Supporting information

Reductive opening of a cyclopropane ring in the Ni(II) coordination environment: a route to functionalized dehydroalanine and cysteine derivatives

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1. *Experimental details*

^{1}H (400.0 MHz) and ^{13}C (100.6 MHz) NMR spectra (including COSY, HMBC, HSQC) were recorded using an Aglient 400-MR spectrometer in $CDCl_3$. Chemical shifts were referenced to the nondeuterated aliquot of the solvent.

Mass spectra. CH_3CN (LC–MS grade) for ESI–MS experiments was ordered from Merck and used as received. Sodium formate (for HPLC) for calibration was ordered from Sigma-Aldrich. The samples for ESI–MS experiments were prepared in 1.8 mL glass vials/screw top caps with PTFE septa for HPLC experiments (Agilent Technologies).

Preparative electrolysis was performed with AutoLab PGSTAT100N potentiostat in a two-compartment cell of 10 ml volume. The WE was glassy carbon plate (300 mm^2); the CE was a stainless steel wire. The solution was stirred with an argon flow.

Voltammetric experiments were performed with Biologic BP-300 potentiostat, in a ALS Co. three-electrode cell of 2 ml with a platinum wire counter electrode (CE) and anhydrous Ag/0.01 M $AgNO_3$ (MeCN) reference electrode (RE). Ferrocene was used as internal standard in each experiment and all measured potentials were converted to the $Ag/AgCl,KCl_{(sat.)}$ reference electrode (in the latter scale, the potential for the $Fc^{0/+}$ redox couple is equal to 0.475 V in acetonitrile). A Pt disk electrode with active surface area of 0.077 cm^2 was used as the working electrode (WE). The Pt electrode was polished with Al_2O_3 suspension SP-A 0.3 mm on a polishing pad (Metrohm, Germany), washed with sulfuric acid and rinsed with water and acetone. Hardware ohmic drop compensation was employed. All solutions were thoroughly deaerated by passing an argon flow through the solution prior to the CV experiments and above the solution during the measurements, the supporting electrolyte in all experiments was 0.1M n-Bu_4NBF_4 (Aldrich, purity > 99%), which has been recrystallized from water and dried by gentle heating under reduced pressure (0.05 Torr) prior to use. Acetonitrile (AN, Aldrich spectroscopic quality, < 0.02% water content) was distilled over P_2O_5 and stored under argon.

All reactants and solvents were commercially available and purified prior to experiments. Complex **1-3** were synthesized according to Ref[1]. Silicagel 60M 0.04-0.063 mm was used for column chromatography.

Computational details

Stationary-point structures were optimized using the ORCA quantum chemistry package. A composite PBEh-3c method[2] accounting for basis set superposition error and dispersion effects was applied. A threshold of $1\cdot10^{-8}$ Hartree was used for SCF convergence; thresholds of $1\cdot10^{-6}$ Hartree and $3\cdot10^{-5}$ Hartree $Bohr^{-1}$ on energy and RMS gradient, respectively, were employed in optimization procedures. SMD continuous solvation model[3] with dimethylformamide as solvent was applied.

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[1] Levitskiy, O. A.; Aglamazova, O. I.; Grishin, Y. K.; Nefedov, S. E.; Magdesieva, T. V. *Electrochim. Acta* **2022**, *409*, 139980. doi:10.1016/j.electacta.2022.139980.
Levitskiy, O. A.; Aglamazova, O. I.; Grishin, Y. K.; Paseshnichenko, K. A.; Soloshonok, V. A.; Moriwaki, H.; Magdesieva, T. V. *Dalt. Trans.* **2020**, *49* (25), 8636–8644. doi:10.1039/d0dt01578d.

[2] S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, *J. Chem. Phys.*, **2015**, 143, 054107

[3] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, **2009**, 113, 6378

2. Synthesis of complex 4

Synthesis was performed in an argon atmosphere using the standard Schlenk technique. The solution of Δ-AlaNi (1.142 g, 2.24 mmol) in toluene (10 ml) was degassed, then $BrCH(COOMe)_2$ (709 mg, 3.36 mmol, 1.5 eq) was added. After 5 minutes NaH (136 mg, 3.4 mmol, 60% suspension in a mineral oil) was added. The reaction mixture was stirred at room temperature for 30 min. Afterwards, the reaction mixture was poured onto water; organic compounds were extracted with ethyl acetate. The combined organic fractions were dried over anhydrous Na_2SO_4; the solvent was evaporated under reduced pressure. The residue was separated using column chromatography. The first fraction was eluted with a $CHCl_3$/AcMe = 10:1 (the minor isomer); the second (major) fraction corresponding to the (*S*)-isomer was eluted with a $CHCl_3$/AcMe = 1:1 mixture). After removal of the solvent, (*S*)-**4** (1.17 g, 82%) was obtained.

(*S*)-**4**

HRMS (ESI): m/z 640.1582 ($M+H^+$, 640.1588 calculated for $C_{33}H_{32}N_3NiO_7$).

^{1}H NMR ($CDCl_3$ δ, ppm): 8.21 (dd, ^3J = 8.7 Hz, ^4J = 0.9 Hz, 1H (H-8)), 8.16-8.11 (m, 2H (H-17,21)), 7.54-7.48 (m, 1H (H-25)), 7.47-7.40 (m, 2H (H-24,26)), 7.26-7.13 (m, 4H (H-18,20,23,27)), 7.10-7.00 (m, 2H (H-7,19)), 6.83 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 1H (H-5)), 6.69-6.64 (m, 1H (H-6)), 4.33-4.17 (m, 2H (H-13,15)), 3.77 (s, 3H (H-31)), 3.72 (s, 3H (H-33)), 3.60-3.53 (m, 1H (H-14)), 3.44 (dd, ^3J = 11.0 Hz, ^3J = 5.8 Hz, 1H (H-11)), 3.31 (d, ^2J = 12.5 Hz, 1H (H-15)), 2.79-2.68 (m, 1H (H-12)), 2.64-2.51 (m, 1H (H-12)), 2.30-2.19 (m, 1H (H-13)), 2.16-2.06 (m, 1H (H-14)), 1.90 (d, ^2J = 7.6 Hz, 1H (H-29)), 0.93 (d, ^2J = 7.6 Hz, 1H (H-29)).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.31 (C-10), 172.49 (C-3), 171.54 (C-1), 165.90 (C-30), 165.54 (C-32), 143.73 (C-9), 134.84 (C-22), 134.36 (C-5), 133.97 (C-16), 133.25 (C-7), 131.21 (C-17,21), 130.55 (C-23), 130.44 (C-25), 129.30 (C-27), 128.95 (C-18,20), 128.68 (C-19), 128.45 (C-24), 128.28 (C-26), 126.48 (C-4), 122.46 (C-8), 120.51 (C-6), 71.50 (C-11), 63.33 (C-15), 63.30 (C-28), 57.85 (C-14), 53.56 (C-33), 53.26 (C-31), 45.68 (C-2), 31.21 (C-12), 25.89 (C-29), 23.33 (C-13).

3. Reductive ring opening of complex 4

Solution of Bu_4NBF_4 (10 ml 0.09 M) in DMF was placed into the two-compartment electrochemical cell equipped with the magnetic stirrer. In the working electrode compartment, complex **4** (50 mg, 0.078 mmol) and azobenzene (method A: no azobenzene; method B: 15 mg (0.082 mmol)) were added. Potentiostatic electrolysis (E = −1.70 V (method A), E = −1.50 V (method B) *vs.* Ag/AgCl, $KCl_{(sat.)}$) of the solution deaerated with an argon flow was performed using a carbon felt as a working electrode and a Fe-rod as a counter electrode. The color of the solution was changed from red to dark purple during the electrolysis. After a charge of 7.5 C (1 F/mol of complex **4**, method A) or 18 C (2.4 F/mol of complex **4**, method B) was passed through the solution, $PhNEt_2 \cdot HCl$ (31 mg, 0.167 mmol) was added. After 5 minutes the solution from the working electrode compartment was poured onto water (15 ml) and extracted with ethyl acetate (3 x 15 ml). Organic fractions were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified using column chromatography (hexane/acetone = 1:1). After evaporation of the solvent and drying in vacuum the following complexes were isolated:

Method A: complexes **6** (20 mg, 40%), complex **7** (20 mg, 40%).

Method B: complexes **6** (42.5 mg, 85%), complex **7** (5 mg, 10%).

Complexes **6** were characterized as a mixture of α-β alkene (**6a**) and β-γ alkene (**6b**).

Characteristic signals of α-β alkene (**6a**):

^{1}H NMR ($CDCl_3$ δ, ppm): 5.46 (d, J = 10.0 Hz, 1H), 5.22 (d, J = 10.0 Hz, 1H), 4.31 (d, J = 12.6 Hz, 1H), 3.71 (s, 3H), 3.53 (s, 3H).

^{13}C NMR ($CDCl_3$ δ, ppm): 168.65, 168.53, 167.64, 167.18, 122.81, 48.78,

Characteristic signals of β-γ alkene (**6b**):

^{1}H NMR ($CDCl_3$ δ, ppm): 5.06 (d, J = 7.9 Hz, 1H), 4.42 (d, J = 12.6 Hz, 1H), 3.79 (s, 3H), 3.50 (s, 3H).

^{13}C NMR ($CDCl_3$ δ, ppm): 174.24, 173.70, 164.00, 163.97.

4. Reductive ring opening followed by the reaction with electrophiles (AcOH or MeI)

Solution of Bu_4NBF_4 (10 ml 0.09 M) in DMF was placed into the two-compartment electrochemical cell equipped with the magnetic stirrer. In the working electrode compartment, complex **3** (60 mg, 0.1 mmol) was added. Potentiostatic electrolysis (E = −1.70 V *vs.* Ag/AgCl, $KCl_{(sat.)}$) of the solution deaerated with an argon flow was performed using a carbon felt as a working electrode and a Fe-rod as a counter electrode. The color of the solution was changed from red to dark purple during the electrolysis. After a charge of 10 C (1 F/mol of complex **3**) was passed through the solution, 1 ml of DMF containing acetic acid (13 mkl, 0.2 mmol) or MeI (64 mkl, 1 mmol) was added to the reaction mixture. Then the reaction mixture was poured onto water (15 ml) and extracted with ethyl acetate (3 x 15 ml). Organic fractions were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was separated with column chromatography, using the following eluents: $CHCl_3$/AcMe = 5:1 (in the experiment with AcOH as an electrophilic additive), CCl_4/*i*-PrOH = 10:1 (in the experiment with MeI addition). After evaporation of the solvent and drying in vacuum the following complexes were isolated:

After protonation: complex **8** (10 mg, 20%), complex **5** (10 mg, 20%, diastereomer 1 solely).

After methylation: complex **9** (25 mg, 42%), complex **5** (15 mg, 25%, diastereomer 1 solely).

Electrolysis in the presence of AcCl allows obtaining the complex **5** in the form of two diastereomers (dr = 1:1) with a total yield of 40%

Complex **5**, diastereomer 1:

HRMS (ESI): m/z 582.1534 ($M+H^+$, 582.1533 calculated for $C_{31}H_{30}N_3NiO_5$).

^{1}H NMR ($CDCl_3$ δ, ppm): 8.00-7.95 (m, 2H (H-17,21)), 7.91-7.86 (m, 2H (H-8,24)), 7.51-7.47 (m, 3H (H-18,19,20)), 7.29-7.21 (m, 4H (H-5,7,25,26)), 7.14 (dd, ^{3}J = 8.2 Hz, ^{3}J = 6.9 Hz 1H (H-6)), 7.01-6.95 (m, 2H (H-23,27)), 4.26-4.15 (m, 2H (H-14,28)), 3.95 (d, ^{2}J = 12.7 Hz, 1H (H-15)), 3.70-3.53 (m, 2H (H-11,29)), 3.28 (s, 3H (H-31)), 3.07 (dd, ^{3}J = 20.3 Hz, ^{3}J = 9.7 Hz, 1H (H-29)), 3.03-2.97 (m, 1H (H-14)), 2.95 (d, ^{2}J = 12.7 Hz, 1H (H-15)), 2.27-2.18 (m, 1H (H-13)), 2.04-1.86 (m, 3H (H-12,12,13)).

^{13}C NMR ($CDCl_3$ δ, ppm): 179.04 (C-10), 177.03 (C-2), 169.31 (C-30), 166.75 (C-1), 142.12 (C-22), 136.97 (C-9), 133.58 (C-16), 131.43 (C-17,21), 131.26 (C-4), 129.34, 129.31 (C-18,19,20), 128.77, 128.72, 128.66 (C-5,7,25,26), 127.48 (C-24), 126.54 (C-8), 126.22 (C-23,27), 122.76 (C-6), 79.36 (C-3), 68.32 (C-11), 59.60 (C-15), 57.94 (C-14), 53.72 (C-28), 52.53 (C-31), 36.22 (C-29), 27.43 (C-13), 22.20 (C-12).

Complex **5**, diastereomer 2:

^{1}H NMR ($CDCl_3$ δ, ppm): 8.25-8.21 (m, 2H (H-17,21)), 7.75-7.70 (m, 2H (H-23,27)), 7.46-7.26 (m, 7H (H-8,18,19,20,24,25,26)), 7.15 (dd, ^{3}J = 7.7 Hz, ^{4}J = 1.6 Hz, 1H (H-5)), 6.98-6.93 (m, 1H (H-7)), 6.88 (td, J = 7.5 Hz, J = 1.4 Hz, 1H (H-6)), 4.30 (d, ^{2}J = 12.5 Hz, 1H (H-15)), 3.88 (dd, ^{3}J = 5.9 Hz, ^{3}J = 1.5 Hz, 1H (H-28)), 3.80-3.66 (m, 1H (H-13)), 3.58 (s, 3H (H-31)), 3.57-3.46 (m, 2H (H-14,15)), 3.33 (dd, ^{3}J = 10.4 Hz, ^{3}J = 6.2 Hz, 1H (H-11)), 2.88 (dd, ^{2}J = 19.1 Hz, ^{3}J = 1.5 Hz, 1H (H-29)), 2.82 (dd, ^{2}J = 19.1 Hz, ^{3}J = 5.9 Hz, 1H (H-29)), 2.50-2.34 (m, 2H (H-12)), 2.33-2.23 (m, 1H (H-13)), 2.23-2.13 (m, 1H (H-14)).

^{13}C NMR ($CDCl_3$ δ, ppm): 179.34 (C-10), 178.59 (C-2), 171.82 (C-30), 166.69 (C-1), 139.46 (C-22), 139.37 (C-9), 133.66 (C-16), 131.54 (C-17,21), 130.42 (C-4), 129.38 (C-19), 129.33 (C-18,20), 129.19 (C-24,26), 128.46 (C-25), 127.37 (C-7), 126.74 (C-8), 125.44 (C-5,23,27), 122.29 (C-6), 77.80 (C-3), 71.75 (C-11), 63.36 (C-15), 57.84 (C-14), 56.52 (C-28), 52.56 (C-31), 36.96 (C-29), 30.55 (C-12), 24.66 (C-13).

Complex **8**:

HRMS (ESI): m/z 582.1541 ($M+H^+$, 582.1533 calculated for $C_{31}H_{30}N_3NiO_5$).

The compound was obtained as an inseparable mixture of stereo- and regioisomeric alkenes with β-γ trans-isomer as a main component. The characteristic signals of the latter are listed below: ^{1}H NMR ($CDCl_3$ δ, ppm) (characteristic signals): 7.02 (dd, J = 15.7, 5.7 Hz, 1H), 6.25 (dd, J = 15.7, 1.7 Hz, 1H), 4.62 (dd, J = 5.1, 1.7 Hz, 1H), 3.77 (s, 3H).

Methylated complex **9**:

HRMS (ESI): m/z 596.1690 ($M+H^+$, 596.1690 calculated for $C_{32}H_{32}N_3NiO_5$).

^{1}H NMR ($CDCl_3$ δ, ppm): 8.12-8.07 (m, 3H (H-8,17,21)), 7.47-7.39 (m, 3H (H-23,24,26)), 7.34-7.29 (m, 2H (H-18,20)), 7.18-7.10 (m, 4H (H-7,19,25,27)), 6.89 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.6 Hz, 1H (H-5)), 6.70 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.2 Hz, 1H (H-6)), 5.02 (d, ^{3}J = 10.3 Hz, 1H (H-28)), 4.36-4.27 (m, 2H (H-15,29)), 3.90-3.77 (m, 1H (H-13)), 3.64 (s, 3H (H-31)), 3.48-3.43 (m, 1H (H-11)), 3.40 (d, ^{3}J = 12.6 Hz, 1H (H-15)), 2.78-2.69 (m, 1H (H-12)), 2.63-2.45 (m, 2H (H-12,14)), 2.25-2.16 (m, 1H (H-13)), 2.11-2.03 (m, 1H (H-14)), 0.74 (d, ^{3}J = 7.1 Hz, 3H (H-32)).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.25 (C-10), 174.26 (C-30), 168.97 (C-1), 167.71 (C-3), 143.46 (C-9), 140.74 (C-2), 135.08 (C-22), 134.09 (C-5), 133.65 (C-16), 132.95 (C-7), 131.49 (C-17,21), 131.35 (C-28), 129.85 (C-24,26), 129.15 (C-25), 129.11 (C-27), 129.07 (C-18,20), 128.97 (C-19), 128.87 (C-23), 127.02 (C-4), 123.67 (C-8), 120.83 (C-6), 70.75 (C-11), 63.04 (C-15), 57.53 (C-14), 52.14 (C-31), 36.16 (C-29), 30.82 (C-12), 24.14 (C-13), 17.28 (C-32).

5. *One-pot electrosynthesis of cysteine derivatives from complex 4*

Solution of Bu_4NBF_4 (10 ml 0.09 M) in DMF was placed into the two-compartment electrochemical cell equipped with the magnetic stirrer. In the working electrode compartment, complex **4** (50 mg, 0.078 mmol) and azobenzene (15 mg, 0.082 mmol) were added.

Potentiostatic electrolysis (E = −1.50 V *vs.* Ag/AgCl, $KCl_{(sat.)}$) of solution deaerated with an argon flow was performed using carbon felt as a working electrode and Fe-rod as a counter electrode. The color of the solution during the electrolysis changed from red to dark purple. After a charge of 18 C (2.4 F/mol of complex **4**) was passed through the solution, $PhNEt_2 \cdot HCl$ (31 mg, 0.167 mmol) was added. After 5 min of intensive stirring, RSH (0.16 mmol) and Et_3N (method B) were added (method A: no Et_3N; method B: 7.26 mg, 0.07 mmol of Et_3N). The solution from the working electrode compartment was transferred to the Schlenk tube preliminary charged with argon and kept at room temperature for 24 h. Then the reaction mixture was poured onto water (15 ml) and extracted with ethyl acetate (3 x 15 ml). Organic fractions were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was separated using column chromatography (Silicagel, $CHCl_3$/AcMe = 15:1 mixture was used as an eluent; for further purification of each diastereomer hexane/AcOEt = 1:5 mixture was used). After evaporation of the solvent and drying in vacuum the following complexes were obtained:

Method A:

TolSH: complex **10** (32 mg, 54%, (*R*,*S*)/(*R*,*R*)=1:5), complexes **6** (20 mg (40%)).

BnSH: complex **12** (38 mg, 64%, (*R*,*S*)/(*R*,*R*)=1:2.6), complexes **6** (10 mg (20%)).

Method B:

TolSH: complex **10** (38 mg, 64%, (*R*,*S*)/(*R*,*R*)=10:1), complexes **6** (8 mg (16%)).

PhSH: complex **11** (47 mg, 88%, (*R*,*S*)/(*R*,*R*)=12:1).

BnSH: complex **12** (25 mg, 42%, pure (*R*,*S*)-diastereomer), complexes **6** (24 mg (48%)) (40°C, 72 hours)

(*R*,*S*)-**10**

HRMS (ESI): m/z 764.1954 ($M+H^+$, 764.1935 calculated for $C_{40}H_{40}N_3NiO_7S$), 786.1774 ($M+Na^+$, 786.1754 calculated for $C_{40}H_{39}N_3NaNiO_7S$).

^{1}H NMR ($CDCl_3$ δ, ppm): 8.37 (dd, ^3J = 8.8 Hz, ^4J = 1.1 Hz, 1H (H-8)), 8.10-8.05 (m, 2H (H-17,21)), 7.53-7.43 (m, 4H (H-25,26,35,39)), 7.36-7.30 (m, 2H (H-18,20)), 7.25-7.11 (m, 4H (H-7,19,24,27), 6.84-6.80 (m, 2H (H-36,38)), 6.57 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 1H (H-6)), 6.41 (dd, ^3J = 8.3 Hz, ^4J = 1.6 Hz, 1H (H-5)), 5.66-5.62 (m, 1H (H-23)), 4.61 (d, ^3J = 5.6 Hz, 1H (H-2)), 4.48 (d, ^2J = 12.6 Hz, 1H (H-15)), 4.06 (d, ^3J = 11.4 Hz, 1H (H-29)), 3.89-3.78 (m, 1H (H-13)), 3.74 (s, 3H (H-31)), 3.71-3.64 (m, 1H (H-14)), 3.61 (d, ^2J = 12.6 Hz, 1H (H-15)), 3.52-3.48 (m, 4H (H-11,33)), 3.41 (dd, ^3J = 11.4 Hz, ^3J = 5.6 Hz, 1H (H-28)), 2.88-2.78 (m, 1H (H-12)), 2.54-2.41 (m, 1H (H-12)), 2.12 (s, 3H (H-40)), 2.15-2.01 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.58 (C-10), 176.57 (C-1), 172.40 (C-3), 168.56 (C-30), 166.63 (C-32), 143.01 (C-9), 138.83 (C-37), 134.28 (C-35,39), 133.71 (C-22), 133.63 (C-5), 133.53 (C-16), 132.44 (C-7), 131.76 (C-17,21), 131.20 (C-34), 129.91 (C-36,38), 129.81 (C-25), 129.07 (C-26), 128.90 (C-19), 128.84 (C-18,20), 128.66 (C-24), 127.37 (C-23), 127.06 (C-27), 125.88 (C-4), 123.58 (C-8), 120.43 (C-6), 70.67 (C-11), 70.06 (C-2), 63.55 (C-15), 57.40 (C-14), 55.26 (C-29), 52.83 (C-31), 52.71 (C-33), 52.24 (C-28), 30.75 (C-12), 23.44 (C-13), 21.03 (C-40).

(*R*,*R*)-**10**

^{1}H NMR ($CDCl_3$ δ, ppm): 8.38 (dd, ^{3}J = 8.8 Hz, ^{4}J = 1.1 Hz, 1H (H-8)), 8.01-7.96 (m, 2H (H-17,21)), 7.54-7.43 (m, 4H (H-24,25,26,27)), 7.28-7.17 (m, 5H (H-18,20,23,35,39)), 7.14 (ddd, ^{3}J = 8.8 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.7 Hz, 1H (H-7)), 7.10-7.05 (m, 1H (H-19)), 6.99-6.95 (m, 2H (H-36,38)), 6.77 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.7 Hz, 1H (H-5)), 6.69 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.1 Hz, 1H (H-6)), 4.78 (dd, ^{3}J = 9.7 Hz, ^{3}J = 4.4 Hz, 1H (H-28)), 4.47 (d, ^{3}J = 4.4 Hz, 1H (H-29)), 4.28 (d, ^{2}J = 12.6 Hz, 1H (H-15)), 4.13 (d, ^{3}J = 9.7 Hz, 1H (H-2)), 3.72 (s, 3H (H-31)), 3.78 (s, 3H (H-33)), 3.38 (d, ^{2}J = 12.6 Hz, 1H (H-15)), 3.35-3.28 (m, 2H (H-11,14)), 3.23-3.07 (m, 1H (H-13)), 2.28 (s, 3H (H-40)), 2.26-2.16 (m, 1H (H-12)), 2.15-2.06 (m, 1H (H-12)), 2.01-1.90 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ, ppm): 179.65 (C-10), 176.80 (C-1), 173.75 (C-3), 168.48 (C-30), 167.29 (C-32), 143.28 (C-9), 138.58 (C-37), 134.61 (C-5), 134.41 (C-22), 133.63 (C-35,39), 133.55 (C-16), 133.07 (C-7), 132.43 (C-34), 131.41 (C-17,21), 130.17 (C-36,38), 128.91 (C-18,20), 128.78 (C-19), 131.78, 129.67,128.69, 128.56, 127.87 (C-23,24,25,26,27), 126.06 (C-4), 122.95 (C-8), 120.57 (C-6), 73.12 (C-2), 70.43 (C-11), 63.19 (C-15), 57.92 (C-28), 57.33 (C-14), 54.26 (C-29), 53.07 (C-31), 52.46 (C-33), 29.94 (C-12), 23.77 (C-13), 21.24 (C-40).

(*R*,*S*)-**11**

^{1}H NMR ($CDCl_3$ δ, ppm): 8.37 (dd, ^{3}J = 8.7 Hz, ^{4}J = 1.1 Hz, 1H), 8.10-8.05 (m, 2H), 7.68-7.63 (m, 2H), 7.53-7.43 (m, 2H), 7.35-7.30 (m, 2H), 7.24-7.05 (m, 5H), 7.04-6.99 (m, 2H), 6.56 (ddd, ^{3}J = 8.2 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.1 Hz, 1H), 6.38 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.6 Hz, 1H), 5.52-5.47 (m, 1H), 4.63 (d, ^{3}J = 5.7 Hz, 1H), 4.48 (d, ^{2}J = 12.6 Hz, 1H), 4.08 (d, ^{3}J = 11.4 Hz, 1H), 3.94-3.80 (m, 1H), 3.75 (s, 3H), 3.71-3.64 (m, 1H), 3.62 (d, ^{2}J = 12.6 Hz, 1H), 3.54-3.48 (m, 4H), dd (dd, ^{3}J = 11.4 Hz, ^{3}J = 5.7 Hz, 1H), 2.91-2.81 (m, 1H), 2.57-2.44 (m, 1H), 2.17-2.03 (m, 2H).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.55, 176.58, 172.45, 168.66, 166.64, 143.03, 134.76, 134.29, 133.65, 133.53, 132.48, 131.76, 129.88, 129.22, 129.08, 128.92, 128.87, 128.63, 128.60, 127.37, 127.07, 125.82, 123.55, 120.46, 70.65, 70.01, 63.58, 57.38, 55.23, 52.90, 52.78, 52.08, 30.74, 23.48.

(*R*,*S*)-**12**

^{1}H NMR ($CDCl_3$ δ, ppm): 8.46 (dd, ^{3}J = 8.7 Hz, ^{4}J = 1.0 Hz, 1H), 8.10-8.03 (m, 2H), 7.57-7.48 (m, 2H), 7.44-7.37 (m, 1H), 7.34-7.10 (m, 7H), 7.06-6.97 (m, 3H), 6.65 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.0 Hz, 1H), 6.52 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.5 Hz, 1H), 6.30-6.24 (m, 1H), 4.46-4.37 (m, 2H), 4.15 (d, ^{3}J = 11.4 Hz), 4.00 (d, J = 11.7 Hz), 3.80 (s, 3H), 3.60-3.51 (m, 2H), 3.44 (s, 3H), 3.41-3.29 (m, 1H), 3.18 (dd, ^{3}J = 11.4, ^{3}J = 4.9 Hz, 1H), 2.68-2.56 (m, 1H), 2.37-2.24 (m, 1H), 2.10-1.99 (m, 1H), 1.88-1.77 (m, 1H), 1.71-1.58 (m, 1H), 1.29-1.22 (m, 1H).

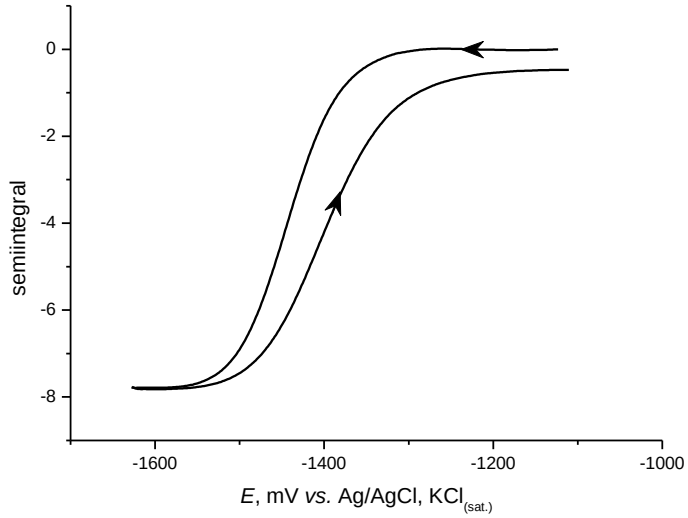
^{13}C NMR ($CDCl_3$ δ, ppm): 180.43, 176.15, 171.95, 168.41, 166.57, 143.50, 136.39, 133.93, 133.67, 132.69, 131.73, 129.89, 129.64, 129.26, 129.10, 128.83, 128.81, 127.87, 127.60, 127.22, 125.98, 123.35, 120.48, 70.85, 69.89, 63.82, 57.36, 55.00, 52.95, 52.73, 46.81, 40.79, 30.43, 23.19.

(*R*,*R*)-**12**

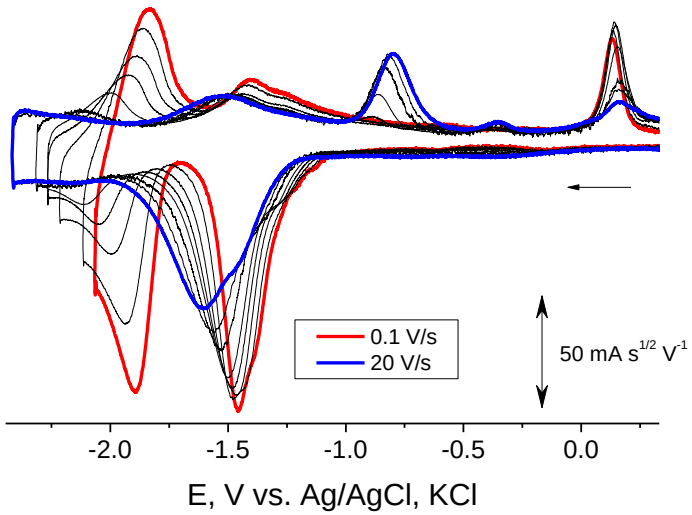
^{1}H NMR ($CDCl_3$ δ, ppm): 8.43 (d, ^{3}J = 8.8 Hz, 1H), 8.09-8.04 (m, 2H), 7.54-7.44 (m, 2H), 7.43-7.37 (m, 1H), 7.32-7.23 (m, H), 7.19-7.07 (m, 5H), 6.99-6.94 (m, 2H), 6.75-6.66 (m, 2H), 4.52-4.38 (m, 3H), 4.19 (d, J = 7.9 Hz), 4.01 (d, J = 10.6 Hz, 1H), 3.93 (d, J = 10.6 Hz, 1H), 3.70 (s, 3H), 3.58-3.43 (m, 7H), 2.75-2.65 (m, 1H), 2.56-2.44 (m, 1H), 2.17-2.06 (m, 2H).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.30, 176.74, 173.76, 168.52, 167.33, 143.09, 136.44, 134.50, 134.37, 133.59, 133.16, 131.49, 131.27, 129.81, 129.20, 128.99, 128.87, 128.84, 128.68, 128.56, 127.84, 127.37, 125.97, 123.04, 120.76, 72.95, 70.82, 63.62, 57.54, 54.39, 53.27, 52.55, 51.52, 41.31, 30.66, 23.91.

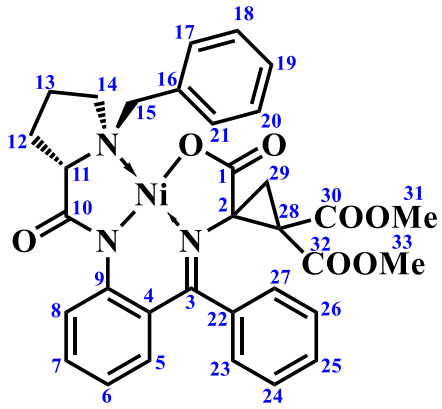
6. *Semi-integral voltammogram for complex 2 (100 mV/s)*



7. *Semi-differential voltammograms for complex 4 at various scan rates*



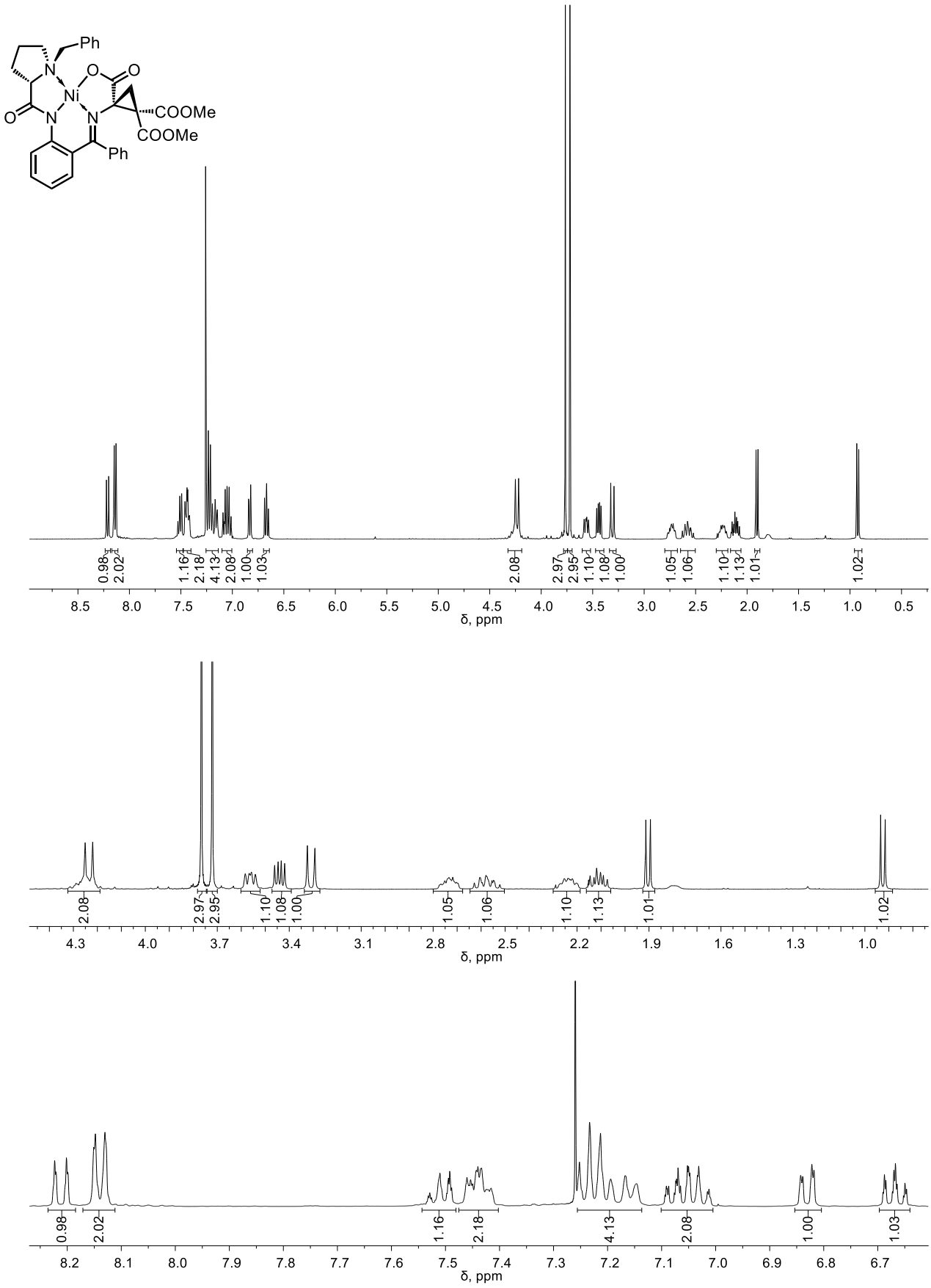
*8. Atom numeration and signal assignment in the NMR spectra of complex (S)-**4***



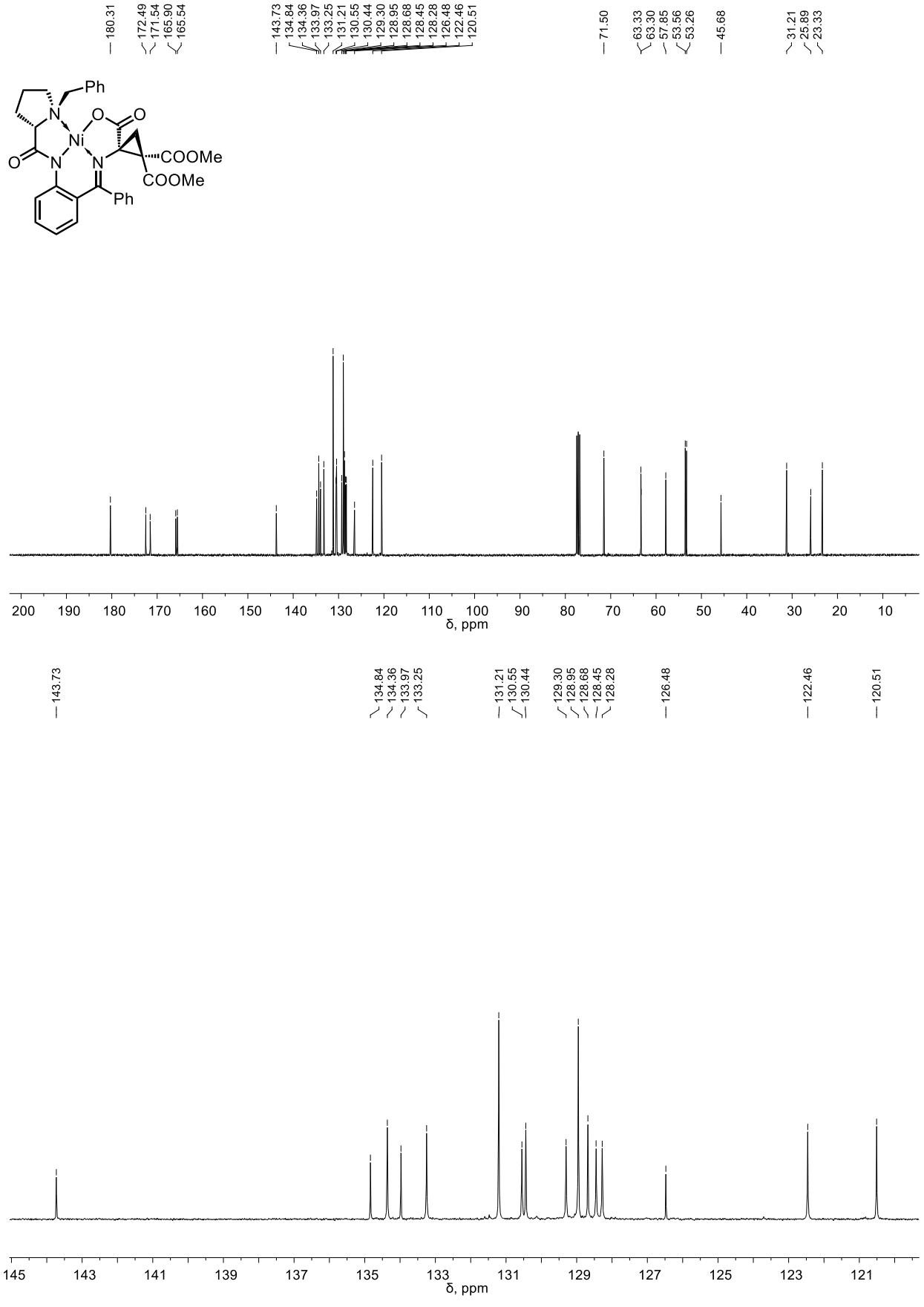
^{1}H NMR ($CDCl_3$ δ, ppm): 8.21 (dd, ^{3}J = 8.7 Hz, ^{4}J = 0.9 Hz, 1H (H-8)), 8.16-8.11 (m, 2H (H-17,21)), 7.54-7.48 (m, 1H (H-25)), 7.47-7.40 (m, 2H (H-24,26)), 7.26-7.13 (m, 4H (H-18,20,23,27)), 7.10-7.00 (m, 2H (H-7,19)), 6.83 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.6 Hz, 1H (H-5)), 6.69-6.64 (m, 1H (H-6)), 4.33-4.17 (m, 2H (H-13,15)), 3.77 (s, 3H (H-31)), 3.72 (s, 3H (H-33)), 3.60-3.53 (m, 1H (H-14)), 3.44 (dd, ^{3}J = 11.0 Hz, ^{3}J = 5.8 Hz, 1H (H-11)), 3.31 (d, ^{2}J = 12.5 Hz, 1H (H-15)), 2.79-2.68 (m, 1H (H-12)), 2.64-2.51 (m, 1H (H-12)), 2.30-2.19 (m, 1H (H-13)), 2.16-2.06 (m, 1H (H-14)), 1.90 (d, ^{2}J = 7.6 Hz, 1H (H-29)), 0.93 (d, ^{2}J = 7.6 Hz, 1H (H-29)).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.31 (C-10), 172.49 (C-3), 171.54 (C-1), 165.90 (C-30), 165.54 (C-32), 143.73 (C-9), 134.84 (C-22), 134.36 (C-5), 133.97 (C-16), 133.25 (C-7), 131.21 (C-17,21), 130.55 (C-23), 130.44 (C-25), 129.30 (C-27), 128.95 (C-18,20), 128.68 (C-19), 128.45 (C-24), 128.28 (C-26), 126.48 (C-4), 122.46 (C-8), 120.51 (C-6), 71.50 (C-11), 63.33 (C-15), 63.30 (C-28), 57.85 (C-14), 53.56 (C-33), 53.26 (C-31), 45.68 (C-2), 31.21 (C-12), 25.89 (C-29), 23.33 (C-13).

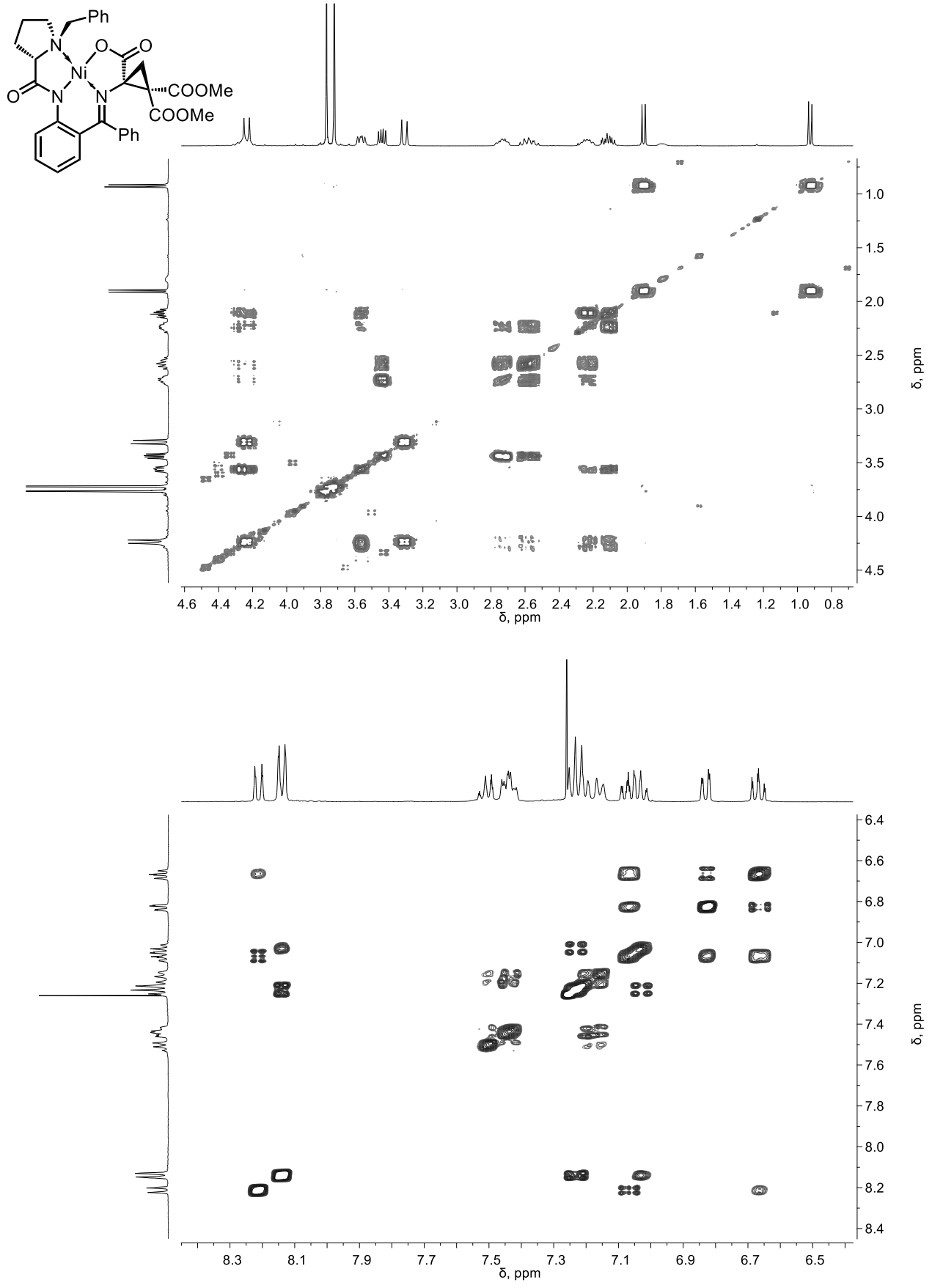
9. *^{1}H NMR spectrum of complex (S)-**4***



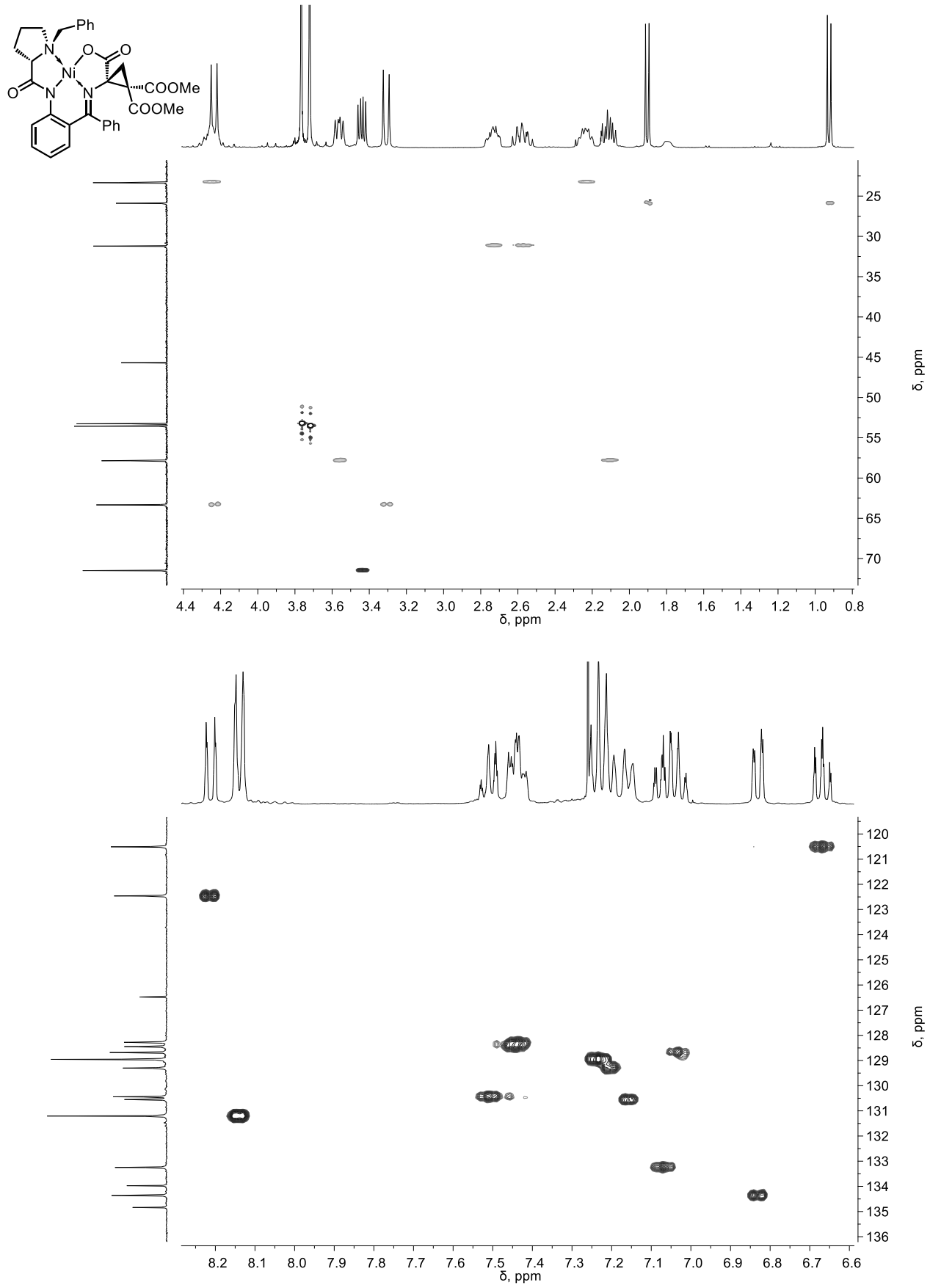
*10. ^{13}C NMR spectrum of complex (S)-**4***



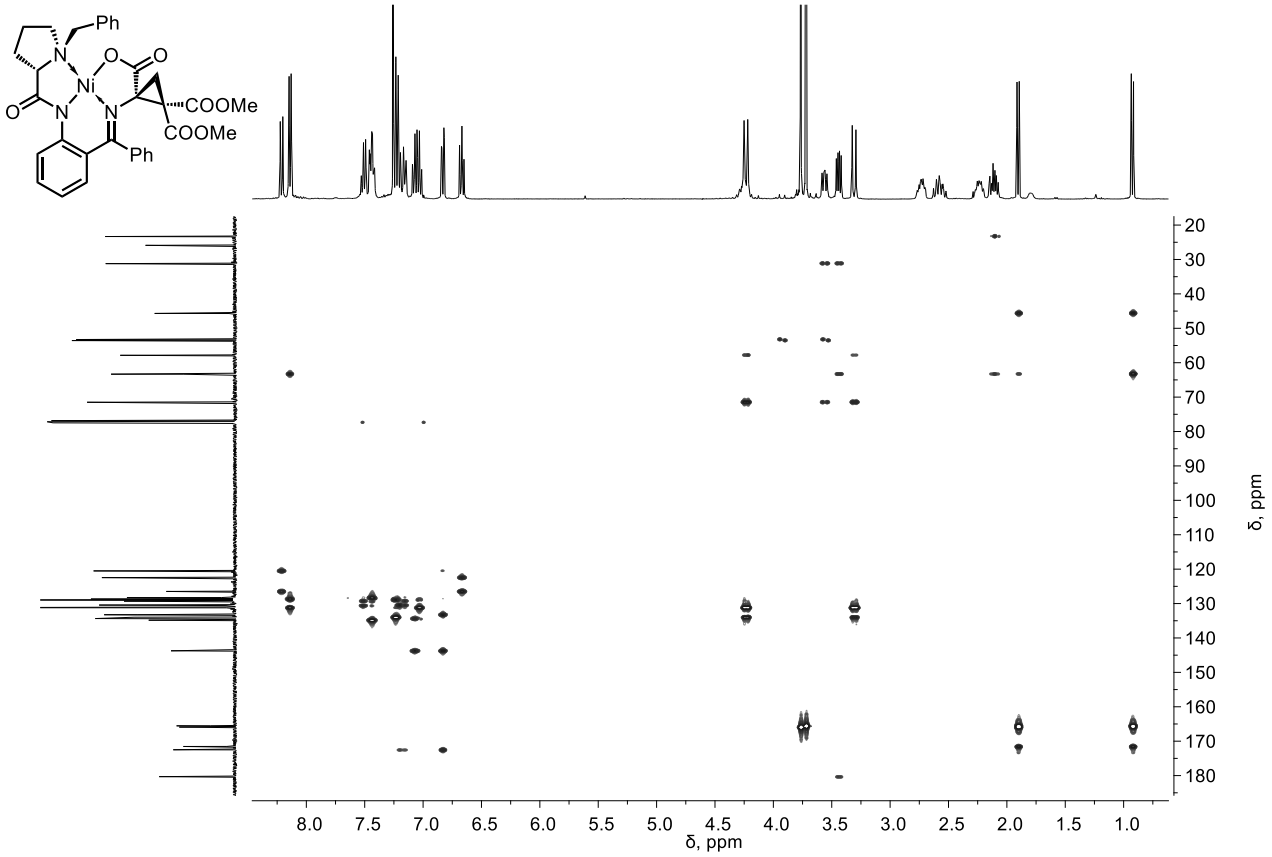
*11. COSY spectrum of complex (S)-**4***



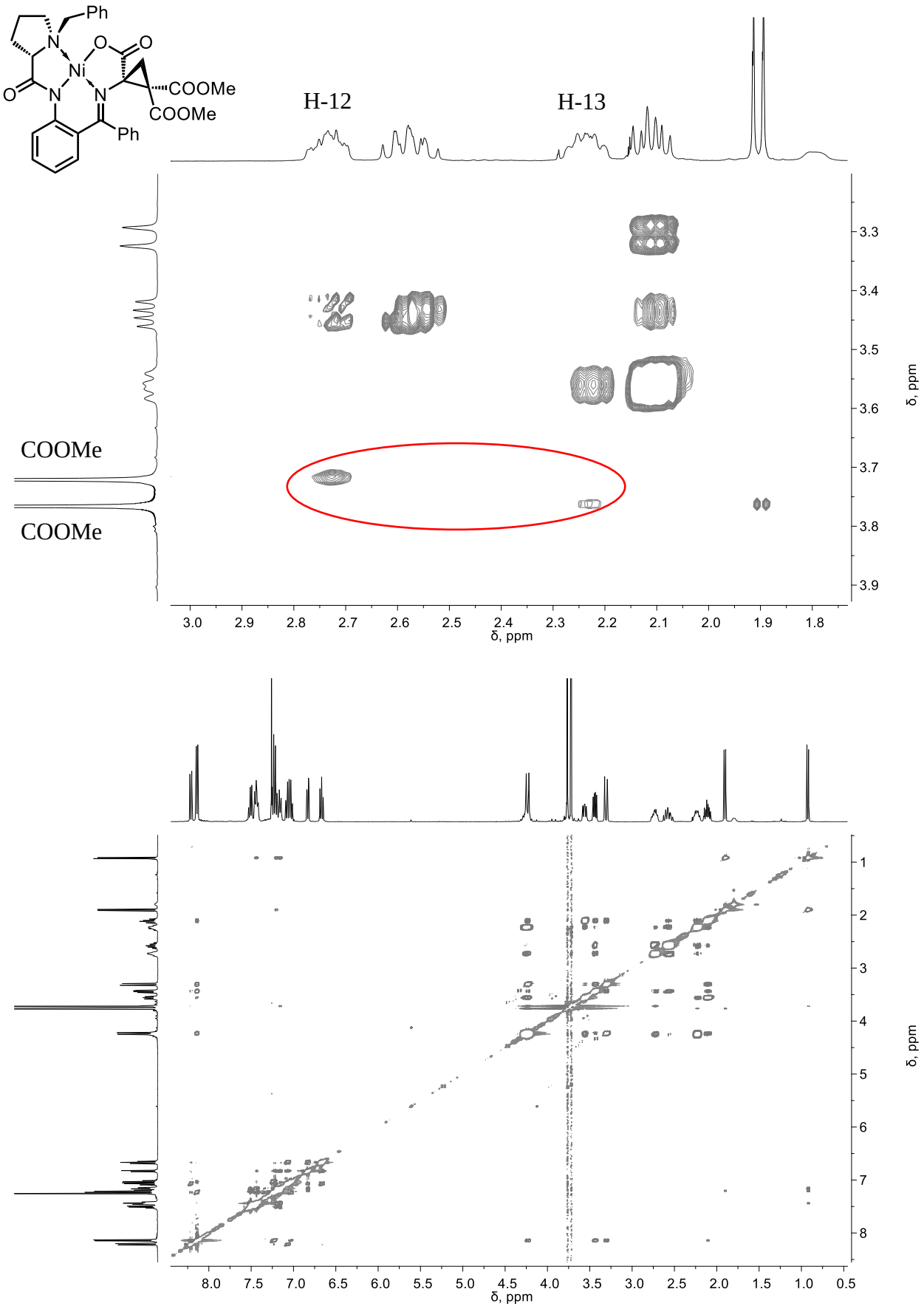
*12. HSQC spectrum of complex (S)-**4***



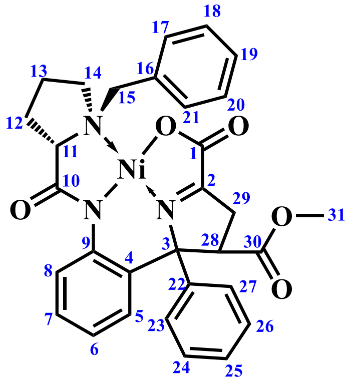
*13. HMBC spectrum of complex (S)-**4***



*14. NOESY spectrum of complex (S)-**4***



15. Atom numeration and signal assignment in the NMR spectra of complex ***5***



Diastereomer 1:

^{1}H NMR ($CDCl_3$ δ, ppm): 8.00-7.95 (m, 2H (H-17,21)), 7.91-7.86 (m, 2H (H-8,24)), 7.51-7.47 (m, 3H (H-18,19,20)), 7.29-7.21 (m, 4H (H-5,7,25,26)), 7.14 (dd, ^{3}J = 8.2 Hz, ^{3}J = 6.9 Hz 1H (H-6)), 7.01-6.95 (m, 2H (H-23,27)), 4.26-4.15 (m, 2H (H-14,28)), 3.95 (d, ^{2}J = 12.7 Hz, 1H (H-15)), 3.70-3.53 (m, 2H (H-11,29)), 3.28 (s, 3H (H-31)), 3.07 (dd, ^{3}J = 20.3 Hz, ^{3}J = 9.7 Hz, 1H (H-29)), 3.03-2.97 (m, 1H (H-14)), 2.95 (d, ^{2}J = 12.7 Hz, 1H (H-15)), 2.27-2.18 (m, 1H (H-13)), 2.04-1.86 (m, 3H (H-12,12,13)).

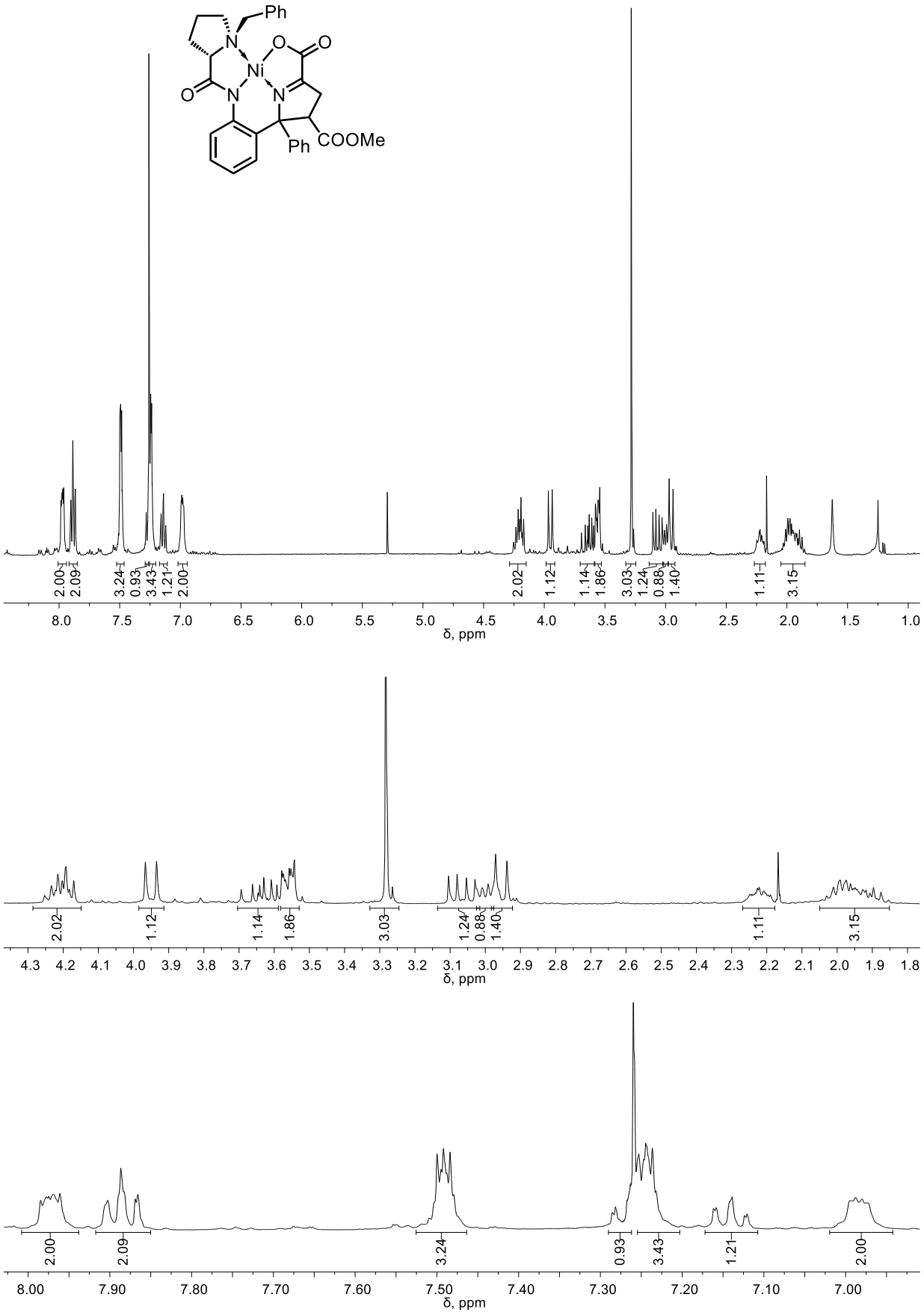
^{13}C NMR ($CDCl_3$ δ, ppm): 179.04 (C-10), 177.03 (C-2), 169.31 (C-30), 166.75 (C-1), 142.12 (C-22), 136.97 (C-9), 133.58 (C-16), 131.43 (C-17,21), 131.26 (C-4), 129.34, 129.31 (C-18,19,20), 128.77, 128.72, 128.66 (C-5,7,25,26), 127.48 (C-24), 126.54 (C-8), 126.22 (C-23,27), 122.76 (C-6), 79.36 (C-3), 68.32 (C-11), 59.60 (C-15), 57.94 (C-14), 53.72 (C-28), 52.53 (C-31), 36.22 (C-29), 27.43 (C-13), 22.20 (C-12).

Diastereomer 2:

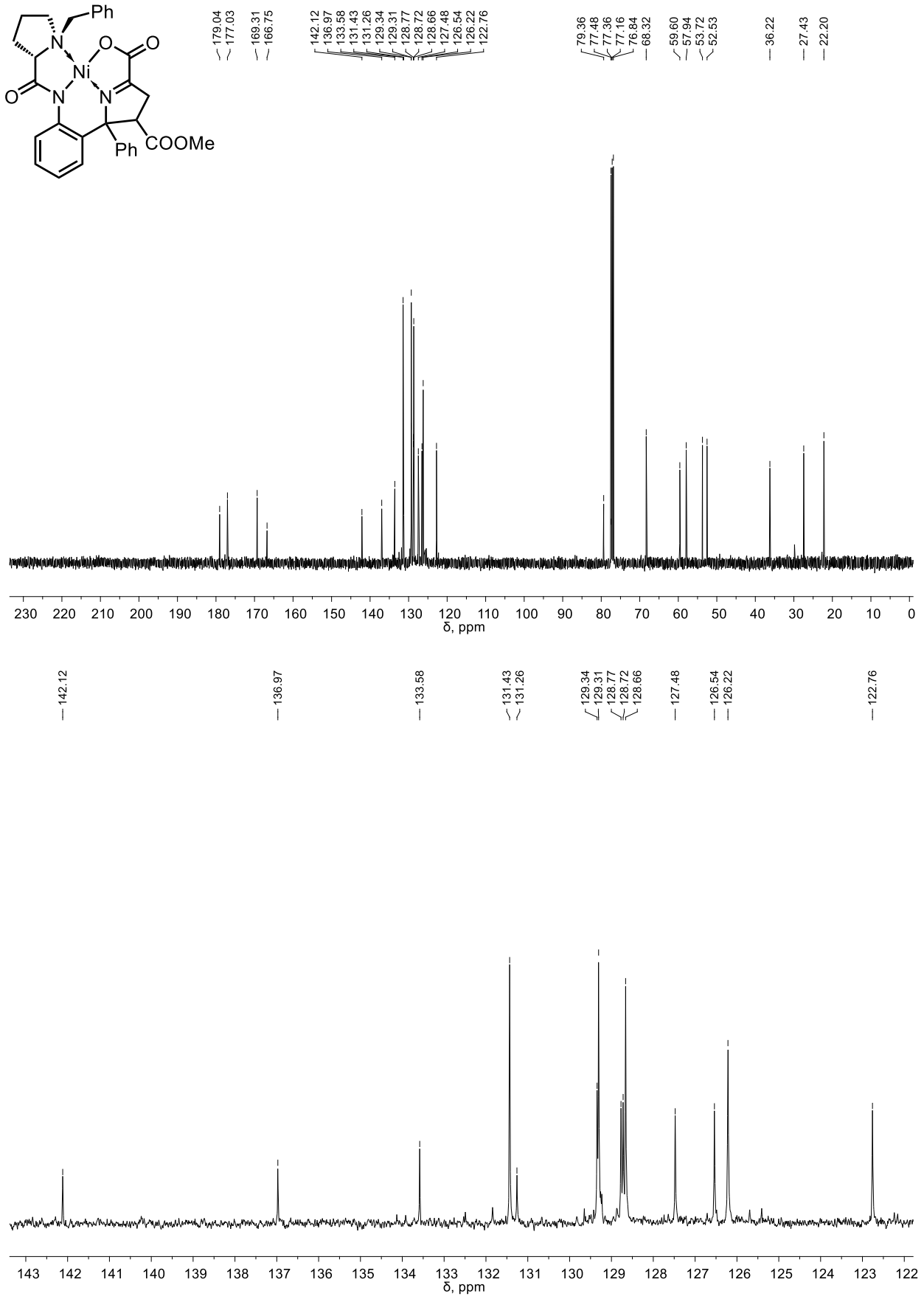
^{1}H NMR ($CDCl_3$ δ, ppm): 8.25-8.21 (m, 2H (H-17,21)), 7.75-7.70 (m, 2H (H-23,27)), 7.46-7.26 (m, 7H (H-8,18,19,20,24,25,26)), 7.15 (dd, ^{3}J = 7.7 Hz, ^{4}J = 1.6 Hz, 1H (H-5)), 6.98-6.93 (m, 1H (H-7)), 6.88 (td, J = 7.5 Hz, J = 1.4 Hz, 1H (H-6)), 4.30 (d, ^{2}J = 12.5 Hz, 1H (H-15)), 3.88 (dd, ^{3}J = 5.9 Hz, ^{3}J = 1.5 Hz, 1H (H-28)), 3.80-3.66 (m, 1H (H-13)), 3.58 (s, 3H (H-31)), 3.57-3.46 (m, 2H (H-14,15)), 3.33 (dd, ^{3}J = 10.4 Hz, ^{3}J = 6.2 Hz, 1H (H-11)), 2.88 (dd, ^{2}J = 19.1 Hz, ^{3}J = 1.5 Hz, 1H (H-29)), 2.82 (dd, ^{2}J = 19.1 Hz, ^{3}J = 5.9 Hz, 1H (H-29)), 2.50-2.34 (m, 2H (H-12)), 2.33-2.23 (m, 1H (H-13)), 2.23-2.13 (m, 1H (H-14)).

^{13}C NMR ($CDCl_3$ δ, ppm): 179.34 (C-10), 178.59 (C-2), 171.82 (C-30), 166.69 (C-1), 139.46 (C-22), 139.37 (C-9), 133.66 (C-16), 131.54 (C-17,21), 130.42 (C-4), 129.38 (C-19), 129.33 (C-18,20), 129.19 (C-24,26), 128.46 (C-25), 127.37 (C-7), 126.74 (C-8), 125.44 (C-5,23,27), 122.29 (C-6), 77.80 (C-3), 71.75 (C-11), 63.36 (C-15), 57.84 (C-14), 56.52 (C-28), 52.56 (C-31), 36.96 (C-29), 30.55 (C-12), 24.66 (C-13).

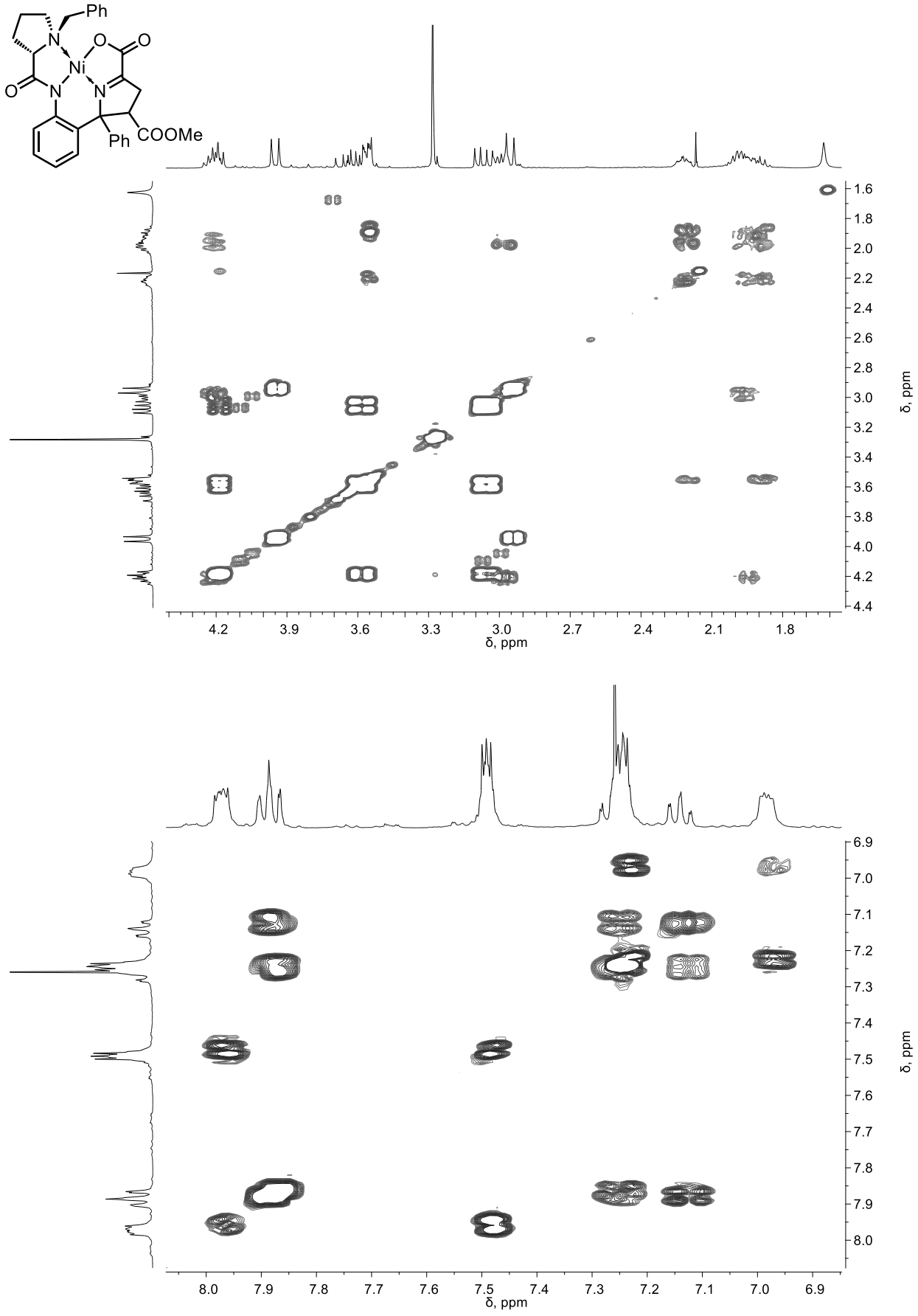
16. *^{1}H NMR spectrum of complex* ***5****, diastereomer 1*



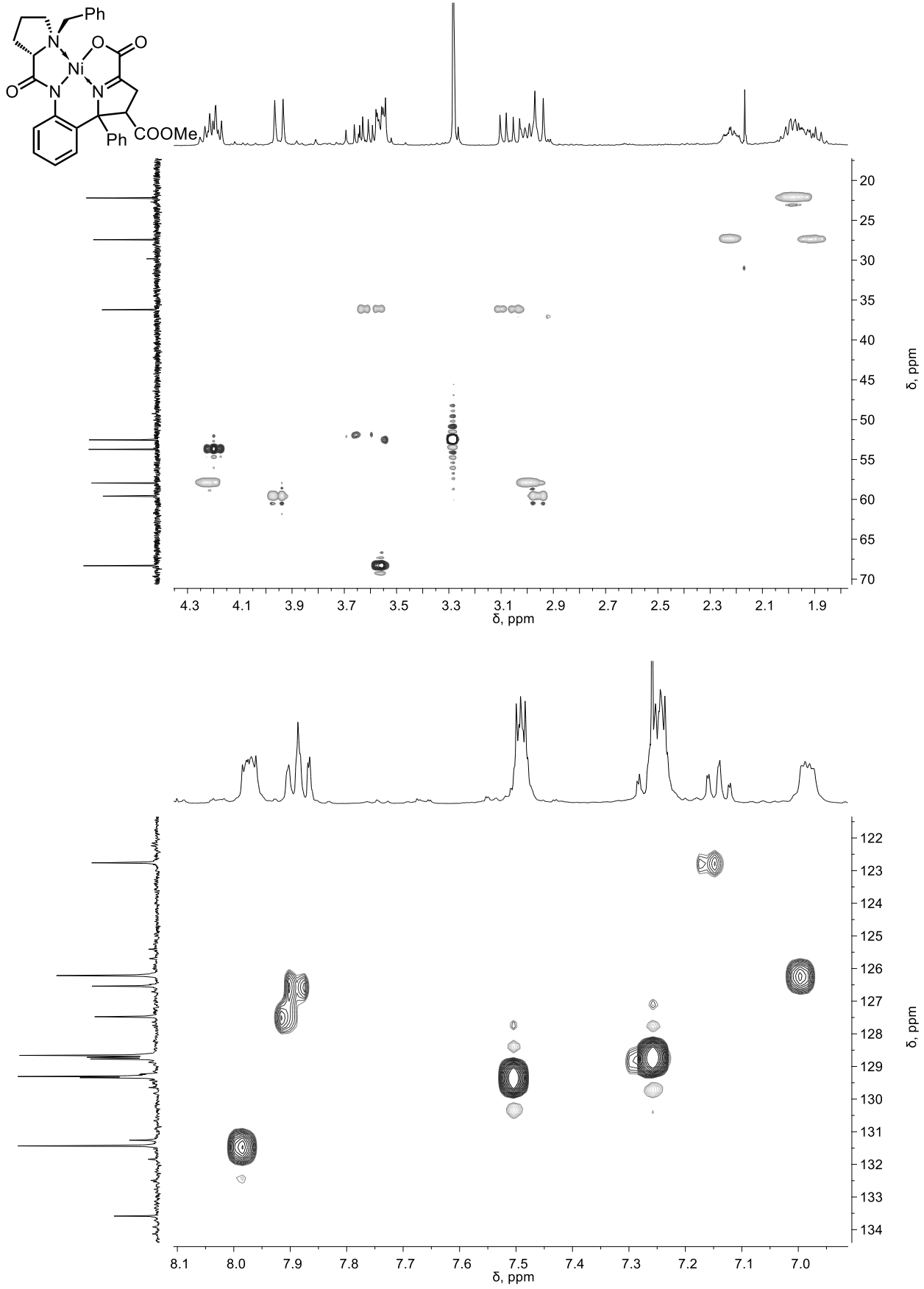
*17. ^{13}C NMR spectrum of complex **5**, diastereomer 1*



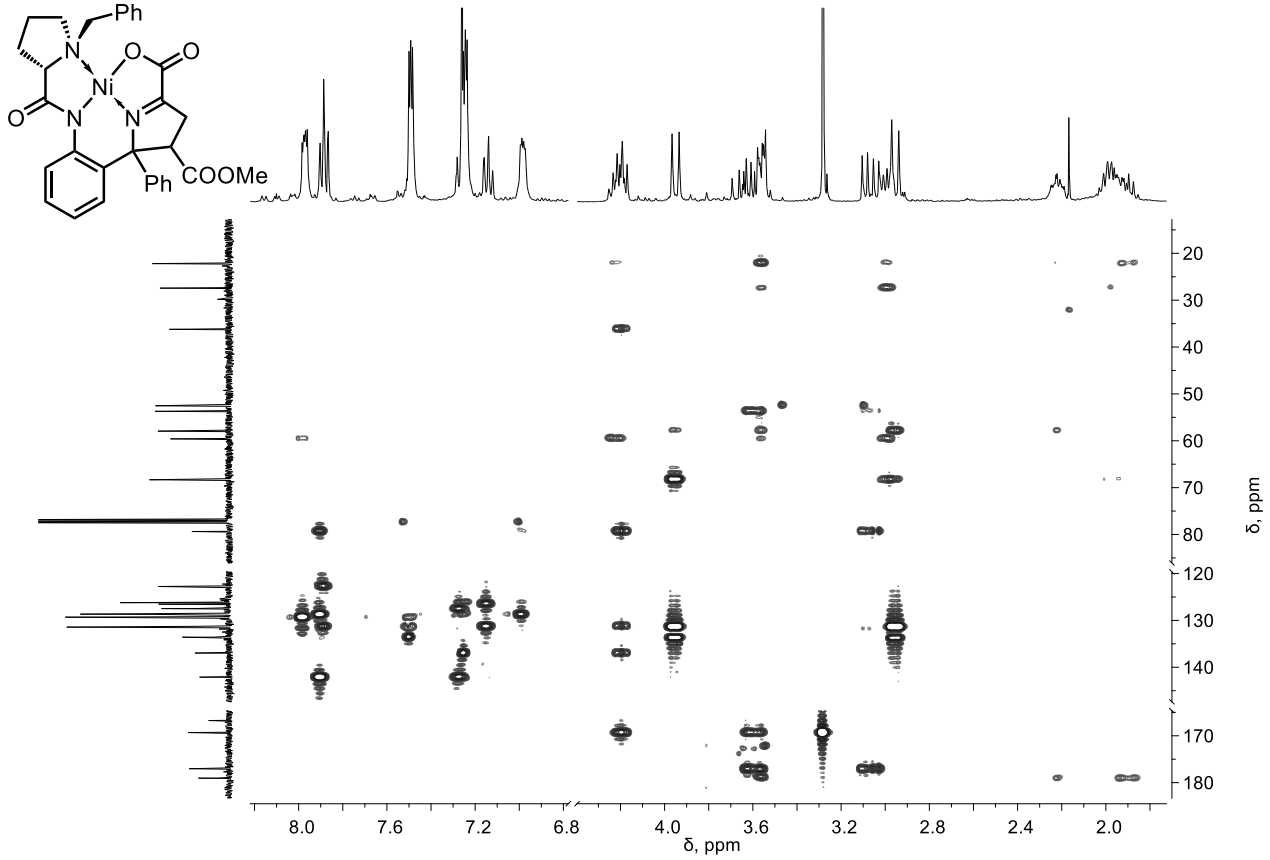
*18. COSY spectrum of complex **5**, diastereomer 1*



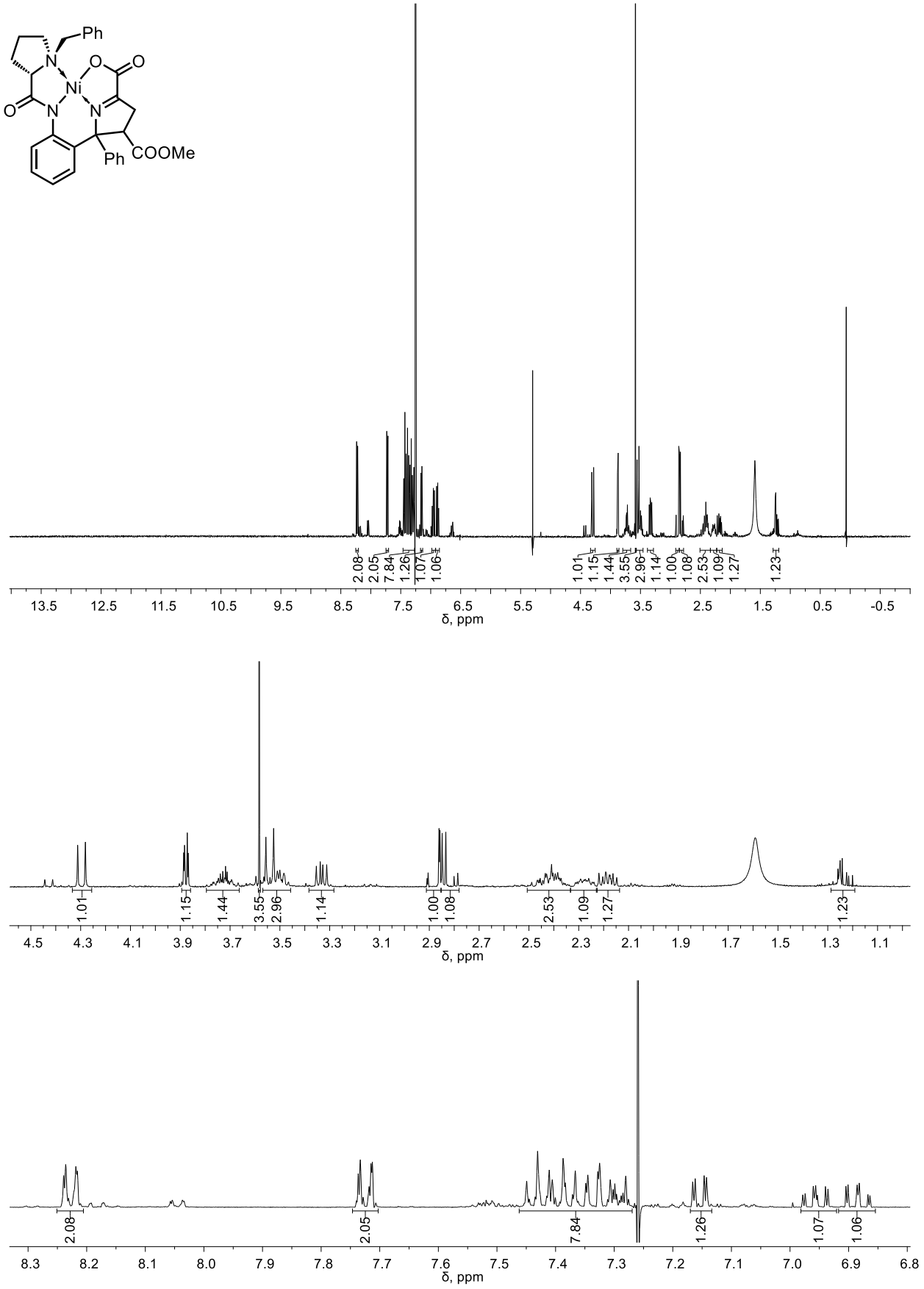
19. HSQC spectrum of complex ***5****, diastereomer 1*



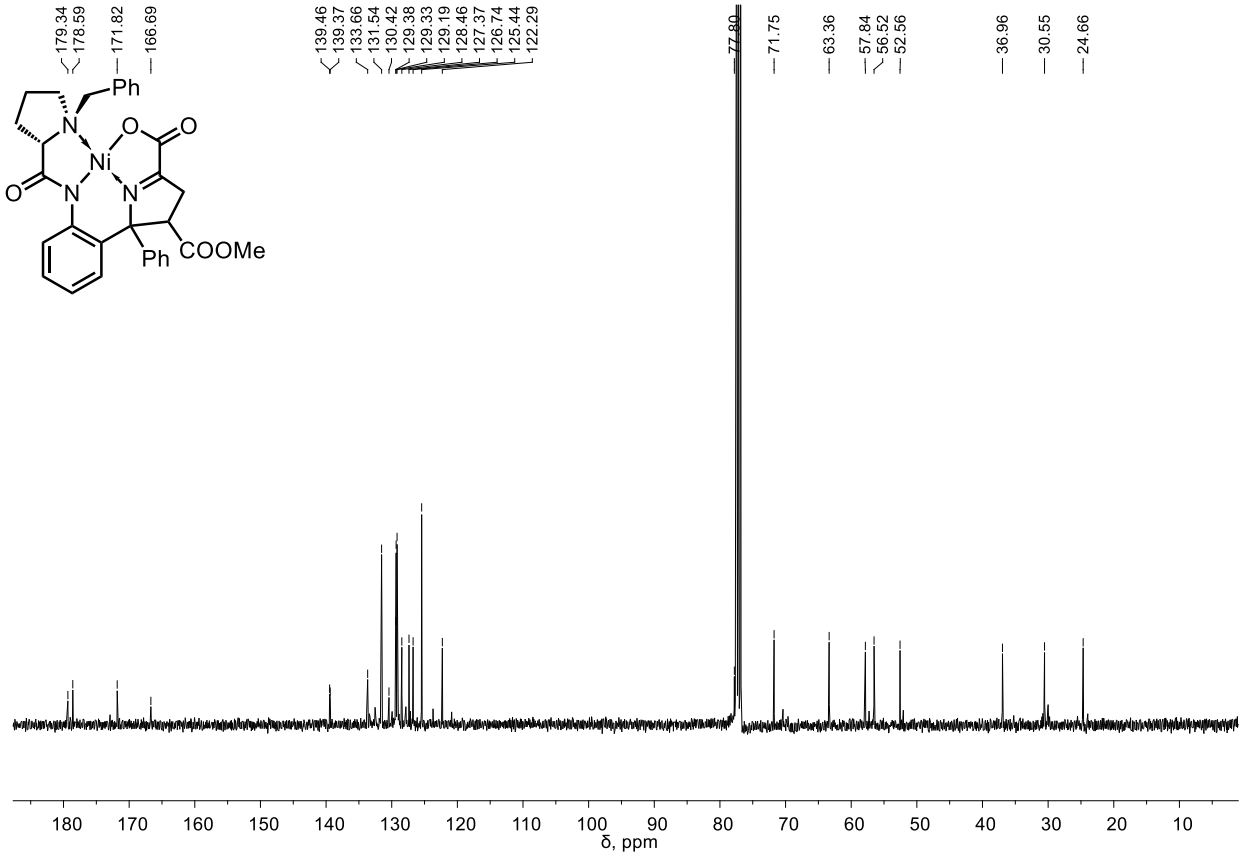
*20. HMBC spectrum of complex **5**, diastereomer 1*

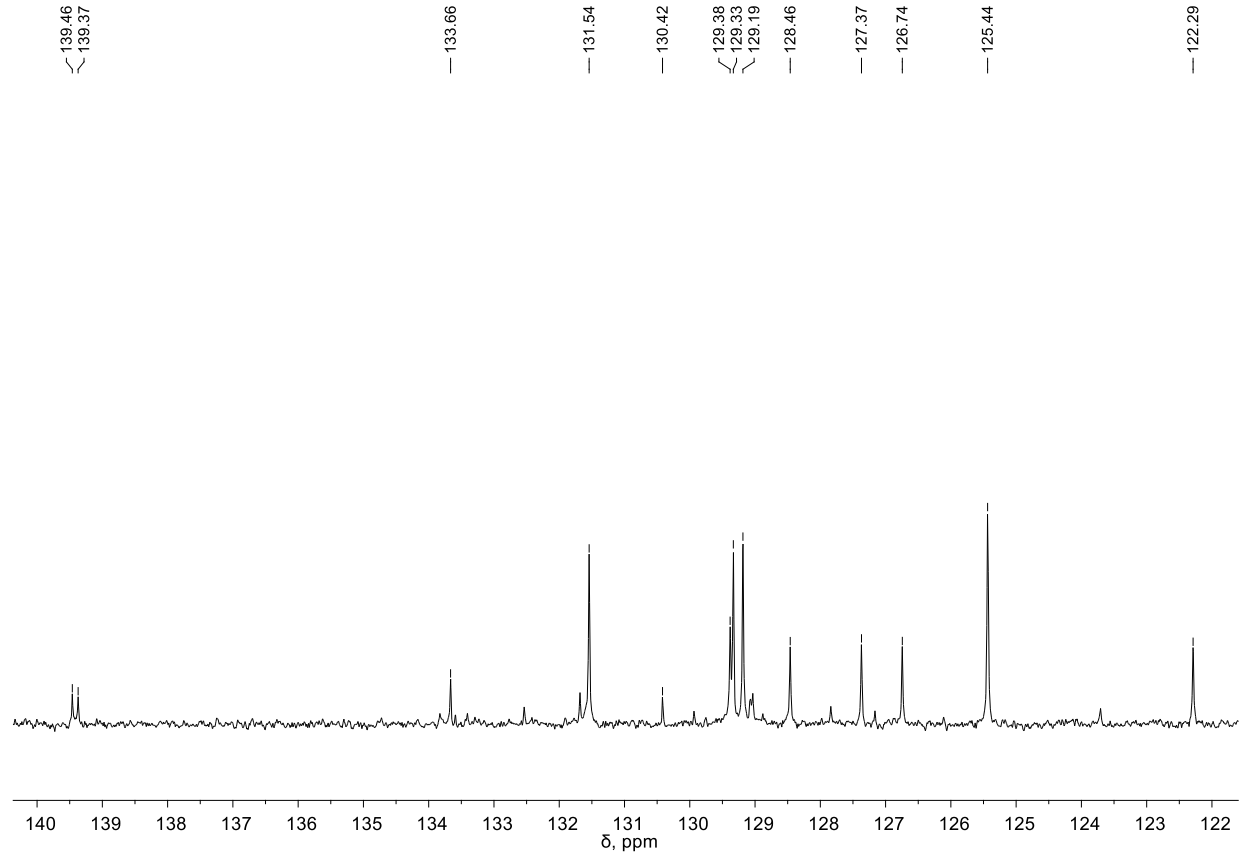


21. *^{1}H NMR spectrum of complex* ***5****, diastereomer 2*

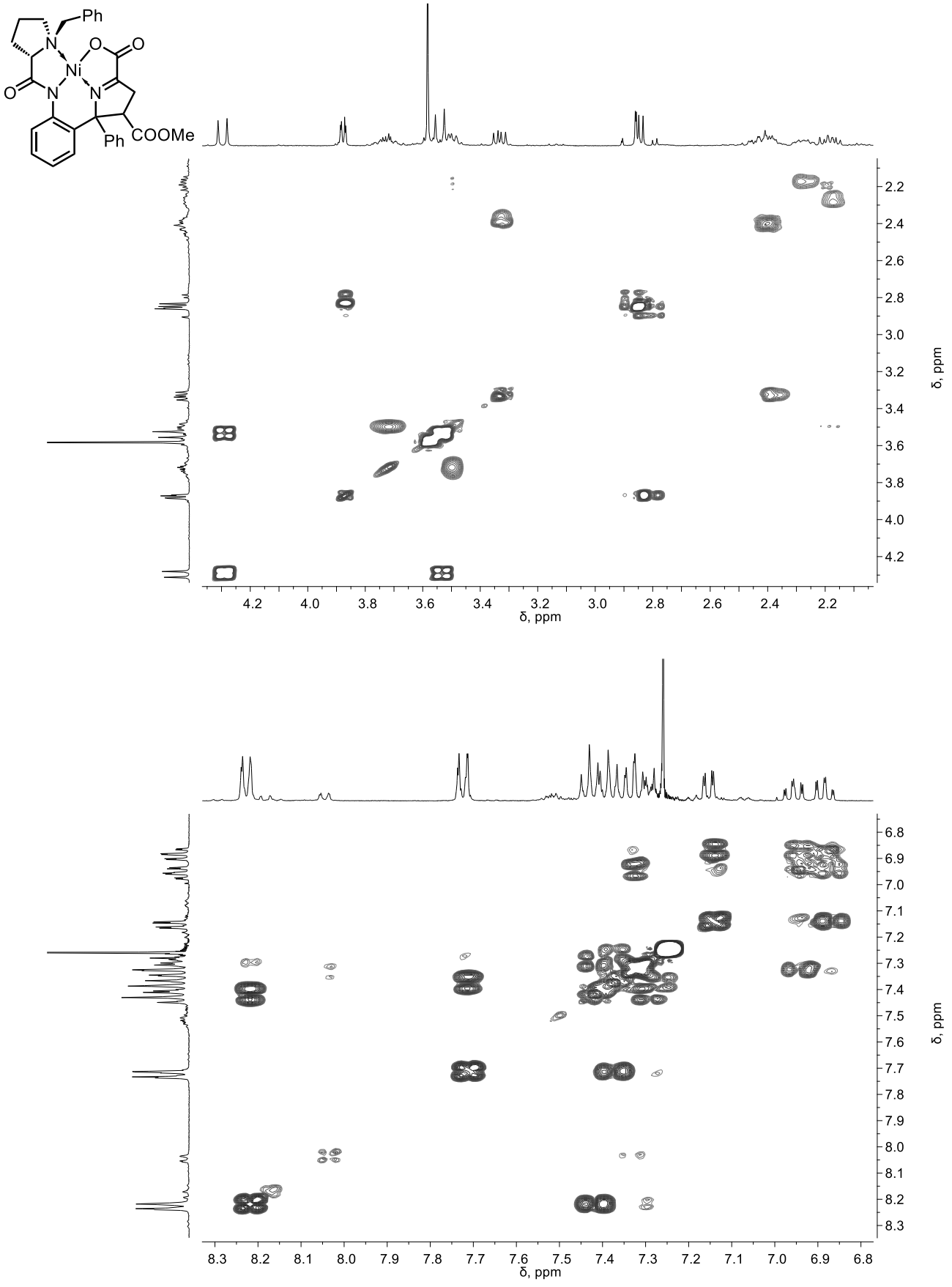


*22. ^{13}C NMR spectrum of complex **5**, diastereomer 2*

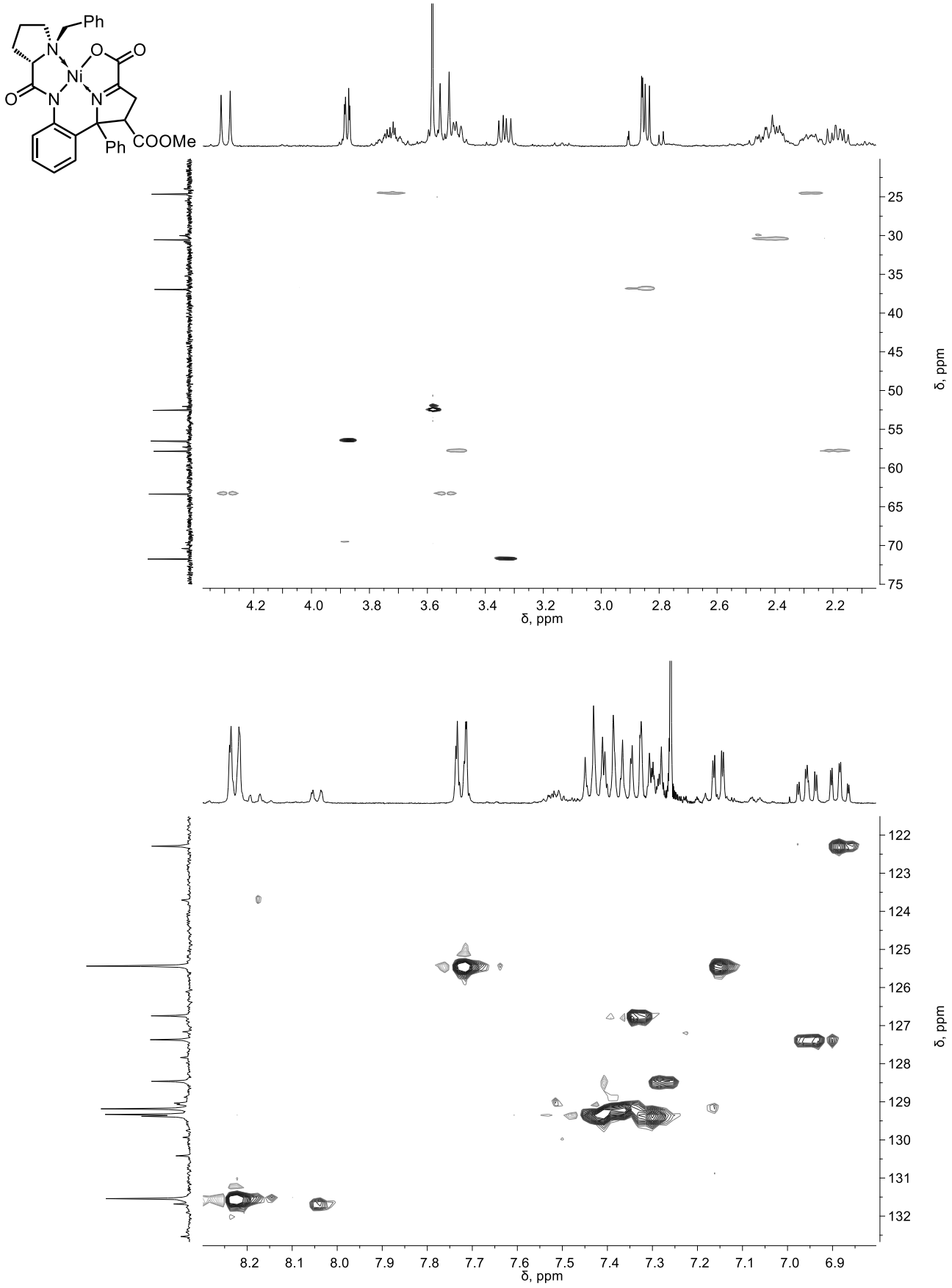




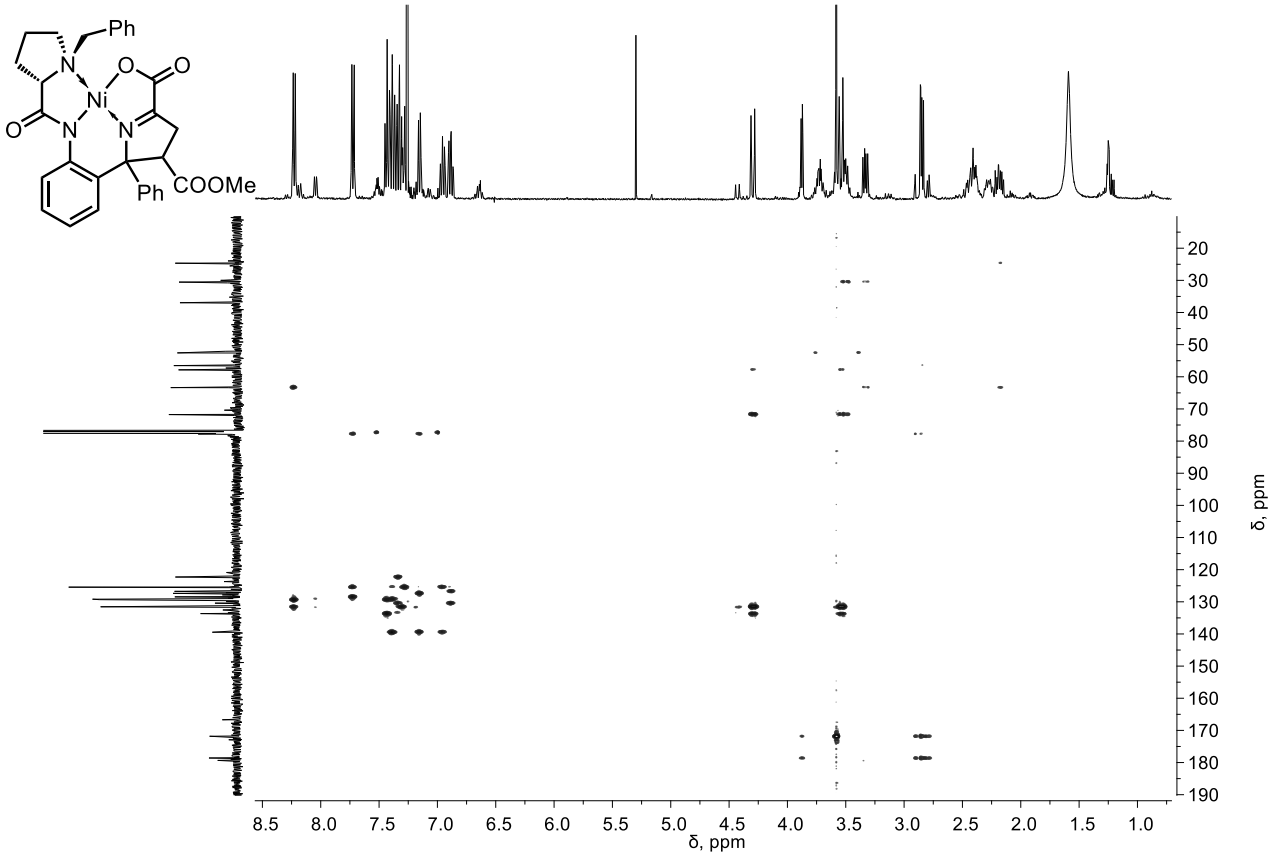
*23. COSY spectrum of complex **5**, diastereomer 2*



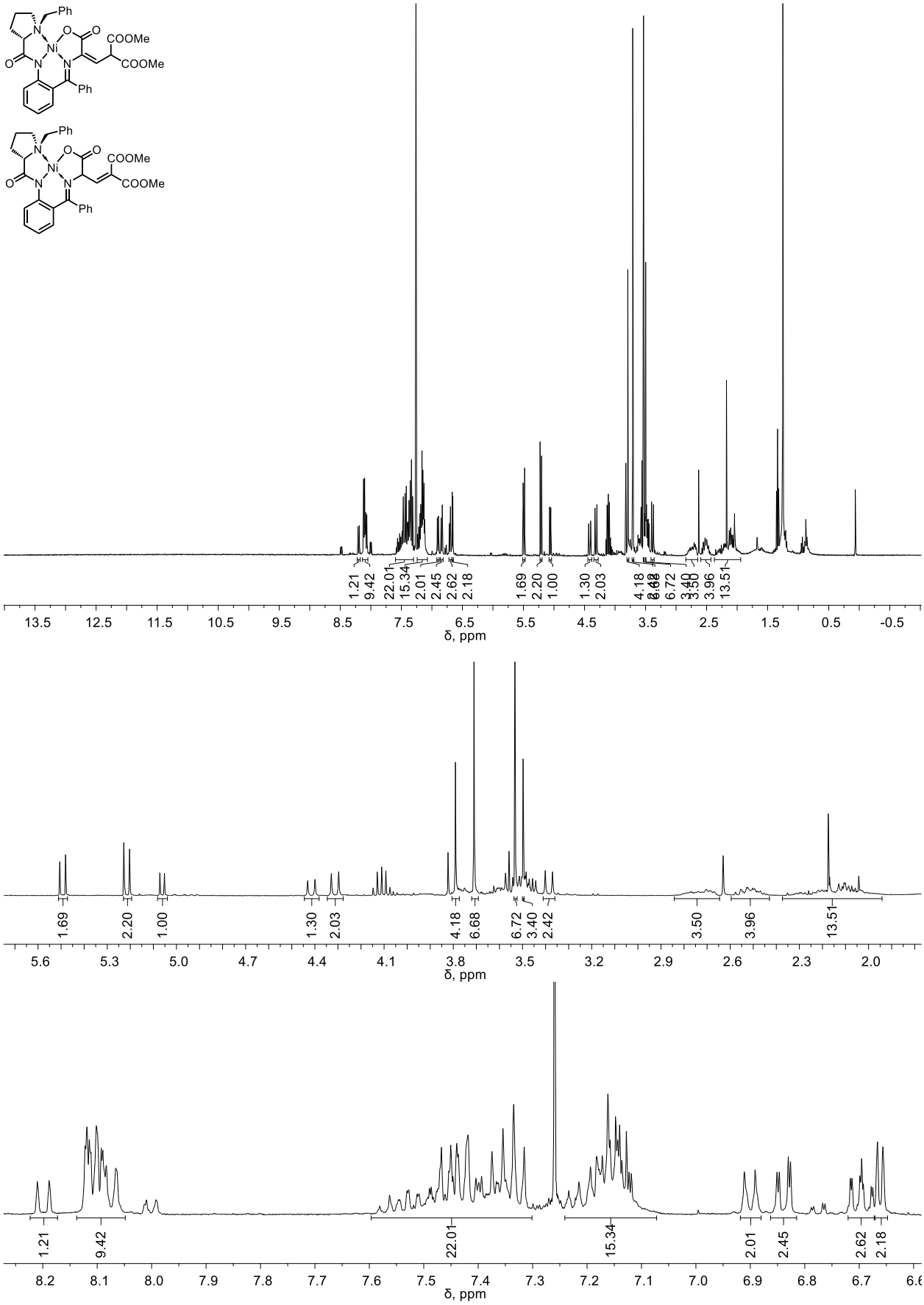
24. HSQC spectrum of complex **5**, *diastereomer 2*



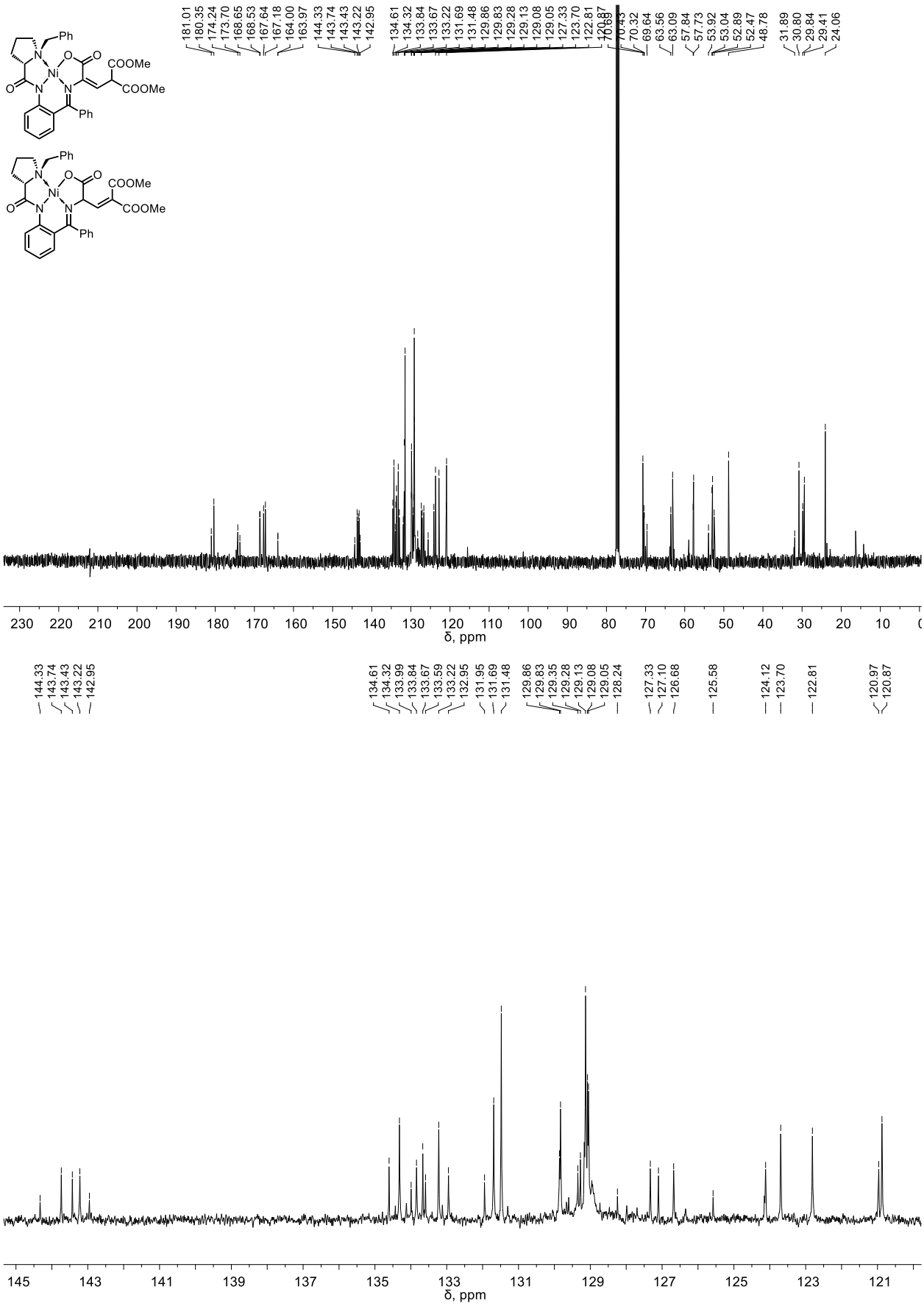
*25. HMBC spectrum of complex **5**, diastereomer 2*



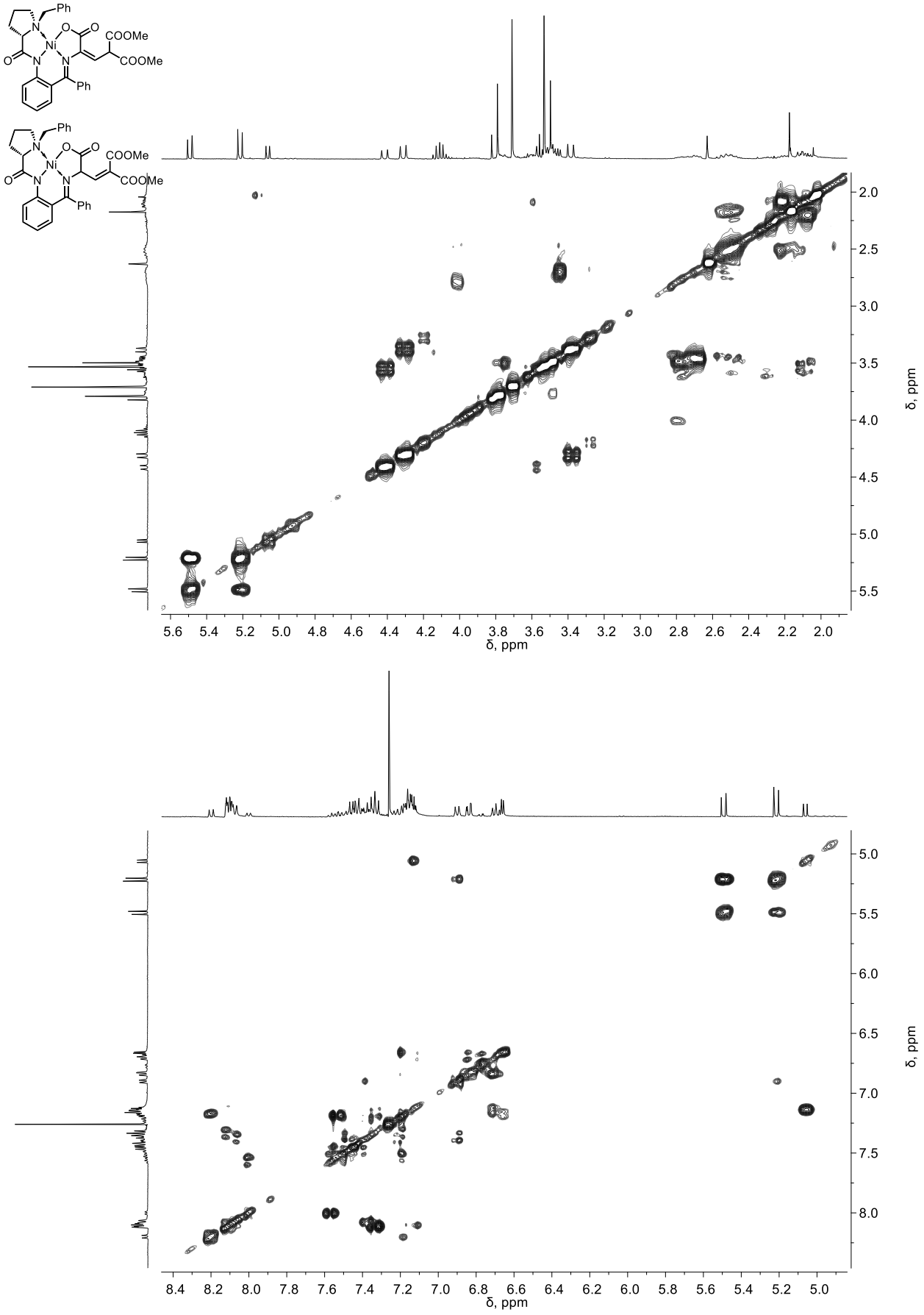
26. *^{1}H NMR spectrum of complexes* ***6***



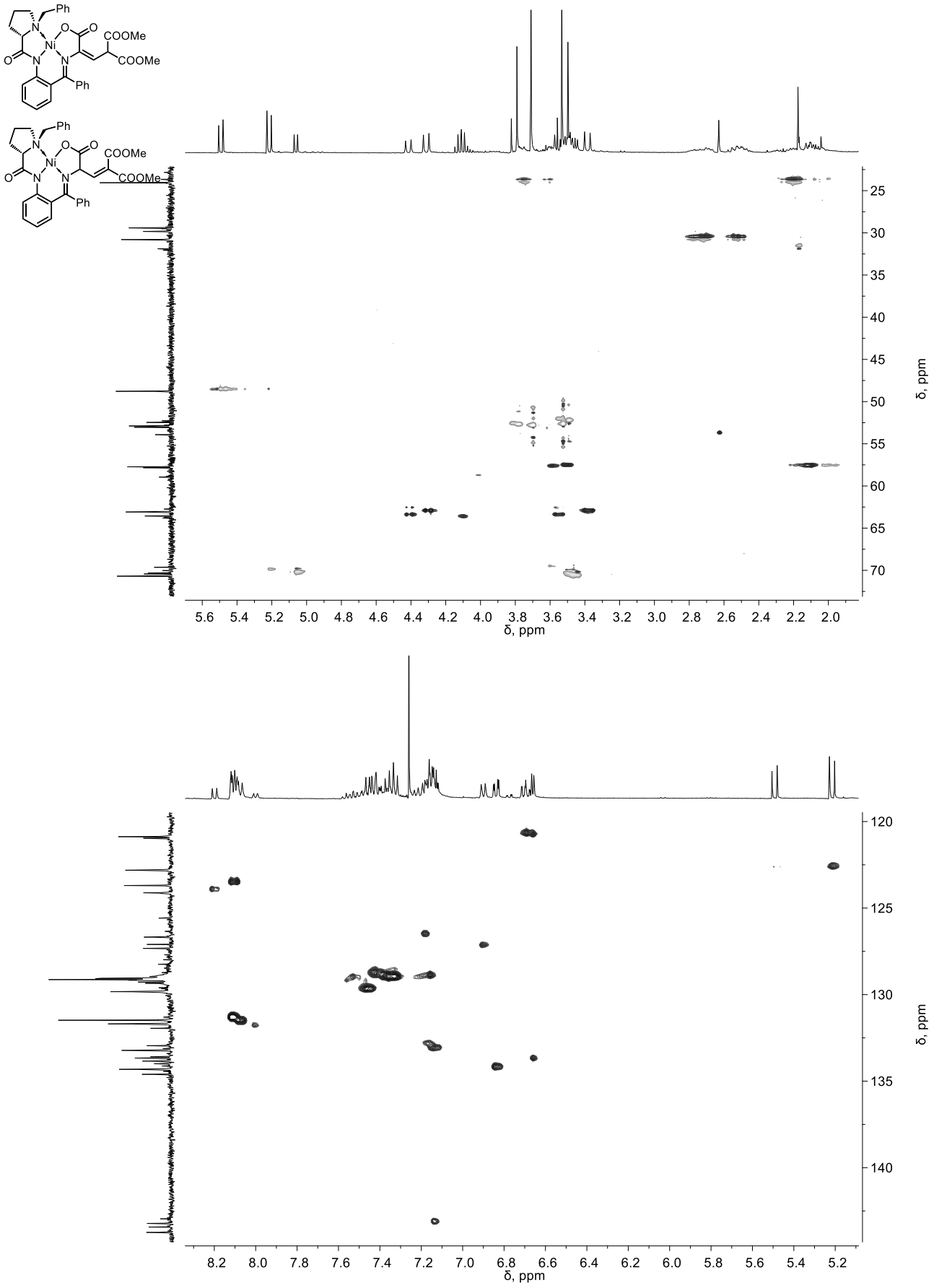
*27. ^{13}C NMR spectrum of complexes **6***



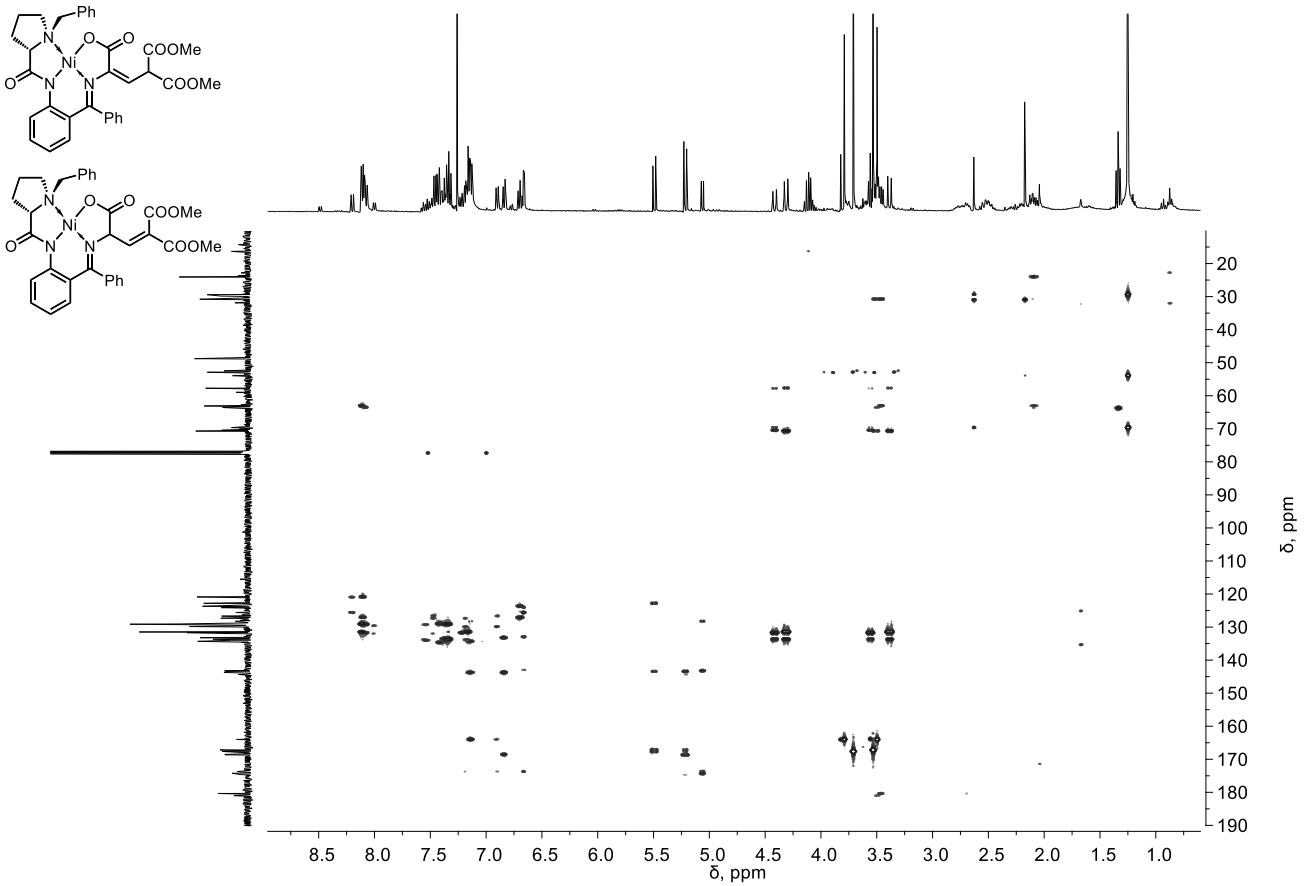
*28. COSY spectrum of complexes **6***

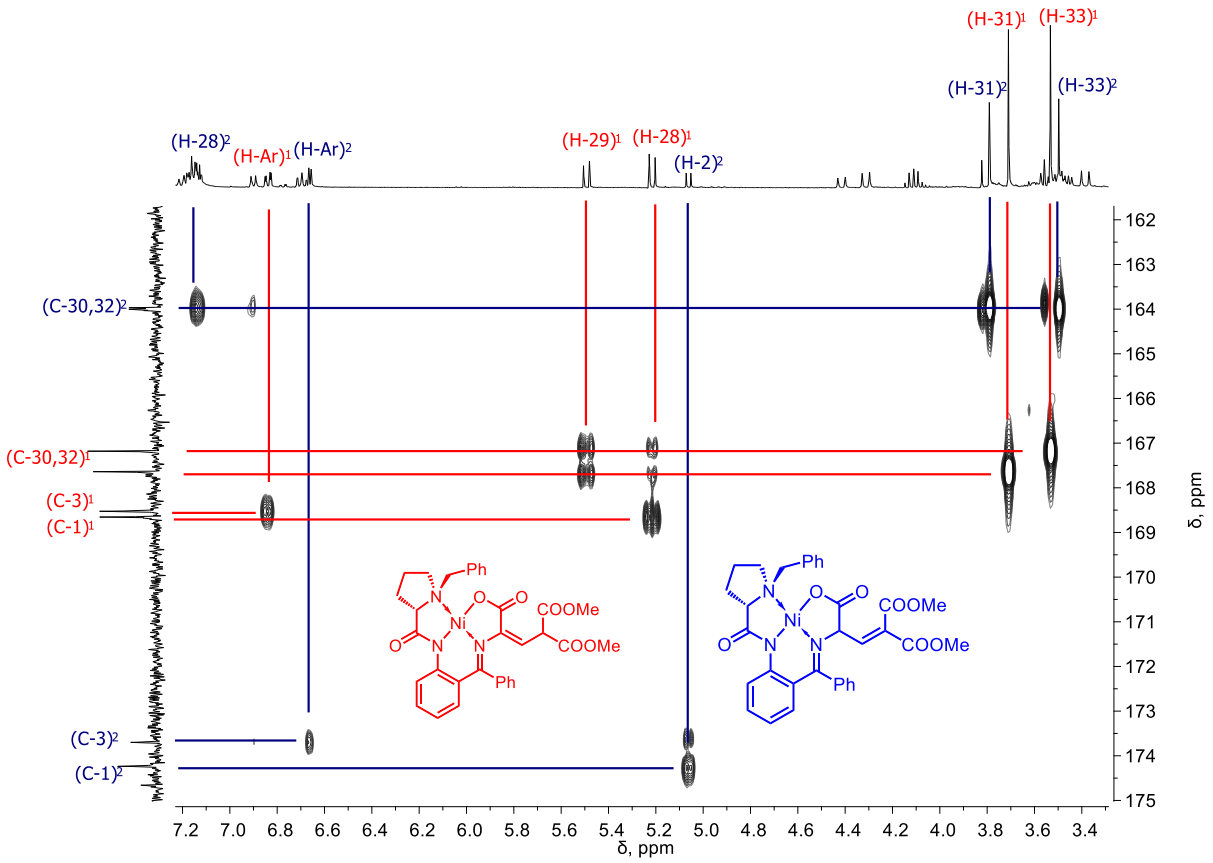


29. HSQC spectrum of complexes ***6***

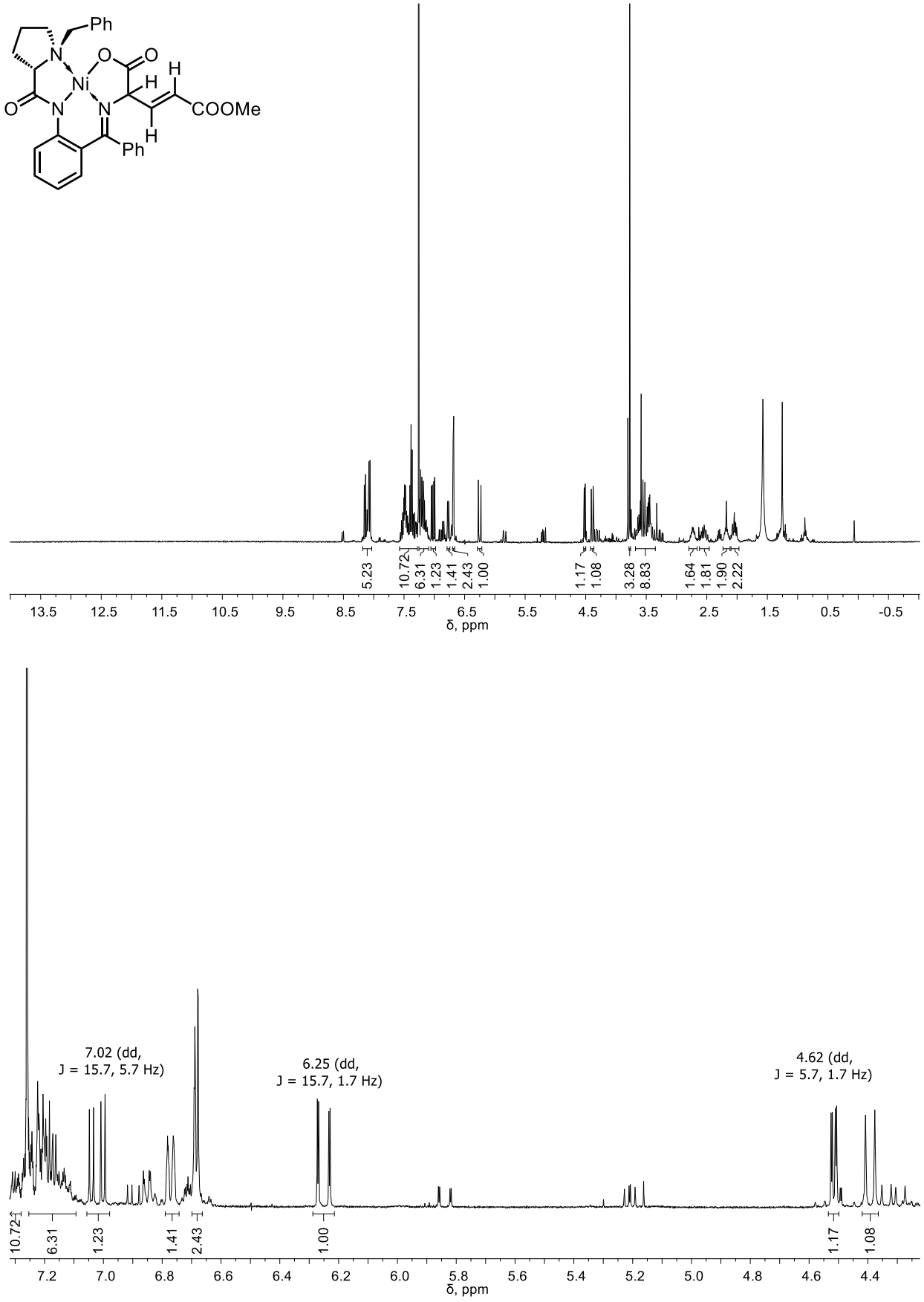


30. HMBC spectrum of complexes ***6***

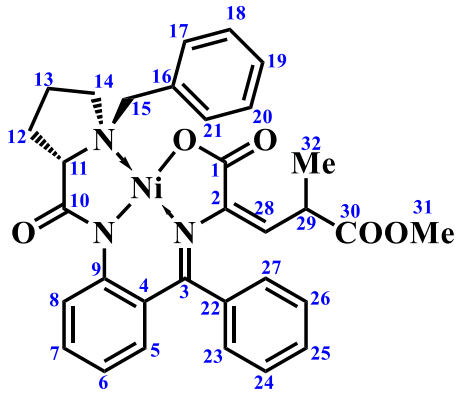




*31. ^{1}H NMR spectrum of complex **8***



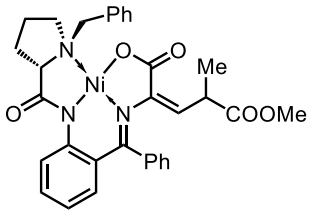
32. Atom numeration and signal assignment in the NMR spectra of complex ***9***

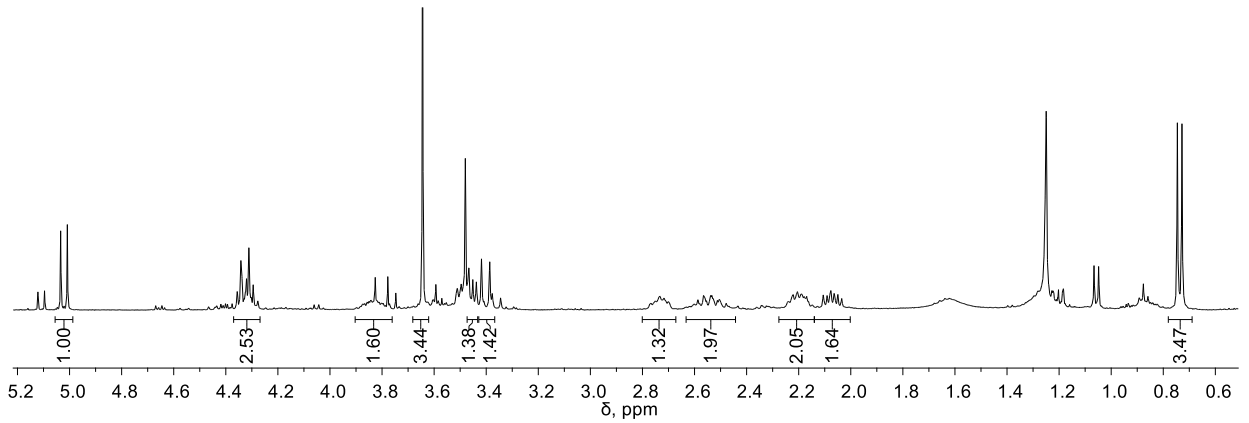


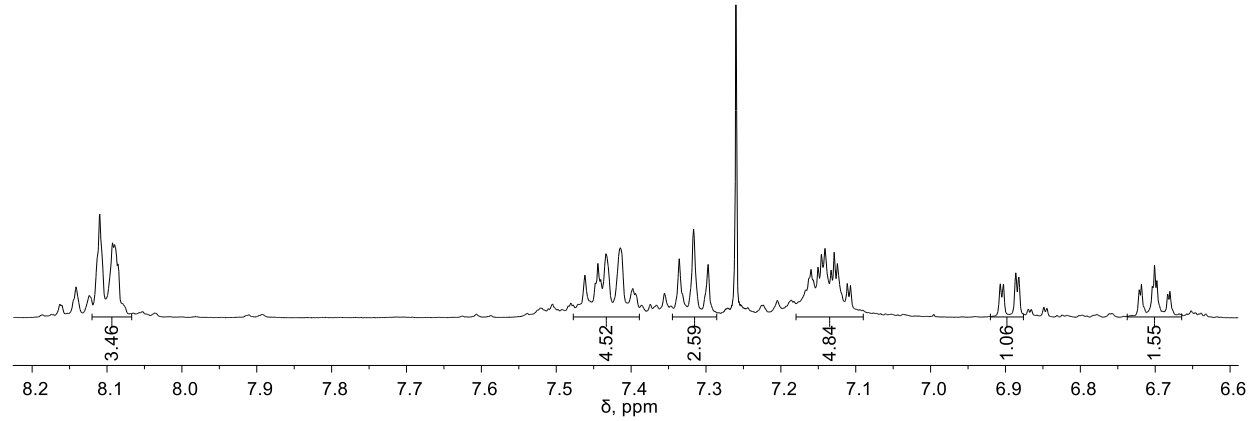
^{1}H NMR ($CDCl_3$ δ, ppm): 8.12-8.07 (m, 3H (H-8,17,21)), 7.47-7.39 (m, 3H (H-23,24,26)), 7.34-7.29 (m, 2H (H-18,20)), 7.18-7.10 (m, 4H (H-7,19,25,27)), 6.89 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.6 Hz, 1H (H-5)), 6.70 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.2 Hz, 1H (H-6)), 5.02 (d, ^{3}J = 10.3 Hz, 1H (H-28)), 4.36-4.27 (m, 2H (H-15,29)), 3.90-3.77 (m, 1H (H-13)), 3.64 (s, 3H (H-31)), 3.48-3.43 (m, 1H (H-11)), 3.40 (d, ^{3}J = 12.6 Hz, 1H (H-15)), 2.78-2.69 (m, 1H (H-12)), 2.63-2.45 (m, 2H (H-12,14)), 2.25-2.16 (m, 1H (H-13)), 2.11-2.03 (m, 1H (H-14)), 0.74 (d, ^{3}J = 7.1 Hz, 3H (H-32)).

^{13}C NMR ($CDCl_3$ δ, ppm): 180.25 (C-10), 174.26 (C-30), 168.97 (C-1), 167.71 (C-3), 143.46 (C-9), 140.74 (C-2), 135.08 (C-22), 134.09 (C-5), 133.65 (C-16), 132.95 (C-7), 131.49 (C-17,21), 131.35 (C-28), 129.85 (C-24,26), 129.15 (C-25), 129.11 (C-27), 129.07 (C-18,20), 128.97 (C-19), 128.87 (C-23), 127.02 (C-4), 123.67 (C-8), 120.83 (C-6), 70.75 (C-11), 63.04 (C-15), 57.53 (C-14), 52.14 (C-31), 36.16 (C-29), 30.82 (C-12), 24.14 (C-13), 17.28 (C-32).

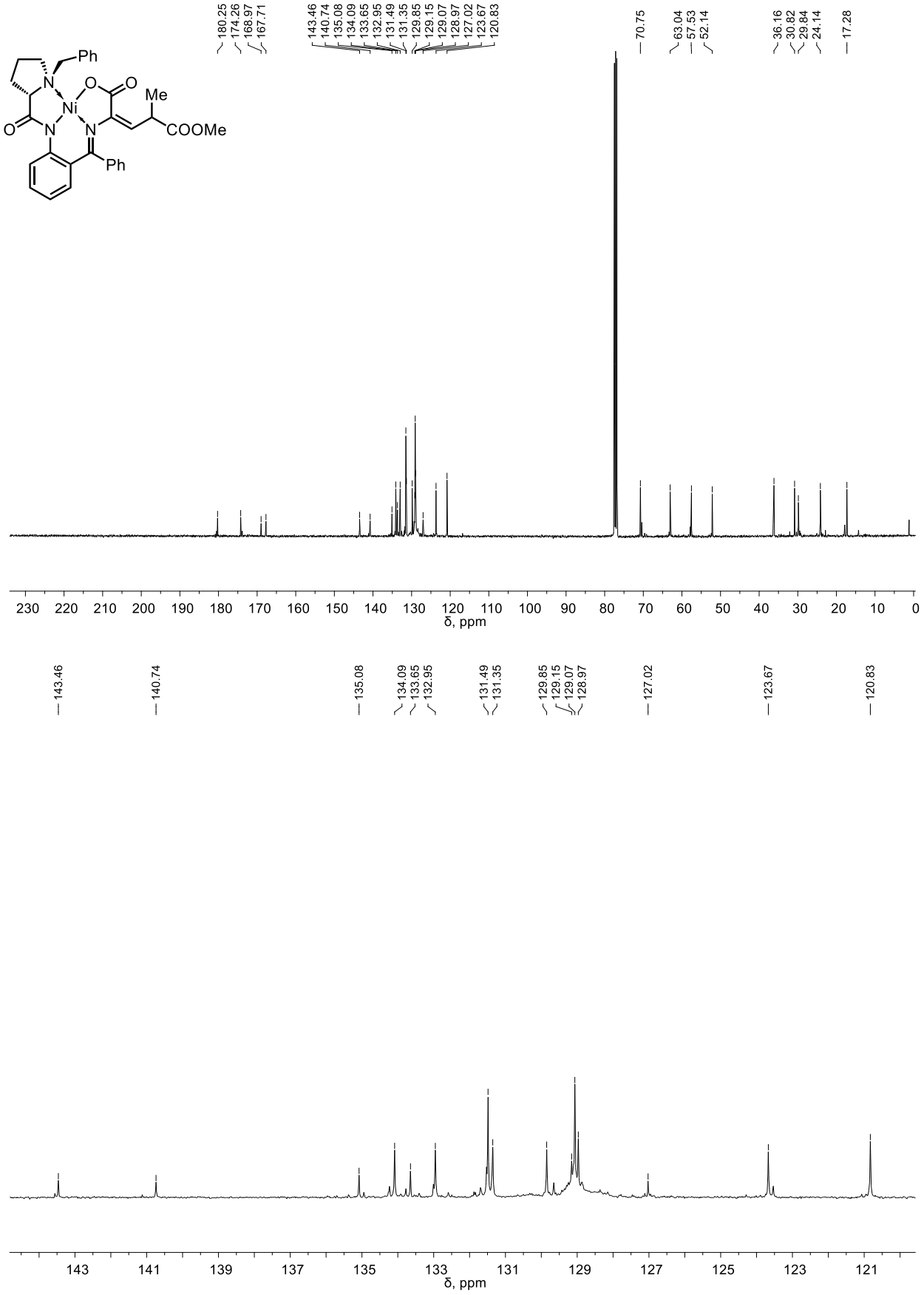
*33. ^{1}H NMR spectrum of complex **9***



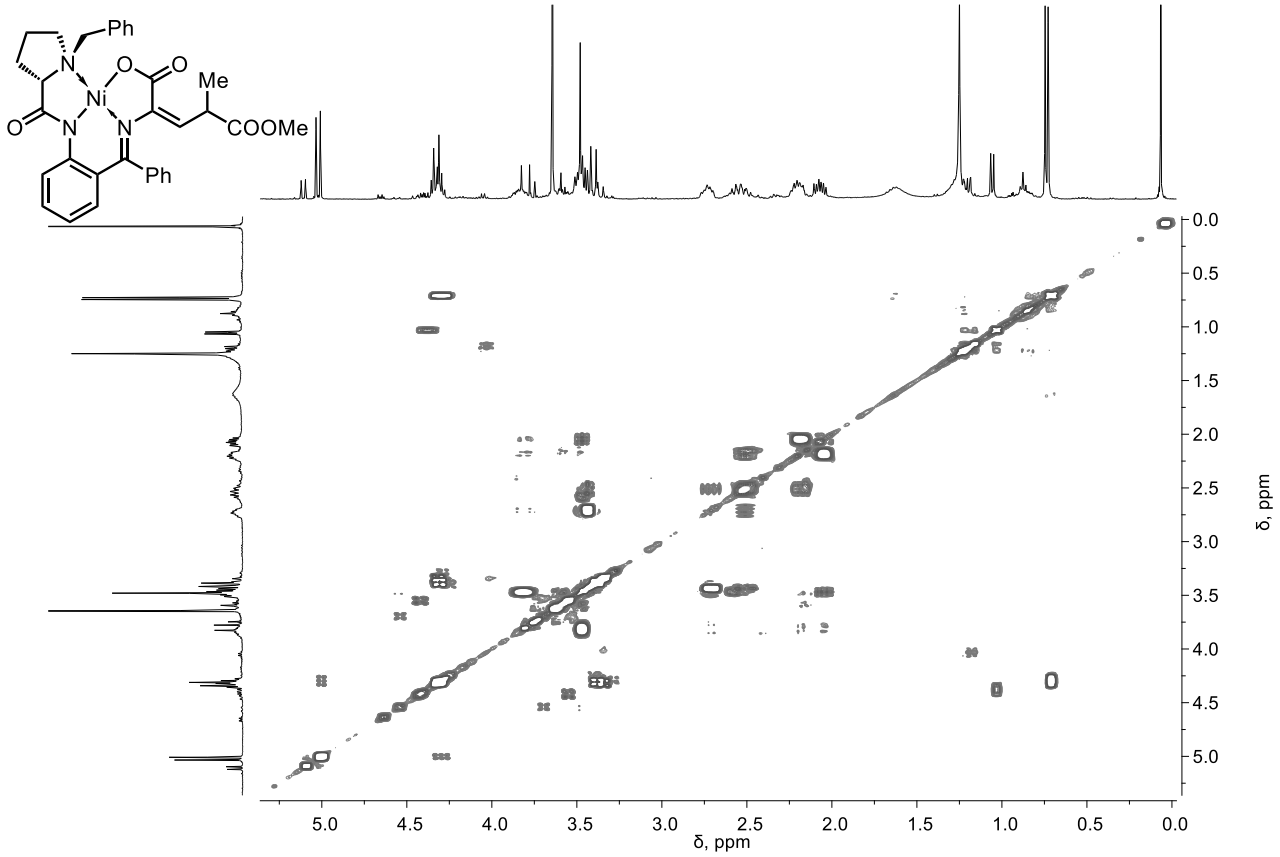




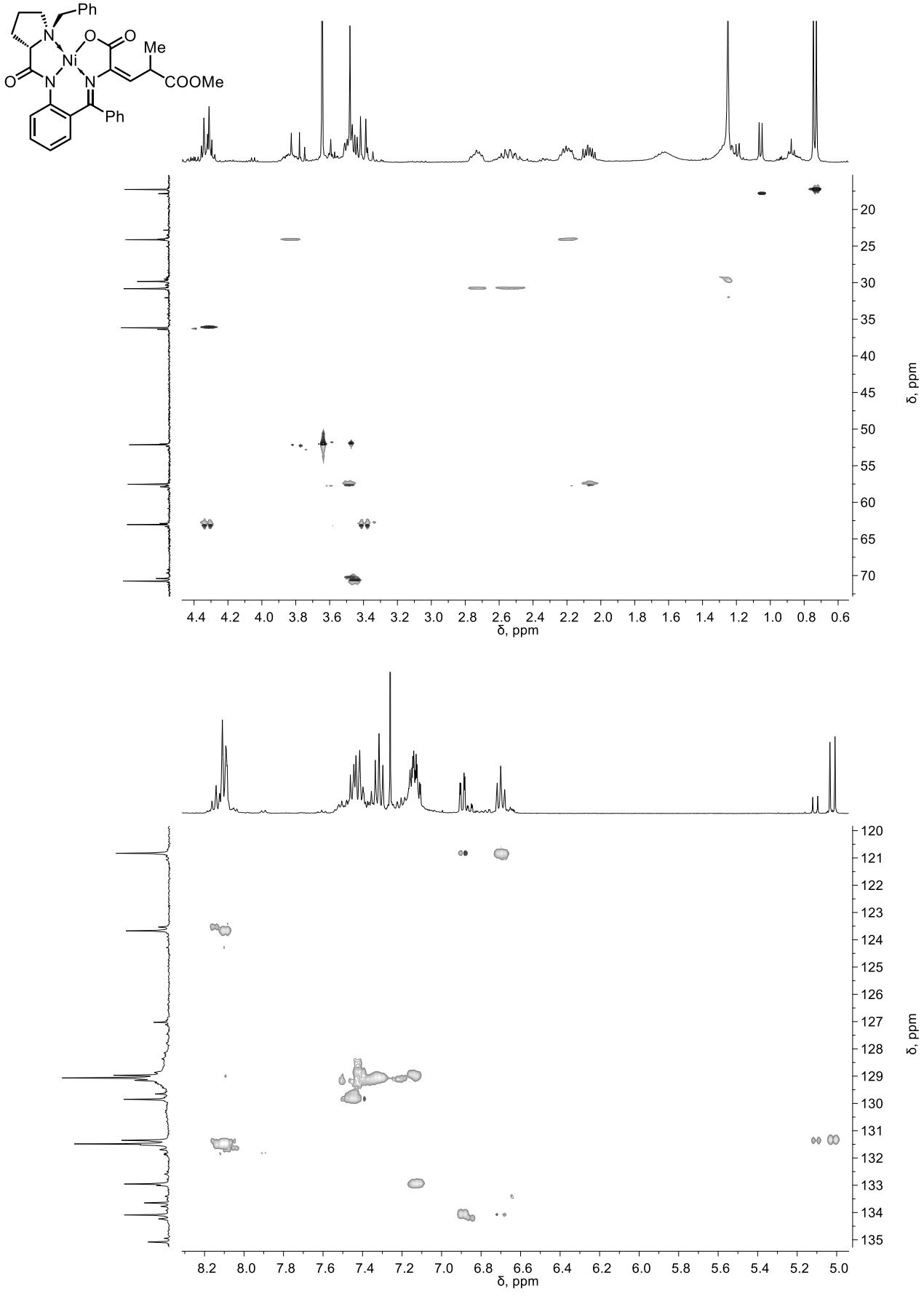
*34. ^{13}C NMR spectrum of complex **9***



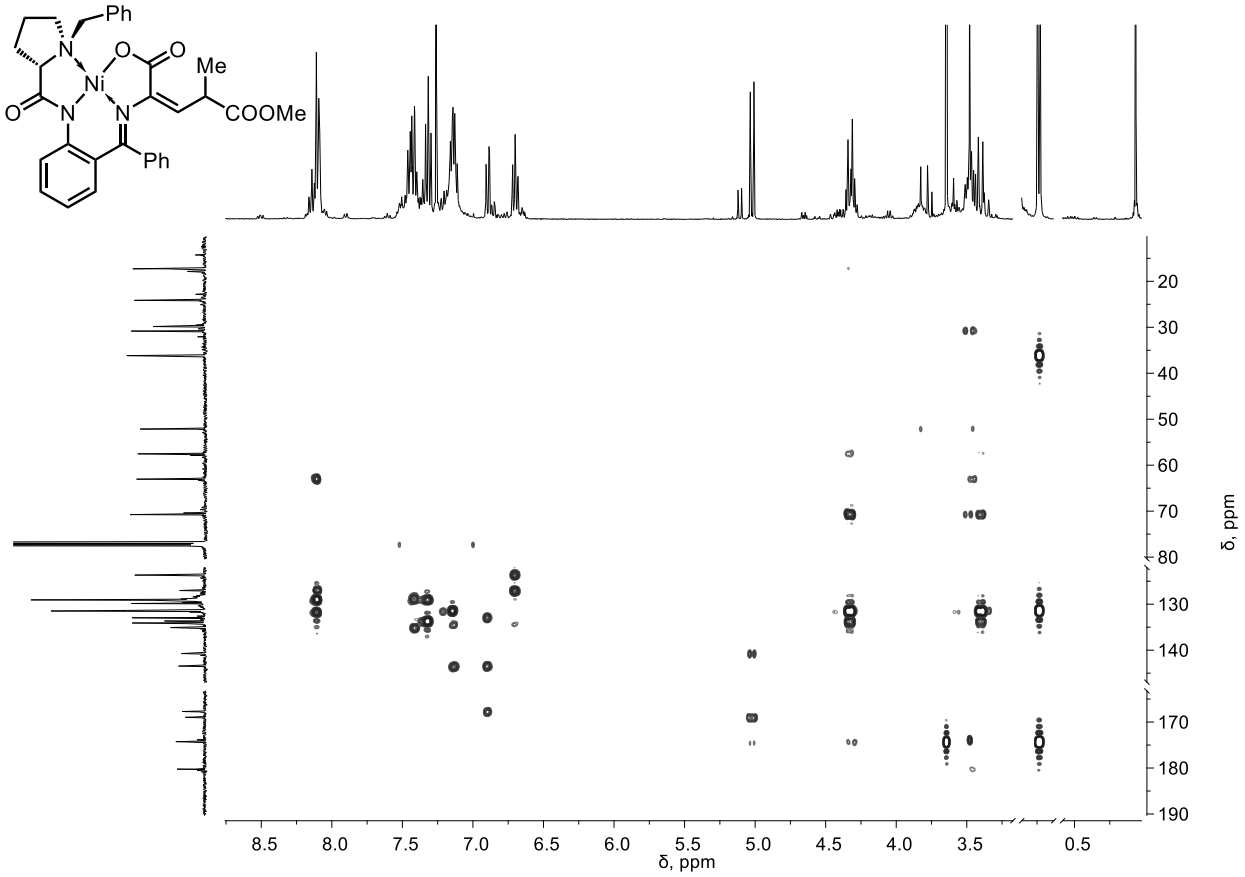
*35. COSY spectrum of complex **9***



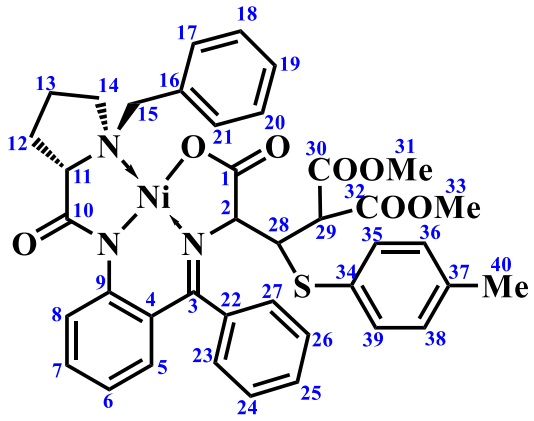
*36. HSQC spectrum of complex **9***



*37. HMBC spectrum of complex **9***



38. *Atom numeration and signal assignment in the NMR spectra of complex (R,S)-**10***



(*R*,*S*)-**10**

^{1}H NMR ($CDCl_3$ δ, ppm): 8.37 (dd, ^{3}J = 8.8 Hz, ^{4}J = 1.1 Hz, 1H (H-8)), 8.10-8.05 (m, 2H (H-17,21)), 7.53-7.43 (m, 4H (H-25,26,35,39)), 7.36-7.30 (m, 2H (H-18,20)), 7.25-7.11 (m, 4H (H-7,19,24,27), 6.84-6.80 (m, 2H (H-36,38)), 6.57 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 7.0 Hz, ^{4}J = 1.1 Hz, 1H (H-6)), 6.41 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.6 Hz, 1H (H-5)), 5.66-5.62 (m, 1H (H-23)), 4.61 (d, ^{3}J = 5.6 Hz, 1H (H-2)), 4.48 (d, ^{2}J = 12.6 Hz, 1H (H-15)), 4.06 (d, ^{3}J = 11.4 Hz, 1H (H-29)), 3.89-3.78 (m, 1H (H-13)), 3.74 (s, 3H (H-31)), 3.71-3.64 (m, 1H (H-14)), 3.61 (d, ^{2}J = 12.6 Hz, 1H (H-15)), 3.52-3.48 (m, 4H (H-11,33)), 3.41 (dd, ^{3}J = 11.4 Hz, ^{3}J = 5.6 Hz, 1H (H-28)), 2.88-2.78 (m, 1H (H-12)), 2.54-2.41 (m, 1H (H-12)), 2.12 (s, 3H (H-40)), 2.15-2.01 (m, 2H (H-13,14)).

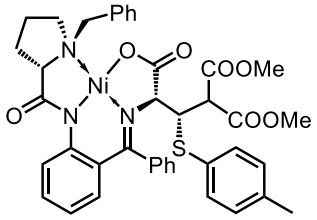
^{13}C NMR ($CDCl_3$ δ, ppm): 180.58 (C-10), 176.57 (C-1), 172.40 (C-3), 168.56 (C-30), 166.63 (C-32), 143.01 (C-9), 138.83 (C-37), 134.28 (C-35,39), 133.71 (C-22), 133.63 (C-5), 133.53 (C-16), 132.44 (C-7), 131.76 (C-17,21), 131.20 (C-34), 129.91 (C-36,38), 129.81 (C-25), 129.07 (C-26), 128.90 (C-19), 128.84 (C-18,20), 128.66 (C-24), 127.37 (C-23), 127.06 (C-27), 125.88 (C-4), 123.58 (C-8), 120.43 (C-6), 70.67 (C-11), 70.06 (C-2), 63.55 (C-15), 57.40 (C-14), 55.26 (C-29), 52.83 (C-31), 52.71 (C-33), 52.24 (C-28), 30.75 (C-12), 23.44 (C-13), 21.03 (C-40).

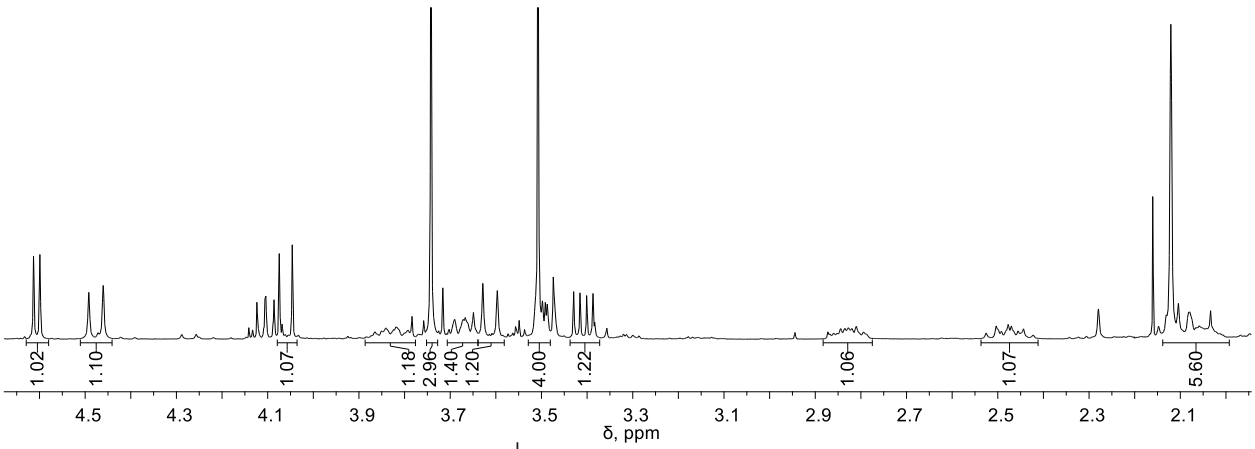
(*R*,*R*)-**10**

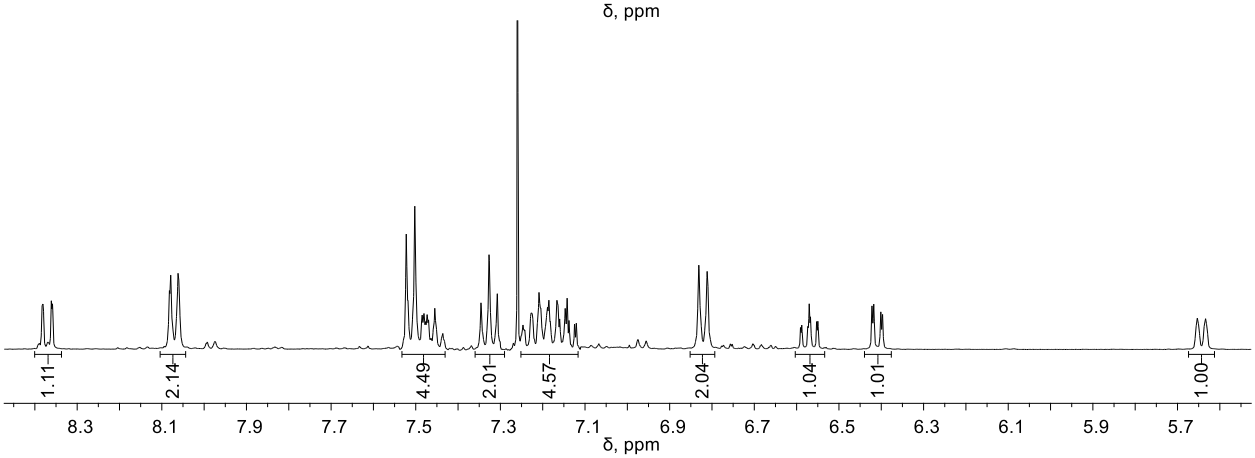
^{1}H NMR ($CDCl_3$ δ, ppm): 8.38 (dd, ^{3}J = 8.8 Hz, ^{4}J = 1.1 Hz, 1H (H-8)), 8.01-7.96 (m, 2H (H-17,21)), 7.54-7.43 (m, 4H (H-24,25,26,27)), 7.28-7.17 (m, 5H (H-18,20,23,35,39)), 7.14 (ddd, ^{3}J = 8.8 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.7 Hz, 1H (H-7)), 7.10-7.05 (m, 1H (H-19)), 6.99-6.95 (m, 2H (H-36,38)), 6.77 (dd, ^{3}J = 8.3 Hz, ^{4}J = 1.7 Hz, 1H (H-5)), 6.69 (ddd, ^{3}J = 8.3 Hz, ^{3}J = 6.9 Hz, ^{4}J = 1.1 Hz, 1H (H-6)), 4.78 (dd, ^{3}J = 9.7 Hz, ^{3}J = 4.4 Hz, 1H (H-28)), 4.47 (d, ^{3}J = 4.4 Hz, 1H (H-29)), 4.28 (d, ^{2}J = 12.6 Hz, 1H (H-15)), 4.13 (d, ^{3}J = 9.7 Hz, 1H (H-2)), 3.72 (s, 3H (H-31)), 3.78 (s, 3H (H-33)), 3.38 (d, ^{2}J = 12.6 Hz, 1H (H-15)), 3.35-3.28 (m, 2H (H-11,14)), 3.23-3.07 (m, 1H (H-13)), 2.28 (s, 3H (H-40)), 2.26-2.16 (m, 1H (H-12)), 2.15-2.06 (m, 1H (H-12)), 2.01-1.90 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ, ppm): 179.65 (C-10), 176.80 (C-1), 173.75 (C-3), 168.48 (C-30), 167.29 (C-32), 143.28 (C-9), 138.58 (C-37), 134.61 (C-5), 134.41 (C-22), 133.63 (C-35,39), 133.55 (C-16), 133.07 (C-7), 132.43 (C-34), 131.41 (C-17,21), 130.17 (C-36,38), 128.91 (C-18,20), 128.78 (C-19), 131.78, 129.67,128.69, 128.56, 127.87 (C-23,24,25,26,27), 126.06 (C-4), 122.95 (C-8), 120.57 (C-6), 73.12 (C-2), 70.43 (C-11), 63.19 (C-15), 57.92 (C-28), 57.33 (C-14), 54.26 (C-29), 53.07 (C-31), 52.46 (C-33), 29.94 (C-12), 23.77 (C-13), 21.24 (C-40).

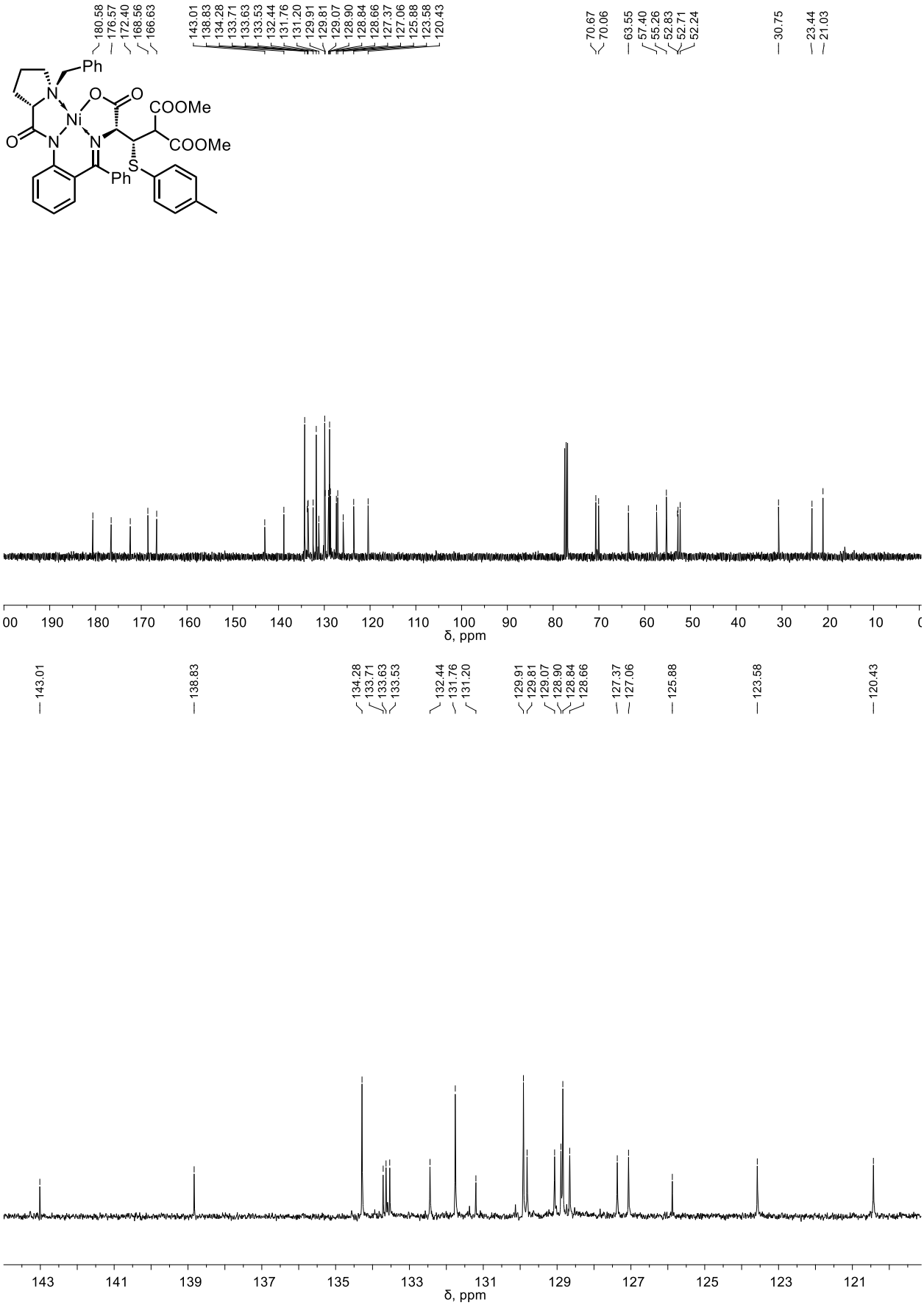
*39. ^{1}H NMR spectrum of complex (R,S)-**10***



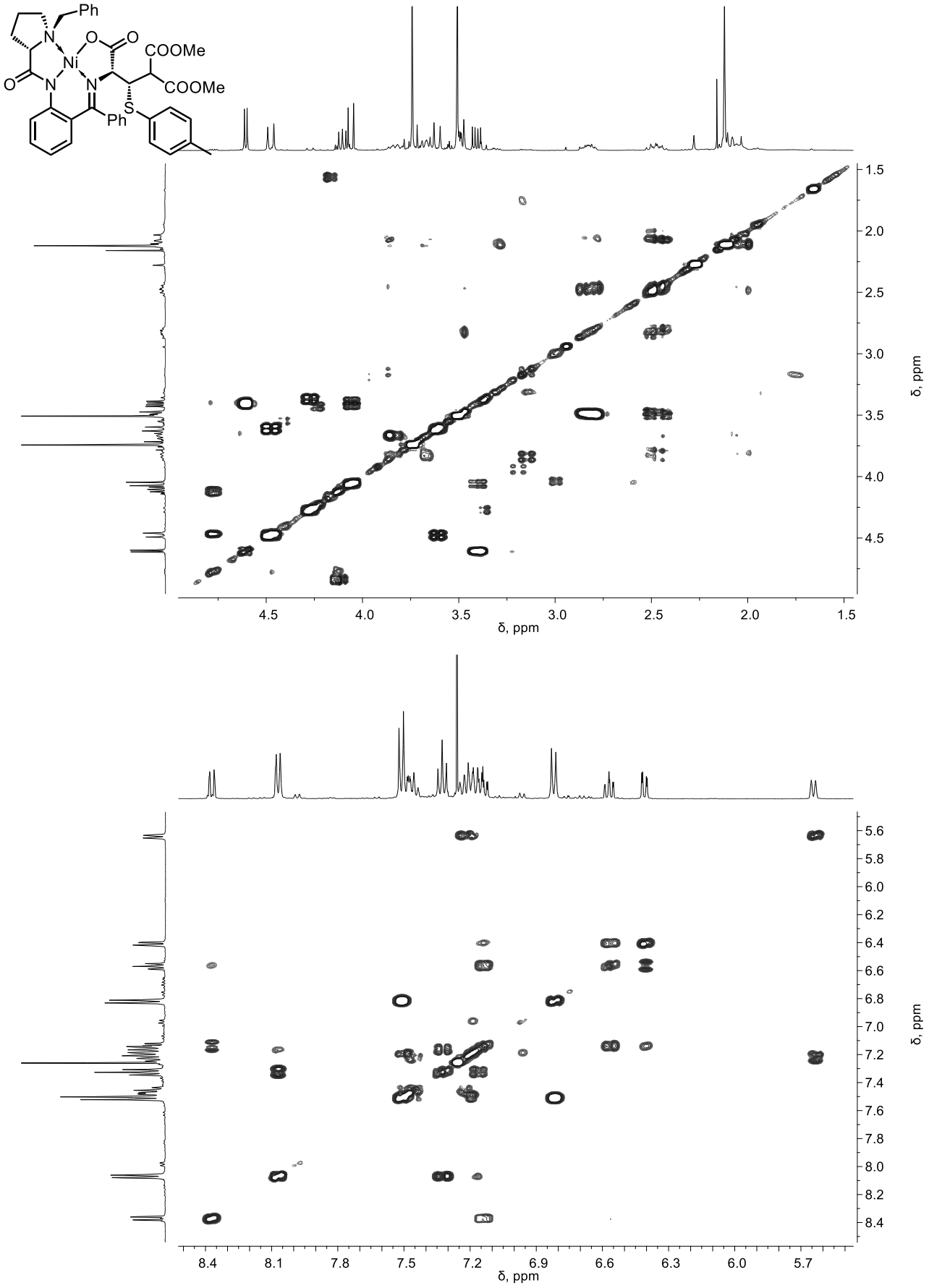




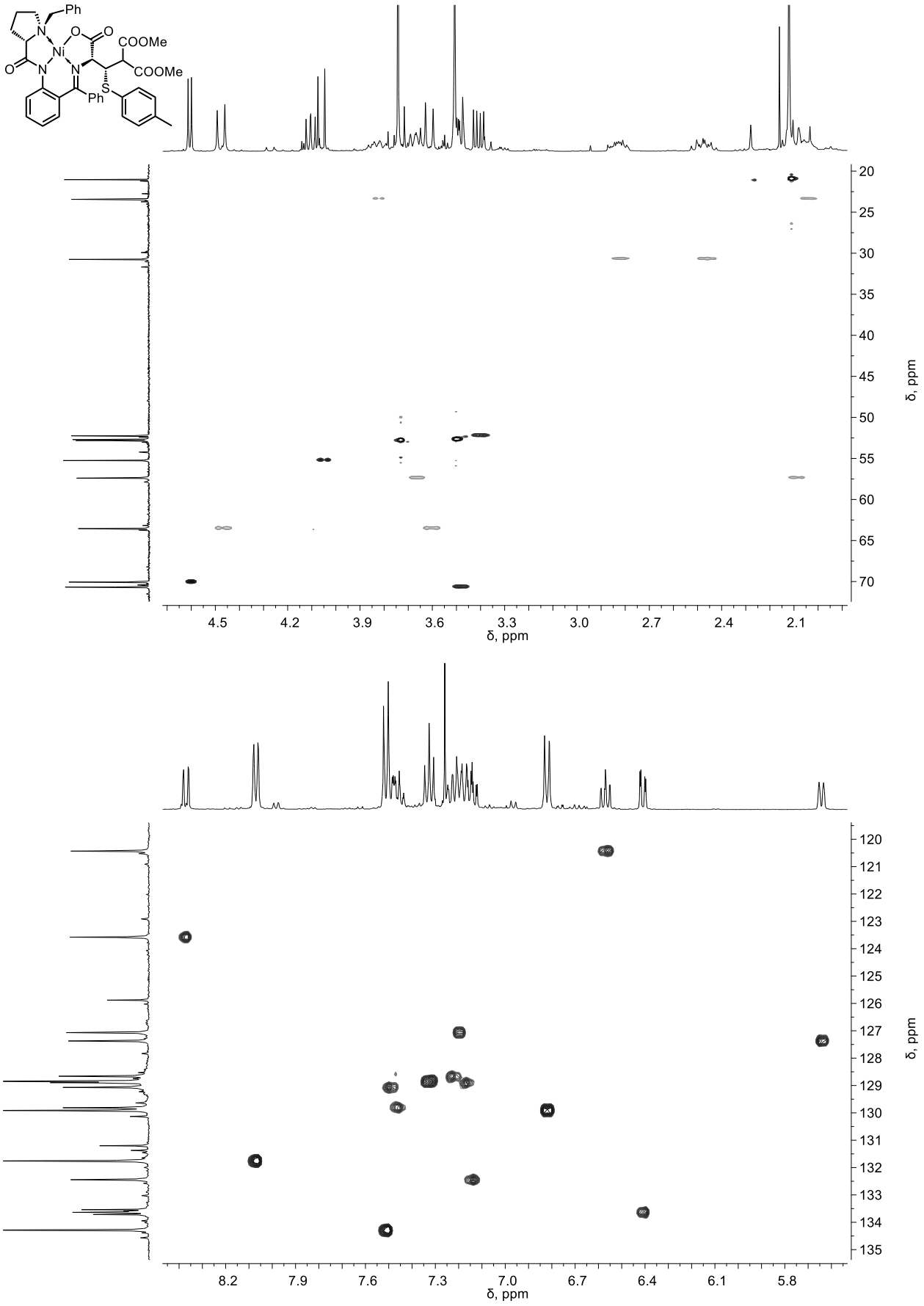
*40. ^{13}C NMR spectrum of complex (R,S)-**10***



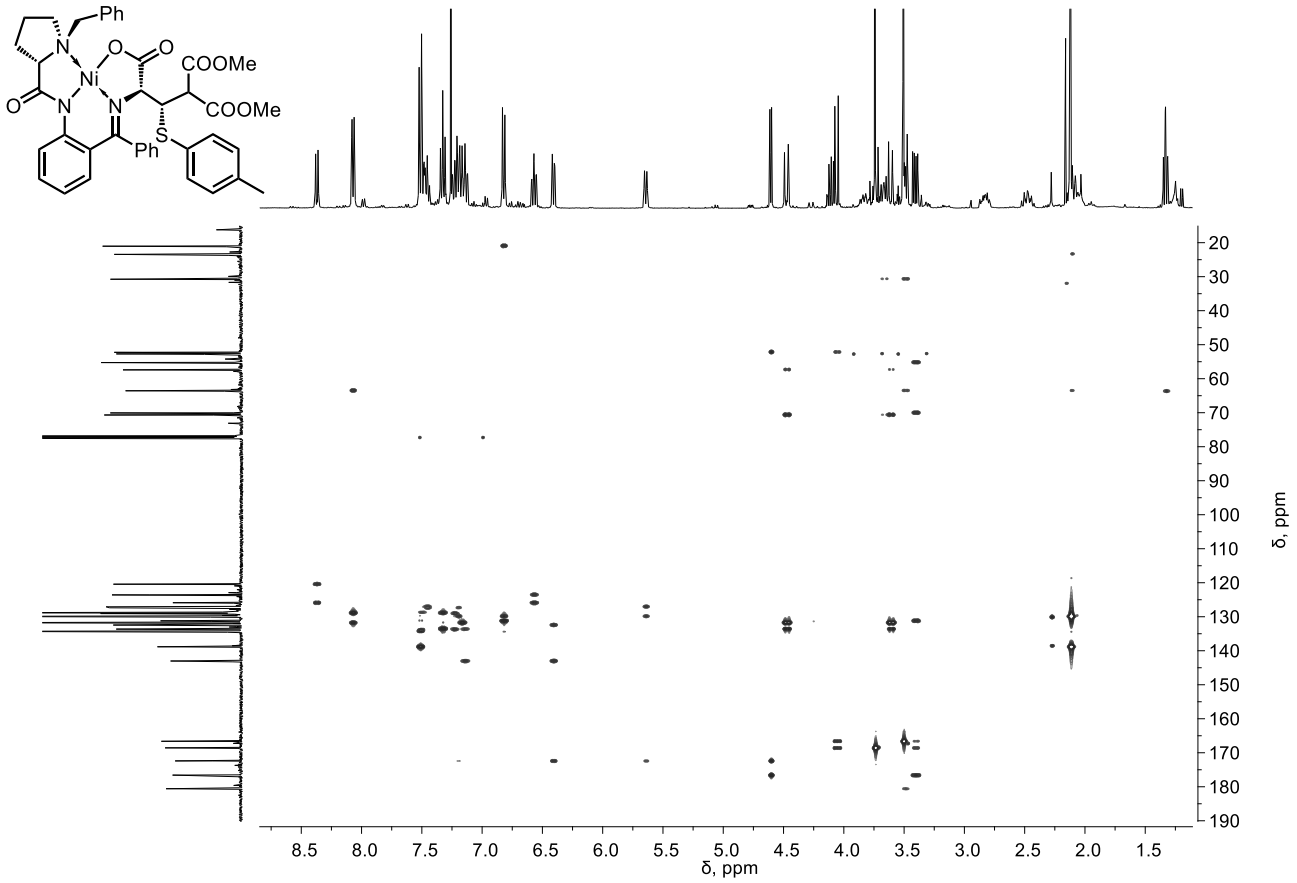
*41. COSY spectrum of complex (R,S)-**10***



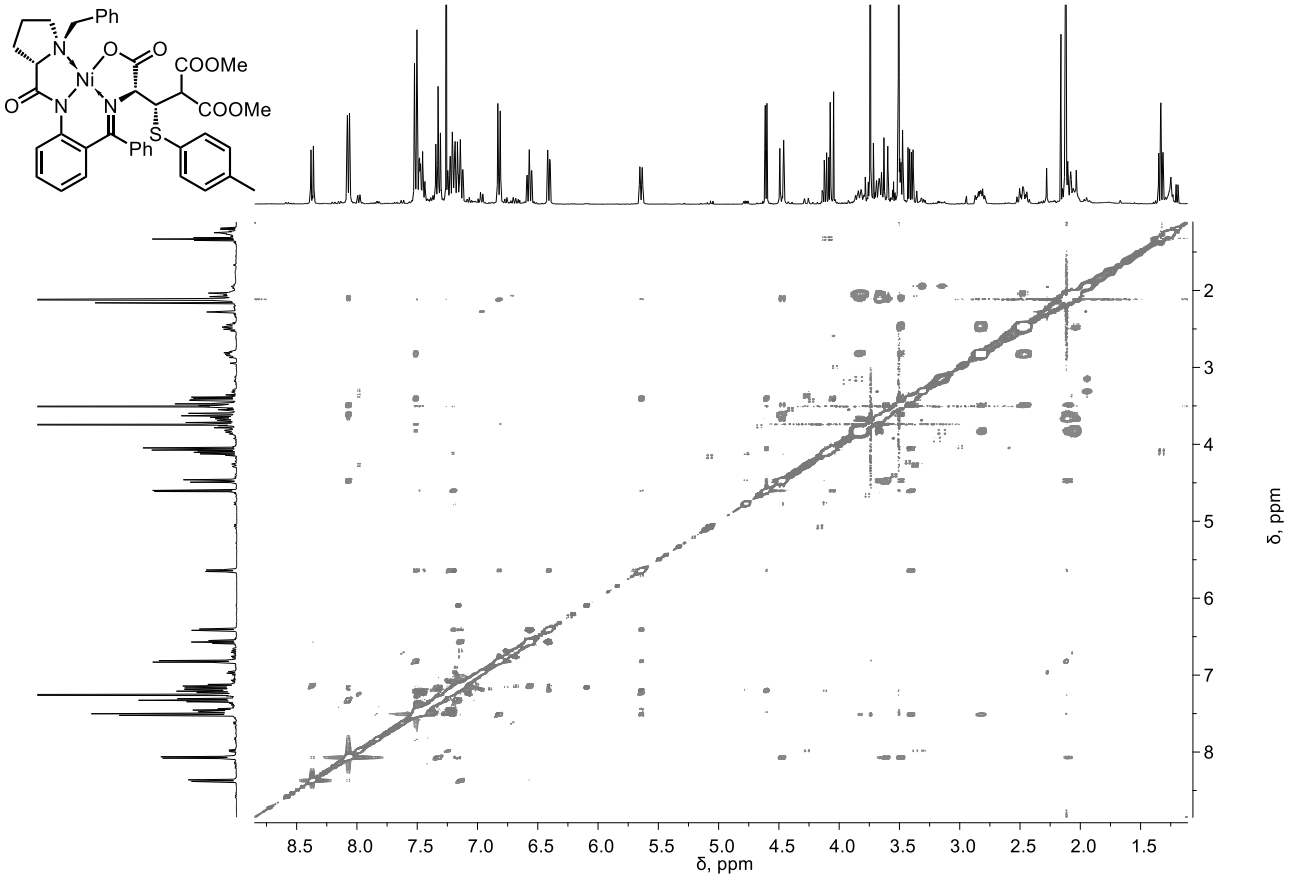
*42. HSQC spectrum of complex (R,S)-**10***

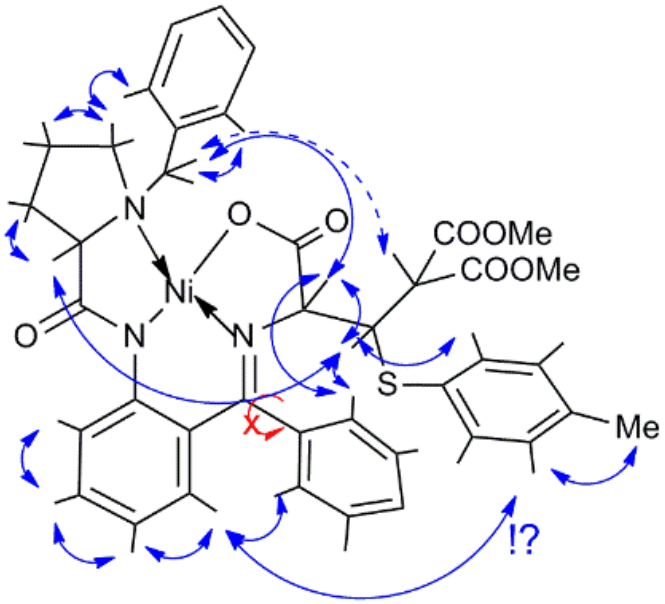


*43. HMBC spectrum of complex (R,S)-**10***

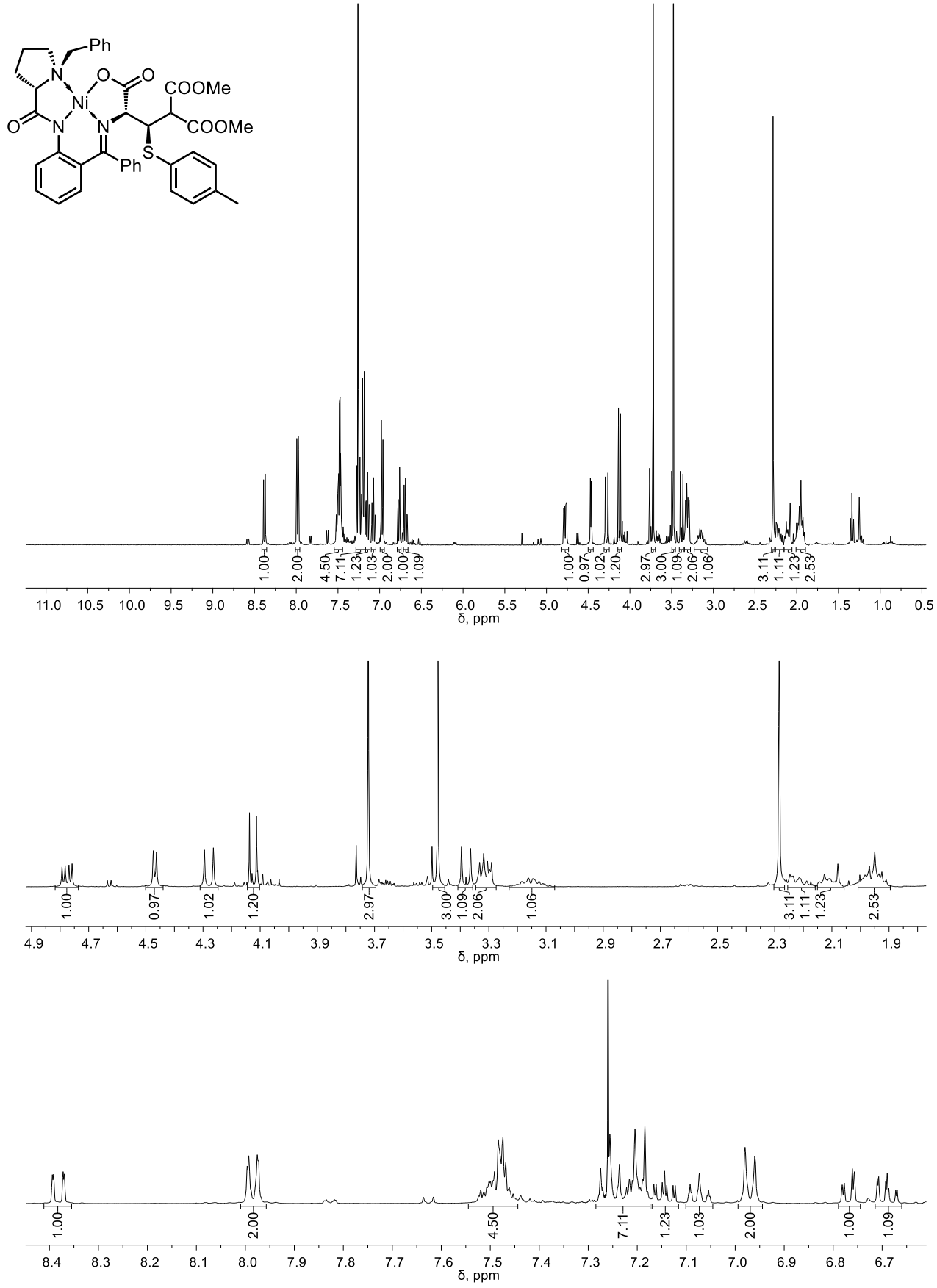


*44. NOESY spectrum of complex (R,S)-**10***

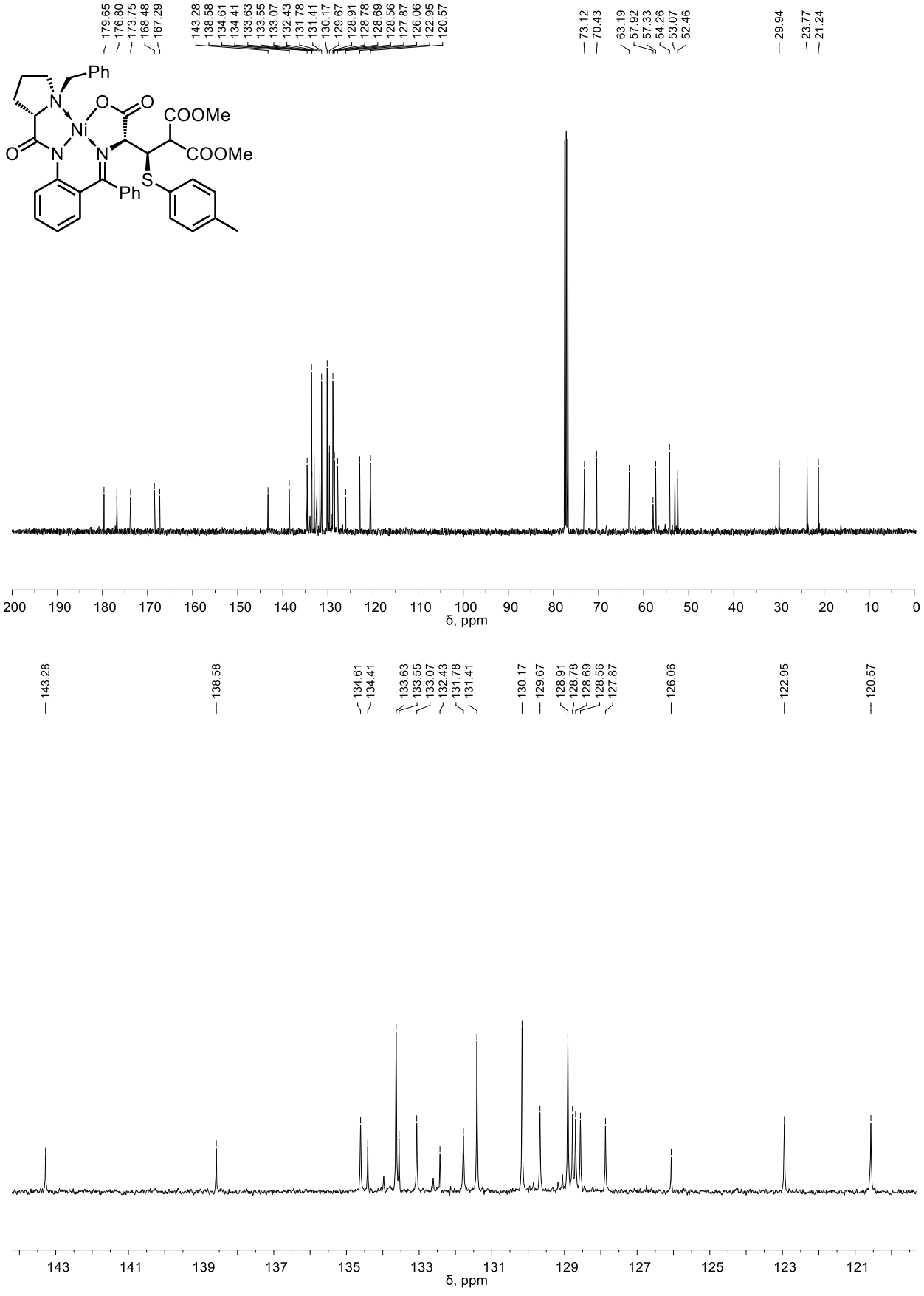




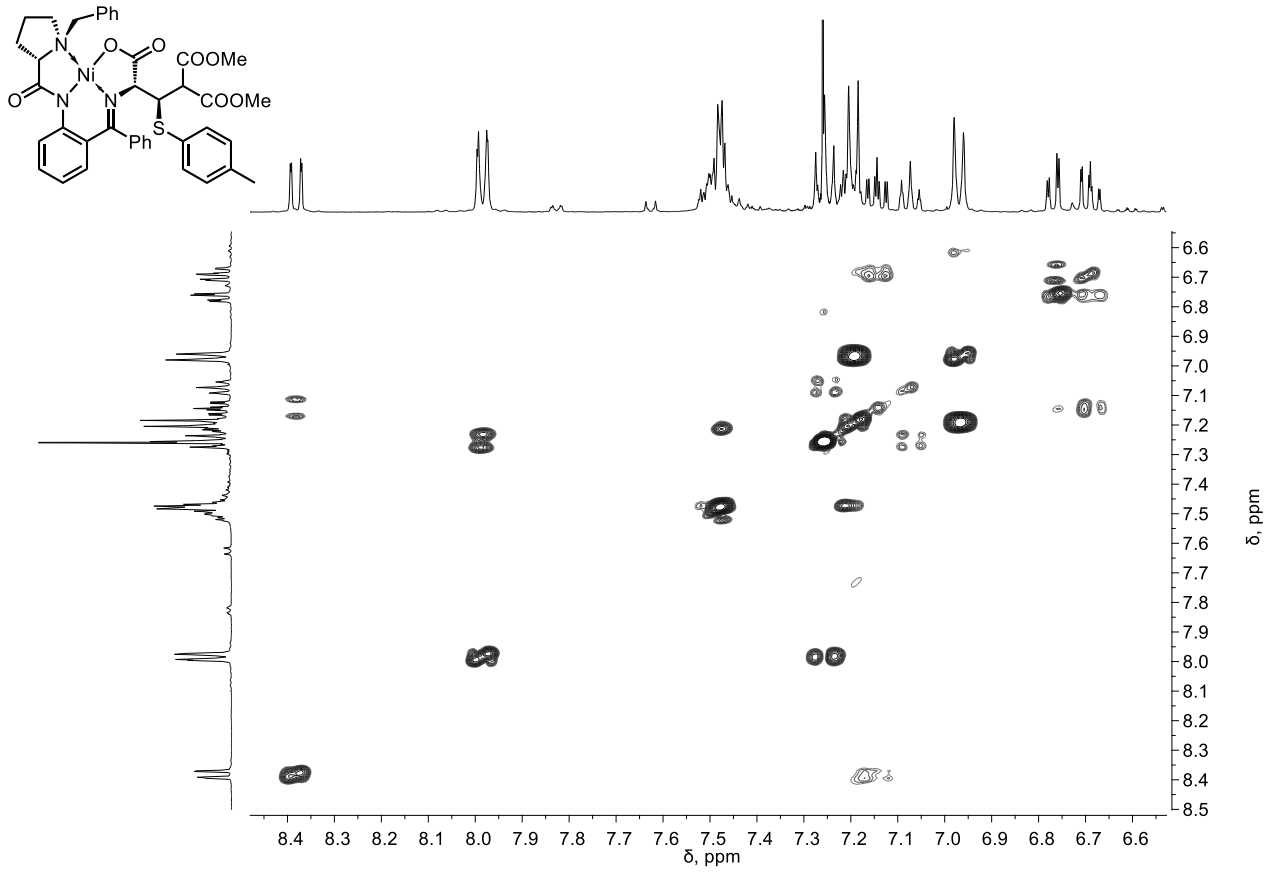
45. *^{1}H NMR spectrum of complex (R,R)-**10***



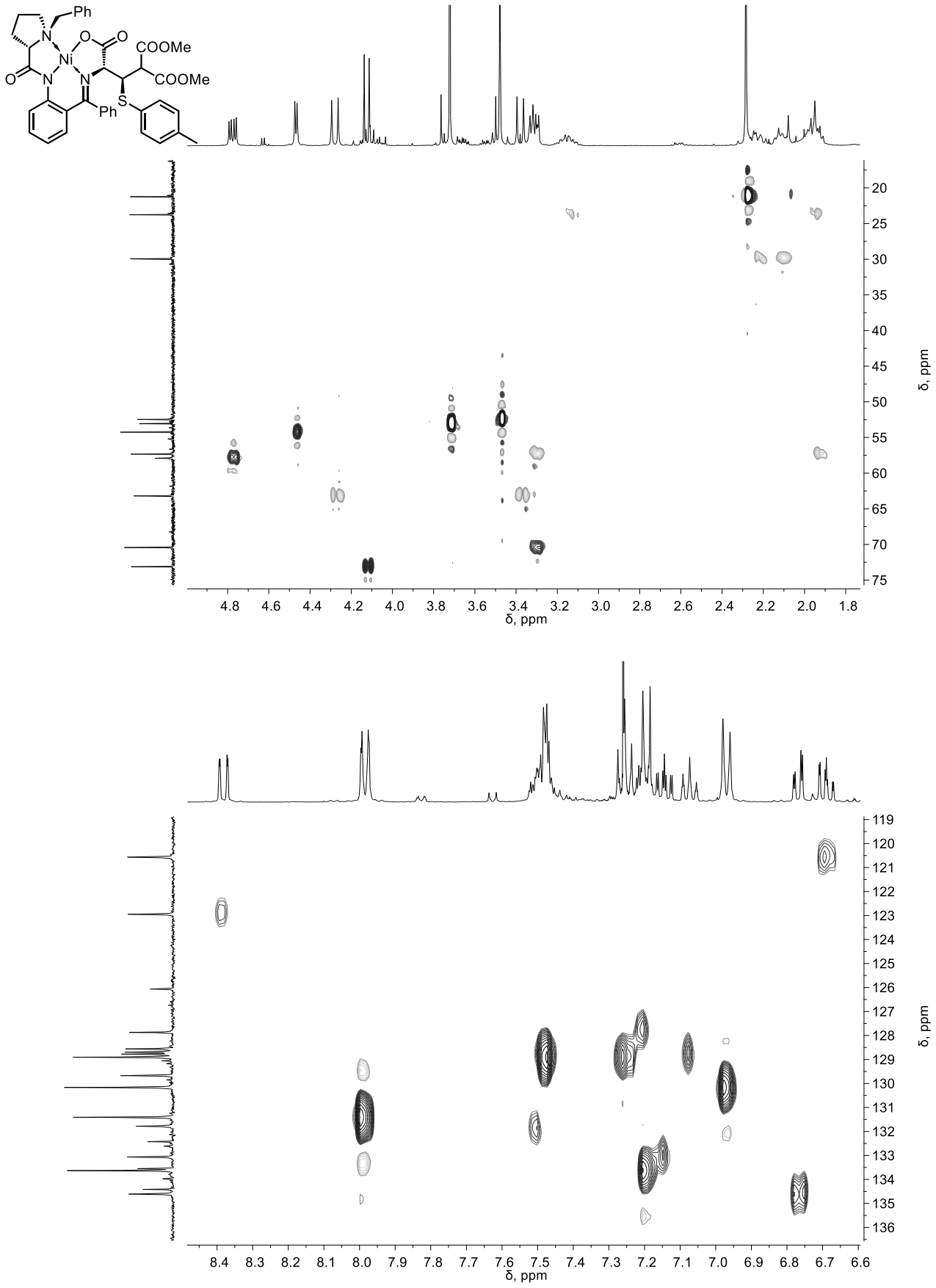
46. *^{13}C NMR spectrum of complex (R,R)-**10***



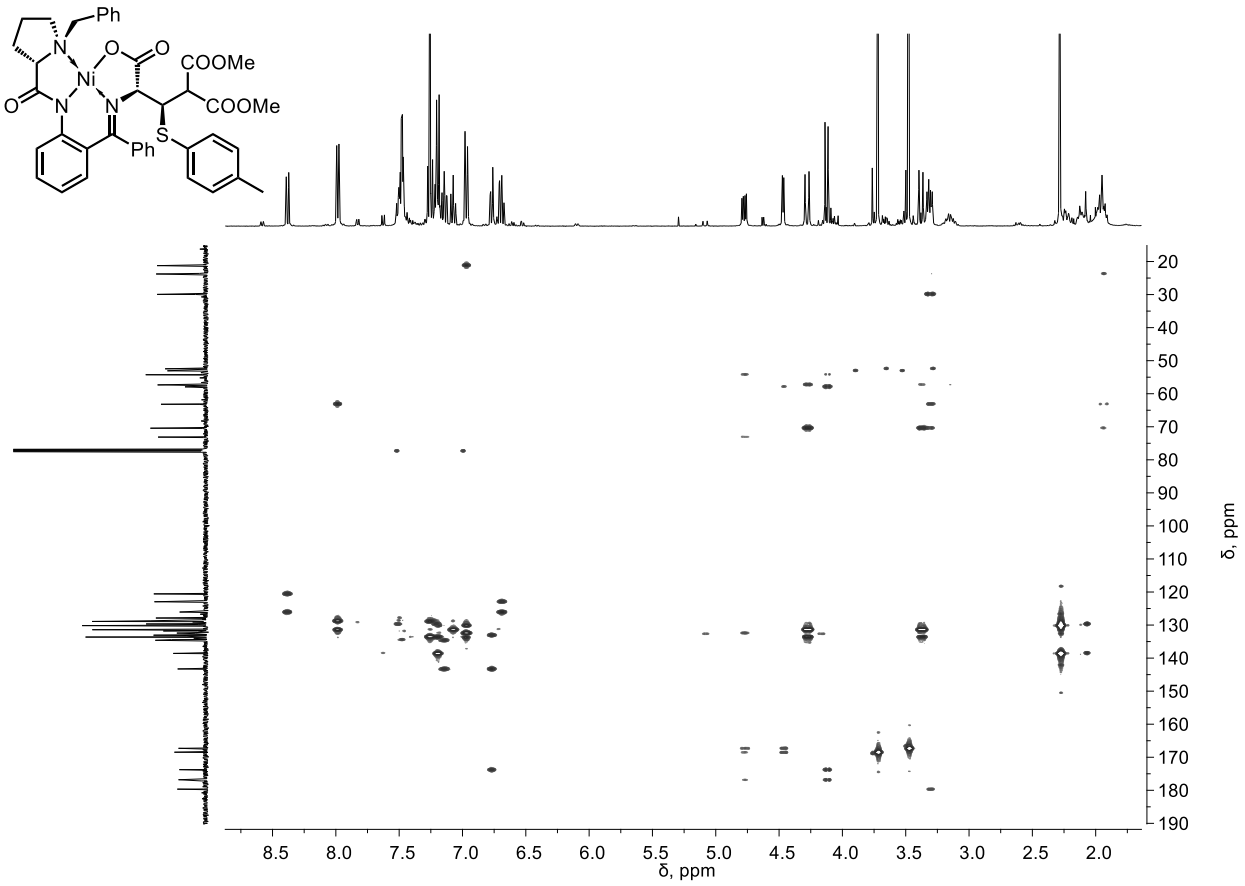
47. *COSY spectrum of complex (R,R)-**10***



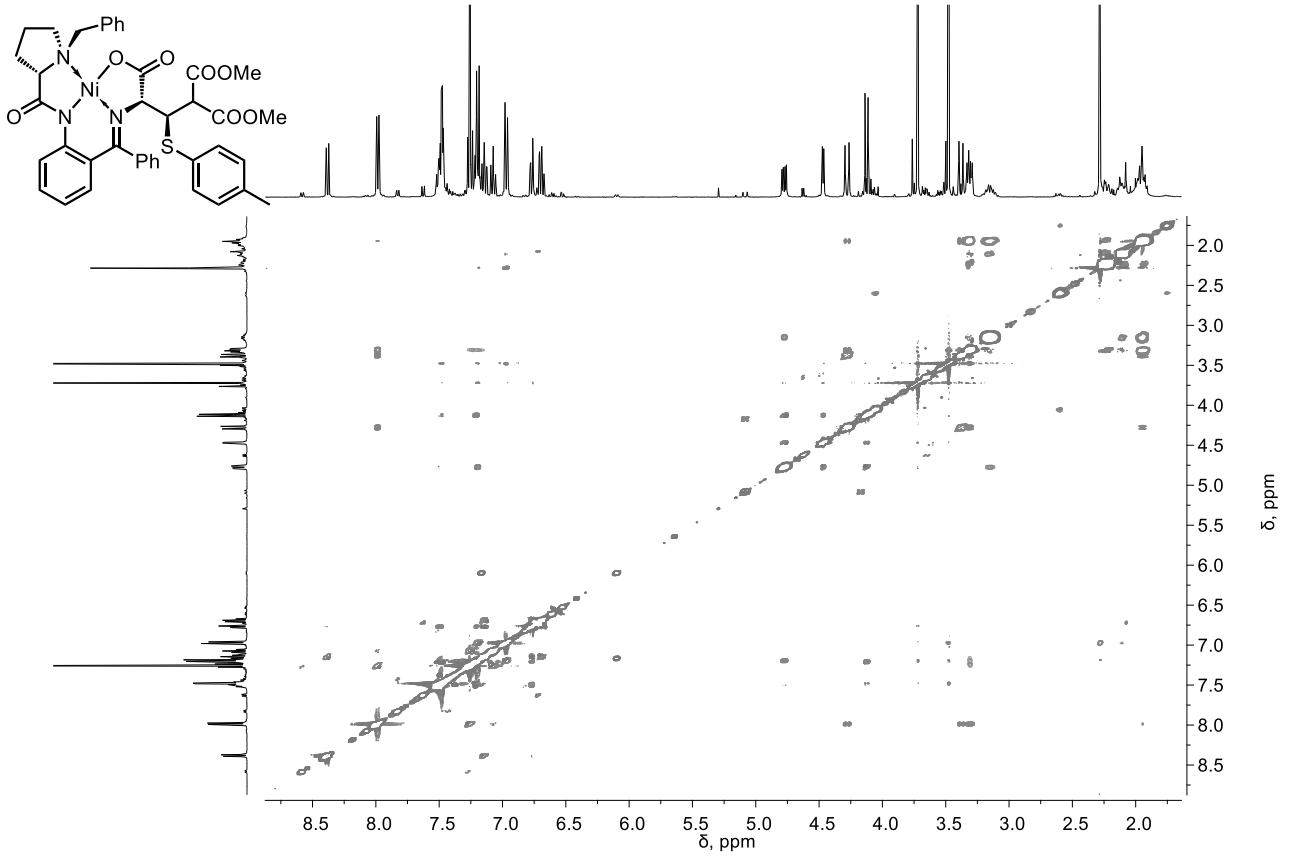
48. *HSQC spectrum of complex (R,R)-**10***

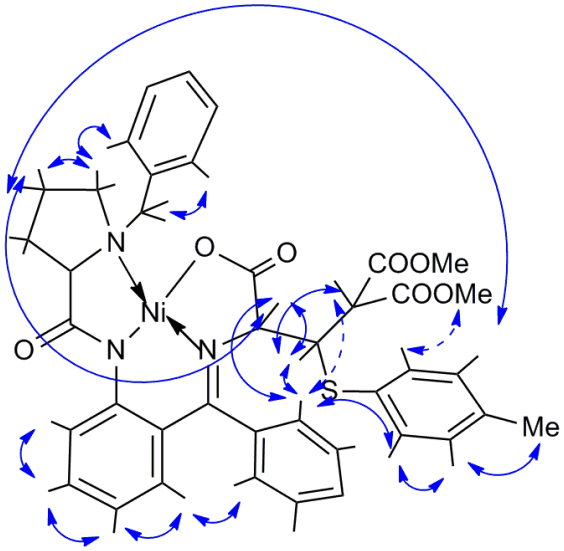


49. *HMBC spectrum of complex (R,R)-**10***

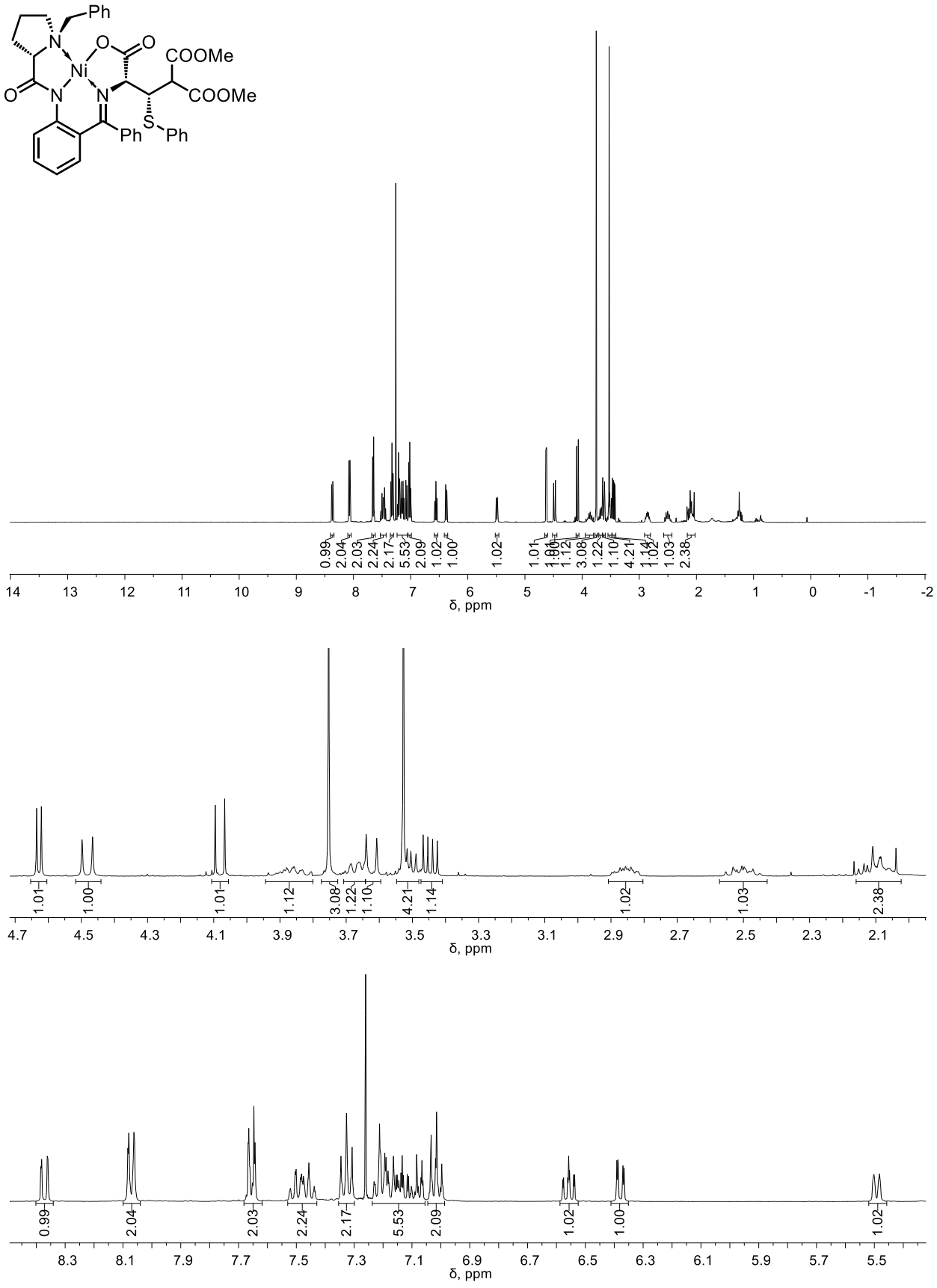


50. *NOESY spectrum of complex (R,R)-**10***

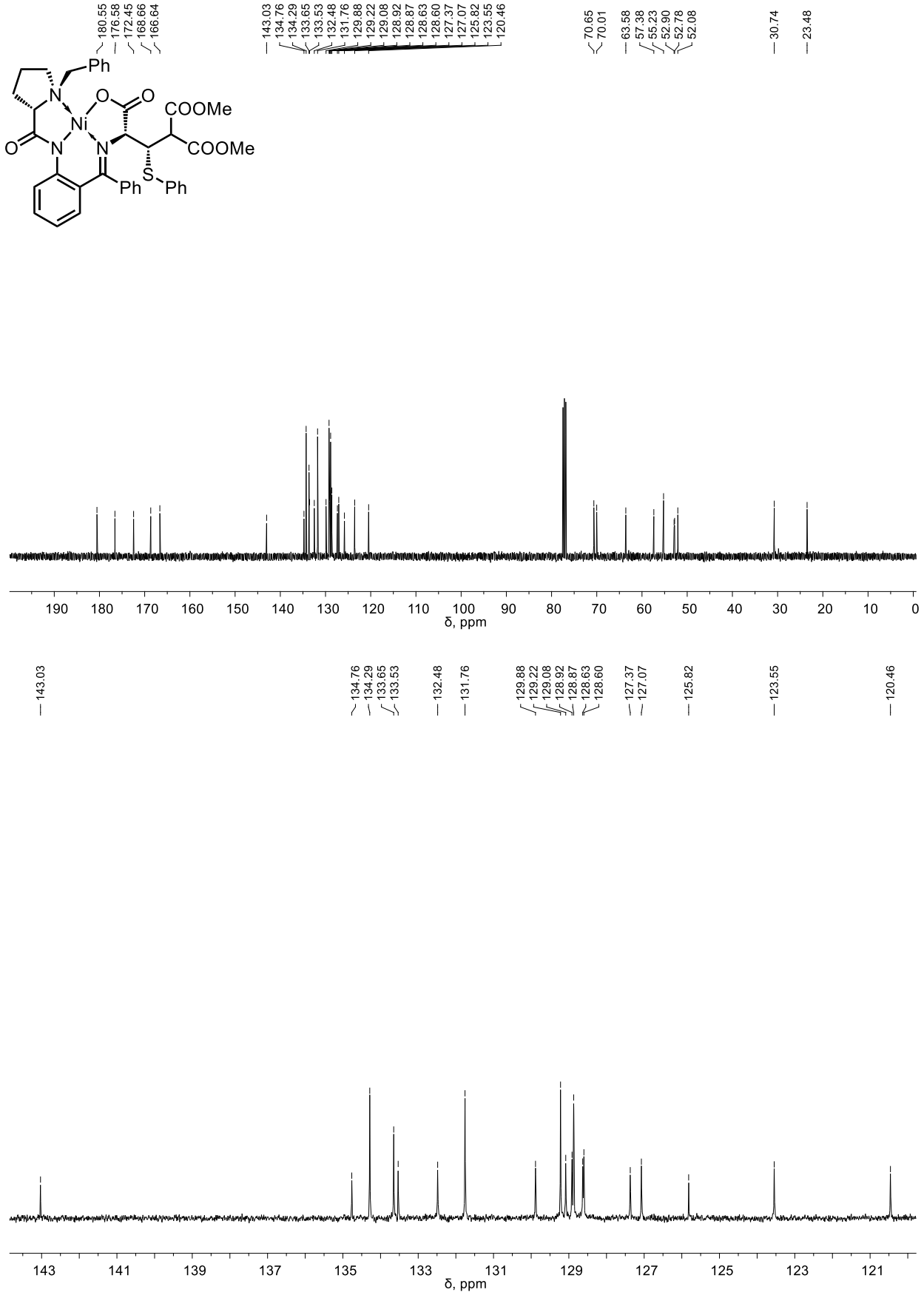




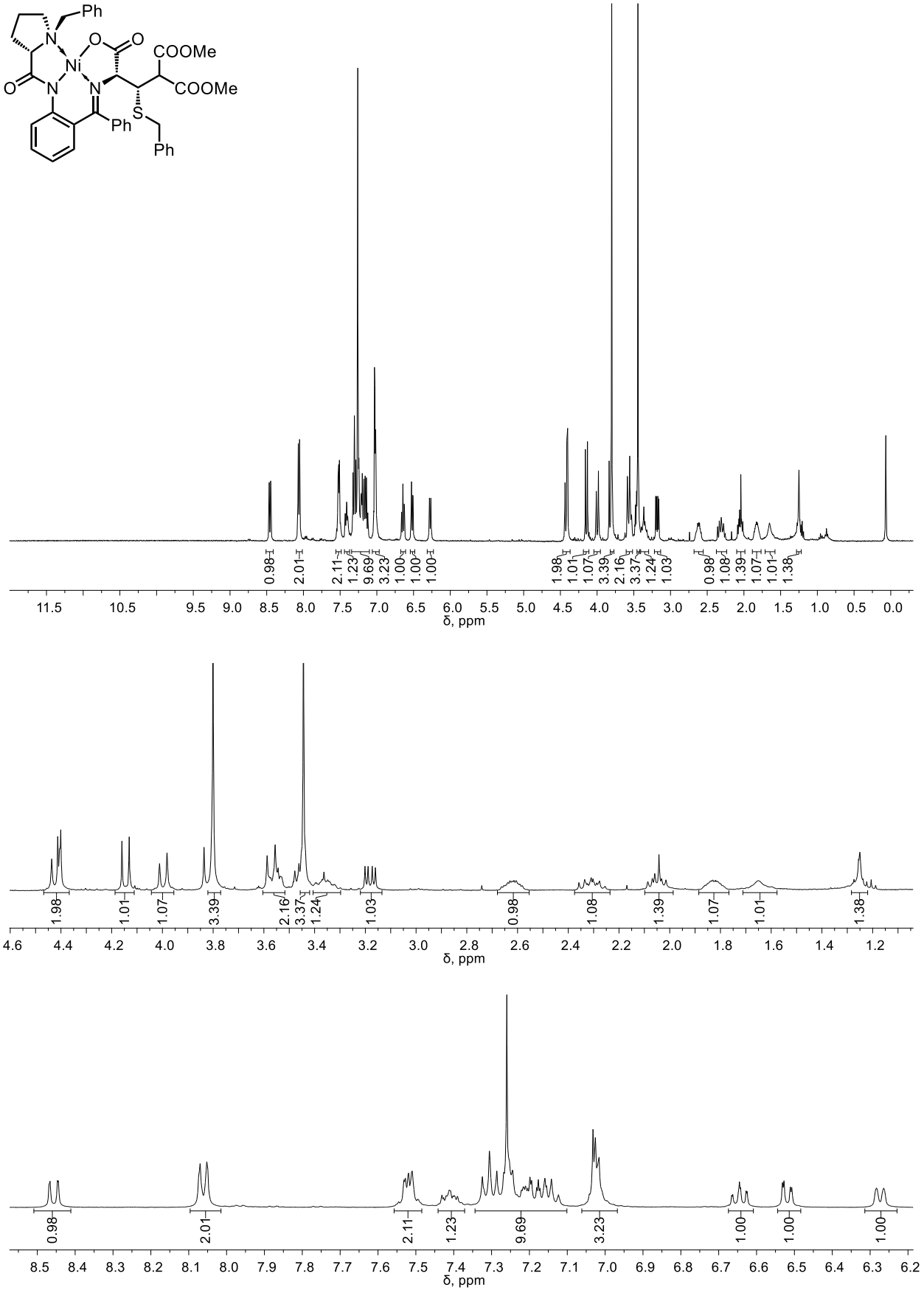
51. *^{1}H NMR spectrum of complex (R,S)-**11***



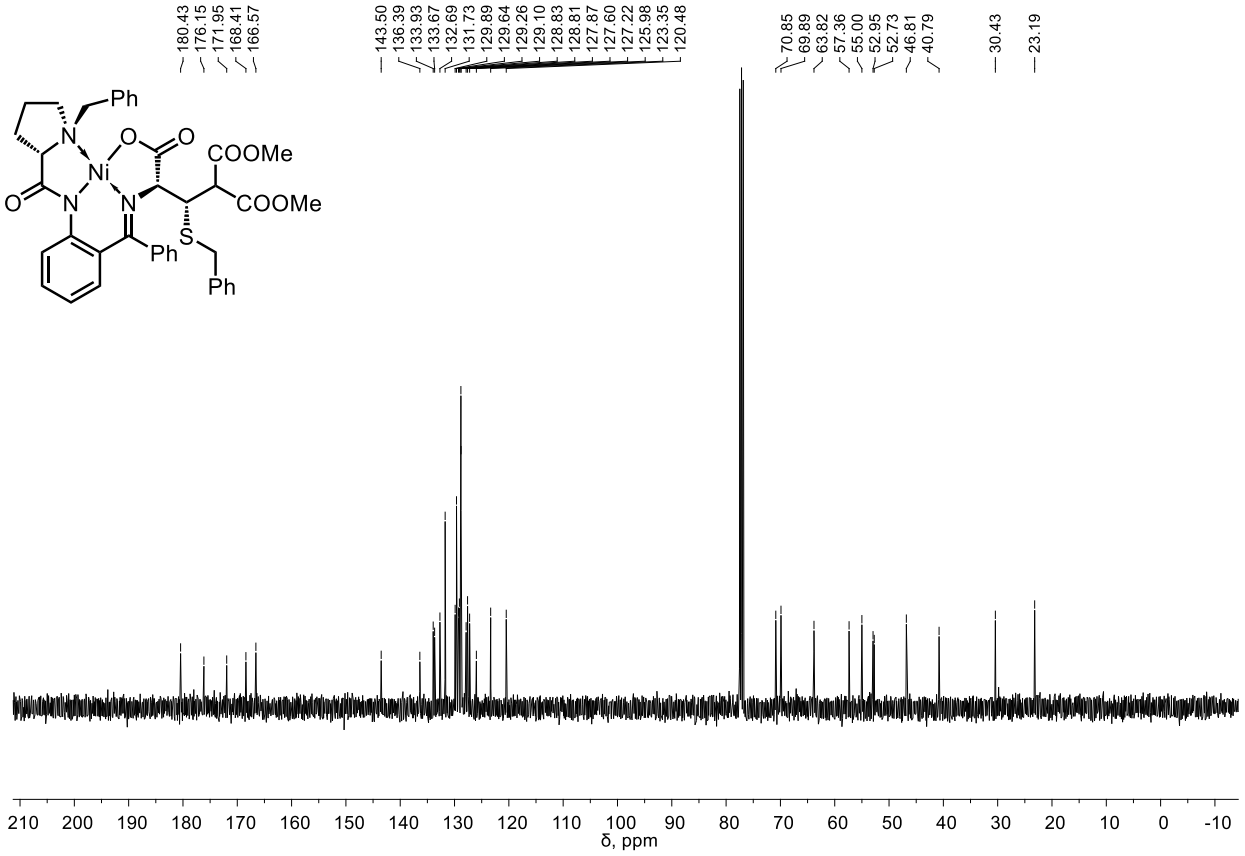
52. *^{13}C NMR spectrum of complex (R,S)-**11***

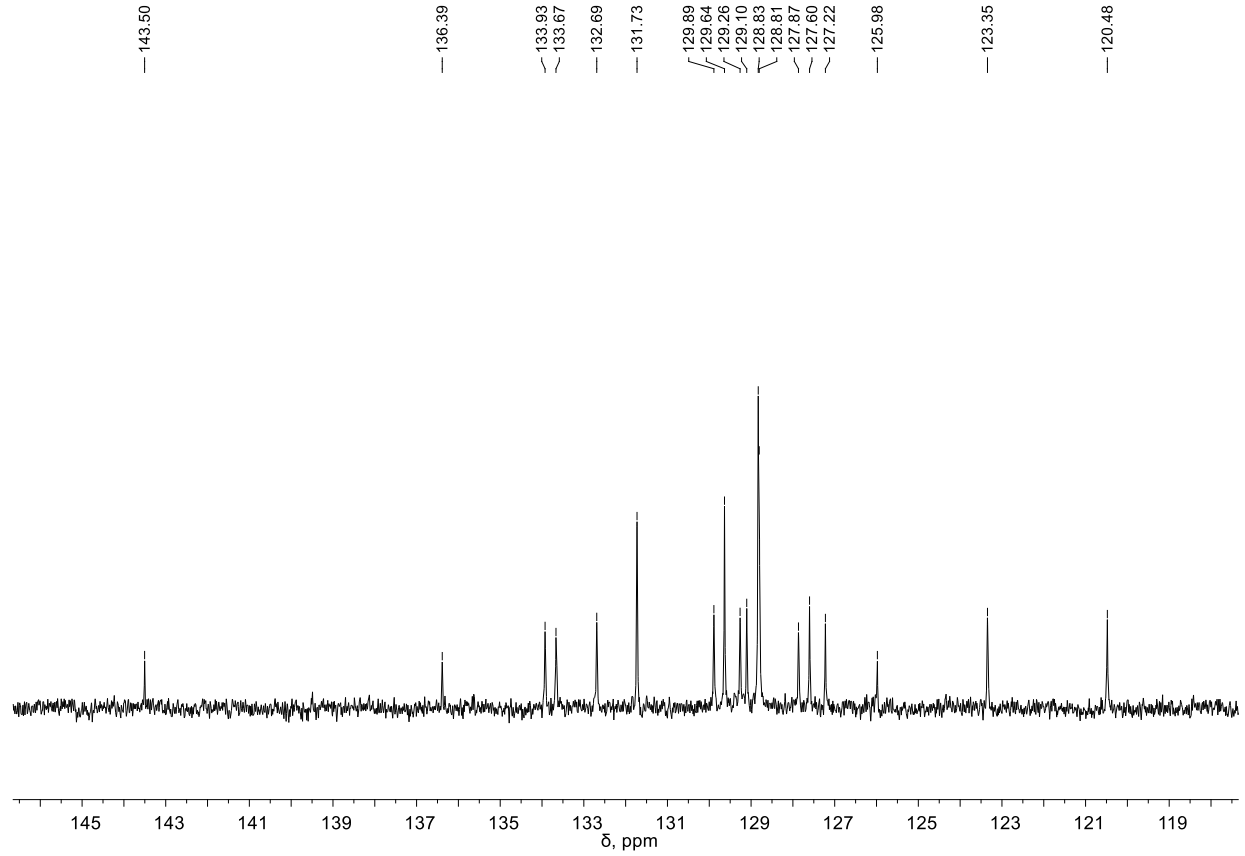


53. *^{1}H NMR spectrum of complex (R,S)-**12***

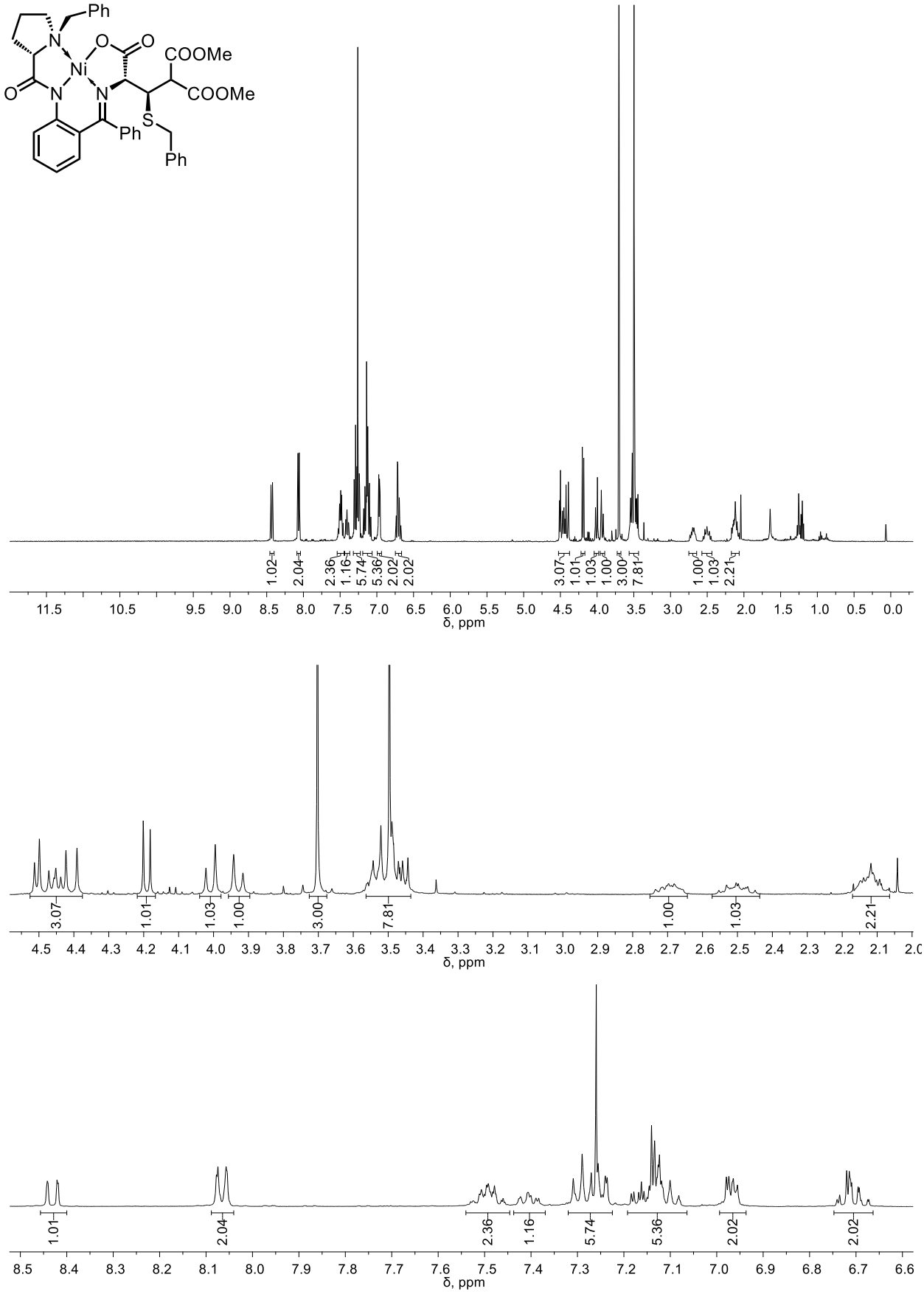


54. *^{13}C NMR spectrum of complex (R,S)-**12***

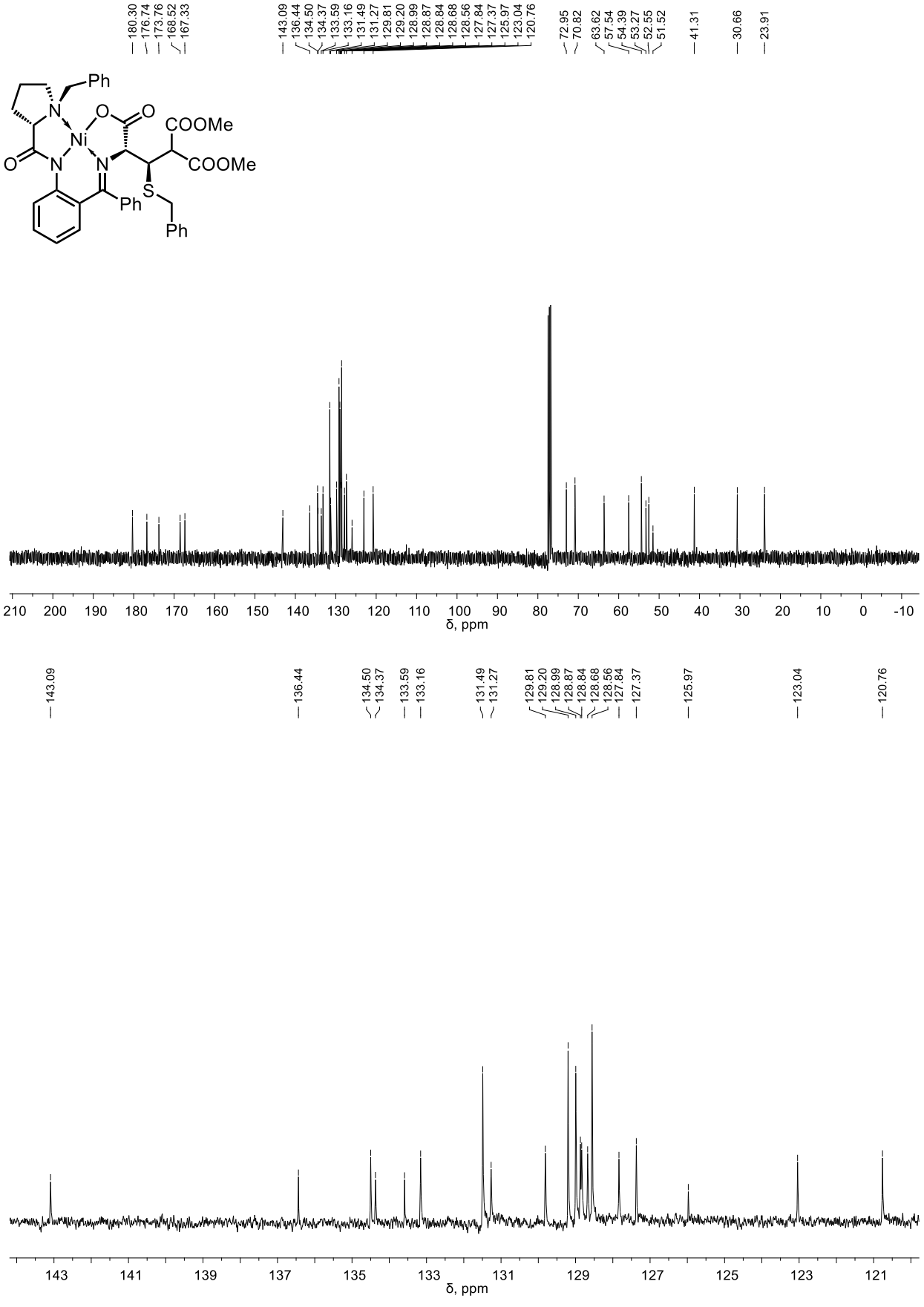




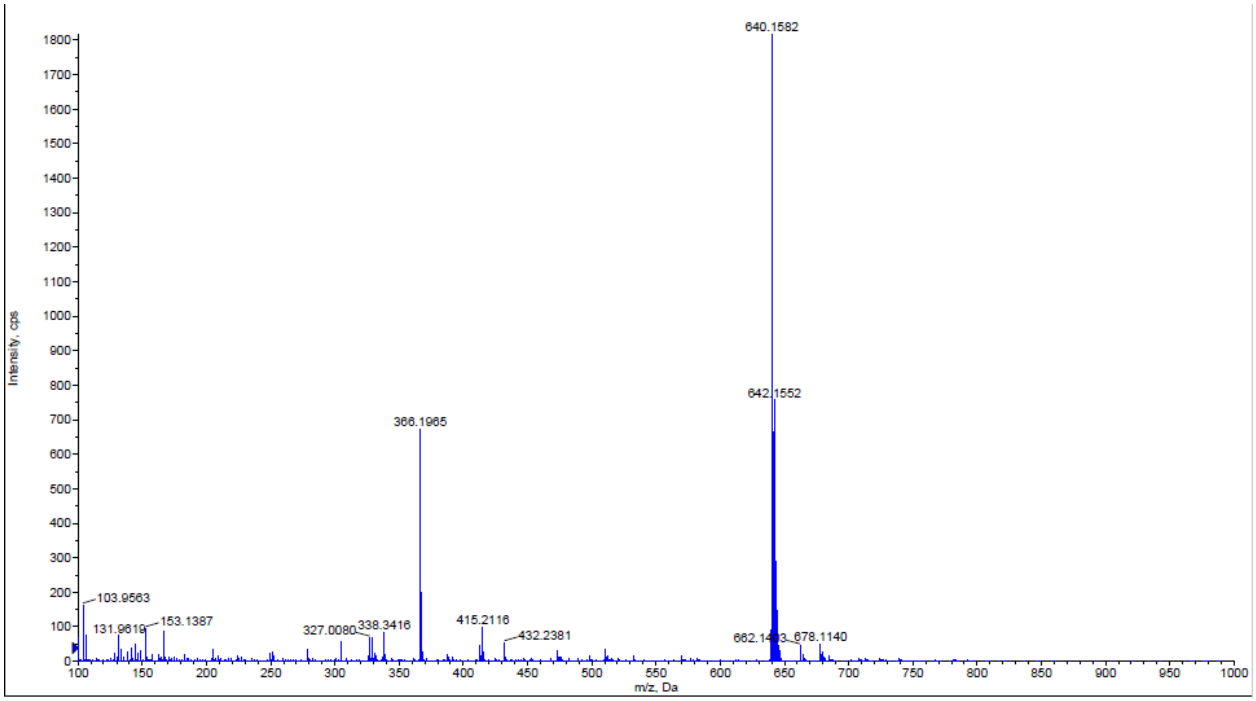
55. *^{1}H NMR spectrum of complex (R,R)-**12***

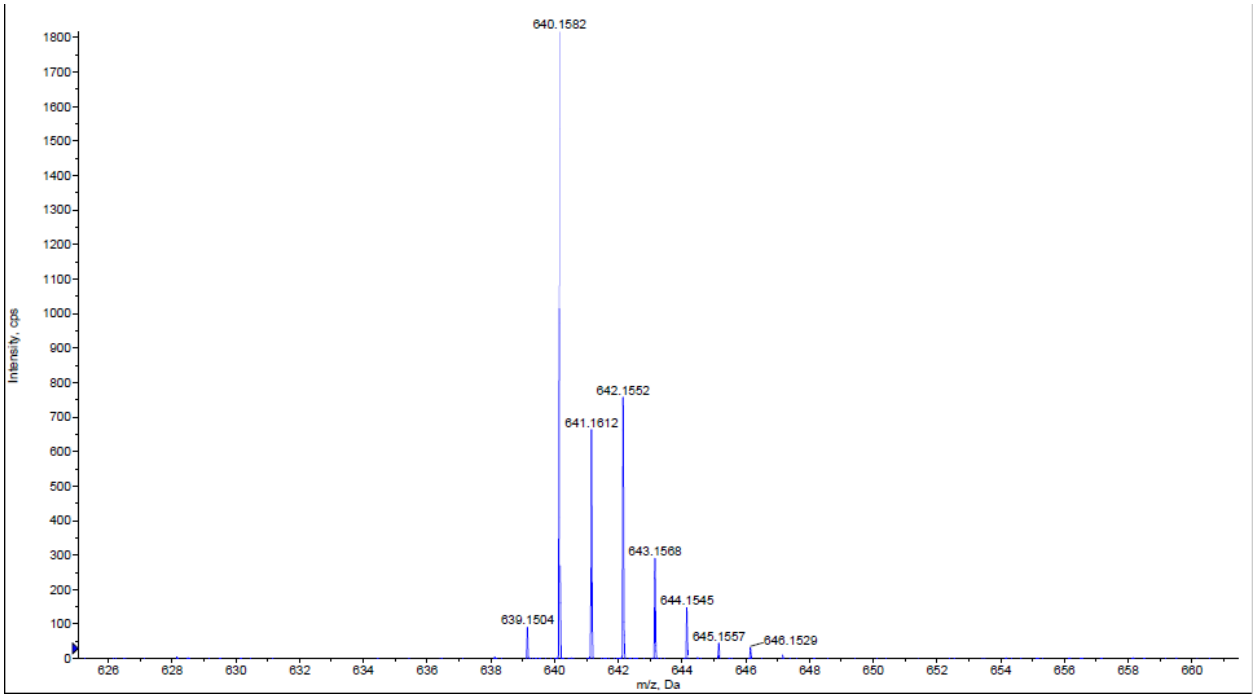


56. *^{13}C NMR spectrum of complex (R,R)-**12***

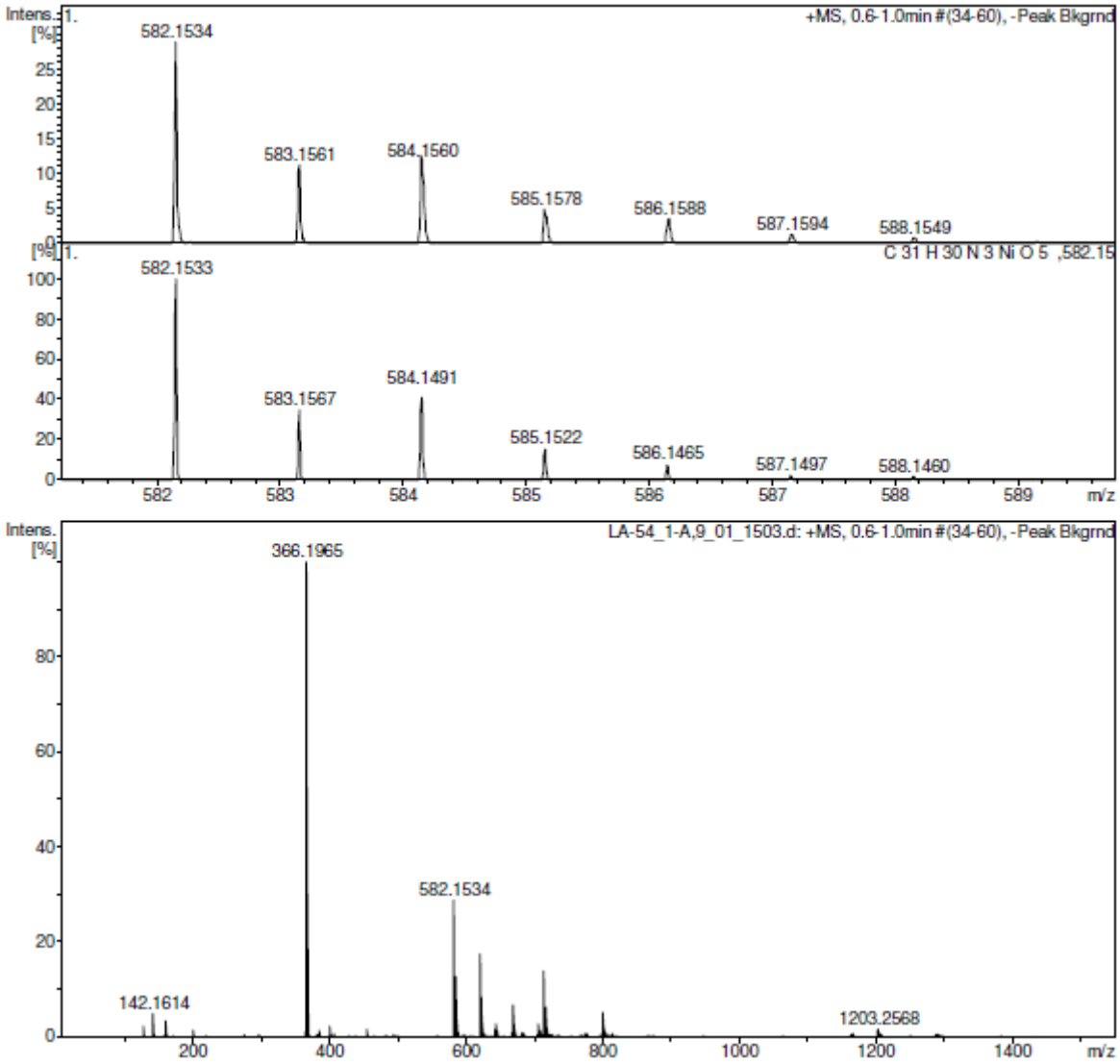


*57. ESI-HRMS data for complex **4***

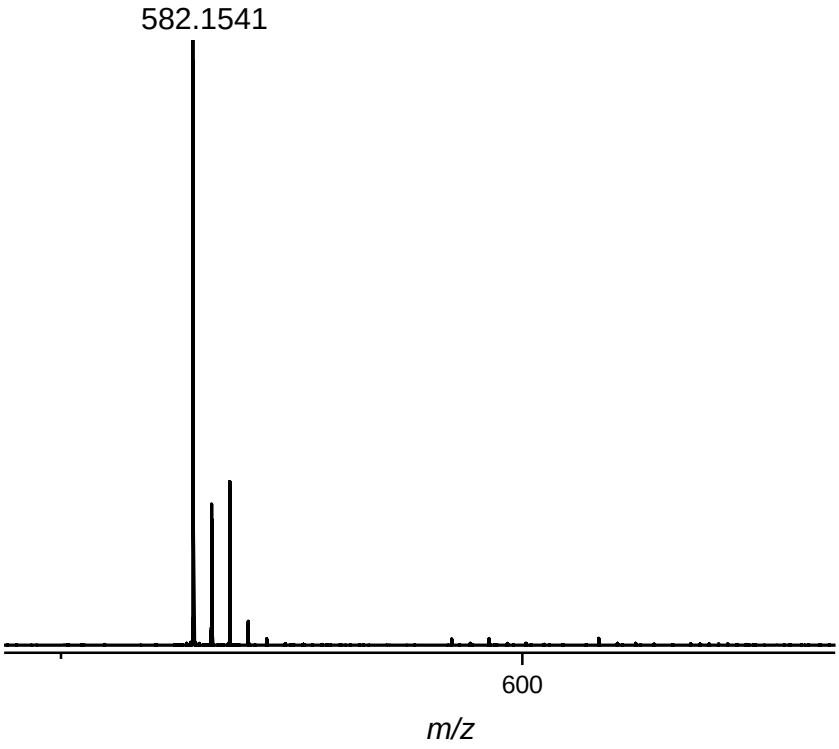




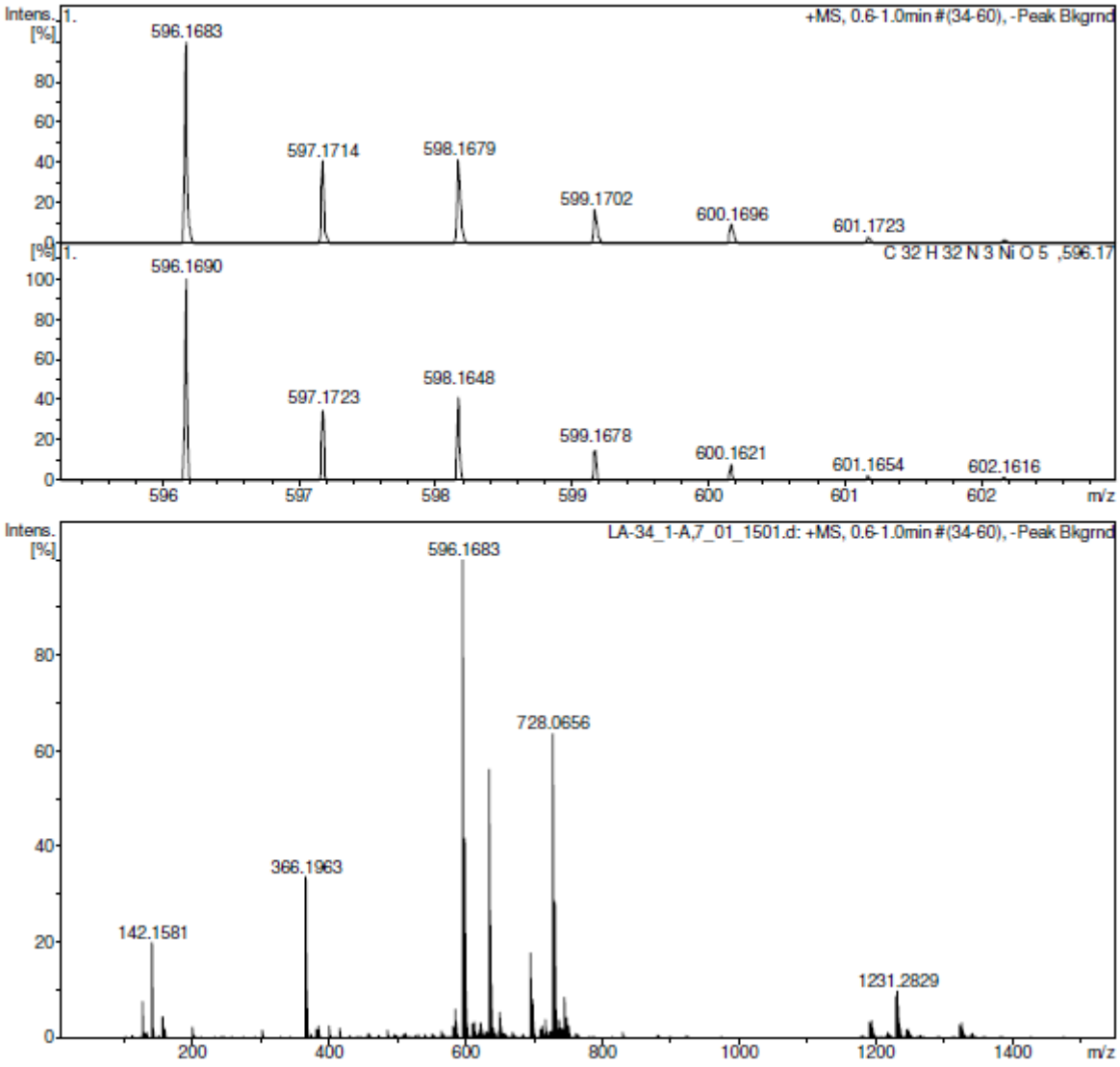
58. ESI-HRMS data for complex ***5****, diastereomer 1*



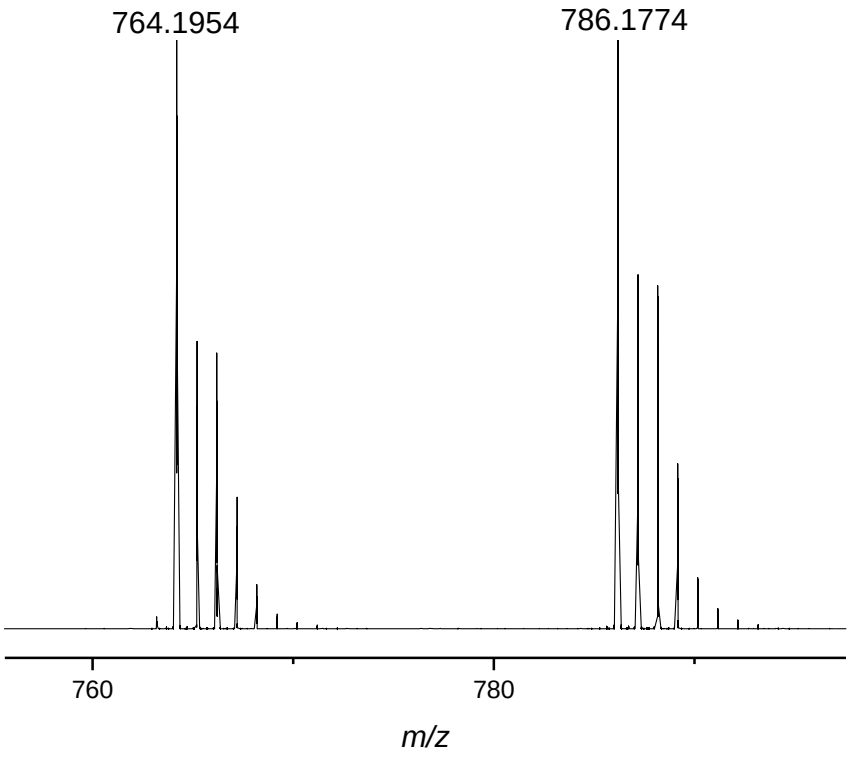
*59. ESI-HRMS data for complex **8***



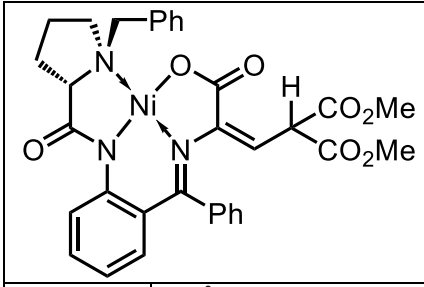
60. ESI-HRMS data for complex ***9***



61. *ESI-HRMS data for complex (R,S)-**10***



62. Results of the quantum chemical calculations



E_e = -3470.401565845330 Hartree

Element	x, Å	y, Å	z, Å
6	1.042189000	-1.402104000	0.697121000
6	1.747990000	-2.196185000	1.618530000
6	1.110668000	-3.053105000	2.484198000
6	-0.276357000	-3.145913000	2.422292000
6	-1.001629000	-2.379957000	1.535671000
6	-0.380249000	-1.460406000	0.667638000
7	-1.105026000	-0.599660000	-0.125584000
6	1.826030000	-0.575329000	-0.210982000
1	2.825036000	-2.121124000	1.664279000
1	1.678940000	-3.640354000	3.192311000
1	-0.805297000	-3.817417000	3.087199000
1	-2.073965000	-2.474359000	1.537251000
6	5.562468000	-0.173128000	-0.052589000
6	5.997593000	-1.371365000	-0.603399000
6	5.071986000	-2.318952000	-1.019611000
6	3.714017000	-2.072420000	-0.883024000
6	3.277710000	-0.864506000	-0.347624000
6	4.205689000	0.084160000	0.070498000
1	3.869905000	1.020932000	0.498242000
1	6.280882000	0.563533000	0.282500000
1	7.057077000	-1.568108000	-0.704435000
1	5.406533000	-3.254521000	-1.448509000
1	2.993170000	-2.814006000	-1.204018000
7	1.286636000	0.397858000	-0.861817000
6	1.908690000	1.200516000	-1.845777000
6	1.397818000	2.611619000	-1.753775000
8	2.005961000	3.543331000	-2.243810000
8	0.274800000	2.692540000	-1.134199000
6	-2.412390000	-0.802758000	-0.444577000
6	-3.040649000	0.423352000	-1.072842000
8	-3.058355000	-1.829496000	-0.343697000
6	-3.022139000	0.338969000	-2.618676000
7	-2.294307000	1.660487000	-0.737904000
1	-4.072189000	0.512117000	-0.718343000
1	-4.034905000	0.175572000	-2.982770000
1	-2.416672000	-0.494517000	-2.975231000
6	-2.731035000	2.299681000	0.525874000
6	-2.585066000	2.569855000	-1.871189000
1	-2.228063000	3.266051000	0.582539000
6	-2.443796000	1.505447000	1.768594000
1	-3.805406000	2.496818000	0.451980000
1	-1.919124000	3.428903000	-1.859793000

1	-3.614022000	2.932056000	-1.767047000
6	-2.461977000	1.686079000	-3.092975000
6	-1.229332000	1.646826000	2.437063000
6	-3.396615000	0.633745000	2.286544000
6	-0.964896000	0.915776000	3.586127000
1	-0.488831000	2.348656000	2.069991000
6	-3.137583000	-0.094995000	3.440443000
1	-4.354365000	0.530456000	1.789980000
1	-3.889969000	-0.768154000	3.831150000
1	-0.015730000	1.034692000	4.092820000
6	-1.919603000	0.041863000	4.090861000
1	-1.715331000	-0.527276000	4.988676000
1	-3.019895000	2.092613000	-3.935245000
1	-1.421659000	1.597797000	-3.409758000
28	-0.445256000	1.046271000	-0.672134000
6	2.664820000	0.731014000	-2.837051000
6	3.243978000	1.551576000	-3.953666000
1	2.874894000	-0.329803000	-2.867525000
6	4.066026000	0.660459000	-4.879278000
6	2.175686000	2.301558000	-4.740966000
1	3.951783000	2.280192000	-3.541755000
8	2.623970000	3.451485000	-5.202650000
8	1.074240000	1.864637000	-4.943840000
8	4.083565000	1.122505000	-6.115558000
8	4.651081000	-0.322344000	-4.513615000
6	1.722202000	4.235473000	-5.976341000
1	2.262088000	5.140685000	-6.242237000
1	1.419932000	3.721075000	-6.889161000
1	0.833180000	4.505968000	-5.405782000
6	4.865486000	0.409510000	-7.076235000
1	4.742188000	0.941427000	-8.015396000
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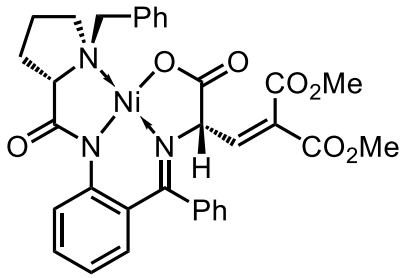

E_e = -3470.401287771888 Hartree

Element	x, Å	y, Å	z, Å
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6	0.468353000	-3.512507000	3.583024000
6	-0.922104000	-3.557289000	3.606410000
6	-1.672852000	-2.780940000	2.750955000
6	-1.075270000	-1.893771000	1.832300000
7	-1.820367000	-1.049129000	1.039995000
6	1.107194000	-1.029399000	0.875604000
1	2.159264000	-2.639388000	2.658620000

1	1.059141000	-4.118103000	4.256488000
1	-1.432174000	-4.204011000	4.309580000
1	-2.745374000	-2.846428000	2.813278000
6	4.863276000	-0.945059000	1.187067000
6	5.227529000	-2.026500000	0.395732000
6	4.252002000	-2.766966000	-0.256584000
6	2.912188000	-2.439632000	-0.108144000
6	2.547491000	-1.358434000	0.686045000
6	3.525732000	-0.607686000	1.331475000
1	3.241244000	0.231901000	1.954019000
1	5.620634000	-0.363761000	1.696748000
1	6.271526000	-2.289968000	0.286092000
1	4.531798000	-3.605747000	-0.880146000
1	2.152292000	-3.027274000	-0.607814000
7	0.575450000	-0.049087000	0.238350000
6	1.332295000	0.739193000	-0.734081000
6	0.642667000	2.118014000	-0.840890000
8	1.196317000	3.038104000	-1.397179000
8	-0.527557000	2.147773000	-0.314077000
6	-3.134607000	-1.274089000	0.765314000
6	-3.796837000	-0.085703000	0.104902000
8	-3.770157000	-2.299780000	0.927687000
6	-3.872562000	-0.259933000	-1.431636000
7	-3.032613000	1.163744000	0.323846000
1	-4.806337000	0.025510000	0.512691000
1	-4.906602000	-0.432486000	-1.724460000
1	-3.295913000	-1.119107000	-1.774509000
6	-3.400514000	1.880572000	1.569931000
6	-3.387614000	2.007136000	-0.842620000
1	-2.881108000	2.839188000	1.548321000
6	-3.072875000	1.151381000	2.842631000
1	-4.474155000	2.090778000	1.531845000
1	-2.723362000	2.863201000	-0.917790000
1	-4.410116000	2.375434000	-0.702041000
6	-3.332690000	1.052029000	-2.014097000
6	-1.831099000	1.308883000	3.455544000
6	-4.014990000	0.320827000	3.441714000
6	-1.529231000	0.630476000	4.627353000
1	-1.097386000	1.981585000	3.025540000
6	-3.718251000	-0.355539000	4.618161000
1	-4.993286000	0.206108000	2.989652000
1	-4.462150000	-0.998453000	5.071228000
1	-0.558864000	0.760288000	5.089177000
6	-2.472579000	-0.206015000	5.210810000
1	-2.238237000	-0.735058000	6.125767000
1	-3.929223000	1.411574000	-2.851375000
1	-2.309101000	0.935618000	-2.374043000
28	-1.177551000	0.554642000	0.351600000
6	2.212722000	-0.214914000	-2.924454000
6	3.650129000	0.094885000	-2.671914000
6	1.841623000	-0.878369000	-4.208662000
8	2.708812000	-0.587049000	-5.163495000

8	0.857135000	-1.551832000	-4.366878000
8	4.406592000	-0.948793000	-2.967005000
8	4.065566000	1.140234000	-2.247360000
6	2.486895000	-1.162256000	-6.450360000
1	3.304671000	-0.818015000	-7.077492000
1	2.501791000	-2.251548000	-6.409165000
1	1.541674000	-0.831446000	-6.881175000
6	5.817375000	-0.797351000	-2.830559000
1	6.246542000	-1.775316000	-3.031428000
1	6.207495000	-0.080926000	-3.555138000
1	6.099791000	-0.481401000	-1.827514000
6	1.232230000	0.060652000	-2.062716000
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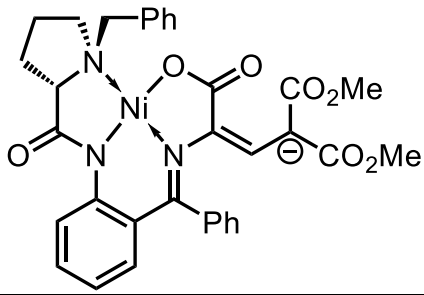

E_e = -3469.918110600138Hartree

Element	x, Å	y, Å	z, Å
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6	0.546812000	-3.368345000	3.643153000
6	-0.835417000	-3.508567000	3.650193000
6	-1.615225000	-2.795802000	2.762179000
6	-1.056333000	-1.902400000	1.828699000
7	-1.837847000	-1.084202000	1.036276000
6	1.085970000	-0.993251000	0.794834000
1	2.195790000	-2.426903000	2.710749000
1	1.167615000	-3.905312000	4.348061000
1	-1.315023000	-4.168351000	4.362808000
1	-2.684339000	-2.918494000	2.807977000
6	4.821945000	-0.564156000	0.865634000
6	5.263856000	-1.791547000	0.386470000
6	4.340862000	-2.765105000	0.029422000
6	2.981255000	-2.513661000	0.150384000
6	2.533870000	-1.282951000	0.623168000
6	3.464169000	-0.310085000	0.981997000
1	3.125292000	0.647323000	1.358870000
1	5.537216000	0.195209000	1.154843000
1	6.324330000	-1.988531000	0.295322000
1	4.678563000	-3.723409000	-0.344013000
1	2.263939000	-3.276908000	-0.125482000
7	0.518846000	-0.032895000	0.138098000
6	1.045599000	0.744978000	-0.909034000
6	0.463349000	2.099013000	-0.881626000
8	0.985947000	3.054719000	-1.433912000
8	-0.618986000	2.194634000	-0.166952000

6	-3.147628000	-1.325417000	0.787894000
6	-3.841130000	-0.127642000	0.172478000
8	-3.770140000	-2.363385000	0.944415000
6	-3.912164000	-0.235663000	-1.369962000
7	-3.108369000	1.130517000	0.446465000
1	-4.853746000	-0.058082000	0.582398000
1	-4.941931000	-0.417941000	-1.672934000
1	-3.316461000	-1.066181000	-1.749078000
6	-3.495986000	1.780580000	1.719047000
6	-3.479446000	2.014490000	-0.682136000
1	-2.992728000	2.747803000	1.747461000
6	-3.169773000	1.003429000	2.964173000
1	-4.572974000	1.976661000	1.684712000
1	-2.829723000	2.884232000	-0.719514000
1	-4.509661000	2.357641000	-0.531512000
6	-3.401992000	1.112691000	-1.894429000
6	-1.938951000	1.157071000	3.599721000
6	-4.110264000	0.145487000	3.526393000
6	-1.648821000	0.455624000	4.760972000
1	-1.205660000	1.845703000	3.195310000
6	-3.825339000	-0.554863000	4.691752000
1	-5.079842000	0.030917000	3.055907000
1	-4.569066000	-1.217136000	5.116434000
1	-0.687257000	0.584956000	5.241214000
6	-2.592735000	-0.403101000	5.310561000
1	-2.368237000	-0.948852000	6.218157000
1	-4.007094000	1.494257000	-2.715919000
1	-2.376138000	1.036818000	-2.257197000
28	-1.231599000	0.564570000	0.418903000
6	1.931645000	0.275811000	-1.866566000
6	2.334763000	0.813358000	-3.082357000
1	2.367021000	-0.698227000	-1.677439000
6	3.287205000	0.053632000	-3.860197000
6	1.642064000	1.939206000	-3.760543000
8	2.451256000	2.964076000	-4.024548000
8	0.488737000	1.912471000	-4.116138000
8	3.395204000	0.520903000	-5.121419000
8	3.925677000	-0.914979000	-3.489417000
6	1.887048000	4.058108000	-4.724777000
1	2.683235000	4.790790000	-4.842655000
1	1.526493000	3.774108000	-5.716160000
1	1.066685000	4.517406000	-4.172106000
6	4.316361000	-0.129378000	-5.976408000
1	4.256229000	0.383440000	-6.934742000
1	5.343138000	-0.061064000	-5.610557000
1	4.072304000	-1.182195000	-6.129766000