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Asymmetric Synthesis of Chiral α-Methyl-α,β-diamino Acid Derivatives via Group-Assisted Purification Chemistry Using *N*-Phosphonyl Imines and a Ni(II)-Complexed Alanine Schiff Base

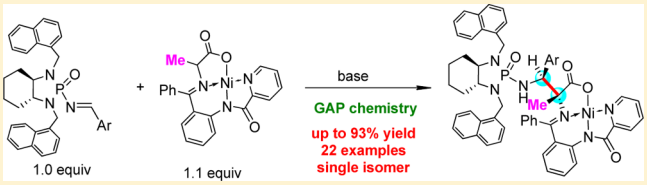
Haowei Zhang,[†] Bing Yang,[†] Zhen Yang,[†] Hongjian Lu,[†] and Guigen Li*[,†,‡]

[†]Institute of Chemistry and BioMedical Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[‡]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States

Supporting Information

ABSTRACT: The Mannich reaction between chiral *N*-phosphonyl imines and a Ni(II)-complexed alanine Schiff base (Ala-Ni) is reported. With a chiral phosphonyl auxiliary, a single isomer of α-methyl-α,β-diamino acid derivative containing vicinal chiral centers, including a chiral quaternary carbon center, can be obtained simply by washing the crude mixture with cosolvents. The absolute stereochemistry of the enantiomerically pure product has been unambiguously determined by X-ray crystallographic analysis.



INTRODUCTION

In current green chemical synthesis,[1,2] designing reagents that can control solubility, reactivity, and stereoselectivity simultaneously remains a challenge. In recent years, our group has devoted great effort to the design and application of new chiral and achiral imines with phosphorus-containing auxiliaries,[3−9] leading to a new concept called group-assisted purification (GAP) chemistry/technology.[3] For example, imines with *N*-phosphonyl, *N*-phosphoryl, and *N*-phosphinyl attachments[4] have been successfully utilized in various reactions, such as an aza-Darzens reaction,[5] a borylation,[6] an aza-MBH reaction,[7] and several others.[8] In these studies, yields and stereochemistry were promoted and controlled by the auxiliaries and pure products can be obtained simply by washing the crude mixture with common solvents without recourse to chromatography or recrystallization. Synthetic chemistry that takes advantage of this concept not only can greatly accelerate the chemical production but also can minimize the use of silica gel, eluents, energy, and manpower, thus saving natural resources.[9]

Chiral α,β-diamino acid compounds have attracted much attention because they are key structural fragments in a number of biologically active compounds.[10] Additionally, the vicinal chiral centers also represent a challenge for synthetic organic chemists, especially in the synthesis of enantiomerically pure materials. A direct Mannich reaction between an α-amino acid equivalent and an imine, in which a C−C bond and two stereogenic centers are created in a single operation, is an attractive and efficient route to chiral α,β-diamino acids. Among different nucleophilic α-amino acid equivalents, the Ni(II) complex derived from an α-amino acid and pyridine-2-carboxylic acid (2-benzoyl-phenyl)-amide (PBP) was described as one of the most useful equivalents[11] because it can be deprotonated by commonly applied organic or inorganic bases, such as NaOH, Et_3N, or DBU (1,8-diazobicyclo[5.4.0]undecene-7).[12−15] For example, Gly-Ni, derived from glycine and PBP, has been successfully utilized in the synthesis of various α-hydrogen α,β-diamino acid analogues[16,17] (Scheme 1). However, aside from Gly-Ni, this type of Mannich reaction involving the Ni(II) complexes derived from other α-amino acids such as alanine, valine, or phenylalanine has not been well documented, possibly because of steric problems. Following previous studies in our laboratory,[8] we would like to report that the Mannich reaction between imines and the Ni(II) complex Ala-Ni leads to the formation of α-methyl-α,β-diamino acid analogues. With a chiral phosphorus-containing auxiliary, a single isomer containing vicinal chiral centers, including a chiral quaternary carbon center, was obtained simply by washing the crude mixture with cosolvents (Scheme 1). We note that a hydrogen atom replaced by the smallest alkyl group, methyl, can significantly affect the biological activities and physical properties of bioactive molecules. This has been called the "magic methyl effect".[18]

RESULTS AND DISCUSSION

The reaction between Ala-Ni (**2**) and the *N*-phosphonyl imine derived from (1*R*,2*R*)-1,2-diphenylethylene diamine (**1a′**) was allowed to proceed in DCM at −78 °C with *t*-BuOK as the base (Table 1, entry 1).[8] No product, even in trace amounts, was produced. Because the α-methyl group of the ester influences the acidity of the α-hydrogen, other bases, including LDA, *n*-BuLi, DBU, and NaOH, were explored (entries 2−5, respectively), but no products were observed in these cases. In light of the structural flexibility of the auxiliaries, other

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Scheme 1. Synthesis of α,β-Diamino Acid Derivatives Using a Ni(II)-Complexed Schiff Base

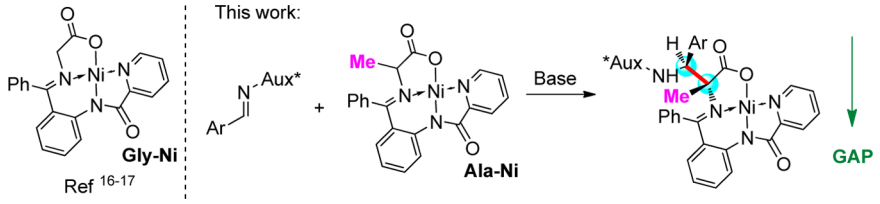
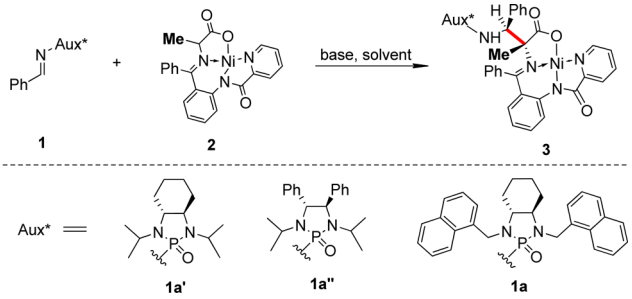


Table 1. Screening of Reaction Conditions



entry[a]	substrate	base	solvent	temp (°C)	yield
1	**1a′** (or **1a″**)	*t*-BuOK	DCM	−78	–[b]
2	**1a′** (or **1a″**)	LDA	DCM	−78	–[b]
3	**1a′** (or **1a″**)	*n*-BuLi	DCM	−78	–[b]
4	**1a′** (or **1a″**)	DBU	DCM	−78	–[b]
5	**1a′** (or **1a″**)	NaOH	DCM	−78	–[b]
6	**1a**	*t*-BuOK	DCM	−78	41% (81%[c])
7	**1a**	LDA	THF	−78	trace
8	**1a**	*n*-BuLi	THF	−78	trace
9	**1a**	DBU	DCM	0	31%
10	**1a**	DABCO	DCM	0	15%
11	**1a**	NaOH	DCM	−78	trace
12	**1a**	*t*-BuOK	DCM	−48	79%[d]
13	**1a**	*t*-BuOK	DCM	0	44%
14	**1a**	*t*-BuOK	THF	−48	24%
15	**1a**	*t*-BuOK	toluene	−48	55%
16	**1a**	*t*-BuOK	acetone	−48	60%

[a]Reactions were performed with imine **1a** (0.2 mmol), Ala-Ni (0.22 mmol, 1.1 equiv), and base (0.24 mmol, 1.2 equiv) in 10 mL of solvent under N_2 for 4 h. [b]Imines **1a′** and **1a″** remained. [c]Isolated yield after the reaction was extended to 24 h. [d]Isolated yield determined by GAP washing. Other conversion rates were determined by ^{31}P NMR analysis of the crude mixture.

N-phosphonyl imines were explored, but the 1,2-diaminocyclohexane-derived, isopropyl-protected imine **1a″** also afforded no product (entries 1−5), suggesting that steric hindrance between the methyl group from the Ni(II) complex and the isopropyl group from the imine may be significant. When the naphthylmethyl-protected imine (**1a**) reacted with Ala-Ni (**2**) in DCM at −78 °C with *t*-BuOK as the base, the desired product (**3a**) was obtained in 41% isolated yield (entry 6). Subsequently, various bases, solvents, and temperatures for the asymmetric addition were examined systematically. Among the bases examined, *t*-BuOK (entry 6) was found to be optimal (41% at −78 °C for 4 h). Strong bases like LDA and *n*-BuLi and the inorganic base NaOH gave only trace amounts of product, because the imine decomposed to form phosphinamide and benzaldehyde. At the same time, some commonly used organic bases, including DBU and DABCO, at higher temperatures (0 °C) can form the product, but with somewhat lower yields (31 and 15%, respectively) because of the incomplete conversion of the imine (entries 9 and 10, respectively). After *t*-BuOK had been selected as the base, the reaction temperature and solvents were changed to obtain higher yields and to make GAP washing more convenient. When the reaction time was prolonged to 24 h at −78 °C (entry 6), the conversion rate was significantly improved to 81%, indicating a slow reaction rate. When the temperature was increased to −48 °C (entry 12), the reaction was completed in 4 h as shown by TLC, and more importantly, a yield of 79% was obtained in this case through GAP washing. The pure individual isomeric product can be obtained simply by washing the crude products with the cosolvents hexane and ethyl acetate [2/1 (v/v)] without the use of chromatography or recrystallization. Interestingly, an increase in the reaction temperature to 0 °C (entry 13) led to an inferior result. Finally, the optimization of solvents revealed that all three solvents, THF, toluene, and acetone, deliver yields lower than that with DCM (entry 12 vs entries 14−16, respectively). Among all the cases described above, only one isomer was obseverd according to the ^{31}P NMR of the reaction mixture.

With the optimized reaction conditions established, the substrate scope was evaluated. As shown in Scheme 2, substrates (**1**) attached to aromatic rings with electron-donating or electron-withdrawing groups at different positions can be efficiently transformed into the α,β-diamino acid derivatives in high yields. Only a single diastereoisomer was found in each case by analysis of the crude products by ^{31}P NMR spectroscopy, and the product was >99/1 dr. Of all the cases, the 4-nitro substituent gave the highest yield (**3h**, 93%). Other electron-withdrawing groups such as 2-CF_3 (**3t**, 84%) and 2-OMe (**3s**, 69%) performed better than electron-donating groups. In addition, 2-furyl-substituted imines can function well in this reaction (**3u**, 77%), proving the high efficiency of the method using *N*-phosphonyl heteroaryl-functionalized imines. It should be emphasized that when treating the Ni(II) complex with α,β-unsaturated *N*-phosphonyl imine, we obtained only one isomer (**3v**) in 67% yield, which underwent 1,2-addition affording γ,δ-unsaturated α,β-diamino acid derivatives. In all of the cases, the pure products were obtained simply by washing the crude mixture with hexane and ethyl acetate [2/1 (v/v)] once or twice without the use of chromatography or recrystallization.

Ni(II) complexes derived from other amino acids were examined, as well, and indicated that the bulk of the substitution groups can inhibit the reaction significantly. If the methyl group is changed to ethyl, the yields decreased from 90 to 59% (Scheme 2) with >99/1 dr. After the methyl group had been changed to isopropyl or benzyl, no products were observed even after the reaction had been prolonged to 24 h.

The absolute configuration of **3q** was determined by X-ray structural analysis (see the Supporting Information), revealing the two vicinal chiral centers retaining a (2*R*,3*S*) configuration (CCDC entry 1482489), consistent with our previous work.[8] In view of the previous report[19] and the observed

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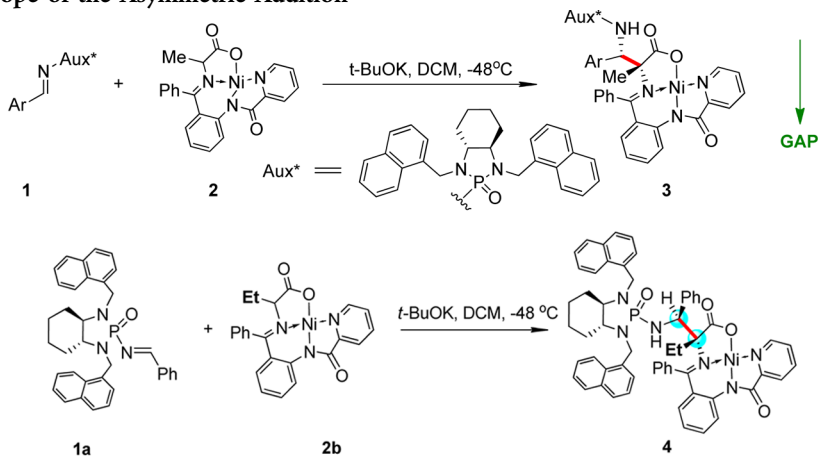
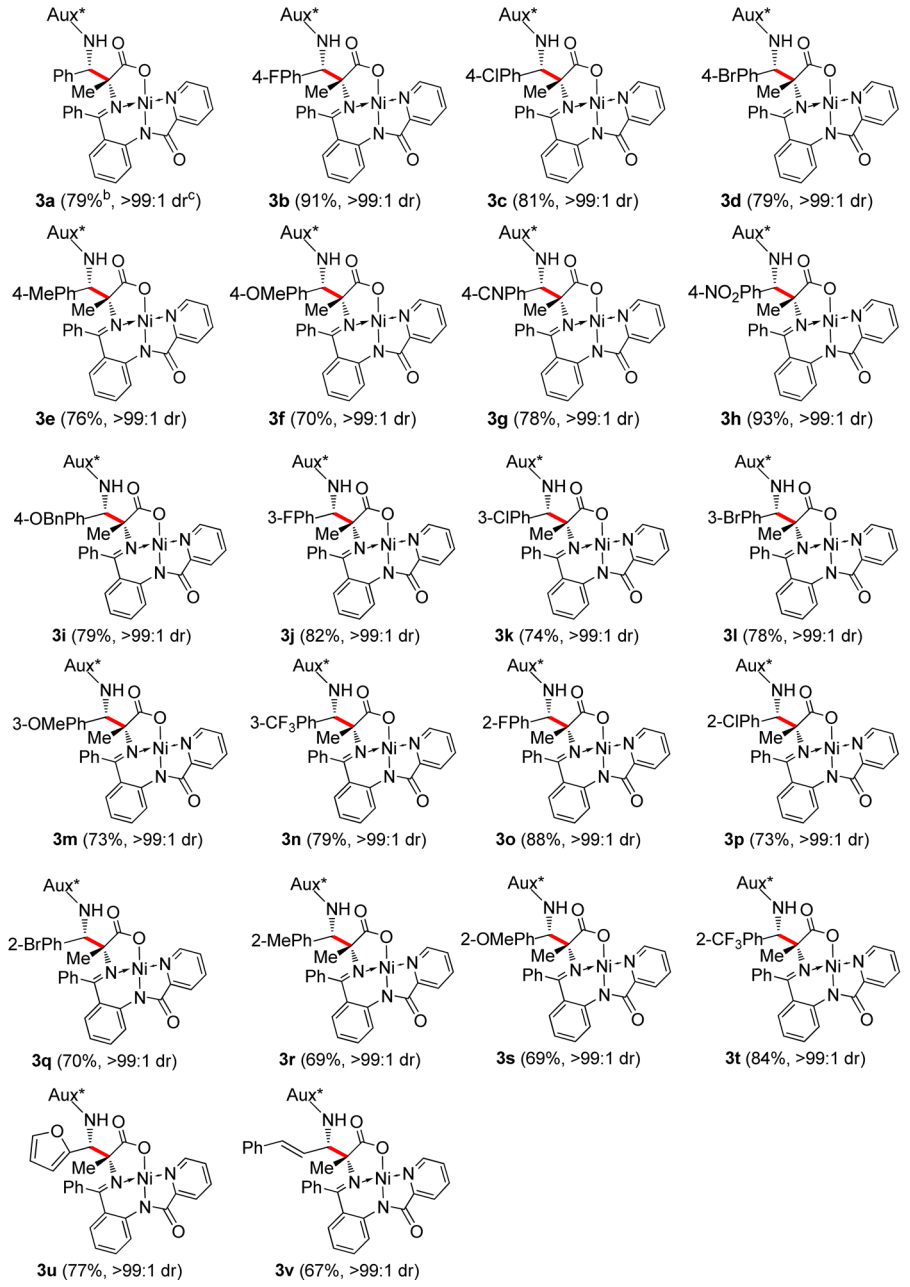
Scheme 2. Substrate Scope of the Asymmetric Addition[a]





[a]Reactions were performed with imine (0.4 mmol), Ala-Ni (0.44 mmol), and *t*-BuOK (0.48 mmol) in dry DCM at −48 °C under N_2 for 4 h. [b]Isolated yields after GAP washing. [c]Based on analysis of ^{1}H NMR and ^{31}P NMR data of the reaction mixture; >99/1 means only one isomer was observed.

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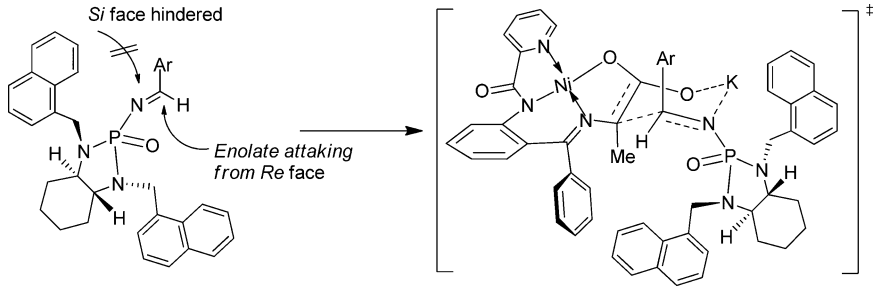
Scheme 3. Proposed Transition State Model



absolute configuration, the asymmetric addition is considered to go through the cyclic six-membered transition state that is shown in Scheme 3. The enolate derived from the Ni(II)-complexed alanine Schiff base has *Z* geometry, which leads to *syn* stereochemistry of the vicinal amino groups. The aromatic ring at the axial position is almost parallel to the planar Ni(II) complex and can thus avoid diaxial interaction.[8a] The *S* configuration at the β position can be explained by the fact that nucleophilic attack occurs from the *re* face of the *N*-phosphonyl imine.

In conclusion, we have developed an efficient protocol for the asymmetric synthesis of α-methyl-α,β-diamino acid derivatives using chiral *N*-phosphonyl imines and a Ni(II)-complexed alanine Schiff base. Good yields and complete diastereoselectivity have been achieved in 21 examples. A single isomer containing vicinal chiral centers and a chiral quaternary carbon center can be obtained simply by washing the crude mixture with hexane and ethyl acetate [2/1 (v/v)] once or twice without the use of chromatography or recrystallization. Finally, the absolute stereochemistry was determined by X-ray analysis. This provides a valuable addition to GAP chemistry.

EXPERIMENTAL SECTION

General Method. All commercially available solvents, unless otherwise mentioned, were used without further purification. Ether, dichloromethane, tetrahydrofuran, and toluene were obtained from the Innovation Technology solvent system. Melting points are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR (TMS used as an internal standard) spectra were recorded with a 400 MHz instrument. Data are represented as follows: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet), coupling constant (*J*, in hertz), and integration. High-resolution mass spectra for all the new compounds were determined with a TOF-MS instrument with an ESI source.

Synthesis of *N*-Phosphonyl Imines 1a–v. These compounds were synthesized according to published procedures.[20] The ^{1}H and ^{31}P NMR data for these compounds agree with the published data.

Typical Procedure for the Asymmetric Synthesis of Products 3a–v through GAP Progress. In an oven-dried and nitrogen-charged 50 mL round-bottom vial, 0.44 mmol of Ala-Ni (**2b**) and 0.48 mmol of *t*-BuOK powder were added with 10 mL of dry DCM. The mixture was stirred in a cold bath at −48 °C for 20 min. Then a solution of *N*-phosphonyl imine **1** (0.4 mmol) in dry DCM (5 mL) was added dropwise via syringe over 10 min. The reaction mixture was stirred for an additional 4 h before the reaction was quenched with a saturated NH_4Cl solution (5 mL). The bilayer was separated and the organic layer washed twice with brine, dried over Na_2SO_4, filtered, and concentrated to dryness. Ethyl acetate (~10 mL) was added to resolve the residue followed by dropwise addition of hexane (~10 mL) to form a precipitate. After filtration, the cake was washed once or twice with hexane and ethyl acetate [2/1 (v/v)] to afford the pure product.

Data for Pure Products 3a–v. *Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-phenylpropanoic Acid Schiff Base Complex (**3a**).* Obtained as a red solid: 364 mg, 79% yield; mp 203.8–204.2 °C; $[\alpha]_D^{20}$ = −1595 (*c* = 0.200, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.5 Hz, 1H), 7.92 (bs, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.80–7.71 (m, 5H), 7.68–7.59 (m, 4H), 7.58–7.48 (m, 4H), 7.47–7.36 (m, 5H), 7.25–7.15 (m, 3H), 7.14–7.04 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.68 (dt, *J* = 14.9, 7.6 Hz, 2H), 6.53 (t, *J* = 7.2 Hz, 2H), 6.29 (t, *J* = 7.2 Hz, 1H), 4.99 (t, *J* = 9.0 Hz, 1H), 4.52 (dd, *J* = 16.6, 11.2 Hz, 1H), 4.38 (t, *J* = 11.2 Hz, 1H), 4.21 (t, *J* = 15.7 Hz, 1H), 4.10–4.00 (m, 1H), 3.91 (dd, *J* = 16.8, 7.7 Hz, 1H), 3.07–2.90 (m, 2H), 1.54–1.37 (m, 4H), 1.21–0.93 (m, 4H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 173.5, 168.9, 153.2, 146.7, 142.0, 139.7, 136.1, 135.4 (d, *J* = 4.7 Hz), 135.0, 134.8 (d, *J* = 5.4 Hz), 133.7, 133.5, 133.1, 131.1, 131.0, 130.3, 129.3, 129.0, 128.9, 128.74, 128.69, 128.6, 127.6, 127.5, 127.3, 127.2, 127.0, 126.2, 125.8, 125.70, 125.67, 125.63, 125.5, 125.4, 125.3, 124.3, 123.6, 123.29, 123.27, 122.7, 121.3, 82.5 (d, *J* = 9.4 Hz), 64.3 (d, *J* = 9.9 Hz), 63.6 (d, *J* = 9.0 Hz), 63.5, 44.5 (d, *J* = 4.4 Hz), 43.3 (d, *J* = 3.1 Hz), 29.8 (d, *J* = 10.2 Hz), 29.5 (d, *J* = 8.5 Hz), 27.6, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.47; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{57}H_{51}N_6NaNiO_4P$ 995.2955, found 995.2962.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-fluorophenyl)propanoic Acid Schiff Base Complex (**3b**).* Red solid: 451 mg, 91% yield; mp 196.8–198.9 °C; $[\alpha]_D^{20}$ = −1437 (*c* = 0.200, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1H), 8.02–7.89 (m, 2H), 7.87–7.70 (m, 6H), 7.67–7.61 (m, 2H), 7.59–7.39 (m, 7H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.25–7.16 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.79 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.69–6.64 (m, 1H), 6.52 (t, *J* = 7.5 Hz, 1H), 6.05 (t, *J* = 8.5 Hz, 2H), 5.08–5.01 (m, 1H), 4.53 (dd, *J* = 16.9, 10.9 Hz, 1H), 4.29–4.15 (m, 2H), 4.10–3.97 (m, 2H), 3.07 (t, *J* = 8.9 Hz, 1H), 2.96 (t, *J* = 10.3 Hz, 1H), 1.55–1.42 (m, 4H), 1.25–0.92 (m, 4H), 1.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 173.7, 168.8, 161.9 (d, *J* = 247.2 Hz), 153.0, 146.6, 142.5, 140.1, 137.9 (d, *J* = 3.1 Hz), 135.8, 135.25 (d, *J* = 4.7 Hz), 135.1 (d, *J* = 6.5 Hz), 134.9, 133.7, 133.5, 133.2, 131.0, 130.8, 130.63, 130.55, 130.1, 129.3, 128.9, 128.8, 128.7, 128.6, 127.4, 127.1, 126.9, 126.2, 125.9, 125.7, 125.60, 125.57, 125.5, 125.2, 123.74, 123.70, 123.5, 123.2, 122.4, 121.43, 114.3, 114.1, 82.4 (d, *J* = 9.3 Hz), 64.2 (d, *J* = 9.6 Hz), 64.1 (d, *J* = 9.1 Hz), 62.9, 44.5 (d, *J* = 4.9 Hz), 43.5 (d, *J* = 3.5 Hz), 29.8 (d, *J* = 11.0 Hz), 29.5 (d, *J* = 8.6 Hz), 27.4, 24.4, 24.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.59; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{57}H_{50}FN_6NaNiO_4P$ 1013.2861, found 1013.2858.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-chlorophenyl)propanoic Acid Schiff Base Complex (**3c**).* Red solid: 407 mg, 81% yield; mp 198.6–201.1 °C; $[\alpha]_D^{20}$ = −1456 (*c* = 0.200, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.5 Hz, 1H), 7.94 (t, *J* = 9.8 Hz, 2H), 7.87–7.71 (m, 6H), 7.66 (d, *J* = 7.0 Hz, 1H), 7.64–7.39 (m, 8H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.25–7.15 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.78 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.69–6.63 (m, 1H), 6.54 (t, *J* = 7.5 Hz, 1H), 6.31 (d, *J* = 8.1 Hz, 2H), 5.05–4.98 (m, 1H), 4.52 (dd, *J* = 16.9, 11.0 Hz, 1H), 4.28–4.15 (m, 2H), 4.08–3.97 (m, 2H), 3.07 (t, *J* = 11.2 Hz, 1H), 2.96 (t, *J* = 11.6 Hz, 1H), 1.56–1.46 (m, 4H), 1.24–0.93 (m, 4H), 1.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 173.6, 168.8, 152.7, 146.4, 142.5, 140.7, 140.2, 135.8, 135.2 (d,

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J = 4.8 Hz), 135.0 (d, J = 6.5 Hz), 134.9, 133.7, 133.5, 133.2, 131.0, 130.8, 130.3, 130.1, 129.3, 128.9, 128.8, 128.7, 128.6, 127.6, 127.4, 127.1, 127.0, 126.9, 126.2, 126.0, 125.9, 125.7, 125.64, 125.59, 125.5, 125.2, 123.8, 123.72, 123.67, 123.2, 122.3, 121.4, 82.3 (d, J = 9.2 Hz), 64.2 (d, J = 10.1 Hz), 64.0 (d, J = 9.5 Hz), 63.0, 44.5(s), 43.4 (d, J = 3.5 Hz), 29.8 (d, J = 9.5 Hz), 29.5 (d, J = 8.5 Hz), 27.4, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.46; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{57}H_{50}ClN_6NaNiO_4P$ 1029.2565, found 1029.2581.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-bromophenyl)propanoic Acid Schiff Base Complex (**3d**).* Red solid: 410 mg, 79% yield; mp 219.1−221.8 °C; $[\alpha]_D^{20}$ = −1518 (c = 0.200, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50−8.43 (m, 1H), 7.97−7.90 (m, 2H), 7.88−7.72 (m, 6H), 7.68 (d, J = 7.6 Hz, 1H), 7.64−7.40 (m, 8H), 7.34 (d, J = 7.6 Hz, 1H), 7.25−7.10 (m, 5H), 7.07 (d, J = 7.8 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.77 (dd, J = 8.5, 1.4 Hz, 1H), 6.65 (t, J = 7.2 Hz, 1H), 6.54 (t, J = 7.5 Hz, 1H), 6.47 (d, J = 7.9 Hz, 2H), 5.03−4.92 (m, 1H), 4.51 (dd, J = 17.0, 11.1 Hz, 1H), 4.30−4.15 (m, 2H), 4.09−3.94 (m, 2H), 3.06 (t, J = 9.1 Hz, 1H), 2.97 (t, J = 9.0 Hz, 1H), 1.58−1.42 (m, 4H), 1.32−0.91 (m, 4H), 1.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 173.6, 168.8, 152.5, 146.4, 142.5, 141.2, 140.2, 135.8, 135.2 (d, J = 4.8 Hz), 134.90, 134.85, 133.6, 133.4, 133.2, 130.9, 130.7, 130.61, 130.59, 130.2, 129.3, 128.8, 128.74, 128.68, 128.5, 127.3, 127.1, 127.0, 126.9, 126.2, 126.1, 125.9, 125.7, 125.64, 125.56, 125.4, 125.1, 123.9, 123.65, 123.63, 123.1, 122.3, 121.7, 121.3, 82.2 (d, J = 9.2 Hz), 64.2 (d, J = 10.1 Hz), 63.9 (d, J = 9.6 Hz), 63.0, 44.4 (d, J = 4.6 Hz), 43.4 (d, J = 3.3 Hz), 29.7 (d, J = 10.8 Hz), 29.4 (d, J = 8.4 Hz), 27.4, 24.32, 24.26; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.41; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{57}H_{50}BrN_6NaNiO_4P$ 1073.2060, found 1073.2057.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-p-tolylpropanoic Acid Schiff Base Complex (**3e**).* Red solid: 365 mg, 76% yield; mp 201.1−202.9 °C; $[\alpha]_D^{20}$ = −1578 (c = 0.218, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.4 Hz, 1H), 7.95−7.89 (m, 2H), 7.85 (d, J = 7.3 Hz, 1H), 7.82−7.77 (m, 4H), 7.75 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 6.4 Hz, 2H), 7.61 (d, J = 7.5 Hz, 1H), 7.57−7.50 (m, 4H), 7.48−7.40 (m, 3H), 7.28−7.12 (m, 7H), 6.86−6.77 (m, 2H), 6.68 (t, J = 7.6 Hz, 1H), 6.27 (d, J = 7.5 Hz, 2H), 5.00−4.92 (m, 1H), 4.56 (dd, J = 17.0, 11.1 Hz, 1H), 4.34 (t, J = 11.3 Hz, 1H), 4.25−4.14 (m, 1H), 4.05 (dd, J = 17.5, 5.3 Hz, 1H), 3.91 (dd, J = 17.0, 8.3 Hz, 1H), 3.09−2.92 (m, 2H), 1.56−1.44 (m, 4H), 1.42 (s, 3H), 1.30−0.90 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 173.2, 168.7, 153.0, 146.8, 142.6, 139.5, 139.1, 137.3, 136.1, 135.4 (d, J = 4.9 Hz), 135.0, 134.9 (d, J = 5.9 Hz), 133.6, 133.5, 133.1, 131.0, 130.9, 130.3, 129.3, 129.1, 128.9, 128.7, 128.6, 128.3, 127.3, 127.1, 127.0, 126.9, 126.1, 125.8, 125.7, 125.6, 125.5, 125.3, 125.2, 124.2, 123.5, 123.2, 123.0, 122.6, 121.3, 82.6 (d, J = 9.7 Hz), 64.4 (d, J = 10.0 Hz), 63.5 (d, J = 9.2 Hz), 63.4, 44.4 (d, J = 4.7 Hz), 43.3 (d, J = 3.6 Hz), 29.8 (d, J = 7.9 Hz), 29.6 (d, J = 8.3 Hz), 27.5, 24.4, 24.3, 20.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.66; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{58}H_{53}N_6NaNiO_4P$ 1009.3112, found 1009.3109.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-methoxyphenyl)propanoic Acid Schiff Base Complex (**3f**).* Red solid: 317 mg, 70% yield; mp 160.3−161.6 °C; $[\alpha]_D^{20}$ = −1348 (c = 0.231, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 8.5 Hz, 1H), 7.99−7.91 (m, 2H), 7.87−7.73 (m, 6H), 7.70−7.61 (m, 3H), 7.59−7.50 (m, 4H), 7.48−7.39 (m, 3H), 7.30−7.20 (m, 5H), 7.14−7.08 (m, 2H), 6.81 (dd, J = 8.4, 1.4 Hz, 1H), 6.78−6.73 (m, 1H), 6.73−6.67 (m, 1H), 6.00 (d, J = 8.3 Hz, 2H), 5.02−4.94 (m, 1H), 4.58 (dd, J = 16.9, 11.0 Hz, 1H), 4.34−4.20 (m, 2H), 4.10−3.94 (m, 2H), 3.13 (s, 3H), 3.09−2.94 (m, 2H), 1.56−1.43 (m, 4H), 1.24−0.96 (m, 4H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 173.3, 168.9, 158.9, 153.0, 146.7, 142.6, 139.8, 136.0, 135.39 (d, J = 5.0 Hz), 135.0, 134.9, 134.1, 133.7, 133.5, 133.1, 131.0, 130.9, 130.25, 130.22, 129.4, 128.83, 128.77, 128.6, 127.3, 127.2, 127.0, 126.1, 125.9, 125.71, 125.68, 125.6, 125.5, 125.4, 125.2, 124.2, 123.6, 123.2, 123.1, 122.64, 121.4, 112.8, 82.7 (d, J = 9.7 Hz), 64.4 (d, J = 10.1 Hz), 63.7 (d, J = 9.7 Hz), 63.2, 54.4, 44.5 (d, J = 4.5 Hz), 43.4, 29.7 (d, J = 10.0 Hz), 29.6 (d, J = 7.9 Hz), 27.5, 24.40, 24.35; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.75; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{58}H_{53}N_6NaNiO_5P$ 1025.3061, found 1025.3069.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-cyanophenyl)propanoic Acid Schiff Base Complex (**3g**).* Red solid: 378 mg, 78% yield; mp 210.5−213.2 °C; $[\alpha]_D^{20}$ = −1356 (c = 0.205, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46−8.38 (m, 1H), 7.96 (s, 2H), 7.91−7.74 (m, 5H), 7.72−7.67 (m, 2H), 7.61−7.48 (m, 7H), 7.43−7.39 (m, 1H), 7.30 (d, J = 7.7 Hz, 1H), 7.25−7.17 (m, 4H), 7.05 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 7.8 Hz, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.78 (dd, J = 8.5, 1.5 Hz, 1H), 6.69−6.64 (m, 1H), 6.47 (s, 1H), 6.45 (s, 1H), 6.40 (t, J = 7.5 Hz, 1H), 5.11 (dd, J = 10.1, 8.7 Hz, 1H), 4.53 (dd, J = 17.0, 11.0 Hz, 1H), 4.26−4.06 (m, 3H), 3.95 (dd, J = 18.0, 5.7 Hz, 1H), 3.14 (t, J = 8.9 Hz, 1H), 2.97 (t, J = 9.1 Hz, 1H), 1.61−1.50 (m, 4H), 1.33−1.05 (m, 4H), 1.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 174.2, 168.7, 152.6, 147.2, 146.4, 142.4, 140.7, 135.4, 135.2 (d, J = 6.3 Hz), 135.0, 134.9, 133.7, 133.41, 133.38, 131.0, 130.9, 130.6, 130.0, 129.5, 129.4, 128.9, 128.82, 128.79, 128.4, 127.5, 127.3, 127.0, 126.9, 126.4, 126.2, 126.1, 126.0, 125.67, 125.66, 125.5, 125.1, 123.9, 123.8, 123.13, 123.08, 122.0, 121.6, 117.8, 111.0, 82.1 (d, J = 8.9 Hz), 64.5 (d, J = 9.4 Hz), 64.1 (d, J = 10.2 Hz), 63.3, 44.4 (d, J = 4.3 Hz), 43.6 (d, J = 3.2 Hz), 29.8 (d, J = 10.9 Hz), 29.4 (d, J = 8.5 Hz), 27.2, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.56; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{58}H_{50}N_7NaNiO_4P$ 1020.2908, found 1020.2919.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-nitrophenyl)propanoic Acid Schiff Base Complex (**3h**).* Red solid: 441 mg, 93% yield; mp 215.1−218.4 °C; $[\alpha]_D^{20}$ = −1379 (c = 0.201, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.4 Hz, 1H), 8.04−7.90 (m, 2H), 7.88−7.65 (m, 6H), 7.62−7.38 (m, 8H), 7.34−7.19 (m, 6H), 7.17−7.07 (m, 2H), 7.04−6.89 (m, 3H), 6.79 (d, J = 8.2 Hz, 1H), 6.66 (t, J = 7.5 Hz, 1H), 6.46 (t, J = 7.3 Hz, 1H), 5.16 (t, J = 9.2 Hz, 1H), 4.56 (dd, J = 16.6, 11.1 Hz, 1H), 4.30−4.05 (m, 3H), 3.92 (dd, J = 17.9, 5.2 Hz, 1H), 3.15 (t, J = 9.3 Hz, 1H), 2.97 (t, J = 9.5 Hz, 1H), 1.56 (s, 4H), 1.38−1.06 (m, 4H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 174.2, 168.5, 152.6, 149.0, 146.5, 146.3, 142.4, 140.3, 135.4, 135.1 (d, J = 6.0 Hz), 135.0, 134.9, 133.7, 133.4, 133.3, 131.0, 130.4, 129.9, 129.6, 129.4, 129.0, 128.8, 128.7, 128.4, 127.5, 127.3, 127.0, 126.9, 126.4, 126.03, 126.01, 125.8, 125.7, 125.4, 125.1, 123.8, 123.3, 123.1, 123.0, 122.2, 121.8, 121.5, 82.1 (d, J = 8.4 Hz), 64.6 (d, J = 9.5 Hz), 64.0 (d, J = 10.2 Hz), 63.1, 44.4 (d, J = 4.0 Hz), 43.6 (d, J = 2.3 Hz), 29.8 (d, J = 11.2 Hz), 29.4 (d, J = 8.4 Hz), 27.2, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.73; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{57}H_{50}N_7NaNiO_6P$ 1040.2806, found 1040.2813.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(4-benzyloxyphenyl)propanoic Acid Schiff Base Complex (**3i**).* Red solid: 426 mg, 79% yield; mp 182.4−186.1 °C; $[\alpha]_D^{20}$ = −1403 (c = 0.211, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.5 Hz, 1H), 7.99−7.88 (m, 2H), 7.84−7.71 (m, 5H), 7.68 (d, J = 8.2 Hz, 1H), 7.63−7.49 (m, 7H), 7.42−7.28 (m, 8H), 7.24−7.18 (m, 4H), 7.15−7.06 (m, 3H), 6.78 (d, J = 8.4 Hz, 1H), 6.73 (t, J = 7.1 Hz, 1H), 6.65 (t, J = 7.7 Hz, 1H), 6.07 (d, J = 7.9 Hz, 2H), 4.97 (t, J = 9.1 Hz, 1H), 4.56 (dd, J = 16.8, 11.0 Hz, 1H), 4.35−4.19 (m, 4H), 4.05 (dd, J = 17.5, 4.2 Hz, 1H), 3.95 (dd, J = 16.9, 8.0 Hz, 1H), 3.07−2.91 (m, 2H), 1.53−1.41 (m, 4H), 1.26−0.92 (m, 4H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 173.2, 168.8, 158.0, 152.7, 146.6, 142.4, 139.7, 136.9, 135.9, 135.3 (d, J = 4.6 Hz), 134.9, 134.8, 134.4, 133.6, 133.4, 133.0, 130.9, 130.8, 130.2, 129.3, 128.84, 128.76, 128.7, 128.6, 128.5, 127.8, 127.24, 127.17, 127.01, 126.95, 126.9, 126.0, 125.8, 125.62, 125.60, 125.5, 125.4, 125.2, 124.1, 123.5, 123.2, 123.1, 122.5, 121.3, 113.4, 82.6 (d, J = 9.0 Hz), 68.8, 64.2 (d, J = 10.1 Hz), 63.6 (d, J = 9.1 Hz), 63.1, 44.4, 43.3, 29.7 (d, J = 10.1 Hz), 29.5 (d, J = 8.4 Hz), 27.4, 24.3, 24.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.64; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{64}H_{57}N_6NaNiO_5P$ 1101.3374, found 1101.3376.

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*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(3-fluorophenyl)propanoic Acid Schiff Base Complex (**3j**).* Red solid: 396 mg, 82% yield; mp 201.5−202.6 °C; $[\alpha]_D^{20}$ = −1263 (*c* = 0.200, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.86−7.63 (m, 9H), 7.59−7.48 (m, 4H), 7.45−7.36 (m, 3H), 7.25−7.18 (m, 3H), 7.16−7.00 (m, 4H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.69−6.56 (m, 3H), 5.96 (t, *J* = 7.4 Hz, 1H), 5.05 (t, *J* = 9.3 Hz, 1H), 4.55 (dd, *J* = 16.8, 11.1 Hz, 1H), 4.35−4.22 (m, 2H), 4.12−3.98 (m, 2H), 3.05 (t, *J* = 9.2 Hz, 1H), 2.95 (t, *J* = 9.1 Hz, 1H), 1.55−1.40 (m, 4H), 1.22−0.92 (m, 4H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 173.2, 168.9, 162.7 (d, *J* = 247.6 Hz), 153.0, 146.7, 144.6 (d, *J* = 6.3 Hz), 142.6, 140.0, 135.8, 135.2 (d, *J* = 4.8 Hz), 135.0, 134.6 (d, *J* = 6.2 Hz), 133.7, 133.6, 133.3, 131.0, 130.8, 130.2, 129.4, 129.2 (d, *J* = 8.0 Hz), 128.9, 128.8, 128.6, 128.5, 127.4, 127.1, 127.0, 126.5, 125.9, 125.70, 125.67, 125.6, 125.4, 125.3, 125.2 (d, *J* = 2.5 Hz), 124.0, 123.7, 123.4, 123.3, 122.5, 121.4, 115.6 (d, *J* = 21.9 Hz), 114.3 (d, *J* = 21.1 Hz), 82.1 (d, *J* = 9.0 Hz), 64.2 (d, *J* = 10.2 Hz), 63.9 (d, *J* = 9.6 Hz), 63.1, 44.5 (d, *J* = 4.7 Hz), 43.5 (d, *J* = 3.1 Hz), 29.8 (d, *J* = 10.5 Hz), 29.5 (d, *J* = 8.5 Hz), 27.5, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.50; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{57}H_{50}FN_6NaNiO_4P$ 1013.2861, found 1013.2861.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(3-chlorophenyl)propanoic Acid Schiff Base Complex (**3k**).* Red solid: 363 mg, 74% yield; mp 203.1−203.8 °C; $[\alpha]_D^{20}$ = −1251 (*c* = 0.205, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.94−7.90 (m, 1H), 7.84−7.65 (m, 9H), 7.59−7.48 (m, 5H), 7.46−7.41 (m, 2H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.25−7.15 (m, 4H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.78 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.69−6.60 (m, 2H), 6.54 (t, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.05−4.98 (m, 1H), 4.53 (dd, *J* = 16.9, 11.0 Hz, 1H), 4.39−4.25 (m, 2H), 4.09 (dd, *J* = 17.4, 5.1 Hz, 1H), 4.00 (dd, *J* = 17.0, 8.0 Hz, 1H), 3.07−2.92 (m, 2H), 1.52−1.39 (m, 4H), 1.23−0.92 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 173.8, 169.0, 152.9, 146.7, 144.4, 142.7, 139.9, 135.9, 135.2 (d, *J* = 5.1 Hz), 134.6, 134.5 (d, *J* = 6.2 Hz), 133.7, 133.3, 131.0, 130.9, 130.2, 129.4, 129.0, 128.9, 128.8, 128.68, 128.67, 128.4, 127.7, 127.5, 127.4, 127.2, 127.1, 127.0, 126.6, 125.9, 125.8, 125.69, 125.66, 125.6, 125.4, 125.2, 124.1, 123.7, 123.4, 123.3, 122.5, 121.4, 82.1 (d, *J* = 9.0 Hz), 64.3 (d, *J* = 10.1 Hz), 63.7 (d, *J* = 9.5 Hz), 63.1, 44.5 (d, *J* = 4.5 Hz), 43.3 (d, *J* = 3.0 Hz), 29.7 (d, *J* = 10.9 Hz), 29.4 (d, *J* = 8.5 Hz), 27.6, 24.34, 24.30; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.36; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{57}H_{50}ClN_6NaNiO_4P$ 1029.2565, found 1029.2558.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(3-bromophenyl)propanoic Acid Schiff Base Complex (**3l**).* Red solid: 409 mg, 78% yield; mp 207.5−208.3 °C; $[\alpha]_D^{20}$ = −1186 (*c* = 0.234, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 6.9 Hz, 1H), 7.87−7.64 (m, 11H), 7.60−7.42 (m, 6H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.25−7.22 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.11−7.01 (m, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.49 (t, *J* = 7.6 Hz, 1H), 4.99 (t, *J* = 9.3 Hz, 1H), 4.52 (dd, *J* = 16.8, 11.1 Hz, 1H), 4.42−4.28 (m, 2H), 4.11 (dd, *J* = 17.4, 5.0 Hz, 1H), 3.99 (dd, *J* = 16.9, 8.0 Hz, 1H), 3.08−2.93 (m, 2H), 1.54−1.39 (m, 4H), 1.22−0.91 (m, 4H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 173.8, 169.1, 152.9, 146.8, 144.8, 142.8, 139.9, 136.0, 135.3 (d, *J* = 5.1 Hz), 135.0, 134.5 (d, *J* = 6.1 Hz), 133.71, 133.69, 133.4, 131.5, 131.02, 130.97, 130.8, 130.3, 129.4, 129.3, 128.9, 128.8, 128.7, 128.4, 128.0, 127.4, 127.2, 127.1, 127.0, 126.8, 125.9, 125.82, 125.75, 125.7, 125.6, 125.4, 125.2, 124.2, 123.7, 123.5, 123.3, 122.8, 122.6, 121.4, 82.1 (d, *J* = 9.1 Hz), 64.3 (d, *J* = 10.1 Hz), 63.7 (d, *J* = 9.6 Hz), 63.1, 44.5 (d, *J* = 4.4 Hz), 43.3 (d, *J* = 3.4 Hz), 29.7 (d, *J* = 10.6 Hz), 29.4 (d, *J* = 8.7 Hz), 27.6, 24.35, 24.32; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.25; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{57}H_{50}BrN_6NaNiO_4P$ 1073.2060, found 1073.2059.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(3-methoxyphenyl)propanoic Acid Schiff Base Complex (**3m**).* Red solid: 345 mg, 73% yield; mp 202.3−204.2 °C; $[\alpha]_D^{20}$ = −1399 (*c* = 0.234, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.5 Hz, 1H), 7.94−7.86 (m, 2H), 7.85−7.67 (m, 8H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.56−7.41 (m, 7H), 7.27−7.12 (m, 5H), 7.07 (s, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.83−6.73 (m, 2H), 6.65 (t, *J* = 7.6 Hz, 1H), 6.54 (t, *J* = 7.7 Hz, 1H), 5.99 (d, *J* = 6.9 Hz, 1H), 4.93 (t, *J* = 9.3 Hz, 1H), 4.58−4.45 (m, 2H), 4.36−4.25 (m, 1H), 4.13 (dd, *J* = 17.2, 4.9 Hz, 1H), 3.86 (dd, *J* = 16.8, 7.8 Hz, 1H), 3.11 (s, 3H), 2.98 (d, *J* = 8.7 Hz, 2H), 1.51−1.36 (m, 4H), 1.26−0.90 (m, 4H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 173.2, 168.8, 159.3, 153.0, 146.5, 143.6, 142.6, 139.7, 136.1, 135.3 (d, *J* = 5.1 Hz), 134.9, 134.3 (d, *J* = 5.5 Hz), 133.5, 133.1, 130.9, 130.4, 129.4, 128.9, 128.8, 128.7, 128.64, 128.56, 127.2, 127.1, 126.99, 126.96, 126.2, 125.8, 125.6, 125.5, 125.3, 125.0, 124.4, 123.5, 123.2, 123.1, 122.6, 121.4, 121.2, 114.2, 113.2, 82.2 (d, *J* = 9.6 Hz), 64.4 (d, *J* = 10.1 Hz), 63.5, 63.0 (d, *J* = 9.9 Hz), 44.3 (d, *J* = 5.0 Hz), 42.9 (d, *J* = 3.5 Hz), 29.6 (d, *J* = 10.9 Hz), 29.4 (d, *J* = 8.1 Hz), 27.7, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.35; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{58}H_{53}N_6NaNiO_5P$ 1025.3061, found 1025.3068.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(3-trifluoromethylphenyl)propanoic Acid Schiff Base Complex (**3n**).* Red solid: 381 mg, 79% yield; mp 201.5−202.0 °C; $[\alpha]_D^{20}$ = −1099 (*c* = 0.206, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 6.9 Hz, 1H), 7.80−7.57 (m, 10H), 7.55−7.35 (m, 8H), 7.20−7.13 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.75−6.58 (m, 4H), 6.49 (t, *J* = 7.4 Hz, 1H), 5.08 (t, *J* = 9.3 Hz, 1H), 4.51−4.38 (m, 2H), 4.29−4.18 (m, 1H), 4.07−3.94 (m, 2H), 2.99 (t, *J* = 9.2 Hz, 1H), 2.91 (t, *J* = 10.0 Hz, 1H), 1.47−1.30 (m, 4H), 1.15−0.79 (m, 4H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 174.3, 169.1, 152.8, 146.5, 143.4, 142.8, 140.0, 136.0, 135.2 (d, *J* = 5.3 Hz), 135.1, 134.3 (d, *J* = 5.9 Hz), 133.7, 133.6, 133.5, 132.6, 131.0, 130.9, 130.4 (q, *J* = 32.2 Hz), 130.0, 129.5, 128.9, 128.8, 128.7, 128.3, 128.2, 127.4, 127.3, 127.2, 127.0, 126.6, 126.0, 125.8, 125.7, 125.64, 125.59, 125.4, 125.3, 125.1 (q, *J* = 3.1 Hz), 124.2 (q, *J* = 4.1 Hz), 124.1, 123.7, 123.6 (q, *J* = 274.2 Hz), 123.5, 123.3, 122.4, 121.4, 81.9 (d, *J* = 8.6 Hz), 64.3 (d, *J* = 10.1 Hz), 63.6 (d, *J* = 9.7 Hz), 63.2, 44.5 (d, *J* = 4.3 Hz), 43.1 (d, *J* = 3.3 Hz), 29.6 (d, *J* = 10.2 Hz), 29.3 (d, *J* = 8.5 Hz), 27.5, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.16; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{58}H_{50}F_3N_6NaNiO_4P$ 1063.2829, found 1063.2830.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(2-fluorophenyl)propanoic Acid Schiff Base Complex (**3o**).* Red solid: 414 mg, 88% yield; mp 209.5−210.2 °C; $[\alpha]_D^{20}$ = −1499 (*c* = 0.211, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.5 Hz, 1H), 7.93−7.87 (m, 2H), 7.86−7.68 (m, 7H), 7.66−7.41 (m, 9H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.25−7.15 (m, 3H), 7.14−7.09 (m, 2H), 6.88−6.70 (m, 3H), 6.66 (t, *J* = 7.7 Hz, 1H), 6.34 (dd, *J* = 12.7, 6.6 Hz, 1H), 5.86 (s, 1H), 5.41 (t, *J* = 9.4 Hz, 1H), 4.55−4.38 (m, 2H), 4.33−4.22 (m, 1H), 4.11 (dd, *J* = 17.4, 5.5 Hz, 1H), 3.86 (dd, *J* = 16.9, 7.6 Hz, 1H), 3.07−2.91 (m, 2H), 1.56−1.38 (m, 4H), 1.27−0.91 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.4, 174.9, 168.8, 161.3 (d, *J* = 245.8 Hz), 153.2, 146.7, 142.6, 139.8, 136.2, 135.3 (d, *J* = 4.8 Hz), 135.0, 134.5 (d, *J* = 4.9 Hz), 133.63, 133.56, 133.1, 130.97, 130.94, 130.2, 130.0 (d, *J* = 13.7 Hz), 129.9, 129.6, 129.3, 129.2, 129.0 (d, *J* = 8.7 Hz), 128.9, 128.8, 128.6, 127.3, 127.2 (d, *J* = 7.7 Hz), 127.1, 126.8, 126.2, 125.8, 125.74, 125.70, 125.68, 125.5, 125.4, 125.2, 124.3, 123.4 (d, *J* = 2.7 Hz), 123.3, 123.24, 123.19, 122.6, 121.2, 115.1 (d, *J* = 23.4 Hz), 82.2 (d, *J* = 8.7 Hz), 64.4 (d, *J* = 9.9 Hz), 63.4 (d, *J* = 9.0 Hz), 56.0, 44.3 (d, *J* = 4.2 Hz), 43.0 (d, *J* = 3.2 Hz), 29.6 (d, *J* = 10.2 Hz), 29.5 (d, *J* = 8.6 Hz), 27.5, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.15; HRMS (ESI-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{57}H_{50}FN_6NaNiO_4P$ 1013.2861, found 1013.2858.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(2-chlorophenyl)propanoic Acid Schiff Base Complex (**3p**).* Red solid: 327 mg, 73% yield; mp 164.2−166.8 °C; $[\alpha]_D^{20}$ = −1384 (*c* = 0.212,

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$CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 7.4 Hz, 1H), 7.85−7.60 (m, 11H), 7.48 (dd, J = 17.3, 5.8 Hz, 7H), 7.16 (dd, J = 27.7, 20.1 Hz, 6H), 6.86−6.73 (m, 2H), 6.65 (t, J = 7.5 Hz, 1H), 6.20 (t, J = 6.9 Hz, 1H), 6.08 (s, 1H), 5.43 (t, J = 8.2 Hz, 1H), 4.49 (dd, J = 16.0, 10.6 Hz, 1H), 4.37−4.20 (m, 2H), 4.13 (d, J = 15.8 Hz, 1H), 3.80 (dd, J = 17.6, 5.3 Hz, 1H), 3.09 (t, J = 9.3 Hz, 1H), 3.00 (t, J = 9.0 Hz, 1H), 1.60−1.35 (m, 4H), 1.07 (s, 4H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1, 174.5, 168.6, 153.2, 146.7, 143.1, 140.4, 139.8, 136.7, 135.8, 135.4 (d, J = 3.7 Hz), 135.1, 134.2, 133.6, 133.2, 131.0, 130.9, 130.5, 130.2, 129.4, 129.3, 129.11, 129.06, 128.8, 128.7, 128.5, 127.3, 127.13, 127.08, 126.7, 126.20, 126.15, 125.8, 125.73, 125.67, 125.5, 125.4, 125.1, 124.5, 123.3, 123.07, 122.99, 122.6, 121.1, 83.5 (d, J = 11.1 Hz), 64.5 (d, J = 10.0 Hz), 62.9 (d, J = 10.0 Hz), 59.5, 44.2, 42.8, 29.6 (d, J = 8.1 Hz), 29.5 (d, J = 10.1 Hz), 27.3, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.21; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{57}H_{50}ClN_6NaNiO_4P$ 1029.2565, found 1029.2566.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(2-bromophenyl)propanoic Acid Schiff Base Complex (**3q**).* Red solid: 360 mg, 70% yield; mp 206.0−210.1 °C; $[\alpha]_D^{20}$ = −1654 (c = 0.229, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.5 Hz, 1H), 7.85 (t, J = 8.1 Hz, 2H), 7.78−7.64 (m, 7H), 7.60 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 5.2 Hz, 1H), 7.49−7.37 (m, 7H), 7.24 (d, J = 7.8 Hz, 1H), 7.19−7.00 (m, 5H), 6.80−6.70 (m, 2H), 6.60 (t, J = 7.6 Hz, 1H), 6.11 (t, J = 5.6 Hz, 1H), 6.01 (t, J = 7.2 Hz, 1H), 5.30 (t, J = 9.8 Hz, 1H), 4.45 (dd, J = 16.9, 11.4 Hz, 1H), 4.28−4.14 (m, 2H), 4.07 (dd, J = 17.5, 6.0 Hz, 1H), 3.78 (dd, J = 16.9, 7.9 Hz, 1H), 3.09 (t, J = 9.2 Hz, 1H), 2.96 (t, J = 9.4 Hz, 1H), 1.53−1.33 (m, 4H), 1.01 (s, 4H), 1.23−0.84 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 174.3, 168.5, 153.3, 146.7, 143.2, 141.9, 139.7, 136.8, 135.4 (d, J = 5.0 Hz), 135.1, 134.2 (d, J = 5.1 Hz), 133.6, 133.2, 132.4, 131.0, 130.9, 130.8, 130.2, 129.4, 129.3, 129.2, 128.8, 128.7, 127.2, 127.12, 127.06, 126.8, 126.1, 125.8, 125.7, 125.6, 125.5, 125.4, 125.0, 124.4, 123.3, 123.0, 122.9, 122.6, 121.1, 83.8 (d, J = 9.2 Hz), 64.5 (d, J = 10.3 Hz), 62.9 (d, J = 9.2 Hz), 61.9, 44.2 (d, J = 4.5 Hz), 42.8 (d, J = 2.6 Hz), 29.6 (d, J = 8.5 Hz), 29.5 (d, J = 10.4 Hz), 27.2, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.00; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{57}H_{50}BrN_6NaNiO_4P$ 1073.2060, found 1073.2057.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-o-tolylpropanoic Acid Schiff Base Complex (**3r**).* Red solid: 310 mg, 69% yield; mp 206.8−206.9 °C; $[\alpha]_D^{20}$ = −1641 (c = 0.266, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 7.8 Hz, 1H), 7.98−7.92 (m, 1H), 7.91−7.77 (m, 4H), 7.73−7.66 (m, 2H), 7.61 (d, J = 7.0 Hz, 1H), 7.58−7.49 (m, 6H), 7.46−7.34 (m, 4H), 7.24−7.18 (m, 2H), 7.13−7.08 (m, 1H), 7.02 (d, J = 4.5 Hz, 2H), 6.82−6.75 (m, 2H), 6.70 (d, J = 7.0 Hz, 1H), 6.63 (t, J = 7.7 Hz, 1H), 6.38−6.31 (m, 1H), 5.82−5.71 (m, 2H), 5.21 (t, J = 9.6 Hz, 1H), 4.64 (dd, J = 17.0, 10.9 Hz, 1H), 4.16−3.80 (m, 4H), 3.08−2.91 (m, 2H), 2.37 (s, 3H), 1.55−1.34 (m, 4H), 1.24−1.01 (m, 4H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 173.0, 168.7, 153.0, 146.7, 142.9, 141.0, 139.4, 137.5, 136.0, 135.4 (d, J = 4.3 Hz), 135.1, 135.0, 133.6, 133.5, 133.2, 131.0, 130.8, 129.9, 129.8, 129.2, 129.0, 128.8, 128.6, 128.5, 127.8, 127.2, 127.0, 126.8, 126.2, 126.0, 125.9, 125.8, 125.5, 125.4, 125.3, 125.0, 123.9, 123.2, 123.1, 123.0, 122.6, 121.1, 84.4 (d, J = 10.0 Hz), 64.5 (d, J = 10.2 Hz), 63.9 (d, J = 9.2 Hz), 60.0, 44.5 (d, J = 4.2 Hz), 43.3 (d, J = 3.4 Hz), 29.8 (d, J = 12.6 Hz), 29.7 (d, J = 9.0 Hz), 27.4, 24.4, 24.3, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.41; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{58}H_{53}N_6NaNiO_4P$ 1009.3112, found 1009.3118.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(2-methoxyphenyl)propanoic Acid Schiff Base Complex (**3s**).* Red solid: 361 mg, 69% yield; mp 237.5−238.2 °C; $[\alpha]_D^{20}$ = −1321 (c = 0.208, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.1 Hz, 1H), 7.85−7.62 (m, 11H), 7.58 (d, J = 7.4 Hz, 1H), 7.52−7.39 (m, 7H), 7.31−7.24 (m, 2H), 7.18−7.11 (m, 3H), 6.99 (t, J = 7.3 Hz, 1H), 6.74−6.58 (m, 3H), 6.46 (t, J = 7.5 Hz, 1H), 5.97 (t, J = 7.4 Hz, 1H), 5.47 (t, J = 9.5 Hz, 1H), 4.53 (t, J = 11.0 Hz, 1H), 4.38 (dd, J = 16.8, 11.1 Hz, 1H), 4.27 (t, J = 16.0 Hz, 1H), 4.15 (dd, J = 17.1, 5.6 Hz, 1H), 3.50 (dd, J = 17.0, 6.0 Hz, 1H), 3.22 (s, 3H), 2.98−2.84 (m, 2H), 1.56−1.34 (m, 3H), 1.27−1.15 (m, 2H), 1.07 (s, 3H), 1.01−0.77 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3, 173.8, 168.9, 157.3, 153.1, 146.8, 142.5, 139.6, 137.0, 135.6 (d, J = 5.3 Hz), 134.8, 133.8 (d, J = 3.4 Hz), 133.6, 133.5, 132.7, 131.13, 131.10, 130.9, 130.4, 129.8, 129.3, 129.2, 128.88, 128.86, 128.8, 128.7, 127.2, 127.1, 127.0, 126.9, 126.2, 125.8, 125.7, 125.6, 125.4, 125.3, 125.1, 125.0, 123.2, 123.1, 122.7, 121.1, 119.9, 109.8, 82.8 (d, J = 9.1 Hz), 64.5 (d, J = 10.1 Hz), 62.2 (d, J = 9.4 Hz), 55.5, 54.6, 44.0 (d, J = 3.8 Hz), 42.3 (d, J = 2.8 Hz), 29.5 (d, J = 8.4 Hz), 29.3 (d, J = 9.5 Hz), 27.5, 24.5, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.98; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{58}H_{53}N_6NaNiO_5P$ 1025.3061, found 1025.3049.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-(2-trifluoromethylphenyl)propanoic Acid Schiff Base Complex (**3t**).* Red solid: 420 mg, 84% yield; mp 196.7−198.2 °C; $[\alpha]_D^{20}$ = −1315 (c = 0.200, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 9.5 Hz, 2H), 7.77 (dt, J = 16.6, 7.7 Hz, 4H), 7.64 (d, J = 8.1 Hz, 1H), 7.60−7.46 (m, 8H), 7.44−7.33 (m, 4H), 7.20 (t, J = 8.4 Hz, 1H), 7.14 (t, J = 6.5 Hz, 1H), 7.08−6.96 (m, 4H), 6.81 (d, J = 8.4 Hz, 1H), 6.67−6.59 (m, 2H), 6.22 (t, J = 7.5 Hz, 1H), 5.96 (t, J = 7.6 Hz, 1H), 5.43 (t, J = 10.0 Hz, 1H), 4.70 (dd, J = 17.0, 10.6 Hz, 1H), 4.26 (dt, J = 17.1, 11.4 Hz, 2H), 3.96 (dd, J = 17.8, 5.4 Hz, 1H), 3.88 (t, J = 10.8 Hz, 1H), 3.12 (t, J = 9.9 Hz, 1H), 2.99 (t, J = 11.4 Hz, 1H), 1.57−1.41 (m, 4H), 1.21−1.00 (m, 4H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 174.7, 168.3, 153.3, 146.5, 142.7, 140.5, 139.7, 136.4, 135.23 (d, J = 4.2 Hz), 135.18, 135.1 (d, J = 6.6 Hz), 133.7, 133.4, 133.2, 130.1, 130.64, 130.61, 130.0, 129.7, 129.4, 129.2, 128.9, 128.8, 128.7 (q, J = 30.3 Hz), 128.4, 127.4, 126.82, 126.75 (q, J = 2.6 Hz), 126.7, 125.98, 125.97, 125.8, 125.7, 125.62 (q, J = 3.1 Hz), 125.55, 125.4, 125.3, 125.2, 123.42, 123.35, 123.0, 122.9, 122.4, 121.1, 84.5 (d, J = 8.0 Hz), 64.4 (d, J = 9.6 Hz), 64.2 (d, J = 10.5 Hz), 59.6, 44.2 (d, J = 4.9 Hz), 43.3 (d, J = 3.2 Hz), 29.8 (d, J = 11.2 Hz), 29.5 (d, J = 7.7 Hz), 27.6, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.94; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{58}H_{50}F_3N_6NaNiO_4P$ 1063.2829, found 1063.2837.

*Ni(II)-PBP/(2R,3S)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-3-furan-2-ylpropanoic Acid Schiff Base Complex (**3u**).* Red solid: 370 mg, 77% yield; mp 204.3−204.9 °C; $[\alpha]_D^{20}$ = −1241 (c = 0.205, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 5.2 Hz, 1H), 7.94−7.71 (m, 9H), 7.62−7.44 (m, 8H), 7.40 (t, J = 7.5 Hz, 1H), 7.36−7.32 (m, 1H), 7.28−7.24 (m, 1H), 7.17−7.08 (m, 2H), 6.93 (t, J = 7.1 Hz, 1H), 6.88 (s, 1H), 6.82−6.76 (m, 1H), 6.70 (t, J = 7.3 Hz, 1H), 6.30 (d, J = 3.1 Hz, 1H), 5.61−5.53 (m, 1H), 5.17 (t, J = 9.6 Hz, 1H), 4.64−4.38 (m, 3H), 4.19 (dd, J = 17.2, 5.2 Hz, 1H), 4.07 (dd, J = 16.7, 8.0 Hz, 1H), 3.06−2.93 (m, 2H), 1.55−1.37 (m, 4H), 1.16 (s, 3H), 1.13−0.88 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.2, 174.6, 169.2, 155.7, 153.4, 146.8, 142.5, 141.8, 140.2, 136.0, 135.3 (d, J = 5.2 Hz), 134.9, 134.8 (d, J = 6.3 Hz), 133.7, 133.6, 133.0, 131.1, 131.0, 130.1, 129.5, 129.05, 129.03, 128.73, 128.68, 128.0, 127.4, 127.0, 126.9, 126.5, 125.9, 125.8, 125.69, 125.66, 125.6, 125.5, 125.4, 124.7, 123.6, 123.5, 123.4, 122.8, 121.4, 110.1, 108.7, 80.7 (d, J = 8.7 Hz), 64.1 (d, J = 10.3 Hz), 63.8 (d, J = 9.3 Hz), 57.4, 44.5 (d, J = 4.4 Hz), 43.6 (d, J = 3.7 Hz), 29.7 (d, J = 10.8 Hz), 29.5 (d, J = 8.9 Hz), 27.3, 24.4, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.85; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{55}H_{49}N_6NaNiO_5P$ 985.2748, found 985.2738.

*Ni(II)-PBP/(2R,3S,E)-2-Amino-2-methyl-3-[(1aR,2aR)-N,N′-dinaphthylmethyl-cyclohexyldiaminophosphonyl]amino-5-phenylpent-4-enoic Acid Schiff Base Complex (**3v**).* Red solid: 334 mg, 67% yield; mp 184.9−186.1 °C; $[\alpha]_D^{20}$ = −1126 (c = 0.215, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 8.6 Hz, 1H), 8.05−8.00 (m, 1H), 7.92 (d, J = 5.3 Hz, 2H), 7.83−7.70 (m, 6H), 7.64−7.48 (m, 5H), 7.36 (t, J = 7.4 Hz, 1H), 7.31−7.20 (m, 5H), 7.14−7.09 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.90 (dd, J = 15.9, 7.9 Hz, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.76 (d, J = 15.9 Hz, 1H), 6.72−6.64 (m, 3H), 6.46 (t, J = 7.5 Hz, 2H), 6.39 (d, J = 7.7 Hz, 2H), 4.86 (dd, J = 16.9, 14.3 Hz, 1H), 4.67 (dd, J = 17.8, 8.6 Hz, 1H), 4.59 (dd, J = 16.7, 11.0 Hz, 1H), 4.25 (dd, J = 17.6, 5.0 Hz, 1H), 4.17−4.13

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(m, 1H), 3.67 (t, J = 11.0 Hz, 1H), 3.11−2.94 (m, 2H), 1.59−1.41 (m, 4H), 1.05 (s, 3H), 1.17−0.91 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.0, 173.9, 169.2, 152.7, 146.4, 142.7, 139.7, 135.8, 135.6, 135.4 (d, J = 5.1 Hz), 135.2 (d, J = 6.5 Hz), 134.9, 133.8, 133.7, 133.6, 133.1, 131.1, 130.9, 130.0, 129.9, 129.3, 129.0, 128.9, 128.7, 128.6, 127.9, 127.7, 127.4, 127.1, 126.80, 126.77, 126.2, 125.9, 125.85, 125.76, 125.64, 125.60, 125.57, 125.45, 125.42, 123.9, 123.61, 123.56, 123.4, 122.5, 121.4, 81.7 (d, J = 9.2 Hz), 64.4 (d, J = 7.9 Hz), 64.3 (d, J = 8.7 Hz), 61.5, 44.8 (d, J = 4.7 Hz), 44.2 (d, J = 3.5 Hz), 29.9 (d, J = 10.6 Hz), 29.6 (d, J = 8.5 Hz), 26.6, 24.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.24; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{59}H_{53}N_6NaNiO_4P$ 1021.3112, found 1021.3119.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01385.

^{1}H and ^{13}C NMR spectra for all pure products (PDF)
CheckCIF/PLATON report (PDF)
X-ray crystal data for **3q** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: guigen.li@ttu.edu.

Notes

The authors declare no competing financial interest.

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