Supplementary Information (SI) for ChemComm.

Supporting information

One-Pot Enantioselective Cyclopropanation Process from Inactivated Aldehydes Mediated by Organocatalysis

Camille Rocq and Sylvain Canesi*

Laboratoire de Méthodologie et Synthèse de Produit Naturels Université du Québec à Montréal, C.P.8888, Succ. Centre-Ville, Montréal. H3C 3P8, Québec, Canada.

**E-mail: canesi.sylvain@uqam.ca*

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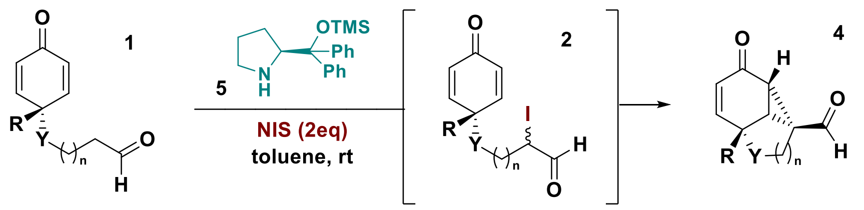
I. General Information

Reaction methods: unless otherwise stated, non-aqueous reactions were performed in dried glassware under positive argon pressure. Reaction vessels were equipped with a magnetic stirrer bar. Air- and moisture-sensitive liquids were transferred via syringe or cannula through rubber septa using standard techniques. Solids were either added under an inert gas flow or dissolved in an appropriate solvent before being treated as liquids. Solvents used in reactions were dried using an LC Technical SP-1 solvent purification system. Solvents used for extraction and purification by flash column chromatography were used as received. Flash column chromatography was performed using the indicated solvent system (v/v%) and CLS ZEOPrep HYD 40–63 µm silica gel. Reactions performed at ambient temperature were conducted without heating or cooling, at an ambient temperature typically of 23 °C, depending on weather conditions (ca. 18–28 °C). Reagents were purchased from commercial sources and used as received, unless otherwise noted. Concentration under reduced pressure (in vacuo) was performed by rotary evaporation (bath temperature 40–60 °C). Reactions were monitored by thin-layer chromatography.

Characterization: TLC plates were visualised using UV fluorescence quenching (with a source of either 254 or 360 nm) followed by staining with either Hannessian's stain or $KMnO_4$ stain and heating. Optical rotation was measured using a Jasco P-1010 automatic polarimeter with the Na-D line (589 nm), with the concentration (c) of the solution expressed in g/100 mL at room temperature. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{19}F NMR (282 MHz) nuclear magnetic resonance spectra were determined on a Bruker Ultrashield spectrometer at room temperature. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm) downfield from tetramethylsilane (δ) as the internal standard, with coupling constants expressed in hertz (Hz). The following abbreviations are used to indicate spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Chemical shifts for ^{13}C NMR are reported in ppm relative to the centre of a triplet at 77.16 ppm for deuteriochloroform. Some spectra include minor impurities of water, solvent and grease, which do not affect the assignments. Accurate mass measurements were performed on a LC-TOF 6224 instrument from Agilent technologies with electrospray ionization. Aliquots of 0.1 uL were injected into the mass spectrometer using a 0.5 mL/min flow of 50% methanol/ 50% water mixture. The capillary voltage was set at 3000 V and mass spectra were acquired from 100 to 3000 m/z. Protonated molecular ions $[M+H]^+$ were used for accurate mass calculation in positive mode. Enantiomeric excess values were determined by SFC using a WHELK-O1 column, eluting with CO_2 and EtOH (flow rate = 3mL/min, λ = 210 nm).

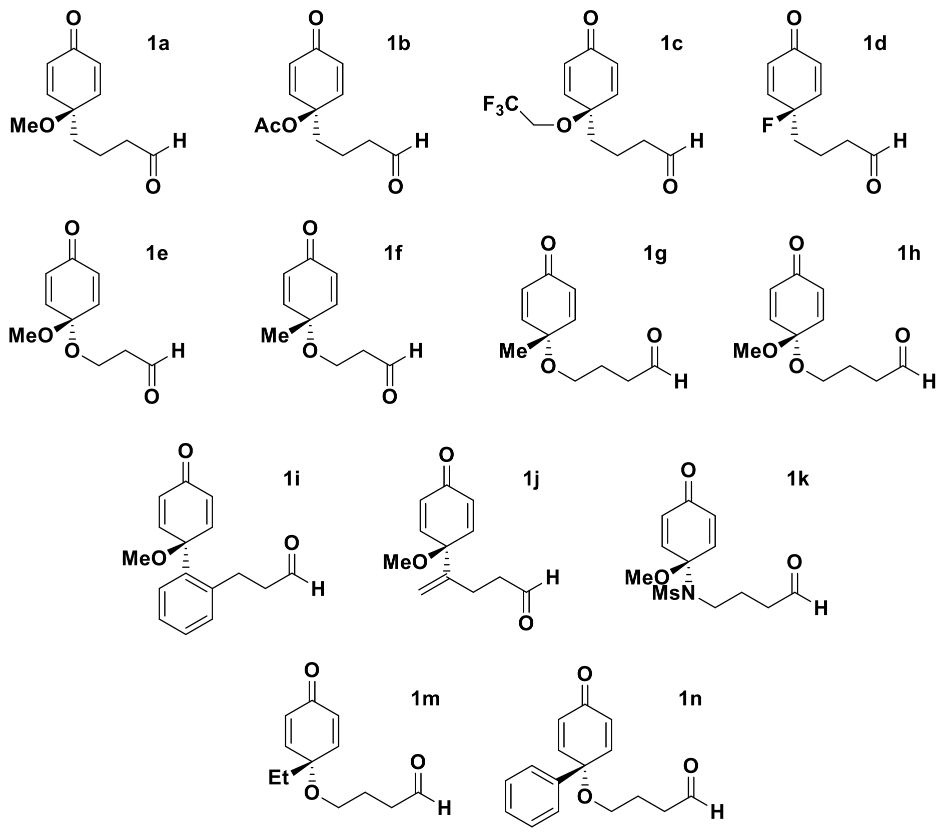
II. Experimental procedures and characterization

General procedure for organocatalytic enantioselective cyclopropanation



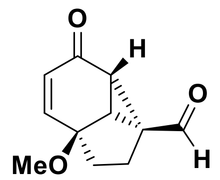
To a solution of aldehyde **1** (1 equiv.) in dry toluene (0.05 M) under argon, were added subsequently N-iodosuccinimide (2equiv.) and organocatalyst **(S)-5** (20 mol%) at room temperature. The resulting mixture was stirred between 8 hours and 5 days (monitored by NMR analysis). Once complete, an aqueous saturated ammonium chloride was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by silica gel chromatography to obtain product **4**.

Structures of dienone precursors (1a – 1n)



All dienone precursors are prepared according to procedures described by Gaunt[1] and Rovis[2].

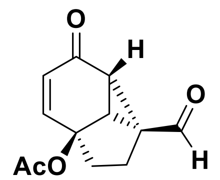
(2aS,2a[1]S,2bS,5aS)-5a-methoxy-3-oxo-1,2,2a[1],2b,3,5a-hexahydro-2aH-cyclopropa[cd]indene-2a-carbaldehyde **(+)-4a:**



Starting from dienone **1a** (20 mg, 0.103 mmol), the reaction was stirred overnight. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 70:30) afforded cyclopropane **4a** as a colorless oil (15 mg, 76% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 6.78 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.21 (dd, *J* = 10.4, 1.2 Hz, 1H), 3.44 (s, 3H), 2.88 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.72 (m, 2H), 2.55 (m, 1H), 1.99 – 1.90 (dd, *J* = 12.3, 5.5 Hz, 1H), 1.35 (ddd, *J* = 14.3, 12.3, 5.8 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 191.1, 151.3, 130.6, 82.3, 54.9, 49.6, 49.0, 40.6, 36.9, 18.7.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 6.5 min, t_R (minor) = 8.2 min, 99% ee.
$[\alpha]_D$ ^{21} = +54.8 (*c* 0.13, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{11}H_{12}O_3$ $(M+H)^+$: 193.0859; found: 193.0861.

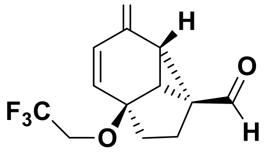
(2aS,2a[1]S,2bS,5aS)-2a-formyl-3-oxo-1,2,2a,2a[1],2b,3-hexahydro-5aH-cyclopropa[cd]inden-5a-yl acetate **(+)-4b**:



Starting from dienone **1b** (28 mg, 0.126 mmol), the reaction was stirred for 8 hours. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 70:30) afforded cyclopropane **4b** as a colorless oil (19 mg, 69% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (s, 1H), 6.71 (dd, *J* = 10.4, 1.3 Hz, 1H), 6.08 (dd, *J* = 10.4, 1.1 Hz, 1H), 2.96 (dd, *J* = 8.7, 1.3 Hz, 1H), 2.86 – 2.58 (m, 3H), 2.14 (s, 3H), 2.10 (m, 1H), 1.34 (ddd, *J* = 14.4, 12.5, 5.4 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 190.5, 170.3, 149.5, 127.3, 80.6, 49.7, 48.4, 42.6, 35.9, 21.2, 17.9.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 7.1 min, t_R (minor) = 9.1 min, >99% ee.
$[\alpha]_D$ ^{21} = +100.9 (*c* 1.0, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{12}H_{12}O_4$ $(M+H)^+$: 243.0628; found: 243.0621.

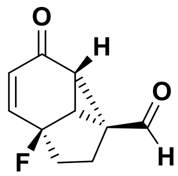
(2aS,2a1S,2bS,5aS)-3-oxo-5a-(2,2,2-trifluoroethoxy)-1,2,2a1,2b,3,5a-hexahydro-2aH-cyclopropa[cd] indene-2a-carbaldehyde **(+)-4c:**



Starting from dienone **1c** (20 mg, 0.076 mmol), the reaction was stirred for 10 hours. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 80:20) afforded cyclopropane **4c** as a colorless oil (15 mg, 76% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 6.74 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.24 (dd, *J* = 10.4, 1.2 Hz, 1H), 3.95 (q, *J* = 8.3 Hz, 2H), 2.85 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.81 – 2.58 (m, 3H), 2.03 (ddd, *J* = 12.2, 6.1, 1.3 Hz, 1H), 1.46 – 1.29 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) 195.8, 190.1, 148.7, 131.3, 123.4 (q, *J* = 277.6 Hz), 83.0, 65.3 (q, *J* = 35.1 Hz), 49.5, 49.0, 40.6, 36.6, 18.8.
^{19}F NMR (282 MHz, $CDCl_3$) δ-74.28 (t, *J* = 8.4 Hz).
SFC: WHELK-O1 column (CO_2/MeOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 4.0 min, t_R (minor) = 5.1 min, 93% ee.
$[\alpha]_D$ ^{21} = +22.5 (*c* 1.0, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{12}H_{11}F_3O_3$ $(M+H)^+$: 261.0733; found: 261.0740.

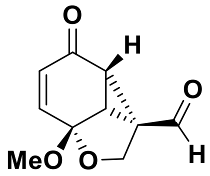
(2aR,2a1S,2bS,5aS)-5a-fluoro-3-oxo-1,2,2a1,2b,3,5a-hexahydro-2aH-cyclopropa[cd]indene-2a-carbaldehyde **(-)-4d**:



Starting from dienone **1d** (20 mg, 0.110 mmol), the reaction was stirred for 2 days. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 80:20) afforded cyclopropane **4d** as a colorless oil (13 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 6.89 (td, *J* = 10.3, 1.4 Hz, 1H), 6.11 (dd, *J* = 10.3, 1.1 Hz, 1H), 3.10 (ddd, *J* = 13.2, 8.6, 1.4 Hz, 1H), 2.89 – 2.61 (m, 3H), 2.17 (dd, *J* = 11.8, 6.0 Hz, 1H), 1.38 – 1.19 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 190.3, 146.9 (d, *J* = 31.9 Hz), 128.8, 95.3 (d, *J* = 189.5 Hz), 49.4, 48.4 (d, *J* = 24.2 Hz), 41.7 (d, *J* = 34.6 Hz), 35.2 (d, *J* = 3.0 Hz), 18.2 (d, *J* = 8.7 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ-139.24 – 158.98 (m)
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 3.5 min, t_R (minor) = 4.1 min, 90% ee.
$[\alpha]_D$ ^{21} = -16.5 (*c* 0.17, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{10}H_9FO_2$ $(M+H)^+$: 181.0659; found: 181.0660.

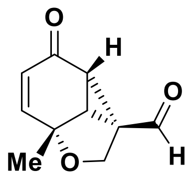
(2aR,2a1S,2bS,5aR)-5a-methoxy-3-oxo-2a1,2b,3,5a-tetrahydrocyclopropa[cd]benzofuran-2a(2H)-carbaldehyde **(-)-4e:**



Starting from dienone **1e** (20 mg, 0.102 mmol), the reaction was stirred for 4 days. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 75:25) afforded cyclopropane **4e** as a colorless oil (11 mg, 56% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (s, 1H), 6.60 (dd, *J* = 10.3, 1.1 Hz, 1H), 6.14 (dd, *J* = 10.3, 1.3 Hz, 1H), 4.83 (dd, *J* = 10.7, 0.7 Hz, 1H), 3.55 (s, 3H), 3.47 (d, *J* = 10.7 Hz, 1H), 3.22 (dd, *J* = 8.2, 1.1 Hz, 1H), 2.90 (ddd, *J* = 8.2, 1.3, 0.7 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 190.3, 143.6, 129.0, 102.7, 61.6, 53.3, 50.4, 38.3, 36.3.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 2.7 min, t_R (minor) = 3.1 min, >99% ee.
$[\alpha]_D$ ^{21} = -14.9 (*c* 0.4, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{16}H_{14}O_3$ $(M+H)^+$: 255.1016; found: 255.1021.

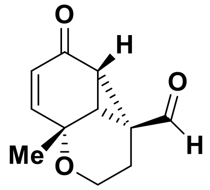
(2aS,2a1S,2bS,5aR)-5a-methyl-3-oxo-2a1,2b,3,5a-tetrahydrocyclopropa[cd]benzofuran-2a(2H)-carbaldehyde **(-)-4f**:



Starting from dienone **1f** (20 mg, 0.111 mmol), the reaction was stirred for 3 days. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 80:20) afforded cyclopropane **4f** as a colorless oil (13 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.12 (s, 1H), 6.35 (dd, *J* = 10.2, 0.9 Hz, 1H), 6.16 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.70 (d, *J* = 10.9 Hz, 1H), 3.52 (d, *J* = 10.9 Hz, 1H), 2.93 (dd, *J* = 7.7, 0.9 Hz, 1H), 2.86 (dd, *J* = 7.7, 1.2 Hz, 1H), 1.65 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 190.7, 145.3, 128.9, 76.9, 62.8, 55.6, 43.3, 38.9, 25.1.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 2.9 min, t_R (minor) = 3.2 min, 99% ee.
$[\alpha]_D$ ^{21} = -46.9 (*c* 0.9, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{10}H_{10}O_3$ $(M+H)^+$: 179.0703; found: 179.0693.

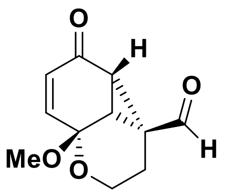
(3aS,3a1S,3bS,6aR)-6a-methyl-4-oxo-2,3,3a1,3b,4,6a-hexahydro-3aH-cyclopropa[de]chromene-3a-carbaldehyde **(+)-4g:**



Starting from dienone **1g** (15 mg, 0.077 mmol), the reaction was stirred for 5 days. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 80:20) afforded cyclopropane **4g** as a colorless oil (7 mg, 47% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.79 (s, 1H), 6.41 (dd, *J* = 10.2, 1.3 Hz, 1H), 6.05 (dd, *J* = 10.2, 1.3 Hz, 1H), 3.70 (m, 1H), 3.54 (m, 1H), 2.70 (m, 1H), 2.39 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.09 (dd, *J* = 8.2, 1.3 Hz, 1H), 1.57 (s, 3H), 1.64 – 1.49 (m, 1H).
^{13}C NMR (75 MHz, CDCl$_3$) δ 197.3, 191.6, 151.6, 129.7, 65.4, 58.8, 35.5, 30.2, 29.4, 27.4, 14.5.
SFC: WHELK-O1 column (CO_2/MeOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (minor) = 4.6 min, t_R (major) = 5.7 min, 97% ee.
$[\alpha]_D$ ^{21} = +20.3 (*c* 0.4, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{11}H_{12}O_3$ $(M+H)^+$: 193.0859; found: 193.0859.

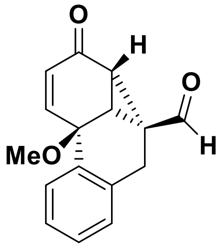
(3aR,3a1S,3bS,6aR)-6a-methoxy-4-oxo-2,3,3a1,3b,4,6a-hexahydro-3aH-cyclopropa[de]chromene-3a-carbaldehyde **(-)-4h**:



Starting from dienone **1h** (20 mg, 0.095 mmol), the reaction was stirred overnight. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 75:25) afforded cyclopropane **4h** as a colorless oil (8 mg, 41% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.85 (s, 1H), 6.59 (dd, *J* = 10.3, 1.5 Hz, 1H), 6.14 (dd, *J* = 10.3, 1.2 Hz, 1H), 3.90 – 3.65 (m, 2H), 3.49 (s, 3H), 2.70 (m, 1H), 2.47 (dd, *J* = 8.6, 1.2 Hz, 1H), 2.38 (dd, *J* = 8.6, 1.5 Hz, 1H), 1.62 – 1.47 (m, 1H).
^{13}C NMR (75 MHz, CDCl$_3$) δ 196.5, 190.9, 146.4, 129.8, 91.6, 61.5, 49.6, 37.2, 28.9, 24.8, 16.0.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 3.5 min, t_R (minor) = 5.0 min, >99% ee.
$[\alpha]_D$ ^{21} = -12.4 (*c* 0.15, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{11}H_{12}O_4$ $(M+H)^+$: 209.0808; found: 209.0815.

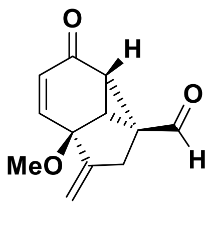
(3aS,3a1S,3bS,8bS)-8b-methoxy-3-oxo-3a,3a1,4,8b-tetrahydrocyclopropa[jk]phenanthrene-3b(3H)-carbaldehyde **(-)-4i:**



Starting from dienone **2i** (50 mg, 0.195 mmol), the reaction was stirred for 3 days. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10) afforded cyclopropane **4i** as a colorless oil (20 mg, 41% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.17 (m, 3H), 6.28 – 6.03 (m, 2H), 3.85 (d, *J* = 16.9 Hz, 1H), 3.59 (d, *J* = 0.7 Hz, 3H), 2.72 (d, *J* = 8.0, 0.9 Hz, 1H), 2.45 (dd, *J* = 8.0, 1.9 Hz, 1H), 2.13 (d, *J* = 16.8 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.5, 190.9, 147.2, 137.3, 136.5, 129.1, 128.6, 128.1, 128.0, 124.4, 72.3, 52.4, 40.2, 32.7, 32.2, 22.8.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 5.4 min, t_R (minor) = 6.4 min, 95% ee.
$[\alpha]_D$ ^{21} = -229.7 (*c* 0.95, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{16}H_{14}O_3$ $(M+H)^+$: 255.1016; found: 255.1020.

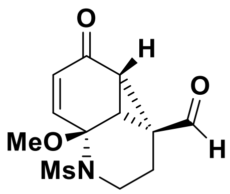
(2aS,2a1S,2bS,5aS)-5a-methoxy-1-methylene-3-oxo-1,2,2a1,2b,3,5a-hexahydro-2aH-cyclopropa[cd] indene-2a-carbaldehyde **(-)-4j**:



Starting from dienone **1j** (20 mg, 0.097 mmol), the reaction was stirred overnight. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 75:25) afforded cyclopropane **4j** as a colorless oil (10 mg, 51% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (s, 1H), 6.59 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.06 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.11 (dd, *J* = 2.9, 1.3 Hz, 1H), 4.99 (dd, *J* = 2.5, 1.3 Hz, 1H), 3.50 (s, 3H), 3.43 – 3.29 (m, 1H), 2.96 (dd, *J* = 8.4, 1.4 Hz, 1H), 2.78 (dt, *J* = 8.4, 0.8 Hz, 1H), 2.19 (dt, *J* = 17.7, 2.7 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 190.6, 155.4, 151.00, 128.1, 108.7, 81.6, 53.7, 45.4, 38.9, 35.3, 25.8.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 5.5 min, t_R (minor) = 6.7 min, >99% ee.
$[\alpha]_D$ ^{21} = -228.7 (*c* 0.35, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{12}H_{12}O_3$ $(M+H)^+$: 205.0859; found: 205.0851.

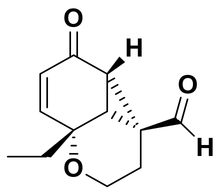
(3aS,3a[1]S,3bS,6aS)-6a-methoxy-1-(methylsulfonyl)-4-oxo-2,3,3a[1],3b,4,6a-hexahydrocyclopropa[de]quinoline-3a(1H)-carbaldehyde **(-)-4k:**



Starting from dienone **1k** (20 mg, 0.070 mmol), the reaction was stirred for 2 days. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 80:20 to 50:50) afforded cyclopropane **4k** as a colorless oil (11 mg, 55% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.34 – 7.23 (m, 1H), 6.20 (dd, *J* = 10.5, 1.3 Hz, 1H), 3.87 (dt, *J* = 11.9, 4.2 Hz, 1H), 3.49 (s, 3H), 3.35 – 3.24 (m, 1H), 3.13 (s, 3H), 2.83 (dt, *J* = 15.2, 3.9 Hz, 1H), 2.61 (dd, *J* = 8.1, 1.3 Hz, 1H), 2.42 (dd, *J* = 8.1, 1.8 Hz, 1H), 1.67 – 1.50 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 189.5, 149.3, 130.5, 84.0, 51.9, 45.0, 44.4, 38.0, 30.7, 28.8, 16.8.
SFC: WHELK-O1 column (CO_2/MeOH, 95:5), flow rate 3 ml/min, *λ* = 210 nm; t_R (major) = 9.5 min, t_R (minor) = 11.3 min, >99% ee.
$[\alpha]_D$ ^{21} = -58.2 (*c* 0.3, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{12}H_{15}NO_5S$ $(M+H)^+$: 286.0744; found: 286.0745.

(3aS,3a[1]S,3bS,6aR)-6a-ethyl-4-oxo-2,3,3a[1],3b,4,6a-hexahydro-3aH-cyclopropa[de]chromene-3a-carbaldehyde **(+)-4m**:

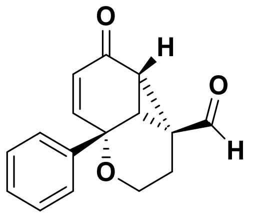


Starting from dienone **1m** (30 mg, 0.144 mmol), the reaction was stirred for overnight. An aqueous saturated ammonium chloride was then added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 70:30) to produce iodinated intermediate **2m** (19 mg, 0.057 mmol). It was dissolved in dry toluene (0.1 M) under argon and organocatalyst **(S)-5** (20 mol%) was added at room temperature. The resulting mixture was stirred for 3 days (monitored by NMR analysis). Once complete, an aqueous saturated ammonium chloride was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10) afforded cyclopropane **4m** as a colorless oil (6 mg, 51% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.84 (s, 1H), 6.42 (dd, *J* = 10.3, 1.3 Hz, 1H), 6.14 (dd, *J* = 10.3, 1.3 Hz, 1H), 3.85 – 3.54 (m, 2H), 2.73 (ddd, *J* = 15.4, 8.1, 5.0 Hz, 1H), 2.43 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.10 (dd, *J* = 8.2, 1.3 Hz, 1H), 1.86 (qd, *J* = 7.6, 2.2 Hz, 2H), 1.62 (m, 1H), 0.99 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.4, 191.9, 151.4, 131.0, 68.5, 59.0, 34.8, 31.1, 30.3, 26.1, 14.8, 7.3.

SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 5.0 min, t_R (minor) = 6.1 min, 95% ee.
$[\alpha]_D$ ^{21} = +58.0 (*c* 0.12, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{12}H_{14}O_3$ $(M+H)^+$: 207.1016; found: 207.1017.

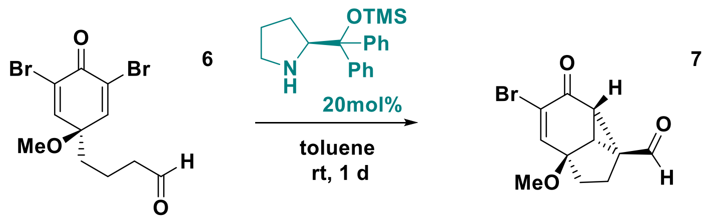
(3aS,3a^{1}S,3bS,6aR)-4-oxo-6a-phenyl-2,3,3a^1,3b,4,6a-hexahydro-3aH-cyclopropa[de]chromene-3a-carbaldehyde **(+)-4n**:



Starting from dienone **1n** (19 mg, 0.074 mmol), the reaction was stirred for 3 days. An aqueous saturated ammonium chloride was then added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 75:25) to produce iodinated intermediate **2n** (10 mg, 0.026 mmol). It was dissolved in dry toluene (0.1 M) under argon and organocatalyst **(S)-5** (20 mol%) was added at room temperature. The resulting mixture was stirred for 4 days (monitored by NMR analysis). Once complete, an aqueous saturated ammonium chloride was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10) afforded cyclopropane **4n** as a colorless oil (4 mg, 61% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.59 – 7.29 (m, 5H), 6.53 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.19 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.04 – 3.80 (m, 2H), 2.88 (m, 1H), 2.59 (dd, *J* = 8.2, 1.3 Hz, 1H), 2.41 (dd, *J* = 8.2, 1.4 Hz, 1H), 1.74 (dt, *J* = 15.6, 7.9 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 191.5, 151.2, 144.1, 129.0, 128.9, 128.4, 125.0, 69.2, 59.51, 35.6, 30.0, 28.9, 14.5.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, λ = 210 nm; t_R (major) = 8.3 min, t_R (minor) = 11.1 min, 97% ee.
$[\alpha]_D$ ^{21} = +91.6 (*c* 0.1, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{16}H_{14}O_3$ $(M+H)^+$: 255.1016; found: 255.1021.

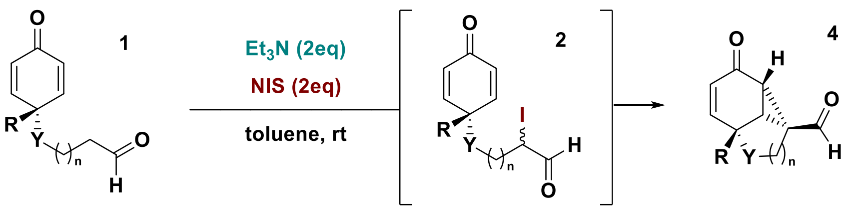
Bromo-dienone cyclopropanation procedure



To a solution of bromo-dienone **6** (25 mg, 0.071 mmol) in dry toluene (0.05 M) under argon, organocatalyst **(S)-5** (20 mol%) was added at room temperature. The resulting mixture was stirred overnight (monitored by NMR analysis). Once complete, an aqueous saturated ammonium chloride was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 90:10 to 80:20) afforded cyclopropane **7** as a colorless oil (14 mg, 74% yield).

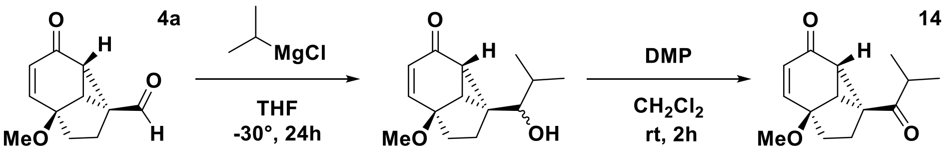
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.22 (d, *J* = 1.3 Hz, 1H), 3.48 (s, 3H), 2.96 (dd, *J* = 8.3, 1.3 Hz, 1H), 2.90 (dd, *J* = 8.3, 1.1 Hz, 1H), 2.76 (dd, *J* = 14.6, 8.7 Hz, 1H), 2.56 (td, *J* = 12.4, 8.8 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.39 (ddd, *J* = 14.6, 12.4, 5.7 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 184.0, 152.0, 123.9, 84.8, 77.6, 77.2, 76.8, 55.3, 49.9, 49.1, 41.4, 37.1, 19.1.
SFC: WHELK-O1 column (CO_2/EtOH, 95:5), flow rate 3 ml/min, *λ* = 210 nm; t_R (minor) = 6.3 min, t_R (major) = 7.9 min, 5% ee.
$[\alpha]_D^{21}$ = +11.22 (*c* 0.9, CH_2Cl_2).
HRMS (ESI): *m/z* Calc. for $C_{11}H_{11}BrO_3$ $(M+H)^+$: 270.9964; found: 270.9964.

General procedure for racemic cyclopropanation



To a solution of aldehyde **1** (1 equiv.) in dry toluene (0.05 M) under argon, were added subsequently N-iodosuccinimide (2equiv.) and triéthylamine (2equiv.) at room temperature. The resulting mixture was stirred overnight (monitored by NMR analysis). Once complete, an aqueous saturated ammonium chloride was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by silica gel chromatography to obtain racemic product **4**.

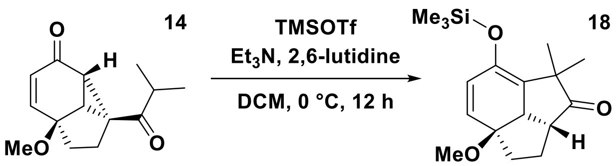
From cyclopropane 4a to ketone 14



To a solution of cyclopropane **4a** (1 equiv.) in dry THF under argon, was added isopropylmagnesium chloride (2equiv.) at -30°. After 24 hours, an aqueous saturated ammonium chloride was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then dissolved in dry CH_2Cl_2 under argon. DMP was added and the mixture was stirred for 2h. The mixture was then filtrated under a short pad of silica and concentrated under reduced pressure. Purification by silica gel flash chromatography (*n*-Hex/EtOAc, 80:20) afforded ketone **14** as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.16 (dd, *J* = 10.3, 1.2 Hz, 1H), 3.42 (s, 3H), 2.94 – 2.81 (m, 2H), 2.66 – 2.45 (m, 3H), 1.90 (m, 1H), 1.60 – 1.42 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 210.4, 192.3, 151.6, 130.9, 82.1, 77.6, 77.2, 76.7, 54.9, 49.1, 47.3, 42.1, 39.2, 36.5, 21.6, 19.0, 18.7.
HRMS (ESI): *m/z* Calc. for $C_{14}H_{18}O_3$ $(M+H)^+$: 235.1329; found: 235.1319.

Vinylcyclopropane rearrangement procedure



To a solution of ketone **14** (1 equiv.) in dry CH_2Cl_2 (0.1 M) under argon, were added subsequently Et_3N (2 equiv.), lutidine (2 equiv.) and TMSOTf (2 equiv.) at 0°. After 24 hours, water was added, followed by EtOAc. The organic layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by silica gel chromatography (95:5 *n*-Hex/EtOAc) to afford product **18** (20% yield, 44% brsm).

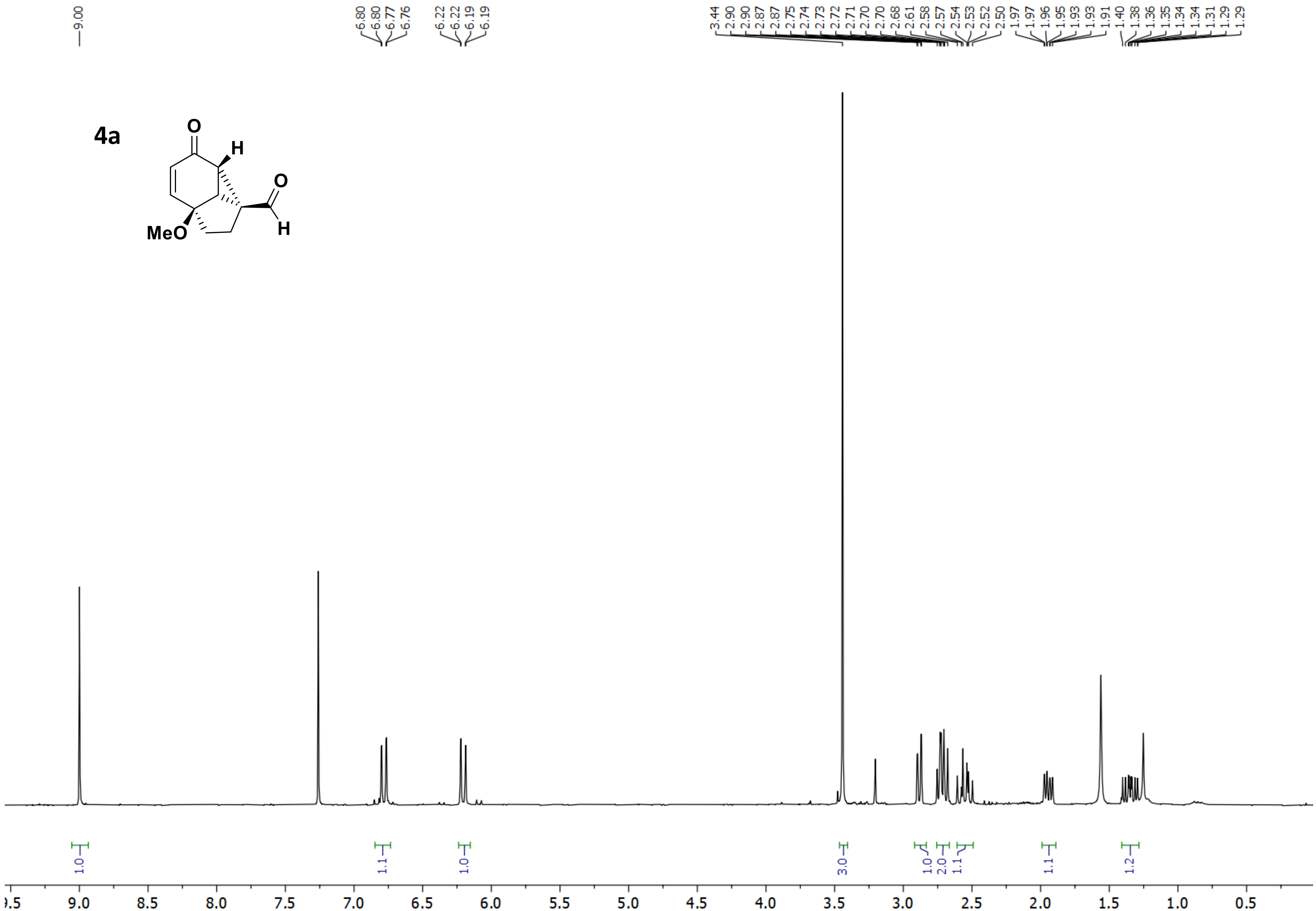
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (dd, *J* = 10.1, 1.2 Hz, 1H), 5.71 (d, *J* = 10.2 Hz, 1H), 3.64 (d, *J* = 8.5 Hz, 1H), 3.26 (s, 3H), 3.04 (ddd, *J* = 11.7, 8.4, 2.7 Hz, 1H), 2.34 – 2.02 (m, 1H), 1.95 – 1.84 (m, 1H), 1.79 (t, *J* = 4.9 Hz, 1H), 1.32 (s, 3H), 1.13 (s, 3H), 1.10 – 0.83 (m, 1H), 0.21 (s, 9H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 223.9, 140.7, 131.4, 126.8, 122.3, 88.6, 51.4, 50.9, 50.1, 46.5, 35.1, 29.28, 24.0, 21.7, 1.0.
HRMS (ESI): *m/z* Calc. for $C_{17}H_{26}O_3Si$ $(M+H)^+$: 307.1724; found: 307.1731.

III. References

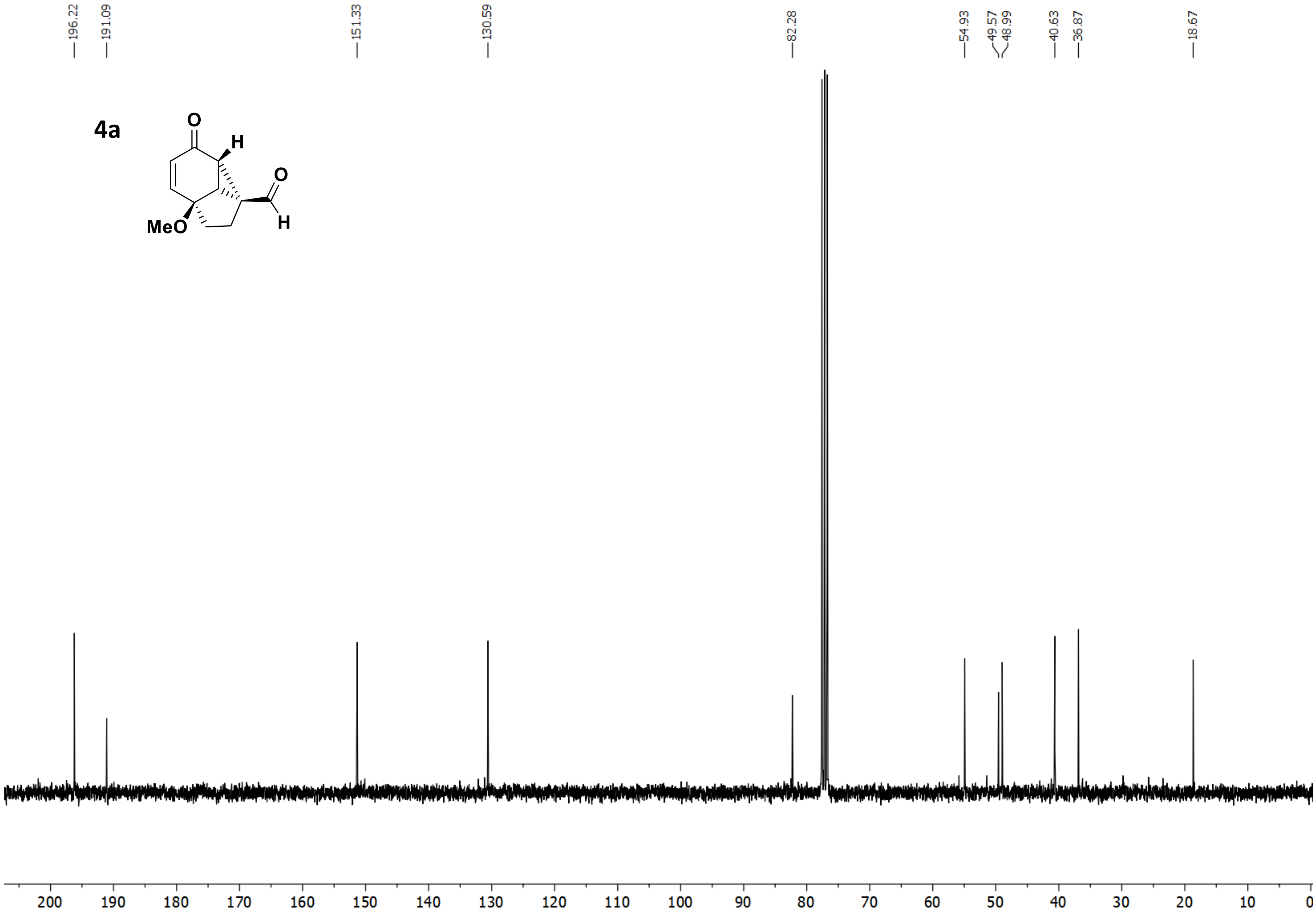
1. N. T. Vo, R. D. M. Pace, F. O'Hara and M. J. Gaunt, J. Am. Chem. Soc., 2008, 130, 404.
2. Q. Liu and T. Rovis, J. Am. Chem. Soc., 2006, 128, 2552.

IV. NMR Spectra

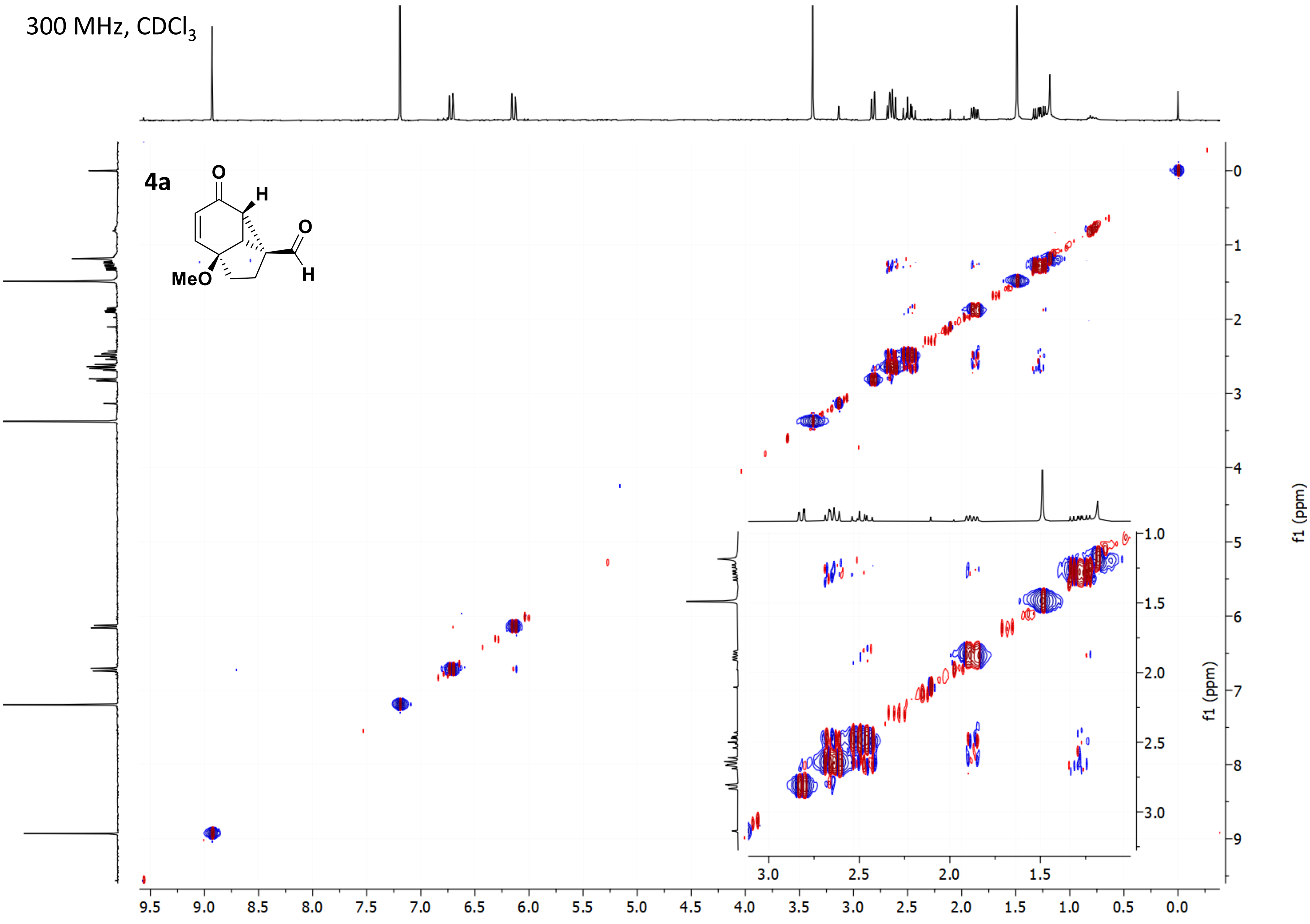
300 MHz, $CDCl_3$



75 MHz, $CDCl_3$

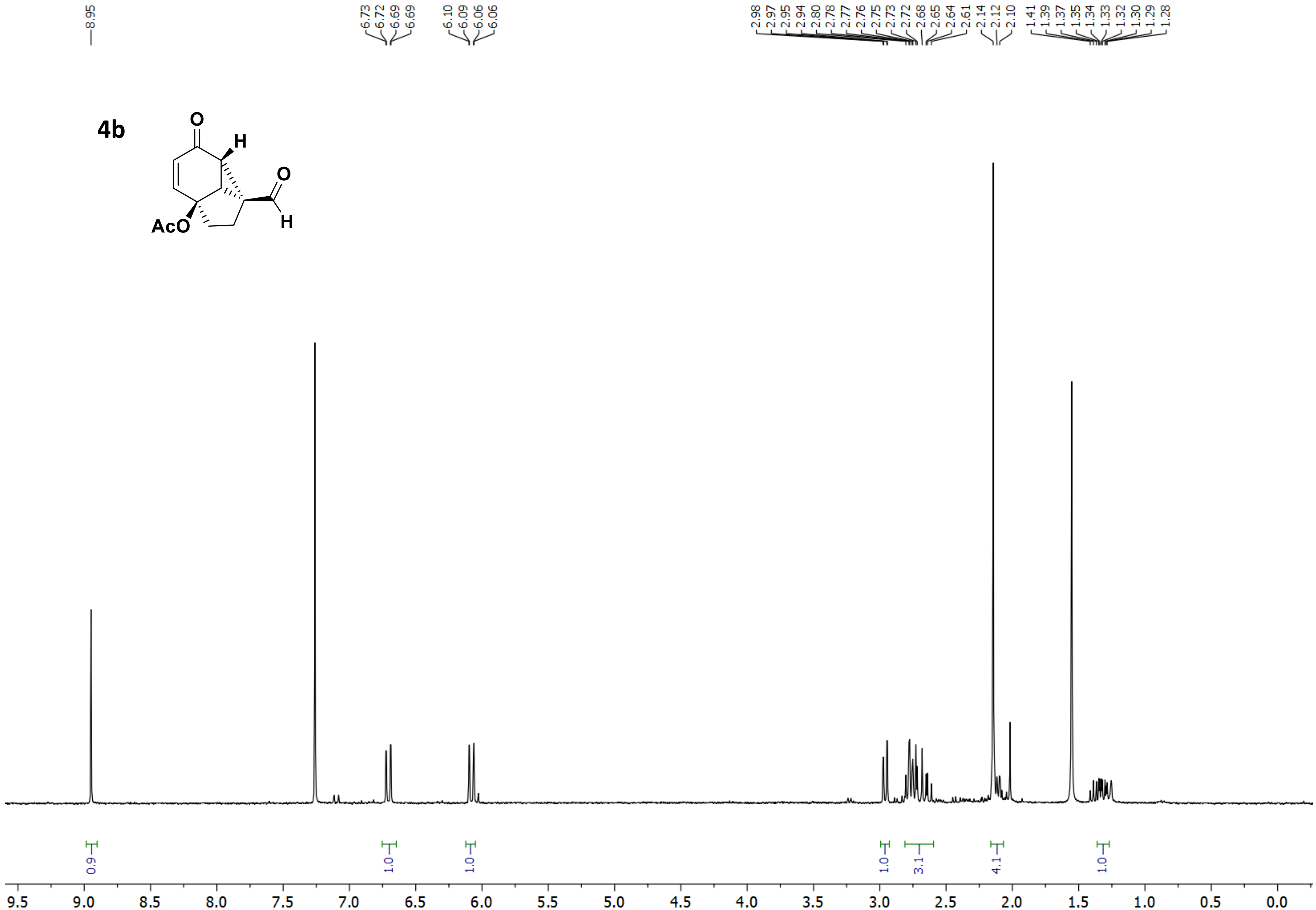


196.22
191.09
151.33
130.59
82.28
54.93
49.57
48.99
40.63
36.87
18.67
4a
O
H
O
H
MeO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

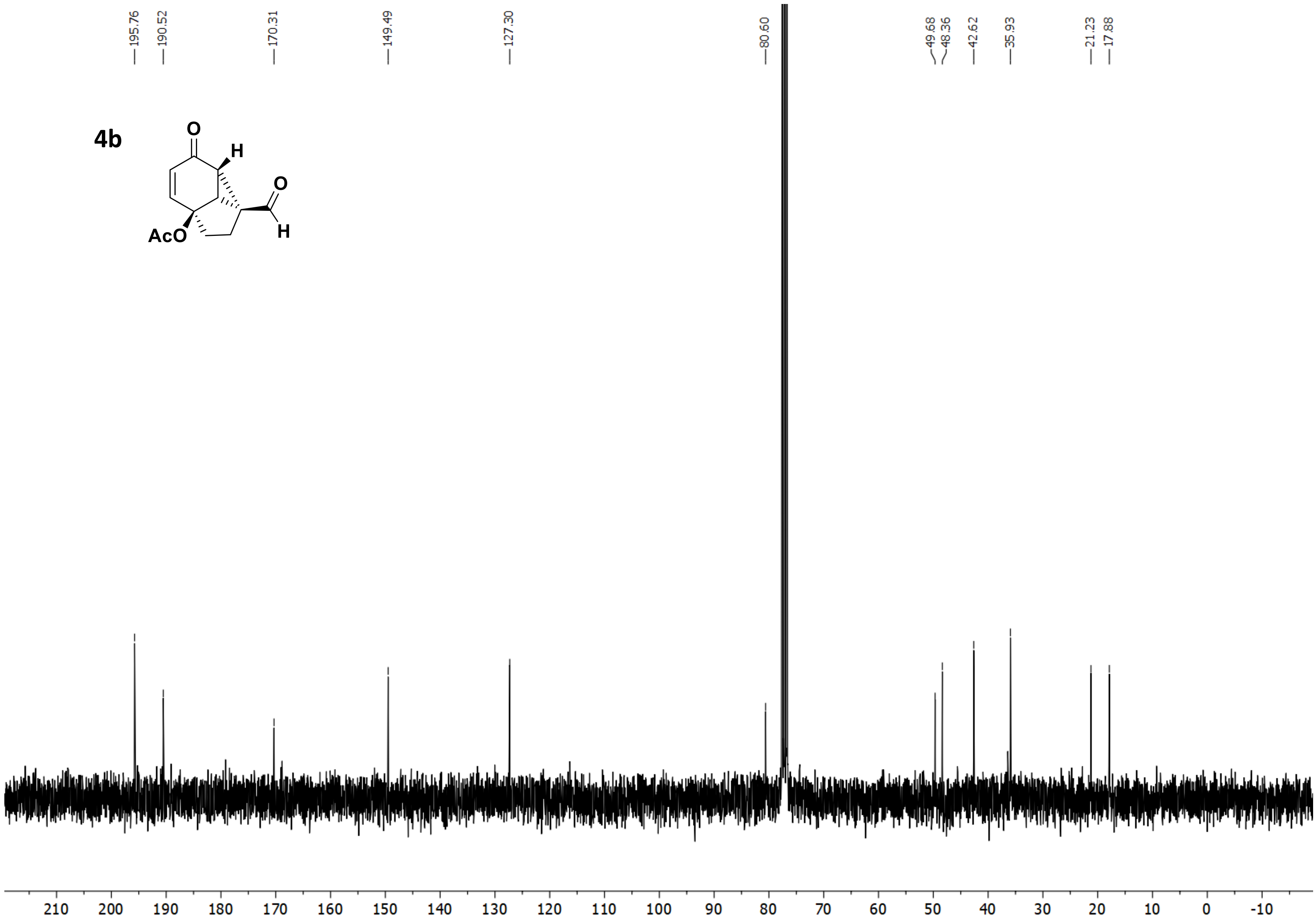

300 MHz, CDCl3
4a
O
H
O
H
MeO
f1 (ppm)
f1 (ppm)

300 MHz, $CDCl_3$

4b

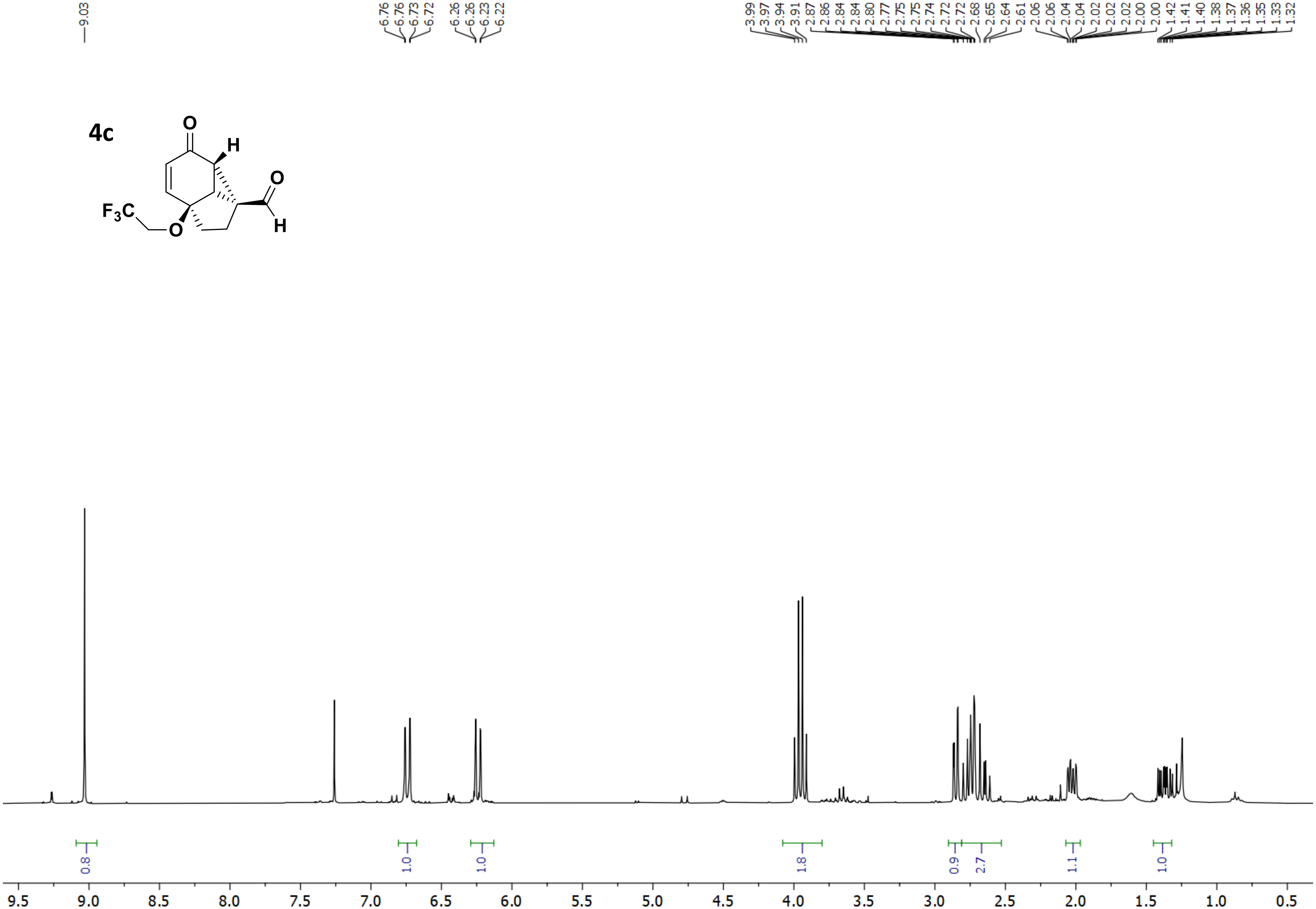


75 MHz, $CDCl_3$

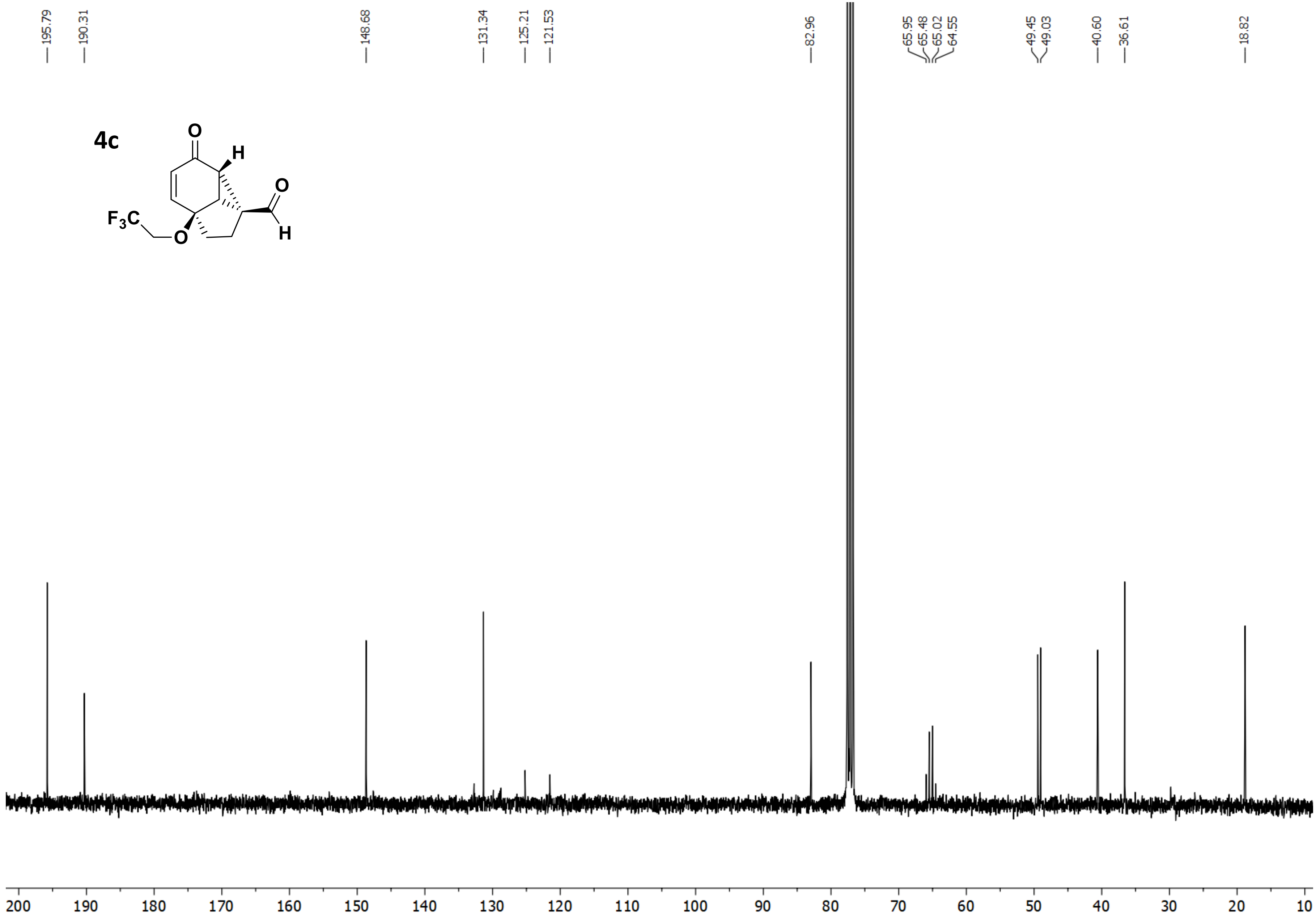

4b
O
H
O
H
AcO
195.76
190.52
170.31
149.49
127.30
80.60
49.68
48.36
42.62
35.93
21.23
17.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

300 MHz, $CDCl_3$

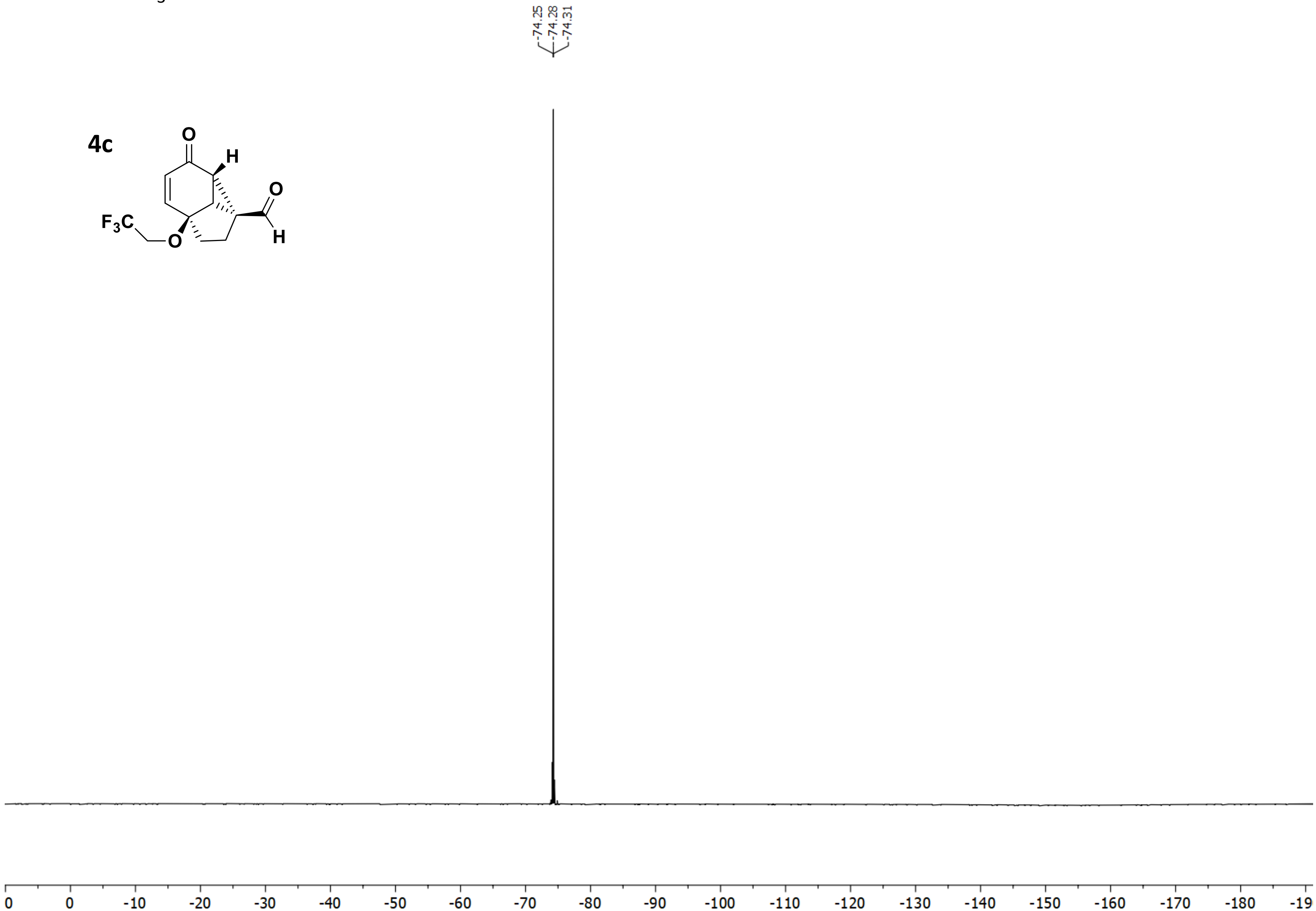
4c



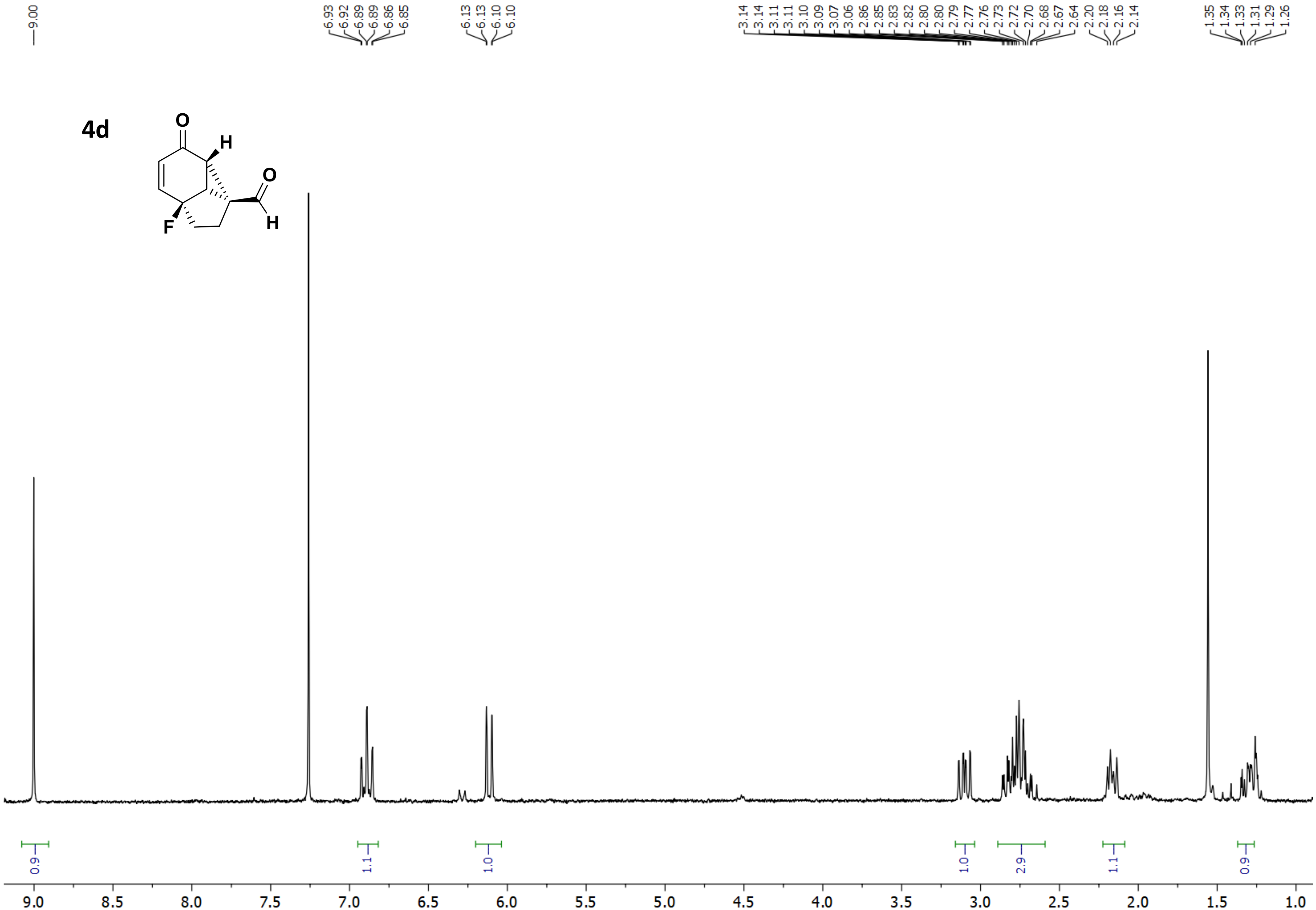
75 MHz, $CDCl_3$


195.79
190.31
148.68
131.34
125.21
121.53
82.96
65.95
65.48
65.02
64.55
49.45
49.03
40.60
36.61
18.82
4c
O
H
O
H
F3C
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

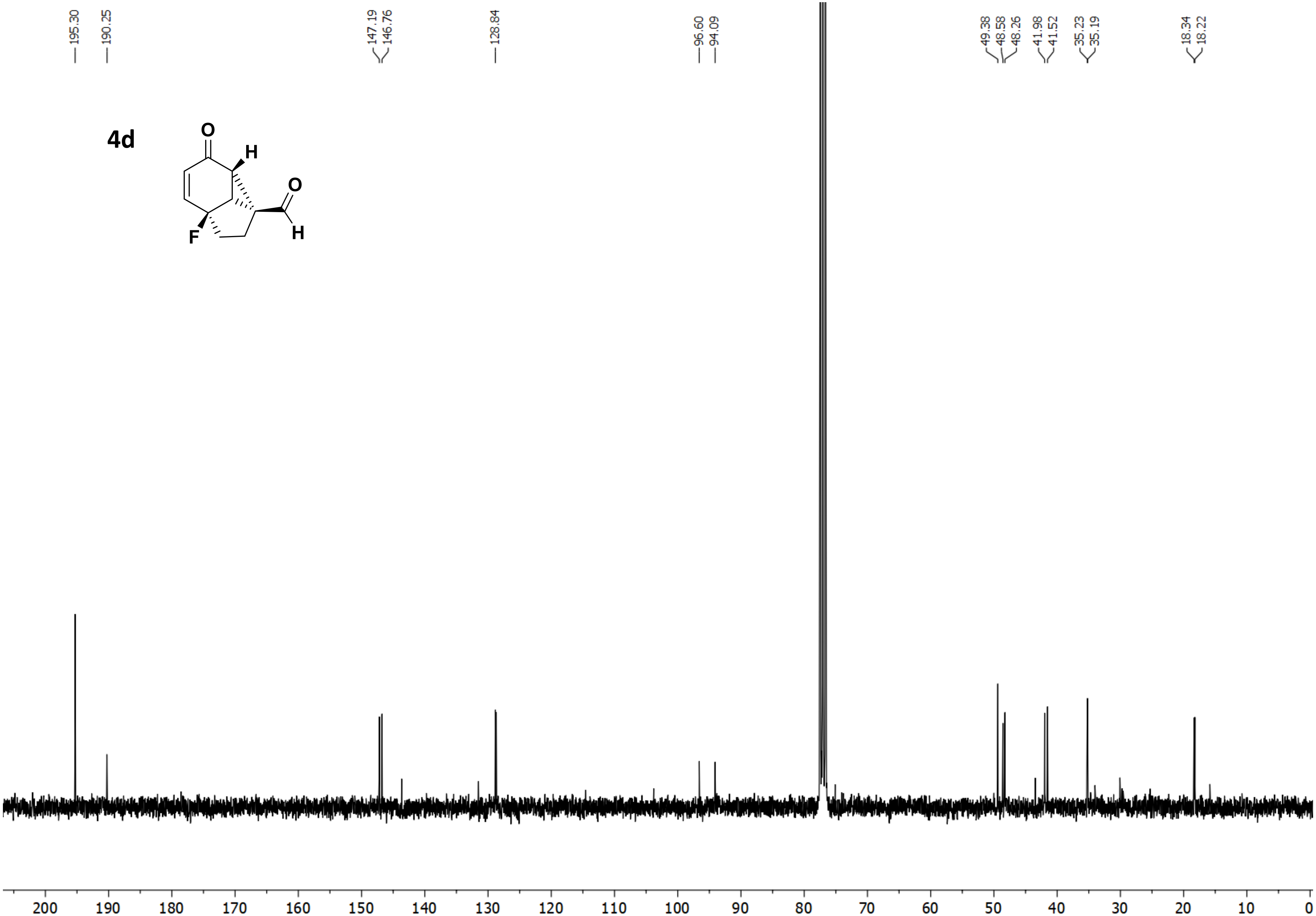
282 MHz, $CDCl_3$



300 MHz, $CDCl_3$

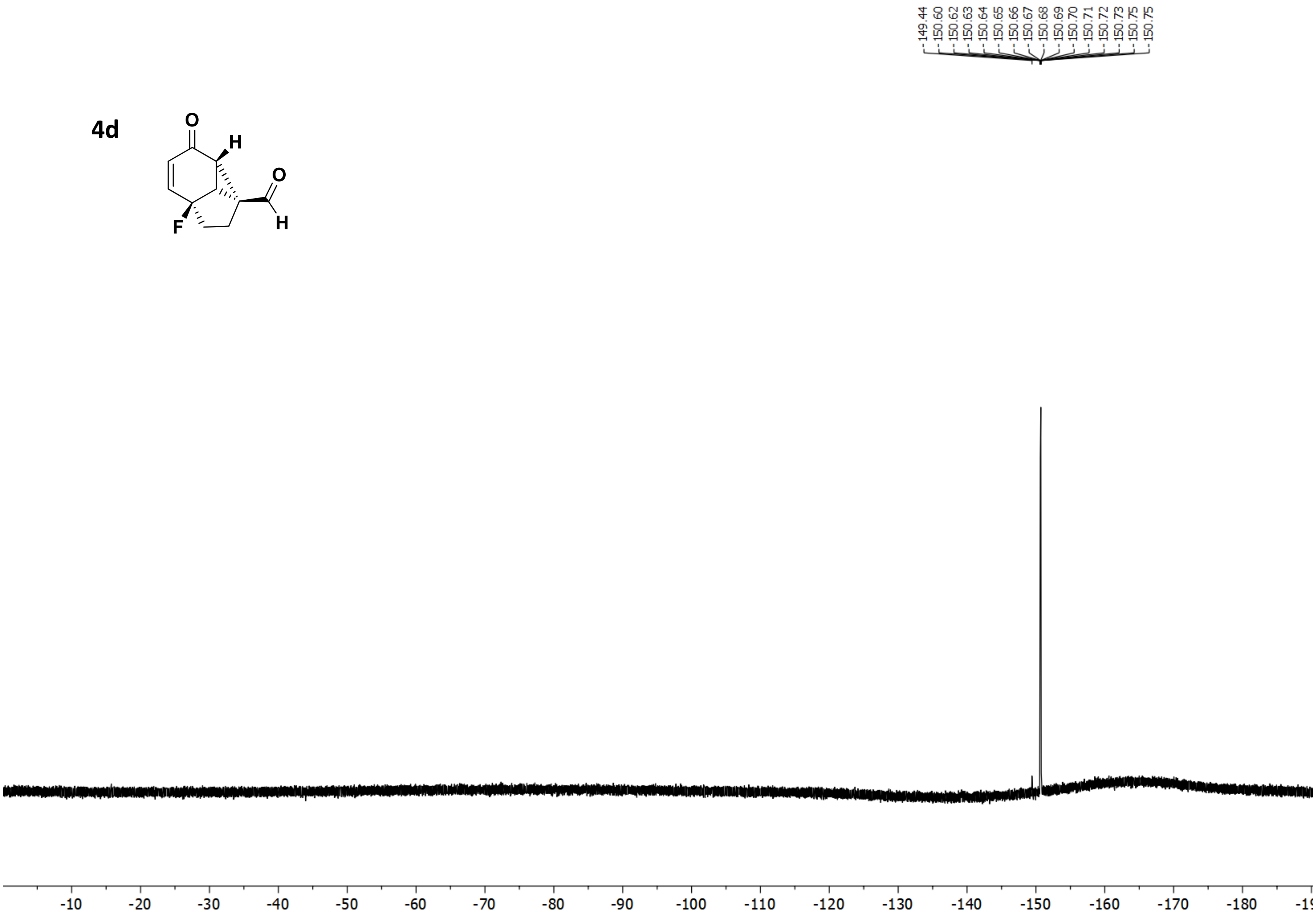


75 MHz, $CDCl_3$


195.30
190.25
147.19
146.76
128.84
96.60
94.09
49.38
48.58
48.26
41.98
41.52
35.23
35.19
18.34
18.22
4d
O
H
O
H
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

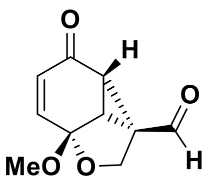
282 MHz, $CDCl_3$

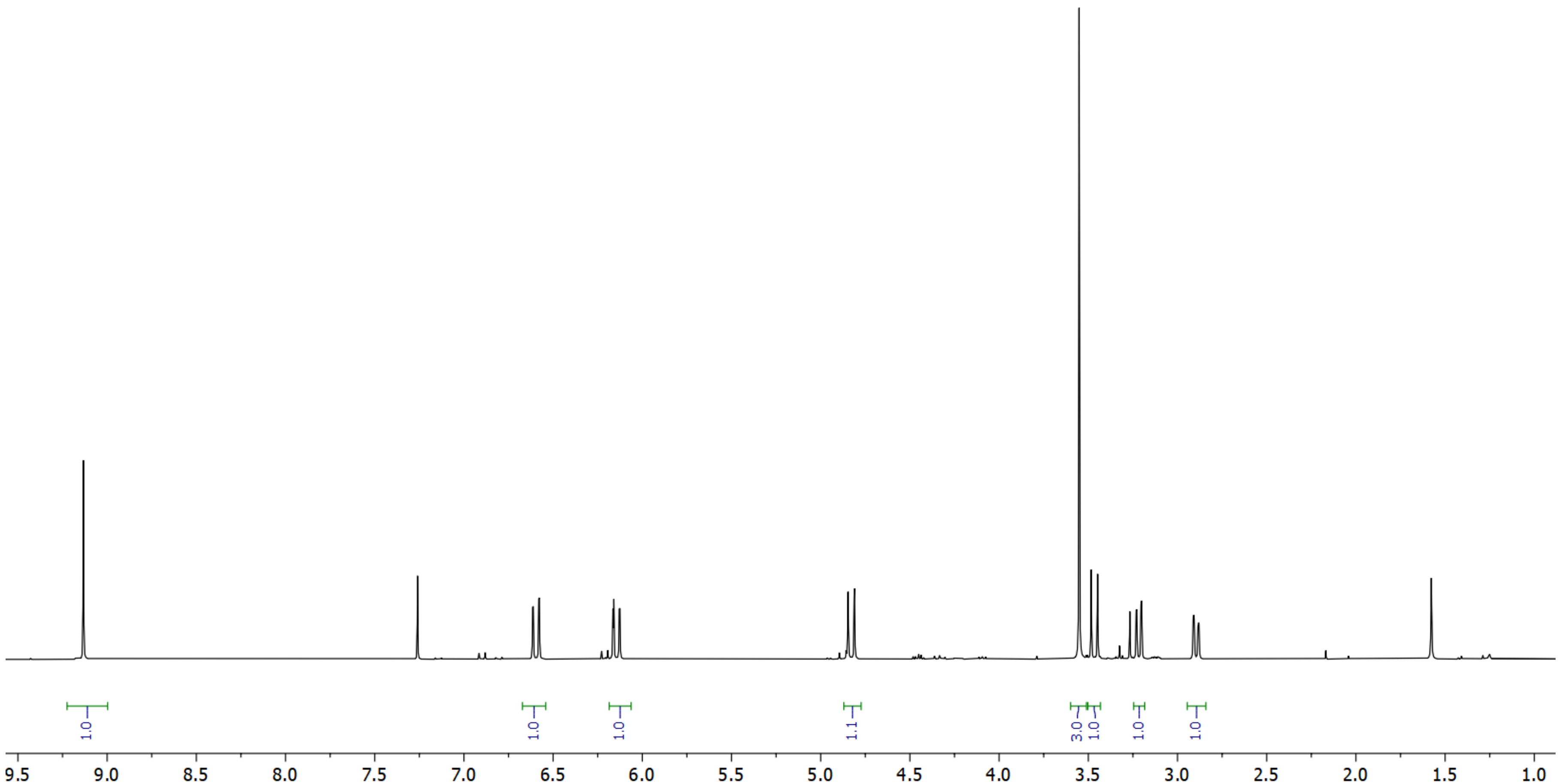
4d



300 MHz, $CDCl_3$

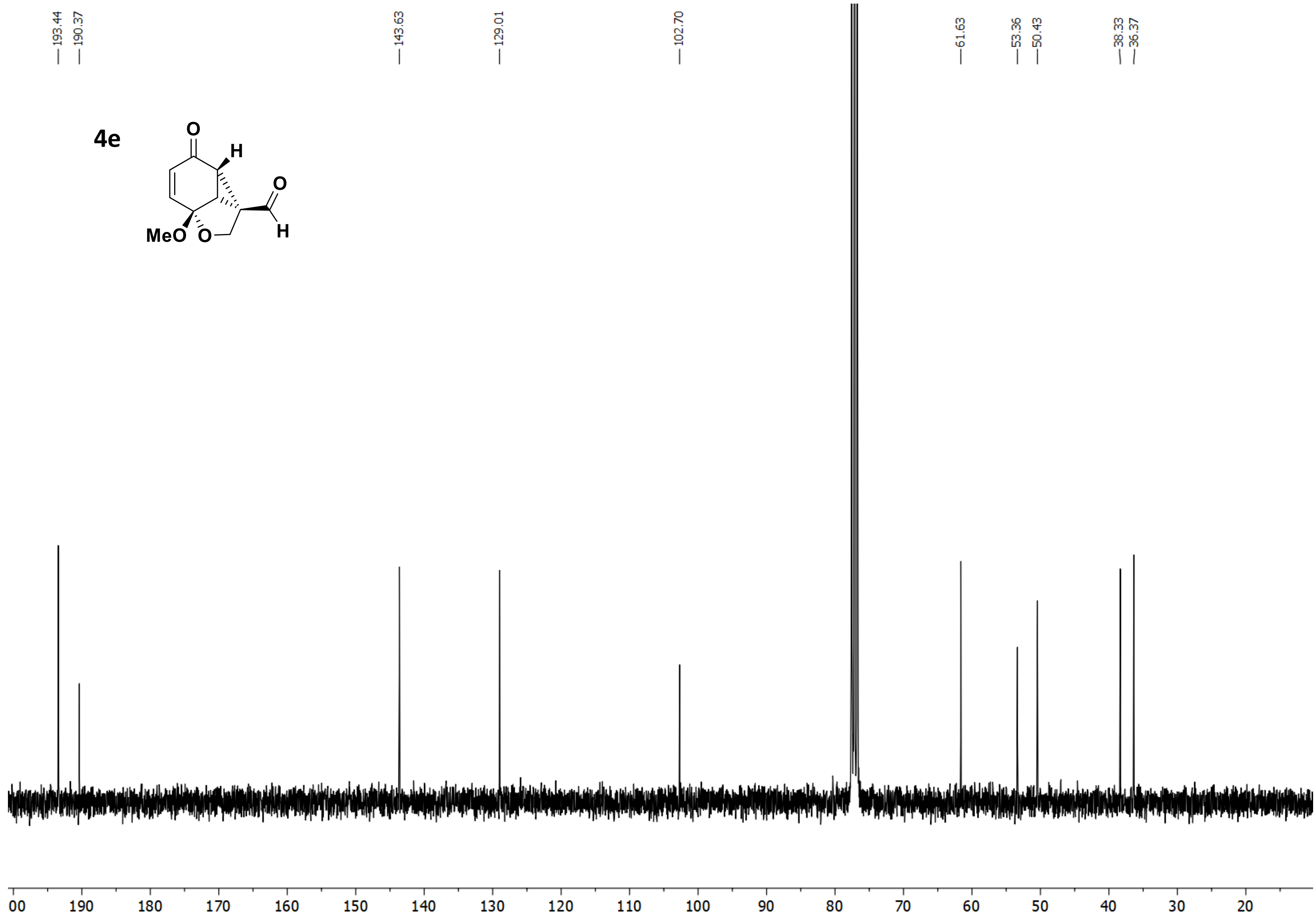
4e



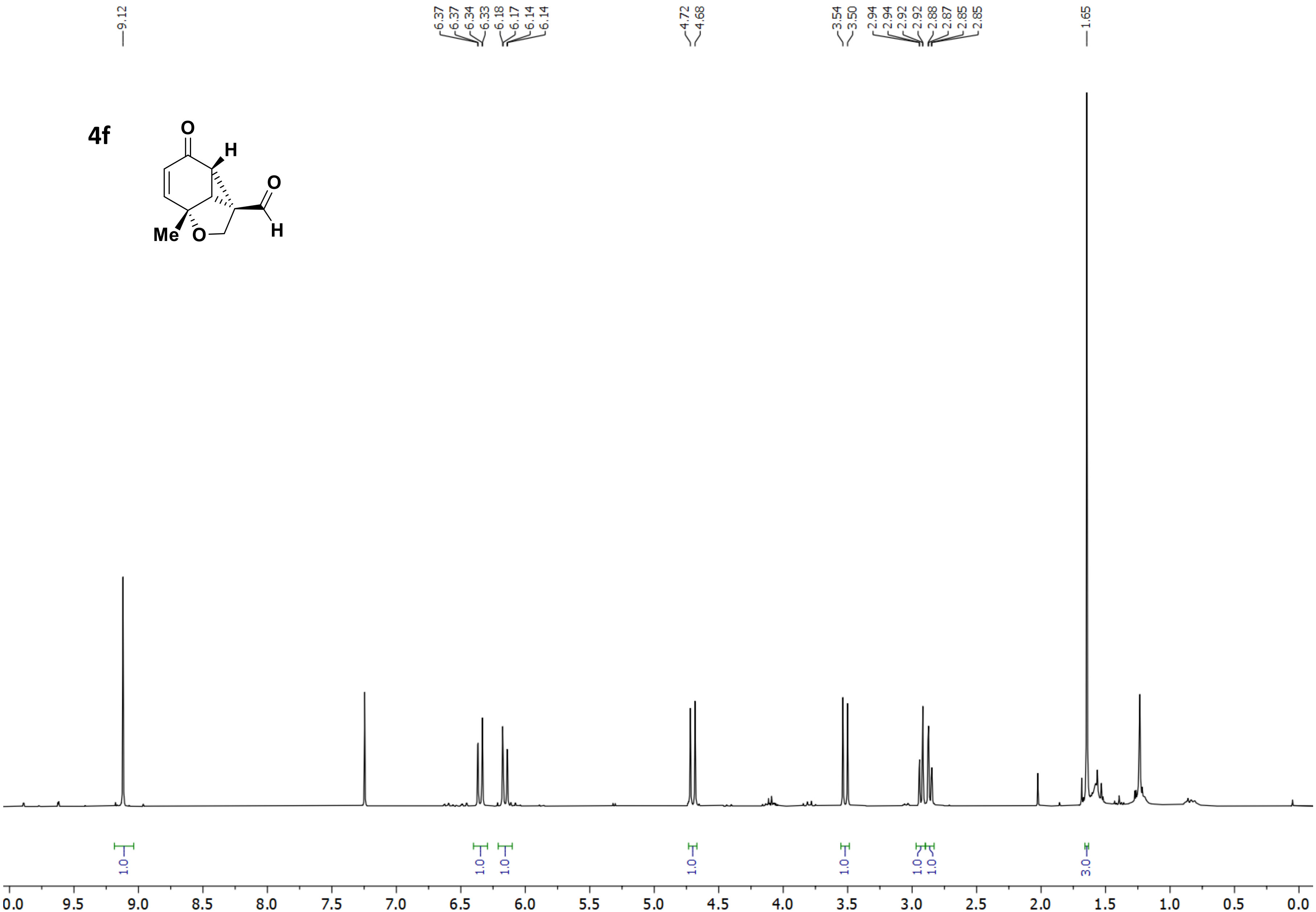


75 MHz, $CDCl_3$

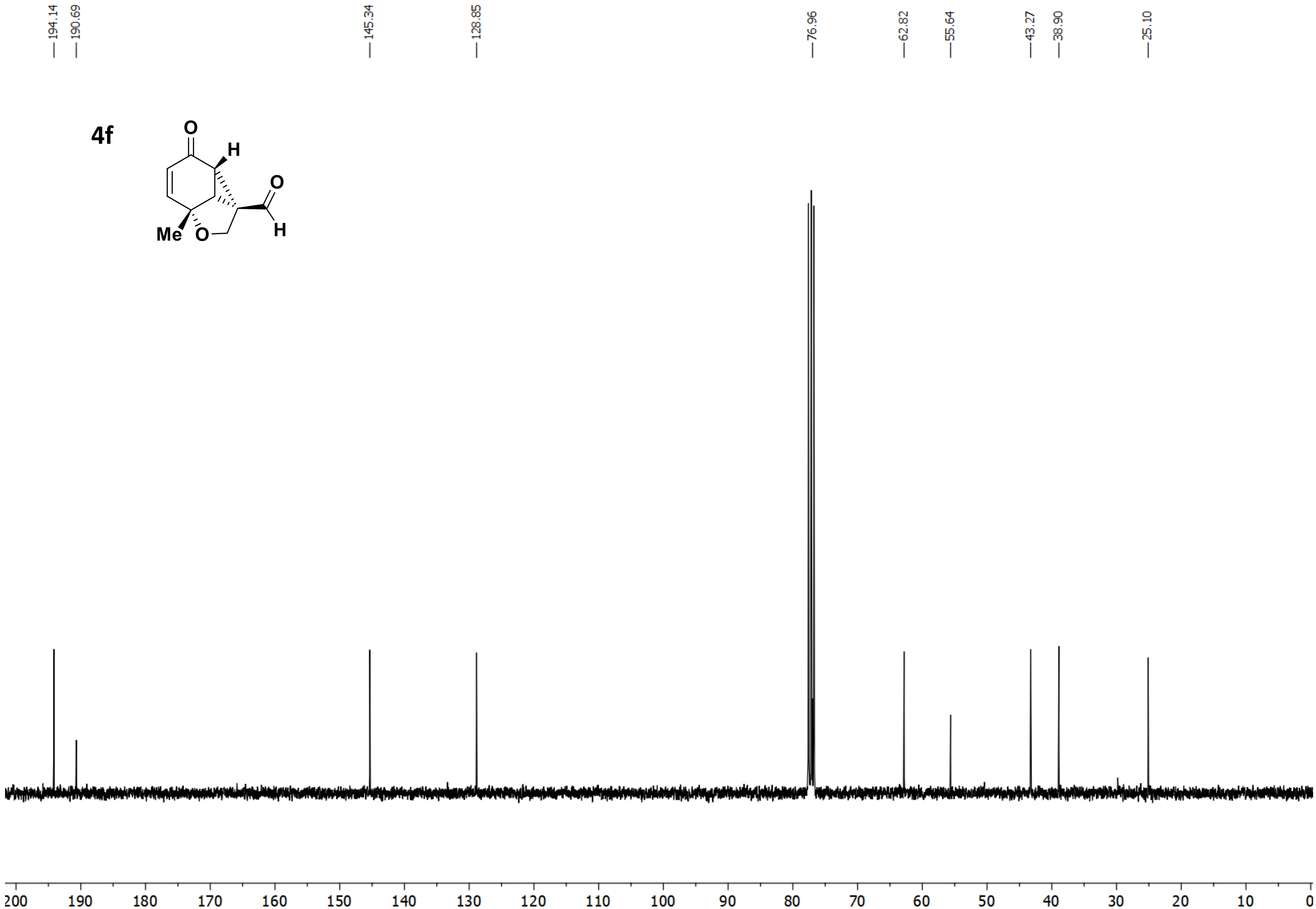
4e



300 MHz, $CDCl_3$



75 MHz, $CDCl_3$


194.14
190.69
145.34
128.85
76.96
62.82
55.64
43.27
38.90
25.10
4f
O
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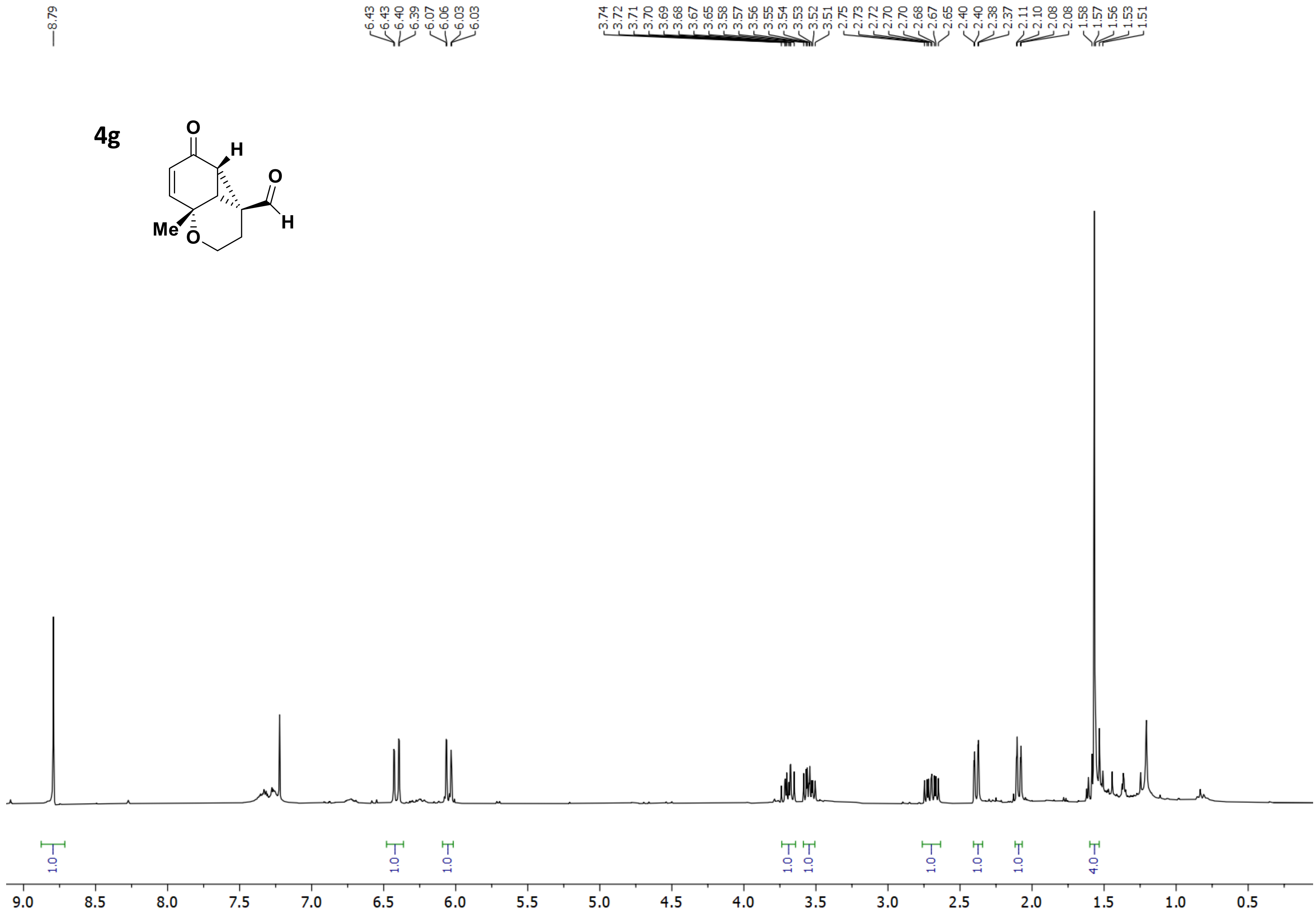
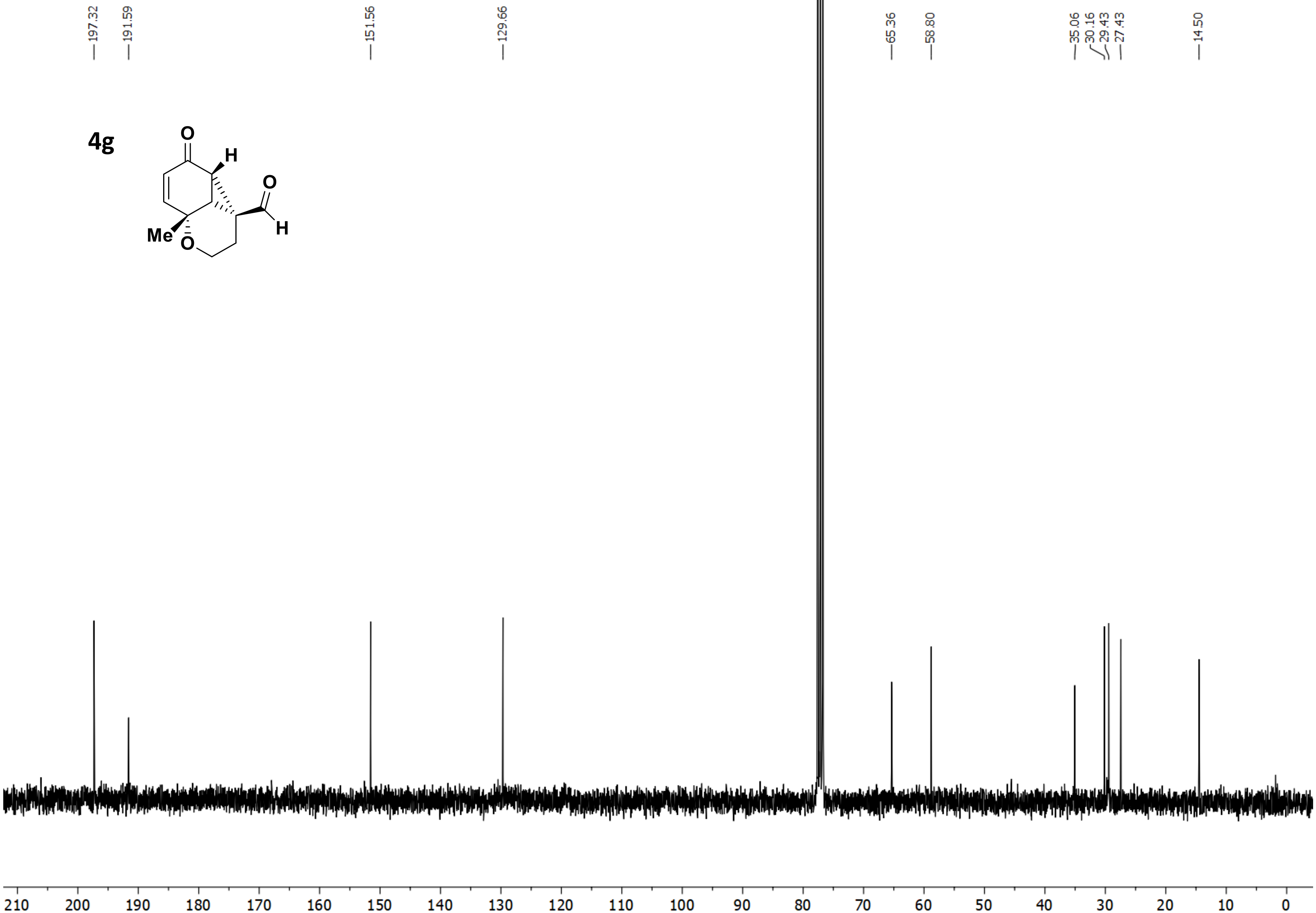
O
H
Me
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

300 MHz, $CDCl_3$

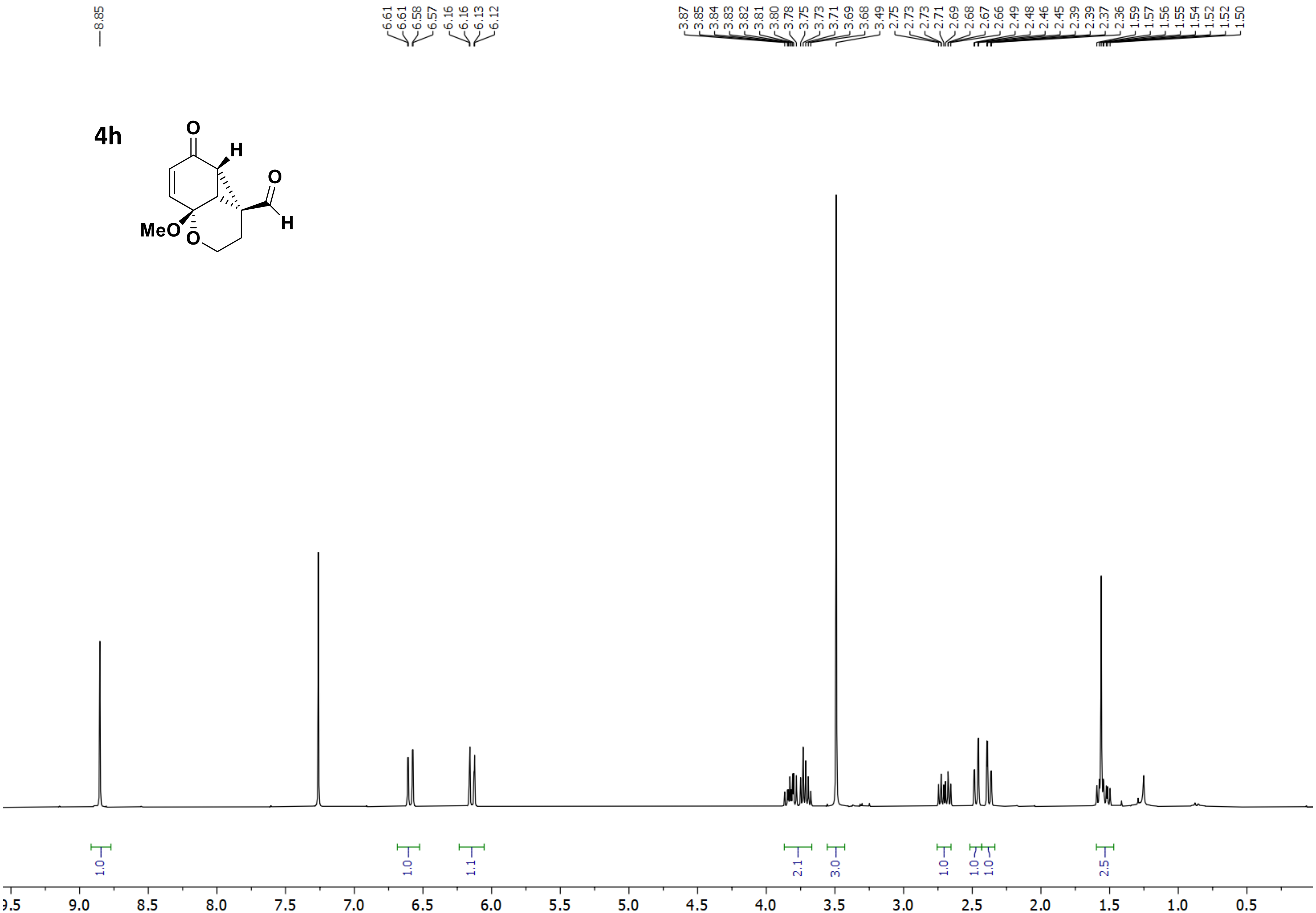


75 MHz, $CDCl_3$

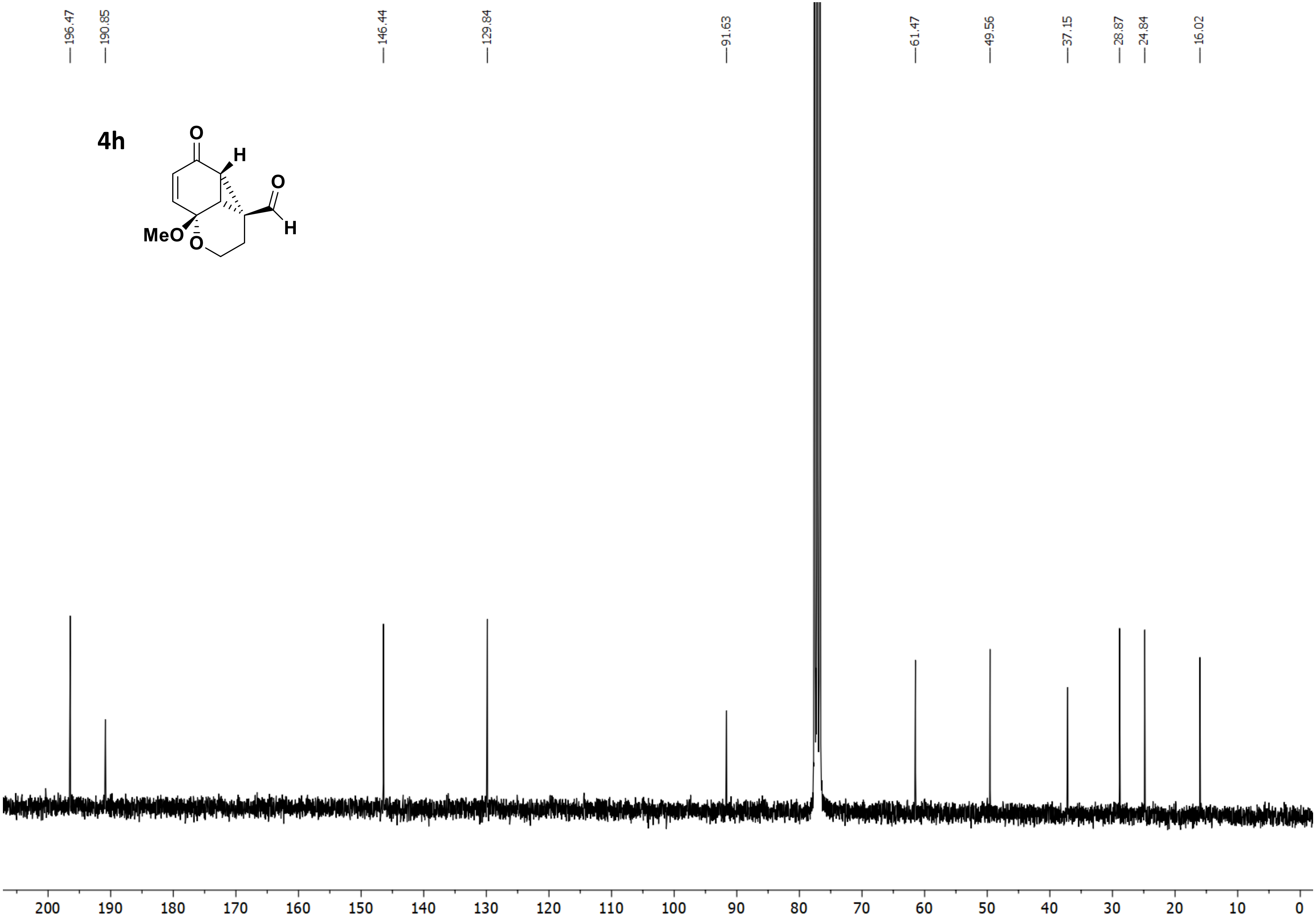
4g



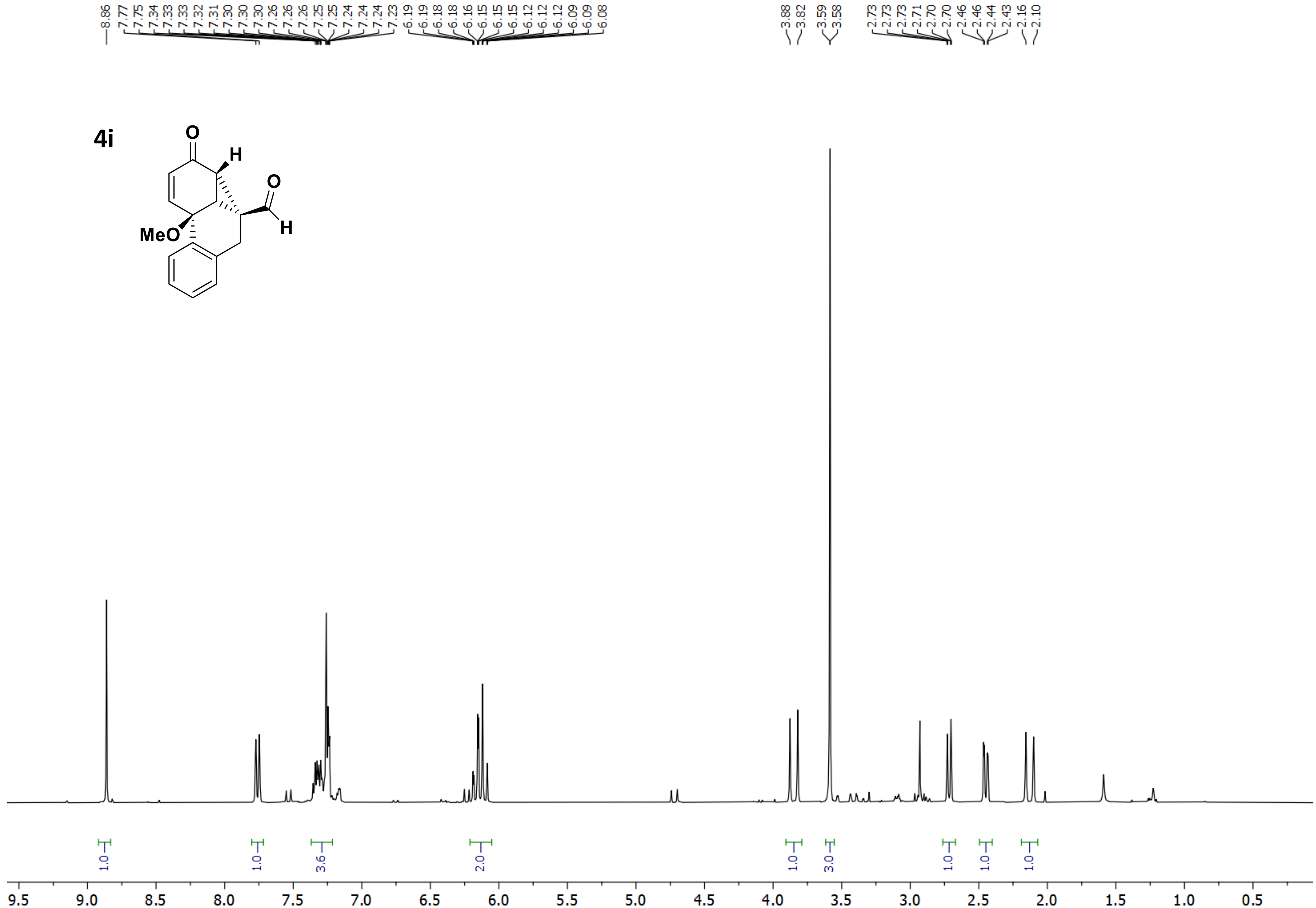
300 MHz, $CDCl_3$



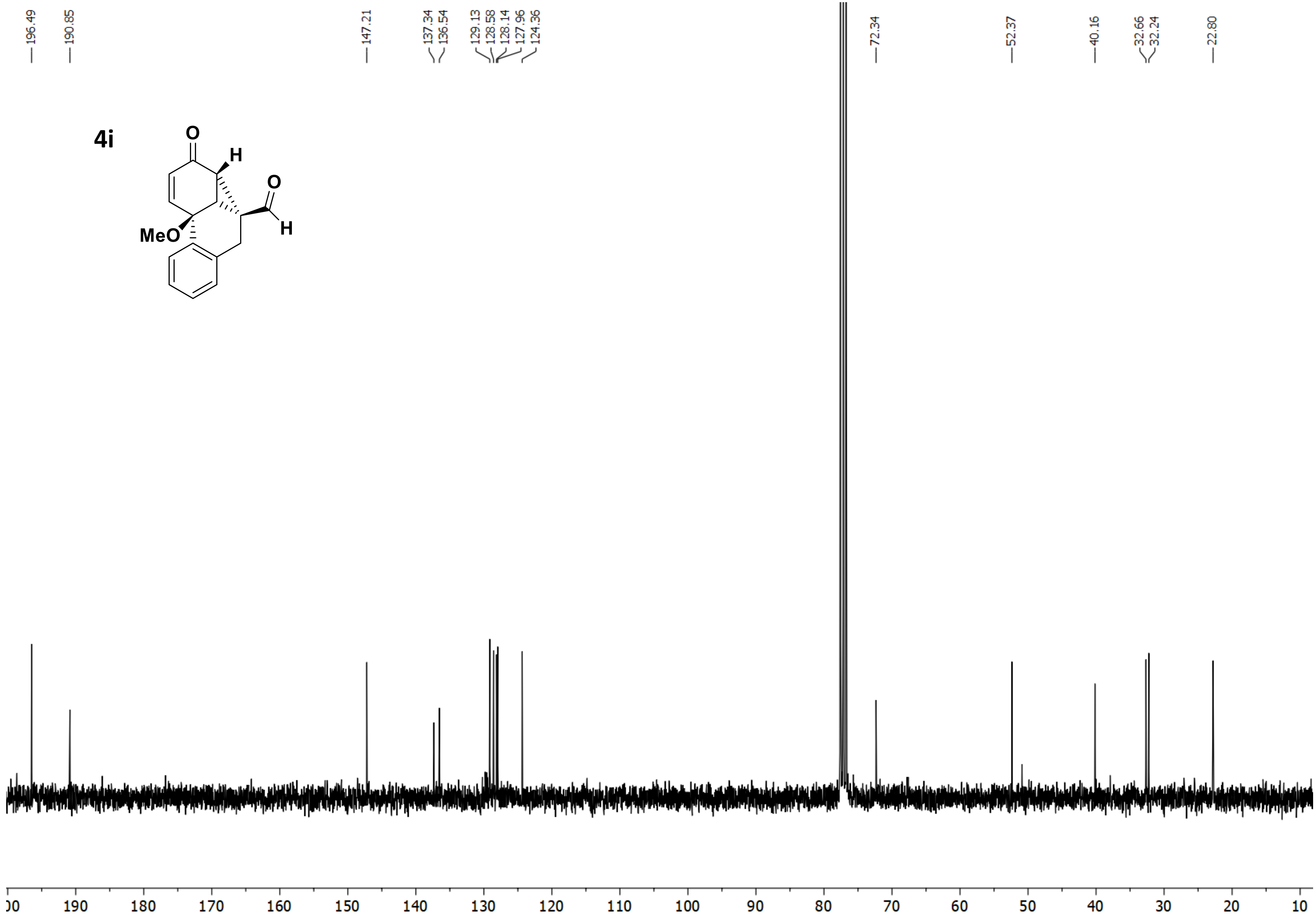
75 MHz, $CDCl_3$


196.47
190.85
146.44
129.84
91.63
61.47
49.56
37.15
28.87
24.84
16.02
4h
O
H
O
H
MeO
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

300 MHz, $CDCl_3$



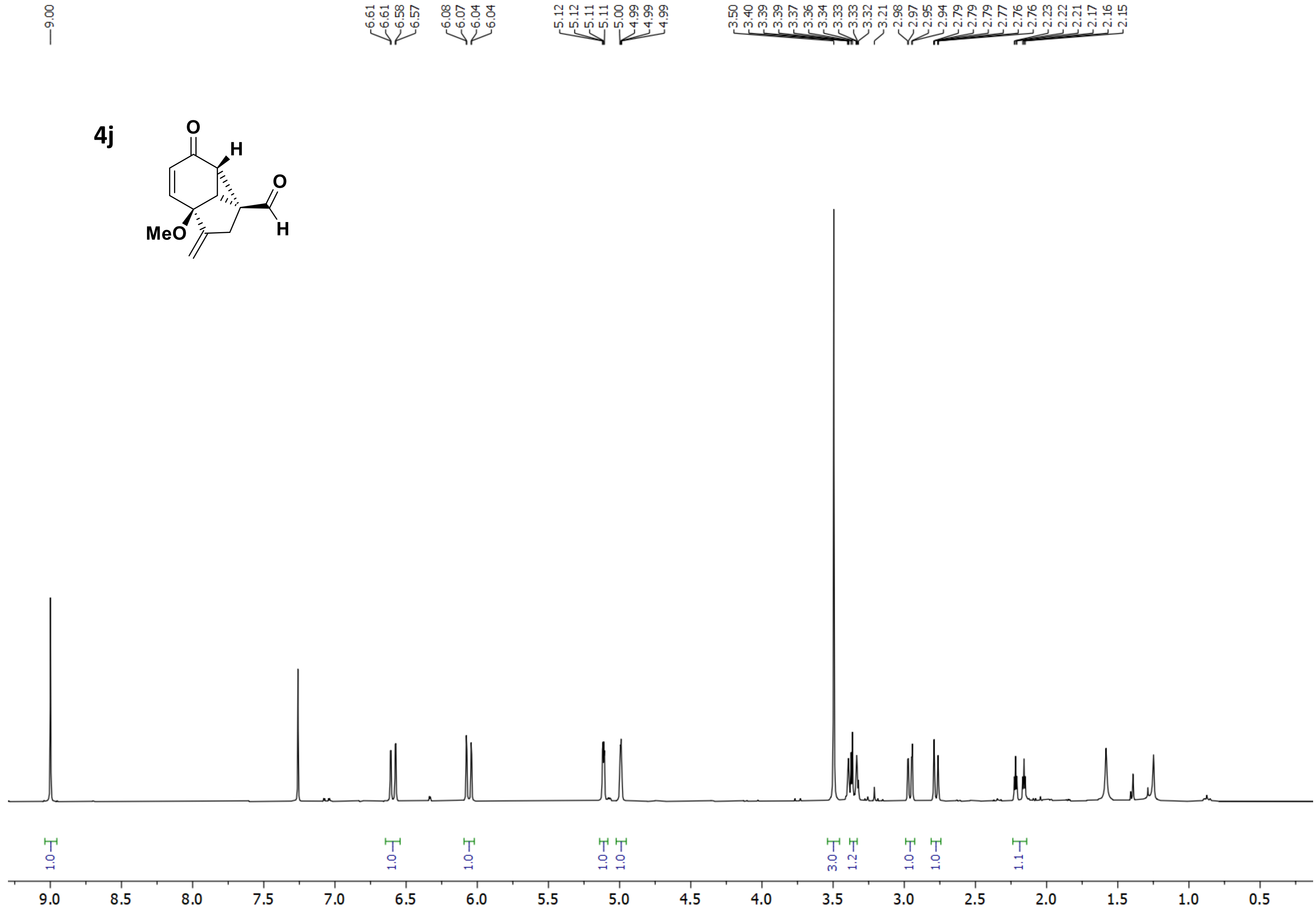
75 MHz, $CDCl_3$



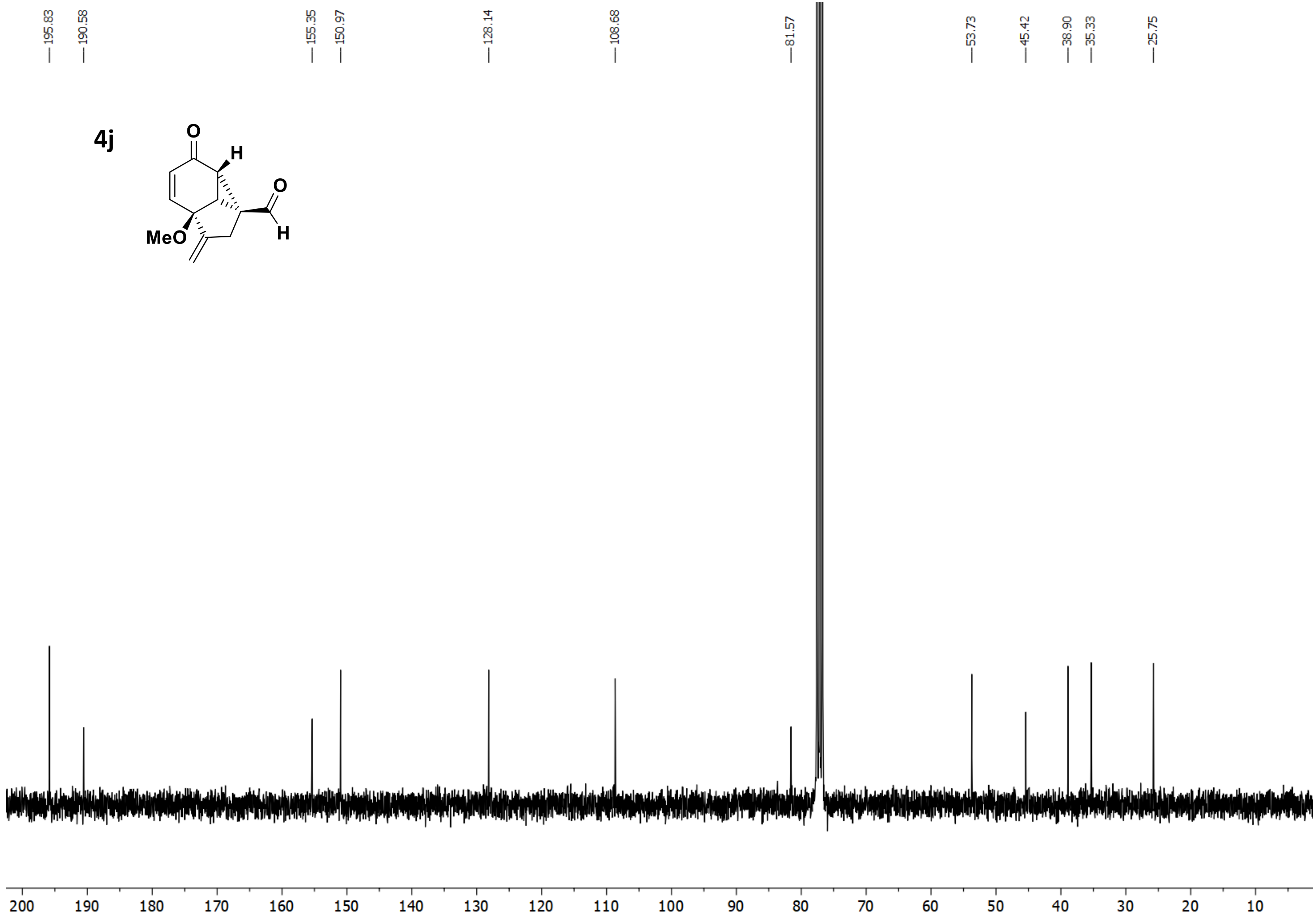
196.49
190.85
147.21
137.34
136.54
129.13
128.58
128.14
127.96
124.36
72.34
52.37
40.16
32.66
32.24
22.80
4i
O
H
O
H
MeO
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

300 MHz, $CDCl_3$

4j

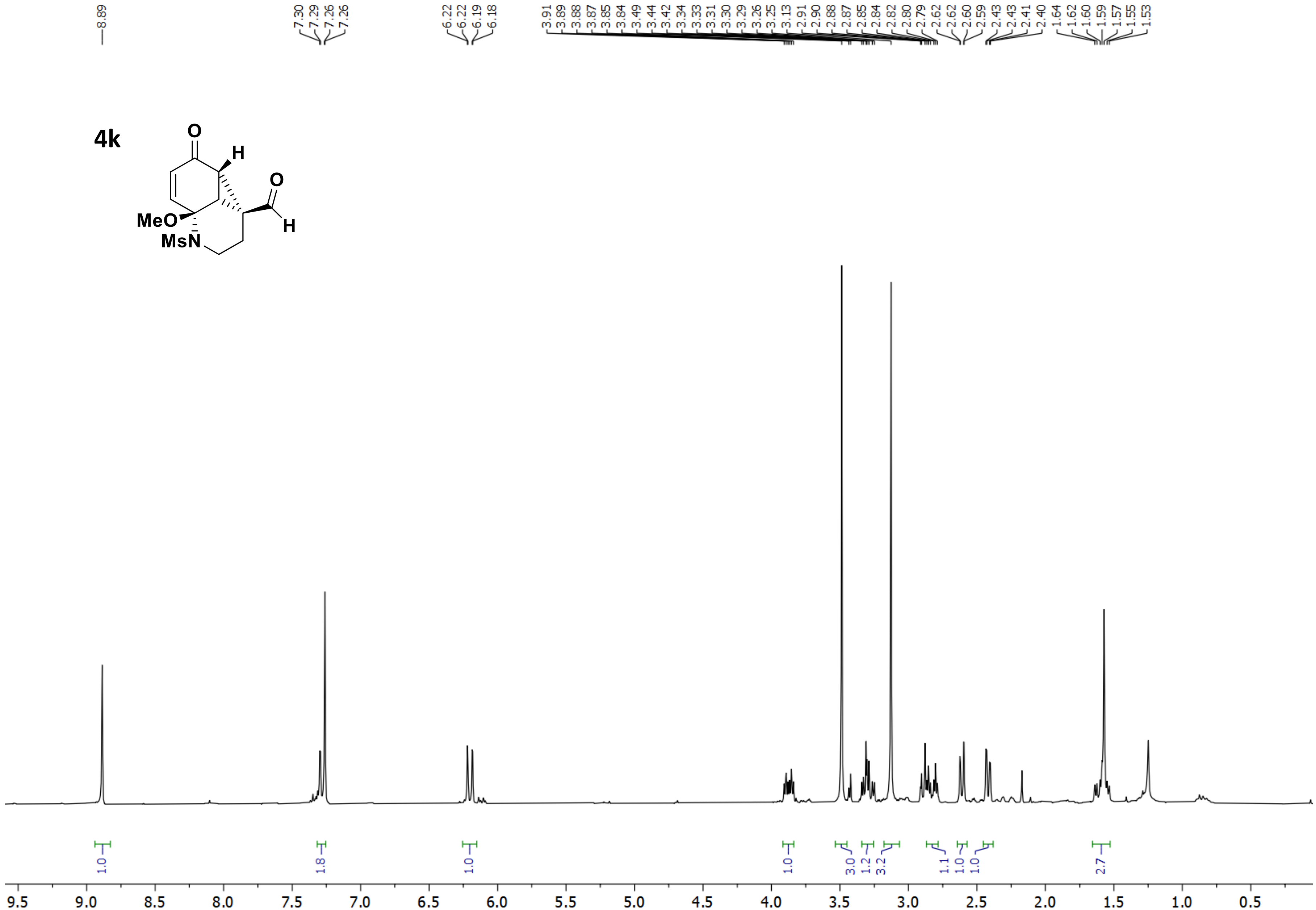


75 MHz, $CDCl_3$


195.83
190.58
155.35
150.97
128.14
108.68
81.57
53.73
45.42
38.90
35.33
25.75
4j
O
H
O
H
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

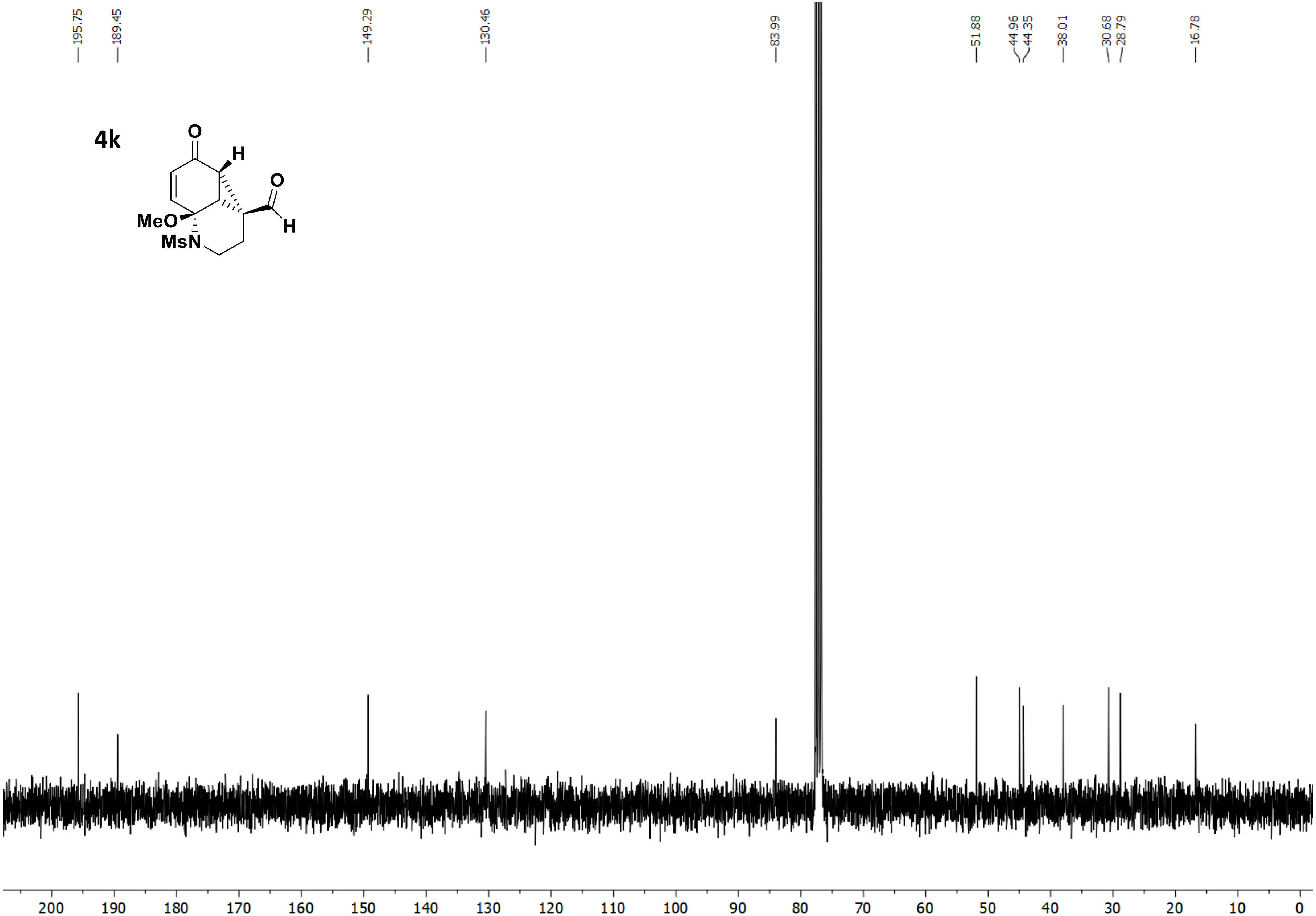
300 MHz, $CDCl_3$

4k



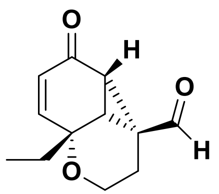
75 MHz, $CDCl_3$

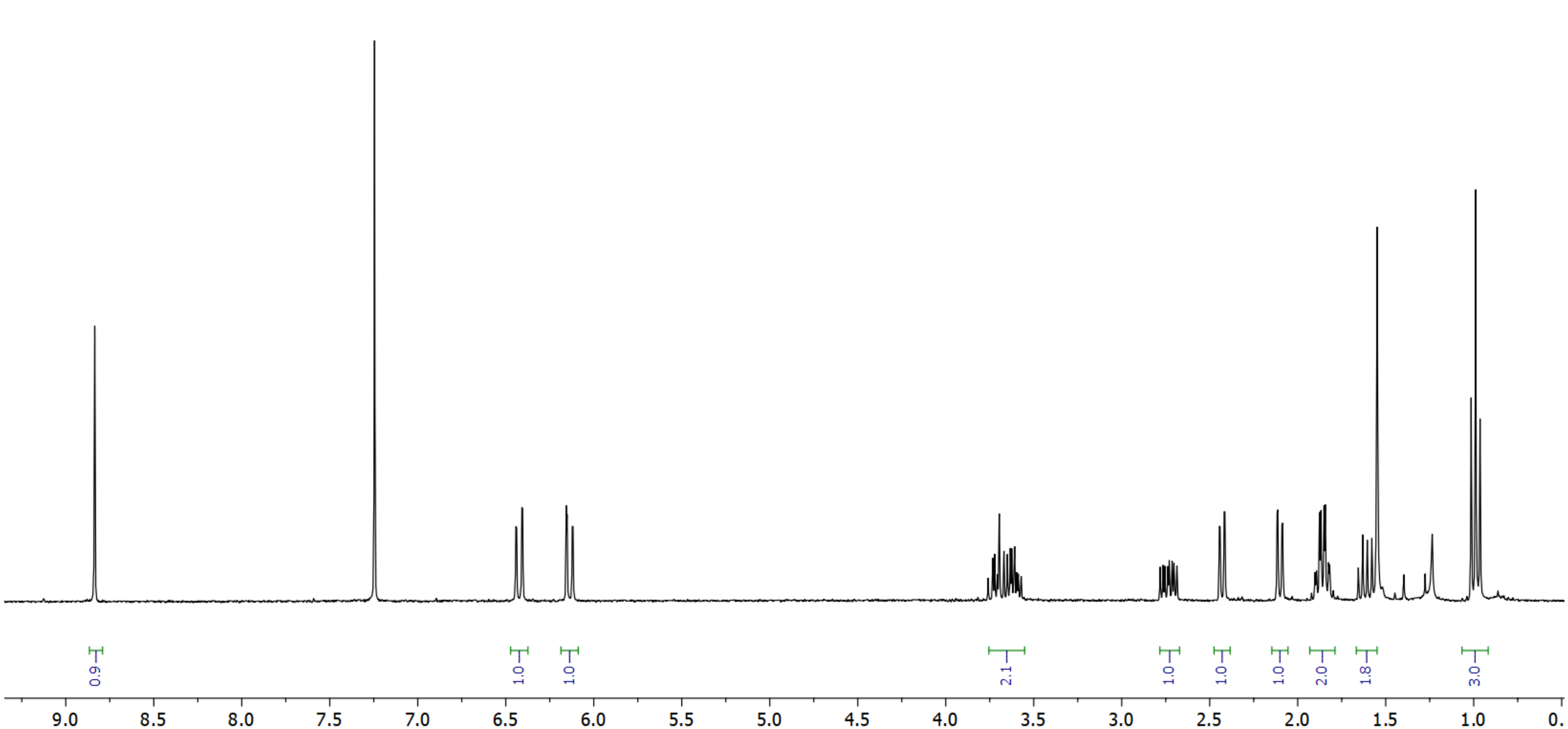
4k



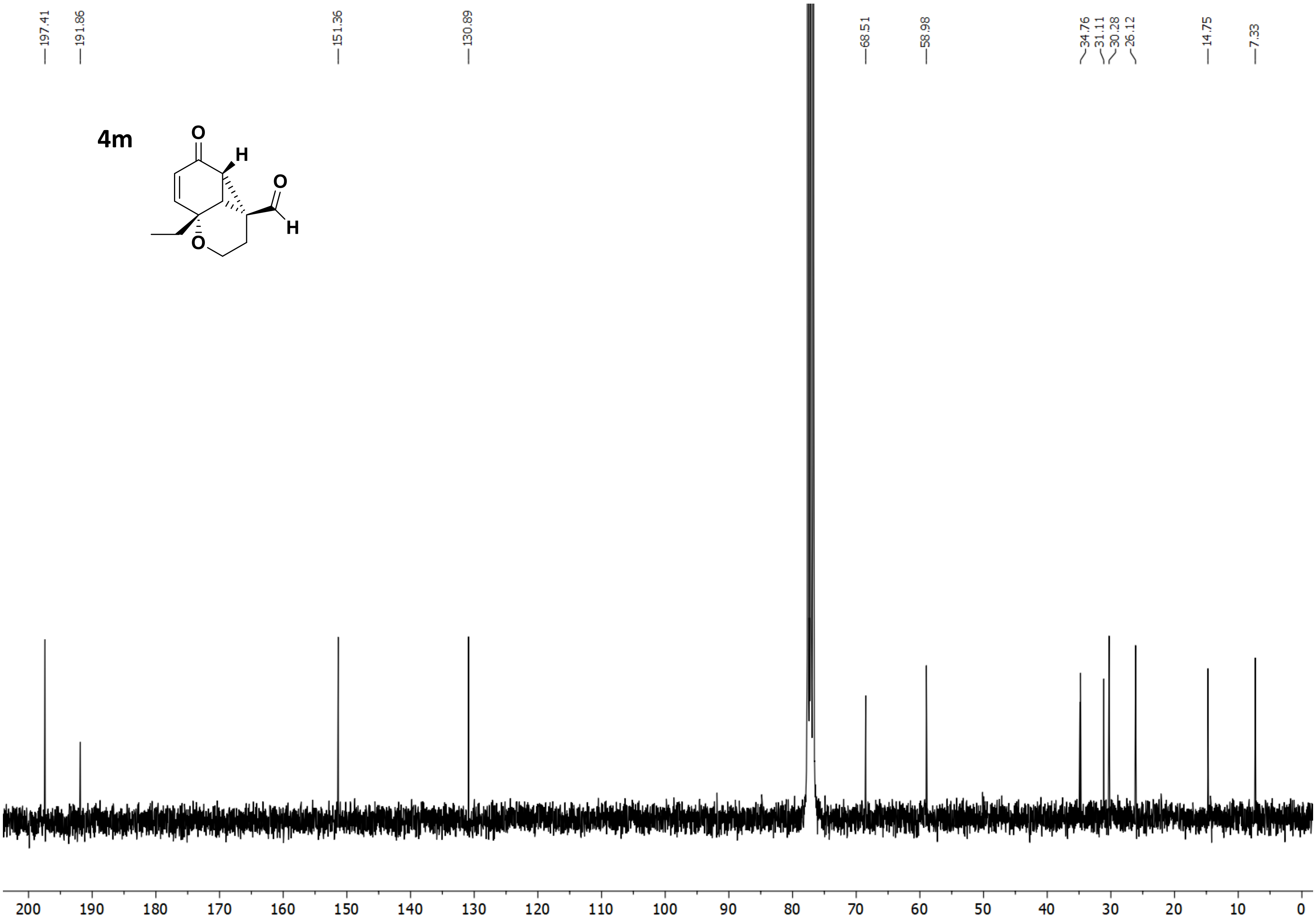
300 MHz, $CDCl_3$

4m

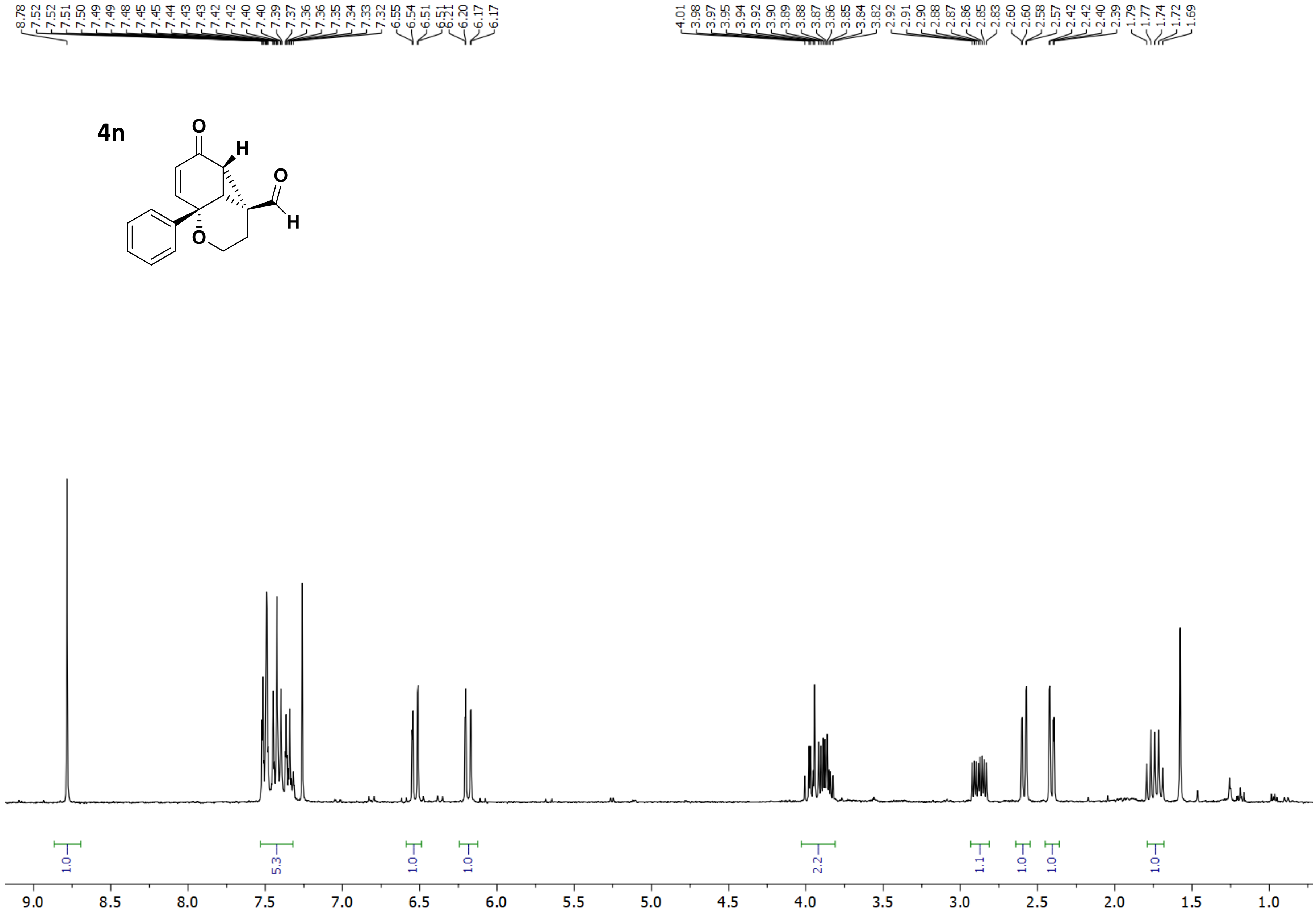




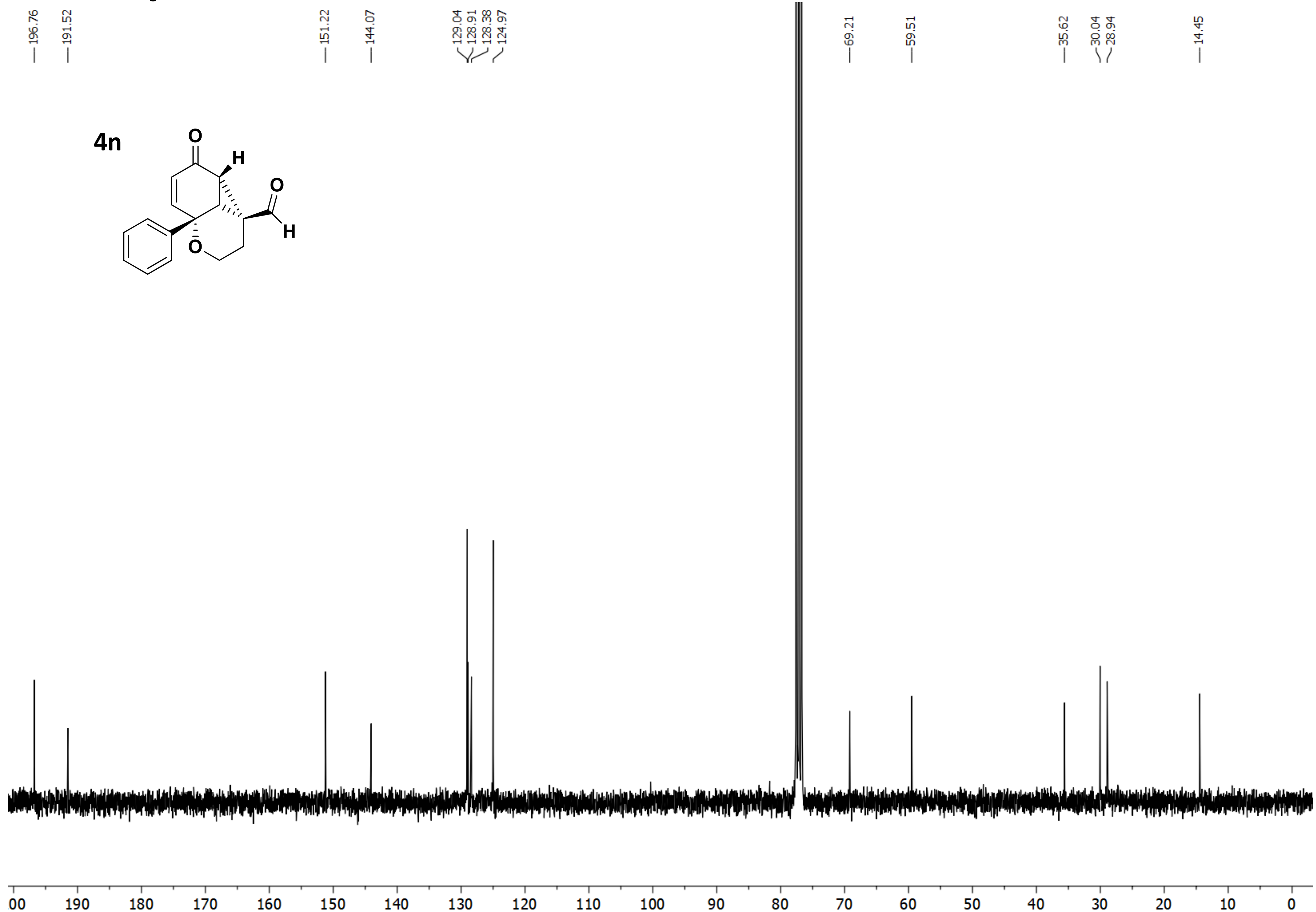
75 MHz, $CDCl_3$


197.41
191.86
151.36
130.89
68.51
58.98
34.76
31.11
30.28
26.12
14.75
7.33
4m
O
H
O
H
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

300 MHz, $CDCl_3$

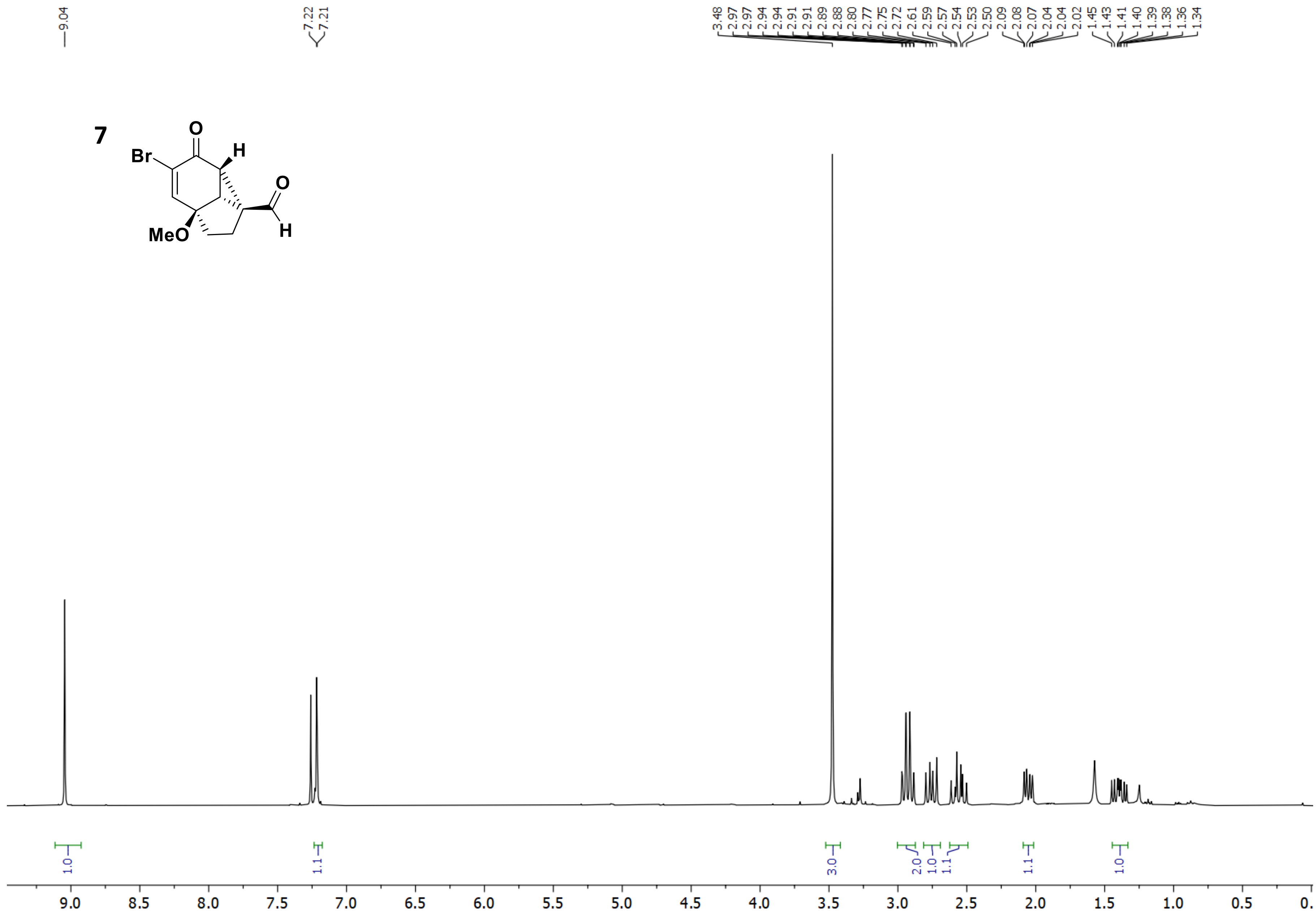


75 MHz, $CDCl_3$

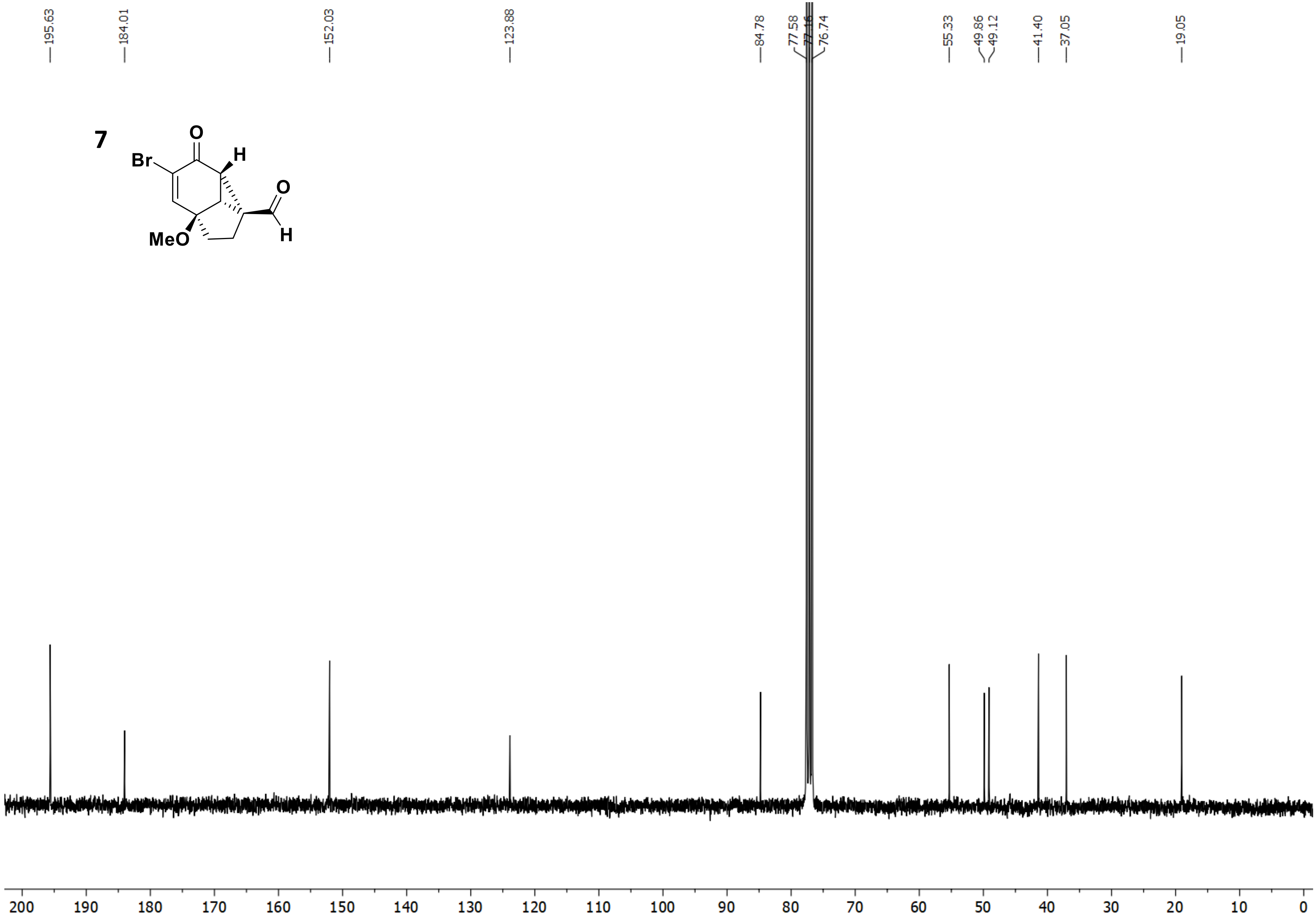

196.76
191.52
151.22
144.07
129.04
128.91
128.38
124.97
69.21
59.51
35.62
30.04
28.94
14.45
4n
O
H
O
H
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

300 MHz, $CDCl_3$

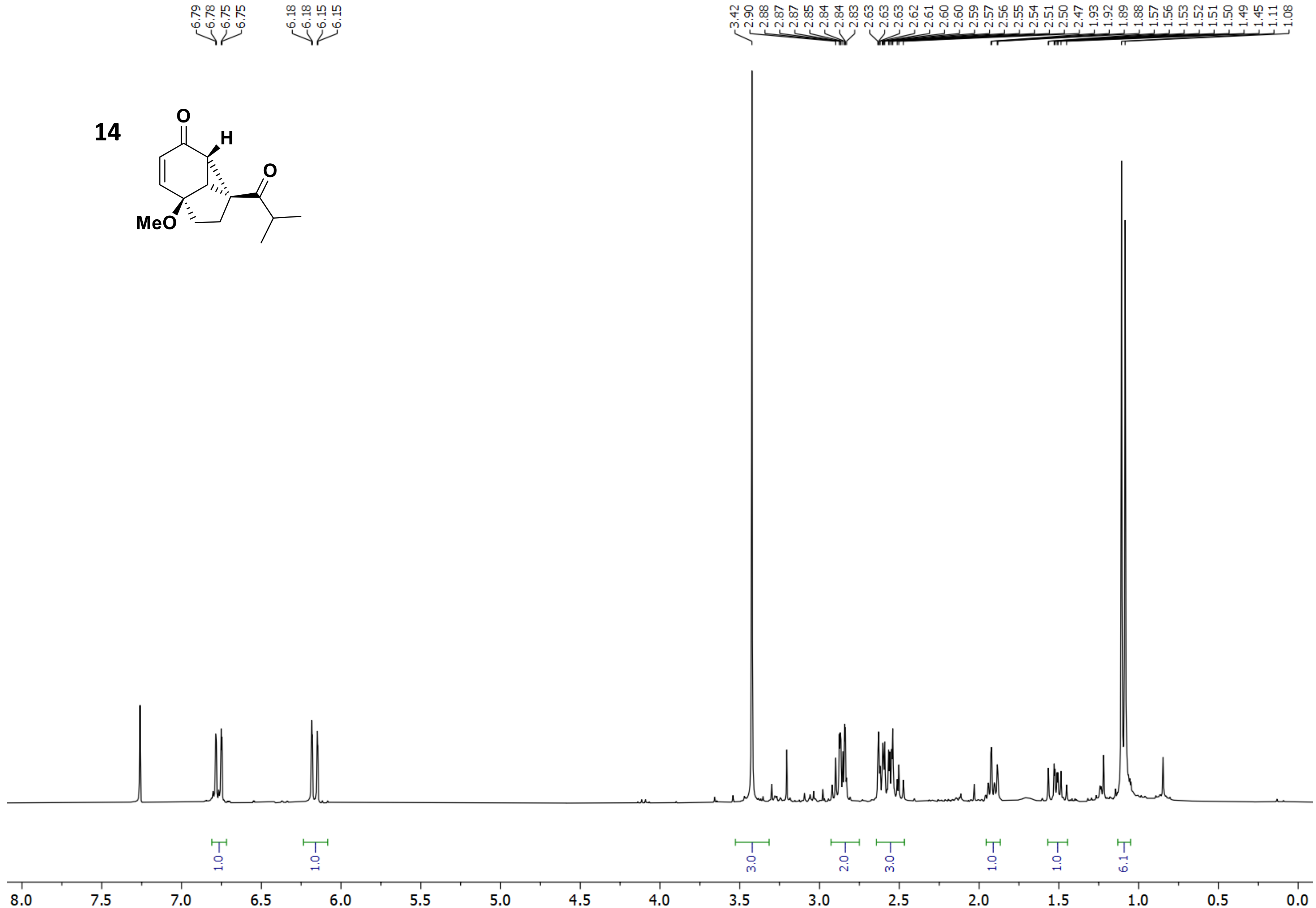
7



75 MHz, $CDCl_3$

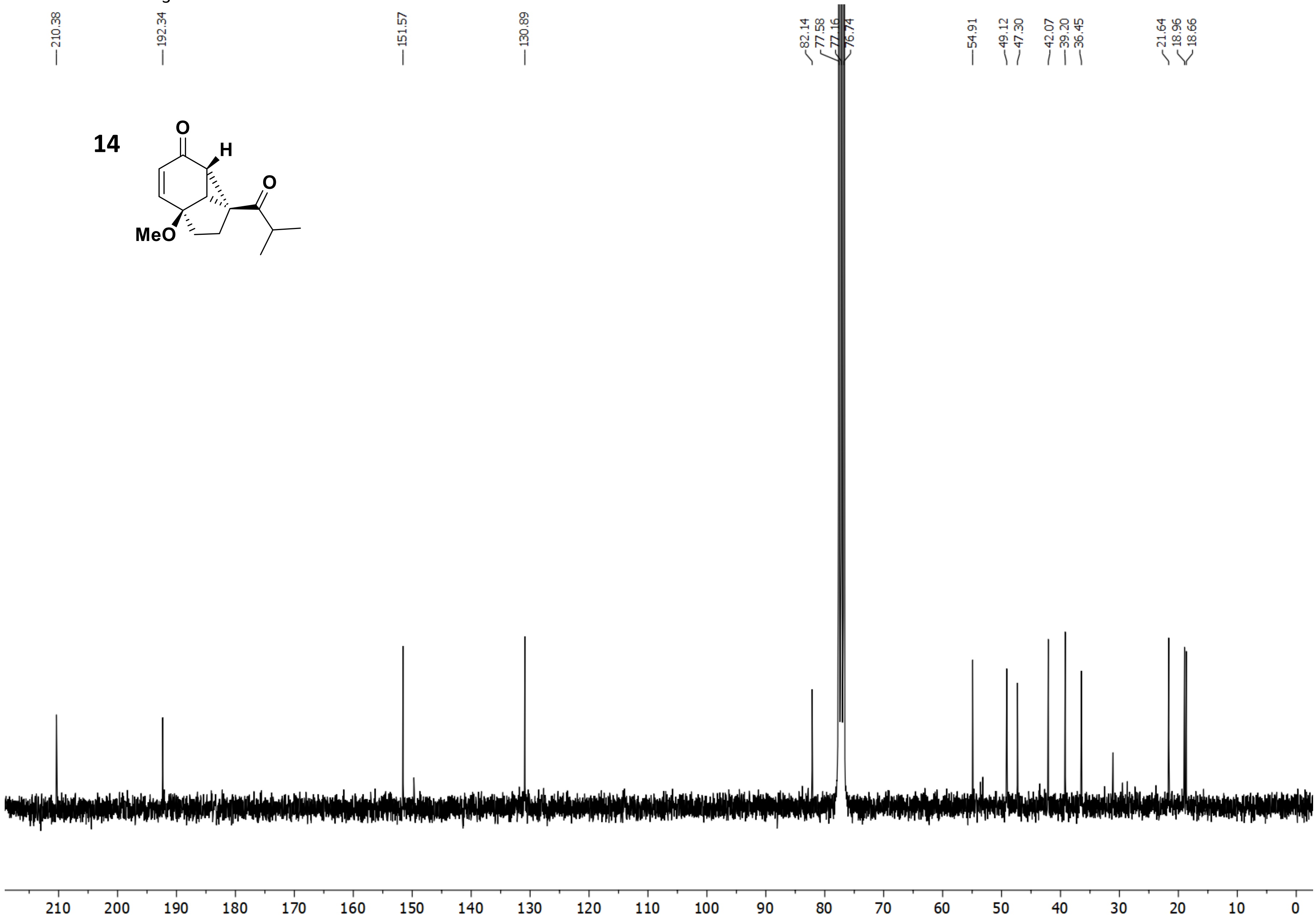

195.63
184.01
152.03
123.88
84.78
77.58
77.16
76.74
55.33
49.86
49.12
41.40
37.05
19.05
7
Br
O
H
O
H
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

300 MHz, $CDCl_3$



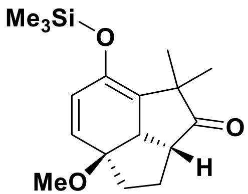
300 MHz, $CDCl_3$

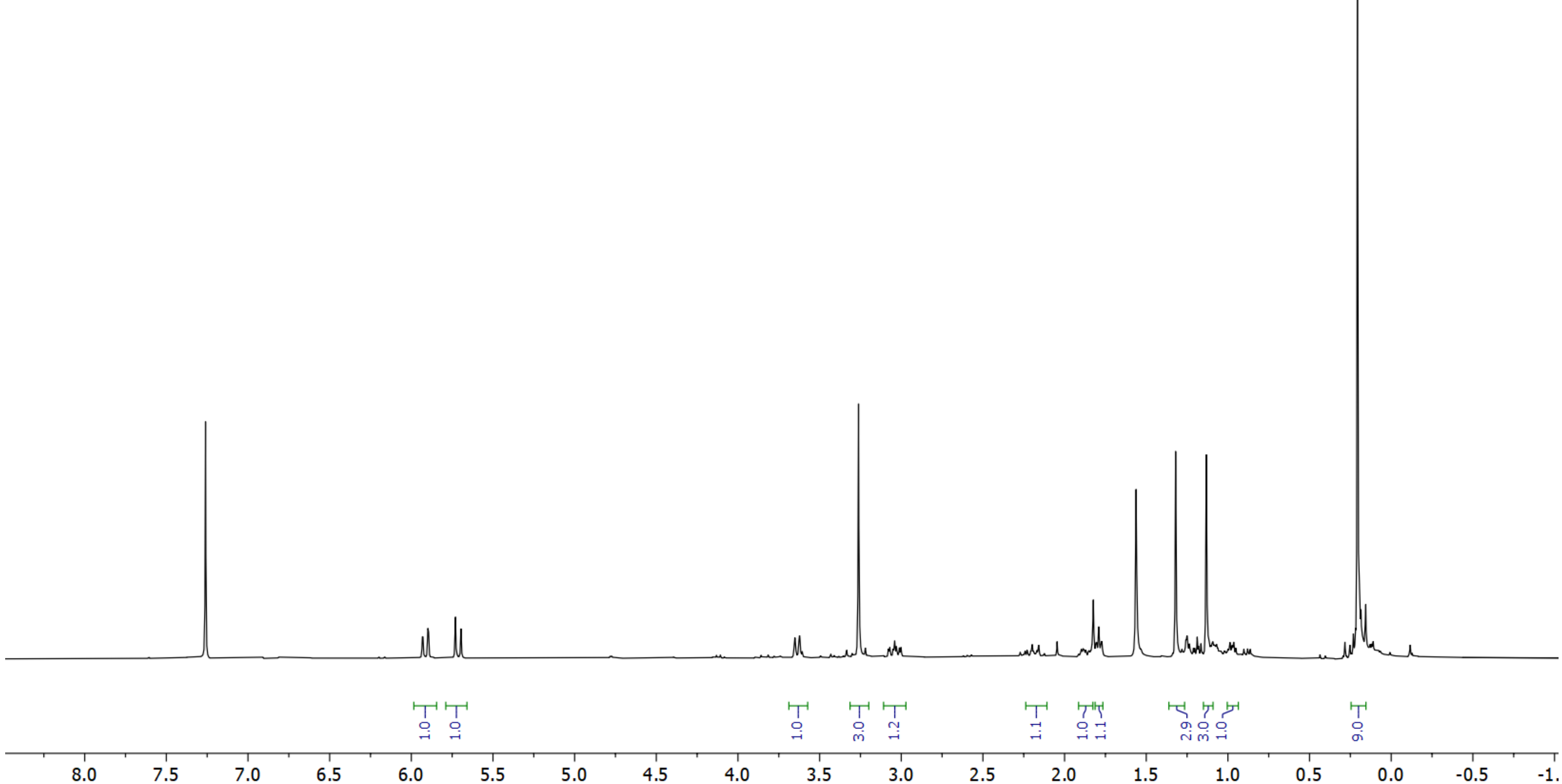
14



300 MHz, $CDCl_3$

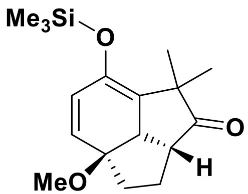
18

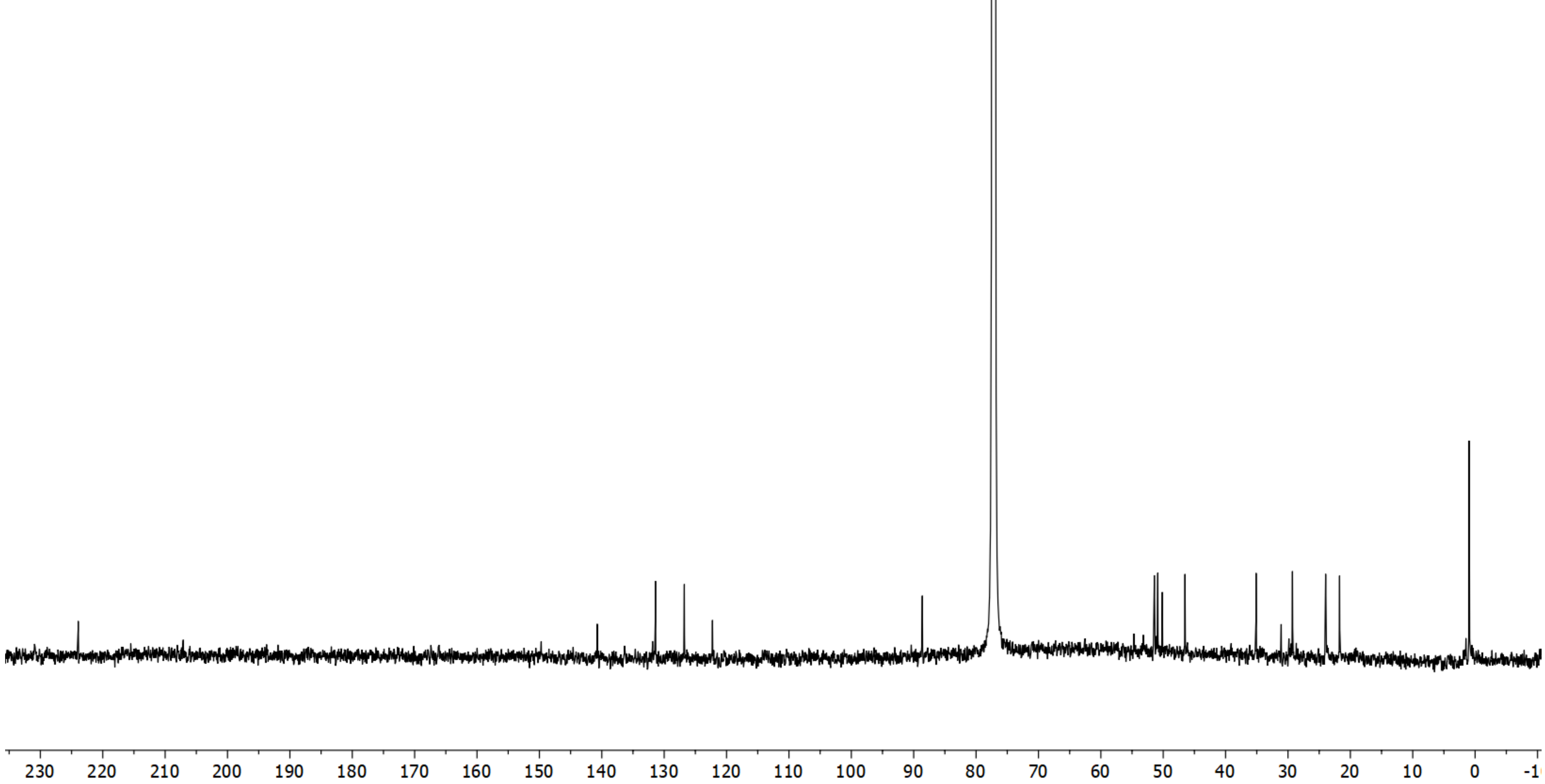




150 MHz, $CDCl_3$

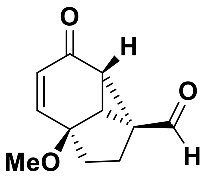
18

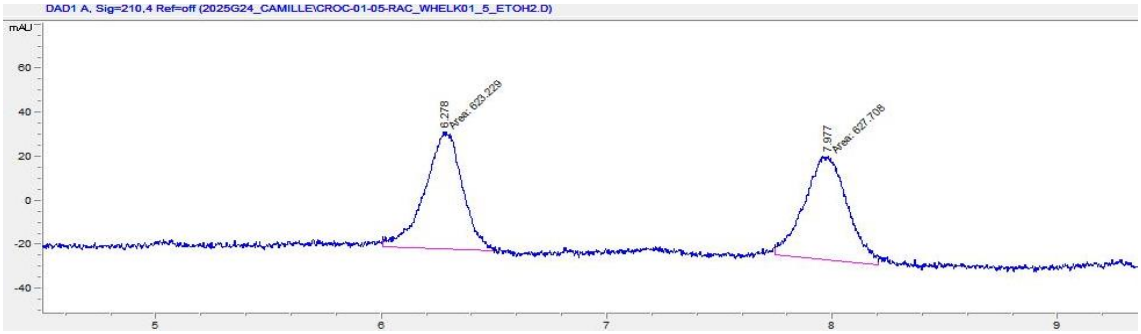




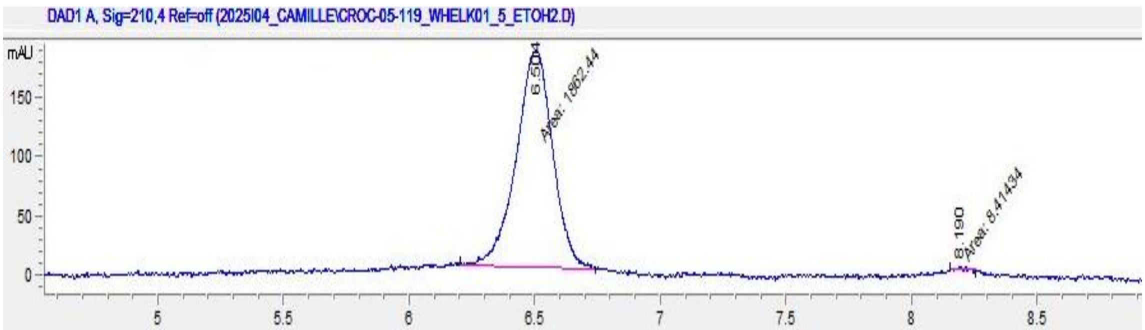
V. SFC Data

4a



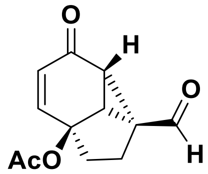


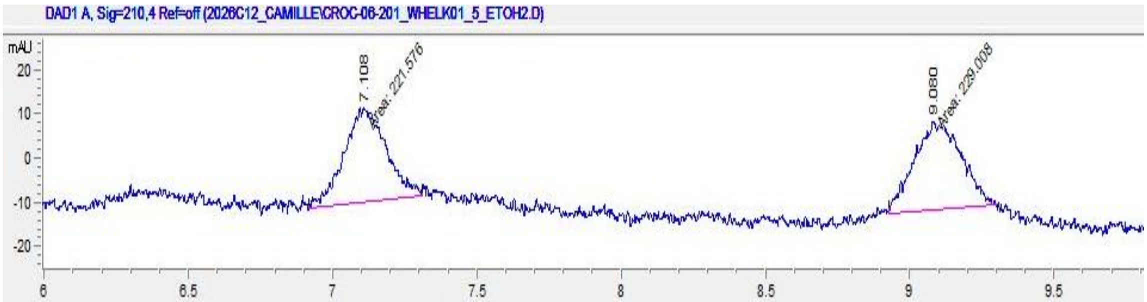
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.278	MM	0.1939	623.22888	53.56251	49.8210
2	7.977	MM	0.2210	627.70813	47.34914	50.1790



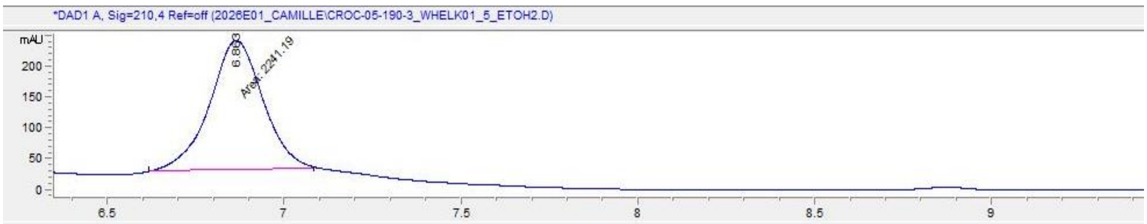
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.504	MM	0.1690	1862.43933	183.69395	99.5502
2	8.190	MM	0.0391	8.41434	3.58861	0.4498

4b



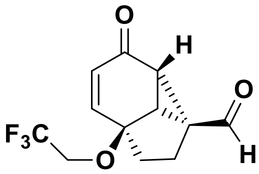


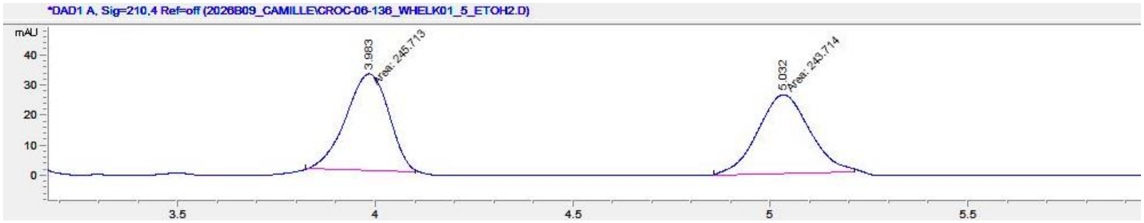
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.108	MM	0.1733	221.57628	21.30997	49.1753
2	9.080	MM	0.1892	229.00830	20.17492	50.8247



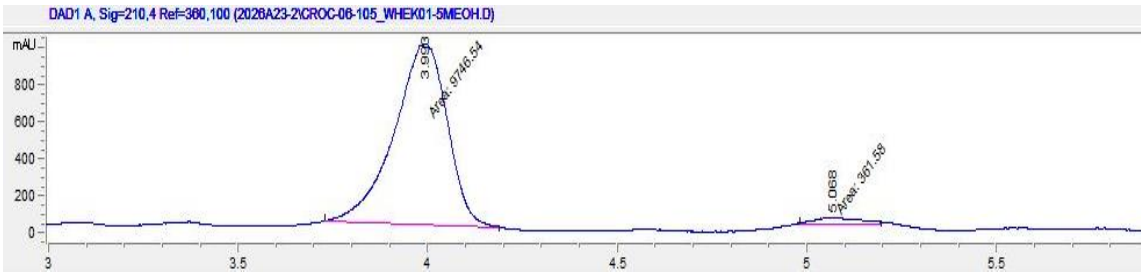
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.863	MM	0.1769	2241.18677	211.20183	100.0000

4c



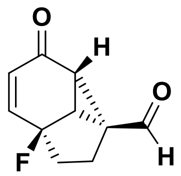


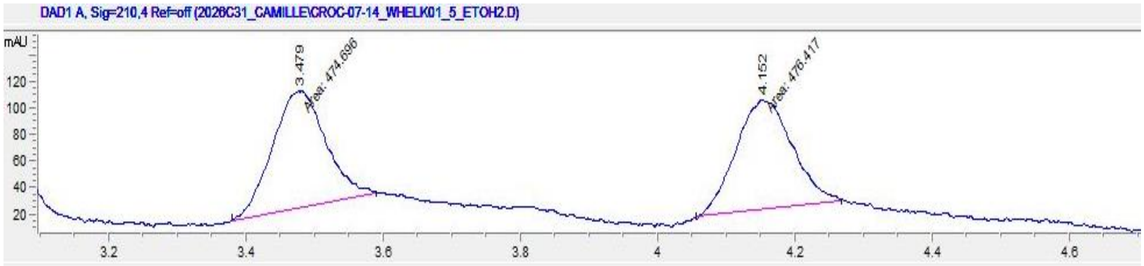
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.983	MM	0.1269	245.71318	32.25959	50.2043
2	5.032	MM	0.1538	243.71353	26.40890	49.7957



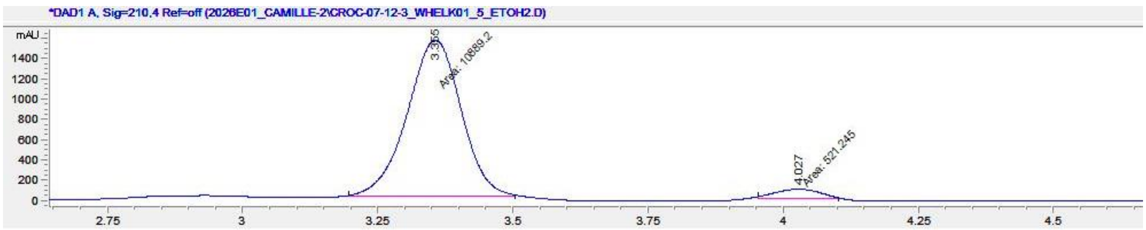
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.993	MM	0.1649	9746.53613	985.09729	96.4229
2	5.068	MM	0.1524	361.57983	39.53909	3.5771

4d



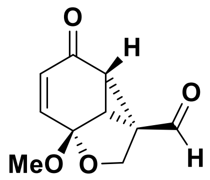


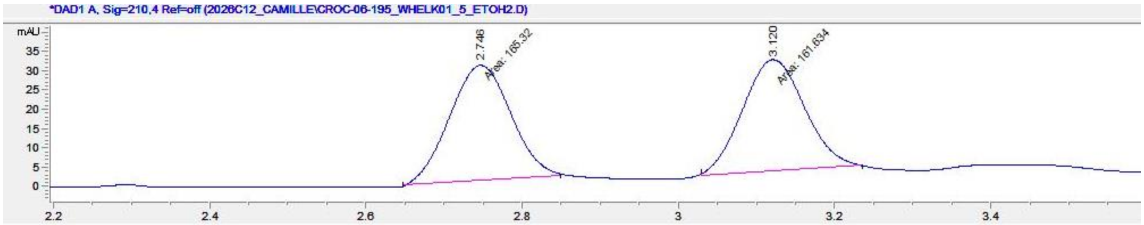
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.479	MM	0.0902	474.69595	87.67290	49.9095
2	4.152	MM	0.0963	476.41663	82.48325	50.0905



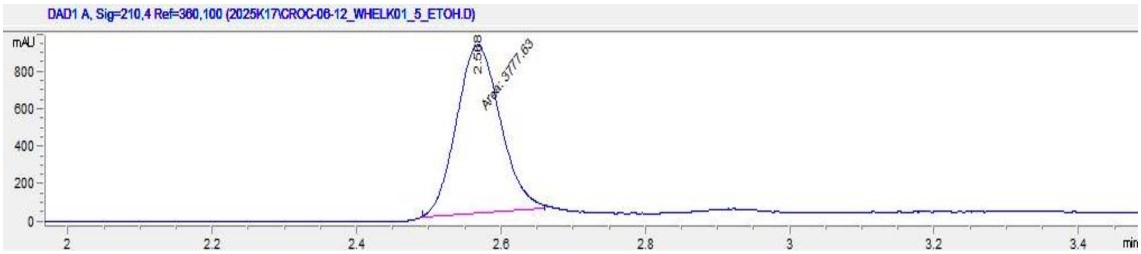
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.355	MM	0.1167	1.08892e4	1554.89746	95.4319
2	4.027	MM	0.0950	521.24524	91.43199	4.5681

4e



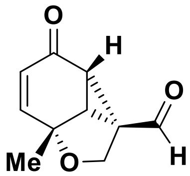


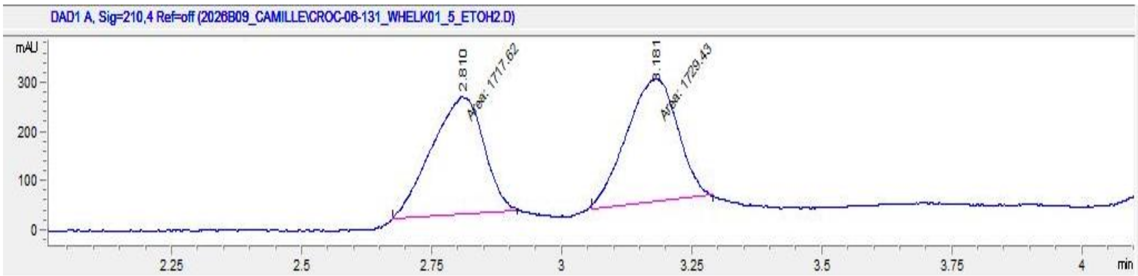
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.746	MM	0.0914	165.32037	30.15174	50.5638
2	3.120	MM	0.0923	161.63367	29.18751	49.4362



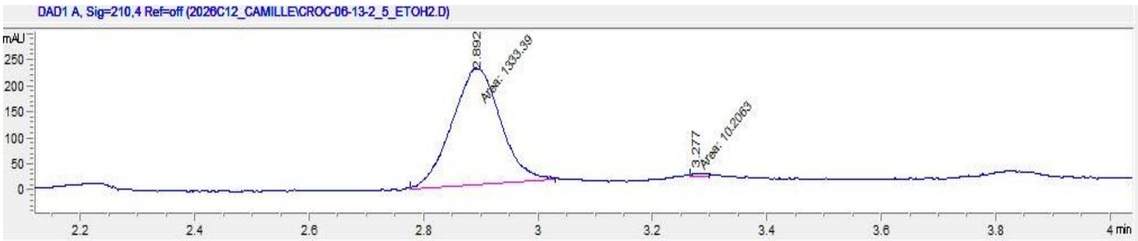
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.568	MM	0.0700	3777.62793	899.01526	100.0000

4f



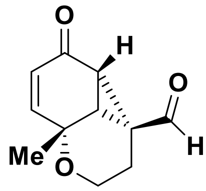


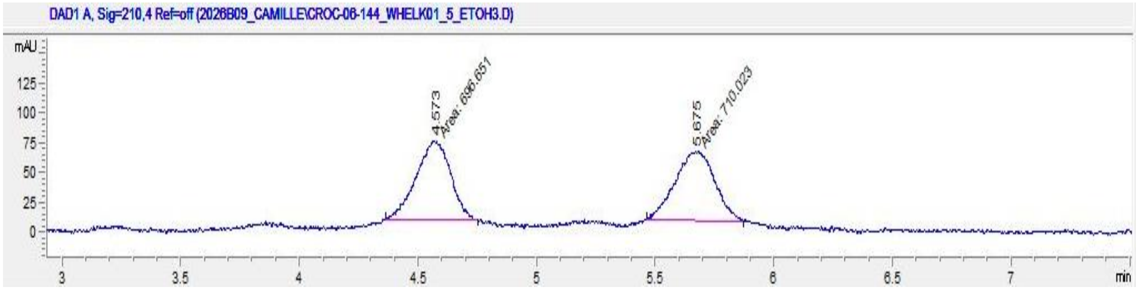
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.810	MM	0.1185	1717.62158	241.54477	49.8288
2	3.181	MM	0.1143	1729.42566	252.27144	50.1712



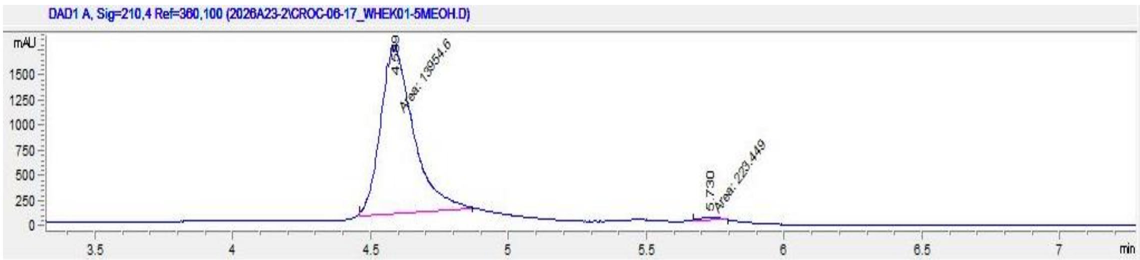
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.892	MM	0.0990	1333.38916	224.57745	99.2404
2	3.277	MM	0.0268	10.20633	6.34251	0.7596

4g



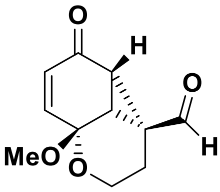


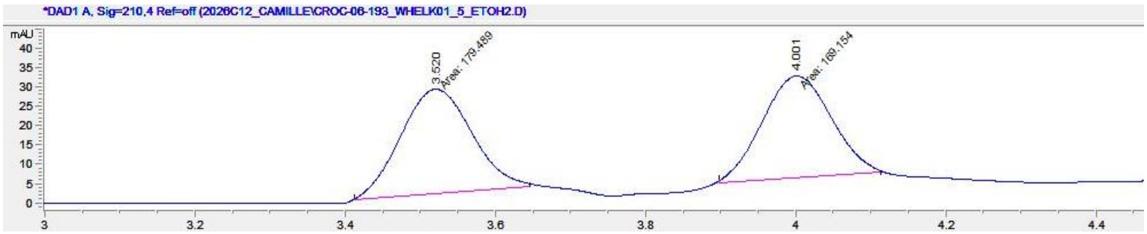
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.573	MM	0.1730	696.65051	67.13091	49.5247
2	5.675	MM	0.2010	710.02289	58.86599	50.4753



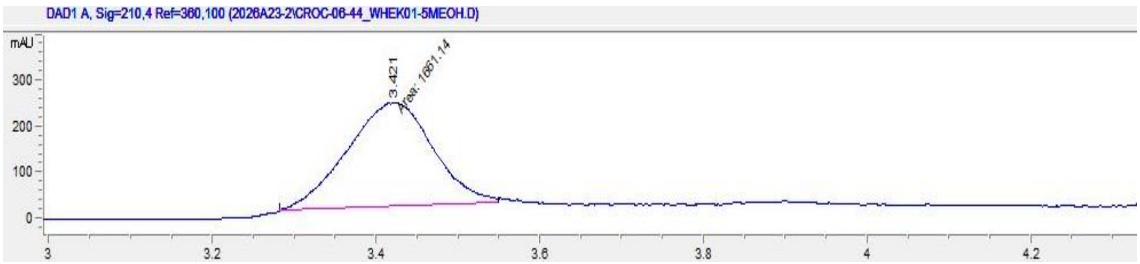
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.589	MM	0.1366	1.39546e4	1702.69104	98.4240
2	5.730	MM	0.0901	223.44878	41.34848	1.5760

4h



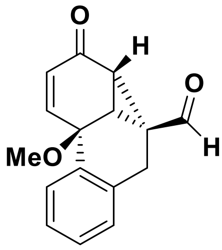


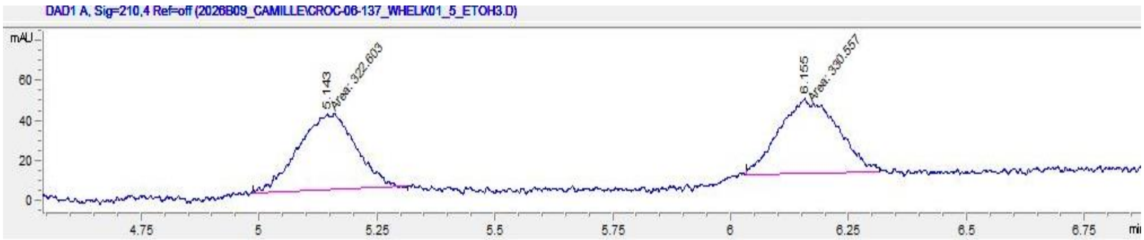
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.520	MM	0.1101	179.48927	27.16604	51.4822
2	4.001	MM	0.1066	169.15430	26.45795	48.5178



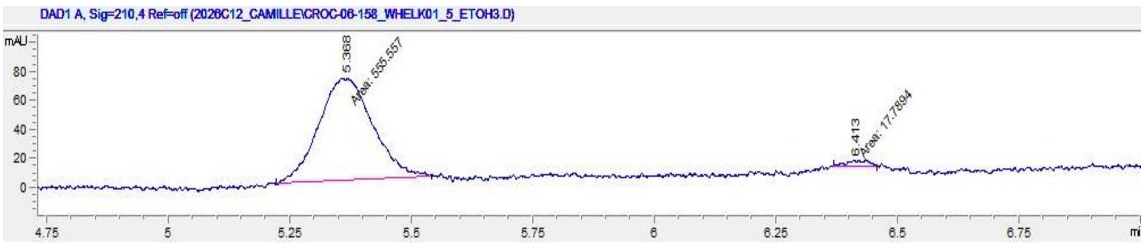
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.421	MM	0.1230	1661.13525	225.10950	100.0000

4i



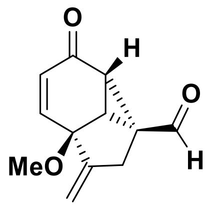


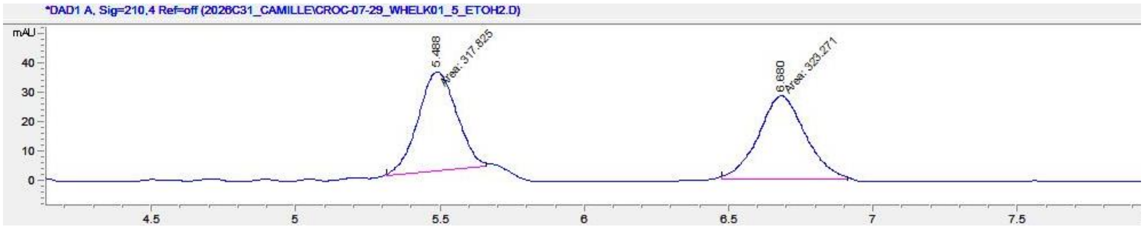
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.143	MM	0.1428	322.60297	37.65620	49.3911
2	6.155	MM	0.1457	330.55746	37.80771	50.6089



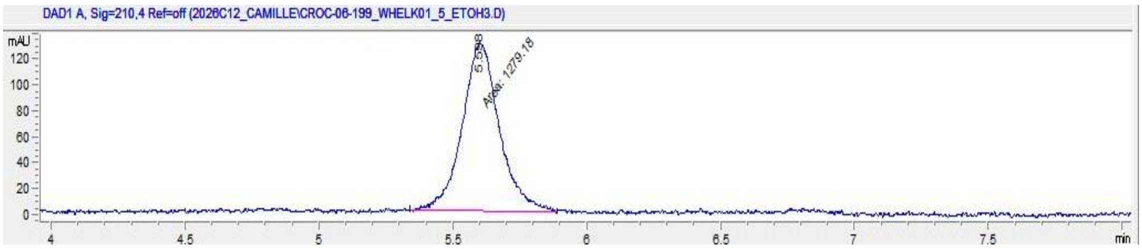
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.368	MM	0.1304	555.55688	71.00947	96.8973
2	6.413	MM	0.0578	17.78943	4.77731	3.1027

4j



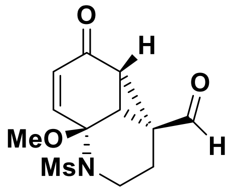


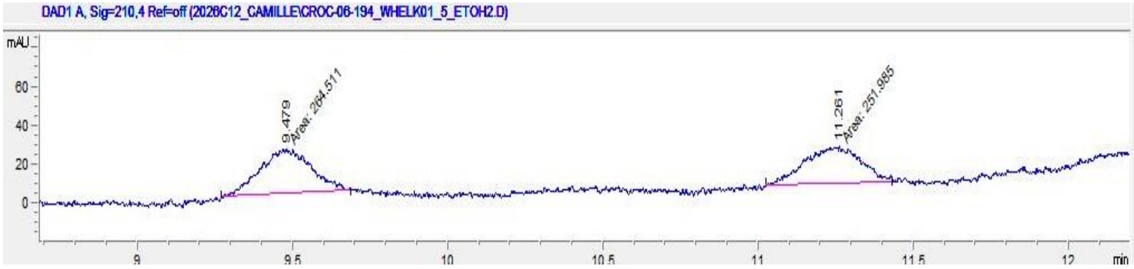
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.488	MM	0.1560	317.82529	33.95380	49.5753
2	6.680	MM	0.1895	323.27106	28.43896	50.4247



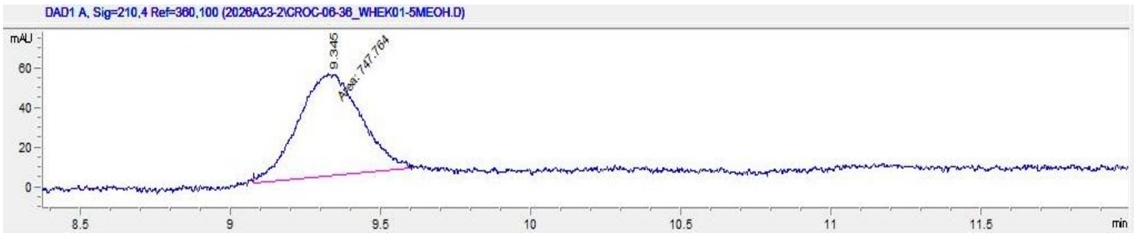
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.598	MM	0.1629	1279.17725	130.86551	100.0000

4k



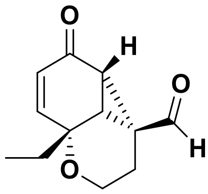


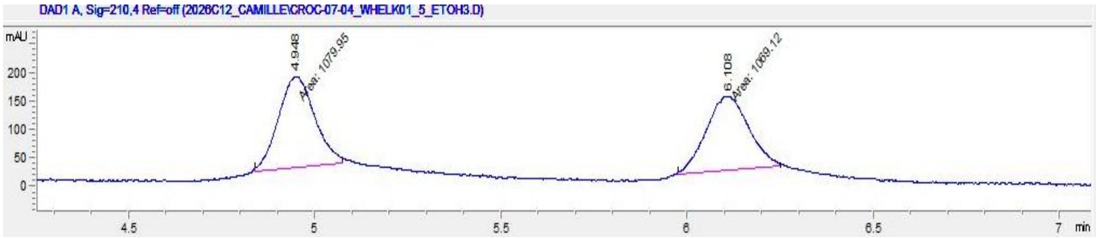
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.479	MM	0.1926	264.51114	22.88813	51.2126
2	11.261	MM	0.2176	251.98503	19.30073	48.7874



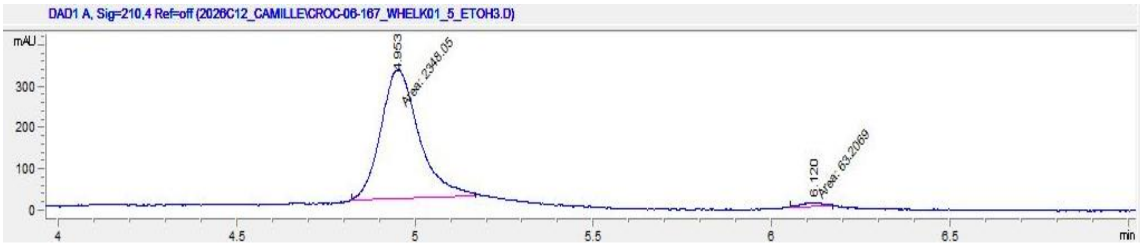
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.345	MM	0.2438	747.76410	51.10913	100.0000

4m



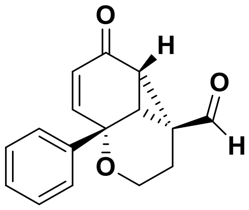


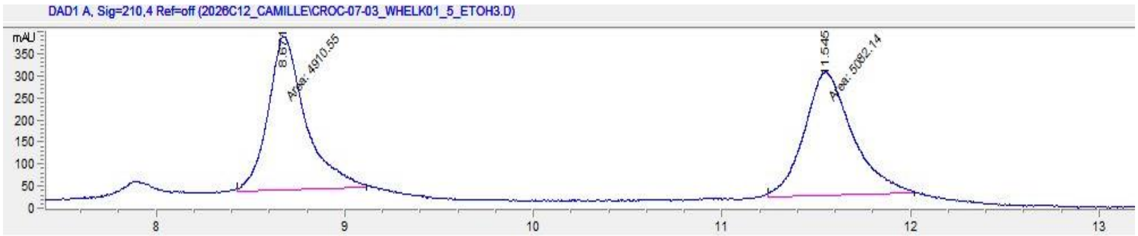
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.948	MM	0.1125	1079.95032	159.99591	50.2520
2	6.108	MM	0.1344	1069.12109	132.54465	49.7480



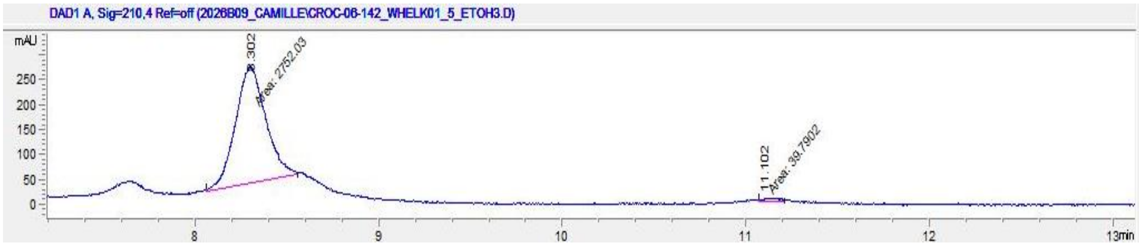
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.953	MM	0.1248	2348.05078	313.45291	97.3787
2	6.120	MM	0.0824	63.20691	12.78045	2.6213

4n



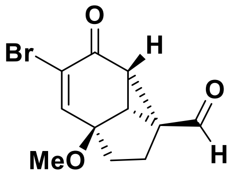


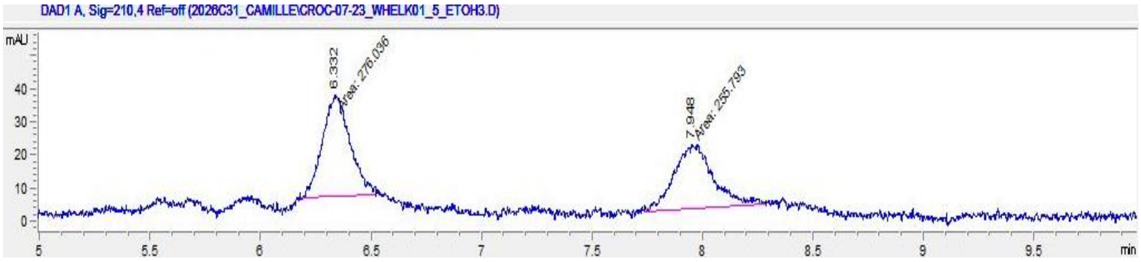
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.671	MM	0.2325	4910.55176	351.97272	49.0758
2	11.545	MM	0.2976	5082.13525	284.64313	50.7906



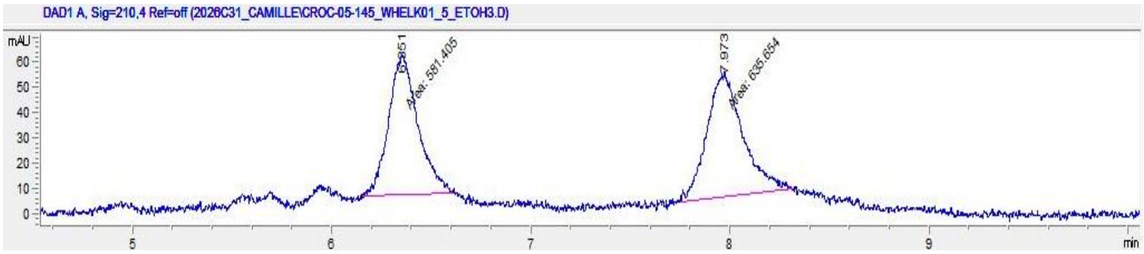
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.302	MM	0.1944	2752.02759	235.89568	98.5748
2	11.102	MM	0.0935	39.79016	7.09435	1.4252

7





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.332	MM	0.1483	276.03586	31.02280	51.9031
2	7.948	MM	0.2135	255.79294	19.97233	48.0969



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.351	MM	0.1735	581.40460	55.86452	47.7713
2	7.973	MM	0.2135	635.65350	49.62439	52.2287