Electronic supplementary information

A General Synthesis of Unnatural α-Amino Acids by Iron-Catalyzed Olefin-Olefin Coupling via Generated Radicals

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1. General remarks

Whenever the use of dry solvents is mentioned below the reactions were conducted under an atmosphere of argon using *Schlenk*-line techniques in flame-dried glassware. The reported catalytic reactions were performed in Schlenk tubes (10 mL). All solvents were purchased from commercial suppliers. The Ni(II) complex **2** (*S*)-BPB-Ni-Δ-Ala was synthesized according to a literature procedure.[1] Methyl methyl(vinyl)phosphinate **3r** was synthesized according to a published procedures.[2,3] Purchased reagents from commercial suppliers were used without further purification. If not stated otherwise, flash column chromatography was performed with silica gel 60 M from Macherey-Nagel.

2. Instrumentation

Proton nuclear magnetic resonance (^{1}H-NMR) spectra and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Bruker Avance III-400 NMR spectrometer (operating at 400/101 MHz respectively referring to ^{1}H/^{13}C nucleus). Chemical shifts are reported in ppm relative to the residual solvent peak ($CDCl_3$: δ = 7.26 ppm for ^{1}H-NMR, δ = 77.2 for ^{13}C-NMR; D_2O: δ = 4.79 ppm for ^{1}H-NMR). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant, integration, and nucleus. High-resolution mass spectra were recorded on a AB Sciex TripleTOF 5600+ instrument using ESI ionization method (DuoSpray source). Optical rotations were measured on Schmidt+Haensch Polartronic H532 polarimeter in a 10-cm cell. X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer [λ(MoKα) = 0.71073 Å, ω-scans, 2θ<58^o].

3. General procedure for the olefin-olefin coupling of a chiral Ni(II) complex of dehydroalanine Schiff base 2 ((*S*)-BPB-Ni-Δ-Ala) with different olefins

A Schlenk tube (10 mL) was charged with a chiral Ni(II) complex **2** (51.0 mg, 0.1 mmol, 1.0 equiv.), catalyst $Fe(acac)_3$ (10.5 mg, 0.03 mmol), and vacuumed and purged with argon (3 times). Then, to a mixture were added 1,2-dichloroethane (0.75 mL), proton source (2.7 mmol, 27.0 equiv., in case of EtOH (0.16 mL)), olefin (0.5 mmol, 5 equiv.) and phenylsilane (0.06 mL, 0.15 mmol, 1.5 equiv.), and the mixture stirred at room temperature under argon atmosphere for 16 h. Full conversion for each reaction confirmed by TLC analysis. Then the solvent was evaporated and the residue was purified by preparative TLC or column flash chromatography on SiO_2 to afford the desired product.

Ni(II) complex (*S*,*S*)-4a

Starting from a chiral Ni(II) complex **2** and 1-methyl-1-cyclohexene **3a** with applying the general procedure, the desired product (*S*,*S*)-**4a** was isolated as a red powder (54.8 mg, yield 90%, *dr* >20:1). Eluent: $CHCl_3$/acetone (5:1).

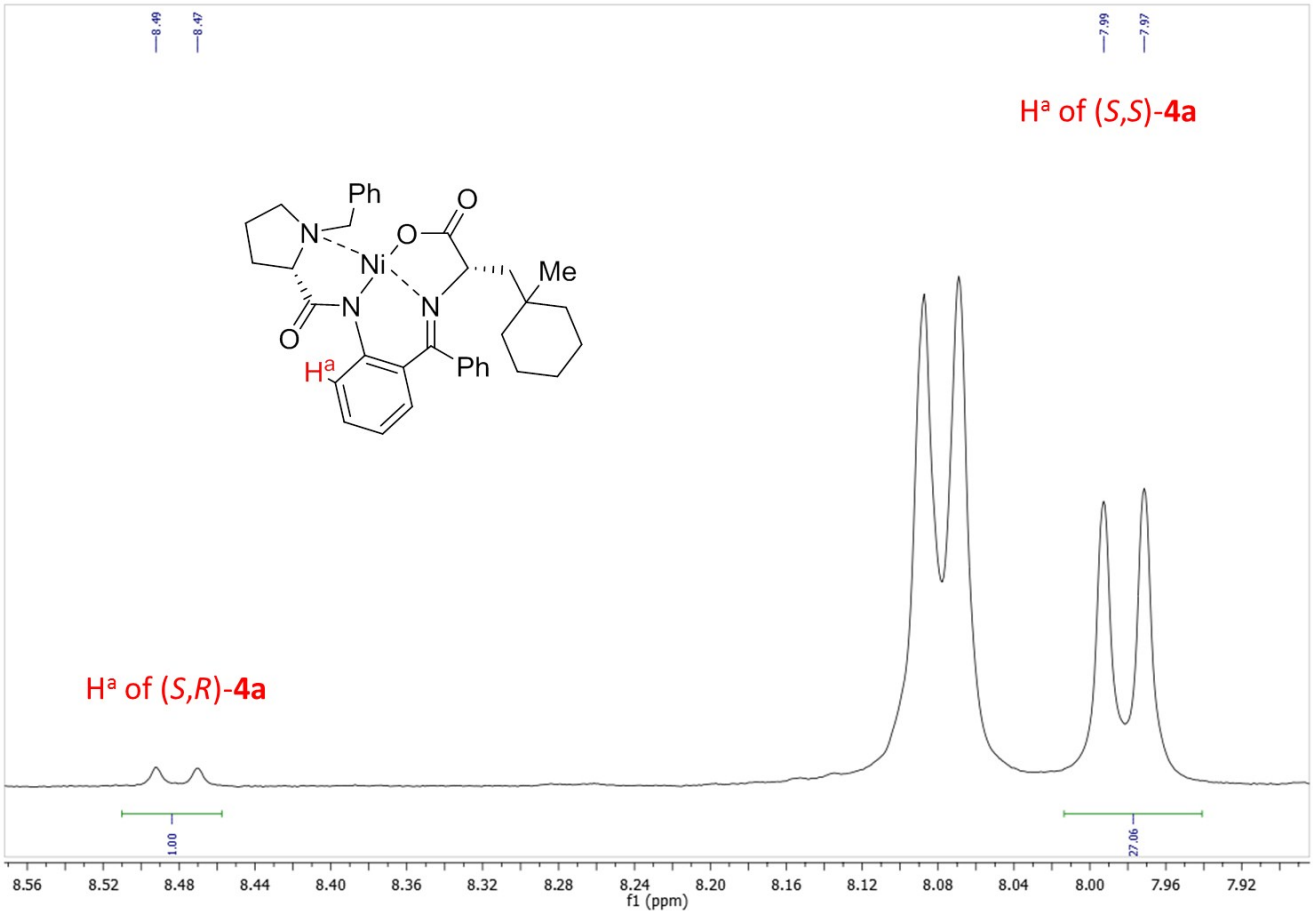
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.3 Hz, 2H), 7.97 (d, J = 8.5 Hz, 1H), 7.53–7.40 (m, 3H), 7.33 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 6.9 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.14–7.06 (m, 1H), 6.93 (d, J = 7.2 Hz, 1H), 6.67–6.55 (m, 2H), 4.42 (d, J = 12.6 Hz, 1H), 3.89 (dd, J = 11.1, 3.7 Hz, 1H), 3.84–3.70 (m, 1H), 3.57–3.43 (m, 3H), 3.05–2.93 (m, 1H), 2.84–2.71 (m, 1H), 2.60–2.47 (m, 1H), 2.29–2.17 (m, 1H), 2.13–2.04 (m, 1H), 1.53 (dd, J = 13.8, 3.7 Hz, 1H), 1.37–1.17 (m, 8H), 1.05–0.94 (m, 1H), 0.87–0.74 (m, 1H), 0.67 (s, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 180.1, 168.7, 142.0, 133.5, 133.3, 133.1, 131.9, 131.6, 131.3, 129.8, 129.1, 129.0, 128.9, 127.9, 127.8, 126.9, 123.9, 120.9, 70.3, 68.3, 63.0, 57.2, 49.0, 38.2, 37.5, 33.0, 30.8, 26.0, 25.1, 24.1, 21.8, 21.7 ppm.

HRMS (ESI, m/z) calcd. for $C_{35}H_{40}N_3NiO_3^+$ $[M+H]^+$: 608.2418, found: 608.2441.

The structure of (S,S)-**4a** was determined by single crystal X-ray analysis (see Scheme 2 in main text and Part 5 in the SI).

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^{a} in (S,S)-**4a** and (S,R)-**4a** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* >20:1 for (S,S)-**4a**/(S,R)-**4a**.



Ni(II) complex (*S*,*S*)-4b

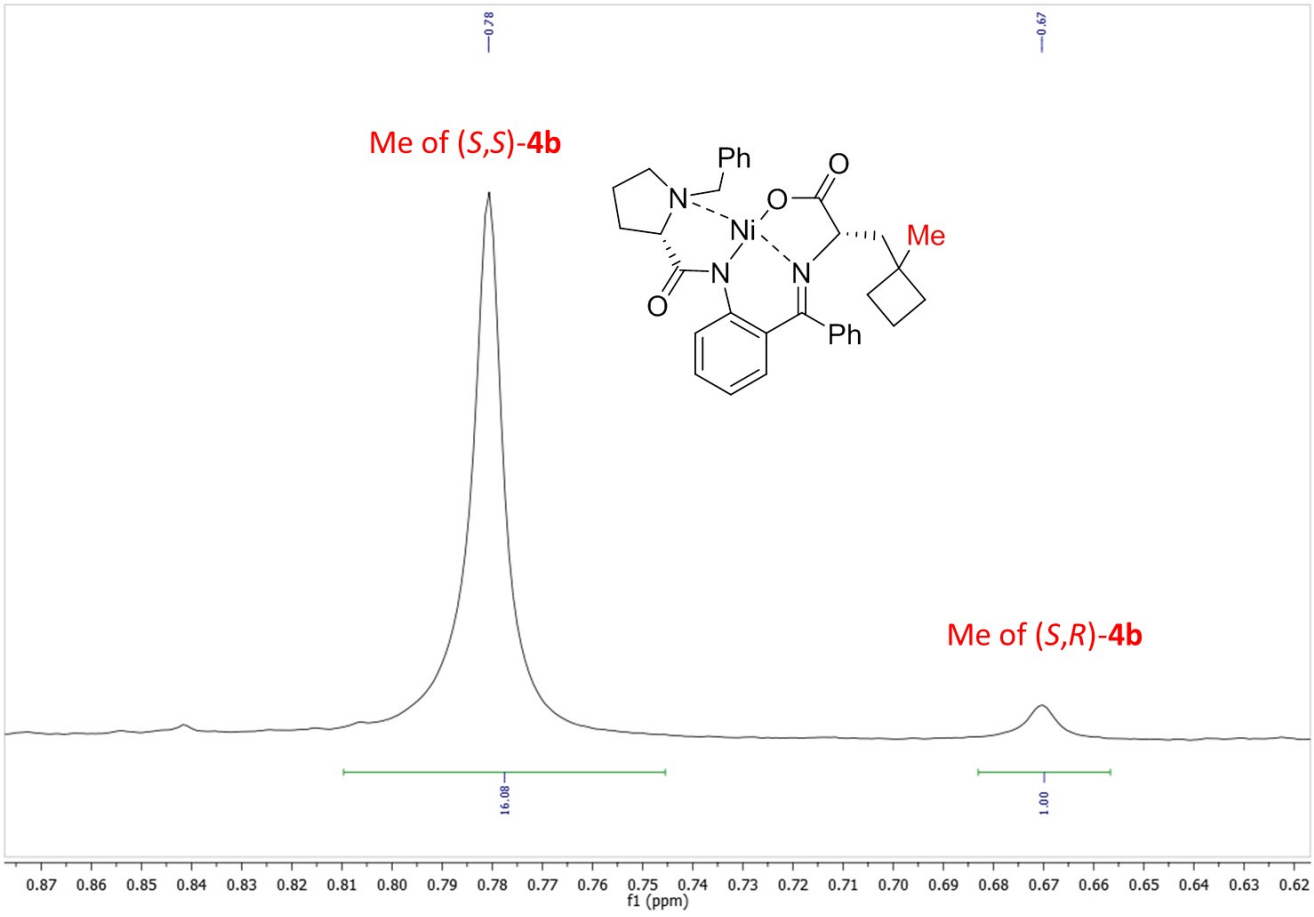
Starting from a chiral Ni(II) complex **2** and methylenecyclobutane **3b** with applying the general procedure, the desired product (*S*,*S*)-**4b** was isolated as a red powder (40.0 mg, yield 69%, *dr* 16:1). Eluent: $CHCl_3$/acetone (5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09–7.99 (m, 3H), 7.54–7.41 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30–7.27 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.16–7.09 (m, 1H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.69–6.60 (m, 2H), 4.44 (d, *J* = 12.7 Hz, 1H), 3.92–3.73 (m, 2H), 3.57 (d, *J* = 12.7 Hz, 1H), 3.55–3.44 (m, 2H), 3.06 (dd, *J* = 13.2, 11.3 Hz, 1H), 2.88–2.76 (m, 1H), 2.64–2.50 (m, 1H), 2.31–2.20 (m, 1H), 2.13–2.03 (m, 1H), 1.89–1.79 (m, 2H), 1.79–1.68 (m, 2H), 1.66–1.54 (m, 3H), 0.78 (s, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.3, 179.0, 169.0, 142.0, 133.4, 133.3, 133.1, 131.9, 131.6, 129.7, 128.9, 128.88, 128.84, 127.7, 127.6, 126.6, 123.9, 120.8, 70.3, 68.2, 63.0, 57.1, 50.2, 37.4, 35.1, 33.7, 30.8, 24.2, 24.1, 15.6 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{33}H_{36}N_3NiO_3^+$ $[M+H]^+$: 580.2105, found: 580.2110.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of Me group in (*S*,*S*)-**4b** and (*S*,*R*)-**4b** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 16:1 for (*S*,*S*)-**4b**/(*S*,*R*)-**4b**.



Ni(II) complex (*S*,*S*)-4c

Starting from a chiral Ni(II) complex **2** and α-methyl styrene **3c** with applying the general procedure, the desired product (*S*,*S*)-**4c** was isolated as a red powder (58.0 mg, yield 92%, *dr* >20:1). Eluent: $CHCl_3$/acetone (5:1).

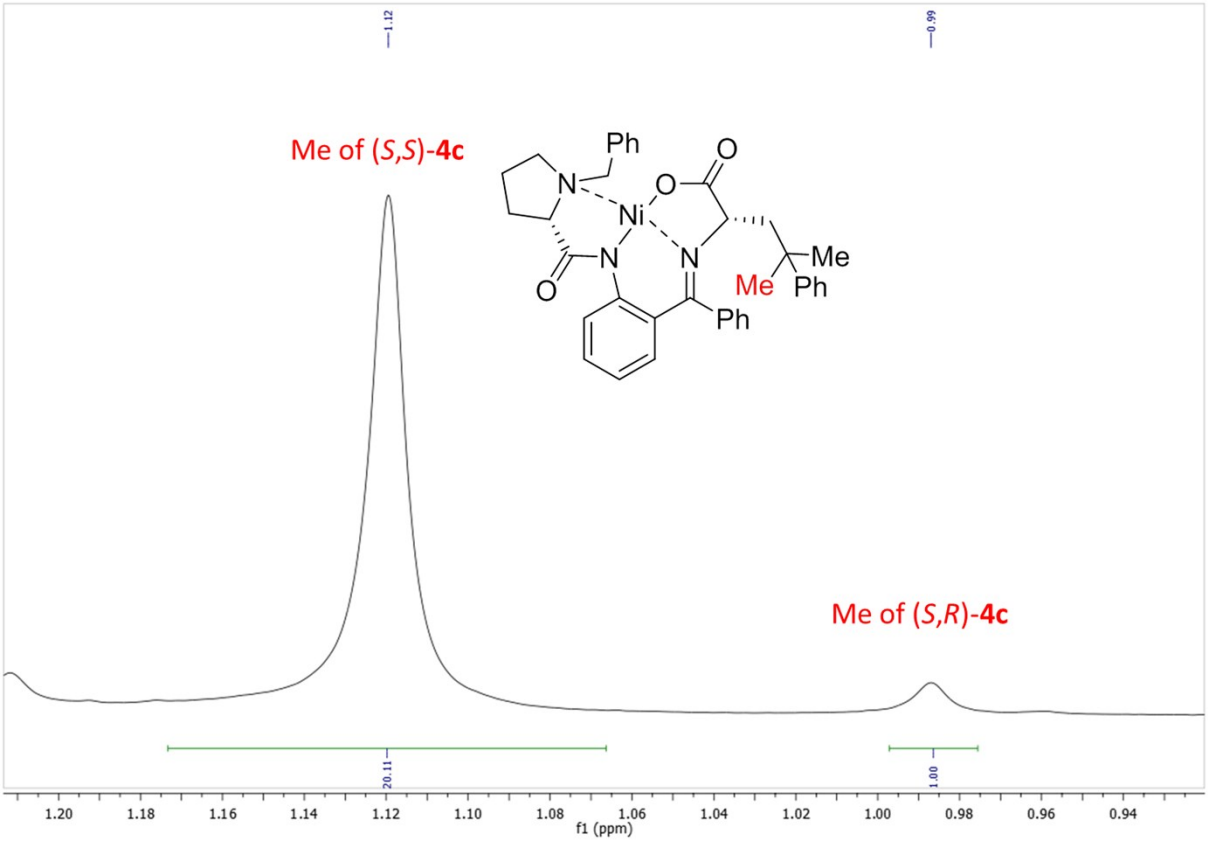
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.4 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.56–7.43 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24–7.14 (m, 4H), 7.14–7.05 (m, 4H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.65–6.58 (m, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 4.40 (d, *J* = 12.6 Hz, 1H), 3.89–3.74 (m, 2H), 3.58–3.43 (m, 3H), 3.38–3.27 (m, 1H), 2.82–2.72 (m, 1H), 2.64–2.48 (m, 1H), 2.33–2.23 (m, 1H), 2.12–2.03 (m, 1H), 1.93 (dd, *J* = 13.8, 4.0 Hz, 1H), 1.26 (s, 3H), 1.12 (s, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.3, 178.9, 169.0, 148.4, 142.1, 133.4, 133.3, 133.1, 132.0, 131.6, 129.8, 129.1, 128.9, 128.87, 128.0, 127.9, 127.6, 126.7, 125.7, 125.3, 123.8, 120.8, 70.2, 68.7, 63.0, 57.2, 51.6, 37.2 30.8, 27.6, 24.2 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_3^+$ $[M+H]^+$: 630.2261, found: 630.2285.

The structure of (*S*,*S*)-**4c** was determined by single crystal X-ray analysis (see Scheme 2 in main text and Part 5 in the SI).

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of Me group in (*S*,*S*)-**4c** and (*S*,*R*)-**4c** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* >20:1 for (*S*,*S*)-**4c**/(*S*,*R*)-**4c**.



Ni(II) complex (*S*,*S*)-4d

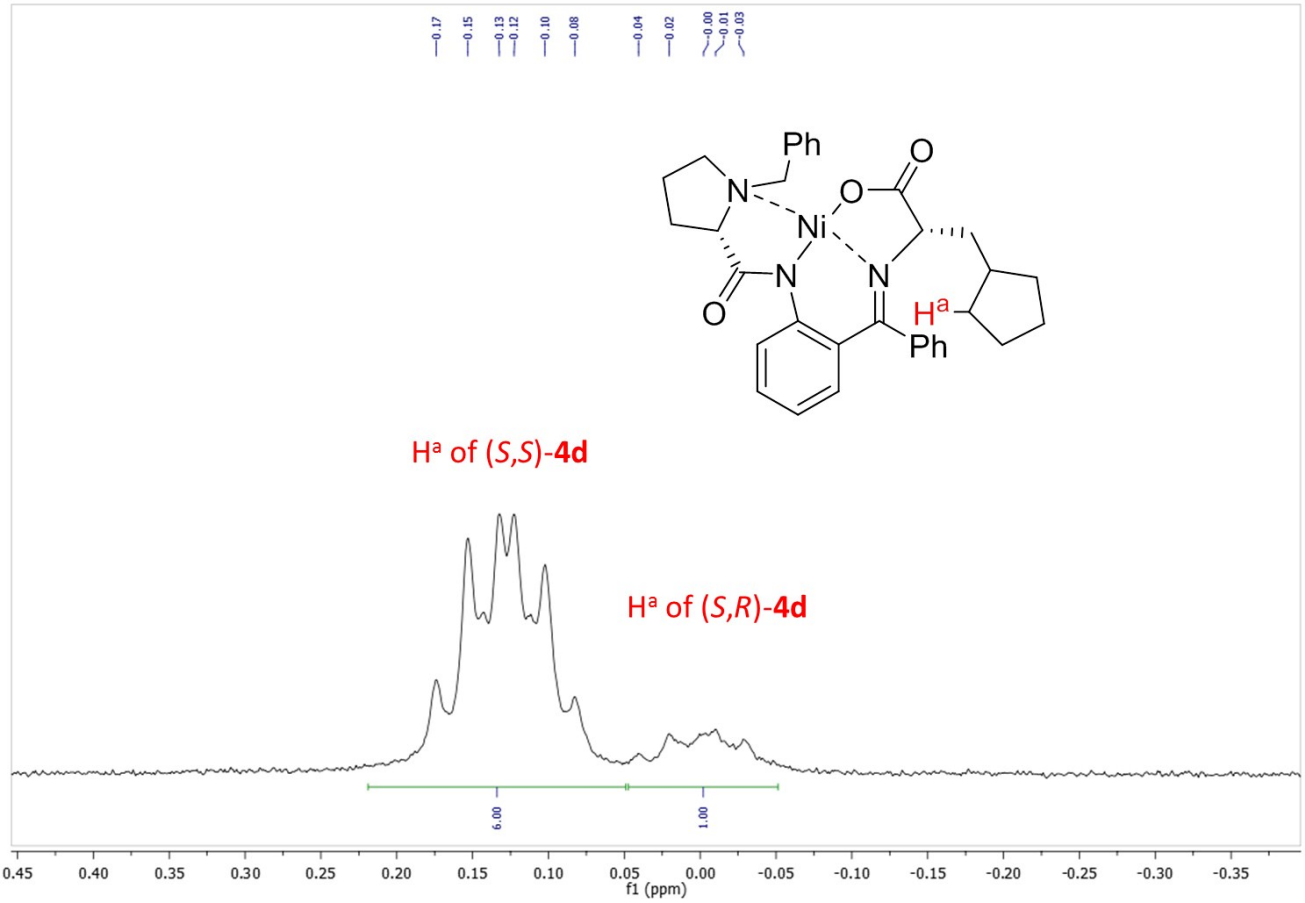
Starting from a chiral Ni(II) complex **2** and cyclopentene **3d** with applying the general procedure, the desired product (*S*,*S*)-**4d** was isolated as a red powder (43.5 mg, yield 75%, *dr* 6:1). Eluent: $CHCl_3$/acetone (5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.14–7.99 (m, 3H), 7.53–7.41 (m, 3H), 7.34 (t, J = 7.6 Hz, 2H), 7.30–7.26 (m, 1H), 7.18 (t, J = 7.5 Hz, 1H), 7.15–7.08 (m, 1H), 6.92 (d, J = 7.3 Hz, 1H), 6.68–6.57 (m, 2H), 4.46 (d, J = 12.6 Hz, 1H), 3.87 (dd, J = 10.2, 3.5 Hz, 1H), 3.71–3.60 (m, 1H), 3.58–3.42 (m, 3H), 2.81–2.66 (m, 1H), 2.56–2.44 (m, 2H), 2.26–2.18 (m, 1H), 2.11–2.01 (m, 1H), 1.96–1.85 (m, 1H), 1.57–1.27 (m, 7H), 1.07–0.94 (m, 1H), 0.20–0.06 (m, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.4, 169.8, 142.1, 133.7, 133.3, 133.1, 132.0, 131.6, 129.7, 129.1, 128.9, 128.88, 128.86, 127.8, 127.6, 126.6, 123.8, 120.7, 70.2, 70.1, 63.0, 57.2, 42.9, 36.0, 33.7, 31.2, 30.7, 25.0, 24.8, 24.0 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{33}H_{36}N_3NiO_3^+$ $[M+H]^+$: 580.2105, found: 580.2118.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a in (*S*,*S*)-**4d** and (*S*,*R*)-**4d** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 6:1 for (*S*,*S*)-**4d**/(*S*,*R*)-**4d**.



Ni(II) complex (*S*,*S*)-4e

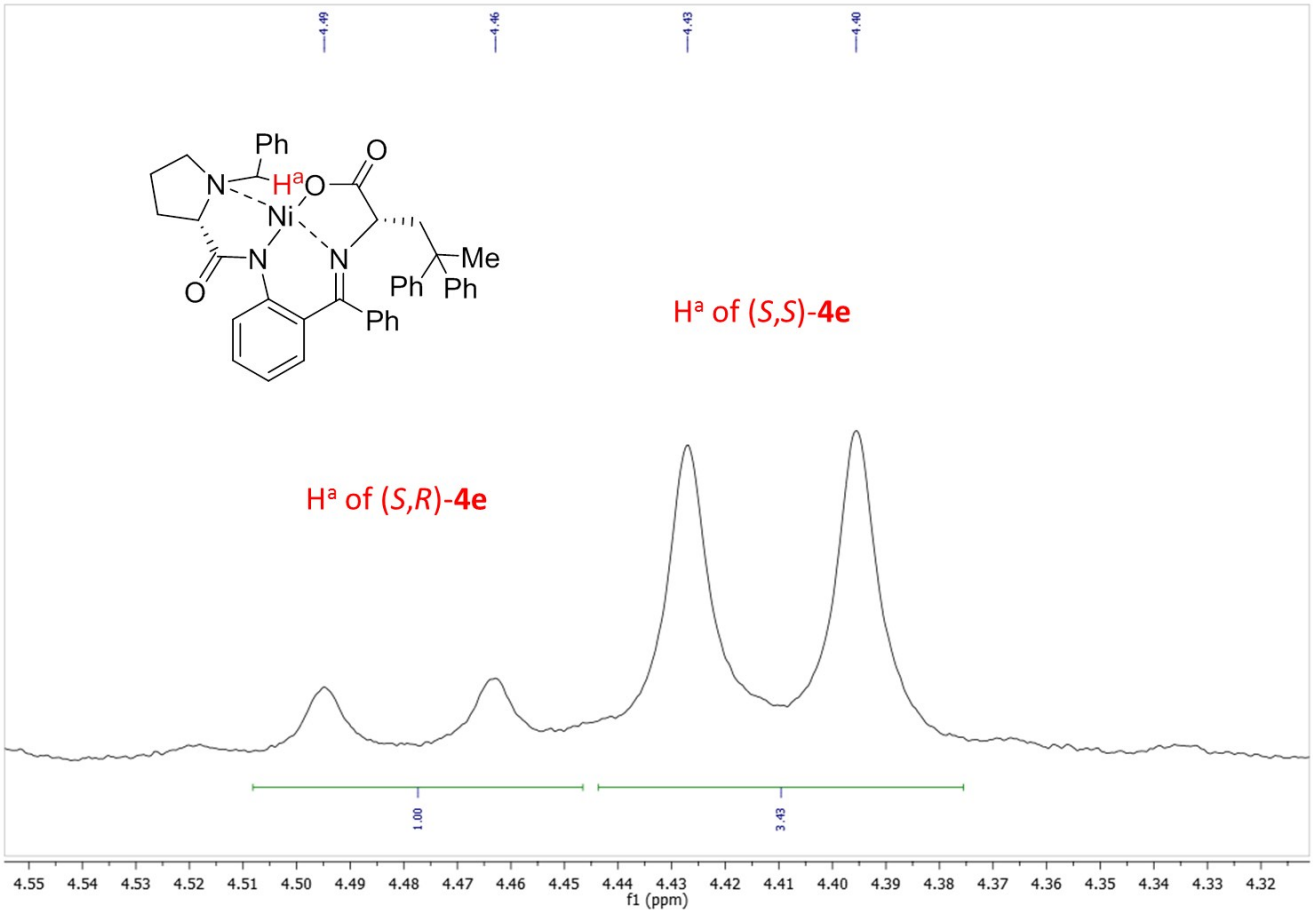
Starting from a chiral Ni(II) complex **2** and 1,1-diphenylethylene **3e** with applying the general procedure, the desired product (*S*,*S*)-**4e** was isolated as a red powder (20.8 mg, yield 30%, *dr* 3.4:1). Eluent: $CHCl_3$/acetone (7:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07–8.03 (m, 3H), 7.53–7.47 (m, 1H), 7.47–7.40 (m, 1H), 7.38–7.29 (m, 4H), 7.25–7.16 (m, 6H), 7.15–7.09 (m, 2H), 7.08–6.99 (m, 3H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.81–6.75 (m, 1H), 6.67–6.61 (m, 1H), 6.56–6.49 (m, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 4.06–3.84 (m, 2H), 3.73–3.64 (m, 1H), 3.60–3.47 (m, 3H), 2.90–2.81 (m, 1H), 2.62–2.55 (m, 1H), 2.51 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.37–2.26 (m, 1H), 2.13–2.05 (m, 1H), 1.57 (s, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 178.3, 169.2, 149.9, 146.9, 142.1, 133.3, 133.2, 132.1, 131.7, 131.6, 129.8, 129.1, 129.0, 128.92, 128.90, 128.0, 127.9, 127.6, 127.0, 126.7, 125.9, 125.7, 125.3, 123.8, 120.8, 120.1, 70.3, 68.6, 63.0, 57.2, 48.8, 45.2, 30.9, 27.0, 24.3 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{42}H_{40}N_3NiO_3^+$ $[M+H]^+$: 692.2418, found: 692.2402.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a in (*S*,*S*)-**4e** and (*S*,*R*)-**4e** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 3.4:1 for (*S*,*S*)-**4e**/(*S*,*R*)-**4e**.



Ni(II) complex (*S*,*S*)-4f

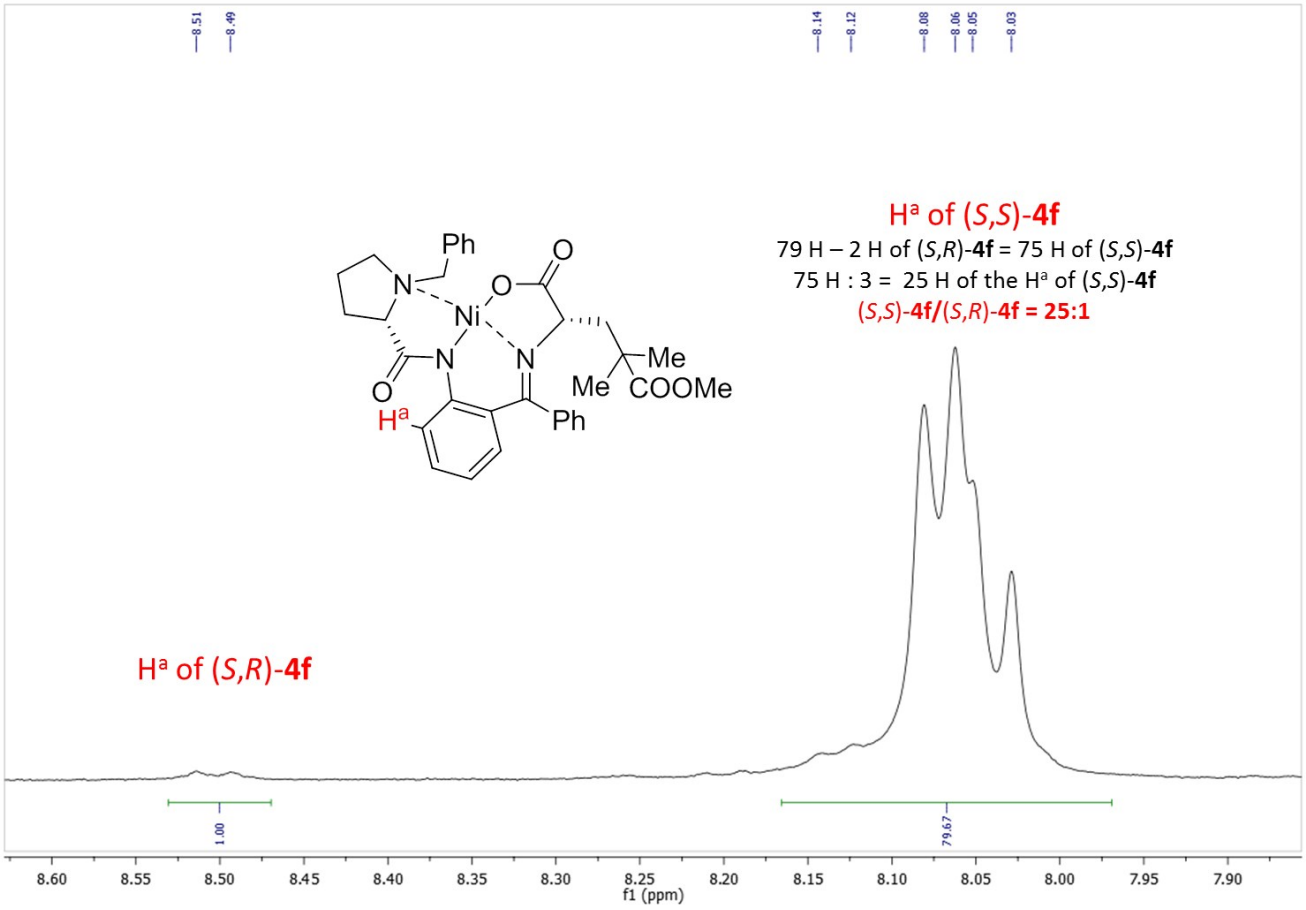
Starting from a chiral Ni(II) complex **2** and methyl methacrylate **3f** with applying the general procedure, the desired product (*S*,*S*)-**4f** was isolated as a red powder (54.5 mg, yield 89%, *dr* >20:1). Eluent: $CHCl_3$/acetone (5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11–7.99 (m, 3H), 7.58–7.42 (m, 3H), 7.41–7.31 (m, 2H), 7.31–7.27 (m, 1H), 7.22–7.09 (m, 2H), 6.97 (d, J = 7.3 Hz, 1H), 6.71–6.60 (m, 2H), 4.41 (d, J = 12.6 Hz, 1H), 3.94–3.85 (m, 2H), 3.58 (s, 3H), 3.55–3.43 (m, 3H), 2.86–2.74 (m, 1H), 2.61–2.47 (m, 1H), 2.36–2.23 (m, 1H), 2.14–2.03 (m, 1H), 1.88–1.65 (m, 1H), 1.41 (dd, J = 13.4, 4.1 Hz, 1H), 1.08 (s, 3H), 0.75 (s, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 178.4, 176.6, 169.7, 142.2, 133.4, 133.3, 133.1, 132.1, 131.6, 129.9, 129.0, 128.9, 128.8, 127.7, 127.6, 126.5, 123.9, 120.8, 70.4, 67.8, 63.0, 57.4, 51.7, 45.4, 40.5, 30.9, 23.8, 21.6 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{33}H_{36}N_3NiO_5^+$ $[M+H]^+$: 612.2003, found: 612.2028.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a in (*S*,*S*)-**4f** and (*S*,*R*)-**4f** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* >20:1 for (*S*,*S*)-**4f**/(*S*,*R*)-**4f**.



Ni(II) complex (*S*,*S*)-4g

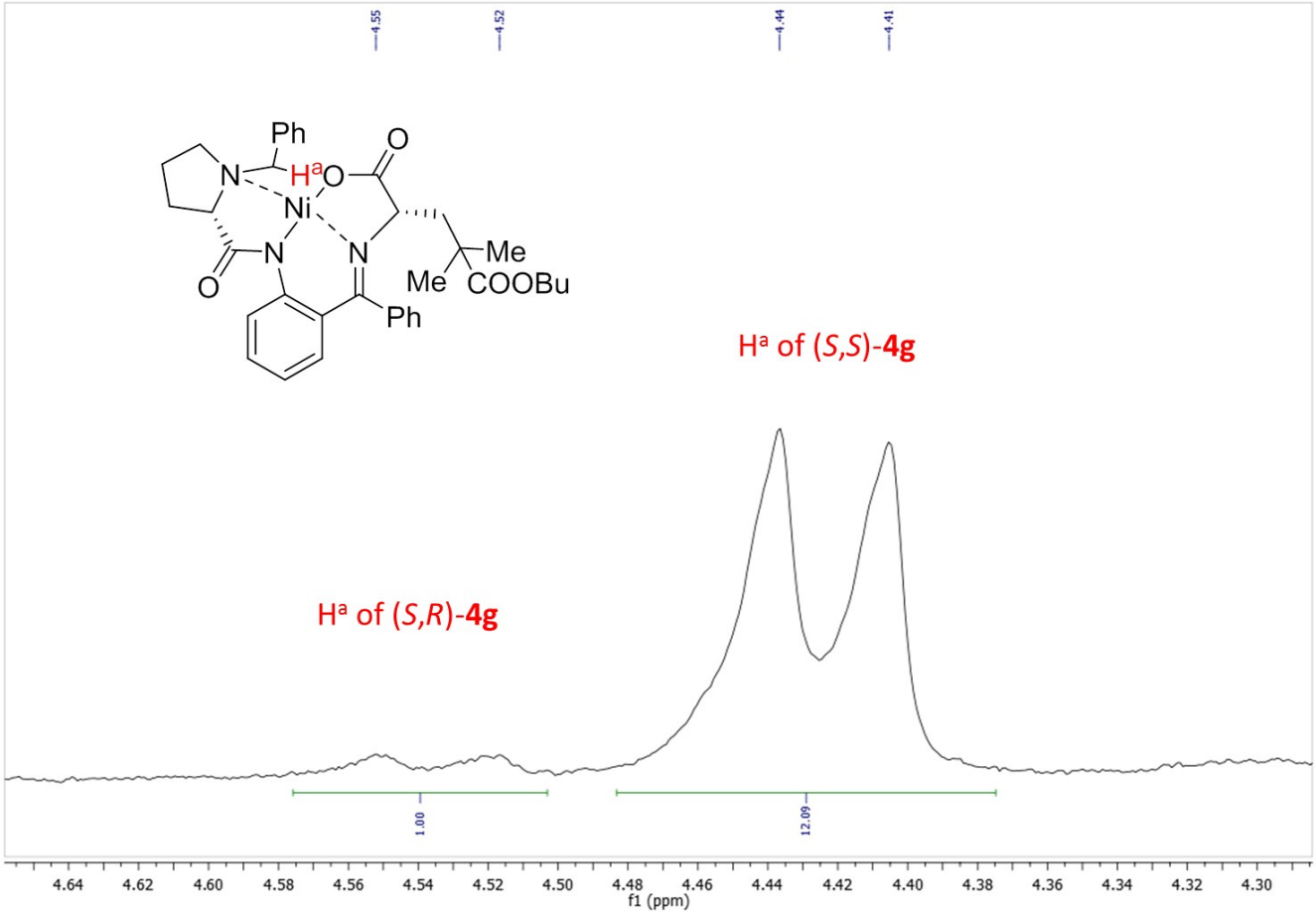
Starting from a chiral Ni(II) complex **2** and butyl methacrylate **3g** with applying the general procedure, the desired product (*S*,*S*)-**4g** was isolated as a red powder (55.6 mg, yield 85%, *dr* 12:1). Eluent: $CHCl_3$/acetone (5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11–8.02 (m, 3H), 7.56–7.43 (m, 3H), 7.34 (t, J = 7.5 Hz, 2H), 7.31–7.27 (m, 1H), 7.24–7.08 (m, 2H), 7.02–6.93 (m, 1H), 6.70–6.60 (m, 2H), 4.42 (d, J = 12.6 Hz, 1H), 4.12–4.00 (m, 1H), 3.99–3.83 (m, 3H), 3.66–3.56 (m, 1H), 3.56–3.38 (m, 3H), 2.87–2.72 (m, 1H), 2.65–2.46 (m, 1H), 2.33–2.21 (m, 1H), 2.16–2.03 (m, 1H), 1.64–1.52 (m, 2H), 1.47–1.30 (m, 3H), 1.05 (s, 3H), 0.90 (t, J = 7.3 Hz, 3H), 0.72 (s, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.5, 178.4, 176.2, 169.6, 142.2, 133.5, 133.4, 133.1, 132.1, 131.6, 129.8, 129.0, 128.9, 128.8, 127.7, 127.6, 126.5, 123.9, 120.7, 70.4, 67.7, 64.4, 63.0, 57.5, 45.5, 40.6, 30.9, 30.6, 29.4, 24.0, 21.6, 19.2, 13.8 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{36}H_{42}N_3NiO_5^+$ $[M+H]^+$: 654.2472, found: 654.2460.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a in (*S*,*S*)-**4g** and (*S*,*R*)-**4g** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 12:1 for (*S*,*S*)-**4g**/(*S*,*R*)-**4g**.



Ni(II) complex (*S*,*S*)-4h

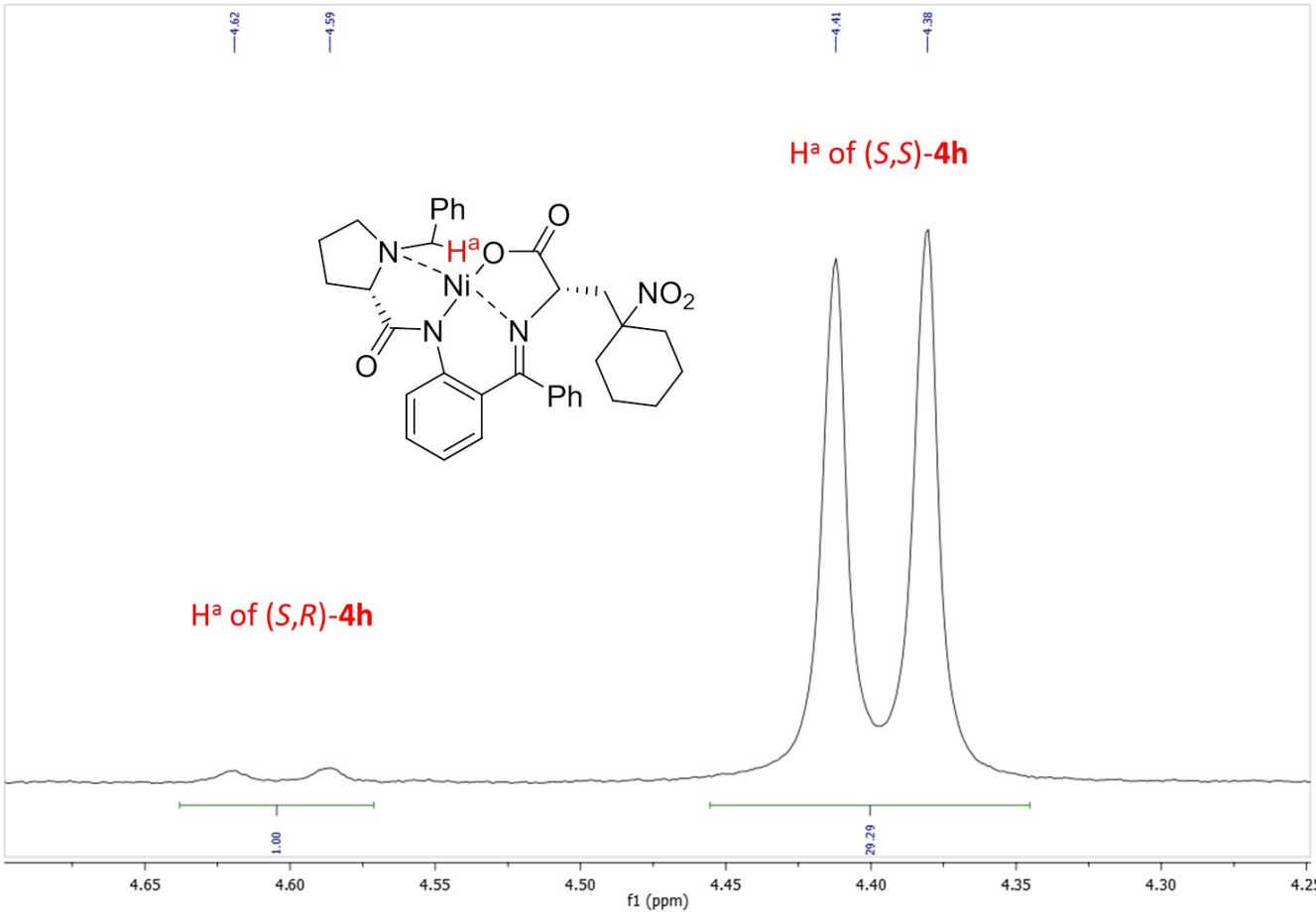
Starting from a chiral Ni(II) complex **2** and 1-nitrocyclohex-1-ene **3h** with applying the general procedure, the desired product (*S*,*S*)-**4h** was isolated as a red powder (26.9 mg, yield 42%, *dr* >20:1). Eluent: $CHCl_3$/acetone (5:1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 7.8 Hz, 2H), 8.04 (d, J = 8.7 Hz, 1H), 7.58–7.46 (m, 3H), 7.38–7.28 (m, 3H), 7.22–7.10 (m, 2H), 7.01 (d, J = 7.5 Hz, 1H), 6.65 (t, J = 7.6 Hz, 1H), 6.61–6.52 (m, 1H), 4.40 (d, J = 12.6 Hz, 1H), 4.03–3.89 (m, 2H), 3.76–3.58 (m, 2H), 3.56–3.46 (m, 2H), 2.83–2.72 (m, 1H), 2.63–2.49 (m, 1H), 2.36–2.24 (m, 2H), 2.16–1.97 (m, 3H), 1.87–1.71 (m, 2H), 1.55–1.43 (m, 1H), 1.40–1.17 (m, 4H), 0.26–0.04 (m, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.6, 177.6, 170.3, 142.5, 133.6, 133.4, 133.2, 132.4, 131.6, 130.1, 129.3, 129.1, 128.9, 127.8, 127.7, 126.4, 123.9, 120.8, 89.6, 70.5, 65.8, 63.2, 57.7, 40.0, 37.5, 30.8, 30.3, 24.3, 24.0, 22.5, 21.1 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{34}H_{37}N_4NiO_5^+$ $[M+H]^+$: 639.2112, found: 639.2122.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a in (*S*,*S*)-**4h** and (*S*,*R*)-**4h** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* >20:1 for (*S*,*S*)-**4h**/(*S*,*R*)-**4h**.



Ni(II) complexes 4i

Starting from a chiral Ni(II) complex **2** and styrene **3i** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4i** and (*S,S,R*)-**4i** were isolated in a ratio of *dr* 1:1 as a red powders (combined yield of both diastereomers 45.0 mg, 73%). Diastereoselective ratio (*dr* value) was determined according to chemical yields of the isolated diastereomers. Yield of the first eluting diastereomer was 22.6 mg and yield of the second eluting was 22.4 mg. Preparative TLC, eluent: $CHCl_3$/acetone (10:1).

1st diastereomer

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11–8.02 (m, 3H), 7.59–7.49 (m, 3H), 7.35 (t, J = 7.5 Hz, 3H), 7.31–7.27 (m, 2H), 7.19 (t, J = 7.3 Hz, 2H), 7.16–7.08 (m, 3H), 7.02–6.96 (m, 1H), 6.71–6.63 (m, 2H), 4.45 (d, J = 12.6 Hz, 1H), 4.01 (dd, J = 11.6, 3.2 Hz, 1H), 3.63–3.41 (m, 4H), 3.16–3.04 (m, 1H), 2.81 (t, J = 11.5 Hz, 1H), 2.68–2.57 (m, 1H), 2.52–2.38 (m, 1H), 2.15–2.01 (m, 2H), 1.78–1.67 (m, 1H), 0.59 (d, J = 6.6 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.5, 179.0, 169.9, 147.3, 142.2, 133.6, 133.3, 133.1, 132.1, 131.6, 129.9, 129.1, 129.0, 128.9, 128.6, 127.8, 127.6, 126.6, 126.5, 126.2, 123.9, 120.8, 70.2, 68.7, 63.1, 57.3, 45.3, 35.1, 30.7, 24.1, 19.2 ppm.

HRMS (ESI, *m/z*) calcd. for $C_{36}H_{36}N_3NiO_3^+$ $[M+H]^+$: 616.2105, found: 616.2120.

2nd diastereomer

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.12–7.99 (m, 3H), 7.38–7.28 (m, 4H), 7.19–7.07 (m, 3H), 7.03–6.98 (m, 3H), 6.95 (d, J = 7.3 Hz, 1H), 6.86–6.75 (m, 3H), 6.60 (t, J = 7.6 Hz, 1H), 6.45 (d, J = 8.1 Hz, 1H), 4.43 (d, J = 12.6 Hz, 1H), 3.79–3.67 (m, 1H), 3.65–3.43 (m, 4H), 3.13–3.00 (m, 1H), 2.95–2.84 (m, 1H), 2.82–2.71 (m, 1H), 2.62–2.48 (m, 1H), 2.32–2.18 (m, 1H), 2.12–2.02 (m, 1H), 1.93–1.82 (m, 1H), 1.22 (d, J = 6.9 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.3, 178.7, 169.7, 144.7, 142.0, 133.3, 133.2, 133.0, 131.9, 131.6, 129.7, 128.9, 128.8, 128.2, 127.3, 127.2, 126.9, 126.7, 125.7, 123.7, 120.7, 70.3, 68.7, 63.1, 57.2, 45.4, 35.5, 30.7, 24.1, 23.3 ppm.

HRMS (ESI, *m/z*) calcd. for $C_{36}H_{36}N_3NiO_3^+$ $[M+H]^+$: 616.2105, found: 616.2118.

Ni(II) complex 4j

Starting from a chiral Ni(II) complex **2** and *ortho*-isopropoxystyrene **3j** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4j** and (*S,S,R*)-**4j** were isolated in a ratio of *dr* 5.5:1 as a red powders (combined yield of both diastereomers 58.0 mg, 86%). Eluent: $CHCl_3$/acetone (5:1).

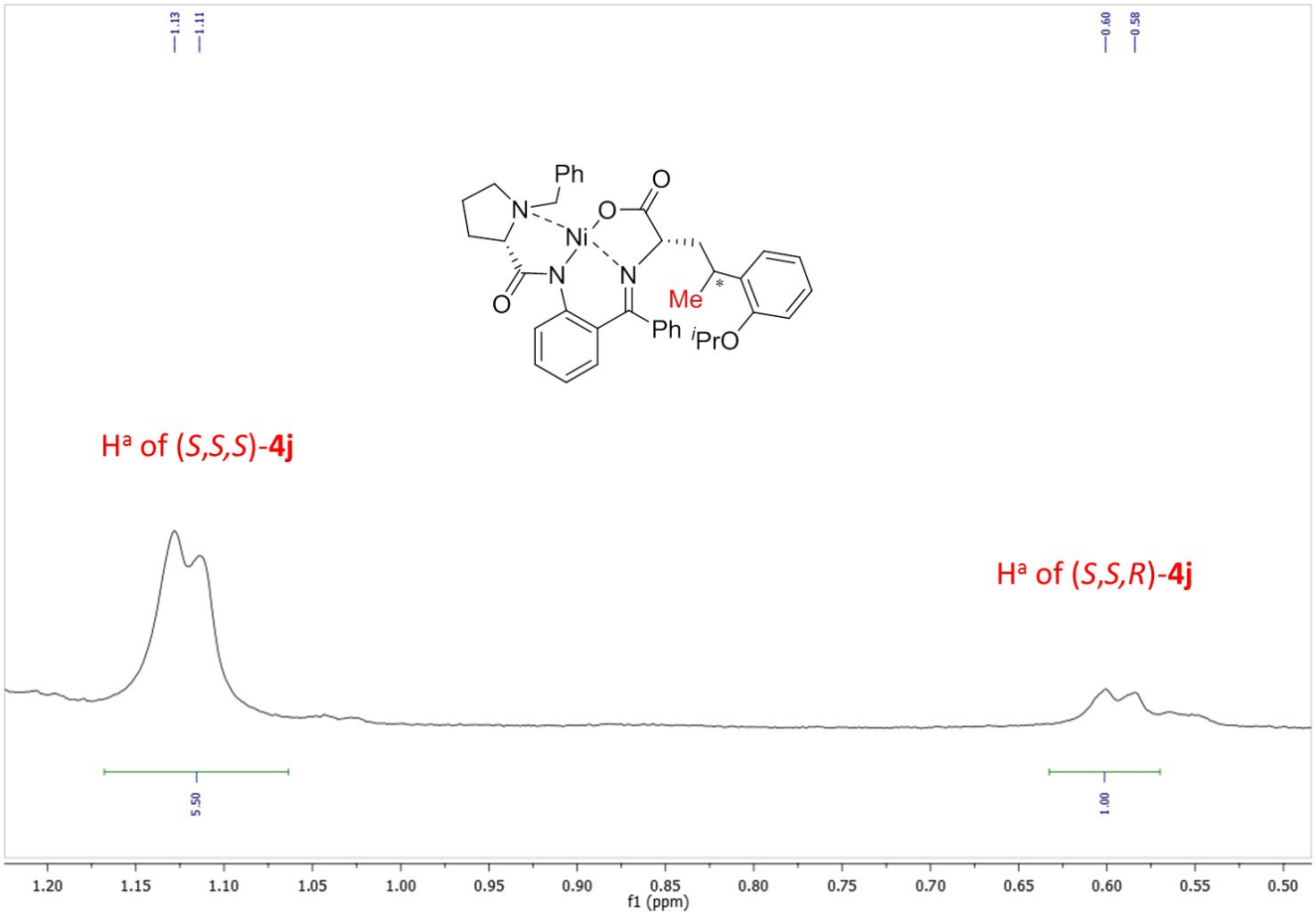
major diastereomer

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.14–8.02 (m, 3H), 7.46–7.29 (m, 5H), 7.23–7.08 (m, 4H), 7.06–6.95 (m, 2H), 6.72 (d, J = 8.2 Hz, 1H), 6.64 (t, J = 7.4 Hz, 1H), 6.59–6.53 (m, 1H), 6.51–6.43 (m, 1H), 4.52–4.39 (m, 2H), 3.91–3.80 (m, 1H), 3.76–3.62 (m, 1H), 3.59–3.44 (m, 3H), 3.42–3.32 (m, 1H), 2.82–2.65 (m, 2H), 2.58–2.48 (m, 1H), 2.42–2.30 (m, 1H), 2.28–2.19 (m, 1H), 2.12–2.02 (m, 1H), 1.26 (dd, J = 11.3, 6.0 Hz, 6H), 1.12 (d, J = 5.7 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 210.9, 180.3, 178.7, 169.7, 142.5, 142.0, 133.3, 133.1, 133.0, 132.0, 131.5, 131.3, 129.7, 128.9, 128.85, 128.8, 128.4, 127.2, 126.8, 125.9, 123.8, 120.7, 70.3, 68.4, 63.1, 60.9, 57.2, 44.0, 40.1, 38.1, 30.7, 29.3, 24.2 ppm.

HRMS (ESI, *m/z*) calcd. for $C_{39}H_{42}N_3NiO_4^+$ $[M+H]^+$: 674.2523, found: 674.2547.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of Me group in (*S,S,S*)-**4j** and (*S,S,R*)-**4j** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 5.5:1 for (*S,S,S*)-**4j**/(*S,S,R*)-**4j**.



Ni(II) complexes 4k

Starting from a chiral Ni(II) complex **2** and 3-phenylprop-2-en-1-ol **3k** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4k** and (*S,S,R*)-**4k** were isolated in a ratio of *dr* 2:1 as a

red powders (combined yield of both diastereomers 58.8 mg, 91%). Diastereoselective ratio (*dr* value) was determined according to chemical yields of the isolated diastereomers. Yield of the first eluting diastereomer was 19.6 mg and yield of the second eluting was 39.2 mg. Eluent: $CHCl_3$/acetone (5:1 to 3:1).

1st diastereomer (major)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.14–7.99 (m, 3H), 7.65–7.49 (m, 3H), 7.40–7.32 (m, 3H), 7.32–7.27 (m, 2H), 7.24–7.16 (m, 2H), 7.16–7.08 (m, 3H), 7.00–6.93 (m, 1H), 6.72–6.60 (m, 2H), 4.40 (d, *J* = 12.5 Hz, 1H), 4.18–4.10 (m, 1H), 3.55 (d, *J* = 12.5 Hz, 1H), 3.51–3.39 (m, 3H), 3.28–3.14 (m, 2H), 3.09–2.99 (m, 1H), 2.74 (t, *J* = 12.5 Hz, 1H), 2.63–2.56 (m, 1H), 2.50–2.38 (m, 1H), 2.12–2.00 (m, 2H), 1.92–1.81 (m, 1H), 1.20–1.12 (m, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.4, 170.1, 145.6, 142.2, 133.6, 133.3, 133.2, 132.2, 131.6, 130.0, 129.2, 129.0, 128.9, 128.7, 127.7, 127.6, 127.2, 126.5, 126.4, 123.9, 120.9, 70.2, 68.6, 63.2, 60.7, 57.3, 43.9, 38.0, 37.2, 30.6, 24.1 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_4^+$ $[M+H]^+$: 646.2210, found: 646.2228.

2nd diastereomer (minor)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.1 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.37–7.27 (m, 4H), 7.18–7.06 (m, 3H), 7.04–6.97 (m, 3H), 6.92 (d, *J* = 7.1 Hz, 1H), 6.82 (d, *J* = 6.4 Hz, 1H), 6.79–6.71 (m, 2H), 6.65–6.57 (m, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.82–3.69 (m, 1H), 3.60–3.42 (m, 6H), 3.11–2.97 (m, 2H), 2.81–2.72 (m, 1H), 2.61–2.48 (m, 1H), 2.32–2.20 (m, 1H), 2.13–2.02 (m, 1H), 1.94–1.68 (m, 4H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.3, 178.7, 169.7, 142.5, 142.0, 133.3, 133.1, 132.9, 132.0, 131.6, 129.7, 128.9, 128.87, 128.8, 128.77, 128.4, 127.2, 126.9, 125.9, 123.8, 120.7, 70.3, 63.1, 60.9, 57.2, 53.8, 44.0, 40.1, 38.1, 30.7, 24.2 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_4^+$ $[M+H]^+$: 646.2210, found: 646.2221.

Ni(II) complexes 4l

Starting from a chiral Ni(II) complex **2** and indene **3l** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4l** and (*S,S,R*)-**4l** were isolated in a ratio of *dr* 2.5:1 as a red powders (combined yield of both diastereomers 54.8 mg, 87%). Diastereoselective ratio (*dr* value) was determined according to chemical yields of the isolated diastereomers. Yield of the first eluting diastereomer was 39.1 mg and yield of the second eluting was 15.7 mg. Preparative TLC, eluent: ethyl acetate.

1st diastereomer (major)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.15–8.00 (m, 3H), 7.59–7.46 (m, 2H), 7.44–7.29 (m, 4H), 7.24–7.08 (m, 6H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.70–6.53 (m, 2H), 4.48 (d, *J* = 12.7 Hz, 1H), 4.01–3.90 (m, 1H), 3.89–3.74 (m, 1H), 3.64–3.40 (m, 4H), 3.13 (t, *J* = 12.1 Hz, 1H), 2.84–2.47 (m, 4H), 2.37–2.24 (m, 1H), 2.14–1.92 (m, 2H), 1.65–1.48 (m, 1H), 0.47 (td, *J* = 15.7, 7.8 Hz, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.0, 169.9, 146.2, 143.8, 142.1, 133.5, 133.3, 133.1, 132.1, 131.6, 129.8, 129.1, 129.0, 128.9, 127.7, 127.6, 126.6, 126.5, 126.3, 124.6, 123.9, 123.1, 120.8, 70.2, 69.4, 63.0, 57.3, 42.5, 41.0, 31.1, 30.8, 30.7, 24.2 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{36}N_3NiO_3^+$ $[M+H]^+$: 628.2105, found: 628.2117.

2nd diastereomer (minor)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.51 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 7.1 Hz, 2H), 7.59–7.48 (m, 5H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.39–7.30 (m, 2H), 7.21–7.13 (m, 5H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.73–6.69 (m, 1H), 4.49 (d, *J* = 13.1 Hz, 1H), 4.40–4.30 (m, 1H), 3.95 (dd, *J* = 11.7, 3.4 Hz, 1H), 3.72 (dd, *J* = 9.1, 3.6 Hz, 1H), 3.48 (d, *J* = 13.1 Hz, 1H), 3.43–3.34 (m, 1H), 2.90 (t, *J* = 12.5 Hz, 1H), 2.84–2.74 (m, 2H), 2.70–2.61 (m, 1H), 2.59–2.48 (m, 2H), 2.32–2.22 (m, 1H), 2.01–1.87 (m, 2H), 1.48 (dd, *J* = 17.2, 8.0 Hz, 1H), 0.47–0.34 (m, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 181.9, 180.4, 170.6, 146.3, 143.8, 142.8, 134.0, 133.8, 133.7, 132.5, 131.6, 131.4, 129.7, 129.2, 128.9, 128.8, 128.1, 127.4, 126.5, 126.1, 125.9, 124.5, 123.7, 123.3, 120.8, 69.4, 68.9, 61.1, 59.0, 41.4, 40.8, 31.2, 30.4, 30.3, 23.2 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_4^+$ $[M+H]^+$: 628.2105, found: 628.2127.

Ni(II) complexes 4m

Starting from a chiral Ni(II) complex **2** and acrylonitrile **3m** with applying the general procedure, the mixture of diastereomers (*S*,*S*,*S*)-**4m** and (*S*,*S*,*R*)-**4m** were isolated in a ratio of *dr* 1:1 as a red powders (combined yield of both diastereomers 40.7 mg, 72%). Diastereoselective ratio (*dr* value) was determined according to chemical yields of the isolated diastereomers. Yield of the first eluting diastereomer was 20.4 mg and yield of the second eluting was 20.3 mg. Preparative TLC, eluent: $CHCl_3$/acetone (5:1).

1st diastereomer

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 7.4 Hz, 2H), 7.57–7.49 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31–7.27 (m, 1H), 7.24–7.12 (m, 2H), 7.03–6.96 (m, 1H), 6.69–6.60 (m, 2H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.84 (dd, *J* = 11.3, 3.1 Hz, 1H), 3.73–3.61 (m, 1H), 3.60–3.44 (m, 3H),

3.13–3.00 (m, 1H), 2.84–2.67 (m, 2H), 2.59–2.47 (m, 1H), 2.30–2.21 (m, 1H), 2.13–2.01 (m, 1H), 1.77–1.64 (m, 1H), 0.67 (d, J = 6.9 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.5, 178.1, 171.3, 142.5, 133.4, 133.3, 132.6, 131.5, 131.2, 130.1, 129.3, 129.1, 129.0, 128.9, 127.7, 127.3, 126.1, 124.0, 122.5, 120.9, 70.2, 66.4, 63.2, 57.4, 39.1, 30.7, 24.3, 21.2, 15.8 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{31}H_{31}N_4NiO_3^+$ $[M+H]^+$: 565.1744, found: 565.1762.

2nd diastereomer

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.12–8.03 (m, 3H), 7.63–7.47 (m, 3H), 7.41–7.29 (m, 3H), 7.23–7.11 (m, 2H), 6.93 (d, J = 7.4 Hz, 1H), 6.71–6.61 (m, 2H), 4.42 (d, J = 12.6 Hz, 1H), 4.10–3.98 (m, 1H), 3.67–3.46 (m, 4H), 3.09–2.94 (m, 1H), 2.77–2.64 (m, 1H), 2.60–2.42 (m, 2H), 2.29–2.19 (m, 1H), 2.13–2.02 (m, 1H), 1.89–1.78 (m, 1H), 1.26 (d, J = 6.9 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 176.8, 171.7, 142.3, 133.5, 133.3, 132.9, 132.5, 131.5, 130.5, 129.6, 129.4, 129.03, 129.0, 127.2, 126.9, 126.3, 123.8, 121.0, 120.8, 70.2, 68.0, 63.3, 57.4, 40.7, 30.7, 24.3, 22.3, 18.6 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_4^+$ $[M+H]^+$: 565.1744, found: 565.1751.

Ni(II) complexes 4n

Starting from a chiral Ni(II) complex **2** (153.0 mg, 0.3 mmol) and acrylamide **3n** with applying the general procedure, the mixture of diastereomers (*S*,*S*,*S*)-**4n** and (*S*,*S*,*R*)-**4n** were isolated in a ratio of *dr* 2:1 as a red powders (combined yield of both diastereomers 78.6 mg, 45%). Diastereoselective ratio (*dr* value) was determined according to chemical yields of the isolated diastereomers. Yield of the first eluting diastereomer was 52.4 mg and yield of the second eluting (*S*,*S*,*R*)-**4n** was 26.2 mg. Eluent: $CHCl_3$/acetone (5:1 to 1:5).

1st diastereomer (major)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.6 Hz, 1H), 8.05 (d, J = 7.4 Hz, 2H), 7.57–7.46 (m, 3H), 7.35 (t, J = 7.6 Hz, 2H), 7.23–7.11 (m, 3H), 6.94 (d, J = 7.1 Hz, 1H), 6.73 (br.s, 1H), 6.69–6.62 (m, 2H), 4.93 (br.s, 1H), 4.39 (d, J = 12.6 Hz, 1H), 3.93 (dd, J = 11.5, 4.6 Hz, 1H), 3.74–3.61 (m, 1H), 3.57 (d, J = 12.6 Hz, 1H), 3.52–3.41 (m, 2H), 2.81–2.71 (m, 1H), 2.67–2.46 (m, 3H), 2.29–2.20 (m, 1H), 2.14–2.02 (m, 1H), 1.85–1.73 (m, 1H), 1.10 (d, J = 6.0 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.3, 179.6, 176.2, 170.8, 142.1, 133.4, 133.2, 132.7, 132.3, 131.5, 130.1, 129.6, 129.0, 128.9, 128.7, 127.4, 126.7, 126.2, 123.8, 120.9, 70.3, 68.8, 63.1, 57.2, 41.5, 31.8, 30.7, 24.2, 17.5 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{31}H_{33}N_4NiO_4^+$ $[M+H]^+$: 583.1850, found: 583.1870.

2nd diastereomer (minor)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.10–8.03 (m, 3H), 7.55–7.45 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.29–7.26 (m, 1H), 7.22–7.09 (m, 2H), 7.04–6.98 (m, 1H), 6.69–6.59 (m, 2H), 5.71 (br.s, 1H), 5.42 (br.s, 1H), 4.39 (d, *J* = 12.6 Hz, 1H), 3.87–3.76 (m, 2H), 3.75–3.63 (m, 1H), 3.53 (d, *J* = 12.6 Hz, 1H), 3.50–3.41 (m, 2H), 2.89 (t, *J* = 12.8 Hz, 2H), 2.77–2.66 (m, 1H), 2.61–2.44 (m, 2H), 2.11–2.00 (m, 1H), 1.68–1.56 (m, 1H), 0.51 (d, *J* = 6.2 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.5, 179.4, 178.2, 170.6, 142.2, 133.4, 133.3, 133.2, 132.3, 131.6, 129.9, 129.3, 129.0, 128.9, 128.89, 127.9, 127.3, 126.34, 123.9, 120.8, 115.5, 70.3, 69.6, 63.1, 57.4, 40.0, 31.8, 30.7, 24.2, 16.3 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_4^+$ $[M+H]^+$: 583.1850, found: 583.1873.

The structure of (*S,S,R*)-**4n** was determined by single crystal X-ray analysis (see Scheme 2 in main text and Part 5 in SI).

Ni(II) complexes 4o

Starting from a chiral Ni(II) complex **2** and β-methyl styrene **3o** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4o** and (*S,S,R*)-**4o** were isolated in a ratio of *dr* 1.5:1 as a red powders (combined yield of both diastereomers 49.2 mg, 78%). Eluent: $CHCl_3$/acetone (5:1). The diastereomers wasn't separated.

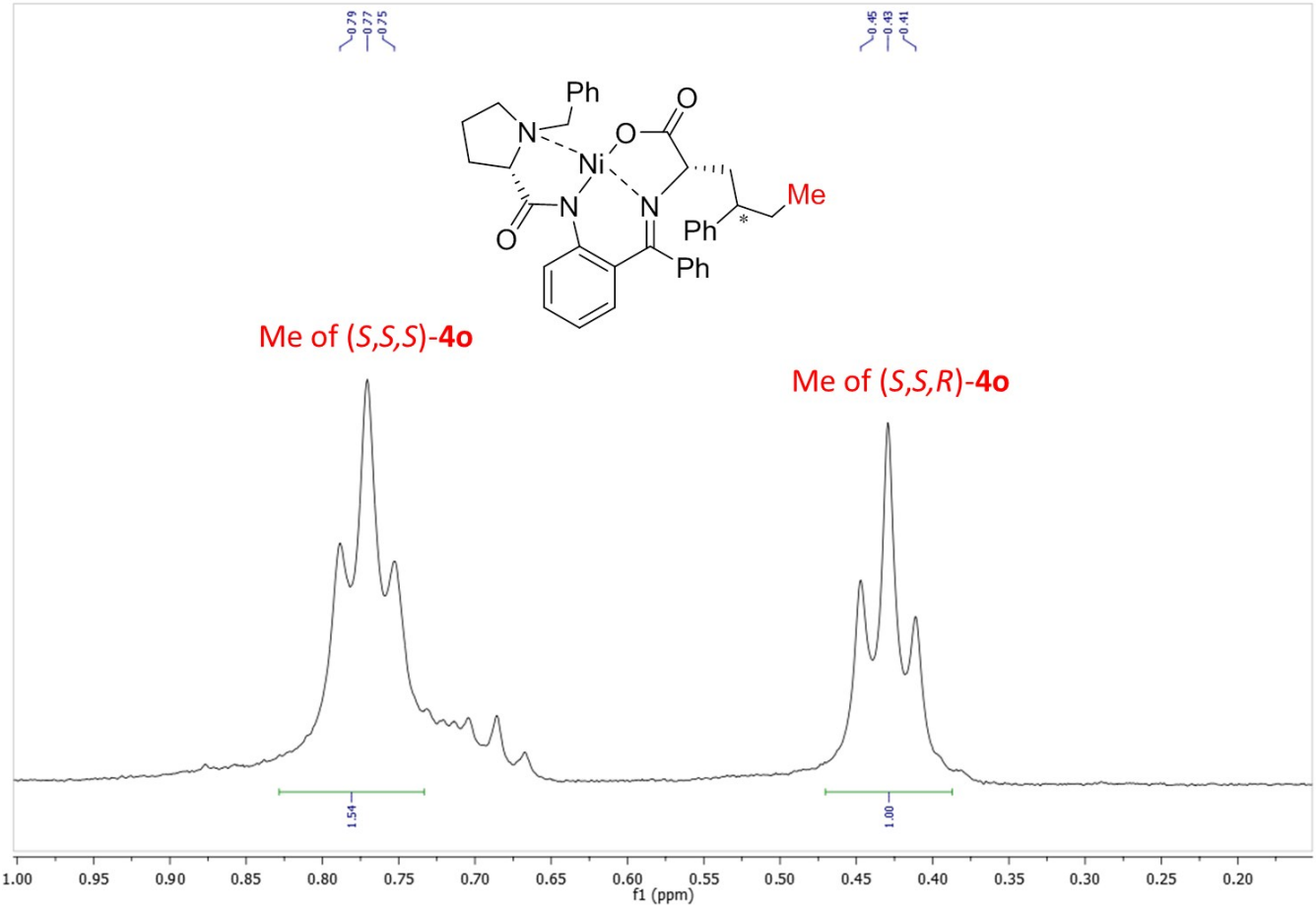
NMR of the mixture of (*S,S,S*)-4o and (*S,S,R*)-4o

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09–7.98 (m, 6H), 7.57–7.47 (m, 3H), 7.40–7.28 (m, 8H), 7.20–7.07 (m, 8H), 7.02–6.96 (m, 4H), 6.95–6.88 (m, 2H), 6.87–6.80 (m, 1H), 6.75–6.69 (m, 2H), 6.68–6.57 (m, 3H), 6.45 (d, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 12.7 Hz, 2H), 4.07–3.99 (m, 1H), 3.82–3.69 (m, 1H), 3.64–3.51 (m, 4H), 3.52–3.41 (m, 4H), 3.13–3.01 (m, 1H), 2.95–2.84 (m, 1H), 2.84–2.68 (m, 3H), 2.61–2.51 (m, 1H), 2.51–2.39 (m, 1H), 2.30–2.20 (m, 1H), 2.12–2.00 (m, 3H), 1.89–1.78 (m, 2H), 1.68–1.58 (m, 2H), 1.56–1.45 (m, 1H), 1.23–1.12 (m, 1H), 0.78 (t, *J* = 7.1 Hz, 3H), 0.73–0.65 (m, 1H), 0.43 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 180.3, 179.0, 178.6, 169.9, 169.5, 145.2, 143.0, 142.2, 142.0, 133.7, 133.3, 133.3, 133.1, 133.0, 132.1, 131.9, 131.6, 131.6, 129.8, 129.7, 129.0, 128.98, 128.9, 128.8, 128.4, 128.1, 127.8, 127.6, 127.5, 127.3, 127.3, 127.0, 126.5, 126.2, 125.6, 123.9, 123.8, 120.8, 120.7, 70.3, 70.1, 68.8, 68.6, 63.0, 57.2, 57.1, 44.0, 43.7, 42.9, 42.5, 30.7, 30.66, 30.3, 26.2, 24.1, 24.0, 12.0, 11.5 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{38}N_3NiO_3^+$ $[M+H]^+$: 630.2261, found: 630.2276.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of Me group in (*S*,*S*,*S*)-**4o** and (*S*,*S*,*R*)-**4o** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 1.5:1 for (*S*,*S*,*S*)-**4o**/(*S*,*S*,*R*)-**4o**.



Ni(II) complexes 4p

Starting from a chiral Ni(II) complex **2** and safrole **3p** with applying the general procedure, the mixture of diastereomers (*S*,*S*,*R*)-**4p** and (*S*,*S*,*S*)-**4p** were isolated in a ratio of *dr* 1.1:1 as a red powders (combined yield of both diastereomers 28.3 mg, 42%). Eluent: $CHCl_3$/acetone (5:1). The diastereomers wasn't separated.

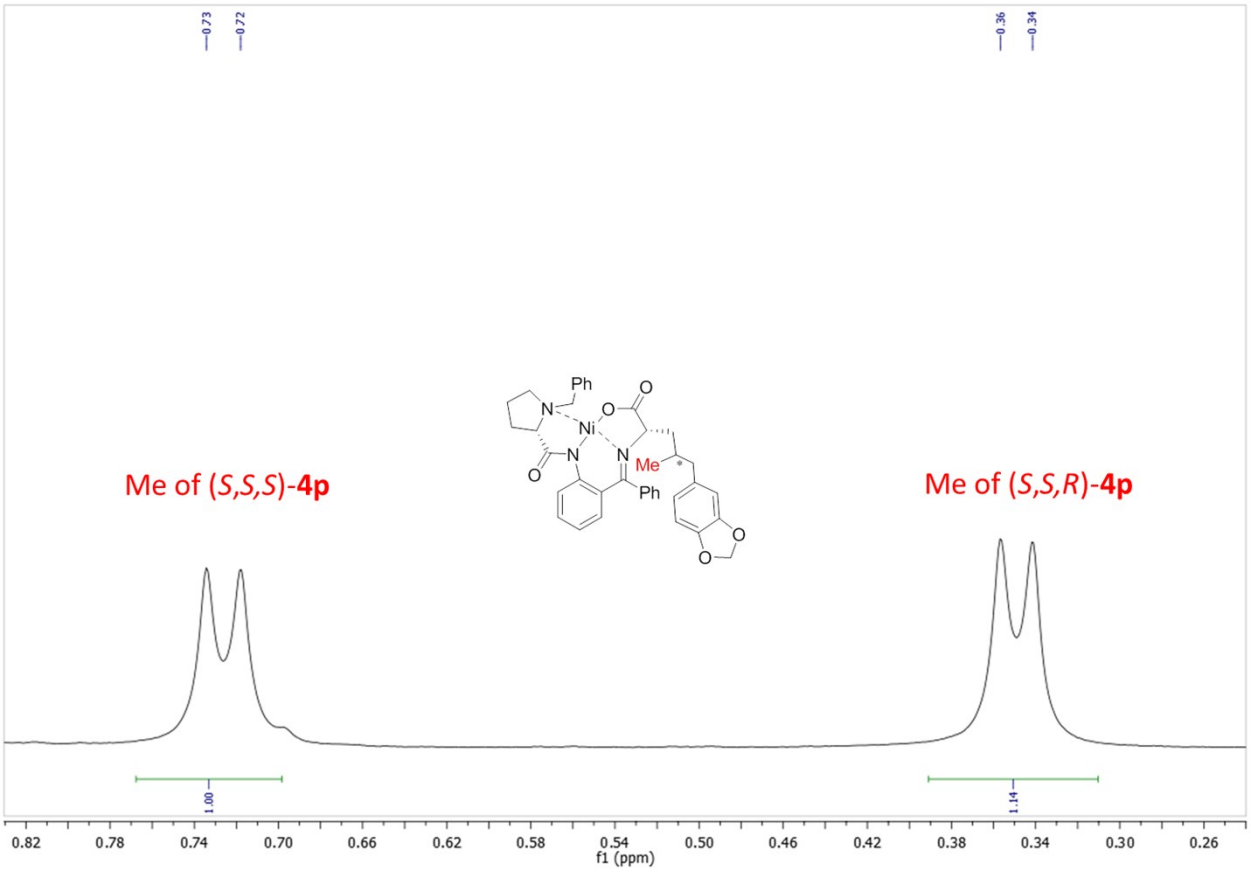
NMR of the mixture of (*S*,*S*,*S*)-4p and (*S*,*S*,*R*)-4p

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.10–7.97 (m, 6H), 7.54–7.41 (m, 7H), 7.39–7.29 (m, 5H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 2H), 6.92 (d, *J* = 6.4 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.69–6.59 (m, 7H), 6.53 (s, 1H), 6.45 (d, *J* = 7.7 Hz, 1H), 5.91–5.85 (m, 4H), 4.43 (d, *J* = 12.7 Hz, 1H), 4.35 (d, *J* = 12.6 Hz, 1H), 4.03–3.94 (m, 1H), 3.88–3.79 (m, 1H), 3.68–3.35 (m, 7H), 3.34–3.25 (m, 1H), 3.20–3.05 (m, 1H), 2.75–2.60 (m, 3H), 2.57–2.40 (m, 4H), 2.32–2.20 (m, 2H), 2.14–2.04 (m, 2H), 1.99–1.89 (m, 3H), 1.70–1.60 (m, 1H), 1.48 (dd, *J* = 13.2, 9.6 Hz, 1H), 1.12 (t, *J* = 10.4 Hz, 1H), 0.73 (d, *J* = 6.5 Hz, 3H), 0.35 (d, *J* = 6.1 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 180.4, 180.3, 179.0, 178.3, 169.8, 169.5, 147.5, 147.4, 145.7, 145.6, 142.2, 142.0, 134.4, 134.3, 133.5, 133.4, 133.3, 133.2, 133.19, 133.1, 132.1, 132.0, 131.6, 129.8, 129.76, 129.0, 128.9, 128.88, 127.9, 127.7, 127.6, 126.7, 126.6, 123.9, 123.8, 122.1, 121.9, 120.8, 120.8, 109.7, 109.5, 108.1, 107.9, 100.7, 100.68, 70.3, 69.0, 63.0, 62.9, 57.1, 57.0, 44.3, 43.9, 43.0, 41.2, 31.6, 30.9, 30.7, 30.65, 24.0, 23.4, 20.2, 18.7 ppm.

HRMS (ESI, *m/z*) calcd. for $C_{38}H_{38}N_3NiO_5^+$ $[M+H]^+$: 674.2159, found: 674.2164.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of Me group in (*S,S,S*)-**4p** and (*S,S,R*)-**4p** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 1.1:1 for (*S,S,R*)-**4p**/(*S,S,S*)-**4p**.



Ni(II) complexes 4q

Starting from a chiral Ni(II) complex **2** and chalcone **3q** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4q** and (*S,S,R*)-**4q** were isolated in a ratio of *dr* 1:1 as a red powders (combined yield of both diastereomers 43.2 mg, 60%). Eluent: $CHCl_3$/acetone (5:1). The diastereomers wasn't separated.

NMR of the mixture of (*S,S,S*)-4q and (*S,S,R*)-4q

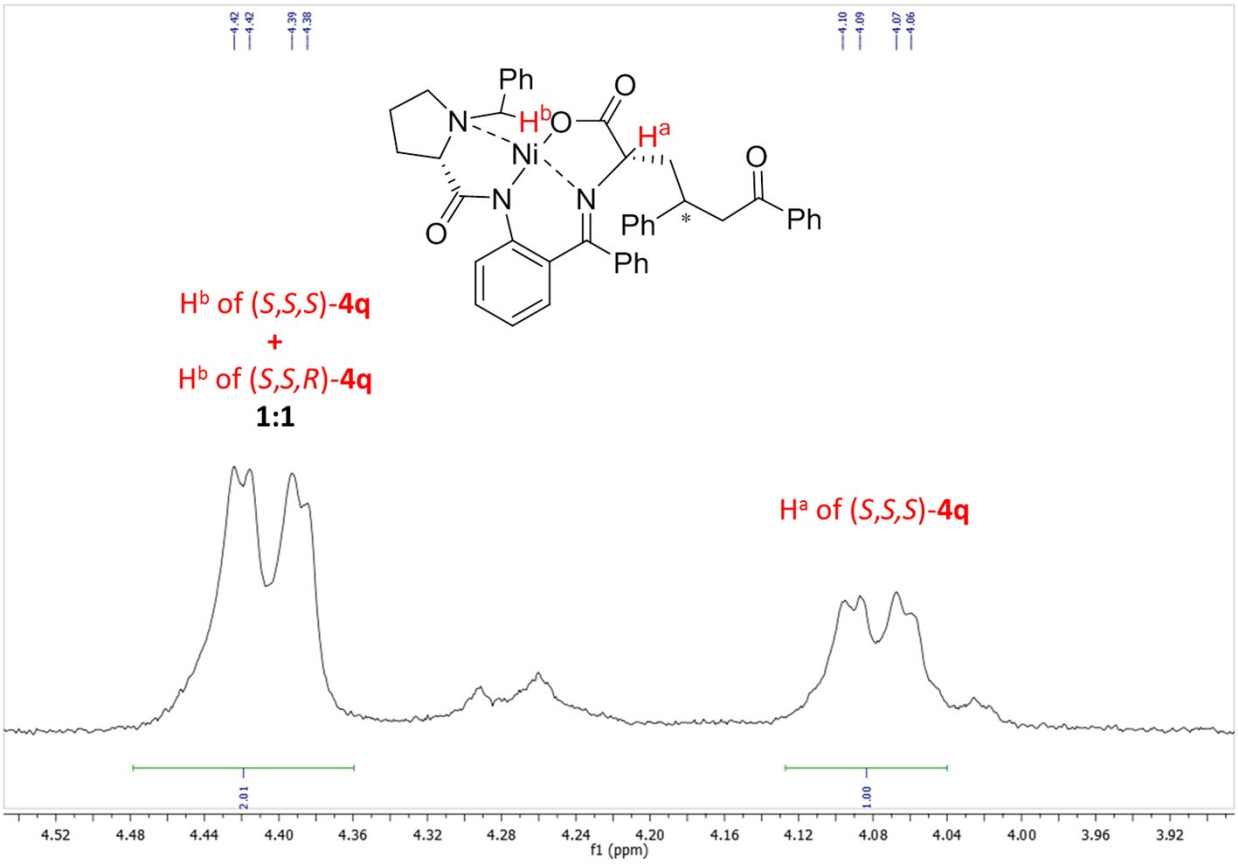
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.15–8.04 (m, 6H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.63–7.53 (m, 4H), 7.49–7.29 (m, 10H), 7.25–7.11 (m, 9H), 7.06–7.00

(m, 5H), 7.00–6.94 (m, 2H), 6.93–6.87 (m, 1H), 6.87–6.76 (m, 2H), 6.72–6.57 (m, 3H), 6.47 (d, J = 8.0 Hz, 1H), 4.47–4.37 (m, 2H), 4.13–4.03 (m, 1H), 3.79–3.66 (m, 2H), 3.64–3.51 (m, 5H), 3.50–3.42 (m, 3H), 3.41–3.31 (m, 1H), 3.26–3.16 (m, 1H), 3.15–2.99 (m, 2H), 2.94–2.78 (m, 1H), 2.77–2.60 (m, 2H), 2.58–2.41 (m, 2H), 2.40–2.30 (m, 1H), 2.28–2.20 (m, 1H), 2.12–1.98 (m, 4H), 1.95–1.84 (m, 1H), 1.80–1.68 (m, 1H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 198.4, 198.1, 180.5, 178.9, 178.7, 178.1, 170.2, 169.4, 143.4, 142.4, 142.3, 142.1, 136.9, 136.7, 133.6, 133.5, 133.3, 133.2, 133.1, 132.8, 132.3, 131.9, 131.7, 131.6, 131.4, 130.0, 129.7, 129.5, 129.1, 129.0, 129.02, 128.97, 128.9, 128.86, 128.6, 128.5, 128.4, 128.39, 128.3, 128.1, 127.9, 127.6, 127.4, 127.37, 127.1, 126.9, 126.6 126.3, 126.1, 123.9, 123.9, 120.8, 120.7, 70.5, 70.3, 68.4, 63.1, 63.1, 57.5, 57.3, 45.8, 43.7, 42.9, 42.1, 38.0, 37.3, 30.8, 30.7, 29.7, 24.1 ppm.

HRMS (ESI, *m/z*) calcd. for $C_{38}H_{38}N_3NiO_5^+$ $[M+H]^+$: 674.2159, found: 674.2164.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a and H^b in (*S,S,S*)-**4q** and (*S,S,R*)-**4q** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 1:1 for (*S,S,R*)-**4q**/(*S,S,S*)-**4q**.



Ni(II) complexes 4r

Starting from a chiral Ni(II) complex **2** and methyl methyl(vinyl)phosphinate **3r** with applying the general procedure, the mixture of diastereomers (*S,S,S*)-**4r** and (*S,S,R*)-**4r** were isolated in a ratio of *dr*

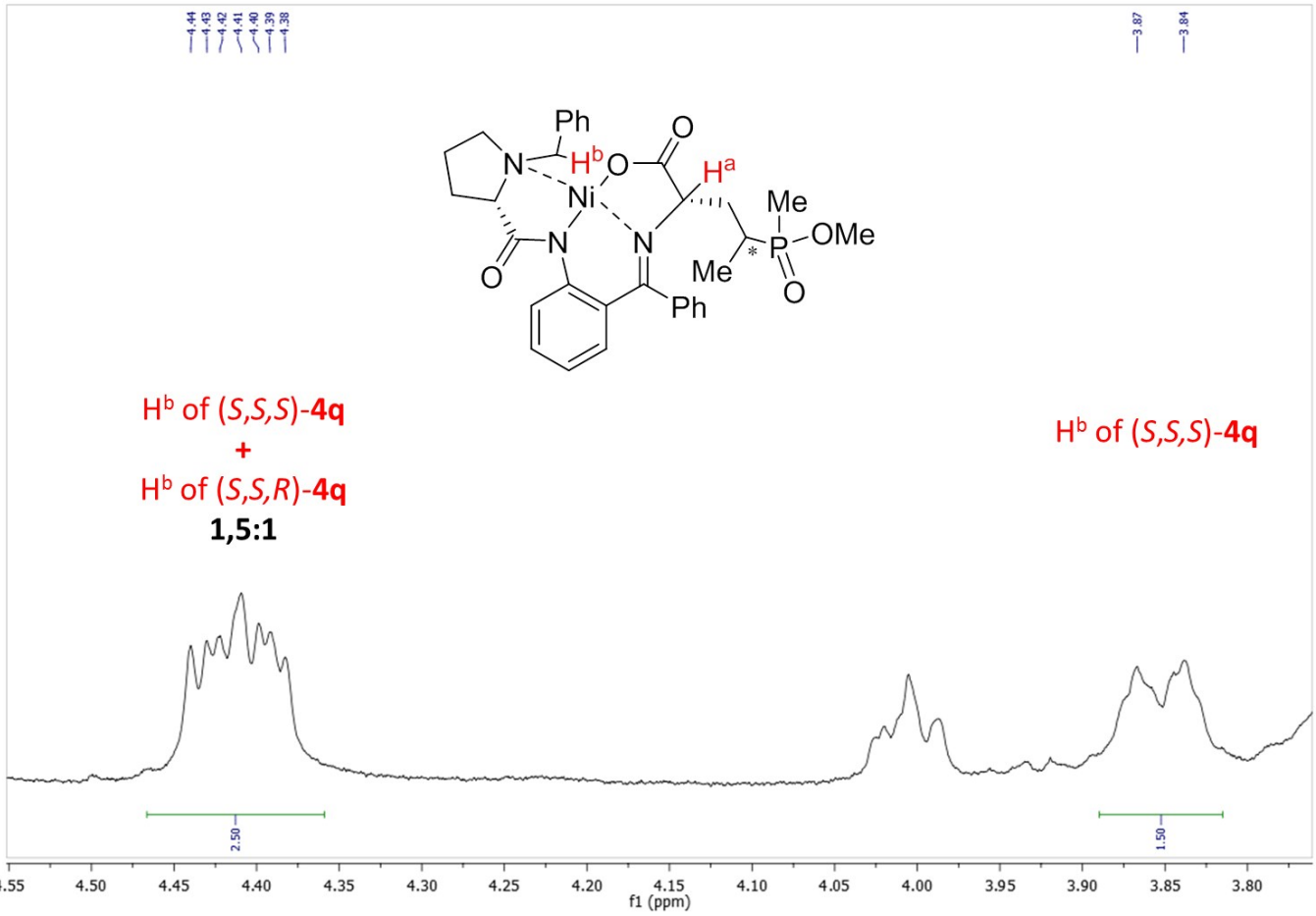
1.5:1 as a red powders (combined yield of both diastereomers 33.5 mg, 53%). Eluent: $CHCl_3$/acetone (1:1) to methanol. The diastereomers wasn't separated.

NMR of the mixture of (*S*,*S*,*S*)-4r and (*S*,*S*,*R*)-4r (contains the starting **3r** as an inpurity!)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.14–7.99 (m, 6H), 7.57–7.43 (m, 6H), 7.40–7.31 (m, 4H), 7.31–7.27 (m, 2H), 7.23–7.16 (m, 2H), 7.16–7.08 (m, 2H), 6.97 (t, J = 6.7 Hz, 2H), 6.70–6.63 (m, 3H), 6.61–6.54 (m, 1H), 4.47–4.36 (m, 2H), 4.06–3.96 (m, 1H), 3.90–3.80 (m, 1H), 3.74–3.69 (m, 4H), 3.69–3.64 (m, 4H), 3.59 (d, J = 10.5 Hz, 2H), 3.52–3.44 (m, 6H), 3.19–3.02 (m, 1H), 2.83–2.66 (m, 2H), 2.60–2.47 (m, 2H), 2.43–2.32 (m, 1H), 2.27–2.17 (m, 3H), 2.12–2.01 (m, 3H), 1.38 (d, J = 12.7 Hz, 3H), 1.23–1.18 (m, 3H), 1.13 (d, J = 13.0 Hz, 3H), 0.48 (dd, J = 17.7, 7.0 Hz, 3H) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{32}H_{37}N_3NiO_5P^+$ $[M+H]^+$: 632.1819, found: 632.1814.

Diastereoselective ratio (*dr* value) was determined according to the ^{1}H NMR peak areas of H^a and H^b in (*S*,*S*,*S*)-**4r** and (*S*,*S*,*R*)-**4r** from the isolated mixture of products (partial ^{1}H NMR of the diastereoisomers is shown below), *dr* 1.5:1 for (*S*,*S*,*R*)-**4r**/(*S*,*S*,*S*)-**4r**.



NMR of the Ni(II) complex (*S*,*R*)-5

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, J = 8.7 Hz, 1H), 8.12 (d, J = 7.0 Hz, 2H), 7.60–7.43 (m, 6H), 7.26–7.21 (m, 1H), 7.21–7.14 (m, 1H), 7.01 (d, J = 6.7 Hz, 1H), 6.78–6.61 (m, 2H), 4.37 (d, J =

12.4 Hz, 1H), 4.28–4.17 (m, 1H), 3.98–3.83 (m, 1H), 3.74–3.61 (m, 1H), 3.44 (d, *J* = 12.4 Hz, 1H), 2.75–2.51 (m, 2H), 2.34–2.20 (m, 2H), 2.04–1.90 (m, 1H), 1.39 (d, *J* = 7.0 Hz, 3H) ppm.

NMR of the Ni(II) complex (*S*,*S*)-5

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11–8.02 (m, 3H), 7.55–7.41 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26–7.23 (m, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.16–7.09 (m, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.69–6.58 (m, 2H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.91 (dd, *J* = 13.6, 6.8 Hz, 1H), 3.81–3.64 (m, 1H), 3.60–3.43 (m, 3H), 2.79–2.67 (m, 1H), 2.60–2.45 (m, 1H), 2.26–2.18 (m, 1H), 2.12–2.01 (m, 1H), 1.59 (d, *J* = 7.0 Hz, 3H) ppm.

4. General procedure for the decomposition of the Ni(II) complexes (*S*,*S*)-4a, (*S*,*S*)-4c and 4r leading to amino acids isolation

To a suspension of the Ni(II) complex **4** (1.96 mmol) in methanol (30.0 mL) was added 6*N* HCl (20.0 mL) and water (30.0 mL) and the whole was heated at 60 ^{o}C. Upon disappearance of the red color of the starting complex, the reaction was stopped. Afterward, the solution was changed to a suspension due to a white precipitate (HCl salt of (*S*)-**BPB**) appearing. The precipitate was filtered and washed with water (50.0 mL). The remaining amount of (*S*)-**BPB** was extracted with DCM. The aqueous layer was quenched by 25% aqueous NH_3 solution (12.0 mL) until pH = 7 and concentrated to dryness and the residue was chromatographed with a cation exchange resin (Dowex 50X8, H^+-form) (eluent: water and then 5% aqueous solution of ammonia) to afford the desired amino acid as a white powder.

(*S*)-2-amino-3-(1-methylcyclohexyl)propanoic acid (6a)

Starting from the chiral Ni(II) complex (*S*,*S*)-**4a** with applying the general procedure, the desired product **6a** was isolated as a white powder (301.0 mg, yield 80%).

^{1}H-NMR (400 MHz, D_2O): δ = (t, *J* = 5.7 Hz, 1H), 1.93 (dd, *J* = 15.1, 5.3 Hz, 1H), 1.53 (dd, *J* = 15.1, 6.2 Hz, 1H), 1.43–1.24 (m, 5H), 1.24–1.01 (m, 5H), 0.82 (s, 3H) ppm.

^{13}C-NMR (101 MHz, D_2O): δ = 173.2, 49.7, 42.6, 37.1, 36.7, 32.2, 25.5, 23.4, 21.3, 21.25 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{10}H_{20}NO_2^+$ $[M+H]^+$: 186.1489, found: 186.1491.

$[\alpha]_D^{20}$ –12.5 (*c* 0.2, MeOH), (>99% *ee*, (*S*)-isomer).

(*S*)-2-amino-4-methyl-4-phenylpentanoic acid (6c)

Starting from the chiral Ni(II) complex (*S*,*S*)-**4c** with applying the general procedure, the desired product **6c** was isolated as a white powder (316.9 mg, yield 78%).

^{1}H-NMR (400 MHz, D_2O+CD_3OD): δ = 7.48 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 3.37 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.52 (dd, *J* = 15.0, 3.8 Hz, 1H), 2.00 (dd, *J* = 15.0, 8.2 Hz, 1H), 1.44 (d, *J* = 5.8 Hz, 6H) ppm.

^{13}C-NMR (101 MHz, D_2O+CD_3OD): δ = 171.8, 146.4, 128.7, 126.7, 126.0, 50.7, 43.8, 36.5, 28.3, 27.9 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{12}H_{18}NO_2^+$ $[M+H]^+$: 208.1332, found: 208.1336.

$[\alpha]_D^{20}$ –7.5 (*c* 0.2, MeOH), (>99% *ee*, (*S*)-isomer).

2-amino-4-(methoxy(methyl)phosphoryl)pentanoic acid (6r)

Starting from the mixture of diastereomers of the Ni(II) complexes (*S,S,S*)-**4r** and (*S,S,R*)-**4r** with applying the general procedure, the mixture of diastereomers (*S,S*)-**6r** and (*S,R*)-**6r** were isolated in a ratio of *dr* 1:1 as a white powder (217.3 mg, yield 53%).

NMR of the mixture of (*S,S*)-4r and (*S,R*)-4r

^{1}H-NMR (400 MHz, D_2O+CD_3OD): δ = 3.84–3.65 (m, 8H), 2.42–2.20 (m, 3H), 2.20–2.00 (m, 2H), 1.93–1.77 (m, 1H), 1.59–1.50 (m, 6H), 1.37–1.16 (m, 6H) ppm.

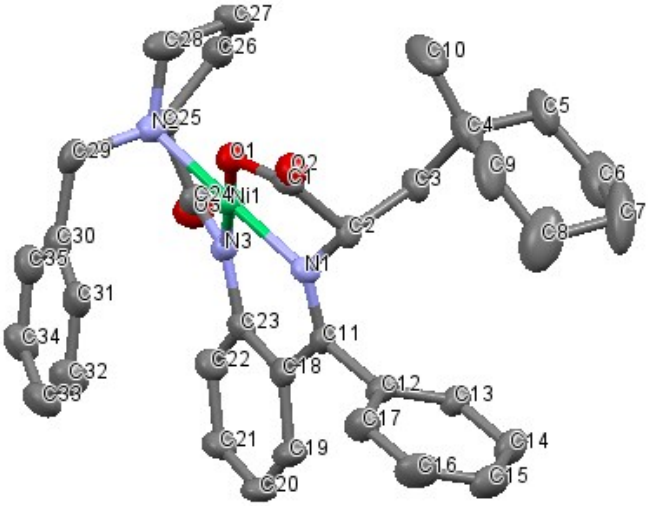
^{13}C-NMR (101 MHz, D_2O+CD_3OD): δ = 173.0, 172.6, 52.6, 50.7 (d, *J* = 7.2 Hz), 50.61 (d, *J* = 7.0 Hz), 31.5, 31.3, 31.0, 30.1 (d, *J* = 51.4 Hz), 29.1 (d, *J* = 51.4 Hz), 12.3 (d, *J* = 2.0 Hz), 12.2 (d, *J* = 3.0 Hz), 8.82 (d, *J* = 53.0 Hz), 7.93 (d, *J* = 53.0 Hz) ppm.

^{31}P-NMR (162 MHz, D_2O+CD_3OD): δ = 64.12 (d, *J* = 19.7 Hz), 63.30 (d, *J* = 26.8 Hz).

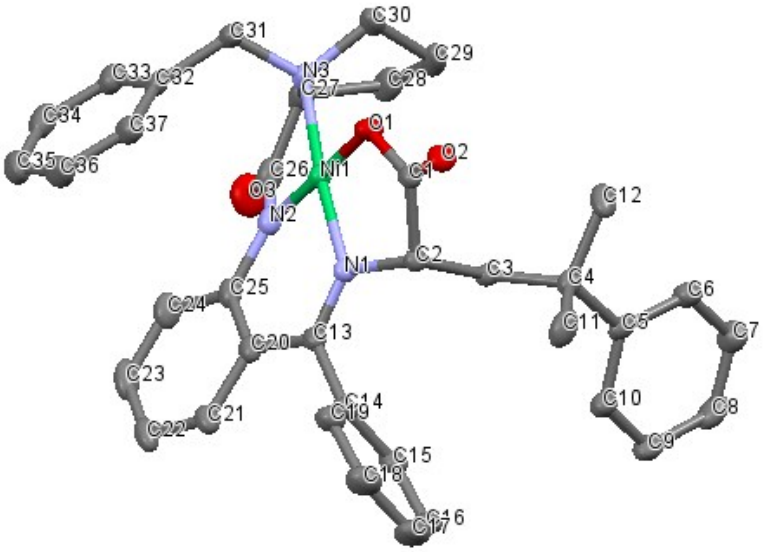
HRMS (ESI, *m*/*z*) calcd. for $C_7H_{17}NO_4P^+$ $[M+H]^+$: 210.0890, found: 210.0891.

5. X-ray diffraction study of Ni(II) complexes (*S,S*)-4a, (*S,S*)-4c and (*S,S,S*)-4n

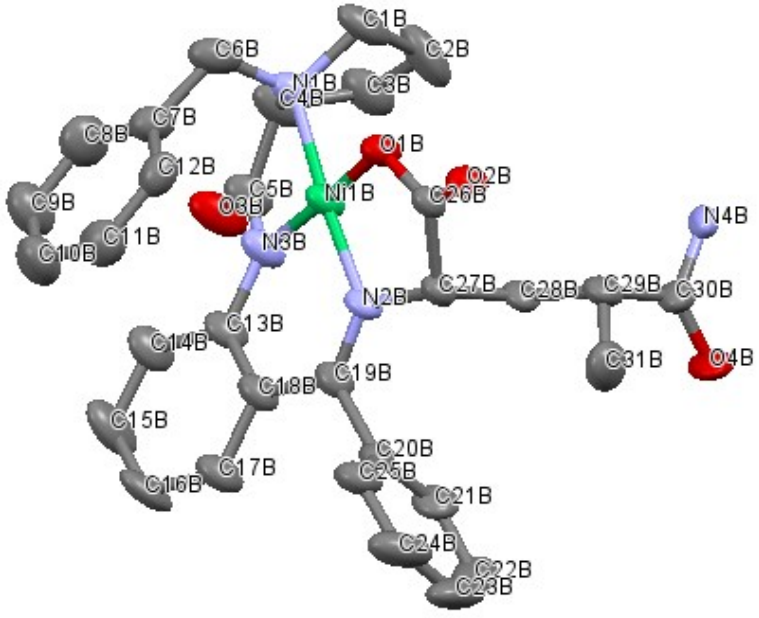
Single-crystal X-ray diffraction experiments for the Ni(II) complexes (*S,S*)-**4a,** (*S,S*)-**4c** and (*S,S,R*)-**4n** were carried out with a Bruker APEX-II CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, ω-scan technique). The APEX II software[4] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction. All calculations (space group and structure determination, refinements, graphics, and structure reporting) were made using the SHELXL2014[5] and OLEX2[6] program packages. Experimental details and crystal parameters are listed in Table S1. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors calculations in the riding motion approximation. The contribution of (*S,S,R*)-**4n** to structure factors was excluded using SQUEEZE[7] routine implemented in PLATON software.[8] CCDC 1892731 ((*S,S,R*)-**4n**), 1892732 ((*S,S*)-**4c**) and 1892733 ((*S,S*)-**4a**) data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.



Structure of the Ni(II) complex (*S*,*S*)-**4a**



Structure of the Ni(II) complex (*S*,*S*)-**4c**



Structure of the Ni(II) complex (*S*,*S*,*R*)-**4n**

Table S1. Crystallographic data and structure refinement parameters

Compound	(*S*,*S*)-**4a**	(*S*,*S*)-**4c**	(*S*,*S*,*R*)-**4n**
Formula moiety	$C_{35}H_{39}N_3NiO_3$,CCl_4	$(C_{37}H_{37}N_3NiO_3)_{0,5}$, $(H_2O)_{0,5}$	$C_{31}H_{32}N_4NiO_4$, $(CH_2Cl_2)_{0,5}$, $(CCl_4)_{0.5}$
Brutto formula	$C_{36}H_{39}Cl_4N_3NiO_3$	$C_{18.50}H_{19.50}N_{1.50}Ni_{0.50}O_2$	$C_{32}H_{33}Cl_3N_4NiO_4$
Molecular weight	762.21	324.21	702.68
Diffractometer	Bruker APEX-II CCD	Bruker APEX-II CCD	Bruker APEX-II CCD
Anode [Wavelength, Å]	MoKα [0.71073] sealed tube	MoKα [0.71073] sealed tube	MoKα [0.71073] sealed tube
Crystal system	Orthorhombic	monoclinic	triclinic
Space group	$P2_12_12_1$	$P12_11$	$P1$
a (Å)	11.4520(9)	9.8460(4)	9.3743(5)
b (Å)	13.8346(12)	12.0451(5)	13.3790(7)
c (Å)	22.8016(19)	14.2648(6)	14.9327(8)
α, °	90	90	81.0080(10)
β, °	90	110.1810(10)	89.6580(10)
γ, °	90	90	80.2760(10)
V (Å^3)	3612.5(5)	1587.89(11)	1822.85(17)
Z	4	4	2
Density, g cm^{-3}	1.401	1.356	1.280
T, K	120	120	120
θ range (deg)	1.89–27.0		
μ, mm^{-1}	0.872	0.656	0.790
F(000)	1584	684	728
Absorption correction	SADABS		
$T_{max.}/T_{min.}$	0.5675/0.7461	0.6893/0.7459	0.6851/0.7461
Collected reflections	29481	20201	17604
Independent reflections	7088	8940	14086
Observed reflections ($I > 2\sigma(I)$)	5554	7901	12635
Parameters	425	408	801
R_{int}	0.0752	0.0301	0.0158
2θmin - 2θmax, °	3.444 - 52.000	3.042 - 59.366	3.128 - 51.998
$R1^a$ (on *F* for obs. refls)	0.0634	0.0372	0.0545
$wR2^b$ (on F^2 for all refls)	0.1773	0.0899	0.1513
GOF[c]	1.031	1.005	1.037
P_{min}/ρ_{max}, eÅ^{-3}	-0.983/1.654	-0.686/0.774	-0.556/0.868

[a] $R = \Sigma \big| \, |F_o| - |F_c| \, \big| / \Sigma |F_o|$, [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2))]^{1/2}$,

[c] $\mathrm{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$

6. References

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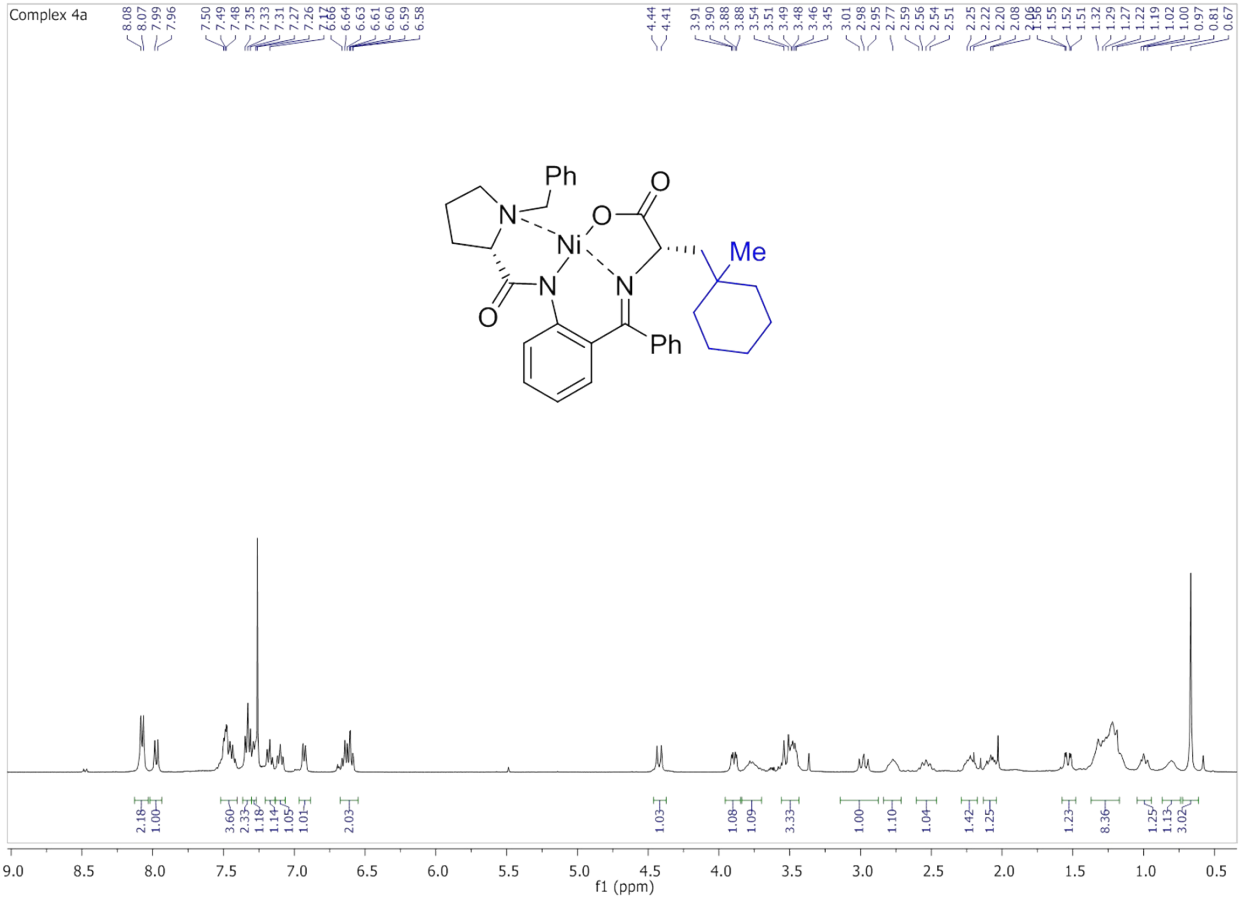
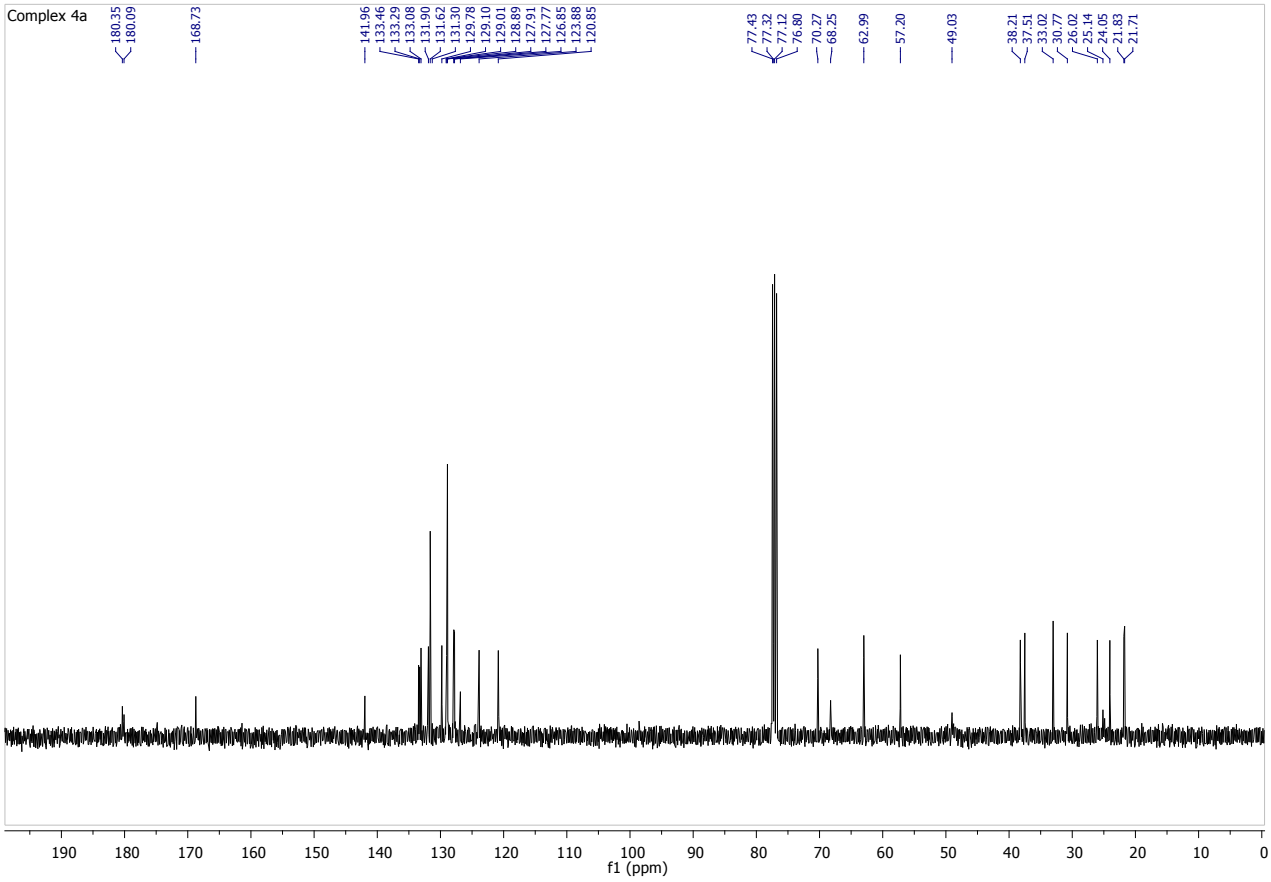
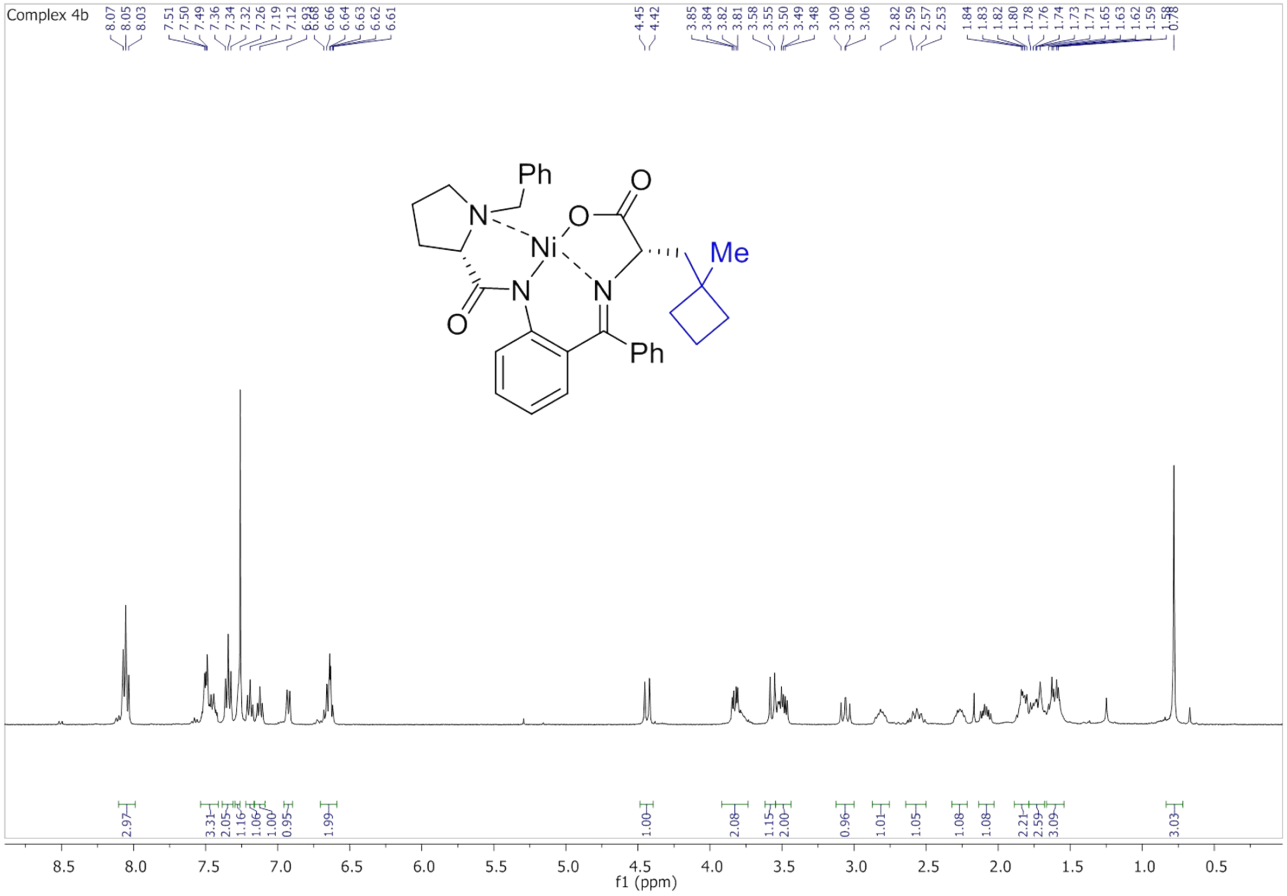
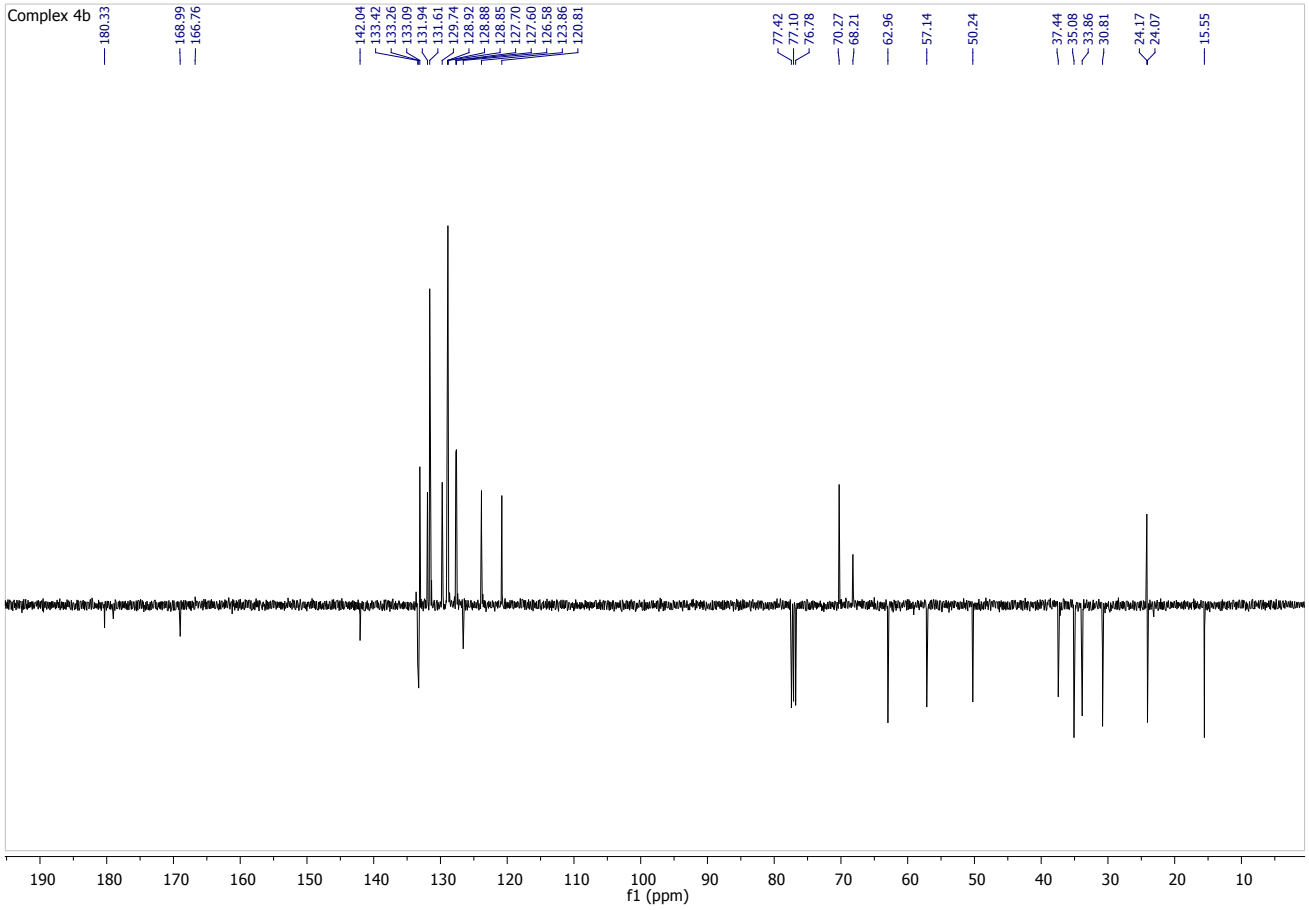
7. Copies of ^{1}H- and ^{13}C-NMR spectra



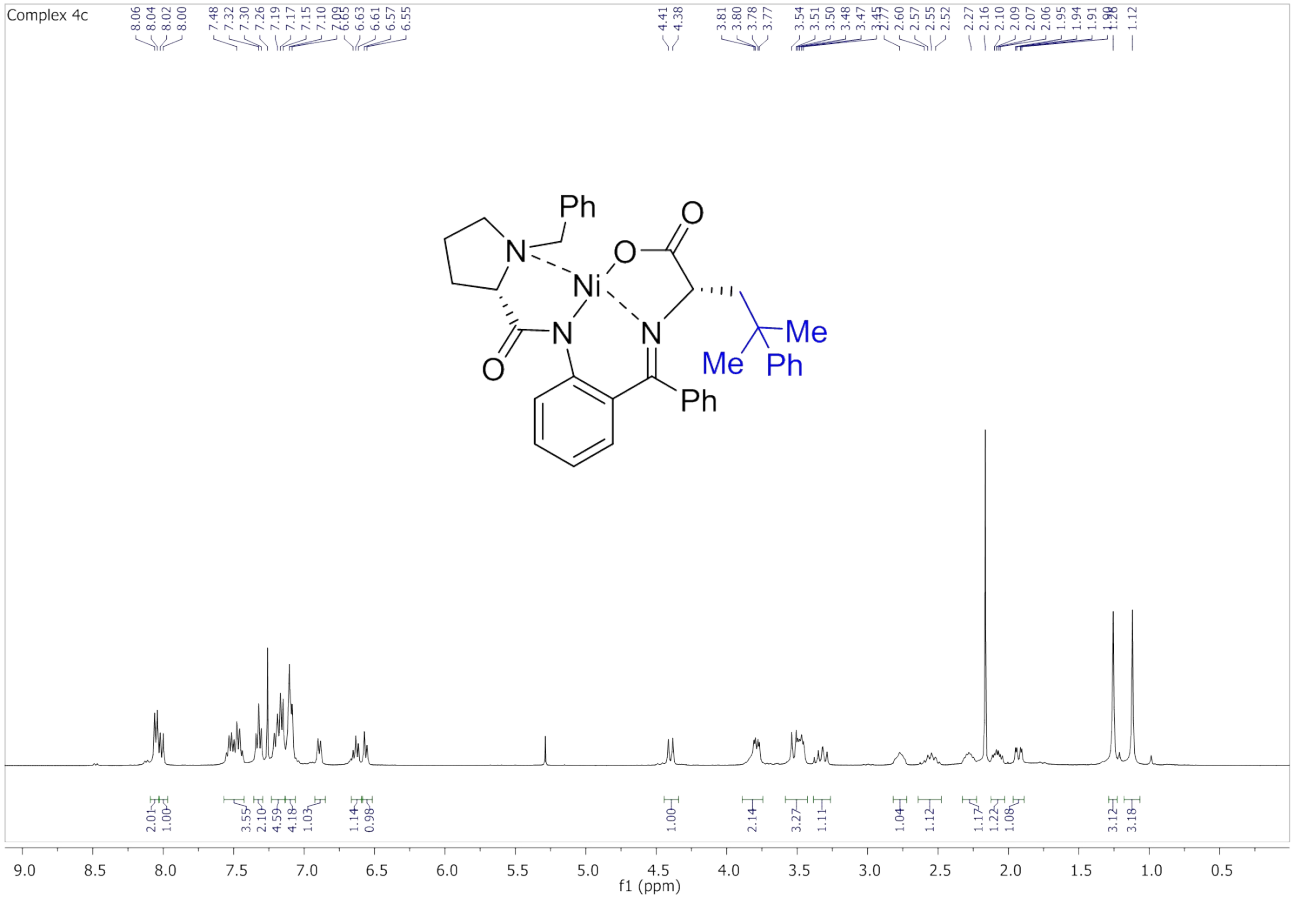


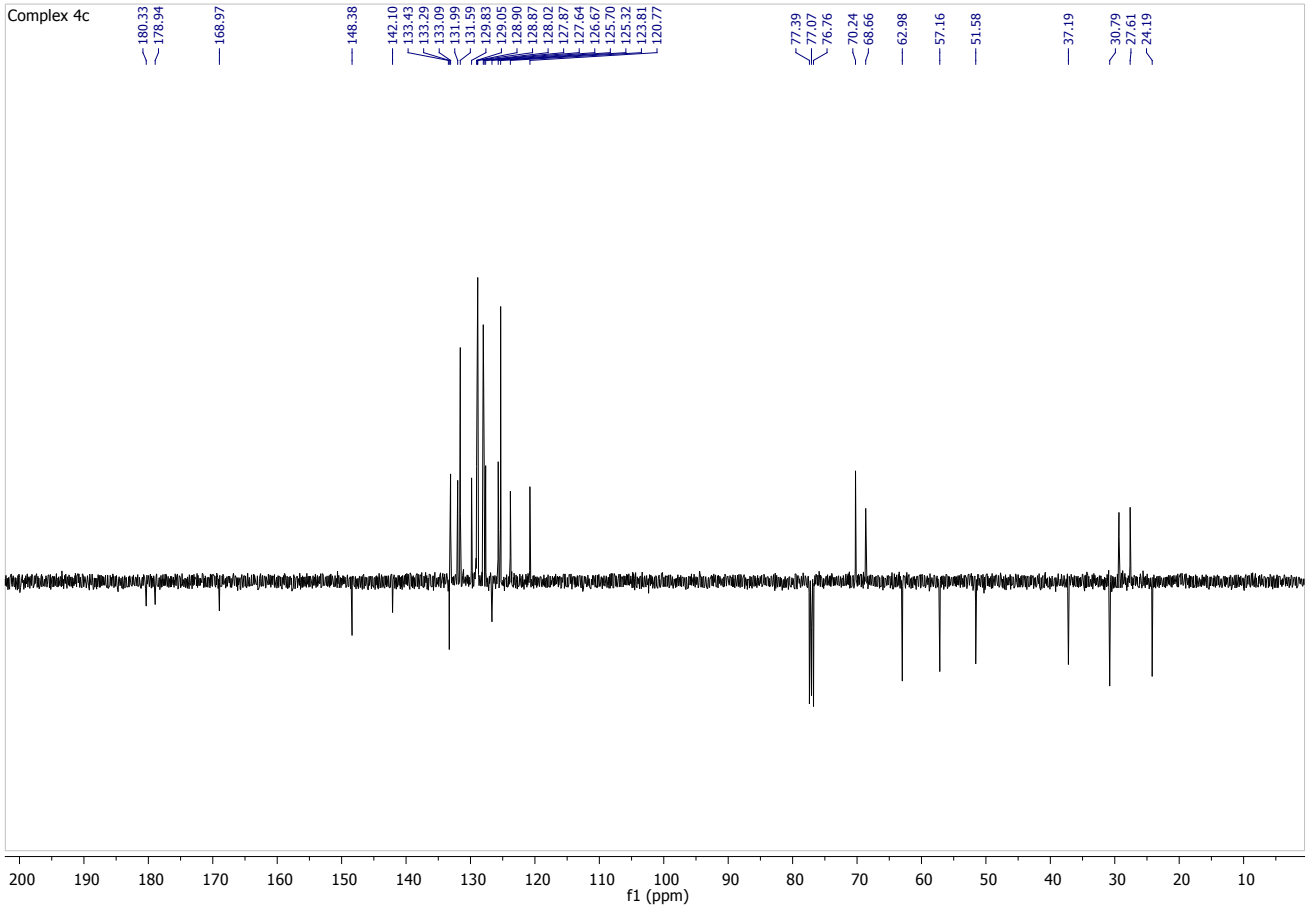
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4a**



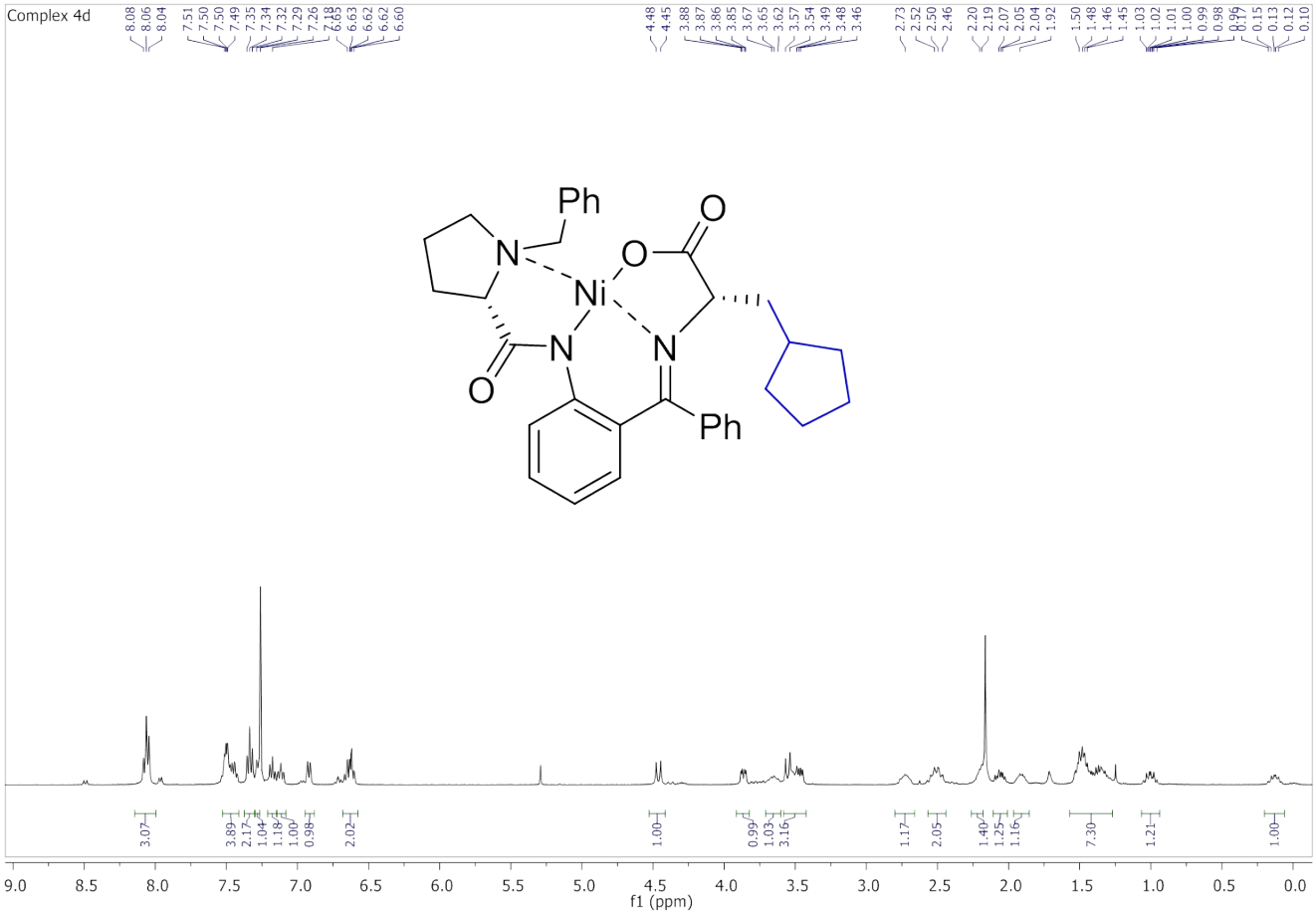


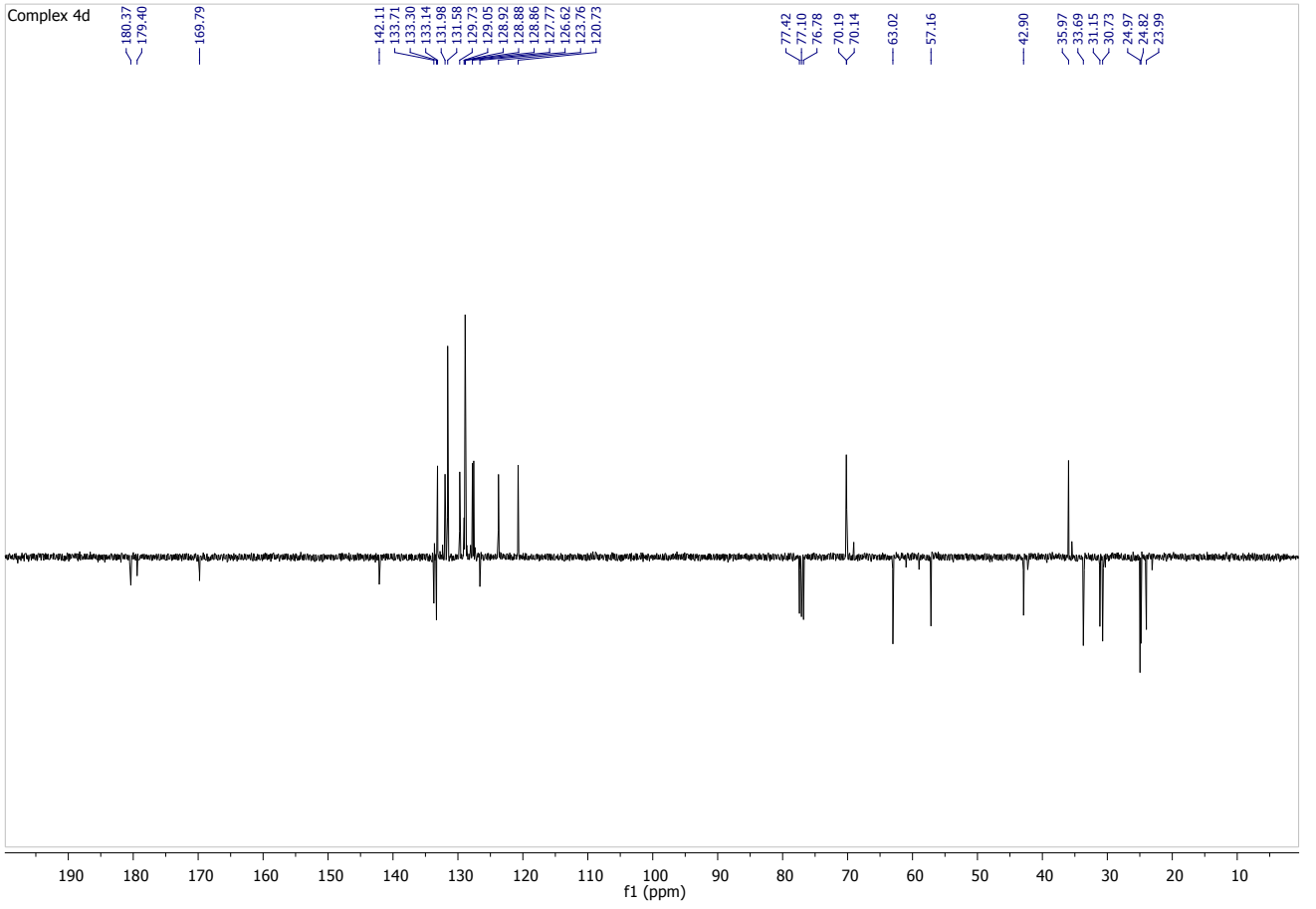
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4b**



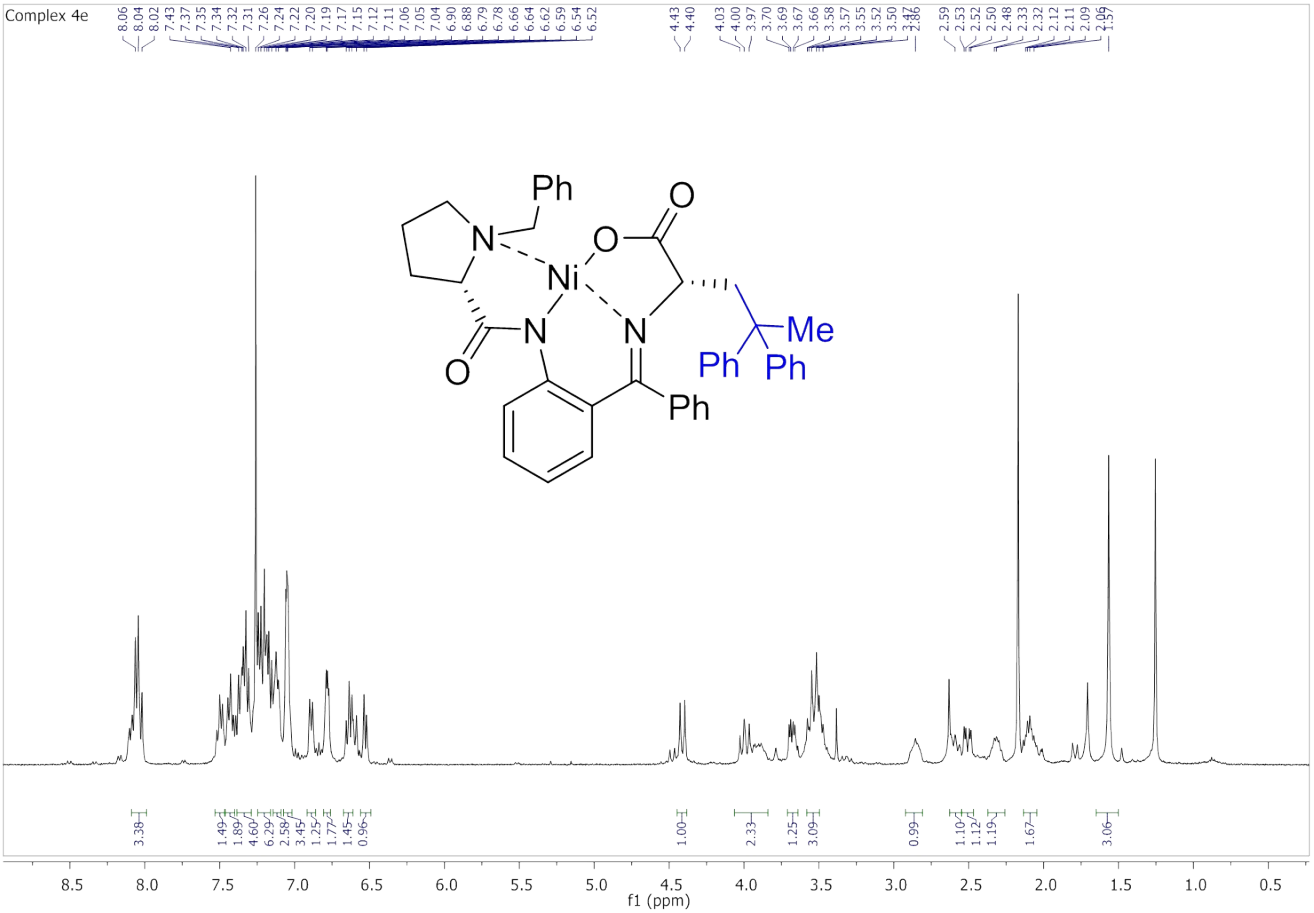


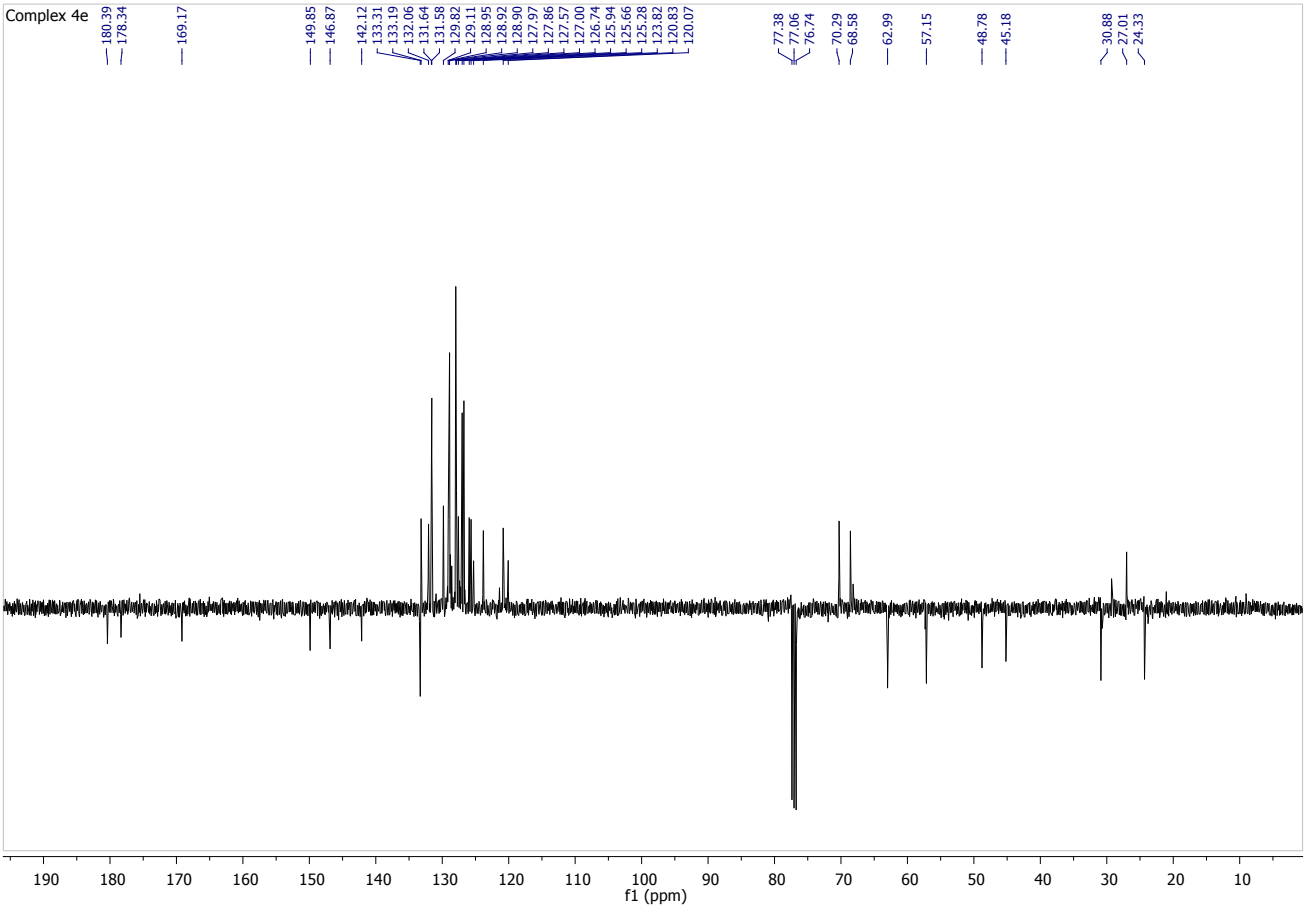
^{1}H and ^{13}C NMR spectra of a Ni(II) the complex **4c**



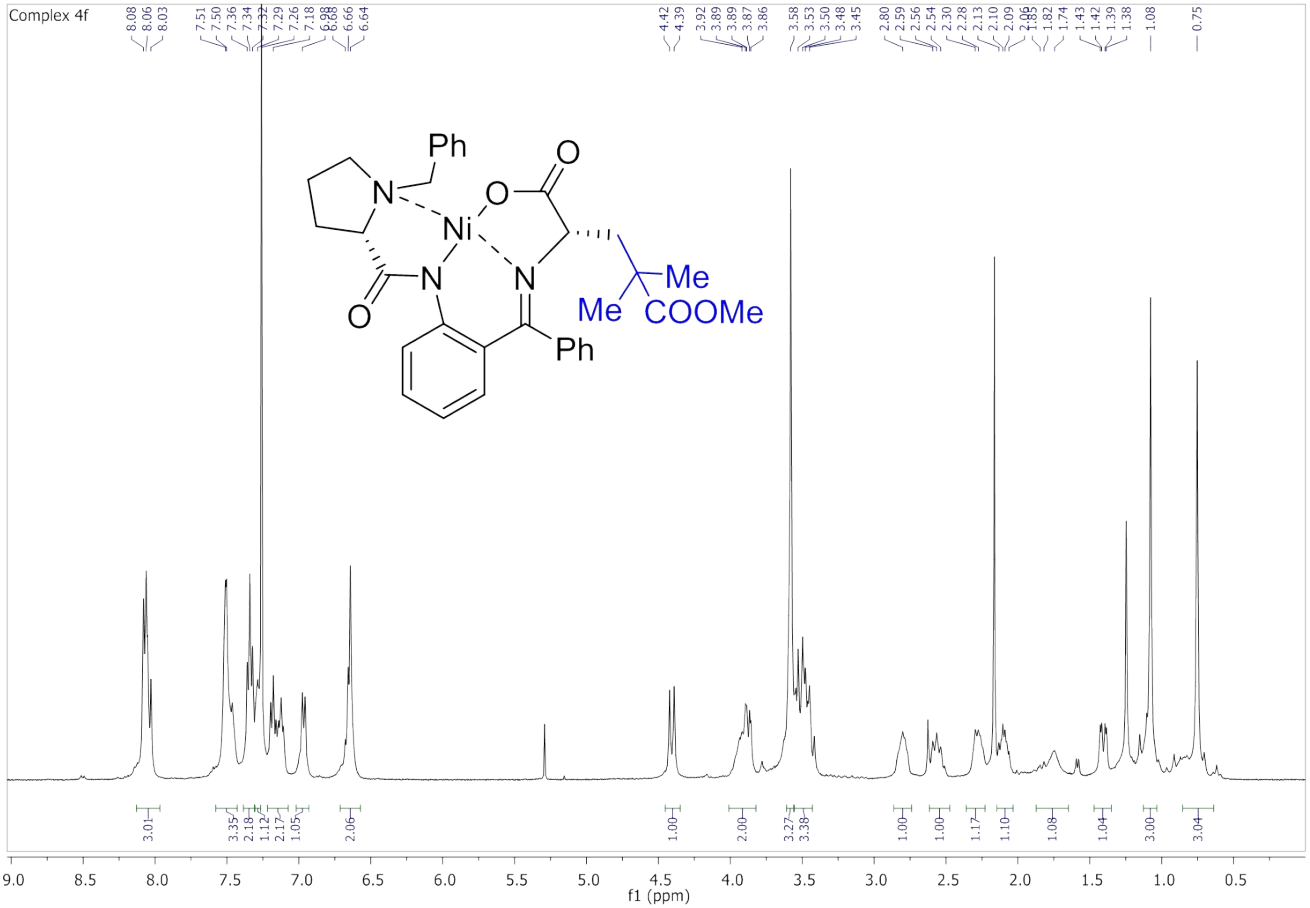


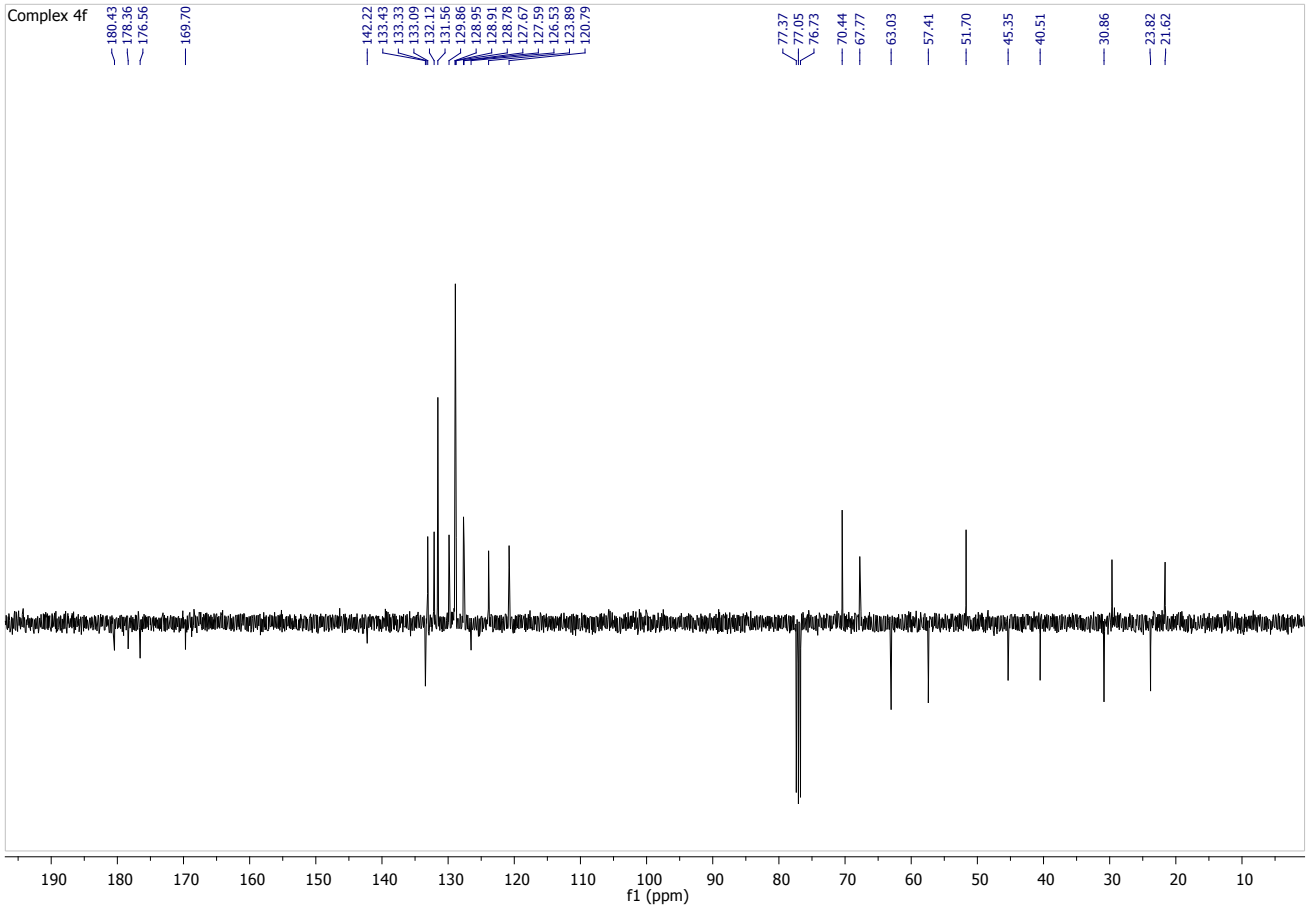
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4d**



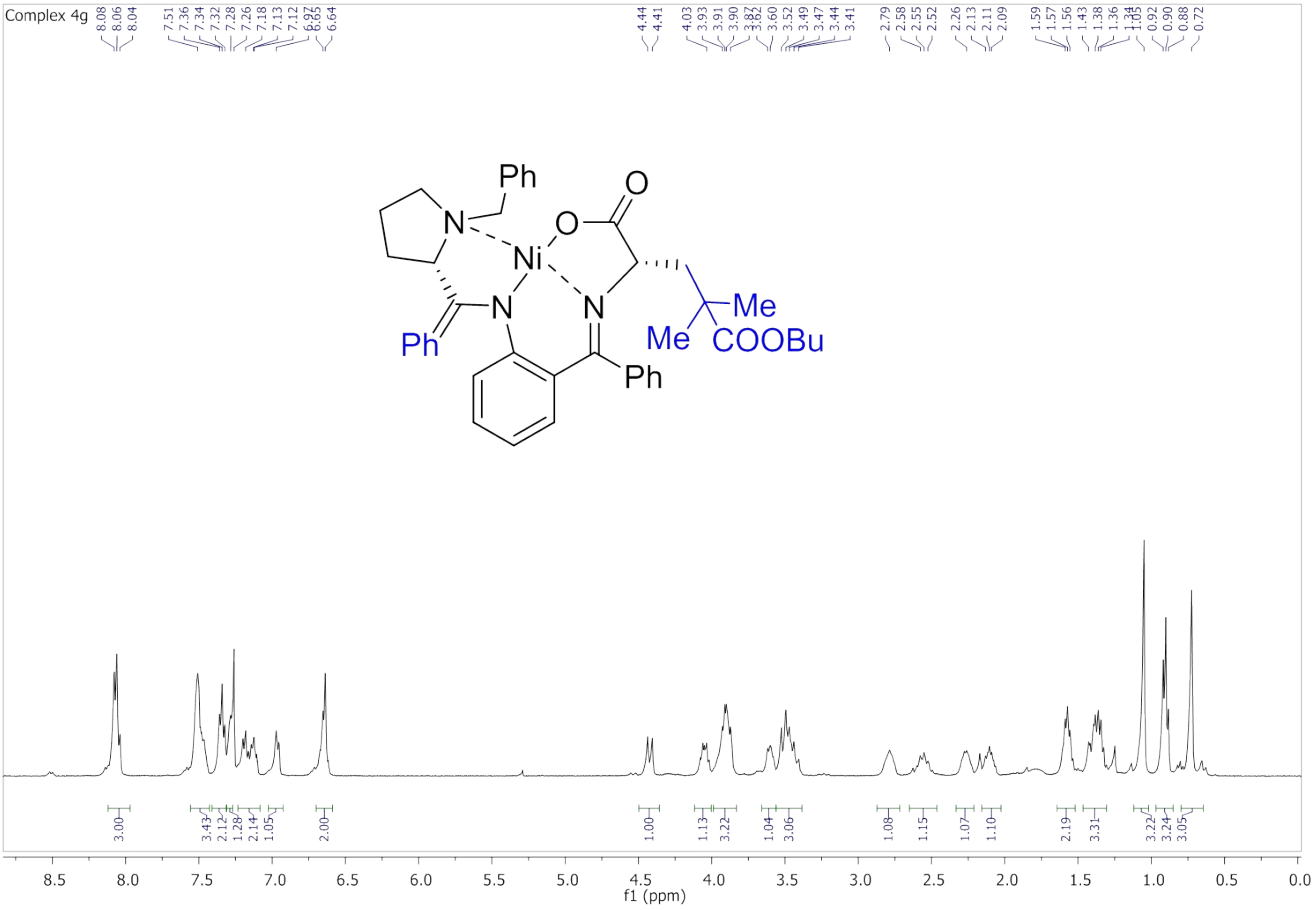


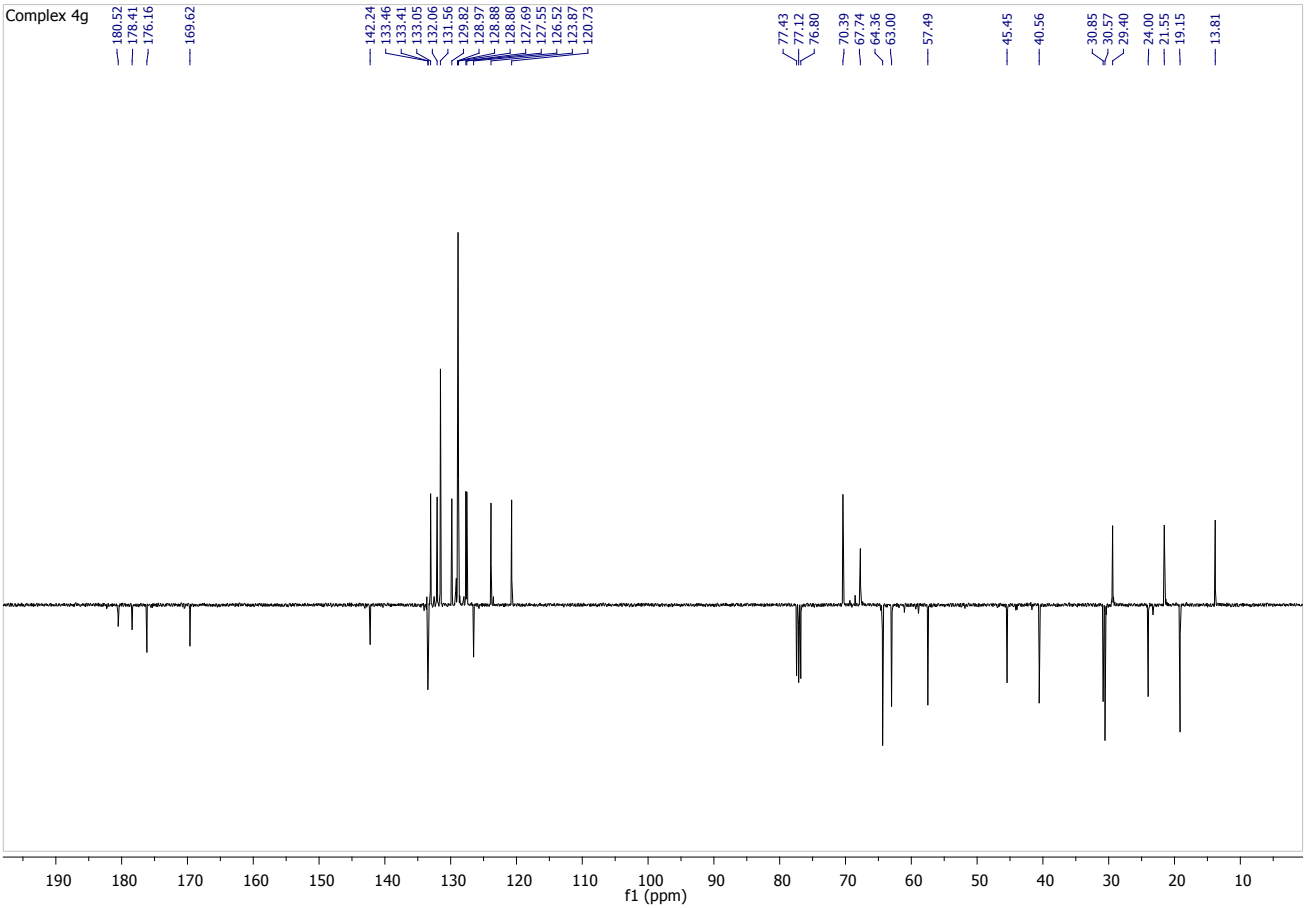
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4e**



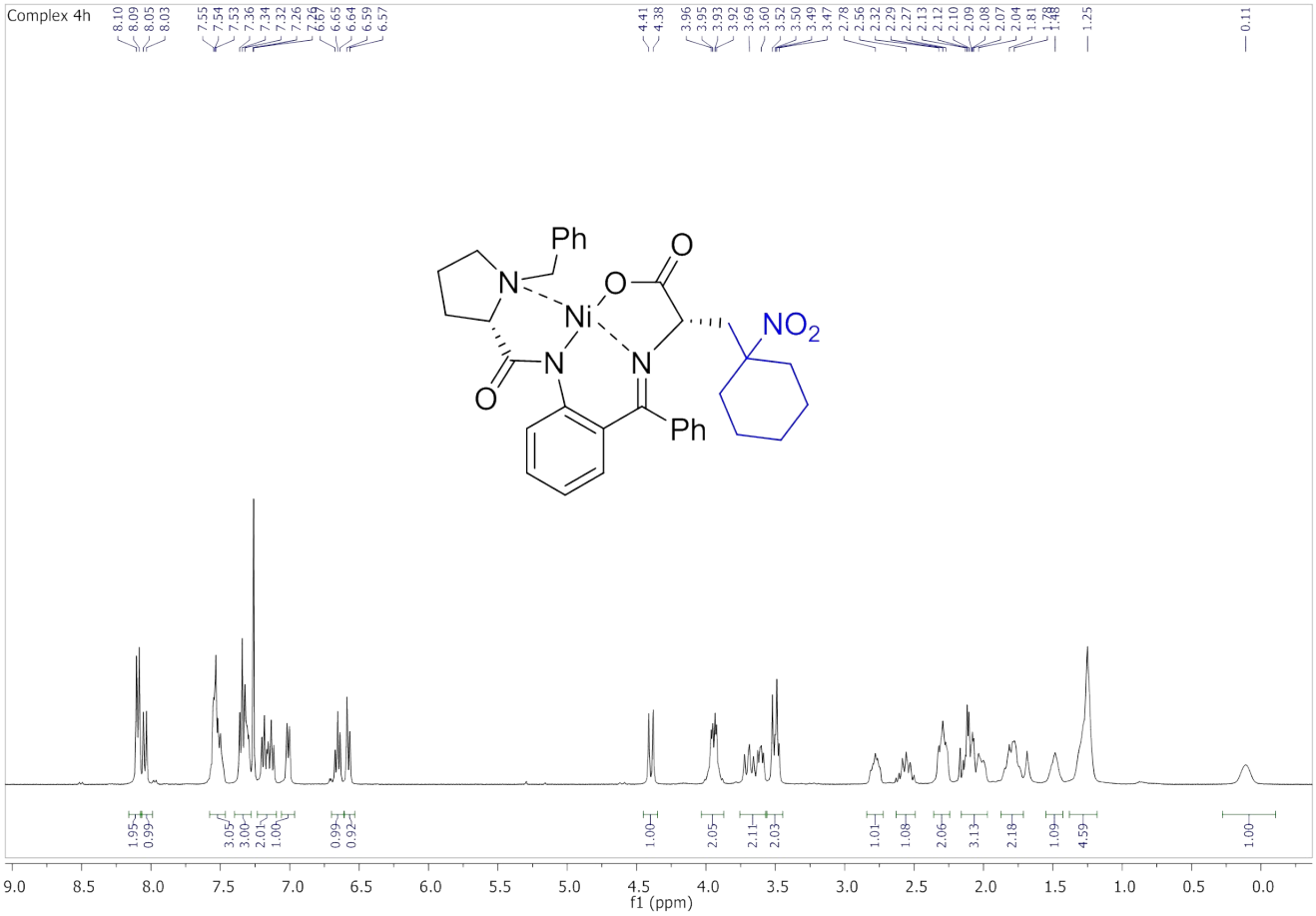


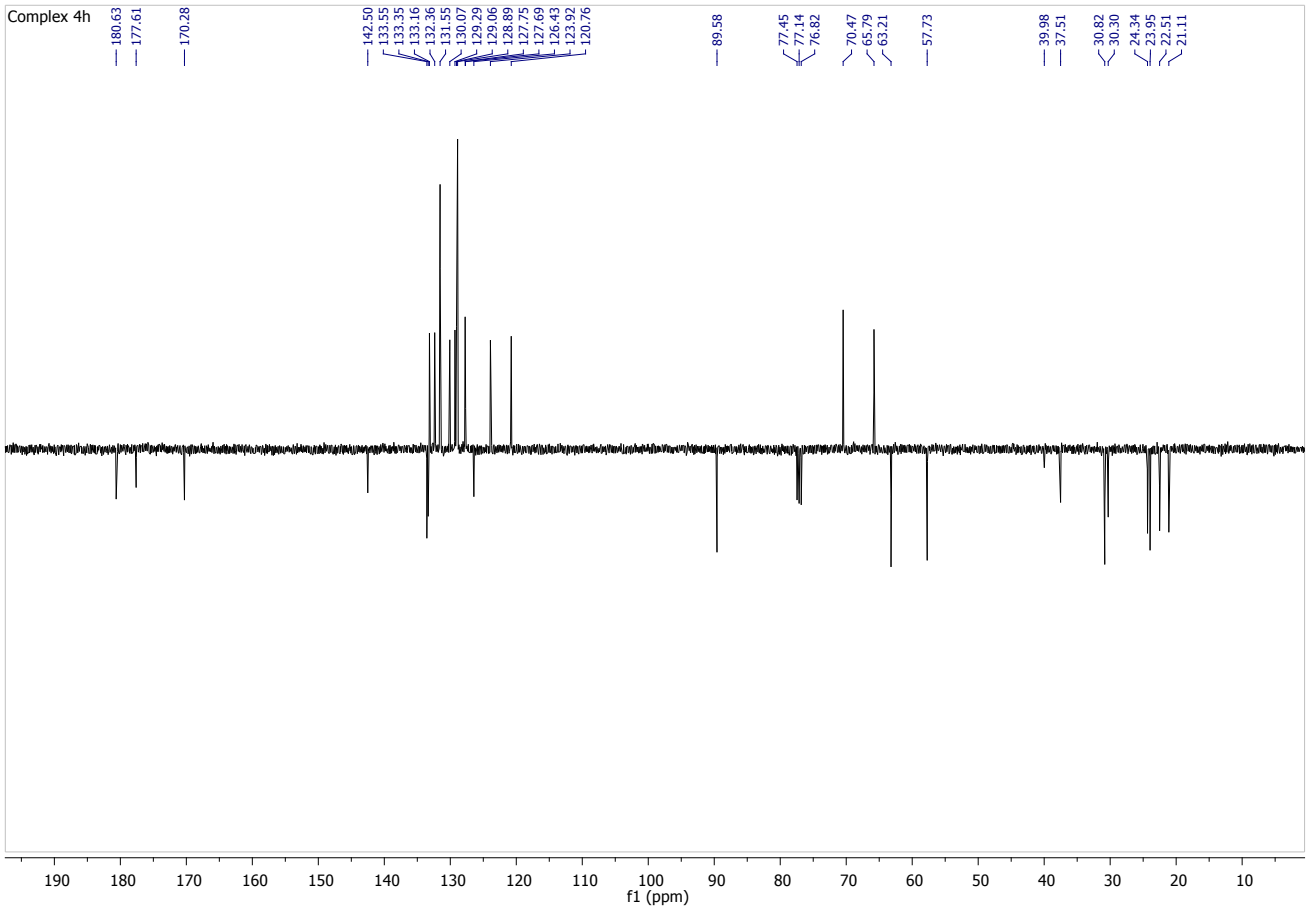
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4f**



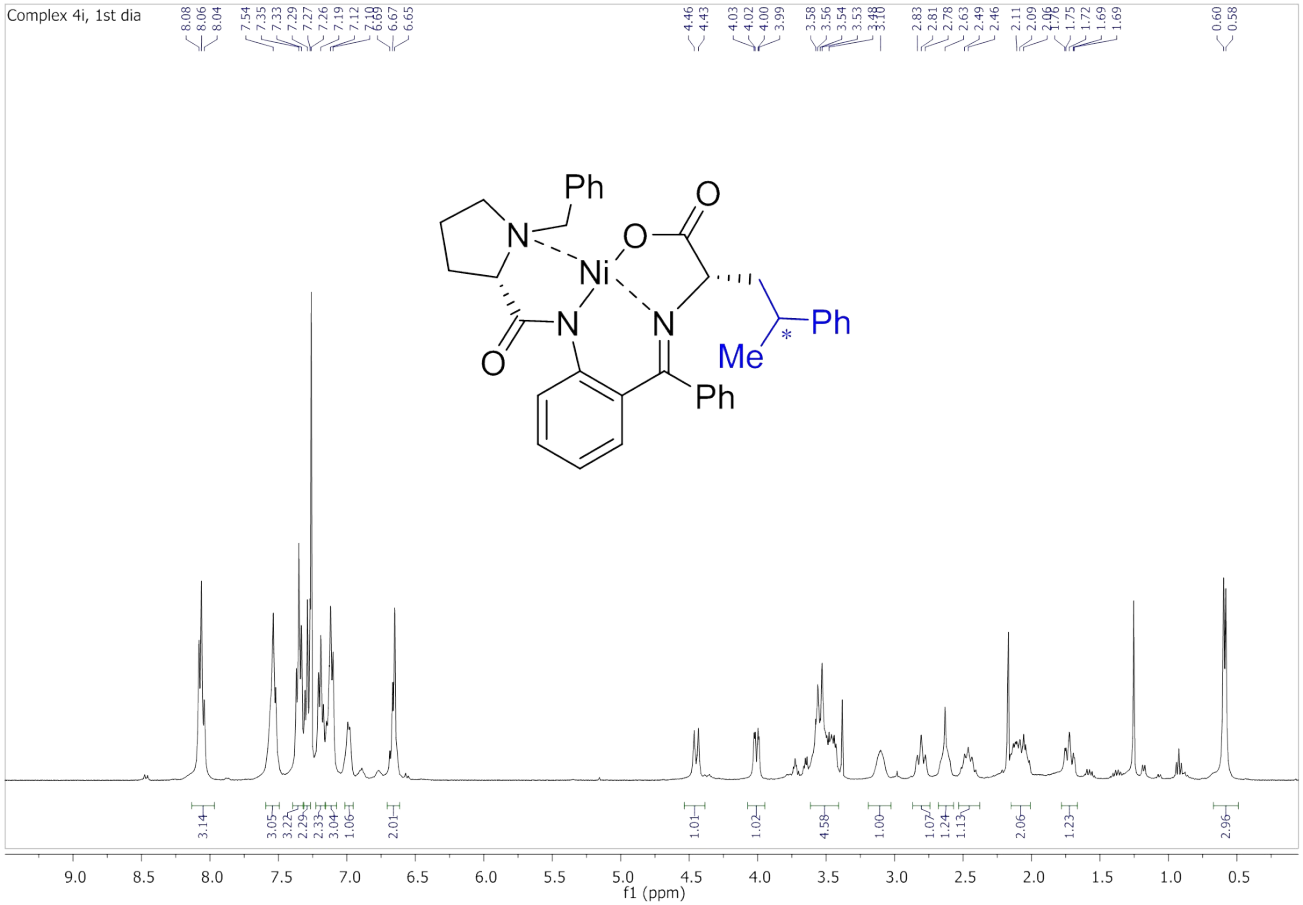


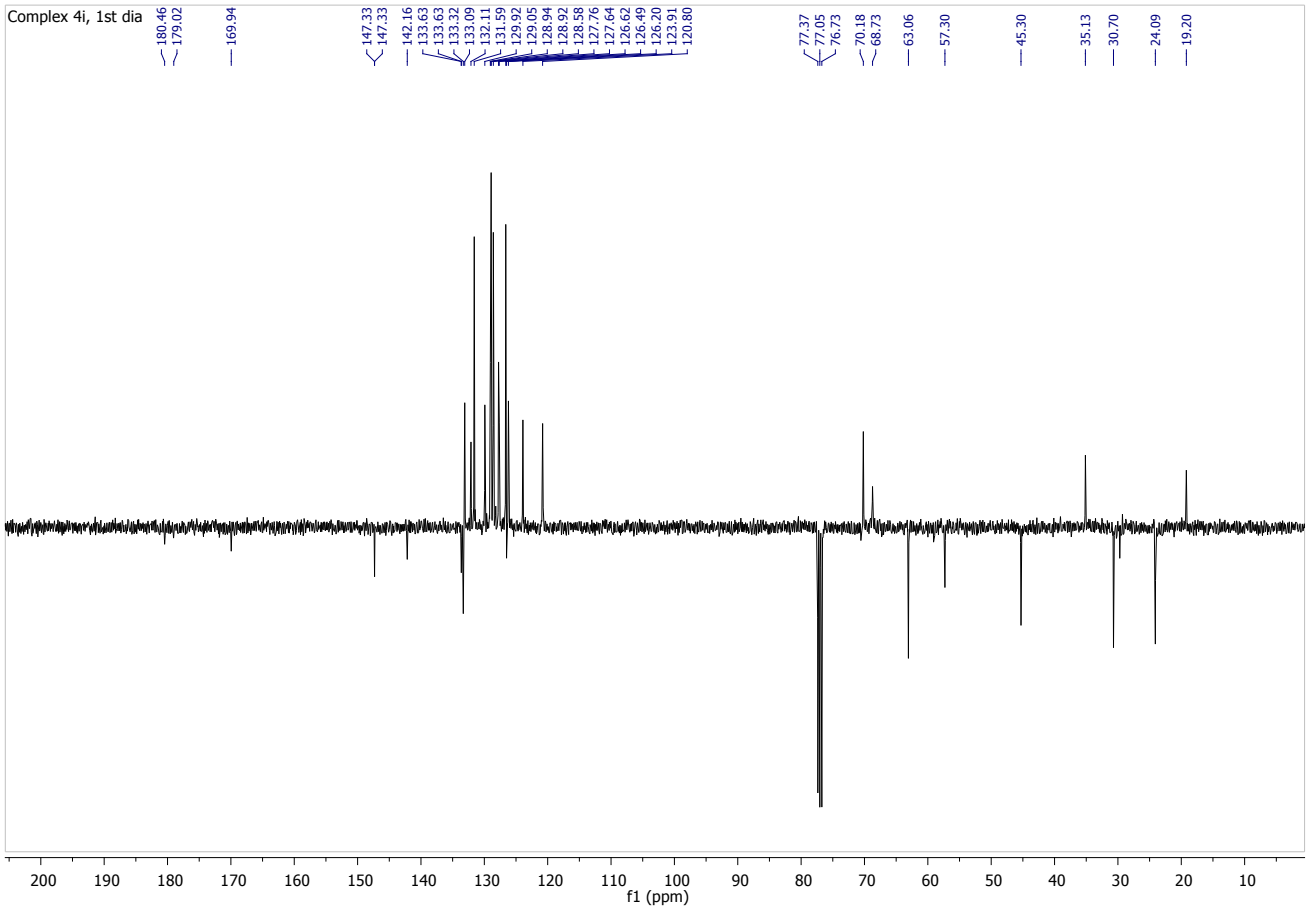
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4g**



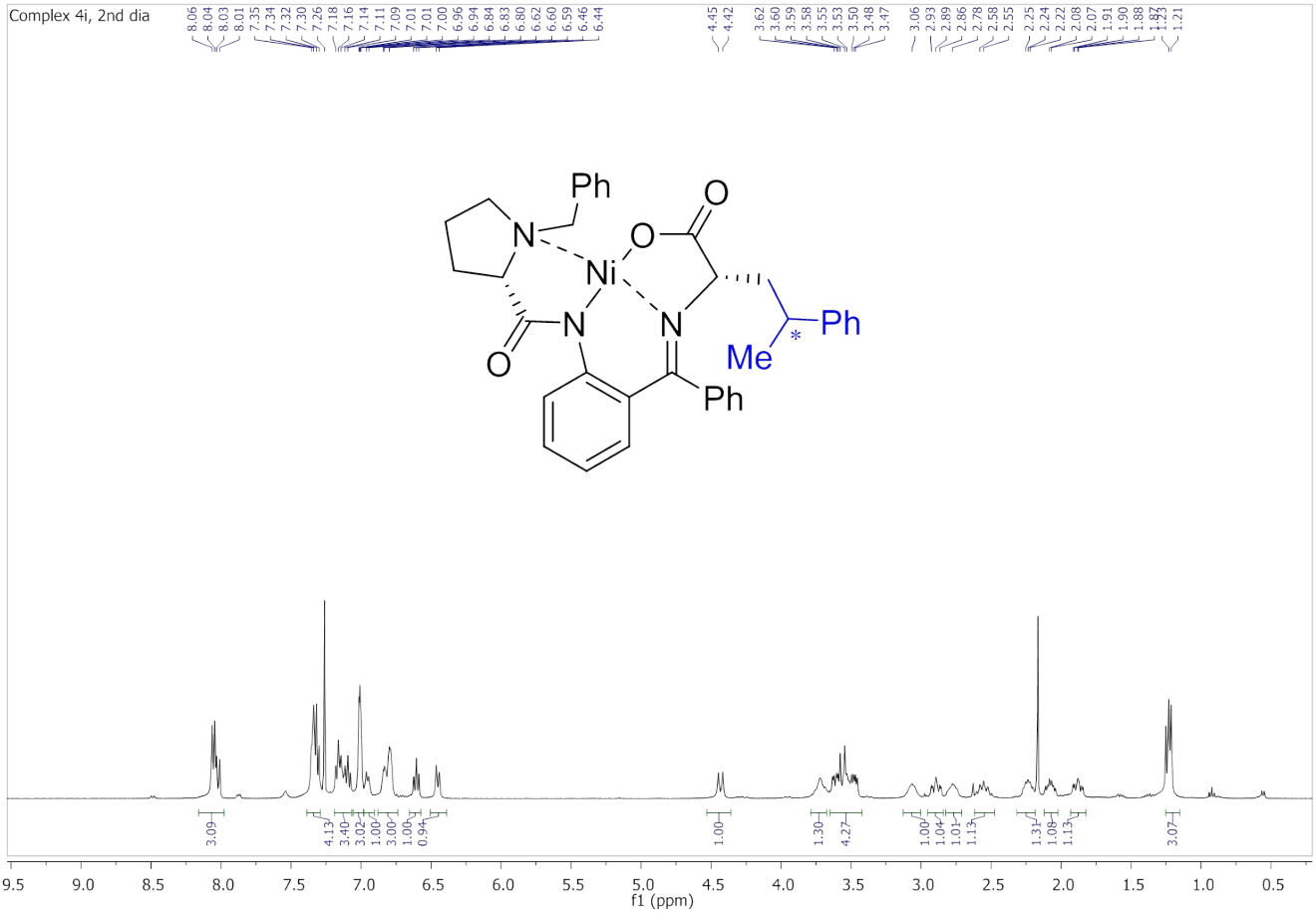


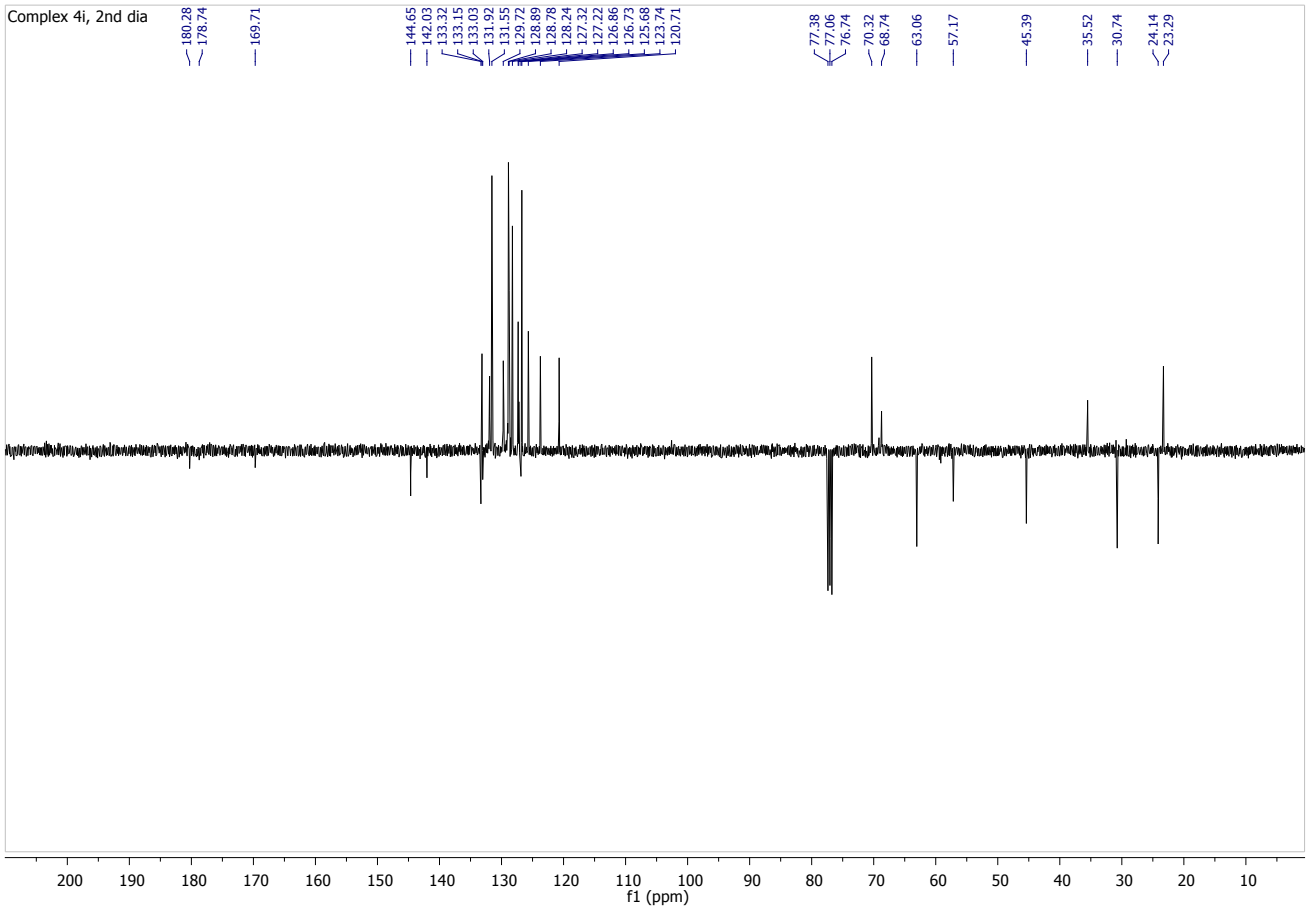
^{1}H and ^{13}C NMR spectra of the Ni(II) complex **4h**



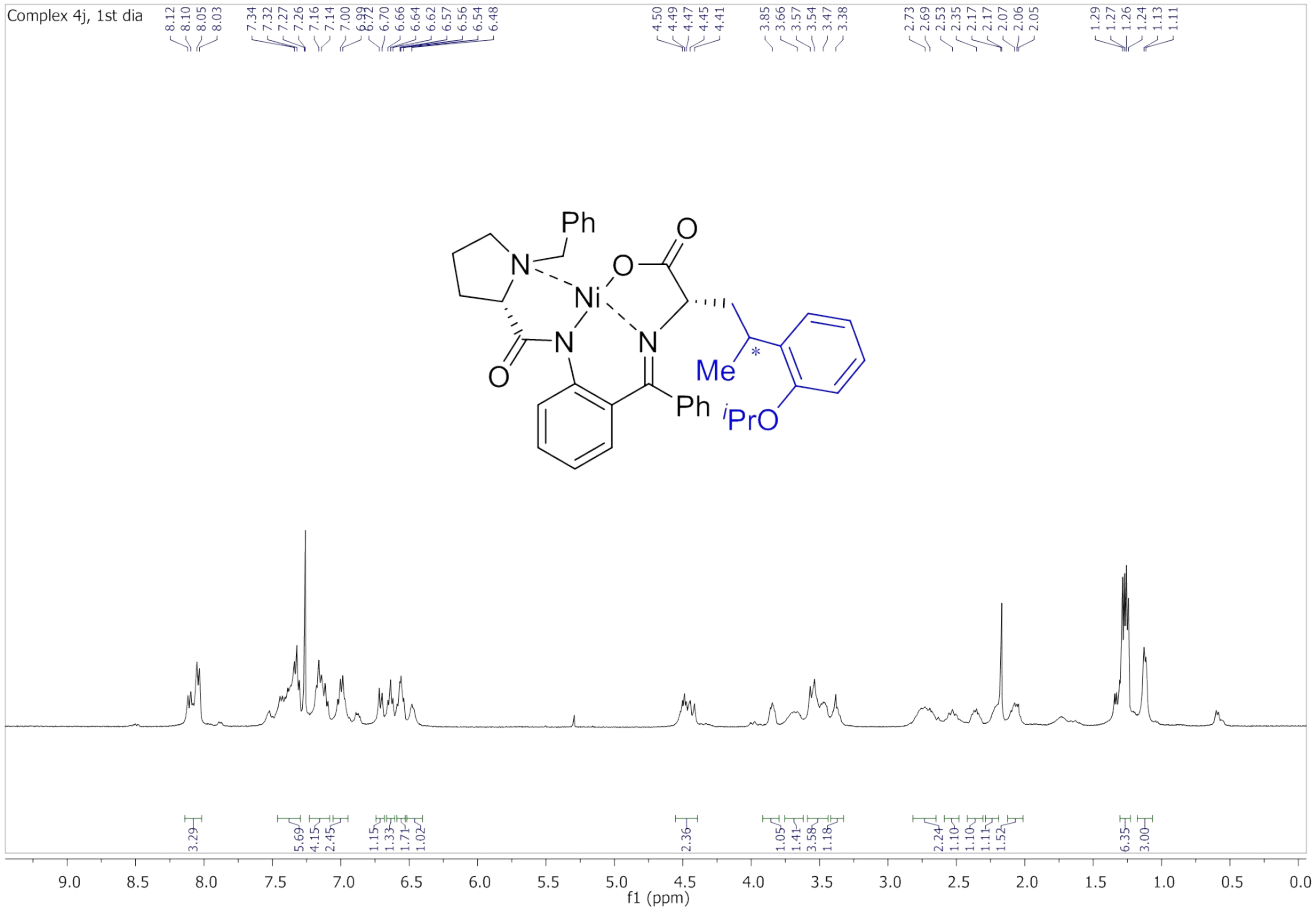


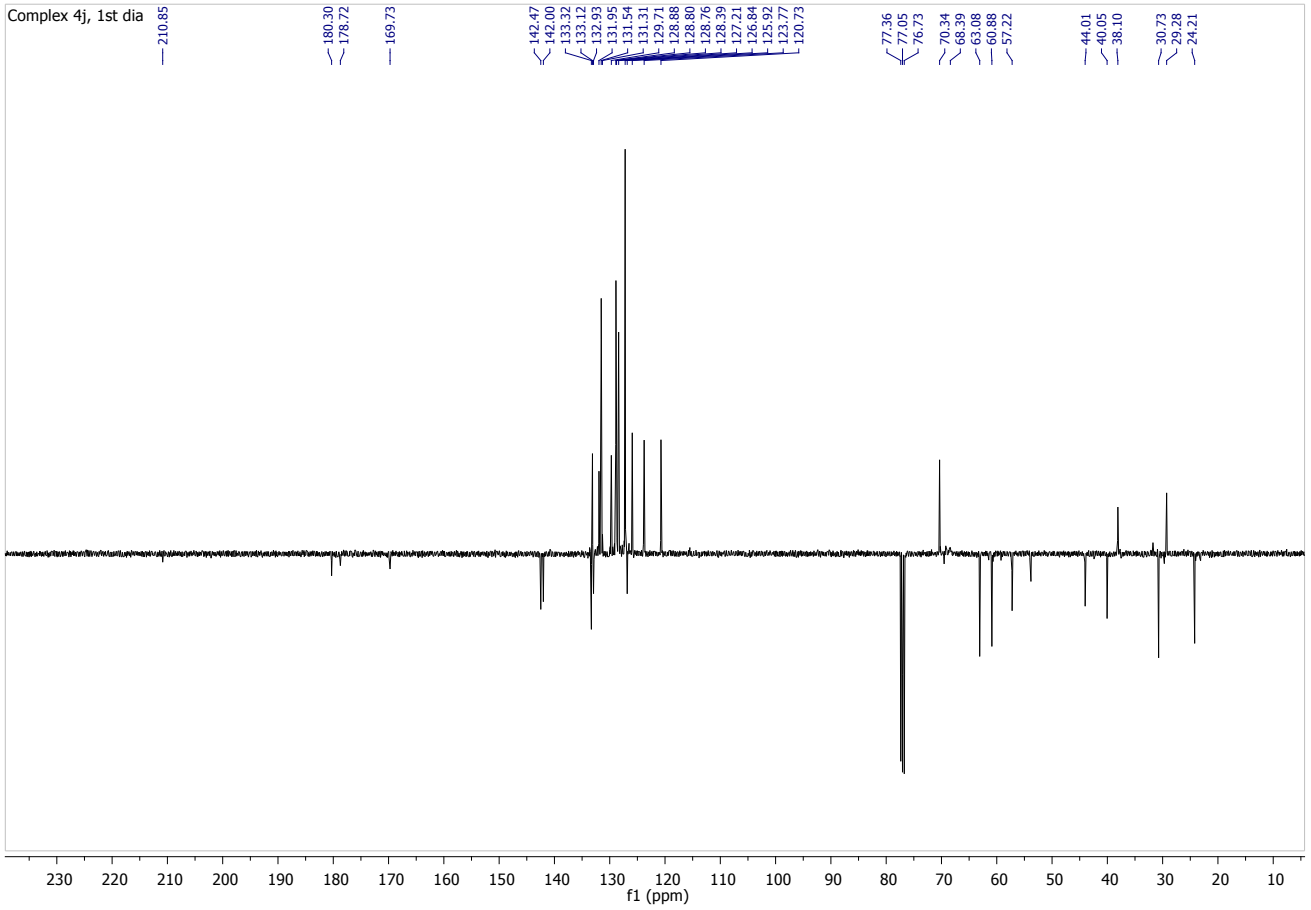
^{1}H and ^{13}C NMR spectra of the 1st diastereomer of the Ni(II) complex **4i**



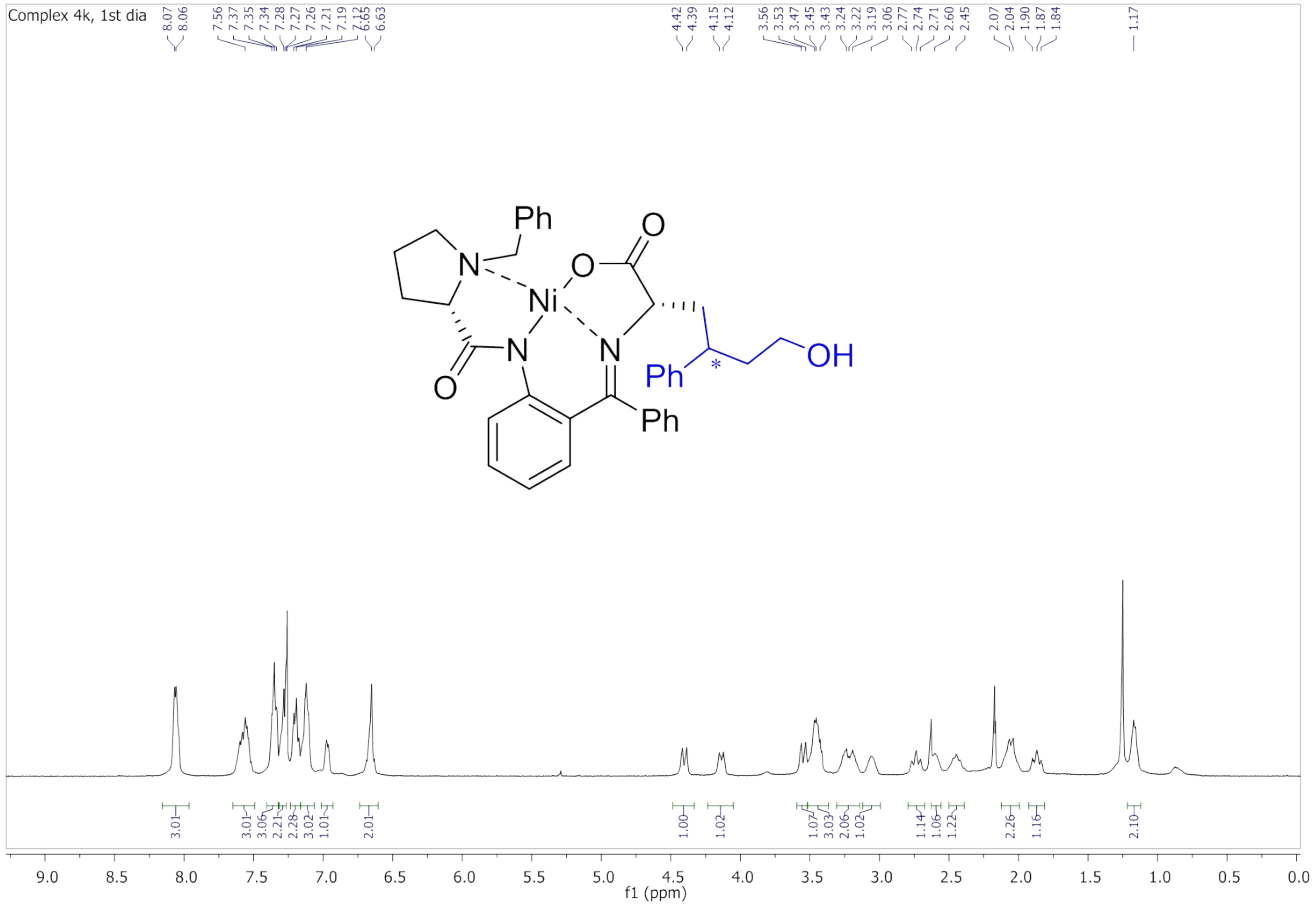


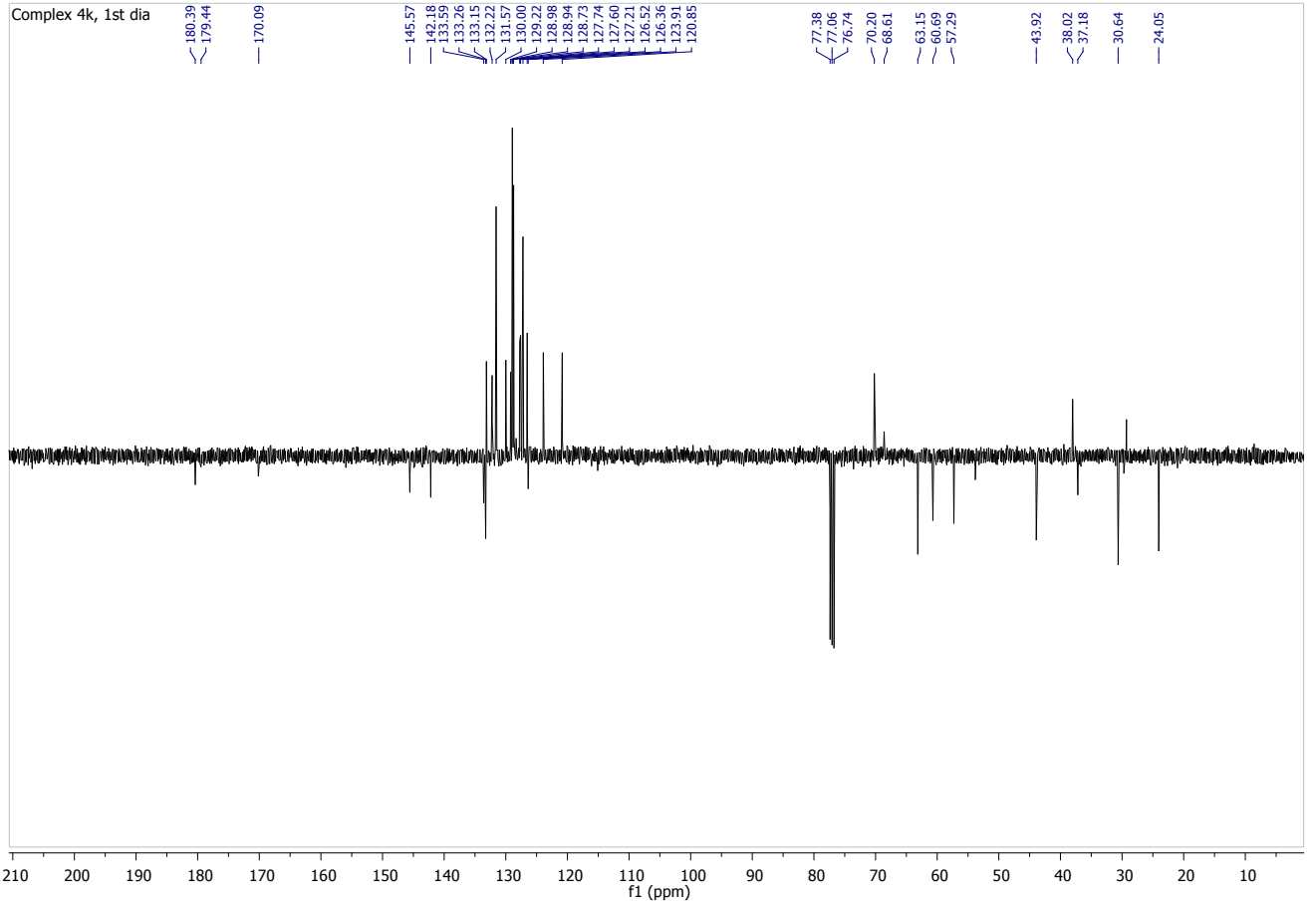
^{1}H and ^{13}C NMR spectra of the 2nd diastereomer of the Ni(II) complex **4i**



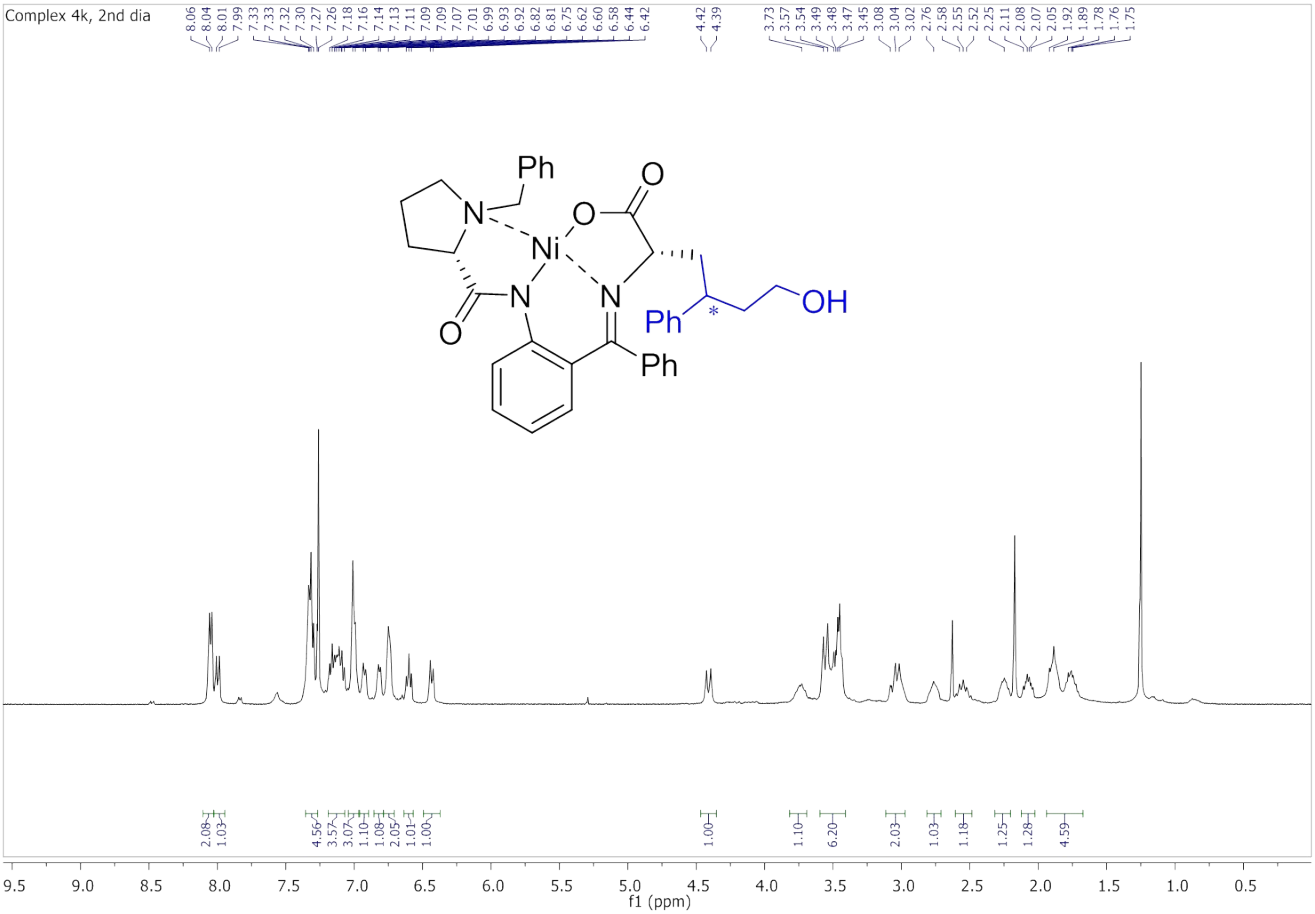


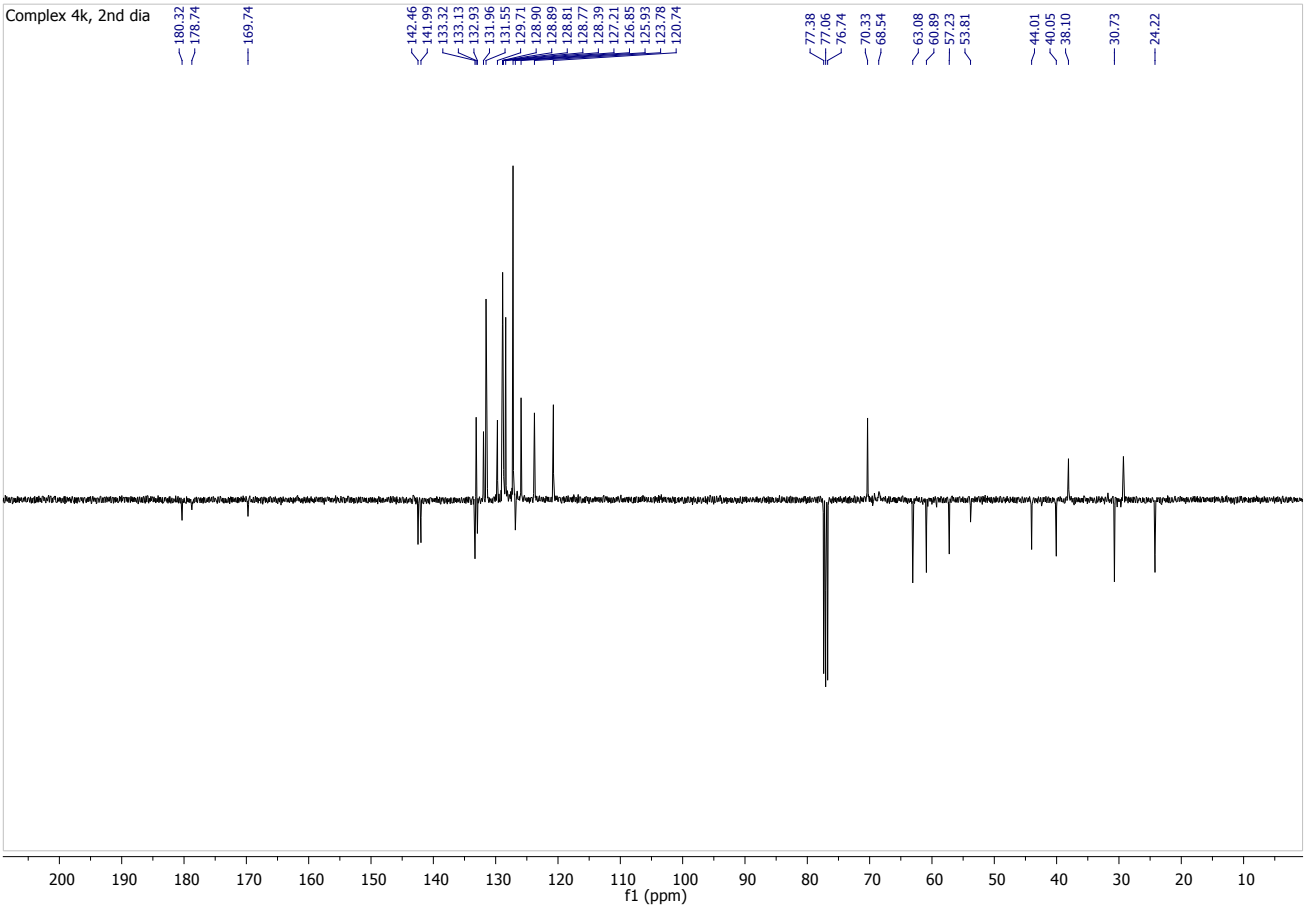
^{1}H and ^{13}C NMR spectra of the 1st diastereomer (*major*) of the Ni(II) complex **4j**



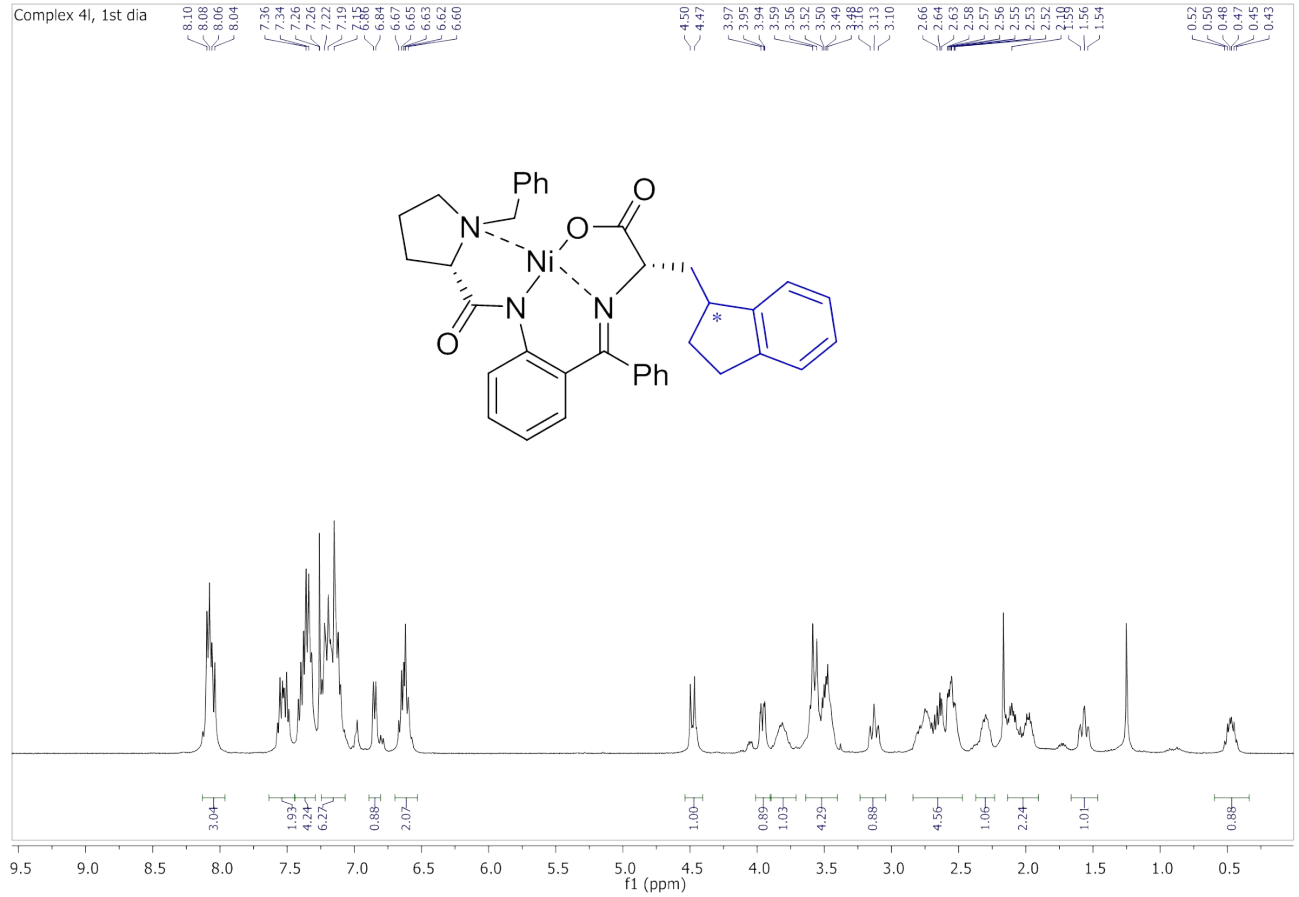


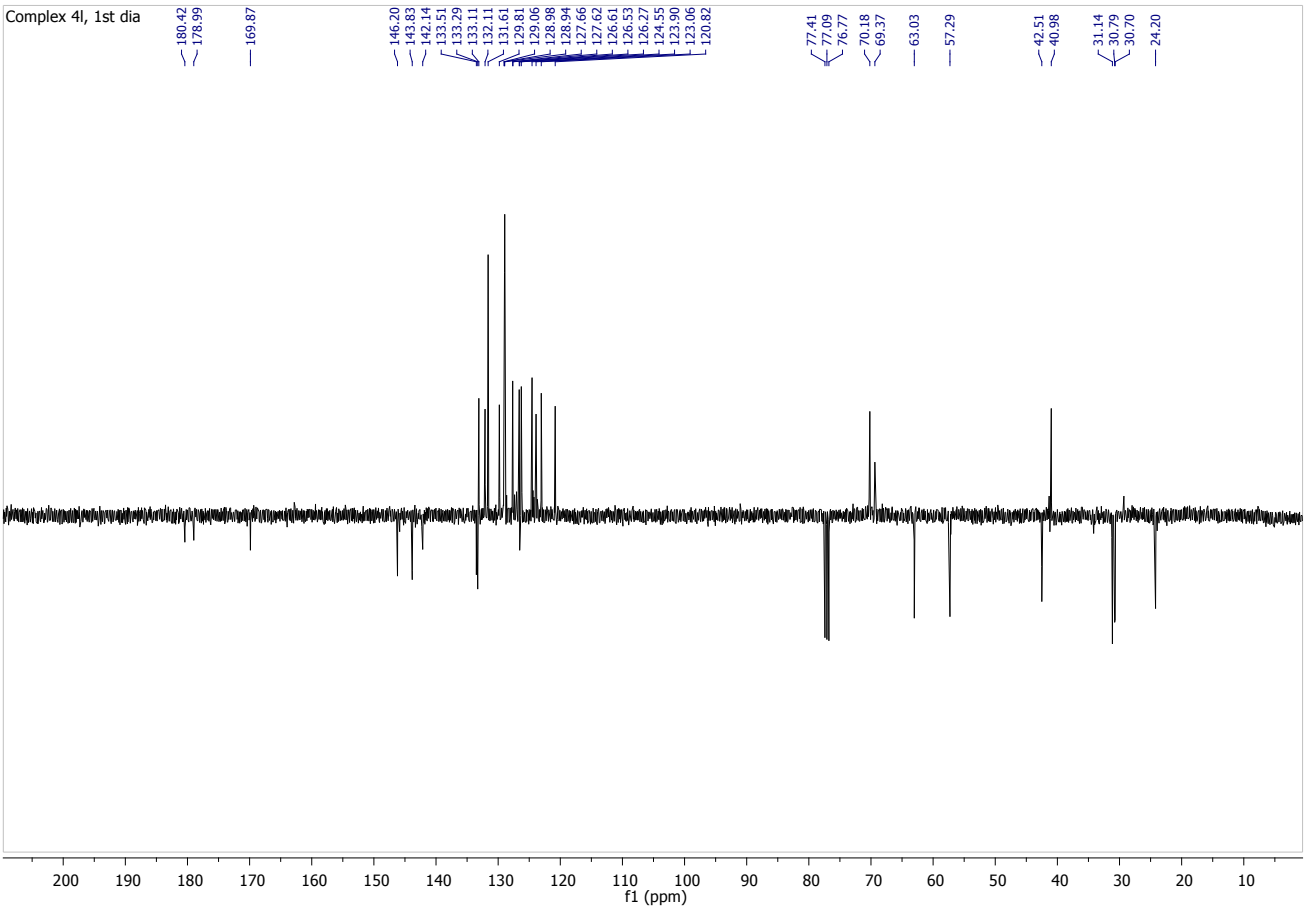
^{1}H and ^{13}C NMR spectra of the 1st diastereomer (*major*) of the Ni(II) complex **4k**



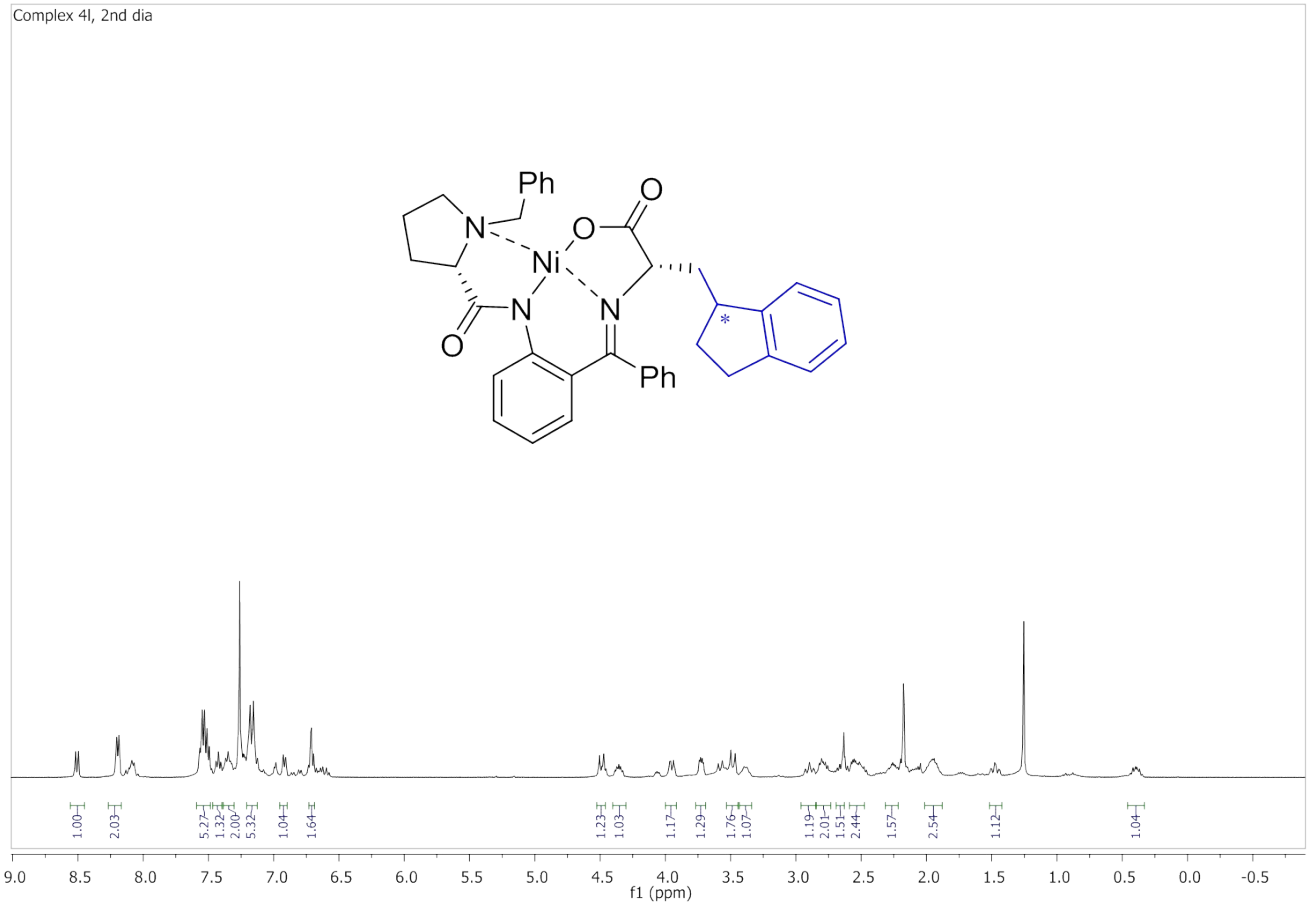


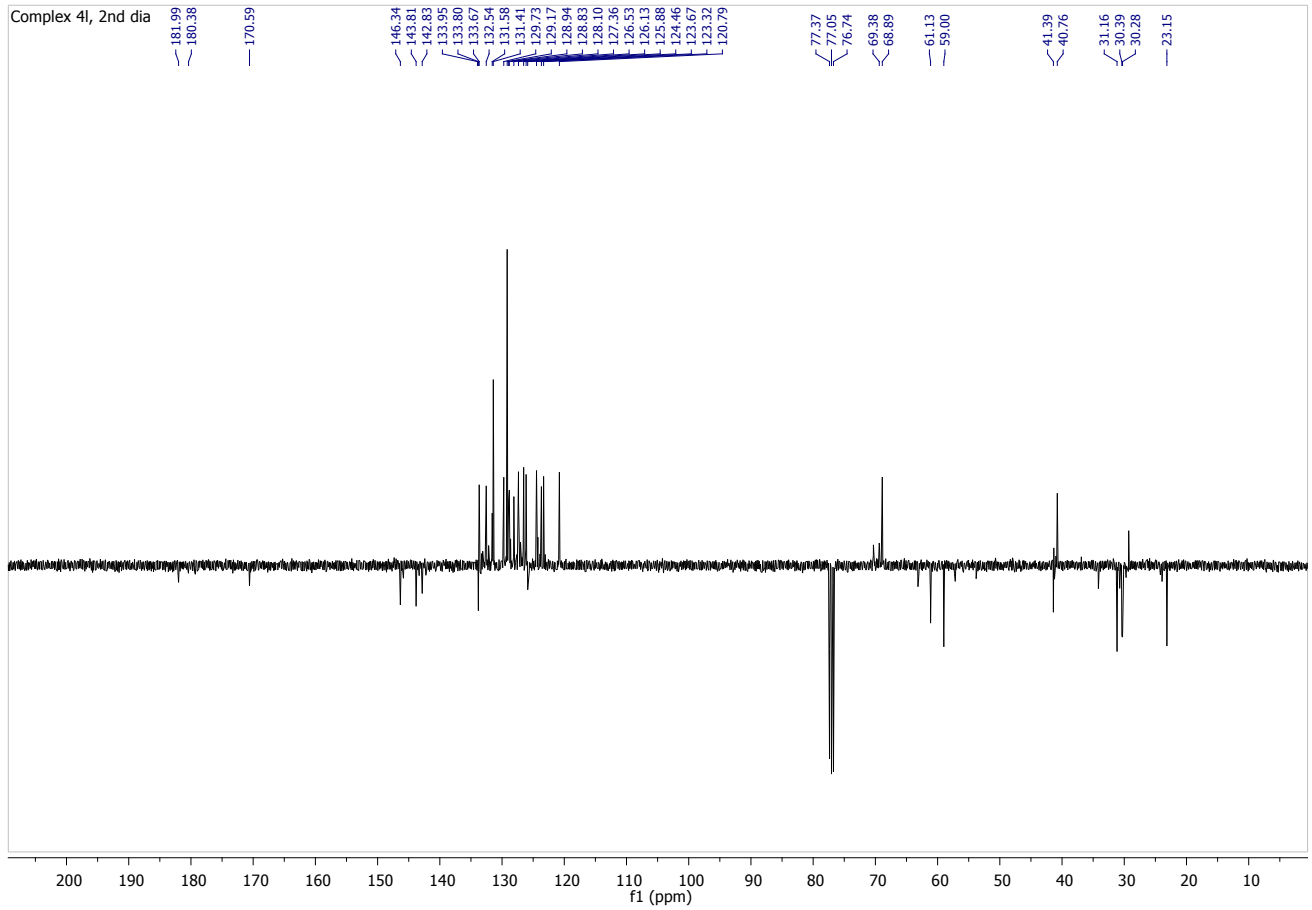
^{1}H and ^{13}C NMR spectra of the 2nd diastereomer (*minor*) of the Ni(II) complex **4k**



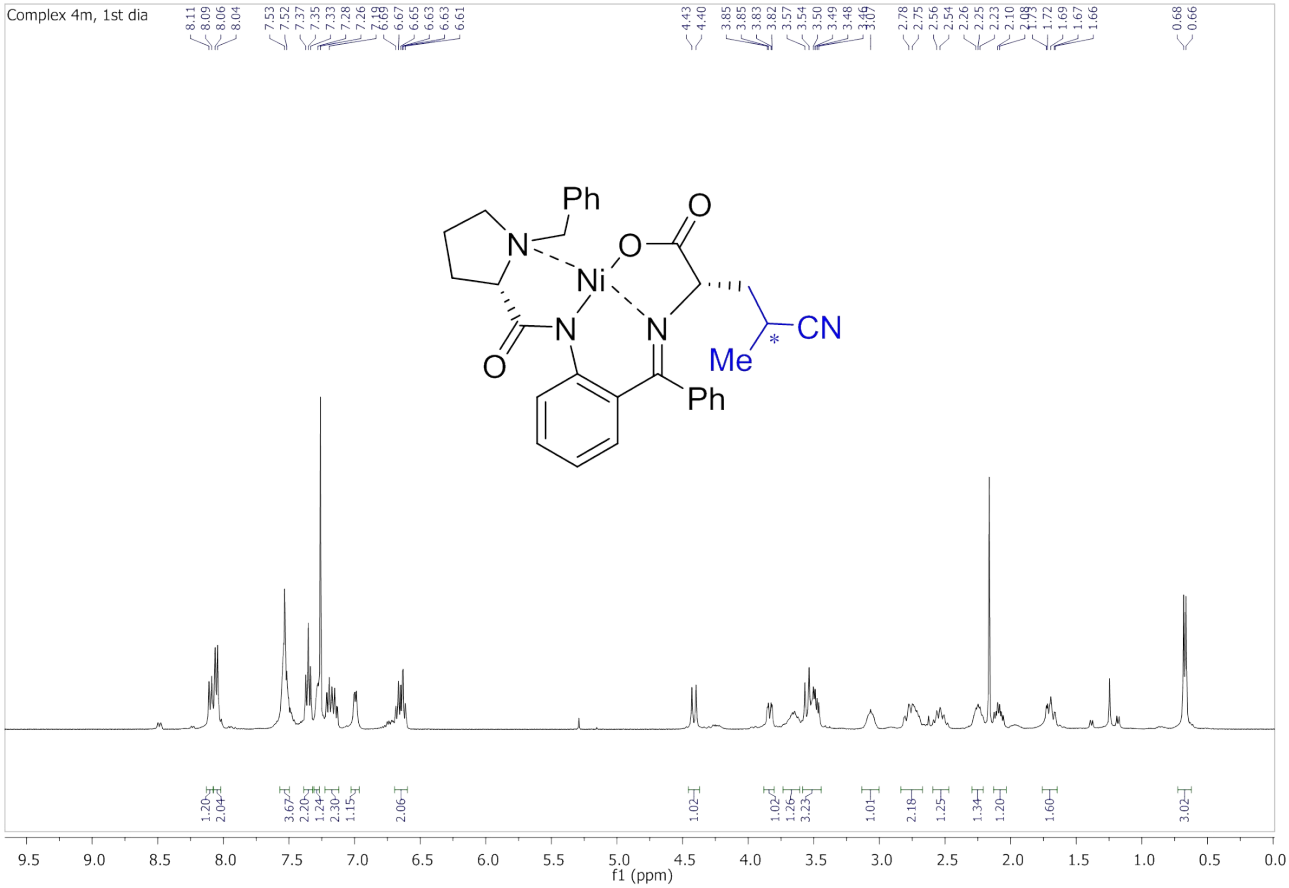


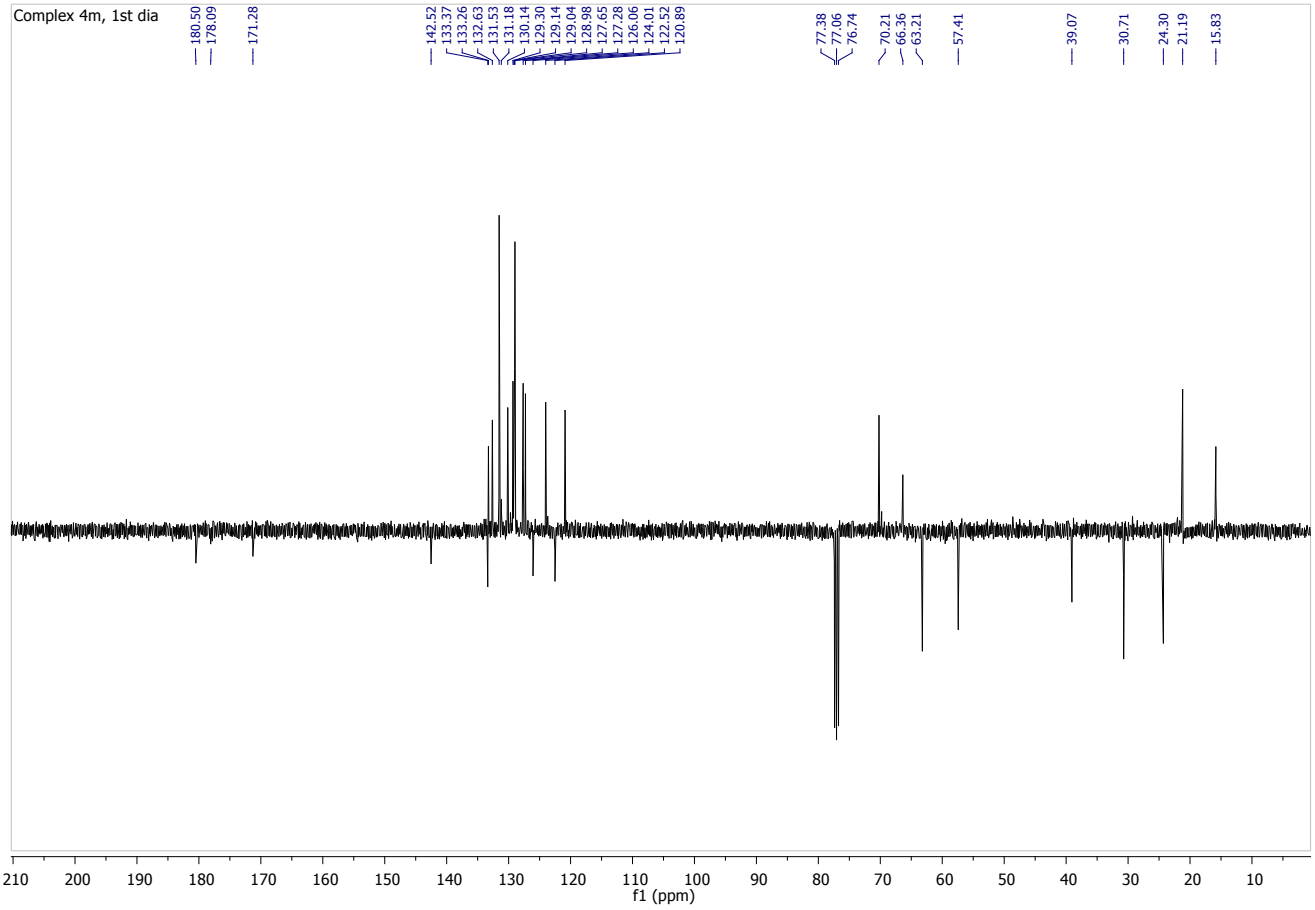
^{1}H and ^{13}C NMR spectra of the 1st diastereomer (*major*) of the Ni(II) complex **4l**



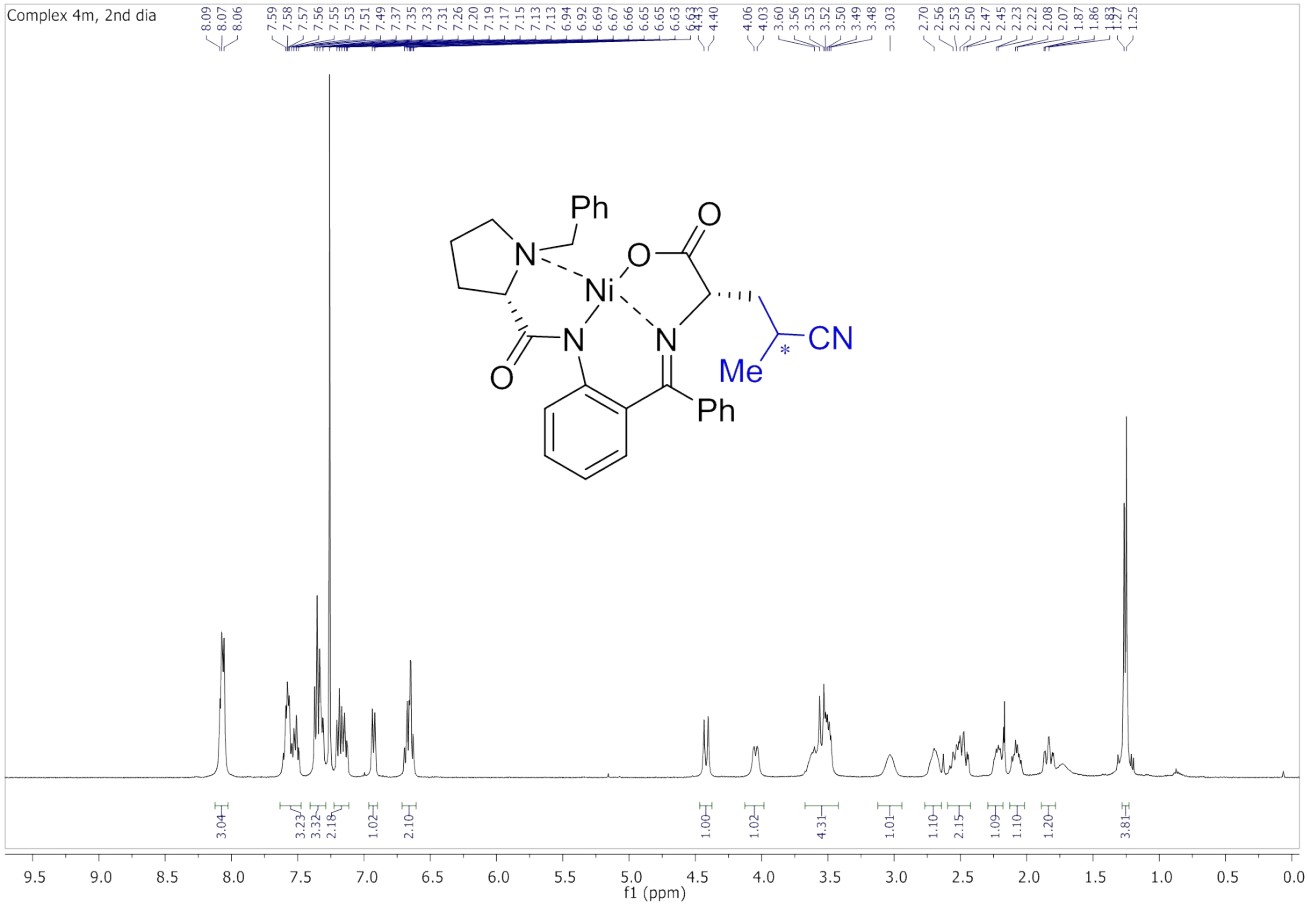


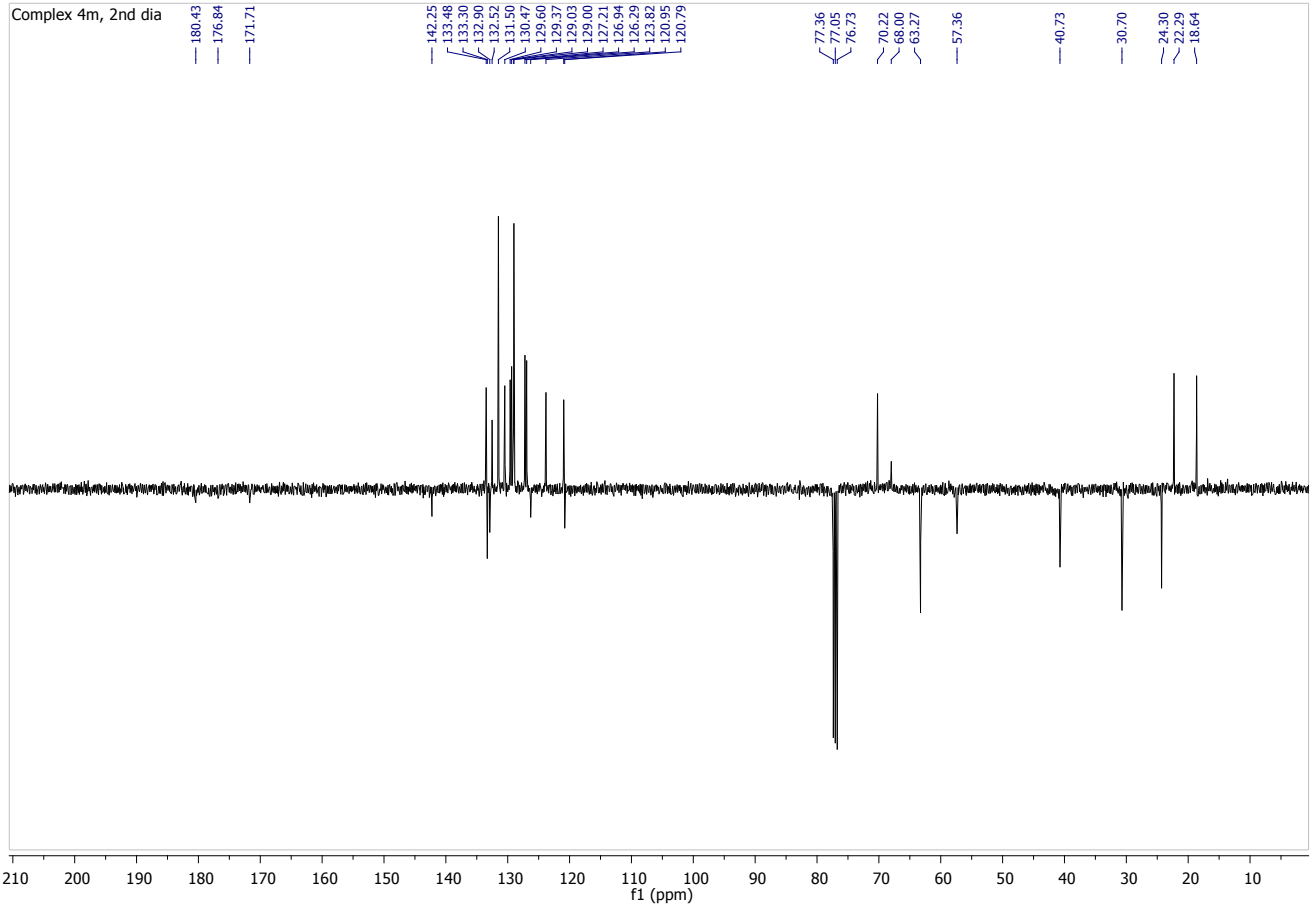
^{1}H and ^{13}C NMR spectra of the 2nd diastereomer (*minor*) of the Ni(II) complex **4l**



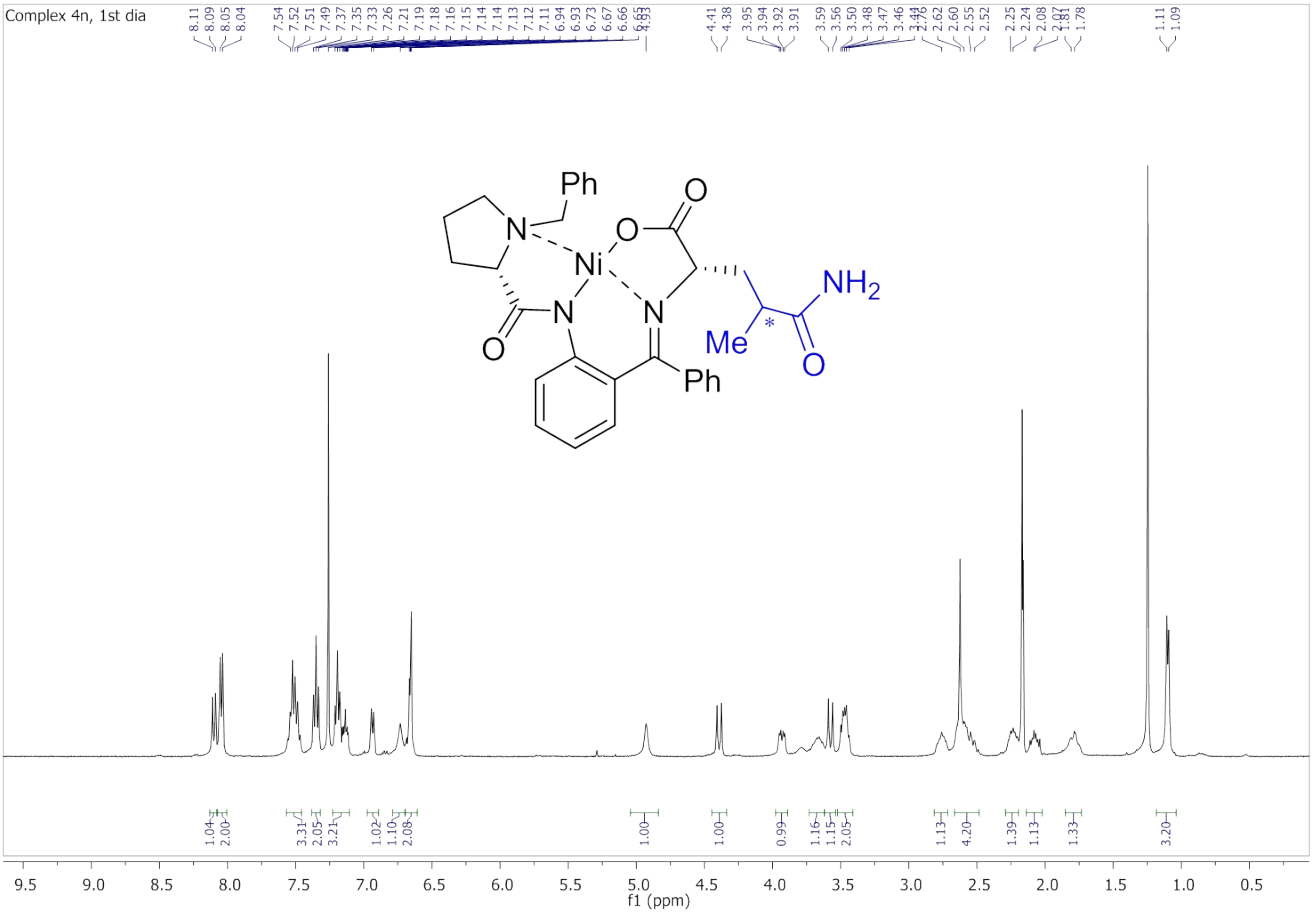


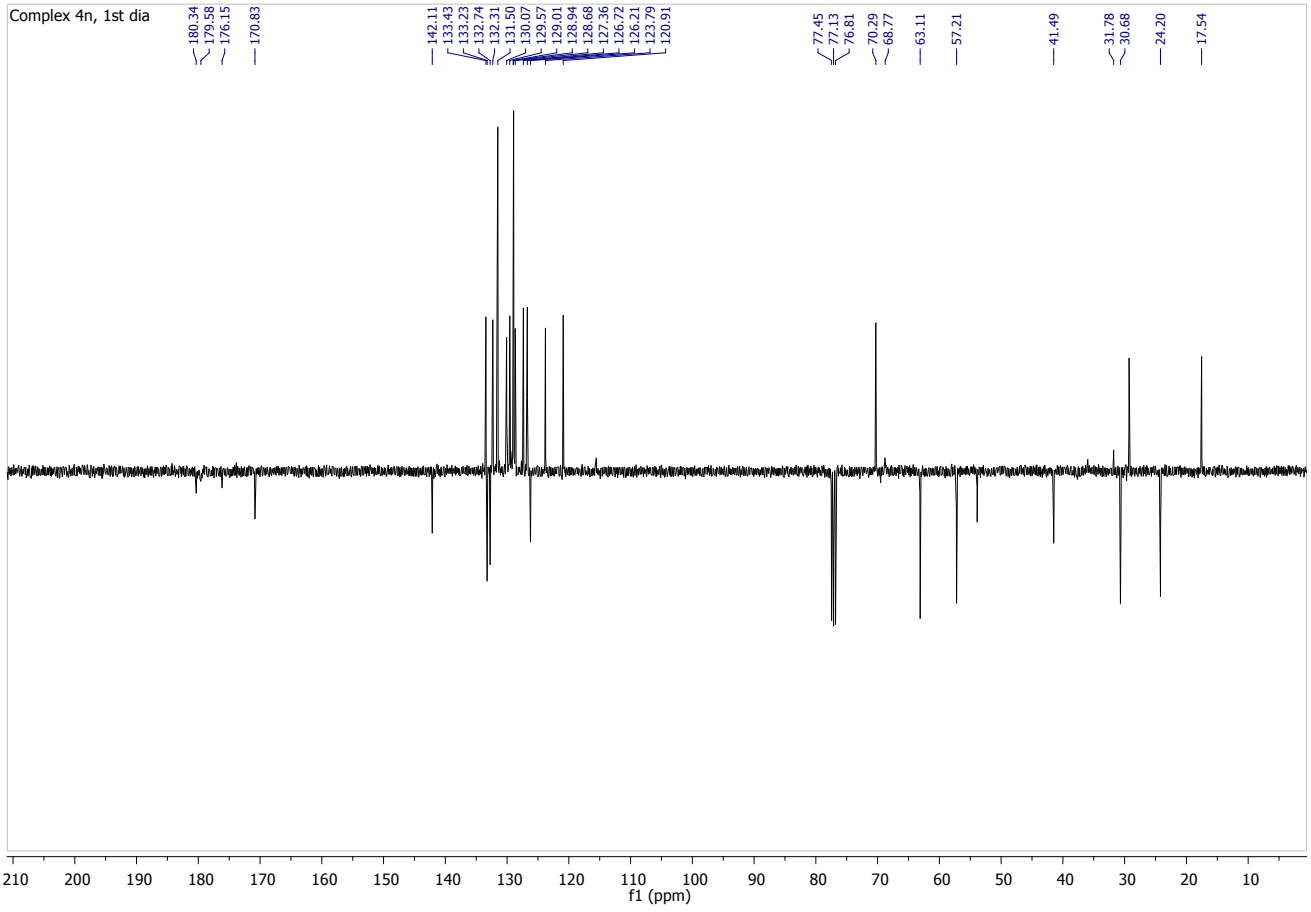
^{1}H and ^{13}C NMR spectra of the 1st diastereomer of the Ni(II) complex **4m**



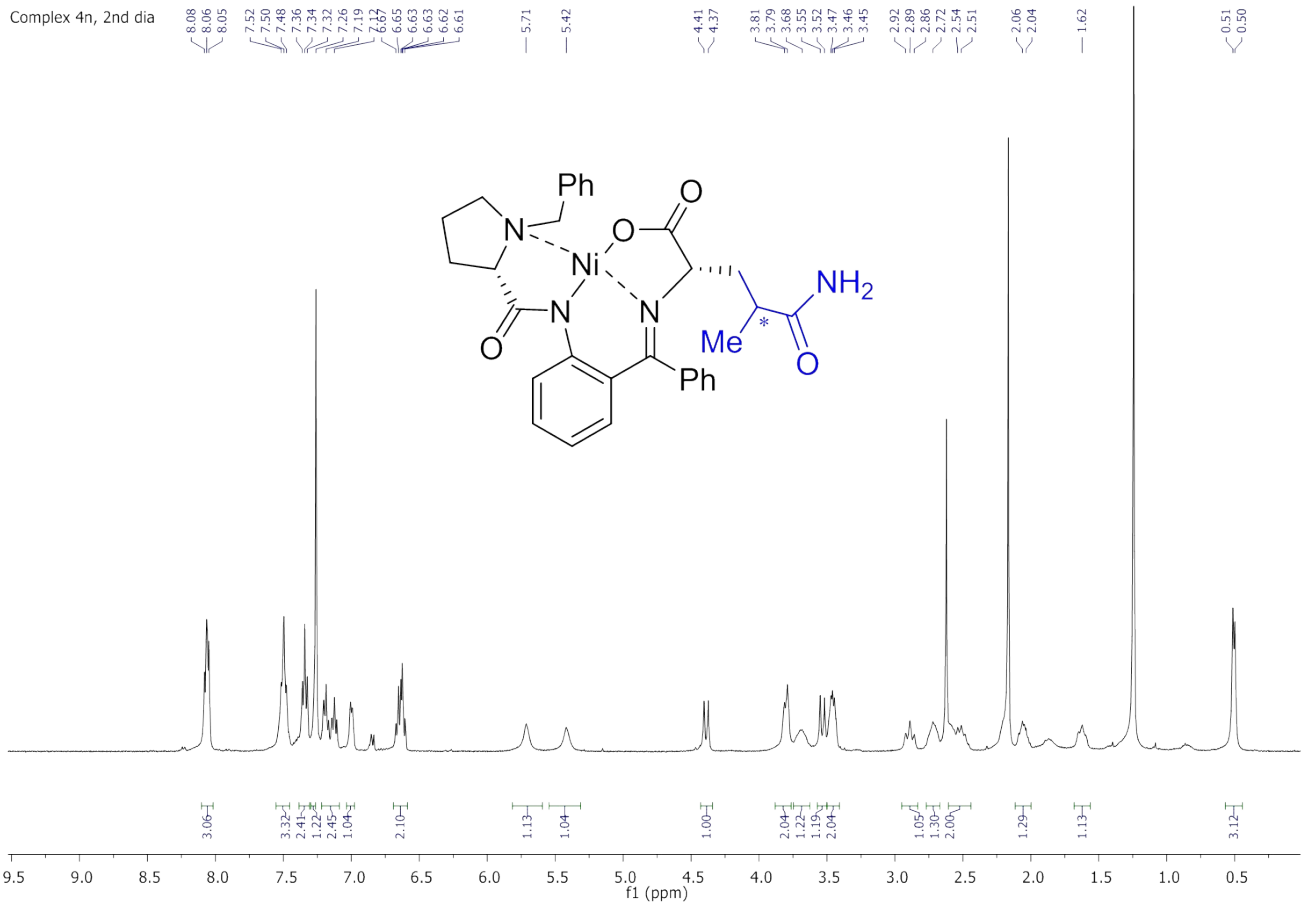


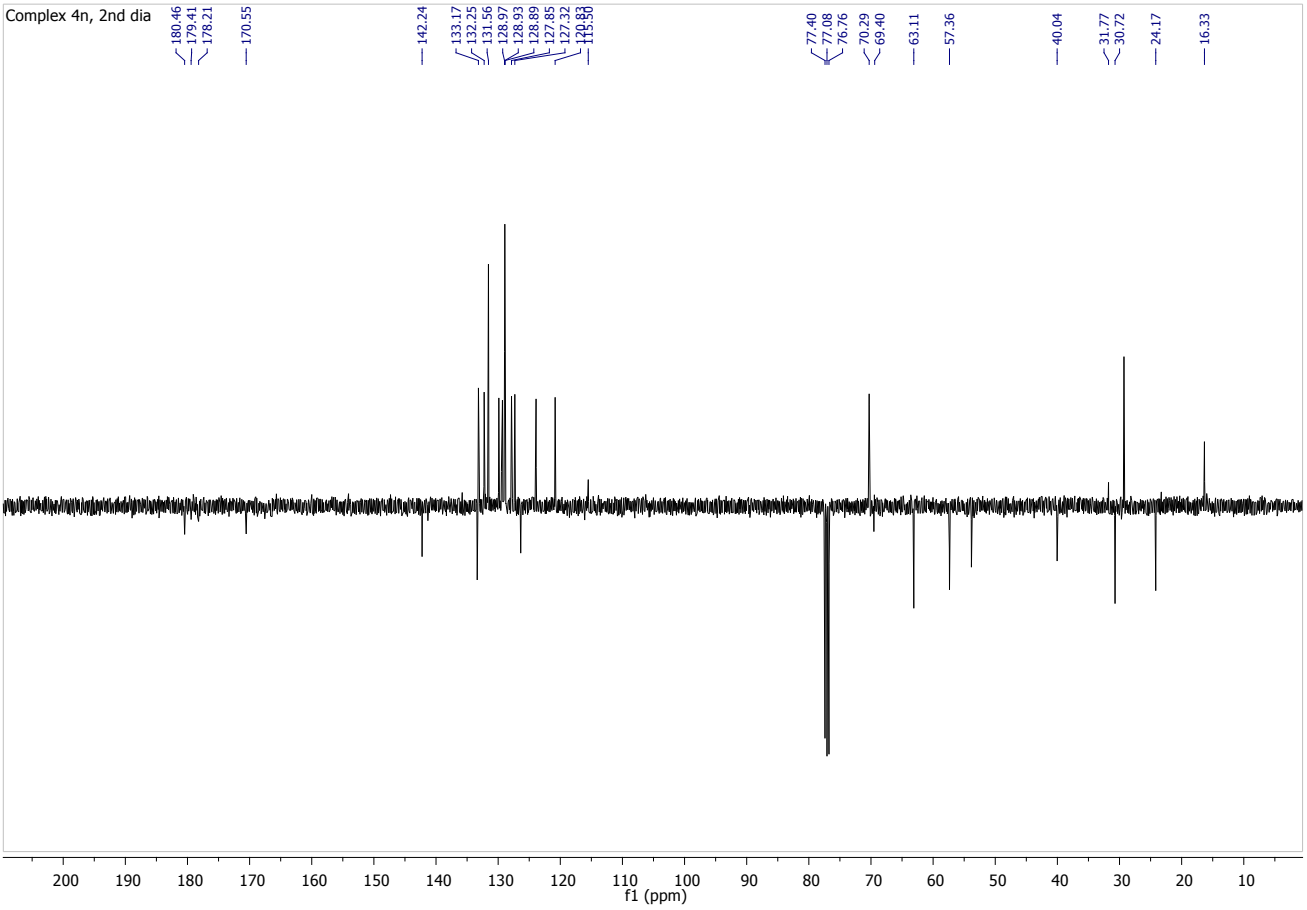
^{1}H and ^{13}C NMR spectra of the 2nd diastereomer of the Ni(II) complex **4m**



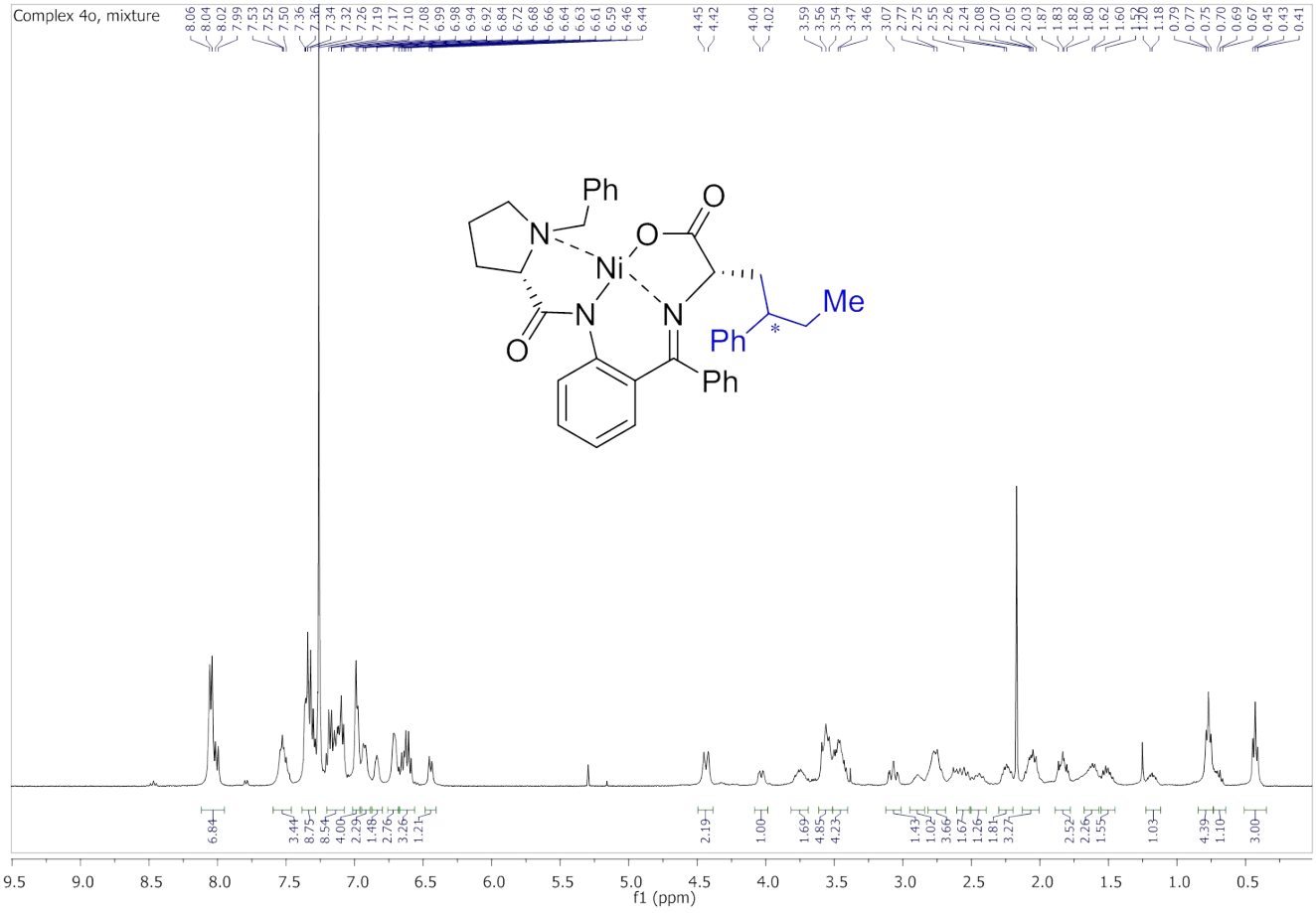


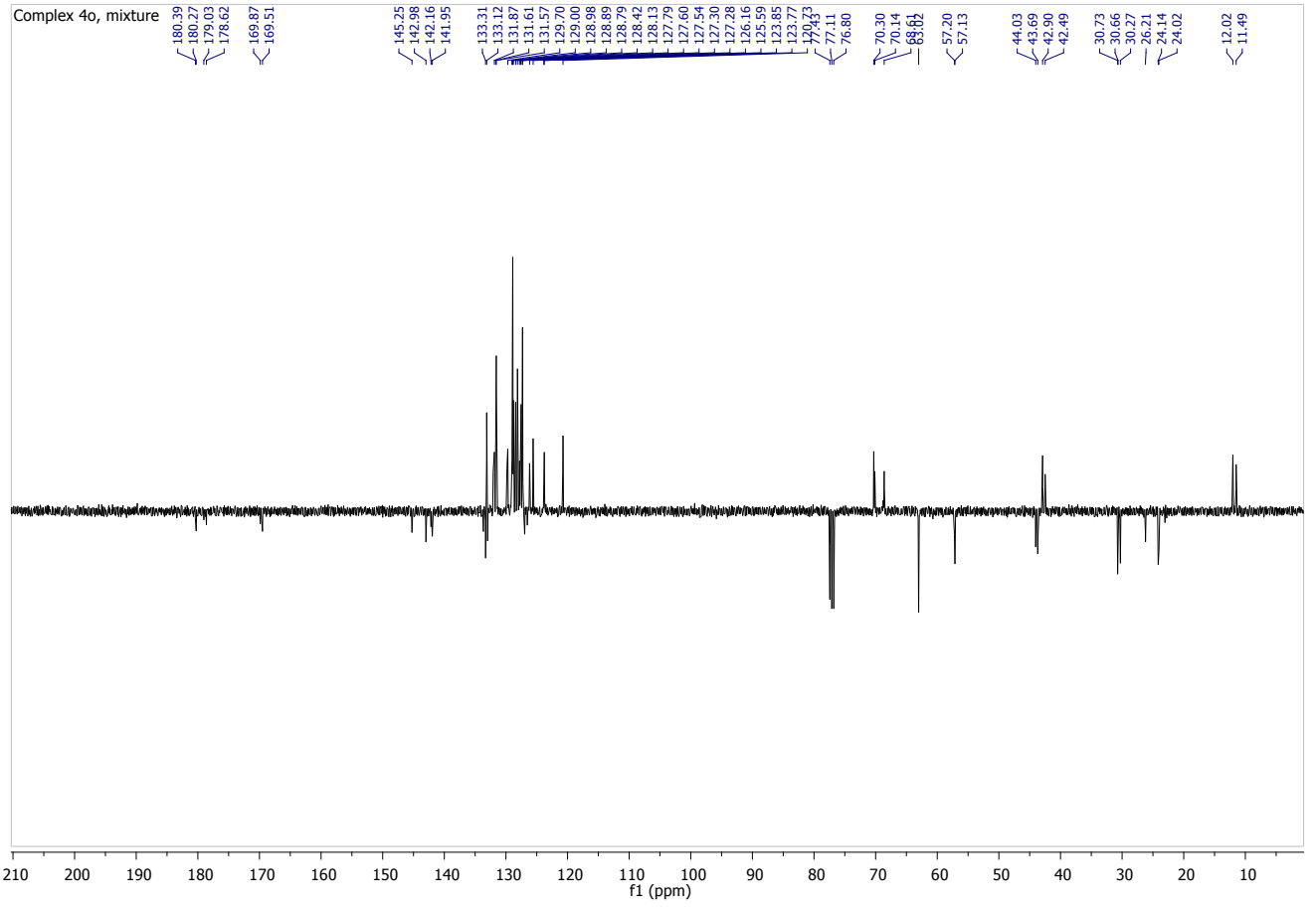
^{1}H and ^{13}C NMR spectra of the 1st diastereomer (*major*) of the Ni(II) complex **4n**



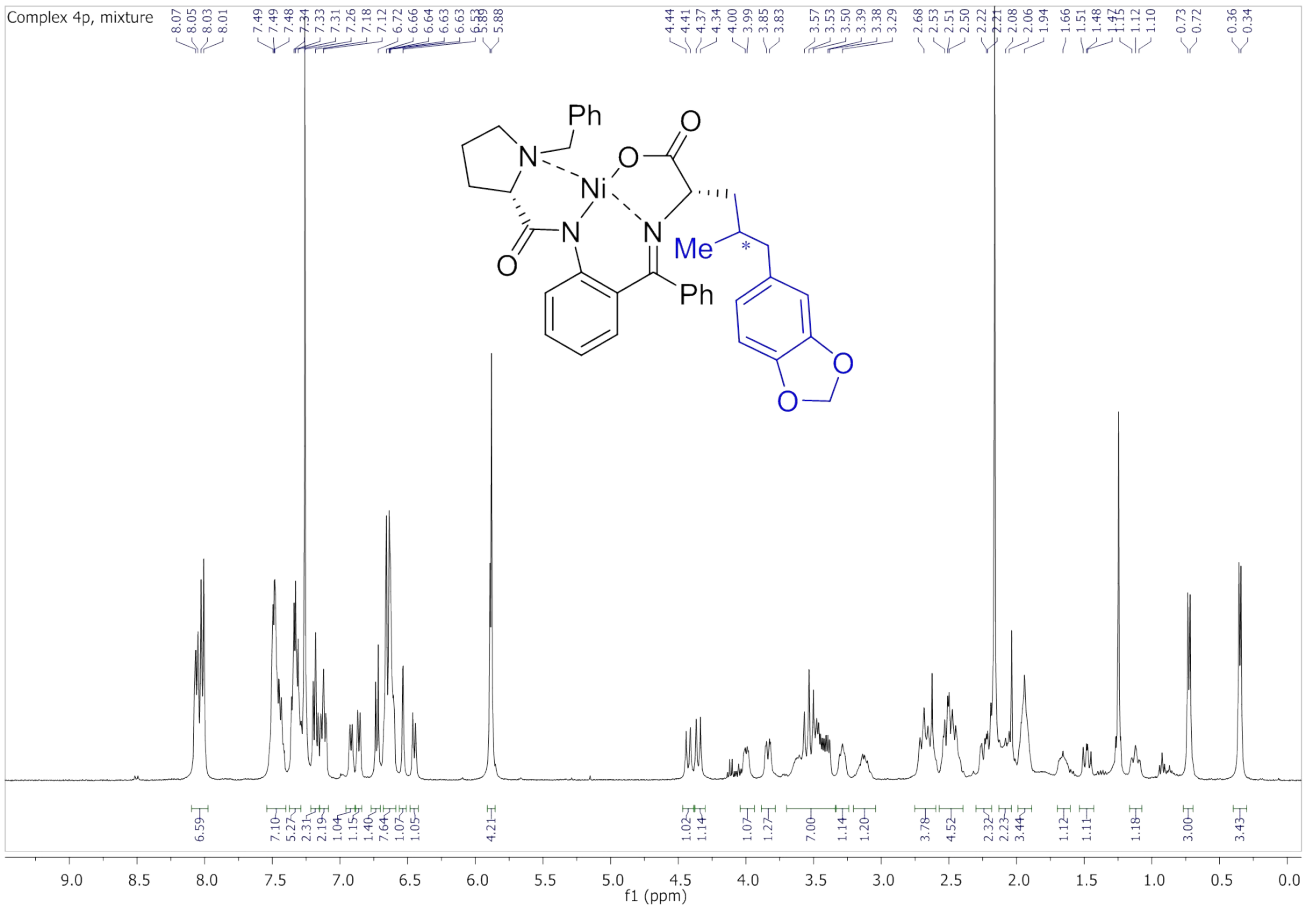


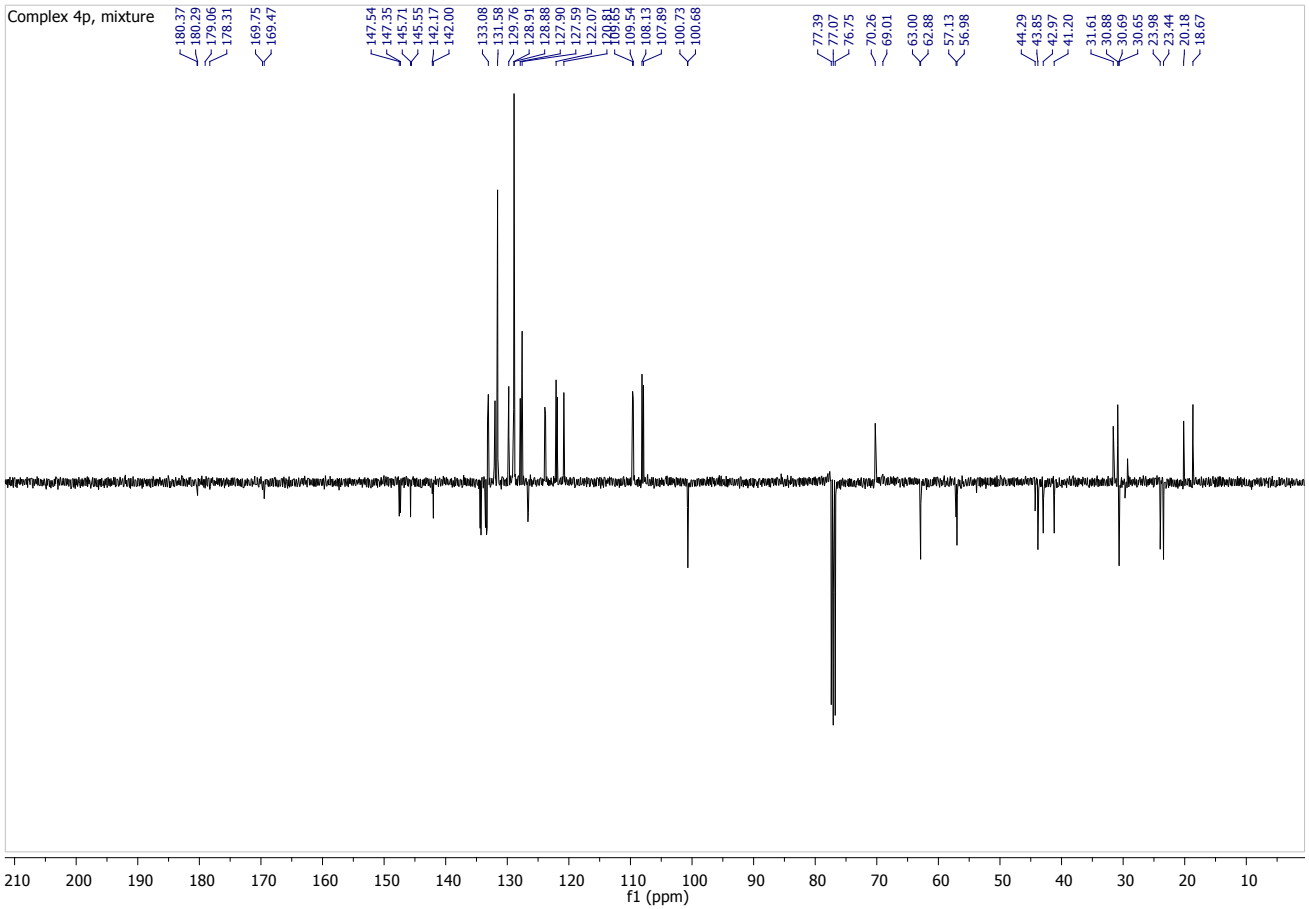
^{1}H and ^{13}C NMR spectra of the 2nd diastereomer (*minor*) of the Ni(II) complex **4n**



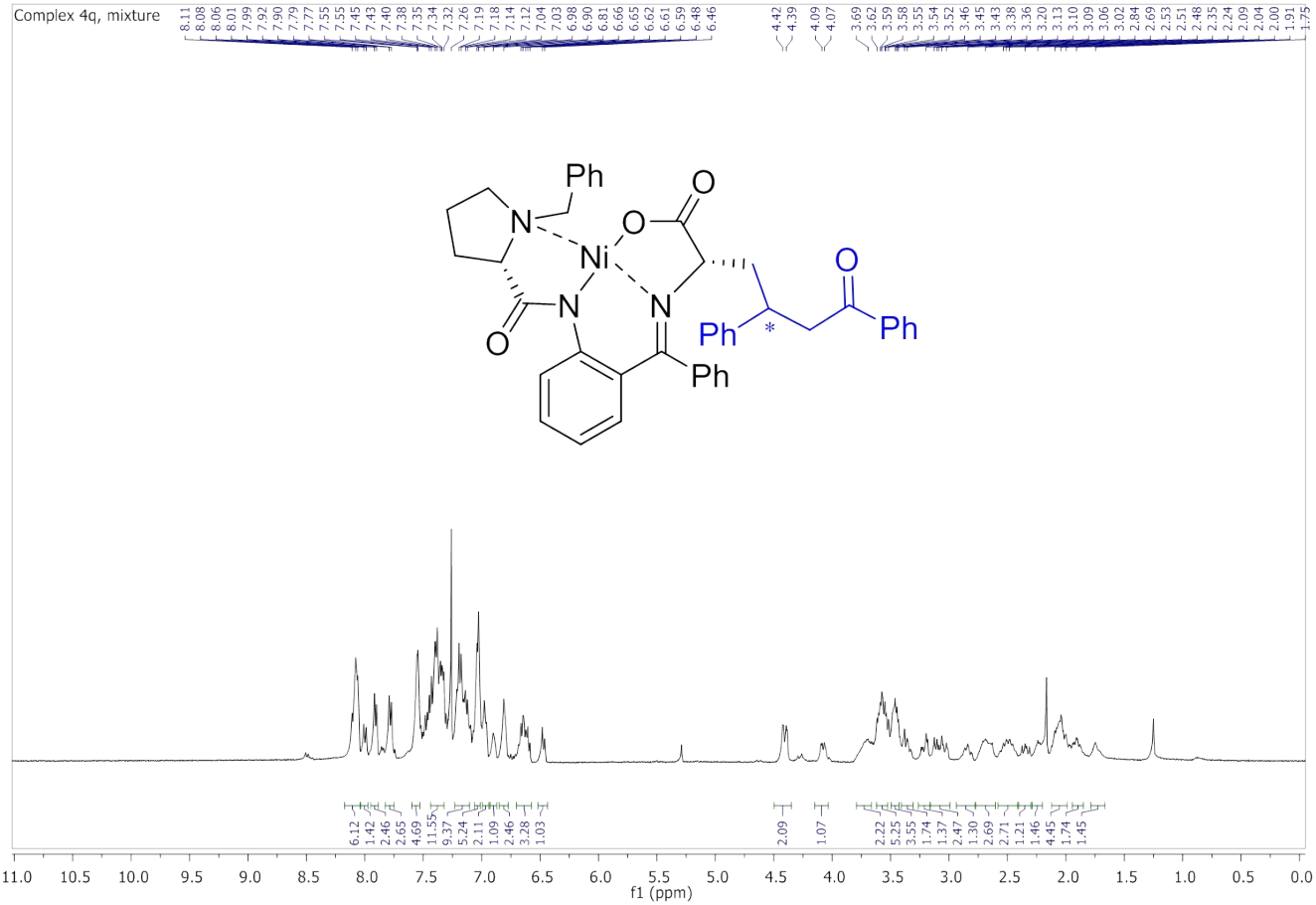


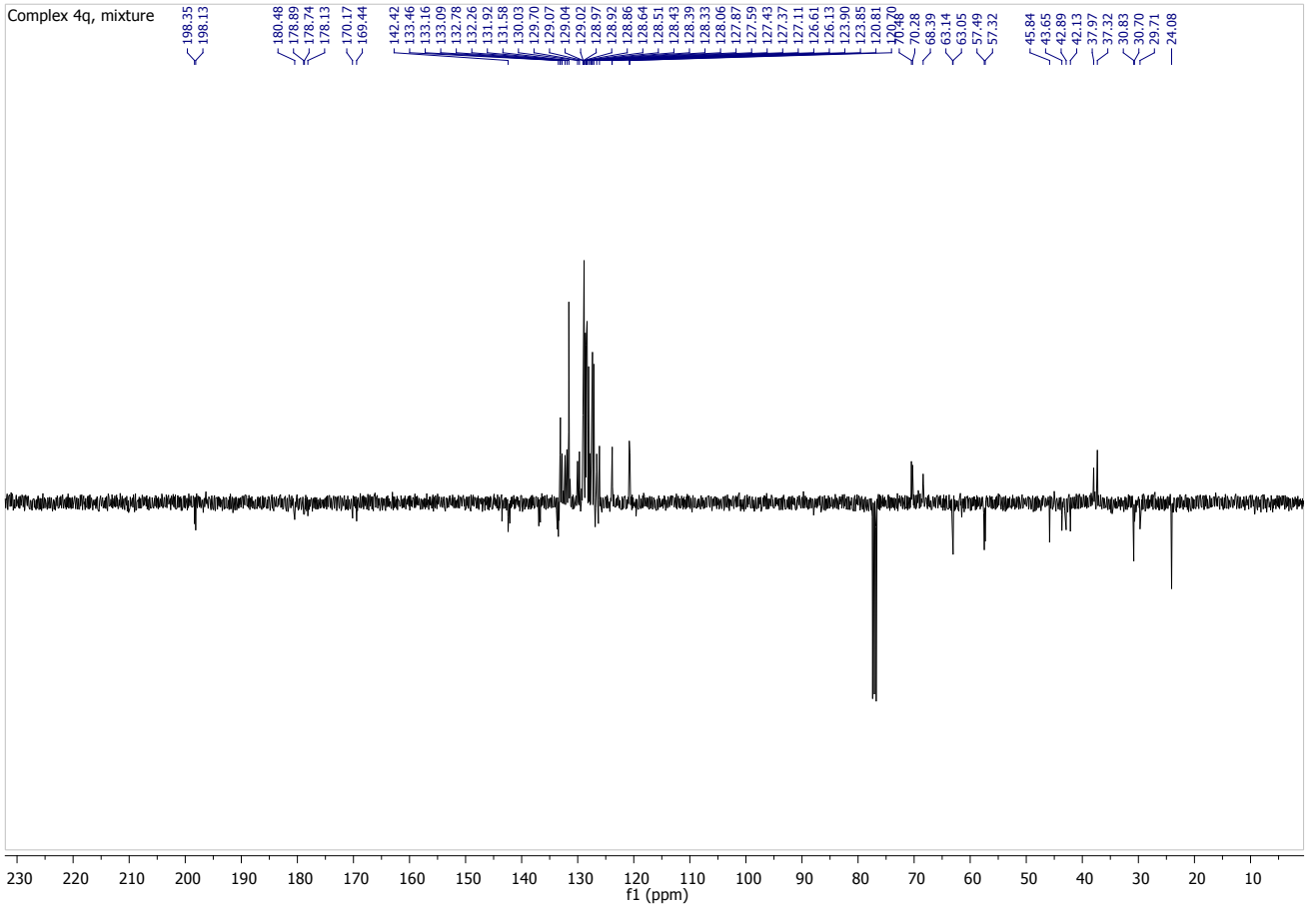
^{1}H and ^{13}C NMR spectra of the mixture of the diastereomers of the Ni(II) complex **4o**



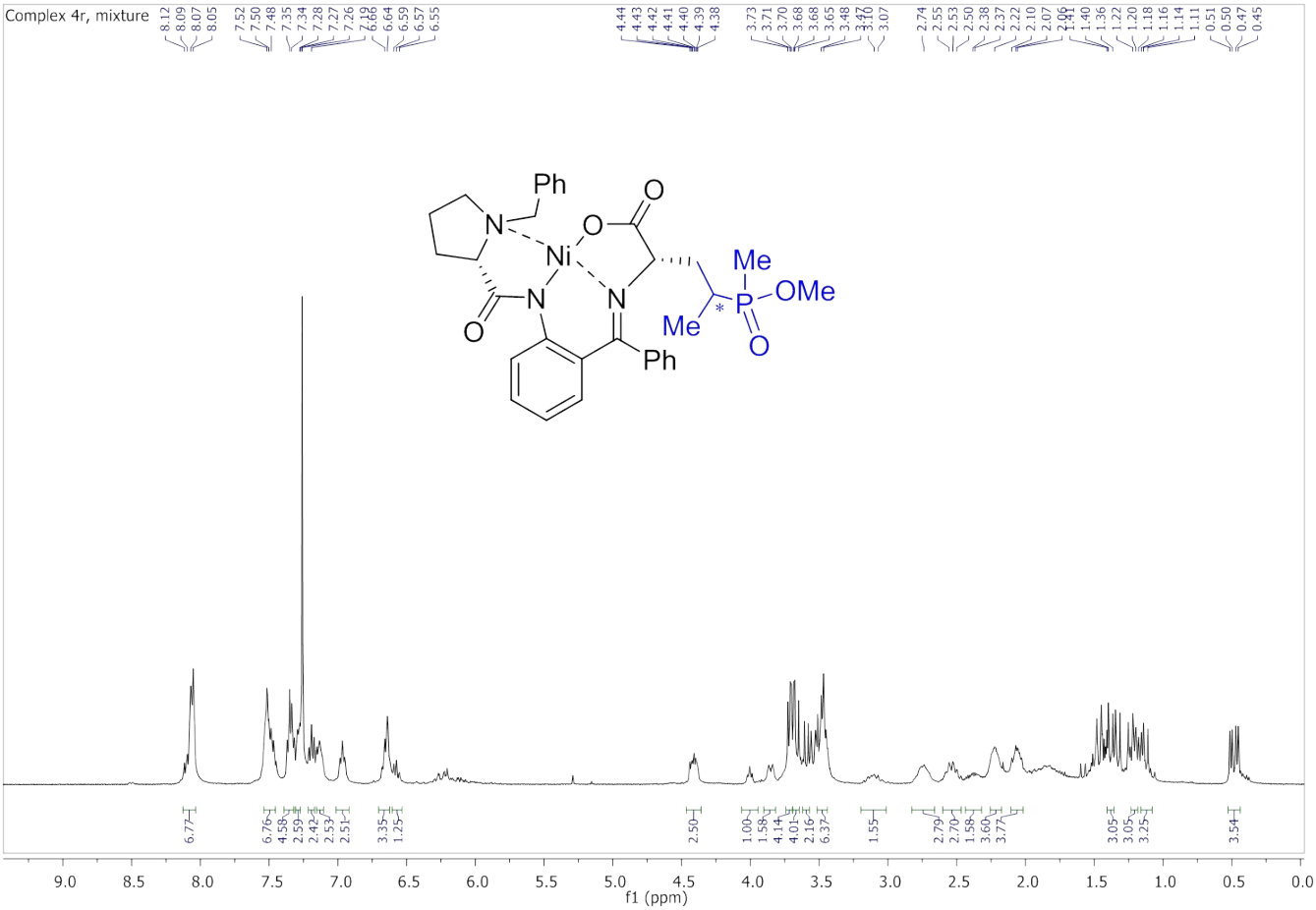


^{1}H and ^{13}C NMR spectra of the mixture of the diastereomers of the Ni(II) complex **4p**



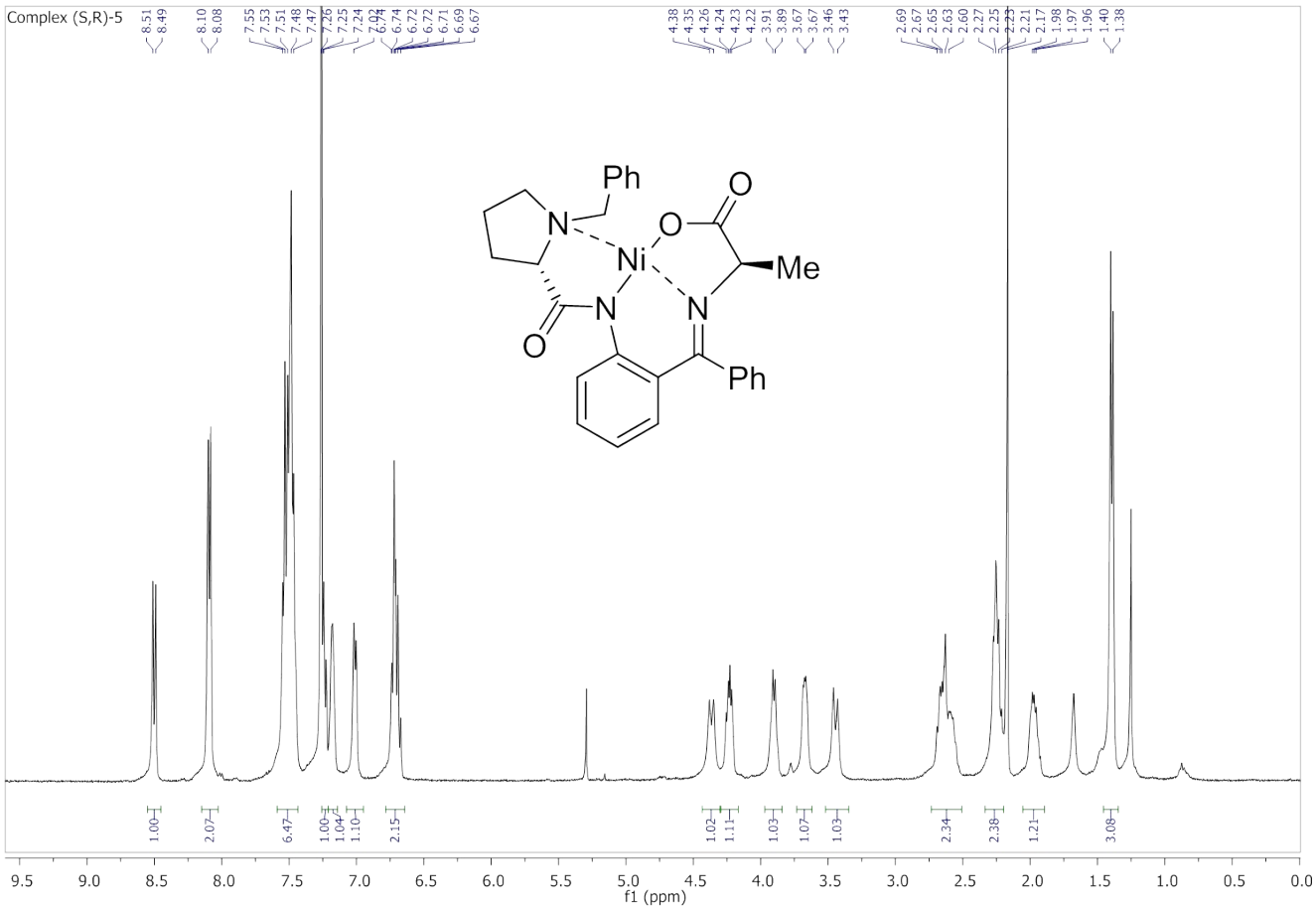


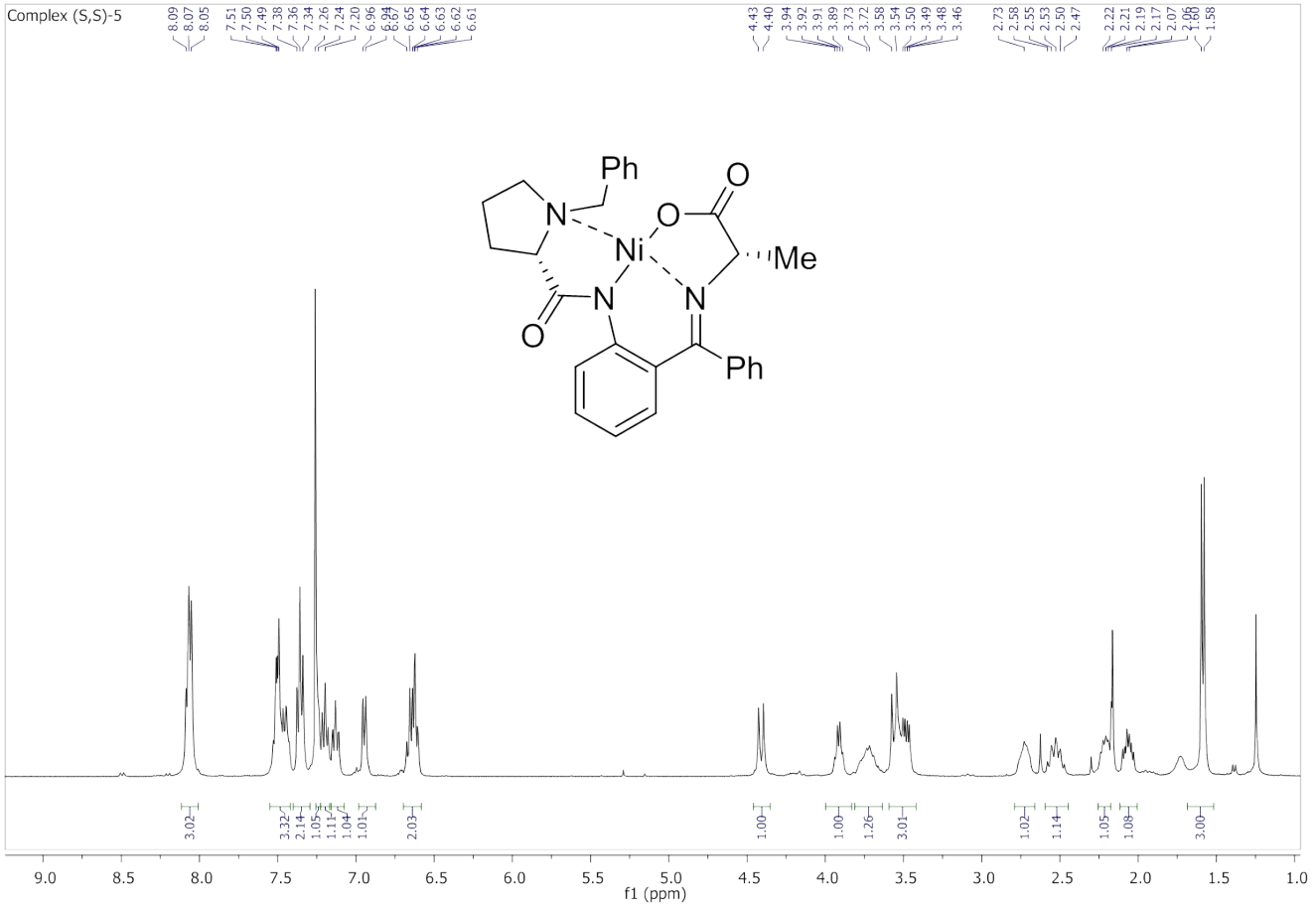
^{1}H and ^{13}C NMR spectra of the mixture of the diastereomers of the Ni(II) complex **4q**



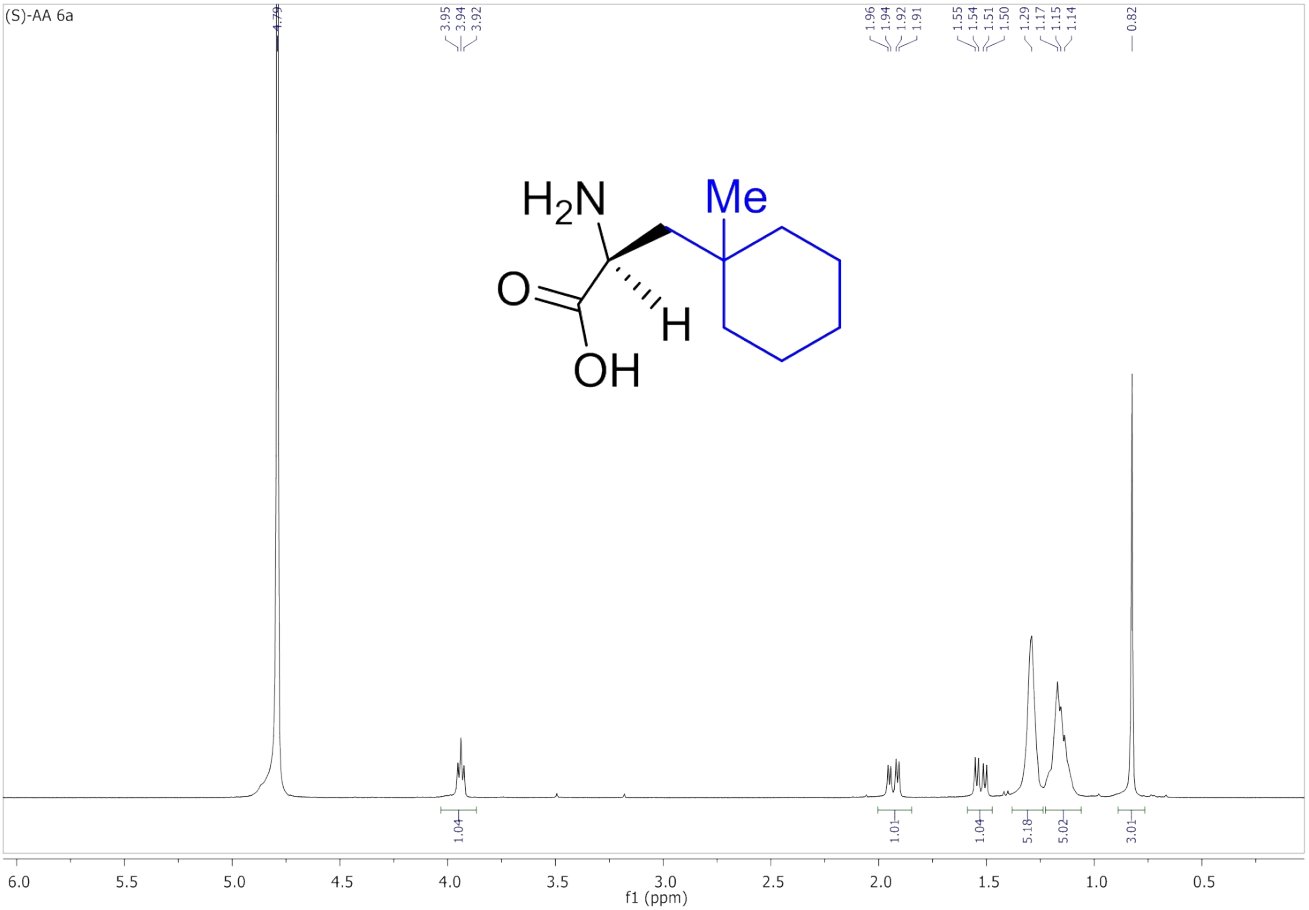
^{1}H NMR spectra of the mixture of the diastereomers of the Ni(II) complex (*S*,*S*.*S*)-**4r** and (*S*,*S*,*R*)-**4r**

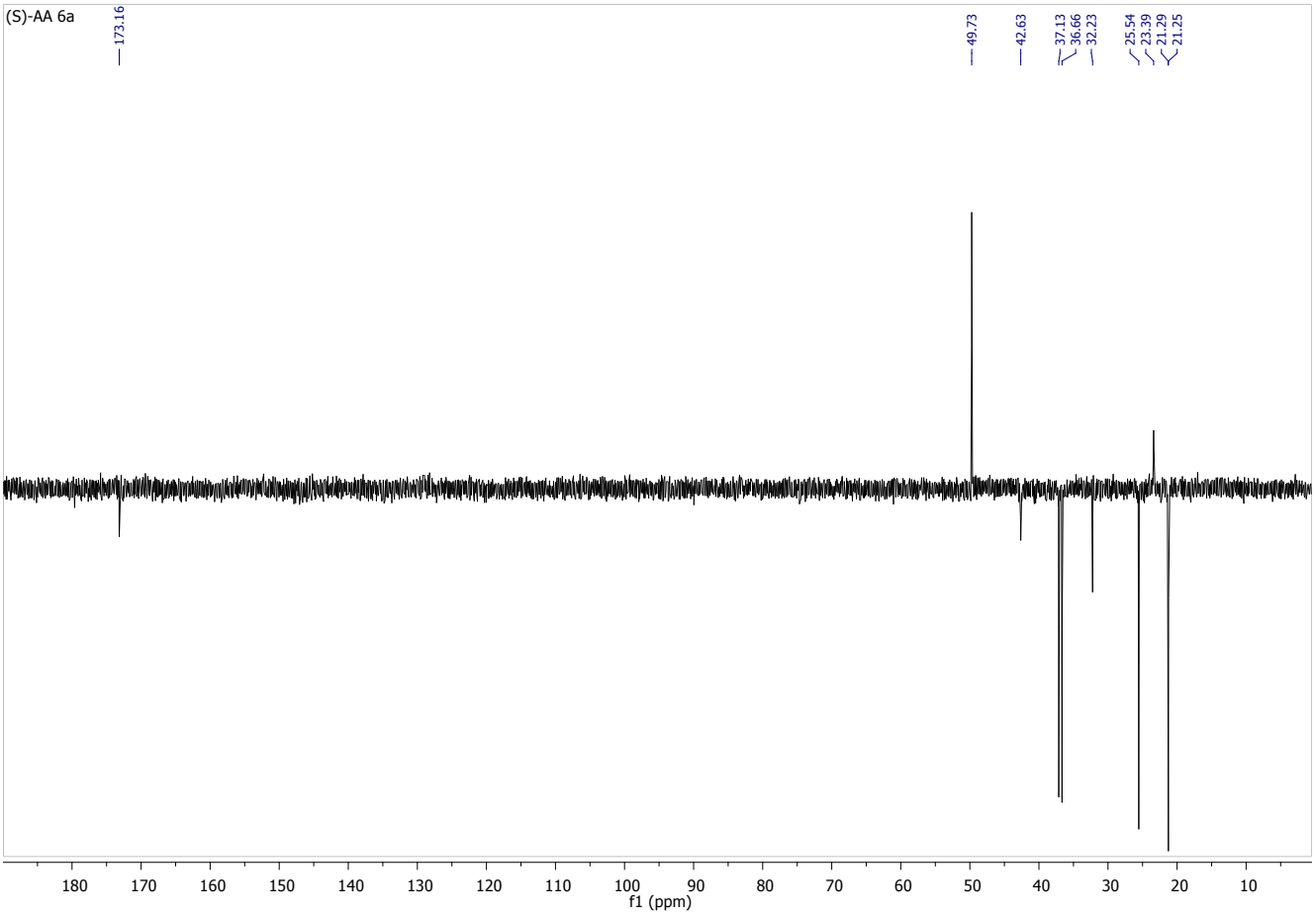
(contains the starting **3r** as an inpurity!)



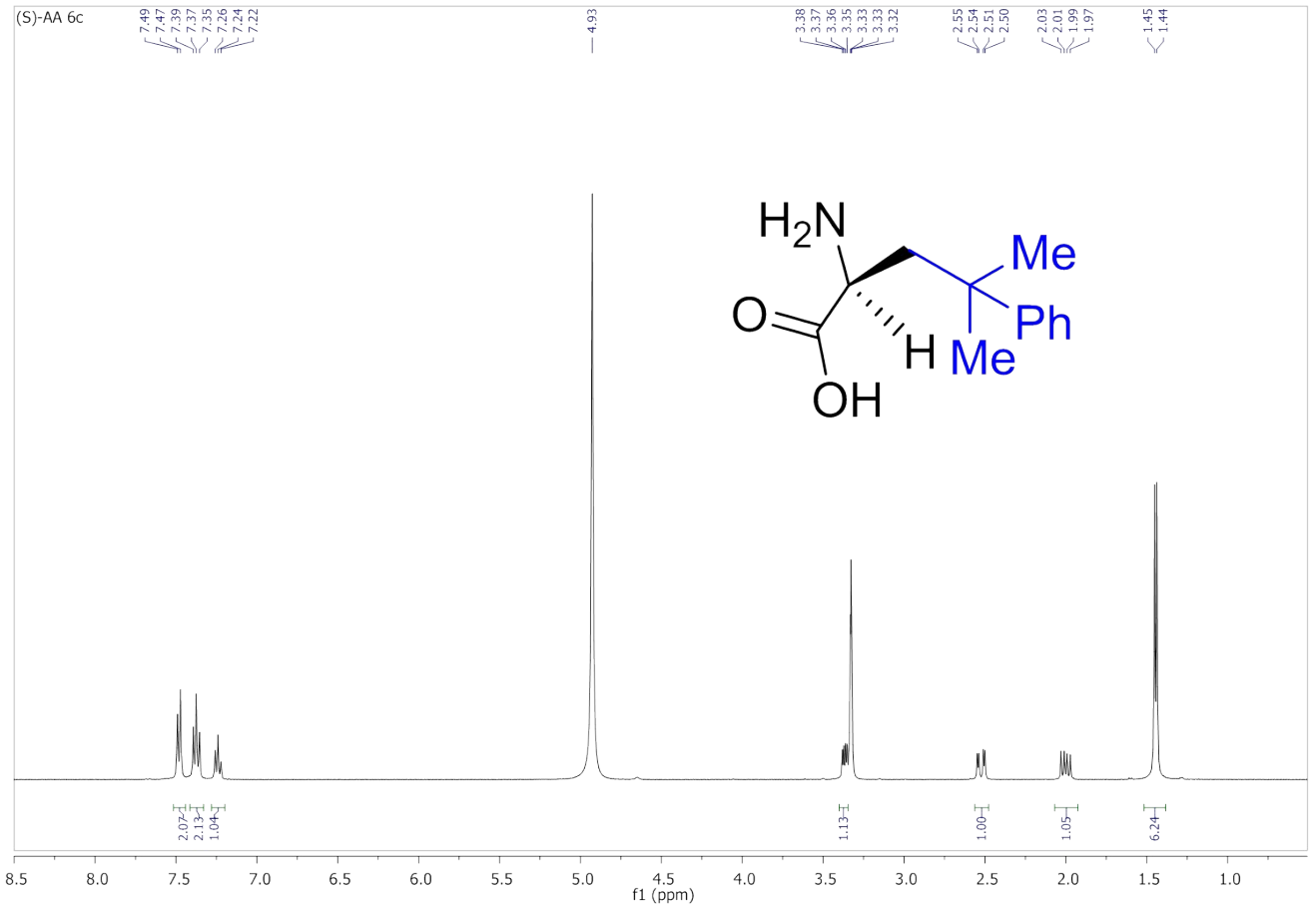


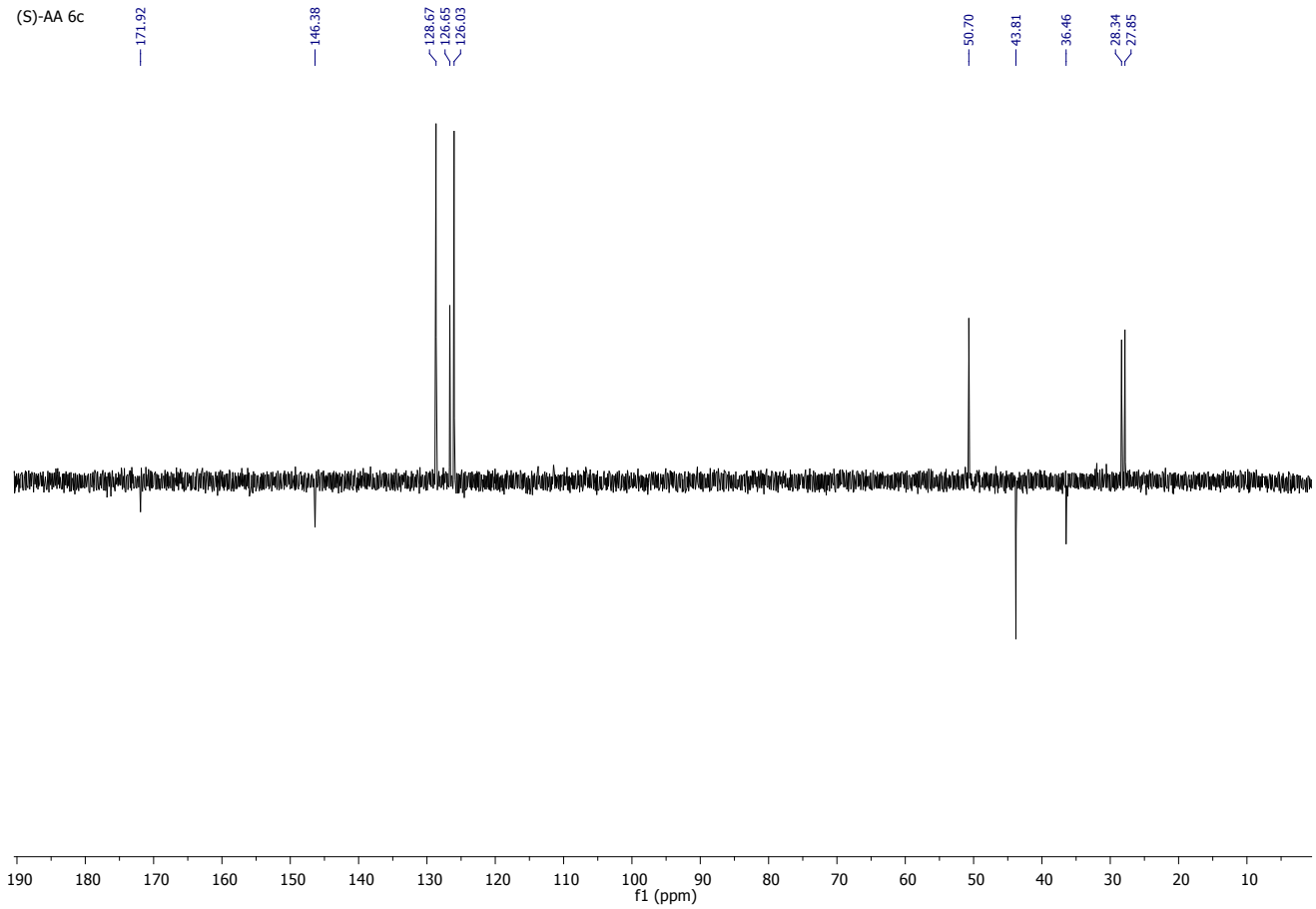
1H NMR spectra of the Ni(II) complex (*S*,*R*)-**5** and (*S*,*S*)-**5**



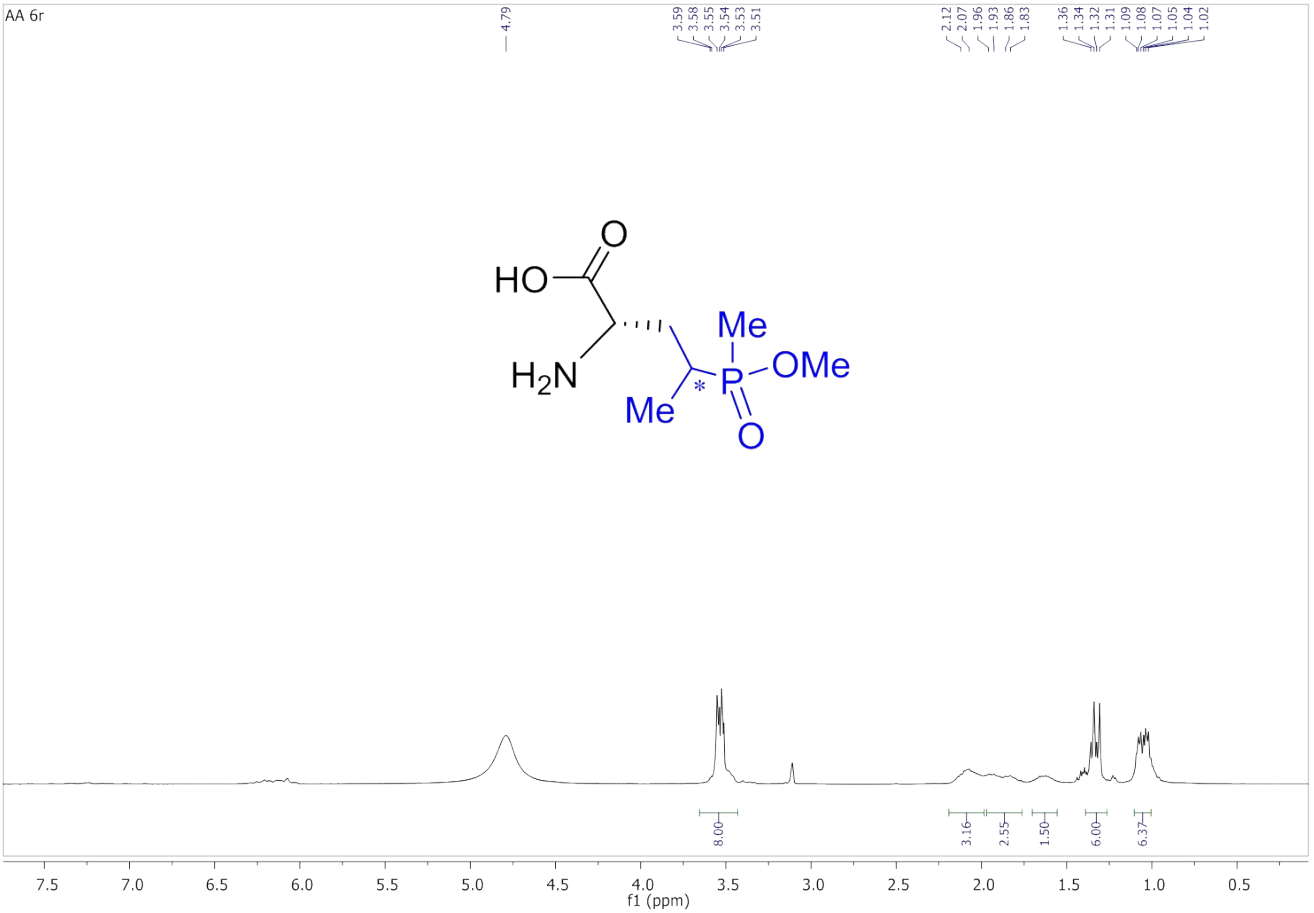


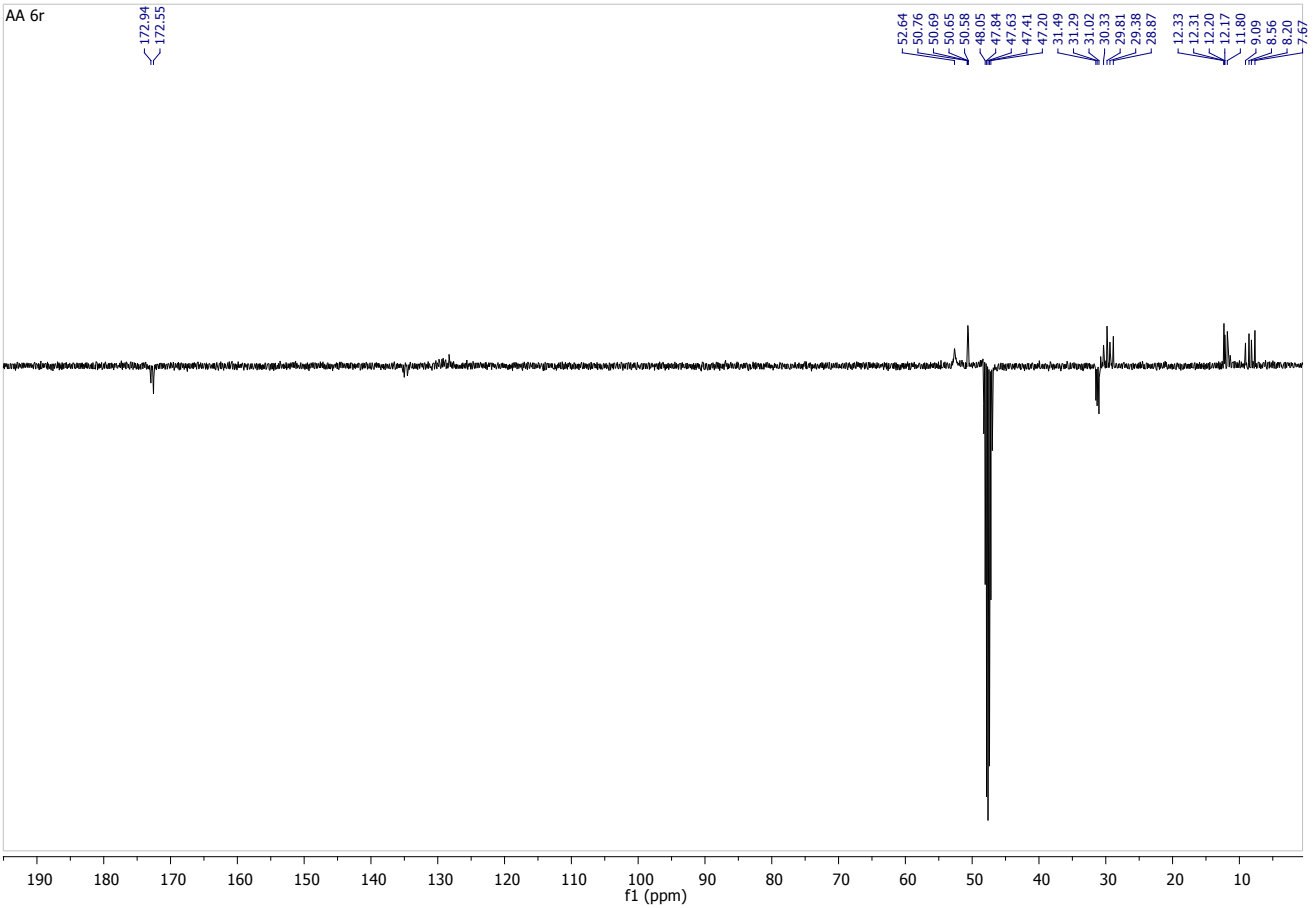
^{1}H and ^{13}C NMR spectra of the amino acid (*S*,*S*)-**6a**



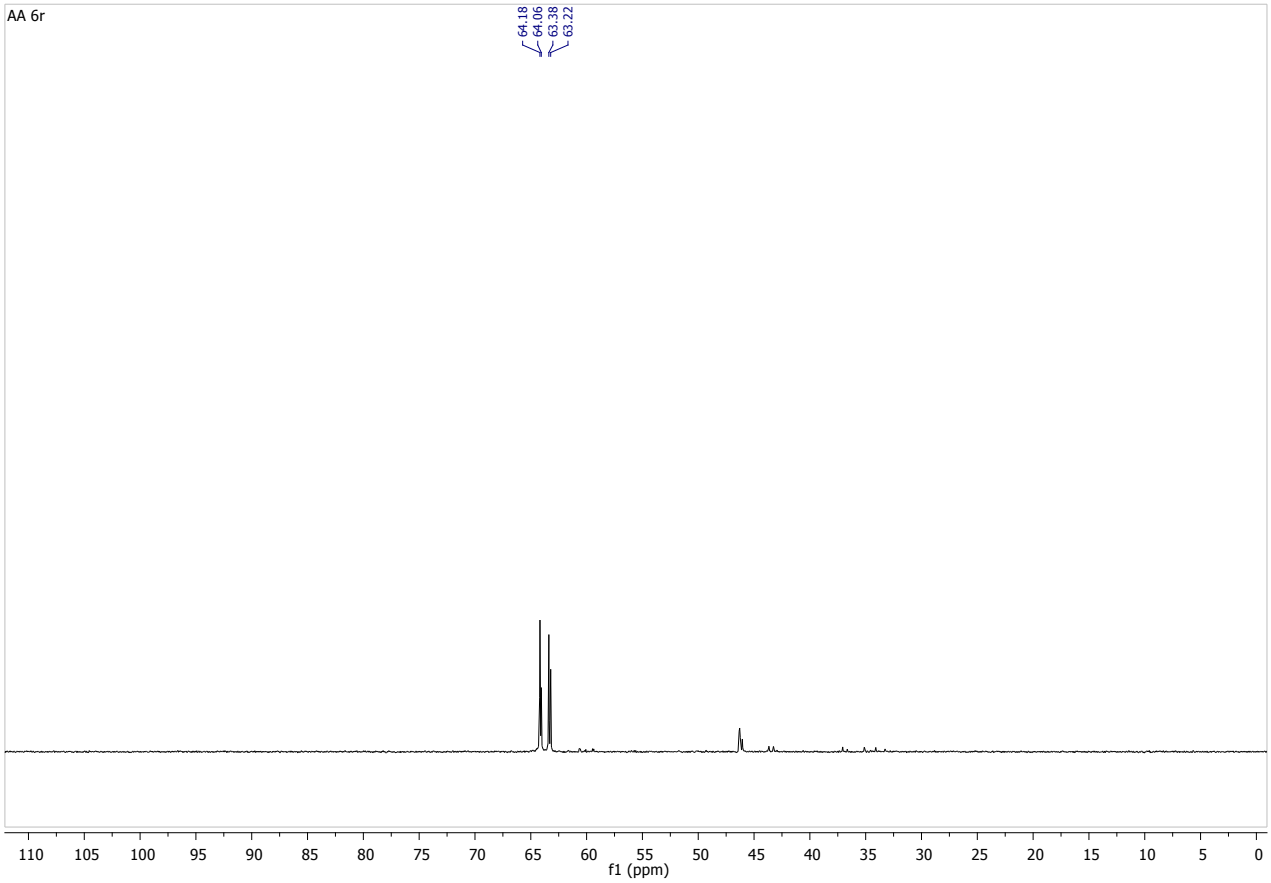


^{1}H and ^{13}C NMR spectra of the amino acid (*S*,*S*)-**6c**





^{1}H and ^{13}C NMR spectra of the mixture of the diastereomers of the amino acid **6r**



^{31}P NMR spectra of the mixture of the diastereomers of the amino acid **6r**