Highly diastereoselective synthesis of 3-indolylglycines via asymmetric oxidative heterocoupling reaction of chiral nickel(II) complex and indoles

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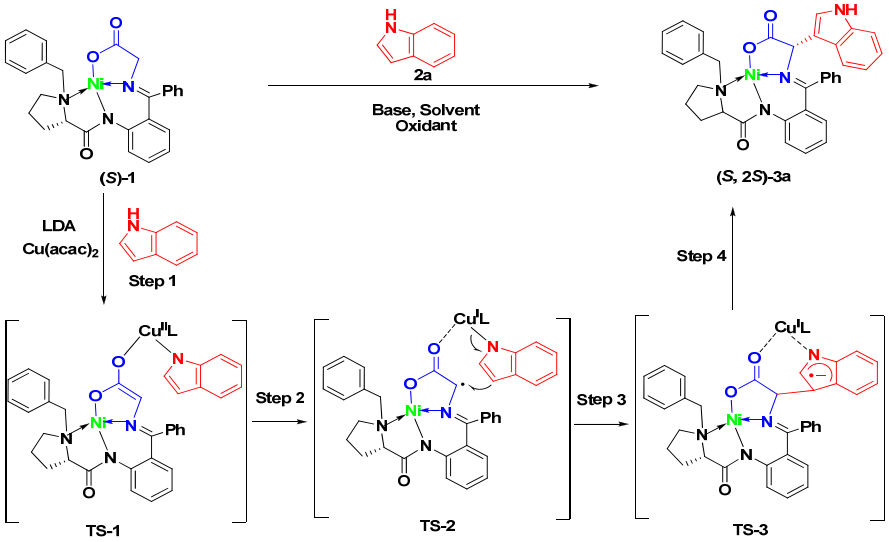
(A) A Proposed Mechanism

We proposed a mechanism of this oxidative coupling reaction (Scheme S1). Under the basic condition, the nickel complex enolate and an indole anion initially coordinate to the copper(II) center, giving the chelated intermediate **TS-1**, the chelate **TS-1** can undergo single-electron transfer to form the chelated nickel(II) complex radical **TS-2**. Due to its proximity to the indole anion, the radical is attacked by this nucleophilic species, resulting in radical anion **TS-3**. This intermediate **TS-3** can then be further oxidized by the proximal copper(I) to generate the product **3a** and copper(0).

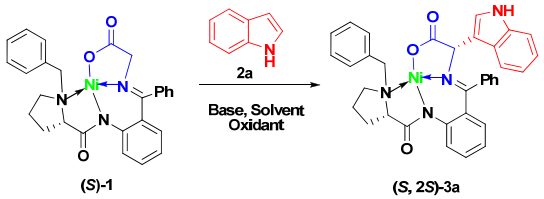


Scheme S1

(B) Optimization of the Reaction Conditions

Copper(II) were considered to be good oxidants for this reaction (in Table 1, entry). We also explored copper(II) oxidants listed in Table S1, $CuCl_2$ and $CuSO_4$ afforded the target product in very low yield due to the poor conversion (entries 1 and 2). A higher yield and diastereoselectivity was observed with $Cu(acac)_2$ as the oxidant than with $Cu(OMs)_2$, $Cu(OAc)_2$, $Cu(OTf)_2$.

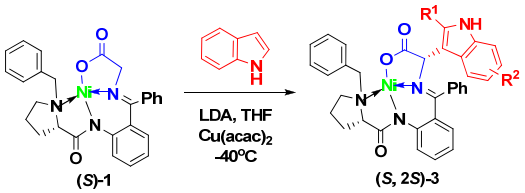
Table S1 Optimization of the Oxidants



Entry	Base	Solution	Oxidant	Temp/°C	Yield (%)	de[b] (%)
1	LDA	THF	$CuCl_2$	-40	15	ND
2	LDA	THF	$CuSO_4$	-40	trace	ND
3	LDA	THF	$Cu(OMs)_2$	-40	30	ND[c]
4	LDA	THF	$Cu(acac)_2$	-40	59	>99
5	LDA	THF	$Cu(OTf)_2$	-40	48	98
6	LDA	THF	$Cu(OAc)_2$	-40	42	98

The equivalents of the base, oxidant and indole were also optimized, which were listed in Table S2. The reactions were run under with 0.20 mmol of (*S*)-**1** and **2a** in 10 mL of THF with LDA for 0.5 h, then added $Cu(acac)_2$ for 1h at -40°C. 3.3 and 3.5 equiv. of LDA yields the best product (entries 3 and 6). Decreasing LDA would lower the yield due to the poor conversion(entries 1-2), and increasing the base would also lower the chemical yield due to the side reactions(entries 4-5), 1.5 equiv. of $Cu(acac)_2$ demonstrated the best performance among the screening the equiv. of the oxidant (entries 6-8). The yields enhanced when the equiv. of indole increased (entries 9-11). From the viewpoint of practical applications, we chose 3.3 equiv. of LDA, 1.5 equiv. of $Cu(acac)_2$, and 4 equiv. of indole to carry out the reaction.

Table S2 Optimization of the equivalents of base, oxidant, and indole



Entry	Equiv. of LDA	Equiv. of $Cu(acac)_2$	Equiv. of indole	Yield (%)
1	2	1.2	2	12
2	3	1.2	2	34
3	3.5	1.2	2	38
4	4	1.2	2	22
5	5	1.2	2	trace
6	3.3	1.2	2	38
7	3.3	1.5	2	42
8	3.3	2	2	35
9	3.3	1.5	3	47
10	3.3	1.5	4	59
11	3.3	1.5	5	60

(C) The Absolute Configuration of 3a and Quantum Chemical Calculation

X-ray Single Crystal Stucture Analysis of (*S*, 2*S*)-**3a**:

X-ray crystallographic data of (*S*, 2*S*)-**3a** were solutions at T = 293(2) K: $C_{35}H_{30}N_4NiO_3$, M_r = 613.34, monoclinic. Space group *P2* (1), a = 11.435 (5) Å, b = 9.023 (4) Å, c = 15.152 (7) Å, α = 90°, β = 99.011 (10)°, γ = 90°, V = 1544.2 (13) Å^3, Z = 2.

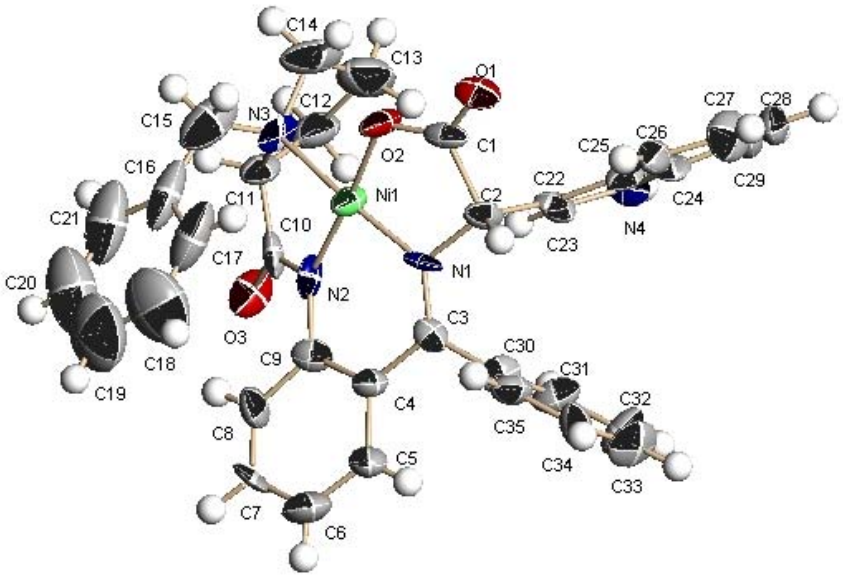


Figure S1. The crystal structure of (*S*, 2*S*)-**3a** by X-ray analysis.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, the CCDC number is 909566.

(D) General Methods

The reagents (chemicals) were purchased from commercial sources, and used without further purification. Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). All products were characterized by their NMR and MS spectra. ^{1}H and ^{13}C NMR spectra were recorded in deuterochloroform ($CDCl_3$) on a 300 MHz or 400 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were measured on spectrometer. Optical rotations were reported as follows: $[\alpha]_D^{20}$ (c: g/100 mL, in solvent).

(E) General Procedure for the Asymmetric Reactions

General Procedure for the Synthesis of (*S*, 2*S*)-3a. The nickel(II) complex of glycine (*S*)-**1** (100 mg, 0.201 mmol) and indole (94 mg, 0.803mmol)was dissolved in tetrahydrofuran (10 mL), and stirred at -40^{o}C under nitrogen. LDA (0.33 mL, 2M, 0.662 mmol) were added and the reaction mixture was stirred for 30 min. Then, the $Cu(acac)_2$ (78.8 mg, 0.301mmol) was added at -40^{o}C. The reaction was moved out of the cool bath, and allowed to warm to room temperature naturally and to stir for 1 h. The reaction was quenched by pouring the crude reaction mixture over 30 mL of aq. sat. NH_4Cl. The suspension was extracted with ethyl acetate (3 times). The combined organic layers were dried with $MgSO_4$, concentrated, and purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give (*S*,2*S*)-**3a** as a red solid.

Procedure for the Synthesis of (2*S*,3*R*)-4a: The crystallized complex (*S*, 2*S*)-**3a** (1 g, 1.64 mmol) was dissolved in THF/MeOH (1:1, v/v) 50 mL, and aqueous 1 N HCl (2 mL) was added. The reaction mixture was stirred for 6 h at room temperature, until the red color of the solution disappeared. The reaction was evaporated to dryness. Water (20 mL) was added to the residue to form a clear solution, and this solution was then separated by column chromatography on C_{18}-reversed phase (230-400 mesh) silica gel. Pure water as an eluent was employed to remove the green $NiCl_2$ and excess HCl; water was then used to obtain optically pure product (*S*)-**4a** (288 mg,

93%). The ligand BPB that decomposed from (*S*, 2*S*)-**3a** was recovered by MeOH eluent (608 mg, 97%), and the column chromatography was washed with 100 mL of MeOH for further use.

(F) Analytical Characterization Data of Products

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(1H-indol-3-yl)acetic acid Schiff Base Complex 3a.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 63%. Mp > 280 ºC; $[\alpha]_D^{20}$ = +2440 (c = 0.10 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ 11.12 (s, 1H), 8.42 (d, J = 7.6 Hz, 2H), 8.02-7.96 (m, 2H), 7.56-7.54(m, 3H), 7.43-7.39 (m, 2H), 7.35-7.31 (m, 2H), 7.21-7.17(m, 1H), 7.12-7.03 (m, 2H), 6.95-6.89 (m, 2H), 6.64 (t, J = 7.6 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.16 (d, J = 8.0 Hz, 1H), 4.91 (s, 1H), 4.14 (d, J = 12.4 Hz, 1H), 3.63-3.57 (m, 2H), 3.32-3.23 (m, 2H), 2.57-2.50 (m, 2H), 2.16-2.08 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.9, 177.1, 171.1, 143.1, 136.4, 135.2, 134.2, 133.0, 132.0, 131.7, 129.5, 129.0, 128.9, 128.8, 127.2, 124.0, 123.4, 121.8, 120.6, 119.7, 119.0, 113.0, 112.1, 70.2, 69.0, 63.3, 57.9, 30.8, 23.8 ppm. LRMS (ESI) $[M+H]^+$ found m/z 613. HRMS (ESI) $[M+Na]^+$ found m/z 635.1559, calcd for $C_{35}H_{30}N_4NiO_3Na$ 635.1569. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 16.22 min, de > 99%.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-methoxy-1H-indol-3-yl)acetic acid Schiff Base Complex 3b.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 60%. Mp >280 ºC; $[\alpha]_D^{20}$ = +1773 (c = 0.11 g/100 mL, $CHCl_3$).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.97 (s, 1H), 8.41 (d, J = 7.5 Hz, 2H), 8.05 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 2.1 Hz, 1H), 7.55 (d, J = 4.2 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.35-7.32 (m, 1H), 7.30-7.07 (m, 4H), 6.91 (t, J = 7.8 Hz, 1H), 6.73-6.62 (m, 2H), 6.52 (dd, J = 8.4, 1.5 Hz, 1H), 6.17 (d, J = 7.5 Hz, 1H), 4.86 (s, 1H), 4.14 (d, J = 12.0 Hz, 1H), 3.61-3.57 (m, 5H), 3.29-3.22 (m,2H), 2.56-2.53 (m, 2H), 2.17-2.04 (m, 2H).8.34 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.90 (s, 1H), 7.65 (s, 1H), 7.54-7.52 (m, 2H), 7.45-7.31 (m, 5H), 7.19-7.07 (m, 5H), 6.97-6.95 (m, 1H), 6.81-6.66 (m, 5H), 4.76 (d, J = 2.1 Hz, 1H), 4.41 (d, J = 1.8 Hz, 1H), 4.25 (d, J = 12.3 Hz, 1H), 3.44-3.29 (m, 2H), 2.82-2.73 (m, 1H), 2.38-2.24 (m, 5H), 2.04-1.98 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.0, 177.1, 171.0, 153.4, 143.1, 135.2, 134.2, 133.0, 132.1, 131.8, 131.6, 129.0, 128.9, 128.8, 127.2, 124.0, 123.9, 120.6, 112.8, 112.6, 111.6, 101.8, 70.1, 69.0, 63.2, 57.9, 55.8, 30.8, 23.9 ppm. LRMS (ESI) $[M+H]^+$ found m/z 643. HRMS (ESI) $[M+Na]^+$ found m/z 665.1656, calcd for $C_{36}H_{32}N_4NiO_4Na$ 665.1675. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 15.58 min, de > 99%.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-fluoro-1H-indol-3-yl)acetic acid Schiff Base Complex 3c.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 40%. Mp >280 ºC; $[\alpha]_D^{20}$ = +2210 (c = 0.10 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.22 (s, 1H), 8.43 (d, J = 7.5 Hz, 2H), 8.03 (d, J = 8.7 Hz, 1H), 7.66-7.55 (m, 4H), 7.45-7.31 (m, 4H), 7.23-7.09 (m, 2H), 6.97-6.89 (m, 2H),

6.66 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 6.18 (d, *J* = 7.5 Hz, 1H), 4.90 (s, 1H), 4.16 (d, *J* = 12.3 Hz, 1H), 3.64-3.59 (m, 2H), 3.31-3.24 (m, 2H), 2.60-2.56 (m, 2H), 2.20-2.07 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ^{13}C NMR (126 MHz, DMSO) δ 180.9, 177.0, 171.3, 157.0 (d, *J* = 230.1 Hz), 143.1, 135.2, 134.2, 133.1, 132.0, 131.8, 129.5, 129.0, 128.9, 128.3, 127.2, 126.2, 125.5, 124.0, 120.6, 113.1 (d, *J* = 8.0 Hz), 110.0 (d, *J* = 25.5 Hz), 104.2 (d, *J* = 23.8 Hz), 70.2, 68.7, 63.3, 57.8, 30.7, 23.8. ppm. LRMS (ESI) $[M+H]^+$ found m/z 631. HRMS (ESI) $[M+Na]^+$ found m/z 653.1498, calcd for $C_{35}H_{29}N_4NiO_3NaF$ 653.1475. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.97 min, de > 99%.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-chloro-1H-indol-3-yl)acetic acid Schiff Base Complex 3d.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 35%. Mp >280 ºC; $[\alpha]_D^{20}$ = +1764 (c = 0.11 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) *δ* 11.30 (s, 1H), 8.43 (d, *J* = 7.8 Hz, 2H), 8.02 (d, *J* = 12.3 Hz, 2H), 7.59-7.51 (m, 3H), 7.45-7.36 (m, 4H), 7.23-7.05 (m, 3H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.16 (d, *J* = 8.1 Hz, 1H), 4.91 (s, 1H), 4.16 (d, *J* = 12.9 Hz, 1H), 3.65-3.59 (m, 2H), 3.30-3.27 (m, 2H), 2.68-2.57 (m, 2H), 2.20-2.14 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) *δ* 180.5, 176.5, 170.9, 142.6, 134.7, 134.4, 133.8, 132.6, 131.6, 131.3, 129.0, 128.6, 128.4, 127.9, 126.8, 126.7, 125.9, 125.6, 125.0, 123.5, 123.3, 121.3, 118.2, 113.2, 112.1,

69.6, 68.0, 62.8, 57.4, 30.3, 23.4 ppm. LRMS (ESI) $[M+H]^+$ found m/z 647. HRMS (ESI) $[M+Na]^+$ found m/z 669.1160, calcd for $C_{35}H_{29}N_4NiO_3NaCl$ 669.1179. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.03 min, de > 99%.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-bromo-1H-indol-3-yl)acetic acid Schiff Base Complex 3e.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 33%. Mp 180-182 ºC; $[\alpha]^{20}_D$ = +1790 (c = 0.10 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.31 (s, 1H), 8.43 (d, *J* = 7.2 Hz, 2H), 8.10 (s, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.59-7.55 (m, 2H), 7.51 (s, 1H), 7.45-7.31 (m, 4H), 7.23-7.16 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.15 (d, *J* = 7.5 Hz, 1H), 4.91 (s, 1H), 4.16 (d, *J* = 12.3 Hz, 1H), 3.65-3.59 (m, 2H), 3.18-3.13 (m, 2H), 2.65-2.59 (m, 2H), 2.20-2.09 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.0, 177.0, 171.4, 143.1, 135.2, 135.1, 134.3, 133.1, 132.1, 131.8, 129.5, 129.1, 128.9, 128.4, 127.3, 127.2, 127.1, 126.1, 125.3, 124.3, 124.0, 121.7, 120.6, 114.2, 112.5, 111.8, 70.1, 68.5, 63.3, 57.9, 30.8, 24.0 ppm. LRMS (EI) $[M]^+$ found m/z 690. HRMS (EI) $[M]^+$ found m/z 690.0721, calcd for $C_{35}H_{29}N_4NiO_3Br$ 690.0777. HPLC (Chiralpak IA, *n*-hexane/ *i*-propanol 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 14.03 min, de > 99%.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(4-methyl-1H-indol-3-yl)acetic acid Schiff Base

Complex 3g.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 62%. Mp 242-244 ºC; $[\alpha]_D^{20}$ = +1250 (c = 0.10 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) δ 11.25 (s, 1H), 8.84 (s, 1H), 8.43 (d, J = 7.8 Hz, 2H), 8.09 (d, J = 8.7 Hz, 1H), 7.62-7.51 (m, 2H), 7.43 (t, J = 7.2 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.23-7.10 (m, 3H), 6.90-6.77 (m, 2H), 6.66 (t, J = 7.5 Hz, 1H), 6.57-6.50 (m, 2H), 6.09 (d, J = 7.5 Hz, 1H), 5.13 (s, 1H), 4.16 (d, J = 12.0 Hz, 1H), 3.67-3.59 (m, 2H), 3.49-3.37 (m, 2H), 2.65-2.57 (m, 2H), 2.21-2.14 (m, 2H), 1.99 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.1, 177.4, 171.1, 143.1, 136.1, 135.3, 134.6, 133.0, 132.0, 131.8, 130.3, 129.4, 129.1, 128.9, 128.5, 127.1, 126.7, 125.9, 124.2, 124.0, 122.4, 121.7, 120.7, 120.6, 115.9, 109.9, 70.3, 68.6, 63.2, 57.9, 30.8, 24.0, 19.5 ppm. LRMS (ESI) $[M+H]^+$ found m/z 627. HRMS (ESI) $[M+Na]^+$ found m/z 627.1756, calcd for $C_{36}H_{32}N_4NiO_3Na$ 649.1726. HPLC (Chiralpak AD, *n*-hexane/*i*-propanol = 75/25, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.73 min, de > 99 %.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3h.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 56%. Mp 232-234 ºC; $[\alpha]_D^{20}$ = +1600 (c = 0.10 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ 10.96 (s, 1H), 8.43 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 9.0 Hz, 1H), 7.70 (s, 1H), 7.59-7.55 (m, 2H), 7.43-7.33 (m, 4H), 7.25-7.17 (m, 2H), 7.14-7.08 (m, 1H), 6.98-6.88 (m, 2H), 6.65 (t, J = 7.5 Hz, 1H), 6.52 (d, J = 8.4

Hz, 1H), 6.15 (d, *J* = 7.8 Hz, 1H), 4.89 (s, 1H), 4.17 (d, *J* = 12.0 Hz, 1H), 3.65-3.60 (m, 2H), 3.26-3.17 (m, 2H), 2.60-2.57 (m, 2H), 2.32 (s, 3H), 2.20-2.09 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.9, 177.1, 171.0, 143.0, 135.2, 134.8, 134.3, 133.0, 132.1, 131.7, 129.4, 129.0, 128.9, 128.4, 127.4, 127.3, 127.2, 126.2, 125.6, 123.9, 123.6, 123.4, 120.5, 119.2, 112.3, 111.7, 70.1, 69.0, 63.3, 57.8, 30.8, 23.9, 21.7 ppm. LRMS (ESI) $[M+H]^+$ found m/z 627. HRMS (ESI) $[M+H]^+$ found m/z 627.1890, calcd for $C_{36}H_{33}N_4NiO_3$ 627.1906. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 15.62 min, de > 99 %.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(6-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3i.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 60 %. Mp 238-240ºC; $[\alpha]_D^{20}$ = +2206 (c = 0.16 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.93 (s, 1H), 8.42 (d, *J* = 6.9 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.56-7.54 (m, 2H), 7.45-7.31 (m, 4H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14-7.08 (m, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 9.3 Hz, 1H), 6.65 (t, *J* = 6.6 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 6.16 (d, *J* = 8.4 Hz, 1H), 4.87 (s, 1H), 4.15 (d, *J* = 12.6 Hz, 1H), 3.64-3.59 (m, 2H), 3.28-3.23 (m, 2H), 2.60-2.57 (m, 2H), 2.36 (s, 3H), 2.18-2.10 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.9, 177.0, 171.0, 143.1, 136.9, 135.2, 134.2, 133.0, 132.1, 131.7, 130.8, 129.5, 129.0, 128.9, 128.8, 128.4, 127.2, 126.2, 124.0, 123.3, 122.8, 120.8, 120.6, 119.5, 112.8, 111.8, 70.2, 69.2, 63.3, 57.8, 30.8, 23.8, 21.8 ppm. LRMS (ESI) $[M+H]^+$ found

m/z 627. HRMS (ESI) $[M+Na]^+$ found m/z 649.1744, calcd for $C_{36}H_{32}N_4NiO_3Na$ 649.1726. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 16.20 min, de > 99 %.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(7-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3j.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 54%. Mp 229-231 ºC; $[\alpha]_D^{20}$ = +1890 (c = 0.15 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.11 (s, 1H), 8.43 (d, *J* = 7.2 Hz, 2H), 8.04 (d, *J* = 8.7 Hz, 1H), 7.89-7.85 (m, 1H), 7.58-7.52 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35-7.33 (m, 1H), 7.23-7.17 (m, 1H), 7.14-7.09 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.88-6.86 (m, 2H), 6.70-6.63 (m, 1H), 6.53 (d, *J* = 9.6 Hz, 1H), 6.19 (d, *J* = 7.2 Hz, 1H), 4.90 (s, 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 3.64-3.59 (m, 4H), 2.61-2.57 (m, 2H), 2.45 (s, 3H), 2.19-2.13 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.0, 177.3, 171.2, 142.9, 136.0, 135.3, 134.1, 133.0, 132.6, 132.0, 131.8, 129.6, 129.2, 129.1, 128.9, 128.4, 127.1, 126.2, 125.0, 124.0, 122.4, 121.1, 120.7, 119.3, 117.4, 113.3, 70.4, 69.1, 63.4, 57.9, 30.8, 23.8, 17.2 ppm. LRMS (ESI) $[M+H]^+$ found m/z 627. HRMS (ESI) $[M+Na]^+$ found m/z 649.1734, calcd for $C_{36}H_{32}N_4NiO_3Na$ 649.1726. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 6.75 min, t_{major} = 16.32 min, de = 98 %.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(2-methyl-1H-indol-3-yl)acetic acid Schiff Base

Complex 3k.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 65%. Mp 186-188 ºC; $[\alpha]_D^{20}$ = +1340 (c = 0.10 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) δ 10.81 (s, 1H), 10.09 (d, *J* = 8.1 Hz, 1H), 8.46 (d, *J* = 7.5 Hz, 2H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.56-7.54 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39-7.34 (m, 1H), 7.30-7.03 (m, 5H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.59 (t, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 5.64 (d, *J* = 7.2 Hz, 1H), 4.98 (s, 1H), 4.20 (d, *J* = 12.3 Hz, 1H), 3.73-3.63 (m, 2H), 3.27-3.22 (m, 2H), 2.66-2.61 (m, 2H), 2.22-2.07 (m, 2H), 1.65 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.0, 178.1, 171.8, 143.0, 135.5, 135.3, 134.9, 134.6, 133.0, 132.1, 131.8, 129.3, 129.1, 129.0, 128.9, 128.1, 126.7, 126.5, 126.1, 125.9, 123.9, 120.7, 120.5, 119.4, 118.8, 111.5, 107.7, 70.4, 68.7, 63.8, 57.7, 30.8, 23.4, 11.2 ppm. LRMS (ESI) $[M+H]^+$ found m/z 627. HRMS (ESI) $[M+Na]^+$ found m/z 649.1724, calcd for $C_{36}H_{32}N_4NiO_3Na$ 649.1726. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 6.85 min, t_{major} = 15.53 min, de = 98 %.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(2-(ethoxycarbonyl)-1H-indol-3-yl)acetic acid Schiff Base Complex 3l.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 55%. Mp 172-174 ºC; $[\alpha]_D^{20}$ = +1168 (c = 0.19 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) δ 11.54 (s, 1H), 10.47 (s, 1H), 8.48 (d, *J* = 7.5 Hz, 2H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.48-7.42 (m, 5H), 7.34-7.20 (m, 4H), 7.14-7.08 (m,

1H), 6.81 (t, *J* = 7.8 Hz, 1H), 6.59 (t, *J* = 7.8 Hz, 1H), 6.40 (d, *J* = 8.1 Hz, 1H),6.07 (s, 1H), 5.49 (d, *J* = 7.8 Hz, 1H), 4.24 (d, *J* = 12.3 Hz, 1H), 4.19-3.99 (m, 2H), 3.73 (d, *J* = 12.3 Hz, 1H), 3.66 (t, *J* = 8.7 Hz, 1H), 3.26-3.15 (m, 2H), 2.68-2.59 (m, 2H), 2.26-2.08 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.0, 176.7, 172.5, 160.6, 143.1, 136.4, 135.2, 135.1, 133.1, 132.2, 131.9, 129.1, 129.0, 128.9, 127.5, 126.9, 126.0, 125.9, 125.2, 124.7, 124.0, 122.2, 120.6, 120.3, 118.2, 113.7, 70.3, 67.5, 63.7, 60.5, 57.7, 30.8, 23.5, 14.6 ppm. LRMS (ESI) $[M+H]^+$ found m/z 685. HRMS (ESI) $[M+H]^+$ found m/z 685.1972, calcd for $C_{38}H_{35}N_4NiO_5$ 685.1961. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 10.63 min, t_{major} = 21.82 min, de = 96 %.

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(2-phenyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3m.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 74 %. Mp 222-224 ºC; $[\alpha]_D^{20}$ = +2080 (c = 0.10 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.23 (s, 1H), 10.98 (d, *J* = 8.1 Hz, 1H), 8.52 (d, *J* = 7.2 Hz, 2H), 8.13-8.08 (m, 1H), 7.56-7.53 (m, 2H), 7.45-7.40 (m, 3H), 7.32-7.30 (m, 4H), 7.23-7.14 (m, 2H), 7.08-7.03 (m, 2H), 6.97-6.88 (m, 2H), 6.74 (t, *J* = 6.0 Hz, 1H), 6.54-6.47 (m, 1H), 6,19 (d, *J* = 7.5 Hz, 1H), 5.50-5.42 (m, 1H), 5.30 (s, 1H), 4.25 (d, *J* = 12.3 Hz, 1H), 3.76-3.67 (m, 2H), 3.53-3.45 (m, 1H), 3.27-3.20 (m, 1H), 2.73-2.64 (m, 2H), 2.31-2.16 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.8, 178.5, 172.3, 143.0, 137.4, 136.5, 135.2, 134.4, 133.0, 132.2, 132.1, 131.7, 131.2,

129.2, 129.0, 128.8, 128.1, 128.0, 127.7, 127.6, 126.0, 125.9, 125.6, 123.7, 121.9, 121.0, 120.3, 119.1, 112.3, 108.5, 70.5, 67.6, 64.0, 57.8, 30.8, 23.4 ppm. LRMS (ESI) $[M+H]^+$ found m/z 689. HRMS (ESI) $[M+Na]^+$ found m/z 711.1882, calcd for $C_{41}H_{34}N_4NiO_3Na$ 711.1882. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.83 min, t_{major} = 30.52 min, de = 97 %

Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-methoxy-2-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3n.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 60 %. Mp 242-244ºC; $[\alpha]_D^{20}$ = +2120 (c = 0.20 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ 10.64 (s, 1H), 9.08 (s, 1H), 8.47 (d, J = 6.8 Hz, 2H), 8.18 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 4.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 7.35-7.30 (m, 1H), 7.21-7.14 (m, 2H), 7.09 (t, J = 8.4 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.72 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 6.58 (t, J = 7.6 Hz, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.60 (d, J = 8.0 Hz, 1H), 4.95 (s, 1H), 4.20 (d, J = 11.6 Hz, 1H), 3.69-3.63 (m, 5H), 3.46-3.44 (m, 1H), 3.22-3.15 (m, 1H), 2.60-2.53 (m, 2H), 2.24-2.17 (m, 2H), 1.70 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.8, 177.7, 171.3, 153.1, 142.6, 135.0, 134.8, 134.4, 132.6, 131.7, 131.5, 130.3, 128.7, 128.6, 128.4, 127.4, 126.3, 126.1, 125.2, 123.2, 120.0, 111.3, 108.5, 106.9, 103.1, 69.7, 68.3, 63.3, 57.5, 55.9 30.1, 23.2, 11.1 ppm. LRMS (ESI) $[M+H]^+$ found m/z 657. HRMS (ESI) $[M+Na]^+$ found m/z 679.1841, calcd for $C_{37}H_{34}N_4NiO_4Na$ 679.1831. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.74 min,

t_{major} = 14.10 min, de = 97 %.

(S)-2-amino-2-(1H-indol-3-yl)acetic acid 4a.

Obtained as a pink solid by column chromatography on C_{18}-reversed phase (230-400 mesh) silica gel (methanol /water = 20/80), yield 93 %. Mp 214-216 ºC; $[\alpha]_D^{20}$ = +113.1 (c = 0.31 g/100 mL, H_2O). ^{1}H NMR (D_2O, 400 MHz): δ 7.53 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.33 (s, 1H), 7.13 (dd, J = 7.6 Hz, 8.0 Hz,1H), 7.04 (dd, J = 7.6 Hz, 8.0 Hz, 1H), 4.96 (s, 1H) ppm. ^{13}C NMR (D_2O, 125 MHz): δ 173.9, 136.2, 126.5, 124.8, 122.3, 119.9, 118.3, 112.1, 107.6 51.2 ppm. LRMS (EI) $[M]^+$ found *m/z* 190. HRMS (EI) $[M]^+$ found *m/z* 190.0739, calcd. for $C_{10}H_{10}N_2O_2$ 190.0742. HPLC (Chirobiotic T, methanol/water = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 9.36 min, t_{minor} =17.36 min, de = 98%.

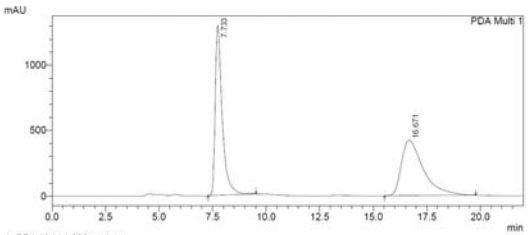
(S)-2-amino-2-(2-phenyl-1H-indol-3-yl)acetic acid 4m.

Obtained as a pink solid by column chromatography on C_{18}-reversed phase (230-400 mesh) silica gel (methanol /water = 20/80), yield 85 %. Mp >300 ºC; $[\alpha]_D^{25}$ = +53.3 (c = 0.10 g/100 mL, H_2O). ^{1}H NMR (D_2O, 400 MHz): δ 7.70-7.66 (m, 3H), 7.60-7.51 (m, 4H), 7.30 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 5.19 (s, 1H) ppm. ^{13}C NMR (D_2O, 125 MHz): δ 174.2, 139.5, 135.8, 131.1, 129.1, 128.9, 128.8, 125.5, 122.5, 120.1, 118.6, 111.7, 104.6 50.8 ppm. LRMS (ESI) $[M]^-$ found *m/z* 265. HRMS (ESI) $[M]^-$ found *m/z* 265.0973, calcd. for $C_{16}H_{13}N_2O_2$ 265.0977. HPLC (Chirobiotic T,

methanol/water = 80/20, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 6.31 min, t_{minor} =20.68 min, de = 97%.

Analytical high performance liquid chromatography was carried out using the Model 410 automated sampler, using the Chiralpak IA column or the Chiralpak AD column. The loading loop was 20 μL. The eluting employed was an isocratic mixture of *n*-hexane and *i*-propanol (60/40 or 75/25 respectively) at a flow of 1 mL/min unless stated. Retention times are reported in minutes. The enantiomeric excess was calculated from the integration of the absorption peaks at 220 nm.

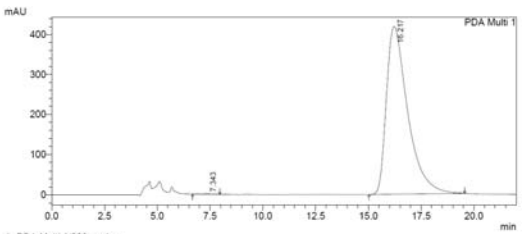
3a



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.733	29644809	1299709	49.763	75.647
2	16.671	29926895	418424	50.237	24.353
Total		59571704	1718133	100.000	100.000



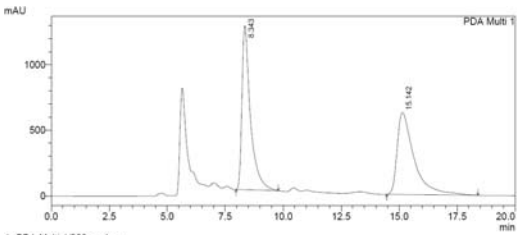
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.343	31649	1185	0.108	0.353
2	16.217	29388186	418982	99.892	99.647
Total		29419836	420166	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 16.22 min, de > 99%.

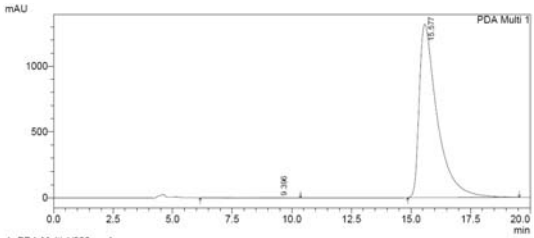
3b



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.343	31758497	1249729	50.229	66.756
2	15.142	31469499	622356	49.771	33.244
Total		63227997	1872085	100.000	100.000



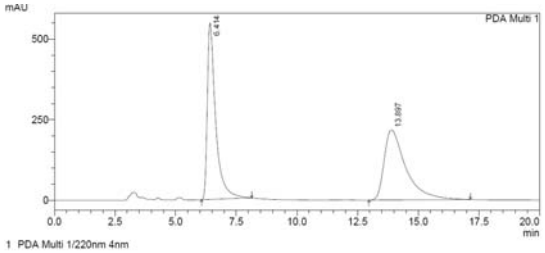
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.396	11334	1058	0.090	0.080
2	15.577	69401730	1319102	99.910	99.920
Total		69413064	1320159	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 15.58 min, de > 99%.

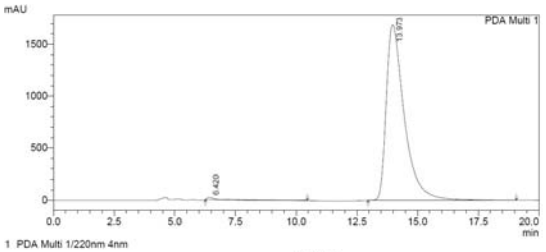
3c



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.414	13130368	546977	49.274	71.562
2	13.897	13517193	217368	50.726	28.438
Total		26647561	761345	100.000	100.000



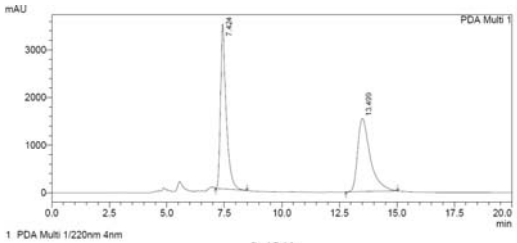
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.420	53356	21225	0.061	1.242
2	13.973	86980663	1688213	99.939	98.758
Total		87034019	1709438	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.97 min, de > 99%.

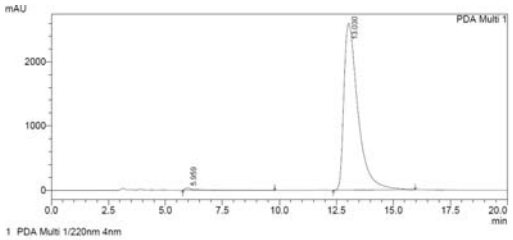
3d



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.424	58663503	3161802	50.007	69.268
2	13.499	58647951	1535927	49.993	30.732
Total		117311153	4997829	100.000	100.000



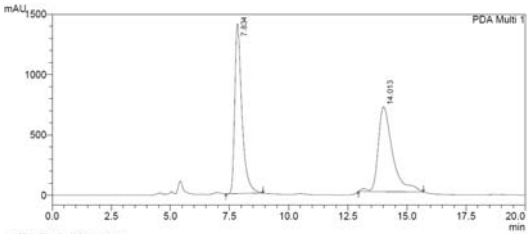
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.959	329970	30744	0.296	1.170
2	13.030	111181214	2597913	99.704	98.830
Total		111511184	2628658	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.03 min, de > 99%.

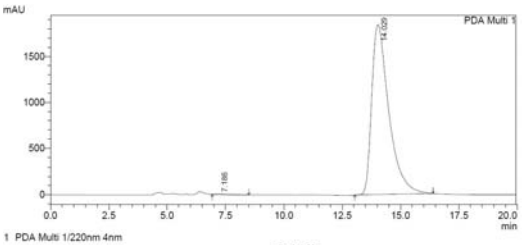
3e



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.831	29652158	1406620	49.887	66.676
2	14.013	29786628	703008	50.113	33.324
Total		59439087	2109628	100.000	100.000



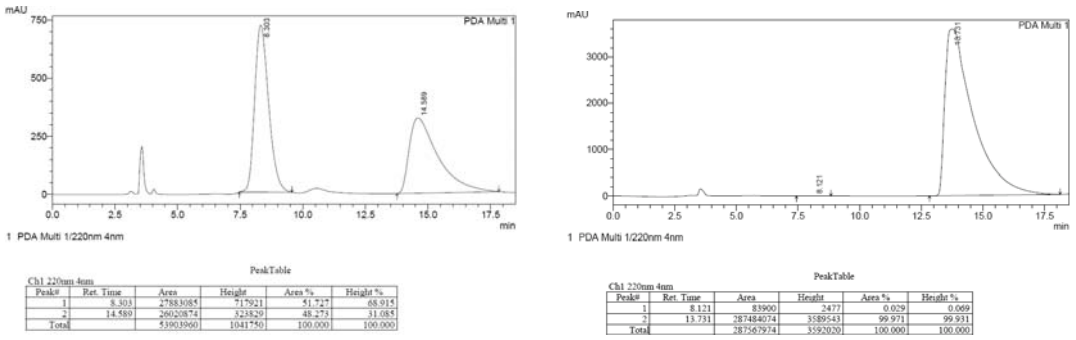
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.186	27108	4667	0.029	0.252
2	14.029	93883630	1844673	99.971	99.748
Total		93910737	1849340	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/ *i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 14.03 min, de > 99%.

3g



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.303	27883085	717921	51.727	68.915
2	14.589	26020874	323829	48.273	31.085
Total		53903960	1041750	100.000	100.000

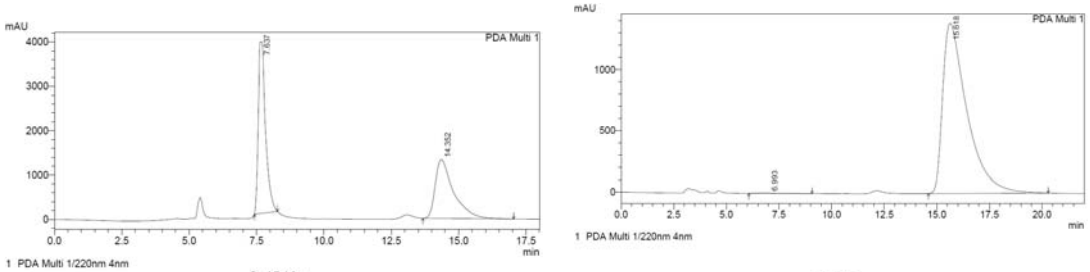
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.121	83900	2477	0.029	0.069
2	13.731	287484074	3589543	99.971	99.931
Total		287567974	3592020	100.000	100.000

HPLC (Chiralpak AD, *n*-hexane/*i*-propanol = 75/25, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.73 min, de > 99%.

3h



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.637	72810705	3865923	53.831	74.427
2	14.352	62447992	1328326	46.169	25.573
Total		135258697	5194249	100.000	100.000

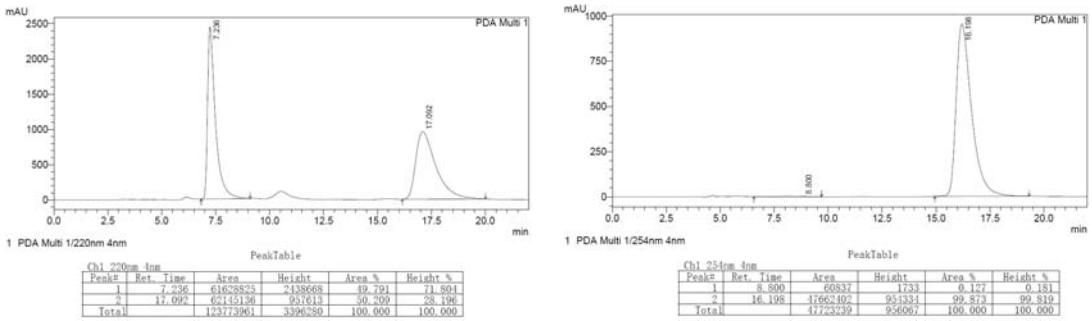
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.993	109405	3015	0.098	0.216
2	15.618	111313602	1390724	99.902	99.784
Total		111423007	1393738	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 15.62 min, de > 99 %.

3i



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.236	61628825	2138668	49.791	71.804
2	17.092	62145136	957613	50.209	28.196
Total		123773961	3396280	100.000	100.000

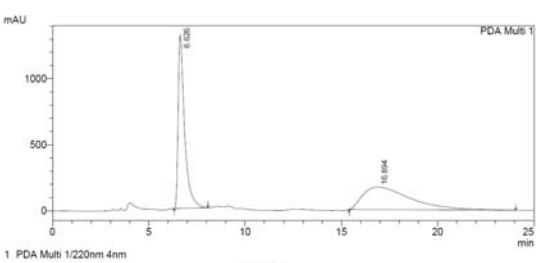
PeakTable

Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.800	60837	1733	0.127	0.181
2	16.198	47662402	953334	99.873	99.819
Total		47723239	956067	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 16.20 min, de > 99%.

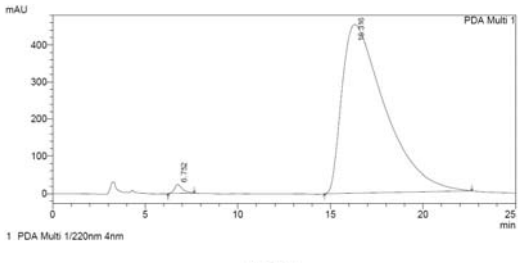
3j



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.626	30409702	1311387	50.724	88.427
2	16.894	29542129	171630	49.276	11.573
Total		59951831	1483017	100.000	100.000



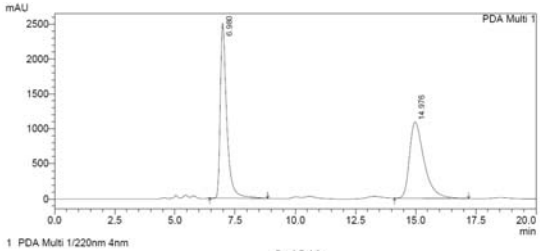
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.752	724501	21141	0.979	5.051
2	16.316	73300593	153849	99.021	94.949
Total		74025097	172990	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 6.75 min, t_{major} = 16.32 min, de = 98 %.

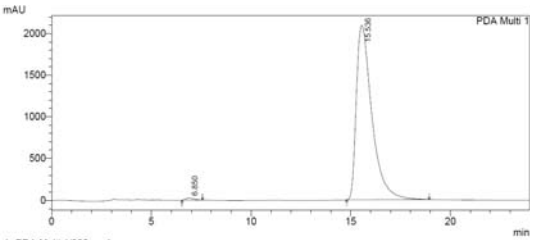
3k



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.980	46179555	2198763	50.419	69.718
2	14.976	45707885	1083785	49.581	30.282
Total		92187440	3582548	100.000	100.000



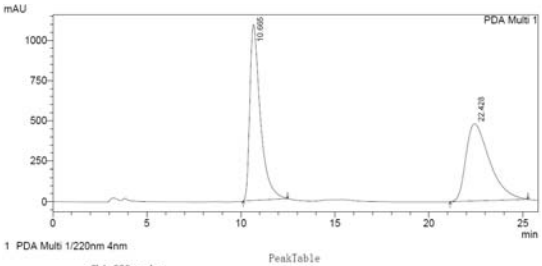
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.850	729999	25836	0.640	1.220
2	15.536	113334635	2092320	99.360	98.780
Total		114064634	2118155	100.000	100.000

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 6.85 min, t_{major} = 15.53 min, de = 98 %.

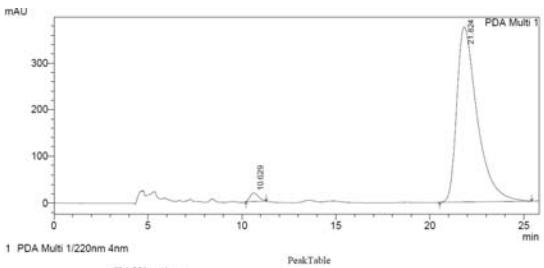
3l



PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.665	42431803	1090912	50.400	69.648
2	22.428	41757980	475115	49.600	30.352
Total		84189783	1566327	100.000	100.000



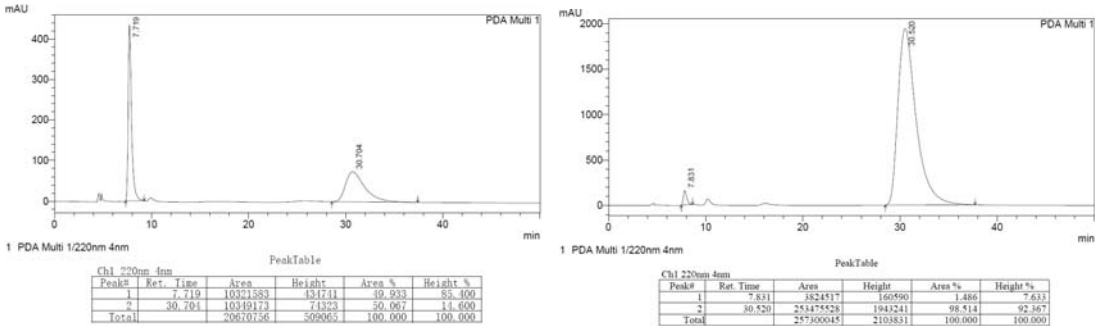
PeakTable

Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.629	565513	18139	1.958	4.607
2	21.824	28313940	375629	98.042	95.393
Total		28879453	393768	100.000	100.000

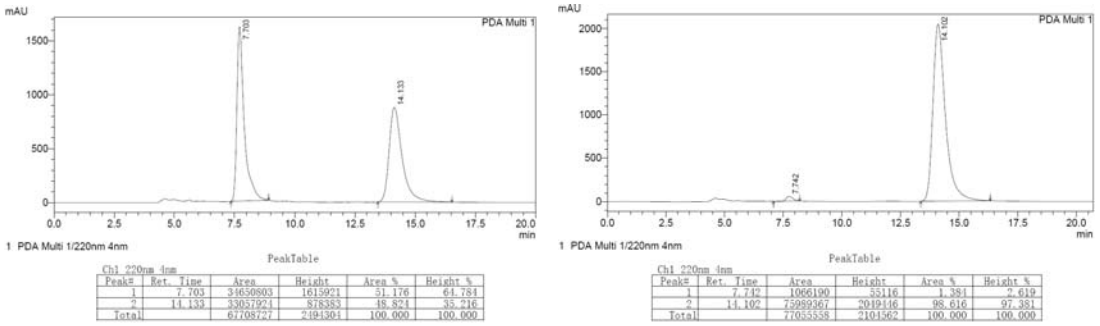
HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 10.63 min, t_{major} = 21.82 min, de = 96%.

3m



HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.83 min, t_{major} = 30.52 min, de = 97%.

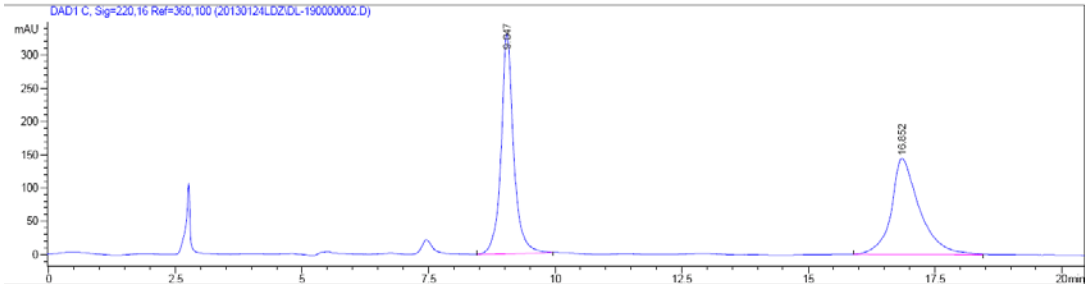
3n



HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.74 min, t_{major} = 14.10 min, de = 97%.

Analytical high performance liquid chromatography was carried out using the Model 410 automated sampler, using the Chirobiotic T column. The loading loop was 10 µL. The eluting employed was an isocratic mixture of methanol and water (60/40 or 80/20 respectively) at a flow of 1.0 mL/min unless stated. Retention times are reported in minutes. The enantiomeric excess was calculated from the integration of the absorption peaks at 220 nm.

rac-**4a**

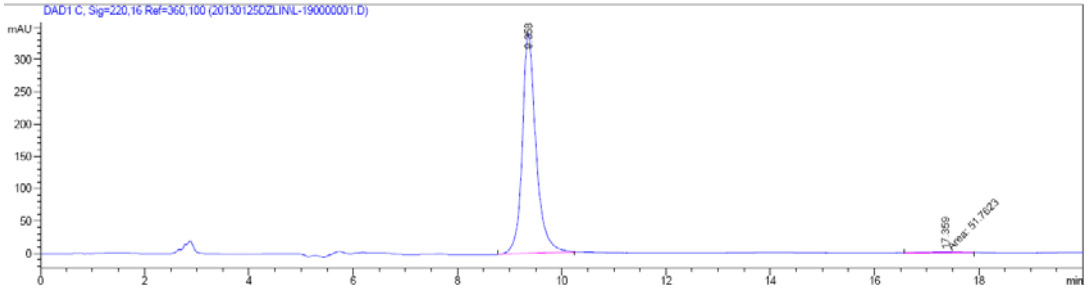


```
Signal 1: DAD1 C, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.047 BB    0.2533 5704.29053  330.60065  50.4806
   2  16.852 BB    0.5345 5595.66602  144.28442  49.5194

Totals :                 1.13000e4   474.88507
```

(*S*)-**4a**



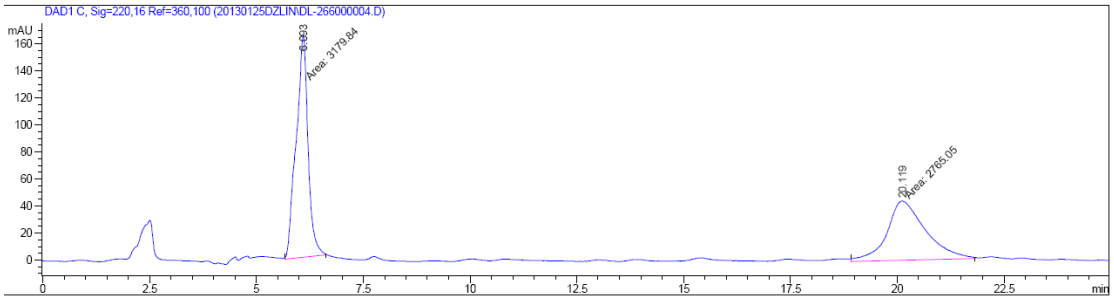

```
Signal 1: DAD1 C, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.358 BB    0.2734 6216.33008  339.80539  99.1742
   2  17.359 MM    0.9366   51.76229 9.21086e-1   0.8258

Totals :                 6268.09237  340.72648
```

HPLC (Chirobiotic T, methanol/water = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 9.36 min, t_{minor} =17.36 min, de = 98%.

rac-**4m**

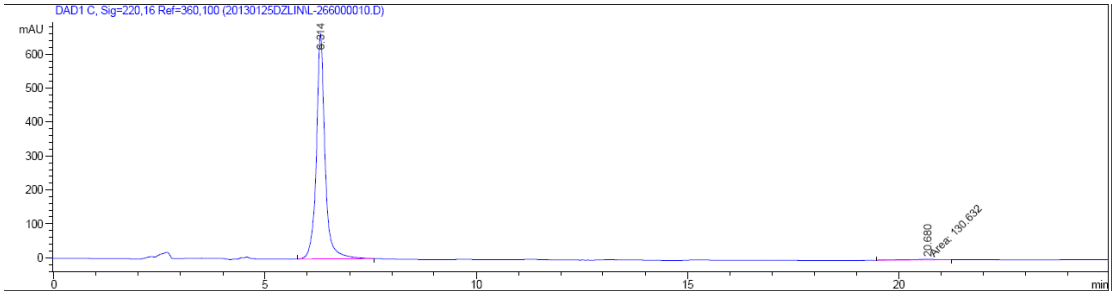



```
Signal 1: DAD1 C, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   6.093 MM    0.3221 3179.84351  164.54597  53.4887
   2  20.119 MM    1.0505 2765.04858   43.87062  46.5113

Totals :                 5944.89209  208.41660
```

(*S*)-**4m**



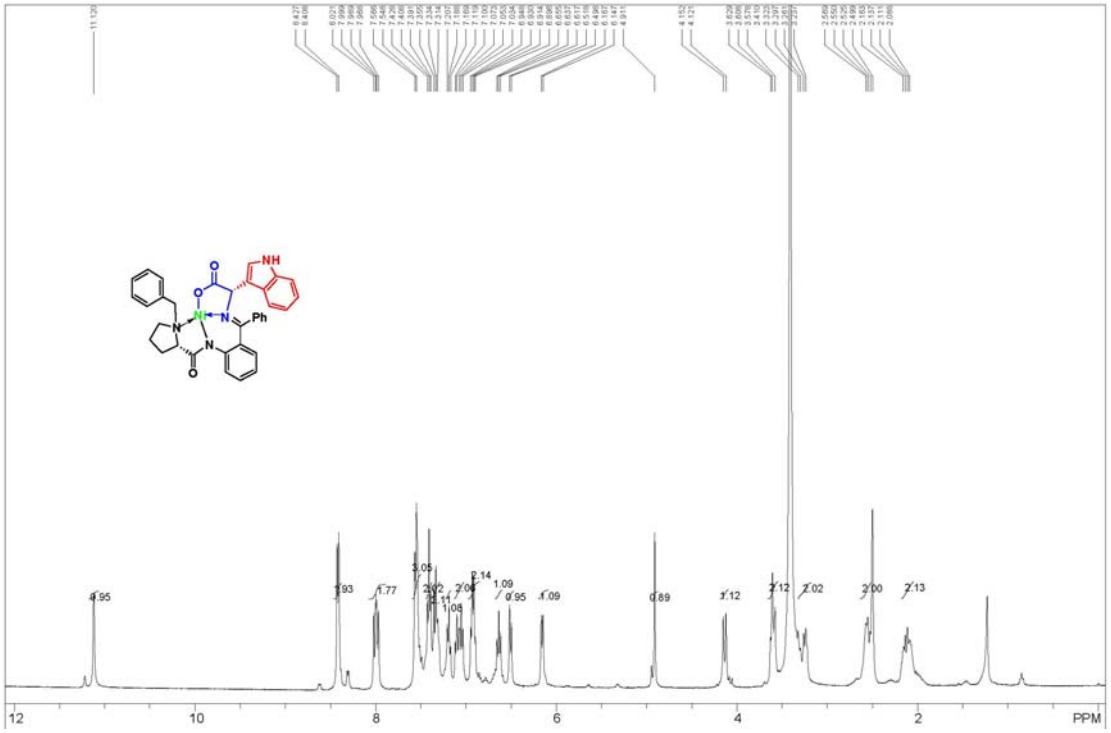
Signal 1: DAD1 C, Sig=220,16 Ref=360,100

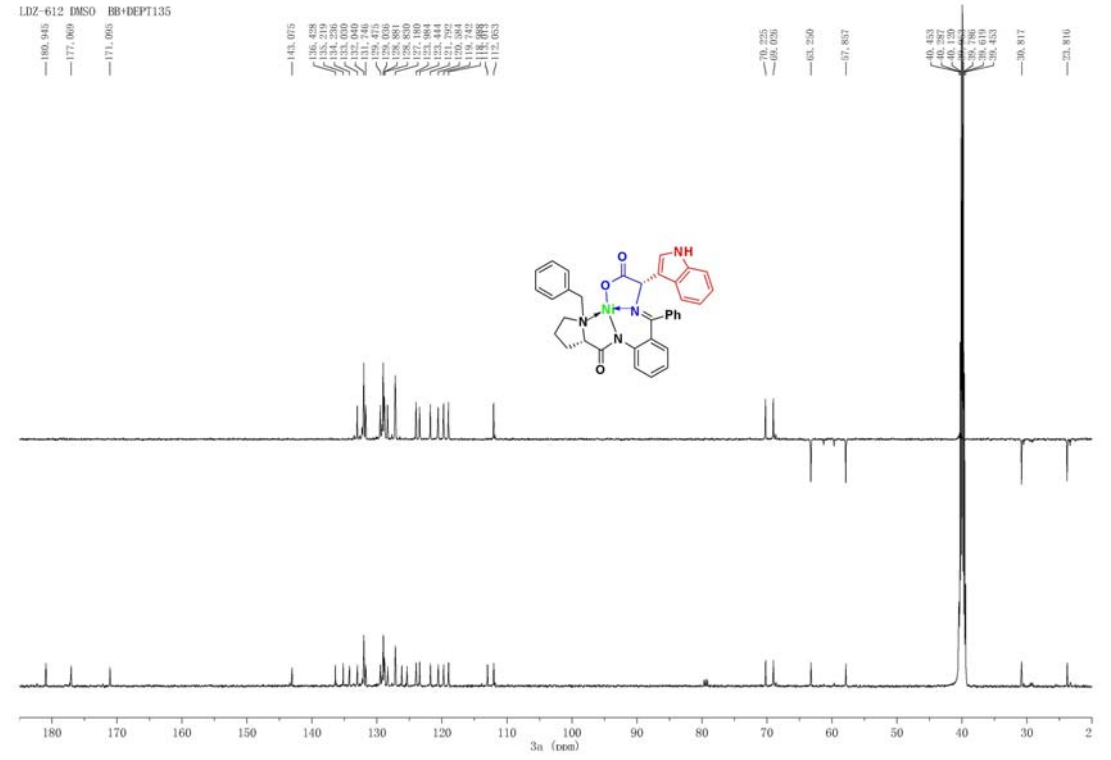
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.314	BB	0.2075	9506.65625	662.25110	98.6445
2	20.680	MM	1.4954	130.63235	1.45597	1.3555
Totals :				9637.28860	663.70707	

HPLC (Chirobiotic T, methanol/water = 80/20, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 6.31 min, t_{minor} =20.68 min, de = 97%.

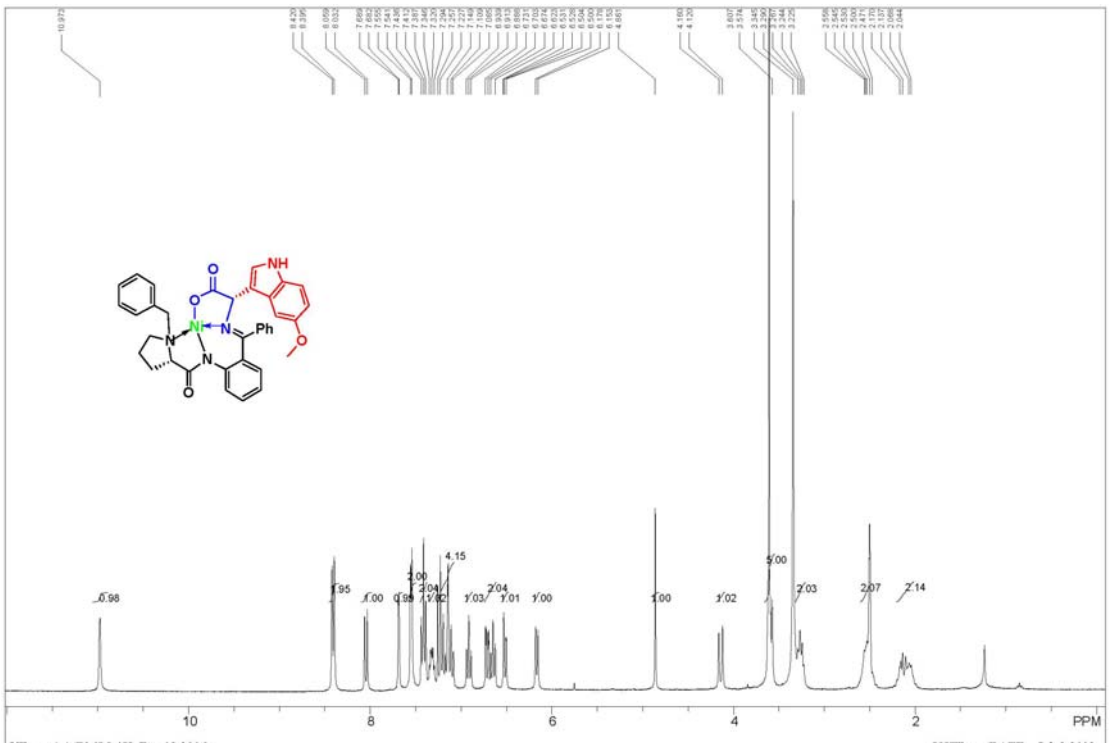
(G) Copies of ^{1}H NMR and ^{13}C NMR Spectra for the Products

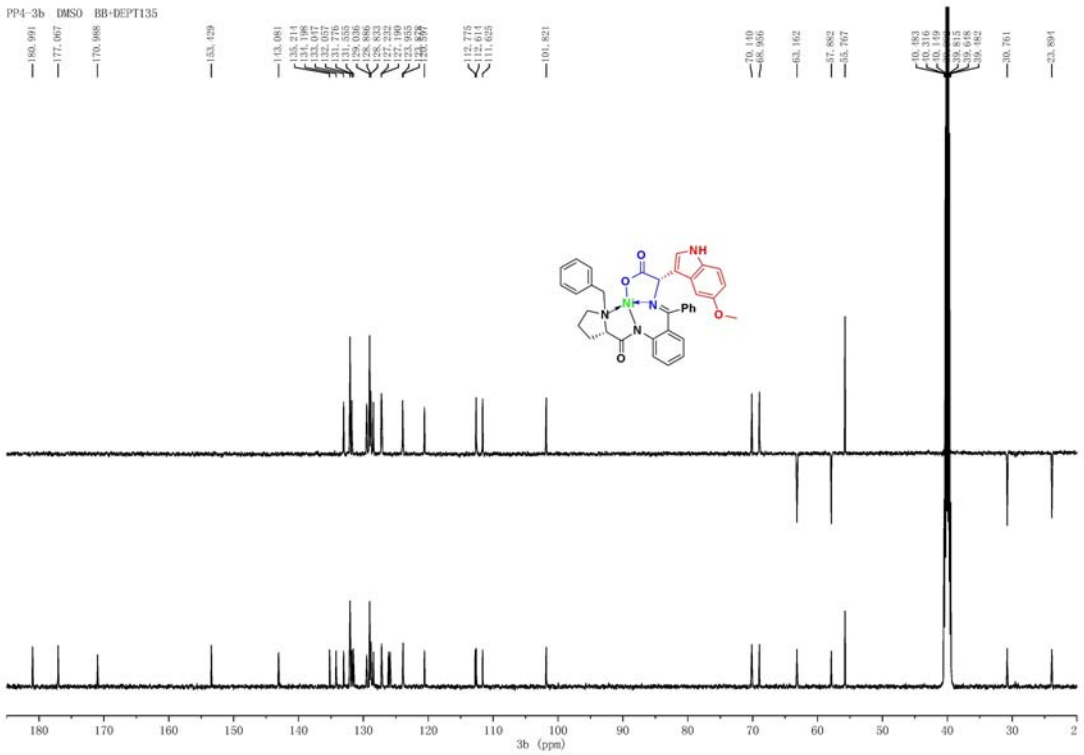
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(1H-indol-3-yl)acetic acid Schiff Base Complex 3a.



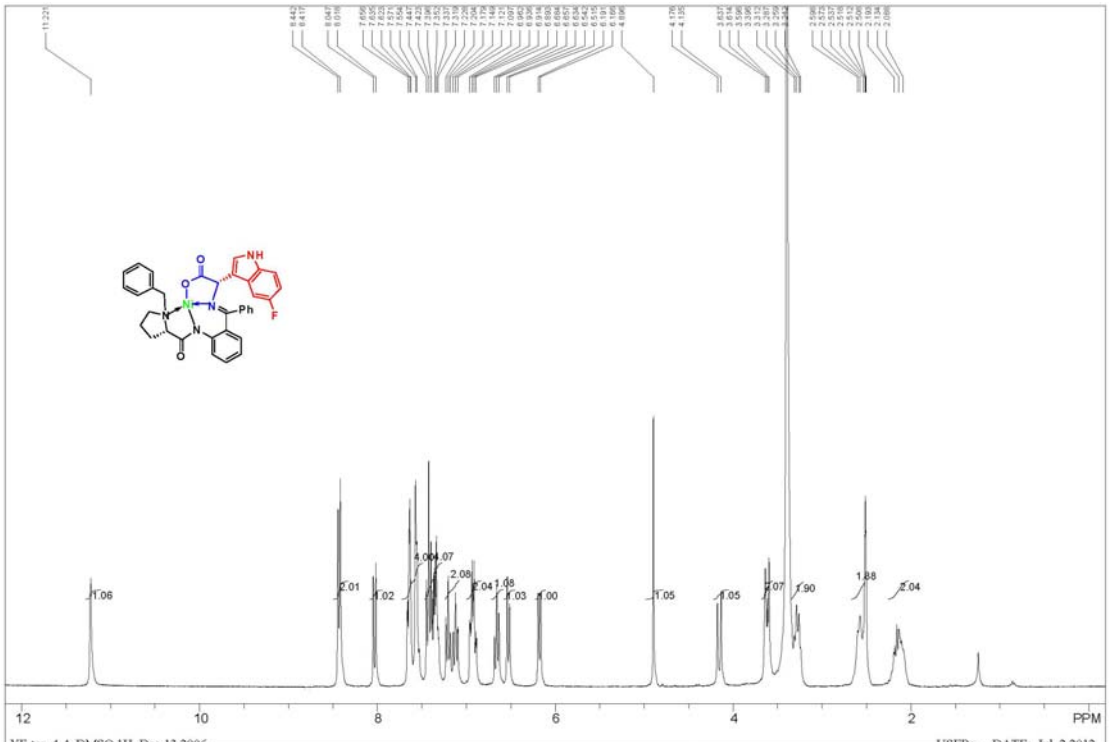


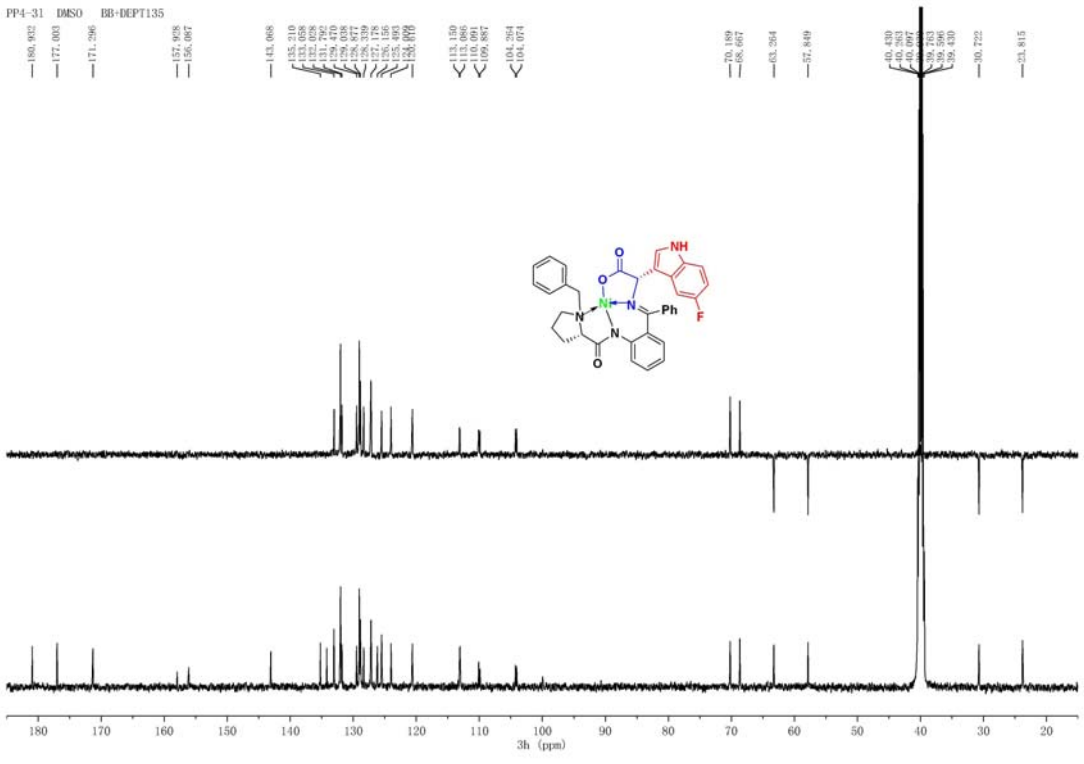
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-methoxy-1H-indol-3-yl)acetic acid Schiff Base Complex 3b.



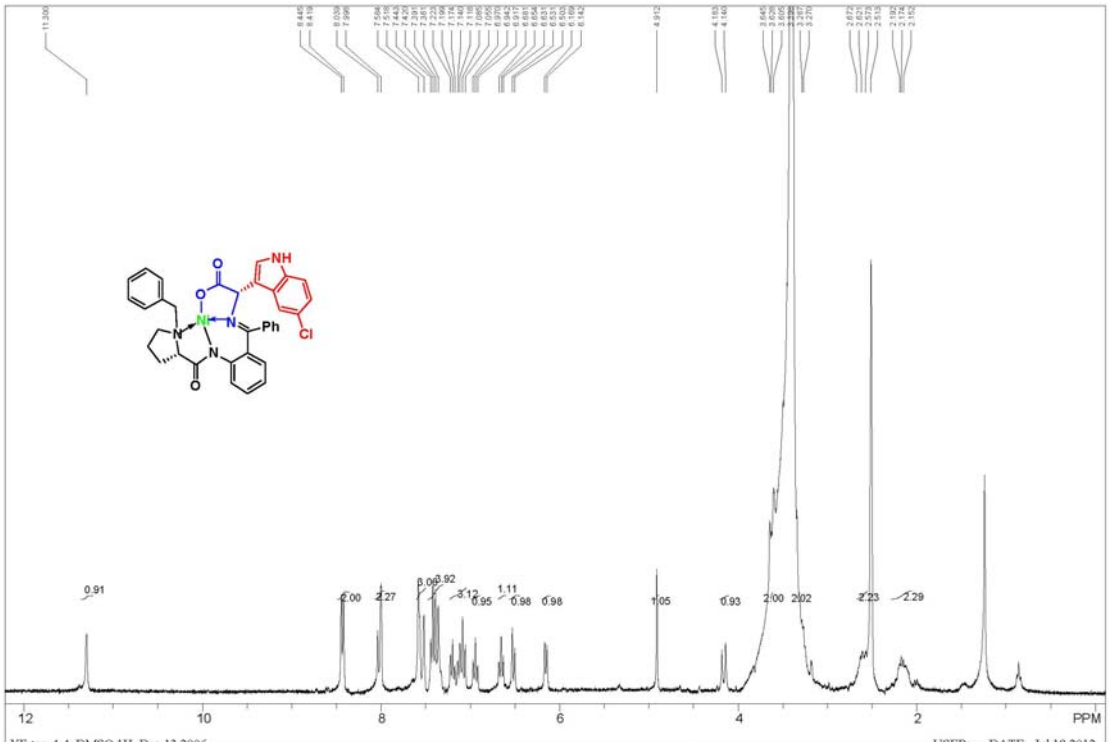


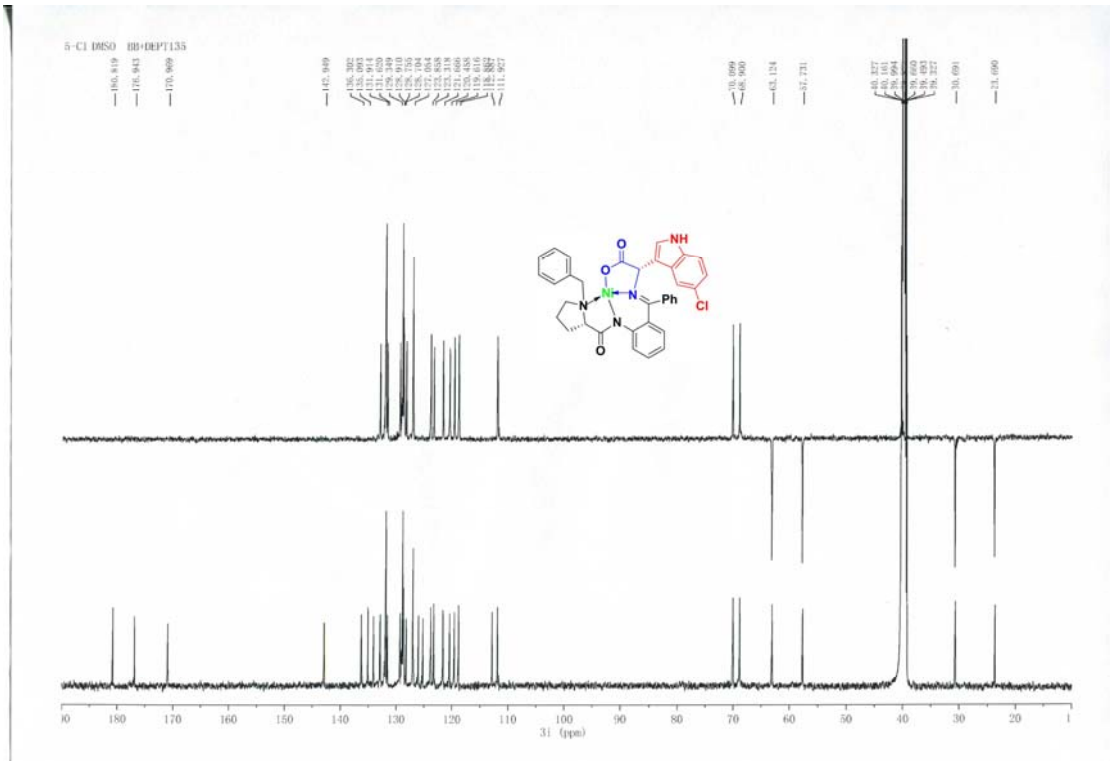
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-fluoro-1H-indol-3-yl)acetic acid Schiff Base Complex 3c.



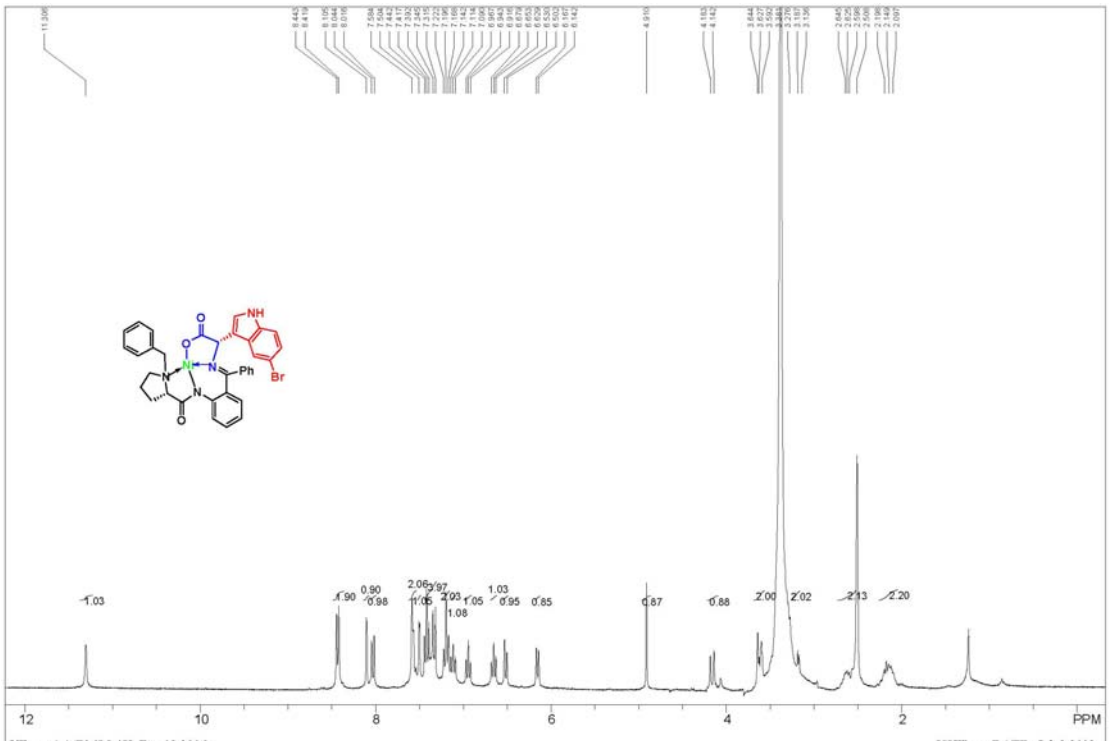


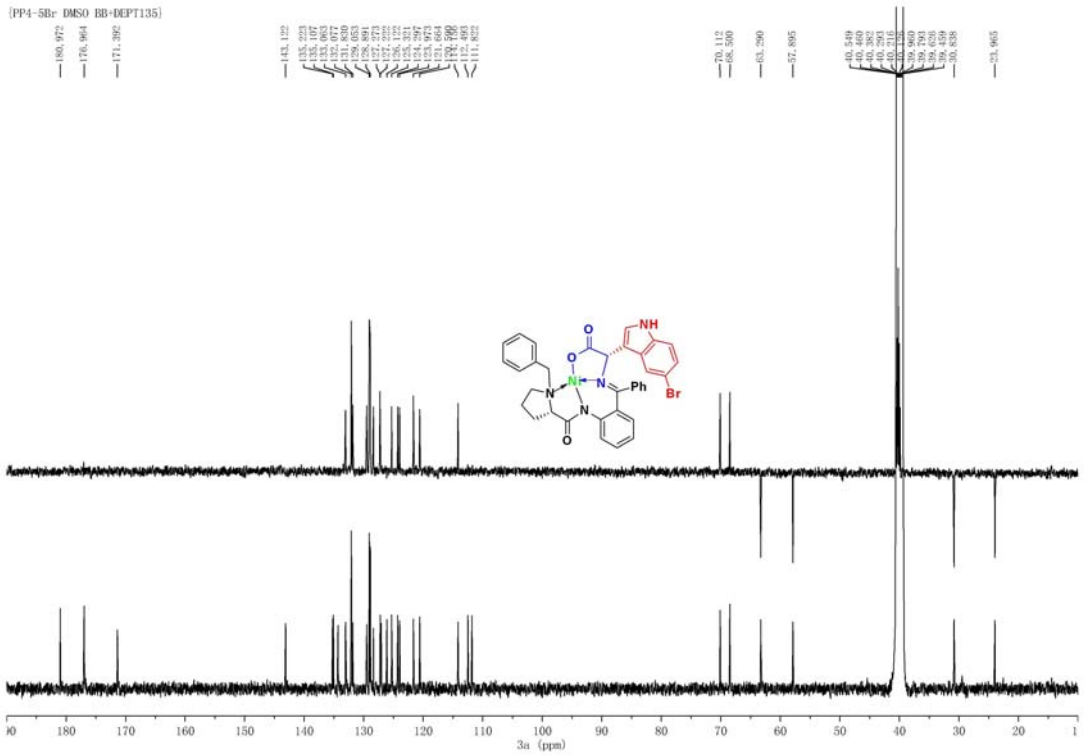
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-chloro-1H-indol-3-yl)acetic acid Schiff Base Complex 3d.



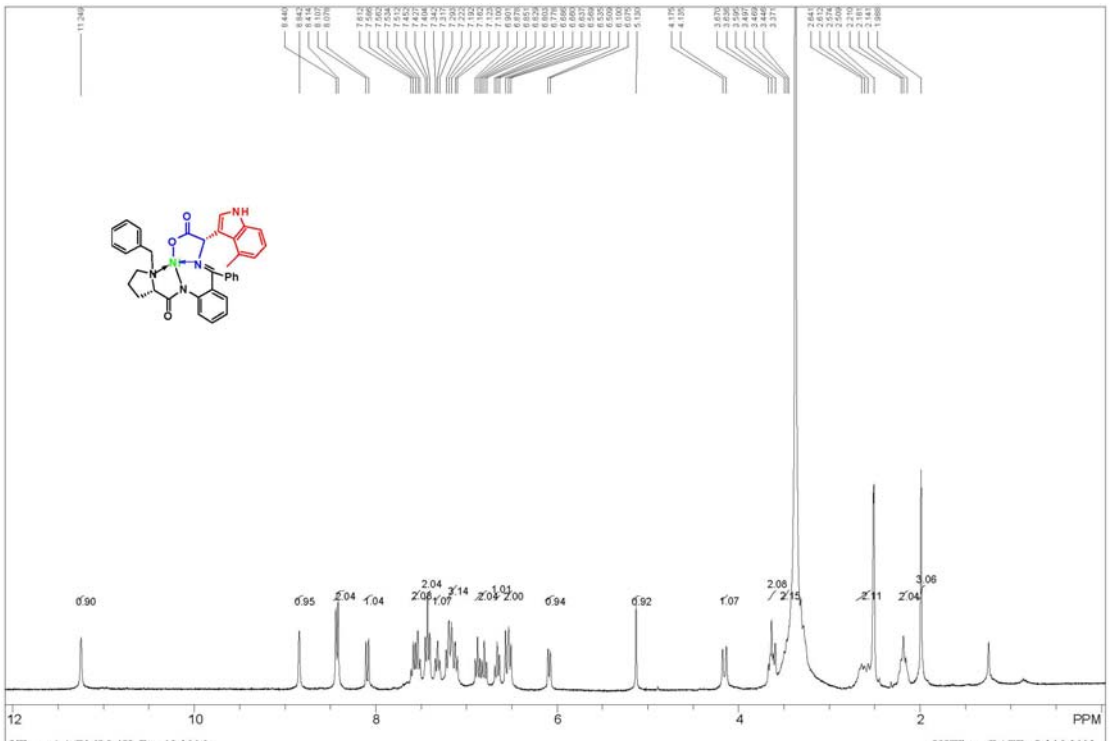


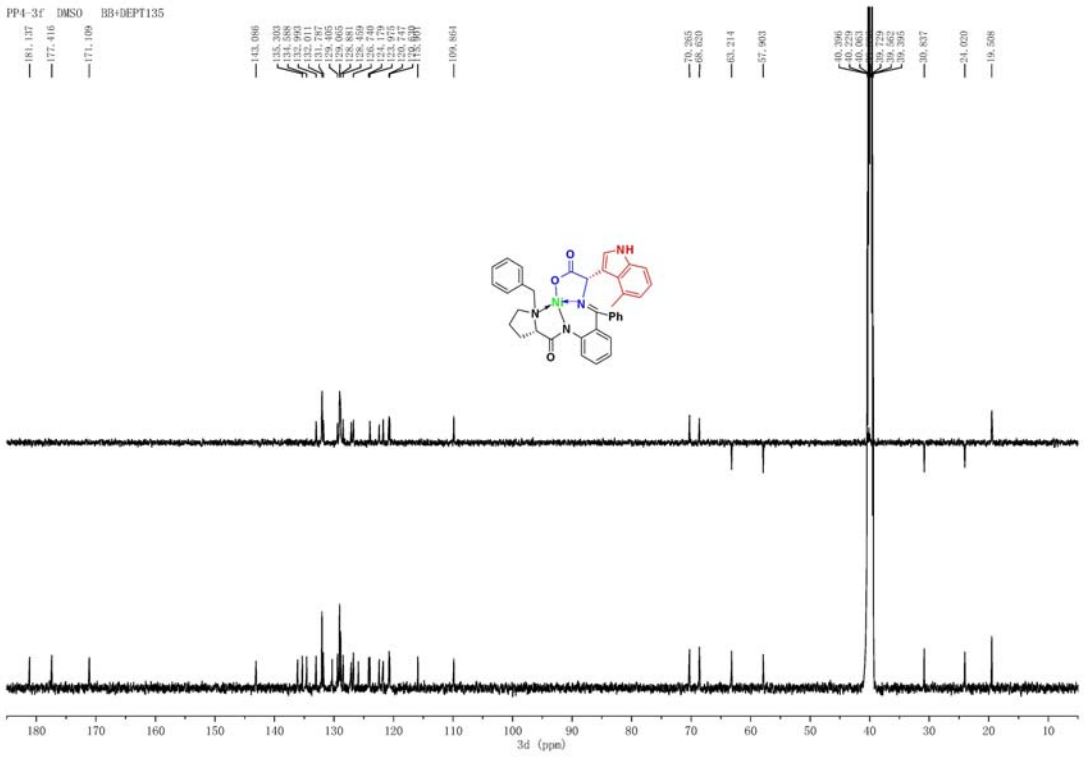
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-bromo-1H-indol-3-yl)acetic acid Schiff Base Complex 3e.



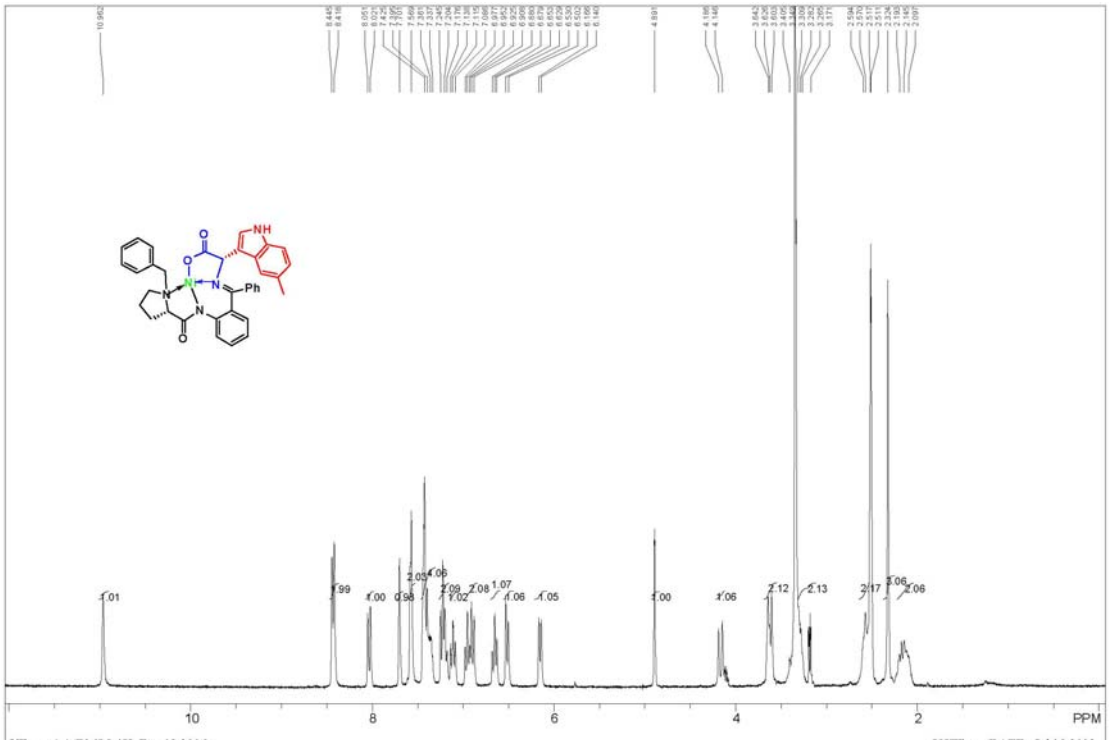


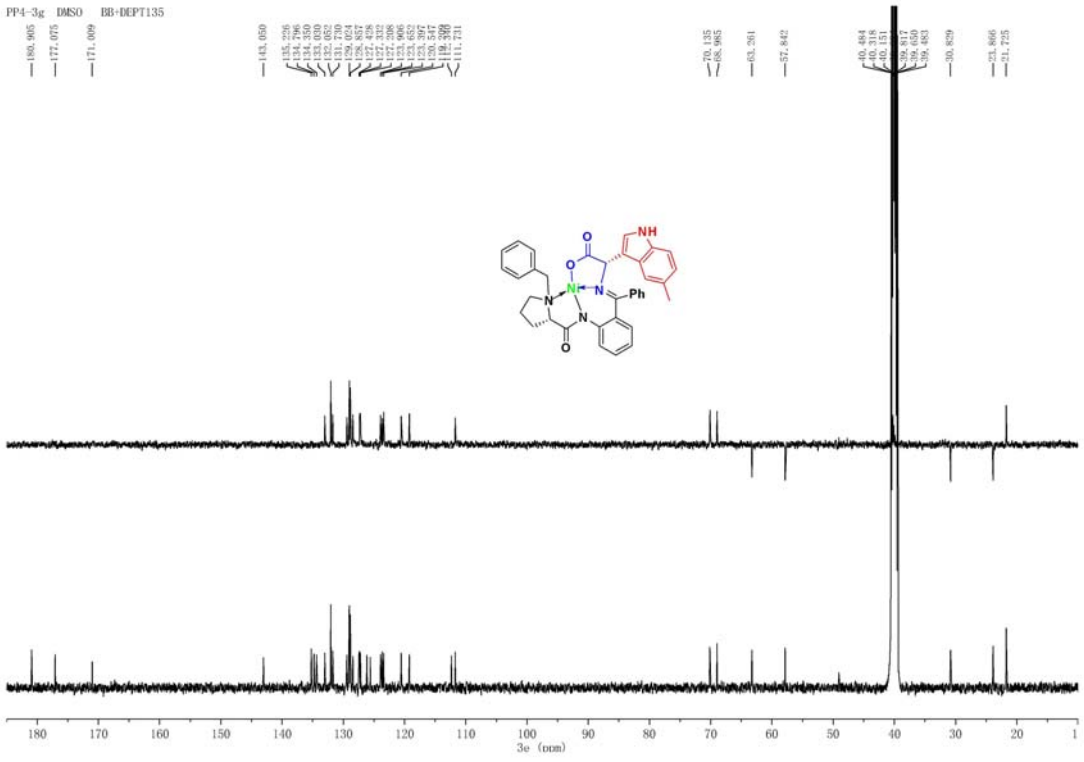
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(4-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3g.



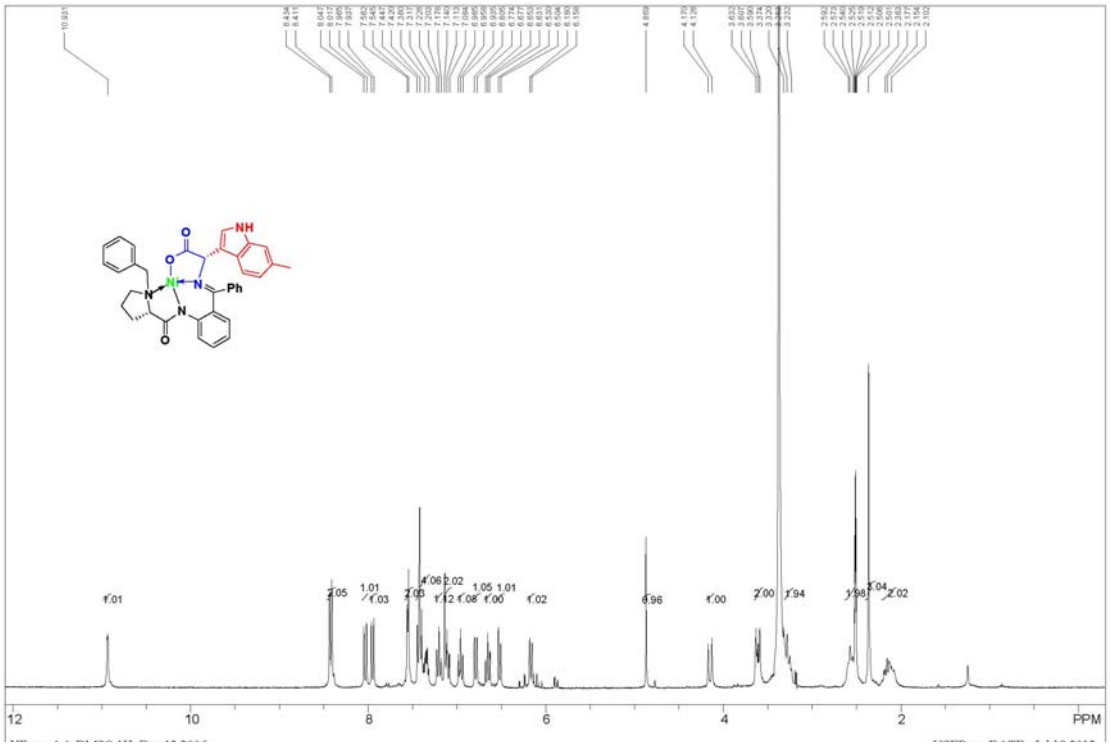


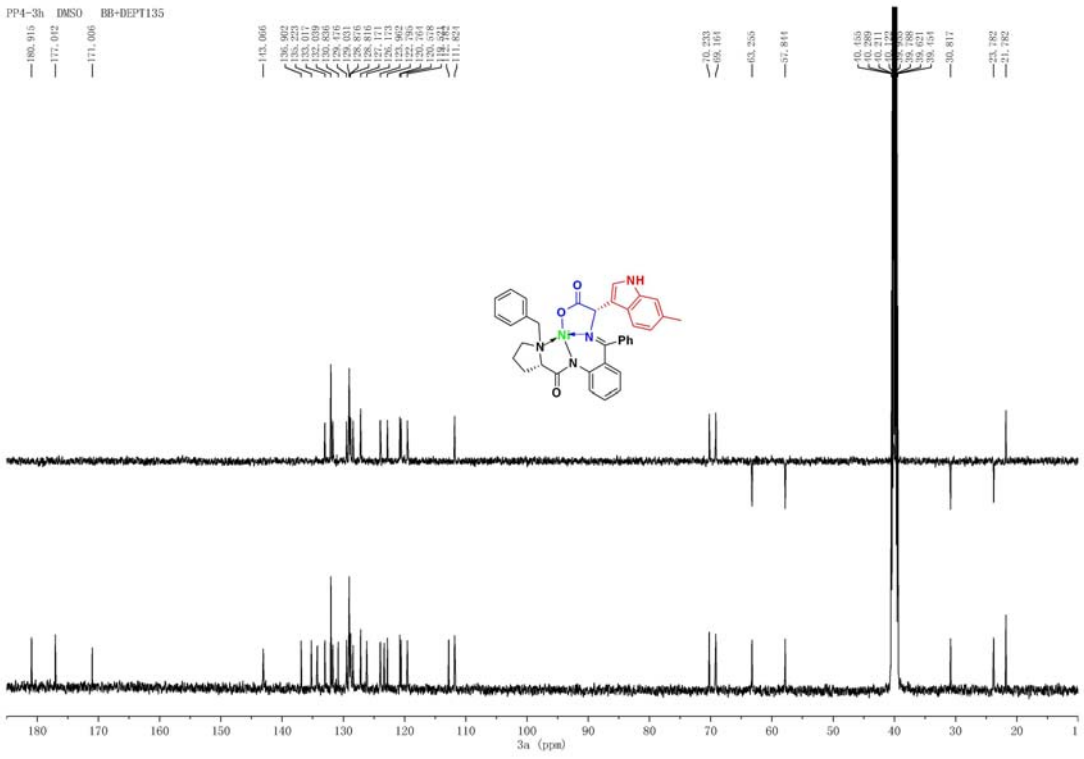
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3h.



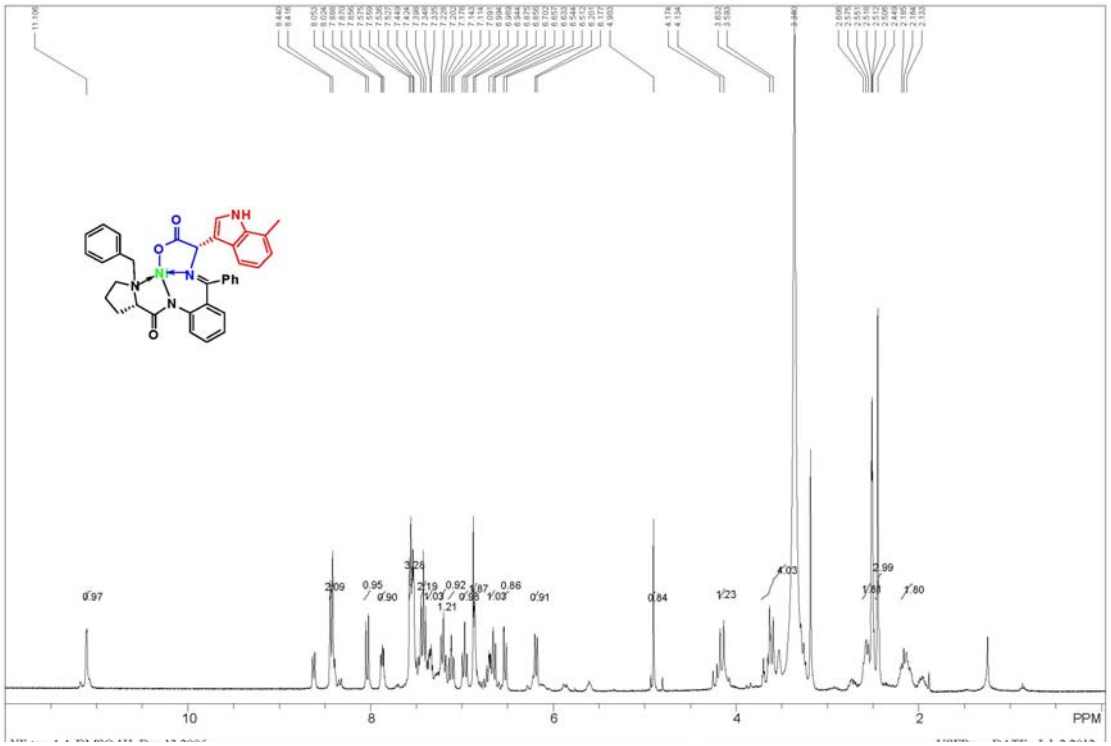


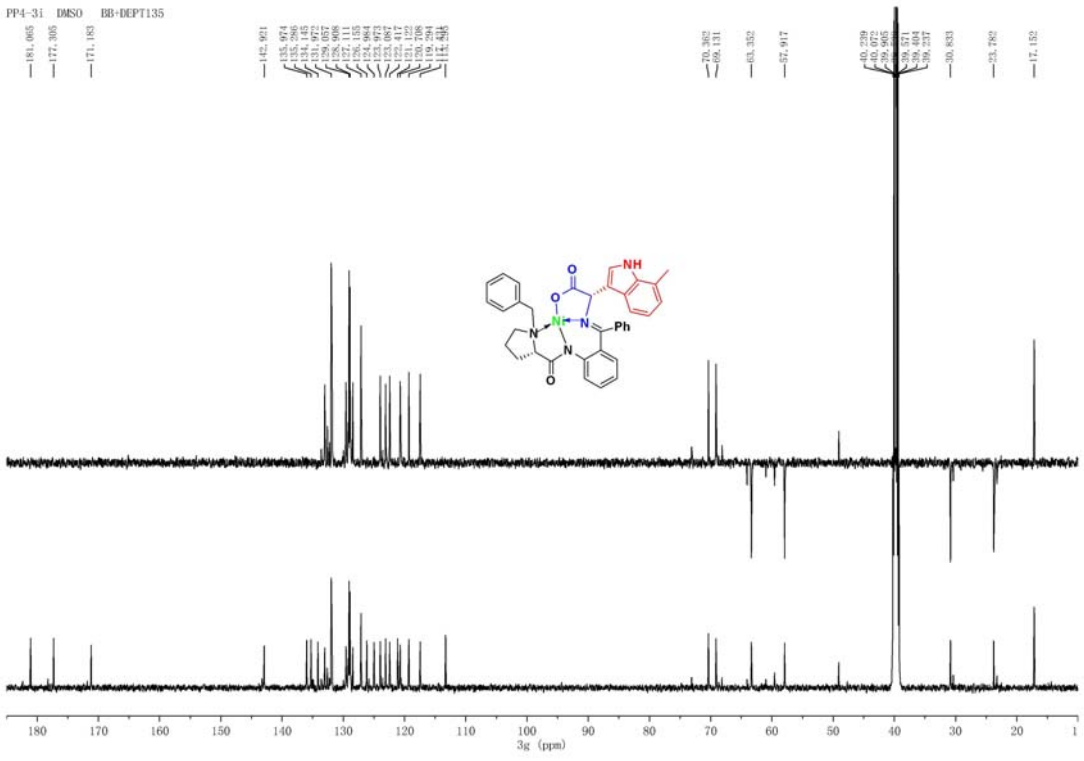
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(6-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3i.



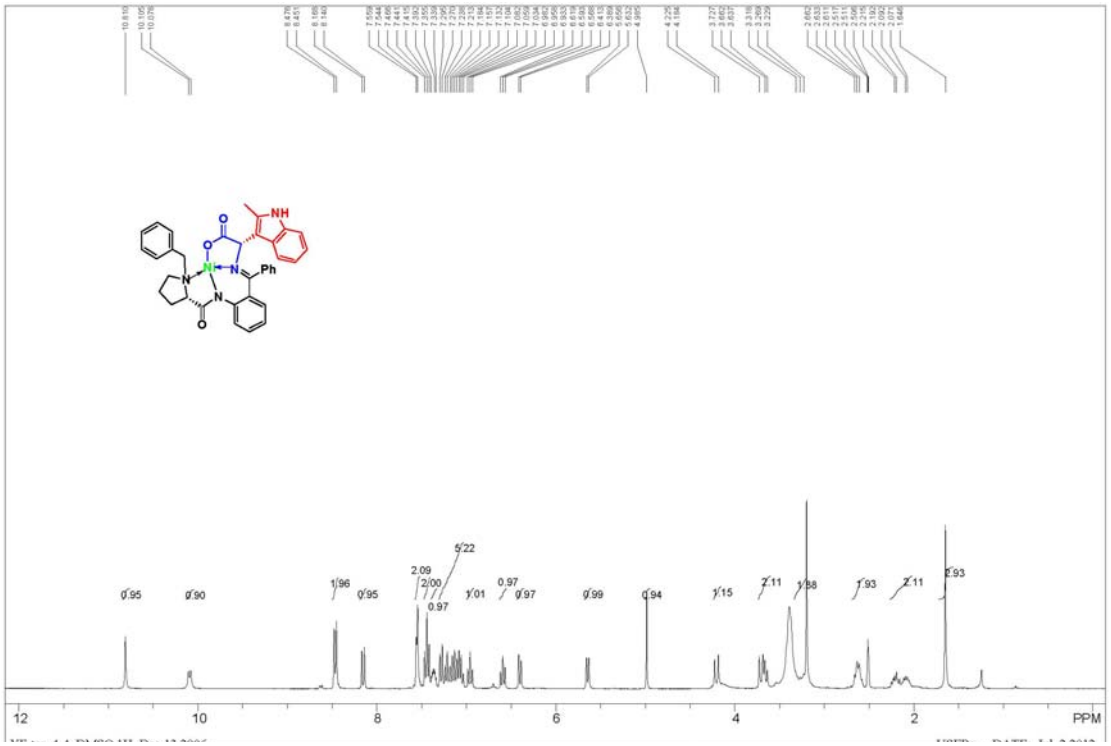


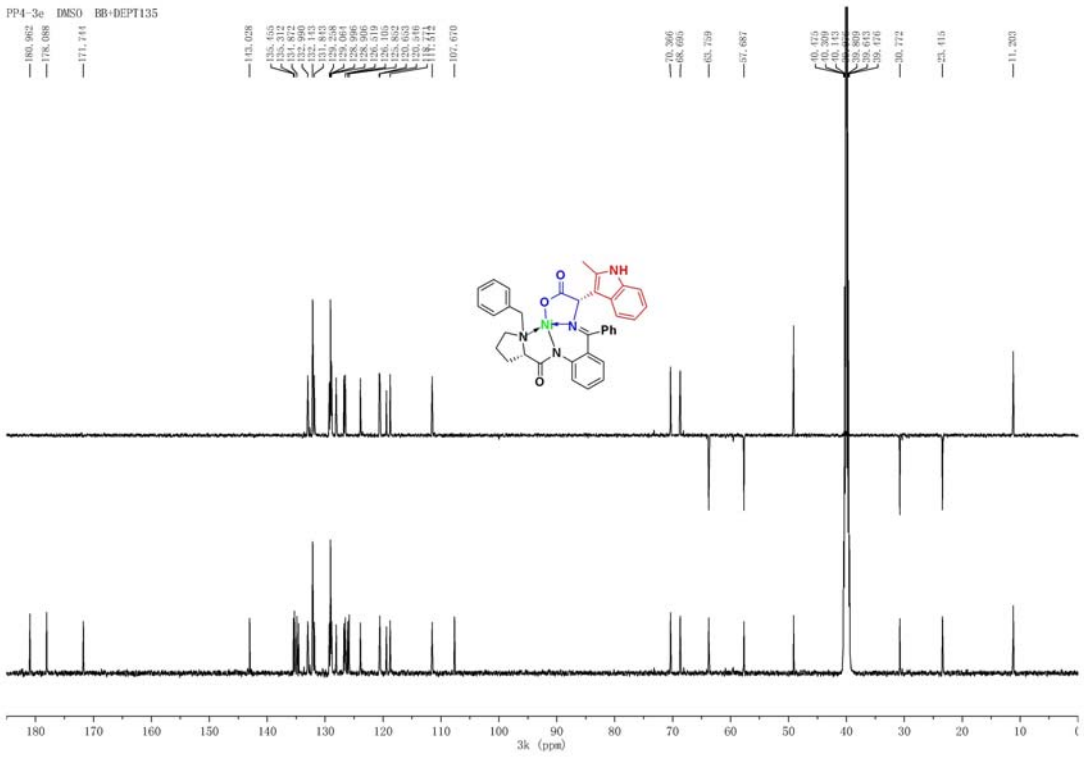
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(7-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3j.



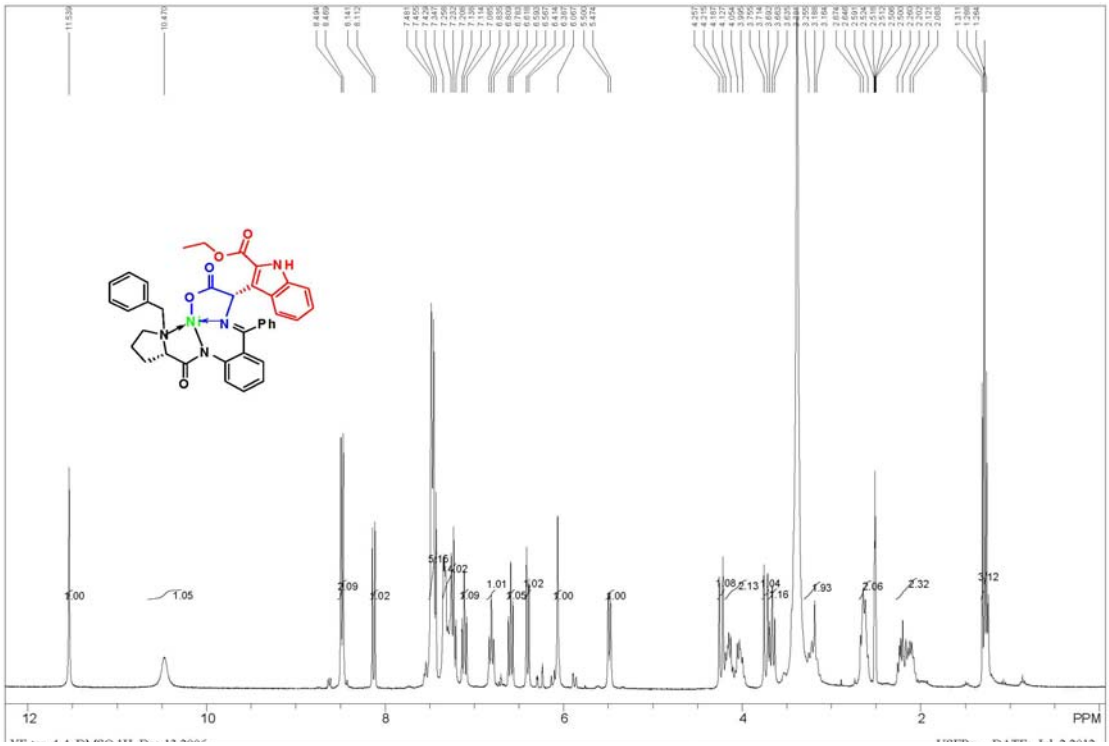


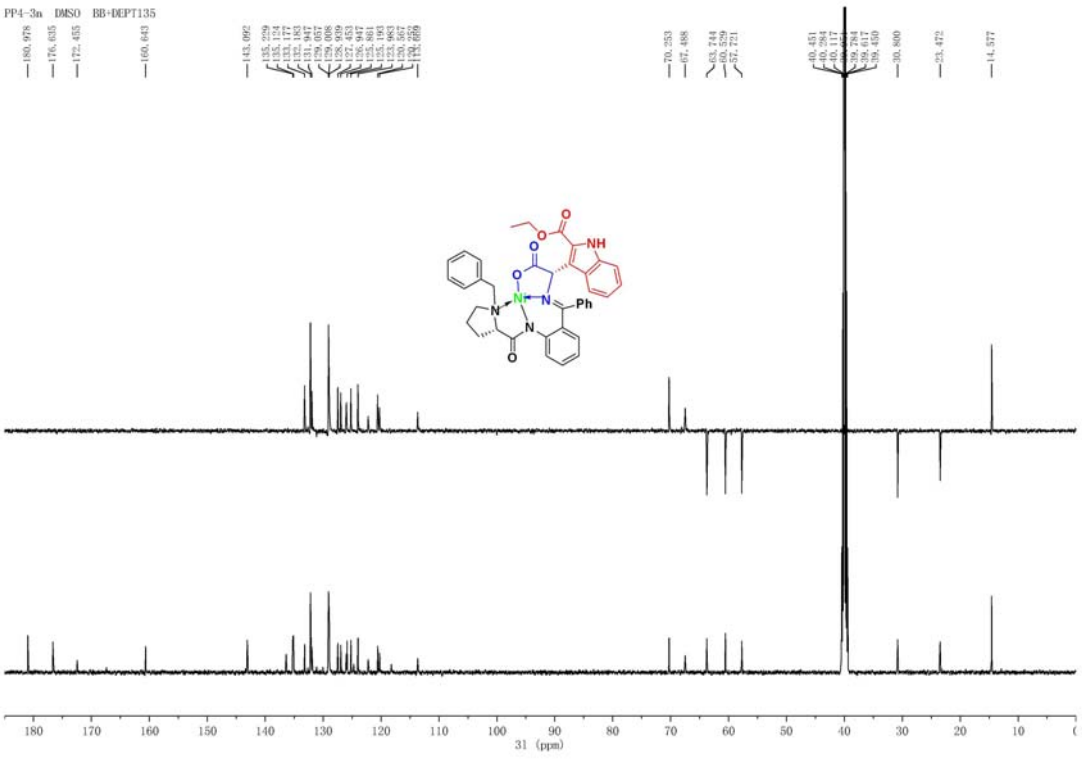
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(2-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3k.



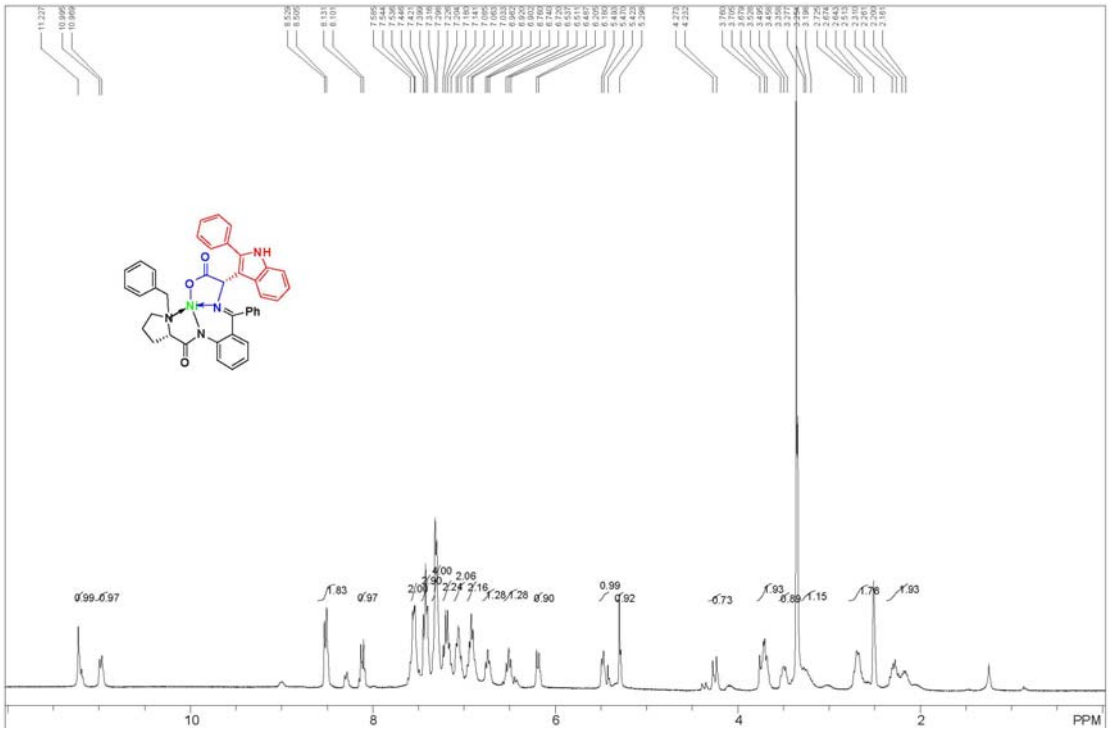


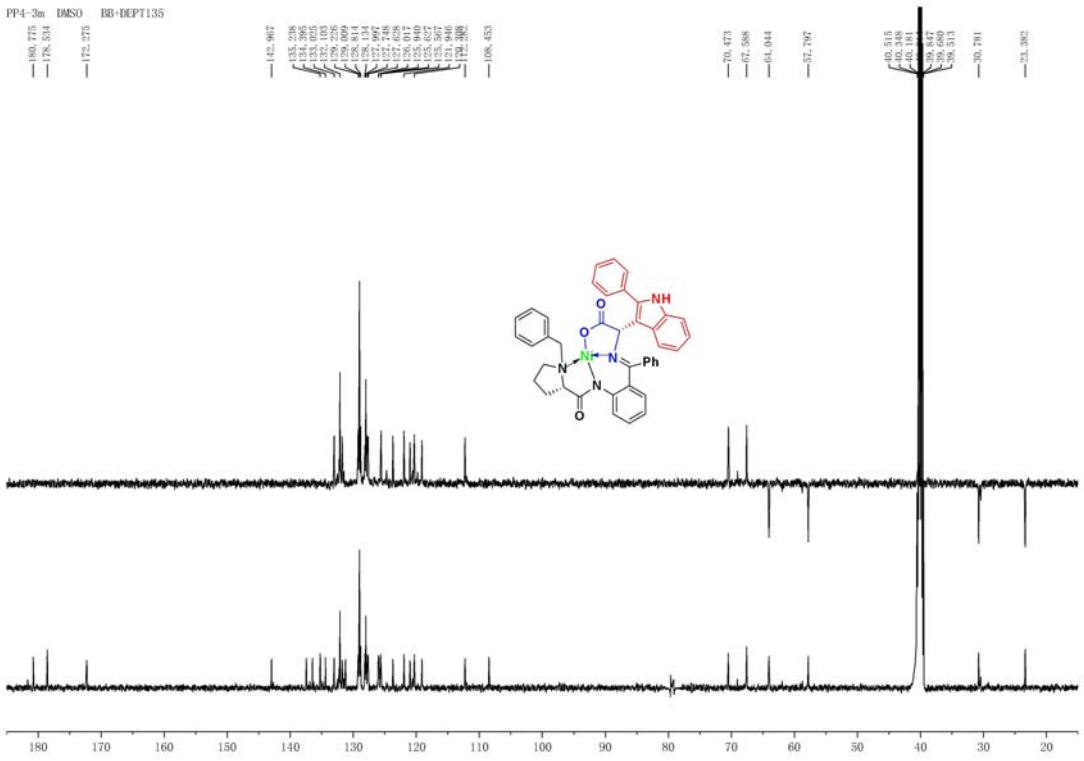
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(2-(ethoxycarbonyl)-1H-indol-3-yl)acetic acid Schiff Base Complex 3l.



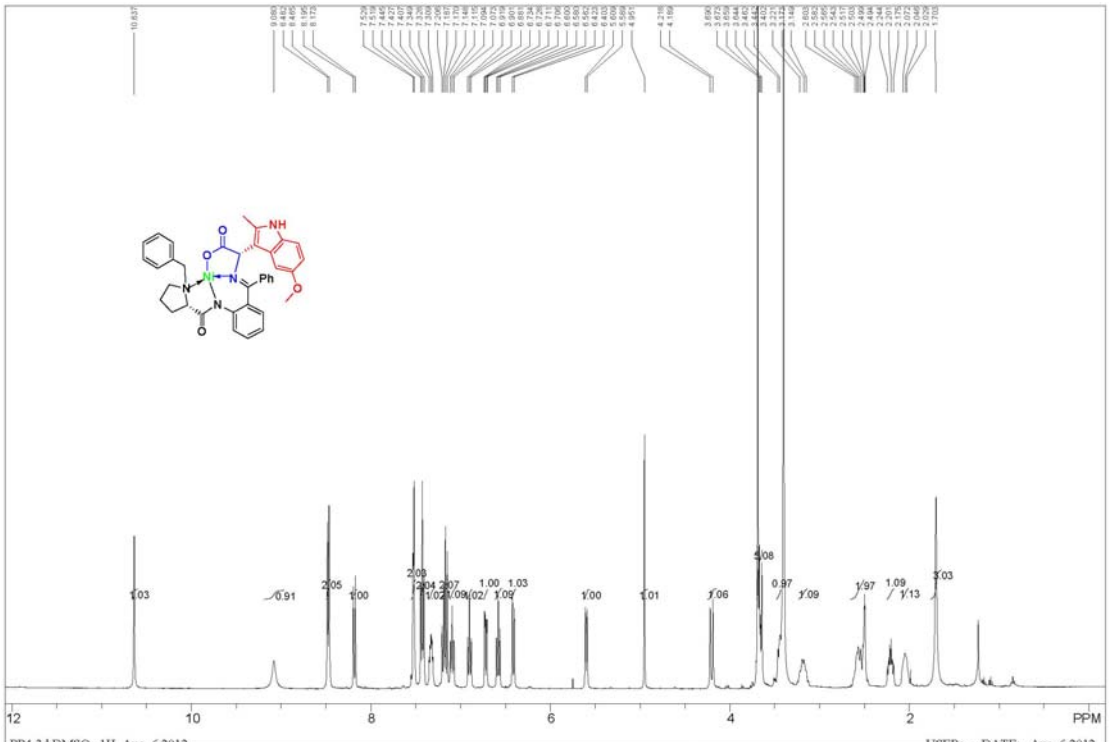


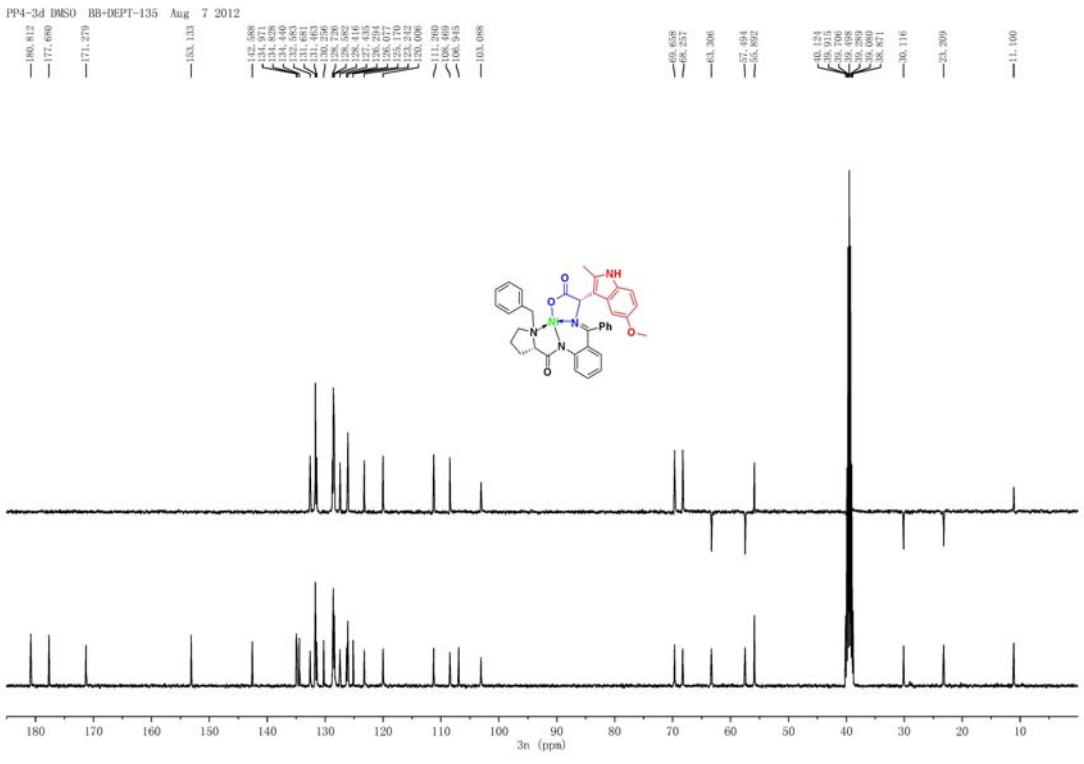
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(2-phenyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3m.



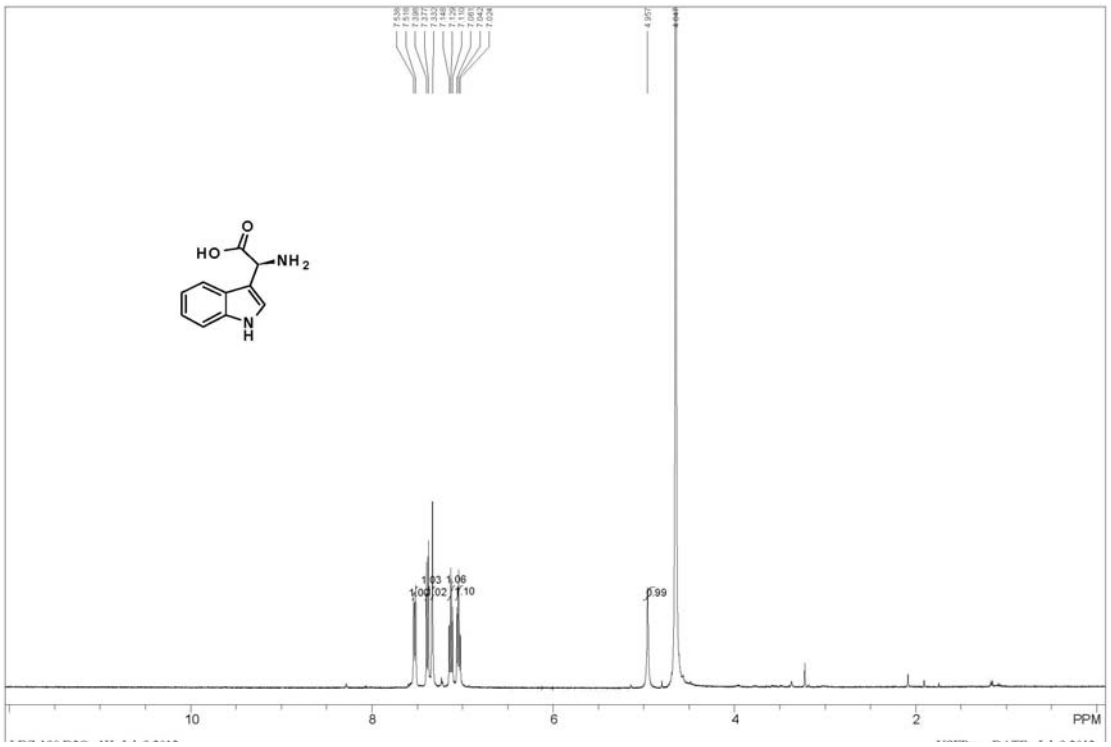


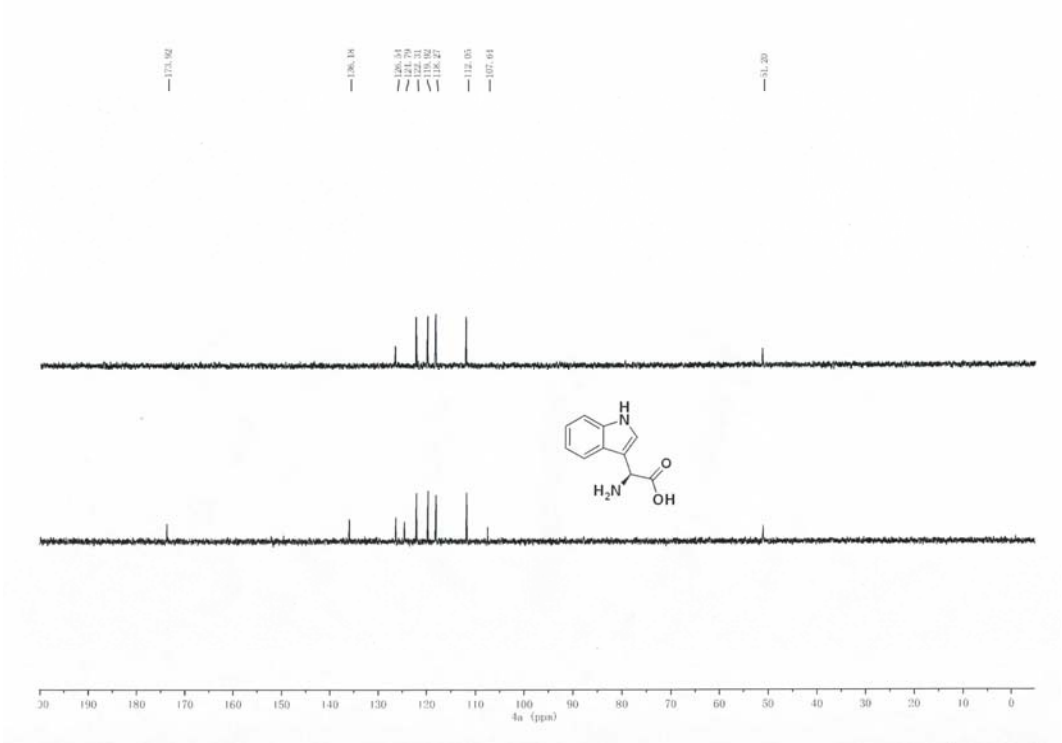
Nickel(II)-(*S*)-BPB/(*S*)-2-amino-2-(5-methoxy-2-methyl-1H-indol-3-yl)acetic acid Schiff Base Complex 3n.



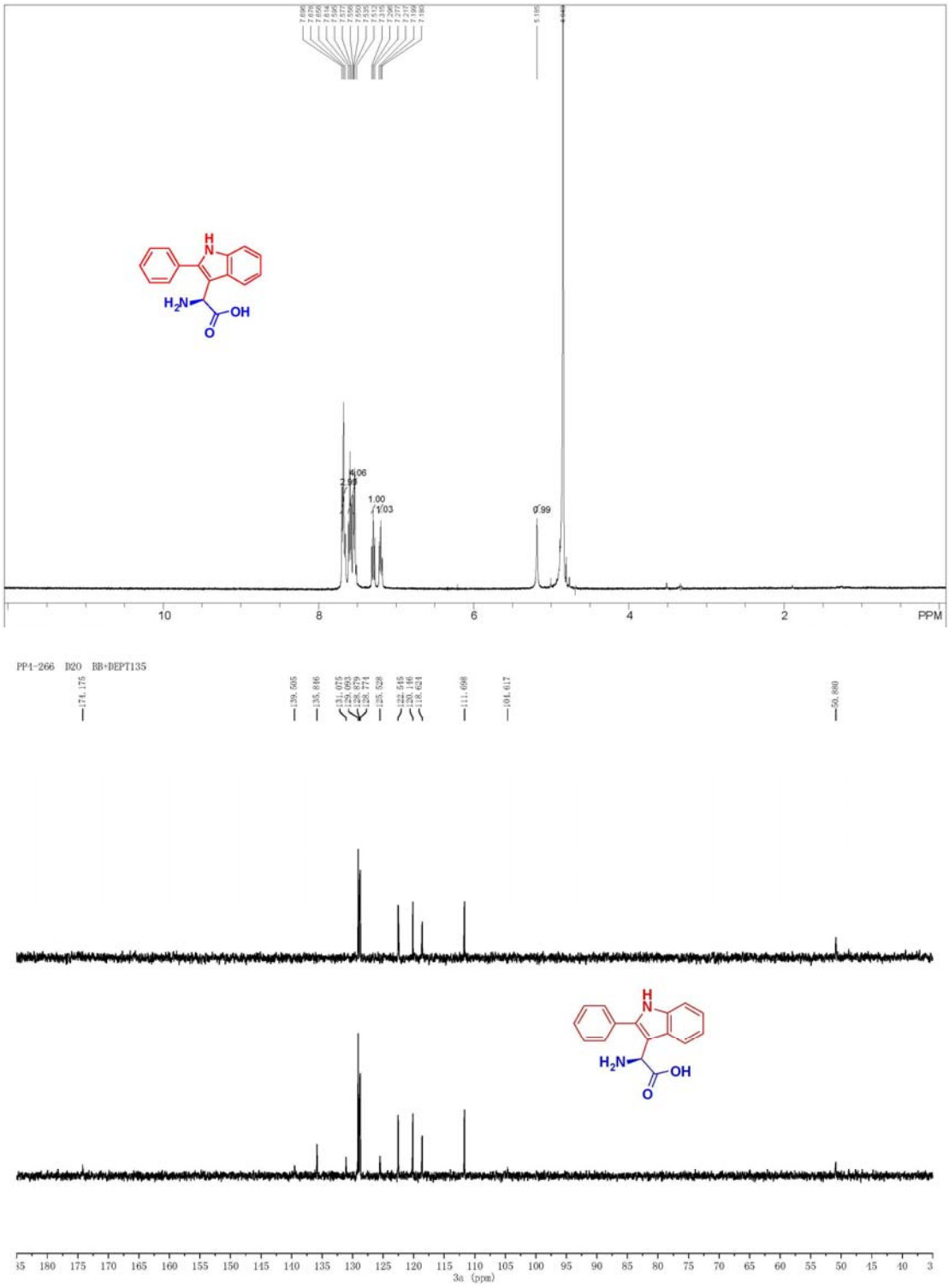


(S)-2-amino-2-(1H-indol-3-yl)acetic acid 4a.





(S)-2-amino-2-(2-phenyl-1H-indol-3-yl)acetic acid 4m.



(H) Reference

1 J. Wang, S. B. Zhou, D. Z. Lin, X. Ding, H. L. Jiang and H. Liu, *Chem. Commun.*, 2011, **47**, 8355