134.3, 138.8, 143.0, 153.0, 170.5, 171.7, 177.1, 180.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{37}N_4NiO_6$ 715.2067, found 715.2079.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-phenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4f): mp 164.0−165.5 °C; $[\alpha]^{25}_D$ −2102 (*c* 0.010, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.11−1.40 (2H, m), 1.79−1.86 (1H, m), 2.00−2.13 (1H, m), 2.46−2.55 (1H, m), 3.10 (1H, part of ABX, *J* = 6.6, 17.6 Hz), 3.33 (1H, part of ABX, *J* = 3.2, 9.5 Hz), 3.43 (1H, part of AB, *J* = 13.9 Hz), 3.48−3.54 (1H, m), 3.62 (1H, part of AB, *J* = 14.2 Hz), 3.66−3.84 (4H, m), 4.28 (2H, t, *J* = 8.3 Hz), 4.34 (1H, d, *J* = 3.9 Hz), 6.73−6.83 (2H, m), 7.15−7.17 (2H, m), 7.24−7.36 (6H, m), 7.50−7.61 (8H, m), 8.44 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.6, 31.3, 36.7, 42.3, 45.2, 55.1, 59.5, 61.8, 68.6, 73.7, 120.7, 123.5, 126.3, 127.2, 128.1, 128.3, 128.7, 128.8, 129.1, 129.3, 129.7, 130.3, 131.7, 131.9, 132.7, 133.9, 134.2, 139.0, 143.2, 153.0, 170.4, 171.6, 176.8, 181.6; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{37}N_4NiO_6$ 715.2067, found 715.2070.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-α-naphthyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3g): mp 185.0−186.0 °C; $[\alpha]^{25}_D$ +1768 (*c* 0.014, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.19−1.33 (2H, m), 1.47−1.59 (1H, m), 1.75−1.94 (2H, m), 2.58 (1H, part of ABX, *J* = 5.8, 11.4 Hz), 2.65 (1H, part of ABX, *J* = 4.4, 17.3 Hz), 3.03 (1H, part of ABX, *J* = 7.8, 9.3 Hz), 3.30, 4.11 (2H, AB, *J* = 12.7 Hz), 3.54−3.71 (2H, m), 4.16−4.34 (3H, m), 4.37 (1H, d, *J* = 2.9 Hz), 4.47−4.53 (1H, m), 6.67−6.80 (2H, m), 7.08−7.34 (8H, m), 7.44−7.63 (6H, m), 7.86−7.96 (4H, m), 8.32 (1H, d, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 22.7, 30.0, 38.6, 39.4, 42.0, 56.9, 61.6, 63.0, 70.0, 75.1, 120.0, 122.7, 123.2, 125.2, 125.7, 126.0, 126.9, 127.3, 127.8, 128.3, 128.5, 128.8, 129.1, 129.4, 131.1, 132.3, 133.0, 133.2, 133.4, 133.8, 133.9, 135.2, 142.8, 152.8, 170.0, 171.5, 176.7, 179.6; HRMS(FAB) $[M + H]^+$ calcd for $C_{43}H_{39}N_4NiO_6$ 765.2223, found 765.2236.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-α-naphthyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4g): mp 255.0−256.0 °C; $[\alpha]^{25}_D$ −1171 (*c* 0.033, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.04−1.30 (2H, m), 1.62−1.78 (1H, m), 1.98−2.32 (2H, m), 2.75−3.06 (4H, m), 3.50−3.76 (3H, m), 4.22−4.57 (5H, m), 6.76−7.01 (4H, m), 7.24−7.62 (13H, m), 7.78 (1H, d, *J* = 8.1 Hz), 7.95−8.01 (2H, m), 8.49 (1H, d, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 23.4, 31.0, 38.2, 40.3, 42.3, 54.3, 58.7, 61.9, 67.9, 75.9, 120.5, 123.6, 123.9, 125.5, 125.8, 126.1,

126.3, 126.5, 127.2, 127.7, 128.1, 128.5, 128.6, 128.9, 129.3, 129.6, 131.4, 131.8, 132.8, 133.6, 133.9, 134.1, 134.2, 135.4, 143.4, 153.1, 170.3, 171.7, 176.9, 181.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{43}H_{39}N_4NiO_6$ 765.2223, found 765.2231.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-*β*-naphthyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3h): mp 159.0−160.0 °C; $[\alpha]^{25}_D$ +1344 (*c* 0.018, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 0.76−1.00 (2H, m), 1.31−1.47 (1H, m), 1.73−1.84 (2H, m), 2.53−2.64 (1H, m), 2.98, 3.94 (2H, ABX, *J* = 5.9, 9.0, 17.3 Hz), 3.07 (1H, t, *J* = 8.6 Hz), 3.25, 4.13 (2H, AB, *J* = 12.5 Hz), 3.58−3.78 (3H, m), 4.18−4.30 (2H, m), 4.36 (1H, d, *J* = 3.9 Hz), 6.65−6.73 (2H, m), 7.08−7.17 (2H, m), 7.22−7.36 (4H, m), 7.43−7.64 (6H, m), 7.89−7.92 (4H, m), 7.96 (2H, d, *J* = 7.8 Hz), 8.23 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 22.3, 30.1, 37.1, 42.1, 44.8, 57.4, 61.7, 63.5, 70.1, 73.5, 120.2, 122.9, 125.7, 126.0, 126.2, 127.0, 127.4, 127.9, 128.1, 128.4, 128.5, 128.8, 129.1, 129.5, 131.3, 132.3, 133.1, 133.2, 133.5, 133.8, 134.1, 136.2, 142.9, 152.9, 170.2, 171.4, 176.9, 180.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{43}H_{39}N_4NiO_6$ 765.2223, found 765.2234.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-*β*-naphthyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4h): mp 162.0−163.0 °C; $[\alpha]^{25}_D$ −1208 (*c* 0.051, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 0.88−1.02 (1H, m), 1.12−1.26 (1H, m), 1.63−1.73 (1H, m), 1.84−2.00 (1H, m), 2.35−2.44 (1H, m), 2.63 (1H, part of AB, *J* = 14.1 Hz), 2.77−2.85 (1H, m), 3.06 (1H, part of AB, *J* = 14.1 Hz), 3.14 (1H, part of ABX, *J* = 6.1, 17.8 Hz), 3.64−3.79 (4H, m), 3.97 (1H, part of ABX, *J* = 8.4, 17.7 Hz), 4.21−4.33 (2H, m), 4.38 (1H, d, *J* = 3.7 Hz), 6.52 (2H, d, *J* = 7.3 Hz), 6.75−6.86 (2H, m), 7.12−7.57 (12H, m), 7.87−7.93 (2H, m), 8.02 (1H, d, *J* = 8.3 Hz), 8.10 (1H, s), 8.44 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 23.5, 31.2, 36.6, 42.2, 45.4, 54.8, 59.4, 61.8, 68.6, 73.9, 120.6, 123.5, 126.2, 126.6, 127.2, 127.7, 128.1, 128.2, 128.4, 128.9, 129.3, 129.7, 131.2, 131.6, 132.7, 133.3, 133.9, 134.1, 136.4, 143.3, 153.0, 170.3, 171.5, 176.7, 181.4; HRMS(FAB) $[M + H]^+$ calcd for $C_{43}H_{39}N_4NiO_6$ 765.2223, found 765.2237.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(2′-methoxyphenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (3i): mp 179.0−180.0 °C; $[\alpha]^{25}_D$ +2329 (*c* 0.018, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.40−1.54 (1H, m), 1.76−1.92 (1H, m), 1.97−2.24 (3H, m), 2.87−2.98 (1H, m), 2.98 (1H, part of ABX, *J* = 6.6, 17.6 Hz), 3.23−3.32 (1H, m), 3.30 (3H, s), 3.44 (1H, part of AB, *J* = 12.5 Hz), 3.64−3.80 (3H, m), 4.20−4.29 (5H, m), 6.64−6.71 (2H, m), 7.04−7.15 (4H, m), 7.24−7.30 (3H, m), 7.37−7.47 (3H, m), 7.51−7.61 (3H, m), 7.99 (2H, d, *J* = 7.1 Hz), 8.30 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 23.0, 30.6, 30.8, 36.5, 42.2, 54.8, 57.2, 61.7, 63.6, 70.1, 73.4, 110.4, 120.1, 121.3, 122.7, 125.9, 127.1, 127.6, 128.5, 128.6, 128.7, 128.9, 129.4, 131.4, 132.0, 133.2, 133.4, 134.4, 142.6, 152.9, 158.0, 170.5, 171.8, 177.3, 180.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{39}N_4NiO_7$ 745.2172, found 745.2180.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-(2′-methoxyphenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (4i): mp 169.0−170.0 °C; $[\alpha]^{25}_D$ −1889 (*c* 0.015, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.09−1.41 (2H, m), 1.78−1.85 (1H, m), 2.02−2.15 (1H, m), 2.45−2.54 (1H, m), 3.16 (1H, part of ABX, *J* = 7.1, 18.3 Hz), 3.30 (1H, part of ABX, *J* = 3.2, 9.5 Hz), 3.38 (3H, s), 3.48 (1H, part of AB, *J* = 14.2 Hz), 3.60−3.86 (5H, m), 4.23−4.31 (4H, m), 6.72−6.83 (2H, m), 7.08−7.36 (9H, m), 7.43−7.58 (6H, m), 8.41 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 23.6, 30.9, 31.2, 35.7, 36.3, 42.2, 54.8, 59.2, 61.7, 68.5, 74.1, 110.3, 120.3, 121.4, 123.2, 126.4, 127.1, 127.9, 128.5, 128.6, 128.7, 128.8, 128.9, 129.4, 129.5, 131.8, 132.1, 133.6, 134.3, 142.9, 153.0, 158.4, 170.5, 171.9, 177.0, 181.5; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{39}N_4NiO_7$ 745.2172, found 745.2185.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(3′-methoxyphenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (3j): mp 271.0−272.0 °C; $[\alpha]^{25}_D$ +2309 (*c* 0.016, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.51−1.63 (1H, m), 1.98−2.27 (4H, m), 2.87 (1H, part of ABX, *J* = 6.0, 17.2 Hz), 2.99 (1H, part of ABX, *J* = 5.8, 10.9 Hz), 3.24−3.29 (1H, m), 3.43 (1H, part of AB, *J* = 12.5 Hz), 3.43−3.49 (1H, m), 3.64−3.85 (3H, m), 3.75 (3H, s), 4.24−4.29 (4H, m), 6.66−6.68 (2H, m), 6.90−7.01 (3H, m), 7.11−7.20 (3H, m), 7.25−7.40 (4H, m), 7.52−7.60 (3H, m), 7.99 (2H, d, *J* = 7.1 Hz), 8.29 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 23.1, 30.7, 37.1, 42.3, 45.1, 55.1, 57.3, 61.8, 63.5, 70.4, 73.4, 114.0, 114.2, 120.4, 122.1, 123.0, 125.8, 127.2, 128.3, 128.6, 128.9, 129.2, 129.6, 129.8, 131.5, 132.4, 133.2, 133.7, 134.2, 140.2, 143.0, 153.0, 159.9, 170.4, 171.6, 177.1, 180.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{39}N_4NiO_7$ 745.2172, found 745.2161.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-(3′-methoxyphenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (4j): mp 267.0−268.0 °C; $[\alpha]^{25}_D$ −2005 (*c* 0.021, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.17−1.43 (2H, m), 1.82−1.89 (1H, m), 2.09−2.18 (1H, m), 2.43−2.52 (1H, m), 3.01 (1H, part of ABX, *J* = 6.3, 17.6 Hz), 3.36 (1H, dd, *J* = 3.4, 9.5 Hz), 3.46−3.51 (1H, m), 3.54 (1H, part of AB, *J* = 14.2 Hz), 3.63 (3H, s), 3.71−3.90 (5H, m), 4.25−4.32 (3H, m), 6.73−6.84 (2H, m), 7.00−7.08 (3H, m), 7.18−7.56 (12H, m), 8.49 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 23.6, 31.2, 36.6, 42.2, 45.3, 54.9, 55.0, 59.5, 61.8, 68.4, 73.7, 114.1, 114.8, 120.6, 122.5, 123.5, 126.1, 127.2, 128.3, 128.7, 129.3, 129.7, 129.8, 131.6, 131.9, 132.7, 133.9, 134.1, 140.4, 143.2, 153.0, 160.1, 170.4, 171.5, 176.8, 181.6; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{39}N_4NiO_7$ 745.2172, found 745.2174.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(4′-methoxyphenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (3k): mp 155.0−156.0 °C; $[\alpha]^{25}_D$ +2294 (*c* 0.013, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.49−1.60 (1H, m), 1.97−2.24 (4H, m), 2.87 (1H, part of ABX, *J* = 5.9, 17.3 Hz), 3.00 (1H, part of ABX, *J* = 5.3, 10.2 Hz), 3.24−3.46 (3H, m), 3.64−3.80 (3H, m), 3.83 (3H, s), 4.23−4.28 (4H, m), 6.66 (2H, d, *J* = 3.9 Hz), 7.02 (2H, d, *J* = 8.1 Hz), 7.10−7.32 (8H, m), 7.52−7.59 (3H, m), 8.00 (2H, d, *J* = 7.3 Hz), 8.25 (1H, d, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$) *δ* 22.9, 30.6, 37.2, 42.2, 44.2, 55.2, 57.4, 61.8, 63.6, 70.4, 73.6, 114.2, 120.4, 122.9, 125.9, 127.2, 128.2, 128.6, 128.8, 129.2, 129.6, 130.6, 131.5, 132.3, 133.2, 133.6, 134.2, 142.9, 153.0, 159.3, 170.4, 171.4, 177.1, 180.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{39}N_4NiO_7$ 745.2172, found 745.2179.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-(4′-methoxyphenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (4k): mp 154.0−155.0 °C; $[\alpha]^{25}_D$ −2047 (*c* 0.018, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.14−1.45 (2H, m), 1.79−2.13 (2H, m), 2.48−2.57 (1H, m), 3.04 (1H, part of ABX, *J* = 6.6, 17.6 Hz), 3.35 (1H, dd, *J* = 3.2, 9.5 Hz), 3.43−3.50 (1H, m), 3.48 (1H, party of AB, *J* = 13.9 Hz), 3.65 (3H, s), 3.71−3.84 (5H, m), 4.25−4.31 (3H, m), 6.73−6.82 (2H, m), 7.09 (2H, part of AB, *J* = 8.5 Hz), 7.17−7.36 (8H, m), 7.44 (2H, part of AB, *J* = 8.8 Hz), 7.54−7.56 (3H, m), 8.44 (1H, d, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) *δ* 23.6, 31.3, 36.7, 42.2, 44.4, 54.9, 55.0, 59.6, 61.8, 68.5, 73.8, 114.2, 120.6, 123.4, 126.3, 127.2, 128.2, 128.6, 128.7, 128.8, 129.2, 129.7, 130.7, 131.2, 131.6, 131.9, 132.6, 133.9, 134.1, 143.2, 153.0, 159.5, 170.4, 171.4, 176.8, 181.6; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{39}N_4NiO_7$ 745.2172, found 745.2181.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(2′-trifluoromethylphenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3l): mp 166.0−167.0 °C; $[\alpha]^{25}_D$ +1989 (*c* 0.019, $CHCl_3$); ^{1}H NMR ($CDCl_3$) *δ* 1.64−1.80 (1H, m), 1.96−2.05 (1H, m), 2.26−2.52 (2H, m), 2.60−2.76 (1H, m), 3.10−3.18 (1H, m), 3.11 (1H, part of ABX, *J* = 6.4, 16.4 Hz), 3.34 (1H, dd, *J* = 7.0, 9.9 Hz), 3.40 (1H, part of AB, *J* = 12.7 Hz), 3.47 (1H, part of ABX, *J* = 7.6, 17.1 Hz), 3.67−3.72 (2H, m), 4.06 (1H, dd, *J* = 8.4, 16.8 Hz), 4.16−4.42 (4H, m), 6.63−6.72 (2H, m), 7.07−7.17 (3H, m), 7.24−7.34 (4H, m), 7.43−7.56 (5H, m), 7.79 (1H, d, *J* = 7.6 Hz), 8.01 (2H, d, *J* = 7.1 Hz), 8.37 (1H, d, *J* = 8.5 Hz); ^{19}F NMR ($CDCl_3$) *δ* −58.2 (3F, s); ^{13}C NMR ($CDCl_3$) *δ* 23.0, 30.5, 38.7, 40.6, 42.1, 57.1, 61.8, 63.2, 70.5, 74.4, 120.1, 122.4, 125.3, 126.1 (q, *J* = 6.0 Hz), 127.1, 127.4, 128.1, 128.3, 128.4, 129.0, 129.1, 129.5, 129.7, 131.1, 132.2, 132.3, 133.3, 133.7, 133.8, 138.2, 142.7, 152.9, 169.3, 172.5, 176.6, 179.9; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{36}F_3N_4NiO_6$ 783.1940, found 783.1934.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-(2′-trifluoromethylphenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4l): mp 160.0−161.5 °C; $[\alpha]^{25}_D$ −1401

(*c* 0.025, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.28−1.42 (2H, m), 1.62−1.78 (1H, m), 1.87−1.96 (1H, m), 2.10−2.22 (1H, m), 2.38−2.64 (1H, m), 3.29 (1H, dd, J = 5.6, 7.8 Hz), 3.53−3.55 (1H, m), 3.63 (1H, part of AB, J = 13.9 Hz), 3.73−3.78 (3H, m), 3.90−4.06 (1H, m), 4.19−4.37 (4H, m), 6.71−6.83 (2H, m), 6.91−7.09 (1H, m), 7.37−7.53 (13H, m), 7.84 (1H, d, J = 7.6 Hz), 8.57 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −58.1 (3F, s); ^{13}C NMR ($CDCl_3$) δ 23.7, 31.4, 38.7, 41.0, 42.3, 55.0, 60.1, 62.0, 68.5, 74.7, 120.6, 123.3, 126.0, 126.6 (q, J = 6.6 Hz), 127.3, 127.7, 128.4, 128.7, 128.9, 129.2, 129.7, 130.4, 131.6, 132.0, 132.5, 132.9, 134.0, 134.1, 138.2, 143.2, 153.2, 169.7, 173.3, 177.2, 181.8; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{36}F_3N_4NiO_6$ 783.1940, found 783.1942.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(3′-trifluoromethylphenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3m): mp 164.0−165.0 °C; $[\alpha]^{25}_D$ +1902 (*c* 0.022, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.54−1.66 (2H, m), 1.92−2.32 (3H, m), 2.92−3.01 (2H, m), 3.28 (1H, part of ABX, J = 6.8, 9.5 Hz), 3.41 (1H, part of AB, J = 12.7 Hz), 3.59−3.82 (4H, m), 4.23−4.30 (4H, m), 6.65−6.72 (2H, m), 7.11−7.22 (3H, m), 7.26−7.37 (3H, m), 7.48−7.72 (7H, m), 7.98 (2H, d, J = 7.1 Hz), 8.32 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −63.4 (3F, s); ^{13}C NMR ($CDCl_3$) δ 22.9, 30.3, 37.2, 42.1, 44.9, 57.2, 61.8, 63.3, 70.1, 73.2, 120.3, 122.8, 124.6 (q, J = 4.1 Hz), 125.4, 127.0, 128.1, 128.5, 128.8, 129.0, 129.2, 129.6, 131.2, 132.5, 133.2, 133.4, 133.6, 133.9, 140.1, 152.9, 169.8, 172.0, 176.5, 180.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{36}F_3N_4NiO_6$ 783.1940, found 783.1959.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-(3′-trifluoromethylphenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4m): mp 166.0−167.0 °C; $[\alpha]^{25}_D$ −957.2 (*c* 0.021, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.33−1.47 (2H, m), 1.87−1.94 (1H, m), 2.23−2.42 (2H, m), 3.00 (1H, part of ABX, J = 5.6, 17.6 Hz), 3.32 (1H, part of ABX, J = 4.2, 9.8 Hz), 3.46 (1H, part of AB, J = 13.7 Hz), 3.59−3.90 (6H, m), 4.28−4.33 (3H, m), 6.75−6.88 (2H, m), 7.13−7.17 (2H, m), 7.29−7.37 (6H, m), 7.56−7.71 (7H, m), 8.58 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −63.4 (3F, s); ^{13}C NMR ($CDCl_3$) δ 23.6, 31.3, 36.7, 42.3, 45.6, 54.7, 59.3, 61.9, 67.9, 73.8, 120.8, 123.6, 124.8, 125.6, 126.6 (q, J = 4.0 Hz), 127.1, 128.4, 128.7, 128.9, 129.4, 130.8, 131.1, 131.5, 132.0, 133.0, 133.2, 133.9, 134.2, 140.2, 143.4, 153.0, 170.0, 172.4, 176.6, 182.0; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{36}F_3N_4NiO_6$ 783.1940, found 783.1939.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(4′-trifluoromethylphenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3n): mp 179.0−180.5 °C; $[\alpha]^{25}_D$ +2152 (*c* 0.028, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.50−1.62 (1H, m), 1.86−1.95 (2H, m), 2.08−2.30 (2H, m), 2.83 (1H, part of ABX, J = 5.5, 17.7 Hz), 2.89−2.94 (1H, m), 3.25 (1H, dd, J = 7.4, 9.6 Hz), 3.43 (1H, part of AB, J = 12.7 Hz), 3.51−3.58 (1H, m), 3.65−3.84 (3H, m), 4.20−4.30 (4H, m), 6.68(2H, d, J = 3.9 Hz), 7.10−7.34 (6H, m), 7.47 (2H, part of AB, J = 8.1 Hz), 7.54−7.64 (3H, m), 7.75 (2H, part of AB, J = 8.1 Hz), 7.97 (2H, d, J = 7.1 Hz), 8.31 (1H, d, J = 8.8 Hz); ^{19}F NMR ($CDCl_3$) δ −63.5 (3F, s); ^{13}C NMR ($CDCl_3$) δ 22.7, 30.5, 37.1, 42.1, 44.7, 57.0, 61.8, 63.4, 70.2, 73.1, 120.4, 122.9, 125.6, 125.7 (q, J = 4.0 Hz), 127.0, 128.1, 128.6, 128.8, 129.3, 129.7, 129.8, 131.3, 132.6, 133.2, 133.6, 134.1, 142.9, 143.0, 152.9, 169.8, 172.0, 176.6, 180.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{36}F_3N_4NiO_6$ 783.1940, found 783.1973.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-(4′-trifluoromethylphenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4n): mp 170.0−171.0 °C; $[\alpha]^{25}_D$ −1690 (*c* 0.014, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.32−1.49 (2H, m), 1.82−1.92 (1H, m), 2.14−2.26 (1H, m), 2.38−2.47 (1H, m), 3.02 (1H, part of ABX, J = 5.9, 17.8 Hz), 3.34 (1H, dd, J = 3.7, 9.5 Hz), 3.50 (1H, part of AB, J = 13.7 Hz), 3.58−3.90 (6H, m), 4.28−4.33 (3H, m), 6.75−6.86 (2H, m), 7.14−7.17 (2H, m), 7.24−7.36 (6H, m), 7.56−7.59 (5H, m), 7.79 (2H, d, J = 8.1 Hz), 8.54 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −63.2 (3F, s); ^{13}C NMR ($CDCl_3$) δ 23.7, 31.4, 36.8, 42.3, 45.3, 54.7, 59.6, 61.9, 68.3, 73.6, 120.8, 123.4, 125.7 (q, J = 4.1 Hz), 127.2, 128.3, 128.7, 128.9, 129.5, 129.9, 130.3, 130.8, 131.9, 133.0, 134.0, 134.2, 143.2, 143.4, 153.0, 170.0, 172.2, 176.7, 182.0; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{36}F_3N_4NiO_6$ 783.1940, found 783.1952.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-[3′-(1′-mesitylenesulfonyl)]indolyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3o): mp 185.0−186.0 °C; $[\alpha]^{25}_D$ +1815 (*c* 0.025, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.12−1.46 (2H, m), 1.52−1.96 (3H, m), 2.26 (3H, s), 2.55 (6H, s), 2.65−2.86 (2H, m), 3.10−3.15 (1H, m), 3.32 (1H, part of AB, J = 12.7 Hz), 3.66−3.91 (4H, m), 4.21−4.34 (4H, m), 6.66−6.77 (2H, m), 6.93 (2H, s), 7.05−7.44 (10H, m), 7.54−7.64 (4H, m), 7.96 (2H, d, J = 7.1 Hz), 8.33 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.9, 22.6, 22.7, 30.1, 37.4, 37.6, 42.3, 57.5, 61.9, 63.2, 70.0, 73.8, 112.3, 117.5, 120.3, 120.7, 122.9, 123.2, 124.6, 125.4, 125.5, 127.1, 128.1, 128.5, 129.0, 129.4, 129.6, 131.3, 132.3, 132.5, 132.7, 133.3, 133.6, 134.2, 134.8, 140.2, 143.1, 143.9, 153.0, 170.0, 171.8, 177.2, 180.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{50}H_{48}N_5NiO_8S$ 936.2577, found 936.2597.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-[3′-(1′-mesitylenesulfonyl)]indolyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4o): mp 174.0−175.0 °C; $[\alpha]^{25}_D$ −1541 (*c* 0.031, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.05−1.38 (2H, m), 1.61−1.88 (2H, m), 2.13 (3H, s), 2.27−2.40 (1H, m), 2.49 (6H, s), 2.57−2.70 (1H, m), 2.86−3.07 (3H, m), 3.74−4.09 (5H, m), 4.29−4.34 (3H, m), 6.76−6.91 (6H, m), 7.22−7.35 (9H, m), 7.55−7.61 (4H, m), 7.75 (1H, d, J = 6.1 Hz), 8.55 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 21.1, 22.6, 23.4, 31.1, 37.1, 38.8, 42.4, 54.5, 58.8, 61.9, 68.2, 74.4, 112.5, 117.6, 120.8, 122.0, 123.0, 124.0, 124.6, 125.5, 125.8, 127.1, 128.2, 128.5, 129.0, 129.5, 129.7, 131.1, 131.9, 132.2, 132.3, 132.9, 133.9, 134.3, 135.3, 140.2, 143.3, 144.0, 153.0, 170.2, 172.1, 177.3, 181.7; HRMS(FAB) $[M + H]^+$ calcd for $C_{50}H_{48}N_5NiO_8S$ 936.2577, found 936.2569.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-pentafluorophenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3p): mp 165.0−166.0 °C; $[\alpha]^{25}_D$ +2008 (*c* 0.042, $CHCl_3$);^1H NMR ($CDCl_3$) δ 2.10−2.36 (2H, m), 2.49−2.63 (1H, m), 2.76−2.88 (1H, m), 3.02, 3.23 (2H, ABX, J = 4.2, 10.5, 18.6 Hz), 3.42, 4.33 (2H, AB, J = 12.7 Hz), 3.48−3.54 (2H, m), 3.72−4.00 (3H, m), 4.09 (1H, d, J = 10.7 Hz), 4.26−4.38 (2H, m), 5.52 (1H, ddd, J = 4.2 Hz), 6.68−6.73 (1H, m), 6.79 (1H, part of ABX, J = 1.7, 8.3 Hz), 7.08−7.18 (2H, m), 7.22−7.34 (4H, m), 7.51−76.0(3H, m), 8.10 (2H, d, J = 7.1 Hz), 8.21 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −162.9 (m), −162.4 (m), −155.9 (m), −142.2 (m), −141.3 (m); ^{13}C NMR ($CDCl_3$) δ 23.5, 30.6, 35.7, 38.0, 42.1, 57.5, 62.2, 63.1, 70.6, 71.1, 112.6 (m), 120.6, 122.6, 125.5, 127.4, 128.5, 128.6, 128.8, 129.0, 129.4, 130.1, 131.0, 132.7, 132.9, 133.5, 134.1, 135.5 (m), 138.6 (m), 141.9 (m), 142.7, 143.2 (m), 147.0 (m), 153.0, 169.8, 172.6, 175.6, 180.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{32}F_5N_4NiO_6$ 805.1595, found 805.1603.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*,3*S*)-3-pentafluorophenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4p): mp 161.5−162.0 °C; $[\alpha]^{25}_D$ −1651 (*c* 0.021, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.60−1.79 (2H, m), 1.97−2.09 (1H, m), 2.15−2.30 (1H, m), 2.75−2.84 (1H, m), 3.21, 3.36 (2H, ABX, J = 4.6, 10.0, 18.3 Hz), 3.72−4.13 (4H, m), 3.78, 4.80 (2H, AB, J = 13.2 Hz), 4.17 (1H, d, J = 10.0 Hz), 4,31−4.43 (2H, m), 5.16 (1H, td, J = 4.6, 10.0 Hz), 6.75−6.80 (1H, m), 6.93 (1H, d, J = 8.1 Hz), 7.22−7.34 (3H, m), 7.40−7.73 (8H, m), 8.60 (1H, d, J = 8.8 Hz); ^{19}F NMR ($CDCl_3$) δ −163.0 (m), −162.4 (m), −156.0 (m), −141.7 (m), −140.6 (m); ^{13}C NMR ($CDCl_3$) δ 23.3, 30.7, 36.0, 37.2, 42.4, 56.6, 60.0, 62.4, 68.3, 71.4, 130.0 (m), 120.9, 122.9, 125.4, 127.5, 128.4, 128.5, 129.1, 129.2, 129.7, 130.2, 131.8, 131.9, 132.0, 132.1, 133.4, 133.5, 134.8, 135.6 (m), 138.9 (m), 140.1 (m), 143.4, 144.8 (m), 147.2 (m), 153.4, 170.0, 173.8, 176.4, 181.9; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{32}F_5N_4NiO_6$ 805.1595, found 805.1609.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*,3*R*)-3-(2′,6′-difluorophenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (3q): mp 168.5−170.0 °C; $[\alpha]^{25}_D$ +2323 (*c* 0.031, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.00−2.17 (2H, m), 2.38−2.68 (2H, m), 3.17 (1H, part of ABX, J = 5.4, 18.3 Hz), 3.30−3.47 (5H, m), 3.76−3.92 (2H, m), 4.19−4.36 (4H, m), 5.10−5.18 (1H, m), 6.65−6.98 (4H, m), 7.08−7.31 (7H, m), 7.50−7.57 (3H, m), 8.06 (2H, d, J = 7.3 Hz), 8.25 (1H, d, J = 8.8 Hz); ^{19}F NMR ($CDCl_3$) δ −113.4 (1F, s), −110.7 (1F, s); ^{13}C NMR ($CDCl_3$) δ 23.2, 30.6, 35.6, 36.9, 42.1, 57.2, 62.0, 63.1,

70.5, 71.5, 111.2 (d, J = 23.2 Hz), 111.9 (d, J = 20.1 Hz), 114.8 (t, J = 17.7 Hz), 120.3, 122.5, 125.6, 127.4, 128.4, 128.5, 128.7, 128.8, 129.0, 129.1, 129.3, 129.7, 131.1, 132.3, 133.3, 133.8, 142.6, 153.0, 159.9 (d, J = 8.1 Hz), 163.2 (d, J = 8.0 Hz), 170.2, 172.1, 176.2, 180.0; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{35}F_2N_4NiO_6$ 751.1878, found 751.1884.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*, 3*S*)-3-(2′,6′-difluorophenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (4q): mp 174.0−175.0 °C; $[\alpha]^{25}_D$ −1587 (*c* 0.052, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.29−1.51 (2H, m), 1.85−1.93 (1H, m), 2.06−2.21 (1H, m), 2.60−2.70 (1H, m), 3.39−3.49 (2H, m), 3.59 (1H, part of ABX, J = 7.6, 18.3 Hz), 3.75−4.01 (4H, m), 4.23−4.34 (4H, m), 4.41−4.51 (1H, m), 6.72−6.84 (2H, m), 6.94−7.16 (2H, m), 7.25−7.46 (9H, m), 7.53−7.56 (3H, m), 8.48 (1H, d, J = 8.8 Hz); ^{19}F NMR ($CDCl_3$) δ −111.8 (1F, s), −107.9 (1F, s); ^{13}C NMR ($CDCl_3$) δ 23.4, 31.1, 35.3, 36.0, 42.2, 55.4, 59.7, 62.0, 68.5, 71.7, 111.8 (m), 112.5 (m), 115.3 (t, J = 17.1 Hz), 120.5, 122.9, 125.9, 127.2, 128.7, 128.8, 129.0, 129.2, 129.3, 129.7, 131.7, 132.6, 133.7, 134.0, 143.1, 153.0, 160.9 (m), 164.0 (m), 170.3, 172.7, 176.6, 181.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{35}F_2N_4NiO_6$ 751.1878, found 751.1896.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*, 3*R*)-3-(2′-fluorophenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3r): mp 272.0−273.0 °C; $[\alpha]^{25}_D$ +2490 (*c* 0.016, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.49−1.72 (1H, m), 1.93−2.28 (4H, m), 2.95−3.05 (2H, m), 3.26 (1H, m), 3.47 (1H, part of AB, J = 12.5 Hz), 3.62−3.82 (3H, m), 3.99−4.06 (1H, m), 4.24−4.34 (4H, m), 6.66 (2H, d, J = 3.9 Hz), 7.11−7.31 (8H, m), 7.40−7.60 (5H, m), 7.96 (2H, d, J = 7.1 Hz), 8.32 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −166.7 (1F, s); ^{13}C NMR ($CDCl_3$) δ 22.8, 30.5, 35.7, 36.5, 42.1, 56.9, 61.7, 63.3, 70.2, 72.5, 115.3, 115.6, 120.1, 122.6, 124.8 (d, J = 3.1 Hz), 125.8, 126.1, 126.9, 128.4, 128.7, 128.8, 129.0, 129.1, 129.3 (d, J = 3.0 Hz), 131.3, 132.2, 133.0, 133.5, 134.0, 142.8, 152.9, 159.8, 163.1, 169.6, 172.4, 176.9, 180.8; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{36}FN_4NiO_6$ 733.1972, found 733.1987.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*, 3*S*)-3-(2′-fluorophenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4q): mp 279.0−280.0 °C; $[\alpha]^{25}_D$ −1887 (*c* 0.025, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.16−1.42 (2H, m), 1.83−1.90 (1H, m), 2.01−2.23 (1H, m), 2.43−2.53 (1H, m), 3.18 (1H, part of ABX, J = 6.8, 17.8 Hz), 3.31 (1H, part of ABX, J = 3.4, 9.5 Hz), 3.51 (1H, part of AB, J = 13.9 Hz), 3.63−3.84 (5H, m), 4.01−4.07 (1H, m), 4.27−4.33 (2H, m), 4.37 (1H, d, J = 4.4 Hz), 6.71−6.81 (2H, m), 7.15−7.18 (2H, m), 7.25−7.61 (13H, m), 8.45 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −116.1 (1F, s); ^{13}C NMR ($CDCl_3$) δ 23.5, 31.2, 36.0, 36.1, 42.2, 54.9, 59.5, 61.8, 68.4, 72.9, 115.6, 115.9, 120.5, 123.2, 125.1 (d, J = 3.0 Hz), 126.3, 126.6, 126.8, 127.0, 128.6, 128.7, 128.8, 129.0, 129.2, 129.3, 129.6, 129.9 (d, J = 3.0 Hz), 131.5, 131.8, 132.5, 133.8, 134.1, 143.1, 153.0, 160.4, 163.6, 170.0, 172.6, 176.8, 181.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{36}FN_4NiO_6$ 733.1972, found 733.1977.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*, 3*R*)-3-(3′,4′-difluorophenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (3s): mp 146.0−147.0 °C; $[\alpha]^{25}_D$ +2581 (*c* 0.023, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.68−1.78 (1H, m), 1.99−2.08 (1H, m), 2.21−2.39 (3H, m), 2.81 (1H, part of ABX, J = 5.4, 17.6 Hz), 3.02−3.11 (1H, m), 3.29−3.34 (1H, m), 3.45 (1H, part of AB, J = 12.7 Hz), 3.50−3.55 (1H, m), 3.62−3.84 (3H, m), 4.23−4.32 (4H, m), 6.68 (2H, d, J = 4.4 Hz), 6.95−7.06 (1H, m), 7.12−7.32 (8H, m), 7.51−7.63 (3H, m), 7.99 (2H, d, J = 7.3 Hz), 8.29 (1H, d, J = 8.8 Hz); ^{19}F NMR ($CDCl_3$) δ −140.1 (1F, m), −137.4 (1F, m); ^{13}C NMR ($CDCl_3$) δ 22.9, 30.8, 37.5, 42.2, 44.4, 57.3, 61.9, 63.6, 70.4, 73.2, 117.4 (d, J = 16.1 Hz), 118.0 (d, J = 17.1 Hz), 120.6, 123.1, 125.7, 125.9 (m), 127.1, 128.2, 128.7, 128.9, 129.4, 129.8, 131.4, 132.7, 133.2, 133.7, 134.1, 136.0 (m), 143.0, 148.8 (m), 152.1 (m), 153.0, 170.0, 172.0, 176.7, 180.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{35}F_2N_4NiO_6$ 751.1878, found 751.1856.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*, 3*S*)-3-(3′,4′-difluorophenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (4s): mp 151.0−152.0 °C; $[\alpha]^{25}_D$ −1618 (*c* 0.020, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.29−1.49 (3H, m), 1.87−1.94 (1H, m), 2.09−2.24 (1H, m), 2.52−2.64 (1H, m), 2.94−3.02 (1H, m), 3.45 (1H, part of ABX, J = 3.4, 9.5 Hz), 3.51−3.57 (1H, m), 3.63 (1H, part of AB, J = 13.9 Hz), 3.70−3.89 (3H, m), 3.94 (1H, part of AB, J = 13.7 Hz), 4.27−4.34 (3H, m), 6.74−6.84 (2H, m), 7.12−7.40 (11H, m), 7.46−7.62 (3H, m), 8.47 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −139.7 (1F, m), −137.4 (1F, m); ^{13}C NMR ($CDCl_3$) δ 23.5, 31.2, 36.9, 42.2, 44.6, 55.3, 60.1, 61.9, 68.4, 73.4, 117.4 (d, J = 17.1 Hz), 118.3 (d, J = 17.1 Hz), 120.7, 123.5, 125.8, 126.2, 127.0, 128.2, 128.4, 128.7, 128.9, 129.4, 129.8, 129.9, 131.2, 131.7, 132.9, 133.9 (m), 136.1 (m), 143.1, 144.2 (m), 146.0 (m), 153.0, 169.9, 172.1, 176.6, 181.5; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{35}F_2N_4NiO_6$ 751.1878, found 751.1876.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*, 3*R*)-3-(4′-methoxy-2′,3′,5′,6′-tetrafluorophenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3t): mp 161.0−162.0 °C; $[\alpha]^{25}_D$ +1873 (*c* 0.034, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.10−2.31 (2H, m), 2,47−2.61 (1H, m), 2.74−2.83 (1H, m), 3.04, 3.25 (2H, ABX, J = 4.4, 10.3, 18.6 Hz), 3.44 (1H, part of AB, J = 12.7 Hz), 3.48−3.54 (2H, m), 3.67−3.99 (3H, m), 4.02 (3H, s), 4.11 (1H, d, J = 10.3 Hz), 4.25−4.35 (2H, m), 4.34 (1H, part of AB, J = 12.5 Hz), 5.43 (1H, dt, J = 4.2, 10.3 Hz), 6.67−6.99 (2H, m), 7.09−7.18 (2H, m), 7.23−7.32 (4H, m), 7.46−7.61 (3H, m), 8.09 (2H, d, J = 7.3 Hz), 8.22 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −159.0 (2F, m), −158.3 (1F, m), −143.4 (1F, m); ^{13}C NMR ($CDCl_3$) δ 23.5, 30.7, 35.8, 37.9, 42.2, 57.5, 61.8, 62.2, 63.2, 70.6, 71.4, 110.5 (t, J = 16.1 Hz), 120.6, 122.6, 125.6, 127.5, 128.3, 128.6, 128.7, 128.9, 129.0, 129.4, 129.9, 130.1, 131.1, 131.7, 132.7, 133.1, 133.4, 134.2, 137.5 (m), 139.0 (m), 142.3 (m), 142.7, 143.8 (m), 146.9 (m), 153.1, 170.0, 172.4, 175.9, 180.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{35}F_4N_4NiO_7$ 817.1795, found 817.1800.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*, 3*S*)-3-(4′-methoxy-2′,3′,5′,6′-tetrafluorophenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4t): mp 163.0−164.0 °C; $[\alpha]^{25}_D$ −909.8 (*c* 0.022, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.54−1.69 (2H, m), 1.97−2.05 (1H, m), 2.14−2.28 (1H, m), 2.71−2.80 (1H, m), 3.26, 3.41 (2H, ABX, J = 5.1, 9.3, 18.3 Hz), 3.49 (1H, d, J = 4.4 Hz), 3.69 (1H, dd, J = 3.5, 9.1 Hz), 3.83 (1H, part of AB, J = 13.4 Hz), 3.88−4.11 (2H, m), 4.00 (3H, s), 4.20 (1H, d, J = 8.8 Hz), 4.33−4.39 (2H, m), 4.72 (1H, part of AB, J = 13.4 Hz), 4.96 (1H, ddd, J = 5.6, 8.8, 9.3 Hz), 6.74−6.92 (2H, m), 7.24−7.61 (11H, m), 8.57 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −159.0 (2F, m), −158.3 (1F, m), −142.2 (1F, m); ^{13}C NMR ($CDCl_3$) δ 23.2, 30.7, 35.7, 36.8, 42.2, 56.1, 59.9, 61.8, 62.1, 68.2, 71.4, 110.7 (t, J = 16.1 Hz), 120.7, 122.8, 125.4, 127.2, 128.6, 128.9, 129.0, 129.2, 129.9, 131.7, 133.0, 133.5, 134.4, 137.5 (m), 138.9 (m), 142.1 (m), 143.2, 144.2 (m), 147.5 (m), 153.2, 169.9, 173.3, 176.4, 181.5; HRMS(FAB) $[M + H]^+$ calcd for $C_{40}H_{35}F_4N_4NiO_7$ 817.1795, found 817.1894.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*, 3*R*)-3-(3′,4′-dichlorophenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (3u): mp 166.0−167.0 °C; $[\alpha]^{25}_D$ +1942 (*c* 0.031, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.01−2.35 (5H, m), 2.83 (1H, part of ABX, J = 5.5, 17.7 Hz), 2.99−3.06 (1H, m), 3.30 (1H, dd, J = 7.5, 9.2 Hz), 3.40−3.47 (2H, m), 3.65−3.83 (3H, m), 4.22−4.33 (4H, m), 6.68 (2H, d, J = 3.9 Hz), 7.11−7.18 (4H, m), 7.26−7.32 (4H, m), 7.47 (1H, d, J = 2.0 Hz), 7.53−7.63 (3H, m), 8.00 (2H, d, J = 8.3 Hz), 8.30 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 22.9, 30.8, 37.2, 42.2, 44.3, 57.6, 61.9, 63.7, 70.4, 73.2, 120.5, 123.1, 125.6, 127.1, 128.1, 128.7, 128.9, 129.3, 129.4, 129.8, 130.7, 131.0, 131.4, 132.3, 132.7, 133.2, 133.3, 133.7, 134.1, 139.3, 143.1, 153.0, 169.9, 172.0, 176.6, 180.3; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{35}Cl_2N_4NiO_6$ 785.1261, found 785.1281.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*, 3*S*)-3-(3′,4′-dichlorophenyl)-5-[3′-(2′-oxazolidinonyl)]-glutamic acid (4u): mp 174.0−175.0 °C; $[\alpha]^{25}_D$ −1271 (*c* 0.023, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.26−1.44 (2H, m), 1.84−1.91 (1H, m), 2.11−2.20 (1H, m), 2.49−2.58 (1H, m), 2.95 (1H, part of AB, J = 5.8, 18.0 Hz), 3.42−3.52 (2H, m), 3.59 (1H, part of AB, J = 13.7 Hz), 3.71−3.86 (5H, m), 4.26−4.75 (3H, m), 6.74−6.84 (2H, m), 7.24−7.38 (9H, m), 7.56−7.65 (5H, m), 8.53 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.6, 31.3, 36.5, 42.2, 44.6, 54.9, 59.9, 61.9, 68.5, 73.4, 120.7, 123.5, 125.7, 127.0,

128.1, 128.6, 128.8, 129.2, 129.4, 129.8, 130.6, 131.0, 131.5, 132.0, 132.2, 132.9, 133.2, 133.9, 139.3, 143.3, 153.0, 169.8, 172.1, 176.4, 181.7; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{35}Cl_2N_4NiO_6$ 785.1261, found 785.1260.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*S*, 3*R*)-3-(4′-nitrophenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (3v): mp 175.0−176.0 °C; $[\alpha]^{25}_D$ +2906 (*c* 0.024, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.55−1.68 (1H, m), 1.91−2.31 (4H, m), 2.84 (1H, dd, J = 3.4, 16.1 Hz), 2.94−2.99 (1H, m), 3.29 (1H, dd, J = 7.2, 9.6 Hz), 3.42 (1H, part of AB, J = 12.5 Hz), 3.67−3.82 (4H, m), 4.22−4.32 (4H, m), 6.69−6.70 (2H, m), 7.11−7.34 (6H, m), 7.50 (2H, part of AB, J = 8.8 Hz), 7.53−7.64 (3H, m), 7.98 (2H, d, J = 7.8 Hz), 8.29 (1H, d, J = 9.3 Hz), 8.32 (2H, part of AB, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 22.8, 30.6, 37.2, 42.1, 45.1, 57.2, 61.9, 63.5, 70.2, 73.1, 120.5, 122.9, 123.8, 125.4, 127.0, 128.0, 128.6, 128.9, 129.4, 129.8, 130.3, 131.2, 132.7, 133.1, 133.7, 133.9, 142.9, 146.7, 147.6, 152.9, 169.7, 172.2, 176.3, 180.1; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{36}N_5NiO_8$ 760.1917, found 760.1921.

Ni(II) complex of the Schiff base of (*S*)-BPB and (2*R*, 3*S*)-3-(4′-nitrophenyl)-5-[3′-(2′-oxazolidinonyl)]glutamic acid (4v): mp 179.0−180.0 °C; $[\alpha]^{25}_D$ −2739 (*c* 0.021, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.34−1.46 (2H, m), 1.86−1.93 (1H,m), 2.17−2.26 (1H, m), 2.43−2.52 (1H, m), 2.97 (1H, dd, J = 5.0, 17.7 Hz), 3.34 (1H, dd, J = 3.7, 9.3 Hz), 5.49 (1H, part of AB, J = 13.7 Hz), 3.69−3.91 (6H, m), 4.27−4.34 (3H, m), 6.75−6.87 (2H, m), 7.15−7.36 (8H, m), 7.58−7.63 (5H, m), 8.34 (2H, d, J = 8.8 Hz), 8.51 (1H, d, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 23.6, 31.2, 37.1, 42.2, 45.6, 55.2, 59.9, 62.0, 68.1, 73.6, 120.9, 123.5, 123.9, 125.7, 127.2, 128.3, 128.9, 129.1, 129.6, 130.0, 130.8, 131.6, 133.2, 134.0, 143.4, 146.9, 147.9, 153.1, 169.9, 172.6, 176.4, 181.9; HRMS(FAB) $[M + H]^+$ calcd for $C_{39}H_{36}N_5NiO_8$ 760.1917, found 760.1933.

Ni(II) Complex of the Chiral Schiff Base of Glycine with (*S*)-*o*-[*N*-(*N*-Benzylprolyl)amino]acetophenone (5). Chiral ligand (*S*)-*o*-[*N*-(*N*-benzylprolyl)amino]-acetophenone (BPA) and the corresponding Ni(II)-complex (*S*)-**5** were synthesized following the standard procedure (ref 21) for preparing BPB−(*S*)-**10** and (*S*)-**1** with the difference that instead of *o*-aminobenzophenone the *o*-aminoacetophenone was used.

Michael Addition Reactions between Complex (*S*)-5 and 2f,p. For the reactions of the acetophenone-derived complex (*S*)-**5** with phenyl- (**2f**) and pentafluorophenyl-containing derivatives **2p**, the general procedure described for the reactions of complex (S)-**1** with Michael acceptors was followed. Yields and physicochemical and NMR data of the diastereomeric products **6f**,**p** and **7f**,**p** are listed below.

Ni(II) complex of the Schiff base of (*S*)-BPA and (2*S*,3*R*)-3-phenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (6f): yield 71%; mp 273.0−274.0 °C; $[\alpha]^{25}_D$ +1875 (*c* 0.033, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.43−1.54 (1H, m), 1.81−2.21 (4H, m), 2.82 (3H, s), 2.85−2.93 (1H, m), 3.18 (1H, t, J = 8.7 Hz), 3.29 (1H, part of AB, J = 12.7 Hz), 3.42 (1H, part of ABX, J = 3.91, 18.6 Hz), 3.60 (1H, td, J = 4.3, 10.3 Hz), 3.95−4.03 (2H, m), 4.14 (1H, part of AB, J = 12.5 Hz), 4.38−4.47 (3H, m), 4.61 (1H, d, J = 4.4 Hz), 6.88−6.93 (1H, m), 7.08−7.34 (6H, m), 7.49−7.53 (3H, m), 7.71 (1H, d, J = 8.3 Hz), 8.00 (2H, d, J = 7.1 Hz), 8.11 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 18.6, 23.0, 30.0, 37.1, 42.3, 44.2, 57.5, 62.0, 63.6, 70.2, 72.3, 120.6, 123.3, 125.1, 127.9, 128.4, 128.9, 129.4, 129.9, 131.3, 131.6, 133.1, 138.9, 141.8, 153.1, 169.2, 172.3, 177.3, 179.8; HRMS(FAB) $[M + H]^+$ calcd for $C_{34}H_{35}N_4NiO_6$ 653.1910, found 653.1917.

Ni(II) complex of the Schiff base of (*S*)-BPA and (2*R*,3*S*)-3-phenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (7f): yield 23%; mp 181.0−182.0 °C; $[\alpha]^{25}_D$ −259.5 (*c* 0.044, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.51−1.60 (2H, m), 1.96−2.05 (1H, m), 2.19−2.26 (1H m), 2.36−2.46 (1H, m), 2.83 (3H, s), 3.24 (1H, dd, J = 4.6, 9.8 Hz), 3.34 (1H, part of AB, J = 13.4 Hz), 3.42 (1H, part of ABX, J = 3.9, 18.8 Hz), 3.57 (1H, td, J = 4.2, 6.1 Hz), 3.62−3.69 (1H, m), 3.83 (1H, part of AB, J = 13.4 Hz), 3.95−4.09 (2H, m), 4.38−4.49 (3H, m), 4.77 (1H, d, J = 4.4 Hz), 6.93−7.02 (1H, m), 7.24−7.28 (8H, m), 7.47−7.52 (3H, m), 7.71 (1H, dd, J = 1.2, 8.3 Hz), 8.06 (1H, dd, J = 1.0, 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.4, 23.5, 30.8, 36.9, 42.2, 44.6, 55.8, 60.9, 62.1, 68.6, 72.1, 121.3, 124.7, 127.1, 128.1, 128.6, 128.7, 128.9, 129.4, 130.0, 131.7, 131.9, 132.0, 138.9, 141.4, 153.2, 170.8, 172.5, 177.7, 180.8; HRMS(FAB) $[M + H]^+$ calcd for $C_{34}H_{35}N_4NiO_6$ 653.1910, found 653.1915.

Ni(II) complex of the Schiff base of (*S*)-BPA and (2*S*, 3*R*)-3-pentafluorophenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (6p): yield 73%; mp 168.0−169.0 °C; $[\alpha]^{25}_D$ +1862 (*c* 0.036, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.06−2.28 (2H, m), 2.47−2.55 (1H, m), 2.58 (3H, s), 2.69−2.80 (1H, m), 3.22 (1H, part of ABX, J = 6.8, 18.6 Hz), 3.33 (1H, part of AB, J = 12.5 Hz), 3.45 (1H, part of ABX, J = 5.9, 11.0 Hz), 3.50−3.54 (1H, m), 3.61 (1H, part of ABX, J = 6.7, 18.5 Hz), 3.71−3.94 (4H, m), 4.18−4.26 (1H, m), 4.27 (1H, part of AB, J = 12.7 Hz), 4.44 (1H, d, J = 10.7 Hz), 5.54 (1H, ddd, J = 6.8, 6.8, 10.7 Hz), 6.88−6.93 (1H, m), 7.07−7.16 (2H, m), 7.23−7.28 (2H, m), 7.61 (1H, dd, J = 1.5, 8.3 Hz), 7.98 (1H, dd, J = 1.0, 8.5 Hz), 8.09 (2H, d, J = 6.8 Hz); ^{19}F NMR ($CDCl_3$) δ −162.5 (1F, m), −161.9 (1F, m), −155.3 (1F, m), −141.5 (2F, m); ^{13}C NMR ($CDCl_3$) δ 18.9, 23.7, 30.5, 35.2, 37.1, 42,1, 58.0, 62.2, 63.6, 70.7, 71.0, 113.1 (m), 121.2, 123.5, 125.0, 128.6, 128.7, 129.7, 131.1, 132.1, 133.6, 135.9 (m), 139.0 (m), 141.5, 142.4 (m), 143.7 (m), 147.1 (m), 153.2, 169.4, 170.1, 176.0, 180.0; HRMS(FAB) $[M + H]^+$ calcd for $C_{34}H_{30}F_5N_4NiO_6$ 743.1439, found 743.1437.

Ni(II) complex of Schiff base of (*S*)-BPA and (2*R*,3*S*)-3-pentafluorophenyl-5-[3′-(2′-oxazolidinonyl)]glutamic acid (7p): yield 23%; mp 144.0−145.0 °C; $[\alpha]^{25}_D$ +181.9 (*c* 0.029, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.74−1.85 (1H, m), 1.91−2.04 (1H, m), 2.11−2.25 (1H, m), 2.30−2.39 (1H, m), 2.56−2.64 (1H, m), 2.75 (3H, s), 3.31 (1H, part of ABX, J = 5.9, 18.8 Hz), 3.42 (1H, dd, J = 4.6, 10.0 Hz), 3.67 (1H, part of AB, J = 13.2 Hz), 3.78−3.86 (1H, m), 3.91−4.00 (3H, m), 4.26−4.42 (2H, m), 4.55 (1H, part of AB, J = 12.9 Hz), 4.56−4.62 (1H, m), 4.71 (1H, d, J = 8.1 Hz), 6.96−7.01 (1H, m), 7.25−7.31 (1H, m), 7.37−7.39 (3H, m), 7.67 (1H, dd, J = 1.2, 8.5 Hz), 7.73−7.76 (2H, m), 8.08 (1H, d, J = 8.5 Hz); ^{19}F NMR ($CDCl_3$) δ −162.2 (2F, m), −154.9 (1F, m), −141.0 (1F, m), −137.8 (1F, m); ^{13}C NMR ($CDCl_3$) δ 19.9, 23.4, 29.2, 30.5, 35.5, 42.3, 57.1, 61.9, 62.2, 68.7, 69.8, 112.8 (m), 121.6, 124.8, 126.9, 128.8, 129.2, 129.7, 131.7, 132.1, 132.3, 136.0 (m), 139.0 (m), 141.3, 142.4 (m), 144.1 (m), 146.7 (m), 153.3, 170.8, 173.0, 177.1, 181.2; HRMS(FAB) $[M + H]^+$ calcd for $C_{34}H_{30}F_5N_4NiO_6$ 743.1439, found 743.1442.

Decomposition of Diastereomerically Pure Complexes 3 and 4. Isolation of Pyroglutamic Acids 8 and 9 and Recovery of Chiral Ligand BPB (*S*)-10 and Oxazolidin-2-one (11). Diastereomerically pure complex **3** or **4** (2.3 mmol) was dissolved in methanol (20 mL) and added to a 1/1 mixture (40 mL) of 3 N HCl and water at 70 °C. After the decomposition of the complex was completed (disappearance of the orange color), the mixture was evaporated in vacuo, treated with concentrated ammonia, and extracted with $CHCl_3$ to remove ligand BPB (*S*)-**10** (95−99% yield). The aqueous phase was evaporated in vacuo, and the solid residue was washed with acetone to remove 2-oxazolidinone (**11**) (90−97% yield). The resultant product was dissolved in water and loaded on a Dowex ion-exchange resin column, which was washed with H_2O/EtOH (2/1). The acidic fraction which emerged from the column was collected and evaporated to afford pyroglutamic acid **8** or **9**, which was recrystallized from THF/hexanes to give an analytically pure sample. Yields and physicochemical and NMR data of the amino acids are listed below.

(2*S*,3*S*)-3-Methylpyroglutamic acid (8a): yield 96%; mp 110.0−111.5 °C; $[\alpha]^{25}_D$ +41.2 (*c* 1.18, CH_3OH) [lit.[1e] $[\alpha]^{25}_D$ +41.0 (*c* 1.16, CH_3OH)]; ^{1}H NMR (CD_3OD) δ 1.27 (3H, d, J = 6.4 Hz), 1.99, 2.54 (2H, ABX, J = 8.5, 9.3, 20.0 Hz), 2.50−2.59 (1H, m), 3.82 (1H, d, J = 4.9 Hz); ^{13}C NMR (CD_3OD) δ 20.1, 34.8, 38.4, 63.1, 174.0, 178.3; HRMS(FAB) $[M + H]^+$ calcd for $C_6H_{10}NO_3$ 144.0661, found 144.0660.

(2*R*,3*R*)-3-Methylpyroglutamic acid (9a): yield 97%; mp 110.5−112.0 °C; $[\alpha]^{25}_D$ −40.7 (*c* 1.02, CH_3OH); ^{1}H NMR and ^{13}C NMR (CD_3OD) spectra are identical to those of (2*S*,3*S*)-**8a**.

(2*S*,3*R*)-3-Phenylpyroglutamic acid (8f): yield 95%; mp 139.0−140.0 °C; $[\alpha]^{25}_D$ +82.5 (*c* 1.11, CH_3OH) [lit.[1e] $[\alpha]^{25}_D$ +82.8 (*c* 1.10, CH_3OH)]; ^{1}H NMR (CD_3OD) δ 2.34, 2.75 (2H, ABX, J

= 16.8, 9.3, 6.3 Hz), 3.72 (1H, ddd, J = 9.3, 6.3, 5.1 Hz), 4.25 (1H, d, J = 5.1 Hz), 7.25−7.41 (5H, m); ^{13}C NMR (CD_3OD) δ 38.7, 44.9, 63.1, 127.8, 127.9, 129.6, 143.9, 173.5, 176.4; HRMS(FAB) $[M + H]^+$ calcd for $C_{11}H_{12}NO_3$ 206.0817, found 206.0809.

(2*R*,3*S*)-3-Phenylpyroglutamic acid (9f): yield 93%; mp 139.5−140.5 °C; $[\alpha]^{25}_D$ −82.3 (*c* 1.10, CH_3OH); ^{1}H NMR and ^{13}C NMR (CD_3OD) spectra are identical to those of (2*S*,3*R*)-**8f**.

(2*S*,3*R*)-3-(3′,4′-Difluorophenyl)pyroglutamic acid (8s): yield 85%; mp 185.0−186.0 °C; $[\alpha]^{25}_D$ +57.8 (*c* 0.81, CH_3OH); ^{1}H NMR (CD_3OD) δ 2.32, 2.71 (2H, ABX, J = 6.8, 9.3, 17.1 Hz), 3.60 (1H, ddd, J = 5.8, 6.6, 9.3 Hz), 4.11 (1H, d, J = 5.6 Hz), 7.01−7.22 (3H, m); ^{19}F NMR (CD_3OD) δ −143.9 (1F, m), −141.0 (1F, m); ^{13}C NMR (CD_3OD) δ 39.3, 44.8, 64.2, 117.2 (d, J = 18.2 Hz), 118.4 (d, J = 17.1 Hz), 124.6 (dd, J = 3.5, 6.5 Hz), 141.1 (m), 149.5 (dd, J = 12.6, 60.4 Hz), 152.8 (dd, J = 13.1, 61.5 Hz), 174.4, 179.0; HRMS(FAB) $[M + H]^+$ calcd for $C_{11}H_{10}F_2NO_3$ 242.0629, found 242.0620.

(2*S*,3*R*)-3-(3′,4′-Dichlorophenyl)pyroglutamic acid (8u): yield 84%; mp 216.0−217.0 °C; $[\alpha]^{25}_D$ +60.7 (*c* 0.22, CH_3OH); ^{1}H NMR (CD_3OD) δ 2.32, 2.71 (2H, ABX, J = 6.8, 9.3, 17.3 Hz), 3.60 (1H, ddd, J = 5.4, 6.8, 9.3 Hz), 4.12 (1H, d, J = 5.4 Hz), 7.18 (1H, dd, J = 2.2, 8.3 Hz), 7.39 (1H, d, J = 8.3 Hz), 7.42 (1H, d, J = 2.2 Hz); ^{13}C NMR (CD_3OD) δ 39.1, 44.8, 64.0, 128.0, 130.5, 132.0, 132.2, 144.4, 174.3, 178.9; HRMS(FAB) $[M + H]^+$ calcd for $C_{11}H_{10}Cl_2NO_3$ 274.0038, found 274.0033.

Hydrolysis of (2*S*,3*R*)-3-Phenylpyroglutamic Acid (8f) to (2*S*,3*R*)-3-Phenylglutamic Acid (12f). (2*S*,3*R*)-3-Phenylpyroglutamic acid **8f** (0.205 g, 1.00 mmol) was refluxed with 6 N HCl (10 mL) overnight. After the solvent was evaporated, the residue was dissolved in ethanol (2 mL). The resulting solution was then refluxed with propylene oxide (3 mL) for 30 min and cooled to room temperature. The white precipitate was filtered out, washed with ethanol, and dried in vacuo to give (2*S*,3*R*)-3-phenylglutamic acid **12f** (0.220 g): yield 99%; mp 158.0−158.5 °C; $[\alpha]^{25}_D$ +16.7 (*c* 1.36, 6 N HCl); ^{1}H NMR (D_2O) δ 2.86, 2.96 (2H, ABX, J = 5.6, 10.0, 16.4 Hz), 3.52−3.59 (1H, m), 3.90 (1H, d, J = 4.9 Hz), 7.62−7.31 (5H, m); ^{13}C NMR (D_2O) δ 31.5, 37.8, 54.1, 123.8, 124.0, 124.8, 132.2, 167.7, 171.6; HRMS(FAB) $[M + H]^+$ calcd for $C_{11}H_{14}NO_4$ 224.0923, found 224.0923.

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Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **3a**−**d**,**f**−**v**, **4a**−**d**,**f**−**v**, **6f**,**p**, **7f**,**p**, **8a**,**f**,**s**,**u**, and **12f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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