Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information (ESI)

Lewis/Brønsted acid promoted highly diastereoselective access to polyfunctionalized 1,3-oxazines

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Experimental section for the synthesis and characterization of compounds and copies of ^{1}HNMR and ^{13}CNMR spectra of the compounds

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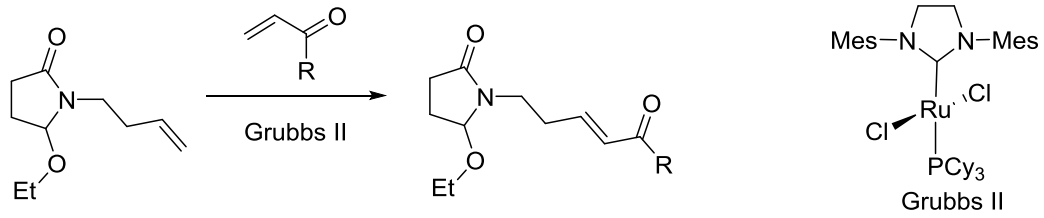
Experimental

General information

Reactions were carried out under argon with magnetic stirring and degassed solvents. Et_2O, CH_2Cl_2 and THF were distilled over alumina on a dry solvent station GT S100. Thin layer chromatography (TLC) was carried out on silica gel plates (Merck 60F254) and the spots were visualized under UV lamp (254 or 365 nm) and sprayed with phosphomolybdic acid solution (25 g phosphomolybdic acid, 10 g cerium sulfate, 60 mL H_2SO_4, 940 mL H_2O) followed by heating on a hot plate. For column chromatography, silica gel (Merck Si 60 40-60 µm) was used. IR spectra were recorded on Bruker Alpha (ATR) spectrophotomer. The melting points were measured using a Bibby Stuart Scientific model 7SMP3. ^{1}H NMR spectra were recorded at 500 MHz (Bruker AC-500) and ^{13}C NMR spectra at 125 MHz (Bruker AC-500) using the signal of the residual non deuterated solvent as internal reference. Significant 1H NMR data are tabulated in the following order: chemical shift (δ) expressed in ppm, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constants in hertz, number of protons. High-resolution mass spectra (HRMS) were performed on an Agilent 6520 Accurate Mass Q-TOF.

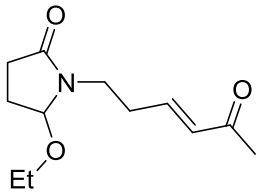
General procedure for the formation of α,β-unsaturated ketones 1a, 1c-j, (+)-6, (+)-7, (+)-8, 17-20



General remark : Grubbs II was always used as cross metathesis catalyst;

A solution of 1-(but-3-en-1-yl)-5-ethoxypyrrolidin-2-one (1.0 eq)[1], the corresponding keto derivative (2.5 eq), and Grubbs second-generation catalyst (0.03 eq) in CH_2Cl_2 (c = 0.1 M) was stirred at 40 °C for 3h. After concentration, the crude product was purified by silica-gel column chromatography (CH_2Cl_2/acetone 90/10 to 70/30)

*Compound **1a : (E)-5-ethoxy-1-(5-oxohex-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{12}H_{19}NO_3$
Exact Mass: 225,1365
Colorless oil
yield: 89 %

^{1}H NMR (500 MHz, $CDCl_3$)

[1] Koseki, Y.; Fujino, K.; Takeshita, A.; Sato, H.; Nagasaka, T. *Tetrahedron: Asymmetry* **2007**, *18*, 1533-1539

δ= 1.16 (t, J = 7.0 Hz, 3H) ; 1.92 (m, 1H) ; 2.08 (m, 1H) ; 2.17 (s, 3H) ; 2.23 (m, 1H) ; 2.44 (m, 3H) ; 3.27 (m, 1H) ; 3.4 (m, 2H) ; 3.50 (m, 1H) ; 4.87 (dd, J = 6.4 Hz, 1.6 Hz, 1H) ; 6.02 (dt, J = 16.0 Hz, 1.6 Hz, 1H) ; 6.70 (dt, J = 16.1 Hz, 7.1 Hz, 1H) ppm.

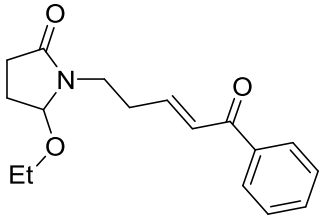
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 15.3 (CH_3) ; 24.8 (CH_2) ; 26.8 (CH_3) ; 28.9 (CH_2) ; 31.2 (CH_2) ; 39.3 (CH_2) ; 61.5 (CH_2) ; 89.4 (CH) ; 132.7 (=CH) ; 144.6 (=CH) ; 175.0 (CON) ; 198.5 (CO) ppm.

iR (ATR) : ν (CO) = 1672, 1627 cm^{-1}, ν (HC=CH) = 926 cm^{-1}.

HRMS (ESI) m/z : $C_{12}H_{19}NO_3$ $[M + Na]^+$ calc. 248.1263, found. 248.1257

*Compound **1c : (E)-5-ethoxy-1-(5-oxo-5-phenylpent-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{17}H_{21}NO_3$
Exact Mass: 287,1521

Colorless oil
yield: 79 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.20 (t, J = 7.0 Hz, 3H) ; 1.96 (m, 1H) ; 2.10 (m, 1H) ; 2.27 (ddd, J = 17.3 Hz, 9.8 Hz, 3.2 Hz, 1H) ; 2.54 (m, 3H) ; 3.33 (m, 1H) ; 3.44 (q, J = 7.0 Hz, 2H) ; 3.62 (m, 1H) ; 4.92 (dd, J = 6.3 Hz, 1.6 Hz, 1H) ; 6.94 (m, 2H) ; 7.43 (m, 2H) ; 7.53 (m, 1H) ; 7.41 (m, 2H) ppm.

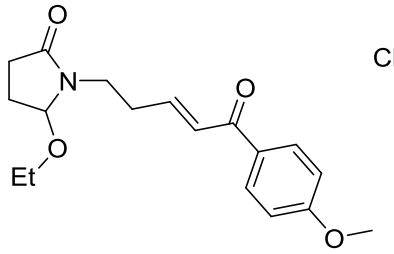
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 15.3 (CH_3) ; 24.8 (CH_2) ; 28.9 (CH_2) ; 31.2 (CH_2) ; 39.4 (CH_2) ; 61.6 (CH_2) ; 89.5 (CH) ; 127.5 (=CH) ; 128.6 (4 =CH) ;132.8 (=CH) ; 137.6 (Cq) ; 145.5 (=CH) ; 175.0 (CON) ; 190.5 (CO) ppm.

iR (ATR) : ν (CO) = 1694, 1671 cm^{-1}

HRMS (ESI) m/z : $C_{17}H_{21}NO_3$ $[M +K]^+$ calc. 326.1158, found. 326.1153

*Compound **1d : (E)-5-ethoxy-1-(5-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{18}H_{23}NO_4$
Exact Mass: 317,1627

Colorless oil
yield: 88 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.19 (t, J = 7.0 Hz, 3H) ; 1.94 (m, 1H) ; 2.09 (m, 1H) ; 2.27 (ddd, J = 17.3 Hz, 10.0 Hz, 3.1 Hz, 1H) ; 2.53 (m, 3H) ; 3.31 (m, 1H) ; 3.44 (q, J = 7.0 Hz, 2H) ; 3.64 (m, 1H) ; 3.83 (s, 3H) ; 4.92 (dd, J = 6.4 Hz, 1.5 Hz, 1H) ; 6.92 (m, 4H) ; 7.92 (d, J = 9.0 Hz, 2H) ppm.

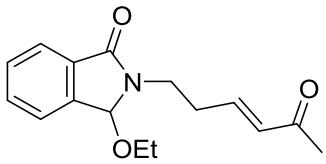
^{13}C NMR (125 MHz, $CDCl_3$)

δ = 15.3 (CH_3) ; 24.8 (CH_2) ; 29.0 (CH_2) ; 31.1 (CH_2) ; 39.4 (CH_2) ; 55.5 (CH_3) ; 61.6 (CH_2) ; 89.5 (CH) ; 113.8 (2 =CH) ; 127.2 (=CH) ; 130.5 (Cq) ; 131.0 (2 =CH) ; 144.4 (=CH) ; 163.4 (Cq) ; 175.1 (CON) ; 188.7 (CO) ppm.

IR (ATR) : ν (CO) = 1693, 1598 cm^{-1}

HRMS (ESI) m/z : $C_{18}H_{23}NO_4$ $[M+Na]^+$ calc. 340.1525, found. 340.1519

*Compound **1e : (E)-3-ethoxy-2-(5-oxohex-3-en-1-yl) isoindolin-1-one**



Chemical Formula: $C_{16}H_{19}NO_3$
Exact Mass: 273,1365

Colorless oil
yield: 80 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.11 (t, J = 7.1 Hz, 3H) ; 2.21 (s, 3H) ; 2.60 (m, 2H) ; 2.97 (m, 1H) ; 3.12 (m, 1H) ; 3.43 (m, 1H) ; 3.89 (m, 1H) ; 5.83 (s, 1H) ; 6.1 (d, J = 16.2 Hz, 1H) ; 6.79 (m, 1H) ; 7.51 (m, 3H) ; 7.78 (d, J = 7.3 Hz, 1H) ppm.

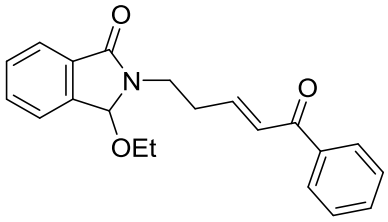
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 15.1 (CH_3) ; 26.9 (CH_3) ; 31.6 (CH_2) ; 38.2 (CH_2) ; 57.8 (CH_2) ; 86.2 (CH) ; 123.4 (=CH) ; 123.5 (=CH) ; 130.0 (=CH) ; 132.2 (=CH) ; 132.5 (Cq) ; 133.0 (=CH) ; 140.9 (Cq) ; 144.3 (=CH) ; 167.7 (CON) ; 198.4 (CO) ppm.

iR (ATR) : ν (CO) = 1696, 1673 cm^{-1}, ν (Ar) = 745 cm^{-1}.

HRMS (ESI) m/z : $C_{16}H_{19}NO_3$ $[M + Na]^+$ calc. 296.1263, found. 296.1257

*Compound **1f : (E)-3-ethoxy-2-(5-oxo-5-phenylpent-3-en-1-yl) isoindolin-1-one**



Chemical Formula: $C_{21}H_{21}NO_3$
Exact Mass: 335,1521
Colorless oil
yield: 89 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.11 (t, J = 7.0Hz, 3H) ; 2.71 (m, 2H) ; 2.98 (m, 1H) ; 3.14 (m, 1H) ; 3.48 (qt, J = 7.0Hz, 1H) ; 3.97 (qt, J = 7.0 Hz, 1H) ; 5.86 (s, 1H) ; 7.00 (m, 2H) ; 7.47 (m, 6H) ; 7.80 (d, J = 7.0 Hz, 1H) ; 7.87 (d, J = 7.8 Hz, 2H) ppm.

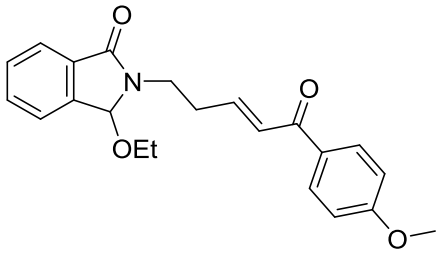
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 14.1 (CH_3) ; 31.6 (CH_2) ; 38.2 (CH_2) ; 57.8 (CH_2) ; 86.3 (CH) ; 123.4 (=CH) ; 123.5 (=CH) ; 127.7 (=CH) ; 128.6 (2 =CH) ; 128.7 (2 =CH) ; 130.0 (=CH) ; 132.1 (=CH) ; 132.7 (Cq) ; 132.8 (=CH) ; 137.6 (Cq) ; 140.9 (Cq) ; 145.2 (=CH) ; 167.6 (CON) ; 190.5 (CO) ppm.

iR (ATR) : ν (CO) = 1698, 1670 cm^{-1}, ν (Ar) = 745, 695 cm^{-1}.

HRMS (ESI) m/z : $C_{21}H_{21}NO_3$ $[M + Na]^+$ calc. 358.1419, found. 358.1414

*Compound **1g : (E)-3-ethoxy-2-(5-(4-methoxyphenyl)-5-oxopent-3-en-1-yl) isoindolin-1-one**



Chemical Formula: $C_{22}H_{23}NO_4$
Exact Mass: 365,1627
Colorless oil
yield: 84 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.11 (t, J = 7.0Hz, 3H) ; 2.69 (m, 2H) ; 2.98 (m, 1H) ; 3.14 (m, 1H) ; 3.47 (qu, J = 7.0Hz, 1H) ; 3.82 (s, 3H) ; 3.96 (qu, J = 7.0 Hz, 1H) ; 5.86 (s, 1H) ; 6.89 (d, J = 8.9 Hz, 2H) ; 6.99 (m, 2H) ; 7.51 (m, 3H) ; 7.79 (d, J = 7.4 Hz, 1H) ; 7.89 (d, J = 8.9 Hz, 1H) ppm.

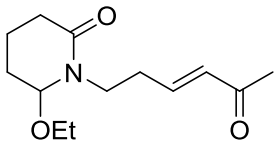
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 15.1 (CH_3) ; 31.5 (CH_2) ; 38.3 (CH_2) ; 55.5 (CH_3) ; 57.8 (CH_2) ; 86.3 (CH) ; 113.8 (2 =CH) ; 123.4 (=CH) ; 123.5 (=CH) ; 127.4 (=CH) ; 129.9 (=CH) ; 130.4 (Cq) ; 130.9 (2 =CH) ; 132.1 (=CH) ; 132.7 (Cq) ; 140.9 (Cq) ; 144.0 (=CH) ; 163.4 (Cq) ; 167.6 (CON) ; 188.6 (CO) ppm.

iR (ATR) : ν (CO) = 1699, 1597 cm^{-1}, ν (Ar) = 746 cm^{-1}.

HRMS (ESI) m/z : $C_{22}H_{23}NO_4$ $[M + Na]^+$ calc. 388.1525, found. 388.1519

*Compound **1h : (E)-6-ethoxy-1-(5-oxohex-3-en-1-yl) piperidin-2-one**



Chemical Formula: $C_{13}H_{21}NO_3$
Exact Mass: 239,1521
Colorless liquid
yield: 88 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.19 (t, J = 7.0 Hz, 3H, C**H$_3$**CH_2O) ; 1.66 (m, 2H) ; 1.95 (m, 2H) ; 2.19 (s, 3H, C**H$_3$**-CO) ; 2.25 (m, 1H) ; 2.45 (m, 3H) ; 3.32 (m, 1H) ; 3.40 (m, 1H) ; 3.49 (m, 1H) ; 3.60 (m, 1H) ; 4.51 (t, J = 3.01 Hz, 1H, OCHN) ; 6.02 (dt , J = 16.1 Hz, 1.6 Hz, 1H, CH=C**H**-CO) ; 6.74 (dt, J = 16.1 Hz, 7.1 Hz, 1H, C**H**=CH-CO) ppm.

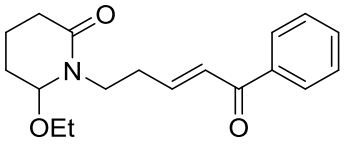
^{13}C NMR (125 MHz, $CDCl_3$)

δ = 15.4 (**C**H_3-CH_2O) ; 15.8 (-CH_2-**C**H_2-CH_2-) ; 26.8 (**C**H_3-CO) ; 27.1 (CH_2) ; 31.5 (CH_2) ; 32.4 (CH_2) ; 44.8 (CH_2-**C**H_2N) ; 63.3 (CH_3-**C**H_2O) ; 86.9 (O**C**HN) ; 132.5 (CH=**C**H-CO) ; 145.2 (**C**H=CH-CO) ; 170.3 (CON) ; 198.6 (CO) ppm.

iR (ATR) : ν (CO) : 1672, 1648 cm^{-1}.

HRMS (ESI) m/z : $C_{13}H_{21}NO_3$ $[M + Na]^+$ calc. 262.1419, found. 262.1414

*Compound **1i : (E)-6-ethoxy-1-(5-oxo-5-phenylpent-3-en-1-yl)piperidin-2-one**



Chemical Formula: $C_{18}H_{23}NO_3$
Exact Mass: 301,1678
Colorless oil
yield: 71 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.21 (t, J = 7.0 Hz, 3H, C**H**$_3$CH$_2$O) ; 1.64 (m, 2H) ; 1.98 (m, 2H) ; 2.28 (m, 1H) ; 2.43 (m, 1H) ; 2.63 (m, 2H) ; 3.34 (m, 1H) ; 3.44 (m, 1H, CH$_3$C**H**$_2$O) ; 3.50 (m, 1H) ; 3.72 (m, 1H, CH$_3$C**H**$_2$O) ; 4.54 (t, J = 3.0 Hz, 1H, OC**H**N) ; 6.95 (m, 2H) ; 7.44 (m, 2H) ; 7.53 (m, 1H) ; 7.91 (d, J = 8.3 Hz, 2H) ppm.

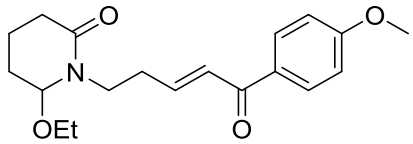
^{13}C NMR (125 MHz, CDCl$_3$)

δ = 15.4 (**C**H$_3$CH$_2$O) ; 15.9 ((-CH$_2$-**C**H$_2$-CH$_2$-) ; 27.0 (CH$_2$) ; 31.7 (CH$_2$) ; 32.5 (CH$_2$) ; 45.2 (CH$_2$-**C**H$_2$N) ; 63.4 (CH$_3$**C**H$_2$O) ; 87.4 (O**C**HN) ; 127.4 (=CH) ; 128.6 (4 =CH) ; 132.8 (=CH) ; 137.7 (Cq) ; 146.2 (=CH) ; 170.4 (CON) ; 190.7 (CO) ppm.

iR (ATR) : ν (CO) : 1649, 1621 cm^{-1} , ν (Ar) : 697 cm^{-1}

HRMS (ESI) m/z : C$_{18}$H$_{23}$NO$_3$ [M + Na]$^+$ calc. 324.1576, found. 324.1570

*Compound **1j : (E)-6-ethoxy-1-(5-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)piperidin-2-one**



Chemical Formula: C$_{19}$H$_{25}$NO$_4$
Exact Mass: 331,1784
Colorless oil
yield: 86 %

^{1}H NMR (500 MHz, CDCl$_3$)

δ = 1.21 (t, J = 7.0 Hz, 3H, C**H**$_3$CH$_2$O) ; 1.63 (m, 2H) ; 1.97 (m, 2H) ; 2.27 (m, 1H) ; 2.44 (m, 1H) ; 2.63 (m, 2H) ; 3.31 (m, 1H) ; 3.47 (m, 2H, CH$_3$C**H**$_2$O) ; 3.74 (m, 1H) ; 3.84 (s, 3H, OC**H**$_3$) ; 4.54 (t, J = 3.0 Hz, 1H, OC**H**N) ; 6.92 (m, 4H) ; 7.92 (d, J = 8.9 Hz, 2H) ppm.

^{13}C NMR (125 MHz, CDCl$_3$)

δ = 15.4 (**C**H$_3$CH$_2$O) ; 15.9 ((-CH$_2$-**C**H$_2$-CH$_2$-) ; 27.0 (CH$_2$) ; 31.6 (CH$_2$) ; 32.4 (CH$_2$) ; 45.3 (CH$_2$-**C**H$_2$N) ; 55.5 (**C**H$_3$O) ; 63.4 (CH$_3$**C**H$_2$O) ; 87.4 (O**C**HN) ; 113.8 (2 =CH) ; 127.1 (=CH) ; 130.5 (Cq) ; 130.9 (2 =CH) ; 145.1 (=CH) ; 163.4 (Cq) ; 170.4 (CON) ; 188.8 (CO) ppm.

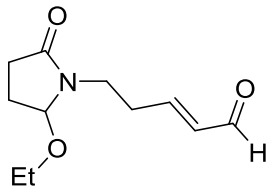
iR (ATR) : ν (CO) : 1648, 1598 cm^{-1}.

HRMS (ESI) m/z : C$_{19}$H$_{25}$NO$_4$ [M + Na]$^+$ calc. 354.1682, found. 354.1676

α,β-unsaturated aldehyde **1b**

A solution of alkene (110 mg, 0.60 mmol), acrolein (0.10 mL, 1.5 mmol), and Grubbs second-generation catalyst (15 mg, 0.018 mmol) in CH$_2$Cl$_2$ (6 mL) was stirred at 40 °C for 3h. After concentration, purification of the crude product by column chromatography (CH$_2$Cl$_2$/acetone 85/15 to 70/30) afforded **1b** (83 mg, 0.39 mmol, 65%).

Compound **1b : (E)-5-(2-ethoxy-5-oxopyrrolidin-1-yl)pent-2-enal**



Chemical Formula: $C_{11}H_{17}NO_3$
Exact Mass: 211,1208
Colorless oil
yield: 84 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.21 (t, J = 7.0 Hz, 3H) ; 1.97 (m, 1H) ; 2.12 (m, 1H) ; 2.29 (ddd, J = 17.3 Hz, 9.9 Hz, 3.1 Hz, 1H) ; 2.49 (m, 1H) ; 2.61 (m, 2H) ; 3.43 (m, 3H) ; 3.56 (m, 1H) ; 4.91(dd, J = 6.3 Hz, 1.6 Hz, 1H) ; 6.12 (ddt, J = 15.7 Hz, 7.8 Hz, 1.5 Hz, 1H) ; 6.81 (dt, J = 15.7 Hz, 7.0 Hz, 1H) ; 9.48 (d, J = 7.8 Hz, 1H) ppm.

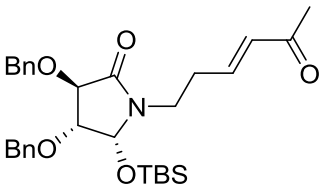
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 15.3 (CH_3) ; 24.8 (CH_2) ; 28.9 (CH_2) ; 31.5 (CH_2) ; 39.2 (CH_2) ; 61.5 (CH_2) ; 89.6 (CH) ; 134.3 (=CH) ; 154.7 (=CH) ; 175.1 (CON) ; 193.8 (CHO) ppm.

iR (ATR) : ν (CO) = 1687 cm^{-1}

HRMS (ESI) m/z : $C_{11}H_{17}NO_3$ $[M+H]^+$ calc. 212.1286 , found. 212.1281

*Compound **(+)-6 : (3R,4R,5R)-3,4-bis(benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-1-((E)-5-oxohex-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{30}H_{41}NO_5Si$
Exact Mass: 523,2754
Colorless oil
87 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 0.08 (s, 3H) ; 0.1 (s, 3H) ; 0.86 (s, 9H) ; 2.21 (s, 3H, C(O)C**H$_3$**) ; 2.48 (m, 2H, NCH_2C**H$_2$**) ; 3.29 (m, 1H, NC**H**$_2CH_2$) ; 3.48 (m, 1H, NC**H**$_2CH_2$) ; 3.87 (dd, J = 5.1 Hz, 3.1 Hz, 1H) ; 4.07 (d, J = 5.1 Hz, 1H) ; 4.46 (d, J = 11.2 Hz, 1H) ; 4.54 (d, J = 11.2 Hz, 1H) ; 4.79

(d, J = 11.5 Hz, 1H) ; 4.95 (d, J = 3.1 Hz, 1H) ; 5.1 (d, J = 11.5 Hz, 1H) ; 6.07 (d, J = 16.0 Hz, 1H) ; 6.71 (dt, J = 16.0 Hz, 7.0 Hz, 1H) ; 7.25 (m, 2H) ; 7.31 (m, 6H) ; 7.40 (m, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

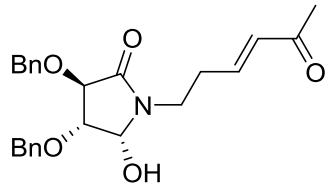
δ = -4.9 (CH_3) ; -4.3 (CH_3) ; 17.9 (Cq) ; 25.6 (3 CH_3) ; 26.9 (CH_3, C(O)**C**H_3) 31.0 (CH_2, NCH_2**C**H_2) ; 38.0 (CH_2, N**C**H_2CH_2) ; 72.2 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 79.6 (CH) ; 84.9 (CH) ; 86.2 (CH) ; 128.0 (=CH) ; 128.1 (3 =CH) ; 128.4 (2 =CH) ; 128.5 (2 =CH) ; 128.6 (2 =CH) ; 132.9 (=CH) ; 137.0 (=C) ; 137.4 (=C) ; 143.8 (=CH) ; 170.1 (CON) ; 198.4 (CO) ppm.

iR (ATR) : ν (CO) = 1704, 1676 cm^{-1}, ν (OTBS) = 1069, 838 cm^{-1}, ν (Ar) = 736 cm^{-1}.

HRMS (ESI) m/z : $C_{30}H_{41}NO_5Si$ $[M + Na]^+$ calc. 546.2652, found. 546.2646

$[\alpha]_D^{25}$: +44.6 (*c*=0.5, $CHCl_3$)

***Compound** **(+)-6a : (3R,4R,5R)-3,4-bis(benzyloxy)-5-hydroxy-1-((E)-5-oxohex-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{24}H_{27}NO_5$
Exact Mass: 409.1889
Colorless oil
88 %

To a solution of alkene **(+)-4** (0.500 g, 1.36 mmol) and methyl vinyl ketone **15** (0.3 mL, 3.6 mmol) in CH_2Cl_2 (15 mL) was added Grubbs second-generation catalyst (35 mg, 0.043 mmol) at room temperature. Then, the mixture was stirred at 40 °C for 3h. After concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (petroleum ether/AcOEt 70/30) to afford compound **(+)-6a** (0.490 g, 1.19 mmol, 88 %)

^{1}H NMR (500 MHz, $CDCl_3$): 2.16 (s, 3H, C(O)C**H**$_3$); 2.47 (m, 2H); 3.36 (m, 1H, NC**H**$_2$); 3.52 (m, 1H, NC**H**$_2$); 3.72 (d, J = 10.1 Hz, 1H); 3.87 (dd, J = 4.3 Hz, 2.8 Hz, 1H); 4.01 (d, J= 4.3 Hz, 1H); 4.53 (m, 2H, OC**H**$_2$Ph); 4.71 (d, J = 11.3 Hz, 1H); 4.9 (m, 1H, OC**H**$_2$Ph); 6.04 (dt, *J* = 16.1 Hz, 1.5 Hz, 1H, CH=C**H**-CO); 6.70 (dt, *J* = 16.0 Hz, 7.1 Hz, 1H, C**H**=CH-CO); 7.24-7.35 (m, 10H) ppm.

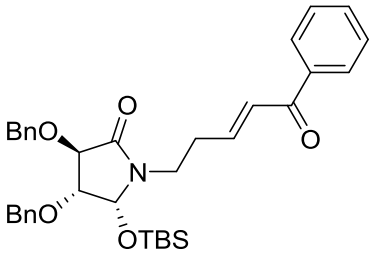
^{13}C NMR (125 MHz, $CDCl_3$): 27.0 (CH_3, C(O)**C**H_3) 30.9 (CH_2, NCH_2**C**H_2); 38.3 (CH_2, N**C**H_2CH_2); 72.3 (CH_2, O**C**H_2Ph); 72.8 (CH_2, O**C**H_2Ph); 79.1 (CH, **C**HOBn); 88.6 (CH, **C**HOBn); 85.3 (CH, O**C**HN); 127.9 (2 =CH); 128.1 (2 =CH); 128.3 (2 =CH); 128.5 (2 =CH); 128.6 (2 =CH); 132.8 (=CH); 137.0 (=C); 137.1 (=CH); 144.4 (=CH); 170.4 (CON); 198.9 (CO) ppm.

iR (ATR): ν (OH) = 3326 cm^{-1} ; ν (CO) = 1672, 1626 cm^{-1}

HRMS (ESI) m/z: $C_{24}H_{27}NO_5$ $[M + Na]^+$ calc.432.1787, found. 432.1791

$[\alpha]^{20}_D$: + 36.8 (*c* = 0.5, $CHCl_3$)

*Compound **(+)-7 : (3R,4R,5R)-3,4-bis(benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-1-((E)-5-oxo-5-phenylpent-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{35}H_{43}NO_5Si$
Exact Mass: 585,2911
Colorless oil
yield: 64 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 0.04 34(s, 3H) ; 0.08 (s, 3H) ; 0.84 (s, 9H) ; 2.52 (m, 2H, $NCH_2C\mathbf{H_2}$) ; 3.28 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.54 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.83 (dd, J = 5.1 Hz, 3.1 Hz, 1H, C**H**OBn) ; 4.04 (d, J = 5.1 Hz, 1H, C**H**OBn) ; 4.41 (d, J = 11.0 Hz, 1H) ; 4.48 (d, J = 11.0 Hz, 1H) ; 4.76 (d, J = 11.4 Hz, 1H) ; 4.94 (d, J = 3.1 Hz, 1H, OC**H**N) ; 5.07 (d, J = 11.4 Hz, 1H) ; 6.89 (m, 2H) ; 7.16 (m, 2H) ; 7.25 (m, 6H) ; 7.36 (m, 4H) ; 7.48 (m, 2H) ; 7.84 (m, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

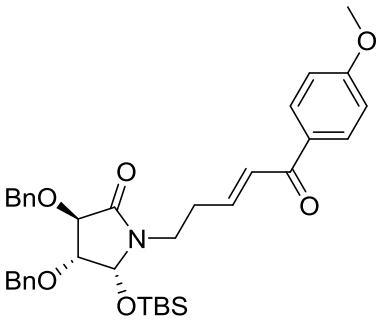
δ = -4.8 (CH_3) ; -4.3 (CH_3) ; 17.9 (Cq) ; 25.6 (3 CH_3) ; 31.1 (CH_2, $NCH_2\mathbf{C}H_2$) ; 38.0 (CH_2, $N\mathbf{C}H_2CH_2$) ; 72.2 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 79.7 (O**C**H) ; 84.8 (O**C**H) ; 86.3 (OC**H**N) ; 127.7 (=CH) ; 128.0 (=CH) ; 128.1 (2 =CH) ; 128.4 (2 =CH) ; 128.5 (2 =CH) ; 128.6 (2 =CH) ; 128.7 (3 =CH) ; 132.8 (=C) ; 137.1 (=C) ; 137.4 (=C) ; 137.6 (=C) ; 144.7 (=CH) ; 170.3 (CON) ; 190.4 (CO) ppm.

iR (ATR) : ν (CO) = 1706, 1672 cm^{-1}, ν (OTBS) = 1069, 856 cm^{-1}, ν (Ar) = 736 cm^{-1}.

HRMS (ESI) m/z : $C_{35}H_{43}NO_5Si$ $[M + Na]^+$ calc. 608.2809, found. 608.2803

$[\alpha]^{25}_D$: +34.2 (*c*=0.5, $CHCl_3$)

*Compound **(+)-8 : (3R,4R,5R)-3,4-bis(benzyloxy)-5-((tert-butyldimethylsilyl)oxy)-1-((E)-5-(4-methoxyphenyl)-5-oxopent-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{36}H_{45}NO_6Si$
Exact Mass: 615,3016
Colorless oil
yield: 76 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 0.09 (s, 3H) ; 0.12 (s, 3H) ; 0.88 (s, 9H) ; 2.55 (m, 2H, $NCH_2C\mathbf{H_2}$) ; 3.30 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.58 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.84 (s, 3H, OCH_3) ; 3.88 (dd, J = 5.3 Hz, 3.1 Hz, 1H, C**H**OBn) ; 4.08 (d, J = 5.1 Hz, 1H, C**H**OBn) ; 4.46 (d, J = 11.2 Hz, 1H) ; 4.53 (d, J = 11.2 Hz, 1H) ; 4.80 (d, J = 11.2 Hz, 1H) ; 4.95 (d, J = 3.1 Hz, 1H, OC**H**N) ; 5.12 (d, J = 11.2 Hz, 1H) ; 6.92 (m, 4H) ; 7.20 (m, 2H) ; 7.30 (m, 6H) ; 7.40 (m, 2H) ; 7.90 (m, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

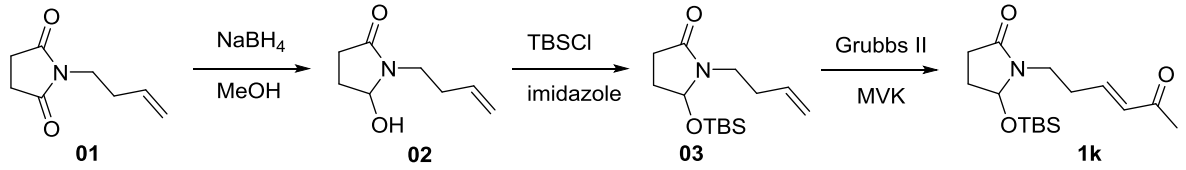
δ = -4.8 (CH_3) ; -4.3 (CH_3) ; 17.9 (Cq) ; 25.6 (3 CH_3) ; 31.0 (CH_2, $NCH_2\mathbf{C}H_2$) ; 38.0 (CH_2, $N\mathbf{C}H_2CH_2$) ; 55.5 (CH_3, $O\mathbf{C}H_3$) ; 72.1 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 79.6 (O**C**H) ; 84.9 (O**C**H) ; 86.2 (OC**H**N) ; 113.8 (2 =CH) ; 127.4 (=CH) ; 128.0 (=CH) ; 128.1 (3 =CH) ; 128.4 (2 =CH) ; 128.5 (2 =CH) ; 128.7 (2 =CH) ; 130.5 (=C) ; 130.9 (2 =CH) ; 137.1 (=C) ; 137.4 (=C) ; 143.6 (CH) ; 163.4 (=C) ; 170.2 (CON) ; 188.6 (CO) ppm.

iR (ATR) : ν (CO) = 1706, 1598 cm^{-1}, ν (OTBS) = 1070, 856 cm^{-1}, ν (Ar) = 736 cm^{-1}.

HRMS (ESI) m/z : $C_{36}H_{45}NO_6Si$ $[M + Na]^+$ calc. 638.2914, found. 638.2908

$[\alpha]_D^{25}$: +36.8 (*c*=0.5, $CHCl_3$)

*Compound **1k**:

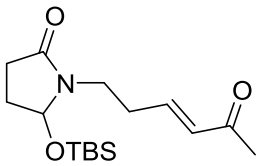


To a solution of 1-(but-3-en-1-yl) pyrrolidine-2.5-dione **01**[1] (300 mg, 1.9 mmol) in MeOH (10 mL) was added $NaBH_4$ (280 mg, 7.52 mmol) at 0 °C. The solution was stirred for 1 h at 0 °C and for 1 h at room temperature. Then, the reaction was quenched with saturated aqueous

$NaHCO_3$ (5 mL) and water (5 mL). CH_2Cl_2 (20 mL) was added, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (twice). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product **02** was dissolved in anhydrous CH_2Cl_2 (7 mL), imidazole (390 mg, 5.8 mmol) and TBSCl (0.32 mg, 2.1 mmol) were added at room temperature. The solution was stirred at room temperature for 4 h. Then, the solution was quenched with water (10 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (thrice). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (CH_2Cl_2/acetone 90/10) afforded compound **03** (320 mg, 1.18 mmol, 61%).

A solution of compound **03** (200 mg, 0.74 mmol), methyl vinyl ketone (0.15 mL, 1.8 mmol), and Grubbs second-generation catalyst (19 mg, 0.022 mmol) in CH_2Cl_2 (8 mL) were stirred at 40 °C for 3 h. After concentration, the purification of the crude product by column chromatography (CH_2Cl_2/acetone 90/10) afforded **1k** (311 mg, 0.56 mmol, 76%).

Compound **1k : (E)-5-((tert-butyldimethylsilyl)oxy)-1-(5-oxohex-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{16}H_{29}NO_3Si$
Exact Mass: 311,1917
Colorless oil
yield: 76 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 0.08 (s, 3H) ; 0.09 (s, 3H) ; 0.87 (s, 9H) ; 1.79 (m, 1H) ; 2.16 (m, 1H) ; 2.21 (s, 3H) ; 2.27 (m, 1H) ; 2.40 (m, 1H) ; 2.51 (m, 2H) ; 3.22 (m, 1H) ; 3.50 (m, 1H) ; 5.20 (dd, J = 5.8 Hz, 2.4 Hz, 1H) ; 6.05 (dt, J = 16.1 Hz, 1.6 Hz, 1H) ; 6.71 (dt, J = 16.1 Hz, 7.0Hz, 1H) ppm.

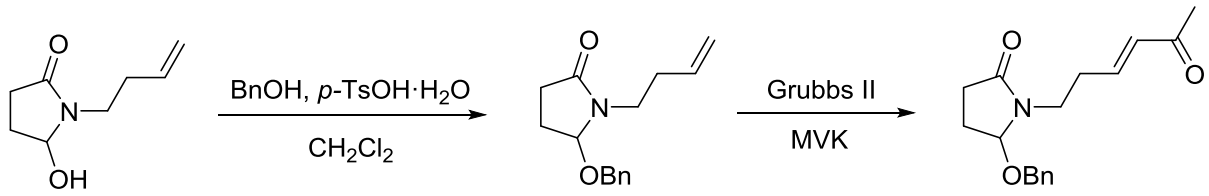
^{13}C NMR (125 MHz, $CDCl_3$)

δ = -4.7 ($SiCH_3$) ; -4.9 ($SiCH_3$) ; 17.9 (Cq) ; 25.6 (3 CH_3) ; 26.9 (CH_3) ; 28.9 (CH_2) ; 29.2 (CH_2) ; 31.3 (CH_2) ; 38.6 (CH_2) ; 83.7 (CH) ; 132.8 (=CH) ; 144.4 (=CH) ; 174.7 (CON) ; 198.5 (CO) ppm.

iR (ATR) : ν (CO) = 1695, 1675 cm^{-1} ; ν (OTBS) = 1060, 837 cm^{-1} .

HRMS (ESI) m/z : $C_{16}H_{29}NO_3Si$ $[M+Na]^+$ calc. 334.1815, found. 334.1809

*Compound **1l**

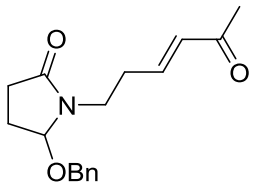


02 **04** **1l**

To a solution of compound **02**[1] (400 mg, 2.18 mmol) and benzyl alcohol (3.3 mL, 32.7 mmol) in in CH_2Cl_2 (7 mL) was added *p*-TsOH·H_2O (37 mg, 0.21 mmol). The reaction was stirred at room temperature for 3 h. Then, the solution was quenched with water (15 mL) and saturated aqueous $NaHCO_3$ (15 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (petroleum ether/AcOEt 50/50 to 40/60) afforded compound **04** (420 mg, 1.71 mmol, 78 %).

A solution of compound **04** (400 mg, 1.6 mmol), methyl vinyl ketone (0.33 mL, 4.0 mmol), and Grubbs second-generation catalyst (28 mg, 0.048 mmol) in CH_2Cl_2 (14 mL) were stirred at 40 °C for 3h. After concentration, purification of the crude product by column chromatography (CH_2Cl_2/acetone 90/10) afforded **1l** (381 mg, 1.32 mmol, 81%).

Compound **1l : (E)-5-(benzyloxy)-1-(5-oxohex-3-en-1-yl)pyrrolidin-2-one**



Chemical Formula: $C_{17}H_{21}NO_3$
Exact Mass: 287,1521
Colorless oil
yield: 81 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 2.04 (m, 1H) ; 2.15 (m, 1H) ; 2.18 (s, 3H, COC**H$_3$**) ; 2.30 (ddd, J = 16.9 Hz, 9.6 Hz, 3.3 Hz, 1H) ; 2.42 (m, 2H) ; 2.54 (m, 1H) ; 3.27 (m, 1H; NC**H**$_2$) ; 3.55 (m, 1H; NC**H**$_2$) ; 4.44 (d, J = 11.7 Hz, 1H, OC**H**$_2$Ar) ; 4.52 (d, J = 11.7 Hz, 1H, OC**H**$_2$Ar) ; 5.00 (dd, J = 6.2 Hz, 1.5 Hz, 1H, CO**H**N) ; 6.01 (dt, J = 16.1 Hz, 1.6 Hz, 1H, CH=C**H**=CO) ; 6.67 (dt, J = 16.1 Hz, 7.0 Hz, 1H, C**H**=CH=CO) ; 7.31 (m, 5H) ppm.

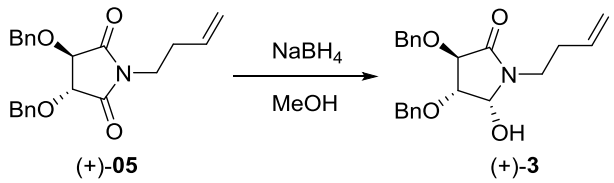
^{13}C NMR (125 MHz, $CDCl_3$)

δ = 24.8 (CH_2) ; 26.8 (CH_3) ; 28.8 (CH_2) ; 31.1 (CH_2) ; 39.3 (CH_2, N**C**H_2) ; 68.4 (CH_2, OBn) ; 88.9 (CH, O**C**HN) ; 127.7 (2 =CH) ; 128.2 (=CH) ; 128.7 (2 =CH) ; 132.9 (=CH) ; 137.2 (Cq) ; 144.4 (CH) ; 175.1 (CON) ; 198.5 (CO) ppm.

iR (ATR) : ν (CO) = 1696, 1673 cm^{-1} ; ν (Ar) = 741 cm^{-1} .

HRMS (ESI) m/z : $C_{17}H_{21}NO_3$ $[M+Na]^+$ calc. 310.1419, found. 310.1414

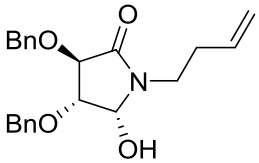
*Compound **(+)-4**[2]



(+)-**05** (+)-**3**

To a solution of compound (+)-**05** (1000 mg, 2.7 mmol) in MeOH (14 mL) was added in 5 portions $NaBH_4$ (100 mg, 2.7 mmol) at 0 °C. The mixture was stirred at 0 °C for 2 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (25 mL) and water (25 mL). CH_2Cl_2 (50 mL) was added, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2x50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (petroleum ether/AcOEt 70/30) afforded **(+)-4** (900 mg, 2.44 mmol, 90%).

Compound **(+)-4 : (3R,4R,5R)-3,4-bis(benzyloxy)-1-(but-3-en-1-yl)-5-hydroxypyrrolidin-2-one**



Chemical Formula: $C_{22}H_{25}NO_4$
Exact Mass: 367,1784
Colorless oil
yield: 90 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 2.33 (m, 2H, $NCH_2C\mathbf{H_2}$) ; 3.29 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.56 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.83 (dd, J = 3.7 Hz, 2.8 Hz, 1H) ; 4.01 (d, J = 3.7 Hz, 1H) ; 4.57 (m, 2H) ; 4.73 (d, J = 11.6 Hz, 1H) ; 4.93 (m, 2H) ; 5.04 (m, 2H) ; 5.74 (m, 1H) ; 7.30 (m, 10H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

δ = 31.8 (CH_2, $NCH_2\mathbf{C}H_2$) ; 37.7 (CH_2, $N\mathbf{C}H_2CH_2$) ; 72.2 (CH_2, OBn) ; 72.9 (CH_2, OBn) ; 79.4 (CH) ; 84.9 (CH) ; 85.0 (CH) ; 117.3 (=CH_2) ; 135.0 (=CH) ; 127.8 (2 =CH) ; 128.1 (2 =CH) ; 128.3 (2 =CH) ; 128.5 (2 =CH) ; 128.6 (2 =CH) ; 137.1 (=C) ; 137.3 (=C) ; 170.2 (CON).

iR (ATR) : ν (OH) = 3338 , ν (CO) : 1676 , ν (Ar) : 735 cm^{-1}.

HRMS (ESI) m/z : $C_{22}H_{25}NO_4$ $[M+H]^+$ calc. 368.1862, found. 368.1856

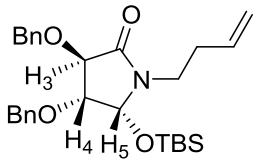
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{25}}$: +51.6 (*c*=0.5, $CHCl_3$)

[2] Thaharn, W.; Bootwicha, T.; Soorukram, D.; Kuhakarn, C.; Prabpai, S.; Kongsaeree,P.; Tuchinda, P.; Reutrakul, V.; Pohmakotr, M. *J. Org. Chem.* **2012**, *77*, 8465-8479.

*Compound **(+)-5**

To a solution of **(+)-3** (400 mg, 1.09 mmol) in CH_2Cl_2 (6 mL) was added TBSCl (320 mg, 2.17 mmol), imidazole (440 mg, 6.5 mmol) and DMAP (26 mg, 0.21 mmol). The mixture was stirred at room temperature for 6 h. Then, the reaction was quenched with water (15 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by column chromatography (CH_2Cl_2/acetone 90/10) afforded **(+)-5** (480 mg, 0.99 mmol, 90%).

Compound **(+)-5: (3R,4R,5R)-3,4-bis(benzyloxy)-1-(but-3-en-1-yl)-5-((tert butyldimethylsilyl)oxy)pyrrolidin-2-one**



Chemical Formula: $C_{28}H_{39}NO_4Si$
Exact Mass: 481,2648

Colorless oil
yield: 87 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 0.02 (s, 3H) ; 0.06 (s, 3H) ; 0.81 (s, 9H) ; 2.20 (m, 2H, $NCH_2C\mathbf{H_2}$) ; 3.06 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.46 (m, 1H, $NC\mathbf{H}_2CH_2$) ; 3.81 (dd, J = 5.2 Hz, 3.1 Hz, 1H) ; 4.03 (d, J = 5.2 Hz, 1H) ; 4.41 (d, J = 11.3 Hz, 1H) ; 4.49 (d, J = 11.3 Hz, 1H) ; 4.74 (d, J = 11.5 Hz, 1H) ; 4.91 (d, J = 3.1 Hz, 1H) ; 5.1 ‘m, 2H) ; 5.07 (d, J = 11.4 Hz, 1H) ; 5.65 (m, 1H) ; 7.15 (m, 2H) ; 7.25 (m, 6H) ; 7.35 (m, 2H) ppm.

4.91 (d, J = 3.1 Hz, H_5) and 3.81 (dd, J = 5.2 Hz, 3.1 Hz, H_4): the coupling constant J H_4H_5=3.1 Hz indicates a *cis* relationship between H_4 and H_5

3.81 (dd, J = 5.2 Hz, 3.1 Hz, H_4) ; 4.03 (d, J = 5.2 Hz, H_3): the coupling constant J H_4H_3=5.2 Hz indicates a *trans* relationship between H_4 and H_3

^{13}C NMR (125 MHz, $CDCl_3$)

δ = -4.9 (CH_3) ; -4.3 (CH_3) ; 17.9 (Cq) ; 25.6 (3 CH_3) ; 31.9 (CH_2, $NCH_2\mathbf{C}H_2$) ; 38.4 (CH_2, $N\mathbf{C}H_2CH_2$) ; 72.2 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 79.9 (CH) ; 84.4 (CH) ; 86.5 (CH) ; 117.1 (=CH_2) ; 128.0 (2 =CH) ; 128.1 (2 =CH) ; 128.4 (2 =CH) ; 128.5 (2 =CH) ; 128.6 (2 =CH) ; 134.8 (=CH) ; 137.2 (=C) ; 137.6 (=C) ; 170.1 (CON) ppm.

iR (ATR) : ν (CO) = 1707 cm^{-1}, ν (OTBS) = 1068, 836 cm^{-1}, ν (Ar) = 733 cm^{-1}.

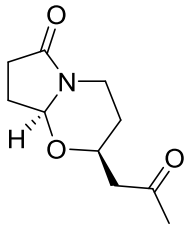
HRMS (ESI) m/z : $C_{28}H_{39}NO_4Si[M + H]^+$ calc. 482.2726, found. 482.2721

$[\alpha]_D^{25}$: +52.8 (*c*=0.5, $CHCl_3$)

General procedure for the formation of 1,3-oxazines 2a-j with *p*-TsOH·H_2O

To a solution of enone (**1a-j**) (1 eq) in CH_2Cl_2 (*c* = 0.1 M) was added *p*-TsOH·H_2O (0.5 eq). The reaction mixture was stirred at room temperature for 7 h. The reaction was quenched with addition of sat. aqueous NH_4Cl. The layers were separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/acetone 90/10 to 70/30)

*Compound **2a : 2-(2-oxopropyl)tetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one**



Chemical Formula: $C_{10}H_{15}NO_3$
Exact Mass: 197,11
White Solid
yield: 95 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.32 (m, 1H) ; 1.52 (m, 1H) ; 2.11 (s, 3H) ; 2.18 (m, 1H) ; 2.29 (m, 1H) ; 2.40 (m, 2H) ; 2.66 (dd, J = 16.6 Hz, 7.5 Hz, 1H) ; 2.94 (td, J = 12.9 Hz, 3.8 Hz, 1H) ; 4.04 (m, 1H) ; 4.1 (ddd J = 13.9 Hz, 4.4 Hz, 1.9 Hz, 1H) ; 4.92 (dd, J = 6.6 Hz, 2.6 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

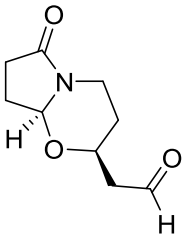
δ= 24.5 (CH_2) ; 28.8 (CH_2) ; 29.7 (CH_2) ; 31.0 (CH_3) ; 38.1 (CH_2) ; 49.2 (CH_2) ; 72.8 (CH) ; 87.7 (CH) ; 173.7 (CON) ; 206.1 (CO) ppm.

iR (ATR) : ν (CO) = 1688 cm^{-1}.

HRMS (ESI) m/z : $C_{10}H_{15}NO_3$ $[M + Na]^+$ calc. 220.095, found. 220.0944

mp (°C) : 46.2

*Compound **2b : 2-(6-oxohexahydro-2H-pyrrolo[2,1-b][1,3]oxazin-2-yl)acetaldehyde**



Chemical Formula: $C_9H_{13}NO_3$
Exact Mass: 183,09
White Solid
yield: 95 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.46 (m, 1H) ; 1.60 (m, 1H) ; 1.88 (m, 1H) ; 2.24 (m, 1H) ; 2.35 (m, 1H) ; 2.48 (m, 2H) ; 2.64 (m, 1H) ; 3.0 (td, J = 12.5 Hz, 3.7 Hz, 1H) ; 4.18 (m, 2H, NC**H$_2$**) ; 5.00 (dd, J = 6.7 Hz, 2.5 Hz, 1H, NC**H**O) ; 9.75 (t, J = 1.5 Hz, 1H, C**H**O) ppm.

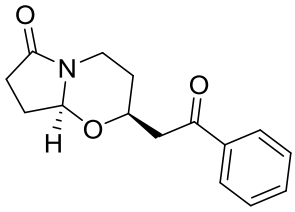
^{13}C NMR (125 MHz, $CDCl_3$)

δ= 24.5 (CH_2) ; 28.8 (CH_2) ; 29.7 (CH_2) ; 38.1 (CH_2) ; 49.2 (CH_2, N**C**H_2) ; 71.8 (CH) ; 87.9 (CH) ; 173.8 (CON) ; 199.9(CHO) ppm.

iR (ATR) : ν (CO) = 1721, 1691 cm^{-1}.

HRMS (ESI) m/z : $C_9H_{13}NO_3$ $[M + H]^+$ calc. 184.0973, found. 184.0968

*Compound **2c : 2-(2-oxo-2-phenylethyl)tetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one**



Chemical Formula: $C_{15}H_{17}NO_3$
Exact Mass: 259,12
White solid
yield: 74 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.48 (qd, J = 12.4 Hz, 5.5 Hz, 1H) ; 1.71 (ddt, J = 13.1 Hz, 3.9 Hz, 1.9 Hz, 1H) ; 1.85 (m, 1H) ; 2.42 (m, 1H) ; 2.34 (m, 1H) ; 2.46 (m, 1H) ; 2.96 (dd, J = 16.9 Hz, 5.8 Hz, 1H) ; 3.05 (dt, J = 13.0 Hz, 4.1 Hz, 1H) ; 3.33 (dd, J = 16.8 Hz, 6.6 Hz, 1H) ; 4.19 (dd, J = 13.5 Hz, 5.1 Hz, 1H) ; 4.32 (m, 1H) ; 5.03 (dd, J = 6.8 Hz, 2.6 Hz, 1H) ; 7.45 (m, 2H) ; 7.56 (m, 1H) ; 7.93 (m, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

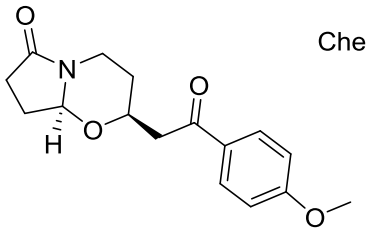
δ = 24.6 (CH_2) ; 28.9 (CH_2) ; 30.1 (CH_2) ; 38.3 (CH_2) ; 44.4 (CH_2) ; 73.2 (CH) ; 87.9 (CH) ; 128.2 (2 =CH) ; 128.7 (2 =CH) ;133.4 (=CH) ; 136.9 (Cq) ; 173.8 (CON) ; 197.2 (CO) ppm.

iR (ATR) : ν (CO) = 1684 cm^{-1}

HRMS (ESI) m/z : $C_{15}H_{17}NO_3$ $[M+H]^+$ calc. 260.1286, found. 260.1281

Mp : 114.9 °C

*Compound **2d : 2-(2-(4-methoxyphenyl)-2-oxoethyl)tetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one**



Chemical Formula: $C_{16}H_{19}NO_4$
Exact Mass: 289,13

White solid
yield: 74 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.46 (qd, J = 12.2 Hz, 5.8 Hz, 1H) ; 1.70 (m, 1H) ; 1.84 (m, 1H) ; 2.22 (m, 1H) ; 2.33 (m, 1H) ; 2.45 (m, 1H) ; 2.89 (dd, J = 16.6 Hz, 5.8 Hz, 1H) ; 3.03 (td, J = 12.8 Hz, 3.8 Hz, 1H) ; 3.27 (dd, J = 16.6 Hz, 6.5 Hz, 1H) ; 3.84 (s, 3H) ; 4.18 (ddd, J = 13.5 Hz, 5.4 Hz, 1.8 Hz, 1H) ; 4.29 (m, 1H) ; 5.01 (dd, J = 6.7 Hz, 2.5 Hz, 1H) ; 6.91 (d, J = 8.9 Hz, 2H) ; 7.91 (d, J = 8.9 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

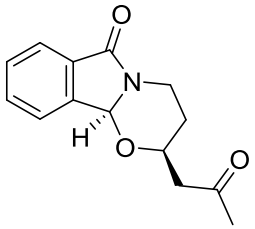
δ = 24.6 (CH_2) ; 28.9 (CH_2) ; 30.1 (CH_2) ; 38.3 (CH_2) ; 44.1 (CH_2) ; 55.5 (CH_3) ; 73.4 (CH) ; 87.9 (CH) ; 113.8 (2 =CH) ; 130.0 (Cq) ; 130.5 (2 =CH) ; 163.8 (Cq) ; 173.7 (CON) ; 195.7 (CO) ppm.

iR (ATR) : ν (CO) = 1693, 1679 cm^{-1}

HRMS (ESI) m/z : $C_{16}H_{19}NO_4$ $[M+H]^+$ calc. 290.1392, found. 290.1387

Mp : 119.3 °C

*Compound **2e : 2-(2-oxopropyl)-3,4-dihydro-2H-[1,3]oxazino[2,3-a]isoindol-6(10bH)-one**



Chemical Formula: $C_{14}H_{15}NO_3$
Exact Mass: 245,11

White solid
yield: 85 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.47 (m, 1H) ; 1.74 (m, 1H) ; 2.18 (s, 3H) ; 2.52 (dd, J = 16.9 Hz, 5.2 Hz, 1H) ; 2.82 (dd, J = 16.9 Hz, 7.3 Hz, 1H) ; 3.27 (td, J = 13.2 Hz, 7.3 Hz, 1H) ; 4.37 (m, 1H) ; 4.44 (dd, J = 13.2 Hz, 3.5 Hz, 1H) ; 5.61 (s, 1H) ; 7.52 (m, 3H) ; 7.79 (d, 7.1 Hz, 1H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

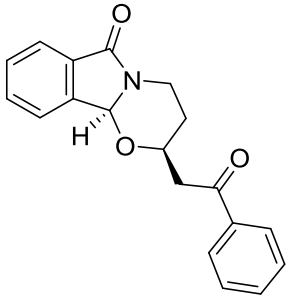
δ= 29.8 (CH_2) ; 31.2 (CH_3) ; 37.5 (CH_2) ; 48.9 (CH_2) ; 73.4 (CH) ; 85.1 (CH) ; 123.3 (=CH) ; 123.7 (=CH) ; 130.1 (=CH) ; 131.9 (=CH) ; 132.7 (Cq) ; 140.9 (Cq) ; 166.0 (CON) ; 205.9 (CO) ppm.

iR (ATR) : ν (CO) = 1700 cm^{-1}, ν (Ar) = 748 cm^{-1}.

HRMS (ESI) m/z : $C_{14}H_{15}NO_3$ $[M + Na]^+$ calc. 268.0950, found. 268.0944

Mp : 97.4 °C

*Compound **2f : 2-(2-oxo-2-phenylethyl)-3,4-dihydro-2H-[1,3]oxazino[2,3-a]isoindol-6(10bH)-one**



Chemical Formula: $C_{19}H_{17}NO_3$
Exact Mass: 307,12

White solid
yield: 85 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.55 (qd, J = 12.3 Hz, 5.4 Hz, 1H) ; 1.89 (m, 1H) ; 3.02 (dd, J = 17.1 Hz, 6.1 Hz, 1H) ; 3.34 (td, J = 13.0 Hz, 4.0 Hz, 1H) ; 3.44 (dd, J = 17.1 Hz, 6.3 Hz, 1H) ; 4.48 (dd, J = 13.7 Hz, 5.4 Hz, 1H) ; 4.59 (m, 1H) ; 5.66 (s, 1H) ; 5.70 (m, 6H) ; 7.80 (m, 1H) ; 7.93 (d, J = 7.7 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

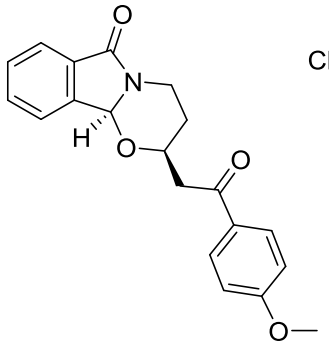
δ= 30.1 (CH_2) ; 37.6 (CH_2) ; 44.4 (CH_2) ; 73.7 (CH) ; 85.2 (CH) ; 123.3 (=CH) ; 123.6 (=CH) ; 128.2 (2 =CH) ; 128.7 (2 =CH) ; 130.0 (=CH) ; 131.9 (=CH) ; 132.7 (Cq) ; 133.5 (=CH) ; 136.8 (Cq) ; 141.0 (Cq) ; 166.0 (CON) ; 197.1 (CO) ppm.

iR (ATR) : ν (CO) = 1701, 1697 cm^{-1}, ν (Ar) = 747, 691 cm^{-1}.

HRMS (ESI) m/z : $C_{19}H_{17}NO_3$ $[M + Na]^+$ calc. 330.1106, found. 330.1101

Mp : 150.1 °C

*Compound **2g : 2-(2-(4-methoxyphenyl)-2-oxoethyl)-3,4-dihydro-2H-[1,3]oxazino[2,3-a]isoindol-6(10bH)-one**



Chemical Formula: $C_{20}H_{19}NO_4$
Exact Mass: 337,13

White solid
yield: 85 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ= 1.54 (qd, J = 12.3 Hz, 5.1 Hz, 1H) ; 1.89 (dt, J = 13.3 Hz, 2.0 Hz, 1H) ; 2.97 (dd, J = 16.9 Hz, 6.2 Hz, 1H) ; 3.33 (dt, J = 13.0 Hz, 3.7 Hz, 1H) ; 3.38 (dd, J = 16.9 Hz, 6.2 Hz, 1H) ; 3.84 (s, 3H) ; 4.47 (dd, J = 13.0 Hz, 5.1 Hz, 1H) ; 4.57 (m, 1H) ; 5.66 (s, 1H) ; 6.91 (d, J = 8.9 Hz, 2H) ; 7.50 (m, 3H) ; 7.79 (m, 1H) ; 7.91 (d, J = 8.9 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

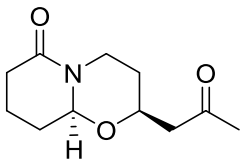
δ= 30.2 (CH_2) ; 37.6 (CH_2) ; 44.0 (CH_2) ; 55.6 (CH_3) ; 85.2 (CH) ; 113.8 (2 =CH) ; 123.3 (=CH) ; 123.6 (=CH) ; 130.0 (=CH) ; 130.5 (2 =CH) ; 131.9 (=CH) ; 132.8 (Cq) ; 141.1 (Cq) ; 163.8 (Cq) ; 166.0 (CON) ; 195.6 (CO) ppm.

iR (ATR) : ν (CO) = 1702, 1677 cm^{-1}, ν (Ar) = 746 cm^{-1}.

HRMS (ESI) m/z : $C_{19}H_{17}NO_3$ $[M + H]^+$ calc. 338.1392, found. 338.1397

Mp : 149.8 °C

*Compound **2h : 2-(2-oxopropyl)hexahydro-2H,6H-pyrido[2,1-b][1,3]oxazin-6-one**



Chemical Formula: $C_{11}H_{17}NO_3$
Exact Mass: 211,12
Colorless liquid
yield: 86 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.44 (qd, J = 12.4 Hz, 4.5 Hz, 1H) ; 1.61 (m, 2H) ; 1.75 (m, 1H) ; 1.86 (m, 1H) ; 1.96 (m, 1H) ; 2.15 (s, 3H , C**H**$_3$-CO) ; 2.34 (m, 2H) ; 2.44 (dd, J = 16.4 Hz, 5.2 Hz, 1H) ; 4.09 (m, 1H) ; 4.72 (m, 2H) ppm

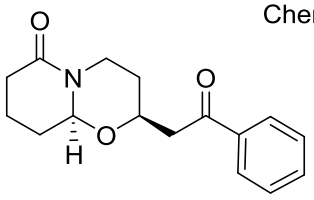
^{13}C NMR (125 MHz, $CDCl_3$)

δ = 17.4 (CH_2) ; 29.1 (CH_2) ; 30.8 (CH_2) ; 31.1 (**C**H_3-CO) ; 32.8 (CH_2) ; 40.5 (CH_2) ; 49.3 (CH_2N) ; 73.7 ((CH_2)$_2$**C**HO) ; 85.7 (O**C**HN) ; 169.4 (CON) ; 206.3 (CO) ppm.

iR (ATR) : ν (CO) : 1714, 1647 cm^{-1}.

HRMS (ESI) m/z : $C_{11}H_{17}NO_3$ $[M + H]^+$ calc. 212.1286, found. 212.1281

*Compound **2i : 2-(2-oxo-2-phenylethyl)hexahydro-2H,6H-pyrido[2,1-b][1,3]oxazin-6-one**



Chemical Formula: $C_{16}H_{19}NO_3$
Exact Mass: 273,14
Colorless liquid
yield: 86 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.53 (qd, J = 12.0 Hz, 5.0 Hz, 2H) ; 1.62 (m, 1H) ; 1.75 (m, 2H) ; 1.87 (m, 1H) ; 1.97 (m, 1H) ; 2.34 (m, 2H) ; 2.78 (td, J = 12.9 Hz, 3.2 Hz, 1H) ; 2.95 (dd, J = 16.7 Hz, 5.9 Hz, 1H) ; 3.32 (dd, J = 16.7 Hz, 5.9 Hz, 1H) ; 4.30 (m, 1H) ; 4.75 (m, 2H) ; 7.44 (m, 2H) ; 7.55 (m, 1H) ; 7.92 (m, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

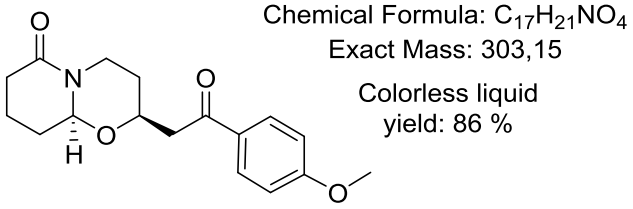
δ = 17.5 (CH_2) ; 29.1 (CH_2) ; 31.1 (CH_2) ; 32.8 (CH_2) ; 40.6 (CH_2) ; 44.5 (CH_2) ; 73.9 ((CH_2)$_2$**C**HO) ; 85.8 (O**C**HN) ; 128.2 (2 =CH) ; 128.60 (2 =CH) ; 133.4 (=CH) ; 137.0 (Cq) ; 169.5 (CON) ; 197.4 (CO) ppm.

iR (ATR) : ν (CO) : 1683, 1645 cm^{-1}, ν (Ar) : 754 cm^{-1}

HRMS (ESI) m/z : $C_{16}H_{19}NO_3$ $[M + H]^+$ calc. 274.1443, found. 274.1438

mp : 90.2 °C

*Compound **2j : 2-(2-(4-methoxyphenyl)-2-oxoethyl)hexahydro-2H,6H-pyrido[2,1-b][1,3]oxazin-6-one**



^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.57 (m, 2H) ; 1.89 (m, 2H) ; 2.36 (q, J = 5.9 Hz, 2H) ; 2.79 (td, J = 13.1 Hz, 3.2 Hz, 1H) ; 2.91 (dd, J = 16.5 Hz, 6.1 Hz, 1H) ; 3.29 (dd, J = 16.5 Hz, 6.5 Hz, 1H) ; 3.86 (s, C**H$_3$**O) ; 4.31 (m, 1H) ; 4.78 (m, 2H) ; 6.93 (d, J = 8.9 Hz, 2H) ; 7.93 (d, J = 8.9 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

δ = 17.5 (CH_2) ; 29.1 (CH_2) ; 31.1 (CH_2) ; 32.8 (CH_2) ; 40.6 (CH_2) ; 44.1 (CH_2) ; 55.5 (O**C**H$_3$) ; 74.2 ((CH_2)$_2$**C**HO) ; 85.8 (O**C**HN) ; 113.7 (2 =CH) ; 130.2 (Cq) ; 130.5 (2 =CH) ; 163.7 (Cq) ; 169.4 (CON) ; 195.9 (CO) ppm.

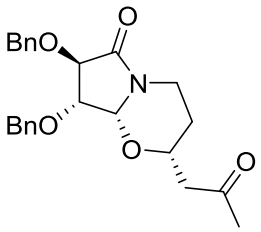
iR (ATR) : ν (CO) : 1647, 1599 cm^{-1}.

HRMS (ESI) m/z : $C_{17}H_{21}NO_4$ $[M + H]^+$ calc. 304.1549, found. 304.1543
mp : 111.8 °C

II-3 General procedure for the formation of 1,3-oxazines **(+)-9a**, **(+)-10a** and **(+)-11a** with TBAF treatment

To a solution of enones **(+)-6-(+)-8** (1 eq) in THF (0.05 M) was added dropwise a solution of TBAF in THF (1 eq) at 0 °C. The mixture was stirred at 0 °C for 2 h. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C, the mixture was allowed to warm to room temperature. CH_2Cl_2 was added and the layers were separated. Latter, the aqueous layer was extracted with CH_2Cl_2 (thrice). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH_2Cl_2/acetone 90/10 to 80/20)

*Compound **(+)-9a : (2R,7R,8R,8aR)-7,8-bis(benzyloxy)-2-(2-oxopropyl)tetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one**



Chemical Formula: $C_{24}H_{27}NO_5$
Exact Mass: 409,1889

Colorless oil
yield: 69 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.44 (qd, J = 12.3 Hz, 5.6 Hz, 1H) ; 1.64 (m, 1H) ; 2.13 (s, 3H, C(O)C**H$_3$**) ; 2.49 (dd, J = 16.8 Hz, 5.3 Hz, 1H) ; 2.77 (dd, J = 16.8 Hz, 7.2 Hz, 1H) ; 2.95 (td, J = 13.4 Hz, 3.8 Hz, 1H) ; 3.97 (dd, J = 5.1 Hz, 3.1 Hz, 1H) ; 4.10 (m, 1H, NC**H**$_2$CH$_2$) ; 4.16 (dd, J = 5.1 Hz, 1.1 Hz, 1H) ; 4.19 (dd, J = 13.2 Hz, 4.9 Hz, 1H, NC**H**$_2$CH$_2$) ; 4.50 (d, J = 11.7 Hz, 1H) ; 4.62 (d, J = 11.7 Hz, 1H) ; 4.76 (d, J = 12.0 Hz, 1H) ; 4.82 (d, J = 3.1 Hz, 1H) ; 4.98 (d, J = 12.0 Hz, 1H) ; 7.31 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$)

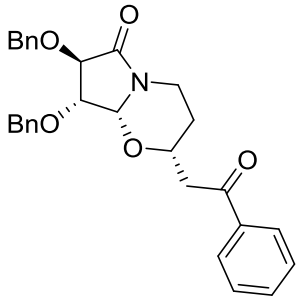
δ = 29.2 (CH_2) ; 21.1 (CH_3, C(O)**C**H$_3$) 37.2 (CH_2) ; 49.0 (CH_2, N**C**H$_2$CH$_2$) ; 72.1 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 72.7 (OC**H**) ; 79.8 (OCH) ; 83.6 (OCH) ; 88.4 (OC**H**N) ; 127.9 (2 =CH) ; 128.0 (2 =CH) ; 128.3 (2 =CH) ; 128.4 (2 =CH) ; 128.5 (2 =CH) ; 137.1 (=C) ; 137.5 (=C) ; 168.3 (CON) ; 205.7 (CO) ppm.

iR (ATR) : ν (CO) = 1708 cm^{-1}, ν (Ar) = 739 cm^{-1}.

HRMS (ESI) m/z : $C_{24}H_{27}NO_5$ $[M + Na]^+$ calc. 410.1967, found. 410.1962

$[\alpha]_D^{25}$: +61.0 (*c*=0.5, $CHCl_3$)

*Compound **(+)-10a : (2R,7R,8R,8aR)-7,8-bis(benzyloxy)-2-(2-oxo-2-phenylethyl)tetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one**



Chemical Formula: $C_{29}H_{29}NO_5$
Exact Mass: 471,2046
Colorless oil
yield: 63 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.55 (qd, J = 12.1 Hz, 4.6 Hz, 1H) ; 1.79 (dt, J = 13.1 Hz, 2.3 Hz, 1H) ; 2.95 (dd, J = 16.1 Hz, 4.9 Hz, 1H, NCH_2CH_2) ; 3.01 (td, J = 12.6 Hz, 4.9 Hz, 1H) ; 3.40 (dd, J = 16.6 Hz, 6.8 Hz, 1H, NCH_2CH_2) ; 3.96 (dd, J = 5.4 Hz, 3.2 Hz, 1H, C**H**OBn) ; 4.16 (dd, J = 5.4 Hz, 1.4 Hz, 1H, C**H**OBn) ; 4.23 (dd, J = 13.4 Hz, 5.0 Hz, 1H, NCH_2CH_2) ; 4.30 (m, 1H, NCH_2CH_2) ; 4.41 (d, J = 10.9 Hz, 1H) ; 4.55 (d, J = 10.9 Hz, 1H) ; 4.75 (d, J = 11.1 Hz, 1H) ; 4.85 (d, J = 3.2 Hz, 1H, OC**H**N) ; 4.96 (d, J = 11.1 Hz, 1H) ; 7.19 (m, 2H) ; 7.24 (m, 4H) ; 7.31 (m, 2H) ; 7.35 (m, 2H) ; 746 (m, 2H) ; 7.58 (m, 1H) ; 7.96 (d, J = 8.0 Hz, 2H) ppm.

^{13}C NMR (125 MHz, $CDCl_3$)

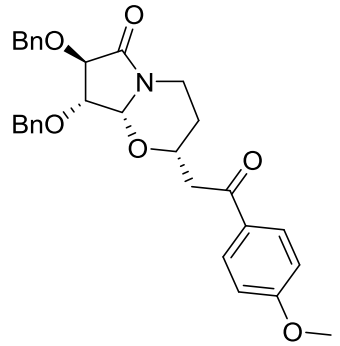
δ = 29.5 (CH_2) ; 37.3 (CH_2, NCH_2CH_2) ; 44.2 (CH_2, NCH_2CH_2) ; 72.0 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 73.3 (OC**H**) ; 79.7 (OC**H**) ; 83.6 (OC**H**) ; 88.5 (OC**H**N) ; 127.8 (=CH) ; 127.9 (=CH) ; 128.0 (2 =CH) ; 128.2 (4 =CH) ; 128.4 (4 =CH) ; 128.7 (2 =CH) ; 133.5 (=CH) ; 130.9 (=C) ; 137.1 (=C) ; 137.5 (=C) ; 168.3 (CON) ; 197.3 (CO) ppm.

iR (ATR) : ν (CO) = 1712, 1685 cm^{-1}, ν (Ar) = 738 cm^{-1}.

HRMS (ESI) m/z : $C_{35}H_{43}NO_5Si$ $[M + H]^+$ calc. 472.2124, found. 472.2118

$[\alpha]_D^{25}$: +46 (*c*=0.5, $CHCl_3$)

*Compound **(+)-11a : (2R,7R,8R,8aR)-7,8-bis(benzyloxy)-2-(2-(4-methoxyphenyl)-2-oxoethyl)tetrahydro-2H-pyrrolo[2,1-b][1,3]oxazin-6(7H)-one**



Chemical Formula: $C_{30}H_{31}NO_6$
Exact Mass: 501,2151
Colorless oil
yield: 66 %

^{1}H NMR (500 MHz, $CDCl_3$)

δ = 1.41 (qd, J = 12.2 Hz, 5.3 Hz, 1H) ; 1.64 (dt, J = 13.5 Hz, 1.6 Hz, 1H) ; 2.76 (dd, J = 16.3 Hz, 5.1 Hz, 1H, NCH_2CH_2) ; 2.87 (td, J = 12.6 Hz, 3.5 Hz, 1H) ; 3.22 (dd, J = 16.3 Hz, 6.8 Hz, 1H, NCH_2CH_2) ; 3.72 (s, 3H, OCH_3) ; 3.82 (dd, J = 5.8 Hz, 3.2 Hz, 1H, CHOBn) ; 4.04 (dd, J = 5.7 Hz, 1.6 Hz, 1H, CHOBn) ; 4.08 (dd, J = 13.8 Hz, 5.0 Hz, 1H, NCH_2CH_2) ; 4.15 (m, 1H, NCH_2CH_2) ; 4.28 (d, J = 11.6 Hz, 1H) ; 4.42 (d, J = 11.6 Hz, 1H) ; 4.62 (d, J = 11.5 Hz, 1H) ; 4.70 (d, J = 3.2 Hz, 1H, OCHN) ; 4.83 (d, J = 11.5 Hz, 1H) ; 6.80 (d, J = 10.4 Hz, 2H) ; 7.05(m, 2H) ; 7.12 (m, 4H) ; 7.18 (m, 2H) ; 7.22 (m, 2H) ; 7.81 (d, J = 10.4 Hz, 2H) ppm.

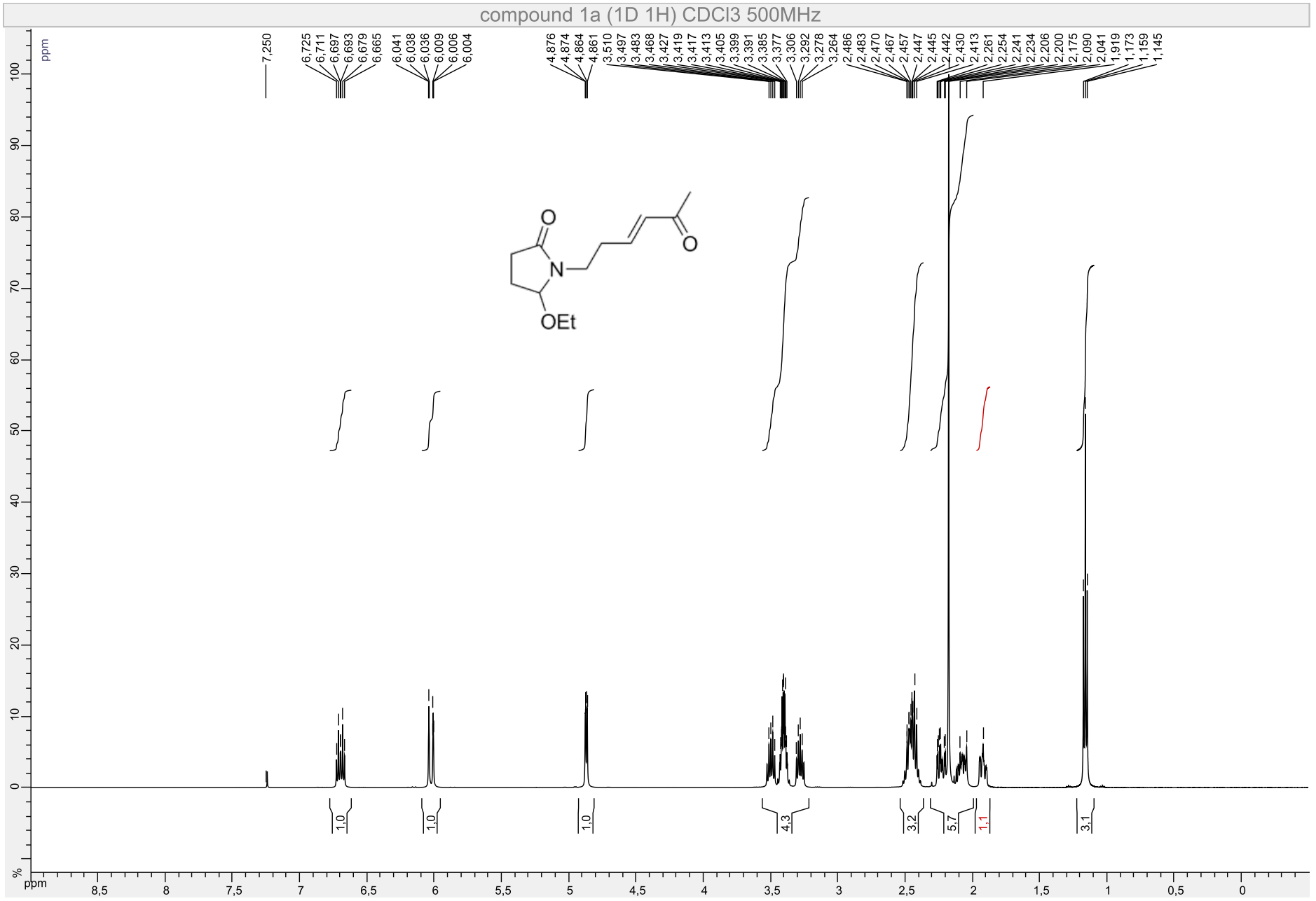
^{13}C NMR (125 MHz, $CDCl_3$)

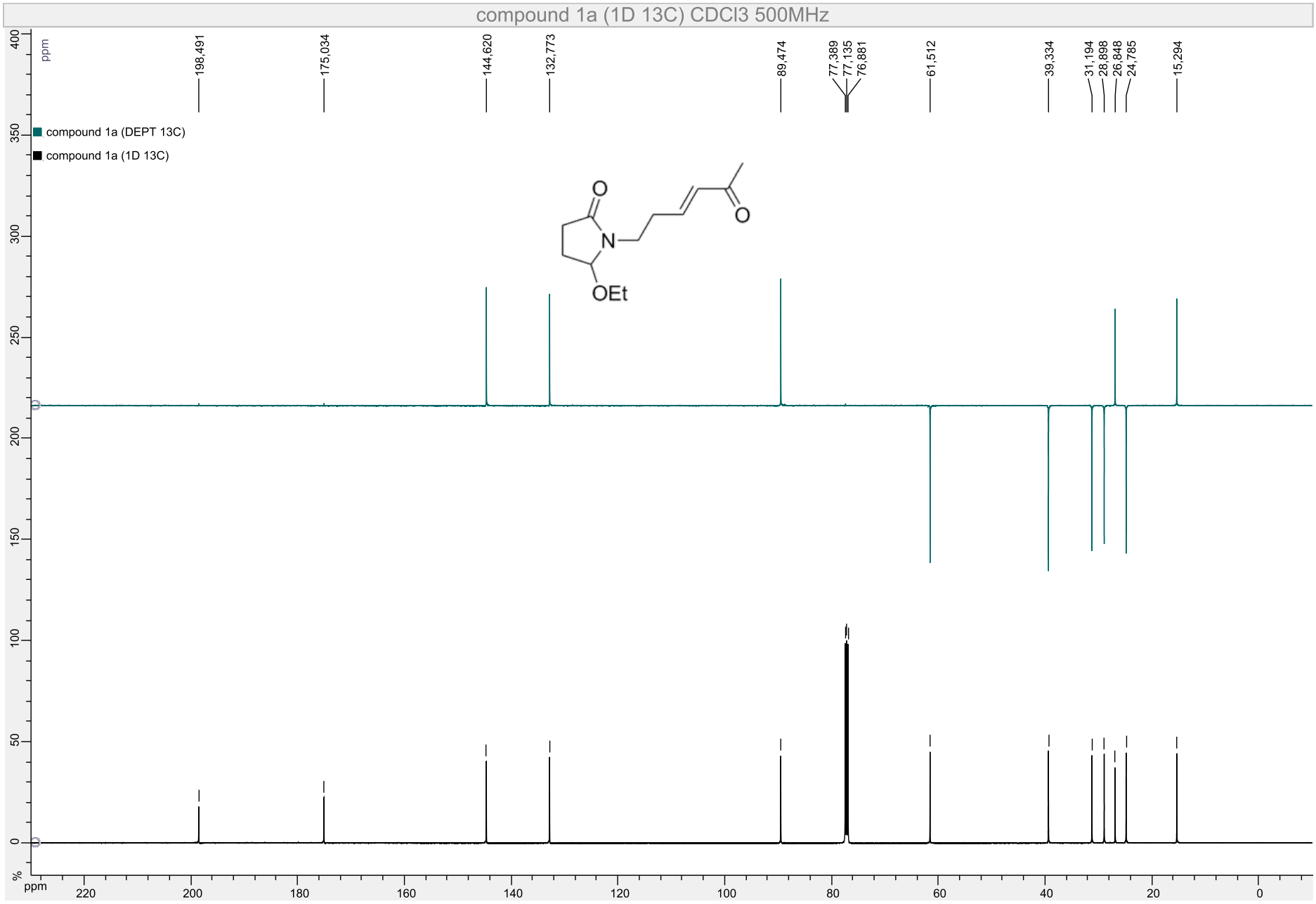
δ = 29.5 (CH_2) ; 37.3 (CH_2, NCH_2CH_2) ; 43.9 (CH_2, NCH_2CH_2) ; 55.6 (CH_3, OCH_3) ; 72.0 (CH_2, OBn) ; 72.6 (CH_2, OBn) ; 73.5 (OCH) ; 79.7 (OCH) ; 83.6 (OCH) ; 88.5 (OCHN) ; 113.8 (2 =CH) ; 127.8 (=CH) ; 127.9 (=CH) ; 128.0 (2 =CH) ; 128.2 (2 =CH) ; 128.4 (4 =CH) ; 130.1 (=C) ; 130.6 (2 =CH) ; 137.1 (=C) ; 137.5 (=C) ; 168.3 (CON) ; 195.8 (CO) ppm.

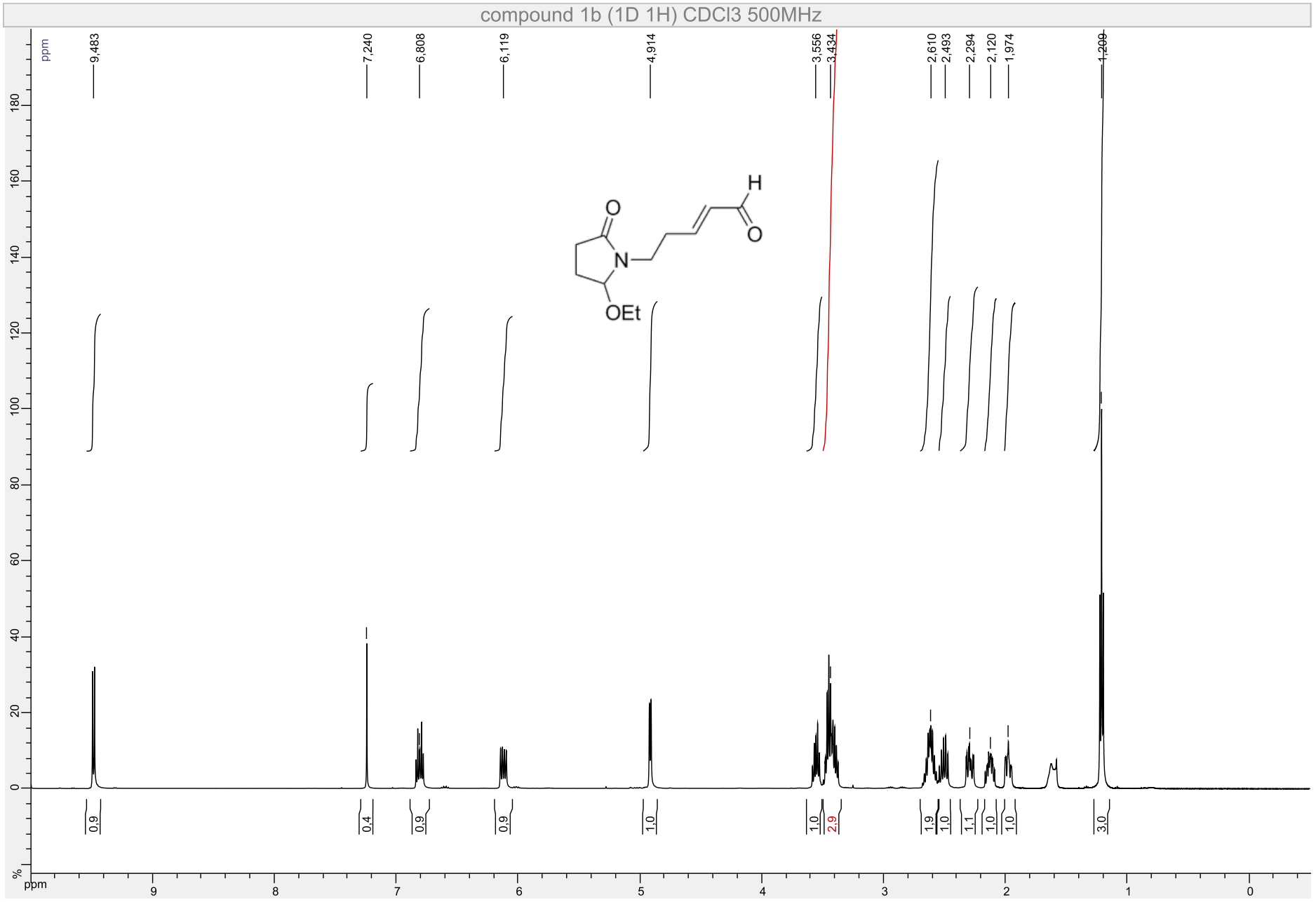
iR (ATR) : ν (CO) = 1709, 1674 cm^{-1}, ν (Ar) = 733 cm^{-1}.

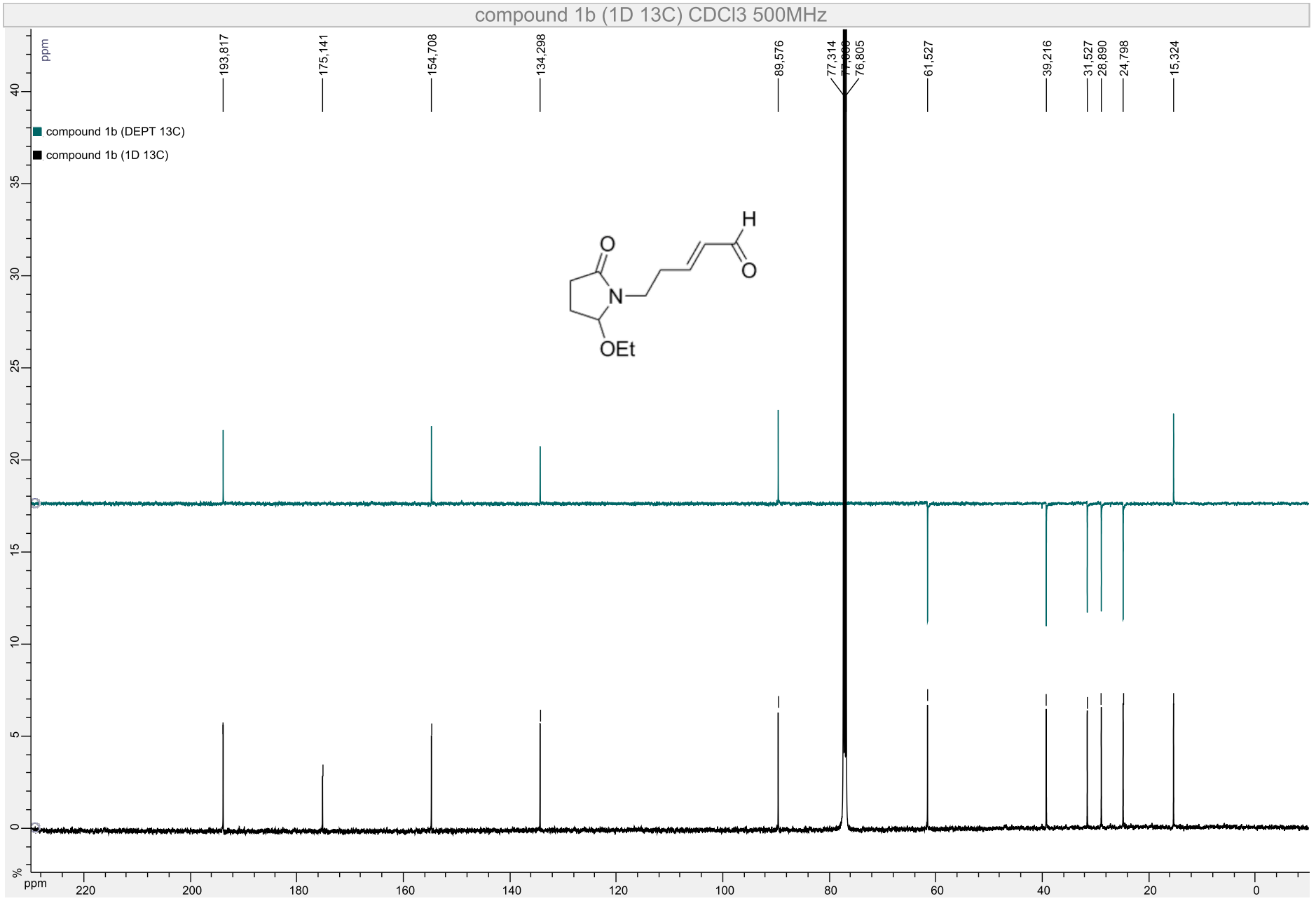
HRMS (ESI) m/z : $C_{30}H_{31}NO_6$ $[M + Na]^+$ calc. 524.2049, found. 524.2044

$[\alpha]_D^{25}$: +36.6 (*c*=1, $CHCl_3$)

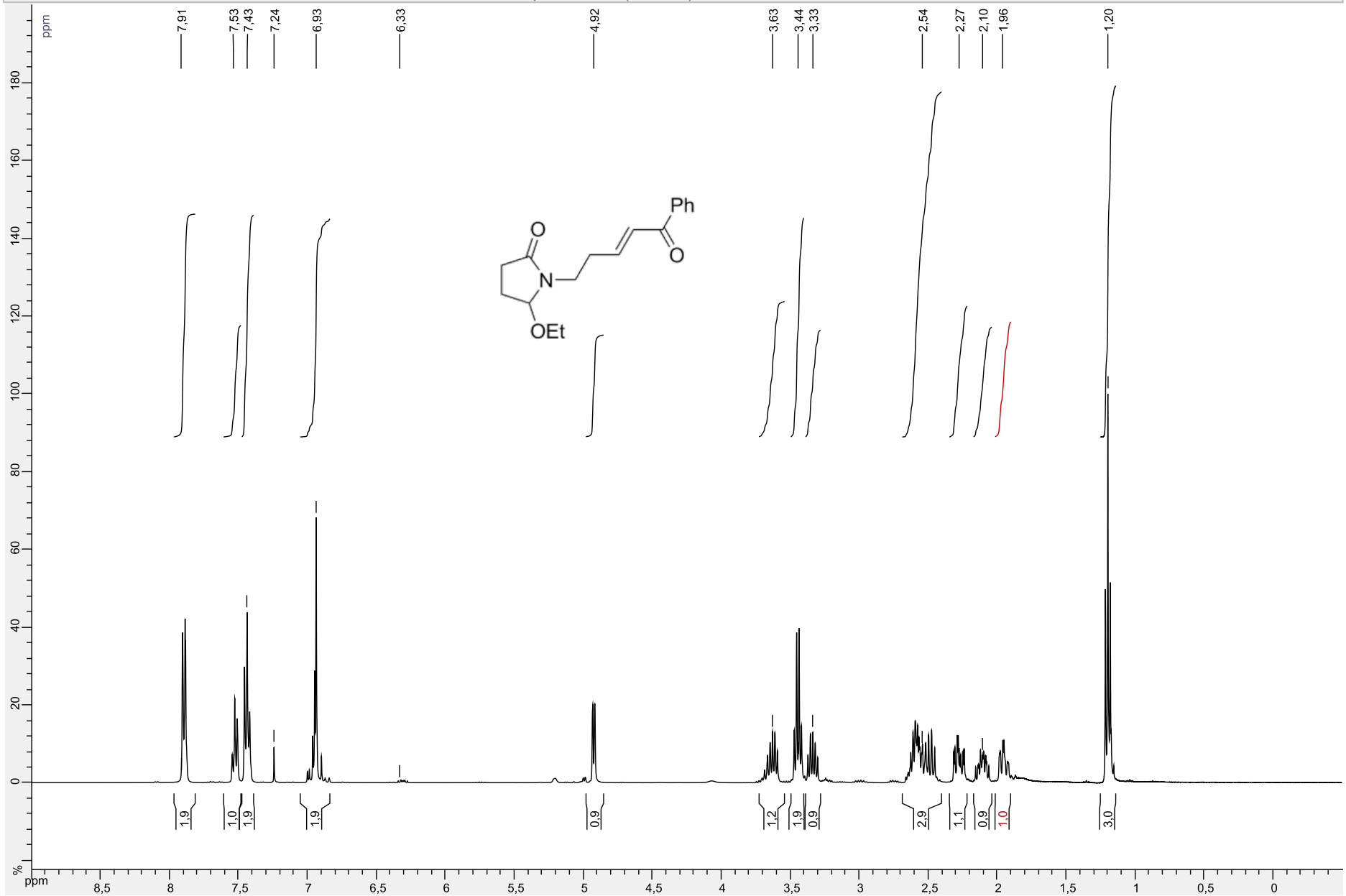

compound 1a (1D 1H) CDCl3 500MHz
ppm
7,250
6,725
6,711
6,697
6,693
6,679
6,665
6,041
6,038
6,036
6,009
6,006
6,004
4,876
4,874
4,864
4,861
3,510
3,497
3,483
3,468
3,427
3,419
3,417
3,413
3,405
3,399
3,391
3,385
3,377
3,306
3,292
3,278
3,264
2,486
2,483
2,470
2,467
2,457
2,447
2,445
2,442
2,430
2,413
2,261
2,254
2,241
2,234
2,206
2,200
2,175
2,090
2,041
1,919
1,173
1,159
1,145
O
N
O
OEt
1,0
1,0
1,0
4,3
3,2
5,7
1,1
3,1
%
ppm

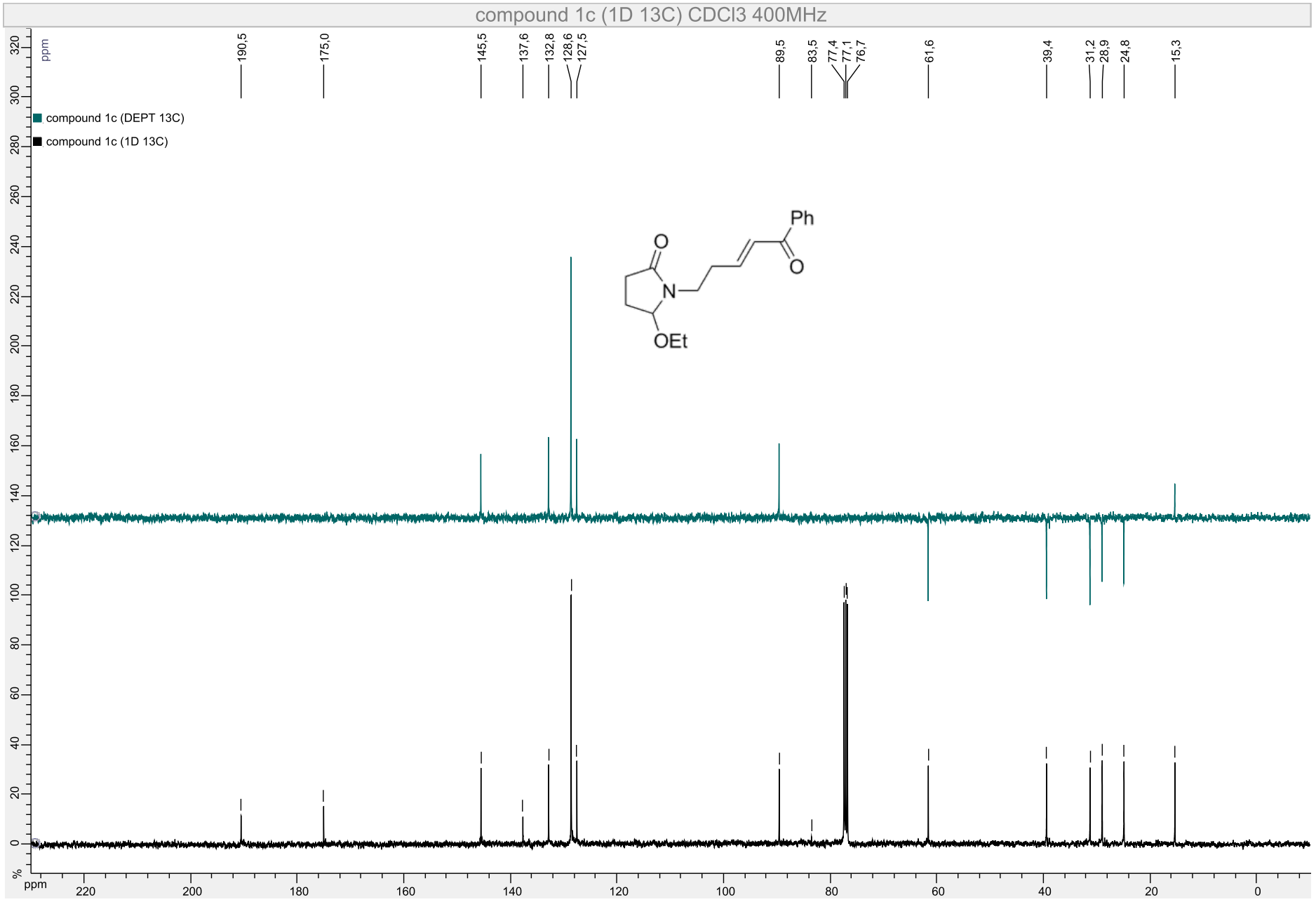

compound 1a (1D 13C) CDCl3 500MHz
ppm
198,491
175,034
144,620
132,773
89,474
77,389
77,135
76,881
61,512
39,334
31,194
28,898
26,848
24,785
15,294
compound 1a (DEPT 13C)
compound 1a (1D 13C)
O
N
O
OEt
%
400
350
300
250
200
150
100
50
0
ppm
220
200
180
160
140
120
100
80
60
40
20
0


compound 1b (1D 1H) CDCl3 500MHz
ppm
9,483
7,240
6,808
6,119
4,914
3,556
3,434
2,610
2,493
2,294
2,120
1,974
1,299
O
H
O
N
OEt
0,9
0,4
0,9
0,9
1,0
1,0
2,9
1,9
1,0
1,1
1,0
1,0
3,0
%
ppm

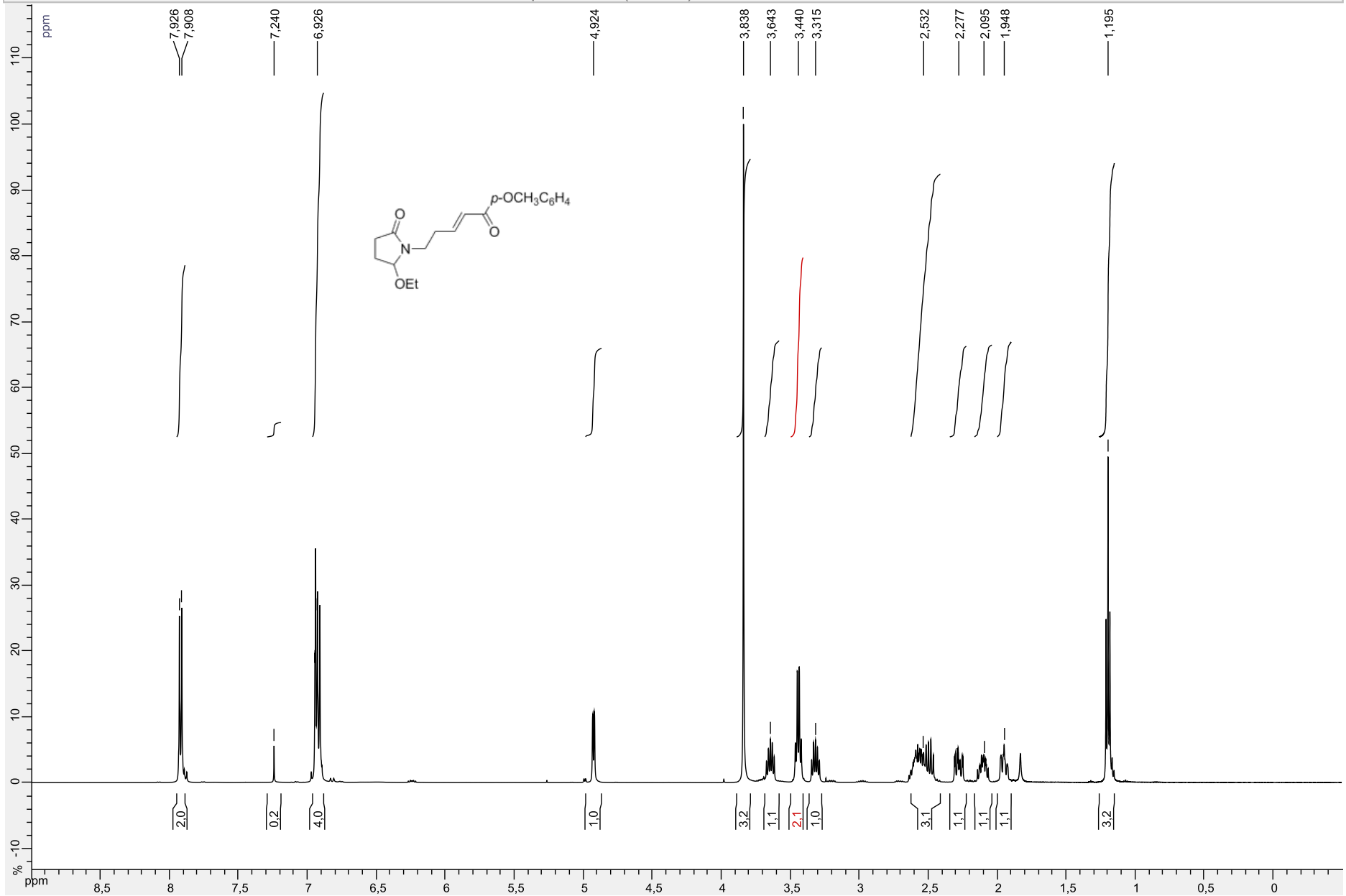

compound 1b (1D 13C) CDCl3 500MHz
ppm
193,817
175,141
154,708
134,298
89,576
77,314
77,000
76,805
61,527
39,216
31,527
28,890
24,798
15,324
compound 1b (DEPT 13C)
compound 1b (1D 13C)
O
H
O
N
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

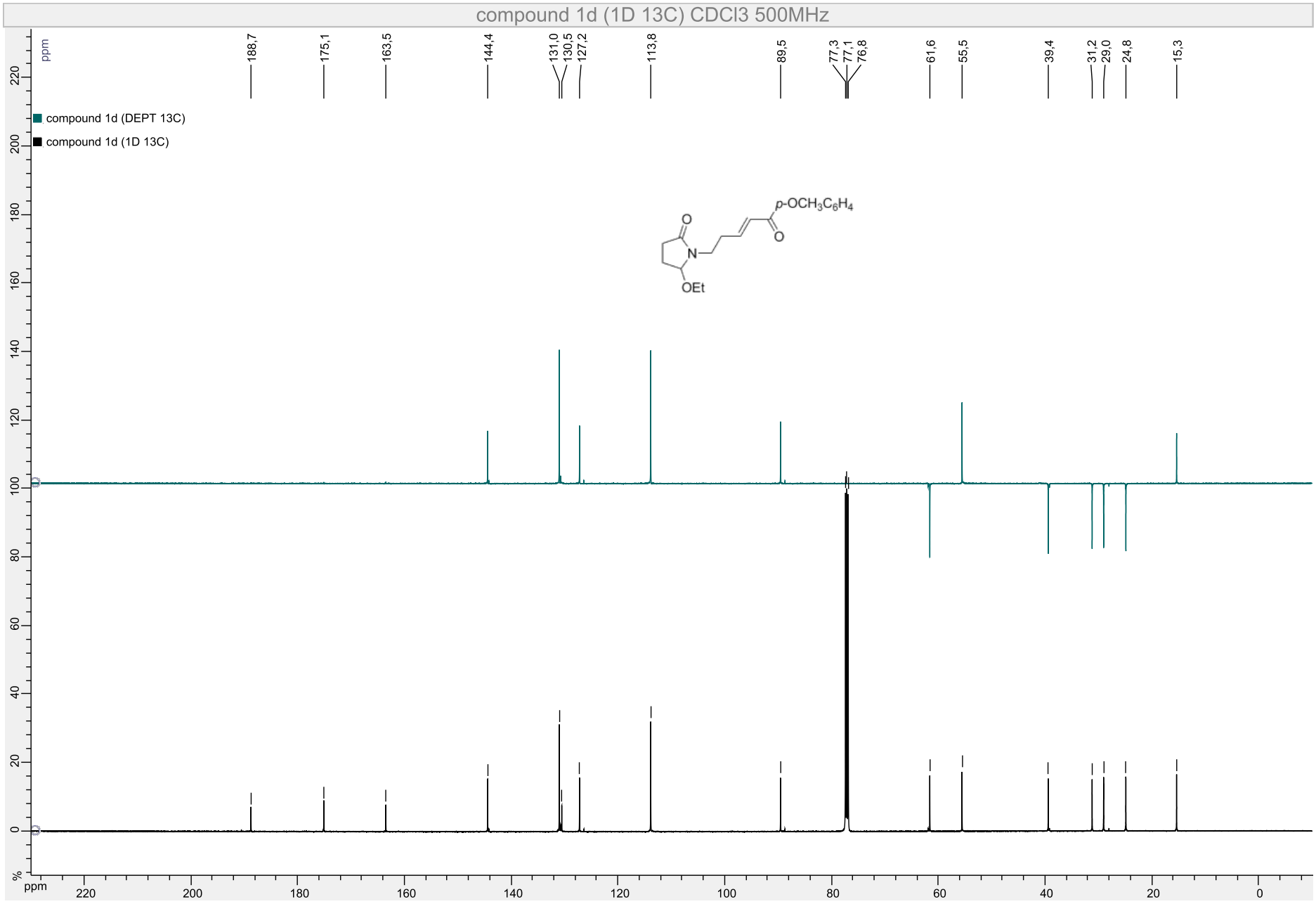
compound 1c (1D 1H) CDCl3 400MHz

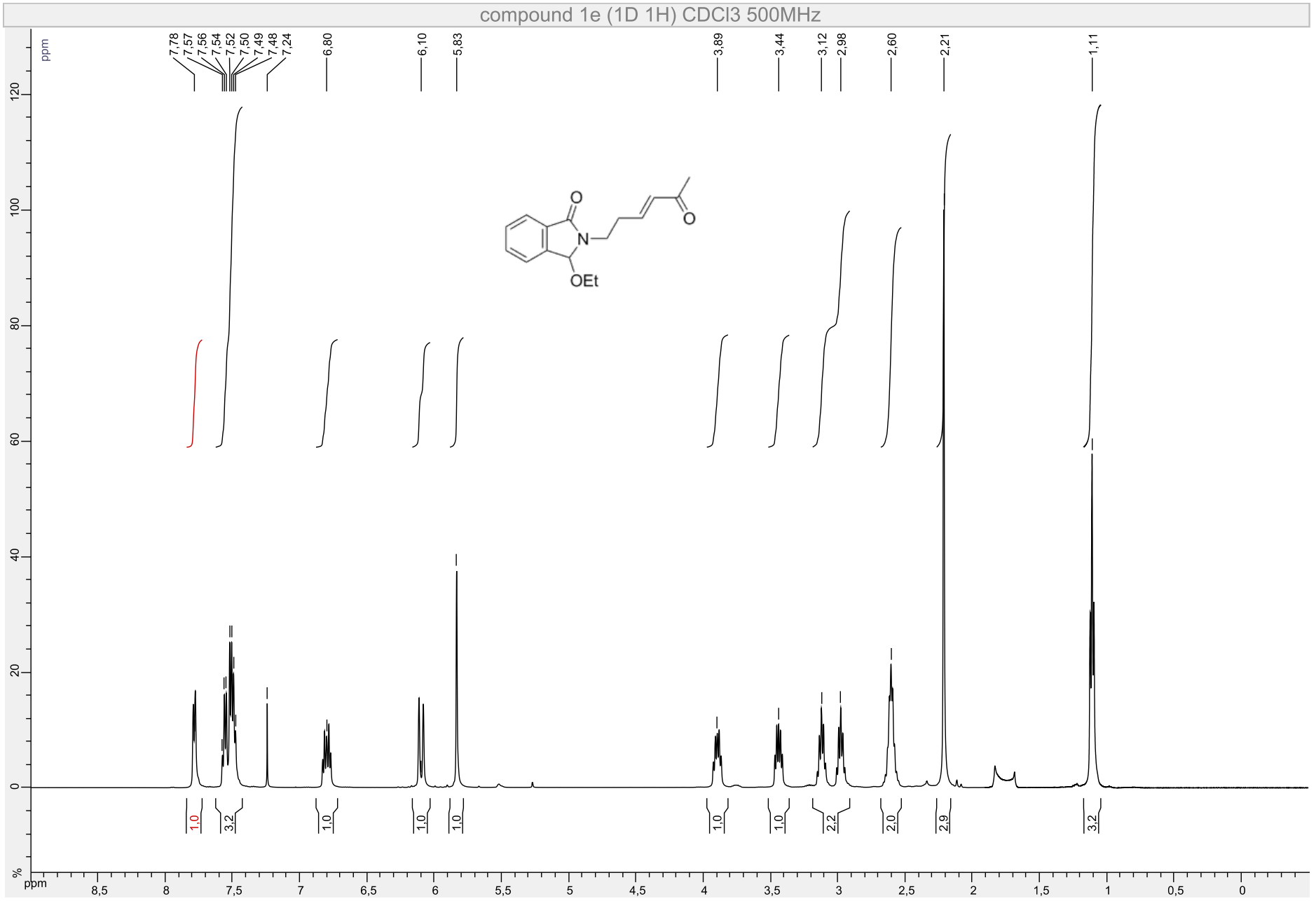


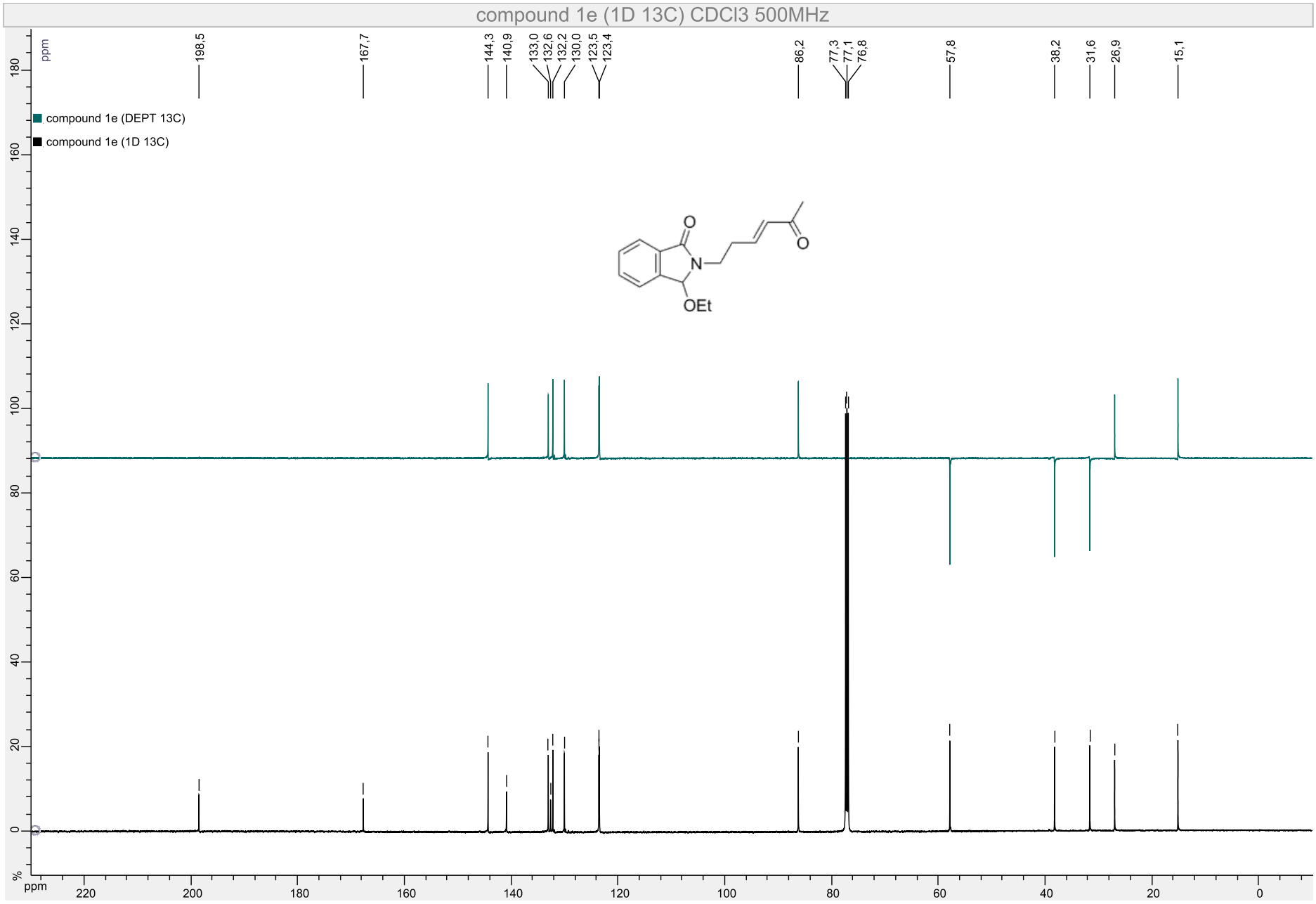

compound 1c (1D 13C) CDCl3 400MHz
ppm
190,5
175,0
145,5
137,6
132,8
128,6
127,5
89,5
83,5
77,4
77,1
76,7
61,6
39,4
31,2
28,9
24,8
15,3
compound 1c (DEPT 13C)
compound 1c (1D 13C)
Ph
O
O
N
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

compound 1d (1D 1H) CDCl3 500MHz

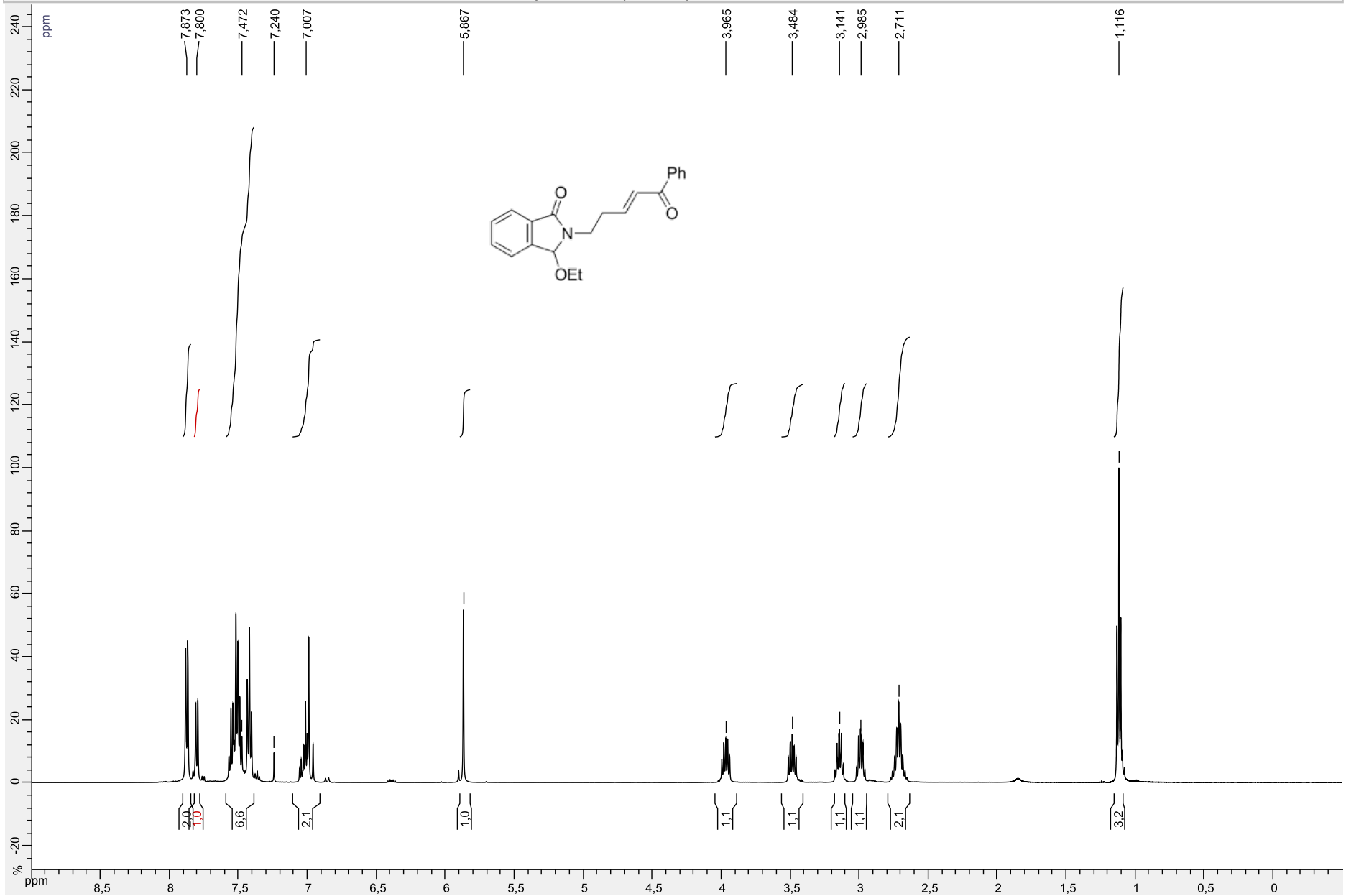


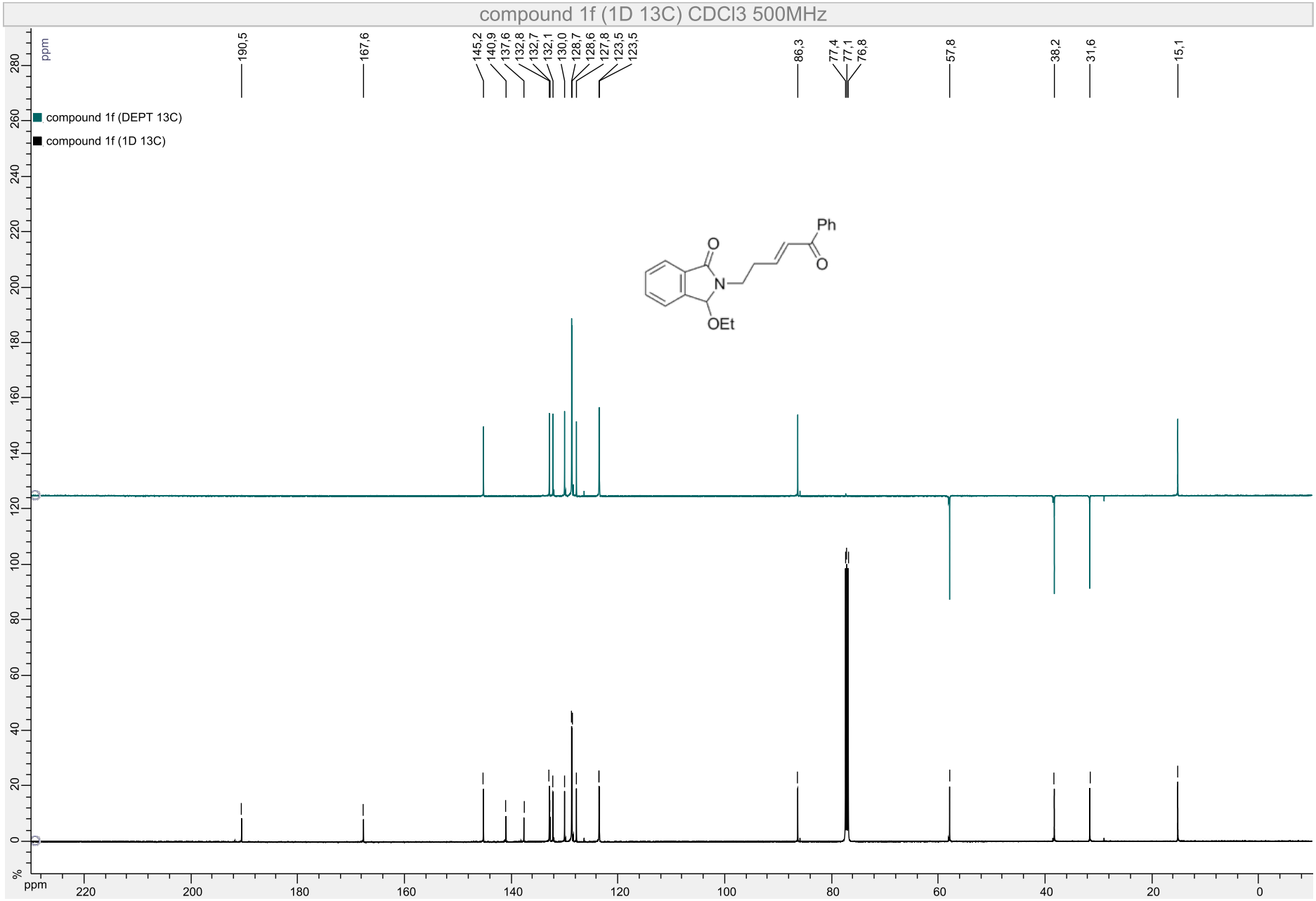

compound 1d (1D 13C) CDCl3 500MHz
ppm
188,7
175,1
163,5
144,4
131,0
130,5
127,2
113,8
89,5
77,3
77,1
76,8
61,6
55,5
39,4
31,2
29,0
24,8
15,3
compound 1d (DEPT 13C)
compound 1d (1D 13C)
p-OCH3C6H4
O
O
N
OEt
%
220
200
180
160
140
120
100
80
60
40
20
0


compound 1e (1D 1H) CDCl3 500MHz
ppm
7,78
7,57
7,56
7,54
7,52
7,50
7,49
7,48
7,24
6,80
6,10
5,83
3,89
3,44
3,12
2,98
2,60
2,21
1,11
O
N
O
OEt
1,0
3,2
1,0
1,0
1,0
1,0
2,2
2,0
2,9
3,2
%
120
100
80
60
40
20
0
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

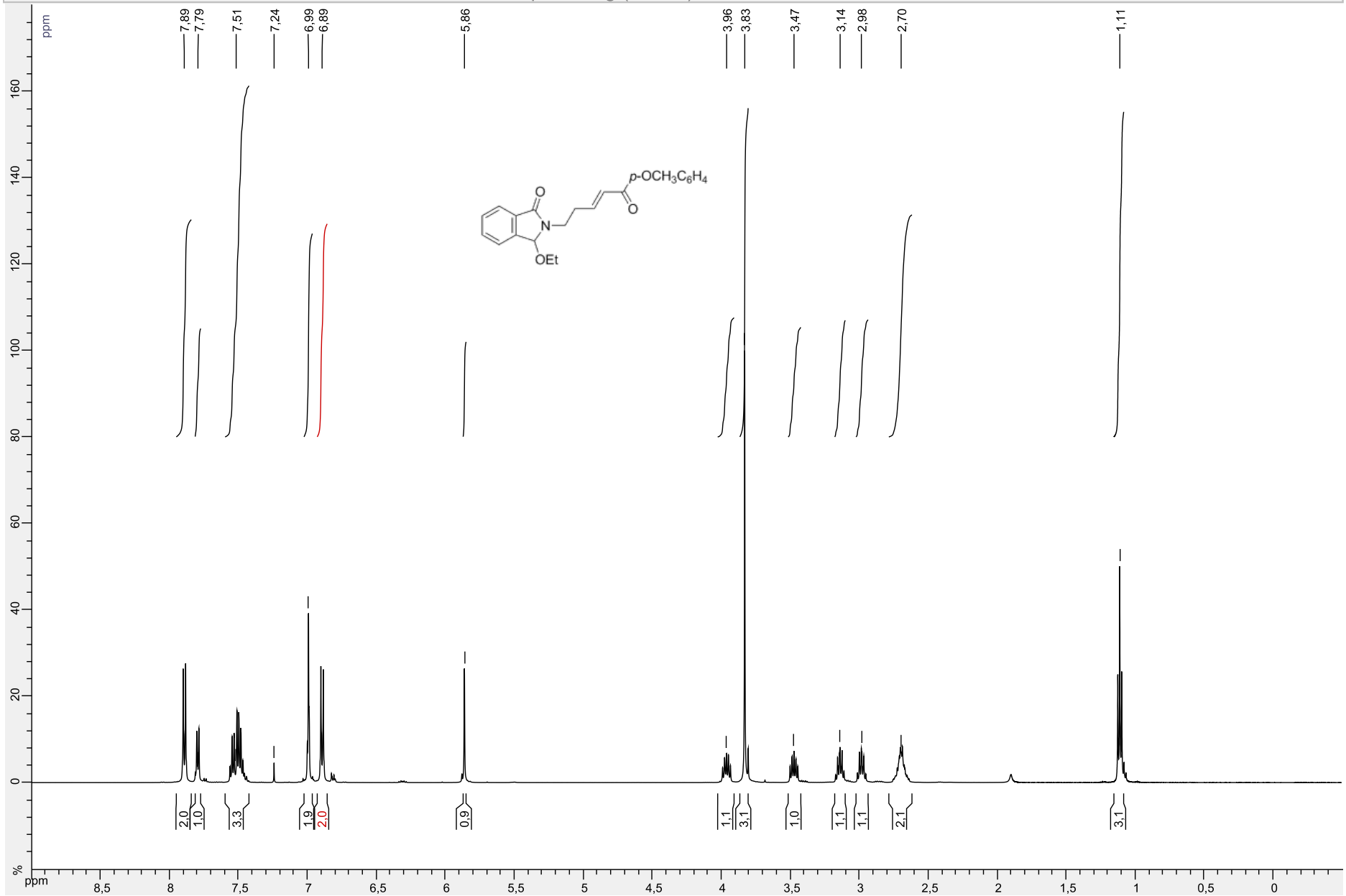

compound 1e (1D 13C) CDCl3 500MHz
ppm
198,5
167,7
144,3
140,9
133,0
132,6
132,2
130,0
123,5
123,4
86,2
77,3
77,1
76,8
57,8
38,2
31,6
26,9
15,1
compound 1e (DEPT 13C)
compound 1e (1D 13C)
O
N
O
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

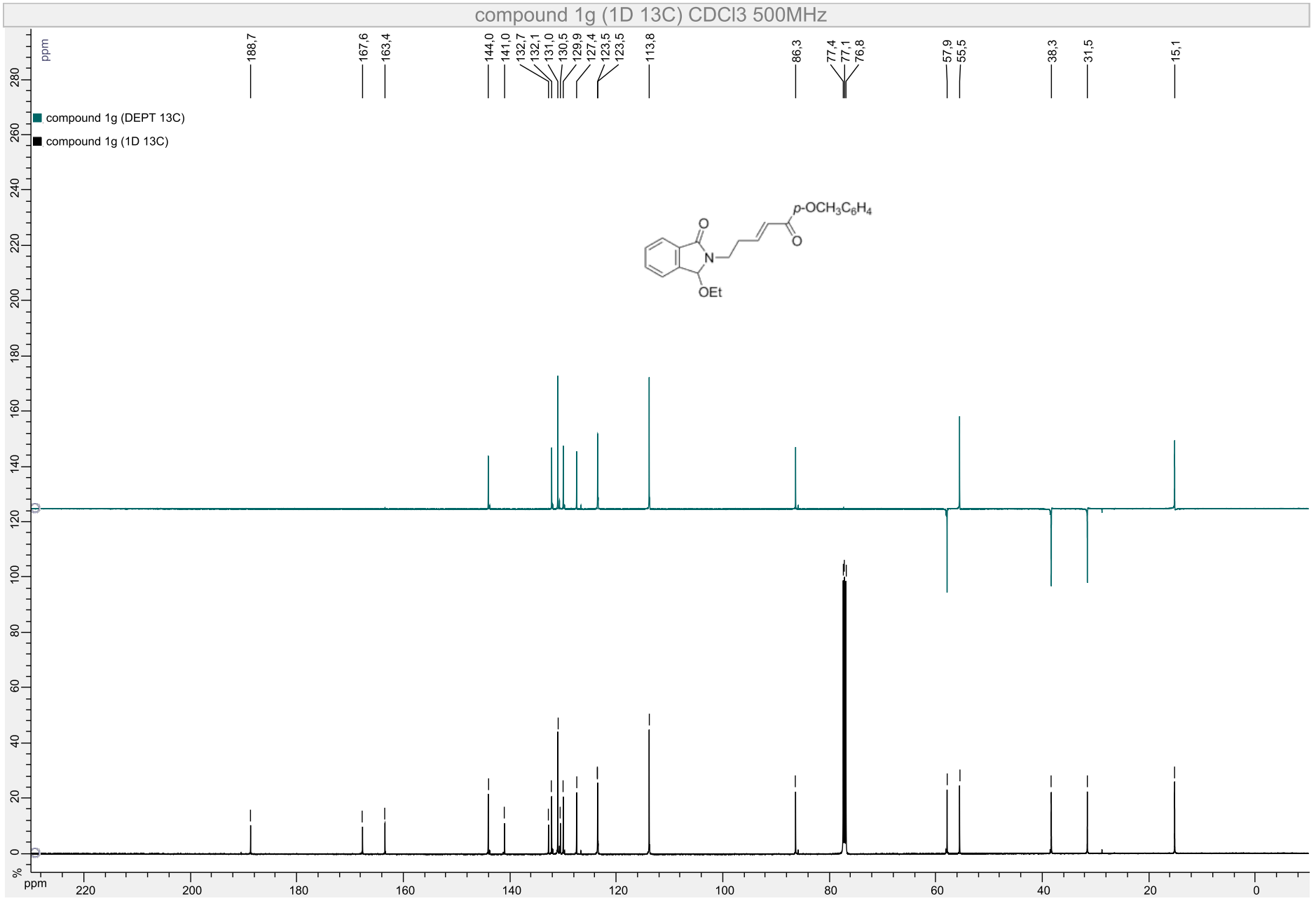
compound 1f (1D 1H) CDCl3 500MHz

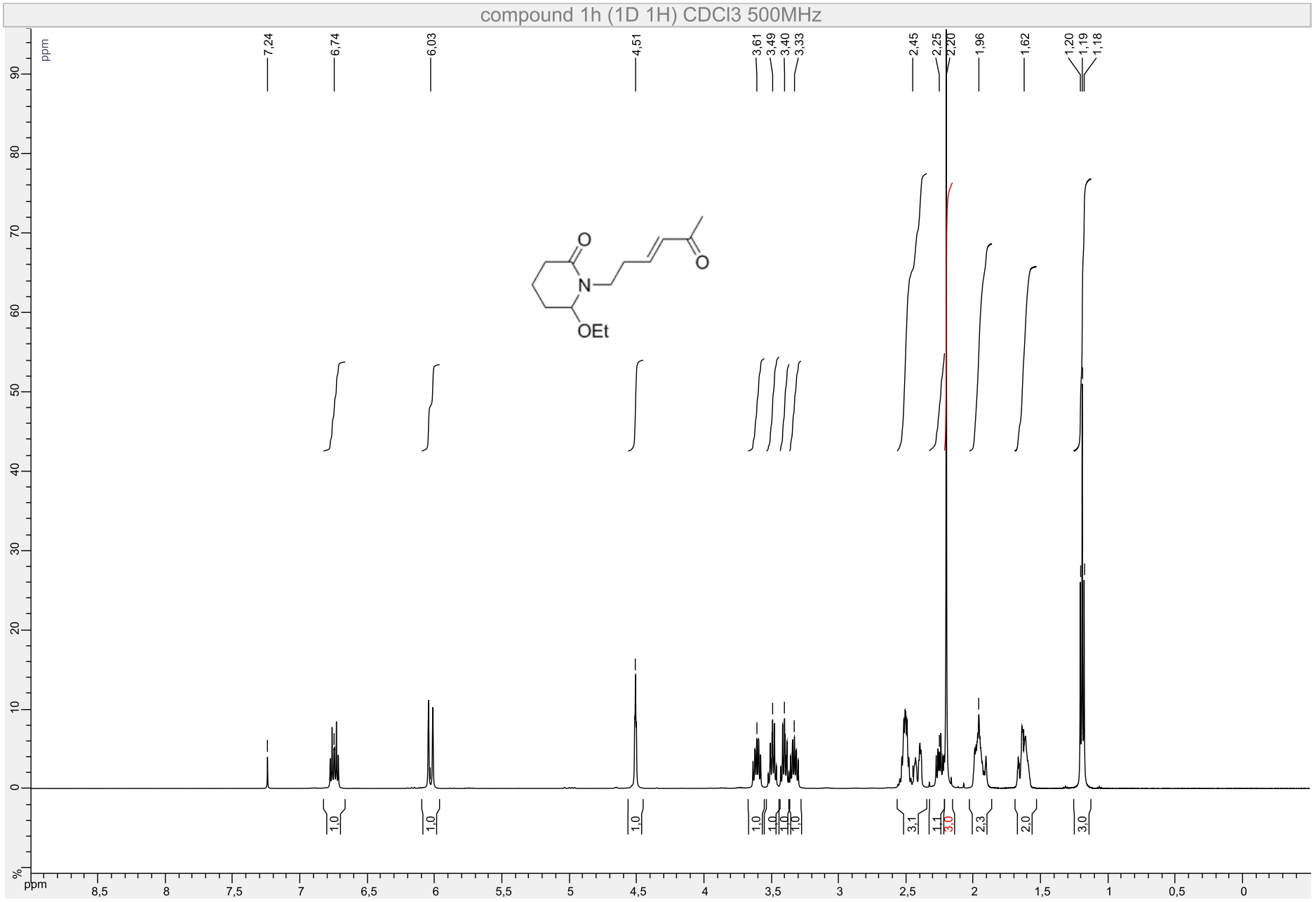


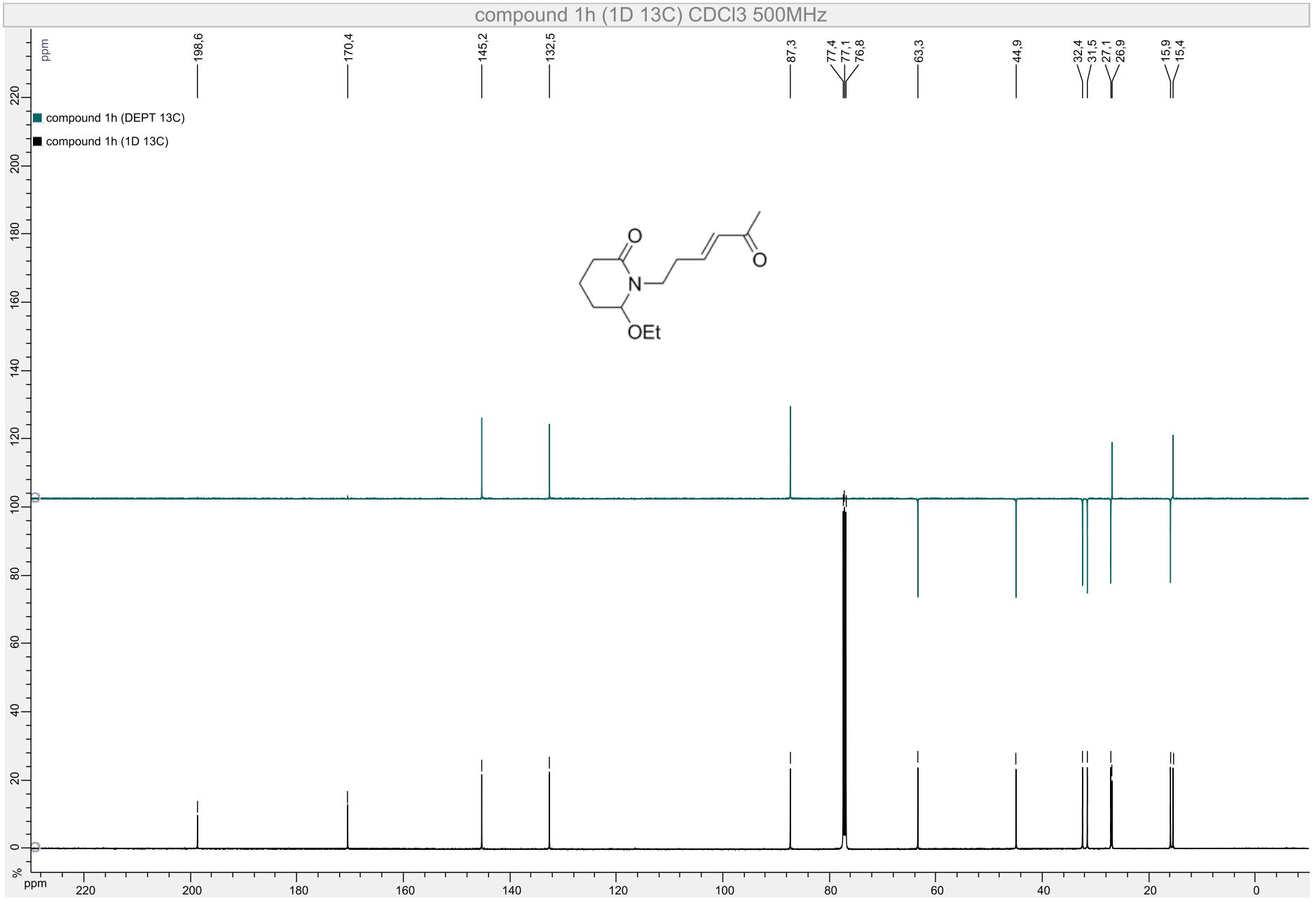

compound 1f (1D 13C) CDCl3 500MHz
ppm
190,5
167,6
145,2
140,9
137,6
132,8
132,7
132,1
130,0
128,7
128,6
127,8
123,5
123,5
86,3
77,4
77,1
76,8
57,8
38,2
31,6
15,1
compound 1f (DEPT 13C)
compound 1f (1D 13C)
Ph
O
O
N
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

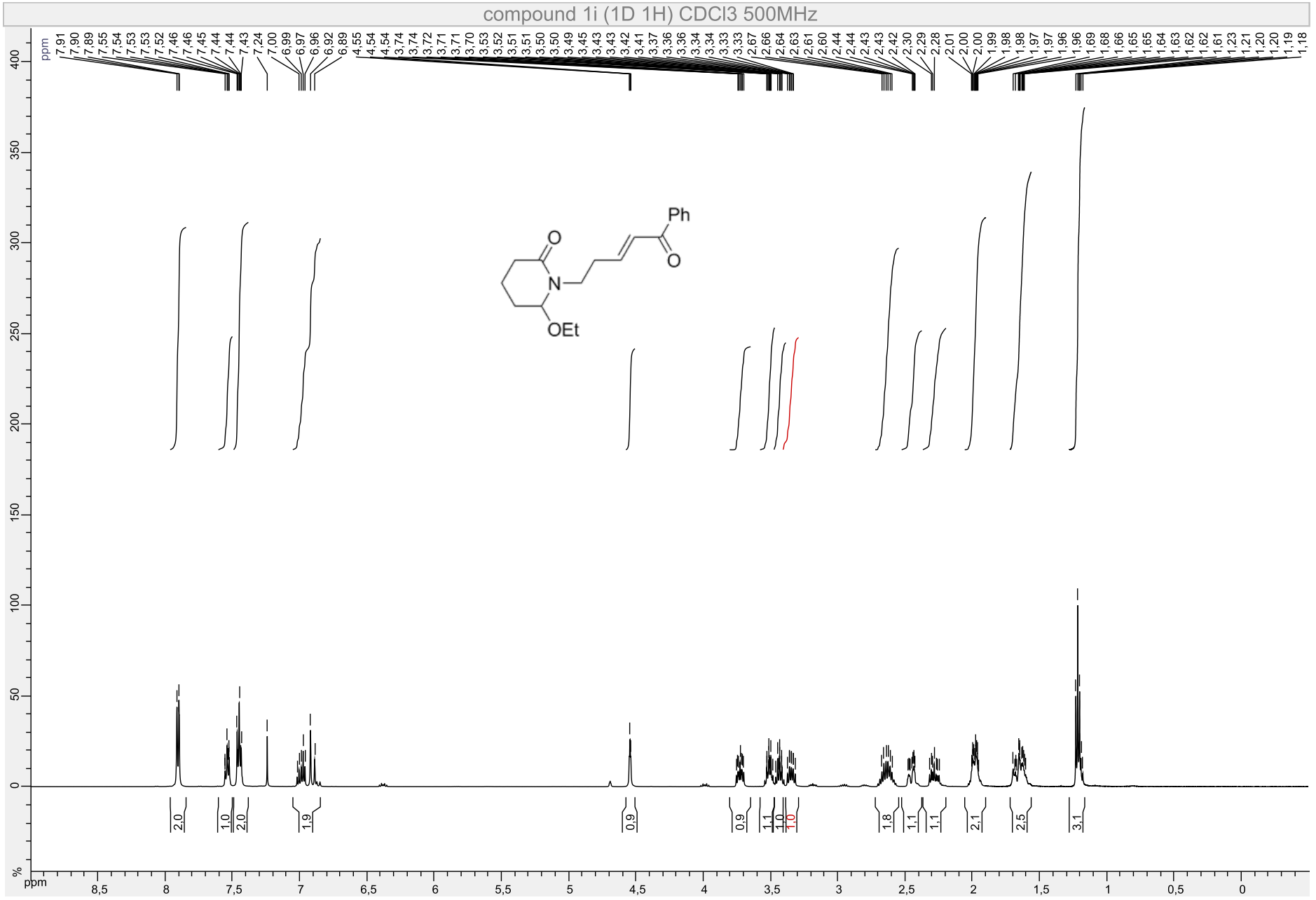
compound 1g (1D 1H) CDCl3 500MHz

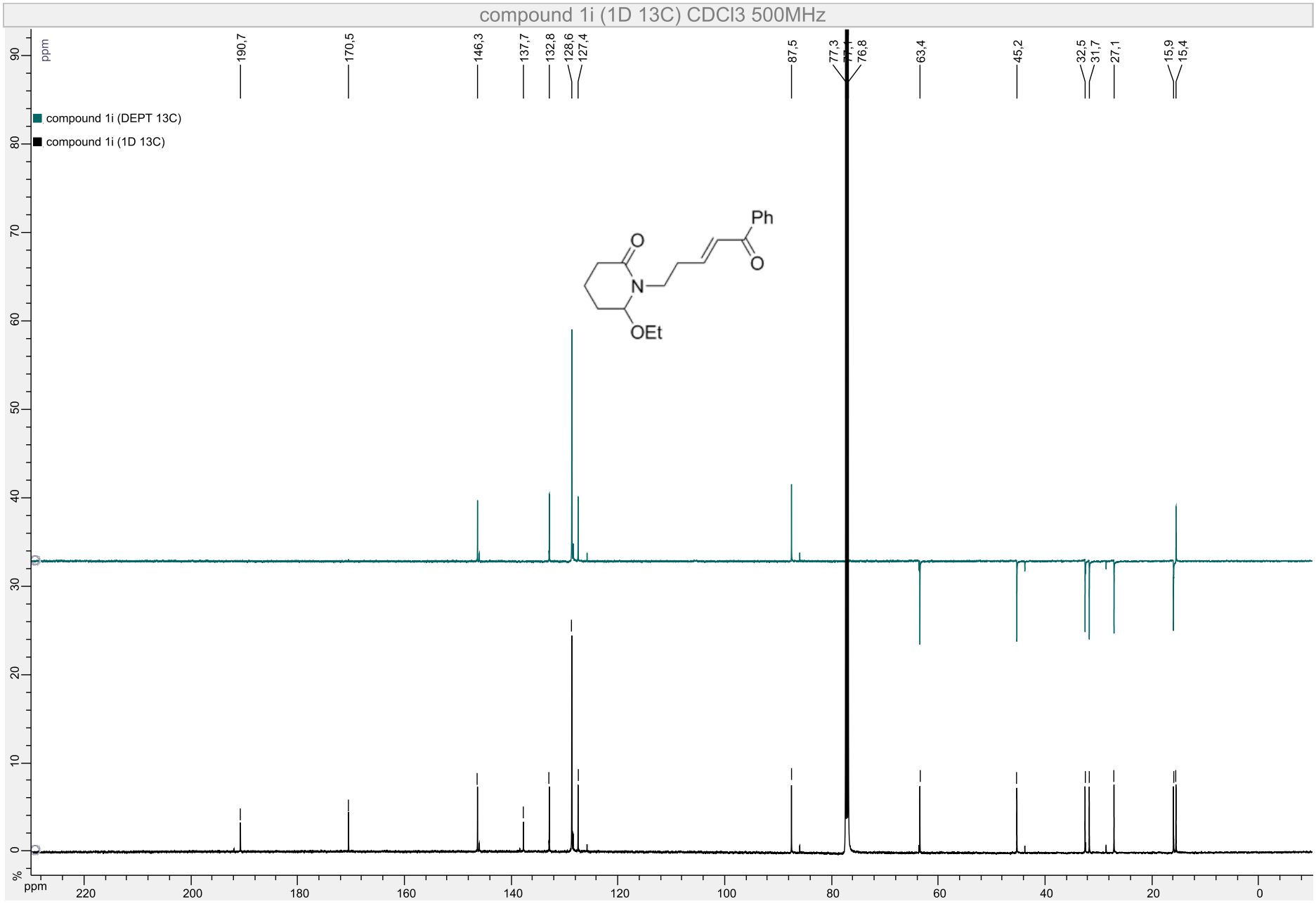



compound 1g (1D 13C) CDCl3 500MHz
ppm
188,7
167,6
163,4
144,0
141,0
132,7
132,1
131,0
130,5
129,9
127,4
123,5
123,5
113,8
86,3
77,4
77,1
76,8
57,9
55,5
38,3
31,5
15,1
compound 1g (DEPT 13C)
compound 1g (1D 13C)
p-OCH3C6H4
O
O
N
O
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

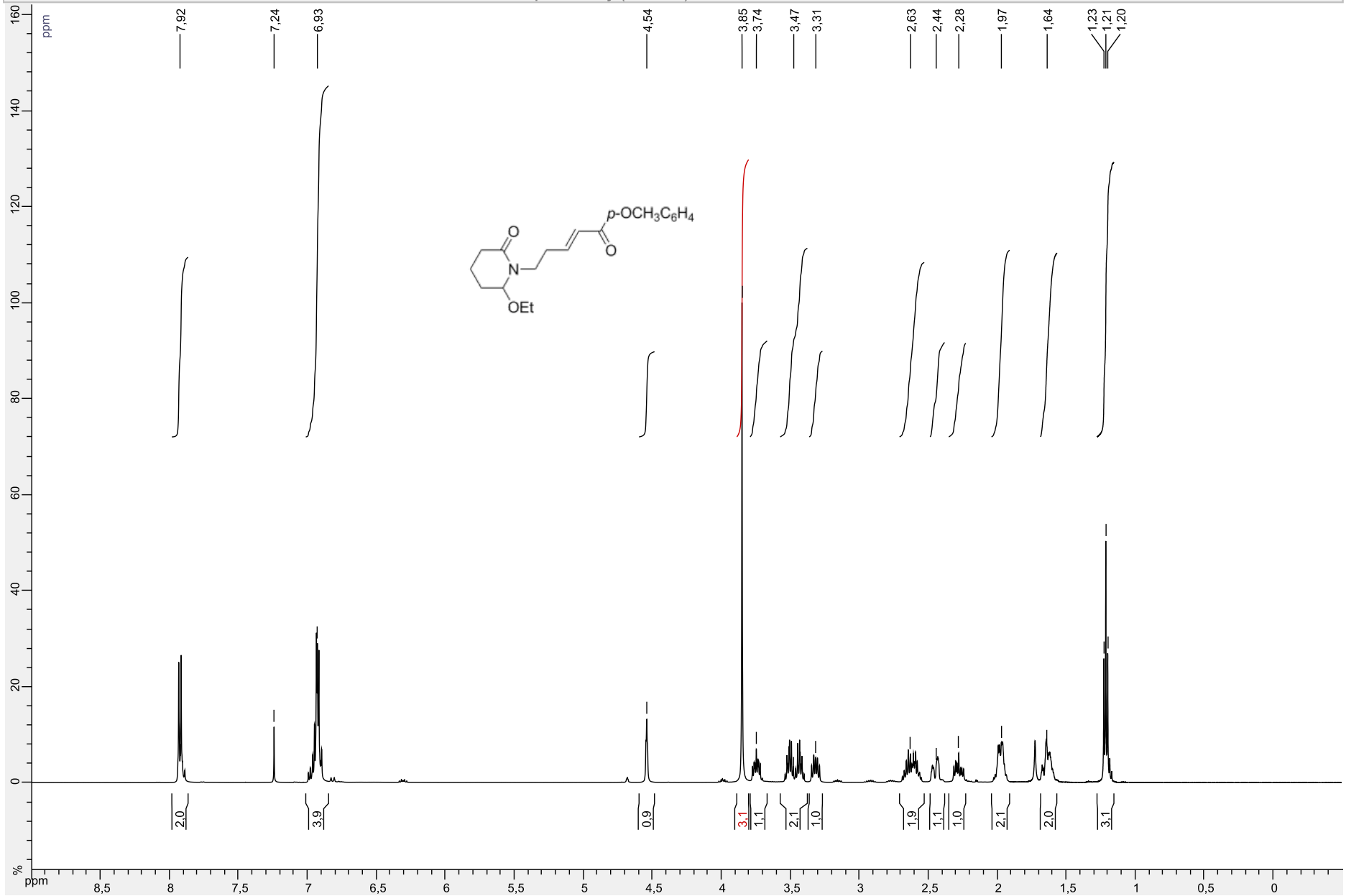

compound 1h (1D 1H) CDCl3 500MHz
ppm
7,24
6,74
6,03
4,51
3,61
3,49
3,40
3,33
2,45
2,25
2,20
1,96
1,62
1,20
1,19
1,18
O
N
OEt
O
1,0
1,0
1,0
1,0
1,0
1,0
1,0
3,1
1,1
3,0
2,3
2,0
3,0
%
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

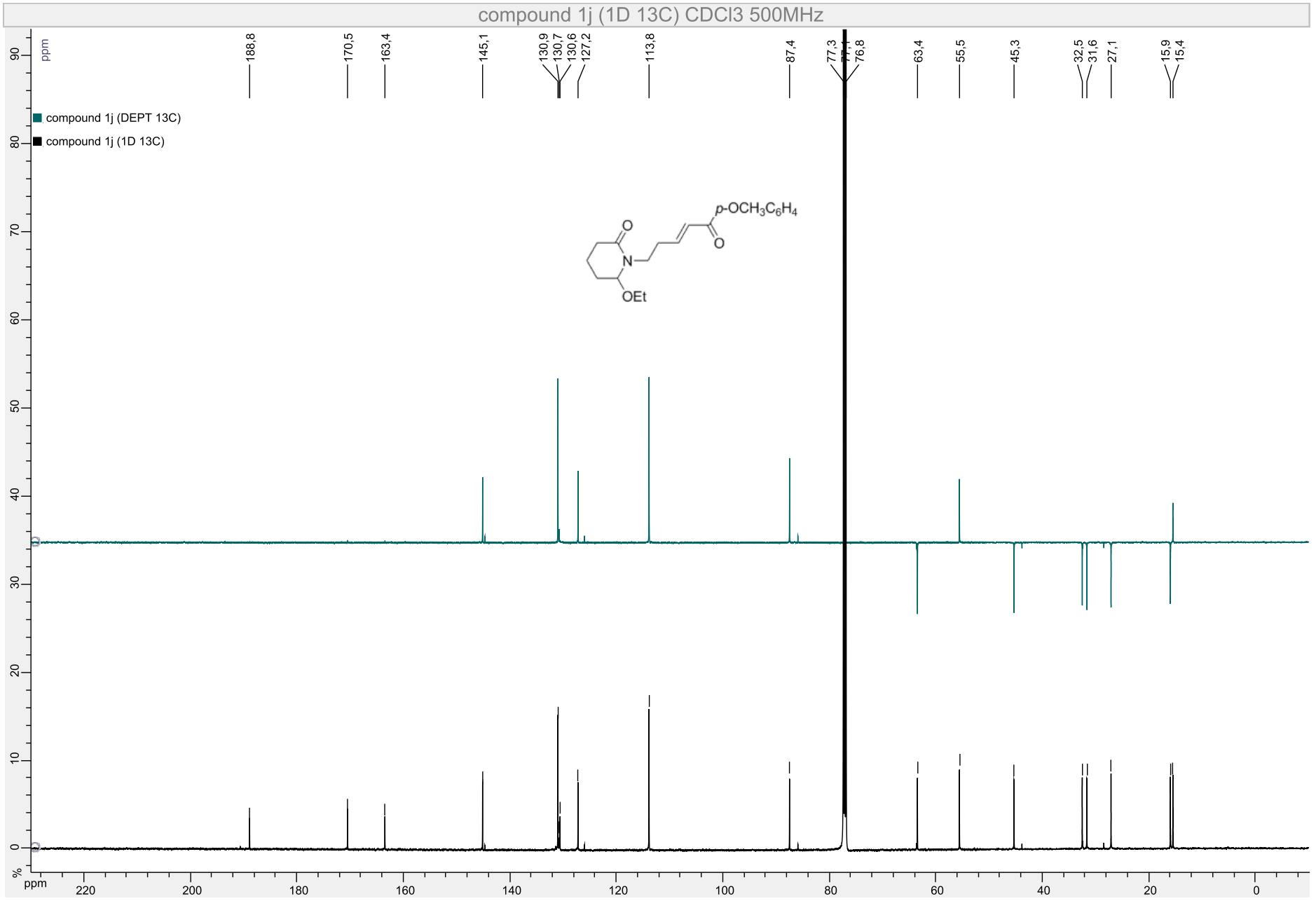

compound 1h (1D 13C) CDCl3 500MHz
ppm
198,6
170,4
145,2
132,5
87,3
77,4
77,1
76,8
63,3
44,9
32,4
31,5
27,1
26,9
15,9
15,4
compound 1h (DEPT 13C)
compound 1h (1D 13C)
O
N
O
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

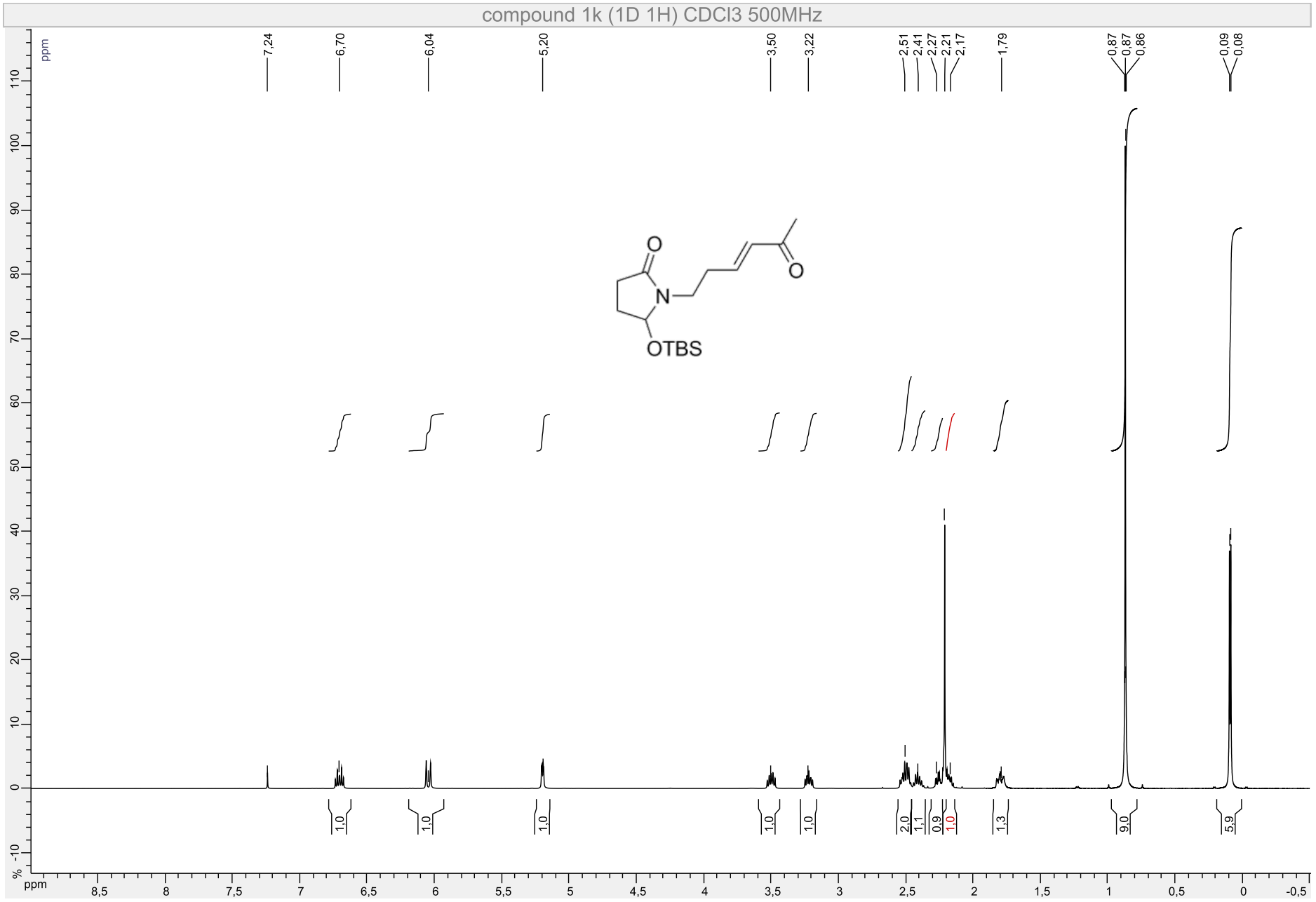

compound 1i (1D 1H) CDCl3 500MHz
ppm
7,91 7,90 7,89 7,55 7,54 7,53 7,53 7,52 7,46 7,46 7,45 7,44 7,44 7,43 7,24 7,00 6,99 6,97 6,96 6,92 6,89 4,55 4,54 4,54 3,74 3,74 3,72 3,71 3,71 3,70 3,53 3,52 3,51 3,51 3,50 3,50 3,49 3,45 3,43 3,43 3,42 3,41 3,37 3,36 3,36 3,34 3,34 3,33 3,33 2,67 2,66 2,64 2,63 2,61 2,60 2,44 2,44 2,43 2,43 2,42 2,30 2,29 2,28 2,01 2,00 2,00 1,99 1,98 1,98 1,97 1,97 1,96 1,96 1,69 1,68 1,66 1,65 1,65 1,64 1,63 1,62 1,62 1,61 1,23 1,21 1,20 1,20 1,19 1,18
Ph
O
N
O
OEt
2,0
1,0
2,0
1,9
0,9
0,9
1,1
1,0
1,0
1,8
1,1
1,1
2,1
2,5
3,1
%
ppm
8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0

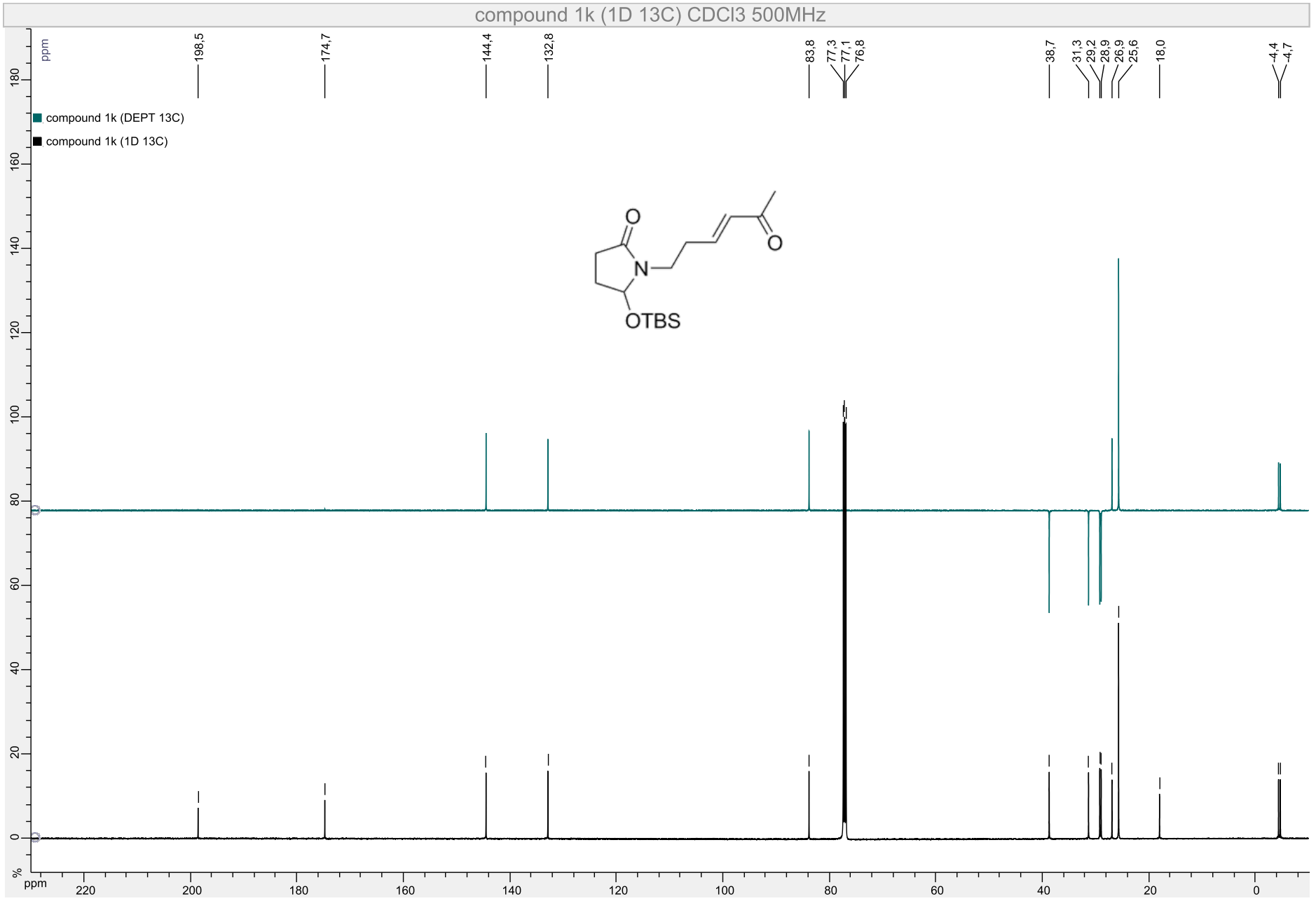

compound 1i (1D 13C) CDCl3 500MHz
ppm
190,7
170,5
146,3
137,7
132,8
128,6
127,4
87,5
77,3
77,1
76,8
63,4
45,2
32,5
31,7
27,1
15,9
15,4
compound 1i (DEPT 13C)
compound 1i (1D 13C)
Ph
O
N
O
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

compound 1j (1D 1H) CDCl3 500MHz

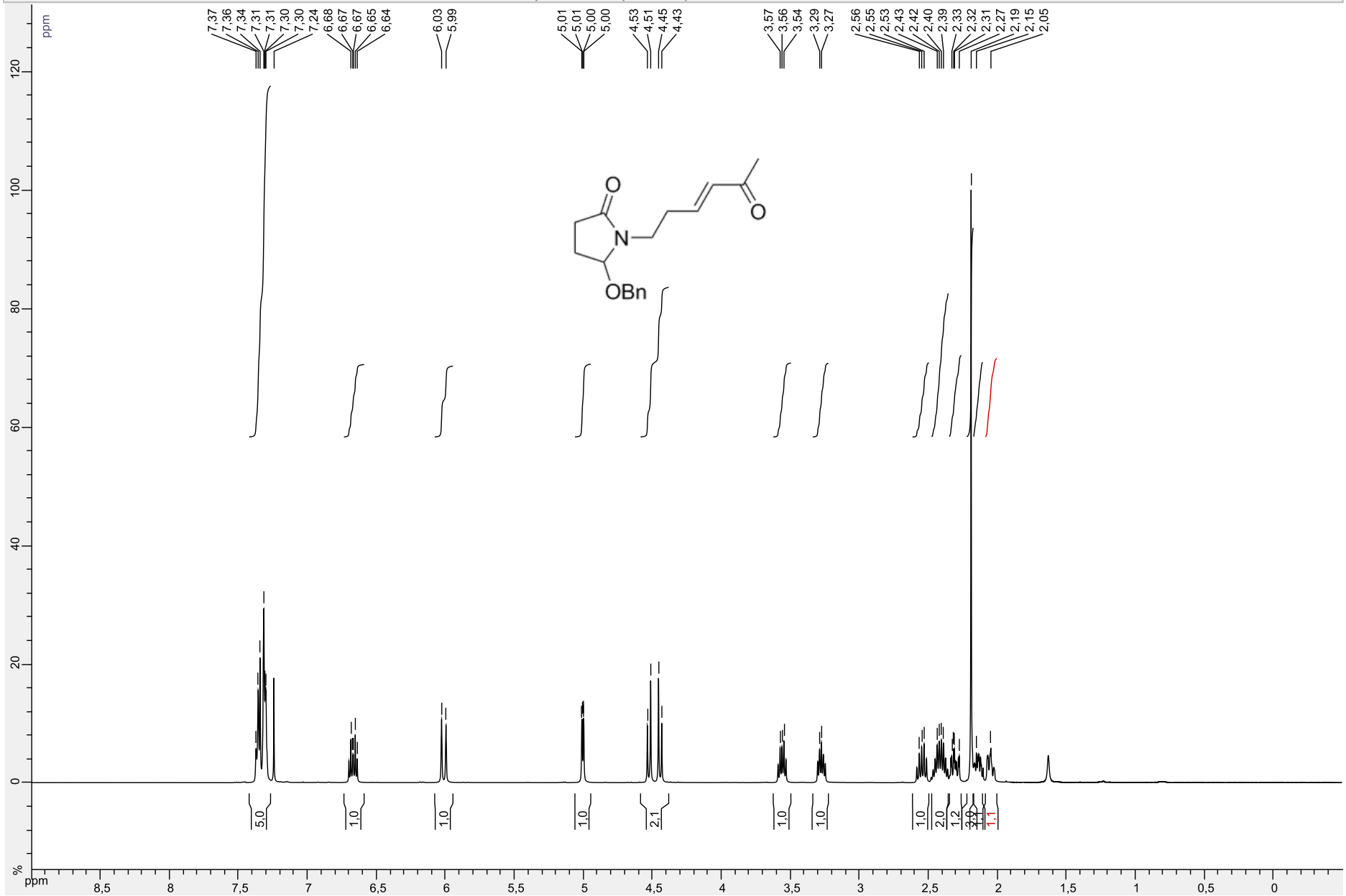


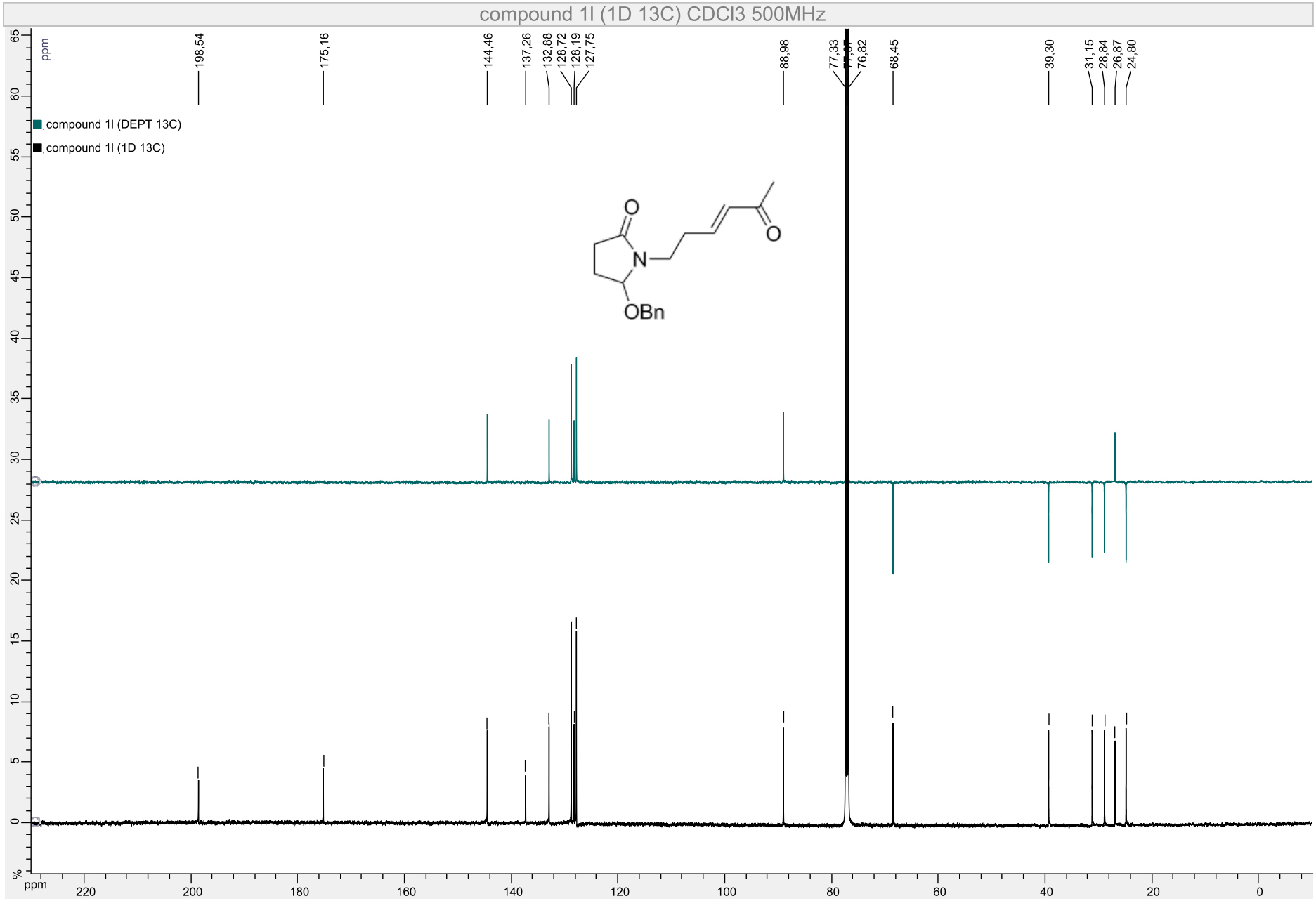

compound 1j (1D 13C) CDCl3 500MHz
ppm
188,8
170,5
163,4
145,1
130,9
130,7
130,6
127,2
113,8
87,4
77,3
77,1
76,8
63,4
55,5
45,3
32,5
31,6
27,1
15,9
15,4
compound 1j (DEPT 13C)
compound 1j (1D 13C)
p-OCH3C6H4
O
O
N
OEt
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

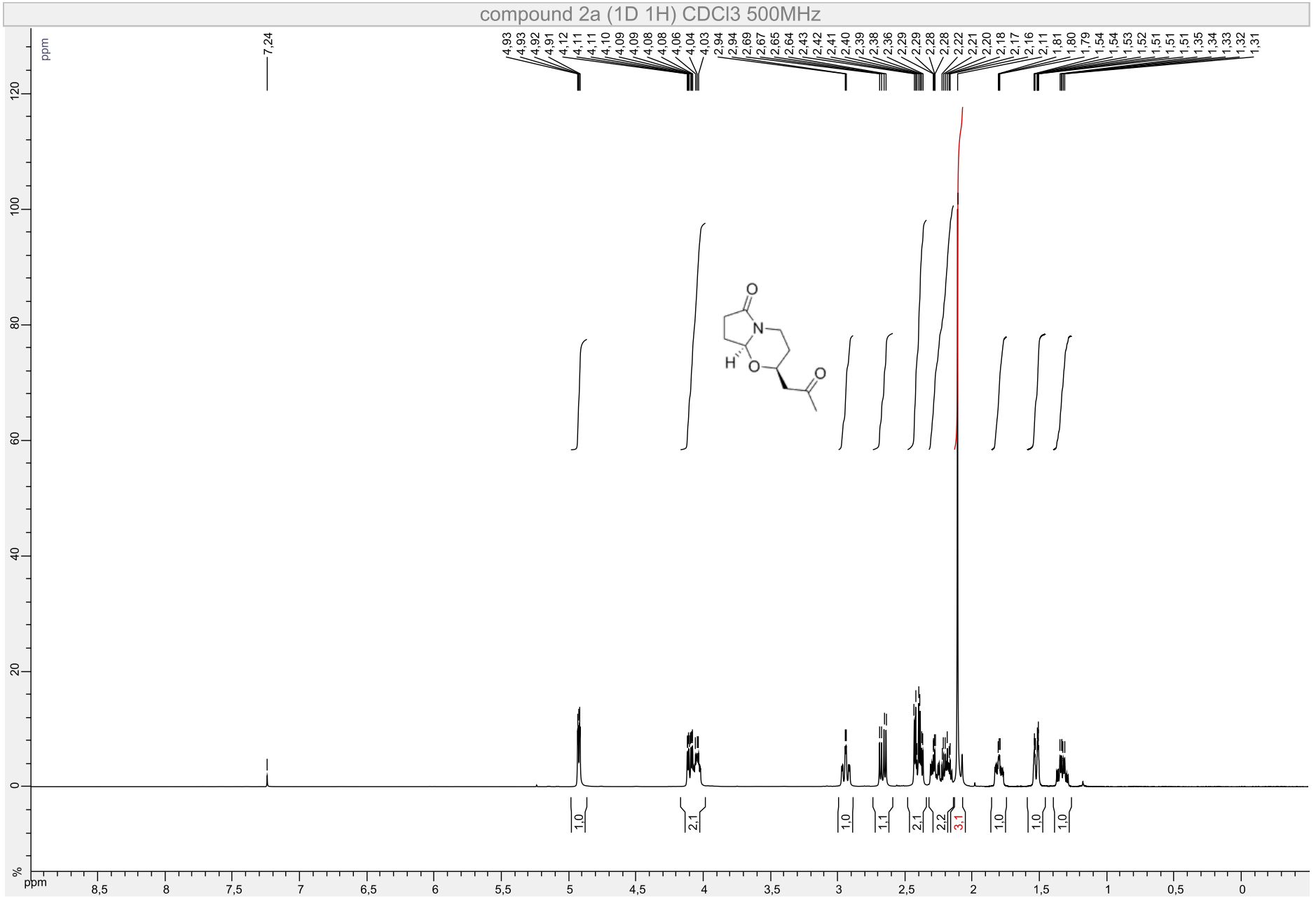

compound 1k (1D 1H) CDCl3 500MHz
ppm
7,24
6,70
6,04
5,20
3,50
3,22
2,51
2,41
2,27
2,21
2,17
1,79
0,87
0,87
0,86
0,09
0,08
O
O
N
OTBS
1,0
1,0
1,0
1,0
1,0
2,0
1,1
0,9
1,0
1,3
9,0
5,9
% 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm 8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0 -0,5

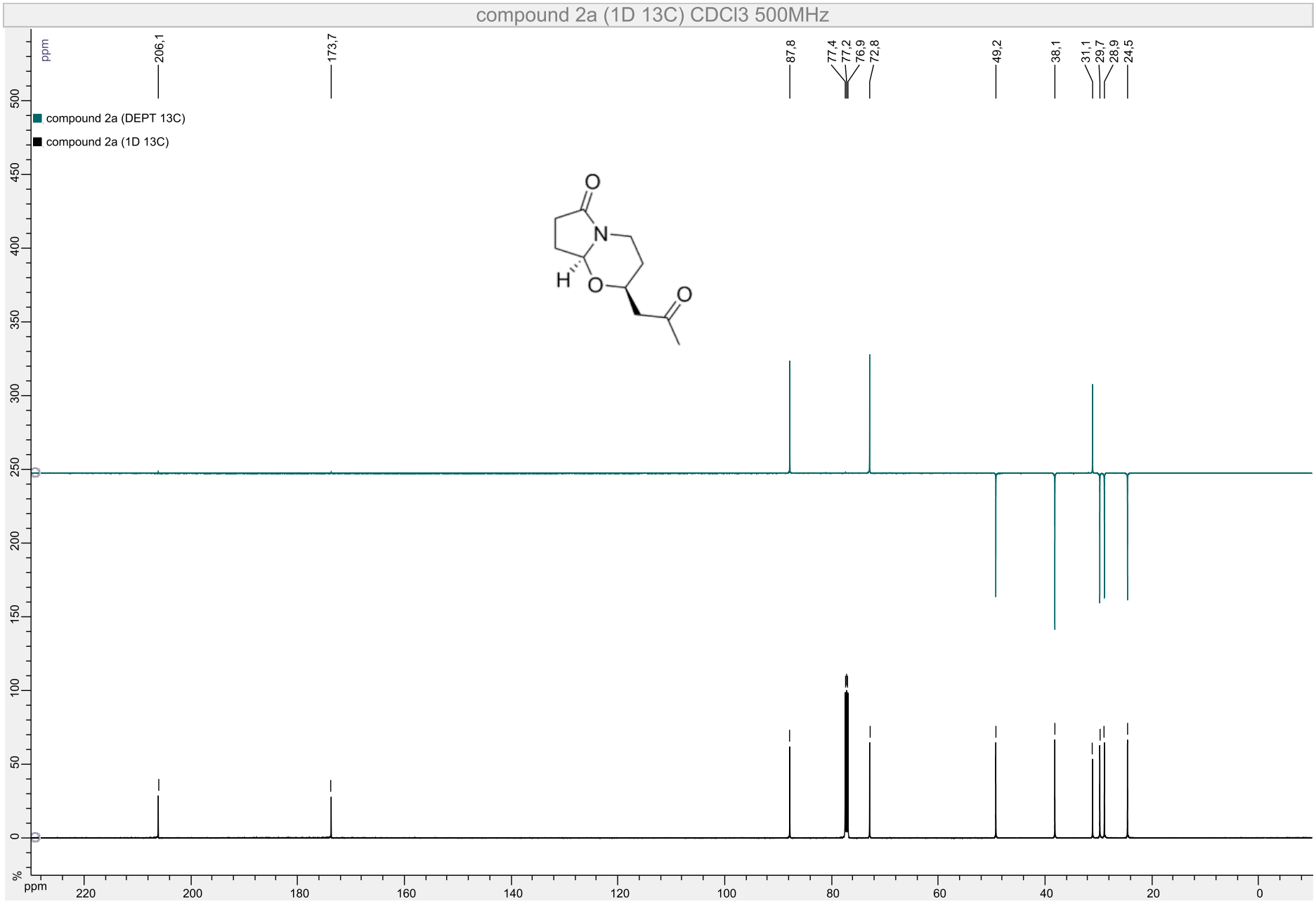

compound 1k (1D 13C) CDCl3 500MHz
ppm
198,5
174,7
144,4
132,8
83,8
77,3
77,1
76,8
38,7
31,3
29,2
28,9
26,9
25,6
18,0
-4,4
-4,7
compound 1k (DEPT 13C)
compound 1k (1D 13C)
O
N
O
OTBS
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

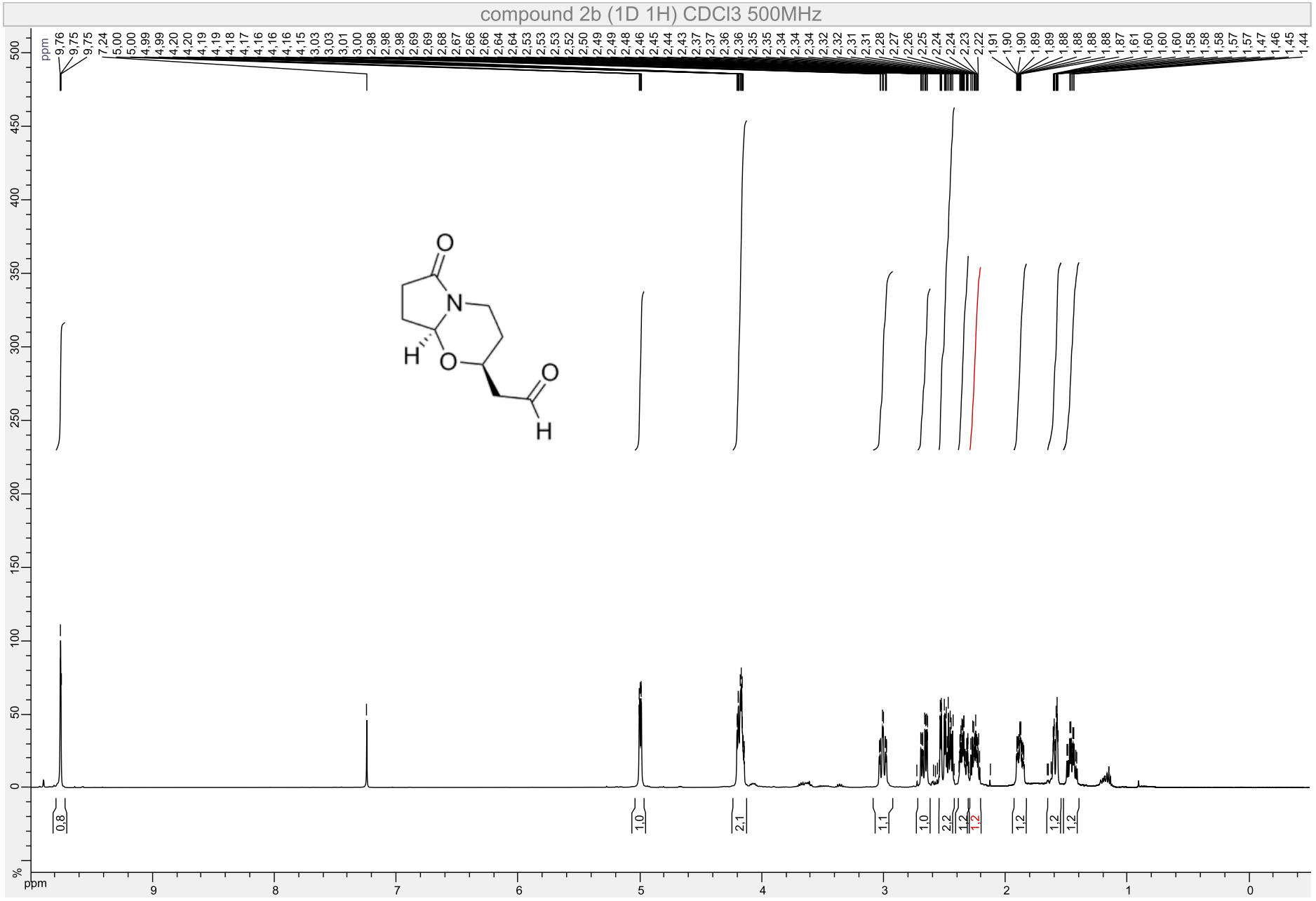
compound 1l (1D 1H) CDCl3 500MHz

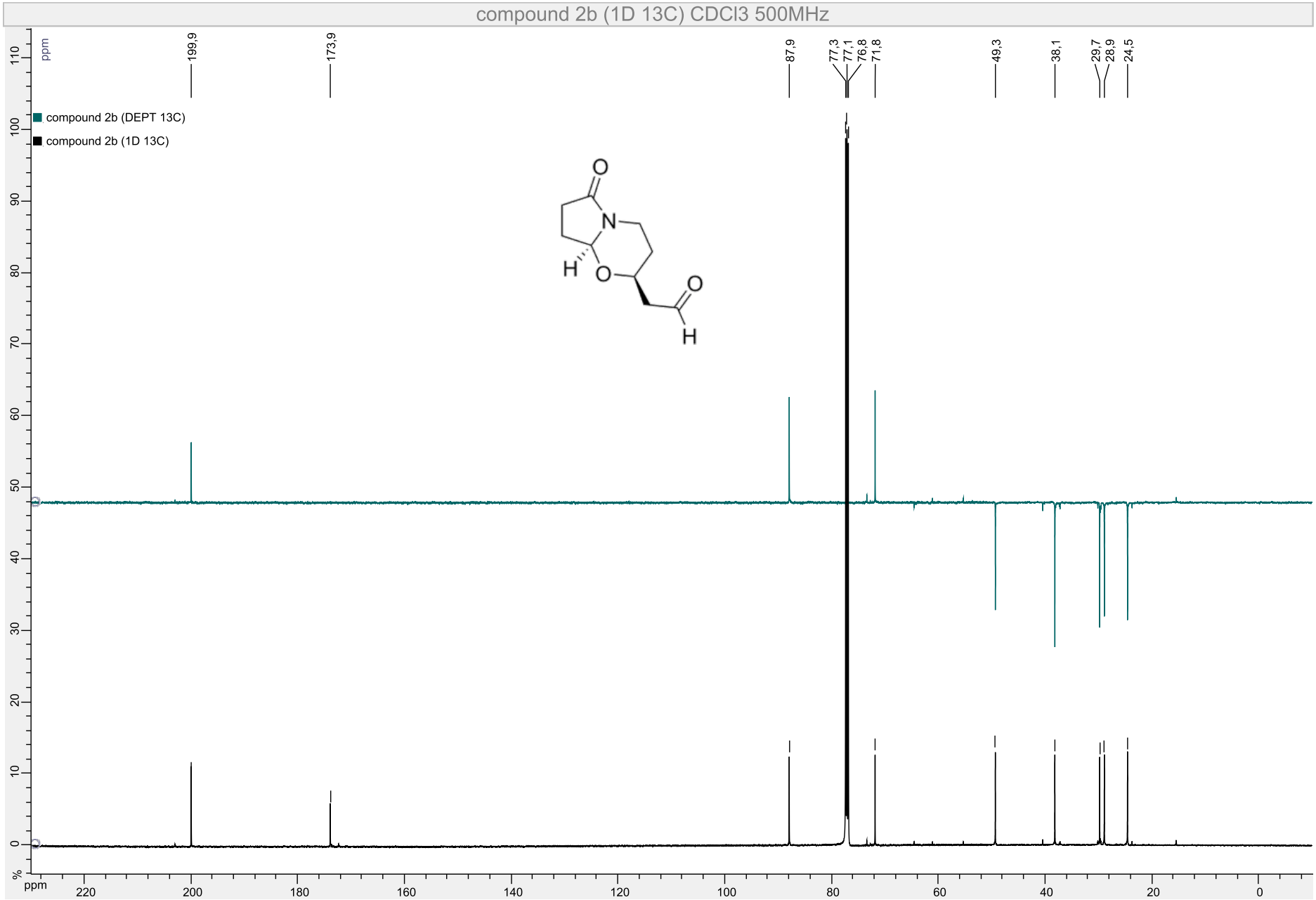



compound 1l (1D 13C) CDCl3 500MHz
ppm
198,54
175,16
144,46
137,26
132,88
128,72
128,19
127,75
88,98
77,33
77,07
76,82
68,45
39,30
31,15
28,84
26,87
24,80
compound 1l (DEPT 13C)
compound 1l (1D 13C)
O
N
O
OBn
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

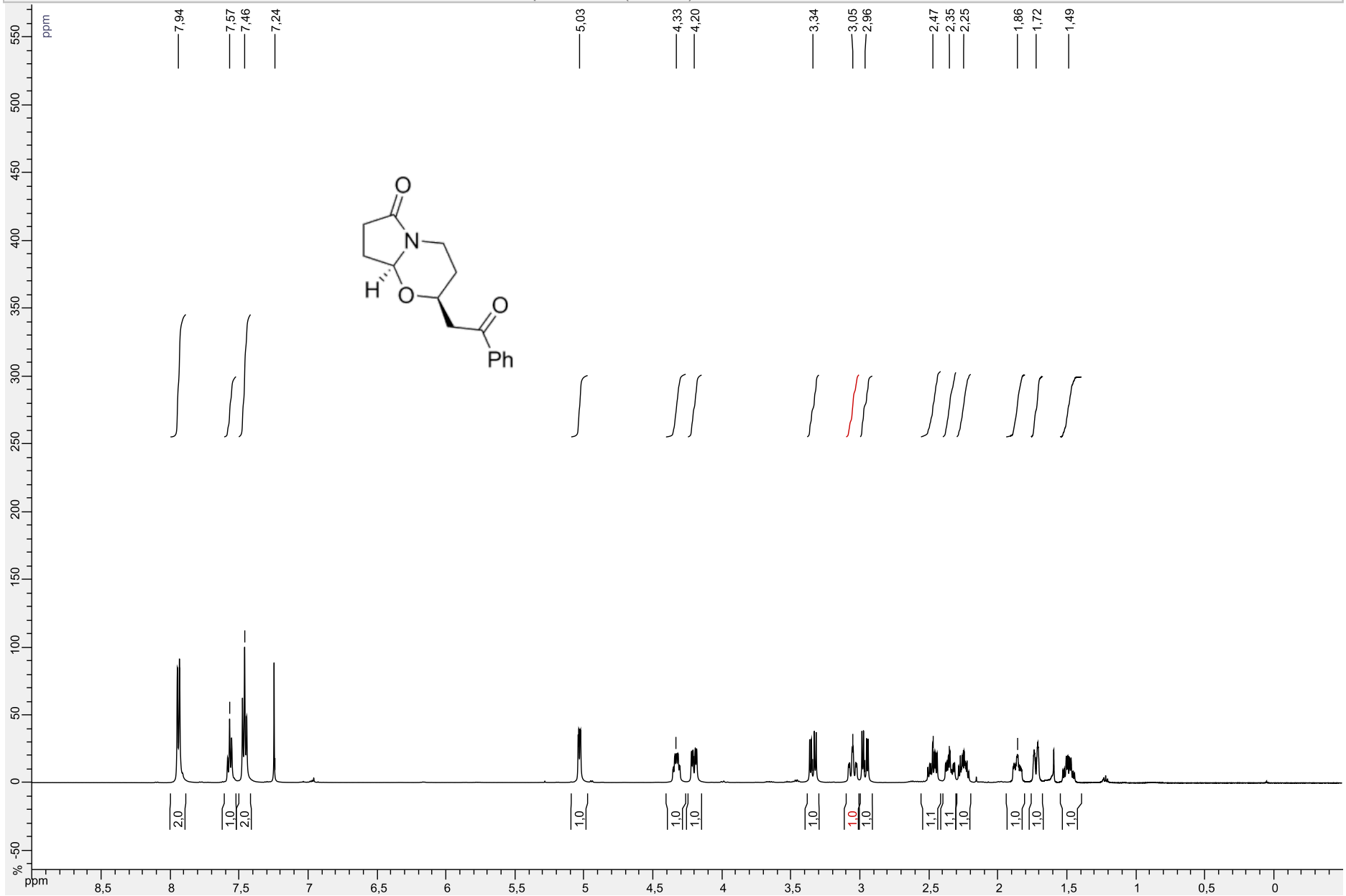

compound 2a (1D 1H) CDCl3 500MHz
ppm
7,24
4,93 4,93 4,92 4,91 4,12 4,11 4,11 4,10 4,09 4,09 4,08 4,08 4,06 4,04 4,03
2,94 2,94 2,69 2,67 2,65 2,64 2,43 2,42 2,41 2,40 2,39 2,38 2,36 2,29 2,29 2,28 2,28 2,22 2,21 2,20 2,18 2,17 2,16 2,11 1,81 1,80 1,79 1,54 1,54 1,53 1,52 1,51 1,51 1,51 1,35 1,34 1,33 1,32 1,31
O
N
H
O
O
1,0
2,1
1,0
1,1
2,1
2,2
3,1
1,0
1,0
1,0
%
120
100
80
60
40
20
0
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

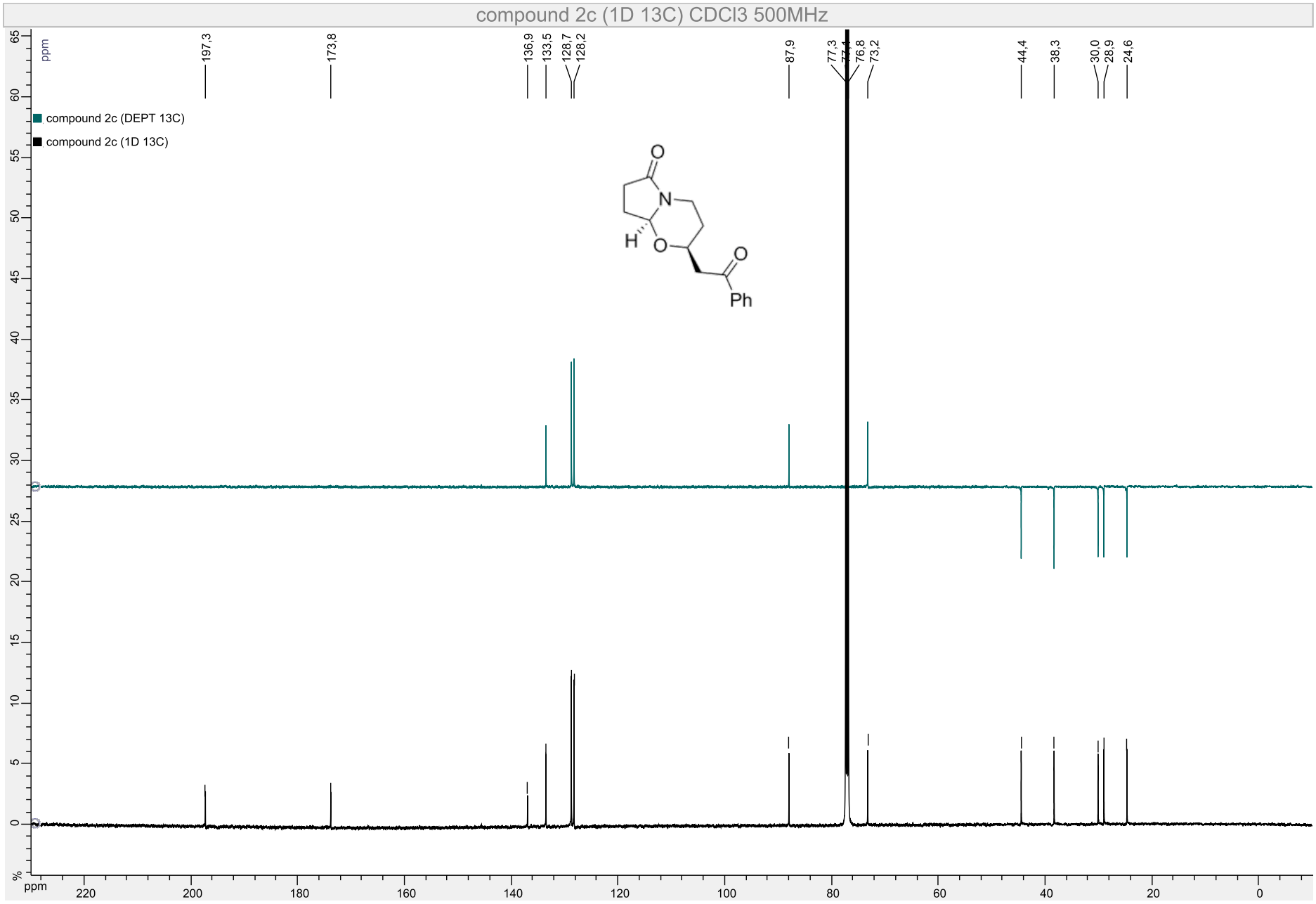

compound 2a (1D 13C) CDCl3 500MHz
ppm
206,1
173,7
87,8
77,4
77,2
76,9
72,8
49,2
38,1
31,1
29,7
28,9
24,5
compound 2a (DEPT 13C)
compound 2a (1D 13C)
O
N
H
O
O
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0


compound 2b (1D 1H) CDCl3 500MHz
ppm
9,76 9,75 9,75 7,24 5,00 5,00 4,99 4,99 4,20 4,20 4,19 4,19 4,18 4,17 4,16 4,16 4,16 4,15 3,03 3,03 3,01 3,00 2,98 2,98 2,98 2,69 2,69 2,68 2,67 2,66 2,66 2,64 2,64 2,53 2,53 2,53 2,52 2,50 2,49 2,49 2,48 2,46 2,45 2,44 2,43 2,37 2,37 2,36 2,36 2,35 2,35 2,34 2,34 2,34 2,32 2,32 2,31 2,31 2,28 2,27 2,26 2,25 2,24 2,24 2,24 2,23 2,22 1,91 1,90 1,90 1,89 1,89 1,88 1,88 1,88 1,87 1,87 1,61 1,60 1,60 1,60 1,58 1,58 1,58 1,57 1,57 1,47 1,46 1,45 1,44
O
N
H
O
O
H
0,8
1,0
2,1
1,1
1,0
2,2
1,2
1,2
1,2
1,2
1,2
%
ppm
9
8
7
6
5
4
3
2
1
0

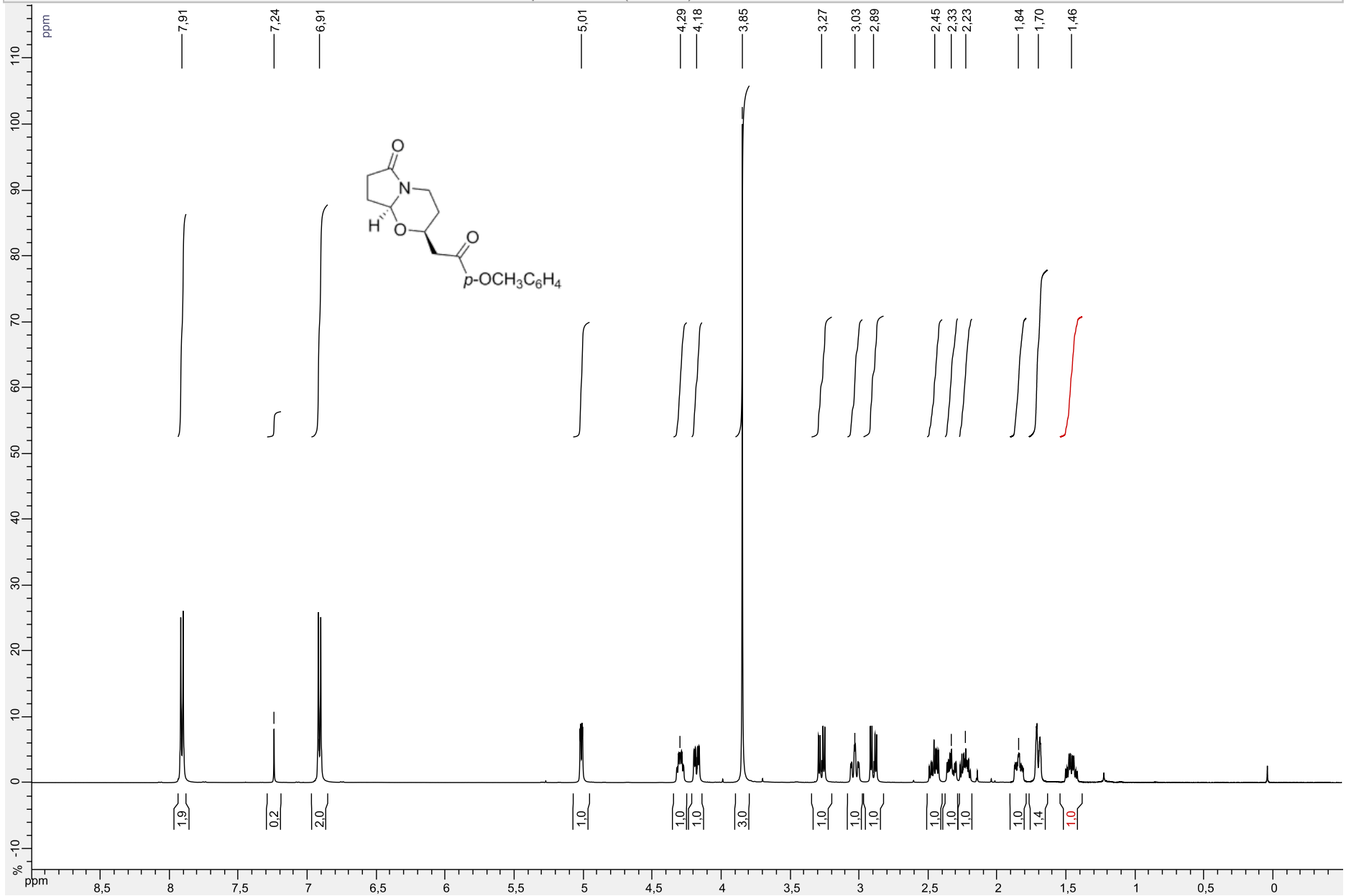

compound 2b (1D 13C) CDCl3 500MHz
ppm
199,9
173,9
87,9
77,3
77,1
76,8
71,8
49,3
38,1
29,7
28,9
24,5
compound 2b (DEPT 13C)
compound 2b (1D 13C)
O
N
H
O
O
H
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

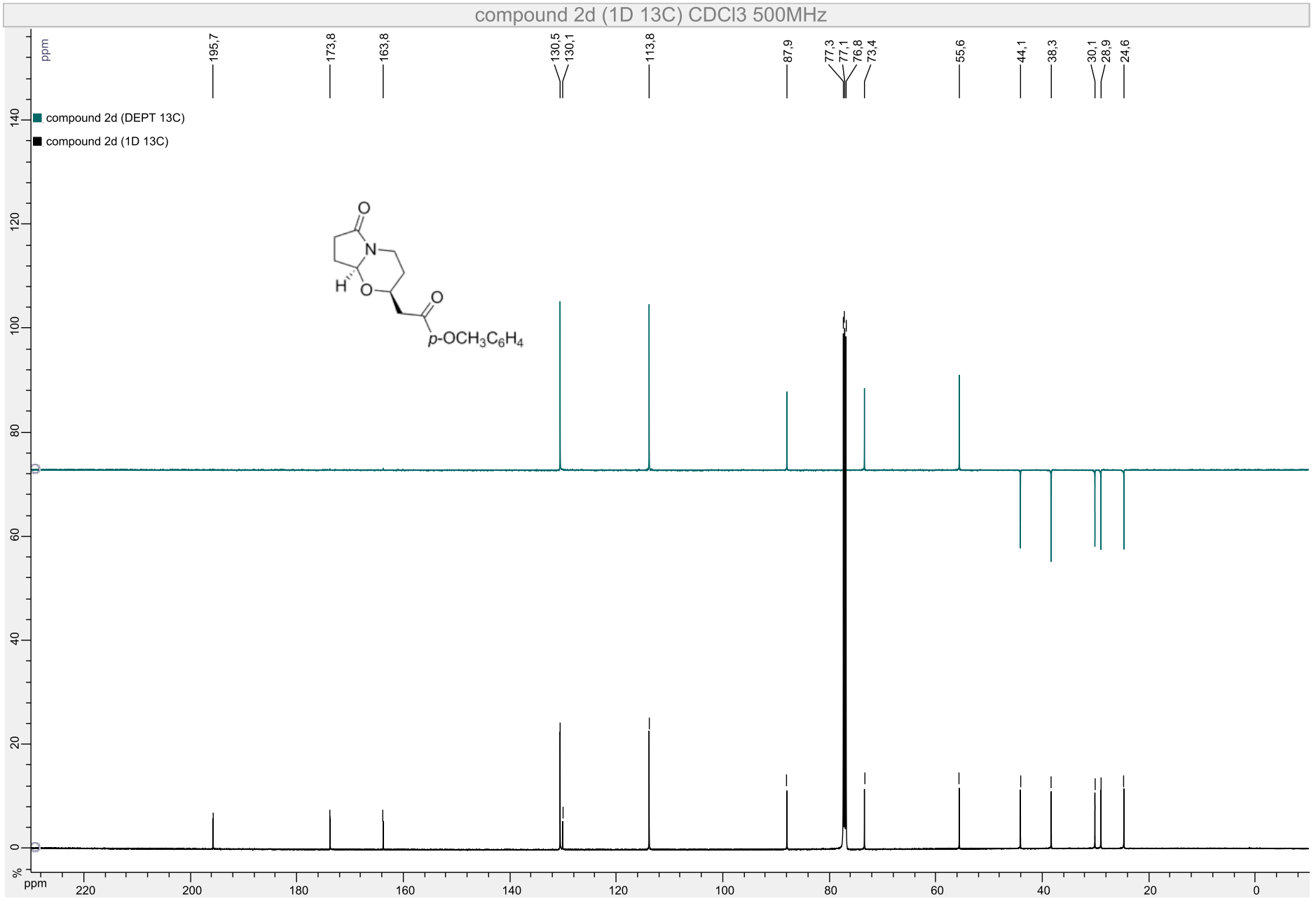
compound 2c (1D 1H) CDCl3 500MHz



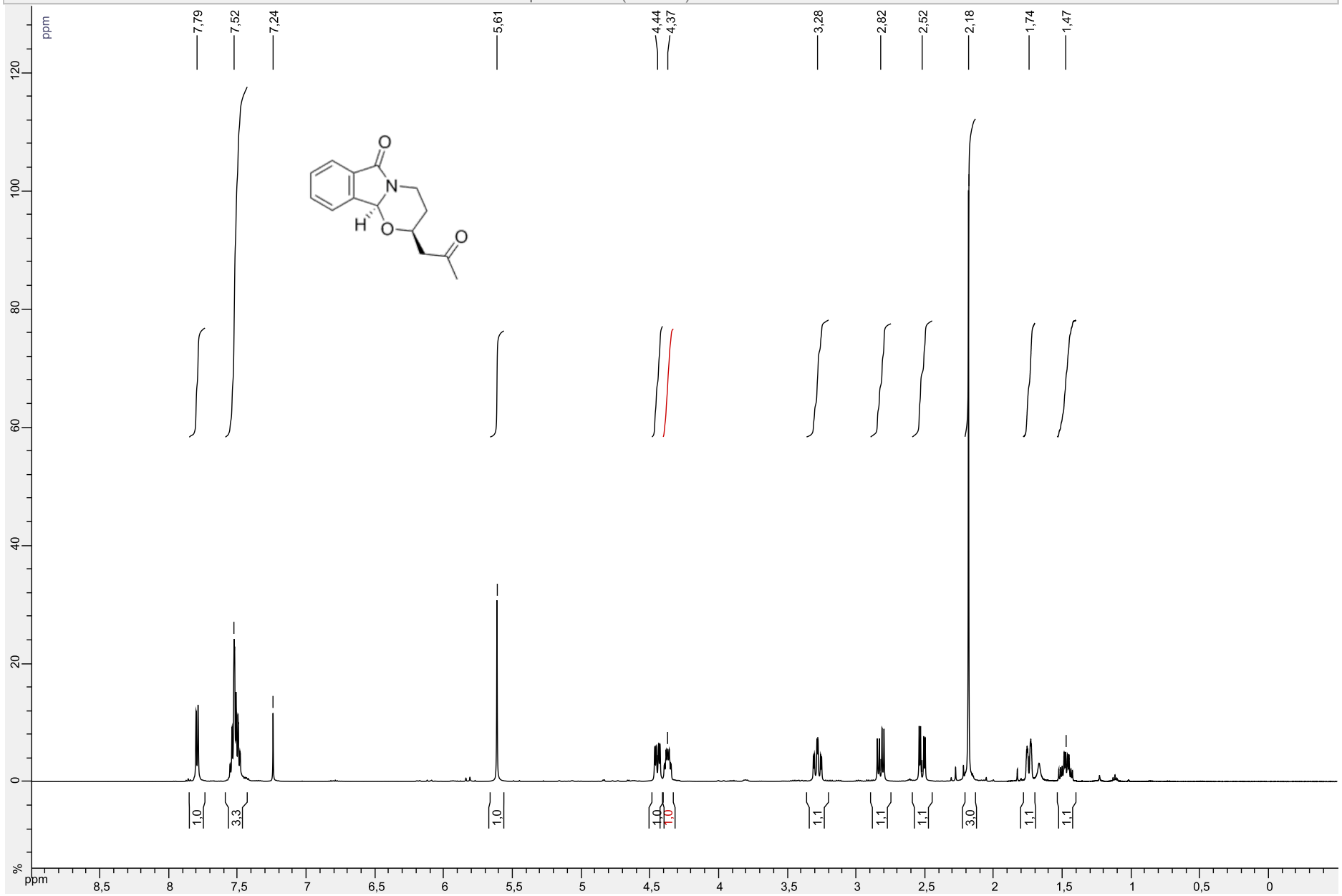

compound 2c (1D 13C) CDCl3 500MHz
ppm
197,3
173,8
136,9
133,5
128,7
128,2
87,9
77,3
77,1
76,8
73,2
44,4
38,3
30,0
28,9
24,6
compound 2c (DEPT 13C)
compound 2c (1D 13C)
O
N
H
O
O
Ph
%
65
60
55
50
45
40
35
30
25
20
15
10
5
0
ppm
220
200
180
160
140
120
100
80
60
40
20
0

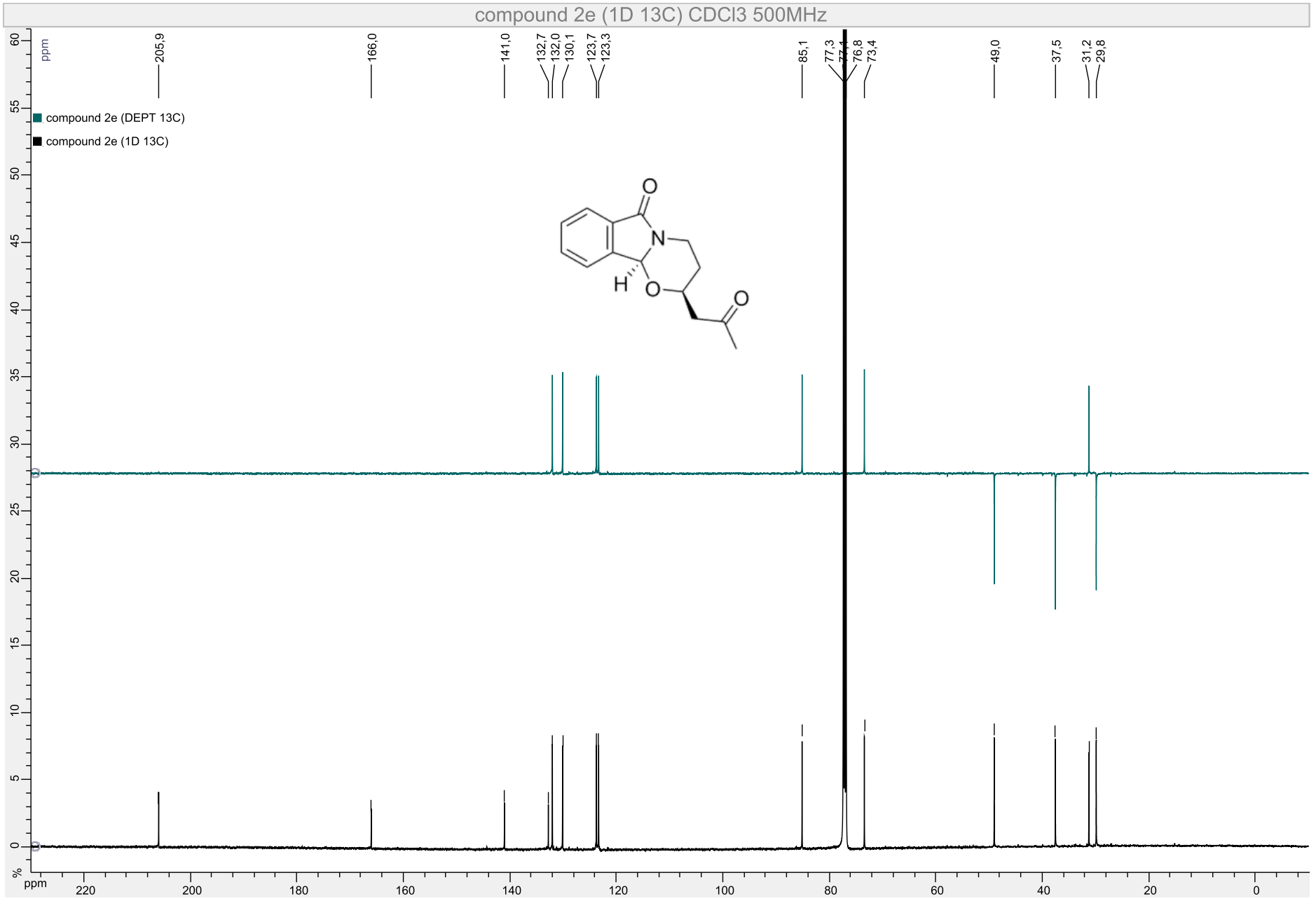
compound 2d (1D 1H) CDCl3 500MHz

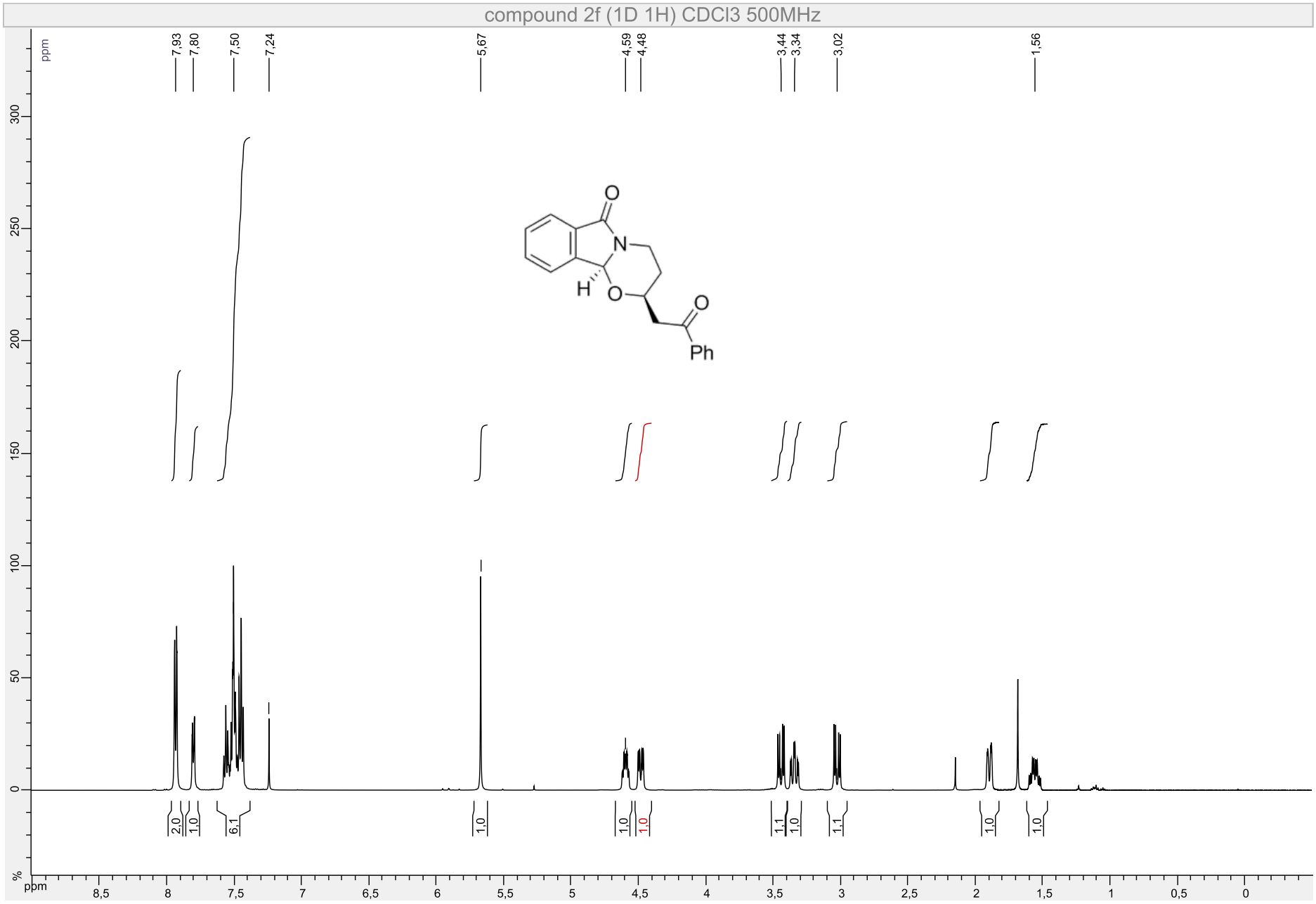


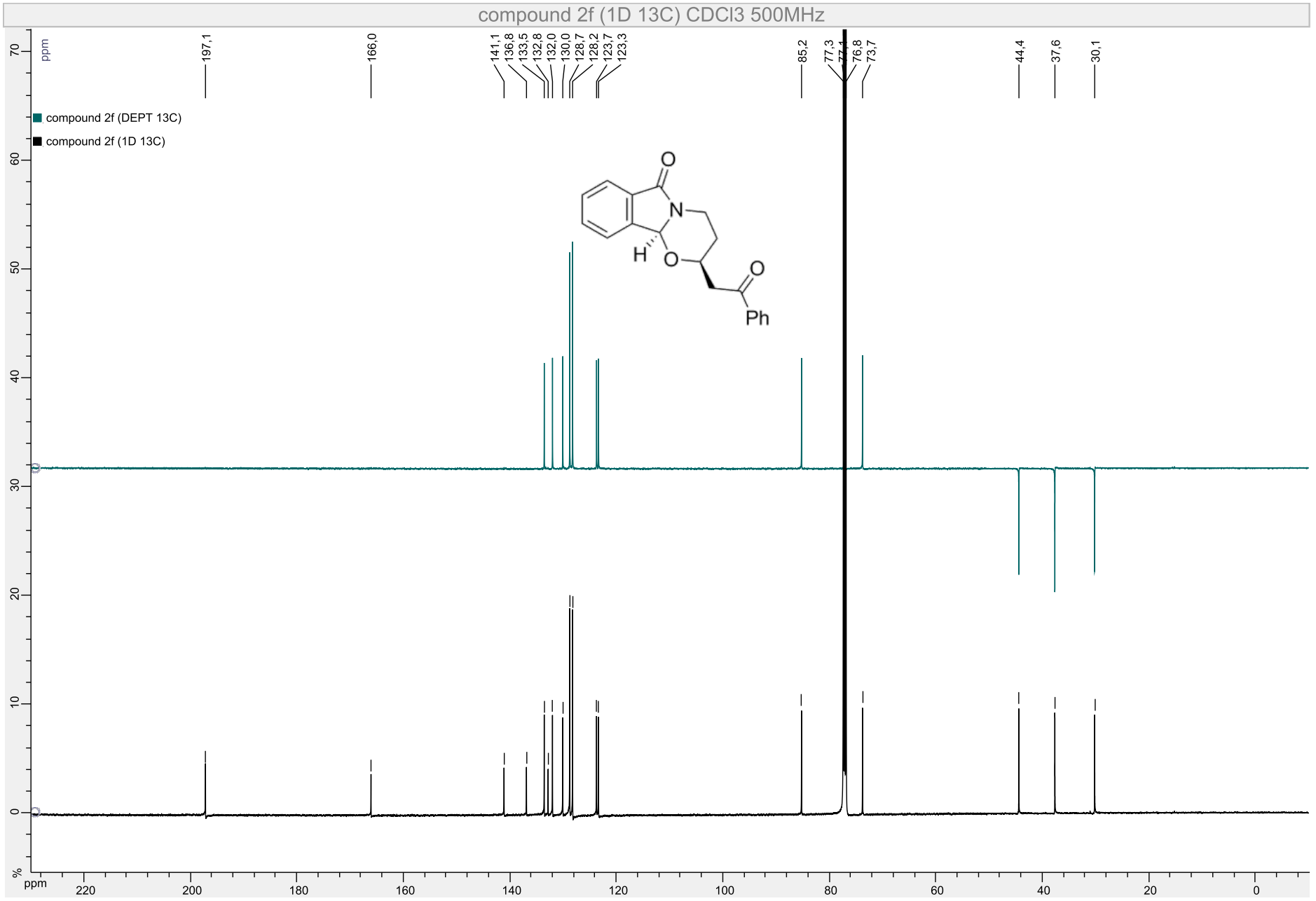

compound 2d (1D 13C) CDCl3 500MHz
ppm
195,7
173,8
163,8
130,5
130,1
113,8
87,9
77,3
77,1
76,8
73,4
55,6
44,1
38,3
30,1
28,9
24,6
compound 2d (DEPT 13C)
compound 2d (1D 13C)
O
N
H
O
O
p-OCH3C6H4
140
120
100
80
60
40
20
0
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

compound 2e (1D 1H) CDCl3 500MHz

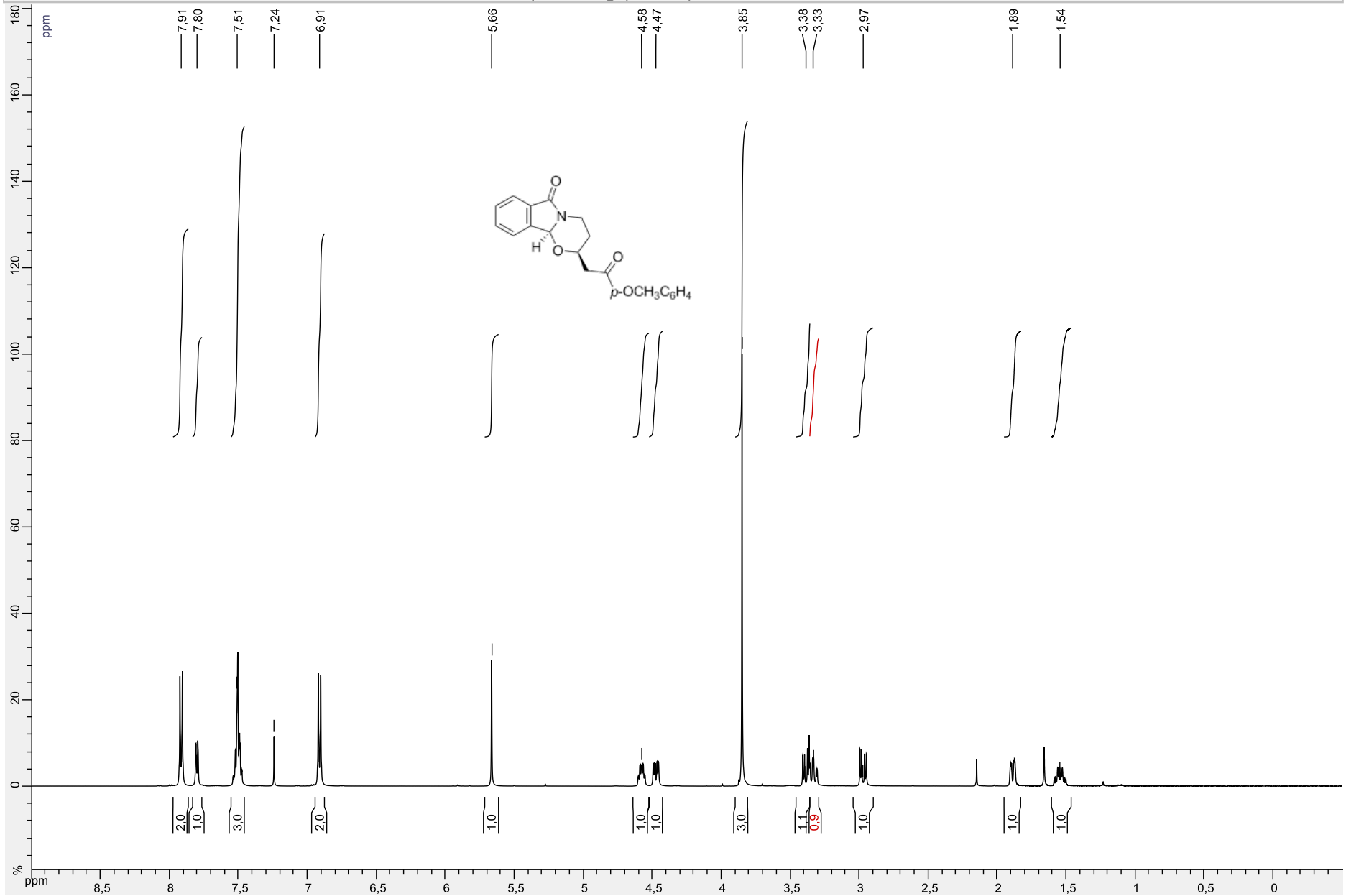


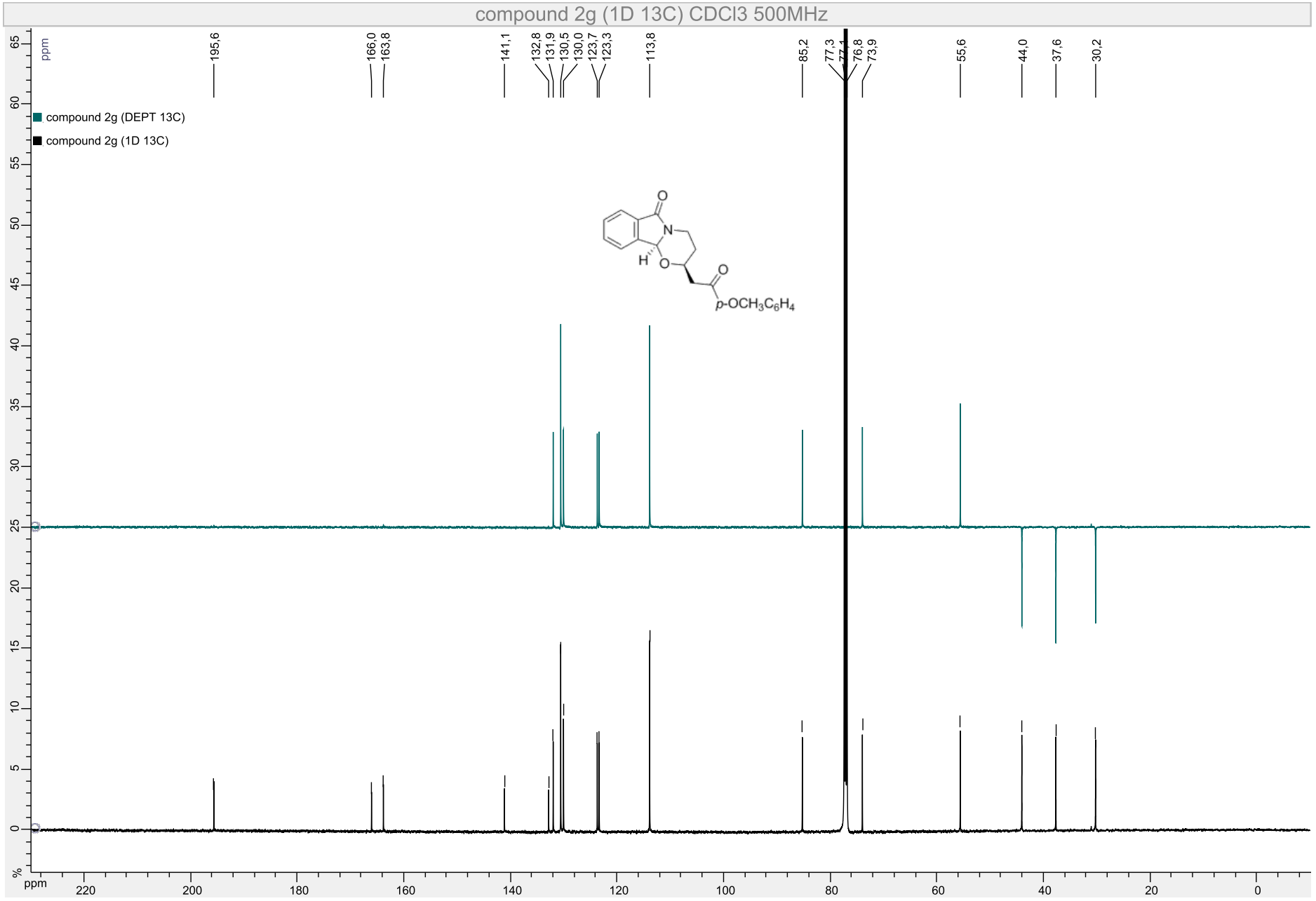

compound 2e (1D 13C) CDCl3 500MHz
ppm
205,9
166,0
141,0
132,7
132,0
130,1
123,7
123,3
85,1
77,3
77,1
76,8
73,4
49,0
37,5
31,2
29,8
compound 2e (DEPT 13C)
compound 2e (1D 13C)
O
N
H
O
O
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0


compound 2f (1D 1H) CDCl3 500MHz
ppm
7,93
7,80
7,50
7,24
5,67
4,59
4,48
3,44
3,34
3,02
1,56
O
N
H
O
O
Ph
2,0
1,0
6,1
1,0
1,0
1,0
1,1
1,0
1,1
1,0
1,0
%
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

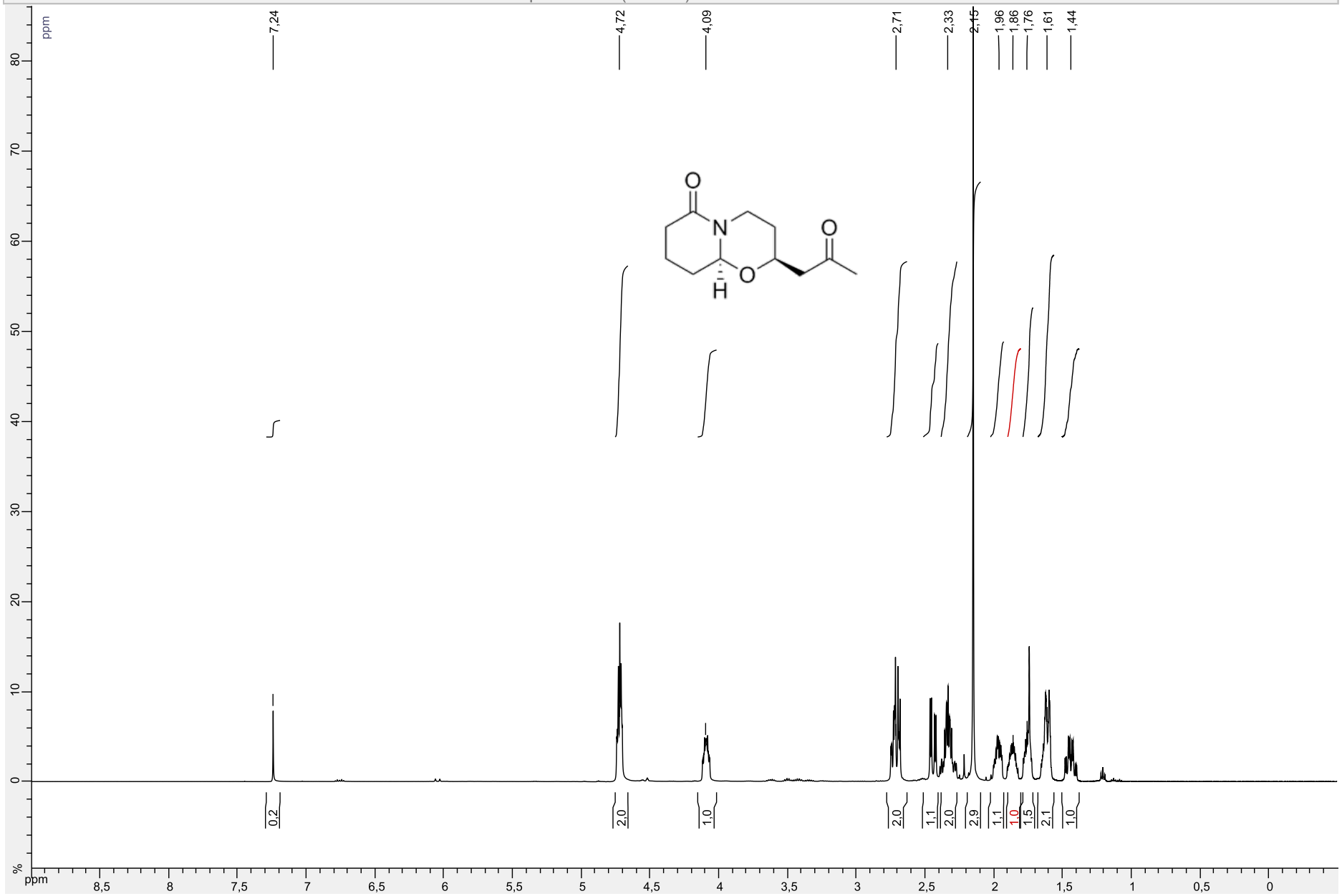

compound 2f (1D 13C) CDCl3 500MHz
ppm
197,1
166,0
141,1
136,8
133,5
132,8
132,0
130,0
128,7
128,2
123,7
123,3
85,2
77,3
76,8
73,7
44,4
37,6
30,1
compound 2f (DEPT 13C)
compound 2f (1D 13C)
O
N
H
O
O
Ph
%
70
60
50
40
30
20
10
0
220
200
180
160
140
120
100
80
60
40
20
0

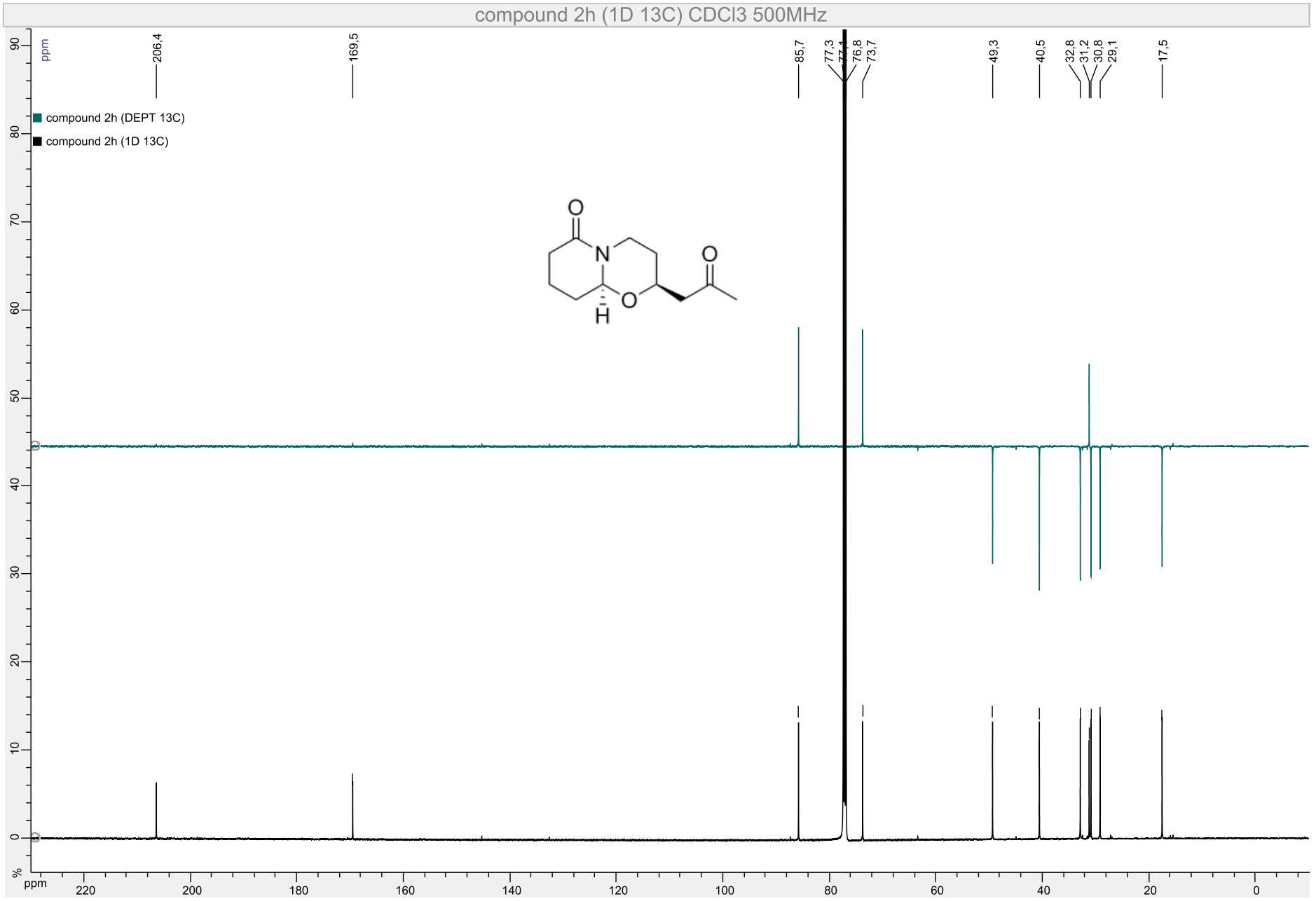
compound 2g (1D 1H) CDCl3 500MHz

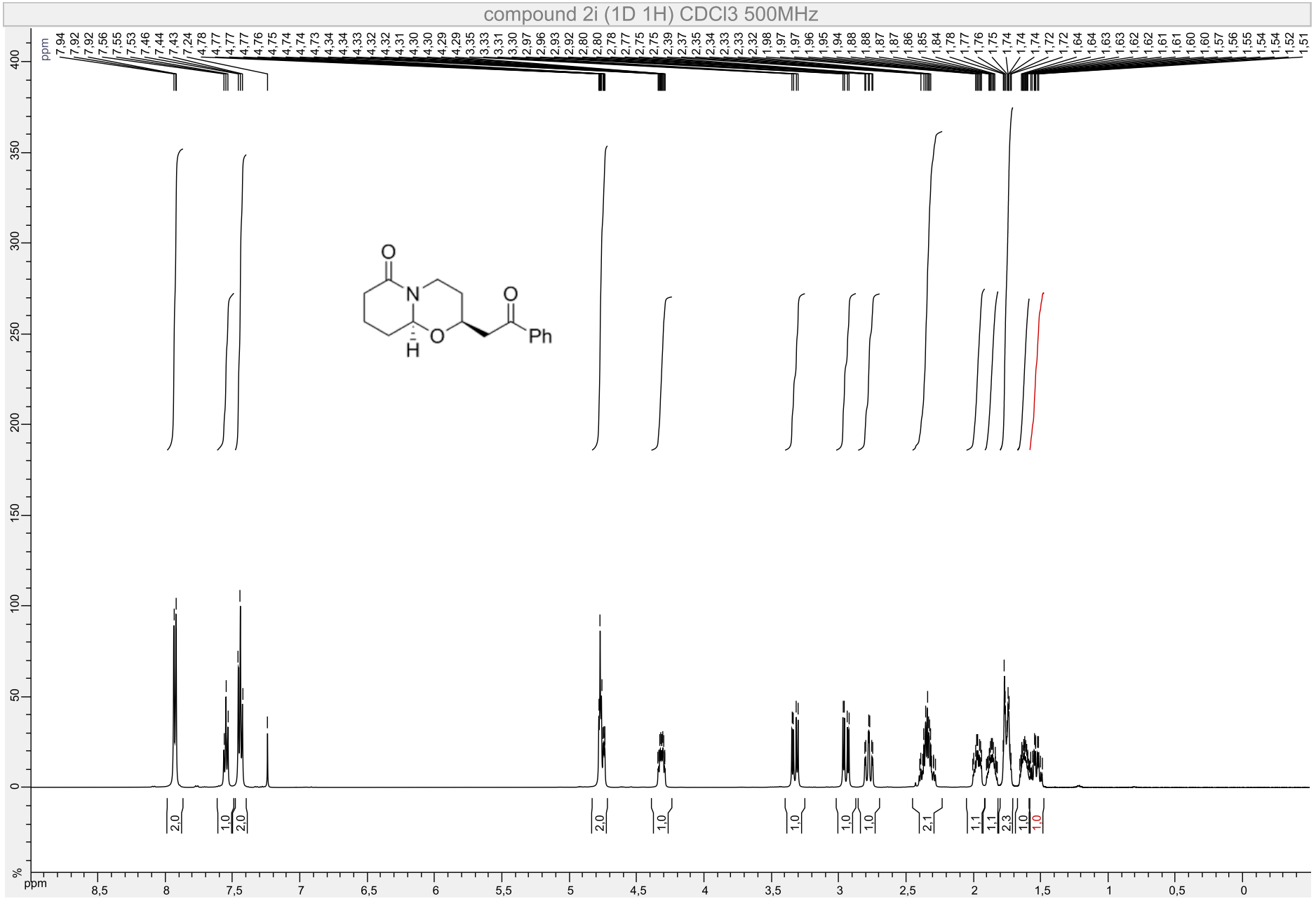


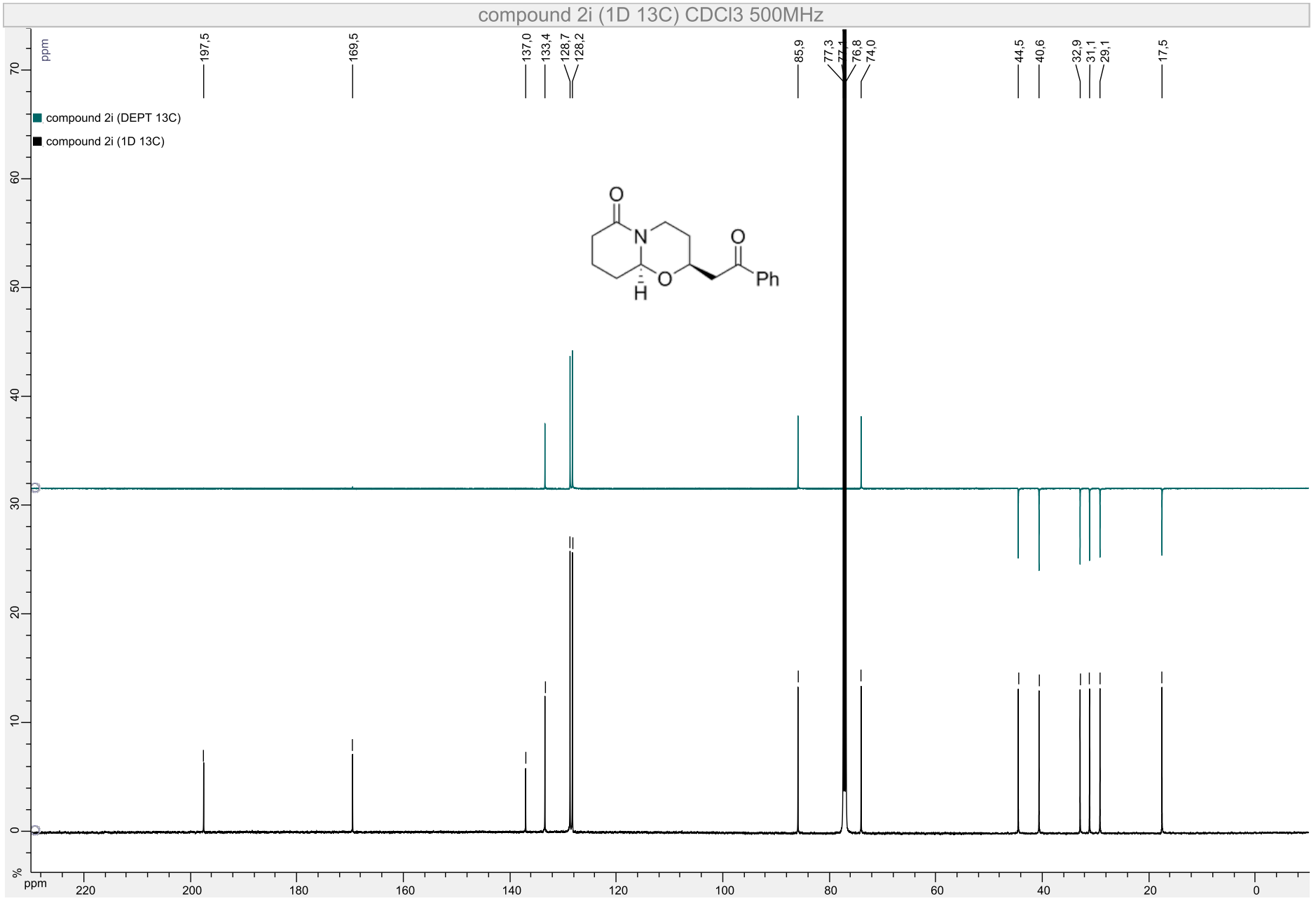

compound 2g (1D 13C) CDCl3 500MHz
ppm
195,6
166,0
163,8
141,1
132,8
131,9
130,5
130,0
123,7
123,3
113,8
85,2
77,3
76,8
73,9
55,6
44,0
37,6
30,2
compound 2g (DEPT 13C)
compound 2g (1D 13C)
O
N
H
O
O
p-OCH3C6H4
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

compound 2h (1D 1H) CDCl3 500MHz

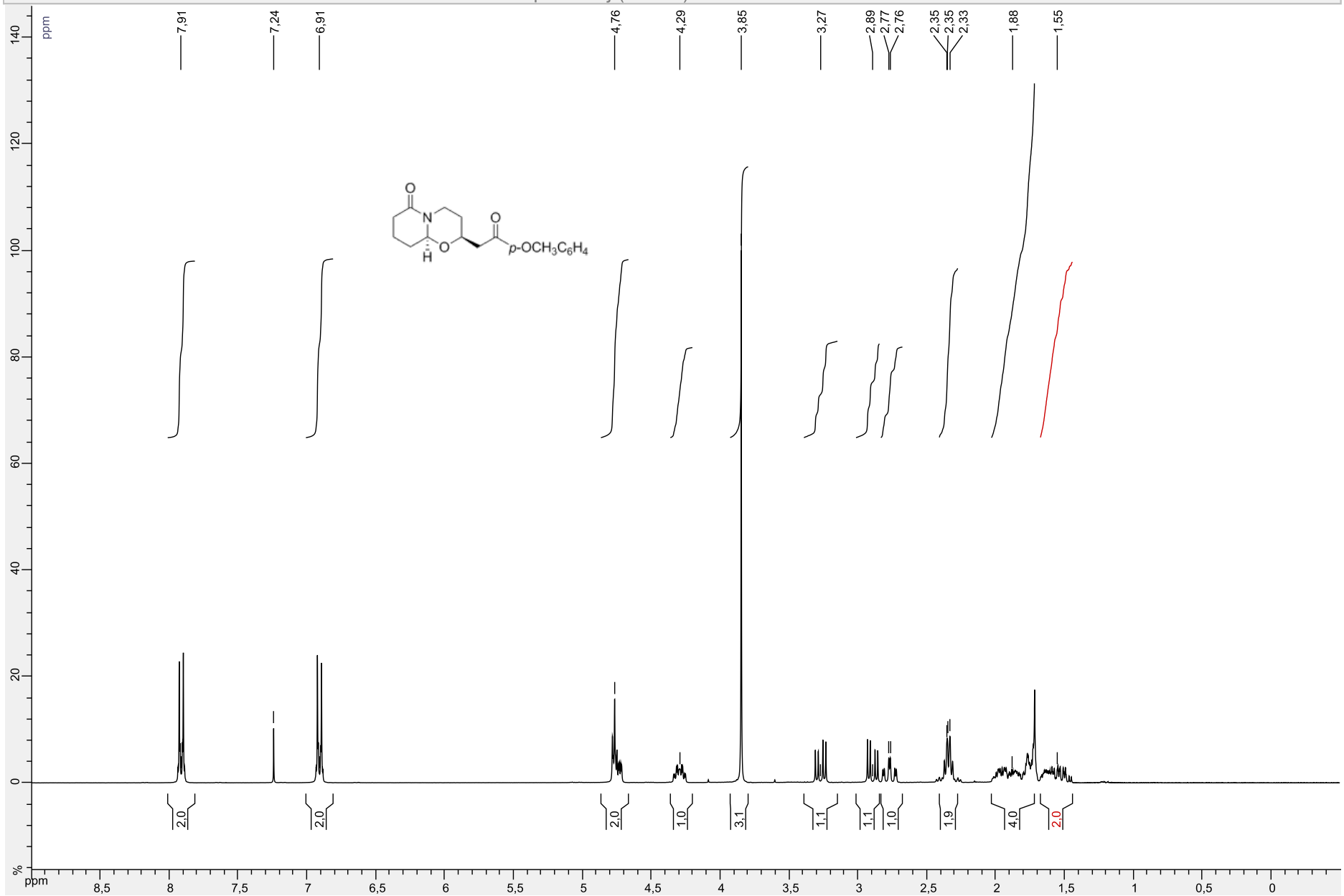


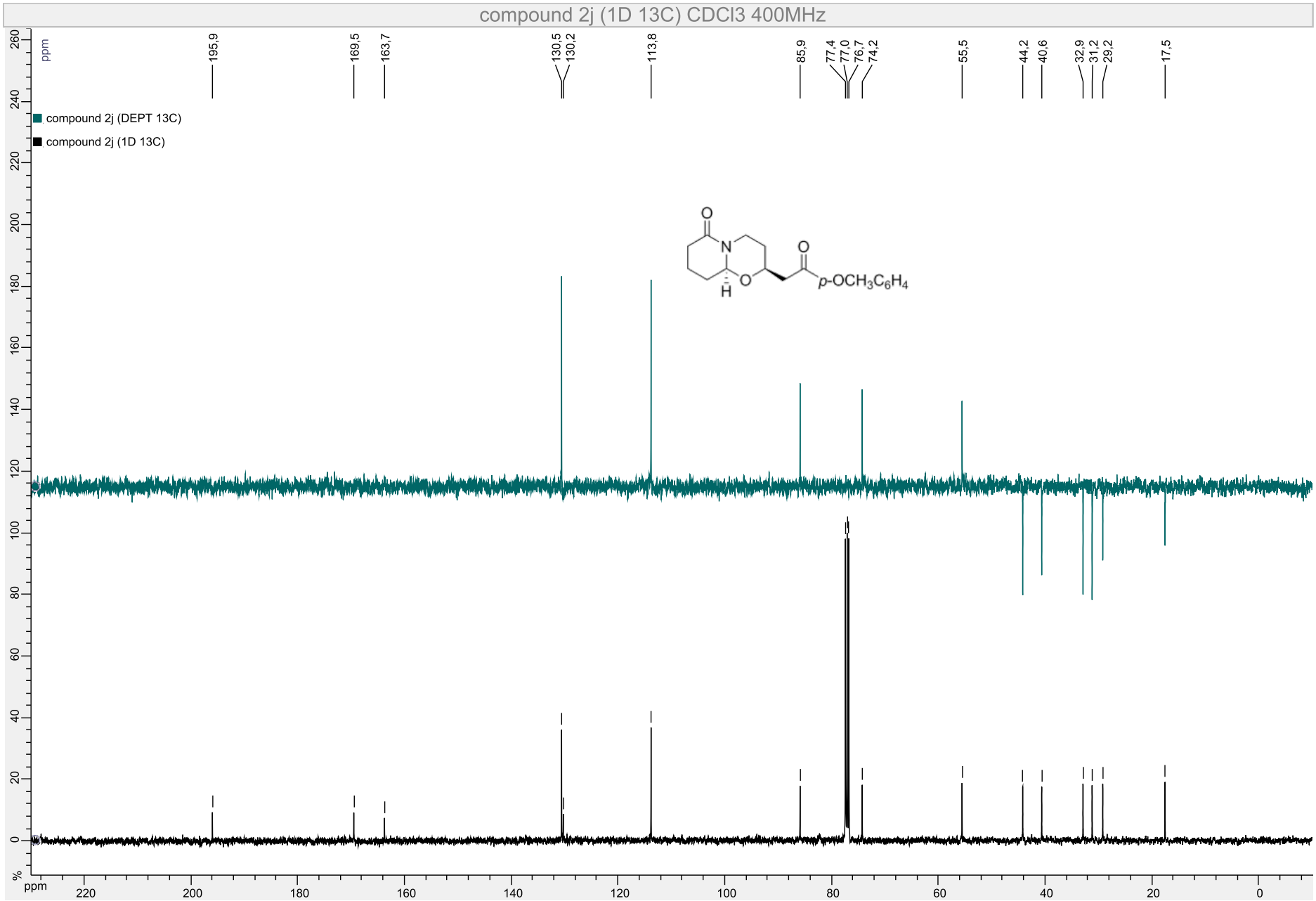

compound 2h (1D 13C) CDCl3 500MHz
ppm
206,4
169,5
85,7
77,3
77,1
76,8
73,7
49,3
40,5
32,8
31,2
30,8
29,1
17,5
compound 2h (DEPT 13C)
compound 2h (1D 13C)
O
N
O
O
H
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

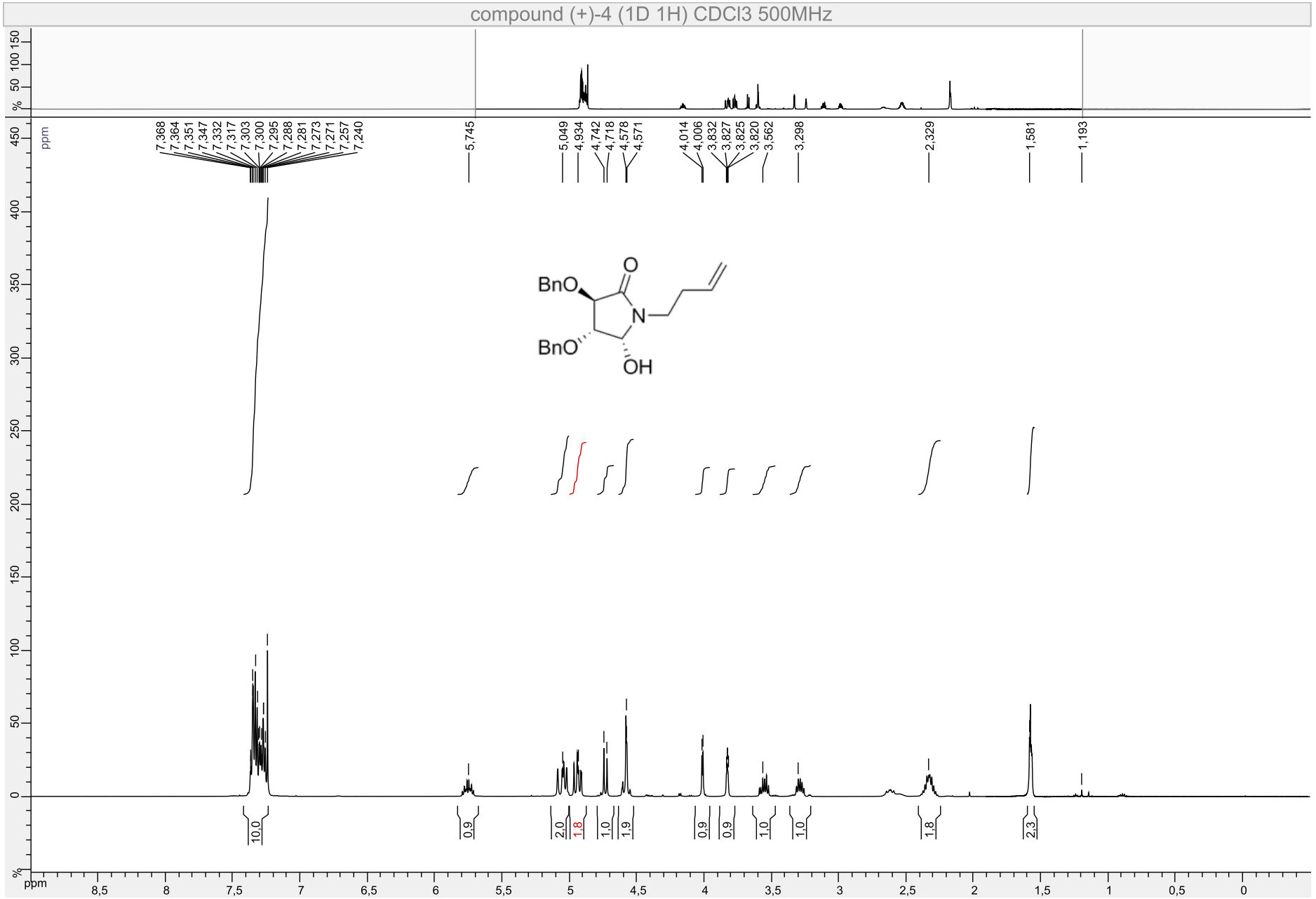

compound 2i (1D 1H) CDCl3 500MHz
ppm
7,94 7,92 7,92 7,56 7,55 7,53 7,46 7,44 7,43 7,24 4,78 4,77 4,77 4,77 4,76 4,75 4,74 4,74 4,73 4,34 4,34 4,33 4,32 4,32 4,31 4,30 4,30 4,29 4,29 3,35 3,33 3,31 3,30 2,97 2,96 2,93 2,92 2,80 2,80 2,78 2,77 2,75 2,75 2,39 2,37 2,35 2,34 2,33 2,33 2,32 1,98 1,97 1,97 1,96 1,95 1,94 1,88 1,88 1,87 1,87 1,86 1,85 1,84 1,78 1,77 1,76 1,75 1,74 1,74 1,74 1,72 1,72 1,64 1,64 1,63 1,63 1,62 1,62 1,61 1,61 1,60 1,60 1,57 1,56 1,55 1,54 1,54 1,52 1,51
O
N
O
O
H
Ph
2,0 1,0 2,0 2,0 1,0 1,0 1,0 1,0 2,1 1,1 1,1 2,3 1,0 1,0
%
ppm
8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0

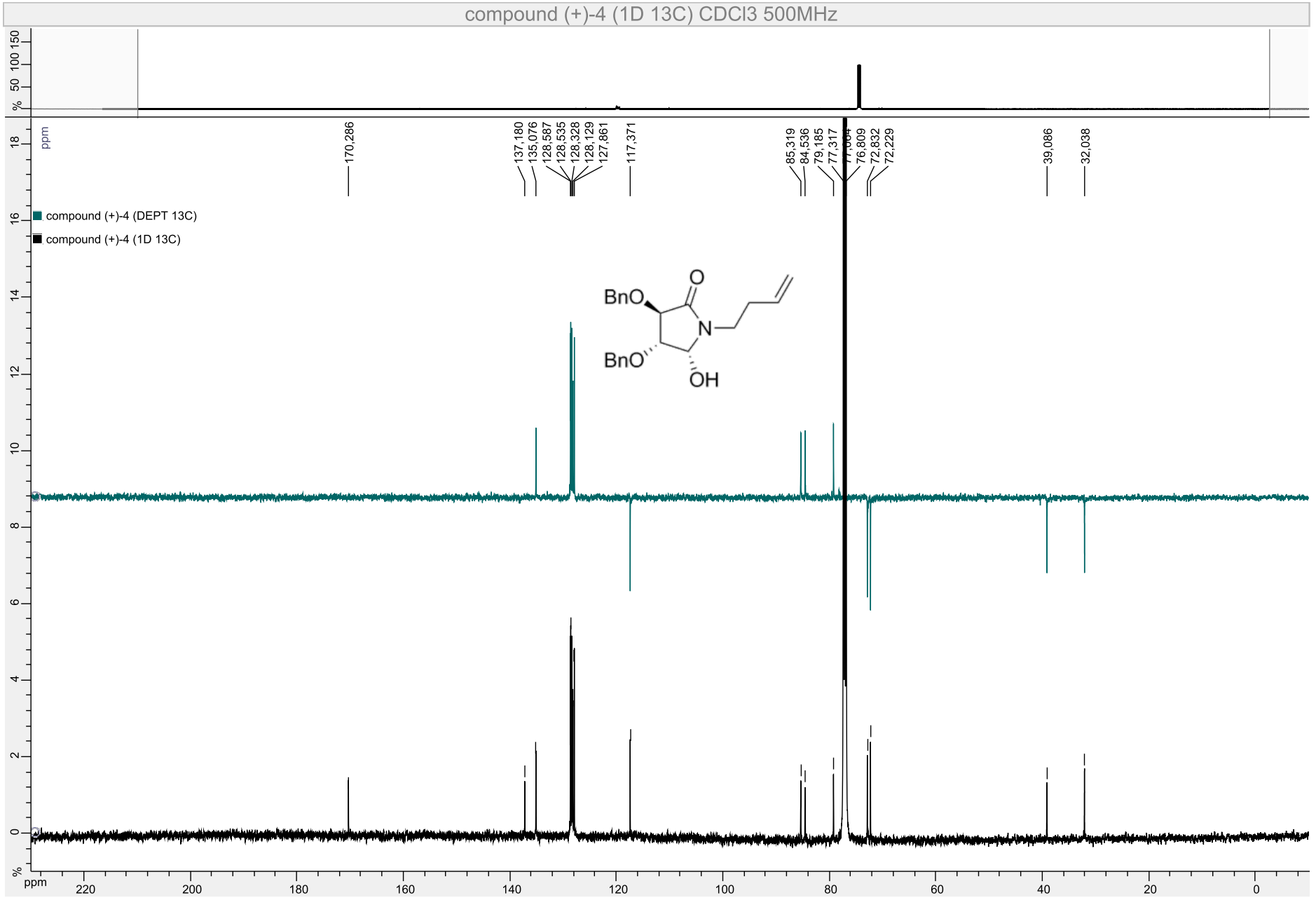

compound 2i (1D 13C) CDCl3 500MHz
ppm
197,5
169,5
137,0
133,4
128,7
128,2
85,9
77,3
76,8
74,0
44,5
40,6
32,9
31,1
29,1
17,5
compound 2i (DEPT 13C)
compound 2i (1D 13C)
O
N
O
O
H
Ph
%
70
60
50
40
30
20
10
0
220
200
180
160
140
120
100
80
60
40
20
0

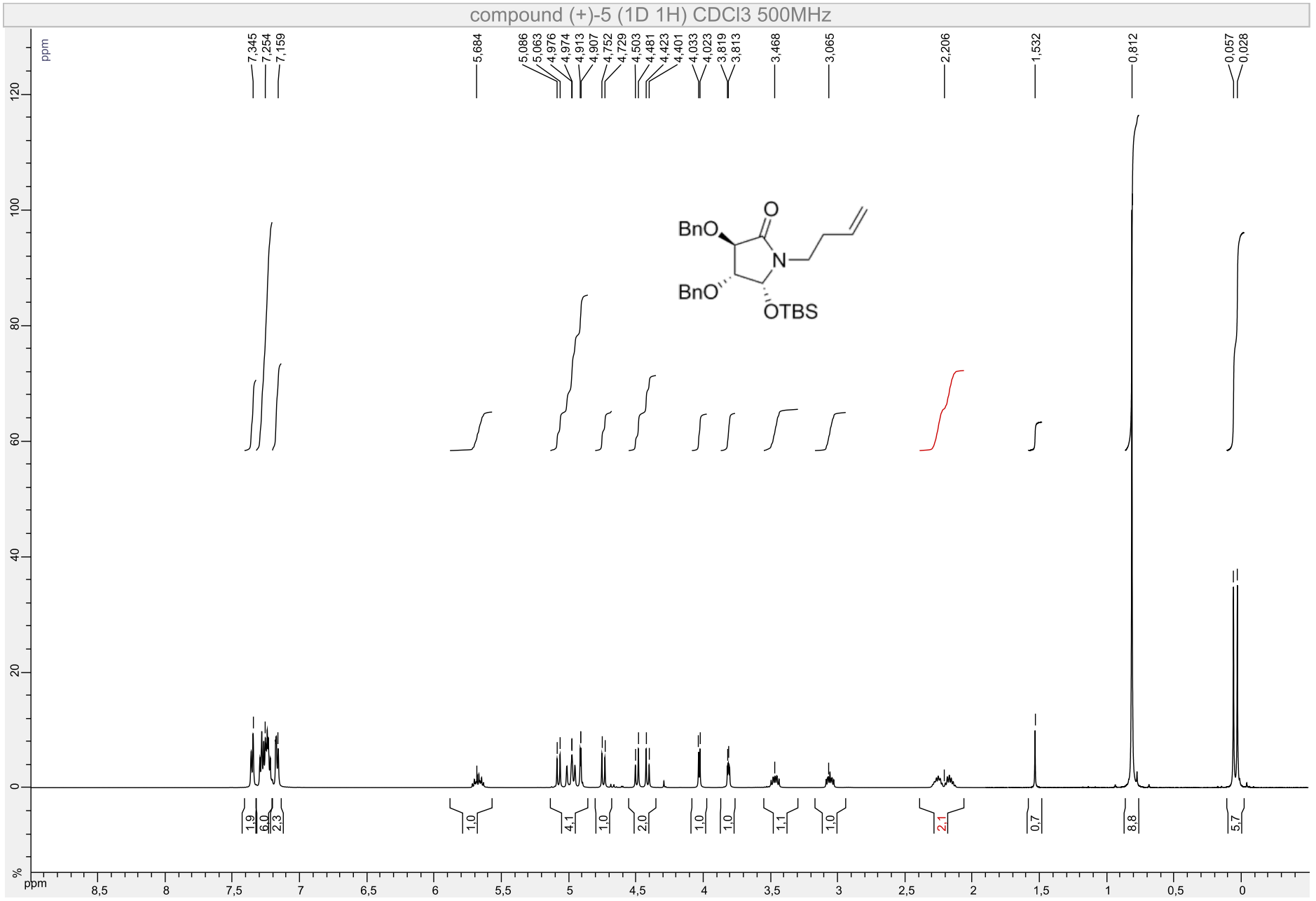
compound 2j (1D 1H) CDCl3 300MHz

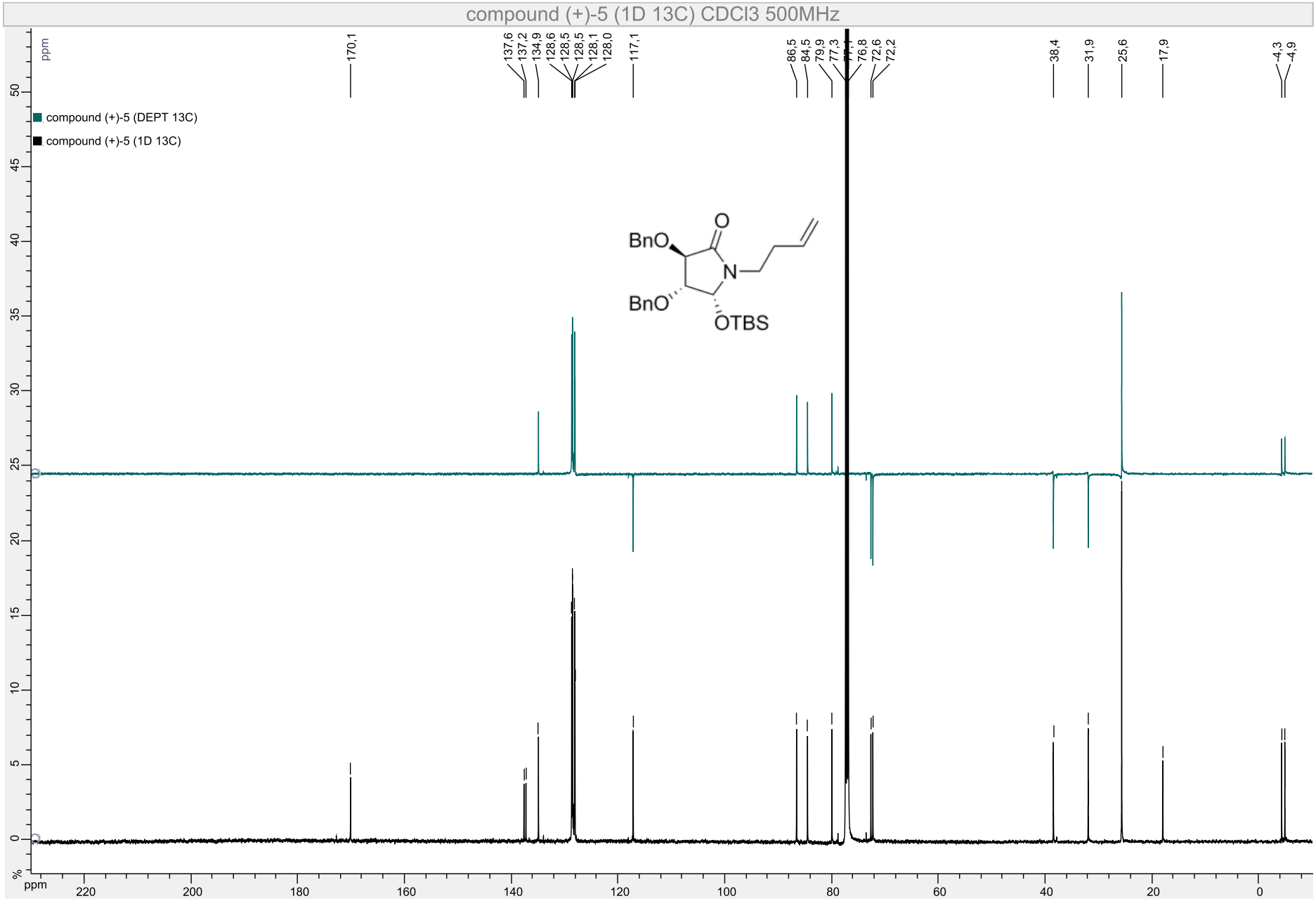


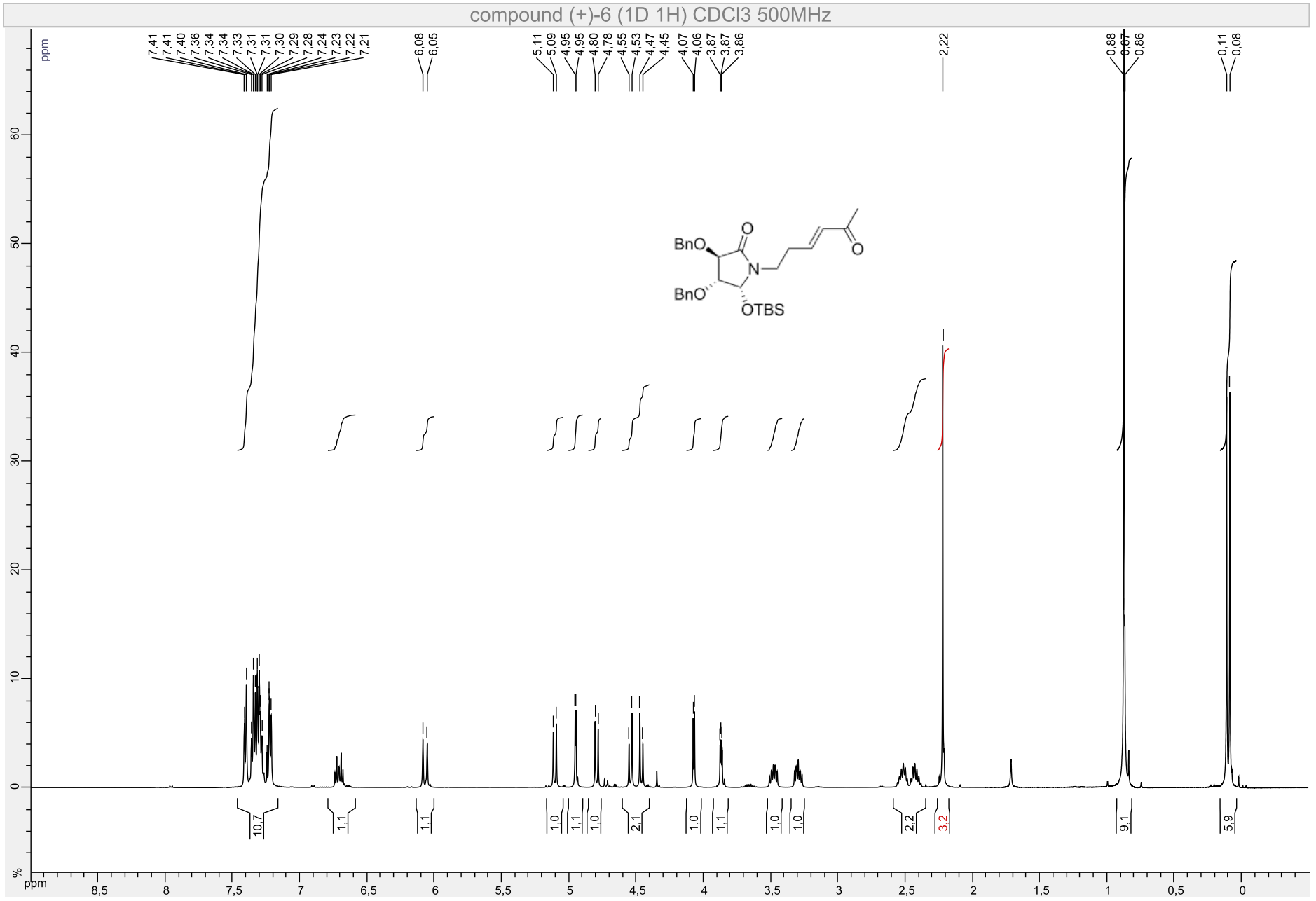

compound 2j (1D 13C) CDCl3 400MHz
ppm
195,9
169,5
163,7
130,5
130,2
113,8
85,9
77,4
77,0
76,7
74,2
55,5
44,2
40,6
32,9
31,2
29,2
17,5
compound 2j (DEPT 13C)
compound 2j (1D 13C)
p-OCH3C6H4
%
ppm

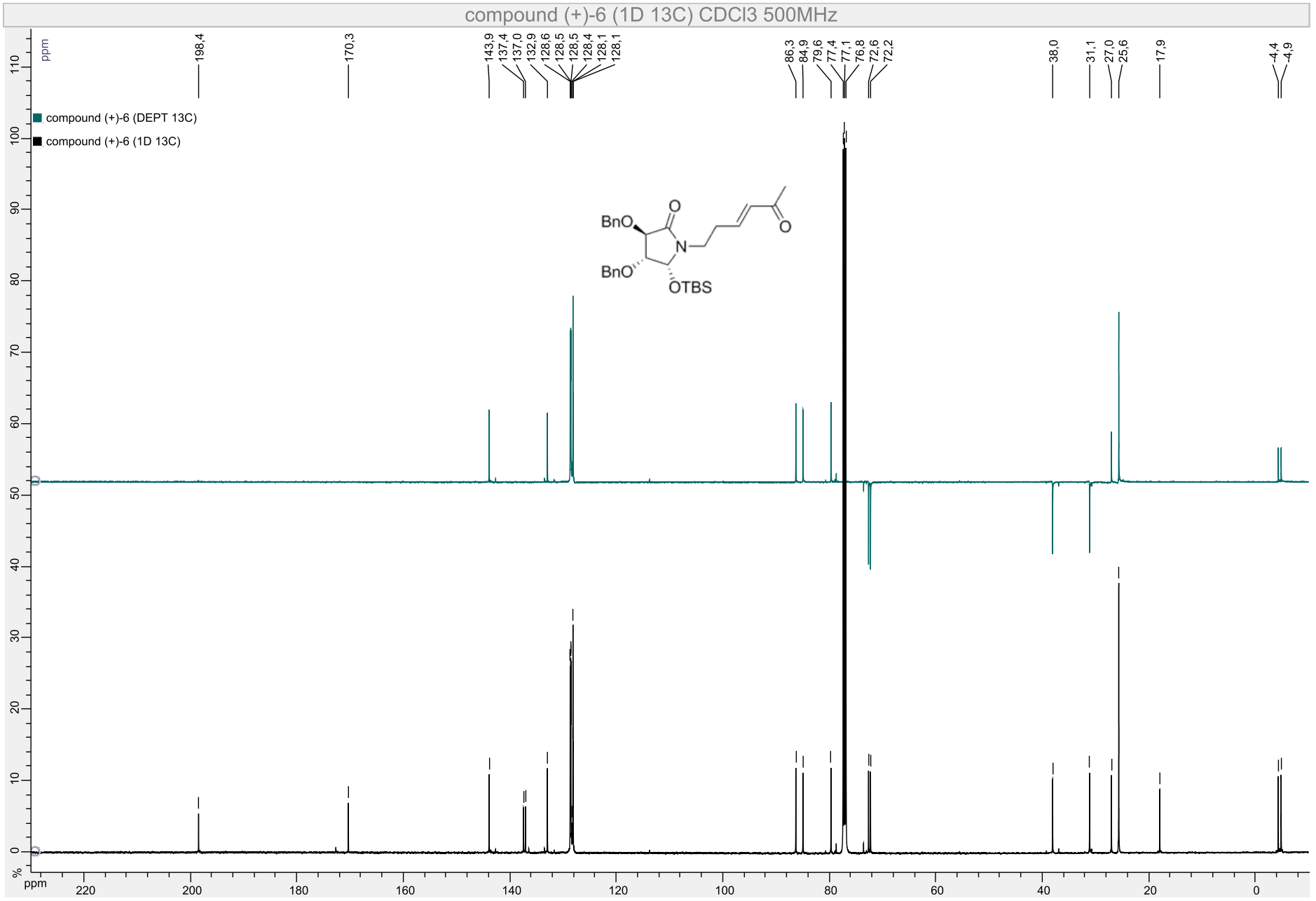

compound (+)-4 (1D 1H) CDCl3 500MHz
ppm
7,368
7,364
7,351
7,347
7,332
7,317
7,303
7,300
7,295
7,288
7,281
7,273
7,271
7,257
7,240
5,745
5,049
4,934
4,742
4,718
4,578
4,571
4,014
4,006
3,832
3,827
3,825
3,820
3,562
3,298
2,329
1,581
1,193
BnO
O
N
BnO
OH
10,0
0,9
2,0
1,8
1,0
1,9
0,9
0,9
1,0
1,0
1,8
2,3

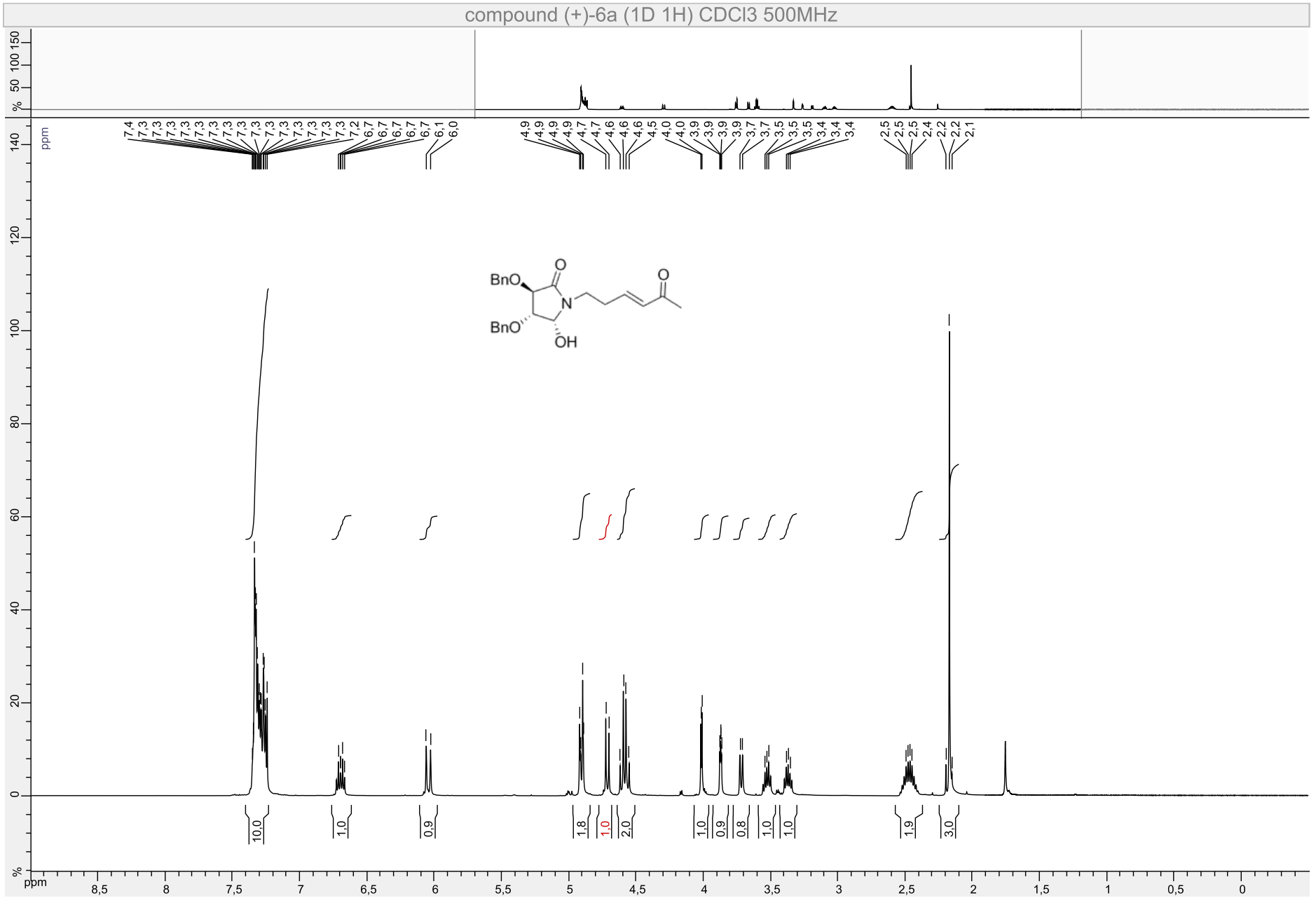

compound (+)-4 (1D 13C) CDCl3 500MHz
ppm
170,286
137,180
135,076
128,587
128,535
128,328
128,129
127,861
117,371
85,319
84,536
79,185
77,317
76,809
72,832
72,229
39,086
32,038
compound (+)-4 (DEPT 13C)
compound (+)-4 (1D 13C)
BnO
BnO
O
N
OH

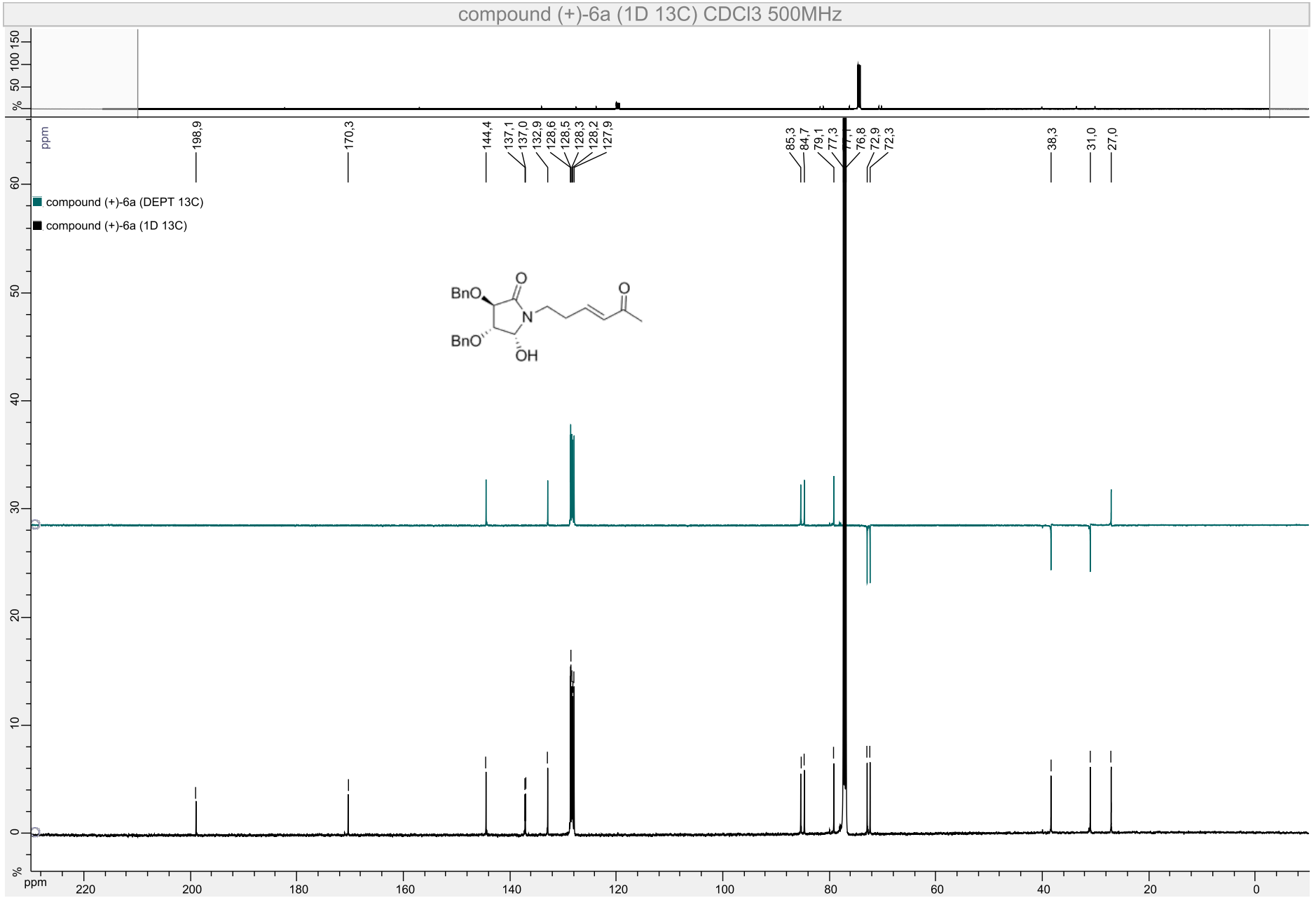

compound (+)-5 (1D 1H) CDCl3 500MHz
ppm
7,345
7,254
7,159
5,684
5,086
5,063
4,976
4,974
4,913
4,907
4,752
4,729
4,503
4,481
4,423
4,401
4,033
4,023
3,819
3,813
3,468
3,065
2,206
1,532
0,812
0,057
0,028
BnO
O
N
BnO
OTBS
1,9
6,0
2,3
1,0
4,1
1,0
2,0
1,0
1,0
1,1
1,0
2,1
0,7
8,8
5,7
%
ppm

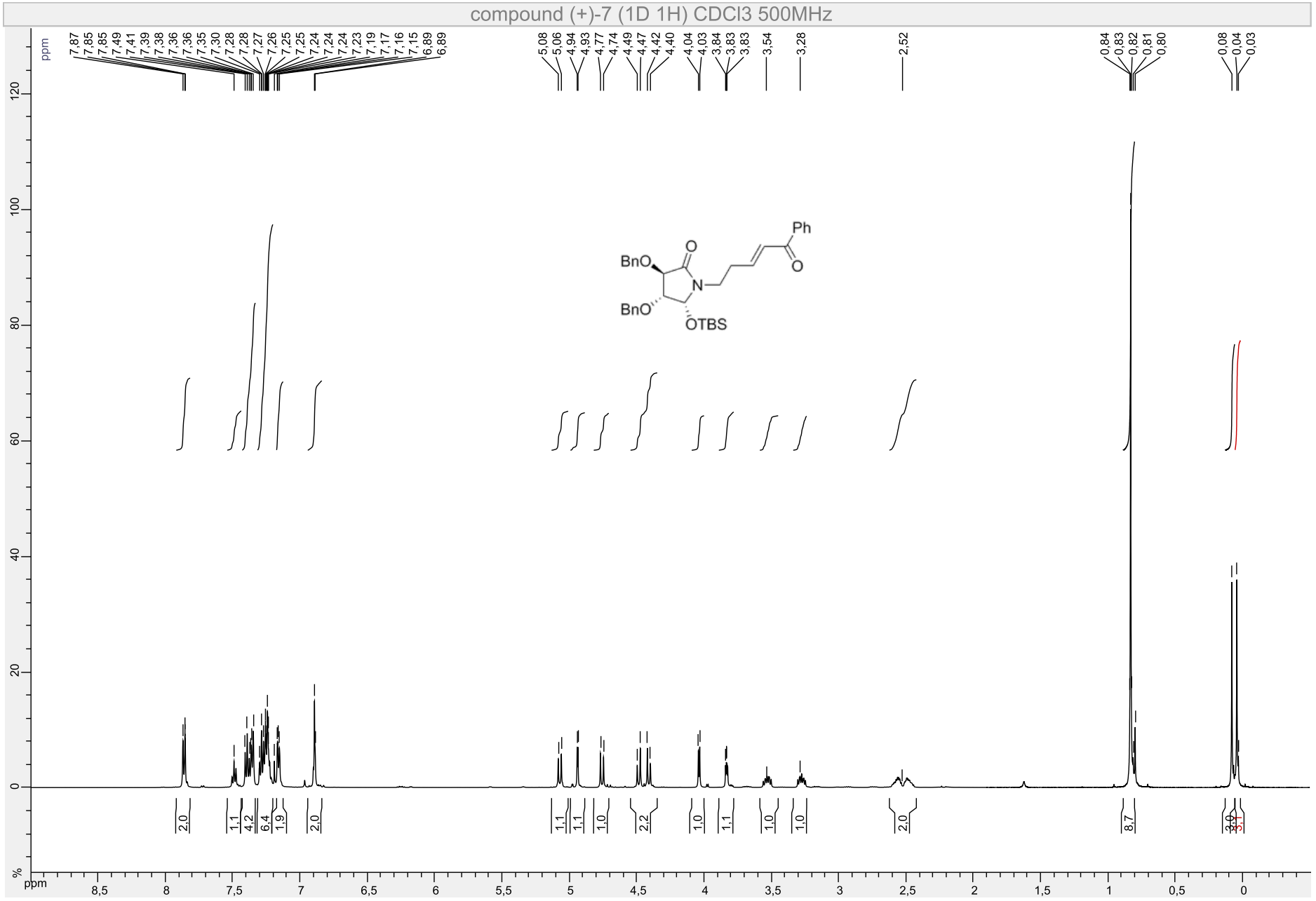

compound (+)-5 (1D 13C) CDCl3 500MHz
ppm
170,1
137,6
137,2
134,9
128,6
128,5
128,5
128,1
128,0
117,1
86,5
84,5
79,9
77,3
77,1
76,8
72,6
72,2
38,4
31,9
25,6
17,9
-4,3
-4,9
compound (+)-5 (DEPT 13C)
compound (+)-5 (1D 13C)
BnO
BnO
O
N
OTBS
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

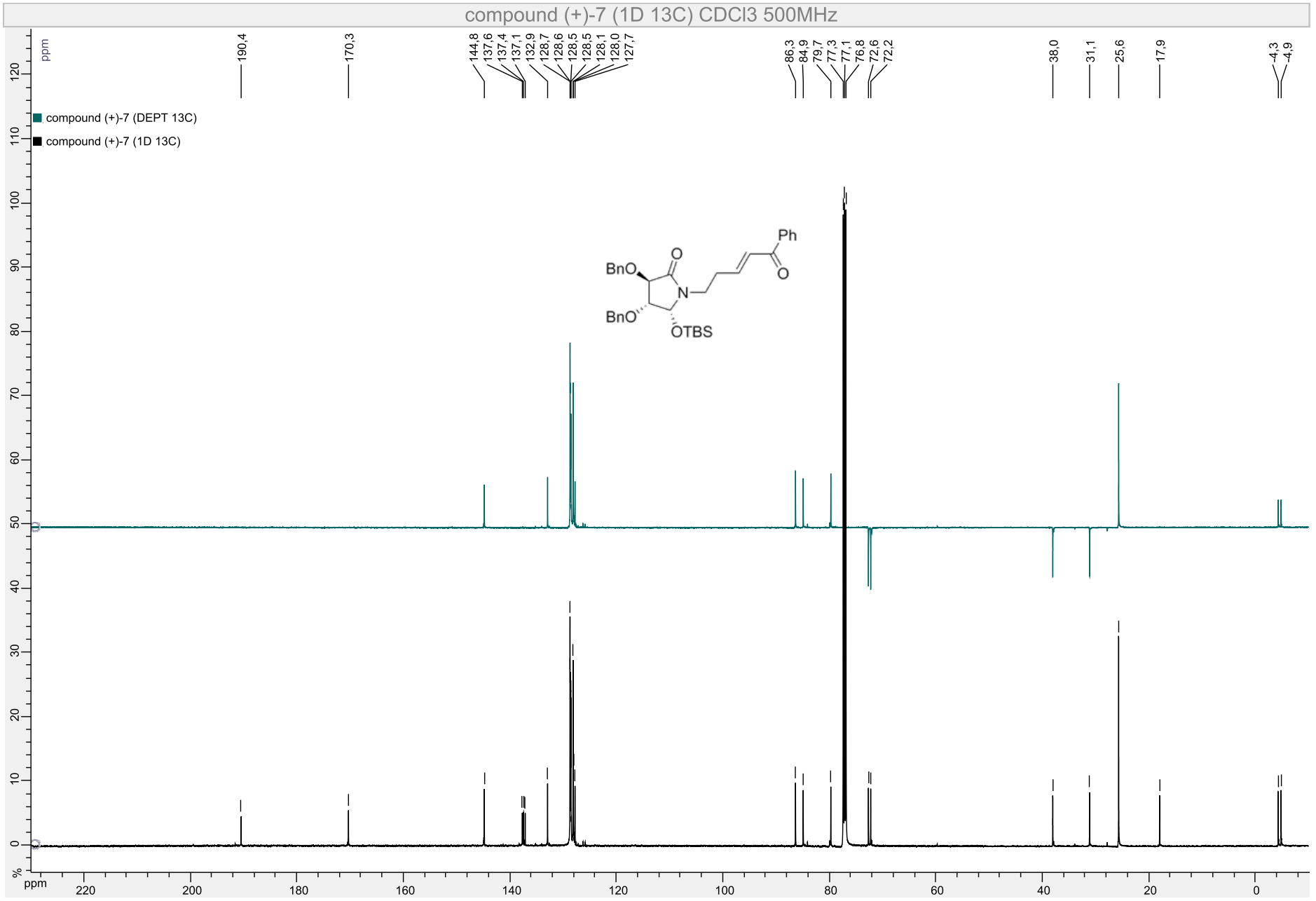

compound (+)-6 (1D 1H) CDCl3 500MHz
ppm
7,41
7,41
7,40
7,36
7,34
7,34
7,33
7,31
7,31
7,30
7,29
7,28
7,24
7,23
7,22
7,21
6,08
6,05
5,11
5,09
4,95
4,95
4,80
4,78
4,55
4,53
4,47
4,45
4,07
4,06
3,87
3,87
3,86
2,22
0,88
0,87
0,86
0,11
0,08
BnO
BnO
OTBS
O
N
O
10,7
1,1
1,1
1,0
1,1
1,0
2,1
1,0
1,1
1,0
1,0
2,2
3,2
9,1
5,9
%
ppm


compound (+)-6 (1D 13C) CDCl3 500MHz
ppm
198,4
170,3
143,9
137,4
137,0
132,9
128,6
128,5
128,5
128,4
128,1
128,1
86,3
84,9
79,6
77,4
77,1
76,8
72,6
72,2
38,0
31,1
27,0
25,6
17,9
-4,4
-4,9
compound (+)-6 (DEPT 13C)
compound (+)-6 (1D 13C)
BnO
BnO
OTBS
O
O
N
%
ppm

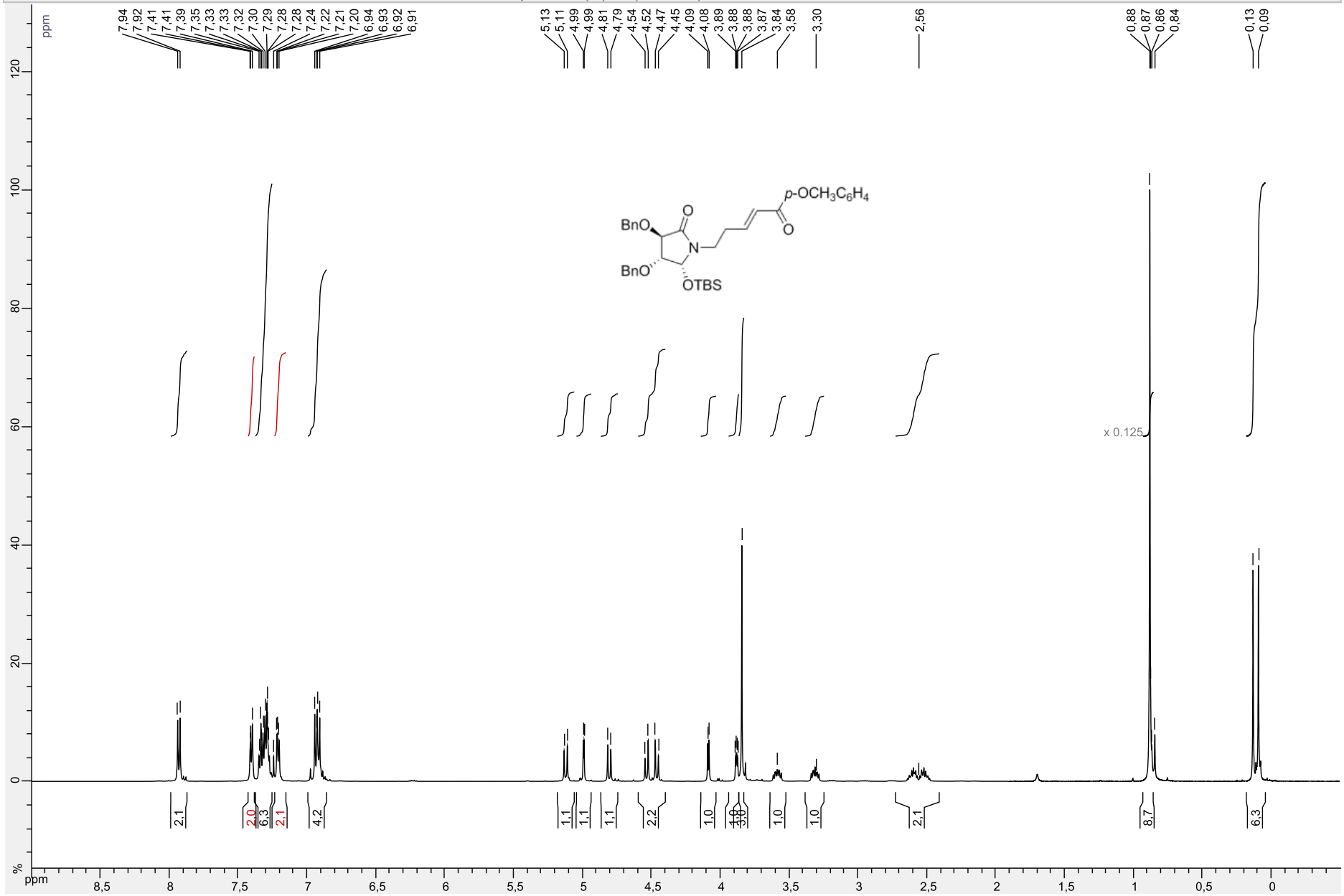

compound (+)-6a (1D 1H) CDCl3 500MHz
BnO
BnO
OH
O
N
O
ppm
10,0
1,0
0,9
1,8
1,0
2,0
1,0
0,9
0,8
1,0
1,0
1,9
3,0

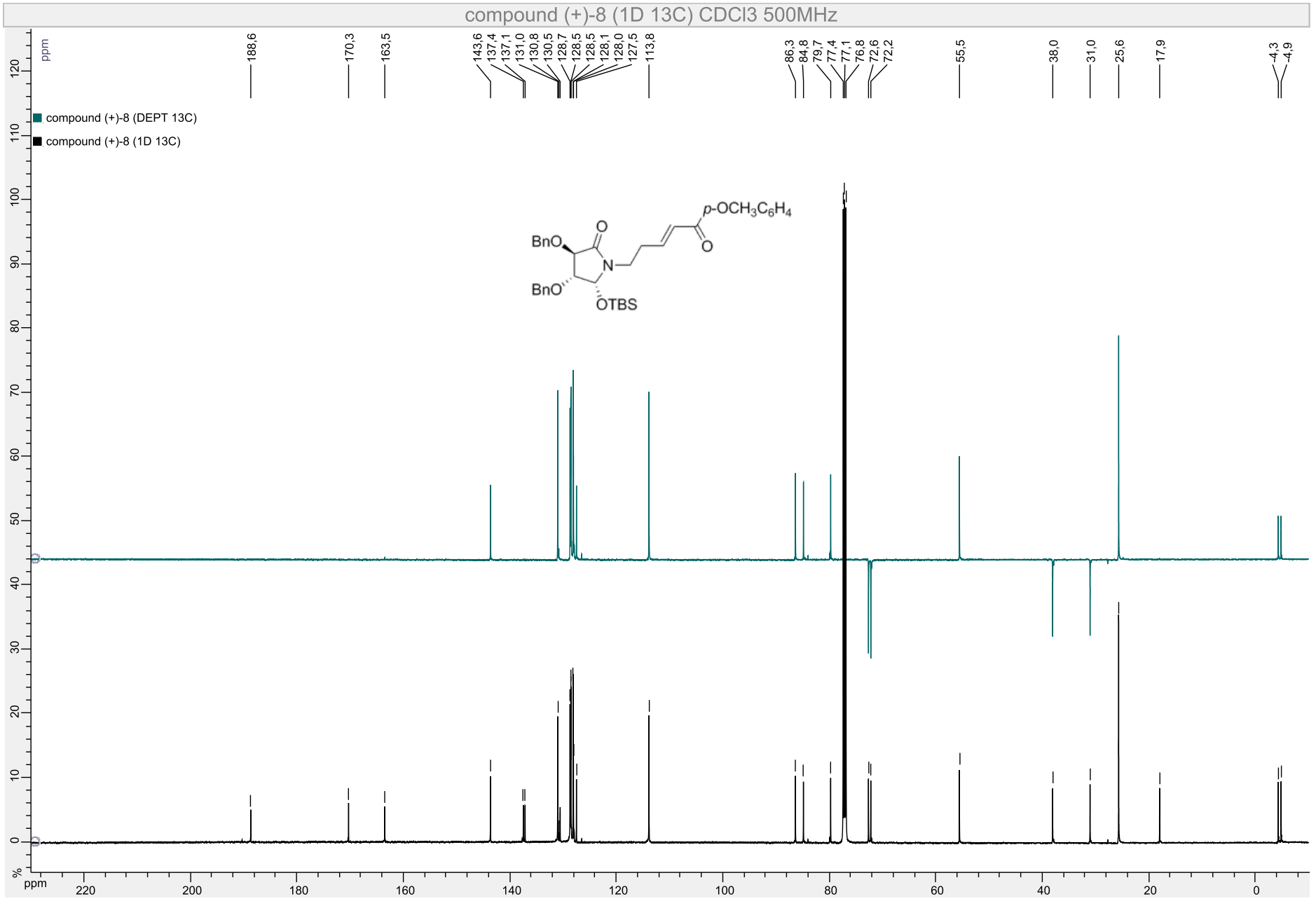

compound (+)-6a (1D 13C) CDCl3 500MHz
ppm
198,9
170,3
144,4
137,1
137,0
132,9
128,6
128,5
128,3
128,2
127,9
85,3
84,7
79,1
77,3
76,8
72,9
72,3
38,3
31,0
27,0
compound (+)-6a (DEPT 13C)
compound (+)-6a (1D 13C)
BnO
BnO
OH
N
O
O
220
200
180
160
140
120
100
80
60
40
20
0

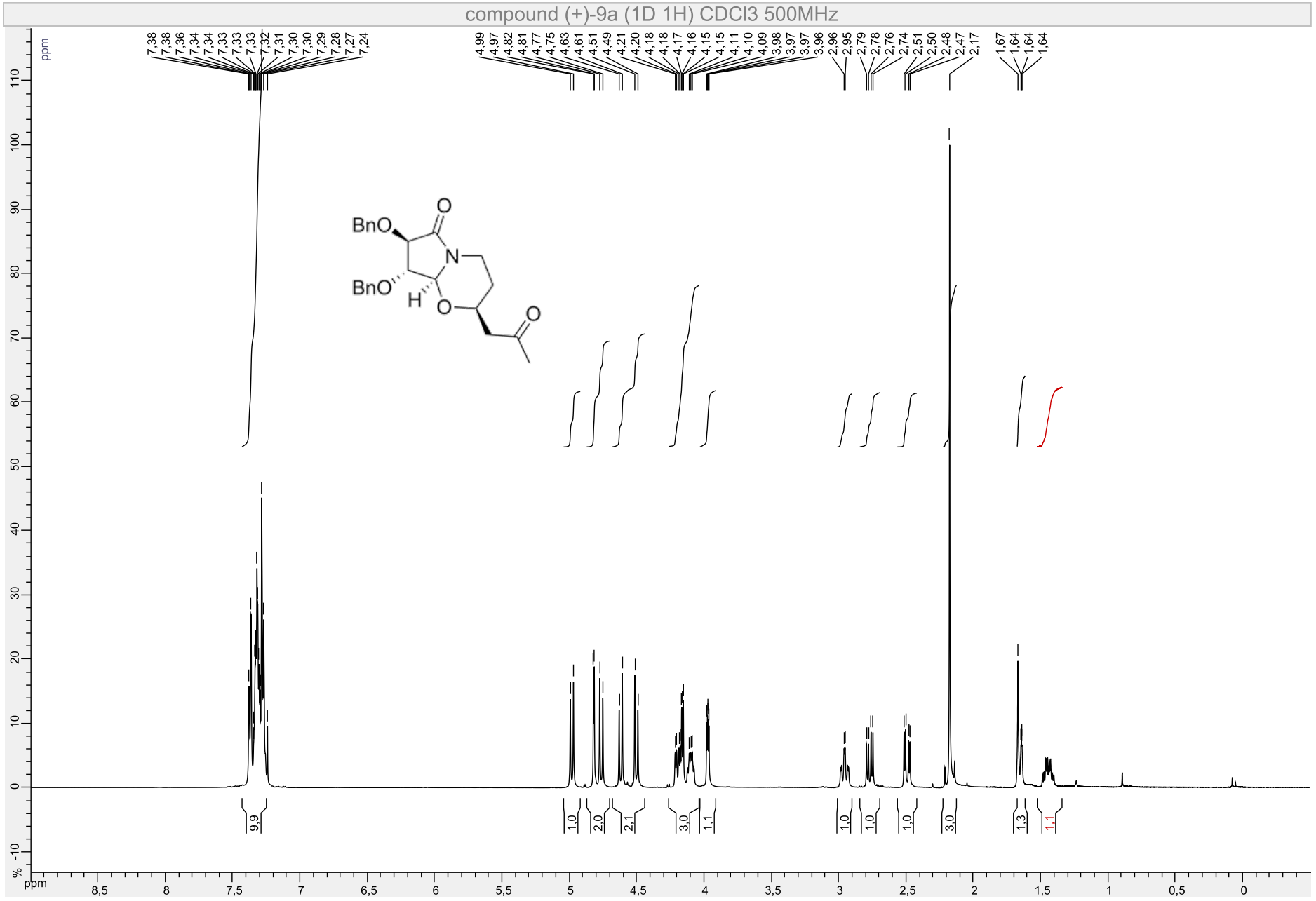

compound (+)-7 (1D 1H) CDCl3 500MHz
ppm
7,87 7,85 7,85 7,49 7,41 7,39 7,38 7,36 7,36 7,35 7,30 7,28 7,28 7,27 7,26 7,25 7,25 7,24 7,24 7,24 7,23 7,19 7,17 7,16 7,15 6,89 6,89
5,08 5,06 4,94 4,93 4,77 4,74 4,49 4,47 4,42 4,40 4,04 4,03 3,84 3,83 3,83 3,54 3,28 2,52 0,84 0,83 0,82 0,81 0,80 0,08 0,04 0,03
BnO
BnO
OTBS
N
O
O
Ph
2,0 1,1 4,2 6,4 1,9 2,0 1,1 1,1 1,0 2,2 1,0 1,1 1,0 1,0 2,0 8,7 3,0 3,1
%
ppm
8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0

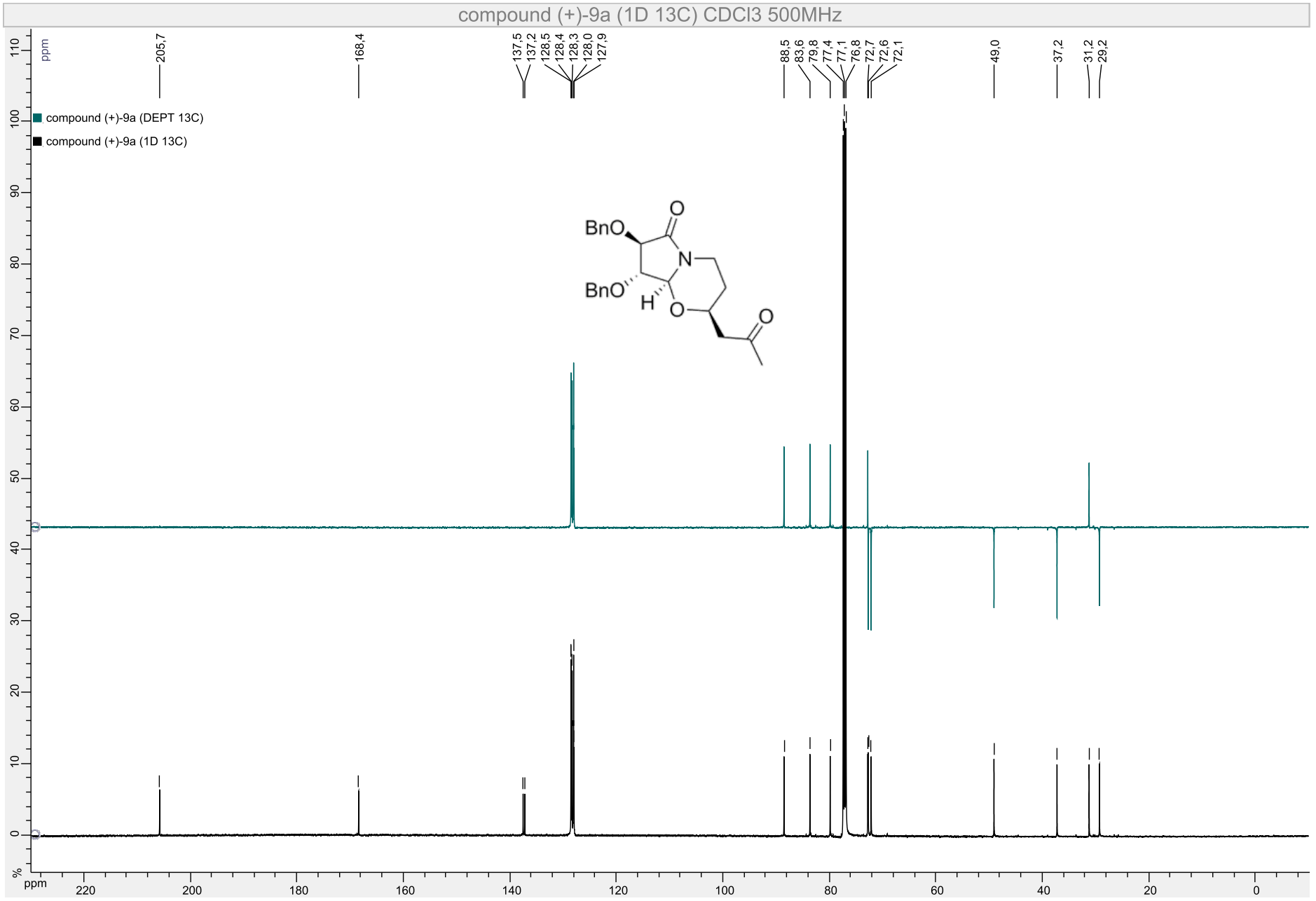

compound (+)-7 (1D 13C) CDCl3 500MHz
ppm
190,4
170,3
144,8
137,6
137,4
137,1
132,9
128,7
128,6
128,5
128,5
128,1
128,0
127,7
86,3
84,9
79,7
77,3
77,1
76,8
72,6
72,2
38,0
31,1
25,6
17,9
-4,3
-4,9
compound (+)-7 (DEPT 13C)
compound (+)-7 (1D 13C)
BnO
BnO
OTBS
O
N
O
Ph
%
ppm

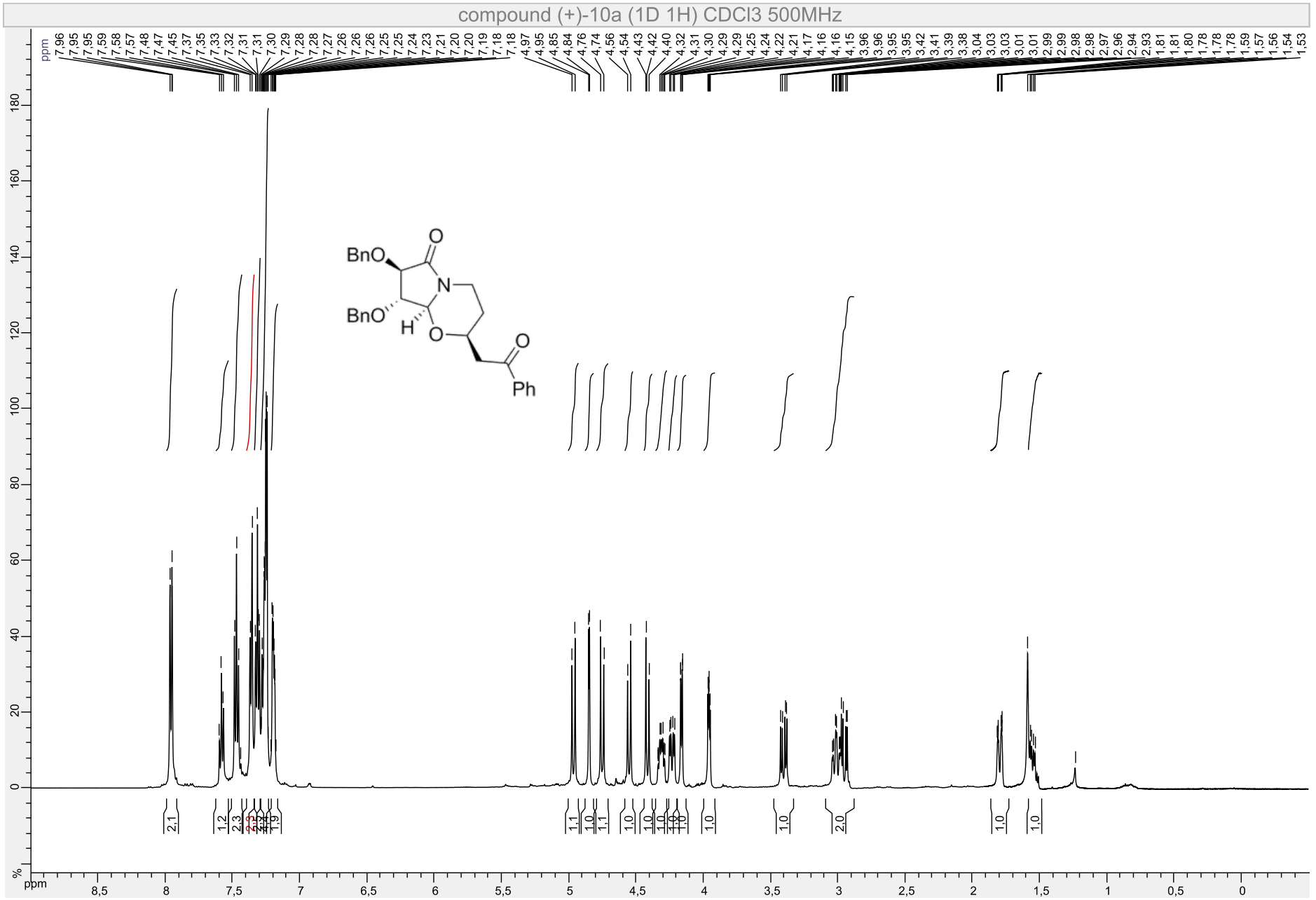
compound (+)-8 (1D 1H) CDCl3 500MHz

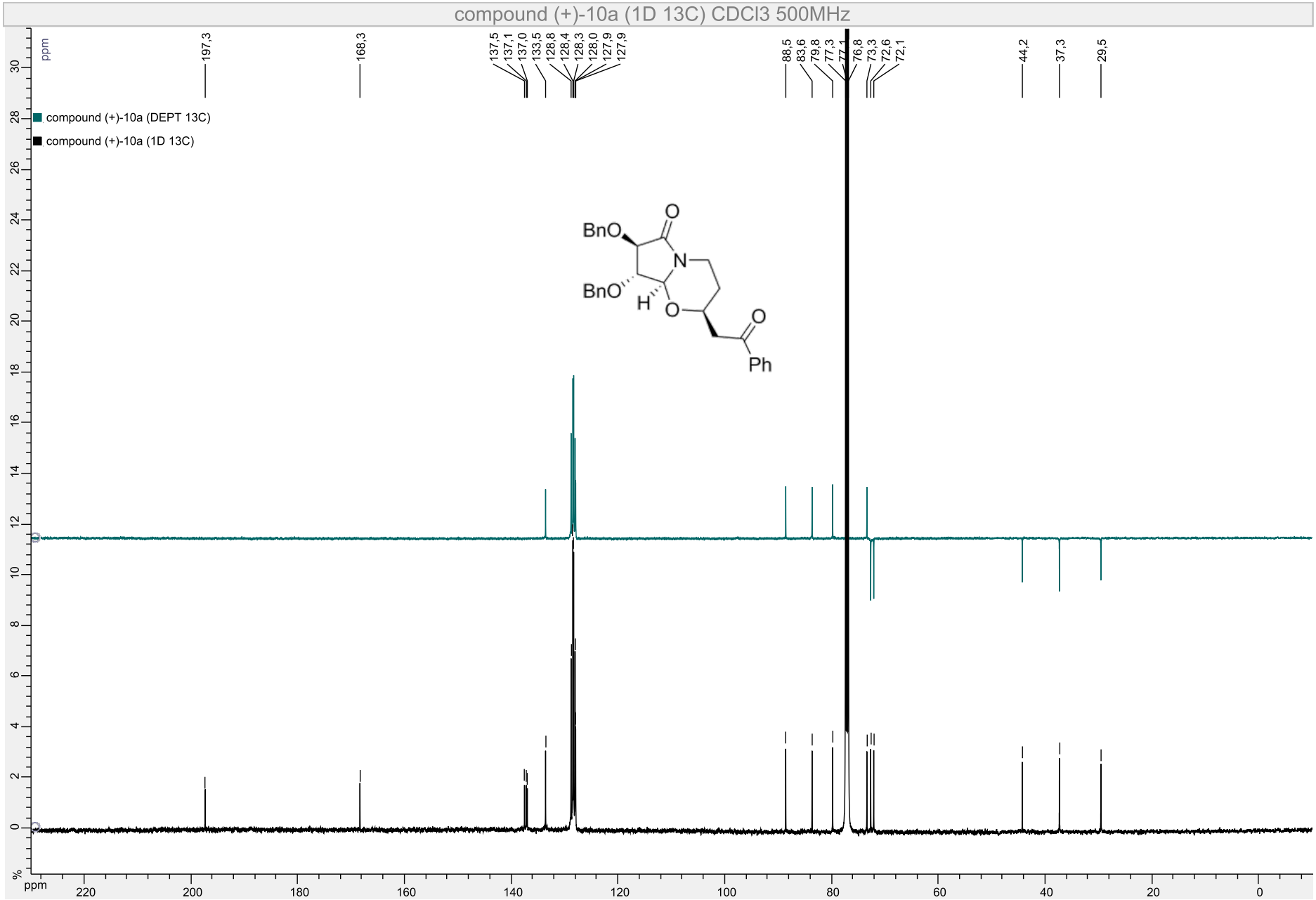


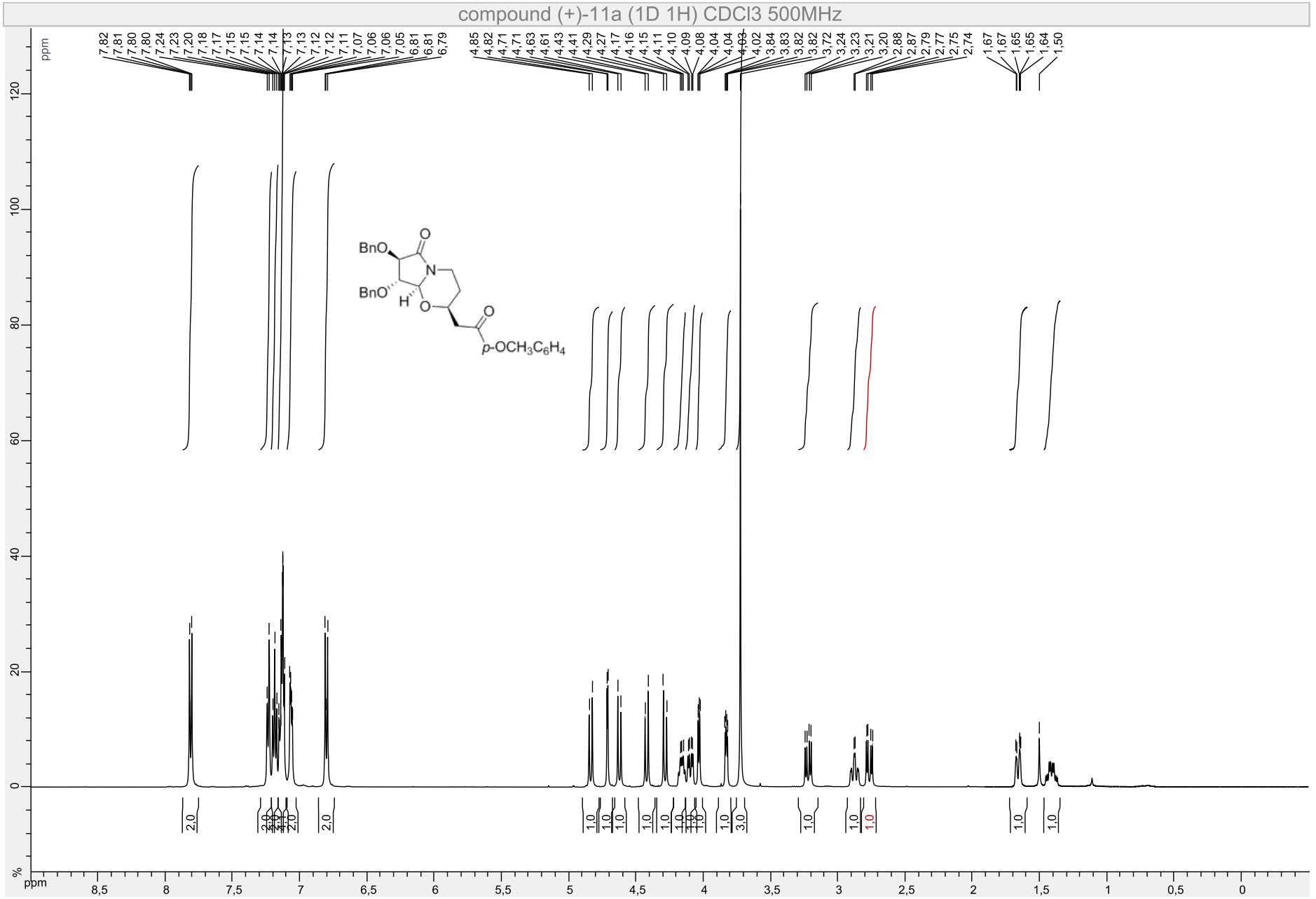

compound (+)-8 (1D 13C) CDCl3 500MHz
ppm
188,6
170,3
163,5
143,6
137,4
137,1
131,0
130,8
130,5
128,7
128,5
128,5
128,1
128,0
127,5
113,8
86,3
84,8
79,7
77,4
77,1
76,8
72,6
72,2
55,5
38,0
31,0
25,6
17,9
-4,3
-4,9
compound (+)-8 (DEPT 13C)
compound (+)-8 (1D 13C)
p-OCH3C6H4
BnO
BnO
OTBS
O
O
O
N
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0

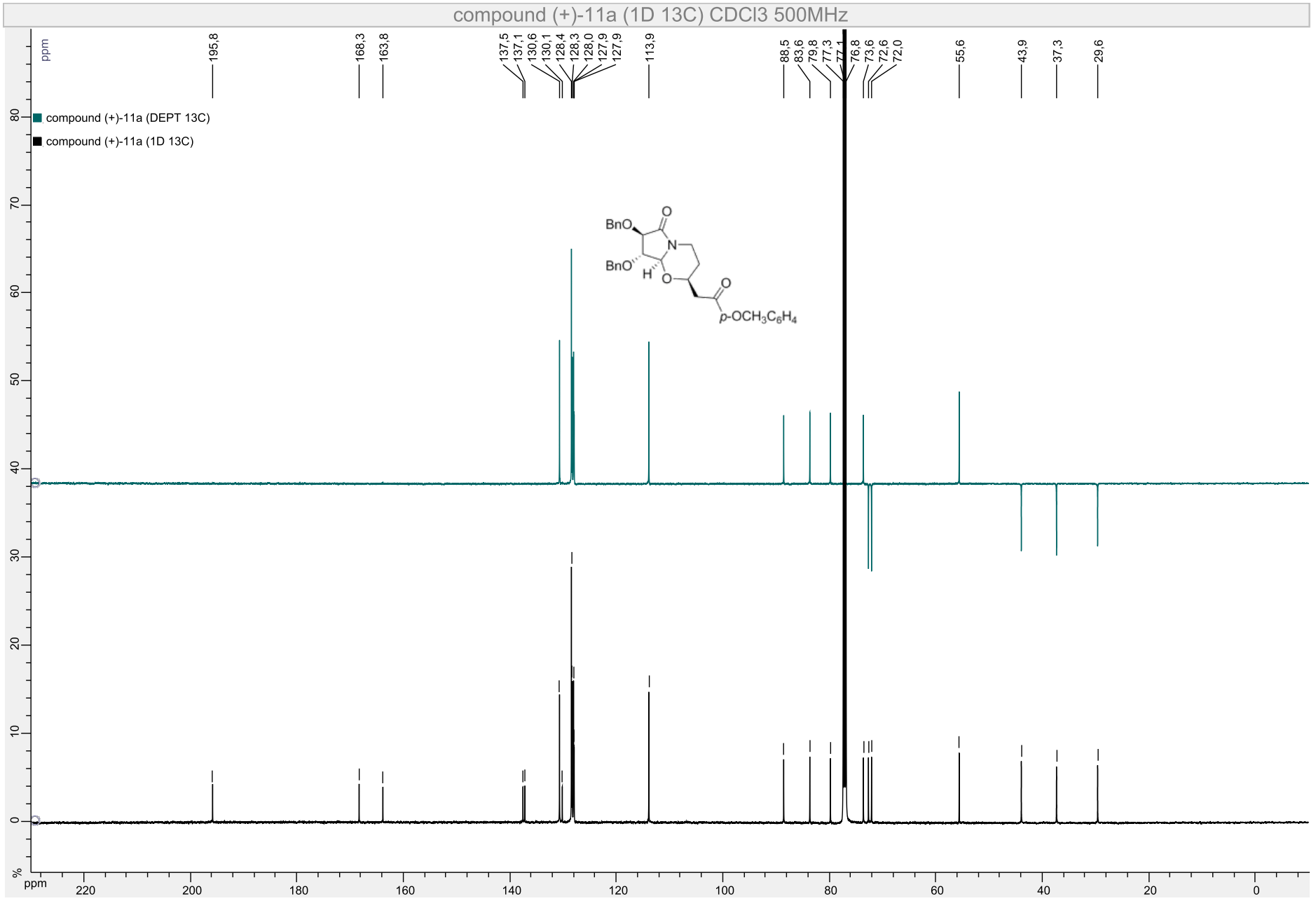

compound (+)-9a (1D 1H) CDCl3 500MHz
ppm
7,38
7,38
7,36
7,34
7,34
7,33
7,33
7,33
7,32
7,31
7,30
7,30
7,29
7,28
7,27
7,24
4,99
4,97
4,82
4,81
4,77
4,75
4,63
4,61
4,51
4,49
4,21
4,20
4,18
4,18
4,17
4,16
4,15
4,15
4,11
4,10
4,09
3,98
3,97
3,97
3,96
2,96
2,95
2,79
2,78
2,76
2,74
2,51
2,50
2,48
2,47
2,17
1,67
1,64
1,64
1,64
BnO
BnO
H
O
N
O
O
9,9
1,0
2,0
2,1
3,0
1,1
1,0
1,0
1,0
3,0
1,3
1,1
ppm
8,5
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0
%
110
100
90
80
70
60
50
40
30
20
10
0
-10


compound (+)-9a (1D 13C) CDCl3 500MHz
ppm
205,7
168,4
137,5
137,2
128,5
128,4
128,3
128,0
127,9
88,5
83,6
79,8
77,4
77,1
76,8
72,7
72,6
72,1
49,0
37,2
31,2
29,2
compound (+)-9a (DEPT 13C)
compound (+)-9a (1D 13C)
BnO
BnO
H
N
O
O
O
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0


compound (+)-10a (1D 1H) CDCl3 500MHz
ppm
7.96 7.95 7.95 7.59 7.58 7.57 7.48 7.47 7.45 7.37 7.35 7.33 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.25 7.24 7.23 7.21 7.20 7.20 7.19 7.18 7.18 4.97 4.95 4.85 4.84 4.76 4.74 4.56 4.54 4.43 4.42 4.40 4.32 4.31 4.30 4.29 4.29 4.25 4.24 4.22 4.21 4.17 4.16 4.16 4.15 3.96 3.96 3.95 3.95 3.42 3.41 3.39 3.38 3.04 3.03 3.03 3.01 3.01 2.99 2.99 2.98 2.98 2.97 2.96 2.94 2.93 1.81 1.81 1.80 1.78 1.78 1.78 1.59 1.57 1.56 1.54 1.53
BnO
BnO
H
O
N
O
O
Ph
2,1
1,2
2,3
1,1
1,0
1,1
1,0
1,0
1,0
1,8
1,0
1,0
2,0
1,0
1,0
%
ppm
8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0


compound (+)-10a (1D 13C) CDCl3 500MHz
ppm
197,3
168,3
137,5
137,1
137,0
133,5
128,8
128,4
128,3
128,0
127,9
127,9
88,5
83,6
79,8
77,3
77,1
76,8
73,3
72,6
72,1
44,2
37,3
29,5
compound (+)-10a (DEPT 13C)
compound (+)-10a (1D 13C)
BnO
BnO
H
O
N
O
O
Ph
%
ppm
220
200
180
160
140
120
100
80
60
40
20
0


compound (+)-11a (1D 1H) CDCl3 500MHz
ppm
7,82 7,81 7,80 7,80 7,24 7,23 7,20 7,18 7,17 7,15 7,15 7,14 7,14 7,13 7,13 7,12 7,12 7,11 7,07 7,06 7,06 7,05 6,81 6,81 6,79
4,85 4,82 4,71 4,71 4,63 4,61 4,43 4,41 4,29 4,27 4,17 4,16 4,15 4,11 4,10 4,09 4,08 4,04 4,04 4,03 4,02 3,84 3,83 3,82 3,82 3,72 3,24 3,23 3,21 3,20 2,88 2,87 2,79 2,77 2,75 2,74
1,67 1,67 1,65 1,65 1,64 1,50
BnO
BnO
H
O
N
O
O
p-OCH3C6H4
2,0 2,0 2,0 1,0 1,0 1,0 1,0 1,0 1,0 1,0 1,0 1,0 3,0 1,0 1,0 1,0 1,0 1,0
%
120 100 80 60 40 20 0
ppm
8,5 8 7,5 7 6,5 6 5,5 5 4,5 4 3,5 3 2,5 2 1,5 1 0,5 0


compound (+)-11a (1D 13C) CDCl3 500MHz
ppm
195,8
168,3
163,8
137,5
137,1
130,6
130,1
128,4
128,3
128,0
127,9
127,9
113,9
88,5
83,6
79,8
77,3
77,1
76,8
73,6
72,6
72,0
55,6
43,9
37,3
29,6
compound (+)-11a (DEPT 13C)
compound (+)-11a (1D 13C)
BnO
BnO
H
O
N
O
O
O
p-OCH3C6H4
%
80
70
60
50
40
30
20
10
0
220
200
180
160
140
120
100
80
60
40
20
0