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Highly Diastereo- and Enantioselective Synthesis of *syn*-β-Substituted Tryptophans via the Reaction of a Chiral Equivalent of Nucleophilic Glycine and Sulfonylindoles

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(A) 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: $[\alpha]_D^{22}$ (c: g/100 mL, in solvent).

(B) General Procedure for the Asymmetric Reactions

General Procedure for the Synthesis of (*S*)(2*S*,3*R*)-3a. The nickel(II) complex of glycine (*S*)-**1** (100 mg, 0.201 mmol) was dissolved in dichloromethane (10 mL). Sulfonylindole derived from benzaldehyde **2a** [1](76 mg, 0.211 mmol) and DBU (37 μL, 0.241 mmol) were added at ambient temperature. The reaction mixture was stirred 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*,3*R*)-**3a** as a red solid.

Procedure for the Synthesis of (2*S*,3*R*)-4a: The crystallized complex (*S*)(2*S*,3*R*)-**3a** (1 g, 1.42 mmol) was decomposed by refluxing a suspension in a mixture of aqueous 6 N HCl (1 mL) and MeOH (15 mL) for 30 min, until the red color of the solution disappeared, as described previously. The reaction was cooled to room temperature and then 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 (2*S*,3*R*)-**4a** (398 mg, 96%). The ligand BPB that decomposed from

(*S*)(2*S*,3*R*)-**3a** was recovered by MeOH eluent (608 mg, 96%), and the column chromatography was washed with 100 mL of MeOH for further use.

Procedure for the synthesis of (*S*)-1. [2]

(*S*)-BPB (1 g, 2.60 mmol), Gly (976 mg, 13.0 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (1.52 g, 5.21 mmol), MeOH (50 mL) was added as solvent. And NaH (55-65% in oil, 1.04 g, 26 mmol), KOH (437 mg, 7.81 mmol) were added successively. The resulting mixture was refluxed for 2 h and then the reaction was terminated and cooled. The solution was neutralized with acetic acid. After 12 h the separated crystalline solid was filtered and washed with 100 mL of ethanol, followed by stirring in methane/water (v/v) 1:2, 200 mL), then filtered to form a red crystal (1.27 g, yield 98%). The complex was sufficiently pure for further use without additional purification.

(C) Analytical Characterization Data of Products

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3a.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 82%. Mp 183-185 ºC; $[\alpha]^{24}_{D}$ = +1792 (c = 0.25 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.34 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 9.3 Hz, 3H), 7.62 (d, J = 2.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.45-7.29 (m, 6H), 7.26-7.19 (m, 4H), 7.15-7.02 (m, 2H), 6.99-6.92 (m, 1H), 6.87-6.80 (m, 2H), 6.71-6.64 (m, 2H), 4.76 (d, J = 2.7 Hz, 1H), 4.44 (d, J = 2.7 Hz, 1H), 4.25 (d, J = 12.6 Hz, 1H), 3.49-3.40 (m, 2H), 2.80-2.76 (m, 1H), 2.40-2.31 (m, 2H), 2.01-1.87 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.6, 171.6, 143.0, 140.8, 135.5, 134.2, 133.8, 133.3, 132.5, 131.6, 130.4, 129.3, 128.9, 128.8, 128.7, 127.8, 127.4, 126.7, 126.5, 126.1, 123.8, 123.1, 121.4, 120.5, 118.6, 115.2, 110.7, 96.6, 74.7, 70.6, 63.7, 57.5, 49.8, 30.9, 23.2 ppm. LRMS (ESI) $[M+H]^+$ found m/z 703. HRMS (ESI) $[M+Na]^+$ found m/z 725.2045, calcd for $C_{42}H_{36}N_4NiO_3Na$ 725.2039. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.6 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-*o*-tolyl-propanoic Acid Schiff Base Complex 3b.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl

acetate = 1/1), yield 88%. Mp 174-176 ºC; $[\alpha]^{21}_{D}$ = +1017 (c = 0.18 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 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 ($CDCl_3$, 100 MHz) δ 180.5, 180.4, 170.3, 141.9, 133.4, 133.3, 132.0, 131.5, 129.7, 128.9, 127.4, 127.1, 126.4, 123.8, 120.8, 70.2, 66.5, 63.0, 57.2, 30.7, 24.1, 21.8 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2179, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.5 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-*m*-tolyl-propanoic Acid Schiff Base Complex 3c.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 89%. Mp 177-179ºC; $[\alpha]^{20}_{D}$ = +1979 (c = 0.14 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.46 (s, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 7.2 Hz, 2H), 7.35-7.29 (m, 1H), 7.24-7.20 (m, 2H), 7.15-7.01 (m, 2H), 7.15-7.01 (m, 11H), 6.66-6.57 (m, 3H), 4.90 (d, J = 1.2 Hz, 1H), 4.79 (d, J = 3.6 Hz, 1H), 4.22-4.09 (m, 2H), 3.49 (s, 3H), 3.38-3.34 (m, 1H), 3.26-3.20 (m, 1H), 2.76-2.71 (m, 1H), 2.04 (s, 2H), 1.89-1.84 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 181.4, 177.3, 171.6, 142.5, 134.6, 133.3, 133.2, 132.2, 131.7, 129.7, 129.6, 129.3, 129.1,

128.9, 126.2, 125.6, 125.2, 124.2, 120.8, 69.9, 63.1, 61.3, 57.5, 30.7, 23.7 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2192, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 12.2 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-*p*-tolyl-propanoic Acid Schiff Base Complex 3d.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 87%. Mp 171-173 ºC; $[\alpha]^{20}_D$ = +1467 (c = 0.12 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (s, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.03 (d, J = 7.2 Hz, 2H), 7.35-7.29 (m, 2H), 7.24-7.20 (m, 5H), 7.15-7.01 (m, 8H), 6.84 (d, J = 7.1 Hz, 1H), 6.66-6.57 (m, 2H), 6.15 (d, J = 7.6 Hz, 1H), 5.53 (d, J = 8.8 Hz, 1H), 4.70 (d, J = 4.4 Hz, 1H), 4.27 (d, J = 12.8 Hz, 1H), 3.40 (d, J = 12.4 Hz, 1H), 3.31-3.27 (m, 1H), 2.92-2.86 (m, 1H), 2.67 (s, 3H), 2.32-2.25 (m, 3H), 2.21-2.10 (m, 1H), 2.07-2.05 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 181.3, 177.3, 171.6, 142.4, 134.6, 133.3, 133.2, 132.2, 131.7, 129.7, 129.6, 129.3, 129.1, 128.9, 126.2, 125.6, 125.2, 124.2, 120.8, 69.9, 63.1, 61.2, 57.4, 30.7, 23.7 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2188, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 12.2 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-methoxy-phenyl)-pro

panoic Acid Schiff Base Complex 3e.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 90%. Mp 180-182 ºC; $[\alpha]^{20}_{D}$ = +1590 (c = 0.20 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.31-8.29 (m, 1H), 8.04 (d, J = 5.7 Hz, 2H), 7.55 (s, 1H), 7.43-7.35 (m, 3H), 7.30-7.29 (m, 2H), 7.24-7.14 (m, 5H), 7.07-7.00 (m, 2H), 6.98-6.91 (m, 3H), 6.83-6.81(m, 2H), 6.67-6.65 (m, 2H), 4.72 (d, J = 2.1 Hz, 1H), 4.39 (d, J = 2.1 Hz, 1H), 4.23(d, J = 9.3 Hz, 1H), 3.78 (s, 3H), 3.42-3.29 (m, 3H), 2.87-2.81 (m, 1H), 2.44-2.34 (m, 2H), 2.05-2.02 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.6, 177.9, 171.6, 159.1, 142.9, 135.6, 134.1, 133.8, 133.4, 132.4, 132.1, 131.5, 131.3, 129.3, 129.0, 128.8, 128.7, 127.8, 126.7, 126.5, 126.1, 123.7, 123.1, 121.3, 120.5, 118.7, 118.6, 115.2, 114.1, 110.7, 74.7, 70.7, 63.8, 57.6, 55.2, 50.7, 48.9, 30.8, 23.0 ppm. LRMS (ESI) $[M+H]^+$ found m/z 733. HRMS (ESI) $[M+Na]^+$ found m/z 755.2141, calcd for $C_{43}H_{38}N_4NiO_4Na$ 755.2144. HPLC (Chiralpak IA, *n*-hexane/ *i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.6 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-nitro-phenyl)-propan oic Acid Schiff Base Complex 3f.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 67%. Mp 184-186 ºC; $[\alpha]^{20}_{D}$ = +1815 (c = 0.13 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 7.6 Hz, 2H), 7.97 (s, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.36-7.30 (m, 5H), 7.23-7.10 (m, 4H), 7.05-7.04 (m, 2H), 6.92-6.85 (m, 3H), 6.70-6.67 (m, 2H),

4.74-4.73 (m, 1H), 4.41-4.40 (m, 1H), 4.29-4.26 (m, 1H), 3.65 (s, 1H), 3.49-3.33 (m, 4H), 2.87-2.83 (m, 1H), 2.45-2.41 (m, 2H), 2.03-2.01 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 178.3, 170.9, 143.1, 142.8, 133.8, 133.2, 131.5, 129.3, 128.8, 128.7, 128.6, 128.5, 128.0, 127.7, 127.1, 126.1, 121.8, 114.0, 109.6, 75.7, 70.6, 63.3, 57.2, 50.1, 30.7, 29.7, 23.4, 21.1 ppm. LRMS (ESI) $[M+H]^+$ found m/z 748. HRMS (ESI) $[M+Na]^+$ found m/z 770.1892, calcd for $C_{42}H_{35}N_5NiO_5Na$ 770.1889. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 5.5 min, t_{major} = 11.4 min, de = 80%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-chloro-phenyl)-propanoic Acid Schiff Base Complex 3g.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 91%. Mp 175-177 ºC; $[\alpha]^{20}_D$ = +2400 (c = 0.11 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.34 (d, J = 8.8 Hz, 1H), 8.19 (s, 1H), 8.03 (d, J = 7.6 Hz, 2H), 7.64-7.62 (m, 2H), 7.53-7.29 (m, 6H), 7.15-7.05 (m, 5H), 6.97-6.95 (m, 1H), 6.80-6.74 (m, 2H), 6.68-6.66 (m, 3H), 4.77-4.74 (m, 1H), 4.43-4.41 (m, 1H), 4.31-4.23 (m, 1H), 4.15-4.09 (m, 1H), 3.47-3.26 (m, 4H), 2.79-2.75 (m, 2H), 1.89-1.84 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 178.1, 171.4, 143.0, 139.8, 136.0, 134.0, 133.8, 133.3, 132.5, 132.2, 131.5, 129.9, 129.4, 128.9, 128.7, 128.1, 127.8, 127.2, 126.0, 124.5, 123.1, 122.5, 120.5, 120.2, 119.0, 113.7, 111.3, 74.5, 70.4, 63.5, 60.4, 57.2, 48.7, 30.3, 23.0, 21.0, 14.2 ppm. LRMS (ESI) $[M+H]^+$ found m/z 737. HRMS (ESI) $[M+Na]^+$ found m/z 759.1633, calcd for $C_{42}H_{35}N_4NiO_3ClNa$

759.1649. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.4 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-bromo-phenyl)-propanoic Acid Schiff Base Complex 3h.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 90%. Mp 186-188ºC; $[\alpha]^{20}_{D}$ = +1856 (c = 0.16 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 7.2 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.30-7.28 (m, 2H), 7.26-7.21 (m, 5H), 7.19-7.05 (m, 7H), 6.67-6.62 (m, 3H), 4.90 (d, J = 3.6 Hz, 1H), 4.78 (d, J = 3.6 Hz, 1H), 4.18 (d, J = 12.4 Hz, 1H), 3.35 (d, J = 12.4 Hz, 1H), 3.25-3.21 (m, 1H), 2.75-2.72 (m, 1H), 2.15-2.08 (m, 1H), 1.92-4384 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 178.1, 171.4, 160.5, 143.0, 140.3, 136.1, 133.9, 133.8, 133.3, 132.5, 131.5, 131.1, 130.3, 129.4, 128.9, 128.7, 128.1, 127.8, 127.2, 126.1, 124.6, 123.1, 122.5, 120.5, 120.4, 120.1, 119.0, 113.5, 111.4, 96.6, 74.5, 70.4, 63.5, 57.2, 48.8, 30.3, 23.0 ppm. LRMS (ESI) $[M+H]^+$ found m/z 781. HRMS (ESI) $[M+Na]^+$ found m/z 803.1147, calcd for $C_{42}H_{35}N_4NiO_3BrNa$ 803.1144. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.2 min, t_{major} = 12.8 min, de = 70%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-furan-2-yl-propanoic Acid Schiff Base Complex 3i.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 61%. Mp 183-185ºC; $[\alpha]^{24}_{D}$ = +2100 (c = 0.12 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.34 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.57 (m, 1H), 7.34-7.28 (m, 6H), 7.23-7.11 (m, 4H), 7.02-6.98 (m, 2H), 6.90-6.82 (m, 4H), 6.68-6.63 (m, 2H), 4.74 (s, 1H), 4.43 (s, 1H), 4.26-4.21 (m, 1H), 3.48-3.29 (m, 2H), 2.29-2.18 (m, 6H), 2.03-1.91 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 176.7, 172.8, 162.5, 148.9, 143.5, 143.1, 133.8, 133.7, 132.9, 132.8, 131.5, 130.3, 129.4, 129.3, 128.8, 128.7, 127.9, 126.5, 125.7, 123.3, 120.6, 111.3, 109.7, 74.4, 70.3, 70.1, 63.5, 56.9, 39.7, 36.4, 31.4, 30.5, 22.9 ppm. LRMS (ESI) $[M+H]^+$ found m/z 693. HRMS (ESI) $[M+Na]^+$ found m/z 715.1812, calcd for $C_{40}H_{34}N_4NiO_4Na$ 715.1831. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.9 min, t_{major} = 11.3 min, de > 97%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-cyclohexyl-propanoic Acid Schiff Base Complex 3j.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 53%. Mp 180-182 ºC; $[\alpha]^{20}_{D}$ = +1580 (c = 0.15 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.51 (s, 1H), 8.33-8.16 (m, 1H), 7.95-7.89 (m, 3H), 7.59-7.49 (m, 5H), 7.36-7.34 (m, 2H), 7.21-7.08 (m, 4H), 7.00-6.90 (m, 1H), 6.69-6.67 (m, 2H), 4.69 (s, 1H), 4.51 (s, 1H), 4.12 (d, J = 12.6 Hz, 1H), 3.38-3.30 (m, 2H), 3.01-2.93 (m, 1H), 2.75-2.69 (m, 2H), 2.49-2.41 (m, 2H), 2.12-2.06 (m, 2H), 1,82-1.64 (m, 3H), 1.51-1.38 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 179.8,

135.9, 134.9, 134.5, 133.4, 133.1, 132.2, 131.9, 131.5, 129.9, 129.6, 129.3, 129.2, 128.9, 128.6, 128.5, 127.9, 125.9, 123.2, 123.1, 122.9, 122.4, 122.2, 120.2, 120.0, 118.9, 114.7, 113.7, 111.2, 70.1, 63.5, 56.9, 51.2, 48.1, 39.9, 35.4, 31.5, 29.7, 26.1, 22.7 ppm. LRMS (ESI) $[M+H]^+$ found m/z 709. HRMS (ESI) $[M+Na]^+$ found m/z 731.2515, calcd for $C_{42}H_{42}N_4NiO_3Na$ 731.2508. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 12.8 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(2-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3k.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 64%. Mp 181-183 ºC; $[\alpha]^{20}_D$ = +2500 (c = 0.12 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.36 (d, *J* = 8.8 Hz, 1H), 8.04-7.98 (m, 3H), 7.55-7.53 (m, 3H), 7.43-7.28 (m, 5H), 7.26-7.03 (m, 6H), 6.84-6.82 (m, 2H), 6.69-6.65 (m, 3H), 4.73 (d, *J* = 2.8 Hz, 1H), 4.51 (d, *J* = 2.8 Hz, 1H), 4.27 (d, *J* = 12.8 Hz, 1H), 3.44-3.33 (m, 2H), 2.83-2.78 (m, 1H), 2.46-2.43 (m, 1H), 2.36-2.32 (m, 1H), 2.25 (s, 3H), 2.00-1.98 (m, 2H), 1.53-1.48 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.5, 177.7, 171.5, 143.0, 140.1, 133.8, 132.4, 131.6, 130.2, 129.2, 128.8, 128.7, 128.6, 127.9, 127.3, 126.7, 123.1, 122.9, 120.4, 110.3, 70.5, 63.6, 57.4, 49.8, 30.9, 23.3, 21.4 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2186, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, n-hexane/i-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), tmajor = 11.4 min,

de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(4-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3l.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 76%. Mp 178-180 ºC; $[\alpha]^{20}_{D}$ = +2570 (c = 0.10 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.78 (s, 1H), 8.30 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 7.5 Hz, 2H), 7.31-7.29 (m, 2H), 7.26-7.01 (m, 13H), 6.85-6.82 (m, 1H), 6.64-6.64 (m, 2H), 6.18-6.16 (m, 1H), 4.72-4.71 (m, 1H), 4.26 (d, J = 12.6 Hz, 1H), 3.42-3.28 (m, 2H), 2.92-2.84 (m, 1H), 2.67 (s, 3H), 2.34-2.21 (m, 1H), 2.08-2.01 (m, 1H), 1.91-1.86 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.3, 178.4, 170.9, 143.1, 142.8, 136.1, 133.8, 133.2, 132.4, 131.5, 129.9, 129.3, 128.8, 128.7, 128.6, 128.5, 128.0, 127.7, 127.1, 126.1, 126.0, 125.8, 125.3, 123.0, 121.9, 121.7, 120.5, 113.9, 109.6, 75.7, 70.6, 63.3, 57.2, 50.1, 30.7, 29.7, 23.3, 21.1 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2215, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 9.1 min, t_{major} = 17.5 min, de = 96%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(5-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3m.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 88%. Mp 180-182ºC; $[\alpha]^{21}_{D}$ = +1400 (c = 0.15 g/100 mL,

$CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz) δ 8.38 (d, J = 8.7 Hz, 1H), 8.10-8.02 (m, 3H), 7.68-7.65 (m, 1H), 7.54-7.31 (m, 7H), 7.26-7.00 (m, 7H), 6.84-6.81 (m, 2H) 6.69-6.65 (m, 2H), 4.73-4.72 (m, 1H), 4.52-4.45 (m, 1H), 4.26 (d, J = 12.0 Hz, 1H), 4.13-4.09 (m, 1H), 3.45-3.30 (m, 2H), 2.84-2.75 (m, 1H), 2.39-2.25 (m, 5H), 3.05-1.99 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.5, 177.8, 171.5, 143.0, 140.1, 134.1, 133.8, 133.7, 133.3, 132.4, 131.5, 130.2, 129.2, 128.8, 128.7, 128.6, 127.9, 127.8, 127.3, 126.8, 126.7, 126.1, 124.0, 123.0, 122.9, 120.4, 118.2, 114.5, 110.4, 74.9, 70.6, 63.6, 57.4, 49.8, 30.8, 23.2, 21.4 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2200, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.8 min, t_{major} = 13.0 min, de = 97%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(5-chloro-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3n.

Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 84%. Mp 179-181ºC; $[\alpha]^{20}_D$ = +1302 (c = 0.30 g/100 mL, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.33 (d, J = 9.2 Hz, 1H), 8.02 (d, J = 7.6 Hz, 3H), 7.78 (d, J = 2.4 Hz, 1H), 7.56-7.29 (m, 5H), 7.20-7.10 (m, 8H), 7.00-6.95 (m, 1H), 6.75-6.65 (m, 4H), 4.72 (d, J = 2.4 Hz, 1H), 4.30-4.24 (m, 2H), 3.64 (s, 1H), 3.49-3.42 (m, 2H), 3.33-3.28 (m, 1H), 2.79-2.75 (m, 1H), 2.40-2.32 (m, 3H), 2.01-1.98 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 176.7, 172.4, 143.1, 134.5, 133.7, 133.6, 133.1, 132.8, 131.4, 130.2, 129.4, 128.9, 128.7, 128.6, 127.7,

126.6, 125.5, 123.1, 120.6, 71.4, 70.3, 63.6, 60.3, 57.2, 46.3, 30.5, 22.9, 21.0, 14.1 ppm. LRMS (ESI) $[M+H]^+$ found m/z 737. HRMS (ESI) $[M+Na]^+$ found m/z 759.1655, calcd for $C_{42}H_{35}N_4NiO_3ClNa$ 759.1649. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.5 min, de > 99%.

Nickel(II)-(*S*)-BPB/(2*S*,3*R*)-2-Amino-3-(7-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3o.

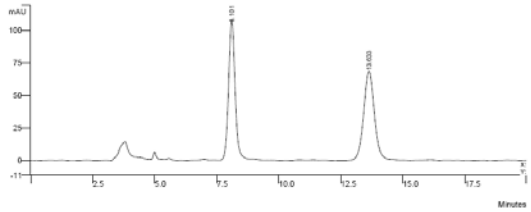
Obtained as a red solid by flash column chromatography (petroleum ether/ethyl acetate = 1/1), yield 86%. Mp 184-186 ºC; $[\alpha]^{21}_D$ = +1420 (c = 0.20 g/100 mL, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (d, J = 8.4 Hz, 1H), 8.32 (d, J = 7.2 Hz, 2H), 7.59 (s, 1H), 7.45-7.28 (m, 8H), 7.17-7.14 (m, 4H), 7.06-6.99 (m, 2H), 6.93-6.91 (m, 1H), 6.86-6.68 (m, 2H) 6.68-6.64 (m, 2H), 4.76 (d, J = 2.4 Hz, 1H), 4.39 (d, J = 2.4 Hz, 1H), 4.24 (d, J = 12.8 Hz, 1H), 4.14-4.09 (m, 2H), 3.43-3.34 (m, 2H), 2.86-2.81 (m, 1H), 2.42-2.35 (m, 2H), 2.06-2.01 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.5, 177.7, 171.6, 143.1, 140.2, 135.1, 134.2, 133.8, 133.3, 132.4 131.6, 130.4, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 127.8, 127.4, 126.7, 126.1, 123.5, 123.1, 121.9, 120.4, 119.8, 119.0, 116.3, 115.5, 96.6, 74.7, 70.6, 63.7, 57.5, 49.9, 30.8, 23.2, 16.5 ppm. LRMS (ESI) $[M+H]^+$ found m/z 717. HRMS (ESI) $[M+Na]^+$ found m/z 739.2220, calcd for $C_{43}H_{38}N_4NiO_3Na$ 739.2195. HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 14.7 min, de >99%.

(2*S*,3*R*)-2-amino-3-(*1H*-indol-3-yl)-3-phenylpropanoic acid 4a.

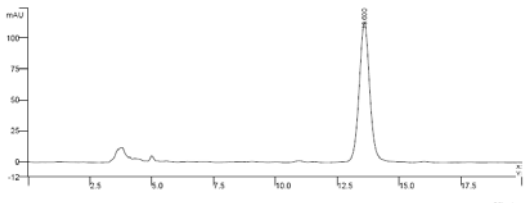
Obtained as a pink solid by column chromatography on C_{18}-reversed phase (230-400 mesh) silica gel (methanol /water = 1/1), yield 96%. Mp 147-179 ºC; $[\alpha]_D^{20}$ = +23.7 (c = 0.38 g/100 mL, 6 N HCl). ^{1}H NMR (DMSO, 300 MHz): δ 11.02 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.75-7.48 (m, 5H), 7.45-7.09 (m, 5H), 3.73 (d, J = 12.9 Hz, 1H), 3.52 (d, J = 13.2 Hz, 1H) ppm. ^{13}C NMR (DMSO, 100 MHz): δ 173.2, 138.2, 137.9, 137.6, 133.0, 132.9, 131.6, 129.8, 128.9, 128.6, 127.9, 126.9, 126.2, 122.8, 121.4 53.5, 30.2 ppm. LRMS (ESI) $[M-H]^+$ found *m/z* 279. HRMS (ESI) $[M-H]^+$ found *m/z* 279.1134, calcd. for $C_{17}H_{15}N_2O_2$ 279.1134.

Analytical high performance liquid chromatography was carried out using the Model 410 automated sampler, using the Chiralpak IA column. The loading loop was 20 µL. The eluting employed was an isocratic mixture of *n*-hexane and *i*-propanol (60:40 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



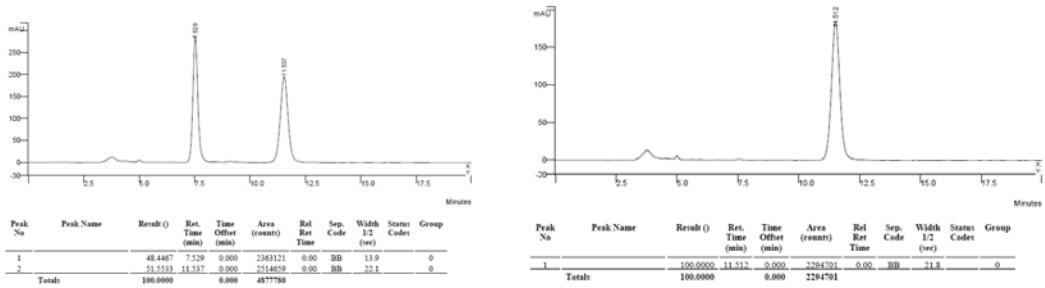
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		48.9338	8.101	0.000	1014791	0.00	BB	16.2		0
2		51.0662	13.633	0.000	1059013	0.00	BB	27.0		0
Totals		100.0000		0.000	2073804					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	13.600	0.000	1703615	0.00	BB	26.7		0
Totals		100.0000		0.000	1703615					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.6 min, de > 99%.

3b

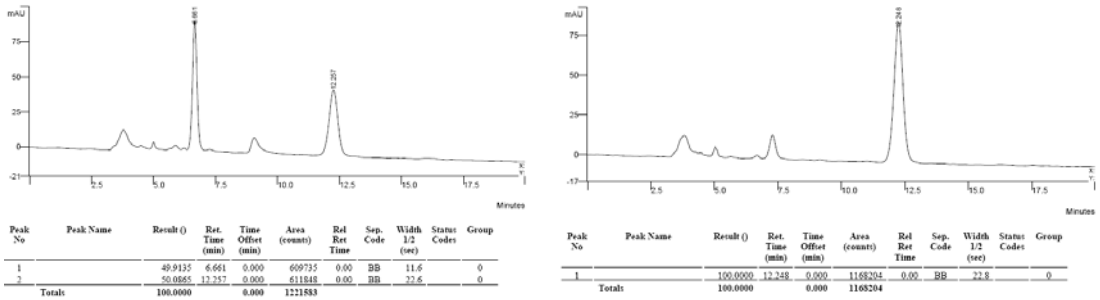


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		48.4467	7.529	0.000	2363121	0.00	BB	13.9		0
2		51.5533	11.537	0.000	2514659	0.00	BB	22.1		0
Totals		100.0000		0.000	4877780					

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	11.512	0.000	2294701	0.00	BB	21.8		0
Totals		100.0000		0.000	2294701					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.5 min, de > 99%.

3c

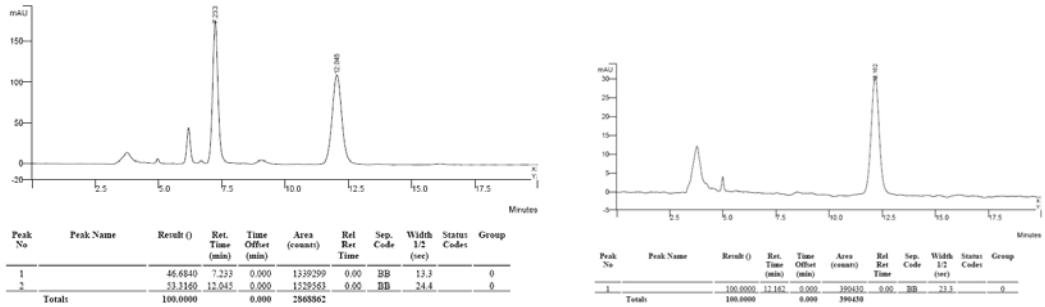


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		49.9135	6.661	0.000	609735	0.00	BB	11.6		0
2		50.0865	12.257	0.000	611848	0.00	BB	22.6		0
Totals		100.0000		0.000	1221583					

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	12.248	0.000	1168204	0.00	BB	22.8		0
Totals		100.0000		0.000	1168204					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 12.2 min, de > 99%.

3d



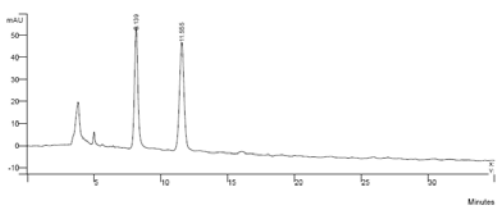
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		46.6840	7.233	0.000	1339299	0.00	BB	13.3		0
2		53.3160	12.045	0.000	1529563	0.00	BB	24.4		0
Totals		100.0000		0.000	2868862					

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	12.162	0.000	390430	0.00	BB	23.3		0
Totals		100.0000		0.000	390430					

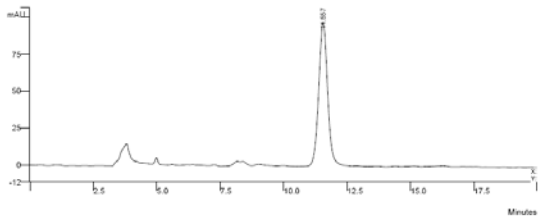
HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm),

t_{major} = 12.2 min, de > 99%.

3e



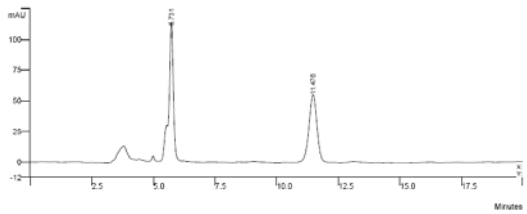
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		45.4693	8.139	0.000	516491	0.00	BB	16.4		0
2		54.5307	11.555	0.000	619421	0.00	BB	21.9		0
Totals		100.0000		0.000	1135912					



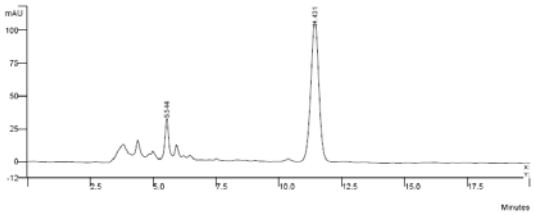
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	11.557	0.000	1224364	0.00	BB	22.0		0
Totals		100.0000		0.000	1224364					

HPLC (Chiralpak IA, *n*-hexane/ *i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.6 min, de > 99%.

3f



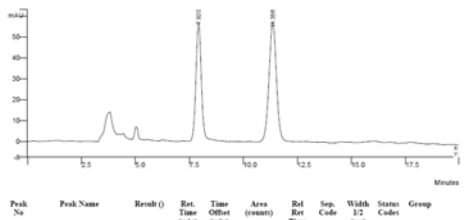
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		54.4139	5.731	0.000	776853	0.00	BB	9.7		0
2		45.5861	11.476	0.000	650820	0.00	BB	20.6		0
Totals		100.0000		0.000	1427673					



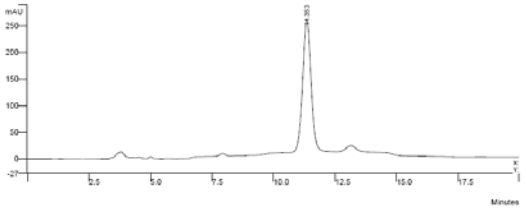
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		10.5980	5.544	0.000	149462	0.00	BB	8.9		0
2		89.4020	11.431	0.000	1260831	0.00	BB	20.5		0
Totals		100.0000		0.000	1410293					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 5.5 min, t_{major} = 11.4 min, de = 80%.

3g



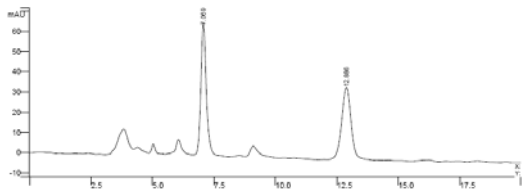
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		41.1830	7.920	0.000	500416	0.00	BB	15.7		0
2		58.8170	11.356	0.000	714630	0.00	BB	21.8		0
Totals		100.0000		0.000	1215046					



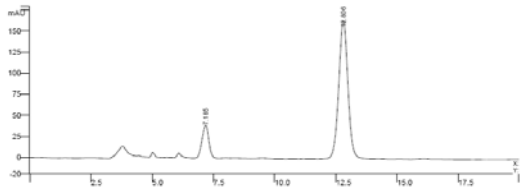
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	11.353	0.000	3080886	0.00	BB	21.8		0
Totals		100.0000		0.000	3080886					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.4 min, de > 99%.

3h



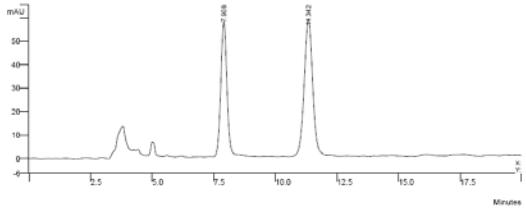
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		51.5451	7.069	0.000	522321	0.00	BB	13.3		0
2		48.4549	12.886	0.000	491007	0.00	BB	24.0		0
Totals		100.0000		0.000	1013328					



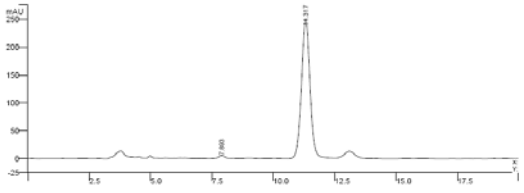
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		15.0394	7.185	0.000	392681	0.00	BB	18.2		0
2		84.9606	12.806	0.000	2218328	0.00	BB	23.7		0
Totals		100.0000		0.000	2611009					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.2 min, t_{major} = 12.8 min, de = 70%.

3i



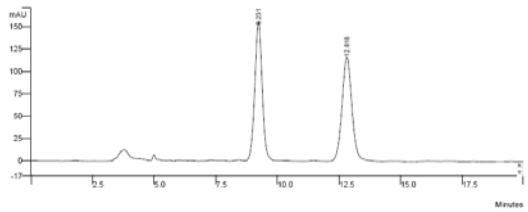
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		41.2220	7.908	0.000	510142	0.00	BB	15.7		0
2		58.7780	11.342	0.000	727406	0.00	BB	21.8		0
Totals		100.0000		0.000	1237548					



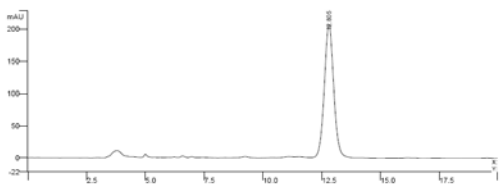
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.3754	7.893	0.000	43682	0.00	BB	15.7		0
2		98.6246	11.317	0.000	3132281	0.00	BB	21.8		0
Totals		100.0000		0.000	3175963					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.9 min, t_{major} = 11.3 min, de > 97%.

3j



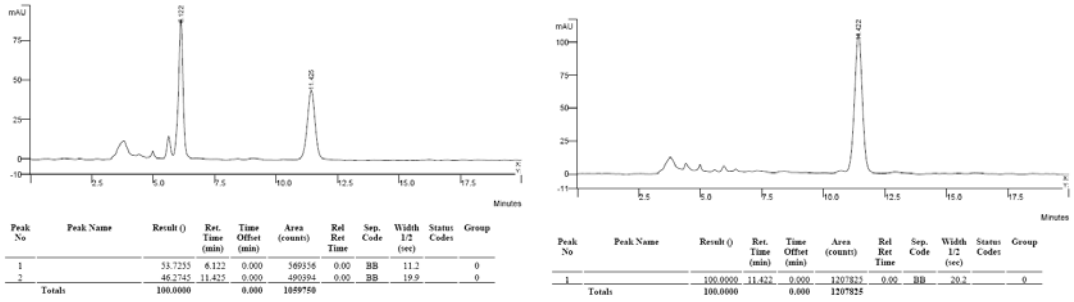
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		50.0515	9.231	0.000	1697944	0.00	BB	19.0		0
2		49.9485	12.818	0.000	1694453	0.00	BB	25.4		0
Totals		100.0000		0.000	3392397					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	12.805	0.000	2985958	0.00	BB	25.2		0
Totals		100.0000		0.000	2985958					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 12.8 min, de > 99%.

3k

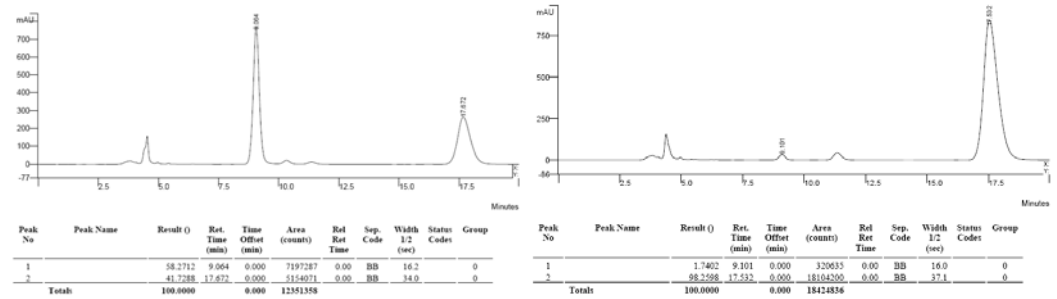


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		53.7255	6.122	0.000	569356	0.00	BB	11.2		0
2		46.2745	11.425	0.000	490394	0.00	BB	19.9		0
Totals		100.0000		0.000	1059750					

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	11.422	0.000	1207825	0.00	BB	20.2		0
Totals		100.0000		0.000	1207825					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 11.4 min, de > 99%.

3l

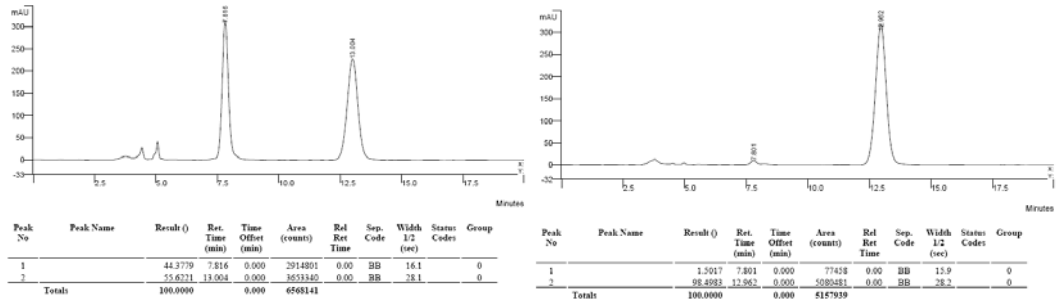


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		58.2712	9.064	0.000	7197287	0.00	BB	16.2		0
2		41.7288	17.672	0.000	5154071	0.00	BB	34.0		0
Totals		100.0000		0.000	12351358					

Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.7402	9.101	0.000	320635	0.00	BB	16.0		0
2		98.2598	17.532	0.000	18104200	0.00	BB	37.1		0
Totals		100.0000		0.000	18424836					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 9.1 min, t_{major} = 17.5 min, de = 96%.

3m

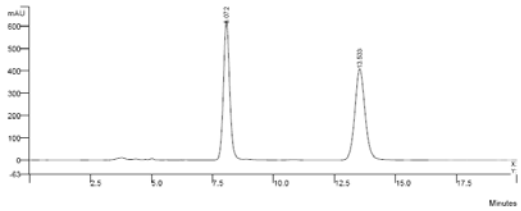


Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		44.3779	7.816	0.000	2914801	0.00	BB	16.1		0
2		55.6221	13.004	0.000	3653340	0.00	BB	28.1		0
Totals		100.0000		0.000	6568141					

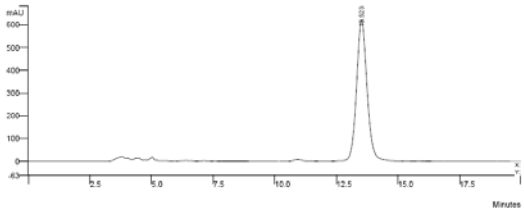
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		1.5017	7.801	0.000	77458	0.00	BB	15.9		0
2		98.4983	12.962	0.000	5080481	0.00	BB	28.2		0
Totals		100.0000		0.000	5157939					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{minor} = 7.8 min, t_{major} = 13.0 min, de = 97%.

3n



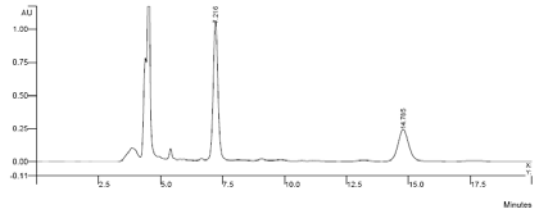
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		47.8968	8.072	0.000	5754456	0.00	BB	16.1		0
2		52.1032	13.533	0.000	6259826	0.00	BB	26.3		0
Totals		100.0000		0.000	12014282					



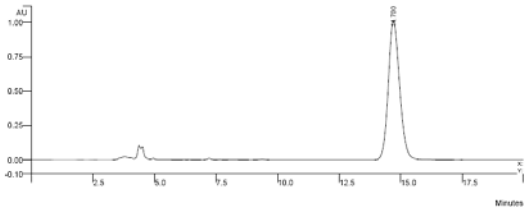
Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	13.523	0.000	9470490	0.00	BB	26.6		0
Totals		100.0000		0.000	9470490					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 13.5 min, de > 99%.

3o



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		66.2159	7.216	0.000	7323454	0.00	BB	12.0		0
2		33.7841	14.785	0.000	3736505	0.00	BB	27.4		0
Totals		100.0000		0.000	11059959					



Peak No	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)	Status Codes	Group
1		100.0000	14.700	0.000	16844082	0.00	BB	29.4		0
Totals		100.0000		0.000	16844082					

HPLC (Chiralpak IA, *n*-hexane/*i*-propanol = 60/40, flow rate 1.0 mL/min, λ= 220 nm), t_{major} = 14.7 min, de >99%.

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

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

X-ray crystallographic data of (*S*)(2*S*,3*R*)-**3a** were solutions at T = 293(2) K: $C_{42}H_{36}N_4NiO_3$, M_r = 702.21, monoclinic. Space group *P2* (1), a = 9.5816 (5) Å, b = 12.4509 (7) Å, c = 16.5961 (9) Å, α = 90°, β = 104.6403 (7)°, γ = 90°, V = 1915.62 (18) Å^3, Z = 2.

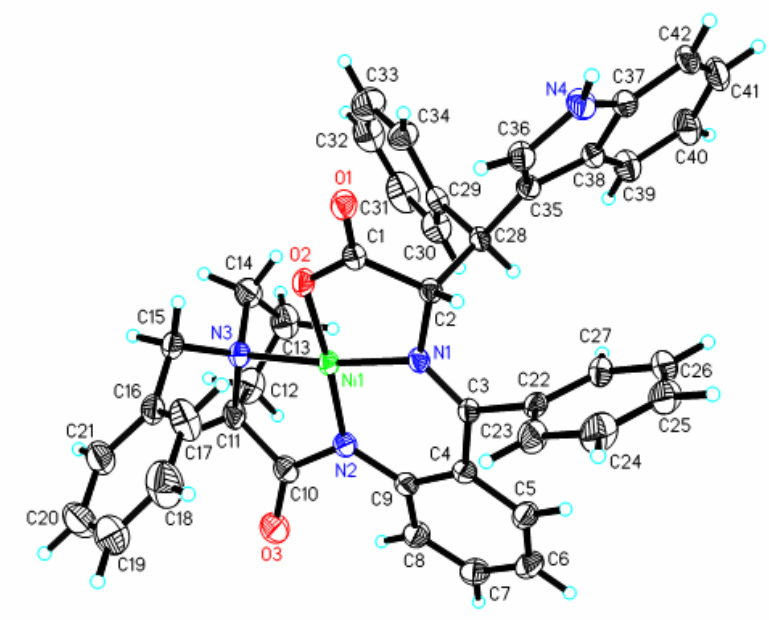
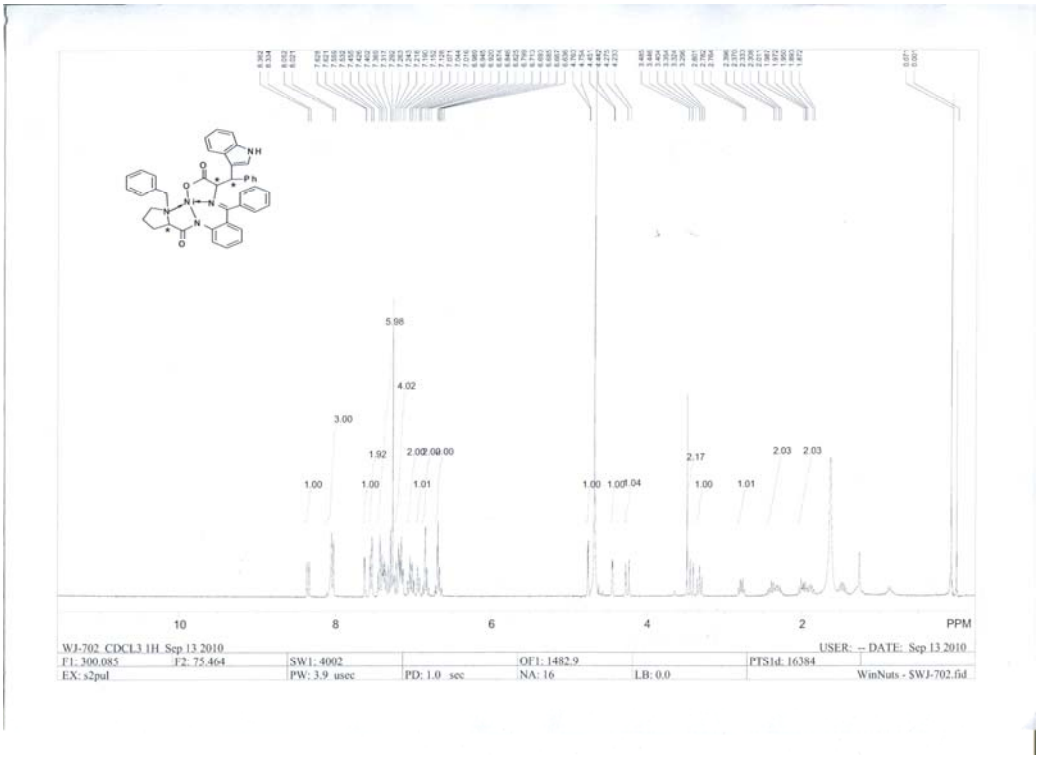


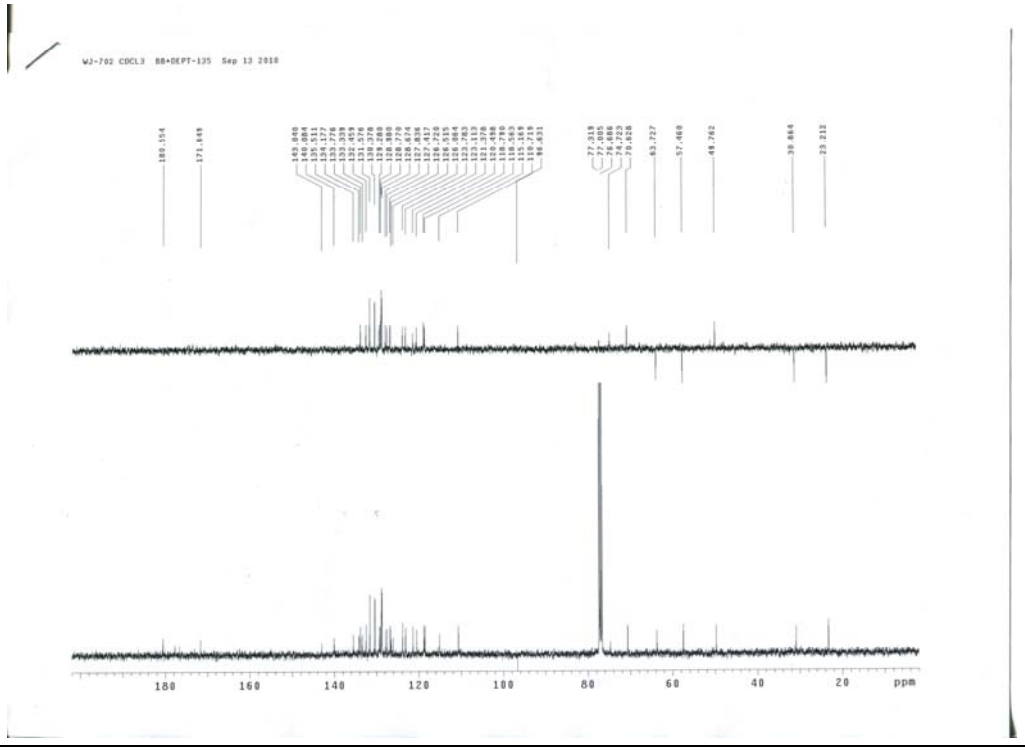
FIGURE S1. The crystal structure of (*S*)(2*S*,3*R*)-**3a** by X-ray analysis.

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 796799.

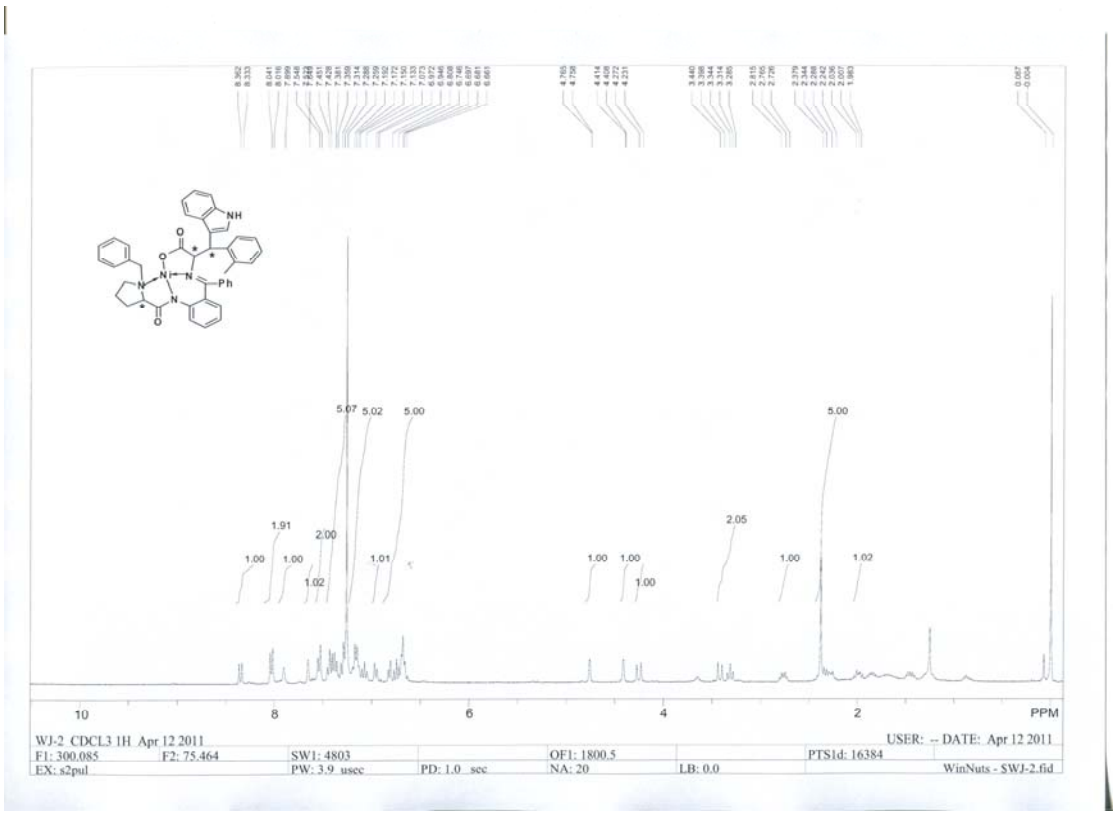
(E) Copies of ^{1}H NMR and ^{13}C NMR Spectra for the Products

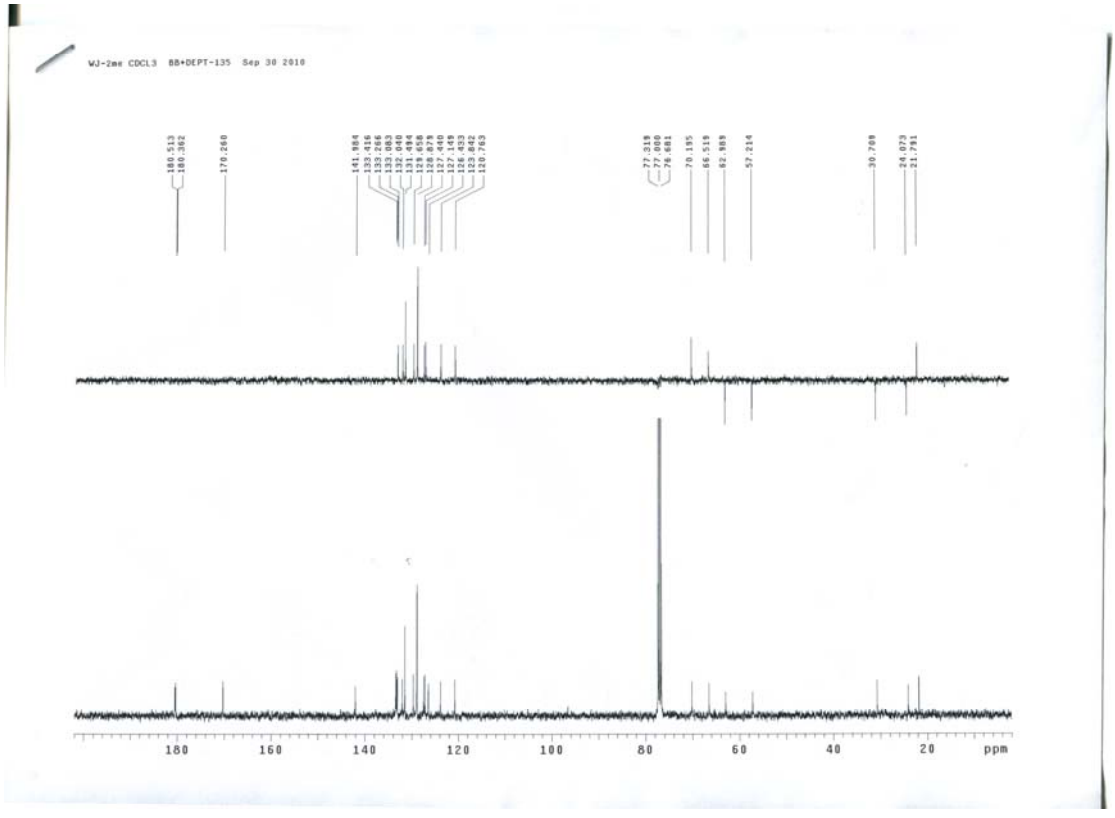
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3a.



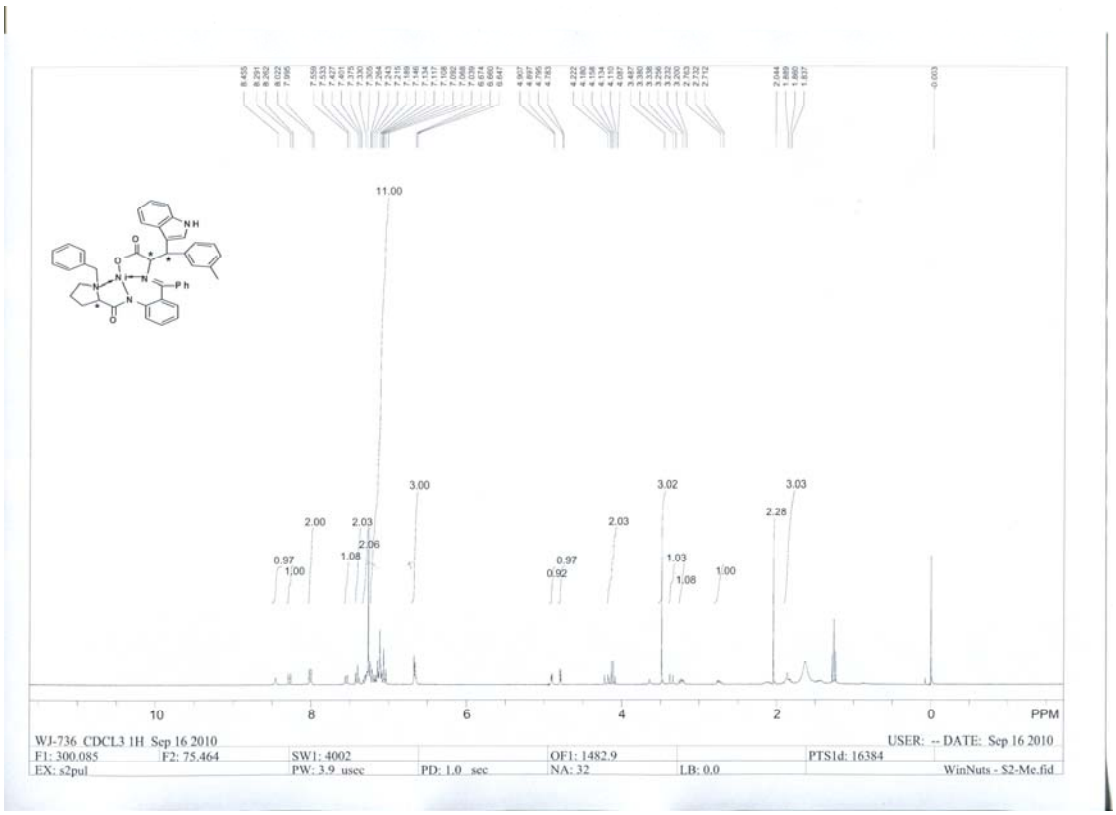


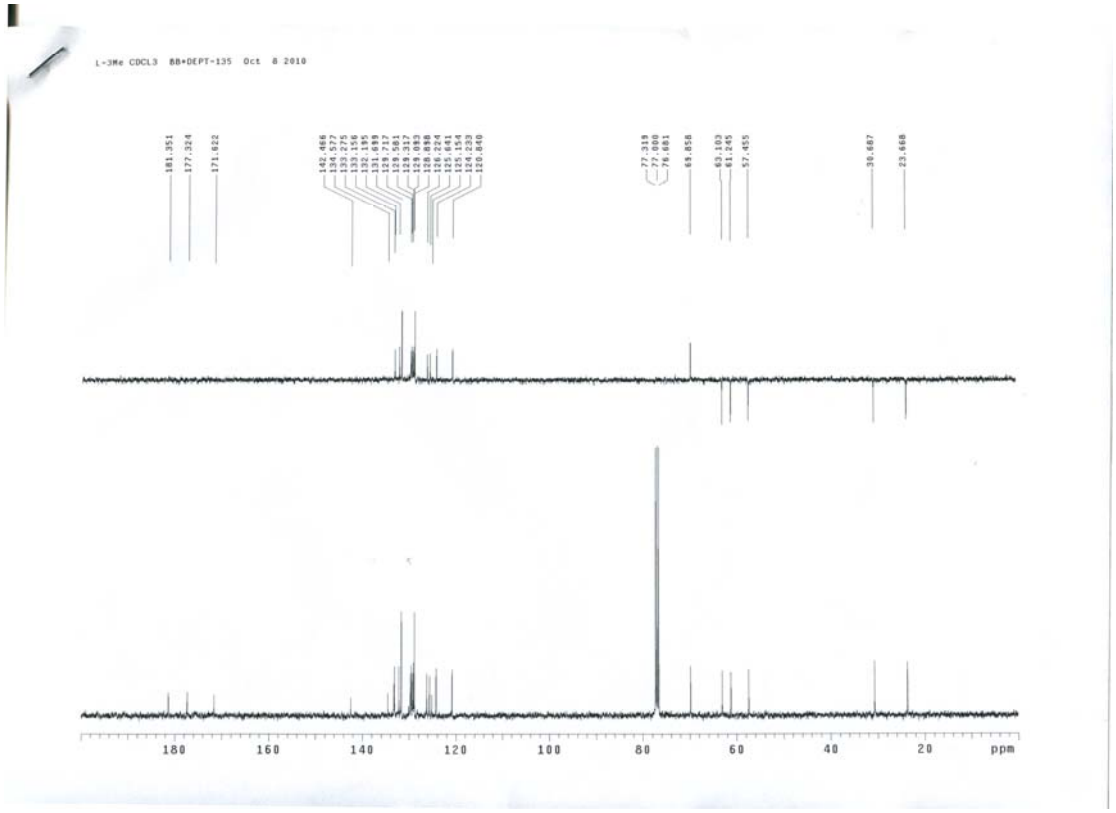
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-*o*-tolyl-propanoic Acid Schiff Base Complex 3b.



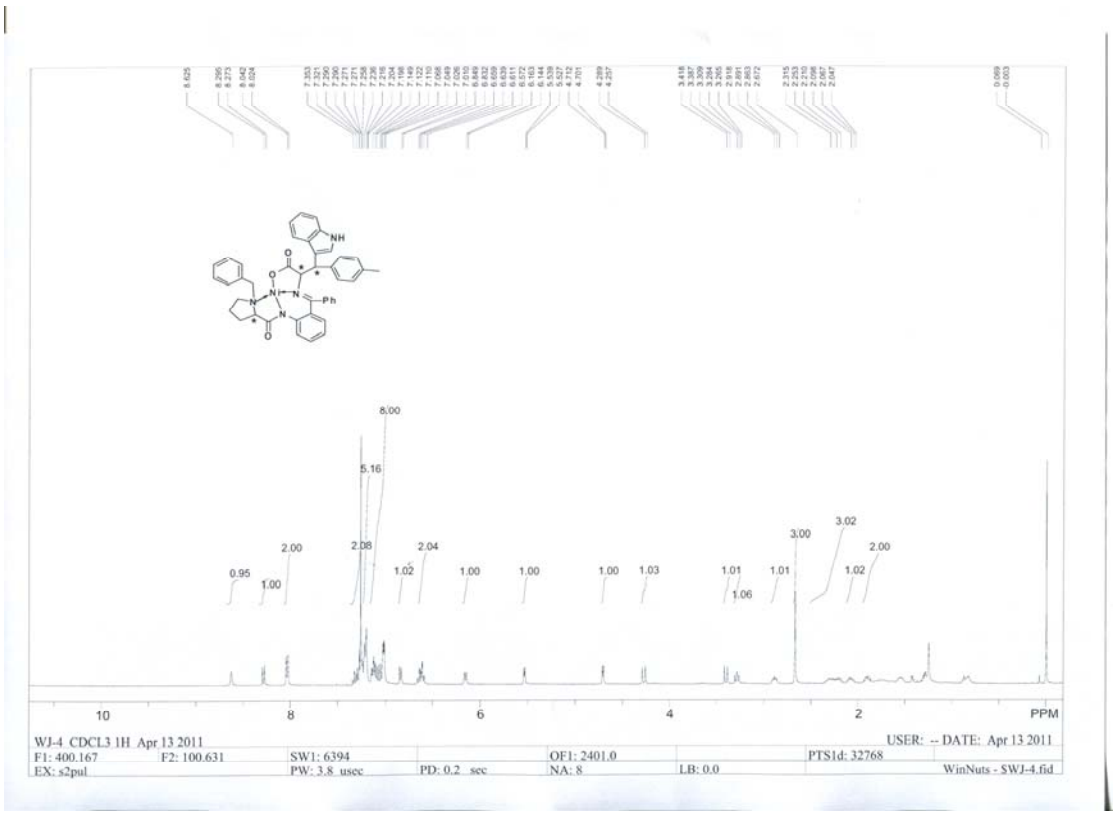


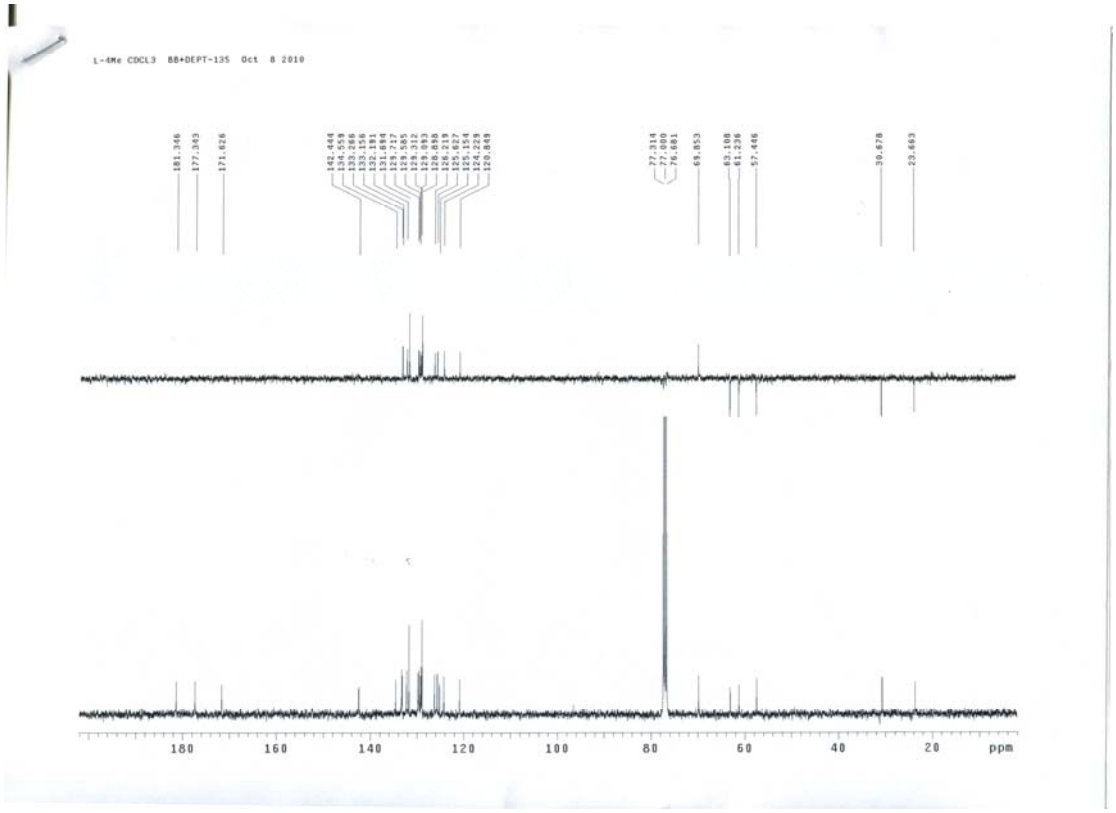
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-*m*-tolyl-propanoic Acid Schiff Base Complex 3c.



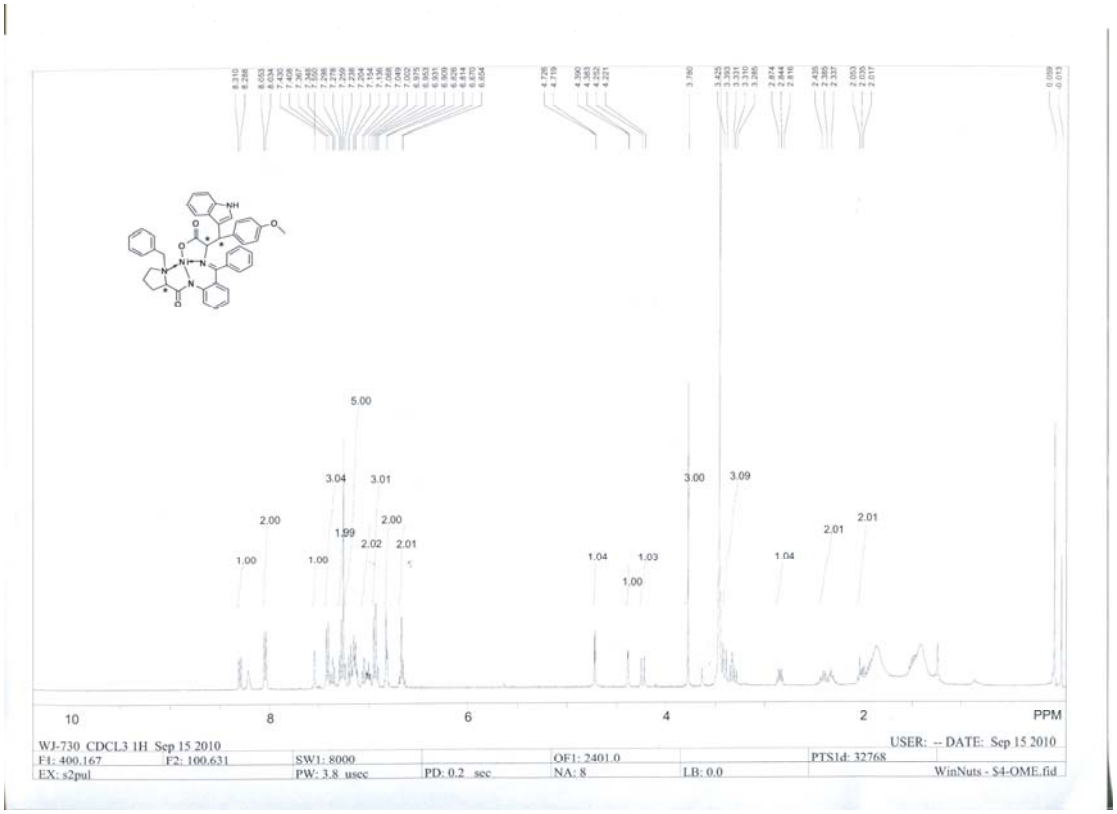


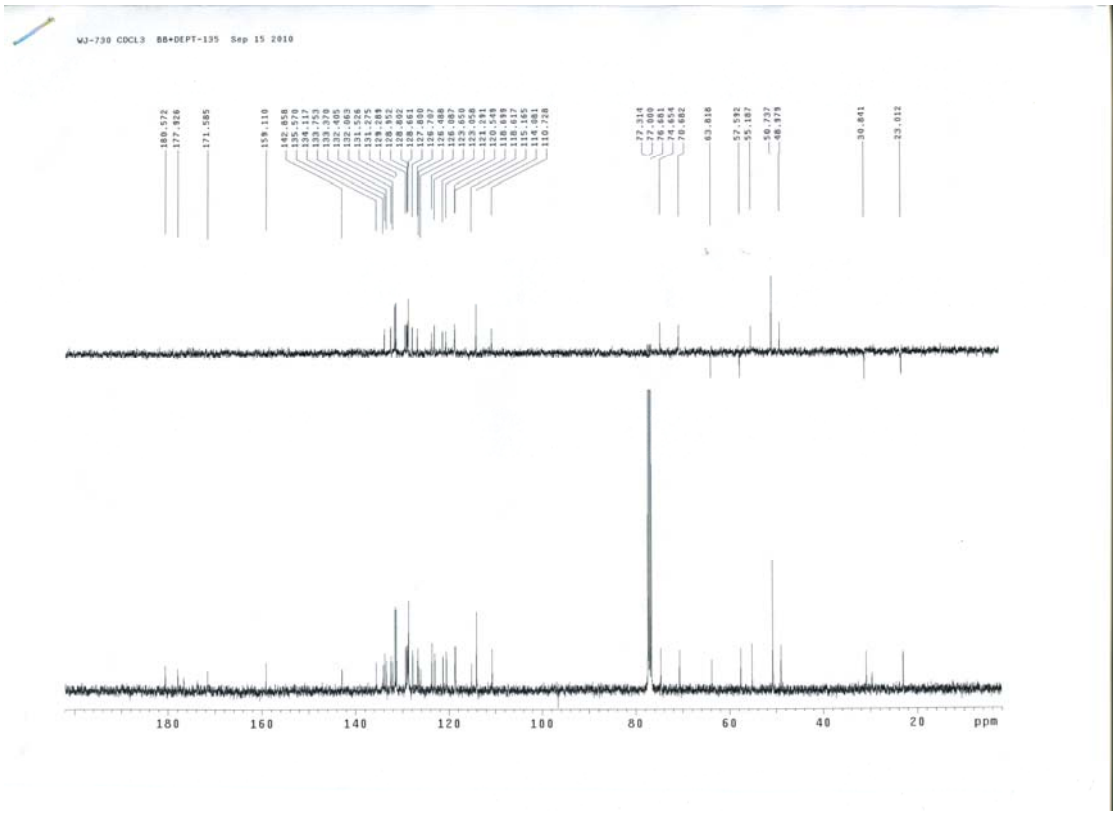
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-*p*-tolyl-propanoic Acid Schiff Base Complex 3d.



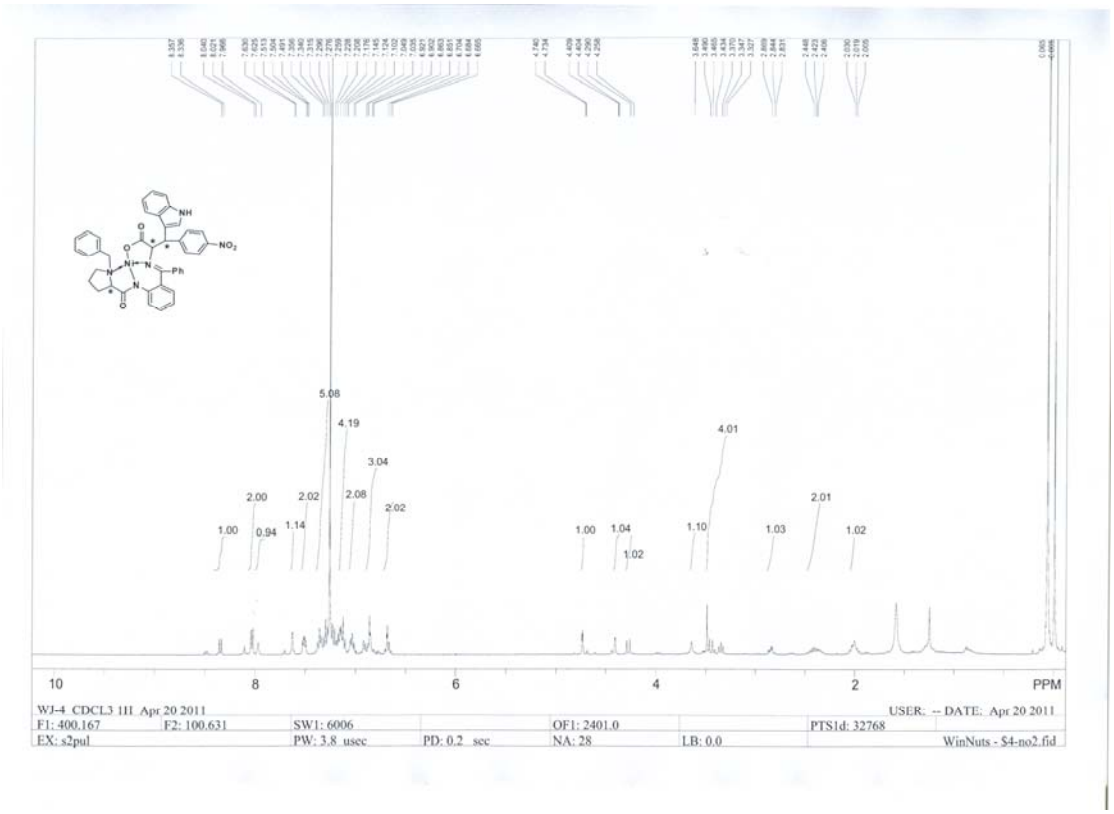


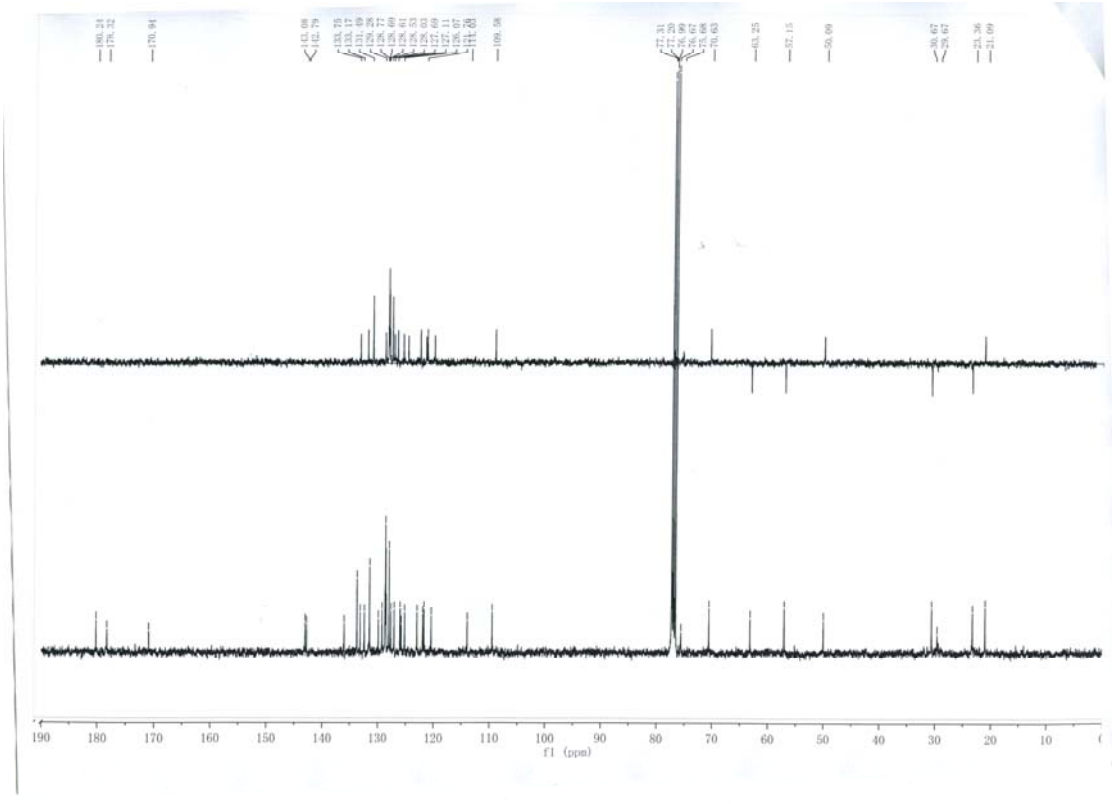
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-methoxy-phenyl)-propanoic Acid Schiff Base Complex 3e.



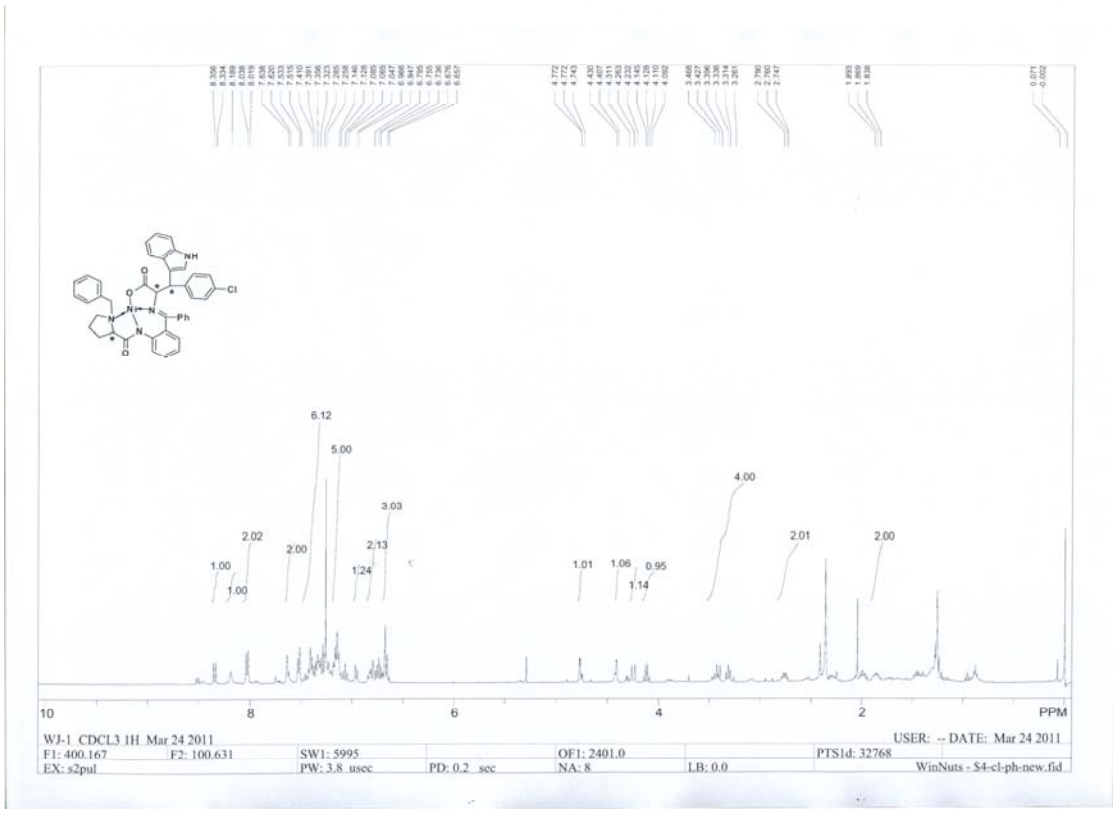


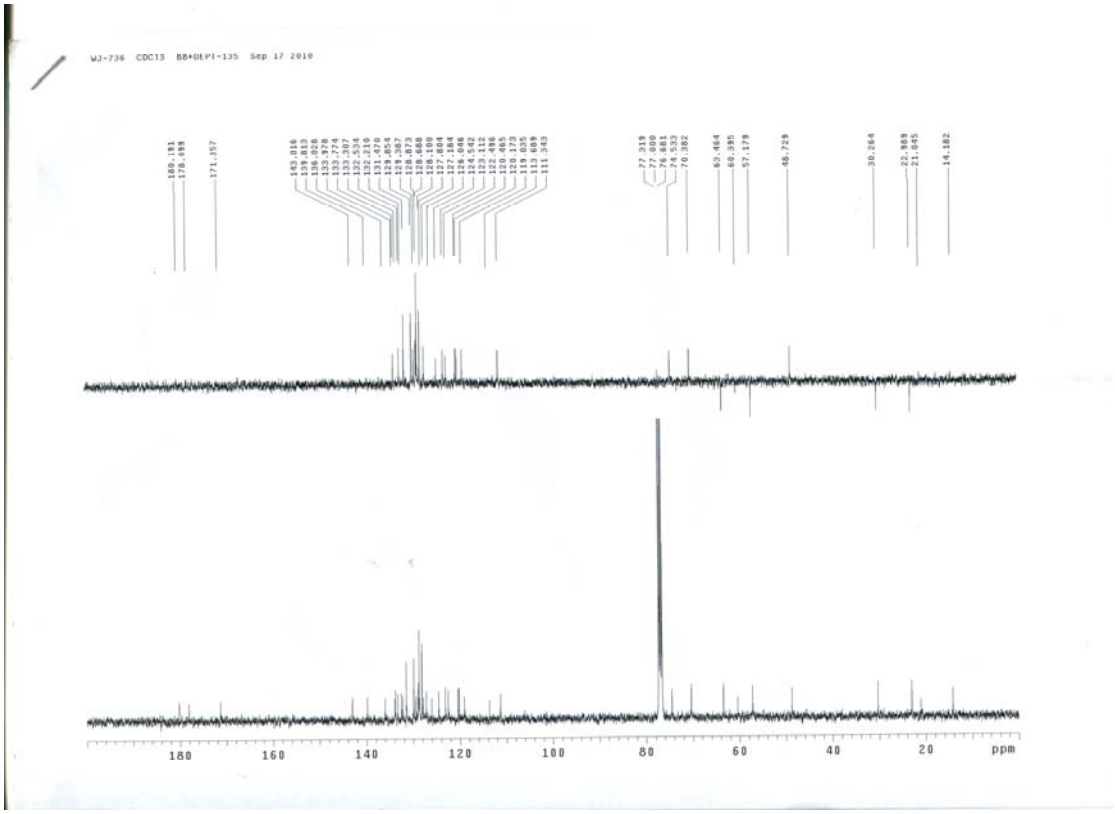
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-nitro-phenyl)-propanoic Acid Schiff Base Complex 3f.



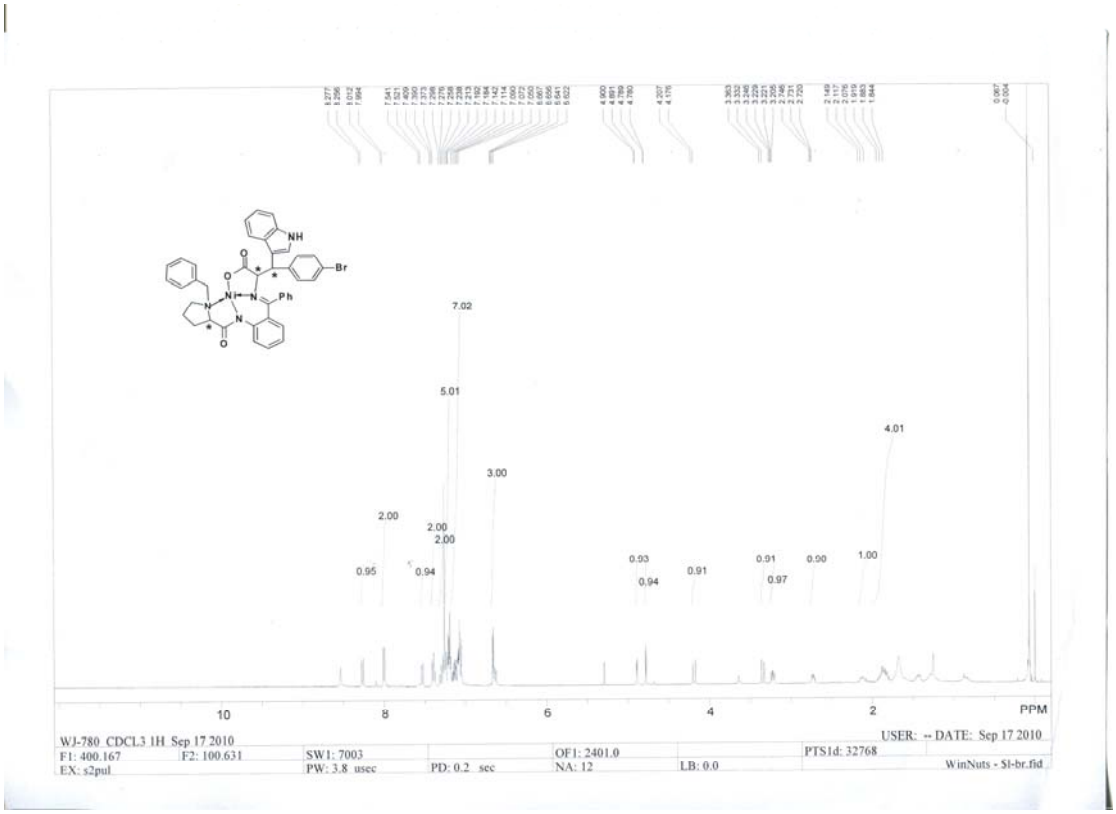


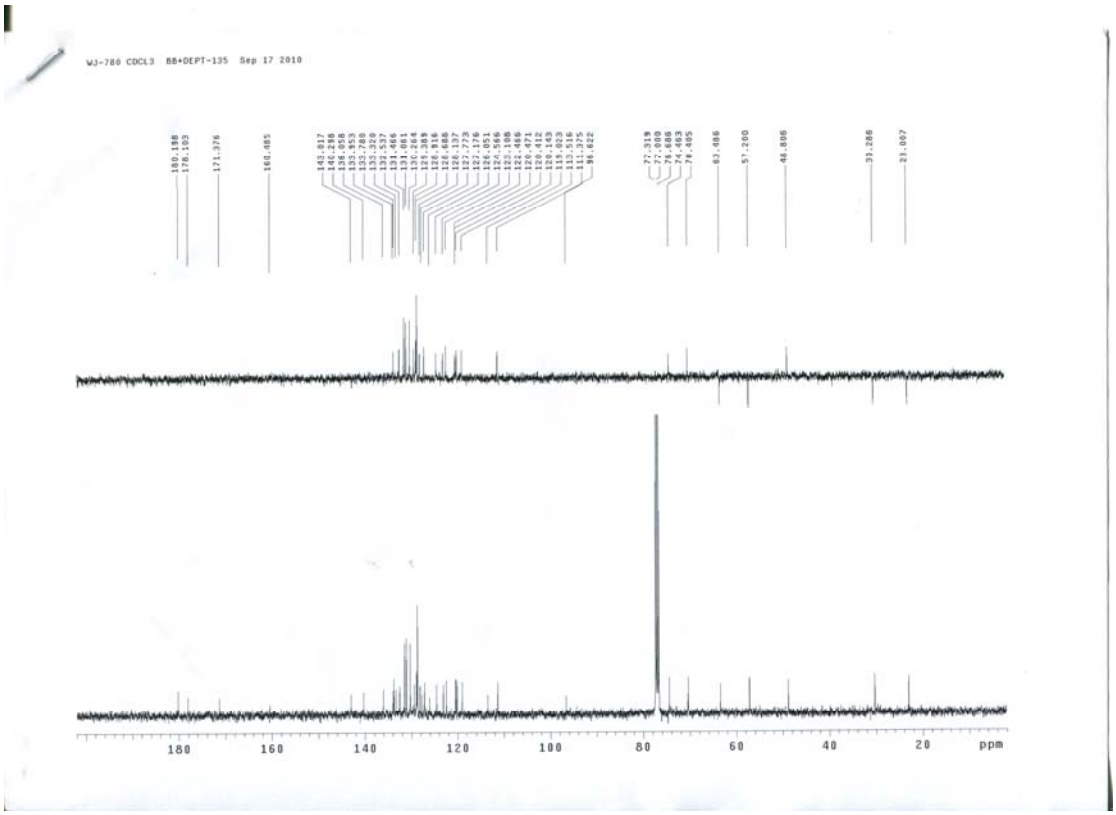
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-chloro-phenyl)-propanoic Acid Schiff Base Complex 3g.



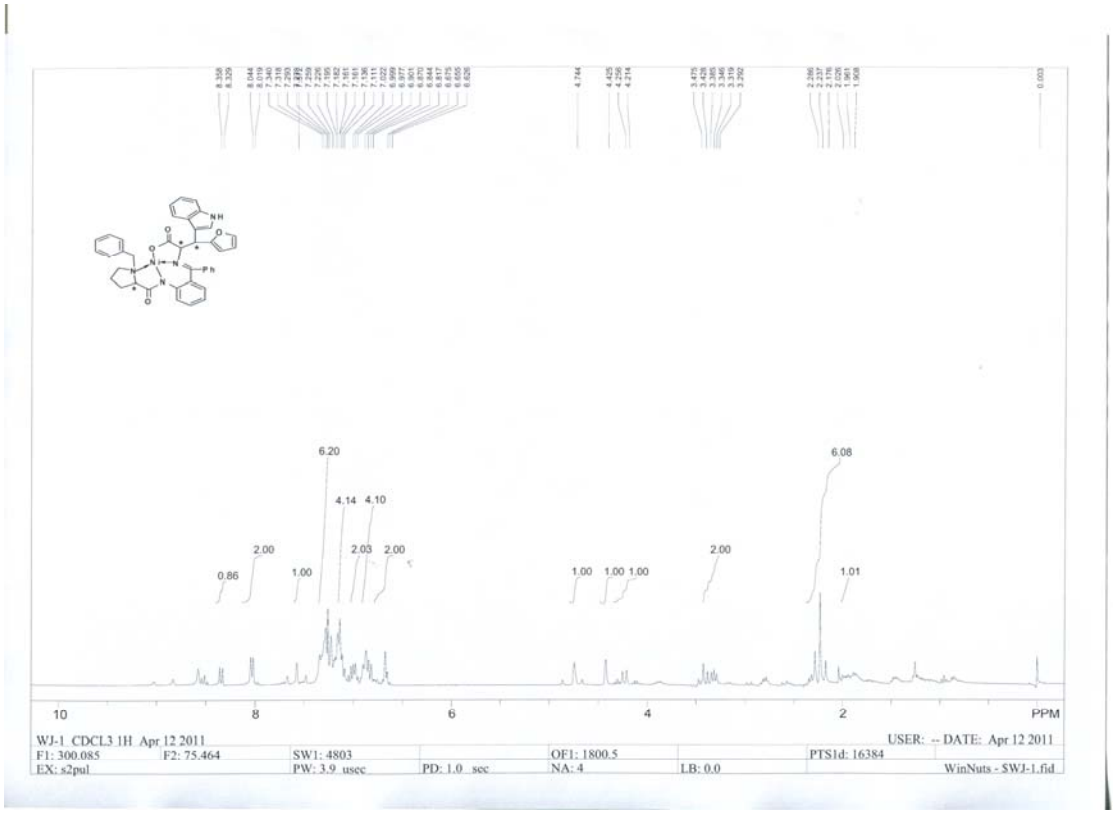


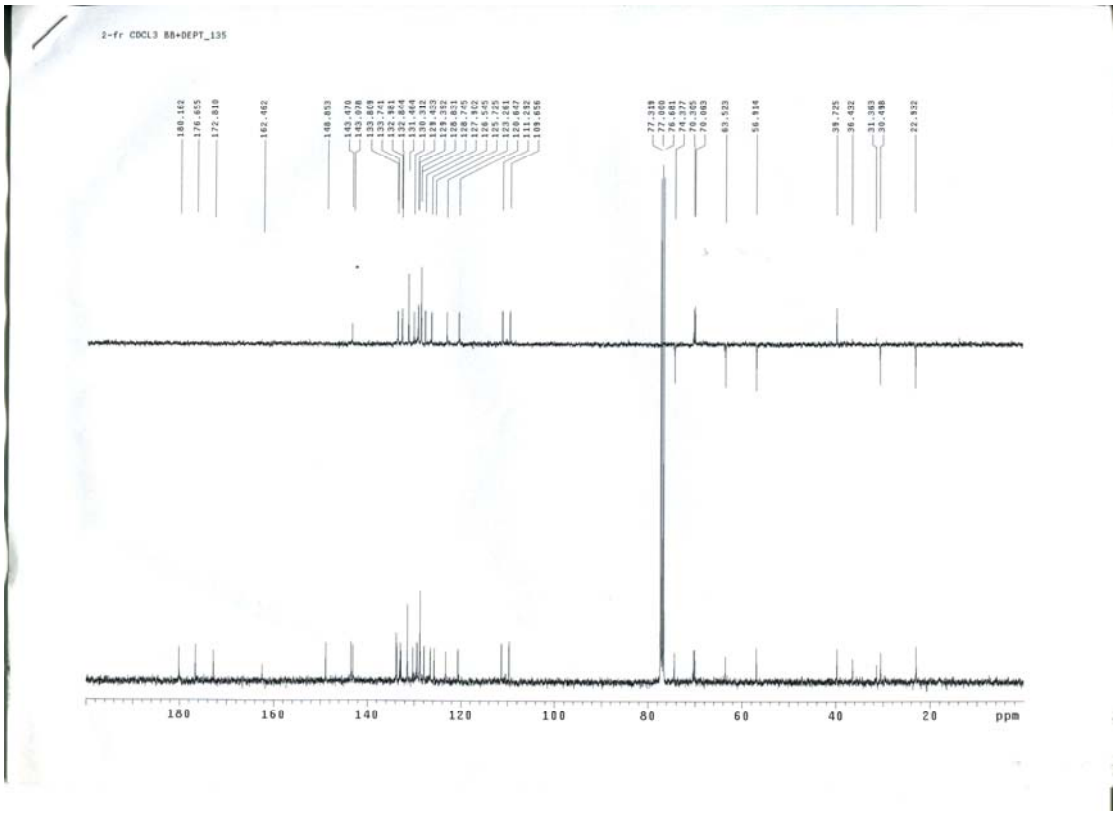
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-(4-bromo-phenyl)-propanoic Acid Schiff Base Complex 3h.



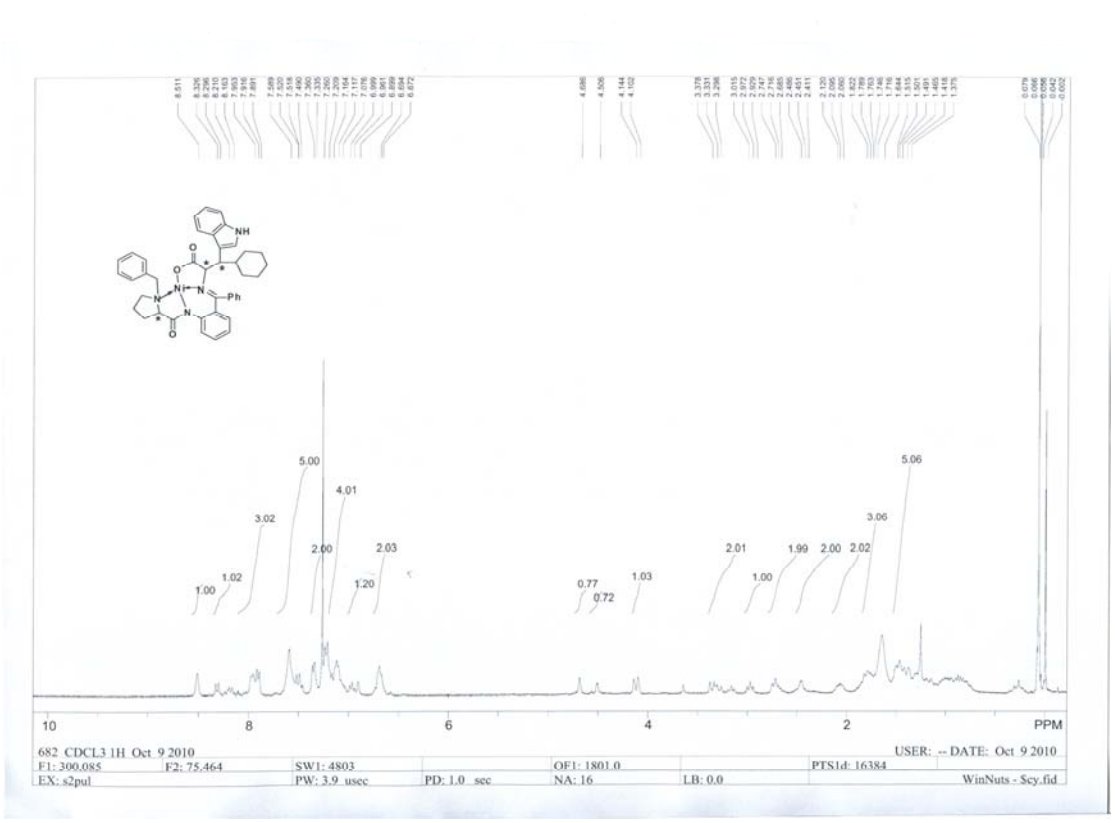


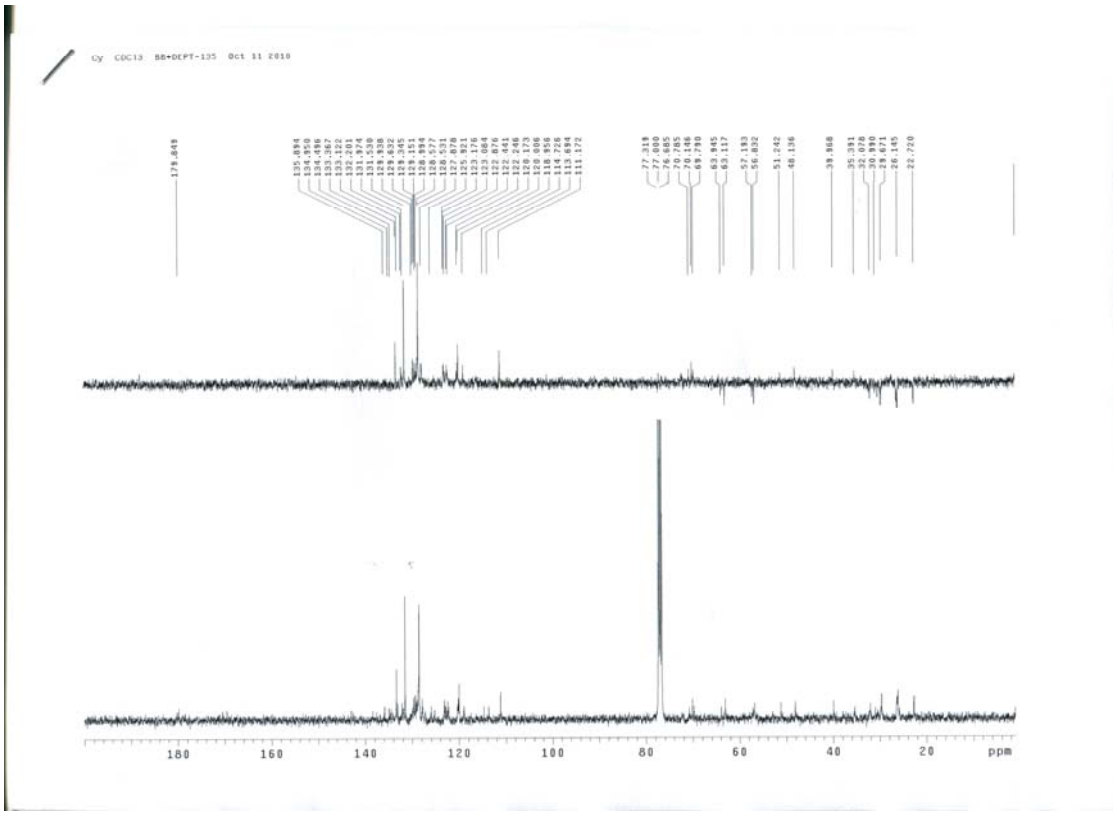
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-furan-2-yl-propanoic Acid Schiff Base Complex 3i.



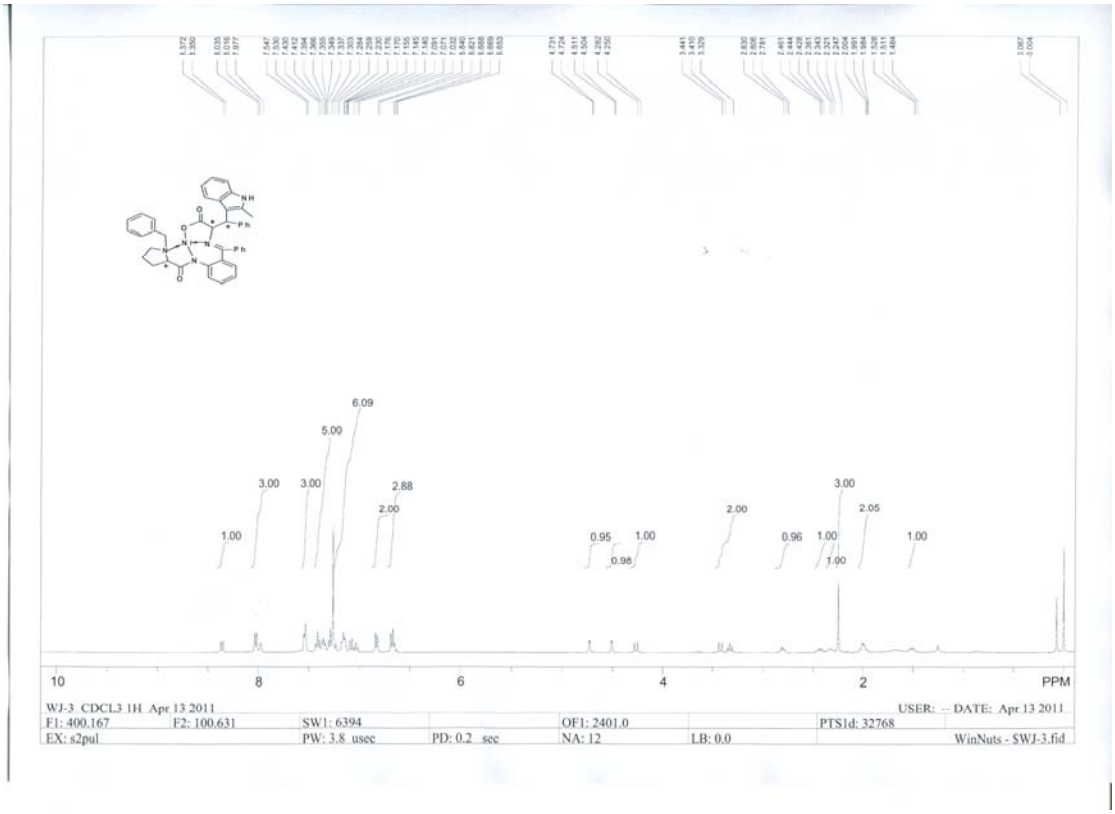


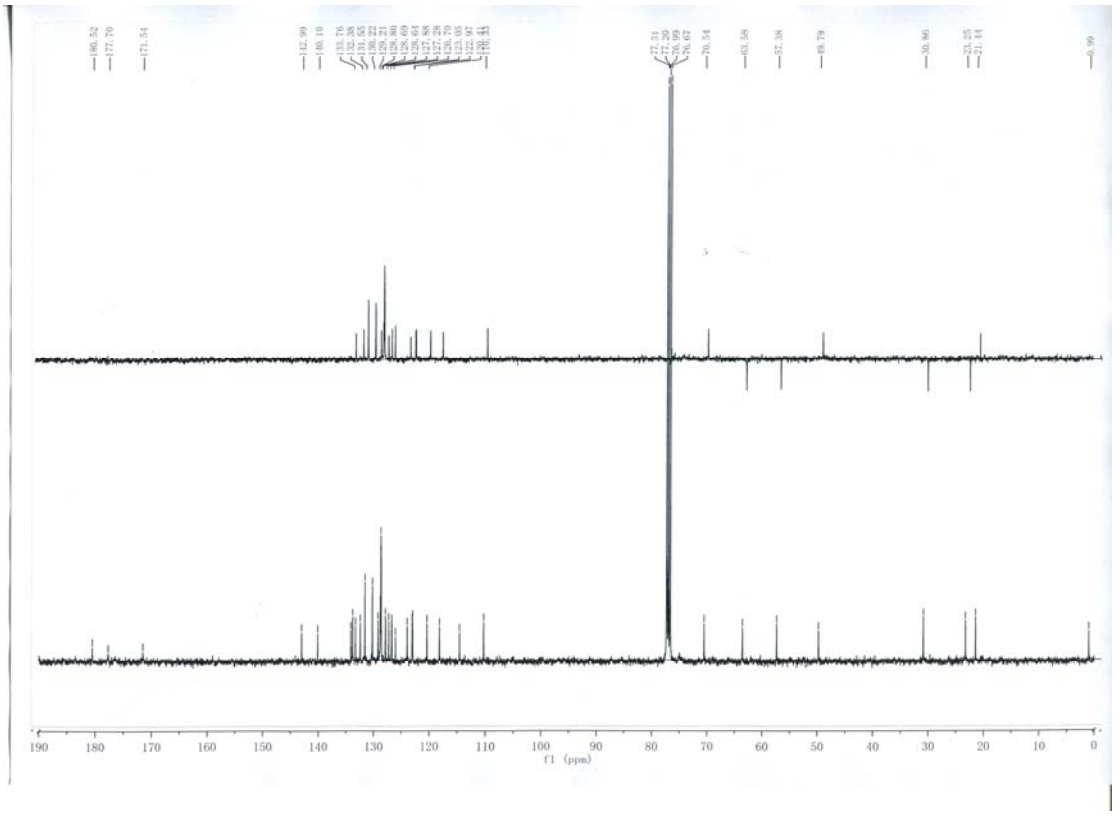
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(1*H*-indol-3-yl)-3-cyclohexyl-propanoic Acid Schiff Base Complex 3j.



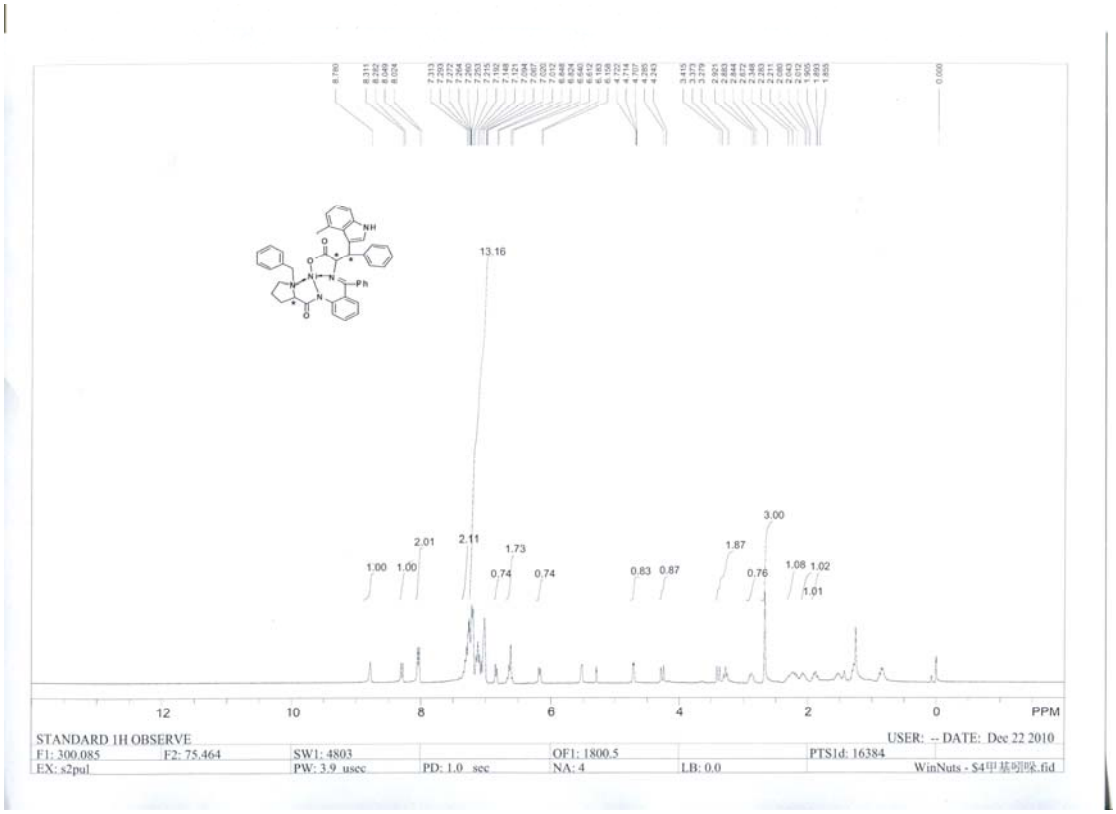


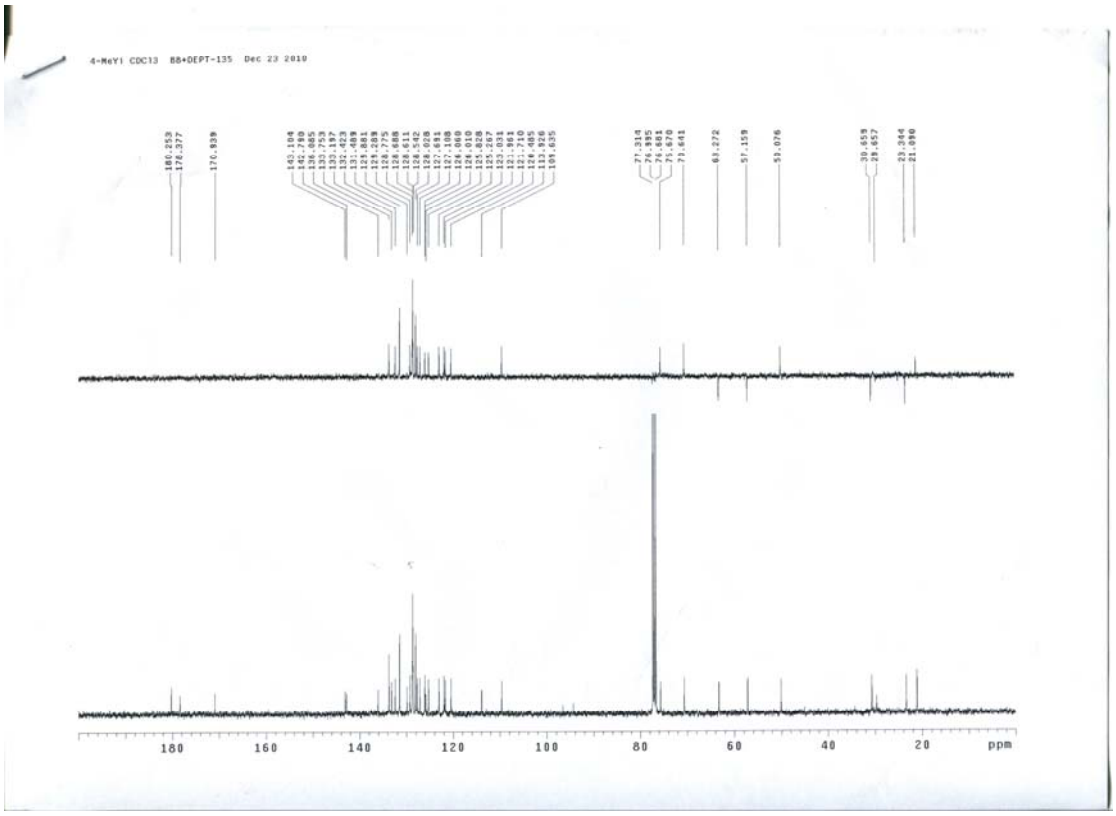
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(2-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3k.



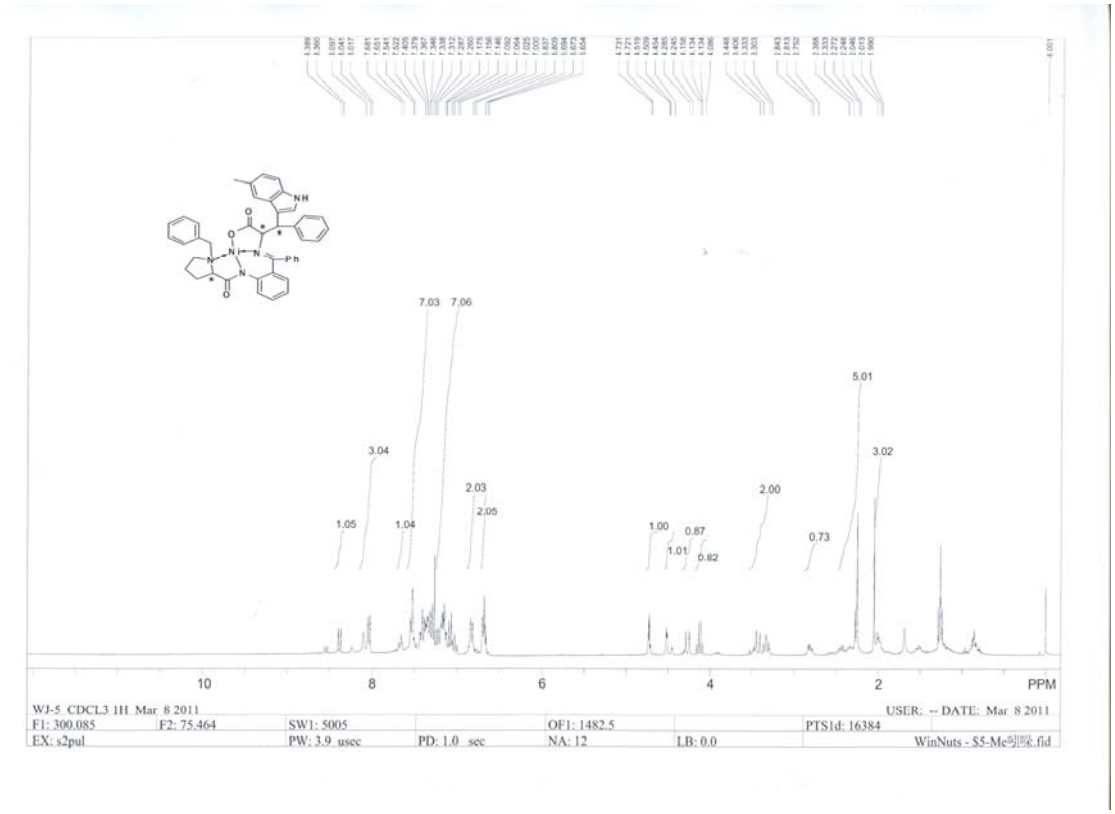


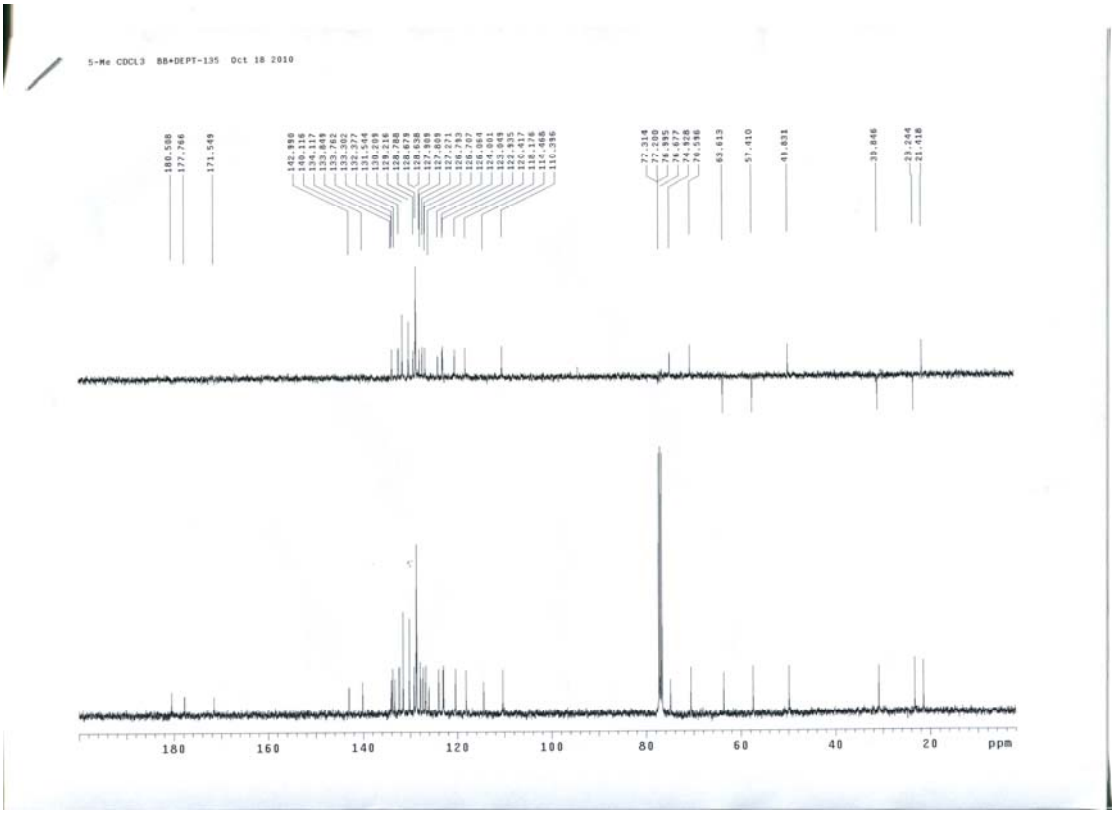
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(4-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3l.



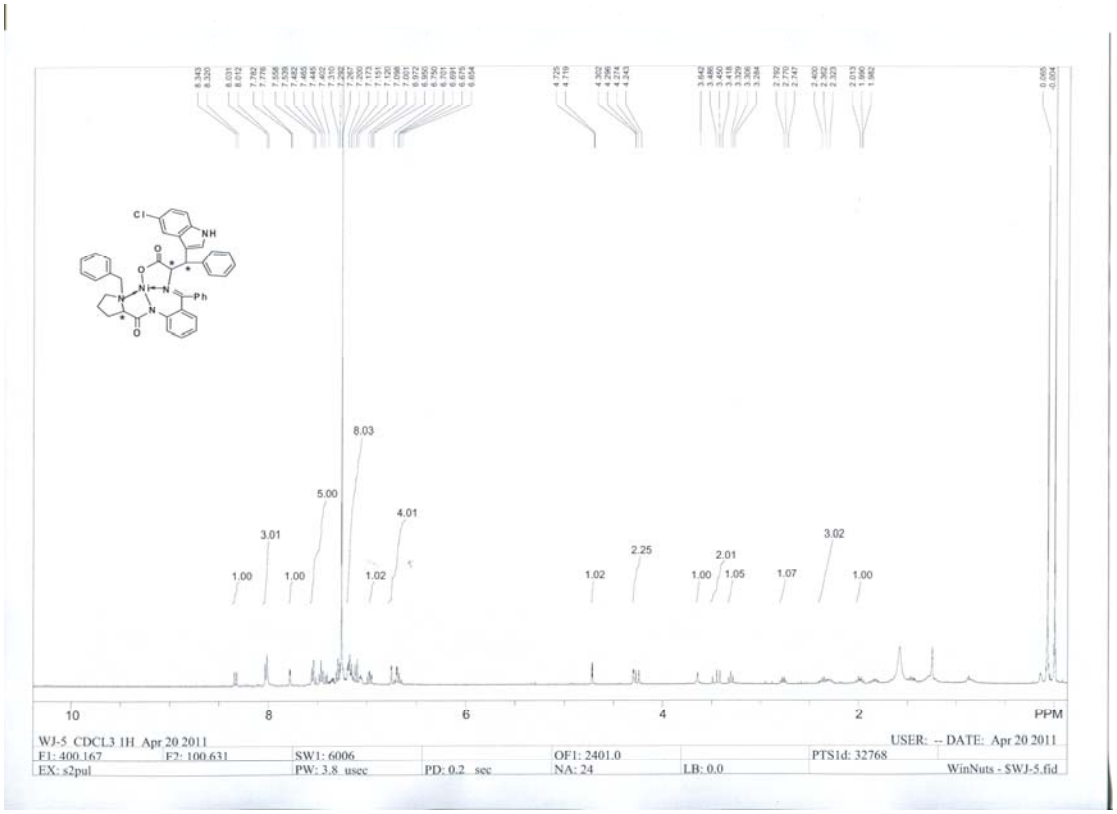


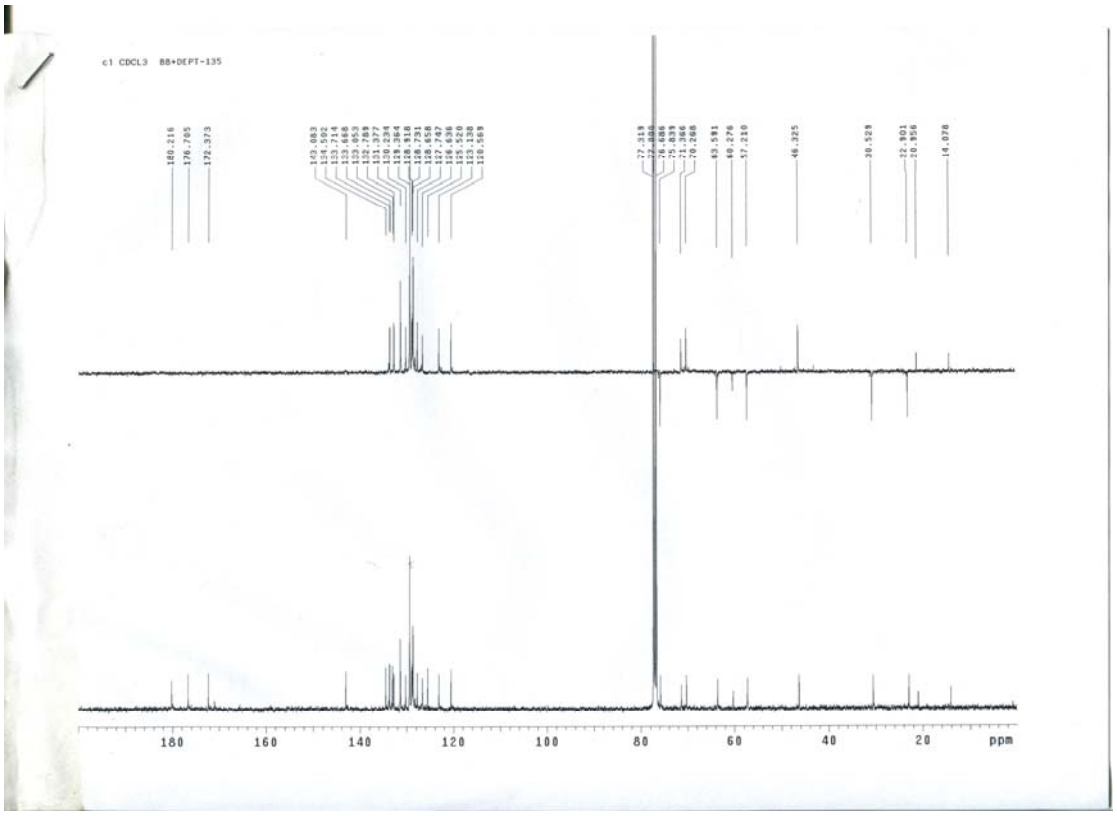
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(5-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3m.



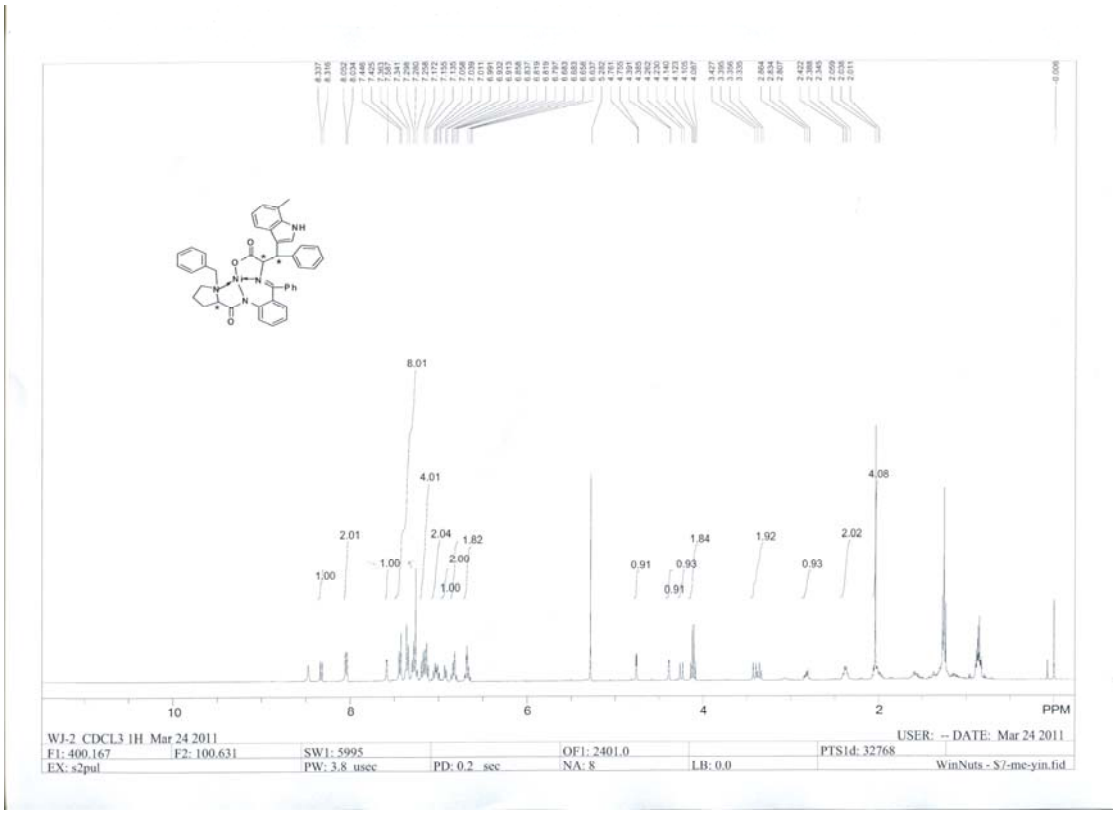


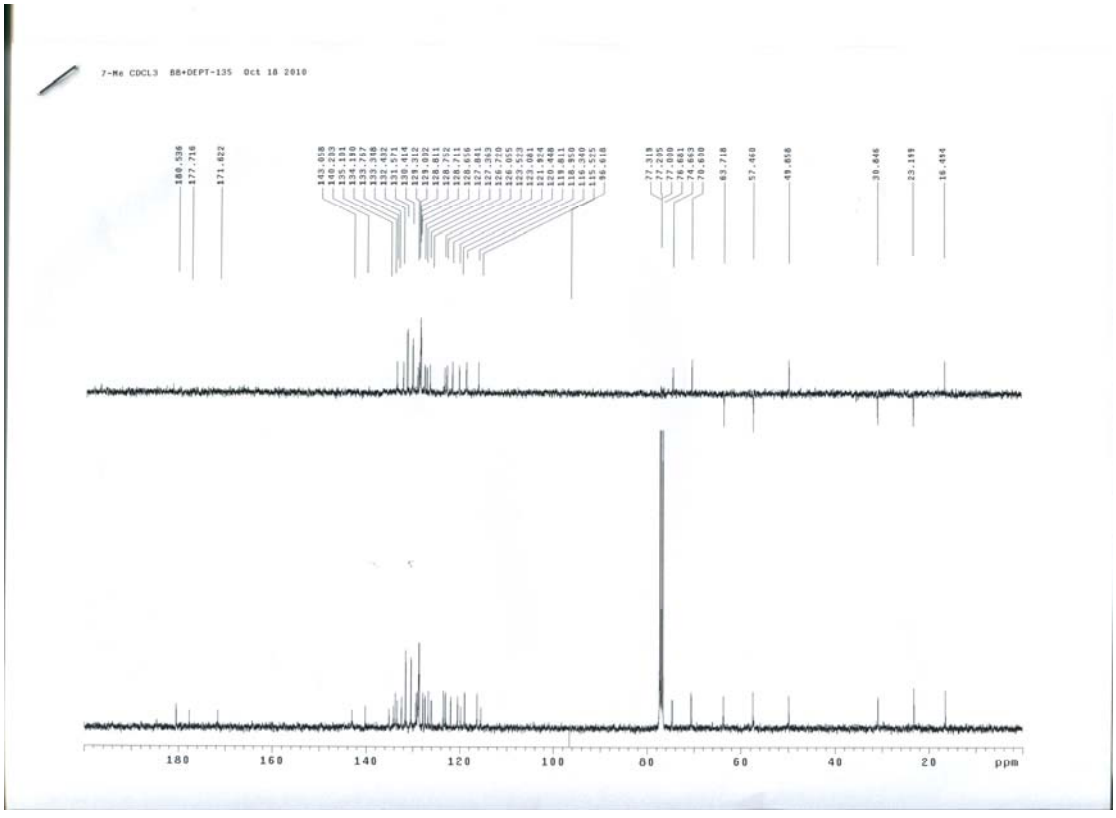
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(5-chloro-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3n.



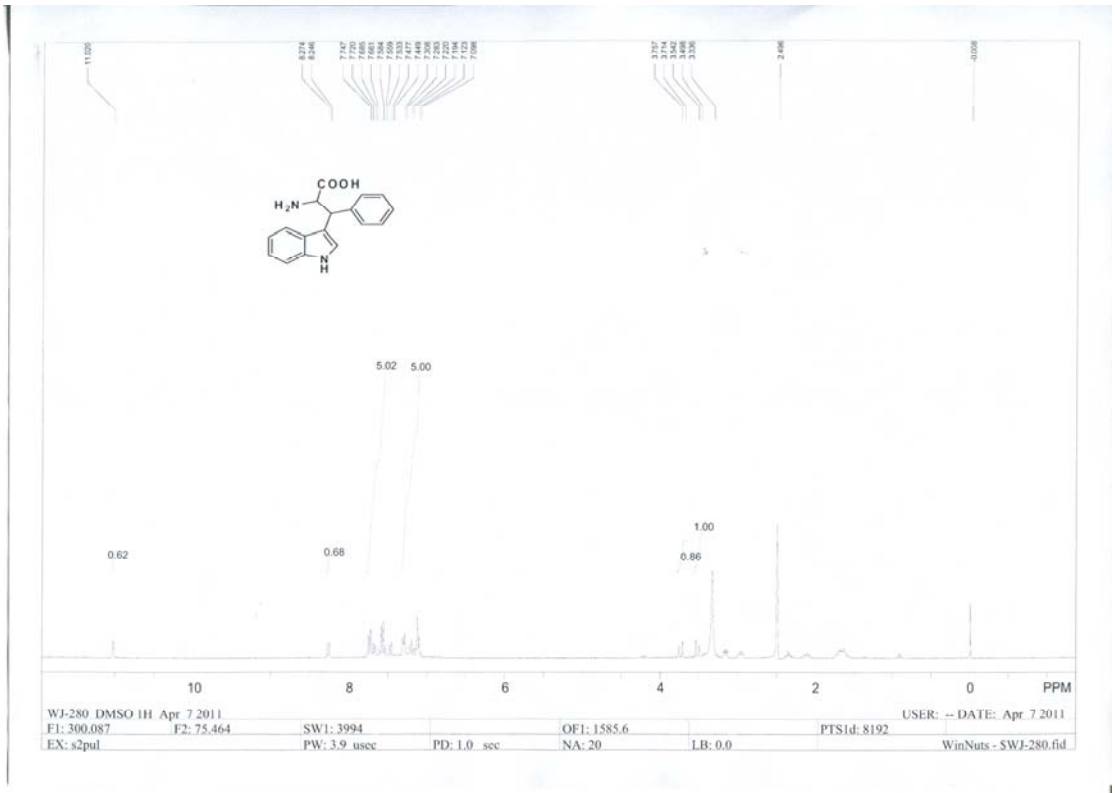


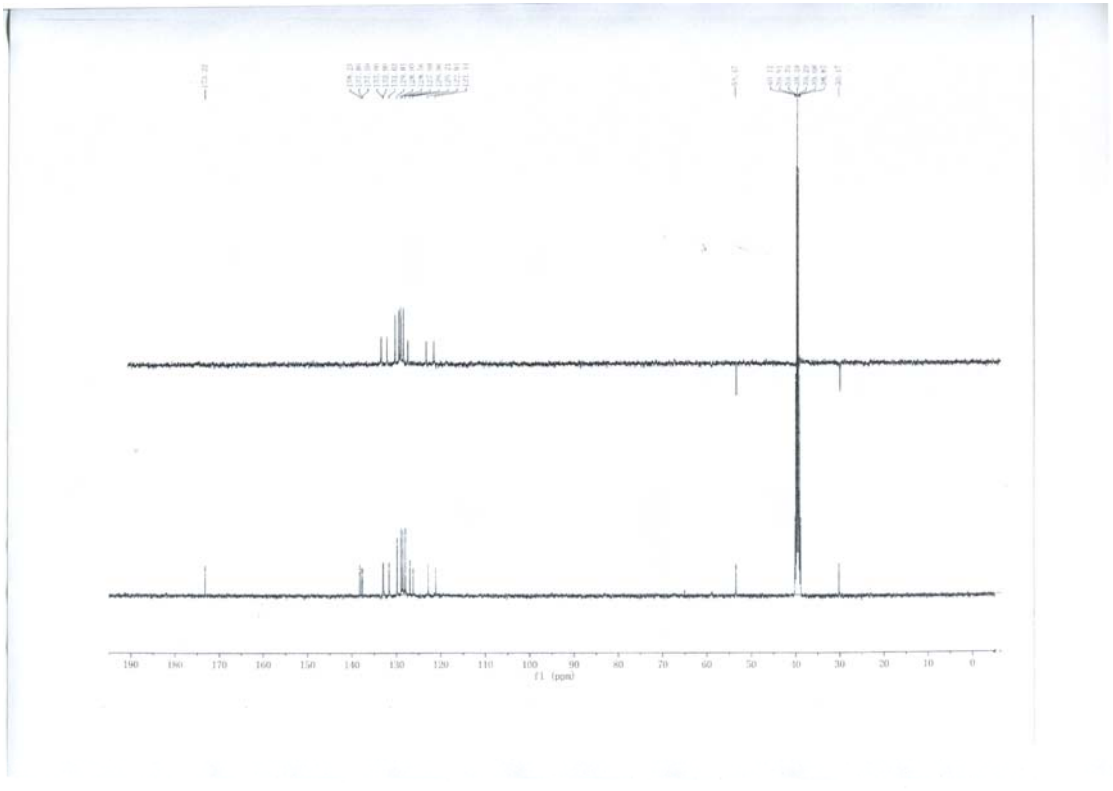
Nickel(II)-(S)-BPB/(2*S*,3*R*)-2-Amino-3-(7-methyl-1*H*-indol-3-yl)-3-phenyl-propanoic Acid Schiff Base Complex 3o.





(2*S*,3*R*)-2-amino-3-(*1H*-indol-3-yl)-3-phenylpropanoic acid 4a.





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