

Electronic Supplementary Information

The Synthetic Route to Artificial Chiral α -Amino Acids Featuring a 3,4-Dihydroisoquinolone Core through a Rh(III)-Catalyzed Functionalization of Allyl Group in the Chiral Ni(II) Complexes

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General information

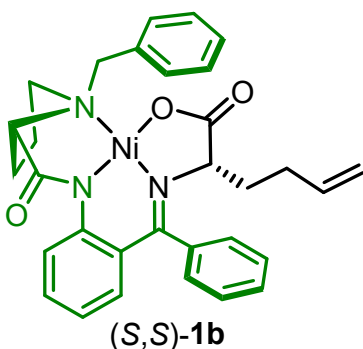
The reported catalytic reactions were performed in a 10 mL round-bottom flask. All solvents were purchased from commercial suppliers (Acros or Sigma-Aldrich). The Ni(II) complex (*S,S*)-**1a** and (*S,S*)-**1c** were synthesized according to a literature procedures.^[S1-S3] Catalysts $[\text{Cp}^*\text{RhCl}_2]_2$, $[\text{Cp}^{\text{tBu}}\text{RhCl}_2]_2$ and $[\text{Cp}^{\text{tBu}}\text{RhI}_2]_2$, as well as aryl hydroxamates were prepared as described in the literature.^[S4-S6] Purchased reagents from commercial suppliers were used without further purification. If not stated otherwise, column chromatography was performed with silica gel 60 M from Macherey-Nagel.

Instrumentation

Proton nuclear magnetic resonance (^1H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian Inova 400, Bruker Avance 400 and Avance 300 spectrometers operating at 400 (300) MHz (^1H), 376 MHz (^{19}F) and 101 MHz ($^{13}\text{C}\{^1\text{H}\}$). Chemical shifts are reported in ppm relative to the residual solvent peak (CDCl_3 : $\delta = 7.26$ ppm for ^1H NMR, $\delta = 77.1$ for ^{13}C NMR; D_2O : $\delta = 4.79$ ppm for ^1H NMR). NMR data are reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, etc.), coupling constant, integration, and nucleus. High-resolution mass spectra were recorded on Bruker MicroTOF II instrument using ESI ionization method. Optical rotations were measured on Krüss P3000 Automatic polarimeter in a 10 cm cell. X-ray crystallography diffraction data were collected on a Bruker APEX-II CCD diffractometer [$\lambda(\text{MoK}_\alpha) = 0.71073 \text{ \AA}$, ω -scans, $2\theta < 58^\circ$] at 120 K. Chiral HPLC was performed with Agilent 1200.

Synthesis and characterization of the complexes (*S,S*)-**1b,c,d** and (*S,R*)-**1d**

Ni(II) complex (*S,S*)-**1b**



A flame dried Schlenk flask equipped with a stir bar was charged with a solution of a chiral glycine Ni(II) complex^[S1] (1 g, 1.0 equiv., 2.0 mmol) in 20 mL of DMF followed by the addition of NaOH (240 mg, 3.0 equiv., 6.0 mmol). The mixture was stirred at 0°C under an Ar atmosphere for 15 min and then 3-butenyl bromide (0.245 mL, 1.2 equiv., 2.4 mmol) was added. The mixture was stirred at room temperature under an Ar atmosphere for 1 hour. Full conversion for reaction was confirmed by

TLC analysis. Afterward, 30 mL of DCM was added to the reaction mixture. The organic layer was washed with H_2O (3x20 mL), brine (2x20 mL), dried over Na_2SO_4 and the solvent was evaporated on a rotary evaporator. The resulting residue was purified by column flash chromatography on silica gel (eluent: DCM/acetone 3:1) to afford the desired chiral Ni(II) complex (*S,S*)-**1b** as an red powder (0.96 g, 87% yield, *dr* 90:10). Next, the *dr* ratio of Ni(II) complexes was improved by epimerization of the diastereoisomeric mixture with MeONa in MeOH. A flask equipped with a stir bar was charged with a solution of a chiral Ni(II) complex (*S,S*)-**1b** (0.88 g, 1.0 equiv., 1.6 mmol) in 16 mL of MeOH followed by the addition of 2.2N MeONa (0.145 mL, 0.2 equiv., 0.32 mmol). The mixture was stirred at room

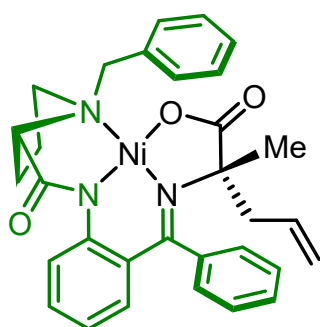
temperature for 24 hours. Afterward, the solvent was evaporated on a rotary evaporator. The purification of the mixture through the short pad of a silica gel (eluent: DCM/acetone 3:1) afforded the desired chiral Ni(II) complex (*S,S*)-**1b** as a red powder (0.84 g, 95% yield, *dr* >20:1).

¹H NMR (300 MHz, CDCl₃): δ = 8.07 (dd, *J* = 15.8, 7.9 Hz, 3H), 7.54–7.39 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25–7.21 (m, 1H), 7.21–7.07 (m, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.69–6.57 (m, 2H), 5.60–5.42 (m, 1H), 4.90 (dd, *J* = 26.2, 13.6 Hz, 2H), 4.42 (d, *J* = 12.6 Hz, 1H), 3.89 (dd, *J* = 8.4, 3.4 Hz, 1H), 3.67–3.40 (m, 4H), 2.82–2.61 (m, 2H), 2.60–2.43 (m, 1H), 2.33–1.99 (m, 4H), 1.74–1.57 (m, 1H) ppm.

[α]_D²⁵ +2500 (c 0.02, MeOH).

The spectroscopic data are consistent with those reported in literature.^[S7]

Ni(II) complex (*S,S*)-**1c**



(*S,S*)-**1c**

Complex (*S,S*)-**1c** was synthesized according to a literature procedure.^[S3]

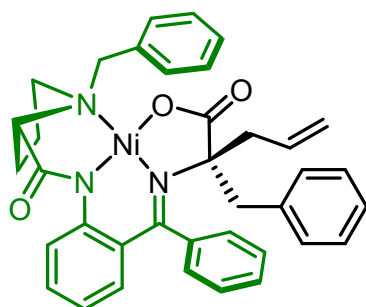
¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, *J* = 7.5 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.53–7.43 (m, 2H), 7.42–7.30 (m, 4H), 7.29–7.20 (m, 1H), 7.16–7.09 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.69–6.54 (m, 3H), 5.46 (d, *J* = 10.2 Hz, 1H), 5.35 (d, *J* = 17.1 Hz, 1H), 4.48 (d, *J* = 12.7 Hz, 1H), 3.70 (d, *J* = 12.7 Hz, 1H), 3.64–3.54 (m, 1H), 3.41 (dd, *J* = 10.6, 6.2 Hz, 1H), 3.37–3.22 (m, 1H), 2.79–2.56 (m, 1H), 2.55–2.40 (m, 3H), 2.10–1.95 (m, 2H), 1.20 (s, 3H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 182.1, 180.7, 172.7, 141.5, 136.5, 133.6, 133.4, 133.0, 131.8 (2C), 130.6, 129.6, 129.1, 129.0 (2C), 128.7, 128.1, 127.6, 127.1, 124.1, 121.0, 119.8, 78.2, 70.3, 63.6, 57.1, 44.6, 30.6, 29.3, 23.3 ppm.

Procedure for the synthesis of chiral Ni(II) complexes **1d**

A flame dried Schlenk flask equipped with a stir bar was charged with a solution of a chiral Phe-Ni(II) complex (prepared according to a literature procedure)^[S8] (3 g, 1.0 equiv., 5.1 mmol) in 30 mL of DMF followed by the addition of NaH (3.0 equiv., 15.3 mmol) and allyl bromide (1.5 equiv., 7.65 mmol). The mixture was stirred at room temperature under an Ar atmosphere for 2 h. Full conversion for reaction was confirmed by TLC analysis. Then, the reaction mixture was dissolved with H₂O and the precipitate formed was collected by filtration. The resulting residue was purified by column flash chromatography on silica gel by DCM/acetone 10:1 to afford the desired Ni(II) complex (*S,S*)-**1d** and (*S,R*)-**1d** (*dr* 2:1).

Ni(II) complex (*S,S*)-**1d**



(*S,S*)-**1d**

The desired product (*S,S*)-**1d** was isolated as a red powder (1.8 g, 60% yield), eluent: CH₂Cl₂/acetone (10:1).

¹H NMR (400 MHz, CDCl₃): δ = 8.10 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.58–7.39 (m, 9H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.25–7.18 (m, 2H), 7.16–7.07 (m, 1H), 6.64–6.54 (m, 2H), 5.87–5.72 (m, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 5.26 (d, *J* = 17.2 Hz, 1H), 4.16 (d, *J* = 12.5 Hz, 1H), 3.46 (d, *J* = 12.5 Hz, 1H), 3.28–3.17 (m, 1H), 3.13–2.99 (m, 2H), 2.82 (d, *J* =

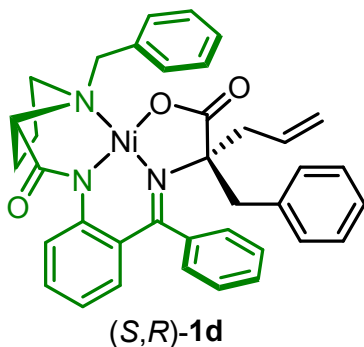
14.1 Hz, 1H), 2.65–2.51 (m, 1H), 2.34–2.12 (m, 3H), 1.95–1.75 (m, 2H), 1.60–1.44 (m, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3): δ = 180.4, 180.0, 172.3, 142.3, 136.9, 136.8, 134.1, 133.7, 132.3, 131.7, 131.5 (2C), 130.9 (2C), 129.8, 129.0, 128.9 (2C), 128.8 (2C), 128.2, 128.1, 127.9, 127.5, 127.3, 123.8, 120.6, 119.2, 82.4, 70.7, 64.2, 57.7, 43.9, 43.7, 30.5, 22.7 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{37}\text{H}_{36}\text{N}_3\text{NiO}_3^+$ $[\text{M}+\text{H}]^+$: 628.2105, found: 628.2107.

$[\alpha]_{\text{D}}^{25} +2050$ (c 0.02, MeOH).

Ni(II) complex (S,R)-1d



The desired product (*S,R*)-**1d** was isolated as a red powder (965 mg, 30% yield); eluent: CH_2Cl_2 /acetone (10:1).

^1H NMR (400 MHz, CDCl_3): δ = 7.99 (d, J = 7.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.47–7.37 (m, 4H), 7.36–7.29 (m, 4H), 7.25–7.16 (m, 2H), 7.14–7.01 (m, 2H), 6.73–6.55 (m, 3H), 5.51 (d, J = 10.2 Hz, 1H), 5.41 (d, J = 17.1 Hz, 1H), 4.28 (d, J = 12.5 Hz, 1H), 3.77–3.64 (m, 1H), 3.42–3.29 (m, 2H), 3.26 (d, J = 12.5 Hz, 1H), 3.05 (q, J = 15.5 Hz, 2H), 2.62–2.34 (m, 3H), 2.33–2.21 (m, 1H), 2.11–1.95 (m, 2H)

ppm.

^{13}C NMR (101 MHz, CDCl_3): δ = 180.9, 180.6, 173.1, 141.5, 136.9, 136.6, 134.2, 133.0, 132.7, 131.7 (2C), 131.4, 129.9, 129.8 (2C), 129.3, 129.0 (2C), 128.9, 128.7 (2C), 128.6, 128.2, 127.9, 127.4, 126.9, 124.4, 120.9, 120.0, 81.5, 70.3, 64.2, 58.5, 46.0, 42.8, 30.9, 23.5 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{37}\text{H}_{36}\text{N}_3\text{NiO}_3^+$ $[\text{M}+\text{H}]^+$: 628.2105, found: 628.2118.

$[\alpha]_{\text{D}}^{25} +1900$ (c 0.02, MeOH).

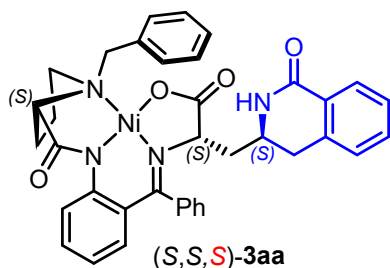
General procedure for the Rh(III)-catalyzed C–H Activation/Annulation of Aryl Hydroxamates with Ni(II) complexes

A chiral Ni(II) complex **1** (1.0 equiv., 0.10 mmol), corresponding aryl hydroxamate **2** (1.0 equiv., 0.10 mmol), catalyst $[\text{Cp}^*\text{RhCl}_2]_2$ (1.2 mg, 0.002 mmol, 4 mol% on Rh) and CsOAc (38 mg, 2.0 equiv., 0.20 mmol) were dissolved in methanol (1 mL). The reaction mixture was stirred at room temperature under standard air atmosphere overnight (≈ 16 h). Full conversion for each reaction was confirmed by TLC analysis. Afterwards, the solvent was removed in vacuo and the residue was purified by column chromatography on SiO_2 (~ 20 cm). Desired products **3** were eluted by CH_2Cl_2 /*i*PrOH mixture (*see below for specific ratios*). In the case of benzyl-substituted derivatives, regioisomers **4da** and **3da** were separated using CH_2Cl_2 /acetone (3:1) as eluent. The mixture of diastereomers **3da** was additionally chromatographed on silica column by a mixture of dichloromethane/isopropanol (*see below for specific ratios*).

Characterization of the complexes **3** and **4**

Ni(II) complex (*S,S,S*)-**3aa**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S,S*)-**3aa** (the first eluting diastereomer) was isolated as an orange powder (15 mg, 23% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.09 (d, *J* = 7.2 Hz, 2H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.61–7.40 (m, 3H), 7.51–7.33 (m, 3H), 7.25–7.19 (m, 2H), 7.15–7.10 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.67–6.61 (m, 1H), 6.56 (d, *J* = 8.2 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 6.11 (d, *J* = 3.7 Hz, 1H, NH), 4.43 (d, *J* = 12.4 Hz, 1H), 4.01 (dd, *J* = 11.5, 4.9 Hz, 2H), 3.66–3.45 (m, 4H), 3.30 (dd, *J* = 16.0, 6.2 Hz, 1H), 2.75–2.66 (m, 2H), 2.59–2.48 (m, 1H), 2.34 (td, *J* = 12.5, 3.8 Hz, 1H), 2.28–2.19 (m, 1H), 2.13–2.08 (m, 1H), 1.90–1.83 (m, 1H) ppm.

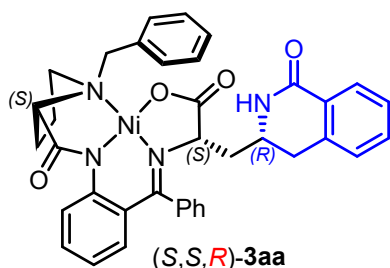
¹³C NMR (101 MHz, CDCl₃): δ = 180.5, 178.9, 171.0, 163.7, 136.5, 133.4 (2C, overlapped), 132.7, 132.4, 132.2, 131.7, 131.6 (2C), 130.4, 129.2, 129.1, 129.0 (2C), 128.9, 128.4, 128.2, 127.9, 126.9 (2C overlapped), 126.3, 123.9, 121.0, 70.3, 67.2, 63.4, 57.4, 46.8, 39.8, 33.4, 30.8, 24.4 ppm. The signal of one carbon atom in ¹³C {¹H} NMR overlapped.

HRMS (ESI, *m/z*) calcd. for C₃₇H₃₄N₄NiO₄⁺ [M+H]⁺: 657.2006, found: 657.2011.

[α]_D²⁵ +1850 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,R*)-**3aa**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S,R*)-**3aa** (the second eluting diastereomer) was isolated as an orange powder (44 mg, 67% yield); eluent: CH₂Cl₂/*i*PrOH (5:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.14–7.98 (m, 4H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.50–7.46 (m, 2H), 7.41–7.25 (m, 6H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.69–6.55 (m, 2H), 4.40 (d, *J* = 12.6 Hz, 1H), 3.96 (dd, *J* = 11.0, 3.6 Hz, 1H), 3.77–3.67 (m, 2H), 3.54–3.47 (m, 3H), 2.84 (td, *J* = 12.9, 5.4 Hz, 1H), 2.73–2.61 (m, 2H), 2.56–2.46 (m, 1H), 2.24–2.03 (m, 3H), 1.88–1.81 (m, 1H) ppm.

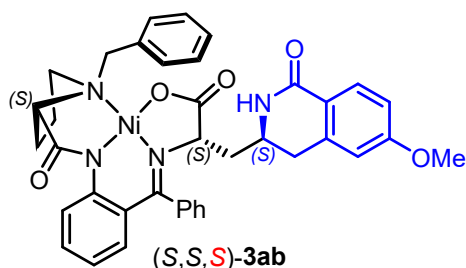
¹³C {¹H} NMR (101 MHz, CDCl₃): δ = 180.6, 179.1, 170.6, 166.0, 142.3, 137.1, 133.4, 133.3, 133.2, 132.4, 132.2, 131.5 (2C), 130.0, 129.3, 129.1, 129.0, 128.9 (2C), 128.4, 127.7, 127.7, 127.4, 127.3, 127.0, 126.2, 123.9, 120.9, 70.2, 67.6, 63.2, 57.5, 48.4, 41.7, 32.9, 30.7, 24.3 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₇H₃₄N₄NiO₄⁺ [M+H]⁺: 657.2006, found: 657.1985.

[α]_D²⁵ +1800 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,S*)-3ab

Starting from a chiral Ni(II) complex (*S,S*)-1a and 4-methoxy-*N*-(pivaloyloxy)benzamide 2b, the desired product (*S,S,S*)-3ab (the first eluting diastereomer) was isolated as an orange powder (12 mg, 17% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.11–8.00 (m, 3H), 7.79 (d, *J* = 8.6 Hz, 1H), 7.59–7.52 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.24–7.17 (m, 2H), 7.14–7.07 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.65–6.59 (m, 2H), 6.58–6.52 (m, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.88 (d, *J* = 4.3 Hz, 1H, NH), 4.41 (d, *J* = 12.6 Hz, 1H), 3.97 (dd, *J* = 11.4, 4.7 Hz, 2H), 3.82 (s, 3H), 3.68–3.43 (m, 4H), 3.25 (dd, *J* = 15.8, 6.0 Hz, 1H), 2.76–2.61 (m, 2H), 2.61–2.48 (m, 1H), 2.37–2.30 (m, 1H), 2.25–2.20 (m, 1H), 2.13–2.06 (m, 1H), 1.91–1.83 (m, 1H) ppm.

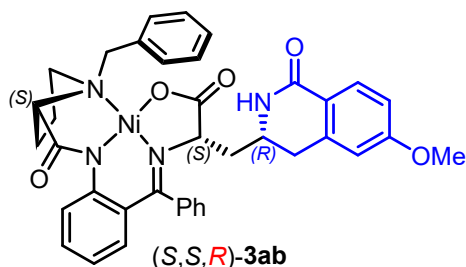
¹³C NMR (101 MHz, CDCl₃): δ = 180.4, 178.9, 171.0, 163.7, 162.7, 142.2, 138.7, 133.4, 133.3, 132.8, 132.4, 131.6 (2C), 130.5, 130.4, 129.3, 129.2, 129.1 (2C), 129.0, 126.9, 126.8, 126.3, 123.9, 121.1, 121.0, 112.8, 112.5, 70.3, 67.3, 63.4, 57.4, 55.5, 46.9, 40.0, 33.9, 30.8, 24.4 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₈H₃₆N₄NiO₅⁺ [M+H]⁺: 687.2112, found: 687.2111.

[α]_D²⁵ +2100 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,R*)-3ab

Starting from a chiral Ni(II) complex (*S,S*)-1a and 4-methoxy-*N*-(pivaloyloxy)benzamide 2b, the desired product (*S,S,R*)-3ab (the second eluting diastereomer) was isolated as an orange powder (49 mg, 72% yield); eluent: CH₂Cl₂/*i*PrOH (5:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.12–8.00 (m, 3H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.40–7.26 (m, 4H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.92–6.68 (m, 3H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.6 Hz, 1H), 6.41 (s, 1H), 4.41 (d, *J* = 12.5 Hz, 1H), 3.93 (d, *J* = 9.6 Hz, 1H), 3.84 (s, 3H), 3.74–3.58 (m, 2H), 3.56–3.43 (m, 3H), 2.80–2.60 (m, 3H), 2.58–2.44 (m, 1H), 2.27–2.12 (m, 2H), 2.11–2.02 (m, 1H), 1.93–1.78 (m, 1H) ppm.

¹³C {¹H} NMR (101 MHz, CDCl₃): δ = 180.6, 179.1, 170.7, 162.6, 142.4, 139.1, 133.4, 133.3, 133.2, 132.5, 131.6 (2C), 130.1 (2C, overlapped), 129.3, 129.2, 129.1, 129.0 (3C, overlapped), 127.5, 127.4, 126.3, 124.0, 121.0, 113.2, 112.2, 70.3, 67.8, 63.2, 57.5, 55.5, 48.5, 41.9, 33.4, 30.8, 24.4 ppm. The signal of one carbon atom in ¹³C {¹H} NMR overlapped.

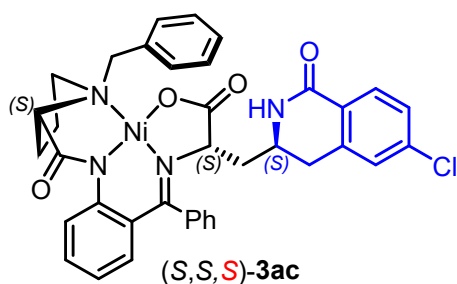
HRMS (ESI, *m/z*) calcd. for C₃₈H₃₆N₄NiO₅⁺ [M+H]⁺: 687.2112, found: 687.2102.

[α]_D²⁵ +1700 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,S*)-3ac

Starting from a chiral Ni(II) complex (*S,S*)-1a and 4-chloro-*N*-(pivaloyloxy)benzamide 2c, the desired product (*S,S,S*)-3ac (the first eluting diastereomer) was isolated as an orange powder (14 mg, 20% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).

Comment: A gram-scale reaction was performed with 2.42 mmol of the Ni(II) complex (*S,S*)-**1a** (1.30 g) by the addition of **2e** (0.638 g, 2.50 mmol), [Cp**RhCl*₂]₂ (0.030 g, 0.048 mmol) and CsOAc (0.920 g, 4.84 mmol) in 20 mL of MeOH. Yield 0.38 g (23%).



¹H NMR (400 MHz, CDCl₃): δ = 8.09–8.00 (m, 3H), 7.77 (dd, *J* = 8.4, 2.8 Hz, 1H), 7.54 (t, *J* = 6.6 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.38–7.27 (m, 3H), 7.25–7.06 (m, 4H), 6.94 (td, *J* = 7.6, 2.6 Hz, 1H), 6.61 (td, *J* = 7.6, 2.4 Hz, 1H), 6.56–6.46 (m, 2H), 6.10 (s, 1H, NH), 4.40 (d, *J* = 12.5 Hz, 1H), 4.03–3.91 (m, 2H), 3.68–3.42 (m, 4H), 3.23 (dd, *J* = 16.0, 6.2 Hz, 1H), 2.72–2.60 (m, 2H), 2.58–2.45 (m, 1H), 2.33 (t, *J* = 12.5 Hz, 1H), 2.27–2.17 (m, 1H), 2.13–2.02

(m, 1H), 1.85–1.77 (m, 1H) ppm.

¹³C NMR (101 MHz, CDCl₃): δ = 180.4, 178.6, 170.9, 162.7, 142.2, 138.3, 138.1, 133.3, 133.2, 132.7, 132.4, 131.5 (2C), 130.2, 129.9, 129.2, 129.0, 128.9 (2C), 128.8, 127.9, 127.1, 126.9, 126.8, 126.7, 126.2, 123.8, 120.9, 70.2, 67.0, 63.3, 57.4, 46.7, 39.7, 33.1, 30.7, 24.3 ppm.

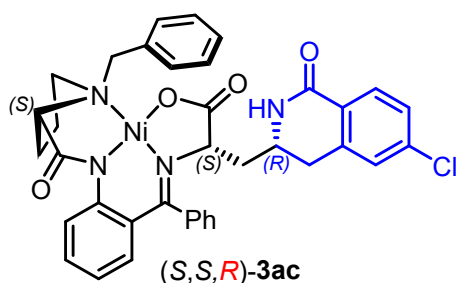
HRMS (ESI, *m/z*) calcd. for C₃₇H₃₃ClN₄NiO₄⁺ [M+H]⁺: 691.1617, found: 691.1622.

[α]_D²⁵ +1250 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,R*)-**3ac**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and 4-chloro-*N*-(pivaloyloxy)benzamide **2c**, the desired product (*S,S,R*)-**3ac** (the second eluting diastereomer) was isolated as an orange powder (49 mg, 71% yield); eluent: CH₂Cl₂/*i*PrOH (5:1).

Comment: A gram-scale reaction was performed with 2.42 mmol of the Ni(II) complex (*S,S*)-**1a** (1.30 g) by the addition of **2e** (0.638 g, 2.50 mmol), [Cp**RhCl*₂]₂ (0.030 g, 0.048 mmol) and CsOAc (0.920 g, 4.84 mmol) in 20 mL MeOH. Yield 1.05 g (63%).



¹H NMR (400 MHz, CDCl₃): δ = 8.09–8.01 (m, 3H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.60–7.49 (m, 2H), 7.38–7.25 (m, 5H), 7.22–7.15 (m, 2H), 7.14–7.08 (m, 1H), 6.86 (s, 1H, NH), 6.81 (d, *J* = 7.7 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.58–6.53 (m, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.92 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.75–3.63 (m, 2H), 3.56–3.44 (m, 3H), 2.78 (dt, *J* = 12.8, 5.2 Hz, 1H), 2.67 (dd, *J* = 15.7, 5.3 Hz, 2H), 2.57–2.44 (m, 1H), 2.24–2.13 (m, 2H), 2.12–2.02 (m, 1H),

1.86–1.77 (m, 1H) ppm.

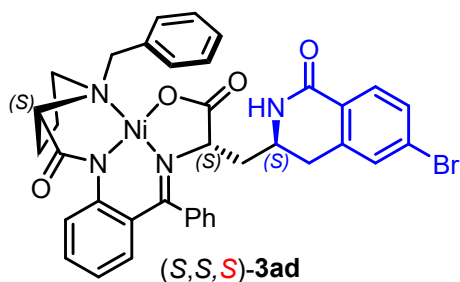
¹³C {¹H} NMR (101 MHz, CDCl₃): δ = 180.5, 178.9, 170.8, 164.9, 142.5, 138.7, 138.3, 133.4, 133.3, 133.2, 132.6, 131.6 (2C), 130.2, 129.6, 129.3, 129.2, 129.1, 129.0 (2C), 127.9, 127.5, 127.4, 127.3, 126.9, 126.3, 124.0, 121.0, 70.3, 67.7, 63.3, 57.5, 48.4, 41.6, 32.5, 30.8, 24.4 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₇H₃₃ClN₄NiO₄⁺ [M+H]⁺: 691.1617, found: 691.1615.

[α]_D²⁵ +1800 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,S*)-**3ad**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and 4-bromo-*N*-(pivaloyloxy)benzamide **2d**, the desired product (*S,S,S*)-**3ad** (the first eluting diastereomer) was isolated as an orange powder (19 mg, 26% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).



^1H NMR (400 MHz, CDCl_3): δ = 8.06 (d, J = 7.2 Hz, 2H), 8.00 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.53 (t, J = 7.3 Hz, 1H), 7.49–7.41 (m, 2H), 7.38–7.28 (m, 3H), 7.24–7.14 (m, 2H), 7.12–7.05 (m, 1H), 6.93 (t, J = 7.4 Hz, 1H), 6.60 (t, J = 7.4 Hz, 1H), 6.55–6.45 (m, 2H), 6.17 (d, J = 3.8 Hz, 1H, NH), 4.39 (d, J = 12.6 Hz, 1H), 3.97 (dd, J = 11.5, 4.8 Hz, 2H), 3.68–3.42 (m, 4H), 3.23 (dd, J = 15.9, 6.0 Hz, 1H), 2.71–2.60 (m, 2H), 2.57–2.43 (m, 1H), 2.38–2.27 (m, 1H), 2.26–2.17 (m, 1H), 2.11–2.03 (m, 1H), 1.86–1.74 (m, 1H) ppm.

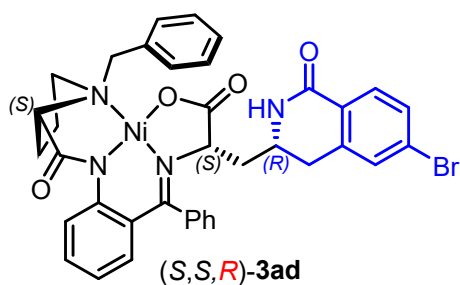
^{13}C NMR (101 MHz, CDCl_3): δ = 180.4, 178.8, 171.0, 162.8, 142.2, 138.5, 133.3, 133.2, 132.7, 132.4, 131.6 (2C), 130.9, 130.3, 130.2, 130.1, 129.2, 129.1, 129.0 (2C), 128.9, 127.1, 126.9, 126.8, 126.7, 126.2, 123.9, 120.9, 70.2, 67.0, 63.3, 57.4, 46.7, 39.6, 33.0, 30.7, 24.4 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{37}\text{H}_{33}\text{BrN}_4\text{NiO}_4^+$ [$\text{M}+\text{H}$] $^+$: 735.1111, found: 735.1138.

$[\alpha]_{\text{D}}^{25}$ +1850 (c 0.02, MeOH).

Ni(II) complex (S,S,R)-3ad

Starting from a chiral Ni(II) complex (S,S)-1a and 4-bromo-*N*-(pivaloyloxy)benzamide 2d, the desired product (S,S,R)-3ad (the second eluting diastereomer) was isolated as an orange powder (49 mg, 67% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (5:1).



^1H NMR (400 MHz, CDCl_3): δ = 8.11–8.00 (m, 3H), 7.86 (d, J = 8.2 Hz, 1H), 7.62–7.55 (m, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.39–7.31 (m, 4H), 7.24–7.18 (m, 2H), 7.12 (t, J = 7.7 Hz, 1H), 7.03 (s, 1H, NH), 6.80 (d, J = 7.7 Hz, 1H), 6.63 (t, J = 7.5 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 4.41 (d, J = 12.6 Hz, 1H), 3.92 (dd, J = 11.1, 3.7 Hz, 1H), 3.74–3.67 (m, 2H), 3.53 (d, J = 12.6 Hz, 1H), 3.53–3.46 (m, 2H), 2.85–2.75 (m, 1H), 2.67 (dd, J = 15.7, 5.3 Hz, 2H), 2.60–2.46 (m, 1H), 2.24–2.16 (m, 2H), 2.13–2.07 (m, 1H), 1.88–1.82 (m, 1H) ppm.

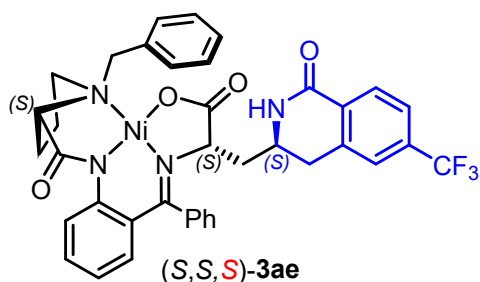
^{13}C NMR (101 MHz, CDCl_3): δ = 180.5, 179.0, 170.7, 165.0, 142.4, 138.8, 133.3 (2C, overlapped), 133.2, 132.6, 131.6 (2C), 130.9, 130.5, 130.2, 129.7, 129.3, 129.2, 129.1, 129.0 (2C), 127.4, 127.3 (2C, overlapped), 126.9, 126.3, 124.0, 121.0, 70.3, 67.6, 63.3, 57.5, 48.3, 41.6, 32.4, 30.8, 24.4 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{37}\text{H}_{33}\text{BrN}_4\text{NiO}_4^+$ [$\text{M}+\text{H}$] $^+$: 735.1111, found: 735.1114.

$[\alpha]_{\text{D}}^{25}$ +1800 (c 0.02, MeOH).

Ni(II) complex (S,S,S)-3ae

Starting from a chiral Ni(II) complex (S,S)-1a and 4-trifluoromethyl-*N*-(pivaloyloxy)benzamide 2e, the desired product (S,S,S)-3ae (the first eluting diastereomer) was isolated as an orange powder (22 mg, 30% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (25:1).



^1H NMR (400 MHz, CDCl_3): δ = 8.06 (d, J = 7.4 Hz, 2H), 8.00 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.46–7.38 (m, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 7.9 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.8 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 6.60 (t, J = 7.6 Hz, 1H), 6.53–6.43 (m, 2H), 6.33 (d, J = 4.5 Hz, 1H, NH), 4.39 (d, J = 12.5 Hz, 1H), 4.00 (dd, J = 11.8, 5.1 Hz, 2H), 3.68–3.46 (m,

4H), 3.30 (dd, $J = 16.1, 6.3$ Hz, 1H), 2.75 (d, $J = 16.1$ Hz, 1H), 2.70–2.62 (m, 1H), 2.59–2.47 (m, 1H), 2.37 (td, $J = 12.7, 3.9$ Hz, 1H), 2.28–2.23 (m, 1H), 2.13–2.06 (m, 1H), 1.81 (td, $J = 12.5, 5.0$ Hz, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3): $\delta = 180.4, 178.8, 171.0, 162.2, 142.2, 137.3, 133.3, 133.2, 132.8, 132.5, 131.6$ (2C), 130.3, 129.2, 129.1, 129.0 (2C), 128.9, 128.7, 127.0, 126.9, 126.2, 124.9 (q, $J_{\text{CF}} = 3.5$ Hz), 123.9, 123.7 (q, $J_{\text{CF}} = 3.6$ Hz), 121.0, 70.3, 66.9, 63.4, 57.5, 46.6, 39.5, 33.1, 30.7, 24.4 ppm. The signals of three carbon atoms in ^{13}C NMR overlapped.

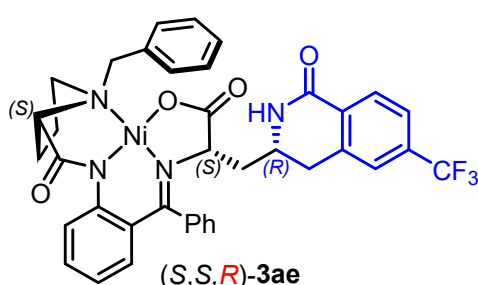
^{19}F NMR (376 MHz, CDCl_3): $\delta = -63.02$ (s, CF_3) ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{38}\text{F}_3\text{H}_{33}\text{N}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 725.1880, found: 725.1878.

$[\alpha]_{\text{D}}^{25} +1600$ (c 0.02, MeOH).

Ni(II) complex (*S,S,R*)-3ae

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and 4-trifluoromethyl-*N*-(pivaloyloxy)benzamide **2e**, the desired product (*S,S,R*)-**3ae** (the second eluting diastereomer) was isolated as an orange powder (44 mg, 61% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (5:1).



^1H NMR (400 MHz, CDCl_3): $\delta = 8.14$ – 8.02 (m, 4H), 7.70 (s, 1H), 7.62–7.47 (m, 3H), 7.38–7.30 (m, 4H), 7.24–7.08 (m, 3H), 6.85 (d, $J = 7.6$ Hz, 1H), 6.69–6.51 (m, 2H), 4.38 (d, $J = 12.6$ Hz, 1H), 3.94 (dd, $J = 11.0, 3.5$ Hz, 1H), 3.79–3.66 (m, 2H), 3.58–3.44 (m, 3H), 2.90–2.61 (m, 3H), 2.59–2.45 (m, 1H), 2.26–2.04 (m, 3H), 1.89–1.82 (m, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3): $\delta = 180.5, 179.0, 170.8, 164.5, 142.3, 137.7, 133.6$ (q, $J_{\text{CF}} = 32.0$ Hz), 133.3, 133.2, 132.5, 131.5 (2C), 131.4, 130.1, 129.2, 129.1, 129.0, 128.9 (2C), 128.4, 127.4, 127.3, 126.2, 124.7 (q, $J_{\text{CF}} = 3.1$ Hz), 124.0 (2C, overlapped), 123.7 (q, $J_{\text{CF}} = 271.0$ Hz), 121.0, 70.2, 67.5, 63.2, 57.5, 48.2, 41.5, 32.5, 30.7, 24.3 ppm. The signal of one carbon atom in ^{13}C NMR overlapped.

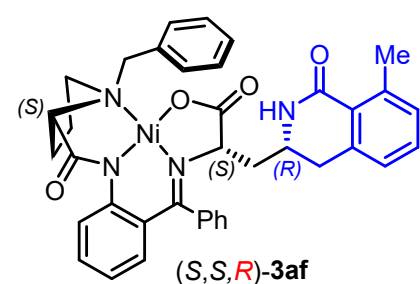
^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.82$ (s, CF_3) ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{38}\text{F}_3\text{H}_{33}\text{N}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 725.1880, found: 725.1870.

$[\alpha]_{\text{D}}^{25} +1800$ (c 0.02, MeOH).

Ni(II) complex (*S,S,R*)-3af

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and 2-methyl-*N*-(pivaloyloxy)benzamide **2f**, the desired product (*S,S,R*)-**3af** (the second eluting diastereomer) was isolated as an orange powder (46 mg, 68% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (25:1).



^1H NMR (400 MHz, CDCl_3): $\delta = 8.12$ – 8.07 (m, 3H), 7.58 (t, $J = 7.5$ Hz, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.42–7.34 (m, 3H), 7.31 (d, $J = 7.5$ Hz, 1H), 7.27–7.07 (m, 4H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.80 (d, $J = 7.4$ Hz, 1H), 6.70–6.64 (m, 1H), 6.62–6.59 (m, 2H), 4.43 (d, $J = 12.6$ Hz, 1H), 3.97 (dd, $J = 10.3, 3.4$ Hz, 1H), 3.69–3.61 (m, 1H), 3.60–3.47 (m, 4H), 2.78–2.70 (m, 1H), 2.68 (s, 3H), 2.65–2.45 (m, 3H), 2.31–2.16 (m, 2H), 2.14–2.05 (m, 1H), 1.88–1.80 (m, 1H) ppm.

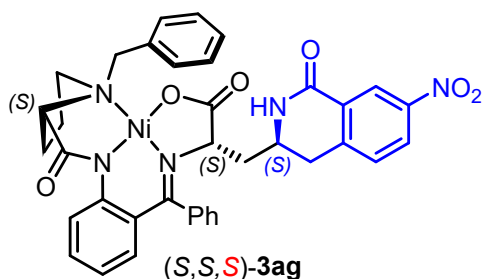
^{13}C NMR (101 MHz, CDCl_3): δ = 180.6, 179.2, 170.8, 166.4, 142.5, 141.1, 138.3, 133.6, 133.4, 133.3, 132.6, 131.6 (2C), 131.2, 131.0, 130.2, 129.4, 129.3, 129.11, 129.07, 127.5, 127.4, 127.1 (2C), 126.3, 125.7, 124.0, 121.0, 70.3, 68.0, 63.3, 57.5, 48.3, 41.9, 35.0, 30.8, 24.3, 22.3 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{38}\text{H}_{36}\text{N}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 671.2163, found: 671.2159.

$[\alpha]_{\text{D}}^{25} +2550$ (c 0.02, MeOH).

Ni(II) complex (S,S,S)-3ag

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and 3-nitro-*N*-(pivaloyloxy)benzamide **2g**, the desired product (*S,S,S*)-**3ag** (the first eluting diastereomer) was isolated as an orange powder (23 mg, 33% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (25:1).



^1H NMR (400 MHz, CDCl_3): δ = 8.66 (d, J = 2.4 Hz, 1H), 8.28 (dd, J = 8.3, 2.5 Hz, 1H), 8.12–8.06 (m, 2H), 8.00 (d, J = 8.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.40–7.31 (m, 3H), 7.30–7.25 (m, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.15–7.09 (m, 1H), 6.78 (t, J = 7.5 Hz, 1H), 6.63 (t, J = 7.6 Hz, 1H), 6.52–6.39 (m, 3H), 4.43 (d, J = 12.6 Hz, 1H), 4.12–4.03 (m, 2H), 3.71–3.62 (m, 1H), 3.60–3.44 (m, 3H), 3.37 (dd, J = 16.2, 6.3 Hz, 1H), 2.83 (dd, J = 16.2, 2.3 Hz, 1H), 2.73–2.67 (m, 1H), 2.63–2.47 (m, 1H), 2.35 (dd, J = 12.4, 4.0 Hz, 1H), 2.29–2.19 (m, 1H), 2.15–2.05 (m, 1H), 1.76 (dd, J = 12.4, 5.1 Hz, 1H) ppm.

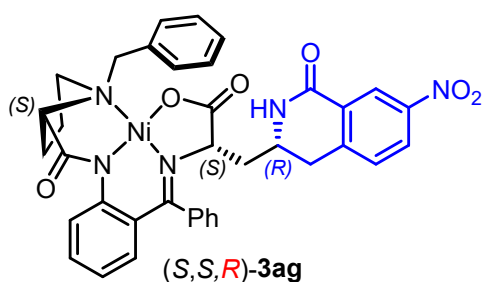
^{13}C NMR (101 MHz, CDCl_3): δ = 180.4, 178.7, 171.1, 161.3, 147.3, 143.5, 142.3, 133.3, 132.8, 132.6, 131.6 (2C), 130.4, 129.7, 129.5, 129.3, 129.22, 129.15 (2C), 128.5, 127.1 (2C), 126.5, 124.0 (2C), 121.1, 70.3, 66.7, 63.5, 57.5, 46.6, 38.9, 33.3, 30.8, 24.5 ppm. The signals of two carbon atoms in ^{13}C NMR overlapped.

HRMS (ESI, m/z) calcd. for $\text{C}_{37}\text{H}_{33}\text{N}_5\text{NiO}_6^+$ $[\text{M}+\text{H}]^+$: 702.1857, found: 702.1870.

$[\alpha]_{\text{D}}^{25} +1238$ (c 0.021, MeOH).

Ni(II) complex (S,S,R)-3ag

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and 3-nitro-*N*-(pivaloyloxy)benzamide **2g**, the desired product (*S,S,R*)-**3ag** (the second eluting diastereomer) was isolated as an orange powder (42 mg, 60% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (5:1).



^1H NMR (400 MHz, CDCl_3): δ = 8.85 (d, J = 2.4 Hz, 1H), 8.26 (dd, J = 8.3, 2.5 Hz, 1H), 8.10–8.06 (m, 3H), 7.63–7.48 (m, 3H), 7.41–7.33 (m, 4H), 7.25–7.12 (m, 3H), 6.92 (d, J = 7.6 Hz, 1H), 6.67 (t, J = 7.5 Hz, 1H), 6.60 (dd, J = 8.2, 1.8 Hz, 1H), 4.44 (d, J = 12.6 Hz, 1H), 3.99 (dd, J = 10.6, 3.3 Hz, 1H), 3.80–3.46 (m, 5H), 2.84–2.68 (m, 3H), 2.65–2.47 (m, 1H), 2.36–2.25 (m, 2H), 2.19–2.06 (m, 1H), 1.87–1.79 (m, 1H) ppm.

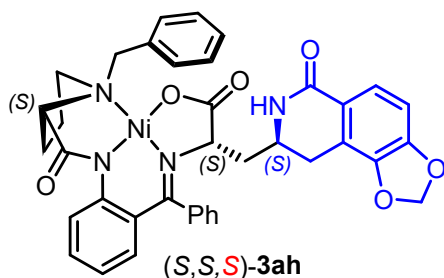
^{13}C NMR (101 MHz, CDCl_3): δ = 180.6, 179.2, 171.0, 163.7, 147.6, 144.0, 142.6, 133.7, 133.4, 133.3, 132.7, 131.7 (2C), 130.2, 130.0, 129.4, 129.3, 129.2, 129.1 (2C), 129.0, 127.5 (2C, overlapped), 126.7, 126.2, 124.2, 123.3, 121.1, 70.3, 67.6, 63.4, 57.6, 48.6, 41.7, 33.3, 30.8, 24.5 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{37}\text{H}_{33}\text{N}_5\text{NiO}_6^+$ $[\text{M}+\text{H}]^+$: 702.1857, found: 702.1854.

$[\alpha]_{\text{D}}^{25} +1917$ (c 0.012, MeOH).

Ni(II) complex (*S,S,S*)-**3ah**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and *N*-(pivaloyloxy)benzo[*d*][1,3]dioxole-5-carboxamide **2h**, the desired product (*S,S,S*)-**3ah** (the first eluting diastereomer) was isolated as an orange powder (32 mg, 46% yield); eluent: CH₂Cl₂/*i*PrOH (20:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.09–8.05 (m, 3H), 7.63–7.44 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.25–7.18 (m, 2H), 7.15–7.10 (m, 1H), 7.08–7.00 (m, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.60–6.51 (m, 2H), 6.03 (d, *J* = 1.3 Hz, 1H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.91 (d, *J* = 4.3 Hz, 1H), 4.43 (d, *J* = 12.6 Hz, 1H), 4.05–3.97 (m, 2H), 3.66–3.62 (m, 1H), 3.59–3.46 (m, 3H), 3.07 (dd, *J* = 16.1, 6.1 Hz, 1H), 2.85 (dd, *J* = 16.1, 3.2 Hz, 1H), 2.70–2.65 (m, 1H), 2.62–2.44 (m, 1H), 2.41–2.31 (m, 1H), 2.29–2.17 (m, 1H), 2.14–2.05 (m, 1H), 1.92–1.82 (m, 1H) ppm.

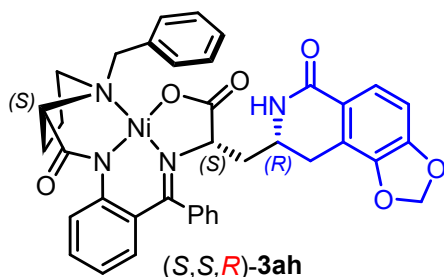
¹³C NMR (101 MHz, CDCl₃): δ = 180.4, 178.8, 171.1, 163.2, 150.5, 144.6, 142.3, 133.4, 132.8, 132.4, 131.7, 131.6 (2C), 130.4, 129.3, 129.2, 129.1 (2C), 129.0, 126.9 (2C, overlapped), 126.3, 123.9, 123.8, 122.5, 121.0, 117.6, 106.6, 102.0, 70.3, 67.2, 63.4, 57.4, 46.7, 40.1, 30.8, 27.0, 24.4 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₈H₃₄N₄NiO₆⁺ [M+H]⁺: 701.1905, found: 701.1917.

[α]_D²⁵ +1692 (*c* 0.013, MeOH).

Ni(II) complex (*S,S,R*)-**3ah**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and *N*-(pivaloyloxy)benzo[*d*][1,3]dioxole-5-carboxamide **2h**, the desired product (*S,S,R*)-**3ah** (the second eluting diastereomer) was isolated as an orange powder (34 mg, 48% yield); eluent: CH₂Cl₂/*i*PrOH (5:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.09 (d, *J* = 8.0 Hz, 3H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.41–7.29 (m, 4H), 7.25–7.10 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 6.78–6.75 (m, 2H), 6.71–6.58 (m, 2H), 6.07 (d, *J* = 1.4 Hz, 1H), 6.00 (d, *J* = 1.5 Hz, 1H), 4.44 (d, *J* = 12.6 Hz, 1H), 3.97 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.77–3.60 (m, 2H), 3.59–3.43 (m, 3H), 2.82–2.59 (m, 3H), 2.59–2.43 (m, 1H), 2.29–2.18 (m, 1H), 2.16–2.02 (m, 2H), 1.91–

1.83 (m, 1H) ppm.

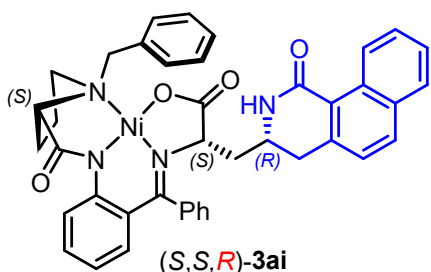
¹³C NMR (101 MHz, CDCl₃): δ = 180.6, 179.1, 170.9, 165.5, 150.6, 144.1, 142.5, 133.5, 133.4, 133.3, 132.6, 131.7 (2C), 130.1, 129.3, 129.2, 129.12, 129.08 (2C), 127.5, 127.4, 126.3, 124.1, 123.3, 122.7, 121.0, 118.2, 106.9, 101.9, 70.3, 67.8, 63.3, 57.6, 48.5, 42.0, 30.8, 26.7, 24.4 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₈H₃₄N₄NiO₆⁺ [M+H]⁺: 701.1905, found: 701.1902.

[α]_D²⁵ +2048 (*c* 0.021, MeOH).

Ni(II) complex (*S,S,R*)-**3ai**

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and *N*-(pivaloyloxy)-1-naphthamide **2i**, the desired product (*S,S,R*)-**3ai** (the second eluting diastereomer) was isolated as an orange powder (38 mg, 54% yield); eluent: CH₂Cl₂/*i*PrOH (5:1).



¹H NMR (400 MHz, CDCl₃): δ = 9.40 (d, *J* = 8.7 Hz, 1H), 8.13–8.01 (m, 3H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.61–7.51 (m, 2H), 7.53–7.44 (m, 2H), 7.39–7.34 (m, 2H), 7.33–7.26 (m, 2H),

7.19 (t, $J = 7.5$ Hz, 1H), 7.13 (t, $J = 7.4$ Hz, 1H), 7.06 (d, $J = 8.2$ Hz, 1H), 6.83 (d, $J = 7.6$ Hz, 1H), 6.64 (t, $J = 7.6$ Hz, 1H), 6.58 (dd, $J = 8.3, 1.6$ Hz, 1H), 4.40 (d, $J = 12.4$ Hz, 1H), 4.04–3.94 (m, 1H), 3.69–3.40 (m, 5H), 2.83–2.62 (m, 2H), 2.56–2.42 (m, 2H), 2.21–2.00 (m, 2H), 1.93–1.84 (m, 1H), 1.82–1.71 (m, 1H) ppm. The signal of NH proton in ^1H NMR overlapped.

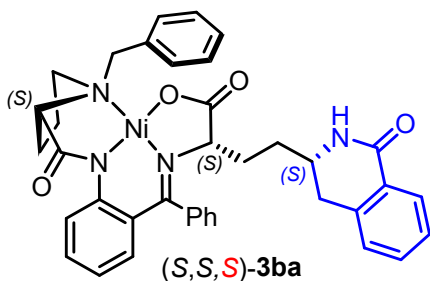
^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 180.6, 179.3, 170.9, 166.4, 142.5, 138.1, 133.6, 133.4, 133.32, 133.30, 133.0, 132.6, 131.7, 131.6$ (2C), 130.2, 129.3 (2C, overlapped), 129.1, 129.0 (2C), 128.3, 128.0, 127.5, 127.4, 126.9, 126.3, 125.9, 125.7, 124.1, 123.3, 121.0, 70.3, 68.0, 63.3, 57.5, 48.0, 41.6, 35.4, 30.8, 24.4 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{41}\text{H}_{36}\text{N}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 707.2163, found: 707.2150.

$[\alpha]_{\text{D}}^{25} +1700$ (c 0.02, MeOH).

Ni(II) complex (*S,S,S*)-3ba

Starting from a chiral Ni(II) complex (*S,S*)-1b and *N*-(pivaloyloxy)benzamide 2a, the desired product (*S,S,S*)-3ba (the first eluting diastereomer) was isolated as an orange powder (35 mg, 52% yield); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (20:1).



^1H NMR (400 MHz, CDCl_3): $\delta = 8.10\text{--}8.05$ (m, 4H), 7.51–7.43 (m, 3H), 7.42–7.33 (m, 3H), 7.23–7.17 (m, 4H), 7.16–7.10 (m, 1H), 6.69–6.53 (m, 3H), 6.36 (d, $J = 4.4$ Hz, 1H, NH), 4.42 (d, $J = 12.6$ Hz, 1H), 3.75 (dd, $J = 9.6, 3.1$ Hz, 1H), 3.59–3.46 (m, 5H), 3.04 (dt, $J = 12.4, 3.7$ Hz, 1H), 2.79–2.62 (m, 2H), 2.56–2.45 (m, 1H), 2.32–2.20 (m, 2H), 2.16–2.02 (m, 2H), 1.68–1.48 (m, 2H) ppm.

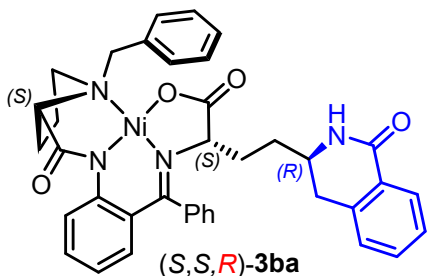
^{13}C NMR (101 MHz, CDCl_3): $\delta = 180.5, 179.2, 170.6, 165.7, 142.3, 142.0, 133.5, 133.34, 133.26, 132.3, 132.2, 131.6$ (2C), 129.9, 129.13, 129.05 (2C), 129.0 (2C), 128.4, 128.2, 127.5, 127.4, 127.12, 127.05, 126.4, 123.9, 120.9, 70.3, 69.9, 63.2, 57.2, 44.2, 36.9, 33.9, 30.9, 29.6, 24.0 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{38}\text{H}_{36}\text{N}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 671.2163, found: 671.2165.

$[\alpha]_{\text{D}}^{25} +1750$ (c 0.02, MeOH).

Ni(II) complex (*S,S,R*)-3ba

Starting from a chiral Ni(II) complex (*S,S*)-1b and *N*-(pivaloyloxy)benzamide 2a, the desired product (*S,S,R*)-3ba (the second eluting diastereomer) was isolated as an orange powder (12 mg, 18% yield or 42 mg, 63% for *R*- $\text{Cp}^{\text{tBu}}\text{RhI}_2$); eluent: $\text{CH}_2\text{Cl}_2/i\text{PrOH}$ (10:1).



^1H NMR (400 MHz, CDCl_3): $\delta = 8.08\text{--}8.03$ (m, 4H), 7.51–7.30 (m, 7H), 7.26–7.22 (m, 1H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.13–7.05 (m, 2H), 6.77 (d, $J = 7.6$ Hz, 1H), 6.69 (d, $J = 4.3$ Hz, 1H, NH), 6.63 (t, $J = 7.5$ Hz, 1H), 6.60–6.54 (m, 1H), 4.37 (d, $J = 12.6$ Hz, 1H), 3.92 (dd, $J = 7.9, 3.6$ Hz, 1H), 3.66 (dd, $J = 12.6, 4.3$ Hz, 1H), 3.50 (d, $J = 12.8$ Hz, 1H), 3.39 (dd, $J = 10.6, 6.1$ Hz, 2H), 3.31 (dt, $J = 12.6, 4.0$ Hz, 1H), 3.25–3.18 (m, 1H), 2.75–2.71 (m, 1H), 2.54–2.47 (m, 2H), 2.42–2.39

(m, 1H), 2.09–1.87 (m, 4H), 1.75–1.69 (m, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3): $\delta = 180.4, 178.9, 170.5, 165.7, 142.4, 142.2, 133.7, 133.3, 133.2, 132.2$ (2C, overlapped), 131.6 (2C), 129.8, 129.1, 129.0, 128.92, 128.89 (2C), 128.3, 128.2, 127.3 (2C,

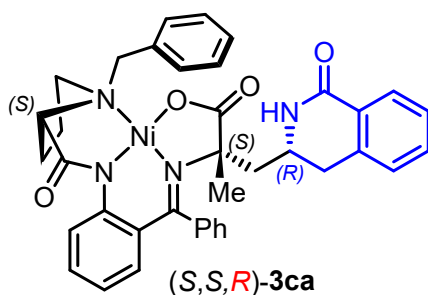
overlapped), 127.2, 127.0, 126.4, 123.8, 120.8, 70.3, 70.1, 63.2, 57.2, 43.9, 37.6, 33.0, 30.8, 29.2, 23.5 ppm.

HRMS (ESI, m/z) calcd. for $C_{38}H_{36}N_4NiO_4^+$ $[M+H]^+$: 671.2163, found: 671.2157.

$[\alpha]_D^{25} +1650$ (c 0.02, MeOH).

Ni(II) complex (S,S,R)-3ca

Starting from a chiral Ni(II) complex (*S,S*)-**1c** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S,R*)-**3ca** (the first eluting diastereomer) was isolated as an orange powder (37 mg, 55% yield); eluent: $CH_2Cl_2/iPrOH$ (25:1).



1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.3 Hz, 2H), 8.06 (d, J = 7.5 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.54–7.46 (m, 3H), 7.44–7.38 (m, 4H), 7.32–7.25 (m, 3H), 7.13–7.10 (m, 1H), 6.93 (d, J = 7.7 Hz, 1H), 6.60 (d, J = 4.2 Hz, 2H), 6.45 (s, 1H, NH), 4.41 (d, J = 12.6 Hz, 1H), 4.17–4.13 (m, 1H), 3.67 (dd, J = 10.2, 6.4 Hz, 1H), 3.60 (d, J = 12.6 Hz, 1H), 3.43 (dd, J = 10.7, 5.7 Hz, 1H), 3.31 (dd, J = 15.7, 4.9 Hz, 1H), 3.16–3.10 (m, 1H), 2.82 (dd, J = 15.6, 7.7 Hz, 1H), 2.54–2.35 (m, 3H), 2.17–1.99 (m, 3H), 1.21 (s, 3H) ppm.

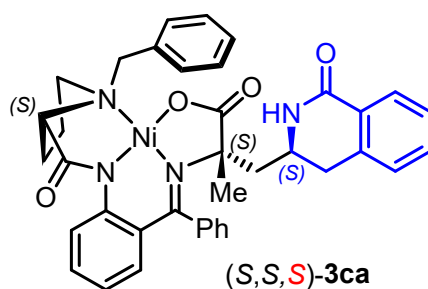
^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.8, 180.8, 172.8, 165.5, 141.8, 137.4, 136.4, 133.7, 133.5, 132.6, 132.1, 131.7 (2C), 130.4, 129.8, 129.2, 129.1 (2C), 128.8, 128.2, 128.1, 128.0, 127.7, 127.5 (2C, overlapped), 127.4, 124.1, 120.9, 75.8, 70.2, 63.7, 57.9, 48.2, 47.1, 35.4, 30.6, 29.1, 24.1 ppm.

HRMS (ESI, m/z) calcd. for $C_{38}H_{36}N_4NiO_4^+$ $[M+H]^+$: 671.2163, found: 671.2132.

$[\alpha]_D^{25} +1750$ (c 0.02, MeOH).

Ni(II) complex (S,S,S)-3ca

Starting from a chiral Ni(II) complex (*S,S*)-**1c** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S,S*)-**3ca** (the second eluting diastereomer) was isolated as an orange powder (24 mg, 36% yield); eluent: $CH_2Cl_2/iPrOH$ (5:1).



1H NMR (400 MHz, $CDCl_3$): δ = 8.15–7.98 (m, 4H), 7.52–7.34 (m, 6H), 7.32–7.20 (m, 3H), 7.16–7.10 (m, 2H), 6.67–6.54 (m, 3H), 6.43 (s, 1H, NH), 4.74–4.60 (m, 1H), 4.40 (d, J = 12.6 Hz, 1H), 3.73–3.58 (m, 2H), 3.43 (dd, J = 10.0, 6.4 Hz, 1H), 3.24–3.00 (m, 3H), 2.45–2.34 (m, 2H), 2.17 (dd, J = 14.6, 4.4 Hz, 1H), 2.15–2.02 (m, 3H), 1.22 (s, 3H) ppm.

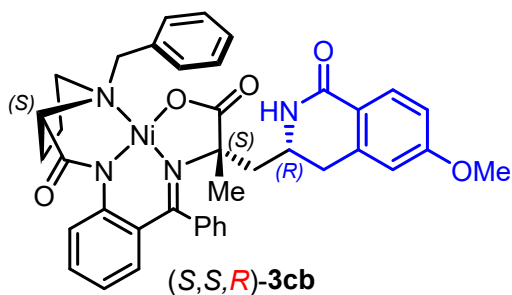
^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.9, 180.8, 173.3, 165.4, 141.8, 137.4, 136.3, 133.7, 132.5, 132.1, 131.7 (2C), 130.5, 129.7, 129.2, 129.1 (2C), 128.2, 128.1, 128.0, 127.7, 127.5, 127.4, 127.3, 124.0, 120.9, 75.8, 70.3, 63.8, 57.8, 49.1, 45.1, 35.6, 30.7, 30.3, 23.7 ppm. The signal of two Ar carbon atoms in ^{13}C $\{^1H\}$ NMR overlapped.

HRMS (ESI, m/z) calcd. for $C_{38}H_{36}N_4NiO_4^+$ $[M+H]^+$: 671.2163, found: 671.2150.

$[\alpha]_D^{25} +1600$ (c 0.02, MeOH).

Ni(II) complex (S,S,R)-3cb

Starting from a chiral Ni(II) complex (*S,S*)-**1c** and 4-methoxy-*N*-(pivaloyloxy)benzamide **2b**, the desired product (*S,S,R*)-**3cb** (the first eluting diastereomer) was isolated as an orange powder (34 mg, 48% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.11 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.55–7.48 (m, 2H), 7.46–7.41 (m, 3H), 7.35–7.30 (m, 2H), 7.15–7.11 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.89 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.60 (d, *J* = 4.3 Hz, 2H), 6.11 (s, 1H, NH), 4.43 (d, *J* = 12.5 Hz, 1H), 4.16–4.03 (m, 1H), 3.86 (s, 3H), 3.73–3.69 (m, 1H), 3.61 (d, *J* = 12.6 Hz, 1H), 3.44 (dd, *J* = 10.8, 5.6 Hz, 1H), 3.29 (dd, *J* = 15.5, 4.5 Hz, 1H), 3.22–3.05 (m, 1H), 2.76 (dd, *J* = 15.6, 7.5 Hz, 1H), 2.55–2.38 (m, 3H), 2.22–1.99 (m, 3H), 1.22 (s, 3H) ppm.

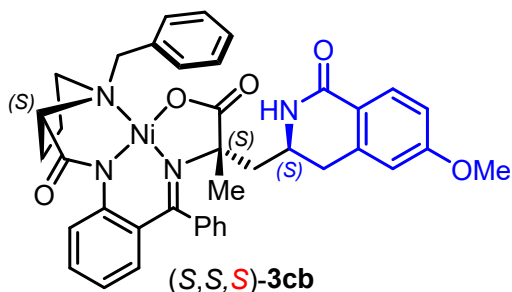
¹³C NMR (101 MHz, CDCl₃): δ = 181.8, 180.8, 172.8, 165.5, 163.0, 141.9, 139.6, 136.5, 133.7, 133.6, 132.1, 131.7 (2C), 130.4, 130.3, 129.8, 129.2, 129.1 (2C), 128.3, 128.2, 127.5, 127.4, 124.2, 121.6, 120.9, 113.1, 112.7, 75.8, 70.2, 63.8, 58.0, 55.6, 48.2, 47.3, 35.9, 30.7, 29.2, 24.2 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₉H₃₈N₄NiO₅⁺ [M+H]⁺: 701.2268, found: 701.2291.

[α]_D²⁵ +1350 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,S*)-**3cb**

Starting from a chiral Ni(II) complex (*S,S*)-**1c** and 4-methoxy-*N*-(pivaloyloxy)benzamide **2b**, the desired product (*S,S,S*)-**3cb** (the second eluting diastereomer) was isolated as an orange powder (23 mg, 33% yield); eluent: CH₂Cl₂/*i*PrOH (5:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.08 (d, *J* = 7.4 Hz, 2H), 8.01 (t, *J* = 8.1 Hz, 2H), 7.48–7.42 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28–7.22 (m, 3H), 7.12 (t, *J* = 7.7 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.64–6.55 (m, 4H), 6.11 (s, 1H, NH), 4.75–4.65 (m, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.70 (s, 3H), 3.69–3.62 (m, 2H), 3.48–3.35 (m, 2H), 3.19 (dd, *J* = 15.5, 4.1 Hz, 1H), 3.12–2.98 (m, 1H), 2.52–2.32 (m, 2H), 2.21 (dd, *J* = 14.8, 4.6 Hz, 1H), 2.13–1.96 (m, 3H), 1.20 (s, 3H) ppm.

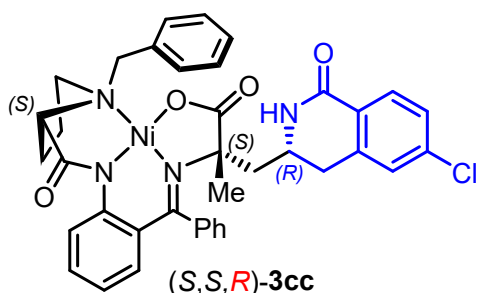
¹³C NMR (101 MHz, CDCl₃): δ = 181.9, 180.7, 173.3, 165.4, 163.0, 141.9, 139.5, 136.3, 133.7, 133.6, 132.2, 131.7 (2C), 130.6, 130.2, 129.8, 129.2, 129.1 (2C), 128.3, 128.1, 127.5, 127.4, 124.1, 121.6, 121.0, 113.6, 112.3, 75.9, 70.3, 63.9, 57.7, 55.5, 49.2, 45.2, 36.1, 30.7, 30.5, 23.7 ppm.

HRMS (ESI, *m/z*) calcd. for C₃₉H₃₈N₄NiO₅⁺ [M+H]⁺: 701.2268, found: 701.2262.

[α]_D²⁵ +1250 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,R*)-**3cc**

Starting from a chiral Ni(II) complex (*S,S*)-**1c** and 4-chloro-*N*-(pivaloyloxy)benzamide **2c**, the desired product (*S,S,R*)-**3cc** (the first eluting diastereomer) was isolated as an orange powder (42 mg, 60% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.13 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.55–7.49 (m, 2H), 7.44–7.37 (m, 4H), 7.33–7.26 (m, 3H), 7.15–7.11 (m, 1H), 6.95

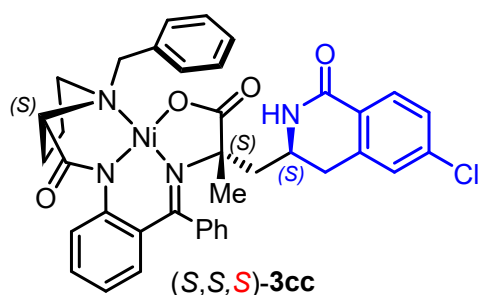
(d, $J = 7.7$ Hz, 1H), 6.63 (d, $J = 4.3$ Hz, 2H), 6.40 (s, 1H, NH), 4.46 (d, $J = 12.6$ Hz, 1H), 4.13–4.09 (m, 1H), 3.73–3.68 (m, 1H), 3.63 (d, $J = 12.6$ Hz, 1H), 3.52–3.45 (m, 1H), 3.30 (dd, $J = 15.8, 4.9$ Hz, 1H), 3.21–3.04 (m, 1H), 2.81 (dd, $J = 15.8, 7.5$ Hz, 1H), 2.54–2.39 (m, 3H), 2.23–2.01 (m, 3H), 1.24 (s, 3H) ppm.

^{13}C NMR (101 MHz, CDCl_3): $\delta = 181.8, 180.8, 172.8, 164.6, 141.9, 139.2, 138.7, 136.4, 133.6, 133.5, 132.2, 131.7$ (2C), 130.4, 129.9, 129.7, 129.2, 129.1 (2C), 128.2, 128.1, 127.9, 127.8, 127.6, 127.4 (2C, overlapped), 124.2, 120.9, 75.7, 70.2, 63.8, 58.0, 48.1, 47.2, 35.3, 30.7, 29.0, 24.2 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{38}\text{H}_{35}\text{ClN}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 705.1773, found: 705.1762.

$[\alpha]_{\text{D}}^{25} +1850$ (c 0.02, MeOH).

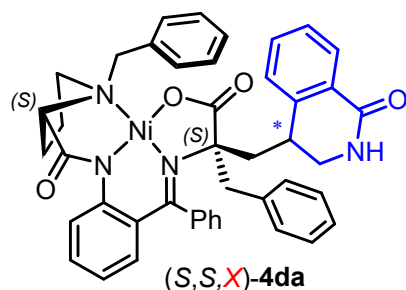
Ni(II) complex (S,S,S)-3cc



The desired product (*S,S,S*)-3cc (the second eluting diastereomer) was not isolated in pure form. We provided the NMR spectra of the mixture of diastereomers (see Figure S36, below).

Ni(II) complex (S,S,X)-4da

Starting from a chiral Ni(II) complex (*S,S*)-1d and *N*-(pivaloyloxymethyl)benzamide 2a, the desired product (*S,S,X*)-4da (the first eluting regioisomer) was isolated as an orange powder (24 mg, 32% yield); eluent: $\text{CH}_2\text{Cl}_2/\text{acetone}$ (3:1).



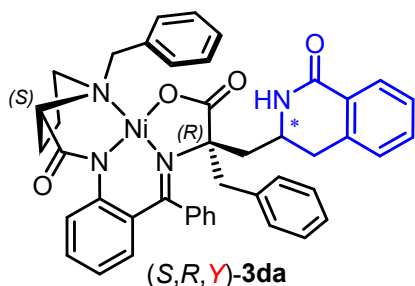
^1H NMR (400 MHz, CDCl_3): $\delta = 8.14\text{--}8.05$ (m, 3H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.60–7.54 (m, 2H), 7.54–7.43 (m, 7H), 7.42–7.23 (m, 6H), 7.18–7.07 (m, 2H), 6.67–6.55 (m, 2H), 5.66 (s, 1H, NH), 4.23 (d, $J = 12.4$ Hz, 1H), 3.93–3.77 (m, 1H), 3.45 (d, $J = 12.5$ Hz, 1H), 3.29–3.15 (m, 3H), 3.04–2.85 (m, 2H), 2.82 (d, $J = 13.9$ Hz, 1H), 2.30–2.07 (m, 3H), 1.96–1.87 (m, 1H), 1.80–1.69 (m, 2H), 1.58–1.45 (m, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3): $\delta = 180.4, 180.0, 173.4, 166.2, 142.5, 138.2, 136.56, 136.2, 133.9$ (2C), 132.8, 132.3, 131.5 (2C), 131.3 (2C), 130.4, 129.2 (3C, overlapped), 129.1 (2C), 129.0, 128.7, 128.5, 128.2, 128.0, 127.9 (2C), 127.88, 127.8, 127.5, 124.2, 121.0, 80.2, 70.7, 64.5, 58.1, 48.5, 44.8 (2C, overlapped), 34.4, 30.5, 22.8 ppm.

HRMS (ESI, m/z) calcd. for $\text{C}_{44}\text{H}_{40}\text{N}_4\text{NiO}_4^+$ $[\text{M}+\text{H}]^+$: 747.2476, found: 747.2462.

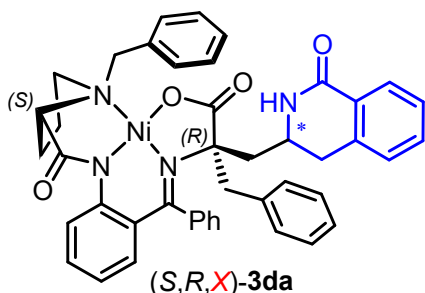
$[\alpha]_{\text{D}}^{25} +1770$ (c 0.11, MeOH).

Ni(II) complex (*S,R,Y*)-3da



Unfortunately, the desired product (*S,R,Y*)-3da (the first eluting diastereomer) was not isolated in pure form.

Ni(II) complex (*S,R,X*)-3da



Starting from a chiral Ni(II) complex (*S,S*)-1d and *N*-(pivaloyloxy)benzamide 2a, the desired product (*S,R,X*)-3da (the second eluting diastereomer) was isolated as an orange powder (36 mg, 48% yield); eluent: CH₂Cl₂/*i*PrOH (25:1).

¹H NMR (400 MHz, CDCl₃): δ = 8.06–7.97 (m, 3H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.59–7.40 (m, 9H), 7.29–7.24 (m, 2H), 7.20–7.08 (m, 4H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 8.3 Hz,

1H), 6.33 (s, 1H, NH), 4.53 (d, *J* = 9.1 Hz, 1H), 4.04 (d, *J* = 12.5 Hz, 1H), 3.54 (d, *J* = 12.5 Hz, 1H), 3.25–3.13 (m, 2H), 3.04–2.95 (m, 1H), 2.83 (d, *J* = 14.1 Hz, 1H), 2.28–2.12 (m, 2H), 2.03–1.90 (m, 2H), 1.86–1.74 (m, 2H), 1.71–1.48 (m, 3H) ppm.

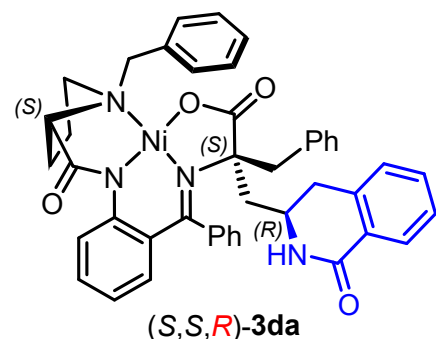
¹³C NMR (101 MHz, CDCl₃): δ = 180.5, 180.2, 172.6, 170.5, 147.6, 142.4, 136.6, 136.4, 134.0, 133.9, 132.2, 132.1, 131.4 (2C), 131.0 (2C), 130.3, 129.03 (2C), 129.0, 128.94, 128.9 (2C), 128.7, 128.4, 127.9 (2C, overlapped), 127.8, 127.7, 124.3, 123.9, 122.7, 120.8, 82.4, 70.9, 64.3, 57.4, 56.4, 44.2, 37.3, 30.6, 30.4, 22.7 ppm. The signal of one Ar carbon atom in ¹³C NMR overlapped.

HRMS (ESI, *m/z*) calcd. for C₄₄H₄₀N₄NiO₄⁺ [M+H]⁺: 747.2476, found: 747.2479.

[α]_D²⁵ +1650 (*c* 0.02, MeOH).

Ni(II) complex (*S,S,R*)-3da

Starting from a chiral Ni(II) complex (*S,R*)-1d and *N*-(pivaloyloxy)benzamide 2a, the desired product (*S,S,R*)-3da (the first eluting diastereomer) was isolated as an orange powder (51 mg, 69% yield); eluent: CH₂Cl₂/*i*PrOH (50:1).



¹H NMR (400 MHz, CDCl₃): δ = 8.07 (d, *J* = 7.0 Hz, 1H), 7.76 (d, *J* = 6.2 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.53–7.49 (m, 5H), 7.43–7.33 (m, 4H), 7.26–7.21 (m, 6H), 7.06–7.04 (m, 2H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.61 (t, *J* = 6.8 Hz, 1H), 5.84 (s, 1H, NH), 4.40–4.28 (m, 1H), 4.24 (d, *J* = 12.5 Hz, 1H), 3.79–3.67 (m, 1H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.33–3.27 (m, 1H), 3.21 (d, *J* = 12.5 Hz, 1H), 3.17–2.90 (m, 4H), 2.36–2.11 (m, 3H), 2.11–2.02 (m, 1H), 2.01–1.92 (m, 1H), 1.56 (d, *J* = 14.2 Hz, 1H) ppm.

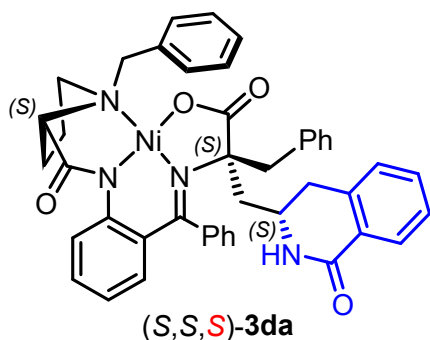
¹³C NMR (101 MHz, CDCl₃): δ = 181.0, 180.5, 173.8, 165.8, 141.7, 137.8, 136.9, 135.7, 133.4, 133.0, 132.6, 131.9, 131.8 (2C), 130.3, 130.1 (2C), 129.0, 128.9 (3C, overlapped), 128.7 (2C), 128.4 (2C, overlapped), 128.1, 127.9 (2C, overlapped), 127.8, 127.5, 127.3, 124.6, 121.0, 79.6, 69.2, 63.6, 58.3, 48.2, 47.0, 43.9, 35.1, 30.6, 24.2 ppm. The signal of one Ar carbon atom in ¹³C NMR overlapped.

HRMS (ESI, m/z) calcd. for $C_{44}H_{40}N_4NiO_4^+$ $[M+H]^+$: 747.2476, found: 747.2483.

$[\alpha]_D^{25} +1550$ (c 0.02, MeOH).

Ni(II) complex (*S,S,S*)-**3da**

Starting from a chiral Ni(II) complex (*S,R*)-**1d** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S,S*)-**3da** (the second eluting diastereomer) was isolated as an orange powder (17 mg, 22% yield); eluent: $CH_2Cl_2/iPrOH$ (25:1).



1H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 7.3 Hz, 2H), 7.59–7.54 (m, 2H), 7.52–7.45 (m, 3H), 7.44–7.35 (m, 5H), 7.32–7.19 (m, 6H), 7.07–7.01 (m, 1H), 6.87 (d, J = 7.6 Hz, 1H), 6.64–6.58 (m, 2H), 6.54 (s, 1H, NH), 4.88 (t, J = 10.3 Hz, 1H), 4.26 (d, J = 12.3 Hz, 1H), 3.82–3.71 (m, 1H), 3.34 (dd, J = 10.7, 5.4 Hz, 1H), 3.20–3.02 (m, 4H), 2.96 (dd, J = 15.3, 11.2 Hz, 1H), 2.83 (dd, J = 15.3, 3.7 Hz, 1H), 2.34–1.98 (m, 5H), 1.78 (d, J = 15.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.2, 181.1, 173.8, 165.6, 141.5, 137.9, 137.0, 135.6, 134.2, 132.9, 132.5, 131.8, 131.6 (2C), 130.1, 129.9 (2C), 129.4, 129.1 (2C), 129.0, 128.7 (2C), 128.5, 128.3 (2C, overlapped), 128.0, 127.9, 127.7, 127.4, 127.3, 124.5, 121.0, 79.4, 70.0, 64.4, 59.3, 49.1, 47.0, 42.5, 36.1, 30.8, 23.9 ppm. The signals of one Ar carbon atom in ^{13}C NMR overlapped.

HRMS (ESI, m/z) calcd. for $C_{44}H_{40}N_4NiO_4^+$ $[M+H]^+$: 747.2476, found: 747.2489.

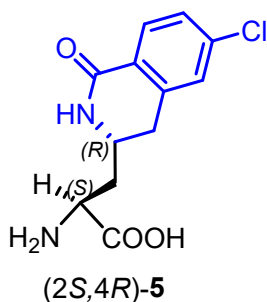
$[\alpha]_D^{25} +1600$ (c 0.02, MeOH).

General procedure for decomposition of the chiral Ni(II) complexes (*S,S,R*)-**3ac** and (*S,S,S*)-**3ac**

To a suspension of the Ni(II) complex **3ac** (0.5 mmol or 0.86 mmol) in methanol (5.0 mL) was added 6*N* HCl (3.5 mL) and water (5.0 mL) and the whole was heated at 60 °C. Upon disappearance of the red color of the starting complex, the reaction was stopped. Afterward, methanol was removed under reduced pressure, the remaining aqueous layer was quenched by 25% aqueous NH_3 solution until pH = 7. During the extraction with DCM, a three-phase system was formed (DCM/emulsion/ H_2O). The (*S*)-**BPB** was extracted with DCM. Two-phase system (emulsion/ H_2O) was passed through a paper filter to afford the desired amino acid as a white powder.

Amino Acid (*2S,4R*)-**5**

Starting from the chiral Ni(II) complex (*S,S,R*)-**3ac** (0.6 g, 0.86 mmol), the desired AA (*2S,4R*)-**5** was isolated as a white powder (147 mg, 64% yield).



1H NMR (400 MHz, D_2O+DCl): δ = 7.10 (d, J = 8.1 Hz, 1H), 6.84–6.77 (m, 2H), 3.64 (t, J = 6.9 Hz, 1H), 3.49–3.40 (m, 1H), 2.71 (dd, J = 16.4, 5.5 Hz, 1H), 2.31 (dd, J = 16.4, 5.5 Hz, 1H), 1.70 (dt, J = 14.8, 7.5 Hz, 1H), 1.46 (dt, J = 14.8, 7.5 Hz, 1H) ppm.

^{13}C NMR (101 MHz, D_2O+DCl): δ = 170.4, 166.3, 138.7, 138.4, 128.2, 127.7, 127.0, 124.5, 49.3, 46.3, 33.8, 31.1 ppm.

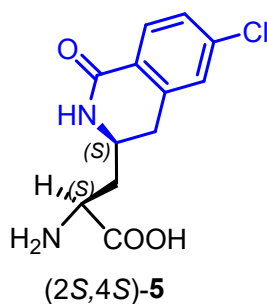
HRMS (ESI, m/z) calcd. for $C_{12}H_{14}ClN_2O_3^+$ $[M+H]^+$: 269.0687, found: 269.0695.

$[\alpha]_D^{25} -80$ (c 0.1, 1*N* HCl).

Enantiomeric purity was established by chiral HPLC analysis (Diasphere-110-Chirasil-E column: Nautilus-R, BioChemMack S&T, 5.0 mkm, 4.0x250 mm, methanol/0.1 M aq. solution of NaH₂PO₄*2H₂O = 20/80, flow rate = 0.8 mL/min, λ = 220 nm, 25 °C), t_R = 12.8 min (see Figure S35).

Amino Acid (2*S*,4*S*)-5

Starting from the chiral Ni(II) complex (*S,S,S*)-**3ac** (0.35 g, 0.5 mmol), the desired AA (2*S*,4*S*)-**5** was isolated as a white powder (74 mg, 55% yield).



¹H NMR (400 MHz, D₂O+DCI): δ = 7.16 (d, *J* = 8.2 Hz, 1H), 6.80–6.73 (m, 2H), 3.64 (t, *J* = 6.4 Hz, 1H), 3.54–3.45 (m, 1H), 2.68 (dd, *J* = 16.4, 5.7 Hz, 1H), 2.26 (dd, *J* = 16.4, 5.7 Hz, 1H), 1.57 (t, *J* = 6.9 Hz, 2H) ppm.

¹³C NMR (101 MHz, D₂O+DCI): δ = 170.8, 166.4, 139.0, 138.6, 128.5, 128.1, 127.3, 125.1, 49.5, 46.2, 33.8, 31.5 ppm.

HRMS (ESI, *m/z*) calcd. for C₁₂H₁₄ClN₂O₃⁺ [M+H]⁺: 269.0688, found: 269.0698.

[α]_D²⁵ +240 (c 0.05, 1*N* HCl).

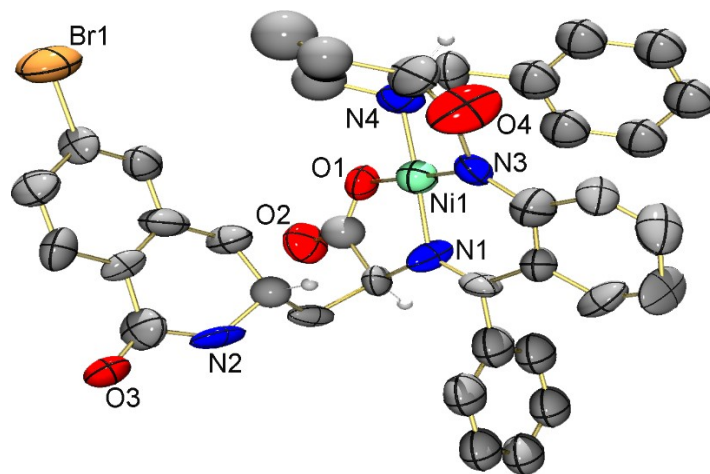
The structure of (2*S*,4*S*)-**5** was unambiguously established by single crystal X-ray analysis (see Figure 2 in the main text and X-Ray part *below*).

Enantiomeric purity was established by chiral HPLC analysis (Diasphere-110-Chirasil-E column: Nautilus-R, BioChemMack S&T, 5.0 mkm, 4.0x250 mm, methanol/0.1 M aq. solution of NaH₂PO₄*2H₂O = 20/80, flow rate = 0.8 mL/min, λ = 254 nm, 25 °C), t_R = 11.7 min (see Figure S35).

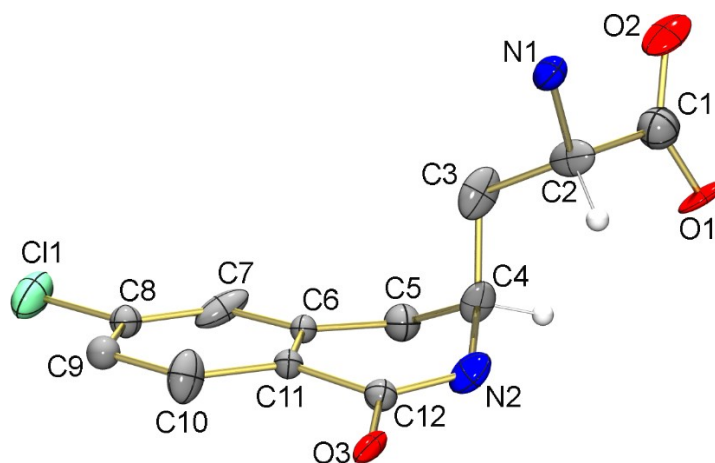
X-ray diffraction study of amino acid (2*S*,4*S*)-5

Single crystal X-ray studies of the Ni(II) complex (*S,S,R*)-**3ad** and amino acid **5** were carried out in Center for molecule composition studies of INEOS RAS. Single crystals of C₃₇H₃₃BrN₄NiO₄ (*S,S,R*)-**3ad** were obtained by crystallization from dichloromethane. Single crystals of C₁₂H₁₃ClN₂O₃ (*S,S*)-**5** were obtained by crystallization from water. A suitable crystals were selected and X-ray diffraction experiments were carried out with Bruker SMART APEX II diffractometer (graphite monochromated MoKα radiation, λ = 0.71073 Å, ω-scan technique). For (*S,S,R*)-**3ad** the crystal was kept at 296.15 K during data collection. The APEX II software^[S9] 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^[S10] and OLEX2^[S11] program packages. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F₂ with the anisotropic thermal parameters for all non-hydrogen atoms. Positions of hydrogen atoms were calculated and all were included in the refinement by the riding model with U_{iso}(H) = 1.5U_{eq}(X) for methyl groups and U_{iso}(H) = 1.2U_{eq}(X) for other atoms. Experimental details and crystal parameters are listed in Tables S1.

CCDC **2303138** contains the supplementary crystallographic data for the complex (*S,S,R*)-**3ad**. CCDC **2278822** contains the supplementary crystallographic data for the amino acid (2*S*,4*S*)-**5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures>.



X-ray structure for (*S,S,R*)-**3ad**



X-ray structure for (*2S,4S*)-**5**

Table S1. Crystallographic data for the complex (<i>S,S,R</i>)- 3ad and amino acid (<i>2S,4S</i>)- 5		
datablock	(<i>S,S,R</i>)- 3ad	(<i>2S,4S</i>)- 5
Empirical formula	C ₃₇ H ₃₃ BrN ₄ NiO ₄	C ₁₂ H ₁₃ ClN ₂ O ₃
Formula weight	736.29	268.69
Temperature/K	296.15	120
Crystal system	monoclinic	monoclinic
Space group	P2 ₁	P2 ₁
a/Å	11.8370(18)	21.160(8)
b/Å	22.263(4)	5.022(2)
c/Å	14.667(2)	21.185(8)
α/°	90	90
β/°	91.310(4)	119.93(2)
γ/°	90	90
Volume/Å ³	3864.2(11)	1951.0(14)
Z	4	6
ρ _{calc} /cm ³	1.266	1.372
μ/mm ⁻¹	1.576	0.295
F(000)	1512.0	840.0
Crystal size/mm ³	0.18×0.09×0.05	0.28×0.22×0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.442 to 56.8	3.846 to 52

Index ranges	-14 ≤ h ≤ 15, -29 ≤ k ≤ 29, -19 ≤ l ≤ 16	-26 ≤ h ≤ 24, -6 ≤ k ≤ 6, -22 ≤ l ≤ 26
Reflections collected	29687	14255
Independent reflections	18182 [R _{int} = 0.1156, R _{sigma} = 0.3441]	7223 [R _{int} = 0.1521, R _{sigma} = 0.3531]
Data/restraints/parameters	18182/93/646	7223/175/490
Goodness-of-fit on F ²	0.854	1.039
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0703, wR ₂ = 0.1422	R ₁ = 0.1480, wR ₂ = 0.2933
Final R indexes [all data]	R ₁ = 0.2411, wR ₂ = 0.1916	R ₁ = 0.2453, wR ₂ = 0.3466
Largest diff. peak/hole / e Å ⁻³	0.35/-0.33	0.74/-0.66
Flack parameter	0.125(16)	0.31(17)

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Determination of structure and configuration of the complexes 3ad and 3ba by 2D NMR analysis

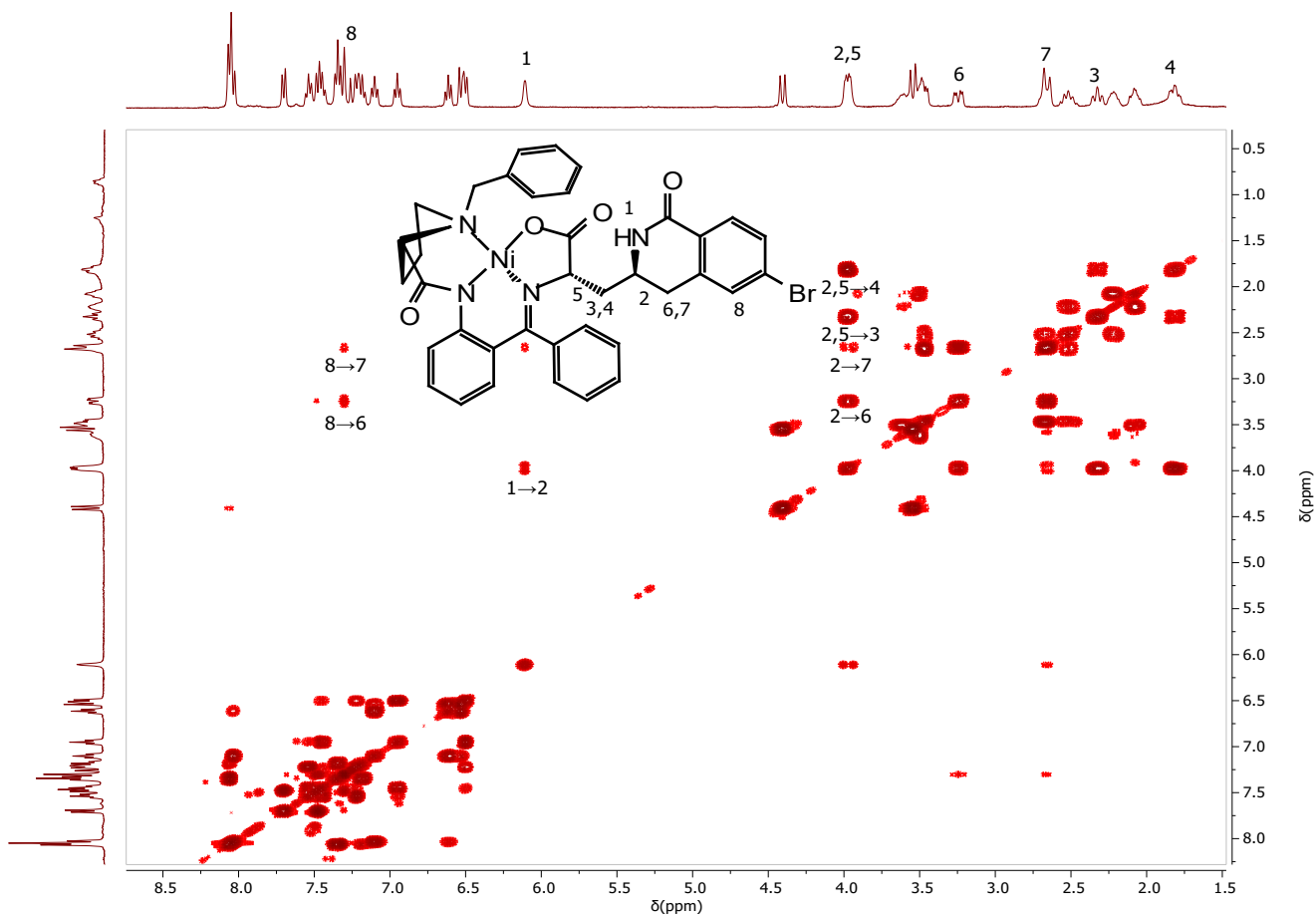
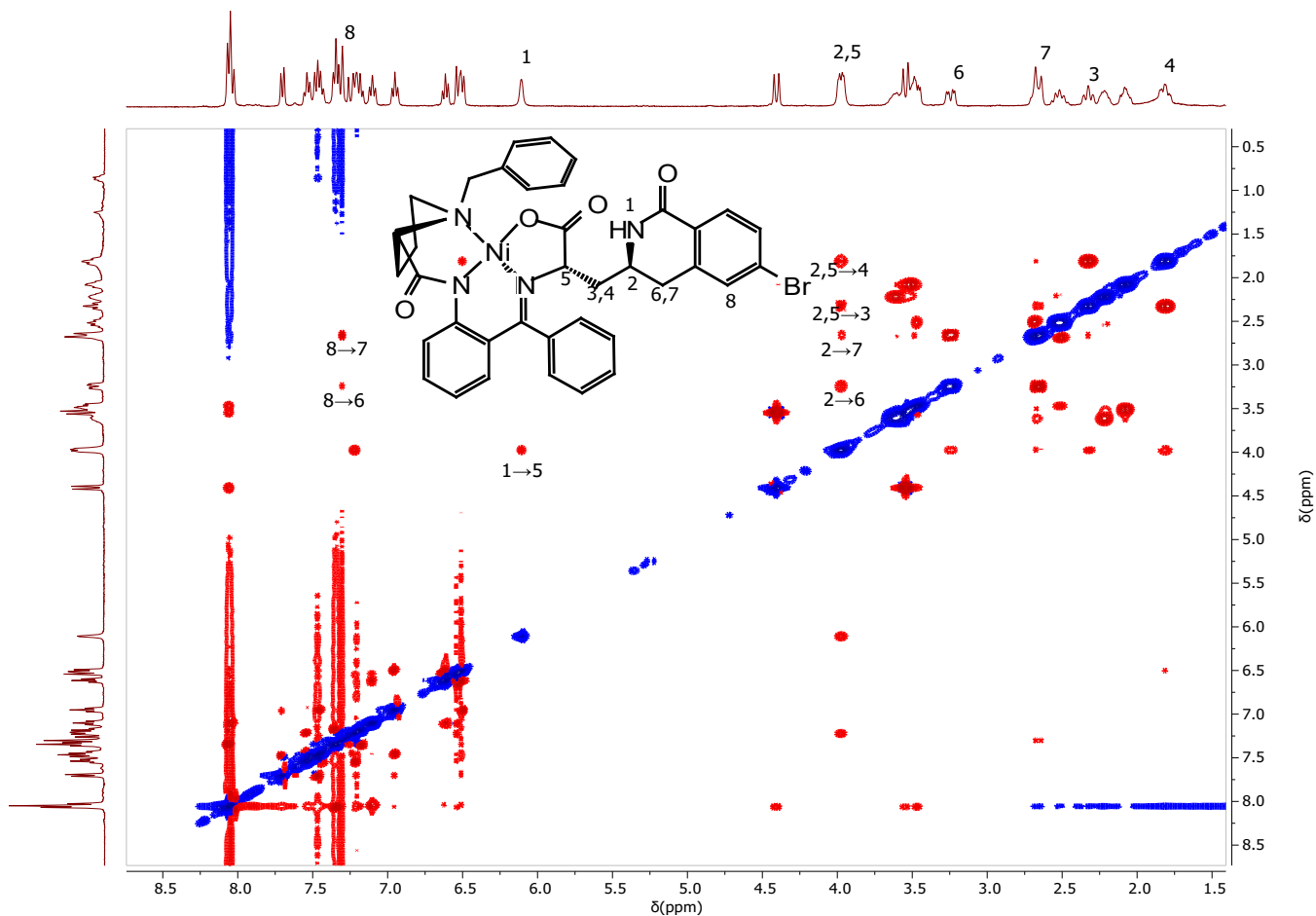


Figure S1. $^1\text{H}^1\text{H}$ -NOESY and $^1\text{H}^1\text{H}$ -COSY NMR spectra of the Ni(II) complex (*S,S,S*)-**3ad** (in CDCl_3)

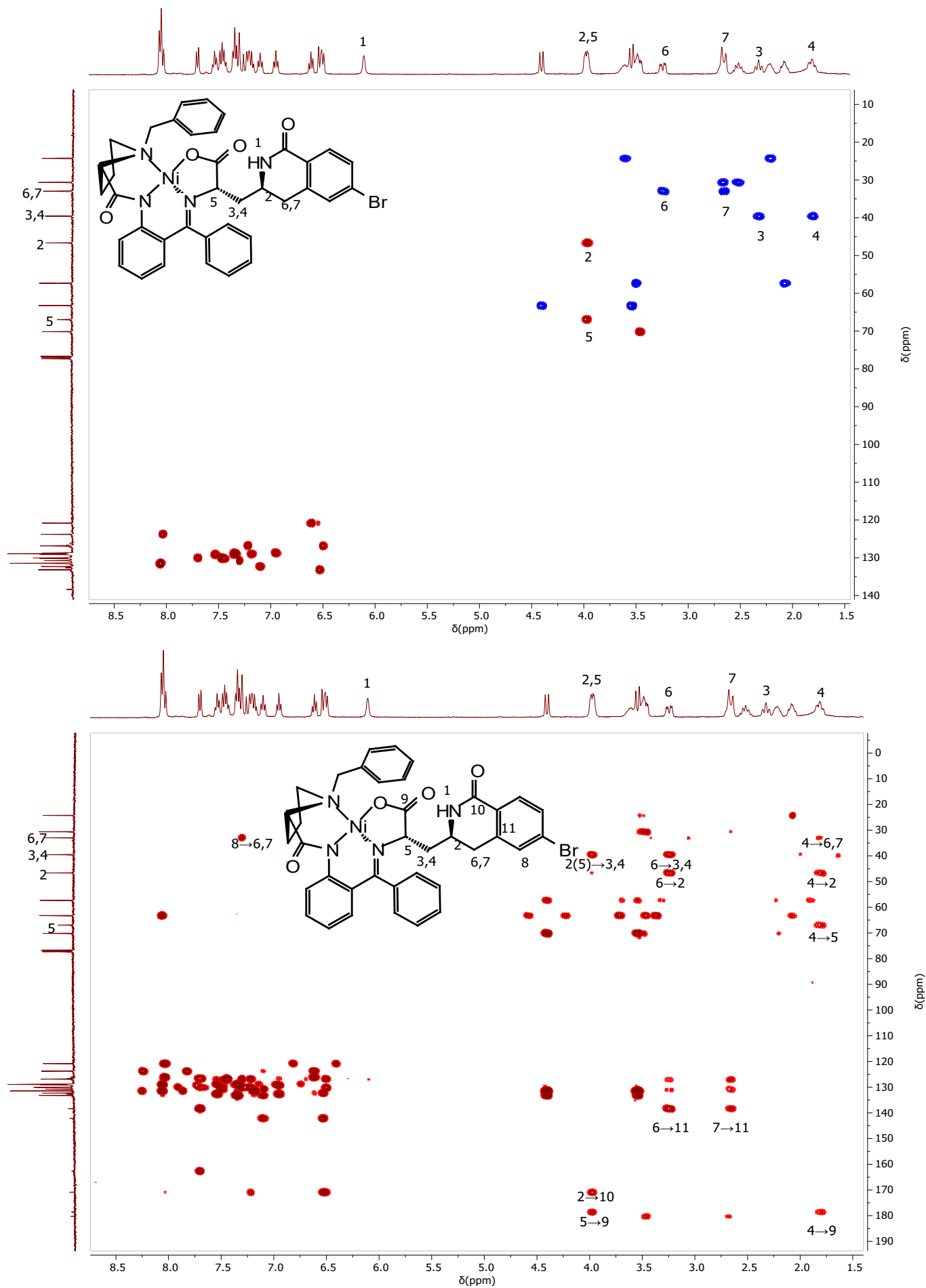
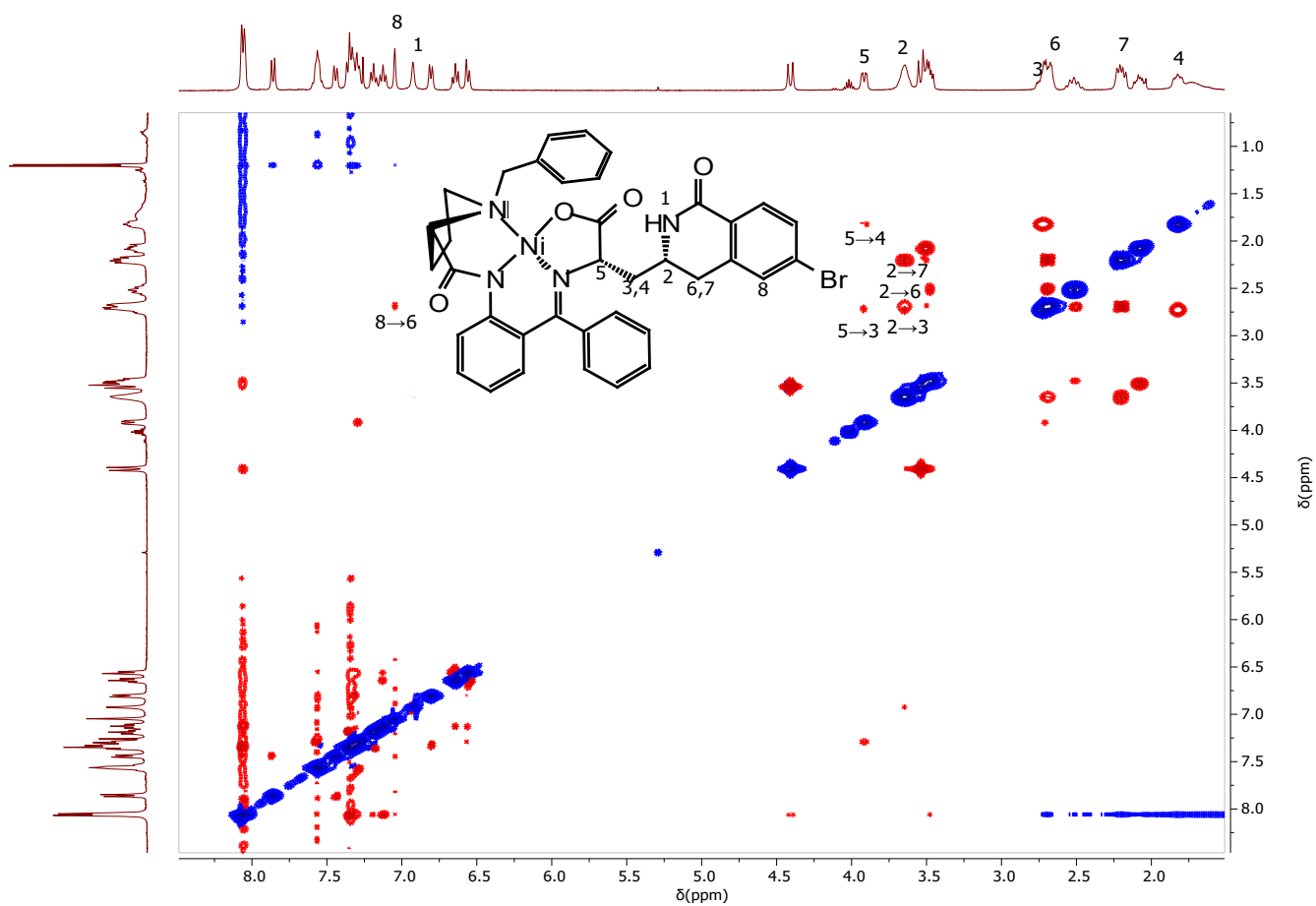


Figure S2. $^1\text{H}^{13}\text{C}$ -HSQC and $^1\text{H}^{13}\text{C}$ -HMBC NMR spectra of the Ni(II) complex (*S,S,S*)-**3ad** (in CDCl_3)



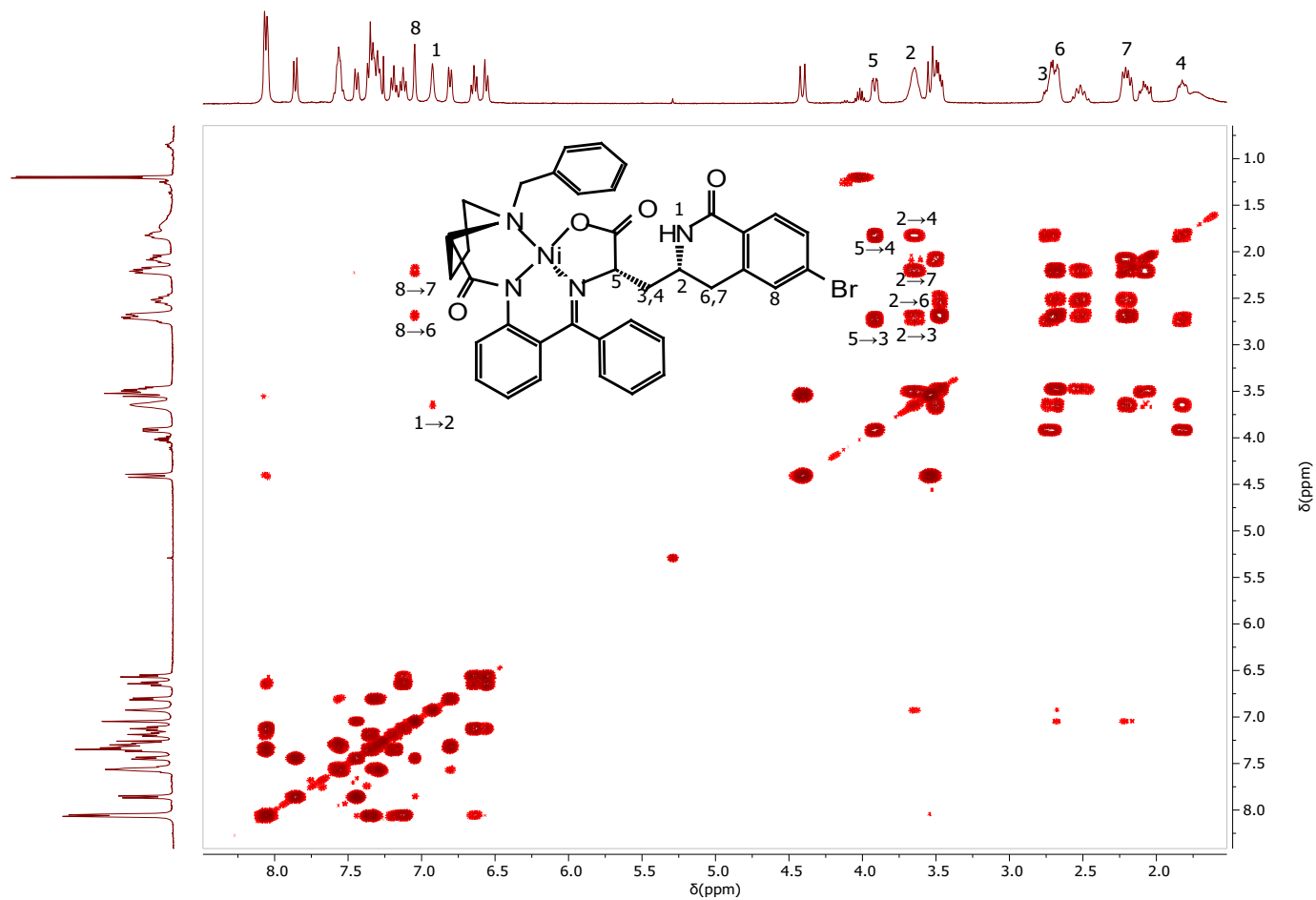


Figure S3. ^1H -NOESY and ^1H -COSY NMR spectra of the Ni(II) complex (S,S,R) -**3ad** (in CDCl_3)

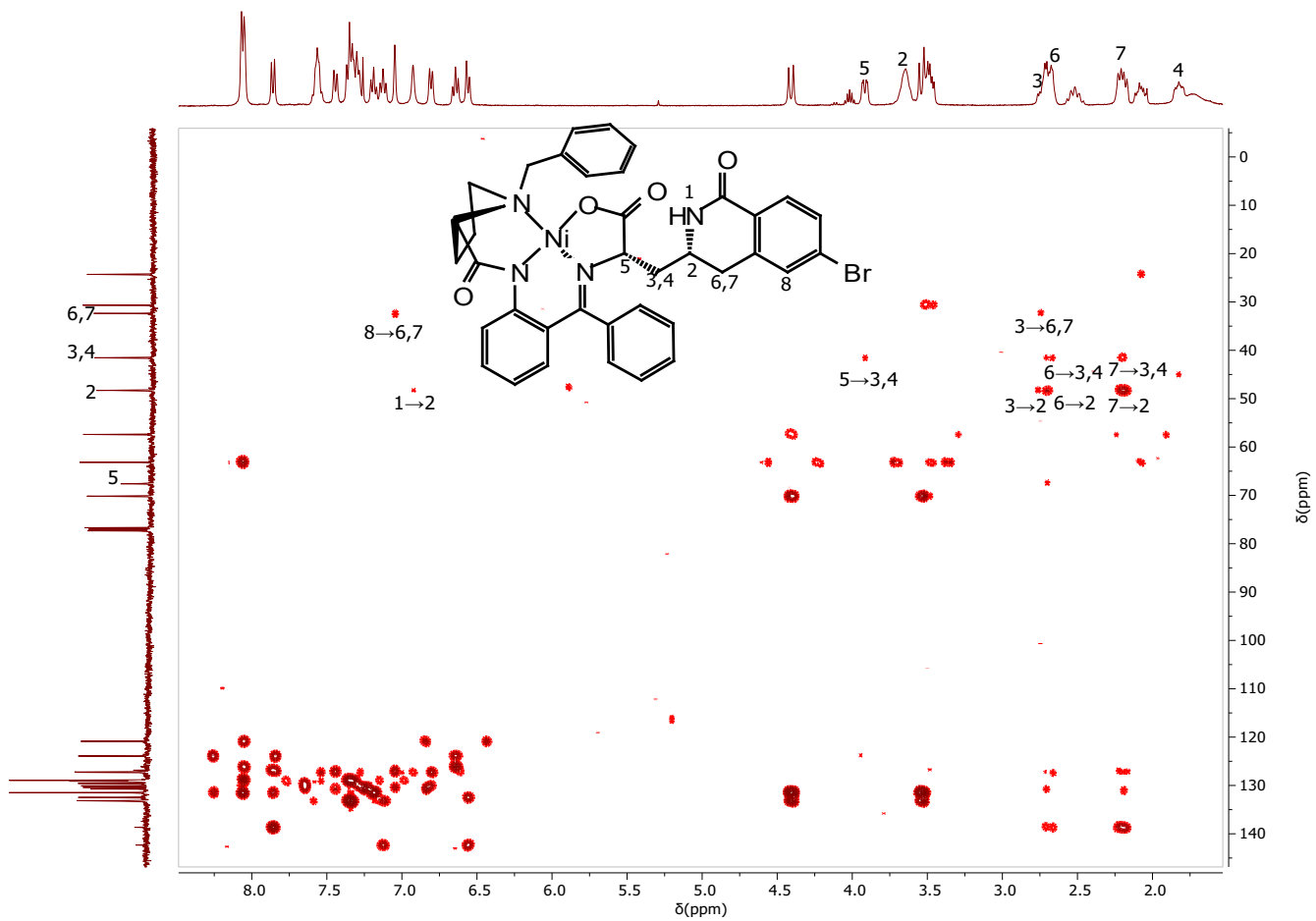
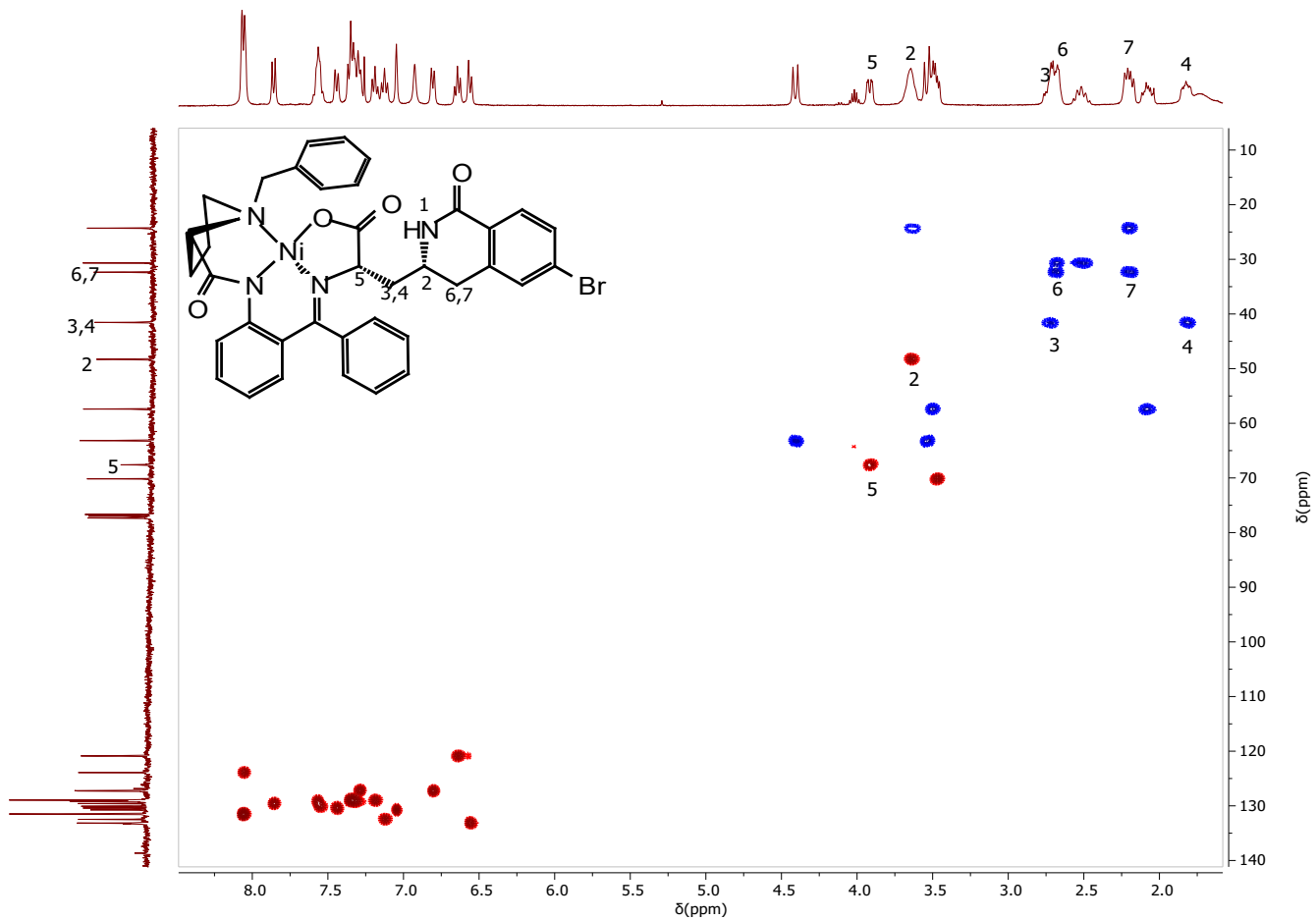
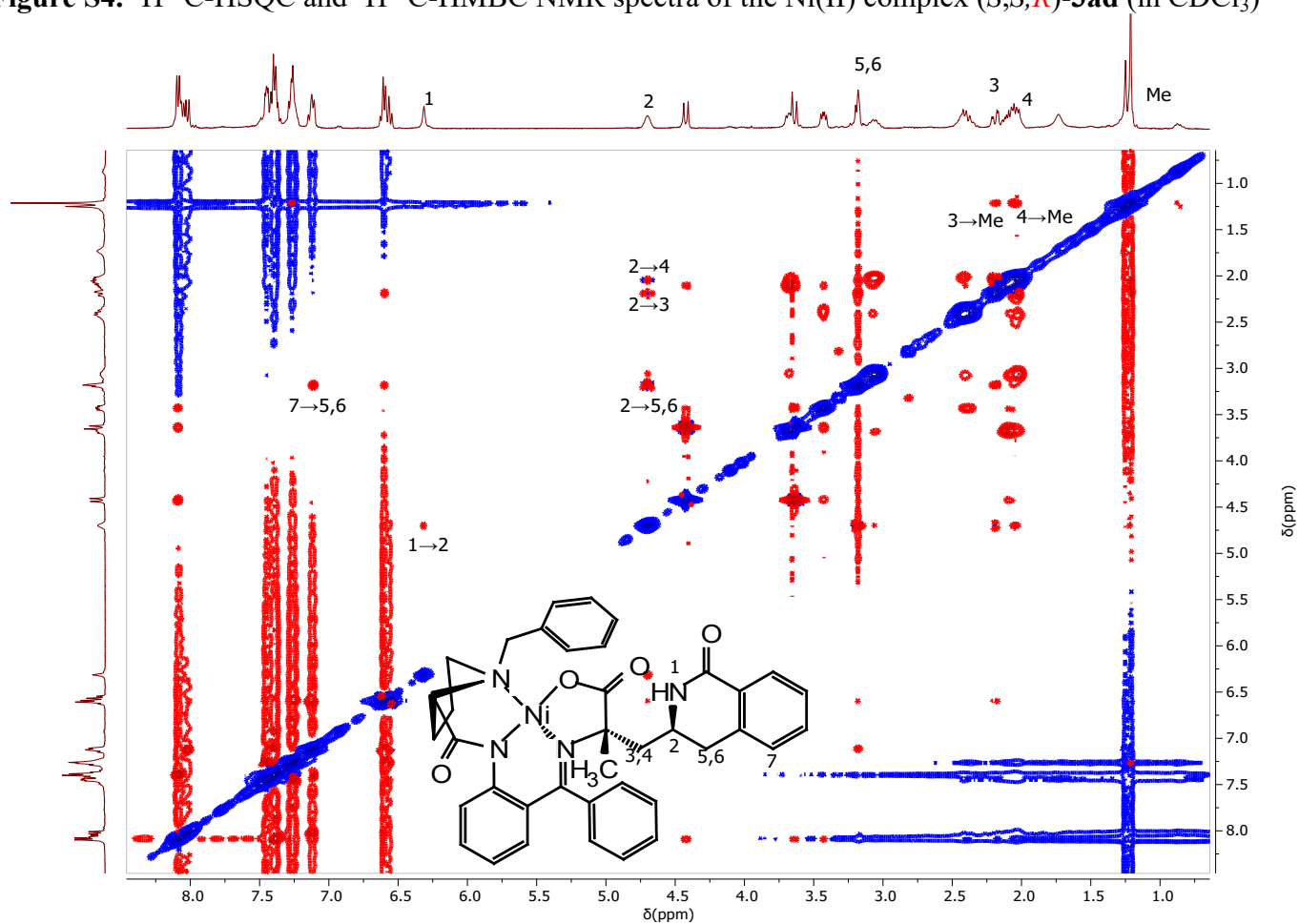


Figure S4. $^1\text{H}^{13}\text{C}$ -HSQC and $^1\text{H}^{13}\text{C}$ -HMBC NMR spectra of the Ni(II) complex (*S,S,R*)-**3ad** (in CDCl_3)



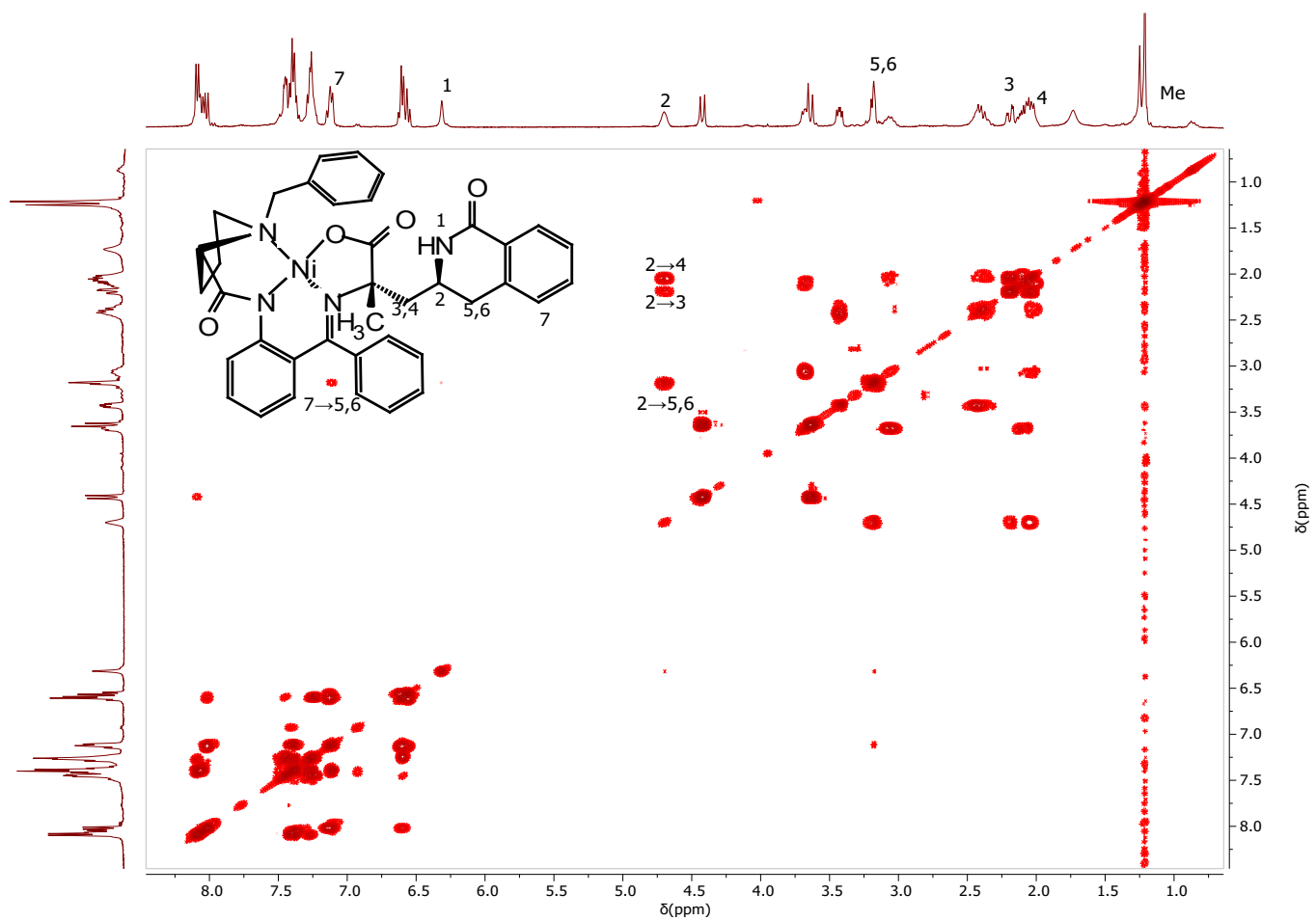


Figure S5. ^1H - ^1H -NOESY and ^1H - ^1H -COSY NMR spectra of the Ni(II) complex (S,S,S) -**3ba** (in CDCl_3)

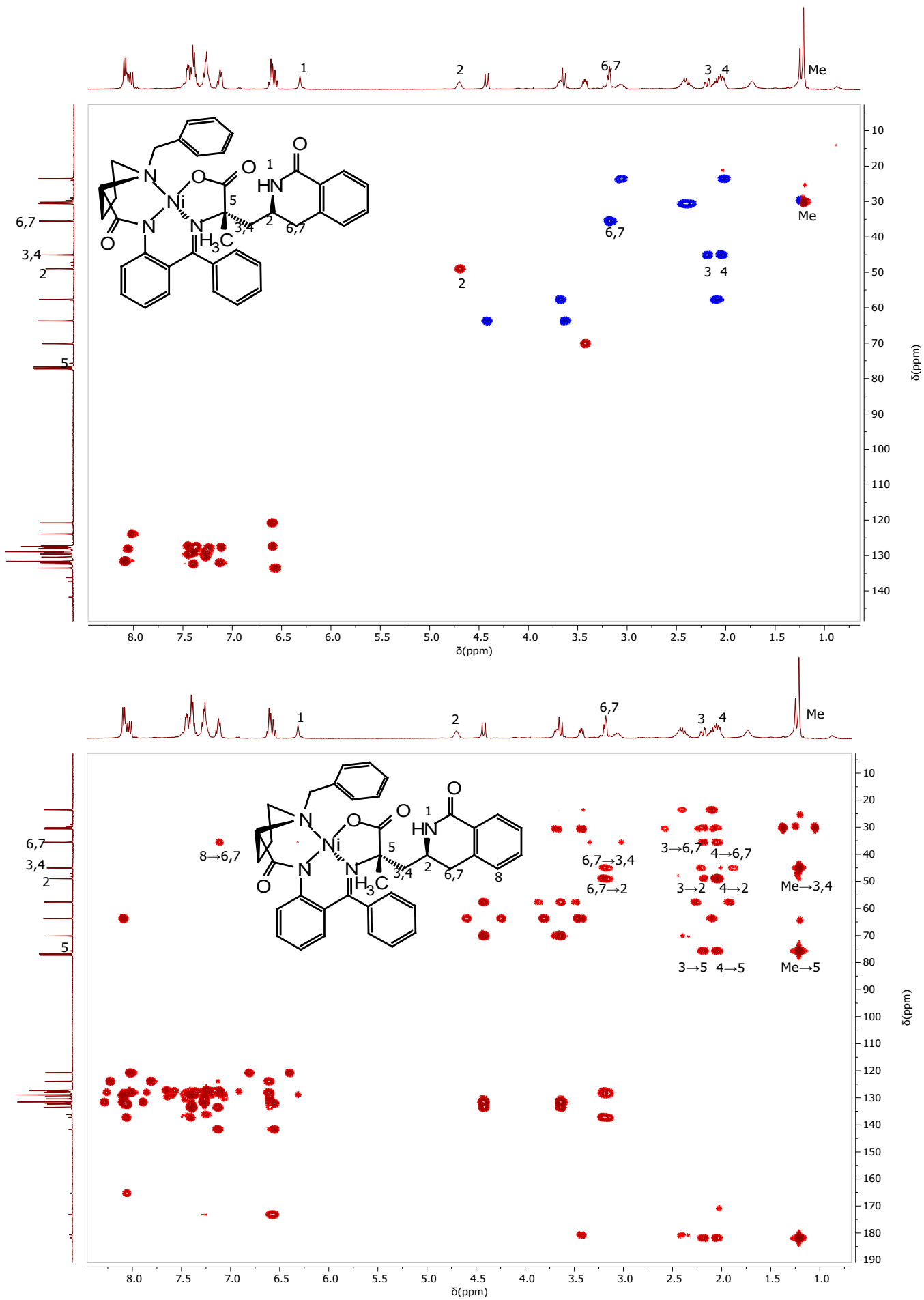
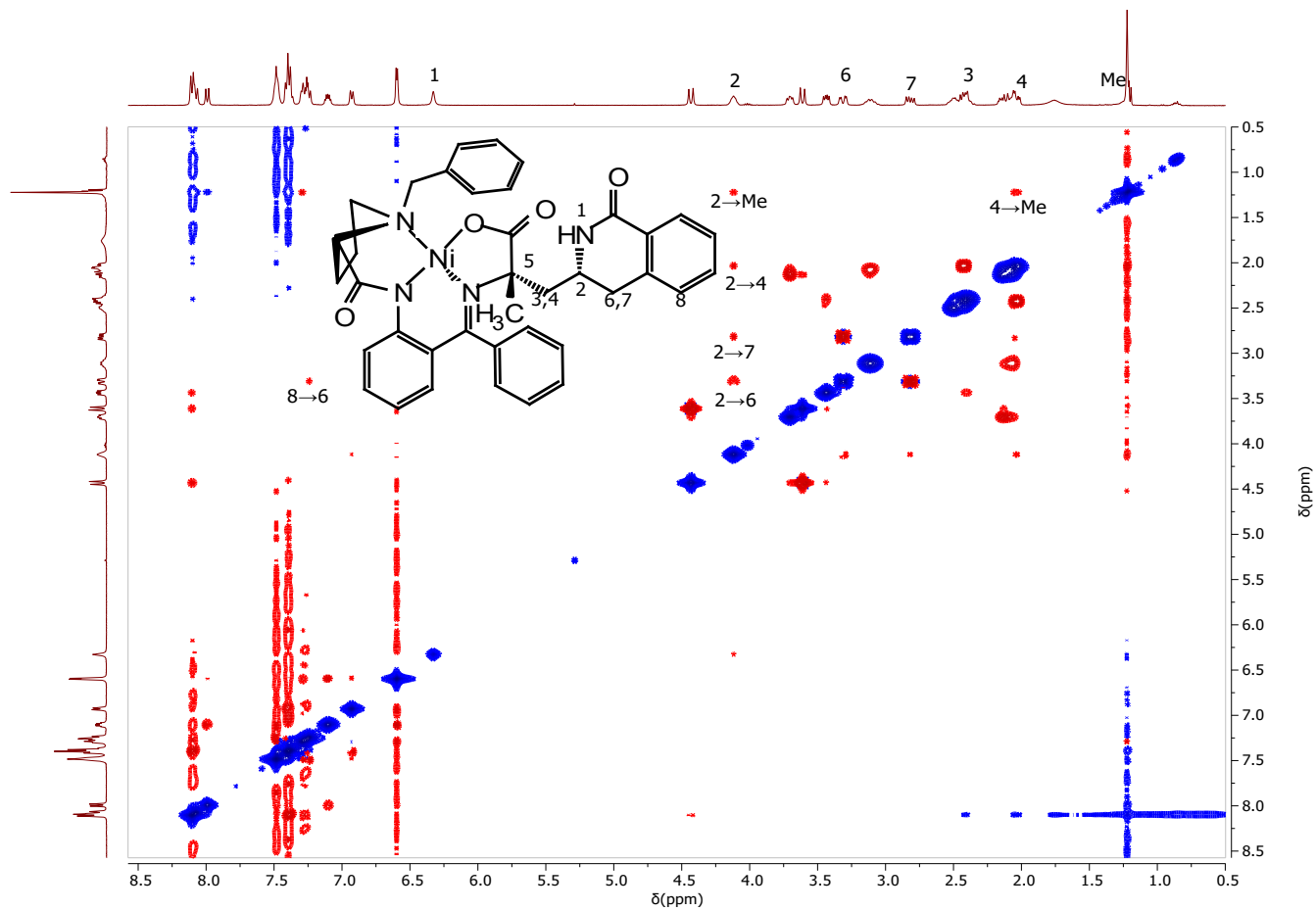


Figure S6. $^1\text{H}^{13}\text{C}$ -HSQC and $^1\text{H}^{13}\text{C}$ -HMBC NMR spectra of the Ni(II) complex (*S,S,S*)-**3ba** (in CDCl_3)



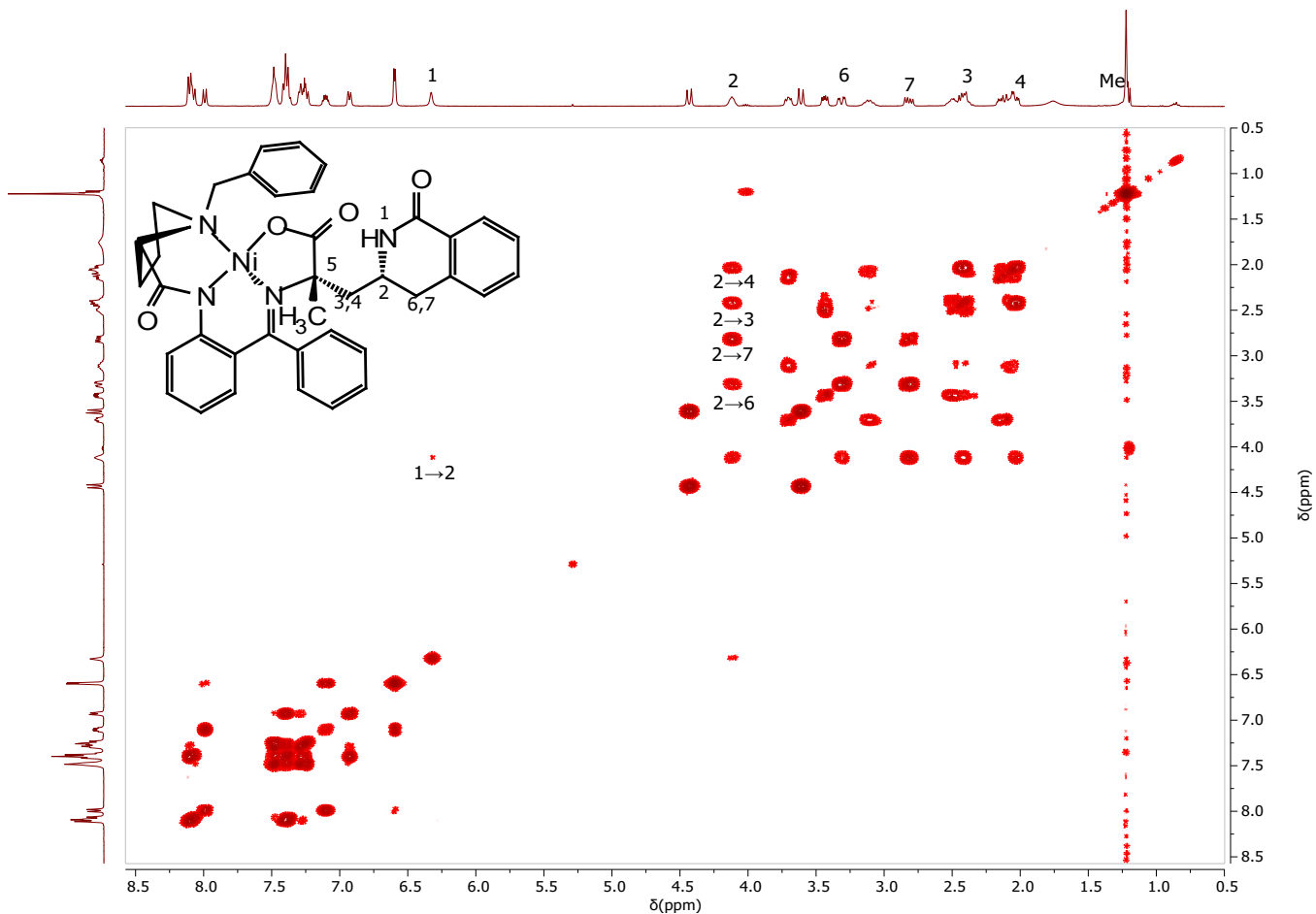
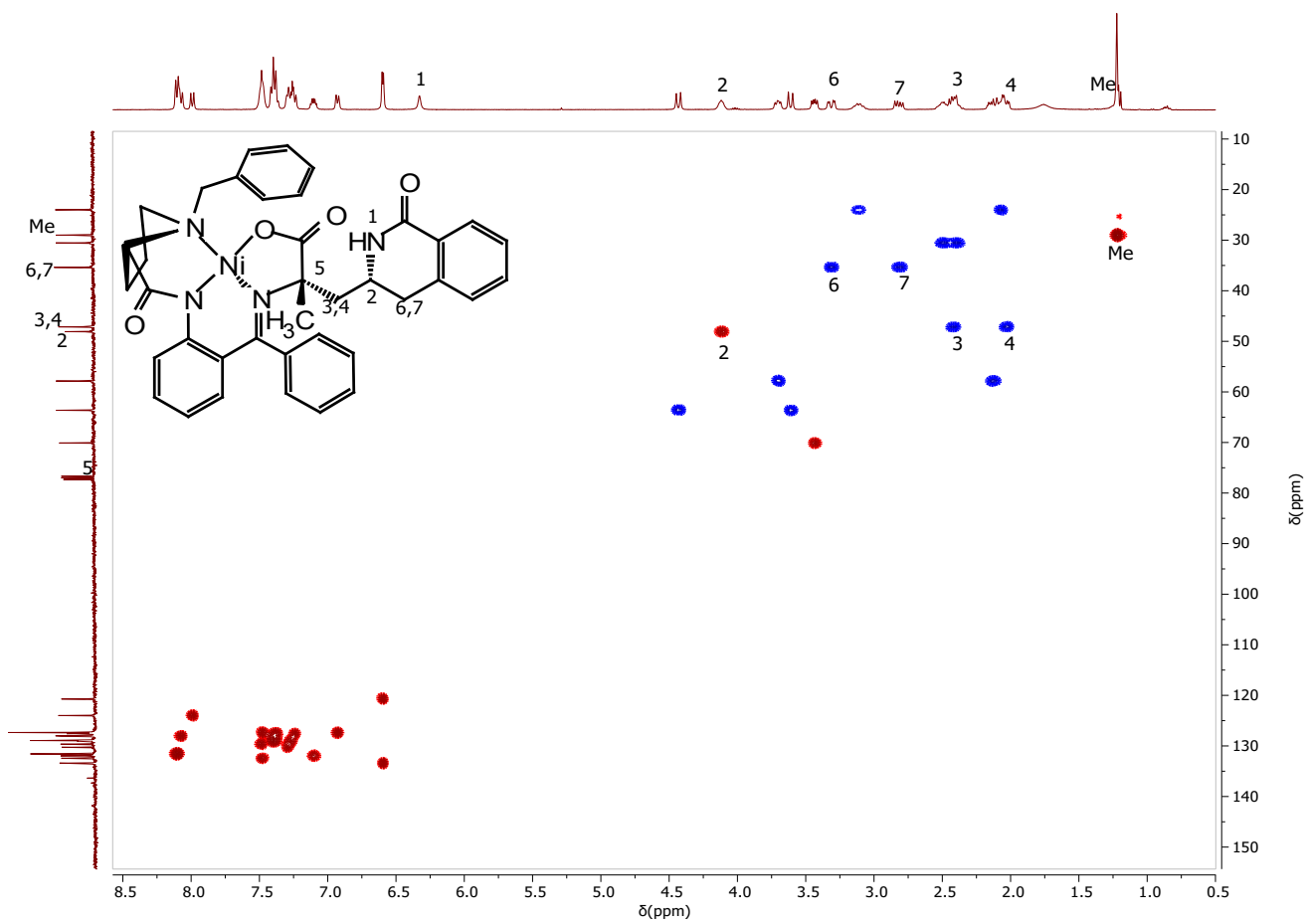


Figure S7. ^1H -NOESY and ^1H -COSY NMR spectra of the Ni(II) complex (*S,S,R*)-**3ba** (in CDCl_3)



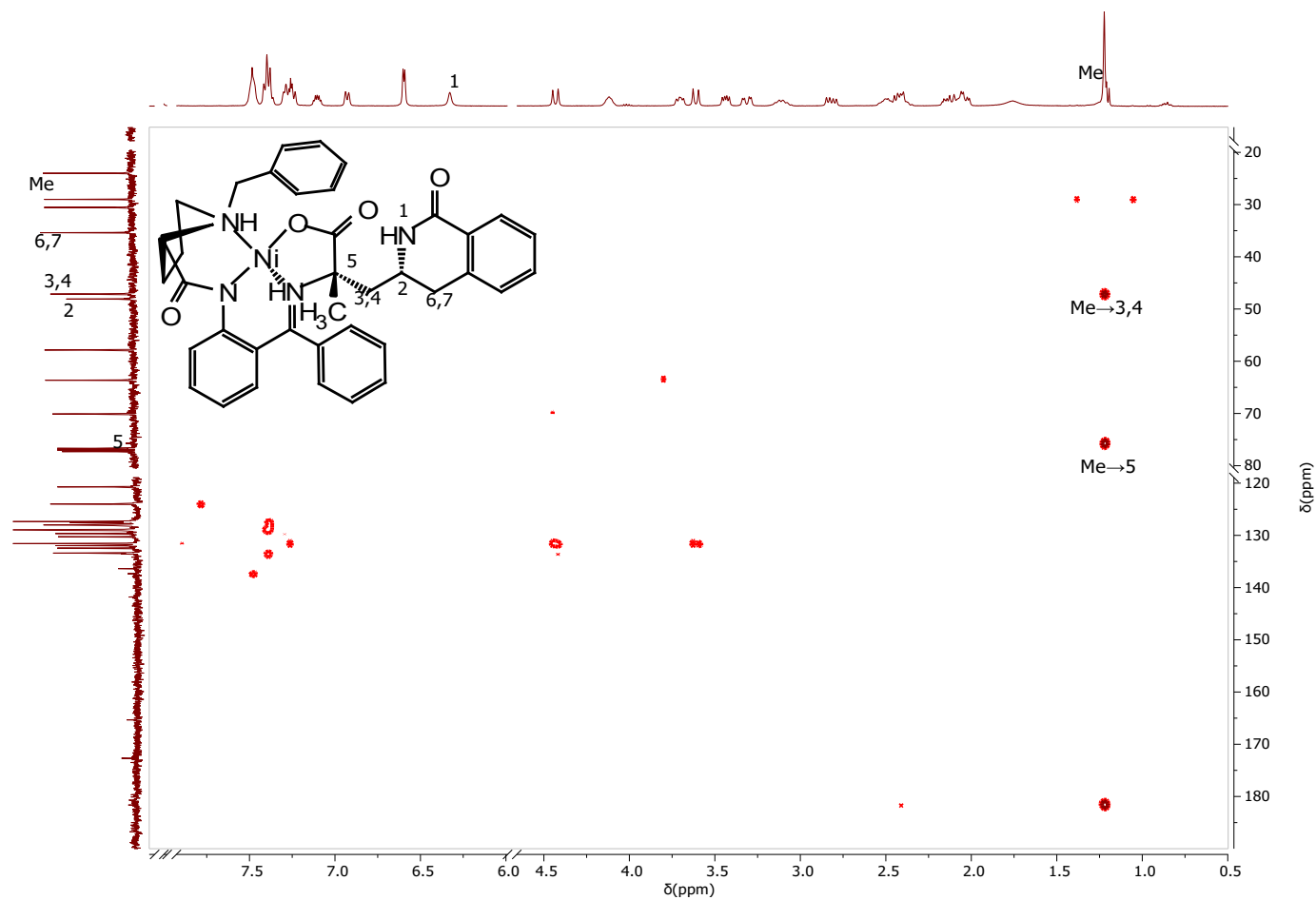


Figure S8. $^1\text{H}^{13}\text{C}$ -HSQC and $^1\text{H}^{13}\text{C}$ -HMBC NMR spectra of the Ni(II) complex (*S,S,R*)-**3ba** (in CDCl_3)

NMR spectra

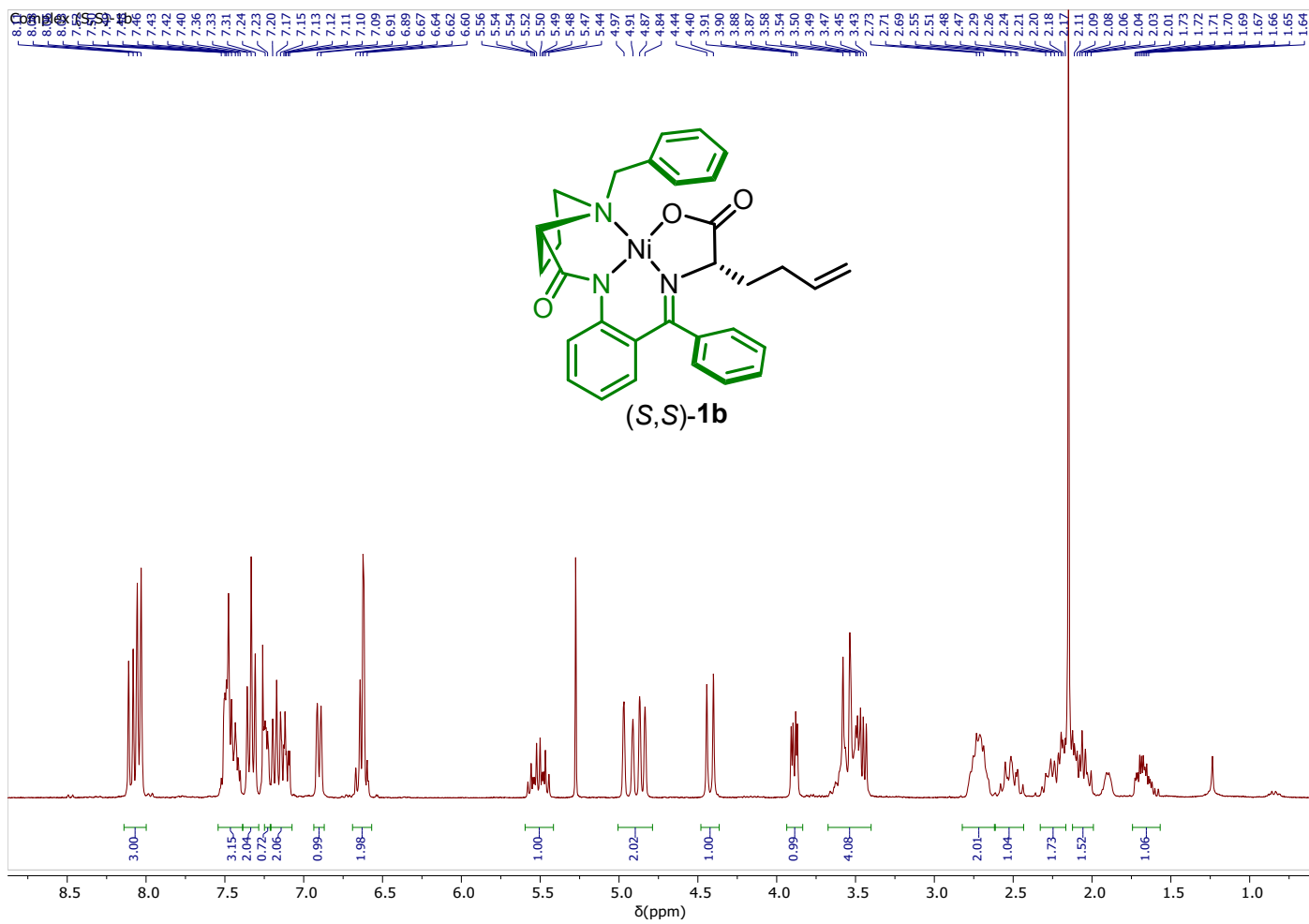
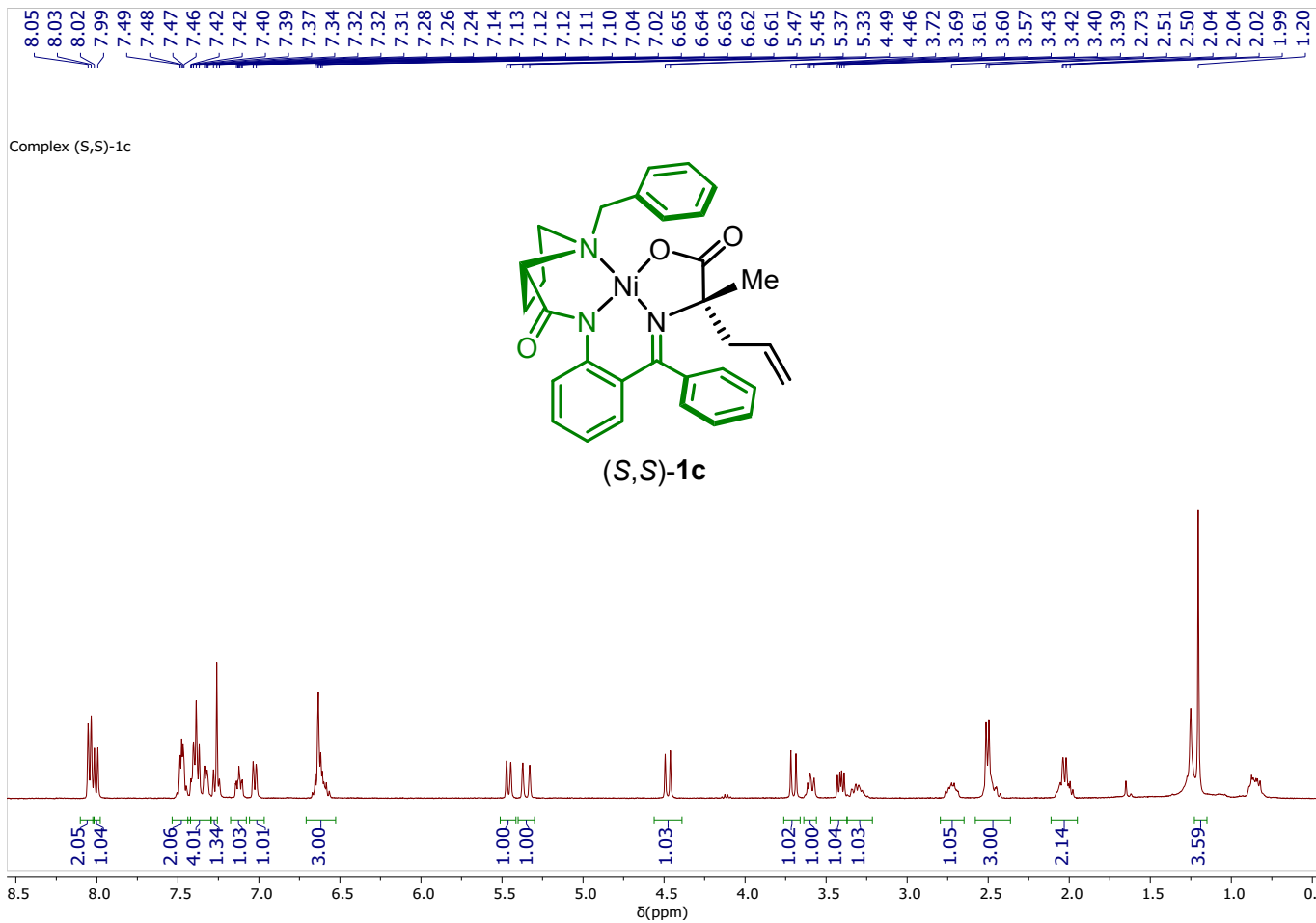


Figure S9. ¹H (300 MHz) NMR spectrum of the Ni(II) complex (S,S)-1b (in CDCl₃)



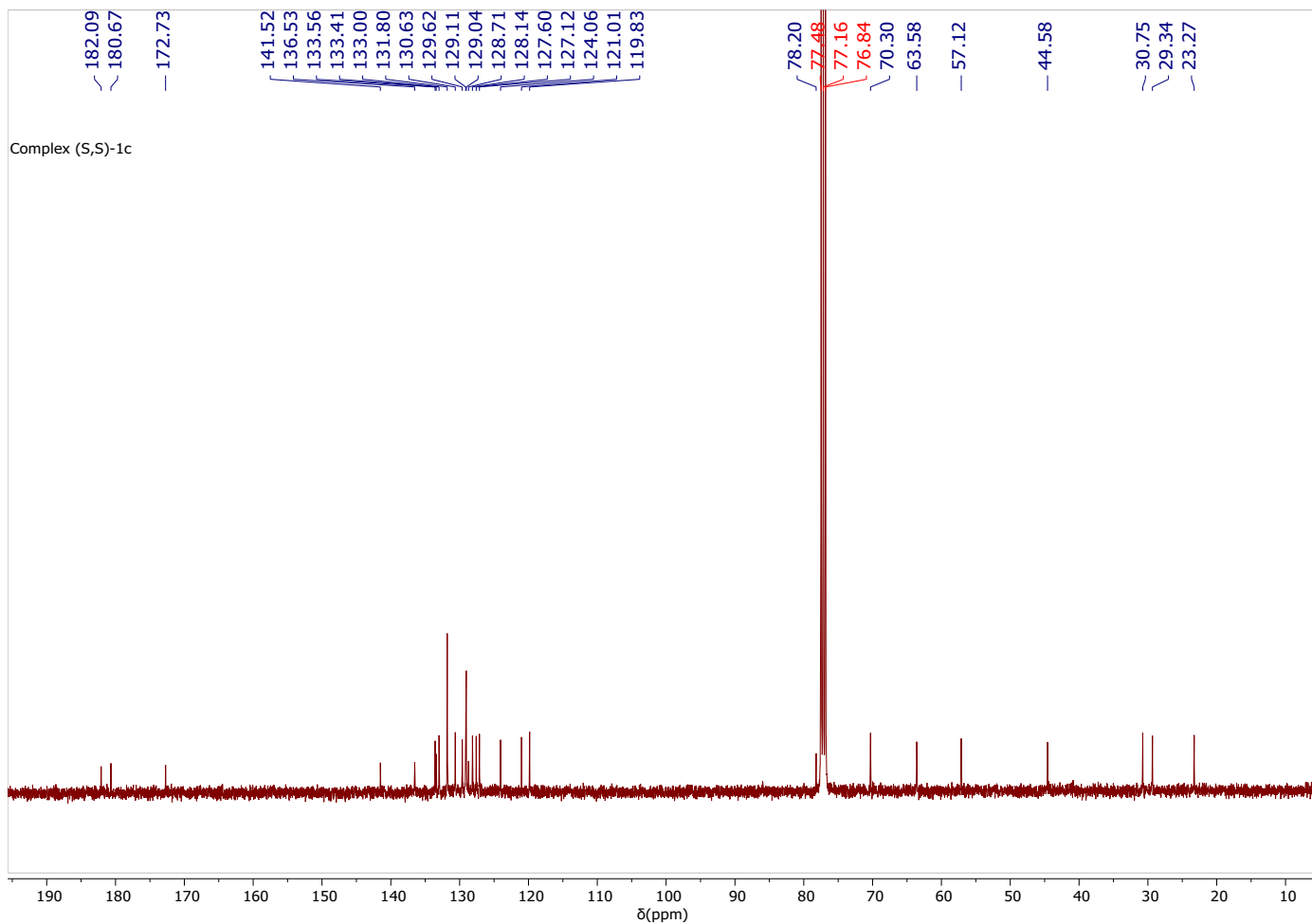
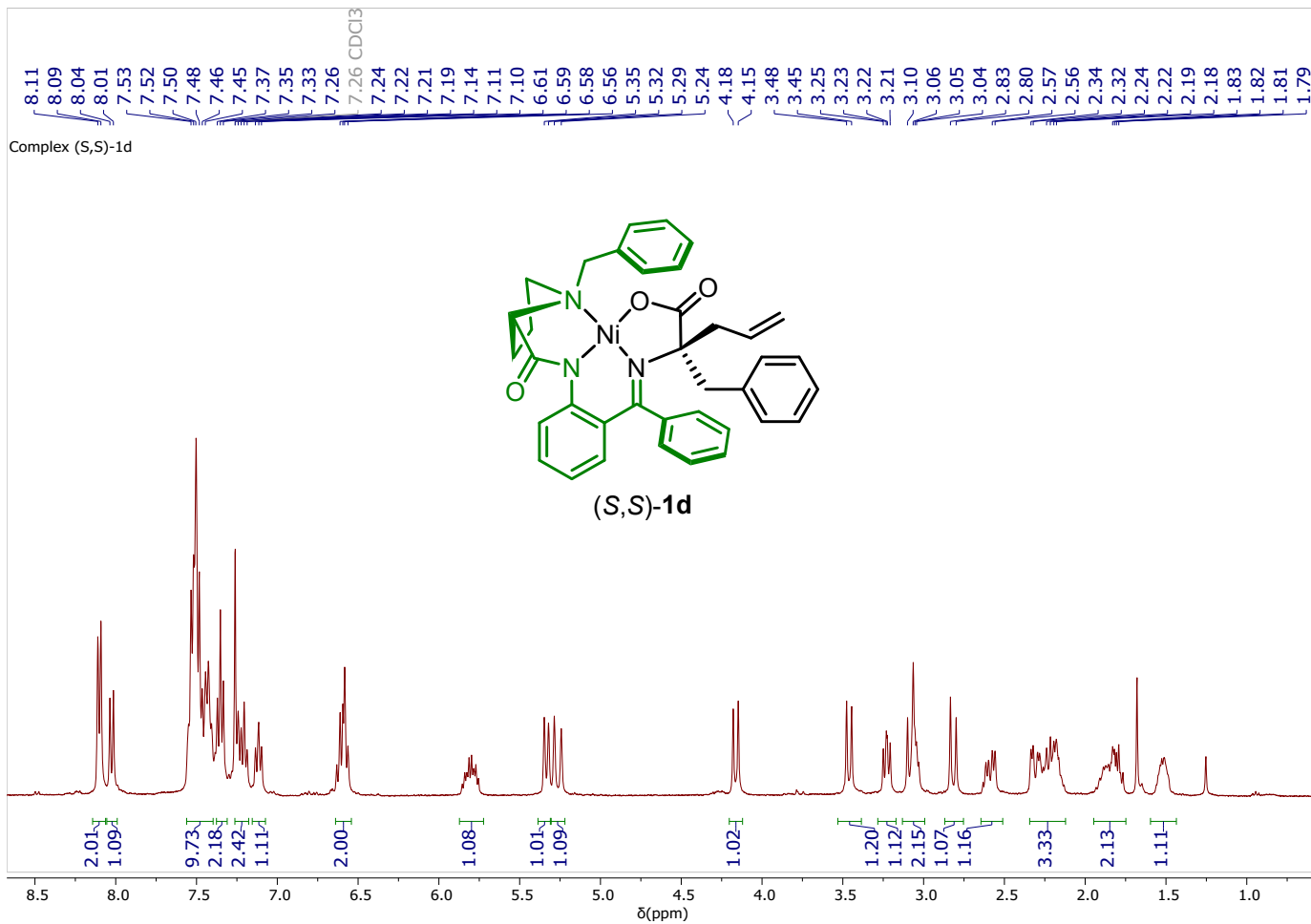


Figure S10. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (S,S)-1c (in CDCl_3)



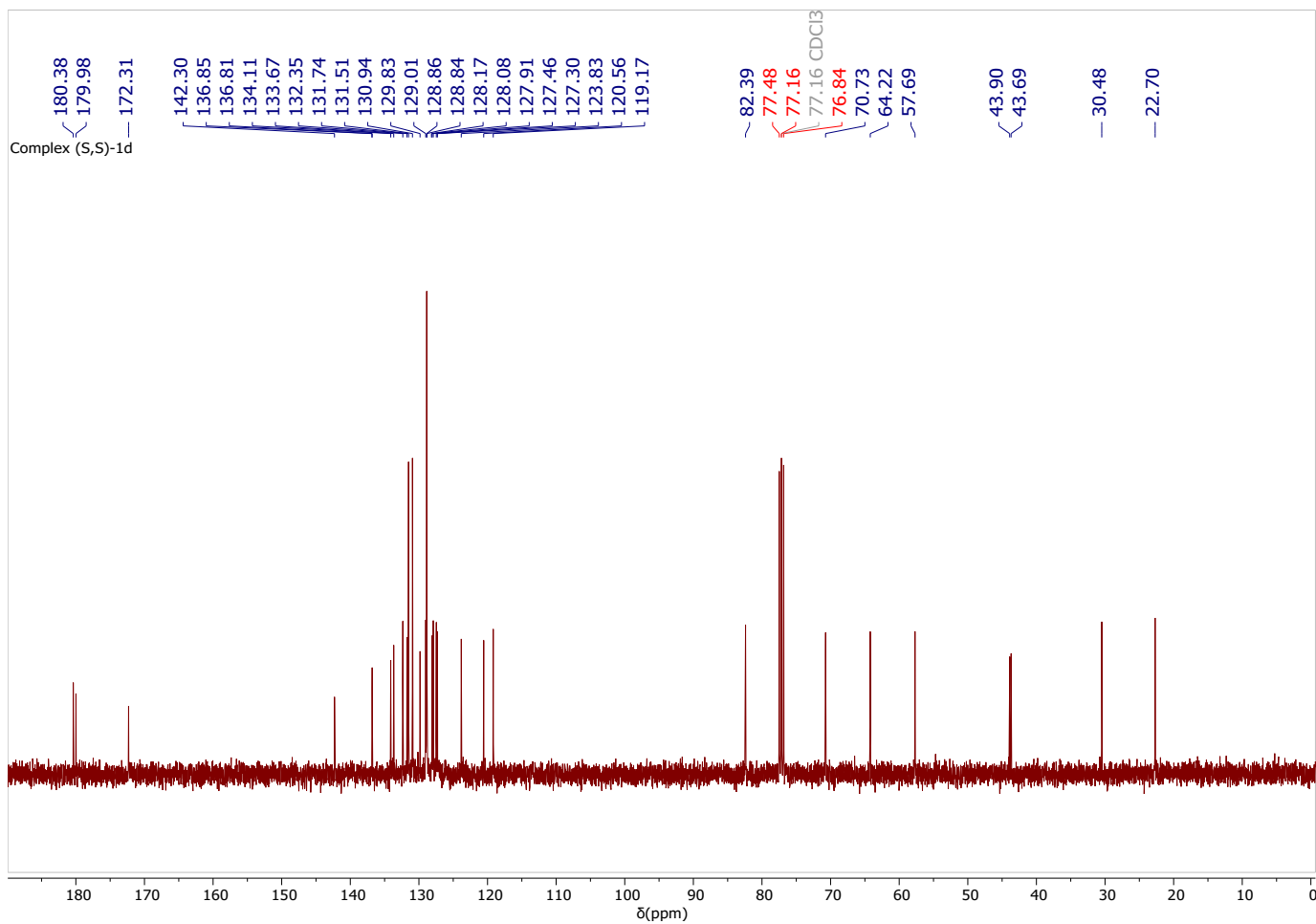
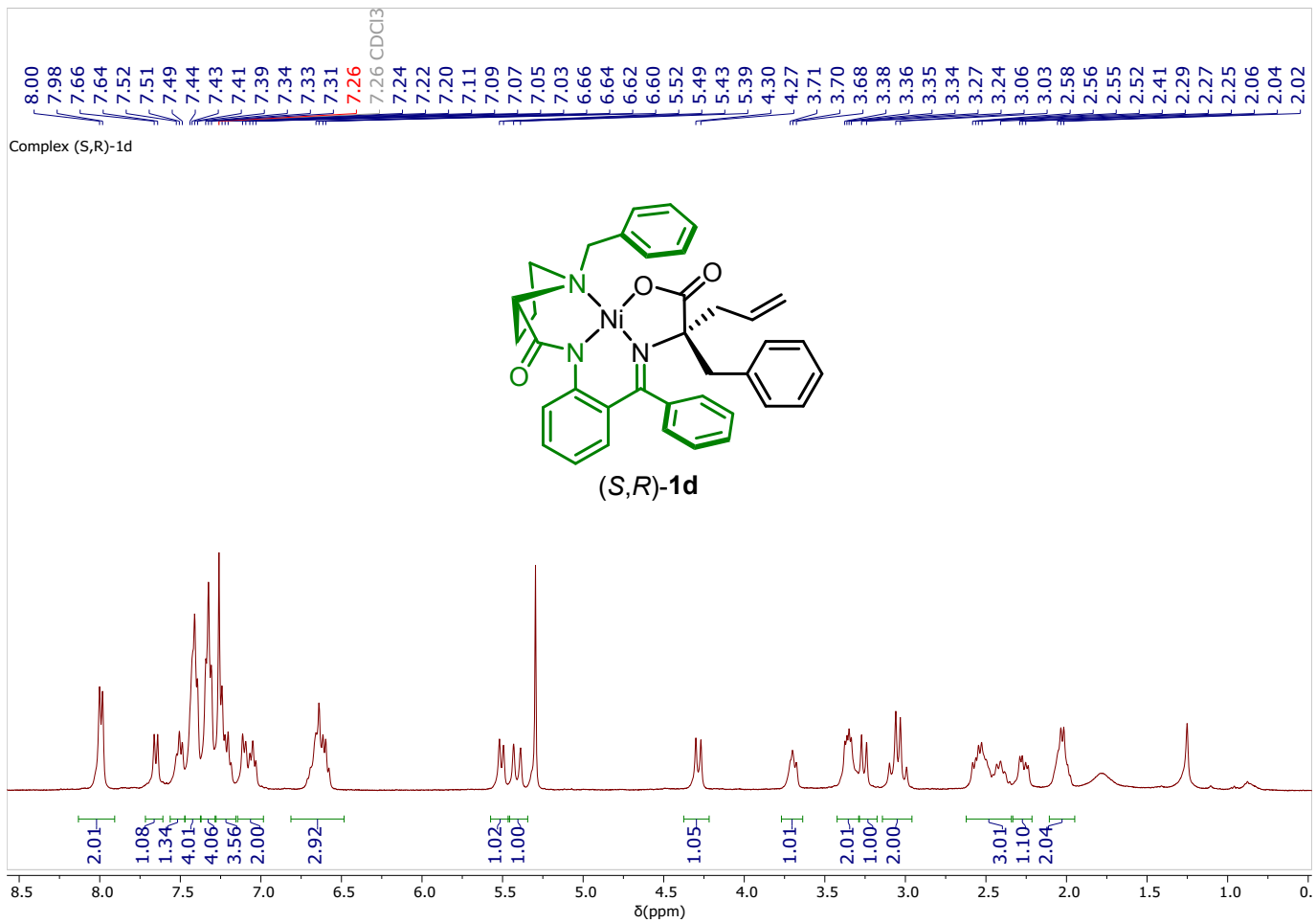


Figure S11. ¹H (400 MHz) and ¹³C (101 MHz) NMR spectra of the Ni(II) complex (*S,S*)-**1d** (in CDCl₃)



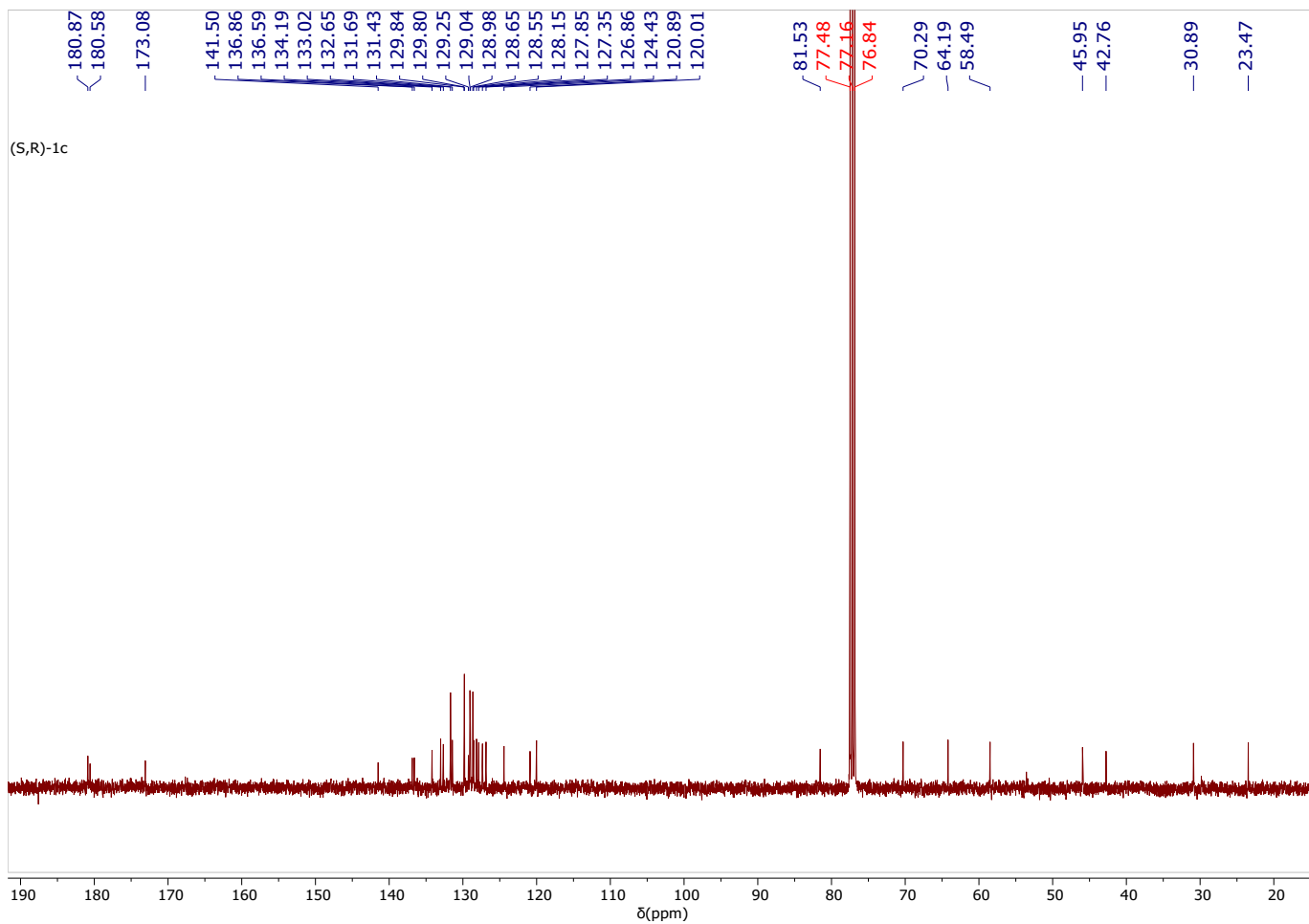
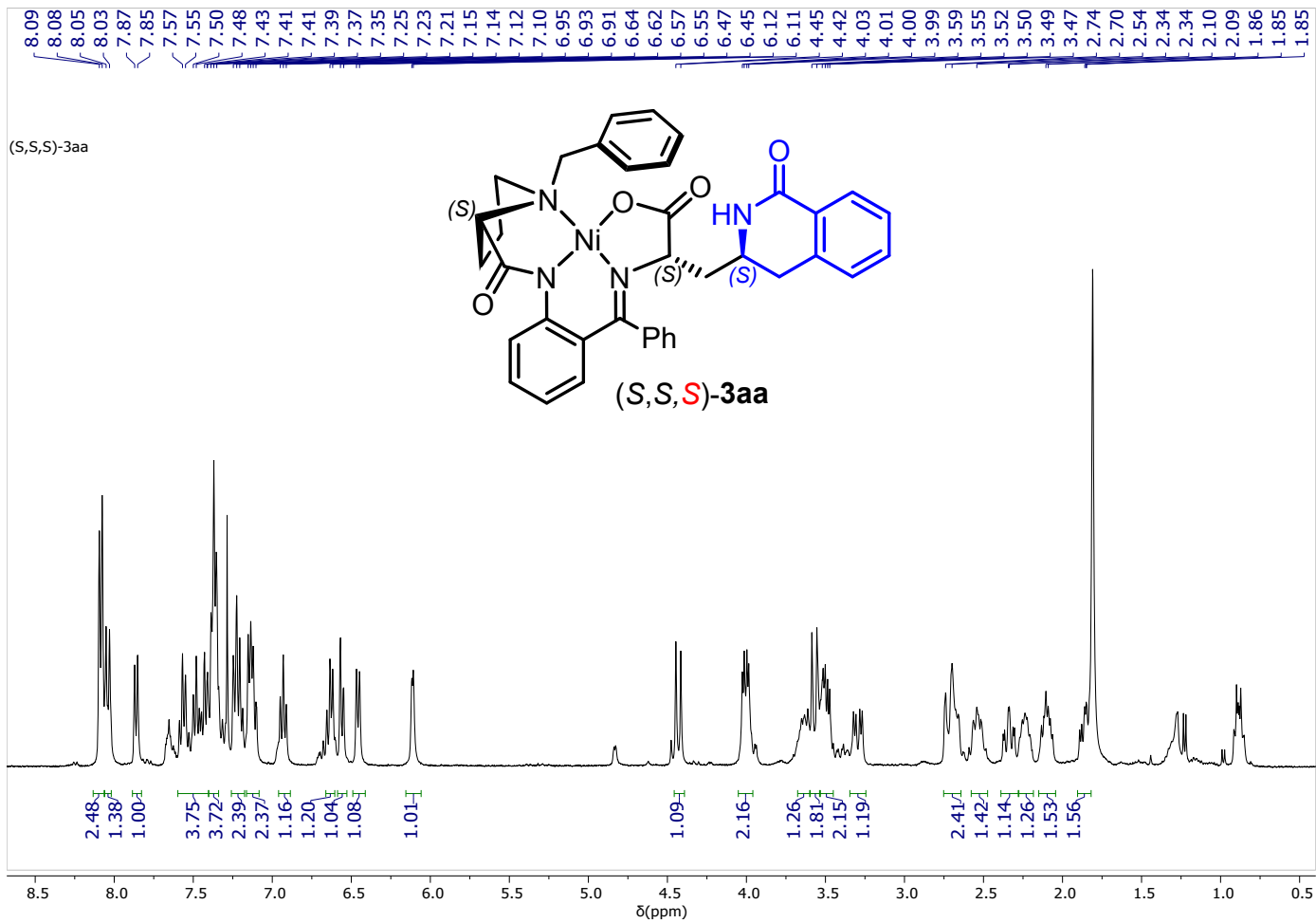


Figure S12. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,R*)-**1d** (in CDCl_3)



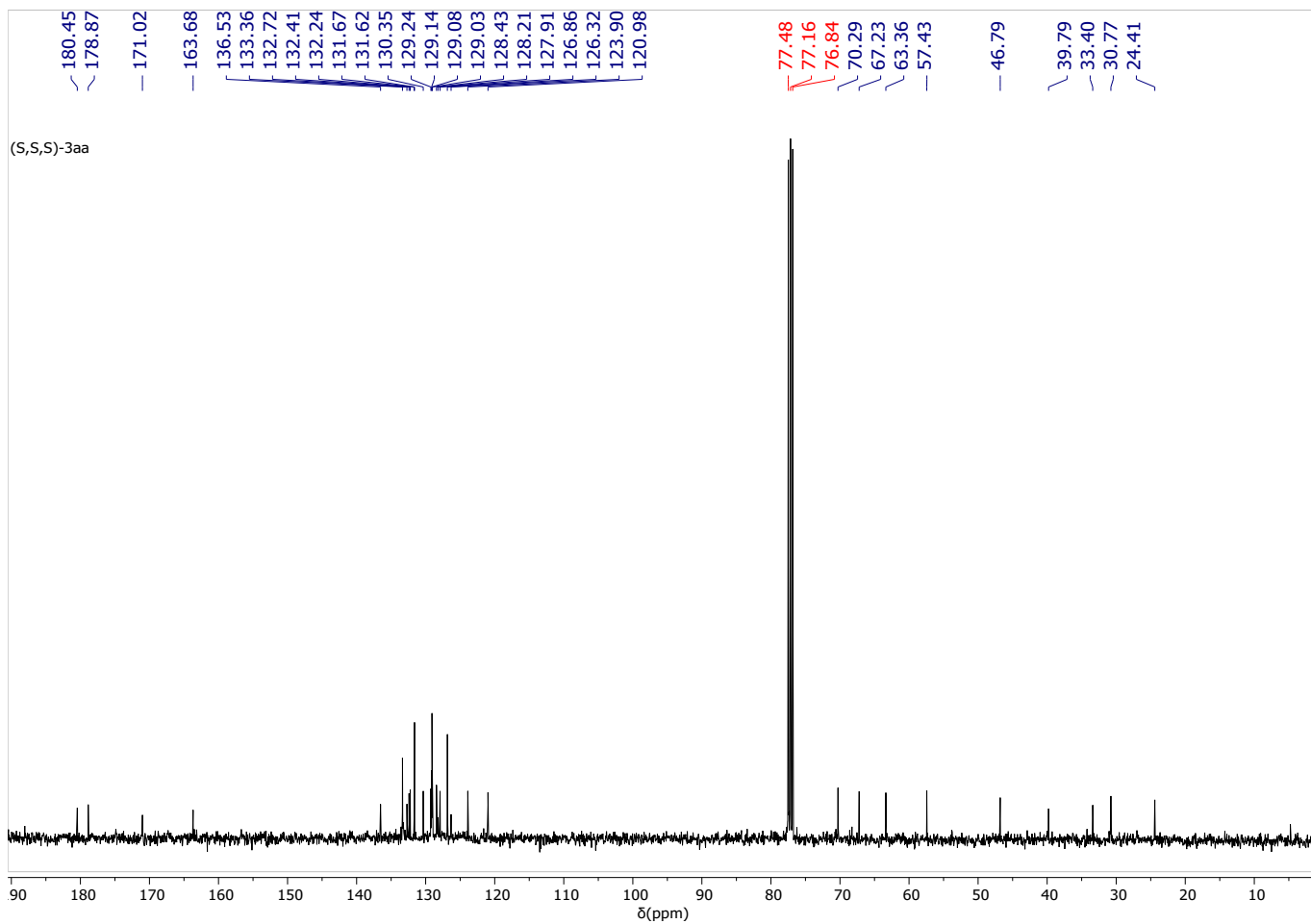


Figure S13. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3aa** (in CDCl_3)

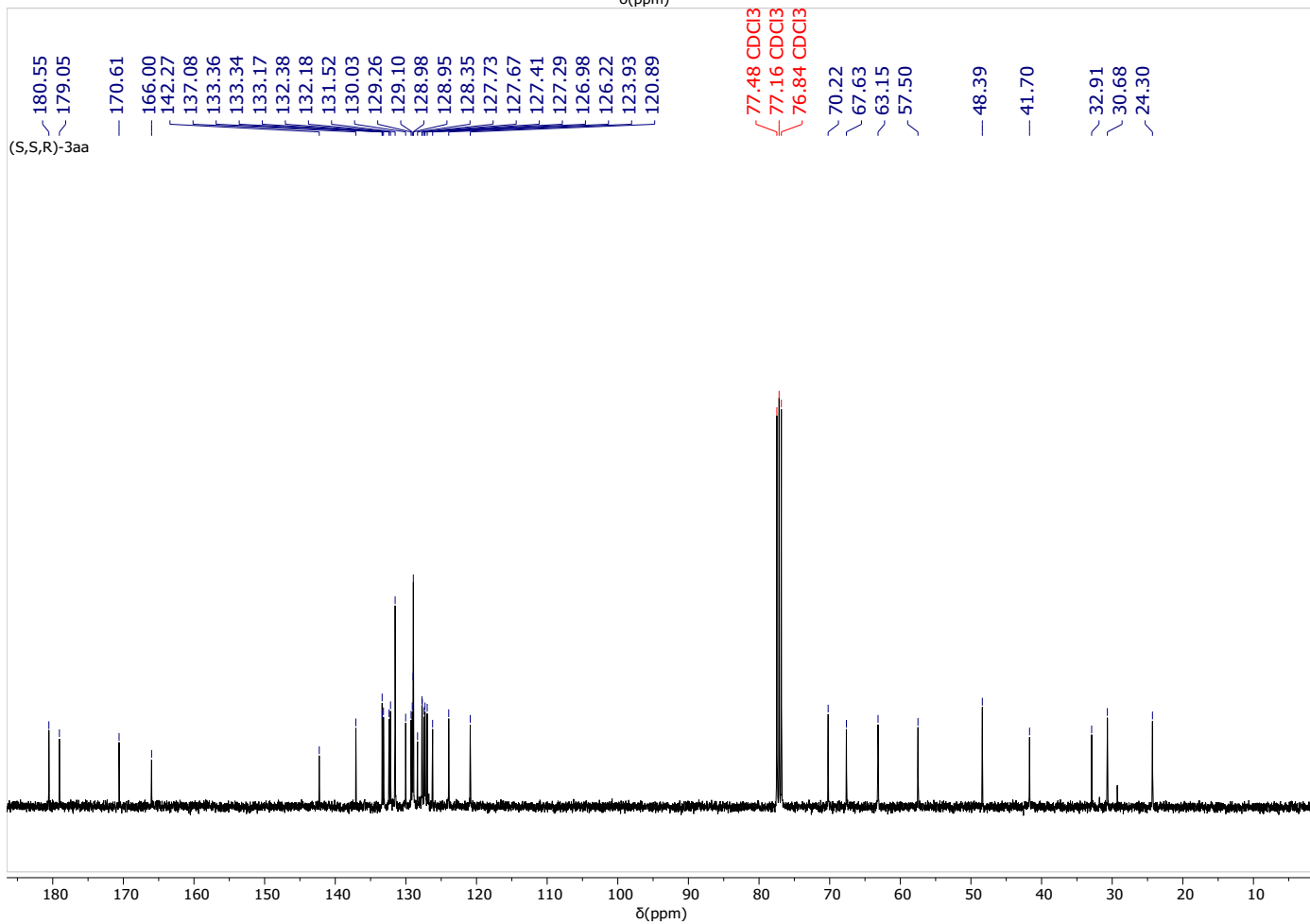
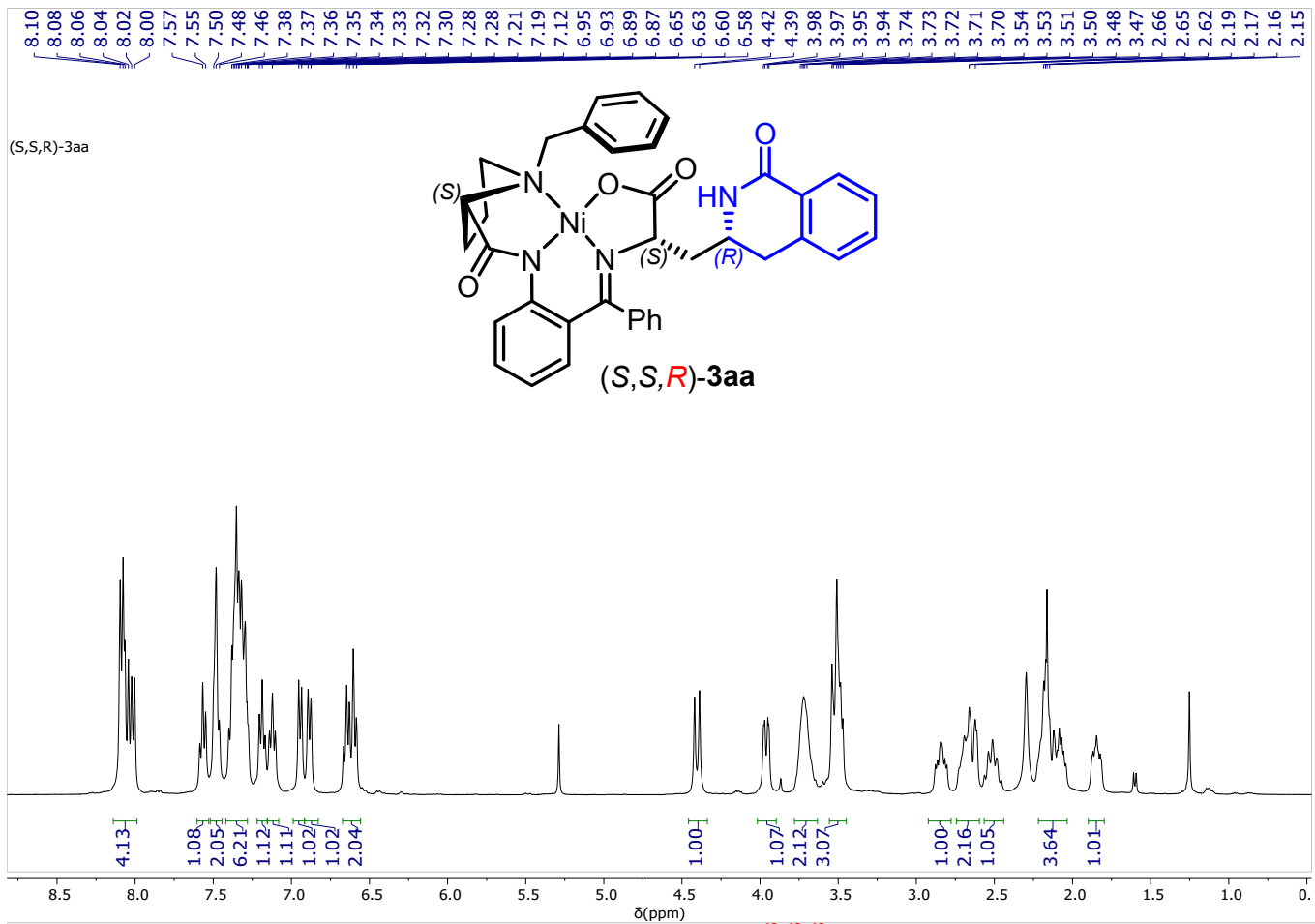
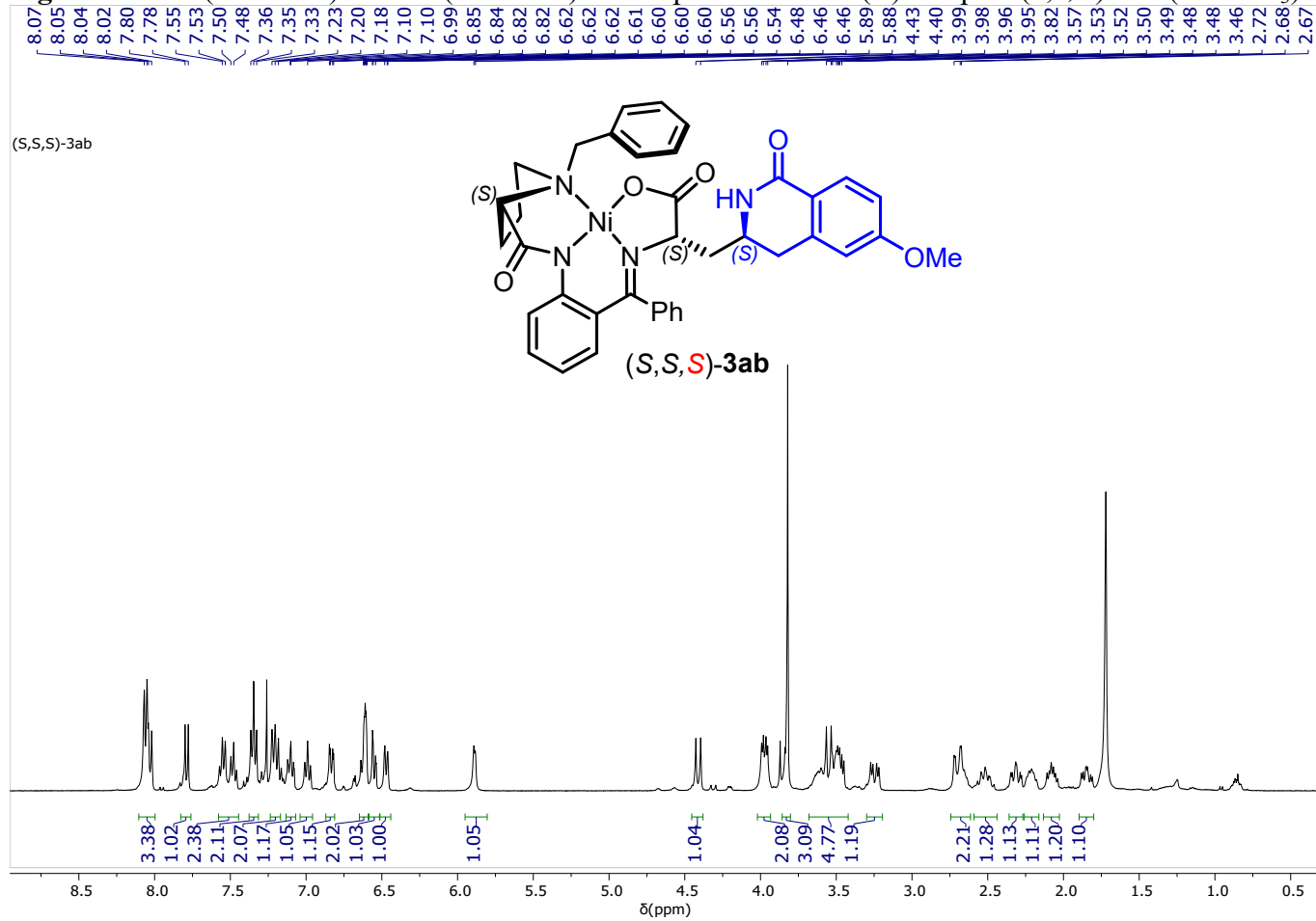


Figure S14. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3aa** (in CDCl_3)



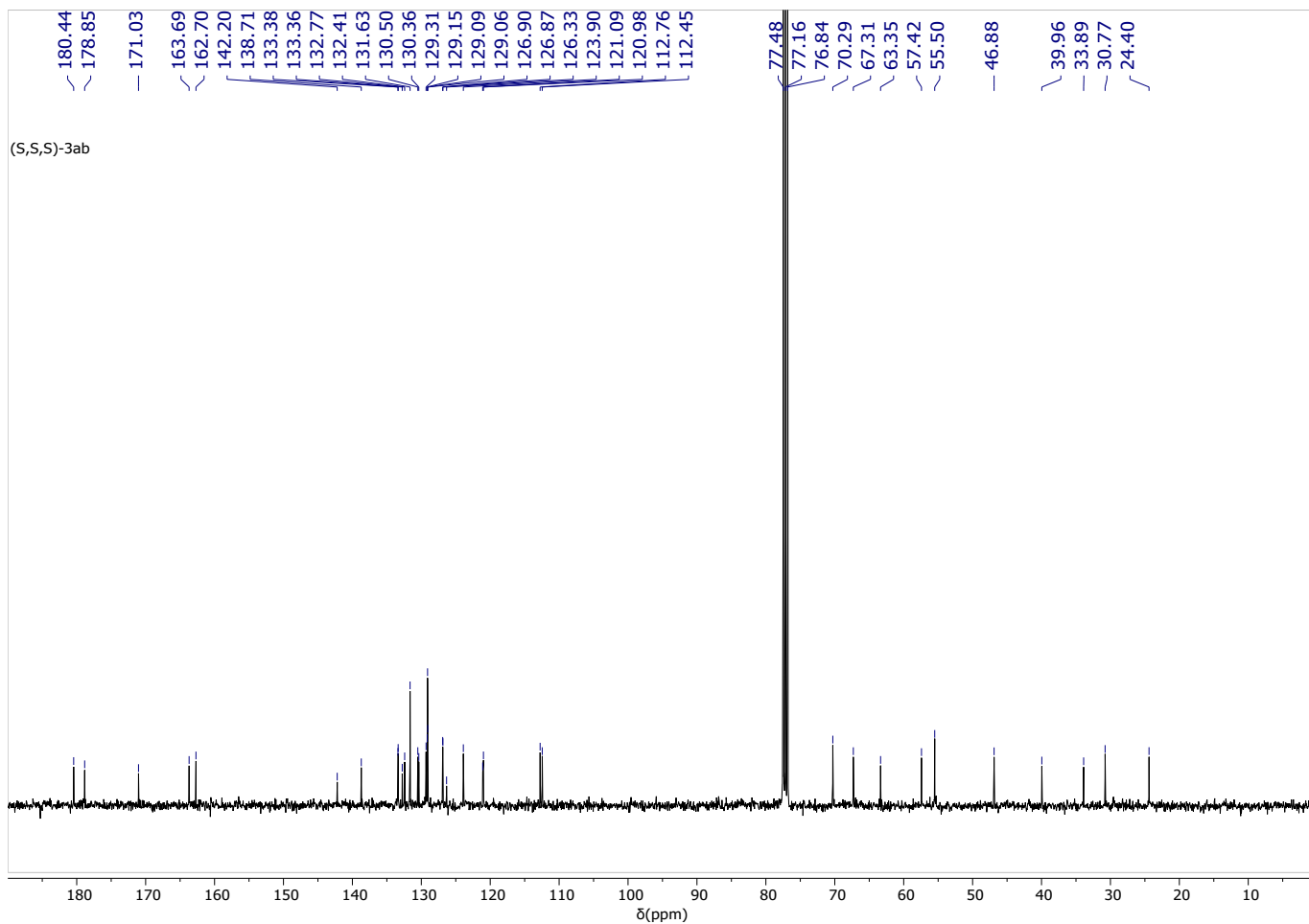
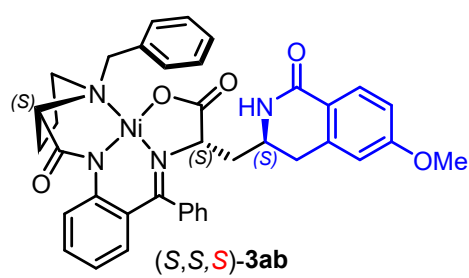


Figure S15. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ab** (in CDCl_3)



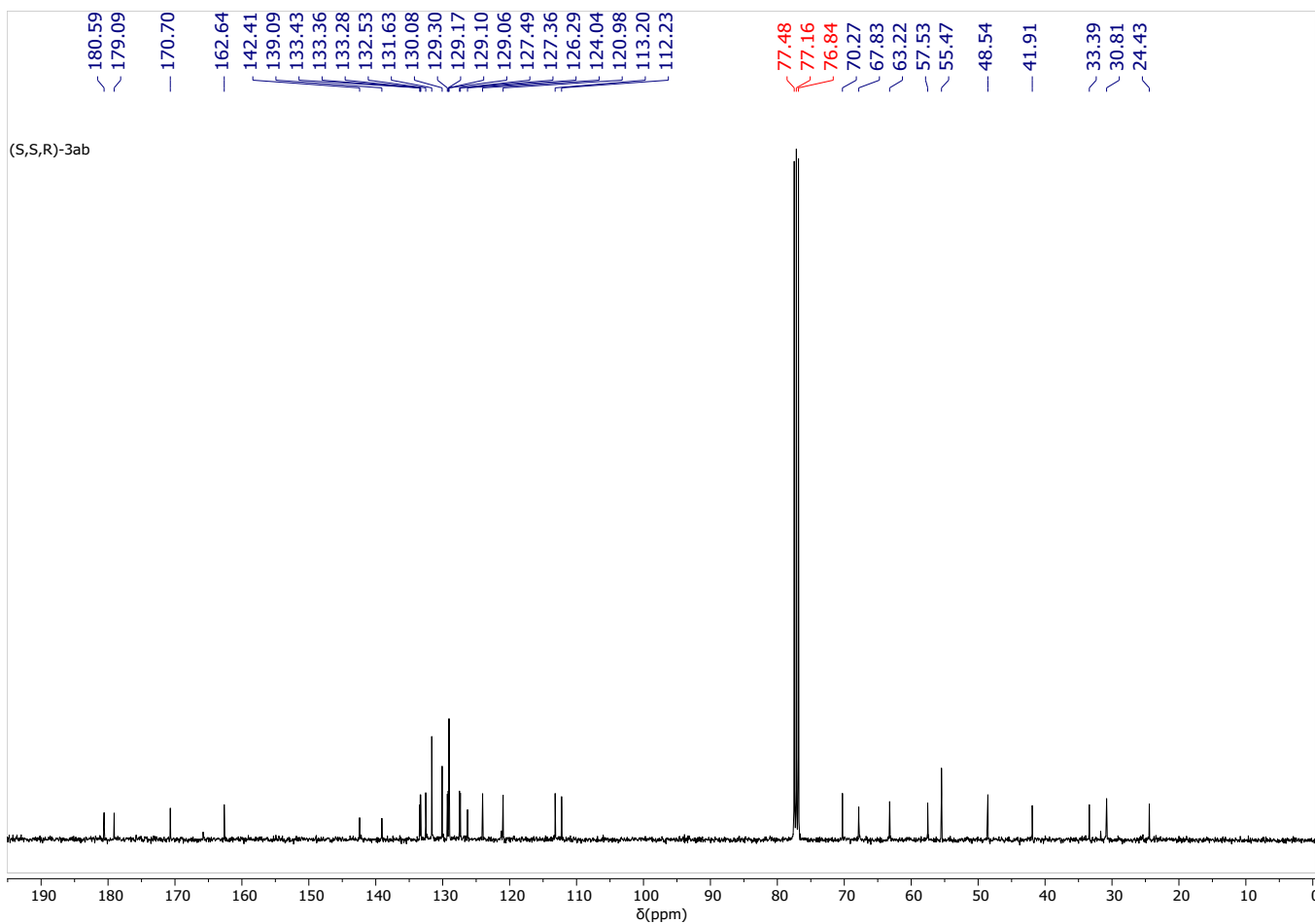
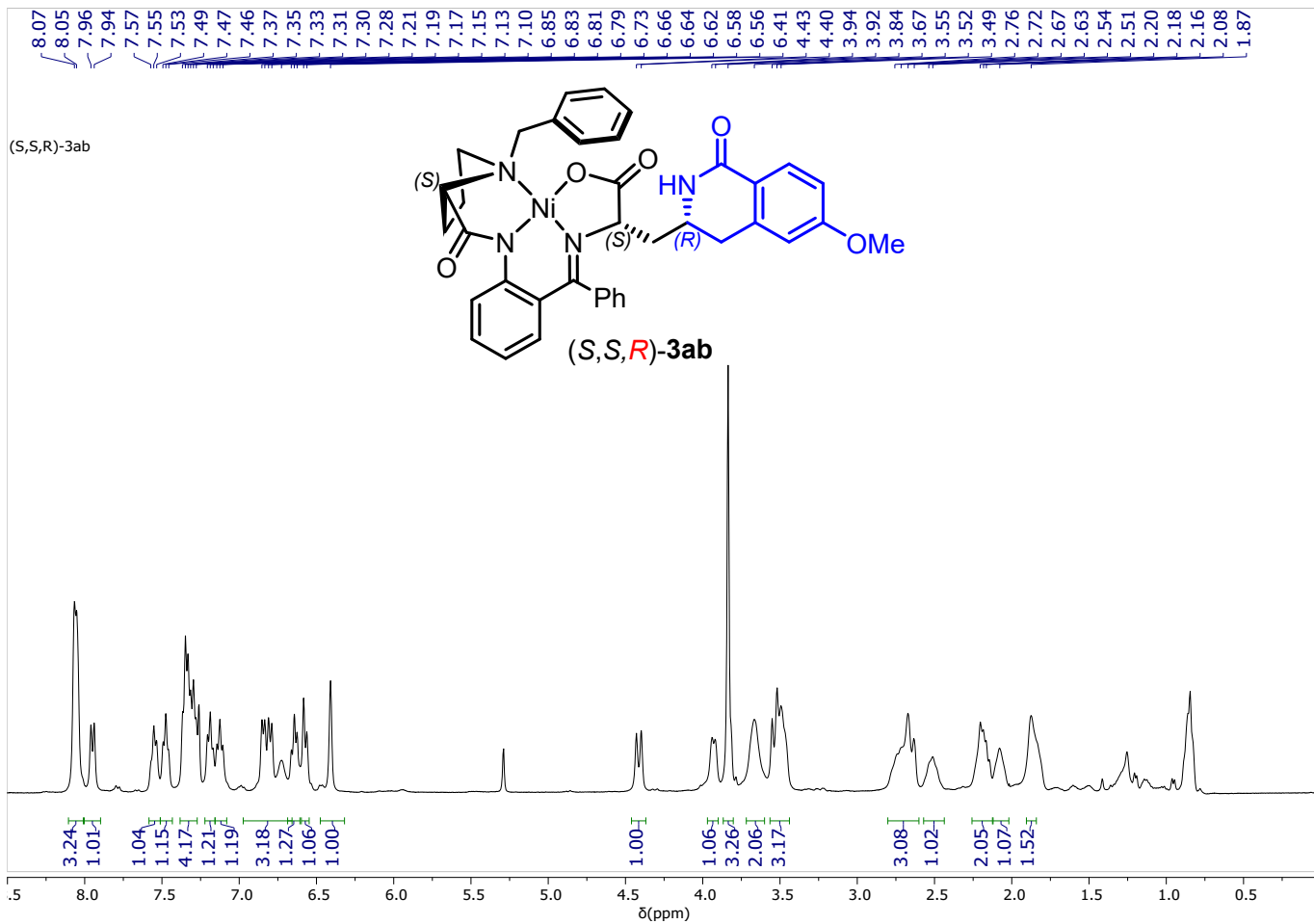
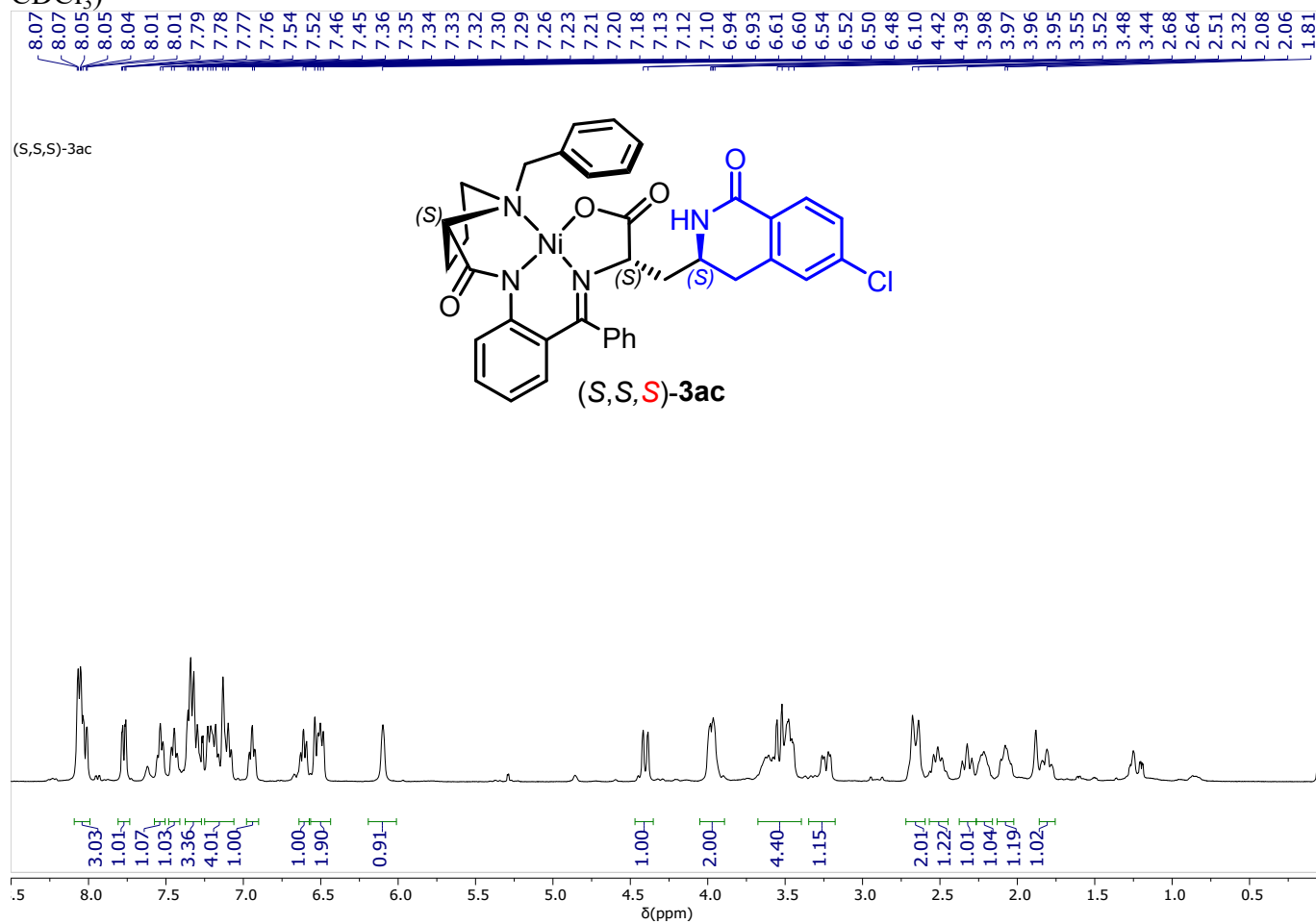


Figure S16. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ab** (in CDCl_3)



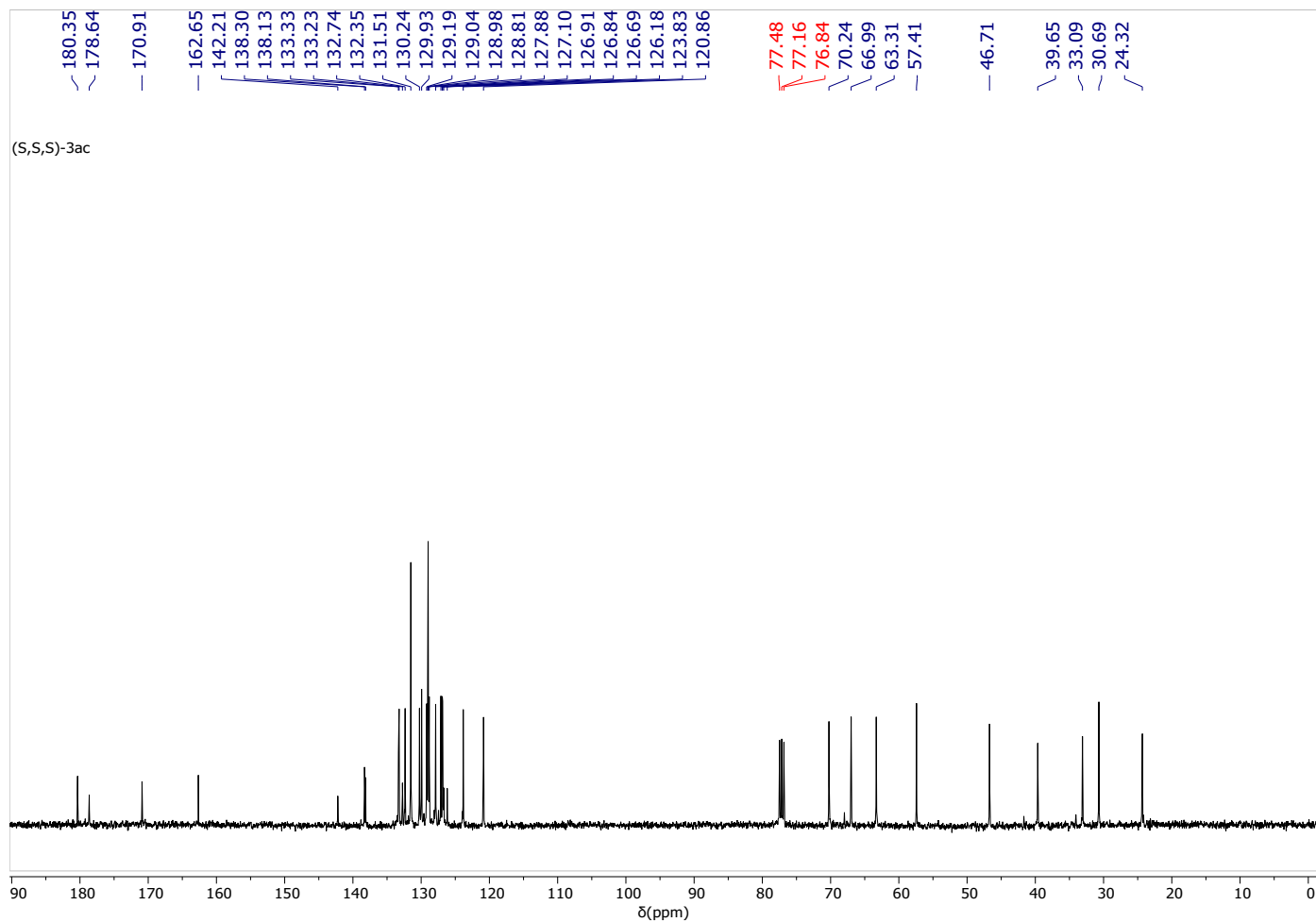
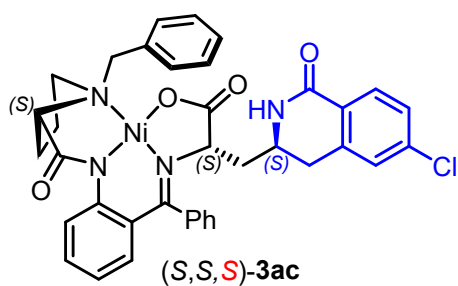
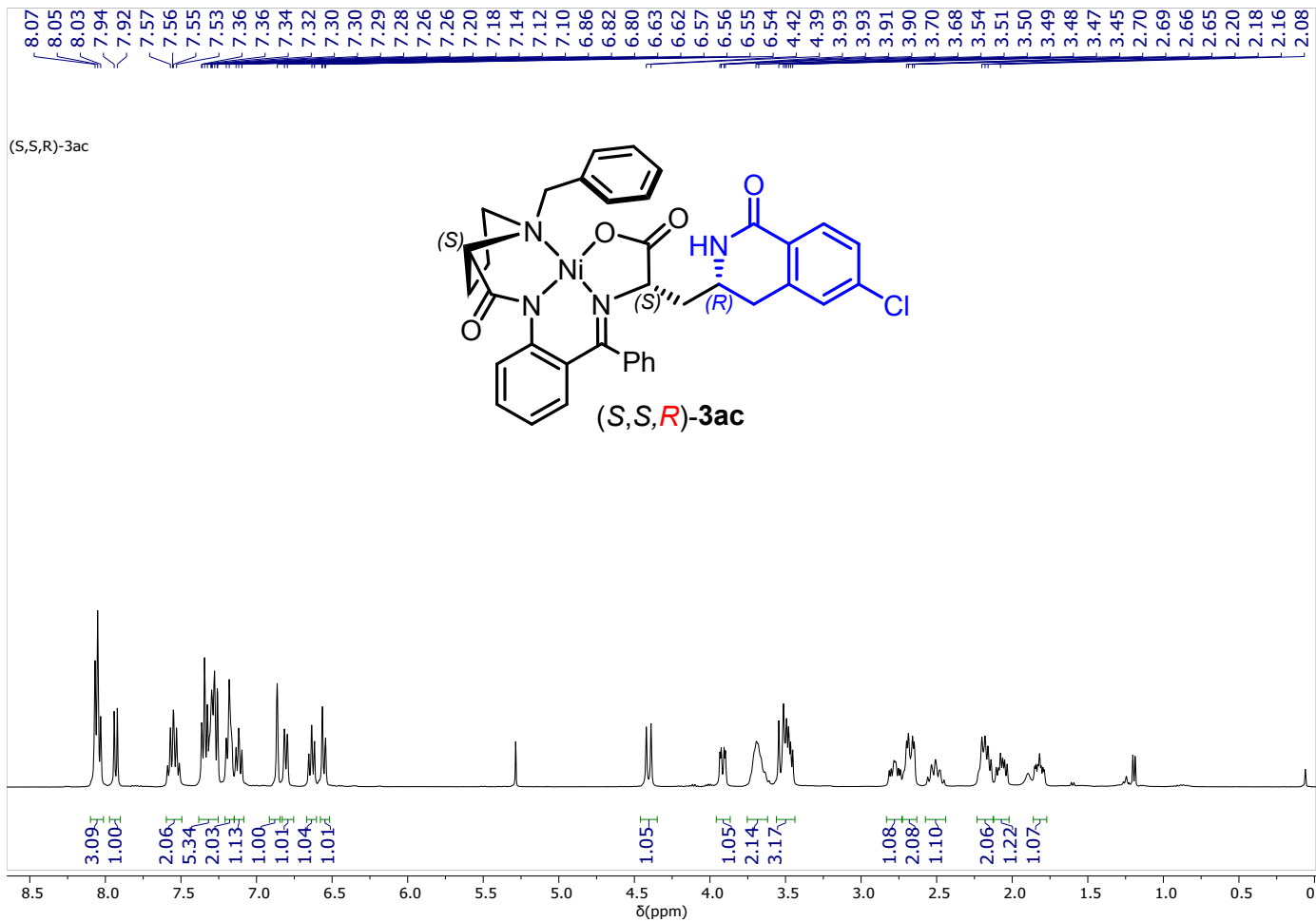


Figure S17. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ac** (in CDCl_3)





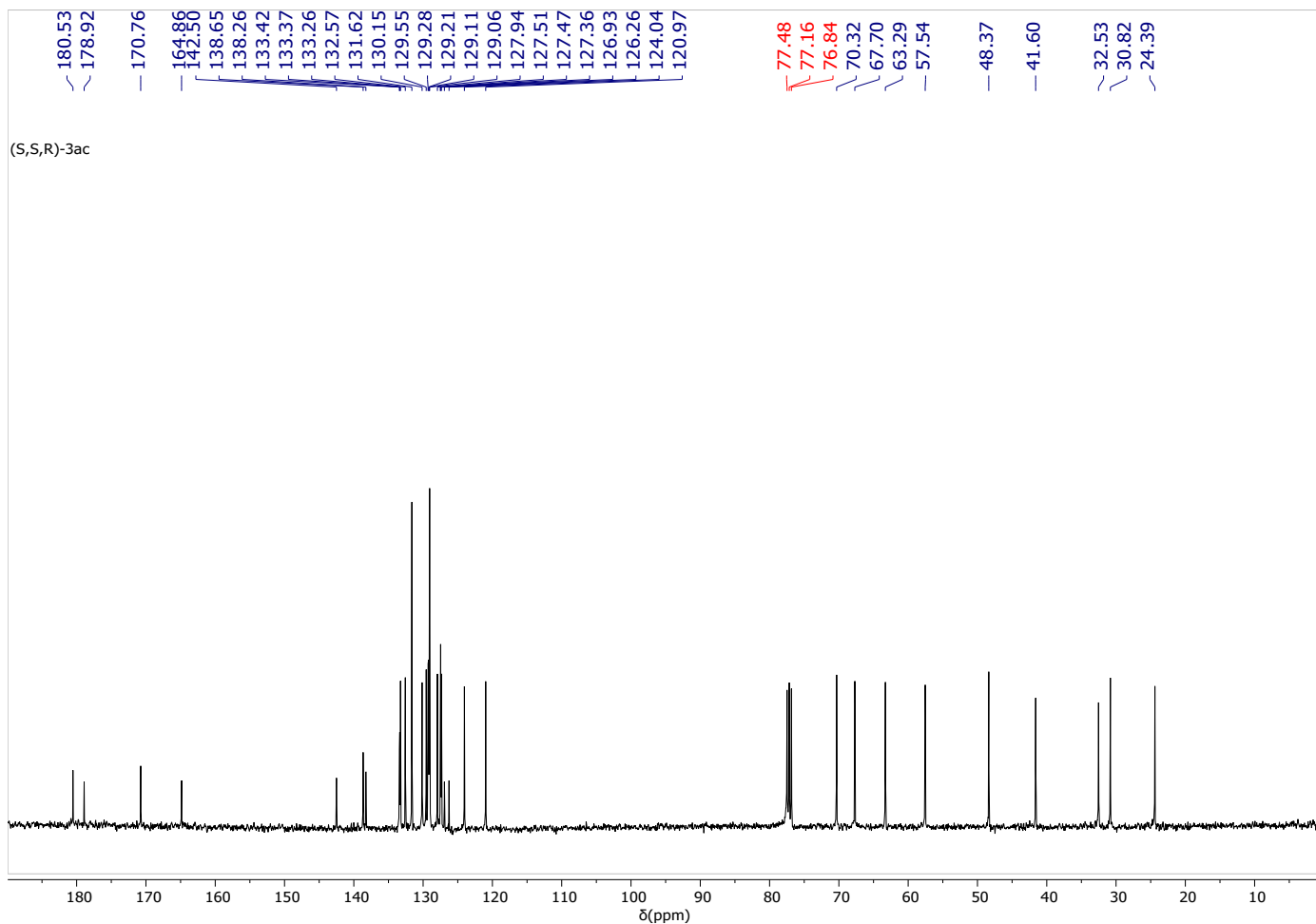
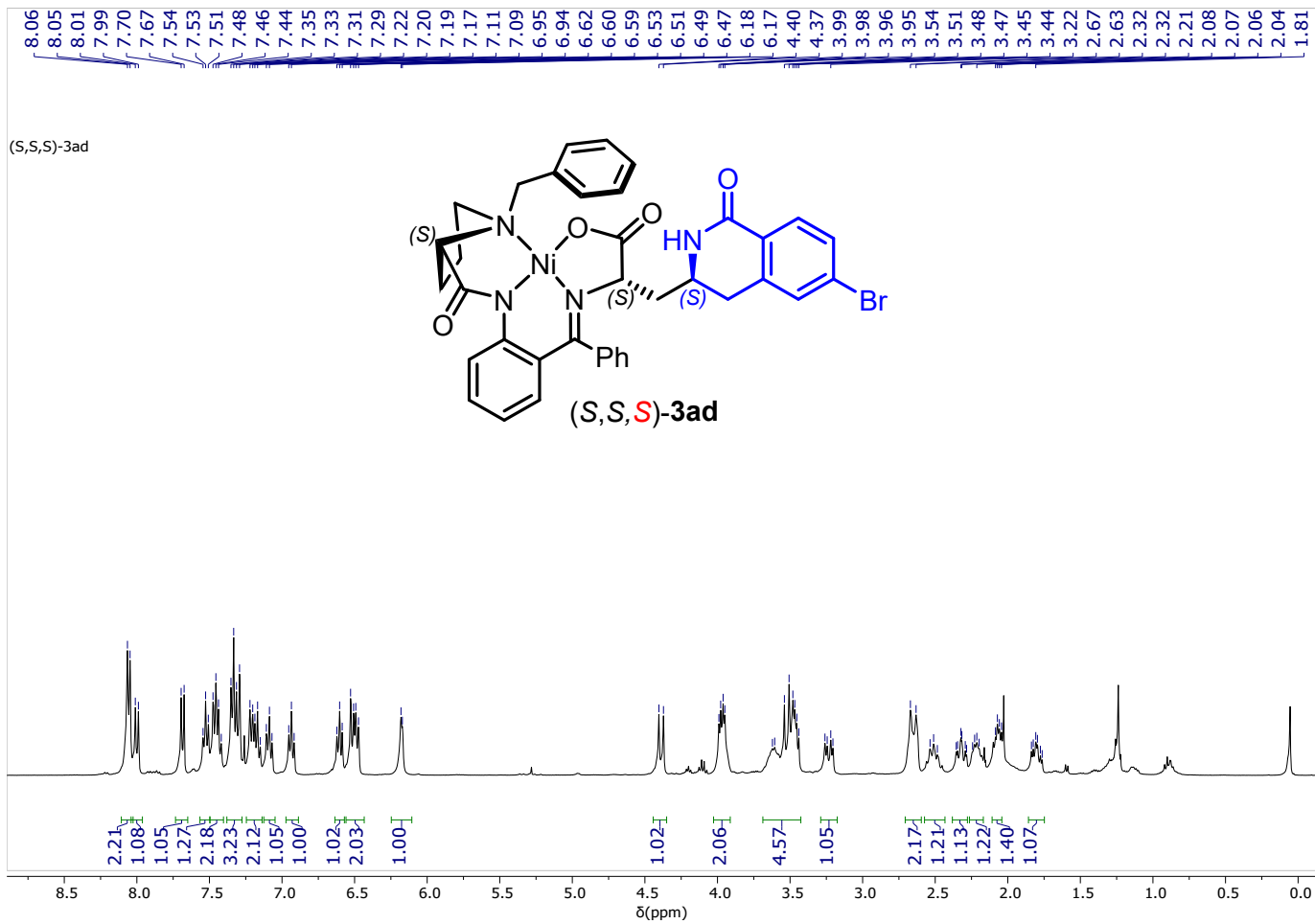


Figure S18. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ac** (in CDCl_3)



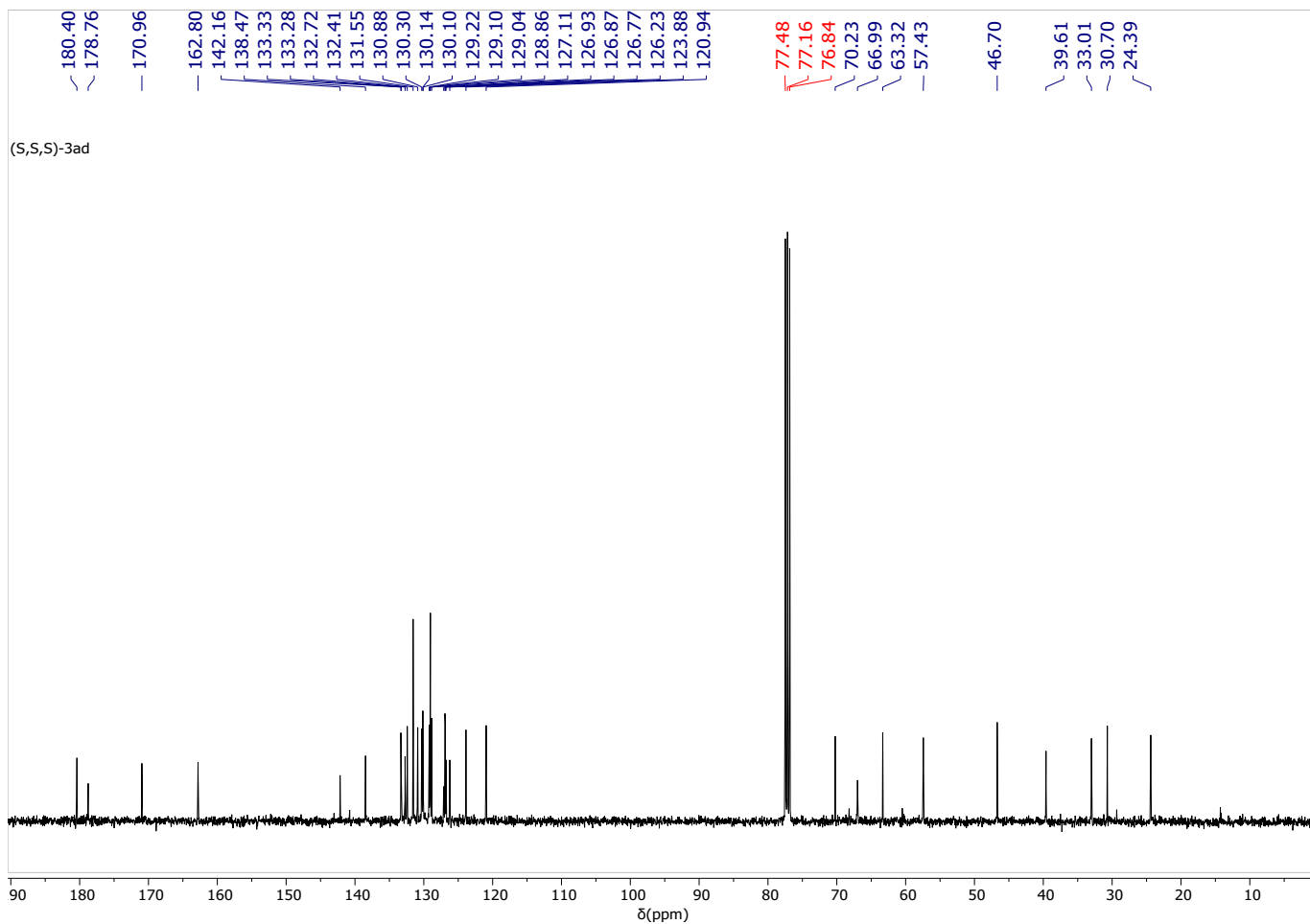


Figure S19. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ad** (in CDCl_3)

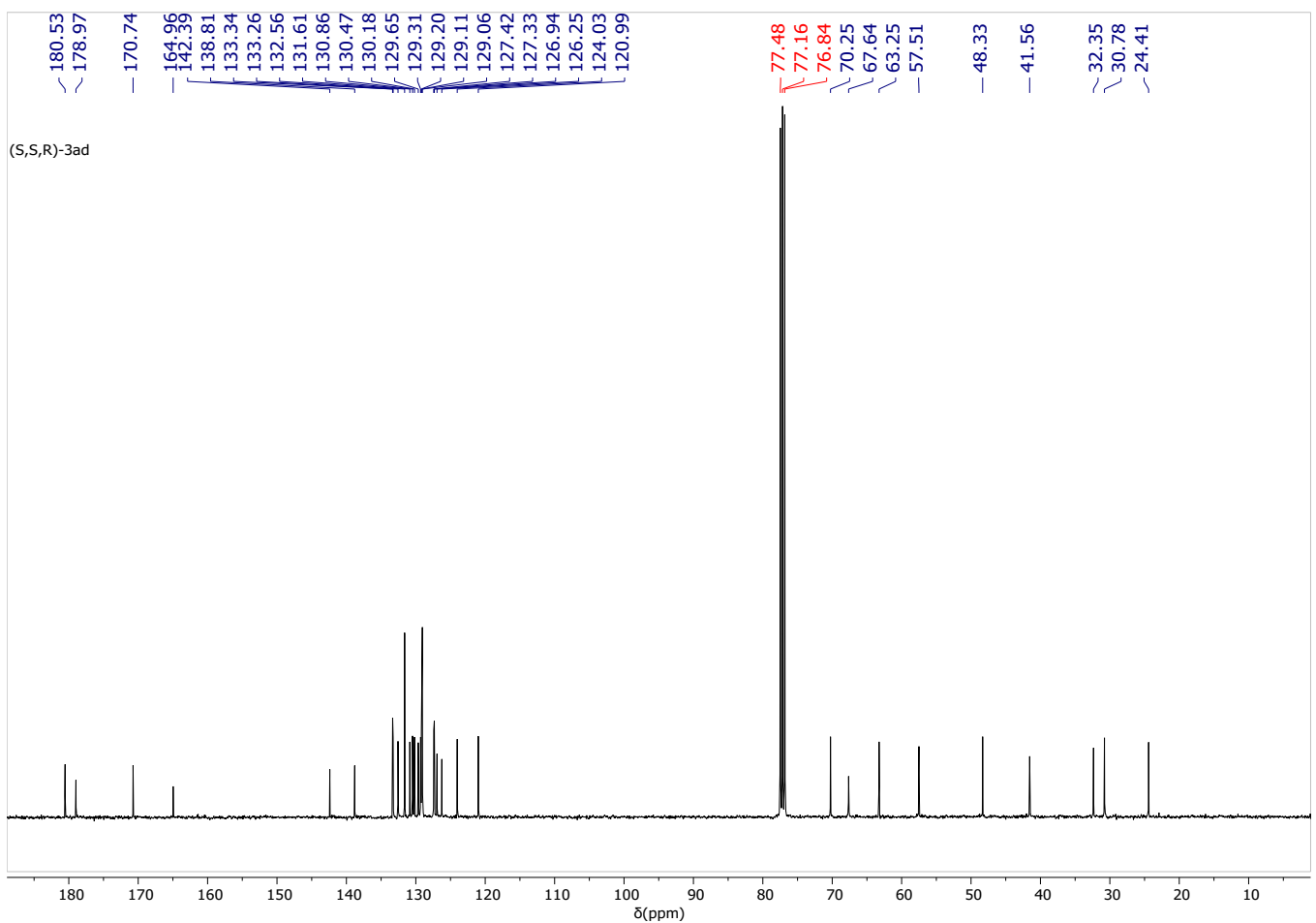
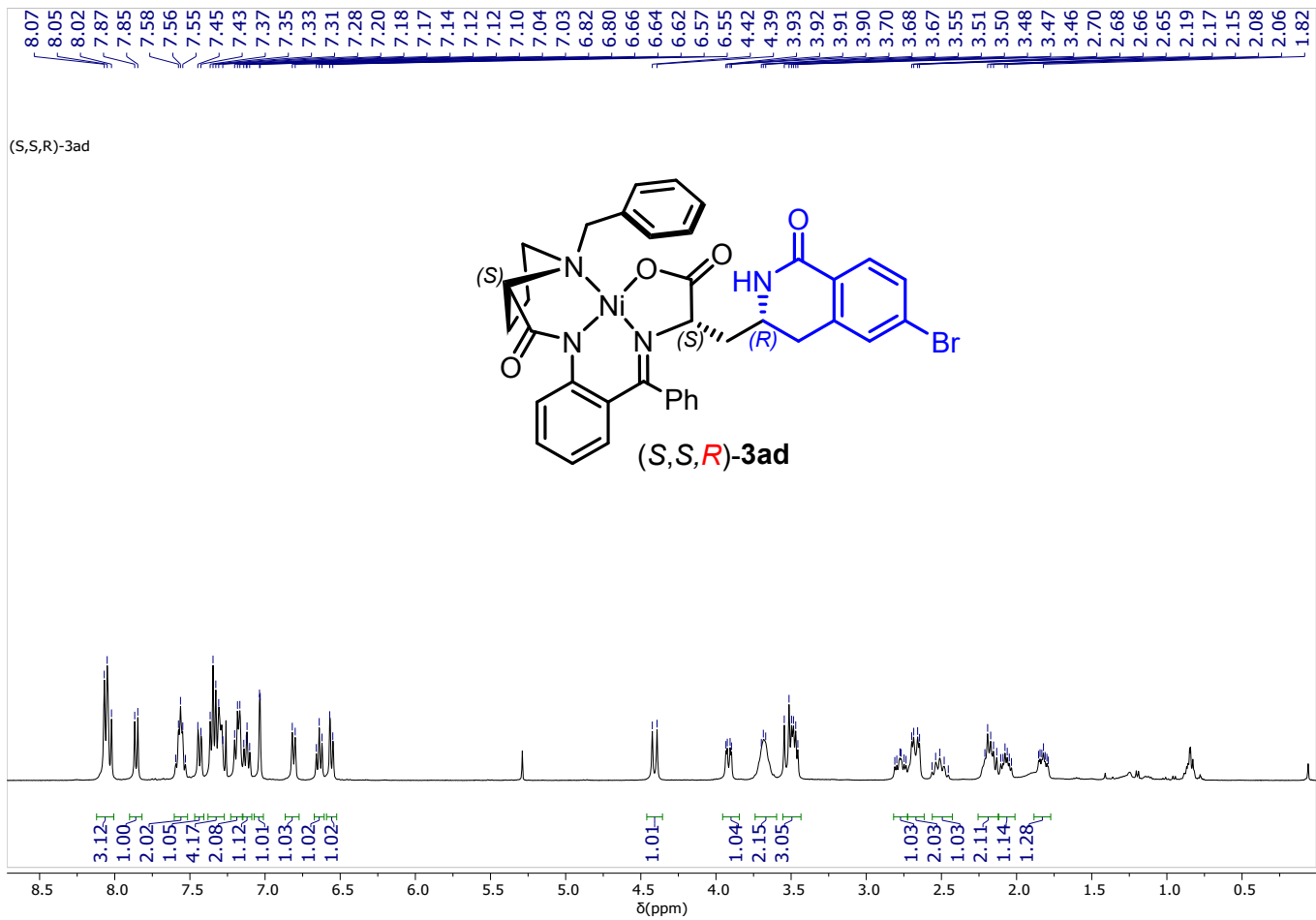
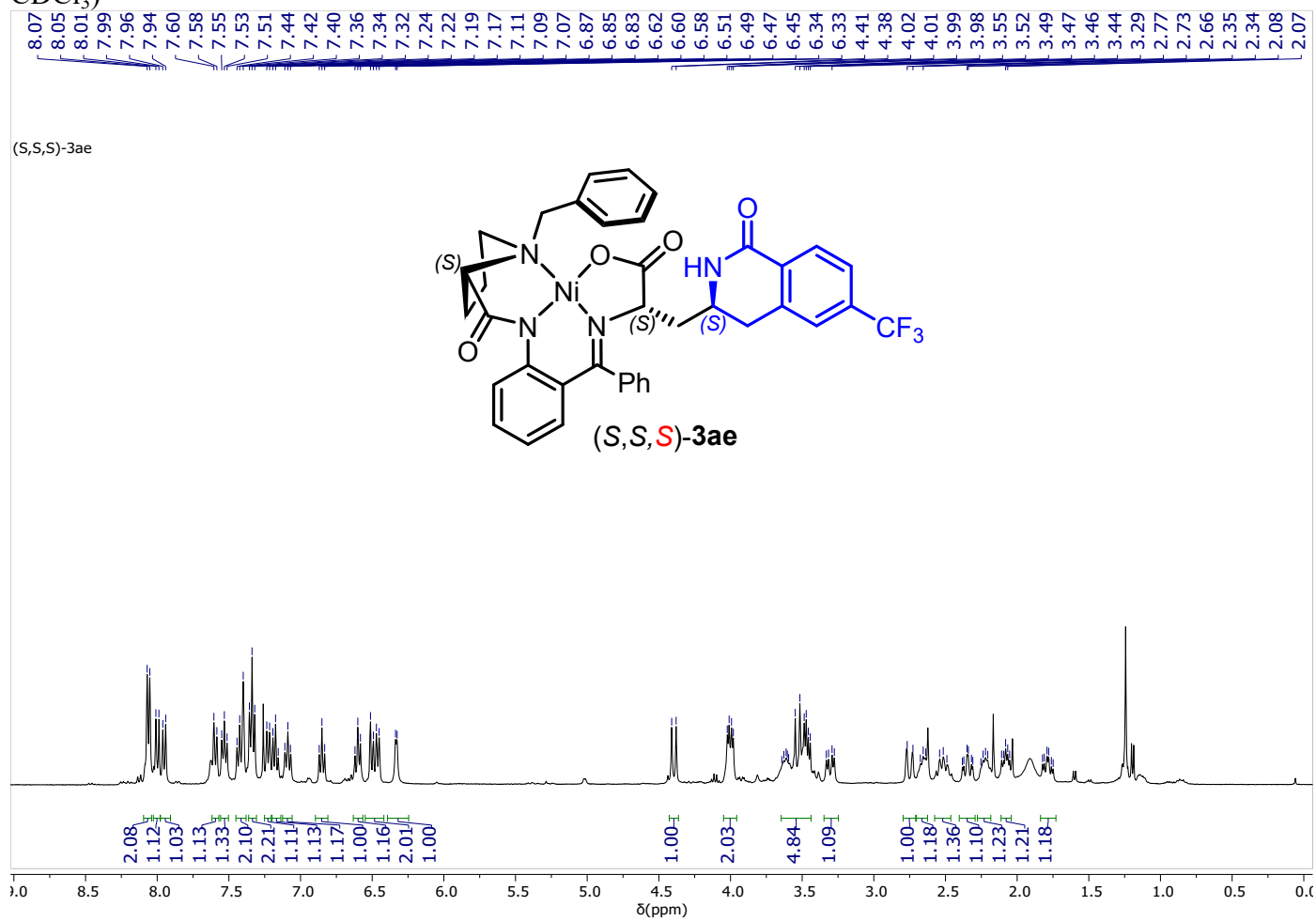
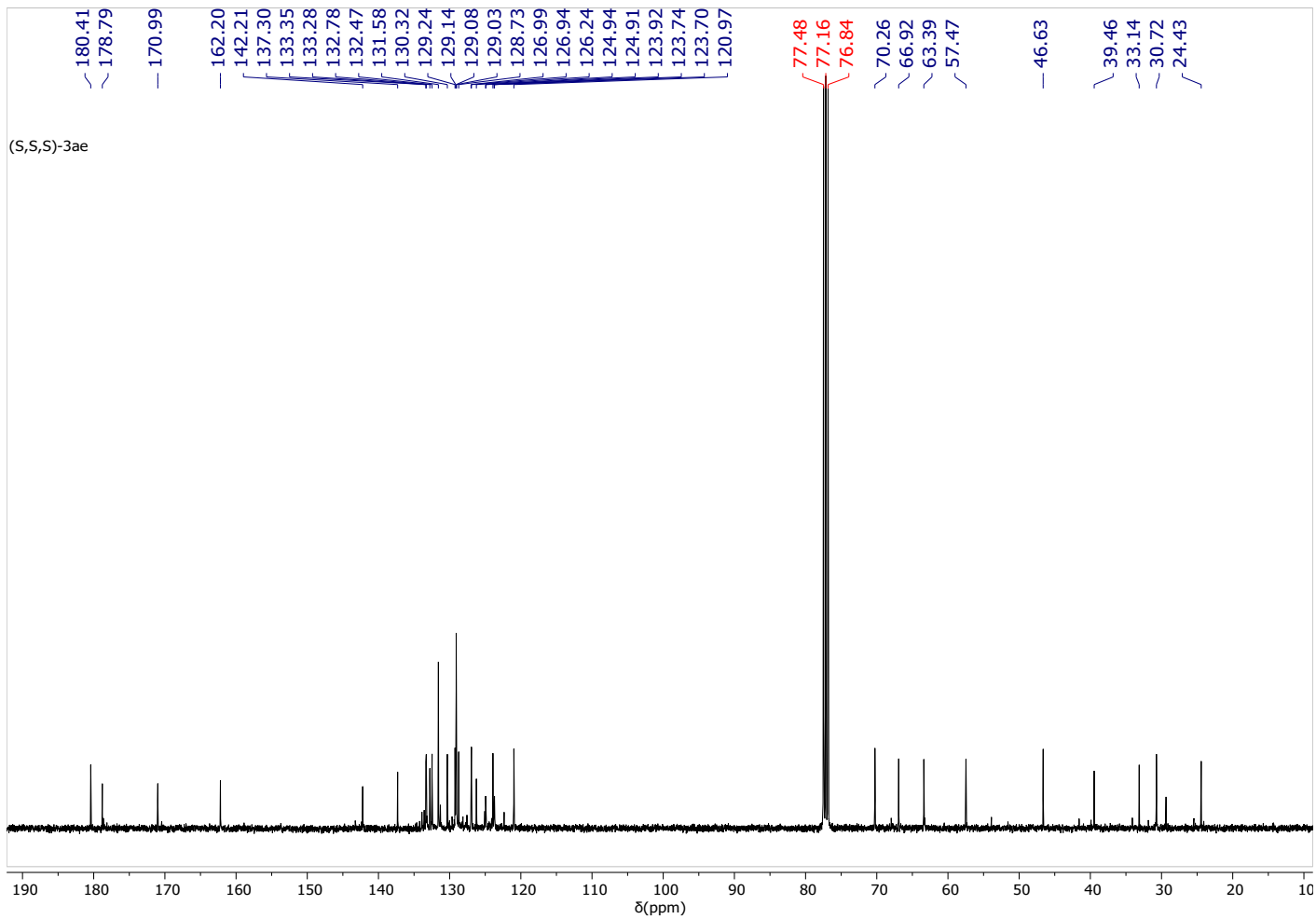


Figure S20. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ad** (in CDCl_3)





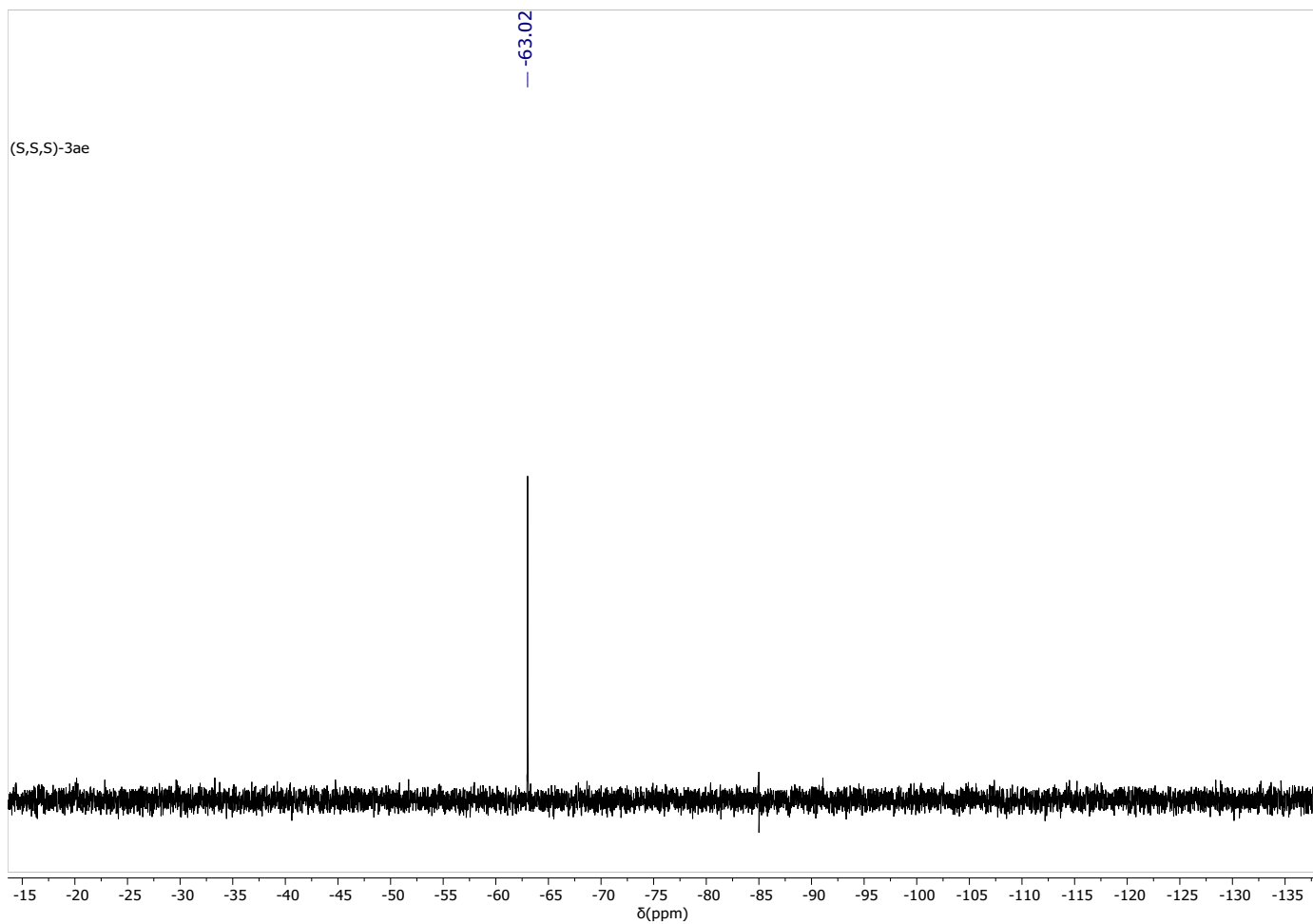
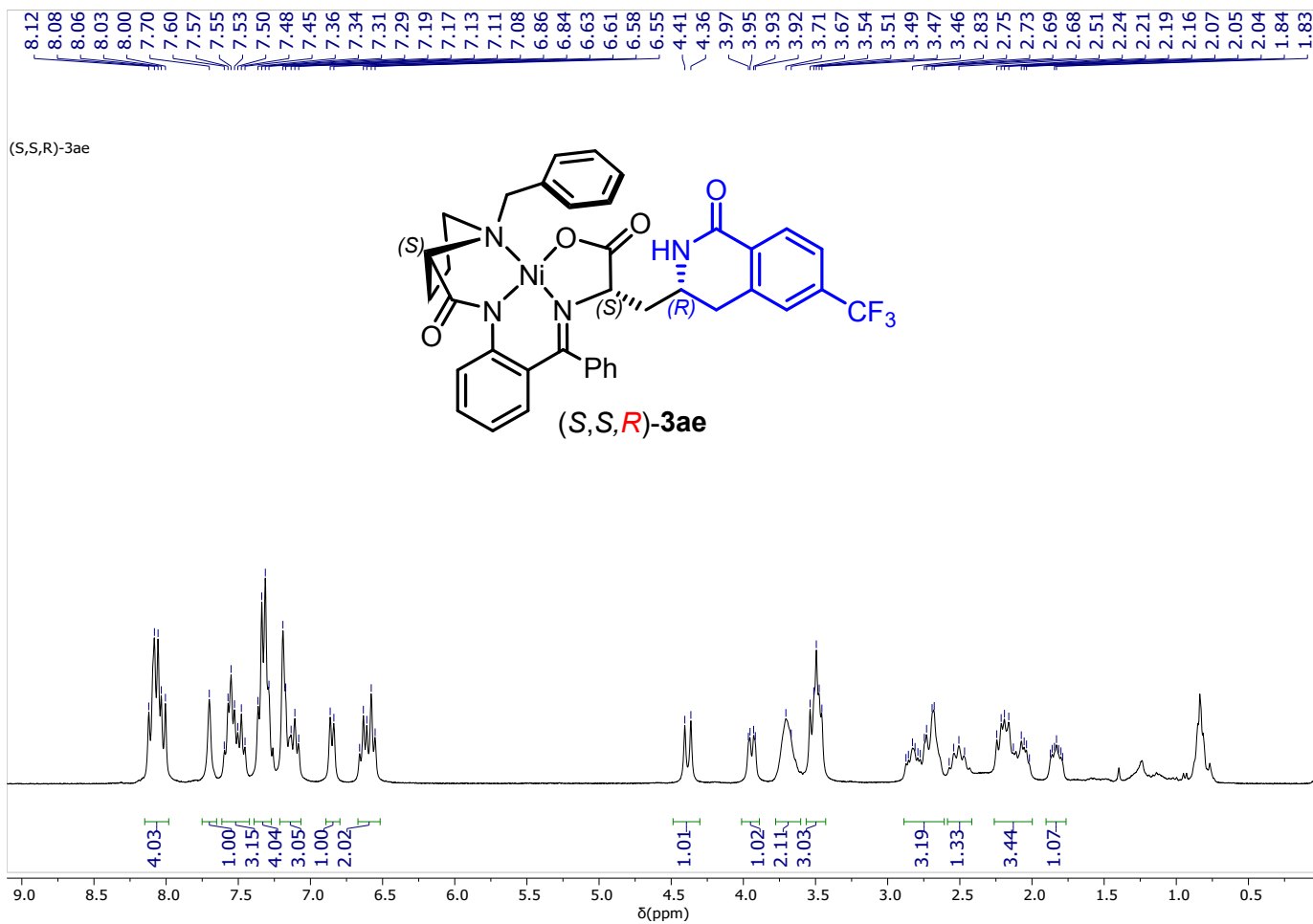


Figure S21. ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (376 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ae** (in CDCl_3)



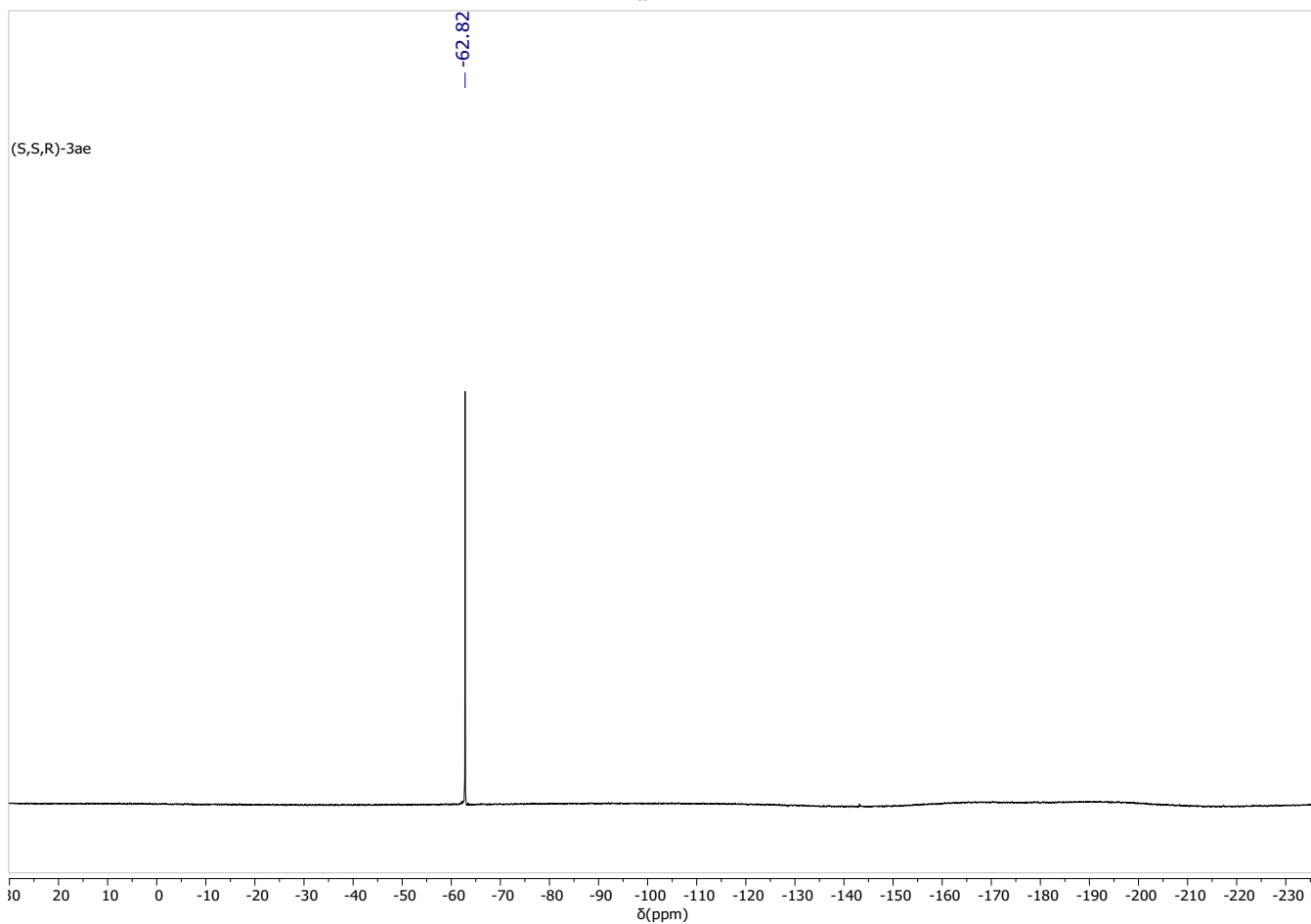
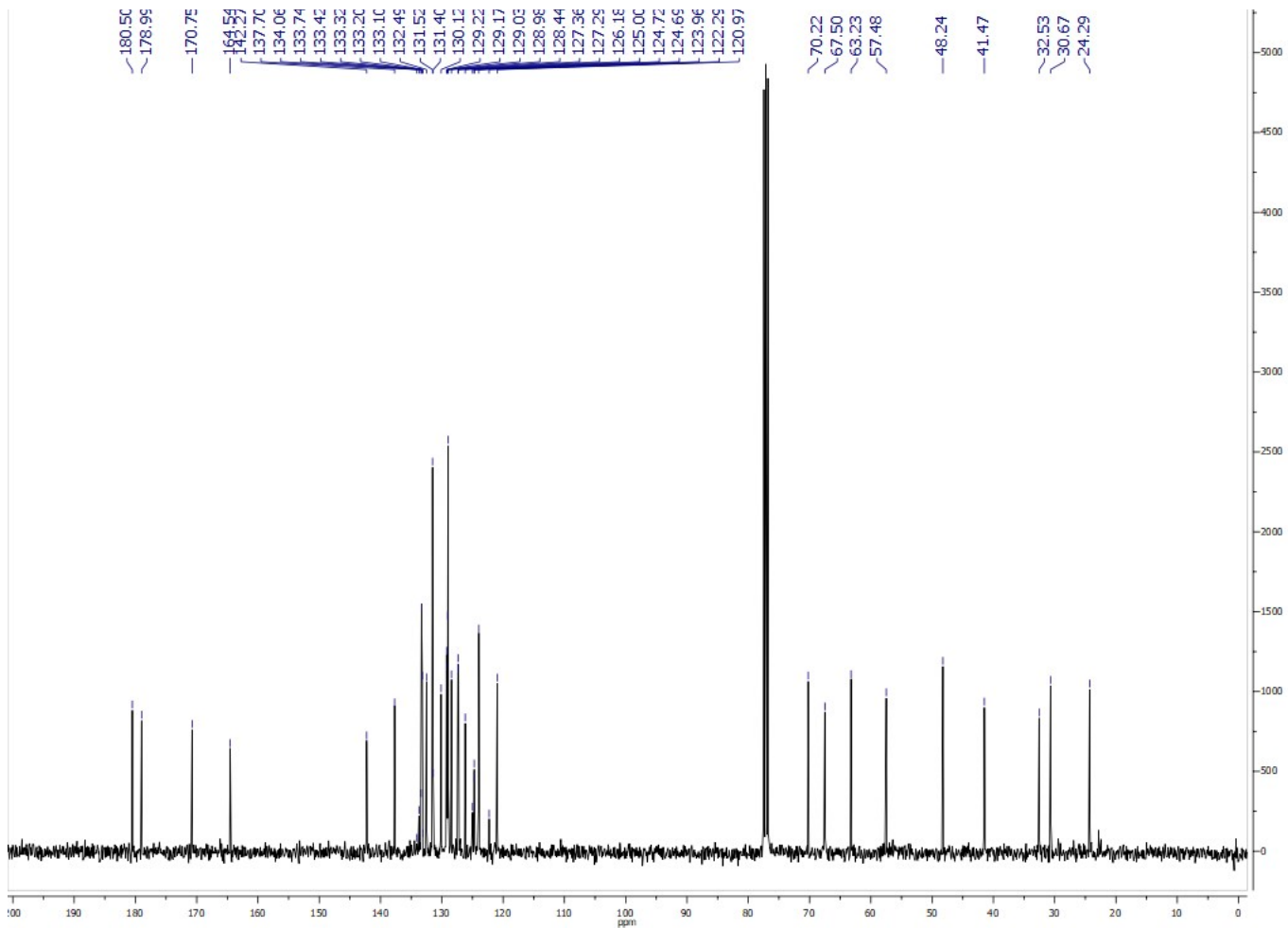


Figure S22. ^1H (400 MHz), ^{13}C (101 MHz) and ^{19}F (376 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ae** (in CDCl_3)

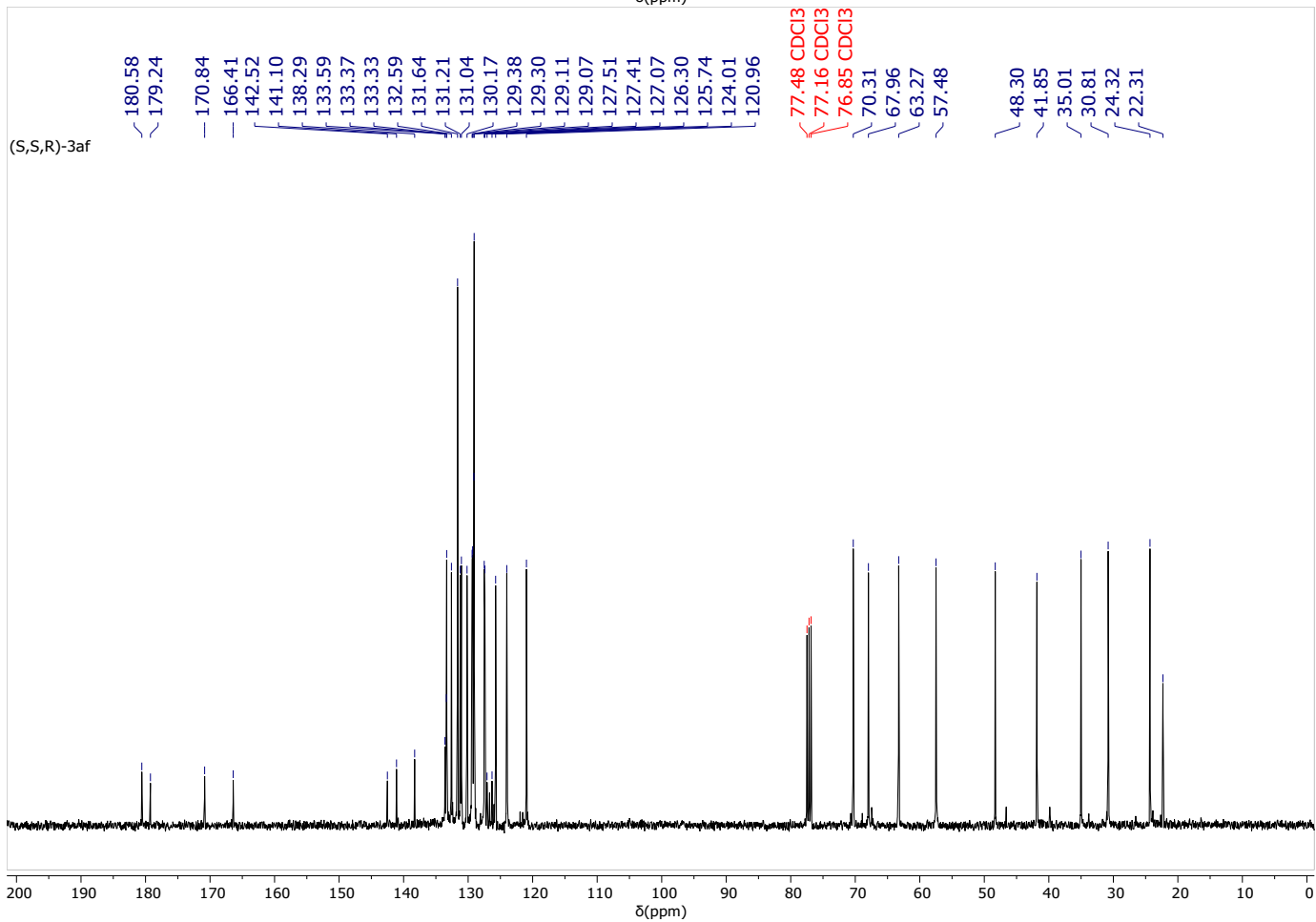
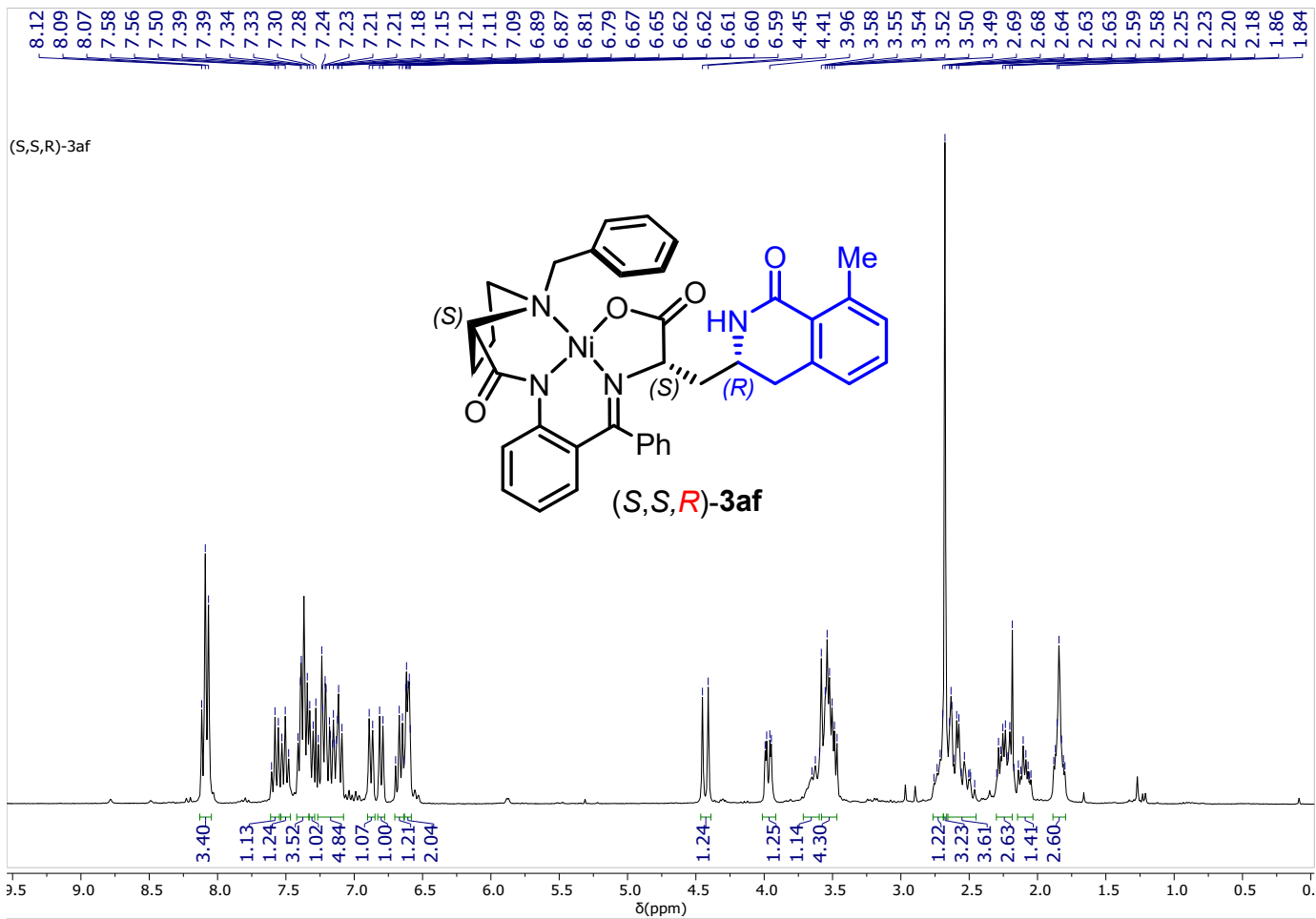
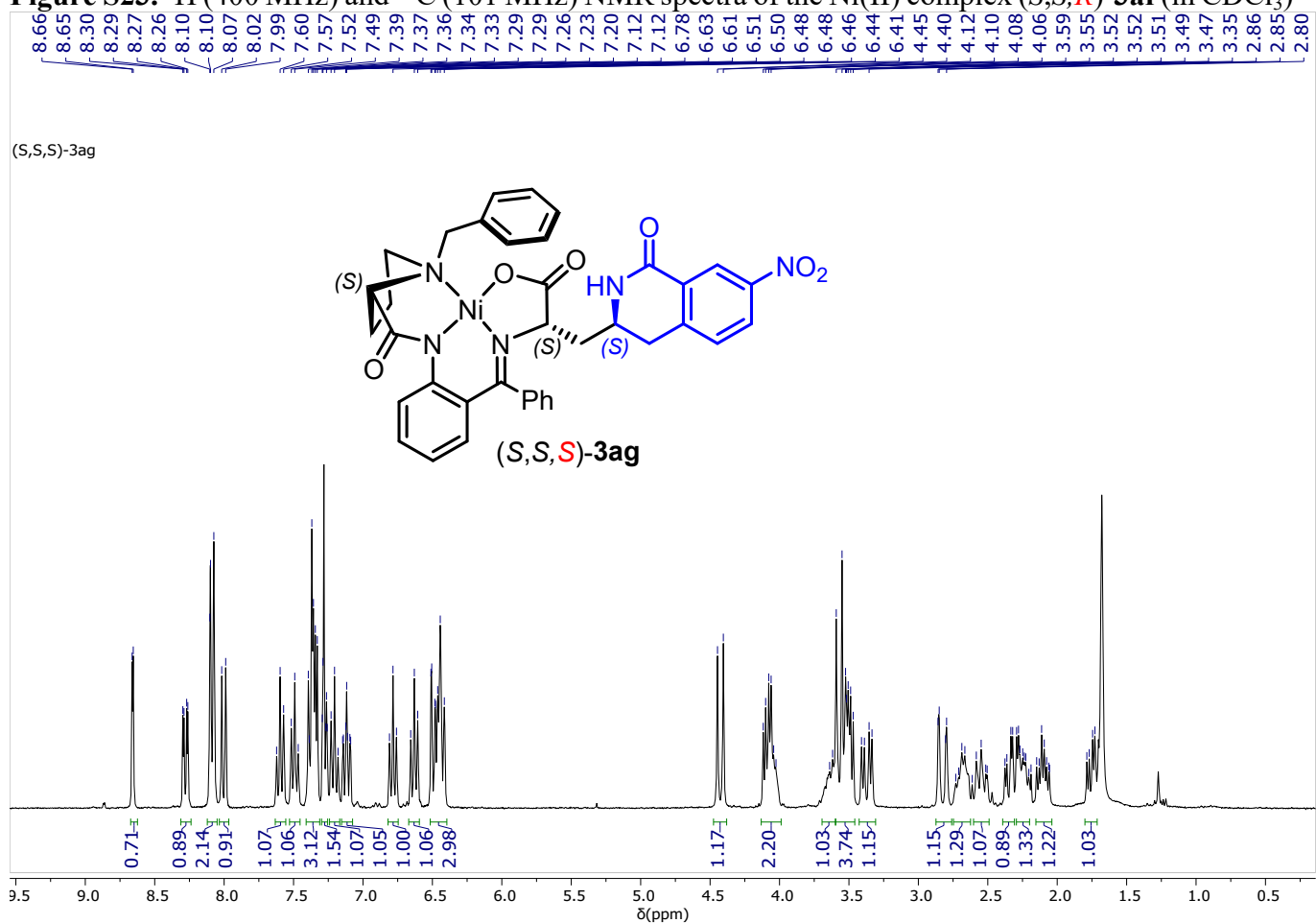


Figure S23. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3af** (in CDCl_3)



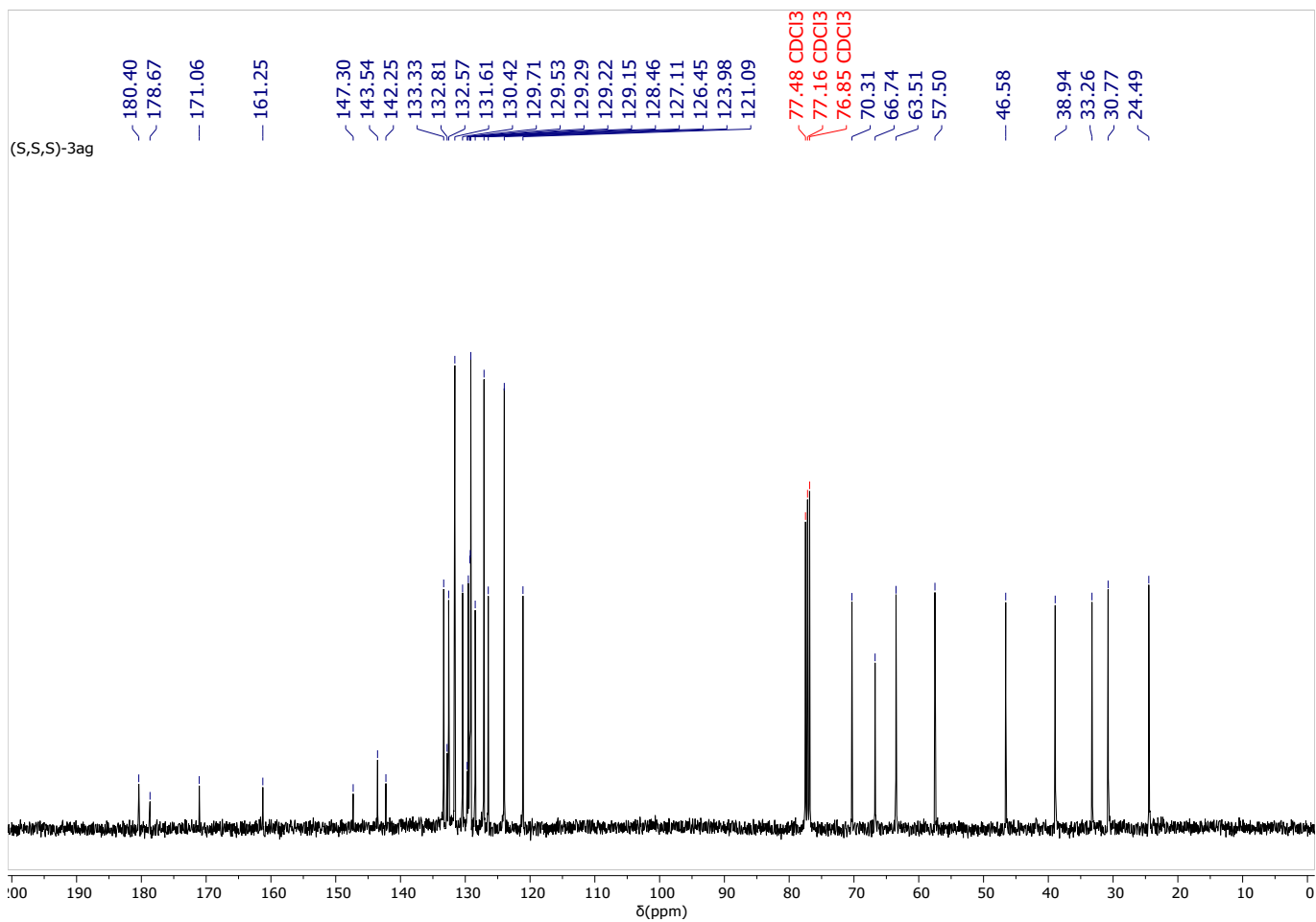
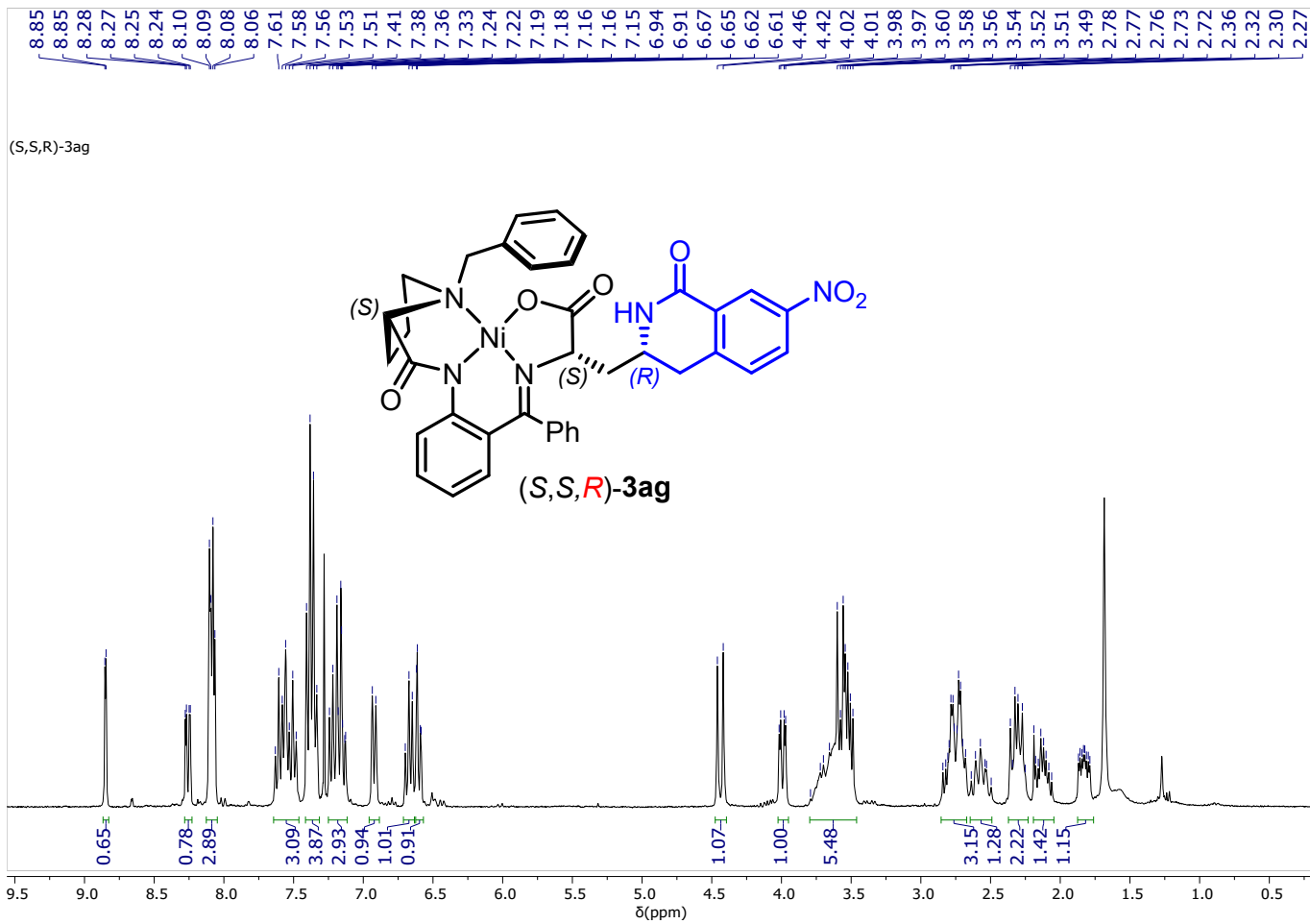


Figure S24. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ag** (in CDCl_3)



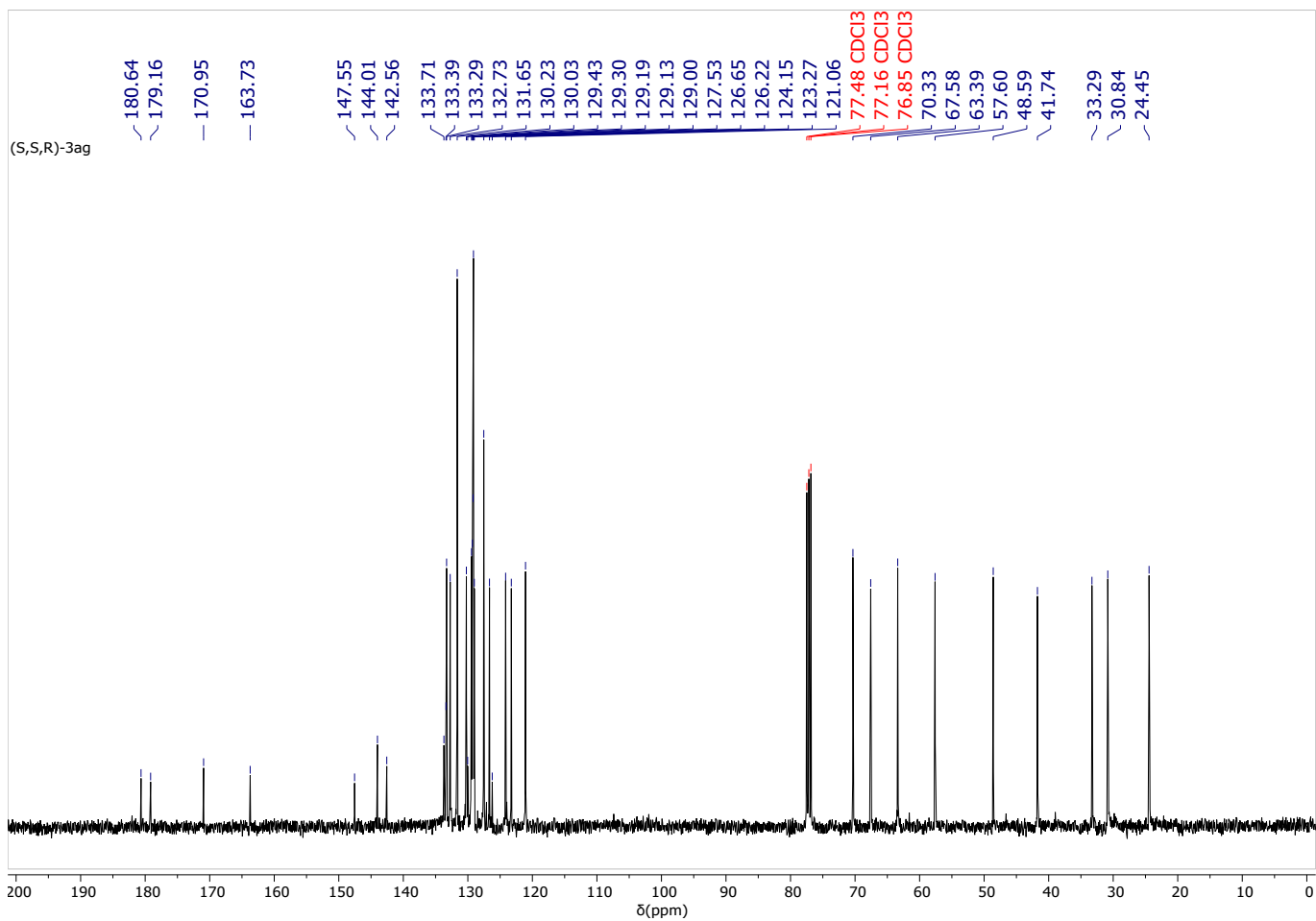


Figure S25. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ag** (in CDCl_3)

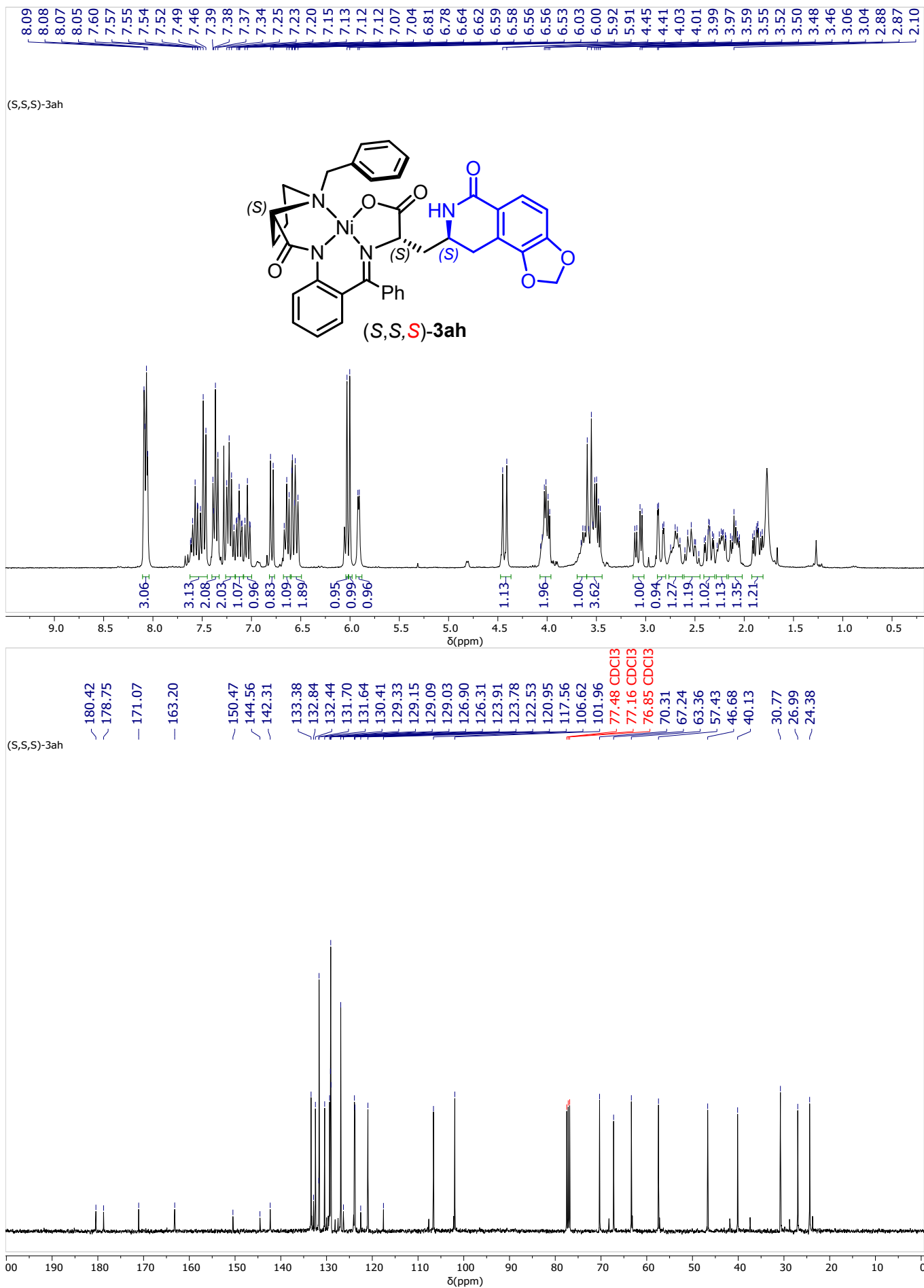
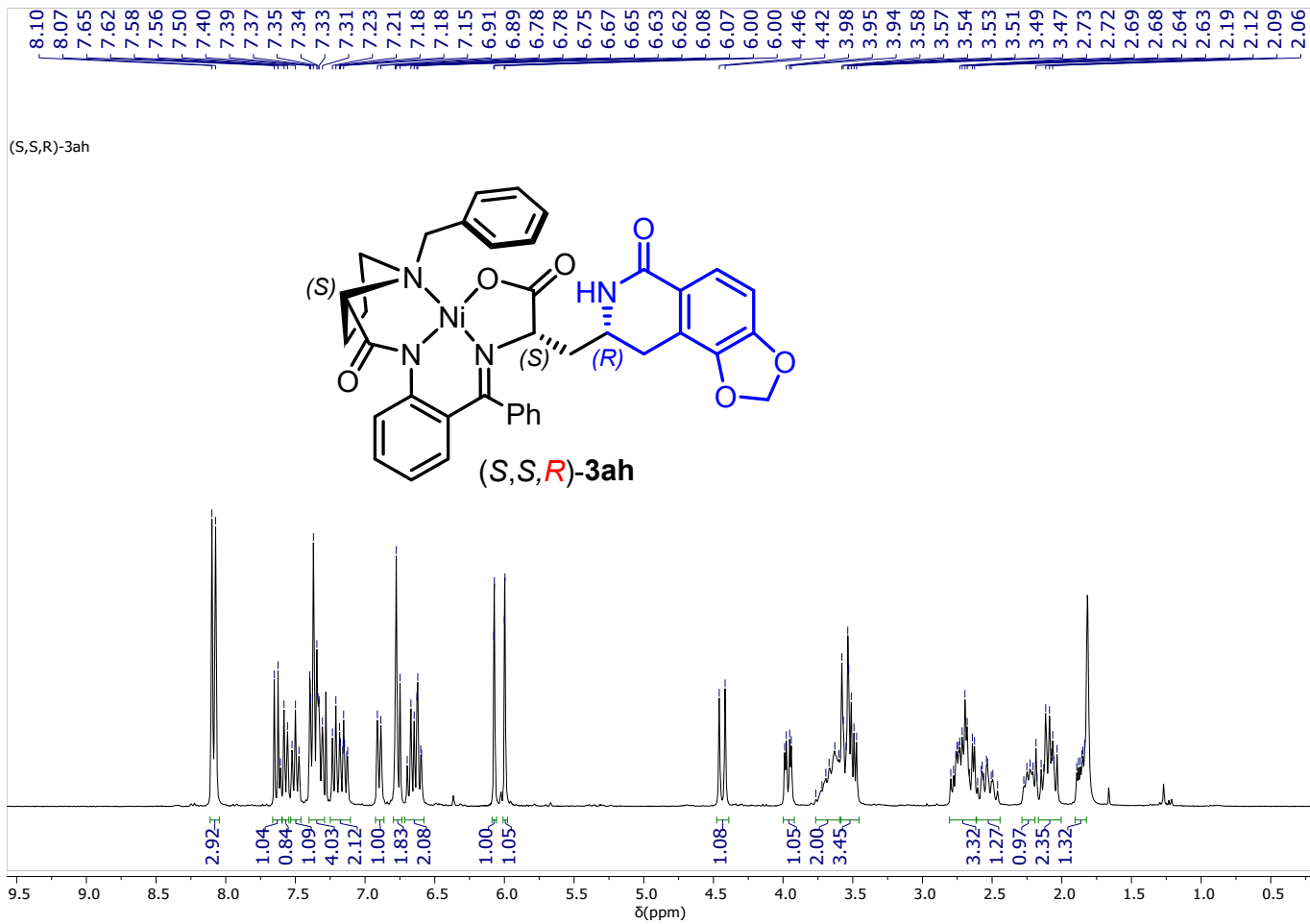


Figure S26. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (S,S,S)-3ah (in CDCl_3)



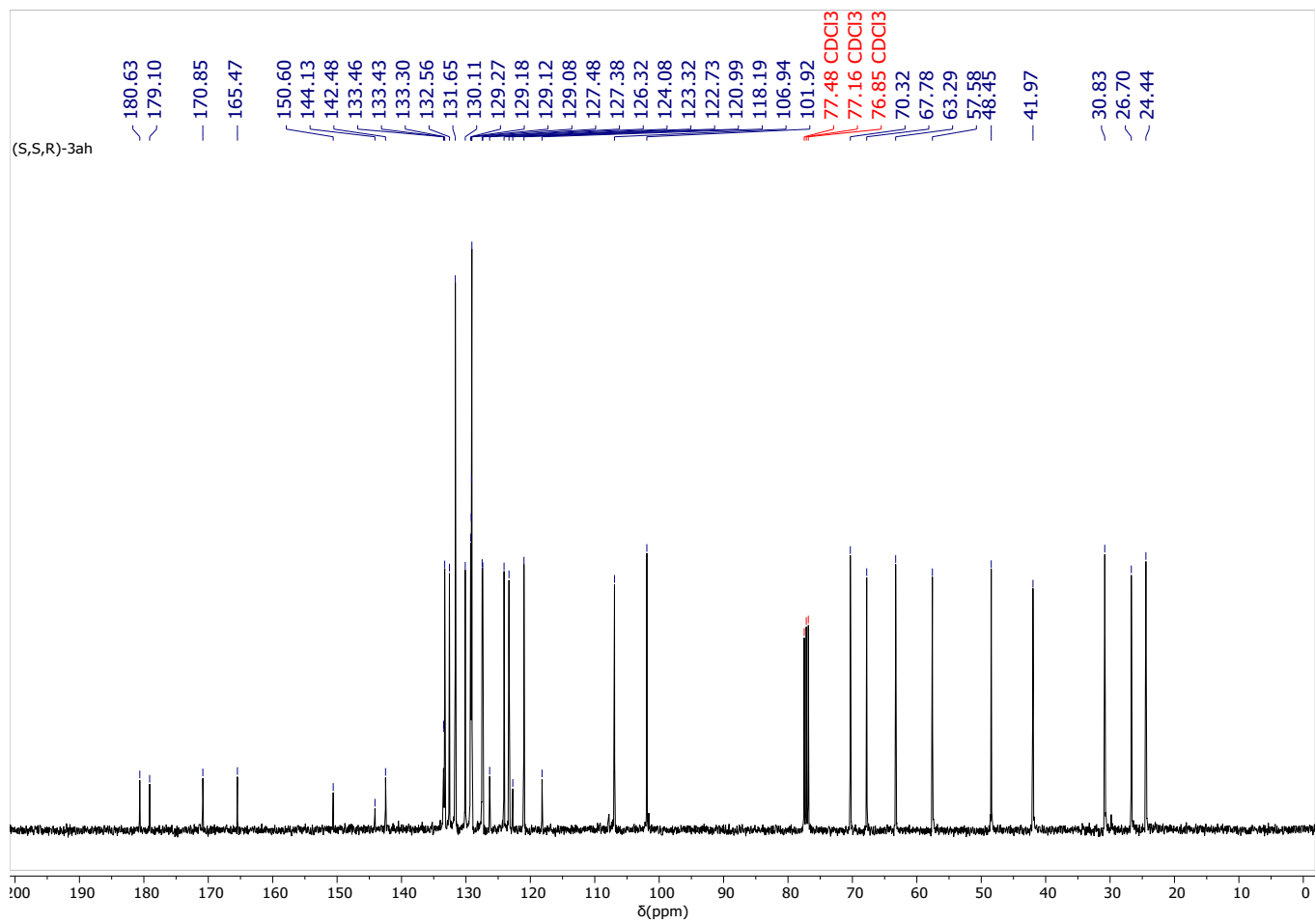
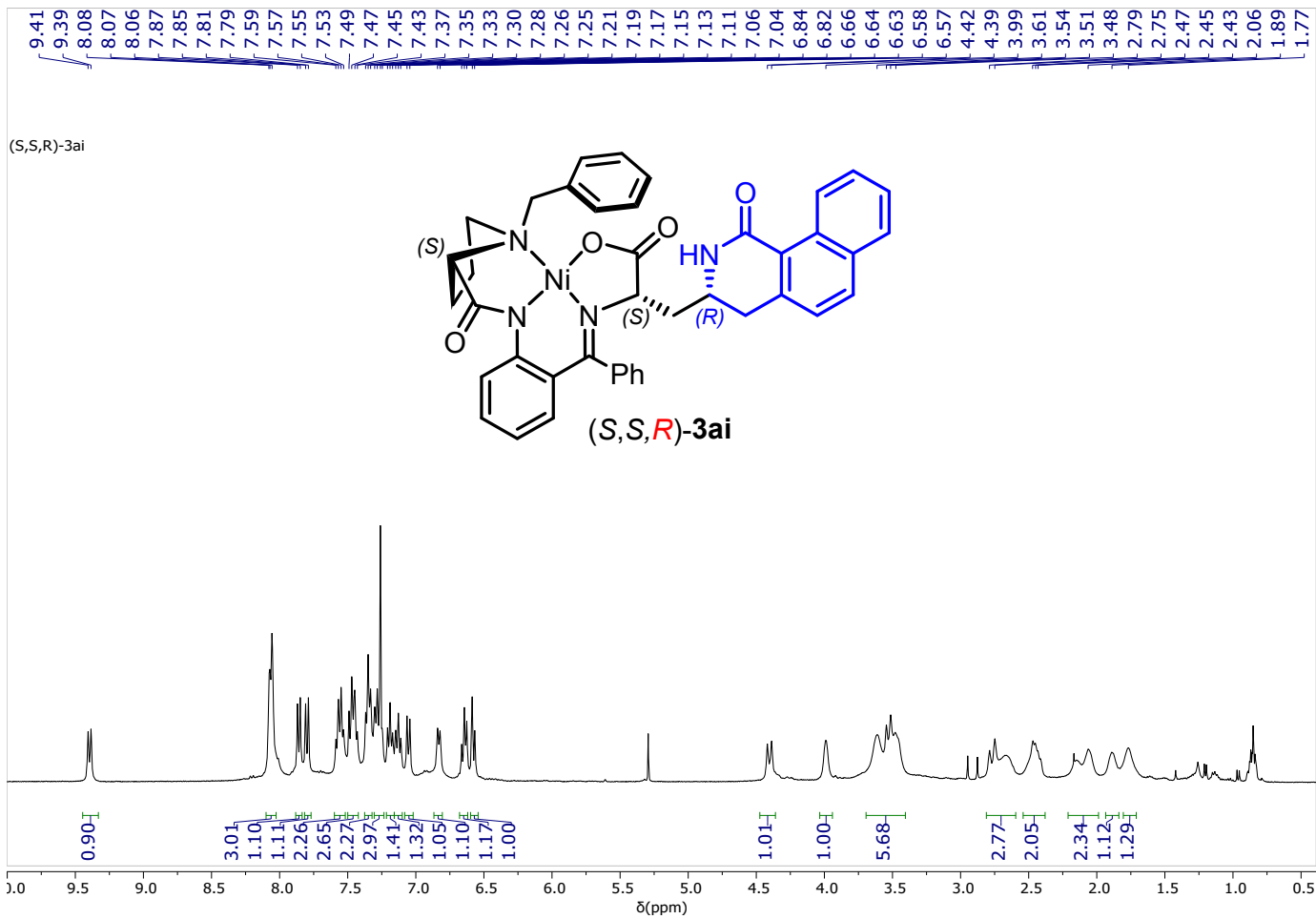


Figure S27. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ah** (in CDCl_3)



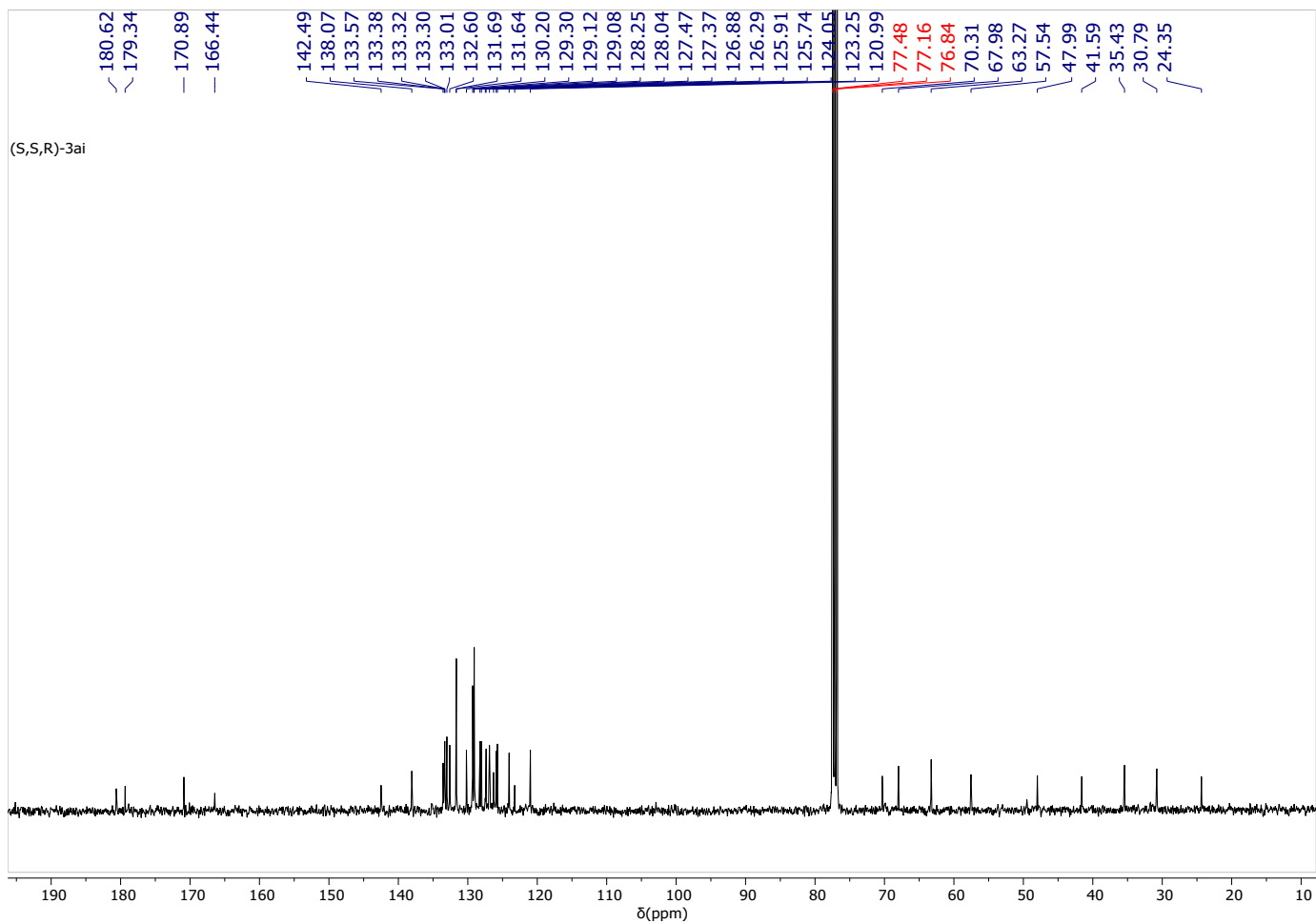
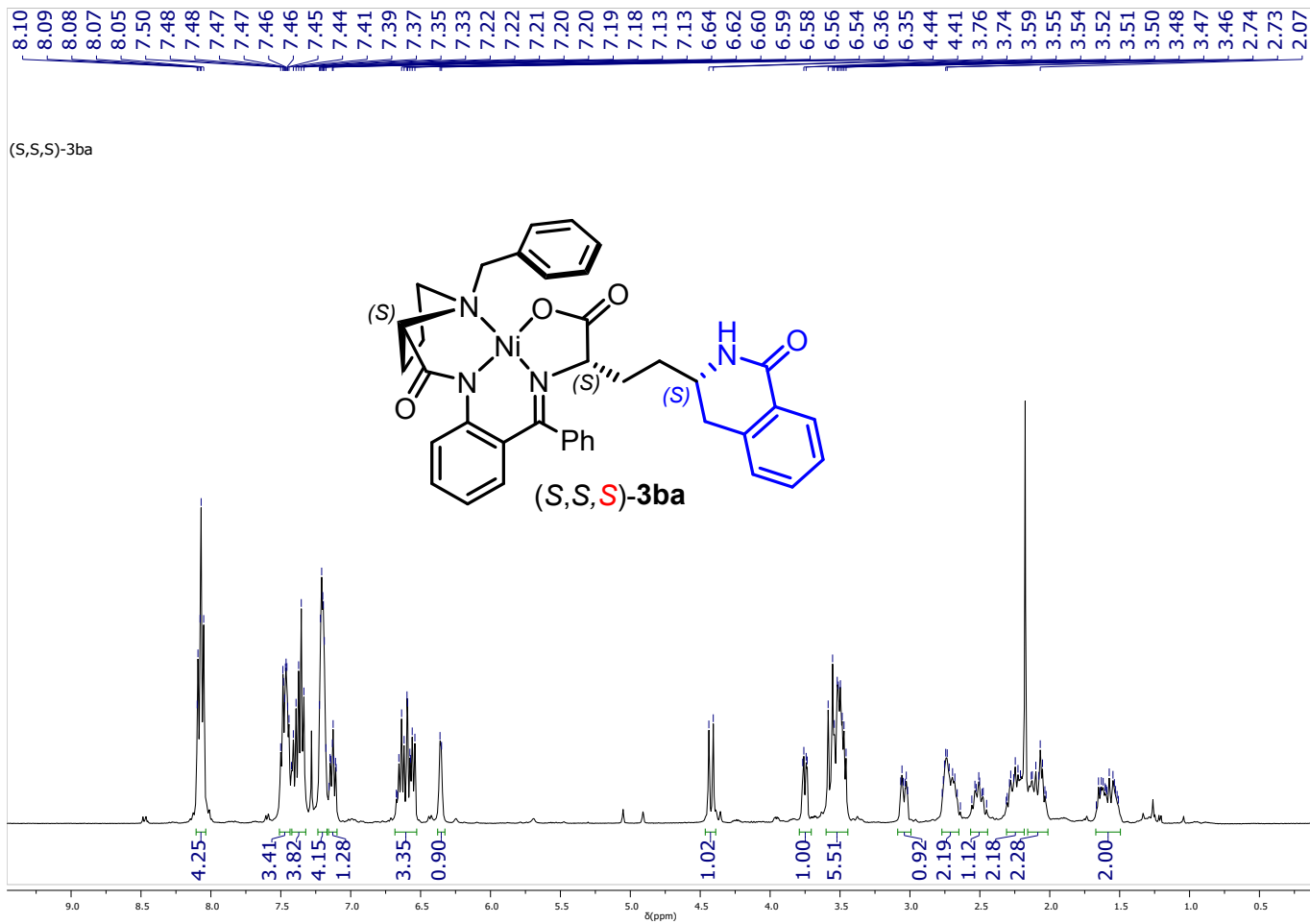


Figure S28. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ai** (in CDCl_3)



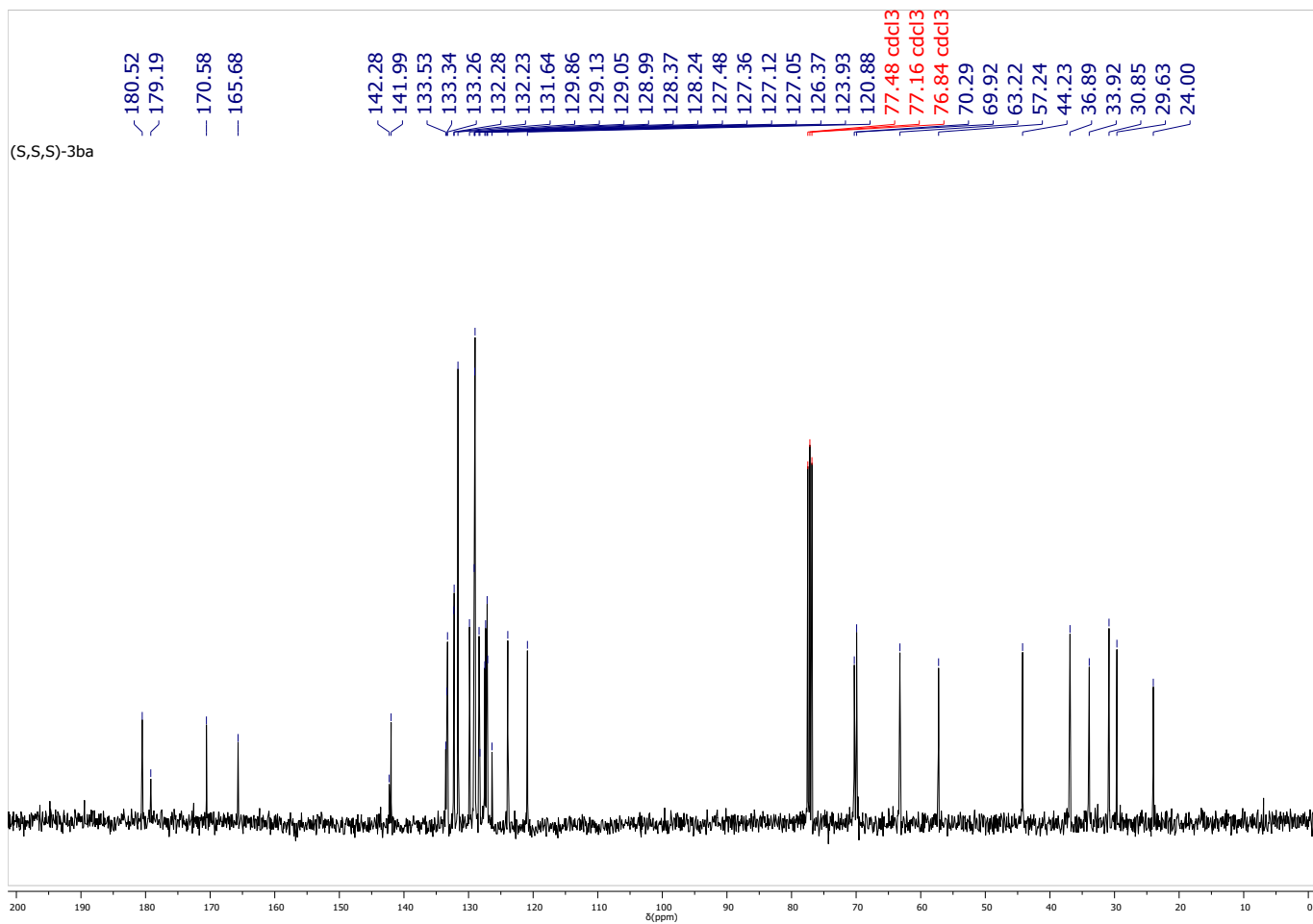
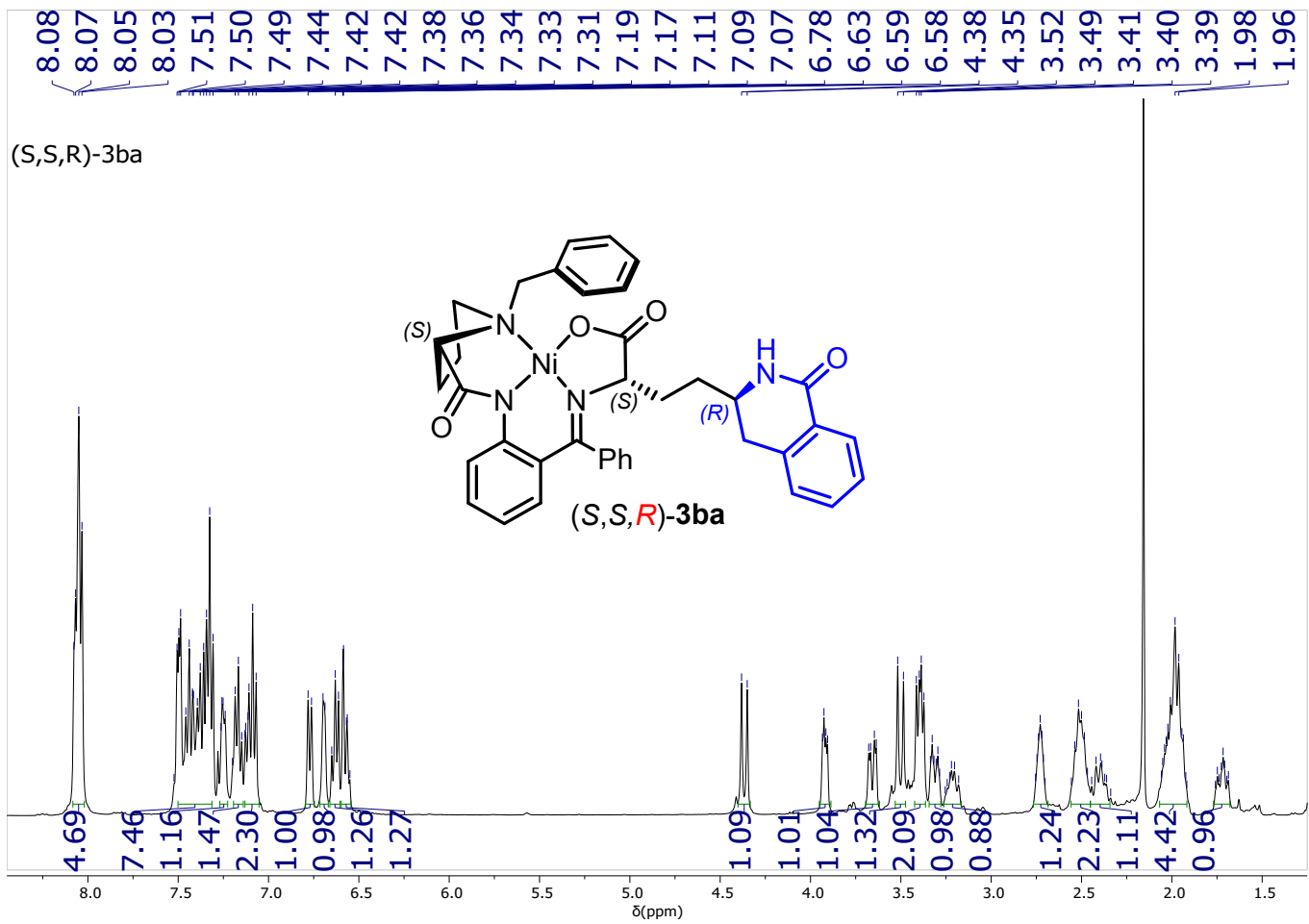


Figure S29. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ba** (in CDCl_3)



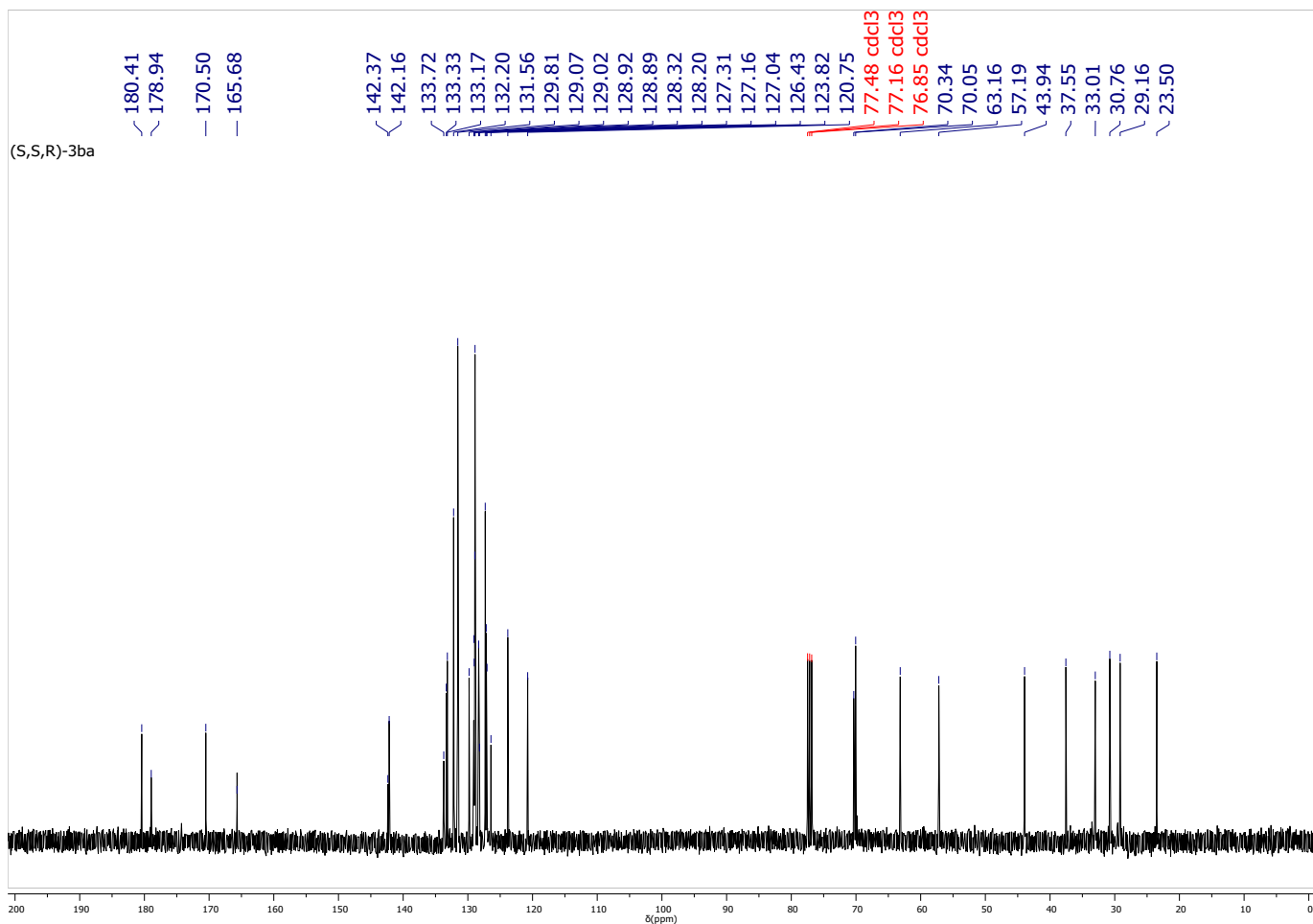


Figure S30. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ba** (in CDCl_3)

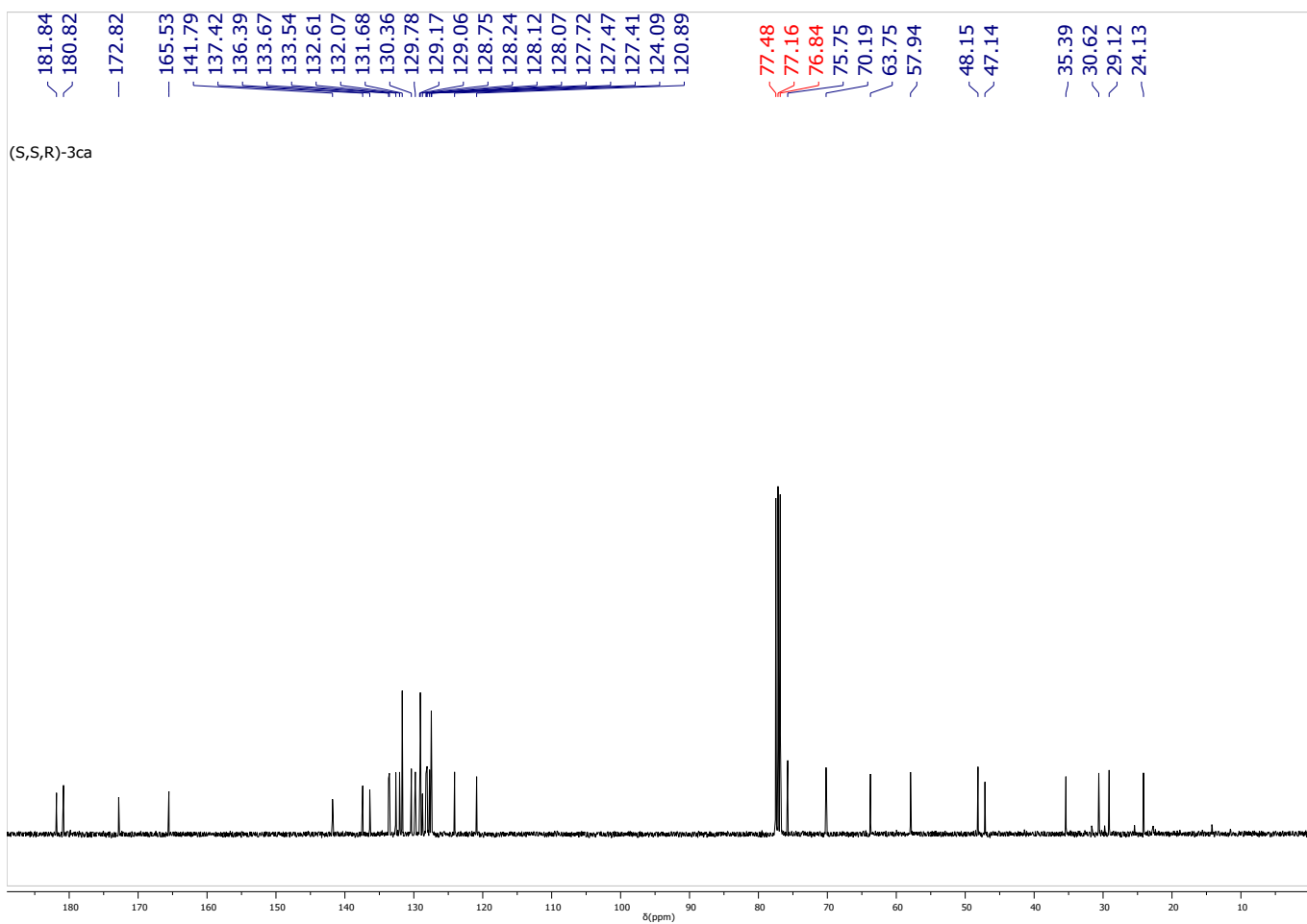
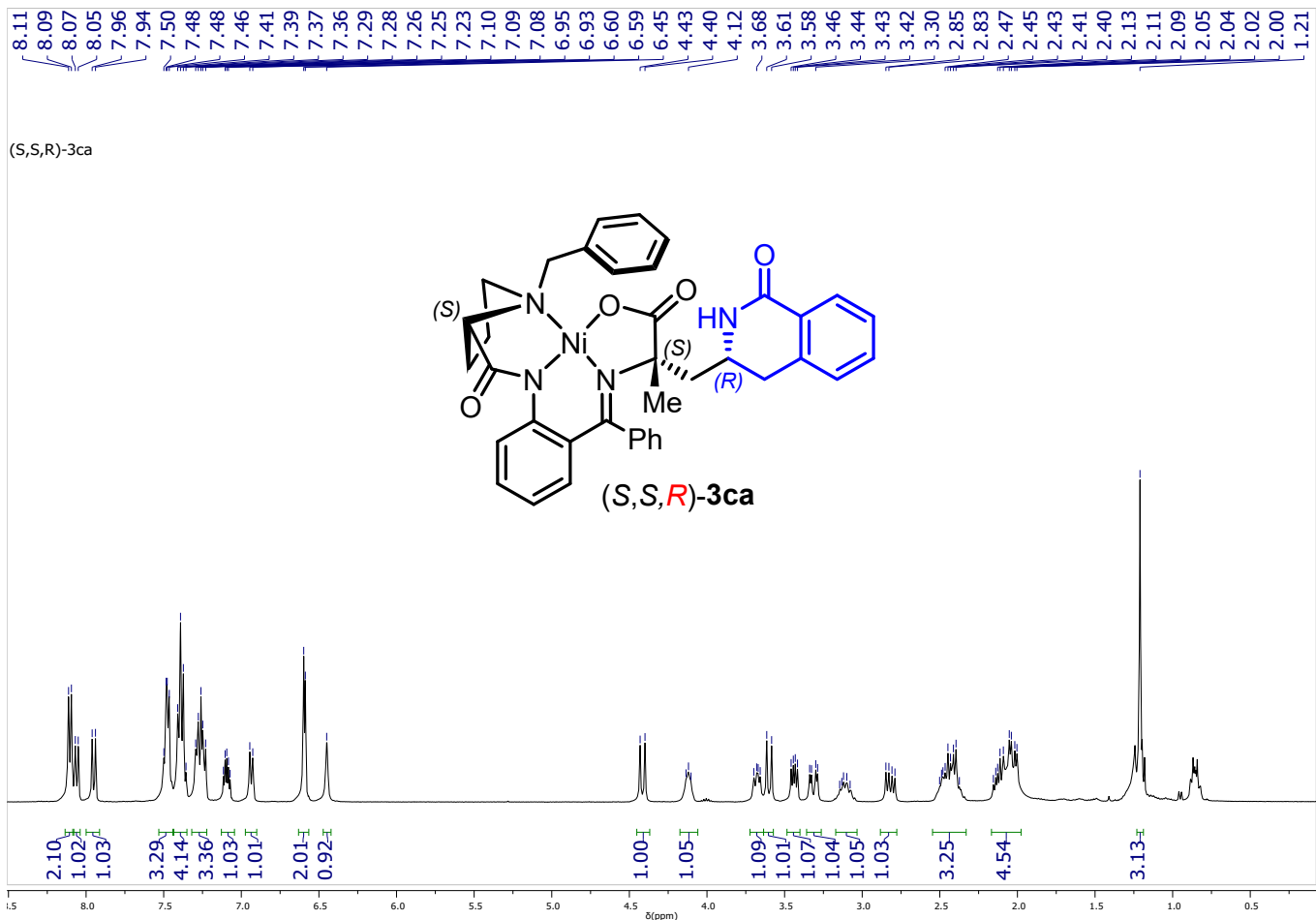
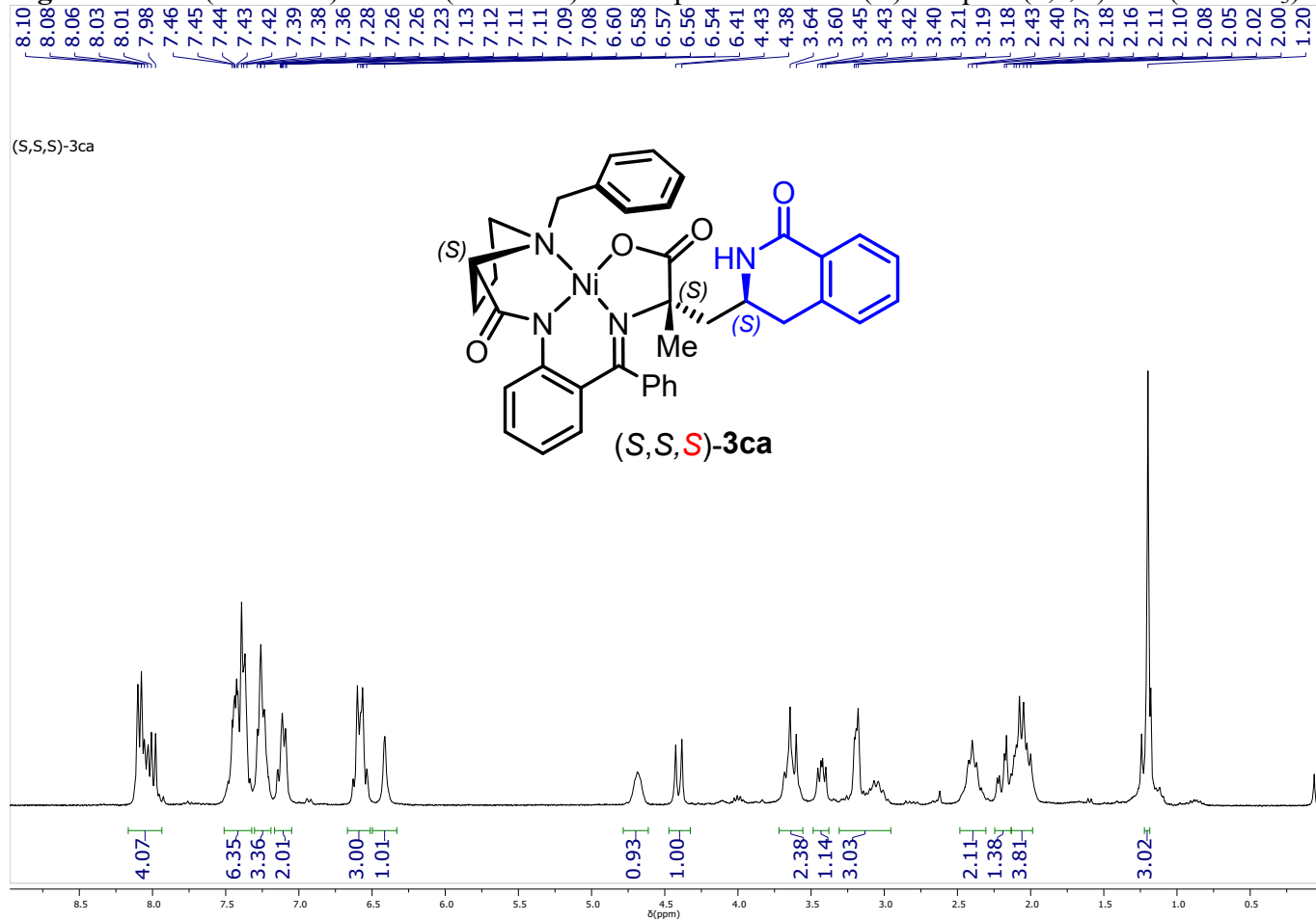


Figure S31. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3ca** (in CDCl_3)



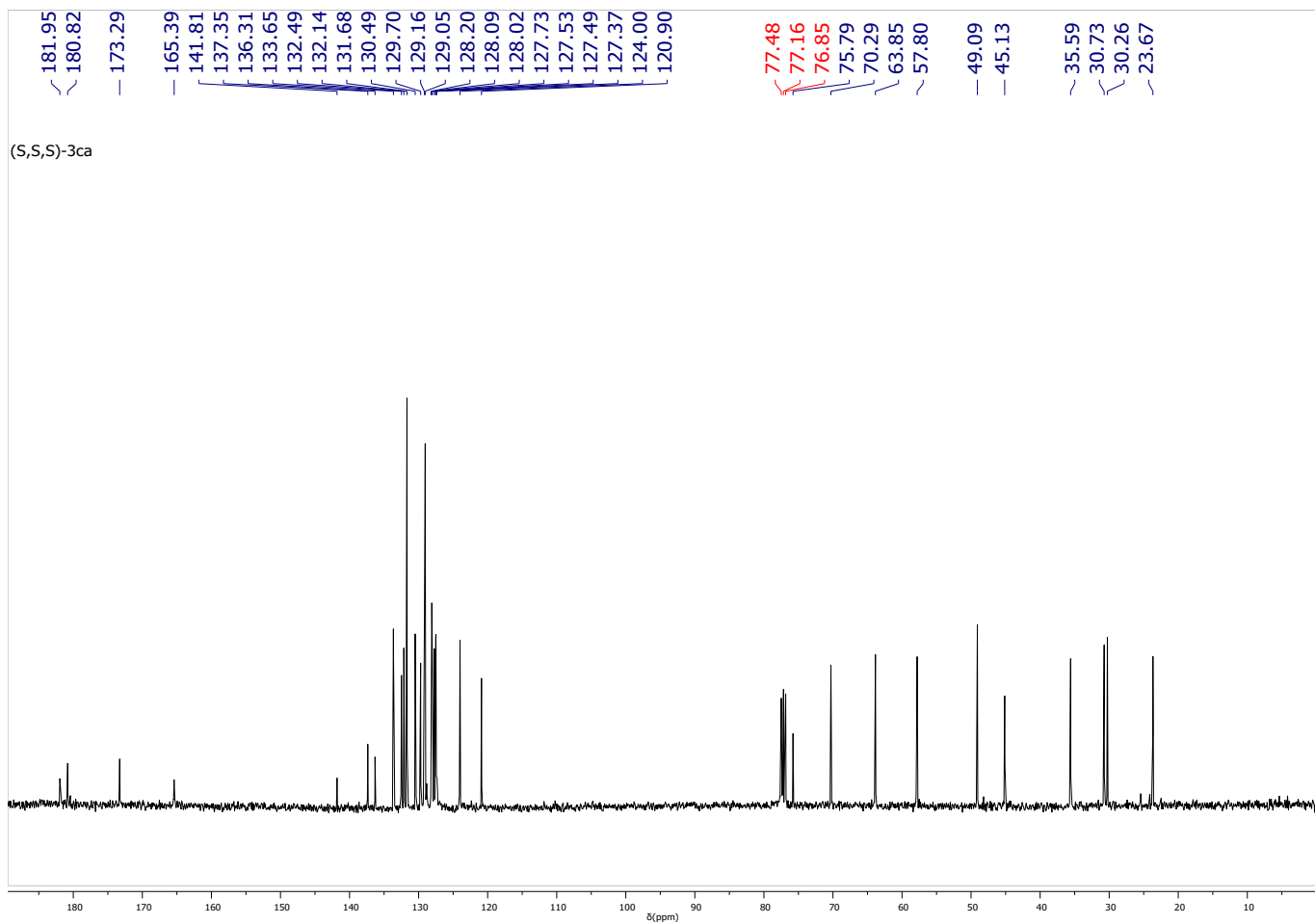


Figure S32. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3ca** (in CDCl_3)

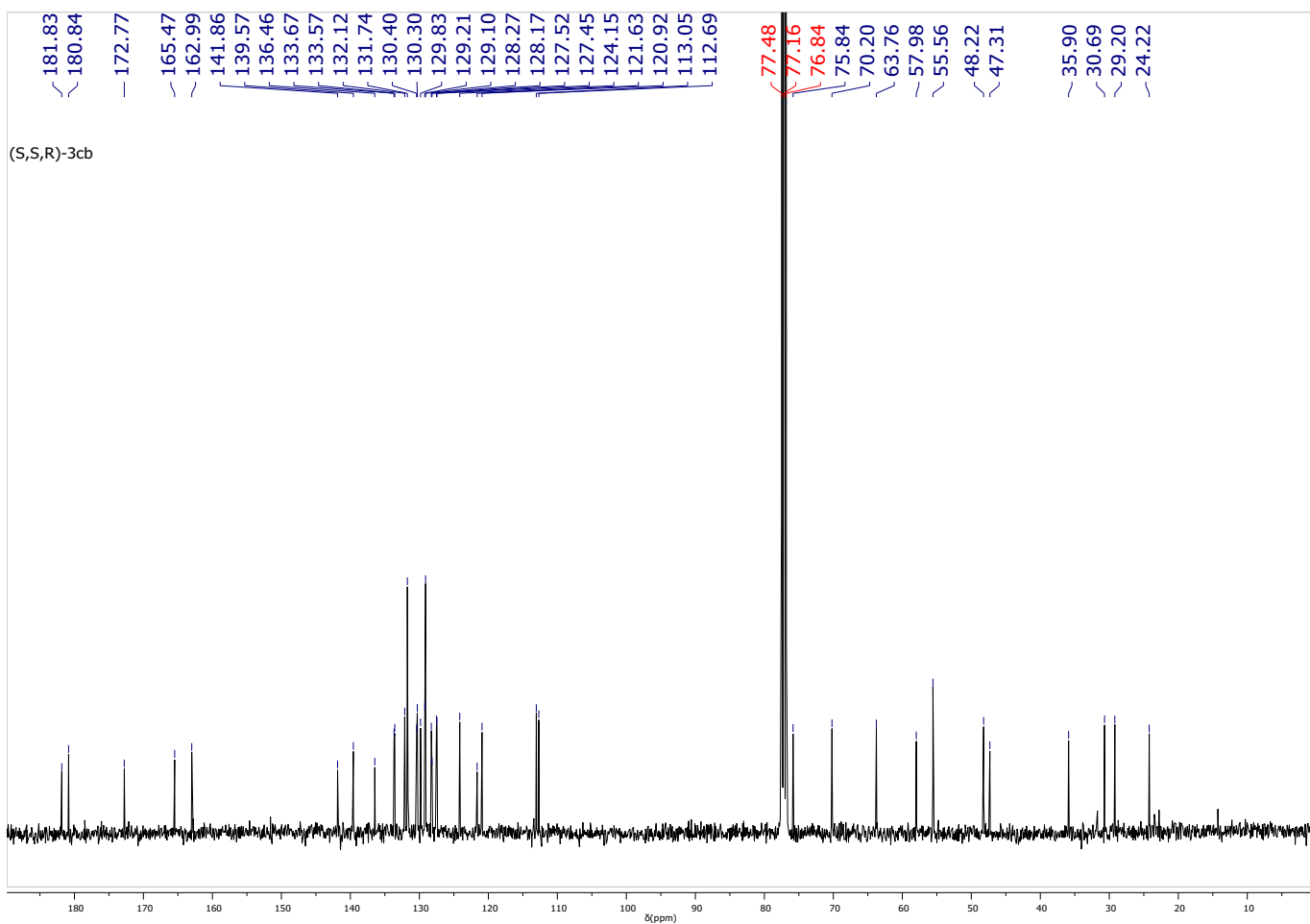
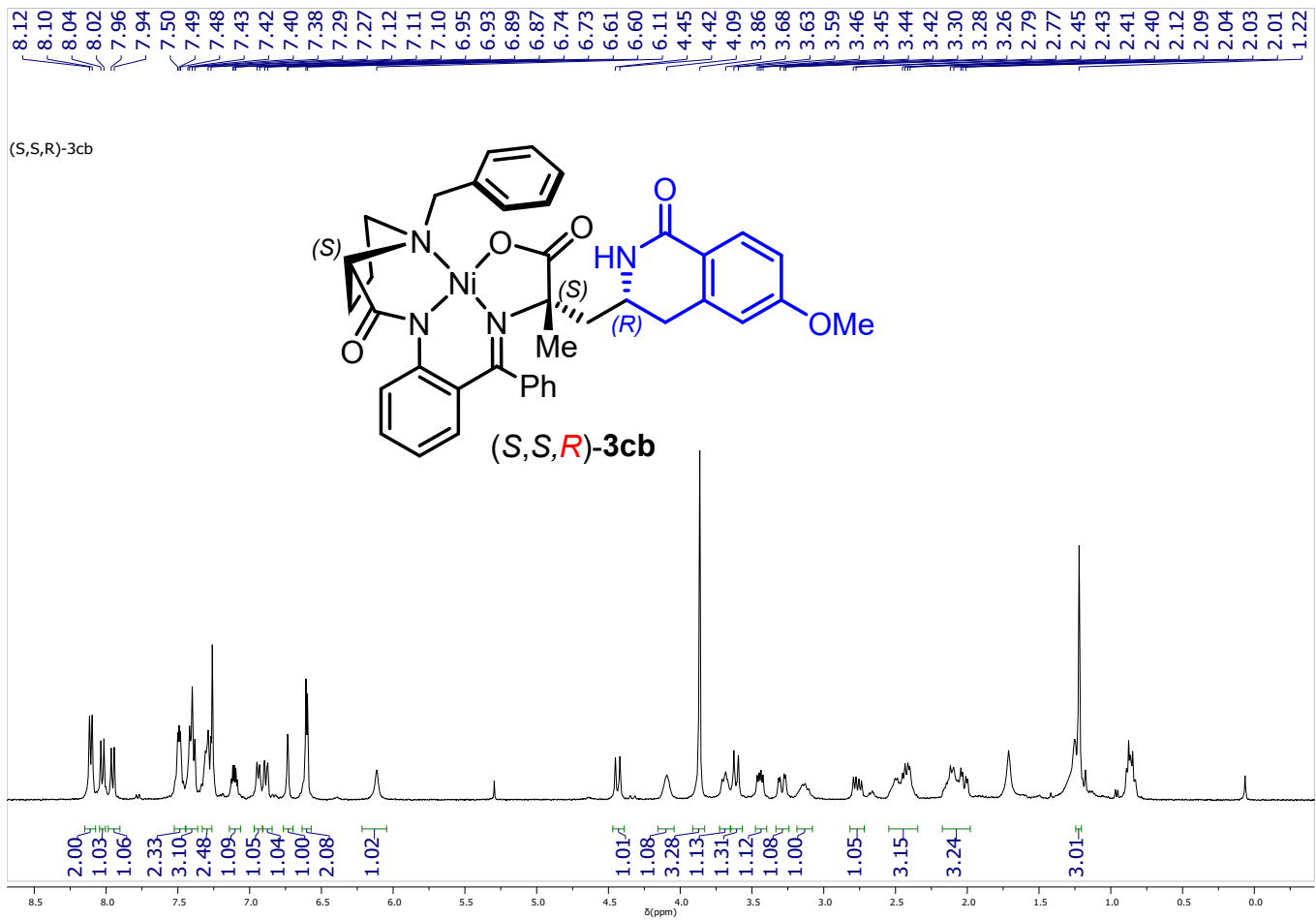
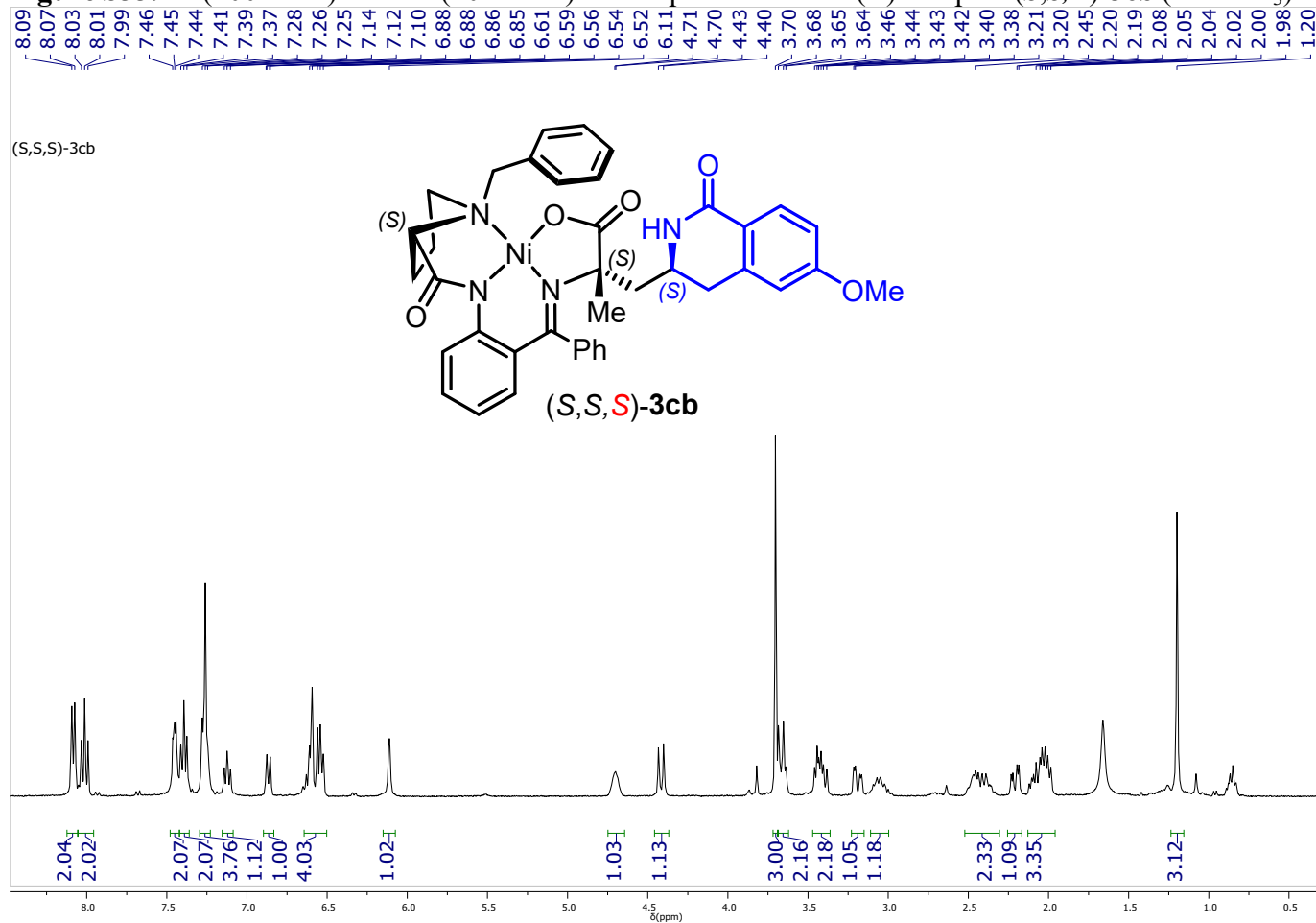


Figure S33. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3cb** (in CDCl_3)



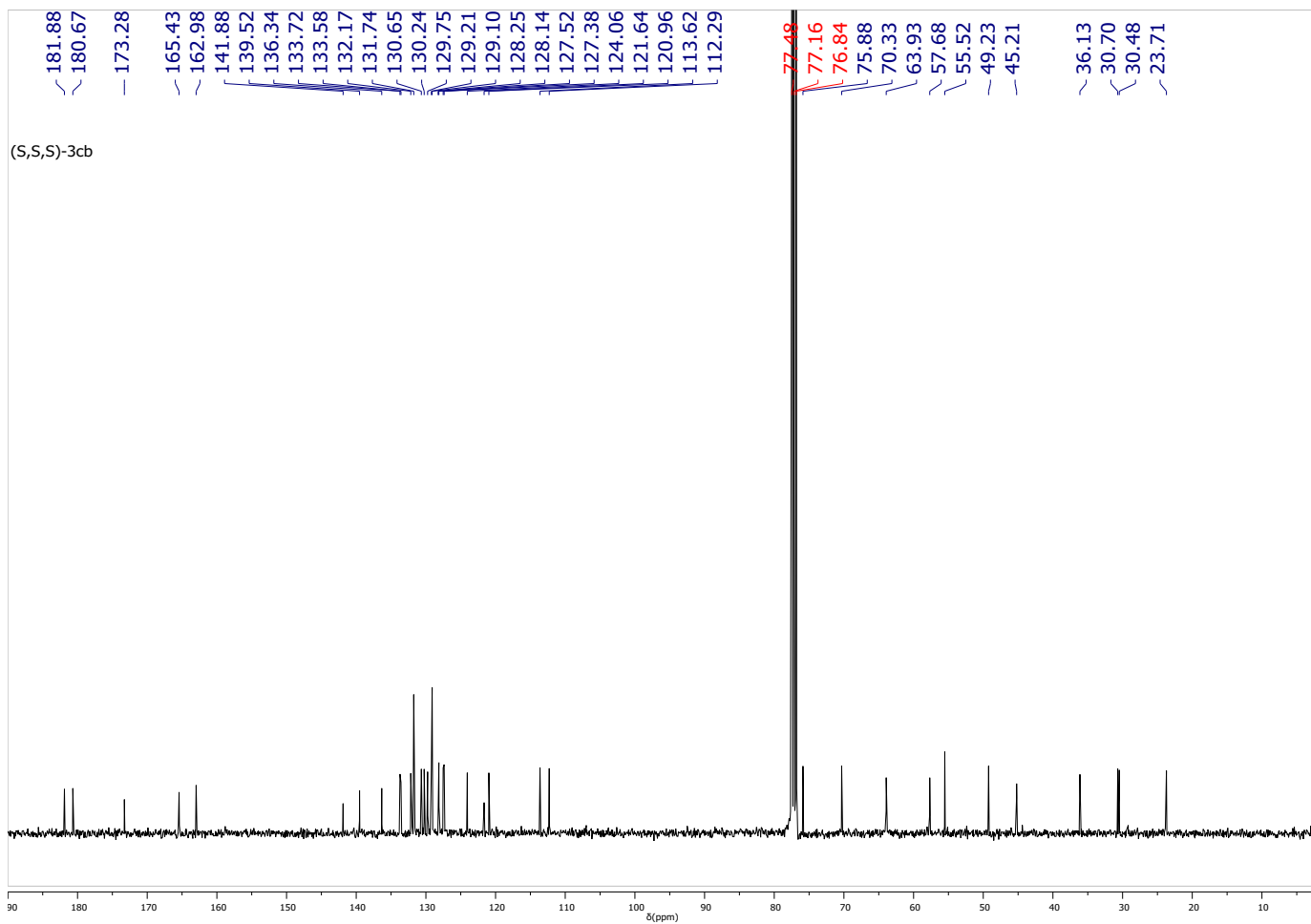
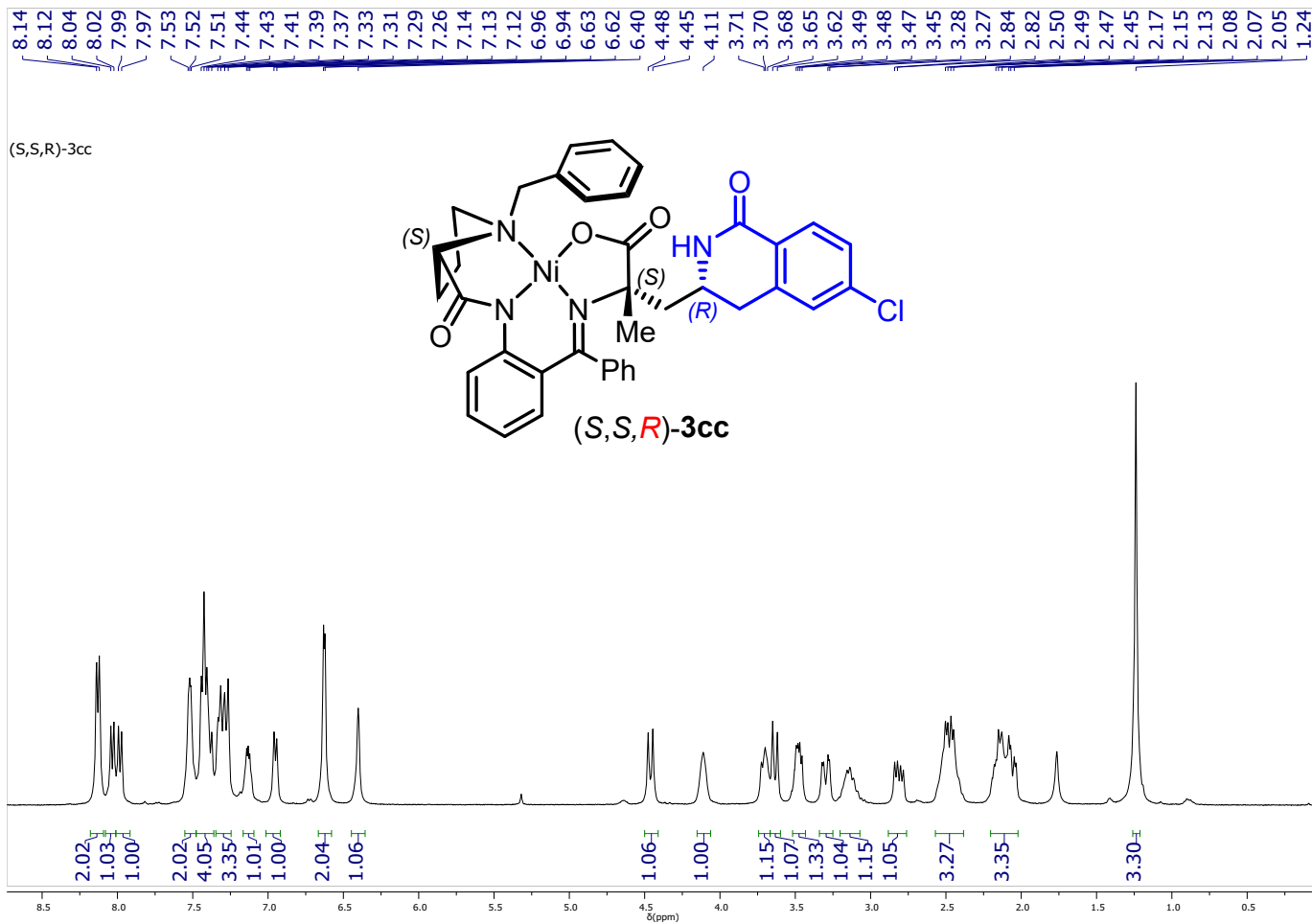


Figure S34. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3cb** (in CDCl_3)



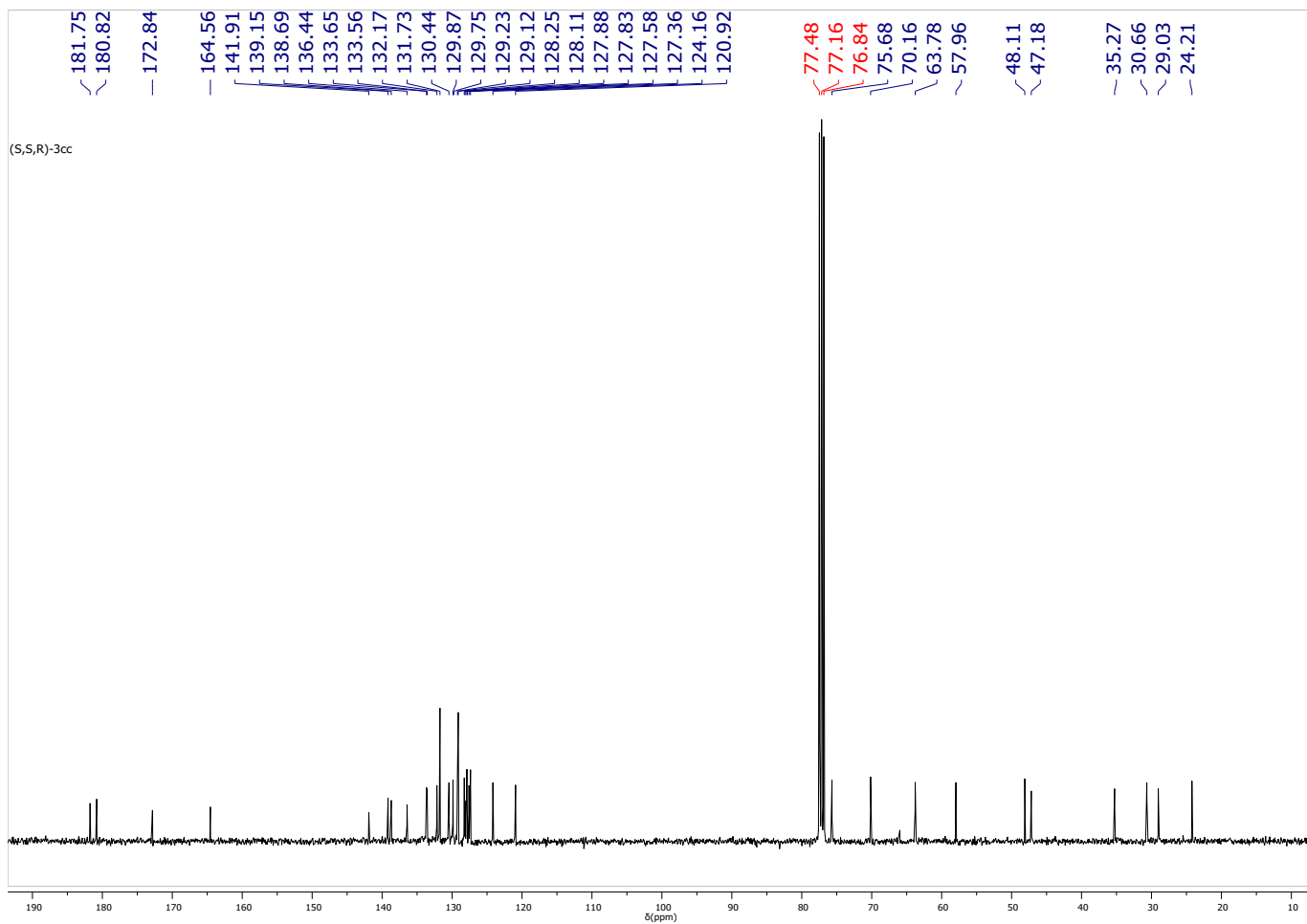


Figure S35. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3cc** (in CDCl_3)

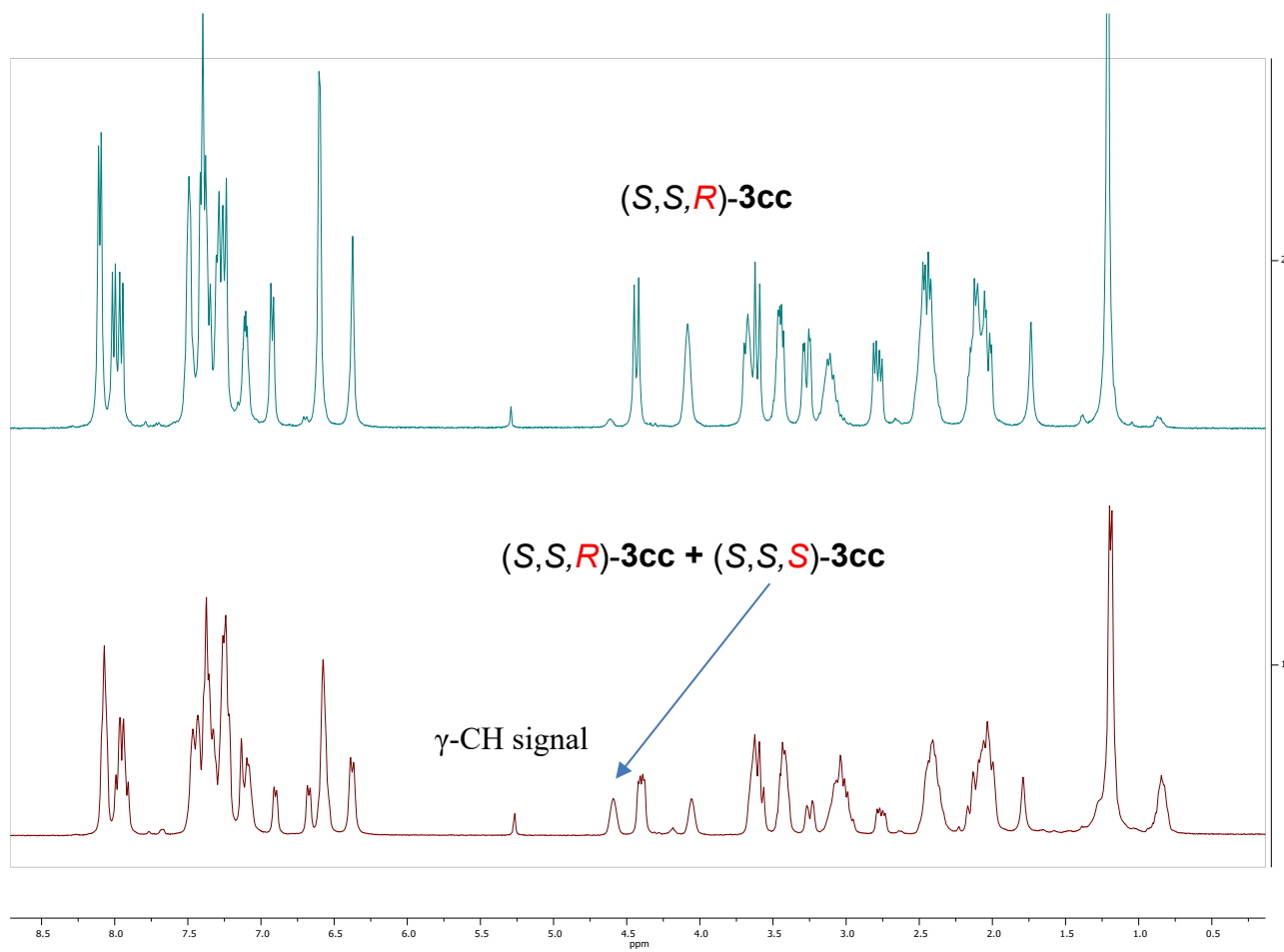
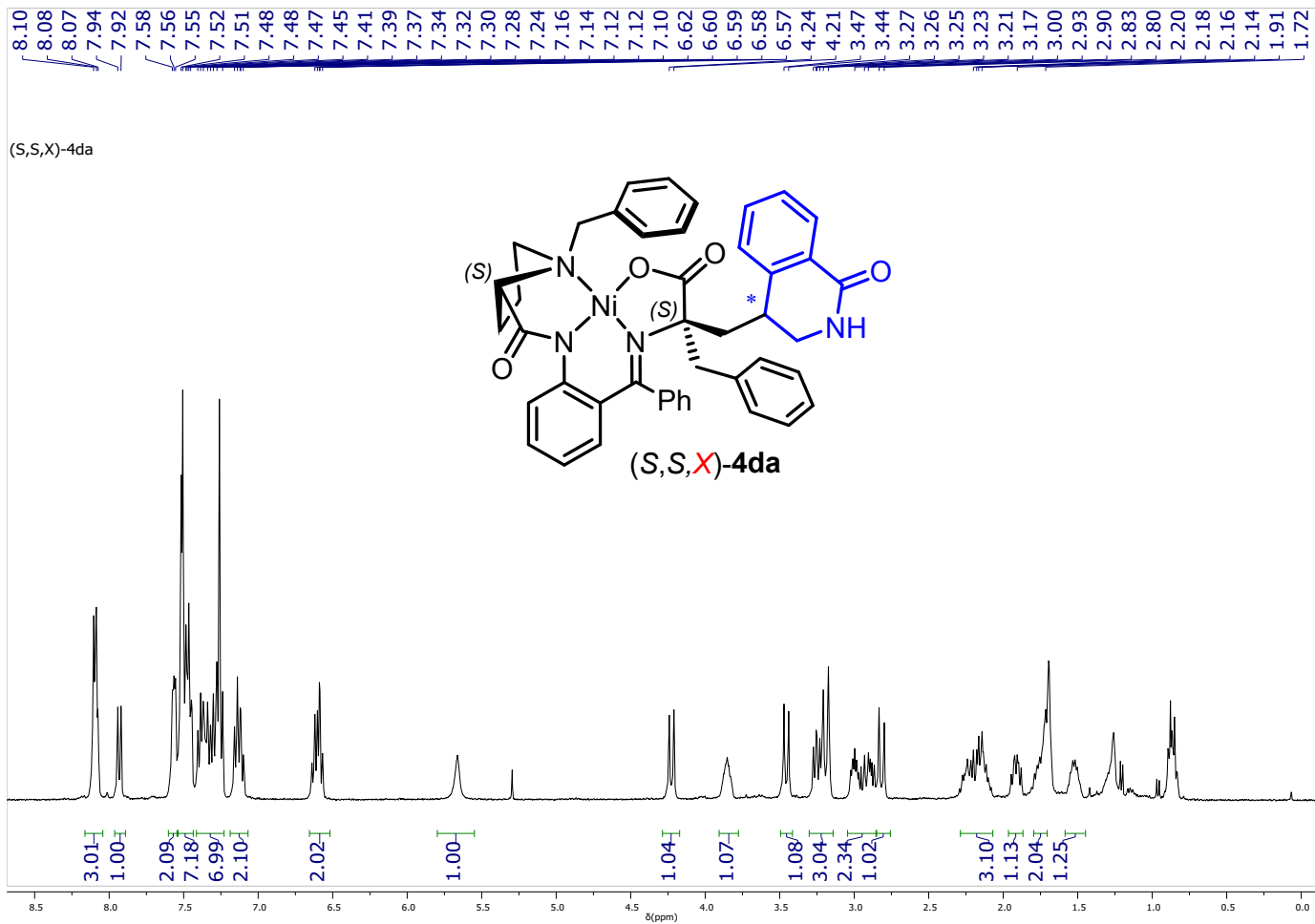


Figure S36. ^1H (400 MHz) NMR spectra of the diastereomeric Ni(II) complexes **3cc** (in CDCl_3)



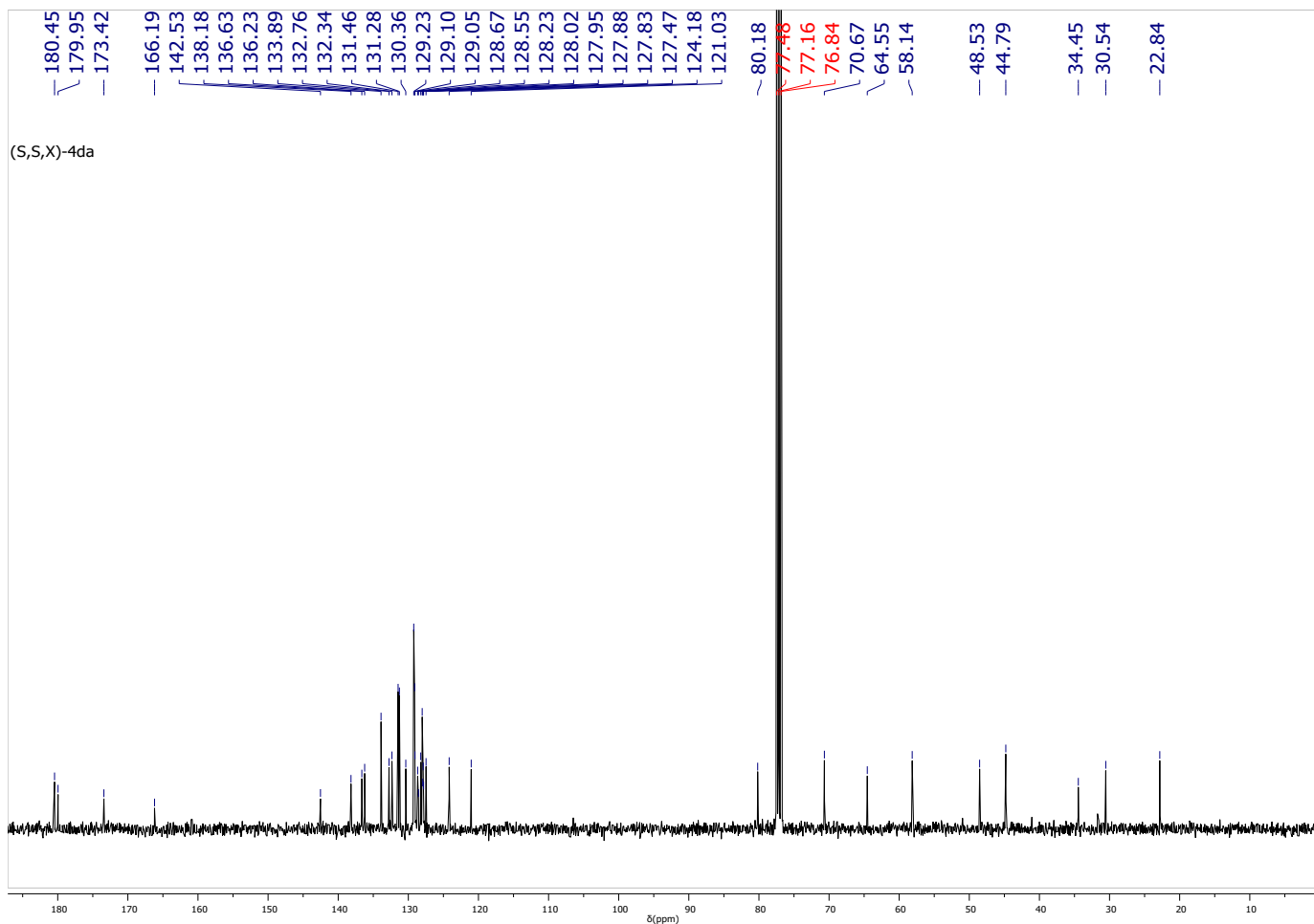
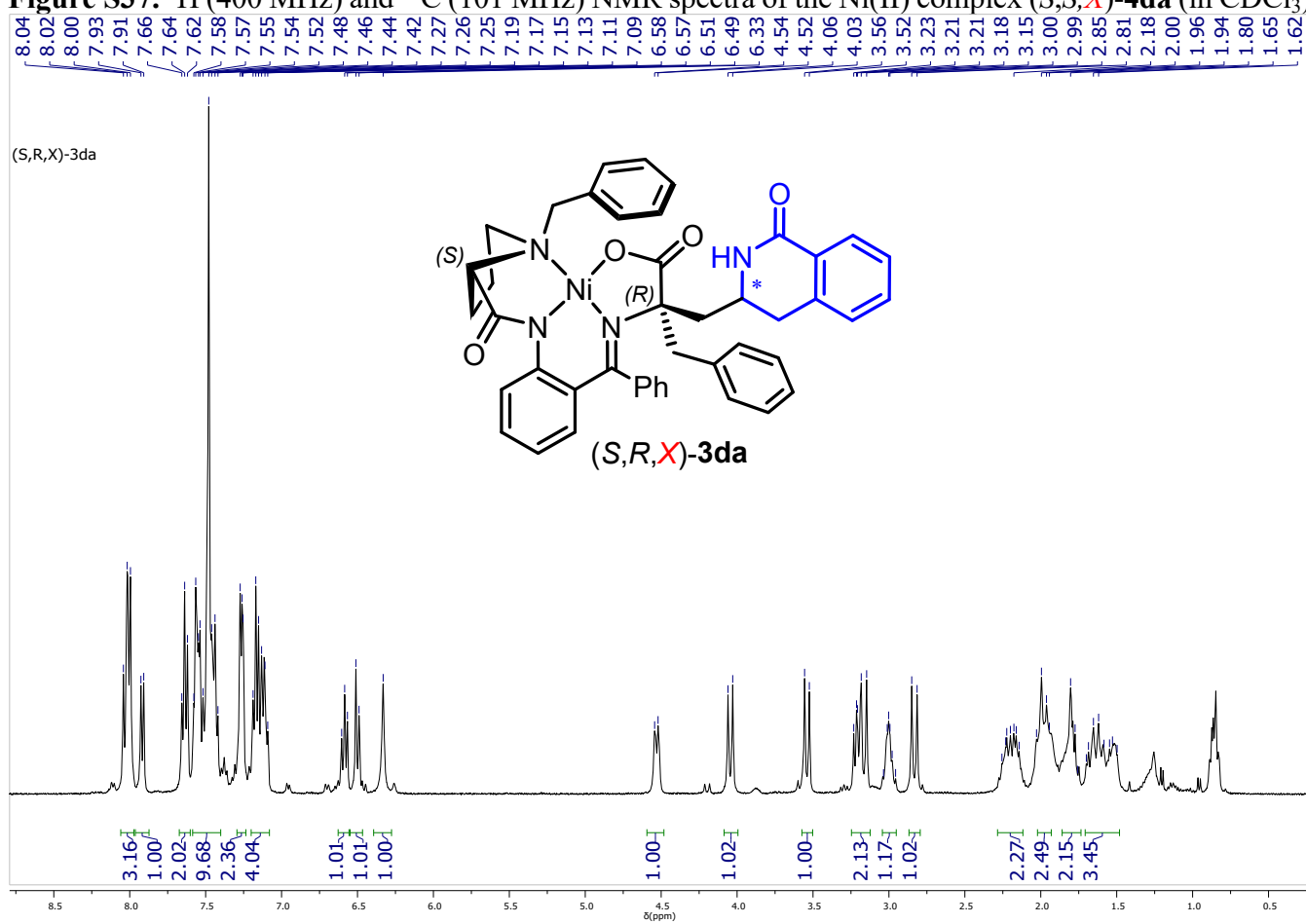


Figure S37. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (S,S,X)-4da (in CDCl_3)



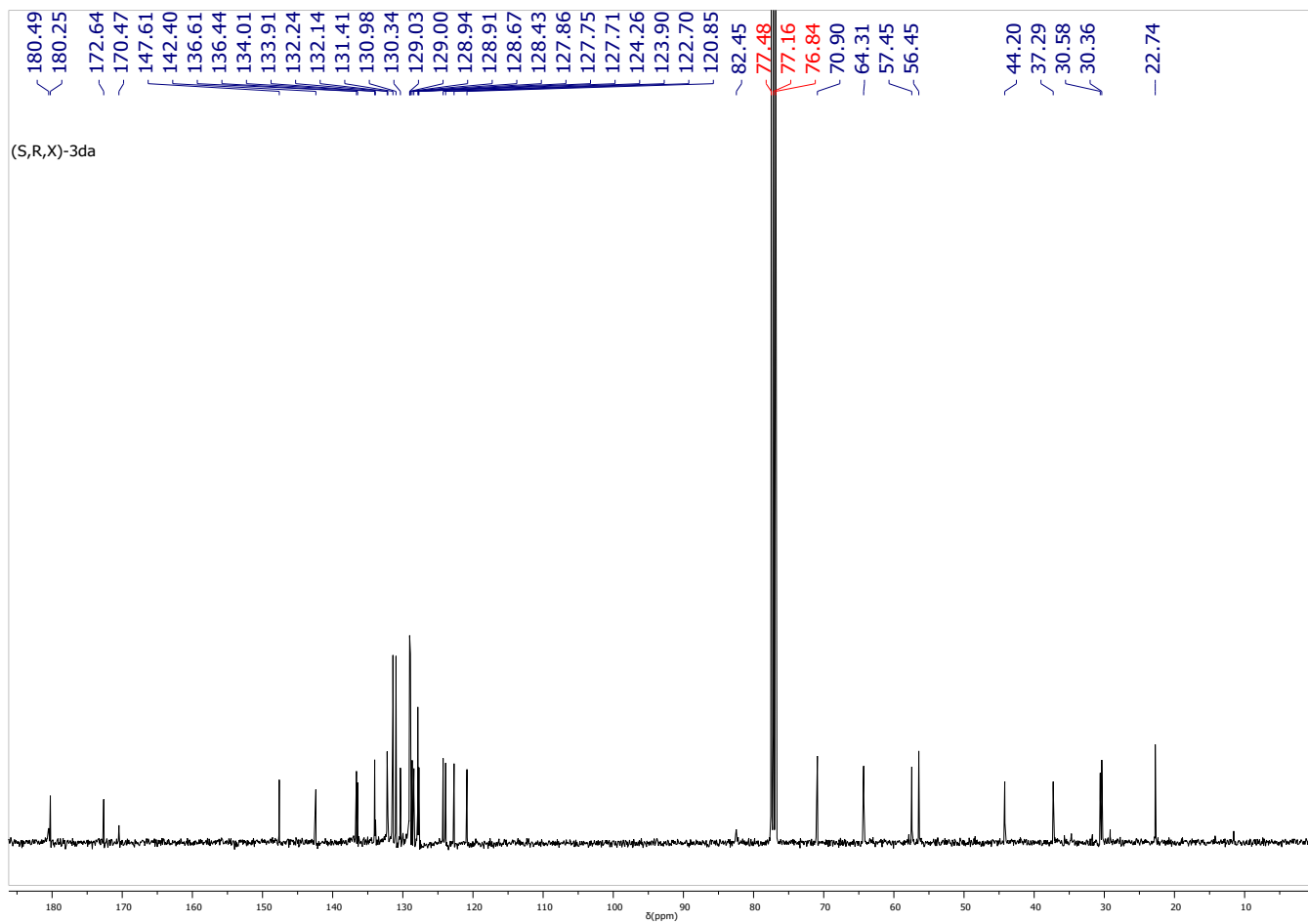
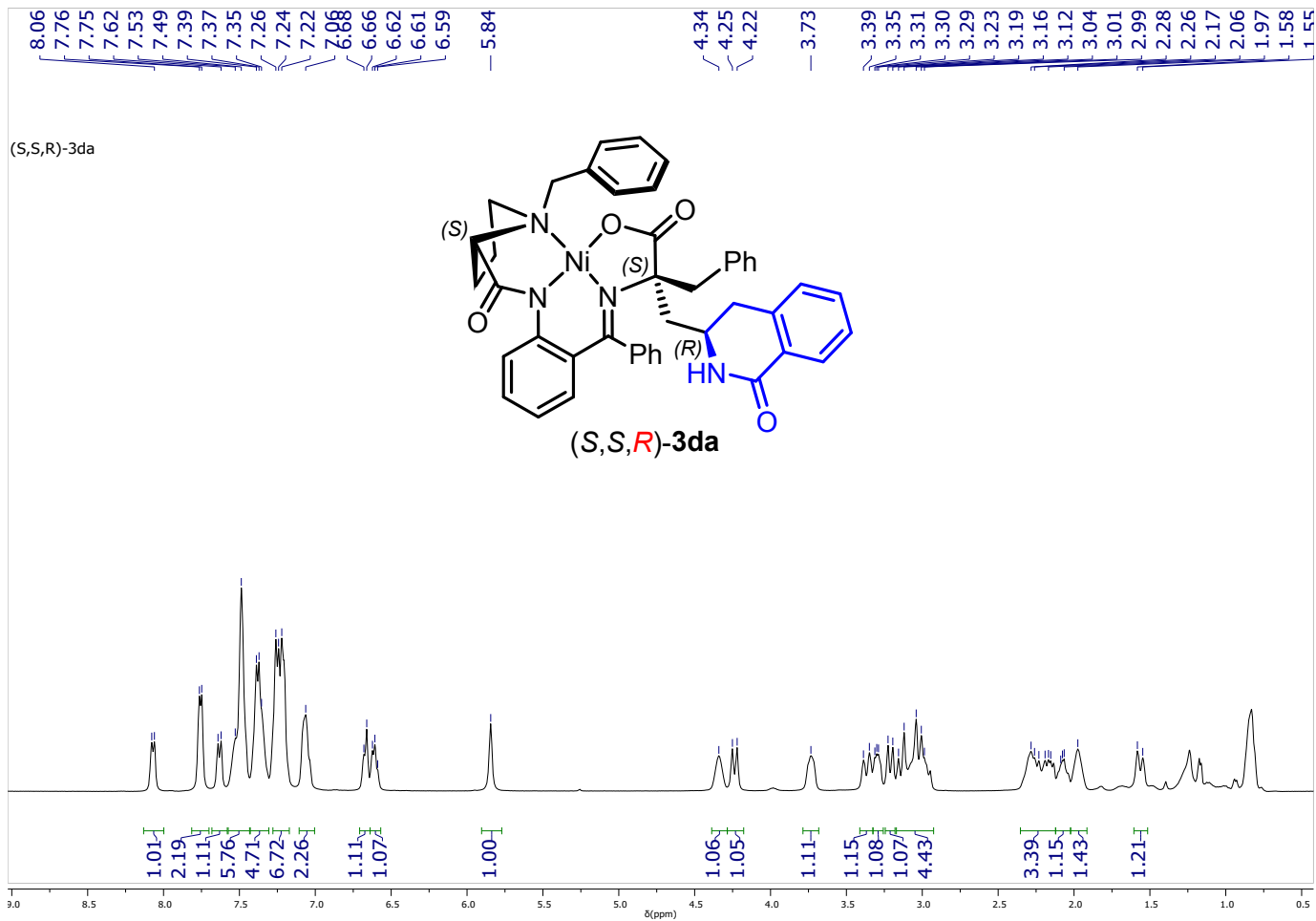


Figure S38. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,R,X*)-**3da** (in CDCl_3)



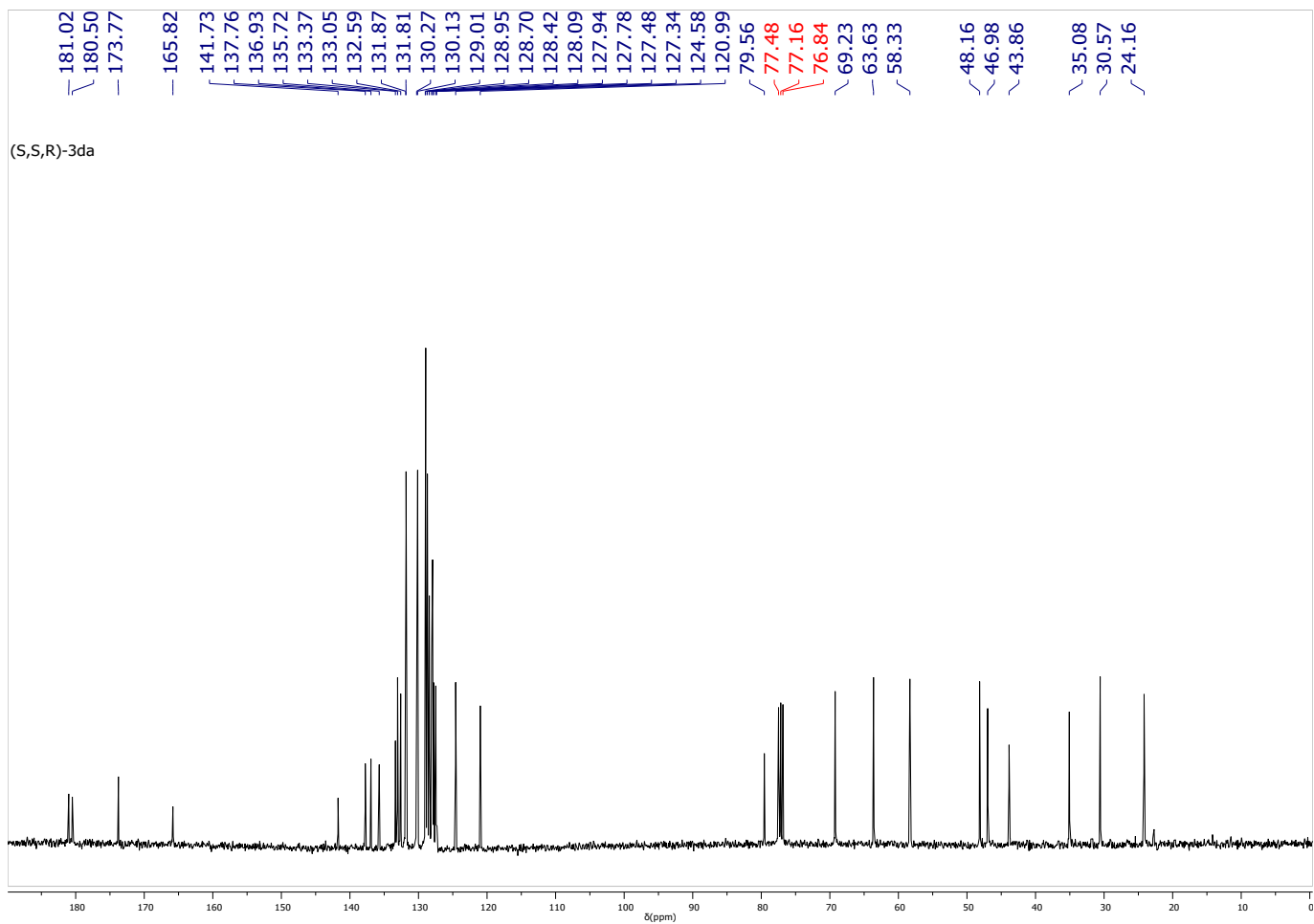
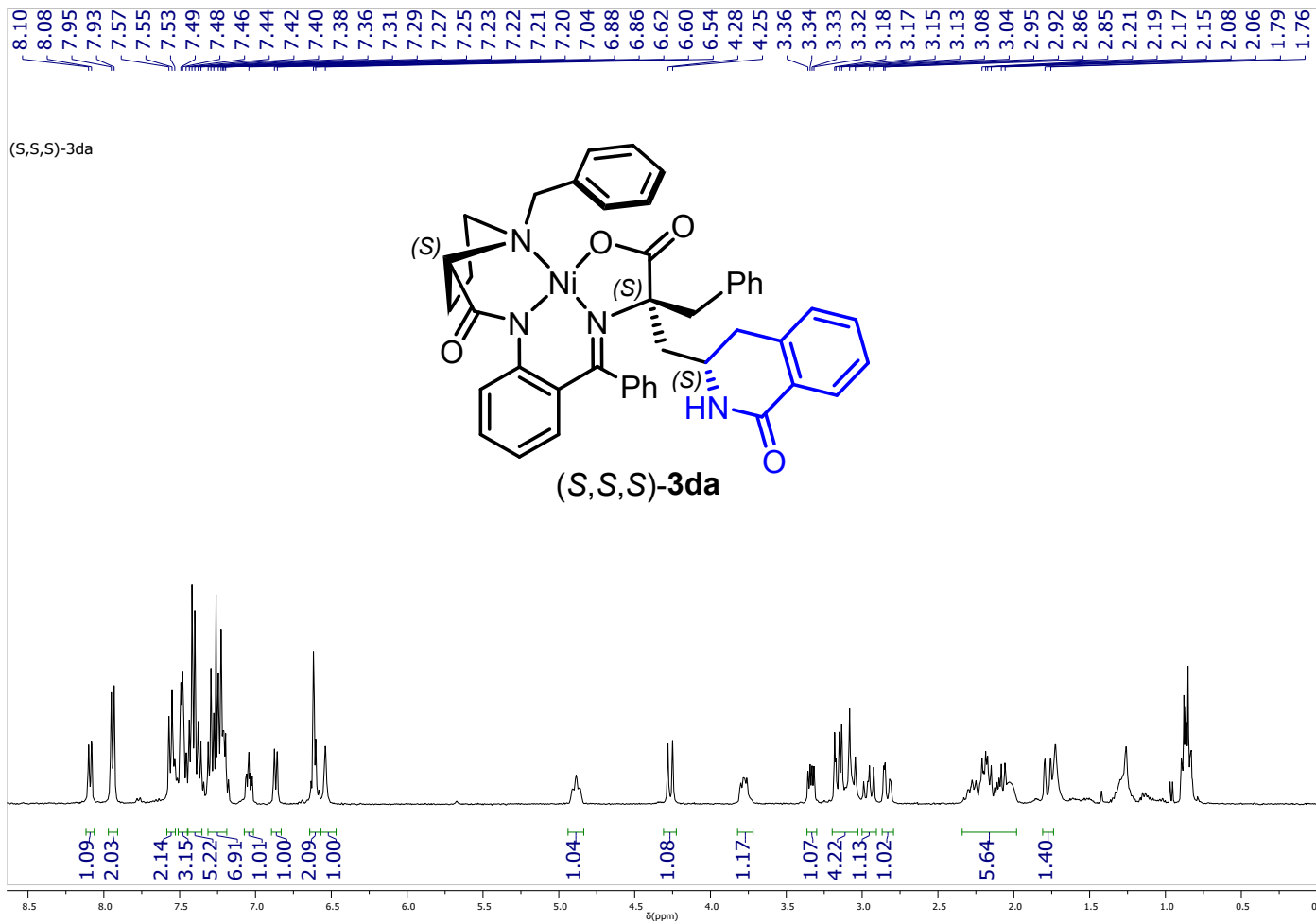


Figure S39. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,R*)-**3da** (in CDCl_3)



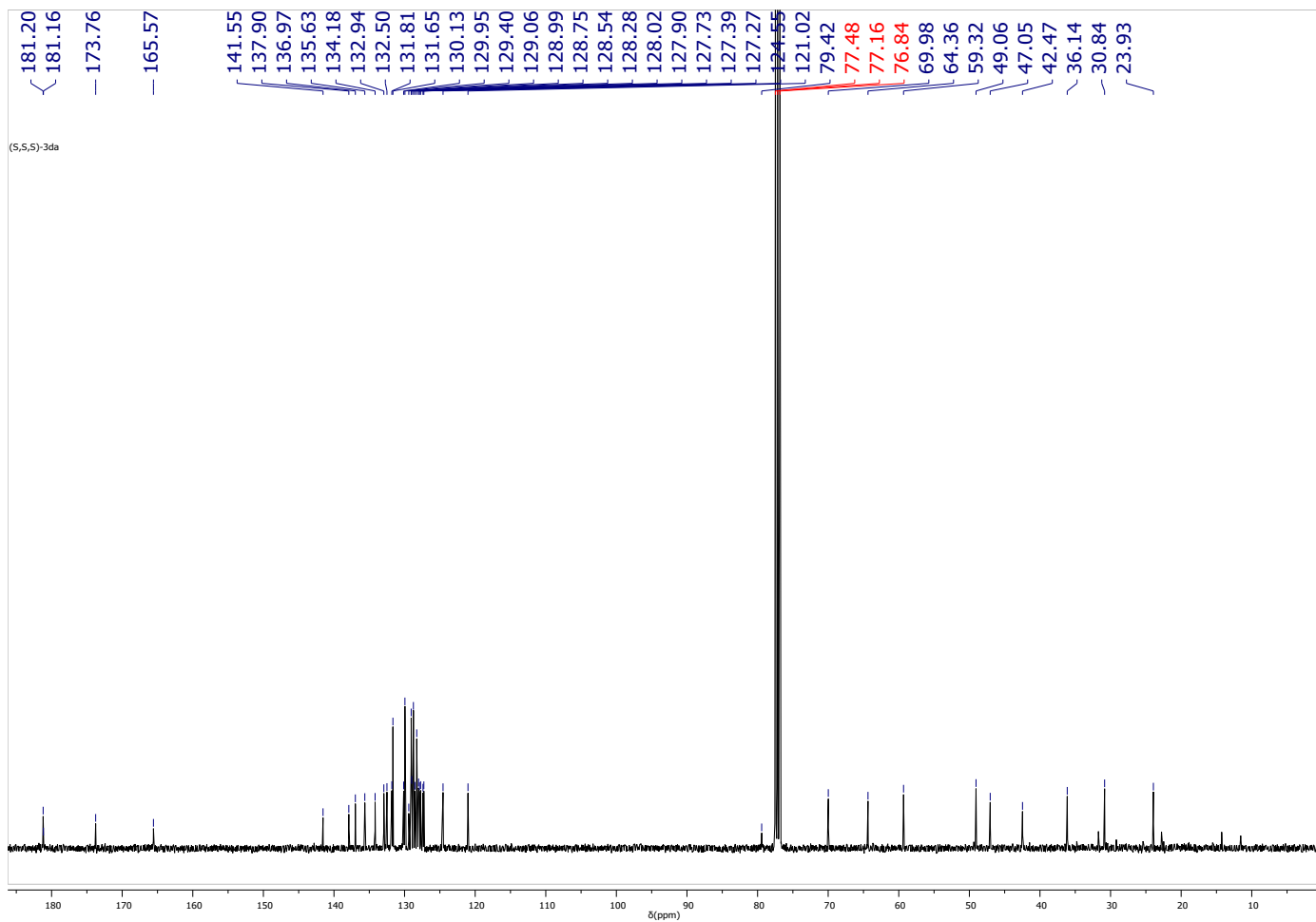
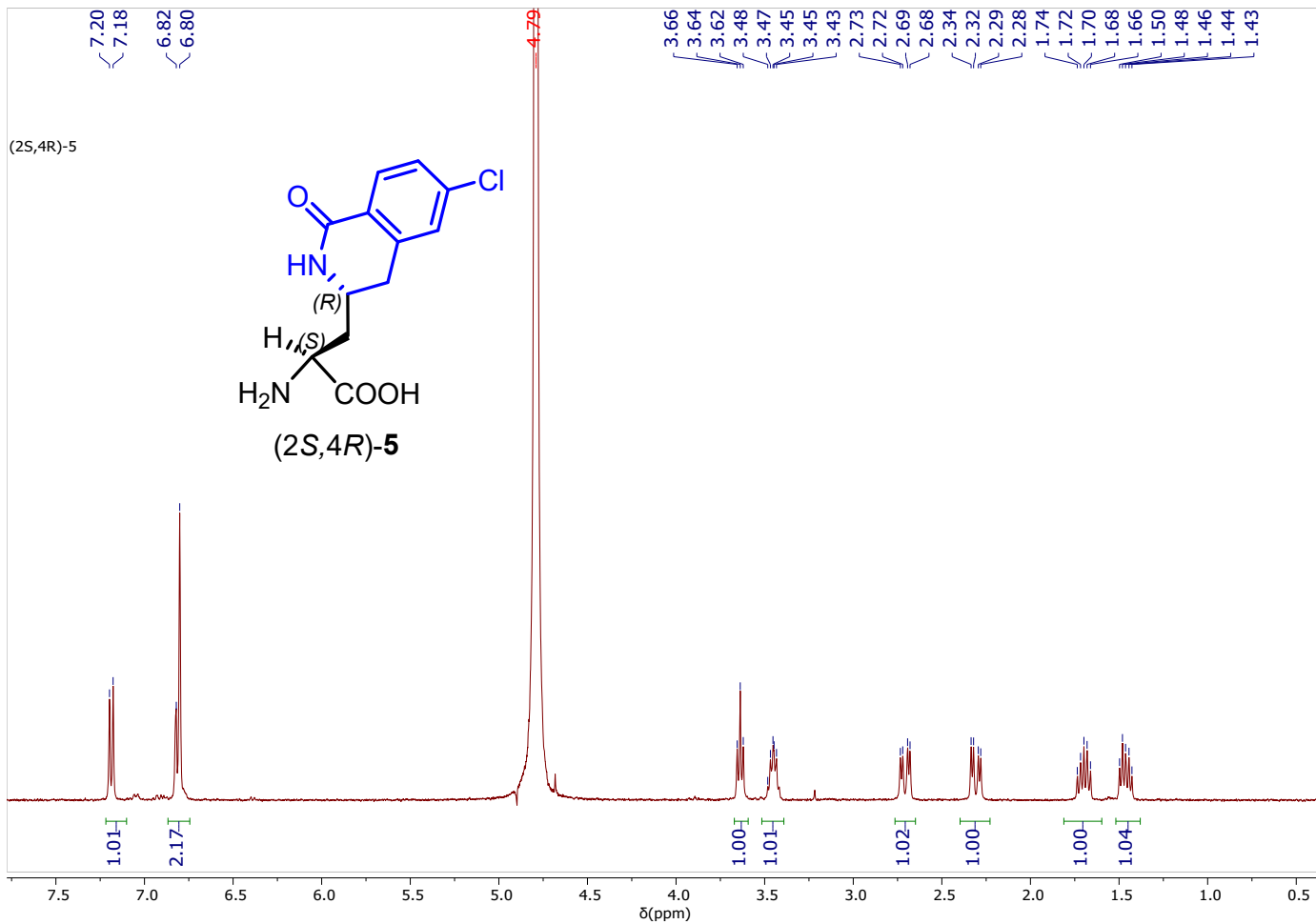


Figure S40. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S,S,S*)-**3da** (in CDCl_3)



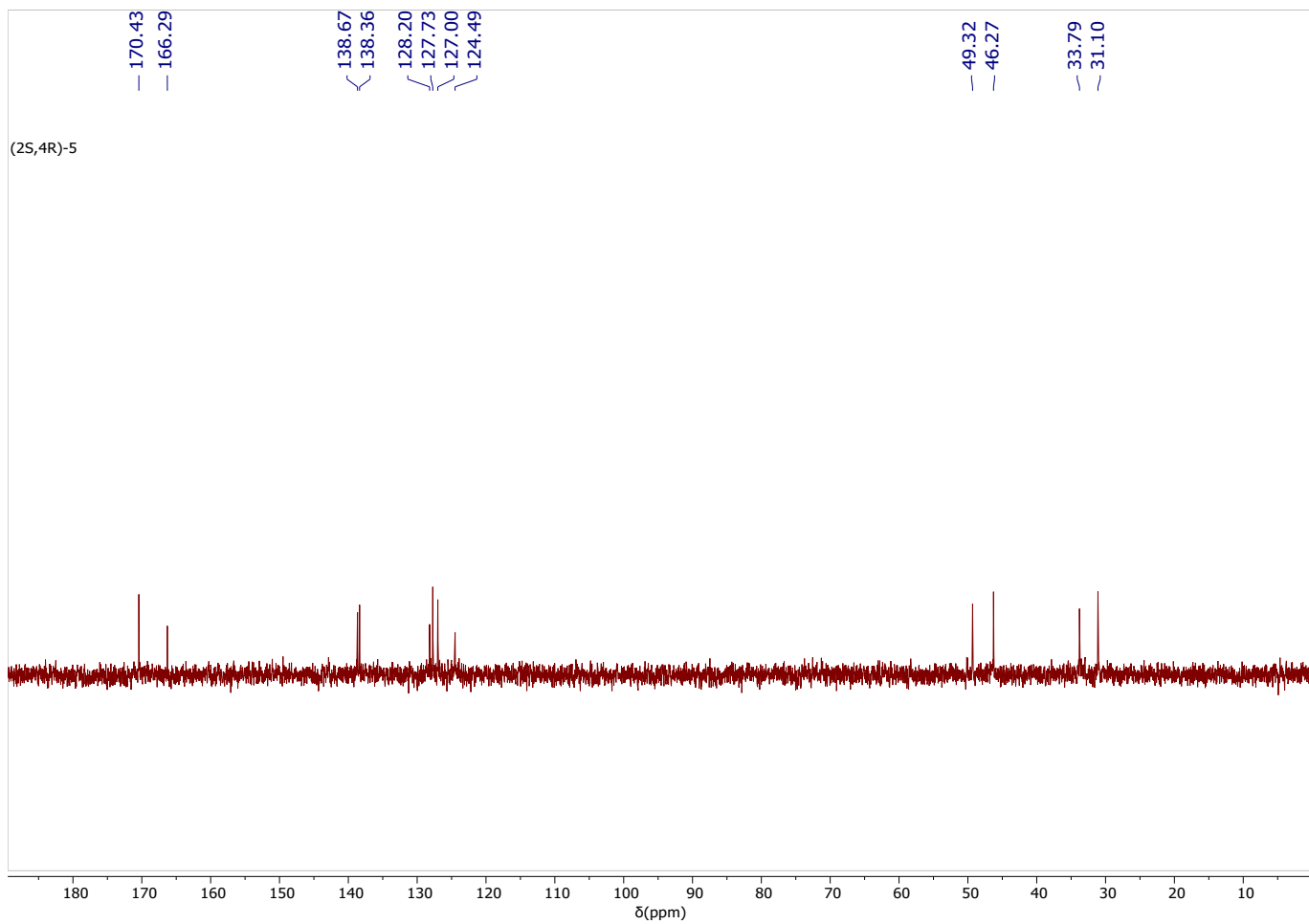
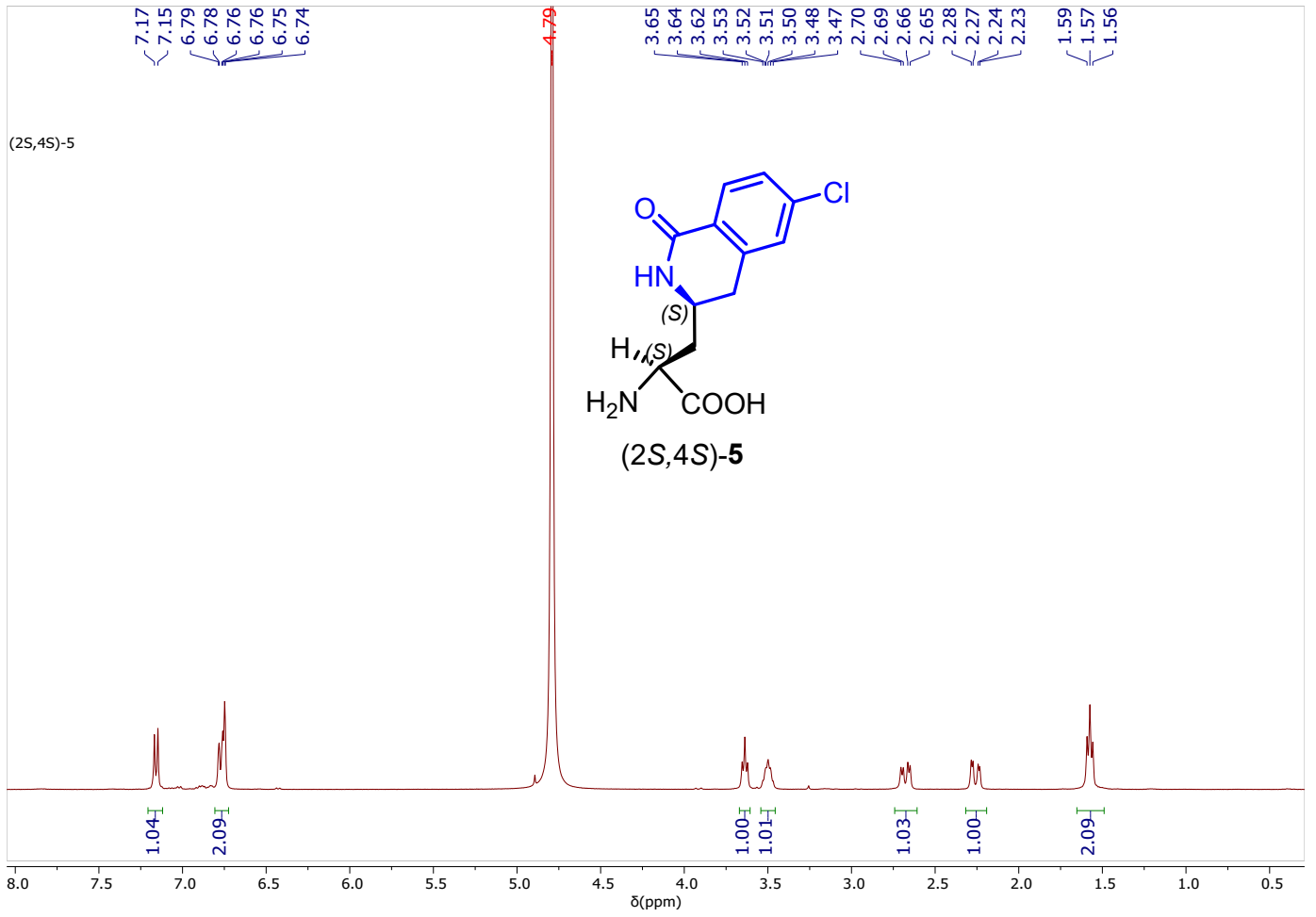


Figure S41. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the AA (2*S*,4*R*)-5 (in $\text{D}_2\text{O}+\text{DCl}$)



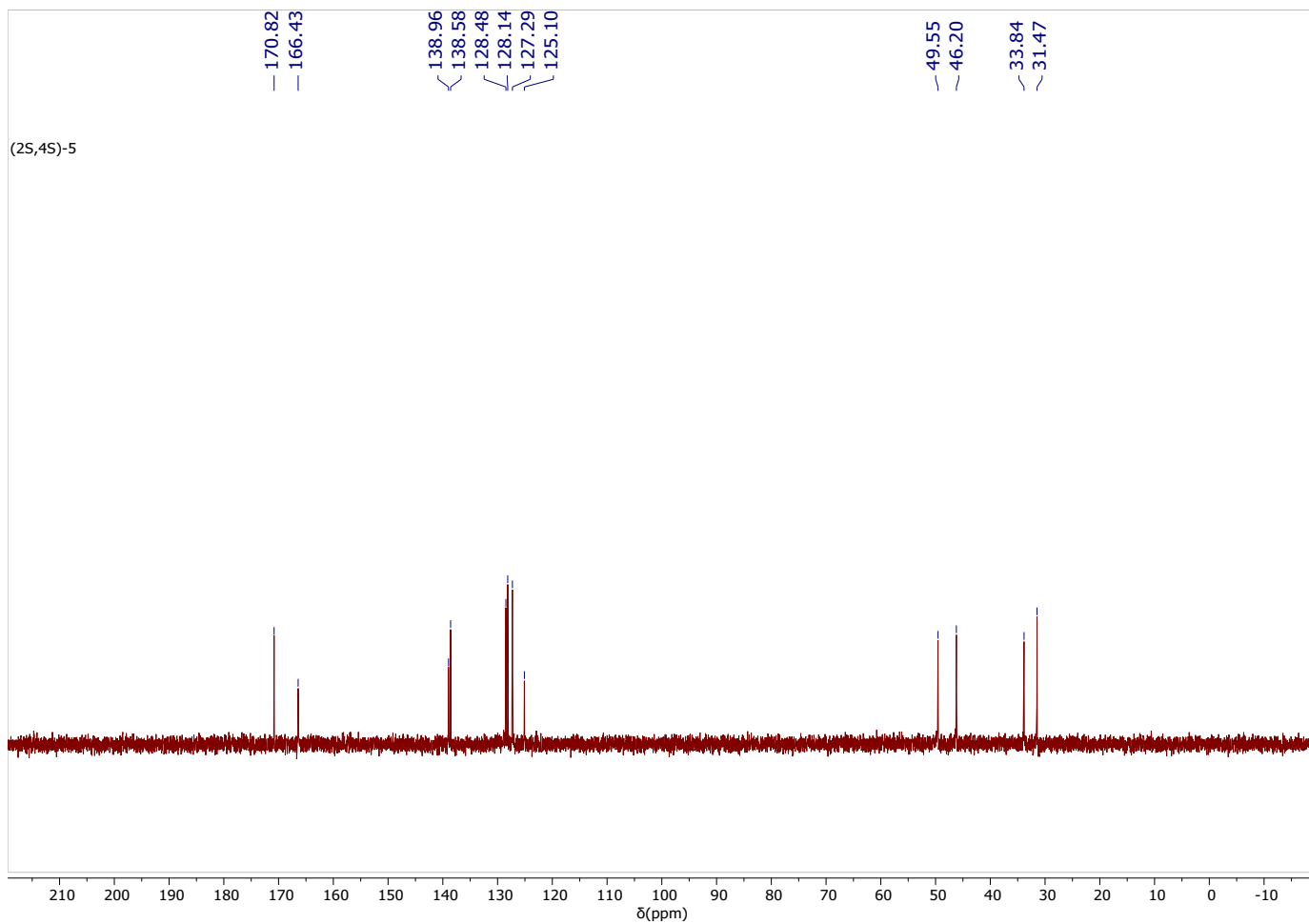


Figure S42. ^1H (400 MHz) and ^{13}C (101 MHz) NMR spectra of the AA (2*S*,4*R*)-5 (in $\text{D}_2\text{O}+\text{DCI}$)

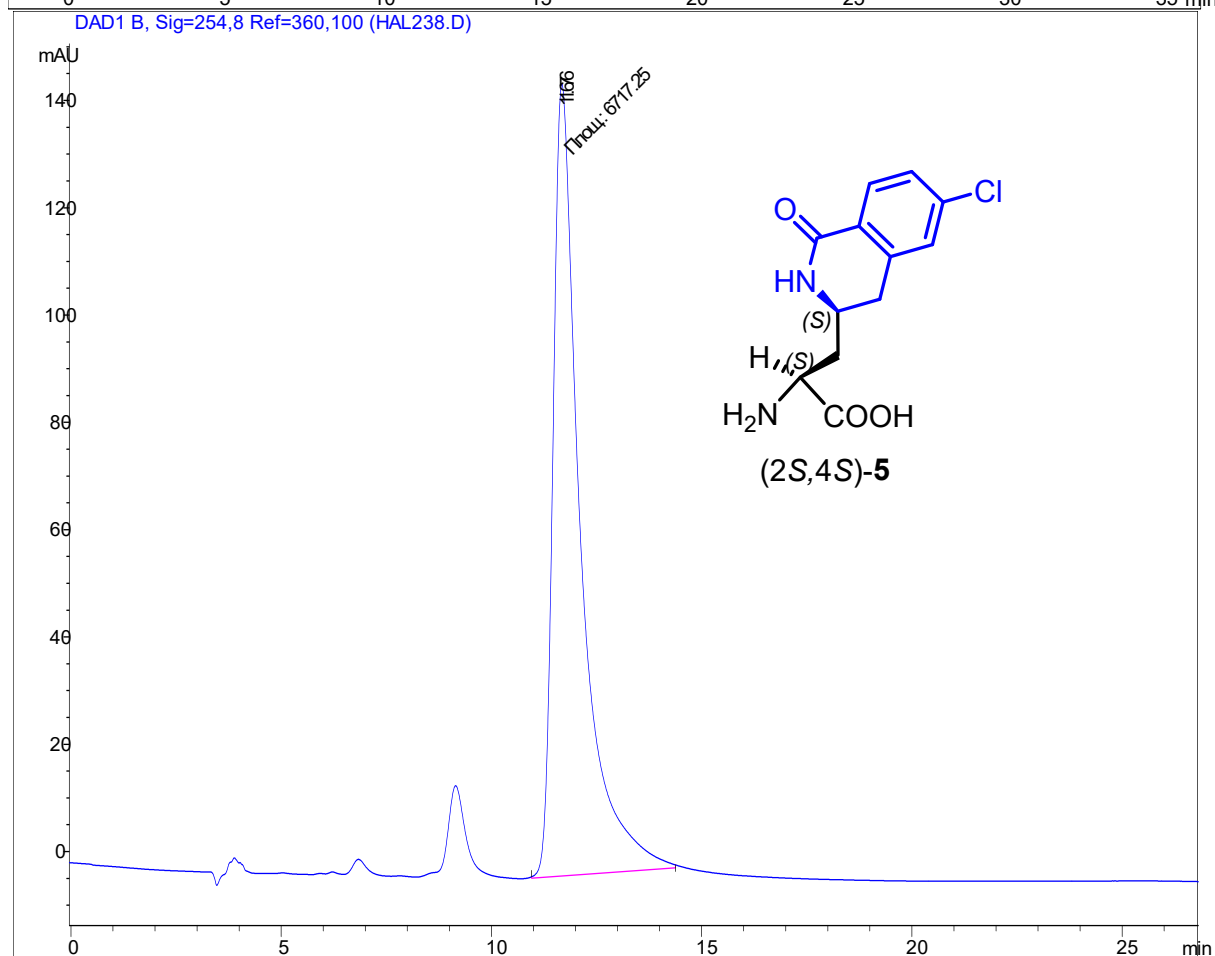
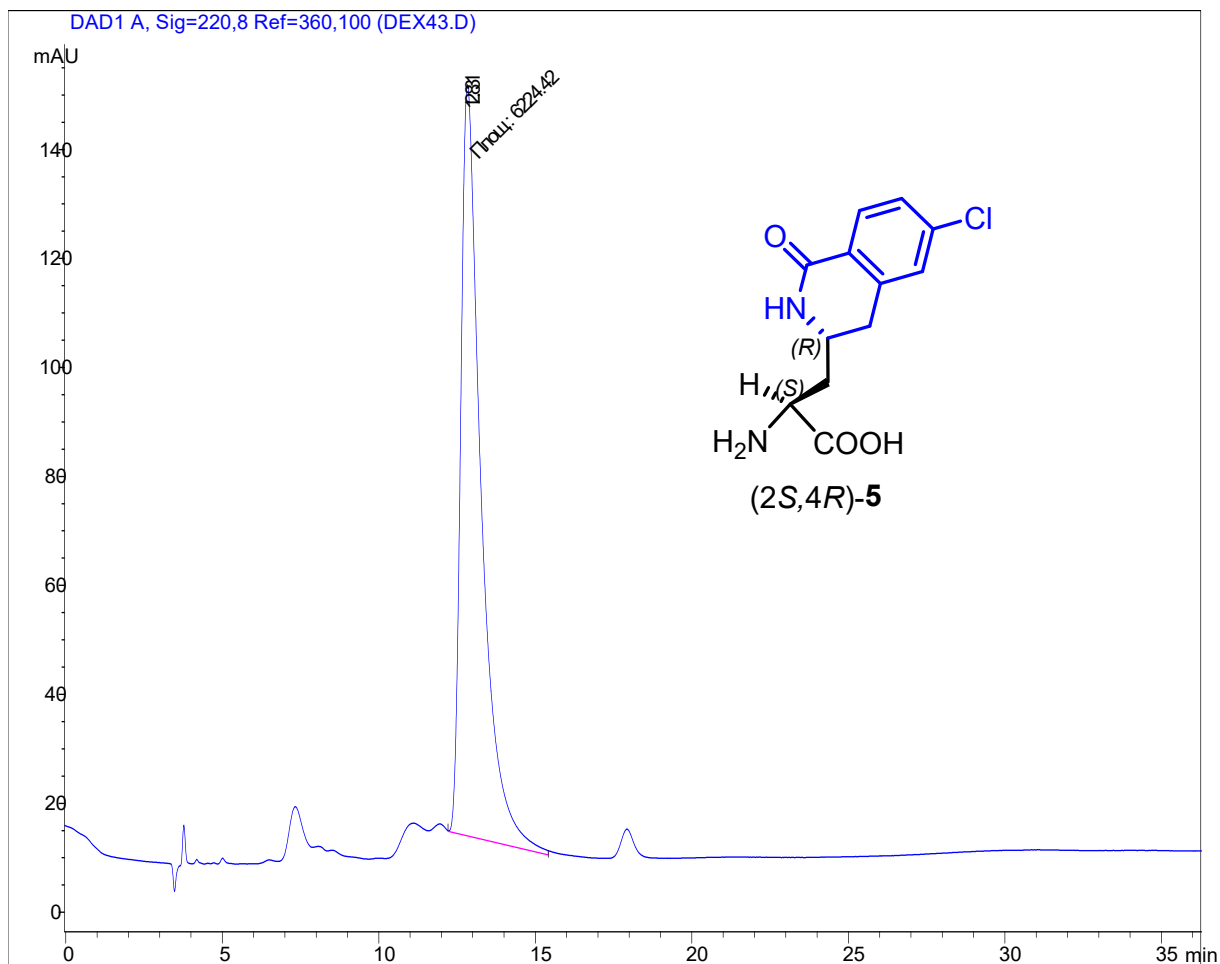


Figure S43. HPLC traces of the enantiopure amino acids (2S,4R)-5 and (2S,4S)-5.