

Stereoselective arylthiolation of dehydroalanine in the Ni^{II} coordination environment: the stereoinductor of choice

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1. Experimental details

^1H (400.0 MHz) and ^{13}C (100.6 MHz) NMR spectra (including COSY, HMBC, HSQC) were recorded using an Agilent 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). No plastics were used for the sample preparation. Aliquot sampling was conducted by using Hamilton syringes.

All reactants and solvents were commercially available from Aldrich and purified prior to experiments. Complex **3** with the (*S*)-BPB-ligand was synthesized as described [Y. Belokon, A. Sagyan, S. Djamgaryan, V. Bakhmutov, V. Belikov. *Tetrahedron*, 1988, **44**, 5507].

Synthesis of 2'

A three-necked 250 ml round-bottom flask equipped with a rubber septum with two electrodes (a glassy carbon anode, 15 cm^2 , and a platinum plate, 10 cm^2) was filled with a solution of KOH (4.5 g) in 150 ml of absolute methanol and connected to a Schlenk line. The solution was deaerated by a freeze-pump-thaw cycling method. Afterwards, complex **1'** (1.5 g) (available from Hamari Chemicals) was added. The 70 mA current (corresponding to current density of 5 mA cm^{-2}) was passed through the solution during 3 h with vigorous stirring. Afterwards, glacial acetic acid (7.5 ml) was added and the mixture was concentrated in vacuum to 1/3 of the initial volume. Then the reaction mixture was diluted with water, extracted with chloroform, washed with NaHCO_3 and dried with Na_2SO_4 . Evaporation of the chloroform solution yields (*S,R*)-**2'** (1.6 g, 98 %). The compound obtained is pure enough for the majority of applications. To obtain analytically pure sample, the complex was further purified by column chromatography (Silicagel, CHCl_3 /acetone, 5:1).

Nickel(II) (2*R*)-2-(5-chloro-2-[(*S*)-1-(3,4-dichlorobenzyl)proplylamido]- α -phenylbenzyliden-amino)-3-hydroxypropanoate (*S,R*)-2'

HRMS (ESI): m/z 630.0255 ($\text{M}+\text{H}^+$, 630.0259 calculated for $\text{C}_{28}\text{H}_{25}\text{Cl}_3\text{N}_3\text{NiO}_4$).

^1H NMR (CDCl_3 δ , ppm): 8.42 (d, $J = 9.3$ Hz, 1H), 8.45 (d, $J = 1.9$ Hz, 1H), 8.20 (dd, $J = 8.2, 1.9$ Hz, 1H), 7.56 (d, $J = 8.2$ Hz), 7.54-7.47 (m, 3H), 7.19-7.10 (m, 2H), 7.14 (dd, $J = 9.3, 2.5$ Hz, 1H), 6.70 (d, $J = 2.5$ Hz), 4.36 (d, $J = 12.9$ Hz, 1H), 4.20-4.11 (m, 1H), 3.97-3.92 (m, 1H), 3.73-3.63 (m, 2H), 3.50 (br. s, 1H), 3.43 (dd, $J = 9.1, 4.8$ Hz, 1H), 3.24 (d, $J = 12.9$ Hz), 2.64-2.51 (m, 2H), 2.26-2.13 (m, 2H), 2.00-1.89 (m, 1H).

^{13}C NMR (CDCl_3 δ , ppm): 181.89, 181.89, 179.22, 172.22, 172.22, 141.46, 133.82, 133.79, 133.61, 133.56, 133.16, 132.53, 132.48, 131.31, 131.23, 130.35, 129.62, 129.12, 128.36, 127.00, 126.42, 125.62, 125.14, 72.43, 68.85, 64.86, 60.72, 59.24, 30.35, 23.27.

Synthesis of 3'

To a solution of (*S,R*)-**2'** (1.5 g, 2.4 mmol) in MeCN (4.5 ml), Na_2CO_3 (1.2 g, 11.3 mmol) and acetic anhydride (1.75 ml, 18.5 mmol) were added. The solution was deaerated by a freeze-pump-thaw cycling method. The stirring was continued at 60°C until complete conversion of the initial complex (9 h), as monitored by TLC (Silicagel, CHCl_3 /acetone = 5:1). The mixture was cooled, filtered, the precipitate was washed with CHCl_3 , the filtrate and washings were combined

and evaporated under reduced pressure, the residue was purified by column chromatography (Silicagel, CHCl₃/acetone, 5:1) to give **3'** (1.02 g, 70%).

Nickel(II) (2R)-2-(5-chloro-2-[(S)-1-(3,4-dichlorobenzyl)proplylamido]- α -phenylbenzylidene-amino)acrylate (S,R)-3'

HRMS (ESI): m/z 612.0154 (M+H⁺, 612.0153 calculated for C₂₈H₂₃Cl₃N₃NiO₃).

Atom numbering is given below.

¹H NMR (CDCl₃ δ , ppm): 8.88 (d, ³J = 2.1 Hz, 1H (H-21)), 8.07 (d, ²J = 9.3 Hz, 1H (H-8)), 7.80 (dd, ²J = 8.2 Hz, ³J = 2.1 Hz, 1H (H-17)), 7.54-7.43 (m, 3H (H-24,25,26)), 7.35 (d, ²J = 8.1 Hz, 1H (H-18)), 7.25-7.15 (m, 1H (H-27)), 7.12 (dd, ²J = 9.3 Hz, ³J = 2.6 Hz, 1H (H-7)), 7.07-6.96 (m, 1H (H-23)), 6.78 (d, ³J = 2.6 Hz, 1H (H-5)), 5.64 (d, ²J = 1.2 Hz, 1H (H-28)), 4.24 (d, ²J = 12.5 Hz, 1H (H-15)), 4.16 (d, ²J = 1.2 Hz, 1H (H-28)), 3.75-3.62 (m, 1H (H-13)), 3.57 (dd, J = 10.3 Hz, J = 6.3 Hz, 1H (H-14)), 3.37 (dd, ³J = 11.1, ³J = 5.7 Hz, 1H (H-11)), 3.14 (d, ²J = 12.5 Hz, 1H (H-15)), 2.72-2.51 (m, 2H (H-12)), 2.27-2.17 (m, 1H (H-13)), 2.11-2.02 (m, 1H (H-14)).

¹³C NMR (CDCl₃ δ , ppm): 179.99 (C-10), 170.26 (C-1), 168.65 (C-3), 146.63 (C-2), 141.78 (C-9), 135.14 (C-16), 134.45 (C-22), 133.59, 133.55 (C-19,20,21), 133.21 (C-7), 132.95 (C-5), 131.20 (C-18), 130.62 (C-25), 129.90 (C-17), 129.4-127.3 (C-23,24,26,27), 128.20 (C-6), 125.93 (C-4), 124.08 (C-8), 115.76 (C-28), 71.54 (C-11), 62.93 (C-15), 58.62 (C-14), 30.94 (C-12), 23.95 (C-13).

Preparative electrolysis was performed with AutoLab PGSTAT100N potentiostat in a two-compartment cell of 10 ml volume. The WE was glassy carbon plate (300 mm²); the CE was a stainless steel wire. The solution was stirred with an argon flow.

Electrochemical thioarylation of 3 and 3' (the general procedure)

Solution of Bu₄NBF₄ (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, azobenzene (18–50 mg, 0.11–0.27 mmol) and ArSH (0.2 – 0.5 mmol) were added. The solution was thoroughly deaerated with an Ar flow and subjected to the potentiostatic electrolysis ($E = -1.4$ V vs. Ag/AgCl, KCl_(sat.)) until a charge corresponding to 1.1 F/mol of the ArSH has been passed through the solution. Afterwards, **3** (100 mg, 0.2 mmol) or **3'** (100 mg, 0.16 mmol) was added to the reaction mixture. In 30 min – 1 h, the reaction mixture was poured into water (15 ml) and extracted with ethylacetate (3 x 15 ml). Organic fractions were washed with water, dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The residue was separated using column chromatography (Silicagel, Hex/AcOEt = 1:5 for **4a**, **4'c**, CHCl₃/AcOEt = 5:1 for **4b-d**, **4'a**, CHCl₃/AcOEt = 2:1 for **4'd**, CHCl₃/acetone = 5:1 for **4'b**, mixtures were used as an eluent). After evaporation of the solvent and drying in vacuum the targeted complexes were obtained.

4a: 94 mg (76%, *dr* = 1.8:1), **4b**: 85 mg (62%, *dr* = 2.8:1, 18% of the initial complex did not react), **4c**: 58 mg (40%, *dr* = 3.1:1, 40% of the initial complex did not react), **4d**: 85 mg (65%, *dr* = 5.5:1, 20% of the initial complex did not react). Conditions: 0.11 mmol azobenzene, 0.2 mmol ArSH.

4a: 84.4 mg (68%, *dr* = 3:1), **4b**: 105 mg (77%, *dr* = 4.5:1), **4c**: 106 mg (73%, *dr* = 5:1), **4d**: 104 mg (80%, *dr* = 8:1), **4'a**: 91 mg (76%), **4'b**: 102 mg (78%), **4'c**: 91 mg (70%, *dr* = 8:1), **4'd**: 87 mg (78%, *dr* = 20:1). Conditions: 0.27 mmol azobenzene, 0.5 mmol ArSH.

Chemical thioarylation of **3** (the general procedure)

To a DMF (3 ml) solution of **3** (20 mg, 0.04 mmol) ArSH (0.098 mmol) was added. The solution was deaerated by a freeze-pump-thaw cycling method. The reaction mixture was stirred for 36 h at room temperature. Afterwards, it was poured into water (15 ml). The organic compounds were extracted with ethylacetate (3 x 10 ml). Organic fractions were washed with water, dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. The residue was separated using column chromatography (Silicagel, Hex/AcOEt = 1:5 for **4a**, CHCl₃/AcOEt = 5:1 for **4d** mixtures were used as an eluent). After evaporation of the solvent and drying in vacuum the targeted complexes were obtained as a mixture of the (*S,S*)- and (*S,R*)-diastereomers: **4a**: 23.6 mg (95%, *dr* = 1.3:1), **4d**: 25 mg (95%, *dr* = 1.3:1).

Nickel(II) (2*R*)-2-{2-[(*S*)-1-benzylprolylamido]- α -phenylbenzylidenamino}-3-(4-methylphenylthio)propanoate (*S,R*)-**4a**

HRMS (ESI): *m/z* 634.1671 (M+H⁺, 634.1669 calculated for C₃₅H₃₄N₃NiO₃S), 656.1490 (M+Na⁺, 656.1488 calculated for C₃₅H₃₃N₃NiO₃SNa).

¹H NMR (CDCl₃ δ , ppm): 8.23 (d, ³J = 8.7 Hz, 1H (H-8)), 8.10-8.04 (m, 2H (H-17,21)), 7.49-7.41 (m, 2H (H-24,26)), 7.38-7.27 (m, 5H (H-18,20,25,30,34)), 7.23-7.19 (m, 2H (H-19,27)), 7.18-7.13 (m, 1H (H-7)), 7.02-6.96 (m, 2H (H-31,33)), 6.66-6.61 (m, 1H (H-6)), 6.56 (dd, ³J = 8.2, ⁴J = 1.5, 1H (H-5)), 6.50 (m, 1H (H-23)), 4.45 (d, ²J = 12.6, 1H (H-15)), 4.26 (dd, ³J = 6.0, ³J = 2.5, 1H (H-2)), 3.74-3.67 (m, 1H (H-13)), 3.61 (d, ²J = 12.6 Hz, 1H (H-15)), 3.64-3.57 (m, 1H (H-14)), 3.46 (dd, J = 10.5, J = 6.5, 1H (H-11)), 3.23 (dd, ²J = 13.3, ³J = 2.5, 1H (H-28)), 2.94-2.85 (m, 1H (H-12)), 2.87 (dd, ²J = 13.3 Hz, ³J = 6.0 Hz, 1H (H-28)), 2.56-2.43 (m, 1H (H-12)), 2.25 (s, 3H (H-35)), 2.12-1.97 (m, 2H (H-13,14)).

¹³C NMR (CDCl₃ δ , ppm): 180.59 (C-10), 178.40 (C-1), 171.76 (C-3), 142.92 (C-9), 137.46 (C-32), 133.99 (C-16), 133.41 (C-5), 133.39 (C-22), 132.50 (C-7), 132.18 (C-29), 132.04 (C-18,20), 131.74 (C-17,21), 129.97 (C-31,33), 129.88 (C-25), 129.00 (C-24,26), 128.98 (C-19), 128.93 (C-30,34), 127.53 (C-23), 126.85, 126.35 (C-4), 123.86 (C-8), 120.68 (C-6), 70.67 (C-11), 69.54 (C-2), 63.43 (C-15), 57.30 (C-14), 39.43 (C-28), 30.87 (C-12), 23.32 (C-13), 21.11 (C-35).

Nickel(II) (2*S*)-2-{2-[(*S*)-1-benzylprolylamido]- α -phenylbenzylidenamino}-3-(4-methylphenylthio)propanoate (*S,S*)-**4a**

HRMS (ESI): *m/z* 634.1656 (M+H⁺, 634.1669 calculated for C₃₅H₃₄N₃NiO₃S), 656.1476 (M+Na⁺, 656.1489 calculated for C₃₅H₃₃N₃NiO₃SNa).

¹H NMR (CDCl₃ δ , ppm): 8.52 (d, ³J = 8.7 Hz, 1H (H-8)), 7.91-7.85 (m, 2H (H-17,21)), 7.49-7.24 (m, 9H (H-7,18,19,20,24,25,26,30,34)), 7.19-7.12 (m, 1H (H-27)), 6.93-6.87 (m, 2H (H-31,33)), 6.71-6.64 (m, 3H (H-5,6,23)), 4.80 (d, ²J = 13.3 Hz, 1H (H-15)), 4.18 (dd, ³J = 6.7 Hz, ³J = 2.9 Hz, 1H (H-2)), 4.15-4.05 (m, 1H (H-14)), 3.86 (d, ²J = 13.3 Hz, 1H (H-15)), 3.65 (dd, J = 9.9 Hz, J = 4.0 Hz, 1H (H-11)), 3.18 (dd, ²J = 13.5 Hz, ³J = 2.9 Hz, 1H (H-28)), 3.00 (dd, ²J = 13.5 Hz, ³J = 6.7 Hz, 1H (H-28)), 2.66-2.52 (m, 2H (H-12,14)), 2.26-2.19 (m, 1H (H-13)), 2.19 (s, 3H (H-35)), 2.08-1.95 (m, 1H (H-13)), 1.88-1.77 (m, 1H (H-12)).

¹³C NMR (CDCl₃ δ , ppm): 182.46 (C-10), 178.60 (C-1), 172.43 (C-3), 143.26, 137.24 (C-32), 134.24, 133.77 (C-5), 132.73, 132.25, 132.02, 131.95 (C-30,34), 131.49, 129.80 (C-31,33), 129.58, 129.25 (C-17,21), 129.18, 129.09, 128.64 (C-29), 128.09 (C-23), 126.68 (C-27), 125.78

(C-4), 124.06 (C-8), 120.75, 69.74 (C-2), 68.66 (C-11), 61.68 (C-15), 57.50 (C-14), 40.08 (C-28), 30.72 (C-13), 23.54 (C-12), 21.07 (C-35).

Nickel(II) (2R)-2-{2-[(S)-1-benzylproplylamido]- α -phenylbenzylidenamino}-3-(4-bromophenylthio)propanoate (S,R)-4b

HRMS (ESI): m/z 698.0611 ($M+H^+$, 698.0617 calculated for $C_{34}H_{31}BrN_3NiO_3S$), 720.0426 ($M+Na^+$, 720.0437 calculated for $C_{34}H_{30}BrN_3NiO_3SNa$).

1H NMR ($CDCl_3$ δ , ppm): 8.20 (dd, $^3J = 8.6$ Hz, $^4J = 0.8$ Hz, 1H (H-8)), 8.08-8.03 (m, 2H (H-17,21)), 7.50-7.44 (m, 2H (H-24,26)), 7.38-7.28 (m, 5H (H-18,20,25,30,34)), 7.27-7.12 (m, 5H (H-7,19,23,31,33)), 6.71-6.61 (m, 2H (H-6,27)), 6.57 (dd, $^3J = 8.3$ Hz, $^4J = 1.7$ Hz, 1H (H-5)), 4.41 (d, $^2J = 12.7$ Hz, 1H (H-15)), 4.25 (dd, $^3J = 6.6$ Hz, $^3J = 2.8$ Hz, 1H (H-2)), 3.70-3.51 (m, 3H (H-13,14,15)), 3.45 (dd, $^3J = 10.6$ Hz, $^3J = 6.4$ Hz, 1H (H-11)), 3.22 (dd, $^2J = 13.2$ Hz, $^3J = 2.8$ Hz, 1H (H-28)), 2.96 (dd, $^2J = 13.2$ Hz, $^3J = 6.3$ Hz, 1H (H-28)), 2.90-2.80 (m, 1H (H-12)), 2.56-2.44 (m, 1H (H-12)), 2.10-1.97 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ , ppm): 180.50 (C-10), 178.00 (C-1), 171.86 (C-3), 142.88 (C-9), 134.81 (C-29), 133.85 (C-22), 133.43 (C-5), 133.34 (C-16), 132.63 (C-7), 132.48 (C-30,34), 132.22 (C-31,33), 131.65 (C-17,21), 130.00 (C-24), 129.11 (C-26), 129.06 (C-25), 128.97 (C-19), 128.92 (C-18,20), 127.41 (C-27), 126.85 (C-23), 126.23 (C-4), 123.83 (C-8), 121.15 (C-32), 120.75 (C-6), 70.61 (C-11), 69.05 (C-2), 63.45 (C-15), 57.26 (C-14), 38.68 (C-28), 30.84 (C-12), 23.34 (C-13).

Nickel(II) (2S)-2-{2-[(S)-1-benzylproplylamido]- α -phenylbenzylidenamino}-3-(4-bromophenylthio)propanoate (S,S)-4b

HRMS (ESI): m/z 698.0602 ($M+H^+$, 698.0617 calculated for $C_{34}H_{31}BrN_3NiO_3S$).

1H NMR ($CDCl_3$ δ , ppm): 8.48 (d, $^3J = 8.6$ Hz, 1H), 7.86 (m, 2H), 7.49-7.39 (m, 6H), 7.23-7.12 (m, 7H), 6.70-6.84 (m, 2H), 4.66 (d, $^2J = 13.3$ Hz, 1H), 4.16-4.06 (m, 3H), 3.76 (d, $J = 13.3$ Hz, 1H), 3.66 (dd, $J = 9.9, 4.0$ Hz, 1H), 3.11 (dd, $J = 13.5, 3.5$ Hz, 1H), 3.04 (dd, $J = 13.3, 7.1$ Hz, 1H), 2.65-2.52 (m, 2H), 2.26-2.17 (m, 1H), 1.88-1.80 (m, 1H).

Nickel(II) (2R)-2-{2-[(S)-1-benzylproplylamido]- α -phenylbenzylidenamino}-3-(2-bromophenylthio)propanoate (S,R)-4c

HRMS (ESI): m/z 698.0598 ($M+H^+$, 698.0617 calculated for $C_{34}H_{31}BrN_3NiO_3S$).

1H NMR ($CDCl_3$ δ , ppm): 8.23 (dd, $^3J = 8.7$ Hz, $^4J = 0.7$ Hz, 1H (H-8)), 8.05 (m, 2H (H-17,21)), 7.55 (dd, $^3J = 7.9$ Hz, $^4J = 1.4$ Hz, 1H (H-31)), 7.51-7.43 (m, 2H (H-19,26)), 7.39-7.31 (m, 3H (H-18,20,24)), 7.25-7.18 (m, 3H (H-25,27,34)), 7.18-7.14 (m, 1H (H-7)), 7.14-7.09 (m, 1H (H-33)), 7.03-6.99 (m, 1H (H-32)), 6.76 (d, $^3J = 7.7$ Hz, 1H (H-23)), 6.68-6.62 (m, 1H (H-6)), 6.60 (dd, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz, 1H (H-5)), 4.43 (d, $^2J = 12.7$ Hz, 1H (H-15)), 4.36 (dd, $^3J = 5.9$ Hz, $^3J = 3.1$ Hz, 1H (H-2)), 3.76-3.65 (m, 1H (H-13)), 3.59 (d, $^2J = 12.7$ Hz, 1H (H-15)), 3.60-3.54 (m, 1H (H-14)), 3.45 (dd, $^3J = 10.5$ Hz, $^3J = 6.6$ Hz, 1H (H-11)), 3.31 (dd, $^2J = 12.9$ Hz, $^3J = 3.1$ Hz, 1H (H-28)), 3.02-2.91 (m, 1H (H-12)), 2.93 (dd, $^2J = 12.9, ^3J = 5.9$ Hz, 1H (H-28)), 2.58-2.46 (m, 1H (H-12)), 2.12-1.97 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ , ppm): 180.56 (C-10), 178.19 (C-1), 172.14 (C-3), 143.10 (C-9), 137.04 (C-29), 133.96 (C-16), 133.55 (C-5), 133.35 (C-22), 133.19 (C-31), 132.70 (C-7), 131.75 (C-17,21), 130.01 (C-27), 129.23 (C-26), 129.13 (C-34), 129.06 (C-18,20), 129.03 (C-19), 128.99 (C-24), 128.12 (C-33), 127.74 (C-32), 127.52 (C-23), 126.87 (C-25), 126.38 (C-4), 124.55 (C-30),

123.91 (C-8), 120.75 (C-6), 70.76 (C-11), 68.67 (C-2), 63.45 (C-15), 57.34 (C-14), 36.72 (C-28), 31.06 (C-12), 23.55 (C-13).

Nickel(II) (2S)-2-{2-[(S)-1-benzylprolylamido]- α -phenylbenzylidenamino}-3-(2-bromophenylthio)propanoate (S,S)-4c

HRMS (ESI): m/z 698.0615 ($M+H^+$), 698.0617 calculated for $C_{34}H_{31}BrN_3NiO_3S$.

1H NMR ($CDCl_3$ δ , ppm): 8.49 (dd, $^3J = 8.7$ Hz, $^4J = 0.8$ Hz, 1H (H-8)), 7.80-7.76 (m, 2H (H-17,21)), 7.49-7.38 (m, 7H), 7.36-7.30 (m, 1H), 7.29-7.25 (m, 1H), 7.21 (dd, $^3J = 7.8$ Hz, $^4J = 1.6$ Hz, 1H), 7.18-7.13 (m, 1H), 7.01 (m, 1H), 6.96-6.91 (m, 1H (H-19)), 6.84 (d, $^3J = 7.3$ Hz, 1H), 6.72 (dd, $^3J = 8.3$ Hz, $^4J = 1.9$ Hz, 1H (H-5)), 6.69 (dd, $^3J = 6.5$ Hz, $^4J = 1.1$ Hz, 1H (H-6)), 4.87 (d, $^2J = 13.4$ Hz, 1H (H-15)), 4.24 (dd, $^3J = 6.2$, 3.7 Hz, 1H (H-2)), 4.05-3.96 (m, 1H), 3.91 (d, $^2J = 13.4$ Hz, 1H (H-15)), 3.66 (dd, $^3J = 9.9$, 4.0 Hz, 1H (H-11)), 3.23 (dd, $^2J = 13.3$ Hz, $^3J = 3.7$ Hz, 1H (H-28)), 3.06 (dd, $^2J = 13.3$ Hz, $^3J = 6.3$ Hz, 1H (H-28)), 2.63-2.48 (m, 2H), 2.22-2.13 (m, 1H), 2.00-1.89 (m, 1H), 1.84-1.73 (m, 1H).

^{13}C NMR ($CDCl_3$ δ , ppm): 182.43 (C-10), 178.24 (C-1), 172.58 (C-3), 143.45, 136.81 (C-29), 134.08 (C-5), 133.95, 133.14, 132.95, 132.81, 132.13 (C-17,21), 129.89, 129.87, 129.24, 129.18, 128.84, 128.33, 128.00, 127.61, 126.81, 125.90, 124.91, 124.03 (C-8), 120.87 (C-6), 68.98 (C-2,11), 61.92 (C-15), 57.40, 37.69 (C-28), 31.02, 29.85, 23.68.

Nickel(II) (2R)-2-{2-[(S)-1-benzylprolylamido]- α -phenylbenzylidenamino}-3-(naphthalen-1-ylthio)propanoate (S,R)-4d

HRMS (ESI): m/z 670.1655 ($M+H^+$), 670.1669 calculated for $C_{38}H_{33}N_3NiO_3S$.

1H NMR ($CDCl_3$ δ , ppm): 8.49-8.43 (m, 1H (H-37)), 8.29 (dd, $^3J = 8.7$ Hz, $^4J = 1.0$ Hz, 1H (H-8)), 8.11-8.07 (m, 2H (H-17,21)), 7.88-7.80 (m, 2H (H-30,34)), 7.73-7.68 (m, 1H (H-32)), 7.52-7.46 (m, 2H (H-35,36)), 7.39-7.33 (m, 3H (H-18,20,24)), 7.29-7.13 (m, 5H (H-7,19,23,25,31)), 6.86-6.80 (m, 1H (H-26)), 6.62 (ddd, $^3J = 8.1$ Hz, $^3J = 7.0$ Hz, $^4J = 1.2$ Hz, 1H (H-6)), 6.50 (dd, $^3J = 8.2$ Hz, $^4J = 1.6$ Hz, 1H (H-5)), 6.00-5.95 (m, 1H (H-27)), 4.48 (d, $^2J = 12.7$ Hz, 1H (H-15)), 4.25 (dd, $^3J = 6.2$ Hz, $^3J = 2.7$ Hz, 1H (H-2)), 3.83-3.70 (m, 1H (H-13)), 3.69-3.61 (m, 2H (H-14,15)), 3.49 (dd, $J = 10.6$ Hz, $J = 6.4$ Hz, 1H (H-11)), 3.34 (dd, $^2J = 13.3$ Hz, $^3J = 2.7$ Hz, 1H (H-28)), 2.95-2.85 (m, 1H (H-12)), 2.83 (dd, $^2J = 13.3$ Hz, $^3J = 6.2$ Hz, 1H (H-28)), 2.56-2.44 (m, 1H (H-12)), 2.14-1.97 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ , ppm): 180.62 (C-10), 178.34 (C-1), 171.77 (C-3), 143.01 (C-9), 134.22 (C-33), 133.71 (C-38), 133.58 (C-22), 133.41 (C-5), 132.52 (C-7), 132.43 (C-29), 131.97, (C-34), 131.74 (C-17,21), 129.72 (C-23 or 25), 128.98 (C-19), 128.94 (C-18,20), 128.87 (C-32), 128.78 (C-30), 128.77 (C-24), 128.61 (C-26), 127.32 (C-27), 127.14, (C-36), 126.64 (C-23 or 25), 126.46 (C-35), 126.26 (C-4), 125.72 (C-31), 125.38 (C-37), 123.85 (C-8), 120.65 (C-6) 70.66 (C-11), 69.42 (C-2), 63.47 (C-15), 57.36 (C-14), 38.59 (C-28), 30.90 (C-12), 23.46 (C-13).

Nickel(II) (2R)-2-(5-chloro-2-[(S)-1-(3,4-dichlorobenzyl)prolylamido]- α -phenylbenzyliden-amino)-3-(4-methylphenylthio)propanoate (S,R)-4'a

HRMS (ESI): m/z 736.0488 ($M+H^+$, 736.0500 calculated for $C_{35}H_{31}Cl_3N_3NiO_3S$), 758.0312 ($M+Na^+$, 758.0319 calculated for $C_{35}H_{30}Cl_3N_3NiO_3SNa$).

1H NMR ($CDCl_3$ δ , ppm): 8.95 (d, $^4J = 2.0$ Hz, 1H (H-21)), 8.16 (d, $^3J = 9.3$ Hz, 1H (H-8)), 7.76 (dd, $^3J = 8.2$ Hz, $^4J = 2.1$ Hz, 1H (H-17)), 7.48 (m, 2H (H-24,26)), 7.37-7.28 (m, 4H (H-20,25,30,34)), 7.25-7.21 (m, 1H (H-27)), 7.12 (dd, $^3J = 9.3$ Hz, $^4J = 2.6$ Hz, 1H (H-7)), 6.98 (d, $^3J = 8.0$ Hz, 2H (H-31,33)), 6.50 (d, $^4J = 2.6$ Hz, 1H (H-5)), 6.39 (d, $^3J = 7.7$ Hz, 1H (H-23)), 4.32 (d, $^2J = 12.5$ Hz, 1H (H-15)), 4.24 (dd, $^3J = 5.9$, 2.6 Hz, 1H (H-2)), 3.86-3.72 (m, 1H (H-14)), 3.67-3.59 (m, 1H (H-13)), 3.36 (dd, $^3J = 10.7$, 6.4 Hz, 1H (H-11)), 3.24 (dd, $^2J = 13.4$, $^3J = 2.6$ Hz, 1H (H-28)), 3.23 (d, $^2J = 12.5$ Hz, 1H (H-15)), 2.82 (dd, $^3J = 13.4$, 5.9 Hz, 1H (H-28)), 2.86-2.79 (m, 1H (H-12)), 2.64-2.53 (m, 1H (H-12)), 2.25 (s, 3H (H-35)), 2.14-2.02 (m, 2H (H-13,14)).

^{13}C NMR ($CDCl_3$ δ , ppm): 180.12 (C-10), 177.96 (C-1), 171.30 (C-3), 141.14 (C-9), 137.76 (C-20), 135.13 (C-32), 133.84 (C-21), 133.49 (C-19), 133.34 (C-22), 133.03 (C-16), 132.59 (C-7), 132.19 (C-5,30,34), 131.95 (C-29), 131.06 (C-18), 130.33 (C-26), 130.05 (C-17,31,33), 129.37 (C-24), 129.27 (C-25), 127.29 (C-23), 127.25 (C-6), 126.92 (C-27), 125.62 (C-4), 124.29 (C-8), 71.80 (C-11), 69.86 (C-2), 63.42 (C-15), 58.67 (C-13), 39.58 (C-28), 31.05 (C-12), 23.25 (C-14), 21.13 (C-35).

Nickel(II) (2R)-2-(5-chloro-2-[(S)-1-(3,4-dichlorobenzyl)prolylamido]- α -phenylbenzyliden-amino)-3-(4-bromophenylthio)propanoate (S,R)-4'b

HRMS (ESI): m/z 799.9443 ($M+H^+$, 799.9448 calculated for $C_{34}H_{28}BrCl_3N_3NiO_3S$), 821.9275 ($M+Na^+$, 821.9268 calculated for $C_{34}H_{27}BrCl_3N_3NiO_3S Na$).

1H NMR ($CDCl_3$ δ , ppm): 8.94 (d, $J = 2.0$ Hz, 1H), 8.13 (d, $J = 9.3$ Hz, 1H), 7.74 (dd, $J = 8.2$ Hz, $J = 2.1$ Hz, 1H), 7.55-7.47 (m, 2H), 7.40-7.30 (m, 4H), 7.26-7.22 (m, 3H), 7.13 (dd, $J = 9.3$ Hz, $J = 2.6$ Hz, 1H), 6.61 (d, $J = 7.7$ Hz, 1H), 6.53 (d, $J = 2.6$ Hz, 1H), 4.31 (d, $J = 12.5$ Hz, 1H), 4.66 (dd, $J = 6.1$, 2.8 Hz, 1H), 3.75-3.63 (m, 1H), 3.54-3.62 (m, 1H), 3.66 (dd, $J = 10.8$, 6.3 Hz, 1H), 3.23 (d, $J = 12.2$ Hz, 1H), 2.97-2.86 (m, 2H), 2.85-2.75 (m, 1H), 2.64-2.52 (m, 1H), 2.15-2.01 (m, 2H).

^{13}C NMR ($CDCl_3$ δ , ppm): 180.05, 177.57, 171.42, 141.09, 135.06, 134.52, 133.75, 133.48, 133.33, 132.88, 132.73, 132.56, 132.30, 132.22, 131.06, 130.46, 129.99, 129.49, 129.37, 127.18, 127.13, 126.91, 125.73, 124.25, 121.39, 71.67, 96.34, 63.36, 58.56, 38.73, 31.00, 23.24.

Nickel(II) (2R)-2-(5-chloro-2-[(S)-1-(3,4-dichlorobenzyl)prolylamido]- α -phenylbenzyliden-amino)-3-(2-bromophenylthio)propanoate (S,R)-4'c

HRMS (ESI): m/z 799.9452 ($M+H^+$, 799.9448 calculated for $C_{34}H_{28}BrCl_3N_3NiO_3S$).

1H NMR ($CDCl_3$ δ , ppm): 8.92 (d, $J = 2.0$ Hz, 1H), 8.15 (d, $J = 9.3$ Hz, 1H), 7.74 (dd, $J = 8.2$, 2.1 Hz, 1H), 7.57-7.44 (m, 3H), 7.37-7.32 (m, 2H), 7.27-7.23 (m, 1H), 7.22 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.13-7.08 (m, 2H), 7.04-6.99 (m, 1H), 6.68-6.64 (m, 1H), 6.53 (d, $J = 2.6$ Hz, 1H), 4.34 (dd, $J = 5.7$, 3.1 Hz, 1H), 4.29 (d, $J = 12.6$ Hz, 1H), 3.80-3.69 (m, 1H), 3.61-3.52 (m, 1H), 3.35 (dd, $J = 10.7$, 6.5 Hz, 1H), 3.31 (dd, $J = 13.0$, 3.1 Hz, 1H), 3.23 (d, $J = 12.6$ Hz, 1H), 2.90 (dd, $J = 13.0$, 5.7 Hz, 1H), 2.96-2.85 (m, 1H), 2.67-2.54 (m, 1H), 2.14-1.99 (m, 2H).

¹³C NMR (CDCl₃ δ, ppm): 179.60, 177.26, 171.17, 140.73, 136.14, 134.56, 133.31, 133.03, 132.90, 132.75, 132.43, 132.27, 131.81, 130.62, 129.92, 129.53, 128.89, 128.47, 127.64, 127.27, 126.93, 126.78, 126.41, 125.22, 124.18, 123.79, 71.36, 68.42, 62.92, 58.20, 36.21, 30.86, 29.28, 22.93.

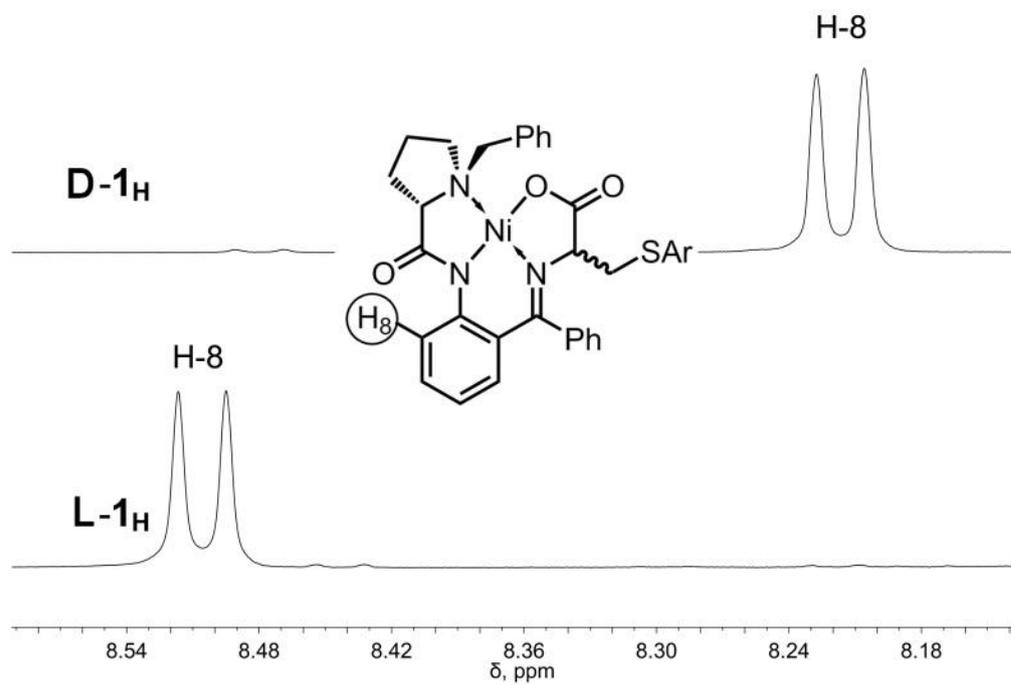
Nickel(II) (2*R*)-2-(5-chloro-2-[(*S*)-1-(3,4-dichlorobenzyl)proplylamido]- α -phenylbenzyliden-amino)-3-(naphthalen-1-ylthio)propanoate (*S,R*)-4'd

HRMS (ESI): *m/z* 772.0482 (M+H⁺, 772.0500 calculated for C₃₈H₃₁Cl₃N₃NiO₃S), 794.0302 (M+Na⁺, 794.0319 calculated for C₃₈H₃₀Cl₃N₃NiO₃SNa).

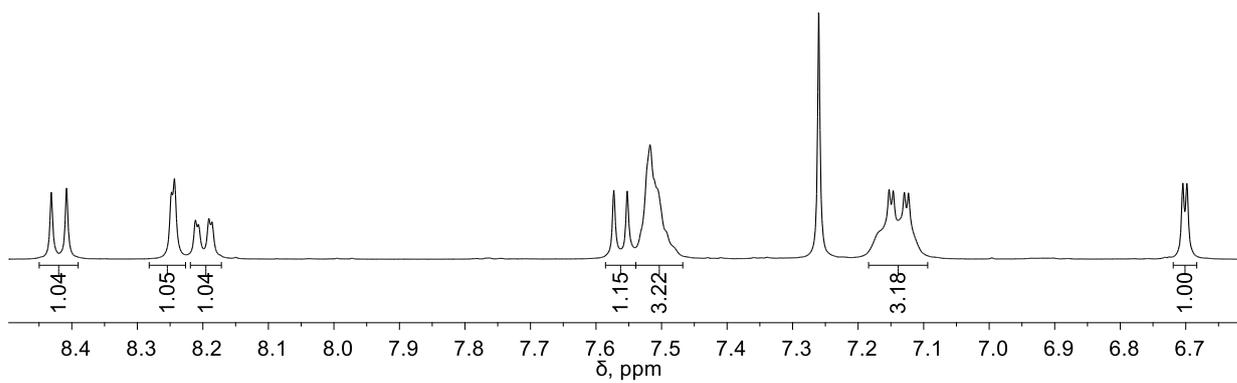
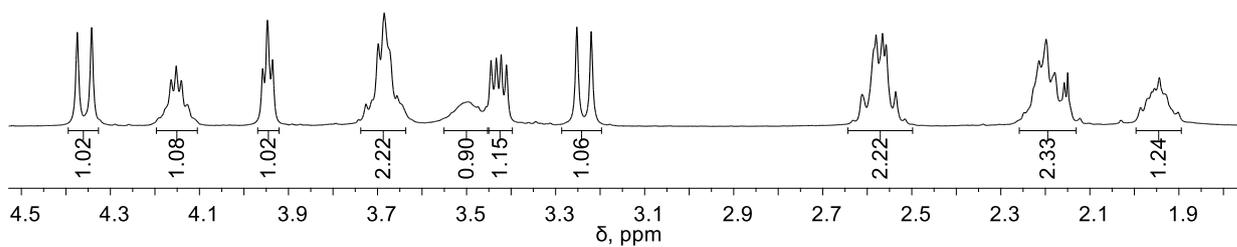
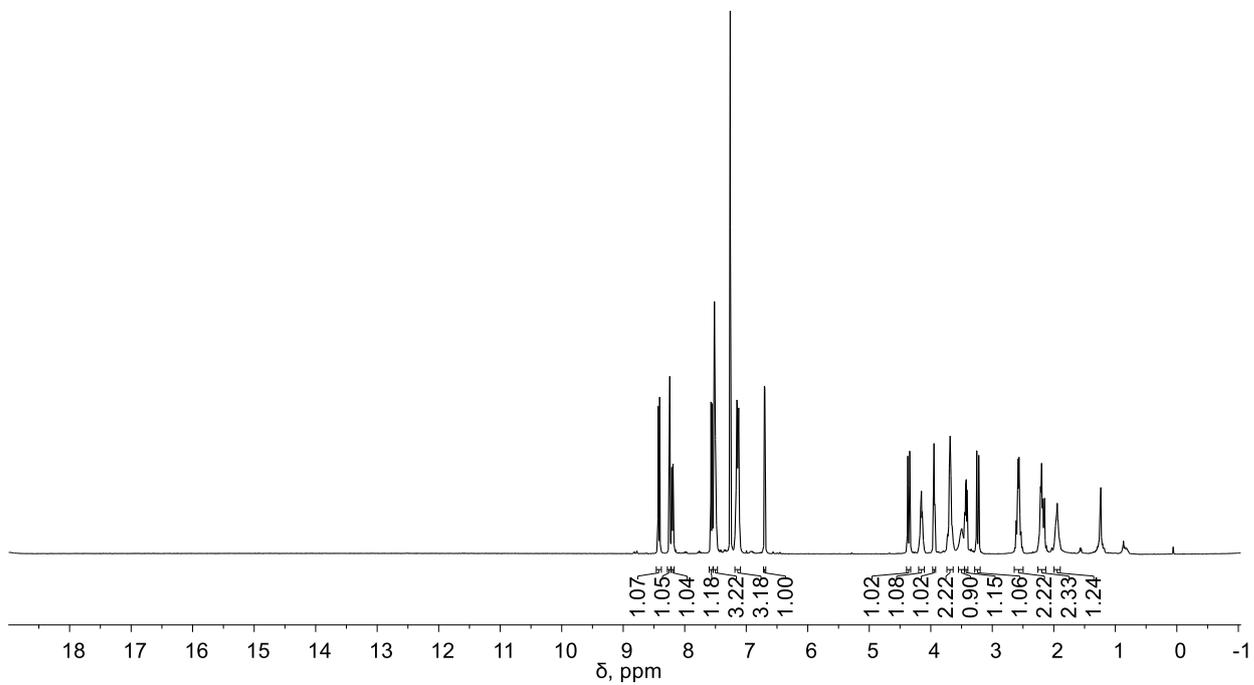
¹H NMR (CDCl₃ δ, ppm): 8.96 (d, *J* = 2.0 Hz, 1H), 8.43-8.38 (m, 1H), 8.19 (d, *J* = 9.3 Hz, 1H), 7.85-7.80 (m, 2H), 7.76 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.53-7.44 (m, 2H), 7.41-7.33 (m, 2H), 7.30-7.24 (m, 1H), 7.18-7.10 (m, 3H), 6.83-6.77 (m, 1H), 6.42 (d, *J* = 2.5 Hz, 1H), 5.79 (d, *J* = 7.7 Hz, 1H), 4.34 (d, *J* = 12.5 Hz, 1H), 4.23 (dd, *J* = 6.0, 2.7 Hz, 1H), 3.89-3.75 (m, 1H), 3.70-3.62 (m, 1H), 3.38 (dd, *J* = 10.8, 6.3 Hz, 1H), 3.32 (dd, *J* = 13.5, 2.7 Hz, 1H), 3.24 (d, *J* = 12.5 Hz, 1H), 2.85-2.74 (m, 1H), 2.76 (dd, *J* = 13.5, 6.0 Hz, 1H), 2.64-2.50 (m, 1H), 2.14-2.04 (m, 2H).

¹³C NMR (CDCl₃ δ, ppm): 179.66, 177.45, 170.82, 140.68, 134.67, 133.75, 133.35, 133.02, 132.99, 132.85, 132.23, 132.12, 131.67, 130.57, 129.67, 129.54, 128.66, 128.62, 128.39, 126.75, 126.51, 126.18, 126.05, 125.15, 125.12, 124.77, 123.79, 71.25, 69.20, 62.93, 58.18, 38.02, 30.54, 22.89.

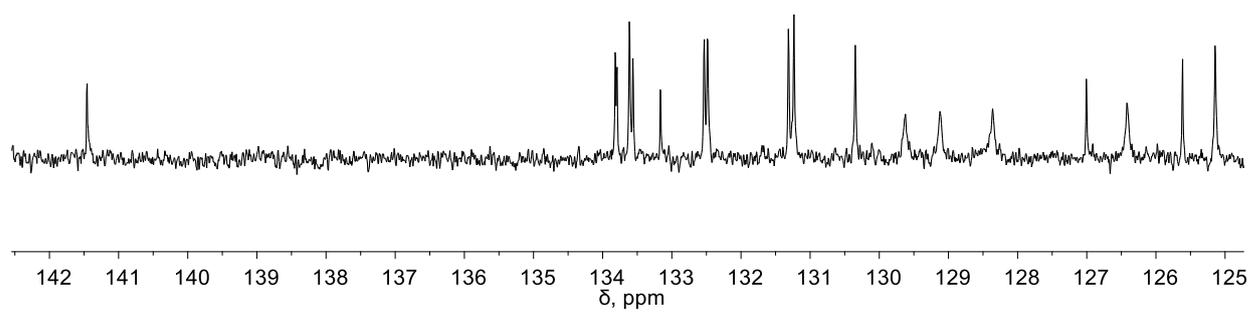
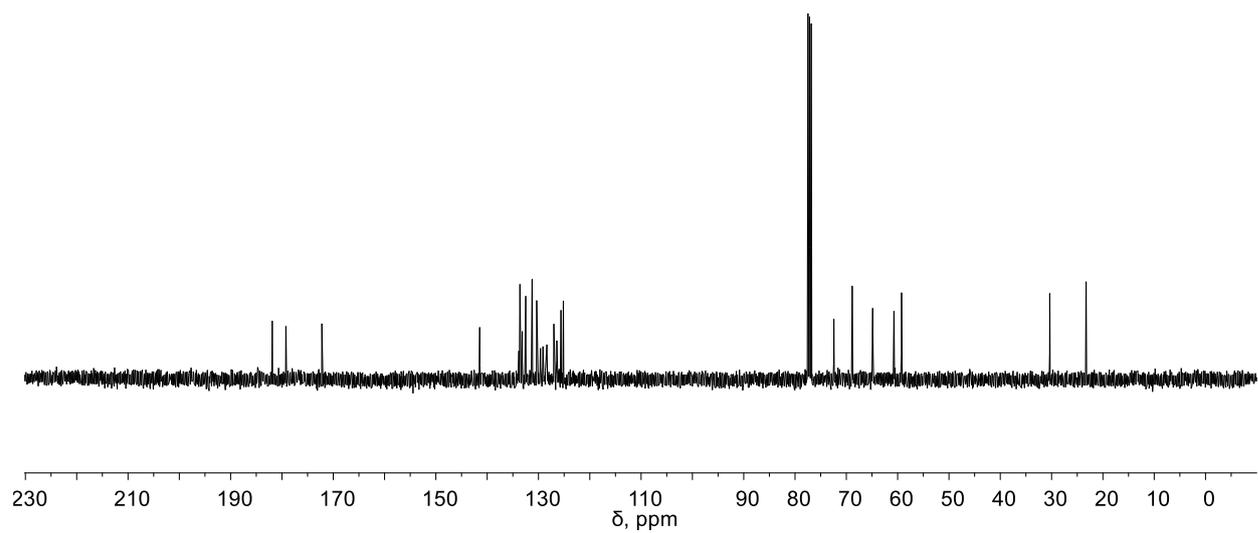
2. **Figure S1.** The characteristic signals of the H₈-protons in the ¹H NMR spectra for (*S,R*)- and (*S,S*)-**4a** complexes



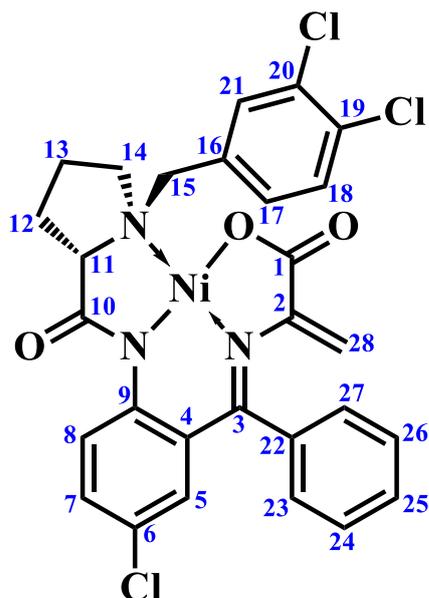
3. ^1H NMR spectrum of **2'**



4. ^{13}C NMR spectrum of **2'**



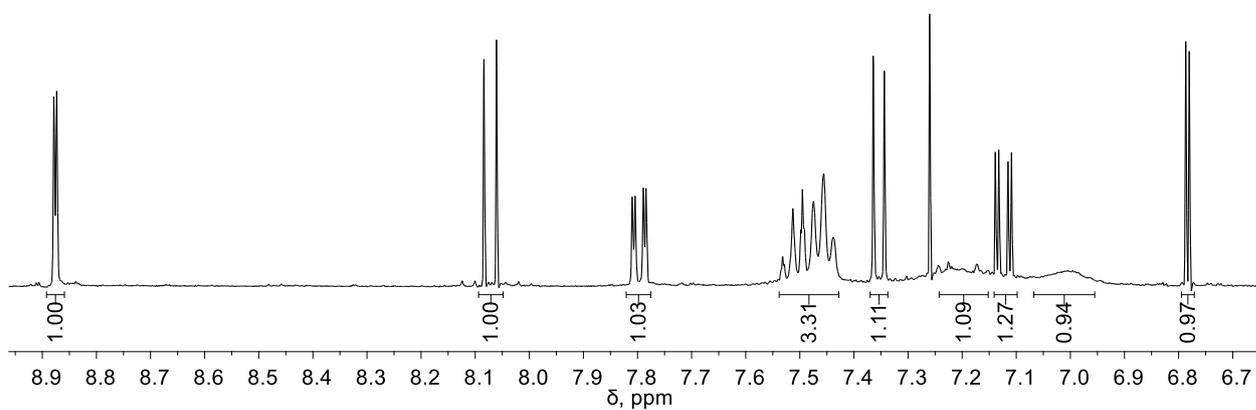
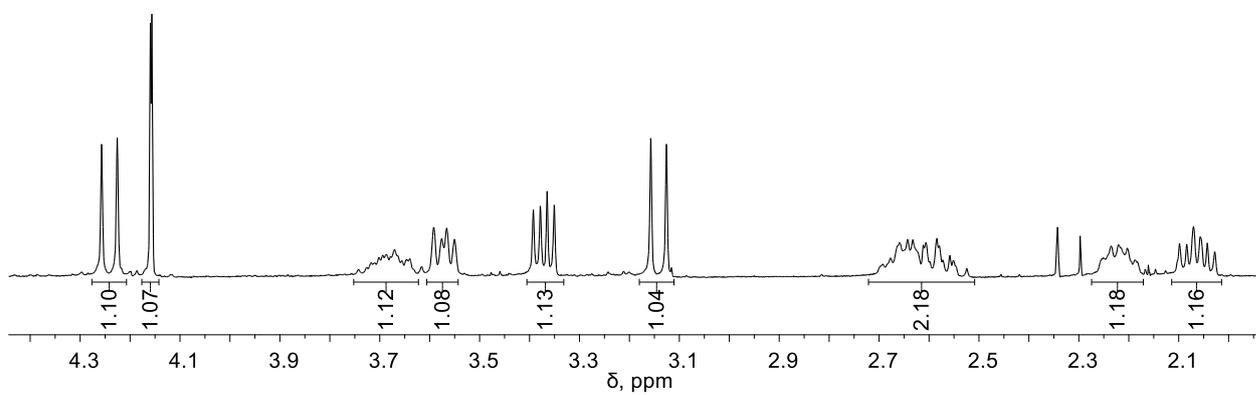
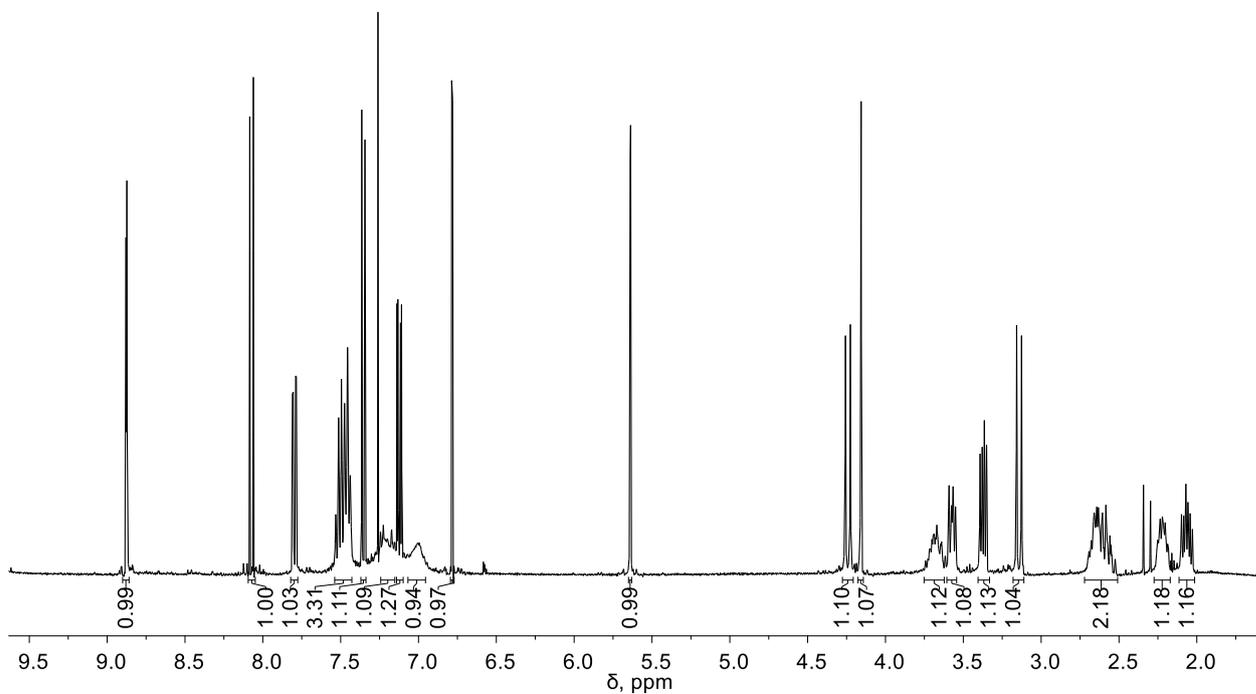
5. Atom numeration and signal assignment in the NMR spectra of **3'**



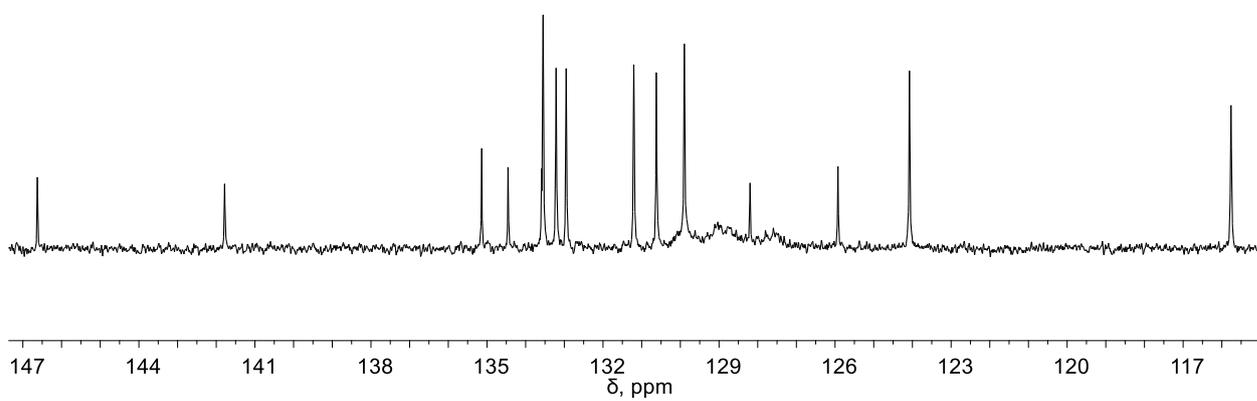
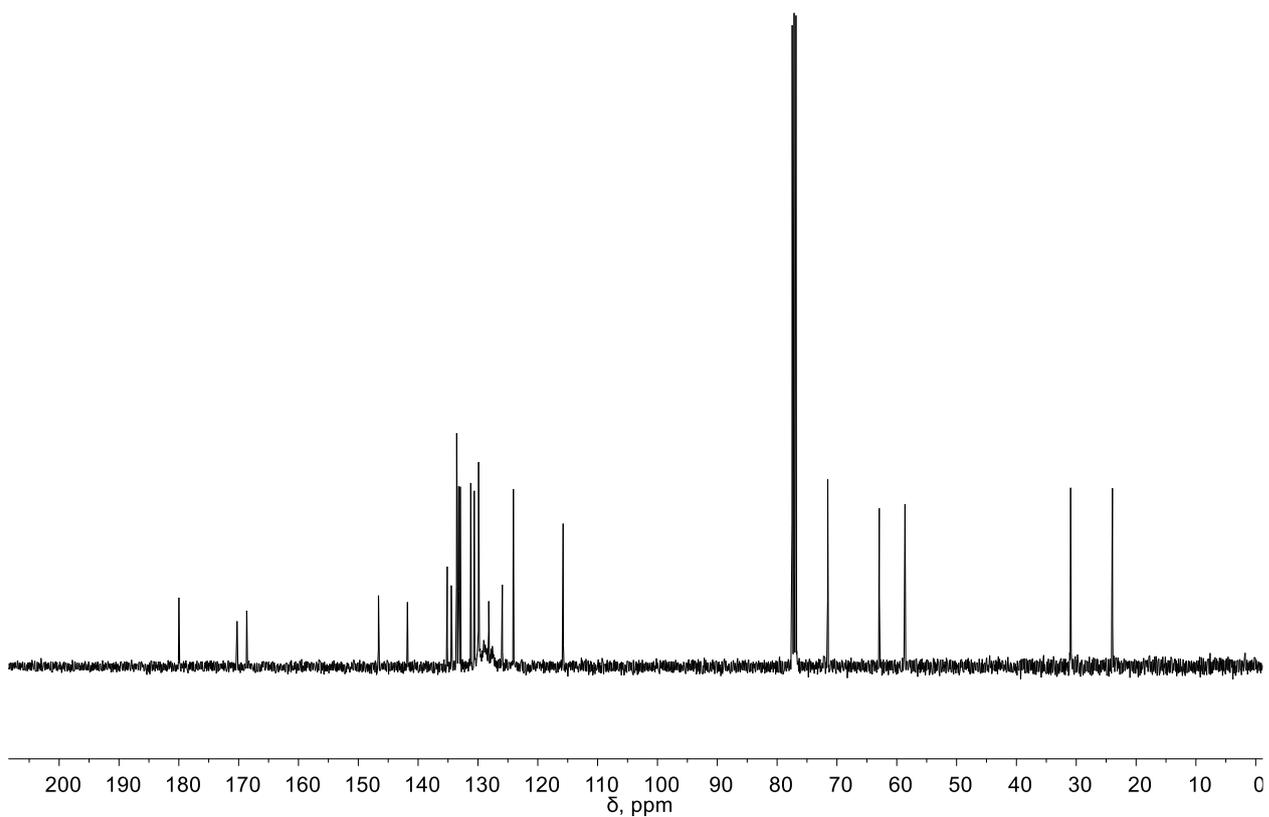
^1H NMR (CDCl_3 δ , ppm): 8.88 (d, $^3J = 2.1$ Hz, 1H (H-21)), 8.07 (d, $^2J = 9.3$ Hz, 1H (H-8)), 7.80 (dd, $^2J = 8.2$ Hz, $^3J = 2.1$ Hz, 1H (H-17)), 7.54-7.43 (m, 3H (H-24,25,26)), 7.35 (d, $^2J = 8.1$ Hz, 1H (H-18)), 7.25-7.15 (m, 1H (H-27)), 7.12 (dd, $^2J = 9.3$ Hz, $^3J = 2.6$ Hz, 1H (H-7)), 7.07-6.96 (m, 1H (H-23)), 6.78 (d, $^3J = 2.6$ Hz, 1H (H-5)), 5.64 (d, $^2J = 1.2$ Hz, 1H (H-28)), 4.24 (d, $^2J = 12.5$ Hz, 1H (H-15)), 4.16 (d, $^2J = 1.2$ Hz, 1H (H-28)), 3.75-3.62 (m, 1H (H-13)), 3.57 (dd, $J = 10.3$ Hz, $J = 6.3$ Hz, 1H (H-14)), 3.37 (dd, $^3J = 11.1$, $^3J = 5.7$ Hz, 1H (H-11)), 3.14 (d, $^2J = 12.5$ Hz, 1H (H-15)), 2.72-2.51 (m, 2H (H-12)), 2.27-2.17 (m, 1H (H-13)), 2.11-2.02 (m, 1H (H-14)).

^{13}C NMR (CDCl_3 δ , ppm): 179.99 (C-10), 170.26 (C-1), 168.65 (C-3), 146.63 (C-2), 141.78 (C-9), 135.14 (C-16), 134.45 (C-22), 133.59, 133.55 (C-19,20,21), 133.21 (C-7), 132.95 (C-5), 131.20 (C-18), 130.62 (C-25), 129.90 (C-17), 129.4-127.3 (C-23,24,26,27), 128.20 (C-6), 125.93 (C-4), 124.08 (C-8), 115.76 (C-28), 71.54 (C-11), 62.93 (C-15), 58.62 (C-14), 30.94 (C-12), 23.95 (C-13).

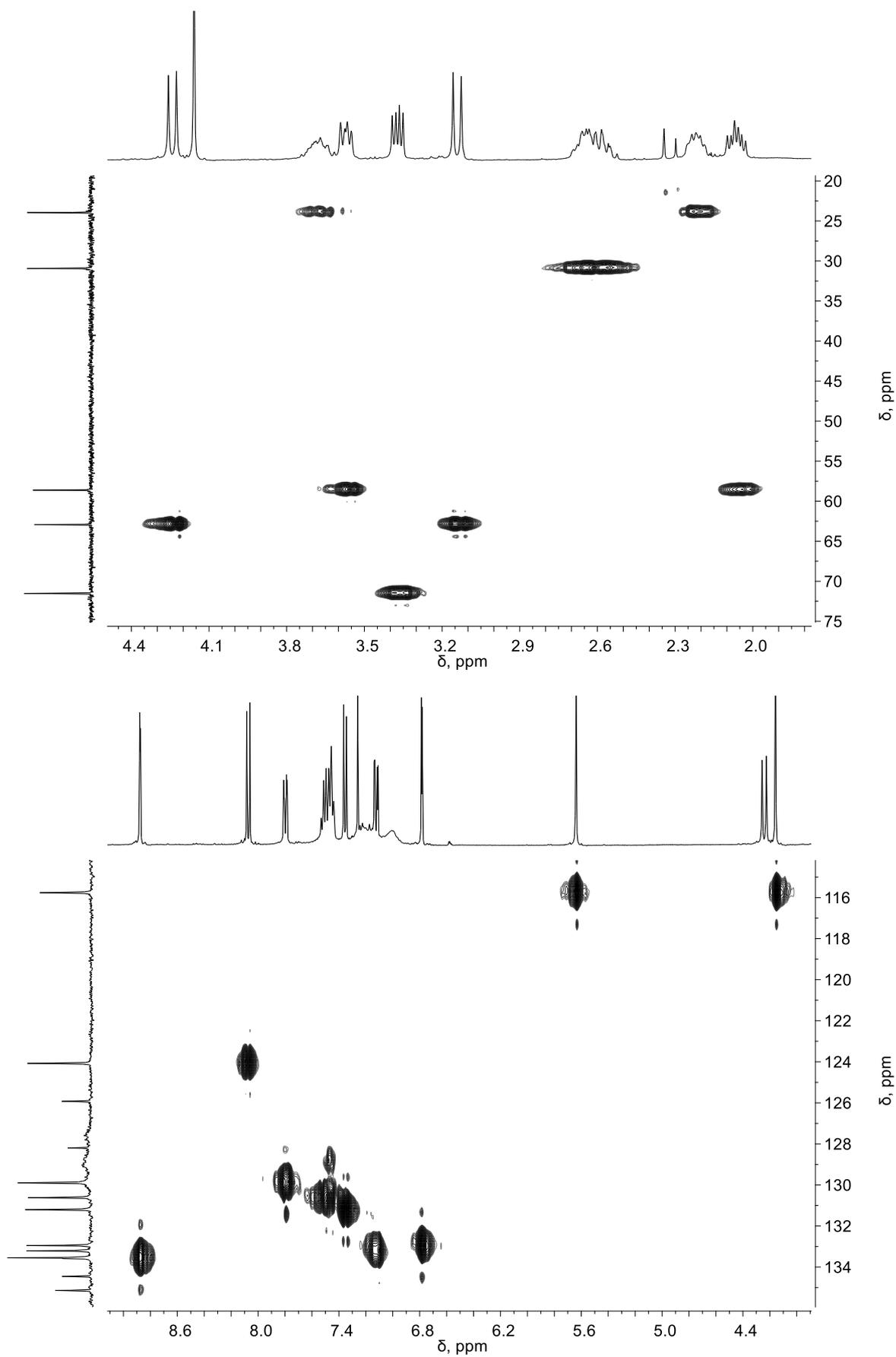
6. ^1H NMR spectrum of **3'**



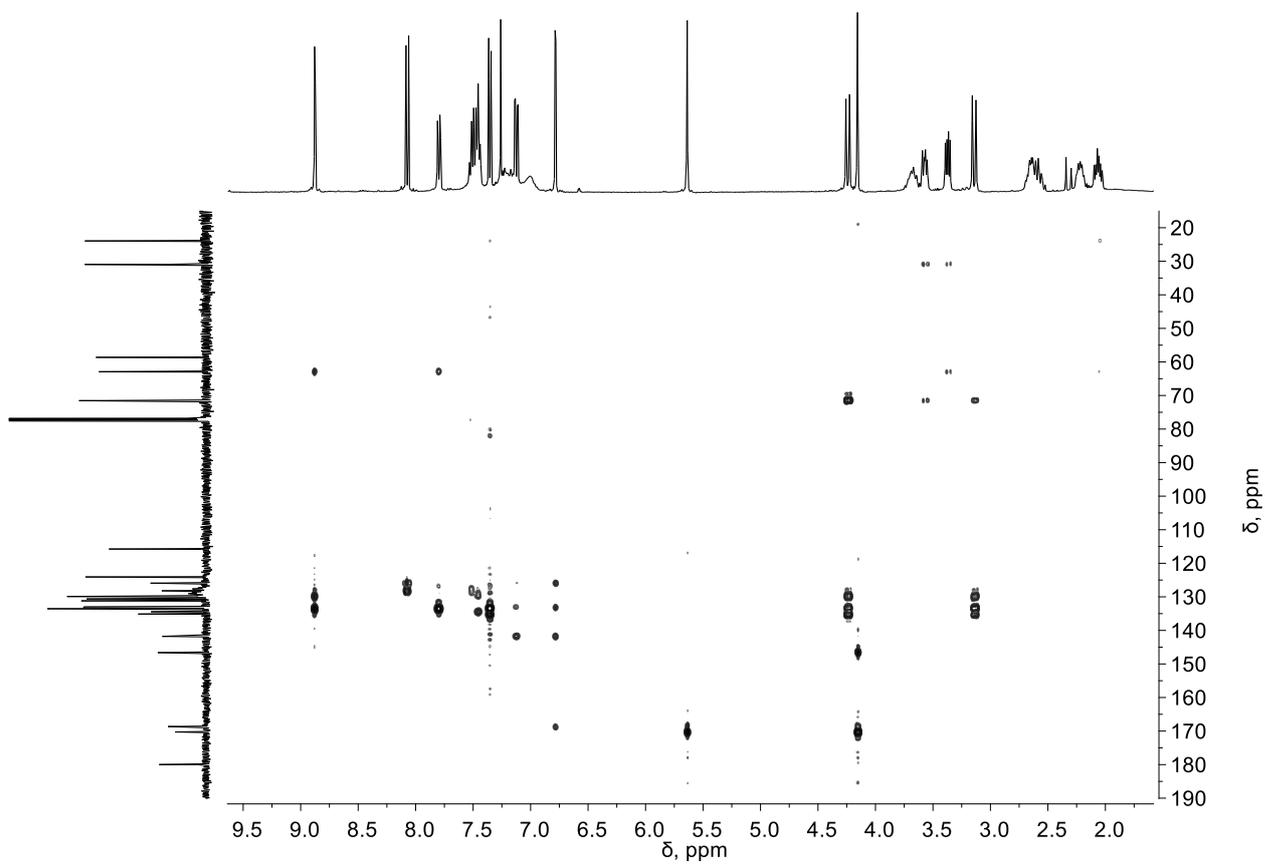
7. ^{13}C NMR spectrum of **3'**



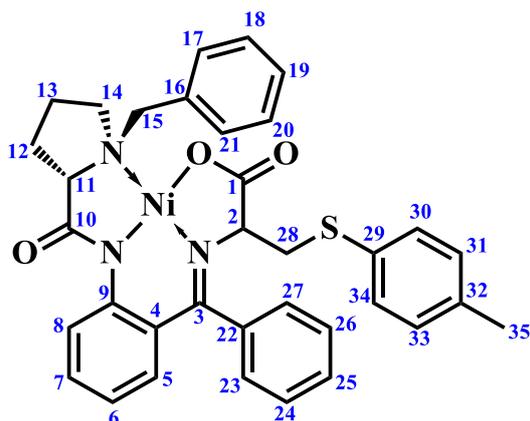
8. HSQC spectrum of 3'



9. HMBC spectrum of 3'



10. Atom numeration and signal assignment in the NMR spectra of **4a**



(S,R)-4a:

^1H NMR (CDCl_3 δ , ppm): 8.23 (d, $^3J = 8.7\text{Hz}$, 1H (H-8)), 8.10-8.04 (m, 2H (H-17,21)), 7.49-7.41 (m, 2H (H-24,26)), 7.38-7.27 (m, 5H (H-18,20,25,30,34)), 7.23-7.19 (m, 2H (H-19,27)), 7.18-7.13 (m, 1H (H-7)), 7.02-6.96 (m, 2H (H-31,33)), 6.66-6.61 (m, 1H (H-6)), 6.56 (dd, $^3J = 8.2$, $^4J = 1.5$, 1H (H-5)), 6.50 (m, 1H (H-23)), 4.45 (d, $^2J = 12.6$, 1H (H-15)), 4.26 (dd, $^3J = 6.0$, $^3J = 2.5$, 1H (H-2)), 3.74-3.67 (m, 1H (H-13)), 3.61 (d, $^2J = 12.6$ Hz, 1H (H-15)), 3.64-3.57 (m, 1H (H-14)), 3.46 (dd, $J = 10.5$, $J = 6.5$, 1H (H-11)), 3.23 (dd, $^2J = 13.3$, $^3J = 2.5$, 1H (H-28)), 2.94-2.85 (m, 1H (H-12)), 2.87 (dd, $^2J = 13.3$ Hz, $^3J = 6.0$ Hz, 1H (H-28)), 2.56-2.43 (m, 1H (H-12)), 2.25 (s, 3H (H-35)), 2.12-1.97 (m, 2H (H-13,14)).

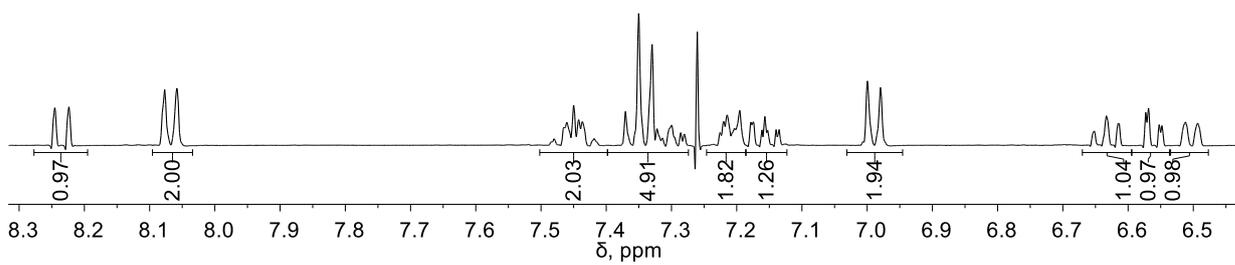
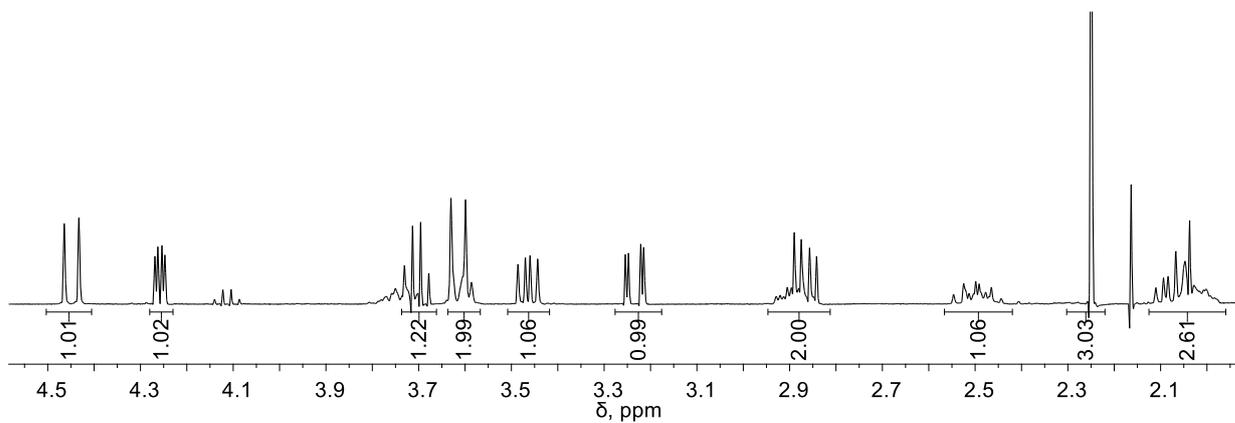
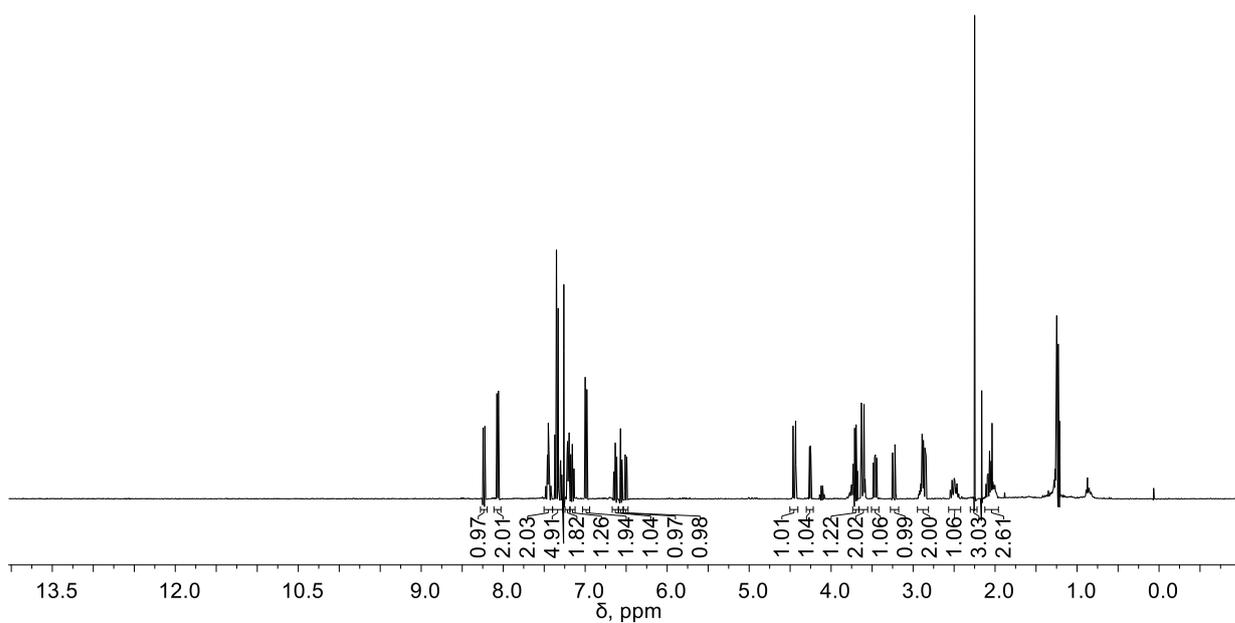
^{13}C NMR (CDCl_3 δ , ppm): 180.59 (C-10), 178.40 (C-1), 171.76 (C-3), 142.92 (C-9), 137.46 (C-32), 133.99 (C-16), 133.41 (C-5), 133.39 (C-22), 132.50 (C-7), 132.18 (C-29), 132.04 (C-18,20), 131.74 (C-17,21), 129.97 (C-31,33), 129.88 (C-25), 129.00 (C-24,26), 128.98 (C-19), 128.93 (C-30,34), 127.53 (C-23), 126.85, 126.35 (C-4), 123.86 (C-8), 120.68 (C-6), 70.67 (C-11), 69.54 (C-2), 63.43 (C-15), 57.30 (C-14), 39.43 (C-28), 30.87 (C-12), 23.32 (C-13), 21.11 (C-35).

(S,S)-4a:

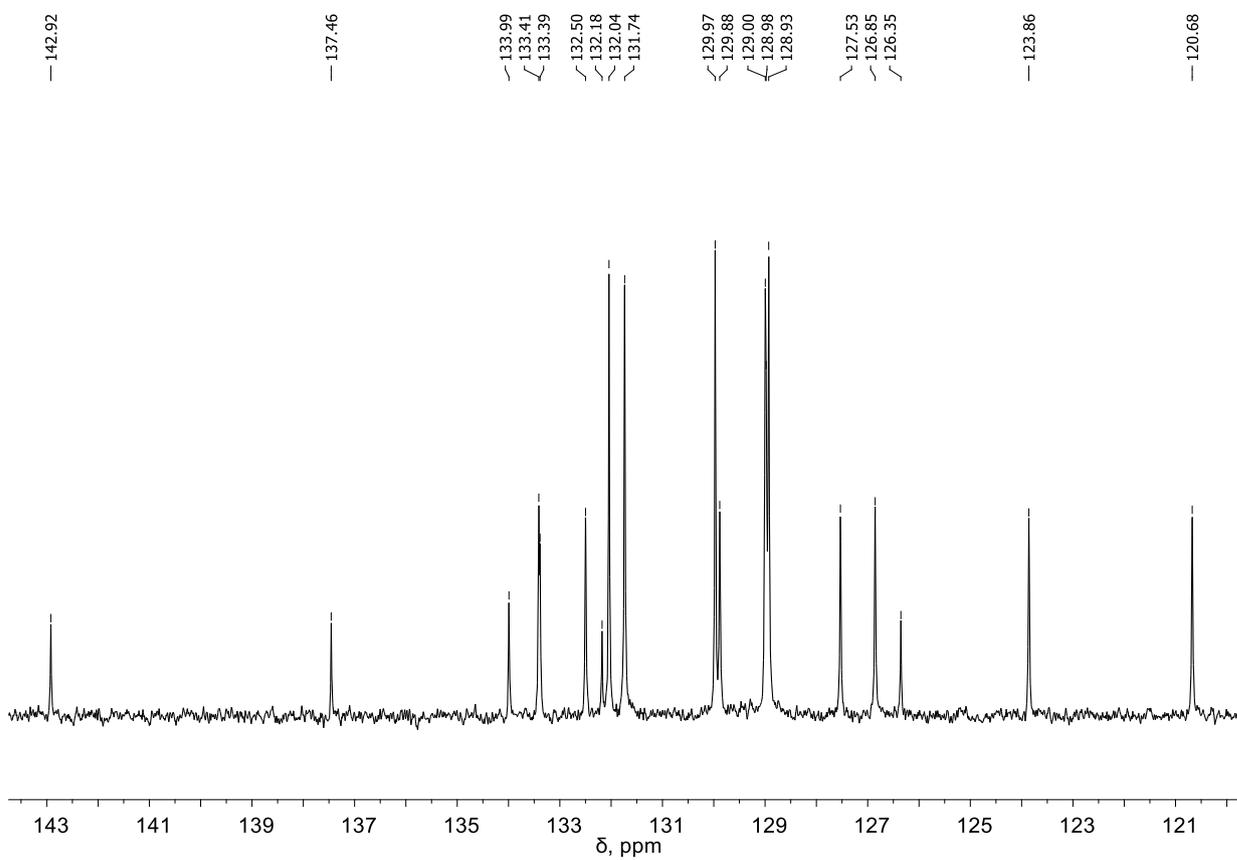
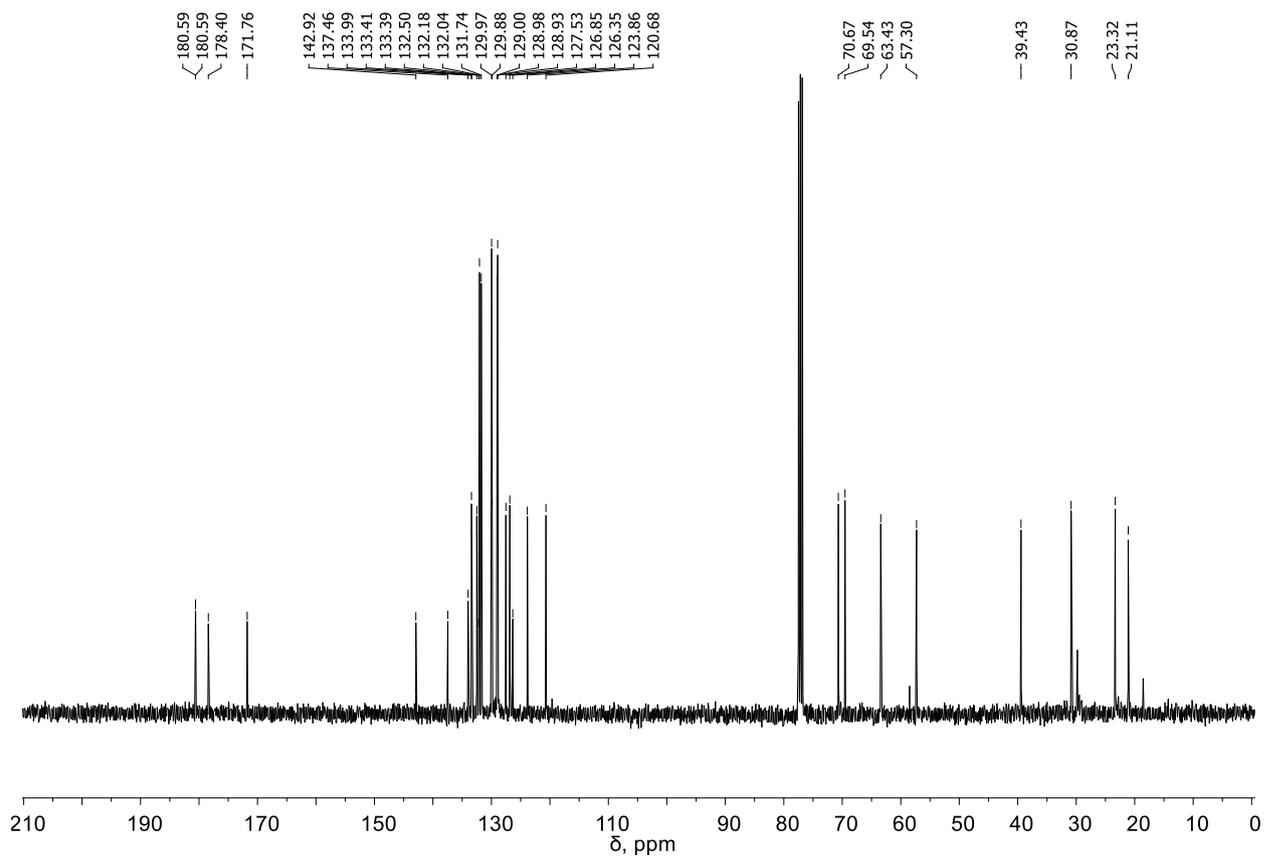
^1H NMR (CDCl_3 δ , ppm): 8.52 (d, $^3J = 8.7$ Hz, 1H (H-8)), 7.91-7.85 (m, 2H (H-17,21)), 7.49-7.24 (m, 9H (H-7,18,19,20,24,25,26,30,34)), 7.19-7.12 (m, 1H (H-27)), 6.93-6.87 (m, 2H (H-31,33)), 6.71-6.64 (m, 3H (H-5,6,23)), 4.80 (d, $^2J = 13.3$ Hz, 1H (H-15)), 4.18 (dd, $^3J = 6.7$ Hz, $^3J = 2.9$ Hz, 1H (H-2)), 4.15-4.05 (m, 1H (H-14)), 3.86 (d, $^2J = 13.3$ Hz, 1H (H-15)), 3.65 (dd, $J = 9.9$ Hz, $J = 4.0$ Hz, 1H (H-11)), 3.18 (dd, $^2J = 13.5$ Hz, $^3J = 2.9$ Hz, 1H (H-28)), 3.00 (dd, $^2J = 13.5$ Hz, $^3J = 6.7$ Hz, 1H (H-28)), 2.66-2.52 (m, 2H (H-12,14)), 2.26-2.19 (m, 1H (H-13)), 2.19 (s, 3H (H-35)), 2.08-1.95 (m, 1H (H-13)), 1.88-1.77 (m, 1H (H-12)).

^{13}C NMR (CDCl_3 δ , ppm): 182.46 (C-10), 178.60 (C-1), 172.43 (C-3), 143.26, 137.24 (C-32), 134.24, 133.77 (C-5), 132.73, 132.25, 132.02, 131.95 (C-30,34), 131.49, 129.80 (C-31,33), 129.58, 129.25 (C-17,21), 129.18, 129.09, 128.64 (C-29), 128.09 (C-23), 126.68 (C-27), 125.78 (C-4), 124.06 (C-8), 120.75, 69.74 (C-2), 68.66 (C-11), 61.68 (C-15), 57.50 (C-14), 40.08 (C-28), 30.72 (C-13), 23.54 (C-12), 21.07 (C-35).

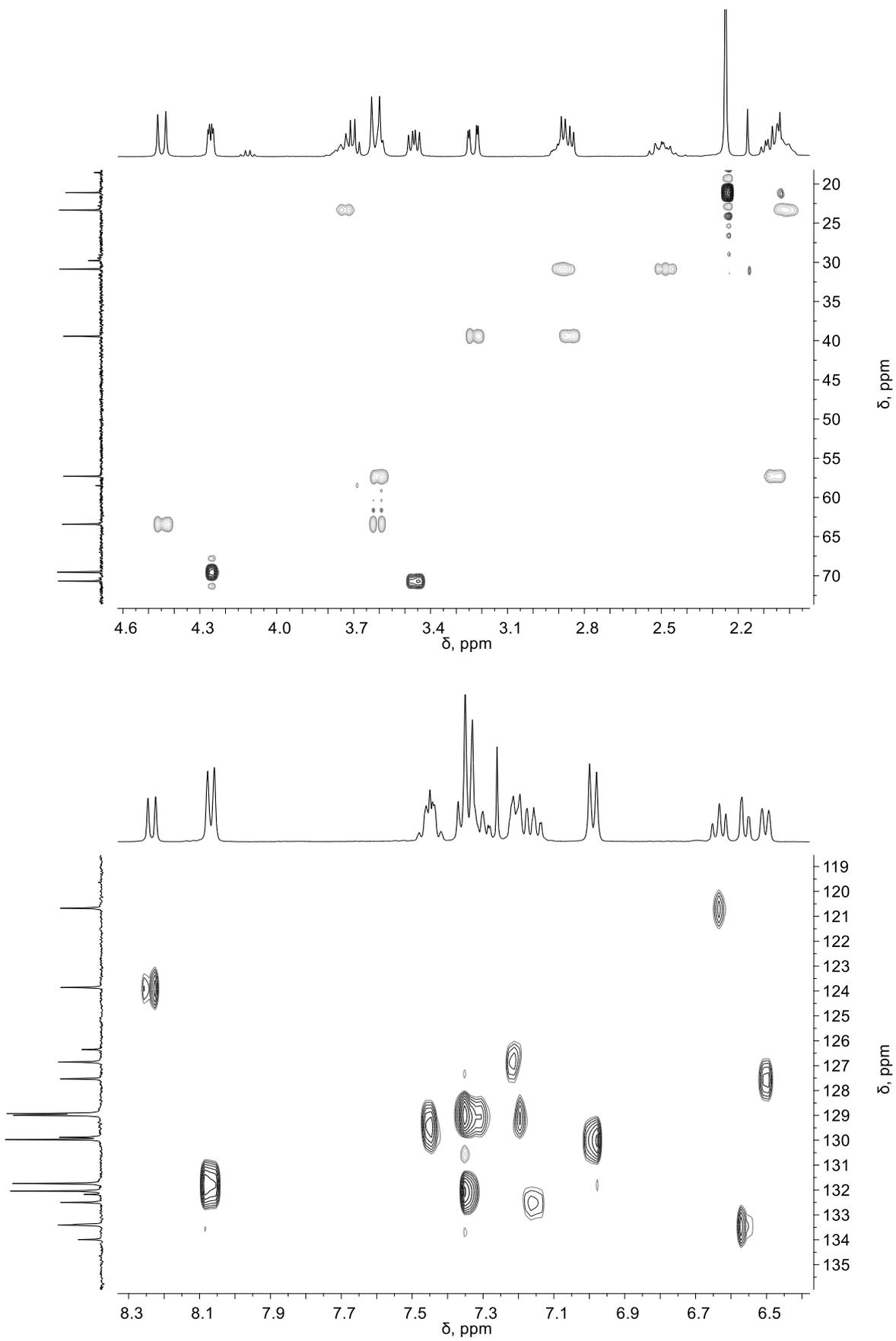
11. ¹H NMR spectrum of (*S,R*)-4a



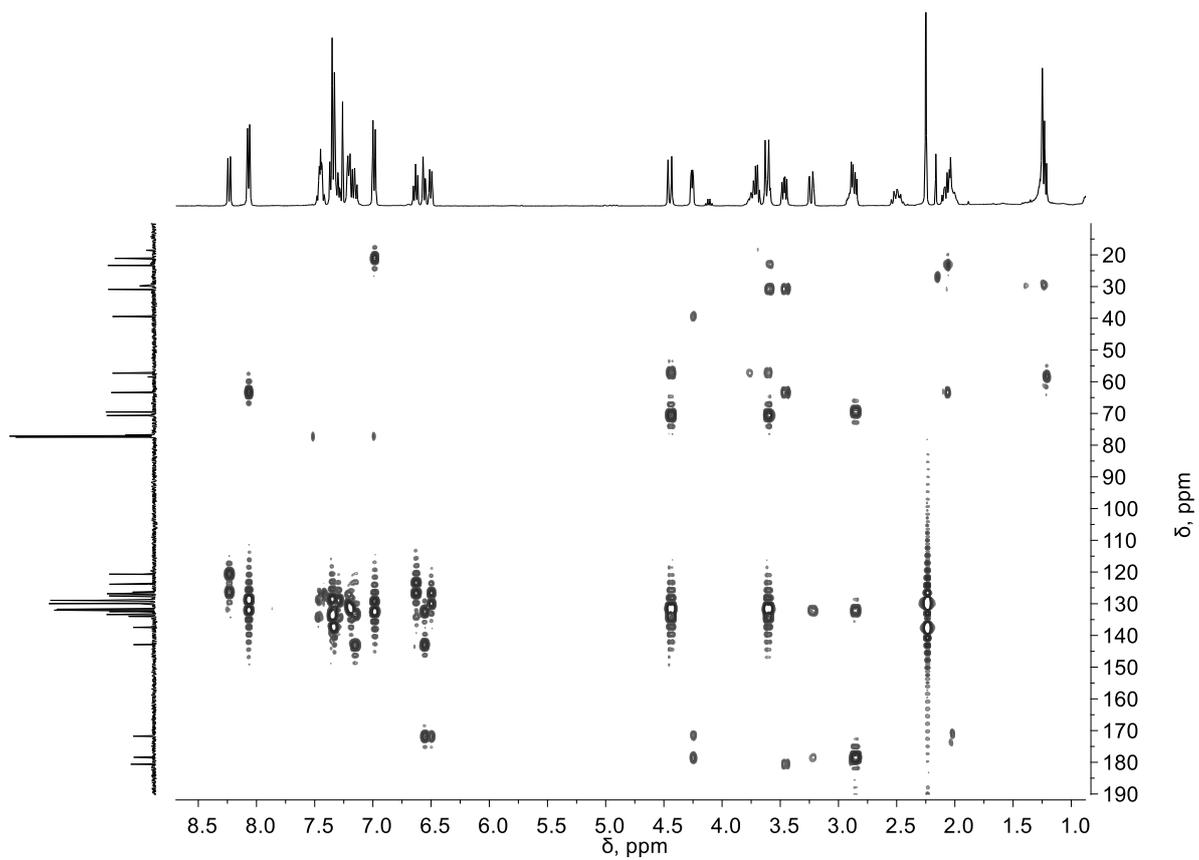
12. ^{13}C NMR spectrum of (*S,R*)-4a



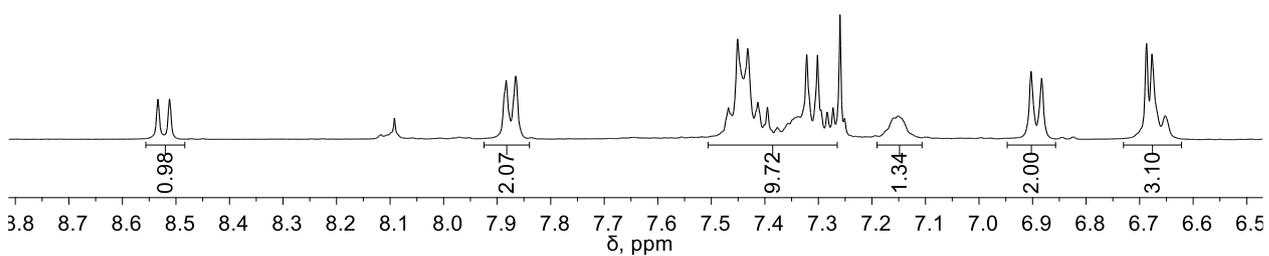
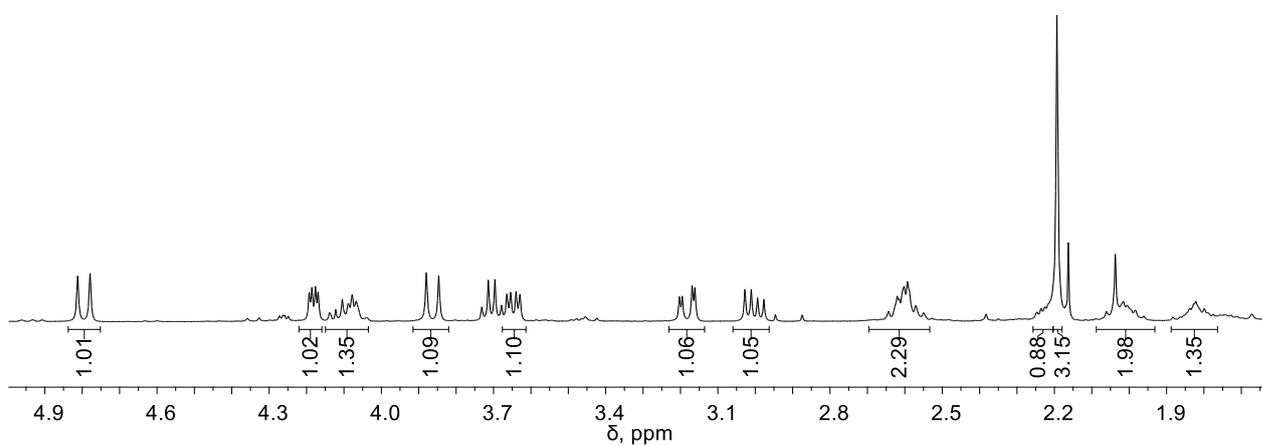
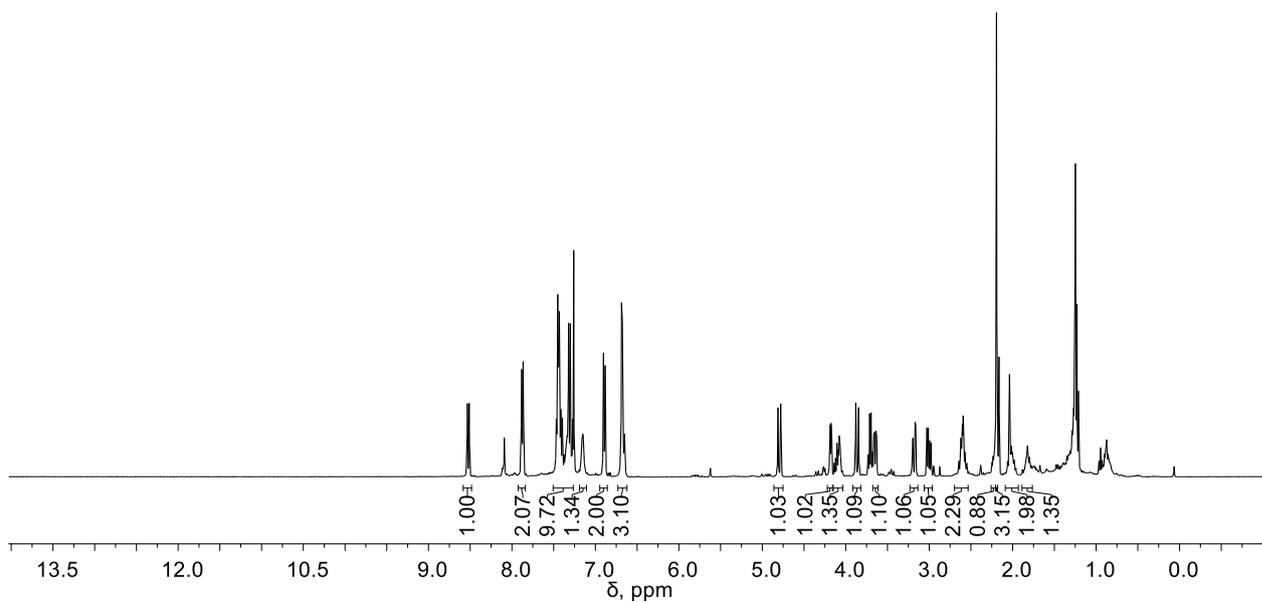
13. HSQC spectrum of (*S,R*)-4a



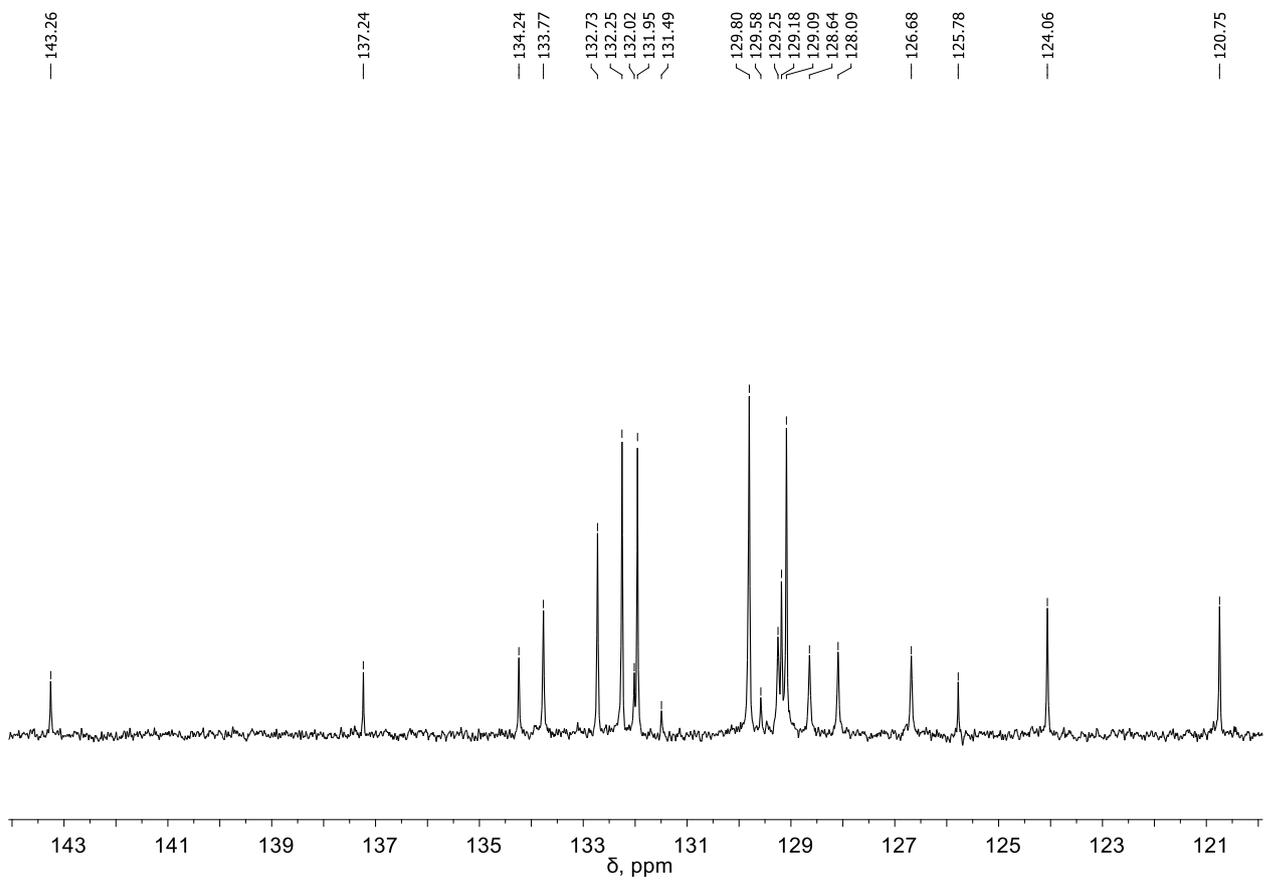
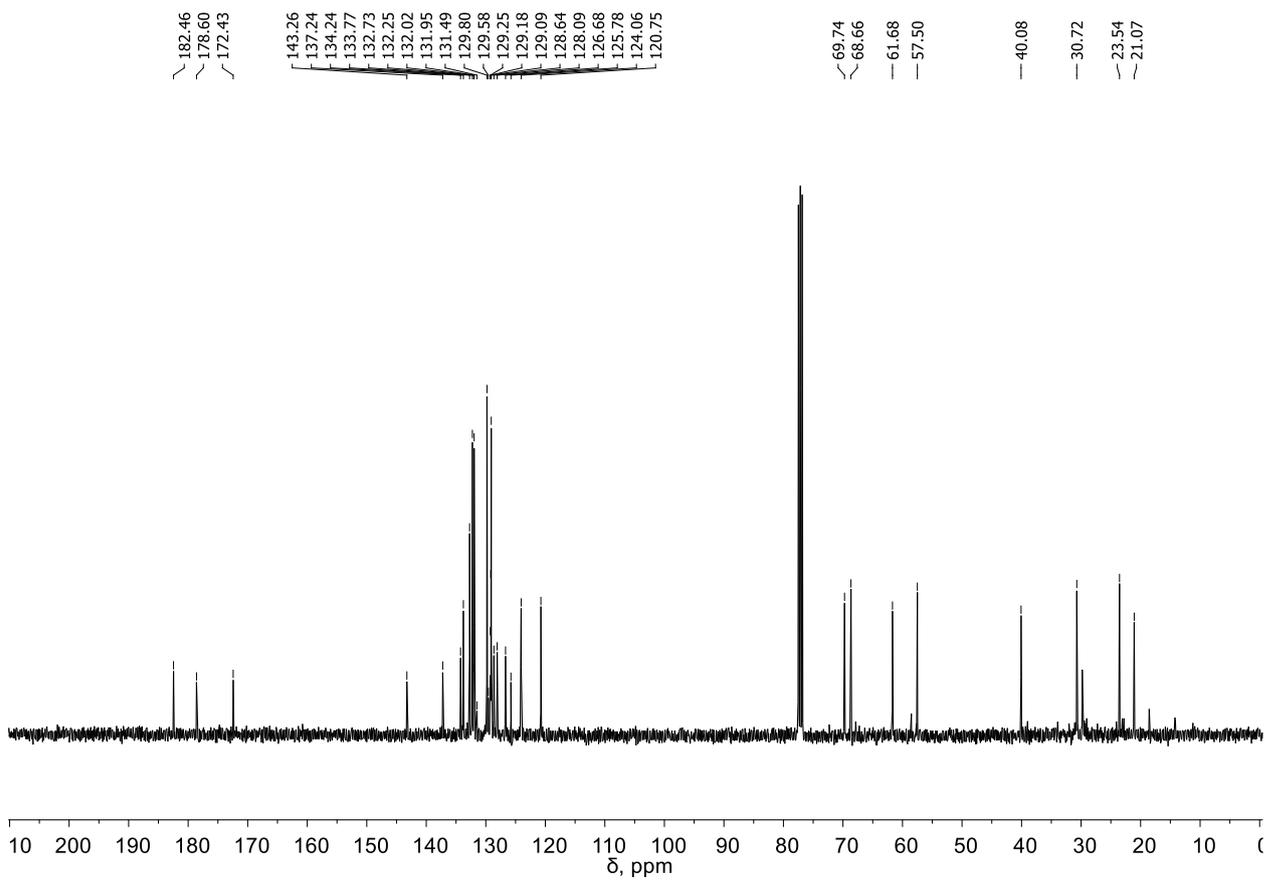
14. HMBC spectrum of (*S,R*)-4a



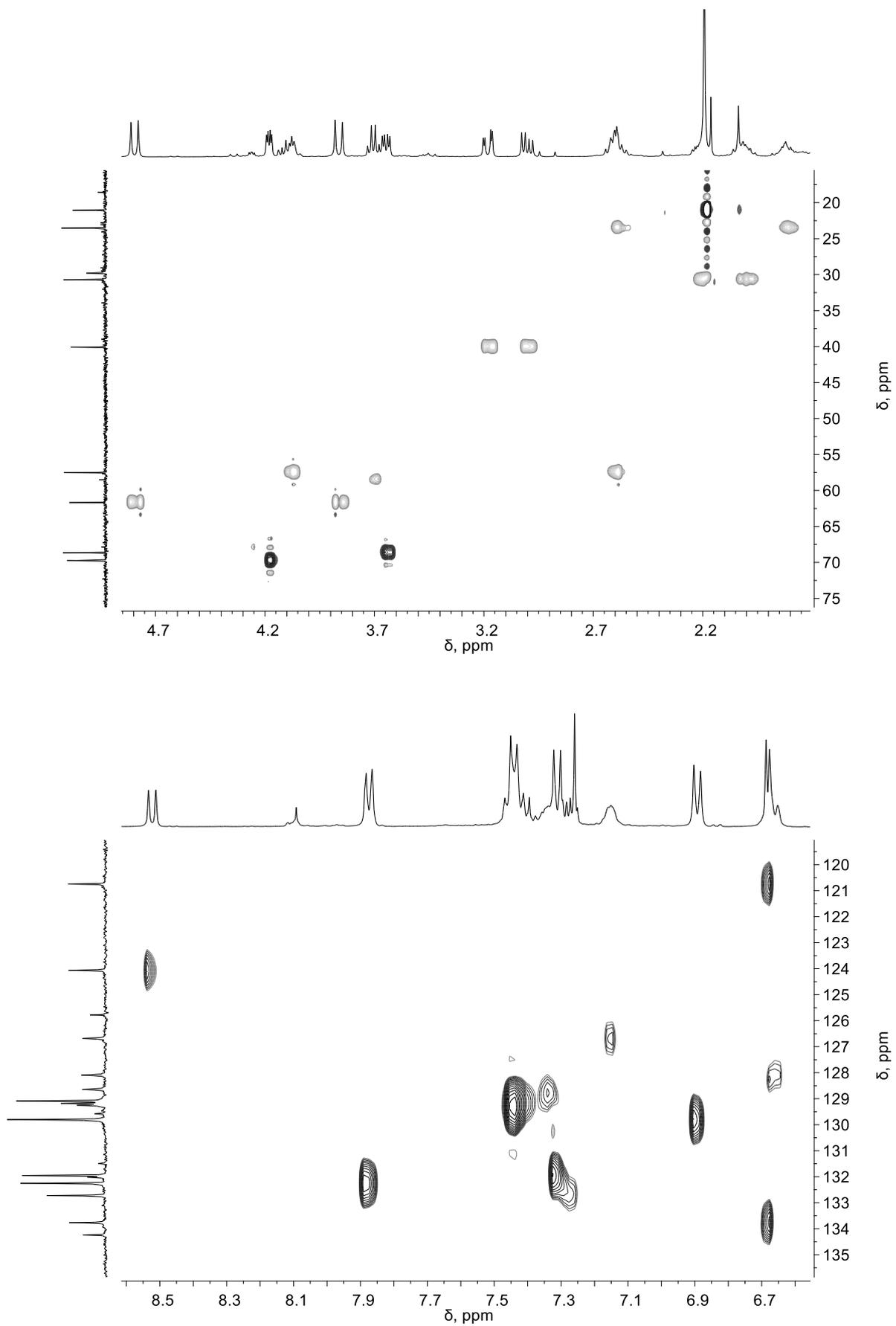
15. ^1H NMR spectrum of (*S,S*)-4a



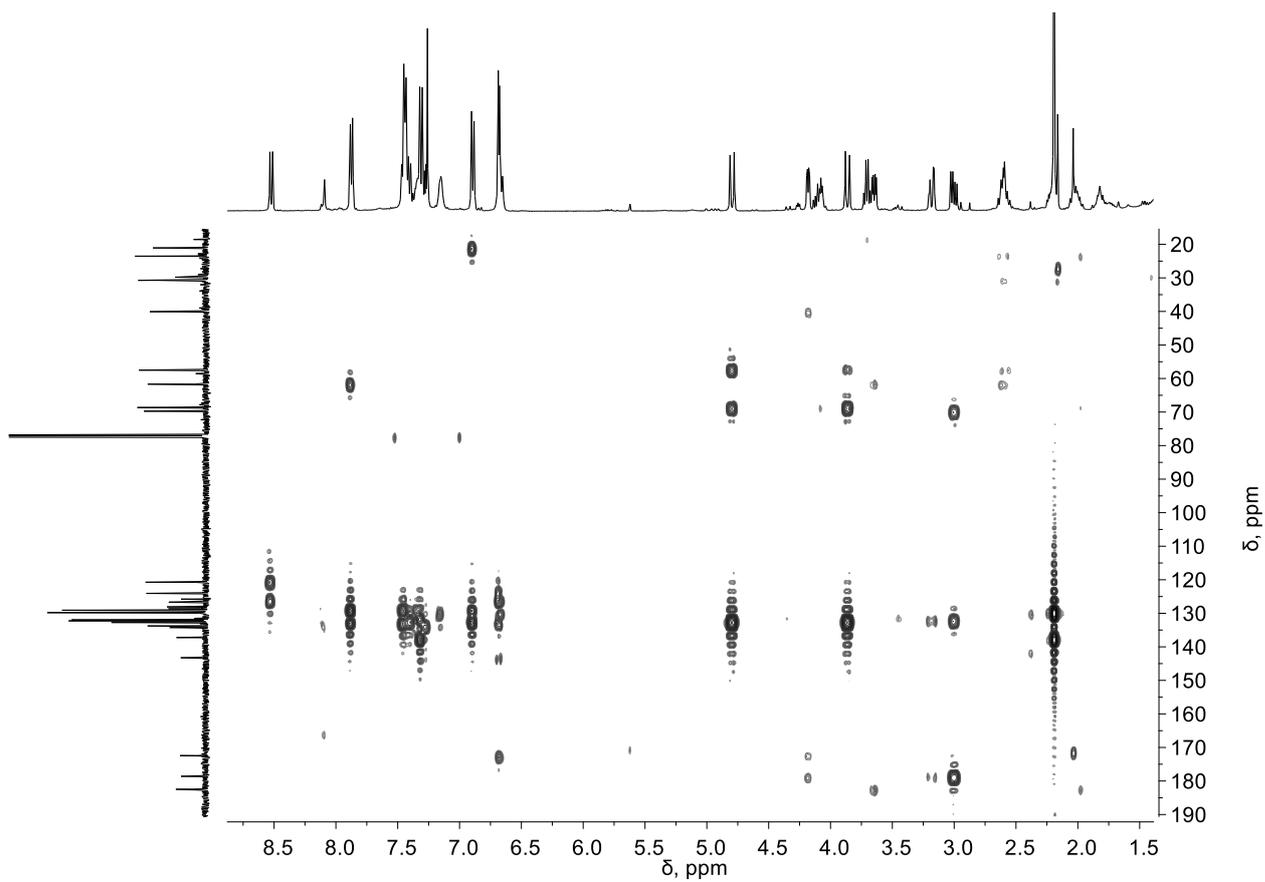
16. ^{13}C NMR spectrum of (*S,S*)-4a



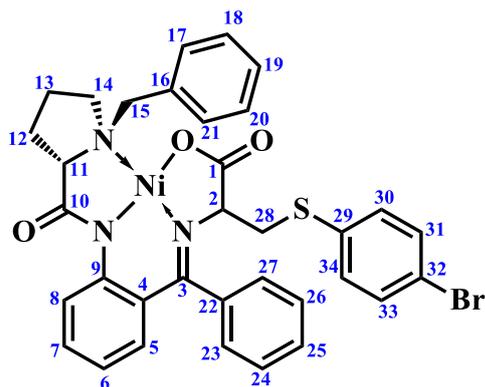
17. HSQC spectrum of (*S,S*)-4a



18. HMBC spectrum of (*S,S*)-4a



19. Atom numeration and signal assignment in the NMR spectra of **4b**



(S,R)-4b:

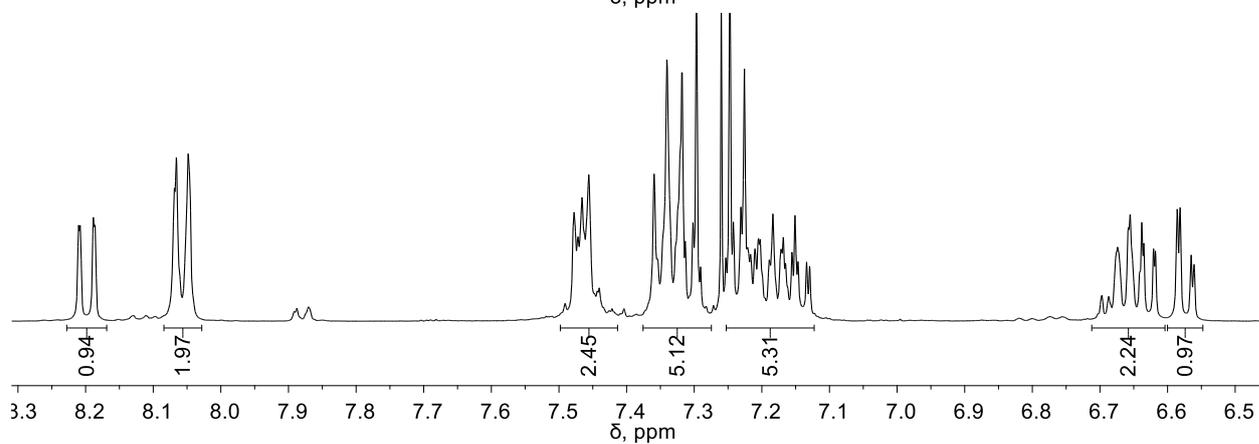
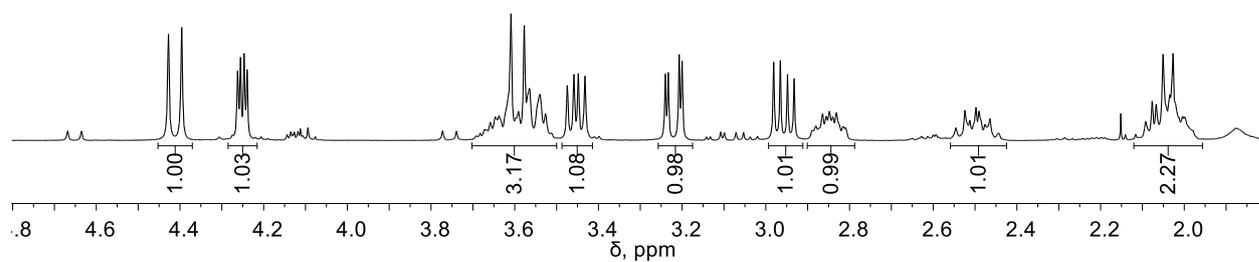
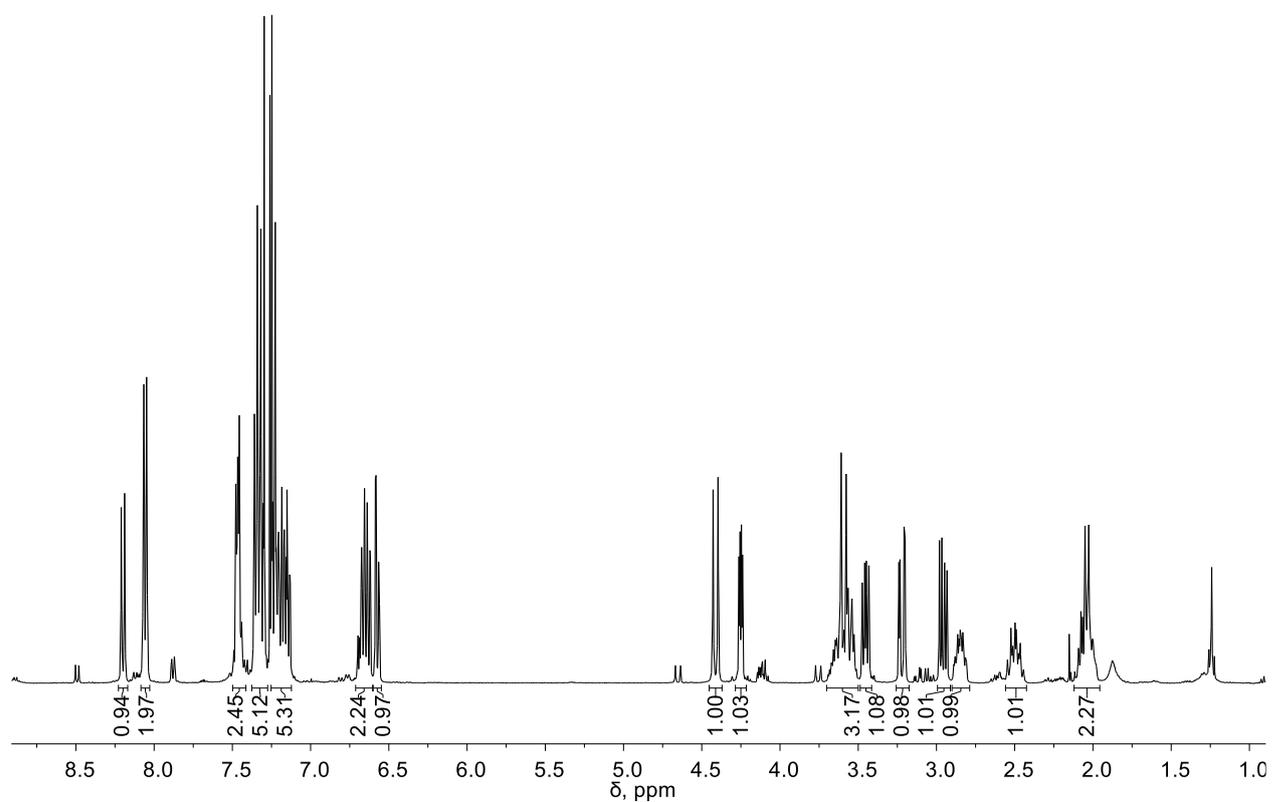
^1H NMR (CDCl_3 δ , ppm): 8.20 (dd, $^3J = 8.6$ Hz, $^4J = 0.8$ Hz, 1H (H-8)), 8.08-8.03 (m, 2H (H-17,21)), 7.50-7.44 (m, 2H (H-24,26)), 7.38-7.28 (m, 5H (H-18,20,25,30,34)), 7.27-7.12 (m, 5H (H-7,19,23,31,33)), 6.71-6.61 (m, 2H (H-6,27)), 6.57 (dd, $^3J = 8.3$ Hz, $^4J = 1.7$ Hz, 1H (H-5)), 4.41 (d, $^2J = 12.7$ Hz, 1H (H-15)), 4.25 (dd, $^3J = 6.6$ Hz, $^3J = 2.8$ Hz, 1H (H-2)), 3.70-3.51 (m, 3H (H-13,14,15)), 3.45 (dd, $^3J = 10.6$ Hz, $^3J = 6.4$ Hz, 1H (H-11)), 3.22 (dd, $^2J = 13.2$ Hz, $^3J = 2.8$ Hz, 1H (H-28)), 2.96 (dd, $^2J = 13.2$ Hz, $^3J = 6.3$ Hz, 1H (H-28)), 2.90-2.80 (m, 1H (H-12)), 2.56-2.44 (m, 1H (H-12)), 2.10-1.97 (m, 2H (H-13,14)).

^{13}C NMR (CDCl_3 δ , ppm): 180.50 (C-10), 178.00 (C-1), 171.86 (C-3), 142.88 (C-9), 134.81 (C-29), 133.85 (C-22), 133.43 (C-5), 133.34 (C-16), 132.63 (C-7), 132.48 (C-30,34), 132.22 (C-31,33), 131.65 (C-17,21), 130.00 (C-24), 129.11 (C-26), 129.06 (C-25), 128.97 (C-19), 128.92 (C-18,20), 127.41 (C-27), 126.85 (C-23), 126.23 (C-4), 123.83 (C-8), 121.15 (C-32), 120.75 (C-6), 70.61 (C-11), 69.05 (C-2), 63.45 (C-15), 57.26 (C-14), 38.68 (C-28), 30.84 (C-12), 23.34 (C-13).

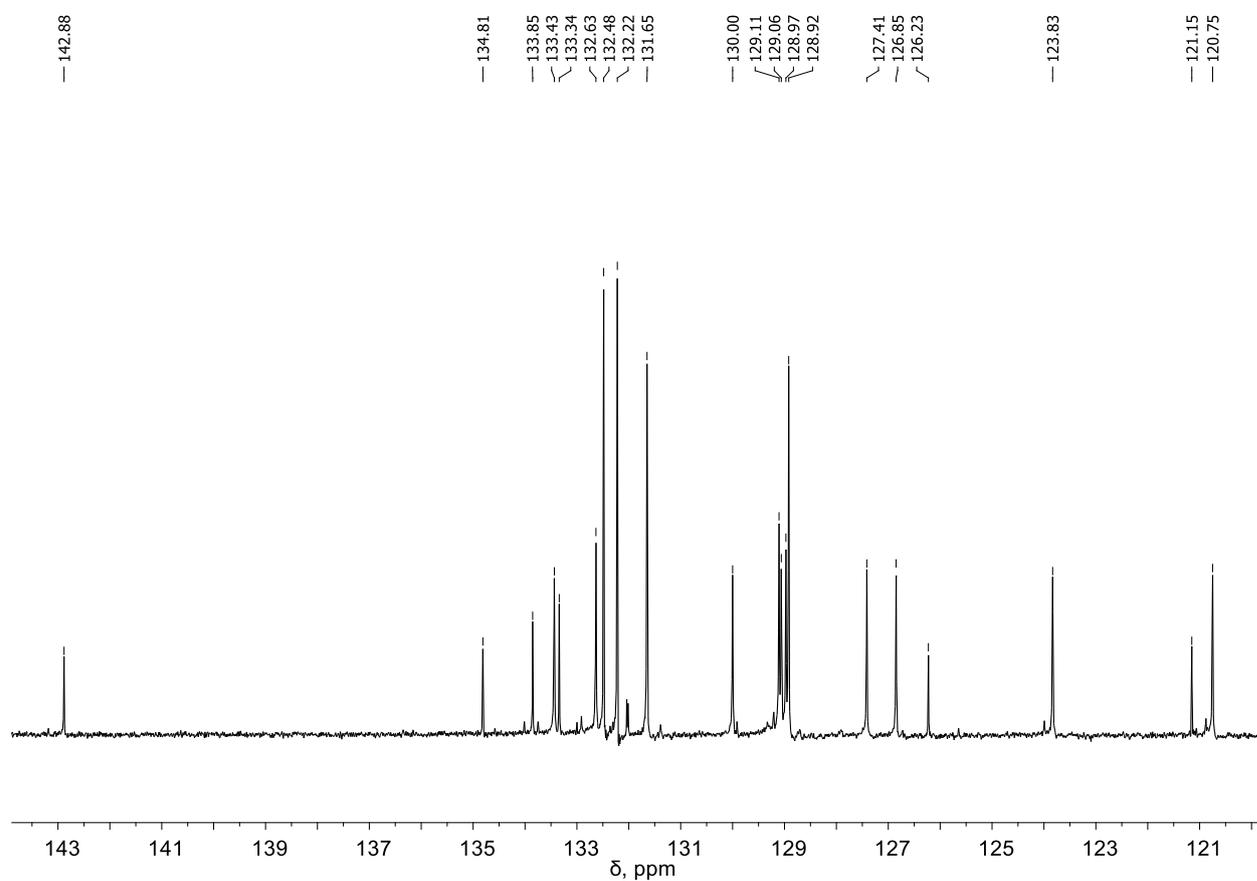
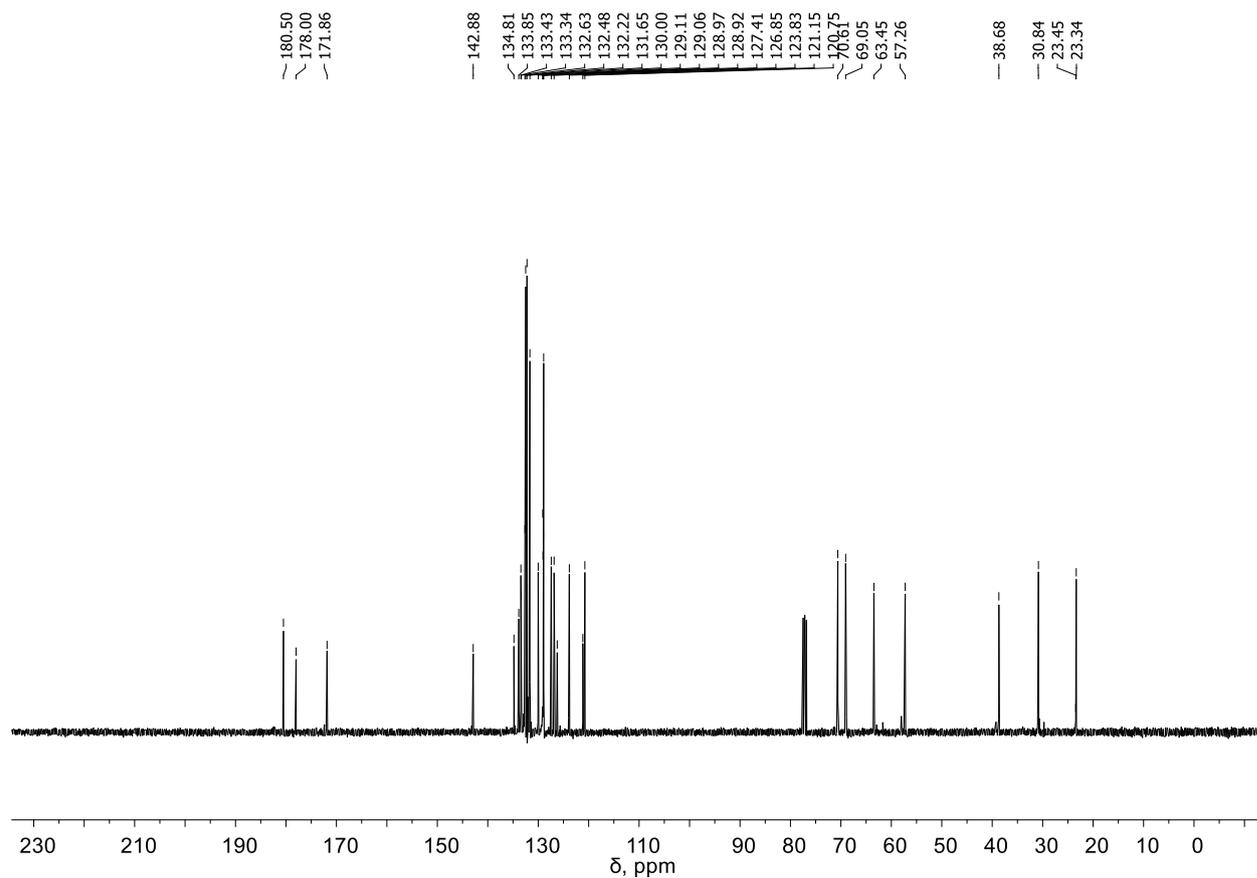
(S,S)-4b:

^1H NMR (CDCl_3 δ , ppm): 8.48 (d, $^3J = 8.6$ Hz, 1H), 7.86 (m, 2H), 7.49-7.39 (m, 6H), 7.23-7.12 (m, 7H), 6.70-6.84 (m, 2H), 4.66 (d, $^2J = 13.3$ Hz, 1H), 4.16-4.06 (m, 3H), 3.76 (d, $J = 13.3$ Hz, 1H), 3.66 (dd, $J = 9.9, 4.0$ Hz, 1H), 3.11 (dd, $J = 13.5, 3.5$ Hz, 1H), 3.04 (dd, $J = 13.3, 7.1$ Hz, 1H), 2.65-2.52 (m, 2H), 2.26-2.17 (m, 1H), 1.88-1.80 (m, 1H).

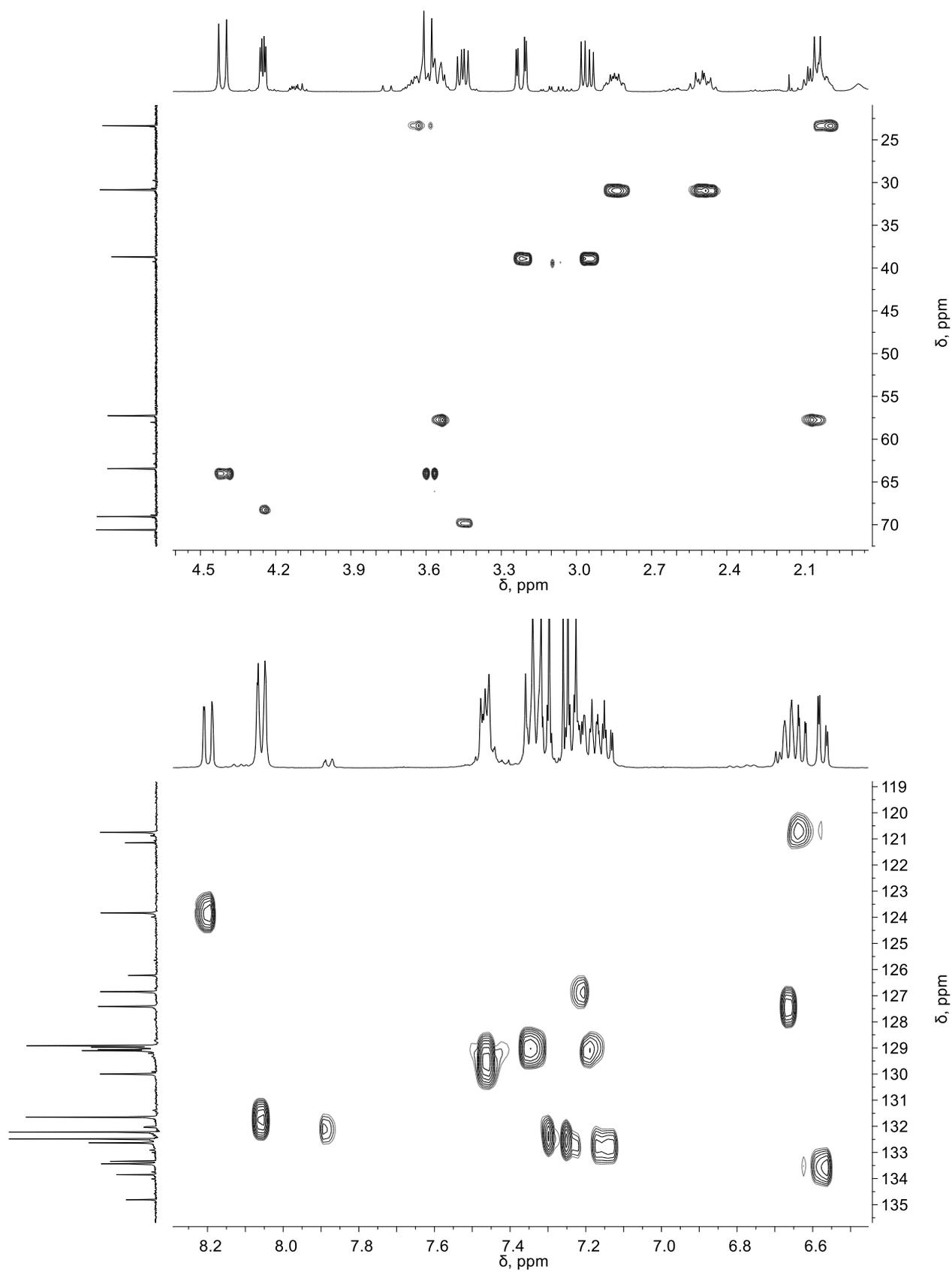
20. ¹H NMR spectrum of (*S,R*)-4b



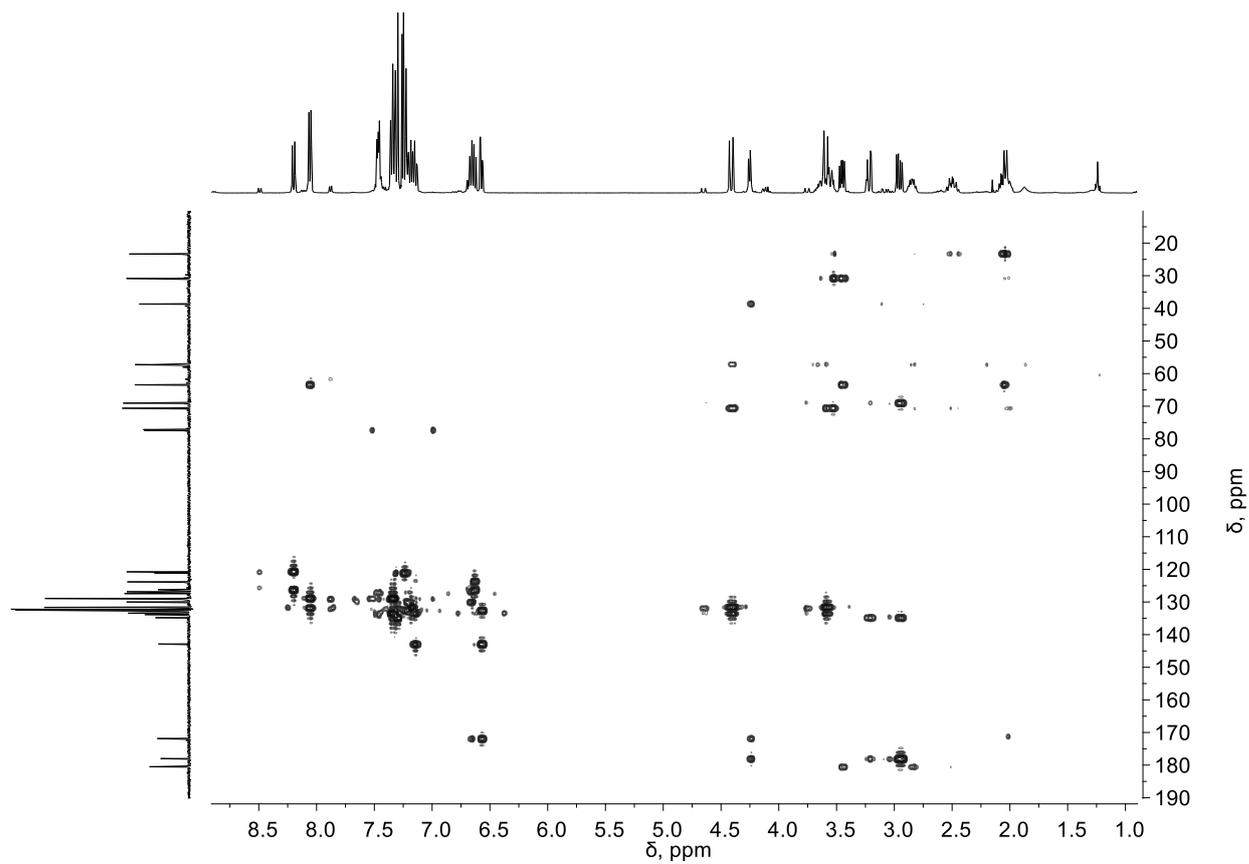
21. ^{13}C NMR spectrum of (*S,R*)-4b



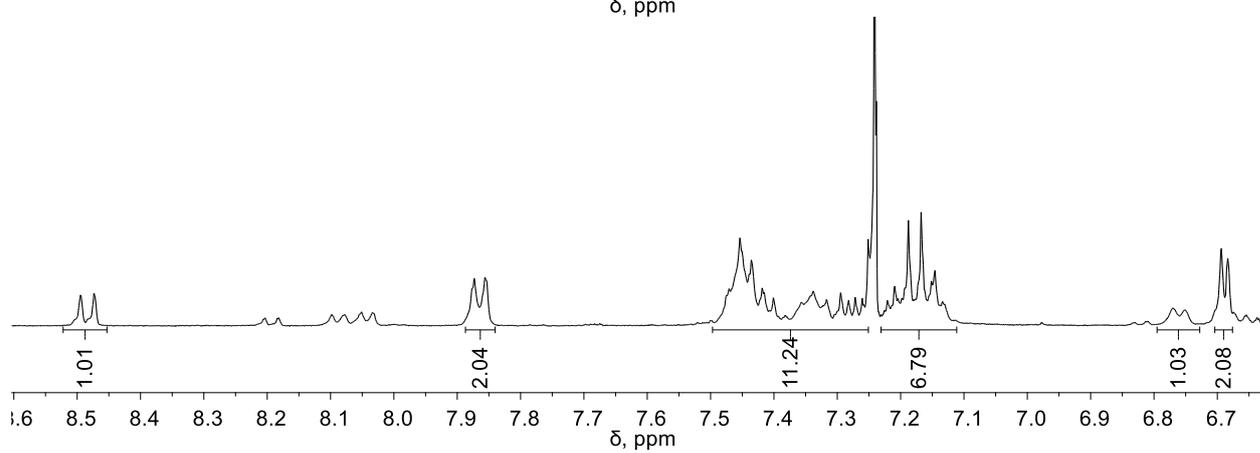
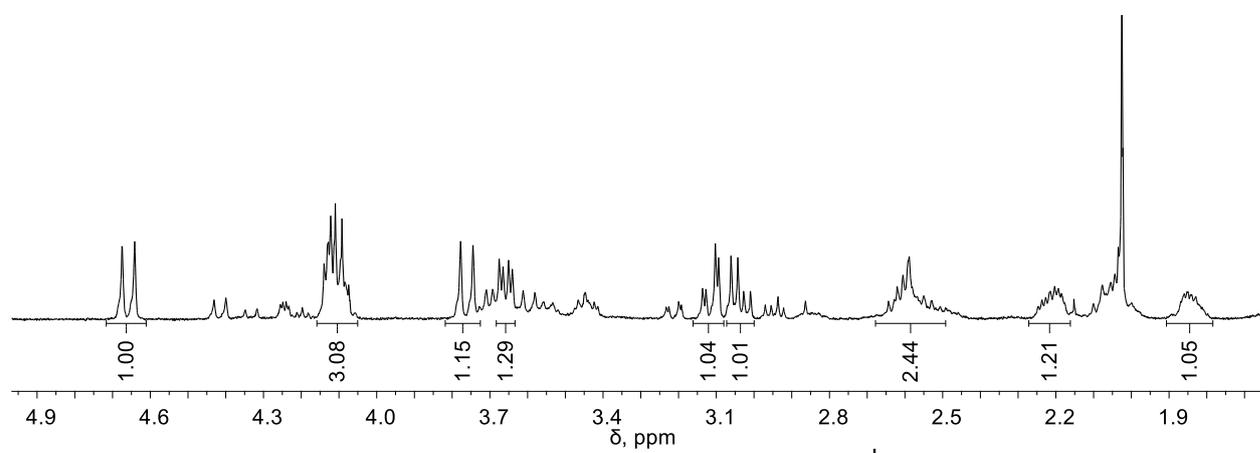
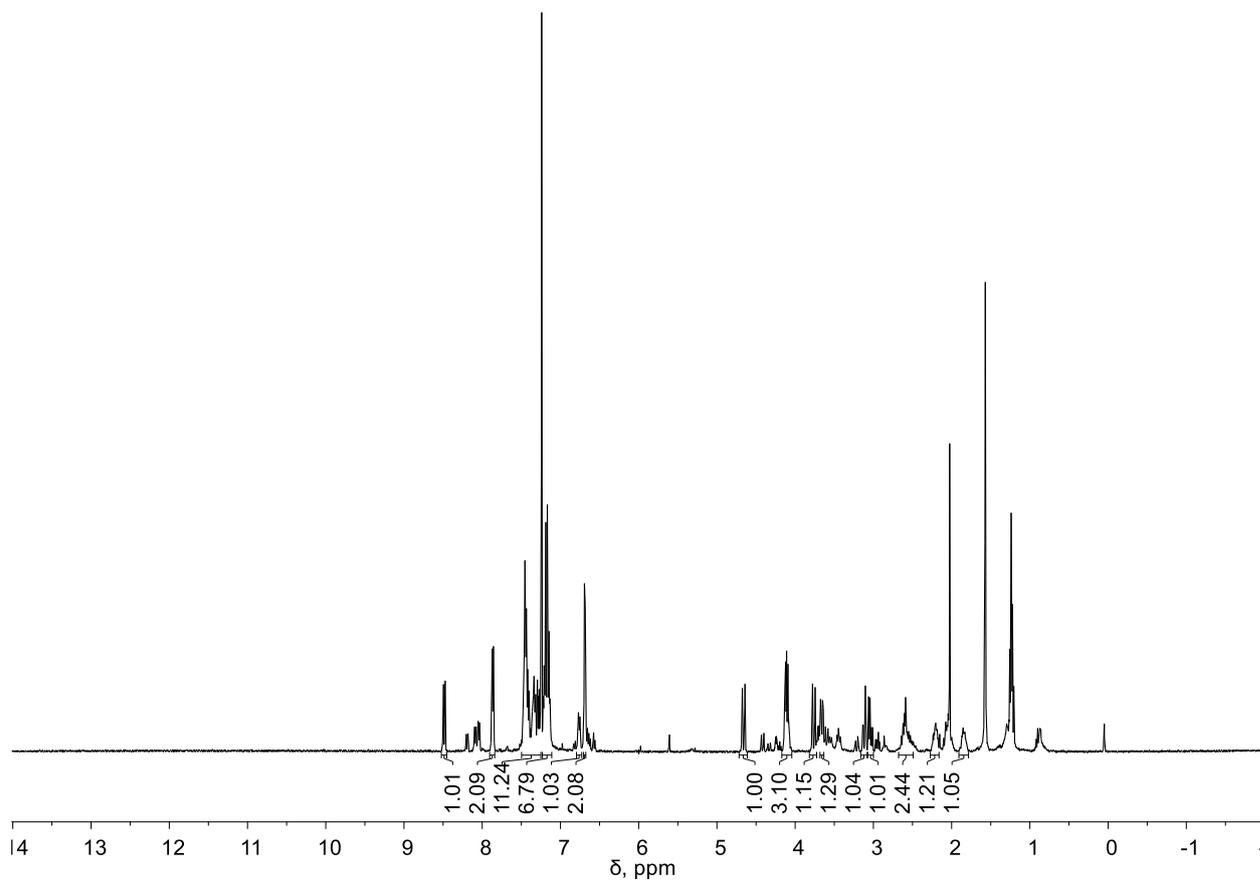
22. HSQC spectrum of (*S,R*)-4b



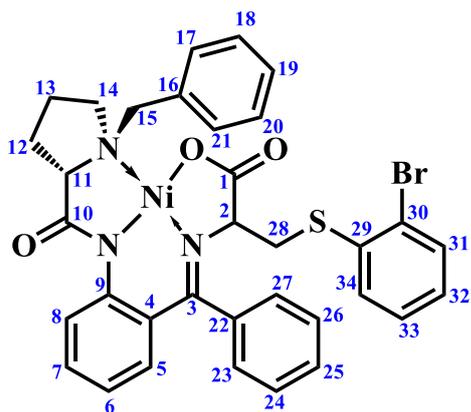
23. HMBC spectrum of (*S,R*)-4b



24. ^1H NMR spectrum of (*S,S*)-**4b**



25. Atom numeration and signal assignment in the NMR spectra of **4c**



(S,R)-4c:

^1H NMR (CDCl_3 δ , ppm): 8.23 (dd, $^3\text{J} = 8.7$ Hz, $^4\text{J} = 0.7$ Hz, 1H (H-8)), 8.05 (m, 2H (H-17,21)), 7.55 (dd, $^3\text{J} = 7.9$ Hz, $^4\text{J} = 1.4$ Hz, 1H (H-31)), 7.51-7.43 (m, 2H (H-19,26)), 7.39-7.31 (m, 3H (H-18,20,24)), 7.25-7.18 (m, 3H (H-25,27,34)), 7.18-7.14 (m, 1H (H-7)), 7.14-7.09 (m, 1H (H-33)), 7.03-6.99 (m, 1H (H-32)), 6.76 (d, $^3\text{J} = 7.7$ Hz, 1H (H-23)), 6.68-6.62 (m, 1H (H-6)), 6.60 (dd, $^3\text{J} = 8.3$ Hz, $^4\text{J} = 1.9$ Hz, 1H (H-5)), 4.43 (d, $^2\text{J} = 12.7$ Hz, 1H (H-15)), 4.36 (dd, $^3\text{J} = 5.9$ Hz, $^3\text{J} = 3.1$ Hz, 1H (H-2)), 3.76-3.65 (m, 1H (H-13)), 3.59 (d, $^2\text{J} = 12.7$ Hz, 1H (H-15)), 3.60-3.54 (m, 1H (H-14)), 3.45 (dd, $^3\text{J} = 10.5$ Hz, $^3\text{J} = 6.6$ Hz, 1H (H-11)), 3.31 (dd, $^2\text{J} = 12.9$ Hz, $^3\text{J} = 3.1$ Hz, 1H (H-28)), 3.02-2.91 (m, 1H (H-12)), 2.93 (dd, $^2\text{J} = 12.9$, $^3\text{J} = 5.9$ Hz, 1H (H-28)), 2.58-2.46 (m, 1H (H-12)), 2.12-1.97 (m, 2H (H-13,14)).

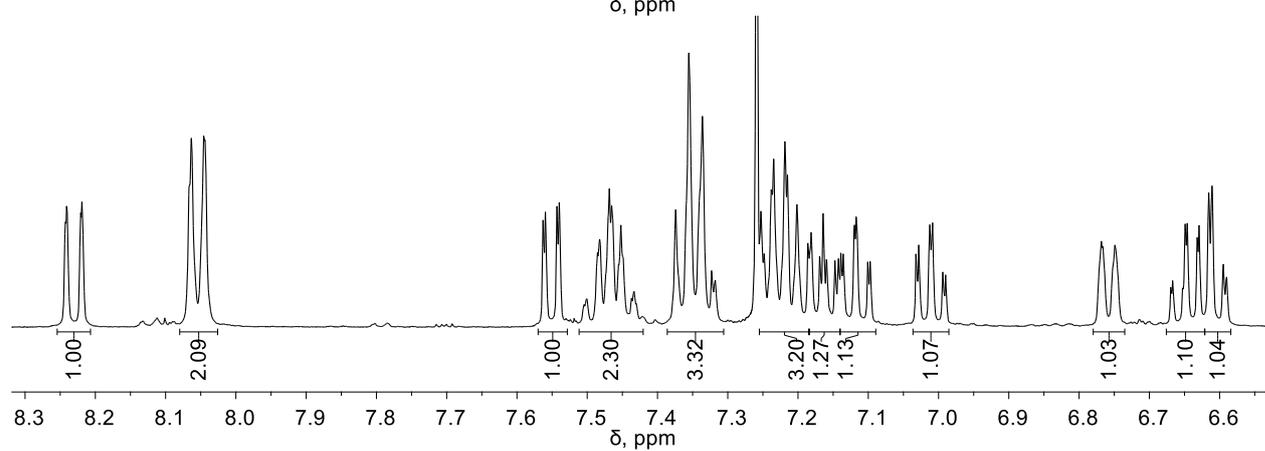
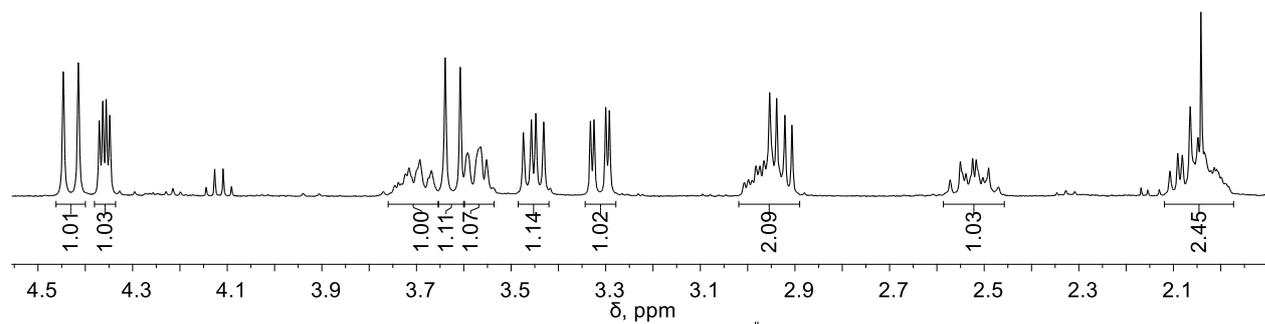
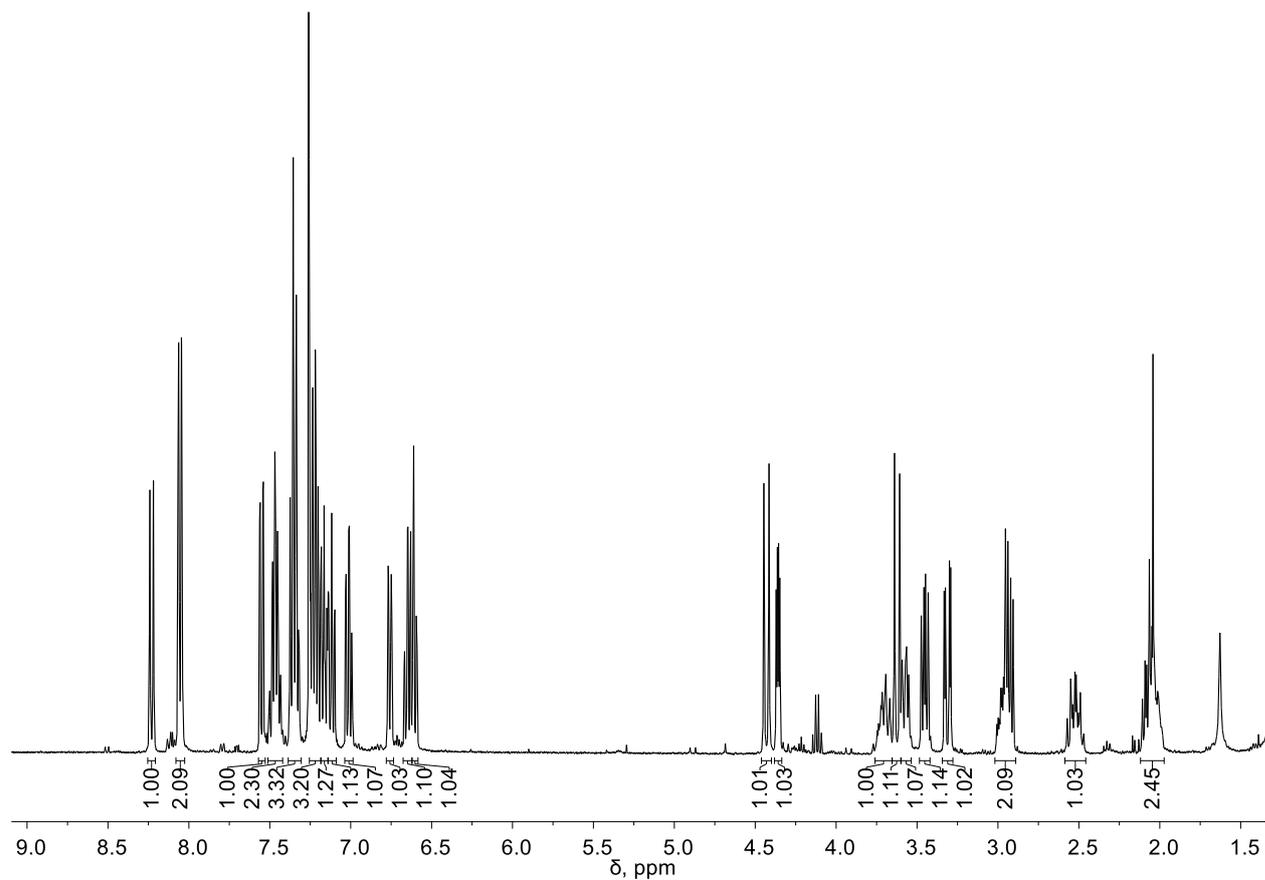
^{13}C NMR (CDCl_3 δ , ppm): 180.56 (C-10), 178.19 (C-1), 172.14 (C-3), 143.10 (C-9), 137.04 (C-29), 133.96 (C-16), 133.55 (C-5), 133.35 (C-22), 133.19 (C-31), 132.70 (C-7), 131.75 (C-17,21), 130.01 (C-27), 129.23 (C-26), 129.13 (C-34), 129.06 (C-18,20), 129.03 (C-19), 128.99 (C-24), 128.12 (C-33), 127.74 (C-32), 127.52 (C-23), 126.87 (C-25), 126.38 (C-4), 124.55 (C-30), 123.91 (C-8), 120.75 (C-6), 70.76 (C-11), 68.67 (C-2), 63.45 (C-15), 57.34 (C-14), 36.72 (C-28), 31.06 (C-12), 23.55 (C-13).

(S,S)-4c:

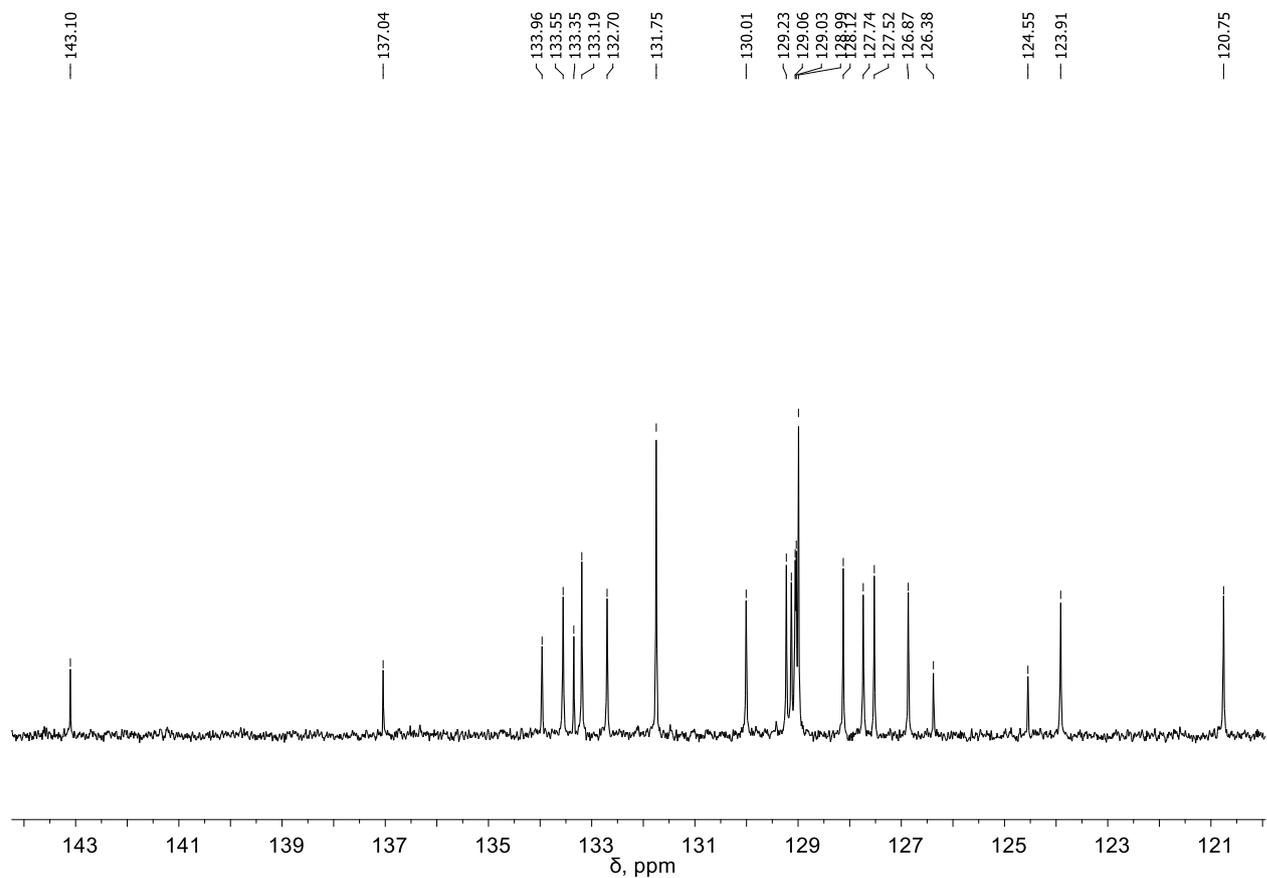
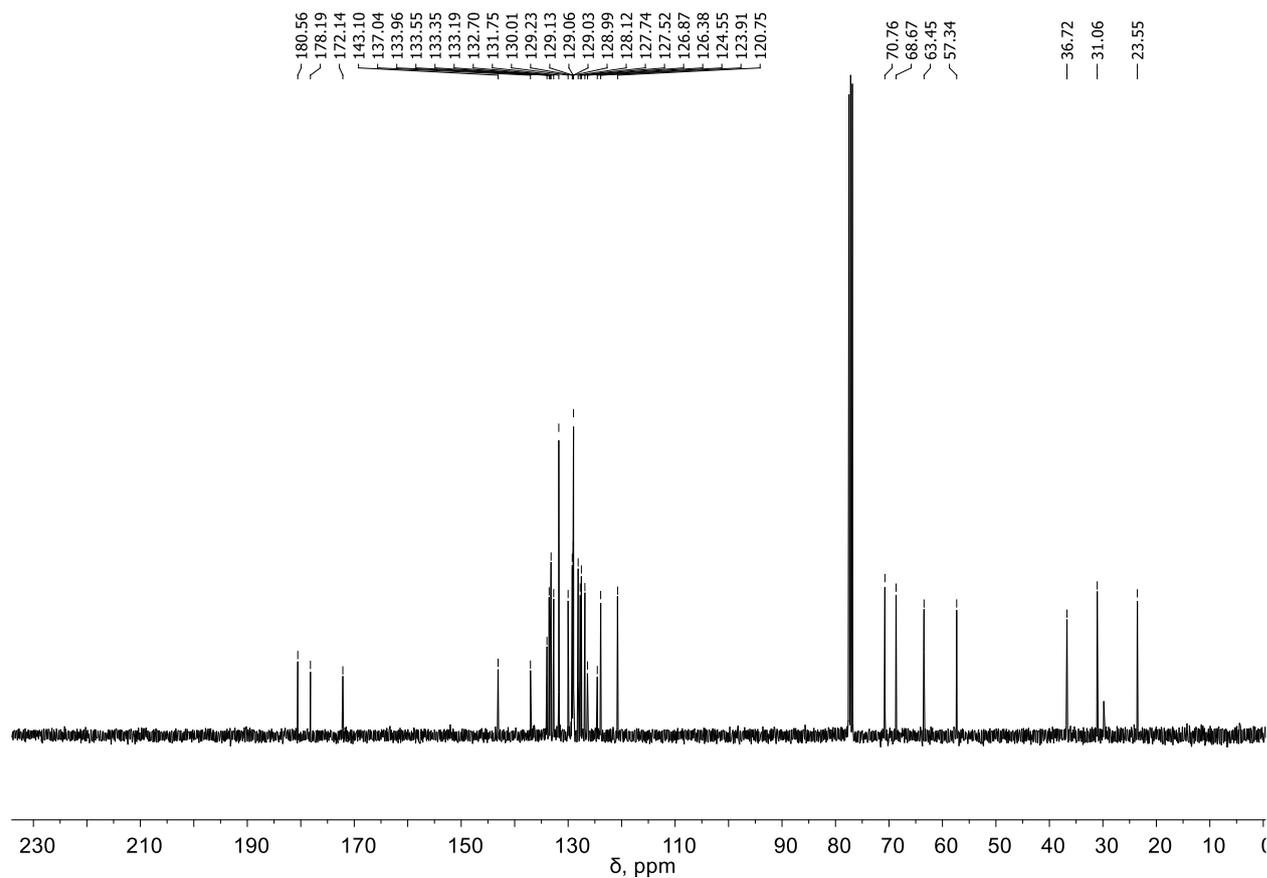
^1H NMR (CDCl_3 δ , ppm): 8.49 (dd, $^3\text{J} = 8.7$ Hz, $^4\text{J} = 0.8$ Hz, 1H (H-8)), 7.80-7.76 (m, 2H (H-17,21)), 7.49-7.38 (m, 7H), 7.36-7.30 (m, 1H), 7.29-7.25 (m, 1H), 7.21 (dd, $^3\text{J} = 7.8$ Hz, $^4\text{J} = 1.6$ Hz, 1H), 7.18-7.13 (m, 1H), 7.01 (m, 1H), 6.96-6.91 (m, 1H (H-19)), 6.84 (d, $^3\text{J} = 7.3$ Hz, 1H), 6.72 (dd, $^3\text{J} = 8.3$ Hz, $^4\text{J} = 1.9$ Hz, 1H (H-5)), 6.69 (dd, $^3\text{J} = 6.5$ Hz, $^4\text{J} = 1.1$ Hz, 1H (H-6)), 4.87 (d, $^2\text{J} = 13.4$ Hz, 1H (H-15)), 4.24 (dd, $^3\text{J} = 6.2$, 3.7 Hz, 1H (H-2)), 4.05-3.96 (m, 1H), 3.91 (d, $^2\text{J} = 13.4$ Hz, 1H (H-15)), 3.66 (dd, $^3\text{J} = 9.9$, 4.0 Hz, 1H (H-11)), 3.23 (dd, $^2\text{J} = 13.3$ Hz, $^3\text{J} = 3.7$ Hz, 1H (H-28)), 3.06 (dd, $^2\text{J} = 13.3$ Hz, $^3\text{J} = 6.3$ Hz, 1H (H-28)), 2.63-2.48 (m, 2H), 2.22-2.13 (m, 1H), 2.00-1.89 (m, 1H), 1.84-1.73 (m, 1H).

^{13}C NMR (CDCl_3 δ , ppm): 182.43 (C-10), 178.24 (C-1), 172.58 (C-3), 143.45, 136.81 (C-29), 134.08 (C-5), 133.95, 133.14, 132.95, 132.81, 132.13 (C-17,21), 129.89, 129.87, 129.24, 129.18, 128.84, 128.33, 128.00, 127.61, 126.81, 125.90, 124.91, 124.03 (C-8), 120.87 (C-6), 68.98 (C-2,11), 61.92 (C-15), 57.40, 37.69 (C-28), 31.02, 29.85, 23.68.

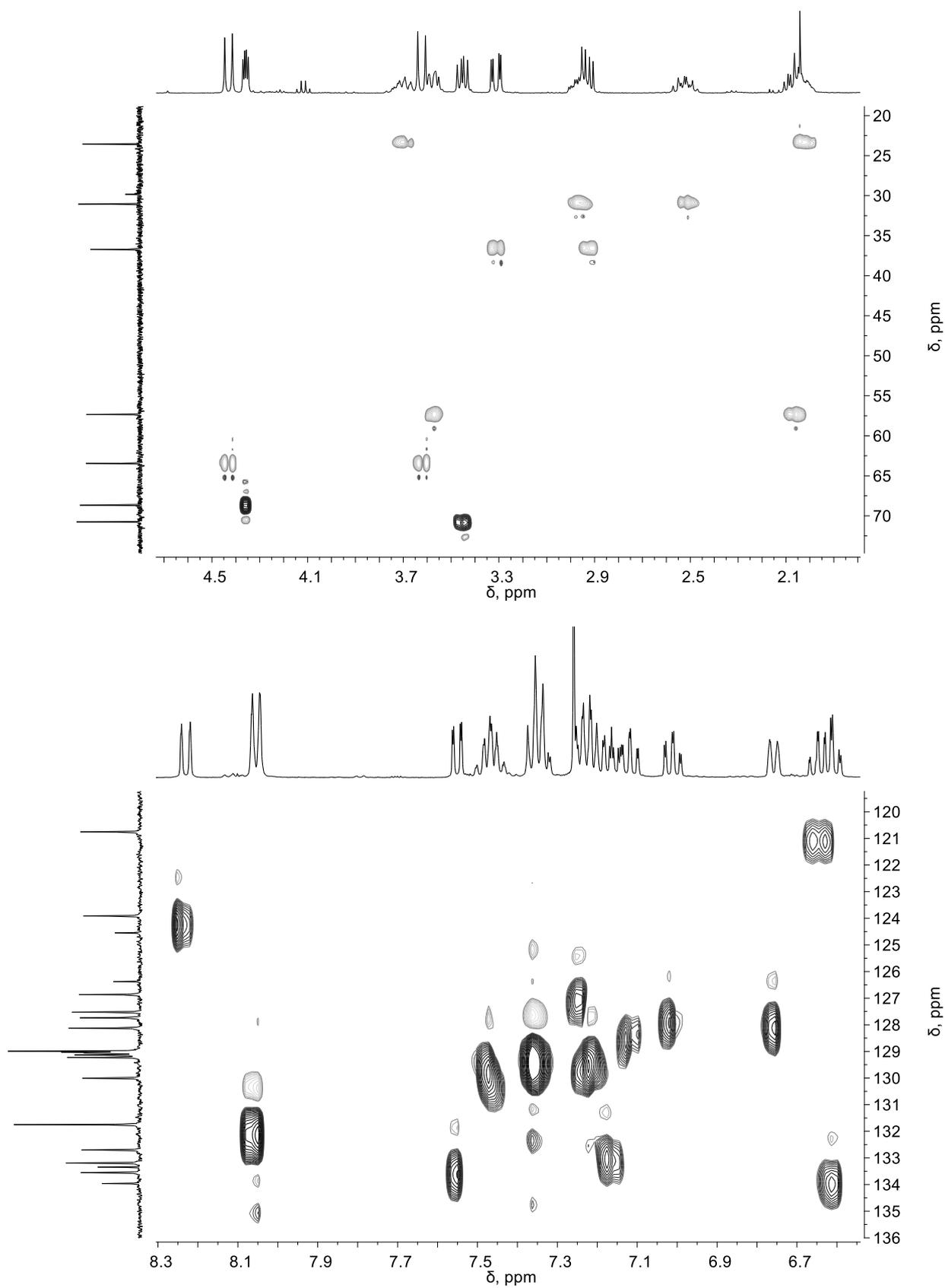
26. ¹H NMR spectrum of (*S,R*)-4c



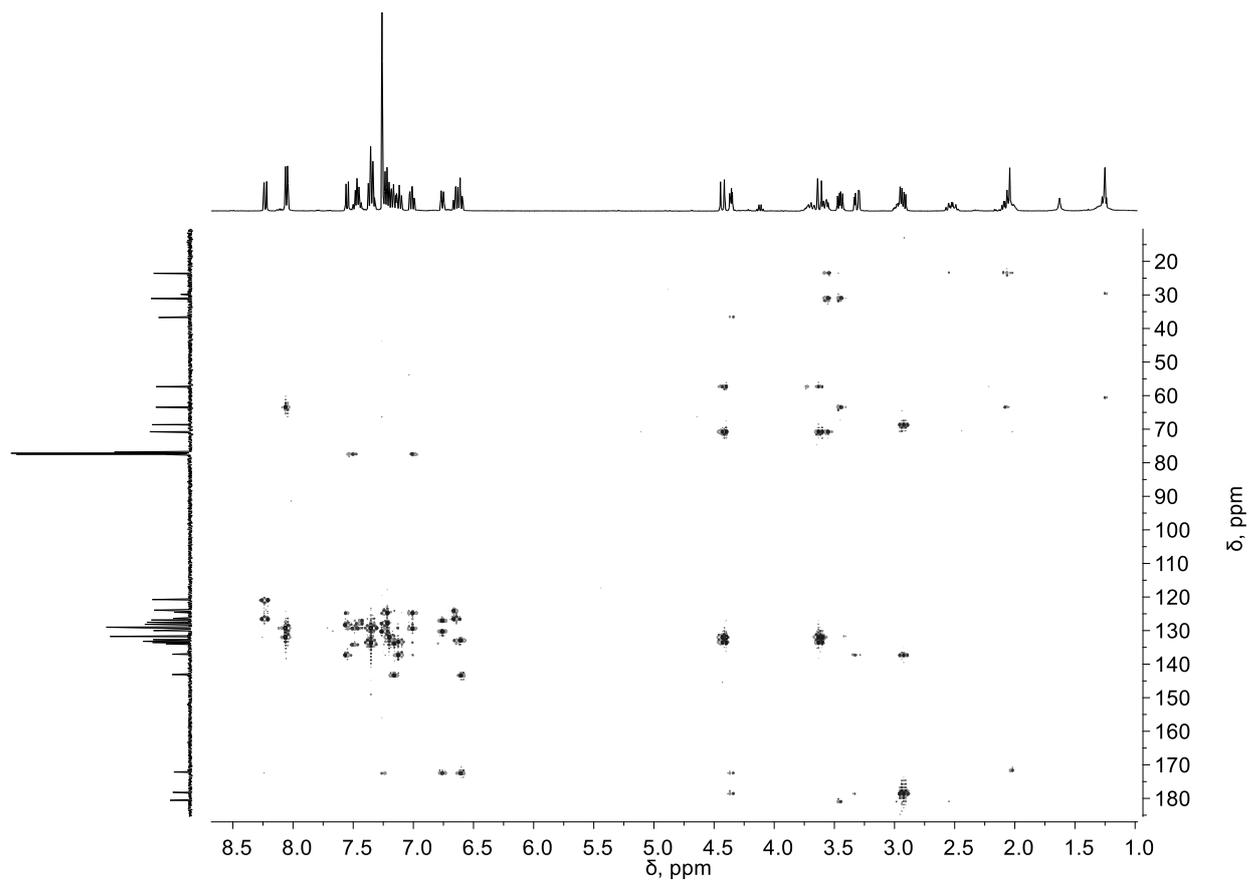
27. ¹³C NMR spectrum of (*S,R*)-4c



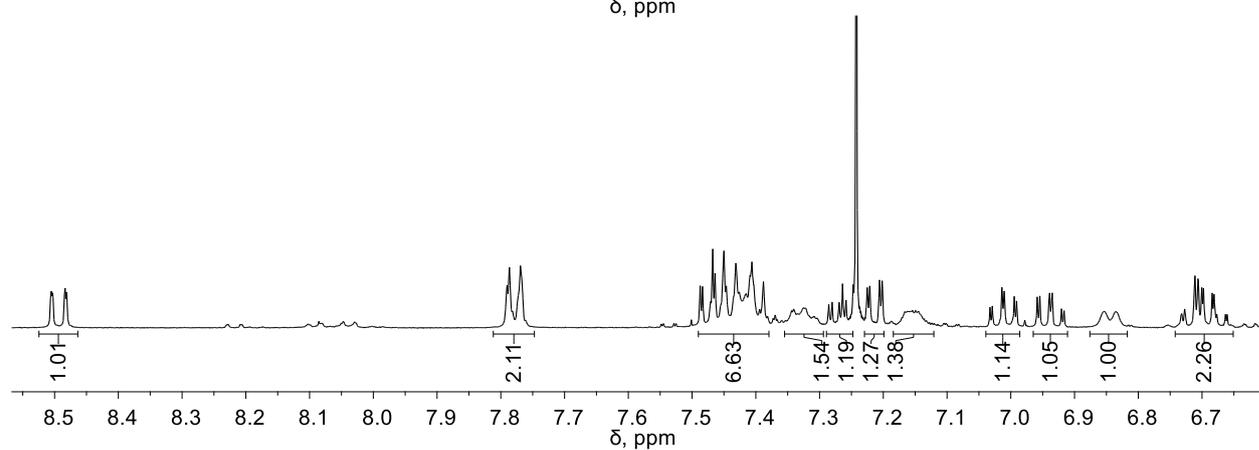
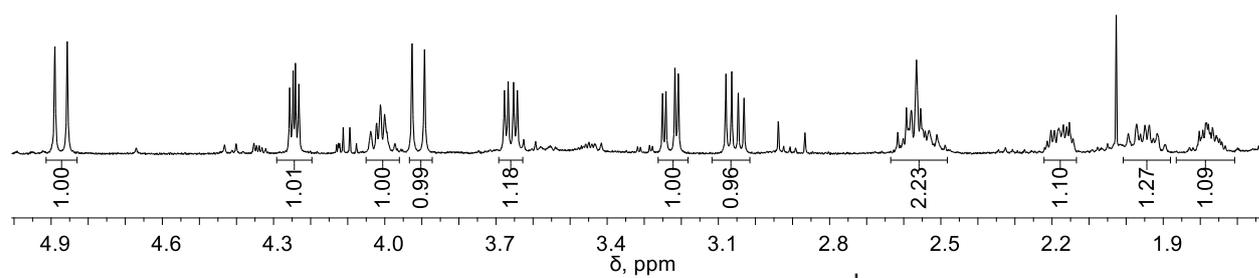
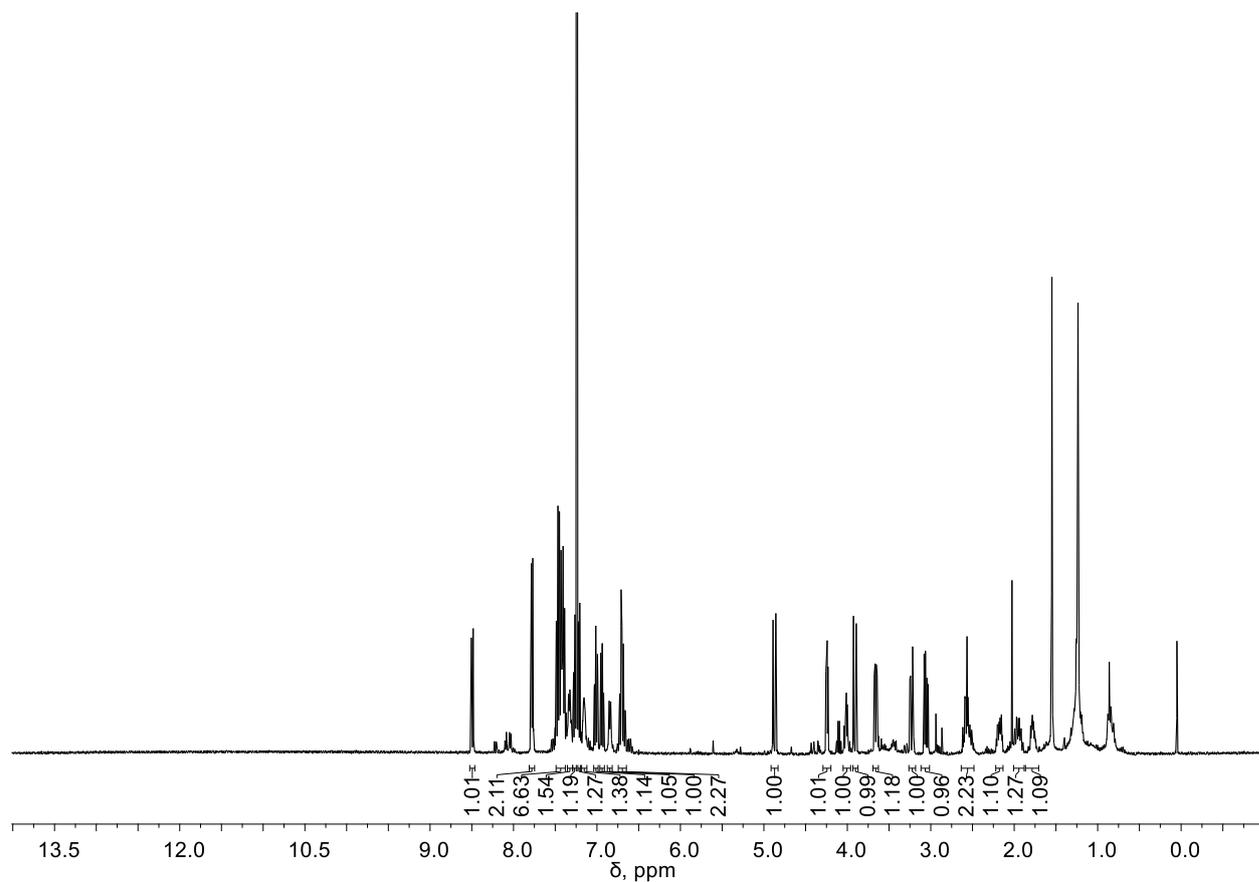
28. HSQC spectrum of (*S,R*)-4c



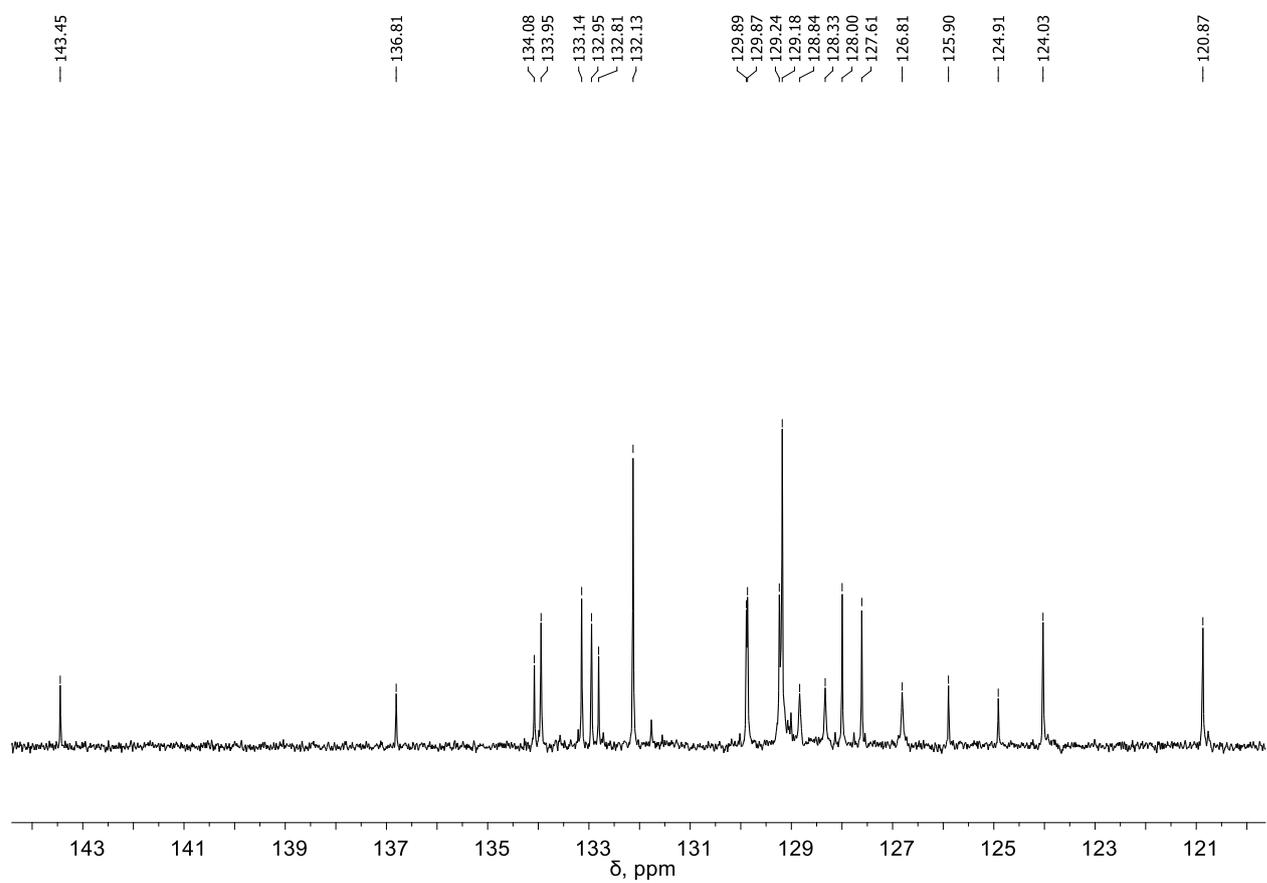
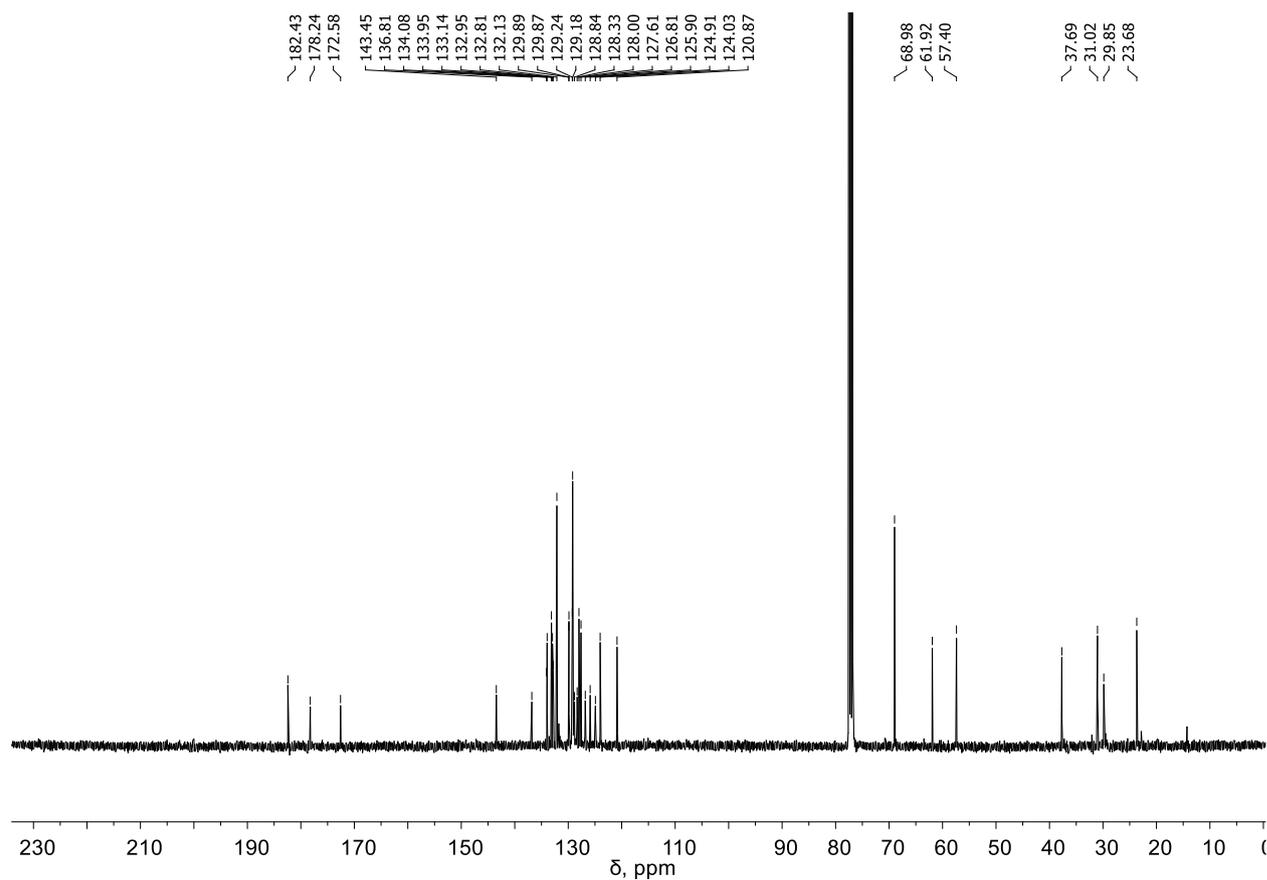
29. HMBC spectrum of (*S,R*)-4c



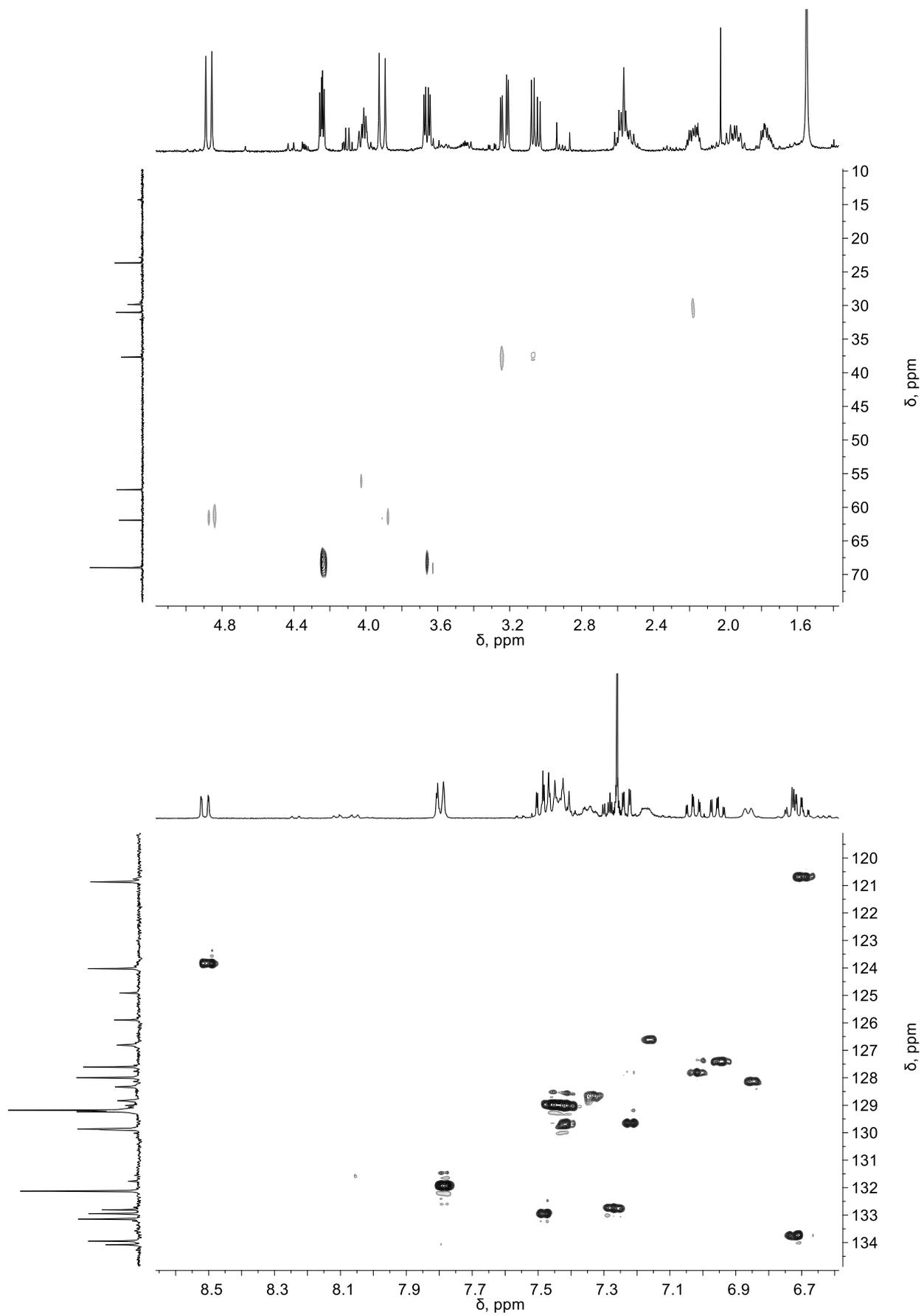
30. ¹H NMR spectrum of (*S,S*)-**4c**



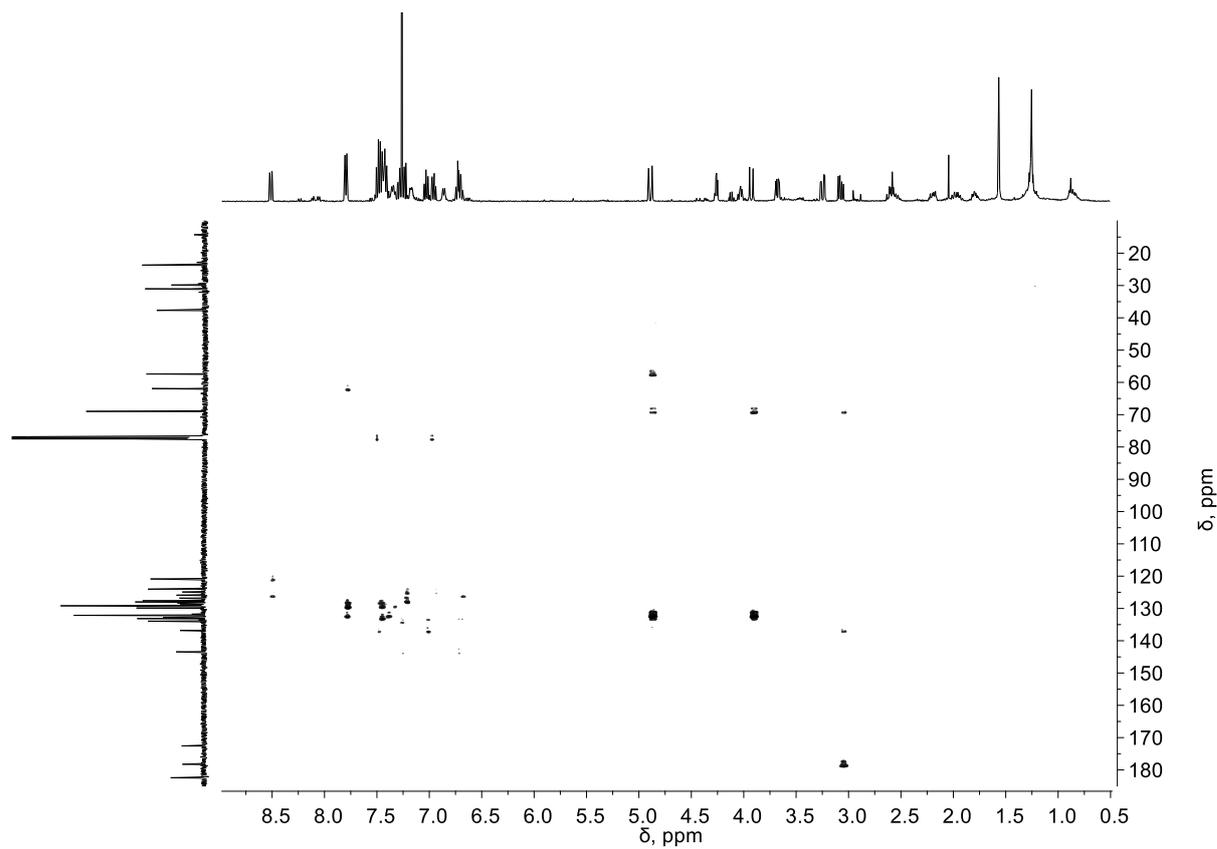
31. ^{13}C NMR spectrum of (*S,S*)-4c



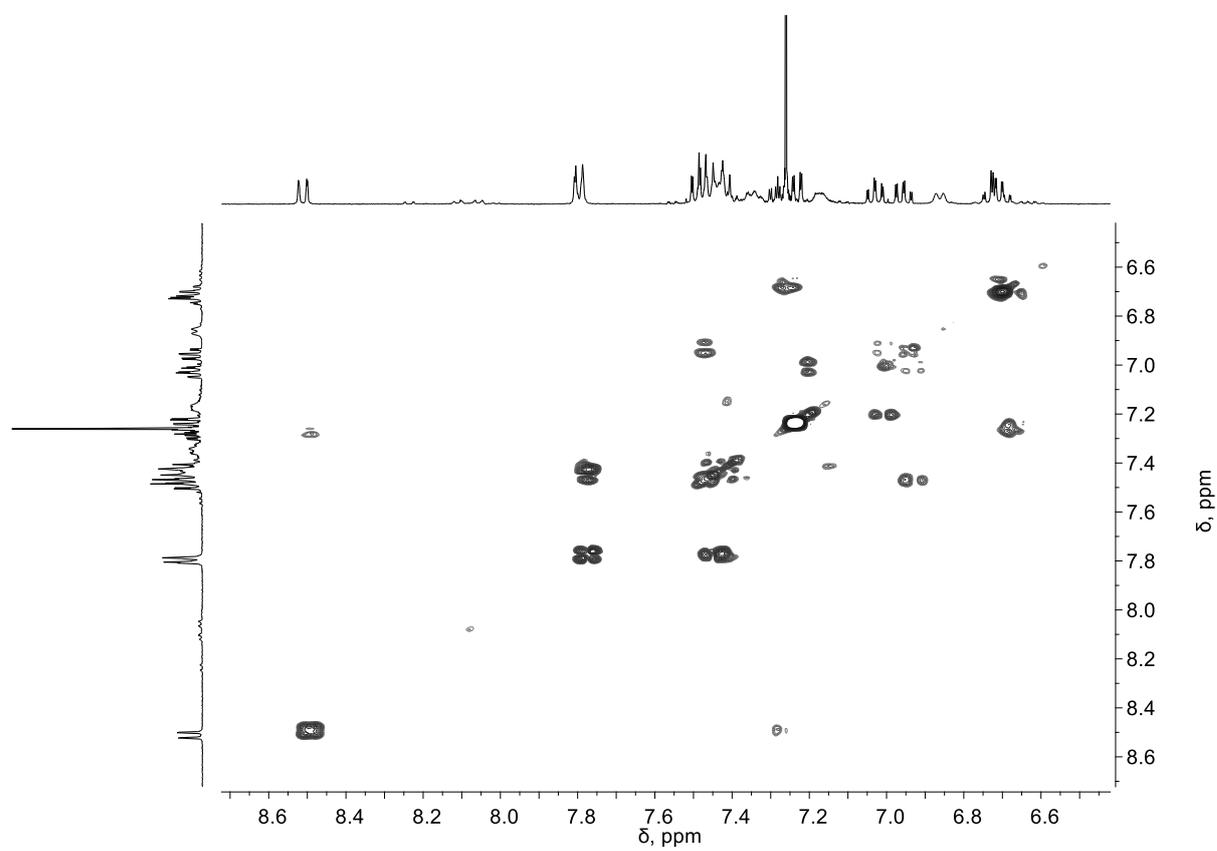
32. HSQC spectrum of (*S,S*)-4c



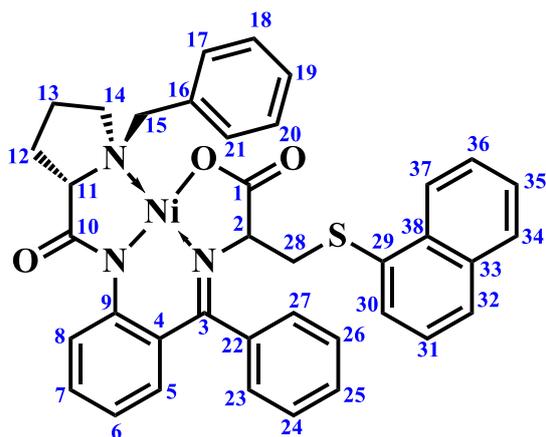
33. HMBC spectrum of (*S,S*)-4c



34. COSY spectrum of (*S,S*)-4c



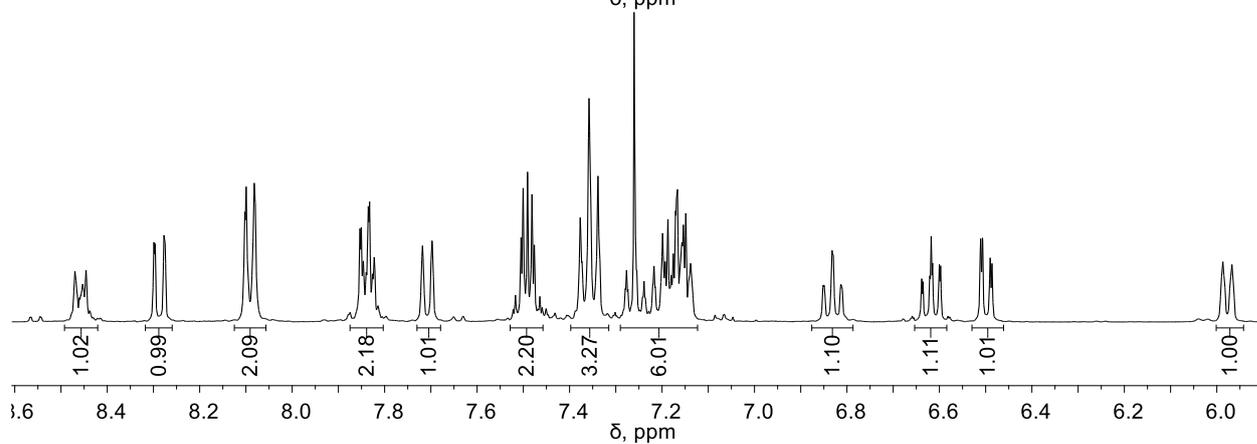
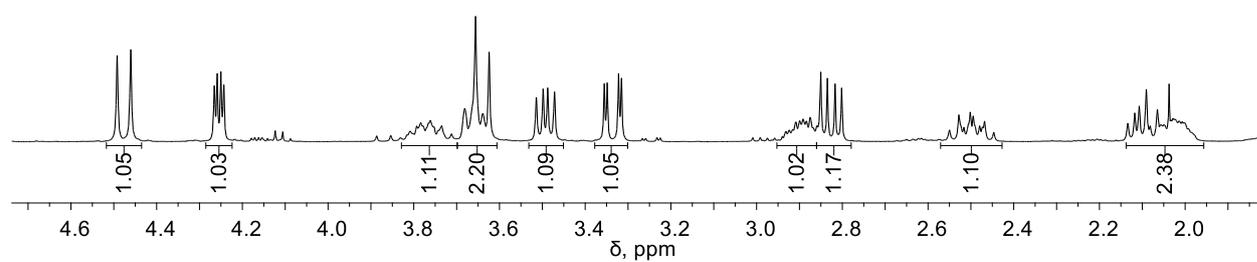
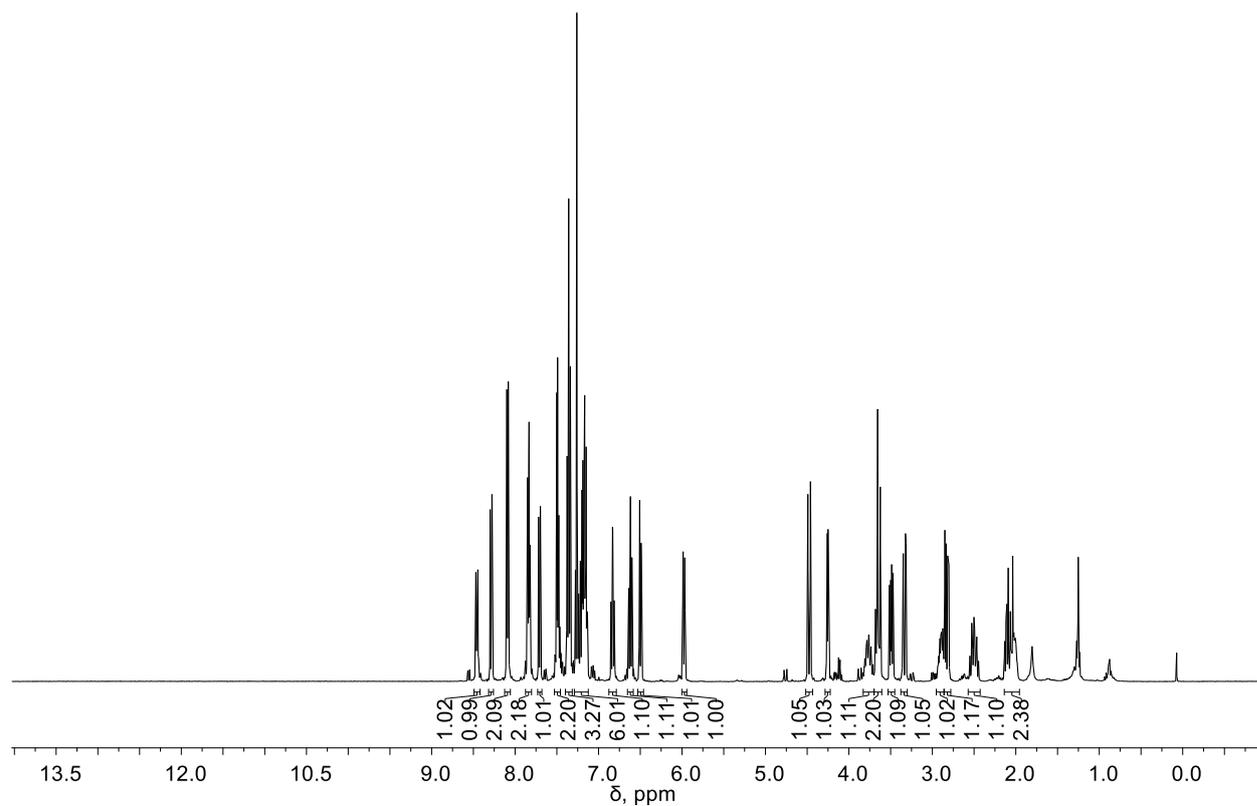
35. Atom numeration and signal assignment in the NMR spectra of **4d**



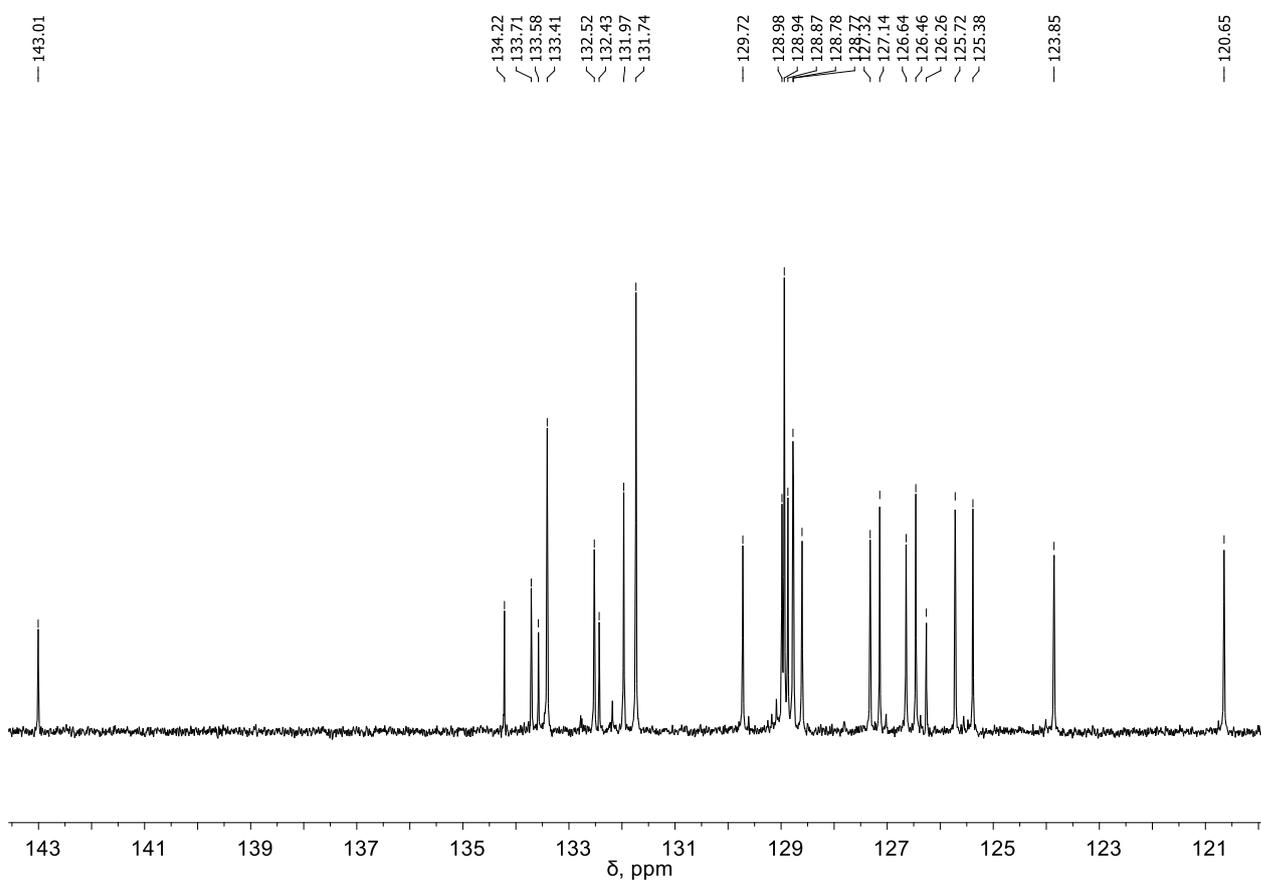
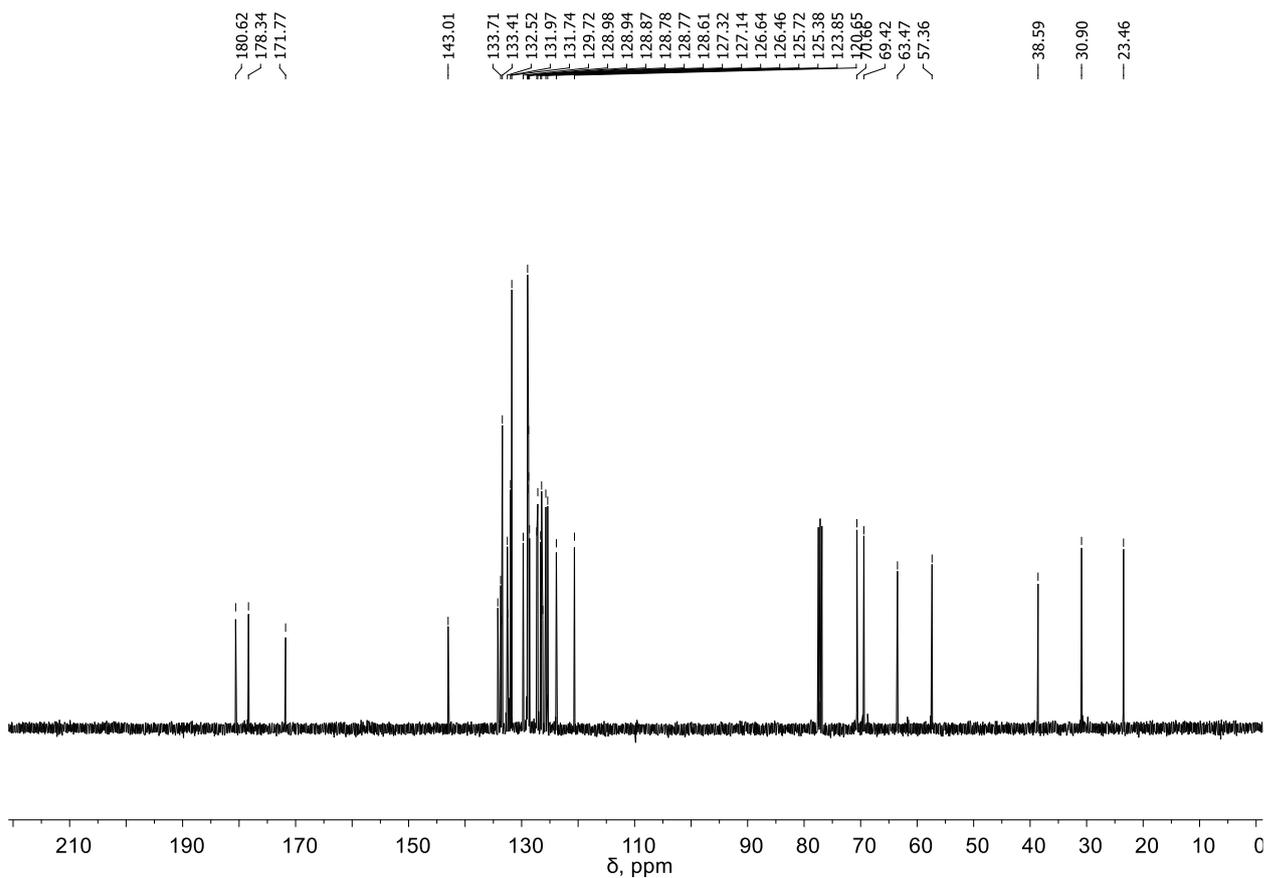
^1H NMR (CDCl_3 δ , ppm): 8.49-8.43 (m, 1H (H-37)), 8.29 (dd, $^3\text{J} = 8.7$ Hz, $^4\text{J} = 1.0$ Hz, 1H (H-8)), 8.11-8.07 (m, 2H (H-17,21)), 7.88-7.80 (m, 2H (H-30,34)), 7.73-7.68 (m, 1H (H-32)), 7.52-7.46 (m, 2H (H-35,36)), 7.39-7.33 (m, 3H (H-18,20,24)), 7.29-7.13 (m, 5H (H-7,19,23,25,31)), 6.86-6.80 (m, 1H (H-26)), 6.62 (ddd, $^3\text{J} = 8.1$ Hz, $^3\text{J} = 7.0$ Hz, $^4\text{J} = 1.2$ Hz, 1H (H-6)), 6.50 (dd, $^3\text{J} = 8.2$ Hz, $^4\text{J} = 1.6$ Hz, 1H (H-5)), 6.00-5.95 (m, 1H (H-27)), 4.48 (d, $^2\text{J} = 12.7$ Hz, 1H (H-15)), 4.25 (dd, $^3\text{J} = 6.2$ Hz, $^3\text{J} = 2.7$ Hz, 1H (H-2)), 3.83-3.70 (m, 1H (H-13)), 3.69-3.61 (m, 2H (H-14,15)), 3.49 (dd, $\text{J} = 10.6$ Hz, $\text{J} = 6.4$ Hz, 1H (H-11)), 3.34 (dd, $^2\text{J} = 13.3$ Hz, $^3\text{J} = 2.7$ Hz, 1H (H-28)), 2.95-2.85 (m, 1H (H-12)), 2.83 (dd, $^2\text{J} = 13.3$ Hz, $^3\text{J} = 6.2$ Hz, 1H (H-28)), 2.56-2.44 (m, 1H (H-12)), 2.14-1.97 (m, 2H (H-13,14)).

^{13}C NMR (CDCl_3 δ , ppm): 180.62 (C-10), 178.34 (C-1), 171.77 (C-3), 143.01 (C-9), 134.22 (C-33), 133.71 (C-38), 133.58 (C-22), 133.41 (C-5), 132.52 (C-7), 132.43 (C-29), 131.97, (C-34), 131.74 (C-17,21), 129.72 (C-23 or 25), 128.98 (C-19), 128.94 (C-18,20), 128.87 (C-32), 128.78 (C-30), 128.77 (C-24), 128.61 (C-26), 127.32 (C-27), 127.14, (C-36), 126.64 (C-23 or 25), 126.46 (C-35), 126.26 (C-4), 125.72 (C-31), 125.38 (C-37), 123.85 (C-8), 120.65 (C-6) 70.66 (C-11), 69.42 (C-2), 63.47 (C-15), 57.36 (C-14), 38.59 (C-28), 30.90 (C-12), 23.46 (C-13).

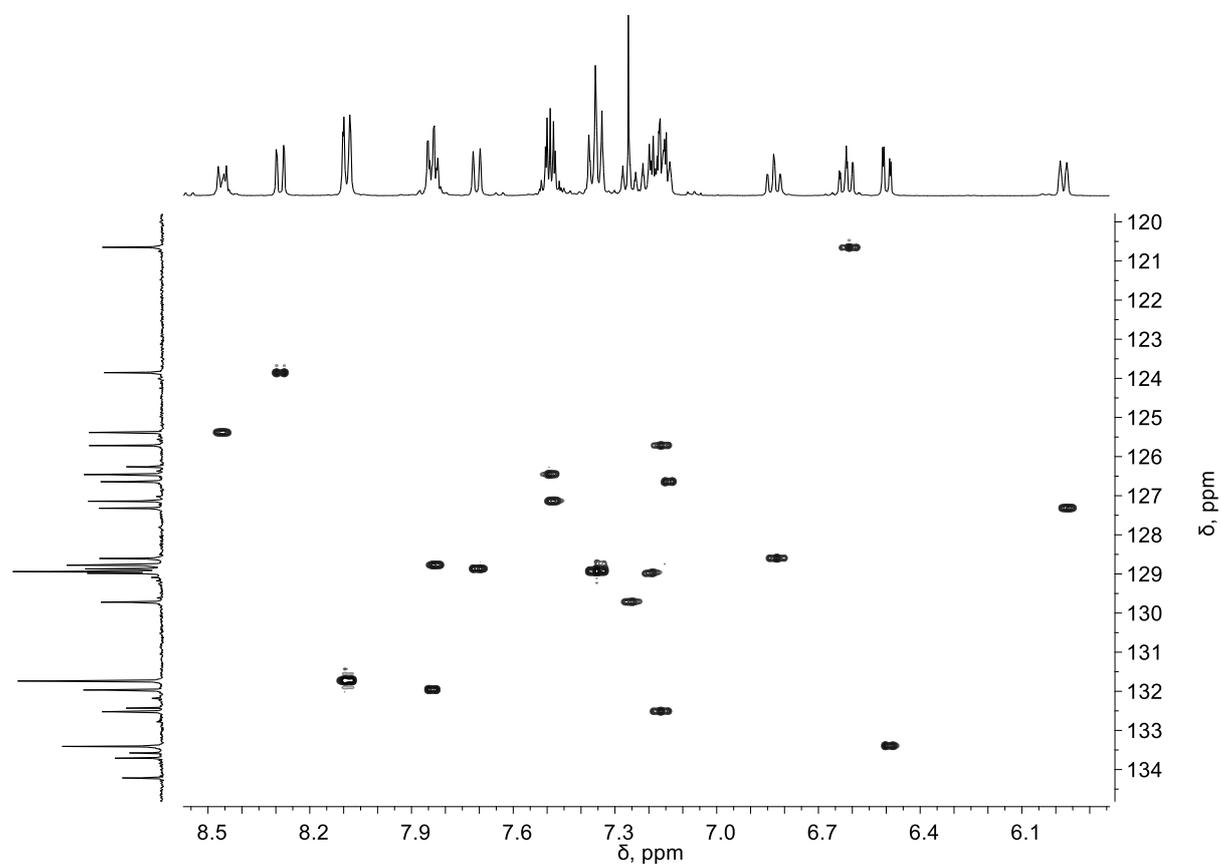
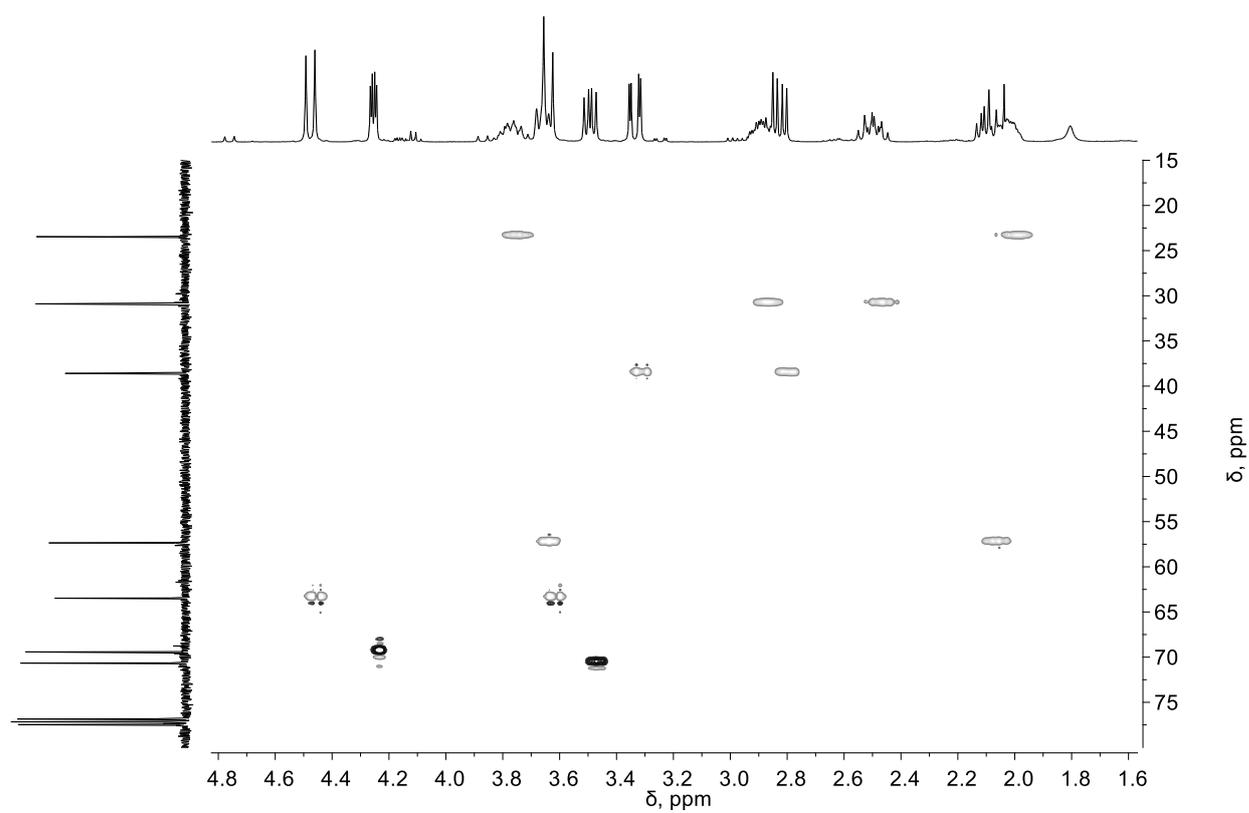
36. ^1H NMR spectrum of (*S,R*)-4d



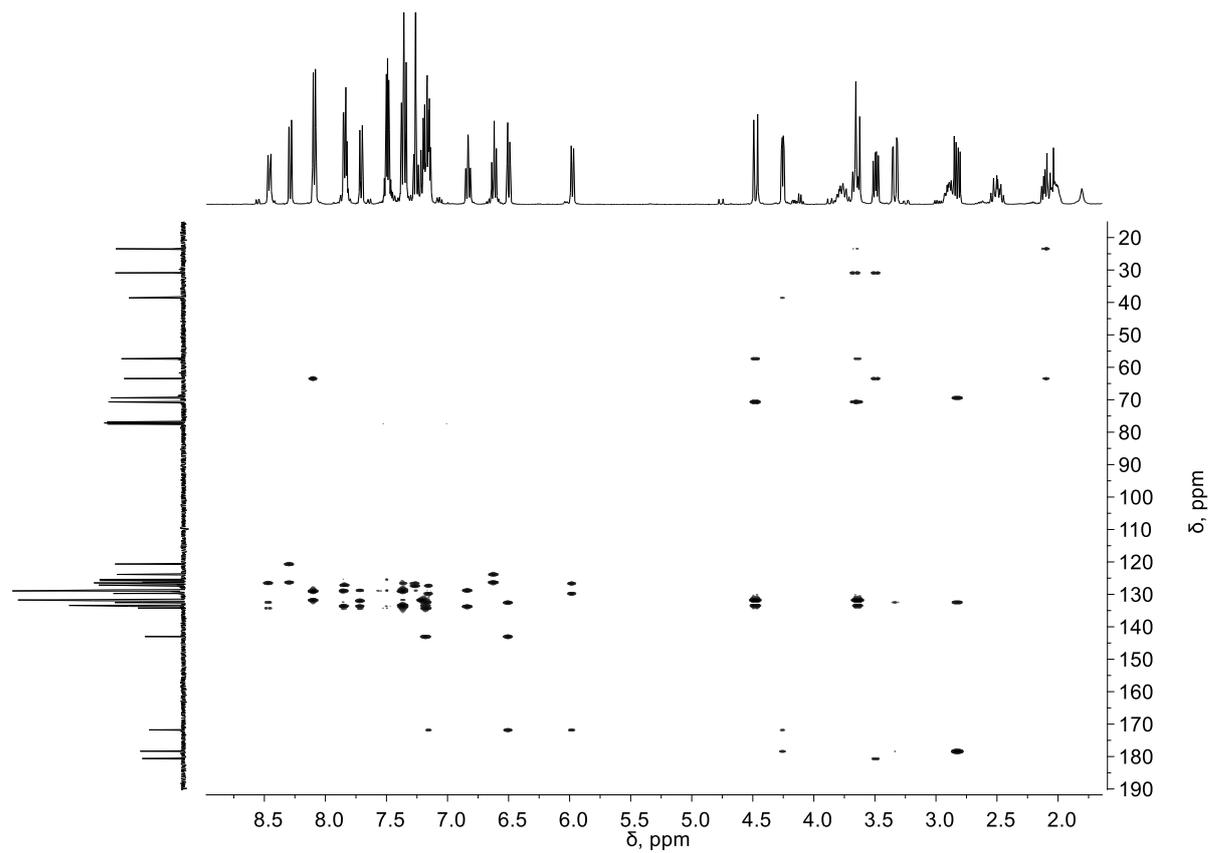
37. ^{13}C NMR spectrum of (*S,R*)-4d



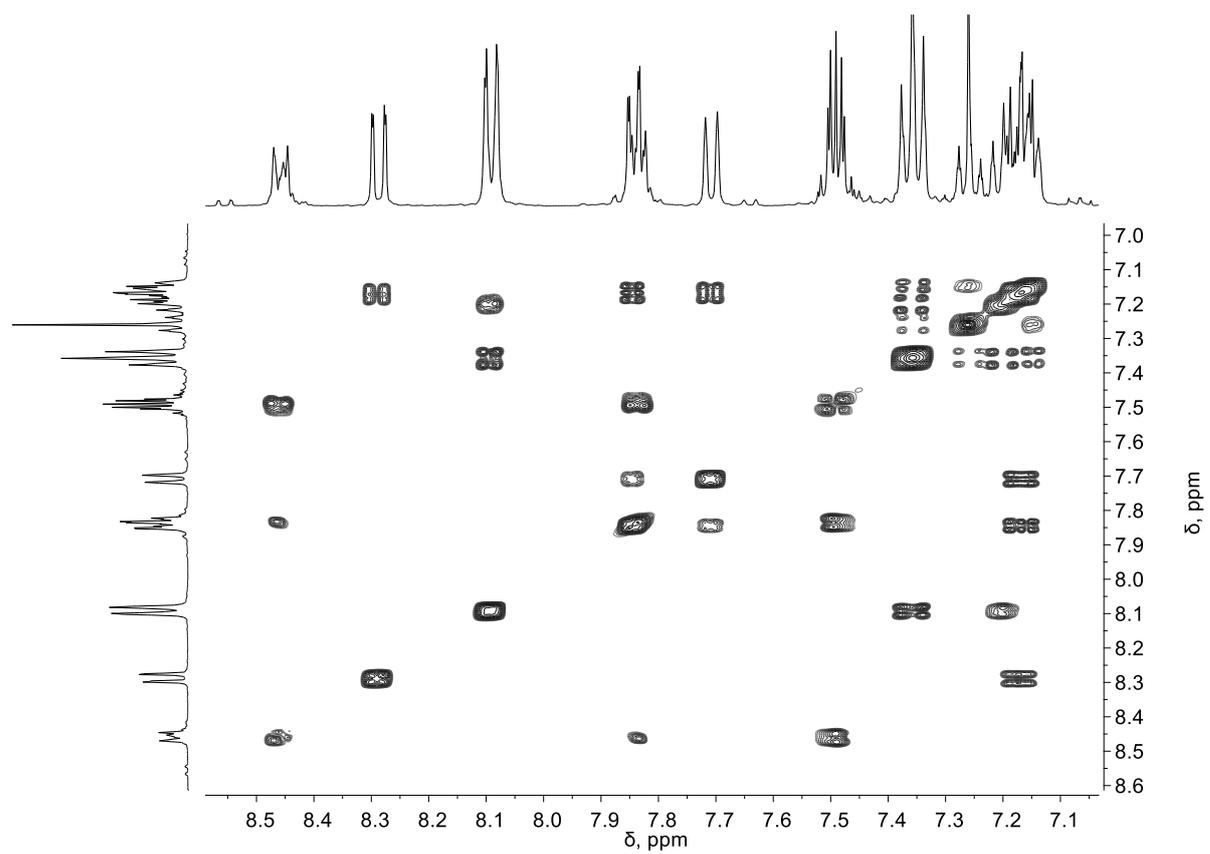
38. HSQC spectrum of (*S,R*)-4d



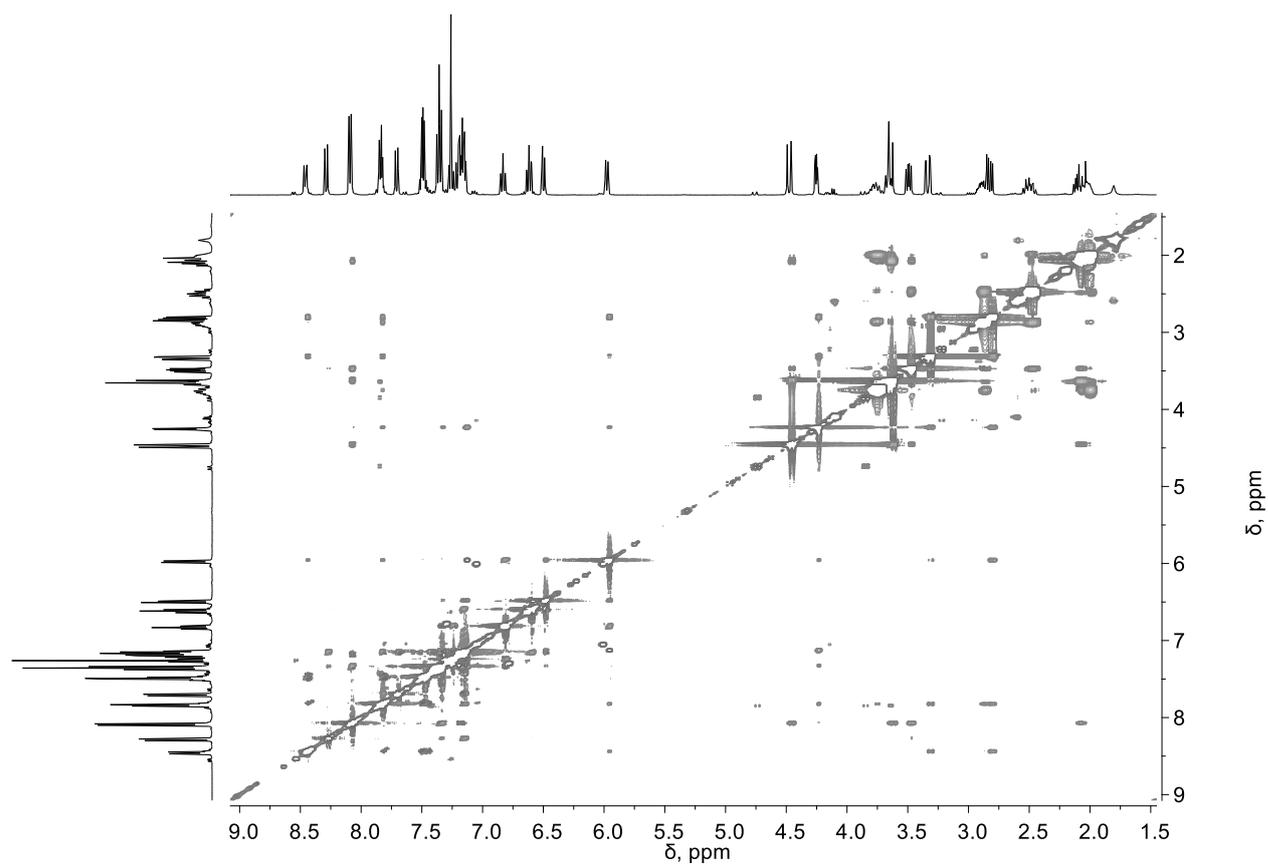
39. HMBC spectrum of (*S,R*)-4d



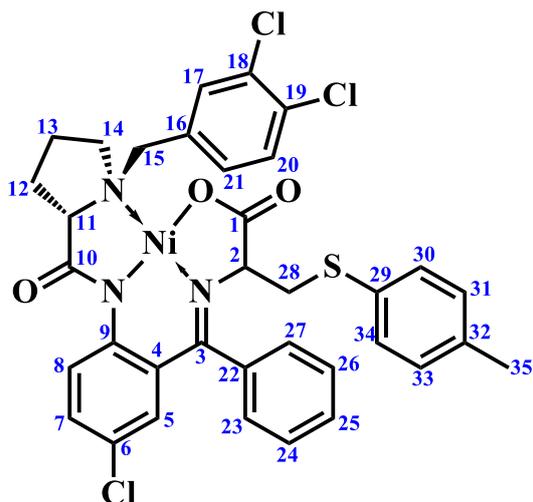
40. COSY spectrum of (*S,R*)-4d



41. NOESY spectrum of (*S,R*)-4d



42. Atom numeration and signal assignment in the NMR spectra of **4'a**

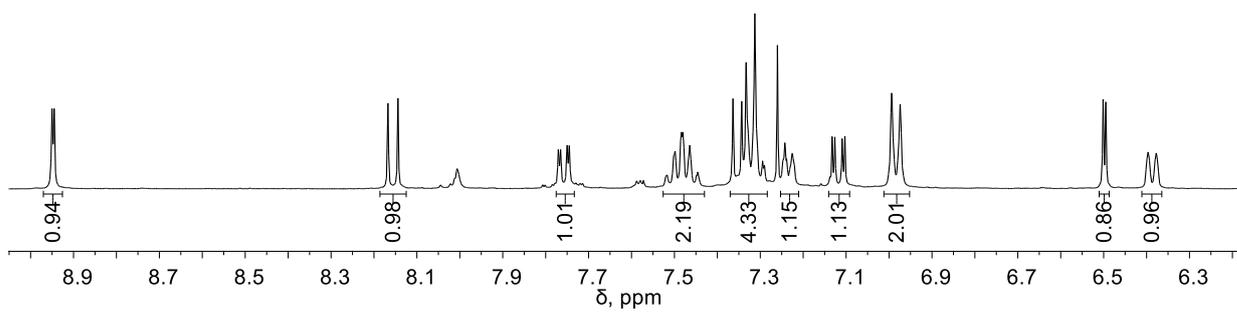
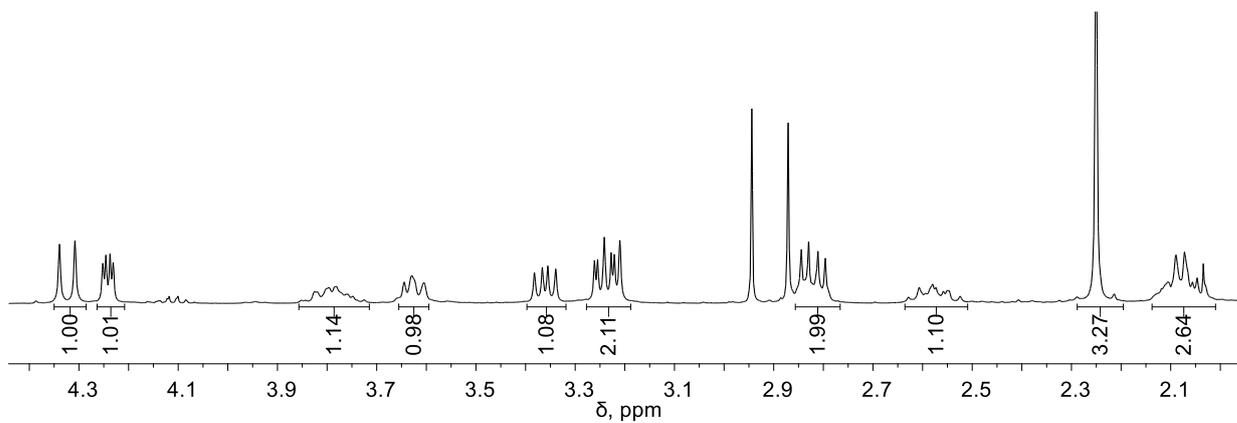
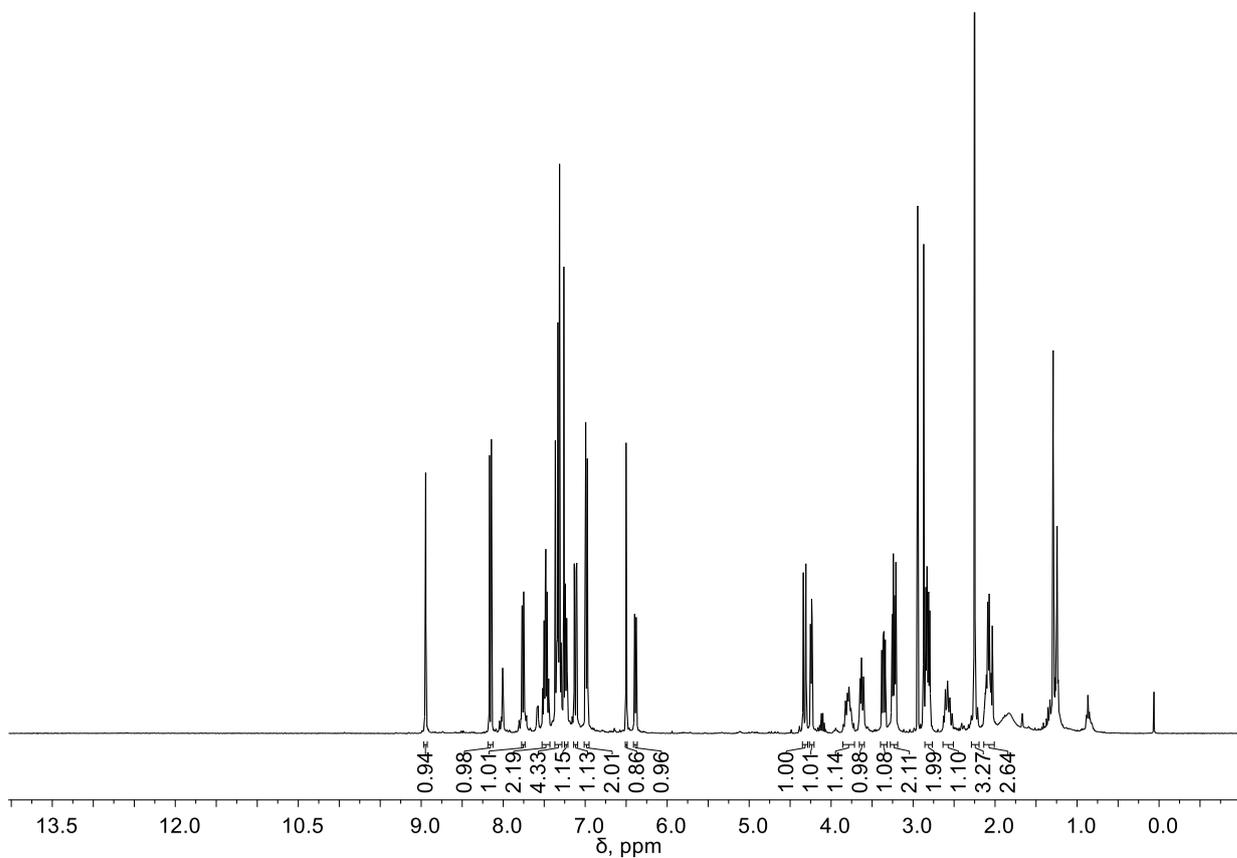


(S,R)-4'a:

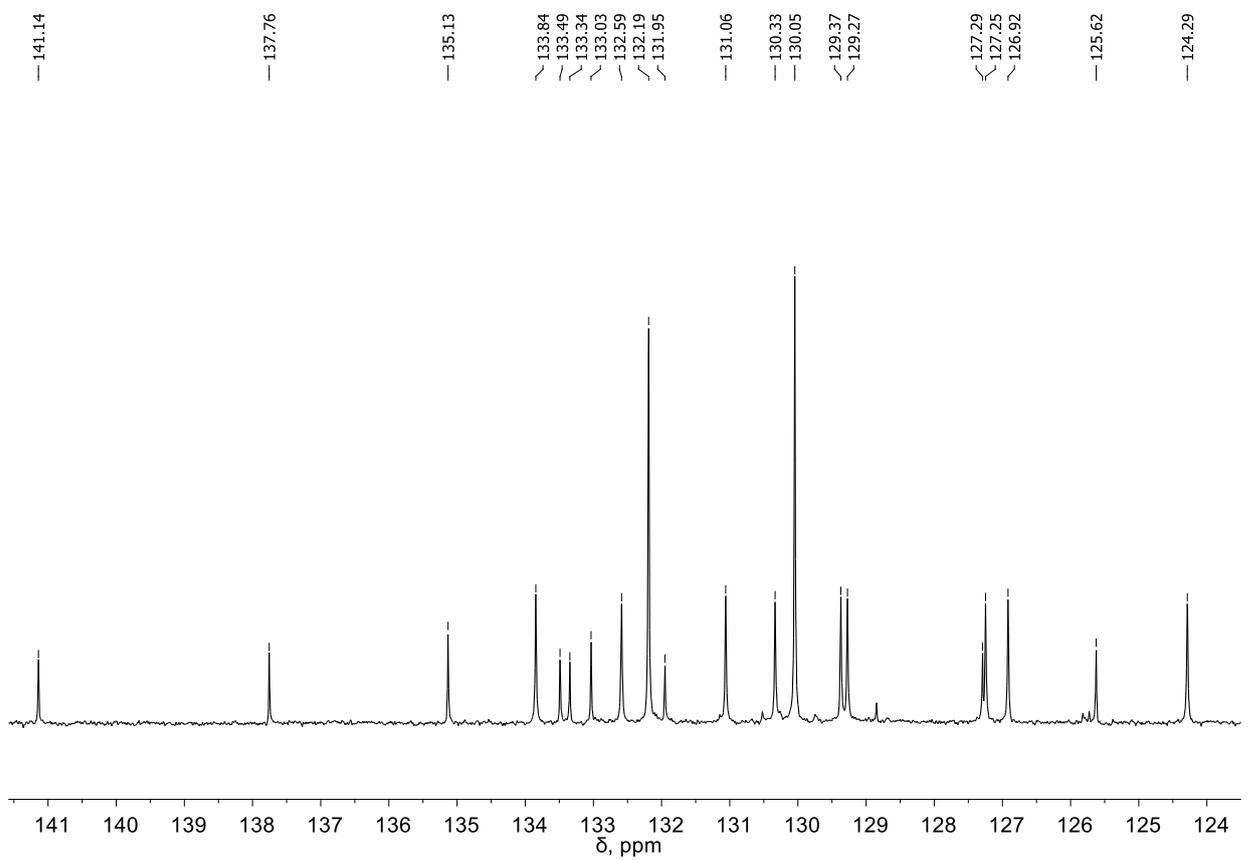
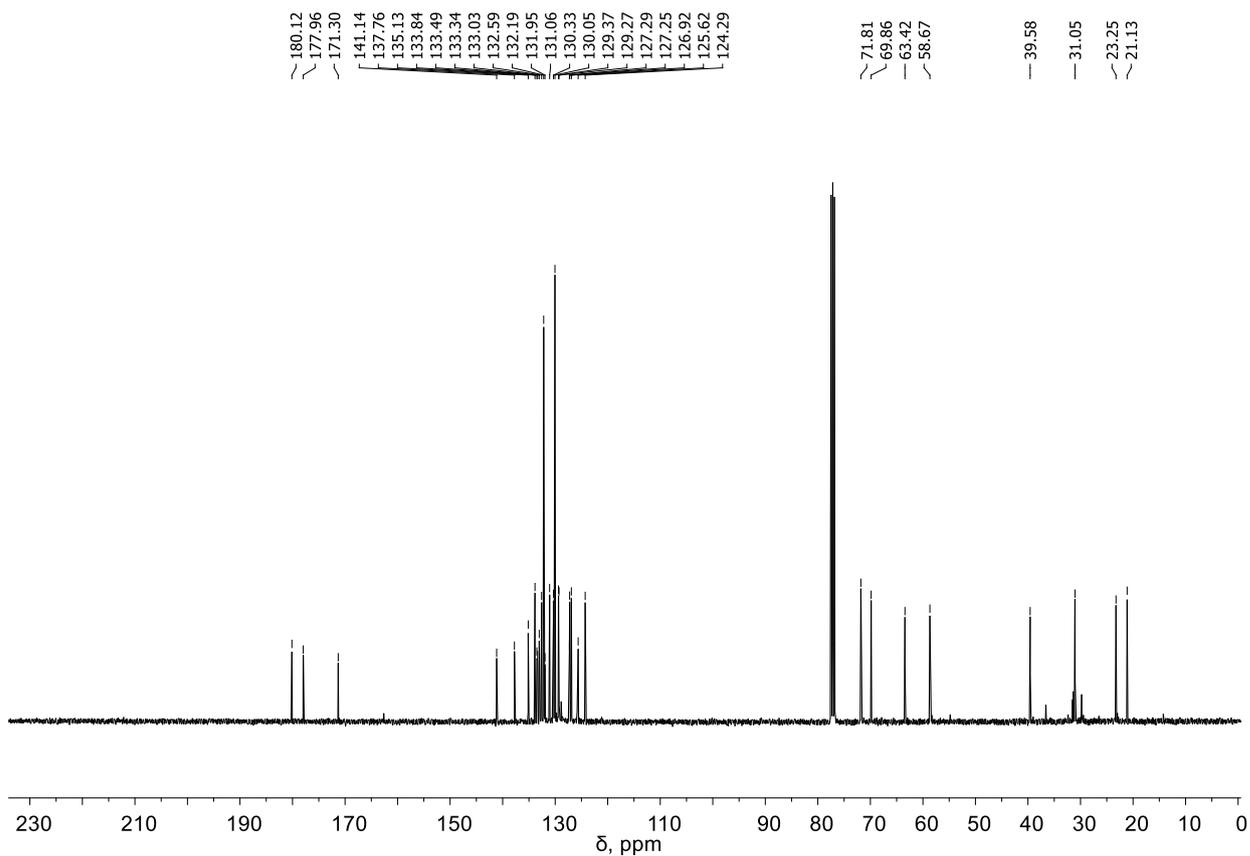
^1H NMR (CDCl_3 δ , ppm): 8.95 (d, $^4\text{J} = 2.0$ Hz, 1H (H-21)), 8.16 (d, $^3\text{J} = 9.3$ Hz, 1H (H-8)), 7.76 (dd, $^3\text{J} = 8.2$ Hz, $^4\text{J} = 2.1$ Hz, 1H (H-17)), 7.48 (m, 2H (H-24,26)), 7.37-7.28 (m, 4H (H-20,25,30,34)), 7.25-7.21 (m, 1H (H-27)), 7.12 (dd, $^3\text{J} = 9.3$ Hz, $^4\text{J} = 2.6$ Hz, 1H (H-7)), 6.98 (d, $^3\text{J} = 8.0$ Hz, 2H (H-31,33)), 6.50 (d, $^4\text{J} = 2.6$ Hz, 1H (H-5)), 6.39 (d, $^3\text{J} = 7.7$ Hz, 1H (H-23)), 4.32 (d, $^2\text{J} = 12.5$ Hz, 1H (H-15)), 4.24 (dd, $^3\text{J} = 5.9, 2.6$ Hz, 1H (H-2)), 3.86-3.72 (m, 1H (H-14)), 3.67-3.59 (m, 1H (H-13)), 3.36 (dd, $^3\text{J} = 10.7, 6.4$ Hz, 1H (H-11)), 3.24 (dd, $^2\text{J} = 13.4, ^3\text{J} = 2.6$ Hz, 1H (H-28)), 3.23 (d, $^2\text{J} = 12.5$ Hz, 1H (H-15)), 2.82 (dd, $^3\text{J} = 13.4, 5.9$ Hz, 1H (H-28)), 2.86-2.79 (m, 1H (H-12)), 2.64-2.53 (m, 1H (H-12)), 2.25 (s, 3H (H-35)), 2.14-2.02 (m, 2H (H-13,14)).

^{13}C NMR (CDCl_3 δ , ppm): 180.12 (C-10), 177.96 (C-1), 171.30 (C-3), 141.14 (C-9), 137.76 (C-20), 135.13 (C-32), 133.84 (C-21), 133.49 (C-19), 133.34 (C-22), 133.03 (C-16), 132.59 (C-7), 132.19 (C-5,30,34), 131.95 (C-29), 131.06 (C-18), 130.33 (C-26), 130.05 (C-17,31,33), 129.37 (C-24), 129.27 (C-25), 127.29 (C-23), 127.25 (C-6), 126.92 (C-27), 125.62 (C-4), 124.29 (C-8), 71.80 (C-11), 69.86 (C-2), 63.42 (C-15), 58.67 (C-13), 39.58 (C-28), 31.05 (C-12), 23.25 (C-14), 21.13 (C-35).

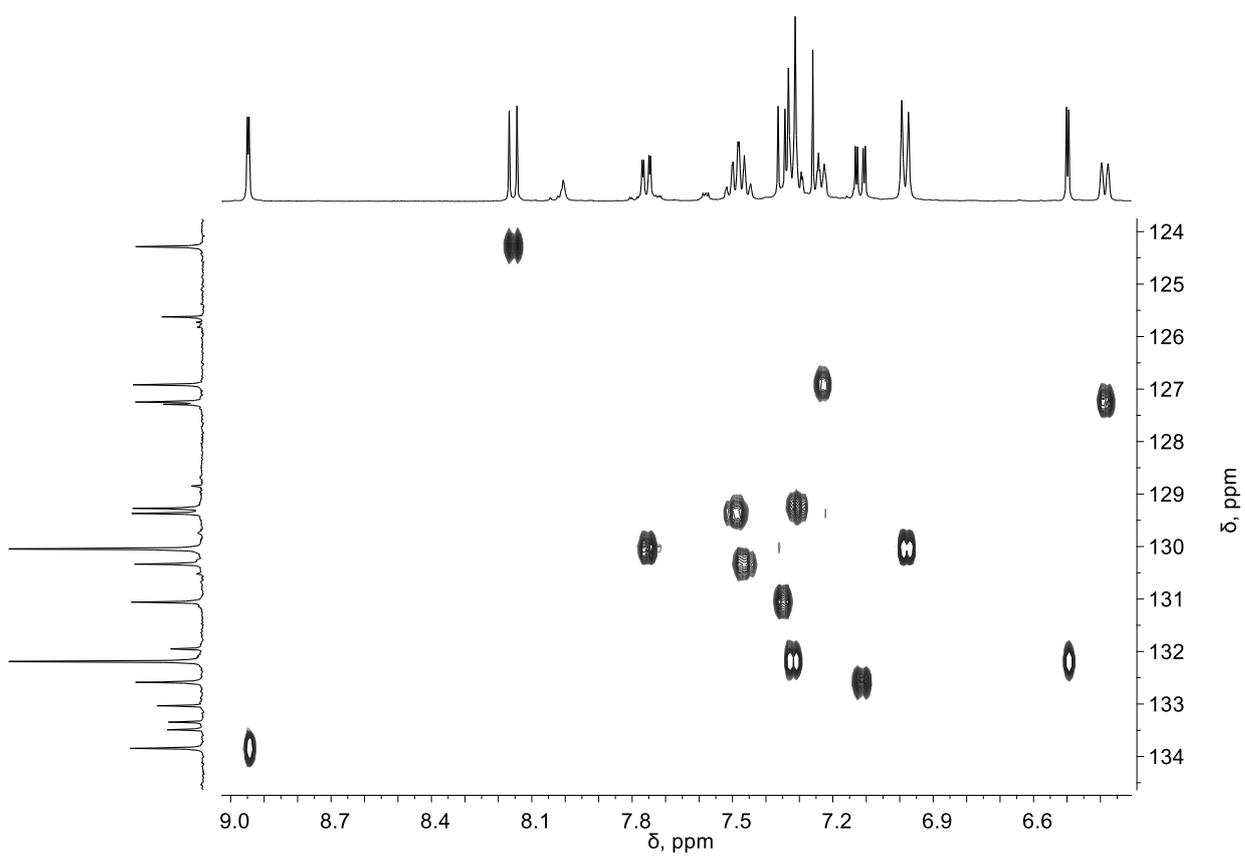
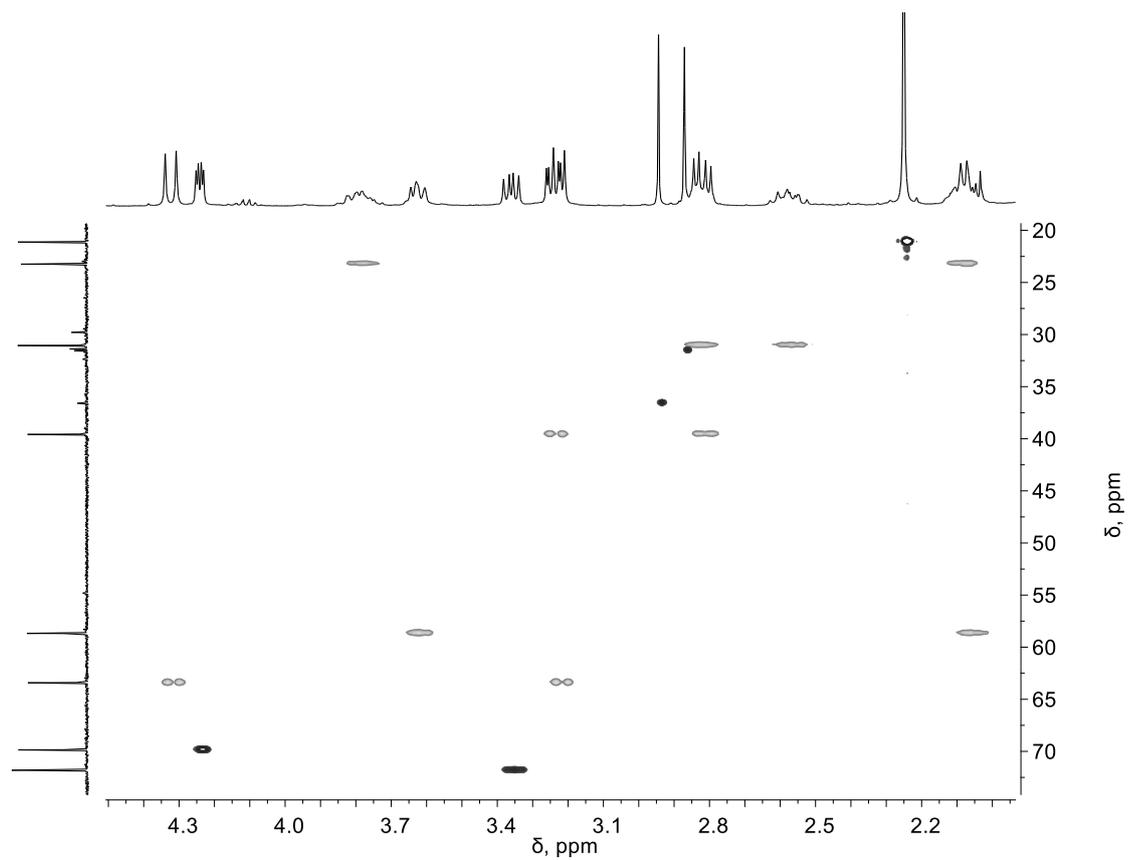
43. ¹H NMR spectrum of (*S,R*)-4'a



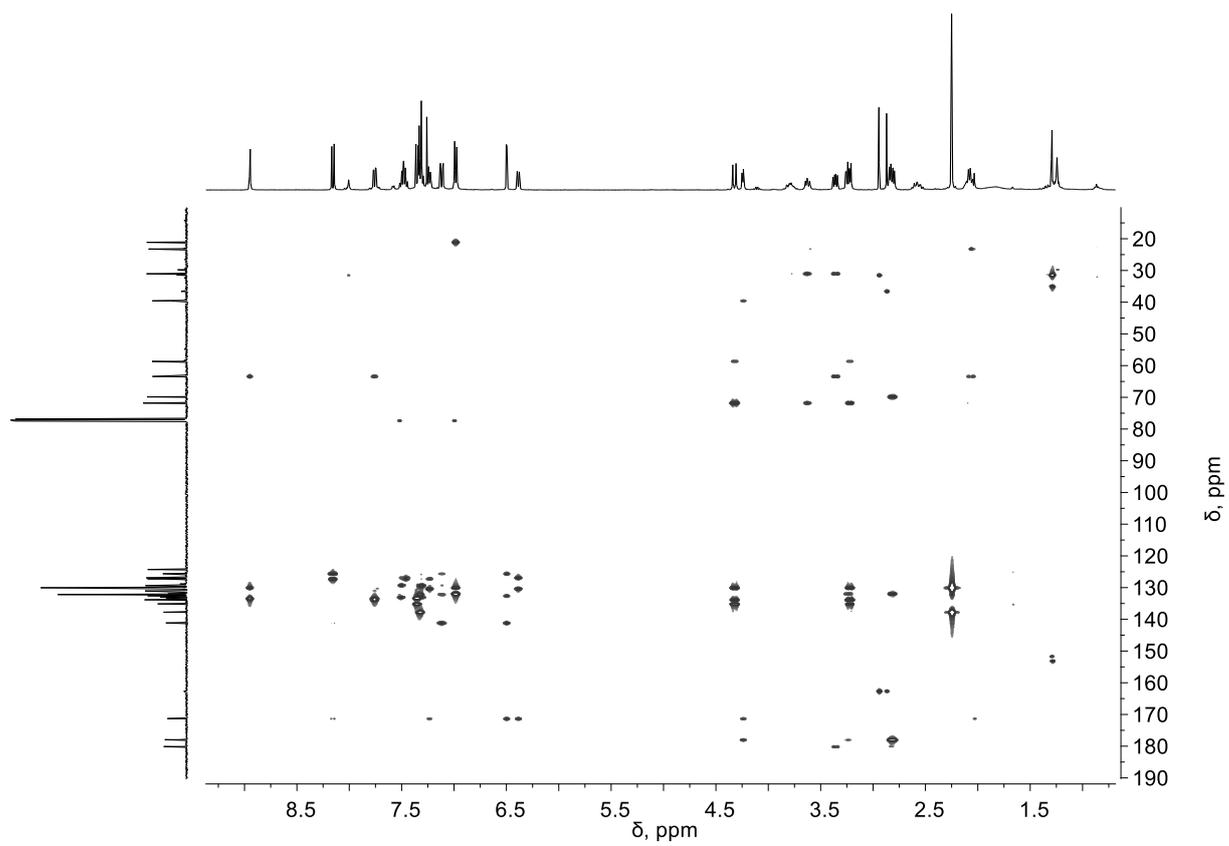
44. ^{13}C NMR spectrum of (*S,R*)-4'a



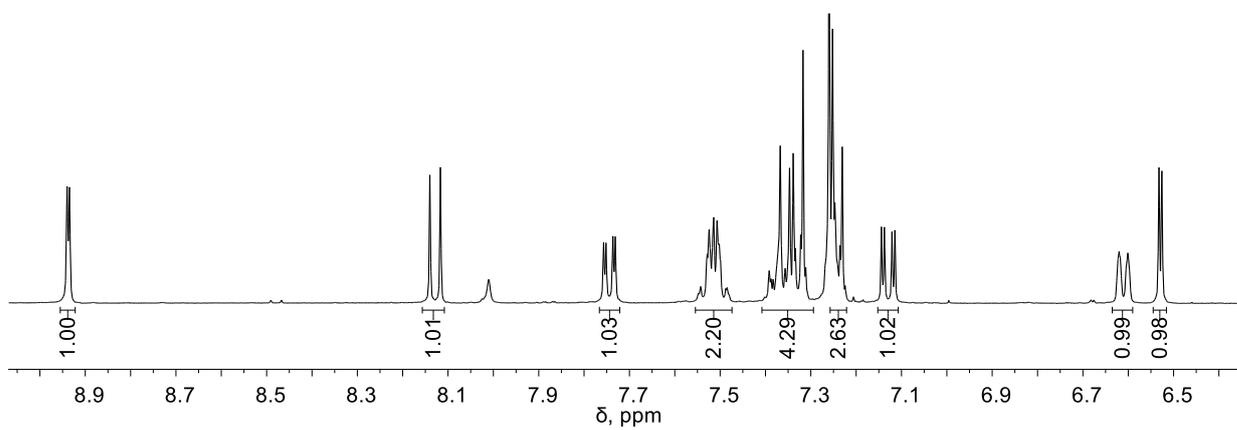
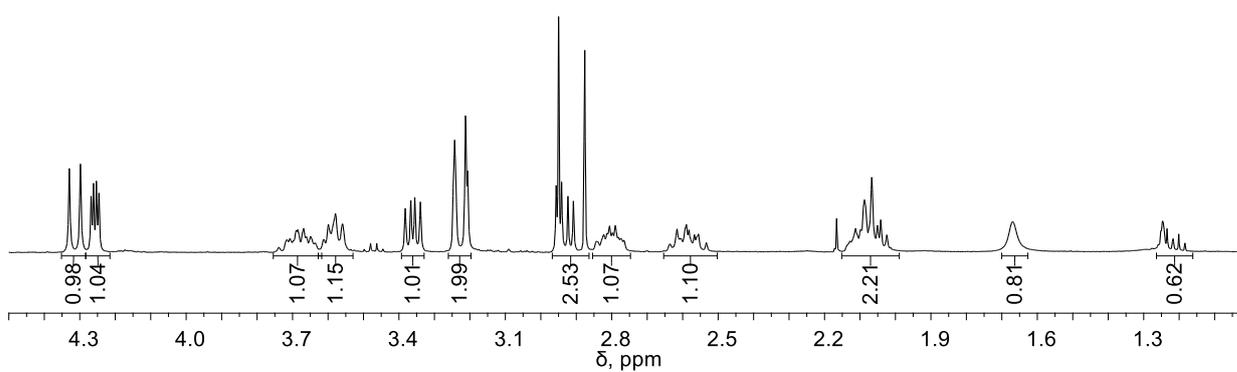
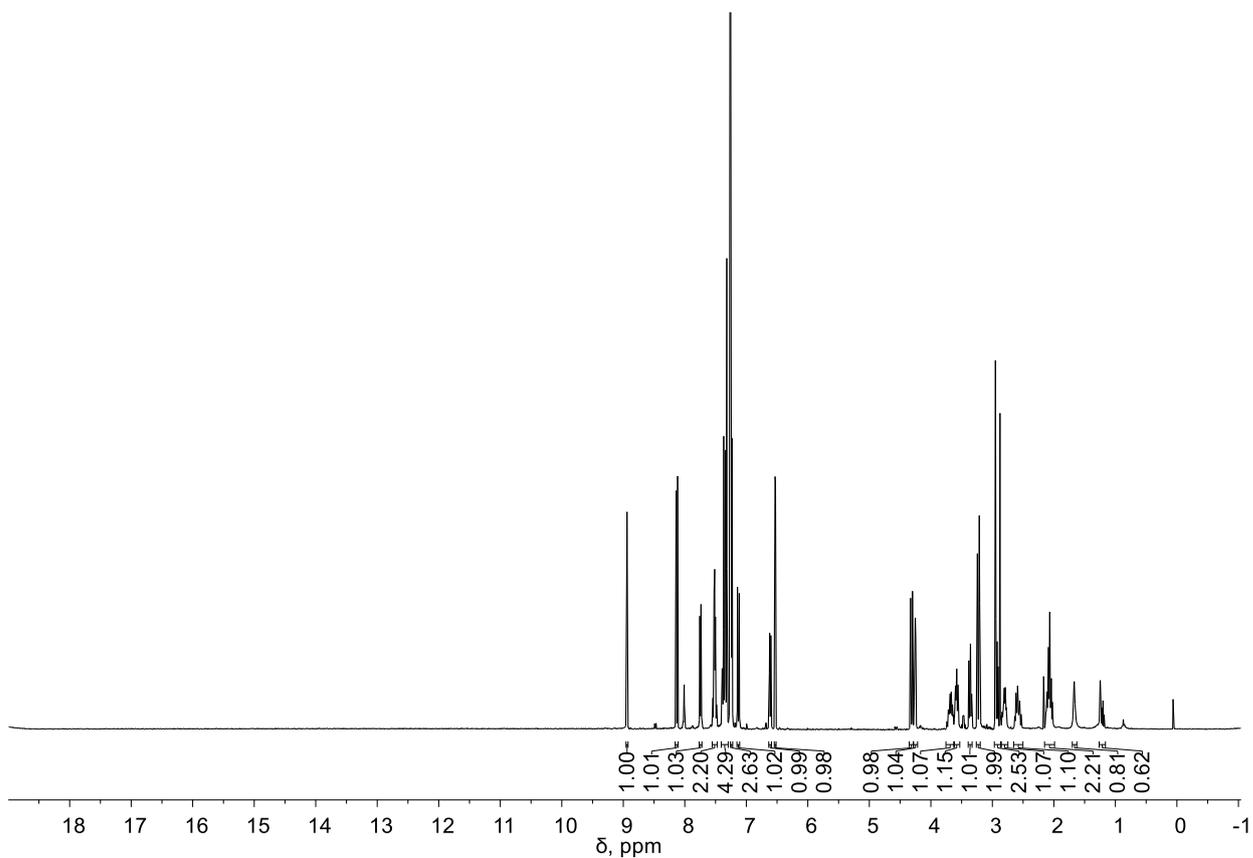
45. HSQC spectrum of (*S,R*)-4'a



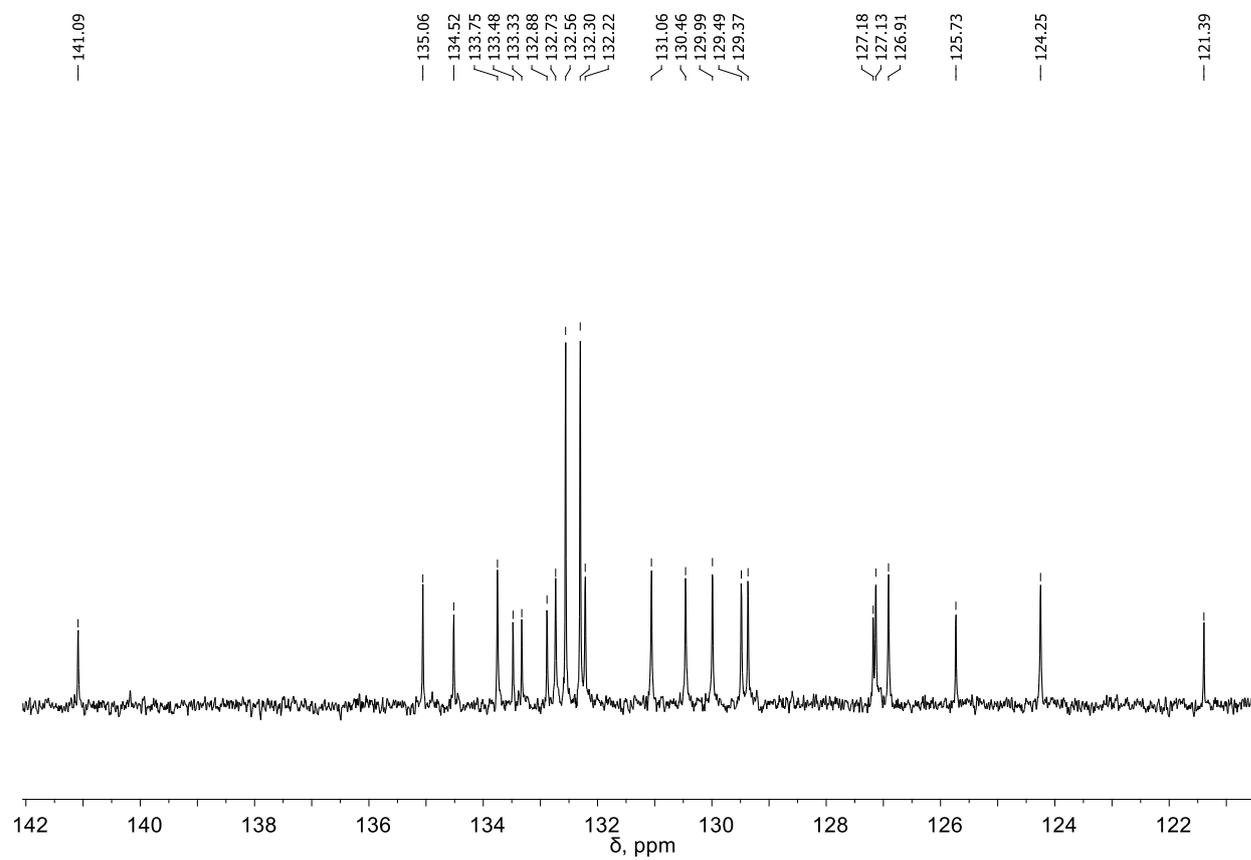
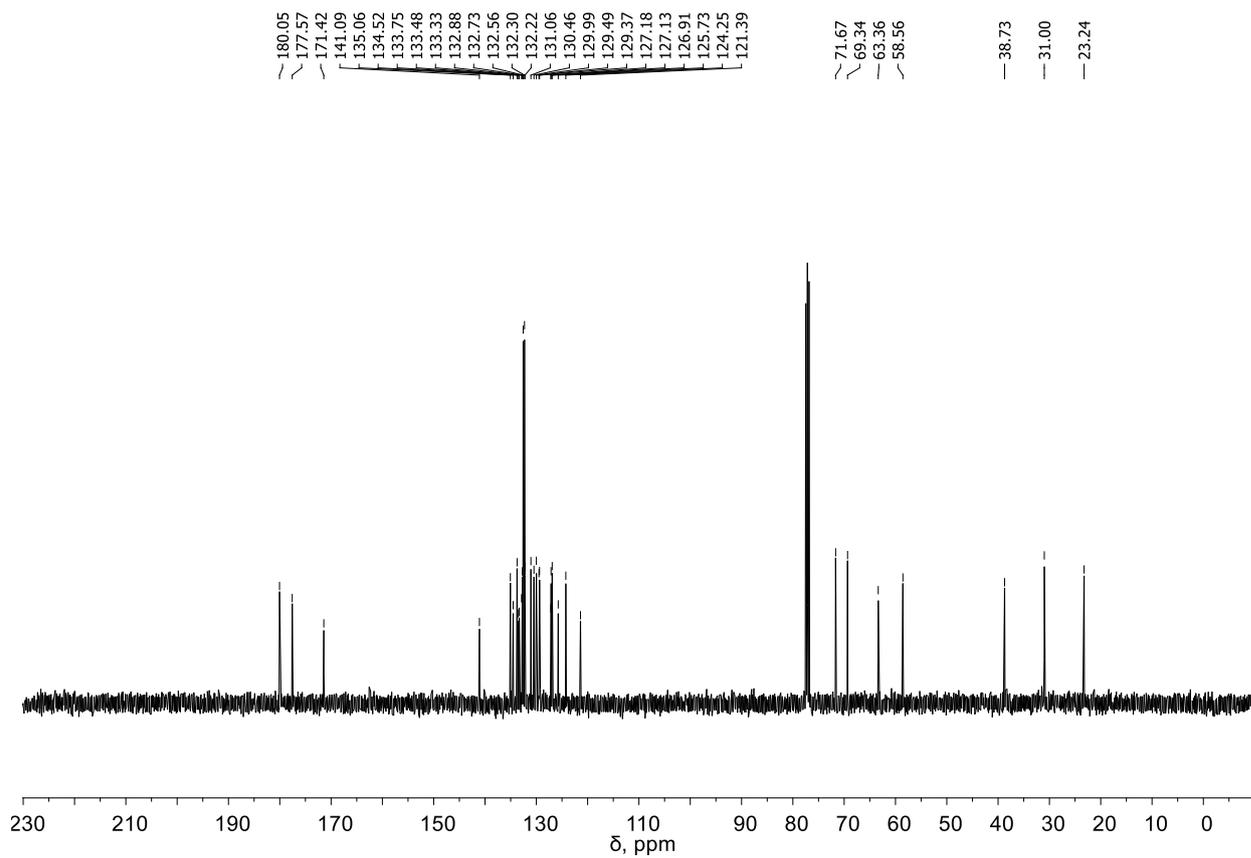
46. HMBC spectrum of (*S,R*)-4'a



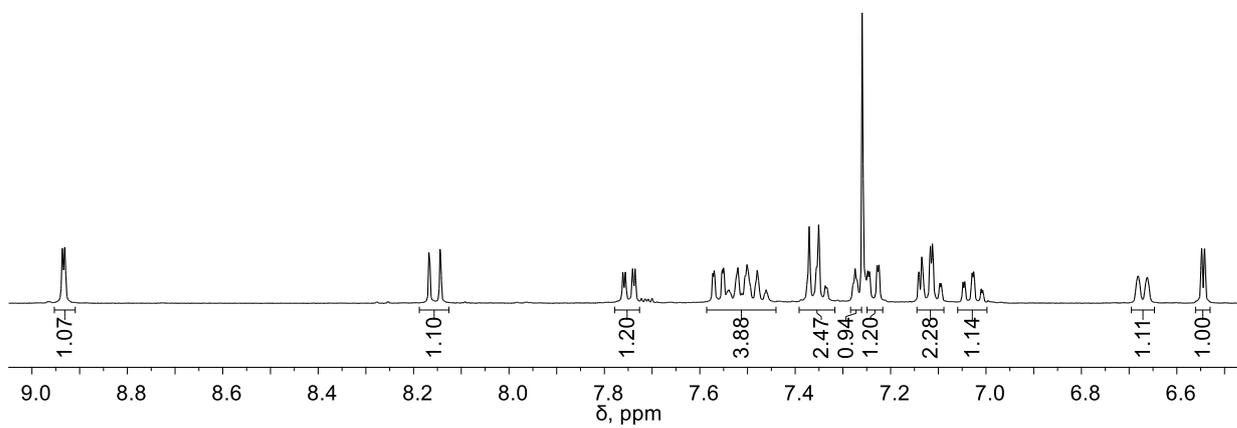
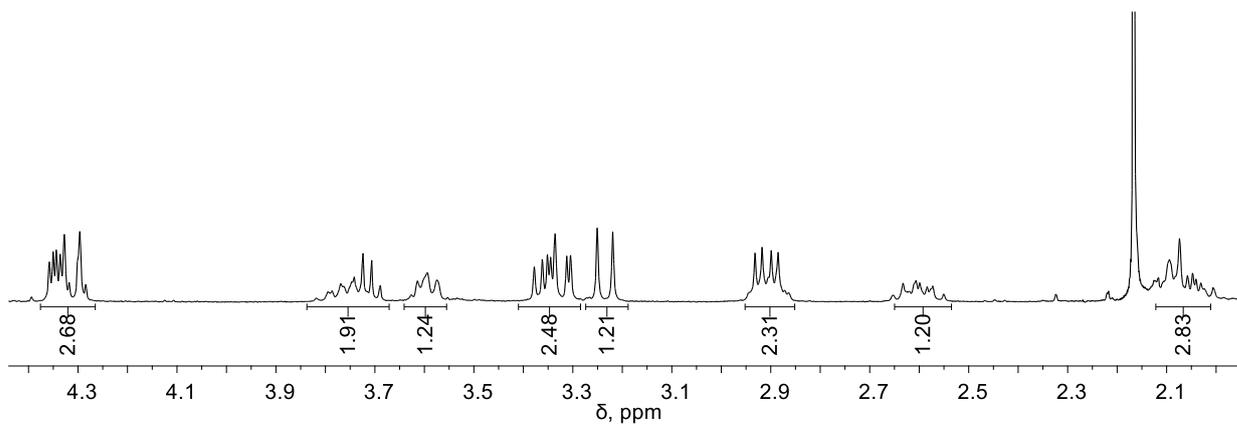
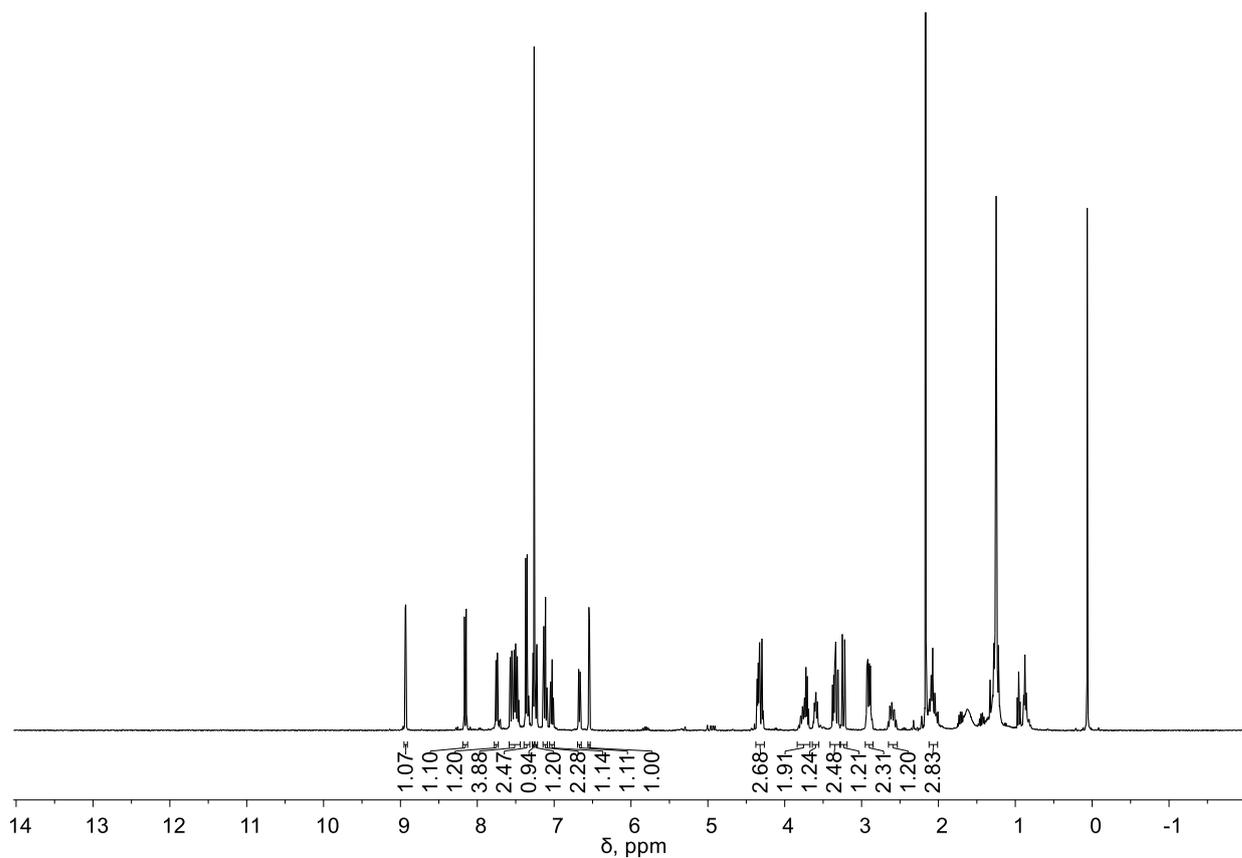
48. ¹H NMR spectrum of (*S,R*)-4'b



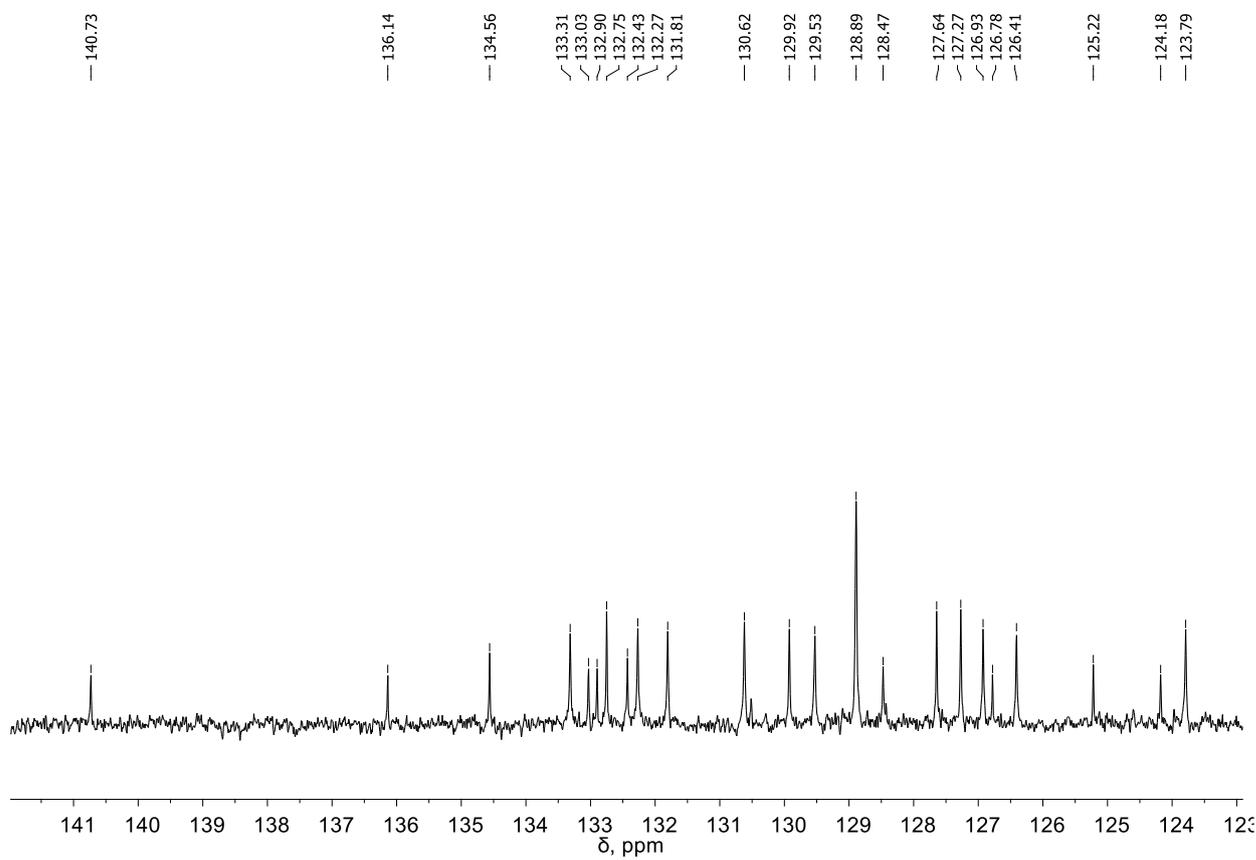
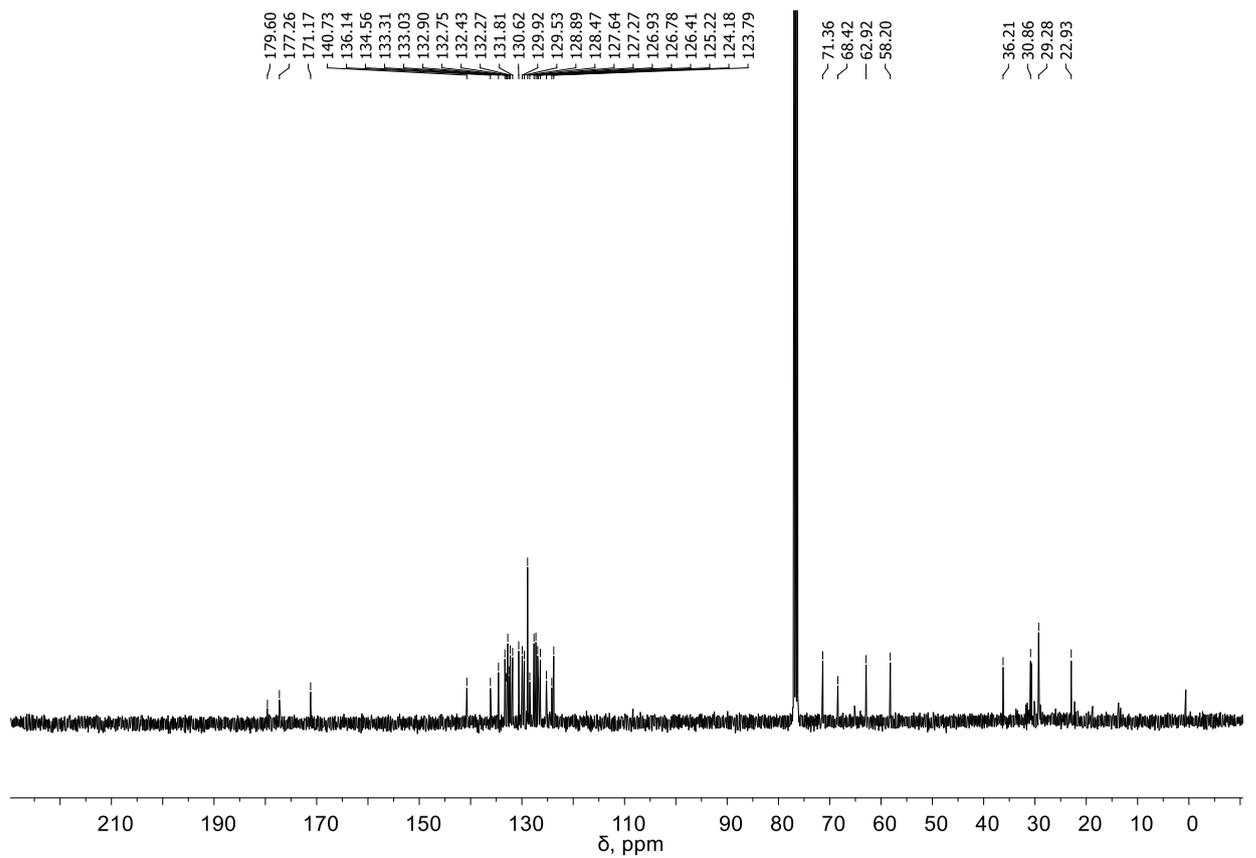
49. ^{13}C NMR spectrum of (*S,R*)-4'b



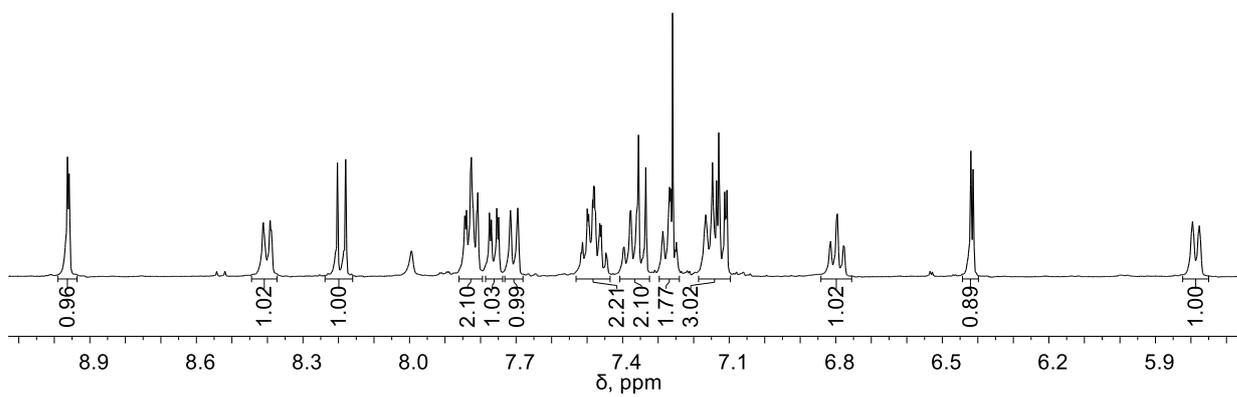
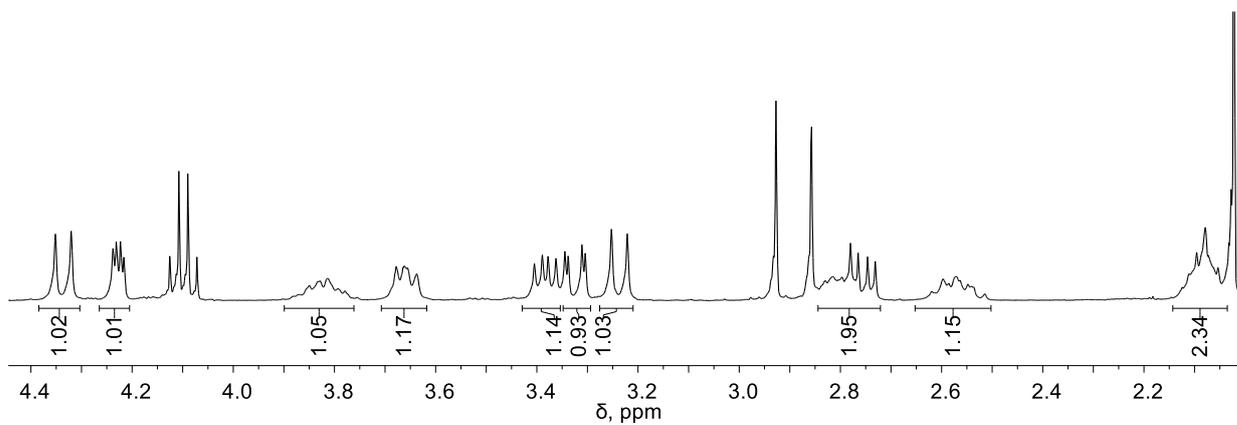
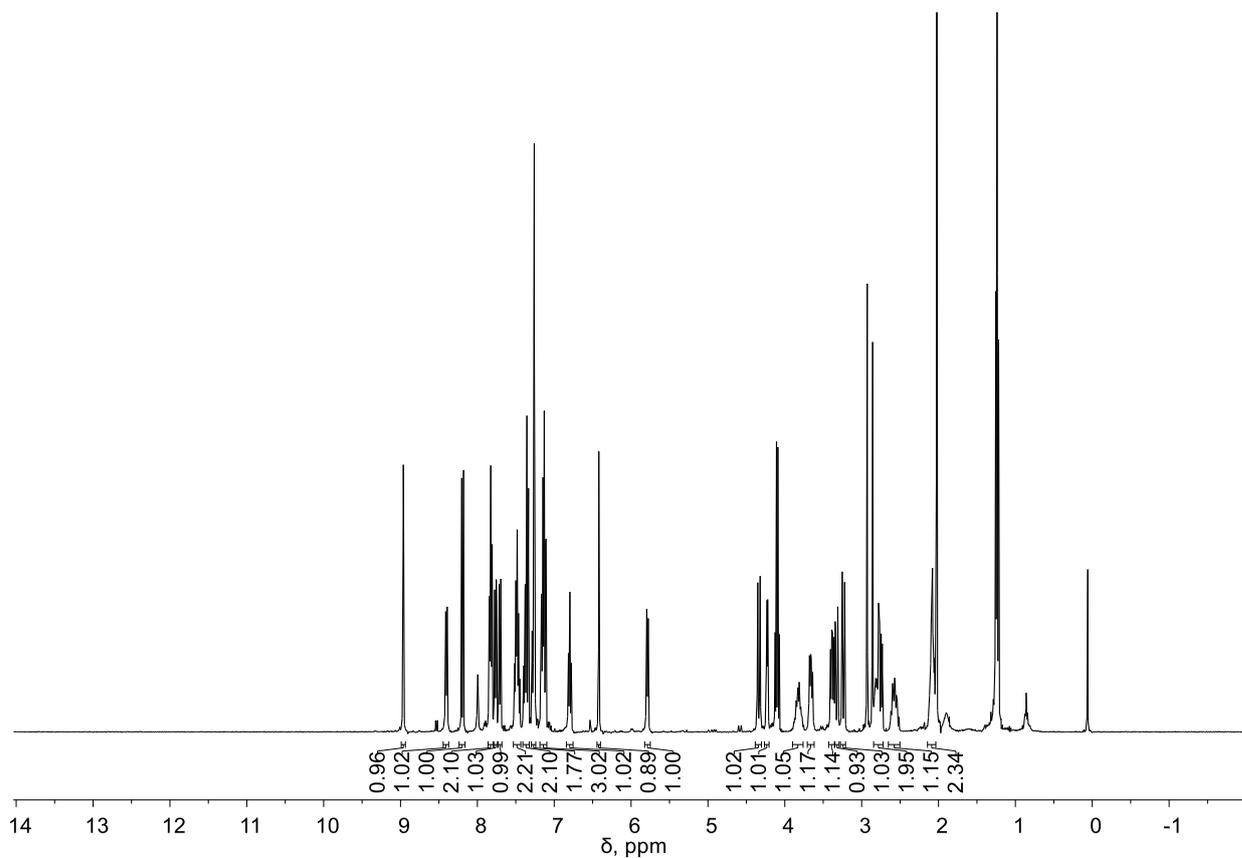
50. ^1H NMR spectrum of (*S,R*)-4'**c**



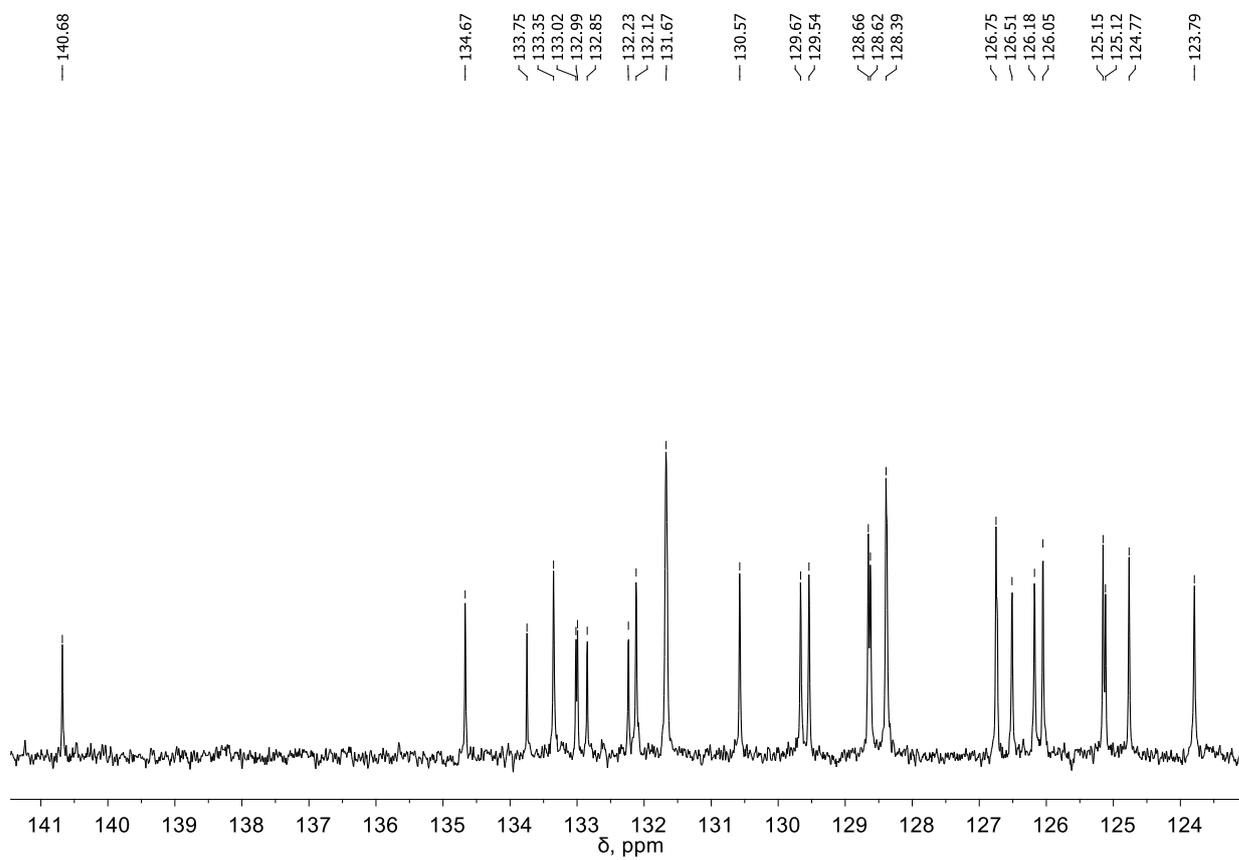
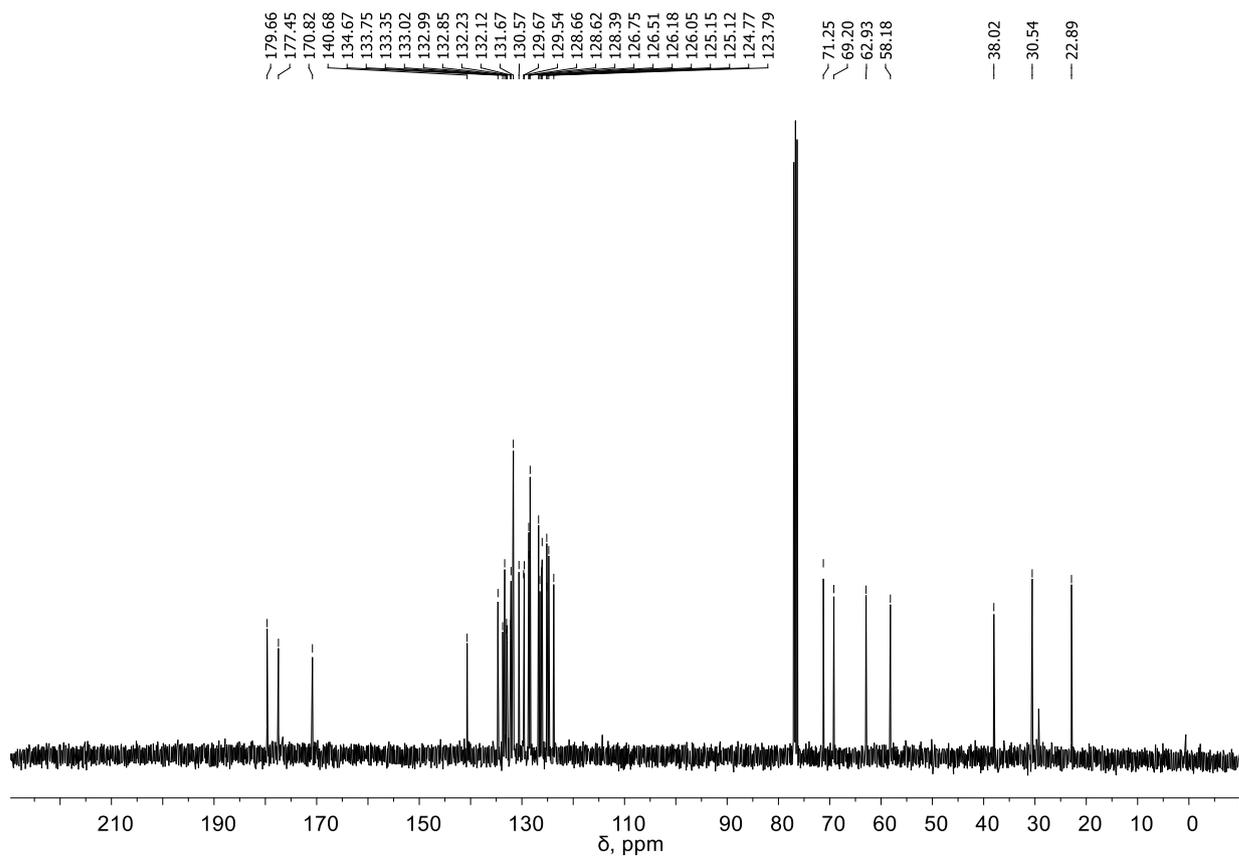
51. ^{13}C NMR spectrum of (*S,R*)-4'**c**



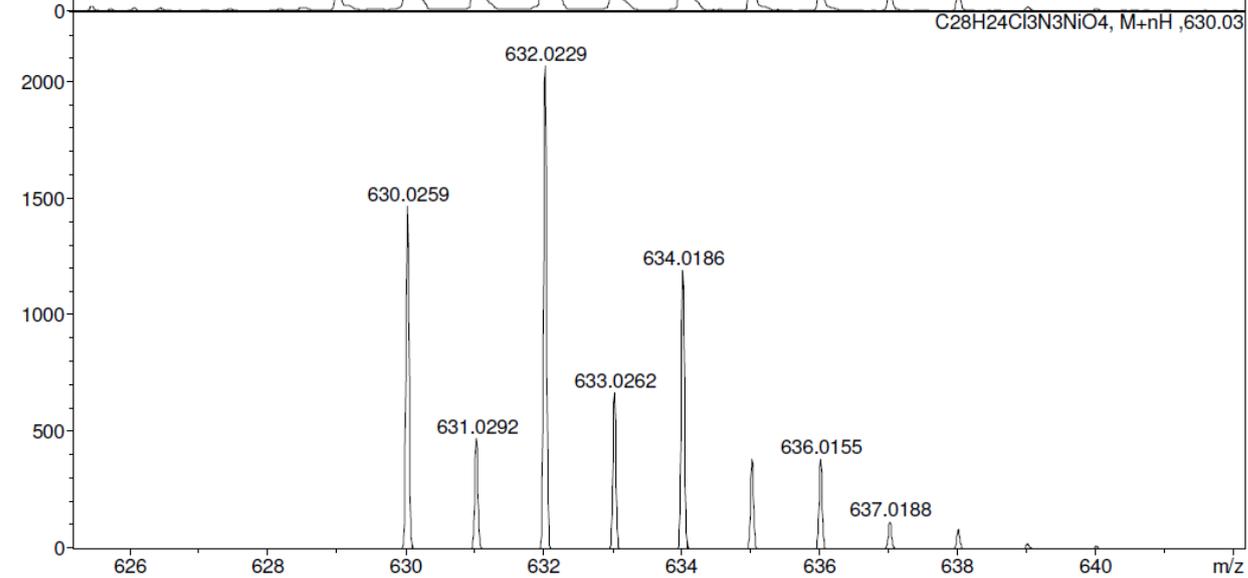
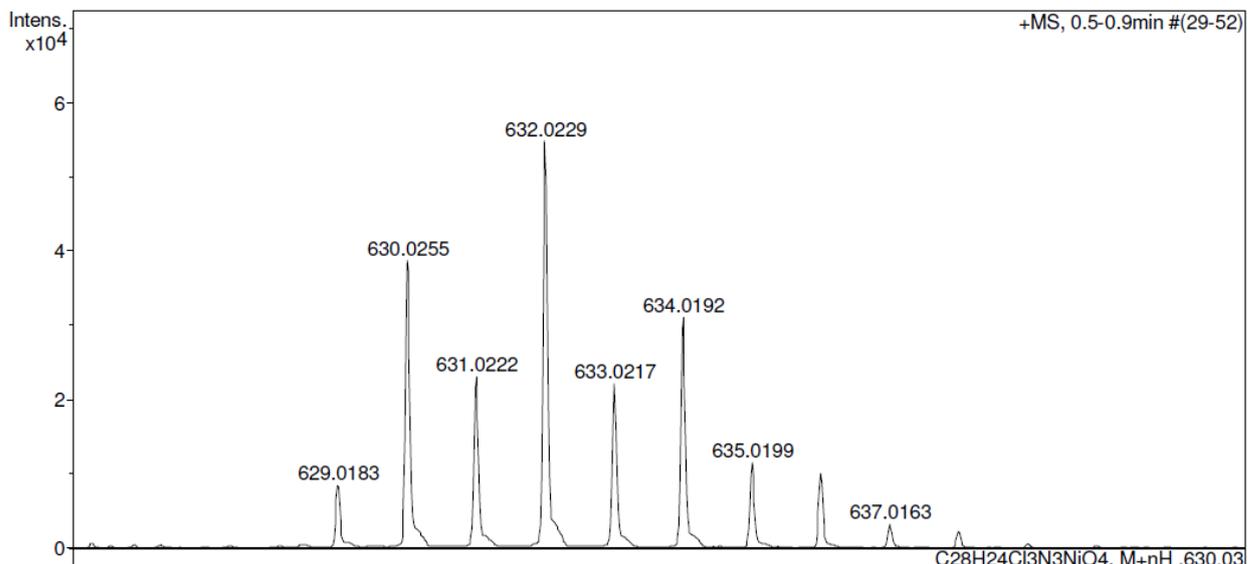
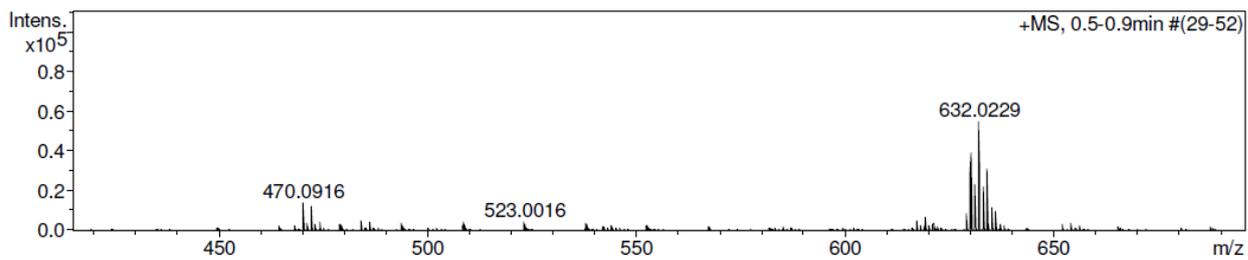
52. ¹H NMR spectrum of (*S,R*)-4'd



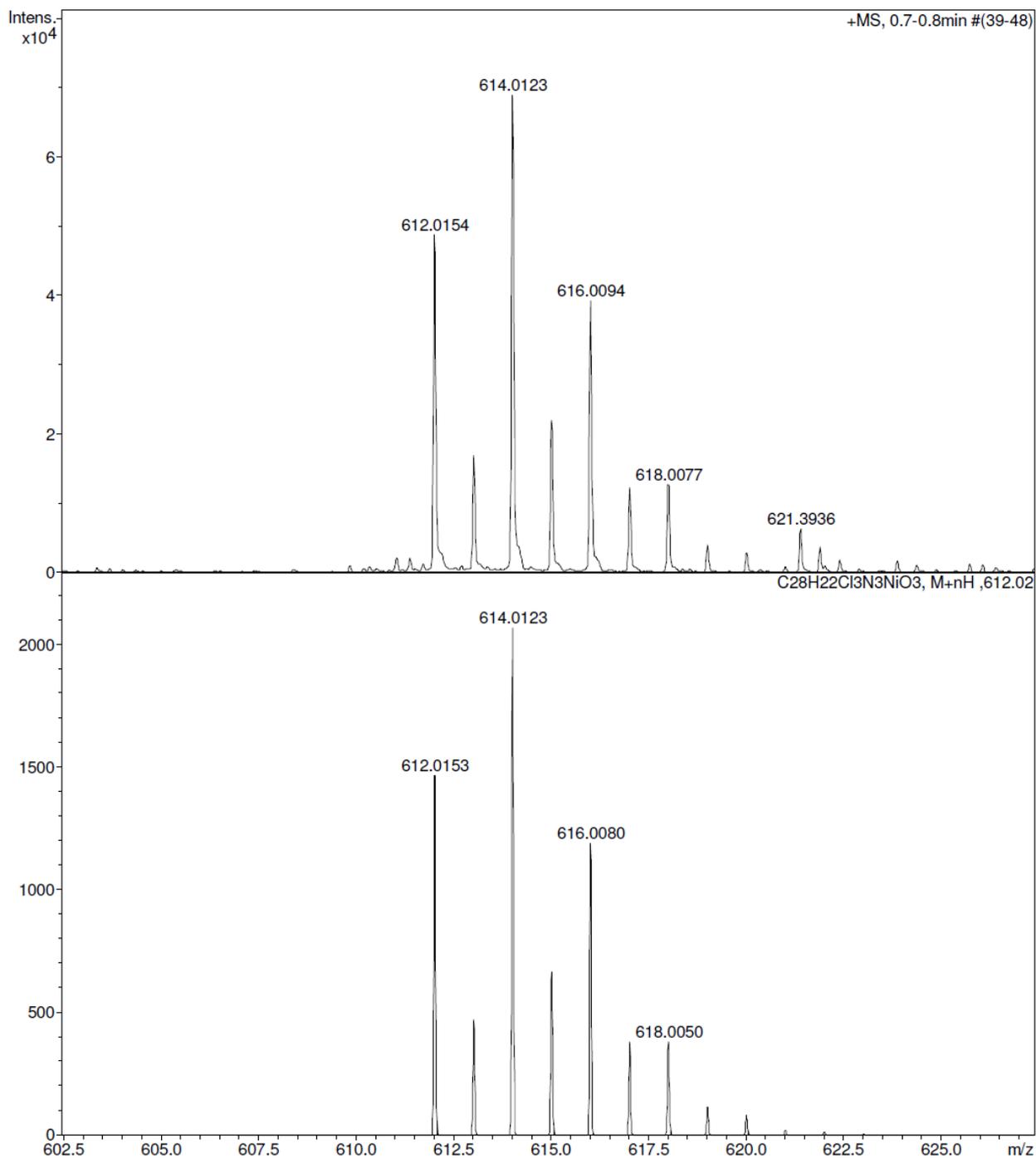
53. ^{13}C NMR spectrum of (*S,R*)-4'd



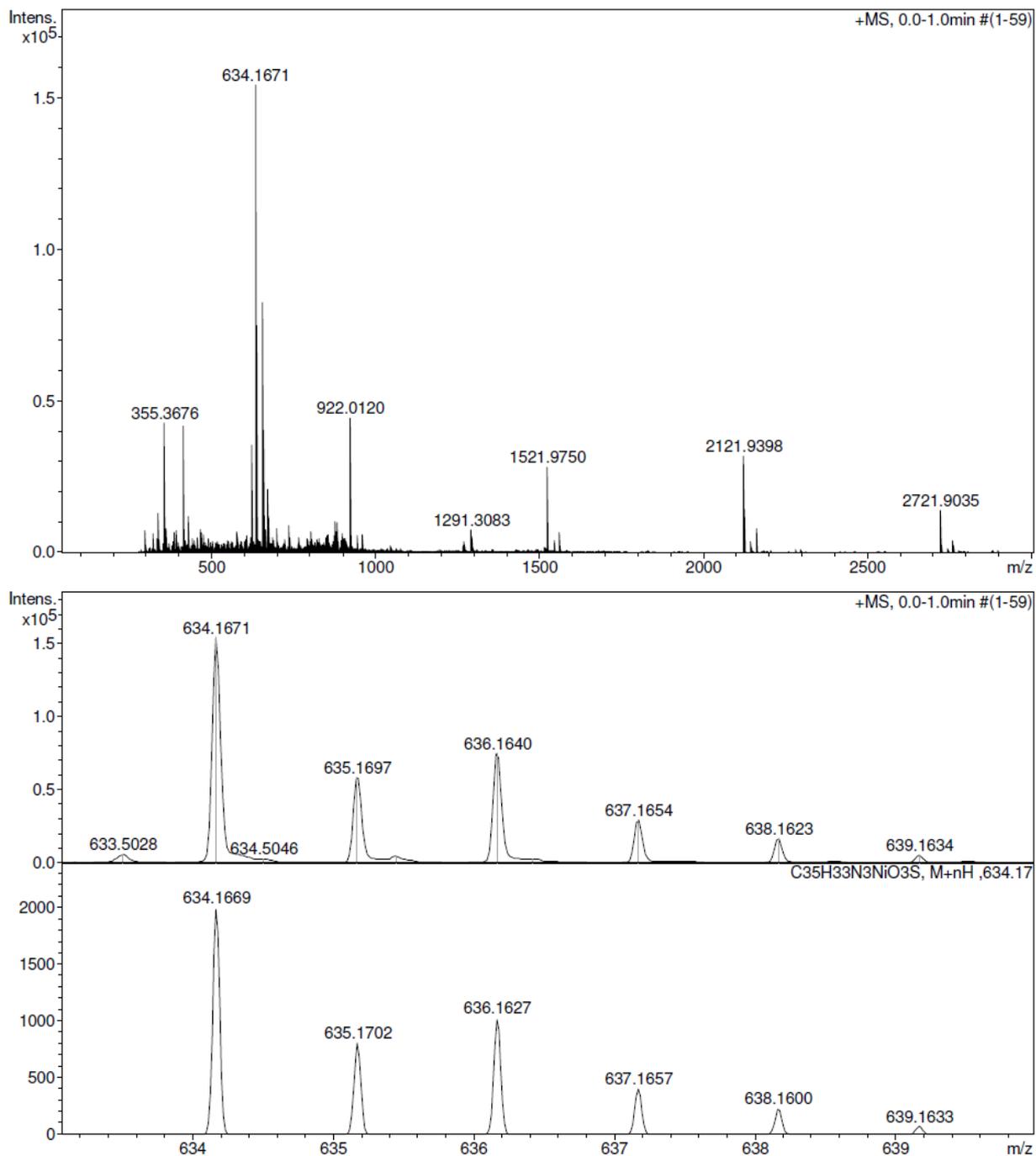
54. ESI-HRMS data for (*S,R*)-2'

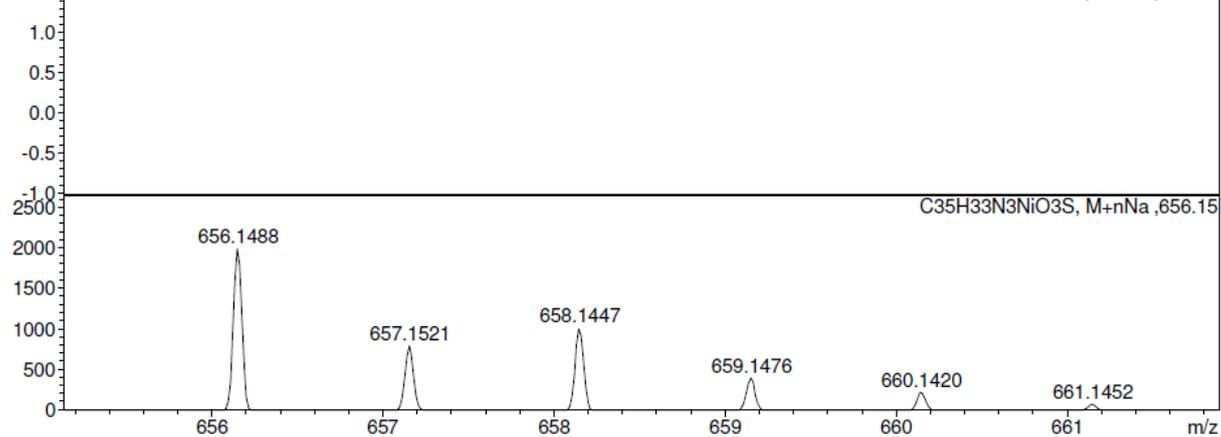
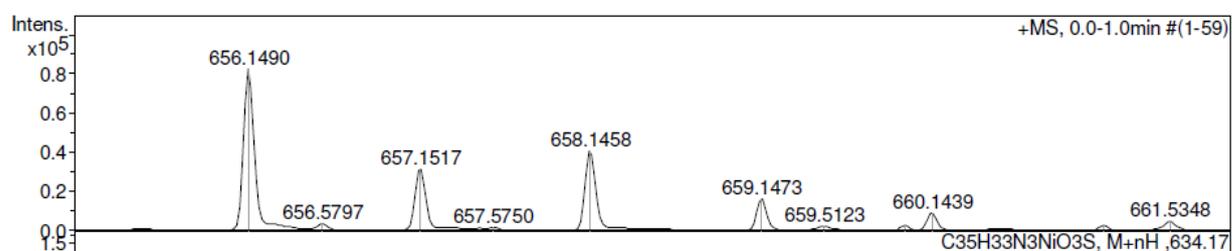
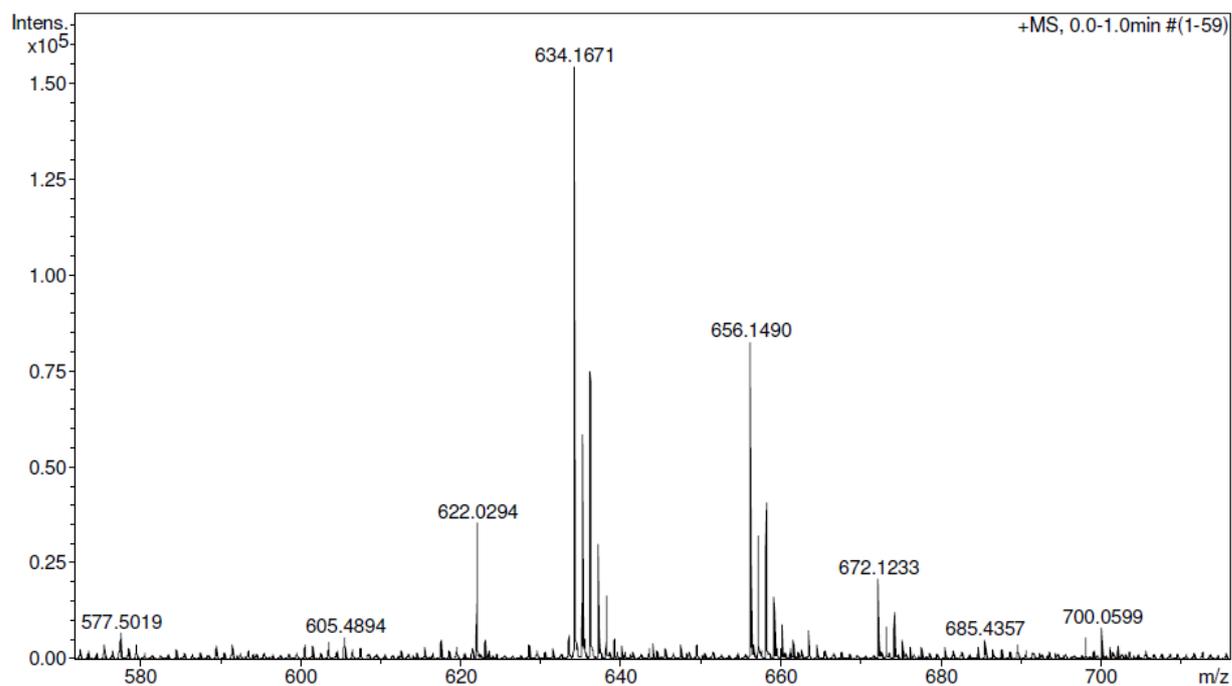


55. ESI-HRMS data for 3'

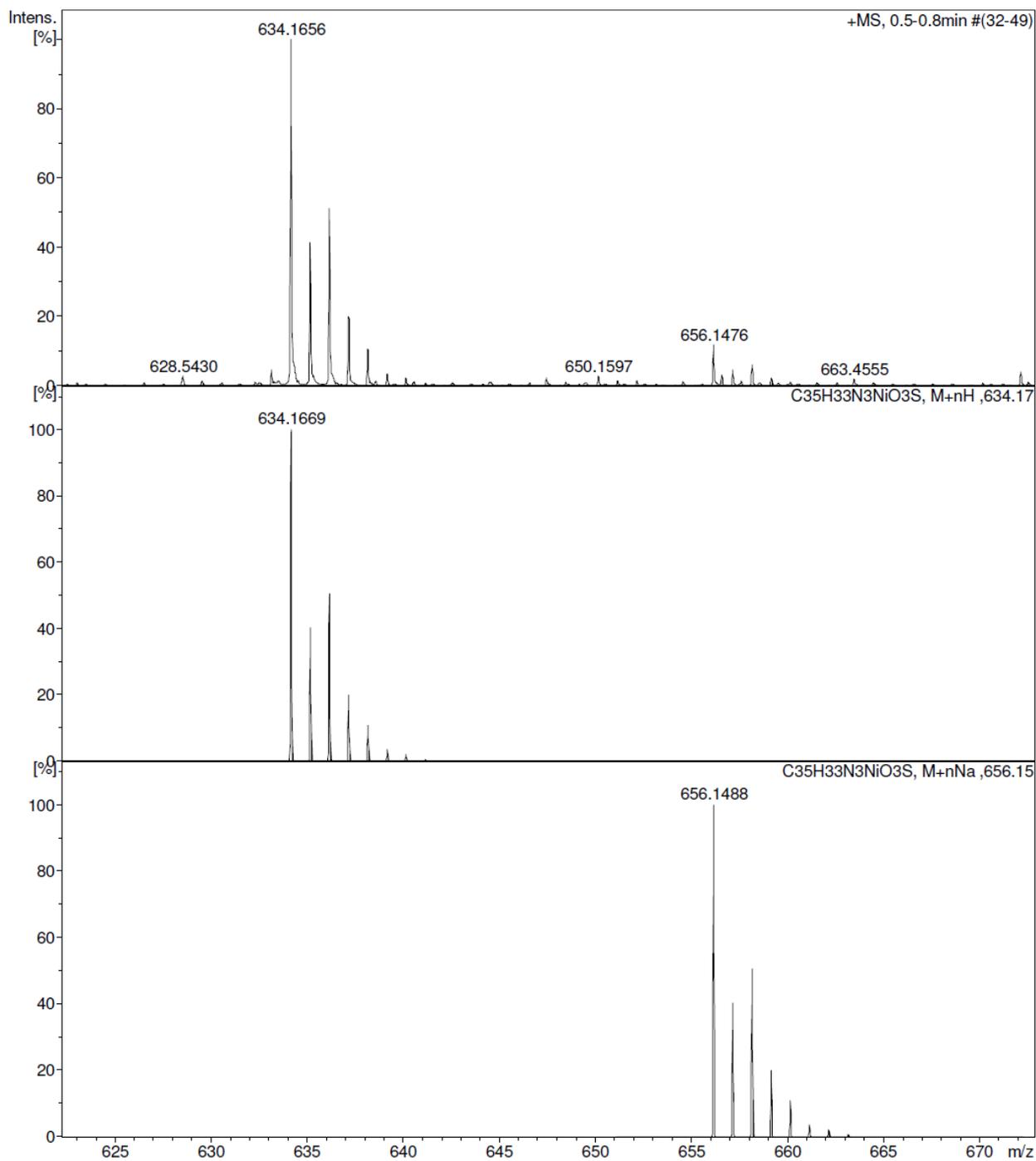


56. ESI-HRMS data for (*S,R*)-4a

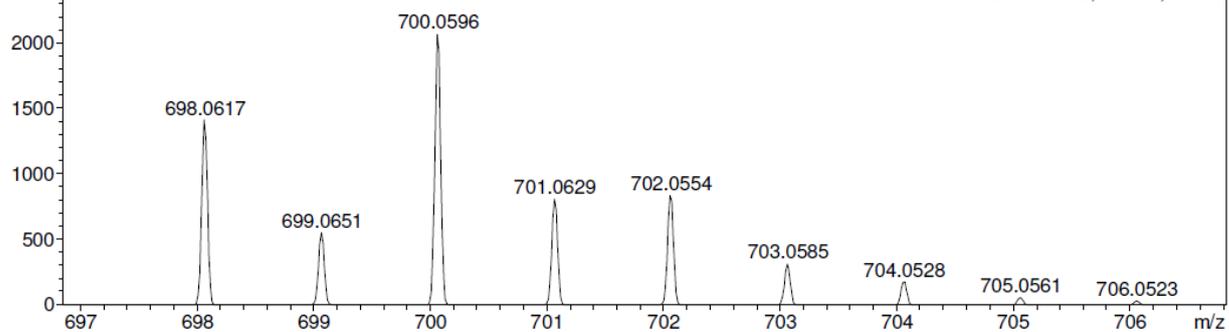
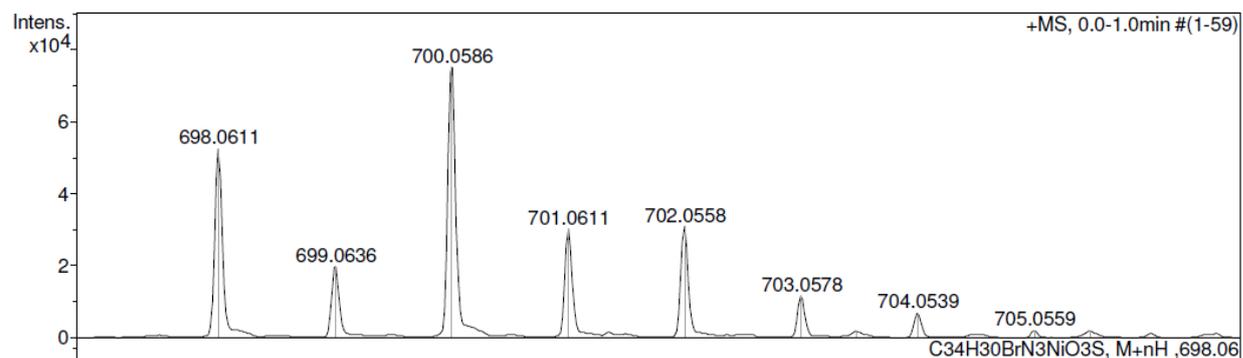
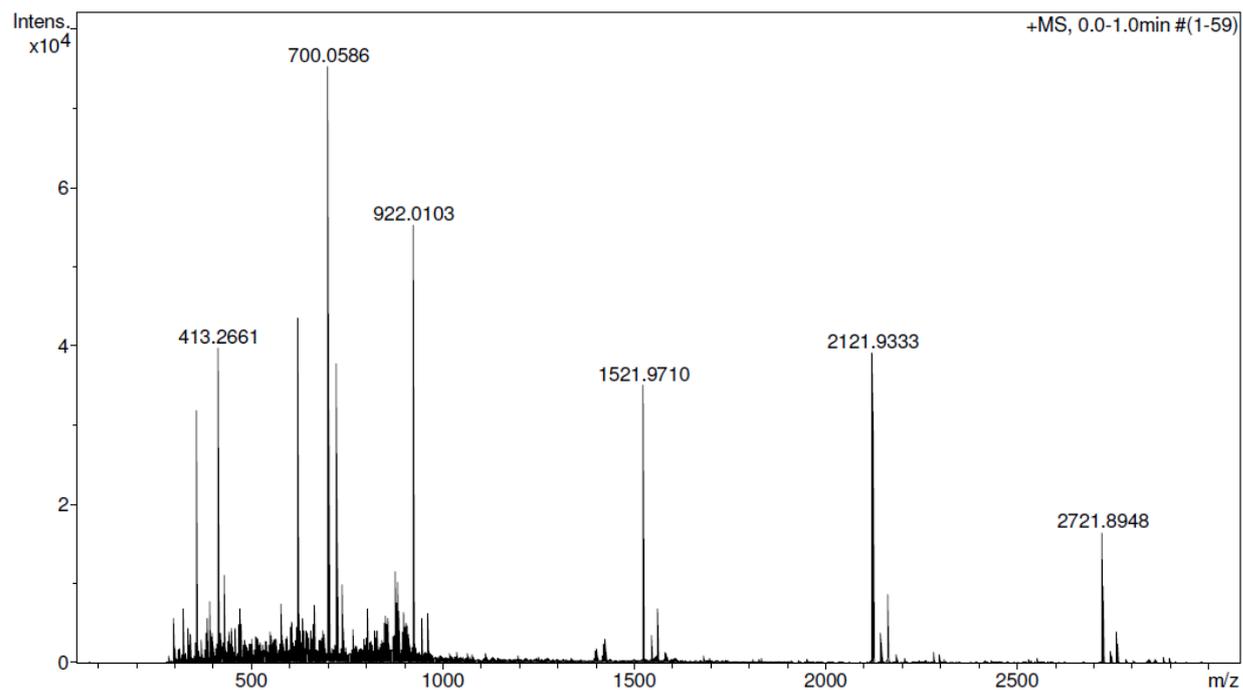


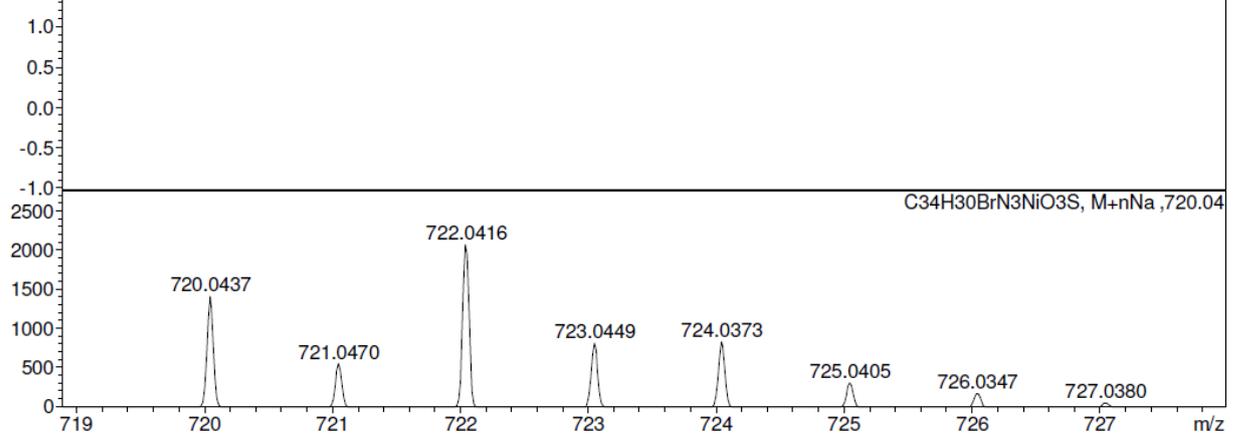
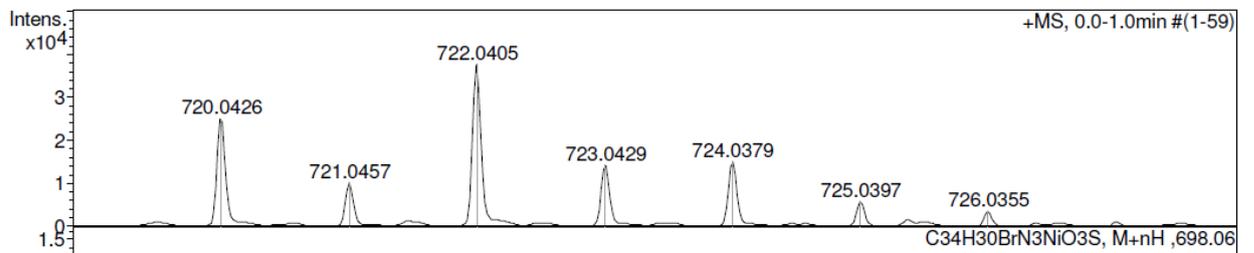
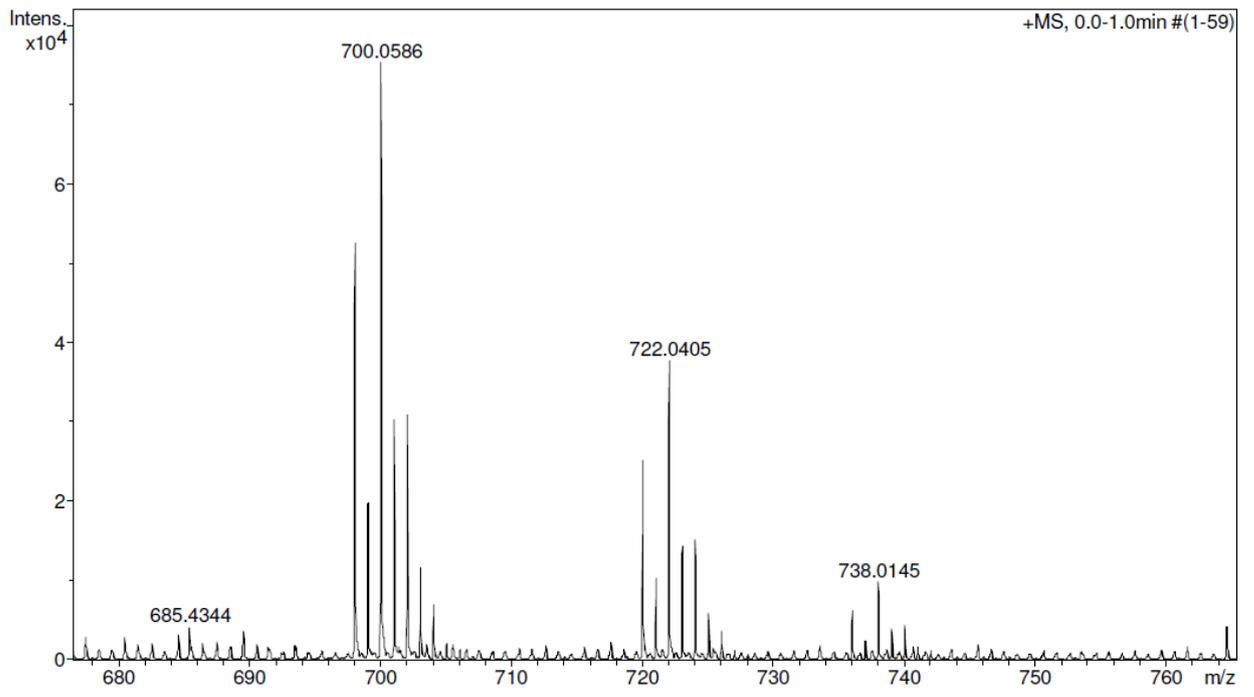


57. ESI-HRMS data for (*S,S*)-4a

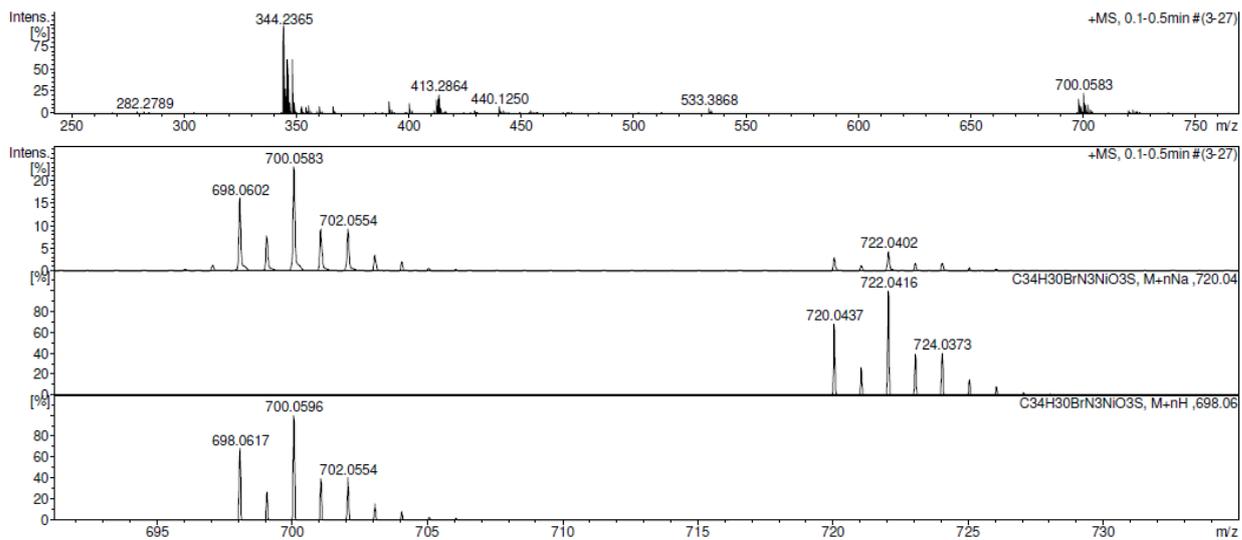


58. ESI-HRMS data for (S,R)-4b

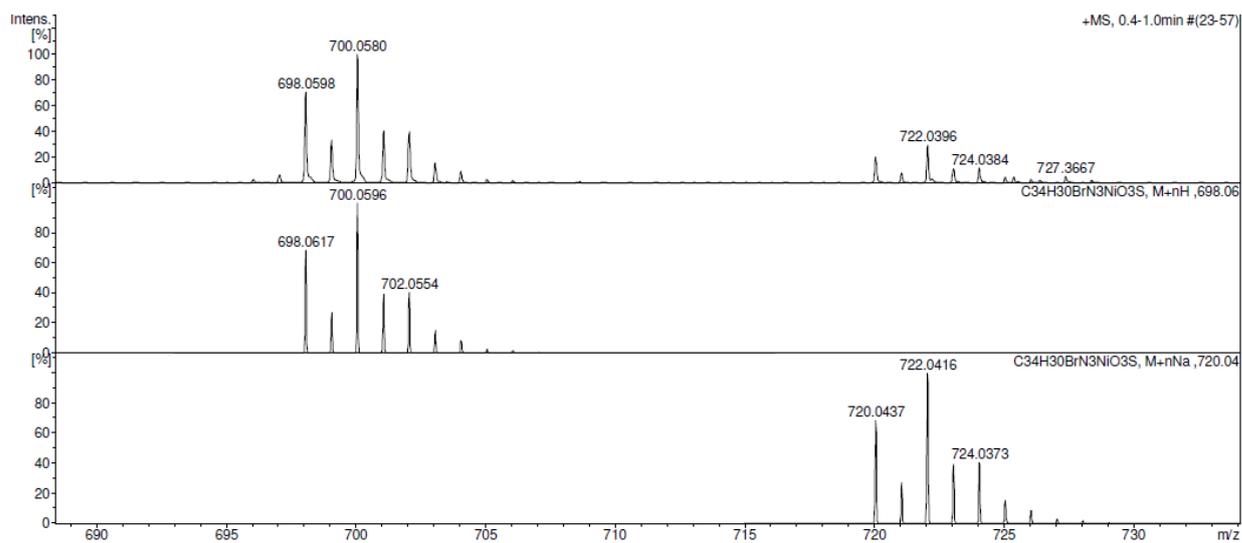




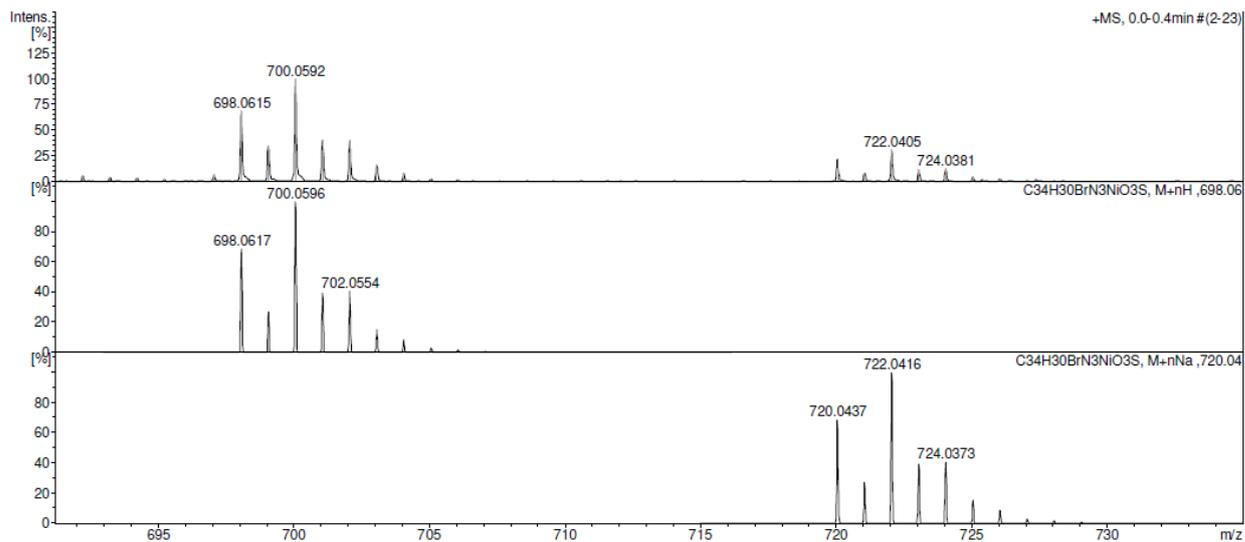
59. ESI-HRMS data for (*S,S*)-4b



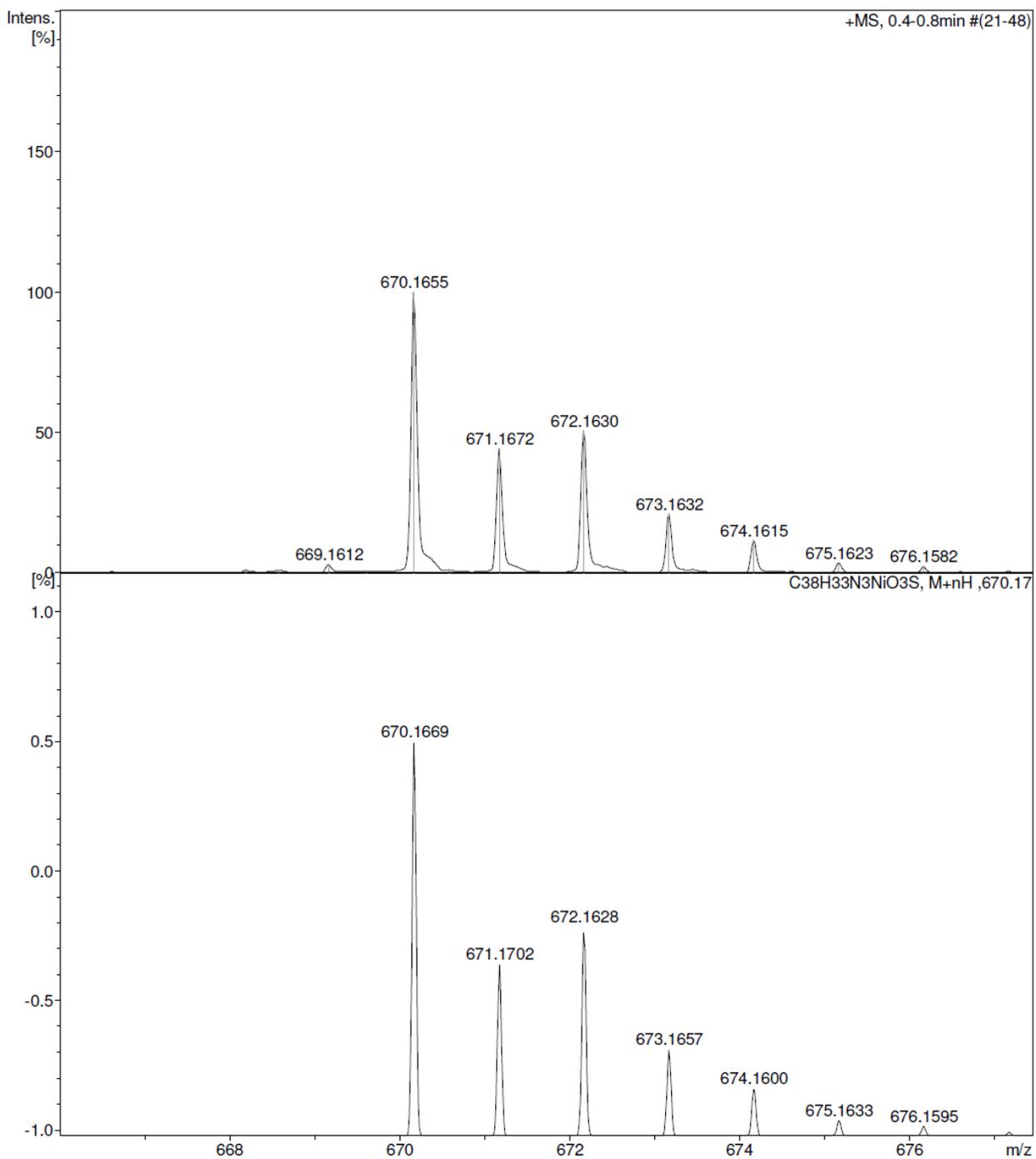
60. ESI-HRMS data for (*S,R*)-4c



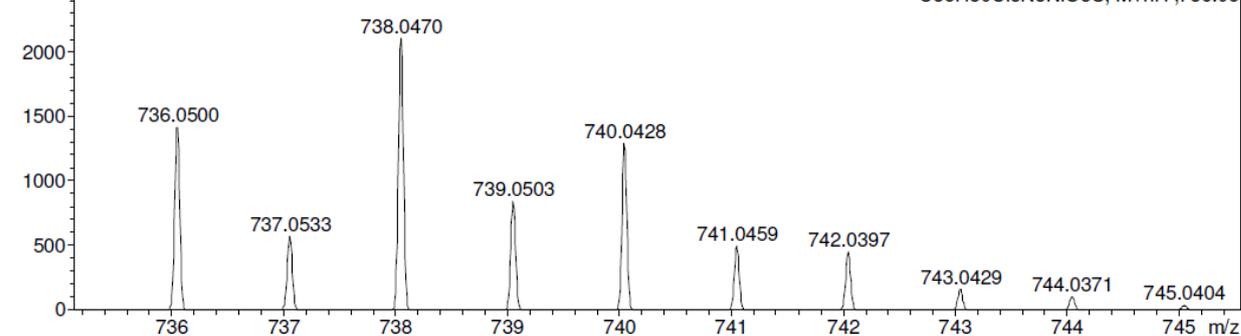
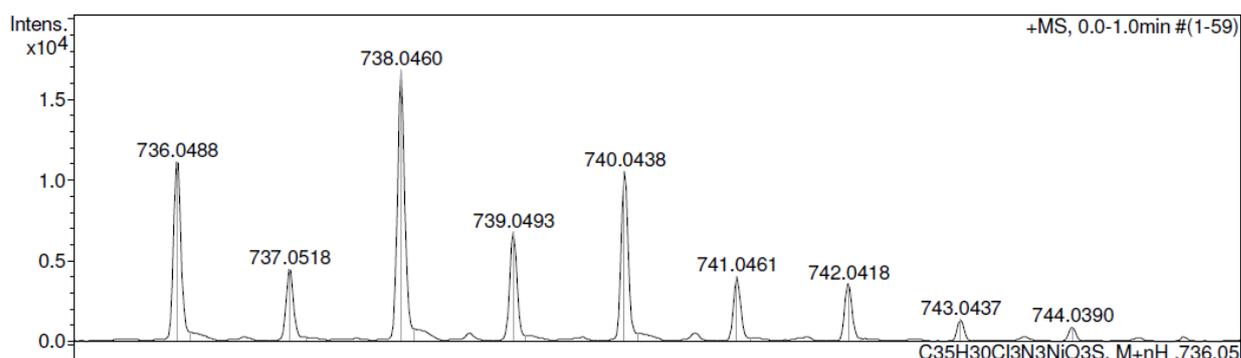
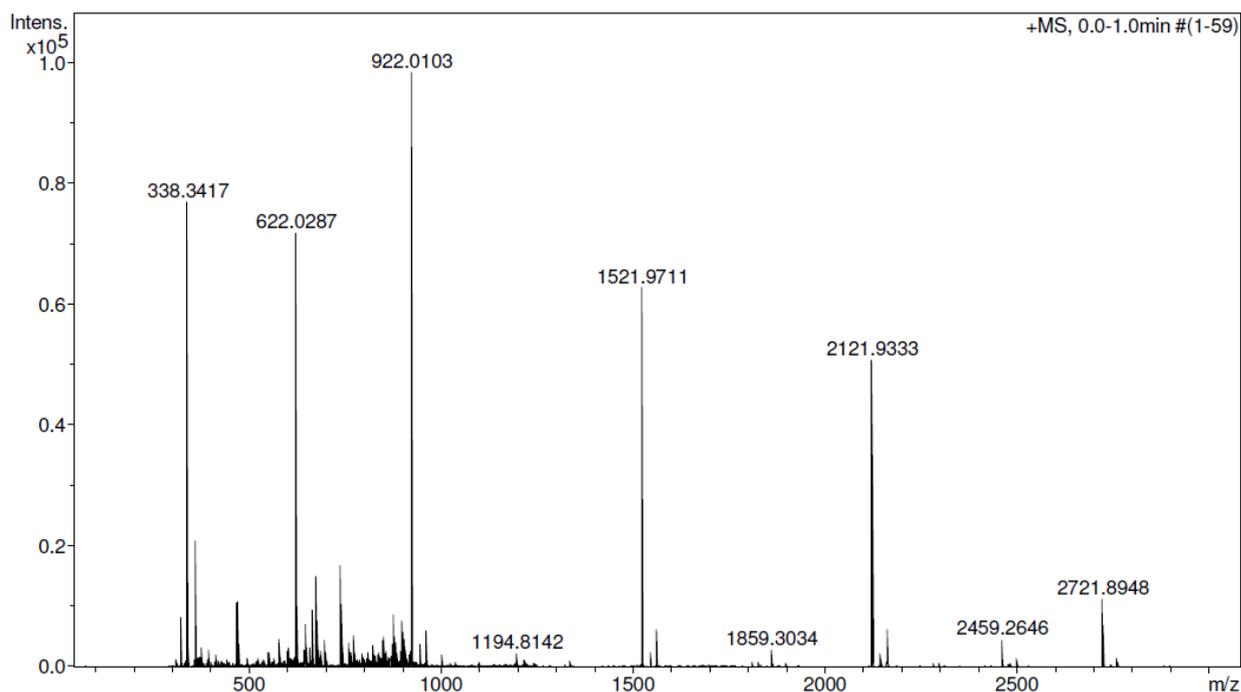
61. ESI-HRMS data for (*S,S*)-4c

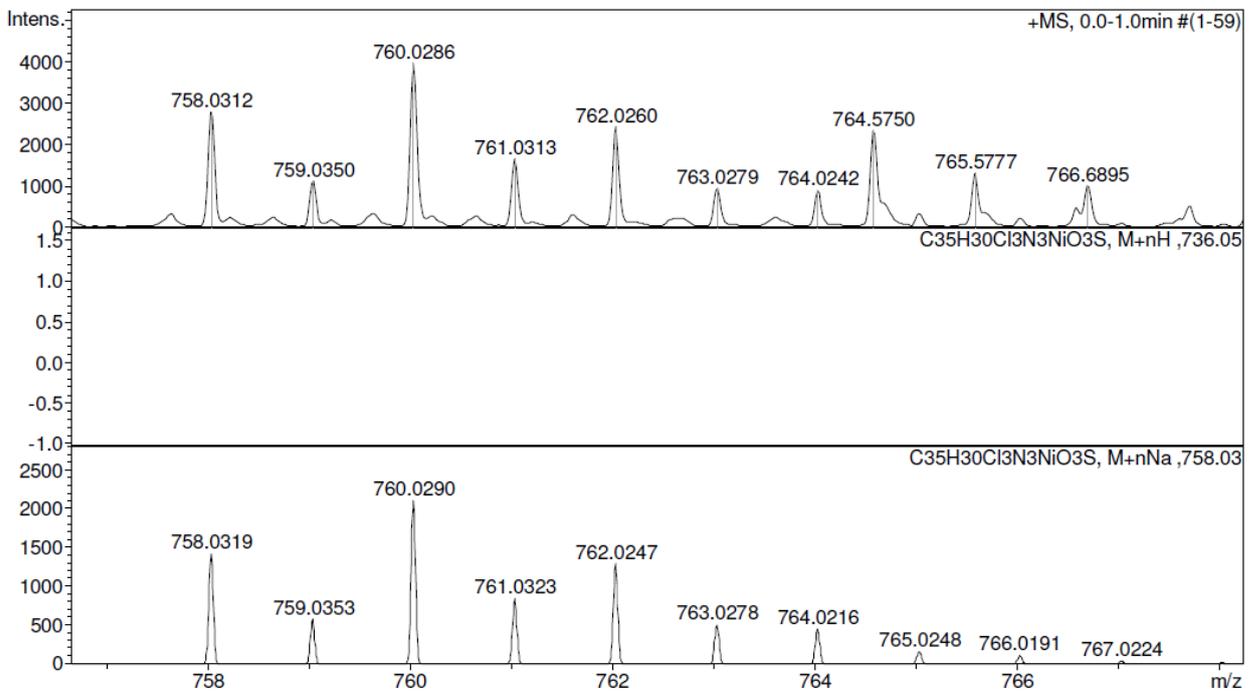
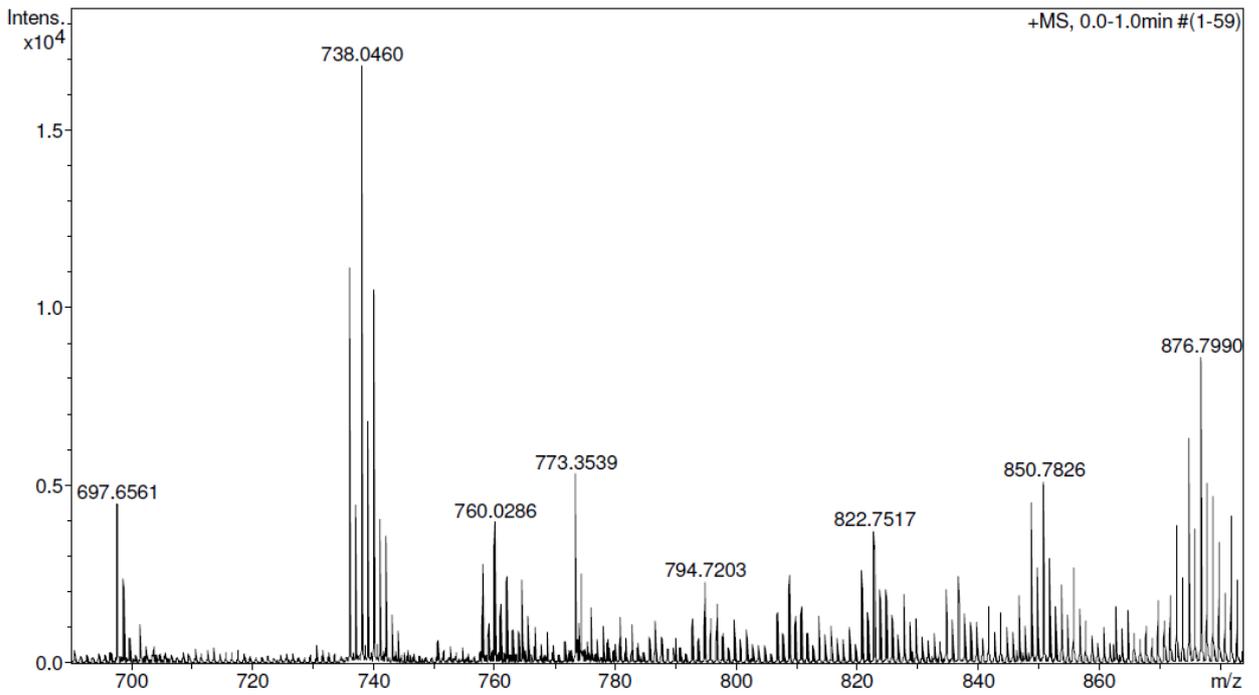


62. ESI-HRMS data for (S,R)-4d

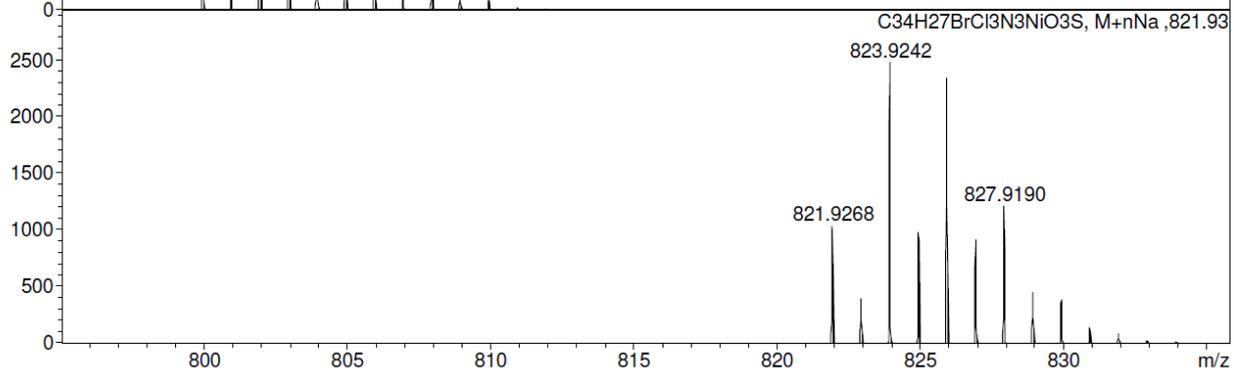
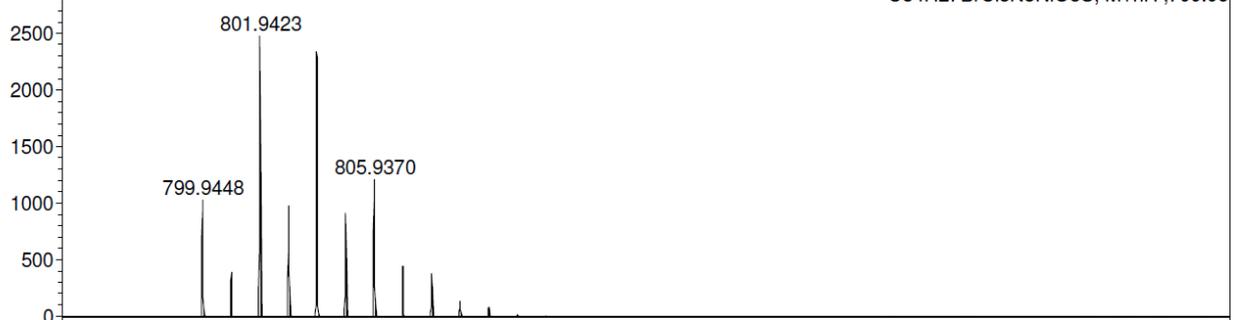
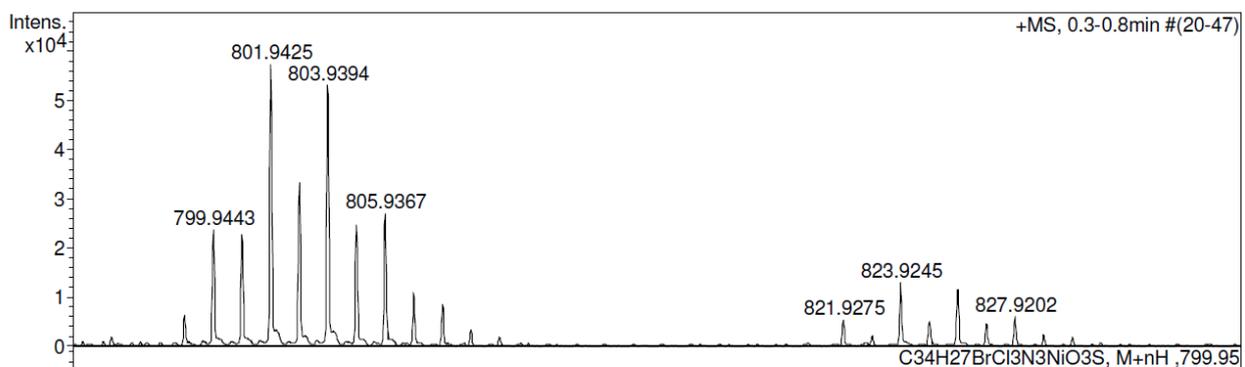
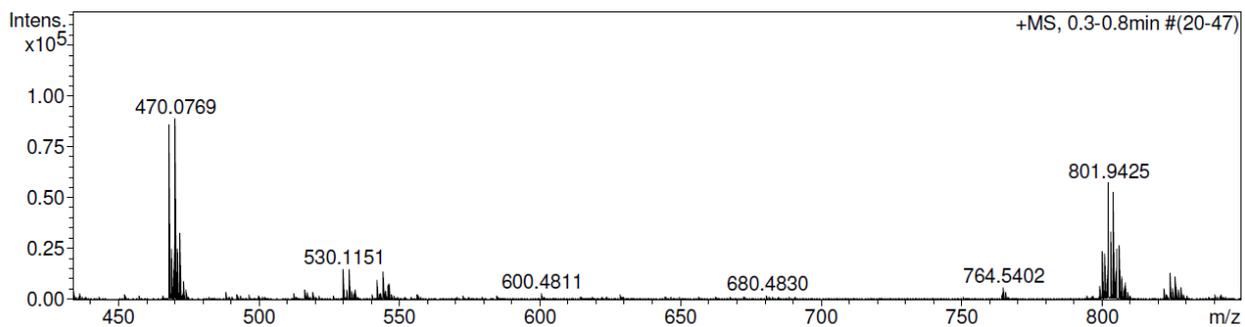


63. ESI-HRMS data for (*S,R*)-4'a

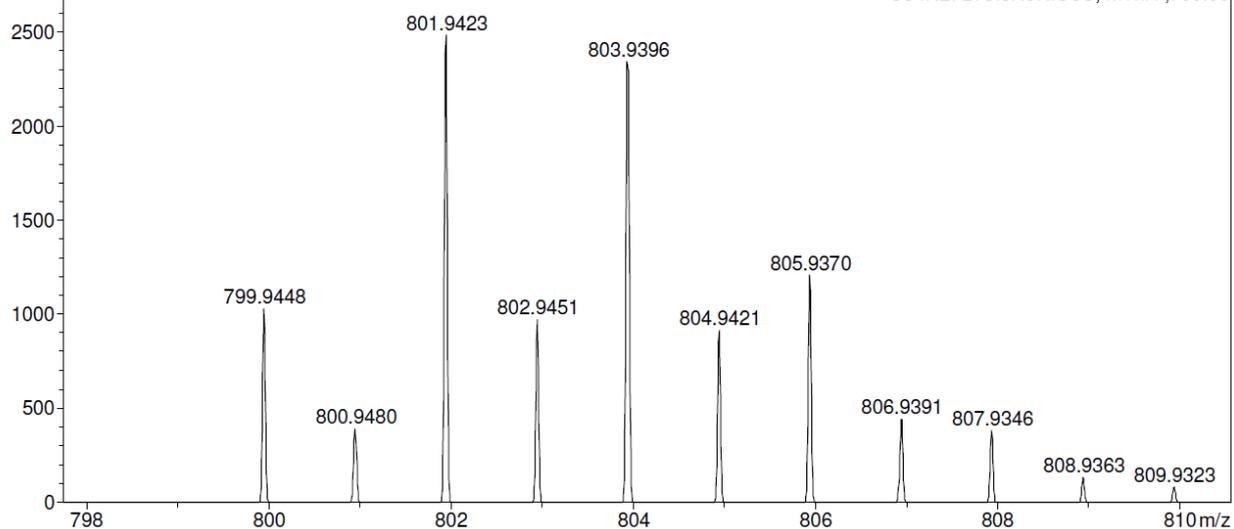
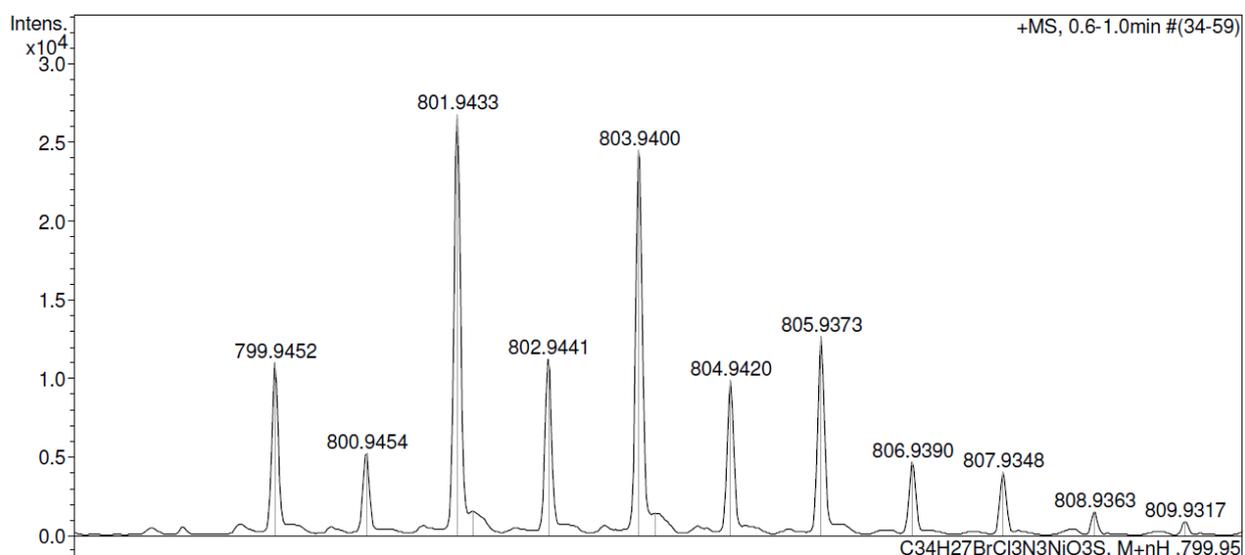
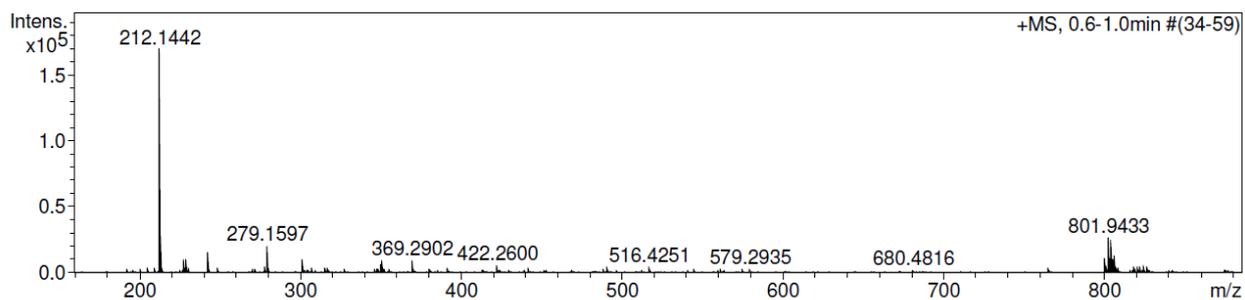




64. ESI-HRMS data for (*S,R*)-4'b



65. ESI-HRMS data for (*S,R*)-4'**c**



66. ESI-HRMS data for (*S,R*)-4'd

