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Electronic Supplementary Information

Asymmetric Metal-Templated Route to Amino Acids with an Isoquinolone Core *via* Rh(III)-Catalyzed Coupling of Aryl Hydroxamates with Chiral Propargylglycine Ni(II) Complexes

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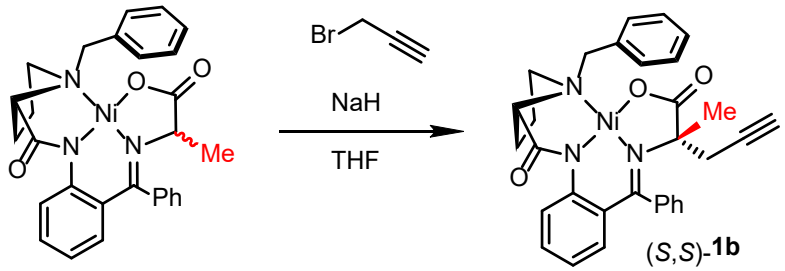
General information

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** was synthesized according to a literature procedure.[S1-S3] Catalyst $[Cp^*RhCl_2]_2$ and 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 (^{1}H 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 (^{1}H), 376 MHz (^{19}F) and 101 MHz (^{13}C{^{1}H}). Chemical shifts are reported in ppm relative to the residual solvent peak ($CDCl_3$: δ = 7.26 ppm for ^{1}H NMR, δ = 77.1 for ^{13}C NMR; acetone-d6: δ = 29.84 and 206.26 ppm 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, etc.), coupling constant, integration, and nucleus. High-resolution mass spectra were recorded on an AB Sciex TripleTOF 5600+ instrument using ESI ionization method (DuoSpray source). 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 [λ(MoK$_\alpha$) = 0.71073 Å, ω-scans, 2θ<58°] at 120 K. Chiral HPLC was performed with Agilent 1200.

Synthesis of the complex (*S*,*S*)-1b



(*S*)-***BBP***-Ni(II)-Ala

A flame dried Schlenk flask equipped with a stir bar was charged with a solution of a chiral (*S*)-**BBP**-Ni(II)-Ala complex (*which was prepared according to a literature procedure*[S1]) (500 mg, 1.0 equiv., 0.98 mmol) in 10 mL of THF followed by the addition of NaH (120 mg, 3.0 equiv., 2.94 mmol) and propargyl bromide (0.17 mL, 2.0 equiv., 1.96 mmol). The mixture was stirred at room temperature under argon for 5 hours. Full conversion for reaction was confirmed by TLC analysis (eluent: $CHCl_3$/EA (1:3)). Afterwards, 30 mL of EA and 30 mL of water were added to the reaction mixture. The aqueous layer was extracted with EA (3x10 mL). The combined organic layers were washed by brine and dried over Na_2SO_4; then, the solvent was evaporated on a rotary evaporator. The resulting residue was purified by column flash chromatography on silica gel (eluent: $CHCl_3$/EA (1:3)) to afford the desired chiral Ni(II) complex (*S*,*S*)-**1b** as a red powder (250 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 7.4 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.54–7.45 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.35–7.27 (m, 3H), 7.19–7.10 (m, 1H), 6.64 (d, *J* = 3.8 Hz, 2H), 4.47 (d, *J* = 12.6 Hz, 1H), 3.75 (d, *J* = 12.6 Hz, 1H), 3.71–3.61 (m, 1H), 3.56–3.37 (m, 2H), 2.81–2.59 (m, 2H), 2.53 (s, 1H), 2.52–2.38 (m, 2H), 2.14–1.92 (m, 3H), 1.34 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 182.2, 180.8, 173.8, 141.6, 136.3, 133.5, 133.4, 131.8, 130.0, 129.8, 129.1, 129.0, 128.7, 128.3, 127.9, 127.0, 124.4, 121.0, 80.5, 76.0, 73.2, 70.2, 63.5, 57.2, 30.7, 29.9, 29.1, 23.2 ppm.

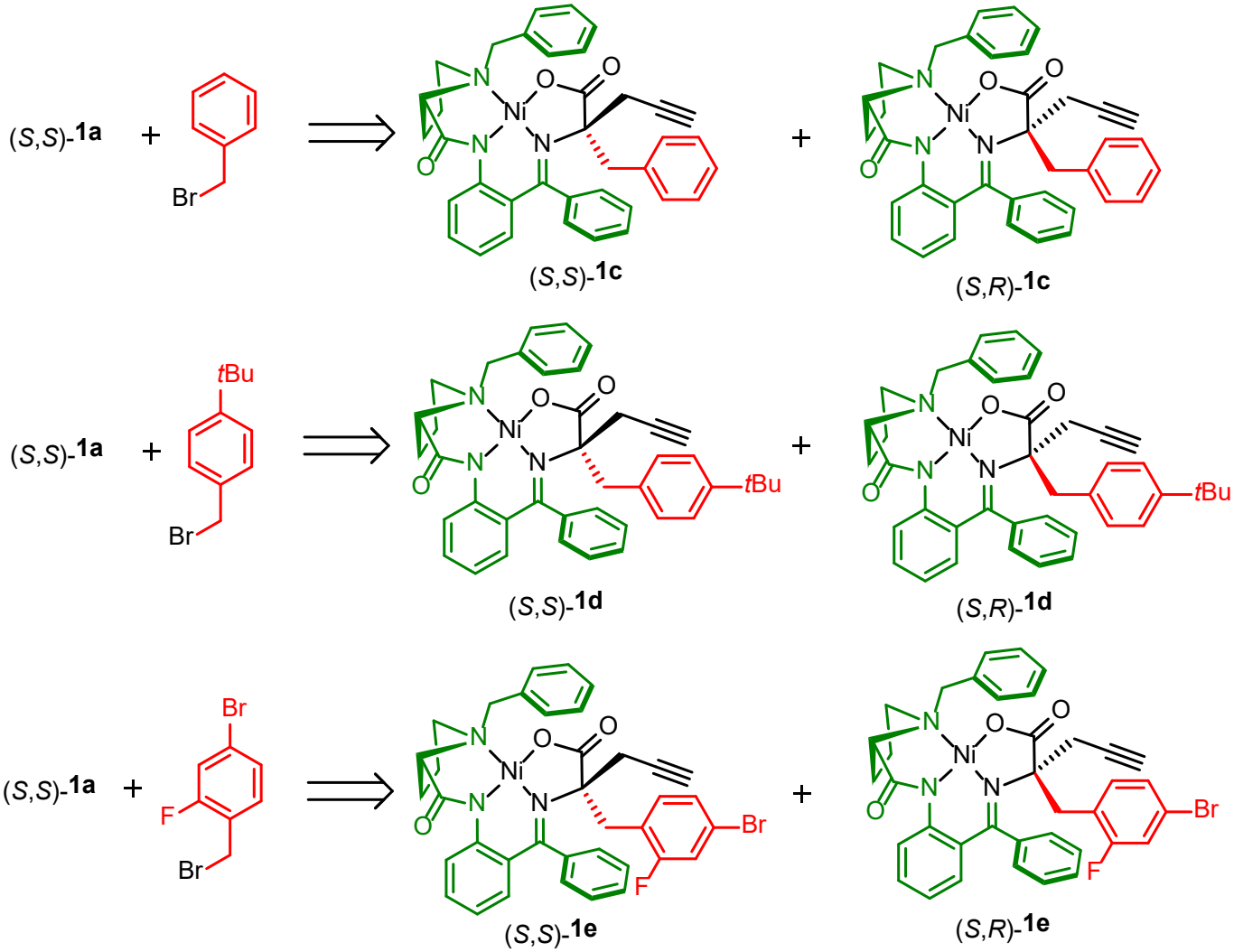
HRMS (ESI, *m/z*) calcd. for $C_{31}H_{30}N_3NiO_3^+$ $[M+H]^+$: 550.1635, found: 550.1638.

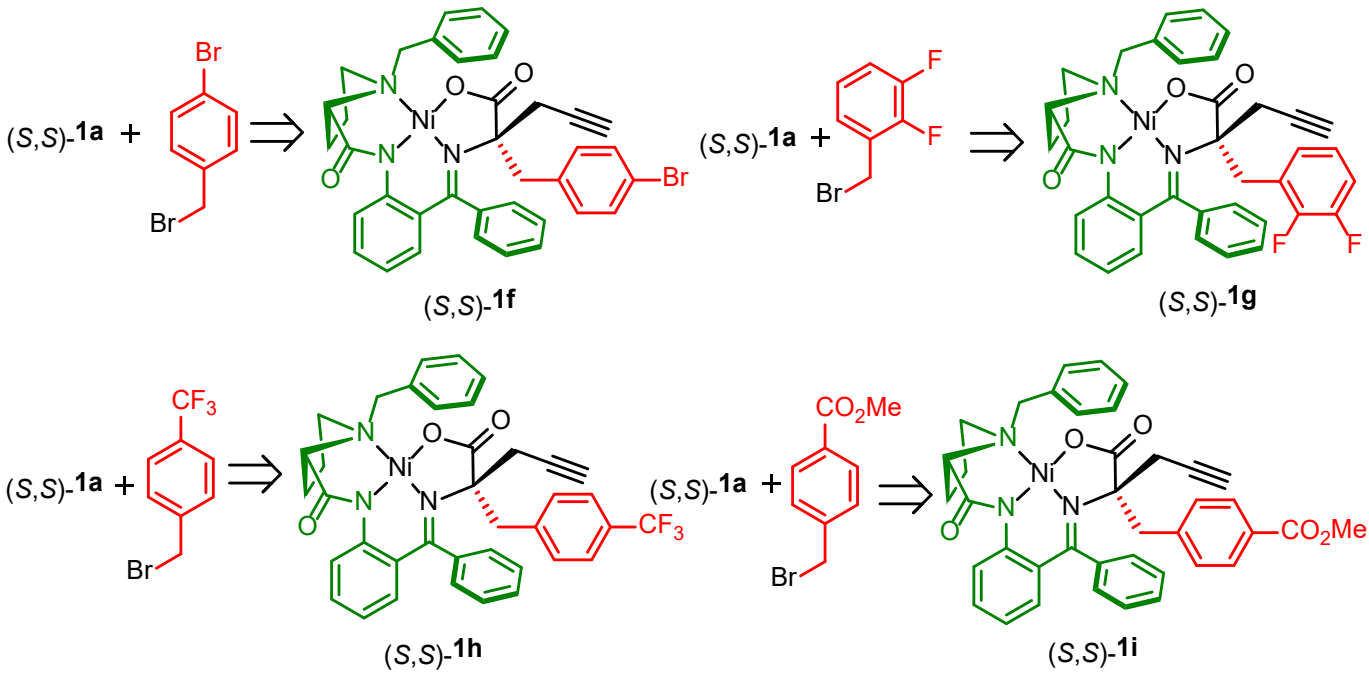
$[\alpha]_D^{25}$ +1700 (*c* 0.02, MeOH).

Preparation and characterization of the complexes 1c-i

General procedure for the benzylation of a chiral Ni(II) complex (*S*,*S*)-1a with different benzyl bromides

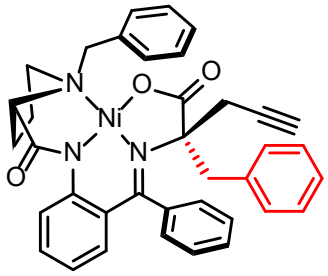
A flame dried Schlenk flask equipped with a stir bar was charged with a solution of a chiral propargylglycine Ni(II) complex (*S*,*S*)-**1a** (300 mg, 1.0 equiv., 0.56 mmol) in 6 mL of DMF followed by the addition of NaOH (3.0 equiv., 1.7 mmol) and benzyl bromide (1.5 equiv., 0.84 mmol). The mixture was stirred at room temperature under argon for 3 hours. Full conversion for each reaction was confirmed by TLC analysis. Then, the reaction mixture was dissolved with H_2O and the precipitate formed was collected by filtration. The resulting residue was purified by column flash chromatography on silica gel to afford the desired Ni(II) complexes **1c-i**.





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

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and benzyl bromide, the product (*S,S*)-**1c** (*the first eluting diastereomer*) was isolated as a red powder (256 mg, 73% yield); eluent: CH_2Cl_2/acetone (10:1).



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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.37–8.23 (m, 2H), 8.01–7.88 (m, 2H), 7.60–7.38 (m, 8H), 7.33–7.20 (m, 3H), 7.16–7.00 (m, 2H), 6.59 (br. s, 2H), 4.24 (d, J = 12.2 Hz, 1H), 3.33–3.15 (m, 2H), 3.12–2.96 (m, 2H), 2.91 (d, J = 17.6 Hz, 1H), 2.72 (d, J = 13.8 Hz, 1H), 2.40 (s, 1H), 2.31–2.18 (m, 1H), 2.15–2.02 (m, 4H), 1.89–1.66 (m, 2H), 1.55–1.41 (m, 1H) ppm.

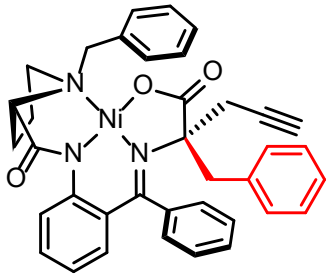
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 179.4, 172.8, 142.4, 136.6, 136.3, 134.4, 133.8, 131.8, 131.5, 131.0, 129.9, 129.5, 129.0, 128.8, 128.7, 128.0, 127.9, 127.8, 127.7, 123.6, 120.4, 80.9, 80.2, 72.9, 70.7, 64.5, 58.3, 43.4, 31.7, 30.6, 22.7 ppm.

HRMS (ESI, m/z) calcd. for $C_{37}H_{34}N_3NiO_3^+$ $[M+H]^+$: 626.1948, found: 626.1944.

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

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

Starting from a chiral Ni(II) complex (*S,S*)-**1a** and benzyl bromide, the product (*S,R*)-**1c** (*the second eluting diastereomer*) was isolated as a red powder (67 mg, 19% yield); eluent: CH_2Cl_2/acetone (10:1).



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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.76 (m, 2H), 7.58–7.21 (m, 14H), 7.07 (br. s, 1H), 6.71 (d, J = 45.2 Hz, 2H), 4.29–4.12 (m, 1H), 3.73 (br. s, 1H), 3.48 (br. s, 1H), 3.34–3.07 (m, 3H), 2.93–2.79 (m, 2H), 2.54 (s, 1H), 2.46–2.24 (m, 2H), 2.05–1.79 (m, 3H) ppm.

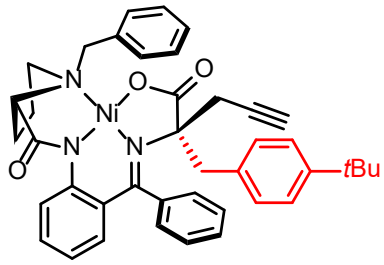
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.9, 180.2, 173.9, 141.4, 136.5, 135.7, 133.9, 132.8, 131.7, 131.4, 130.1, 129.9, 129.1, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 127.3, 127.2, 126.5, 124.6, 120.8, 80.4, 80.1, 73.5, 69.8, 63.8, 58.5, 45.6, 30.8, 29.2, 23.4 ppm.

HRMS (ESI, m/z) calcd. for $C_{37}H_{34}N_3NiO_3^+$ $[M+H]^+$: 626.1948, found: 626.1945.

$[\alpha]_D^{25}$ +1500 (c 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-*tert*-butylbenzyl bromide, the product (*S*,*S*)-**1d** (*the first eluting diastereomer*) was isolated as a red powder (274 mg, 72% yield); eluent: CH_2Cl_2/acetone (10:1).



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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, *J* = 7.4 Hz, 2H), 8.01–7.91 (m, 2H), 7.60–7.46 (m, 4H), 7.45–7.35 (m, 3H), 7.31–7.19 (m, 3H), 7.14–7.01 (m, 2H), 6.64–6.51 (m, 2H), 4.27 (d, *J* = 12.5 Hz, 1H), 3.33 (d, *J* = 12.5 Hz, 1H), 3.21 (dd, *J* = 10.5, 6.7 Hz, 1H), 3.12–3.00 (m, 2H), 2.89 (d, *J* = 17.4 Hz, 1H), 2.68 (d, *J* = 13.8 Hz, 1H), 2.42 (s, 1H), 2.34–2.21 (m, 1H), 2.19–2.10 (m, 2H), 1.81–1.62 (m, 2H), 1.55–1.41 (m, 1H), 1.36 (s, 9H) ppm.

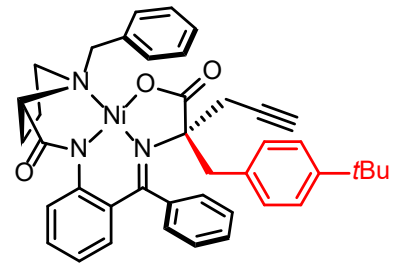
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.6, 172.8, 150.5, 142.3, 136.6, 134.4, 133.8, 133.2, 131.8, 131.5, 130.7, 129.9, 129.4, 128.8, 128.7, 128.0, 127.9, 127.8, 127.7, 126.0, 123.6, 120.5, 80.8, 80.2, 72.9, 70.7, 64.4, 57.7, 42.8, 34.7, 31.9, 31.5, 30.8, 22.4 ppm.

HRMS (ESI, m/z) calcd. for $C_{41}H_{42}N_3NiO_3^+$ $[M+H]^+$: 682.2574, found: 682.2571.

$[\alpha]_D^{25}$ +2150 (c 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-*tert*-butylbenzyl bromide, the product (*S*,*R*)-**1b** (*the second eluting diastereomer*)was isolated as a red powder (70 mg, 18% yield); eluent: CH_2Cl_2/acetone (10:1).



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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.5 Hz, 2H), 7.63–7.42 (m, 8H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.23–7.15 (m, 3H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 4.25 (d, *J* = 12.4 Hz, 1H), 3.71–3.52 (m, 2H), 3.33–3.21 (m, 2H), 3.13 (d, *J* = 12.4 Hz, 1H), 2.88–2.81 (m, 1H), 2.76 (d, *J* = 14.4 Hz, 1H), 2.56 (s, 1H), 2.48–2.36 (m, 2H), 2.05–1.85 (m, 3H), 1.28 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.8, 180.2, 173.8, 150.0, 141.5, 136.5, 134.1, 132.9, 132.6, 131.7, 131.3, 129.9, 129.7, 129.1, 128.9, 128.8, 128.4, 128.3, 128.2, 127.1, 125.6, 124.6, 120.8, 80.5, 80.1, 73.5, 70.0, 64.0, 58.4, 45.1, 34.5, 31.4, 30.8, 29.2, 23.3 ppm.

HRMS (ESI, m/z) calcd. for $C_{41}H_{42}N_3NiO_3^+$ $[M+H]^+$: 682.2574, found: 682.2580.

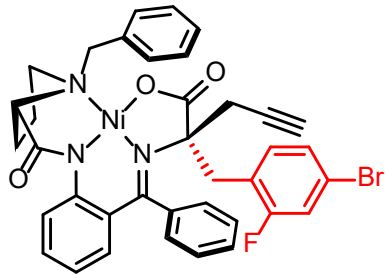
$[\alpha]_D^{25}$ +1650 (c 0.02, MeOH).

Ni(II) complex (S,S)-1e

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-bromo-2-fluorobenzyl bromide, the product (*S*,*S*)-**1e** (*the first eluting diastereomer*) was isolated as a red powder (302 mg, 74% yield); eluent: CH_2Cl_2/acetone (10:1).

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD (few drops)): δ = 8.24 (d, *J* = 7.3 Hz, 2H), 7.89–7.73 (m, 2H), 7.50–7.41 (m, 2H), 7.40–7.33 (m, 3H), 7.31–7.27 (m, 1H), 7.26–7.17 (m, 3H), 7.07–6.94 (m, 2H), 6.57–6.44 (m, 2H), 4.10 (d, *J* = 12.4 Hz, 1H), 3.31–3.17 (m, 3H), 2.95–2.82 (m, 1H), 2.66 (dd, *J* = 17.4, 2.5 Hz,

1H), 2.50 (d, J = 13.8 Hz, 1H), 2.38 (br. s, 1H), 2.34–2.23 (m, 1H), 2.12–2.00 (m, 1H), 1.90–1.75 (m, 3H), 1.67–1.56 (m, 1H) ppm.



(*S*,*S*)-**1e**

^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD (few drops)): δ = 180.9, 179.7, 174.3, 141.8, 136.2, 134.7 (d, J = 5.2 Hz), 134.4, 134.0, 131.9, 131.3, 130.0, 129.3, 128.8, 128.7, 128.3 (d, J = 3.1 Hz), 128.2, 127.7, 127.5, 127.3 (d, J = 8.5 Hz), 123.2, 122.4 (d, J = 7.8 Hz), 122.2 (d, J = 13.2 Hz), 120.7, 119.4 (d, J = 26.3 Hz), 80.8, 79.8, 73.0, 70.9, 64.8, 58.3, 38.2, 30.8, 30.7, 22.6 ppm.

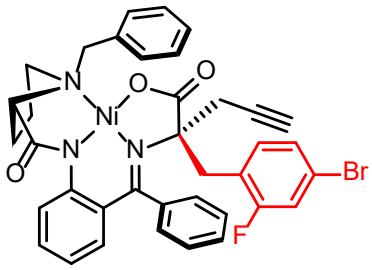
^{19}F NMR (376 MHz, $CDCl_3$+CD_3OD (few drops)): δ = –110.2 (s, 1F) ppm.

HRMS (ESI, m/z) calcd. for $C_{37}H_{32}BrFN_3NiO_3^+$ $[M+H]^+$: 722.0959, found: 722.0963.

$[\alpha]_D^{25}$ +1690 (c 0.026, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-bromo-2-fluorobenzyl bromide, the product (*S*,*R*)-**1e** (*the second eluting diastereomer*) was isolated as a red powder (76 mg, 18% yield); eluent: CH_2Cl_2/acetone (10:1).



(*S*,*R*)-**1e**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.2 Hz, 2H), 7.74–7.64 (m, 1H), 7.60–7.47 (m, 3H), 7.45–7.27 (m, 8H), 7.08 (t, J = 7.2 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.65 (t, J = 7.6 Hz, 1H), 4.23 (d, J = 12.3 Hz, 1H), 3.81–3.67 (m, 1H), 3.58–3.44 (m, 1H), 3.41–3.30 (m, 2H), 3.20 (d, J = 12.3 Hz, 1H), 2.83 (d, J = 15.6 Hz, 1H), 2.67 (d, J = 14.5 Hz, 1H), 2.55 (br. s, 1H), 2.47–2.34 (m, 2H), 2.09–1.94 (m, 2H), 1.80 (d, J = 16.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.8, 179.9, 175.9, 162.6 (d, J = 11.0 Hz), 160.0, 141.2, 136.6, 134.1, 133.0, 131.5, 129.9, 129.7, 129.1, 129.0, 128.3, 128.2, 128.2, 128.1, 127.8 (d, J = 8.8 Hz), 127.6, 124.6, 121.9 (d, J = 15.4 Hz), 121.6 (d, J = 9.8 Hz), 120.9, 118.8 (d, J = 26.8 Hz), 80.3, 79.5, 73.6, 70.0, 64.1, 58.7, 39.9, 30.8, 28.9, 23.4 ppm.

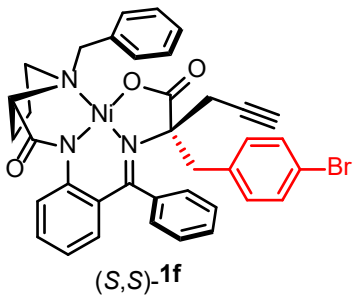
^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.8 (s, 1F) ppm.

HRMS (ESI, m/z) calcd. for $C_{37}H_{32}BrFN_3NiO_3^+$ $[M+H]^+$: 722.0959, found: 722.0956.

$[\alpha]_D^{25}$ +1125 (c 0.024, MeOH).

Ni(II) complex (S,S)-1f

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-bromobenzyl bromide, the product (*S*,*S*)-**1f** was isolated as a red powder (154 mg, 38% yield); eluent: CH_2Cl_2/acetone (3:1).



(*S*,*S*)-**1f**

^{1}H NMR (400 MHz, $CDCl_3$+CD_3OD (few drops)): δ = 8.32 (d, J = 7.2 Hz, 2H), 7.94–7.86 (m, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.57–7.48 (m, 2H), 7.46–7.38 (m, 1H), 7.32–7.27 (m, 2H), 7.26–7.22 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.09–7.01 (m, 2H), 6.63–6.48 (m, 2H), 4.14 (d, J = 12.4 Hz, 1H), 3.30–3.19 (m, 2H), 3.02 (d, J = 13.7 Hz, 1H), 2.97–2.88 (m, 1H), 2.77 (dd, J = 17.4, 2.4 Hz, 1H), 2.62 (d, J = 13.7 Hz, 1H), 2.44 (br. s, 1H), 2.40–2.27 (m, 1H), 2.14–1.99 (m, 2H), 1.92–1.74 (m, 2H), 1.68–1.58 (m, 1H) ppm.

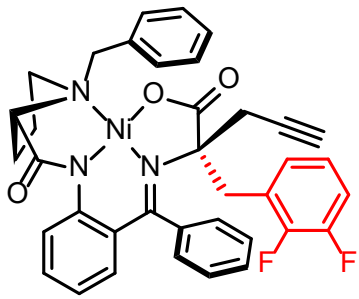
^{13}C NMR (101 MHz, $CDCl_3$+CD_3OD (few drops)): δ = 180.9, 180.0, 173.3, 142.1, 136.2, 134.9, 134.5, 133.8, 132.6, 132.0, 132.0, 131.3, 130.1, 129.3, 128.8, 128.7, 128.1, 127.8, 127.7, 127.4, 123.5, 122.2, 120.9, 80.8, 79.6, 73.0, 70.8, 64.8, 58.5, 42.7, 31.3, 30.6, 22.6 ppm.

HRMS (ESI, m/z) calcd. for $C_{37}H_{33}BrN_3NiO_3^+$ $[M+H]^+$: 704.1053, found: 704.1060.

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

Ni(II) complex (S,S)-1g

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 2,3-difluorobenzyl bromide, the product (*S*,*S*)-**1g** was isolated as a red powder (219 mg, 59% yield); eluent: CH_2Cl_2/acetone (10:1).



(*S*,*S*)-**1g**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 7.4 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.97–7.86 (m, 1H), 7.61–7.49 (m, 2H), 7.49–7.42 (m, 1H), 7.40–7.34 (m, 1H), 7.34–7.27 (m, 4H), 7.24–7.01 (m, 3H), 6.64–6.52 (m, 2H), 4.29 (d, *J* = 12.4 Hz, 1H), 3.47–3.32 (m, 2H), 3.33–3.20 (m, 1H), 3.14–3.03 (m, 1H), 2.87 (d, *J* = 15.4 Hz, 1H), 2.70 (d, *J* = 13.6 Hz, 1H), 2.41 (br. s, 1H), 2.38–2.13 (m, 2H), 2.08–1.79 (m, 3H), 1.68–1.53 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 178.9, 174.0, 151.8 (dd, *J* = 65.0, 11.7 Hz), 149.4 (dd, *J* = 64.0, 12.8 Hz), 142.5, 136.5, 134.2, 133.9, 131.9, 131.6, 129.9, 129.5, 128.9, 128.8, 128.3, 128.2, 127.7, 127.6, 127.5, 125.8 (d, *J* = 12.1 Hz), 124.7, 123.5, 120.4, 116.7 (d, *J* = 16.6 Hz), 80.5, 80.1, 73.1, 70.7, 64.4, 58.1, 38.3, 31.4, 30.8, 22.8 ppm.

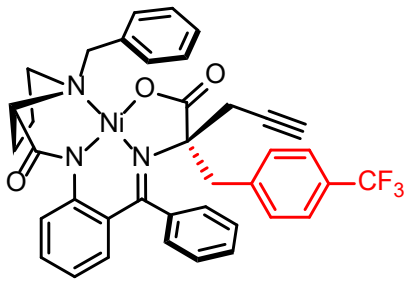
^{19}F NMR (282 MHz, $CDCl_3$): δ = –136.9 (d, *J* = 21.4 Hz, 1F), –137.78 (d, *J* = 21.4 Hz, 1F) ppm.

HRMS (ESI, m/z) calcd. for $C_{37}H_{32}F_2N_3NiO_3^+$ $[M+H]^+$: 662.1760, found: 662.1757.

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

Ni(II) complex (S,S)-1h

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-trifluoromethylbenzyl bromide, the product (*S*,*S*)-**1e** was isolated as a red powder (197 mg, 51% yield); eluent: CH_2Cl_2/acetone (10:1).



(*S*,*S*)-**1h**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 7.5 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 4H), 7.50–7.41 (m, 1H), 7.33–7.26 (m, 2H), 7.21 (d, *J* = 6.9 Hz, 1H), 7.14–7.03 (m, 2H), 6.65–6.52 (m, 2H), 4.24 (d, *J* = 12.5 Hz, 1H), 3.31–3.19 (m, 2H), 3.12 (d, *J* = 13.5 Hz, 1H), 3.06–2.97 (m, 1H), 2.96–2.87 (m, 1H), 2.77 (d, *J* = 13.5 Hz, 1H), 2.44 (br. s, 1H), 2.34–2.20 (m, 1H), 2.12–1.97 (m, 1H), 1.85–1.71 (m, 2H), 1.70–1.45 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 179.1, 173.2, 142.4, 140.4, 136.5, 134.4, 133.8, 132.0, 131.5, 131.4, 130.1, 129.5, 128.9, 128.8, 128.1, 127.9, 127.6, 127.5, 125.9, 125.8, 123.7, 120.6, 80.6, 79.9, 73.2, 70.6, 64.6, 58.2, 43.0, 31.8, 30.7, 22.5 ppm.

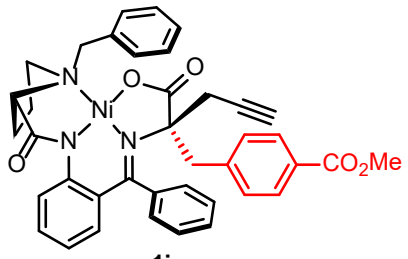
^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.4 (s, 3F) ppm.

HRMS (ESI, m/z) calcd. for $C_{38}H_{33}F_3N_3NiO_3^+$ $[M+H]^+$: 694.1822, found: 694.1818.

$[\alpha]_D^{25}$ +3050 (c 0.02, MeOH).

Ni(II) complex (S,S)-1i

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-methoxycarbonylbenzyl bromide, the product (*S*,*S*)-**1i** was isolated as a red powder (140 mg, 37% yield); eluent: CH_2Cl_2/acetone (3:1).



(*S*,*S*)-**1i**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 7.3 Hz, 2H), 8.13 (d, *J* = 8.2 Hz, 2H), 7.92–7.87 (m, 1H), 7.84 (d, *J* = 8.5 Hz, 1H), 7.55–7.50 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.45–7.38 (m, 1H), 7.25–7.16 (m, 3H), 7.09–7.00 (m, 2H), 6.61–6.50 (m, 2H), 4.15 (d, *J* = 12.4 Hz, 1H), 3.90 (s, 3H), 3.26–3.15 (m, 2H), 3.09 (d, *J* = 13.6 Hz, 1H), 2.92–2.85 (m, 1H), 2.81 (dd, *J* = 17.4, 2.6 Hz, 1H), 2.72 (d, *J* = 13.6 Hz, 1H), 2.41 (t, *J* = 2.4 Hz, 1H), 2.23–2.14 (m, 1H), 2.13–2.05 (m, 1H), 2.02–1.92 (m, 1H), 1.85–1.75 (m, 1H), 1.67–1.55 (m, 1H), 1.50–1.39 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.9, 179.8, 173.4, 167.1, 142.0, 141.4, 136.3, 134.4, 133.8, 132.0, 131.4, 131.0, 130.2, 129.8, 129.4, 128.9, 128.8, 128.1, 127.9, 127.8, 127.5, 123.7, 120.8, 80.8, 79.7, 73.1, 70.7, 64.7, 58.5, 52.3, 43.4, 31.6, 30.5, 22.6 ppm.

HRMS (ESI, m/z) calcd. for $C_{39}H_{36}N_3NiO_5^+$ $[M+H]^+$: 684.2003, found: 684.2000.

$[\alpha]_D^{25}$ +2290 (c 0.024, MeOH).

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

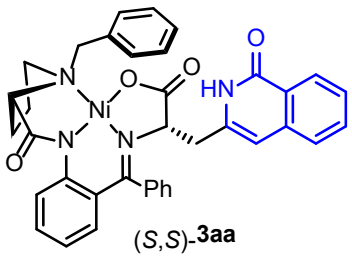
A chiral Ni(II) complex **1** (1.0 equiv., 0.10 mmol), corresponding aryl hydroxamate **2** (1.0 equiv., 0.10 mmol), catalyst $[Cp^*RhCl_2]_2$ (1.2 mg, 0.002 mmol, 4 mol% on Rh) and CsOAc (38 mg, 2.0 equiv., 0.20 mmol) were dissolved in methanol (1 mL). The reaction mixture was stirred at room temperature 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 chromatography on SiO_2 column (~15 cm). CH_2Cl_2 was used as a first eluent to remove traces of unreacted aryl hydroxamate, and then desired products **3** were eluted by CH_2Cl_2/acetone mixture (*see below for specific ratios*). Some of benzyl-substituted derivatives **3** and **4** were isolated as unseparable mixtures of regioisomers using CH_2Cl_2/acetone (1:3) as eluent. In the case of separation of regioisomers **4**, the mixture was additionally chromatographed on silica column by a mixture of CH_2Cl_2/petroleum ether/Et_3N (*see below for specific ratios*).

Characterization of the complexes 3 and 4

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S*)-**3aa** was isolated as an orange powder (53 mg, 81% yield); eluent: CH_2Cl_2/acetone (1:1).

Comment: *A gram-scale reaction was performed with 1.87 mmol of the Ni(II) complex (S,S)-**1a** (1.00 g) by the addition of **2a** (0.411 g, 1.87 mmol), $[Cp^*RhCl_2]_2$ (0.023 g, 0.037 mmol) and CsOAc (0.711 g, 3.74 mmol) in 20 mL of MeOH. Yield 0.87 g (72%).*



(*S*,*S*)-**3aa**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H, NH), 8.35 (d, J = 7.9 Hz, 1H), 8.17 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 7.2 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.51–7.42 (m, 4H), 7.41–7.27 (m, 4H), 7.20–7.07 (m, 2H), 7.00 (d, J = 7.6 Hz, 1H), 6.67–6.57 (m, 2H), 6.16 (s, 1H), 4.36 (t, J = 5.0 Hz, 1H), 4.29 (d, J = 12.7 Hz, 1H), 3.48 (d, J = 12.7 Hz, 1H), 3.37–3.23 (m, 2H), 2.98 (ddd, J = 19.0, 14.8, 5.0 Hz, 2H), 2.80–2.67 (m, 1H), 2.27–2.16 (m, 2H), 2.02–1.92 (m, 1H), 1.73–1.63 (m, 1H) ppm.

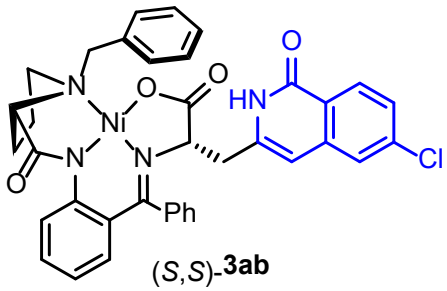
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.5, 179.0, 172.2, 163.3, 143.0, 137.9, 135.6, 133.9, 133.7, 133.4, 132.8, 132.7, 131.6, 130.2, 129.5, 129.2, 129.04, 129.0, 128.0, 127.6, 127.2, 126.8, 126.3, 126.1, 125.6, 123.6, 120.8, 106.6, 70.5, 69.0, 63.5, 57.6, 38.9, 30.7, 23.7 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{33}N_4NiO_4^+$ $[M+H]^+$: 655.1850, found: 655.1849.

$[\alpha]_D^{25}$ +1450 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-chloro-*N*-(pivaloyloxy)benzamide **2b**, the desired product (*S*,*S*)-**3ab** was isolated as an orange powder (54 mg, 78% yield); eluent: CH_2Cl_2/acetone (1:1).



(*S*,*S*)-**3ab**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.08 (s, 1H, NH), 8.21 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 7.5 Hz, 2H), 7.42–7.36 (m, 3H), 7.35–7.27 (m, 3H), 7.25–7.18 (m, 2H), 7.13–7.07 (m, 2H), 7.03 (t, J = 7.6 Hz, 1H), 6.60–6.48 (m, 2H), 6.10 (s, 1H), 4.33 (t, J = 4.6 Hz, 1H), 4.23 (d, J = 12.5 Hz, 1H), 3.44 (d, J = 12.5 Hz, 1H), 3.33 (dd, J = 10.1, 6.7 Hz, 1H), 3.19–3.11 (m, 1H), 3.00 (qd, J = 14.5, 4.6 Hz, 2H), 2.76–2.63 (m, 1H), 2.50–2.38 (m, 1H), 2.37–2.23 (m, 1H), 1.95–1.85 (m, 1H), 1.69–1.58 (m, 1H) ppm.

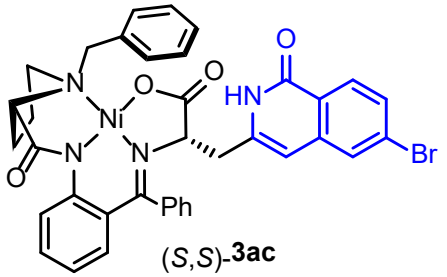
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.3, 178.7, 172.4, 163.4, 142.8, 139.3, 139.1, 137.7, 133.8, 133.6, 133.3, 132.6, 131.5, 130.0, 129.3, 129.2, 129.1, 128.9, 128.1, 127.2, 126.3, 125.3, 123.5, 123.4, 120.6, 105.8, 70.5, 69.4, 63.5, 57.4, 38.9, 30.7, 23.7 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{32}ClN_4NiO_4^+$ $[M+H]^+$: 689.1460, found: 689.1455.

$[\alpha]_D^{25}$ +2550 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-bromo-*N*-(pivaloyloxy)benzamide **2c**, the desired product (*S*,*S*)-**3ac** was isolated as an orange powder (52 mg, 71% yield); eluent: CH_2Cl_2/acetone (1:2).



(*S*,*S*)-**3ac**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.64 (s, 1H, NH), 8.19–8.11 (m, 2H), 8.02 (d, J = 7.4 Hz, 2H), 7.57 (s, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.47–7.39 (m, 2H), 7.47–7.39 (m, 3H), 7.18–7.01 (m, 4H), 6.62–6.52 (m, 2H), 6.05 (s, 1H), 4.36 (t, J = 5.1 Hz, 1H), 4.29 (d, J = 12.6 Hz, 1H), 3.49 (d, J = 12.6 Hz, 1H), 3.38 (dd, J = 10.5, 6.4 Hz, 1H), 3.30–3.21 (m, 1H), 3.04 (ddd, J = 19.2, 14.9, 5.2 Hz, 2H), 2.93–2.82 (m, 1H), 2.52–2.41 (m, 1H), 2.41–2.31 (m, 1H), 2.02–1.91 (m, 1H), 1.81–1.70 (m, 1H) ppm.

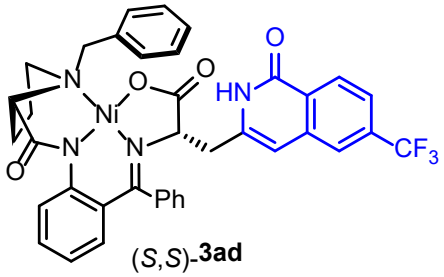
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.3, 178.8, 172.4, 163.4, 142.8, 139.5, 137.8, 133.7, 133.6, 133.3, 132.6, 131.5, 130.0, 129.9, 129.3, 129.1, 129.0, 128.4, 128.1, 127.8, 127.2, 126.3, 123.9, 123.4, 120.6, 105.5, 70.5, 69.3, 63.5, 57.4, 39.1, 30.7, 23.7 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{32}BrN_4NiO_4^+$ $[M+H]^+$: 733.0955, found: 733.0952.

$[\alpha]_D^{25}$ +1900 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-trifluoromethyl-*N*-(pivaloyloxy)benzamide **2d**, the desired product (*S*,*S*)-**3ad** was isolated as an orange powder (61 mg, 85% yield); eluent: CH_2Cl_2/acetone (1:2).



(*S*,*S*)-**3ad**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.32 (s, 1H, NH), 8.39 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 7.5 Hz, 2H), 7.68 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.45–7.36 (m, 2H), 7.32–7.27 (m, 2H), 7.26–7.19 (m, 2H), 7.13–6.99 (m, 3H), 6.59–6.48 (m, 2H), 6.24 (s, 1H), 4.38 (t, *J* = 4.9 Hz, 1H), 4.22 (d, *J* = 12.6 Hz, 1H), 3.45 (d, *J* = 12.6 Hz, 1H), 3.34 (dd, *J* = 10.5, 6.5 Hz, 1H), 3.17–2.97 (m, 3H), 2.78–2.65 (m, 1H), 2.52–2.41 (m, 1H), 2.40–2.25 (m, 1H), 1.97–1.85 (m, 1H), 1.70–1.60 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.2, 178.7, 172.5, 163.2, 142.8, 138.1, 138.0, 134.4, 134.1, 133.7, 133.6, 133.3, 132.6, 131.5, 130.0, 129.3, 129.1, 128.9, 128.5, 128.1, 127.3, 127.2, 126.4, 123.4, 122.5, 122.4, 120.6, 106.3, 70.5, 69.4, 63.5, 57.4, 39.0, 30.7, 23.7 ppm.

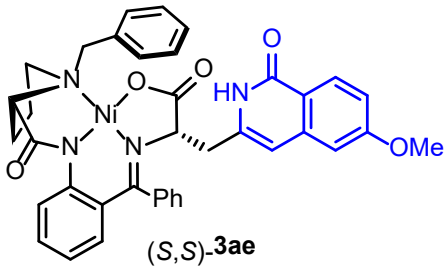
^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.0 (s, 3F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{38}H_{32}F_3N_4NiO_4^+$ $[M+H]^+$: 723.1724, found: 723.1729.

$[\alpha]_D^{25}$ +1500 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-methoxy-*N*-(pivaloyloxy)benzamide **2e**, the desired product (*S*,*S*)-**3ae** was isolated as an orange powder (47 mg, 69% yield); eluent: CH_2Cl_2/acetone (1:2).



(*S*,*S*)-**3ae**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.60 (s, 1H, NH), 8.23 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.46–7.38 (m, 2H), 7.34–7.27 (m, 2H), 7.25–7.18 (m, 2H), 7.14–7.02 (m, 3H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.78 (s, 1H), 6.61–6.52 (m, 2H), 6.22 (s, 1H), 4.36–4.30 (m, 1H), 4.22 (d, *J* = 12.6 Hz, 1H), 3.84 (s, 3H), 3.42 (d, *J* = 12.6 Hz, 1H), 3.33–3.24 (m, 1H), 3.17–3.09 (m, 1H), 2.94 (ddd, *J* = 31.5, 14.5, 4.7 Hz, 2H), 2.57–2.44 (m, 1H), 2.36–2.19 (m, 2H), 1.95–1.85 (m, 1H), 1.60–1.49 (m, 1H) ppm.

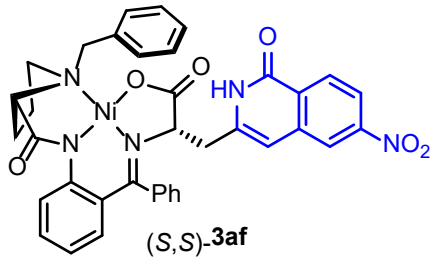
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.4, 178.6, 172.3, 163.5, 163.1, 143.0, 140.2, 136.5, 133.8, 133.7, 133.4, 132.6, 131.6, 130.0, 129.5, 129.2, 129.1, 128.9, 128.2, 127.2, 126.3, 123.5, 120.6, 119.2, 116.6, 106.9, 106.7, 70.6, 69.4, 63.5, 57.6, 55.6, 38.8, 30.7, 23.6 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{38}H_{35}N_4NiO_5^+$ $[M+H]^+$: 685.1955, found: 685.1960.

$[\alpha]_D^{25}$ +1500 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 4-nitro-*N*-(pivaloyloxy)benzamide **2f**, the desired product (*S*,*S*)-**3af** was isolated as an orange powder (53 mg, 76% yield); eluent: CH_2Cl_2/acetone (1:1).



(*S*,*S*)-**3af**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.30 (s, 1H, NH), 8.40 (d, J = 8.7 Hz, 1H), 8.22 (s, 1H), 8.13–8.05 (m, 2H), 8.00 (d, J = 7.5 Hz, 2H), 7.42–7.36 (m, 2H), 7.31–7.20 (m, 4H), 7.09 (t, J = 7.4 Hz, 1H), 7.06–6.97 (m, 2H), 6.57–6.48 (m, 2H), 6.16 (s, 1H), 4.38 (t, J = 5.1 Hz, 1H), 4.23 (d, J = 12.6 Hz, 1H), 3.47 (d, J = 12.6 Hz, 1H), 3.37 (dd, J = 10.6, 6.1 Hz, 1H), 3.24–3.12 (m, 2H), 3.04–2.87 (m, 2H), 2.59–2.48 (m, 1H), 2.45–2.29 (m, 1H), 1.97–1.88 (m, 1H), 1.83–1.73 (m, 1H) ppm.

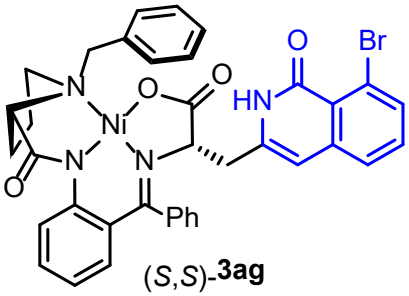
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.2, 179.0, 172.4, 162.5, 150.3, 142.7, 139.2, 138.5, 133.6, 133.3, 132.7, 131.5, 130.1, 129.5, 129.3, 129.02, 129.0, 128.8, 128.1, 127.3, 126.4, 123.5, 121.4, 120.7, 120.0, 105.8, 70.5, 69.0, 63.6, 57.4, 39.3, 30.7, 23.9 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{32}N_5NiO_6^+$ $[M+H]^+$: 700.1701, found: 700.1704.

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

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 2-bromo-*N*-(pivaloyloxy)benzamide **2g**, the desired product (*S*,*S*)-**3ag** was isolated as an orange powder (48 mg, 66% yield); eluent: CH_2Cl_2/acetone (1:1).



(*S*,*S*)-**3ag**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.93 (s, 1H, NH), 9.11 (s, 1H), 8.32 (d, J = 8.3 Hz, 1H), 8.08–7.91 (m, 3H), 7.48–7.34 (m, 4H), 7.31–7.27 (m, 1H), 7.25–7.22 (m, 1H), 7.21 (s, 1H), 7.14–6.94 (m, 3H), 6.63–6.49 (m, 2H), 5.99 (s, 1H), 4.38–4.29 (m, 1H), 4.23 (d, J = 12.5 Hz, 1H), 3.48 (d, J = 12.5 Hz, 1H), 3.39–3.30 (m, 1H), 3.28–3.12 (m, 2H), 3.02–2.83 (m, 2H), 2.42–2.26 (m, 2H), 1.97–1.86 (m, 1H), 1.83–1.74 (m, 1H) ppm.

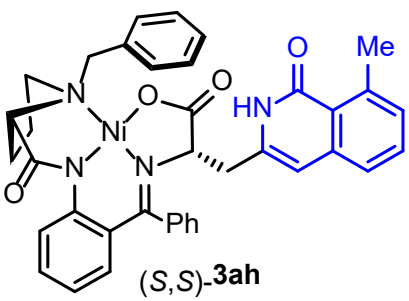
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.3, 179.1, 172.4, 162.5, 145.8, 142.8, 142.4, 141.0, 133.8, 133.7, 133.3, 132.9, 131.5, 130.3, 130.2, 129.7, 129.3, 129.1, 129.0, 127.9, 127.3, 127.2, 126.7, 126.3, 124.1, 123.6, 120.9, 105.2, 70.5, 68.7, 63.7, 57.4, 39.1, 30.6, 23.9 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{32}BrN_4NiO_4^+$ $[M+H]^+$: 733.0955, found: 733.0955.

$[\alpha]_D^{25}$ +1770 (*c* 0.039, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 2-methyl-*N*-(pivaloyloxy)benzamide **2h**, the desired product (*S*,*S*)-**3ah** was isolated as an orange powder (30 mg, 43% yield); eluent: CH_2Cl_2/acetone (2:1).



(*S*,*S*)-**3ah**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1H, NH), 8.14 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 7.3 Hz, 2H), 7.71–7.61 (m, 1H), 7.57–7.42 (m, 3H), 7.37–7.26 (m, 5H), 7.22–7.10 (m, 2H), 6.97 (d, J = 7.8 Hz, 1H), 6.70–6.59 (m, 2H), 5.98 (s, 1H), 4.36–4.25 (m, 2H), 3.51 (d, J = 12.8 Hz, 1H), 3.42–3.33 (m, 2H), 3.06–2.92 (m, 2H), 2.81 (dd, J = 14.7, 3.7 Hz, 1H), 2.34–2.18 (m, 2H), 2.09–1.96 (m, 1H), 1.97–1.84 (m, 1H), 1.65 (s, 3H) ppm.

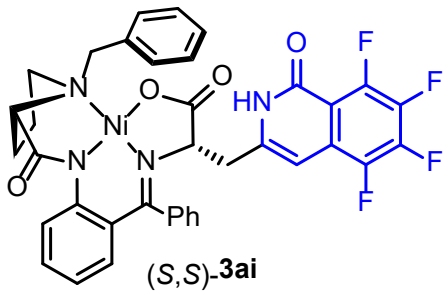
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.5, 179.0, 172.1, 161.4, 142.9, 140.8, 136.5, 133.7, 133.6, 133.5, 133.4, 132.9, 132.7, 131.6, 130.4, 129.6, 129.3, 129.1, 129.0, 127.9, 127.2, 126.3, 126.0, 123.8, 123.0, 122.9, 120.9, 106.1, 70.5, 68.5, 63.6, 57.6, 38.5, 31.1, 30.7, 23.9 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{38}H_{35}N_4NiO_4^+$ $[M+H]^+$: 669.2006, found: 669.2006.

$[\alpha]_D^{25}$ +1625 (*c* 0.016, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 2,3,4,5-tetrafluoro-*N*-(pivaloyloxy)benzamide **2i**, the desired product (*S*,*S*)-**3ai** was isolated as an orange powder (59 mg, 81% yield); eluent: CH_2Cl_2/acetone (2:1).



(*S*,*S*)-**3ai**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.77 (s, 1H, NH), 8.13–8.03 (m, 3H), 7.54–7.39 (m, 3H), 7.39–7.27 (m, 3H), 7.20–7.08 (m, 2H), 6.99 (d, *J* = 6.8 Hz, 1H), 6.69–6.59 (m, 2H), 5.77 (s, 1H), 4.37–4.27 (m, 2H), 3.57 (d, *J* = 12.6 Hz, 1H), 3.50–3.26 (m, 4H), 2.84 (d, *J* = 12.4 Hz, 1H), 2.67–2.58 (m, 1H), 2.54–2.40 (m, 1H), 2.11–2.00 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.5, 172.3, 159.0, 142.7, 139.2, 133.6, 133.5, 133.3, 132.7, 131.5, 130.3, 129.6, 129.3, 129.1, 129.0, 127.8, 127.3, 126.4, 124.7, 124.6, 123.8, 120.9, 110.5, 95.7, 70.4, 68.6, 63.5, 57.4, 39.0, 30.7, 24.1 ppm. The signals of carbon atoms bonded with fluorine atoms were not observed in ^{13}C NMR because of their high multiplicity and low intensity.

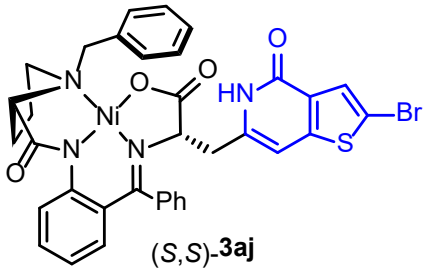
^{19}F NMR (376 MHz, $CDCl_3$): δ = –138.87 (s, 1F), –147.82 (t, *J* = 18.2 Hz, 1F), –149.20 (t, *J* = 19.7 Hz, 1F), –158.52 (t, *J* = 18.8 Hz, 1F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{37}H_{29}F_4N_4NiO_4^+$ $[M+H]^+$: 727.1473, found: 727.1473.

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

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1a** and 5-bromo-*N*-((*tert*-butoxycarbonyl)oxy)thiophene-3-carboxamide **2j**, the desired product (*S*,*S*)-**3aj** was isolated as an orange powder (61 mg, 82% yield); eluent: CH_2Cl_2/acetone (1:2).



(*S*,*S*)-**3aj**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.55 (s, 1H, NH), 8.12 (d, *J* = 8.6 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 2H), 7.49–7.33 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.06–6.98 (m, 1H), 6.63–6.50 (m, 2H), 6.31 (s, 1H), 4.33–4.21 (m, 2H), 3.50 (d, *J* = 12.7 Hz, 1H), 3.38 (dd, *J* = 10.5, 6.4 Hz, 1H), 3.31–3.22 (m, 1H), 3.17 (dd, *J* = 14.7, 5.7 Hz, 1H), 2.99–2.81 (m, 2H), 2.61–2.49 (m, 1H), 2.46–2.32 (m, 1H), 2.05–1.95 (m, 1H), 1.85–1.76 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.3, 178.7, 172.4, 159.2, 150.6, 142.7, 138.2, 133.8, 133.6, 133.3, 132.6, 131.5, 130.0, 129.6, 129.3, 129.2, 129.0, 128.9, 128.0, 127.0, 126.9, 126.1, 123.3, 120.6, 112.0, 101.7, 70.5, 69.3, 63.5, 57.5, 38.8, 30.8, 23.7 ppm.

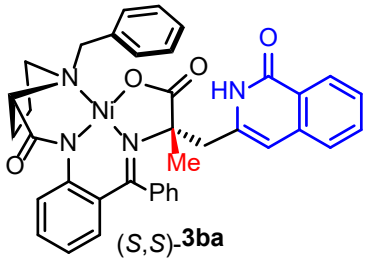
HRMS (ESI, *m*/*z*) calcd. for $C_{35}H_{30}BrN_4NiO_4S^+$ $[M+H]^+$: 741.0499, found: 741.0493.

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

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1b** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*S*)-**3ba** was isolated as an orange powder (57 mg, 82% yield); eluent: CH_2Cl_2/acetone (2:1).

Comment: *A gram-scale reaction was performed with 1.82 mmol of the Ni(II) complex (S,S)-**1b** (1.00 g) by the addition of **2a** (0.40 g, 1.82 mmol), [Cp*RhCl$_2$]$_2$ (0.022 g, 0.036 mmol) and CsOAc (0.692 g, 3.64 mmol) in 20 mL of MeOH. Yield 0.95 g (78%).*



(*S*,*S*)-**3ba**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.18 (s, 1H, NH), 8.38 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.66–7.58 (m, 1H), 7.54–7.39 (m, 5H), 7.36–7.28 (m, 3H), 7.24–7.16 (m, 2H), 7.13–7.06 (m, 1H), 6.65–6.54 (m, 3H), 4.23 (d, *J* = 12.6 Hz, 1H), 3.54 (d, *J* = 12.6 Hz, 1H), 3.30–3.21 (m, 2H), 3.01–2.87 (m, 2H), 2.18–1.98 (m, 2H), 1.95–1.77 (m, 2H), 1.51–1.39 (m, 1H), 1.25 (s, 3H) ppm.

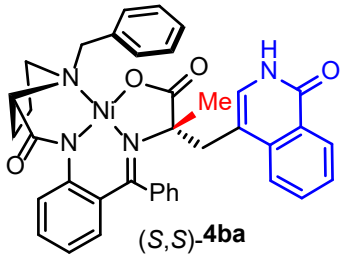
^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.4, 180.4, 173.1, 163.4, 142.1, 137.9, 136.4, 133.8, 133.4, 132.8, 132.1, 131.5, 130.4, 129.7, 128.9, 128.8, 128.3, 127.8, 127.4, 126.7, 126.2, 123.5, 120.6, 106.9, 76.7, 70.1, 63.7, 57.5, 43.4, 30.0, 29.9, 23.1 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{38}H_{35}N_4NiO_4^+$ $[M+H]^+$: 669.2006, found: 669.2007.

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

Ni(II) complex (S,S)-4ba

Starting from a chiral Ni(II) complex (*S*,*S*)-**1b** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*S*)-**4ba** (*the second eluting diastereomer*) was isolated *from a gram-scale reaction* as an orange powder (36 mg, 3% yield); eluent: CH_2Cl_2/acetone (1:3).



(*S*,*S*)-**4ba**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.65 (s, 1H, NH), 8.49–8.42 (m, 1H), 8.09 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.55–7.49 (m, 1H), 7.47–7.39 (m, 5H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29–7.26 (m, 1H), 7.20–7.14 (m, 2H), 7.11–7.03 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.60–6.55 (m, 2H), 4.28 (d, *J* = 12.6 Hz, 1H), 3.52 (d, *J* = 12.6 Hz, 1H), 3.40–3.31 (m, 2H), 3.31–3.23 (m, 1H), 3.08 (d, *J* = 15.4 Hz, 1H), 2.54–2.38 (m, 1H), 2.33–2.18 (m, 1H), 2.12–2.04 (m, 1H), 1.97–1.88 (m, 1H), 1.81–1.70 (m, 1H), 1.19 (s, 3H) ppm.

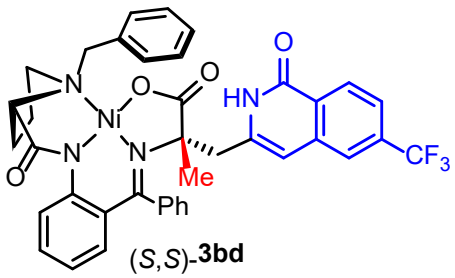
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.7, 180.4, 172.0, 163.4, 141.8, 137.9, 136.5, 133.7, 133.5, 132.4, 131.9, 131.3, 129.8, 129.3, 128.8, 128.7, 128.0, 127.6, 127.4, 127.2, 126.7, 126.5, 125.6, 123.6, 123.4, 120.4, 111.7, 78.2, 70.0, 63.5, 57.3, 40.4, 30.2, 29.3, 23.2 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{38}H_{35}N_4NiO_4^+$ $[M+H]^+$: 669.2006, found: 669.2000.

$[\alpha]_D^{25}$ +1400 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1b** and 4-trifluoromethyl-*N*-(pivaloyloxy)benzamide **2d**, the desired product (*S*,*S*)-**3bd** was isolated as an orange powder (66 mg, 89% yield); eluent: CH_2Cl_2/acetone (2:1).



(*S*,*S*)-**3bd**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70 (s, 1H, NH), 8.45 (d, J = 8.4 Hz, 1H), 8.06–7.97 (m, 3H), 7.78 (s, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.57–7.46 (m, 3H), 7.340–7.30 (m, 3H), 7.26–7.22 (m, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.13–7.08 (m, 1H), 6.59 (d, J = 4.2 Hz, 2H), 6.54 (s, 1H), 4.29 (d, J = 12.6 Hz, 1H), 3.59 (d, J = 12.6 Hz, 1H), 3.46–3.34 (m, 1H), 3.29 (dd, J = 10.4, 6.4 Hz, 1H), 2.97 (dd, J = 50.7, 15.1 Hz, 2H), 2.45–2.37 (m, 1H), 2.19–2.09 (m, 1H), 2.03–1.91 (m, 2H), 1.64–1.60 (m, 1H), 1.32 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.9, 180.5, 173.5, 162.3, 142.3, 138.3, 137.8, 136.5, 133.8, 133.4, 132.4, 131.7, 130.6, 130.0, 129.2, 129.0, 128.7, 128.5, 128.1, 127.7, 127.6, 123.9, 123.5, 122.7, 120.9, 106.3, 76.4, 70.1, 63.8, 57.6, 43.2, 30.4, 30.0, 23.4 ppm.

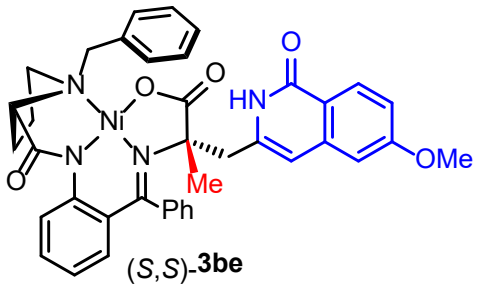
^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.1 (s, 3F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{39}H_{34}F_3N_4NiO_4^+$ $[M+H]^+$: 737.1880, found: 737.1877.

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

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1b** and 4-methoxy-*N*-(pivaloyloxy)benzamide **2e**, the desired product (*S*,*S*)-**3be** was isolated as an orange powder (55 mg, 79% yield); eluent: CH_2Cl_2/acetone (1:1).



(*S*,*S*)-**3be**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (s, 1H, NH), 8.30 (d, J = 8.9 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 8.03 (d, J = 7.1 Hz, 2H), 7.57–7.50 (m, 2H), 7.50–7.43 (m, 1H), 7.38–7.32 (m, 3H), 7.25–7.16 (m, 2H), 7.15–7.09 (m, 1H), 7.02 (dd, J = 8.9, 2.4 Hz, 1H), 6.83 (d, J = 2.4 Hz, 1H), 6.64–6.59 (m, 2H), 6.47 (s, 1H), 4.27 (d, J = 12.6 Hz, 1H), 3.86 (s, 3H), 3.56 (d, J = 12.6 Hz, 1H), 3.36–3.28 (m, 1H), 3.24 (dd, J = 10.3, 6.7 Hz, 1H), 3.02–2.81 (m, 2H), 2.28–2.18 (m, 1H), 2.09–1.98 (m, 1H), 1.98–1.89 (m, 1H), 1.85–1.73 (m, 1H), 1.57–1.46 (m, 1H), 1.28 (s, 3H) ppm.

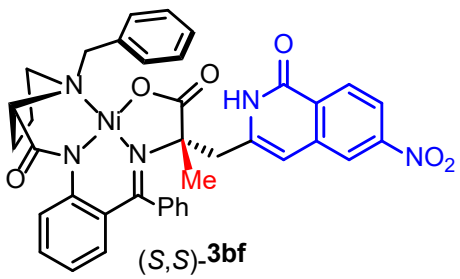
^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.4, 180.4, 173.1, 163.3, 162.9, 142.4, 140.1, 137.0, 136.6, 133.9, 133.5, 132.2, 131.6, 130.7, 129.9, 129.5, 129.0, 128.9, 128.4, 128.0, 127.6, 127.5, 123.8, 120.7, 119.3, 116.8, 106.9, 106.8, 76.8, 70.2, 63.8, 57.6, 55.7, 43.5, 30.2, 30.1, 23.2 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{39}H_{37}N_4NiO_5^+$ $[M+H]^+$: 699.2112, found: 699.2108.

$[\alpha]_D^{25}$ +2200 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1b** and 4-nitro-*N*-(pivaloyloxy)benzamide **2f**, the desired product (*S*,*S*)-**3bf** was isolated as an orange powder (57 mg, 80% yield); eluent: CH_2Cl_2/acetone (2:1).



(*S*,*S*)-**3bf**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.19 (s, 1H, NH), 8.46 (d, J = 8.8 Hz, 1H), 8.36 (s, 1H), 8.16 (d, J = 8.8 Hz, 1H), 8.05 (t, J = 8.4 Hz, 3H), 7.60–7.47 (m, 3H), 7.43–7.33 (m, 3H), 7.30–7.24 (m, 1H), 7.21 (d, J = 7.4 Hz, 1H), 7.15–7.06 (m, 1H), 6.63–6.54 (m, 3H), 4.30 (d, J = 12.6 Hz, 1H), 3.63 (d, J = 12.6 Hz, 1H), 3.50–3.41 (m, 1H), 3.34 (dd, J = 10.3, 6.3 Hz, 1H), 3.04 (dd, J = 32.7, 15.3 Hz,

2H), 2.67–2.52 (m, 1H), 2.32–2.10 (m, 2H), 2.03–1.94 (m, 1H), 1.79–1.67 (m, 1H), 1.34 (s, 3H) ppm.

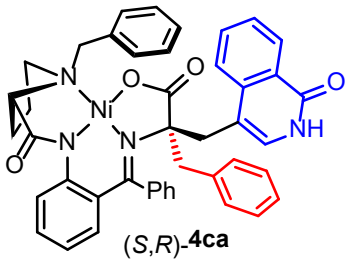
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.9, 173.5, 170.6, 162.7, 150.4, 142.2, 139.1, 136.4, 133.8, 133.4, 132.3, 132.2, 131.6, 131.5, 130.4, 130.0, 129.9, 129.1, 129.0, 128.5, 127.9, 127.7, 123.8, 122.0, 120.8, 120.1, 106.5, 76.7, 70.2, 63.8, 57.5, 43.4, 30.4, 29.8, 23.5 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{38}H_{34}N_5NiO_6^+$ $[M+H]^+$: 714.1857, found: 714.1862.

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

Ni(II) complexes (S,R)-4ca

Starting from a chiral Ni(II) complex (*S*,*S*)-**1c** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*R*)-**4ca** (*the first eluting diastereomer*) was isolated as an orange powder (41 mg, 55% yield); eluent: CH_2Cl_2/PE/Et_3N (4:2:1).



(*S*,*R*)-**4ca**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.65 (s, 1H, NH), 8.22 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 5.5 Hz, 1H), 7.57–7.40 (m, 9H), 7.36–7.23 (m, 3H), 7.18–7.07 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.56 (t, *J* = 7.5 Hz, 2H), 6.48 (d, *J* = 8.3, 1H), 4.69 (d, *J* = 13.0 Hz, 1H), 4.01 (d, *J* = 13.0 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 3.31 (dd, *J* = 9.8, 7.7 Hz, 1H), 3.22 (d, *J* = 17.6 Hz, 1H), 3.08 (d, *J* = 13.4 Hz, 1H), 3.02–2.93 (m, 1H), 2.25 (d, *J* = 17.6 Hz, 1H), 2.16–2.07 (m, 2H), 1.92–1.84 (m, 1H), 1.76–1.70 (m, 1H), 1.46–1.40 (m, 1H) ppm.

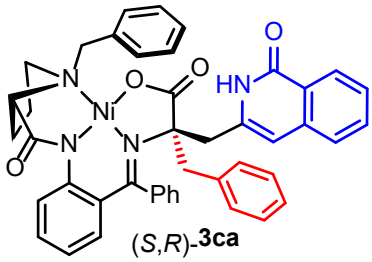
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.6, 172.4, 163.5, 142.9, 137.4, 136.5, 136.2, 134.2, 132.6, 132.5, 132.2, 132.0, 131.6, 129.5, 129.3, 129.1, 129.0, 128.1, 128.0, 127.8, 127.6, 127.5, 126.9, 126.7, 126.2, 125.5, 123.7, 122.7, 120.8, 111.8, 79.8, 69.3, 63.0, 56.5, 47.2, 39.7, 30.1, 22.8 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{39}N_4NiO_4^+$ $[M+H]^+$: 745.2319, found: 745.2322.

$[\alpha]_D^{25}$ +1900 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1c** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*R*)-**3ca** (*the second eluting diastereomer*) was isolated as an orange powder (27 mg, 36% yield); eluent: CH_2Cl_2/PE/Et_3N (4:2:1).



(*S*,*R*)-**3ca**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (br. s, 1H, NH), 8.34 (t, *J* = 8.1 Hz, 3H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.56–7.38 (m, 10H), 7.32–7.23 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.09–7.02 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.77 (s, 1H), 6.58–6.49 (m, 2H), 4.54 (d, *J* = 12.6 Hz, 1H), 3.44–3.25 (m, 4H), 3.06–2.95 (m, 2H), 2.27–2.15 (m, 1H), 2.11–1.96 (m, 3H), 1.80–1.73 (m, 1H), 1.56–1.48 (m, 1H) ppm.

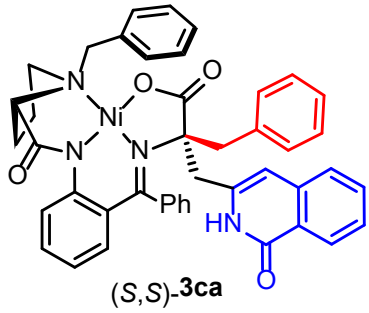
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 179.1, 172.5, 163.1, 142.7, 138.1, 136.4, 136.3, 135.8, 134.0, 133.5, 133.1, 132.3, 131.8, 131.6, 130.3, 129.3, 129.1, 129.0, 128.7, 128.6, 128.2, 127.8, 127.7, 127.3, 127.2, 126.8, 126.2, 124.9, 123.8, 120.7, 105.0, 78.9, 69.6, 64.2, 58.4, 46.8, 43.2, 30.4, 23.1 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{39}N_4NiO_4^+$ $[M+H]^+$: 745.2319, found: 745.2322.

$[\alpha]_D^{25}$ +2042 (*c* 0.07, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*R*)-**1c** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*S*)-**3ca** (*the first eluting diastereomer*) was isolated as an orange powder (52 mg, 70% yield); eluent: CH_2Cl_2/acetone (3:1).



(*S*,*S*)-**3ca**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.28 (s, 1H, NH), 8.41 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.54–7.28 (m, 12H), 7.24–7.19 (m, 1H), 7.13–7.08 (m, 1H), 7.02 (d, *J* = 7.7 Hz, 1H), 6.88 (s, 1H), 6.65–6.59 (m, 2H), 4.14 (d, *J* = 12.9 Hz, 1H), 3.47–3.38 (m, 1H), 3.30 (d, *J* = 12.9 Hz, 1H), 3.22 (dd, *J* = 10.3, 6.2 Hz, 1H), 3.16 (br. s, 2 H), 3.05 (d, *J* = 16.0 Hz, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 2.47–2.34 (m, 1H), 2.02–1.92 (m, 2H), 1.90–1.79 (m, 1H), 1.63–1.52 (m, 1H) ppm.

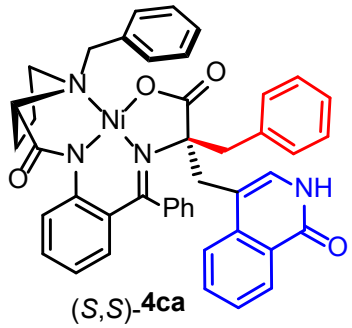
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.9, 180.2, 173.3, 163.3, 142.2, 138.0, 136.6, 136.3, 135.8, 133.6, 133.1, 133.0, 132.1, 131.8, 130.2, 129.0, 128.9, 128.8, 128.4, 128.3, 127.9, 127.8, 127.6, 127.4, 126.9, 126.3, 125.4, 124.3, 120.9, 106.5, 79.6, 69.2, 63.0, 57.6, 47.2, 41.9, 30.6, 23.5 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{39}N_4NiO_4^+$ $[M+H]^+$: 745.2319, found: 745.2320.

$[\alpha]_D^{25}$ +1375 (*c* 0.02, MeOH).

Ni(II) complex (S,S)-4ca

Starting from a chiral Ni(II) complex (*S*,*R*)-**1c** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*S*)-**4ca** (*the second eluting diastereomer*) was isolated as an orange powder (10 mg, 14% yield); eluent: CH_2Cl_2/acetone (1:3).



(*S*,*S*)-**4ca**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.14 (s, 1H, NH), 8.47 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.76 (s, 1H), 7.59–7.28 (m, 12H), 7.26–7.13 (m, 5H), 6.82–6.71 (m, 2H), 6.67–6.59 (m, 2H), 3.94 (d, *J* = 13.3 Hz, 1H), 3.61–3.54 (m, 1H), 3.50–3.44 (m, 1H), 3.32–3.21 (m, 3H), 2.59–2.38 (m, 2H), 2.16–2.09 (m, 2H), 1.96–1.82 (m, 1H), 1.74–1.64 (m, 2H) ppm.

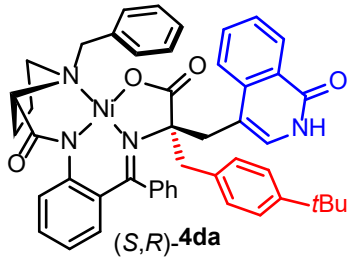
The ^{13}C NMR spectrum was not recorded due to the small amount of (*S*,*S*)-**4ca**.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{39}N_4NiO_4^+$ $[M+H]^+$: 745.2319, found: 745.2316.

$[\alpha]_D^{25}$ +1477 (*c* 0.022, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1d** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*R*)-**4da** (*the first eluting diastereomer*) was isolated as an orange powder (40 mg, 50% yield); eluent: EtOAc/Et_2O (1:1).



(*S*,*R*)-**4da**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.60 (s, 1H, NH), 8.27 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 6.7 Hz, 1H), 7.82 (d, J = 7.1 Hz, 2H), 7.75 (br. s, 1H), 7.61–7.48 (m, 3H), 7.47–7.28 (m, 7H), 7.25–7.20 (m, 1H), 7.20–7.09 (m, 2H), 7.07–6.95 (m, 1H), 6.68–6.52 (m, 3H), 6.46 (d, J = 8.7 Hz, 1H), 4.72 (d, J = 13.2 Hz, 1H), 4.08 (d, J = 13.2 Hz, 1H), 3.44 (d, J = 13.8 Hz, 1H), 3.38–3.16 (m, 2H), 3.12–2.99 (m, 2H), 2.32 (d, J = 17.5 Hz, 1H), 2.23–2.08 (m, 2H), 1.81–1.68 (m, 2H), 1.49–1.40 (m, 1H), 1.37 (s, 9H) ppm.

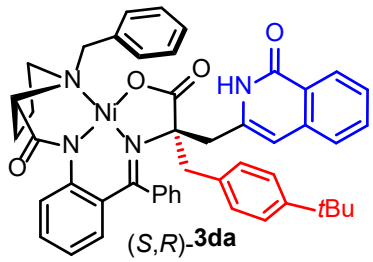
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.8, 172.5, 163.8, 150.8, 142.8, 137.5, 136.5, 134.2, 133.1, 132.4, 132.2, 132.1, 131.2, 129.5, 129.1, 129.0, 128.2, 128.0, 127.8, 127.5, 127.0, 126.7, 126.2, 125.7, 123.7, 122.7, 120.8, 111.9, 79.8, 68.8, 62.4, 55.4, 46.6, 39.9, 34.8, 31.6, 30.5, 22.4 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{48}H_{47}N_4NiO_4^+$ $[M+H]^+$: 801.2945, found: 801.2944.

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

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1d** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*R*)-**3da** (*the second eluting diastereomer*) was isolated as an orange powder (32 mg, 40% yield); eluent: EtOAc/Et_2O (1:1).



(*S*,*R*)-**3da**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.32 (s, 1H, NH), 8.38 (d, J = 6.9 Hz, 2H), 8.22 (d, J = 7.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.79–7.61 (m, 2H), 7.59–7.38 (m, 9H), 7.25–7.20 (m, 1H), 7.18–6.93 (m, 3H), 6.84 (s, 1H), 6.63–6.47 (m, 2H), 4.60 (d, J = 12.6 Hz, 1H), 3.49 (d, J = 12.6 Hz, 1H), 3.41–3.22 (m, 3H), 3.22–3.08 (m, 1H), 2.98 (d, J = 14.0 Hz, 1H), 2.29–2.18 (m, 1H), 2.15–1.99 (m, 2H), 1.94–1.77 (m, 2H), 1.56–1.44 (m, 1H), 1.37 (s, 9H) ppm.

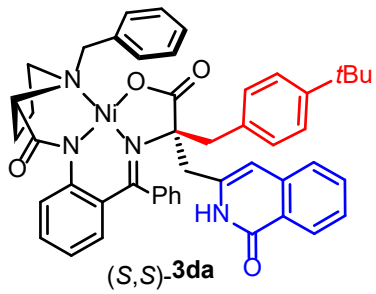
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 179.3, 172.6, 163.2, 150.9, 142.6, 138.3, 136.4, 136.3, 134.0, 133.3, 133.1, 132.7, 132.3, 131.8, 131.2, 130.3, 129.1, 129.0, 128.7, 128.5, 127.7, 127.4, 127.3, 126.8, 126.3, 123.8, 120.8, 105.0, 78.9, 69.6, 63.9, 57.7, 46.2, 43.4, 34.8, 31.6, 30.8, 22.7 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{48}H_{47}N_4NiO_4^+$ $[M+H]^+$: 801.2945, found: 801.2949.

$[\alpha]_D^{25}$ +1800 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*R*)-**1d** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*S*)-**3da** (*the first eluting diastereomer*) was isolated as an orange powder (56 mg, 70% yield); eluent: CH_2Cl_2/acetone (3:1).



(*S*,*S*)-**3da**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.34 (s, 1H, NH), 8.43 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.72–7.60 (m, 2H), 7.57–7.40 (m, 7H), 7.33 (t, J = 7.5 Hz, 2H), 7.29–7.21 (m, 3H), 7.19–7.10 (m, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.97 (s, 1H), 6.70–6.61 (m, 2H), 4.24 (d, J = 12.8 Hz, 1H), 3.38–3.29 (m, 2H), 3.29–3.16 (m, 2H), 3.07 (dd, J = 15.5, 10.1 Hz, 2H), 2.66 (d, J = 16.0 Hz, 1H), 2.56–2.40 (m, 1H), 2.14–2.02 (m, 1H), 1.97–1.82 (m, 2H), 1.67–1.56 (m, 1H), 1.27 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.9, 180.3, 173.3, 163.2, 150.2, 142.2, 137.9, 136.7, 136.5, 136.4, 133.6, 133.0, 132.7, 132.5, 132.0, 131.8, 130.1, 129.8, 129.0, 128.9, 128.6, 128.5, 128.3, 127.8, 127.7,

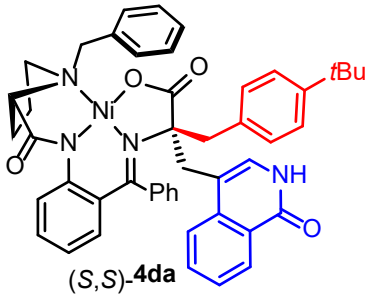
127.6, 126.8, 126.3, 125.6, 125.4, 124.3, 120.9, 106.3, 79.8, 69.0, 62.8, 57.1, 46.9, 41.6, 34.6, 31.4, 30.5, 23.3 ppm.

HRMS (ESI, *m/z*) calcd. for $C_{48}H_{47}N_4NiO_4^+$ $[M+H]^+$: 801.2945, found: 801.2944.

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

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

Starting from a chiral Ni(II) complex (*S,R*)-**1d** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S,S*)-**4da** (*the second eluting diastereomer*) was isolated as an orange powder (17 mg, 21% yield); eluent: CH_2Cl_2/acetone (1:2).



(*S,S*)-**4da**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.04 (s, 1H, NH), 8.45 (d, *J* = 7.6 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 8.05 (s, 1H), 7.56–7.40 (m, 7H), 7.39–7.27 (m, 7H), 7.22 (t, *J* = 6.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.77–6.70 (m, 2H), 6.67–6.59 (m, 2H), 4.22 (d, *J* = 13.2 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.39–3.31 (m, 1H), 3.30–3.20 (m, 3H), 3.13 (d, *J* = 14.3 Hz, 1H), 2.88–2.72 (m, 1H), 2.52–2.33 (m, 2H), 2.28–2.12 (m, 1H), 1.92–1.75 (m, 2H), 1.21 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.3, 180.2, 172.9, 166.5, 150.5, 142.5, 137.8, 136.9, 134.1, 133.1, 132.5, 132.4, 132.3, 132.2, 131.4, 130.3, 129.6, 129.0, 128.8, 128.2, 128.1, 127.9, 127.8, 127.6, 127.0, 126.9, 126.4, 125.7, 124.3, 123.3, 121.0, 112.1, 74.4, 61.3, 55.3, 47.9, 38.5, 34.6, 31.5, 30.8, 23.6 ppm.

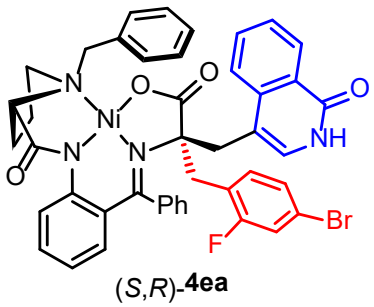
HRMS (ESI, *m/z*) calcd. for $C_{48}H_{47}N_4NiO_4^+$ $[M+H]^+$: 801.2945, found: 801.2942.

$[\alpha]_D^{25}$ +1225 (*c* 0.02, MeOH).

Ni(II) complex (S,R)-4ea

Starting from a chiral Ni(II) complex (*S,S*)-**1e** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S,R*)-**4ea** (*the first eluting diastereomer*) was isolated as an orange powder (55 mg, 65% yield); eluent: CH_2Cl_2/PE/Et_3N (4:8:1).

Comment: *A gram-scale reaction was performed with 1.23 mmol of the Ni(II) complex (S,S)-**1e** (0.89 g) by the addition of **2a** (0.272 g, 1.23 mmol), $[Cp^*RhCl_2]_2$ (0.015 g, 0.025 mmol) and CsOAc (0.467 g, 2.26 mmol) in 20 mL of MeOH. Yield 0.67 g (64%).*



(*S,R*)-**4ea**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 12.15 (d, *J* = 5.0 Hz, 1H, NH), 8.31 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 3H), 7.65 (d, *J* = 5.6 Hz, 1H), 7.50–7.36 (m, 8H), 7.35–7.27 (m, 2H), 7.17–7.10 (m, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.59–6.38 (m, 4H), 4.78 (d, *J* = 13.0 Hz, 1H), 4.11 (d, *J* = 13.0 Hz, 1H), 3.70 (d, *J* = 13.4 Hz, 1H), 3.38 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.15 (d, *J* = 17.7 Hz, 1H), 3.09–3.01 (m, 1H), 2.94 (d, *J* = 13.4 Hz, 1H), 2.39–2.17 (m, 2H), 2.11 (d, *J* = 17.7 Hz, 1H), 2.02–1.89 (m, 2H), 1.68–1.51 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.4, 179.2, 173.8, 163.8, 161.1, 142.9, 137.3, 136.6, 135.2 (d, *J* = 5.1 Hz), 134.3, 132.5, 132.3, 132.1, 129.3, 129.2, 129.1, 128.6, 128.5, 128.3, 127.7 (d, *J* = 10.1 Hz), 127.4, 126.8 (d, *J* = 7.3 Hz), 126.6, 126.0, 125.5, 123.4, 122.6, 122.5. 122.5 (d, *J* = 12.9 Hz), 120.6, 119.6 (d, *J* = 25.9 Hz), 111.9, 79.5, 69.0, 62.8, 56.1, 41.5, 39.3, 30.5, 22.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.4 (s, 1F) ppm.

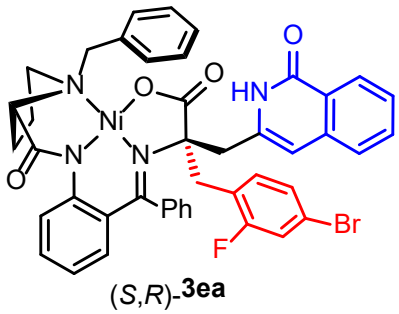
HRMS (ESI, *m/z*) calcd. for $C_{44}H_{37}BrFN_4NiO_4^+$ $[M+H]^+$: 841.1330, found: 841.1324.

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

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

Starting from a chiral Ni(II) complex (*S,S*)-**1e** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,R*)-**3ea** (*the second eluting diastereomer*) was isolated as an orange powder (22 mg, 26% yield); eluent: CH_2Cl_2/PE/Et_3N (4:4:1).

Yield in a gram-scale reaction (0.23 g, 22%).



(*S,R*)-**3ea**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (s, 1H, NH), 8.16 (d, *J* = 7.6 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.30–7.04 (m, 10H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.88–6.79 (m, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.57 (s, 1H), 6.33–6.24 (m, 2H), 4.39 (d, *J* = 12.6 Hz, 1H), 3.41 (d, *J* = 13.7 Hz, 1H), 3.27 (d, *J* = 12.6 Hz, 1H), 3.23–3.03 (m, 2H), 2.95–2.84 (m, 1H), 2.67 (d, *J* = 13.7 Hz, 1H), 2.24–2.08 (m, 1H), 2.05–1.77 (m, 3H), 1.74–1.64 (m, 1H), 1.54–1.41 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 178.7, 173.7, 163.7, 163.3, 142.7, 138.1, 136.6, 136.3, 135.1 (d, *J* = 4.7 Hz), 134.1, 133.4, 133.0, 132.3, 131.8, 130.2, 129.2, 129.0, 128.7, 128.6, 128.4, 127.6 (d, *J* = 7.5 Hz), 127.2, 127.0 (d, *J* = 6.4 Hz), 126.7, 126.2, 124.8, 123.5, 122.7 (d, *J* = 9.6 Hz), 122.2 (d, *J* = 15.7 Hz), 120.6, 119.7 (d, *J* = 26.3 Hz), 104.6, 78.4, 69.7, 64.3, 58.5, 42.7, 41.3, 30.9, 23.2 ppm.

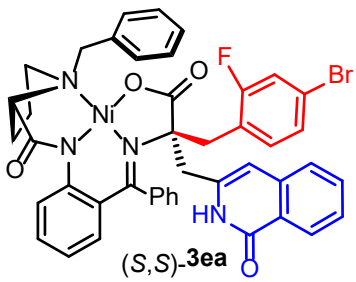
^{19}F NMR (376 MHz, $CDCl_3$): δ = –110.2 (s, 1F) ppm.

HRMS (ESI, *m/z*) calcd. for $C_{44}H_{37}BrFN_4NiO_4^+$ $[M+H]^+$: 841.1330, found: 841.1331.

$[\alpha]_D^{25}$ +1900 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S,R*)-**1e** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S,S*)-**3ea** (*the first eluting diastereomer*) was isolated as an orange powder (55 mg, 66% yield); eluent: CH_2Cl_2/acetone (3:1).



(*S,S*)-**3ea**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.53 (s, 1H, NH), 8.40 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.72–7.59 (m, 2H), 7.54–7.41 (m, 5H), 7.41–7.32 (m, 5H), 7.31–7.25 (m, 1H), 7.18–7.09 (m, 1H), 7.01–6.94 (m, 2H), 6.68–6.57 (m, 2H), 4.23 (d, *J* = 12.8 Hz, 1H), 3.50–3.37 (m, 2H), 3.33–3.18 (m, 2H), 3.03 (dd, *J* = 50.4, 15.8 Hz, 2H), 2.59–2.39 (m, 2H), 2.09–1.92 (m, 3H), 1.70–1.58 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.8, 179.7, 174.7, 163.4, 162.5, 160.0, 142.1, 137.9, 136.6, 136.2, 133.8, 133.1, 133.0, 132.8, 132.2, 131.7, 130.2, 129.1, 129.0, 128.5, 128.3 (d, *J* = 10.8 Hz), 128.0, 127.9, 127.8, 127.6 (d, *J* = 5.5 Hz), 126.9, 126.3, 125.3, 124.2, 122.4 (d, *J* =15.2 Hz), 121.7 (d, *J* =9.8 Hz), 120.9, 119.1 (d, *J* = 26.2 Hz), 106.5, 78.7, 69.2, 63.1, 57.5, 41.8, 40.9, 30.6, 23.5 ppm.

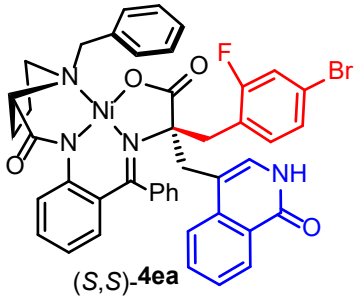
^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.2 (s, 1F) ppm.

HRMS (ESI, *m/z*) calcd. for $C_{44}H_{37}BrFN_4NiO_4^+$ $[M+H]^+$: 841.1330, found: 841.1331.

$[\alpha]_D^{25}$ +1350 (*c* 0.02, MeOH).

Ni(II) complex (S,S)-4ea

Starting from a chiral Ni(II) complex (*S*,*R*)-**1e** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*S*)-**4ea** (*the second eluting diastereomer*) was isolated as an orange powder (18 mg, 21% yield); eluent: CH_2Cl_2/acetone (1:2).



(*S*,*S*)-**4ea**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.49 (s, 1H, NH), 8.46 (d, J = 6.2 Hz, 1H), 8.14–8.07 (m, 1H), 8.01–7.94 (m, 1H), 7.64 (d, J = 6.8 Hz, 2H), 7.54–7.27 (m, 11H), 7.21–7.12 (m, 2H), 6.80–6.70 (m, 2H), 6.66–6.60 (m, 2H), 4.19 (d, J = 13.3 Hz, 1H), 3.59–3.44 (m, 2H), 3.39–3.19 (m, 3H), 3.01 (d, J = 14.9 Hz, 1H), 2.74–2.56 (m, 1H), 2.45 (d, J = 17.0 Hz, 1H), 2.41–2.26 (m, 1H), 2.16–2.03 (m, 2H), 1.84–1.74 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 181.1, 179.5, 174.1, 163.4, 162.8, 160.3, 142.4, 137.8, 136.7, 134.1, 133.3, 132.5, 132.4, 132.3, 131.9, 129.6, 129.1, 129.0, 128.1 (d, J = 9.4 Hz), 128.0, 127.9, 127.4 (d, J = 5.2 Hz), 127.0, 126.9, 126.8, 126.4, 124.2, 123.3, 123.1 (d, J = 15.4 Hz), 121.7 (d, J = 10.2 Hz), 121.0, 119.1 (d, J = 25.9 Hz), 111.9, 79.8, 68.9, 62.4, 56.7, 41.2, 38.9, 30.9, 23.7 ppm.

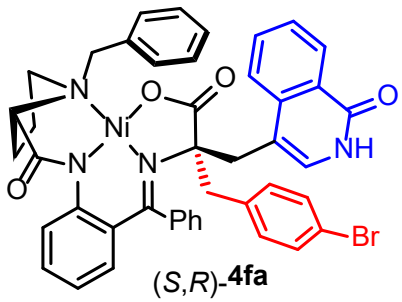
^{19}F NMR (376 MHz, $CDCl_3$): δ = –111.3 (s, 1F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{37}BrFN_4NiO_4^+$ $[M+H]^+$: 841.1330, found: 841.1325.

$[\alpha]_D^{25}$ +1100 (*c* 0.02, MeOH).

Ni(II) complex (S,R)-4fa

Starting from a chiral Ni(II) complex (*S*,*S*)-**1f** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*R*)-**4fa** (*the first eluting diastereomer*) was isolated as an orange powder (44 mg, 54% yield); eluent: CH_2Cl_2/PE/Et_3N (4:4:1).



(*S*,*R*)-**4fa**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.05 (s, 1H, NH), 8.22 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 7.3 Hz, 3H), 7.67 (d, J = 8.1 Hz, 3H), 7.51–7.39 (m, 4H), 7.38–7.32 (m, 3H), 7.32–7.26 (m, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 6.61 (d, J = 7.7 Hz, 1H), 6.55 (t, J = 7.6 Hz, 2H), 6.45 (d, J = 8.2 Hz, 1H), 4.74 (d, J = 13.0 Hz, 1H), 4.03 (d, J = 13.0 Hz, 1H), 3.44–3.30 (m, 2H), 3.19 (d, J = 17.6 Hz, 1H), 3.06–2.93 (m, 2H), 2.31–2.15 (m, 3H), 2.00–1.82 (m, 2H), 1.61–1.49 (m, 1H) ppm.

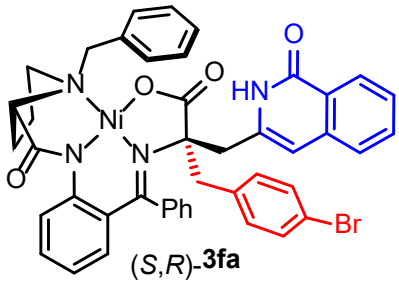
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 179.4, 172.6, 163.7, 142.9, 137.3, 136.4, 135.1, 134.2, 133.2, 132.5, 132.4, 132.3, 132.2, 132.1, 129.6, 129.2, 129.1, 128.1, 128.0, 127.8, 127.7, 127.3, 126.7, 126.1, 125.6, 123.7, 122.6, 122.5, 120.8, 111.6, 79.6, 68.9, 62.9, 56.4, 46.5, 39.7, 30.3, 22.8 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{38}BrN_4NiO_4^+$ $[M+H]^+$: 823.1424, found: 823.1420.

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

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1f** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*R*)-**3fa** (*the second eluting diastereomer*) was isolated as an orange powder (30 mg, 36% yield); eluent: CH_2Cl_2/PE/Et_3N (4:4:1).



(*S*,*R*)-**3fa**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.07 (s, 1H, NH), 8.37 (d, J = 7.4 Hz, 2H), 8.32 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.67–7.59 (m, 3H), 7.50–7.38 (m, 4H), 7.36 (d, J = 8.3 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.24–7.20 (m, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.07–7.00 (m, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.77 (s, 1H), 6.57–6.47 (m, 2H), 4.54 (d, J = 12.6 Hz, 1H), 3.43–3.22 (m, 4H), 3.07–2.97 (m, 1H), 2.91 (d, J = 13.7 Hz, 1H), 2.39–2.23 (m, 1H), 2.16–1.99 (m, 3H), 1.94–1.80 (m, 1H), 1.67–1.59 (m, 1H) ppm.

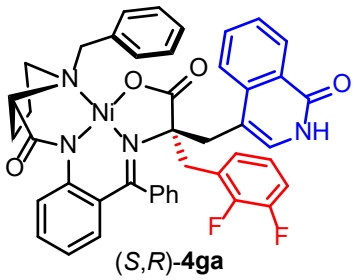
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.7, 178.9, 172.7, 163.4, 142.7, 138.1, 136.5, 136.2, 134.8, 134.0, 133.5, 133.3, 133.0, 132.3, 131.8, 130.3, 129.1, 129.0, 128.6, 128.5, 127.9, 127.7, 127.2, 126.9, 126.6, 126.1, 124.8, 123.8, 122.5, 120.7, 104.7, 78.6, 69.6, 64.4, 58.8, 46.2, 43.1, 30.6, 23.1 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{38}BrN_4NiO_4^+$ $[M+H]^+$: 823.1424, found: 823.1427.

$[\alpha]_D^{25}$ +2167 (*c* 0.012, MeOH).

Ni(II) complex (S,R)-4ga

Starting from a chiral Ni(II) complex (*S*,*S*)-**1g** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*R*)-**4ga** (*the first eluting diastereomer*) was isolated as an orange powder (50 mg, 64% yield); eluent: CH_2Cl_2/PE/Et_3N (4:4:1).



(*S*,*R*)-**4ga**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.16 (s, 1H, NH), 8.30 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 5.6 Hz, 1H), 7.50–7.39 (m, 4H), 7.37–7.20 (m, 6H), 7.17–7.10 (m, 1H), 7.06 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.61–6.51 (m, 2H), 6.51–6.44 (m, 2H), 4.78 (d, J = 13.0 Hz, 1H), 4.11 (d, J = 13.0 Hz, 1H), 3.84 (d, J = 13.4 Hz, 1H), 3.42–3.34 (m, 1H), 3.19–3.06 (m, 3H), 2.36–2.19 (m, 3H), 2.14–2.00 (m, 1H), 1.98–1.86 (m, 1H), 1.69–1.56 (m, 1H) ppm.

^{13}C NMR (101 MHz, acetone-d6): δ = 180.9, 178.3, 173.7, 163.0, 144.4, 138.3, 137.5, 134.4, 134.3, 132.9, 132.3, 130.1, 129.6, 129.5, 129.4, 129.2, 128.7, 128.3, 128.2, 128.1, 127.8 (d, J = 4.9 Hz), 127.4, 127.3, 127.1 (d, J = 12.3 Hz), 126.8, 125.9, 124.5, 123.6, 120.6, 117.6 (d, J = 16.9 Hz), 111.8, 80.0, 69.7, 63.7, 57.4, 42.1, 39.7, 31.2, 23.6 ppm.

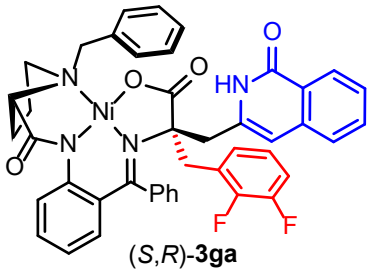
^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.7 (d, J = 21.3 Hz, 1F), –138.2 (d, J = 21.3 Hz, 1F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{37}F_2N_4NiO_4^+$ $[M+H]^+$: 781.2131, found: 781.2129.

$[\alpha]_D^{25}$ +2430 (*c* 0.014, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1g** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*R*)-**3ga** (*the second eluting diastereomer*) was isolated as an orange powder (23 mg, 29% yield); eluent: CH_2Cl_2/PE/Et_3N (4:4:1).



(*S*,*R*)-**3ga**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79 (s, 1H, NH), 8.32 (d, J = 8.1 Hz, 1H), 8.27 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.50–7.41 (m, 3H), 7.40–7.34 (m, 1H), 7.34–7.27 (m, 5H), 7.25–7.15 (m, 2H), 7.10–7.02 (m, 1H), 6.89 (d, J = 7.5 Hz, 1H), 6.72 (s, 1H), 6.59–6.51 (m, 2H), 4.60 (d, J = 12.7 Hz, 1H), 3.73 (d, J = 13.8 Hz, 1H), 3.52 (d, J = 12.7 Hz, 1H), 3.37 (dd, J = 9.7, 6.7 Hz, 1H), 3.30–3.16 (m, 2H), 3.06 (d, J = 13.8 Hz, 1H), 2.42–2.29 (m, 1H), 2.25–2.07 (m, 3H), 2.00 (d, J = 17.9 Hz, 1H), 1.77–1.67 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 178.5, 173.6, 142.7, 136.4, 136.3, 134.0, 133.3, 133.0, 132.4, 131.8, 130.2, 129.4, 129.2, 129.1, 128.7, 128.4, 128.3, 127.7 (d, J = 3.5 Hz), 127.5, 127.4, 127.2, 127.1, 126.8, 126.3, 126.2, 125.4 (d, J = 12.4 Hz), 124.8, 123.8, 123.5, 120.7, 117.1 (d, J = 16.5 Hz), 104.9, 78.3, 69.8, 64.1, 58.1, 42.6, 41.2, 30.8, 23.3 ppm.

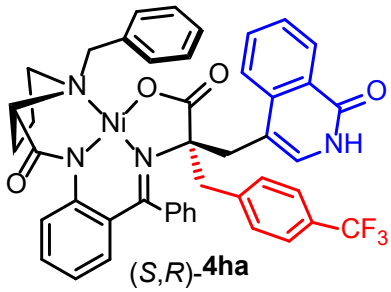
^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.7 (dd, J = 22.6, 20.0 Hz, 1F), –138.1 (dd, J = 57.7, 21.6 Hz, 1F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{44}H_{37}F_2N_4NiO_4^+$ $[M+H]^+$: 781.2131, found: 781.2128.

$[\alpha]_D^{25}$ +2615 (*c* 0.013, MeOH).

Ni(II) complex (S,R)-4ha

Starting from a chiral Ni(II) complex (*S*,*S*)-**1h** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*R*)-**4ha** (*the first eluting diastereomer*) was isolated as an orange powder (44 mg, 54% yield); eluent: CH_2Cl_2/PE/Et_3N (4:4:1).



(*S*,*R*)-**4ha**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.09 (s, 1H, NH), 8.28 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.82 (t, J = 8.0 Hz, 4H), 7.78–7.74 (m, 1H), 7.59 (d, J = 7.4 Hz, 2H), 7.51–7.33 (m, 5H), 7.32–7.26 (m, 1H), 7.25–7.20 (m, 1H), 7.19–7.11 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.60–6.52 (m, 2H), 6.46 (d, J = 8.4 Hz, 1H), 4.78 (d, J = 13.0 Hz, 1H), 4.10 (d, J = 13.0 Hz, 1H), 3.49 (d, J = 13.3 Hz, 1H), 3.34–3.27 (m, 1H), 3.21 (d, J = 17.5 Hz, 1H), 3.11 (d, J = 13.3 Hz, 1H), 3.03–2.92 (m, 1H), 2.29 (d, J = 17.5 Hz, 1H), 2.23–2.11 (m, 1H), 2.08–1.99 (m, 1H), 1.86–1.78 (m, 1H), 1.72–1.56 (m, 1H), 1.51–1.38 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.6, 179.3, 172.9, 163.8, 143.0, 140.3, 137.3, 136.4, 134.3, 132.7, 132.2, 132.1, 132.0, 131.8, 130.6, 130.3, 129.7, 129.2, 129.1, 128.2, 128.1, 127.8, 127.7, 127.2, 126.7, 126.1, 125.8, 125.7, 123.8, 122.6, 120.9, 111.5, 79.6, 68.6, 62.5, 55.7, 46.8, 39.8, 30.2, 22.5 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.4 (s, 3F) ppm.

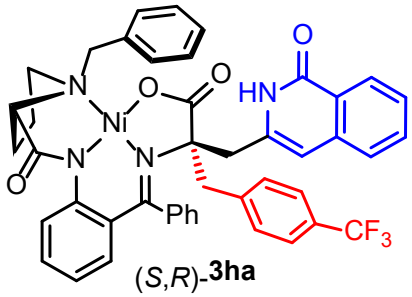
HRMS (ESI, *m*/*z*) calcd. for $C_{45}H_{38}F_3N_4NiO_4^+$ $[M+H]^+$: 813.2193, found: 813.2198.

$[\alpha]_D^{25}$ +1850 (*c* 0.02, MeOH).

The structure of (*S*,*R*)-**4ha** was unambiguously established by single crystal X-ray analysis (see Figure 1 in the main text and X-Ray part *below*).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1h** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*R*)-**3ha** (*the second eluting diastereomer*) was isolated as an orange powder (32 mg, 40% yield); eluent: CH_2Cl_2/PE/Et_3N (8:4:1).



(*S*,*R*)-**3ha**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.49 (s, 1H, NH), 8.37–8.24 (m, 3H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 3H), 7.49–7.39 (m, 4H), 7.31–7.18 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09–7.02 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.59–6.48 (m, 2H), 4.56 (d, *J* = 12.6 Hz, 1H), 3.47–3.26 (m, 4H), 3.05–2.96 (m, 2H), 2.30–2.19 (m, 1H), 2.15 (d, *J* = 14.7 Hz, 1H), 2.04–1.92 (m, 2H), 1.73–1.60 (m, 1H), 1.59–1.48 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.7, 178.9, 173.0, 163.5, 142.7, 140.0, 138.1, 136.5, 136.2, 134.0, 133.3, 133.0, 132.5, 131.9, 131.8, 130.6, 130.4, 130.3, 129.2, 129.0, 128.6, 128.5, 128.0, 127.7, 127.2, 126.9, 126.7, 126.1, 126.08, 126.0, 125.6, 124.8, 123.8, 120.8, 104.8, 78.6, 69.4, 64.1, 58.1, 46.4, 43.3, 30.5, 22.8 ppm.

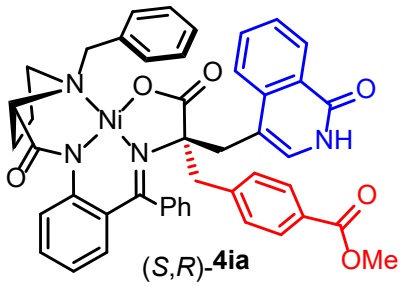
^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.4 (s, 3F) ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{45}H_{38}F_3N_4NiO_4^+$ $[M+H]^+$: 813.2193, found: 813.2199.

$[\alpha]_D^{25}$ +1800 (*c* 0.02, MeOH).

Ni(II) complex (S,R)-4ia

Starting from a chiral Ni(II) complex (*S*,*S*)-**1i** and *N*-(pivaloyloxy)benzamide **2a**, the product (*S*,*R*)-**4ia** (*the first eluting diastereomer*) was isolated as an orange powder (44 mg, 55% yield); eluent: CH_2Cl_2/PE/Et_3N (8:4:1).



(*S*,*R*)-**4ia**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.32 (s, 1H, NH), 8.27–8.17 (m, 3H), 7.95–7.87 (m, 3H), 7.72 (br. s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.53–7.41 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.31–7.23 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.67–6.46 (m, 4H), 4.76 (d, *J* = 13.0 Hz, 1H), 4.04 (d, *J* = 13.0 Hz, 1H), 3.95 (s, 3H), 3.53 (d, *J* = 13.2 Hz, 1H), 3.37–3.29 (m, 1H), 3.22 (d, *J* = 17.6 Hz, 1H), 3.15 (d, *J* = 13.2 Hz, 1H), 3.00–2.92 (m, 1H), 2.29 (d, *J* = 17.6 Hz, 1H), 2.14–2.00 (m, 2H), 1.95–1.85 (m, 1H), 1.76–1.62 (m, 1H), 1.51–1.38 (m, 1H) ppm.

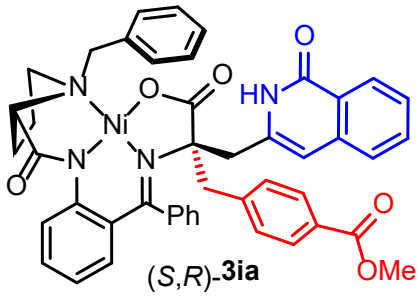
^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.5, 179.3, 172.7, 166.9, 163.8, 142.8, 141.4, 137.3, 136.4, 134.2, 132.5, 132.2, 132.1, 132.0, 131.5, 130.3, 130.0, 129.6, 129.1, 129.0, 128.1, 128.0, 127.7, 127.6, 127.3, 126.7, 126.6, 126.0, 125.7, 123.8, 122.6, 120.8, 111.5, 79.5, 68.8, 62.7, 56.2, 52.4, 47.1, 39.7, 30.1, 22.6 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{46}H_{41}N_4NiO_6^+$ $[M+H]^+$: 803.2374, found: 803.2368.

$[\alpha]_D^{25}$ +1500 (*c* 0.02, MeOH).

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

Starting from a chiral Ni(II) complex (*S*,*S*)-**1i** and *N*-(pivaloyloxy)benzamide **2a**, the desired product (*S*,*R*)-**3ia** (*the second eluting diastereomer*) was isolated as an orange powder (29 mg, 36% yield); eluent: CH_2Cl_2/PE/Et_3N (8:1:1).



(*S*,*R*)-**3ia**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.35 (s, 1H, NH), 8.36–8.26 (m, 3H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.64–7.55 (m, 3H), 7.49–7.38 (m, 4H), 7.31–7.26 (m, 2H), 7.25–7.20 (m, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.08–7.02 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.77 (s, 1H), 6.58–6.50 (m, 2H), 4.52 (d, *J* = 12.6 Hz, 1H), 3.93 (s, 3H), 3.42–3.26 (m, 4H), 3.06 (d, *J* = 13.6 Hz, 1H), 3.02–2.92 (m, 1H), 2.24–2.03 (m, 3H), 2.00–1.92 (m, 1H), 1.77–1.65 (m, 1H), 1.57–1.44 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 180.7, 178.9, 172.8, 166.9, 163.4, 142.7, 141.1, 138.1, 136.5, 136.2, 134.0, 133.4, 133.0, 132.4, 131.8, 131.6, 130.4, 130.3, 130.1, 129.1, 129.0, 128.5, 127.9, 127.7, 127.2, 127.0, 126.7, 126.1, 124.8, 123.9, 120.8, 104.8, 78.7, 69.5, 64.3, 58.5, 52.4, 46.6, 43.2, 30.4, 23.0 ppm.

HRMS (ESI, *m*/*z*) calcd. for $C_{46}H_{41}N_4NiO_6^+$ $[M+H]^+$: 803.2374, found: 803.2373.

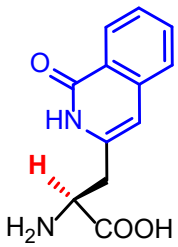
$[\alpha]_D^{25}$ +2100 (*c* 0.02, MeOH).

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

To a suspension of the Ni(II) complex (*S*,*S*)-**3aa**(1.0 mmol) or (*S*,*S*)-**3ba** (1.3 mmol) in methanol (15.0 mL) was added 6*N* HCl (15.0 mL) and water (15 mL) and the whole was heated at 60 °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 (25.0 mL). The remaining amount of (*S*)-**BPB** was extracted with CH_2Cl_2 (2x5 mL). The aqueous layer was quenched by 25% aqueous NH_3 solution (3.0 mL) until pH=7 and concentrated to dryness and the residue was chromatographed with a cation exchange resin (Dowex 50x2, H^+-form) (eluent: water and then 5% aqueous solution of ammonia) to afford the desired amino acid **5** as a white powder.

Amino Acid (S)-5a

Starting from the chiral Ni(II) complex (*S*,*S*)-**3aa** (0.7 g, 1.0 mmol), the desired AA (*S*)-**5a** was isolated as a white powder (163 mg, 70% yield).



(*S*)-**5a**

^{1}H NMR (400 MHz, D_2O): δ = 8.03 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 6.58 (s, 1H), 4.36–4.29 (m, 1H), 3.22 (dd, *J* = 15.0, 5.5 Hz, 1H), 3.04 (dd, *J* = 15.0, 8.8 Hz, 1H) ppm.

^{13}C NMR (101 MHz, D_2O): δ = 170.3, 164.9, 137.8, 133.7, 133.3, 127.5, 126.6, 126.3, 123.6, 109.0, 51.7, 33.1 ppm.

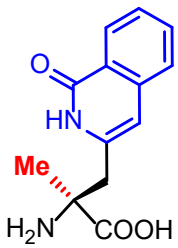
HRMS (ESI, *m*/*z*) calcd. for $C_{12}H_{13}N_2O_3^+$ $[M+H]^+$: 233.0921, found: 233.0922.

$[\alpha]_D^{25}$ +81.55 (*c* 0.233, 1*N* HCl).

Enantiomeric purity (>99% *ee*) was established by chiral HPLC analysis (Diasphere-110-Chirasel-E column: Nautilus-R, BioChemMack S&T, 5.0 mkm, 4.0x250 mm, methanol/0.1 M aq. solution of NaH_2PO_4*$2H_2O$ = 20/80, flow rate = 0.8 mL/min, λ = 220 nm, 25 °C), t_R = 27.5 min (see Figure S111).

Amino Acid (S)-5b

Starting from the chiral Ni(II) complex (*S*,*S*)-**3ba** (0.87 g, 1.3 mmol), the desired AA (*S*)-**5b** was isolated as a white powder (256 mg, 80% yield).



(*S*)-**5b**

^{1}H NMR (400 MHz, D_2O): δ = 7.52 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.07 (s, 1H), 2.66 (dd, J = 40.7, 15.0 Hz, 2H), 1.17 (s, 3H) ppm.

^{13}C NMR (101 MHz, D_2O): δ = 172.2, 164.2, 137.3, 133.5, 132.0, 127.4, 126.4, 125.9, 123.1, 110.0, 59.3, 38.8, 21.1 ppm.

HRMS (ESI, m/z) calcd. for $C_{13}H_{15}N_2O_3^+$ $[M+H]^+$: 247.1077, found: 247.1078.

$[\alpha]_D^{25}$ +9.85 (*c* 0.203, 1*N* HCl).

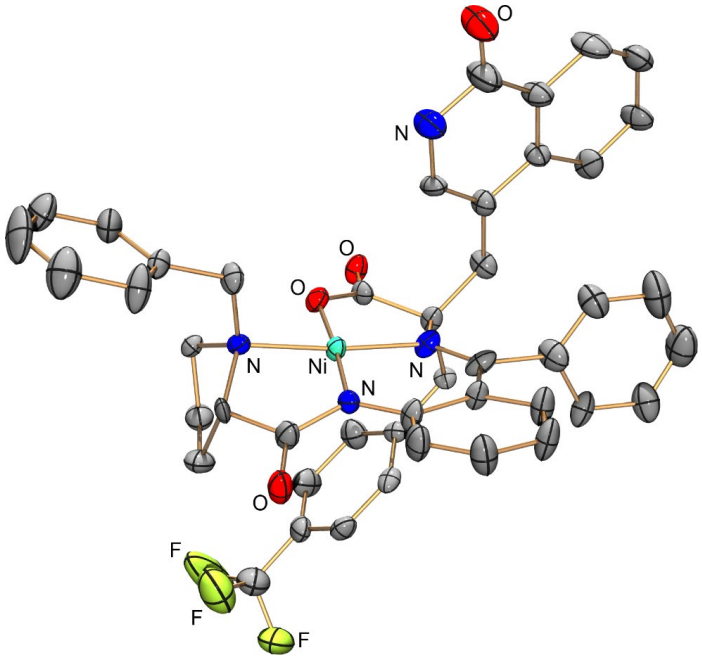
Enantiomeric purity (>99% *ee*) was established by chiral HPLC analysis (Diasphere-110-Chirasel-E column: Nautilus-R, BioChemMack S&T, 5.0 mkm, 4.0x250 mm, methanol/0.1 M aq. solution of NaH_2PO_4*$2H_2O$ = 20/80, flow rate = 0.8 mL/min, λ = 220 nm, 25 °C), t_R = 29.6 min (see Figure S111).

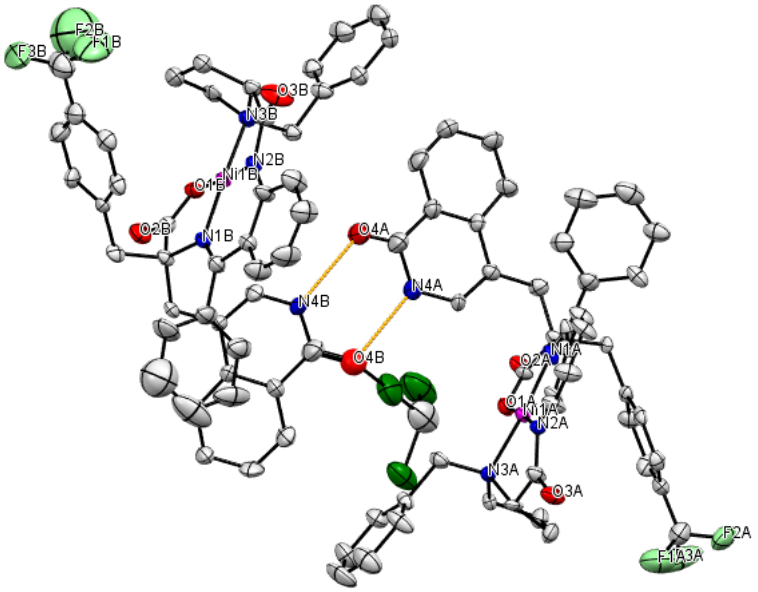
X-ray diffraction study of the Ni(II) complex (*S*,*R*)-4ha

Single crystal X-ray study of the Ni(II) complex was carried out in Center for molecule composition studies of INEOS RAS.

Dark-red single crystals of the Ni(II) complex (*S*,*R*)-**4ha** were obtained by slow interdiffusion of a two-phase system containing hexane and a solution of the compound in $CHCl_3$. Single-crystal X-ray diffraction experiments were carried out with Bruker SMART APEX II diffractometer (graphite monochromated MoK_α radiation, λ = 0.71073 Å, ω-scan technique). The APEX II software[S7] 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[S8] and OLEX2[S9] program packages. 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. Positions of hydrogen atoms were calc 4ulated 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 ***2203331*** contains the supplementary crystallographic data for the complex (*S*,*R*)-**4ha**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.





(*S*,*R*)-**4ha** *(CCDC **2203331**)*

Table S1. Crystallographic data for the complex (*S*,*R*)-**4ha**	
datablock	(*S*,*R*)-**4ha**
Empirical formula	$C_{91}H_{75}Cl_3F_6N_8Ni_2O_8$
Formula weight	1746.36
Anode [λ, Å]	MoKα [0.71073] sealed tube
Crystal size, mm	0.31×0.18×0.04
Crystal system	orthorhombic
a, Å	15.529(2)
b, Å	19.627(3)
c, Å	31.278(4)
α, °	90
β, °	90
γ, °	90
Volume, Å³	9533(2)
Density, g/cm^{-3}	1.217
Temperature, K	120
μ, mm^{-1}	0.545
Space group	$P2_12_12_1$
Z	4
F(000)	3608.0
Reflections collected	172297
Independent reflections	18714
Parameters	1051
R_{int}	0.1473
$2\theta_{min}$ - $2\theta_{max}$, °	2.928–52
wR_2 (all reflections)	0.1194
R_1(I>2σ(I))	0.0998
GOF	1.019
ρ_{min}/ρ_{max}, eÅ^{-3}	-0.78/1.91
Flack parameter	0.139(7)

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NMR spectra

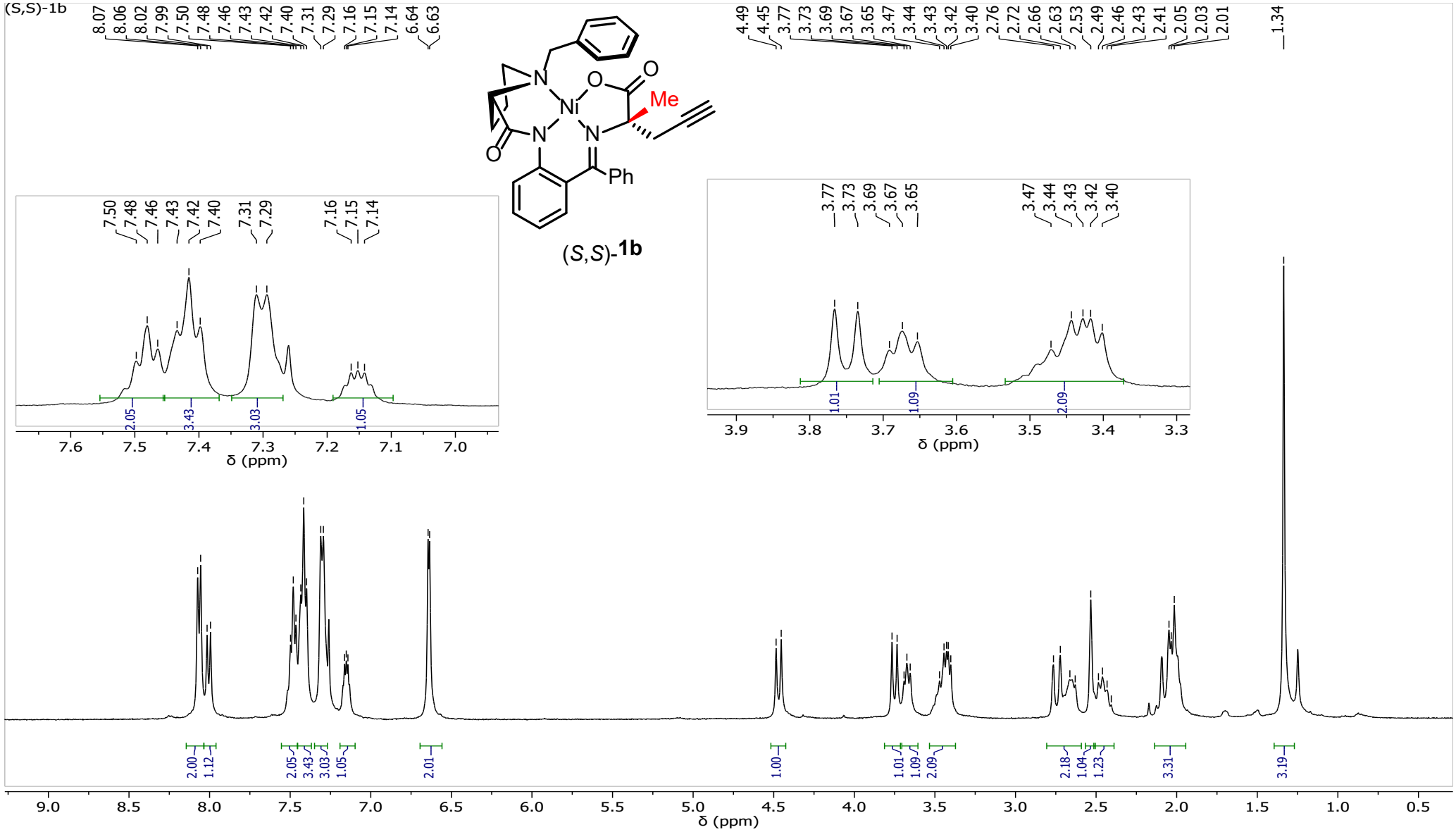

Figure S1. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1b** (in $CDCl_3$)

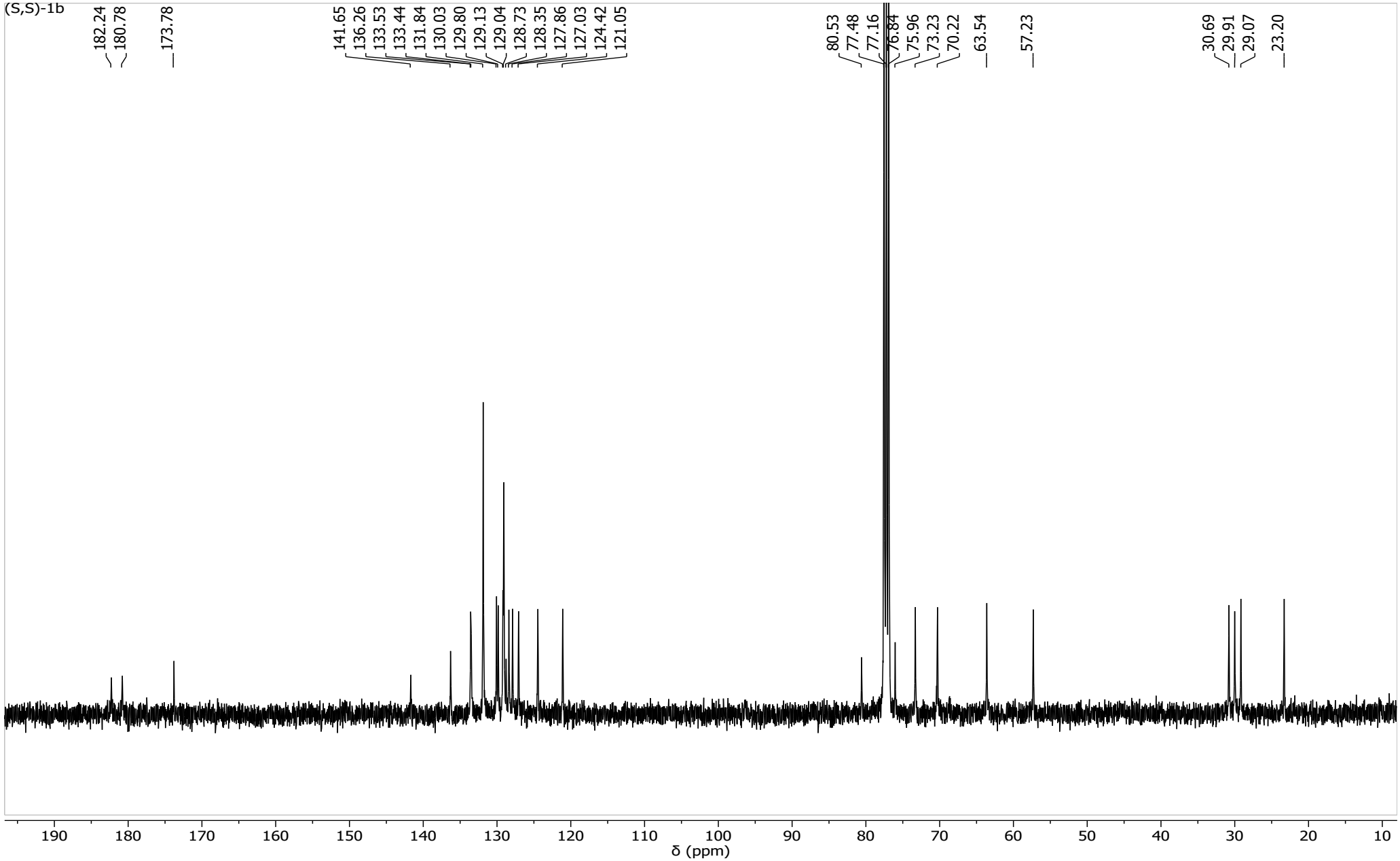

Figure S2. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1b** (in $CDCl_3$)

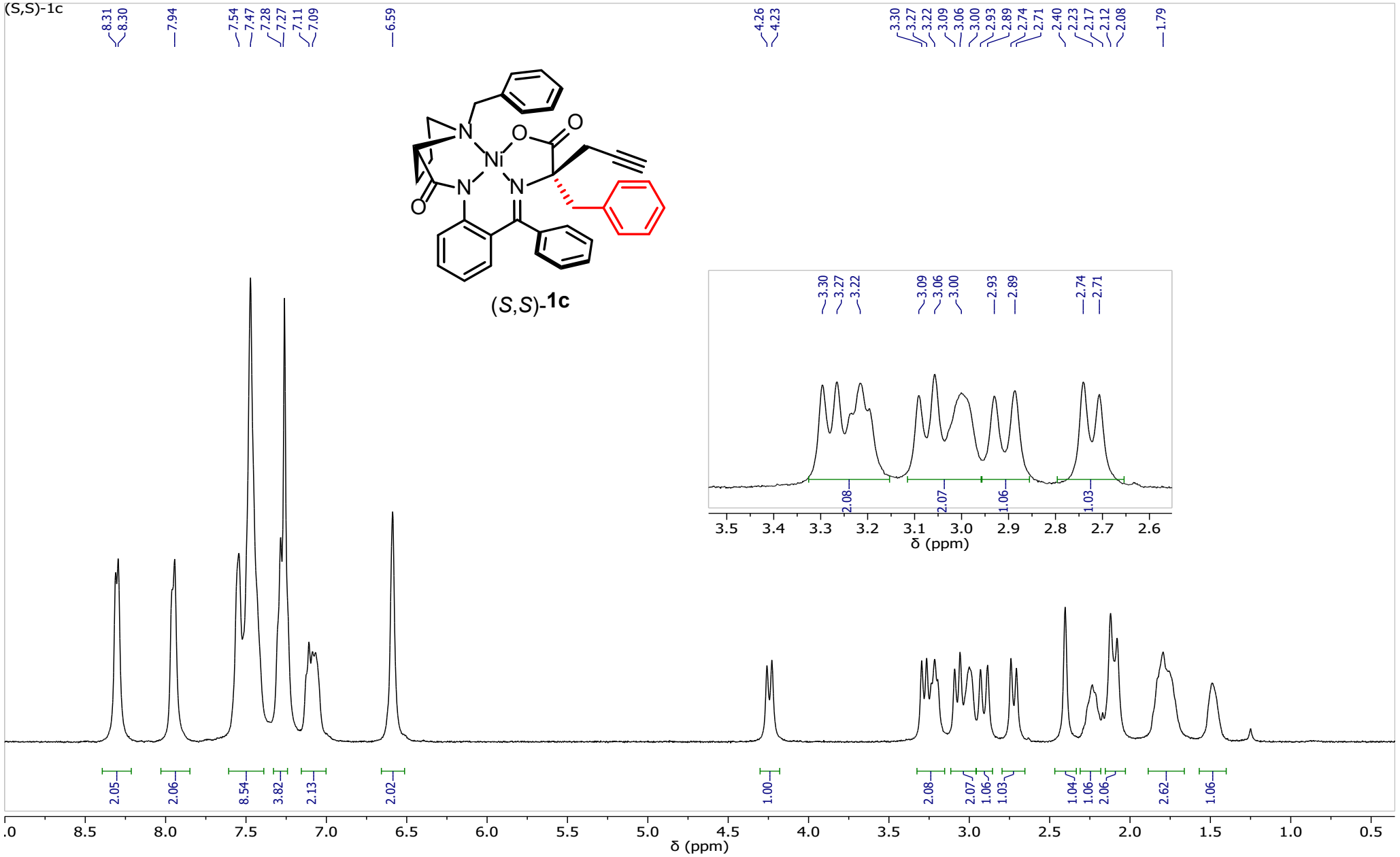

Figure S3. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1c** (in $CDCl_3$)

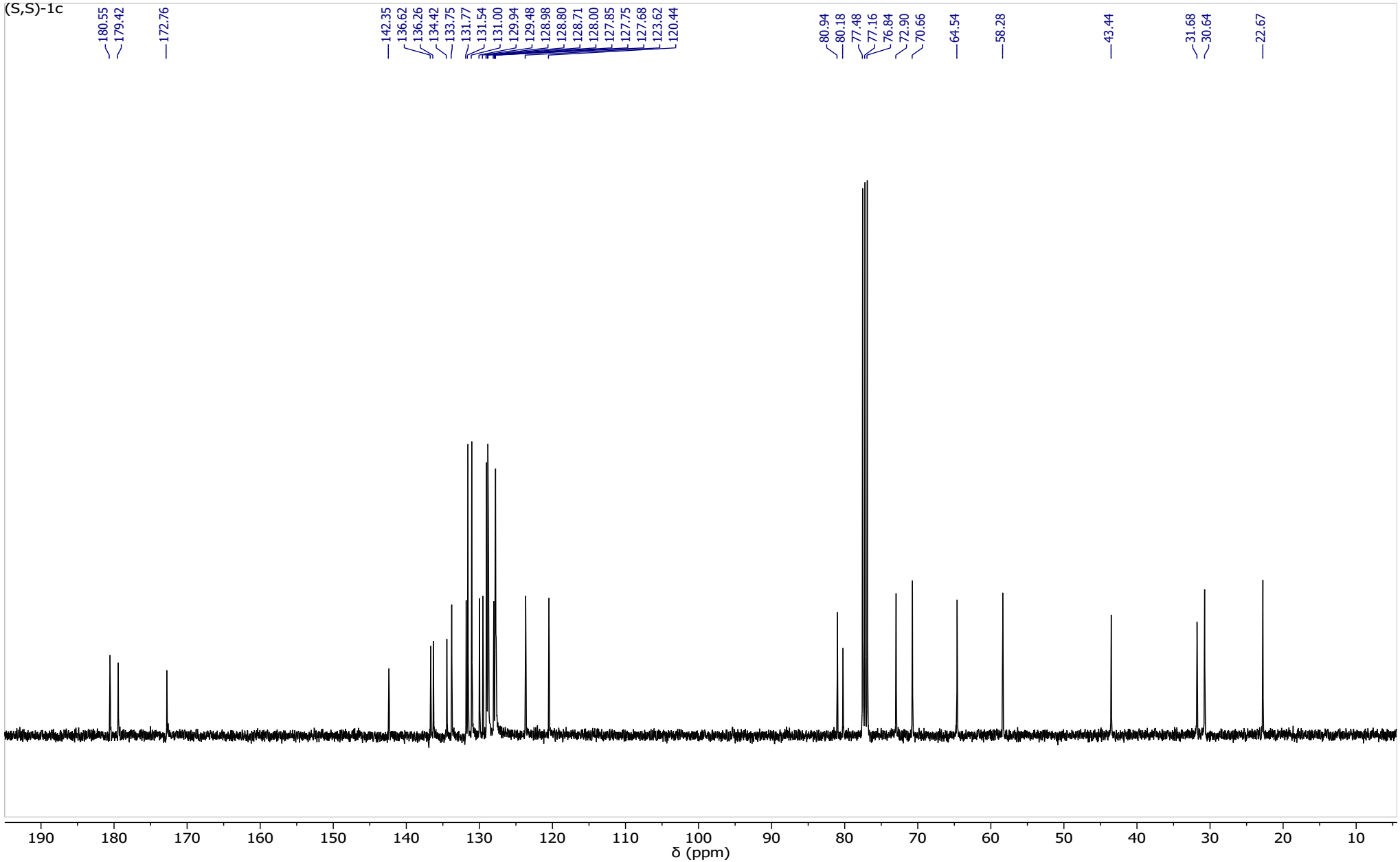

Figure S4. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1c** (in $CDCl_3$)

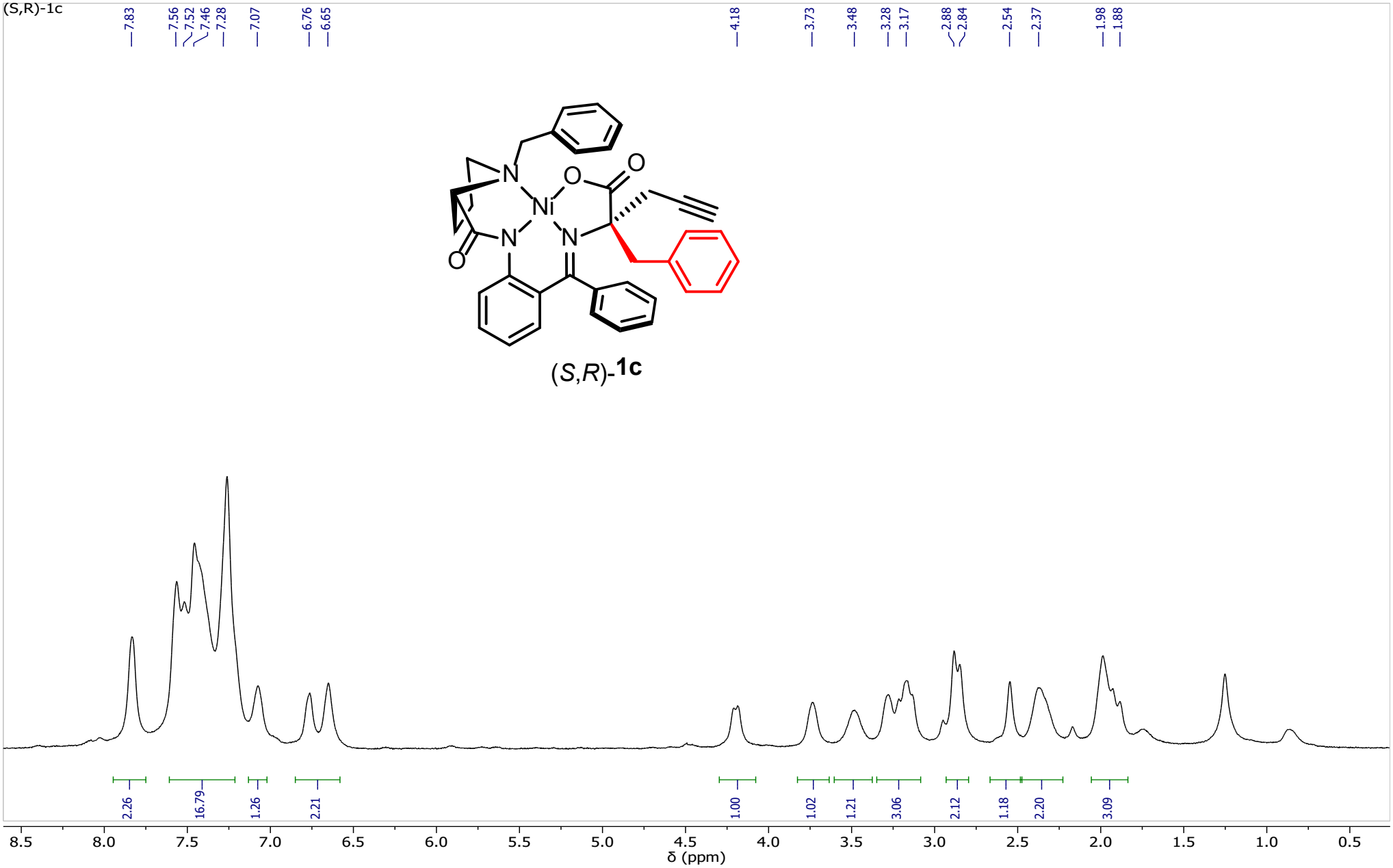

Figure S5. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1c** (in $CDCl_3$)

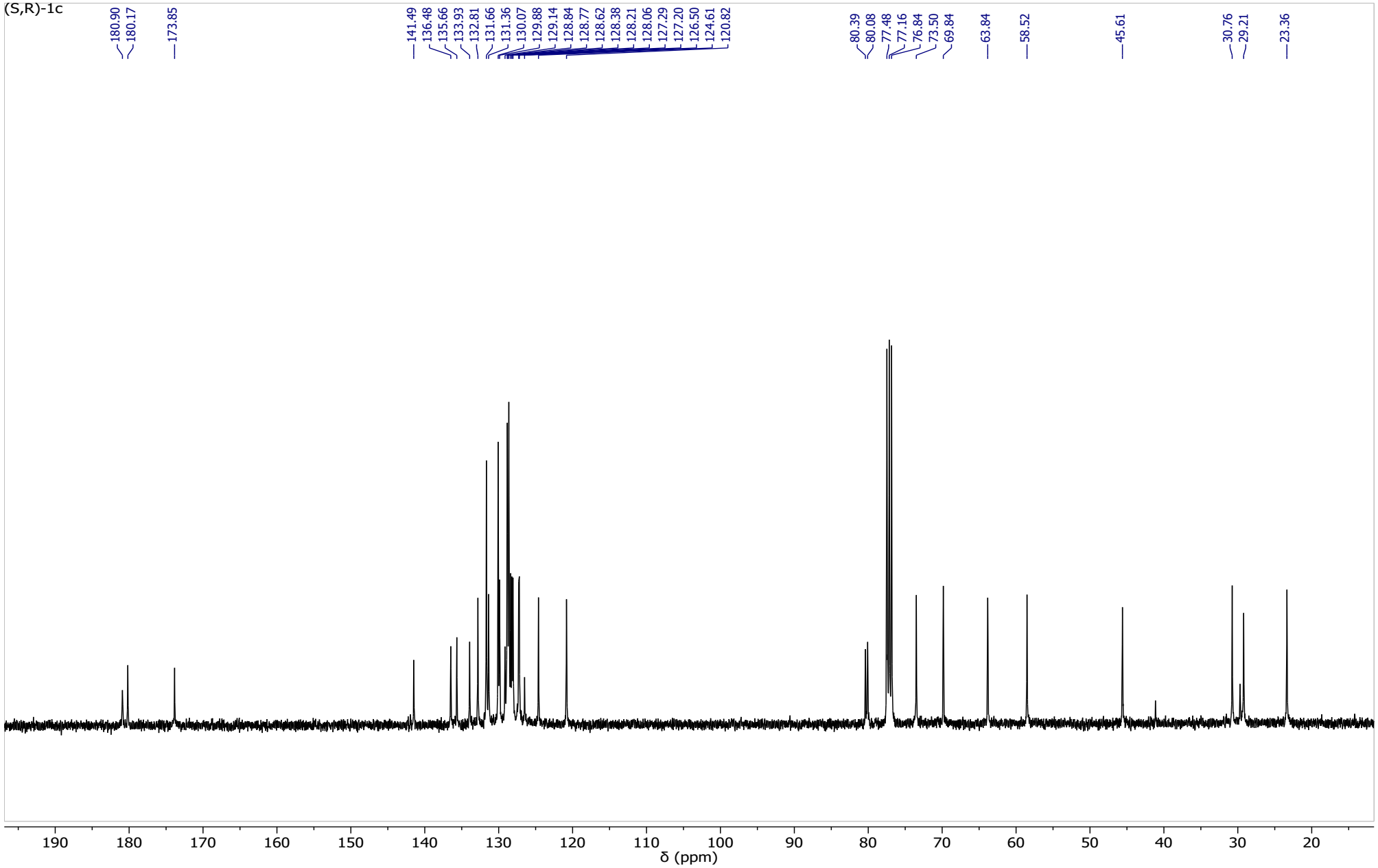

Figure S6. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1c** (in $CDCl_3$)

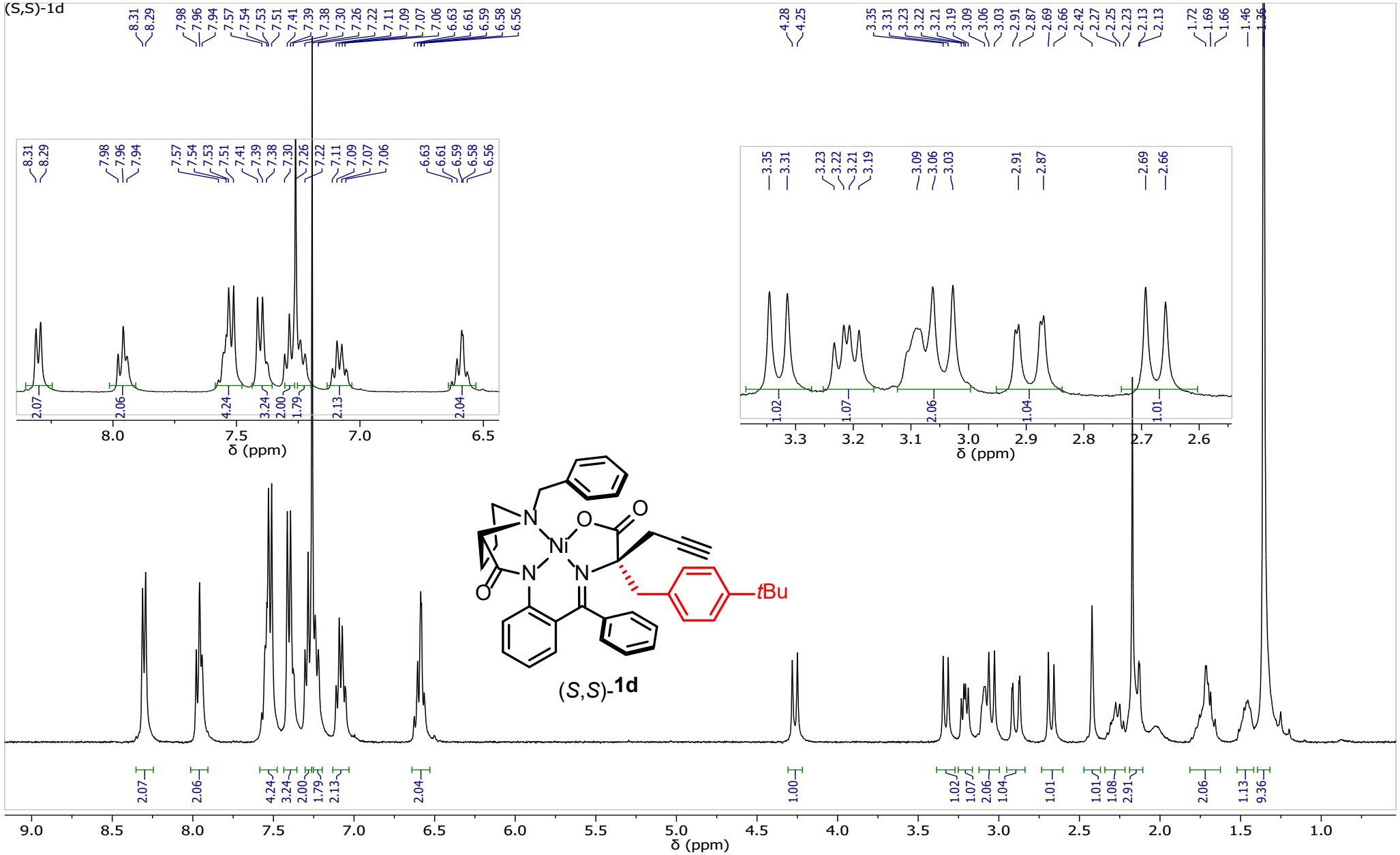

Figure S7. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1d** (in $CDCl_3$)

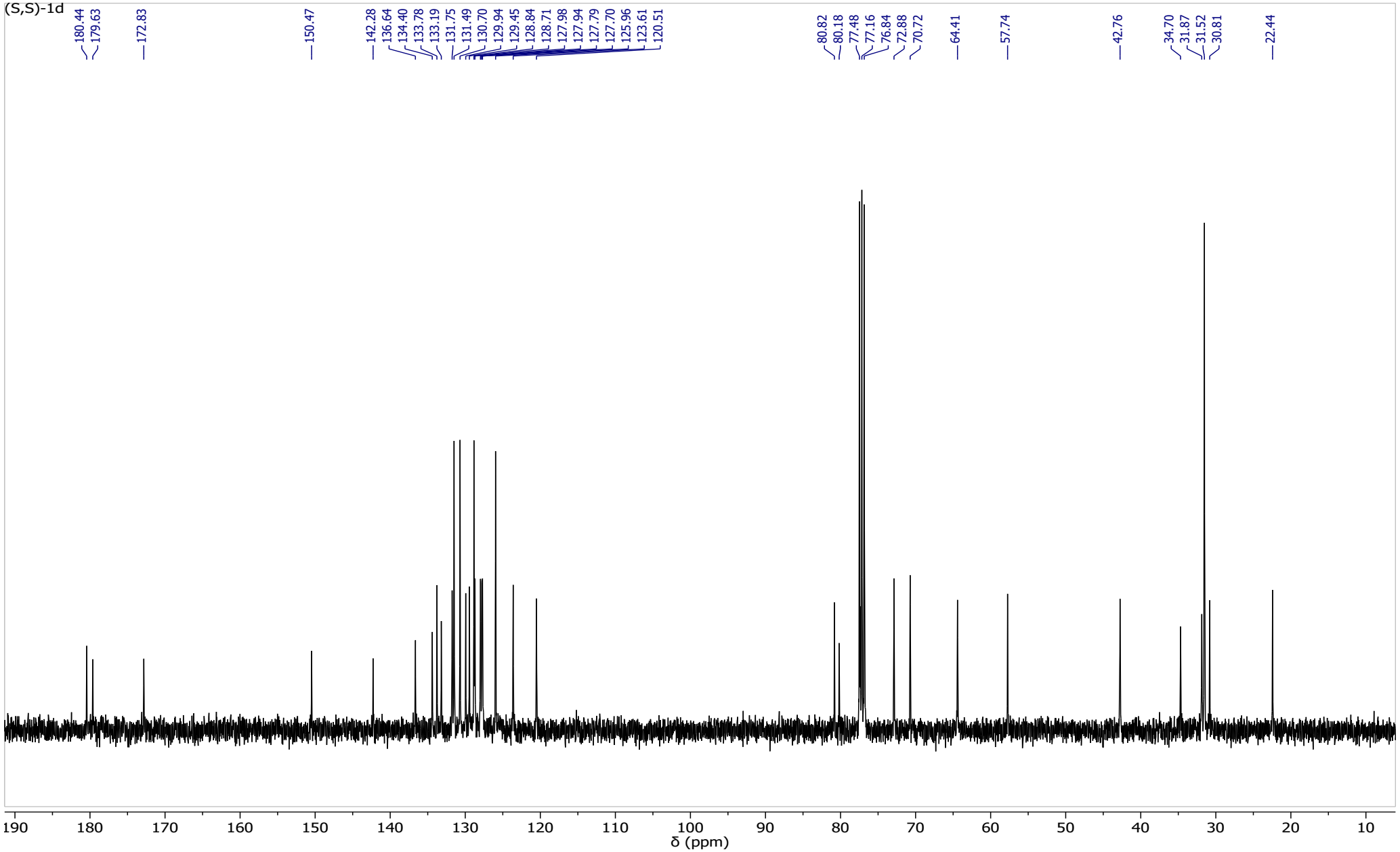

Figure S8. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1d** (in $CDCl_3$)

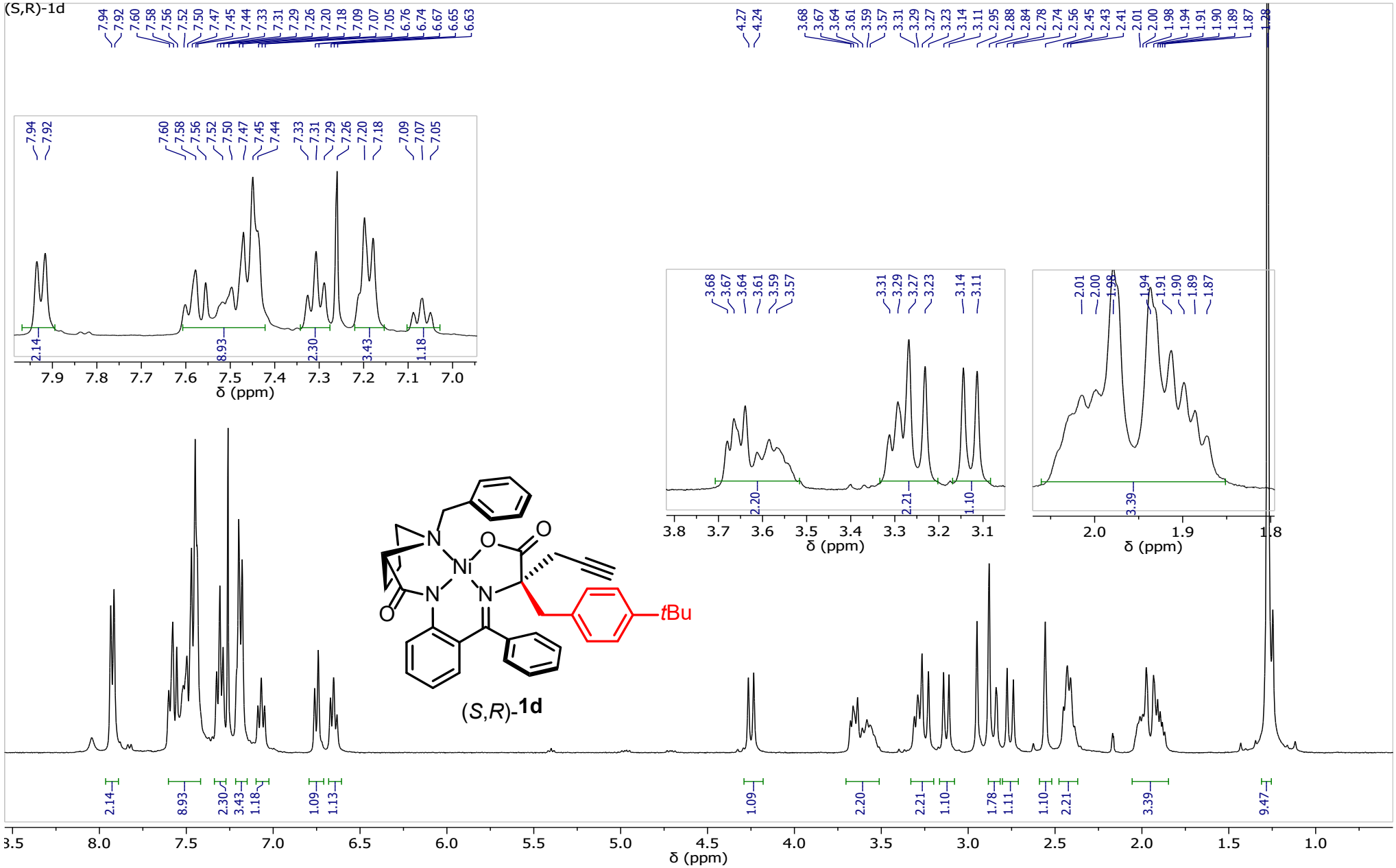

Figure S9. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1d** (in $CDCl_3$)

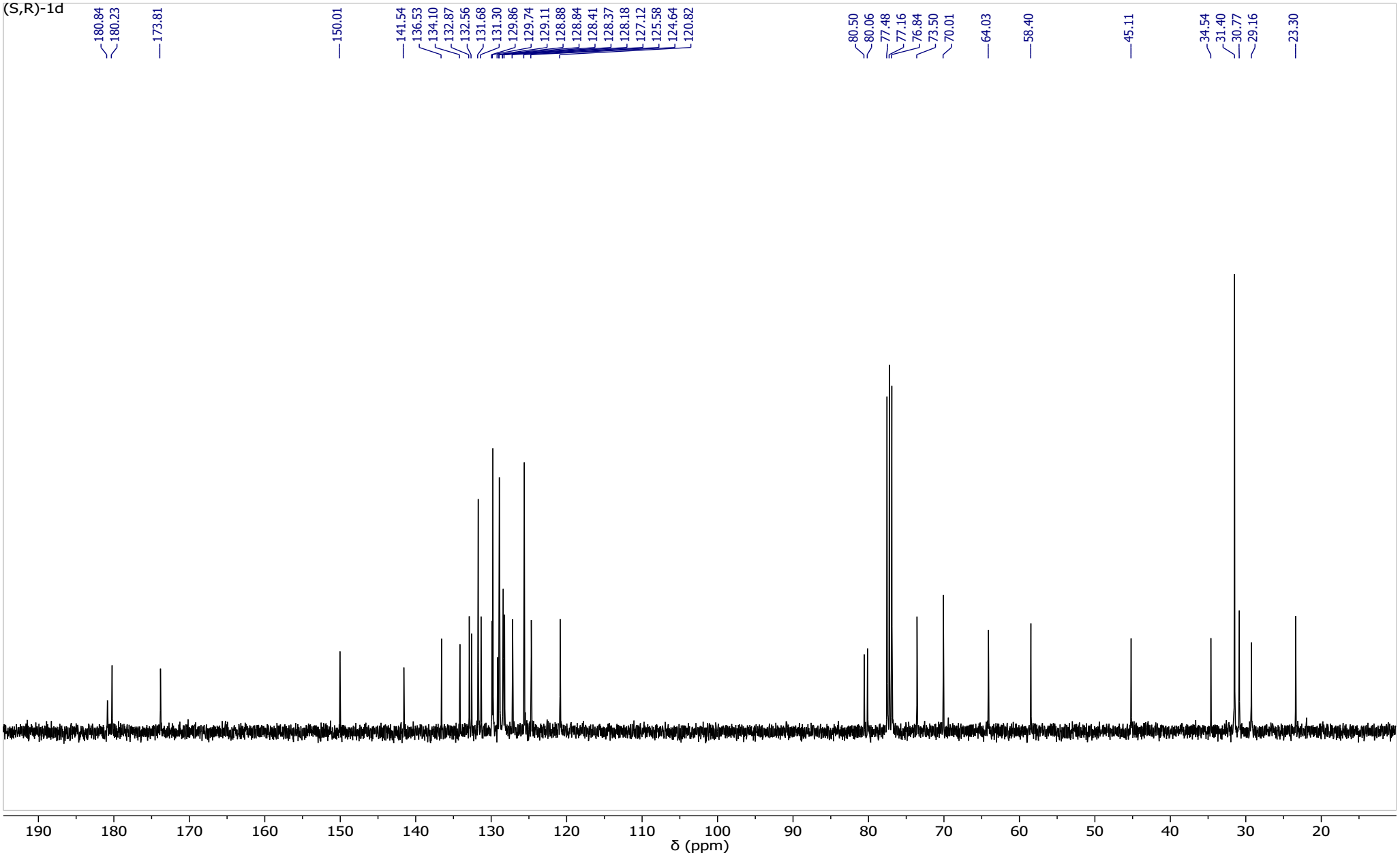

Figure S10. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1d** (in $CDCl_3$)

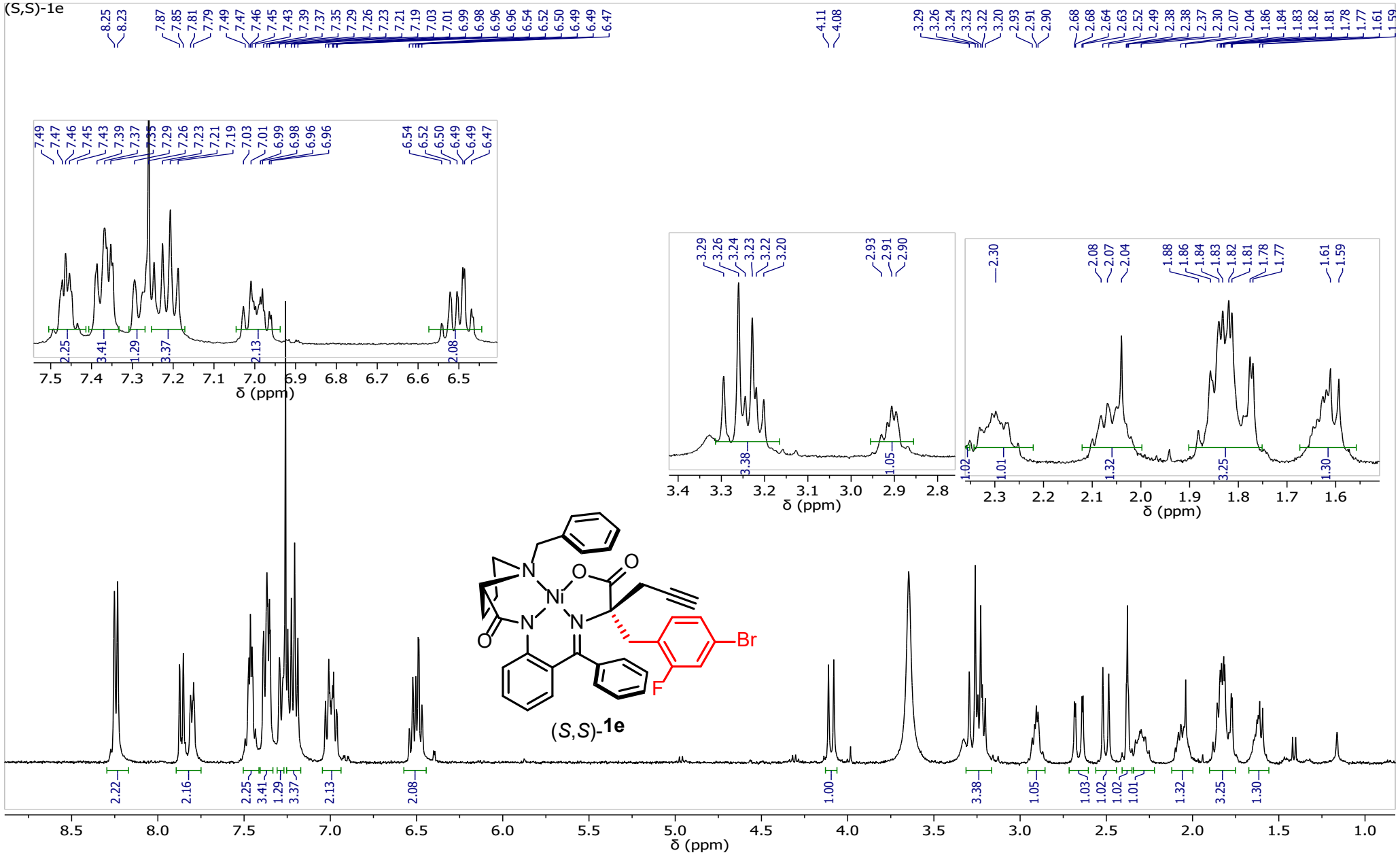

Figure S11. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1e** (in $CDCl_3$+CD_3OD)

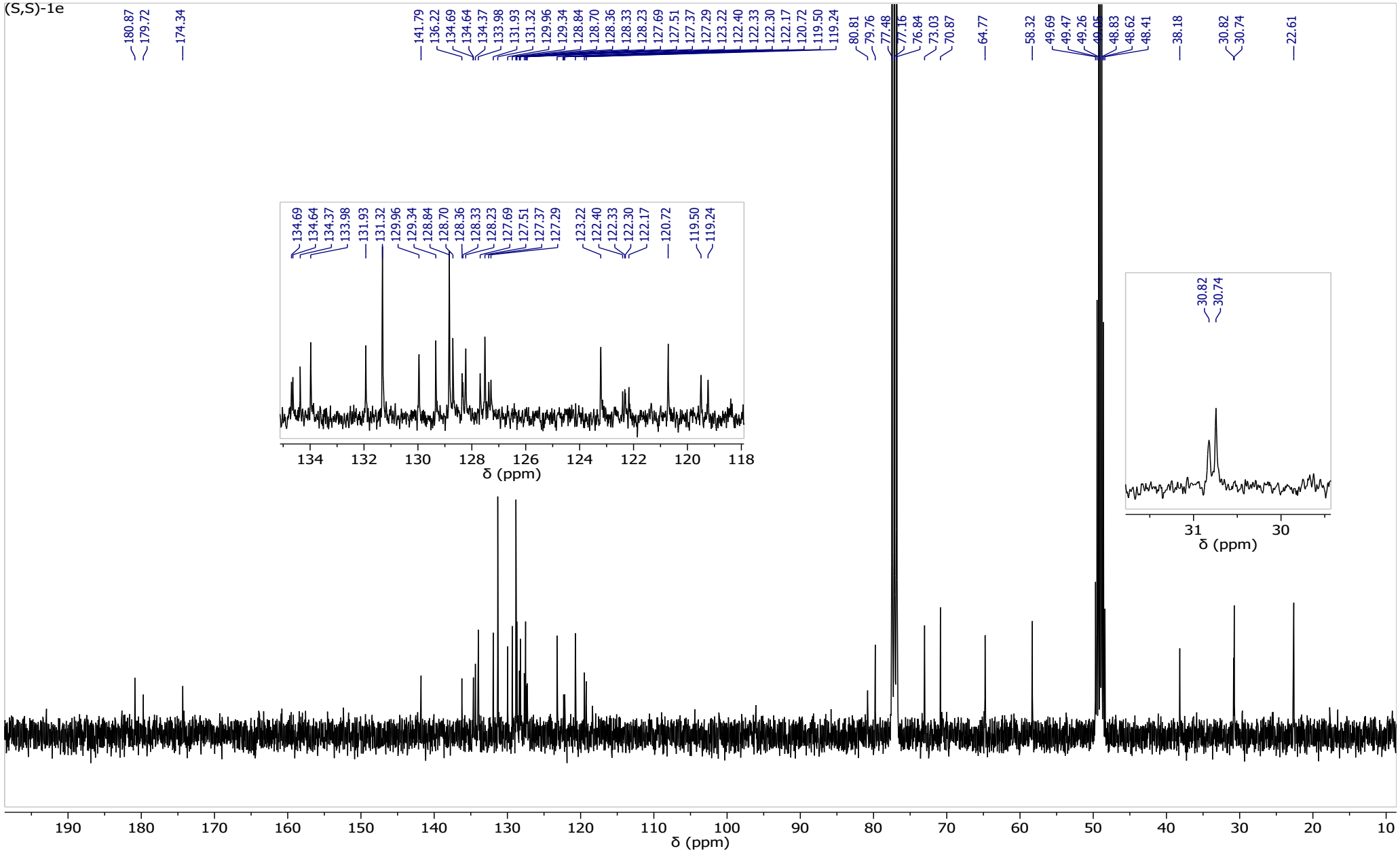

Figure S12. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1e** (in $CDCl_3$+CD_3OD)

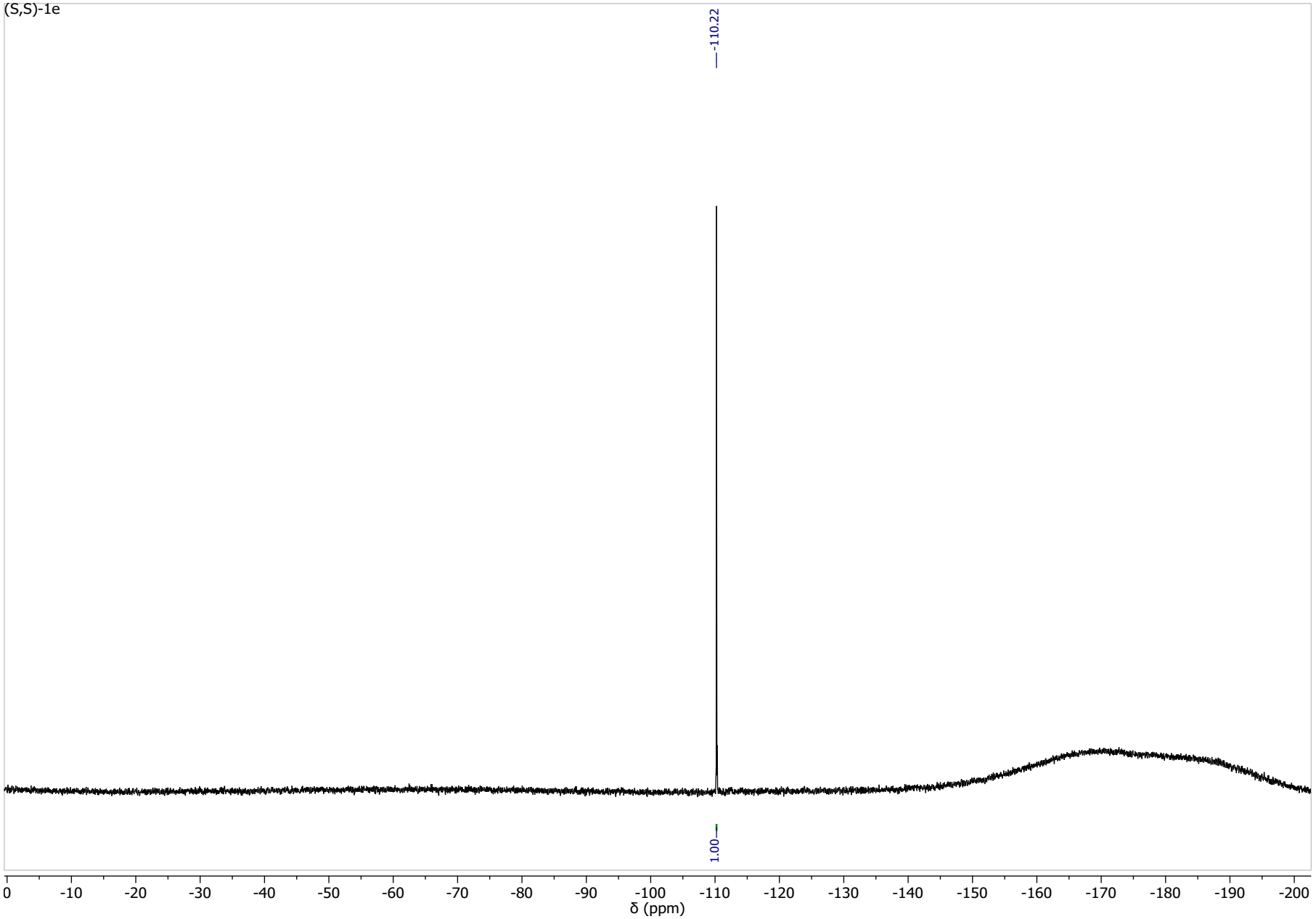

Figure S13. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1e** (in $CDCl_3$+CD_3OD)

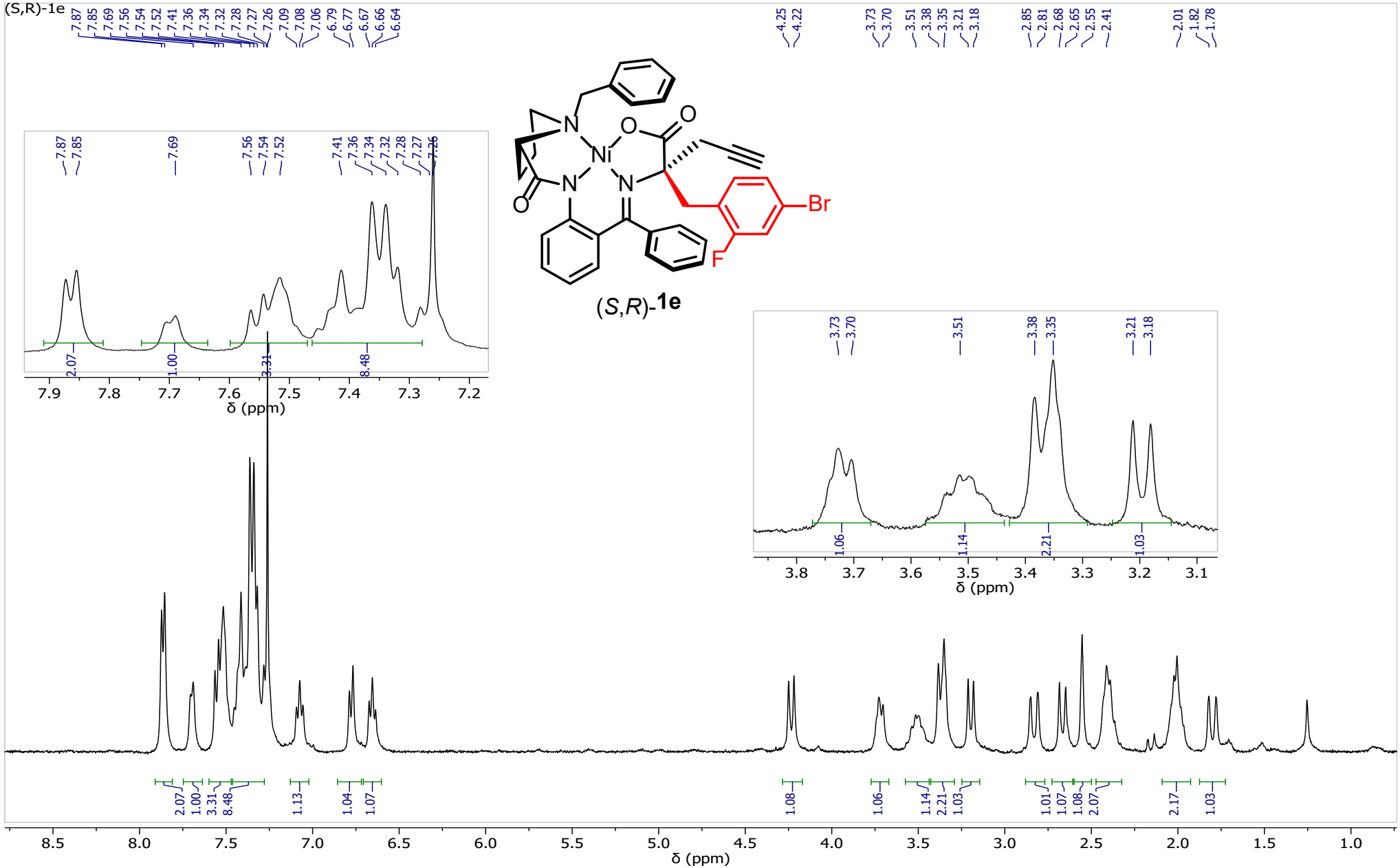

Figure S14. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1e** (in $CDCl_3$)

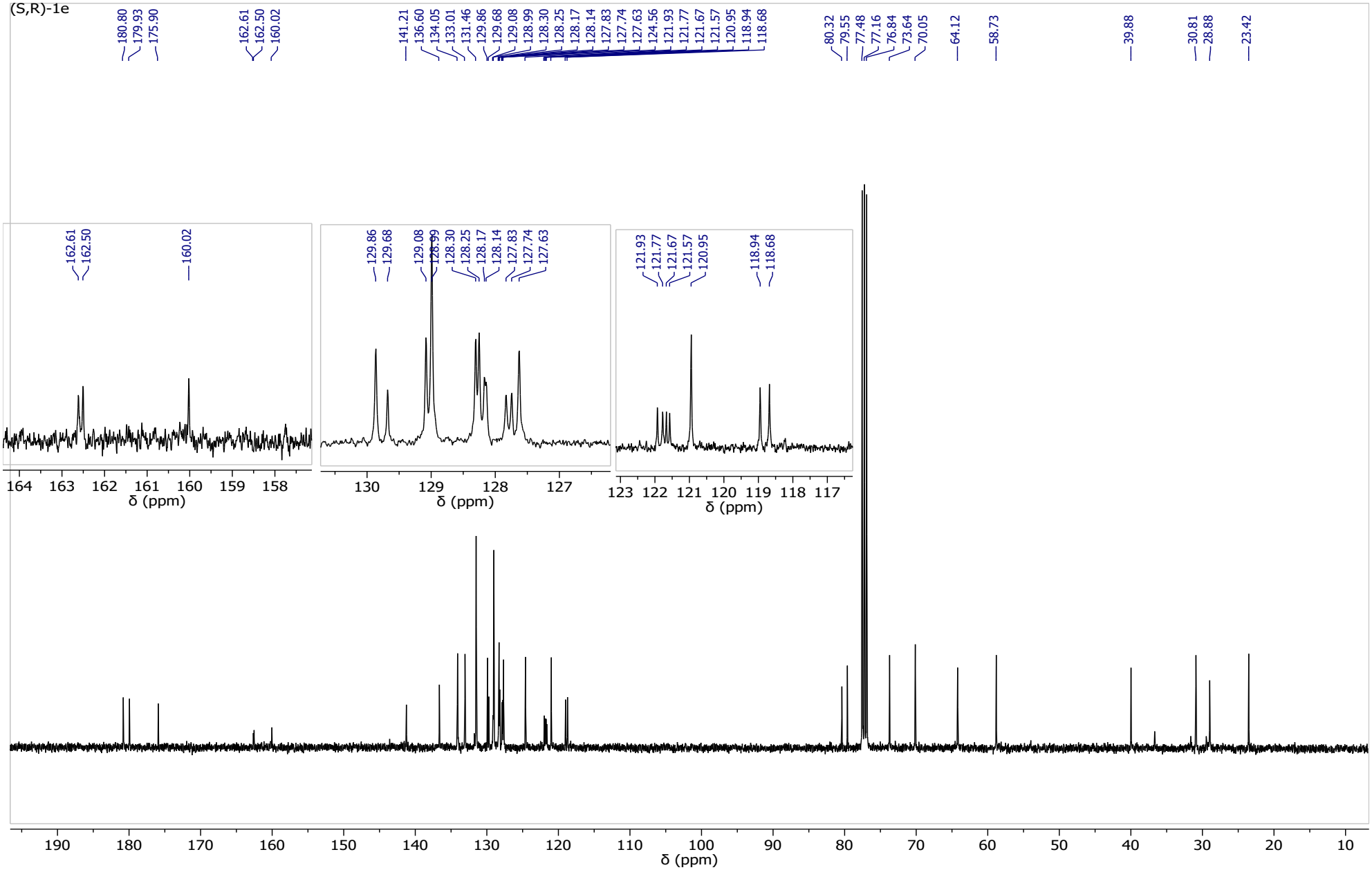

Figure S15. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1e** (in $CDCl_3$)

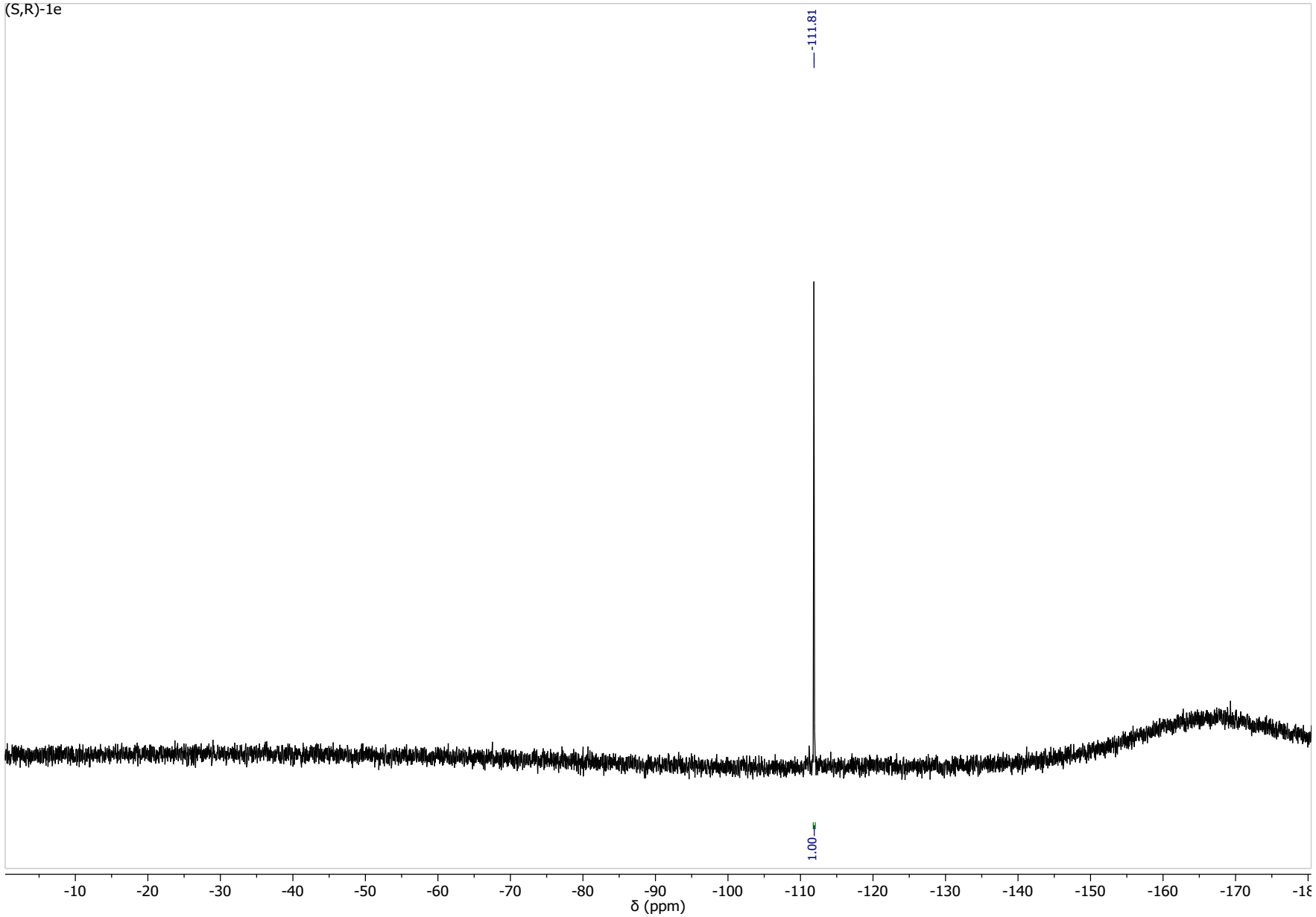

Figure S16. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**1e** (in $CDCl_3$)

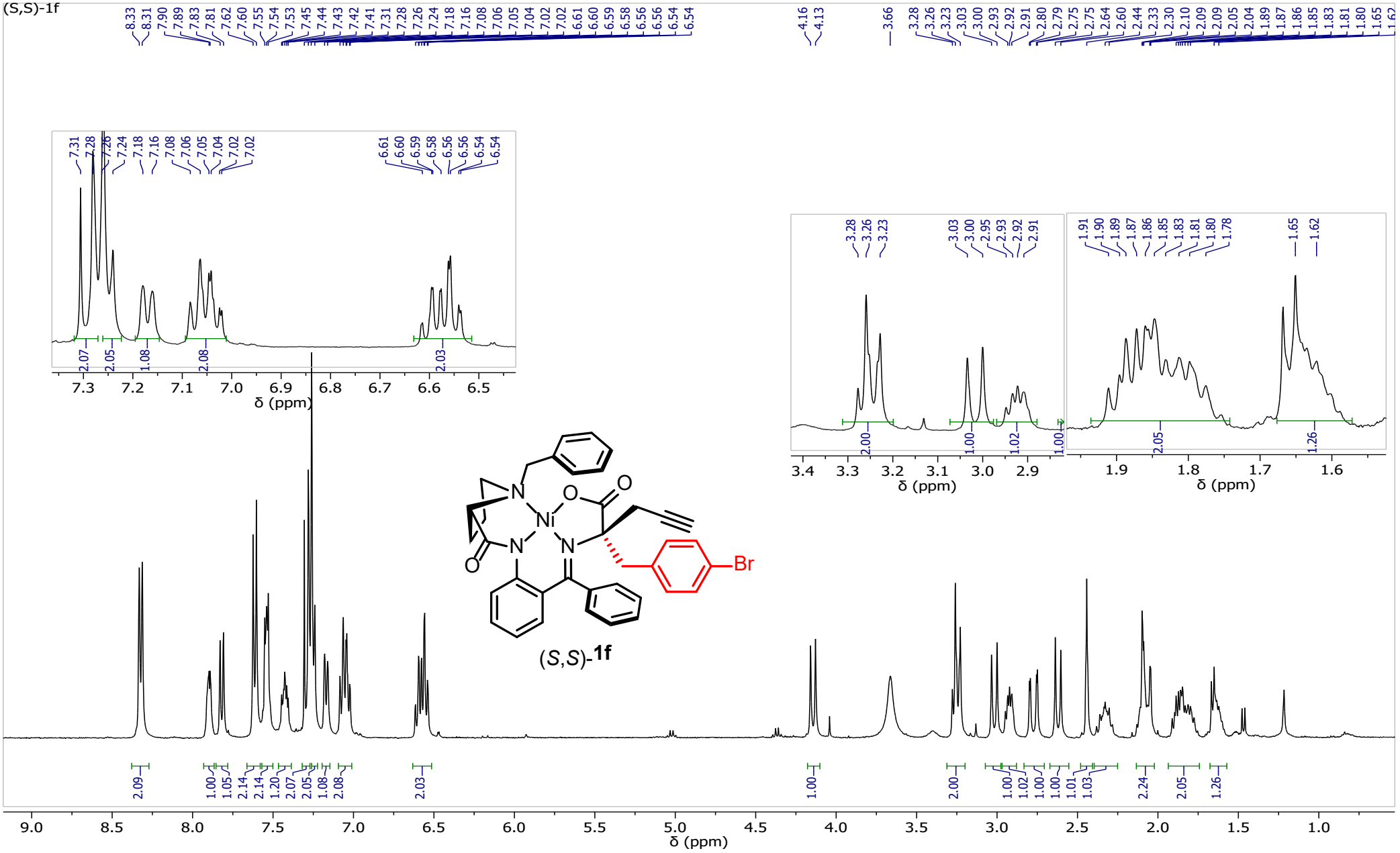

Figure S17. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1f** (in $CDCl_3$+CD_3OD)

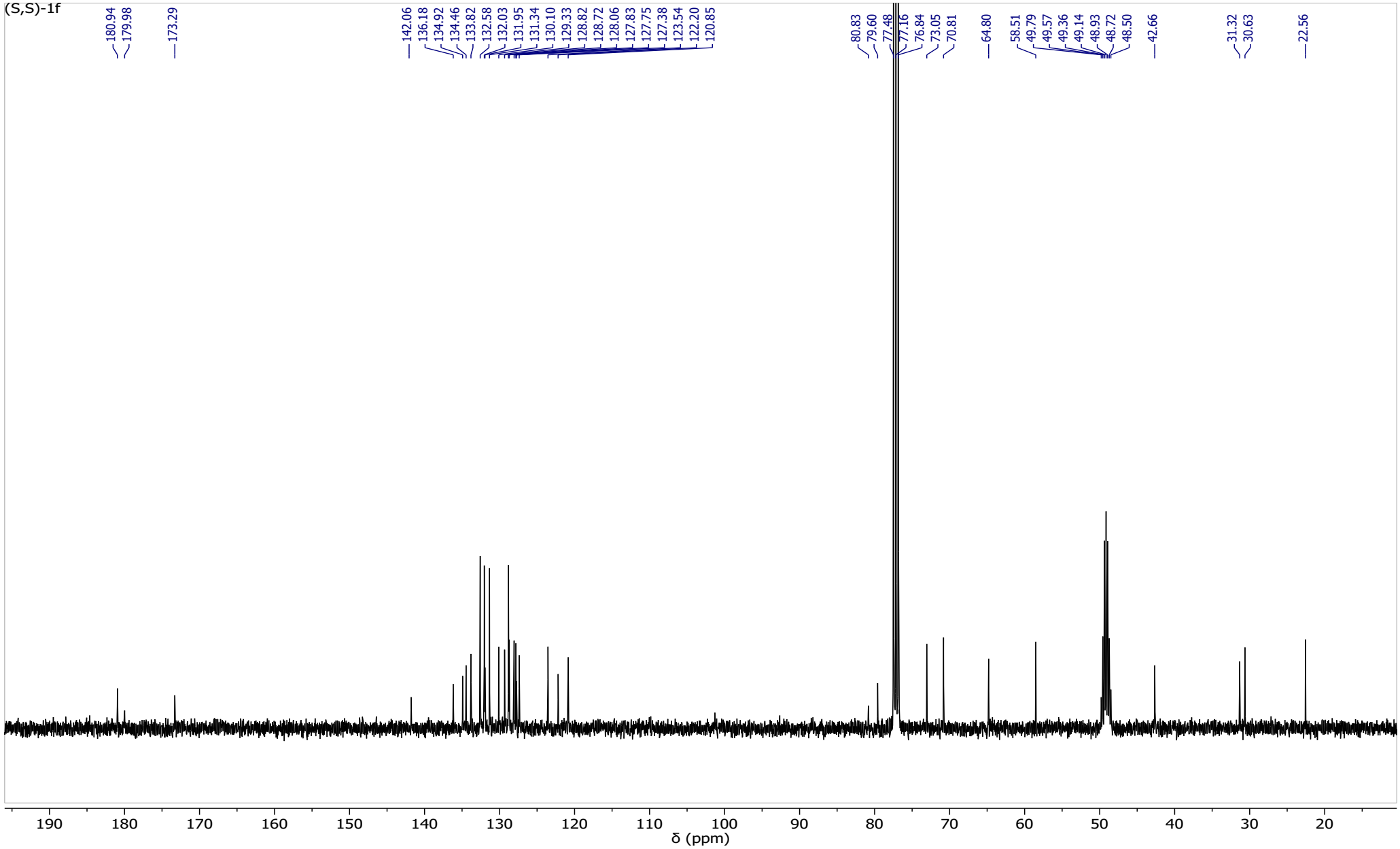

Figure S18. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1f** (in $CDCl_3$+CD_3OD)

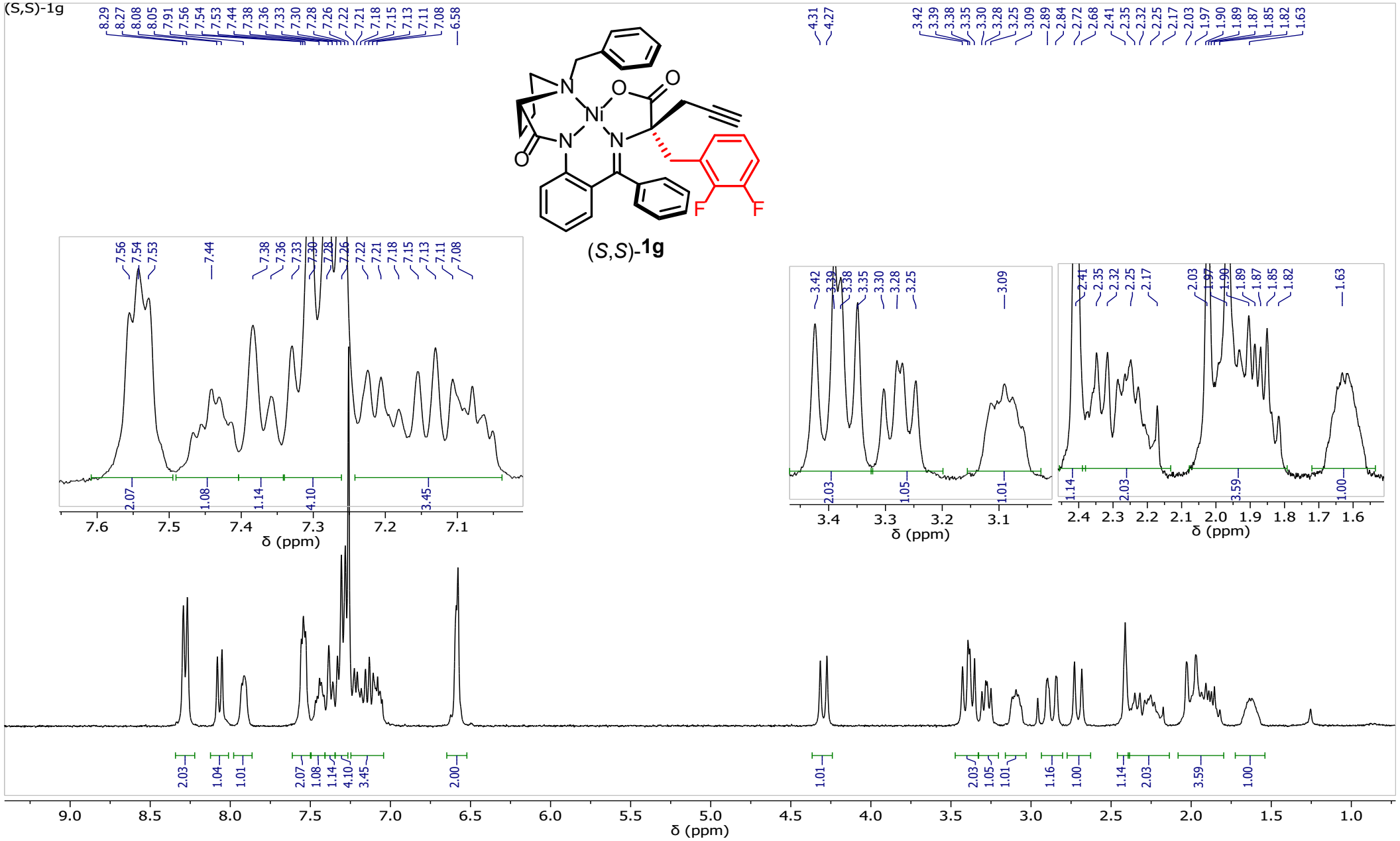

Figure S19. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1g** (in $CDCl_3$)

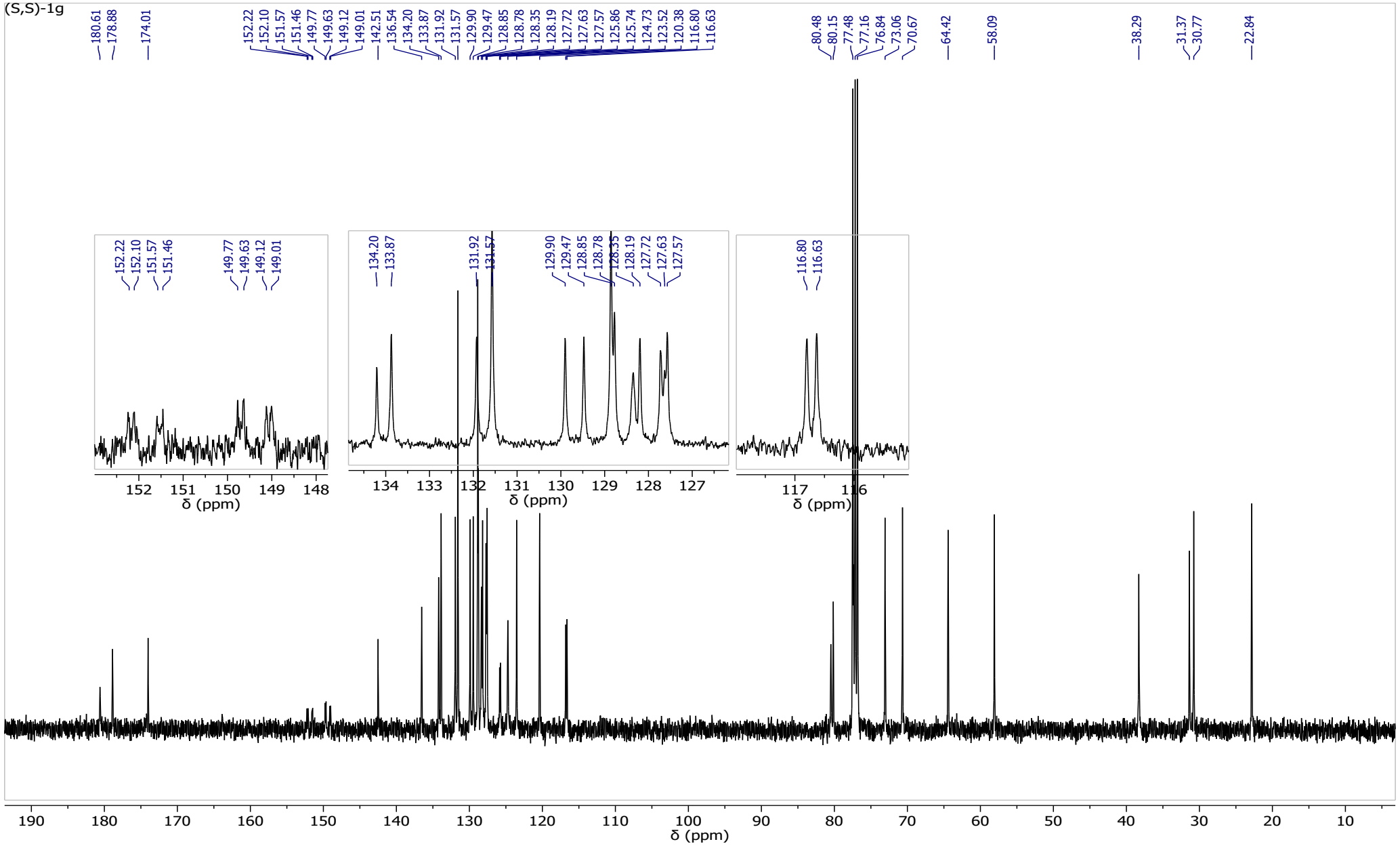

Figure S20. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1g** (in $CDCl_3$)

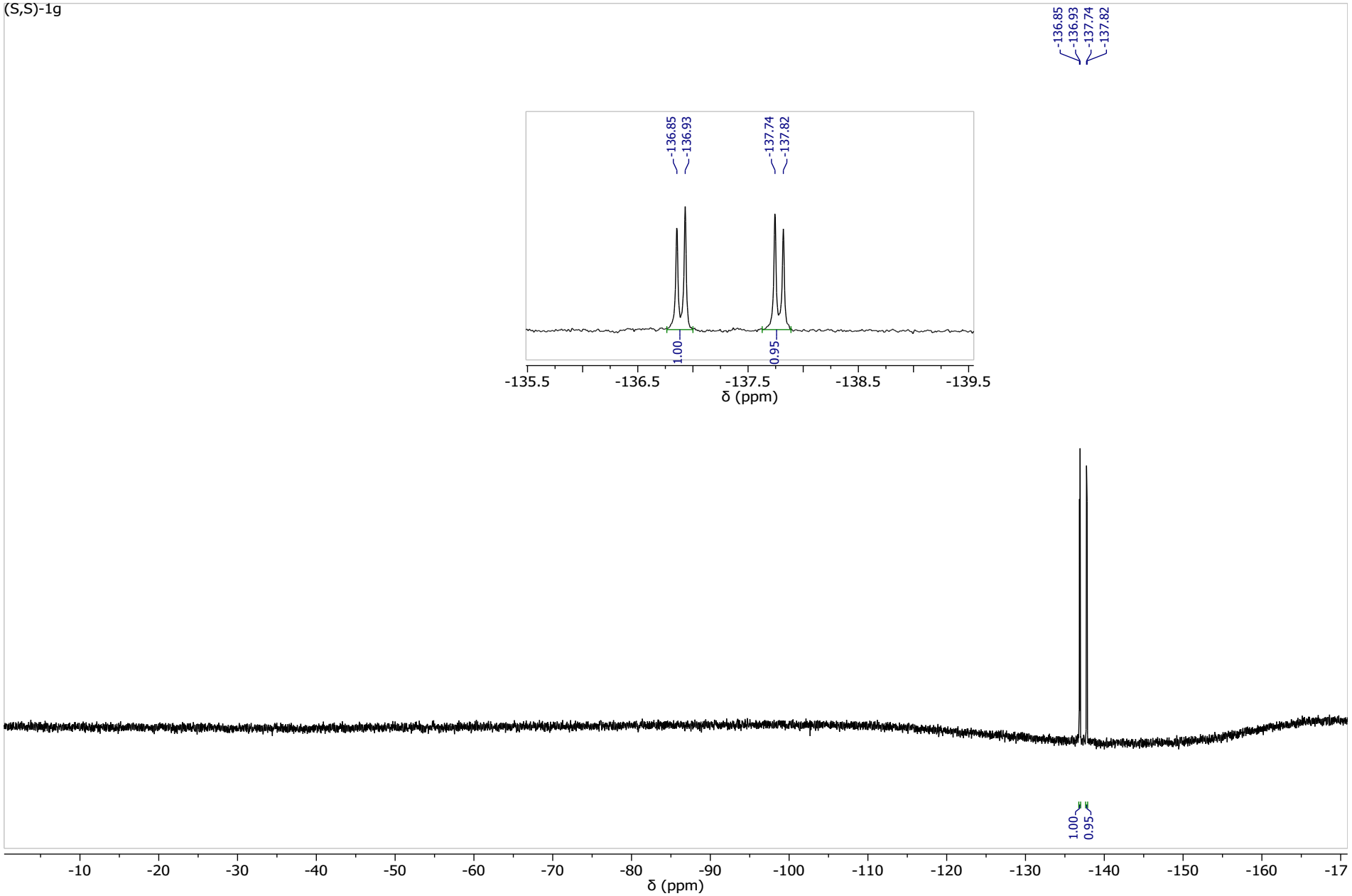

Figure S21. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1g** (in $CDCl_3$)

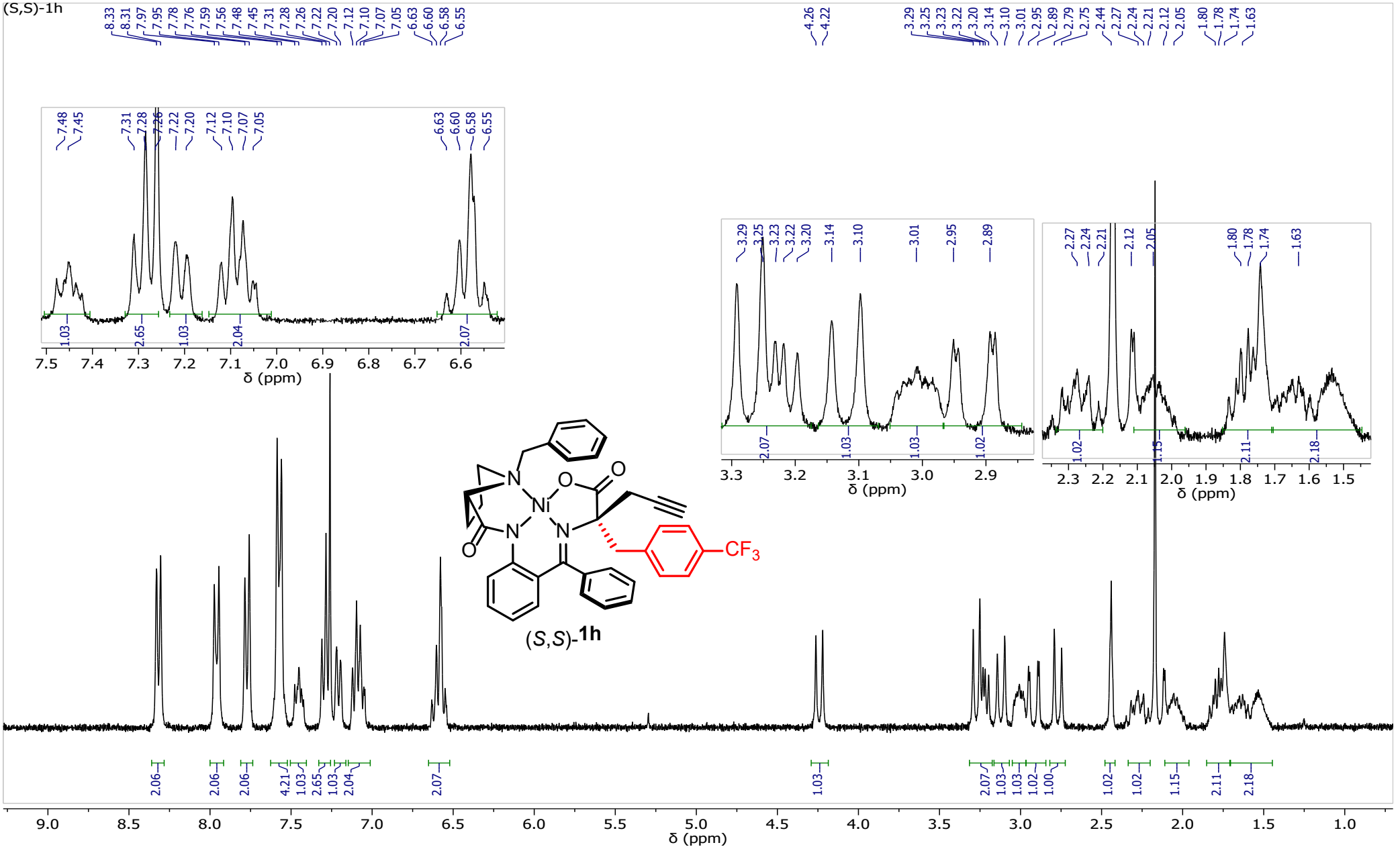

Figure S22. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1h** (in $CDCl_3$)

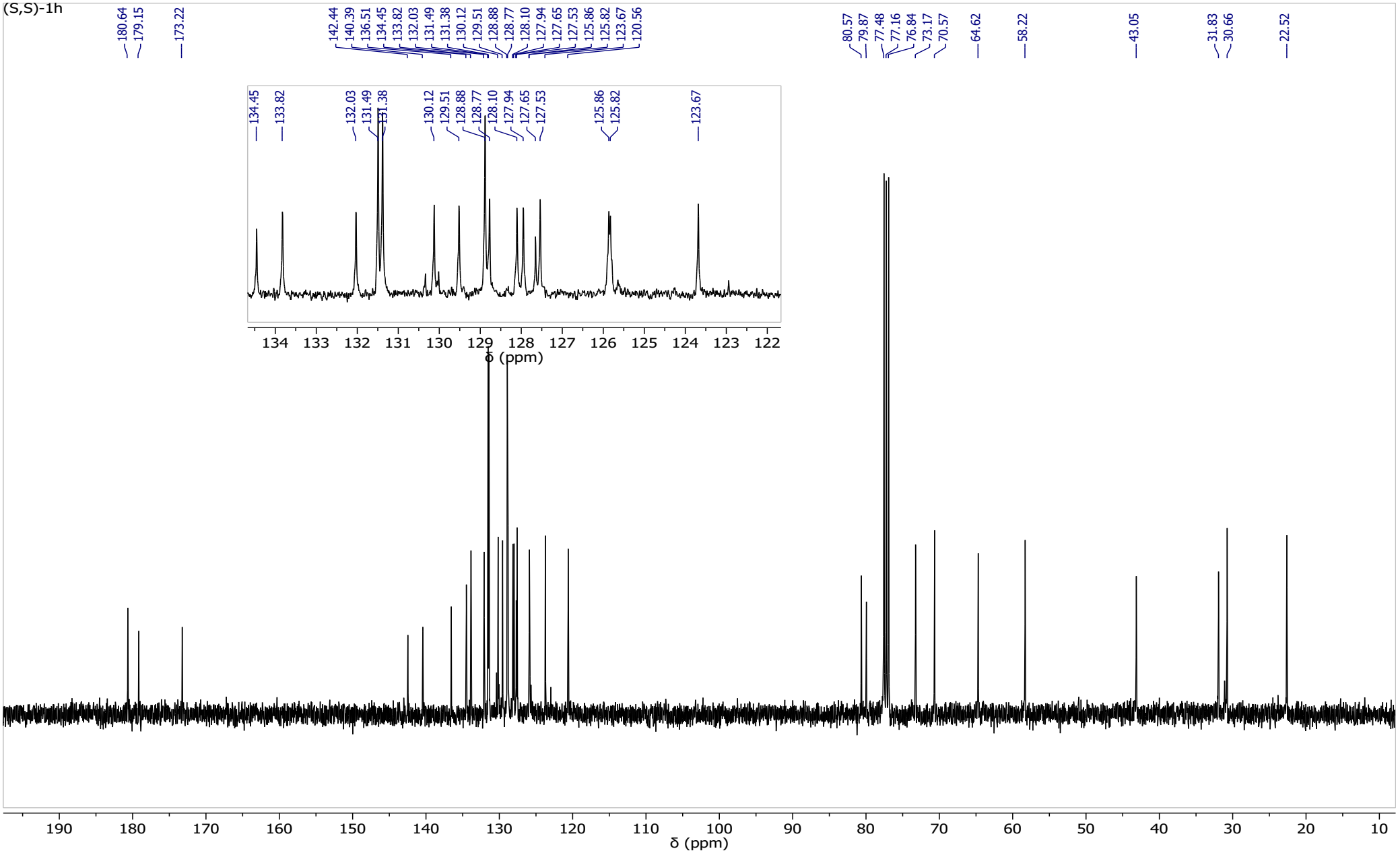

Figure S23. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1h** (in $CDCl_3$)

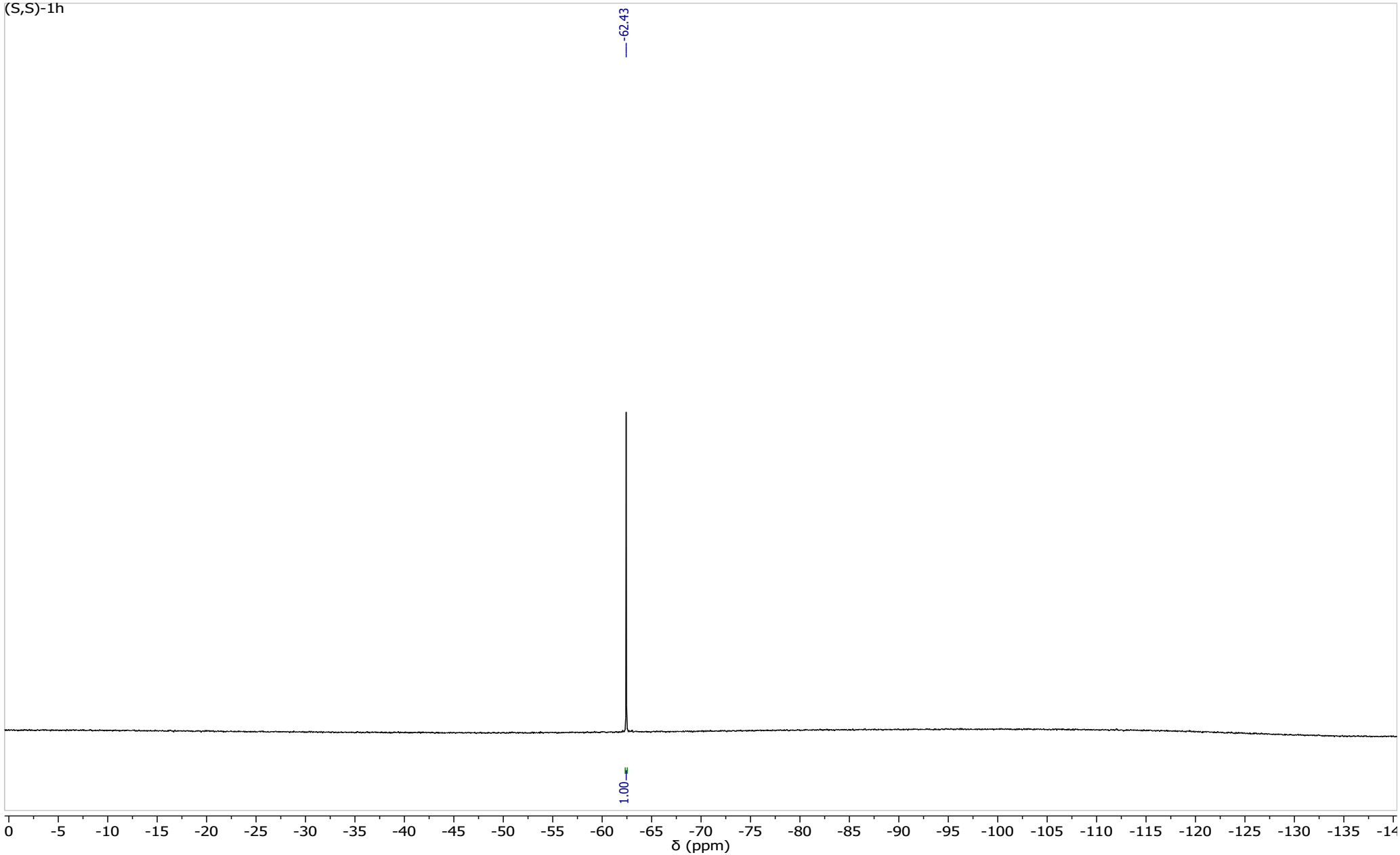

Figure S24. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1h** (in $CDCl_3$)

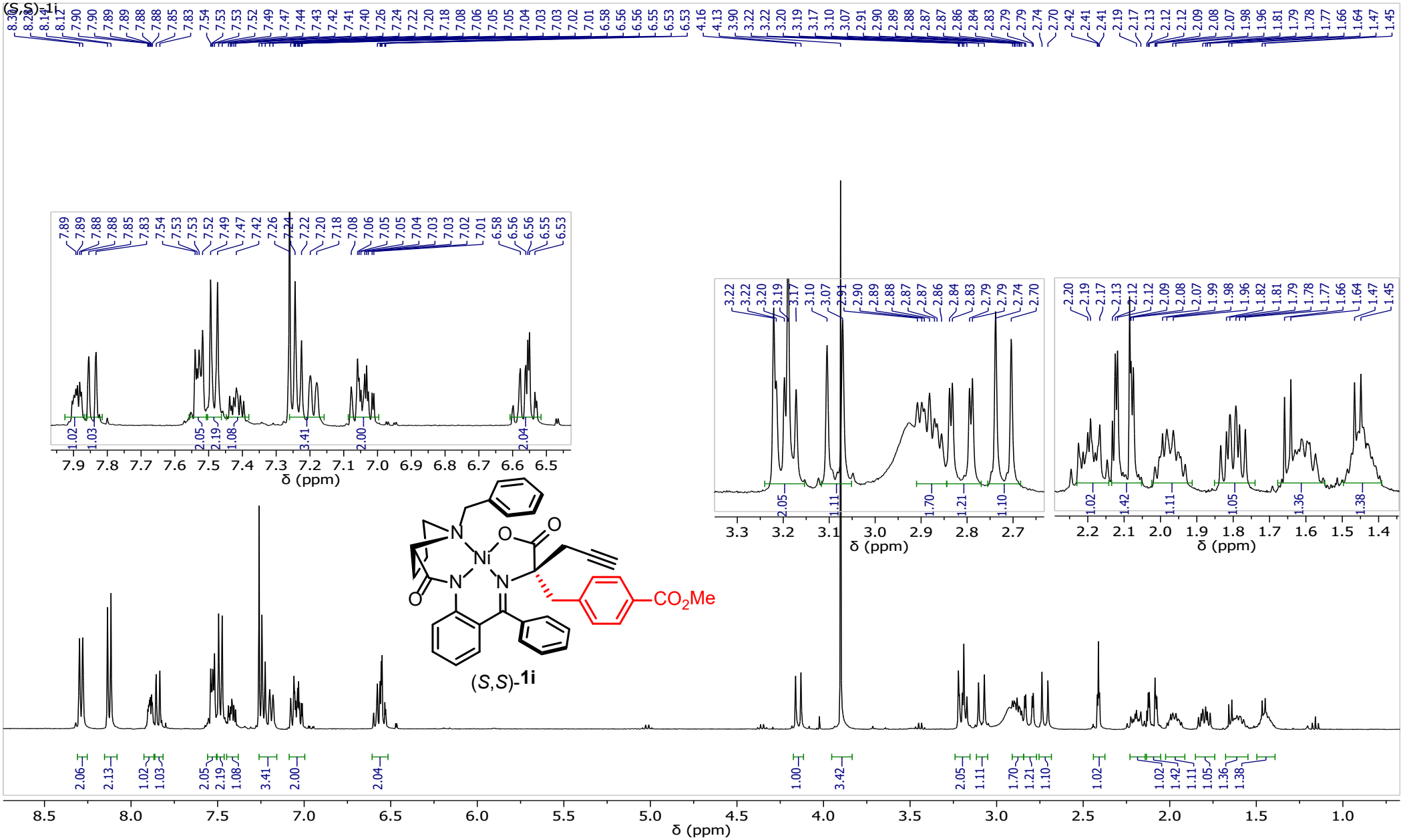

Figure S25. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1i** (in $CDCl_3$+CD_3OD)

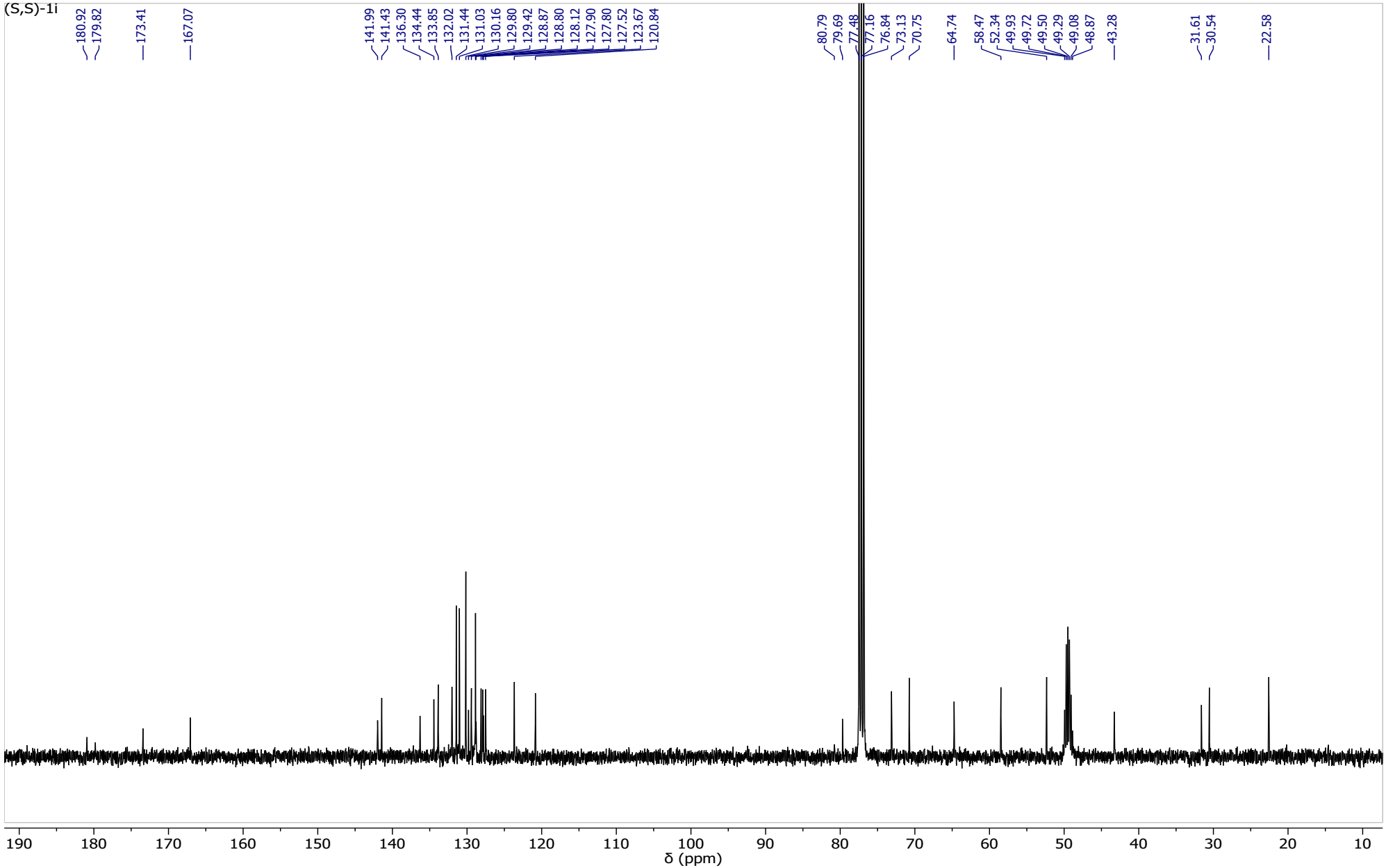

Figure S26. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**1i** (in $CDCl_3$+CD_3OD)

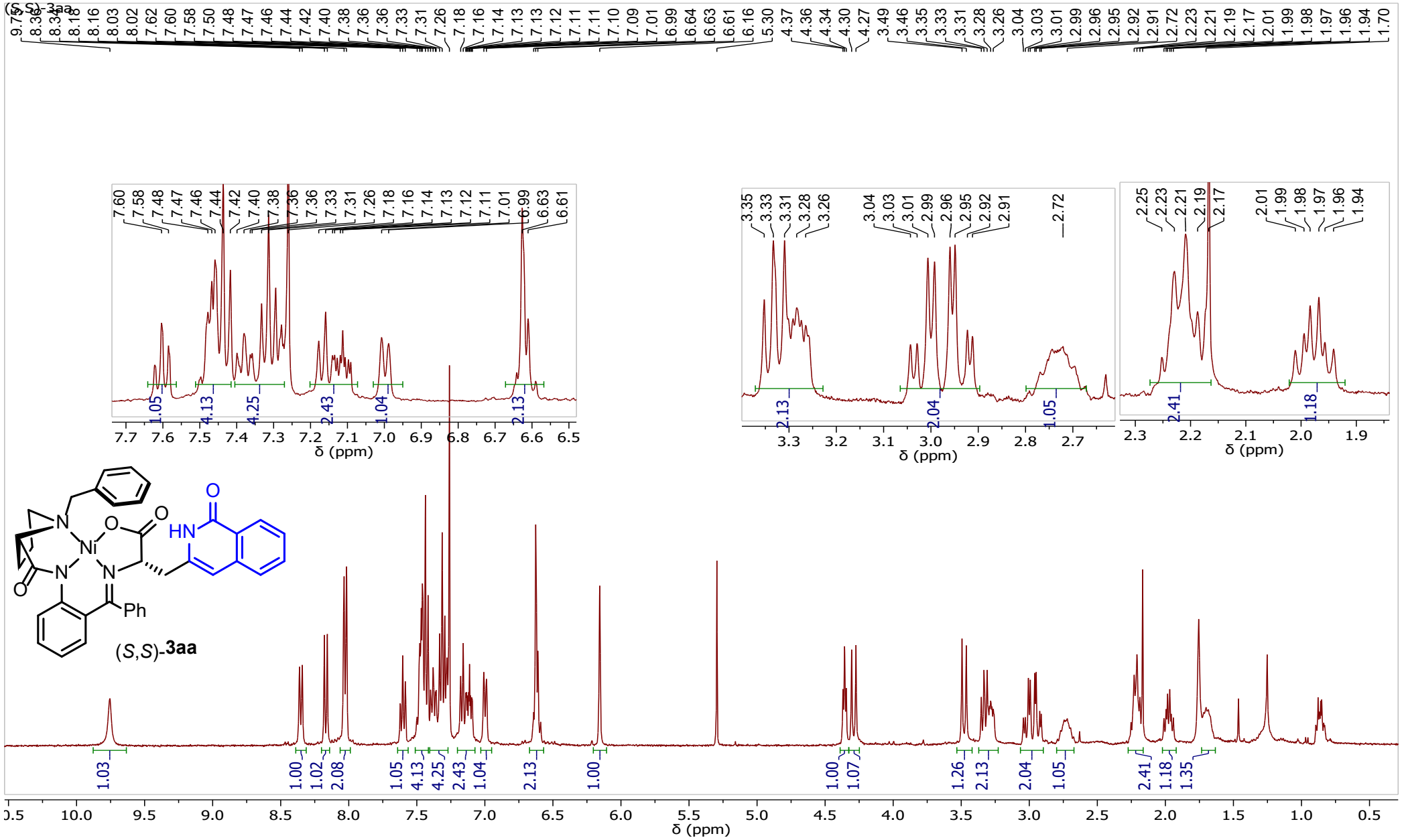

Figure S27. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3aa** (in $CDCl_3$)

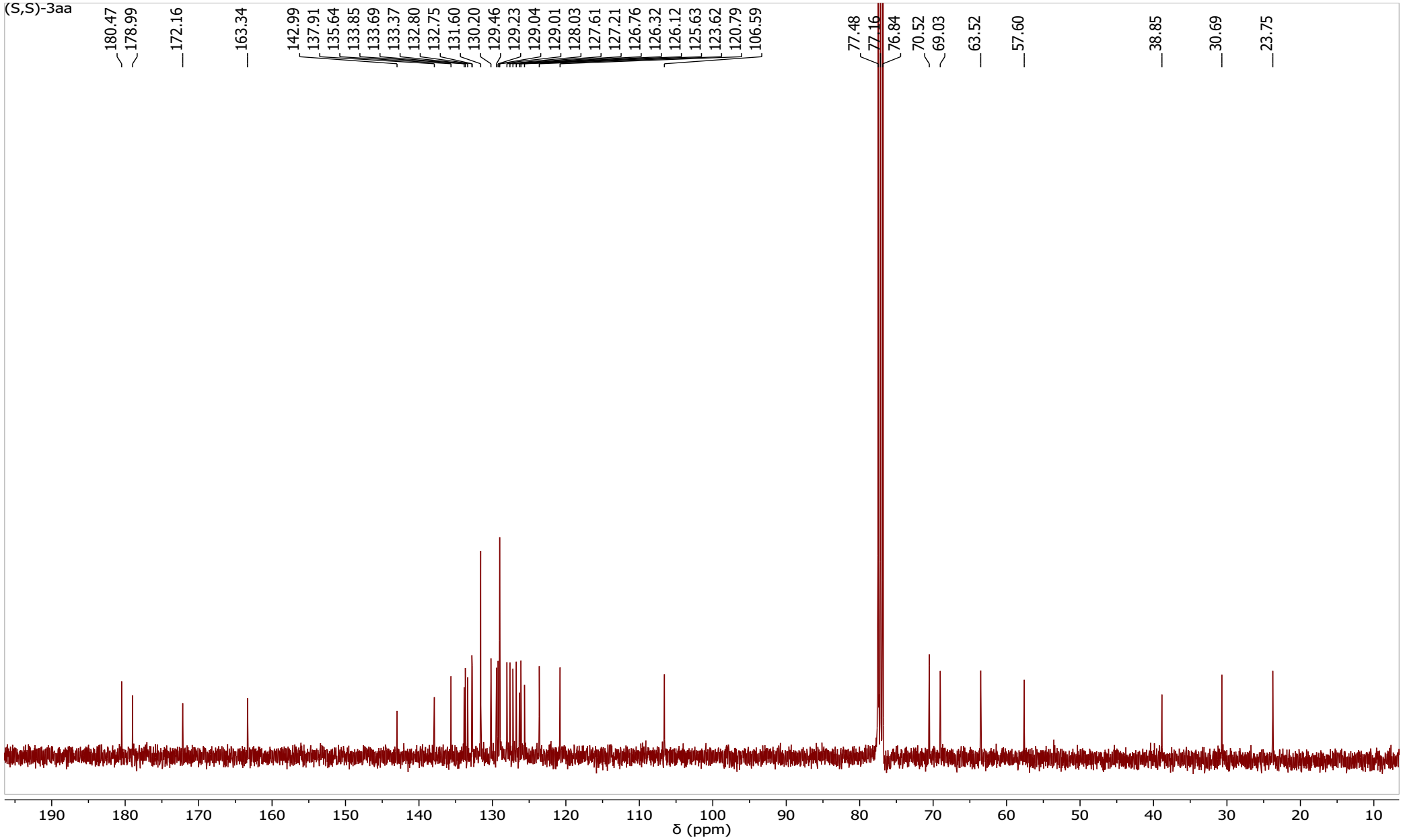

Figure S28. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3aa** (in $CDCl_3$)

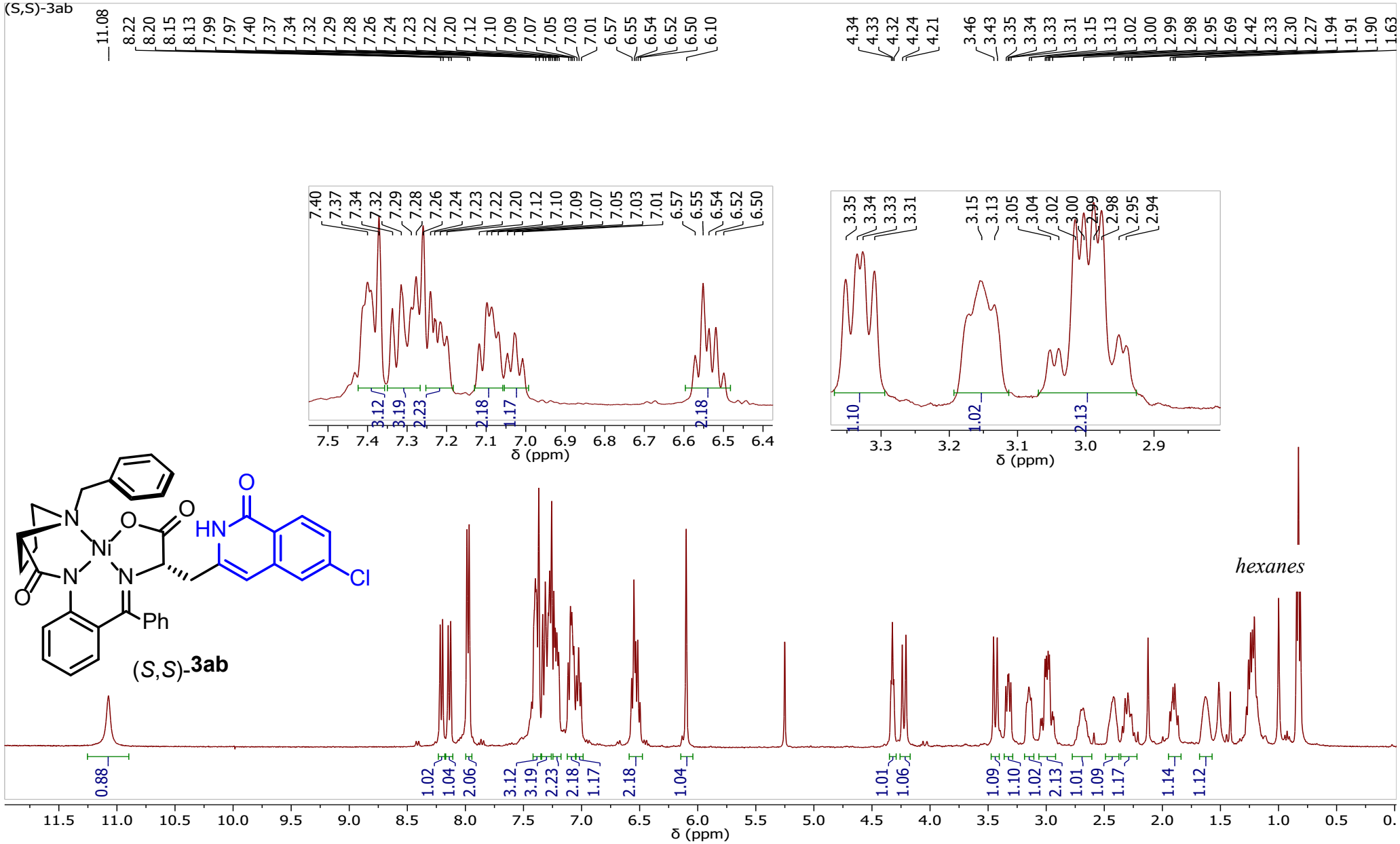

Figure S29. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ab** (in $CDCl_3$)

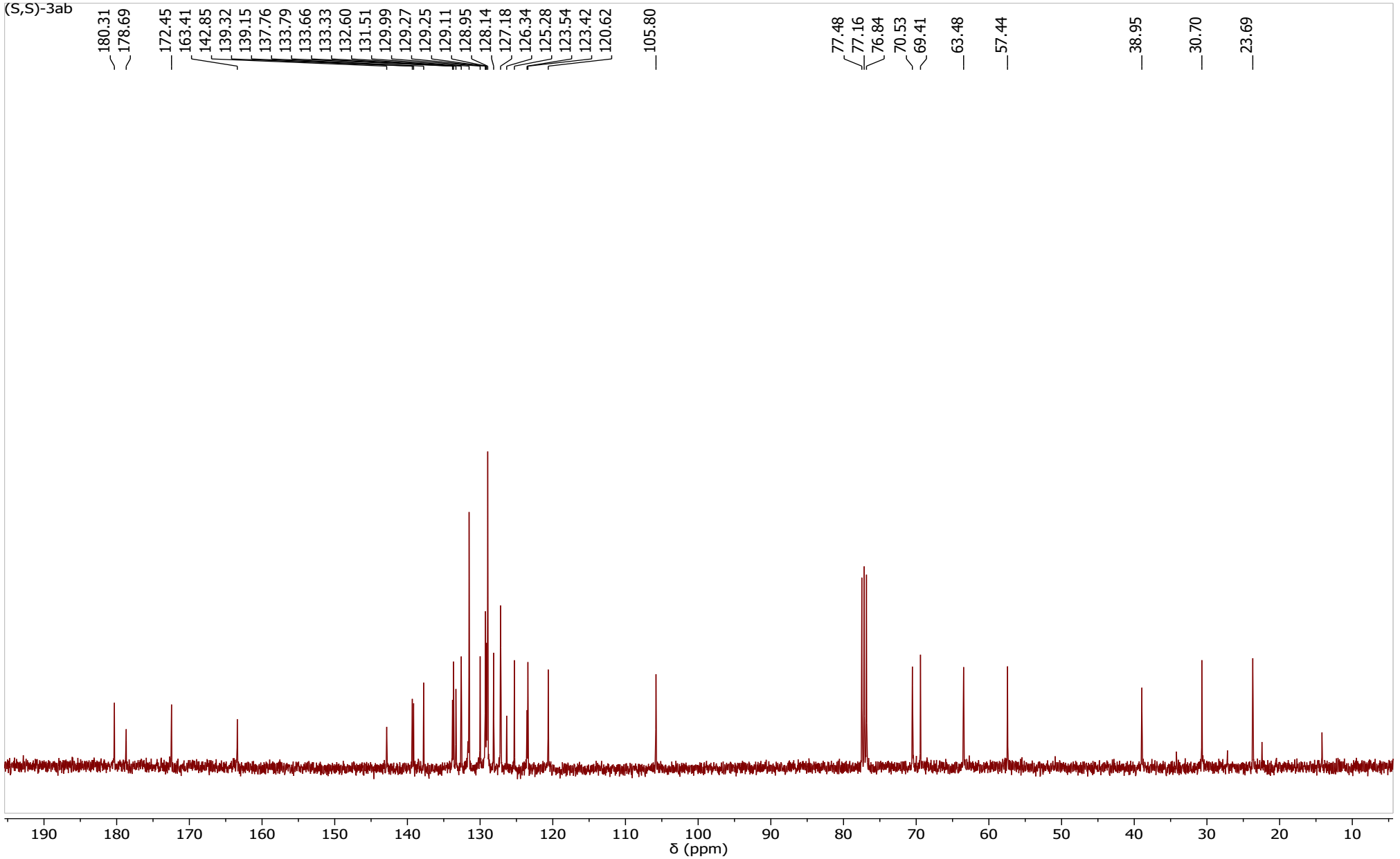

Figure S30. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ab** (in $CDCl_3$)

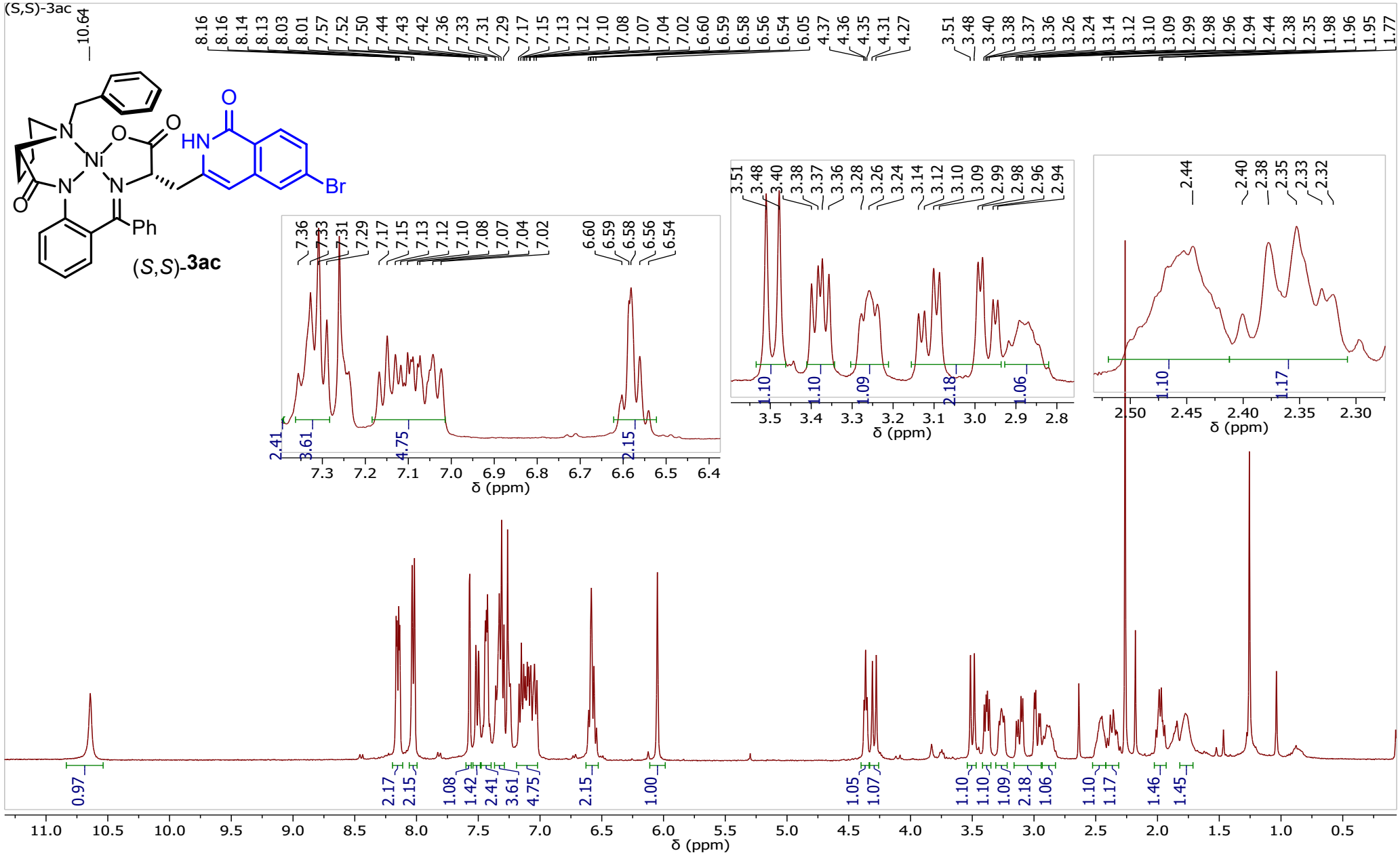

Figure S31. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ac** (in $CDCl_3$)

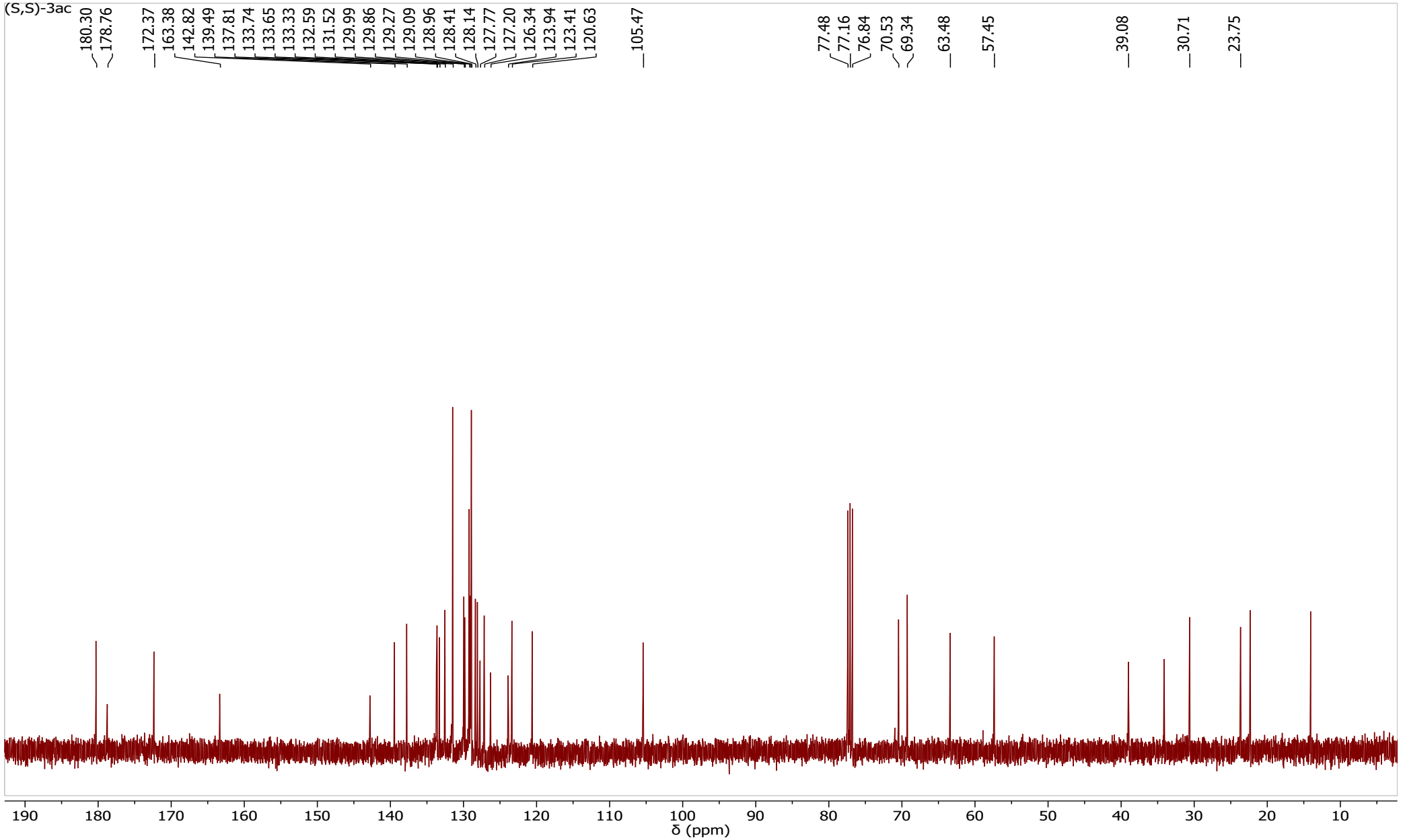

Figure S32. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ac** (in $CDCl_3$)

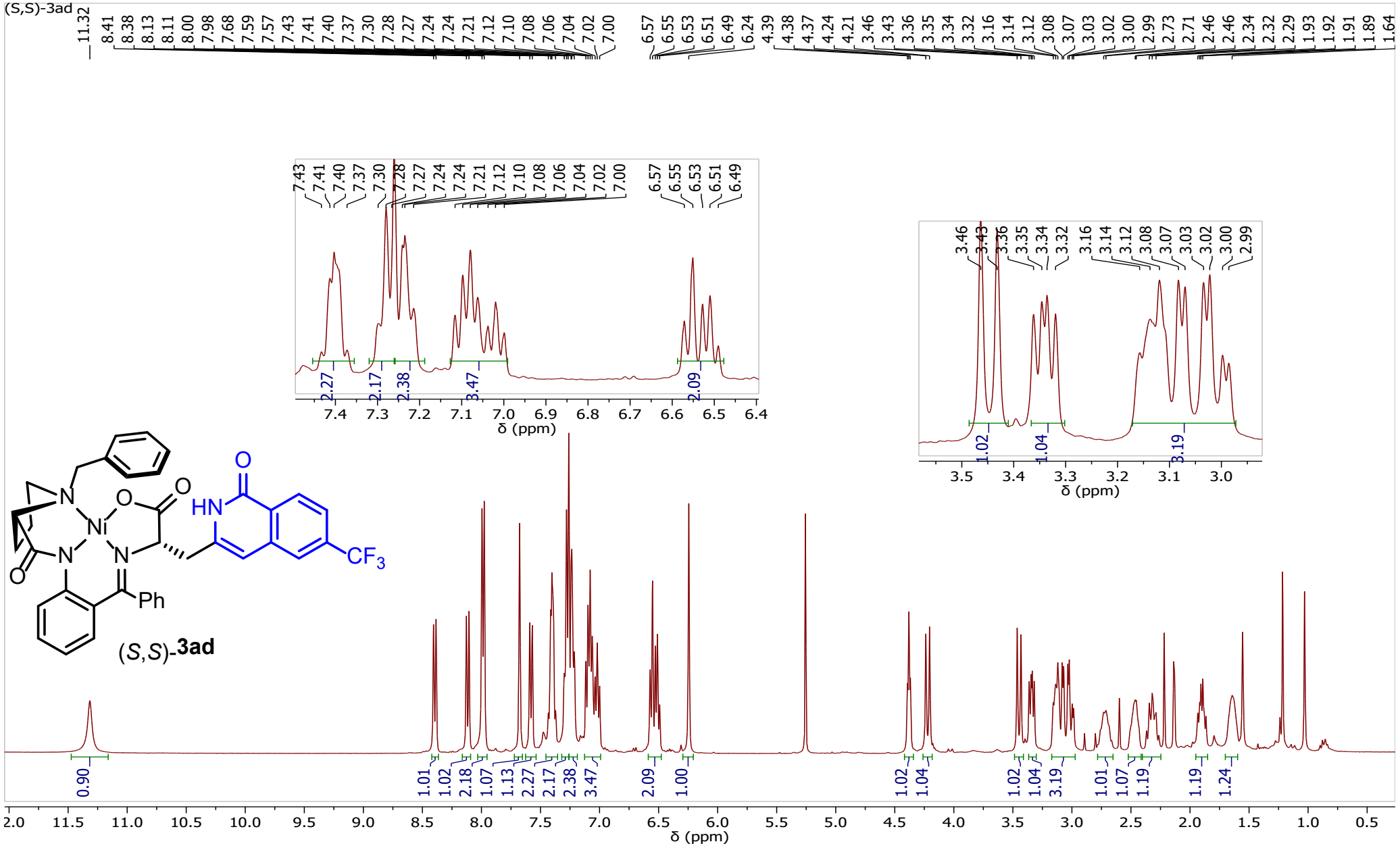

Figure S33. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ad** (in $CDCl_3$)

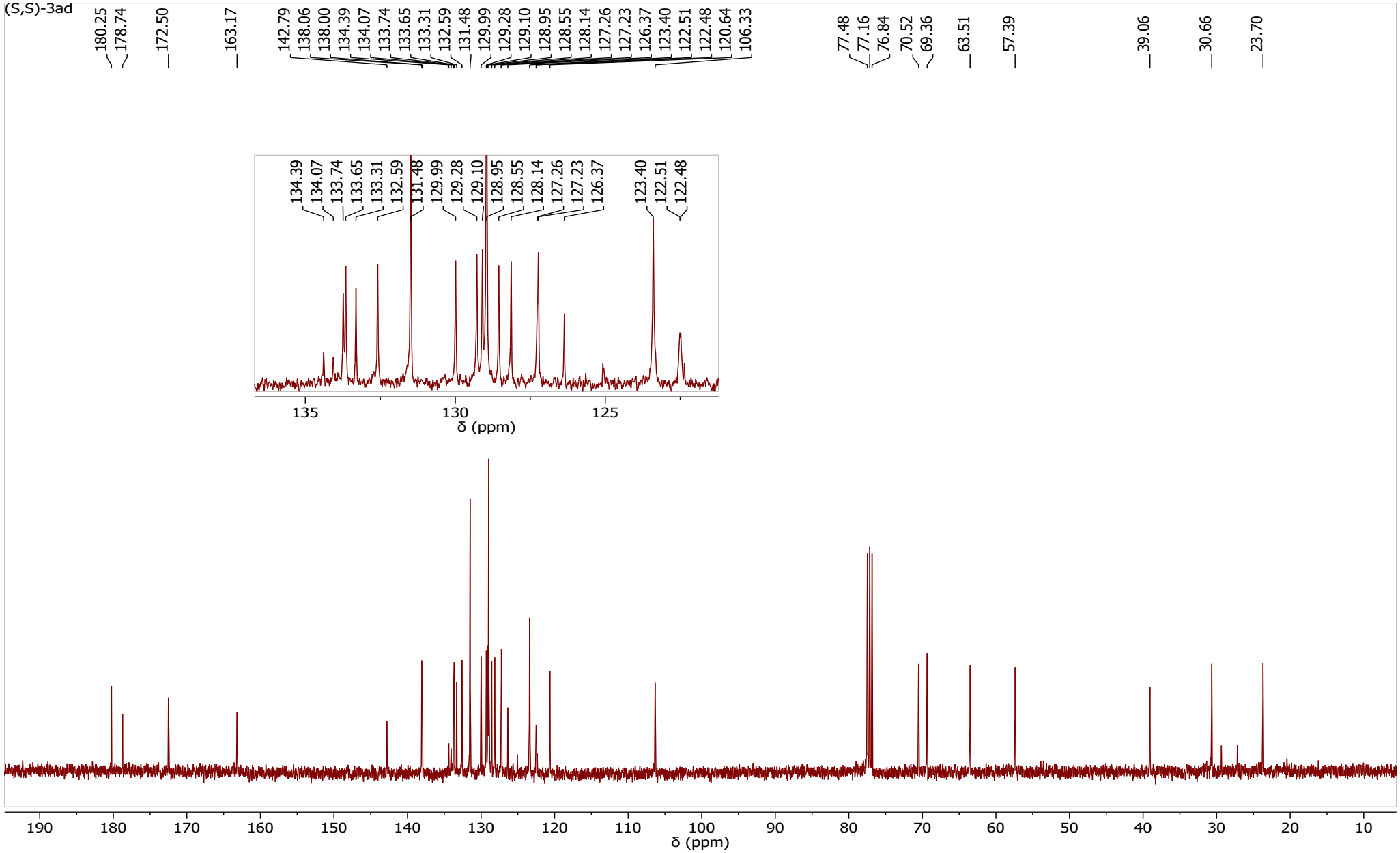

Figure S34. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ad** (in $CDCl_3$)

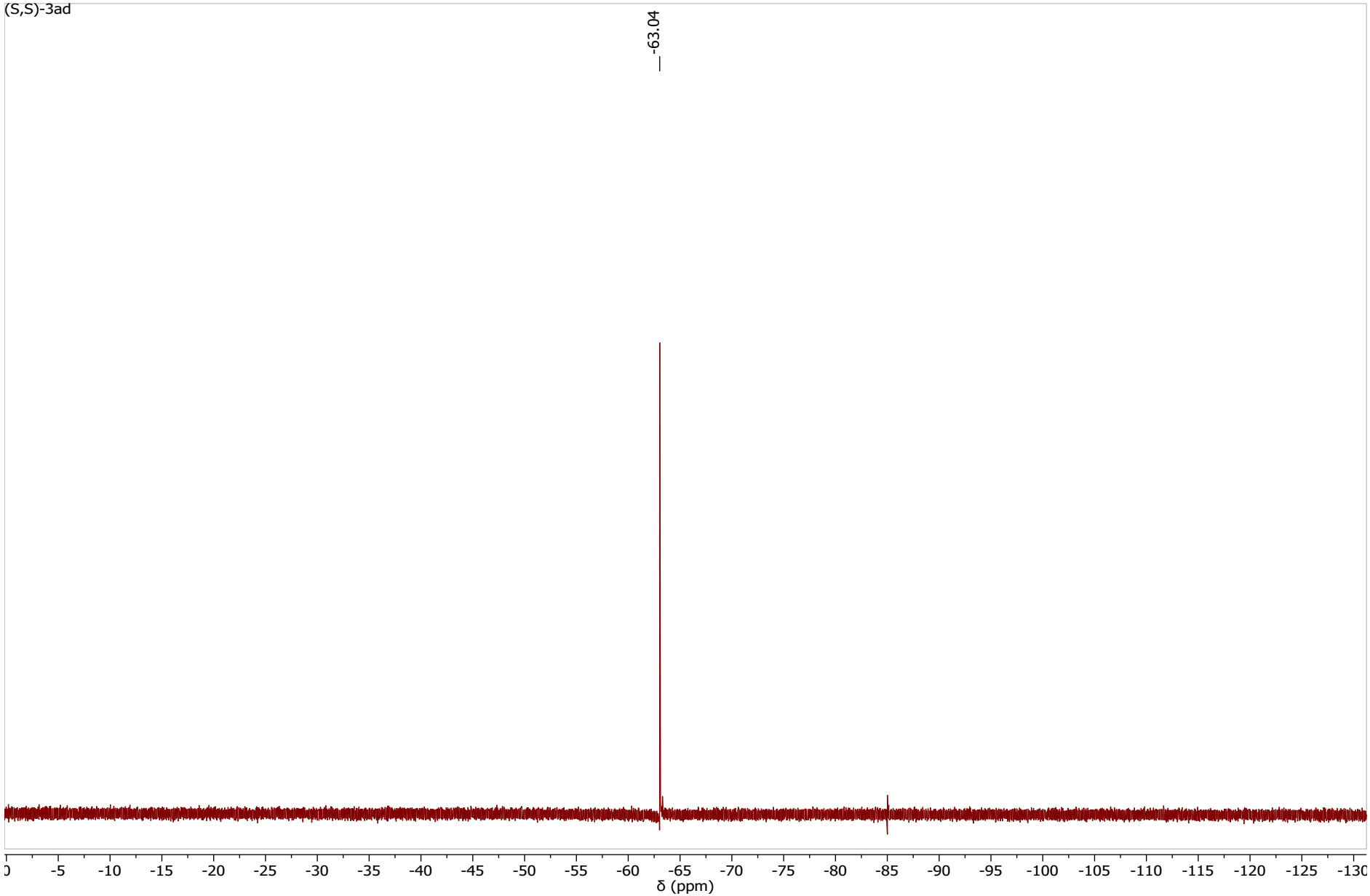

Figure S35. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ad** (in $CDCl_3$)

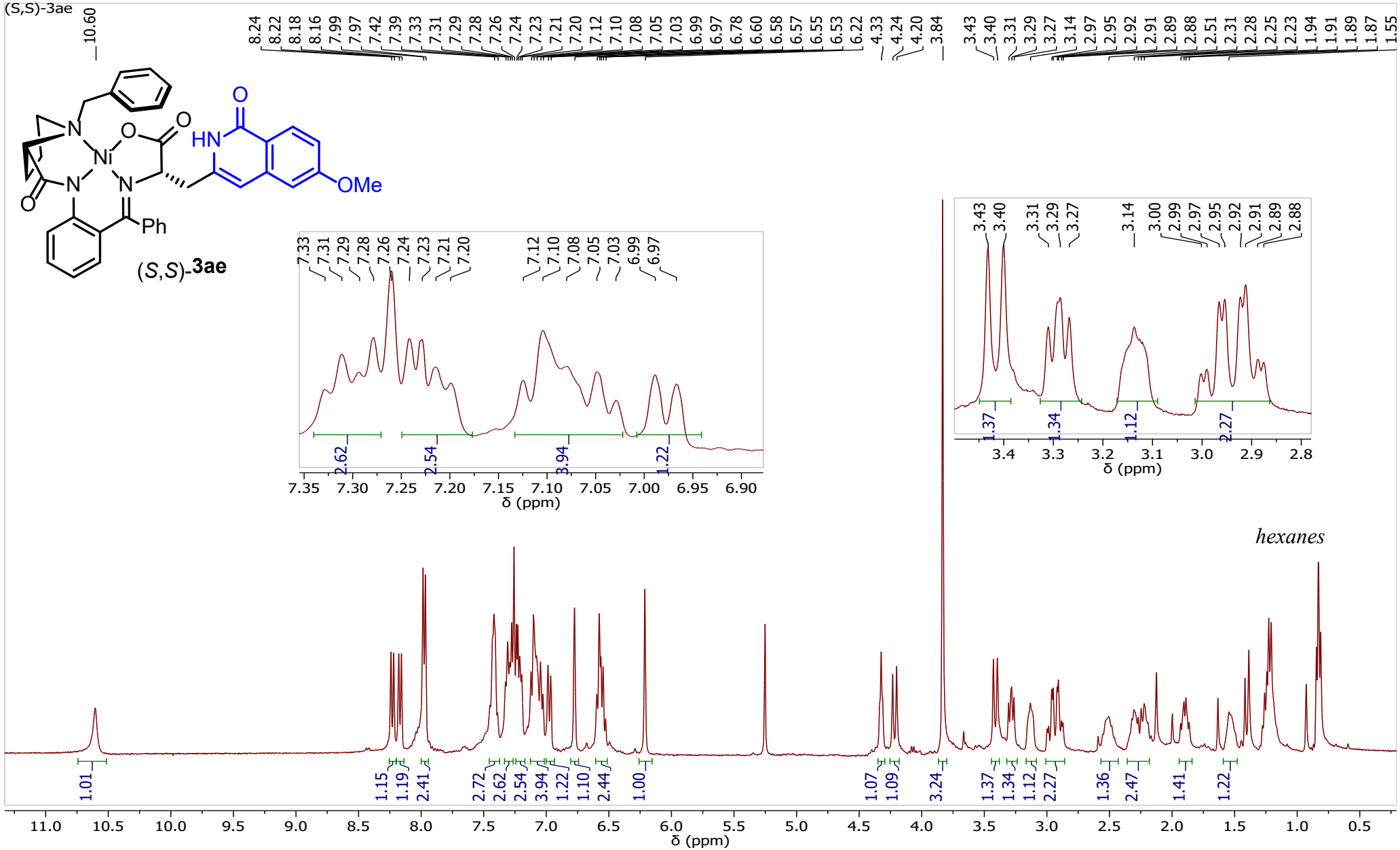

Figure S36. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ae** (in $CDCl_3$)

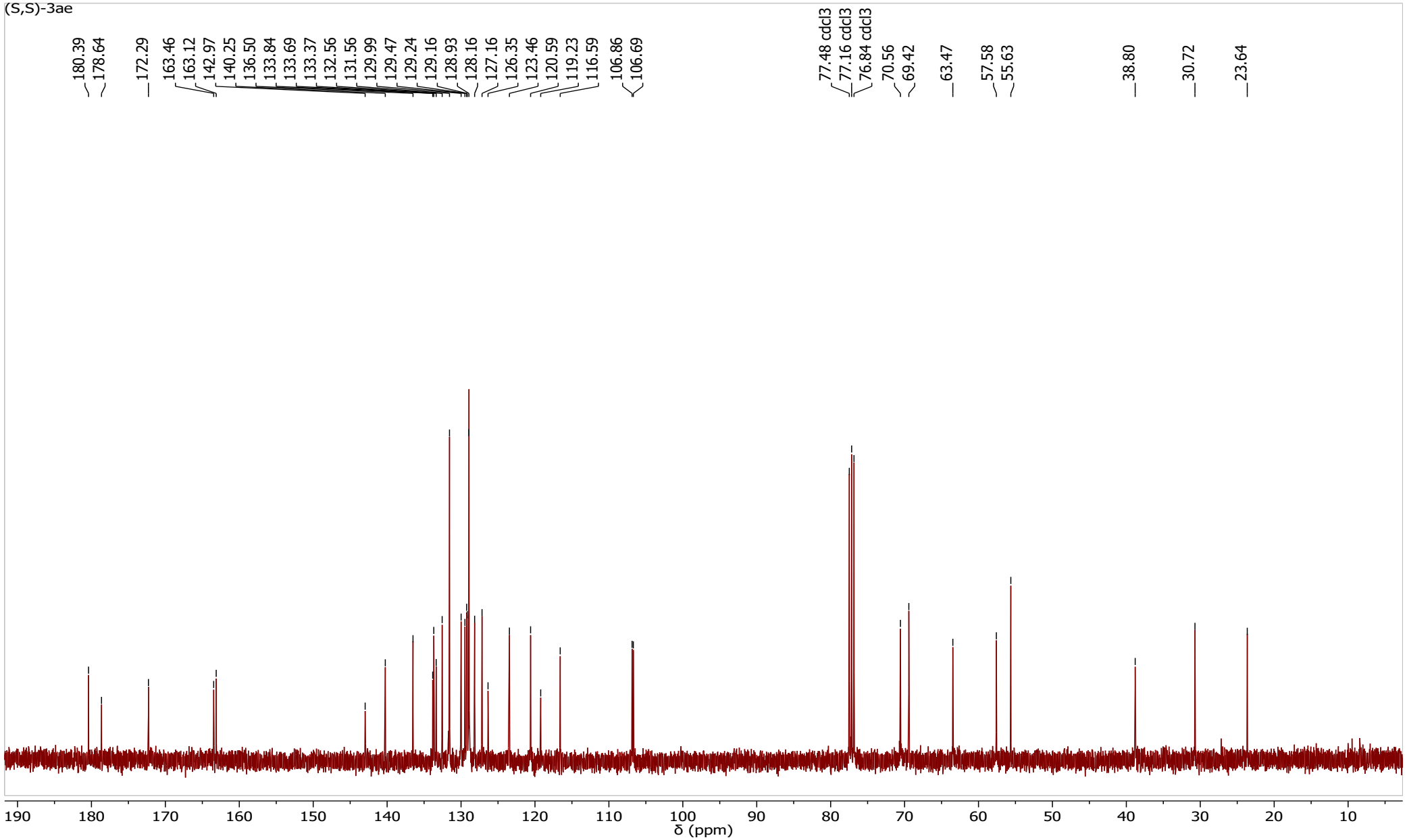

Figure S37. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ae** (in $CDCl_3$)

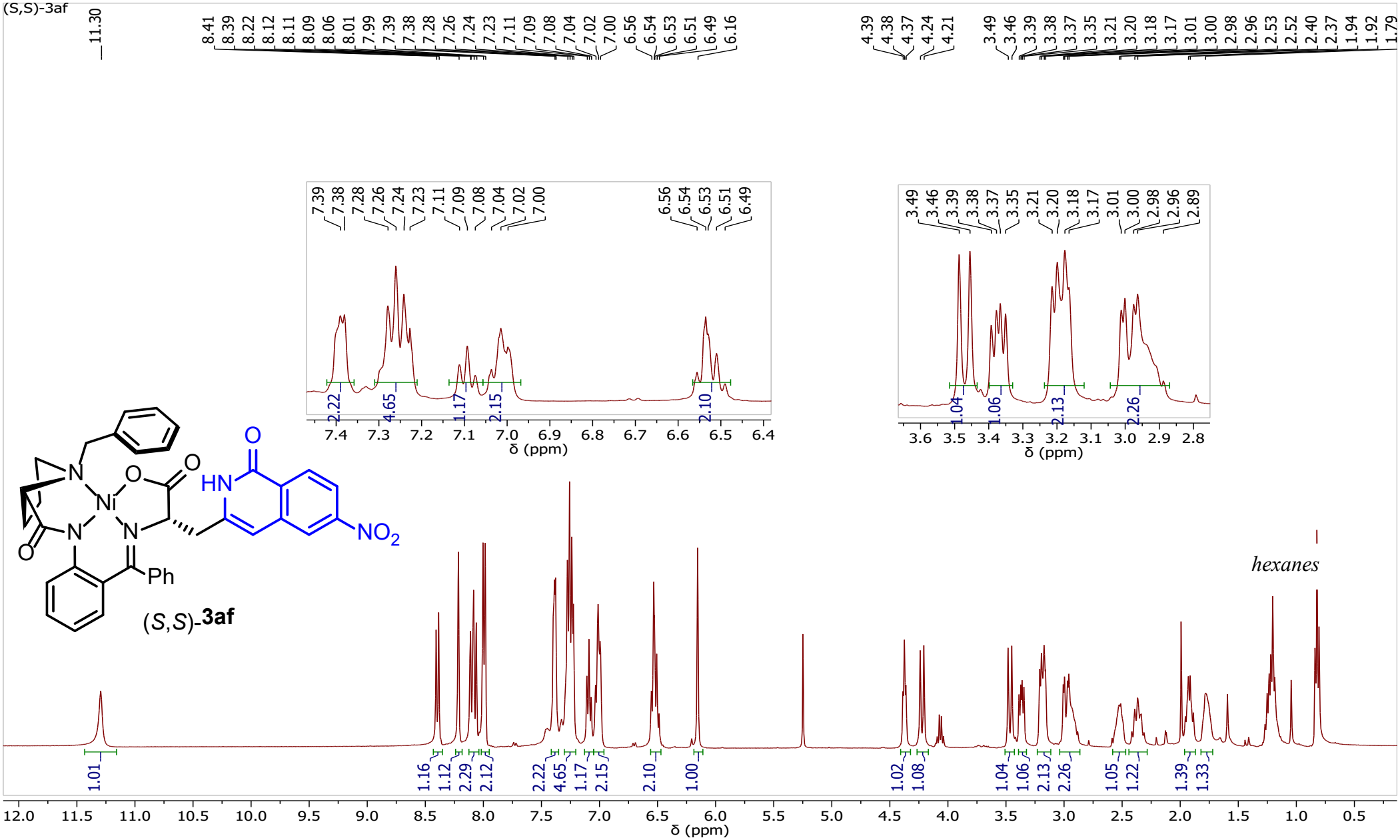

Figure S38. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3af** (in $CDCl_3$)

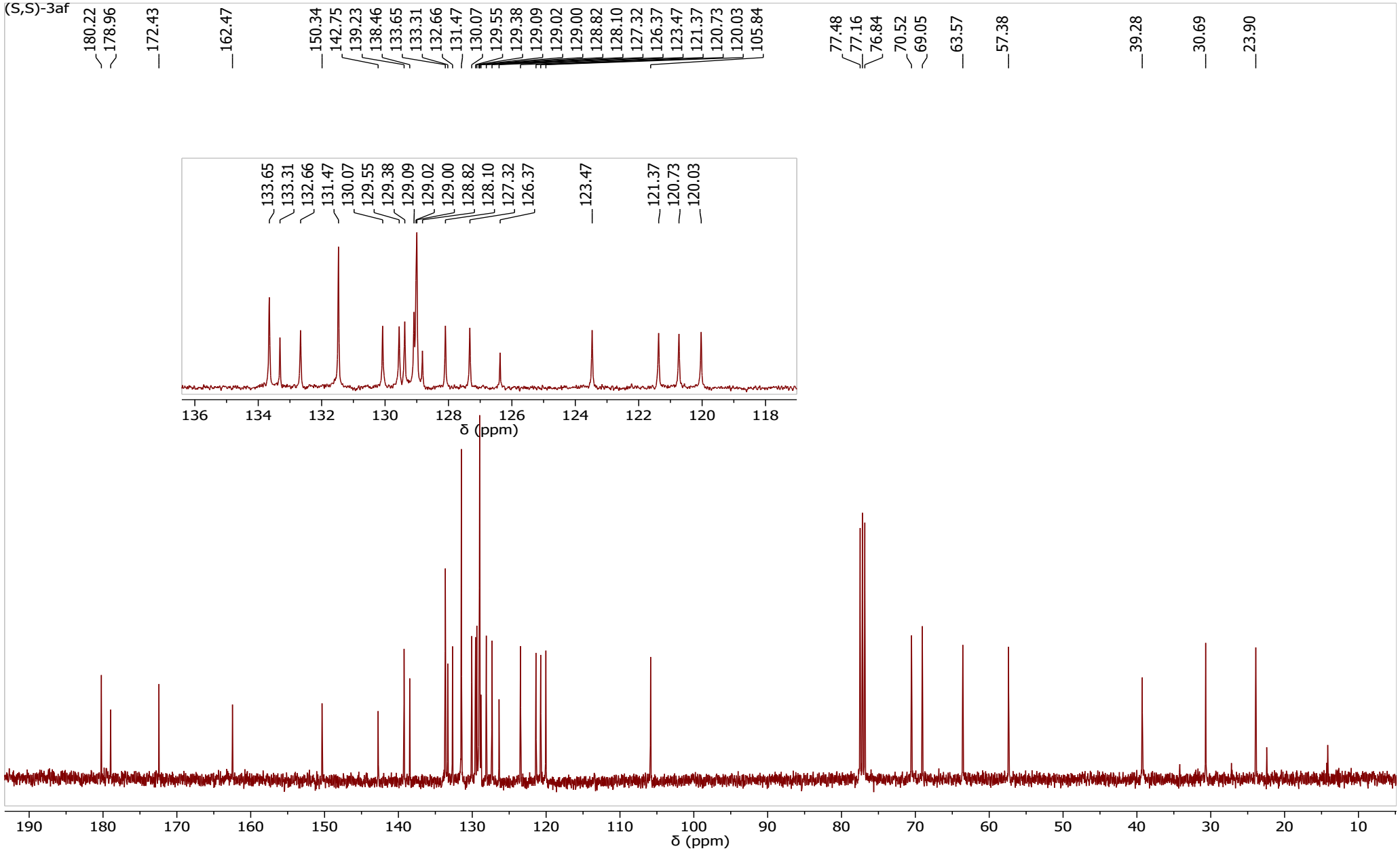

Figure S39. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3af** (in $CDCl_3$)

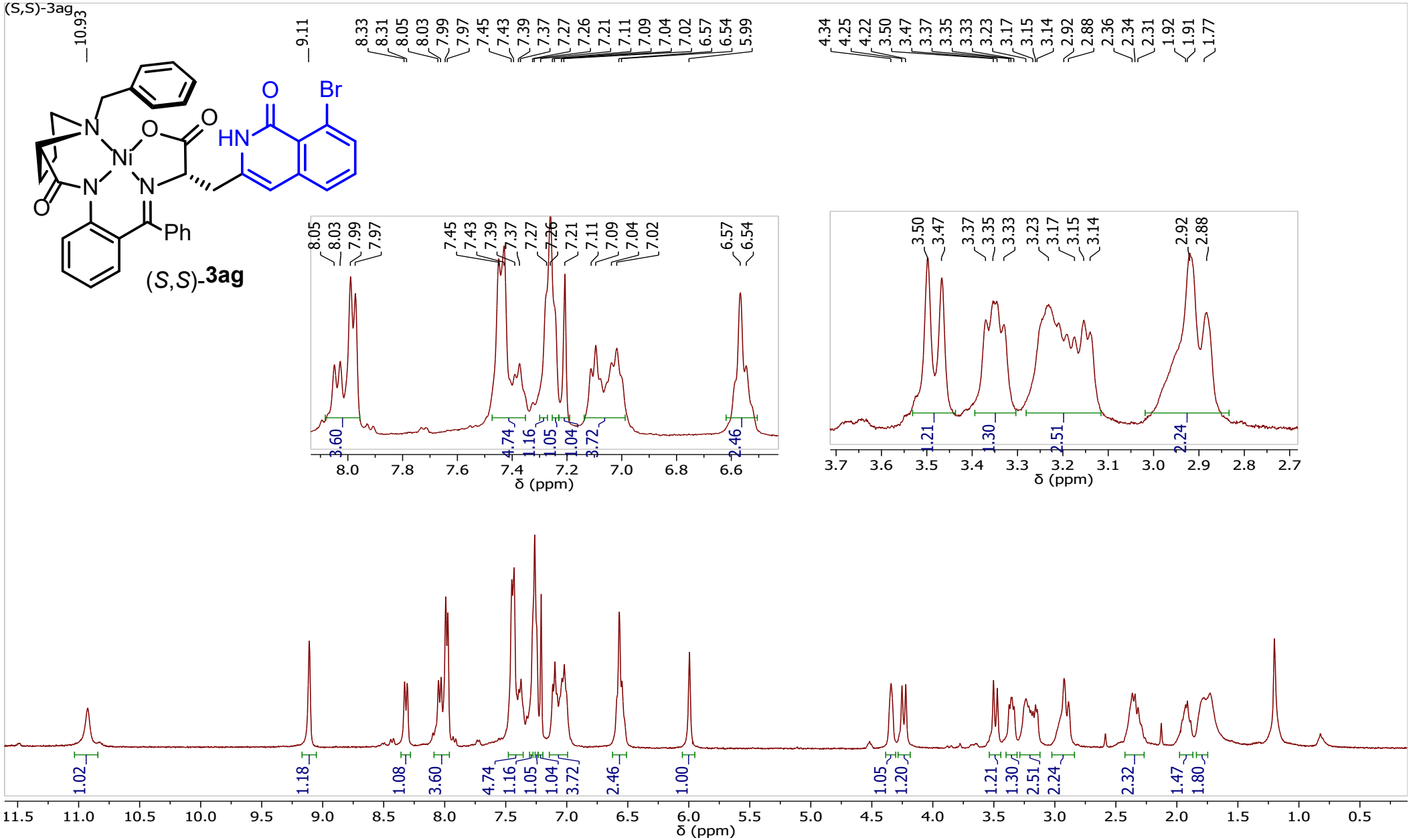

Figure S40. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ag** (in $CDCl_3$)

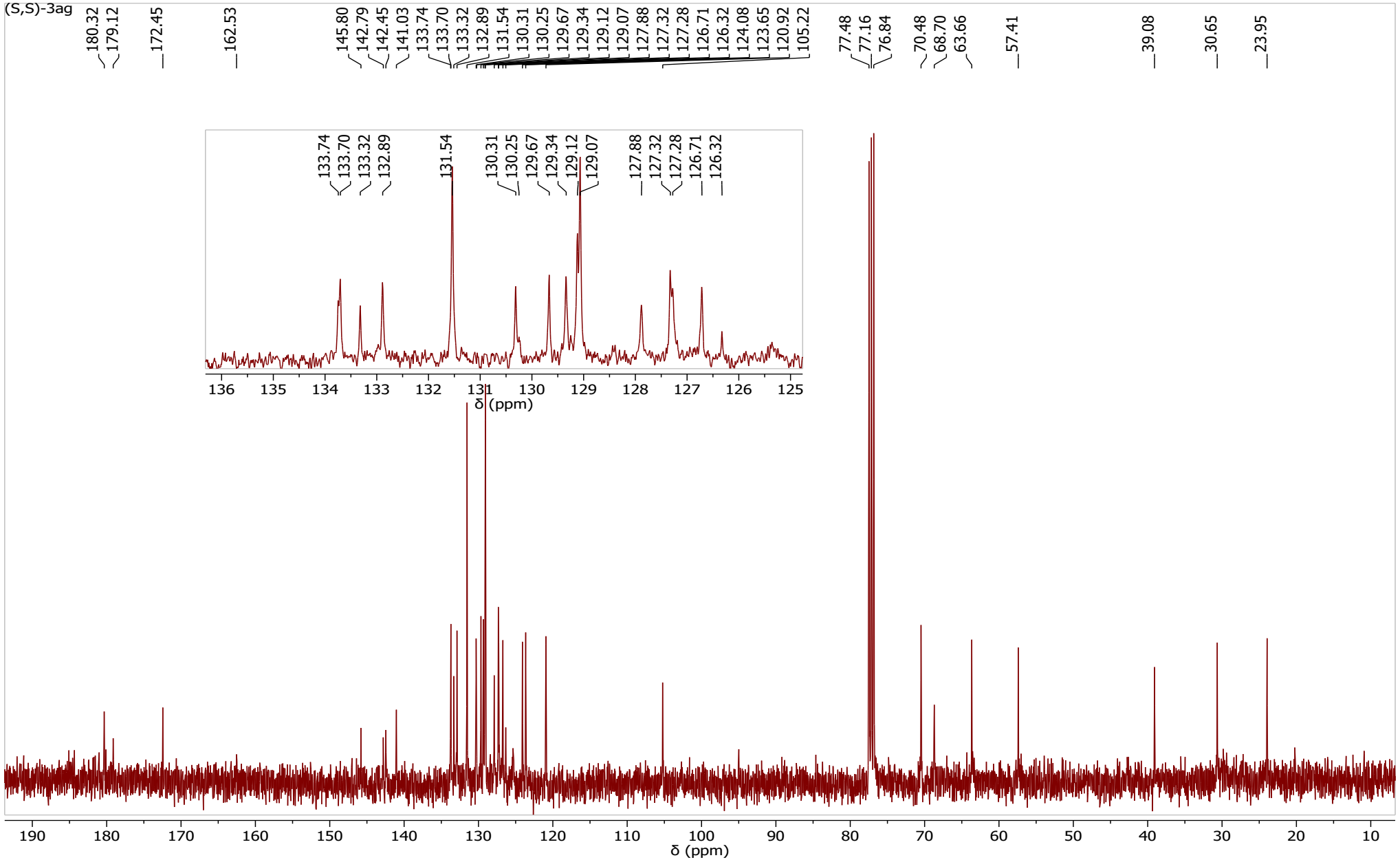

Figure S41. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ag** (in $CDCl_3$)

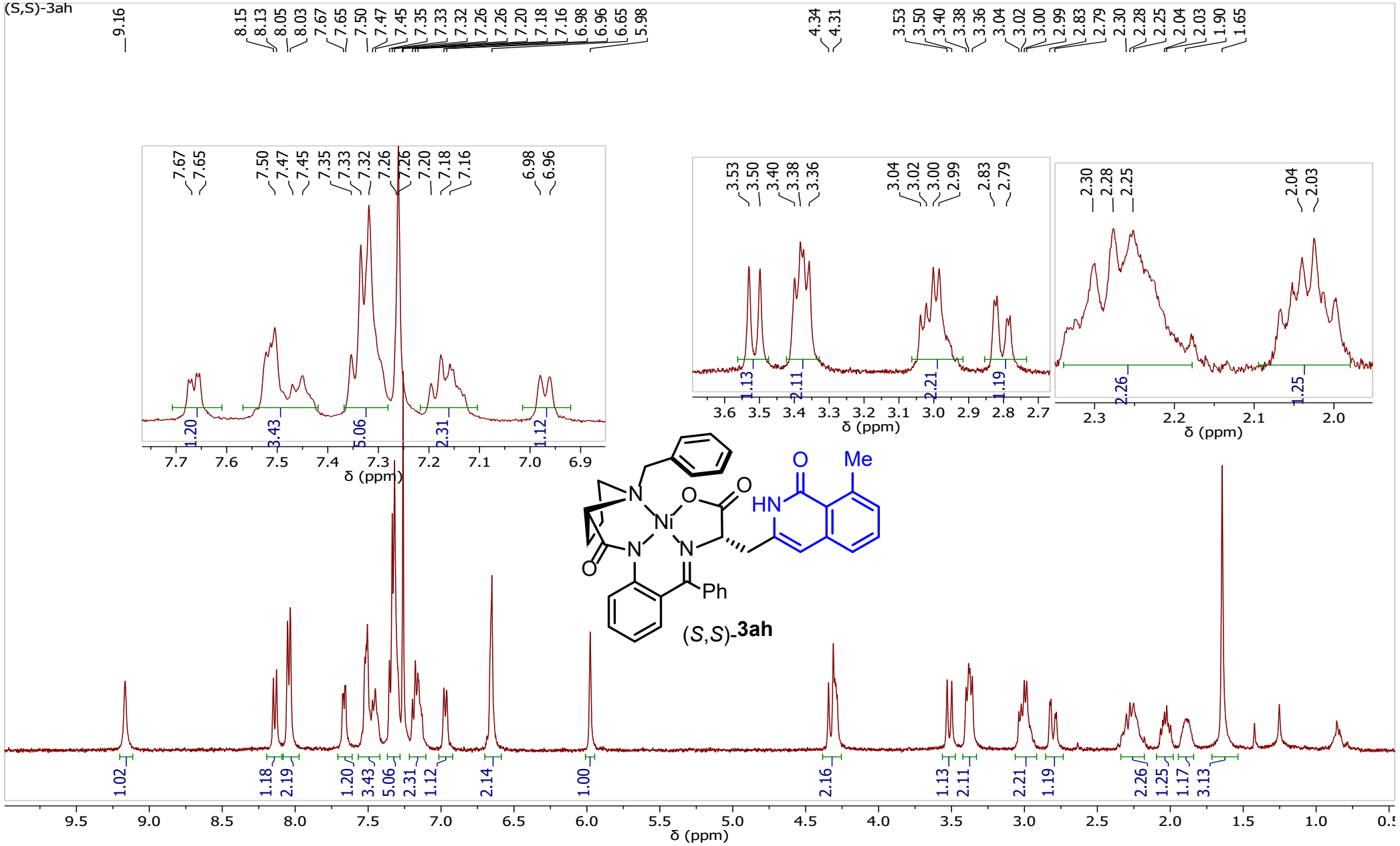

Figure S42. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ah** (in $CDCl_3$)

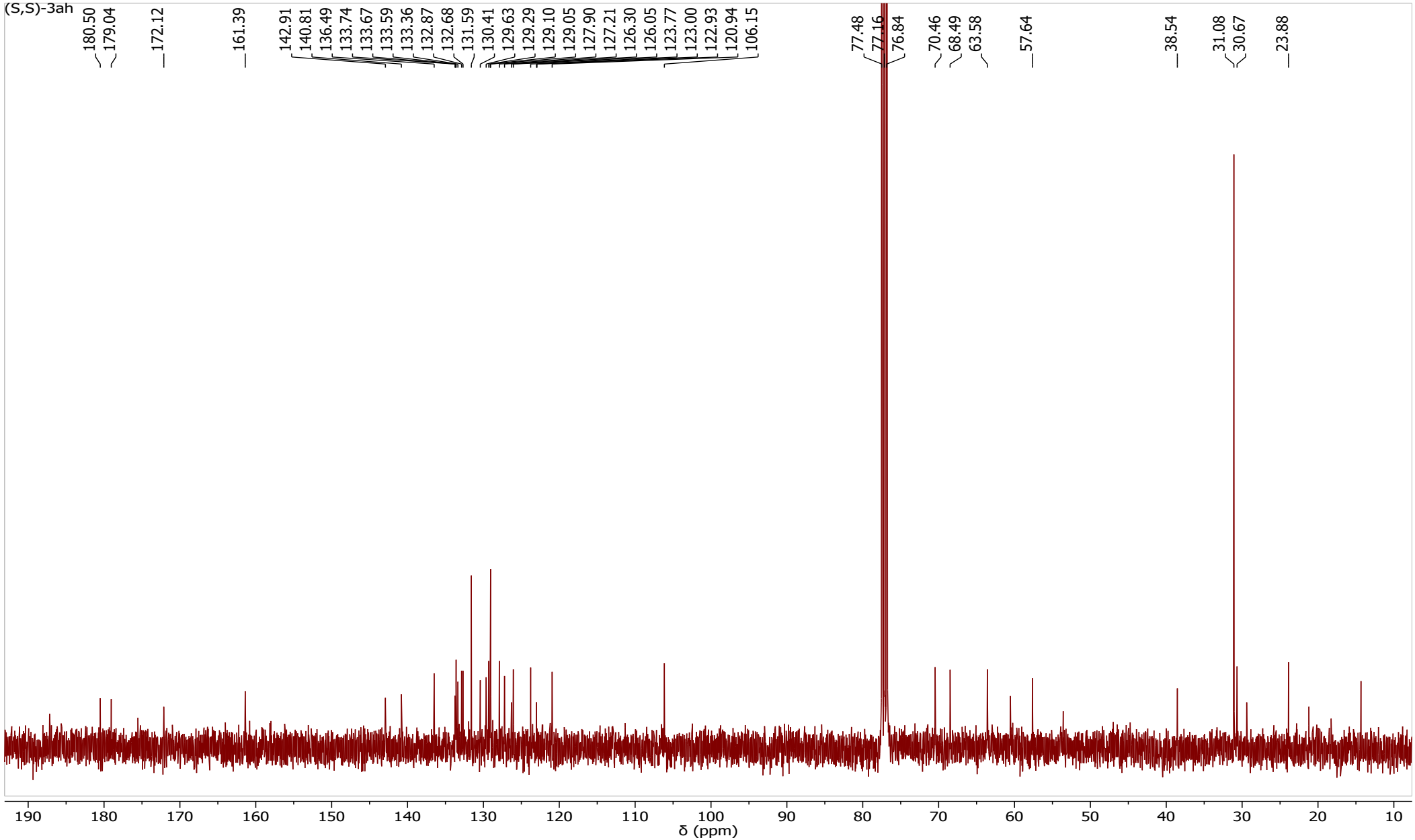

Figure S43. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ah** (in $CDCl_3$)

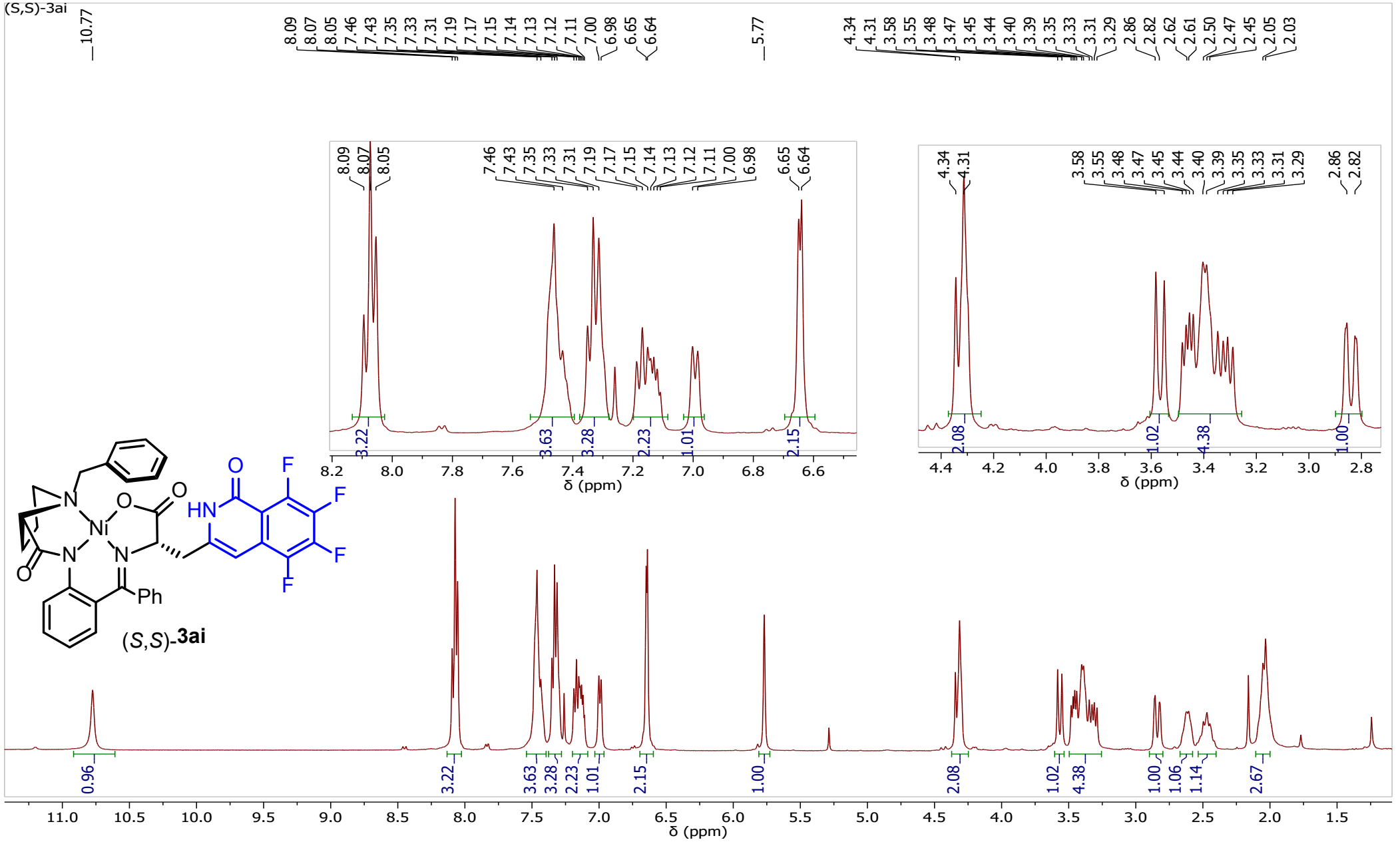

Figure S44. ^{1}H (400 MHz) NMR spectra of the Ni(II) complex (*S*,*S*)-**3ai** (in $CDCl_3$)

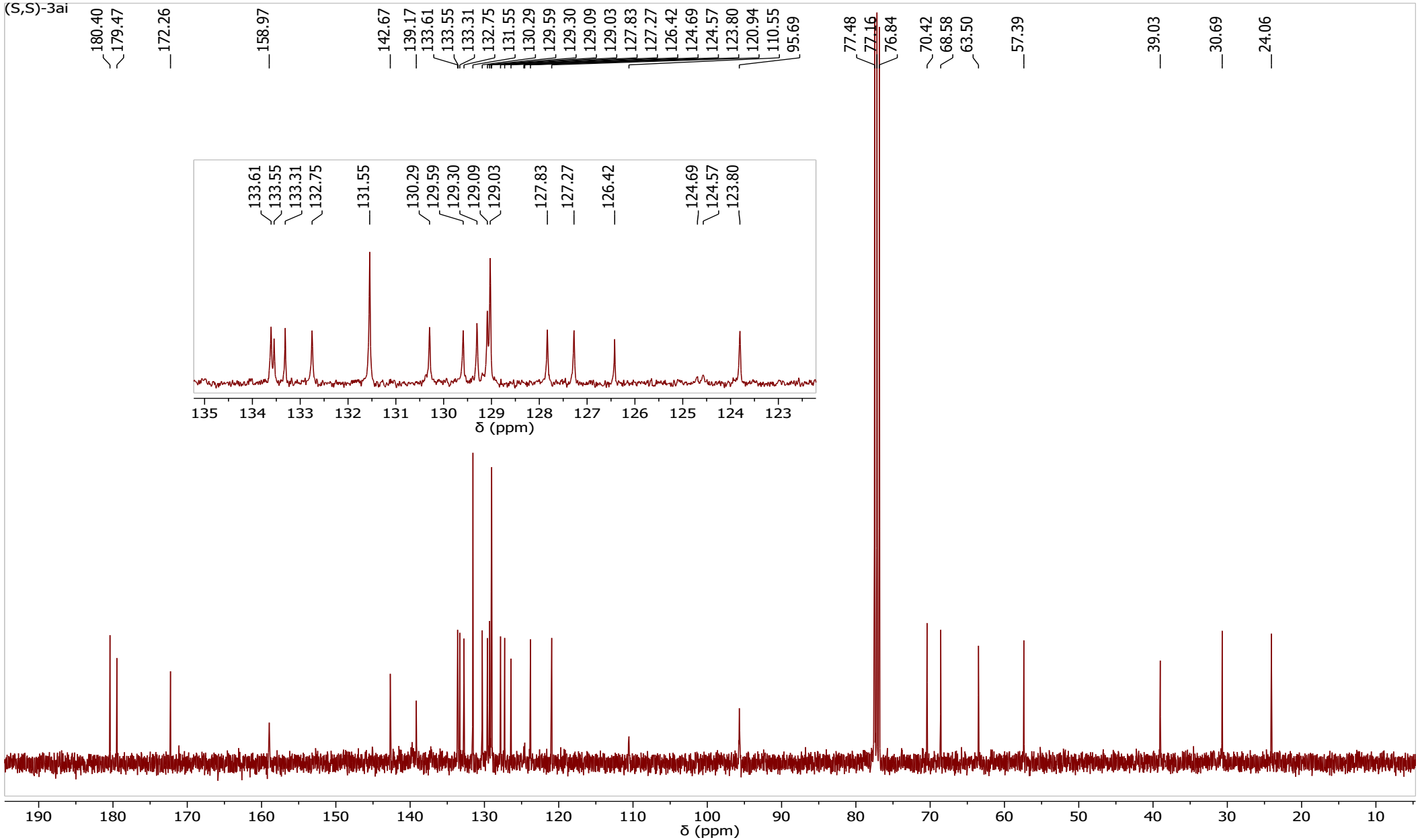

Figure S45. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ai** (in $CDCl_3$)

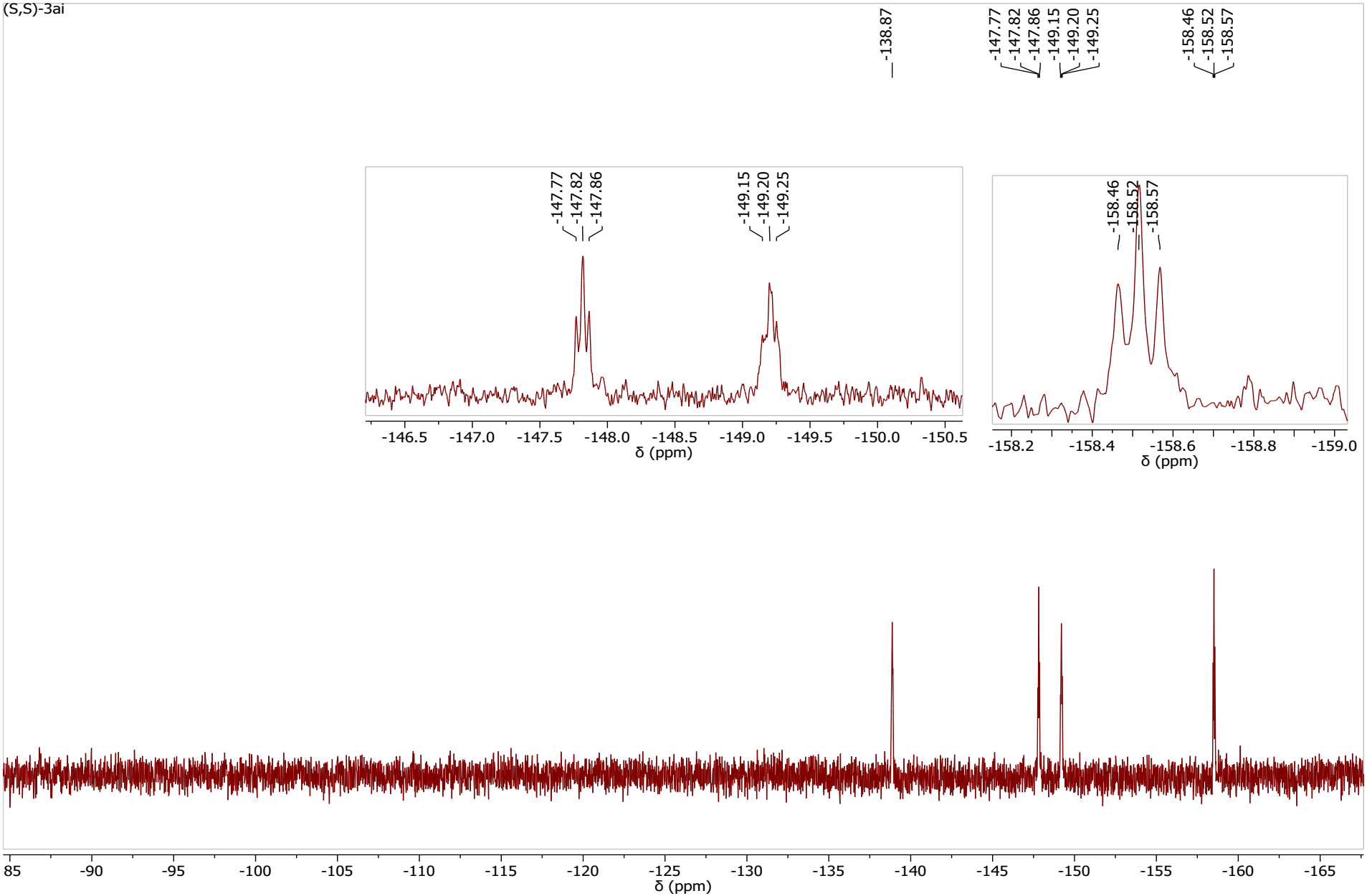

Figure S46. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ai** (in $CDCl_3$)

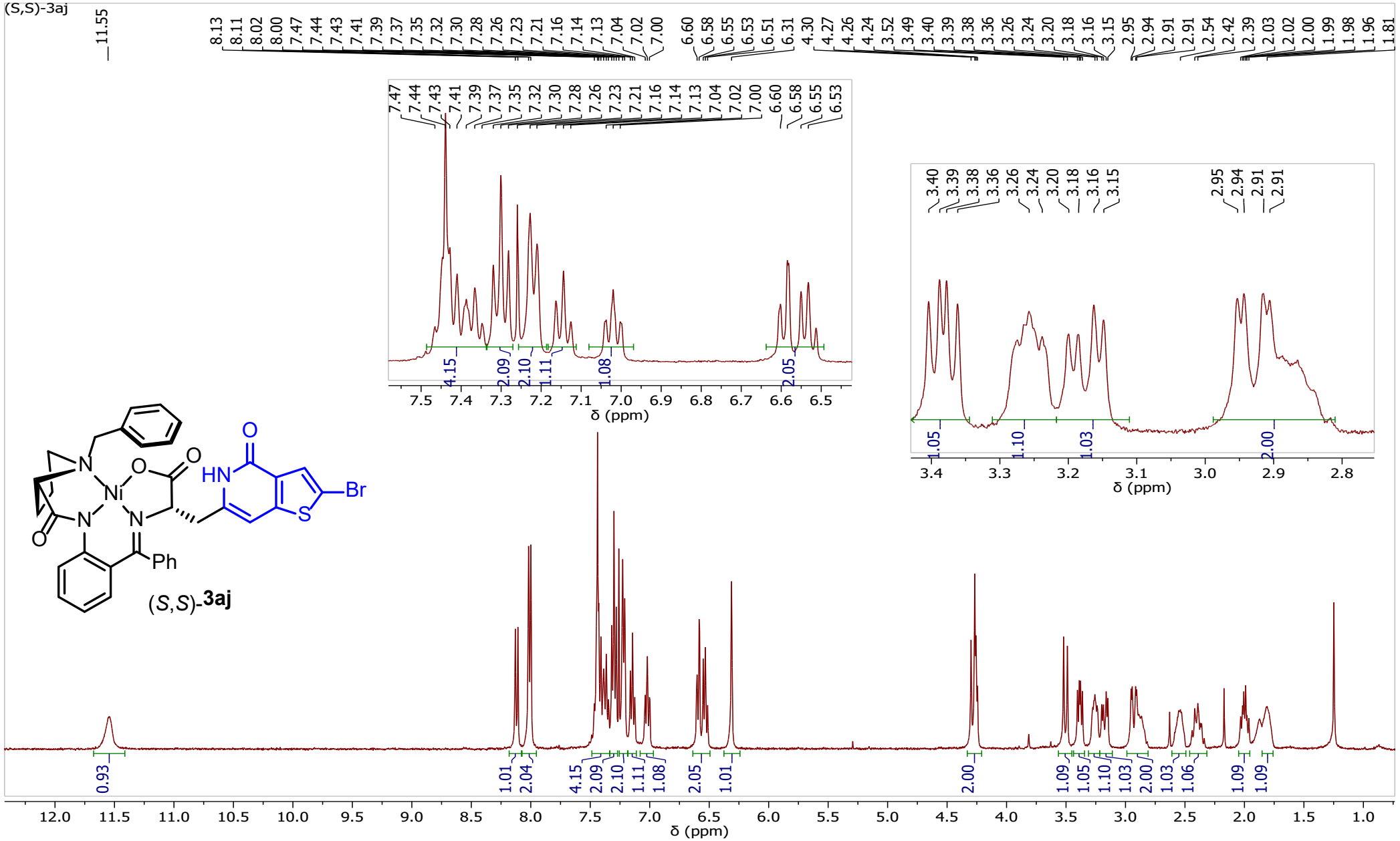

Figure S47. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3aj** (in $CDCl_3$)

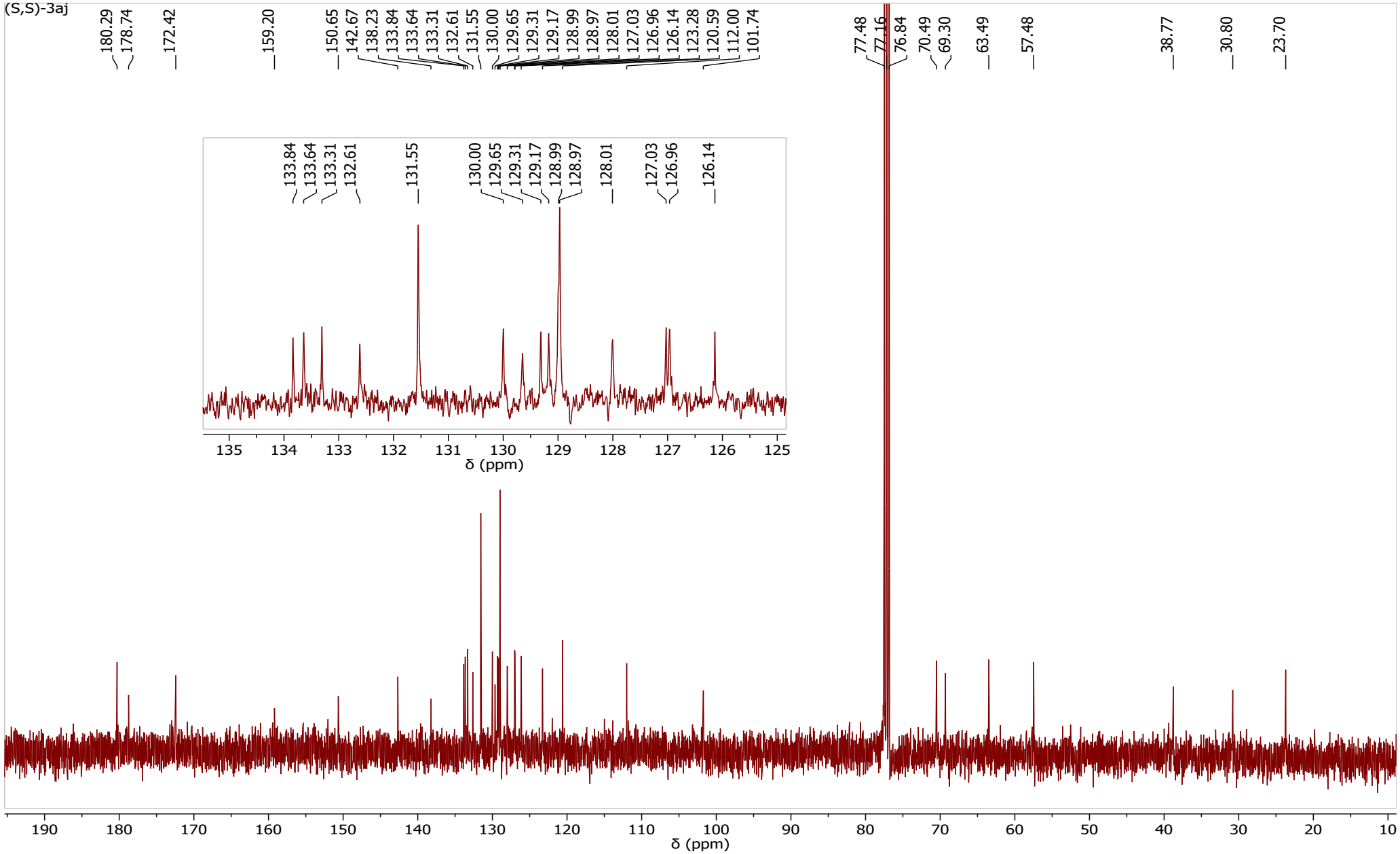

Figure S48. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3aj** (in $CDCl_3$)

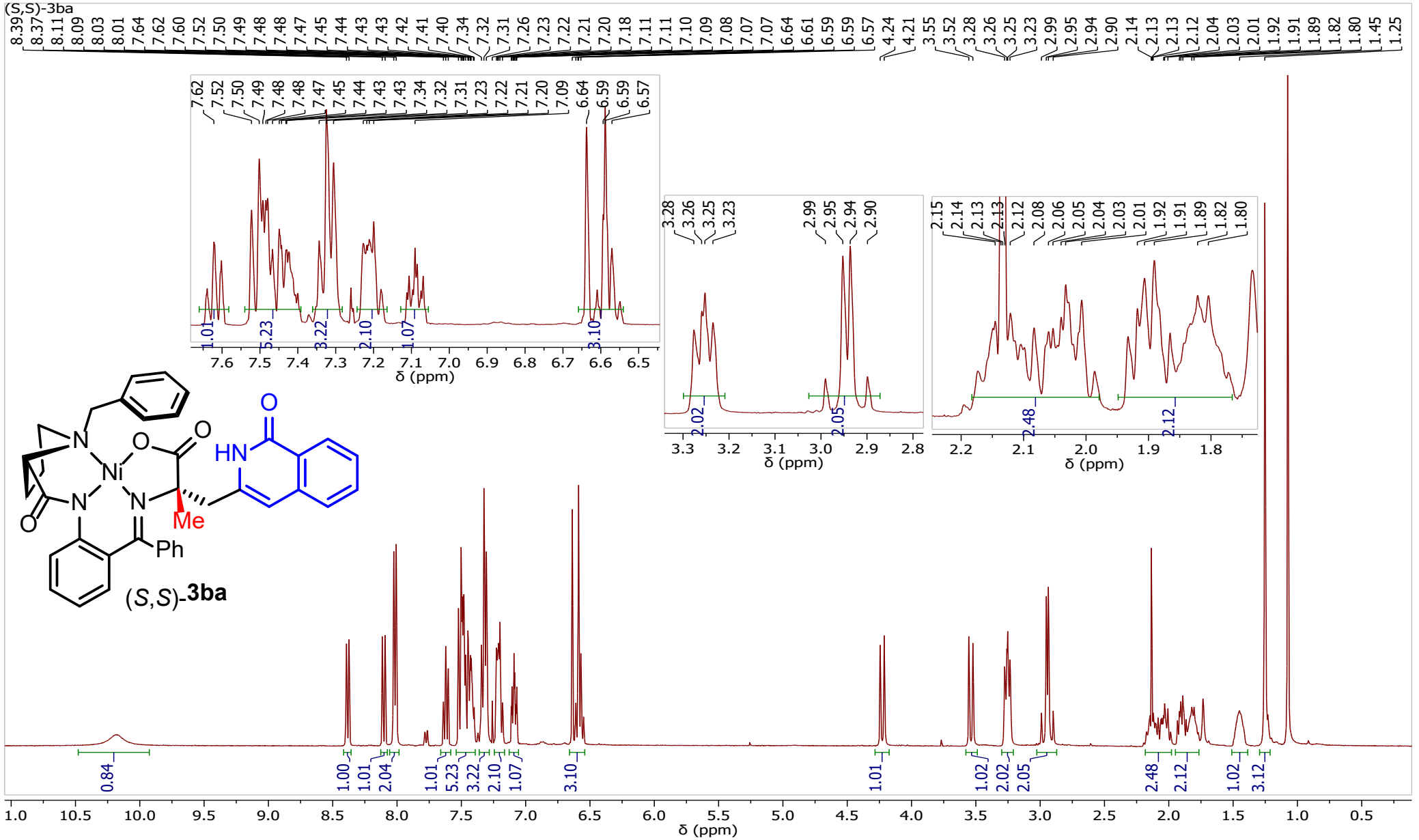

Figure S49. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ba** (in $CDCl_3$)

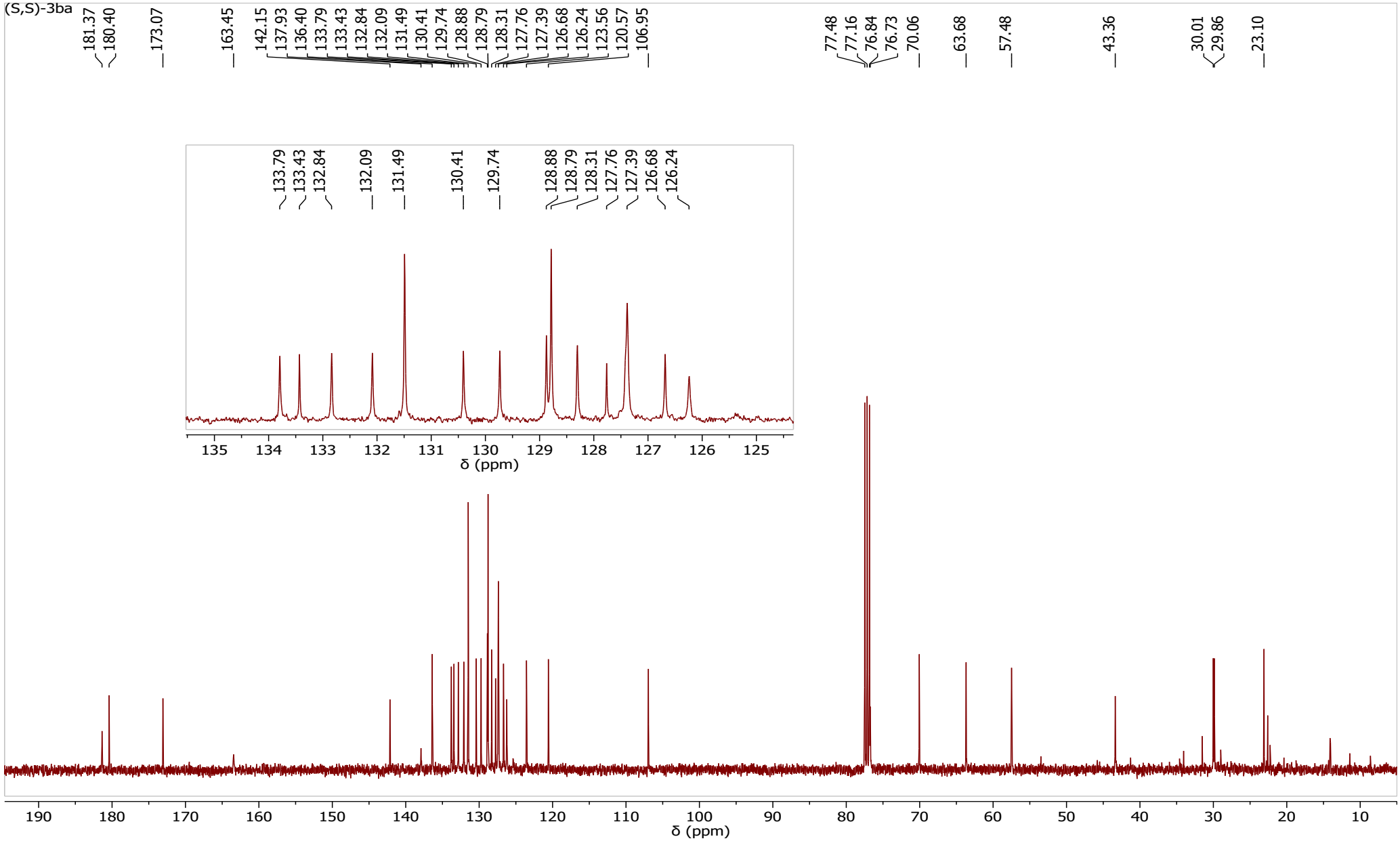

Figure S50. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ba** (in $CDCl_3$)

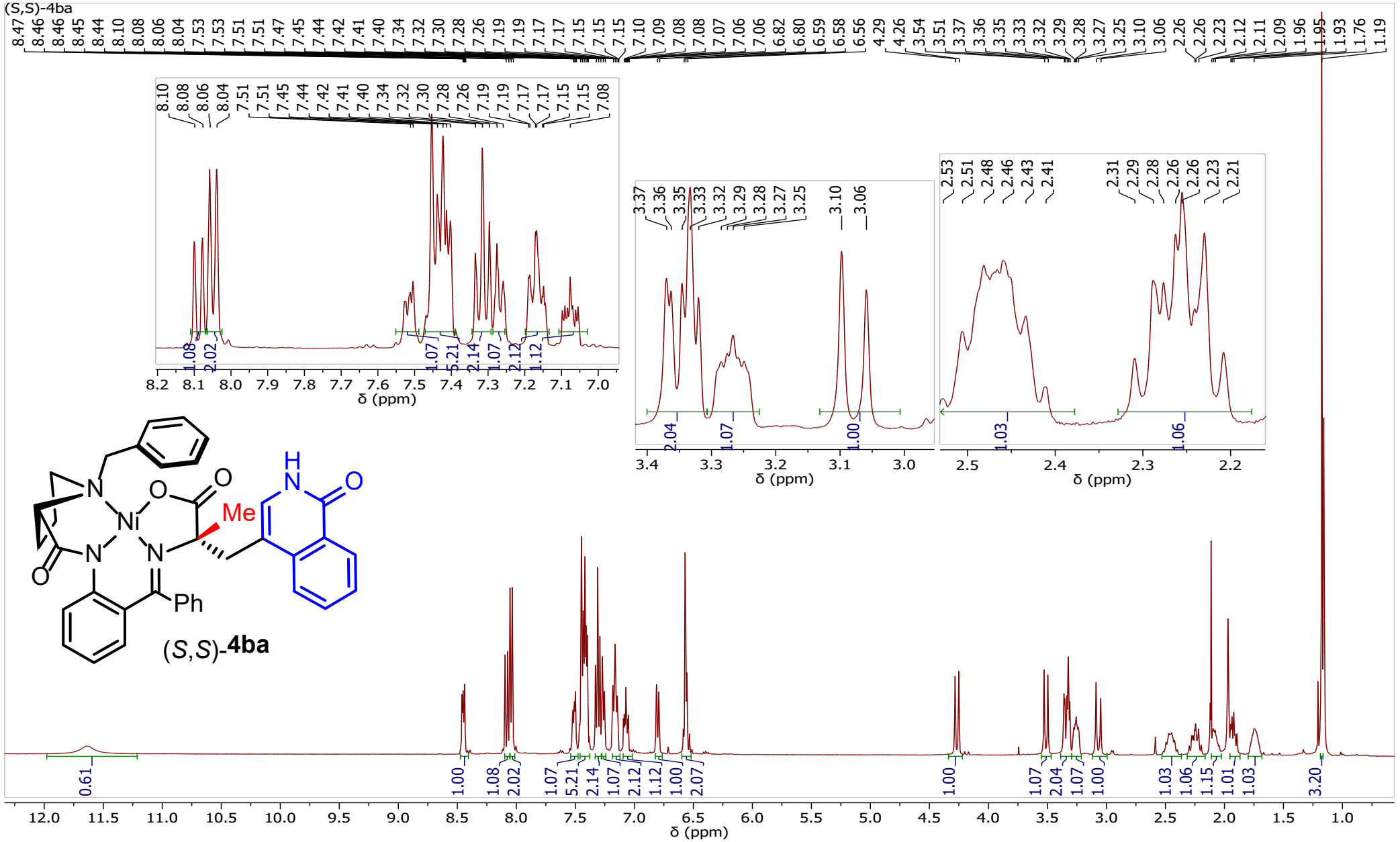

Figure S51. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4ba** (in $CDCl_3$)

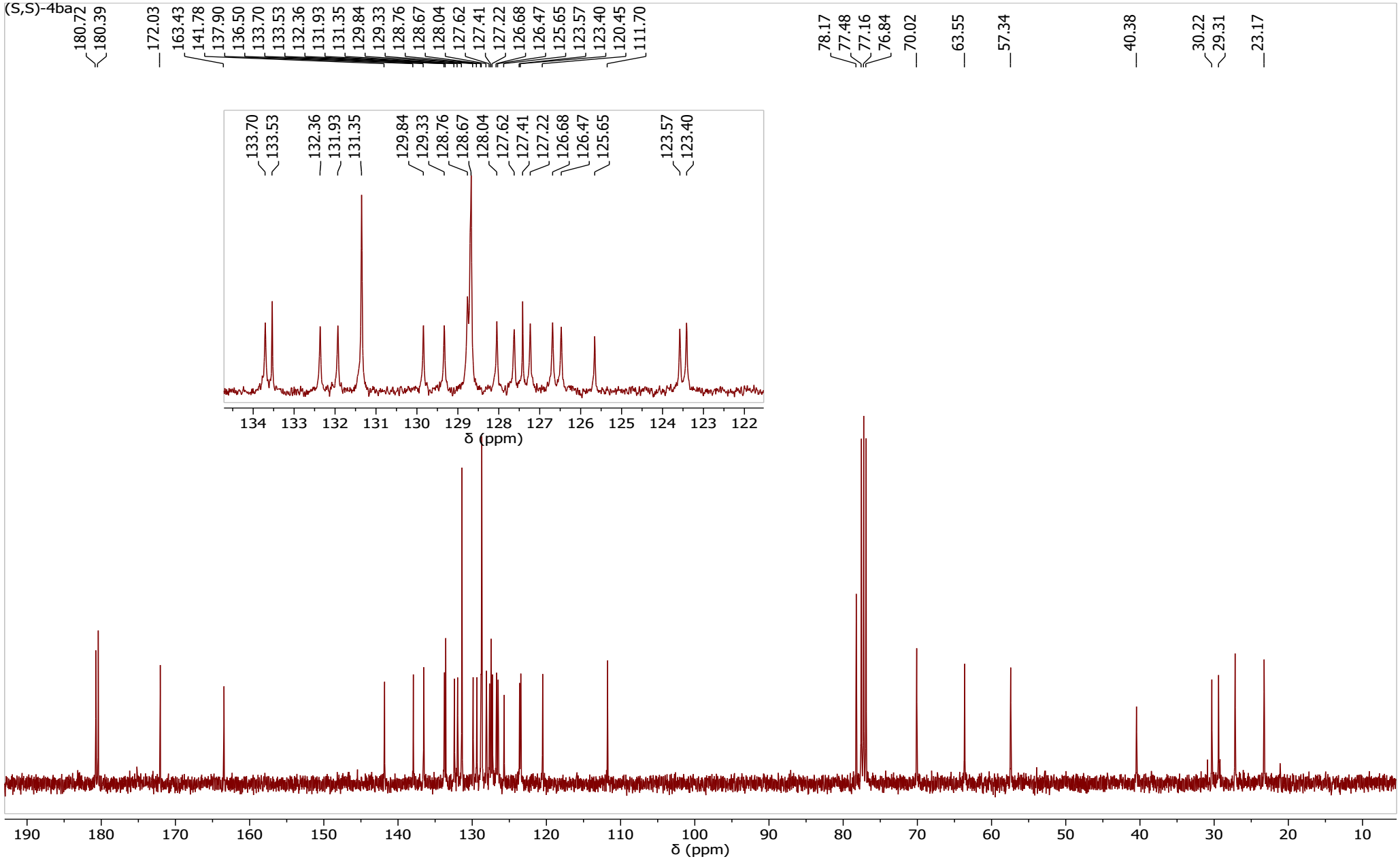

Figure S52. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4ba** (in $CDCl_3$)

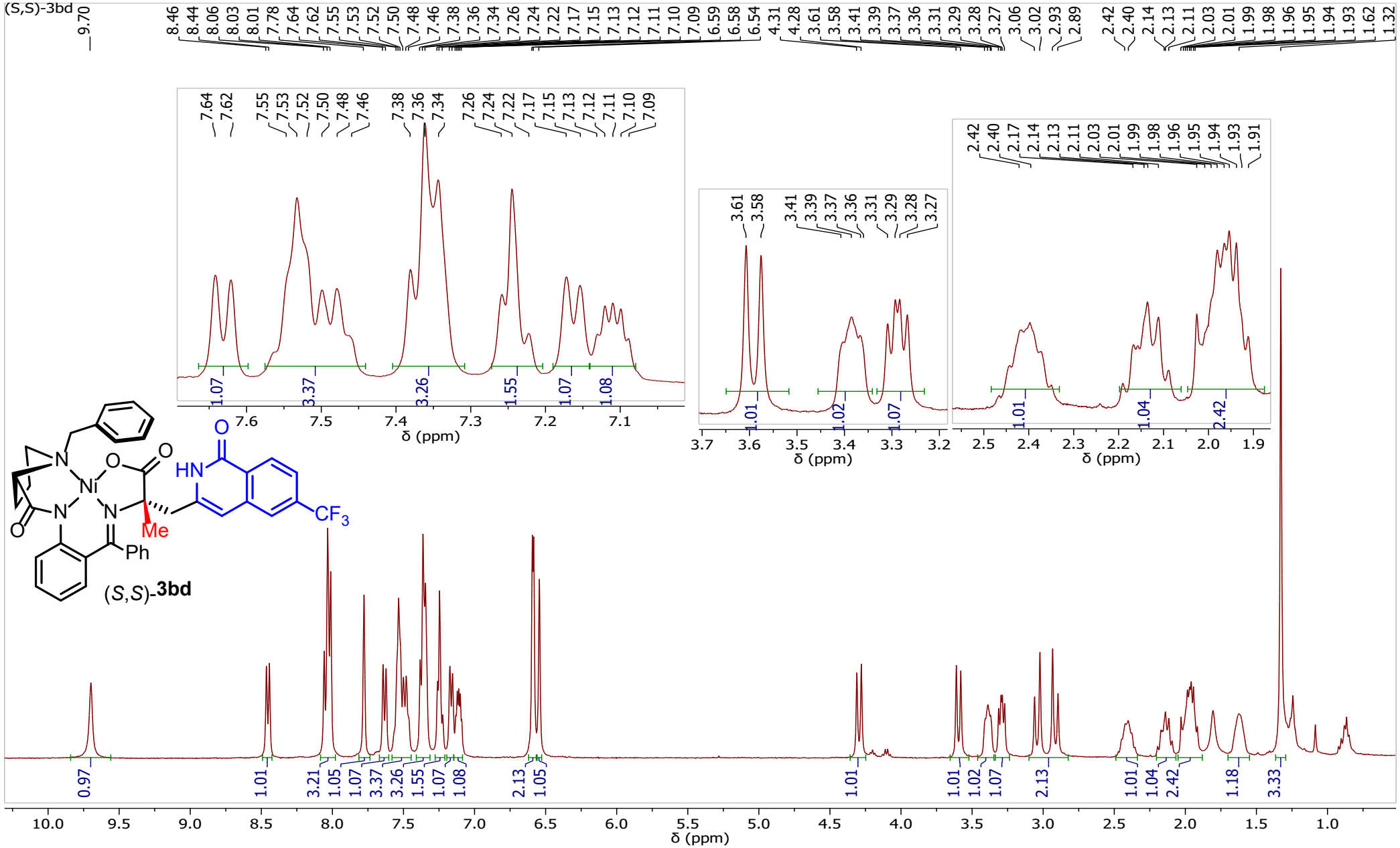

Figure S53. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3bd** (in $CDCl_3$)

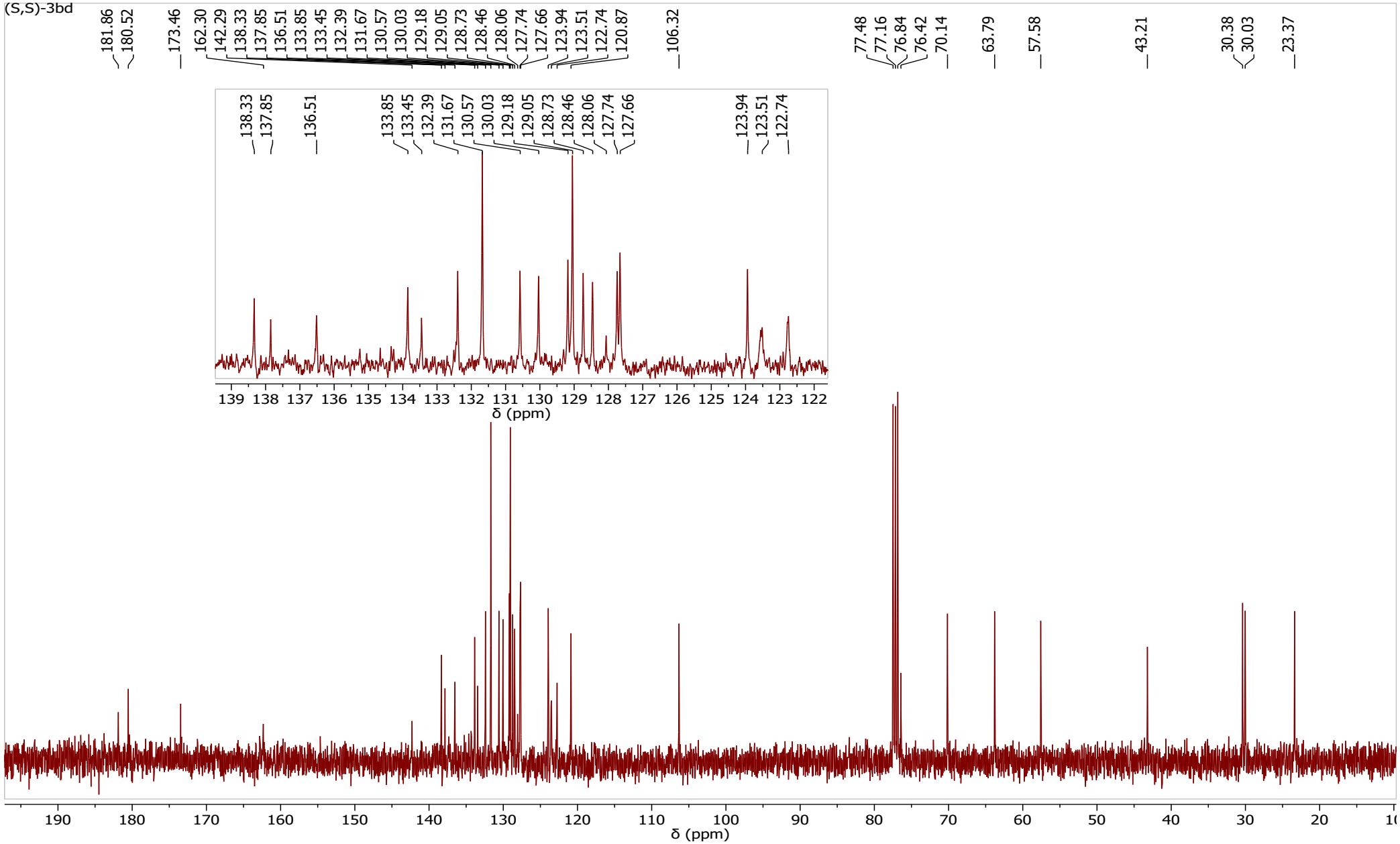

Figure S54. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3bd** (in $CDCl_3$)

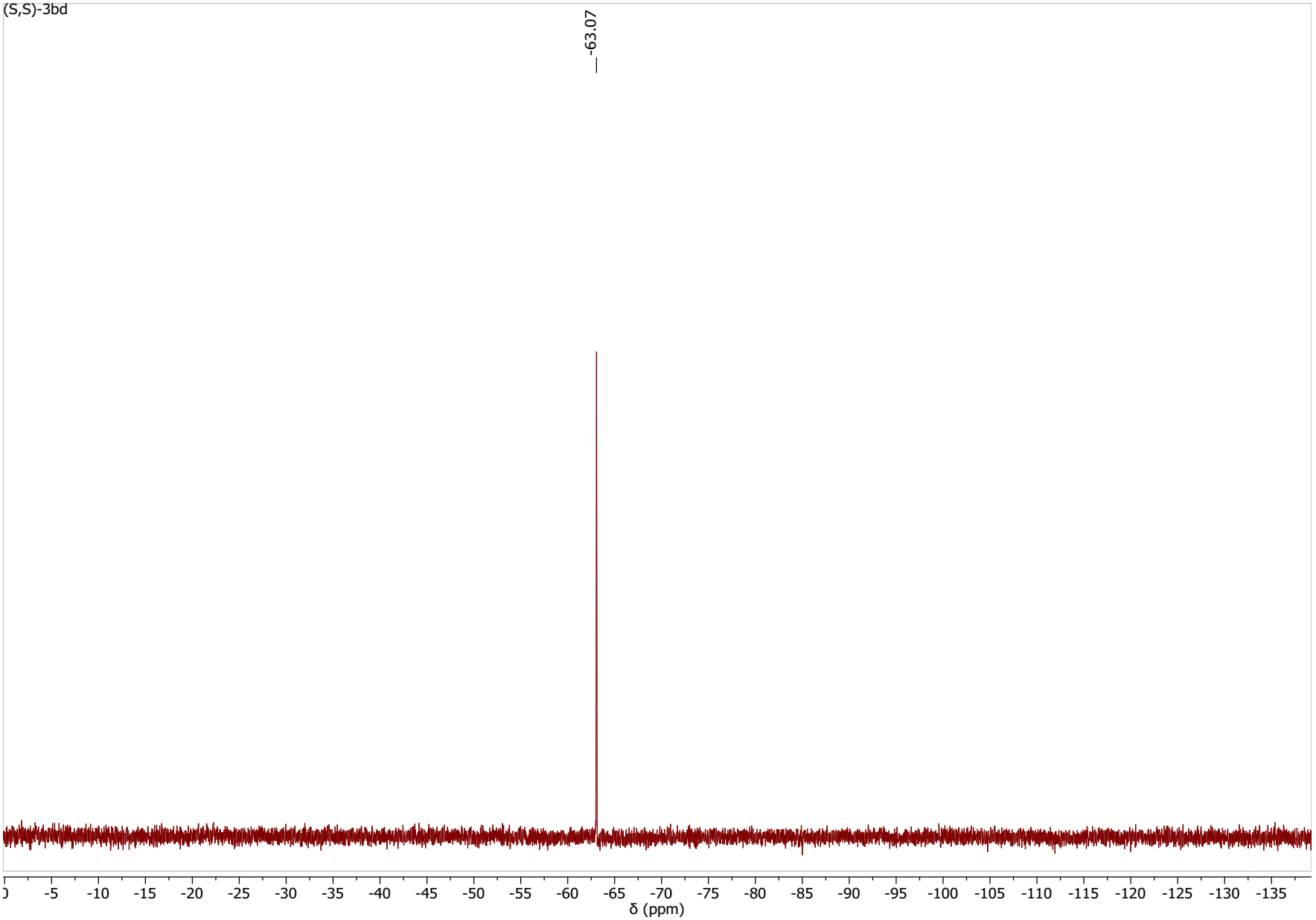

Figure S55. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3bd** (in $CDCl_3$)

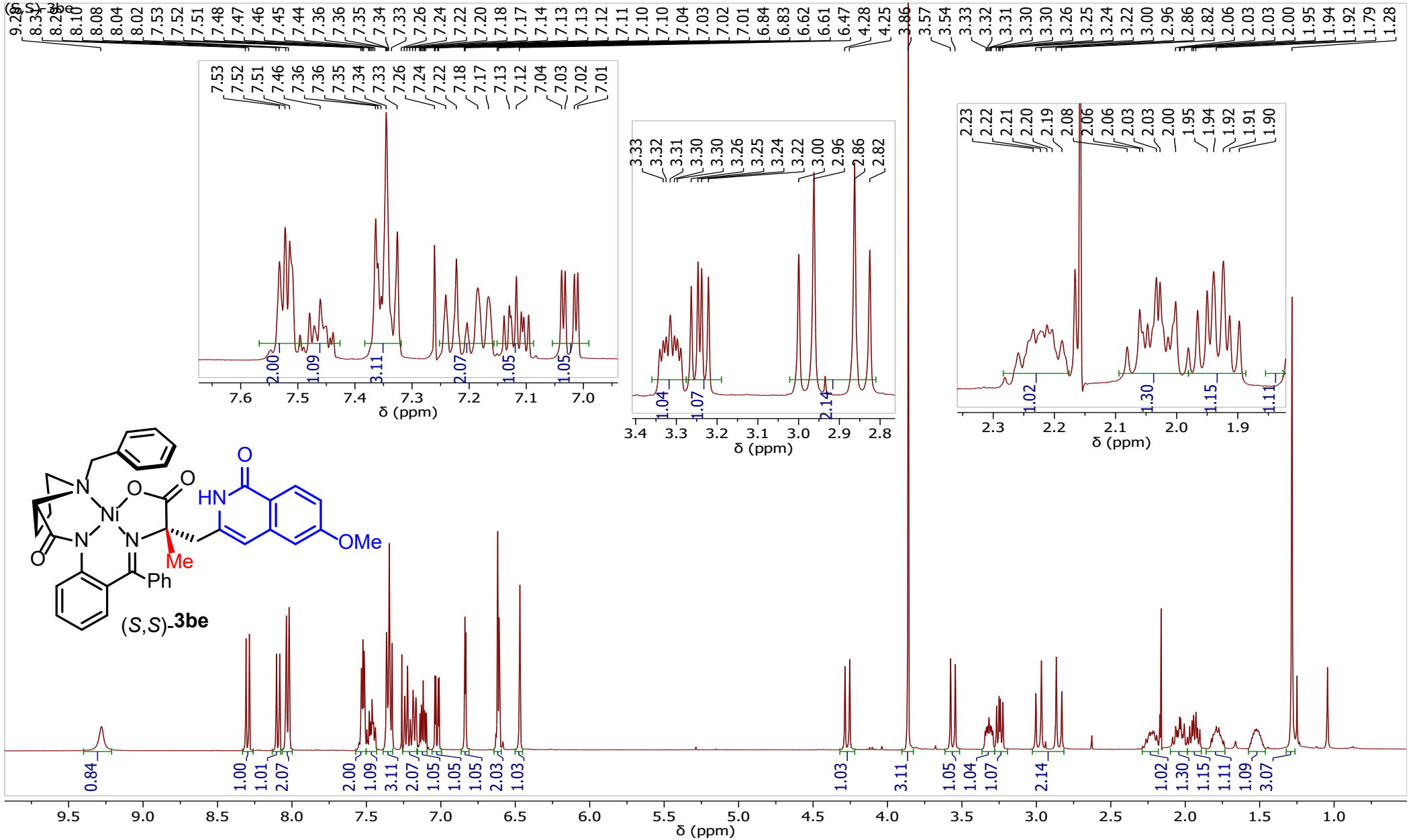

Figure S56. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3be** (in $CDCl_3$)

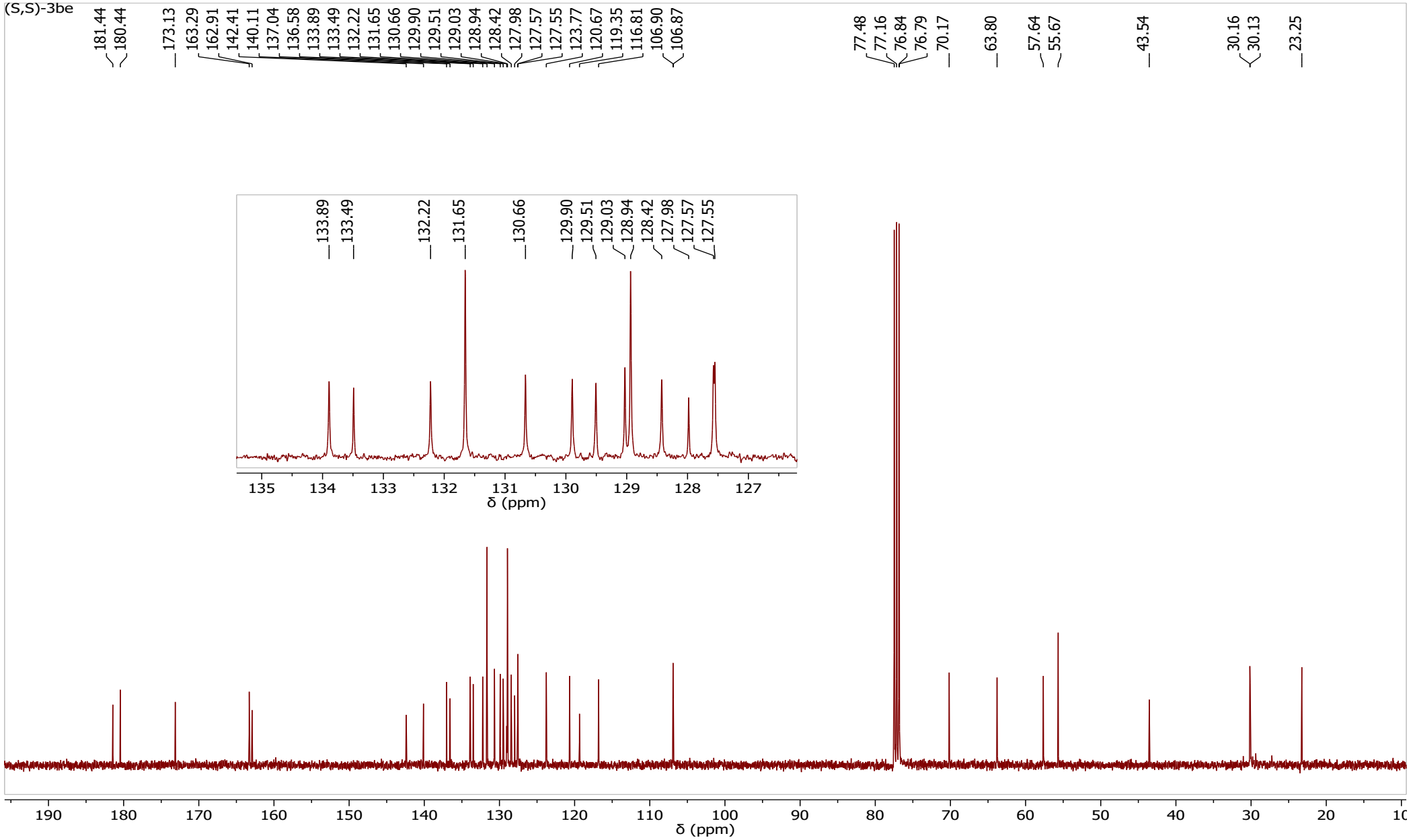

Figure S57. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3be** (in $CDCl_3$)

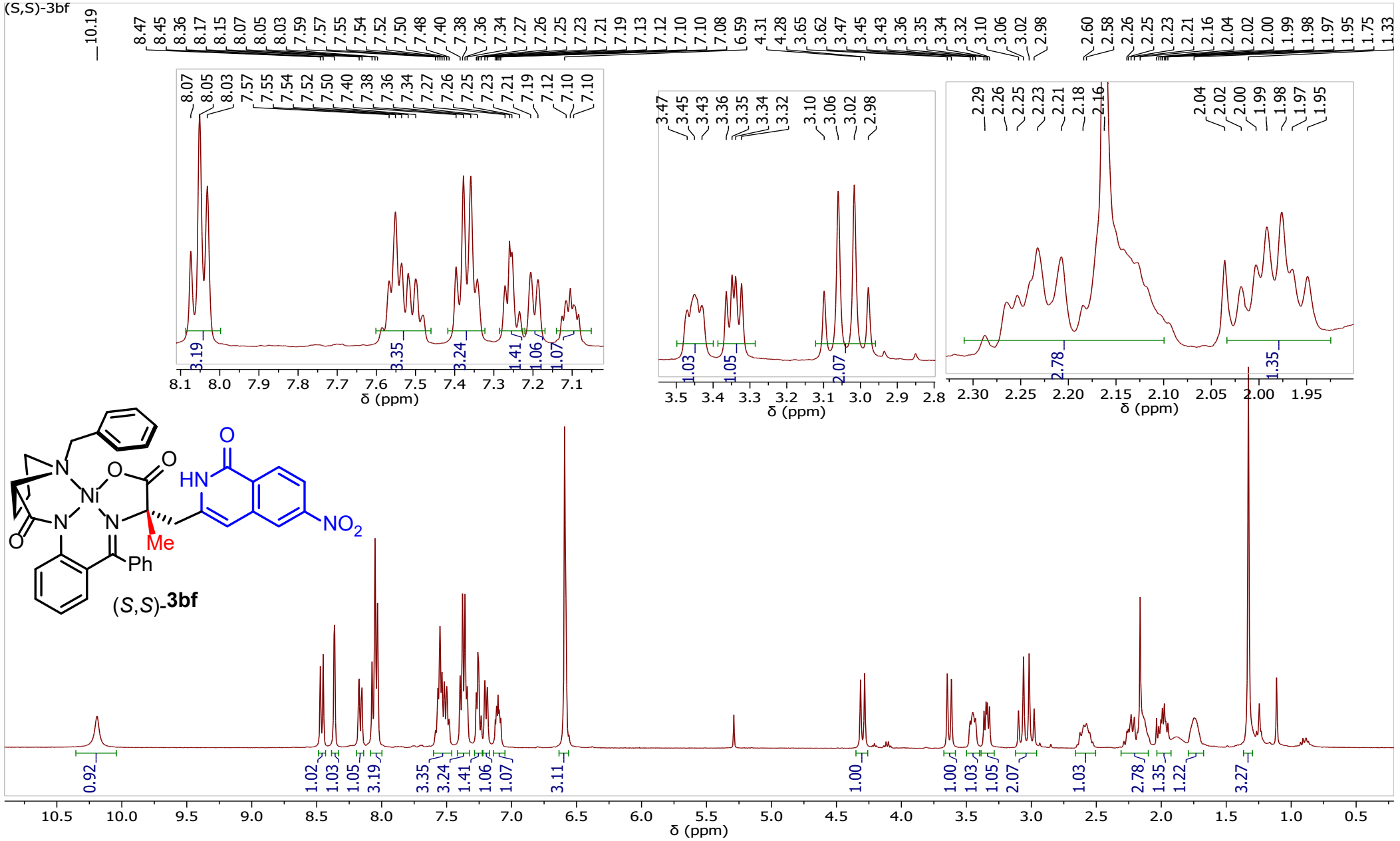

Figure S58. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3bf** (in $CDCl_3$)

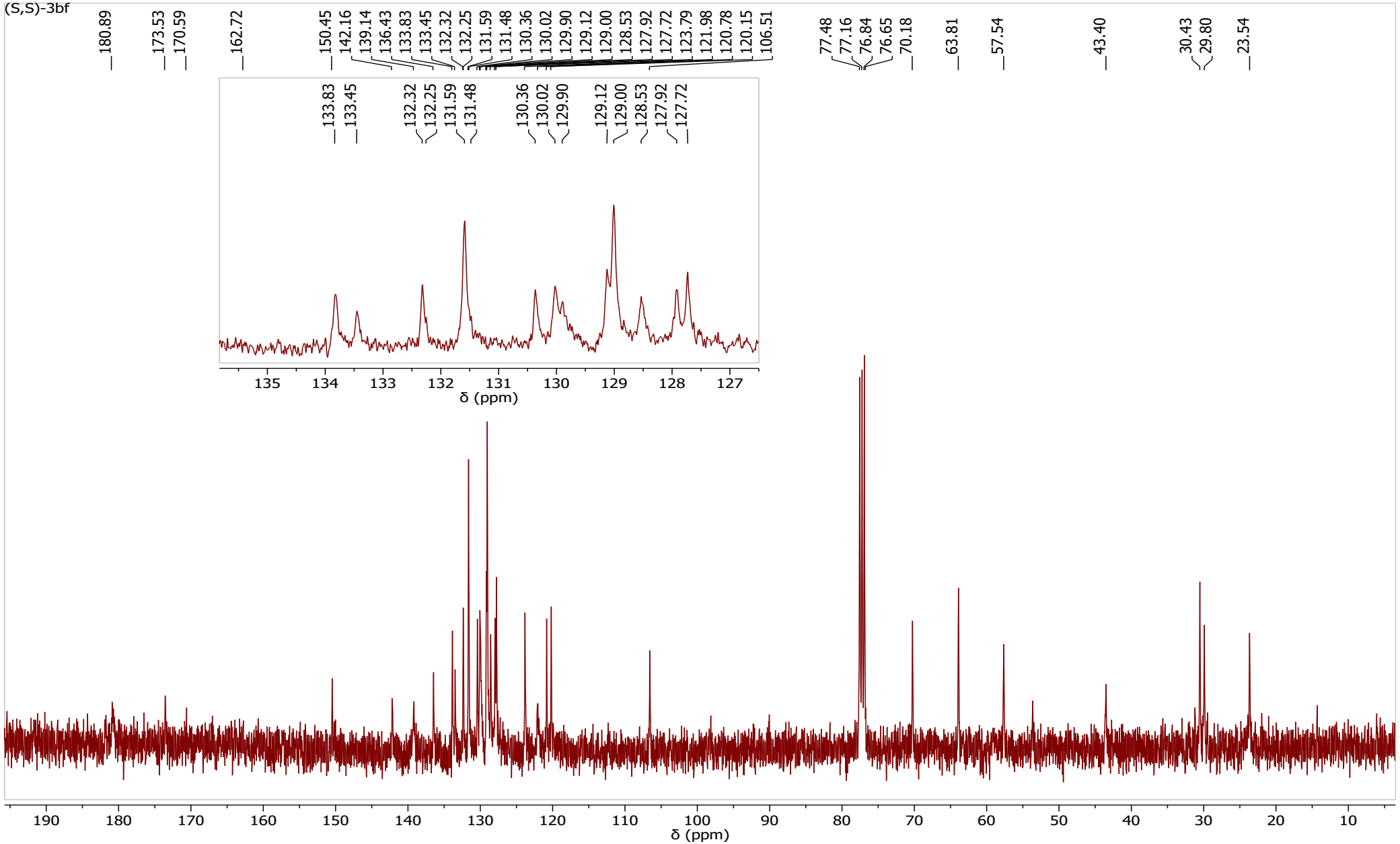

Figure S59. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3bf** (in $CDCl_3$)

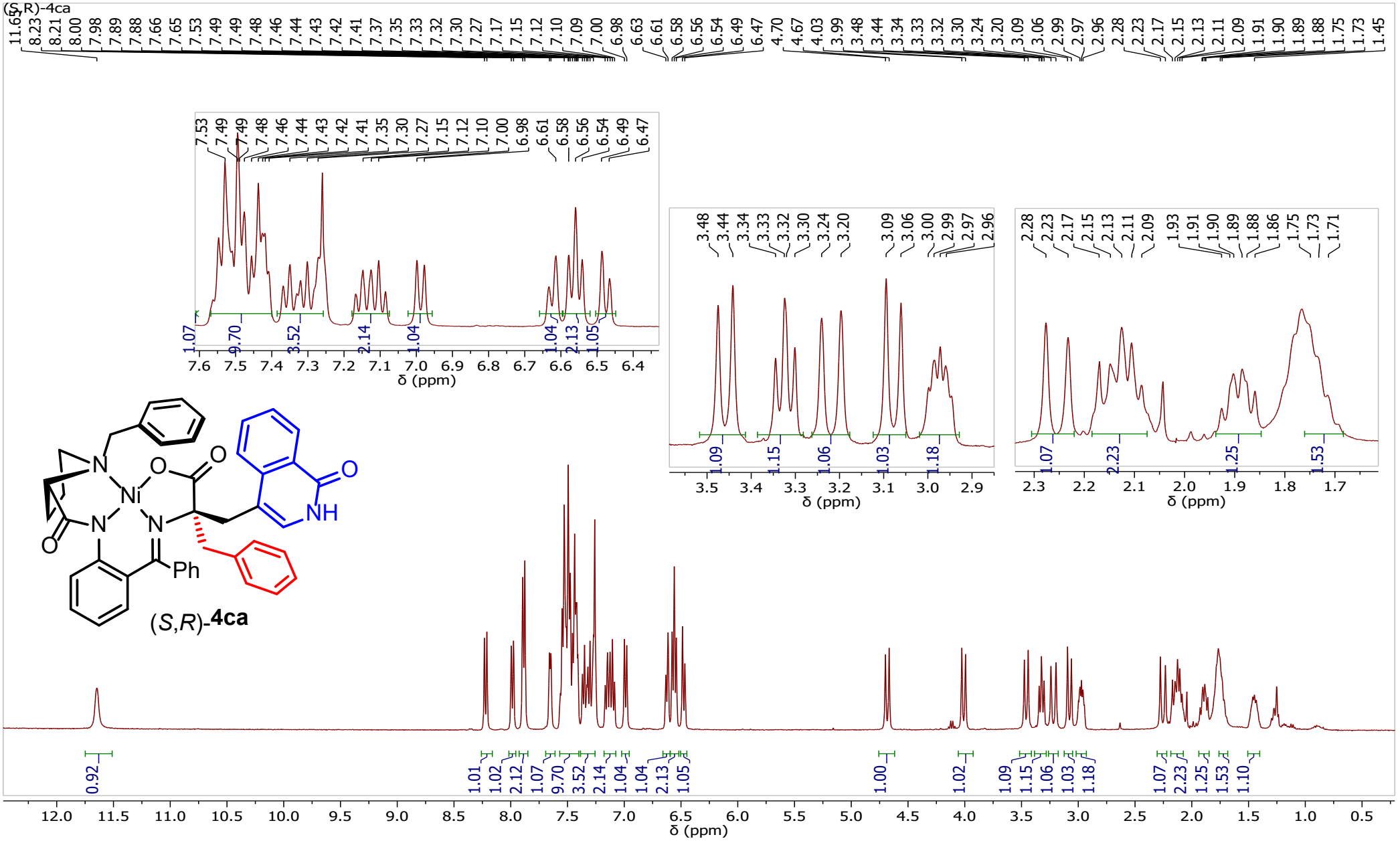

Figure S60. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ca** (in $CDCl_3$)

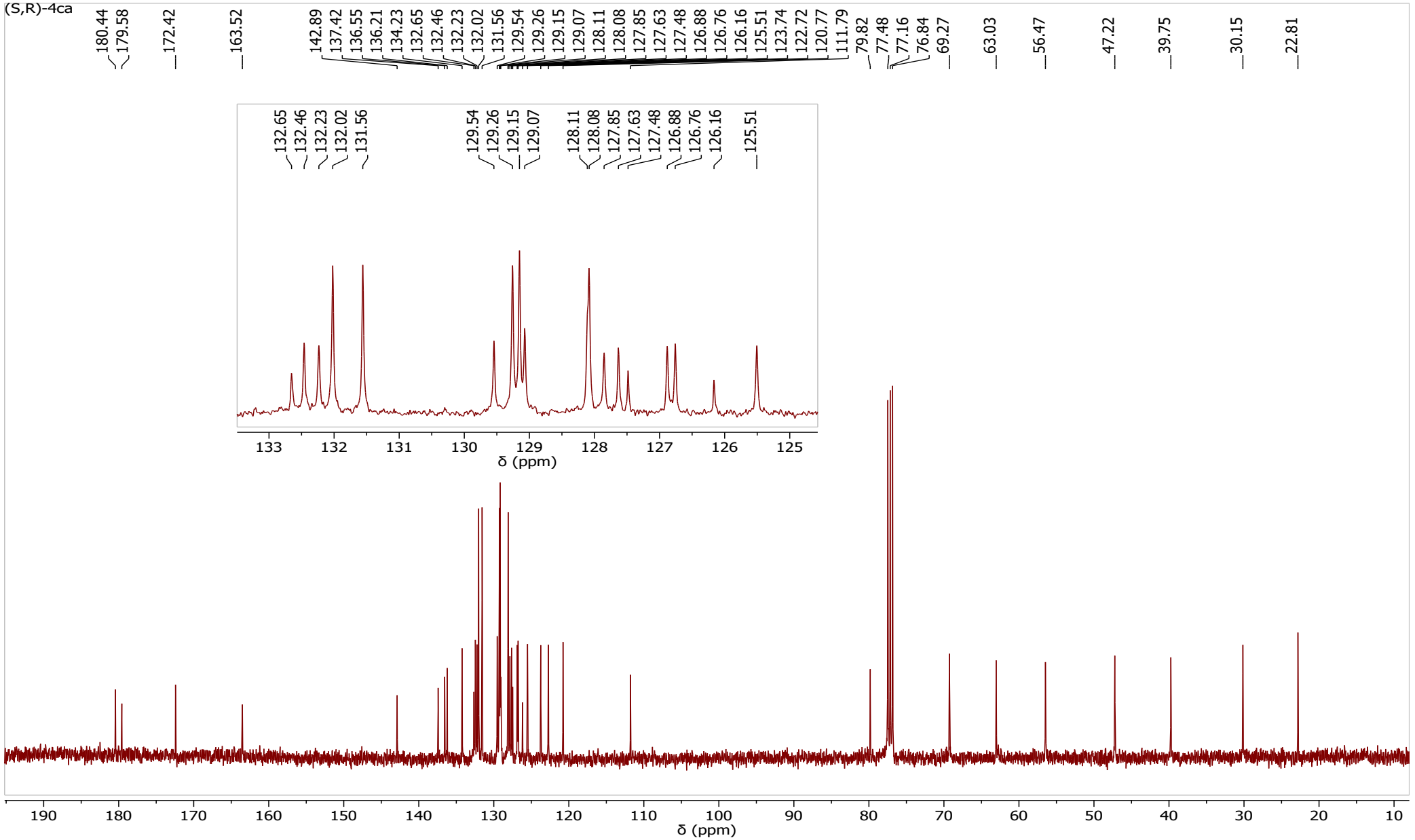

Figure S61. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ca** (in $CDCl_3$)

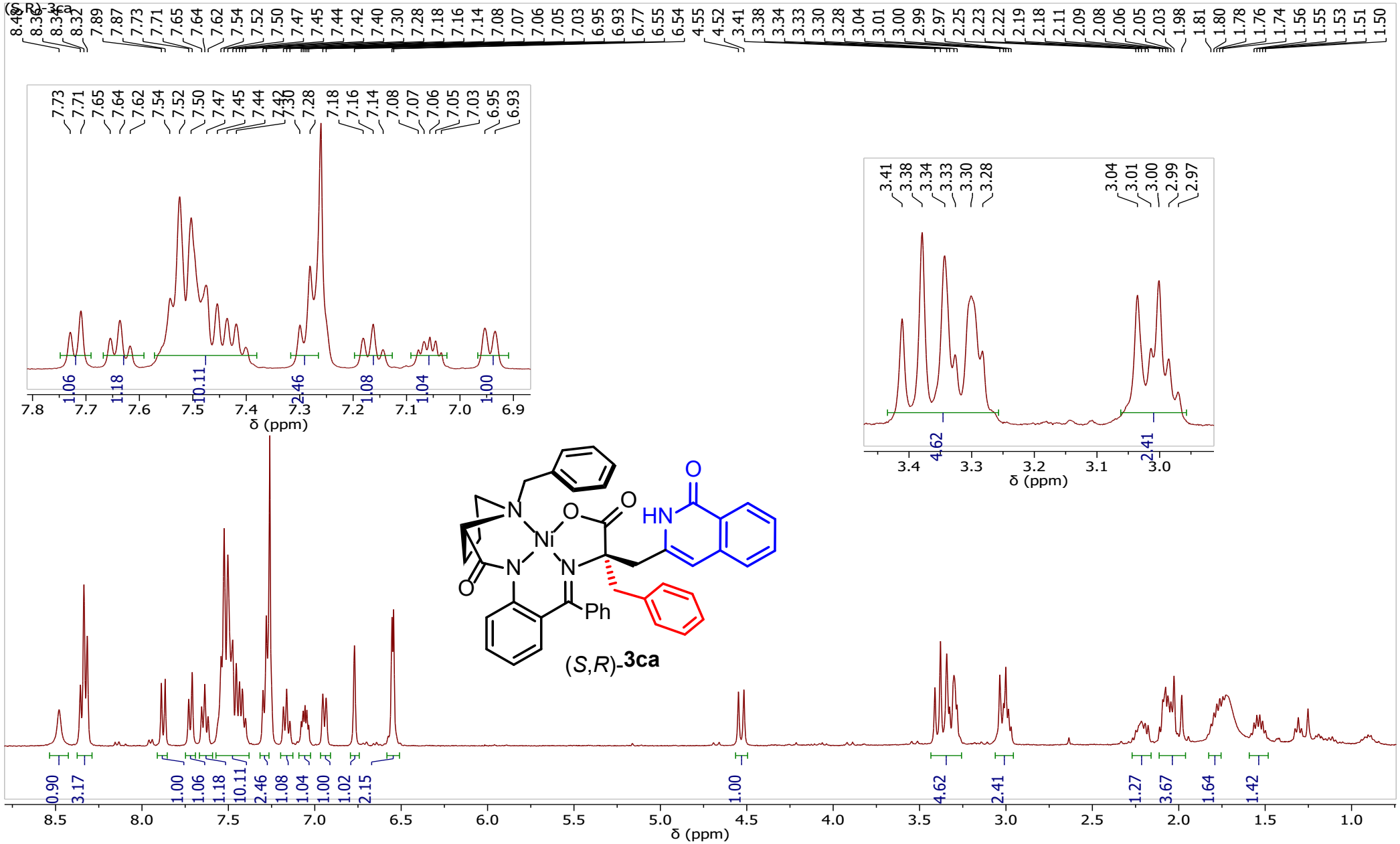

Figure S62. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ca** (in $CDCl_3$)

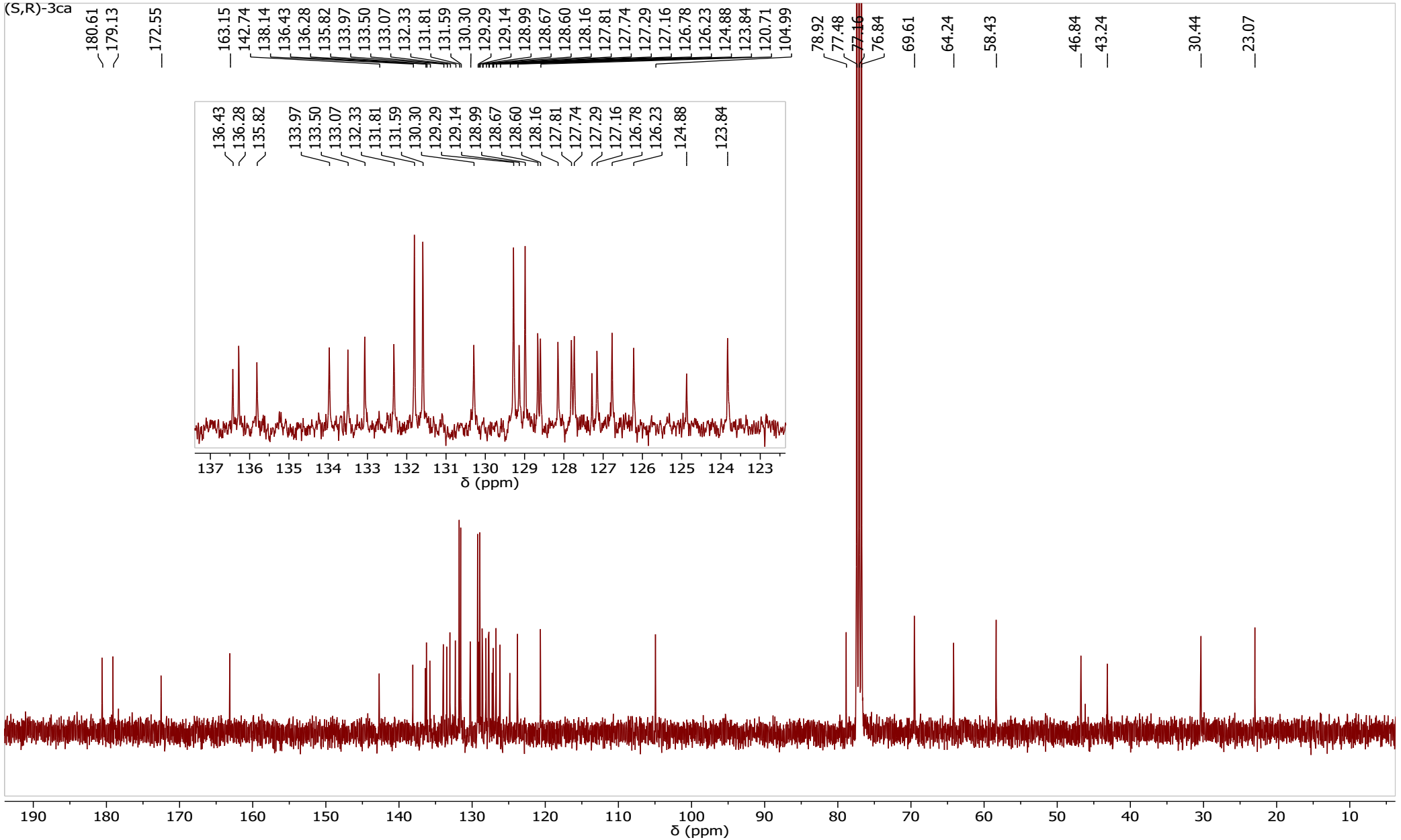

Figure S63. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ca** (in $CDCl_3$)

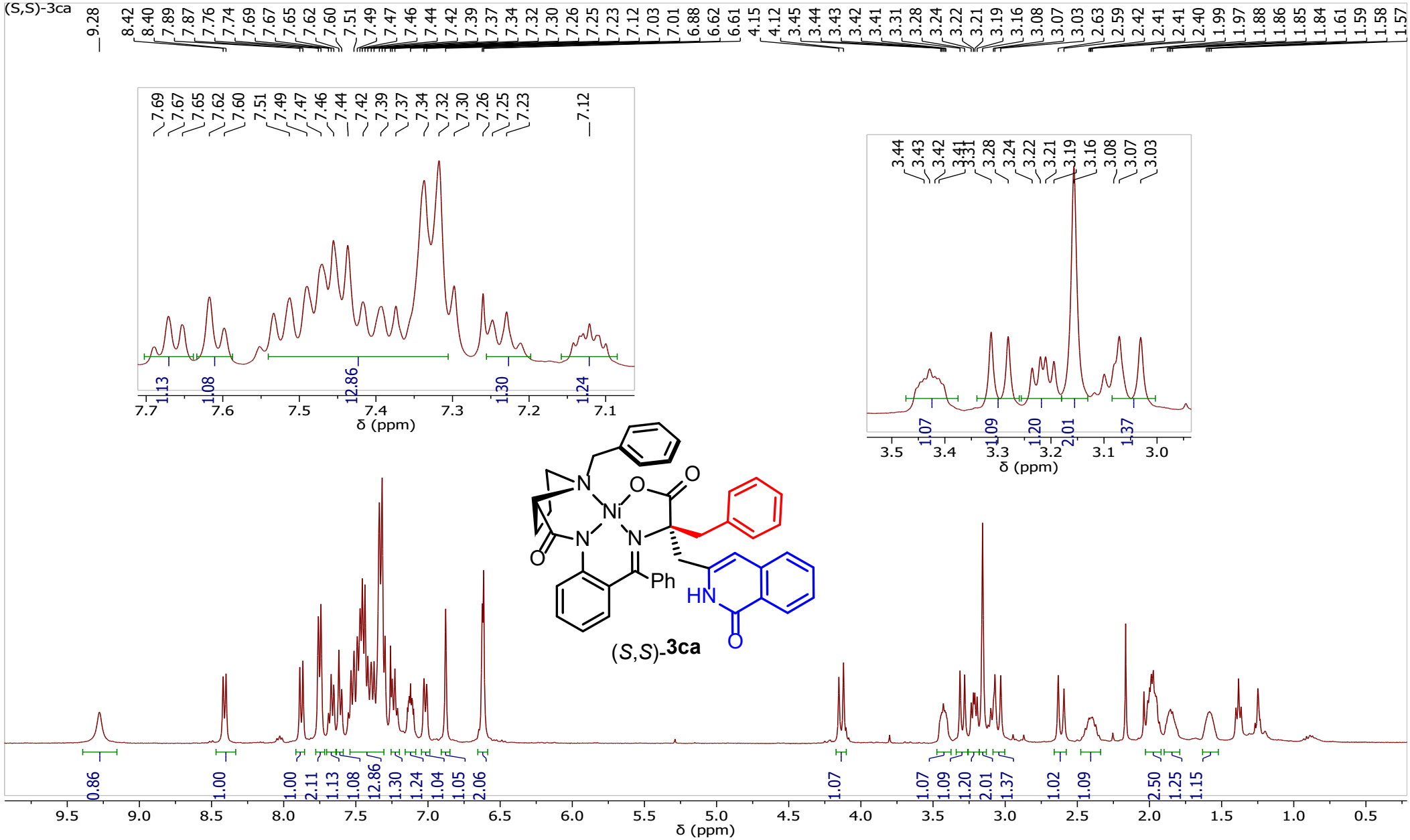

Figure S64. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ca** (in $CDCl_3$)

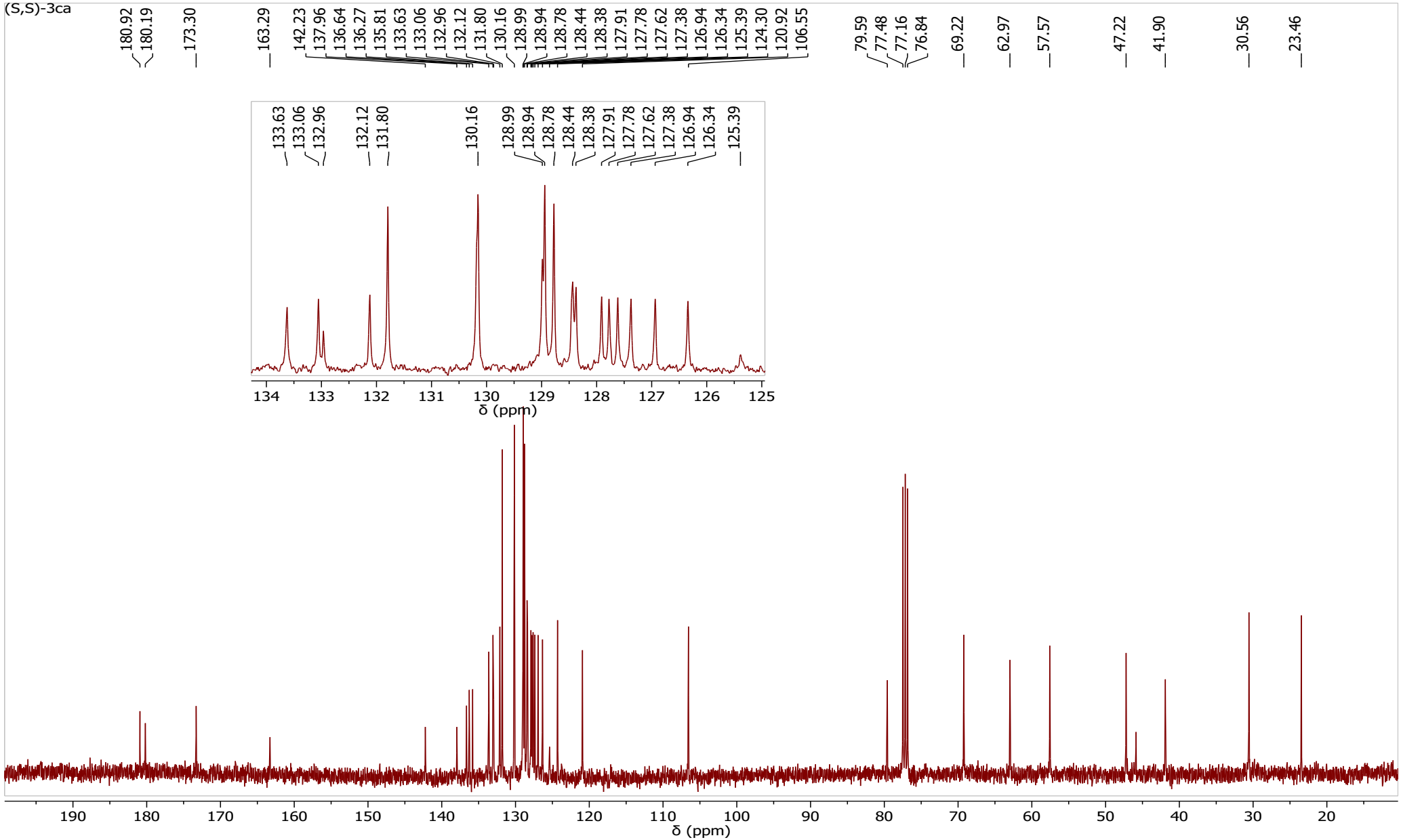

Figure S65. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ca** (in $CDCl_3$)

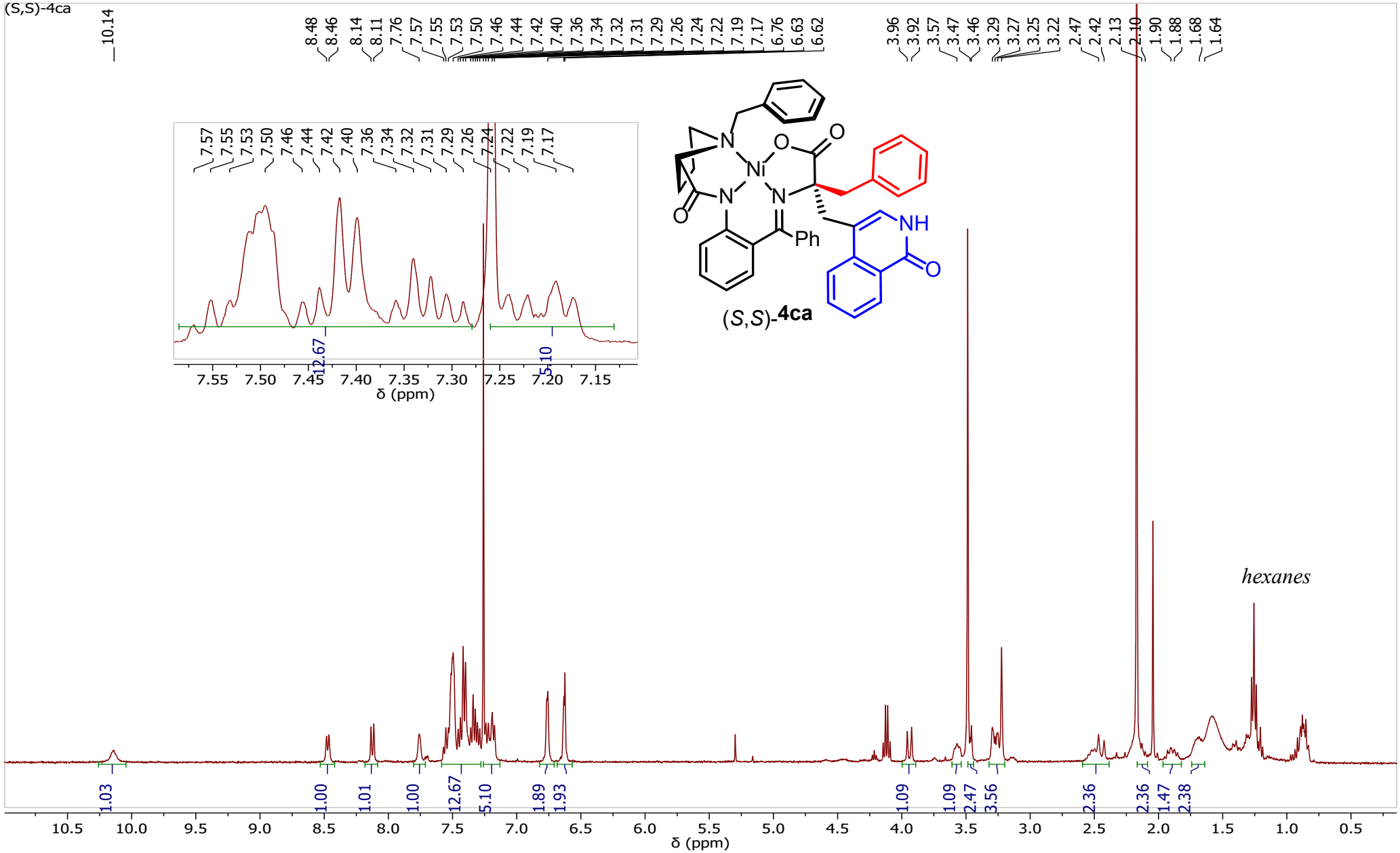

Figure S66. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4ca** (in $CDCl_3$)

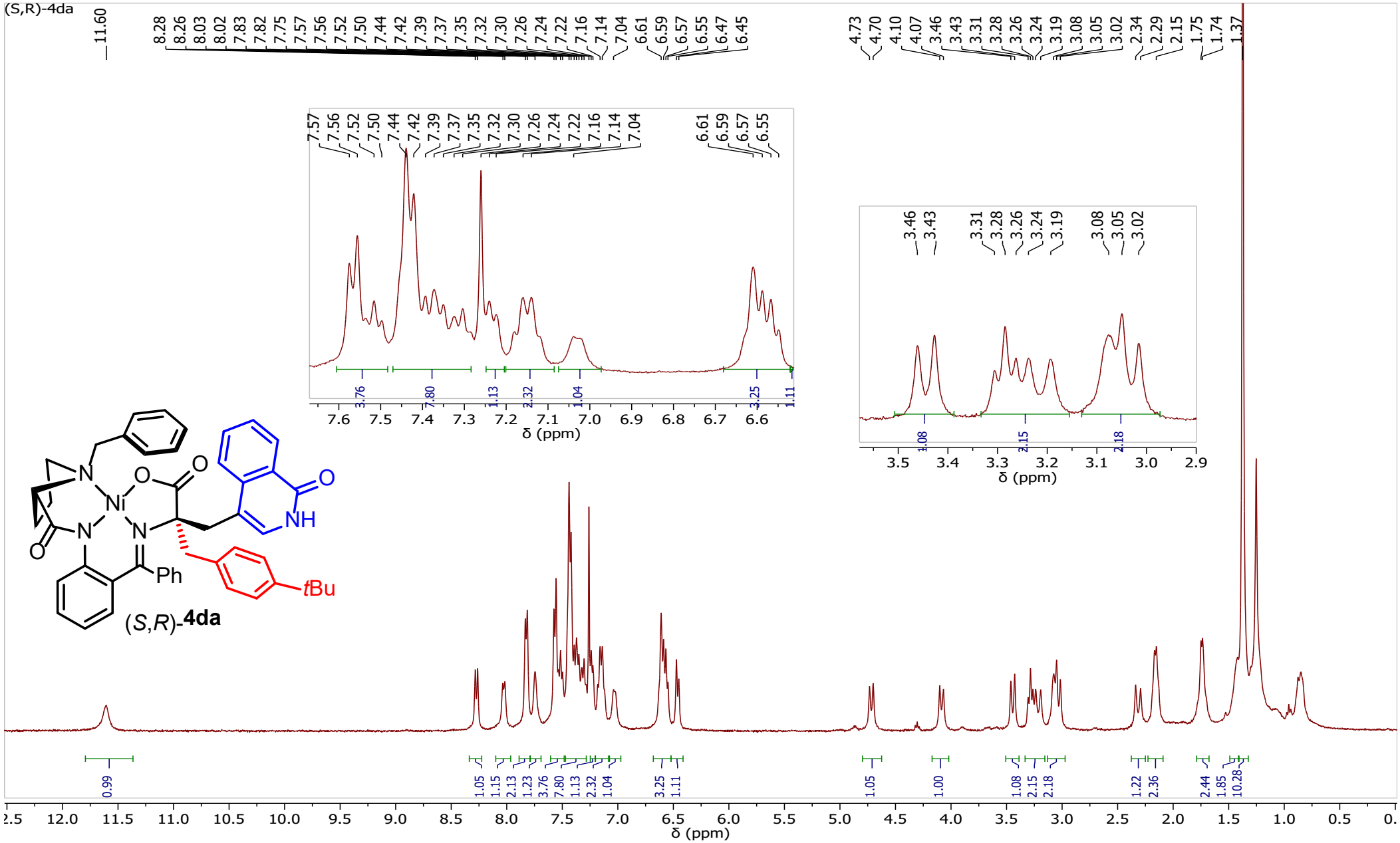

Figure S67. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4da** (in $CDCl_3$)

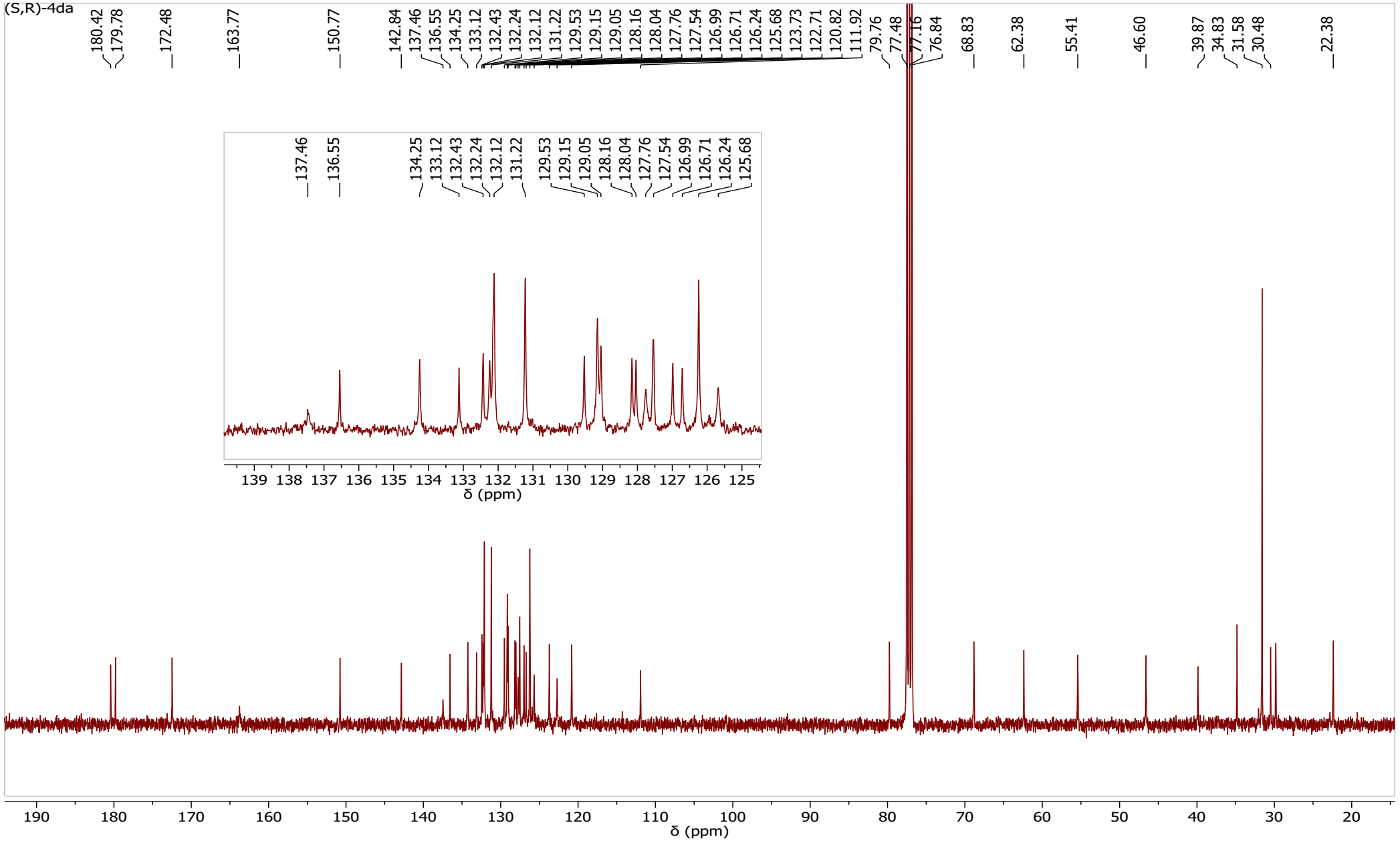

Figure S68. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4da** (in $CDCl_3$)

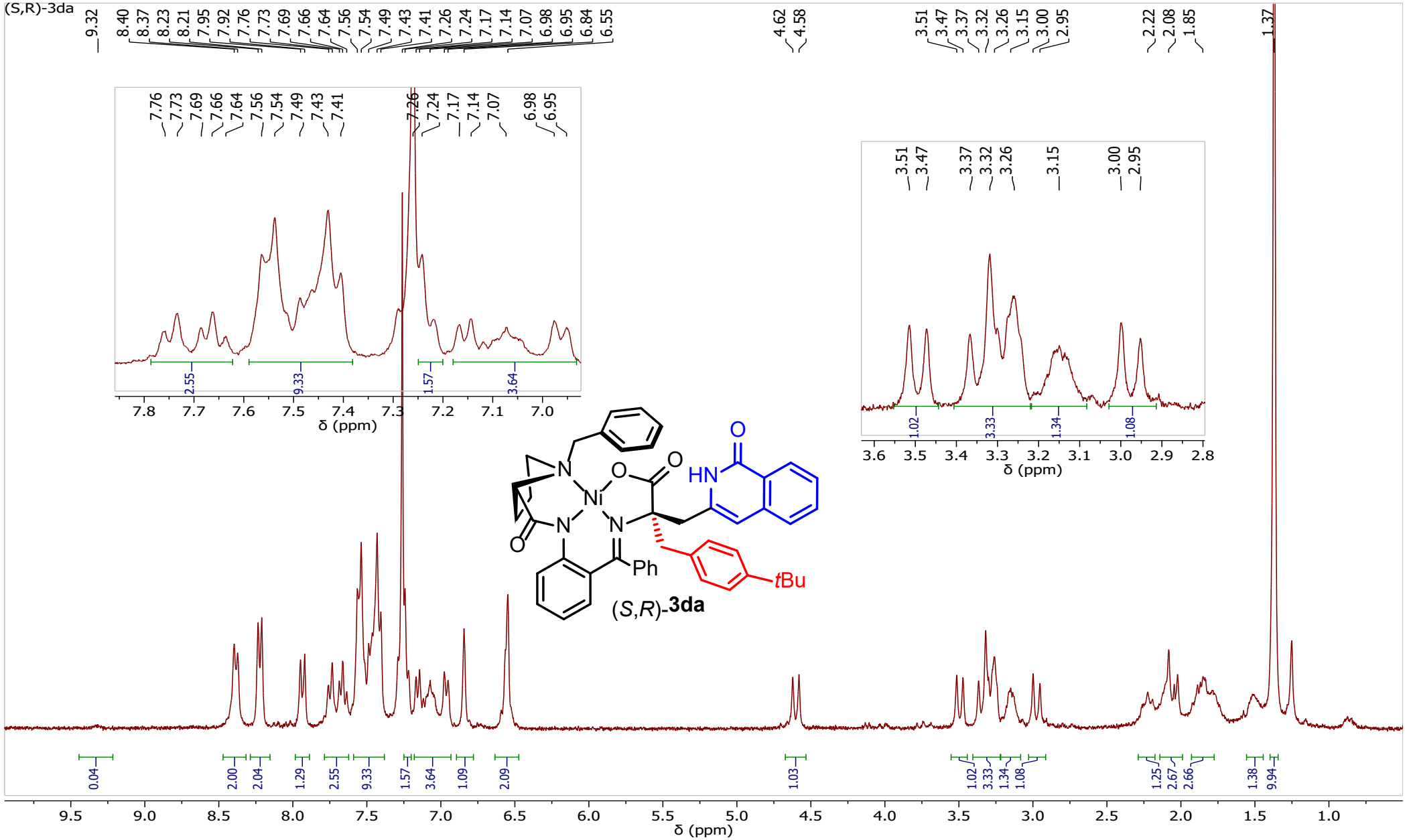

Figure S69. ^{1}H (300 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3da** (in $CDCl_3$)

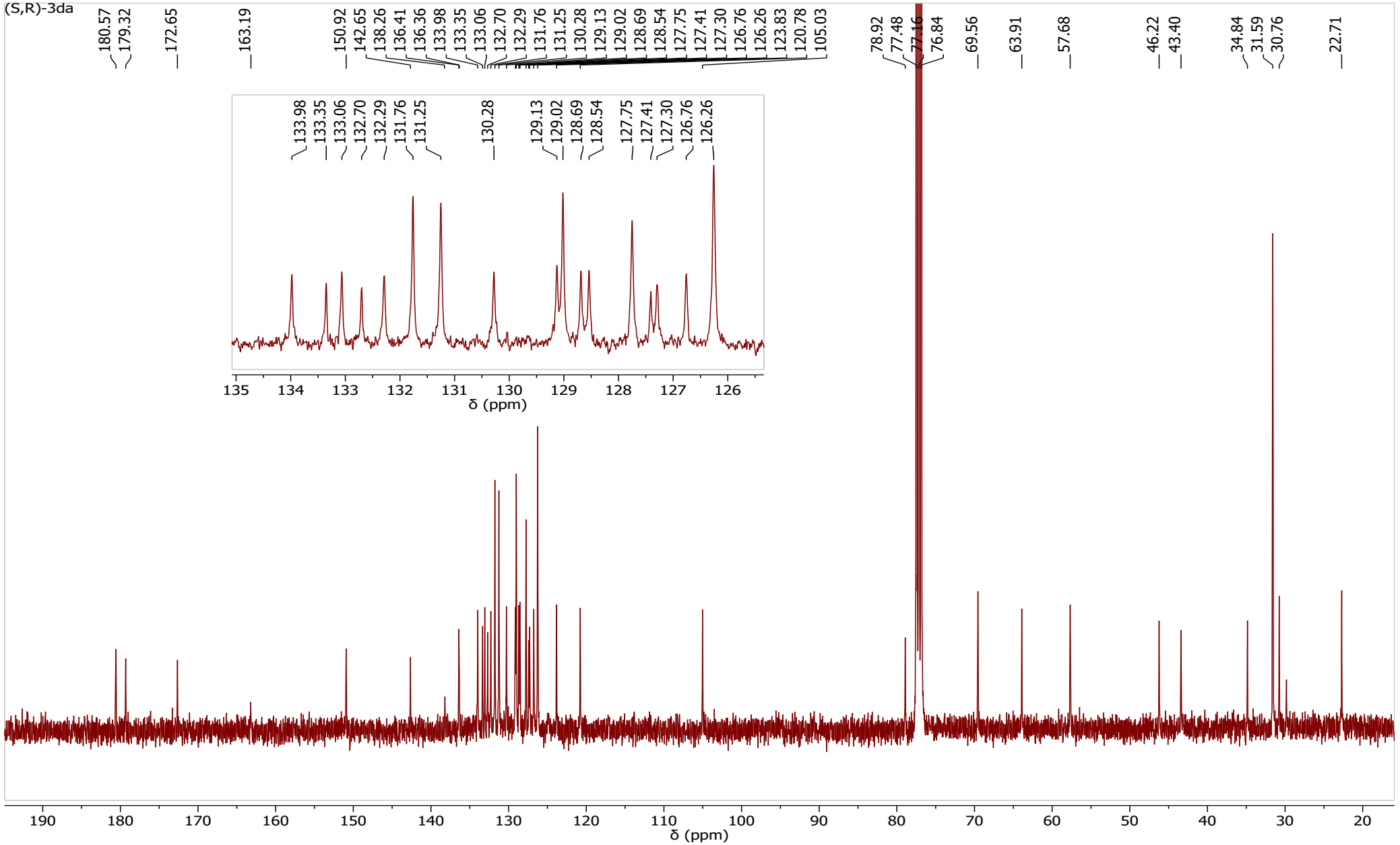

Figure S70. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3da** (in $CDCl_3$)

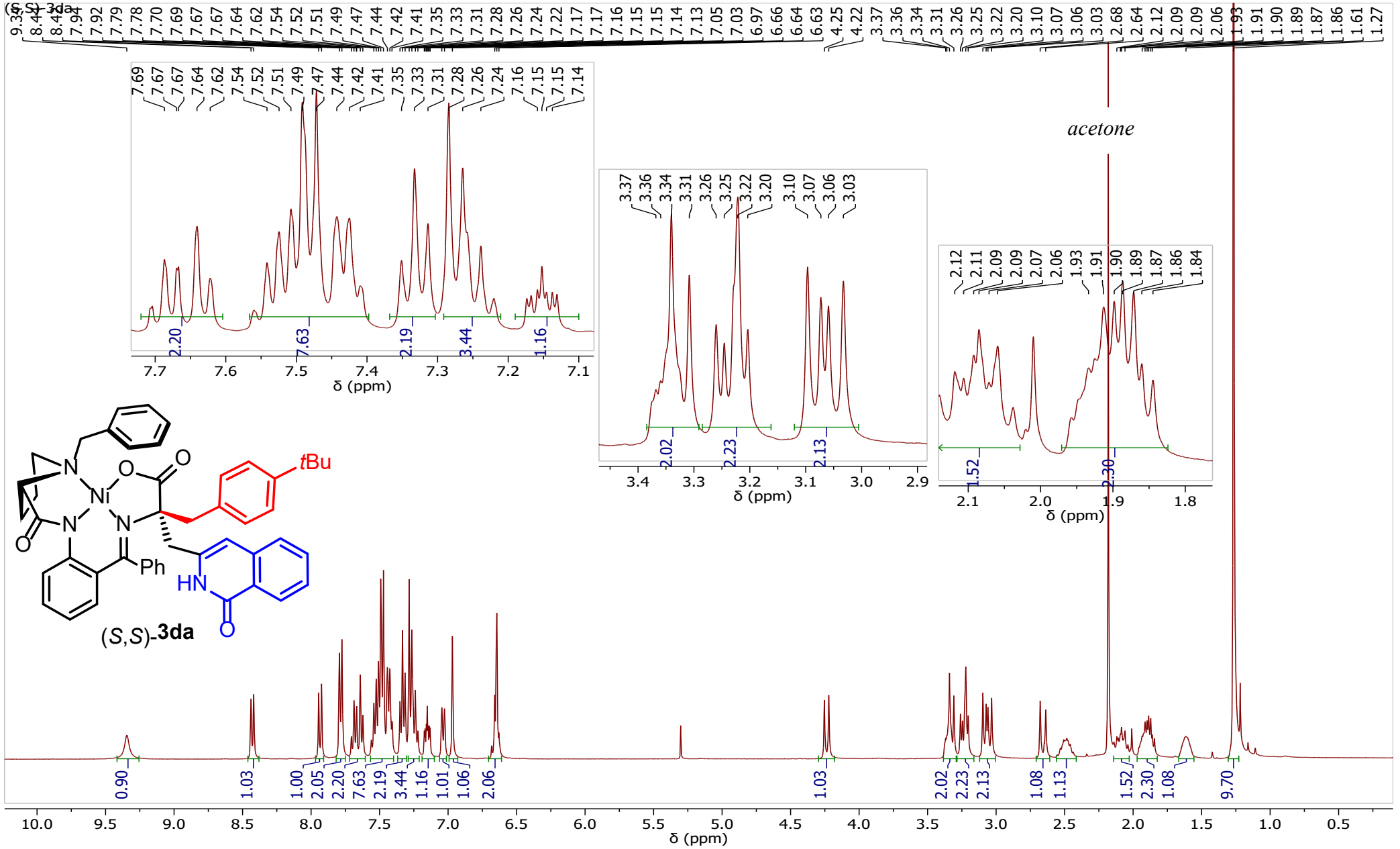

Figure S71. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3da** (in $CDCl_3$)

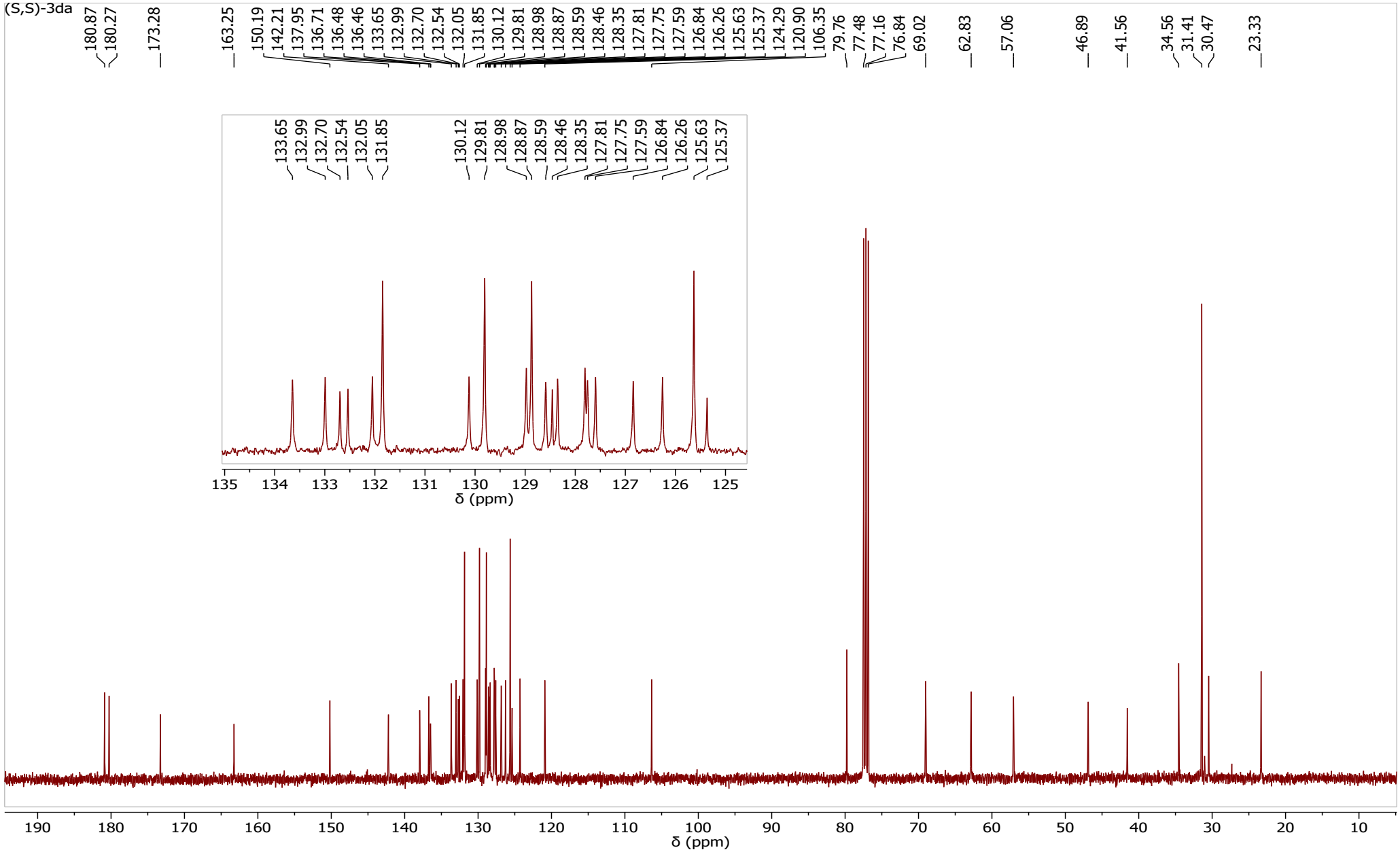

Figure S72. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3da** (in $CDCl_3$)

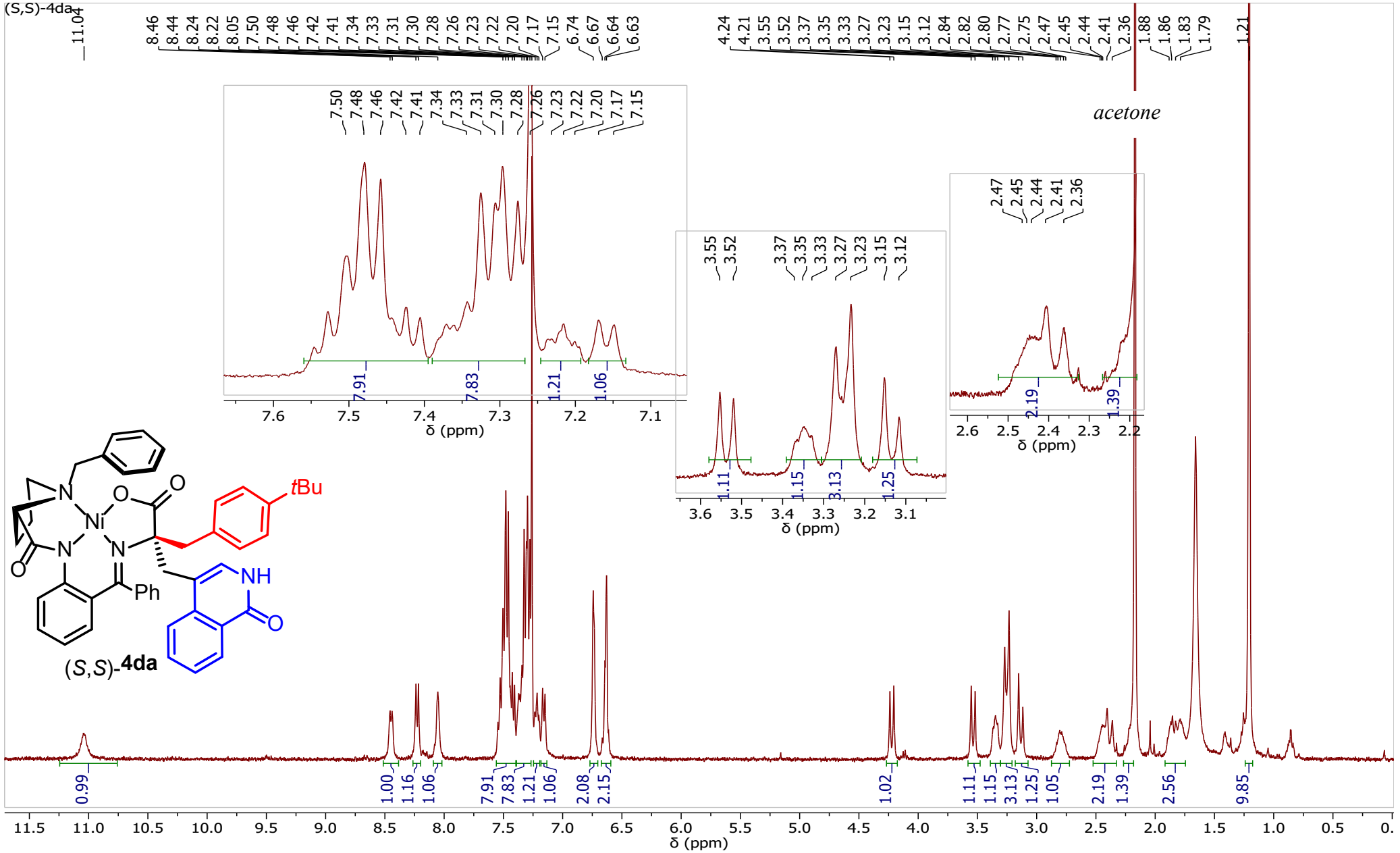

Figure S73. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4da** (in $CDCl_3$)

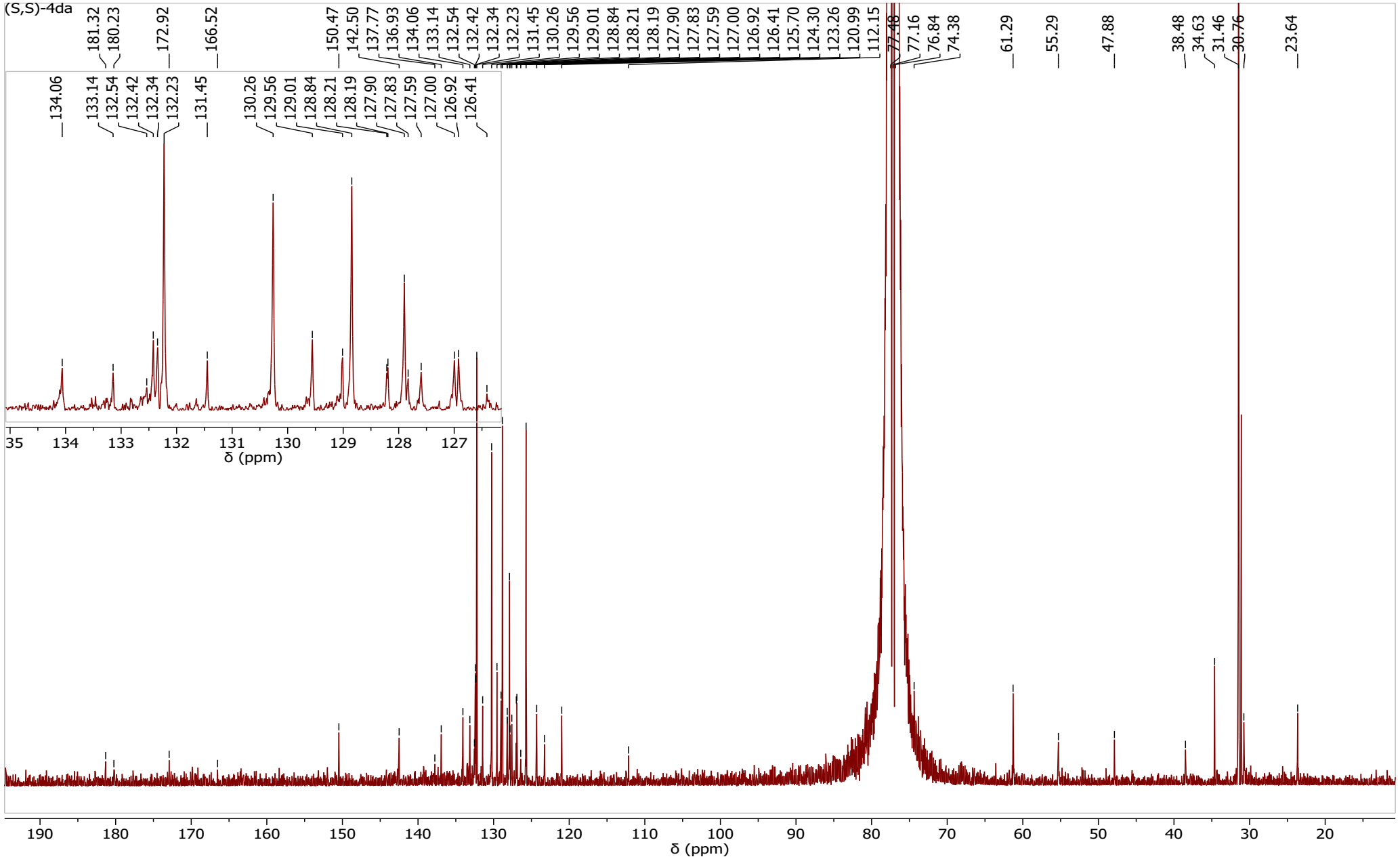

Figure S74. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4da** (in $CDCl_3$)

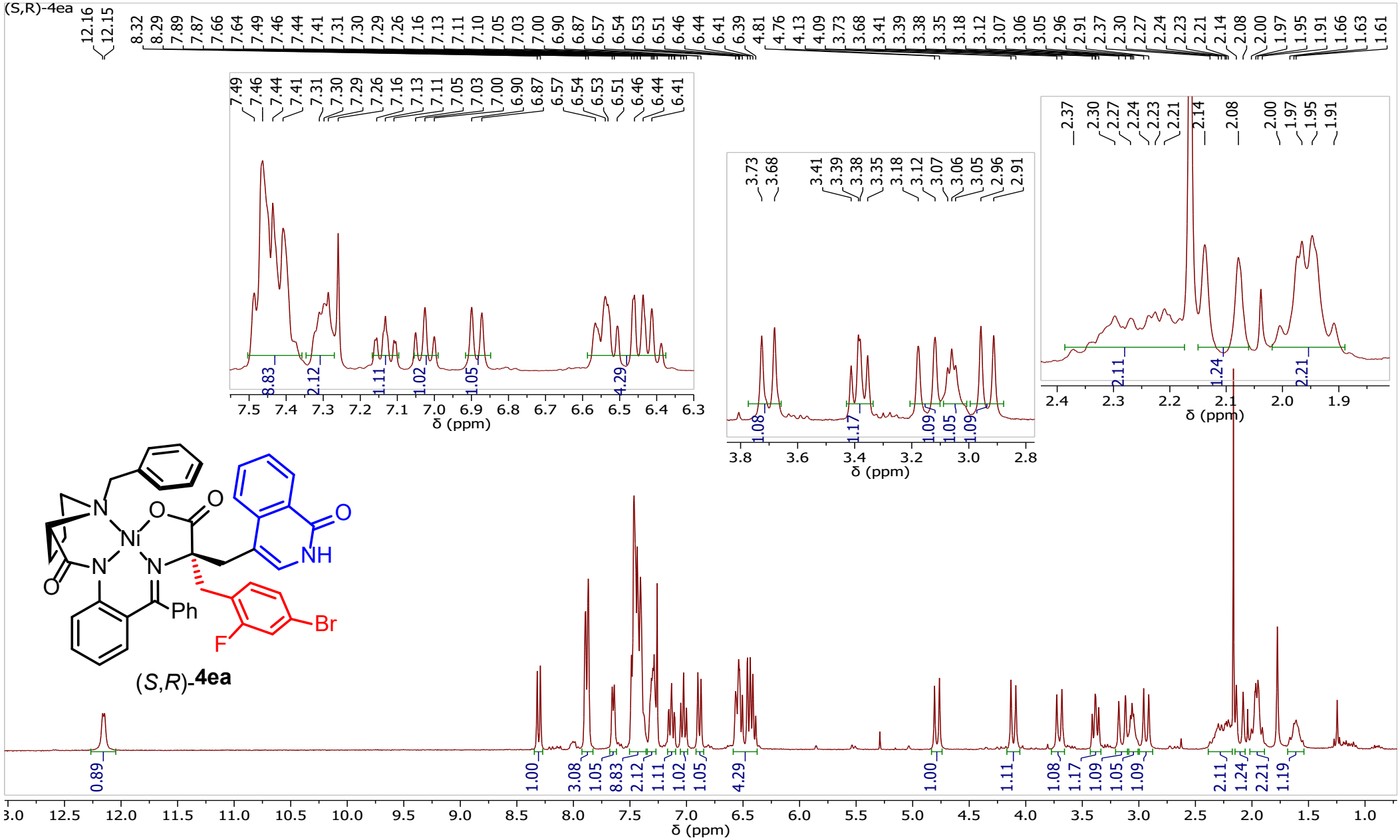

Figure S75. ^{1}H (300 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ea** (in $CDCl_3$)

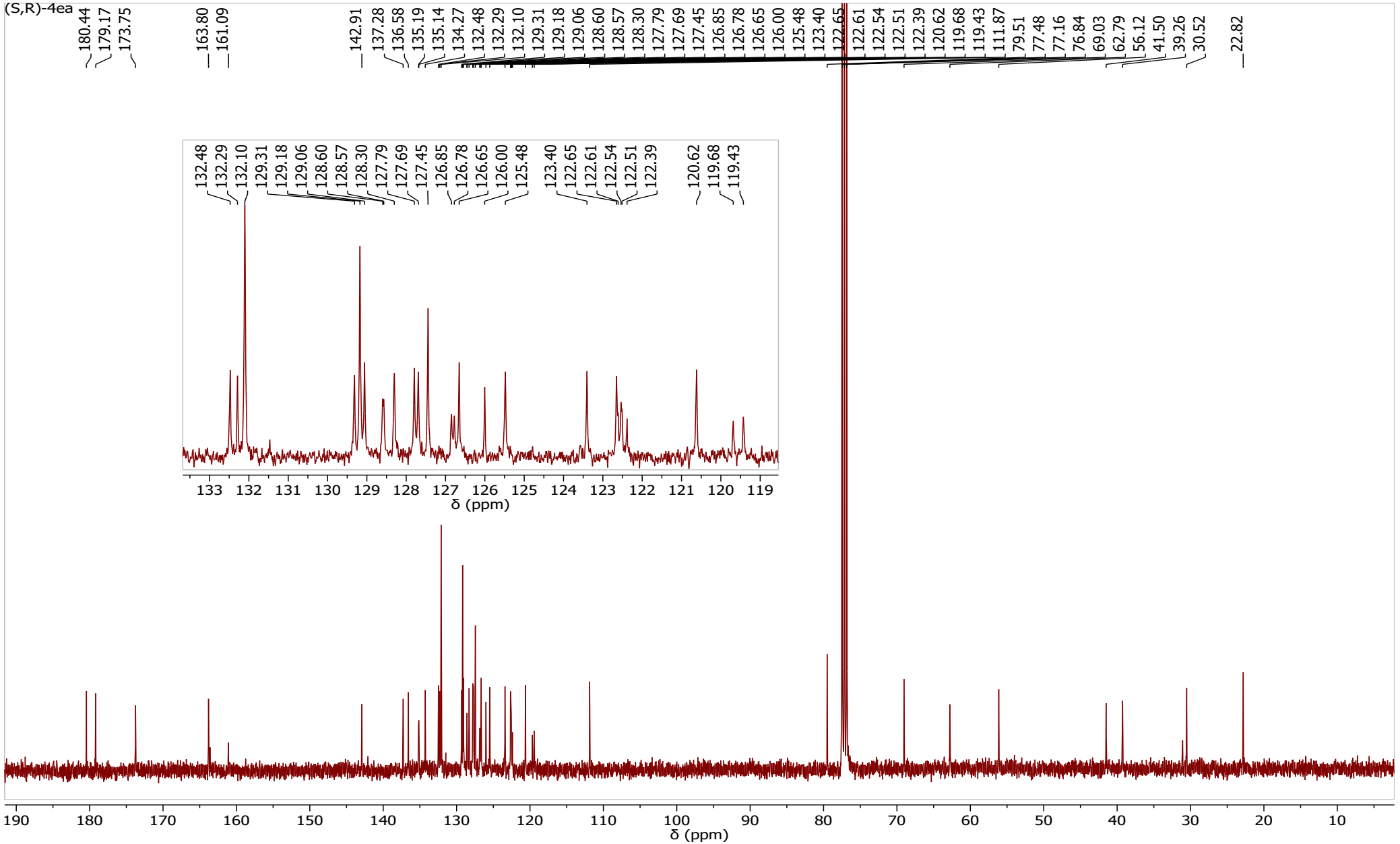

Figure S76. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ea** (in $CDCl_3$)

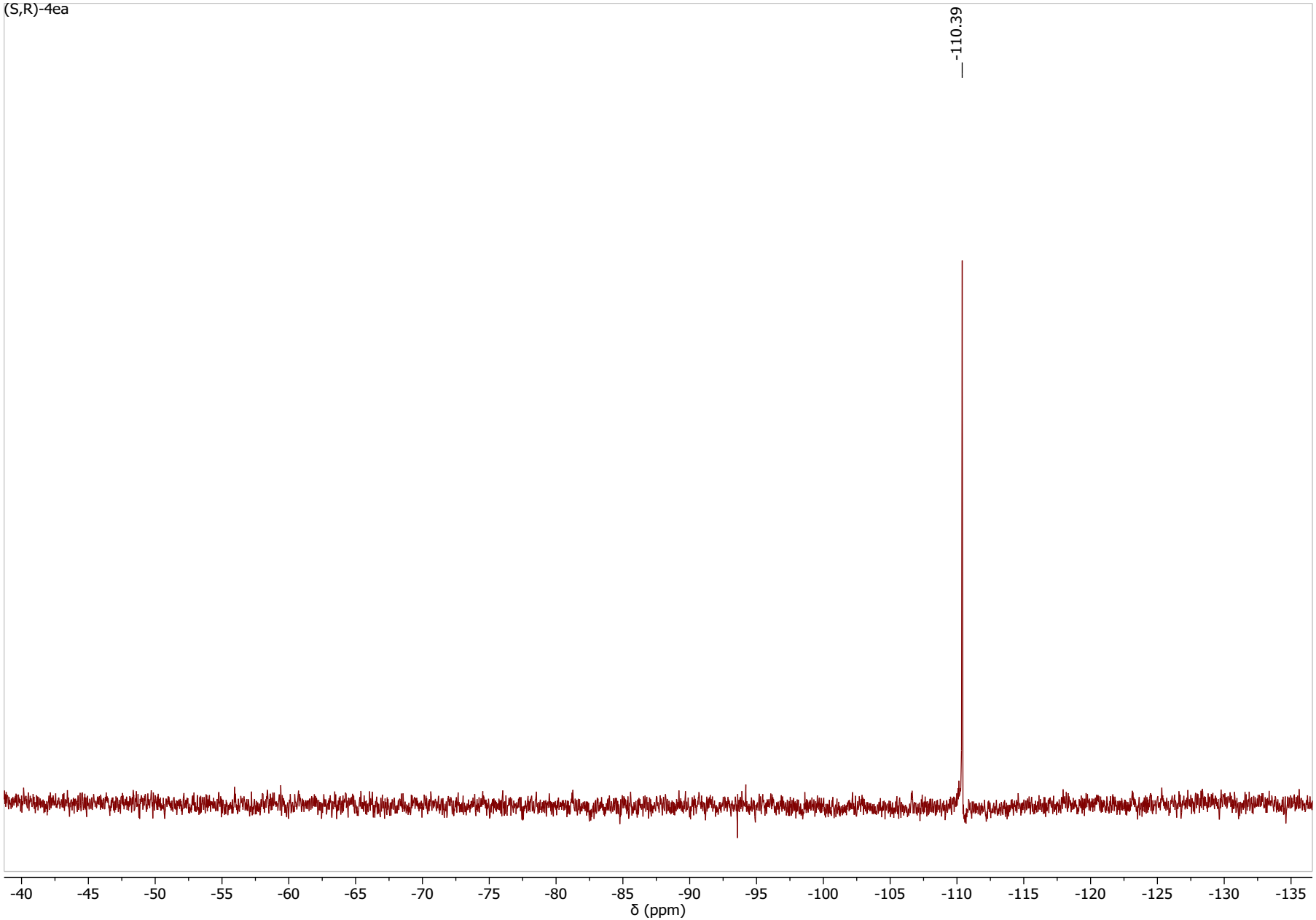

Figure S77. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ea** (in $CDCl_3$)

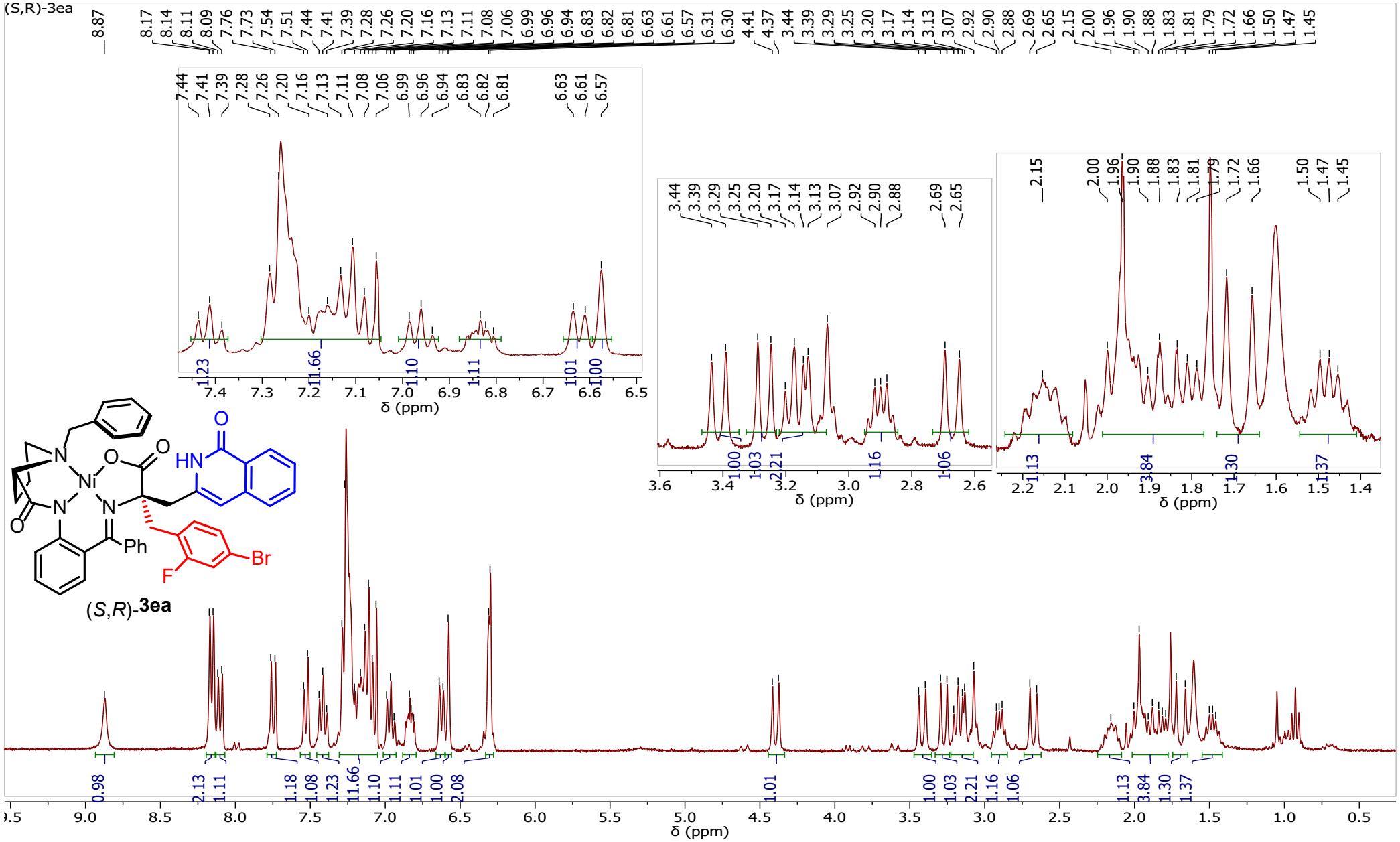

Figure S78. ^{1}H (300 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ea** (in $CDCl_3$)

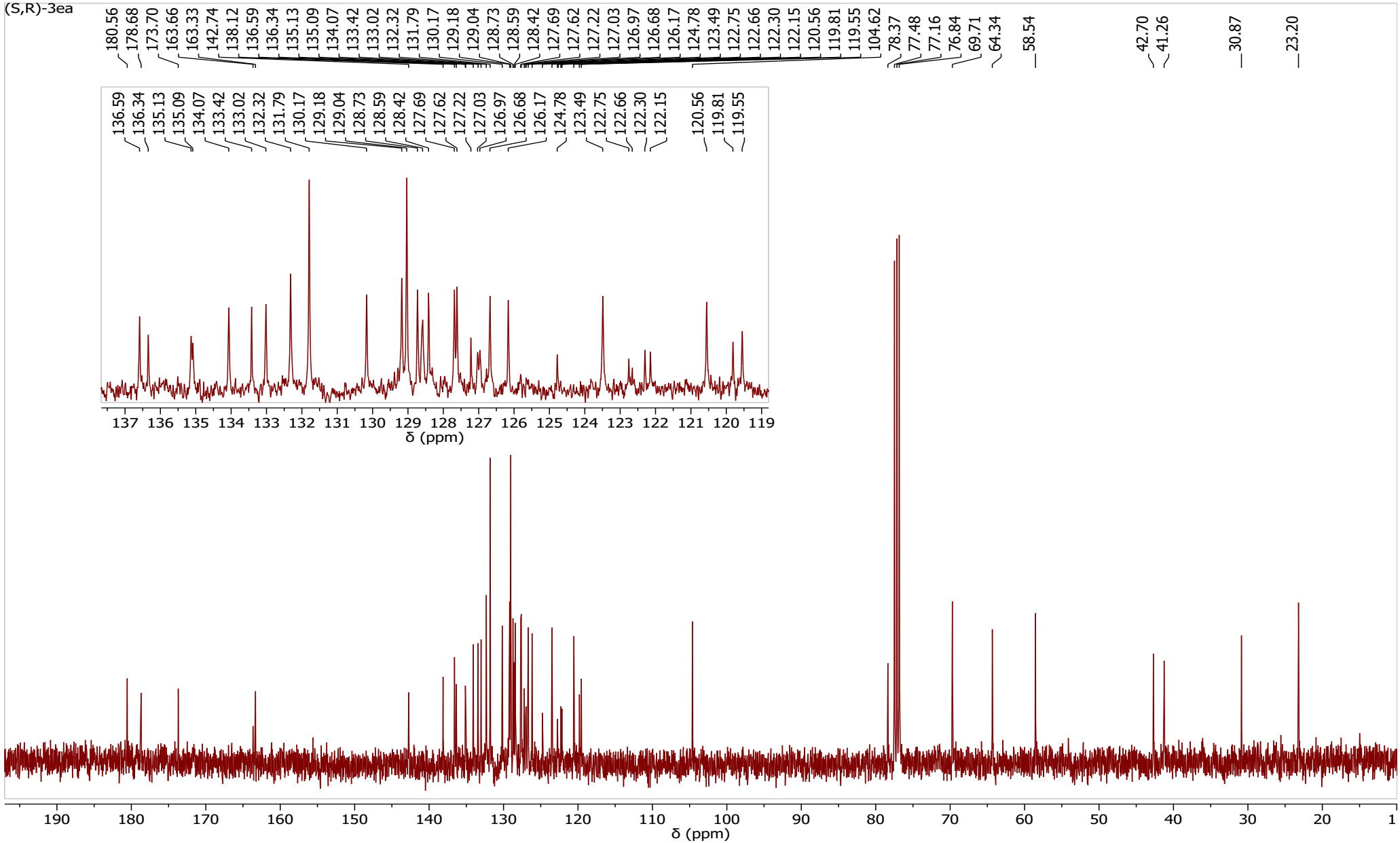

Figure S79. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ea** (in $CDCl_3$)

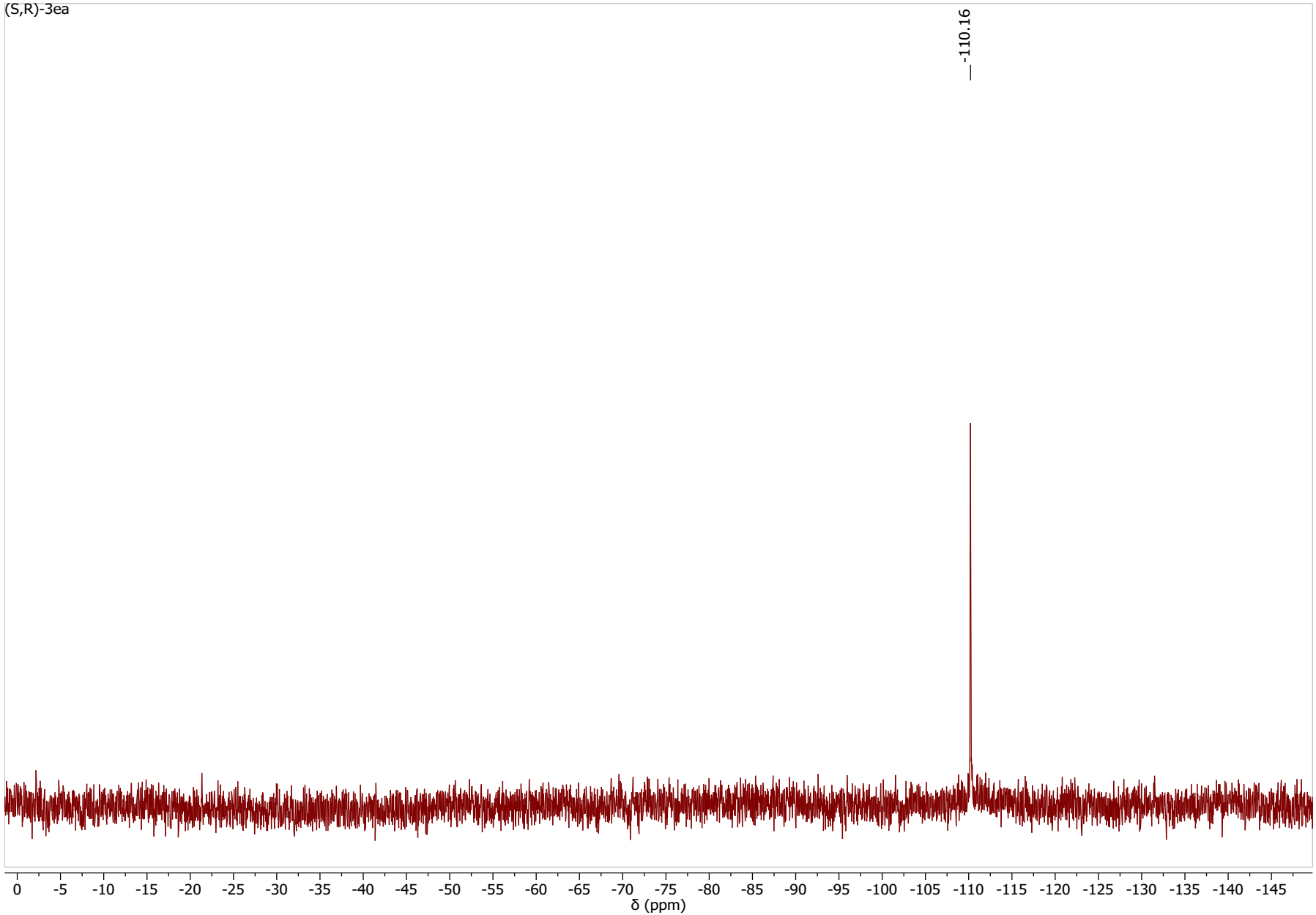

Figure S80. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ea** (in $CDCl_3$)

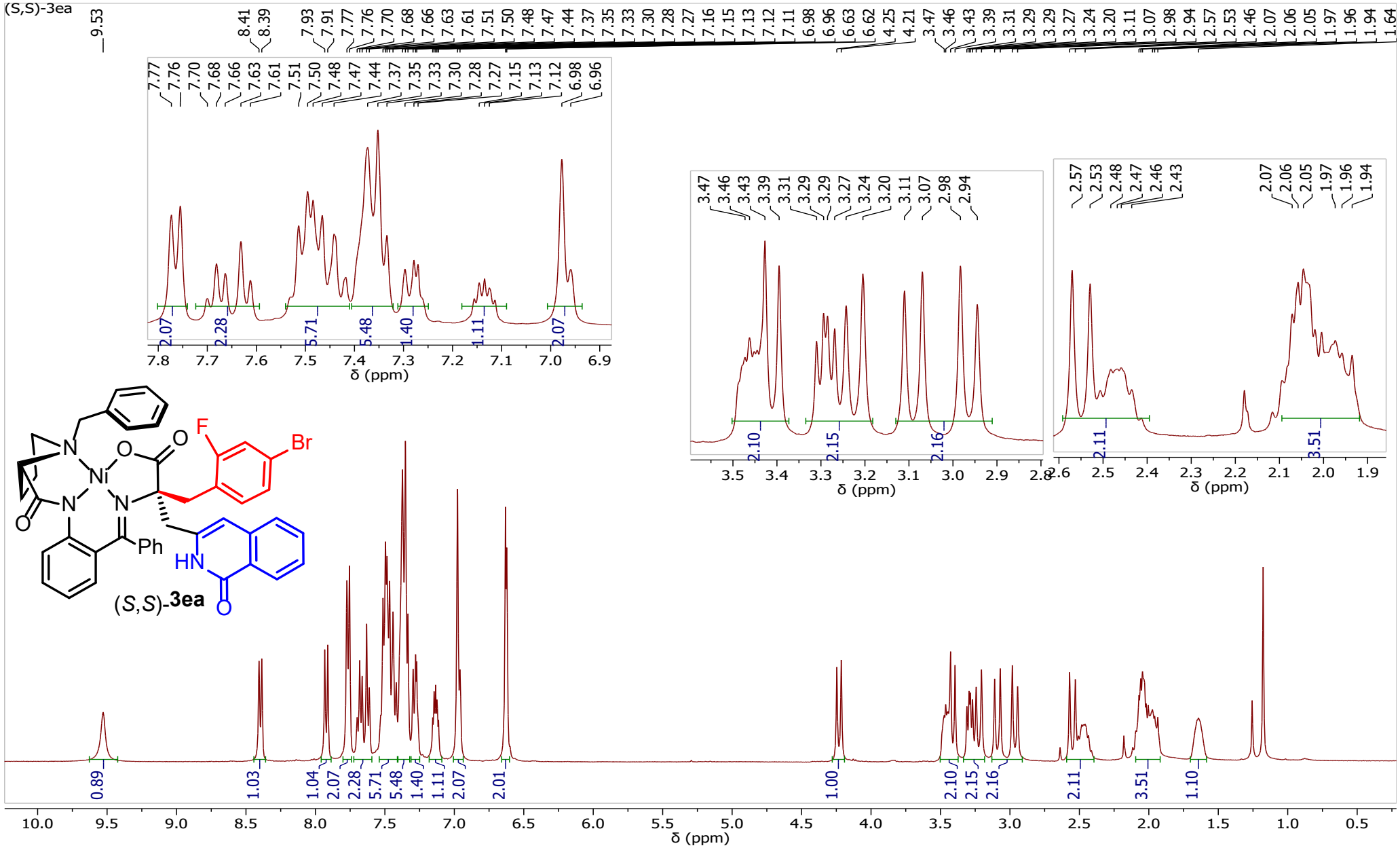

Figure S81. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ea** (in $CDCl_3$)

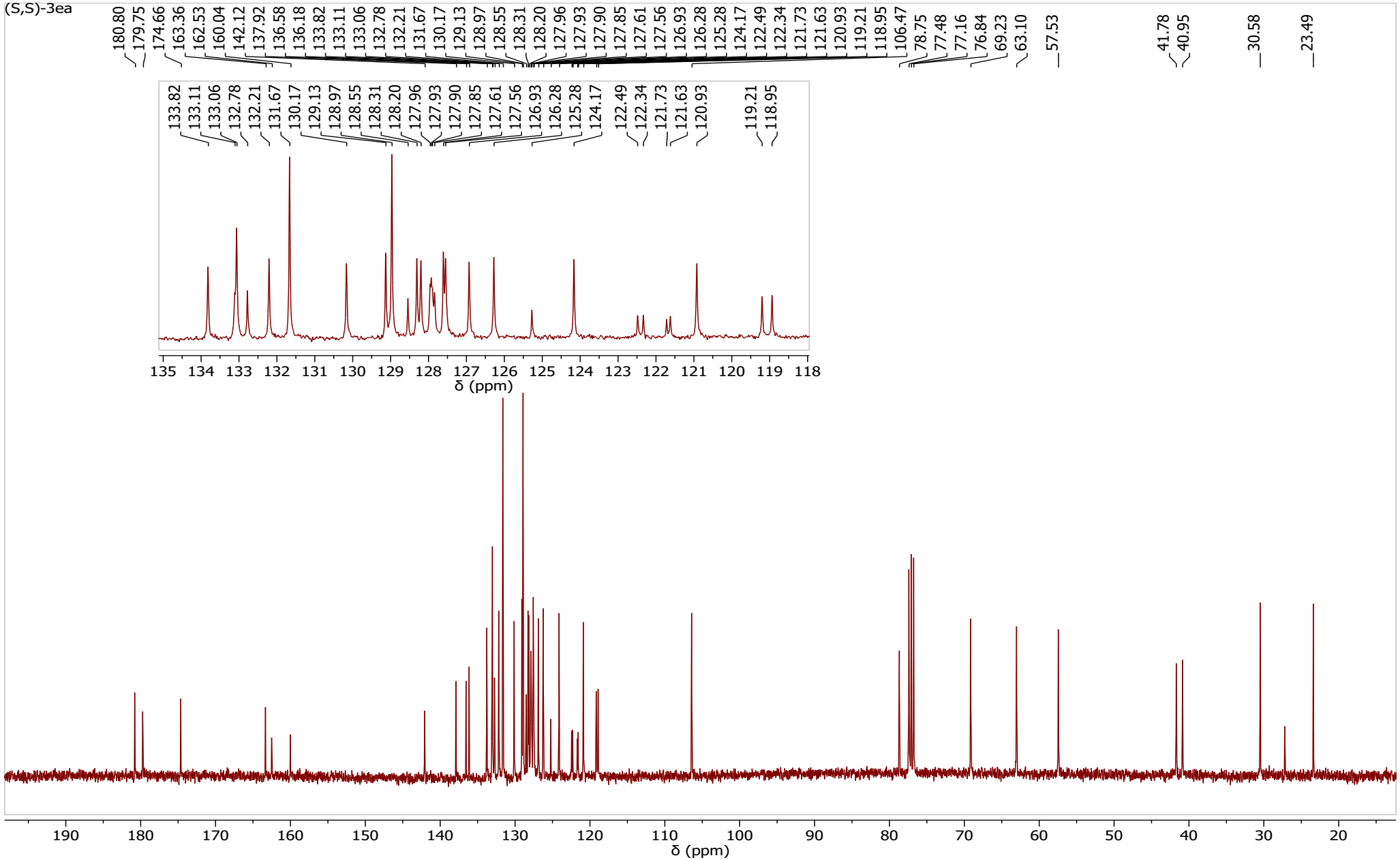

Figure S82. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ea** (in $CDCl_3$)

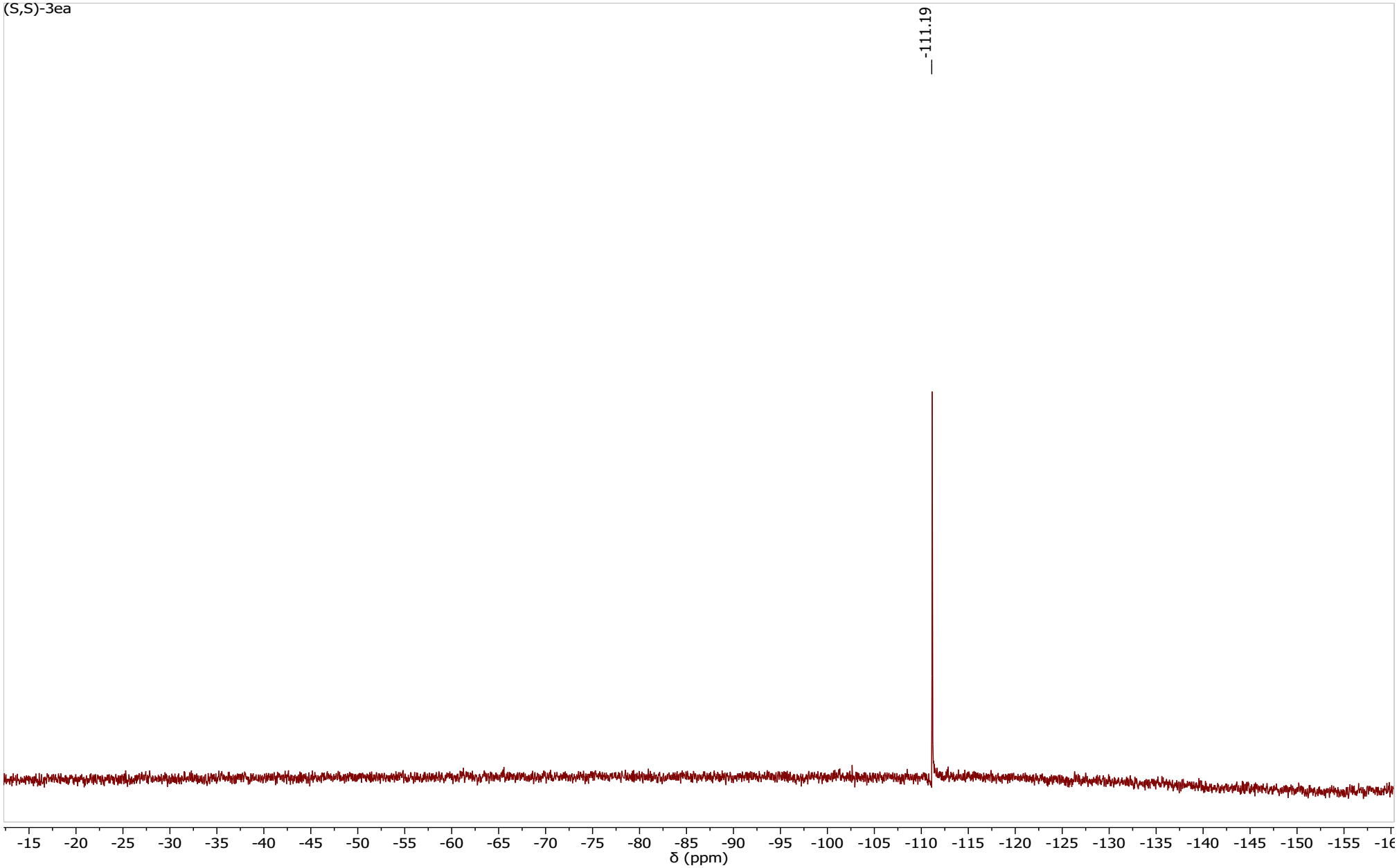

Figure S83. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**3ea** (in $CDCl_3$)

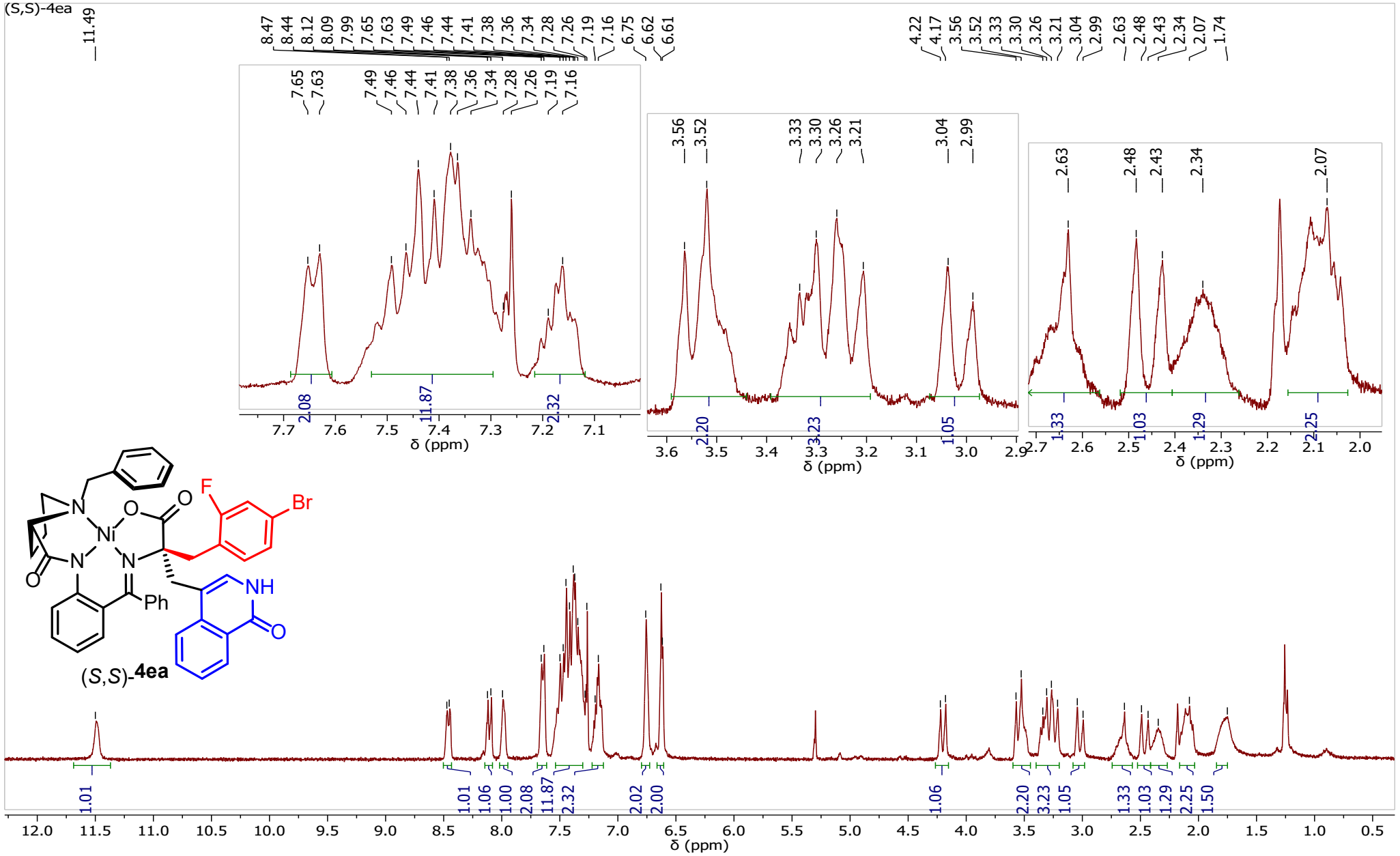

Figure S84. ^{1}H (300 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4ea** (in $CDCl_3$)

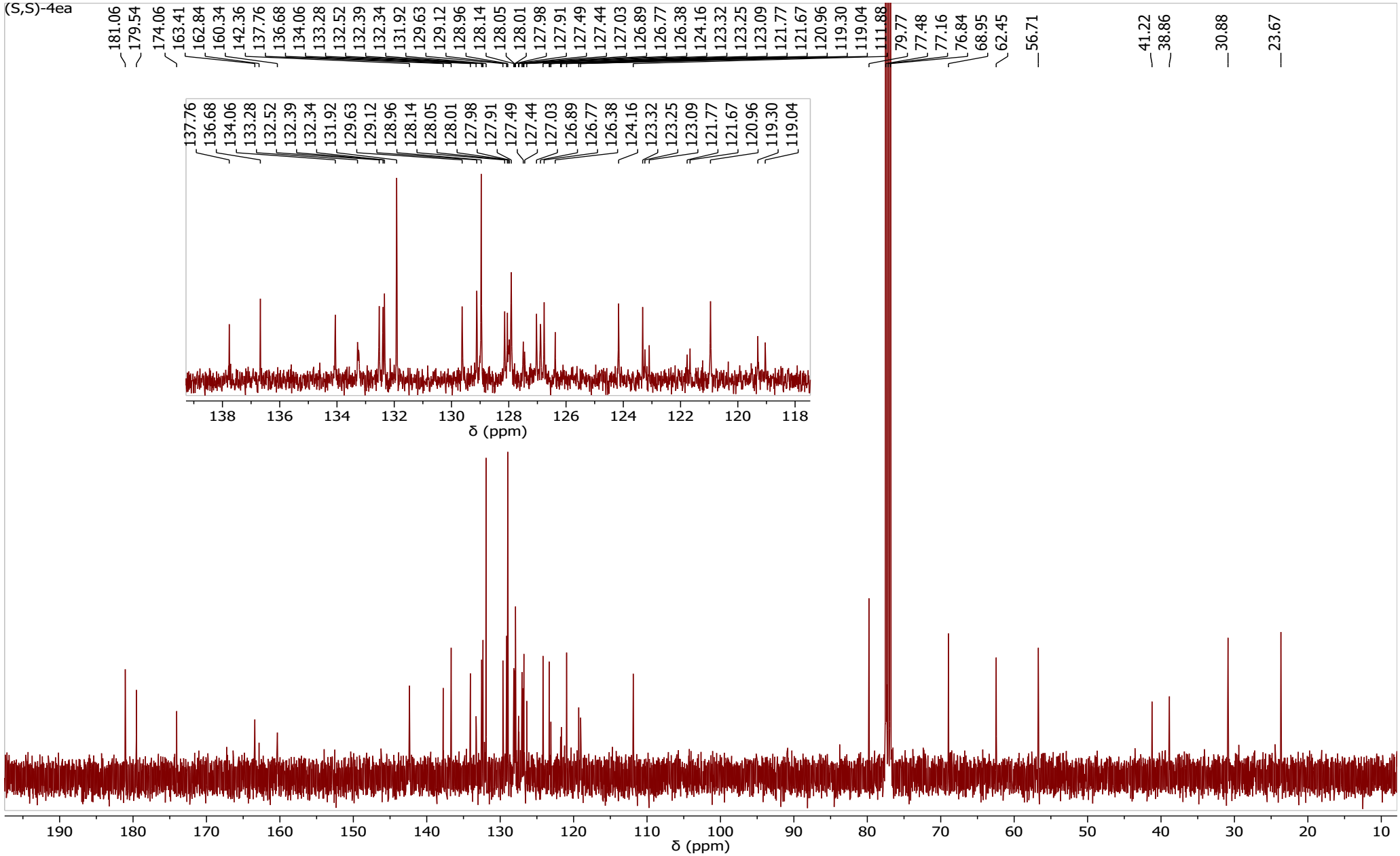

Figure S85. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4ea** (in $CDCl_3$)

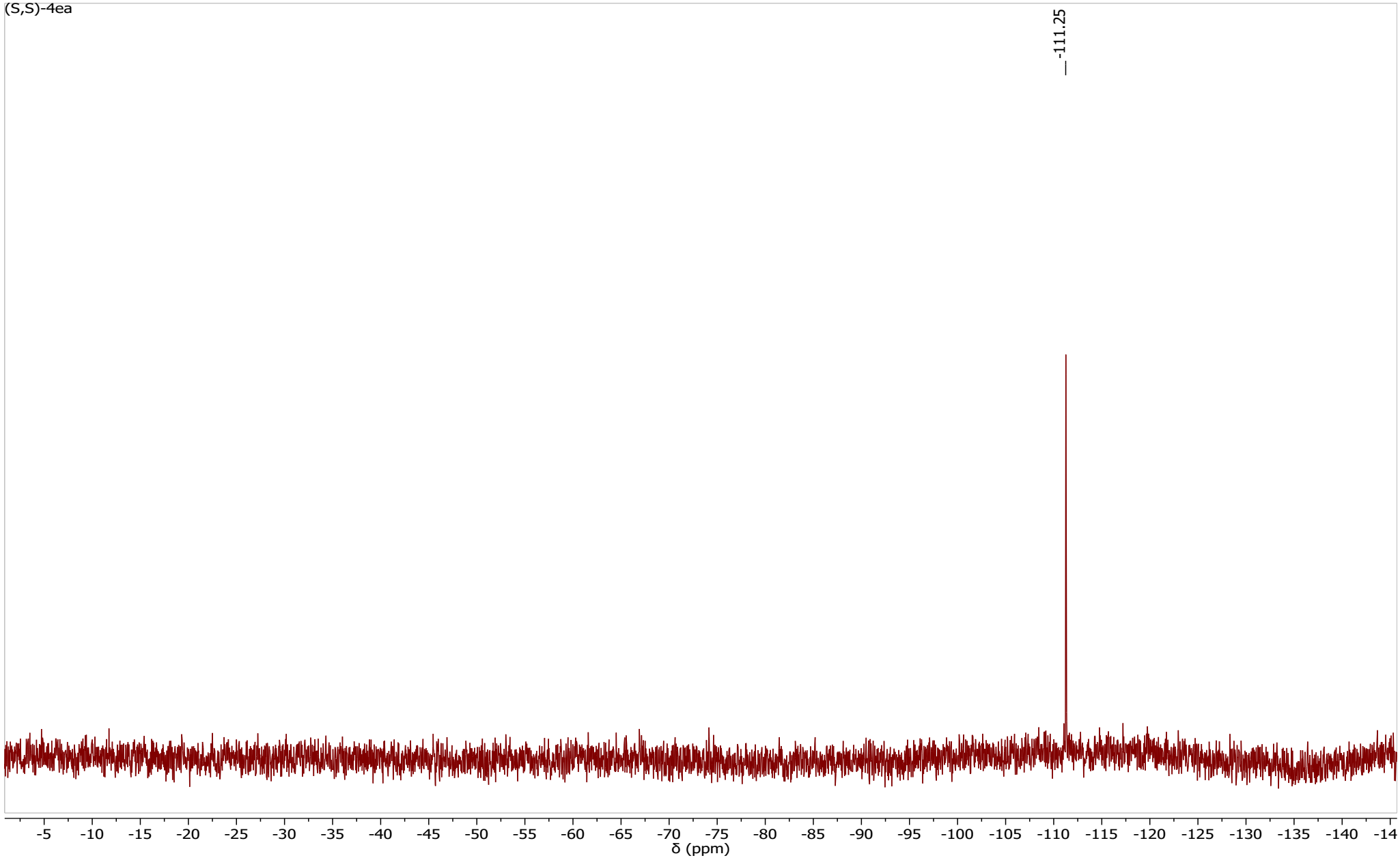

Figure S86. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*S*)-**4ea** (in $CDCl_3$)

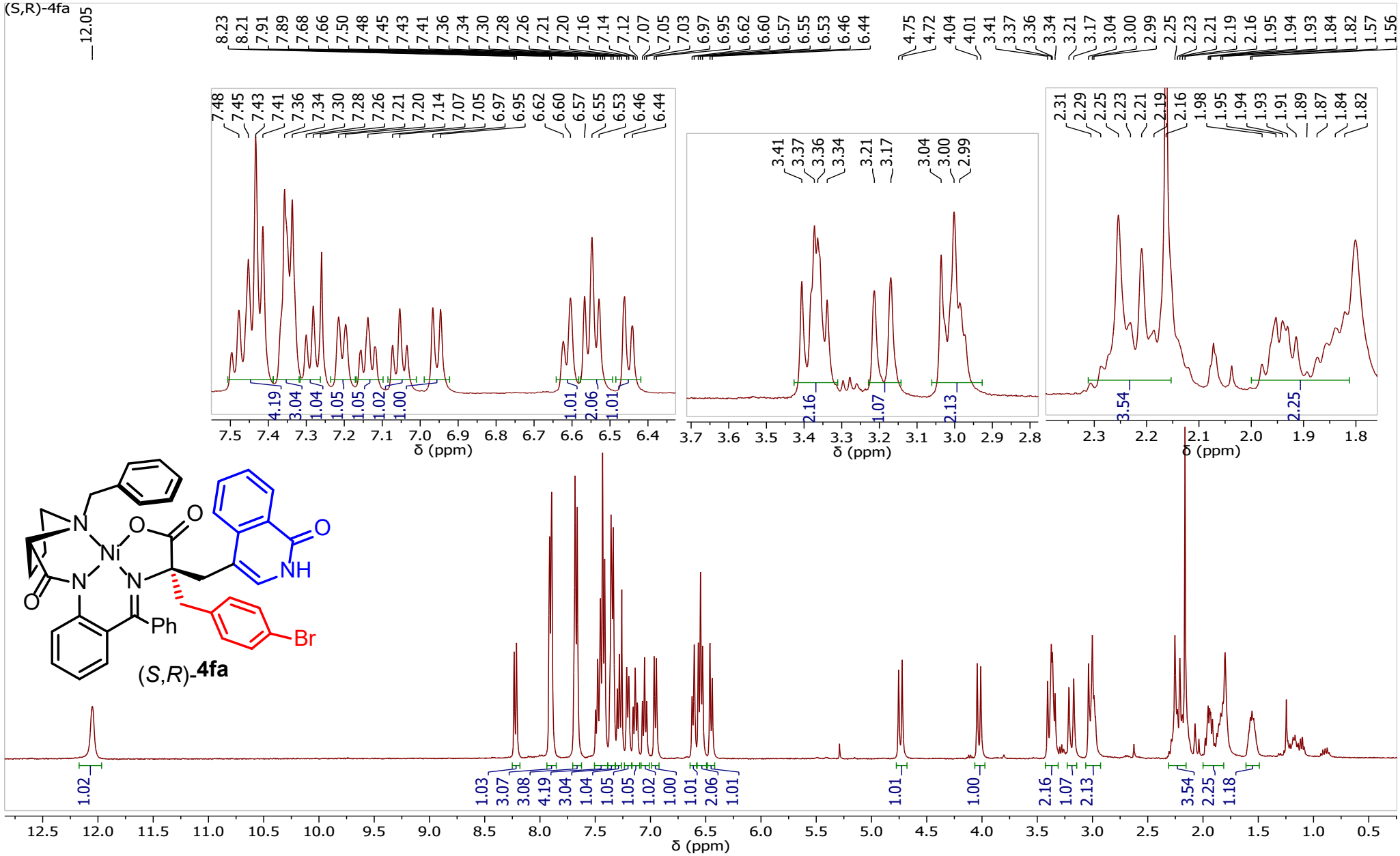

Figure S87. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4fa** (in $CDCl_3$)

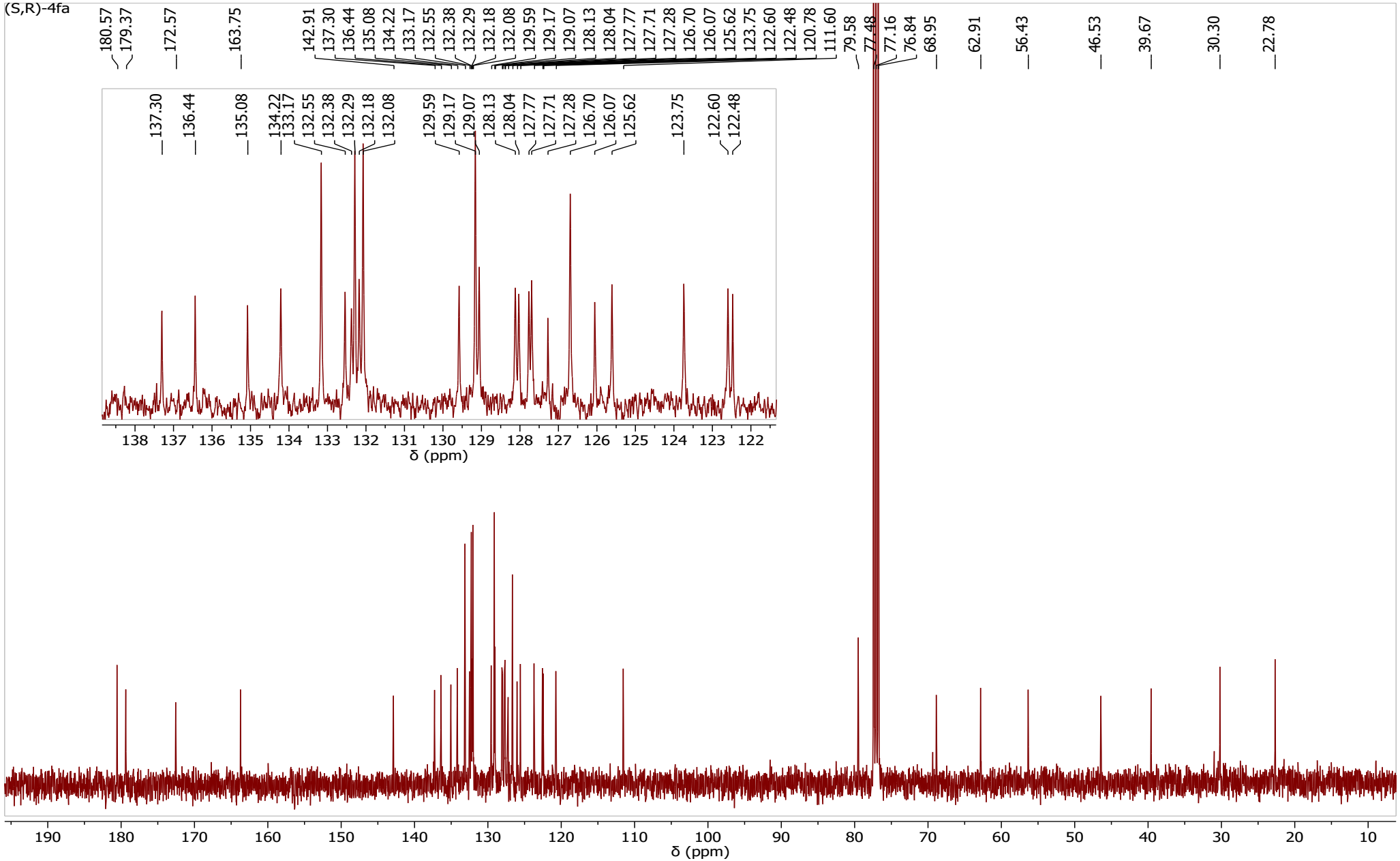

Figure S88. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4fa** (in $CDCl_3$)

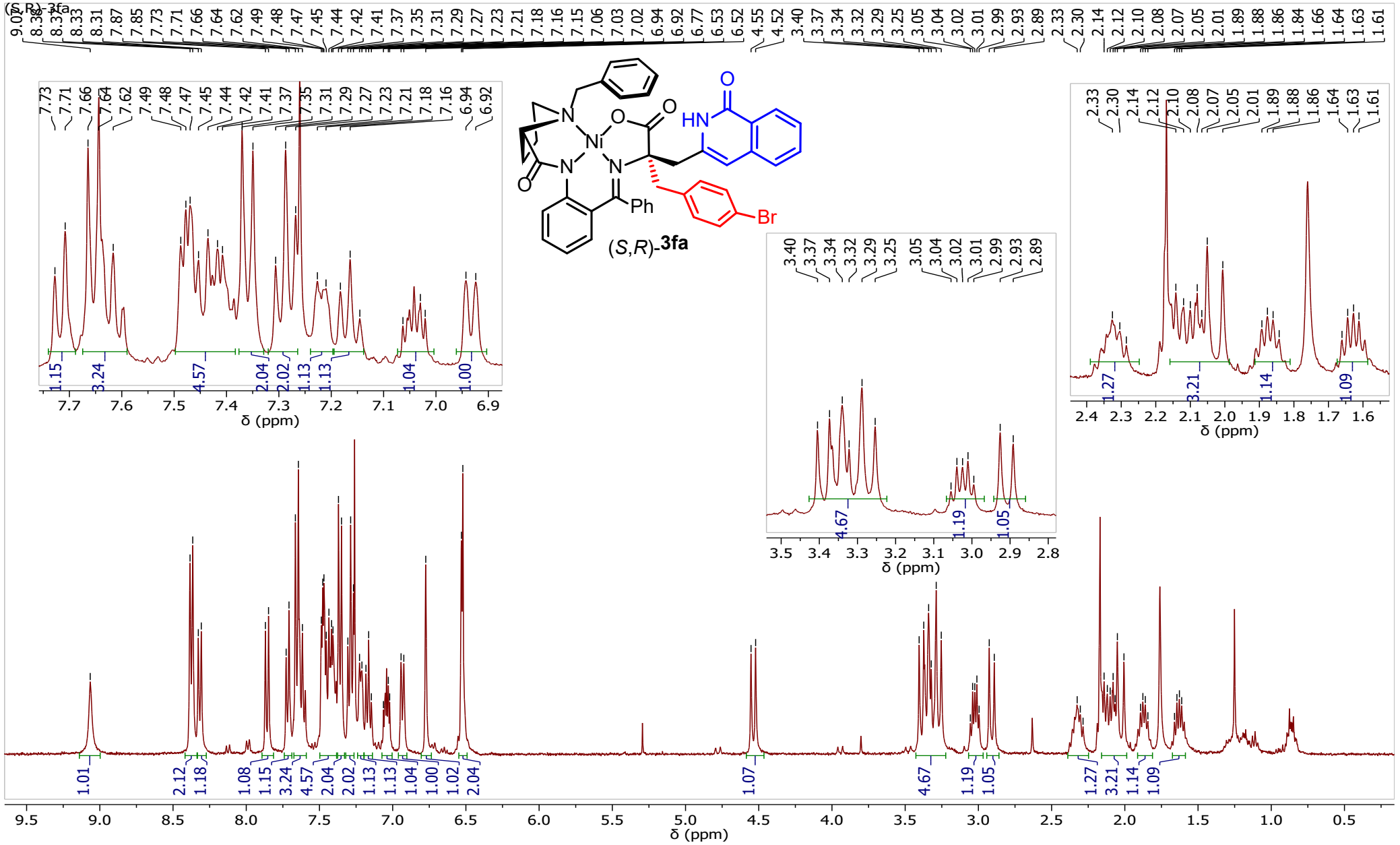

Figure S89. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3fa** (in $CDCl_3$)

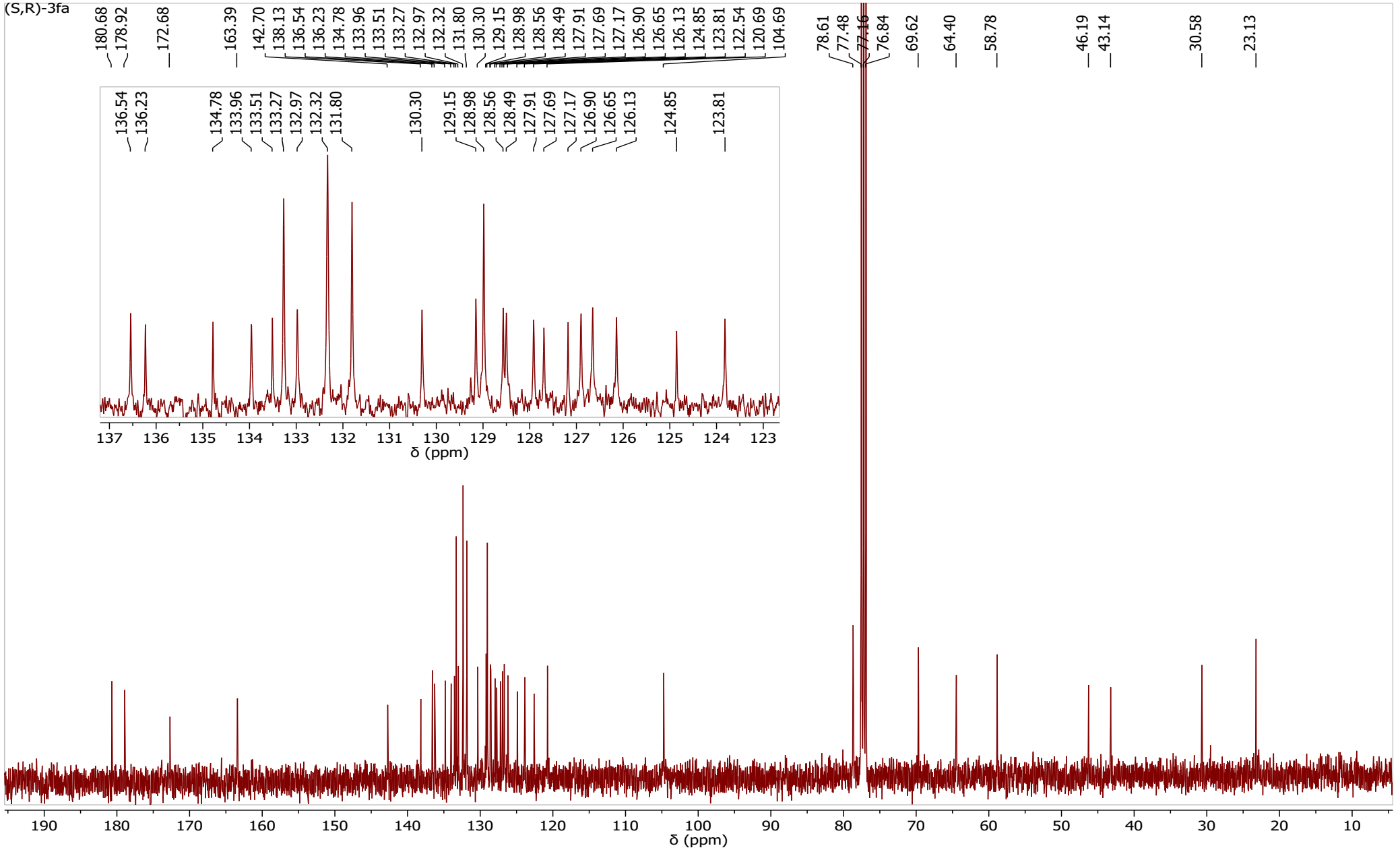

Figure S90. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3fa** (in $CDCl_3$)

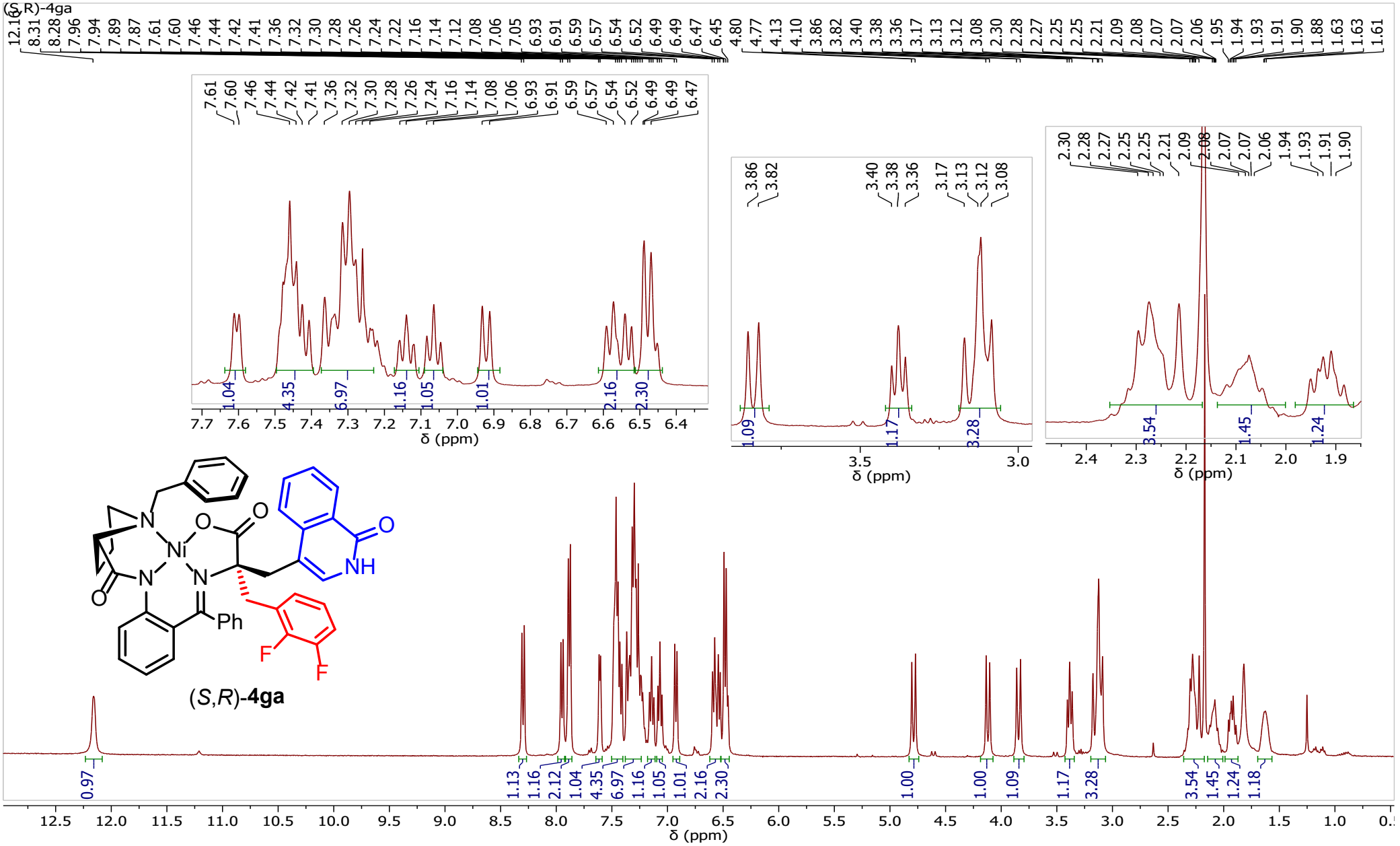

Figure S91. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ga** (in $CDCl_3$)

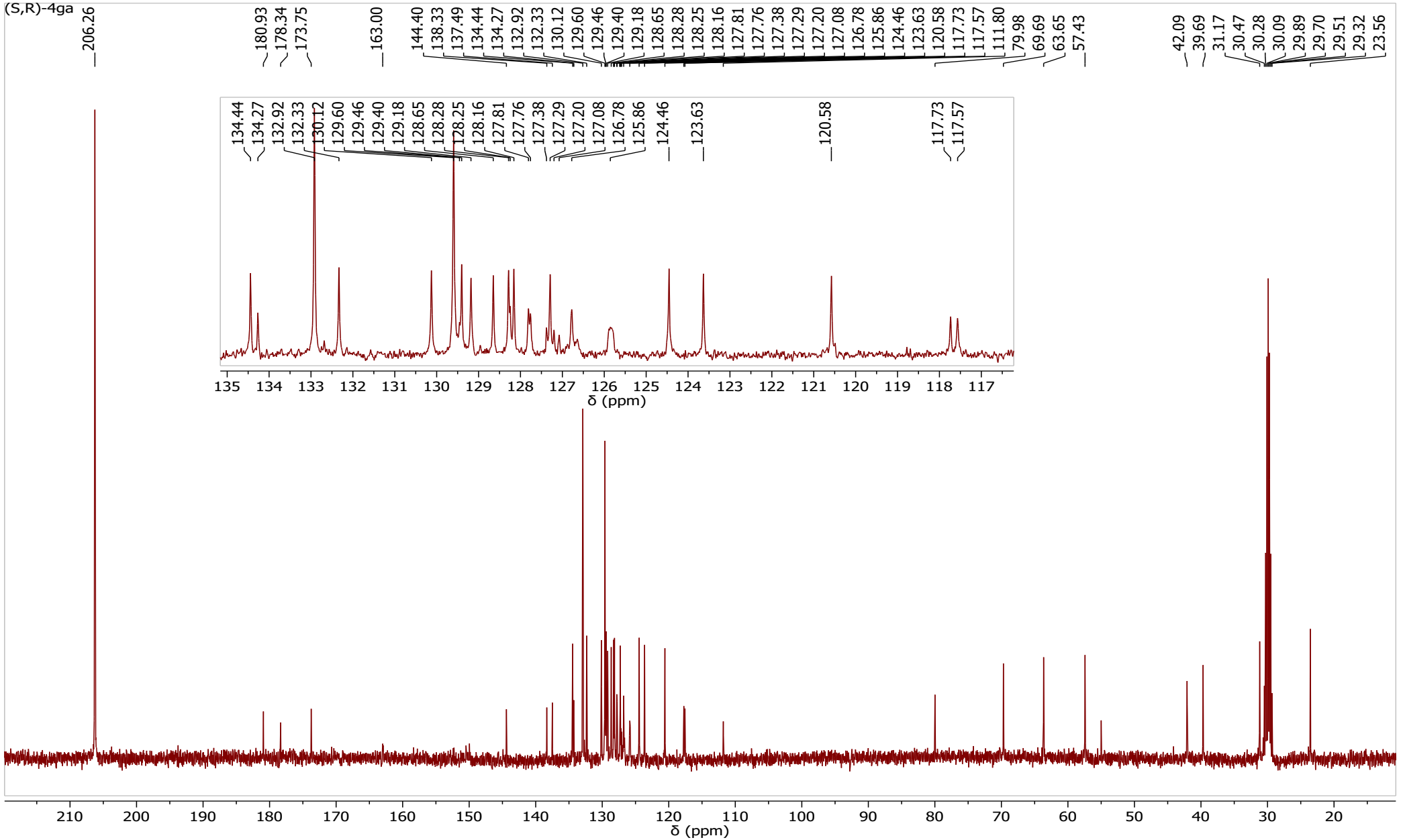

Figure S92. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ga** (in acetone-d6)

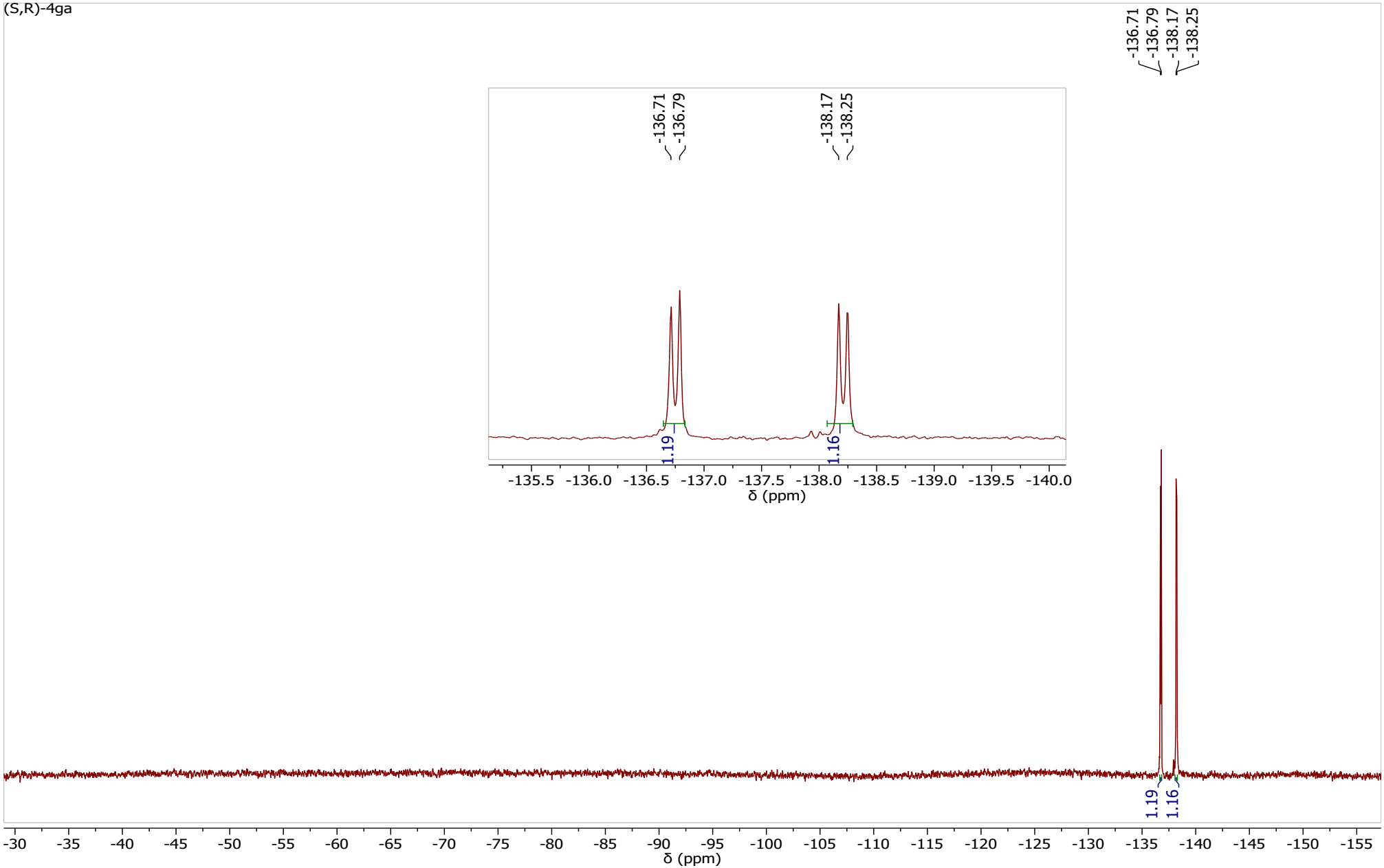

Figure S93. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ga** (in $CDCl_3$)

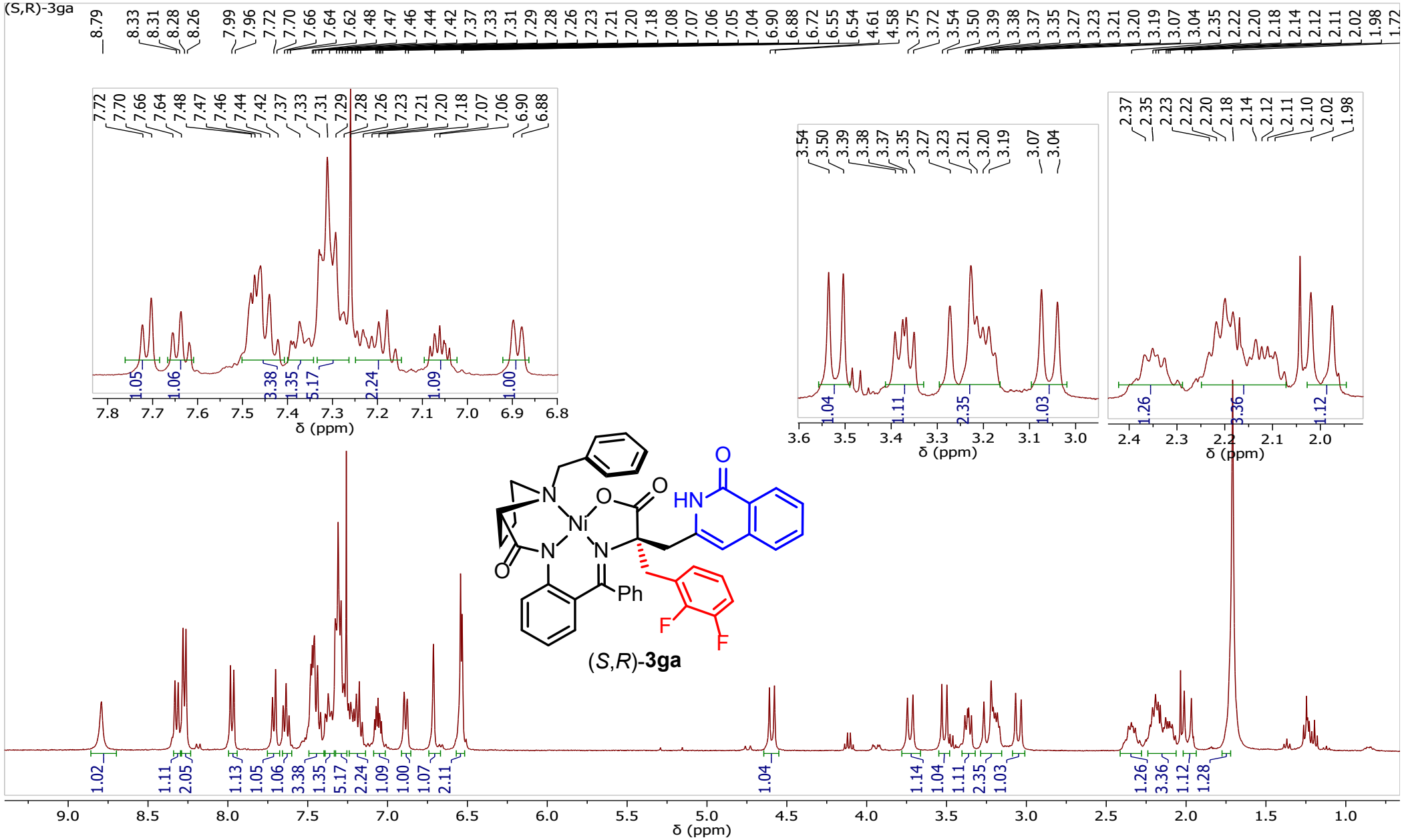

Figure S94. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ga** (in $CDCl_3$)

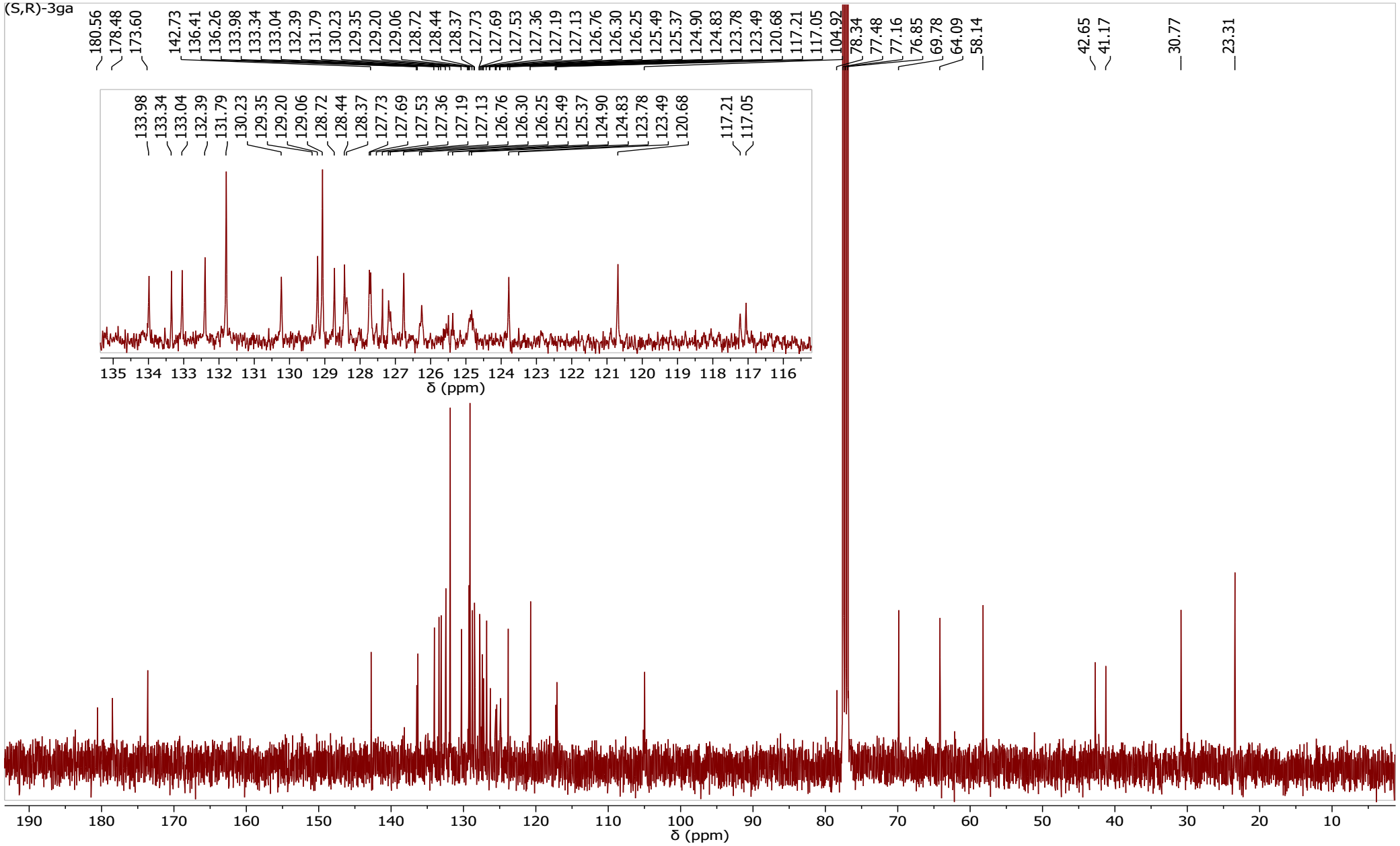

Figure S95. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ga** (in $CDCl_3$)

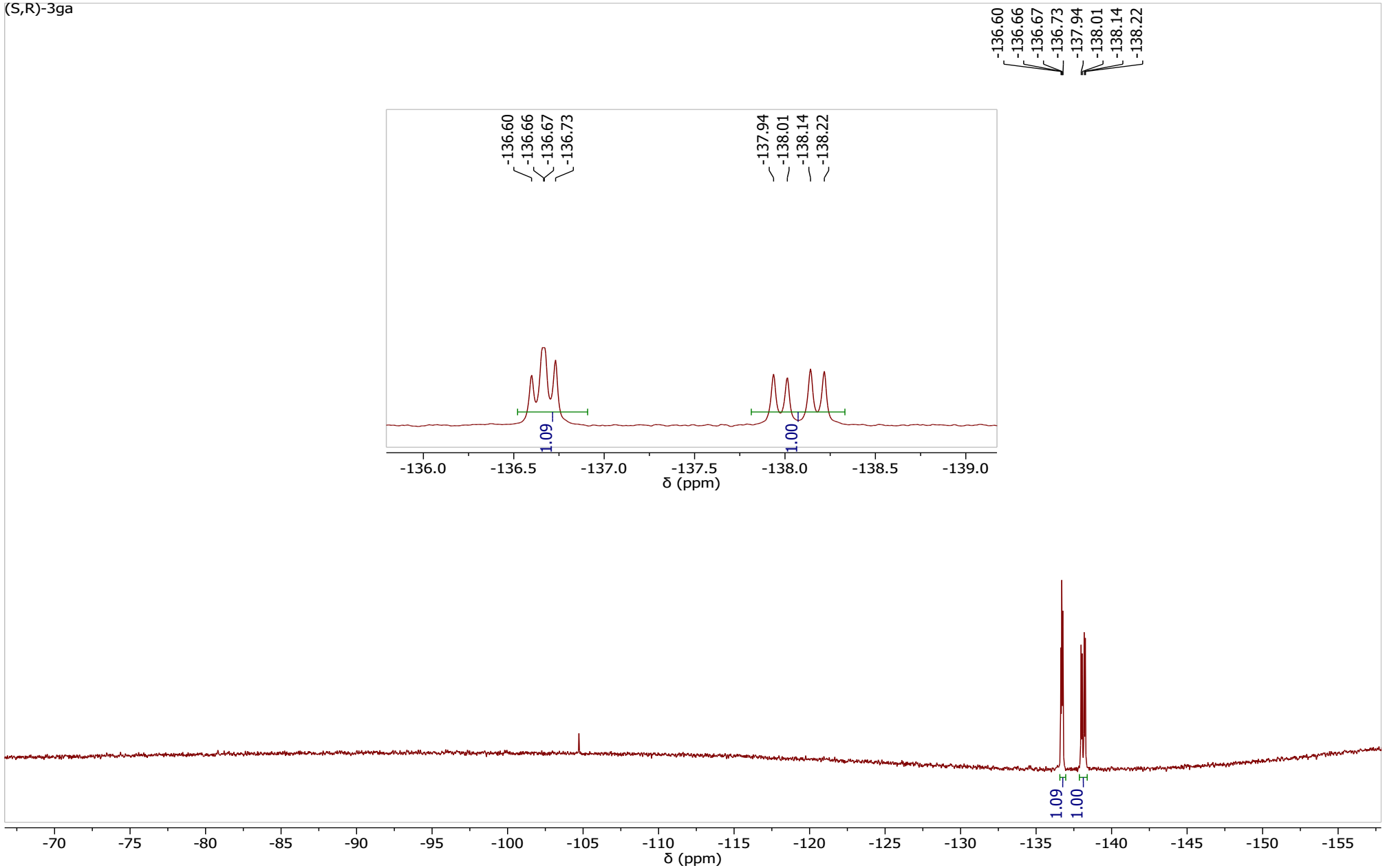

Figure S96. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ga** (in $CDCl_3$)

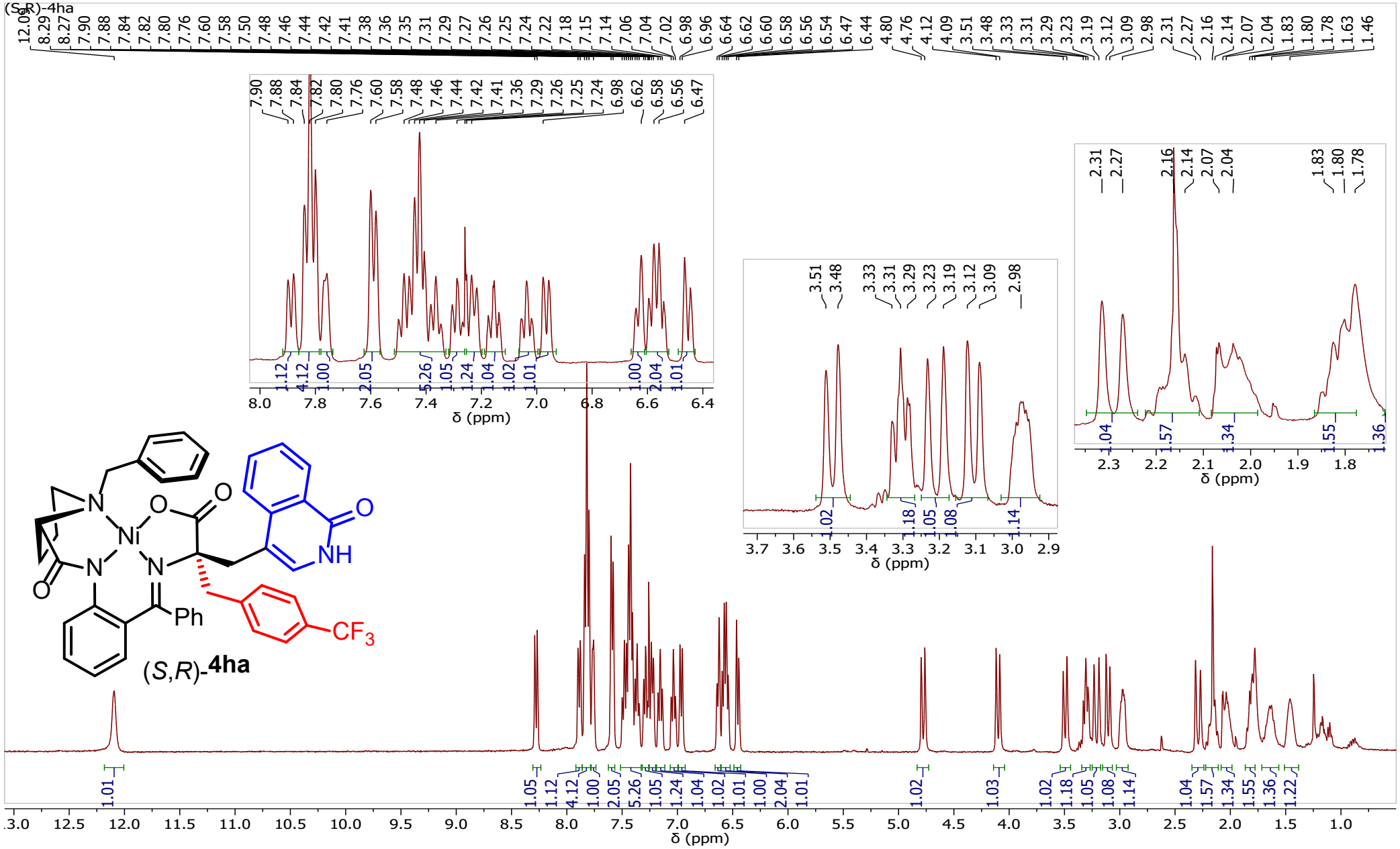

Figure S97. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ha** (in $CDCl_3$)

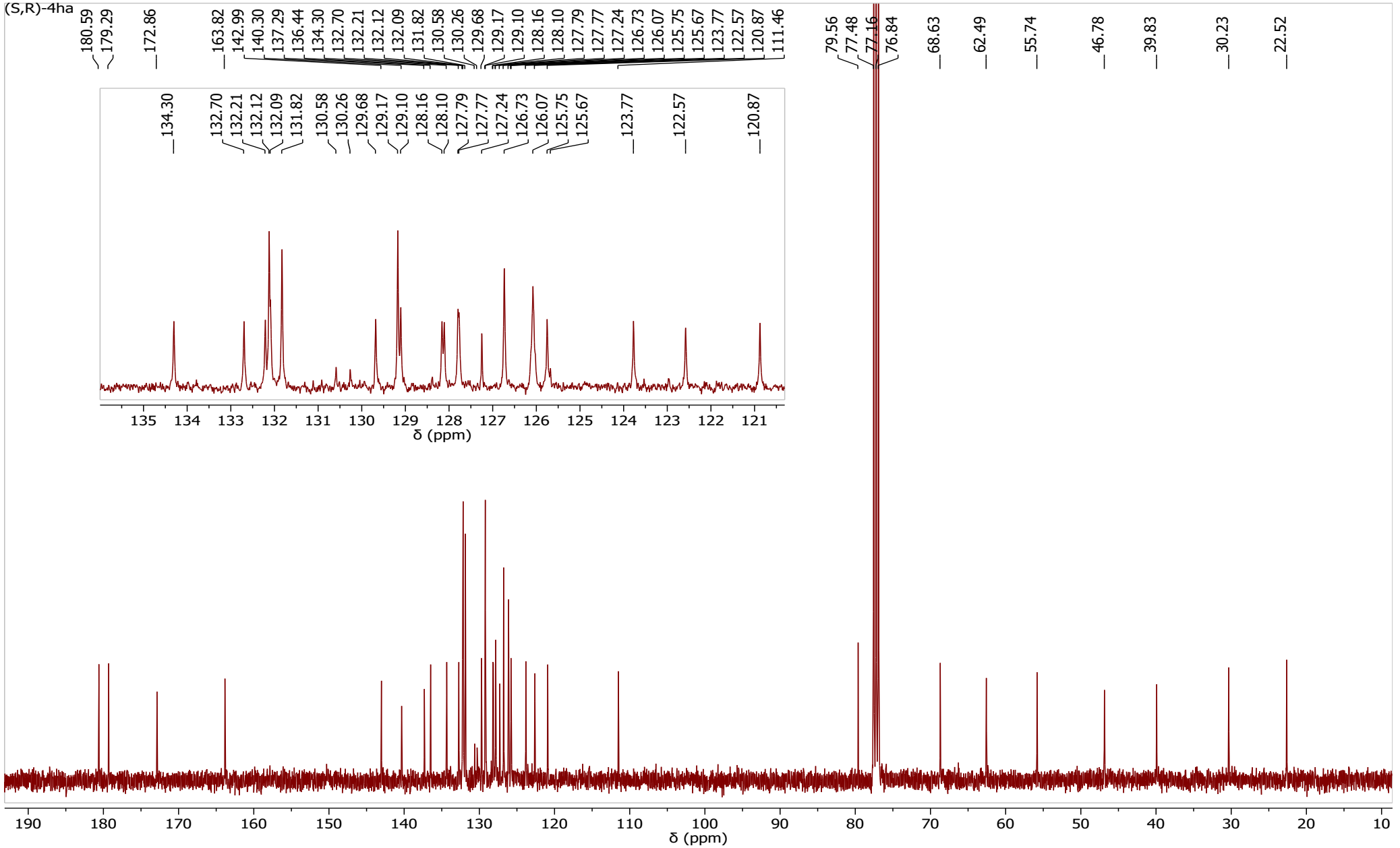

Figure S98. ^{13}C (101 MHz) NMR spectra of the Ni(II) complex (*S*,*R*)-**4ha** (in $CDCl_3$)

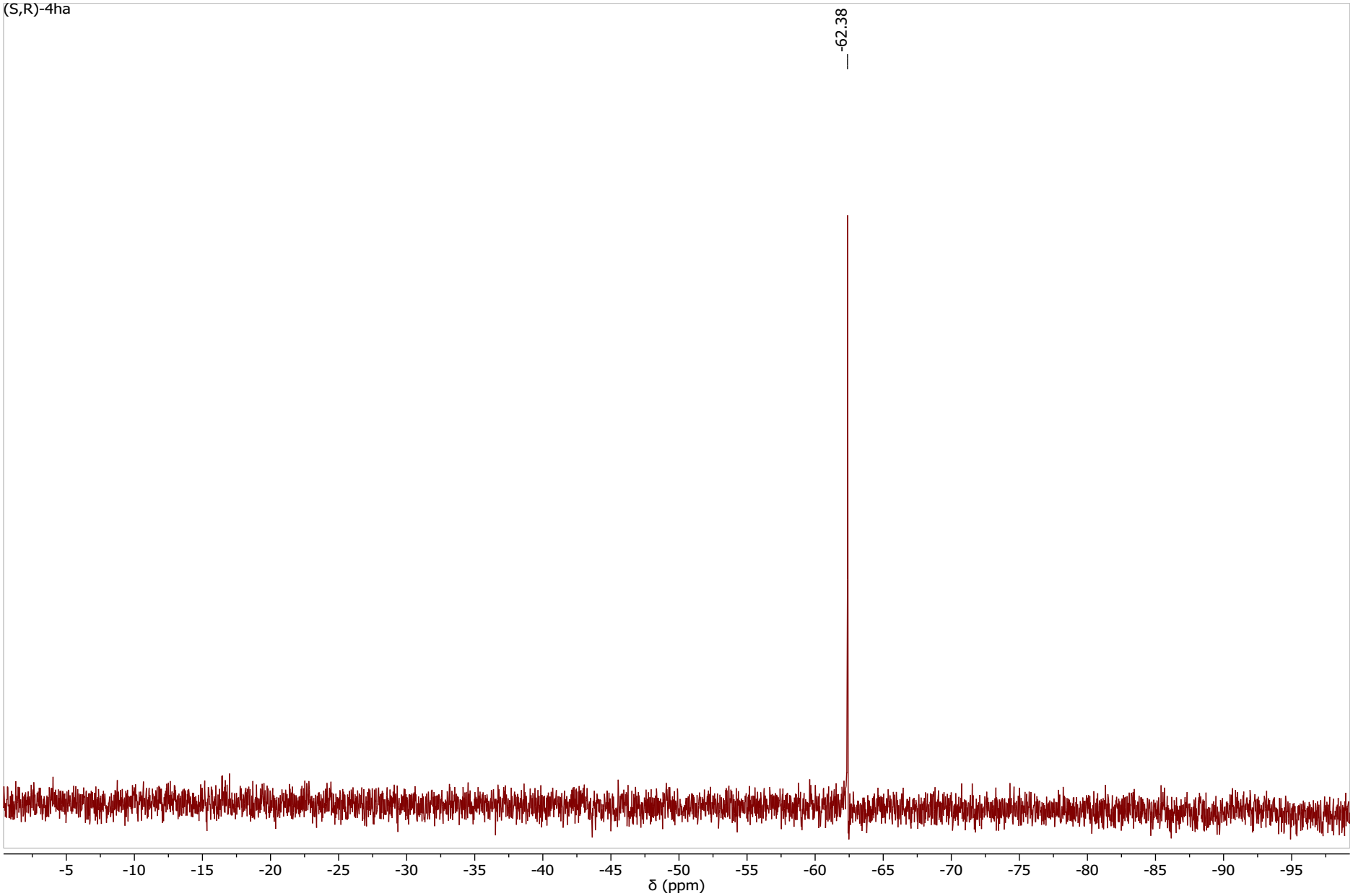

Figure S99. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**4ha** (in $CDCl_3$)

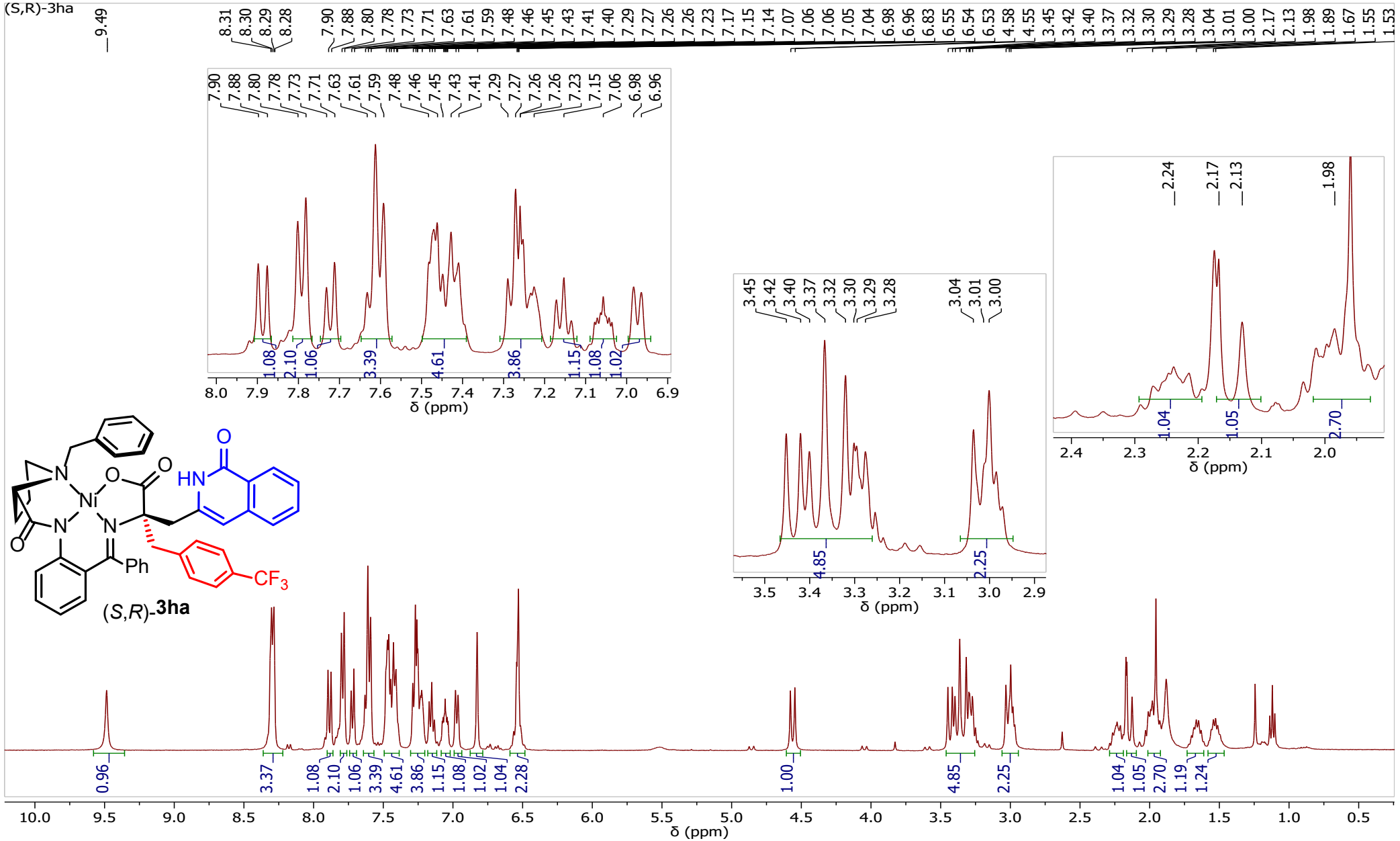

Figure S100. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ha** (in $CDCl_3$)

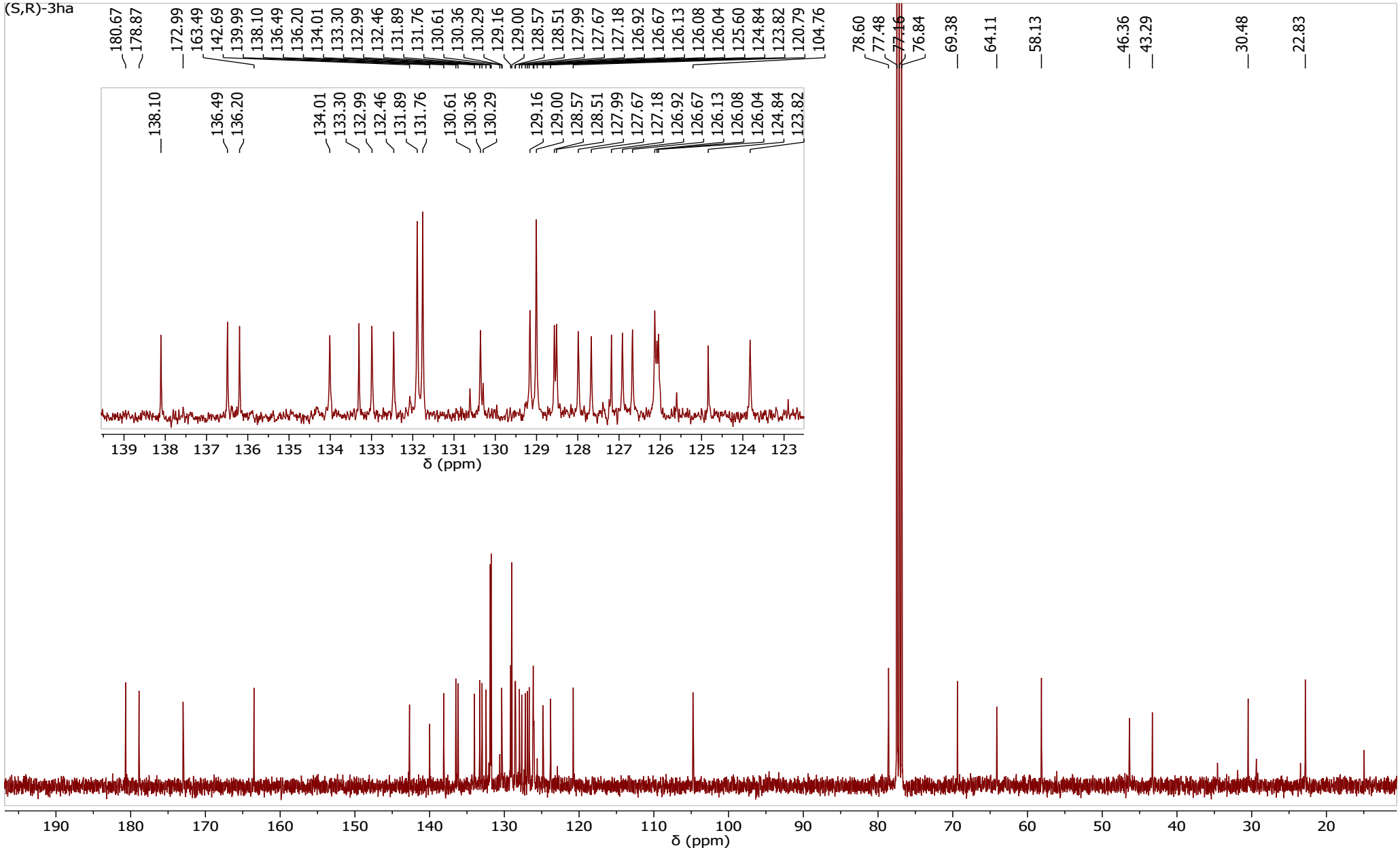

Figure S101. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ha** (in $CDCl_3$)

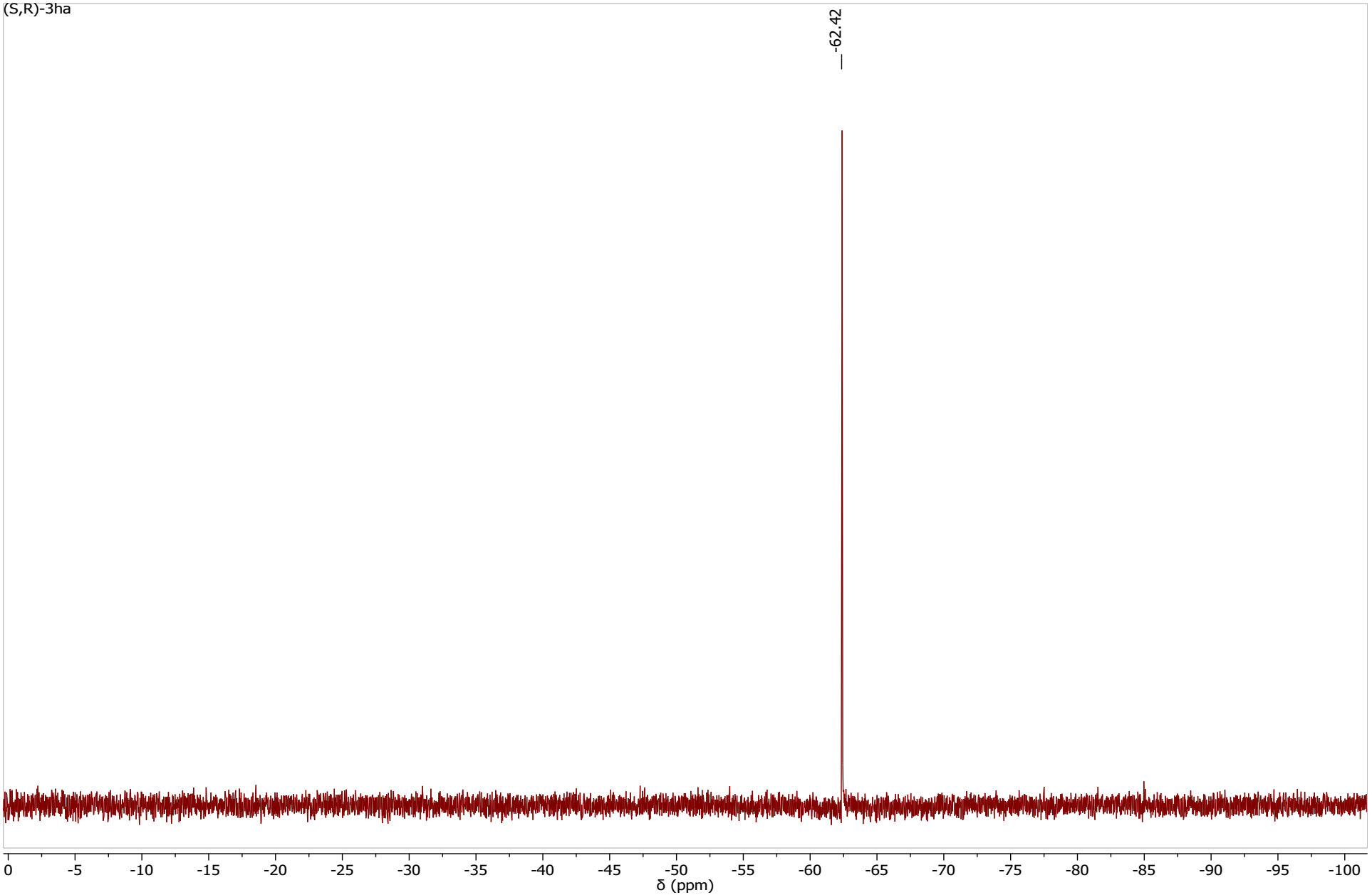

Figure S102. ^{19}F (376 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ha** (in $CDCl_3$)

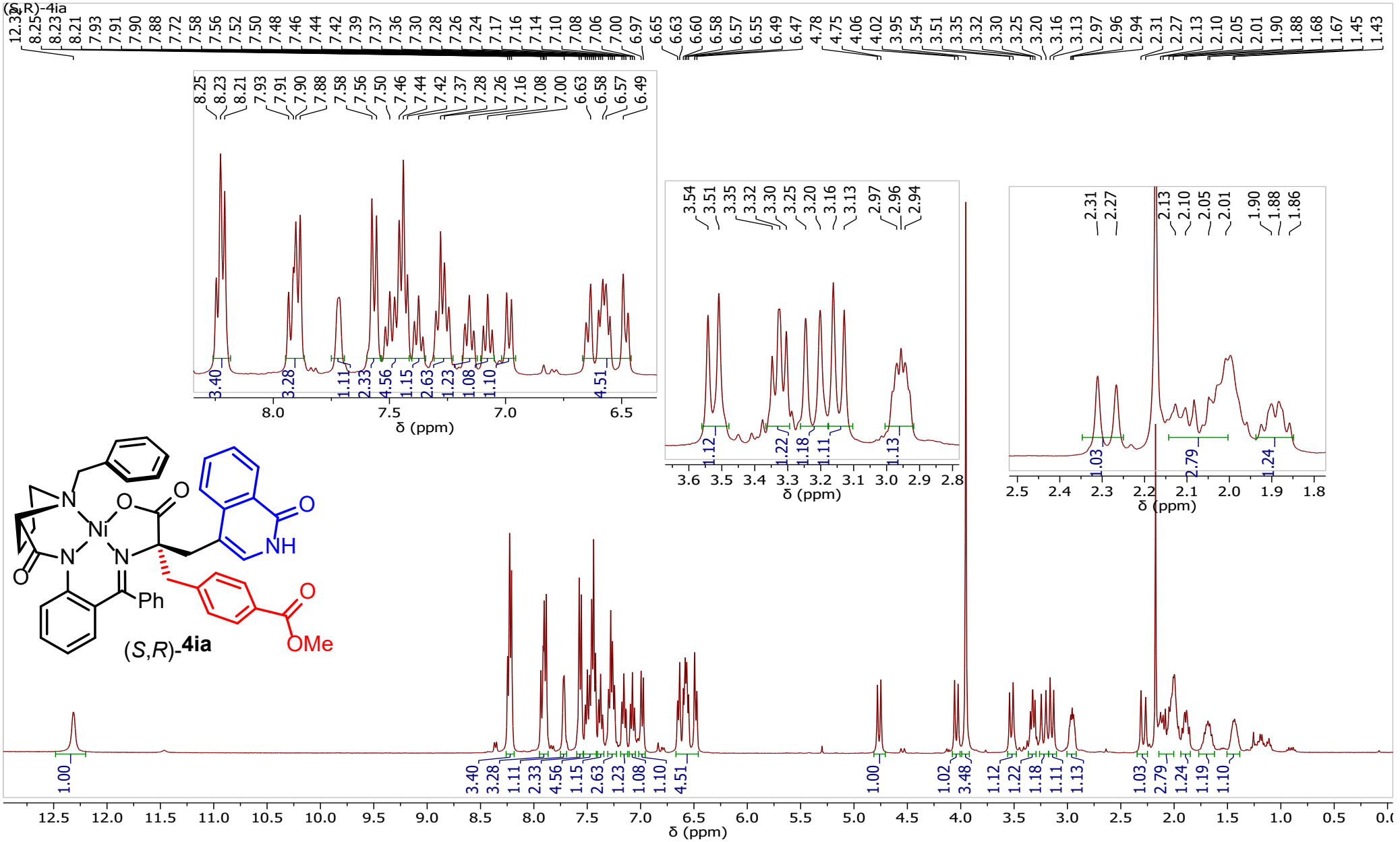

Figure S103. ^{1}H (400 MHz) spectrum of the Ni(II) complex (*S*,*R*)-**34ia** (in $CDCl_3$)

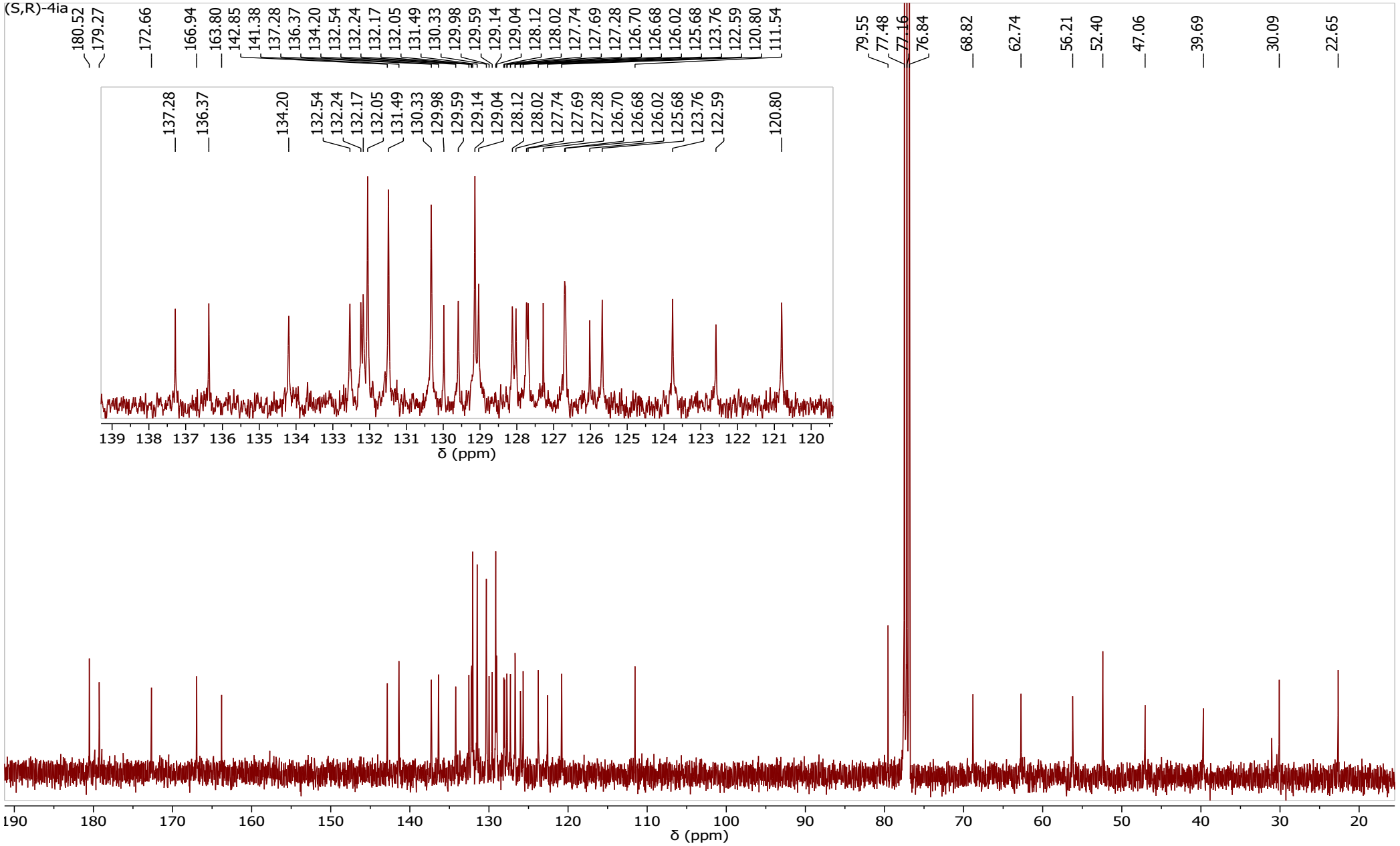

Figure S104. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**34ia** (in $CDCl_3$)

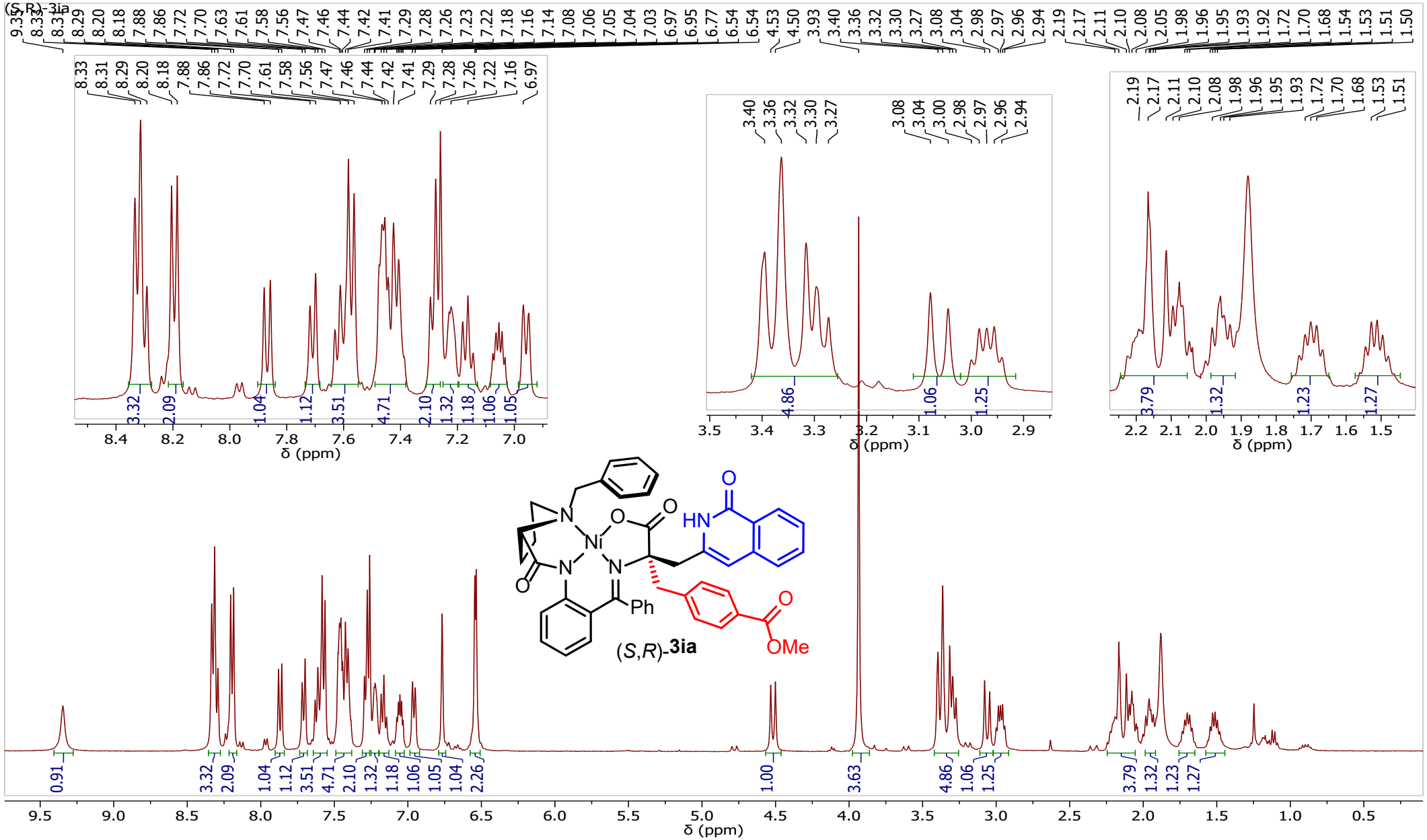

Figure S105. ^{1}H (400 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ia** (in $CDCl_3$)

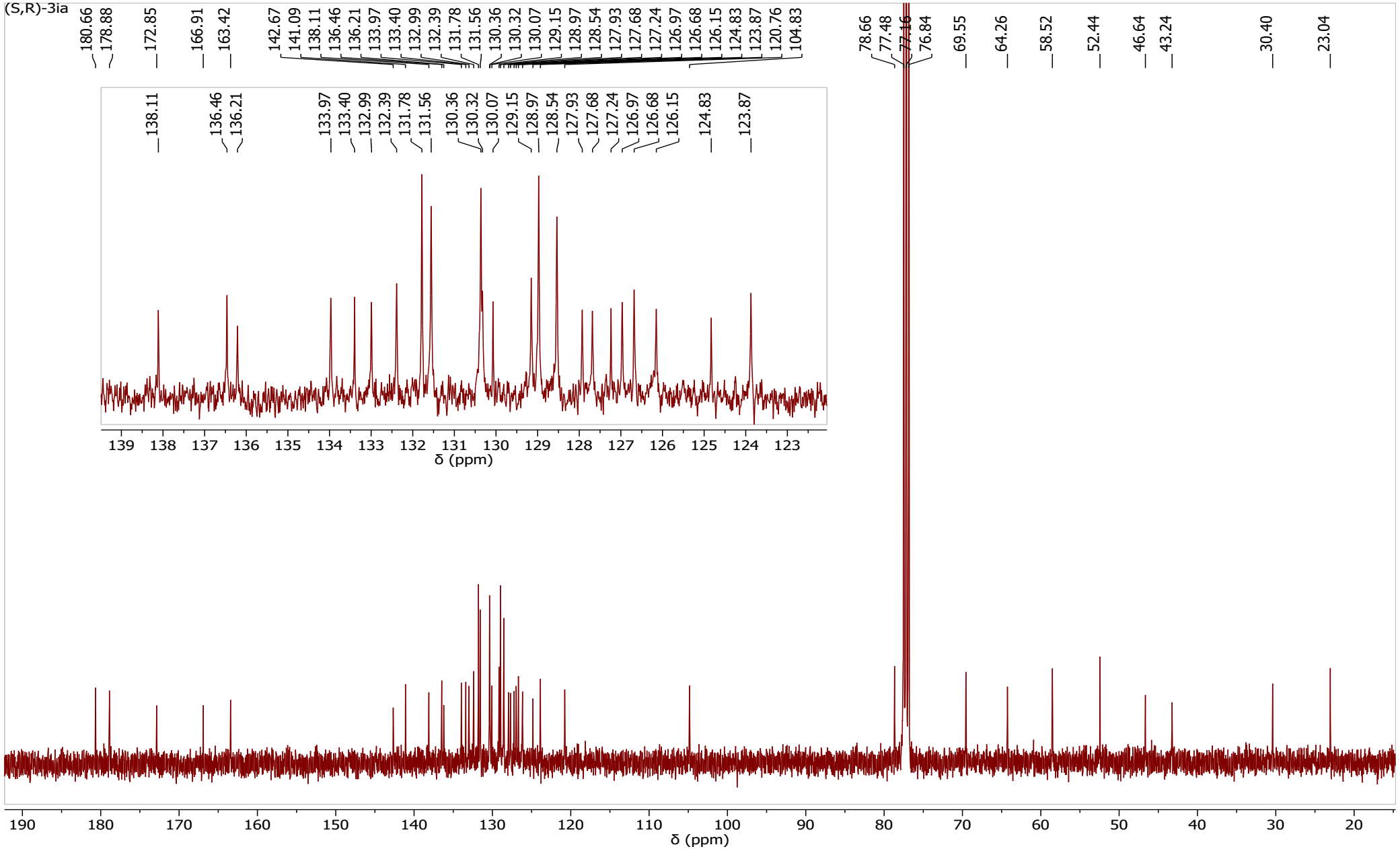

Figure S106. ^{13}C (101 MHz) NMR spectrum of the Ni(II) complex (*S*,*R*)-**3ia** (in $CDCl_3$)

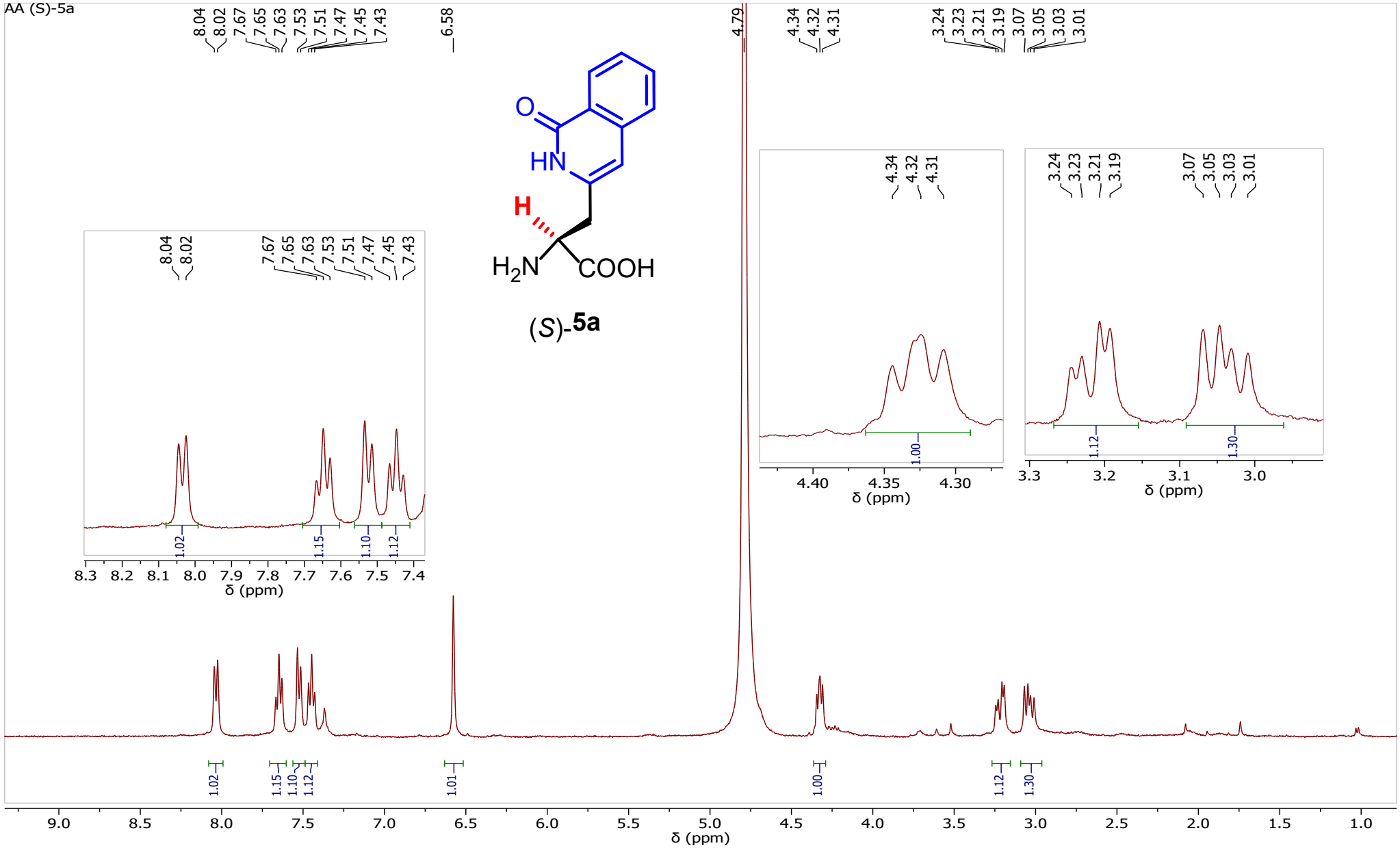

Figure S107. ^{1}H (400 MHz) NMR spectrum of AA (*S*)-**5a** (in D_2O)

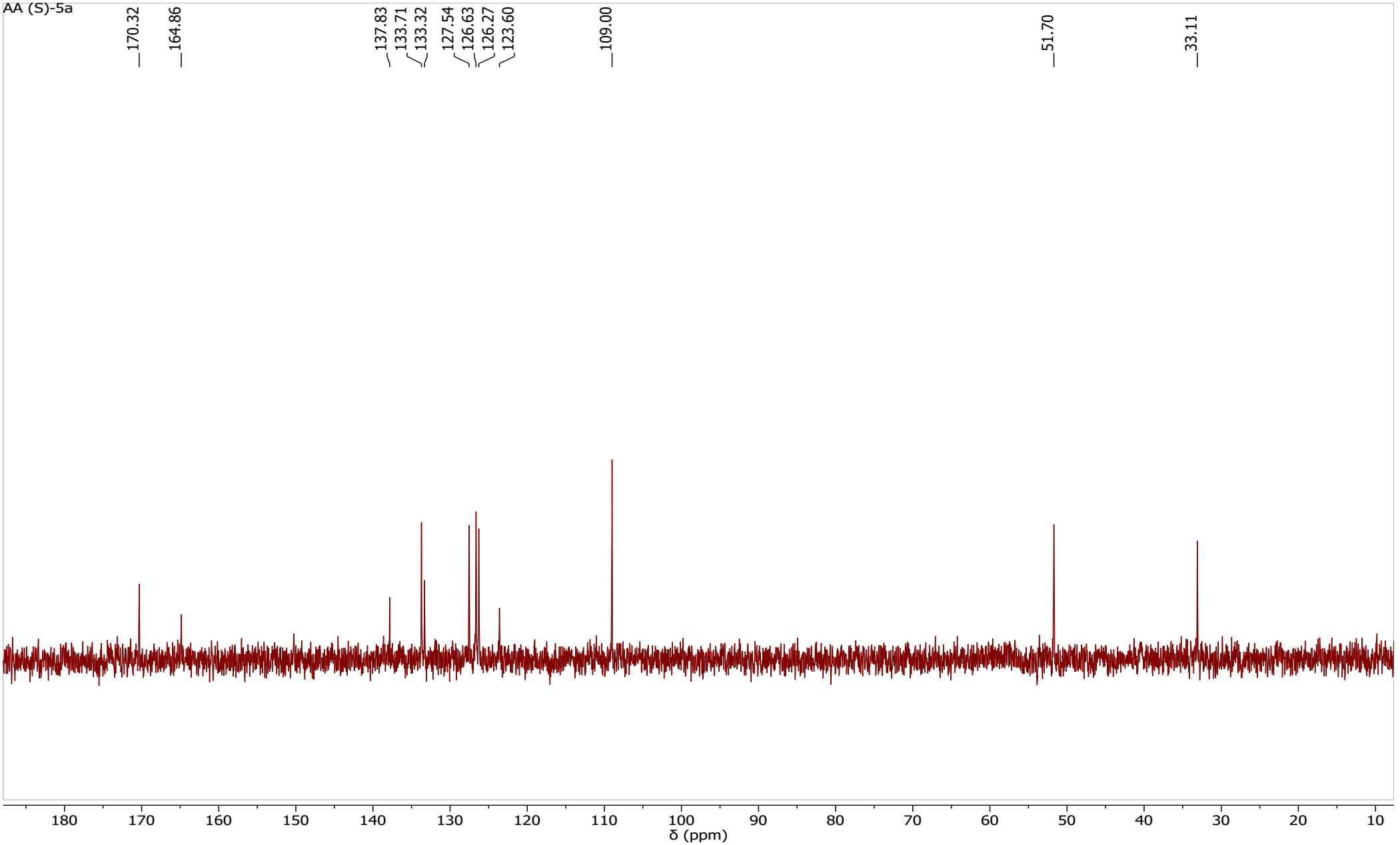

Figure S108. ^{13}C (101 MHz) NMR spectrum of AA (*S*)-**5a** (in D_2O)

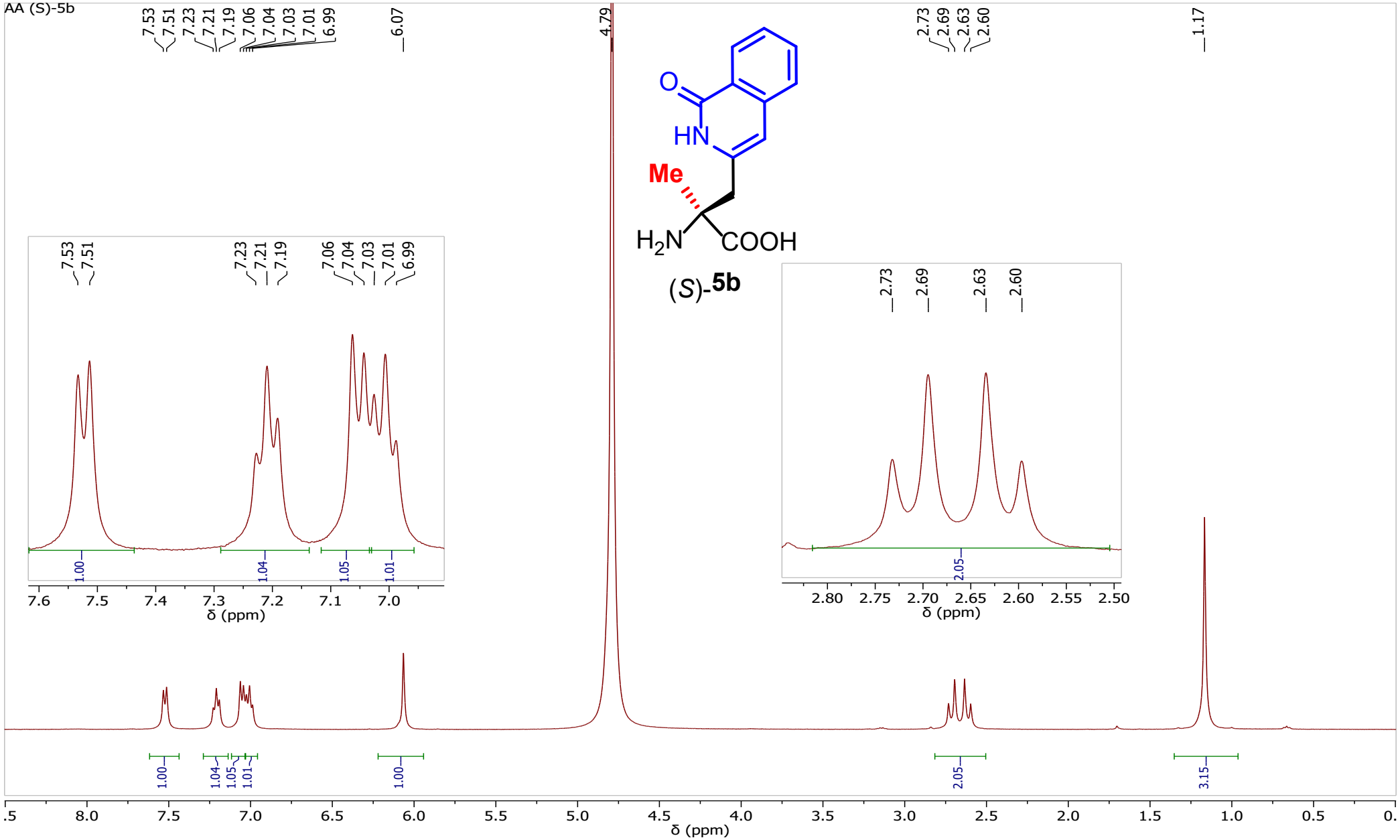

Figure S109. ^{1}H (400 MHz) NMR spectrum of AA (*S*)-**5b** (in D_2O)

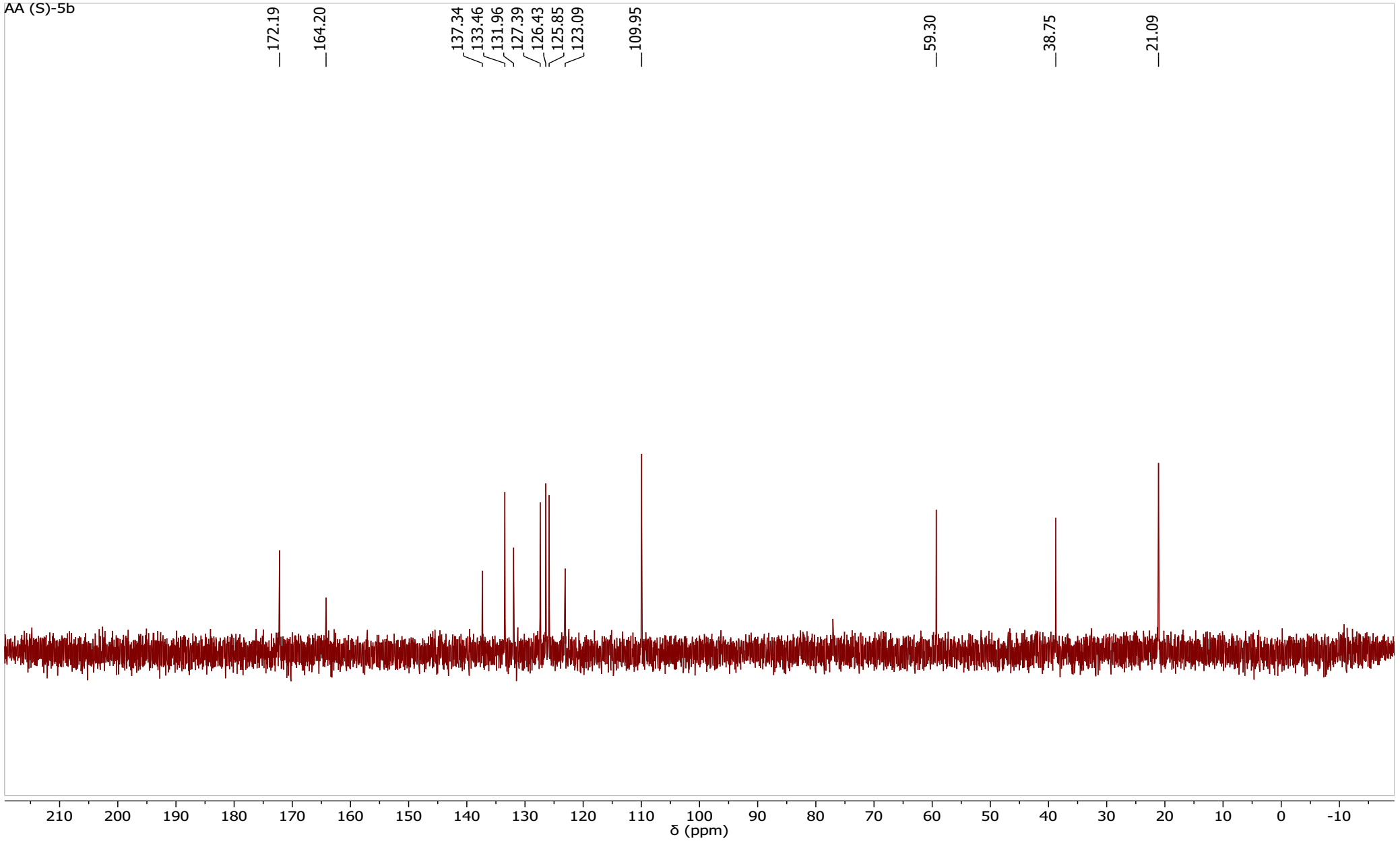

Figure S110. ^{13}C (101 MHz) NMR spectrum of AA (*S*)-**5b** (in D_2O)

HPLC traces of enantiopure amino acid 5a and 5b

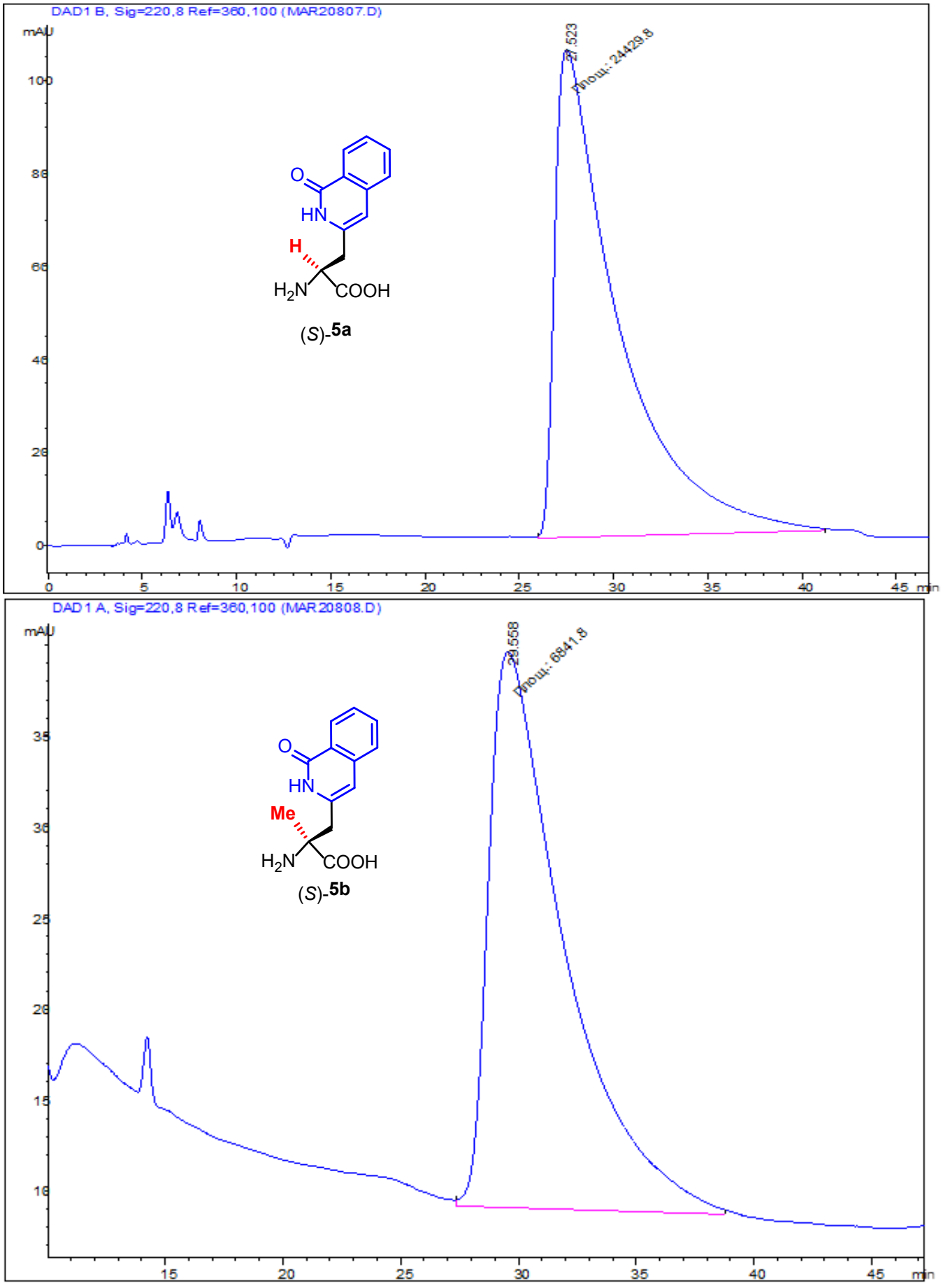

Figure S111. HPLC traces of the enantiopure amino acids **5a** and **5b**.