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NH-type of chiral Ni(II) complexes of glycine Schiff base: design, structural evaluation, reactivity and synthetic applications†

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The work being reported here deals with the design of a new type of "N–H" Ni(II) complexes of glycine Schiff bases and study general aspects of their reactivity. It was confirmed that the presence of NH function in these Ni(II) complexes does not interfere with the homologation of the glycine residue, rendering these derivatives of high synthetic value for the general synthesis of α-amino acids. In particular, the practical application of these NH-type complexes was demonstrated by asymmetric synthesis of various β-substituted pyroglutamic acids *via* Michael addition reactions with chiral Michael acceptors.

Introduction

The synthesis of α-amino acids (α-AAs) has remained a topic of special significance in organic chemistry for decades. The importance of this subject is due to the remarkable multidisciplinary nature of α-AAs and related compounds. One of the key aspects of α-AAs is their extraordinary versatility, as they have been utilized in virtually all life/health-related areas, most notably in pharmaceutical, food and agricultural industries.[1] Currently, the commercial production of α-AAs is a multi-billion industry heavily relying on isolation of α-AAs from natural sources and enzymatic resolution of racemates.[2] In sharp contrast, the asymmetric synthesis of α-AAs is rarely applied for the large-scale production. One of the key reasons is that chemical synthesis is prohibitedly expensive,[3] compared to enzymatic methods which enjoy low cost-structure. Considering that the importance of tailor-made amino acids[4] in healthcare industries is rapidly increasing, the synthetic methodology for preparation of structurally and functionally varied α-AAs continues to evolve. One of the major challenges being addressed is the application of operationally convenient reaction conditions,[5] resulting in the reduced cost of the target compounds.

While the core-structure of amino acid is relatively simple and remain unchanged throughout the family, the synthetic challenge[6] has remained in the development of a single synthetic methodology which would include the flexibility necessary to provide α-AAs with side chains which include various structural, functional, stereochemical, electronic, and physical properties.[7] To date, the most robust of the synthetic approaches offered in the literature is the derivatization of nucleophilic glycine equivalents (NGE).[6,7]

There have been numerous NGEs introduced for the general synthesis of α-AAs. They include examples, such as nitroethanoic acid,[8] dioxopiperazines,[9] alkyl α-isocyanoacetate[10] and α-isocyanoacetamide,[11] glycine derived oxazolidinones[12] and Schiff bases.[13] Although each methodology has demonstrated its advantages, each system does come with its inherent limitations such as, reactivity, generality, cost of the target α-AA and scalability. From the standpoint of operationally convenient reaction conditions, the Ni(II) complex of glycine Schiff base **1**[14,15] (Fig. 1) is of particular practical interest. The major advantage of Ni(II) complex **1** over other NGEs is that its homologation *via* alkyl halide alkylations,[16] Michael,[17] aldol[18] and Mannich[19] addition reactions can be conducted at ambient temperature under expedient reaction conditions. An achiral analogue of **1**, picolinic acid derived Ni(II) complexes **2**[20] has demonstrated similar practicality as its asymmetric alkylations[21] and Michael

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† Electronic supplementary information (ESI) available: Crystallographic data of **18** and copies of NMR spectra. CCDC 962997. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob41959b

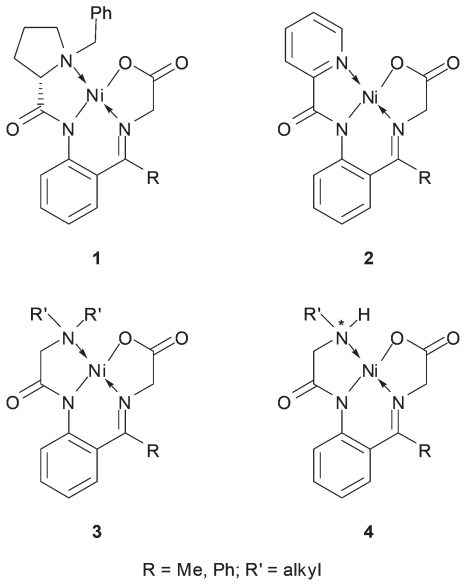


Fig. 1 Structures of various Ni(II) complexes of glycine Schiff base.

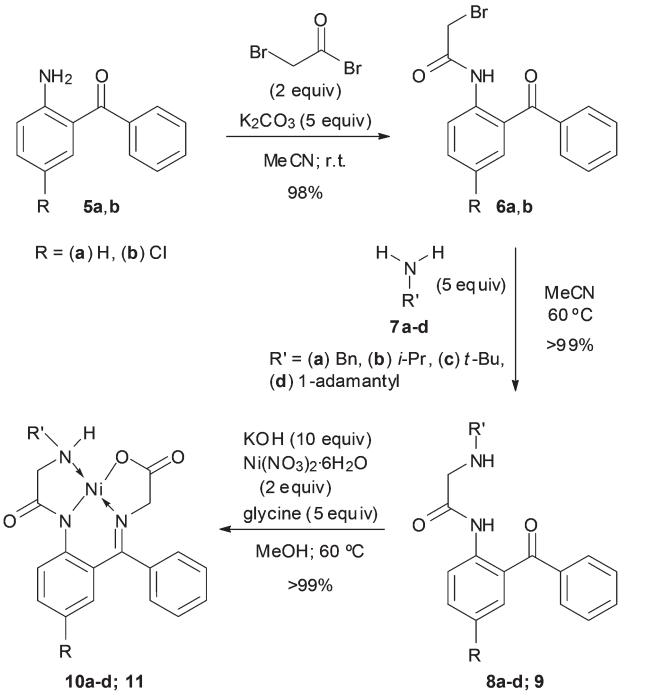
addition reactions[22] can be conducted under operationally convenient conditions.

Despite their practical potential, complexes **1** and **2** also have some disadvantages, related mostly to their poor solubility in common organic solvents. Furthermore, the potential for structural modification of complexes **1** and **2**, to improve their physicochemical properties and reactivity, is rather restricted.[23] Realizing the limitations of complexes **1** and **2**, as well as the broader consideration that a single nucleophilic glycine equivalent will not be suitable for all of the synthetic requirements, we developed a modular approach to Ni(II) complex-based NGE.[24] It is envisioned that this design will allow for tailoring of the physicochemical properties as well as chemical reactivity of the corresponding NGE required for a particular synthetic application.[25] For example, Ni(II) complexes of type **3** (Fig. 1) can be tailored to become soluble in virtually any solvent simply by choosing the appropriate (*N*,*N*-di-alkyl)amine moiety.[26] To date we have demonstrated the practical nature of this design with respect to the preparation of sterically constrained α,α-disubstituted α-amino acids[27] and β-substituted pyroglutamic acid derivatives[28] *via* highly diastereoselective Michael addition reactions.[29] Another area of successful application of complexes of type **3** is the deracemization or resolution of racemic α-AAs.[30] Of the derivatives that have been developed during these studies, the Ni(II) complexes **4** (Fig. 1) which are derived from primary amines rather than the traditional secondary amines are virtually unstudied, however, they seem to be among the most intriguing. From a practical standpoint the availability and cost of primary *versus* secondary amines makes these complexes potentially valuable to the field. In addition, the unusual chemoselectivity and stereochemical aspects of these complexes add to the scientific interest of their study.[31]

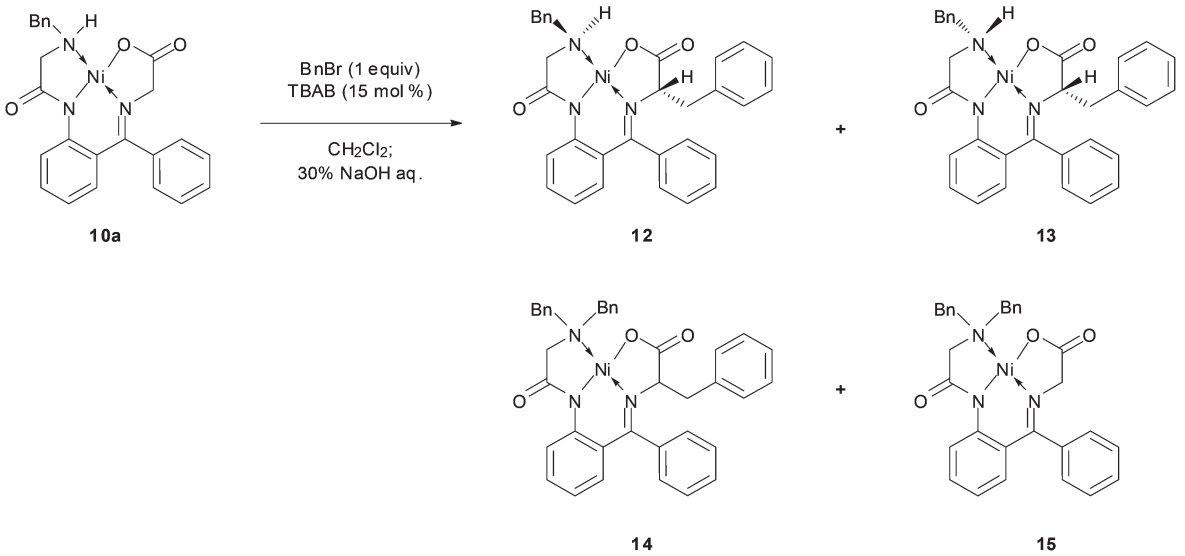
Results and discussion

The preparation of the Ni(II) complexed nucleophilic glycine equivalents containing a secondary rather than a tertiary amine was realized *via* a series of robust and high yielding reactions.[32] The synthesis was initiated by the condensation of *o*-aminobenzophenone **5a**, or its chlorinated analogue **5b**, and bromoacetyl bromide in acetonitrile with potassium carbonate to quench the hydrobromic acid formed (Scheme 1). The resulting 2-bromoacetamide intermediates **6a,b** were treated with a five-fold excess of a primary amine **7a–d** in warm (60 °C) acetonitrile. The resulting ligands **8a–d**, **9** were transformed *in situ* into the corresponding glycine Schiff bases and complexed by the metal after exposure to the appropriate α-amino acid and nickel(II) nitrate in methanol with excess potassium hydroxide to facilitate the reaction. The target Ni(II) complexes **10a–d**, **11** were isolated in high yields and additionally purified by column chromatography.

With ready access to a number of these Ni(II) complexed NGE it was decided to explore their utility with regards to preparation of α-AA derivatives *via* alkylation under phase transfer catalysis (PTC) conditions. The initial complex selected for the study was the *N*-benzyl derivative **10a** (Scheme 2). It was found that treating complex **10a** with benzyl bromide under basic PTC conditions at ambient temperature resulted in the formation of three products (Table 1, entry 1). Two of the compounds obtained from the reaction were



Scheme 1 Synthesis of NH-type Ni(II) complexes of glycine **10a–d** and **11**.



Scheme 2 PTC benzylation of Ni(II) complex **10a** (TBAB: tetra-*N*-butylammonium bromide).

Table 1 Reaction conditions and ratio of products **12–15** in the PTC benzylation of complex **10a**

Entry	Temp (°C)	Time (h)	Ratio **12**, **13**/**14**/**15**[a]
1	25	2	63.3/36.7/0
2	0	2	67.1/19.5/13.4
3	−10	2	83.3/0/16.7

[a] Determined by NMR integration of the crude reaction mixtures.

expected products of the glycine CH_2 group alkylation, diastereomeric complexes **12** and **13**, whereas the third product, complex **14**, resulted from the benzylation of the CH_2 and benzylamino groups. With a goal to eliminate the N-alkylation, we conducted the reaction at a lower temperature (entry 2). As expected, the amount of bis-benzylation product **14** was noticeably decreased, however, quite surprisingly, we observed the formation of one more product, **15**, resulting exclusively from alkylation of the benzylamino group. Further decreases in reaction temperature (−10 °C) (entry 3) provided even more surprising results as the formation of bis-C-/N-alkylation product **14** was completely suppressed while the relative amount of selectively *N*-benzylated complex **15** increased. To explain these results we considered two possible reaction sequences leading to the bis-benzylation product **14**. One approach may include: enolization of **10a**, subsequent alkylation to form complexes **12** and **13**, followed by their N-benzylation; while the alternative path may start with N-benzylation of **10a** forming the secondary amine containing complex **15**, which can be enolized and alkylated to produce the final product **14**. Considering the stereochemical outcome observed at ambient temperature (entry 1) one may agree that it is impossible to make a preference for either reaction sequence and therefore both may take place. On the other hand, considering the reactions conducted at lower temperatures (entries 2 and 3) in particular, the result observed at −10 °C, we can suggest that the second approach, proceeding *via* formation of **15**, is more realistic as the alternative way does not afford complex **15** as the end-product. If this rational is correct, it leads to another very important assumption that NH-type Ni(II) complex **10a** is noticeably more reactive than *N*,*N*-di-alkyl-type **15**. Thus, the results obtained at low temperatures suggest that the formation of enolate from **10a** takes place at a much higher reaction rate than that of the secondary amine derived complex **15**. To verify this assumption, we conducted standard PTC benzylation of 1/1 mixture of **10a** and **15** at 0 °C using only one equivalent of benzyl bromide. The result was overwhelmingly convincing, as virtually all benzylation product obtained was a mixture of diastereomeric complexes **12** and **13**, resulting exclusively from complex **10a**.

The superior reactivity of NH-type complexes over previously used secondary amine derived complexes was rather unexpected. One possible explanation for this noticeable difference in reactivity might be based on the following steric considerations. In the case of NH-type complexes, the corresponding enolate has two non-equivalent diastereotopic faces. One of which is totally open (NH face) and another slightly shielded by the *N*-alkyl group. Obviously, the formation of the corresponding transition state with an incoming electrophile takes place faster on the NH-side, while approach from the opposite *N*-alkyl face is disadvantaged by some repulsive steric interactions. By contrast, in the case of secondary amine derived complexes both sides of the corresponding enolate are equivalent and shielded by *N*-alkyl groups. This conclusion regarding reactivity of NH *vs.* *N*,*N*-di-alkyl types of Ni(II) complexes is of great novelty and may have beneficial implications for the design of more advanced types of Ni(II) complexes of glycine Schiff bases.

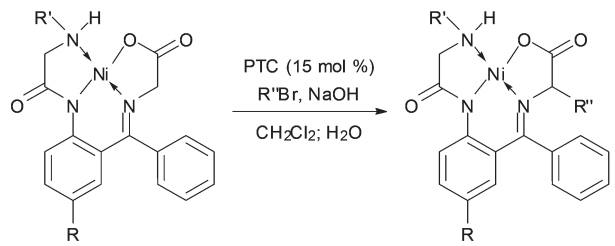
Considering the results obtained, one more important conclusion can be made regarding the configurational stability of

diastereomeric complexes **12** and **13**. These products were obtained in a ratio close to 1/1 and can be easily seen as two well-separated spots on TLC. Therefore, we conducted column chromatography to isolate them in diastereomerically pure form and determine their relative configurations. While we succeeded in separation of pure fractions of **12** and **13**, evaporation of the eluent (acetone–chloroform 1/5) at an elevated temperature resulted in their epimerization giving rise to the mixtures of **12** and **13**. This epimerization was also observed at ambient temperature, although at a slower rate. Considering two stereogenic centers in diastereomers **12** and **13**, we may confidently believe that the stereogenic carbon of the phenylalanine residue is completely configurationally stable under neutral conditions in common organic solvents. This leads us to a conclusion that the stereogenic nitrogen in complexes **12** and **13** is rather configurationally unstable. This finding is of great novelty to be considered in the design of new generations of chiral Ni(II) complexes of glycine and higher amino acids.

Intrigued by the results obtained, we decided to investigate these novel features of reactivity of NH-type Ni(II) complexes in more detail (Scheme 3). During these investigations it was discovered that increasing the steric bulk of the substituent on the amine group from benzyl to isopropyl group was sufficient to achieve the desired chemoselectivity under the room temperature PTC benzylation conditions. Thus, in the alkylation of complex **10b** no products resulting from the corresponding N-benzylation were detected in the crude reaction mixture (Table 2, entry 1). However, the phenylalanine containing complex **16** was obtained as a mixture of epimerizable diastereomers (67% de). With this in mind, it was decided to further increase the steric bulk around the stereogenic nitrogen *via* the incorporation of a *t*-butyl moiety into the complex. Thus, benzylation of complex **10c** resulted in the formation of a single product, the phenylalanine containing Ni(II) complex **17a** in excellent chemical yield (93%) (entry 2).

To assign the relative configuration of the diastereomer **17a** we needed a crystallographic study. Taking advantage that Ni(II) complexes derived from *m*-Cl containing *o*-amino-benzophenone **5b** (Scheme 1) usually have significantly higher crystallinity, we performed synthesis of the corresponding glycine complex **11** and its PTC benzylation. Similar to the reaction of **10c**, alkylation of Cl-containing complex **11** gave only one diastereomeric product **18** in excellent yield (Table 2, entry 3). Using the advantageous physicochemical properties of complex **18**, we obtained suitable crystals and conducted X-ray analysis. The crystallographic structure of **18** is presented in Fig. 2. As one may expect the *N*-*t*-Bu and Bn groups in complex **18** are in *trans*-orientation, thus corresponding to (R_N*,*R**) relative configuration.

The X-ray analysis has also revealed some striking structural features of complex **18**. First of all, while the three Ni(II)-



10b-d, 11 (see Scheme 1) **16, 17a-d, 18, 19a-c**

16: R = H, R' = *i*-Pr, R" = Bn; **17a**: R = H, R' = *t*-Bu, R" = Bn; **17b**: R = H, R' = *t*-Bu, R" = $CH_2CH{=}CH_2$; **17c**: R = H, R' = *t*-Bu, R" = *trans*-$CH_2CH{=}CH{-}Ph$; **17d**: R = H, R' = *t*-Bu, R" = $CH_2C{\equiv}CH$; **18**: R = Cl, R' = *t*-Bu, R" = Bn; **19a**: R = H, R' = 1-adamantyl, R" = Bn; **19b**: R = H, R' = 1-adamantyl, R" = *trans* $CH_2CH{=}CH{-}Ph$; **19c**: R = H, R' = 1-adamantyl, R" = $CH_2C{\equiv}CH$

Scheme 3 PTC alkylations of complexes **10b–d** and **11**.

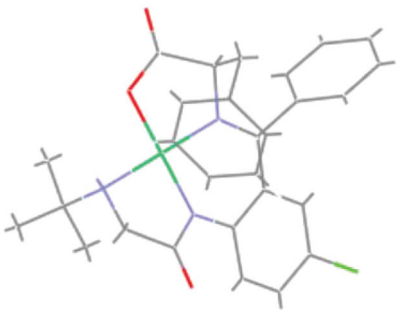
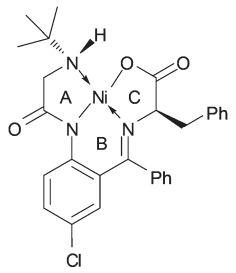


Fig. 2 X-ray structure of (R_N*,*R**)-**18**.

Table 2 Reaction conditions and stereochemical outcome of the PTC alkylations of complexes **10b–d** and **11**

Entry	Starting complex	R	R′	R″	Catalyst	Product	Time (h)	Yield (%)	de[a] (%)
1	**10b**	H	i-Pr	Bn	TBAB	**16**	1.5	91	67
2	**10c**	H	*t*-Bu	Bn	TBAB	**17a**	3	93	>98
3	**11**	Cl	*t*-Bu	Bn	TBAB	**18**	2	90	>98
4	**10c**	H	*t*-Bu	Allyl	TBAB	**17b**	1	96	>98
5	**10c**	H	*t*-Bu	Cinnamyl	TBAB	**17c**	1	94	>98
6	**10c**	H	*t*-Bu	Propargyl	TBAB	**17d**	3	90	>98
7	**10d**	H	1-Adamantyl	Bn	TBAI	**19a**	4	90	>98
8	**10d**	H	1-Adamantyl	Cinnamyl	TBAI	**19b**	4	96	>98
9	**10d**	H	1-Adamantyl	Propargyl	TBAI	**19c**	4	94	>98

[a] The *trans* diastereomer is the favoured product.



(R_N*,R*)-**18**

Fig. 3 A, B and C chelate rings in **18**.

bonded/coordinated nitrogen and one oxygen atoms are normally positioned in the Ni(II) coordination plane, the chelate rings A–C (Fig. 3) are remarkably puckered. Thus, the position of the *N*-*t*-Bu group down the coordination plane pushes the *N*-CH_2 group and the whole chelate ring A up, with a torsion angle Ni–N–CH_2–CO of −33.55(17)°. Consequently, the six-membered ring B is down, with a torsion angle (including imine group) of 23.4(2)°. Finally, the phenylalanine containing ring C is yet again down, providing a torsion angle of Ni–N–CH–C=O −27.44(17)°. This deviation of the chelate rings from planarity is believed to be the main reason for the observed stereochemical outcome, *trans*-positioning the *N*-*t*-Bu and Bn groups away from each other. Thus, considering that both the substituent-bearing rings A and C are up, one may agree that in a hypothetical *cis*-position, *N*-*t*-Bu and Bn groups will be engaged in repulsive steric interactions destabilizing the corresponding diastereomer.

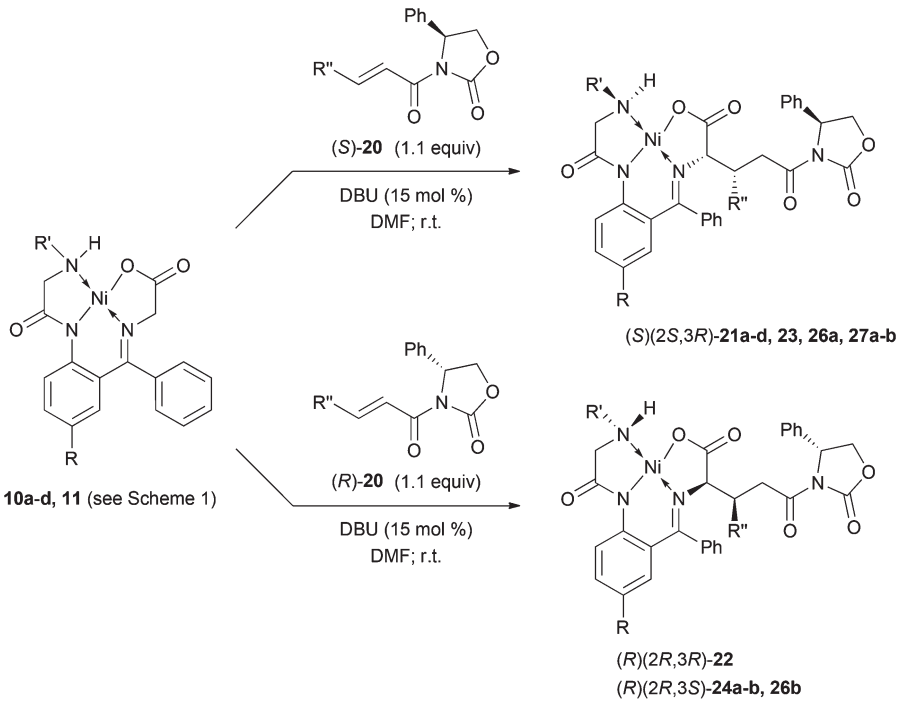
It should be mentioned that in the alkylation chemistry of Ni(II) complexes **1–3** (Fig. 1), the highest levels of diastereoselectivity are usually recorded around 90–95% de.[16] Therefore, the complete (>99% de) stereochemical outcome observed in the PTC benzylations of complexes **10c** and **11** present an obvious novelty deserving a more detailed study. As one can see from Table 2, application of allyl (entry 4), cinnamyl (entry 5) and propargyl (entry 6) bromides as alkylating agents in the reactions with *N*-*t*-butyl derived Ni(II) complex **10c**, resulted in the formation of single, diastereomerically pure products **17b–d**, respectively, isolated in chemical yields above 90%.

In order to evaluate the generality of this stereocontrol and its possible application for the synthesis of various α-AAs, we also prepared the corresponding N–H complex **10d**, derived from 1-adamantylamine. In a series of alkylations of complex **10d** with benzyl (entry 7), cinnamyl (entry 8) and propargyl (entry 9) bromides, equally impressive, complete control over the chemo and diastereoselectivity of the alkylation process was observed. Products **19a–c**, bearing the corresponding α-AA moieties, were isolated as pure diastereomers with yields greater than 90%.

The uncompromised diastereoselectivity in the PTC alkylations of N–H complexes **10c,d**, discovered in this work, is quite a novel and a very important feature of reactivity of this new type of Ni(II) complexes which can be used in the future to advance the design of subsequent generations of chiral Ni(II) complexes of glycine Schiff bases. However, we were eager to find some immediate useful applications of these NH-type Ni(II) complexes for asymmetric synthesis of α-AAs. To this end we considered the Michael addition reactions of complexes **10a–d** and **11** with chiral oxazolidinone derived Michael acceptors **20** (Scheme 4). It is known that in the reactions of chiral *N*-proline containing complex (*S*)- or (*R*)-**1**[33] (Fig. 1) or achiral derivatives **2**, **3**,[34] the chirality of Michael acceptors **20** controls the stereochemical outcome giving rise to (*S*)(2*S*,3*S*) and (*R*)(2*R*,3*R*) configured products in β-aliphatic and (*S*)(2*S*,3*R*) and (*R*)(2*R*,3*S*) in β-aromatic series.[35] In the case of NH-type complexes **10a–d** and **11** under study, we deal with new stereochemical features due to the presence of stereogenic nitrogen in **10a–d** and **11**. These derivatives are racemic and could cause a situation in which matched and mismatched stereochemical preferences in the reactions with chiral Michael acceptors **20** could arise.

The initial reactivity comparison studies were conducted to determine the effect of the alkyl group of the amino moiety of the complexes **10a–d** and **11** with respect to their differences in lipophilicity, as well as their steric properties. The (*R*)-*N*-(*E*-enoyl)-4-phenyl-1,3-oxazolidin-2-one ((*R*)-**20a**) chosen for these experiments included a phenyl substituent in the β-position to limit the reaction rate of the corresponding reactions, by virtue of their corresponding steric contributions, to increase the accuracy while determining the relative reactivity of each of the complexes **10a–d** and **11**. Each of the following reactions discussed in this section were conducted under a set of standard conditions at ambient temperature, which included the use of commercial-grade DMF as the solvent and 15 mol% of DBU as the catalyst (Scheme 4). It was found that the application of Michael acceptor (*R*)-**20a** with the *N*-benzyl derived Ni(II) complex **10a** resulted in the formation of **21a** in fairly good yield (89%) and >98% de in one hour (Table 3, entry 1). Repeating this reaction with the isopropyl derived NGE **10b** yielded similar results, 92% yield and >98% de, in approximately the same amount of time (entry 2). However, the application of Ni(II) complexes with more sterically hindered groups such as **10c** containing *N*-*t*-Bu and **10d** with *N*-Ad groups resulted in longer reaction times in order to reach completion (2 hours). In addition to the increased reaction time, these reactions resulted in slightly decreased yields (84 and 81% respectively) without compromising the diastereoselectivity of the process (entries 3 and 4).

Following the completion of the reactivity profile of the NH Ni(II) complexes **10a–d** it was decided to explore the generality of this process with respect to the application of *N*-(*E*-enoyl)-4-phenyl-1,3-oxazolidin-2-ones which contain various substituents in the β-position. The substituents, ranging from a methyl group to a *t*-butyl group, will aid in generating a reactivity profile with respect to the steric and electronic contributions of the Michael acceptors. The reaction of the β-methyl substituted Michael acceptor (*R*)-**20b** resulted in the preparation of the corresponding product **22** in greater than 95% yield in about two hours (entry 5). However, increasing the steric bulk



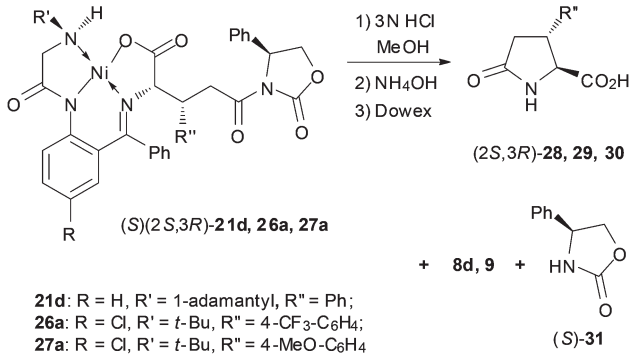
Scheme 4 Michael additions of complexes **10b–d** and **11** to acceptors **20**.

Table 3 Reaction conditions and stereochemical outcome of the Michael additions of complexes **10b–d** and **11** to acceptors **20**

Entry	Starting complex	R	R′	Michael acceptor	R″	Product	Time (h)	Yield (%)	de (%)
1	**10a**	H	Bn	(*S*)-**20a**	Ph	**21a**	1	89	>98
2	**10b**	H	i-Pr	(*S*)-**20a**	Ph	**21b**	1	92	>98
3	**10c**	H	*t*-Bu	(*S*)-**20a**	Ph	**21c**	2	84	>98
4	**10d**	H	1-Adamantyl	(*S*)-**20a**	Ph	**21d**	2	81	>98
5	**10c**	H	*t*-Bu	(*R*)-**20b**	Me	**22**	2	95	>98
6	**11**	Cl	*t*-Bu	(*S*)-**20c**	i-Pr	**23**	4	72	>98
7	**11**	Cl	*t*-Bu	(*R*)-**20d**	α-Naphthyl	**24a**	24	61	>98
8	**11**	Cl	*t*-Bu	(*S*)-**20e**	*t*-Bu	**25**	24	0	NA
9	**11**	Cl	*t*-Bu	(*S*)-**20f**	4-CF_3-C_6H_4	**26a**	2	89	>98
10	**11**	Cl	*t*-Bu	(*S*)-**20g**	4-MeO-C_6H_4	**27a**	3	85	>98
11	**10d**	H	1-Adamantyl	(*R*)-**20d**	α-Naphthyl	**24b**	2	73	>98
12	**10d**	H	1-Adamantyl	(*R*)-**20f**	4-CF_3-C_6H_4	**26b**	1	66	>98
13	**10d**	H	1-Adamantyl	(*S*)-**20g**	4-MeO-C_6H_4	**27b**	1	85	>98

of the β-substituent on the Michael acceptor *via* the substitution of the methyl group by an isopropyl group increased the reaction time necessary to obtain the appropriate product **23** in 72% yield to four hours (entry 6). Increasing the steric hindrance contributed by the β-position of the Michael acceptor *via* the incorporation of an α-naphthyl group drastically decreased reaction rates, 24 hours, however, the expected product was recovered in acceptable yield, 61%, without compromising the diastereoselectivity of the process (entry 7). Increase in the steric contribution of the Michael acceptor culminated with the incorporation of a *t*-butyl group; however, no product **25** could be identified from the reaction mixture (entry 8). To this point the focus of these studies has been concentrated on the steric factors associated with the Michael acceptors; however, an evaluation with respect to the electronic properties of the Michael acceptors also required evaluation. Therefore, *N*-(*E*-enoyl)-4-phenyl-1,3-oxazolidin-2-ones which included a 4-trifluoromethylphenyl **20f** and 4-methoxyphenyl group **20g** in the β-position were utilized for this purpose. These investigations found that the application of a phenyl group with an electron withdrawing (CF_3) or electron donating (OMe) group results in the formation of the expected glutamic acid derivatives **26a**, **27a** in high chemical yield, 89 and 85% yield respectively (entries 9 and 10). However, as expected, shorter reaction times were necessary to reach complete consumption of the starting glycine Ni(II) complex in the reactions with the Michael acceptors bearing the electron withdrawing group.

With the aim to confirm the absolute configuration of the addition products and to demonstrate the preparation of the corresponding enantiomerically pure pyroglutamic acids, we carried out the disassembly of compounds **21d**, **26a** and **27a**.



Scheme 5 Disassembly of products **21d**, **26a** and **27a**.

Heating in 3 N HCl–MeOH resulted in a clean decomposition of the Ni(II) complexes and the formation of the target pyroglutamic acids **28–30** along with chiral auxiliary (*S*)-**31** and NH ligands **8d** or **9** (Scheme 5). Similar to the procedure established for the disassembly of the corresponding glutamic acid derivatives obtained from complexes **1–3**,[17] compounds **8d**, **9** and **31** were isolated by extraction while pyroglutamic acids **28–30** were obtained using ion-exchange resin. Comparison of spectral and chiroptical properties of thus obtained amino acids **28–30** confirmed their expected (2*S*,3*R*) absolute configuration.

Conclusions

The data reported in this work, clearly demonstrate that new N–H type of Ni(II) complexes of glycine Schiff bases holds advantageous structural features and reactivity profile. In particular, they are readily available, very inexpensive, self-stable and can be easily prepared on a large scale. The N–H stereogenic centre in these compounds is relatively configurationally unstable in solution; however, in the case of sterically bulky groups (*t*-Bu, Ad) attached to the N–H function, homologation of the glycine fragment occurs with complete (>99%) diastereoselectivity giving rise to a single reaction product with excellent chemical yield. The synthetic potential of these N–H Ni(II) complexes is demonstrated by an advanced asymmetric synthesis of β-substituted pyroglutamic acids *via* Michael addition reactions with chiral oxazolidinone derived Michael acceptors.

Experimental

General methods

^{1}H, ^{13}C and ^{19}F NMR were performed on Varian Unity-300 (299.94 MHz), Gemini-200 (199.98 MHz) and Brüker Avance 300 spectrometers using TMS, $CDCl_3$ and CCl_3F as internal standards. High resolution mass spectra (HRMS) were recorded on JEOL HX110A and Agilent Synapt G2 instruments. Optical rotations were measured on JASCO P-1010 and P-2000 polarimeters. Melting points (m.p.) are uncorrected and were obtained in open capillaries. All reagents and solvents, unless otherwise stated, are commercially available and were used as received. Chiral (*S*)- or (*R*)-*N*-(*E*-enoyl)-4-phenyl-1,3-oxazoline-2-ones **20** were prepared according to the general method given in ref. 36. Unless otherwise stated, yields refer to isolated yields of products of greater than 95% purity as estimated by ^{1}H, ^{19}F and ^{13}C NMR spectrometry. All new compounds were characterized by ^{1}H, ^{19}F, ^{13}C NMR and HRMS.

General procedure for the synthesis of bromoacetamides 6

A solution of 2-bromoacetyl bromide (104.64 mmol) in acetonitrile (21 mL) was slowly added to a slurry of aminoacetophenone **5** (102.32 mmol) and potassium carbonate (70.71 g, 511.6 mmol) in acetonitrile (240 mL). The reaction was stirred at ambient temperature (room temperature water bath) for one hour, and upon completion (monitored by TLC), the acetonitrile was evaporated *in vacuo*. Water (200 mL) was then added to the crude mixture and extracted with dichloromethane (200 mL) three times. The organic portions were combined, dried and concentrated *in vacuo* to afford the corresponding α-bromoamide product **6** in 98% yield and greater than 99% chemical purity.

***N*-(2-Benzoylphenyl)-2-bromoacetamide (6a).** M.p. 71.7 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.20 (2 H, s), 7.15 (1 H, m), 7.43–7.53 (2 H, m), 7.53–7.63 (3 H, m), 7.63–7.75 (2 H, m), 8.61 (1 H, dd, J = 8.8, 1.2 Hz), 11.60 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 43.0, 121.3, 122.9, 124.0, 128.1, 129.8, 132.4, 133.3, 133.9, 138.1, 139.0, 165.1, 198.8. HRMS: calcd for $C_{15}H_{12}BrNNaO_2$ [M + Na^+] 339.9949, found 339.9955.

***N*-(2-Benzoyl-4-chlorophenyl)-2-bromoacetamide (6b).** M.p. 125.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.02 (2 H, s), 7.45–7.80 (7 H, m), 8.53–8.64 (1 H, m), 11.30 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.3, 123.0, 125.4, 128.3, 128.6, 130.0, 132.6, 133.1, 133.8, 137.5, 137.9, 164.9, 197.9. HRMS: calcd for $C_{15}H_{12}BrClNO_2$ [M + H^+] 351.9740, found 351.9747.

General procedure for the synthesis of ligands 8a–d, 9

To a solution of the corresponding bromoacetamide **6** (1 equiv.) and acetonitrile (10 mL per 1 g of **6**) was added the corresponding primary amine **7a–d** (5 equiv.). The reaction was allowed to proceed for 24 hours at 60–70 °C (monitored by TLC) before the reaction mixture was concentrated *in vacuo*. Water was added to the viscous liquid, followed by extraction with dichloromethane. The organic portions were combined, dried with magnesium sulfate, and concentrated *in vacuo* to afford the corresponding alkylamino-acetamide product **8a–d**, **9** in nearly quantitative yield and high chemical purity >99%.

***N*-(2-Benzoylphenyl)-2-(benzylamino)acetamide (8a).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (1 H, br), 3.45 (2 H, s), 3.86 (2 H, s), 7.10 (1 H, t, J = 7.2 Hz), 7.13–7.29 (3 H, m), 7.03–7.43 (2 H, m), 7.46–7.60 (5 H, m), 7.77 (2 H, d, J = 8.4 Hz), 8.64 (1 H, d, J = 8.4 Hz), 11.66 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 52.9, 54.1, 121.7, 122.3, 124.8, 127.3, 128.3, 128.5, 128.5, 130.2,

132.6, 132.8, 133.7, 138.5, 139.1, 139.3, 171.2, 198.3. HRMS: calcd for $C_{22}H_{21}N_2O_2$ [M + H$^+$], 345.1603, found 345.1606.

***N*-(2-Benzoylphenyl)-2-(isopropylamino)acetamide (8b).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (6 H, d, J = 6.3 Hz), 1.77 (1 H, br), 2.84 (1 H, hept, J = 6.3 Hz), 3.42 (2 H, s), 7.10 (1 H, t, J = 7.8 Hz), 7.45–7.62 (5 H, m), 7.74 (2 H, d, J = 8.1 Hz), 8.68 (1 H, d, J = 8.4 Hz), 11.65 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 22.9, 49.6, 51.2, 121.6, 122.2, 125.0, 128.3, 128.4, 130.0, 130.1, 132.5, 132.7, 133.5, 138.5, 139.2, 172.4, 198.1. HRMS: calcd for $C_{18}H_{21}N_2O_2$ [M + H$^+$], 297.1603, found 297.1601.

***N*-(2-Benzoylphenyl)-2-(*tert*-butylamino)acetamide (8c).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (9 H, s), 3.42 (2 H, s), 7.09 (1 H, t, J = 8.1 Hz), 7.44–7.61 (5 H, m), 7.75 (2 H, d, J = 6.9 Hz), 8.61 (1 H, d, J = 8.4 Hz), 11.67 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 28.8, 47.1, 51.2, 121.5, 122.2, 125.2, 128.3, 130.1, 132.5, 132.6, 133.5, 138.6, 139.1, 173.0, 198.0. HRMS: calcd for $C_{19}H_{23}N_2O_2$ [M + H$^+$] 311.1760, found 311.1764.

***N*-(2-Benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (8d).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60 (6 H, q, J = 13.7 Hz), 1.68 (6 H, br), 2.04 (3 H, br), 3.47 (2 H, s), 4.10 (1 H, br), 7.12 (1 H, td, J = 7.6, 1.1 Hz), 7.46–7.64 (5 H, m), 7.76–7.82 (2 H, m), 8.62 (1 H, d, J = 8.3 Hz), 11.59 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.3, 36.3, 42.0, 44.7, 51.4, 121.6, 122.3, 125.5, 128.2, 130.0, 132.2, 132.5, 133.2, 138.4, 138.7, 172.6, 197.9. HRMS: calcd for $C_{25}H_{29}N_2O_2$ [M + H]$^+$ 389.2229, found 389.2240.

***N*-(2-Benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (9).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (9 H, s), 3.41 (2 H, s), 7.49 (1 H, d, J = 2.5 Hz), 7.51–7.58 (3 H, m), 7.66 (1 H, tt, J = 7.4, 1.3 Hz), 7.70–7.82 (2 H, m), 8.66 (1 H, d, J = 8.9 Hz), 11.60 (1 H, br). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 28.4, 46.6, 50.7, 122.5, 126.2, 126.9, 128.2, 129.7, 131.2, 132.7, 137.1, 137.4, 172.6, 196.0. HRMS: calcd for $C_{19}H_{22}ClN_2O_2$ [M + H]$^+$ 345.1370, found 345.1374.

General procedure for the synthesis of Ni(II) complexes 10a–d, 11

A solution of potassium hydroxide (10 equiv.) in methanol (7 mL per 1 g of KOH) was added to the corresponding ligand **8a–d**, **9** (1 equiv.), glycine (5 equiv.), nickel nitrate hexahydrate (2 equiv.) in methanol (10 mL per 1 g of ligand) at 60–70 °C. Upon complete consumption of the ligand (monitored by TLC), the reaction mixture was poured over slurry of ice and 5% acetic acid. After the complete precipitation, the corresponding product **10a–d**, **11** was filtered and dried, in a low temp. oven (50 °C) overnight. The product was obtained in high chemical yield (99%) and high chemical purity without further purification.

Ni(II) complex of glycine Schiff base with *N*-(2-benzoylphenyl)-2-(benzylamino)acetamide (10a). M.p. >300 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.08 (1 H, br), 3.25 (1 H, d, J = 16.9 Hz), 3.68 (1 H, dd, J = 17.0, 7.3 Hz), 3.79 (2 H, s), 3.97 (1 H, dd, J = 13.6, 10.0 Hz), 4.45 (1 H, d, J = 13.7 Hz), 6.83 (1 H, t, J = 7.5 Hz), 6.94 (1 H, d, J = 8.2 Hz), 7.00–7.07 (1 H, m), 7.18 (1 H, d, J = 7.0 Hz), 7.34–7.49 (6 H, m), 7.52–7.62 (3 H, m), 8.64 (1 H, d, J = 8.5 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 53.0, 55.6, 60.8, 121.2, 124.3, 125.5, 125.7, 126.2, 128.8, 129.1, 129.4, 129.7, 129.8, 132.6, 133.6, 134.7, 142.8, 171.8, 178.0. HRMS: calcd for $C_{24}H_{22}N_3NiO_3$ [M + H]$^+$ 458.1015, found 458.1020.

Ni(II) complex of glycine Schiff base with *N*-(2-benzoylphenyl)-2-(isopropylamino)acetamide (10b). M.p. 292.3 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.56 (3 H, d, J = 6.3 Hz), 1.66 (3 H, d, J = 6.3 Hz), 2.76 (1 H, br), 3.12 (1 H, dq, J = 13.2, 6.3 Hz), 3.29 (1 H, d, J = 17.7 Hz), 3.75 (2 H, s), 3.99 (1 H, dd, J = 17.7, 7.5 Hz), 6.83 (1 H, m), 6.93 (1 H, m), 7.01 (1 H, m), 7.19 (1 H, m), 7.35 (1 H, m), 7.53–7.59 (3 H, m), 8.55 (1 H, d, J = 7.8 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.6, 21.7, 51.7, 53.3, 60.6, 121.3, 128.3, 125.7, 125.8, 136.2, 129.4, 129.7, 129.9, 132.7, 133.6, 134.7, 142.6, 173.2, 177.9, 178.2. HRMS: calcd for $C_{20}H_{21}N_3NaNiO_3$ [M + Na$^+$] 432.0834, found 432.0837.

Ni(II) complex of glycine Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (10c). M.p. >300 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54 (9 H, s), 2.60 (1 H, d, J = 7.8 Hz), 3.41 (1 H, d, J = 17.1 Hz), 3.73 (2 H, d, J = 3.9 Hz), 4.17 (1 H, dd, J = 17.1, 7.5 Hz), 6.84 (1 H, m), 6.93 (1 H, dd, J = 8.1, 1.8 Hz), 6.99 (1 H, m), 7.23 (1 H, m), 7.38 (1 H, m), 7.53–7.60 (3 H, m), 8.37 (1 H, d, J = 7.5 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 28.0, 51.0, 58.2, 60.4, 121.3, 124.2, 125.7, 126.3, 129.4, 129.8, 129.9, 132.7, 133.5, 134.5, 142.4, 171.7, 177.4, 177.7. HRMS: calcd for $C_{21}H_{23}N_3NaNiO_3$ [M + Na$^+$] 446.0991, found 446.1015.

Ni(II) complex of glycine Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (10d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.71 (6 H, br), 2.11 (6 H, br), 2.17 (3 H, br), 3.03 (1 H, d, J = 7.4 Hz), 3.44 (1 H, d, J = 17.0 Hz), 3.68 (1 H, d, J = 20.4 Hz), 3.71 (1 H, d, J = 20.3 Hz), 4.07 (1 H, dd, J = 17.0, 7.6 Hz), 6.80 (1 H, td, J = 7.6, 1.0 Hz), 6.90 (1 H, dd, J = 8.2, 1.5 Hz), 6.93–6.99 (1 H, m), 7.23 (1 H, d, J = 6.6 Hz), 7.34 (1 H, ddd, J = 7.7, 7.0, 1.6 Hz), 7.46–7.58 (3 H, m), 8.39 (1 H, dd, J = 8.5, 0.6 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.3, 35.7, 40.7, 49.0, 58.1, 60.3, 120.9, 124.2, 125.6, 126.0, 126.2, 129.2, 129.5, 129.6, 132.3, 133.2, 134.5, 142.4, 171.3, 177.7, 177.8. HRMS: calcd for $C_{27}H_{30}N_3O_3Ni$ [M + H]$^+$ 502.1641, found 502.1646.

Ni(II) complex of glycine Schiff base with *N*-(2-benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (11). M.p. >300 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (9 H, s), 2.98 (1 H, br), 3.36 (1 H, d, J = 17.1 Hz), 3.55–3.75 (2 H, m), 4.16 (1 H, dd, J = 17.0, 7.5 Hz), 6.85 (1 H, d, J = 2.5 Hz), 6.93–6.99 (1 H, m), 7.22 (1 H, d, J = 6.3 Hz), 7.31 (1 H, dd, J = 9.1, 2.5 Hz), 7.52–7.65 (3 H, m), 8.38 (1 H, d, J = 9.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 30.8, 54.4, 58.0, 60.4, 125.6, 126.1, 127.3, 128.6, 129.3, 129.6, 130.1, 132.1, 132.5, 133.9, 141.2, 171.0, 177.7, 178.1. HRMS: calcd for $C_{21}H_{23}ClN_3NiO_3$ [M + H$^+$] 458.0781, found 458.0780.

General procedure for the PTC alkylations of Ni(II) complexes 10a–d, 11

To a flask containing the corresponding Ni(II) complex **10a–d**, **11** (0.10 g), tetra-*n*-butylammonium iodide (25 mol%), 15 ml of dichloromethane and 5 ml of 30% aqueous sodium hydroxide, alkyl bromide (1.0 equiv.) was added and the reaction mixture was stirred at room temperature. After disappearance of the

starting complex by TLC, 10 mL of water was added and the organic layer was extracted with $CHCl_3$ three times. The combined organic layer was dried over magnesium sulfate, and concentrated *in vacuo* to afford the corresponding products **12–16**, **17a–d**, **18**, **19a–c**.

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoylphenyl)-2-(benzylamino)acetamide (upper diastereomer) (12). M.p. 219.7 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.00 (1 H, t, J = 7.5 Hz), 2.72–2.84 (2 H, m), 3.08–3.16 (2 H, m), 3.66 (1 H, ABX, J = 13.8, 10.2 Hz), 4.04 (1 H, AB, J = 13.8 Hz), 4.37 (1 H, m), 6.84 (1 H, m), 7.08–7.19 (2 H, m), 7.23–7.48 (6 H, m), 7.49 (1 H, m), 7.52–7.65 (6 H, m), 7.74 (1 H, dd, J = 6.6, 2.4 Hz), 8.42 (1 H, d, J = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.5, 53.1, 54.7, 71.3, 121.0, 124.3, 127.1, 127.4, 127.8, 128.8, 129.0, 129.1, 129.3, 129.7, 130.1, 131.7, 132.5, 133.8, 133.9, 134.4, 136.5, 143.0, 170.4, 176.8, 178.3. HRMS: calcd for $C_{31}H_{27}N_3NaNiO_3$ [M + Na$^+$] 570.1304, found 570.1312.

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoylphenyl)-2-(benzylamino)acetamide (lower diastereomer) (13). M.p. 219.7 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (1 H, m), 2.75–2.91 (2 H, m), 3.12–3.23 (2 H, m), 3.65 (1 H, ABX, J = 13.5, 9.6 Hz), 3.96 (1 H, AB, J = 13.5 Hz), 4.35 (1 H, m), 6.77–6.83 (2 H, m), 7.08–7.16 (2 H, m), 7.26–7.37 (5 H, m), 7.42–7.48 (2 H, m), 7.51–7.63 (6 H, m), 7.72 (1 H, dd, J = 5.7, 2.4 Hz), 8.38 (1 H, d, J = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.6, 52.7, 55.4, 71.2, 121.0, 123.7, 126.9, 127.4, 127.7, 127.8, 128.7, 128.8, 128.9, 128.9, 129.1, 129.7, 130.1, 131.5, 132.7, 133.4, 133.8, 136.2, 143.0, 170.4, 176.7, 179.1. HRMS: calcd for $C_{31}H_{27}N_3NaNiO_3$ [M + Na$^+$] 570.1304, found 570.1307.

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoylphenyl)-2-(dibenzylamino)acetamide (14). M.p. 295.2 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (1 H, d, J = 16.4 Hz), 2.73 (1 H, dd, J = 13.5, 5.3 Hz), 3.02 (1 H, d, J = 12.3 Hz), 3.04 (1 H, dd, J = 13.3, 3.4 Hz), 3.17 (1 H, d, J = 14.1 Hz), 3.49 (1 H, d, J = 14.2 Hz), 3.58 (1 H, d, J = 16.3 Hz), 3.83 (1 H, d, J = 12.3 Hz), 4.31 (1 H, dd, J = 5.3, 3.4 Hz), 6.60–6.68 (2 H, m), 6.96–7.09 (3 H, m), 7.17–7.80 (17 H, m), 8.20–8.28 (2 H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.0, 62.3, 62.7, 62.8, 71.3, 120.5, 123.5, 126.2, 127.1, 127.3, 127.5, 128.4, 128.5, 128.6, 128.7, 128.9, 129.7, 130.2, 131.2, 131.6, 131.8, 132.8, 133.5, 134.0, 136.3, 142.0, 170.2, 175.5, 177.6. HRMS: calcd for $C_{38}H_{33}N_3NaNiO_3$ [M + Na$^+$] 660.1773, found 660.1781.

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoylphenyl)-2-(isopropylamino)acetamide (16) (major diastereomer). M.p. 245.9 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (3 H, d, J = 6.3 Hz), 1.46 (3 H, d, J = 6.3 Hz), 1.74 (1 H, br), 2.67–2.73 (2 H, m), 2.93 (1 H, d, J = 16.5 Hz), 3.08 (1 H, dd, J = 13.5, 3.0 Hz), 3.32 (1 H, dd, J = 16.5, 7.2 Hz), 4.33 (1 H, dd, J = 5.4, 3.0 Hz), 6.82 (2 H, d, J = 3.6 Hz), 7.14 (1 H, m), 7.31–7.37 (2 H, m), 7.43–7.46 (2 H, m), 7.55–7.62 (6 H, m), 8.39 (1 H, d, J = 9.0 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.4, 21.7, 39.2, 52.0, 53.1, 71.2, 121.1, 123.6, 127.3, 127.3, 127.7, 127.9, 128.7, 129.1, 129.3, 130.1, 131.5, 132.8, 133.8, 133.8, 136.2, 142.9, 170.3, 176.8, 178.8. HRMS: calcd for $C_{27}H_{28}N_3NiO_3$ [M + H$^+$] 500.1484, found 500.1490. Data for the minor diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (3 H, d, J = 6.3 Hz), 1.07 (3 H, d, J = 6.3 Hz), 2.16 (1 H, br), 2.64–2.76 (1 H, m), 2.87 (1 H, dd, J = 13.7, 5.8 Hz), 3.04 (1 H, dd, J = 13.6, 3.6 Hz), 3.20–3.31 (2 H, m), 4.26 (1 H, dd, J = 5.7, 3.7 Hz), 6.81–6.87 (1 H, m), 6.91 (1 H, dd, J = 8.2, 1.8 Hz), 7.12–7.17 (1 H, m), 7.26–7.33 (4 H, m), 7.37 (1 H, ddd, J = 8.6, 5.3, 1.8 Hz), 7.46–7.52 (2 H, m), 7.54–7.65 (3 H, m), 8.49 (1 H, d, J = 8.6 Hz).

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (17a). M.p. 272.9 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (9 H, s), 1.78 (1 H, d, J = 7.2 Hz), 2.66 (1 H, dd, J = 13.5, 6.0 Hz), 3.03 (1 H, d, J = 16.5 Hz), 3.07 (1 H, dd, J = 13.5, 2.7 Hz), 3.37 (1 H, dd, J = 16.5, 7.2 Hz), 4.33 (1 H, dd, J = 5.4, 3.0 Hz), 6.84 (2 H, d, J = 3.9 Hz), 7.14 (1 H, m), 7.32–7.43 (4 H, m), 7.55–7.63 (6 H, m), 8.26 (1 H, d, J = 8.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.8, 39.0, 50.9, 57.7, 70.8, 121.0, 123.3, 127.3, 127.6, 127.8, 128.0, 128.8, 129.1, 129.3, 130.2, 131.4, 132.9, 133.7, 133.9, 136.1, 142.8, 170.4, 176.3, 178.7. HRMS: calcd for $C_{28}H_{29}N_3NaNiO_3$ [M + Na$^+$] 536.1460, found 536.1472.

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (18). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (9 H, s), 1.95 (1 H, d, J = 7.3 Hz), 2.64 (1 H, dd, J = 13.5, 5.6 Hz), 3.00 (1 H, d, J = 16.6 Hz), 3.08 (1 H, dd, J = 13.5, 2.9 Hz), 3.35 (1 H, dd, J = 16.6, 7.4 Hz), 4.31 (1 H, dd, J = 5.6, 2.9 Hz), 6.77 (1 H, d, J = 2.5 Hz), 7.10–7.15 (1 H, m), 7.28 (1 H, dd, J = 9.1, 2.5 Hz), 7.36–7.42 (3 H, m), 7.56–7.67 (6 H, m), 8.26 (1 H, d, J = 9.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.6, 38.9, 50.7, 57.6, 70.8, 124.5, 125.6, 127.1, 127.7, 127.7, 128.7, 129.2, 129.4, 130.4, 131.1, 132.3, 132.6, 133.0, 135.8, 141.4, 169.5, 176.5, 178.4. HRMS: calcd for $C_{28}H_{29}ClN_3NiO_3$ [M + H]$^+$ 548.1251, found 548.1263.

Ni(II) complex of 2-aminopent-4-enoic acid Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (17b). M.p. 116.3 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (9 H, s), 2.32 (1 H, m), 2.48 (1 H, m), 2.73 (1 H, d, J = 7.5 Hz), 3.41 (1 H, d, J = 16.8 Hz), 4.08 (1 H, dd, J = 6.3, 3.6 Hz), 4.28 (1 H, dd, J = 16.8, 7.5 Hz), 5.26 (1 H, dd, J = 17.1, 1.5 Hz), 5.56 (1 H, dd, J = 10.1, 1.5 Hz), 6.63 (1 H, m), 6.81 (1 H, m), 6.99 (1 H, m), 7.32–7.38 (2 H, m), 7.48–7.55 (3 H, m), 8.33 (1 H, d, J = 8.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 28.0, 38.1, 51.4, 58.0, 69.4, 120.0, 121.1, 123.3, 127.1, 127.7, 128.0, 129.0, 129.2, 130.0, 132.3, 132.9, 133.7, 133.8, 142.6, 170.6, 176.8, 179.0. HRMS: calcd for $C_{24}H_{27}N_3NaNiO_3$ [M + Na$^+$] 486.1304, found 486.1308.

Ni(II) complex of (*E*)-2-amino-5-phenylpent-4-enoic acid Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (17c). M.p. 198.3 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (9 H, s), 2.26 (1 H, d, J = 7.5 Hz), 2.34 (1 H, m), 2.64 (1 H, m), 2.98 (1 H, d, J = 16.8 Hz), 3.23 (1 H, dd, J = 16.8, 7.5 Hz), 4.19 (1 H, dd, J = 5.7, 3.3 Hz), 6.72 (1 H, d, J = 15.9 Hz), 6.82 (2 H, d, J = 4.2 Hz), 7.04–7.15 (2 H, m), 7.30–7.38 (3 H, m), 7.44 (2 H, t, J = 7.2 Hz), 7.50–7.60 (3 H, m), 7.66 (2 H, d, J = 7.5 Hz), 8.34 (1 H, d, J = 8.4 Hz). ^{13}C NMR δ 27.9, 36.6, 50.7, 58.0, 69.9, 121.0, 123.2, 124.0, 126.4, 127.2, 127.7, 128.0, 128.0, 129.1, 129.3, 130.1, 133.0, 133.7, 133.8, 135.4, 137.3, 142.9, 170.5, 176.9, 179.0. HRMS: calcd for $C_{30}H_{31}N_3NaNiO_3$ [M + Na$^+$] 562.1617, found 562.1620.

Ni(II) complex of 2-aminopent-4-ynoic acid Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (17d). M.p. 236.7 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (9 H, s), 2.28 (1 H, dq, J = 19.8, 2.7 Hz), 2.67 (1 H, dt, J = 17.4, 2.7 Hz), 2.81–2.86 (2 H, m), 3.41 (1 H, d, J = 16.5 Hz), 4.05 (1 H, dd, J = 6.3, 3.0 Hz), 4.27 (1 H, dd, J = 16.5, 7.2 Hz), 6.81 (2 H, m), 7.05 (1 H, m), 7.31–7.39 (2 H, m), 7.48–7.58 (3 H, m), 8.32 (1 H, d, J = 8.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.9, 27.9, 51.5, 58.0, 67.2, 74.2, 79.5, 121.1, 123.5, 126.9, 127.7, 127.7, 129.3, 130.2, 133.0, 133.6, 133.7, 142.9, 171.4, 176.9, 178.5. HRMS: calcd for $C_{24}H_{25}N_3NaNiO_3$ [M + Na^+] 484.1147, found 484.1172.

Ni(II) complex of phenylalanine Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (19a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (6 H, br), 1.77 (1 H, d, J = 6.8 Hz), 1.88 (6 H, br), 2.11 (3 H, br), 2.67 (1 H, dd, J = 13.4, 5.5 Hz), 3.07 (1 H, dd, J = 13.7, 2.7 Hz), 3.13 (1 H, d, J = 16.7 Hz), 3.30 (1 H, dd, J = 16.4, 7.1 Hz), 4.29–4.34 (1 H, m), 6.81–6.85 (2 H, m), 7.14 (1 H, d, J = 6.6 Hz), 7.31–7.44 (4 H, m), 7.52–7.64 (6 H, m), 8.28 (1 H, d, J = 8.5 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.2, 35.6, 38.9, 40.6, 48.9, 57.9, 70.6, 120.8, 123.4, 127.2, 127.5, 127.6, 127.9, 128.6, 129.0, 129.2, 130.0, 131.2, 132.7, 133.6, 133.8, 135.9, 142.8, 170.2, 176.5, 178.7. HRMS: calcd for $C_{34}H_{36}N_3O_3Ni$ [M + H]$^+$ 592.2110, found 592.2117.

Ni(II) complex of (*E*)-2-amino-5-phenylpent-4-enoic acid Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)-acetamide (19b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.67 (6 H, br), 1.96 (6 H, br), 2.14 (3 H, br), 2.29–2.40 (2 H, m), 2.60–2.70 (1 H, m), 3.09 (1 H, d, J = 16.7 Hz), 3.20 (1 H, dd, J = 16.7, 7.0 Hz), 4.18 (1 H, dd, J = 5.5, 3.4 Hz), 6.70 (1 H, d, J = 15.9 Hz), 6.82 (2 H, d, J = 3.9 Hz), 7.03–7.08 (1 H, m), 7.12 (1 H, dd, J = 15.7, 7.8 Hz), 7.29–7.46 (5 H, m), 7.49–7.60 (3 H, m), 7.65 (2 H, d, J = 7.2 Hz), 8.36 (1 H, d, J = 8.5 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.3, 35.7, 36.6, 40.7, 48.7, 58.2, 69.8, 120.9, 123.3, 123.9, 126.3, 127.1, 127.6, 127.9, 129.0, 129.1, 129.9, 132.8, 133.6, 133.9, 135.2, 137.2, 142.9, 170.3, 177.0, 179.0. HRMS: calcd for $C_{36}H_{38}N_3O_3Ni$ [M + H]$^+$ 618.2267, found 618.2271.

Ni(II) complex of 2-aminopent-4-ynoic acid Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (19c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.73 (6 H, br), 2.09 (6 H, br), 2.21 (3 H, br), 2.31 (1 H, dd, J = 6.0, 2.6 Hz), 2.57 (1 H, d, J = 6.9 Hz), 2.68 (1 H, dt, J = 17.0, 2.7 Hz), 2.80 (1 H, t, J = 2.5 Hz), 3.54 (1 H, d, J = 16.6 Hz), 4.06 (1 H, dd, J = 6.0, 2.6 Hz), 4.20 (1 H, dd, J = 16.6, 7.4 Hz), 6.79–6.86 (2 H, m), 7.06 (1 H, d, J = 6.7 Hz), 7.33–7.41 (2 H, m), 7.49–7.60 (3 H, m), 8.36 (1 H, d, J = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 23.8, 29.4, 35.8, 40.8, 49.6, 58.2, 67.2, 74.1, 79.5, 120.9, 123.6, 126.8, 127.7, 129.2, 130.1, 132.9, 133.6, 133.7, 143.0, 171.1, 177.0, 178.4. HRMS: calcd for $C_{30}H_{32}N_3O_3Ni$ [M + H]$^+$ 540.1797, found 540.1804.

General procedure for the Michael addition of complexes 10a–d, 11 to acceptors 20

To a flask containing the starting complex **10a–d**, **11** (0.10 g), the corresponding 3-((*E*)-3-alkylacryloyl)oxazolidin-2-one (*R*)- or (*S*)-**20** (1.05 equiv.) and 3 ml of DMF, DBU (15 mol%) was added to the reaction mixture, which was stirred at room temperature and monitored by TLC. After the disappearance of the starting glycine equivalent by TLC, the reaction mixture was poured into a beaker containing 100 mL of ice water. After the ice had melted the solid was filtered from the aqueous solution and dried in an oven to afford the appropriate product in high chemical yields.

Ni(II) complex of (2*S*,3*R*,4′*S*)-3-phenyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-(benzylamino)acetamide (21a). M.p. 146.3 °C. $[\alpha]_D^{25}$ = +1867.2 (c 0.021, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.66–2.89 (4 H, m), 3.25–3.42 (3 H, m), 3.85 (1 H, dd, J = 16.2, 6.0 Hz), 4.18 (1 H, dd, J = 8.7, 3.9 Hz), 4.43 (1 H, d, J = 4.2 Hz), 4.60 (1 H, t, J = 8.7 Hz), 5.18 (1 H, dd, J = 8.7, 3.9 Hz), 6.71–6.84 (3 H, m), 6.97–7.01 (2 H, m), 7.05 (1 H, d, J = 6.9 Hz), 7.11–7.14 (2 H, m), 7.23–7.47 (10 H, m), 7.56–7.59 (2 H, m), 7.67–7.73 (3 H, m), 8.38 (1 H, d, J = 8.7 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 36.4, 45.2, 53.1, 54.7, 57.5, 69.7, 73.4, 121.0, 123.8, 125.7, 125.9, 126.9, 127.0, 127.2, 128.0, 128.3, 128.4, 128.75, 128.9, 129.1, 129.6, 129.8, 130.7, 132.6, 133.5, 133.6, 134.0, 138.7, 132.8, 139.2, 142.9, 169.9, 171.0, 175.9, 176.6, 177.4. HRMS: calcd for $C_{42}H_{36}N_4NaNiO_6$ [M + Na^+] 773.1886, found 773.1886.

Ni(II) complex of (2*S*,3*R*,4′*S*)-3-phenyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-(isopropylamino)acetamide (21b). M.p. 183.1 °C. $[\alpha]_D^{25}$ = +1124.9 (c 0.018, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3 H, d, J = 6.6 Hz), 1.37 (3 H, d, J = 6.6 Hz), 2.67 (1 H, s), 2.74 (1 H, h, J = 6.6 Hz), 2.86 (1 H, d, J = 16.5 Hz), 3.18–3.30 (2 H, m), 3.56 (1 H, dd, J = 18.6, 8.7 Hz), 3.72 (1 H, dd, J = 18.6, 8.7 Hz), 4.20 (1 H, dd, J = 8.7, 3.9 Hz), 4.49 (1 H, d, J = 4.5 Hz), 4.63 (1 H, t, J = 9.0 Hz), 5.18 (1 H, dd, J = 8.7, 3.9 Hz), 6.74 (1 H, d, J = 2.7 Hz), 6.99–7.05 (3 H, m), 7.24 (1 H, d, J = 2.7 Hz), 7.27 (1 H, d, J = 2.7 Hz), 7.28–7.33 (5 H, m), 7.37 (1 H, t, J = 7.2 Hz), 7.47–7.52 (3 H, m), 7.56–7.62 (3 H, m), 8.40 (1 H, d, J = 9.3 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.2, 21.4, 29.3, 44.9, 52.7, 53.8, 57.5, 69.8, 73.3, 124.7, 125.7, 125.9, 127.3, 127.9, 128.3, 128.4, 128.5, 128.7, 128.9, 129.3, 129.4, 130.3, 130.8, 132.6, 132.7, 132.9, 138.8, 139.2, 141.6, 153.3, 169.8, 170.0, 176.9, 177.1. HRMS: calcd for $C_{38}H_{36}N_4NaNiO_6$ [M + Na^+] 725.1886, found 725.1884.

Ni(II) complex of (2*S*,3*R*,4′*S*)-3-phenyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (21c). M.p. 183.1 °C. $[\alpha]_D^{25}$ = +734.2 (c 0.012, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (9 H, s), 2.67 (1 H, s), 2.97 (1 H, d, J = 16.8 Hz), 3.20–3.37 (2 H, m), 3.51 (1 H, dd, J = 17.7, 8.4 Hz), 3.74 (1 H, dd, J = 17.7, 8.4 Hz), 4.17 (1 H, dd, J = 9, 3.9 Hz), 4.46 (1 H, d, J = 4.5 Hz), 4.61 (1 H, t, J = 8.7 Hz), 5.18 (1 H, dd, J = 8.7, 3.6 Hz), 6.79 (1 H, m), 6.98–7.03 (3 H, m), 7.26–7.38 (7 H, m), 7.43–7.49 (3 H, m), 7.54–7.63 (4 H, m), 8.23 (1 H, d, J = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.8, 36.5, 44.9, 50.8, 57.4, 59.7, 69.7, 72.5, 120.9, 123.1, 125.8, 127.3, 127.6, 128.2, 128.3, 128.8, 128.9, 129.0, 129.2, 130.0, 130.6, 132.9, 133.6, 133.9, 138.8, 139.1, 142.8, 153.3, 170.0, 170.8, 176.4, 177.2. HRMS: calcd for $C_{39}H_{38}N_4NaNiO_6$ [M + Na^+] 739.2043, found 739.2078.

Ni(II) complex of (2*S*,3*R*,4′*S*)-3-phenyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (21d). $[\alpha]_D^{25}$ = +1751.3 (*c* 0.052, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.64 (6 H, br), 1.85 (6 H, br), 2.11 (3 H, br), 3.08 (1 H, d, *J* = 16.5 Hz), 3.21–3.31 (2 H, m), 3.46 (1 H, dd, *J* = 18.0, 8.0 Hz), 3.74 (1 H, dd, *J* = 17.9, 6.7 Hz), 4.16 (1 H, dd, *J* = 8.8, 3.7 Hz), 4.46 (1 H, d, *J* = 4.7 Hz), 4.60 (1 H, t, *J* = 8.7 Hz), 5.18 (1 H, dd, *J* = 8.6, 3.6 Hz), 6.75–6.84 (2 H, m), 6.97–7.05 (3 H, m), 7.25–7.39 (6 H, m), 7.42–7.50 (3 H, m), 7.53–7.66 (4 H, m), 8.26 (1 H, d, *J* = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.2, 35.6, 36.5, 40.5, 44.8, 48.8, 57.3, 57.8, 69.6, 72.4, 120.7, 123.1, 125.6, 127.2, 127.5, 128.2, 128.7, 128.9, 129.1, 129.8, 130.5, 132.7, 133.5, 133.8, 138.7, 138.9, 142.7, 153.2, 169.9, 170.6, 176.5, 171.2. HRMS: calcd for $C_{45}H_{45}N_4O_6Ni$ $[M + H]^+$ 795.2693, found 795.2695.

Ni(II) complex of (2*R*,3*R*,4′*R*)-3-methyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-(*tert*-butylamino)acetamide (22). M.p. 153.7 °C. $[\alpha]_D^{25}$ = −1467.9 (*c* 0.005, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.43 (9 H, s), 1.91 (3 H, s), 3.04 (1 H, dd, *J* = 18.3, 7.2 Hz), 3.24 (1 H, dd, *J* = 18.3, 7.2 Hz), 3.39 (1 H, d, *J* = 17.1 Hz), 4.16 (1 H, d, *J* = 4.5 Hz), 4.22 (1 H, dd, *J* = 9.0, 3.6 Hz), 4.39 (1 H, q, *J* = 17.1, 7.2 Hz), 4.61 (1 H, t, *J* = 8.7 Hz), 5.28 (1 H, dd, *J* = 8.7, 3.3 Hz), 6.78 (2 H, d, *J* = 4.8 Hz), 6.94 (1 H, d, *J* = 7.8 Hz), 7.25 (2 H, m), 7.30–7.47 (7 H, m), 7.53 (1 H, t, *J* = 7.8 Hz), 8.37 (1 H, d, *J* = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 16.8, 28.0, 33.7, 38.9, 51.5, 57.5, 57.9, 69.9, 72.3, 121.0, 123.0, 126.1, 127.3, 127.8, 128.6, 128.8, 129.0, 129.1, 129.8, 132.9, 133.7, 134.0, 139.2, 142.7, 153.5, 170.5, 171.2, 177.1, 177.8. HRMS: calcd for $C_{34}H_{36}N_4NaNiO_6$ $[M + Na^+]$ 677.1886, found 677.1918.

Ni(II) complex of (2*S*,3*R*,4′*S*)-3-isopropyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (23). $[\alpha]_D^{25}$ = +766.7 (*c* 0.015, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 0.39 (3 H, d, *J* = 6.7 Hz), 0.81 (3 H, d, *J* = 6.7 Hz), 1.37 (9 H, s), 2.49 (2 H, m), 2.71 (1 H, d, *J* = 7.3 Hz), 3.10 (2 H, m), 3.38 (1 H, d, *J* = 16.6 Hz), 3.83 (1 H, d, *J* = 8.2 Hz), 4.15 (1 H, dd, *J* = 8.8, 2.8 Hz), 4.25 (1 H, t, *J* = 8.5 Hz), 4.52 (1 H, dd, *J* = 16.5, 7.4 Hz), 5.34 (1 H, dd, *J* = 8.2, 2.6 Hz), 6.79 (1 H, d, *J* = 2.4 Hz), 7.21 (4 H, m), 7.38 (4 H, m), 7.52 (3 H, m), 8.45 (1 H, d, *J* = 9.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 15.8, 21.8, 27.5, 27.9, 31.5, 44.4, 51.7, 57.3, 57.9, 70.5, 70.9, 123.9, 125.9, 128.1, 128.4, 128.7, 129.1, 129.2, 129.5, 129.7, 130.5, 132.8, 132.9, 133.2, 139.3, 141.3, 153.9, 170.5, 172.1, 177.7, 178.7. HRMS: calcd for $C_{36}H_{40}ClN_4NiO_6$ $[M + H^+]$ 717.1990, found 717.1988.

Ni(II) complex of (2*R*,3*S*,4′*R*)-3-α-naphthyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (24a). $[\alpha]_D^{25}$ = −720.0 (*c* 0.002, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.15 (9 H, s), 1.66 (1 H, m), 1.85 (1 H, dd, *J* = 16.7, 7.4 Hz), 2.47 (1 H, d, *J* = 16.7 Hz), 3.38 (2 H, m), 3.95 (1 H, m), 4.11 (1 H, dd, *J* = 8.8, 3.8 Hz), 4.43 (1 H, d, *J* = 4.2 Hz), 4.58 (1 H, t, *J* = 8.8 Hz), 5.15 (1 H, dd, *J* = 4.9, 3.8 Hz), 6.73 (1 H, d, *J* = 2.4 Hz), 6.86 (2 H, m), 6.99 (2 H, t, *J* = 7.7 Hz), 7.10 (2 H, m), 7.21 (1 H, dd, *J* = 9.1, 2.4 Hz), 7.46 (7 H, m), 7.95 (2 H, m), 8.19 (1 H, d, *J* = 9.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.6, 36.4, 45.2, 49.7, 57.5, 57.7, 69.7, 72.9, 124.4, 125.5, 125.6, 126.7, 126.8, 127.3, 127.7, 128.1, 128.2, 128.3, 128.4, 128.6, 128.7, 129.3, 129.5, 130.4, 132.6, 132.8, 132.9, 133.3, 133.5, 136.1, 138.5, 141.6, 153.4, 170.0, 170.1, 176.6, 177.1. HRMS: calcd for $C_{43}H_{40}ClN_4NiO_6$ $[M + H^+]$ 801.1990, found 801.1981.

Ni(II) complex of (2*S*,3*R*,4″*S*)-3-(4′-trifluoromethylphenyl)-5-[3″-(4″-phenyl-2″-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (26a). $[\alpha]_D^{25}$ = +506.5 (*c* 0.007, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (9 H, s), 1.96 (1 H, m), 3.00 (1 H, d, *J* = 16.9 Hz), 3.29 (3 H, m), 3.91 (1 H, dd, *J* = 19.1, 9.1 Hz), 4.17 (1 H, m), 4.41 (1 H, m), 4.60 (1 H, t, *J* = 8.6 Hz), 5.17 (1 H, dd, *J* = 7.6, 2.9 Hz), 6.71 (1 H, m), 6.93 (3 H, m), 7.41 (10 H, m), 7.77 (2 H, m), 8.26 (1 H, d, *J* = 8.9 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.7, 36.5, 44.8, 50.3, 57.5, 58.0, 69.8, 72.5, 77.1, 124.3, 125.7, 125.8, 127.2, 128.0, 128.5, 128.9, 129.4, 129.6, 130.5, 130.6, 132.8, 132.9, 133.0, 138.5, 141.6, 143.0, 153.4, 169.6, 170.7, 176.5, 176.7. HRMS: calcd for $C_{40}H_{37}ClF_3N_4NiO_6$ $[M + H^+]$ 819.1707, found 819.1704.

Ni(II) complex of (2*S*,3*R*,4″*S*)-3(4′-methoxyphenyl)-5-[3″-(4″-phenyl-2″-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoyl-4-chlorophenyl)-2-(*tert*-butylamino)acetamide (27a). $[\alpha]_D^{25}$ = +316.4 (*c* 0.003, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.25 (9 H, m), 2.98 (1 H, d, *J* = 16.8 Hz), 3.13 (1 H, m), 3.37 (1 H, dd, *J* = 16.8, 7.6 Hz), 3.44 (1 H, dd, *J* = 17.8, 8.2 Hz), 3.63 (1 H, dd, *J* = 17.8, 6.5 Hz), 3.89 (3 H, s), 4.16 (1 H, dd, *J* = 8.8, 3.4 Hz), 4.40 (1 H, d, *J* = 4.9 Hz), 4.59 (1 H, t, *J* = 8.8 Hz), 5.16 (1 H, dd, *J* = 8.6, 3.3 Hz), 5.30 (1 H, s), 6.72 (1 H, d, *J* = 2.2 Hz), 6.99 (3 H, m), 7.09 (2 H, m), 7.29 (8 H, m), 7.46 (1 H, t, *J* = 7.4 Hz), 7.56 (1 H, t, *J* = 7.6 Hz), 8.18 (1 H, d, *J* = 9.1 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.7, 29.3, 31.0, 44.1, 50.5, 55.5, 57.4, 57.8, 69.7, 114.0, 124.3, 125.6, 129.9, 127.3, 128.0, 128.3, 128.8, 129.2, 129.4, 130.4, 130.6, 131.5, 132.6, 132.9, 138.8, 141.4, 153.3, 159.7, 170.0, 176.6, 177.1. HRMS: calcd for $C_{40}H_{40}ClN_4NiO_7$ $[M + H^+]$ 781.1939, found 781.1929.

Ni(II) complex of (2*R*,3*S*,4′*R*)-3-α-naphthyl-5-[3′-(4′-phenyl-2′-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (24b). $[\alpha]_D^{25}$ = −1584.5 (*c* 0.074, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.63 (6 H, br), 1.87 (6 H, br), 2.01 (1 H, d, *J* = 6.0 Hz), 2.10 (3 H, br), 3.12–3.42 (4 H, m), 3.98 (1 H, dd, *J* = 16.8, 7.2 Hz), 4.16 (1 H, dd, *J* = 8.9, 3.9 Hz), 4.40 (1 H, d, *J* = 4.3 Hz), 4.60 (1 H, t, *J* = 8.8 Hz), 5.19 (1 H, dd, *J* = 8.7, 3.9 Hz), 6.78–6.82 (2 H, m), 6.94–7.00 (3 H, m), 7.20–7.28 (3 H, m), 7.28–7.44 (5 H, m), 7.45–7.63 (5 H, m), 7.79 (2 H, d, *J* = 8.1 Hz), 8.31 (1 H, d, *J* = 8.4 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.2, 35.6, 36.5, 40.5, 44.8, 48.5, 57.3, 58.1, 69.7, 72.2, 120.8, 122.3, 123.1, 125.5, 125.9, 126.1, 126.7, 127.2, 128.1, 128.3, 128.5, 125.6, 128.7, 129.0, 129.2, 130.0, 130.4, 133.0, 133.4, 133.9, 138.4, 143.0, 143.0, 153.3, 169.6, 171.1, 176.4, 176.9. HRMS: calcd for $C_{49}H_{47}N_4O_6Ni$ $[M + H]^+$ 845.2849, found 845.2831.

Ni(II) complex of (2*R*,3*S*,4″*R*)-3-(4′-trifluoromethylphenyl)-5-[3″-(4″-phenyl-2″-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (26b). $[\alpha]_D^{25}$ = −2560.6 (*c* 0.088, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 1.58 (6 H, br), 1.73 (6 H, br), 1.80–1.91 (2 H, m), 2.04

(3 H, br), 2.63 (1 H, d, J = 16.7 Hz), 3.35–3.49 (2 H, m), 3.96–4.08 (1 H, m), 4.12 (1 H, dd, J = 8.8, 3.8 Hz), 4.46 (1 H, d, J = 4.1 Hz), 4.58 (1 H, t, J = 8.8 Hz), 5.18 (1 H, dd, J = 8.6, 3.7 Hz), 6.76–6.91 (4 H, m), 7.00 (2 H, t, J = 7.6 Hz), 7.08–7.17 (2 H, m), 7.30 (1 H, ddd, J = 7.5, 6.6, 2.1 Hz), 7.35–7.44 (2 H, m), 7.50 (2 H, t, J = 7.5 Hz), 7.55–7.65 (3 H, m), 7.93–8.04 (4 H, m), 8.26 (1 H, d, J = 8.5 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.2, 35.6, 36.5, 40.5, 45.3, 47.9, 57.4, 57.9, 69.6, 72.8, 120.7, 123.2, 125.5, 126.5, 126.6, 127.3, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.5, 128.6, 129.0, 129.1, 129.9, 132.8, 133.2, 133.5, 133.7, 133.8, 136.3, 138.5, 143.0, 153.2, 170.1, 170.7, 176.4, 177.1 (the CF_3 peak was obscured due to low intensity). ^{19}F NMR (376.4 MHz, $CDCl_3$): δ −62.1 (s, 3F). HRMS: calcd for $C_{46}H_{44}F_3N_4O_6Ni$ $[M + H]^+$ 863.2566, found 863.2564.

Ni(II) complex of (2*S*,3*R*,4″*S*)-3(4′-methoxyphenyl)-5-[3″-(4″-phenyl-2″-oxazolidinonyl)]glutamic acid Schiff base with *N*-(2-benzoylphenyl)-2-((adamant-1-yl)amino)acetamide (27b). $[\alpha]_D^{25}$ = +1576.2 (c 0.061, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.64 (6 H, br), 1.69 (1 H, d, J = 6.8 Hz), 1.87 (6 H, br), 2.11 (3 H, br), 3.10–3.33 (3 H, m), 3.42 (1 H, dd, J = 17.8, 8.0 Hz), 3.71 (1 H, dd, J = 17.8, 7.0 Hz), 3.92 (3 H, s), 4.16 (1 H, dd, J = 8.8, 3.6 Hz), 4.41 (1 H, d, J = 4.9 Hz), 4.59 (1 H, t, J = 8.7 Hz), 5.18 (1 H, dd, J = 8.6, 3.6 Hz), 6.75–6.84 (2 H, m), 6.98–7.04 (3 H, m), 7.11 (2 H, d, J = 8.7 Hz), 7.25–7.40 (8 H, m), 7.46 (1 H, t, J = 7.5 Hz), 7.56 (1 H, t, J = 7.0 Hz), 8.24 (1 H, d, J = 8.3 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 29.3, 35.7, 36.5, 40.6, 44.2, 48.7, 55.5, 57.4, 57.9, 69.6, 72.4, 113.9, 120.7, 123.1, 125.7, 127.3, 127.5, 128.2, 128.7, 129.9, 130.7, 131.5, 132.7, 133.6, 133.8, 138.8, 142.8, 153.2, 159.6, 170.0, 170.4, 176.4, 177.2. HRMS: calcd for $C_{46}H_{47}N_4O_7Ni$ $[M + H]^+$ 825.2798, found 825.2797.

General procedure for the disassembly of complexes (*S*)(2*S*,3*R*)-21d, 26a, 27a

To a suspension of complex **21d**, **26a** or **27a** (10 mmol) in MeOH (40 mL), a mixture of 3 N HCl and MeOH (80 mL, ratio 1/1) was added with stirring at 70 °C. Red color of the reaction mixture gradually disappeared (~2 h) indicating complete decomposition of the Ni(II) complexes. The reaction mixture was evaporated *in vacuo* to dryness. Water (75 mL) and conc. NH_4OH were added to the crystalline residue to obtain a transparent solution which was extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 extracts were dried over $MgSO_4$ and evaporated *in vacuo* to afford a 1 : 1 mixture (~96%) of chiral auxiliary (*S*)-**31** and ligands **8d** or **9**. The aqueous solution was evaporated *in vacuo*, dissolved in a minimum amount of water, and loaded on a column with cation exchange resin Dowex 50X2 100. The column was washed with water and the target pyroglutamic acids **28–30** were collected in an acidic fraction. Evaporation of water and drying *in vacuo* of the crystalline residue afforded amino acids of at least 95% chemical purity. For analytical purpose products **28–30** were recrystallized from THF–*n*-hexane (1 : 5).

(2*S*,3*R*)-3-Phenylpyroglutamic acid (28). Yield 92%; m.p. 139.0–140.0 °C; $[\alpha]_D^{25}$ = +79.1 (c 1.0, $CHCl_3$), lit.[17b] {$[\alpha]_D^{25}$ = +75.6 (c 0.74, CH_3OH)}. ^{1}H NMR (300 MHz, CD_3OD): δ 2.31 (1 H, dd, J = 17.1, 6.1 Hz), 2.72 (1 H, dd, J = 17.1, 9.3 Hz), 3.57 (1 H, ddd, J = 9.3, 6.1, 4.9 Hz), 4.11 (1 H, d, J = 4.9 Hz), 7.11–7.25 (5 H, m). ^{13}C NMR (75.5 MHz, CD_3OD): δ 39.5, 45.5, 64.5, 128.0, 128.4, 130.1, 143.7, 174.8, 179.9. HRMS: calcd for $C_{11}H_{12}NO_3$ $[M + H]^+$ 206.0817, found 206.0809.

(2*S*,3*R*)-3-(*p*-Trifluoromethylphenyl)pyroglutamic acid (29). Yield 93%; m.p. 172.0–172.5 °C; $[\alpha]_D^{25}$ = +76.0 (c 1.0, $CHCl_3$); lit.[17b] {$[\alpha]_D^{25}$ = +73.3 (c 1.3, $CHCl_3$)}. ^{1}H NMR (CD_3OD): δ 2.48 (1 H, dd, J = 17.0, 6.6 Hz), 2.88 (1 H, dd, J = 17.0, 9.3 Hz), 3.82 (1 H, ddd, J = 9.3, 6.0, 5.6 Hz), 4.27 (1 H, d, J = 5.4 Hz), 7.55, 7.66 (4 H, d, J = 8.3 Hz). ^{19}F NMR (CD_3OD): δ −65.5 (3 F, s). ^{13}C NMR (CD_3OD): δ 39.2, 45.4, 64.1, 126.9 (q, J = 4.0 Hz), 126.7, 128.8, 148.1, 174.5, 179.2. HRMS: calcd for $C_{12}H_{11}F_3NO_3$ $[M + H]^+$ 274.0691, found 274.0691.

(2*S*,3*R*)-3-(*p*-Methoxyphenyl)pyroglutamic acid (30). Yield 90%; m.p. 184.0–186.0 °C; $[\alpha]_D^{25}$ = +85.9 (c 1.0, $CHCl_3$); lit.[17b] {$[\alpha]_D^{25}$ = +87.1 (c 1.6, $CHCl_3$)}. ^{1}H NMR (CD_3OD): δ 2.41 (1 H, dd, J = 17.2, 6.0 Hz), 2.81 (1 H, dd, J = 17.1, 9.3 Hz), 3.64 (1 H, ddd, J = 9.4, 6.0, 5.1 Hz), 3.76 (3 H, s), 4.16 (1 H, d, J = 5.1 Hz), 6.90, 7.23 (4 H, d, J = 8.8 Hz). ^{13}C NMR (CD_3OD): δ 39.5, 45.1, 55.7, 64.8, 115.3, 129.1, 135.7, 160.2, 179.8, 179.9. HRMS: calcd for $C_{12}H_{14}NO_4$ $[M + H]^+$ 236.0923, found 236.0921.

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