

## Electronic Supplementary Information

### A General Asymmetric Synthesis of Artificial Aliphatic and Perfluoroalkylated $\alpha$ -Amino Acids by Luche's Cross-Electrophile Coupling Reaction

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## General information

The reported catalytic reactions were performed in a round-bottom flask (10 mL). All solvents were purchased from commercial suppliers (Acros). Perfluoroalkyl iodides were purchased from SIA "P&M-Invest" Ltd. (Moscow, Russia, <http://en.fluorine1.ru>). The Ni(II) complex **1** was synthesized according to a literature procedure.<sup>[S1]</sup> Purchased reagents from commercial suppliers were used without further purification. If not stated otherwise, flash column chromatography was performed with silica gel 60 M from Macherey-Nagel.

## Instrumentation

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra and carbon nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded on a Bruker Avance 400 spectrometer operating at 400 MHz (<sup>1</sup>H) and 101 MHz (<sup>13</sup>C {<sup>1</sup>H}). Chemical shifts are reported in ppm relative to the residual solvent peak (CDCl<sub>3</sub>:  $\delta = 7.26$  ppm for <sup>1</sup>H NMR,  $\delta = 77.1$  for <sup>13</sup>C NMR). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant, integration, and nucleus. High-resolution mass spectra were recorded on 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 [ $\lambda(\text{MoK}_\alpha) = 0.71073 \text{ \AA}$ ,  $\omega$ -scans,  $2\theta < 58^\circ$ ] at 120 K.

## General procedure for the alkylation of a chiral Ni(II) complex **1** with different alkyl iodides

A round-bottom flask (10 mL) was charged with a solution of a chiral Ni(II) complex **1** (51 mg, 1.0 equiv., 0.10 mmol) in 1 mL of solvent mixture (solvent/H<sub>2</sub>O, 1:1) followed by the addition of Zn dust (23 mg, 3.5 equiv., 0.35 mmol), Cu(OAc)<sub>2</sub> (1.8 mg, 10 mol%, 0.01 mmol), NH<sub>4</sub>Cl (53.5 mg, 10 equiv., 1.0 mmol) and alkyl or perfluoroalkyl iodide **2** (4.0 equiv., 0.40 mmol; *in case of iodides **2 r** and **2 s**, they were added in two portions in 30 mins interval: 2.0 equiv. + 2.0 equiv.*). The mixture stirred at room temperature under standard atmosphere. Full conversion for each reaction was confirmed by TLC analysis. Then, the reaction mixture was dissolved with H<sub>2</sub>O and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated on a rotary evaporator, and the resulting residue was purified by column flash chromatography on silica gel to afford the desired product **3**.

### Ni(II) complex (*S,S*)-**3a**

Starting from a chiral Ni(II) complex **1** and isopropyl iodide **2a** with applying the *General Procedure*, the desired product (*S,S*)-**3a** was isolated as a red powder (46 mg, yield 83%, *dr* >17.7:1), eluent: EtOAc.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.10\text{--}8.00$  (m, 3H), 7.53–7.40 (m, 3H), 7.37–7.26 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.68–6.58 (m, 2H), 4.43 (d, *J* = 12.6 Hz, 1H), 3.87 (dd, *J* = 11.0, 3.8 Hz, 1H), 3.76–3.62 (m, 1H), 3.53 (d, *J* = 12.6 Hz, 1H), 3.51–3.42 (m, 2H),

2.79–2.66 (m, 1H), 2.59–2.42 (m, 2H), 2.25–2.16 (m, 1H), 2.05 (td,  $J = 11.2, 5.9$  Hz, 1H), 1.96–1.81 (m, 1H), 1.39–1.28 (m, 1H), 0.85 (d,  $J = 6.7$  Hz, 3H), 0.31 (d,  $J = 6.4$  Hz, 3H) ppm.

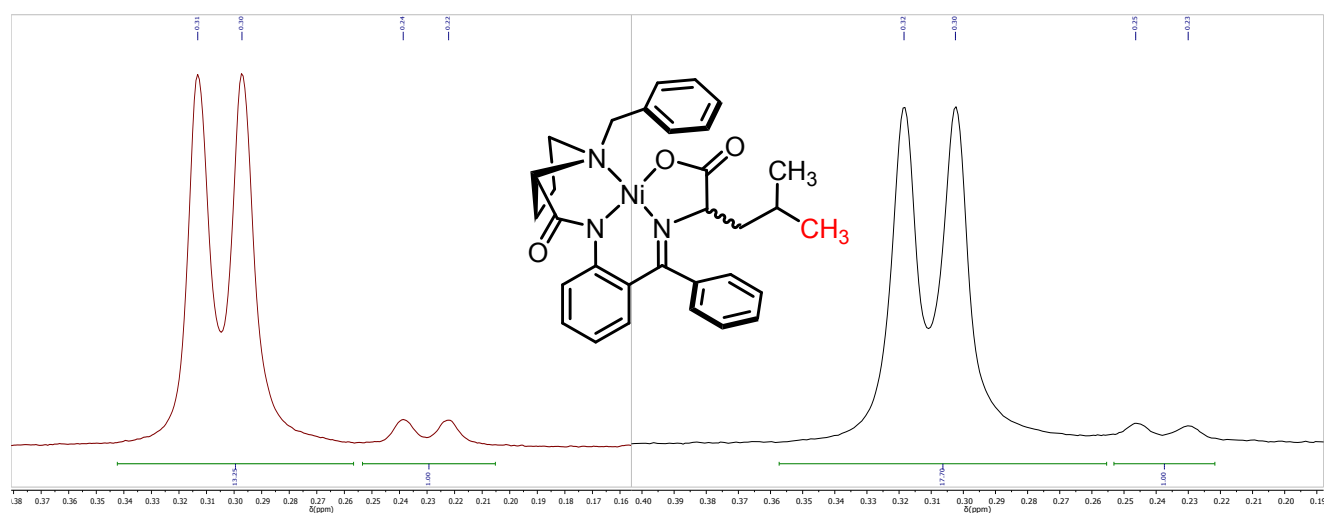
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 180.4, 179.5, 169.7, 142.1, 133.6, 133.4, 133.2, 132.0, 131.6, 129.8, 129.0, 128.9, 127.9, 127.7, 126.7, 123.9, 120.8, 70.3, 69.1, 63.1, 57.3, 46.3, 30.8, 24.5, 24.1, 23.9, 20.1$  ppm.

$[\alpha]_{\text{D}}^{25} +2363$  ( $c$  0.03, MeOH).

The structure of (*S,S*)-**3a** was determined by single crystal X-ray analysis (see Scheme 2 in main text and Part 5 in the SI).

The spectroscopic data were in agreement with the literature.<sup>[S2,S3]</sup>

Diastereoselective ratio (*dr* value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\text{CH}_3$  in (*S,S*)-**3a** and (*S,R*)-**3a** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below), ***dr* 13.2:1** (after reaction) and ***dr* 17.7:1** (after epimerization with MeONa) for (*S,S*)-**3a**/*(S,R)*-**3a**.



### *Ni*(II) complex (*S,S*)-**3b**

Starting from a chiral Ni(II) complex **1** and methyl iodide **2b** with applying the *General Procedure*, the desired product (*S,S*)-**3b** was isolated as a red powder (16 mg, yield 30%), eluent: EtOAc.

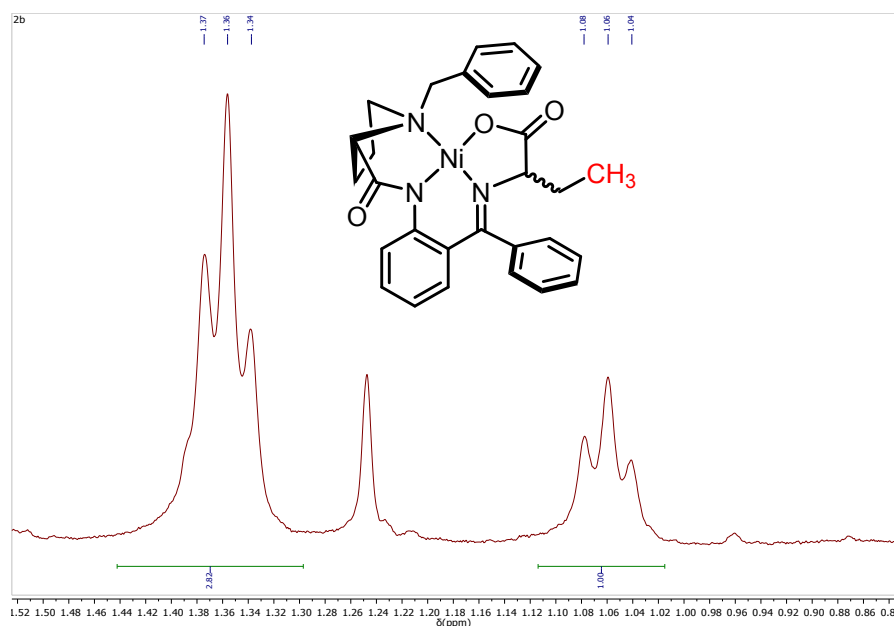
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.13$  (d,  $J = 8.7$  Hz, 1H), 8.04 (d,  $J = 7.5$  Hz, 2H), 7.56–7.39 (m, 3H), 7.34 (t,  $J = 7.6$  Hz, 2H), 7.26–7.22 (m, 1H), 7.19 (t,  $J = 7.5$  Hz, 1H), 7.16–7.10 (m, 1H), 6.92 (d,  $J = 7.4$  Hz, 1H), 6.69–6.60 (m, 2H), 4.43 (d,  $J = 12.7$  Hz, 1H), 3.88 (dd,  $J = 7.6, 3.6$  Hz, 1H), 3.59 (d,  $J = 12.7$  Hz, 1H), 3.55–3.35 (m, 2H), 2.81–2.70 (m, 1H), 2.58–2.45 (m, 1H), 2.19–2.00 (m, 2H), 1.98–1.85 (m, 1H), 1.84–1.63 (m, 2H), 1.35 (t,  $J = 7.4$  Hz, 3H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 180.5, 179.6, 170.7, 142.4, 134.00, 133.4, 133.3, 132.2, 131.7, 129.8, 129.04, 129.02, 128.98, 128.96, 127.7, 127.2, 126.6, 123.8, 120.8, 71.5, 70.4, 63.2, 57.0, 30.9, 28.5, 23.7, 10.1$  ppm.

$[\alpha]_{\text{D}}^{25} +2606$  ( $c$  0.03, MeOH).

The spectroscopic data were in agreement with the literature.<sup>[S3]</sup>

Diastereoselective ratio (*dr* value) was determined according to the <sup>1</sup>H NMR peak areas of **CH<sub>3</sub>** in (*S,S*)-**3b** and (*S,R*)-**3b** from the isolated mixture of products (partial <sup>1</sup>H NMR of the diastereoisomers is shown below), ***dr* 2.8:1** (after reaction) for (*S,S*)-**3b**/*(S,R)*-**3b**.



### *Ni*(II) complex (*S,S*)-**3c**

Starting from a chiral Ni(II) complex **1** and ethyl iodide **2c** with applying the *General Procedure*, the desired product (*S,S*)-**3c** was isolated as a red powder (48 mg, yield 89%, *dr* 23.1:1), eluent: EtOAc.

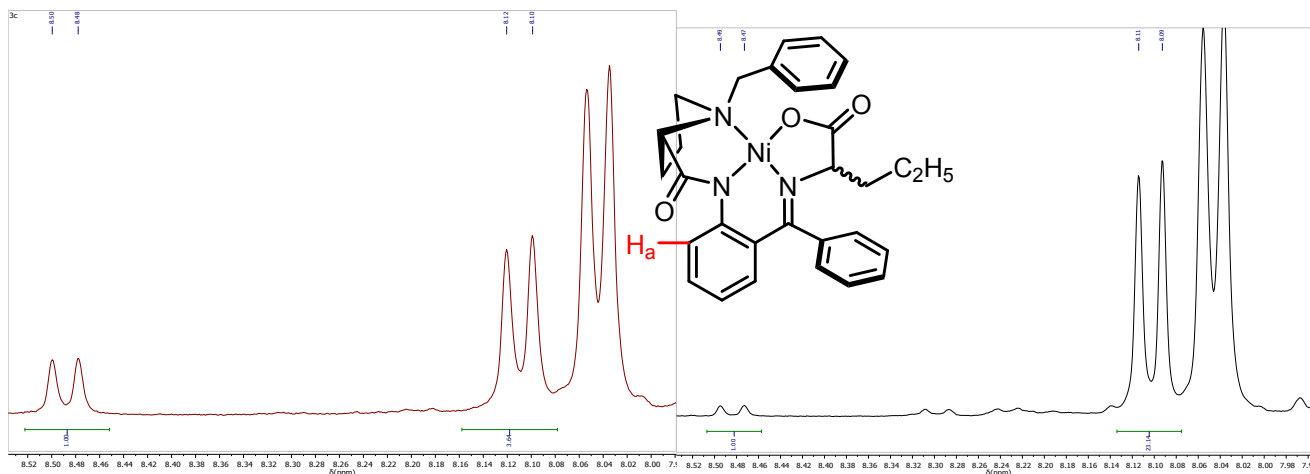
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.10 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.53–7.41 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25–7.20 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.14–7.08 (m, 1H), 6.91 (d, *J* = 7.3 Hz, 1H), 6.67–6.58 (m, 2H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.90 (dd, *J* = 7.9, 2.4 Hz, 1H), 3.63–3.42 (m, 4H), 2.80–2.68 (m, 1H), 2.58–2.43 (m, 1H), 2.20–2.11 (m, 1H), 2.10–1.93 (m, 3H), 1.65–1.53 (m, 2H), 0.77 (t, *J* = 6.9 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.4, 179.6, 170.3, 142.2, 133.9, 133.3, 133.3, 133.2, 132.1, 131.6, 129.7, 129.0, 128.95, 128.9, 127.6, 127.3, 126.6, 123.7, 120.8, 70.3, 70.2, 63.2, 57.1, 37.6, 30.8, 23.7, 18.7, 13.7 ppm.

$[\alpha]_D^{25} +2343$  (*c* 0.03, MeOH).

The spectroscopic data were in agreement with the literature.<sup>[S2]</sup>

Diastereoselective ratio (*dr* value) was determined according to the <sup>1</sup>H NMR peak areas of **H<sub>a</sub>** in (*S,S*)-**3c** and (*S,R*)-**3c** from the isolated mixture of products (partial <sup>1</sup>H NMR of the diastereoisomers is shown below), ***dr* 3.6:1** (after reaction) and ***dr* 23.1:1** (after epimerization with MeONa) for (*S,S*)-**3c**/*(S,R)*-**3c**.



### Ni(II) complex (*S,S*)-**3d**

Starting from a chiral Ni(II) complex **1** and *n*-propyl iodide **2d** with applying the *General Procedure*, the desired product (*S,S*)-**3d** was isolated as a red powder (45 mg, yield 81%, *dr* 27.3:1), eluent: EtOAc.

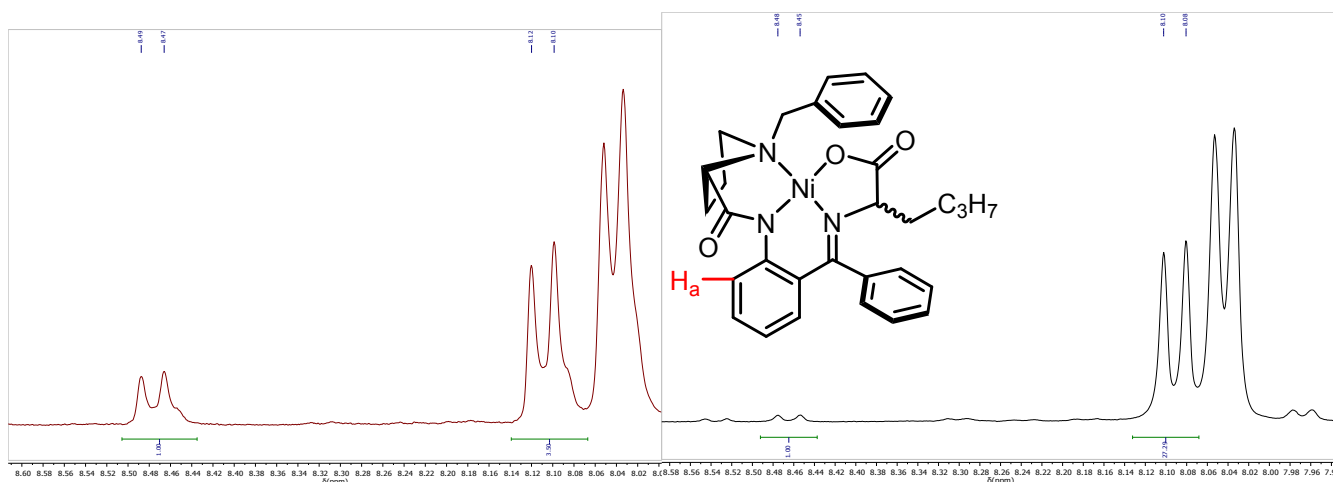
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.09 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.51–7.39 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.25–7.22 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.14–7.08 (m, 1H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.67–6.57 (m, 2H), 4.41 (d, *J* = 12.7 Hz, 1H), 3.91 (dd, *J* = 7.6, 2.6 Hz, 1H), 3.61–3.44 (m, 4H), 2.81–2.69 (m, 1H), 2.59–2.44 (m, 1H), 2.22–2.09 (m, 2H), 2.09–1.99 (m, 1H), 1.96–1.84 (m, 1H), 1.67–1.55 (m, 2H), 1.27–1.09 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H) ppm.

<sup>13</sup>C (*JMOD*) NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.4, 179.7, 170.4, 142.2, 133.8, 133.3, 133.26, 132.1, 131.6, 129.7, 129.0, 128.9, 127.6, 127.2, 126.6, 123.7, 120.8, 70.5, 70.3, 63.2, 57.0, 35.0, 30.8, 27.5, 23.6, 22.5, 13.9 ppm.

$[\alpha]_D^{25}$  +2450 (*c* 0.02, MeOH).

The spectroscopic data were in agreement with the literature.<sup>[S4,S5]</sup>

Diastereoselective ratio (*dr* value) was determined according to the <sup>1</sup>H NMR peak areas of **H<sub>a</sub>** in (*S,S*)-**3d** and (*S,R*)-**3d** from the isolated mixture of products (partial <sup>1</sup>H NMR of the diastereoisomers is shown below), ***dr* 3.5:1** (after reaction) and ***dr* 27.3:1** (after epimerization with MeONa) for (*S,S*)-**3d**/*(S,R)*-**3d**.



### Ni(II) complex (*S,S*)-3e

Starting from a chiral Ni(II) complex **1** and *n*-pentyl iodide **2e** with applying the *General Procedure*, the desired product (*S,S*)-**3e** was isolated as a red powder (43 mg, yield 74%, *dr* 21.6:1), eluent: EtOAc.

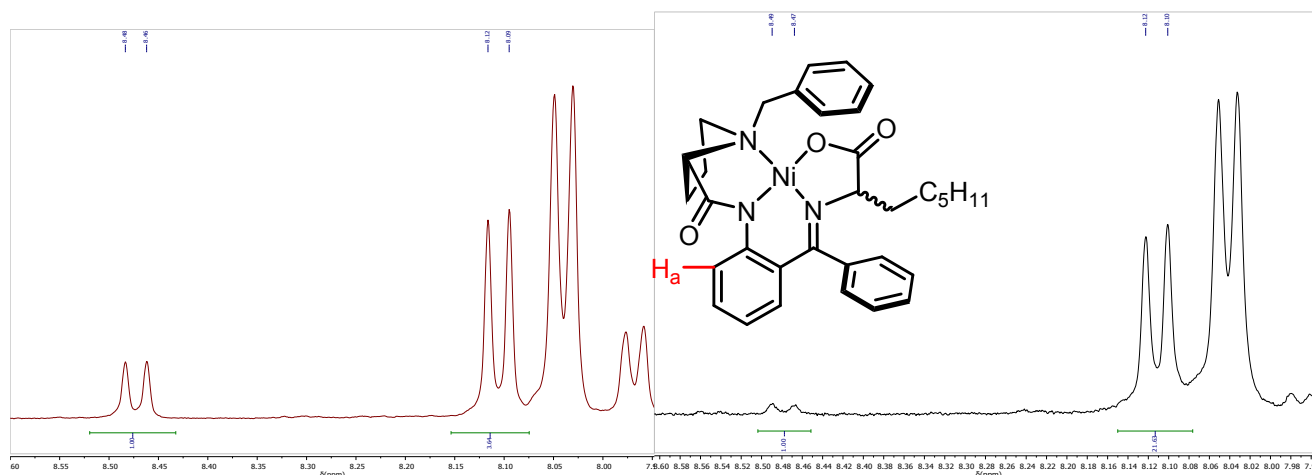
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.11 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.54–7.41 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25–7.22 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.15–7.09 (m, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.68–6.59 (m, 2H), 4.43 (d, *J* = 12.7 Hz, 1H), 3.95–3.87 (m, 1H), 3.61–3.42 (m, 4H), 2.81–2.70 (m, 1H), 2.59–2.45 (m, 1H), 2.21–2.00 (m, 3H), 1.98–1.85 (m, 1H), 1.68–1.54 (m, 2H), 1.28–1.07 (m, 6H), 0.85 (t, *J* = 6.6 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.5, 179.6, 170.4, 142.3, 133.9, 133.3, 132.2, 131.7, 129.8, 129.0, 128.9, 127.7, 127.3, 126.7, 123.8, 120.8, 70.5, 70.4, 63.2, 57.0, 35.4, 31.7, 30.8, 29.1, 25.4, 23.7, 22.7, 14.1 ppm.

HRMS (ESI, *m/z*) calcd. for C<sub>33</sub>H<sub>38</sub>N<sub>3</sub>NiO<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 582.2261, found: 582.2264.

$[\alpha]_D^{25}$  +1571 (*c* 0.03, MeOH).

Diastereoselective ratio (*dr* value) was determined according to the <sup>1</sup>H NMR peak areas of **H<sub>a</sub>** in (*S,S*)-**3e** and (*S,R*)-**3e** from the isolated mixture of products (partial <sup>1</sup>H NMR of the diastereoisomers is shown below), ***dr* 3.6:1** (after reaction) and ***dr* 21.6:1** (after epimerization with MeONa) for (*S,S*)-**3e**/*S,R*)-**3e**.



### Ni(II) complex (*S,S*)-3f

Starting from a chiral Ni(II) complex **1** and *n*-hexyl iodide **2f** with applying the *General Procedure*, the desired product (*S,S*)-**3f** was isolated as a red powder (50 mg, yield 84%, *dr* 26.2:1), eluent: EtOAc.

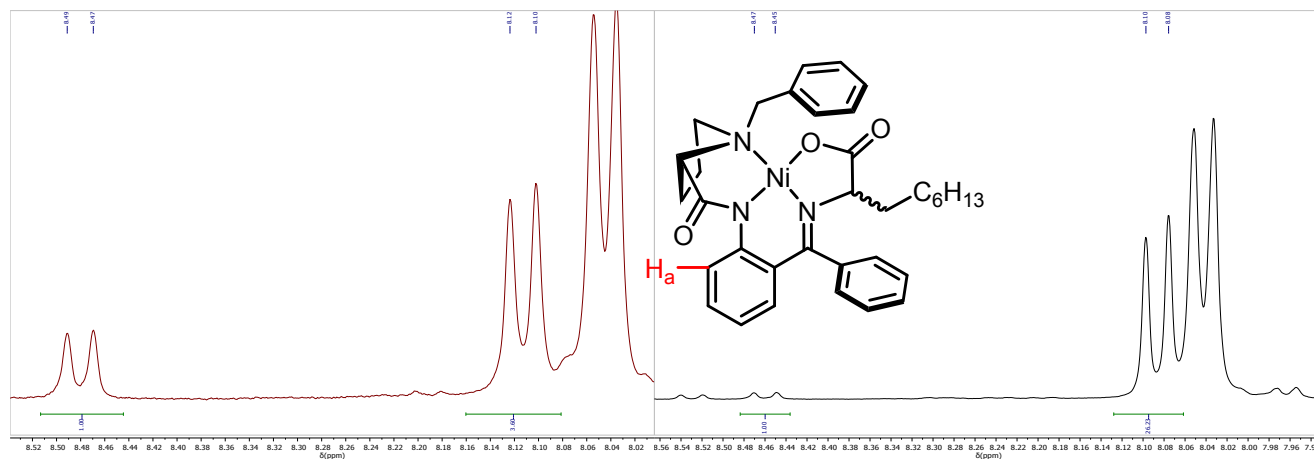
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.12 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.52–7.40 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25–7.22 (m, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.16–7.09 (m, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.68–6.59 (m, 2H), 4.44 (d, *J* = 12.7 Hz, 1H), 3.91 (d, *J* = 7.9 Hz, 1H), 3.62–3.42 (m, 4H), 2.82–2.71 (m, 1H), 2.59–2.45 (m, 1H), 2.20–2.00 (m, 3H), 1.98–1.85 (m, 1H), 1.68–1.55 (m, 2H), 1.28–1.09 (m, 8H), 0.86 (t, *J* = 6.4 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.5, 179.7, 170.4, 142.3, 134.0, 133.3, 133.2, 132.2, 131.7, 129.8, 129.0, 128.9, 127.7, 127.3, 126.7, 123.8, 120.9, 70.5, 70.4, 63.2, 57.0, 35.4, 31.9, 30.9, 29.4, 29.2, 25.5, 23.7, 22.7, 14.2 ppm.

$[\alpha]_D^{25} +2194$  ( $c$  0.04, MeOH).

The spectroscopic data were in agreement with the literature.<sup>[S6]</sup>

Diastereoselective ratio ( $dr$  value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\text{H}_a$  in ( $S,S$ )-**3f** and ( $S,R$ )-**3f** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below),  $dr$  3.6:1 (after reaction) and  $dr$  26.2:1 (after epimerization with MeONa) for ( $S,S$ )-**3f**/ $(S,R)$ -**3f**.



### *Ni(II) complex (S,S)-3g*

Starting from a chiral Ni(II) complex **1** and *n*-octyl iodide **2g** with applying the *General Procedure*, the desired product ( $S,S$ )-**3g** was isolated as a red powder (38 mg, yield 61%), eluent: EtOAc

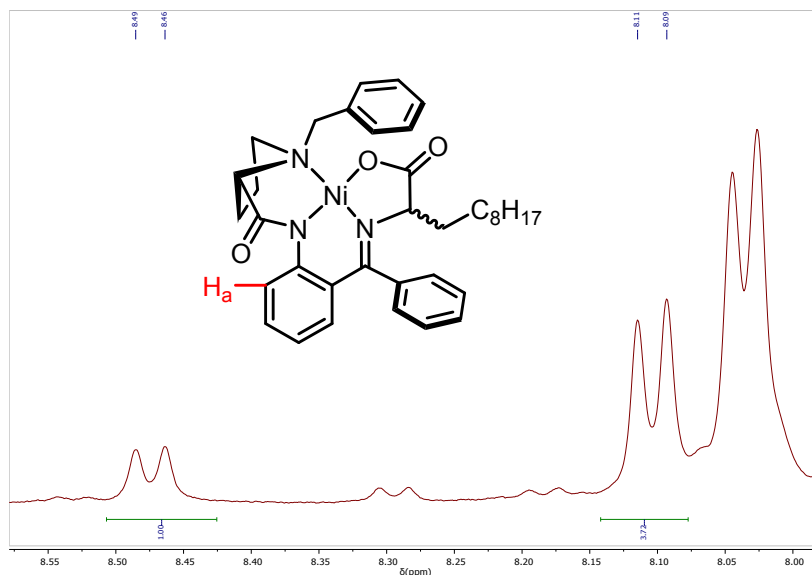
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12 (d,  $J$  = 8.5 Hz, 1H), 8.04 (d,  $J$  = 7.3 Hz, 2H), 7.52–7.40 (m, 3H), 7.34 (t,  $J$  = 7.0 Hz, 2H), 7.25–7.22 (m, 1H), 7.18 (t,  $J$  = 7.4 Hz, 1H), 7.15–7.09 (m, 1H), 6.91 (d,  $J$  = 7.2 Hz, 1H), 6.68–6.59 (m, 2H), 4.44 (d,  $J$  = 12.7 Hz, 1H), 3.95–3.88 (m, 1H), 3.62–3.42 (m, 4H), 2.82–2.70 (m, 1H), 2.59–2.45 (m, 1H), 2.21–2.00 (m, 3H), 1.97–1.85 (m, 1H), 1.67–1.54 (m, 2H), 1.29–1.07 (m, 12H), 0.87 (t,  $J$  = 6.0 Hz, 3H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 180.5, 179.7, 170.4, 142.3, 134.0, 133.4, 133.3, 132.2, 131.7, 129.8, 129.0, 128.9, 127.7, 127.3, 126.7, 123.8, 120.9, 70.6, 70.4, 63.2, 57.0, 35.4, 32.0, 30.9, 29.6, 29.5, 29.4, 29.3, 25.5, 23.7, 22.8, 14.2 ppm.

HRMS (ESI,  $m/z$ ) calcd. for  $\text{C}_{36}\text{H}_{44}\text{N}_3\text{NiO}_3^+$   $[\text{M}+\text{H}]^+$ : 624.2731, found: 624.2732.

$[\alpha]_D^{25} +2222$  ( $c$  0.03, MeOH).

Diastereoselective ratio ( $dr$  value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\text{H}^a$  in ( $S,S$ )-**3g** and ( $S,R$ )-**3g** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below),  $dr$  3.7:1 (after reaction) for ( $S,S$ )-**3g**/ $(S,R)$ -**3g**.



### *Ni(II) complex (S,S)-3h*

Starting from a chiral Ni(II) complex **1** and *n*-decyl iodide **2h** with applying the *General Procedure*, the desired product (*S,S*)-**3h** was isolated as a red powder (42 mg, yield 64%), eluent: EtOAc.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.12 (d,  $J$  = 8.7 Hz, 1H), 8.04 (d,  $J$  = 7.5 Hz, 2H), 7.54–7.41 (m, 3H), 7.34 (t,  $J$  = 7.6 Hz, 2H), 7.25–7.22 (m, 1H), 7.19 (t,  $J$  = 7.4 Hz, 1H), 7.16–7.10 (m, 1H), 6.91 (d,  $J$  = 7.3 Hz, 1H), 6.69–6.59 (m, 2H), 4.44 (d,  $J$  = 12.7 Hz, 1H), 3.92 (dd,  $J$  = 7.9, 2.9 Hz, 1H), 3.62–3.42 (m, 4H), 2.82–2.71 (m, 1H), 2.59–2.46 (m, 1H), 2.20–2.00 (m, 3H), 1.97–1.85 (m, 1H), 1.68–1.55 (m, 2H), 1.29–1.07 (m, 16H), 0.87 (t,  $J$  = 6.7 Hz, 3H) ppm.

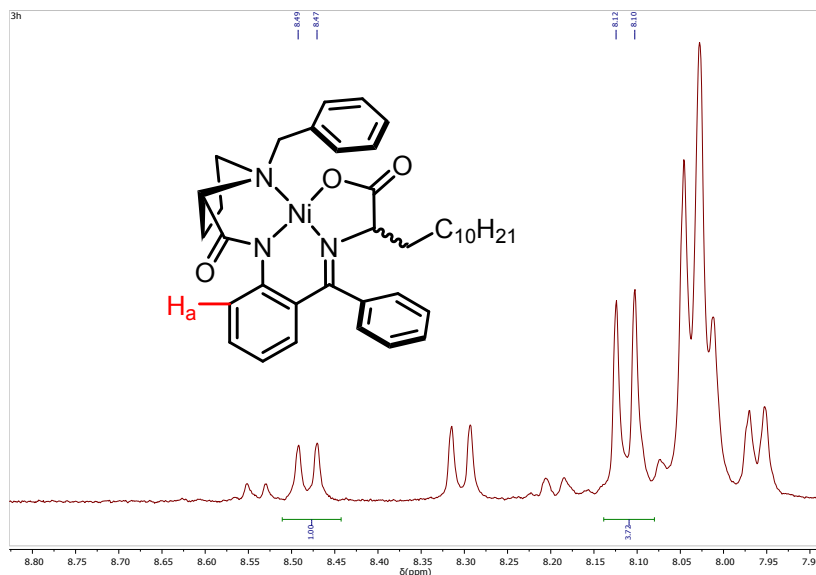
$^{13}\text{C}$  (*JMOD*) NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 180.5, 179.7, 170.4, 142.3, 134.0, 133.4, 133.3, 132.2, 131.7, 129.8, 129.1, 129.0, 127.7, 127.3, 126.7, 123.8, 120.9, 70.6, 70.4, 63.2, 57.0, 35.4, 32.0, 30.9, 29.73, 29.7, 29.6, 29.5, 29.4, 25.5, 23.7, 22.8, 14.3 ppm.

HRMS (ESI,  $m/z$ ) calcd. for  $\text{C}_{38}\text{H}_{48}\text{N}_3\text{NiO}_3^+$  [ $\text{M}+\text{H}$ ] $^+$ : 652.3044, found: 652.3037.

$[\alpha]_{\text{D}}^{25}$  +2269 ( $c$  0.03, MeOH).

Diastereoselective ratio (*dr* value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\text{H}^{\text{a}}$  in (*S,S*)-**3h** and (*S,R*)-**3h** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below), *dr* **3.7:1** for (*S,S*)-**3h**/*(S,R)*-**3h**.





### Ni(II) complex (*S,S*)-**3i**

Starting from a chiral Ni(II) complex **1** and *tert*-butyl iodide **2i** with applying the *General Procedure*, the desired product (*S,S*)-**3i** was isolated as a red powder (54 mg, yield 95%, *dr* 21.3:1), eluent: EtOAc.

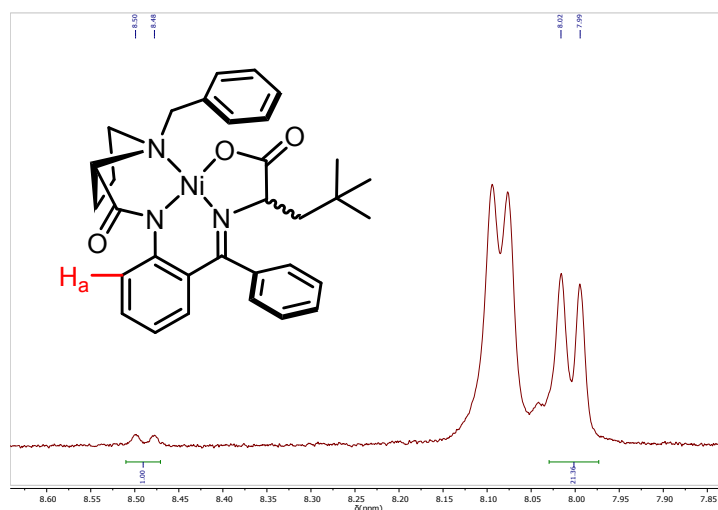
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.09 (d,  $J$  = 7.0 Hz, 2H), 7.99 (d,  $J$  = 7.5 Hz, 1H), 7.55–7.41 (m, 3H), 7.33 (t,  $J$  = 7.5 Hz, 2H), 7.30–7.26 (m, 1H), 7.16 (t,  $J$  = 7.3 Hz, 1H), 7.13–7.06 (m, 1H), 6.90 (d,  $J$  = 7.2 Hz, 1H), 6.68–6.57 (m, 2H), 4.44 (d,  $J$  = 12.1 Hz, 1H), 3.96–3.84 (m, 1H), 3.80–3.66 (m, 1H), 3.60–3.41 (m, 3H), 2.86–2.68 (m, 2H), 2.63–2.45 (m, 1H), 2.28–2.17 (m, 1H), 2.13–2.03 (m, 1H), 1.49 (dd,  $J$  = 13.7, 2.8 Hz, 1H), 0.73 (s, 9H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.4, 169.1, 141.9, 133.5, 133.4, 133.1, 132.0, 131.6, 129.8, 129.0, 128.9, 127.8, 127.7, 126.7, 123.9, 120.9, 70.3, 68.8, 63.0, 57.4, 51.4, 30.8, 30.6, 29.6, 24.1 ppm.

$[\alpha]_D^{25}$  +1714 ( $c$  0.02, MeOH).

The spectroscopic data were in agreement with the literature.<sup>[S2]</sup>

Diastereoselective ratio (*dr* value) was determined according to the <sup>1</sup>H NMR peak areas of **Ha** in (*S,S*)-**3i** and (*S,R*)-**3i** from the isolated mixture of products (partial <sup>1</sup>H NMR of the diastereoisomers is shown below), ***dr* 21.3:1** (*after reaction*) for (*S,S*)-**3i**/*(S,R)*-**3i**.



### Ni(II) complex (S,S)-3j

Starting from a chiral Ni(II) complex **1** and 2-iodobutane **2j** with applying the *General Procedure*, the mixture of diastereomers (S,S,S)-**3j** and (S,S,R)-**3j** were isolated in a ratio of *dr* 1:1 as a red powder (combined yield of both diastereomers 37 mg, yield 65%), eluent: EtOAc. The diastereomers weren't separated.

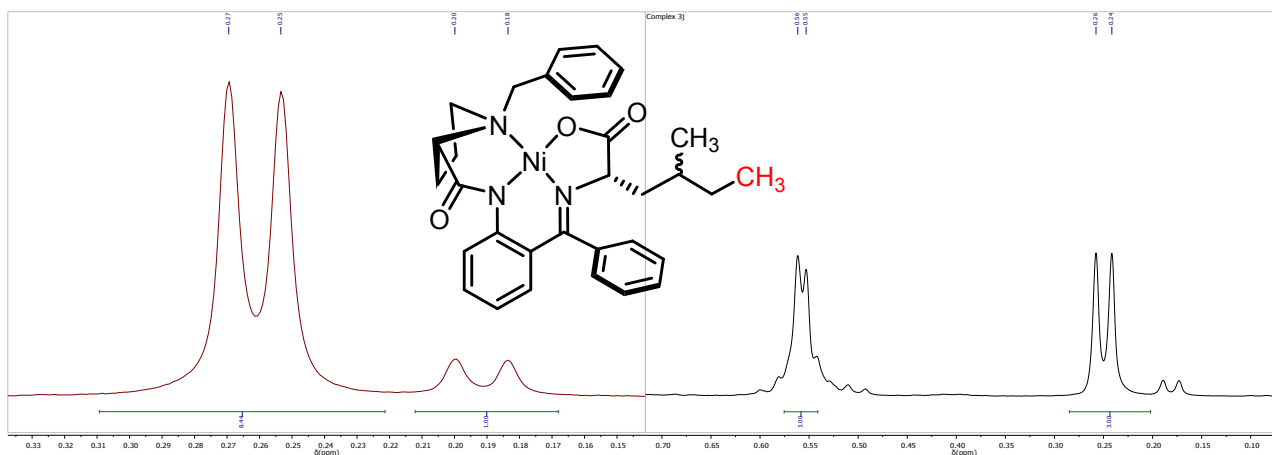
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.09–7.98 (m, 6H), 7.52–7.41 (m, 6H), 7.36–7.26 (m, 6H), 7.20–7.24 (m, 2H), 7.13–7.07 (m, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.68–6.57 (m, 4H), 4.43 (d, *J* = 12.7 Hz, 2H), 3.94–3.83 (m, 2H), 3.76–3.62 (m, 2H), 3.56–3.50 (m, 2H), 3.50–3.45 (m, 4H), 2.79–2.60 (m, 3H), 2.59–2.45 (m, 2H), 2.41–2.32 (m, 1H), 2.25–2.16 (m, 2H), 2.10–2.00 (m, 2H), 1.74–1.53 (m, 4H), 1.29–1.04 (m, 4H), 0.81–0.80 (m, 6H), 0.56 (d, *J* = 3.4 Hz, 3H), 0.25 (d, *J* = 6.5 Hz, 3H) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.5, 180.4, 179.5, 179.4, 169.7, 169.6, 133.6, 133.5, 133.4, 133.3, 133.2, 133.1, 132.1, 132.0, 131.6, 129.8, 129.8, 129.0, 128.9, 127.9, 127.7, 127.67, 127.6, 126.8, 126.7, 123.9, 123.8, 120.9, 120.8, 70.3, 70.2, 69.2, 68.9, 63.1, 57.3, 57.2, 50.8, 44.3, 30.8, 30.6, 30.57, 30.5, 27.6, 24.1, 24.0, 20.2, 17.7, 11.3, 10.6 ppm.

HRMS (ESI, *m/z*) calcd. for C<sub>32</sub>H<sub>36</sub>N<sub>3</sub>NiO<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 568.2105, found: 568.2103.

$[\alpha]_D^{25}$  +2259 (*c* 0.03, MeOH).

Diastereoselective ratio (*dr* value) was determined according to the <sup>1</sup>H NMR peak areas of CH<sub>3</sub> in (S,S)-**3i** and (S,R)-**3i** from the isolated mixture of products (partial <sup>1</sup>H NMR of the diastereoisomers is shown below), *dr* 8.4:1 (after reaction) for (S,S)-**3i**/(S,R)-**3i** and *dr* 1:1 for (S,S,S)-**3j** and (S,S,R)-**3j**.



### Ni(II) complex (S,S)-3k

Starting from a chiral Ni(II) complex **1** and 1-iodo-3-methylbutane **2k** with applying the *General Procedure*, the desired product (S,S)-**3k** was isolated as a red powder (52 mg, yield 89%, *dr* 28.7:1), eluent: EtOAc.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.10 (d, *J* = 8.6 Hz, 1H), 8.04 (d, *J* = 7.4 Hz, 2H), 7.53–7.40 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25–7.22 (m, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.15–7.09 (m, 1H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.69–6.58 (m, 2H), 4.42 (d, *J* = 12.7 Hz, 1H), 3.91 (dd, *J* = 7.9, 3.0 Hz, 1H), 3.63–3.41 (m, 4H),

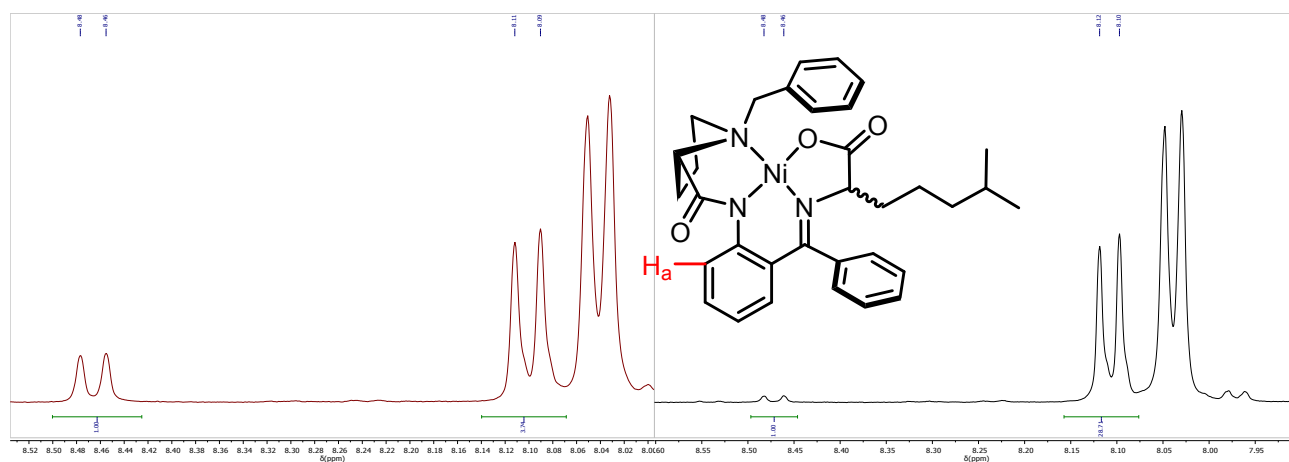
2.80–2.69 (m, 1H), 2.59–2.45 (m, 1H), 2.18–2.00 (m, 3H), 1.98–1.85 (m, 2H), 1.64–1.54 (m, 2H), 1.52–1.42 (m, 1H), 1.04–0.96 (m, 1H), 0.83 (dd,  $J = 6.5, 2.1$  Hz, 6H) ppm.

$^{13}\text{C}$  (JMOD) NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 180.5, 179.7, 170.4, 142.2, 133.9, 133.3, 133.2, 132.2, 131.7, 129.8, 129.0, 128.99, 128.95, 127.7, 127.3, 126.7, 123.8, 120.9, 70.5, 70.3, 63.1, 57.0, 38.6, 35.7, 30.8, 27.9, 23.7, 23.3, 22.7, 22.6$  ppm.

HRMS (ESI,  $m/z$ ) calcd. for  $\text{C}_{33}\text{H}_{38}\text{N}_3\text{NiO}_3^+$   $[\text{M}+\text{H}]^+$ : 582.2261, found: 582.2261.

$[\alpha]_{\text{D}}^{25} +2117$  ( $c$  0.03, MeOH).

Diastereoselective ratio ( $dr$  value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\text{H}_a$  in ( $S,S$ )-**3k** and ( $S,R$ )-**3k** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below),  $dr$  3.7:1 (after reaction) and  $dr$  28.7:1 (after epimerization with MeONa) for ( $S,S$ )-**3k**/ $(S,R)$ -**3k**



### Ni(II) complex ( $S,S$ )-**3l**

Starting from a chiral Ni(II) complex **1** and *cyclo*-hexyl iodide **2l** with applying the *General Procedure*, the desired product ( $S,S$ )-**3l** was isolated as a red powder (52 mg, yield 87%,  $dr$  9.6:1), eluent: EtOAc.

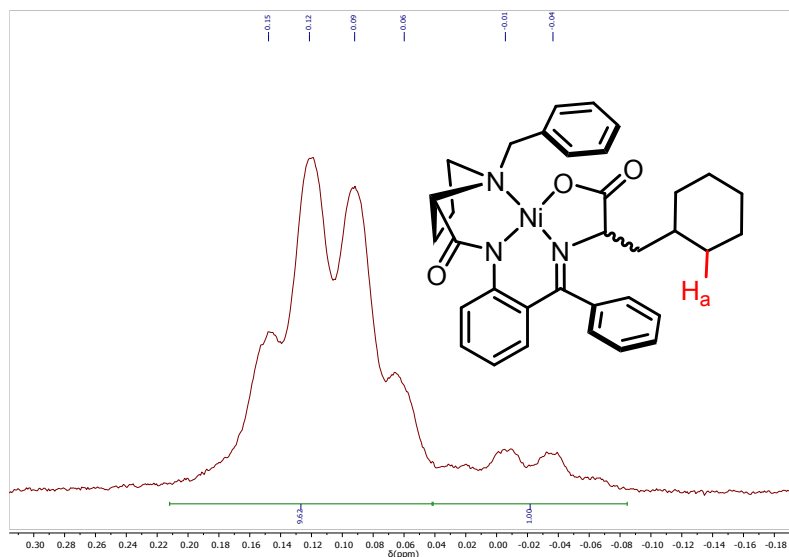
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.08\text{--}8.02$  (m, 3H), 7.52–7.42 (m, 3H), 7.33 (t,  $J = 7.3$  Hz, 2H), 7.29–7.26 (m, 1H), 7.19 (t,  $J = 7.5$  Hz, 1H), 7.14–7.08 (m, 1H), 6.92 (d,  $J = 7.1$  Hz, 1H), 6.68–6.59 (m, 2H), 4.45 (d,  $J = 12.7$  Hz, 1H), 3.92 (dd,  $J = 10.4, 3.6$  Hz, 1H), 3.76–3.61 (m, 1H), 3.55 (d,  $J = 12.7$  Hz, 1H), 3.52–3.43 (m, 2H), 2.80–2.68 (m, 1H), 2.59–2.46 (m, 1H), 2.44–2.35 (m, 1H), 2.24–2.14 (m, 1H), 2.10–2.00 (m, 1H), 1.67–1.50 (m, 4H), 1.49–1.36 (m, 2H), 1.27–1.17 (m, 2H), 1.17–0.93 (m, 2H), 0.89–0.77 (m, 1H), 0.12 (q,  $J = 10.2$  Hz, 1H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 180.4, 179.5, 170.4, 142.1, 133.7, 133.3, 132.2, 132.1, 131.7, 129.8, 129.0, 128.9, 127.9, 127.7, 126.8, 123.8, 120.9, 70.3, 68.6, 63.0, 57.2, 45.1, 34.5, 33.5, 31.7, 30.8, 26.4, 26.1, 25.8, 24.1$  ppm.

HRMS (ESI,  $m/z$ ) calcd. for  $\text{C}_{34}\text{H}_{38}\text{N}_3\text{NiO}_3^+$   $[\text{M}+\text{H}]^+$ : 594.2261, found: 594.2260.

$[\alpha]_{\text{D}}^{25} +1380$  ( $c$  0.02, MeOH).

Diastereoselective ratio ( $dr$  value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\text{H}_a$  in ( $S,S$ )-**3l** and ( $S,R$ )-**3l** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below),  $dr$  9.6:1 (after reaction) for ( $S,S$ )-**3l**/ $(S,R)$ -**3l**.



### *Ni(II) complex (S,S)-3m*

Starting from a chiral Ni(II) complex **1** and benzyl bromide **2m** with applying the *General Procedure*, the desired product (*S,S*)-**3m** was isolated as a red powder (54 mg, yield 90%), eluent: EtOAc.

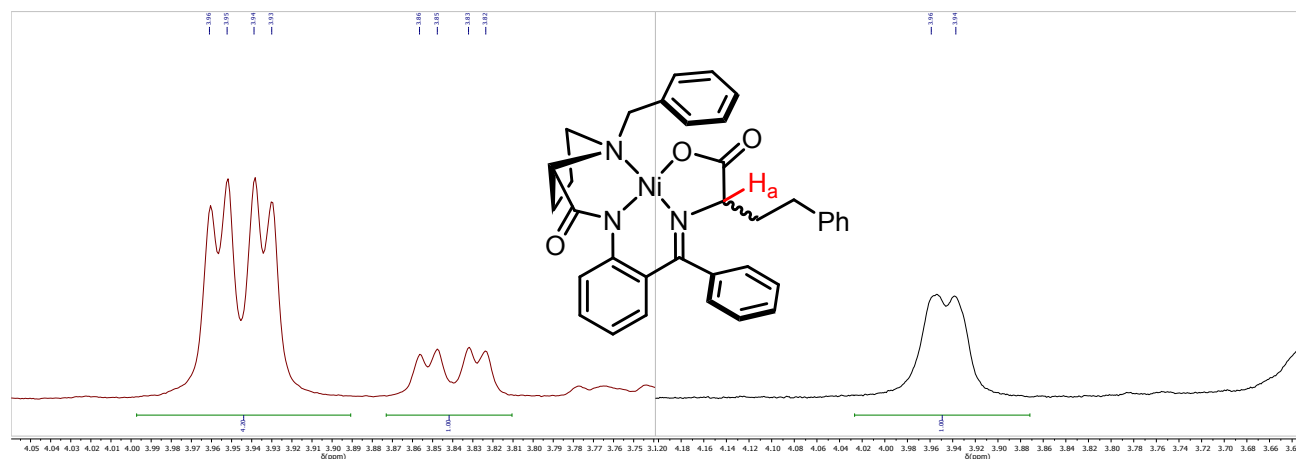
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.16–7.99 (m, 3H), 7.49–7.30 (m, 5H), 7.25–7.10 (m, 6H), 7.10–7.01 (m, 2H), 6.90 (d,  $J$  = 7.1 Hz, 1H), 6.72–6.55 (m, 2H), 4.45 (d,  $J$  = 12.6 Hz, 1H), 3.95 (dd,  $J$  = 8.5, 2.9 Hz, 1H), 3.65–3.44 (m, 4H), 3.36–3.22 (m, 1H), 2.83–2.66 (m, 2H), 2.60–2.43 (m, 1H), 2.42–2.28 (m, 1H), 2.23–2.00 (m, 2H), 1.97–1.83 (m, 1H) ppm.

$^{13}\text{C}$  (*JMOD*) NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 180.5, 179.3, 170.6, 142.3, 140.7, 133.6, 133.3, 133.3, 132.2, 131.6, 129.8, 129.0, 128.9, 128.5, 128.4, 127.4, 127.1, 126.5, 126.1, 123.8, 120.8, 70.3, 70.0, 63.1, 57.1, 37.5, 31.8, 30.8, 23.8 ppm.

$[\alpha]_{\text{D}}^{25} +1757$  ( $c$  0.03, MeOH).

The spectroscopic data were in agreement with the literature.<sup>[S2]</sup>

Diastereoselective ratio (*dr* value) was determined according to the  $^1\text{H}$  NMR peak areas of  $\alpha\text{-H}_a$  in (*S,S*)-**3m** and (*S,R*)-**3m** from the isolated mixture of products (partial  $^1\text{H}$  NMR of the diastereoisomers is shown below), *dr* **4.2:1** (after reaction) and *dr* **>50:1** (after epimerization with MeONa) for (*S,S*)-**3m**/*(S,R)*-**3m**.



### *Ni(II) complex (S,S)-3n*

Starting from a chiral Ni(II) complex **1** and nonafluorobutyl iodide **2n** with applying the *General Procedure*, the desired product (*S,S*)-**3n** was isolated as a red powder (22 mg, yield 30%), eluent: EtOAc.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21 (d,  $J$  = 8.7 Hz, 1H), 8.06 (d,  $J$  = 7.5 Hz, 2H), 7.60–7.53 (m, 2H), 7.52–7.46 (m, 1H), 7.37 (t,  $J$  = 7.5 Hz, 2H), 7.31–7.27 (m, 1H), 7.24–7.14 (m, 2H), 6.93 (d,  $J$  = 7.6 Hz, 1H), 6.70–6.61 (m, 2H), 4.43 (d,  $J$  = 12.6 Hz, 1H), 4.29 (dd,  $J$  = 6.6, 2.3 Hz, 1H), 3.60 (d,  $J$  = 12.6 Hz, 1H), 3.57–3.50 (m, 1H), 3.48–3.33 (m, 2H), 2.86–2.73 (m, 1H), 2.61–2.42 (m, 2H), 2.13–2.02 (m, 3H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = –80.9 (s, 3 F), –108.6 (d,  $J$  = 266 Hz, 1 F), –111.4 (d,  $J$  = 266 Hz, 1 F), –124.5 (s, 2 F), –125.7 (d,  $J$  = 12 Hz, 2F) ppm.

The spectroscopic data were in agreement with the literature.<sup>[S7]</sup>

### *Ni(II) complex (S,S)-3o*

Starting from a chiral Ni(II) complex **1** and *n*-perfluorohexyl iodide **2o** with applying the *General Procedure*, the desired product (*S,S*)-**3o** was isolated as a red powder (20 mg, yield 24%), eluent: EtOAc.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.21 (d,  $J$  = 8.8 Hz, 1H), 8.06 (d,  $J$  = 7.5 Hz, 2H), 7.60–7.52 (m, 2H), 7.52–7.45 (m, 1H), 7.37 (t,  $J$  = 7.6 Hz, 2H), 7.31–7.27 (m, 1H), 7.24–7.14 (m, 2H), 6.92 (d,  $J$  = 8.2 Hz, 1H), 6.70–6.61 (m, 2H), 4.42 (d,  $J$  = 12.8 Hz, 1H), 4.29 (dd,  $J$  = 6.0, 2.5 Hz, 1H), 3.60 (d,  $J$  = 12.8 Hz, 1H), 3.57–3.51 (m, 1H), 3.49–3.36 (m, 2H), 2.87–2.74 (m, 1H), 2.62–2.44 (m, 2H), 2.16–2.02 (m, 3H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = –80.7 (s, 3 F), –108.4 (d,  $J$  = 266 Hz, 1 F), –111.1 (d,  $J$  = 266 Hz, 1 F), –121.6 (s, 2 F), –122.8 (s, 2 F), –123.6 (s, 2 F), –126.1 (s, 2F) ppm.

The spectroscopic data were in agreement with the literature.<sup>[S7]</sup>

### *Ni(II) complex (S,S)-3p*

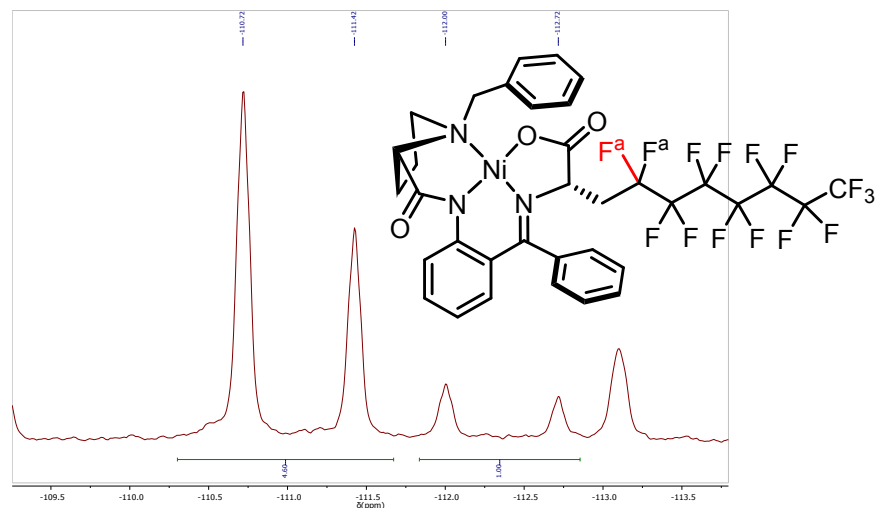
Starting from a chiral Ni(II) complex **1** and *n*-perfluoroheptyl iodide **2p** with applying the *General Procedure*, the desired product (*S,S*)-**3p** was isolated as a red powder (28 mg, yield 32%), eluent: EtOAc.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.20 (d,  $J$  = 8.6 Hz, 1H), 8.06 (d,  $J$  = 7.4 Hz, 2H), 7.59–7.52 (m, 2H), 7.51–7.45 (m, 1H), 7.36 (t,  $J$  = 7.6 Hz, 2H), 7.31–7.26 (m, 1H), 7.23–7.13 (m, 2H), 6.92 (d,  $J$  = 7.8 Hz, 1H), 6.69–6.60 (m, 2H), 4.43 (d,  $J$  = 12.7 Hz, 1H), 4.30–4.21 (m, 1H), 3.59 (d,  $J$  = 12.7 Hz, 1H), 3.57–3.49 (m, 1H), 3.47–3.32 (m, 2H), 2.86–2.72 (m, 1H), 2.62–2.42 (m, 2H), 2.14–2.01 (m, 3H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = –80.7 (s, 3 F), –108.4 (d,  $J$  = 266 Hz, 1 F), –111.1 (d,  $J$  = 266 Hz, 1 F), –121.5 (s, 2 F), –122.0 (s, 2 F), –122.7 (s, 2 F), –123.5 (s, 2 F), –126.1 (s, 2F) ppm.

The spectroscopic data were in agreement with the literature.<sup>[S7]</sup>

Diastereoselective ratio (*dr* value) was determined according to the <sup>19</sup>F NMR peak areas of **F<sup>a</sup>** in (*S,S*)-**3p** and (*S,R*)-**3p** from the isolated mixture of products (partial <sup>19</sup>F NMR of the diastereoisomers is shown below), *dr* 4.6:1 (after reaction) for (*S,S*)-**3p**/*(S,R)*-**3p**.



### *Ni(II) complex (S,S)-3q*

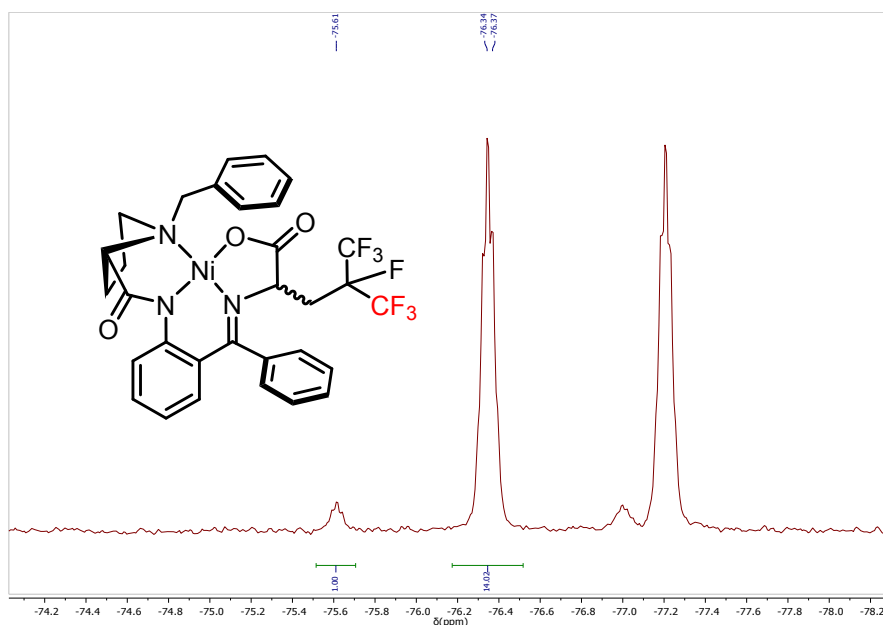
Starting from a chiral Ni(II) complex **1** and *n*-perfluoroisopropyl iodide **2q** with applying the *General Procedure*, the desired product (*S,S*)-**3q** was isolated as a red powder (23 mg, yield 34%), eluent: EtOAc.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.17–8.04 (m, 3H), 7.60–7.52 (m, 2H), 7.51–7.44 (m, 1H), 7.39–7.27 (m, 3H), 7.22–7.12 (m, 2H), 6.91 (d,  $J$  = 7.1 Hz, 1H), 6.70–6.59 (m, 2H), 4.42 (d,  $J$  = 12.6 Hz, 1H), 4.21 (dd,  $J$  = 9.0, 3.7 Hz, 1H), 3.60–3.43 (m, 4H), 3.24–3.10 (m, 1H), 2.84–2.70 (m, 1H), 2.63–2.38 (m, 2H), 2.28–2.18 (m, 1H), 2.14–2.04 (m, 1H) ppm.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –76.4 (s, 3 F), –77.2 (s, 3 F), –184.5 (s, 1 F) ppm.

The spectroscopic data were in agreement with the literature.<sup>[S7]</sup>

Diastereoselective ratio (*dr* value) was determined according to the  $^{19}\text{F}$  NMR peak areas of  $\text{CF}_3$  in (*S,S*)-**3q** and (*S,R*)-**3q** from the isolated mixture of products (partial  $^{19}\text{F}$  NMR of the diastereoisomers is shown below), *dr* **14:1** (after reaction) for (*S,S*)-**3q**/*(S,R)*-**3q**.



### ***Ni(II) complex (S,S)-3r***

Starting from a chiral Ni(II) complex **1** and iodoperfluorocyclohexane iodide **2r** (*were added in two portions during 30 mins*) with applying the *General Procedure*, the desired product (*S,S*)-**3r** was isolated as a red powder (32 mg, yield 40%), eluent: EtOAc.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.20 (d,  $J$  = 8.7 Hz, 1H), 8.06 (d,  $J$  = 7.6 Hz, 2H), 7.59–7.52 (m, 2H), 7.51–7.45 (m, 1H), 7.37–7.28 (m, 3H), 7.20–7.12 (m, 2H), 6.92 (d,  $J$  = 7.1 Hz, 1H), 6.70–6.60 (m, 2H), 4.42 (d,  $J$  = 12.6 Hz, 1H), 4.34–4.27 (m, 1H), 3.55 (d,  $J$  = 12.6 Hz, 1H), 3.52–3.37 (m, 3H), 2.95–2.73 (m, 2H), 2.70–2.48 (m, 2H), 2.19–2.02 (m, 2H) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = –117.5 (d,  $J$  = 298 Hz, 1F), –119.1 (d,  $J$  = 300 Hz, 1F), –122.2 (d,  $J$  = 287 Hz, 2F), –123.9 (d,  $J$  = 276 Hz, 1F), –131.3 (d,  $J$  = 146 Hz, 1F), –132.1 (d,  $J$  = 156 Hz, 1F), –138.5 (d,  $J$  = 164 Hz, 1F), –139.3 (d,  $J$  = 161 Hz, 1F), –142.0 (d,  $J$  = 284 Hz, 1F), –183.0 (s, 1F) ppm.

The spectroscopic data were in agreement with the literature.<sup>[S7]</sup>

### ***Ni(II) complex (S,S)-3s***

Starting from a chiral Ni(II) complex **1** and ethyl 2,2-difluoro-2-iodoacetate **2s** (*were added in two portions during 30 mins*) with applying the *General Procedure*, the desired product (*S,S*)-**3s** was isolated as a red powder (30 mg, yield 46%), eluent: CHCl<sub>3</sub>/acetone (5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.22 (d,  $J$  = 8.7 Hz, 1H), 8.06 (d,  $J$  = 7.4 Hz, 2H), 7.59–7.45 (m, 3H), 7.34 (t,  $J$  = 7.6 Hz, 2H), 7.25–7.21 (m, 1H), 7.20–7.12 (m, 2H), 7.10–7.02 (m, 1H), 6.68–6.60 (m, 2H), 4.38 (d,  $J$  = 12.6 Hz, 1H), 4.21–4.07 (m, 3H), 3.67–3.50 (m, 3H), 3.46 (dd,  $J$  = 10.8, 6.0 Hz, 1H), 2.88–2.61 (m, 2H), 2.57–2.32 (m, 2H), 2.18–2.05 (m, 2H), 1.25 (t,  $J$  = 7.1 Hz, 3H) ppm.

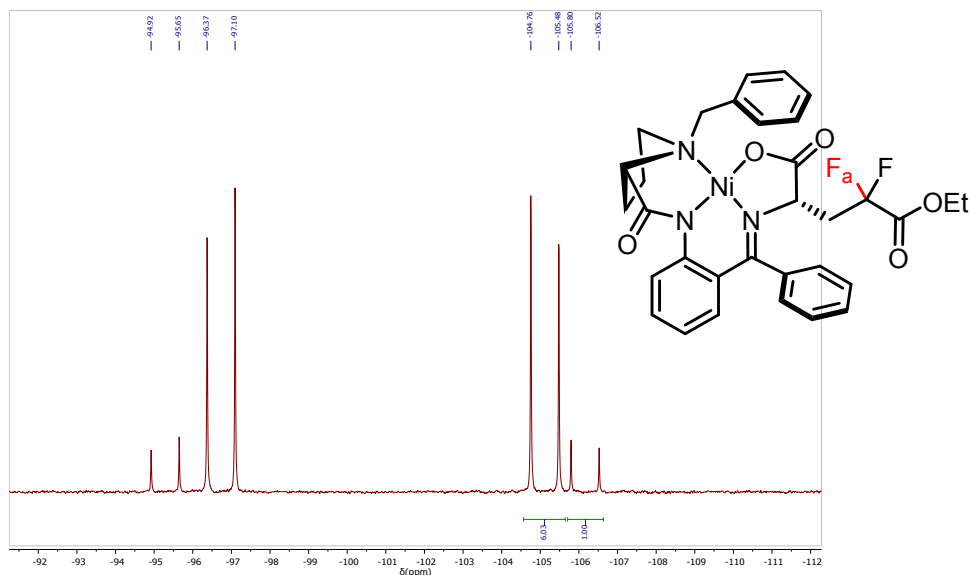
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 180.7, 177.9, 172.8, 163.7–162.7 (m), 143.0, 133.78, 133.7, 133.5, 132.9, 131.7, 130.3, 129.4, 129.3, 129.0, 127.8, 126.9, 126.0, 123.7, 120.8, 70.6, 65.1, 63.5, 60.5, 57.5, 37.2, 30.8, 23.4, 13.9 ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = –97.0 (d,  $J$  = 273 Hz), –105.3 (d,  $J$  = 273 Hz) ppm.

HRMS (ESI,  $m/z$ ) calcd. for C<sub>32</sub>H<sub>32</sub>F<sub>2</sub>N<sub>3</sub>NiO<sub>5</sub><sup>+</sup> [M+H]<sup>+</sup>: 634.1658, found: 634.1662.

$[\alpha]_D^{25}$  +2315 ( $c$  0.06, MeOH).

Diastereoselective ratio (*dr* value) was determined according to the <sup>19</sup>F NMR peak areas of **F<sup>a</sup>** in (*S,S*)-**3s** and (*S,R*)-**3s** from the isolated mixture of products (partial <sup>19</sup>F NMR of the diastereoisomers is shown below), **dr 6:1** (*after reaction*) for (*S,S*)-**3s**/*(S,R)*-**3s**.



### General procedure for the decomposition of the chiral Ni(II) complexes (*S,S*)-**3i** and (*S,S*)-**3l**

To a suspension of the Ni(II) complex **3** (1.0 or 1.85 mmol) in methanol (15.0 mL) was added 6*N* HCl (10.0 mL) and water (15.0 mL) and the whole was heated at 60 °C. Upon disappearance of the red color of the starting complex, the reaction was stopped. Afterward, 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 DCM. The aqueous layer was quenched by 25% aqueous NH<sub>3</sub> solution (6.0 mL) until pH = 7 and concentrated to dryness and the residue was chromatographed with a cation exchange resin (Dowex 50x2, H<sup>+</sup>-form) (eluent: water and then 5% aqueous solution of ammonia) to afford the desired amino acid as a white powder.

#### (*S*)-2-amino-4,4-dimethylpentanoic acid **4i**

Starting from the chiral Ni(II) complex (*S,S*)-**3i** (1.0 mmol) with applying the *General Procedure*, the desired product **4i** was isolated as a white powder (130.0 mg, yield 85%).

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 3.58 (t, *J* = 5.7 Hz, 1H), 1.53 (dd, *J* = 15.0, 5.3 Hz, 1H), 1.21 (dd, *J* = 15.0, 6.2 Hz, 1H), 0.49 (s, 9H) ppm.

<sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 172.7, 50.2, 43.5, 29.4, 28.1 ppm.

The spectroscopic data were in agreement with the literature.<sup>[S2]</sup>

[α]<sub>D</sub><sup>25</sup> +19 (*c* 0.005, MeOH), (>99% *ee*, (*S*)-isomer).

The *ee* and absolute stereochemistry was assigned as (*S*) by comparison of the optical rotation with the following literature value:<sup>[S2]</sup> [α]<sub>D</sub><sup>21</sup> +14.2 (*c* 1.6 in HCl), (for >99% *ee*, (*S*)-isomer).



### ***(S)*-2-amino-3-cyclohexylpropanoic acid 4l**

Starting from the chiral Ni(II) complex (*S,S*)-**3l** (1.85 mmol) with applying the *General Procedure*, the desired product **4l** was isolated as a white powder (210.0 mg, yield 66%).

<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  = 3.80–3.66 (m, 1H), 1.52–1.43 (m, 1H), 1.40–1.16 (m, 6H), 1.12–0.98 (m, 1H), 0.92–0.68 (m, 3H), 0.66–0.49 (m, 2H) ppm.

<sup>13</sup>C (*JMOD*) NMR (101 MHz, D<sub>2</sub>O):  $\delta$  = 172.4, 50.5, 37.1, 32.7, 32.3, 31.6, 25.5, 25.2, 25.1 ppm.

The spectroscopic data were in agreement with the literature.<sup>[S8]</sup>

$[\alpha]_{\text{D}}^{25}$  +20 (*c* 0.05, MeOH), (>99% *ee*, (*S*)-isomer).

The *ee* and absolute stereochemistry was assigned as (*S*) by comparison of the optical rotation with the following literature value:<sup>[S8]</sup>  $[\alpha]_{\text{D}}^{25}$  +5.2 (*c* 0.30, 1.0 M HCl) (for 93% *ee*, (*S*)-isomer).

### **Procedure for decomposition of the chiral Ni(II) complex (*S,S*)-**3r****

To a suspension of the Ni(II) complex (*S,S*)-**3r** (0.35 g, 0.44 mmol) in methanol (10.0 mL) was added 1*N* HCl (10.0 mL) and the final mixture was stirred at room temperature for 3 h. Upon disappearance of red color of the starting complex, the reaction was completed. Afterward, MeOH was evaporated on a rotary evaporator and 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 aqueous layer was treated by 5% aqueous NaOH solution (5.0 mL) until pH = 9–10. The remaining amount of (*S*)-**BPB** was extracted with Et<sub>2</sub>O (2x10 mL). Then, the aqueous layer was quenched by 1*N* HCl until pH = 3–4 and stirred for 10 h. The resulting (*S*)-AA **4r** was precipitated in a HCl salt form. The precipitate was filtered and washed by water affording the desired (*S*)-AA **4r** x HCl as a white powder (0.11 g, 61%).

### ***(S)*-2-amino-3-(perfluorocyclohexyl)propanoic acid 4r**

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 4.25 (br. s, 1H), 2.94 (p, *J* = 16.9, 14.8 Hz, 2H) ppm.

<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 169.4, 113.6–112.4 (m), 111.6–110.0 (m), 109.0–107.0 (m), 106.3–104.8 (m), 93.0–91.8 (m), 90.8–89.5 (m), 47.8, 26.3 (d, *J* = 18.8 Hz) ppm.

<sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = –118.1 (dd, *J* = 304, 107 Hz, 2F), –122.5 (d, *J* = 285 Hz, 2F), –124.0 (d, *J* = 285 Hz, 1F), –132.8 (t, *J* = 292 Hz, 2F), –139.2 (d, *J* = 289 Hz, 2F), –142.1 (d, *J* = 285 Hz, 1F), –185.0 (s, 1F) ppm.

HRMS (ESI, *m/z*) calcd. for C<sub>9</sub>H<sub>7</sub>F<sub>11</sub>NO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 370.0296, found: 370.0306.

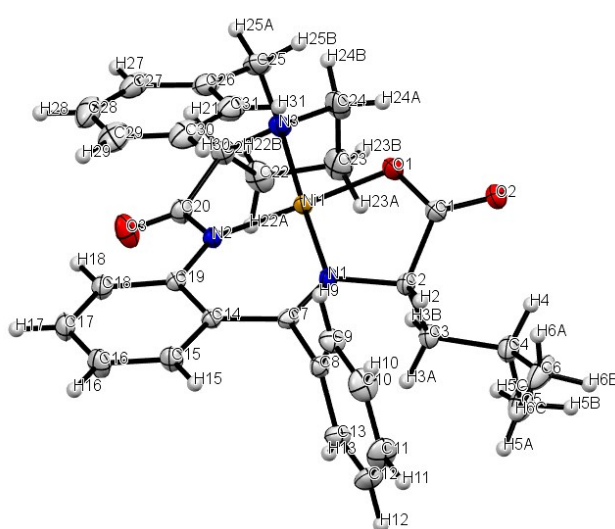
$[\alpha]_{\text{D}}^{25}$  –28.6 (*c* 0.1, MeOH), (>99% *ee*).

## X-ray diffraction study of the Ni(II) complexes (*S,S*)-**3a** and (*S,S*)-**31**

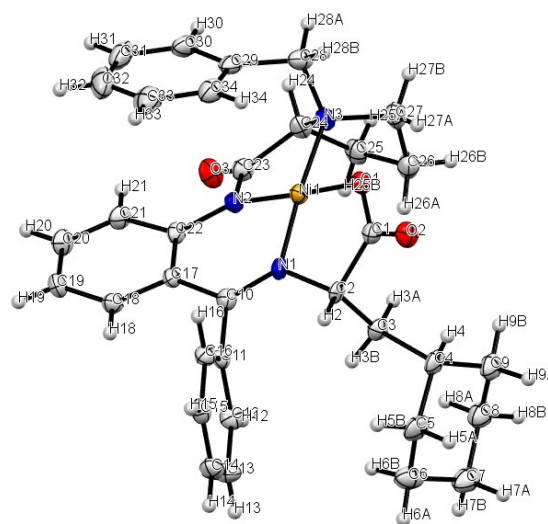
Single crystal X-ray study of the complexes Ni(II) complexes were carried out in Center for molecule composition studies of INEOS RAS.

Dark-red single crystals of the Ni(II) complexes (*S,S*)-**3a** and (*S,S*)-**31** were obtained by slow evaporation from mixture CH<sub>2</sub>Cl<sub>2</sub>/hexane. Single-crystal X-ray diffraction experiments were carried out with Bruker SMART APEX II diffractometer (graphite monochromated MoK<sub>α</sub> radiation, λ = 0.71073 Å, ω-scan technique). The APEX II software<sup>[S9]</sup> 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<sup>[S10]</sup> and OLEX2<sup>[S11]</sup> 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 calculated and all were included in the refinement by the riding model with  $U_{iso}(H) = 1.5U_{eq}(X)$  for methyl groups and  $U_{iso}(H) = 1.2U_{eq}(X)$  for other atoms. Experimental details and crystal parameters are listed in Table S1.

CCDC 2069715-2069716 contain the supplementary crystallographic data for the complexes (*S,S*)-**31** and (*S,S*)-**3a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures>.



(*S,S*)-**3a** (CCDC 2069716)



(*S,S*)-**31** (CCDC 2069715)

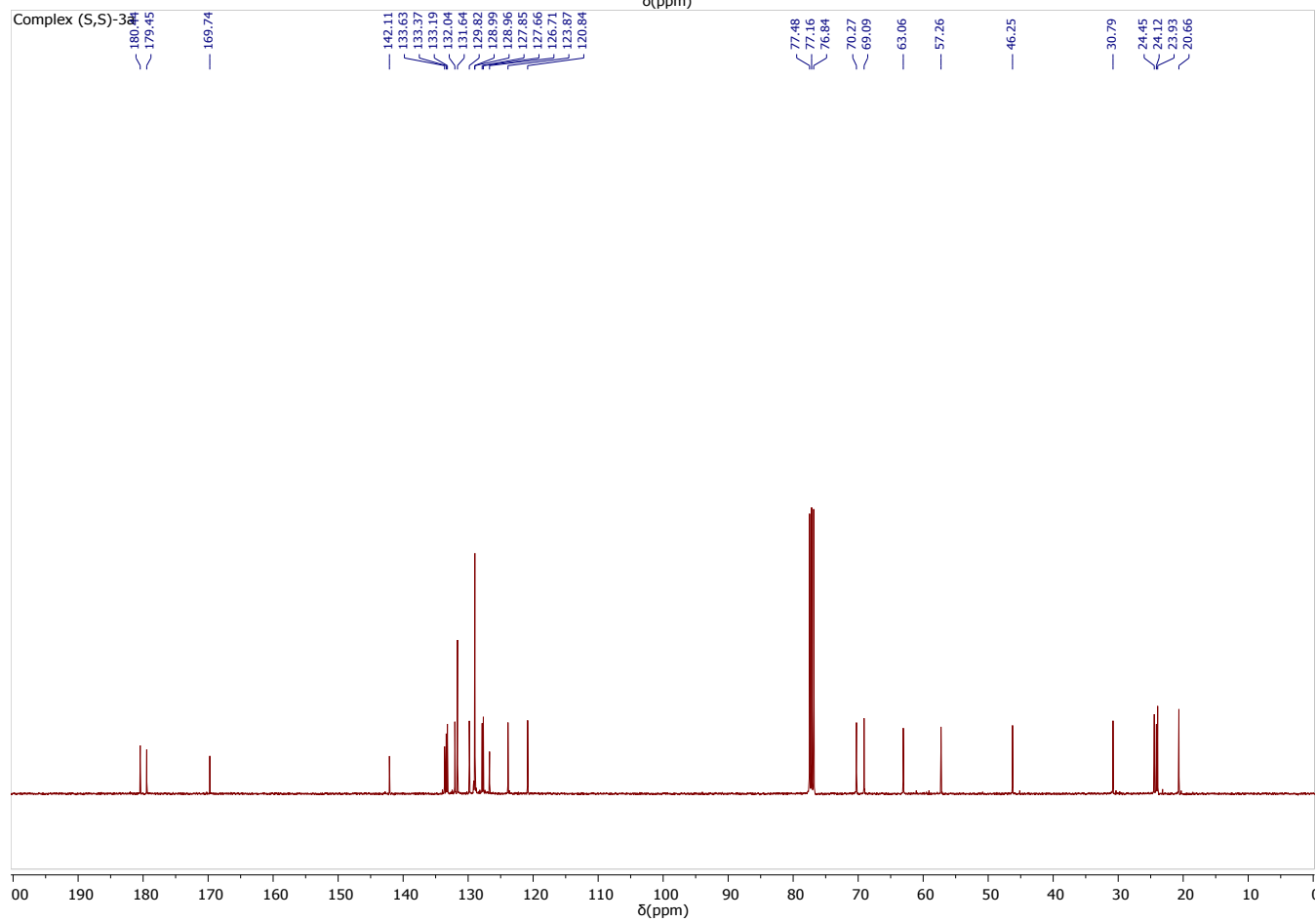
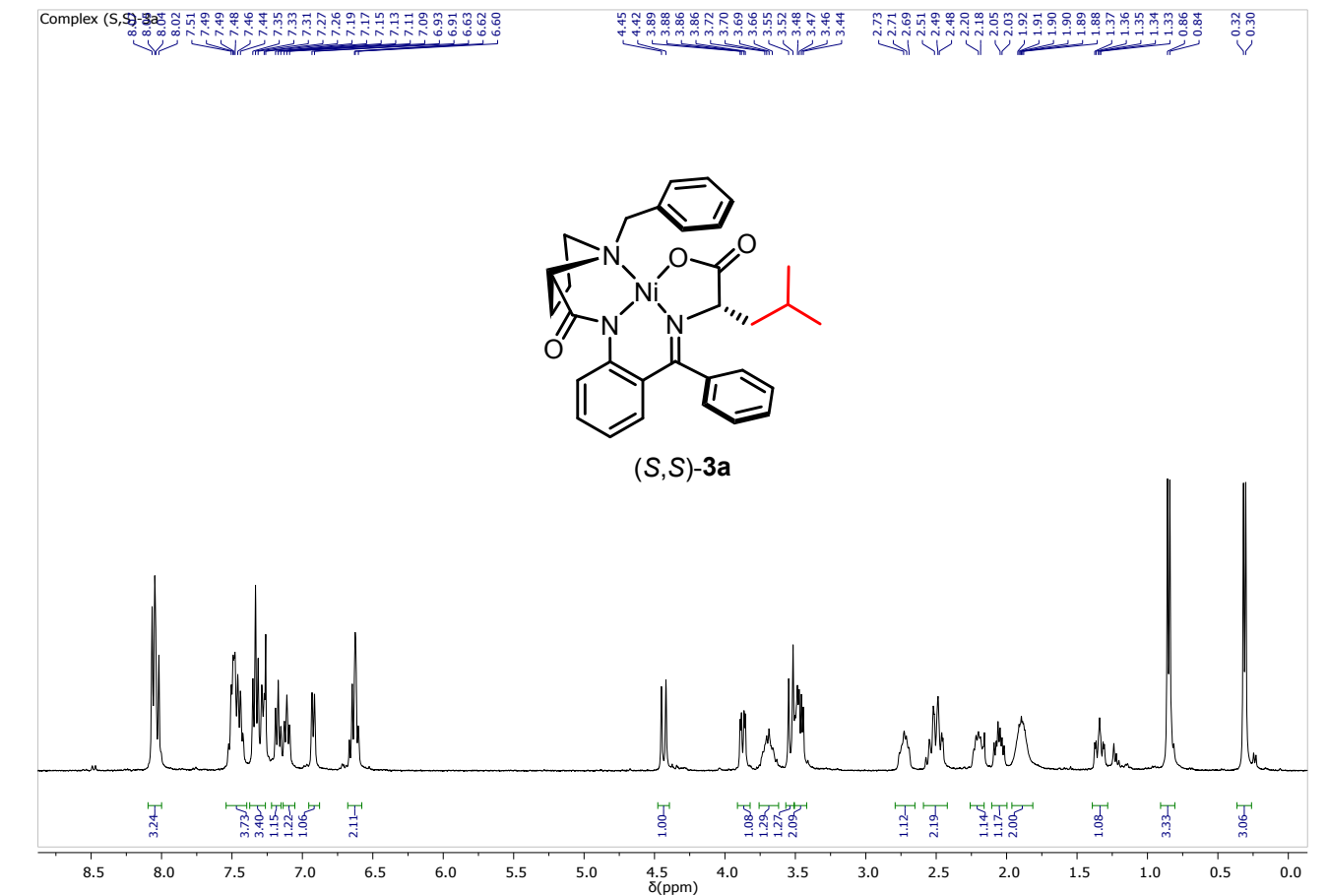
Table S1. Crystallographic data for the complex ( <i>S,S</i> )- <b>3a</b> and ( <i>S,S</i> )- <b>31</b>		
datablock	( <i>S,S</i> )- <b>3a</b>	( <i>S,S</i> )- <b>31</b>
Formula moiety	C <sub>31</sub> H <sub>33</sub> N <sub>3</sub> NiO <sub>3</sub>	C <sub>34</sub> H <sub>37</sub> N <sub>3</sub> NiO <sub>3</sub>
Brutto formula	C <sub>31</sub> H <sub>33</sub> N <sub>3</sub> NiO <sub>3</sub>	C <sub>34</sub> H <sub>37</sub> N <sub>3</sub> NiO <sub>3</sub>
Formula weight	554.31	594.37
Diffractometer	Bruker APEX-II CCD area detector	Bruker APEX-II CCD area detector
Scan mode	φ and ω scans	φ and ω scans
Anode [Wavelength, Å]	MoK <sub>α</sub> [0.71073] sealed	MoK <sub>α</sub> [0.71073] sealed

	tube	tube
Crystal Dimensions, mm	0.38 × 0.3 × 0.2	0.35 × 0.07 × 0.05
Crystal color	Dark red	dark red
Crystal system	orthorhombic	orthorhombic
a, Å	10.1084(4)	11.746(2)
b, Å	12.8143(5)	12.121(2)
c, Å	21.4068(9)	20.783(4)
α, °	90	90
β, °	90	90
γ, °	90	90
Volume, Å <sup>3</sup>	2772.87(19)	2958.9(10)
Density, g/cm <sup>-3</sup>	1.328	1.334
Temperature, K	120	120
μ, mm <sup>-1</sup>	0.736	0.695
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Z	4	4
F(000)	1168	1256
Reflections collected	50870	29023
Independent reflections	8450	5822
Parameters	345	370
R <sub>int</sub>	0.0267	0.1006
2θ <sub>min</sub> - 2θ <sub>max</sub> , °	3.704–60.978	3.89–51.998
wR <sub>2</sub> (all reflections)	0.0730	0.1030
R <sub>1</sub> (I>2σ(I))	0.0280	0.0445
GOF	1.033	1.020
ρ <sub>min</sub> /ρ <sub>max</sub> , eÅ <sup>-3</sup>	-0.22/0.47	-0.64/0.52

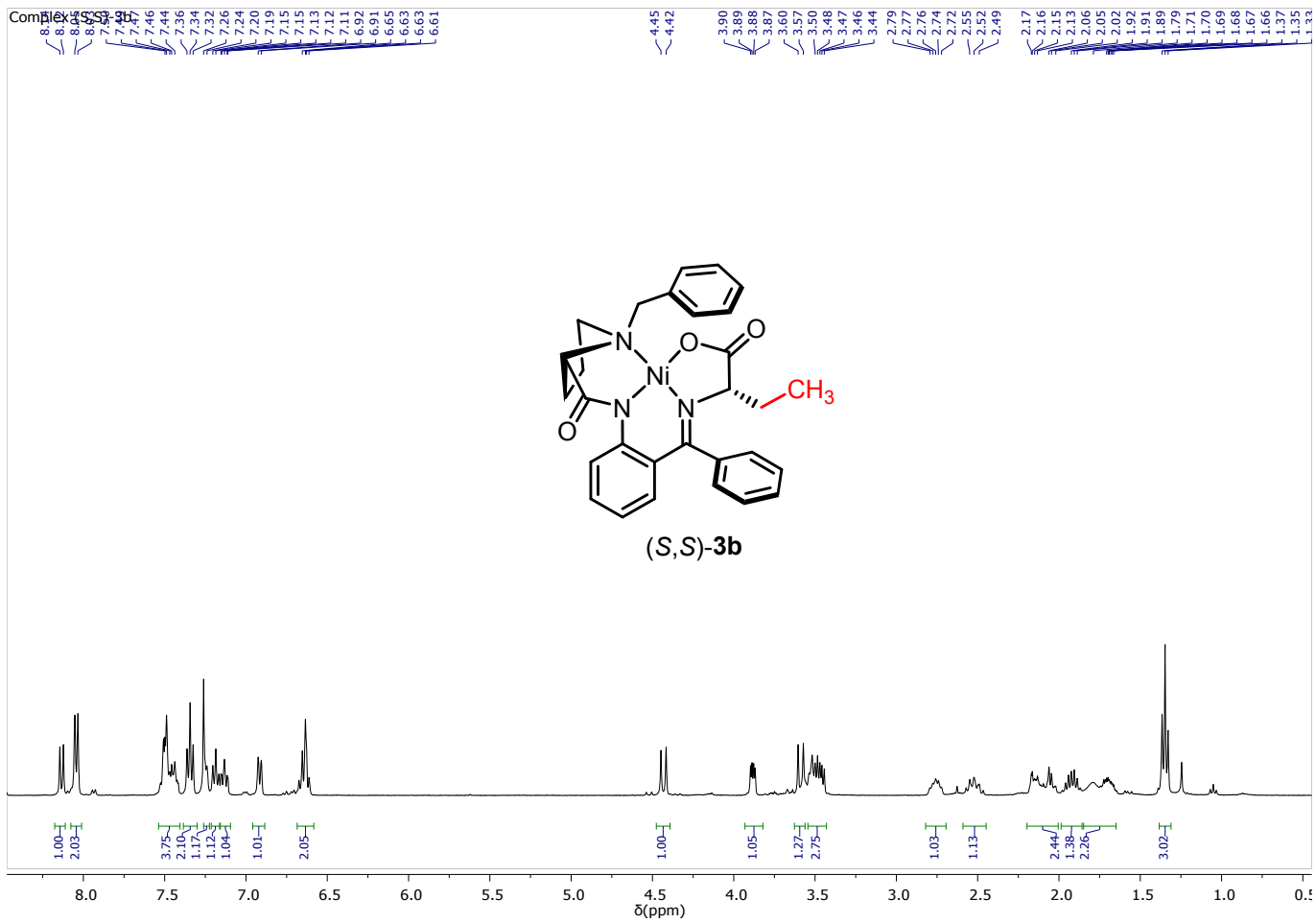
## References

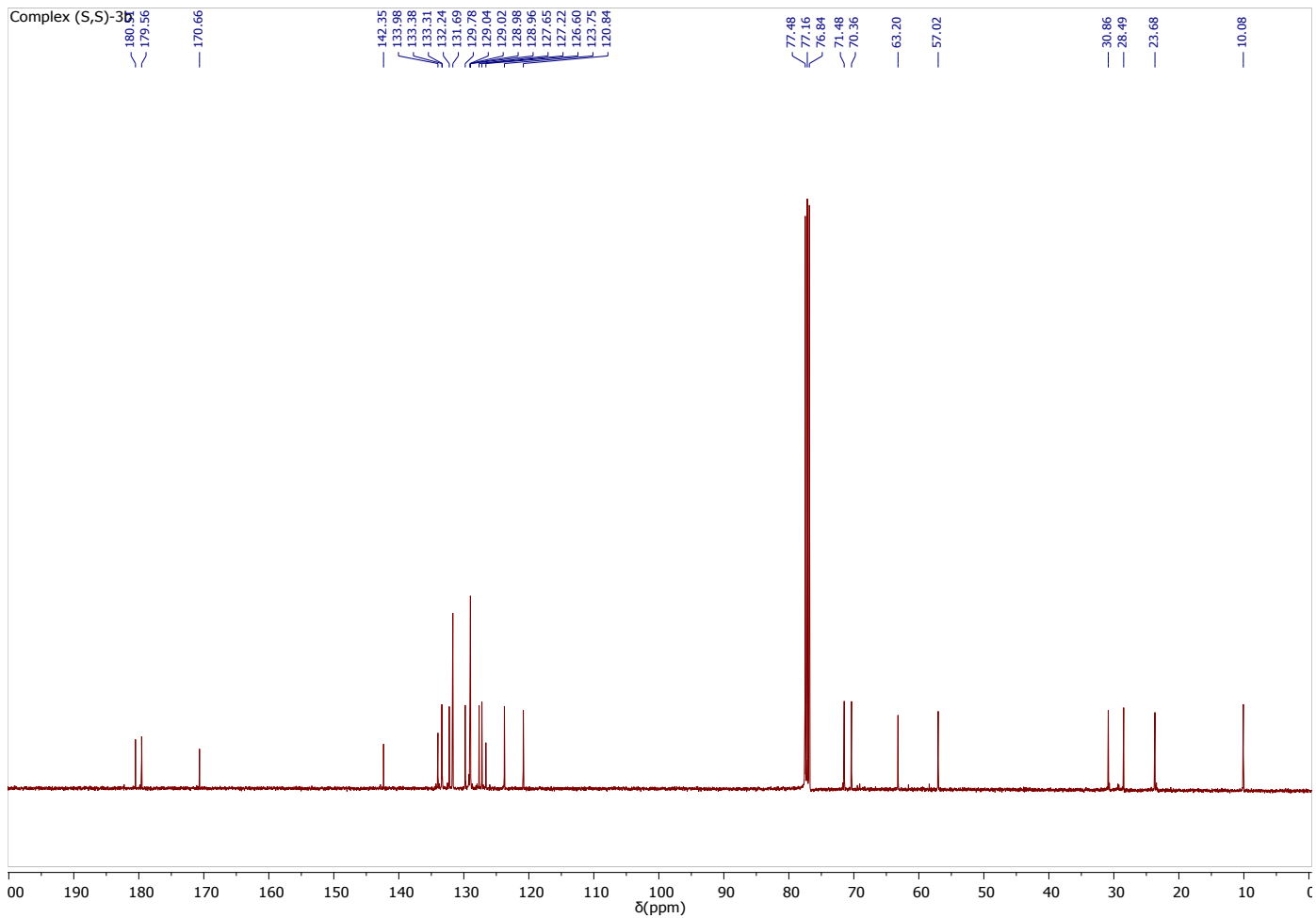
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# NMR spectra

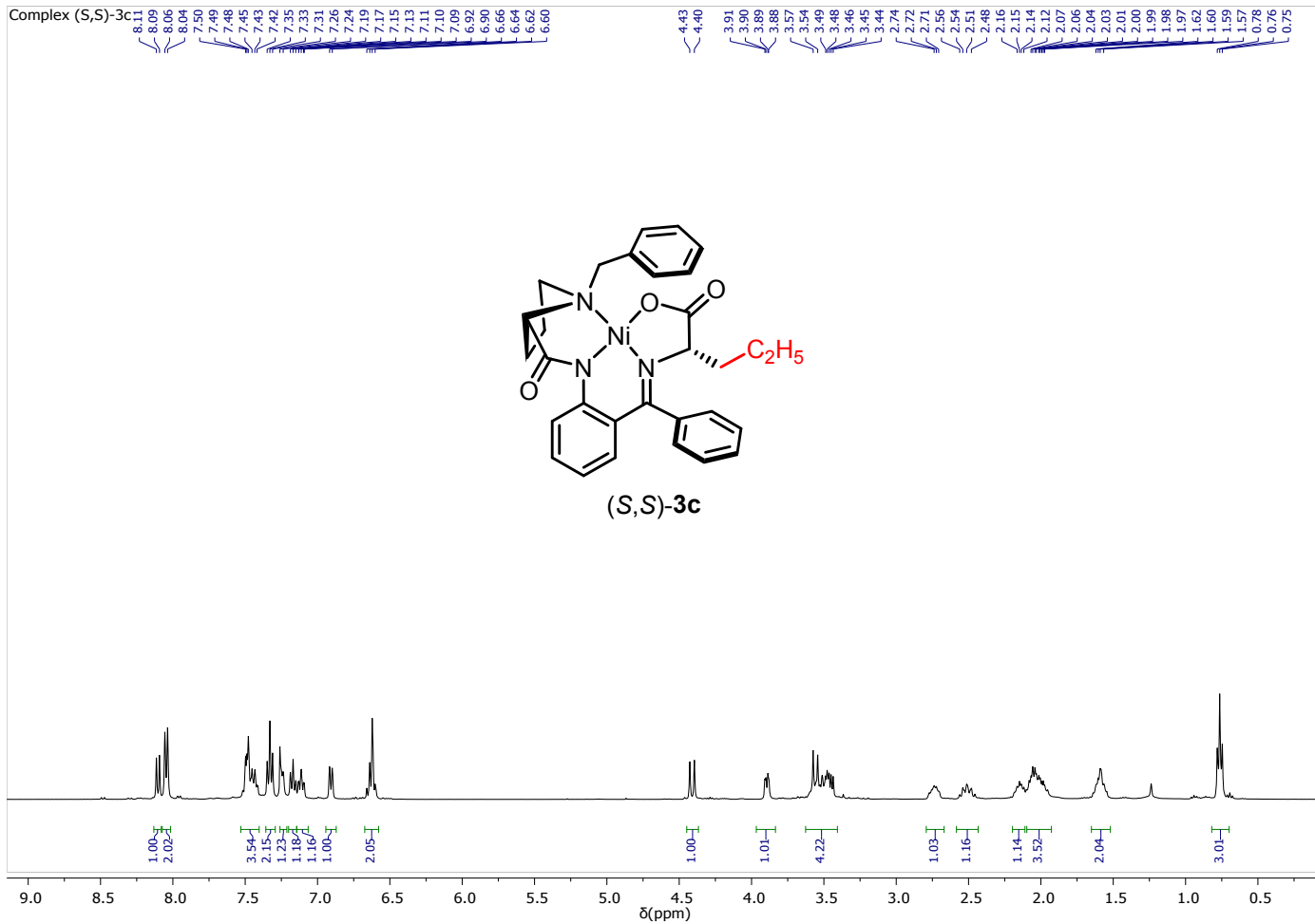


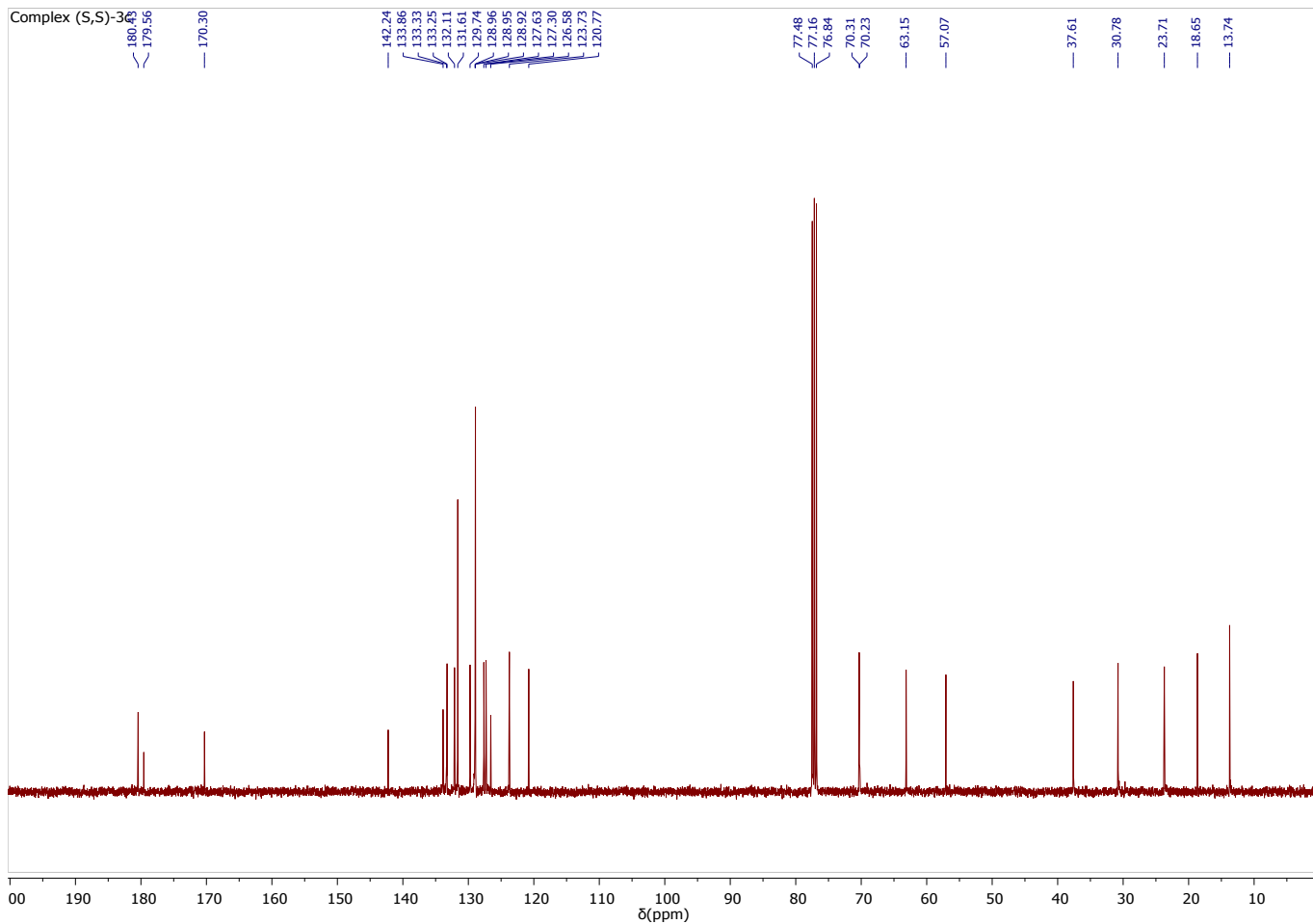
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-3a





*<sup>1</sup>H and <sup>13</sup>C NMR spectra of the Ni(II) complex (S,S)-**3b***

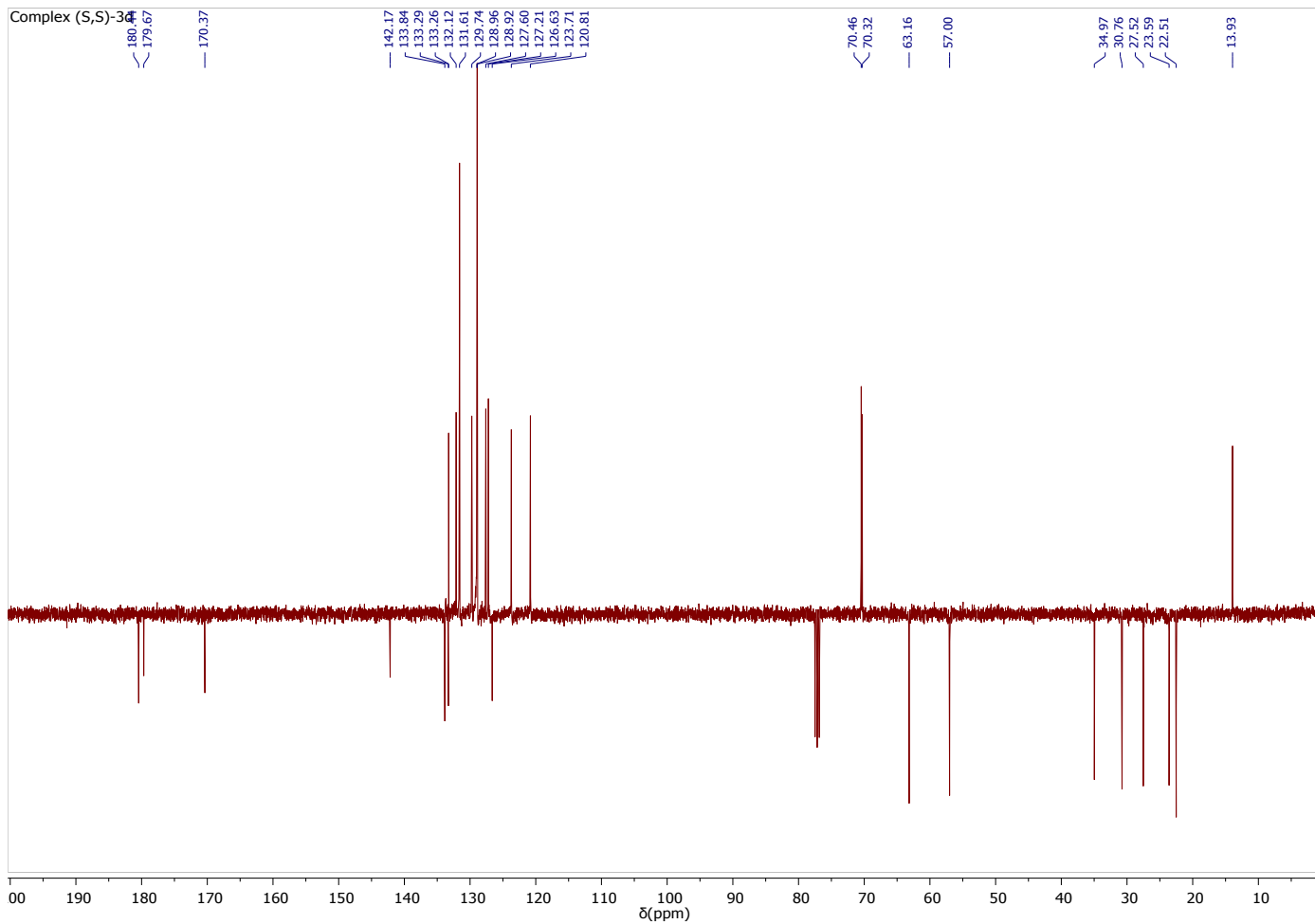




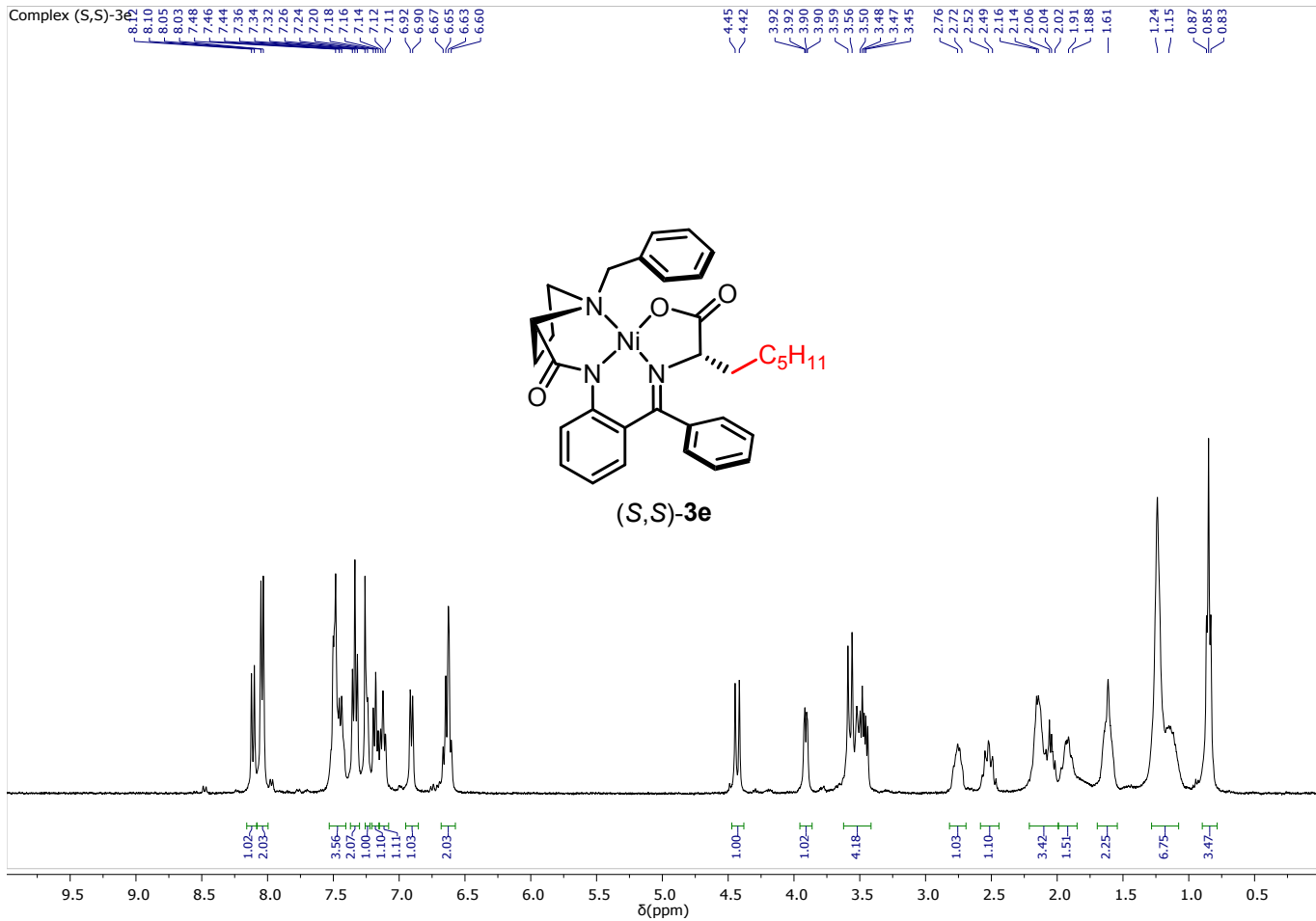
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-**3c**

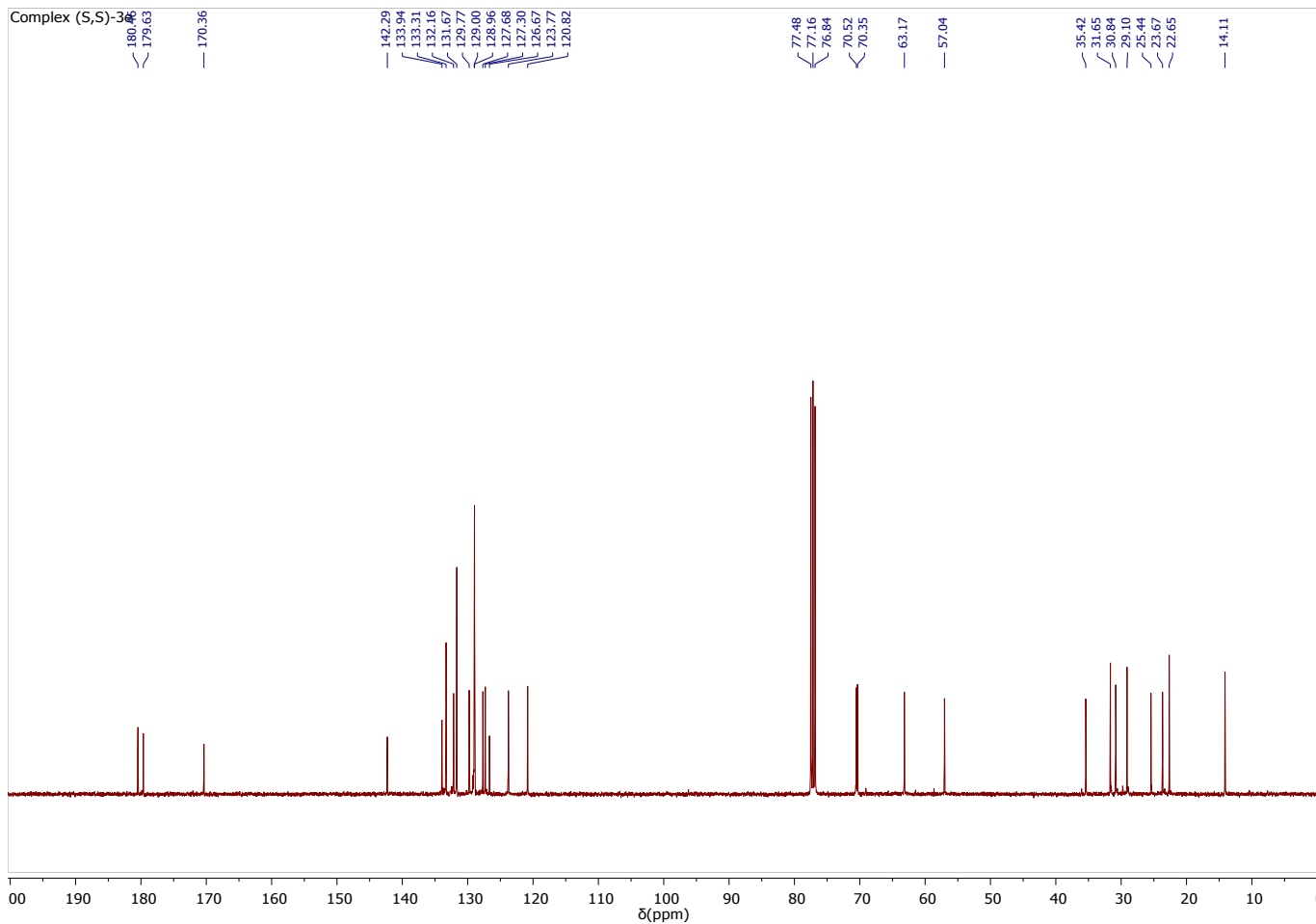






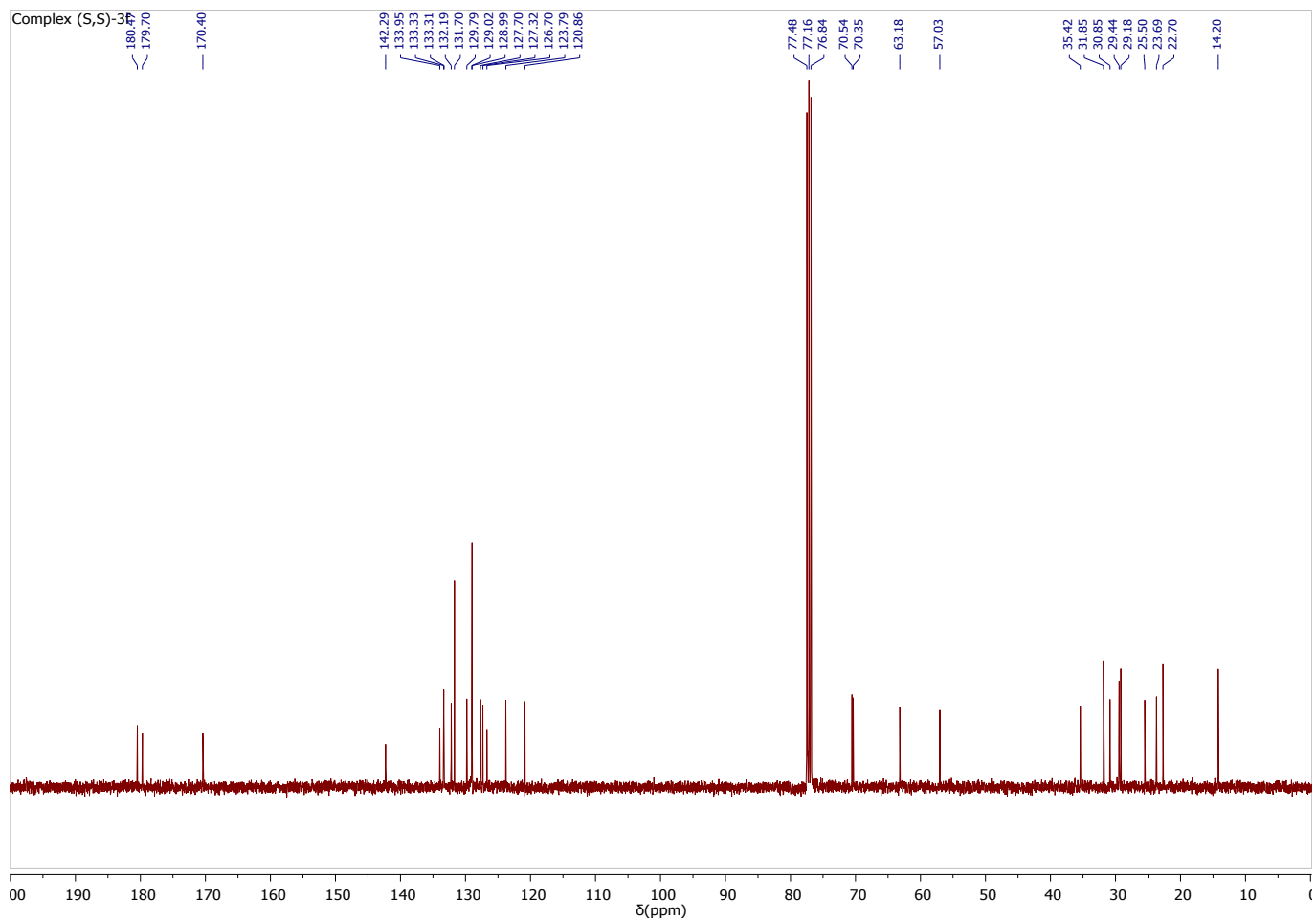
*<sup>1</sup>H and <sup>13</sup>C (JMOD) NMR spectra of the Ni(II) complex (S,S)-**3d***





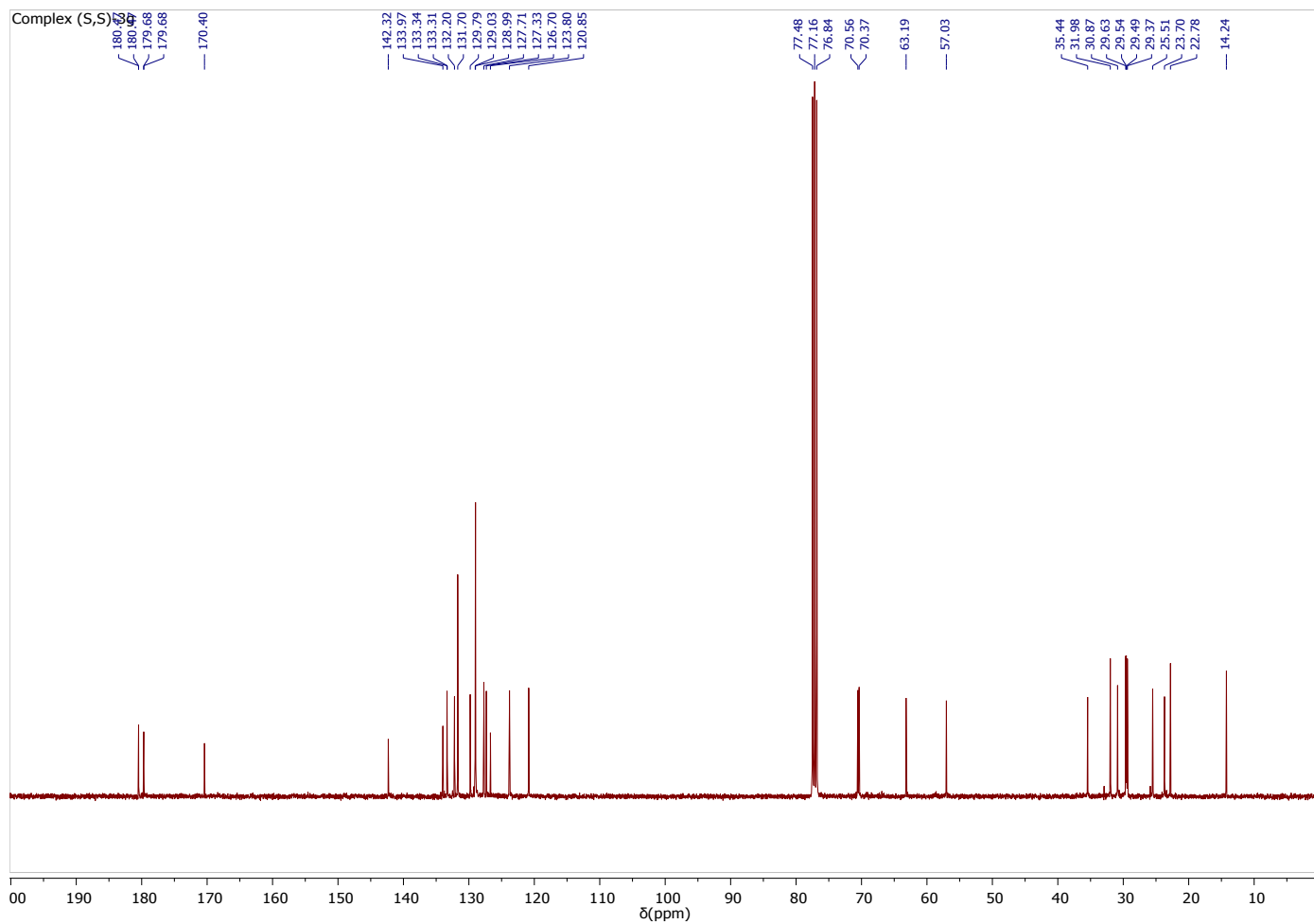
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-**3e**





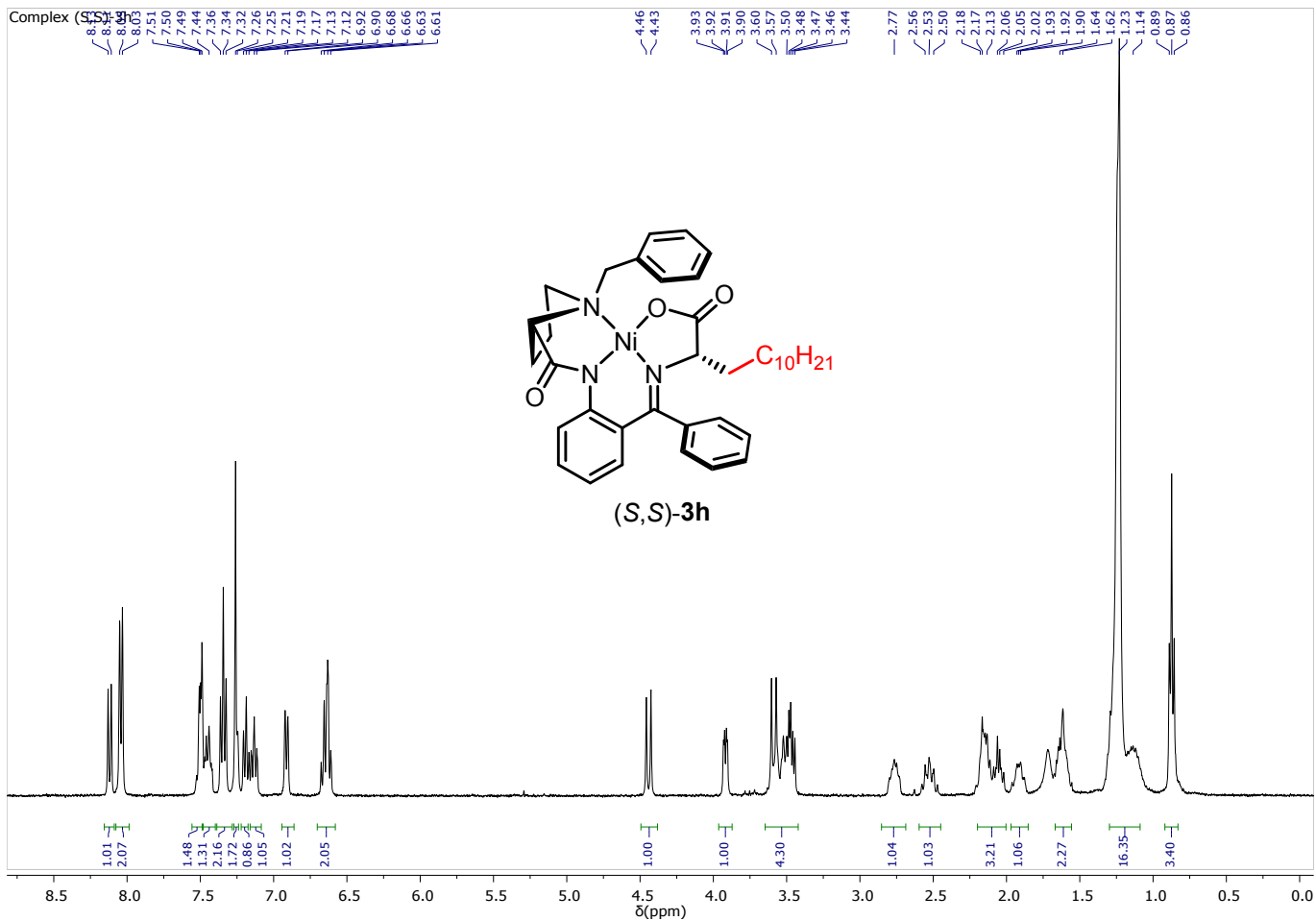
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-3f

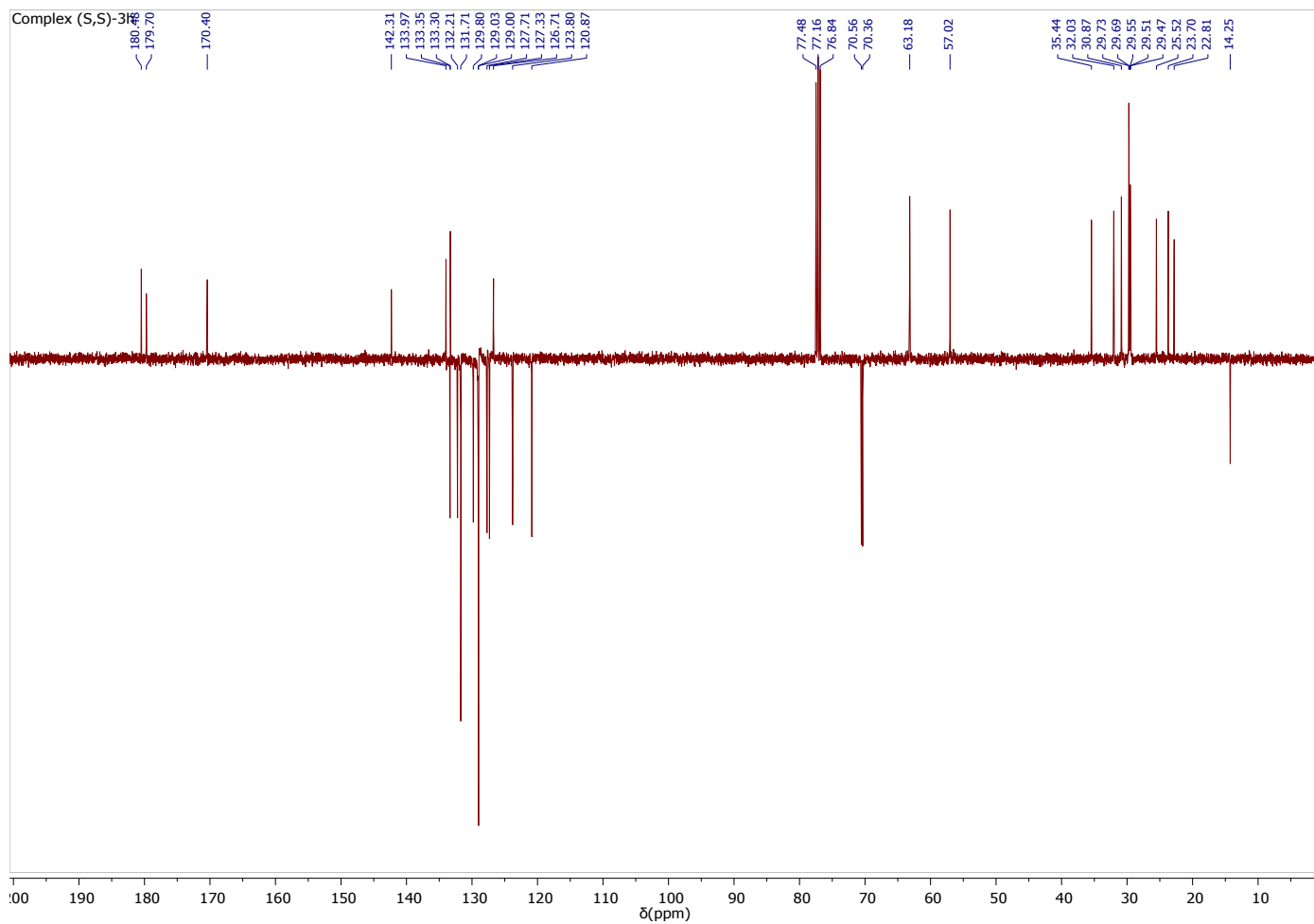




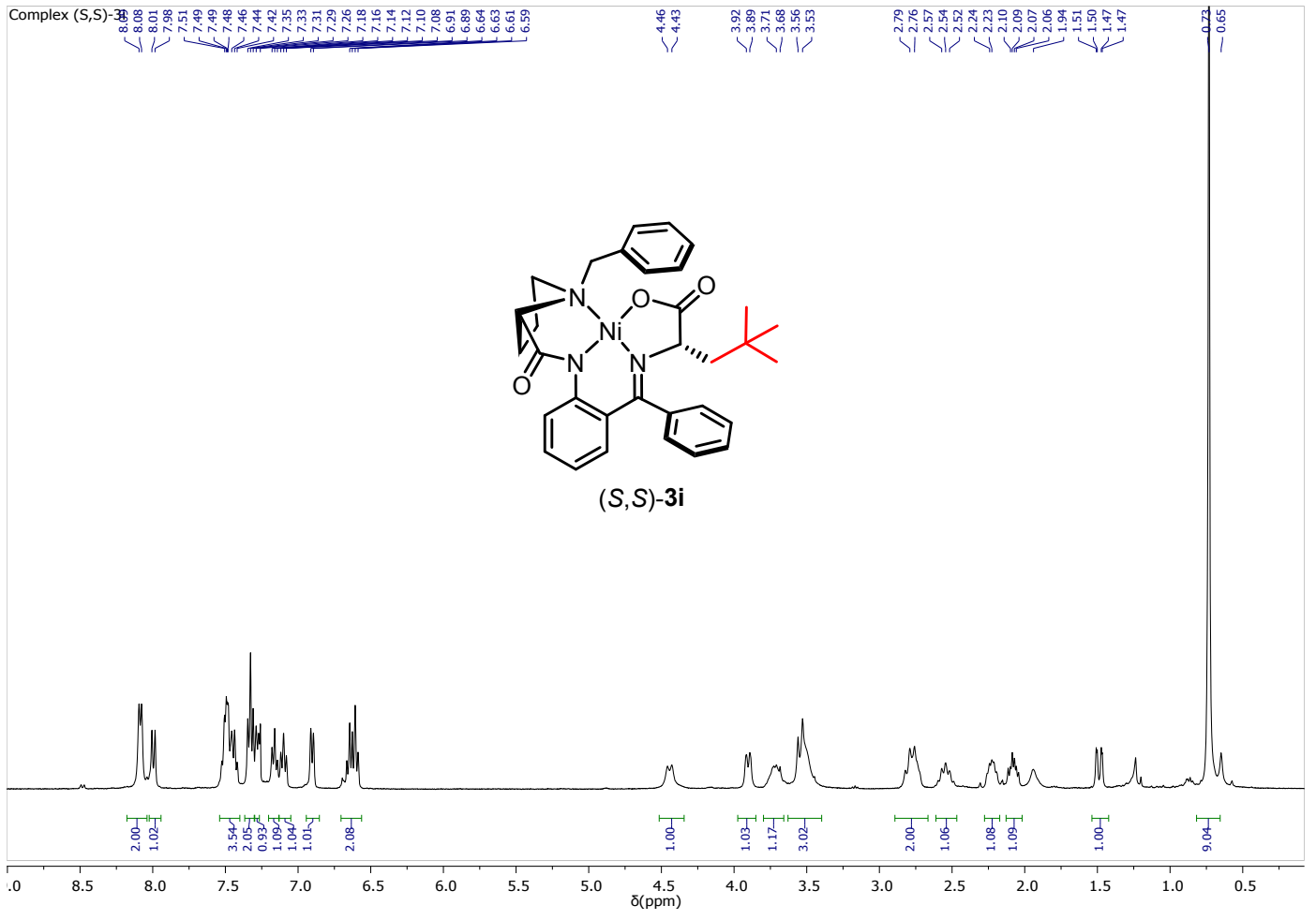
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-**3g**

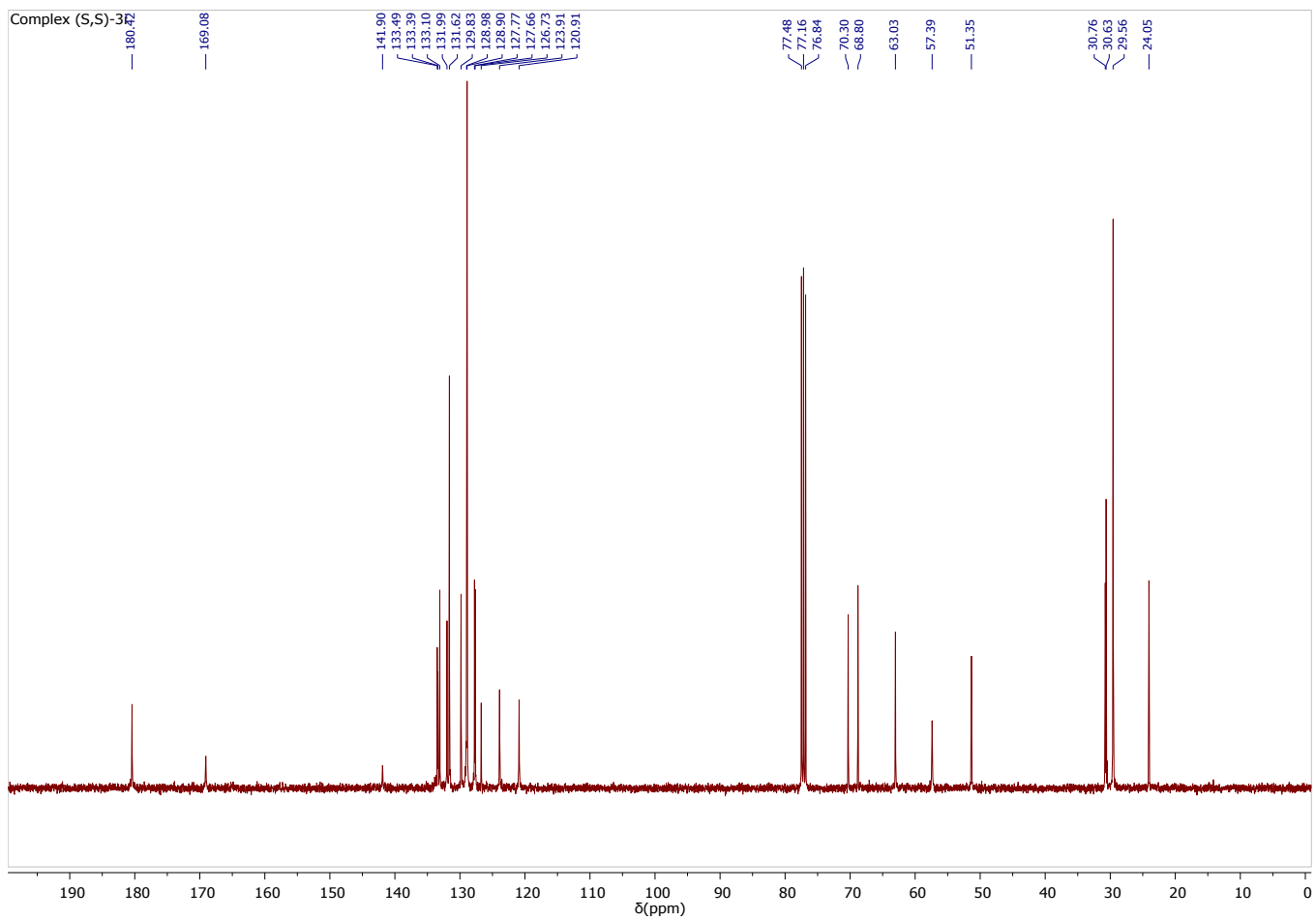




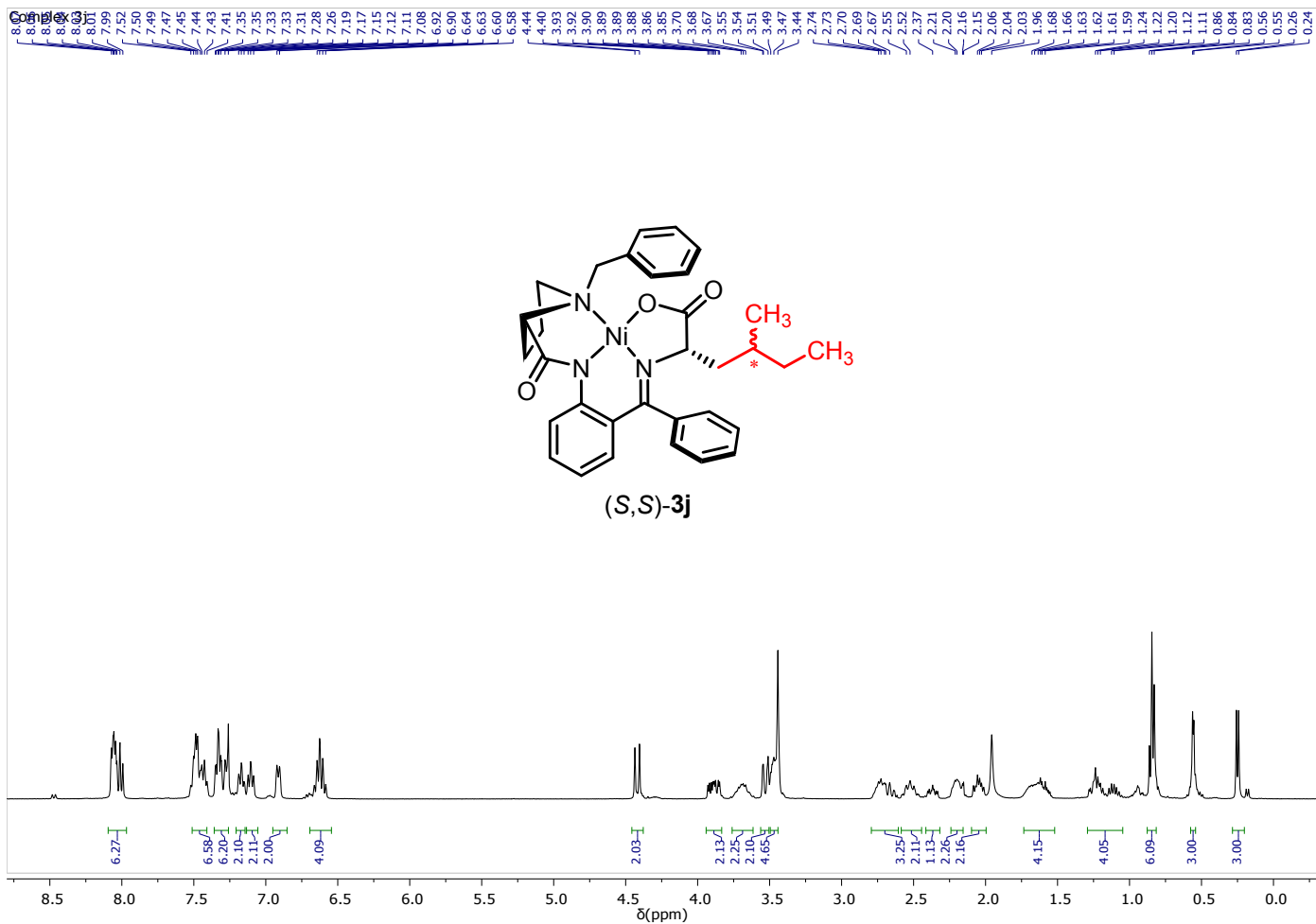


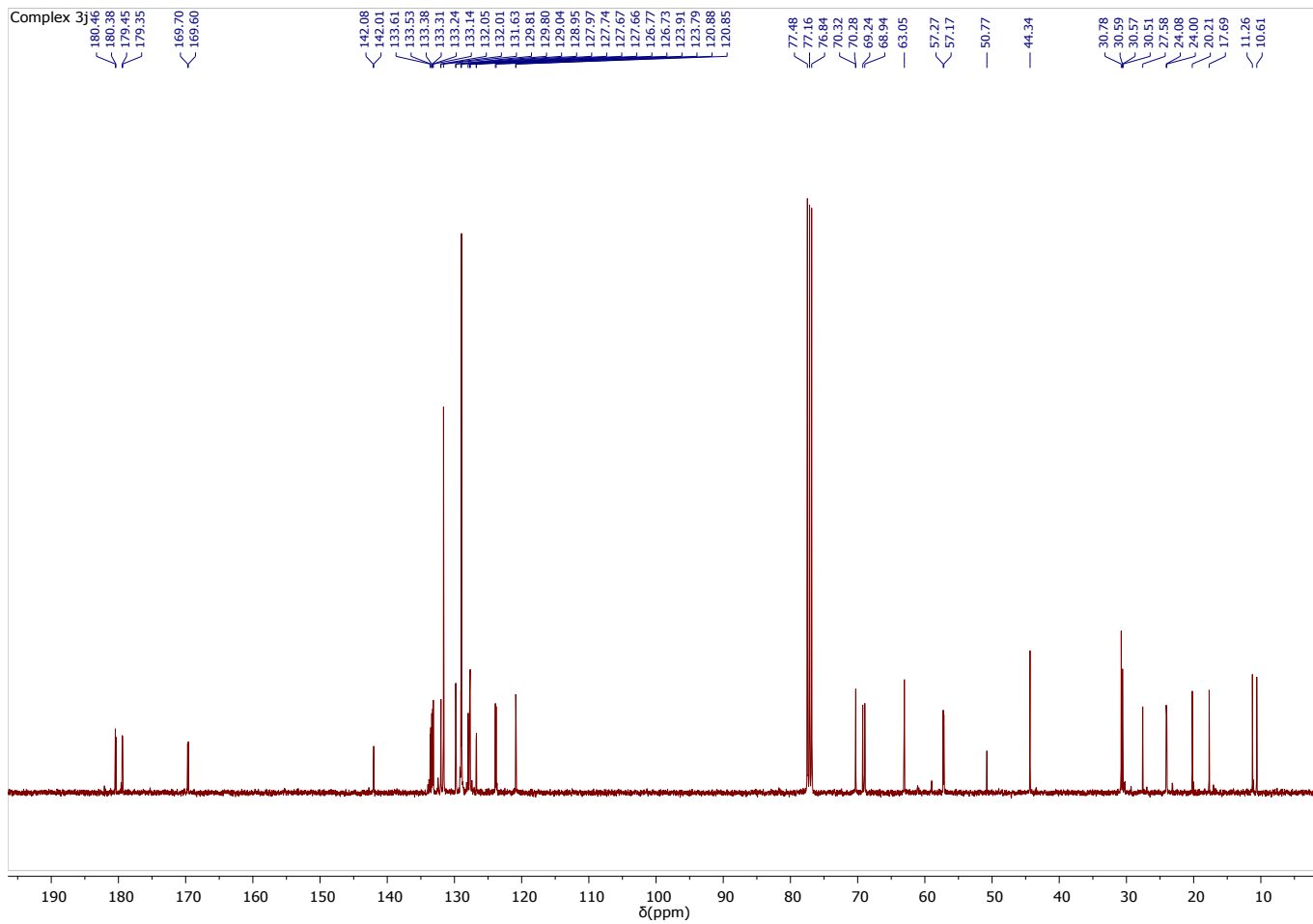
$^1\text{H}$  and  $^{13}\text{C}$  (JMOD) NMR spectra of the Ni(II) complex (S,S)-**3h**



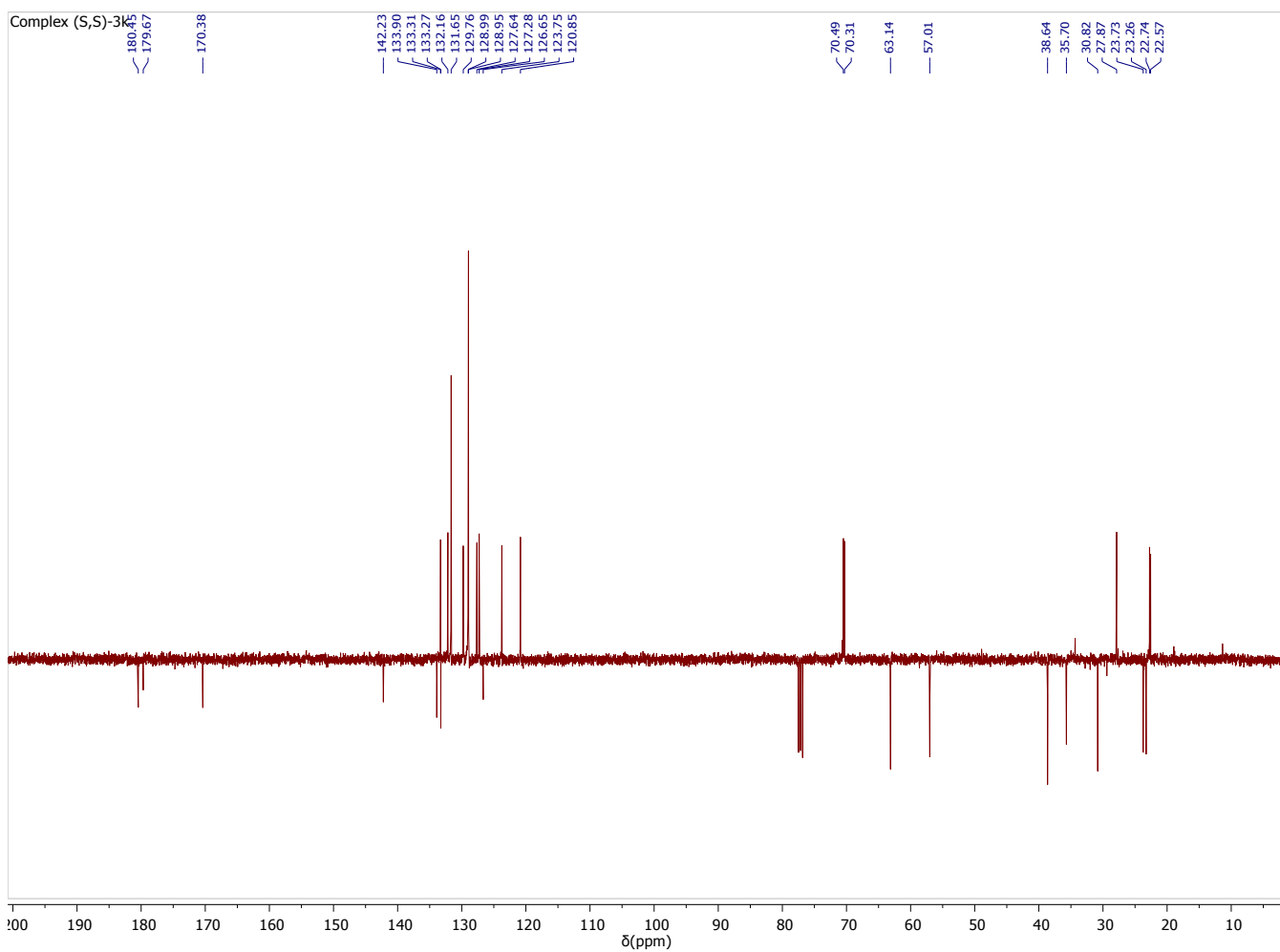
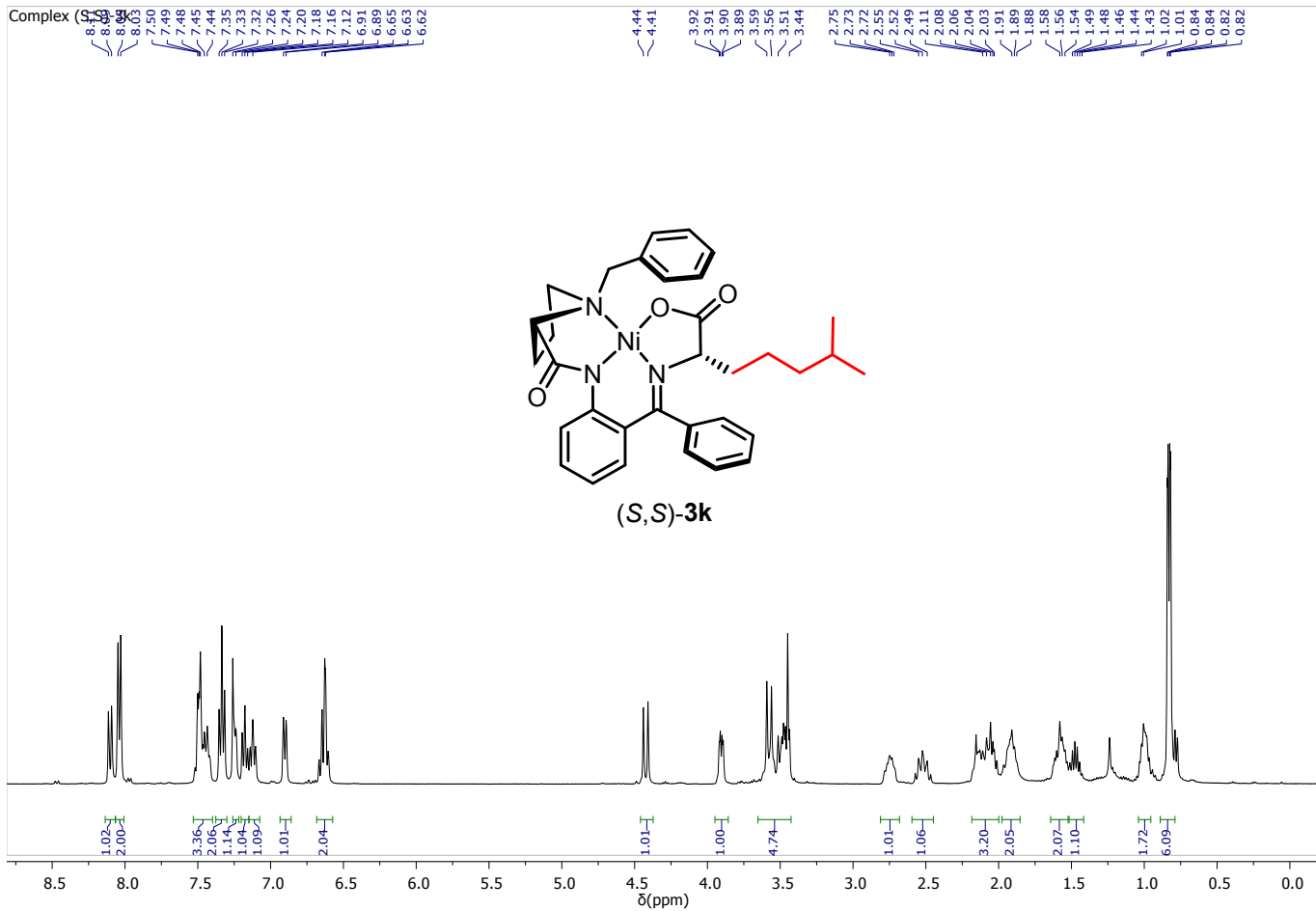


$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-**3i**

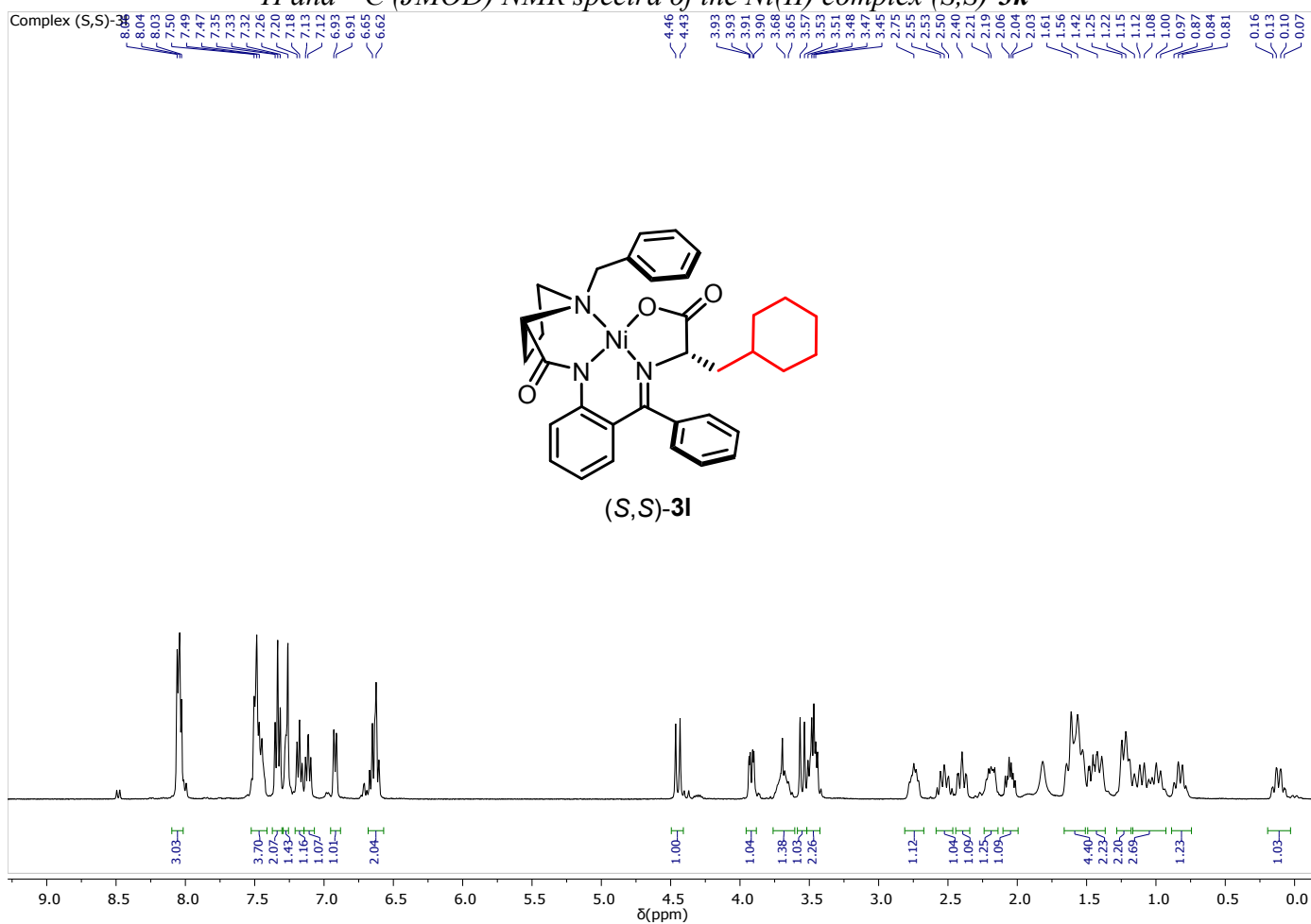




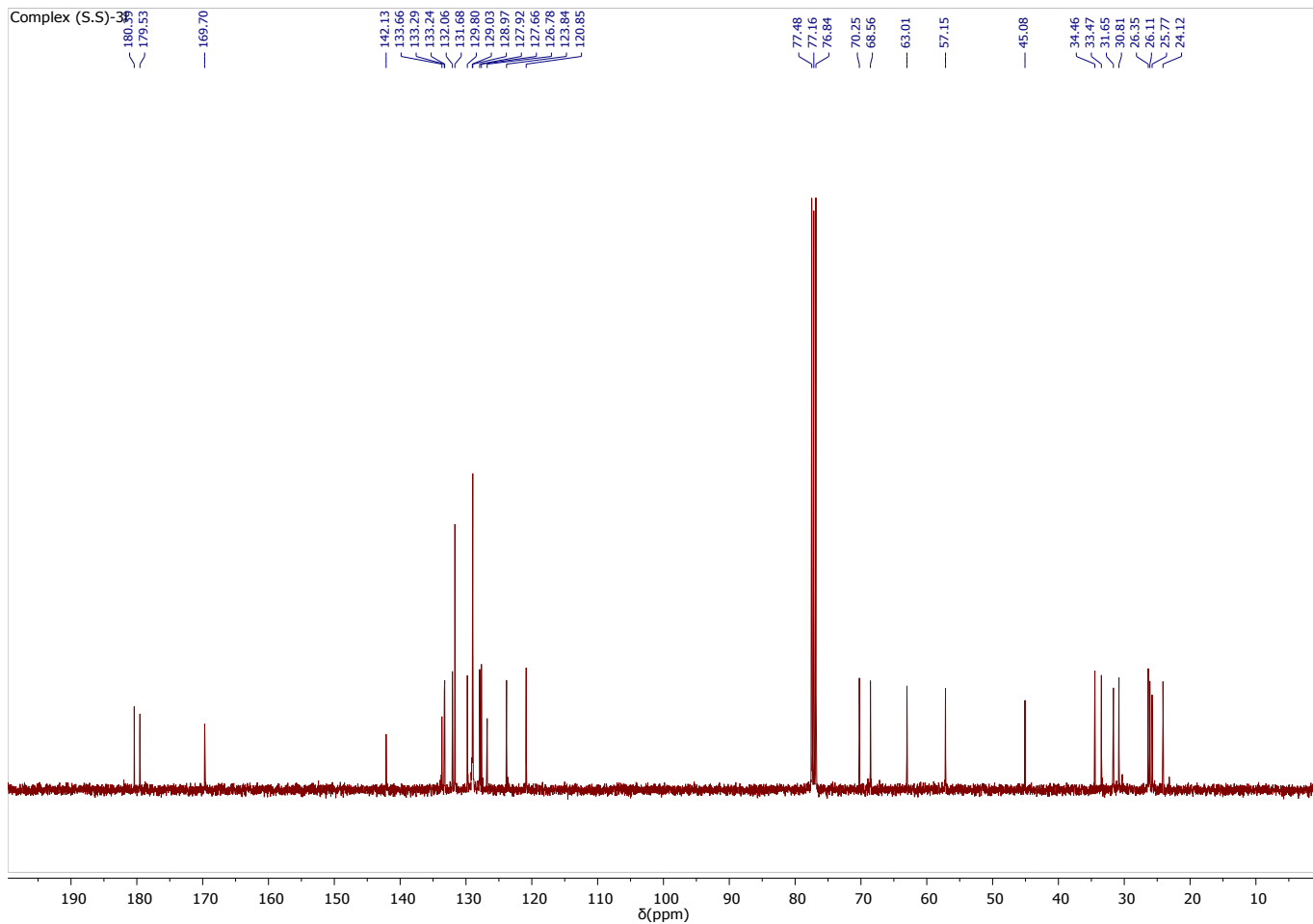
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (*S,S*)-**3j**



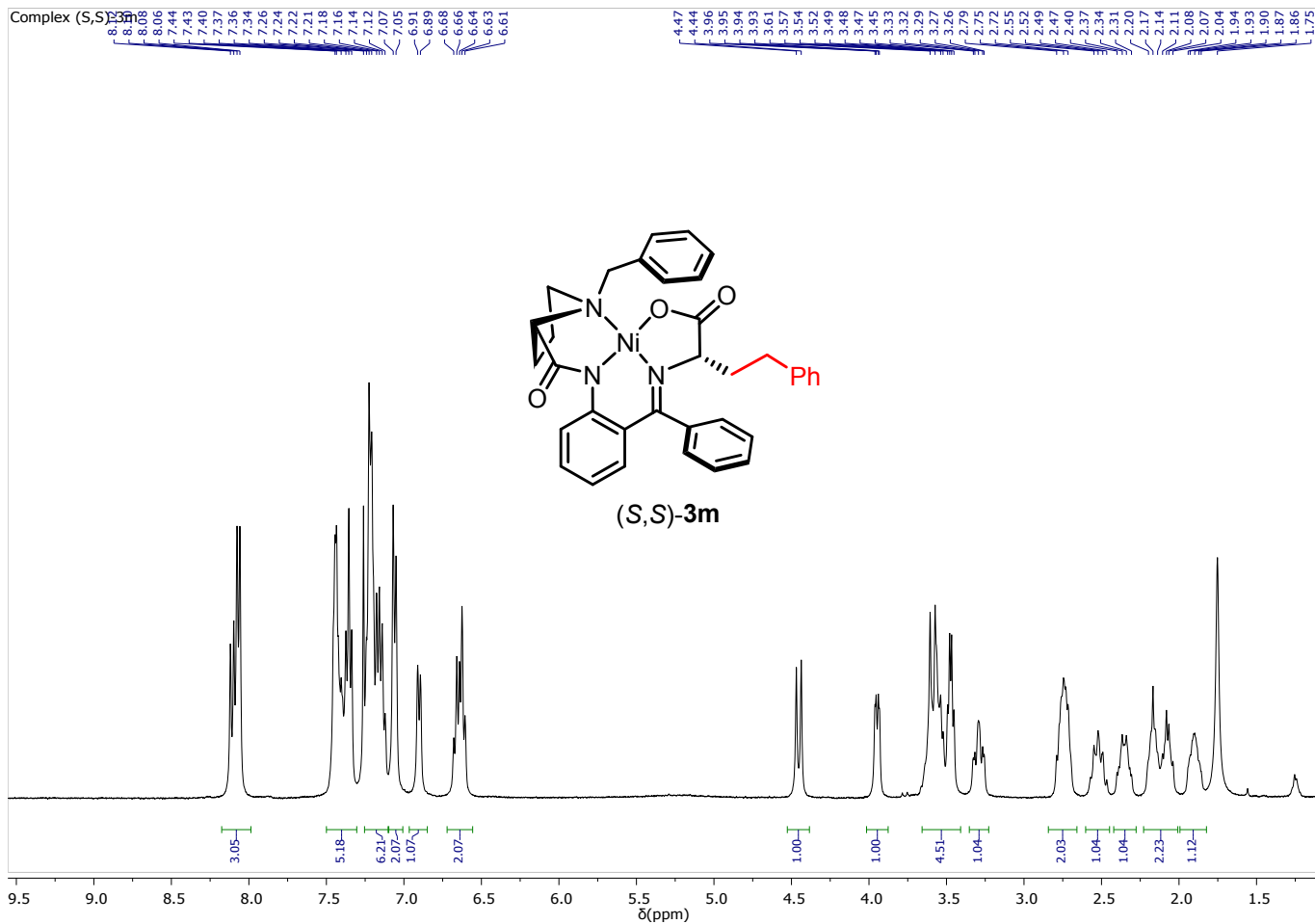
<sup>1</sup>H and <sup>13</sup>C (JMOD) NMR spectra of the Ni(II) complex (S,S)-3k

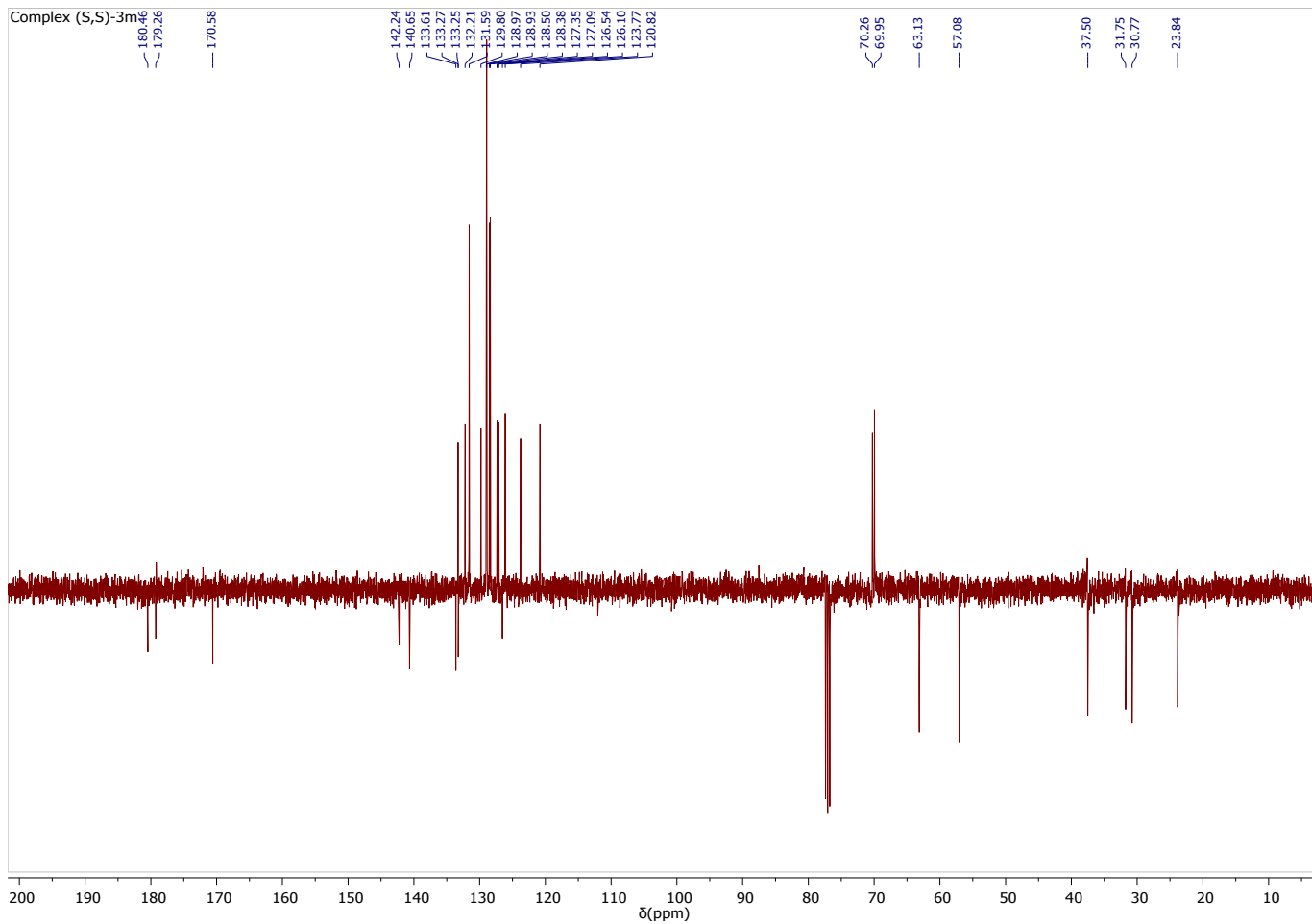




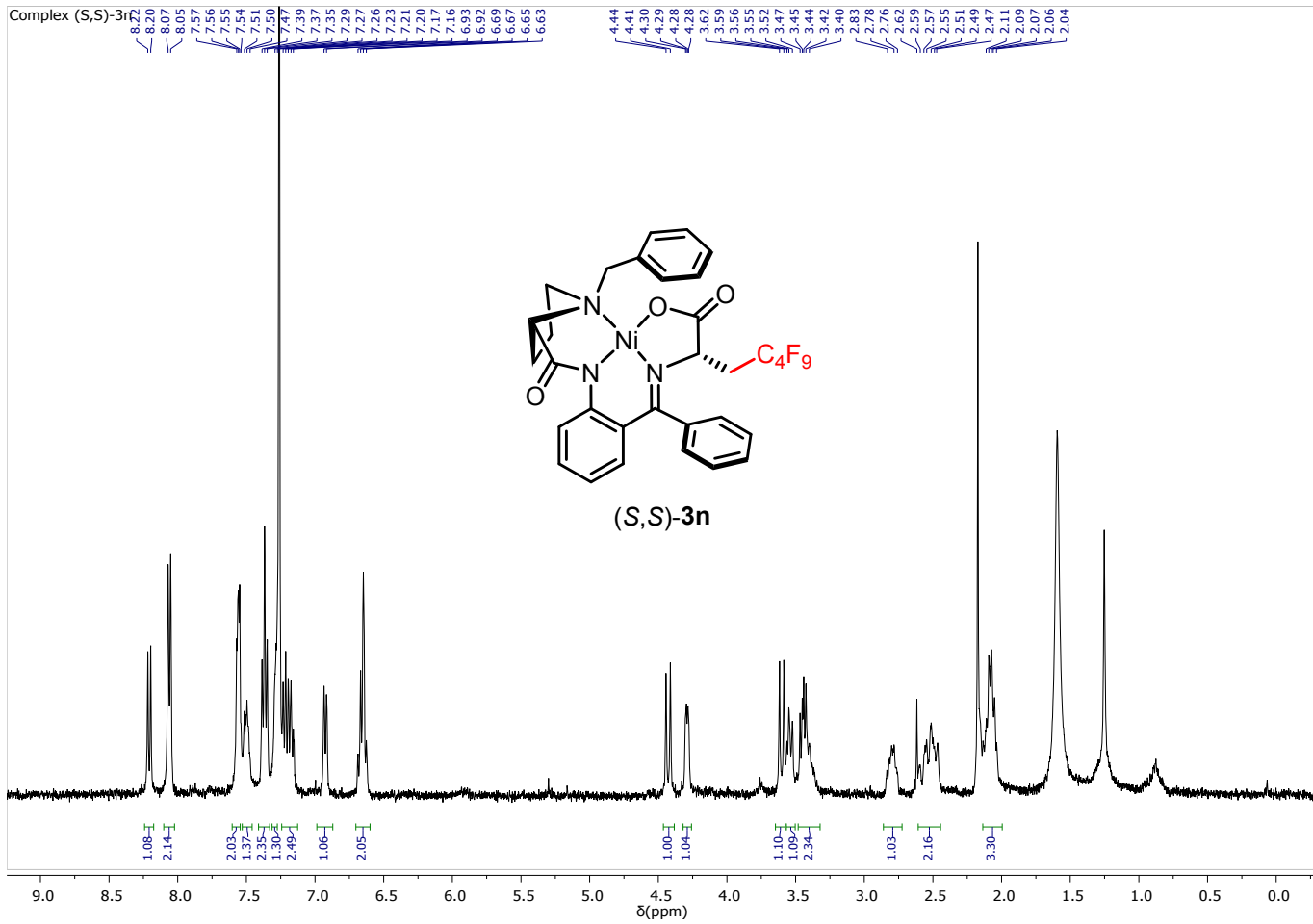


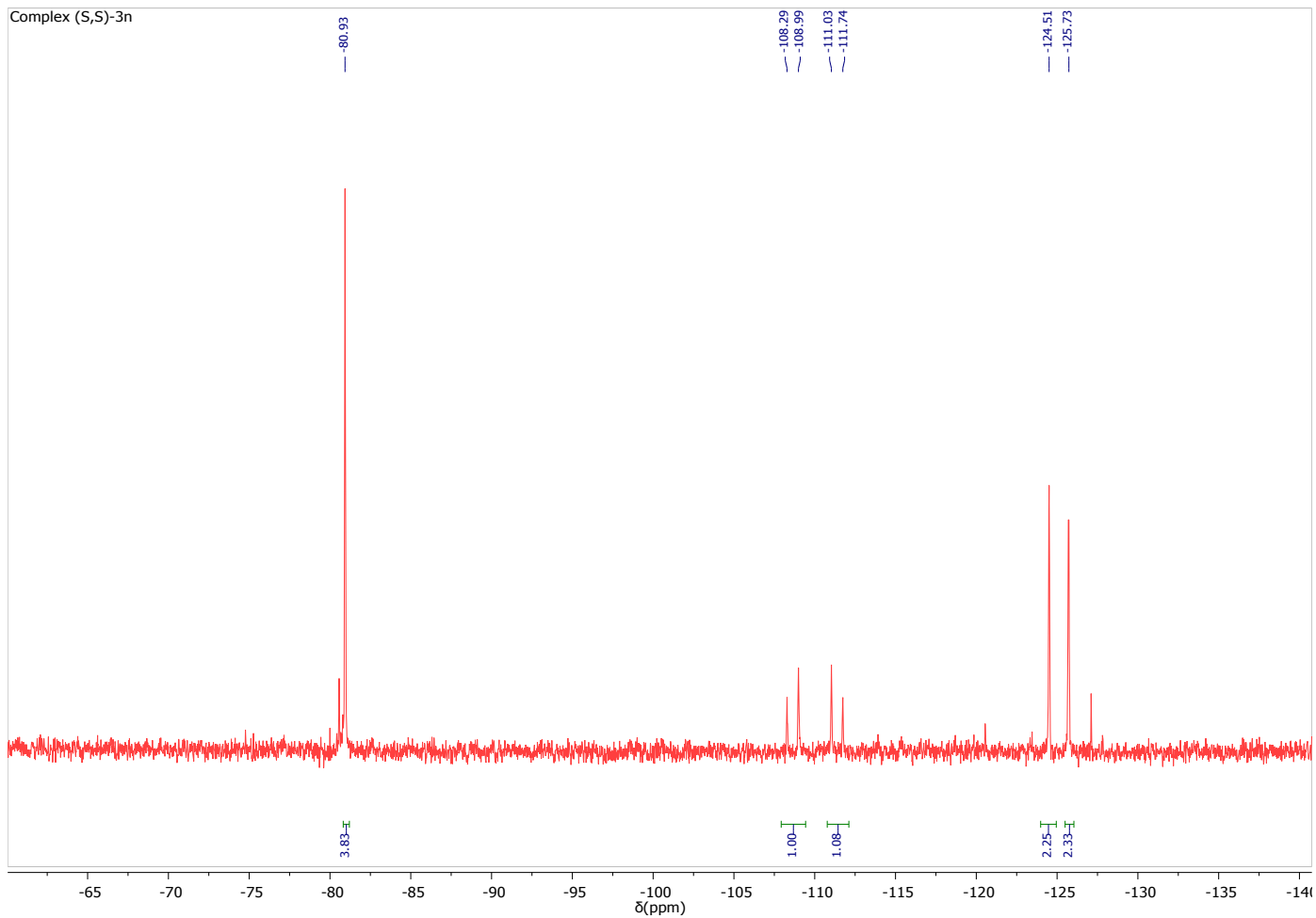
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Ni(II) complex (S,S)-**31**



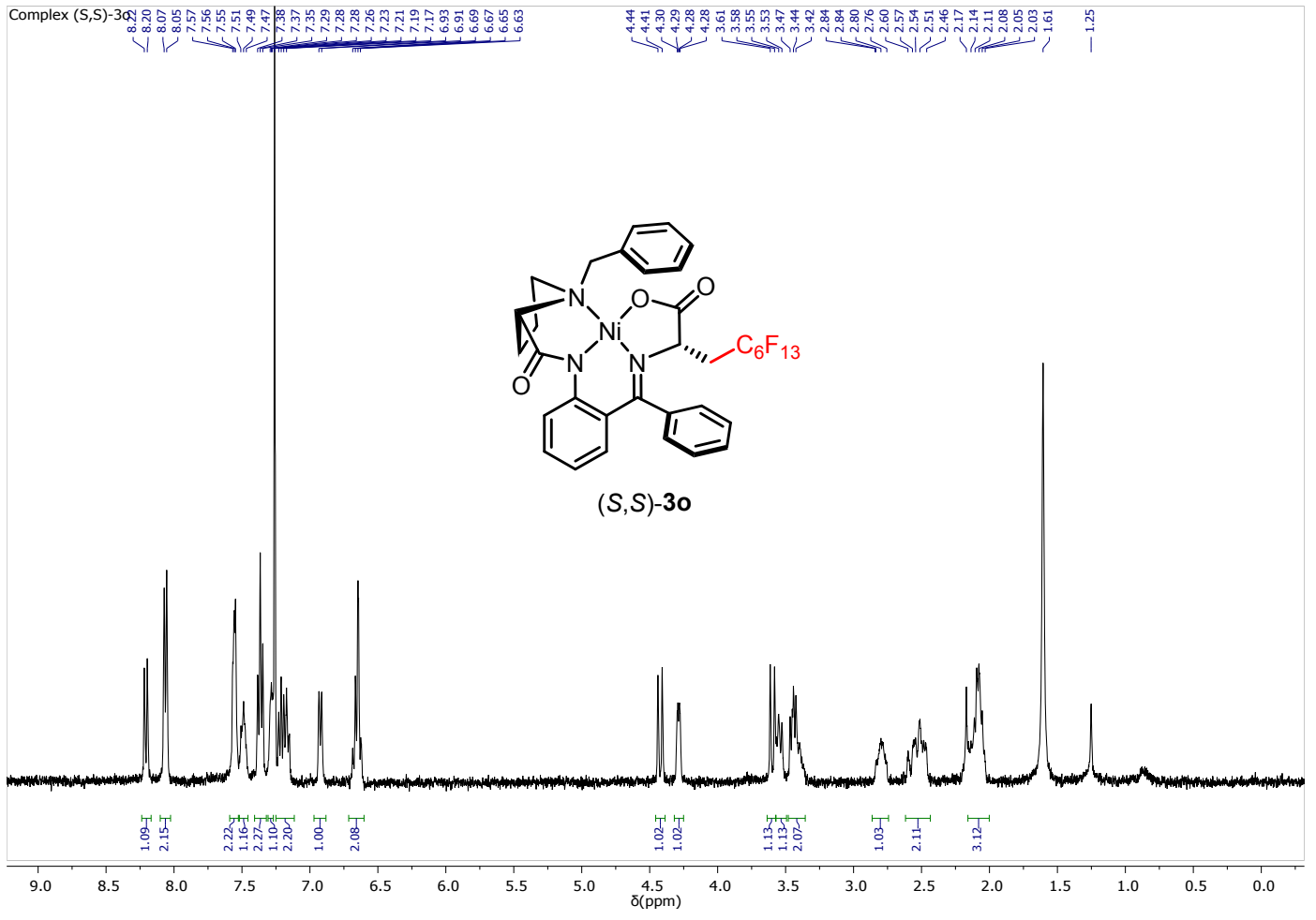


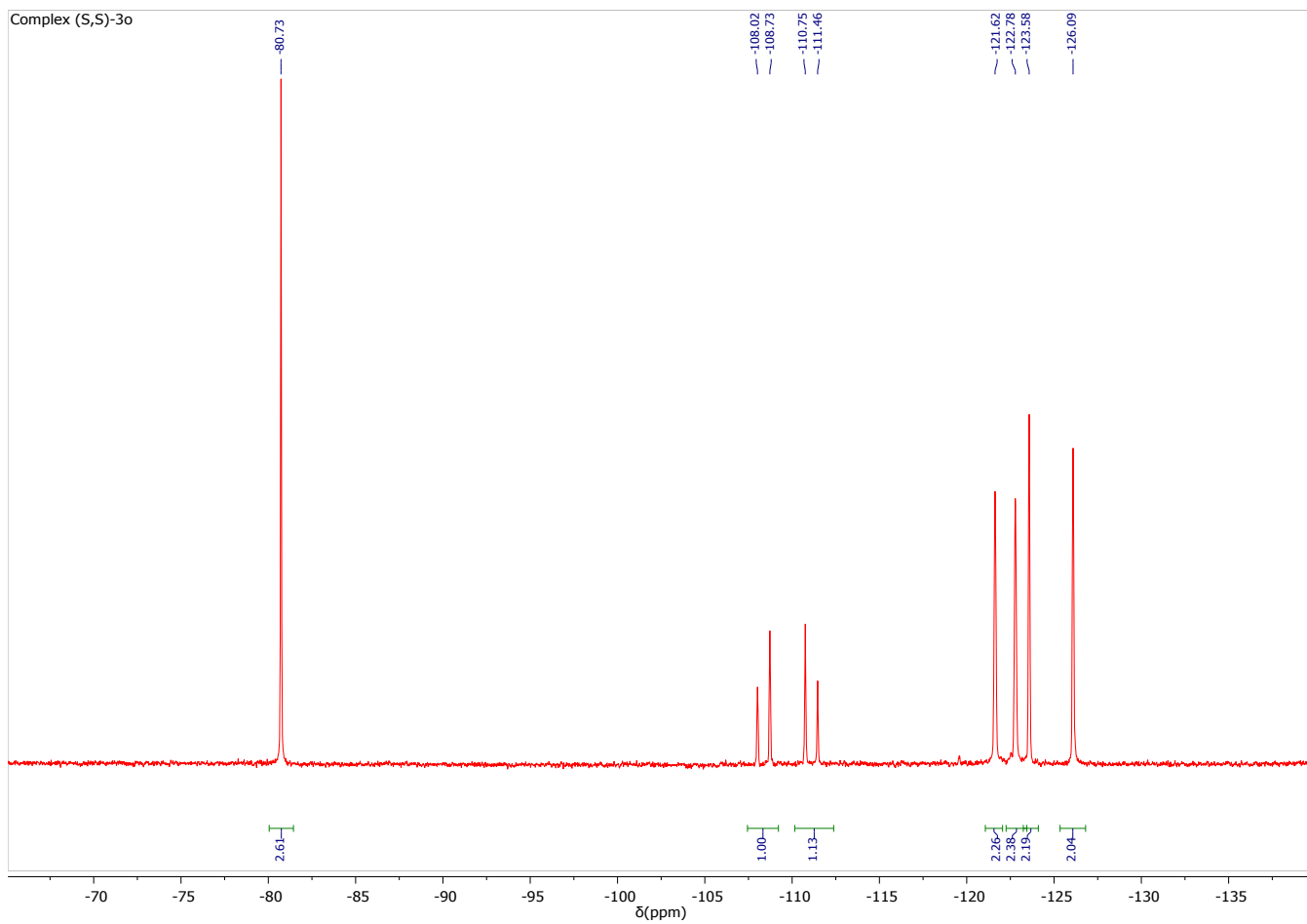
*<sup>1</sup>H and <sup>13</sup>C (JMOD) NMR spectra of the Ni(II) complex (S,S)-3m*



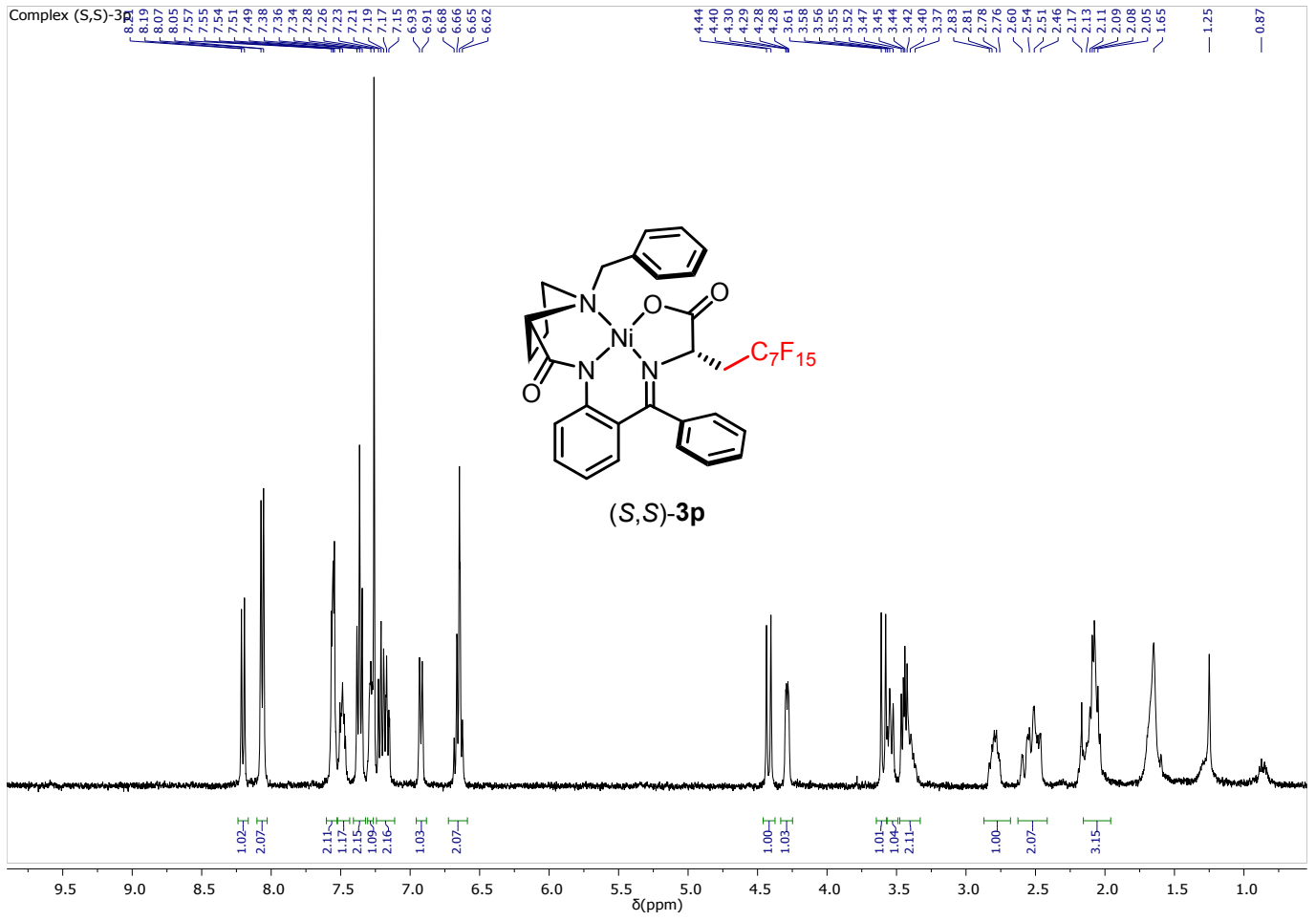


*<sup>1</sup>H and <sup>19</sup>F NMR spectra of the Ni(II) complex (S,S)-3n*

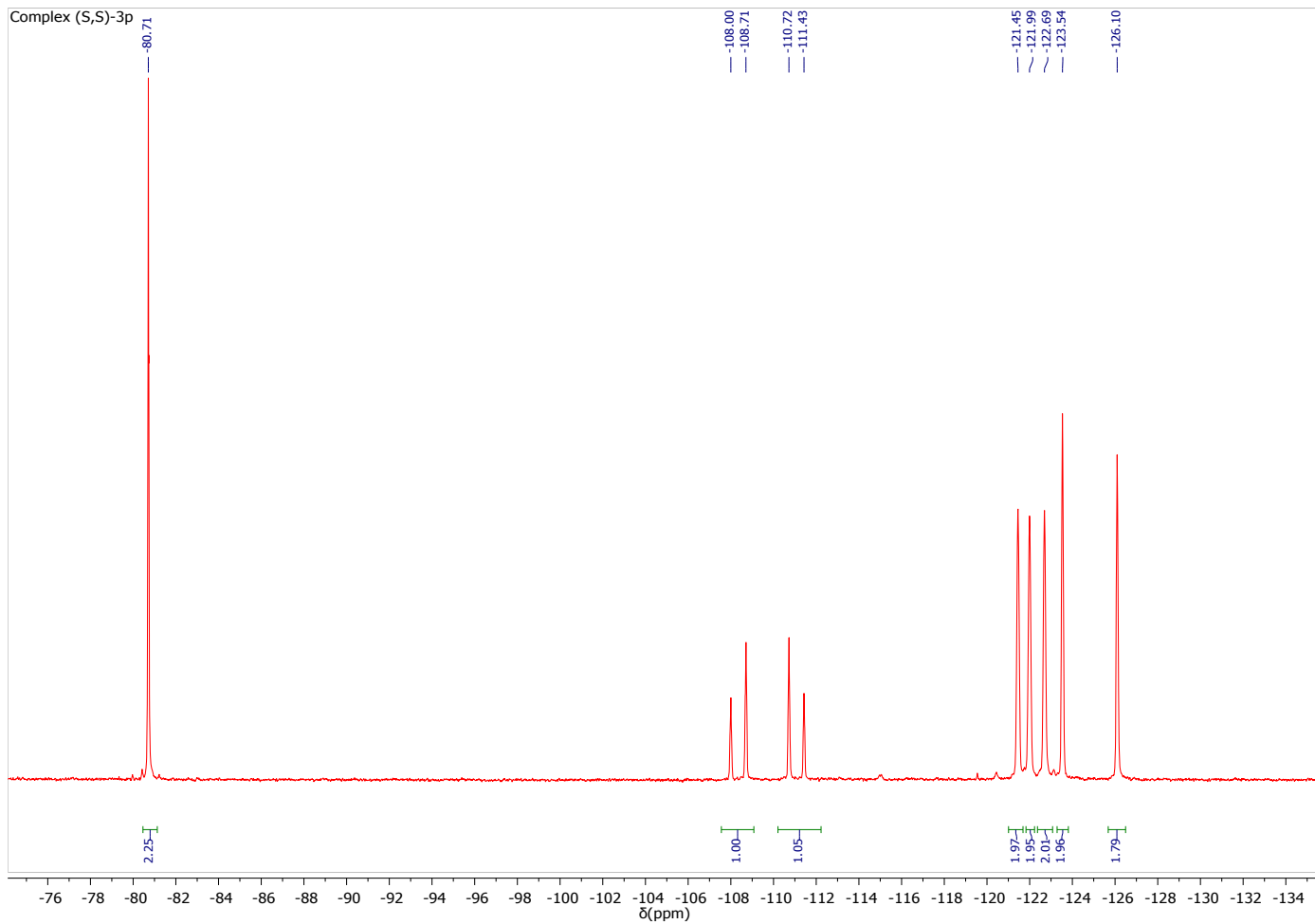




*<sup>1</sup>H and <sup>19</sup>F NMR spectra of the Ni(II) complex (S,S)-3o*

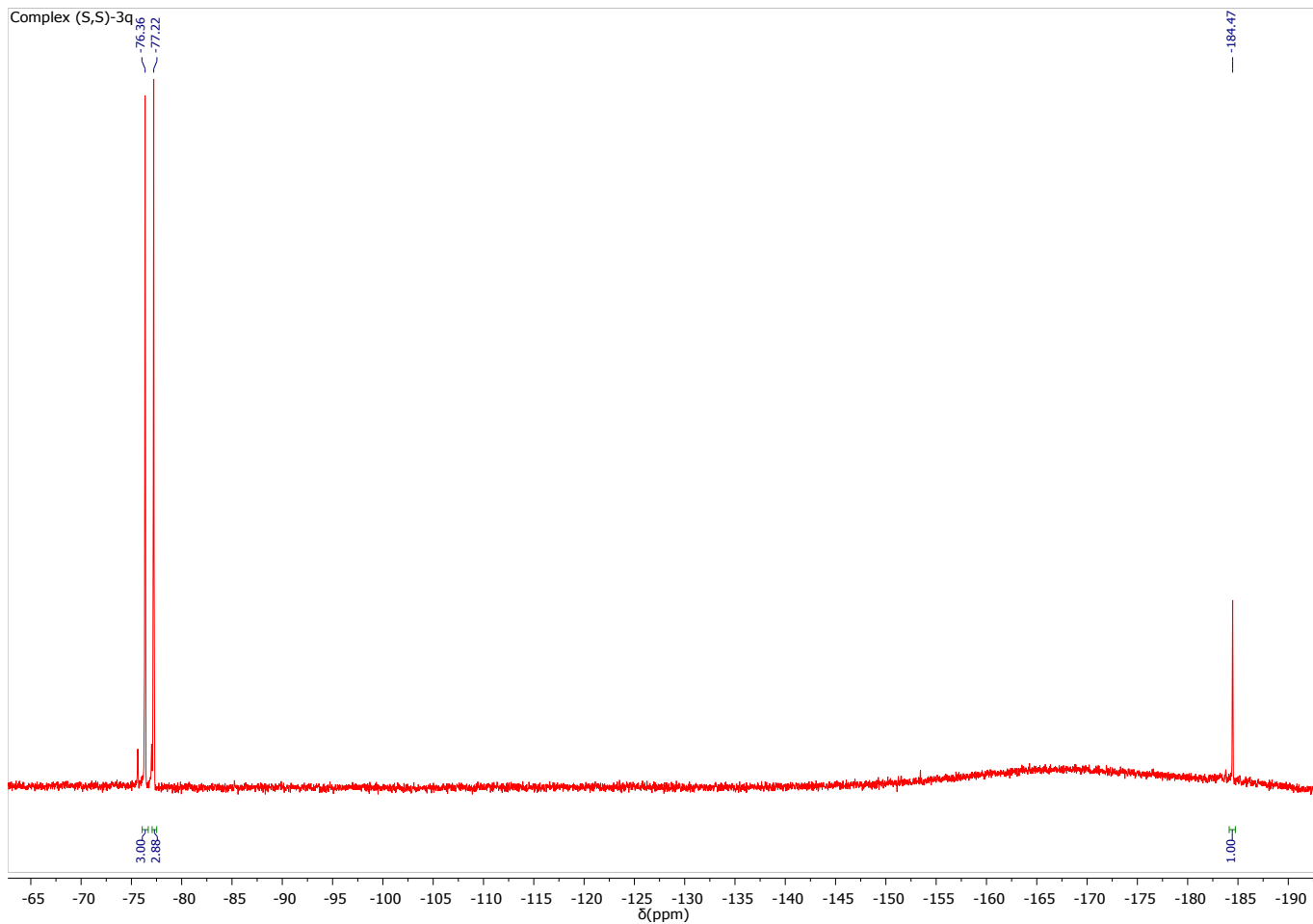




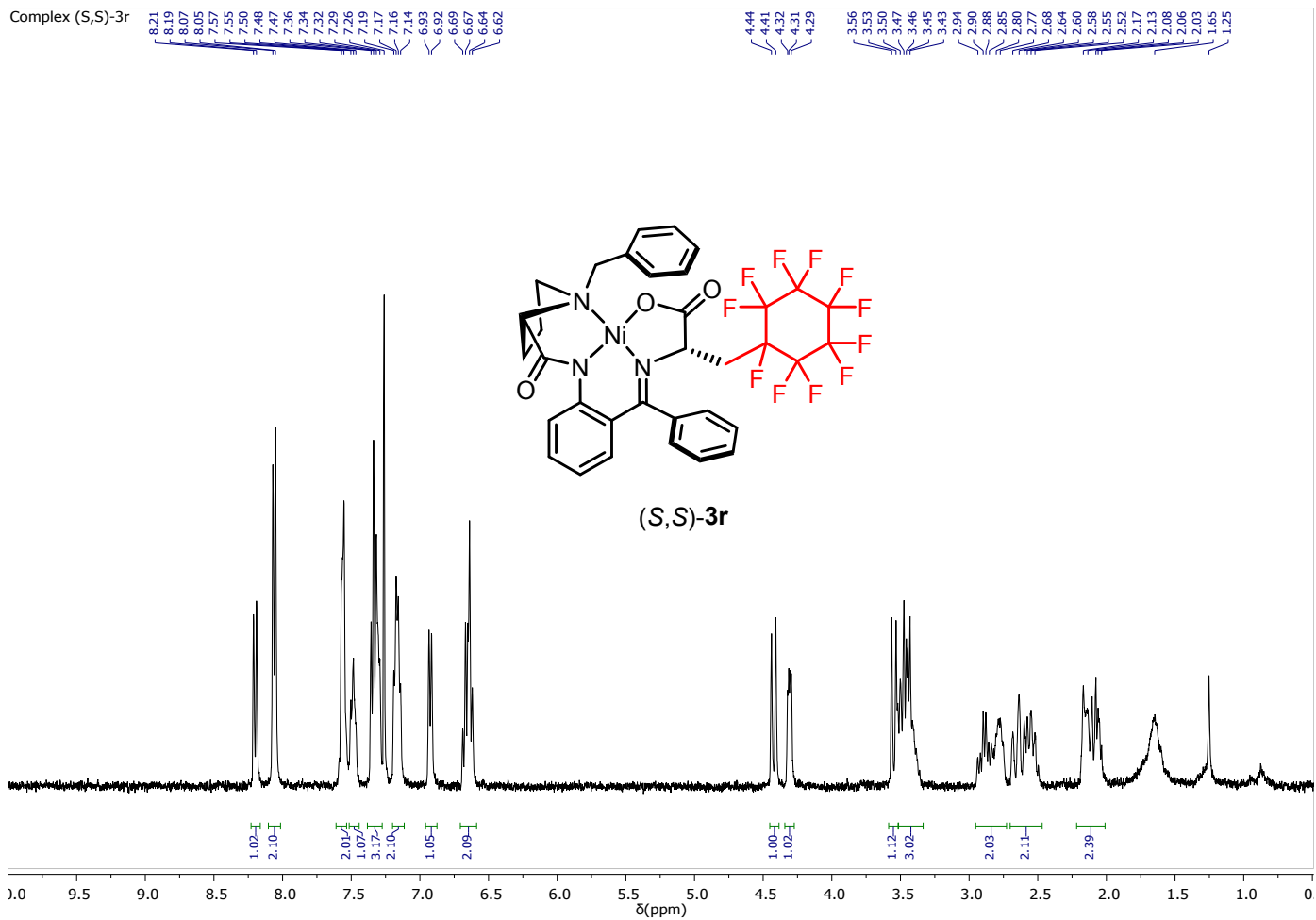


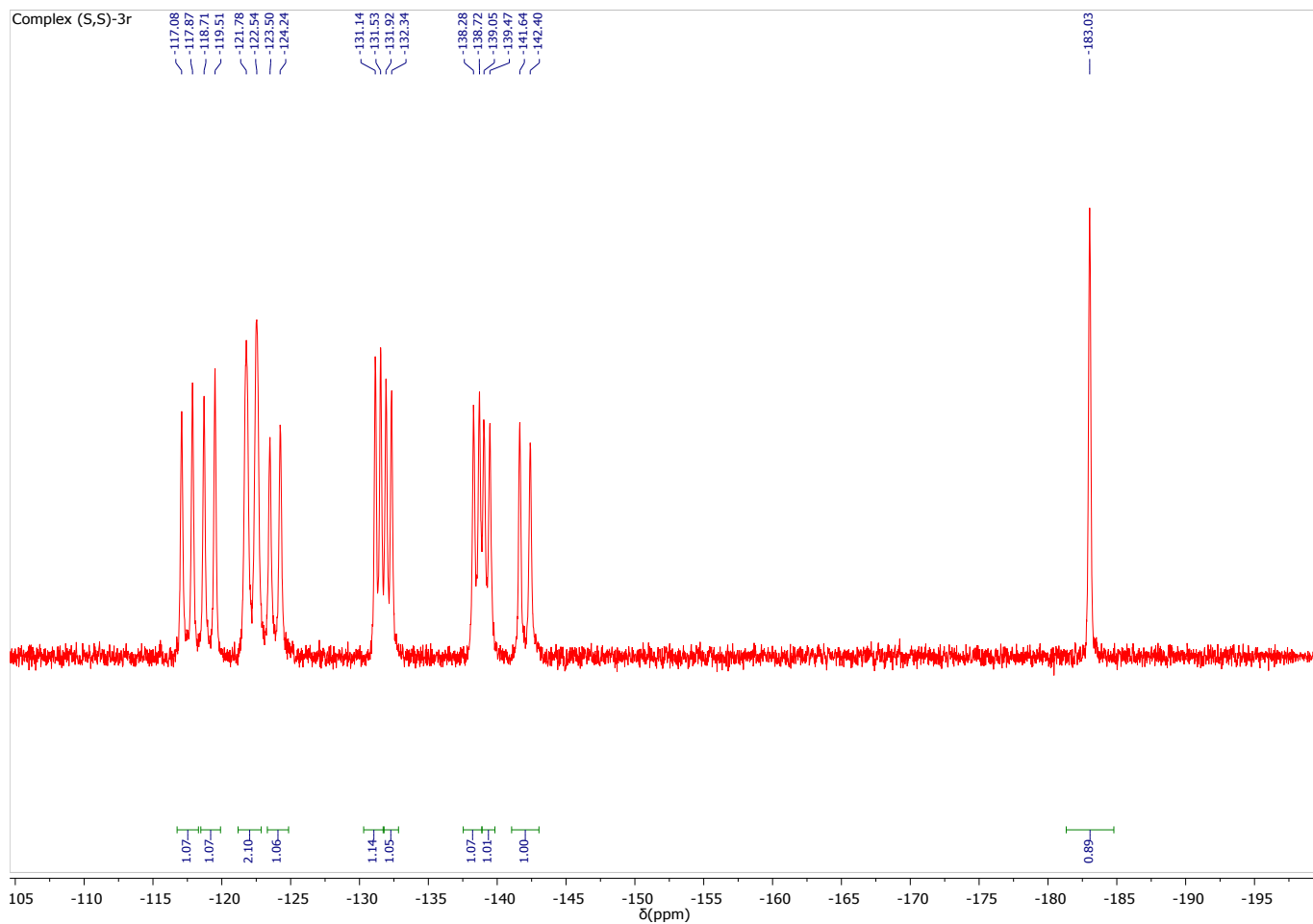
*<sup>1</sup>H and <sup>19</sup>F NMR spectra of the Ni(II) complex (S,S)-3p*



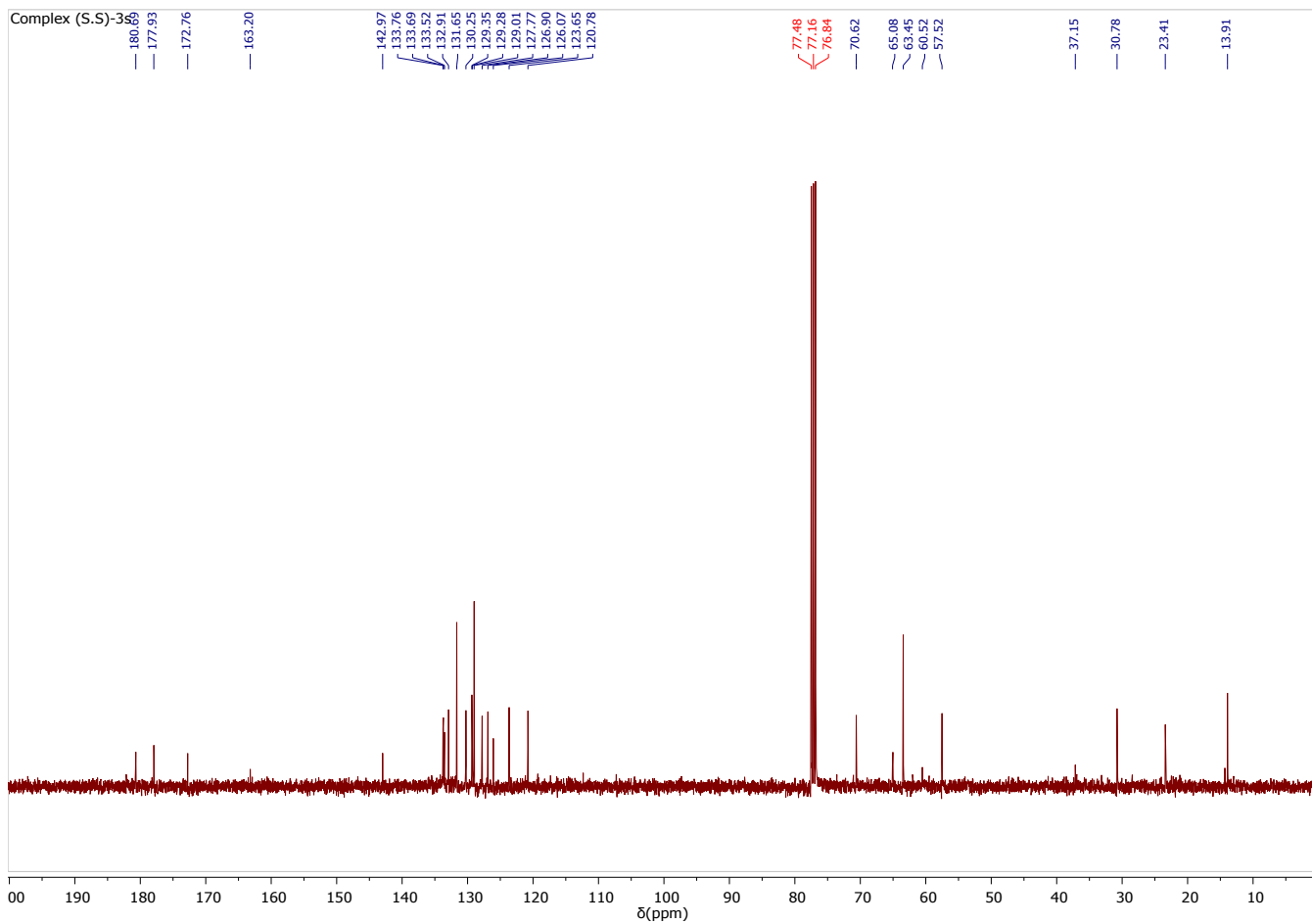
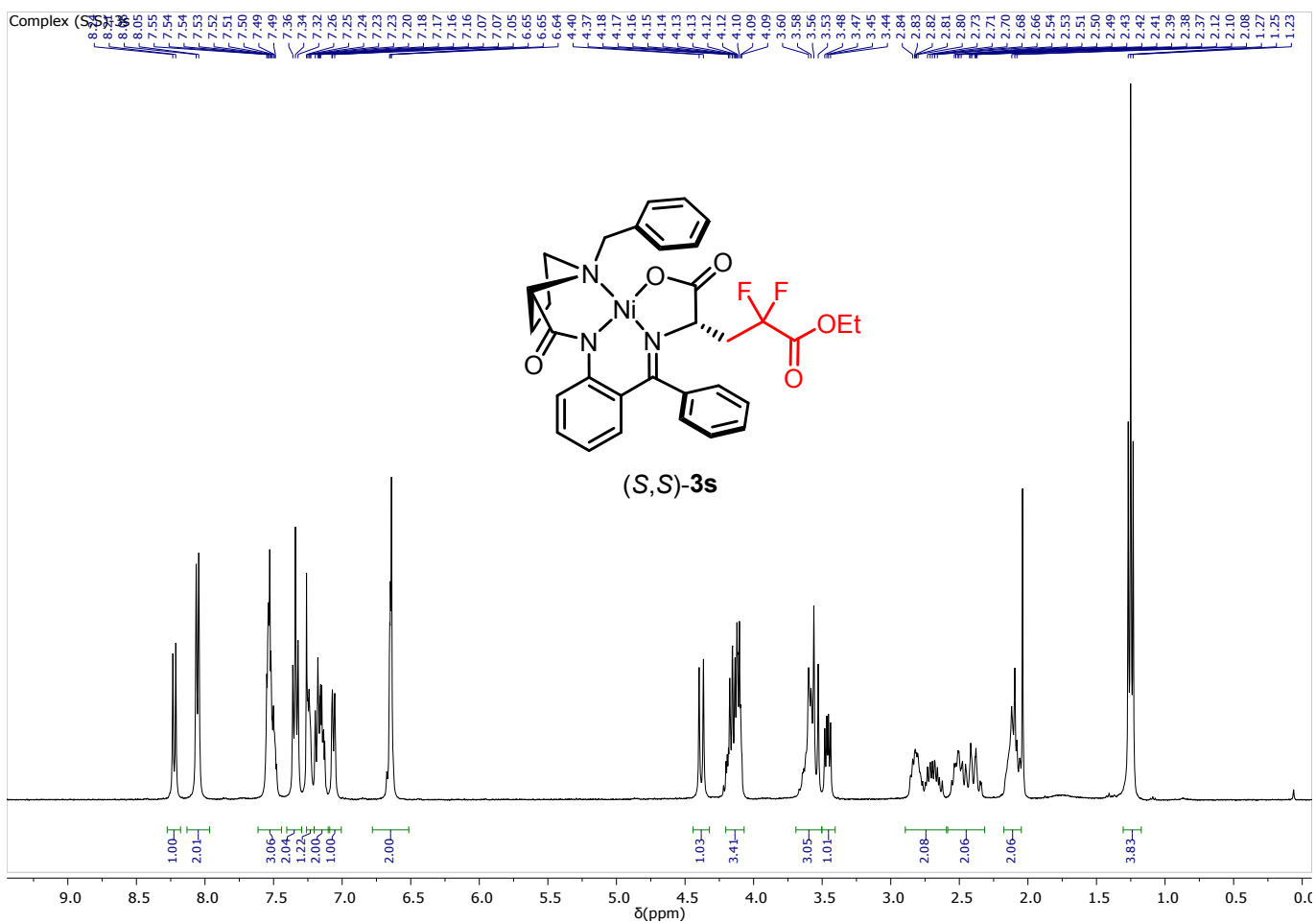


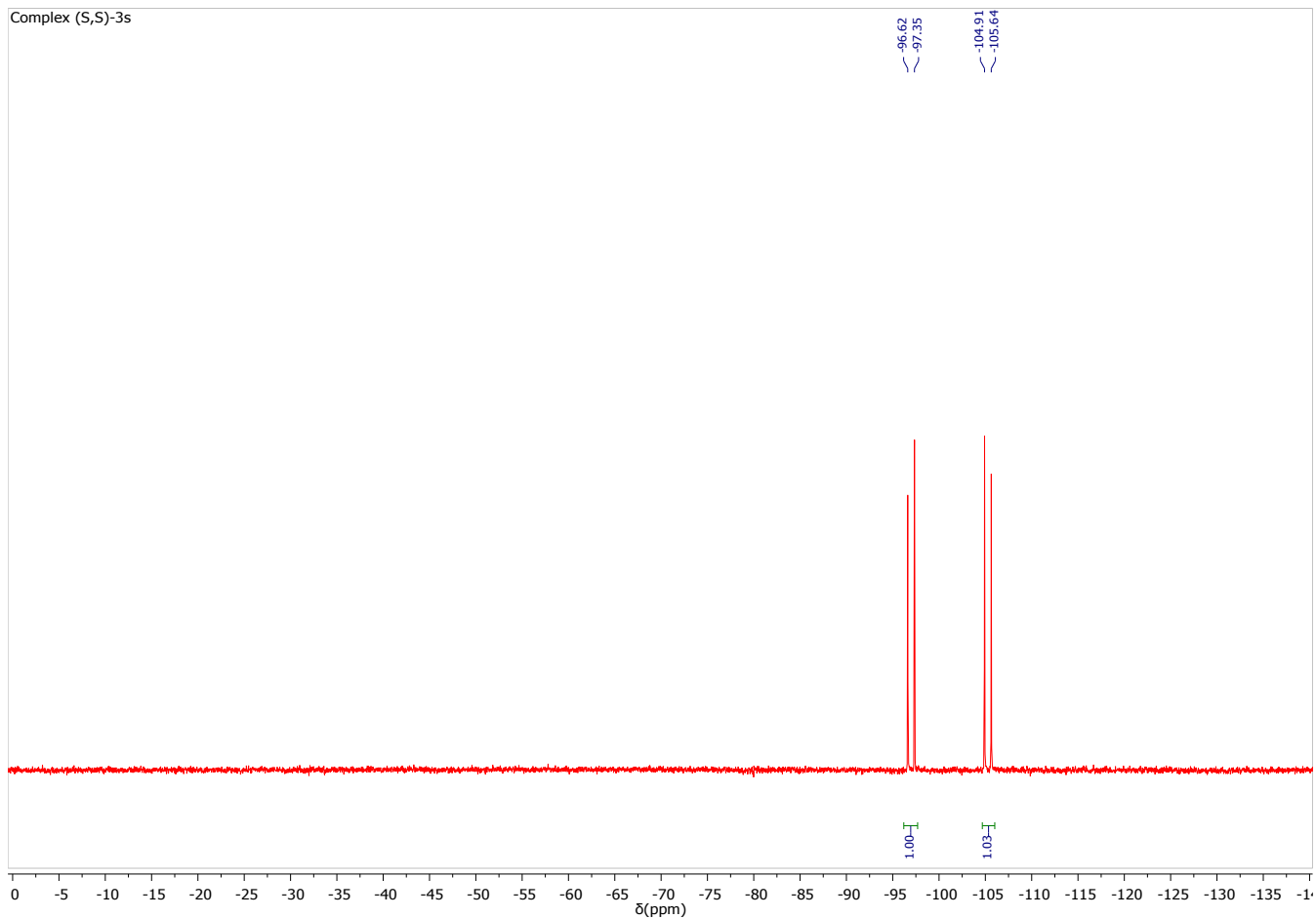
*<sup>1</sup>H and <sup>19</sup>F NMR spectra of the Ni(II) complex (S,S)-3q*



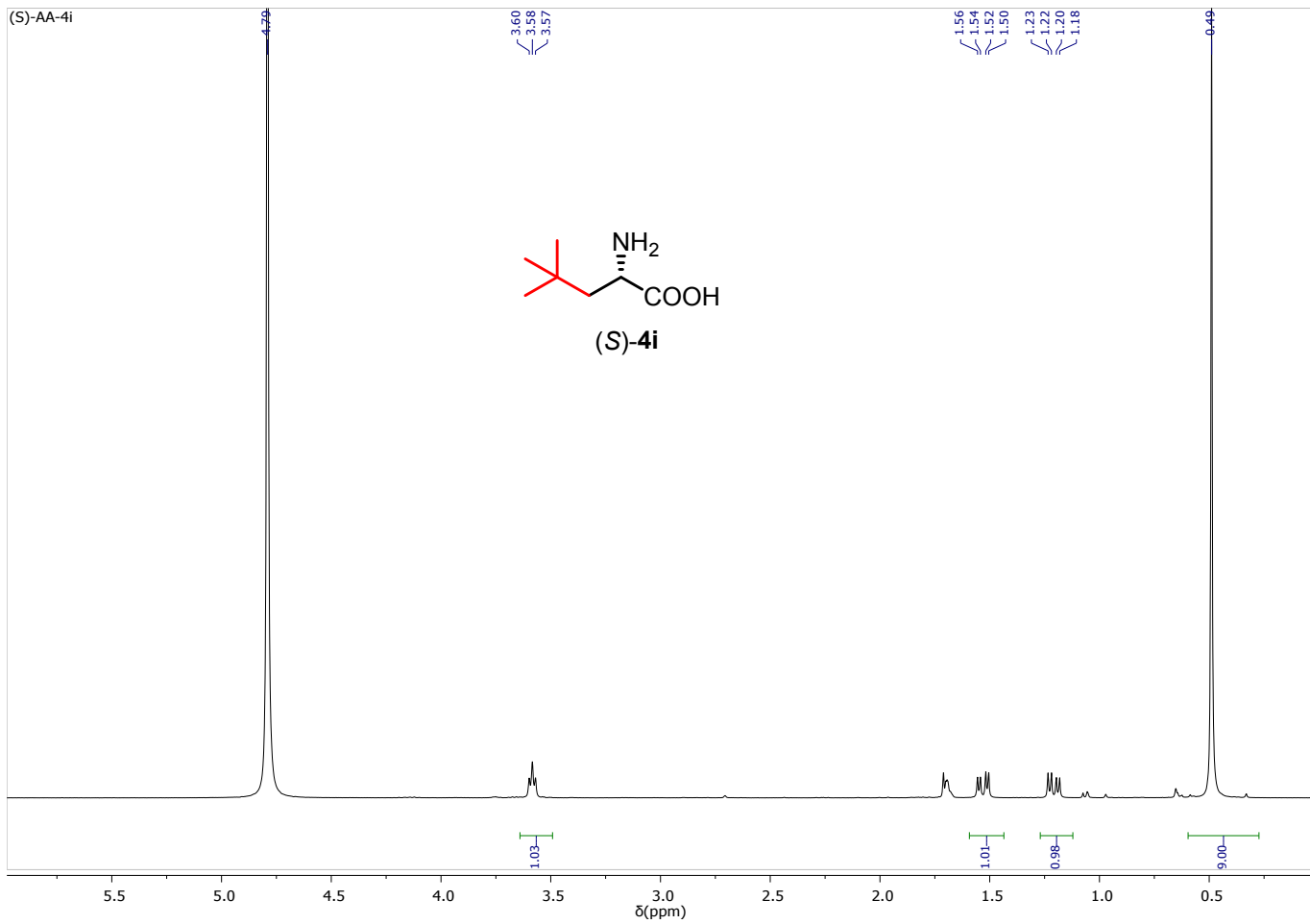


$^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of the Ni(II) complex (S,S)-3r

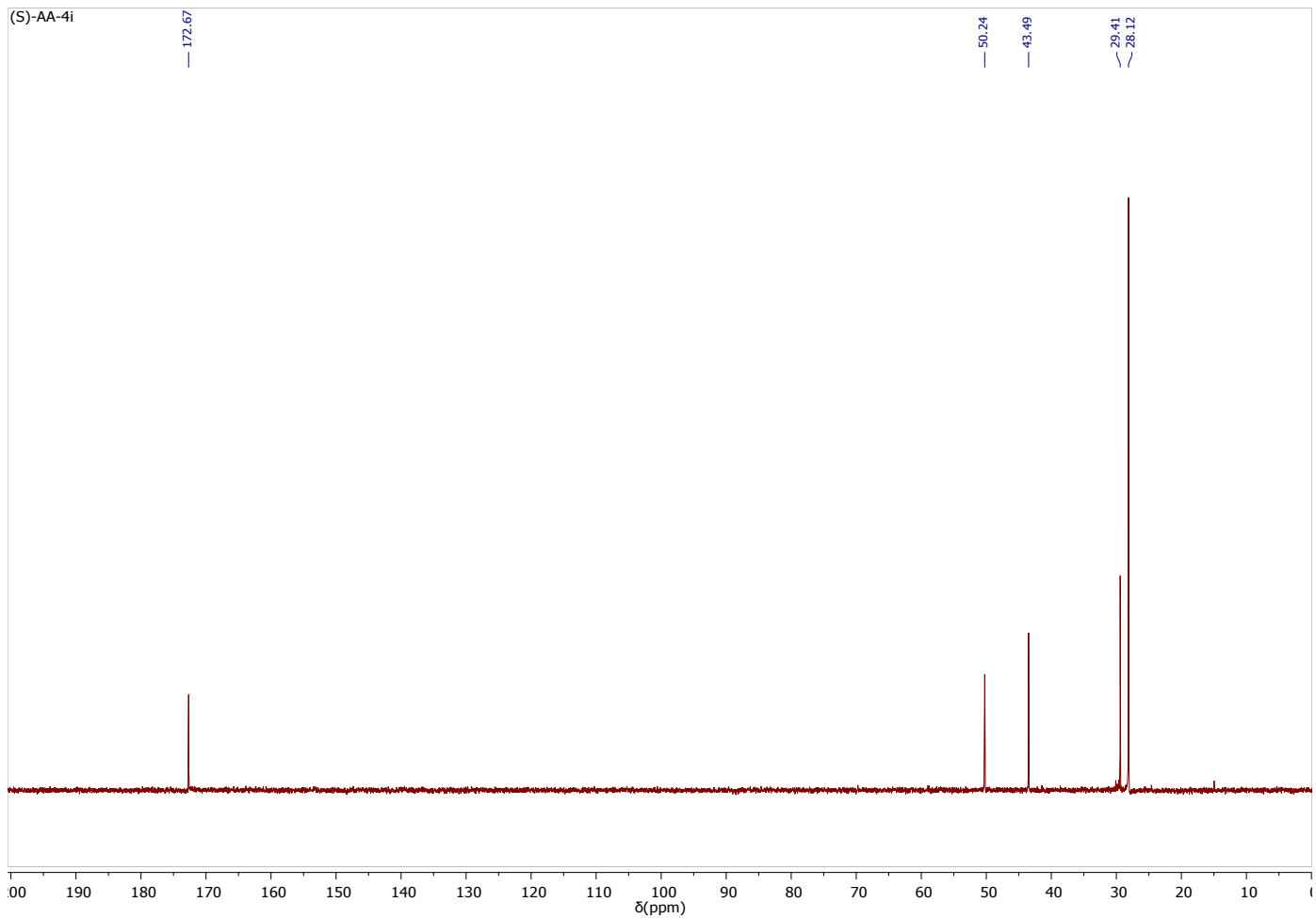




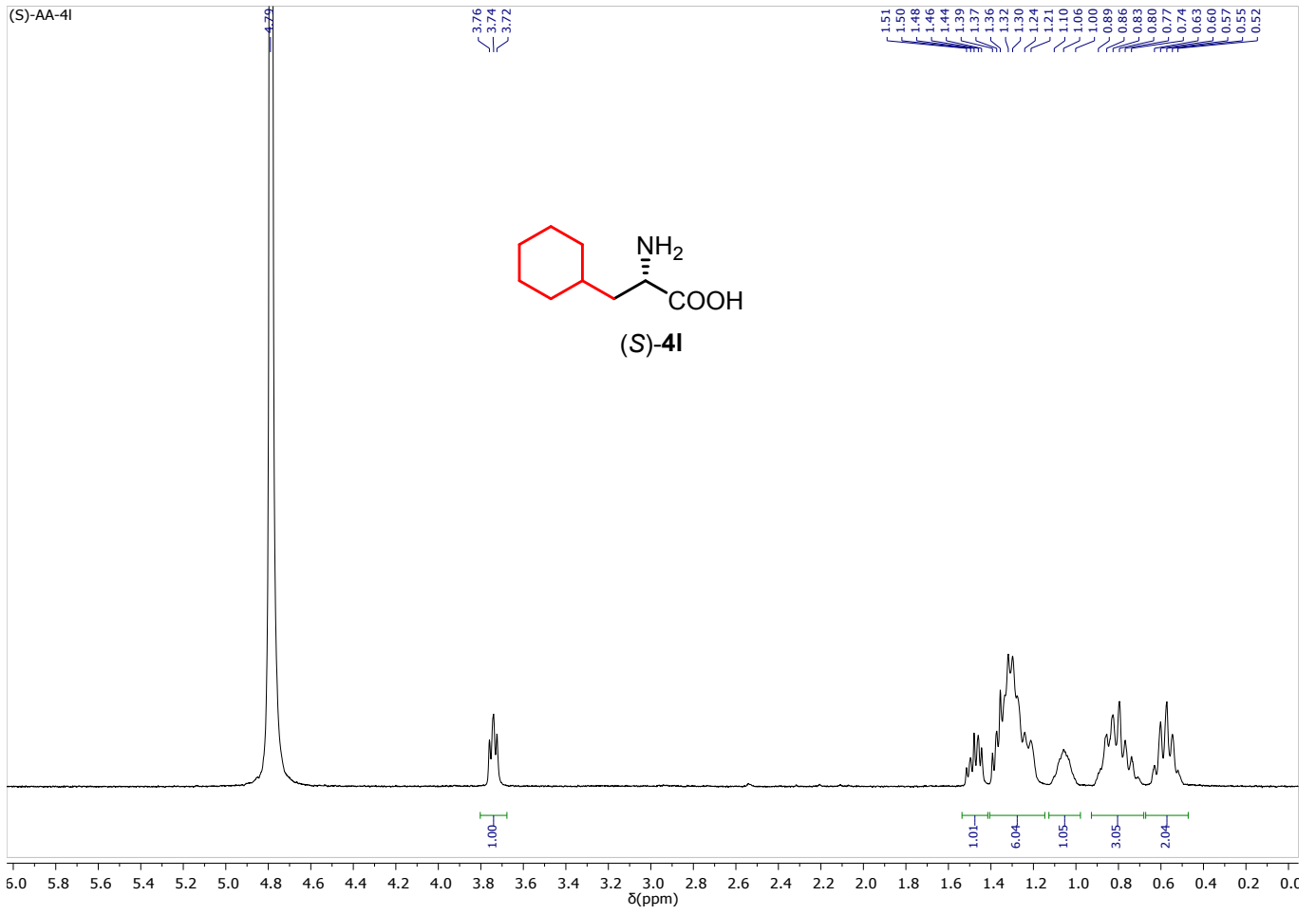
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra of the Ni(II) complex (S,S)-3s

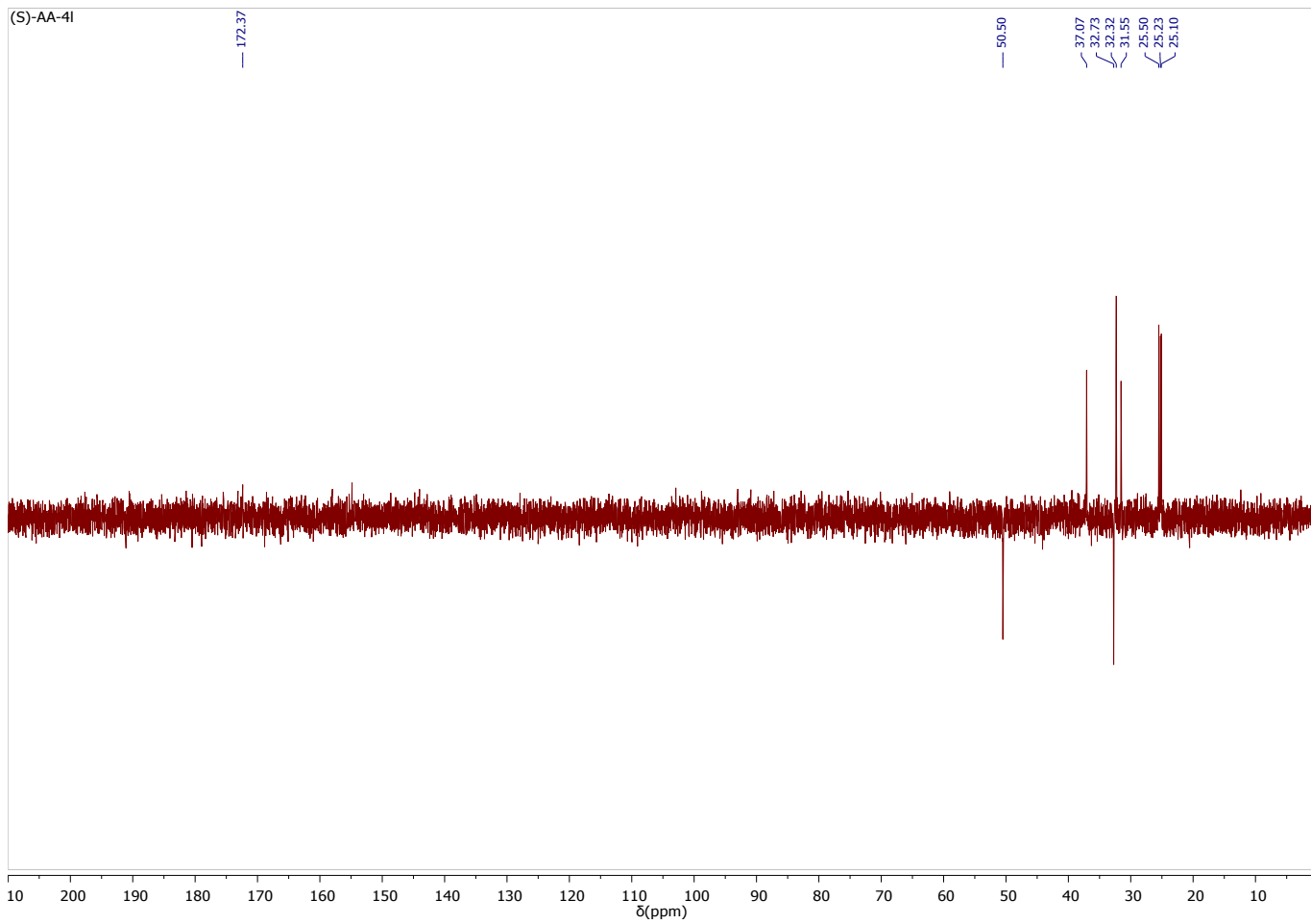




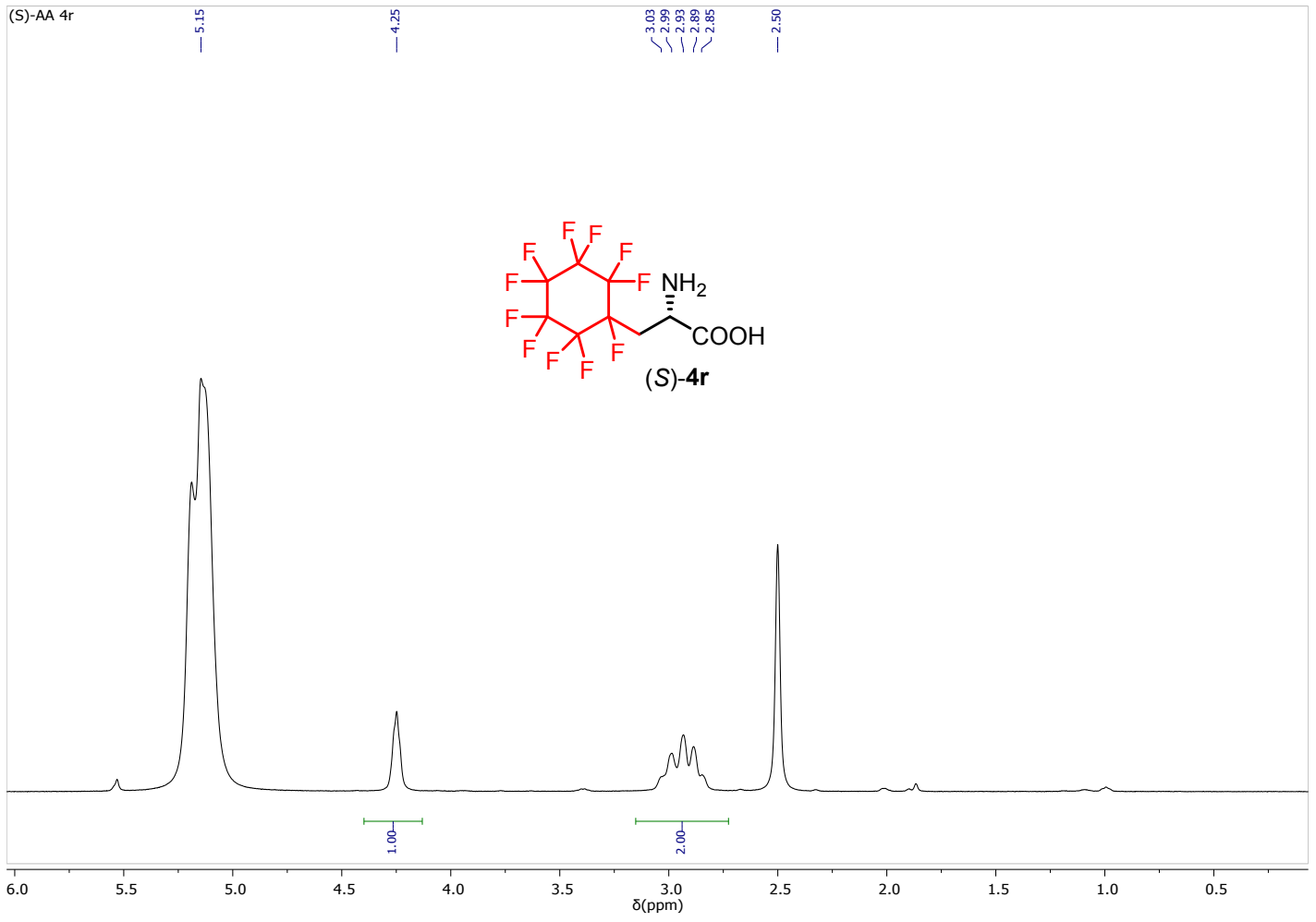


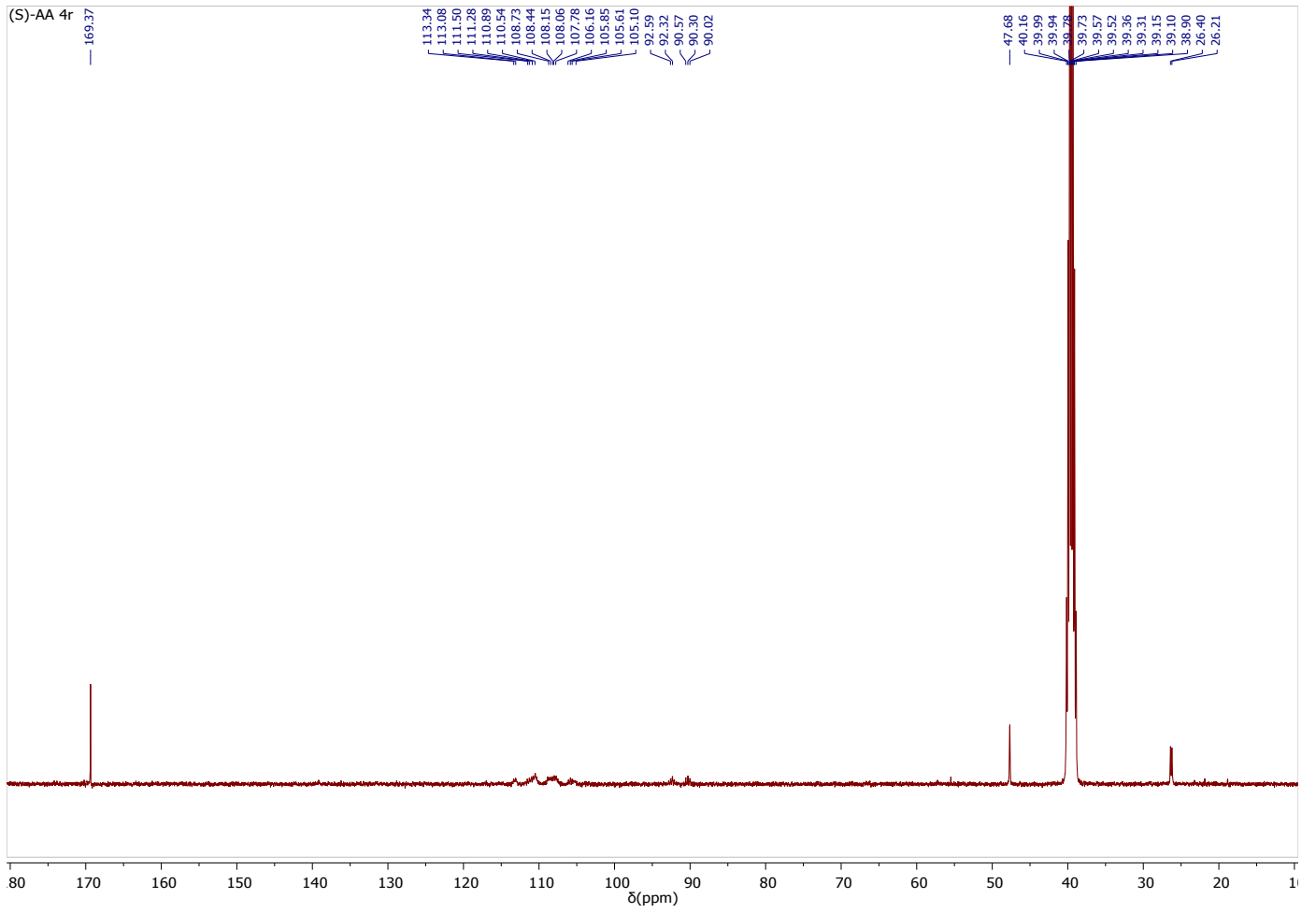
*$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the (S)-AA 4i*

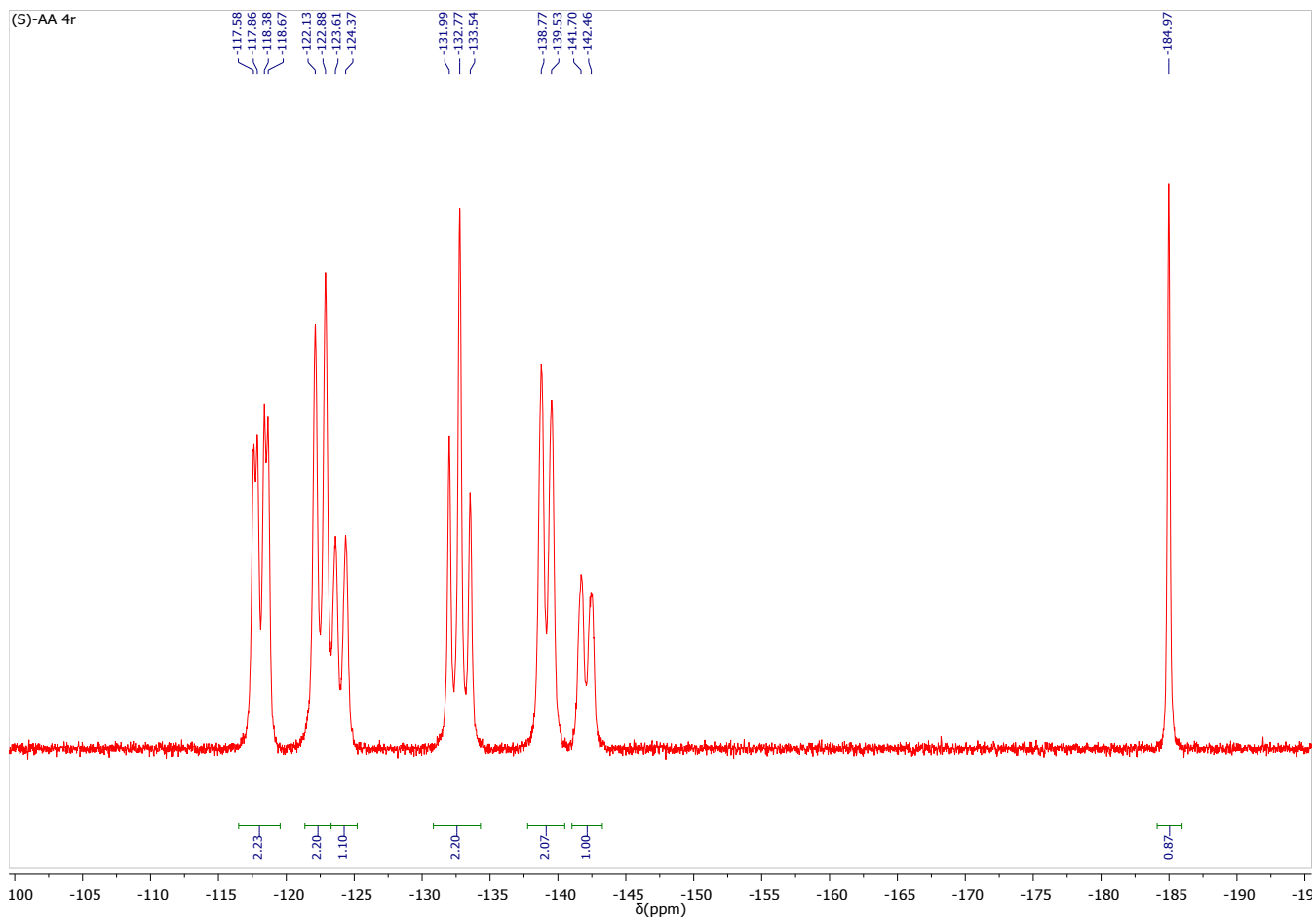




*<sup>1</sup>H and <sup>13</sup>C (JMOD) NMR spectra of the (S)-AA 4I*







$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra of the (S)-AA **4r**