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Stereoselective Synthesis of Arylglycine Derivatives via Palladium-Catalyzed α-Arylation of a Chiral Nickel(II) Glycinate

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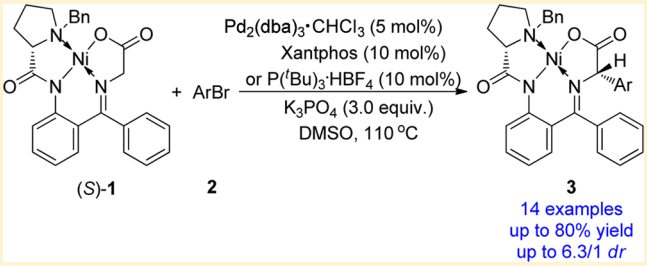
Supporting Information

ABSTRACT: A practical and efficient stereoselective synthesis of arylglycine derivatives was realized via palladium-catalyzed α-arylation of a chiral nickel(II) glycinate complex with aryl bromides. The structurally diverse arylglycine products were obtained in excellent isolated yields and with good diastereoselectivity. A simple acidic hydrolysis furnished optically pure arylglycines in high yield, and the chiral ligand (S)-BPB could be efficiently recovered and reused.



INTRODUCTION

Optically active non-naturally occurring amino acids are highly desirable compounds due to their broad biological properties and versatility as a scaffold that has been used in highly efficient syntheses of numerous peptides, proteins, natural products, and biologically relevant compounds.[1] Among a variety of non-naturally occurring amino acids, substituted arylglycines serve as important structural motifs in many biologically active compounds and natural products, such as P53-MDM2 inhibitor RO-5963,[2] β-lactam antibiotics cephalexin, cefadroxi, and amoxicillin,[3] antiplatelet agents clopidogrel and vicagrel,[4] antibiotics vancomycin and teicoplanin,[5] and HCV NS3/4A protease inhibitor (Figure 1).[6] To date, numerous approaches to racemic arylglycine derivatives have been developed.[7] In contrast, only limited asymmetric approaches toward optically active arylglycines have been reported. These approaches mainly include transition-metal-mediated asymmetric addition of various nucleophiles to α-imino esters,[8] biotransformation,[9] chemical resolution,[10] asymmetric Sommelet−Hauser rearrangement,[11] and aryne-mediated diastereoselective arylation reaction.[12] More recently, Pd-catalyzed enantioselective synthesis of arylglycine derivatives by direct C−H oxidative cross-coupling was reported by Yang et al.[13] Despite the significant development on this field, more efficient and practical methods for convenient construction of various chiral arylglycines are needed.

Chiral nickel(II) complexes of glycine Schiff base (*S*)-**1**, which were initially introduced in 1985 and prepared on large scale starting from (*S*)-proline by simply following the reported procedure,[14] have been widely used to synthesize chiral non-naturally occurring amino acids through various approaches,[15] such as the C-alkylation reaction,[15d,16] aldol reaction,[14a,15e,17] Mannich reaction,[15e,18] Michael addition reaction,[15f,19] Mitsunobu reaction,[20] oxidative heterocoupling reaction,[21] and cross-dehydrogenative coupling cascade reaction.[22] On the other hand, a Pd-catalyzed α-arylation approach to yield racemic protected amino acids derivatives has been explored by the Hartwig group.[23] Herein, we describe a stereoselective synthesis of optically active arylglycine derivatives via Pd-catalyzed α-arylation of chiral nickel(II) glycinate complex (*S*)-**1** with various aryl bromides.

RESULTS AND DISCUSSION

In our initial study, chiral nickel(II) glycinate complex (*S*)-**1** and bromobenzene **2a** were chosen as the model reaction substrates. In the presence of 30 mol % of $Pd(PPh_3)_4$ as a catalyst and K_3PO_4 as a base, reaction of **2a** with complex (*S*)-**1** in DMSO at 110 °C gave the desired product in 58% yield (entry 1, Table 1). Encouraged by this result, different palladium catalysts were investigated (Table 1). When PPh_3 was used as a ligand, $Pd(OAc)_2$ and $PdCl_2$ only gave trace amounts of the desired product (entries 2 and 3, Table 1). When $Pd_2(dba)_3{\cdot}CHCl_3$ was used as the catalyst, the yields were significantly improved, and even the loading of the catalyst was decreased to 5 mol % and the amount of PPh_3 was lowered to 10 mol % (entry 4, Table 1). Therefore, we determined $Pd_2(dba)_3{\cdot}CHCl_3$ as the optimal catalyst to screen ligands (entries 4−8, Table 1). It was found that $P(^tBu)_3{\cdot}HBF_4$ (entry 5, Table 1) and Xantphos (entry 8, Table 1) could provide high yields (85−90% yields) with modest diastereoselectivity. With the optimal catalyst and ligands in hand, we turned our attention to the effect of base in this reaction (see the Supporting Information for details). We found that K_3PO_4 was the best base in terms of isolated yield and dr value. Finally, we established the optimized reaction conditions as follows: $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol %) as the catalyst, $P(^tBu)_3{\cdot}HBF_4$ or Xantphos as the ligand (10 mol %), K_3PO_4 (300 mol %) as the

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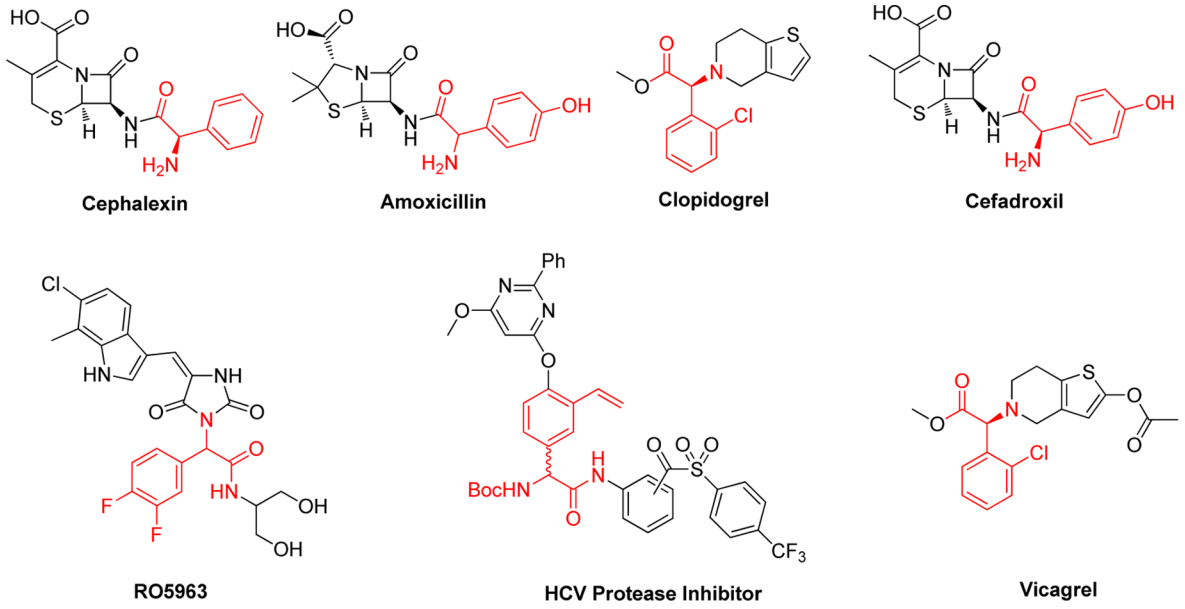
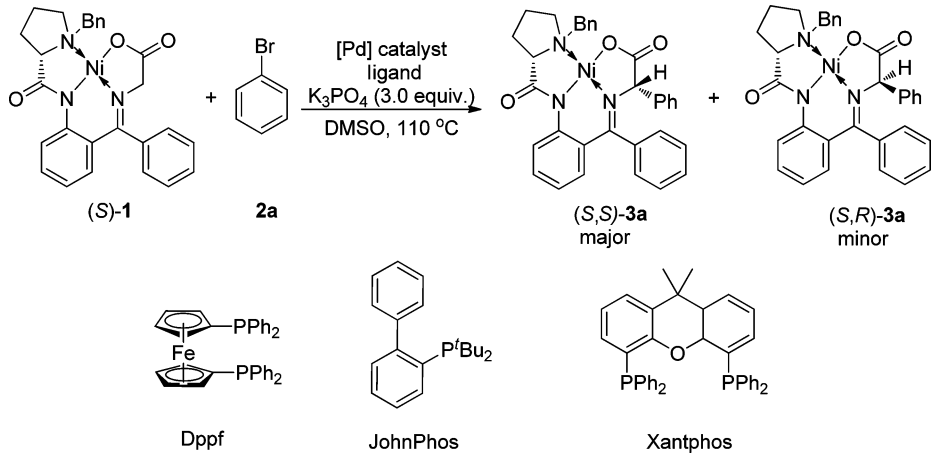


Figure 1. Selected substituted arylglycine derivatives exist as building blocks in many bioactive compounds and natural products.

Table 1. Optimization of the Reaction Conditions[a]



entry	[Pd] (mol %)	ligand (mol %)	yield[b] (%)	dr (*S,S*/*S,R*)[c]
1	$Pd(PPh_3)_4$ (30)	none	58[d]	N.D.
2	$Pd(OAc)_2$ (30)	PPh_3(100)	N.R.	N.D.
3	$PdCl_2$ (30)	PPh_3(100)	11[d]	N.D.
4	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)	PPh_3(10)	37	13.3/1
5	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)	$P(^tBu)_3{\cdot}HBF_4$ (10)	85	4.3/1
6	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)	Dppf (10)	49	4.6/1
7	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)	JohnPhos (10)	37	5.6/1
8	$Pd_2(dba)_3{\cdot}CHCl_3$ (5)	Xantphos (10)	90	3.8/1

[a]Reactions were run with 0.1 mmol of (*S*)-**1a** and 0.3 mmol **2a** in 3 mL of DMSO with 0.3 mmol of K_3PO_4 for 36 h at 110 °C. [b]Total yields of both isomers. [c]dr determined by crude ^1H NMR. [d]Yields determined by crude ^1H NMR. N.R. = no reaction. N.D. = not determined.

base and DMSO as the solvent with temperature at 110 °C. The absolute configuration of the major stereoisomer (*S,S*)-**3a** was confirmed by X-ray crystallography (see the Supporting Information for details; thermal ellipsoids are set at 30% probability). The absolute configuration of the minor diastereomer (*S,R*)-**3a** was determined by CD spectra (see the Supporting Information for the details).

With the optimal reaction conditions in hand, we investigated the scope of the Pd-catalyzed arylation of (*S*)-**1** with regard to the aryl bromide coupling partners (Table 2). Most aryl bromides afforded the desired products (*S,S*)-**3** in good yields (42−80%), and the diastereoisomeric ratios (dr) could be increased to >20/1 after column chromatography except in the case of product **3l**. Analysis of the electronic effect displayed that the aryl bromides with electron-withdrawing substitution at the 4-position (e.g., 4-CN, 4-CF_3, 4-CO_2Me, 4-F, 4-NO_2, 4-CHO, 3,4-F_2) were well tolerated in this reaction (entries 1−8, Table 2). However, the presence of an electron-withdrawing substituent at the 3-position (e.g., 3-Cl) required the use of $P(^tBu)_3{\cdot}HBF_4$, giving the desired product in 80%

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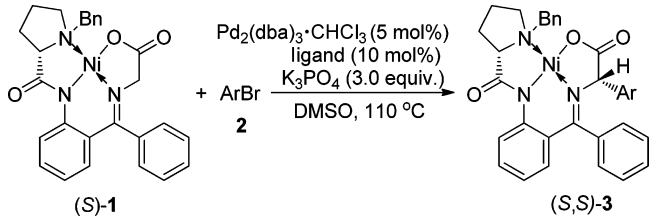
Table 2. Pd-Catalyzed α-Arylation of Chiral Nickel(II) Glycinate Complex (*S*)-1 with Various Aryl Bromides[a]



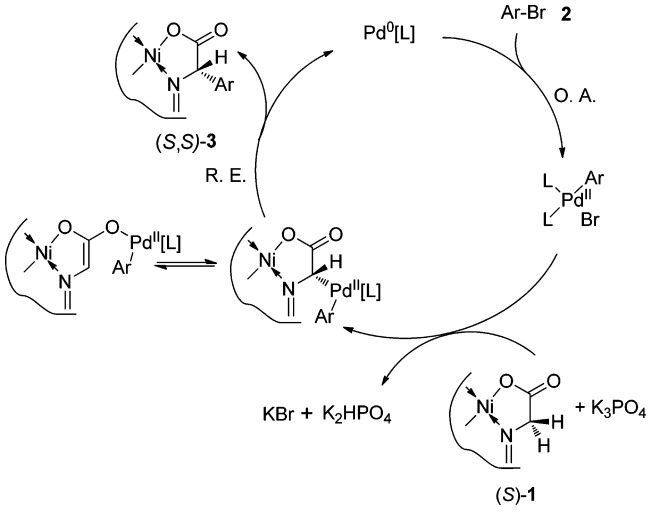
entry	ArBr	ligand	3	yield[b] (%)	dr (*S,S*)/(*S,R*)[c]
1	C_6H_5Br	Xantphos	**3a**	80	4.6/1 (>20/1)
2	4-CN-C_6H_4Br	Xantphos	**3b**	62	4.6/1 (>20/1)
3	4-CF_3-C_6H_4Br	Xantphos	**3c**	54 (59[d])	5.0/1 (>20/1)
4	4-CO_2Me-C_6H_4Br	Xantphos	**3d**	61 (60[d])	4.6/1 (>20/1)
5	4-F-C_6H_4Br	Xantphos	**3e**	49	1.1/1 (>20/1)
6	4-NO_2-C_6H_4Br	Xantphos	**3f**	60 (32[d])	6.3/1 (>20/1)
7	4-CHO-C_6H_4Br	Xantphos	**3g**	80	6.3/1 (>20/1)
8	3,4-F_2-C_6H_3Br	Xantphos	**3h**	76	4.4/1 (>20/1)
9	3-Cl-C_6H_4Br	$P(^tBu)_3$·HBF_4	**3i**	80	4.5/1 (>20/1)
10	2-Me-C_6H_4Br	$P(^tBu)_3$·HBF_4	**3j**	71	4.0/1 (>20/1)
11	4-Me-C_6H_4Br	$P(^tBu)_3$·HBF_4	**3k**	55	1.7/1 (>20/1)
12	3-MeO-C_6H_4Br	Xantphos	**3l**	70[e]	2.9/1
13	4-MeO-C_6H_4Br	$P(^tBu)_3$·HBF_4	**3m**	72	3.7/1 (>20/1)
14	2-bromonaphthalene	Xantphos	**3n**	42	4.8/1 (>20/1)

[a]Reactions were running with 0.1 mmol of (*S*)-**1**, 0.3 mmol aryl bromide **2** in 3 mL of DMSO with 0.3 mmol of K_3PO_4 for 36 h at 110 °C. [b]Yields of (*S,S*)-isomer. [c]The dr value was determined by crude ^1H NMR (dr after column chromatography in the parentheses). [d]$P(^tBu)_3$·HBF_4 as the ligand. [e]Yield of the mixture of (*S,S*)-isomer and (*S,R*)-isomer.

yield and >20/1 dr after column chromatography (entry 9, Table 2). In a similar fashion, aryl bromides bearing electron-donating substituents at the 2- or 4-position worked only with $P(^tBu)_3$·HBF_4 as the ligand (entries 10, 11, and 13, Table 2). In contrast, both ligands provided good results when electron-donating substituents were at the 3-position (entry 12, Table 2). When 2-bromonaphthalene was employed as the substrate, the corresponding product was obtained in only 42% yield and >20/1 dr after column chromatography (entry 14, Table 2).

A proposed catalytic cycle is shown in Scheme 1. According the well-studied Pd-catalyzed arylation of ketones,[23a] the arylation of Ni(II) complex (*S*)-**1** described here most likely occurs via an identical catalytic cycle, involving oxidative addition of aryl bromide, formation of arylpalladium enolate complexes, and reductive elimination. Figure 2 shows the proposed transition state that accounts for the formation of the major diastereomer of the reaction. Formation of the minor diastereomer would suffer from severe repulsion between the substrate and the phenyl residue of Ni (II) complex (*S*)-**1**, which rationalizes why the major diastereomer (*S,S*)-**3** was observed in this arylation reaction.

Scheme 1. Proposed Mechanism



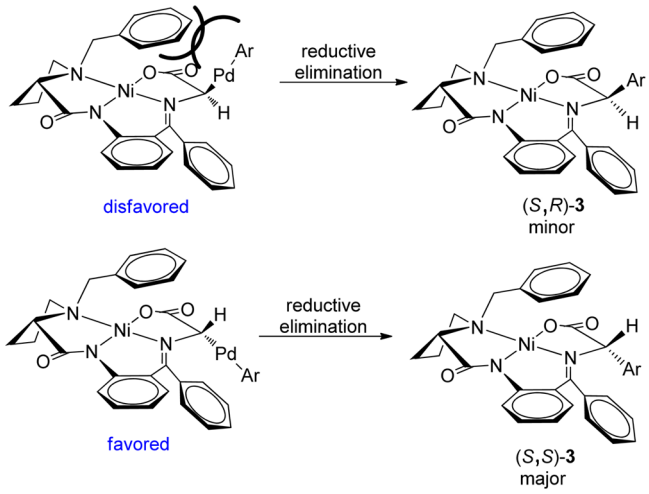


Figure 2. Proposed transition state leading to the major diastereomer. Absolute configuration of (*S,S*)-**3a** (X-ray).

Next, we hydrolyzed the diastereoisomerically pure complex (*S,S*)-**3a** under acidic conditions and obtained(*S*)-phenylglycine (*S*)-**4a** in 90% yield and >99% ee (Scheme 2). The chiral ligand (*S*)-BPB was recovered in quantitative yield and could be reused.

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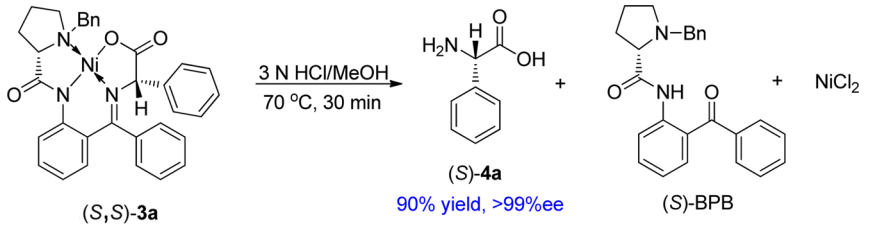
Scheme 2. Hydrolysis of (*S*,*S*)-3a Affords (*S*)-Phenylglycine (*S*)-4a



CONCLUSION

In conclusion, a practical and efficient approach to (*S*)-arylglycine derivatives via palladium-catalyzed α-arylation of a chiral nickel(II) glycinate complex has been developed. To the best of our knowledge, this is the first example for catalytic α-arylation reaction with a chiral nickel(II) glycinate complex. Structurally diverse aryl bromides were well-tolerated in this reaction, affording arylglycine derivatives in moderate to good yields and with >20/1 dr after column chromatography. These diastereoisomerically pure nickel(II) arylglycine complexes could be easily converted to non-naturally occurring arylglycines in high yields and high ee. This methodology provides rapid synthetic access to valuable building blocks for the synthesis of complex molecules as well as drug discovery.

EXPERIMENT SECTION

General Information. ^{1}H NMR and ^{13}C NMR (300 and 75 MHz, respectively) spectra were recorded in $CDCl_3$ and DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm, DMSO-d_6 at 39.51 ppm). (*S*)-**1** was prepared according to the literature.[14b]

General Procedure for Pd-Catalyzed α-Arylation of a Chiral Nickel(II) Glycinate. A solution of (*S*)-**1** (50.0 mg, 0.1 mmol), aryl bromide **2** (0.3 mmol, 3.0 equiv.), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.2 mg, 0.005 mmol, 5 mol %), ligand Xantphos (5.8 mg, 10 mol %) or $P(^tBu)_3{\cdot}HBF_4$ (2.9 mg, 10 mol %), and K_3PO_4 (64.0 mg, 0.3 mmol, 3.0 equiv.) in DMSO (3 mL) were added to a Schlenk tube under Ar conditions. The reaction was stirred at 110 °C for 36 h. After being cooled to room temperature, the mixture was diluted with water (5 mL) and extracted with EtOAc (3 × 10 mL), and the organic phase was dried over sodium sulfate. The solvent was removed under reduced pressure, and residue was purified by flash chromatography using petroleum ether/ethyl acetate (1/1) as the eluent, giving the desired product as a red solid.

(*S*,*S*)-**3a**: red solid (46.4 mg, 80% yield); mp 248–250 °C; $[\alpha]^{25}_D$ = +866.0 (*c* 0.1, CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 7.79–7.77 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.41–7.36 (m, 3H), 7.29–7.20 (m, 5H), 7.18–7.14 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.68–6.65 (m, 2H), 6.09 (d, *J* = 7.8 Hz, 1H), 4.79 (s, 1H), 4.50 (d, *J* = 12.6 Hz, 1H), 3.62 (d, *J* = 12.7 Hz, 1H), 3.53–3.44 (m, 3H), 2.86–2.78 (m, 1H), 2.60–2.52 (m, 1H), 2.13–1.98 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 180.8, 177.8, 172.3, 142.7, 133.8, 133.4, 133.3, 132.4, 131.6, 129.3, 129.0, 128.9, 128.5, 128.4, 128.3, 128.0, 127.1, 126.4, 126.1, 124.0, 120.8, 74.6, 70.4, 63.2, 57.3, 30.9, 23.7; MS (ESI) *m*/*z* 574.2 $[M + H]^+$; HRMS (ESI-TOF) calcd for $C_{33}H_{29}N_3NaNiO_3$ $[M + Na]^+$ *m*/*z* 596.1455, found 596.1453.

(*S*,*S*)-**3b**: red solid (37.2 mg, 62% yield); mp 237–239 °C; $[\alpha]^{25}_D$ = +1122.0 (*c* 0.1, CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.42–7.34 (m, 3H), 7.26 (s, 1H), 7.24 (s, 1H), 7.22–7.17 (m, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 2H), 6.08 (d, *J* = 7.5 Hz, 1H), 4.87 (s, 1H), 4.47 (d, *J* = 12.9 Hz, 1H), 3.62 (d, *J* = 12.6 Hz, 1H), 3.55–3.50 (m, 1H), 3.48–3.43 (m, 2H), 2.83–2.74 (m, 1H), 2.65–2.51 (m, 1H), 2.21–2.09 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 180.8, 176.6, 173.1, 143.3, 142.9, 131.6, 129.1, 128.5, 128.8, 127.0, 126.3, 124.1, 121.1, 118.3, 112.0, 73.9, 70.3, 63.3, 57.4, 30.9, 23.9; MS (ESI) *m*/*z* 621.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{29}N_4NiO_3$ $[M + H]^+$ *m*/*z* 599.1588, found 599.1583.

(*S*,*S*)-**3c**: red solid (34.7 mg, 54% yield); mp 210–212 °C; $[\alpha]^{25}_D$ = +1249.0 (*c* 0.1, CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 8.08–7.97 (m, 1H), 7.92–7.89 (m, 2H), 7.72–7.67 (m, 2H), 7.60–7.54 (m, 2H), 7.51–7.45 (m, 2H), 7.42–7.38 (m, 1H), 7.36–7.31 (m, 1H), 7.27–7.19 (m, 1H), 7.05–6.99 (m, 2H), 6.83–6.78 (m, 1H), 6.70 (d, *J* = 3.9 Hz, 1H), 6.11 (d, *J* = 7.5 Hz, 1H), 4.90 (s, 1H), 4.50 (d, *J* = 12.9 Hz, 1H), 3.90–3.81 (m, 1H), 3.64 (d, *J* = 12.6 Hz, 1H), 3.58–3.47 (m, 2H), 2.88–2.81 (m, 1H), 2.65–2.53 (m, 1H), 2.32–2.17 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 180.4, 176.6, 172.5, 142.3, 142.6, 133.2, 130.0, 132.7, 132.3, 131.1, 129.1, 128.5, 128.2, 128.0, 126.3, 126.1, 125.8, 125.5, 125.1, 125.0, 123.6, 120.5, 73.5, 69.8, 62.8, 56.8, 30.4, 23.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ −36.4 (s); MS (ESI) *m*/*z* 664.2 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{29}F_3N_3NiO_3$ $[M + H]^+$ *m*/*z* 642.1509, found 642.1505.

(*S*,*S*)-**3d**: red solid (38.5 mg, 61% yield); mp 139–141 °C; $[\alpha]^{25}_D$ = +387.0 (*c* 0.1, CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 1H), 8.12 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44–7.34 (m, 3H), 7.26 (s, 1H), 7.25 (s, 1H), 7.22–7.18 (m, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 3.9 Hz, 2H), 6.11 (d, *J* = 7.8 Hz, 1H), 4.89 (s, 1H), 4.50 (d, *J* = 12.6 Hz, 1H), 3.94 (s, 3H), 3.64 (d, *J* = 12.6 Hz, 1H), 3.56–3.44 (m, 3H), 2.89–2.80 (m, 1H), 2.64–2.54 (m, 1H), 2.15–2.10 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 180.7, 177.0, 172.7, 166.5, 143.0, 142.7, 133.7, 133.4, 133.2, 132.6, 131.6, 129.7, 129.4, 129.0, 128.9, 128.5, 128.4, 126.8, 126.2, 126.0, 124.0, 121.0, 73.8, 69.7, 62.9, 51.6, 30.0, 29.2, 23.0; MS (ESI) *m*/*z* 654.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{35}H_{32}N_3NiO_5$ $[M + H]^+$ *m*/*z* 632.1695, found 632.1686.

(*S*,*S*)-**3e**: red solid (29.3 mg, 49% yield); mp 219–221 °C; $[\alpha]^{25}_D$ = +662.0 (*c* 0.1, CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 2H), 7.76–7.72 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.35 (m, 3H), 7.25 (s, 1H), 7.23–7.19 (m, 1H), 7.67–6.98 (m, 3H), 6.68 (d, *J* = 3.3 Hz, 2H), 6.13 (d, *J* = 7.2 Hz, 1H), 4.81 (s, 1H), 4.50 (d, *J* = 12.3 Hz, 1H), 3.65 (d, *J* = 12.6 Hz, 1H), 3.56–3.51 (m, 3H), 2.83–2.81 (m, 1H), 2.63–2.52 (m, 1H), 2.12–2.05 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 180.2, 177.4, 172.1, 163.6, 160.4, 142.1, 133.3, 132.9, 132.7, 132.1, 131.1, 128.6, 128.5, 128.1, 128.0, 127.5, 127.4, 126.5, 125.8, 123.5, 120.5, 115.2, 114.9, 73.3, 69.8, 62.7, 56.7, 30.4, 23.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ −87.5 (m); MS (ESI) *m*/*z* 614.2 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{33}H_{29}FN_3NiO_3$ $[M + H]^+$ *m*/*z* 592.1540, found 592.1541.

(*S*,*S*)-**3f**: red solid (37.4 mg, 60% yield); mp 138–139 °C; $[\alpha]^{25}_D$ = +735.0 (*c* 0.1, CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.8 Hz, 1H), 8.23–8.18 (m, 2H), 8.12 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.71–7.64 (m, 2H), 7.59–7.53 (m, 2H), 7.50–7.48 (m, 1H), 7.45–7.40 (m, 2H), 7.23–7.20 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 3.3 Hz, 1H), 6.12 (d, *J* = 7.2 Hz,

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1H), 4.96 (s, 1H), 4.48 (d, J = 12.3 Hz, 1H), 3.64 (d, J = 12.6 Hz, 1H), 3.58−3.53 (m, 1H), 3.48−3.41 (m, 2H), 2.87−2.81 (m, 1H), 2.68−2.58 (m, 1H), 2.20−2.06 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.8, 176.3, 173.2, 147.5, 142.9, 133.5, 132.9, 131.5, 129.7, 129.1, 129.0, 128.8, 128.6, 127.0, 126.7, 126.3, 124.6, 124.2, 124.0, 123.7, 121.0, 73.8, 70.3, 63.3, 57.4, 30.8, 23.9; MS (ESI) m/z 641.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{33}H_{29}N_4NiO_5$ $[M + H]^+$ m/z 619.1486, found 619.1483.

(*S*,*S*)-**3g**: red solid (48.6 mg, 80% yield); mp 186−188 °C; $[\alpha]^{25}_D$ = +1206.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.18 (d, J = 8.7 Hz, 1H), 8.10 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.42−7.32 (m, 4H), 7.24 (s, 1H), 7.22−7.16 (m, 1H), 6.96 (t, J = 7.8 Hz, 1H), 6.67 (d, J = 3.9 Hz, 2H), 6.09 (d, J = 7.5 Hz, 1H), 4.90 (s, 1H), 4.48 (d, J = 12.6 Hz, 1H), 3.62 (d, J = 12.6 Hz, 1H), 3.55−3.44 (m, 3H), 2.87−2.80 (m, 1H), 2.66−2.51 (m, 1H), 2.16−2.01 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 191.5, 180.8, 176.8, 173.9, 172.9, 144.7, 142.8, 131.6, 129.5, 129.0, 128.5, 126.8, 126.0, 124.0, 121.0, 74.3, 70.3, 63.4, 57.3, 30.9, 23.9; MS (ESI) m/z 624.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{30}N_3NiO_4$ $[M + H]^+$ m/z 602.1584, found 602.1582.

(*S*,*S*)-**3h**: red solid (46.4 mg, 76% yield); mp 251−252 °C; $[\alpha]^{25}_D$ = +831.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 7.2 Hz, 2H), 7.63−7.57 (m, 1H), 7.53−7.37 (m, 6H), 7.23−7.14 (m, 2H), 7.11−7.05 (m, 2H), 6.67 (d, J = 4.2 Hz, 2H), 6.16 (d, J = 7.8 Hz, 1H), 4.77 (s, 1H), 4.47 (d, J = 12.6 Hz, 1H), 3.61 (d, J = 12.9 Hz, 1H), 3.55−3.46 (m, 3H), 2.85−2.79 (m, 1H), 2.65−2.51 (m, 1H), 2.19−2.11 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.8, 177.2, 172.9, 151.9, 151.8, 151.7, 151.6, 148.6, 148.5, 148.4, 148.3, 142.7, 133.7, 133.4, 133.2, 132.7, 131.6, 129.6, 129.1, 129.0, 128.7, 128.5, 126.9, 126.3, 126.0, 124.0, 122.3, 122.2, 122.1, 122.0, 121.0, 117.4, 117.2, 115.7, 115.5, 73.1, 70.4, 63.2, 57.3, 30.7, 24.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ −110.1 (m), −111.8 (m); MS (ESI) m/z 632.2 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{33}H_{28}F_2N_3NiO_3$ $[M + H]^+$ m/z 610.1447, found 610.1443.

(*S*,*S*)-**3i**: red solid (48.8 mg, 80% yield); mp 228−230 °C; $[\alpha]^{25}_D$ = +627.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.7 Hz, 1H), 8.09 (d, J = 7.5 Hz, 2H), 8.00 (s, 1H), 7.53−7.48 (m, 2H), 7.42−7.36 (m, 3H), 7.28 (s, 1H), 7.23 (s, 2H), 7.21−7.20 (m, 1H), 7.18−7.15 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.68−6.64 (m, 2H), 6.14 (d, J = 7.8 Hz, 1H), 4.77 (s, 1H), 4.49 (d, J = 12.6 Hz, 1H), 3.62 (d, J = 12.9 Hz, 1H), 3.54−3.45 (m, 3H), 2.91−2.84 (m, 1H), 2.66−2.52 (m, 1H), 2.20−2.07 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.8, 177.3, 172.7, 142.7, 143.0, 134.5, 133.7, 133.4, 133.2, 132.6, 131.6, 129.8, 129.5, 129.0, 128.6, 128.5, 128.3, 127.0, 126.5, 126.3, 126.1, 124.7, 124.1, 121.0, 73.9, 70.4, 63.2, 57.3, 30.9, 23.6; MS (ESI) m/z 630.2 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{33}H_{29}ClN_3NiO_3$ $[M + H]^+$ m/z 608.1245, found 608.1251.

(*S*,*S*)-**3j**: red solid (41.8 mg, 71% yield); mp 148−150 °C; $[\alpha]^{25}_D$ = +787.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 9.39 (d, J = 7.8 Hz, 1H), 8.22 (d, J = 8.7 Hz 1H), 8.10 (d, J = 7.2 Hz, 2H), 7.51−7.46 (m, 1H), 7.43−7.32 (m, 4H), 7.28 (s, 1H), 7.24 (s, 1H), 7.20−7.12 (m, 2H), 7.00−6.91 (m, 2H), 6.67−6.62 (m, 2H), 5.88 (d, J = 7.2 Hz, 1H), 5.04 (s, 1H), 4.52 (d, J = 12.6 Hz, 1H), 3.66 (d, J = 12.6 Hz, 1H), 3.55−3.50 (m, 3H), 2.97−2.87 (m, 1H), 2.67−2.53 (m, 1H), 2.56−2.00 (m, 2H), 1.71 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.8, 180.0, 172.0, 142.5, 137.9, 137.1, 134.1, 132.3, 131.6, 130.4, 129.0, 128.9, 128.5, 128.4, 127.8, 126.7, 126.4, 126.0, 125.5, 124.0, 120.8, 71.0, 70.4, 63.2, 57.2, 30.9, 23.6, 18.9; MS (ESI) m/z 610.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{32}N_3NiO_3$ $[M + H]^+$ m/z 588.1792, found 588.1789.

(*S*,*S*)-**3k**: red solid (32.6 mg, 55% yield); mp 156−159 °C; $[\alpha]^{25}_D$ = +463.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 6.6 Hz, 2H), 7.78 (d, J = 5.1 Hz, 1H), 7.67 (d, J = 4.5 Hz, 1H), 7.50−7.45 (m, 2H), 7.42−7.34 (m, 3H), 7.24 (s, 1H), 7.23−7.18 (m, 3H), 7.10 (d, J = 7.2 Hz, 1H), 7.03−6.96, (m, 1H), 6.67 (s, 2H), 6.14 (d, J = 7.5 Hz, 1H), 4.76 (s, 1H) 4.49 (d, J = 12.9 Hz, 1H), 3.62 (d, J = 12.9 Hz, 1H), 3.53−3.49 (m, 3H), 2.88−2.80 (m, 1H), 2.64−2.54 (m, 1H), 2.33 (s, 3H), 2.08−2.04 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.7, 178.1, 172.1, 142.5, 137.7, 135.2, 133.8, 133.3, 132.2, 131.6, 129.2, 129.1, 128.9, 128.8, 128.3, 127.0, 126.3, 126.1, 123.8, 120.8, 74.4, 70.3, 63.0, 57.1, 30.8, 23.6, 21.1; MS (ESI) m/z 610.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{32}N_3NiO_3$ $[M + H]^+$ m/z 588.1792, found 588.1791.

(*S*,*S*)-**3l**: red solid (42.7 mg, 70% yield); mp 220−221 °C; $[\alpha]^{25}_D$ = +773.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 8.7 Hz, 1H), 8.08 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 5.4 Hz, 1H), 7.54−7.45 (m, 2H), 7.42−7.33 (m, 3H), 7.26 (s, 1H), 7.23 (s, 1H), 7.20−7.15 (m, 2H), 7.05−6.95 (m, 1H), 6.88 (d, J = 6.3 Hz, 1H), 6.67−6.66 (m, 2H), 6.16 (d, J = 7.5 Hz, 0.61H), 6.10 (d, J = 7.8 Hz, 0.23H), 4.80 (s, 0.25H), 4.76 (s, 0.71H), 4.50 (d, J = 12.6 Hz, 1H), 3.73 (s, 3H), 3.63 (d, J = 12.9 Hz, 1H), 3.53−3.47 (m, 3H), 2.89−2.83 (m, 1H), 2.61−2.50 (m, 1H), 2.09−2.02 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.7, 177.8, 172.3, 159.7, 142.6, 139.6, 131.6, 129.0, 128.4, 127.0, 124.0, 118.5, 113.6, 112.5, 74.5, 70.3, 63.1, 57.1, 55.2, 30.9, 23.6; MS (ESI) m/z 626.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{32}N_3NiO_4$ $[M + H]^+$ m/z 604.1741, found 604.1736.

(*S*,*S*)-**3m**: red solid (43.6 mg, 72% yield); mp 238−240 °C; $[\alpha]^{25}_D$ = +761.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz 1H), 8.08 (d, J = 7.2 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.49−7.45 (m, 1H), 7.41−7.32 (m, 3H), 7.25 (s, 1H), 7.22 (s, 1H), 7.19−7.16 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.4 Hz, 2H), 6.66−6.62 (m, 2H), 6.14 (d, J = 7.5 Hz, 1H), 4.74 (s, 1H), 4.49 (d, J = 12.6 Hz, 1H)3.78 (s, 3H), 3.62 (d, J = 12.9 Hz, 1H), 3.53−3.48 (m, 3H), 2.85−2.81 (m, 1H), 2.57−2.49 (m, 1H), 2.14−2.04 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.7, 178.3, 172.2, 159.3, 142.5, 133.9, 133.3, 132.3, 131.6, 130.4, 129.3, 129.0, 128.4, 128.3, 127.5, 127.1, 126.3, 123.9, 120.8, 113.9, 74.0, 70.3, 63.1, 57.1, 55.3, 30.9, 23.7; MS (ESI) m/z 626.2 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{34}H_{32}N_3NiO_4$ $[M + H]^+$ m/z 604.1741, found 604.1737.

(*S*,*S*)-**3n**: red solid (26.5 mg, 42% yield); mp 128−130 °C; $[\alpha]^{25}_D$ = +565.0 (c 0.1, CH_3OH); ^1H NMR (300 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.21 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 7.5 Hz, 1H), 7.84−7.78 (m, 3H), 7.53−7.48 (m, 3H), 7.41 (t, J = 7.5 Hz, 2H), 7.35−7.30 (m, 2H), 7.25 (s, 1H), 7.22−7.17 (m, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.71−6.64 (m, 2H), 6.05 (d, J = 7.8 Hz, 1H), 4.96 (s, 1H), 4.52 (d, J = 12.6 Hz, 1H), 3.64 (d, J = 12.9 Hz, 1H), 3.57−3.50 (m, 3H), 2.97−2.91 (m, 1H), 2.66−2.55 (m, 1H), 2.12−1.99 (m, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 180.8, 177.9, 172.5, 142.6, 135.7, 133.6, 133.2, 133.0, 132.5, 131.7, 129.4, 129.0, 128.5, 128.0, 127.7, 127.0, 126.5, 126.4, 126.3, 125.3, 124.2, 124.0, 121.0, 74.8, 70.4, 63.2, 57.2, 31.0, 23.7; MS (ESI) m/z 646.3 $[M + Na]^+$; HRMS (ESI-TOF) calcd for $C_{37}H_{32}N_3NiO_3$ $[M + H]^+$ m/z 624.1792, found 624.1790.

General Procedure for the Preparation of (*S*)-4a. A solution of diastereoisomerically pure complex (*S*,*S*)-**3a** (200 mg, 0.35 mmol) in MeOH (1 mL) was slowly added to a stirring solution of aqueous 3 N HCl in MeOH (90 mL, v/v = 1:1) at 70 °C. After disappearance of the red color (about 30 min), the reaction mixture was evaporated in vacuo until dryness. Water (5 mL) was added, and the resultant mixture was treated with an excess of concentrated ammonium hydroxide and extracted with methylene chloride. The organic solution were dried over Na_2SO_4 and evaporated in vacuo to recover (*S*)-BPB. The aqueous solution was evaporated in vacuo, dissolved in a minimum amount of water, and passed through cation exchange resin. The enantiomerically pure amino acids (*S*)-**4a** were determined after N-Boc protection.

(*S*)-**4a**: white solid (47.9 mg, 90% yield, >99% ee); [Chiralpak AD-H column (4.6 mm × 250 mm); *n*-hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; detection wavelength = 220 nm; t_R = 13.85 min (major), t_R = 15.62 min (minor)]; ^1H NMR (300 MHz, D_2O + MeOD) δ 7.43 (m, 5H), 5.04 (s, 1H); MS (ESI) m/z 152.1 $[M + 1]^+$.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra for all new compounds and X-ray structure information for (*S*,*S*)-**3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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