Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

4-Alkenyl-5*H*-1,2,3-oxathiazole 2,2-dioxides in Catalytic and Enantioselective [4+2] Cycloaddition under Iminium Activation. Straightforward Access to the *trans*-Decaline Framework and to Densely Functionalized Cyclohexanes

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General Methods.[1] NMR spectra were acquired on a 300 spectrometer, running at 300 or 500 MHz and 75.4 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR; $CDCl_3$, 77.0 ppm for ^{13}C NMR). The following abbreviations are used to indicate the multiplicity in ^{1}H NMR spectra: s, singlet; d, doublet; t, triplet; m, multiplet; bs, broad signal. ^{13}C NMR spectra were acquired on a broad band decoupled mode. For infrared (IR) spectra only characteristic bands are given in cm^{-1}. Mass spectra (MS) were recorded on a GC-MS spectrometer using electronic impact (EI) techniques (70 eV). High resolution mass spectrometry (HRMS) were recorded under chemical ionization (CI) TOF conditions using GC when necesary. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates and visualized by ultraviolet irradiation, phosphomolybdic acid or potassium permanganate reagent. Melting points (M.p.) are given in ºC. Optical rotations (α value) were measured in the specified solvent at given concentration in g/100 mL. The enantiomeric excess (e.e.) of the products were determined by chiral stationary phase HPLC using photodiode array detector and using the indicated chiral column in each case.

Materials. Analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel was used.

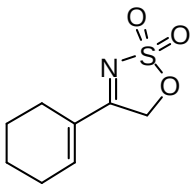
[1] SGIker technical support (MEC, GV/EJ and European Social Fund) is gratefully acknowledged (NMR, Elementary analysis, HRMS analysis and allocation of computational resources).

General procedure for the synthesis of 4-Alkenyl-5*H*-1,2,3-oxathiazole 2,2-dioxides (1a-c).

To a solution of trifluoroacetic acid (2.00 mmol) in a mixture of CH_3CN/H_2O (5:1 mL), the corresponding α,β-unsaturated ketone (1.00 mmol) was added. Then [bis(trifluoroacetoxy)iodo]benzene (2.00 mmol) was added and the reaction was stirred under reflux for the corresponding time in each case and then allowed to reach room temperature. The solvent was removed under reduced pressure and H_2O (5 mL) was added to the obtained crude product. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with saturated solution of $NaHCO_3$ (3 × 30 mL) and then were dry over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure obtaining the corresponding α-hydroxy ketone, which was employed in the following step without further purification.

Chlorosulfonyl amine (2.00 mmol), previously released from chlorosulfonyl isocyanate with formic acid following representative procedure,[2] was added portionwise to a solution of α-hydroxy ketone (1.00 mmol) in dry DMA (3 mL) under Ar atmosphere. After stirring at room temperature for 2 h, the reaction mixture was diluted with EtOAc (10 mL) and washed with brine (10 mL). The solvent was removed under reduced pressure and then *p*-toluensulfonic acid (0.10 mmol) and toluene (3 mL) were added, and the reaction was stirred under reflux for 1 h with a Dean-Stark receiver. The mixture was diluted with EtOAc (10 mL) and washed with $NaHCO_3$ (10 mL). The organic layer was dry over anhydrous Na_2SO_4 and the solvent was evaporated. The crude was purified by flash column chromatography (hexanes/EtOAc gradient from 6:4 to 1:1) to give the corresponding sulfamidate.

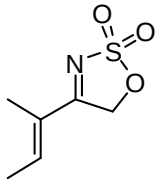
4-(Cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (1a).



Following the general procedure, cyclohex-1-en-1-yl methyl ketone (0.51 mL, 4.00 mmol), [bis(trifluoroacetoxy)iodo]benzene (3.44 g, 8.00 mmol) and trifluoroacetic acid (0.61 mL, 8.00 mmol) in a mixture of CH_3CN/H_2O (20:4 mL) afforded the α-hydroxy ketone after 5 hours. Then to a solution of α-hydroxy ketone in DMA (12 mL), chlorosulfonyl amine (924 mg, 8.00 mmol) was added, and then *p*-toluensulfonic acid (76 mg, 0.40 mmol) and toluene (12 mL) was added, affording the sulfamidate **1a** (283 mg, 1.41 mmol, 35%) as a yellow solid. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.80-6.77 (m, 1H), 5.31 (s, 2H), 2.40-2.35 (m, 4H), 1.81-1.61 (m, 4H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 175.7, 146.8, 131.3, 74.0, 26.9, 24.2, 21.3, 21.1. FTIR (ATR, cm^{-1}): 1632 (C=N st), 1570 (C=C st), 1354 (SO_2 st as), 1186 (SO_2 st sym). MS (70 eV) *m/z* (%): 201 (87), 186 (13), 172 (5), 160 (1), 144 (2), 136 (5), 120 (33), 106 (100), 92 (56), 79 (88), 66 (26), 52 (33). HRMS: calculated for $[C_8H_{12}NO_3S]^+$: 202.0538 $[(M+H)^+]$; found: 202.0525. M.p.: 151-153ºC (hexanes/EtOAc).

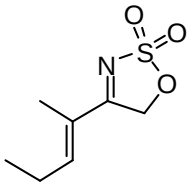
[2] H.-K. Lee, S. Kang, E. B. Choi, *J. Org. Chem.* 2012, **77**, 5454.

4-(1-Methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (1b).



Following the general procedure, 3-methylpent-3-en-2-one (2.34 mL, 20.00 mmol), [bis(trifluoroacetoxy)iodo]benzene (17.73 g, 40.00 mmol) and trifluoroacetic acid (3.06 mL, 40.00 mmol) in a mixture of CH_3CN/H_2O (100:20 mL) afforded the α-hydroxy ketone after 4 hours. Then to a solution of α-hydroxy ketone in DMA (60 mL), chlorosulfonyl amine (4.62 g, 40.00 mmol) was added, and then *p*-toluensulfonic acid (380 mg, 2.00 mmol) and toluene (60 mL) was added, affording the sulfamidate **1b** (544 mg, 3.11 mmol, 16%) as a yellow solid. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.59-6.52 (m, 1H), 5.32 (s, 2H), 2.01-1.99 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 176.6, 144.2, 130.2, 74.1, 15.6, 12.5. FTIR (ATR, cm^{-1}): 1638 (C=N st), 1561 (C=C st), 1351 (SO_2 st as), 1181 (SO_2 st sym). MS (70 eV) *m/z* (%): 175 (39), 160 (1), 135 (1), 110 (4), 94 (14), 81 (100), 75 (1), 66 (21), 54 (46). HRMS: calculated for $[C_6H_{10}NO_3S]^+$:176.0381 $[(M+H)^+]$; found: 176.0376. M.p.: 122-124ºC (hexanes/EtOAc).

4-(1-Methylbut-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide (1c).

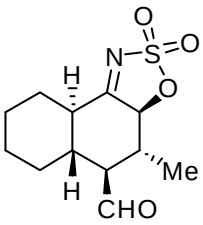


Following the general procedure, 3-methylhex-3-en-2-one (1.14 g, 10.16 mmol), [bis(trifluoroacetoxy)iodo]benzene (9.01 g, 20.32 mmol) and trifluoroacetic acid (1.56 mL, 20.32 mmol) in a mixture of CH_3CN/H_2O (50:10 mL) afforded the α-hydroxy ketone after 2 hours. Then to a solution of α-hydroxy ketone in DMA (30 mL), chlorosulfonyl amine (2.34 g, 20.32 mmol) was added, and then *p*-toluensulfonic acid (194 mg, 1.02 mmol) and toluene (30 mL) was added, affording the sulfamidate **1c** (305 mg, 1.61 mmol, 16%) as a orange solid . ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 6.46-6.40 (m, 1H), 5.33 (s, 2H), 2.42-2.32 (m, 2H), 2.00 (s, 3H), 1.10 (t, *J* = 7.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 176.9, 150.8, 128.7, 74.2, 23.0, 12.6, 12.6. FTIR (ATR, cm^{-1}): 1631 (C=N st), 1563 (C=C st), 1346 (SO_2 st as), 1190 (SO_2 st sym). MS (70 eV) *m/z* (%): 189 (15), 174 (16), 162 (1), 149 (3), 135 (1), 124 (7), 110 (33), 94 (100), 80 (29), 68 (48), 53 (39). HRMS: calculated for $[C_7H_{12}NO_3S]^+$: 190.0538 $[(M+H)^+]$; found: 190.0523. M.p.: 56-58ºC (hexanes/EtOAc).

General procedure for the synthesis of Cycloadducts (4a-i).

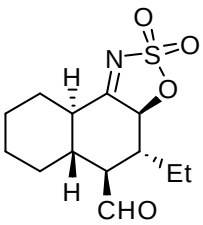
The α,β-unsaturated aldehyde **2** (1.50 or 2.00 mmol) was added to a solution of diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (0.20 mmol), DABCO (0.20 mmol) and the 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (1.00 mmol) in dry $CHCl_3$ (2 mL). The reaction was stirred at the indicated temperature in each case, following its evolution by ^{1}H-NMR. After consumption of the starting material, the product was purified by flash column chromatography with the indicated eluent, yielding the cycloadducts **4a-i**.

(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Methyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4a).



The cycloadduct **4a** (27 mg, 0.10 mmol, 66%, dr: >20:1) was obtained after 48 hours at -30ºC as a white solid, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and crotonaldehyde **2a** (19 µL, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.49 (d, *J* = 4.2 Hz, 1H), 4.81 (d, *J* = 10.6 Hz, 1H), 2.39-2.28 (m, 1H), 2.25-2.17 (m, 3H), 1.97-1.87 (m, 1H), 1.86-1.76 (m, 3H), 1.68-1.54 (m, 1H), 1.36-1.22 (m, 3H), 1.19 (d, *J* = 6.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.4, 185.5, 89.9, 58.5, 44.5, 43.6, 40.7, 31.3, 26.2, 25.0, 24.4, 17.0. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1630 (C=N st), 1368 (SO_2 st as), 1194 (SO_2 st sym). MS (70 eV) *m/z* (%): 271 (5), 243 (12), 227 (46), 214 (3), 201 (25), 192 (15), 178 (58), 162 (31), 150 (29), 134 (9), 122 (16), 108 (36), 91 (19), 81 (49), 71 (100), 55 (37). HRMS: calculated for $[C_{12}H_{18}NO_4S]^+$: 272.0957 $[(M+H)^+]$; found: 272.0946. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; τ_{major} = 22.19 min, τ_{minor} = 35.50 min (96% ee). $[\alpha]_D^{20}$ = +1.2 (*c* = 0.69, CH_2Cl_2). M.p.: 137-139 (*n*-hexane/*i*-PrOH).

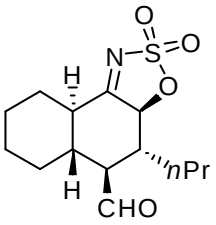
(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Ethyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4b).



The cycloadduct **4b** (28 mg, 0.10 mmol, 66%, dr: >20:1) was obtained after 60 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-pent-2-enal **2b** (29 µL, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.47 (d, *J* = 4.5 Hz, 1H), 5.01 (d, *J* = 10.7 Hz, 1H), 2.40-2.16 (m, 4H), 1.96-1.87 (m, 1H), 1.83-1.76 (m, 3H), 1.74-1.66 (m, 1H), 1.62-1.49 (m, 2H), 1.35-1.21 (m, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.4, 186.2, 87.2, 55.6, 45.6, 44.4, 43.4, 31.4, 26.3, 25.0, 24.4, 23.1, 8.7. FTIR (ATR, cm^{-1}):

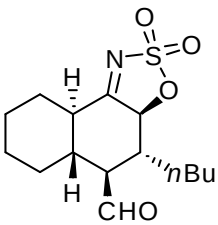
1725 (C=O st), 1631 (C=N st), 1369 (SO_2 st as), 1194 (SO_2 st sym). MS (70 eV) *m/z* (%): 285 (6), 256 (11), 241 (24), 228 (16), 216 (5), 205 (78), 192 (93), 176 (100), 164 (36), 148 (27), 136 (35), 125 (34), 108 (55), 95 (40), 81 (97), 67 (69), 55 (63). The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; τ_{major} = 17.93 min, τ_{minor} = 25.57 min (95% ee). $[\alpha]_D^{20}$ = +1.9 (*c* = 1.00, CH_2Cl_2).

(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Propyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4c).



The cycloadduct **4c** (32 mg, 0.11 mmol, 71%, dr: >20:1) was obtained after 60 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-hex-2-enal **2c** (35 µL, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.47 (d, *J* = 4.4 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 2.37-2.24 (m, 3H), 2.22-2.15 (m, 1H), 1.96-1.88 (m, 1H), 1.86-1.75 (m, 3H), 1.61-1.22 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.4, 185.9, 88.1, 56.6, 44.8, 44.4, 43.5, 33.3, 31.4, 26.3, 25.0, 24.4, 18.3, 14.1. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1631 (C=N st), 1369 (SO_2 st as), 1194 (SO_2 st sym). MS (70 eV) *m/z* (%): 299 (5), 270 (11), 255 (16), 235 (13), 219 (76), 206 (45), 190 (100), 176 (24), 164 (37), 150 (30), 136 (25), 125 (32), 108 (45), 95 (47), 81 (67), 67 (58), 55 (64). HRMS: calculated for $[C_{14}H_{22}NO_4S]^+$: 300.1270 $[(M+H)^+]$; found: 300.1258. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (95:5)]; flow rate 1.0 mL/min; τ_{major} = 30.42 min, τ_{minor} = 43.34 min (96% ee). $[\alpha]_D^{20}$ = +2.8 (c = 1.00, CH_2Cl_2).

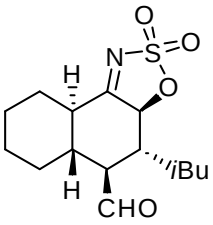
(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Butyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4d).



The cycloadduct **4d** (32 mg, 0.11 mmol, 67%, dr: >20:1) was obtained after 72 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-hept-2-enal **2d** (39 µL, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.47 (d, *J* = 4.4 Hz, 1H), 4.99 (d, *J* = 10.5 Hz, 1H), 2.38-2.24 (m, 3H), 2.21-2.16 (m, 1H), 1.91-1.88 (m, 1H), 1.85-1.76 (m, 3H), 1.65-1.48 (m, 4H), 1.35-1.24 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.5, 186.1, 88.0, 56.4, 44.8, 44.4, 43.5, 31.4, 30.6, 26.8, 26.3, 25.0, 24.4, 22.7, 13.8. FTIR (ATR, cm^{-1}): 1724 (C=O st), 1632 (C=N st), 1371 (SO_2 st as), 1195 (SO_2 st sym). MS (70 eV) *m/z* (%): 313 (3), 233 (45), 220 (28), 204 (100), 190 (16), 176 (15), 164 (25), 148 (17), 125 (23), 109 (22), 95 (29), 81 (43), 67 (39), 55 (45). HRMS: calculated for $[C_{15}H_{24}NO_4S]^+$: 314.1426 $[(M+H)^+]$; found: 314.1420. The ee was determined by HPLC

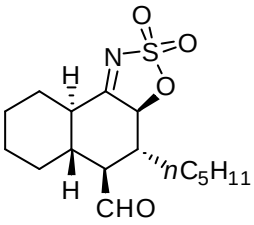
using a Chiralpak IA column [*n*-hexane/*i*-PrOH (95:5)]; flow rate 1.0 mL/min; τ_{major} = 27.02 min, τ_{minor} = 36.08 min (95% ee). $[\alpha]_D^{20}$ = +2.3 (c = 1.00, CH_2Cl_2).

(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Isobutyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4e).



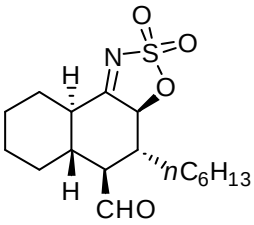
The cycloadduct **4e** (30 mg, 0.10 mmol, 65%, dr: >20:1) was obtained after 60 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-5-methylhex-2-enal **2e** (34 mg, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.46 (d, *J* = 4.4 Hz, 1H), 4.89 (d, *J* = 10.1 Hz, 1H), 2.35-2.16 (m, 4H), 1.94-1.89 (m, 1H), 1.84-1.75 (m, 3H), 1.63-1.46 (m, 3H), 1.34-1.22 (m, 4H), 0.91-0.87 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.4, 185.4, 90.0, 58.4, 44.4, 43.3, 43.0, 42.9, 31.4, 26.3, 25.6, 25.0, 24.4, 23.3, 21.9. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1632 (C=N st), 1368 (SO_2 st as), 1194 (SO_2 st sym). MS (70 eV) *m/z* (%): 233 (82), 204 (46), 176 (61), 162 (11), 146 (95), 120 (100), 106 (40), 91 (32), 77 (30), 64 (19). HRMS: calculated for $[C_{15}H_{24}NO_4S]^+$: 314.1426 $[(M+H)^+]$; found: 314.1421. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (95:5)]; flow rate 1.0 mL/min; τ_{major} = 26.32 min, τ_{minor} = 32.17 min (97% ee). $[\alpha]_D^{20}$ = +5.3 (c = 0.69, CH_2Cl_2).

(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Pentyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4f).



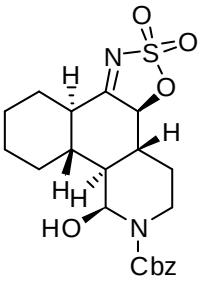
The cycloadduct **4f** (30 mg, 0.09 mmol, 61%, dr: >20:1) was obtained after 72 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 9:1 to 8:2) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-oct-2-enal **2f** (45 µL, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.47 (d, *J* = 4.4 Hz, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 2.38-2.24 (m, 3H), 2.22-2.16 (m, 1H), 1.93-1.88 (m, 1H), 1.85-1.74 (m, 3H), 1.66-1.43 (m, 4H), 1.34-1.22 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.4, 186.0, 88.0, 56.4, 44.9, 44.4, 43.5, 31.7, 31.4, 30.8, 26.3, 25.0, 24.4, 24.3, 22.3, 13.9. FTIR (ATR, cm^{-1}): 1724 (C=O st), 1632 (C=N st), 1372 (SO_2 st as), 1195 (SO_2 st sym). MS (70 eV) *m/z* (%): 327 (6), 281 (38), 234 (89), 207 (100), 164 (33), 136 (49), 108 (34), 81 (68), 55 (90). HRMS: calculated for $[C_{16}H_{26}NO_4S]^+$: 328.1583 $[(M+H)^+]$; found: 328.1585. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (95:5)]; flow rate 1.0 mL/min; τ_{major} = 25.69 min, τ_{minor} = 34.01 min (95% ee). $[\alpha]_D^{20}$ = +3.4 (c = 1.00, CH_2Cl_2).

(3a*S*,4*R*,5*S*,5a*R*,9a*R*)-4-Hexyl-4,5,5a,6,7,8,9,9a-octahydro-3a*H*-naphtho[1,2-*d*][1,2,3]oxathiazole-5-carbaldehyde 2,2-dioxide, (4g).



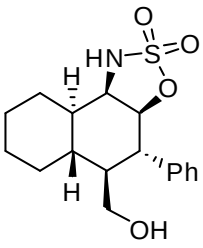
The cycloadduct **4g** (29 mg, 0.08 mmol, 57%, dr: >20:1) was obtained after 72 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 9:1 to 8:2) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-non-2-enal **2g** (50 µL, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.47 (d, *J* = 4.3 Hz, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 2.39-2.23 (m, 3H), 2.21-2.14 (m, 1H), 1.95-1.87 (m, 1H), 1.84-1.75 (m, 3H), 1.66-1.43 (m, 4H), 1.35-1.20 (m, 10H), 0.87 (t, *J* = 6.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.4, 186.0, 88.0, 56.4, 44.9, 44.4, 43.5, 31.5, 31.4, 30.9, 29.2, 26.3, 25.0, 24.7, 24.4, 22.5, 14.0. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1632 (C=N st), 1371 (SO_2 st as), 1197 (SO_2 st sym). MS (70 eV) *m/z* (%): 341 (2), 281 (12), 261 (54), 232 (5), 207 (28), 146 (13), 96 (20), 79 (18), 55 (24). HRMS: calculated for $[C_{17}H_{28}NO_4S]^+$: 342.1739 $[(M+H)^+]$; found: 342.1725. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (95:5)]; flow rate 1.0 mL/min; τ_{major} = 26.36 min, τ_{minor} = 34.75 min (95% ee). $[\alpha]_D^{20}$ = +2.3 (c = 1.01, CH_2Cl_2).

(3a*S*,3b*R*,7*S*,7a*S*,7b*R*,11a*R*)-Benzyl 7-hydroxy-4,5,7,7a,7b,8,9,10,11,11a-decahydro-3a*H*-benzo[*h*][1,2,3]oxathiazolo[5,4-*f*]isoquinoline-6(3b*H*)-carboxylate 2,2-dioxide, (4h).



The cycloadduct **4h** (39 mg, 0.09 mmol, 61%, dr: >20:1) was obtained after 48 hours at room temperature as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and (*E*)-benzyl (5-oxopent-3-en-1-yl)carbamate **2h** (70 µL, 0.30 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.40-7.32 (m, 5H), 5.98-5.92 (m, 1H), 5.15 (s, 2H), 4.73 (d, *J* = 10.8 Hz, 1H), 4.05-3.97 (m, 1H), 3.23-3.17 (m, 1H), 2.46 (bs, 1H), 2.26-2.11 (m, 4H), 1.92-1.83 (m, 2H), 1.72-1.59 (m, 2H), 1.48-1.40 (m, 2H), 1.32-1.24 (m, 3H), 1.18-1.10 (m, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 186.1, 156.1, 136.0, 128.7, 128.4, 128.0, 89.9, 73.6, 67.7, 45.2, 45.1, 44.3, 41.7, 37.5, 29.8, 29.4, 26.2, 25.1, 24.7. FTIR (ATR, cm^{-1}): 3408 (O-H st), 1682 (C=O st), 1629 (C=N st), 1369 (SO_2 st as), 1197 (SO_2 st sym). MS (70 eV) *m/z* (%): 207 (13), 218 (4), 147 (18), 129 (100), 112 (24), 83 (17), 70 (31), 57 (38). The ee was determined by HPLC using a Chiralpak ASH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 32.52 min, τ_{minor} = 63.03 min (94% ee). $[\alpha]_D^{20}$ = +7.1 (c = 1.00, CH_2Cl_2).

(3a*S*,4*S*,5*S*,5a*R*,9a*R*,9b*R*)-5-(Hydroxymethyl)-4-phenyldecahydro-1*H*-naphtho[1,2-*d*][1,2,3]oxathiazole 2,2-dioxide (4i).

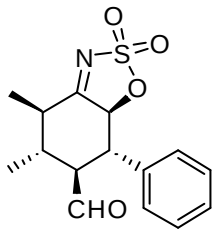


The cycloadduct **4i** (15 mg, 0.05 mmol, 30%, dr: >20:1) was obtained after 48 hours at room temperature as a white solid, according to the general procedure using 4-(cyclohex-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1a** (30 mg, 0.15 mmol) and cinnamaldehyde **2i** (28 µL, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent, following by reduction with $NaBH_4$ (7 mg, 0.18 mmol) in MeOH (2 mL) at 0ºC and then purified by flash column chromatography (hexanes/EtOAc gradient from 6:4 to 1:1). ^{1}H-NMR (MeOD, 300 MHz) δ 7.35-7.23 (m, 5H), 4.92-4.88 (m, 1H), 4.10-4.04 (m, 1H), 3.62 (dd, *J* = 11.2, 2.3 Hz, 1H), 3.40-3.29 (m, 3H), 3.05 (dd, *J* = 11.3, 2.0 Hz, 1H), 2.19-2.10 (m, 1H), 1.87-1.66 (m, 5H), 1.44-1.29 (m, 4H), 1.00-0.86 (m, 1H). ^{13}C-NMR (MeOD, 75 MHz) δ 142.0, 130.2, 129.7, 128.1, 92.0, 61.9, 58.7, 47.9, 47.2, 43.2, 35.8, 31.8, 31.1, 27.6, 27.3. FTIR (ATR, cm^{-1}): 3551 (O-H st), 1339 (SO_2 st as), 1185 (SO_2 st sym). MS (70 eV) *m/z* (%): 281 (38), 239 (13), 207 (100), 179 (13), 148 (60), 117 (24), 91 (44), 64 (26). HRMS: calculated for $[C_{17}H_{24}NO_4S]^+$: 338.1426 $[(M+H)^+]$; found: 338.1431. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 26.01 min, τ_{minor} = 17.56 min (94% ee). $[\alpha]_D^{20}$ = -92.5 (c = 0.44, MeOH). M.p.: 177-179ºC (hexanes/EtOAc).

General procedure for the synthesis of Cycloadducts (5a-o).

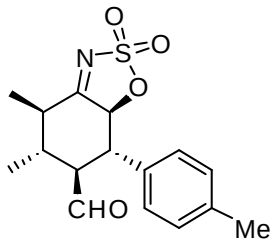
The α,β-unsaturated aldehyde **2** (1.50 mmol) was added to a solution of diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (0.20 mmol), DABCO (0.20 mmol) and the corresponding 4-alkenyl-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b-c** (1.00 mmol) in dry $CHCl_3$ (2 mL). The reaction was stirred at -30ºC, following its evolution by ^{1}H-NMR. After consumption of the starting material, the product was purified by flash column chromatography with the indicated eluent, yielding the cycloadducts **5a-o**.

(4*R*,5*R*,6*S*,7*S*,7a*S*)-4,5-Dimethyl-7-phenyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5a).



The cycloadduct **5a** (30 mg, 0.10 mmol, 66%, dr: >20:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and cinnamaldehyde **2i** (28 µL, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.34 (d, *J* = 3.8 Hz, 1H), 7.40-7.20 (m, 5H), 5.28 (d, *J* = 11.5 Hz, 1H), 3.23 (dd, *J* = 11.7, 11.7 Hz, 1H), 2.95-2.82 (m, 1H), 2.60 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.08-1.93 (m, 1H), 1.43 (d, *J* = 6.4 Hz, 3H), 1.18 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.7, 186.2, 135.0, 129.5, 128.8, 127.8, 89.1, 57.9, 51.5, 41.7, 40.2, 17.6, 13.0. FTIR (ATR, cm^{-1}): 1727 (C=O st), 1631 (C=N st), 1369 (SO_2 st as), 1198 (SO_2 st sym). MS (70 eV) *m/z* (%): 307 (7), 278 (21), 198 (100), 182 (31), 145 (13), 131 (64), 117 (15), 104 (31), 91 (58), 77 (32), 64 (11), 51 (12). HRMS: calculated for $[C_{15}H_{18}NO_4S]^+$: 308.0957 $[(M+H)^+]$; found: 308.0954. The ee was determined by HPLC using a Chiralpak ASH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 50.49 min, τ_{minor} = 39.03 min (98% ee). $[\alpha]_D^{20}$ = -50.3 (c = 1.00, CH_2Cl_2).

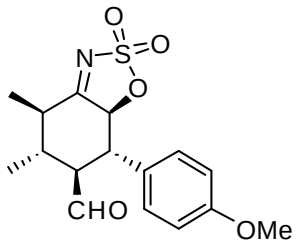
(4*R*,5*R*,6*S*,7*S*,7a*S*)-4,5-Dimethyl-7-(*p*-tolyl)-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5b).



The cycloadduct **5b** (28 mg, 0.09 mmol, 59%, dr: >20:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-methylcinnamaldehyde **2j** (33 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.34 (d, *J* = 3.9 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 5.25 (d, *J* = 11.3 Hz, 1H), 3.20 (dd, *J* = 11.7, 11.7 Hz 1H), 2.91-2.79 (m, 1H), 2.59 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.33 (s, 3H), 2.06-1.92 (m, 1H), 1.43 (d, *J* = 6.4 Hz, 3H), 1.18 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.7, 186.1, 138.8,

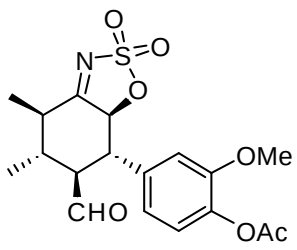
132.0, 130.2, 127.6, 89.2, 58.0, 51.2, 41.7, 40.1, 21.1, 17.7, 13.0. FTIR (ATR, cm^{-1}): 1727 (C=O st), 1626 (C=N st), 1368 (SO_2 st as), 1198 (SO_2 st sym). MS (70 eV) *m/z* (%): 321 (12), 292 (16), 212 (100), 196 (33), 145 (39), 128 (17), 115 (30), 91 (27), 77 (11). HRMS: calculated for $[C_{16}H_{20}NO_4S]^+$: 322.1113 $[(M+H)^+]$; found: 322.1115. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; τ_{major} = 20.88 min, τ_{minor} = - (>99% ee). $[\alpha]_D^{20}$ = -71.8 (c = 1.03, CH_2Cl_2).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(4-Methoxyphenyl)-4,5-dimethyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5c).



The cycloadduct **5c** (33 mg, 0.10 mmol, 65%, dr: >20:1) was obtained after 48 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-methoxycinnamaldehyde **2k** (37 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.33 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.22 (d, *J* = 11.3 Hz, 1H), 3.78 (s, 3H), 3.19 (dd, *J* = 11.7, 11.7 Hz), 1H), 2.90-2.78 (m, 1H), 2.58 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.07-1.89 (m, 1H), 1.42 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.8, 186.2, 159.8, 128.9, 126.9, 114.8, 89.3, 58.1, 55.3, 50.8, 41.7, 40.1, 17.6, 13.0. FTIR (ATR, cm^{-1}): 1726 (C=O st), 1625 (C=N st), 1368 (SO_2 st as), 1197 (SO_2 st sym). MS (70 eV) *m/z* (%): 337 (32), 281 (15), 256 (17), 228 (93), 207 (40), 160 (56), 134 (100), 108 (57), 91 (28), 64 (28). HRMS: calculated for $[C_{16}H_{20}NO_5S]^+$: 338.1062 $[(M+H)^+]$; found: 338.1053. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 21.73 min, τ_{minor} = - (>99% ee). $[\alpha]_D^{20}$ = -60.5 (c = 1.00, CH_2Cl_2).

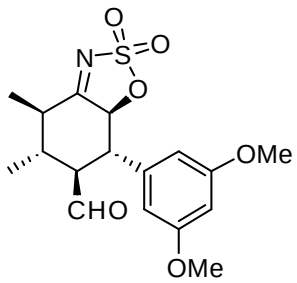
(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(4-Acetoxy-3-methoxyphenyl)-4,5-dimethyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5d).



The cycloadduct **5d** (43 mg, 0.11 mmol, 72%, dr: >20:1) was obtained after 48 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-acetoxy-3-methoxycinnamaldehyde **2l** (52 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.36 (d, *J* = 3.7 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.85-6.76 (m, 2H), 5.23 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 3H), 3.20 (dd, *J* = 11.7, 11.7 Hz, 1H), 2.95-2.86 (m, 1H), 2.59 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.30 (s, 3H), 2.04-1.89 (m, 1H), 1.41 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.6, 185.9, 168.7, 151.7, 140.0, 133.8, 123.7, 119.4, 112.3, 88.9, 57.6, 56.1, 51.3, 41.7, 40.3,

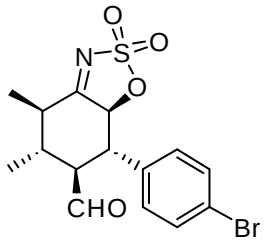
20.7, 17.6, 13.0. FTIR (ATR, cm^{-1}): 1762 (OC=O st), 1727 (C=O st), 1629 (C=N st), 1367 (SO_2 st as), 1196 (SO_2 st sym). MS (70 eV) *m/z* (%): 281 (46), 253 (10), 207 (100), 177 (12), 129 (59), 96 (17), 64 (33). The ee was determined by HPLC using a Chiralpak ASH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 85.52 min, τ_{minor} = - (>99% ee). $[\alpha]_D^{20}$ = -46.1 (c = 1.00, CH_2Cl_2).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(3,5-Dimethoxyphenyl)-4,5-dimethyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5e).



The cycloadduct **5e** (39 mg, 0.11 mmol, 71%, dr: >20:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-3,5-dimethoxycinnamaldehyde **2m** (43 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.38 (d, *J* = 3.6 Hz, 1H), 6.39 (t, *J* = 2.2 Hz, 1H), 6.35 (d, *J* = 2.2 Hz, 2H), 5.27 (d, *J* = 11.3 Hz, 1H), 3.77 (s, 6H), 3.13 (dd, *J* = 11.7, 11.7 Hz, 1H), 2.90-2.77 (m, 1H), 2.57 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.03-1.91 (m, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.18 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.5, 186.0, 161.5, 137.3, 105.9, 100.1, 88.8, 57.8, 55.4, 51.8, 41.7, 40.2, 17.6, 13.0. FTIR (ATR, cm^{-1}): 1726 (C=O st), 1629 (C=N st), 1367 (SO_2 st as), 1197 (SO_2 st sym). MS (70 eV) *m/z* (%): 348 (5), 277 (23), 217 (13), 191 (15), 164 (100), 113 (21), 71 (33). HRMS: calculated for $[C_{17}H_{22}NO_6S]^+$: 368.1168 $[(M+H)^+]$; found: 368.1167. The ee was determined by HPLC using a Chiralpak ASH column [*n*-hexane/*i*-PrOH (80:20)]; flow rate 1.0 mL/min; τ_{major} = 56.28 min, τ_{minor} = 42.95 min (99% ee). $[\alpha]_D^{20}$ = -38.8 (c = 0.90, CH_2Cl_2).

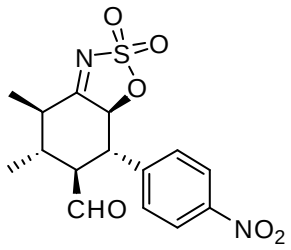
(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(4-Bromophenyl)-4,5-dimethyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5f).



The cycloadduct **5f** (39 mg, 0.10 mmol, 67%, dr: >20:1) was obtained after 60 hours as a orange solid, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-bromocinnamaldehyde **2n** (49 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.35 (d, *J* = 3.8 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 5.23 (d, *J* = 11.3 Hz, 1H), 3.21 (dd, *J* = 11.7, 11.7 Hz, 1H), 2.93-2.81 (m, 1H), 2.60 (dq, *J* = 12.6, 6.3 Hz, 1H), 2.06-1.92 (m, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.19 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.4, 185.9, 134.1, 132.6, 129.5, 122.9, 88.7, 57.7, 50.8, 41.7, 40.3, 17.6, 13.0. FTIR (ATR, cm^{-1}): 1726 (C=O st), 1630 (C=N st), 1369 (SO_2 st as), 1198 (SO_2 st sym). MS (70 eV) *m/z* (%): 305 (53), 281 (36), 207 (89), 180 (29), 147 (59), 119 (3), 84 (100), 51 (41).

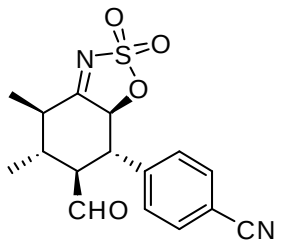
HRMS: calculated for $[C_{15}H_{17}NO_4SBr]^+$: 386.0062 $[(M+H)^+]$; found: 386.0072. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; τ_{major} = 29.41 min, τ_{minor} = 22.99 min (96% ee). $[\alpha]_D^{20}$ = -62.3 (c = 1.00, CH_2Cl_2). M.p.: 110-112ºC (hexanes/EtOAc).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-4,5-Dimethyl-7-(4-nitrophenyl)-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5g).



The cycloadduct **5g** (39 mg, 0.11 mmol, 73%, dr: >20:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 6:4 to 1:1) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-nitrocinnamaldehyde **2o** (41 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.42 (d, *J* = 3.7 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 5.28 (d, *J* = 11.3 Hz, 1H), 3.40 (dd, *J* = 11.7, 11.7 Hz, 1H), 3.02-2.93 (m, 1H), 2.67 (dq, *J* = 12.7, 6.3 Hz, 1H), 2.10-1.97 (m, 1H), 1.45 (d, *J* = 6.4 Hz, 3H), 1.24 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 198.9, 185.5, 148.0, 142.4, 129.0, 124.6, 88.1, 57.5, 50.8, 41.8, 40.6, 17.6, 12.9. FTIR (ATR, cm^{-1}): 1726 (C=O st), 1629 (C=N st), 1521 (NO_2 st as), 1372 (SO_2 st as), 1347 (NO_2 st sym), 1199 (SO_2 st sym). MS (70 eV) *m/z* (%): 281 (34), 245 (40), 207 (100), 170 (41), 142 (69), 115 (57), 91 (25), 64 (33). HRMS: calculated for $[C_{15}H_{17}N_2O_6S]^+$: 353.0807 $[(M+H)^+]$; found: 353.0815. The ee was determined by HPLC using a Chiralpak ADH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 41.51 min, τ_{minor} = 49.45 min (97% ee). $[\alpha]_D^{20}$ = -54.8 (c = 1.00, CH_2Cl_2).

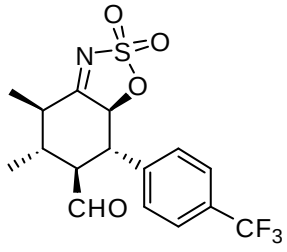
(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(4-Cianophenyl)-4,5-dimethyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5h).



The cycloadduct **5h** (37 mg, 0.11 mmol, 73%, dr: >20:1) was obtained after 48 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 6:4 to 1:1) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-cianocinnamaldehyde **2p** (35 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.39 (d, *J* = 3.7 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 5.24 (d, *J* = 11.3 Hz, 1H), 3.32 (dd, *J* = 11.7, 11.7 Hz, 1H), 2.98-2.86 (m, 1H), 2.64 (dq, *J* = 12.6, 6.4 Hz, 1H), 2.08-1.95 (m, 1H), 1.44 (d, *J* = 6.4 Hz, 3H), 1.23 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 198.9, 185.5, 140.5, 133.1, 128.8, 118.0, 112.9, 88.2, 57.4, 51.1, 41.7, 40.5, 17.6, 12.9. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1627 (C=N st), 1372 (SO_2 st as), 1198 (SO_2 st sym). MS (70 eV) *m/z* (%): 281 (10),

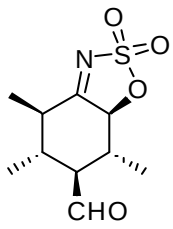
253 (31), 225 (32), 197 (62), 180 (14), 154 (100), 116 (31), 77 (19), 51 (15). HRMS: calculated for $[C_{16}H_{17}N_2O_4S]^+$: 333.0909 $[(M+H)^+]$; found: 333.0917. The ee was determined by HPLC using a Chiralpak ADH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 35.29 min, τ_{minor} = 44.40 min (98% ee). $[\alpha]_D^{20}$ = -59.9 (c = 0.83, CH_2Cl_2).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-4,5-Dimethyl-7-(4-(trifluoromethyl)phenyl)-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5i).



The cycloadduct **5l** (38 mg, 0.10 mmol, 67%, dr: >20:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and (*E*)-4-(trifluoromethyl)cinnamaldehyde **2p** (45 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.39 (d, *J* = 3.7 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 5.26 (d, *J* = 11.3 Hz, 1H), 3.33 (dd, *J* = 11.7, 11.7 Hz, 1H), 3.01-2.87 (m, 1H), 2.70-2.56 (m, 1H), 2.09-1.95 (m, 1H), 1.44 (d, *J* = 6.3 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.1, 185.6, 139.2, 131.1 (q, $^2J_{CF}$ = 32.9 Hz), 128.4, 126.4 (q, $^3J_{CF}$ = 3.5 Hz), 123.7 (q, $^1J_{CF}$ = 272.1 Hz), 88.5, 57.6, 51.0, 41.8, 40.5, 17.6, 12.9. FTIR (ATR, cm^{-1}): 1727 (C=O st), 1622 (C=N st), 1369 (SO_2 st as), 1199 (SO_2 st sym). MS (70 eV) *m/z* (%): 266 (14), 239 (11), 215 (36), 199 (38), 172 (18), 155 (32), 127 (10), 113 (52), 100 (50), 85 (14), 71 (100), 58 (23). HRMS: calculated for $[C_{16}H_{17}NO_4SF_3]^+$: 376.0830 $[(M+H)^+]$; found: 376.0829. The ee was determined by HPLC using a Chiralpak ASH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 27.65 min, τ_{minor} = 22.09 min (98% ee). $[\alpha]_D^{20}$: -33.4 (c = 1.00, CH_2Cl_2).

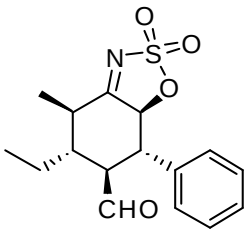
(4*R*,5*R*,6*S*,7*R*,7a*S*)-4,5,7-Trimethyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5j).



The cycloadduct **5j** (14 mg, 0.10 mmol, 36%, dr: >20:1) was obtained after 48 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(1-methylprop-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1b** (26 mg, 0.15 mmol) and crotonaldehyde **2a** (19 µL, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.48 (d, *J* = 4.1 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 2.45 (dq, *J* = 12.7, 6.4 Hz, 1H), 2.23-2.13 (m, 2H), 1.94-1.85 (m, 1H), 1.40 (d, *J* = 6.4 Hz, 3H), 1.19 (d, *J* = 6.0 Hz, 3H), 1.14 (d, *J* = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 200.2, 186.4, 89.8, 59.3, 41.5, 40.1, 39.7, 17.7, 16.9, 13.0. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1629 (C=N st), 1367 (SO_2 st as), 1196 (SO_2 st sym). MS (70 eV) *m/z* (%): 217 (22), 202 (32), 188 (13), 175 (16), 152 (86), 136 (51), 124 (28), 110 (25), 96 (23), 69 (100), 55

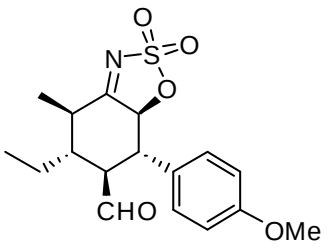
(68). HRMS: calculated for $[C_{10}H_{16}NO_4S]^+$: 246.0800 $[(M+H)^+]$; found: 246.0789. The ee was determined by HPLC using a Chiralpak IA column [*n*-hexane/*i*-PrOH (90:10)]; flow rate 1.0 mL/min; τ_{major} = 18.02 min, τ_{minor} = 20.46 min (91% ee). $[\alpha]_D^{20}$ = -19.5 (c = 0.67, CH_2Cl_2).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-5-Ethyl-4-methyl-7-phenyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5k).



The cycloadduct **5k** (28 mg, 0.09 mmol, 57%, dr: >20:1) was obtained after 60 hours as a yellow solid, after isolation by flash column chromatography (hexanes/EtOAc gradient from 8:2 to 7:3) according to the general procedure using 4-(1-methylbut-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1c** (28 mg, 0.15 mmol) and cinnamaldehyde **2i** (28 µL, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.34 (d, *J* = 4.1 Hz, 1H), 7.40-7.21 (m, 5H), 5.23 (d, *J* = 11.1 Hz, 1H), 3.25 (dd, *J* = 11.5, 11.5 Hz, 1H), 3.12-3.03 (m, *J* = 11.5, 4.1 Hz, 1H), 2.81 (dq, *J* = 12.5, 6.3 Hz, 1H), 2.14-2.05 (m, 1H), 1.82-1.71 (m, 1H), 1.61-1.51 (m, 1H), 1.40 (d, *J* = 6.4 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.3, 186.8, 135.1, 129.5, 128.9, 127.8, 88.9, 53.9, 51.7, 44.9, 37.8, 21.4, 12.6, 7.2. FTIR (ATR, cm^{-1}): 1726 (C=O st), 1626 (C=N st), 1368 (SO_2 st as), 1196 (SO_2 st sym). MS (70 eV) *m/z* (%): 238 (24), 207 (28), 147 (19), 129 (10), 112 (23), 83 (20), 57 (38). HRMS: calculated for $[C_{16}H_{20}NO_4S]^+$: 322.1113 $[(M+H)^+]$; found: 322.1123. The ee was determined by HPLC using a Chiralpak ASH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 51.80 min, τ_{minor} = 60.44 min (96% ee). $[\alpha]_D^{20}$ = -64.1 (c = 0.44, CH_2Cl_2). M.p.: 167-169ºC (hexanes/EtOAc).

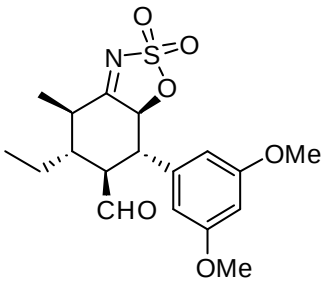
(4*R*,5*R*,6*S*,7*S*,7a*S*)-5-Ethyl-7-(4-methoxyphenyl)-4-methyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5l).



The cycloadduct **5l** (35 mg, 0.10 mmol, 66%, dr: 10:1) was obtained after 60 hours as a yellow solid, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylbut-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1c** (28 mg, 0.15 mmol) and (*E*)-4-methoxycinnamaldehyde **2k** (37 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.32 (d, *J* = 4.1 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.19 (d, *J* = 11.1 Hz, 1H), 3.78 (s, 3H), 3.20 (dd, *J* = 11.5, 11.5 Hz, 1H), 3.08-2.99 (m, 1H), 2.84-2.74 (m, 1H), 2.10-2.00 (m, 1H), 1.80-1.70 (m, 1H), 1.58-1.48 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.6, 187.0, 159.8, 128.9, 127.0, 114.8, 89.2, 55.3, 54.1, 51.0, 44.7, 37.8, 21.4, 12.6, 7.2. FTIR (ATR, cm^{-1}): 1726 (C=O st), 1626 (C=N st), 1370 (SO_2 st as), 1197 (SO_2 st sym). MS (70 eV) *m/z* (%): 244 (12), 215 (100), 187 (12), 175 (26), 134 (28), 121 (25), 91 (13), 77 (8). HRMS: calculated

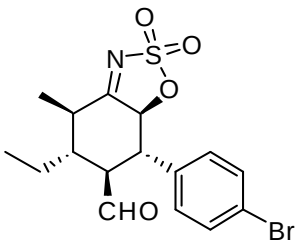
for $[C_{17}H_{22}NO_5S]^+$: 352.1219 $[(M+H)^+]$; found: 352.1236. The ee was determined by HPLC using a Chiralcel OZ3 column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 30.50 min, τ_{minor} = 23.85 min (99% ee). $[\alpha]_D^{20}$ = -68.6 (c = 1.00, CH_2Cl_2). M.p.: 68-70ºC (hexanes/EtOAc).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(3,5-Dimethoxyphenyl)-5-ethyl-4-methyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5m).



The cycloadduct **5m** (35 mg, 0.09 mmol, 61%, dr: 8:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylbut-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1c** (28 mg, 0.15 mmol) and (*E*)-3,5-dimethoxycinnamaldehyde **2m** (43 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.37 (d, *J* = 3.8 Hz, 1H), 6.40-6.34 (m, 3H), 5.26 (d, *J* = 11.0 Hz, 1H), 3.77 (s, 6H), 3.20-3.07 (m, 1H), 3.07-2.97 (m, 1H), 2.85-2.75 (m, 1H), 2.08-1.99 (m, 1H), 1.76-1.68 (m, 1H), 1.59-1.49 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 199.4, 187.0, 161.5, 137.5, 106.0, 100.0, 88.8, 55.4, 53.8, 51.9, 44.9, 37.8, 21.3, 12.6, 7.2. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1627 (C=N st), 1368 (SO_2 st as), 1196 (SO_2 st sym). MS (70 eV) *m/z* (%): 348 (8), 263 (29), 231 (12), 189 (27), 164 (100), 113 (33), 91 (9), 77 (6). HRMS: calculated for $[C_{18}H_{24}NO_6S]^+$: 382.1324 $[(M+H)^+]$; found: 382.1323. The ee was determined by HPLC using a Chiralcel OZ3 column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 17.84 min, τ_{minor} = 32.09 min (99% ee). $[\alpha]_D^{20}$ = -34.4 (c = 1.00, CH_2Cl_2).

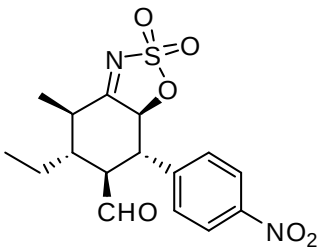
(4*R*,5*R*,6*S*,7*S*,7a*S*)-7-(4-Bromophenyl)-5-ethyl-4-methyl-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5n).



The cycloadduct **5n** (37 mg, 0.09 mmol, 62%, dr: 8:1) was obtained after 60 hours as a yellow oil, after isolation by flash column chromatography (hexanes/EtOAc gradient from 7:3 to 6:4) according to the general procedure using 4-(1-methylbut-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1c** (28 mg, 0.15 mmol) and (*E*)-4-bromocinnamaldehyde **2n** (49 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) (*denotes minor diastereoisomer signals), δ 9.34 (d, *J* = 4.1 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 5.37* (d, *J* = 11.1 Hz, 1H), 5.18 (d, *J* = 11.2 Hz, 1H), 3.49-3.36* (m, 1H), 3.23 (dd, *J* = 11.5, 11.5 Hz, 1H), 3.10-2.98 (m, 1H), 2.81 (dq, *J* = 12.5, 6.3 Hz, 1H), 2.26-2.16* (m, 1H), 2.13-2.01 (m, 1H), 1.84-1.70 (m, 1H), 1.58-1.48 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 3H), 1.31* (d, *J* = 7.3 Hz, 3H), 1.12* (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) (*denotes minor diastereoisomer signals), δ 199.6*, 199.1, 195.6*, 186.8, 134.3*, 134.2,

132.6, 132.3*, 130.5*, 129.5, 122.9, 122.3*, 88.7, 86.6*, 53.7, 52.8*, 51.0, 48.4*, 45.3*, 44.9, 37.8, 35.4*, 23.1*, 21.4, 12.6, 11.2*, 10.9*, 7.2. FTIR (ATR, cm^{-1}): 1724 (C=O st), 1626 (C=N st), 1371 (SO_2 st as), 1198 (SO_2 st sym). MS (70 eV) *m/z* (%): 293 (57), 265 (54), 251 (14), 186 (29), 171 (56), 157 (100), 143 (32), 129 (71), 115 (57), 102 (31), 77 (22), 63 (16). HRMS: calculated for $[C_{16}H_{19}NO_4SBr]^+$: 400.0218 $[(M+H)^+]$; found: 400.0234. The ee was determined by HPLC using a Chiralcel OZ3 column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 21.40 min, τ_{minor} = 14.66 min (97% ee). $[\alpha]_D^{20}$ = -53.5 (c = 1.07, CH_2Cl_2).

(4*R*,5*R*,6*S*,7*S*,7a*S*)-5-Ethyl-4-methyl-7-(4-nitrophenyl)-5,6,7,7a-tetrahydro-4*H*-benzo[*d*][1,2,3]oxathiazole-6-carbaldehyde 2,2-dioxide, (5o).

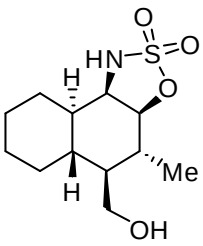


The cycloadduct **5o** (27 mg, 0.07 mmol, 50%, dr: 13:1) was obtained after 60 hours as a yellow solid, after isolation by flash column chromatography (hexanes/EtOAc gradient from 6:4 to 1:1) according to the general procedure using 4-(1-methylbut-1-en-1-yl)-5*H*-1,2,3-oxathiazole 2,2-dioxide **1c** (28 mg, 0.15 mmol) and (*E*)-4-nitrocinnamaldehyde **2o** (41 mg, 0.23 mmol) in the presence of DABCO (3 mg, 0.03 mmol), diphenyl-2-pyrrolidinemethanoltrimethylsilyl ether **3a** (10 mg, 0.03 mmol) and using dry $CHCl_3$ (0.3 mL) as solvent. ^{1}H-NMR ($CDCl_3$, 300 MHz) (*denotes minor diastereoisomer signals), δ 9.43* (d, *J* = 3.8 Hz, 1H), 9.40 (d, *J* = 3.9 Hz, 1H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 5.43* (d, *J* = 11.2 Hz, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 3.41 (dd, *J* = 11.5, 11.5 Hz, 1H), 3.20-3.11 (m, 1H), 2.87 (dq, *J* = 12.5, 6.3 Hz, 1H), 2.16-2.06 (m, 1H), 1.86-1.75 (m, 1H), 1.63-1.51 (m, 1H), 1.40 (d, *J* = 6.3 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 198.7, 186.3, 148.0, 142.5, 129.1, 124.5, 88.1, 53.6, 51.0, 45.3, 37.9, 21.4, 12.5, 7.2. FTIR (ATR, cm^{-1}): 1725 (C=O st), 1627 (C=N st), 1520 (NO_2 st as), 1373 (SO_2 st as), 1348 (NO_2 st sym), 1199 (SO_2 st sym). MS (70 eV) *m/z* (%): 281 (9), 207 (29), 147 (21), 129 (100), 112 (25), 71 (24), 57 (42). The ee was determined by HPLC using a Chiralpak ADH column [*n*-hexane/*i*-PrOH (85:15)]; flow rate 1.0 mL/min; τ_{major} = 61.50 min, τ_{minor} = 41.73 min (94% ee). $[\alpha]_D^{20}$ = -59.4 (c = 1.00, CH_2Cl_2). M.p.: 91-93ºC (hexanes/EtOAc).

General procedure for the synthesis of cyclic sulfamidate amine (6)

$NaBH_4$ (1.20 mmol) was added to a solution of the cycloadduct **4a** (1.00 mmol) in MeOH (10 mL) at 0ºC. The mixture was stirred at 0ºC for 10 minutes, NH_4Cl sat. (10 mL) was added to quenched the reaction and it was stirred for another 5 minutes. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dry with anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The sulfamidate amine **6** were obtained following this procedure, and purified by flash column chromatography (hexanes/EtOAc gradient from 6:4 to 1:1).

(3a*S*,4*R*,5*S*,5a*R*,9a*R*,9b*R*)-5-(Hydroxymethyl)-4-methyldecahydro-1*H*-naphtho[1,2-*d*][1,2,3]oxathiazole 2,2-dioxide (6).

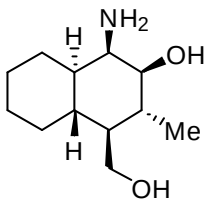


The sulfamidate amine **6** (27 mg, 0.10 mmol, >99%, dr: >20:1) was obtained as a white solid according to the general procedure using $NaBH_4$ (5 mg, 0.12 mmol) and cycloadduct **4a** (27 mg, 0.10 mmol) in MeOH (1 mL). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.27 (d, *J* = 9.0 Hz, 1H), 4.35 (dd, *J* = 10.4, 5.0 Hz, 1H), 4.06-4.00 (m, 1H), 3.88-3.72 (m, 2H), 2.28-2.07 (m, 3H), 1.83-1.72 (m, 3H), 1.59-1.41 (m, 2H), 1.32-1.20 (m, 3H), 1.12 (d, *J* = 6.4 Hz, 3H), 0.87-0.73 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 91.8, 60.2, 57.7, 47.1, 41.9, 34.0, 32.9, 30.4, 29.8, 26.1, 25.8, 15.2. FTIR (ATR, cm^{-1}): 3547 (O-H st), 3261 (N-H st), 1342 (SO_2 st as), 1184 (SO_2 st sym). . MS (70 eV) *m/z* (%): 245 (24), 190 (14), 163 (20), 148 (100), 133 (14), 119 (19), 105 (40), 91 (27), 70 (36), 55 (22). HRMS: calculated for $[C_{12}H_{22}NO_4S]^+$: 276.1270 $[(M+H)^+]$; found: 276.1272. The ee was determined by HPLC using a Chiralpak ADH column [*n*-hexane/*i*-PrOH (98:2)]; flow rate 1.0 mL/min; τ_{major} = 20.14 min, τ_{minor} = 22.86 min (92% ee). $[\alpha]_D^{20}$ = -66.8 (c = 1.00, CH_2Cl_2). M.p.: 155-157ºC (*n*-hexane/EtOAc).

General procedure for the synthesis of β-aminoalcohol (7)

To a suspension of LAH (3.00 mmol) in dry THF (10 mL) the sulfamidate amine **6** (1.00 mmol) in dry THF (20 mL) was added dropwise at 0ºC. The reaction mixture was stirred under reflux for 1 hour, and then HCl 1M (3 mL) was added at room temperature. The reaction was stirred under reflux for 1 hour and then cooled to room temperature. The mixture was washed with CH_2Cl_2 (3 × 10 mL). The aqueous layer was basified with NaOH 1M and then was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dry over Na_2SO_4 and the solvent was removed under reduced pressure, obtaining the β-aminoalcohol **7**.

(1*R*,2*S*,3*R*,4*S*,4a*R*,8a*R*)-1-Amino-4-(hydroxymethyl)-3-methyldecahydronaphthalen-2-ol (7).



The β-aminoalcohol **7** (55 mg, 0.26 mmol, 56%, dr: >20:1) was obtained as a white solid according to the general procedure using LAH (52 mg, 1.38 mmol) and sulfamidate amine **6** (127 mg, 0.46 mmol) in dry THF (5 mL), and then using HCl 1M (1 mL). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.83-3.71 (m, 2H), 3.12 (dd, *J* = 10.6, 4.1 Hz, 1H), 2.86-2.80 (m, 1H), 2.24-2.02 (m, 4H), 1.80-1.72 (m, 2H), 1.62-1.48 (m, 2H), 1.40-1.14 (m, 6H), 1.07 (d, *J* = 6.3 Hz, 3H), 0.86-0.66 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 76.1, 58.6, 56.0, 49.4, 44.8, 33.3, 33.3, 30.6, 30.3, 26.3, 26.2, 15.5. FTIR (ATR, cm^{-1}): 3356 (O-H st). MS (70 eV) *m/z* (%): 207 (94), 129 (100), 84 (23), 57 (52). HRMS: calculated for $[C_{12}H_{24}NO_2]^+$: 214.1807 $[(M+H)^+]$; found: 214.1810. $[\alpha]_D^{20}$ = -37.1 (c = 1.00, CH_2Cl_2). M.p.: 102-104ºC (CH_2Cl_2).

NMR spectra

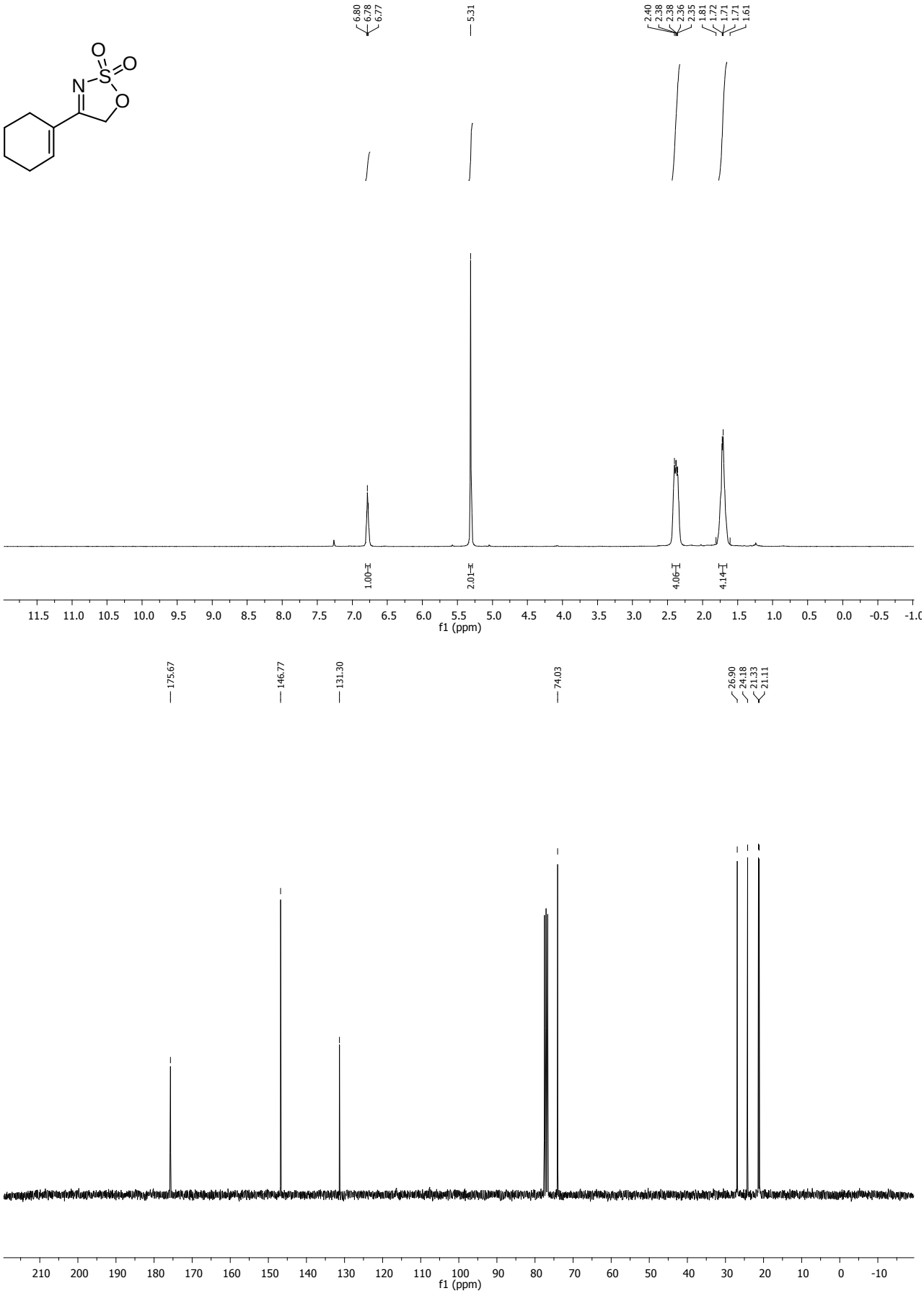


Figure 1: ^{1}H-NMR and ^{13}C-NMR spectra for compound **1a**.

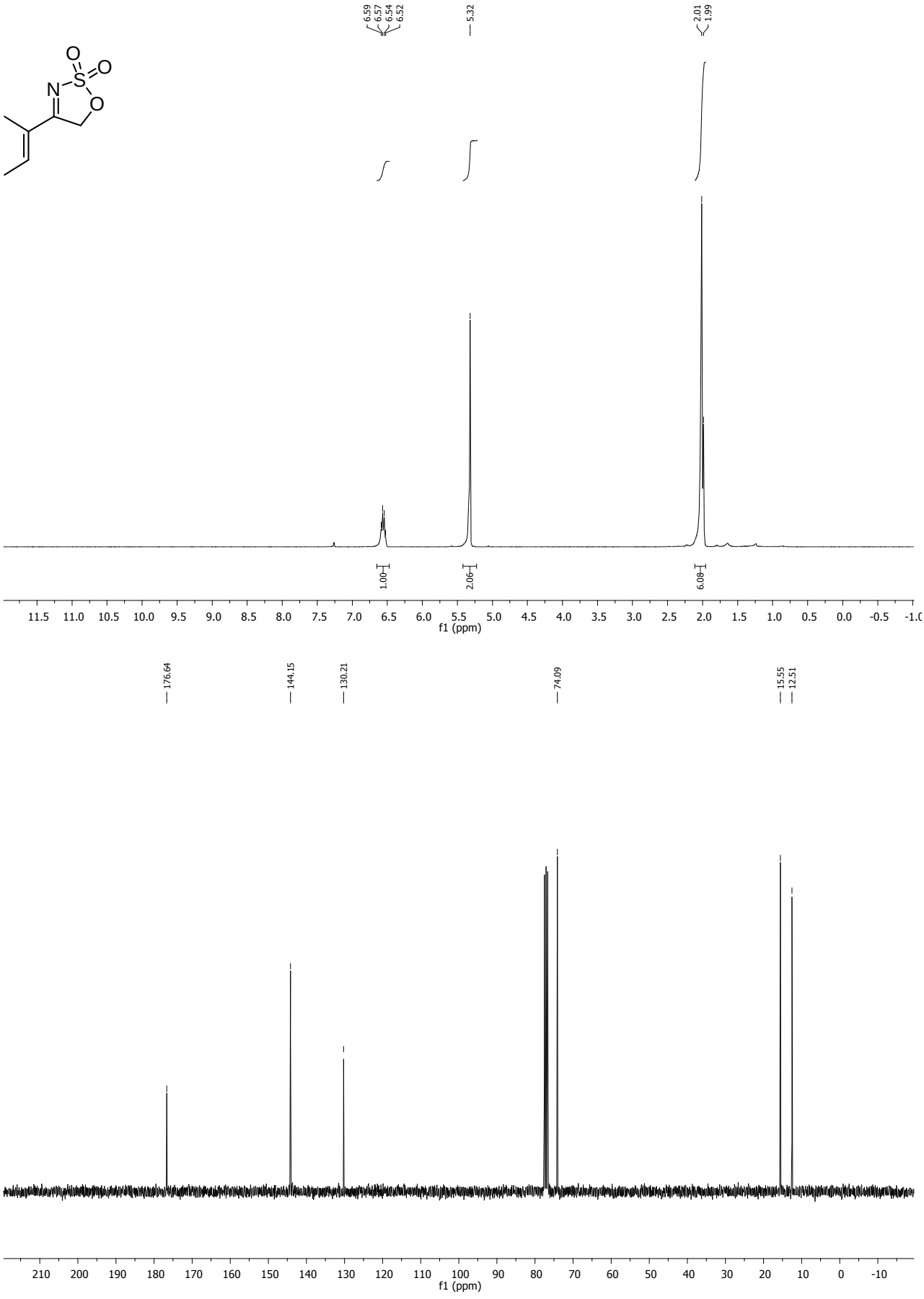


Figure 2: ^{1}H-NMR and ^{13}C-NMR spectra for compound **1b**.

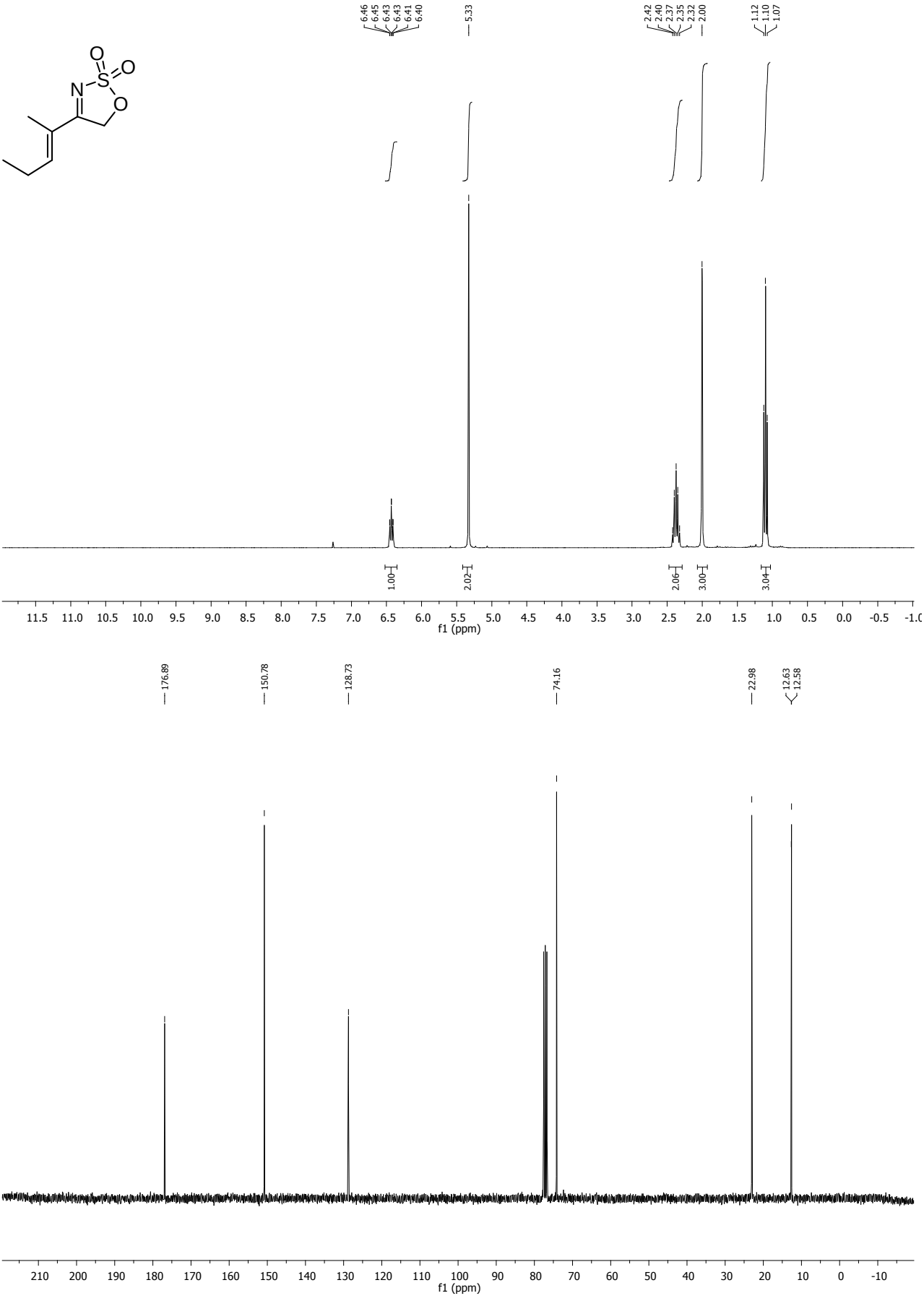


Figure 3: ^{1}H-NMR and ^{13}C-NMR spectra for compound **1c**.

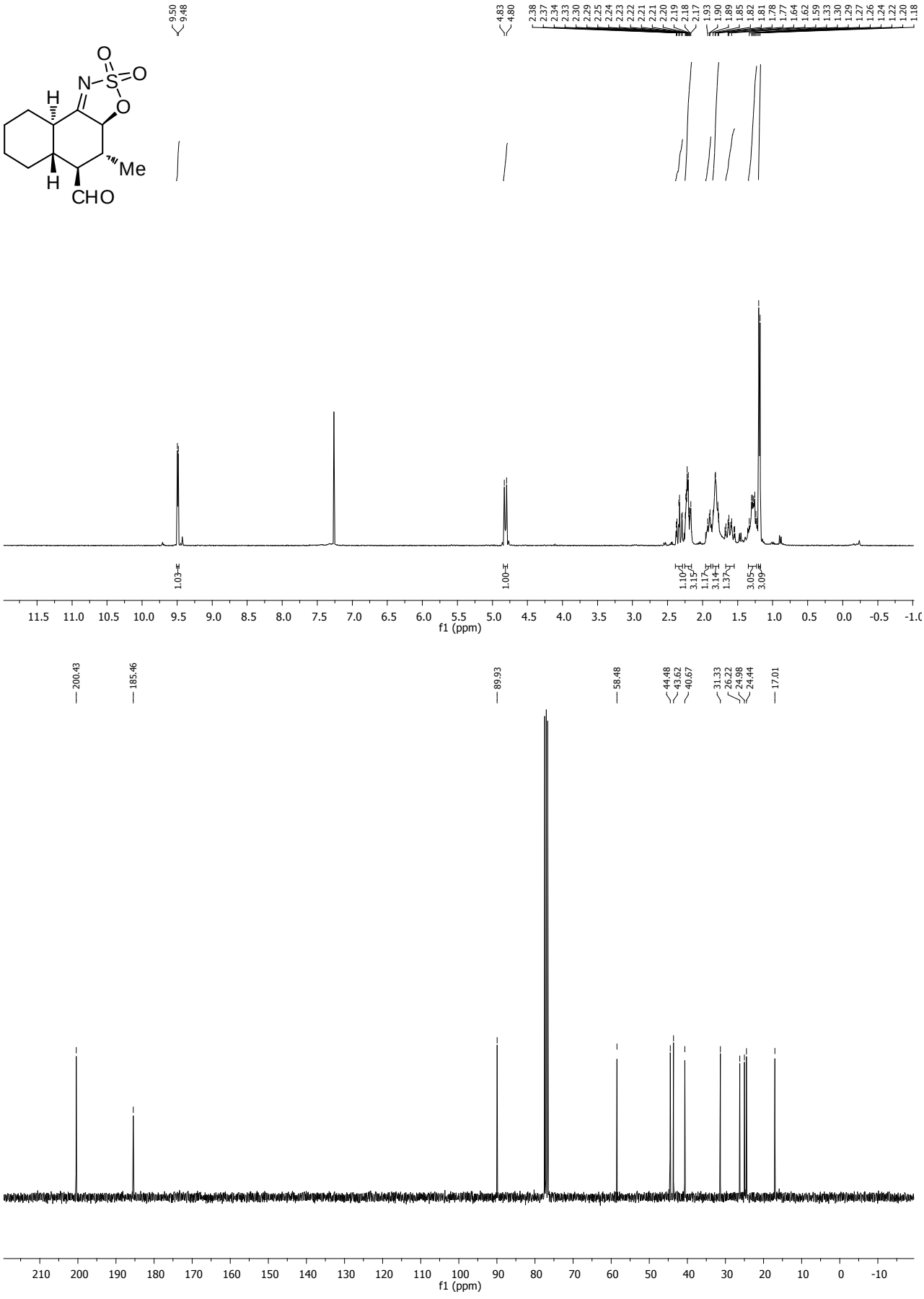


Figure 4: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4a**.

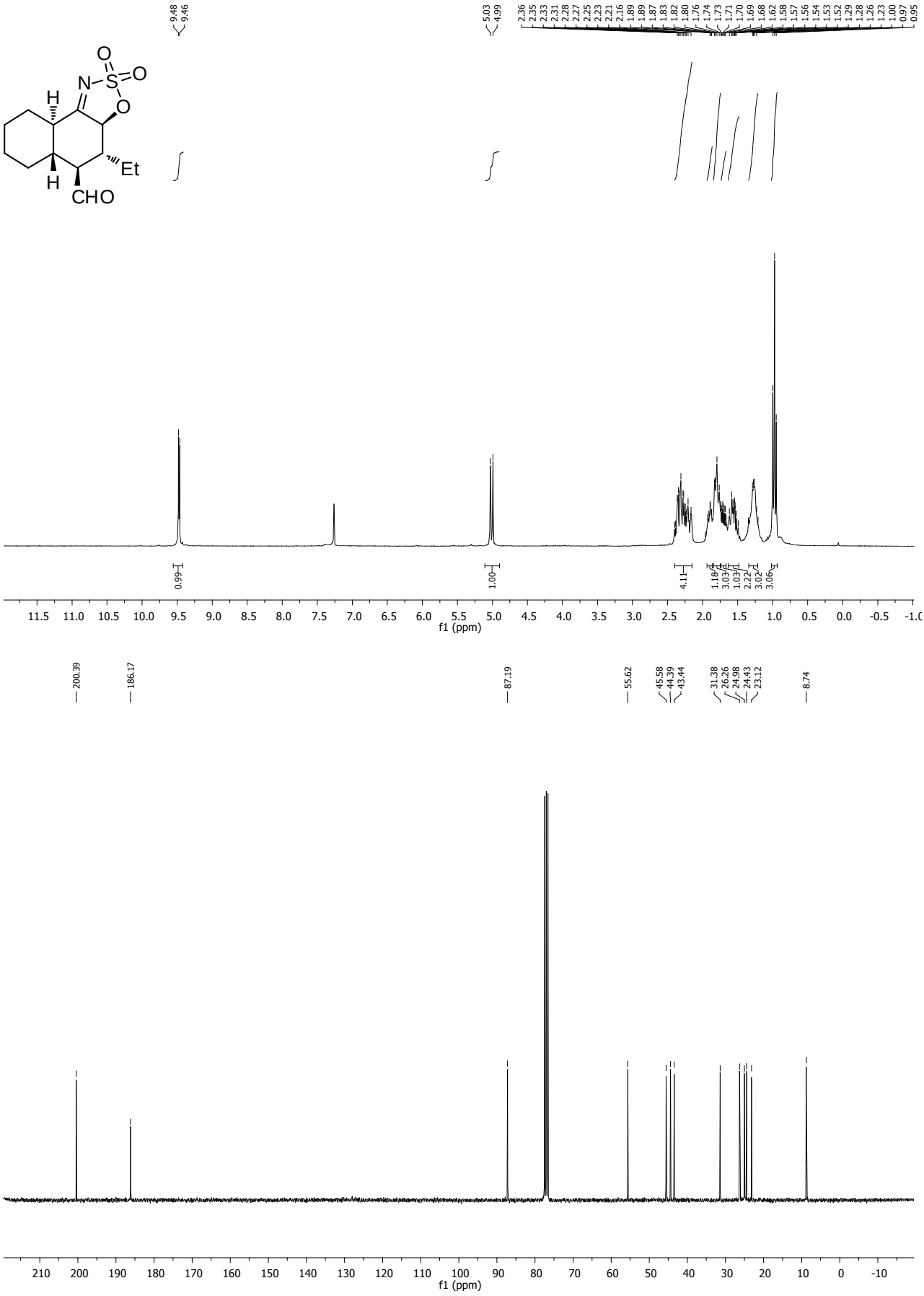


Figure 5: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4b**.

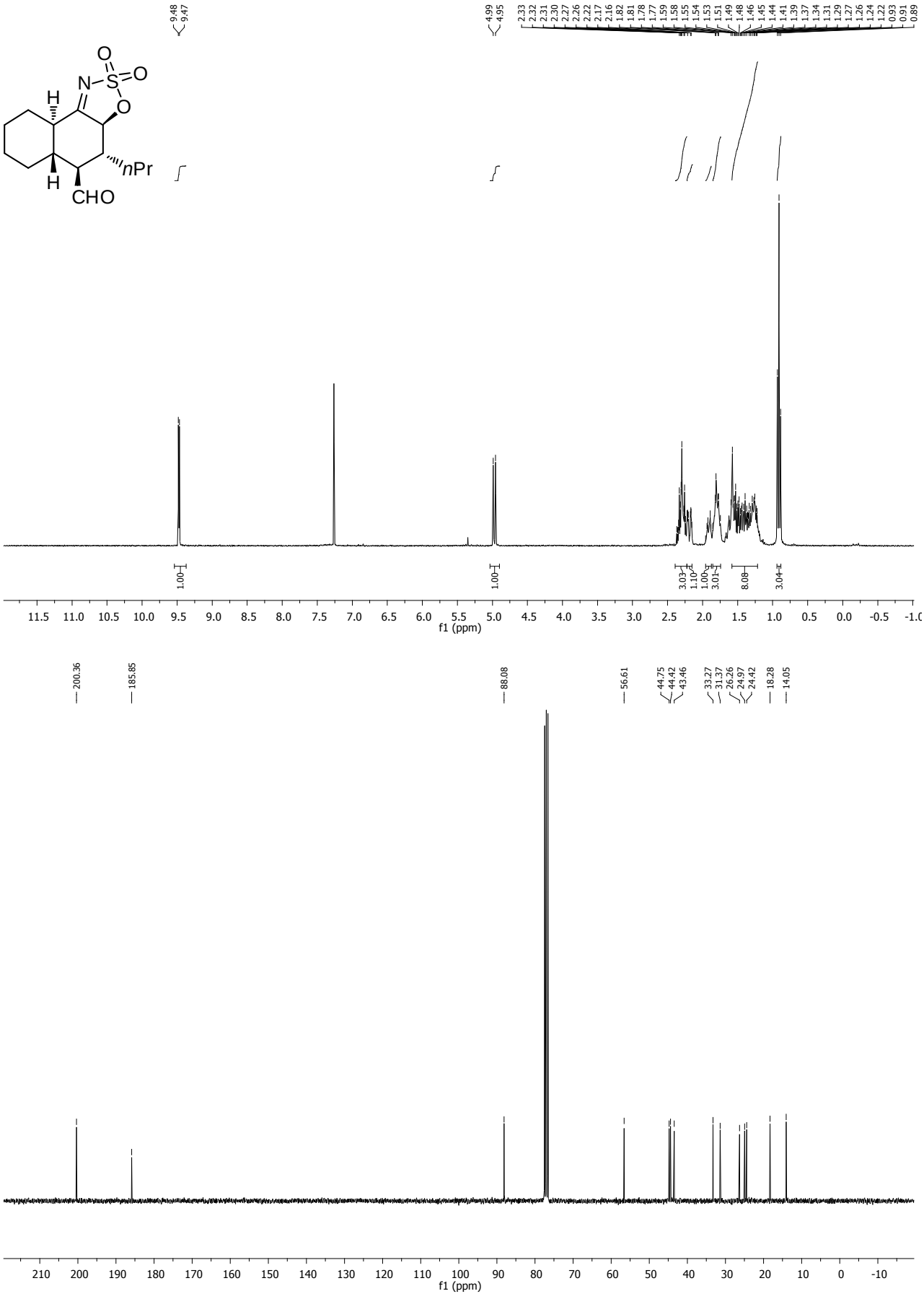


Figure 6: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4c**.

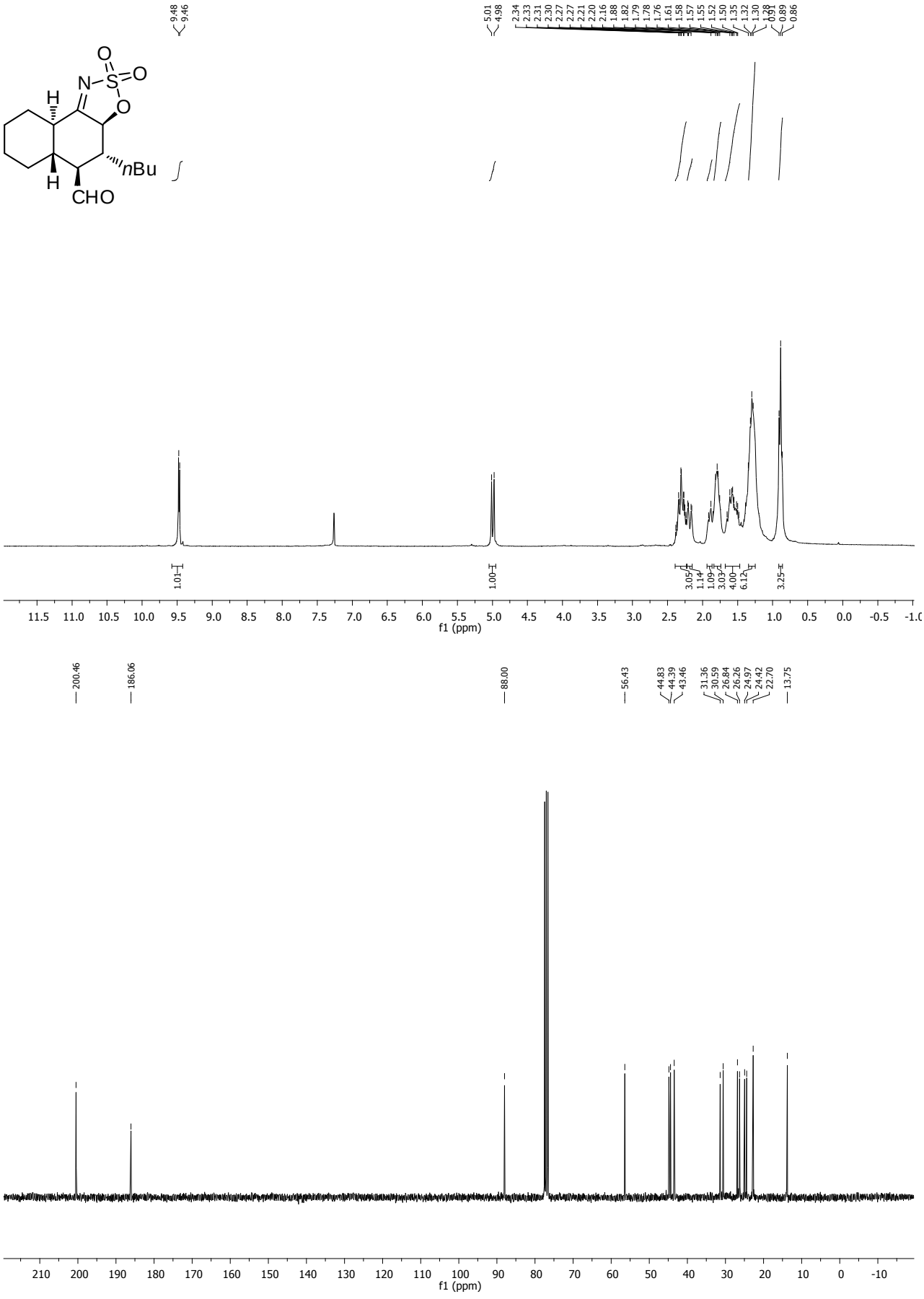


Figure 7: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4d**.

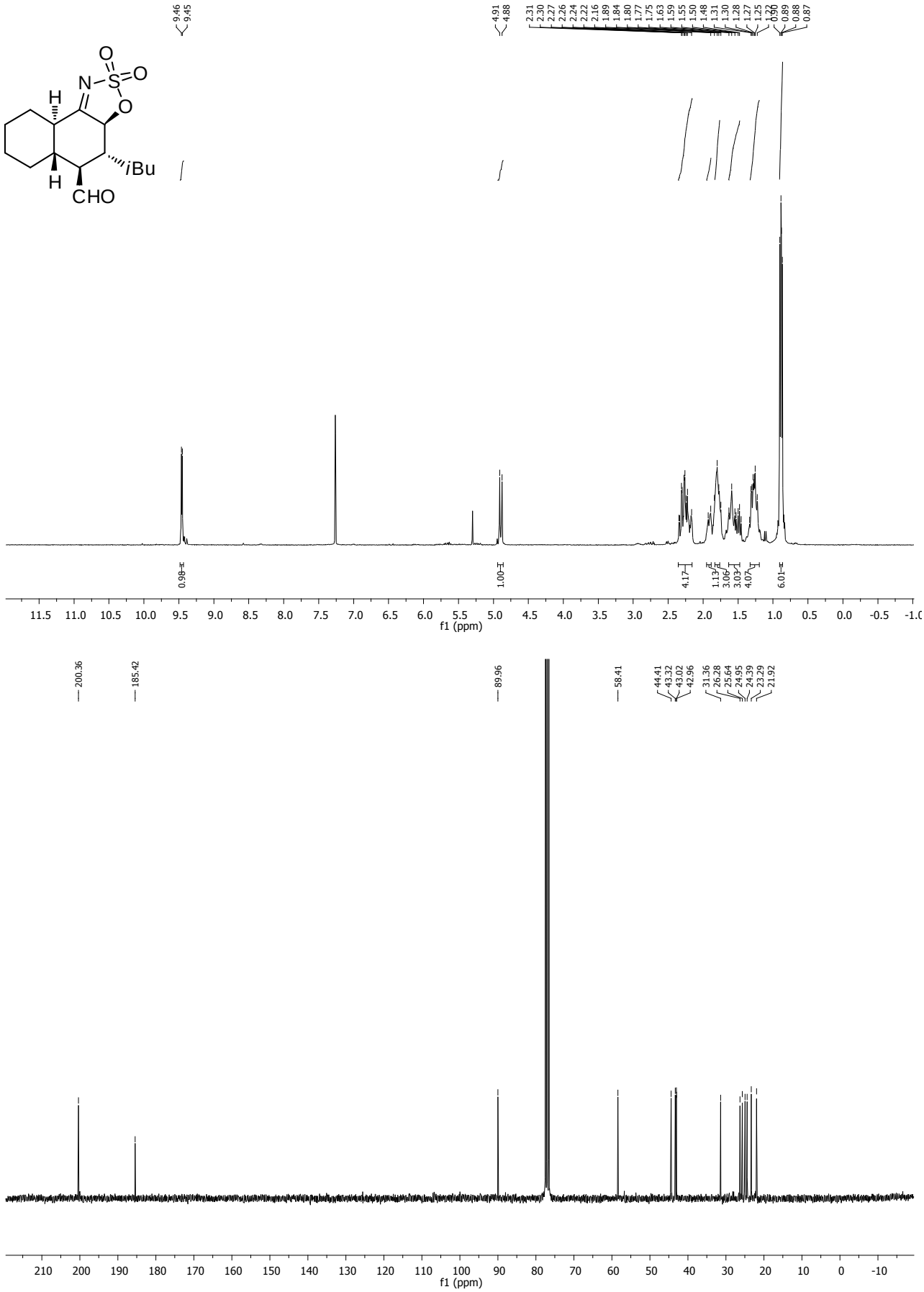


Figure 8: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4e**.

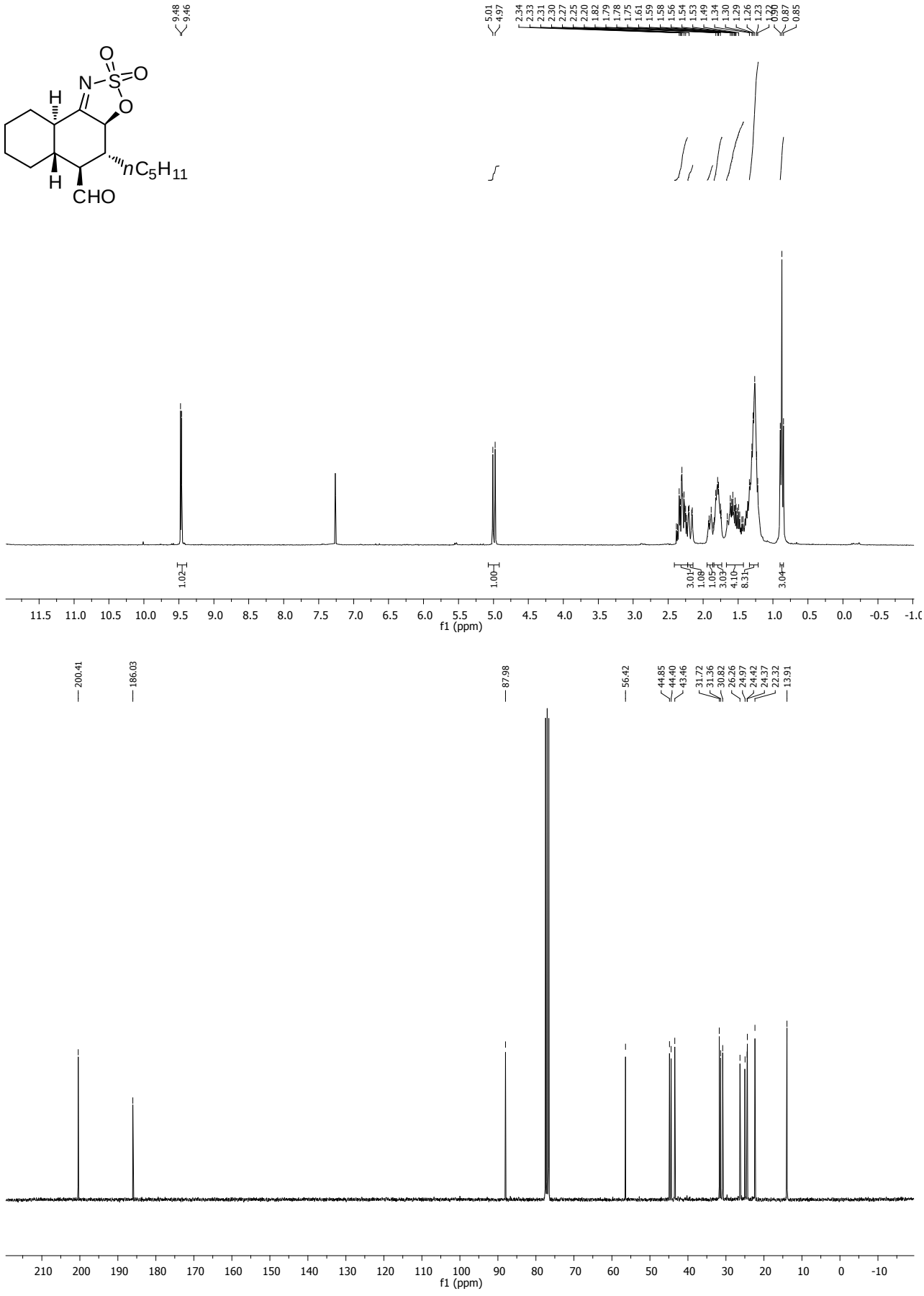


Figure 9: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4f**.

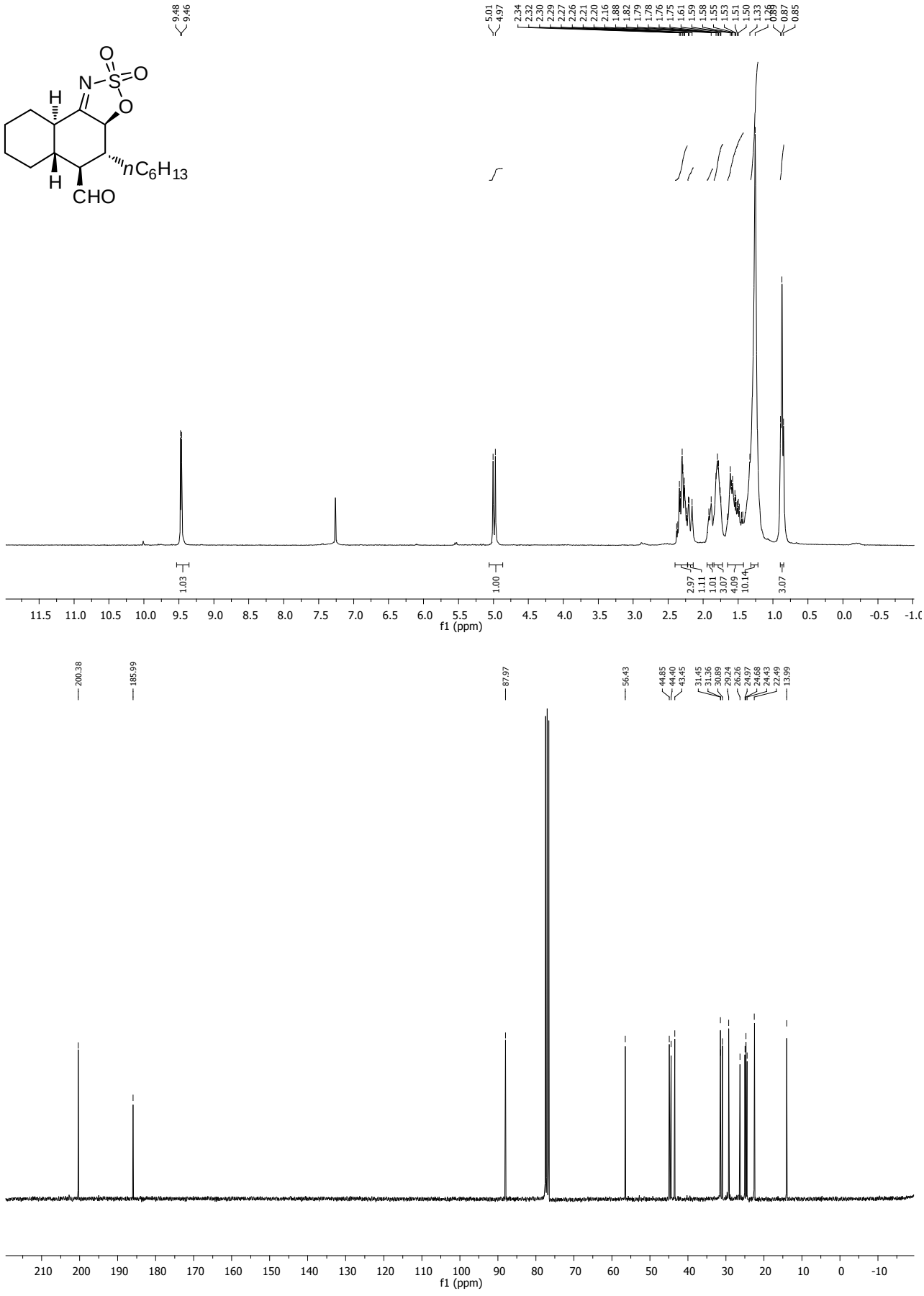
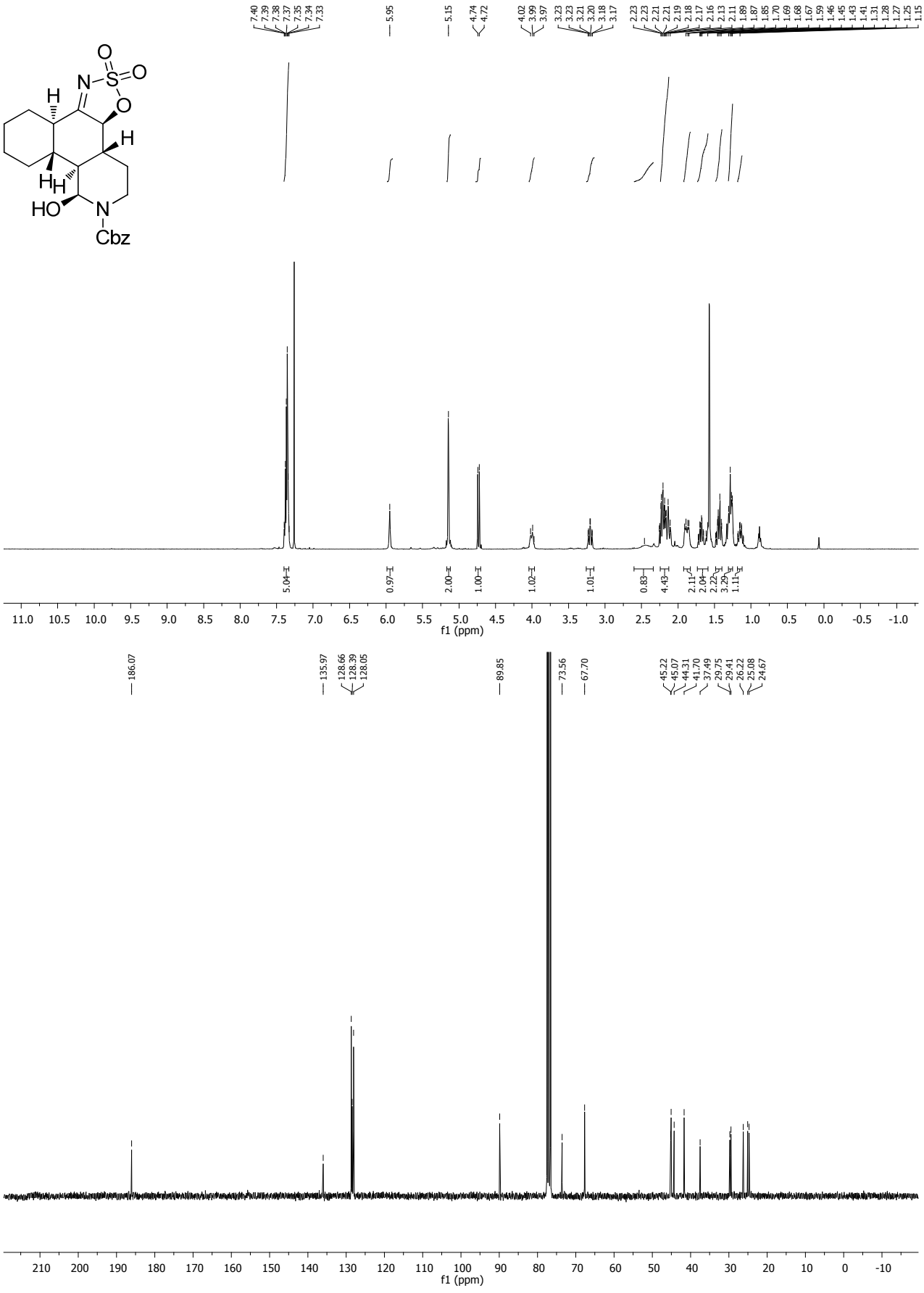


Figure 10: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4g**.


7.40 7.39 7.38 7.37 7.35 7.34 7.33
5.95
5.15
4.74 4.72
4.02 3.99 3.97
3.23 3.23 3.21 3.20 3.18 3.17
2.23 2.23 2.21 2.21 2.19 2.18 2.17 2.16 2.13 2.11 1.89 1.87 1.85 1.70 1.69 1.68 1.67 1.59 1.46 1.45 1.43 1.41 1.31 1.28 1.27 1.25 1.15
O
N
S
O
O
H
H
H
HO
N
Cbz
5.04 0.97 2.00 1.00 1.02 1.01 0.83 4.43 2.11 2.04 2.22 3.29 1.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
186.07
135.97
128.66 128.39 128.05
89.85
73.56
67.70
45.22 45.07 44.31 41.70 37.49 29.75 29.41 26.22 25.08 24.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

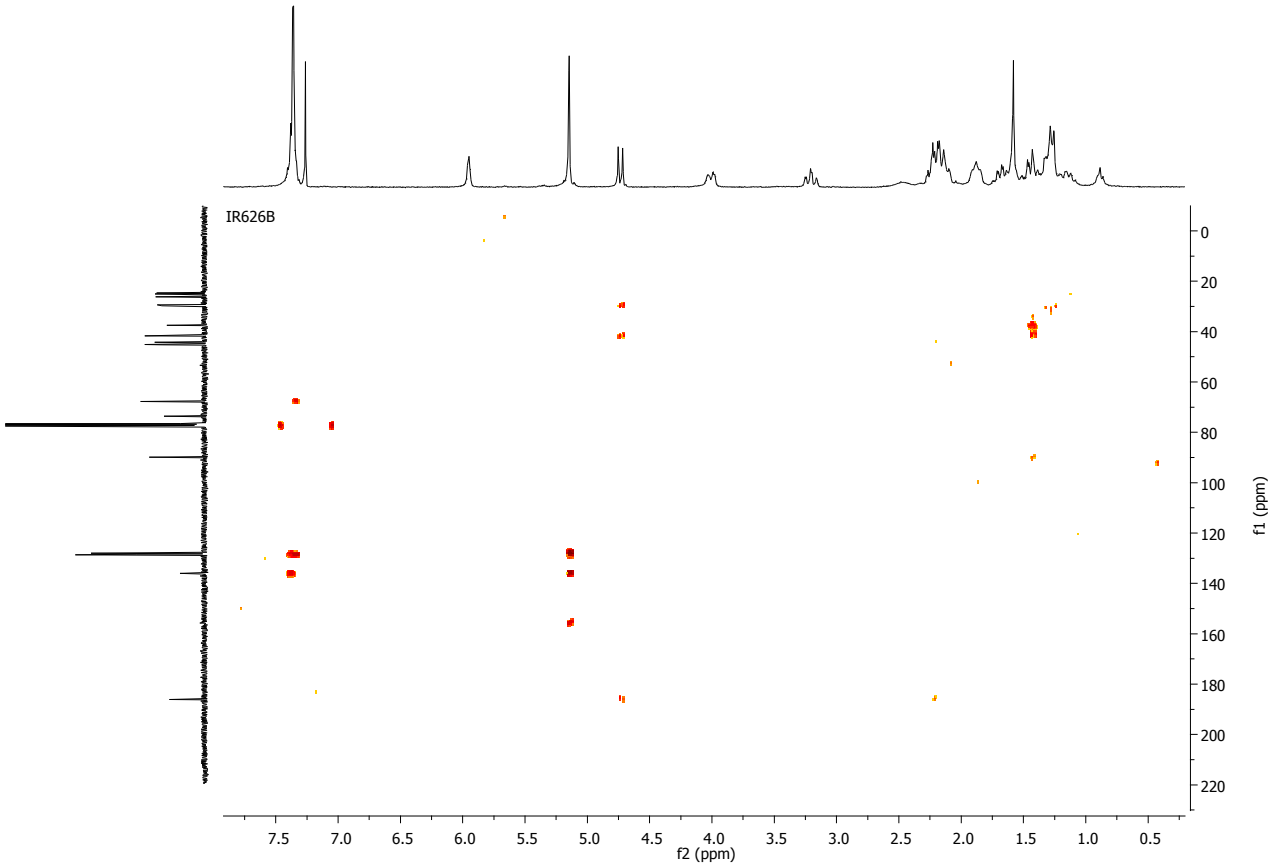


Figure 11: ^{1}H-NMR, ^{13}C-NMR and HMBC spectra for compound **4h**.

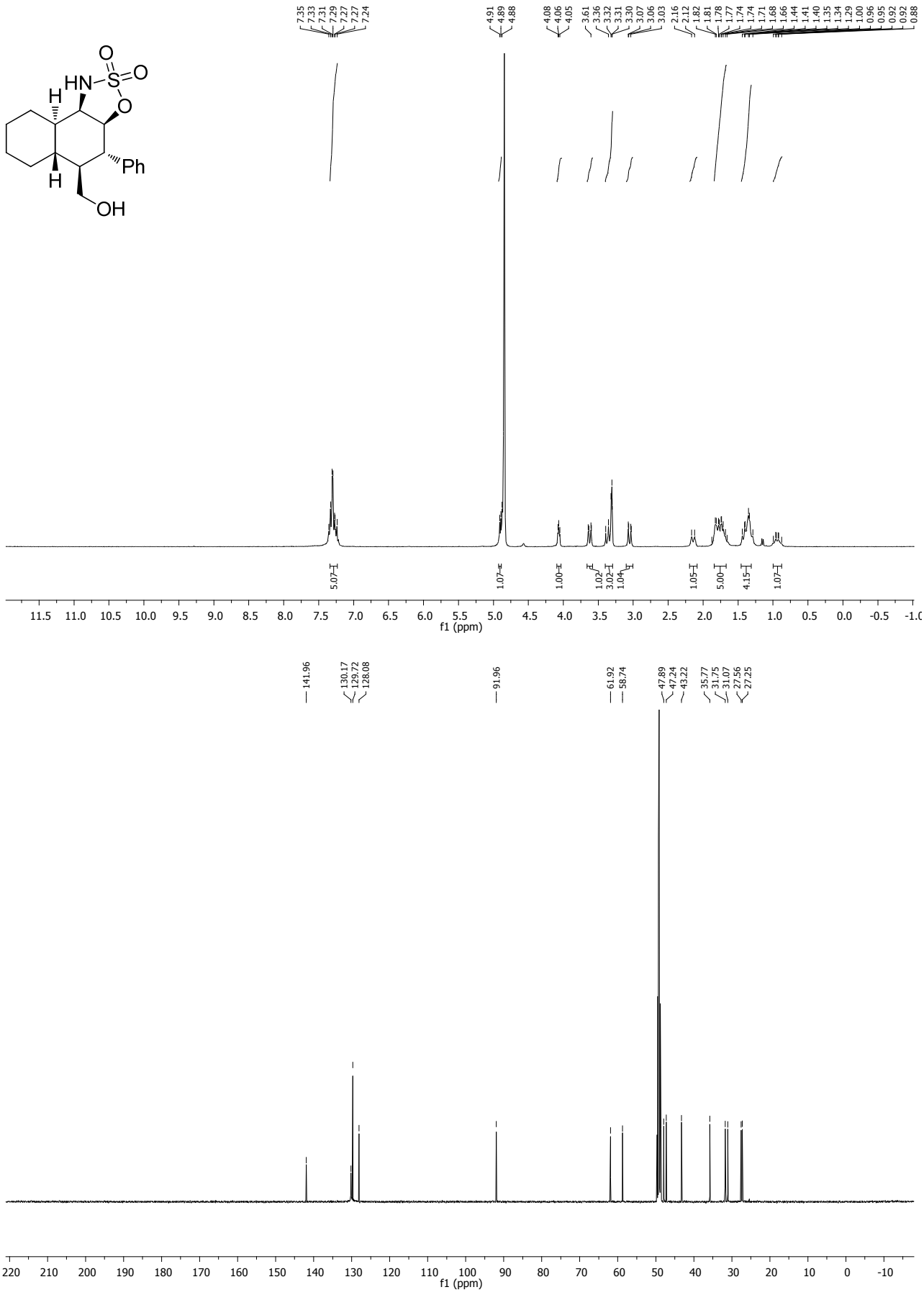


Figure 12: ^{1}H-NMR and ^{13}C-NMR spectra for compound **4i**.

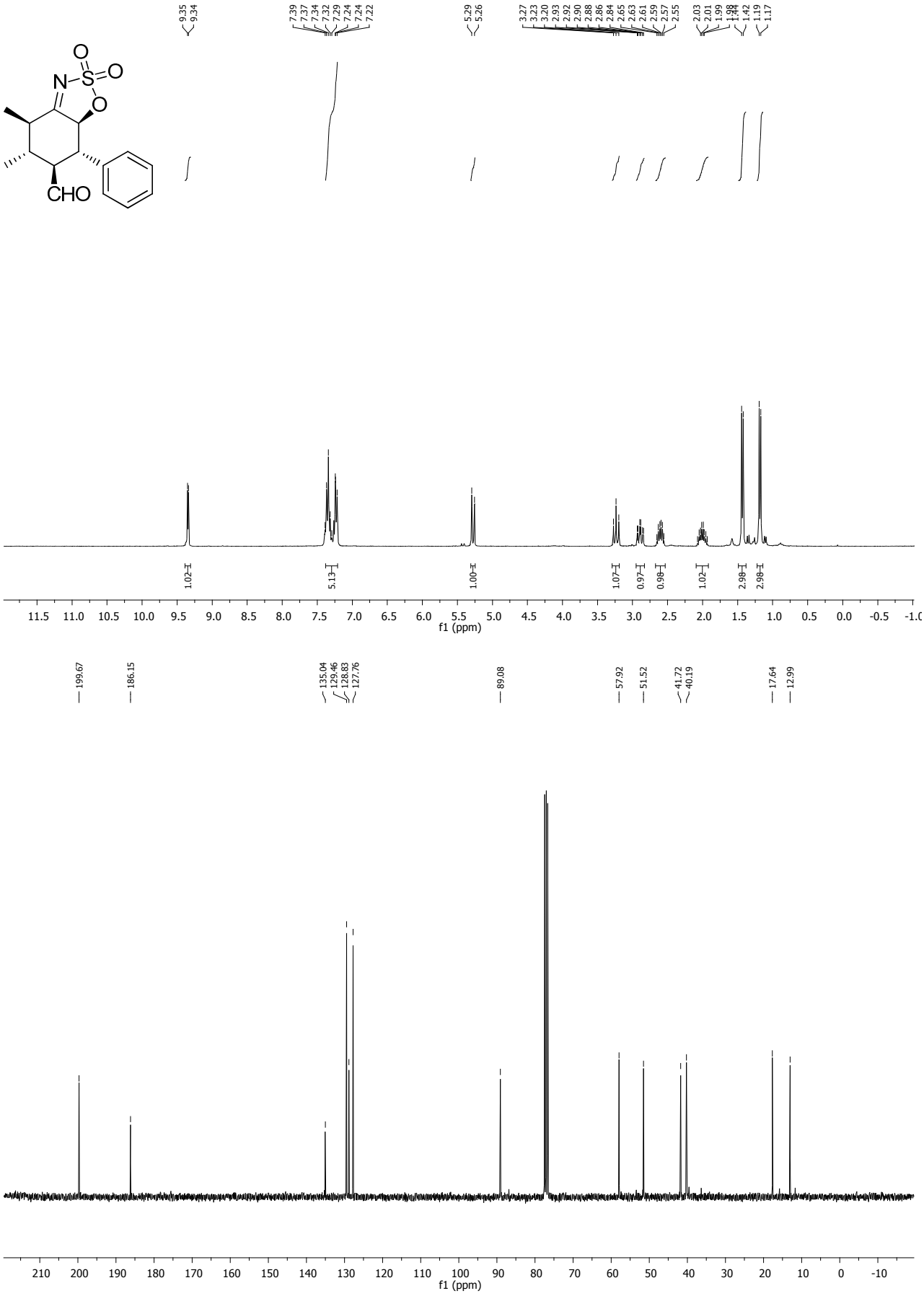


Figure 13: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5a**.

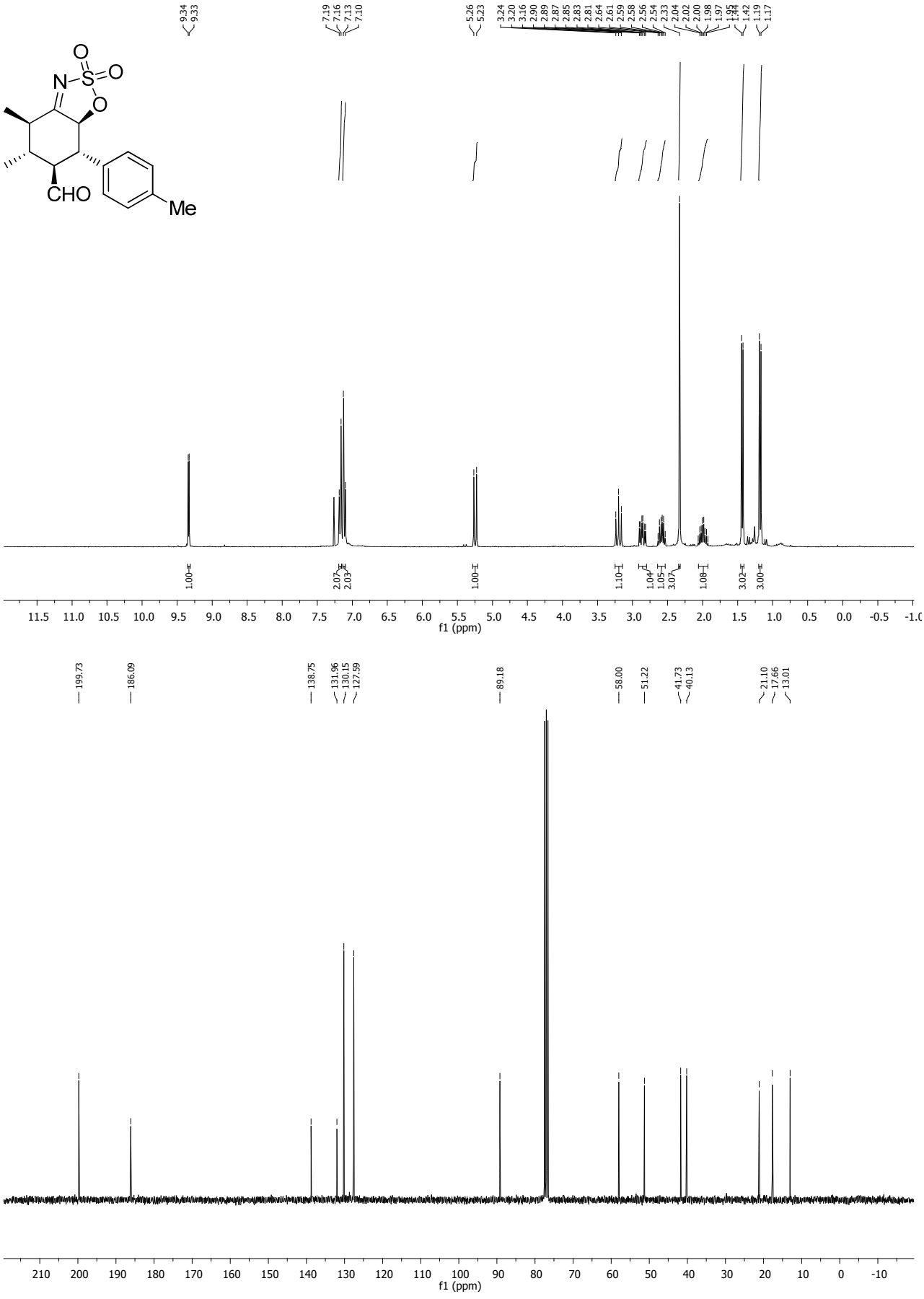


Figure 14: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5b**.

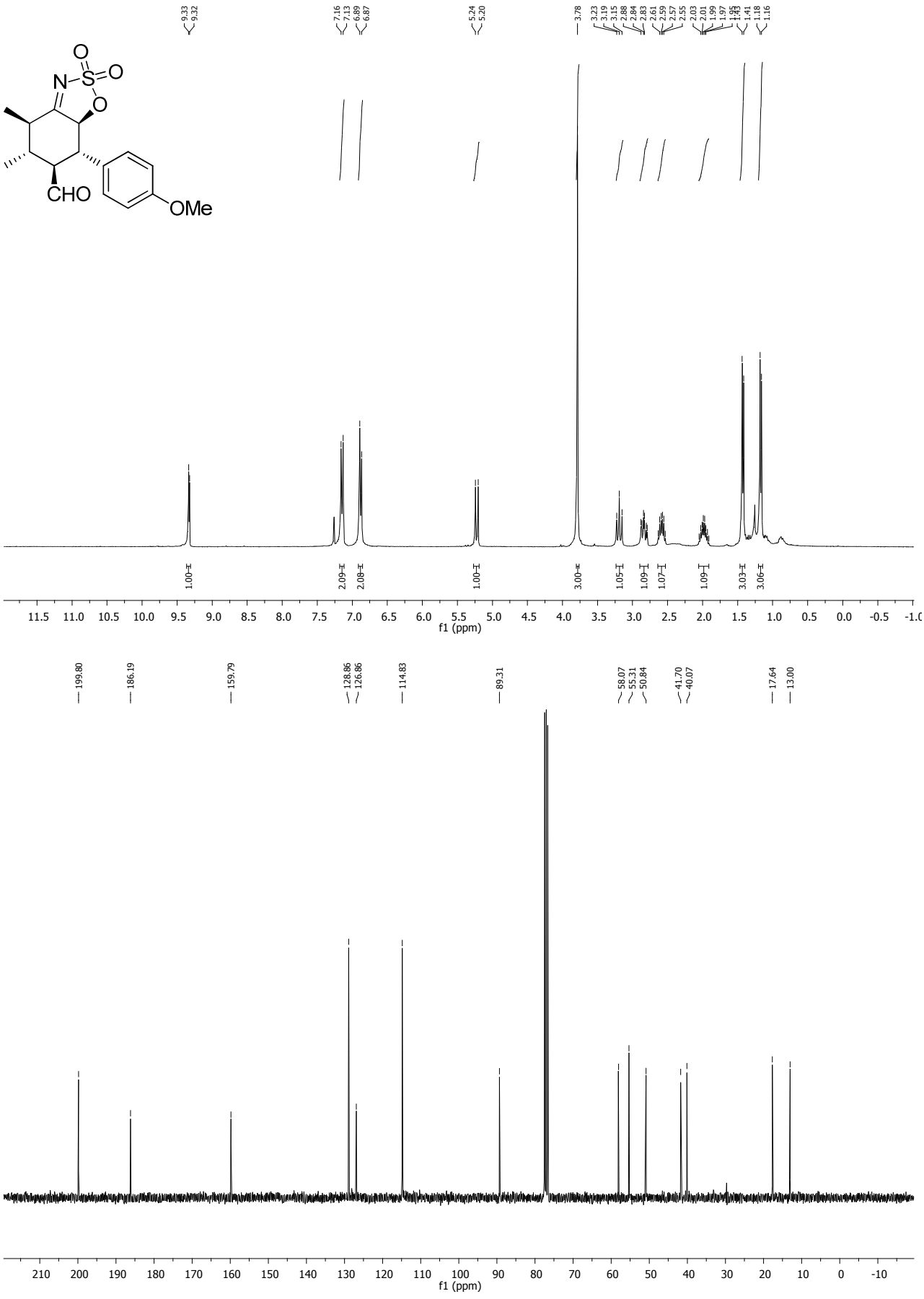


Figure 15: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5c**.

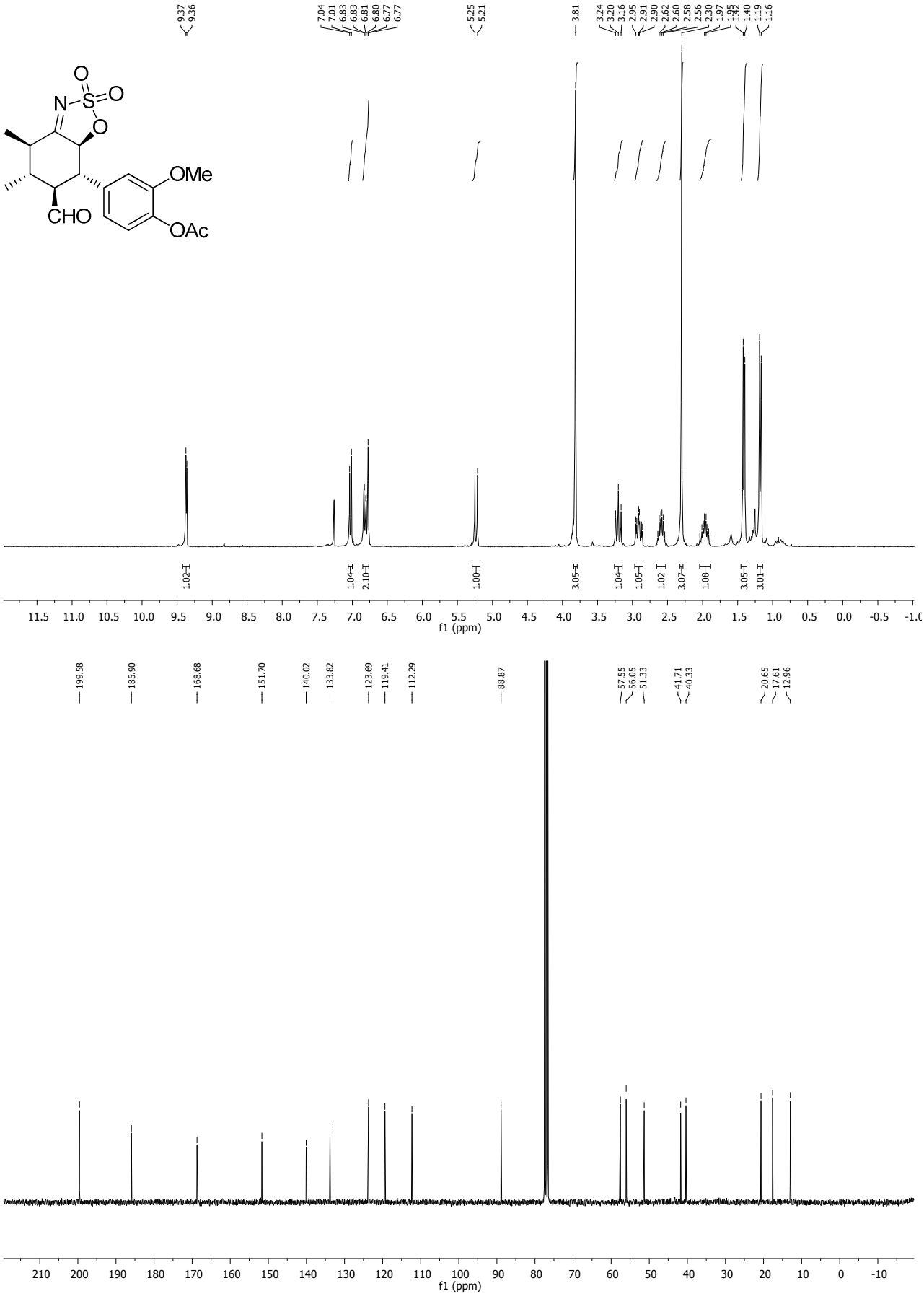


Figure 16: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5d**.

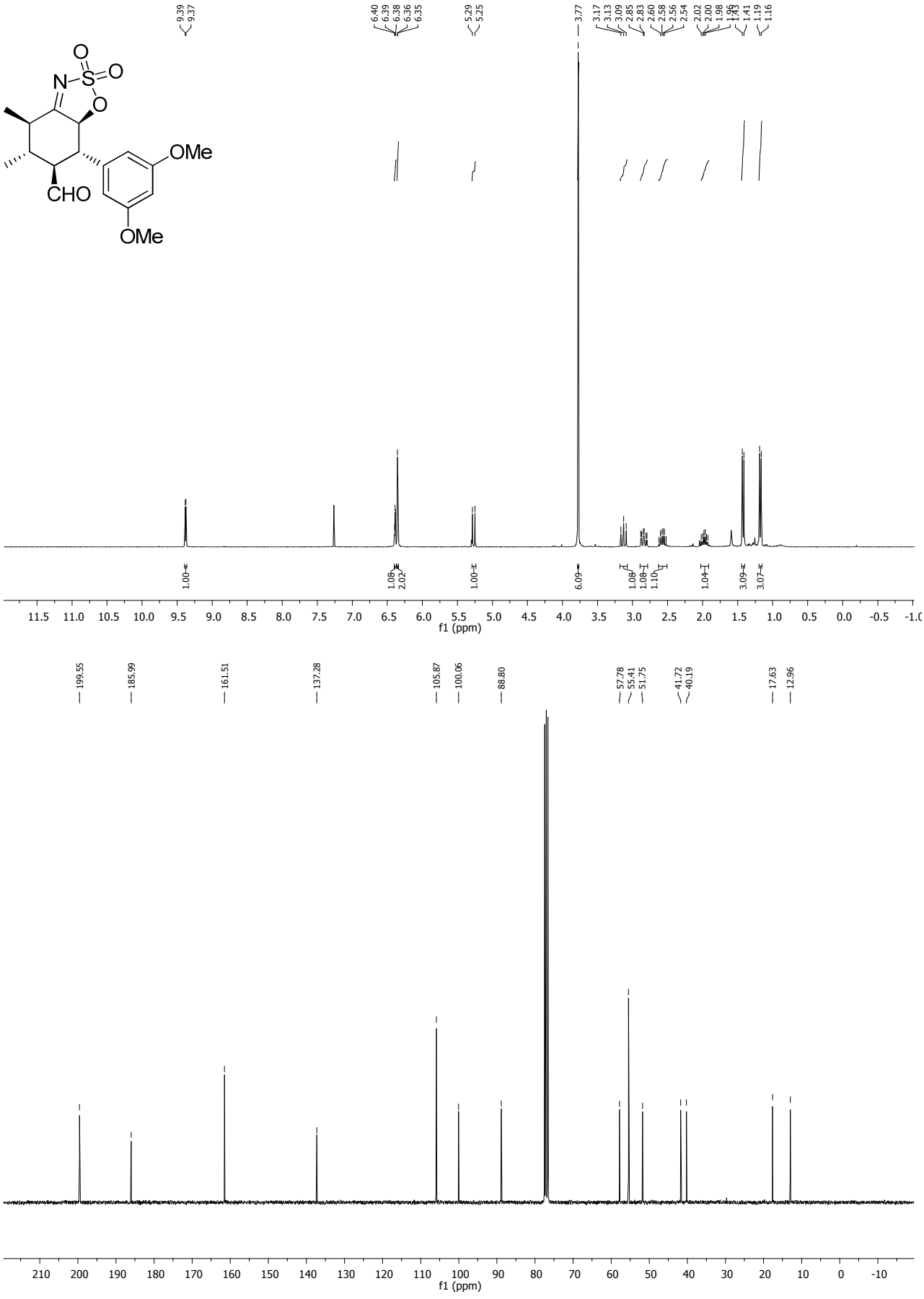


Figure 17: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5e**.

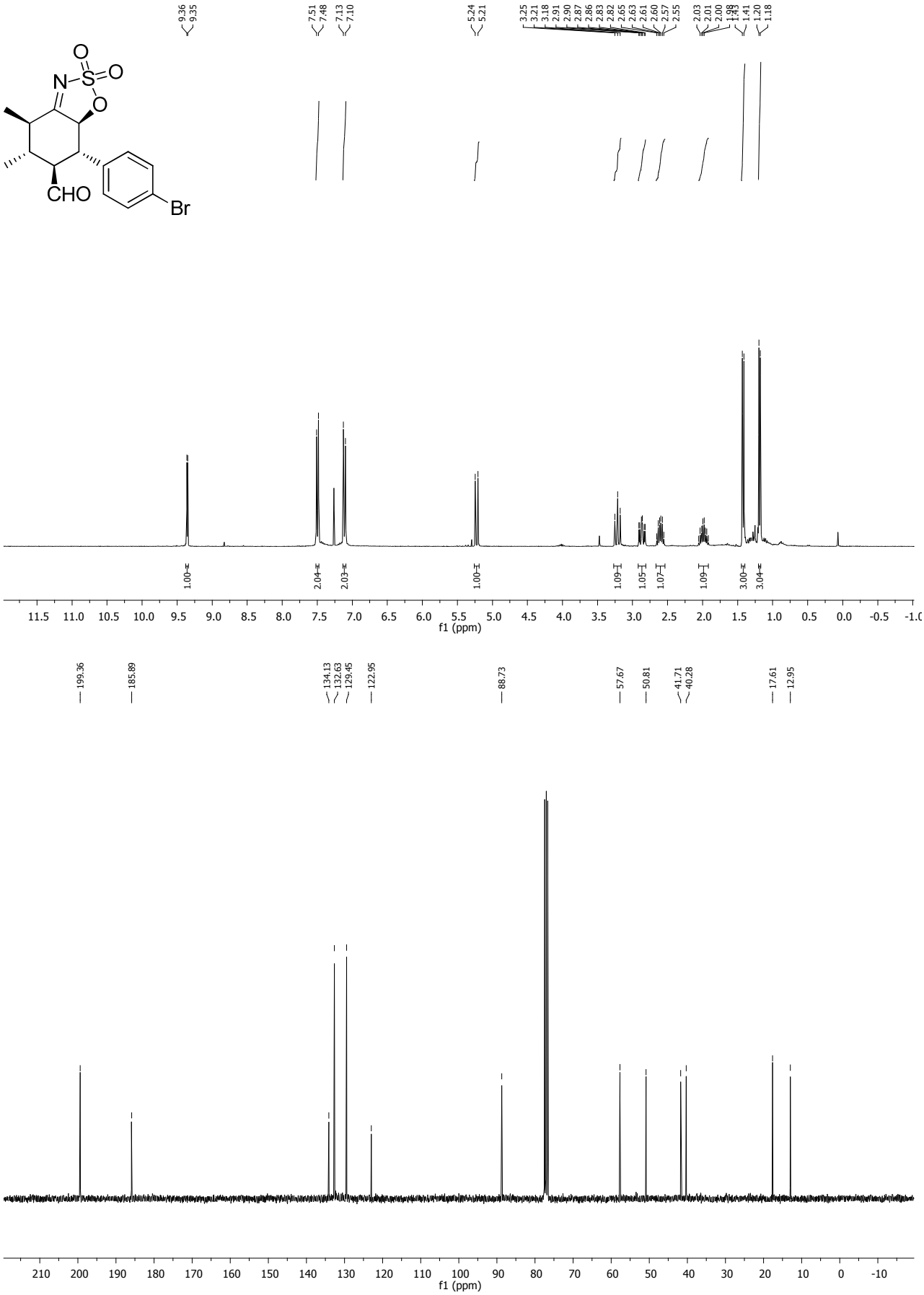


Figure 18: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5f**.

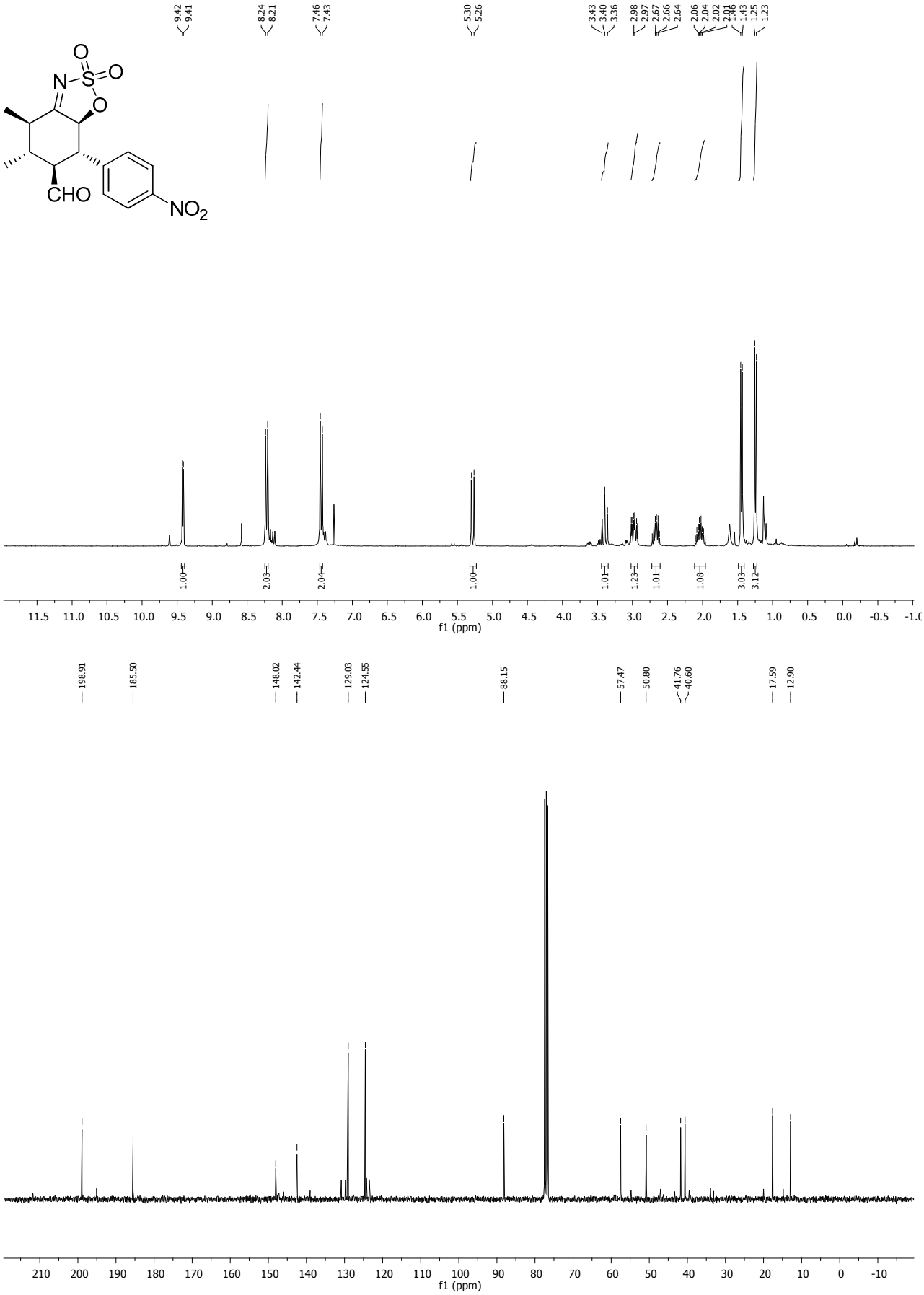


Figure 19: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5g**.

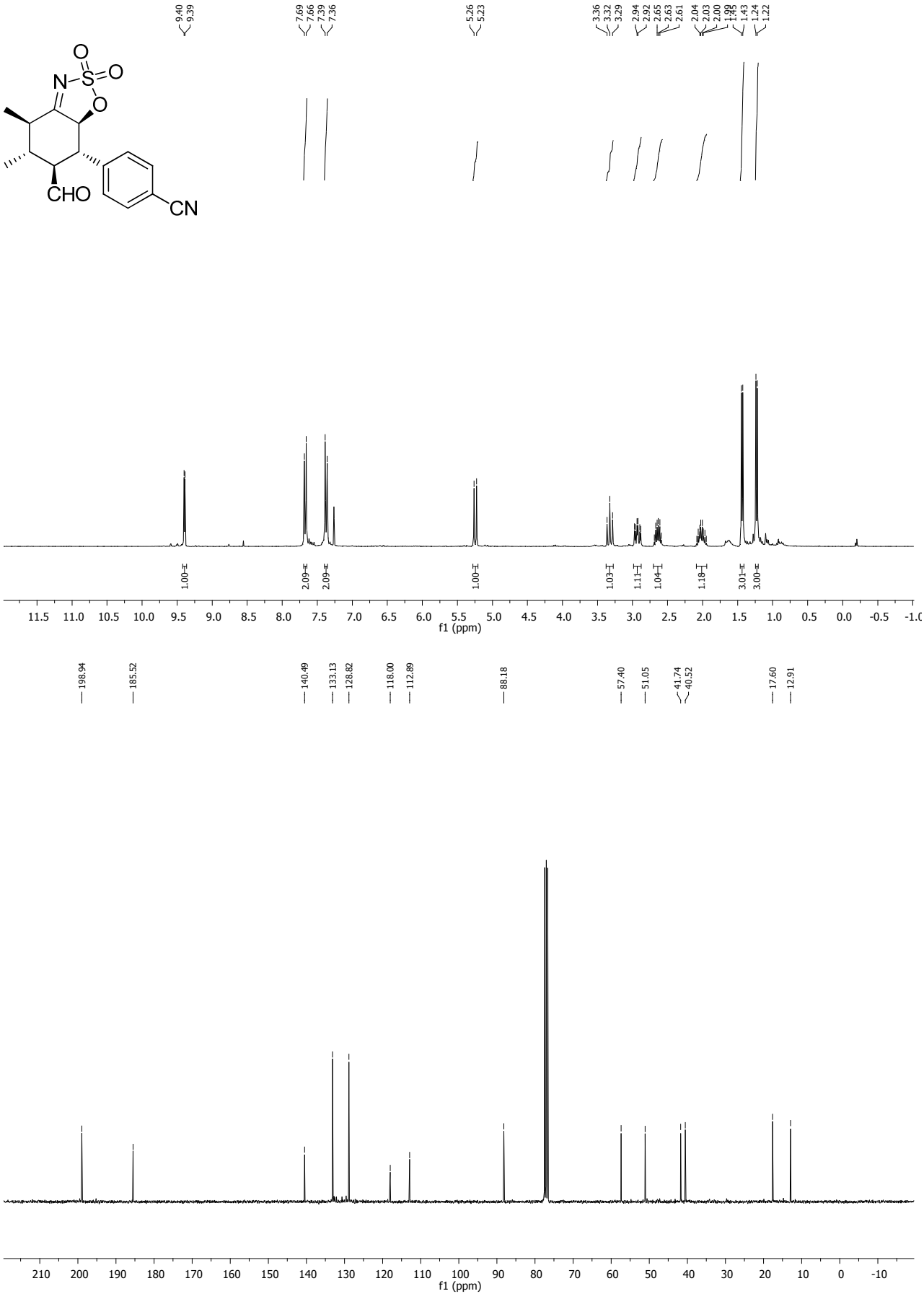


Figure 20: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5h**.

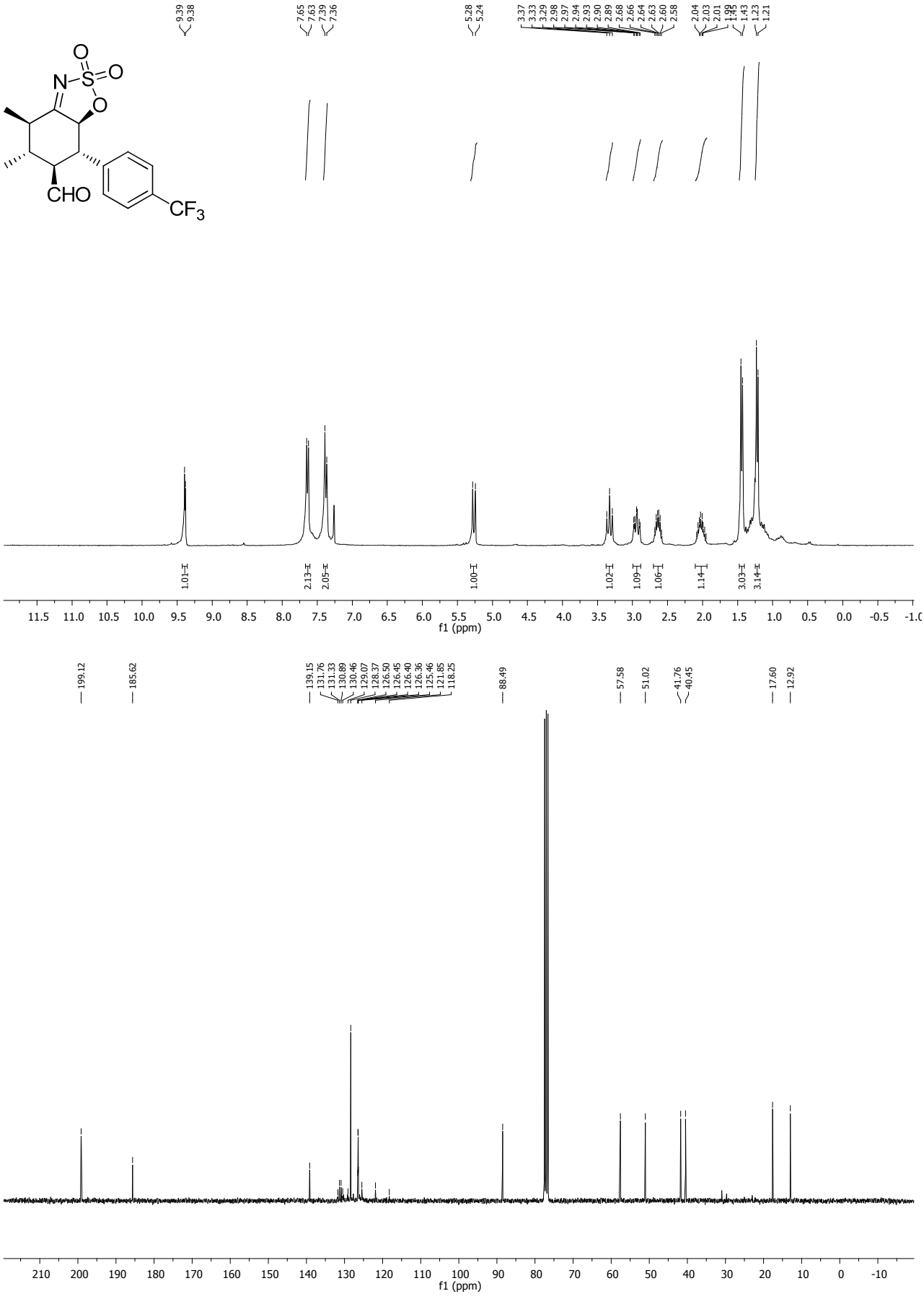


Figure 21: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5i**.

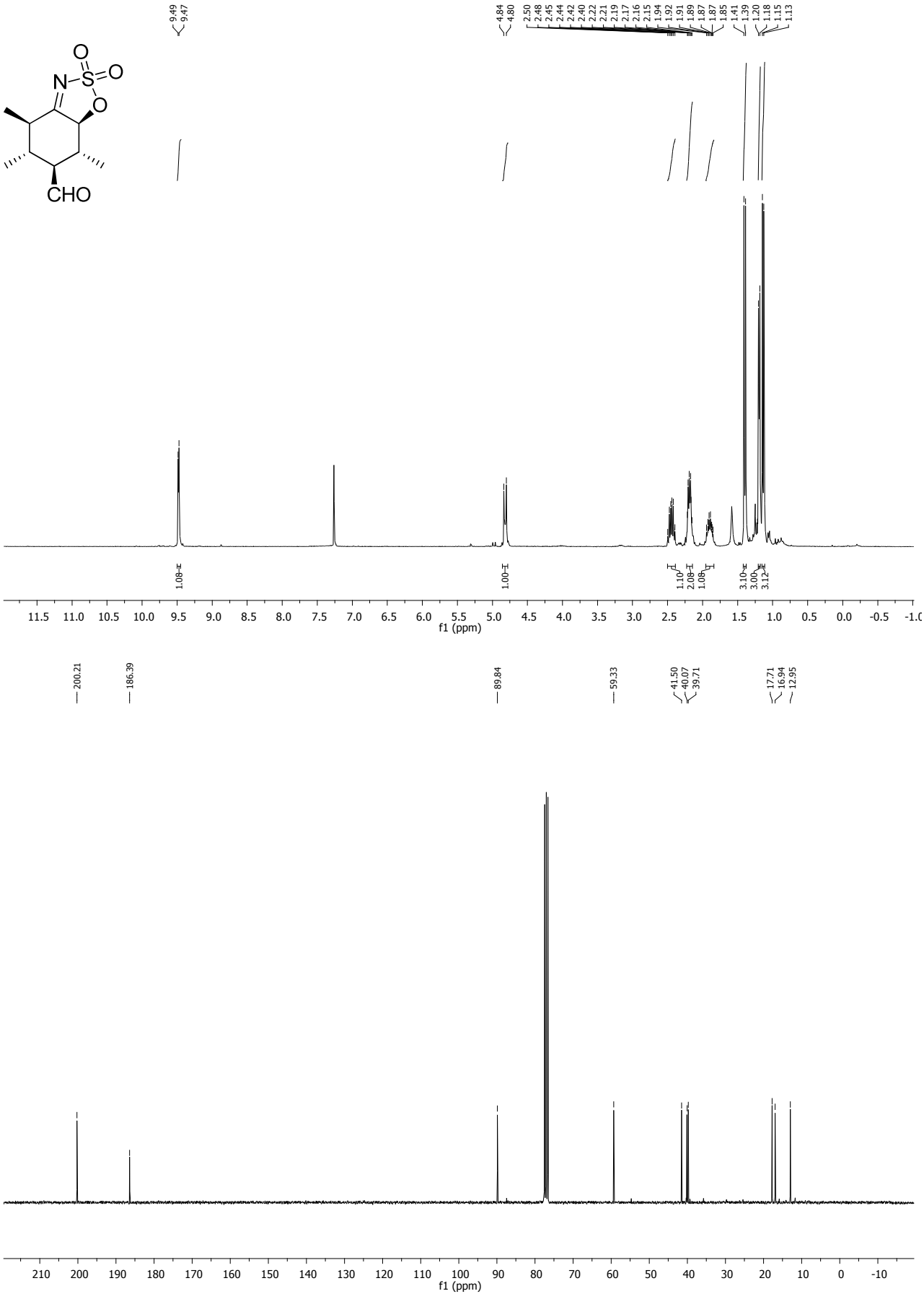


Figure 22: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5j**.

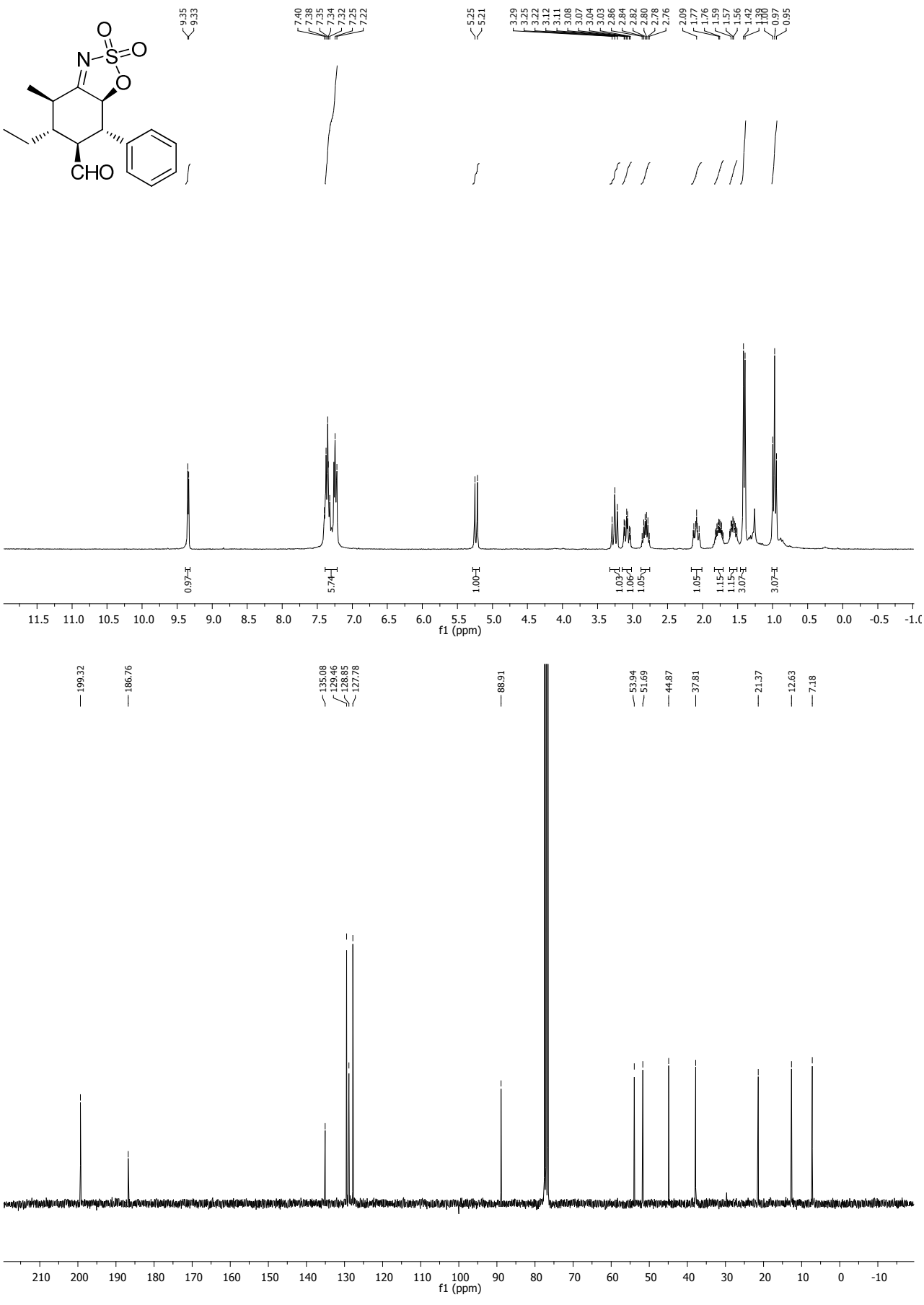


Figure 23: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5k**.

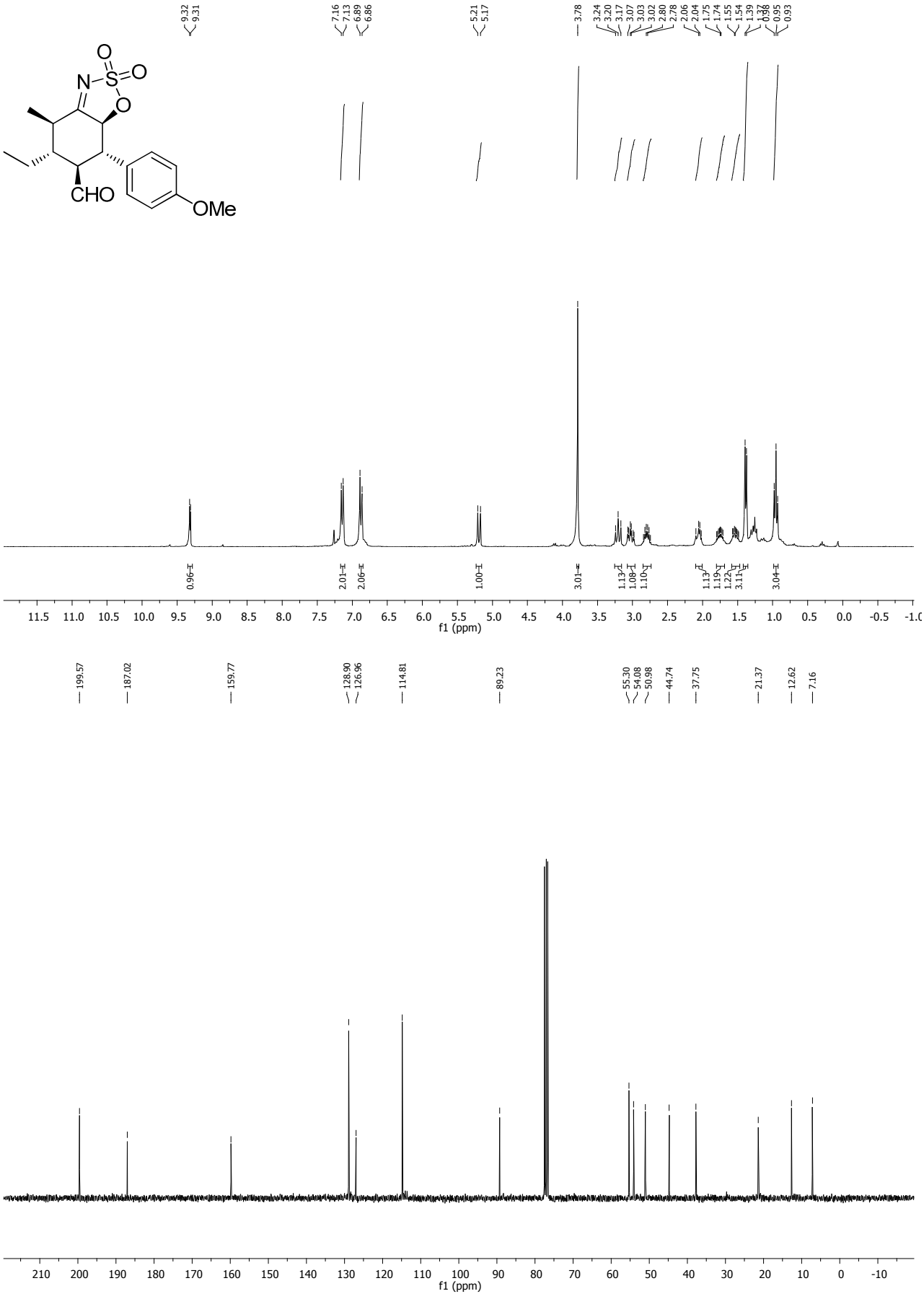


Figure 24: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5l**.

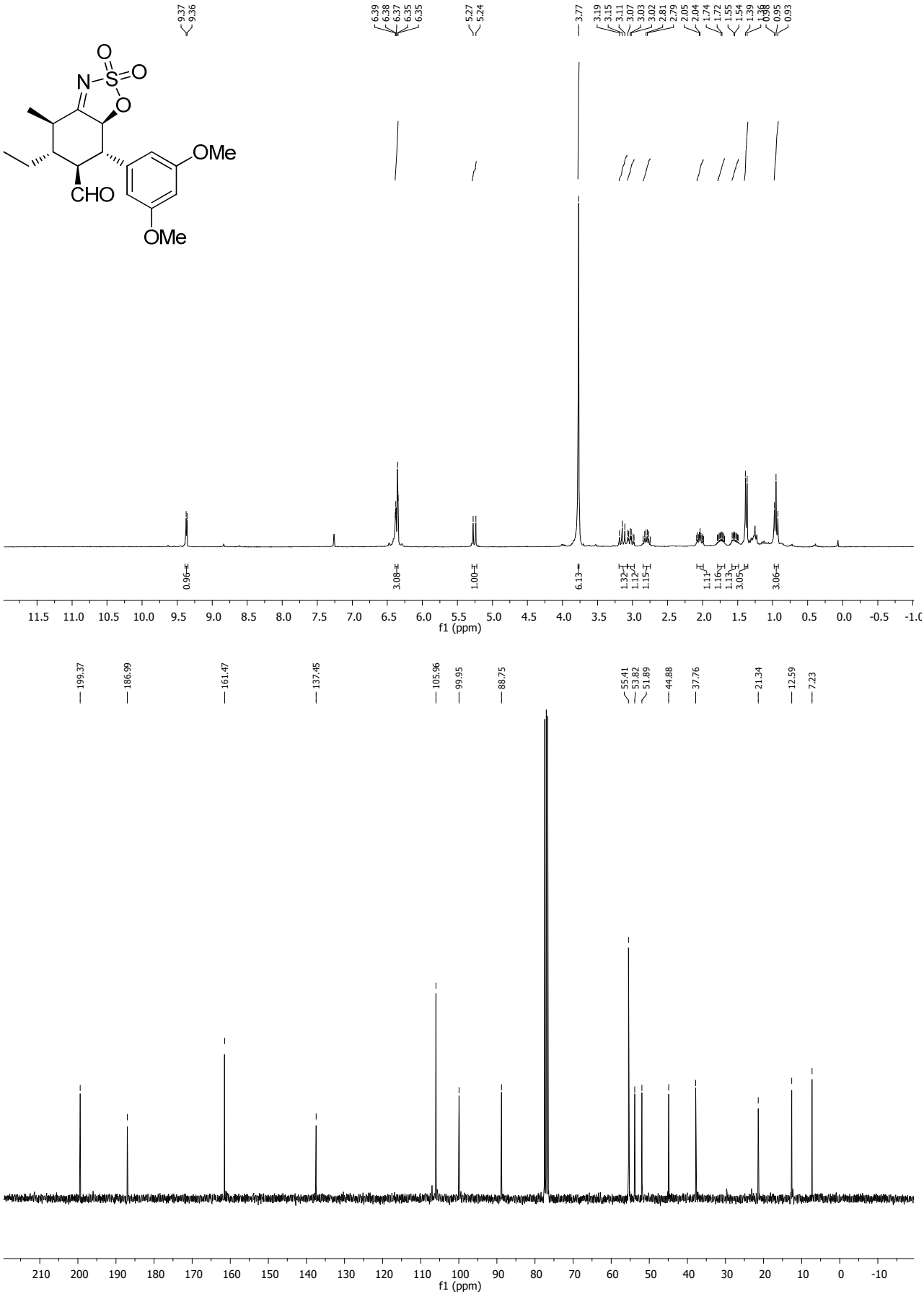


Figure 25: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5m**.

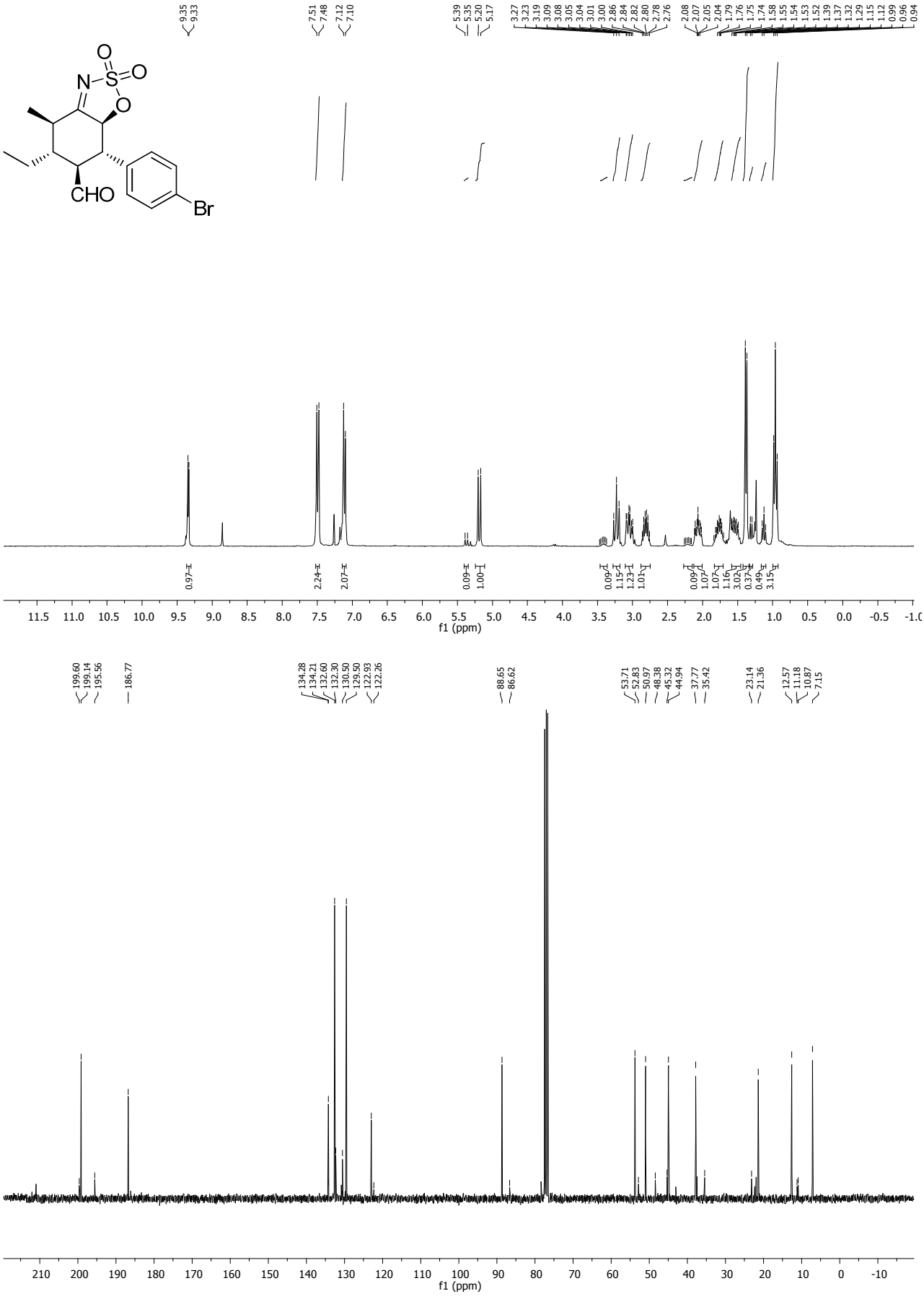


Figure 26: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5n**.

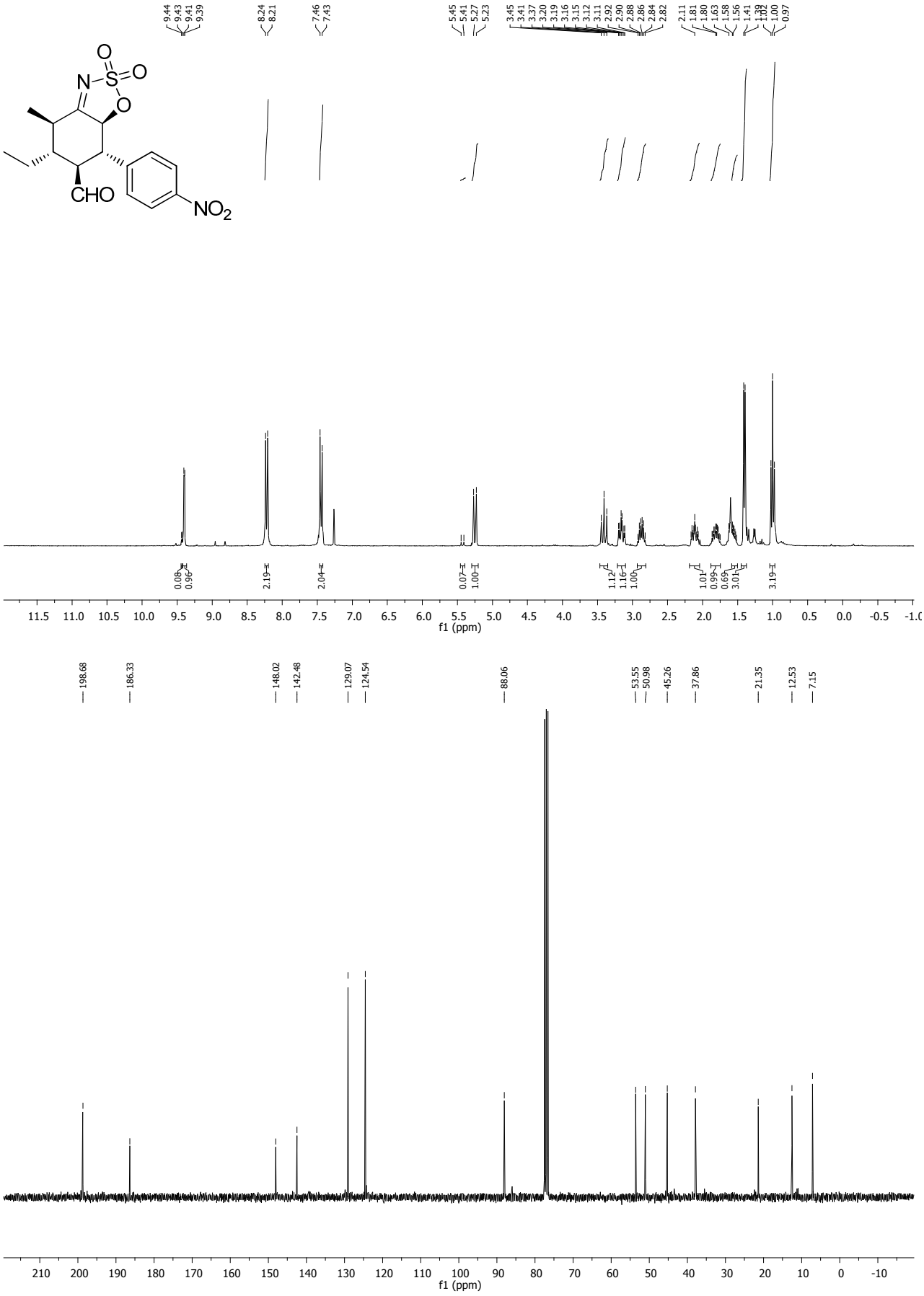


Figure 27: ^{1}H-NMR and ^{13}C-NMR spectra for compound **5o**.

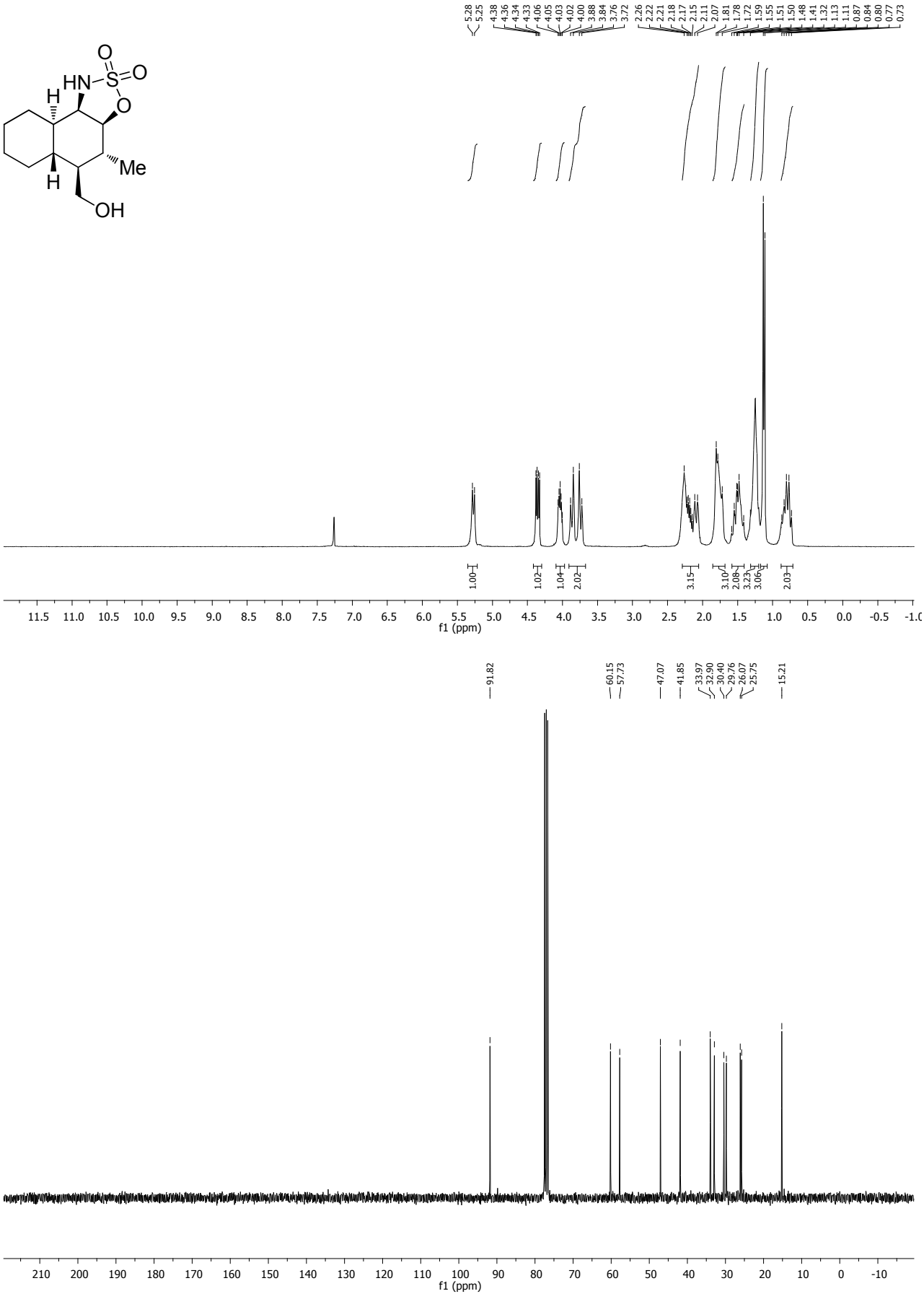


Figure 28: ^{1}H-NMR and ^{13}C-NMR spectra for compound **6**.

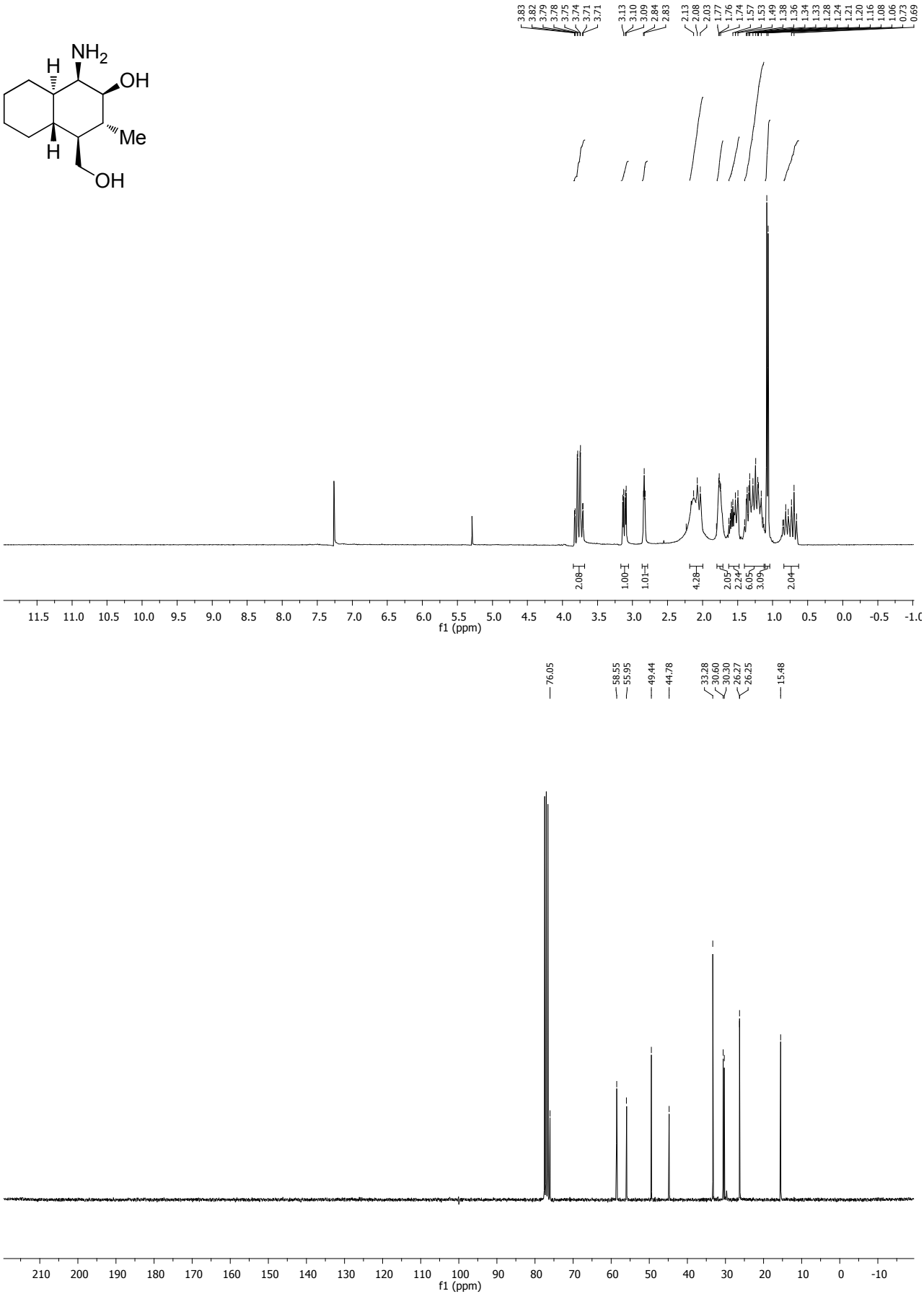
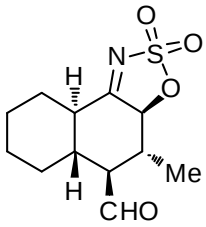


Figure 29: ^{1}H-NMR and ^{13}C-NMR spectra for compound **7**.

HPLC Chromatograms



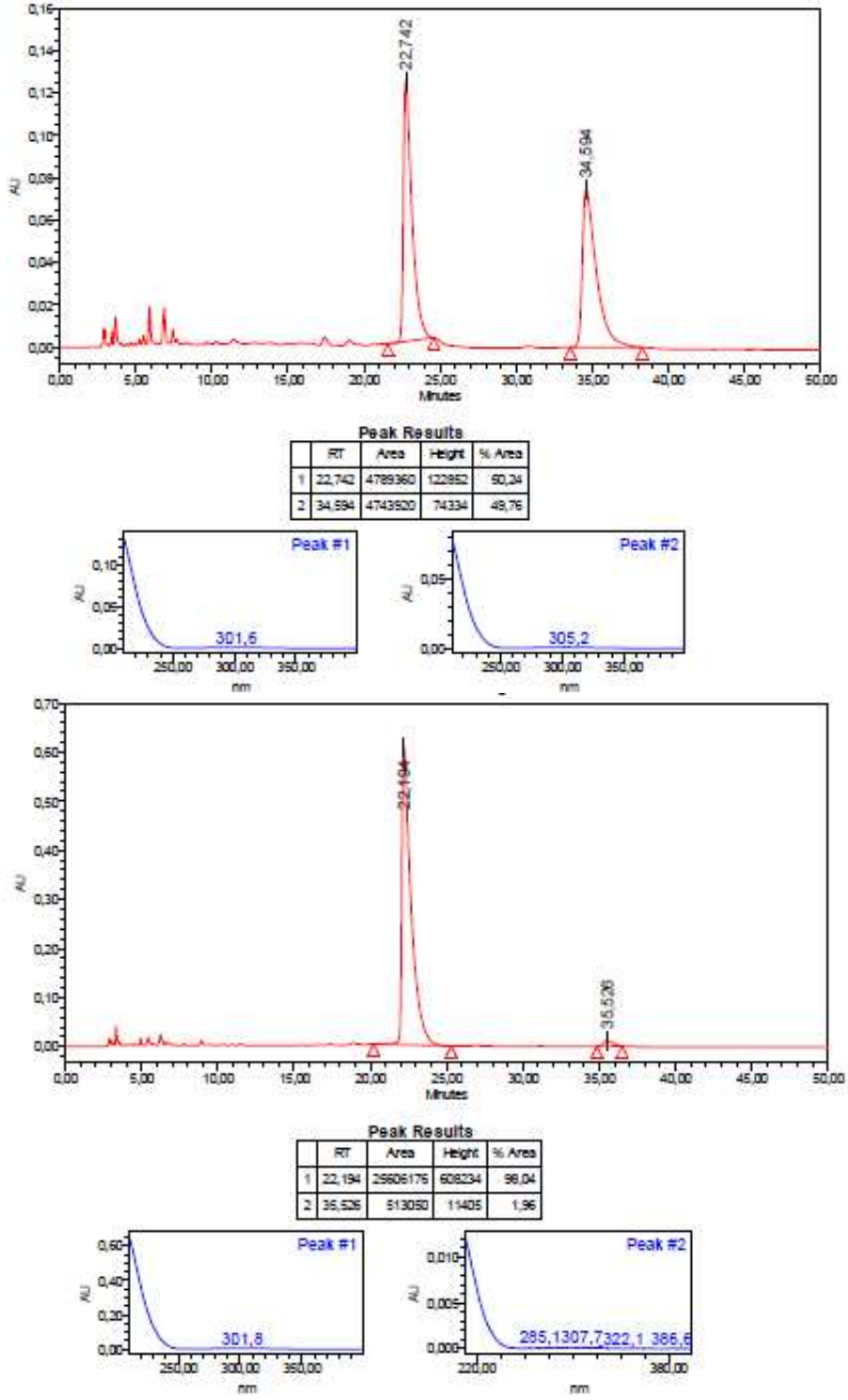
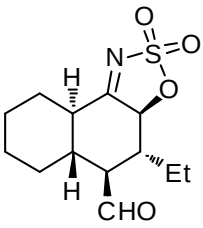


Figure 30: HPLC chromatogram for compounds ***rac*-4a** and **4a**.



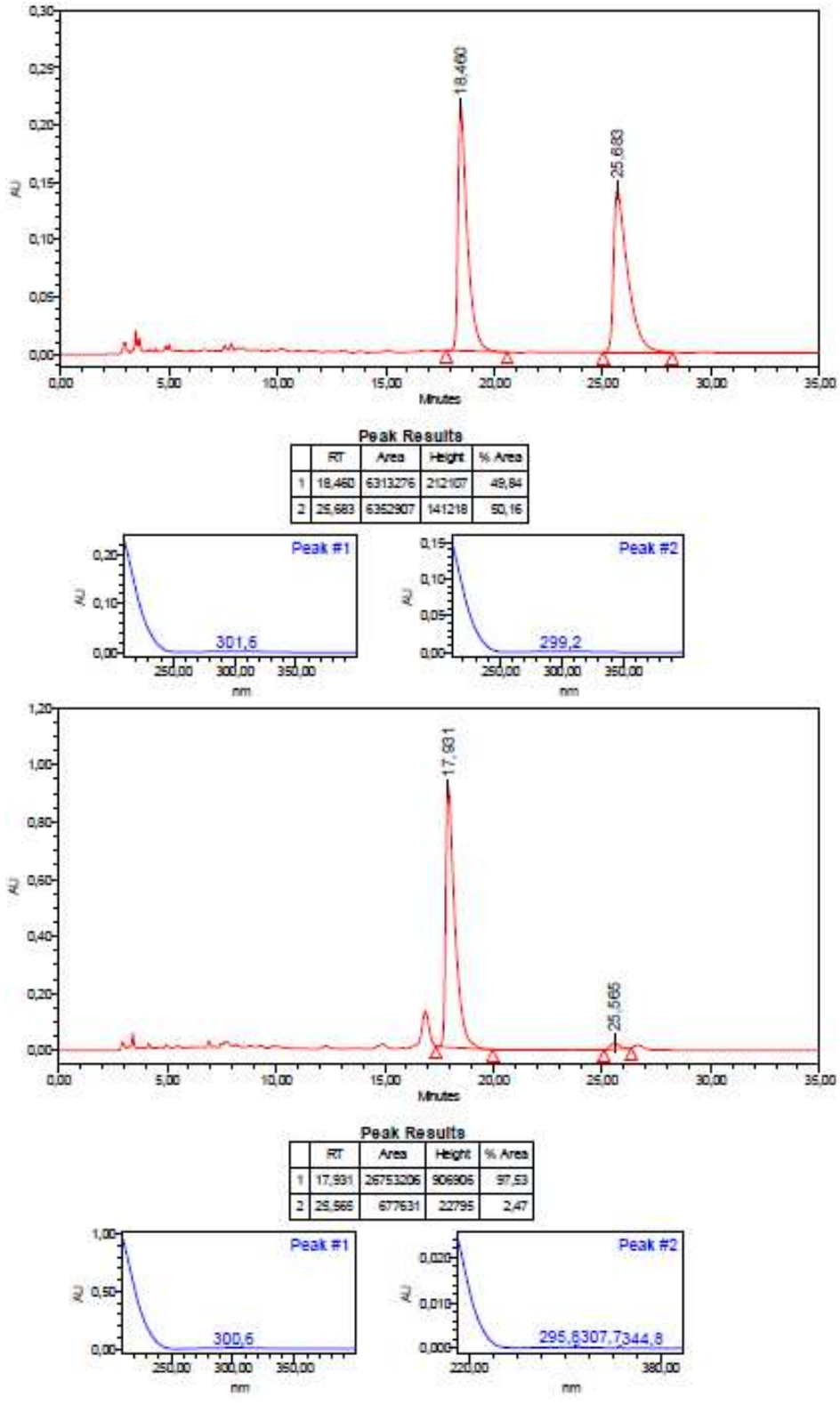
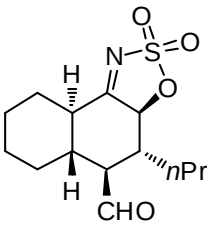
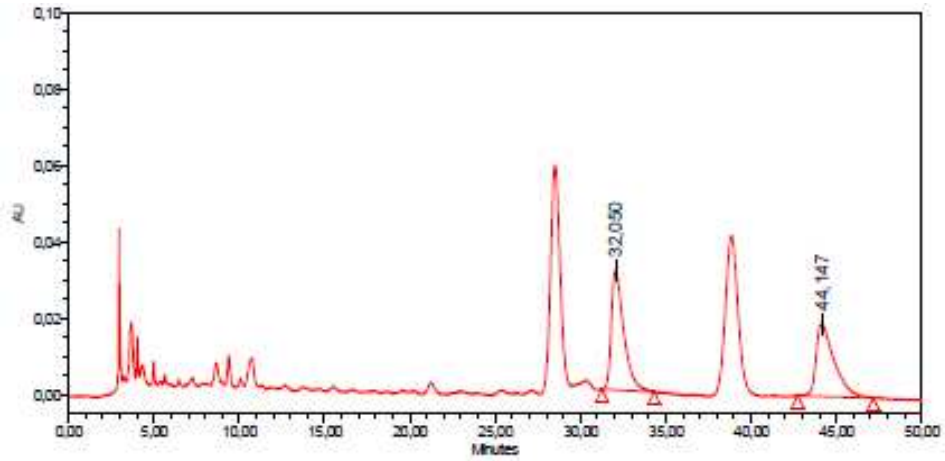


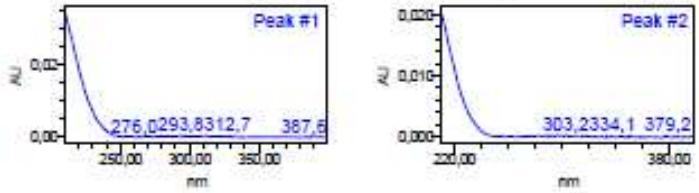
Figure 31: HPLC chromatogram for compounds ***rac*-4b** and **4b**.

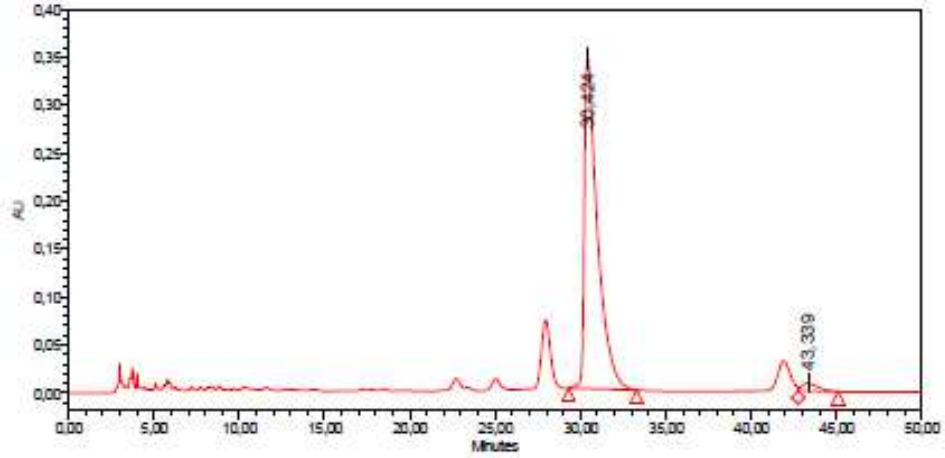




Peak Results

	RT	Area	Height	% Area
1	32,050	1581382	31373	52,93
2	44,147	1406040	19074	47,07





Peak Results

	RT	Area	Height	% Area
1	30,424	18313700	344937	97,23
2	43,339	521786	8041	2,77

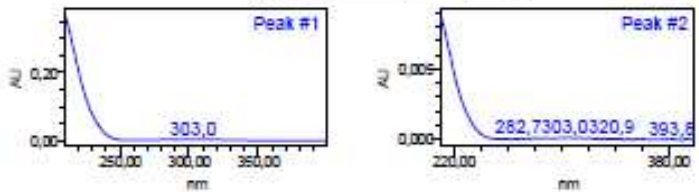
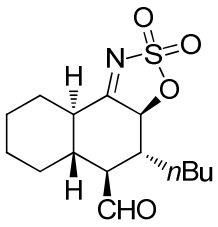
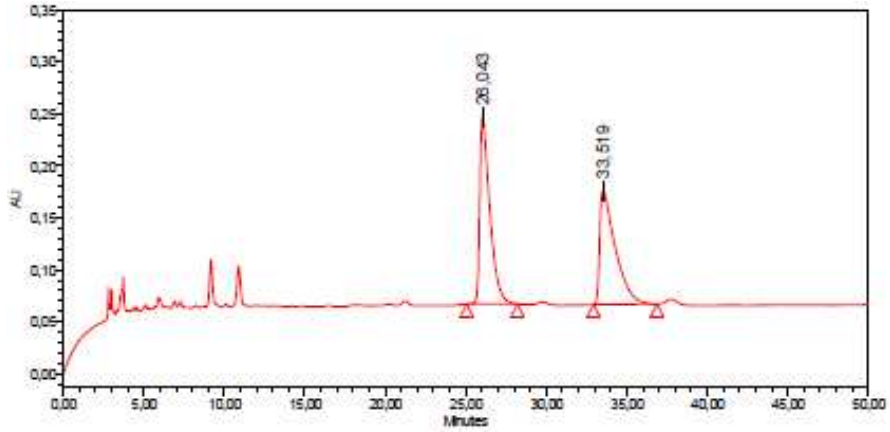


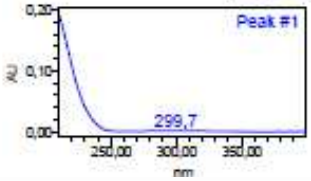
Figure 32: HPLC chromatogram for compounds ***rac*-4c** and **4c**.

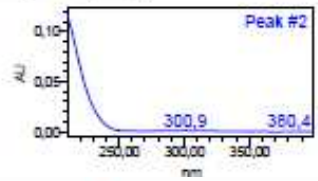


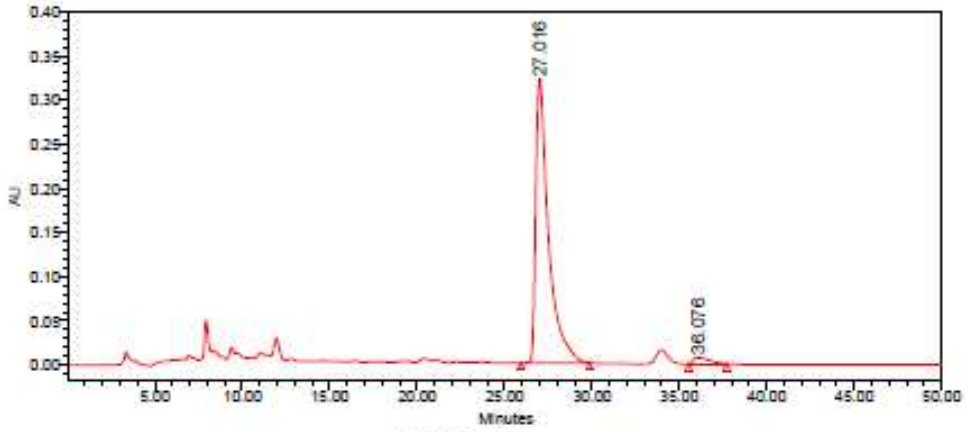


Peak Results

	RT	Area	Height	% Area
1	26.043	7820157	179693	51.53
2	33.519	7355514	109539	48.47

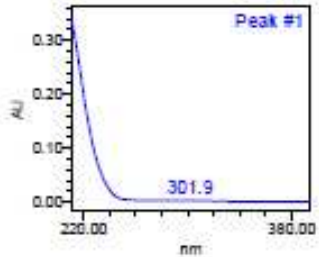






Peak Results

	RT	Area	Height	% Area
1	27.016	16288880	321059	97.38
2	36.076	438468	7407	2.62



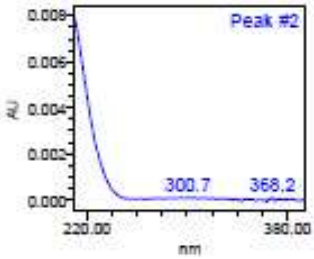
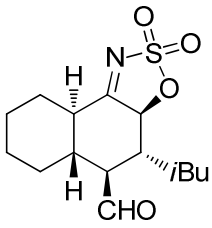


Figure 33: HPLC chromatogram for compounds ***rac*-4d** and **4d**.



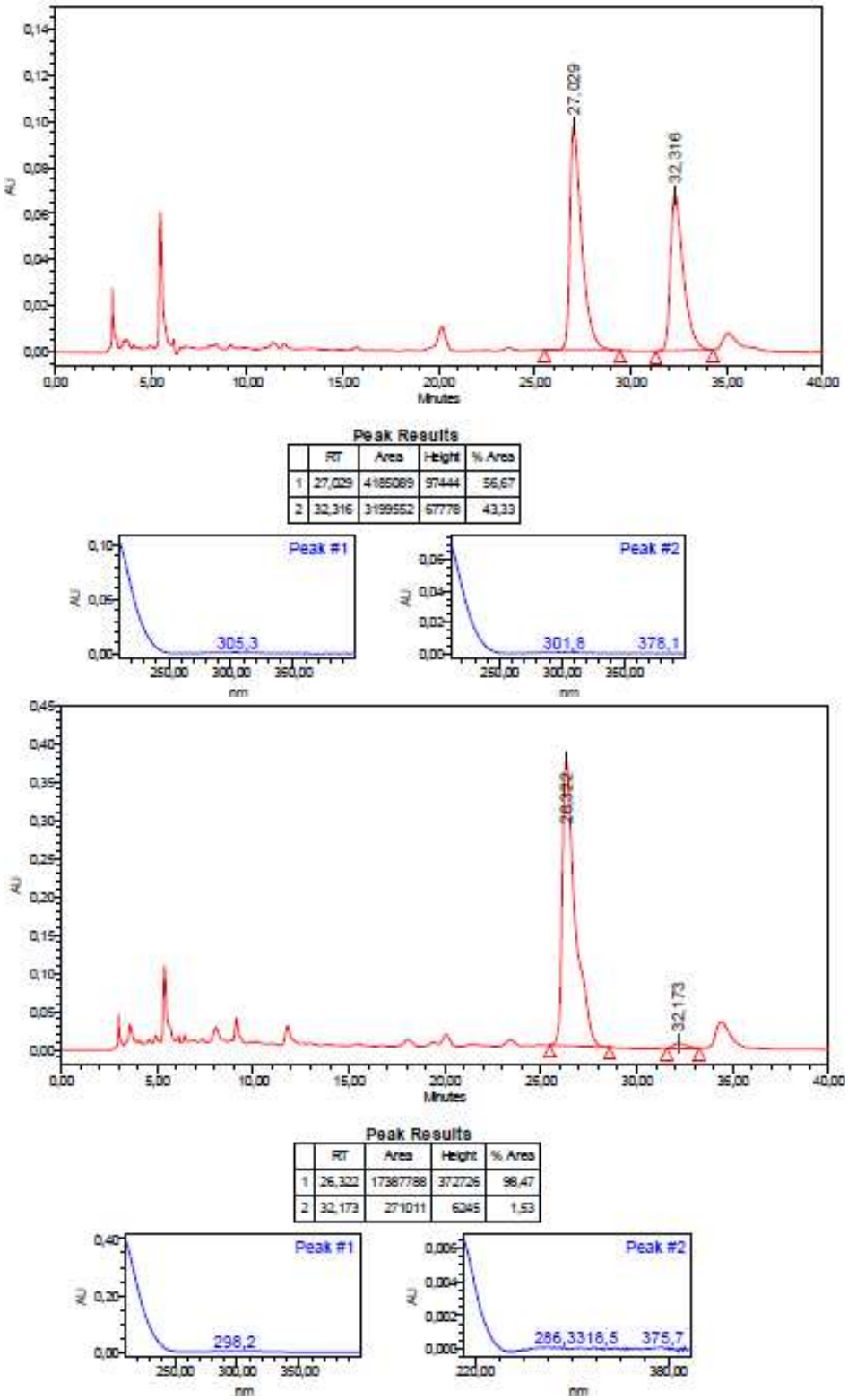
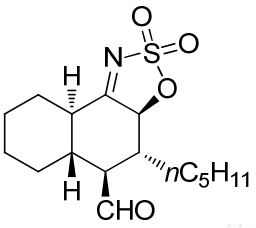
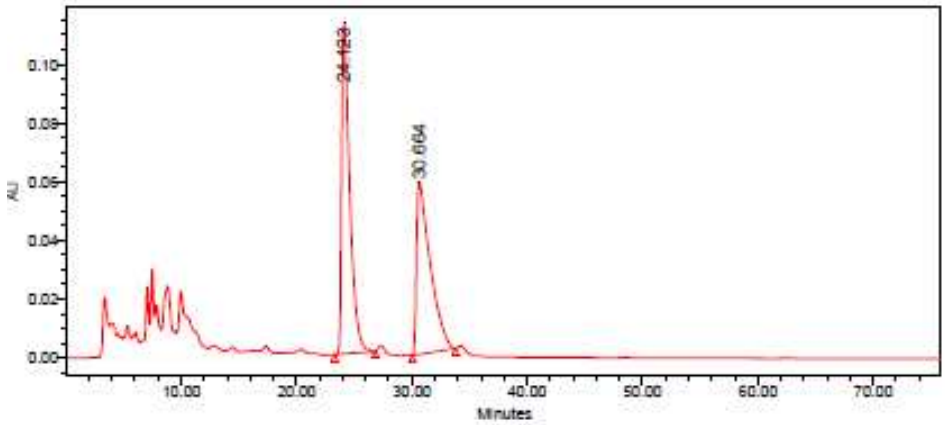


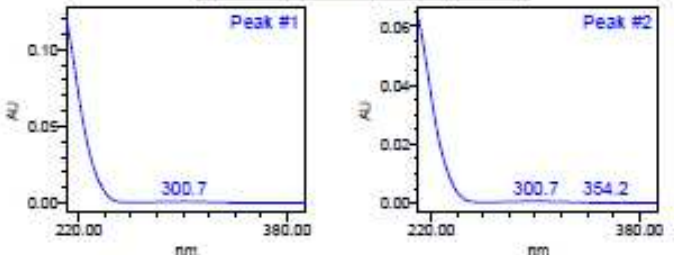
Figure 34: HPLC chromatogram for compounds ***rac*-4e** and **4e**.

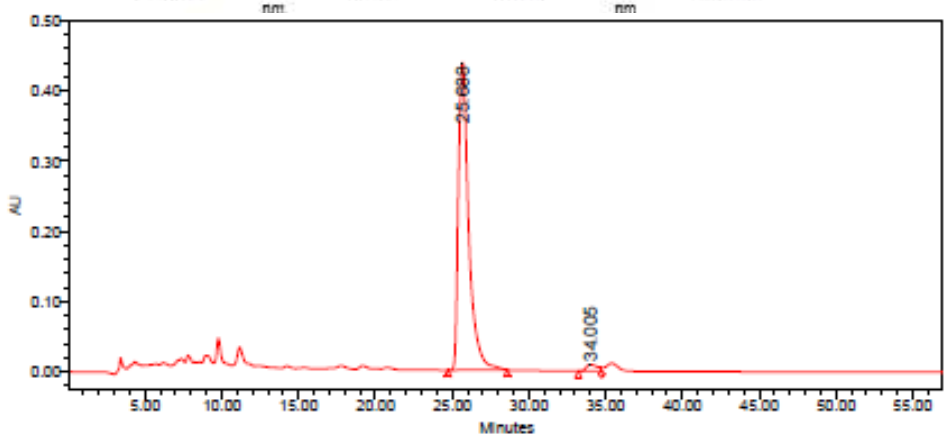




Peak Results

	RT	Area	Height	% Area
1	24.123	5503027	112550	53.11
2	30.664	4857768	58566	46.89





Peak Results

	RT	Area	Height	% Area
1	25.688	20523329	438109	97.78
2	34.005	465631	9289	2.22

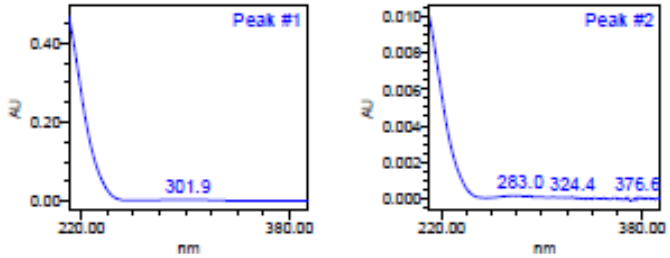
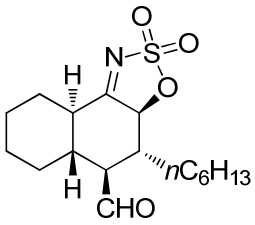
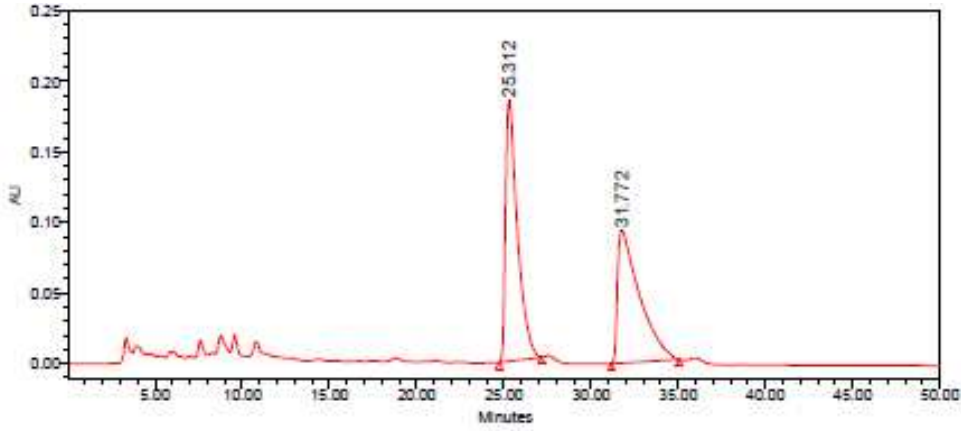


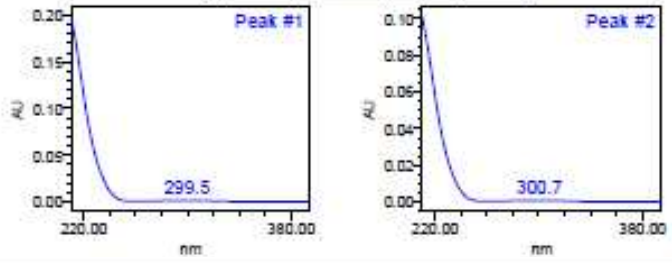
Figure 35: HPLC chromatogram for compounds ***rac*-4f** and **4f**.

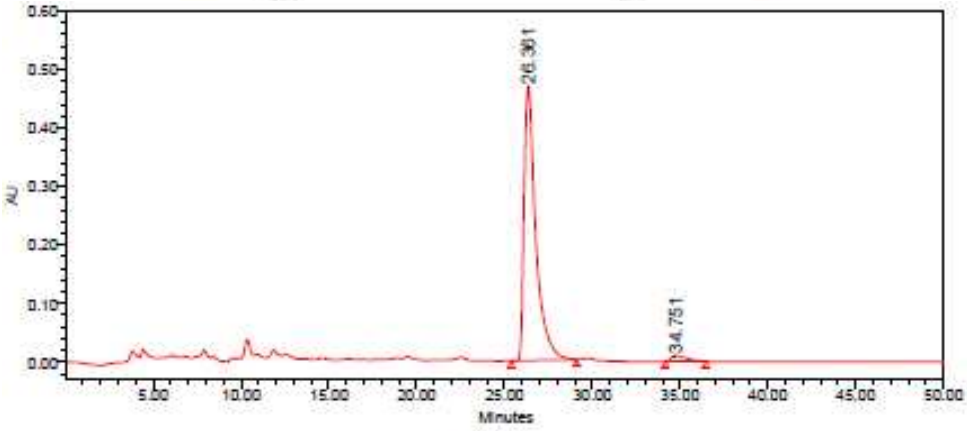




Peak Results

	RT	Area	Height	% Area
1	25.312	8748420	184850	51.55
2	31.772	8223231	94075	48.45





Peak Results

	RT	Area	Height	% Area
1	26.361	21703719	468410	97.42
2	34.751	574235	9722	2.58

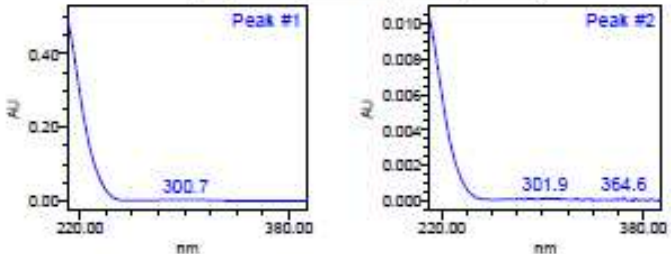
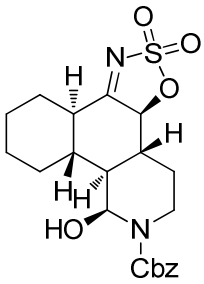
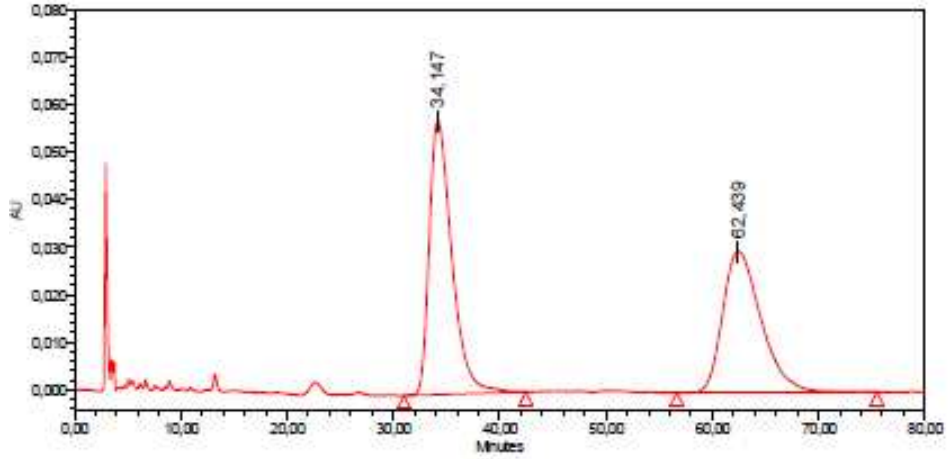


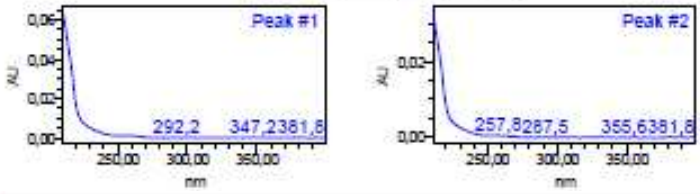
Figure 36: HPLC chromatogram for compounds ***rac*-4g** and **4g**.

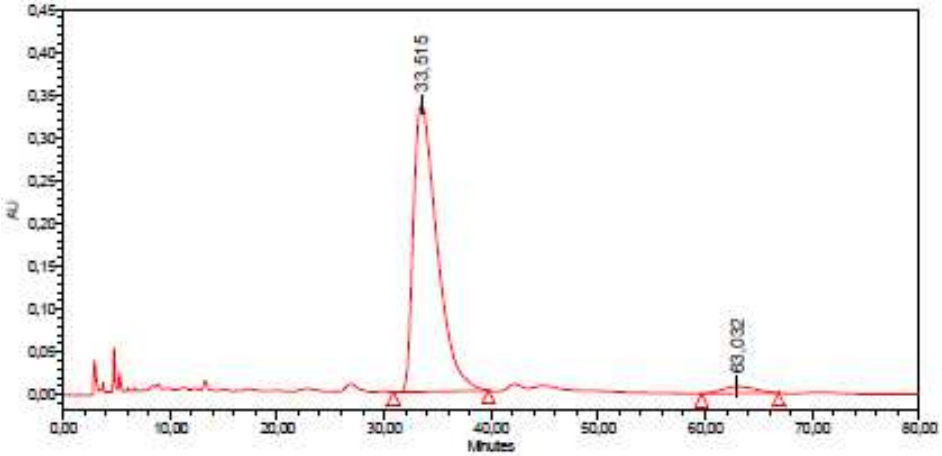




Peak Results

	RT	Area	Height	% Area
1	34,147	8487050	57634	53,28
2	62,439	7442968	29757	46,72





Peak Results

	RT	Area	Height	% Area
1	33,515	51553691	335362	96,83
2	63,032	1688099	8021	3,17

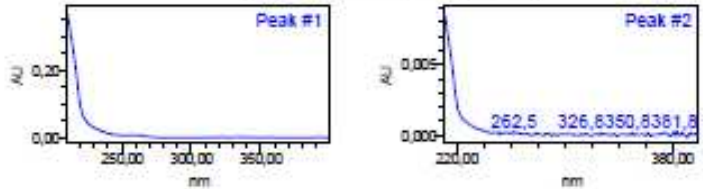
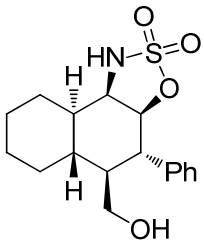
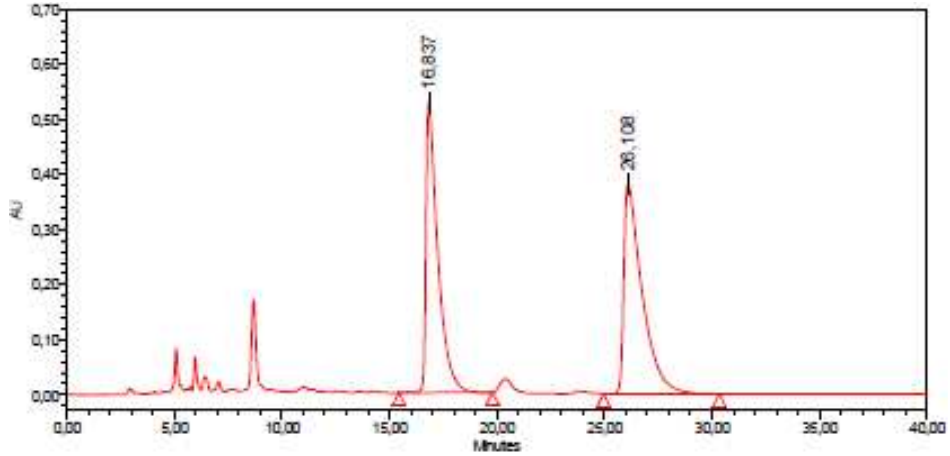


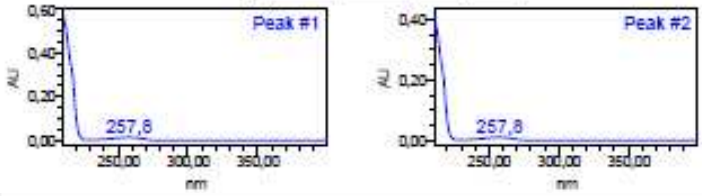
Figure 37: HPLC chromatogram for compounds ***rac*-4h** and **4h**.

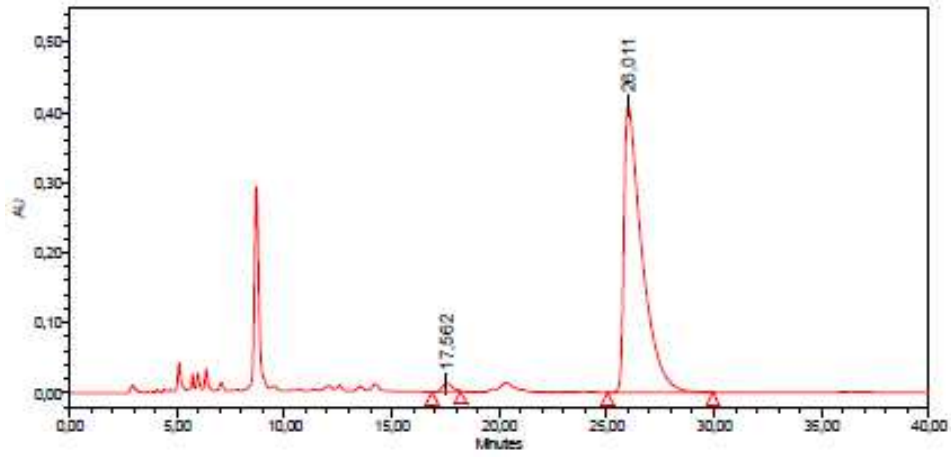




Peak Results

	RT	Area	Height	% Area
1	16,837	20030856	525963	47,14
2	26,108	22463497	381100	52,86





Peak Results

	RT	Area	Height	% Area
1	17,562	350476	11372	1,45
2	26,011	23800853	408669	98,55

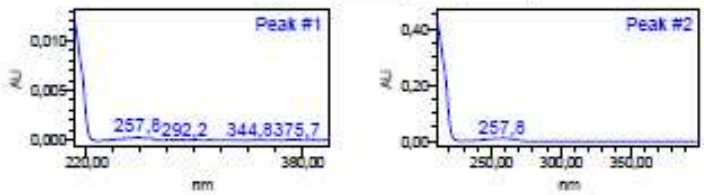
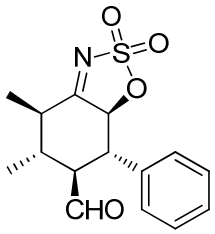


Figure 38: HPLC chromatogram for compounds ***rac*-4i** and **4i**.



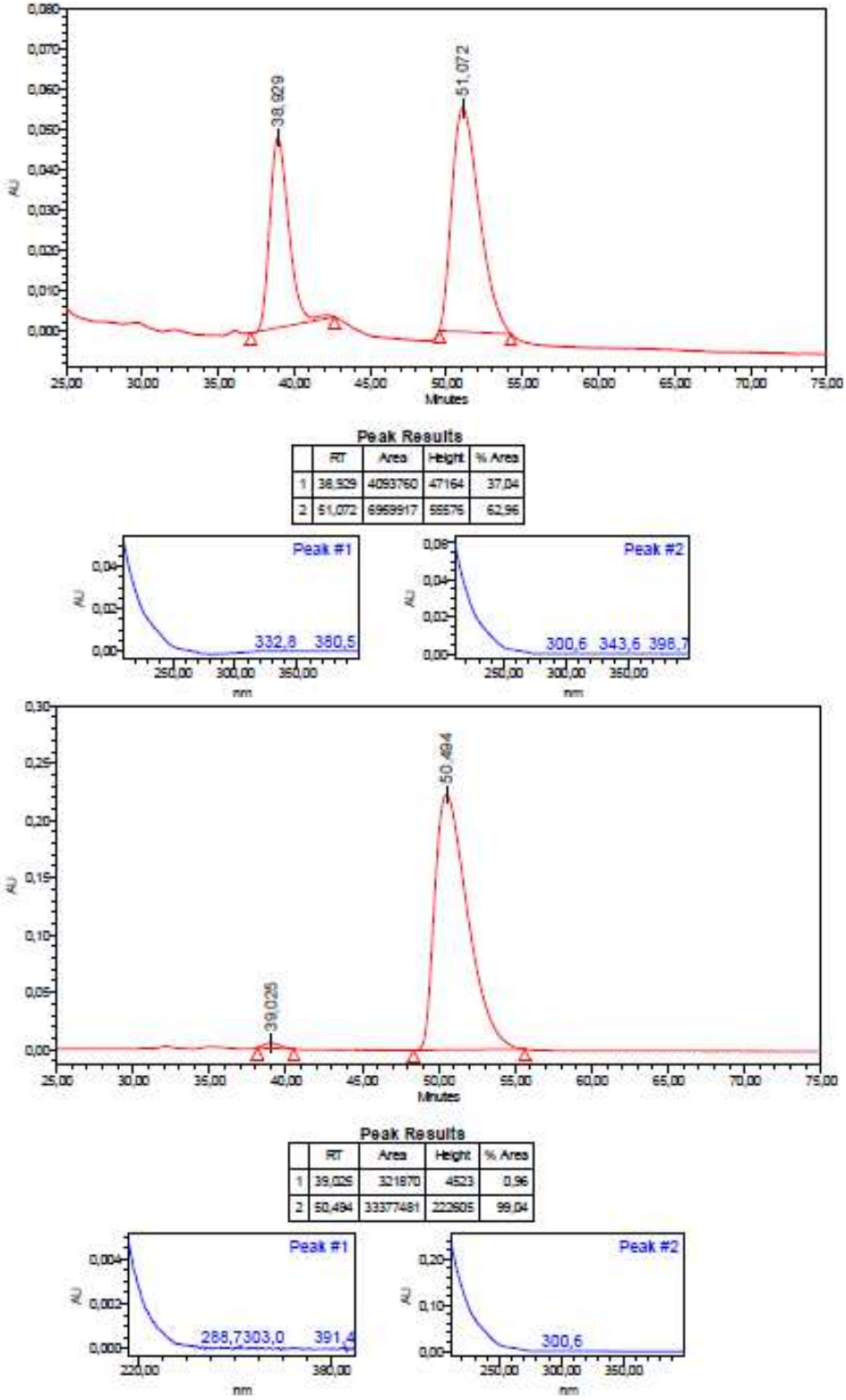
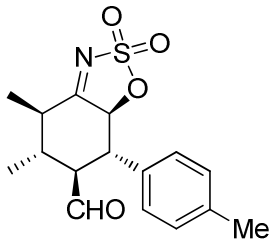


Figure 39: HPLC chromatogram for compounds ***rac*-5a** and **5a**.



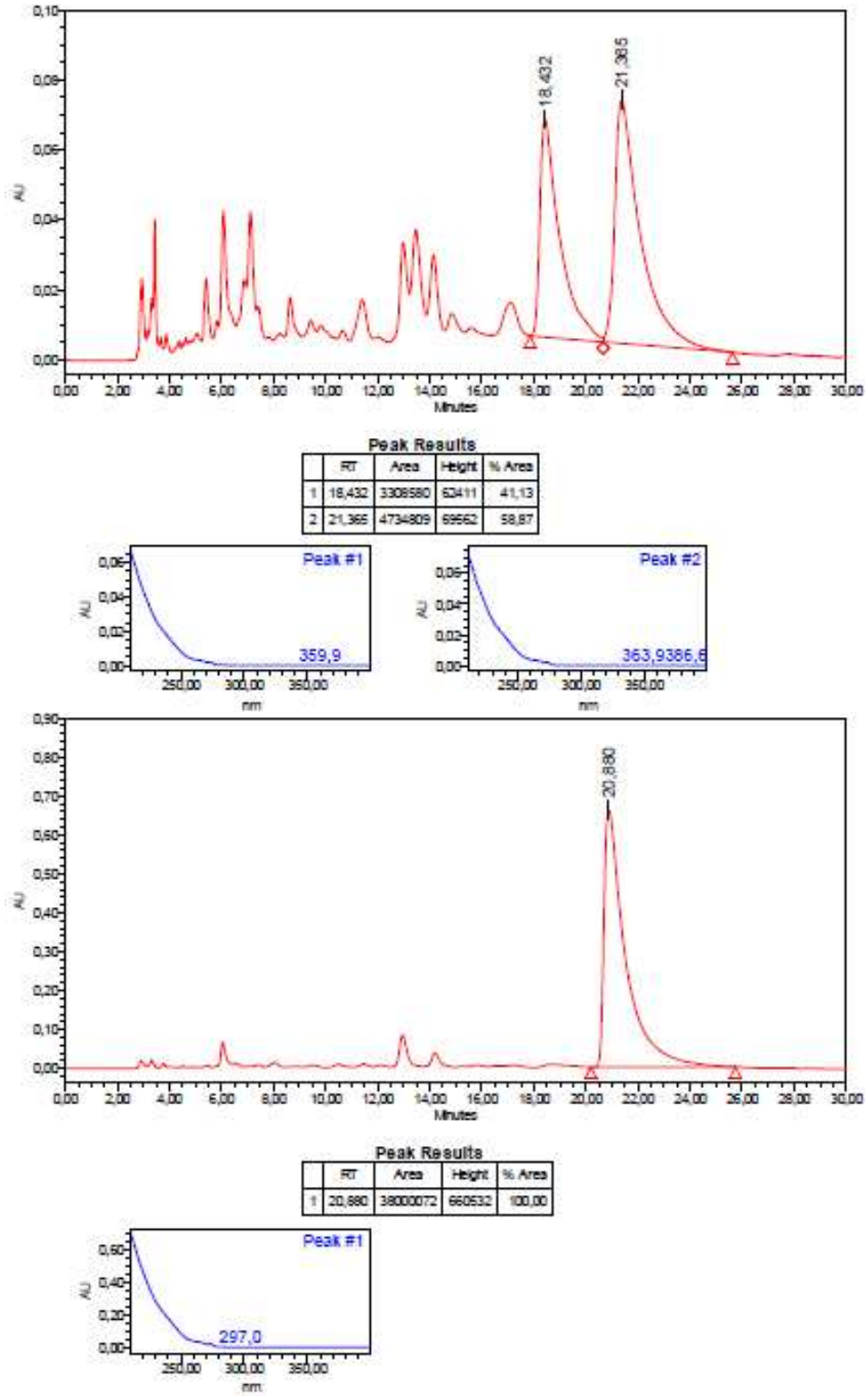
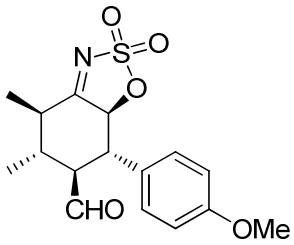
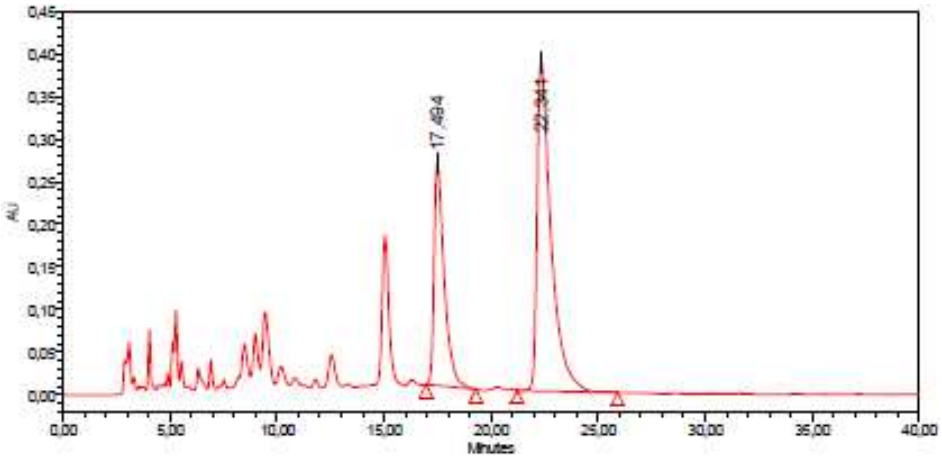


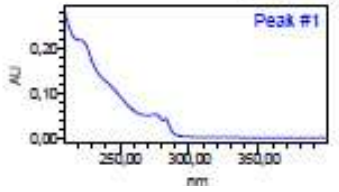
Figure 40: HPLC chromatogram for compounds ***rac*-5b** and **5b**.

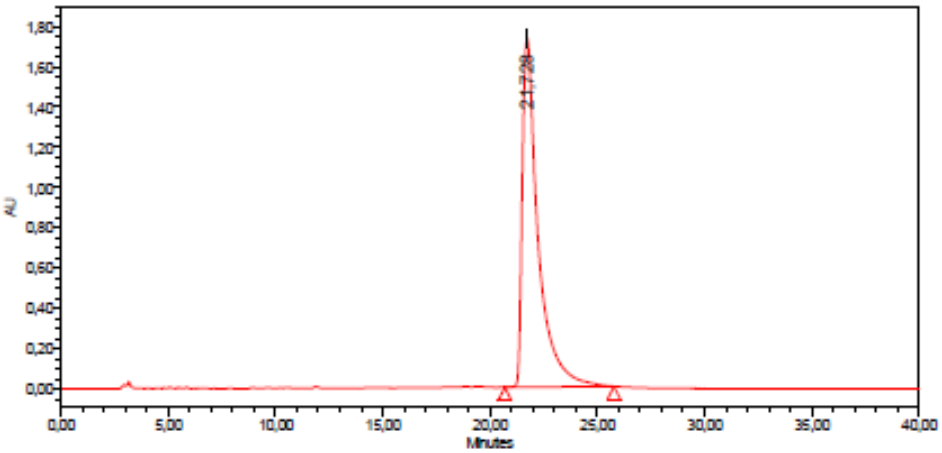




Peak Results

	RT	Area	Height	% Area
1	17,494	8598545	259394	32,82
2	22,341	17597736	385178	67,18





Peak Results

	RT	Area	Height	% Area
1	21,728	88781931	1729052	100,00

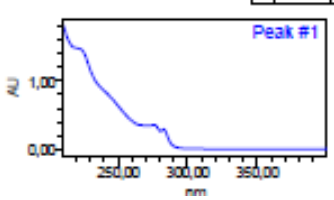
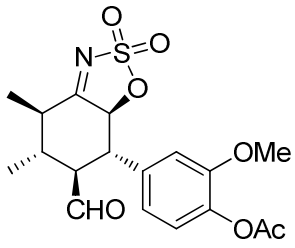
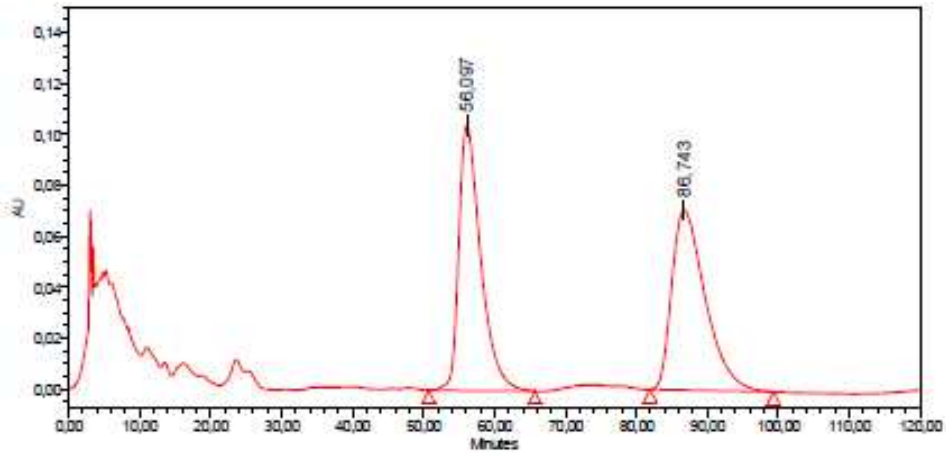


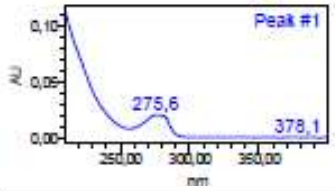
Figure 41: HPLC chromatogram for compounds ***rac*-5c** and **5c**.

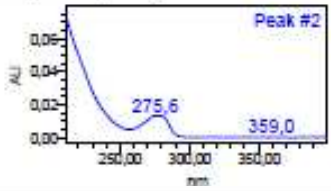


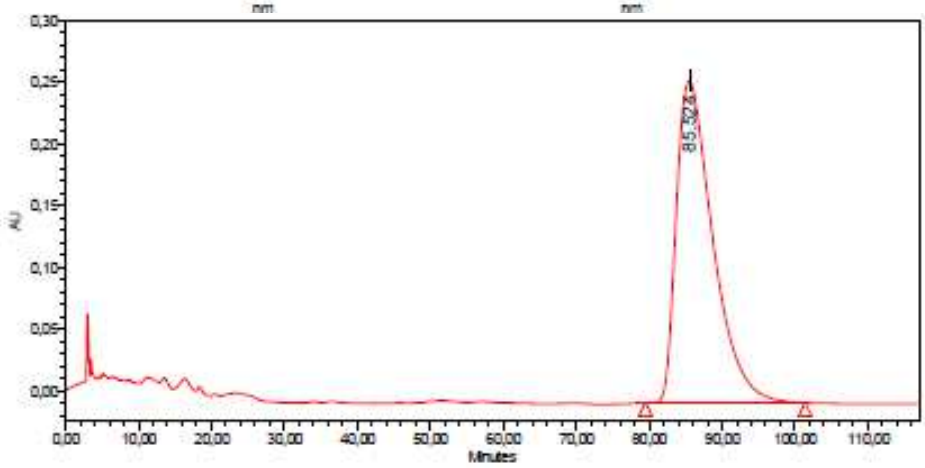


Peak Results

	RT	Area	Height	% Area
1	56,097	22345932	104126	49,05
2	86,743	23214366	70629	50,95







Peak Results

	RT	Area	Height	% Area
1	85,534	90697450	260775	100,00

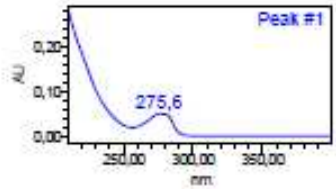


Figure 42: HPLC chromatogram for compounds ***rac*-5d** and **5d**.

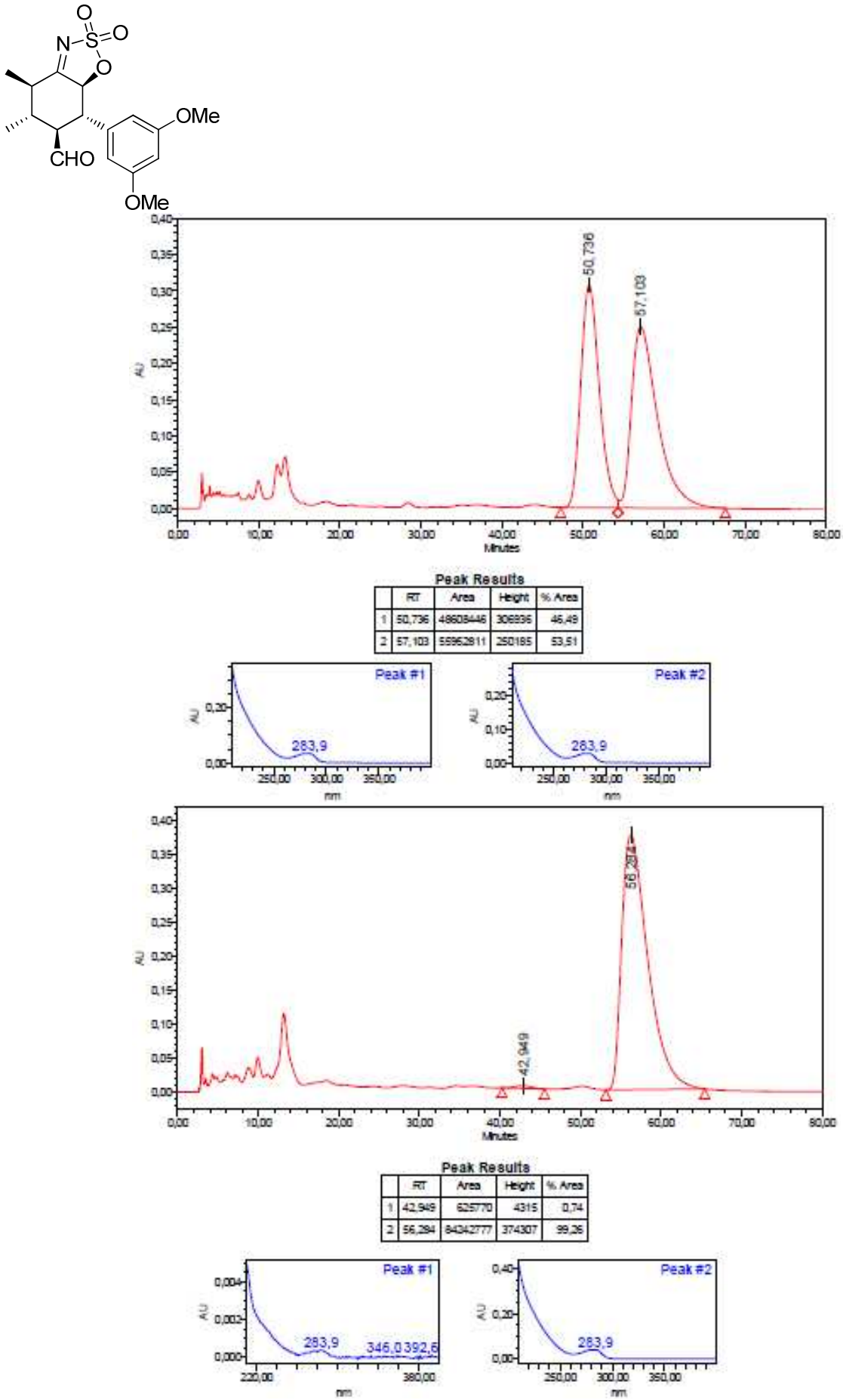
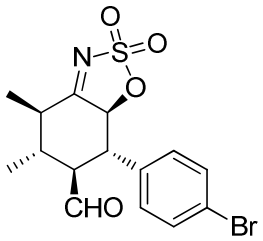
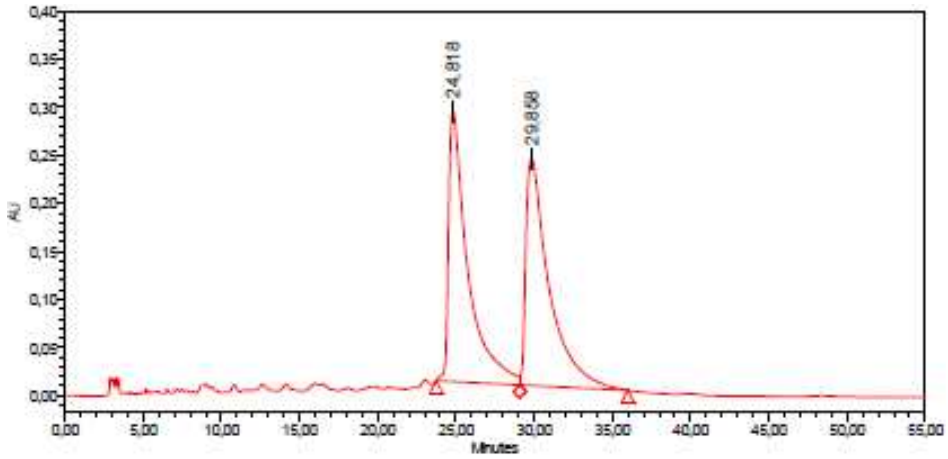


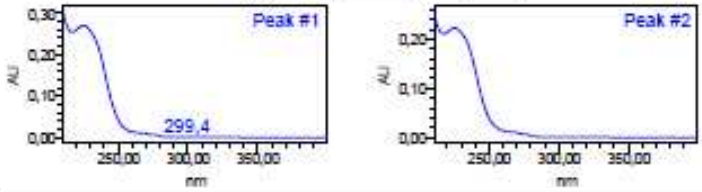
Figure 43: HPLC chromatogram for compounds ***rac*-5e** and **5e**.

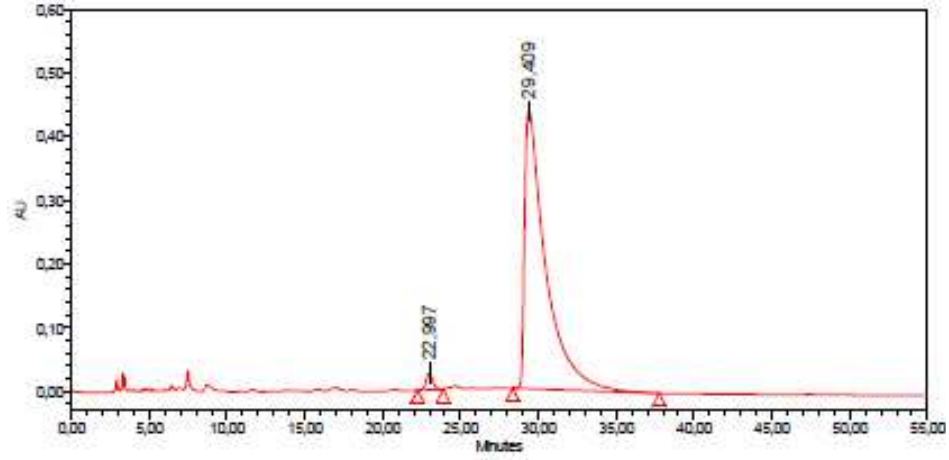




Peak Results

	RT	Area	Height	% Area
1	24,818	23927356	281329	49,62
2	29,858	24298166	236073	50,38





Peak Results

	RT	Area	Height	% Area
1	22,997	774859	25461	1,85
2	29,409	41069774	436562	98,15

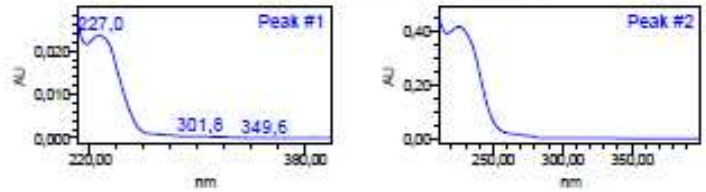


Figure 44: HPLC chromatogram for compounds ***rac*-5f** and **5f**.

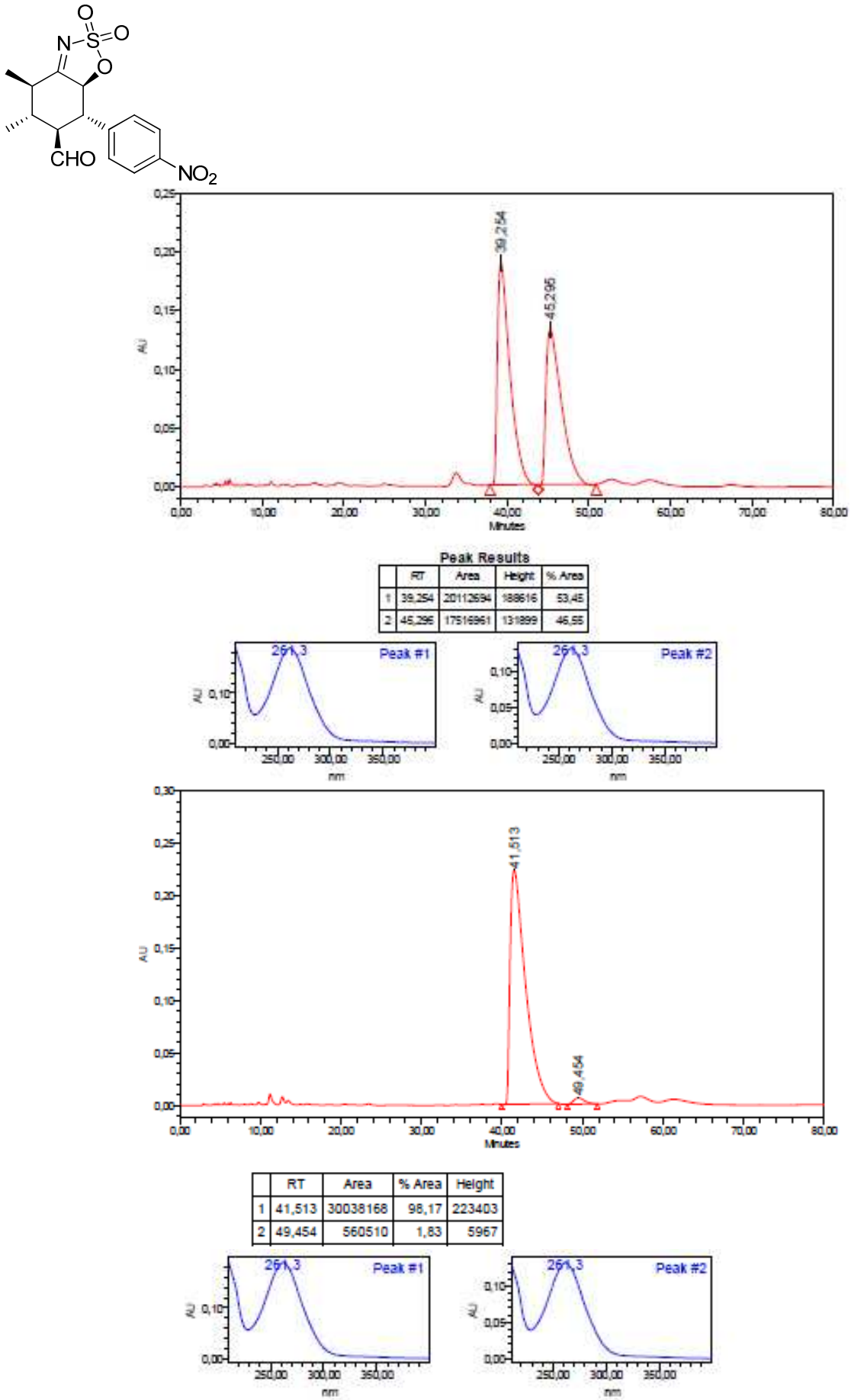
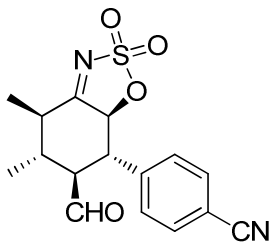
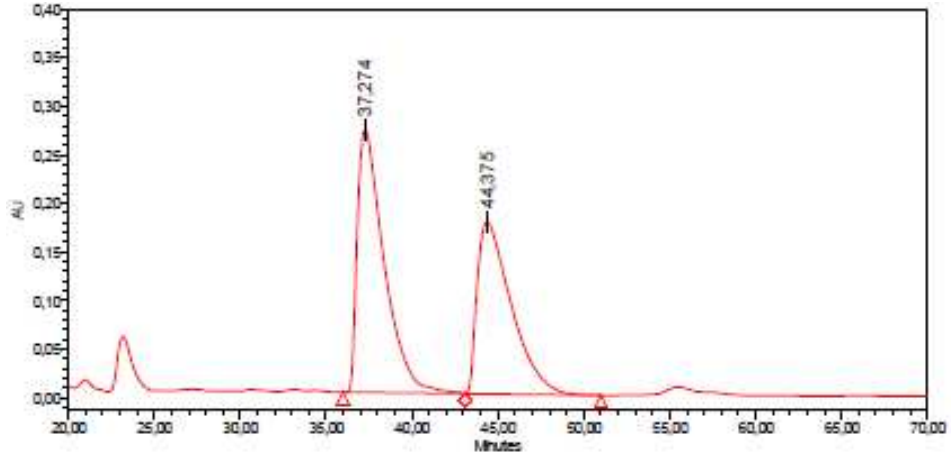


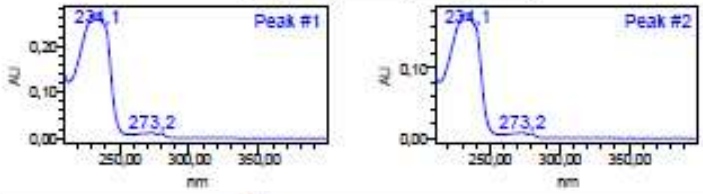
Figure 45: HPLC chromatogram for compounds ***rac*-5g** and **5g**.

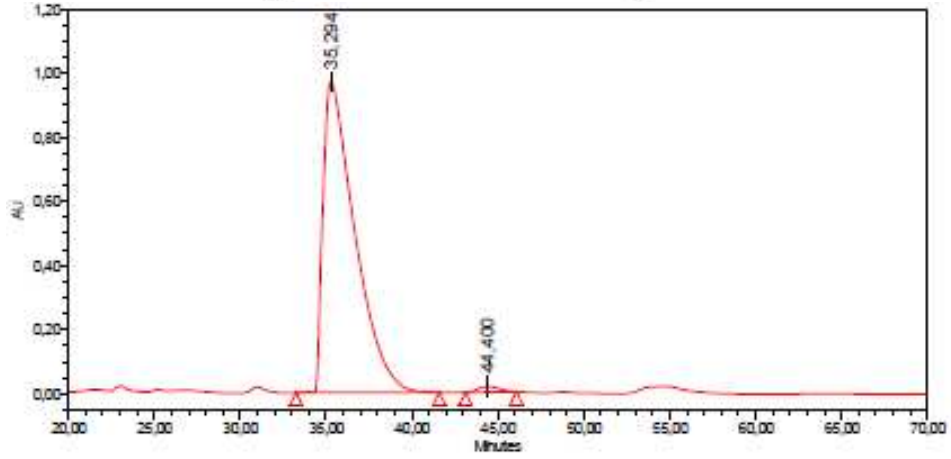




Peak Results

	RT	Area	Height	% Area
1	37,274	29336157	270595	54,50
2	44,375	24485096	177517	45,50





Peak Results

	RT	Area	Height	% Area
1	35,294	134825663	970133	98,79
2	44,400	1532061	17801	1,21

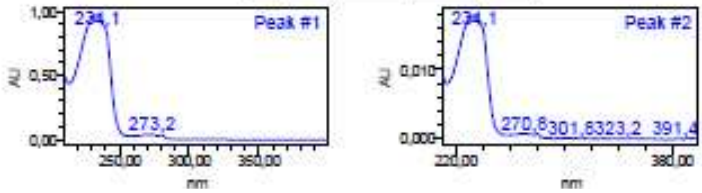


Figure 46: HPLC chromatogram for compounds ***rac*-5h** and **5h**.

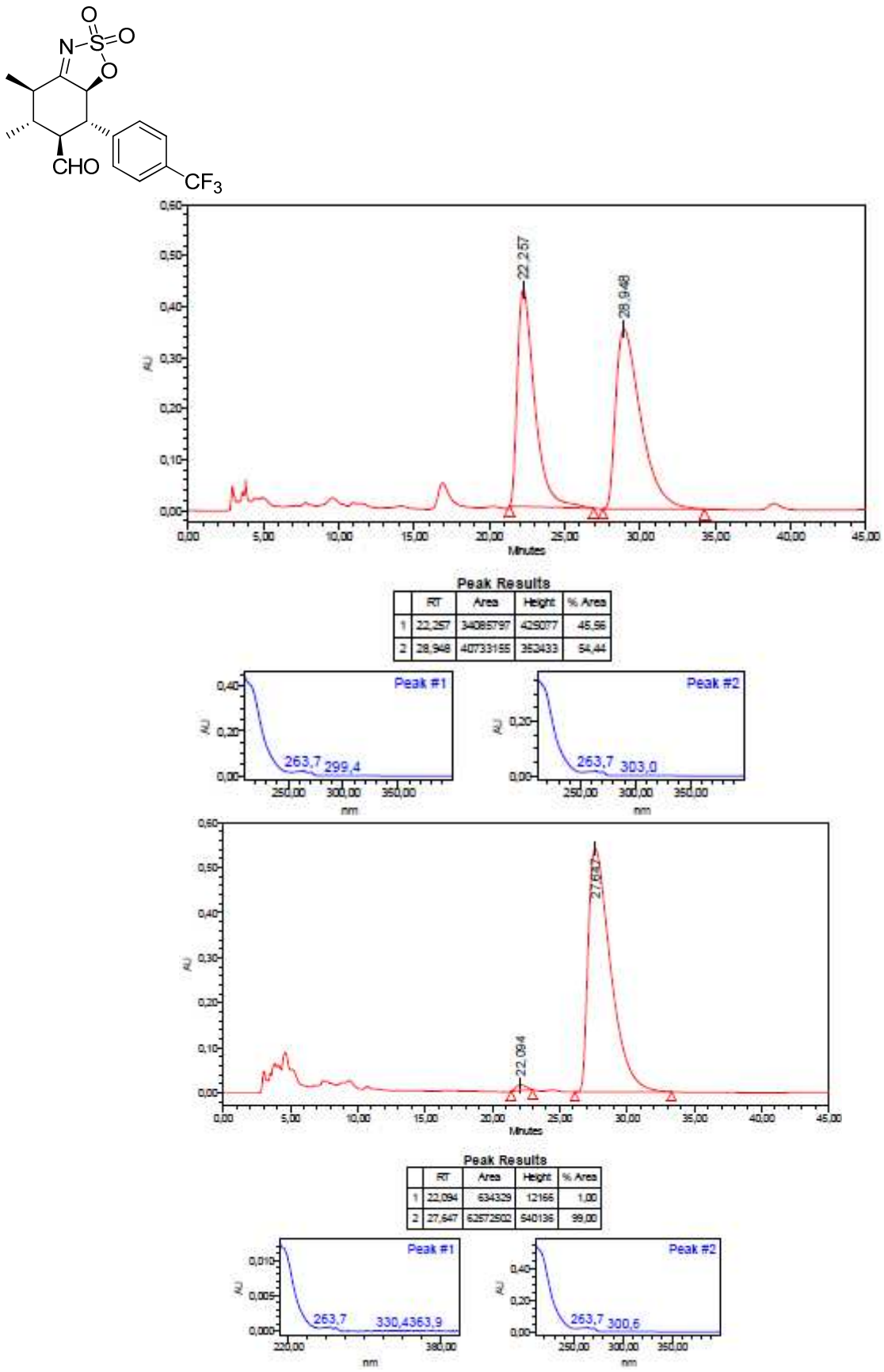
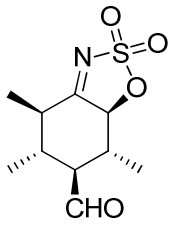


Figure 47: HPLC chromatogram for compounds ***rac*-5i** and **5i**.



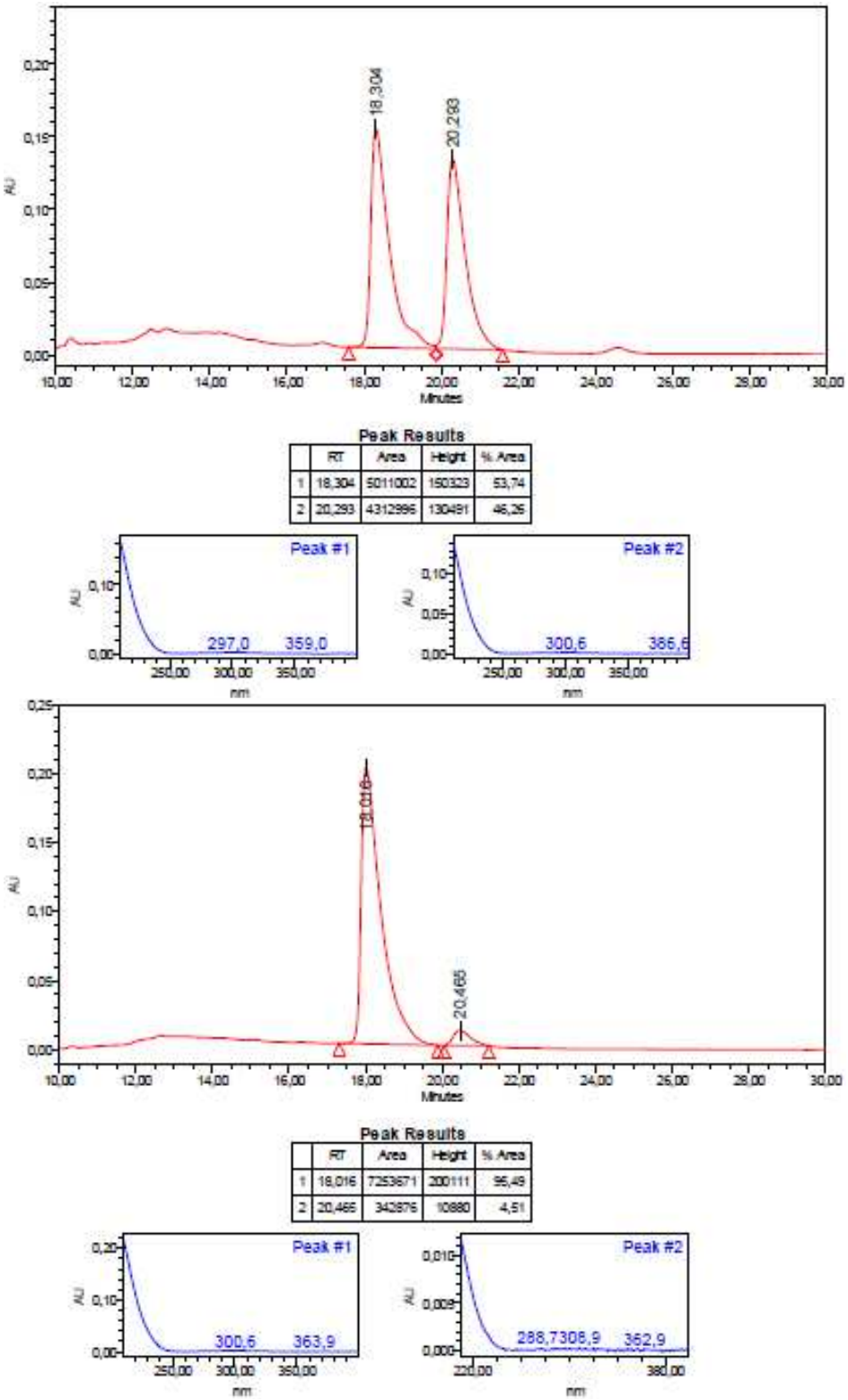
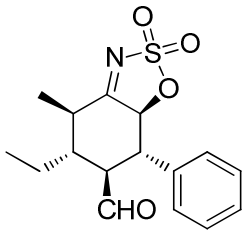
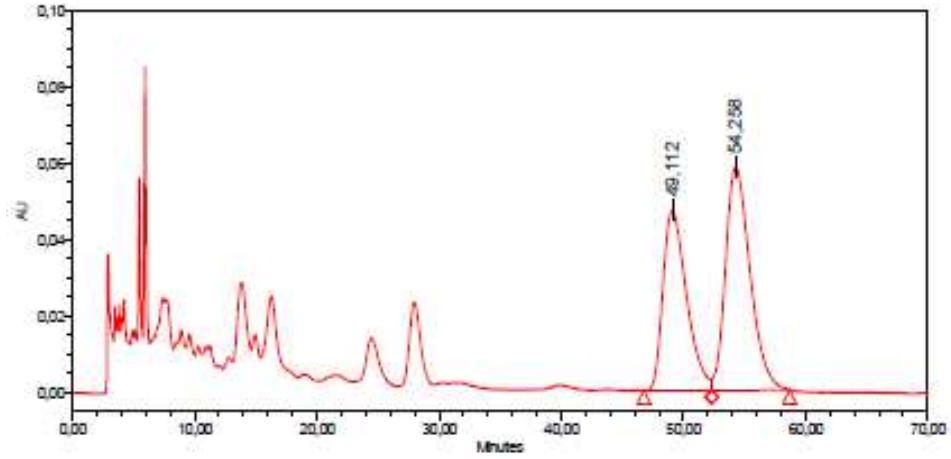


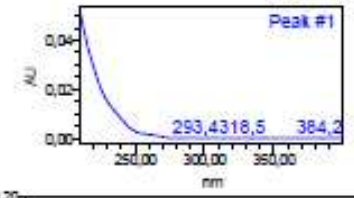
Figure 48: HPLC chromatogram for compounds ***rac*-5j** and **5j**.

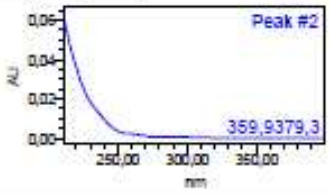


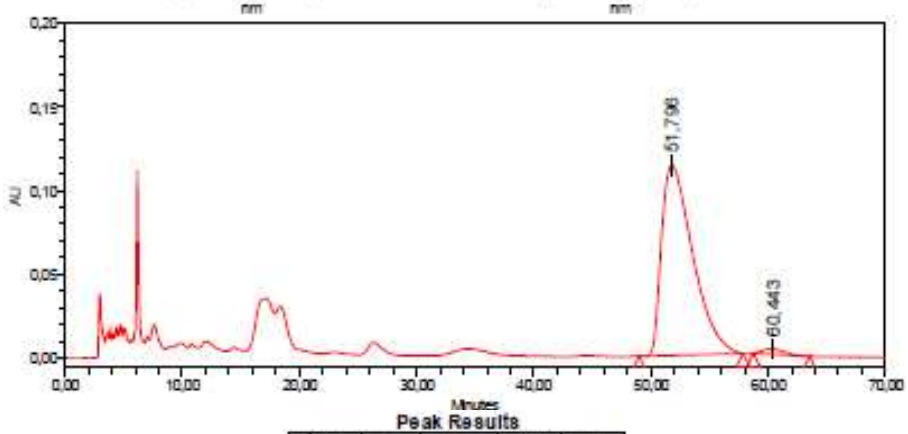


Peak Results

	RT	Area	Height	% Area
1	49,112	6308070	47100	43,54
2	54,258	8180481	58445	56,46



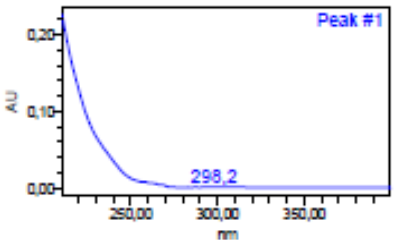




Peak Results

	Name	RT	Area	Height	% Area
1		51,796	21031296	113460	98,05
2		60,443	418660	3261	1,95

Match Plot



Match Plot

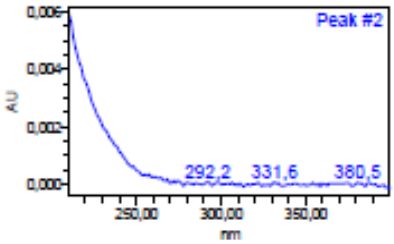
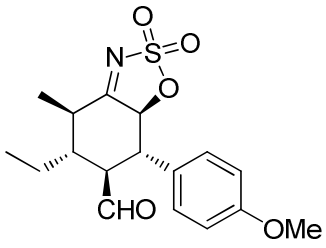
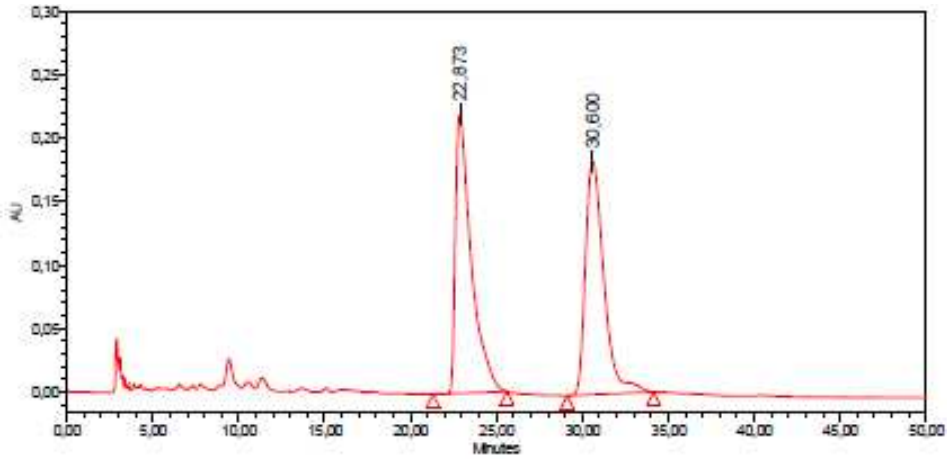


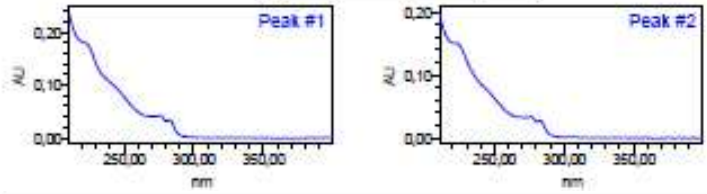
Figure 49: HPLC chromatogram for compounds ***rac*-5k** and **5k**.

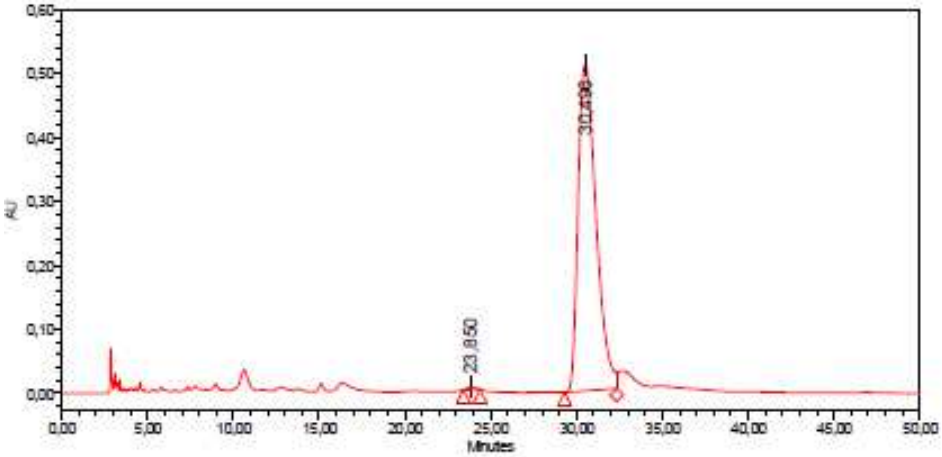




Peak Results

	RT	Area	Height	% Area
1	22,873	14030097	219763	50,61
2	30,600	13693412	183620	49,39





Peak Results

	RT	Area	Height	% Area
1	23,850	138765	4029	0,37
2	30,496	36903502	510027	99,63

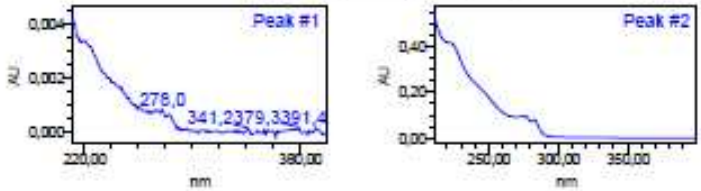


Figure 50: HPLC chromatogram for compounds ***rac*-5l** and **5l**.

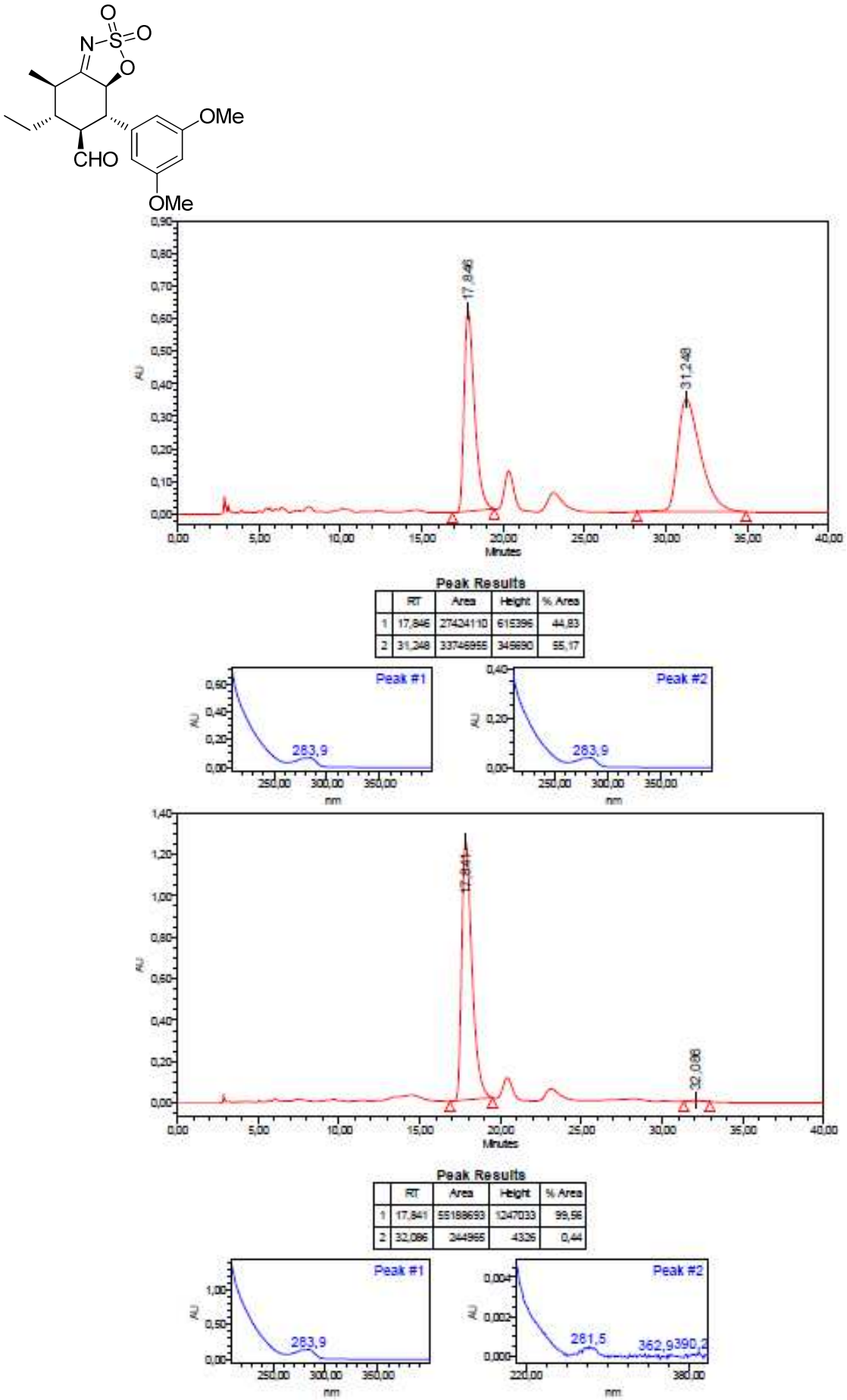
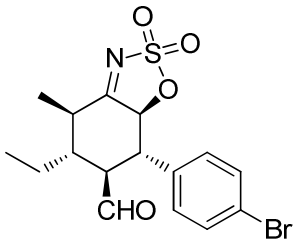
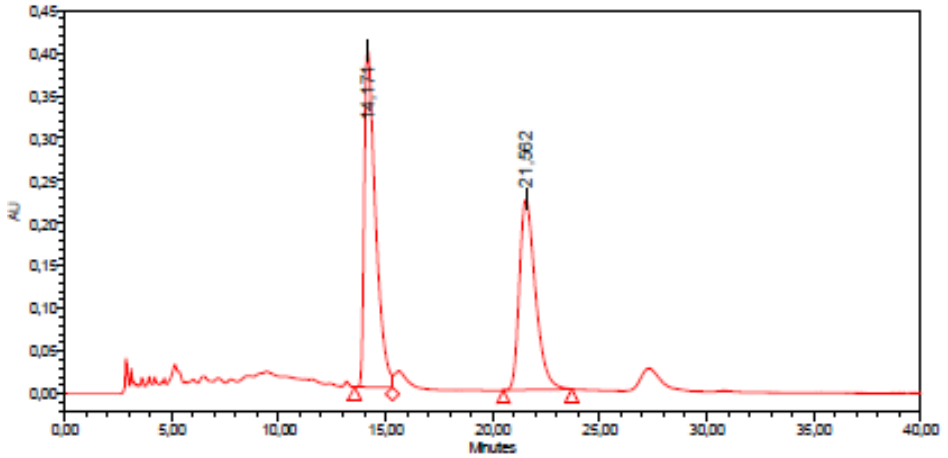


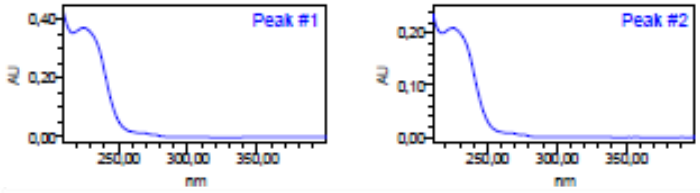
Figure 51: HPLC chromatogram for compounds ***rac*-5m** and **5m**.

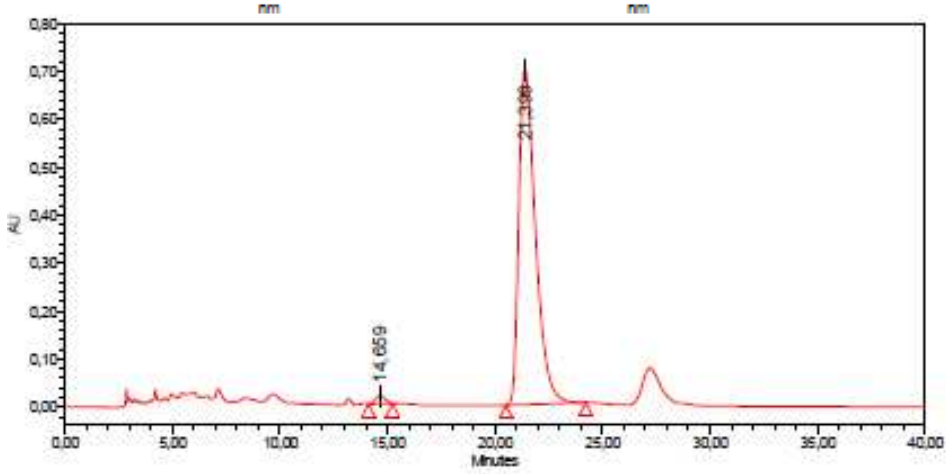




Peak Results

	RT	Area	Height	% Area
1	14,171	14429146	394829	55,31
2	21,562	11660796	223107	44,69





Peak Results

	RT	Area	Height	% Area
1	14,659	533007	17135	1,40
2	21,399	37607284	698724	98,60

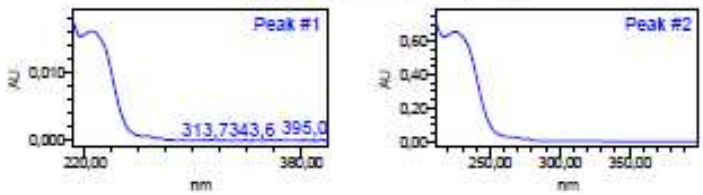
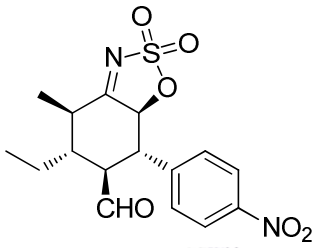
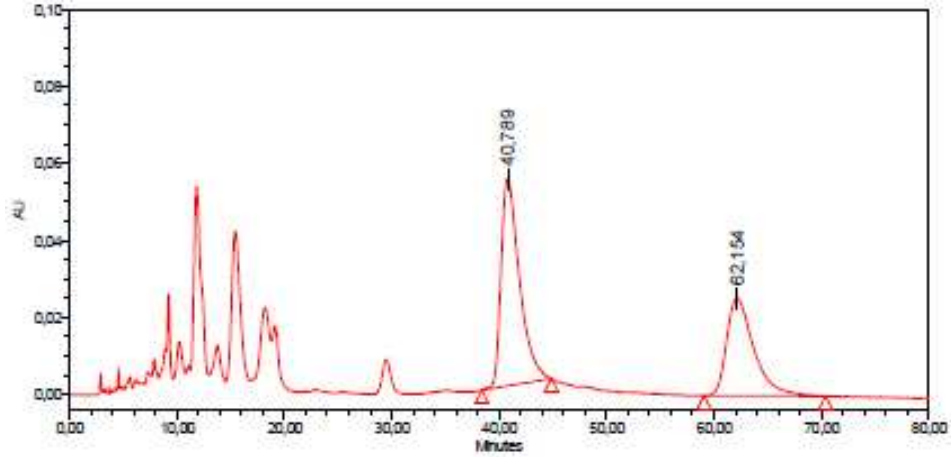


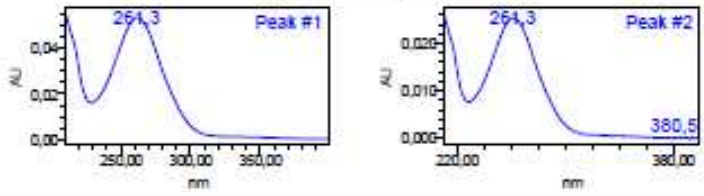
Figure 52: HPLC chromatogram for compounds ***rac*-5n** and **5n**.

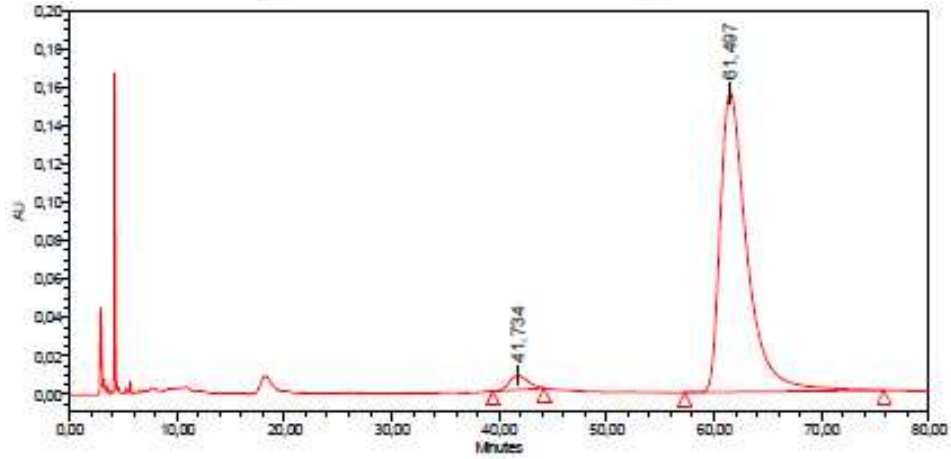




Peak Results

	RT	Area	Height	% Area
1	40,789	6418776	53722	59,01
2	62,154	4458823	26386	40,99





Peak Results

	RT	Area	Height	% Area
1	41,734	890699	7438	3,19
2	61,497	27043713	155971	96,81

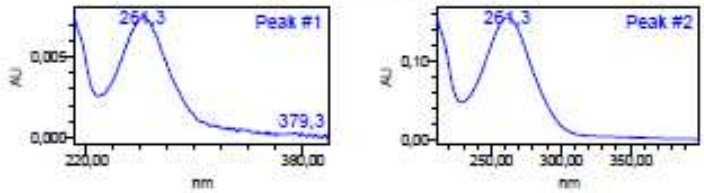
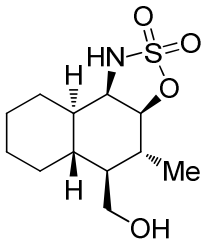
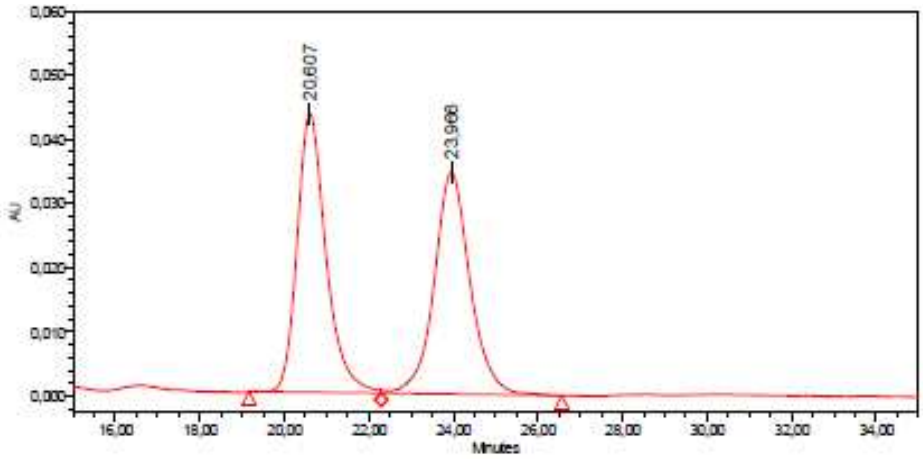


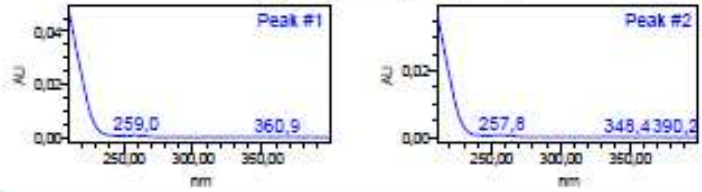
Figure 53: HPLC chromatogram for compounds ***rac*-5o** and **5o**.

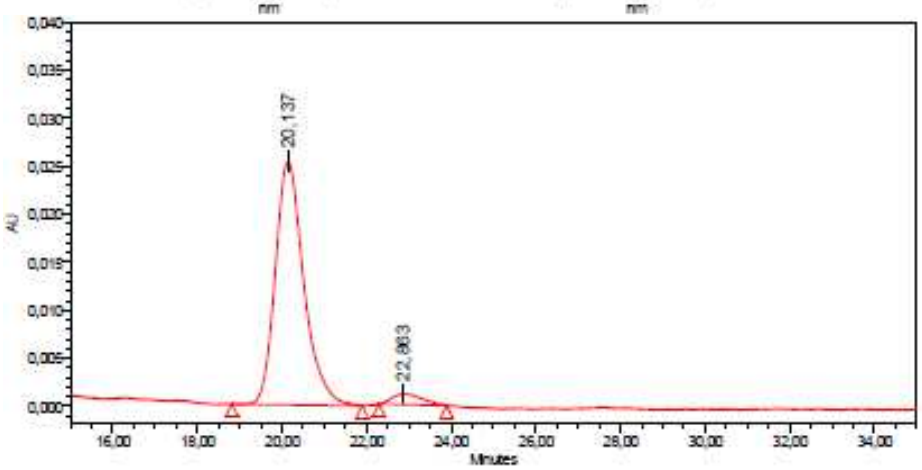




Peak Results

	RT	Area	Height	% Area
1	20,607	2058510	43473	50,18
2	23,966	2043448	34635	49,82





Peak Results

	RT	Area	Height	% Area
1	20,137	1187215	25380	95,55
2	22,863	55304	1137	4,45

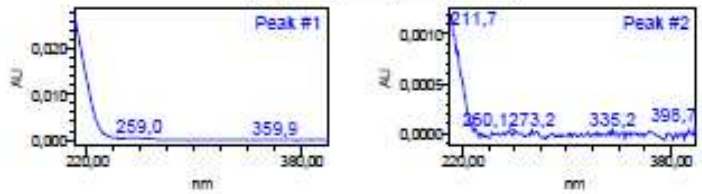


Figure 54: HPLC chromatogram for compounds ***rac*-6** and **6**.