Flow Pd(II)-Catalysed Carbonylative Cyclisation in the Total Synthesis of Jaspine B

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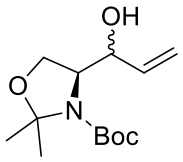
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Synthetic procedures:

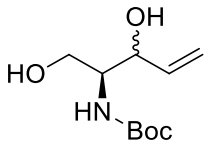
(2*S*)-2*N*,1*O*-isopropylidene-*N*-(*tert*-butoxycarbonyl)-2-amino-pent-4-en-1,3-diol



27-Boc

To a solution of Garner´s aldehyde **26**-Boc (1 g, 4.36 mmol, 1 equiv.) in anhydrous THF (20 mL) was added dropwise a solution of vinylmagnesium bromide (8.72 mL, 1 M in THF, 2 equiv.) at -78 °C. The resulting mixture was stirred for 2 h at the same temperature, and then it was allowed to warm to 0 °C and quenched by addition of saturated aqueous solution of NH_4Cl (20 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (3x30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The purification of crude product by MPLC (isocratic hexanes/EtOAc: 83/17) provided the mixture of diastereomers **27-Boc** (1.02 g, 91%, colorless oil). R_f = 0.23 (hexanes/EtOAc, 7:3); IR (ATR) ν_{max} 1697, 1368, 1260, 1161, 851 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6) δ_H 5.83 (ddd, *J* = 16.7, 10.4, 6.0 Hz, 1H, H-4), 5.22 – 5.14 (m, 1H, H-5_a), 5.05 (d, *J* = 10.4 Hz, 1H, H-5_b), 4.90 (d, *J* = 6.0 Hz, 1H, H-3), 4.16 – 4.02 (m, 1H, H-2) 3.93 (dd, *J* = 8.6, 1.6 Hz, 1H, H-1_a), 3.83 (dd, *J* = 8.6, 6.1 Hz, 1H, H-1_b), 3.76 (s, 1H, OH)), 1.49 (s, 3H, CH_3), 1.45 – 1.40 (m, 12H, CH_3 and $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6) δ_C 151.4, 139.4, 114.2, 93.0, 78.7, 71.5, 63.5, 60.7, 27.8, 26.3 ppm; HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{23}NNaO_4$ 280.1519, found 280.1517.

(4S)-N-(*tert*-butoxycarbonyl)-3,5-dihydroxy-4-aminopent-1-ene



22-Boc

To a solution of alkenes **27-Boc** (10.50 g, 40.80 mmol, 1 equiv.) in MeOH (163 mL) was added in one portion *p*TSA. H_2O (0.78 g, 4.08 mmol, 0.1 equiv.). The resulting mixture was stirred for 1,5 h at 40°C then quenched by addition of saturated solution of $NaHCO_3$ (250 mL) and finally extracted with EtOAc (3x70 mL). Combined organic extracts were washed with brine (150 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The purification of residue by MPLC (isocratic hexanes/EtOAc: 30/70) provided the mixture of diastereomers **22-Boc** (6,64 g, 75% orange oil); All physical and spectral data were in good agreement with the literature:[1] R_f = 0.13 (hexanes/EtOAc, 2:3);

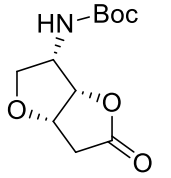
[1] Singh, P.; Panda, G. Intramolecular 5-*endo*-trig aminopalladation of β -hydroxy-γ -alkenylamine: efficient route to apyrrolidine ring and its application for the synthesis of (-)-8,8a-di-*epi*-swainsonine. *RSC Adv*. **2014**, *4*, 2161-2166.

IR (ATR) ν_{max} 3379, 1690, 1514, 1169, 1057 cm^{-1}; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{10}H_{19}NNaO_4$ 240.1206, found 240.1203;

Anti-diastereomer: ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.99–5.86 (m, 1H, H-2), 5.40 (dt, *J* = 17.3, 1.5 Hz, 1H, H-1_a), 5.27 (dt, *J* = 10.6, 1.5 Hz, 1H, H-1_b), 5.34 (s, 1H, NH), 4.42–4.36 (m, 1 H, H-3), 3.94 (dd, *J* = 11.3, 3.5 Hz, 1H, H-5_a), 3.77–3.56 (m, 2H, H-5_b, H-4), 2.77 (s, 1H, OH), 2.50 (s, 1H, OH), 1.45 (s, 9H, $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 156.4, 137.6, 116.6, 80.1, 74.6, 62.4, 55.2, 28.5 ppm

Syn-diastereomer: ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.99–5.86 (m, 1H, H-2), 5.38–5.31 (m, 1H, H-1_a), 5.23 (dt, *J* = 10.5, 1.4 Hz, 1H, H-1_b), 5.14 (s, 1H, NH), 4.46–4.42 (m, 1 H, H-3), 3.85-3.81 (m, 1H, H-5_a), 3.77–3.56 (m, 2H, H-5_b, H-4), 2.68 (s, 1H, OH), 2.50 (s, 1H, OH), 1.44 (s, 9H, $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 156.8, 137.7, 116.4, 80.1, 72.9, 63.8, 55.3, 28.4 ppm;

(1S,5S,8S)-N-(*tert*-butoxycarbonyl)-8-amino-2,6-dioxabicyclo[3.3.0]octane-3-one



major-**21**-Boc

The reaction vial was loaded with mixture of alkenes **22-Boc** (0.11 g, 0.5 mmol, 1 equiv.), $CuCl_2$ (0.26 g, 1.9 mmol, 4 equiv.), LiOAc (0.13 g, 1.9 mmol, 4 equiv.) and AcOH (1.9 mL). The mixture was allowed to stir for 5 min at room temperature. Subsequently $PdCl_2(MeCN)_2$ (0.013 g, 0.048 mmol, 0.1 equiv.) and $Fe(CO)_5$ (0.02 mL, 0.15 mmol, 0.3 equiv.) were added. The reaction vial was immediately closed, and the reaction mixture was stirred for 30 min at 60 °C. After the removal of AcOH in *vacuo*, the crude product was purified by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 50/50 then isocratic hexanes/EtOAc: 50/50) provided mixture of diastereomers **21-Boc** (0.09 g, 77%). Further separation by MPLC (isocratic pentane/Et_2O: 15/85) afforded single all *syn*-diastereomer *major*-**21-Boc** (0.074 g, 60%, white solid).

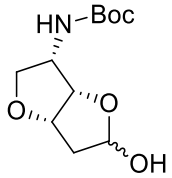
Major diastereomer **21-Boc**: R_f = 0.23 (hexanes/EtOAc, 2:3); mp 106-108 °C; $[\alpha]_D^{25}$ -171.1 (c 0.2, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.00–4.89 (s, 1H, NH), 4.96 (t, *J* = 4.5 Hz, 1H, H-1), 4.82 (ddd, *J* = 6.1, 4.5, 1.0 Hz, 1H, H-5), 4.53–4.36 (m, 1 H, H-8), 4.14 (dd, *J* = 8.7, 7.5 Hz, 1H, H-7_a), 3.53–3.42 (m, 1H, H-7_b), 2.83 (dd, *J* = 18.8, 6.1 Hz, 1H, H-4_a), 2.69 (dd, *J* = 18.8, 1.0 Hz, 1H, H-4_b), 1.45 (s, 9H, $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 175.0, 155.3, 82.5, 80.5, 77.4, 69.2, 53.4, 36.8, 28.4 ppm

Minor diastereomer **21b-Boc**: R_f = 0.28(hexanes/EtOAc, 2:3); mp 137-139 °C; $[\alpha]_D^{25}$ +49.8 (c 0.2, MeOH); ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.01 – 4.91 (m, 1H, H-1), 4.84 (ddd, *J* = 6.0, 4.6, 0.8 Hz, 1H, H-5), 4.75 (s, 1H, NH), 4.35–4.23 (m, 1 H, H-8), 4.04 (dd, *J* = 10.0, 4.9 Hz, 1H, H-7_a), 4.04 (dd, *J* = 10.0, 1.8 Hz, 1H, H-7_b), 2.77 (dd, *J* = 18.8, 6.0 Hz, 1H, H-4_a), 2.65 (d, *J* = 18.8 Hz, 1H, H-4_b), 1.46 (s,

9H, $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 175.2, 155.0, 87.1, 77.1, 71.0, 56.4, 52.3, 35.9, 28.5 ppm;

IR (ATR) ν_{max} 3381, 1798, 1717, 1510, 1155 cm^{-1}; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{11}H_{17}NnaO_5$ 266.0999, found 266.0997;

(1S,5S,8S)-N-(*tert*-butoxycarbonyl)-8-amino-3-hydroxy-2,6-dioxabicyclo[3.3.0]octane



28-Boc

To a solution of lactone *major*-**21-Boc** (0.91 g, 3.73 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (30 mL) was added dropwise DiBAl-H (7.47 mL, 1 M in CH_2Cl_2, 2 equiv.) at -78 °C. The resulting mixture was stirred for 2 h at -78 °C, then quenched by addition of MeOH (15 mL) and allowed to warm to room temperature. Subsequently, a saturated solution of sodium-potassium tartrate (50 mL) was added to the reaction mixture and it was vigorously stirred overnight. The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2 (3x50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The purification of residue by MPLC (hexanes/EtOAc: 60/40 to hexanes/EtOAc: 50/50 then isocratic hexanes/EtOAc: 50/50) provided desired lactol **28-Boc** (0.81 g, 89%, white solid); R_f = 0.17(hexanes/EtOAc, 2:3); mp 158-160 °C; IR (ATR) ν_{max} 3422, 1678, 1523, 1169, 1007 cm^{-1}; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{11}H_{19}NNaO_5$ 268.1155, found 240.1153;

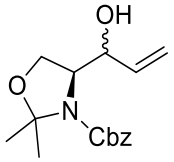
Minor Anomer:

^1H NMR (300 MHz, $CDCl_3$) δ_H 5.68 (dd, *J* = 8.0, 3.5 Hz, 1H, H-3), 5.42 (d, *J* = 6.5 Hz, 1H, NH), 4.89 -4.81 (m, 1H, H-5), 4.68 (t, *J* = 4.9 Hz, 1H, H-1), 4.26 – 4.12 (m, 1H, H-8), 3.99 - 3.84 (m, 1H, H-7_a), 3.38 - 3.30 (m, 1H, H-7_b), 2.81 (s, 1H, OH), 2.30 – 2.09 (m, 2H, H-4), 1.45 (s, 9H, C(CH3)3) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 155.6, 100.4, 83.6, 82.2, 80.9, 69.5, 53.5, 41.1, 28.5 ppm;

Major Anomer :

^1H NMR (300 MHz, $CDCl_3$) δ_H 5.54 (dd, *J* = 8.1, 4.8 Hz, 1H, H-3), 5.04 (d, *J* = 8.2 Hz, 1H, NH), 4.65 – 4.55 (m, 2H, H-5 and H-1), 4.39 – 4.26 (m, 1H, H-8), 4.02 (t, *J* = 7.8 Hz, 1H, H-7_a), 3.99 - 3.84 (m, 1H, H-7_b), 3.56 (d, *J* = 8.4 Hz, 1H, OH), 2.30 – 2.09 (m, 2H, H-4), 1.45 (s, 9H, $C(CH_3)_3$) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 155.7, 100.3, 83.7, 83.2, 79.9, 73.2, 53.4, 42.3, 28.5 ppm.

(2*S*)-2*N*,1*O*-isopropylidene-*N*-(benzyloxycarbonyl)-2-amino-pent-4-en-1,3-diol

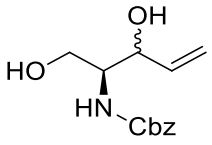


27-Cbz

To a solution of Cbz-protected Garner´s aldehyde **26**-Cbz (0.125 g, 0.48 mmol, 1 equiv.) in anhydrous THF (1 mL) was added dropwise a solution of vinylmagnesium bromide (1 mL, 1 M in THF, 2 equiv.) at -78°C. The resulting mixture was stirred for 1,5 h at −78 °C, and then it was allowed to warm to 0 °C and quenched by addition of saturated aqueous solution of NH4Cl (5 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (3x10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The purification of crude product by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 75/25 then isocratic hexanes/EtOAc: 75/25) provided the mixture of diastereomers **27-Cbz** (0.10 g, 77%, colorless oil). R_f = 0.23 (hexanes/EtOAc, 7:3); IR (ATR) ν_{max} 1701, 1408, 1352, 1070, 842 cm^{-1}; HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{21}NNaO_4$ 314.1363, found 314.1360;

Mixture of anti and syn diastereomers: ^1H NMR (300 MHz, DMSO-d_6) δ_H 7.42 – 7.29 (m, 5H, H_{Ar}), 5.91 – 5.70 (m, 1H, H-4), 5.21 – 4.90 (m, 5H, H-5, H-3, $PhCH_2$), 4.36 (s, 1H, OH), 4.16 (s, 1H, OH), 4.04 – 3.81 (m, 3H, H-2, H-1), 1.54 – 1.38 (m, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6) δ_C 151.9, 151.8, 138.9, 137.2, 136.4, 136.2, 127.9, 127.9, 127.4, 127.3, 127.3, 127.2, 115.4, 114.3, 93.5, 93.3, 71.0, 70.0, 65.6, 63.6, 62.7, 60.6, 60.3, 26.0, 25.5 ppm;

(4S)-N-(benzyloxycarbonyl)-3,5-dihydroxy-4-aminopent-1-ene



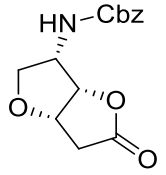
22-Cbz

To a solution of alkenes **27-Cbz** (0.64 g, 2.21 mmol, 1 equiv.) in MeOH (26 mL) was added in one portion *p*TSA. H_2O (0.038 g, 0.22 mmol, 0.1 equiv.). The resulting mixture was stirred for 3 h at room temperature and then quenched by addition of saturated solution of $NaHCO_3$ (10 mL). MeOH was removed in vacuo and the residue was dissolved in the mixture EtOAc (20 mL) and H_2O (20 mL) Organic phase was separated, and aqueous phase was extracted with EtOAc (3x40 mL). Combined organic extracts were washed with brine (40 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The purification of crude product by MPLC (isocratic hexanes/EtOAc: 30/70) provided the mixture of diastereomers **22-Cbz** (0.484 g, 87%, orange oil). R_f = 0.14 (hexanes/EtOAc, 3:7); IR (ATR) ν_{max} 3339, 1692, 1543, 1279, 929 cm^{-1}; HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{13}H_{17}NNaO_4$ 274.1050, found 274.1045;

Anti-diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.40 – 7.29 (m, 5H, H_{Ar}), 5.92 (ddd, *J* = 17.2, 10.6, 5.4 Hz, 1H, H-2), 5.59 (s, 1H, NH), 5.40 (d, *J* = 17.2 Hz, 1H, H-1_a), 5.28 (d, *J* = 10.6 Hz, 1H, H-1_b), 5.12 (s, 2H, $PhCH_2$), 4.45 – 4.36 (m, 1H, H-3), 3.97 (d, *J* = 10.5 Hz, 1H, H-5_a), 3.90 – 3.81 (m, 1H, H-5_b), 3.79 – 3.65 (m, 1H, H-4), 2.59 (s, 1H, OH), 2.35 (s, 1H, OH) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 156.8, 137.3, 136.3, 128.6, 128.3, 128.2, 116.8, 74.2, 67.1, 62.1, 55.6 ppm;

Syn-diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.40 – 7.29 (m, 5H, H_{Ar}), 5.92 (ddd, *J* = 17.2, 10.6, 5.4 Hz, 1H, H-2), 5.39 (s, 1H, NH), 5.34 (d, *J* = 17.2 Hz, 1H, H-1_a), 5.22 (d, *J* = 10.6 Hz, 1H, H-1_b), 5.10 (s, 2H, $PhCH_2$), 4.51 – 4.45 (m, 1H, H-3), 3.79-3.65 (m, 3H, H-5 and H-4), 2.53 (s, 1H, OH), 2.35 (s, 1H, OH) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 157.1, 137.5, 136.3, 128.6, 128.2, 128.1, 116.5, 72.4, 67.1, 63.4, 55.7 ppm.

(1S,5S,8S)-N-(benzyloxycarbonyl)-8-amino-2,6-dioxabicyclo[3.3.0]octane-3-one



major-**21**-Cbz

The reaction vial was loaded with mixture of alkenes **22-Cbz** (0.18 g, 0.73 mmol, 1 equiv.), $CuCl_2$ (0.39 g, 2.9 mmol, 4 equiv.), LiOAc (0.19 g, 2.9 mmol, 4 equiv.) and AcOH (2.9 mL). The mixture was allowed to stir for 5 min at room temperature. Subsequently $PdCl_2$. $(MeCN)_2$ (0.019 g, 0.073 mmol, 0.1 equiv.) and $Fe(CO)_5$ (0.03 mL, 0.22 mmol, 0.3 equiv.) were added. The reaction vial was immediately closed, and the reaction mixture was stirred for 30 min at 60 °C. After the removal of AcOH in *vacuo*, the crude product was purified by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 40/60 then isocratic hexanes/EtOAc: 40/60) provided mixture of diastereomers **21-Cbz** (0.15 g, 75%). Further separation by MPLC (isocratic toluene/Et_2O: 3/97) afforded single diastereomer *major*-**21-Cbz** (0.11 g, 55%, white solid). All physical and spectral data were in good agreement with the literature:[2]

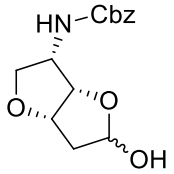
Major diastereomer **21**-Cbz*:* R_f =0.18 (hexanes/EtOAc,2:3); mp 136-137 °C, $[\alpha]_D^{25}$ -124.5 (c 1.0, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.42 – 7.28 (m, 5H, H_{Ar}), 5.24 (d, *J* = 8.5 Hz, 1H, NH), 5.12 (s, 2H, $PhCH_2$), 4.96 (t, *J* = 4.6 Hz, 1H, H-1), 4.87 – 4.78 (m, 1H, H-5), 4.60 – 4.42 (m, 1H, H-8), 4.15 (t, *J* = 8.1 Hz, 1H, H-7_a), 3.56 – 3.43 (m, 1H, H-7_b), 2.82 (dd, *J* = 18.9, 6.2 Hz, 1H, H-4a), 2.68 (dd, *J* = 18.9, 0.6 Hz, 1H, H-4_b) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 174.9, 156.0, 136.1, 128.7, 128.4, 128.2, 82.2, 77.4, 69.0, 67.4, 53.8, 36.7 ppm;

Minor diastereomer **21**-Cbz*:* R_f =0.25 (hexanes/EtOAc,2:3); ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.42 – 7.28 (m, 5H, H_{Ar}) 5.25–5.03 (m, 2H, $PhCH_2$, NH), 5.01–4.89 (m, 1H, H-1), 4.86–4.76 (m, 1 H, H-5), 4.39 – 4.31 (m, 1H, H-8), 4.03 (dd, *J* = 10.0, 4.8 Hz, 1H, H-7_a), 3.81 (d, *J* = 10.0 Hz, 1H, H-7_b), 2.75 (dd, *J* =

[2] Bhaket, P.; Morris, K.; Stauffer, Ch. S.; Datta, A. Total Synthesis of Cytotoxic Anhydrophytosphingosine Pachastrissamine (Jaspine B). *Org. Lett.* **2005**, *7*, 875-876.

18.8, 6.2 Hz, 1H, H-4_a), 2.63 (d, *J* = 18.8 Hz, 1H, H-4_b ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 175.1, 155.6, 136.0, 128.8, 128.6, 128.4, 86.8, 70.8, 67.4, 56.8, 35.7, 29.8 ppm;
IR (ATR) ν_{max} 3318, 1784, 1721, 1541, 1155 cm^{-1}; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{15}NNaO_5$ 300.0842, found 300.0840.

(1S,5S,8S)-N-(benzyloxycarbonyl)-8-amino-3-hydroxy-2,6-dioxabicyclo[3.3.0]octane



28-Cbz

To a solution of lactone *major*-**21-Cbz** (1.50 g, 5,4 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (18 mL) was added dropwise DiBAl-H (6.8 mL, 1 M in CH_2Cl_2, 1.3 equiv.) at -78°C. The resulting mixture was stirred for 0.75 h at -78 °C, then quenched by addition of MeOH (10 mL) and allowed to warm to room temperature. Subsequently, a saturated solution of sodium-potassium tartrate (40 mL) was added to the reaction mixture, and it was vigorously stirred overnight. The organic phase was separated, and the aqueous phase was extracted with EtOAc (3x50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The purification of residue by MPLC (hexanes/EtOAc: 60/40 to hexanes/EtOAc: 50/50 then isocratic hexanes/EtOAc: 50/50) provided desired lactol **28-Cbz** (1.21g, 81%, white solid); All physical and spectral data were in good agreement with the literature:[2] R_f =0.12 (hexanes/EtOAc, 2:3); mp 96-98 °C; IR (ATR) ν_{max} 3309, 1691, 1551, 1261, 976 cm^{-1}; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{14}H_{17}NNaO_5$ 302.0999, found 302.0994.

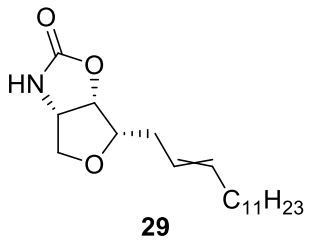
Major anomer:

^1H NMR (300 MHz, $CDCl_3$) δ_H 7.40 – 7.28 (m, 5H, H_{Ar}), 5.69 - 5.64 (m, 1H, H-3), 5.28 (d, *J* = 7.9 Hz, 1H, NH), 5.11 (s, 2H, $PhCH_2$), 4.90 – 4.82 (m, 1H, H-5), 4.69 (t, *J* = 4.8 Hz, 1H, H-1), 4.31 – 4.22 (m, 1H, H-8), 4.04 (t, *J* = 7.7 Hz, 1H, H-7_a), 3.37 (t, *J* = 8.9 Hz, 1H, H-7_b), 2.66 (s, 1H, OH), 2.28 – 2.10 (m, 2H, H-4) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 156.3, 136.5, 128.7, 128.6, 128.3, 100.2, 83.2, 82.3, 72.7, 67.1, 53.8, 41.1 ppm.

Minor anomer:

^1H NMR (300 MHz, $CDCl_3$) δ_H 7.40 – 7.28 (m, 5H, H_{Ar}), 5.70 (s, 1H, NH), 5.53 (dd, *J* = 8.0, 5.3 Hz, 1H, H-3), 5.11 (s, 2H, $PhCH_2$), 4.67 -4.62 (m, 1H, H-5), 4.59 (t, *J* = 4.6 Hz, 1H, H-1), 4.42 – 4.33 (m, 1H, H-8), 3.99 - 3.88 (m, 2H, H-7), 3.47 (d, *J* = 8.4 Hz, 1H, OH), 2.28 – 2.10 (m, 2H, H-4), ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C 156.2, 136.4, 128.7, 128.4, 128.3, 100.4, 83.5, 80.6, 69.3, 67.2, 53.8, 42.2 ppm.

(1S,5S,6S)-6-(tetradec-2-ene-yl)-2-aza-4,7-dioxabicyclo[3.3.0]octane-3-one



29

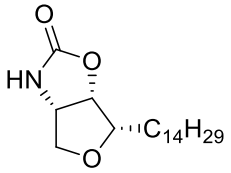
A:

To a solution of dodecyltriphenylphosphonium bromide (7.60 g, 14.9 mmol, 4.5 equiv.) in anhydrous THF (66 mL) was added dropwise solution of *n*-BuLi (5.3 mL, 2.5 M in hexane, 4 equiv.) at -78 °C. Reaction mixture was stirred for 45 min at the same temperature and then solution of lactol **28-Boc** (0.80 g, 3.3 mmol, 1 equiv.) in anhydrous THF (20 mL) was added dropwise. After 2 h of stirring at -78 °C, reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently, the reaction mixture was quenched by addition of saturated solution of NH_4Cl (100 mL). The organic phase was separated, and aqueous phase was extracted with EtOAc (3x50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The purification of residue by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 40/60 then isocratic hexanes/EtOAc: 40:60) provided mixture of olefines **29** (0.45 g, 42%, white solid).

B:

To a solution of dodecyltriphenylphosphonium bromide (1.70 g, 3.40 mmol, 4.5 equiv.) in anhydrous THF (15 mL) was added dropwise solution of *n*-BuLi (1.2 mL, 2.5 M in hexane, 4 equiv.) at -78 °C. Reaction mixture was stirred for 45 min at the same temperature and then solution of lactol **28-Cbz** (0.20 g, 0.75 mmol, 1 equiv.) in anhydrous THF (4.5 mL) was added dropwise. After 2 h of stirring at -78 °C, reaction mixture was allowed to warm to room temperature and stirred overnight. Subsequently, the reaction mixture was quenched by addition of saturated solution of NH_4Cl (30 mL). The organic phase was separated, and aqueous phase was extracted with EtOAc (3x25 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The purification of residue by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 40/60 then isocratic hexanes/EtOAc: 40:60) provided mixture of olefines **29** (0.2 g, 83%, white solid). All physical and spectral data were in good agreement with the literature:[2] R_f = 0.20 (hexanes/EtOAc, 1:4); mp 75-76 °C; IR (ATR) ν_{max} 2916, 2848, 1757, 1469, 1082 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, mixture of *cis*/*trans* isomers) δ_H 5.70 – 5.36 (m, 3H, NH, 6-(H-2 and H-3)), 4.97 (dd, *J* = 7.4, 3.6 Hz, 1H, H-5), 4.38 (dd, *J* = 7.4, 3.7 Hz, 1H, H-1), 3.96 (d, *J* = 10.5 Hz, 1H, H-8_a), 3.59 – 3.47 (m, 2H, H-8_b and H-6), 2.67 – 2.43 (m, 2H, 6-(H-1)), 2.14 – 1.95 (m, 2H, 6-(H-4)), 1.47 – 1.14 (m, 18H, 6-(H-5 to H-13)), 0.88 (t, *J* = 6.7 Hz, 3H, 6-(H-14)) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, mixture of *cis*/*trans* isomers) δ_C 159.4, 134.6, 133.6, 124.3, 123.7, 83.3, 83.1, 80.9, 73.7, 57.2, 57.1, 32.8, 32.1, 31.6, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 27.5, 26.5, 22.8, 14.3 ppm; HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{33}NNaO_3$ 346.2353, found 346.2351.

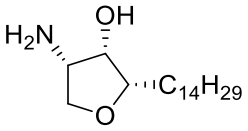
(1s,5s,6s)-6-tetradecyl-2-aza-4,7-dioxabicyclo [3.3.0]octane-3-one



30

To a solution of olefines **29** (0.18 g, 0.56 mmol, 1 equiv.) in EtOAc (8.5 mL) was added Pd/C (0.06 g, 10 wt%, 1 equiv.). The flask was three times evacuated, filled with hydrogen *via* balloon. The mixture was stirred for 2h at room temperature. Subsequently, catalyst was filtered, and reaction mixture concentrated in vacuo. Recrystallization from mixture hexanes/EtOAc: 3/7 offered carbamate **30** (0.18 g, 97%, white solid); All physical and spectral data were in good agreement with the literature:[3] R_f = 0.29 (hexanes/EtOAc, 1:4); $[\alpha]_D^{25}$ +78.5 (c 1.0, $CHCl_3$); mp 125-127 °C (lit.[4.] mp 124-126 °C); IR (ATR) ν_{max} 2920, 2847, 1755, 1464, 1067 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 5.96 (s, 1H, NH), 4.95 (dd, *J* = 7.5, 3.7 Hz, 1H, H-5), 4.37 (dd, *J* = 7.5, 4.0 Hz, 1H, H-1), 3.94 (d, *J* = 10.4 Hz, 1H, H-8_a), 3.57 – 3.45 (m, 2H, H-6 and H-8_b), 1.85 – 1.70 (m, 2H, 6-(H-1)), 1.50 – 1.15 (m, 24H, 6-(H-2 to H-13)), 0.88 (t, *J* = 6.7 Hz, 3H, 6-(H-14)) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C = 159.3, 83.4, 81.1, 73.5, 57.2, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.5, 28.3, 26.2, 22.8, 14.3 ppm; HRMS (ESI) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{35}NNaO_3$ 348.2509, found 348.2506.

(2S,3S,4S)-4-amino-2-tetradecyltetrahydrofuran-3-ol



1

To a solution of carbamate **30** (0.10 g, 0.32 mmol, 1 equiv.) in EtOH (8.5 mL) was added solution of KOH (8.52 mL, 1 M in H_2O,). The reaction mixture was stirred for 4.5 h at 85 °C and then concentrated in *vacuo*. The crude product was purified by MPLC (isocratic $CHCl_3$/MeOH/NH_3: 95/4/1) providing jaspine B (0.065 g, 69%, white solid). All physical and spectral data were in good agreement with the literature:[5] R_f = 0.09 ($CHCl_3$/MeOH/NH_3, 95:4:1); $[\alpha]_D^{25}$ +23.4 (c 1.0, $CHCl_3$); mp 92-93 °C (lit.[6] mp 90-92 °C); IR (ATR) ν_{max} 2916, 2849, 1722, 1467, 873 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ_H 3.92 (dd, *J* = 8.5, 7.3 Hz, 1H, H-5_a), 3.86 (dd, *J* = 4.9, 3.5 Hz, 1H, H-3), 3.73 (ddd, *J* = 7.2, 6.7, 3.5 Hz,

[3] Bae, H.; Jeon, H.; Baek, D. J.; Lee, D.; Kim, S. Stereochemically Reliable Syntheses of Pachastrissamine and Its 2-epi-Congener via Oxazolidinone Precursors from an Established Starting Material N-tert-Butoxycarbonyl-Protected Phytosphingosine. *Synthesis* **2012**, *44*, 3609-3612.

[4] Ichikawa, Y.; Matsunaga, K.; Masuda, T.; Kotsuki, H.; Nakano, K. Stereocontrolled synthesis of cytotoxic anhydrosphingosine pachastrissamine by using [3.3] sigmatropic rearrangement of allyl cyanate. *Tetrahedron* **2008**, *64*, 11313-11318.

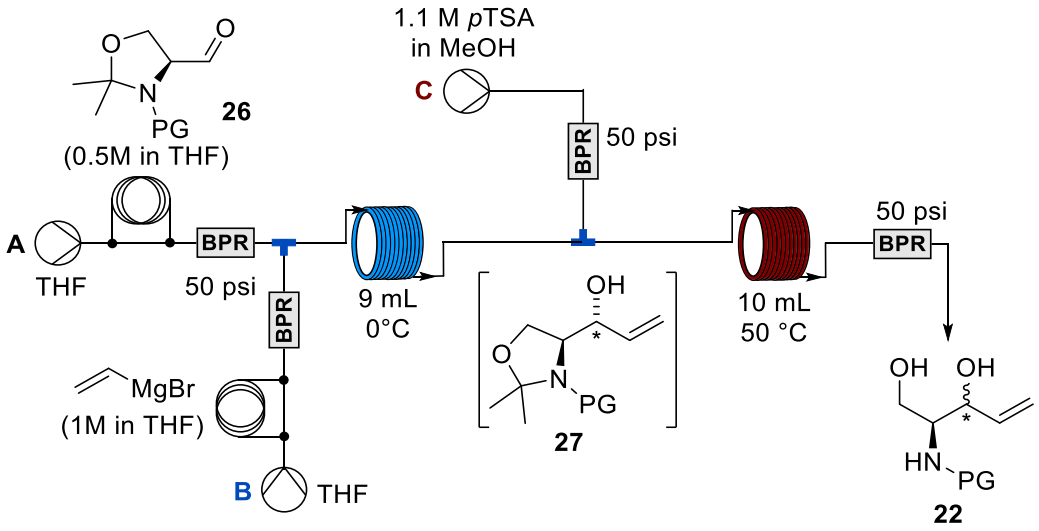
[5] Passiniemi, M.; Koskinen, A. M. P. Asymmetric synthesis of Pachastrissamine (Jaspine B) and its diastereomers via η3-allylpalladium intermediates. *Org. Biomol. Chem.* **2011**, *9*, 1774–1783.

[6] Ghosal, P.; Ajay, S.; Meena, S.; Sinha, S.; Shaw, A. K. Stereoselective total synthesis of Jaspine B (Pachastrissamine)utilizing iodocyclization and an investigation of its cytotoxic activity. *Tetrahedron: Asymmetry* **2013**, *24*, 903–908;

1H, H-4), 3.70 – 3.61 (m, 1H, H-2), 3.51 (dd, J = 8.5, 6.7 Hz, 1H, H-5_b), 1.41 (s, 1H, OH), 1.38 – 1.19 (m, 24H, 2-(H-2 to H-13)), 1.11 (s, 2H, NH_2), 0.88 (t, J = 6.7 Hz, 3H, 2-(H-14)) ppm; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ_C = 83.4, 72.5, 71.9, 54.4, 32.1, 30.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.5, 22.9, 14.3 ppm; HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{18}H_{38}NO_2$ 300.2897, found 300.2893.

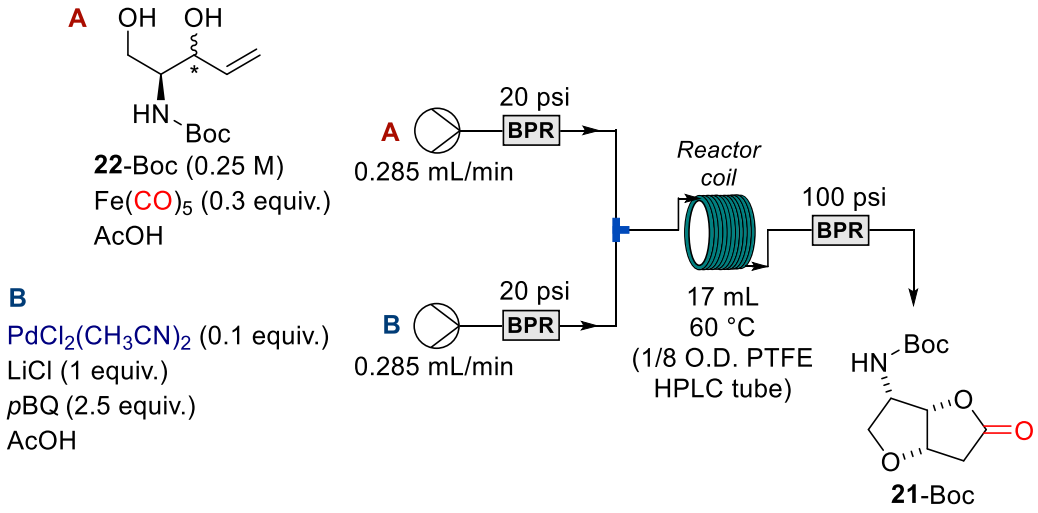
Flow experiments

Grignard addition followed by acetonide cleavage



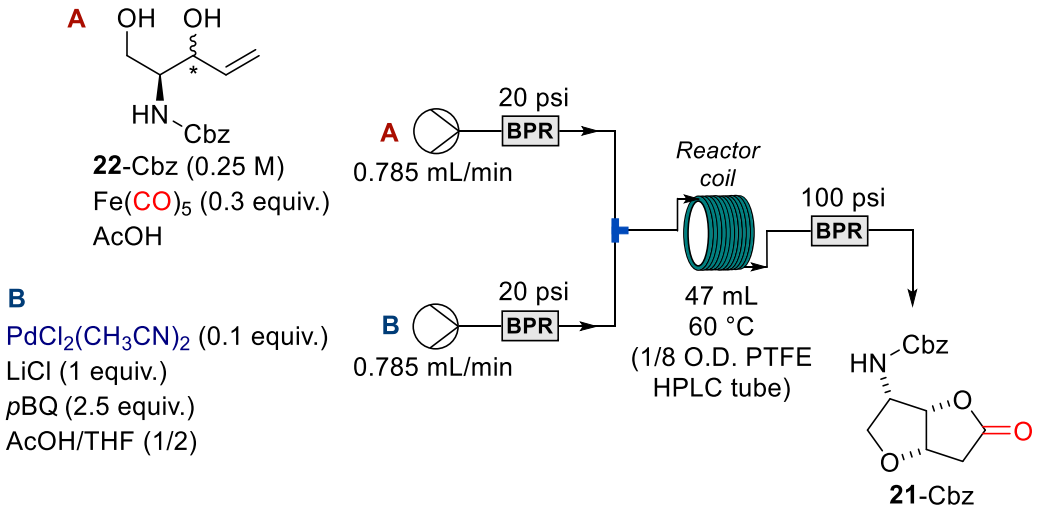
The flow setup consisted of three HPLC pumps (Knauer Azura 4.1S with 10 mL pump head) to introduce a solution of aldehyde (**26**-Boc or **26**-Cbz, 1.983 g or 2.277 g, 8.65 mmol, 0.5 M) in 17.3 mL of anhydrous THF (Feed A), a commercial solution of vinylmagnesium bromide (1.0 M in THF, Sigma-Aldrich, Feed B), and solution of *p*TSA (1.1 M in MeOH, Feed C). Injection loops (PTFE, 0.8 mm i.d., 1.6 mm o.d.; internal volume: 17.3 mL, Feed A, and 18.4 mL, Feed B) were used to deliver the two feeds. Feed C was directly pumped through HPLC pump. To start the experiment, the complete reactor setup was flushed by pumping anhydrous THF with flow rates of Feed A = Feed B = 250 µL/min. Solution of *p*TSA was introduced with Feed C = 250 µL/min. Solutions (Feed A and Feed B) were loaded into their corresponding injection loops and were pumped from the injection loops and mixed in a T-shaped connector (PEEK) in a cooling bath (0 °C). The combined mixture passed through a coil reactor (PTFE, 0.8 mm i.d., 1.6 mm o.d.; internal volume: 9.0 mL) at 0 °C before the mixture was combined with Feed C in a T-shaped connector (PEEK) at the same temperature. The mixture then went through a second coil reactor at 50 °C (PTFE, 1.5 mm i.d., 3.2 mm o.d.; internal volume: 10.0 mL) and left the system through Upchurch BPR (50 psi). Final reaction mixture was collected in the flask filled with appropriate amount of saturated solution of $NaHCO_3$ in water (50 mL) and subsequently extracted with EtOAc (3x100 mL). The residue was purified by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 40/60 then isocratic hexanes/EtOAc: 40/60) providing the mixture of diastereomers **22**-Boc (1.160 g, 62%, pale yellow oil) or **22**-Cbz (1.787 g, 82%, pale yellow oil).

Carbonylative cyclisation of **22**-Boc using *p*BQ/LiCl reoxidation system



The flow setup consisted of two HPLC pumps (Knauer Azura 4.1S with 10 mL pump head) to introduce a solution of **22**-Boc and iron pentacarbonyl in glacial AcOH (Feed A), and solution of pBQ, LiCl and $PdCl_2(MeCN)_2$ in the glacial AcOH (Feed B). Both feeds were directly pumped through the HPLC pumps. To start the experiment, the complete reactor setup was flushed by pumping glacial AcOH with flow rates of Feed A = Feed B = 285 µL/min. Substrate **22**-Boc (5.70 g, 26.25 mmol) and $Fe(CO)_5$ (1.04 mL, 7.88 mmol, 0.3 equiv.) were dissolved in glacial AcOH and diluted to 105 mL in corresponding volumetric flasks (Feed A). LiCl (1.11 g, 26.25 mmmol, 1 equiv.), *p*BQ (7.09 g, 65.62 mmol, 2.5 equiv.) and $PdCl_2(MeCN)_2$ (0.68 g, 2.63 mmol, 0.1 equiv.) were dissolved in glacial AcOH and diluted to 105 mL in corresponding volumetric flasks (Feed B). Feed A and feed B were pumped directly through HPLC pumps and mixed in a T-shaped connector (PEEK). The combined mixture went through a coil reactor (PTFE, 0.8 mm i.d., 1.6 mm o.d.; internal volume: 17.1 mL) at 60 °C before the flow stream left the system through Upchurch BPR (100 psi). Reaction stream was collected in the flask for 6 h (25.65 mmol) and evaporated in vacuo. The residue was purified by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 40/60 then isocratic hexanes/EtOAc: 40/60) providing the mixture of bicyclic lactones **21**-Boc (4.50 g, 72%, pale yellow solid).

Carbonylative cyclisation of **22**-Cbz using *p*BQ/LiCl reoxidation system



The flow setup consisted of two HPLC pumps (Knauer Azura 4.1S with 10 mL pump head) to introduce a solution of **22**-Cbz and iron pentacarbonyl in glacial AcOH (Feed A), and solution of pBQ, LiCl and $PdCl_2(MeCN)_2$ in the mixture of glacial AcOH/THF (1:2) (Feed B). Both feeds were directly pumped through the HPLC pumps. To start the experiment, the complete reactor setup was flushed by pumping glacial AcOH with flow rate of Feed A = 785 µL/min and the mixture of glacial AcOH/THF (1:2) with flow rate of Feed B = 785 µL/min. Substrate **22**-Cbz (7.85 g, 31.24 mmol) and $Fe(CO)_5$ (1.23 mL, 9.37 mmol, 0.3 equiv.) were dissolved in glacial AcOH and diluted to 125 mL in corresponding volumetric flasks (Feed A). LiCl (1.32 g, 31.24 mmmol, 1 equiv.), *p*BQ (8.44 g, 78.09 mmol, 2.5 equiv.) and $PdCl_2(MeCN)_2$ (0.81 g, 3.12 mmol, 0.1 equiv.) were dissolved in the mixture of glacial AcOH/THF (1:2) and diluted to 125 mL in corresponding volumetric flasks (Feed B). Feed A and feed B were pumped directly through HPLC pumps and mixed in a T-shaped connector (PEEK). The combined mixture went through a coil reactor (PTFE, 0.8 mm i.d., 1.6 mm o.d.; internal volume: 47.1 mL) at 60 °C before the flow stream left the system through Upchurch BPR (100 psi). Reaction stream was collected in the flask for 155 min (30.42 mmol) and evaporated in vacuo. The residue was purified by MPLC (hexanes/EtOAc: 100/0 to hexanes/EtOAc: 40/60 then isocratic hexanes/EtOAc: 40/60) providing the mixture of bicyclic lactones **21**-Boc (6.30 g, 75%, pale yellow mixture of oil and solid).

Copies of ^{1}H and ^{13}C NMR spectra

^{1}H, ^{13}C NMR spectrum of compound **27**-Boc...……..…….S14-S15

^{1}H, ^{13}C NMR spectrum of compound **22**-Boc...……..…….S16-S17

^{1}H, ^{13}C NMR spectrum of compound *major*-**21**-Boc……...….S18-S19

^{1}H, ^{13}C NMR spectrum of compound *minor*-**21**-Boc … ……...S20-S21

^{1}H, ^{13}C NMR spectrum of compound **28**-Boc …….S22-S23

^{1}H, ^{13}C NMR spectrum of compound **27**-Cbz...……..…….S24-S25

^{1}H, ^{13}C NMR spectrum of compound **22**-Cbz...……..…….S26-S27

^{1}H, ^{13}C NMR spectrum of compound *major*-**21**-Cbz…...……S28-S29

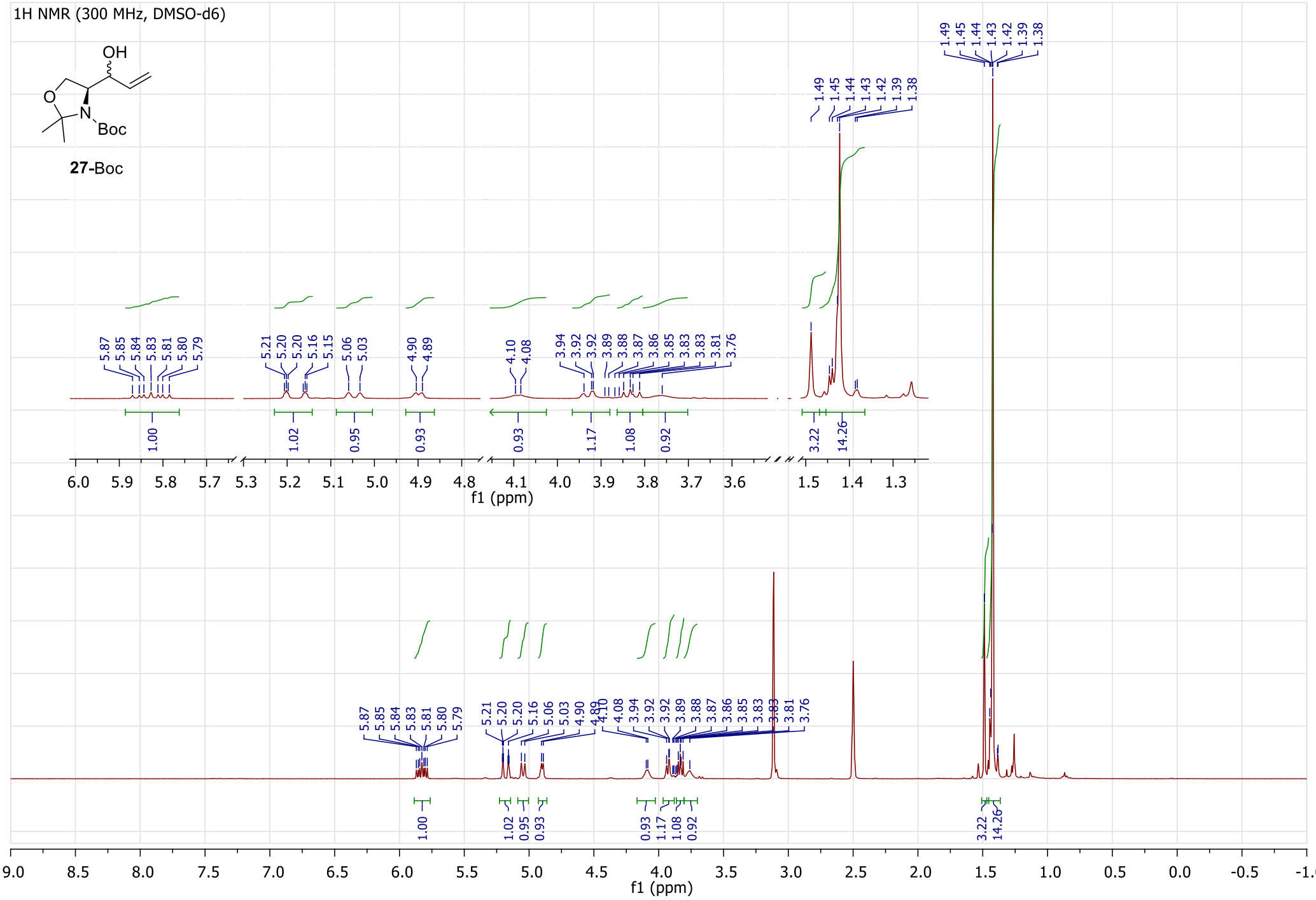
^{1}H, ^{13}C NMR spectrum of compound *minor*-**21**-Cbz……S30-S31

^{1}H, ^{13}C NMR spectrum of compound **28**-Cbz …….S32-S33

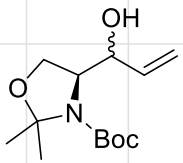
^{1}H, ^{13}C NMR spectrum of compound **29** …….S34-S35

^{1}H, ^{13}C NMR spectrum of compound **30**… …….S36-S37

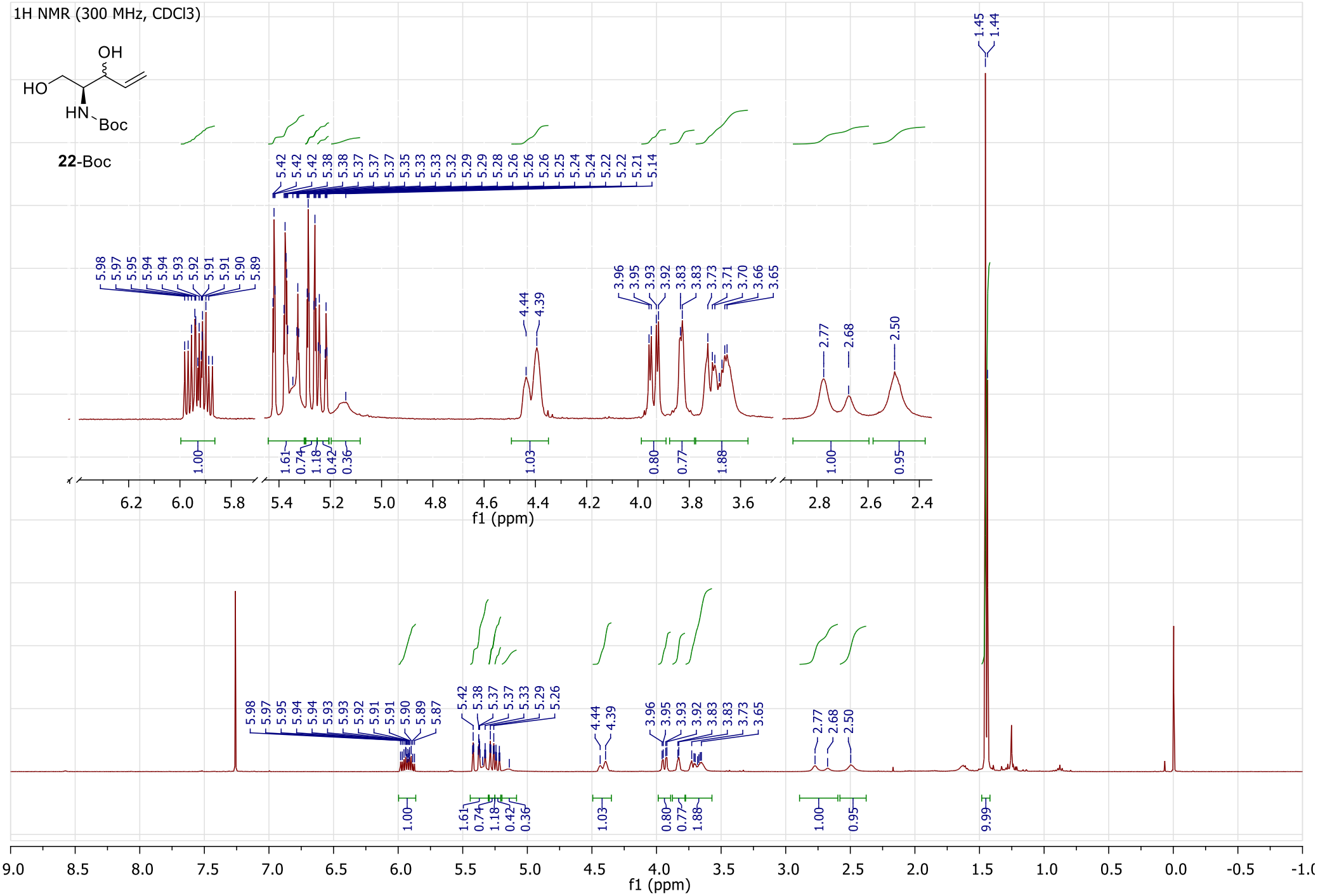
^{1}H, ^{13}C NMR spectrum of compound **1** ……...……...….S38-S39

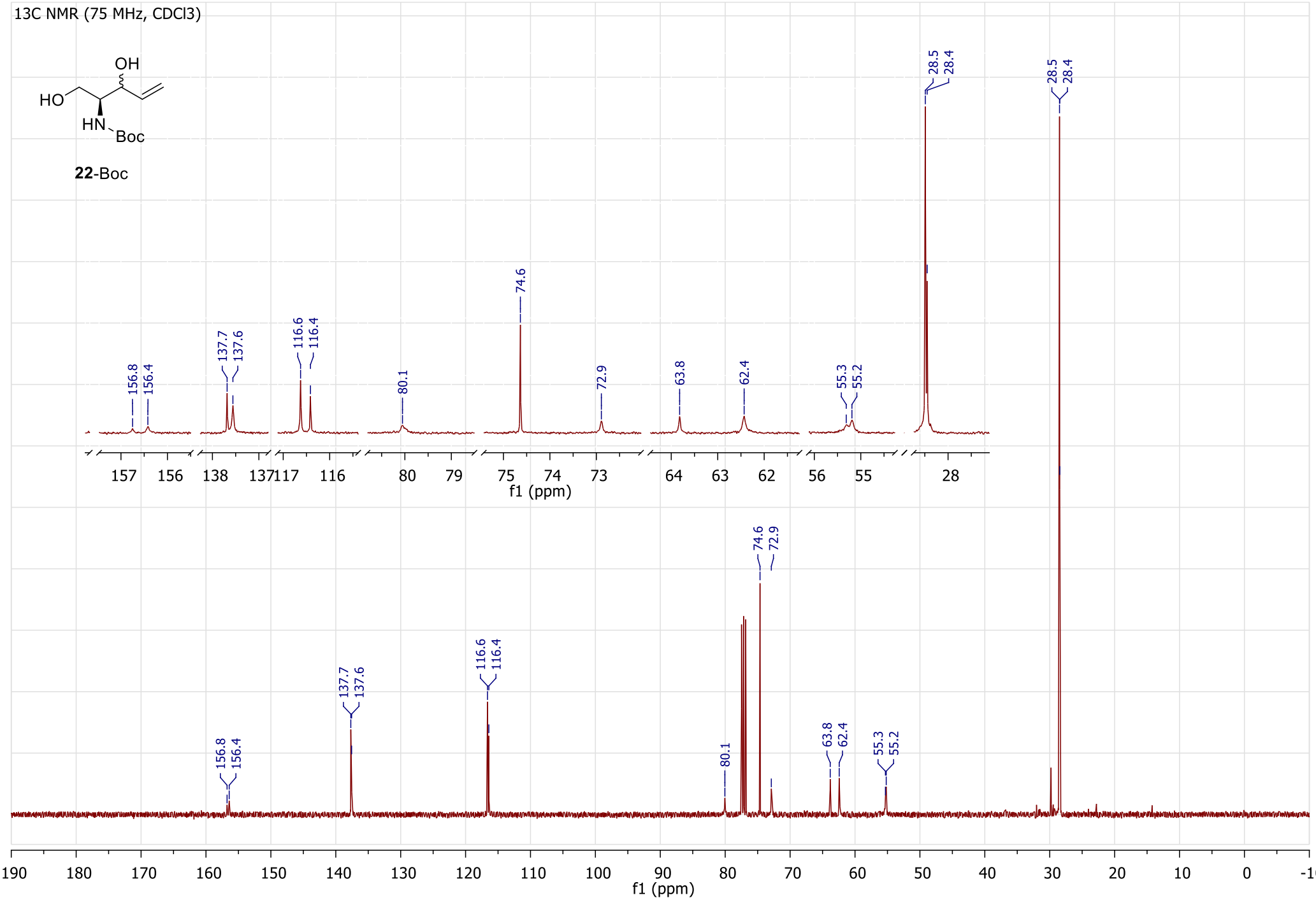

1H NMR (300 MHz, DMSO-d6)
OH
O
N
Boc
27-Boc
f1 (ppm)

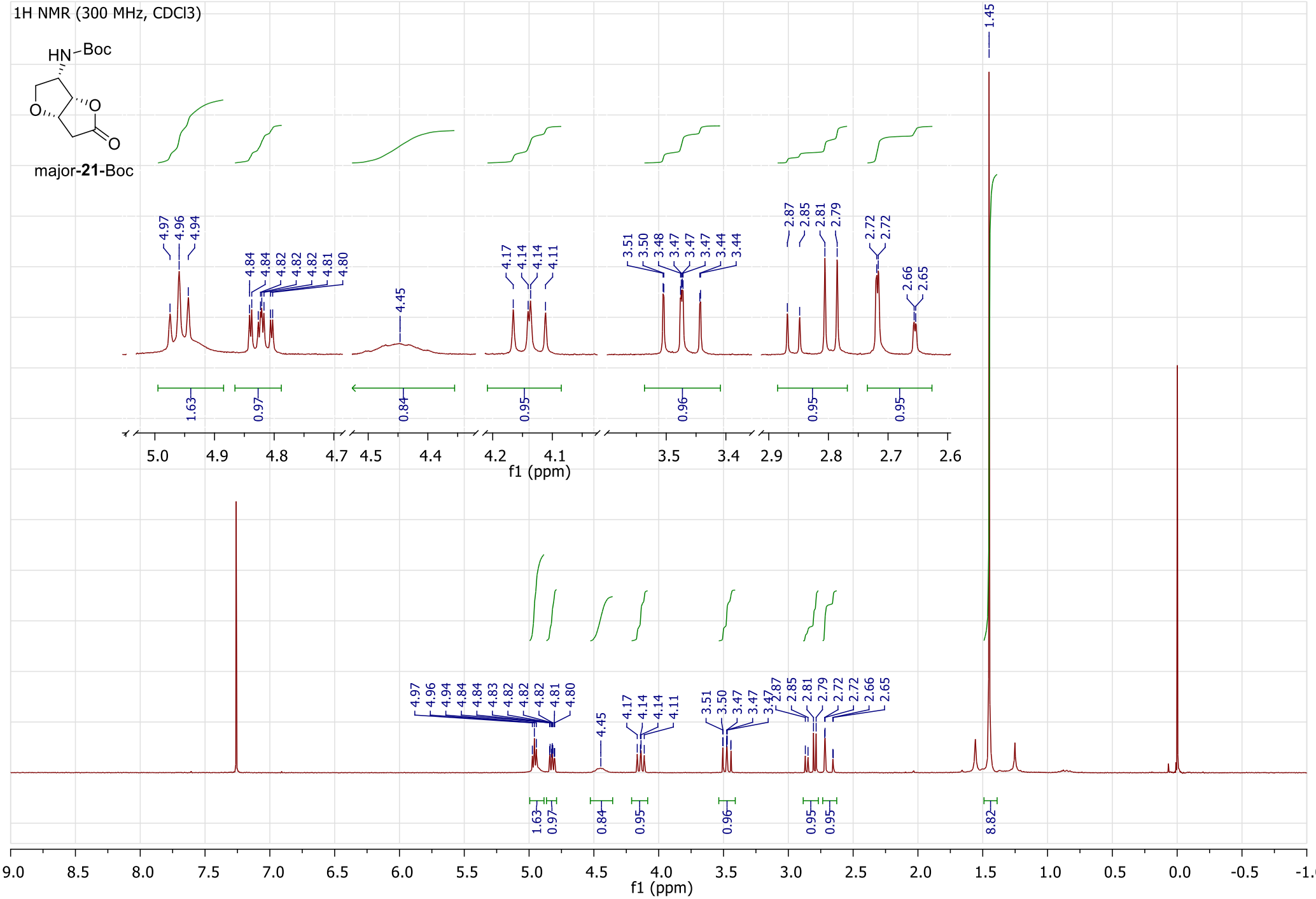
13C NMR (75 MHz, DMSO-d6)

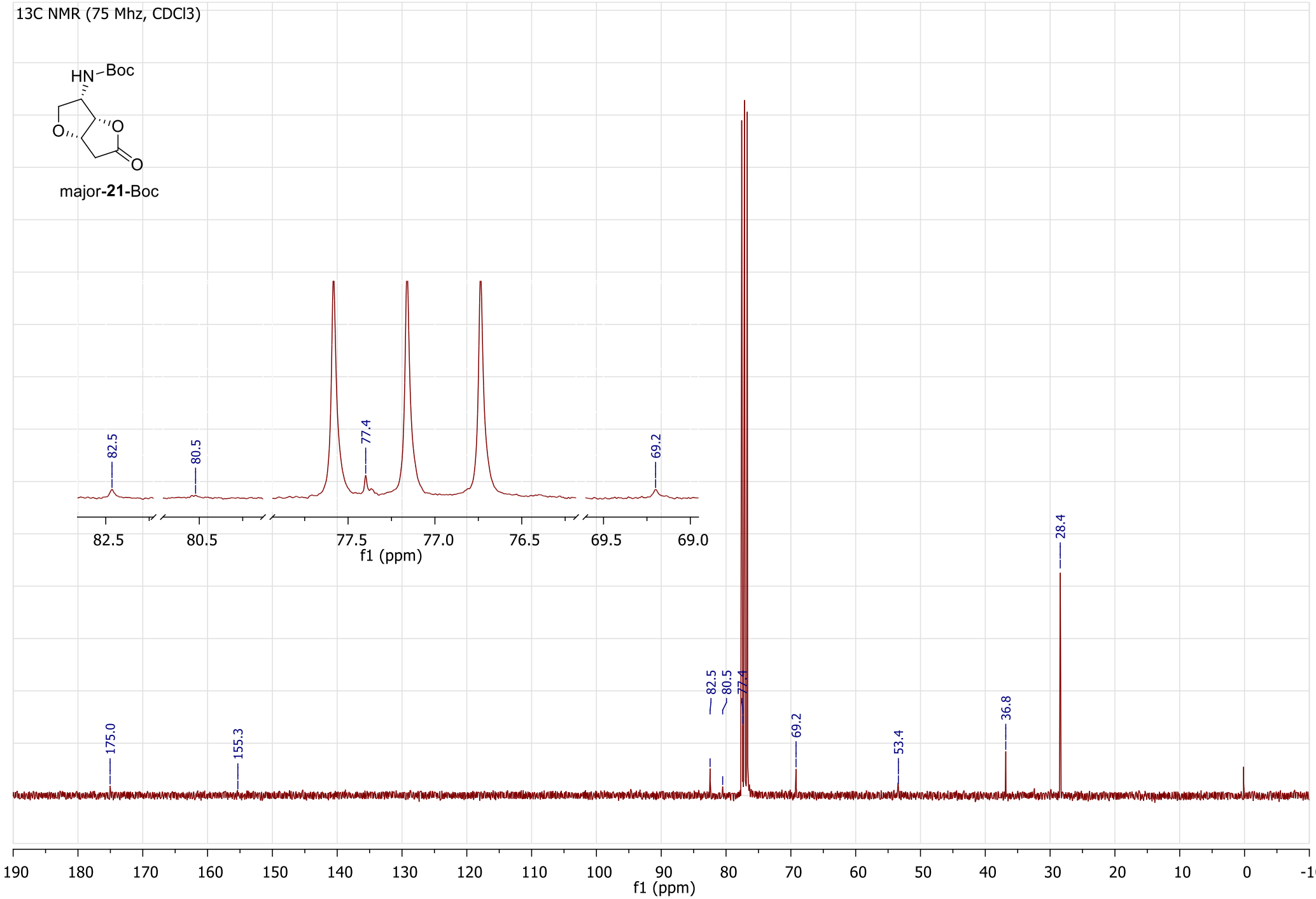


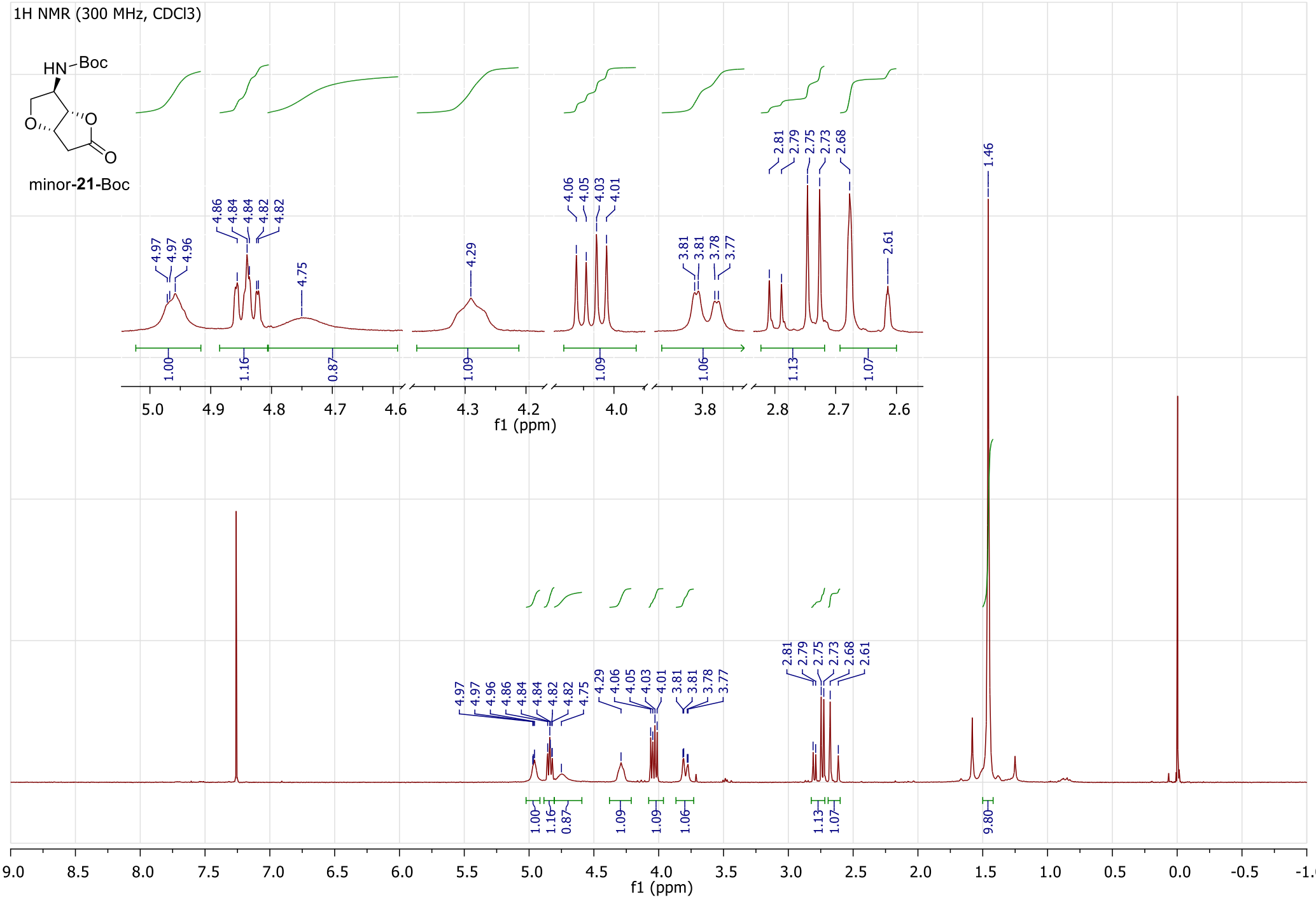
27-Boc

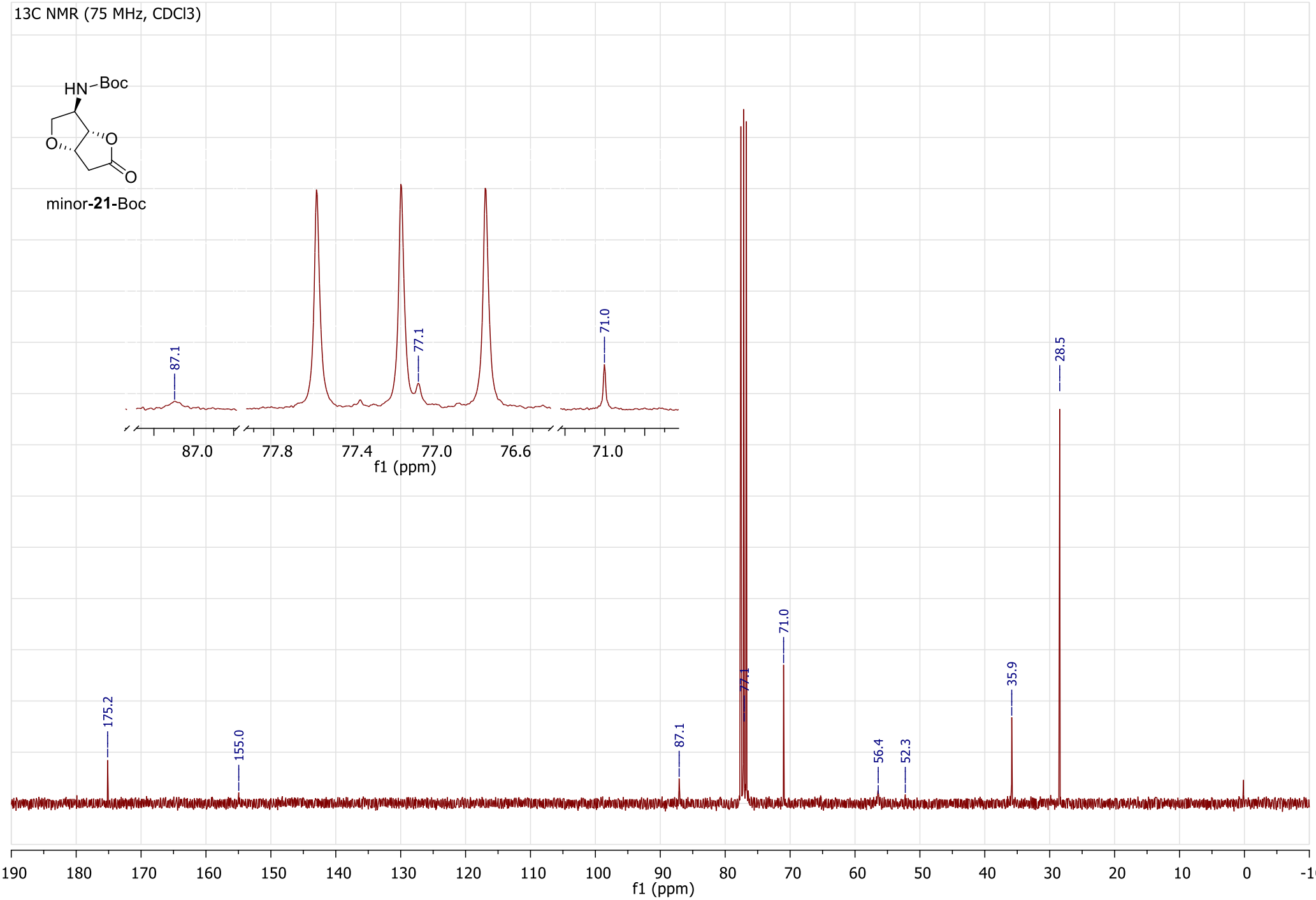

1H NMR (300 MHz, CDCl3)
OH
HO
HN
Boc
22-Boc
f1 (ppm)

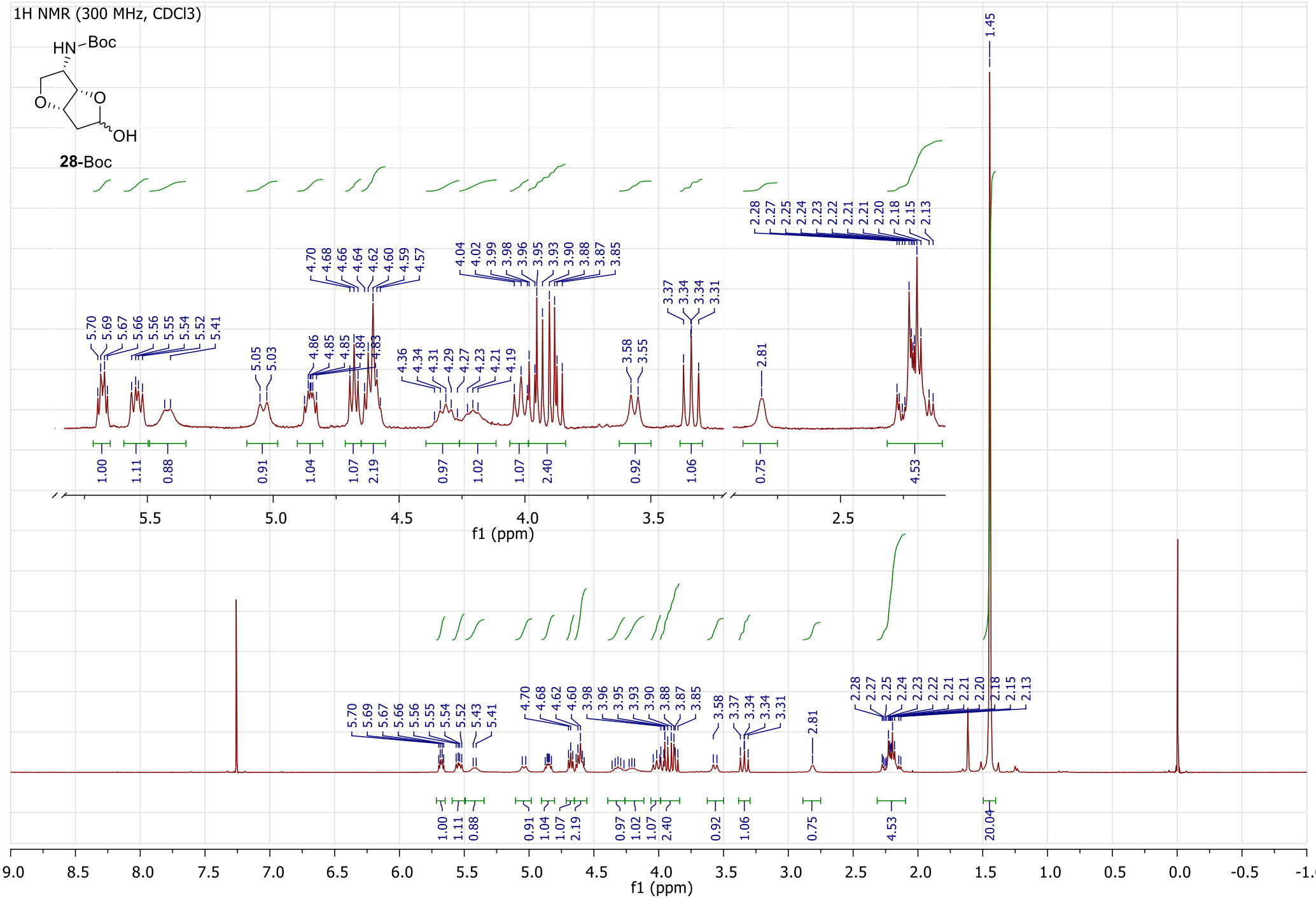

13C NMR (75 MHz, CDCl3)
OH
HO
HN
Boc
22-Boc
156.8
156.4
137.7
137.6
116.6
116.4
80.1
74.6
72.9
63.8
62.4
55.3
55.2
28.5
28.4
f1 (ppm)

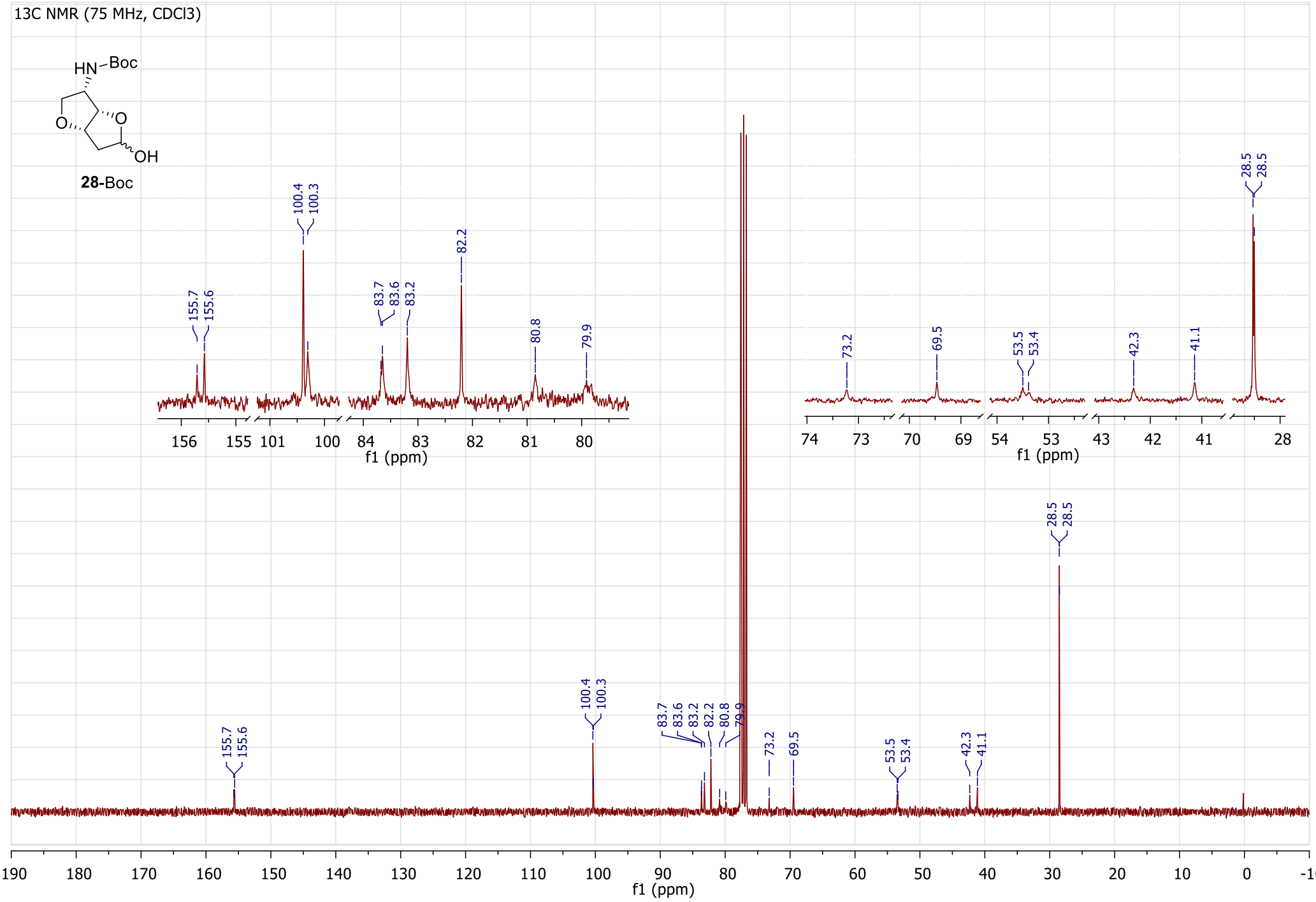

1H NMR (300 MHz, CDCl3)
HN–Boc
O
O
O
major-21-Boc
4.97 4.96 4.94 4.84 4.84 4.82 4.82 4.82 4.81 4.80 4.45 4.17 4.14 4.14 4.11 3.51 3.50 3.48 3.47 3.47 3.47 3.44 3.44 2.87 2.85 2.81 2.79 2.72 2.72 2.66 2.65
1.63 0.97 0.84 0.95 0.96 0.95 0.95
5.0 4.9 4.8 4.7 4.5 4.4 4.2 4.1 3.5 3.4 2.9 2.8 2.7 2.6
f1 (ppm)
1.45
8.82
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

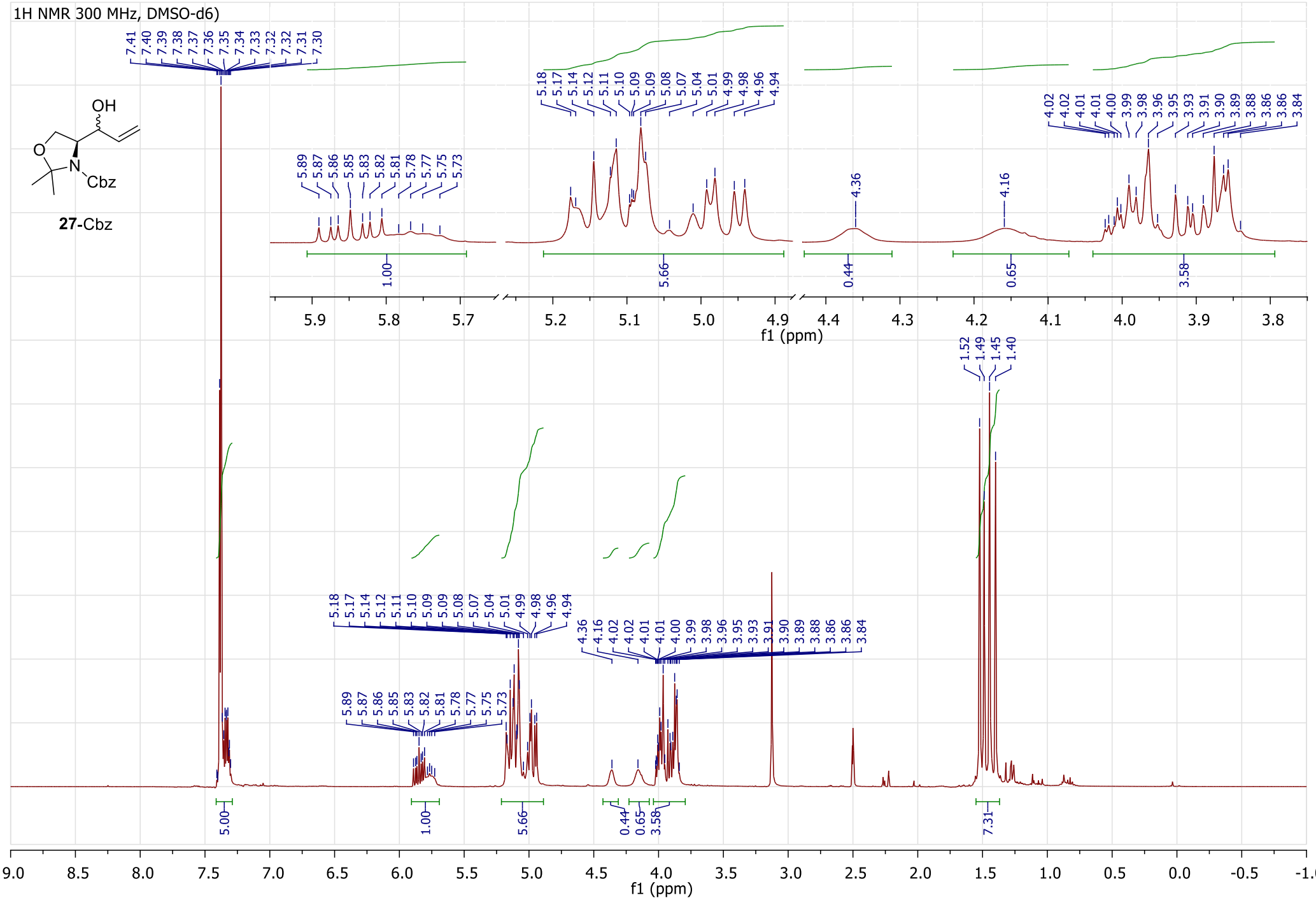

13C NMR (75 Mhz, CDCl3)
HN
Boc
O
O
O
major-21-Boc
82.5
80.5
77.4
69.2
82.5
80.5
77.5
77.0
76.5
69.5
69.0
f1 (ppm)
175.0
155.3
82.5
80.5
77.4
69.2
53.4
36.8
28.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

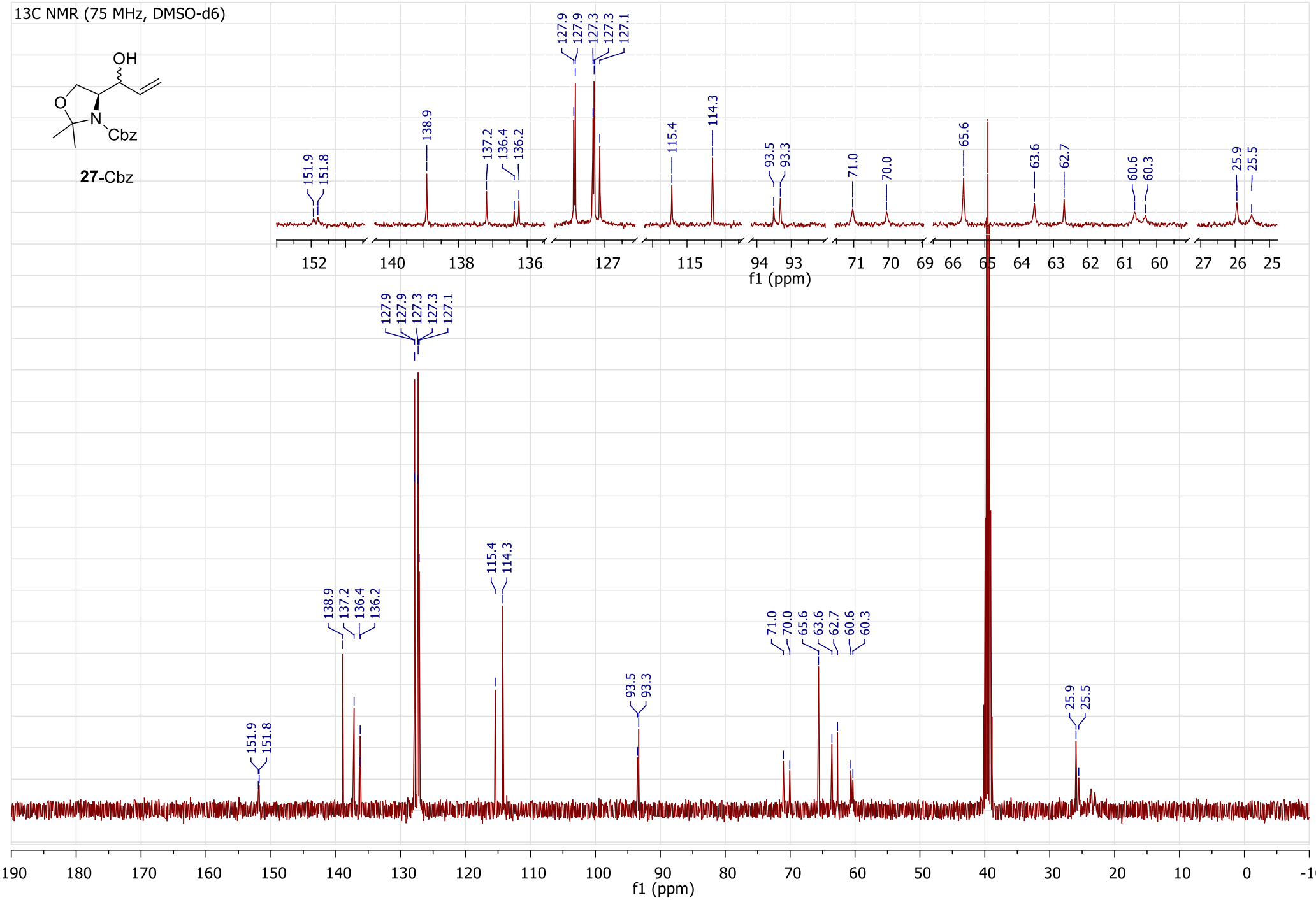

1H NMR (300 MHz, CDCl3)
HN–Boc
O
O
O
minor-21-Boc
4.97
4.97
4.96
4.86
4.84
4.84
4.82
4.82
4.75
4.29
4.06
4.05
4.03
4.01
3.81
3.81
3.78
3.77
2.81
2.79
2.75
2.73
2.68
2.61
1.46
1.00
1.16
0.87
1.09
1.09
1.06
1.13
1.07
9.80
f1 (ppm)

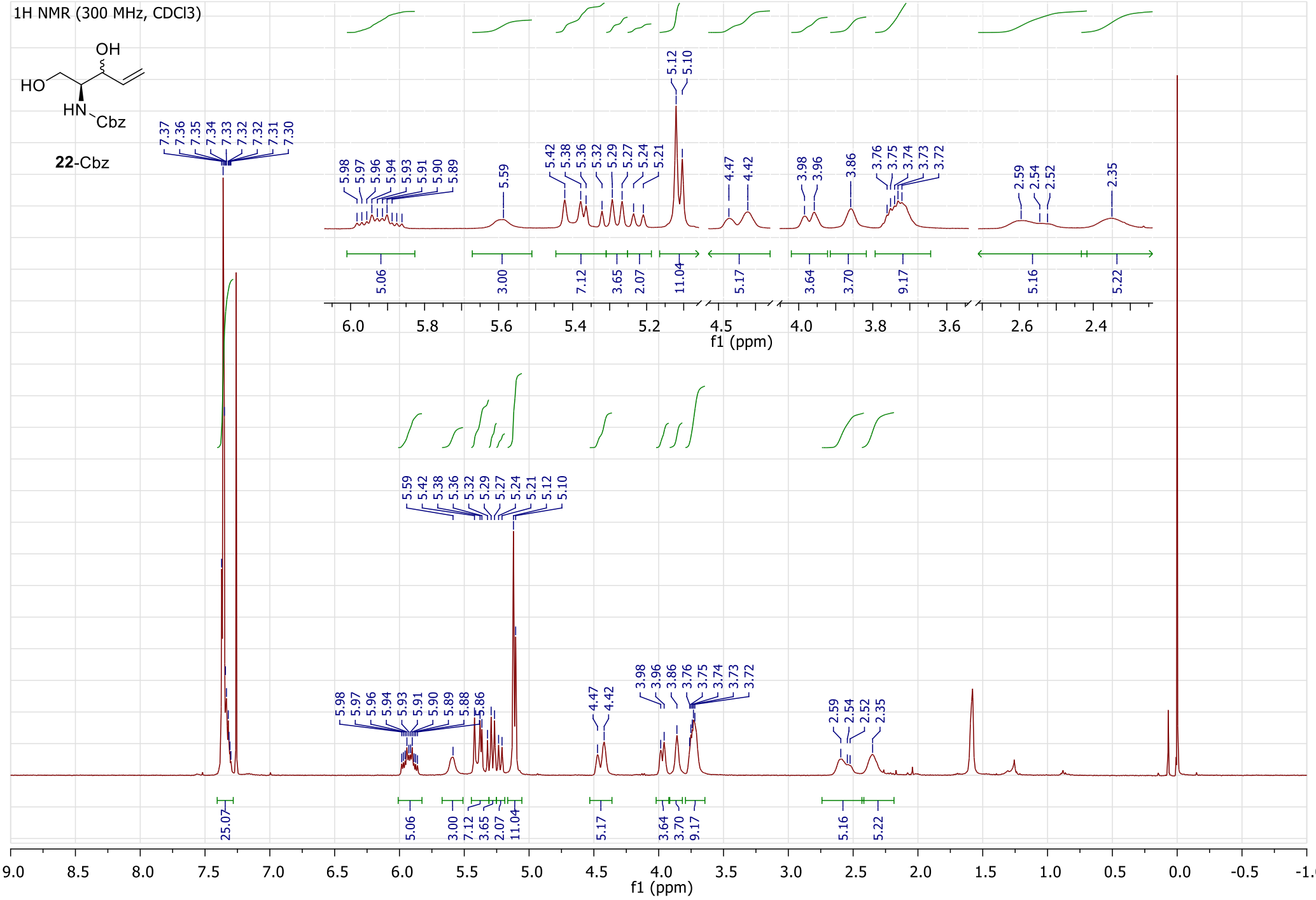

13C NMR (75 MHz, CDCl3)
HN–Boc
O
O
O
minor-21-Boc
87.1
77.1
71.0
87.0
77.8
77.4
77.0
76.6
71.0
f1 (ppm)
175.2
155.0
87.1
77.1
71.0
56.4
52.3
35.9
28.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

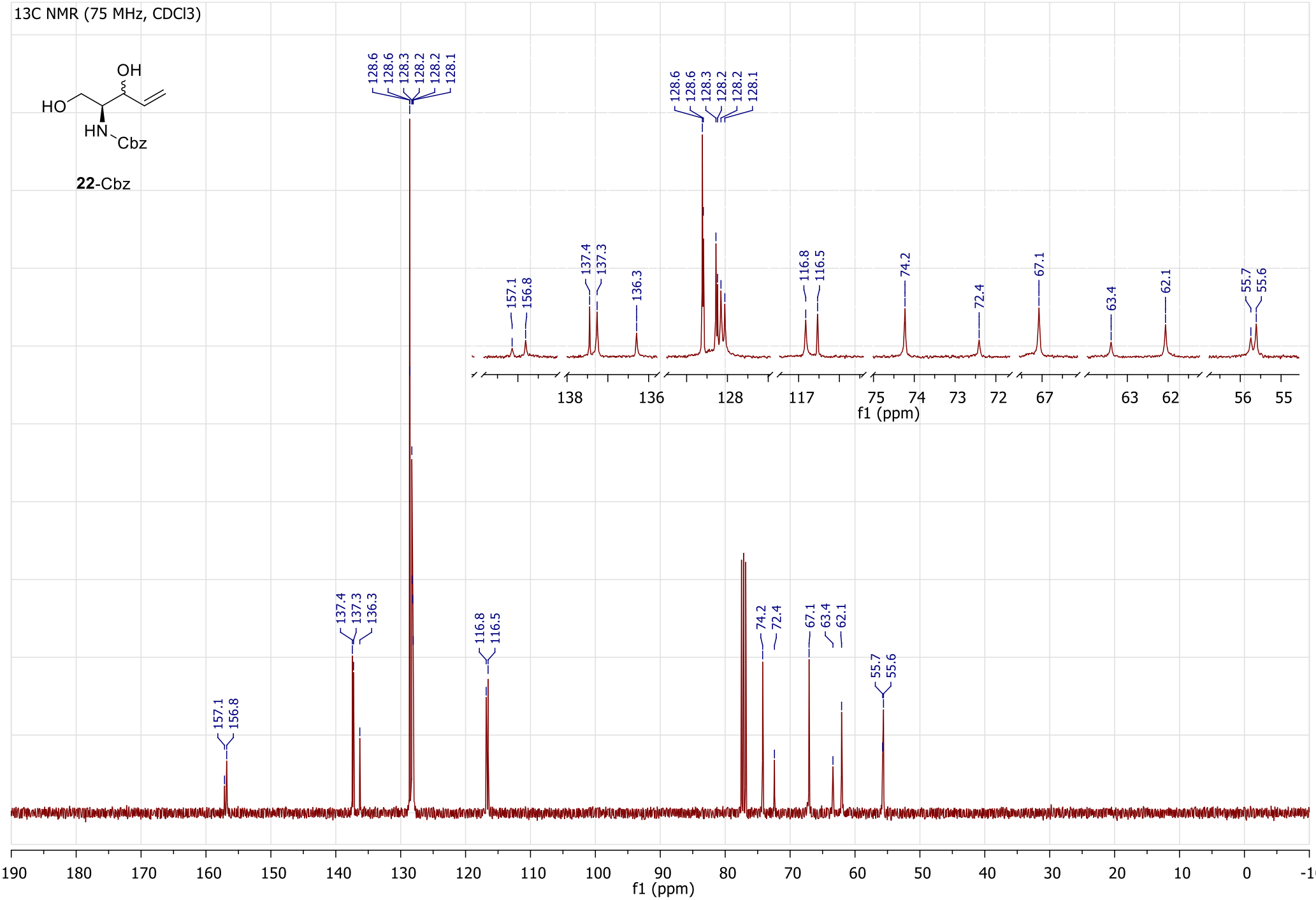

1H NMR (300 MHz, CDCl3)
HN–Boc
O
O
OH
28-Boc
f1 (ppm)
f1 (ppm)

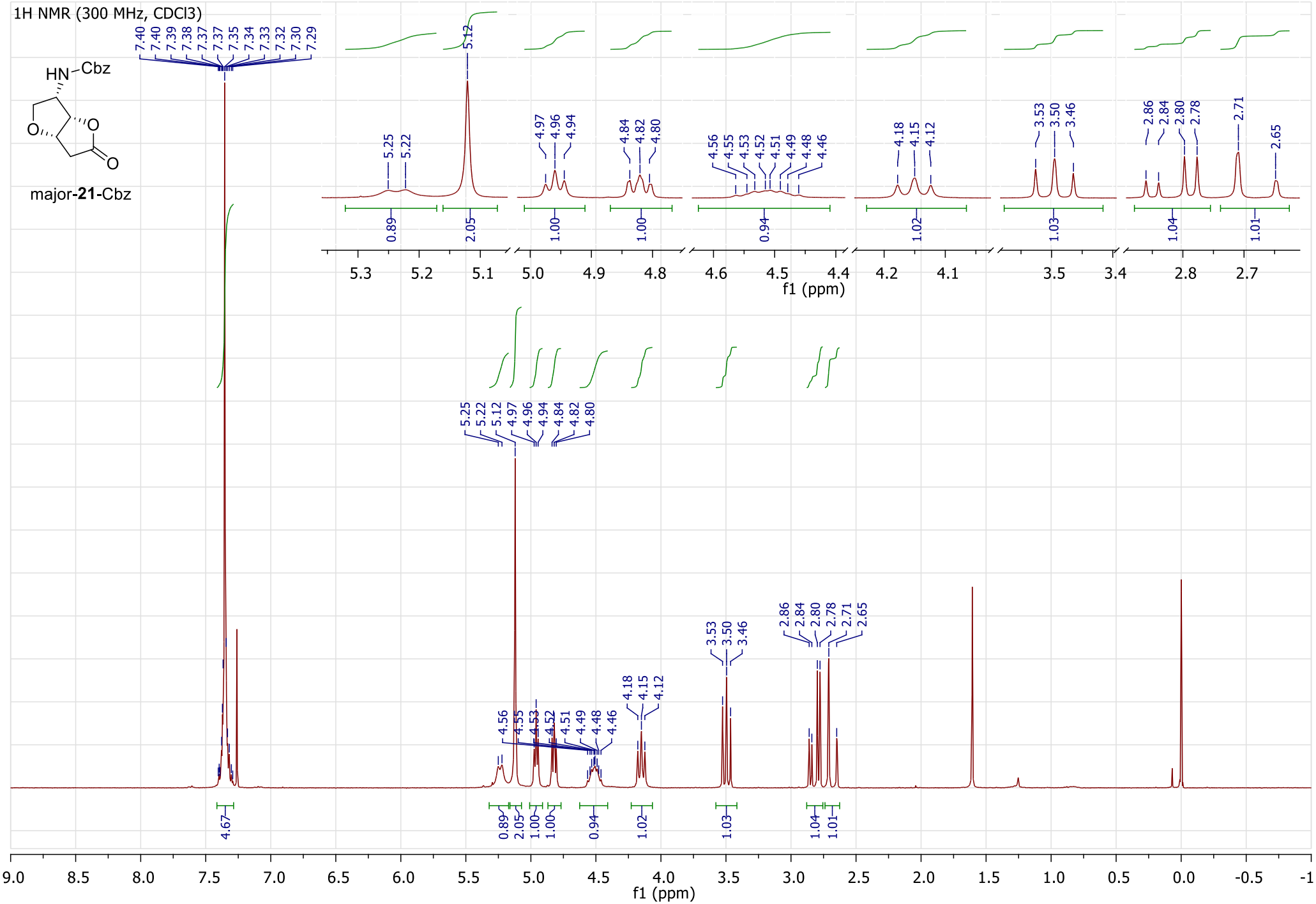

13C NMR (75 MHz, CDCl3)
HN–Boc
O
O
OH
28-Boc
155.7
155.6
100.4
100.3
83.7
83.6
83.2
82.2
80.8
79.9
73.2
69.5
53.5
53.4
42.3
41.1
28.5
28.5
f1 (ppm)

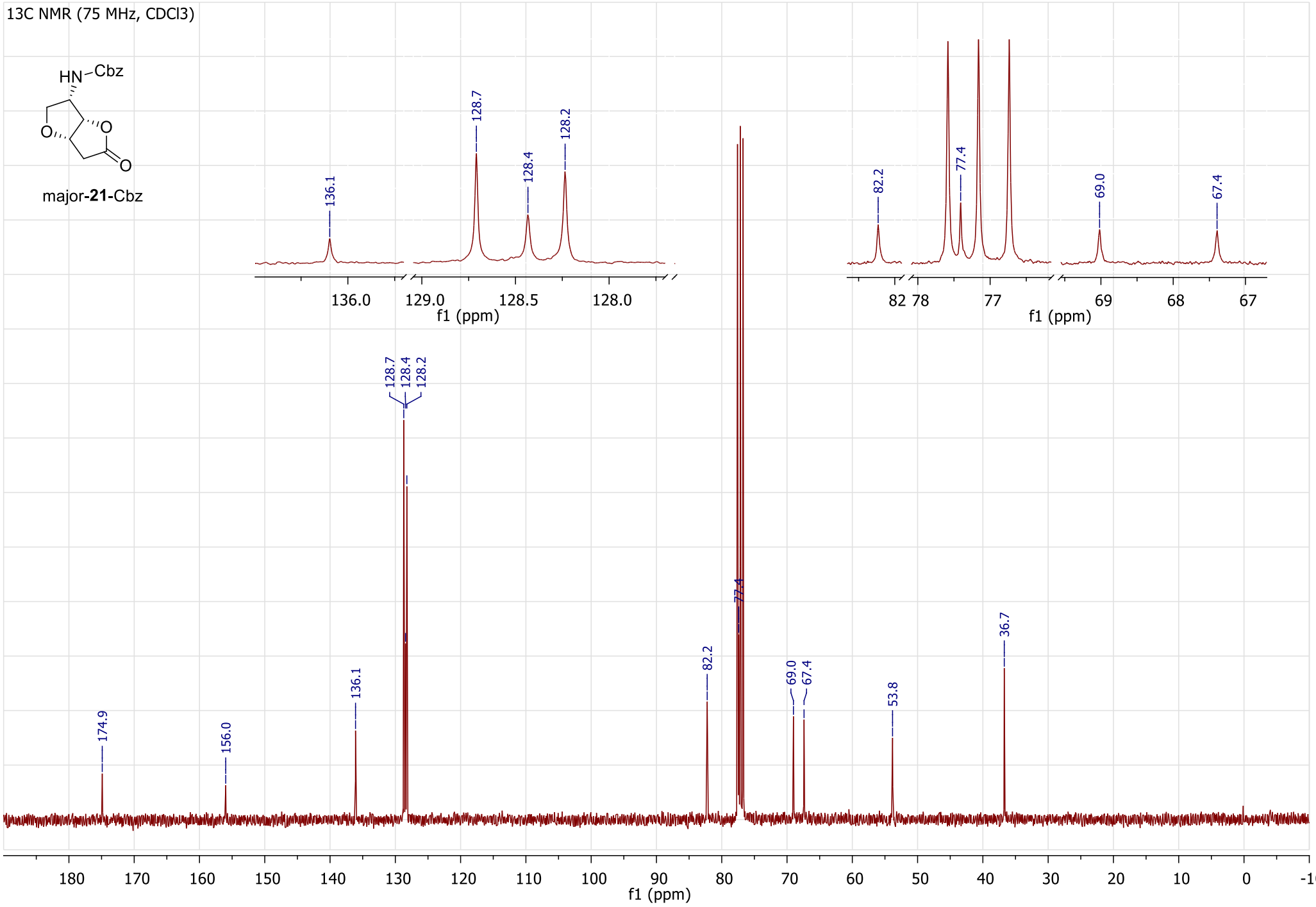

1H NMR 300 MHz, DMSO-d6)
OH
O
N
Cbz
27-Cbz
f1 (ppm)
f1 (ppm)

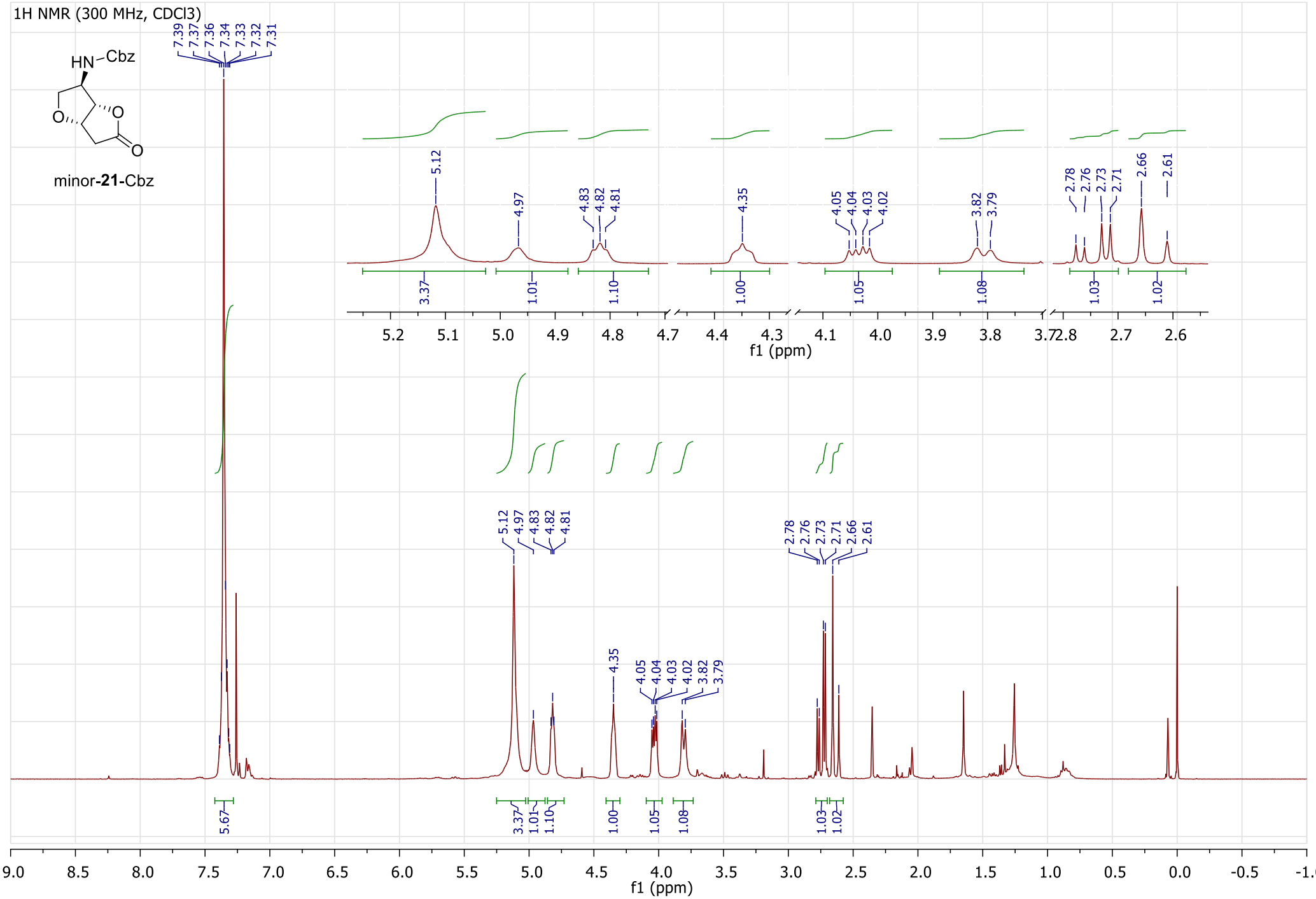

13C NMR (75 MHz, DMSO-d6)
OH
O
N
Cbz
27-Cbz
151.9
151.8
138.9
137.2
136.4
136.2
127.9
127.9
127.3
127.3
127.1
115.4
114.3
93.5
93.3
71.0
70.0
65.6
63.6
62.7
60.6
60.3
25.9
25.5
f1 (ppm)

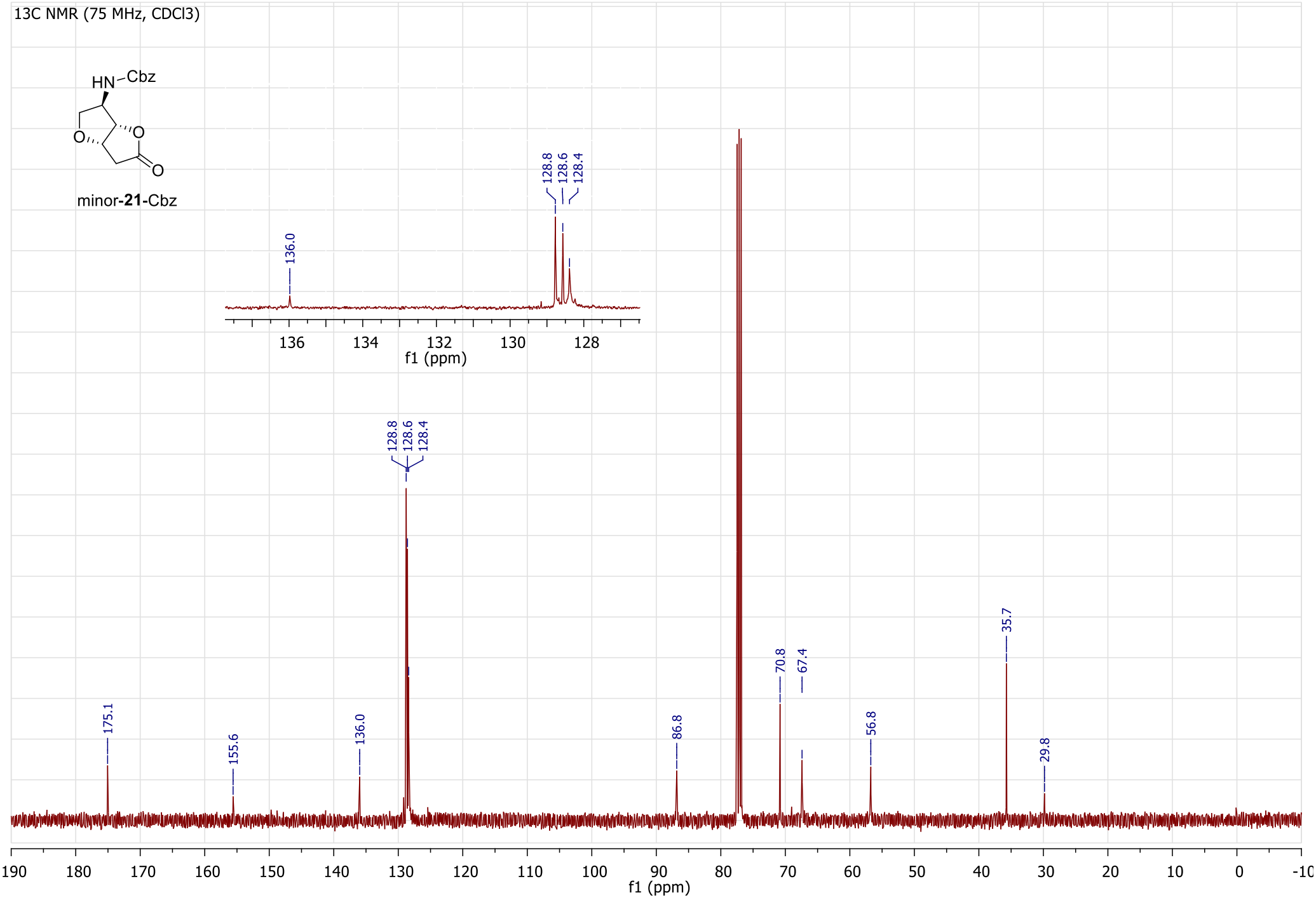

1H NMR (300 MHz, CDCl3)
OH
HO
HN
Cbz
22-Cbz
f1 (ppm)
f1 (ppm)

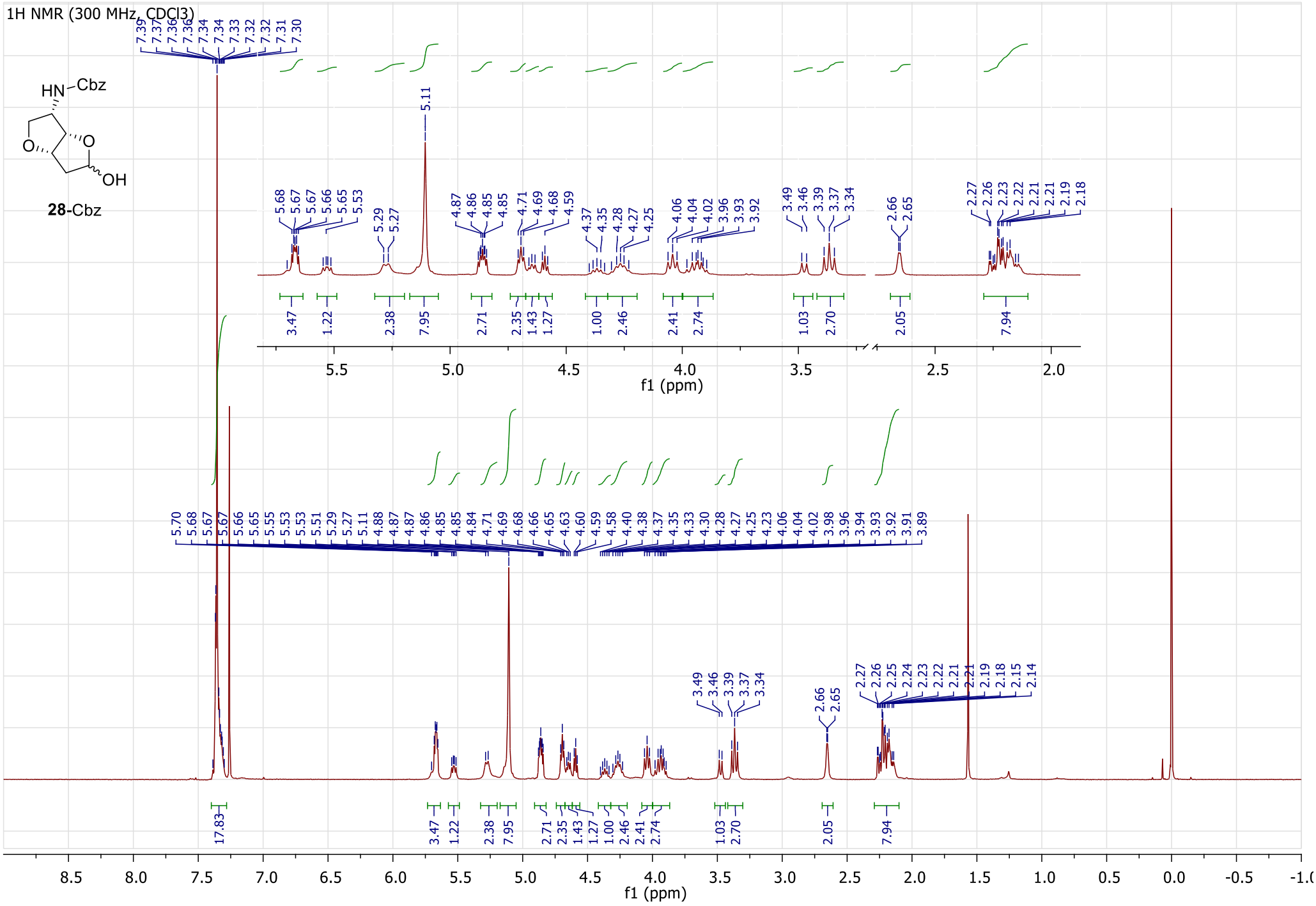

13C NMR (75 MHz, CDCl3)
OH
HO
HN
Cbz
22-Cbz
128.6
128.6
128.3
128.2
128.2
128.1
157.1
156.8
137.4
137.3
136.3
116.8
116.5
74.2
72.4
67.1
63.4
62.1
55.7
55.6
f1 (ppm)

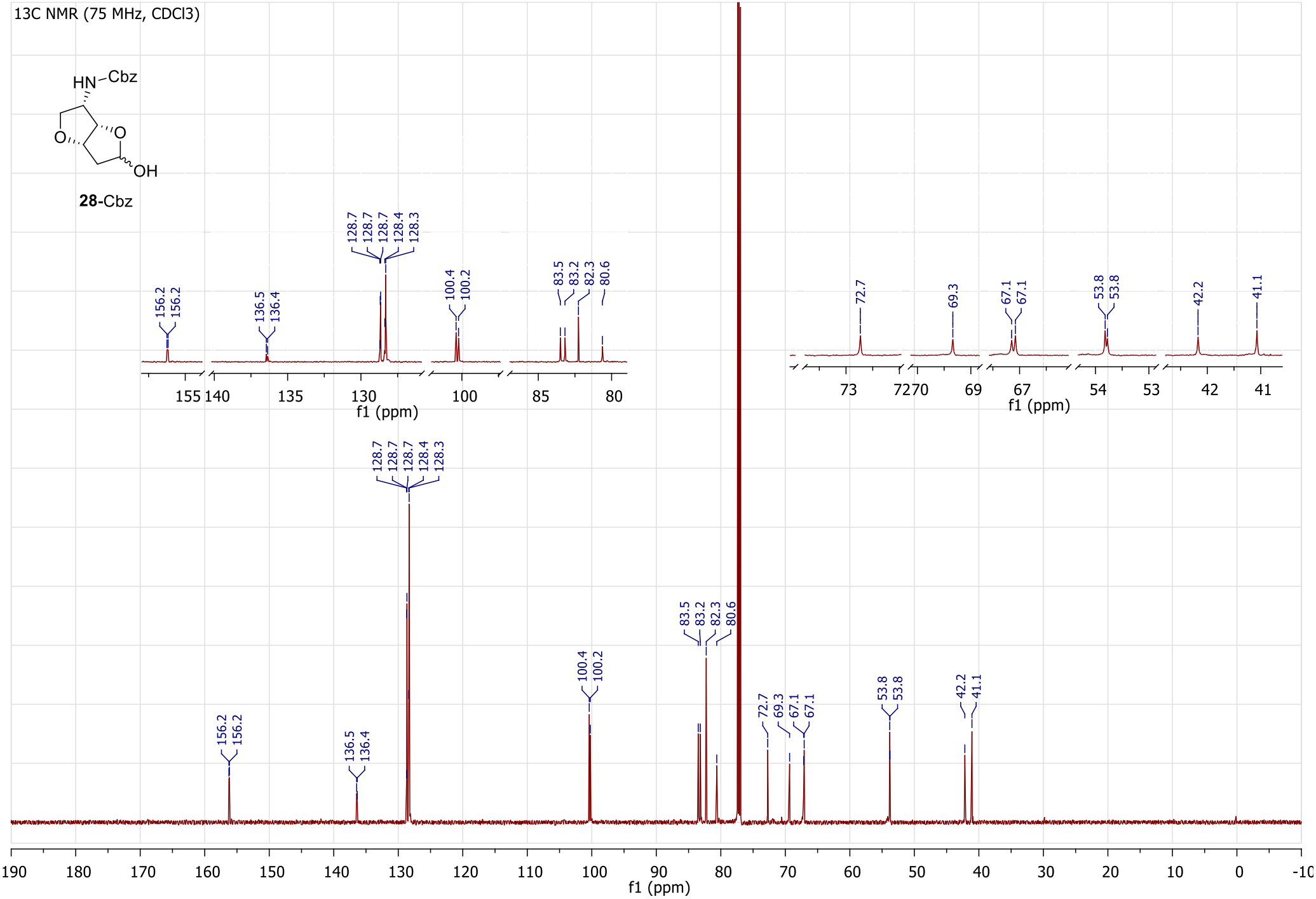

1H NMR (300 MHz, CDCl3)
HN–Cbz
O
O
O
major-21-Cbz
7.40 7.40 7.39 7.38 7.37 7.37 7.35 7.34 7.33 7.32 7.30 7.29
5.25 5.22 5.12 4.97 4.96 4.94 4.84 4.82 4.80 4.56 4.55 4.53 4.52 4.51 4.49 4.48 4.46 4.18 4.15 4.12 3.53 3.50 3.46 2.86 2.84 2.80 2.78 2.71 2.65
4.67 0.89 2.05 1.00 1.00 0.94 1.02 1.03 1.04 1.01
f1 (ppm)

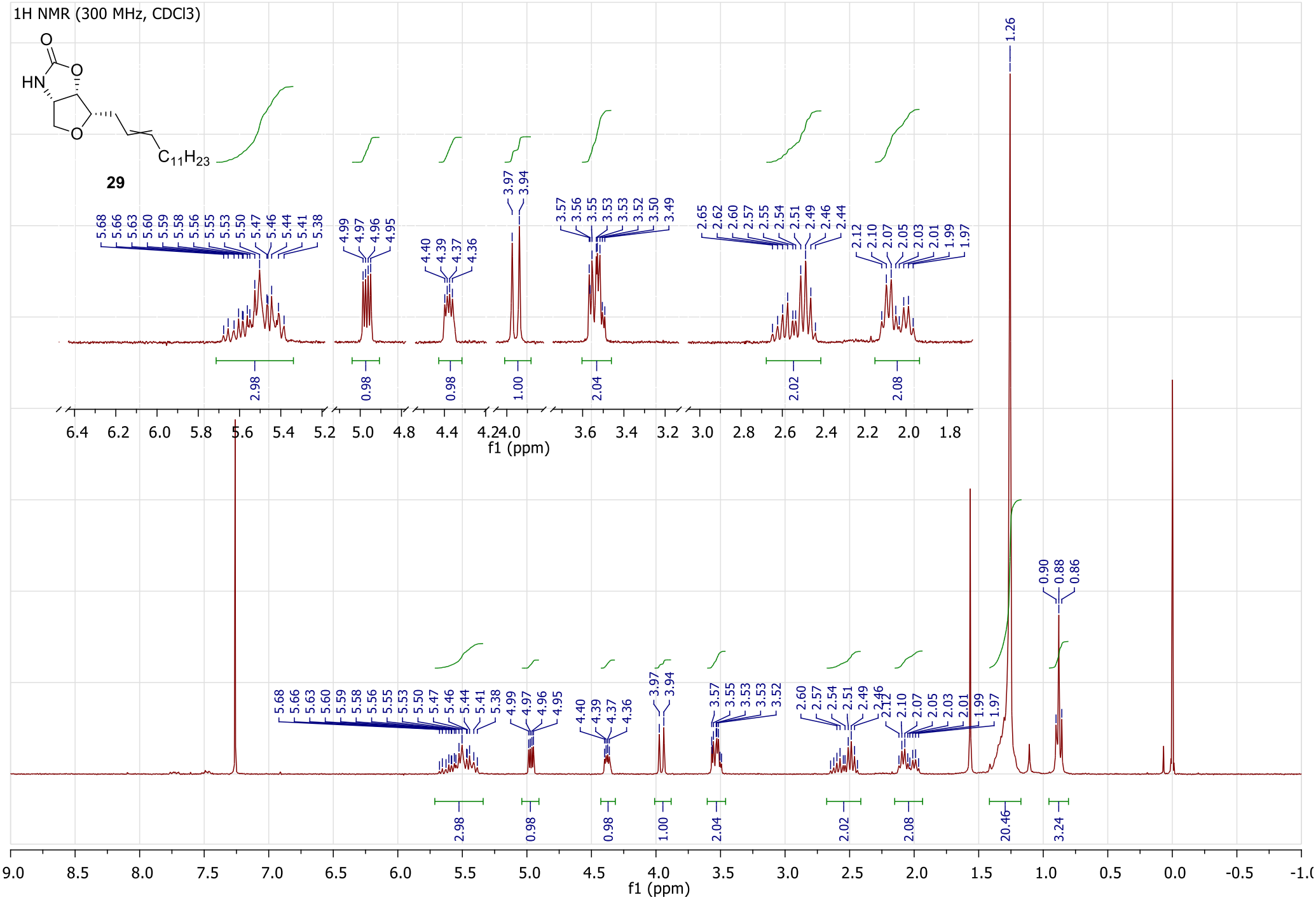

13C NMR (75 MHz, CDCl3)
HN–Cbz
O
O
O
major-21-Cbz
136.1
128.7
128.4
128.2
136.0
129.0
128.5
128.0
f1 (ppm)
82.2
77.4
69.0
67.4
82
78
77
69
68
67
f1 (ppm)
174.9
156.0
136.1
128.7
128.4
128.2
82.2
77.4
69.0
67.4
53.8
36.7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

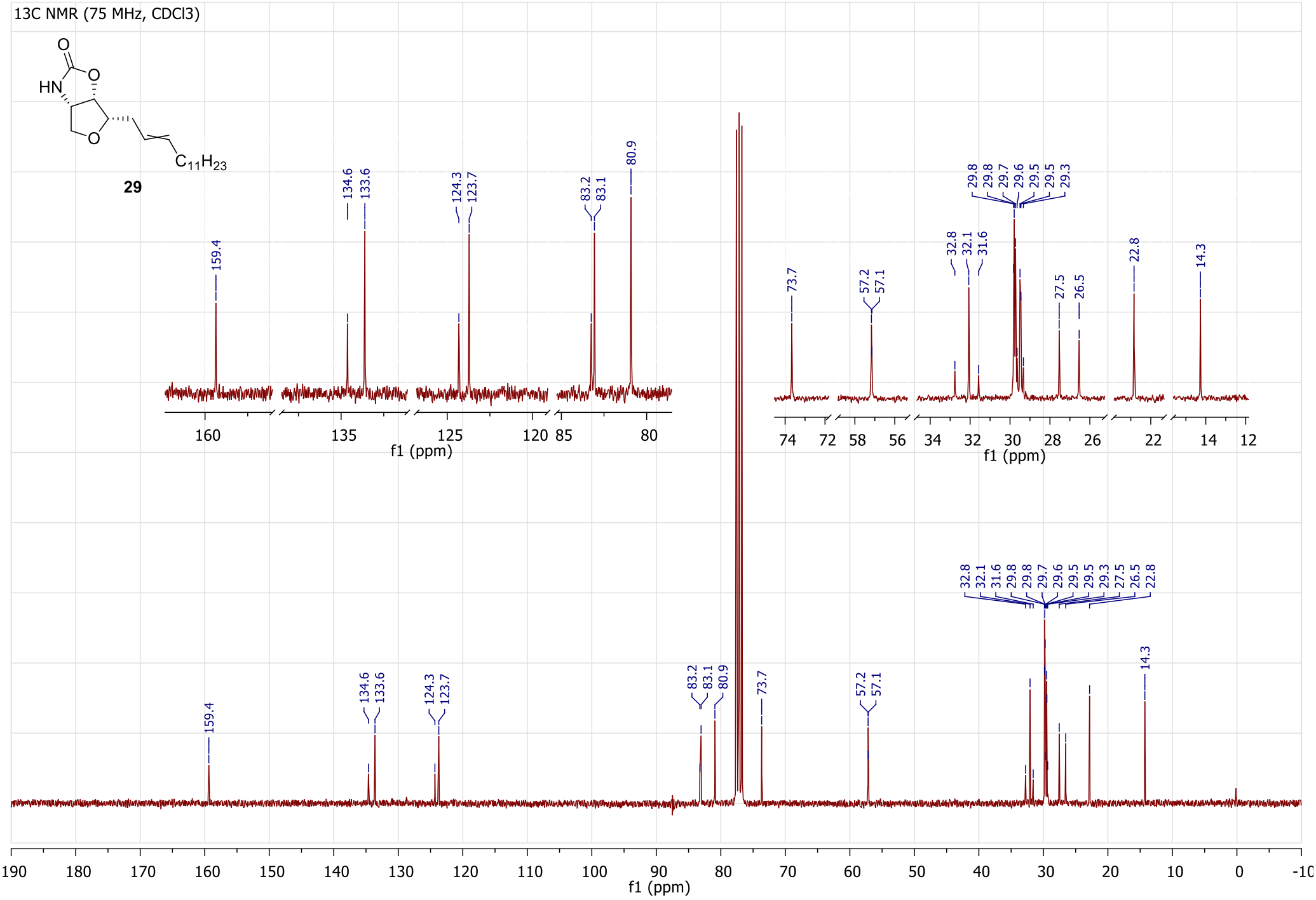

1H NMR (300 MHz, CDCl3)
HN–Cbz
O
O
O
minor-21-Cbz
7.39
7.37
7.36
7.34
7.33
7.32
7.31
5.12
4.97
4.83
4.82
4.81
4.35
4.05
4.04
4.03
4.02
3.82
3.79
2.78
2.76
2.73
2.71
2.66
2.61
3.37
1.01
1.10
1.00
1.05
1.08
1.03
1.02
5.67
f1 (ppm)

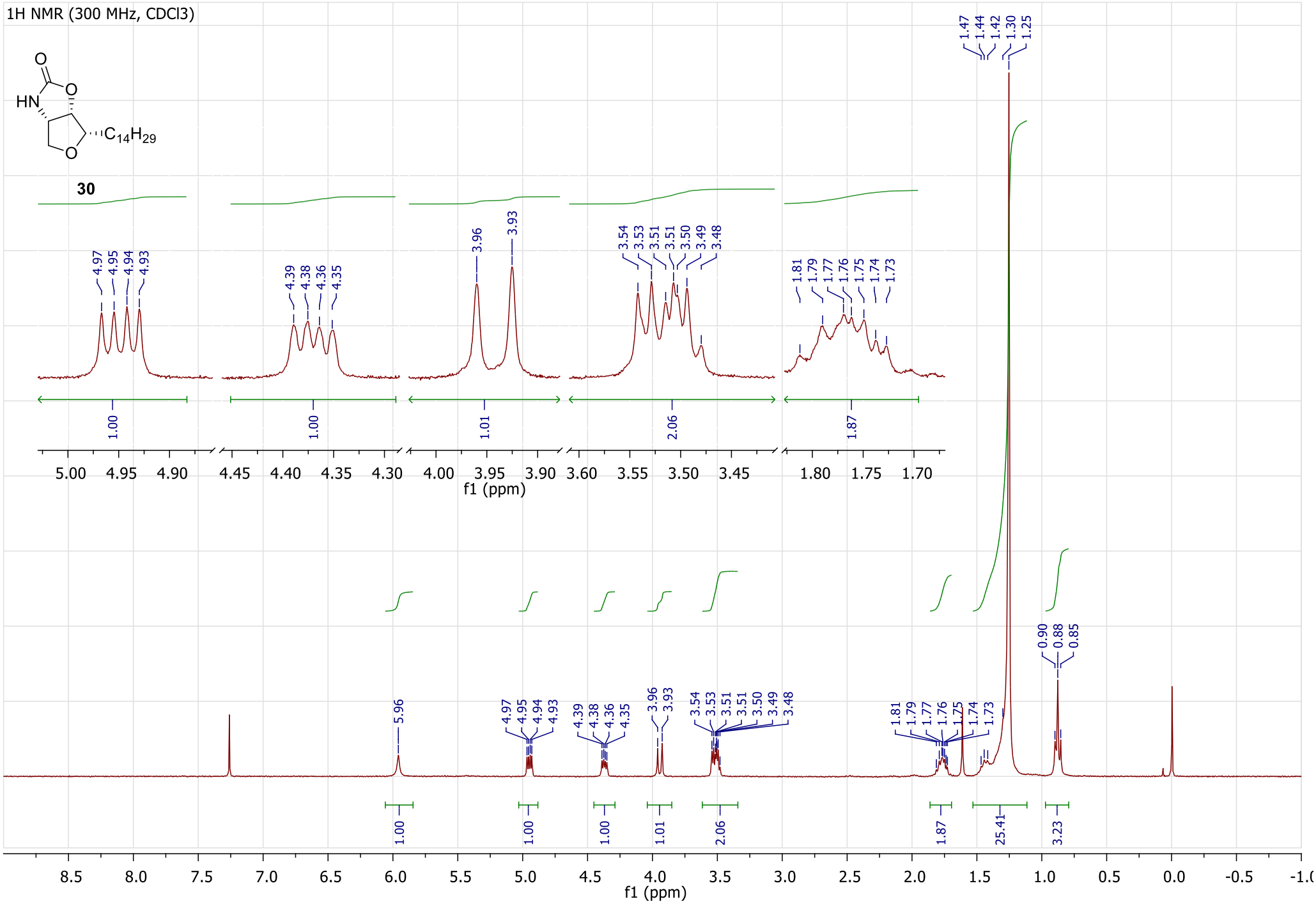

13C NMR (75 MHz, CDCl3)
HN–Cbz
O
O
O
minor-21-Cbz
128.8
128.6
128.4
136.0
136
134
132
130
128
f1 (ppm)
128.8
128.6
128.4
175.1
155.6
136.0
86.8
70.8
67.4
56.8
35.7
29.8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

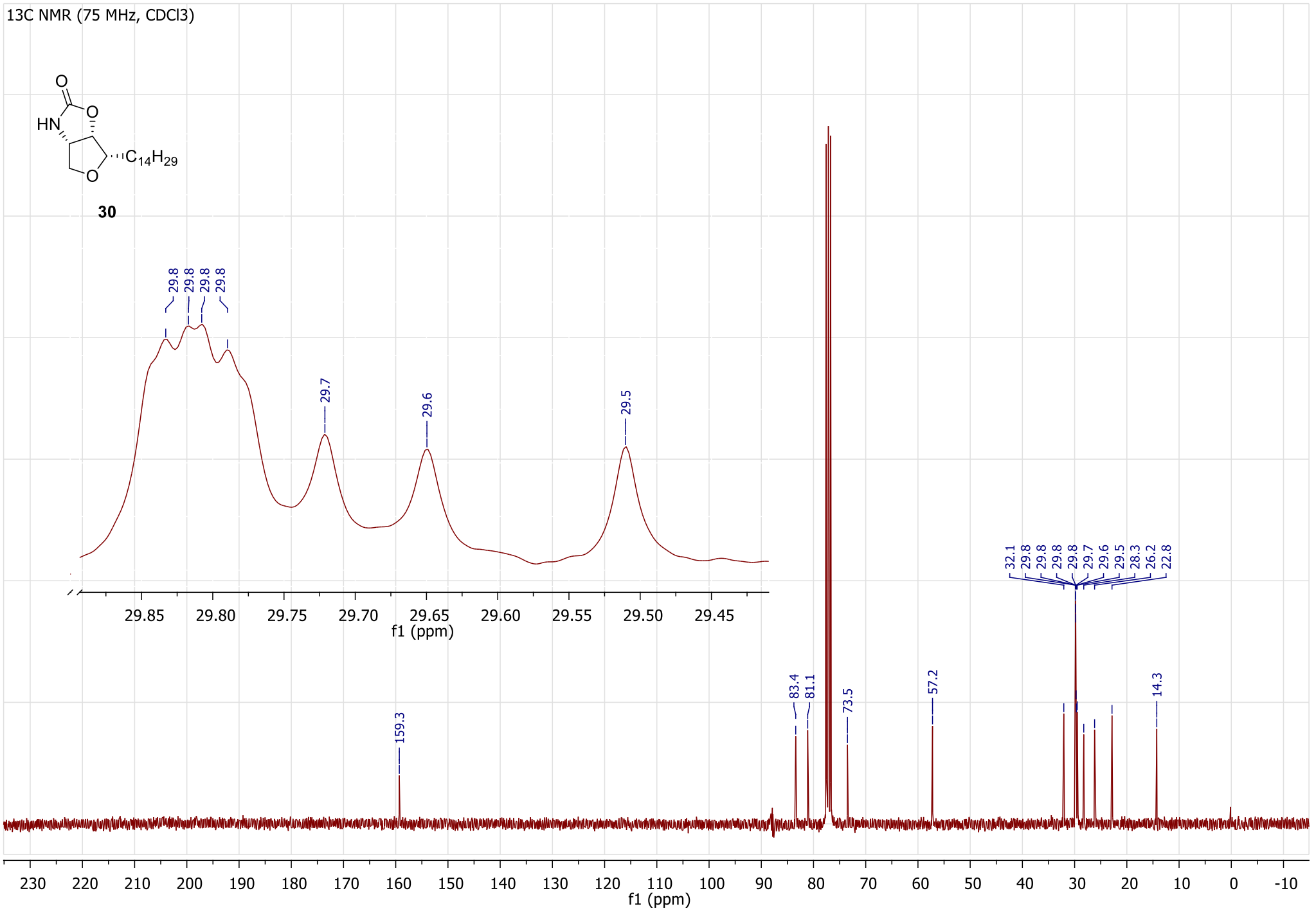

1H NMR (300 MHz, CDCl3)
HN
Cbz
O
O
OH
28-Cbz
f1 (ppm)
f1 (ppm)

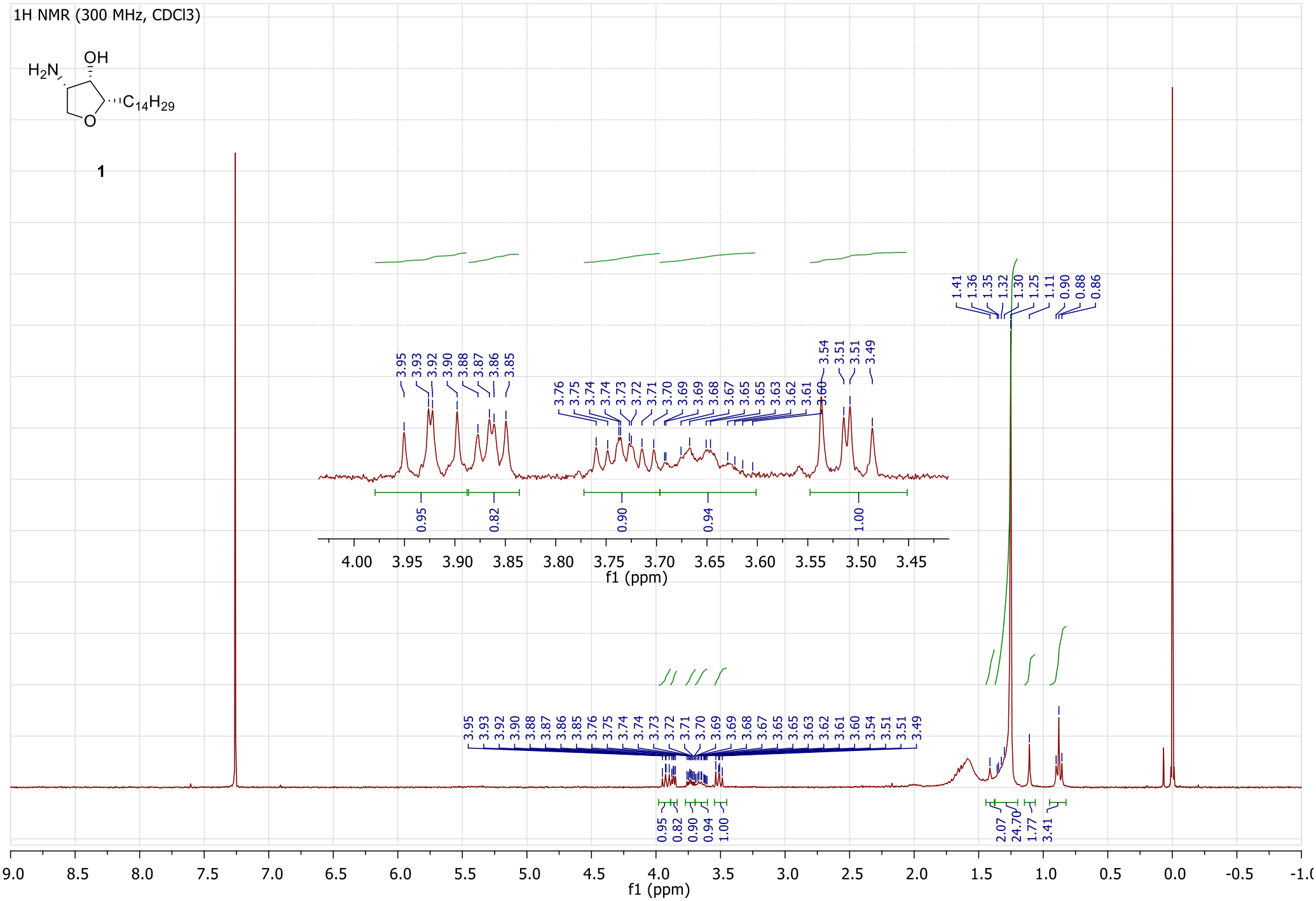

13C NMR (75 MHz, CDCl3)
HN–Cbz
O
O
OH
28-Cbz
156.2
156.2
136.5
136.4
128.7
128.7
128.7
128.4
128.3
100.4
100.2
83.5
83.2
82.3
80.6
72.7
69.3
67.1
67.1
53.8
53.8
42.2
41.1
f1 (ppm)

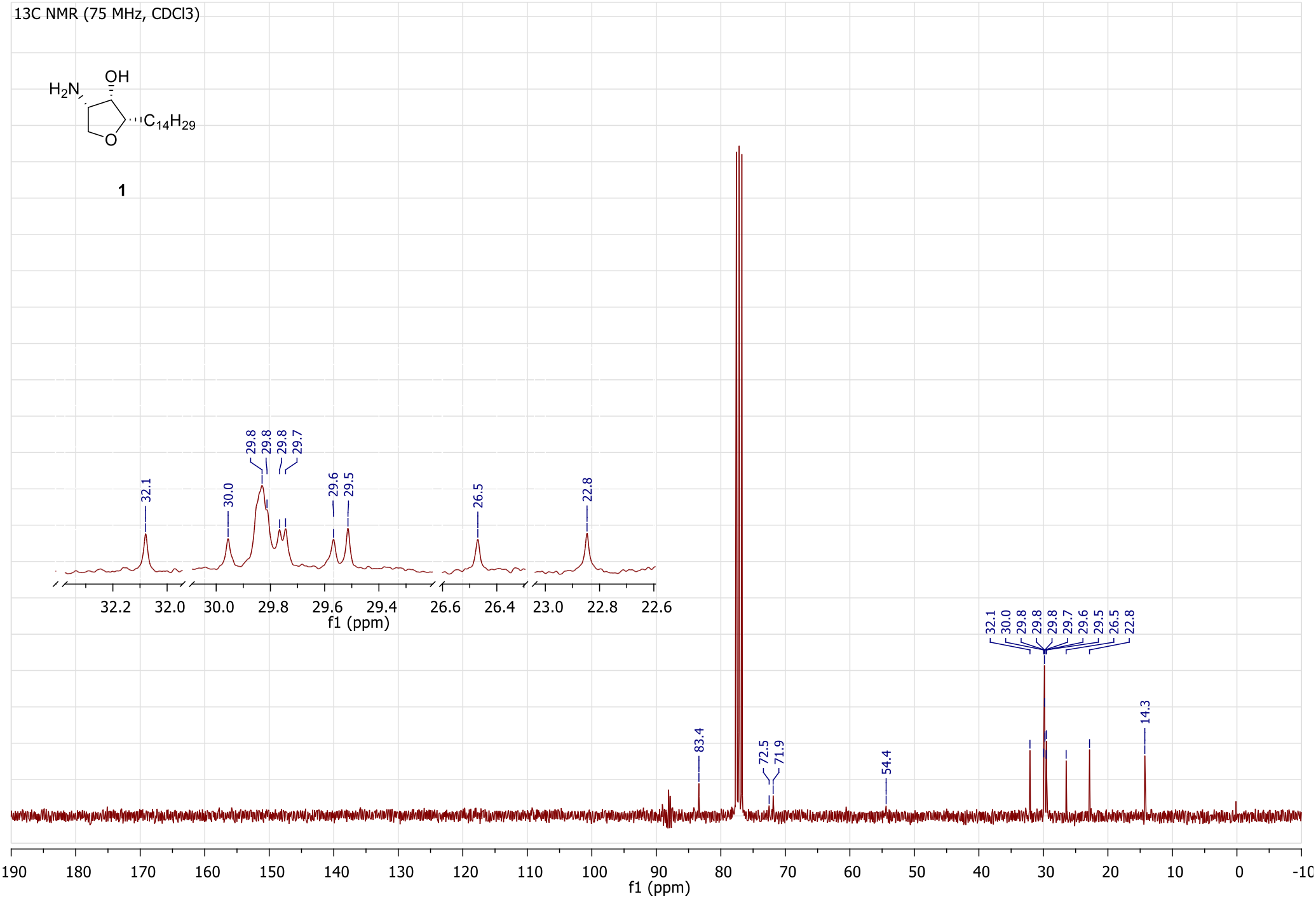

1H NMR (300 MHz, CDCl3)
HN
O
O
O
O
$C_{11}H_{23}$
29
f1 (ppm)


13C NMR (75 MHz, CDCl3)
O
HN
O
O
$C_{11}H_{23}$
29
159.4
134.6
133.6
124.3
123.7
83.2
83.1
80.9
73.7
57.2
57.1
32.8
32.1
31.6
29.8
29.8
29.7
29.6
29.5
29.5
29.3
27.5
26.5
22.8
14.3
f1 (ppm)


1H NMR (300 MHz, CDCl3)
HN
O
O
O
$C_{14}H_{29}$
30
4.97
4.95
4.94
4.93
4.39
4.38
4.36
4.35
3.96
3.93
3.54
3.53
3.51
3.51
3.50
3.49
3.48
1.81
1.79
1.77
1.76
1.75
1.74
1.73
1.00
1.00
1.01
2.06
1.87
f1 (ppm)
1.47
1.44
1.42
1.30
1.25
0.90
0.88
0.85
5.96
1.00
1.00
1.00
1.01
2.06
1.87
25.41
3.23
f1 (ppm)


13C NMR (75 MHz, CDCl3)
O
HN
O
O
C14H29
30
29.8
29.8
29.8
29.8
29.7
29.6
29.5
29.85
29.80
29.75
29.70
29.65
29.60
29.55
29.50
29.45
f1 (ppm)
32.1
29.8
29.8
29.8
29.8
29.7
29.6
29.5
28.3
26.2
22.8
159.3
83.4
81.1
73.5
57.2
14.3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


1H NMR (300 MHz, CDCl3)
OH
H2N
C14H29
O
1
f1 (ppm)


13C NMR (75 MHz, CDCl3)
OH
H2N
C14H29
O
1
32.1
30.0
29.8
29.8
29.8
29.7
29.6
29.5
26.5
22.8
f1 (ppm)
83.4
72.5
71.9
54.4
14.3
f1 (ppm)