Electronic Supplementary Material (ESI) for ChemComm.

Pd-Catalyzed Direct Functionalization of Glycals with Cycloalkenones: Application to the Synthesis of Chiral Phenanthrenones

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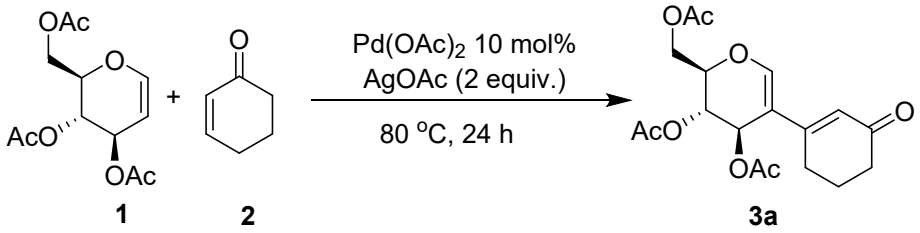
General Consideration

^{1}H and ^{13}C NMR spectra were recorded using 400 to 600 MHz spectrometers with TMS as internal standards. Chemical shifts are expressed in parts per million (δ ppm). Silica gel-coated aluminum plates were used for TLC. The products were purified by column chromatography on silica gel (100-200 mesh) using petroleum ether–ethyl acetate as the eluent to obtain the pure products. All products' exact masses were derived using HRMS having a QTOF analyzer. Reagents used were mostly purchased from Sigma Aldrich.

Variations in the ratio of DMF: DMSO



1 **2** **3a**

Entry	DMF: DMSO ratio	Yield (%)
01	**20:1**	**73**
02	20:0.1	15
03	20:0.3	27
04	20:0.5	51
05	20:0.8	69
06	20:1	73
07	20:1.5	63
08	20:2	47

Experimental procedures for all products

1. **General procedure for the products (3a-3l).**

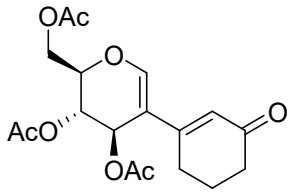
In an oven-dried round bottom flask glycal (0.36 mmol, 1 equiv), $Pd(OAc)_2$ (0.036 mmol, 0.1equiv), and AgOAc (0.73 mmol, 2 equiv.) were dissolved in 2 mL of DMF: DMSO (20:1) at

rt. Finally, the cycloalkenone (0.55 mmol, 1.5 equiv.) was added in an open-air atmosphere and the reaction flask was fitted with a reflux condenser and stirred at 80 ^{o}C in a preheated oil bath for 24 h. Then the reaction mixture was cooled at rt, diluted with ethyl acetate (10 ml), and passed through a small bed of celite. The filtrate was washed with 20 mL of ethyl acetate and brine solution. The organic layer was dried over sodium sulfate; the residue left was purified by column chromatography over silica gel (100-200 mesh) using hexane/ethyl acetate as eluent.

2. General procedure for the products (5a-5e).

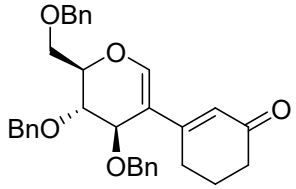
In an oven-dried round bottom flask substrate **5a-5e** (0.098 mmol, 1 equiv) was dissolved in dry acetonitrile under an Ar atmosphere. In the same flask, CsF (0.294 mmol, 3 equiv.) and 2(Trimethylsilyl)phenyl trifluoromethanesulfonate (0.147mmol, 1.5 equiv.) were added and the reaction mixture was stirred at 40 ^{o}C for 24 h. After the completion of the reaction monitored through TLC (thin layer chromatography), the reaction mixture was diluted with ethyl acetate (10 ml) and washed with brine solution. The organic layer was dried over sodium sulfate; the residue left was purified by column chromatography over silica gel (100-200 mesh) using pet ether/ethyl acetate as eluent.

Characterization data



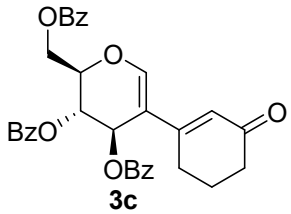
3a

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 6:4) giving colorless oil 99 mg, 74%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 5.72 (s, 1H), 5.52 (d, J = 2.6 Hz, 1H), 5.15 (t, J = 2.6 Hz, 1H), 4.52 – 4.42 (m, 2H), 4.11 (dd, J = 11.0, 3.8 Hz, 1H), 2.49 – 2.33 (m, 4H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 – 2.00 (m, 5H). ^{13}C NMR (126 MHz,) δ 199.2, 170.5, 169.7, 169.4, 154.2, 148.4, 121.8, 110.4, 73.8, 66.2, 62.8, 61.1, 37.4, 25.5, 22.3, 20.9, 20.8, 20.7. HRMS calcd for $C_{18}H_{23}O_8$ $[M + H]^+$367.1393; found 367.1400.



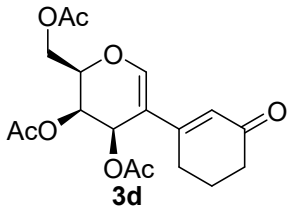
3b

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 94 mg, 77 %.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 13H), 7.16 – 7.12 (m, 2H), 7.09 (s, 1H), 5.94 (s, 1H), 4.67 (d, J = 12.4 Hz, 1H), 4.59 (d, J = 12.0 Hz, 2H), 4.50 – 4.38 (m, 4H), 4.16 (s, 1H), 3.98 (s, 1H), 3.77 – 3.72 (m, 1H), 3.58 (dd, J = 10.1, 5.2 Hz, 1H), 2.41 (m, 4H), 2.04 – 1.97 (m, 2H).^{13}C NMR (126 MHz,) δ 199.7, 156.3, 148.1, 137.8, 137.4, 137.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 121.3, 111.9, 75.8, 73.4, 71.7, 71.4, 69.7, 69.6, 68.2, 37.4, 25.3, 22.4. HRMS calcd for $C_{33}H_{35}O_5$ $[M +H]^+$ 511.2484; found 511.2480.



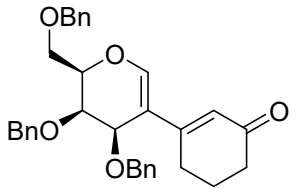
3c

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 6:4) giving colorless oil 43 mg, 71 %.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.9 Hz, 2H), 7.95 (d, J = 7.6 Hz, 2H), 7.88 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.3 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.36 (m, 4H), 7.28 (s, 1H), 5.98 (s, 1H), 5.93 (s, 1H), 5.69 (s, 1H), 4.97 – 4.89 (m, 2H), 4.45 (q, J = 10.0 Hz, 1H), 2.54 (d, J = 5.3 Hz, 2H), 2.42 – 2.36 (m, 2H), 2.10 – 2.01 (m, 2H).^{13}C NMR (126 MHz,) δ 199.2, 166.0, 165.2, 164.9, 154.5, 148.5, 133.8, 133.7, 133.4, 130.0, 129.9, 129.7, 129.2, 129.1, 128.7, 128.6, 128.5, 122.0, 110.3, 73.7, 66.6, 62.8, 61.7, 37.4, 25.6, 22.4. HRMS calcd for $C_{33}H_{28}O_8$ $[M + H]^+$ 553.1862; found553.1863.



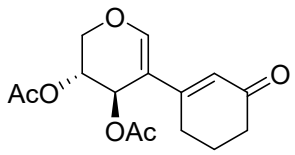
3d

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 6:4) giving colorless oil 50.5 mg,75%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 5.72 (s, 1H), 5.52 (d, *J* = 2.6 Hz, 1H), 5.15 (t, *J* = 2.6 Hz, 1H), 4.52 – 4.42 (m, 2H), 4.11 (dd, *J* = 11.0, 3.8 Hz, 1H), 2.46 – 2.34 (m, 4H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 – 2.00 (m, 5H). ^{13}C NMR (126 MHz,) δ 199.1, 170.7, 170.1, 169.5, 153.8, 148.1, 122.1, 111.7, 77.4, 73.2, 65.1, 61.6, 61.6, 37.3, 25.8, 22.3, 20.8, 20.6. HRMS calcd for $C_{18}H_{23}O_8$ $[M + H]^+$ 367.1393; found 367.1390.



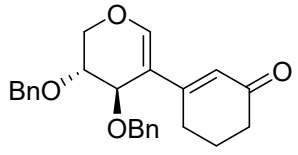
3e

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 46.5 mg,76%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 15H), 6.90 (s, 1H), 5.99 (s, 1H), 5.00 (d, J = 10.4 Hz, 1H), 4.71 (q, J = 12.0 Hz, 2H), 4.65 – 4.57 (m, 3H), 4.42 (dd, J = 22.3, 7.1 Hz, 2H), 4.02 – 3.92 (m, 3H), 2.39 (t, J = 5.7 Hz, 4H), 1.99 (dt, J = 12.6, 6.4 Hz, 2H). ^{13}C NMR (126 MHz,) δ 199.5, 155.8, 147.6, 138.1, 138.0, 137.5, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 121.4, 113.8, 76.2, 75.1, 74.7, 73.5, 72.4, 68.9, 68.3, 37.4, 25.8, 22.5. HRMS calcd for $C_{33}H_{35}O_5$ $[M + H]^+$ 511.2484; found 511.2484.



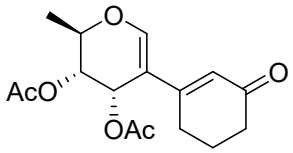
3f

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 6:4) giving colorless oil 108 mg,73 %.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 1H), 5.81 (s, 1H), 5.46 (s, 1H), 4.96 (s, 1H), 4.34 (d, *J* = 12.4 Hz, 1H), 4.00 (d, *J* = 12.5 Hz, 1H), 2.52 – 2.41 (m, 2H), 2.41 – 2.33 (m, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 – 2.01 (m, 2H).^{13}C NMR (126 MHz,) δ 199.5, 169.7, 169.5, 155.2, 150.9, 121.0, 110.0, 65.7, 63.8, 61.6, 37.4, 25.3, 22.3, 21.0, 21.0. HRMS calcd for $C_{15}H_{19}O_6$ $[M + H]^+$ 295.1182; found 295.1187.



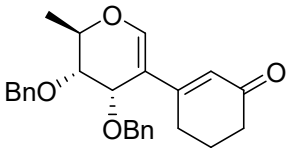
3g

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 88 mg, 67 %.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.5 Hz, 3H), 7.23 – 7.14 (m, 7H), 7.08 (s, 1H), 5.91 (s, 1H), 4.58 (d, *J* = 12.3 Hz, 1H), 4.50 (m, 2H), 4.41 (d, *J* = 10.7 Hz, 1H), 4.21 (dd, *J* = 12.0, 1.2 Hz, 1H), 4.04 (s, 1H), 3.98 (m, 1H), 3.68 (s, 1H), 2.36 (m, 2H), 2.32 (m, 2H), 1.94 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 156.9, 150.1, 128.7, 128.6, 128.2, 128.1, 128.0, 127.9, 127.9, 120.7, 112.1, 77.3, 77.1, 76.9, 71.6, 71.2, 69.4, 68.3, 63.7, 37.3, 25.3, 22.4. HRMS calcd for $C_{25}H_{27}O_4$ $[M + H]^+$ 391.1909; found 391.1909.



3h

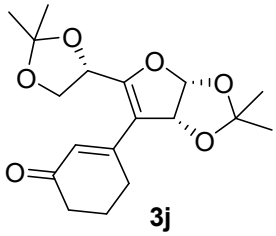
The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 6:4) giving colorless oil 76 mg, 53%.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 1H), 5.67 (s, 1H), 5.48 (s, 1H), 4.96 (s, 1H), 4.35 (d, *J* = 4.7 Hz, 1H), 2.46 – 2.37 (m, 2H), 2.33 (m, 2H), 2.00 (m, 8H), 1.33 (d, *J* = 6.8 Hz, 3H)^{13}C NMR (151 MHz, $CDCl_3$) δ 198.3, 168.9, 168.6, 153.9, 148.0, 120.2, 108.5, 71.5, 69.0, 62.7, 36.3, 28.7, 21.3, 19.9, 19.8, 15.1. HRMS calcd for $C_{16}H_{21}O_6$ $[M + H]^+$ 309.1338; found 309.1316.



3i

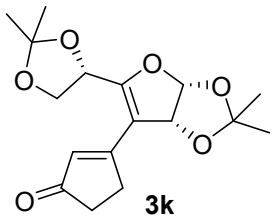
The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 66 mg, 51%.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.17 (m, 10H) 7.00 (s, 1H), 5.90 (s, 1H), 4.57 (d, *J* = 13.8 Hz, 3H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.38 (d, *J* = 11.0 Hz, 1H), 4.15 (s, 1H), 3.66 (s, 1H), 2.38 (m, 2H), 2.32 (m, 2H), 1.94 (m, 2H), 1.30 (d, *J* = 6.6 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 156.6, 148.1, 137.4, 137.3, 128.8, 128.6, 128.5, 128.5, 128.4, 128.4, 128.1, 128.1, 128.0, 127.9,

127.9, 127.8, 127.8, 121.0, 73.0, 73.0, 71.6, 71.1, 70.4, 37.3, 25.2, 22.3, 16.5. HRMS calcd for $C_{26}H_{29}O_4$ $[M + H]^+$ 405.2066; found 405.2042.



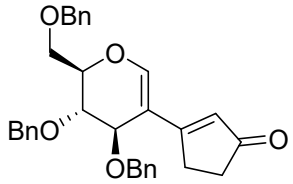
3j

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 94 mg, 68%.^{1}H NMR (500 MHz, $CDCl_3$) δ 6.10 (s, 1H), 6.06 (d, *J* = 5.3 Hz, 1H), 5.36 (d, *J* = 5.3 Hz, 1H), 4.94 (s, 1H), 4.11 (m, 2H), 2.41 (m, 2H), 2.09 – 2.02 (m, 4H), 1.45 (s, 3H), 1.43 (s, 6H), 1.38 (s, 3H). ^{13}C NMR (126 MHz,) 199.5, 168.0, 157.3, 153.0, 129.7, 116.5, 115.4, 110.9, 105.0, 84.2, 69.8, 66.4, 37.3, 28.6, 27.9, 27.9, 25.9, 25.8, 22.7. HRMS calcd for $C_{18}H_{25}O_6$ $[M + H]^+$ 337.1651; found 337.1654.



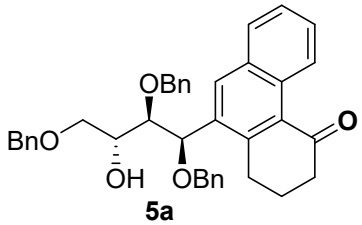
3k

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 81 mg, 61%.^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (s, 1H), 6.12 (d, *J* = 5.4 Hz, 1H), 5.40 (d, *J* = 5.4 Hz, 1H), 5.03 (t, *J* = 6.6 Hz, 1H), 4.16 (dd, *J* = 10.6, 4.2 Hz, 2H), 2.48 – 2.45 (m, 2H), 2.44 – 2.37 (m, 2H), 1.46 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H).^{13}C NMR (126 MHz,) δ 208.9, 166.1, 159.6, 128.5, 113.8, 113.6, 111.1, 105.6, 84.0, 69.7, 66.3, 34.8, 27.9, 27.8, 25.8, 25.8. HRMS calcd for $C_{17}H_{23}O_6$ $[M + H]^+$ 323.1495; found 323.1500.



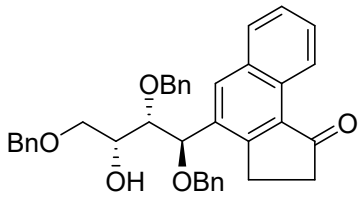
3l

The title compound was prepared according to the general procedure (1) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving colorless oil 31.5 mg, 53%.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 13H), 7.14 (dd, *J* = 7.2, 3.0 Hz, 3H), 5.87 (s, 1H), 4.67 – 4.57 (m, 4H), 4.44 – 4.40 (m, 3H), 4.09 (s, 1H), 3.99 (d, *J* = 2.2 Hz, 1H), 3.76 (dd, *J* = 10.1, 7.4 Hz, 1H), 3.61 (dd, *J* = 10.6, 5.3 Hz, 1H), 2.73 (dd, *J* = 10.7, 4.9 Hz, 2H), 2.44 – 2.41 (m, 2H).13C NMR (126 MHz,) δ 208.9, 172.1, 148.9, 137.7, 137.3, 137.0, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 124.4, 110.3, 76.3, 73.5, 71.9, 71.6, 70.4, 69.9, 68.0, 34.3, 29.7, 26.9.HRMS calcd for $C_{32}H_{33}O_5$ $[M+H]^+$497.2328; found 497.2328.



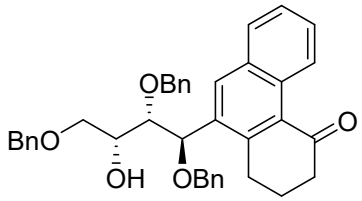
5a

The title compound was prepared according to the general procedure (2) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving white gummy solid 48 mg, 83%.^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, J = 8.9 Hz, 1H), 8.28 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.36 – 7.25 (m, 10H), 7.10 (t, J = 7.3 Hz, 1H), 7.03 (t, J = 7.4 Hz, 2H), 6.63 (d, J = 7.4 Hz, 2H), 5.12 (d, J = 8.8 Hz, 1H), 4.60 – 4.48 (m, 3H), 4.33 (d, J = 11.1 Hz, 2H), 4.14 (d, J = 10.5 Hz, 1H), 3.74 (d, J = 8.7 Hz, 1H), 3.67 – 3.56 (m, 3H), 2.82 (ddd, J = 17.1, 7.5, 4.6 Hz, 1H), 2.73 – 2.64 (m, 2H), 2.60 – 2.52 (m, 1H), 2.00 (ddd, J = 12.6, 8.3, 3.9 Hz, 1H), 1.85 (ddd, J = 12.9, 8.0, 4.0 Hz, 1H).^{13}C NMR (126 MHz) δ 201.1, 146.3, 137.9, 137.6, 136.9, 136.1, 132.5, 131.1, 128.9, 128.6, 128.5, 128.5, 128.4, 128.2, 128.2, 128.1, 128.1, 127.9, 127.9, 126.8, 126.1, 74.9, 73.7, 71.5, 71.1, 69.8, 40.6, 27.4, 22.3.HRMS calcd for $C_{39}H_{39}O_5$ $[M+H]^+$587.2797; found587.2774.



5b

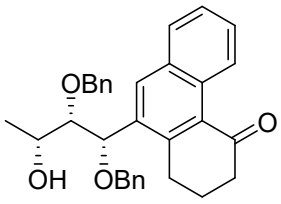
The title compound was prepared according to the general procedure (2) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving white gummy solid 44 mg, 77%.^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, J = 8.3 Hz, 1H), 8.21 (s, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.32 – 7.27 (m, 10H), 7.06 (t, J = 7.4 Hz, 1H), 6.92 (t, J = 7.5 Hz, 2H), 6.73 (d, J = 7.4 Hz, 2H), 5.02 (d, J = 2.2 Hz, 1H), 4.64 (d, J = 11.6 Hz, 2H), 4.49 (d, J = 2.6 Hz, 2H), 4.30 (dd, J = 11.4, 4.5 Hz, 2H), 3.95 (d, J = 11.4 Hz, 1H), 3.65 (ddd, J = 13.9, 9.3, 3.5 Hz, 4H), 2.97 (dt, J = 10.5, 5.1 Hz, 1H), 2.87 – 2.80 (m, 1H), 2.62 (s, 2H).13C NMR (126 MHz,) δ 207.5, 156.7, 148.8, 137.7, 137.3, 137.3, 136.9, 134.7, 133.4, 132.8, 131.4, 128.9, 128.6, 128.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 126.8, 123.9, 79.8, 74.3, 73.6, 71.4, 71.1, 70.2, 36.8, 24.7.HRMS calcd for $C_{38}H_{37}O_5$ $[M+H]^+$573.2641; found 573.2642.



5c

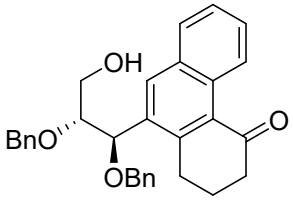
The title compound was prepared according to the general procedure (2) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving white gummy solid 45 mg, 79%.^{1}H NMR (600 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.7 Hz, 1H), 8.24 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.17 (m, 10H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.84 (t, *J* = 7.3 Hz, 2H), 6.63 (d, *J* = 7.4 Hz, 2H), 5.06 (s, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.50 – 4.39 (m, 2H), 4.21 (d, *J* = 11.8 Hz, 1H), 4.13 (d, *J* = 11.0 Hz, 2H), 3.83 (d, *J* = 11.0 Hz, 1H), 3.60 – 3.54 (m, 2H), 3.51 (d, *J* = 7.0 Hz, 1H), 2.77 (m, 1H), 2.70 – 2.56 (m, 2H), 1.99 – 1.87 (m, 2H), 1.61 – 1.46 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 137.7, 137.3, 136.6, 134.3, 133.1, 132.4, 130.9, 128.6, 128.5, 128.4, 128.4, 128.1, 127.9, 127.9, 127.8, 127.6, 126.5,

126.0, 74.1, 73.5, 71.2, 71.1, 70.1, 40.5, 26.6, 22.3. HRMS calcd for $C_{39}H_{39}O_5$ $[M + H]^+$ 587.2797; found 587.2800.



5d

The title compound was prepared according to the general procedure (2) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving white gummy solid 49 mg, 84%.^{1}H NMR (600 MHz, $CDCl_3$) δ 9.28 (d, *J* = 8.7 Hz, 1H), 8.30 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.35 (dt, *J* = 13.3, 6.7 Hz, 3H), 7.30 (d, *J* = 6.9 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.01 (dd, *J* = 15.6, 8.4 Hz, 2H), 6.85 (d, *J* = 7.0 Hz, 2H), 5.08 (s, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 4.26 (d, *J* = 11.9 Hz, 1H), 4.08 (m, 2H), 3.37 (s, 1H), 2.83 – 2.69 (m, 3H), 2.17 – 2.01 (m, 3H), 1.23 (d, *J* = 6.3 Hz, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 200.6, 144.0, 137.3, 137.0, 134.6, 133.0, 132.4, 130.9, 128.8, 128.73, 128.6, 128.5, 128.5, 128.4, 128.1, 127.7, 126.6, 126.2, 83.1, 74.4, 70.9, 67.4, 40.5, 26.8, 22.4, 20.0. HRMS calcd for $C_{32}H_{33}O_4$ $[M + H]^+$ 481.2379; found 481.2368.

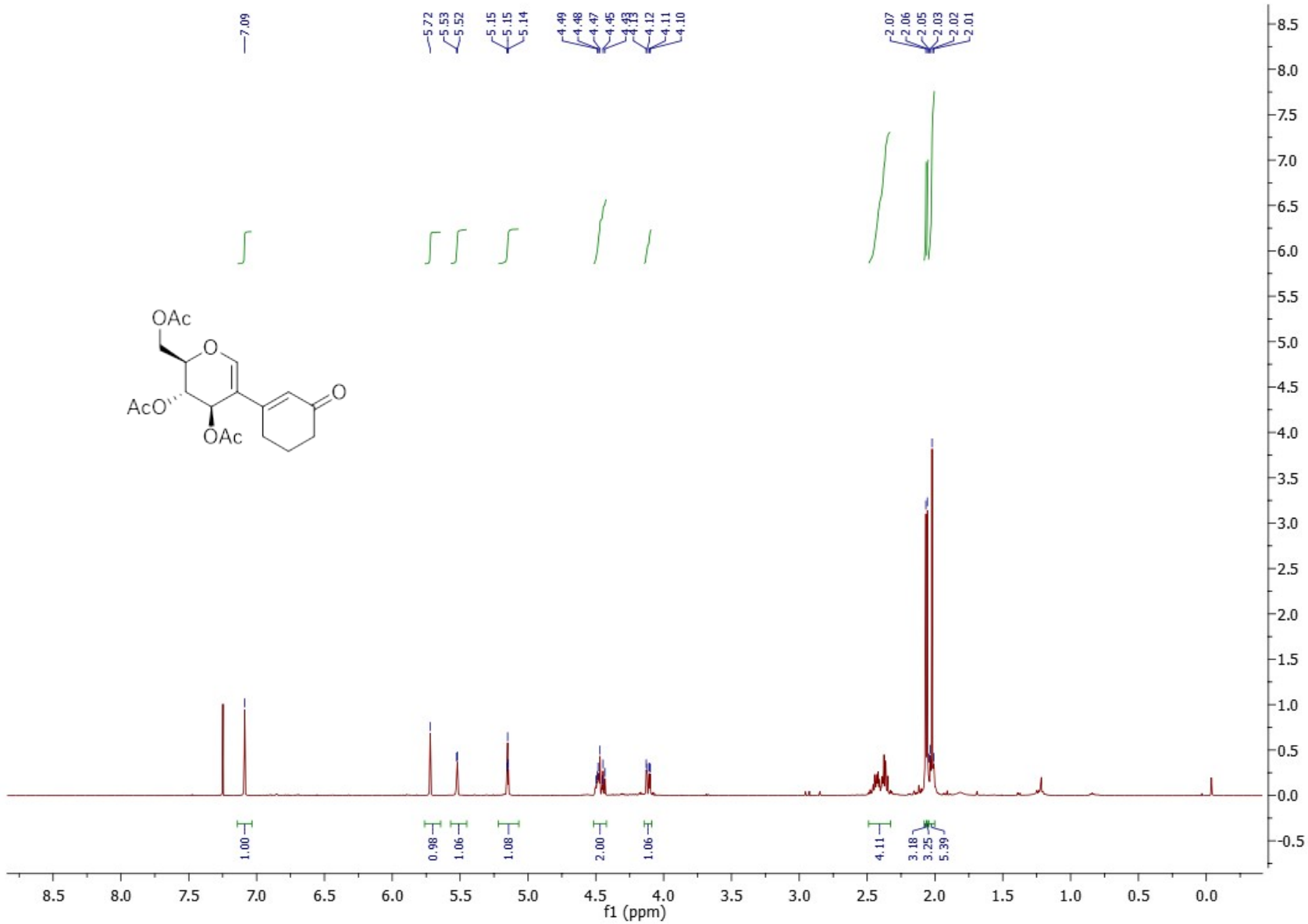


5e

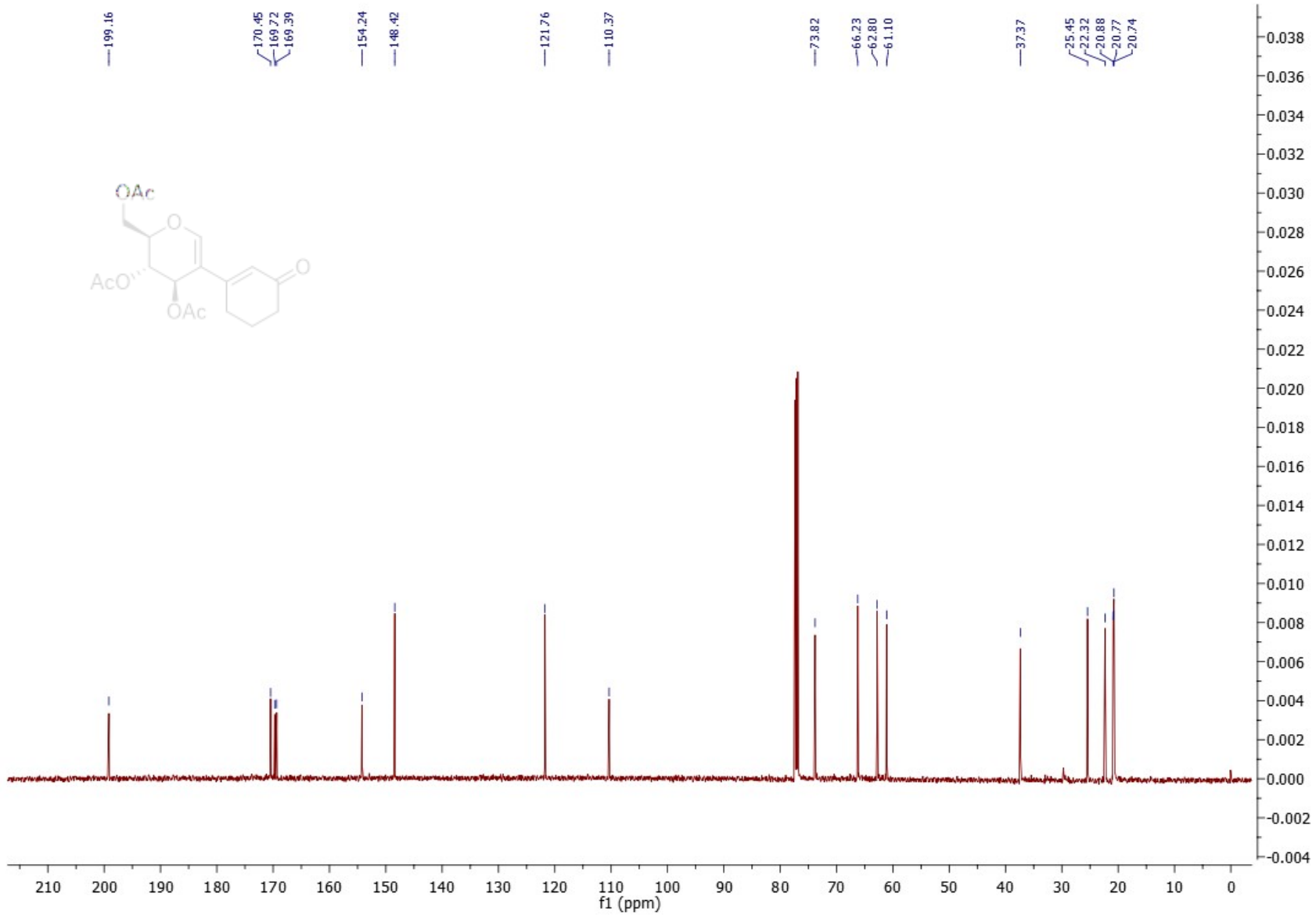
The title compound was prepared according to the general procedure (2) and purified by column chromatography (petroleum ether: ethyl acetate 9:1 to 7:3) giving white gummy solid 49 mg, 85%.^{1}H NMR (600 MHz, $CDCl_3$) δ 9.18 (d, *J* = 8.7 Hz, 1H), 8.14 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 15.4, 8.4 Hz, 1H), 7.30 – 7.17 (m, 5H), 7.14 – 7.11 (m, 1H), 7.08 (t, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 2H), 4.92 (d, *J* = 5.2 Hz, 1H), 4.61 – 4.51 (m, 3H), 4.25 (d, *J* = 11.9 Hz, 1H), 3.69 (d, *J* = 4.5 Hz, 1H), 3.56 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.41 (dd, *J* = 11.4, 4.8 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.70 – 2.61 (m, 2H), 1.98 (m, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 143.5, 136.7, 136.7, 132.9, 132.6, 131.4,

130.0, 127.9, 127.8, 127.5, 127.5, 127.4, 127.3, 127.1, 127.1, 127.0, 126.8, 125.6, 125.1, 80.1, 72.8, 70.0, 60.8, 39.4, 25.9, 21.4. HRMS calcd for $C_{31}H_{31}O_4$ $[M + H]^+$ 467.2222; found 467.2210

NMR Spectra

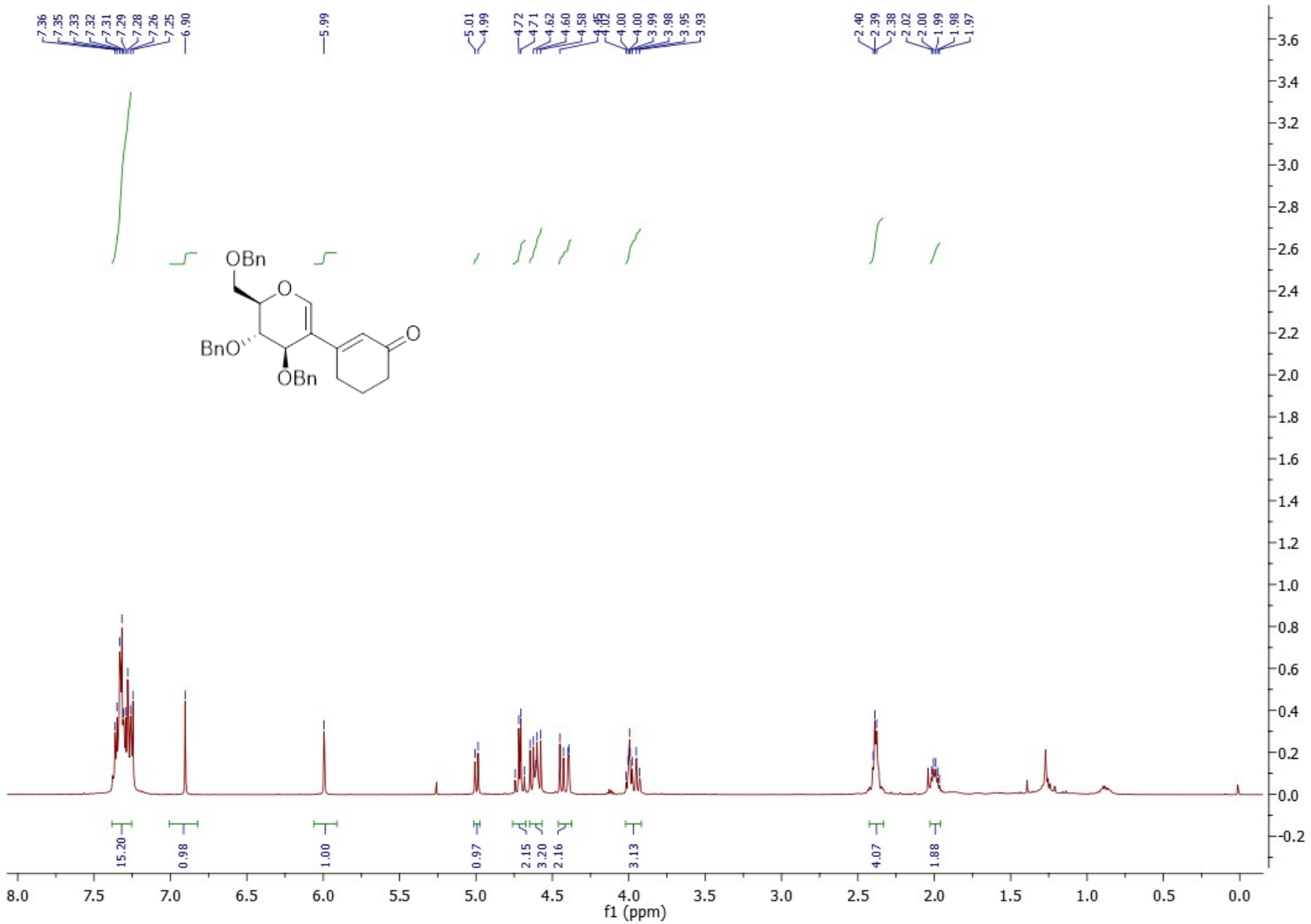


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**

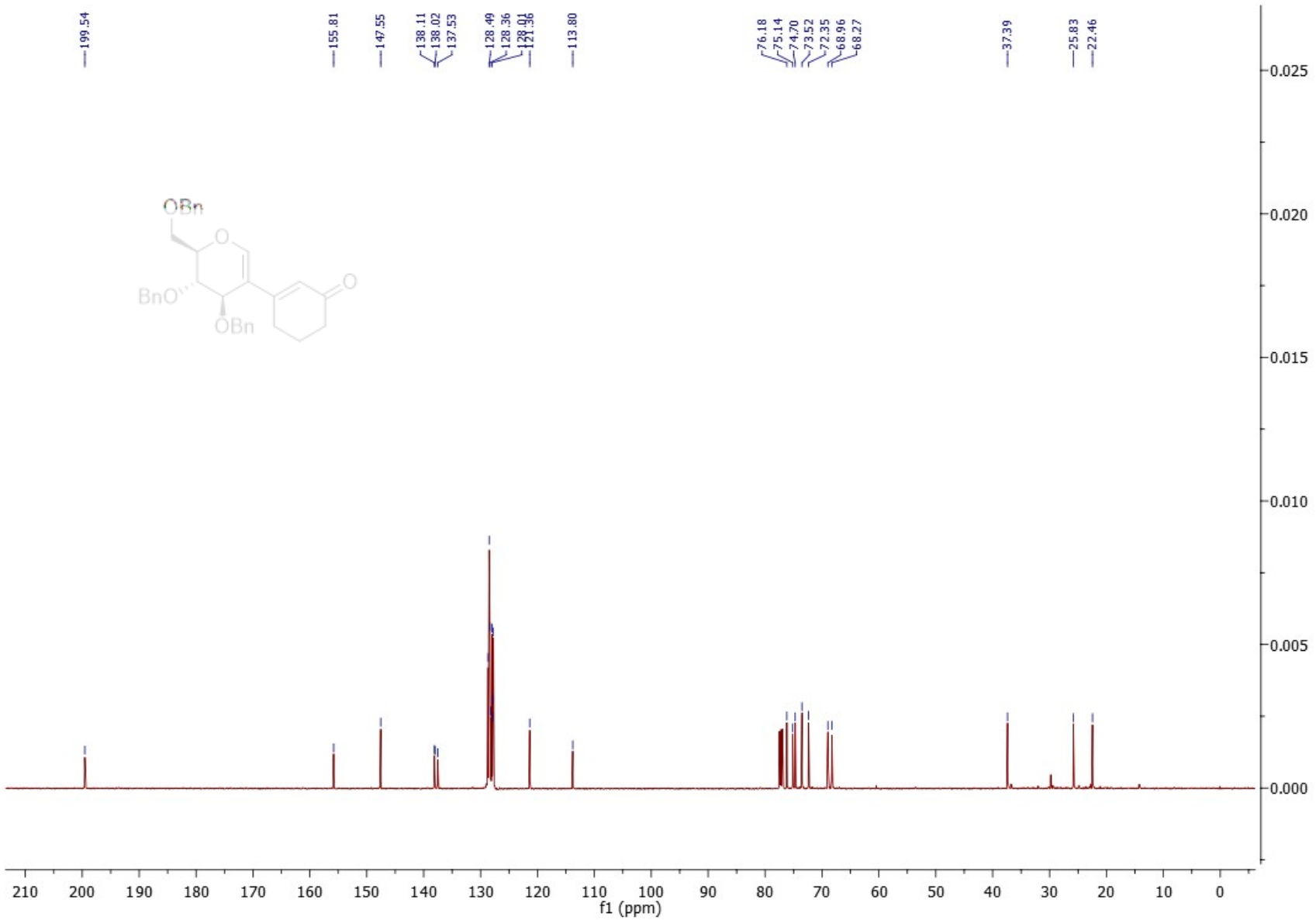

199.16
170.45
169.72
169.39
154.24
148.42
121.76
110.37
73.82
66.23
62.80
61.10
37.37
25.45
22.32
20.88
20.77
20.74
OAc
AcO
OAc
O
O
f1 (ppm)

13

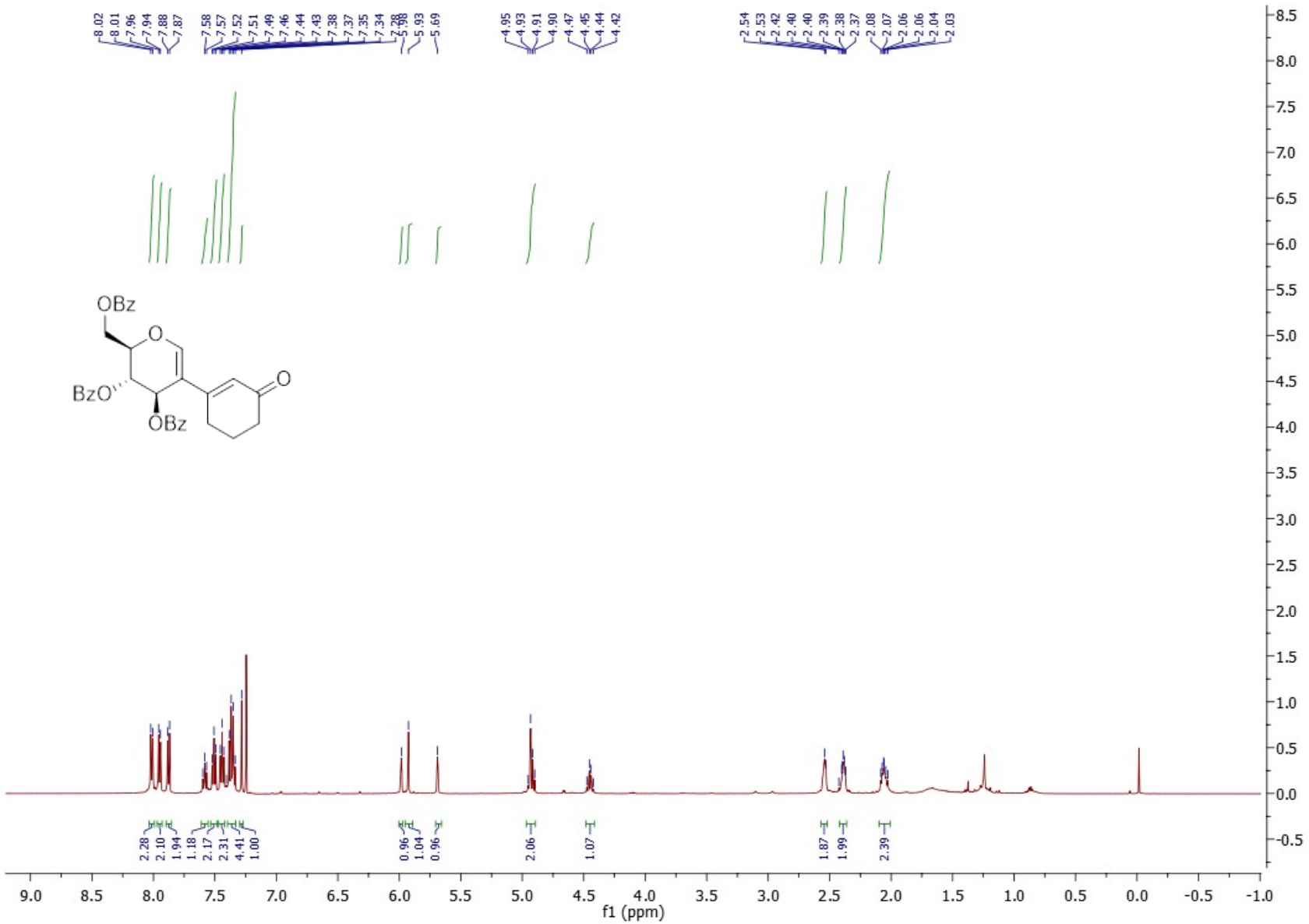
C NMR (126 MHz, $CDCl_3$) of compound **3a**



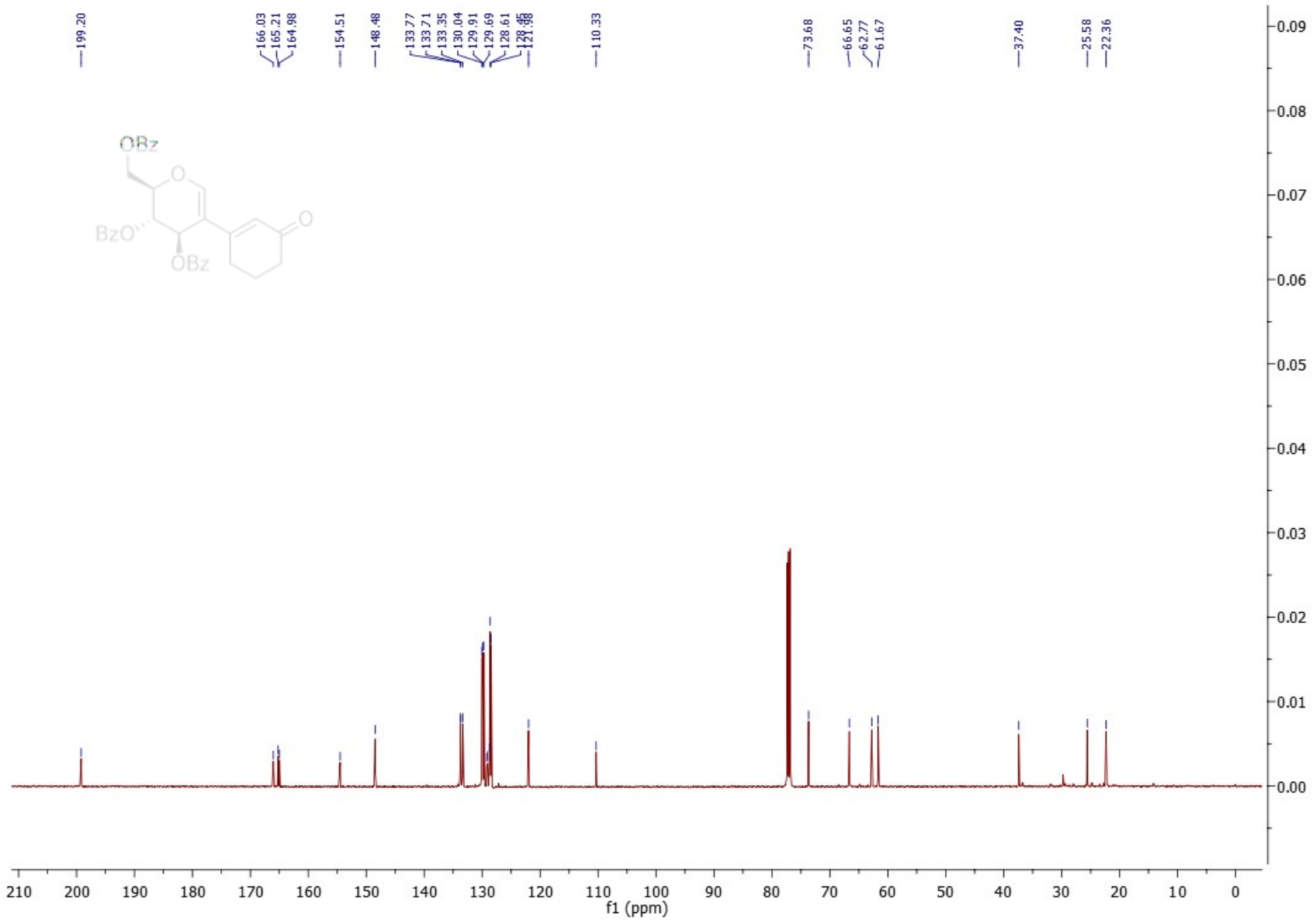
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**



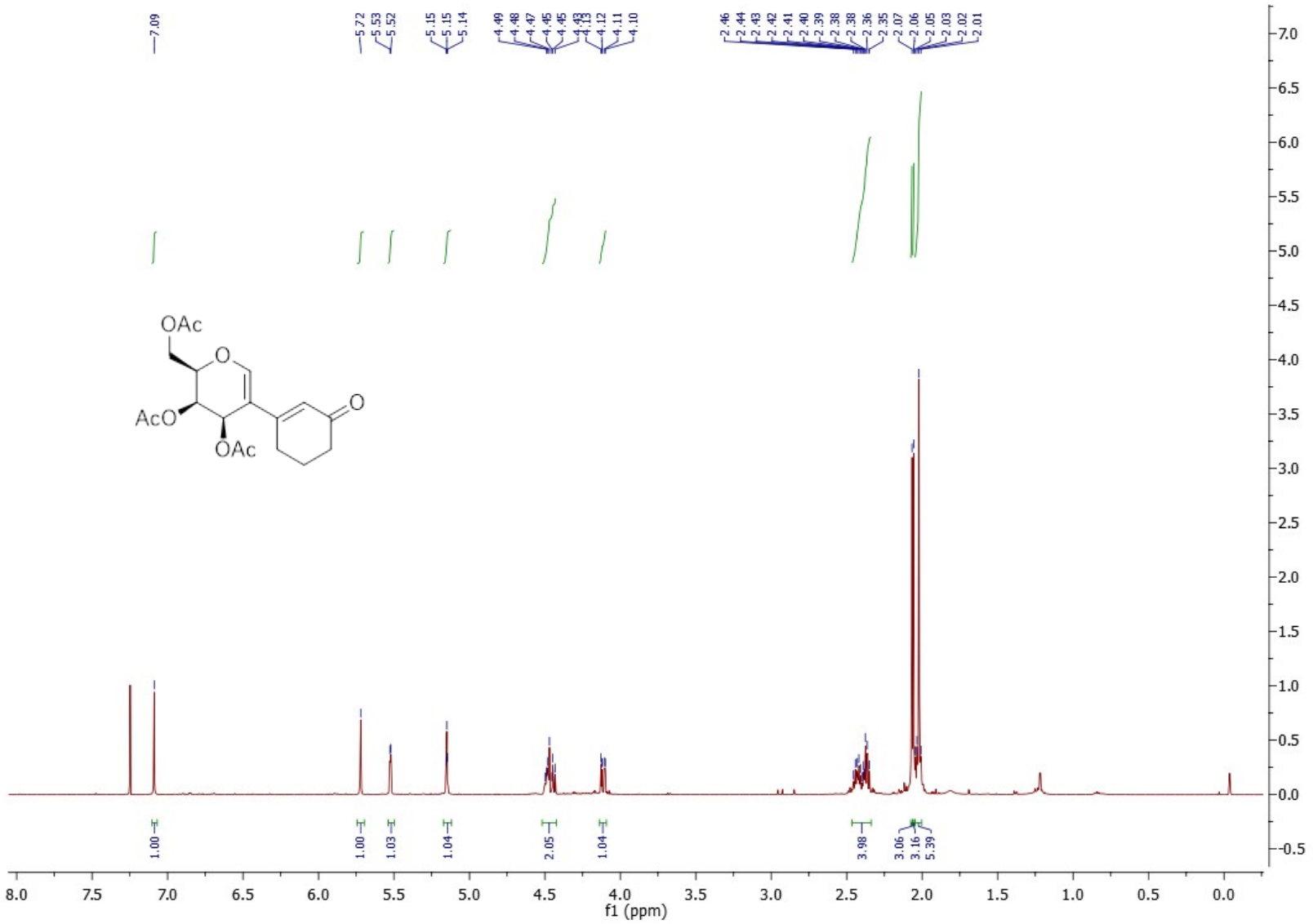
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3b**



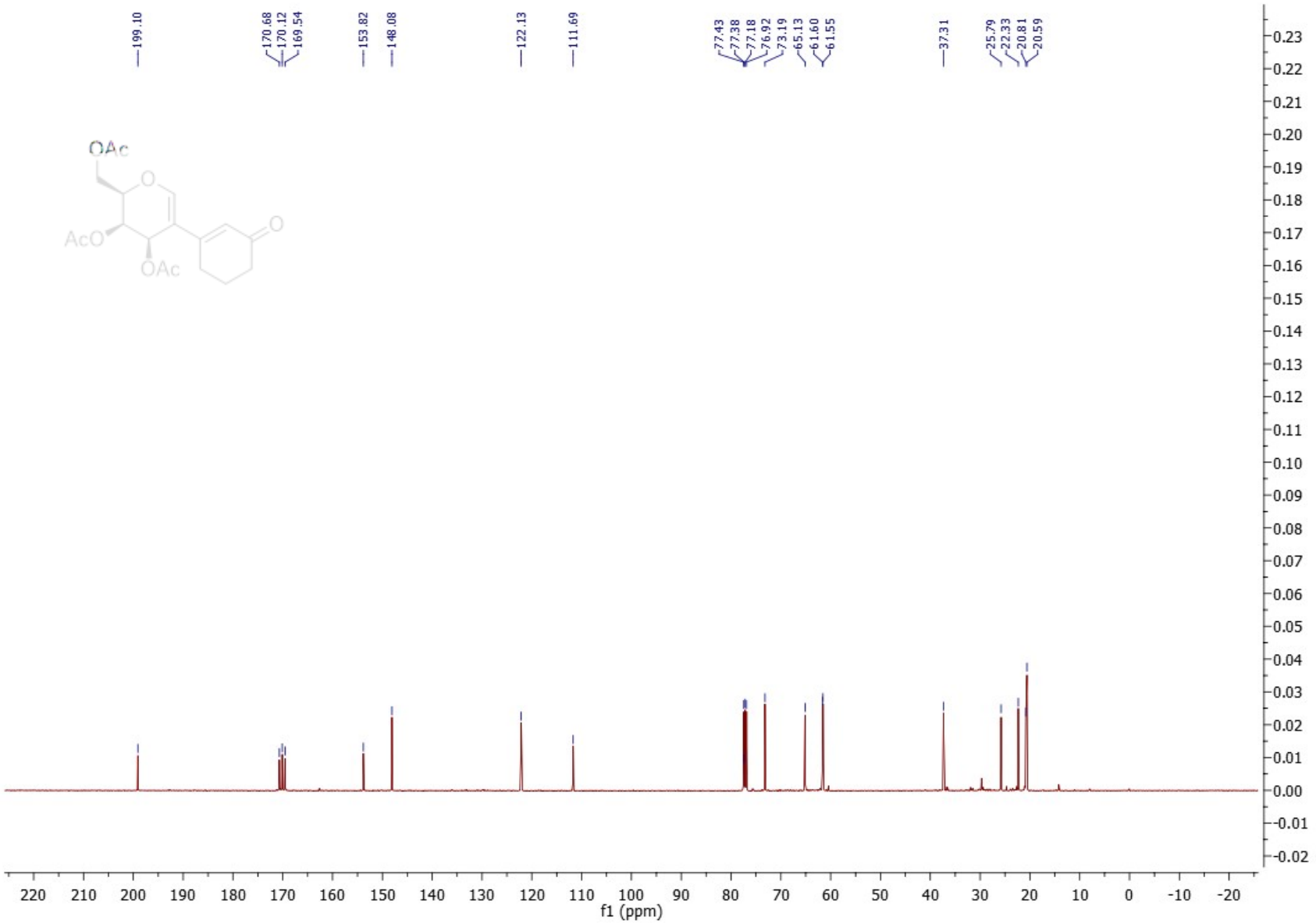
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**



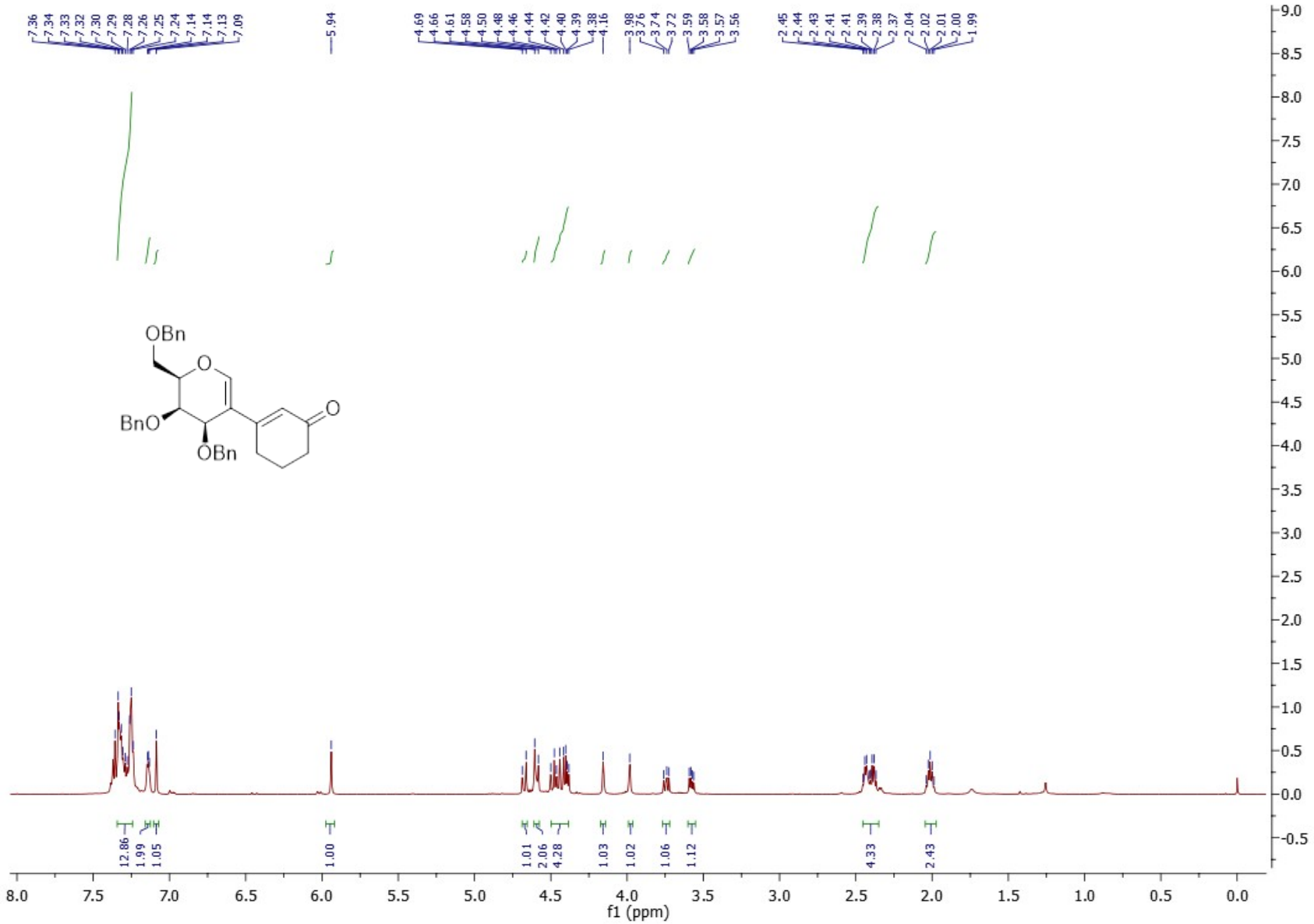
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3c**



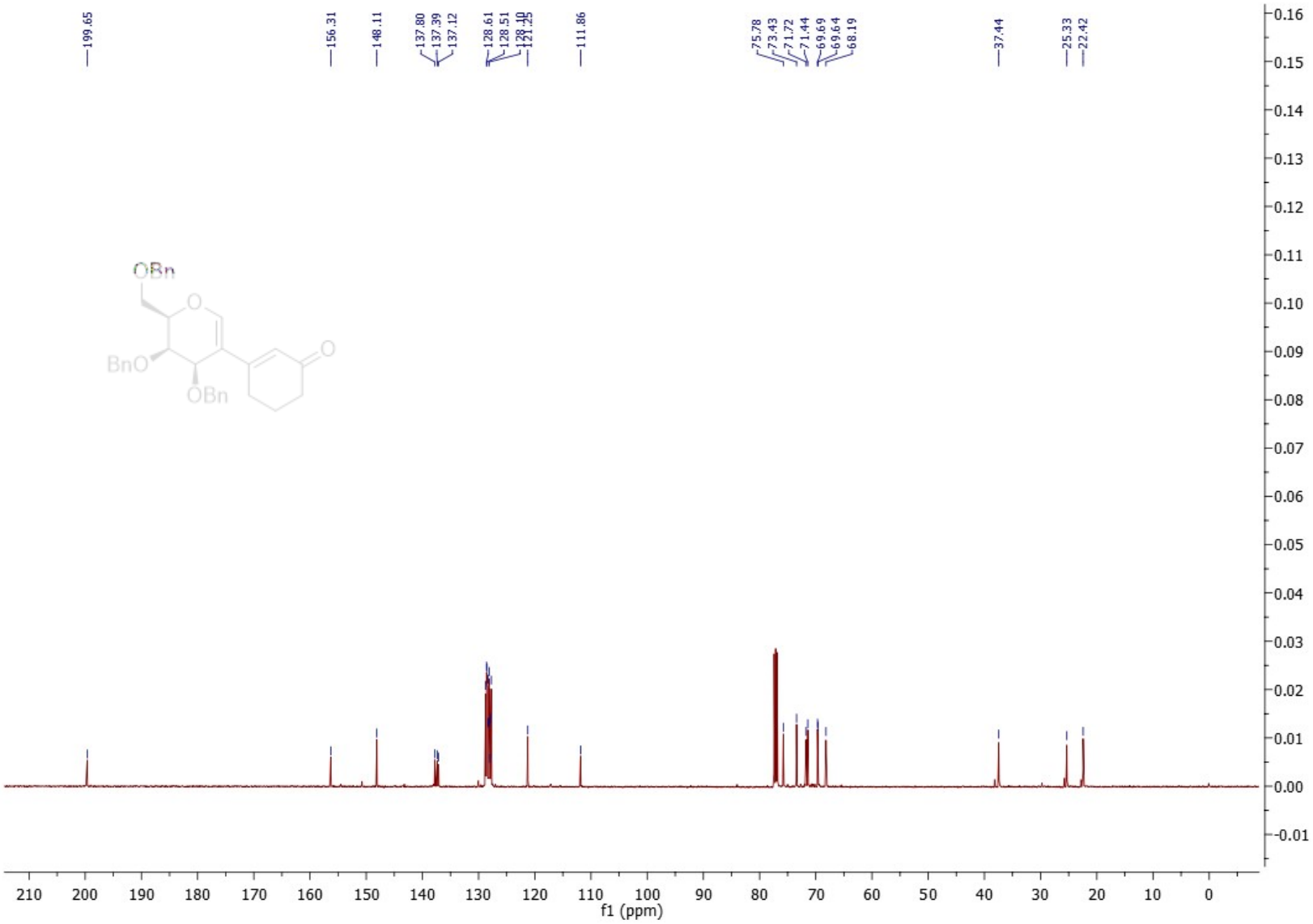
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**



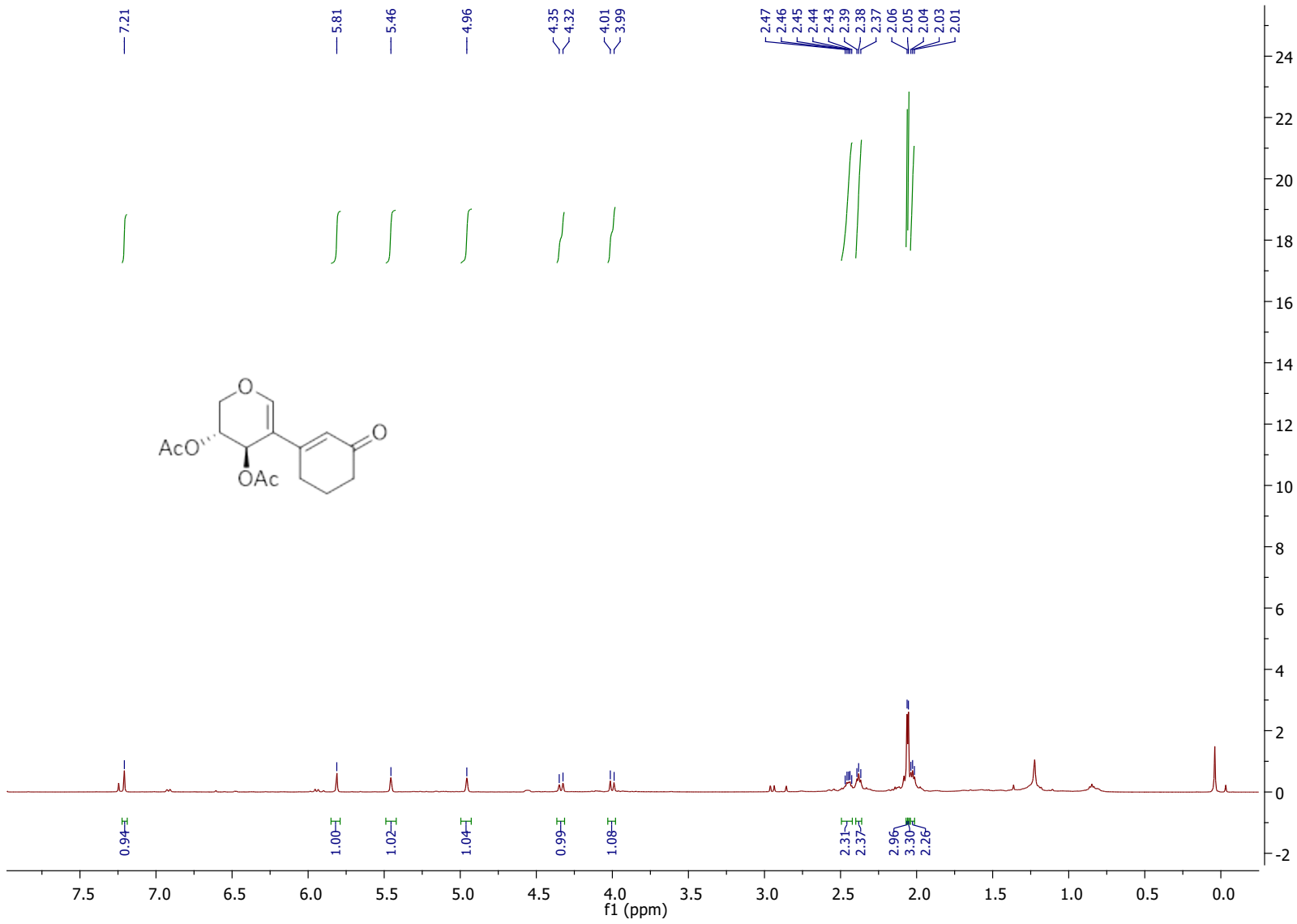
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3d**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**

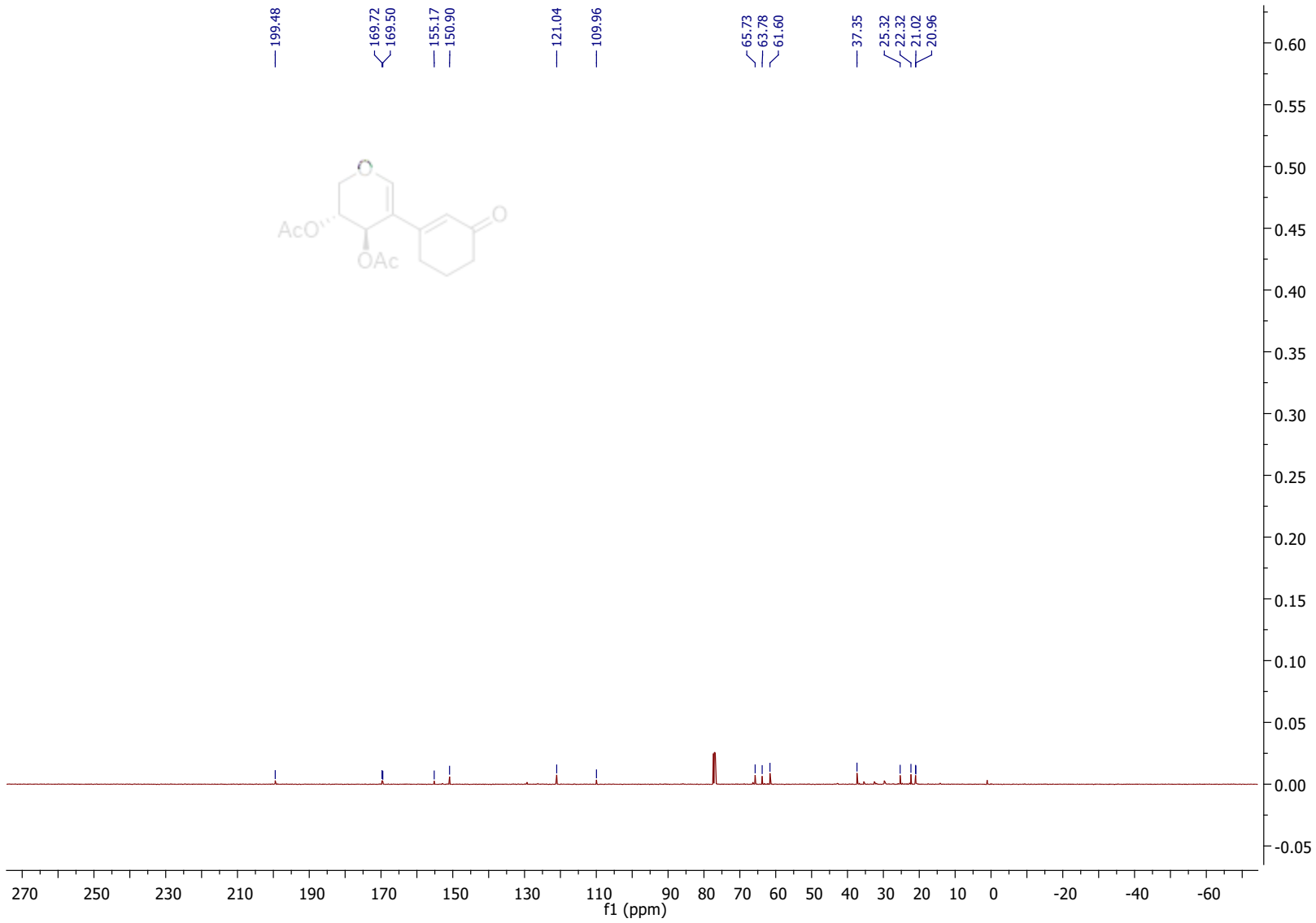


^{13}C NMR (126 MHz, $CDCl_3$) of compound **3e**

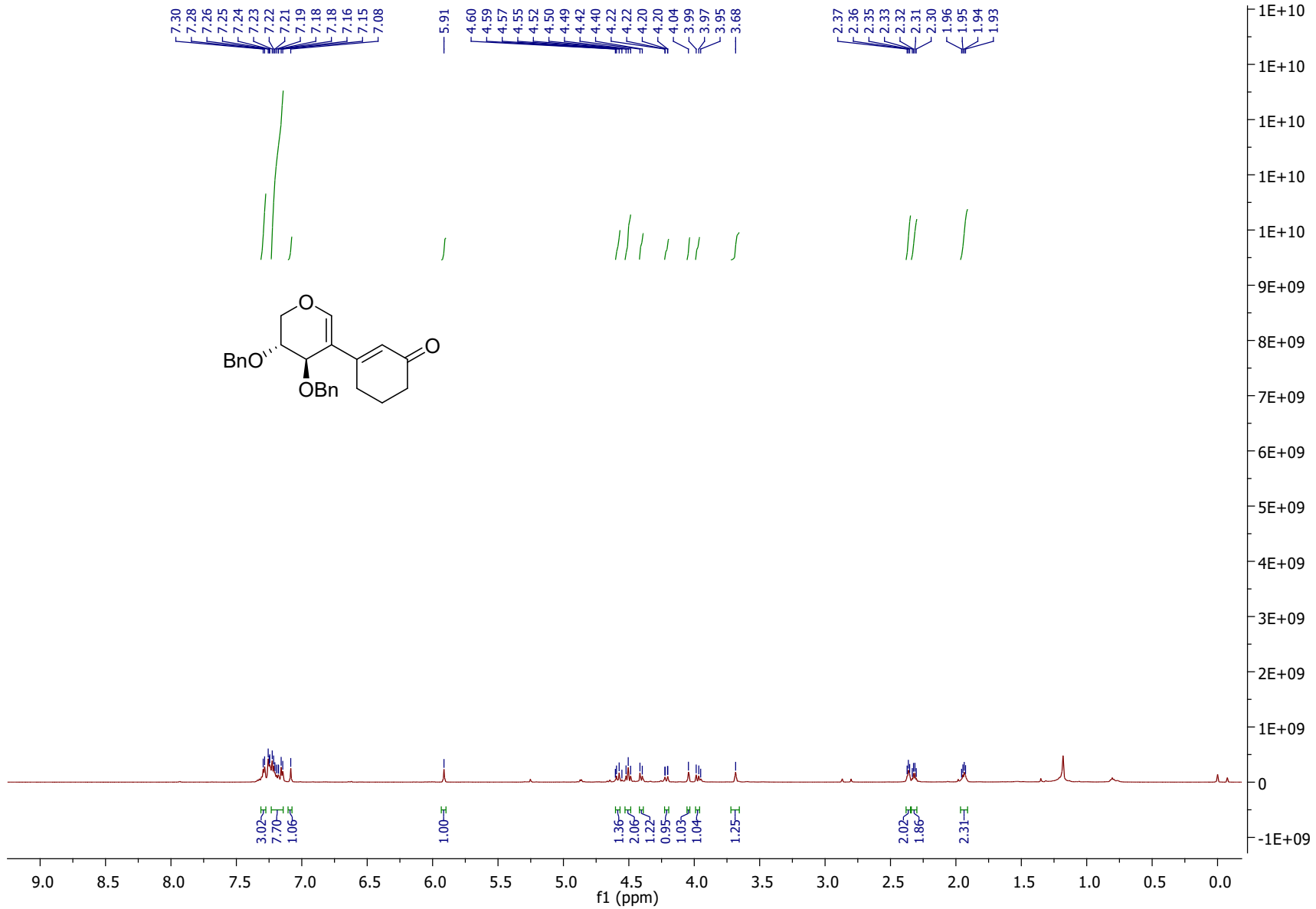


^{1}HN

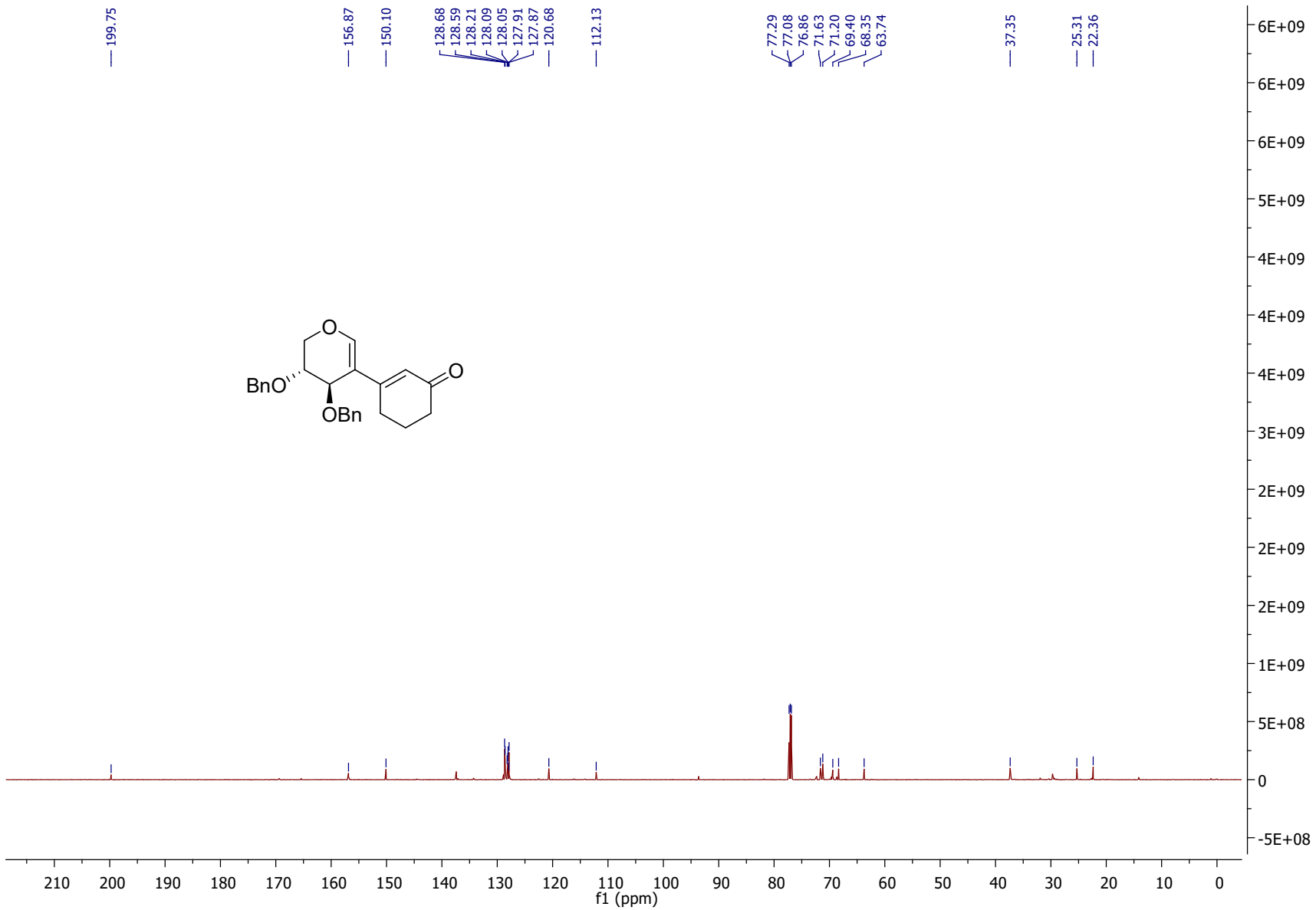
MR (500 MHz, $CDCl_3$) of compound **3f**



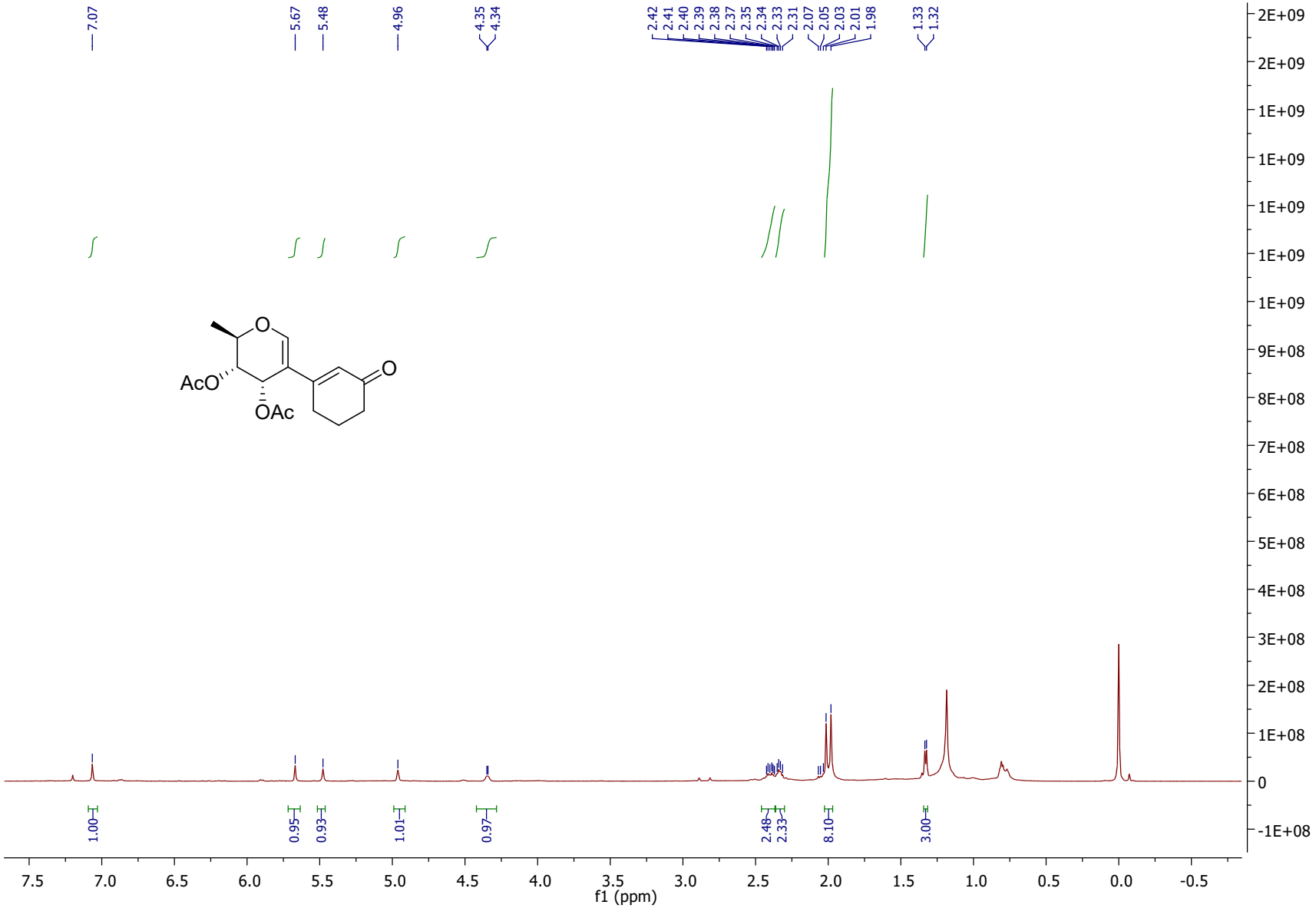
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3f**



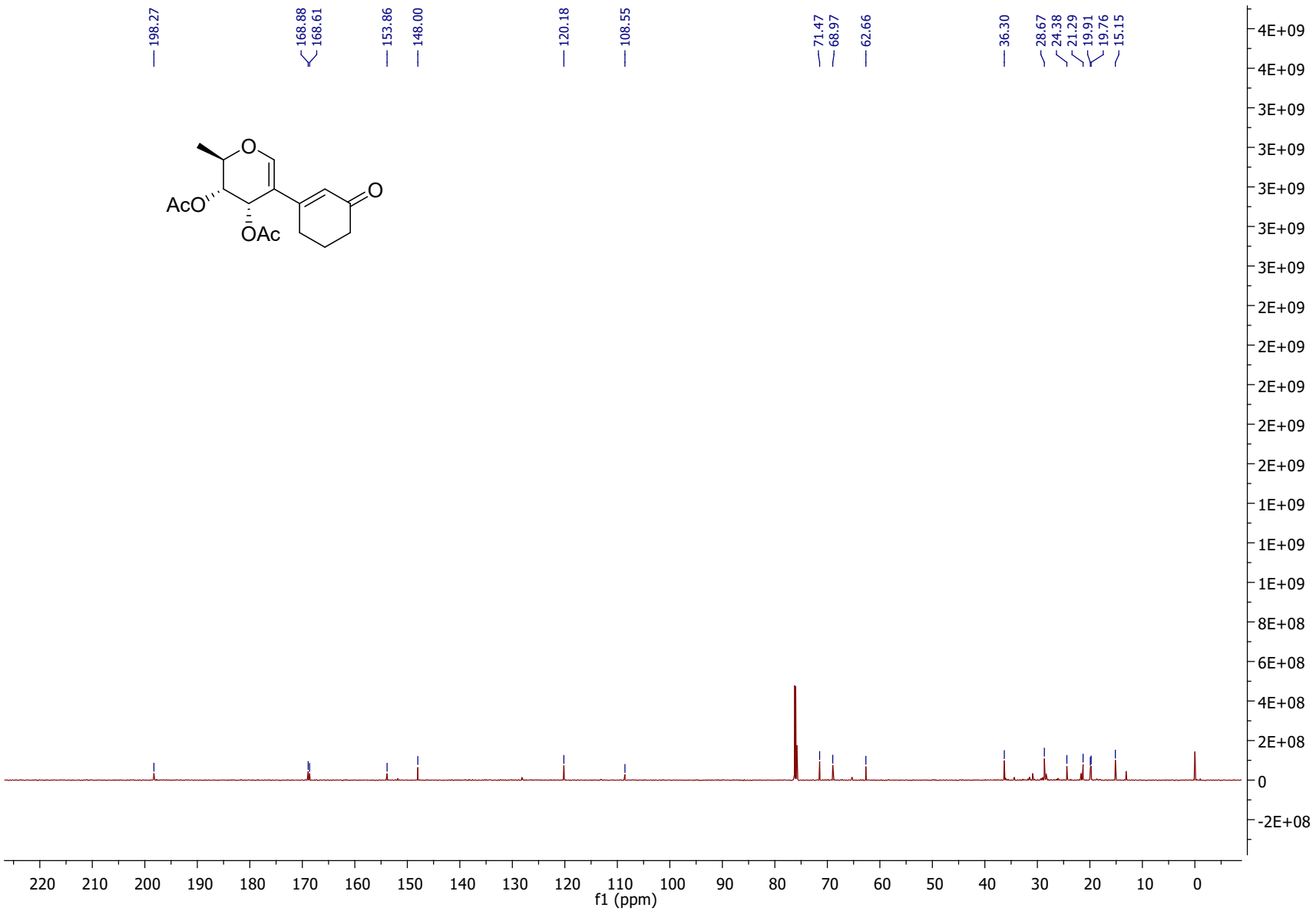
^{1}HNMR (600 MHz, $CDCl_3$) of compound **3g**



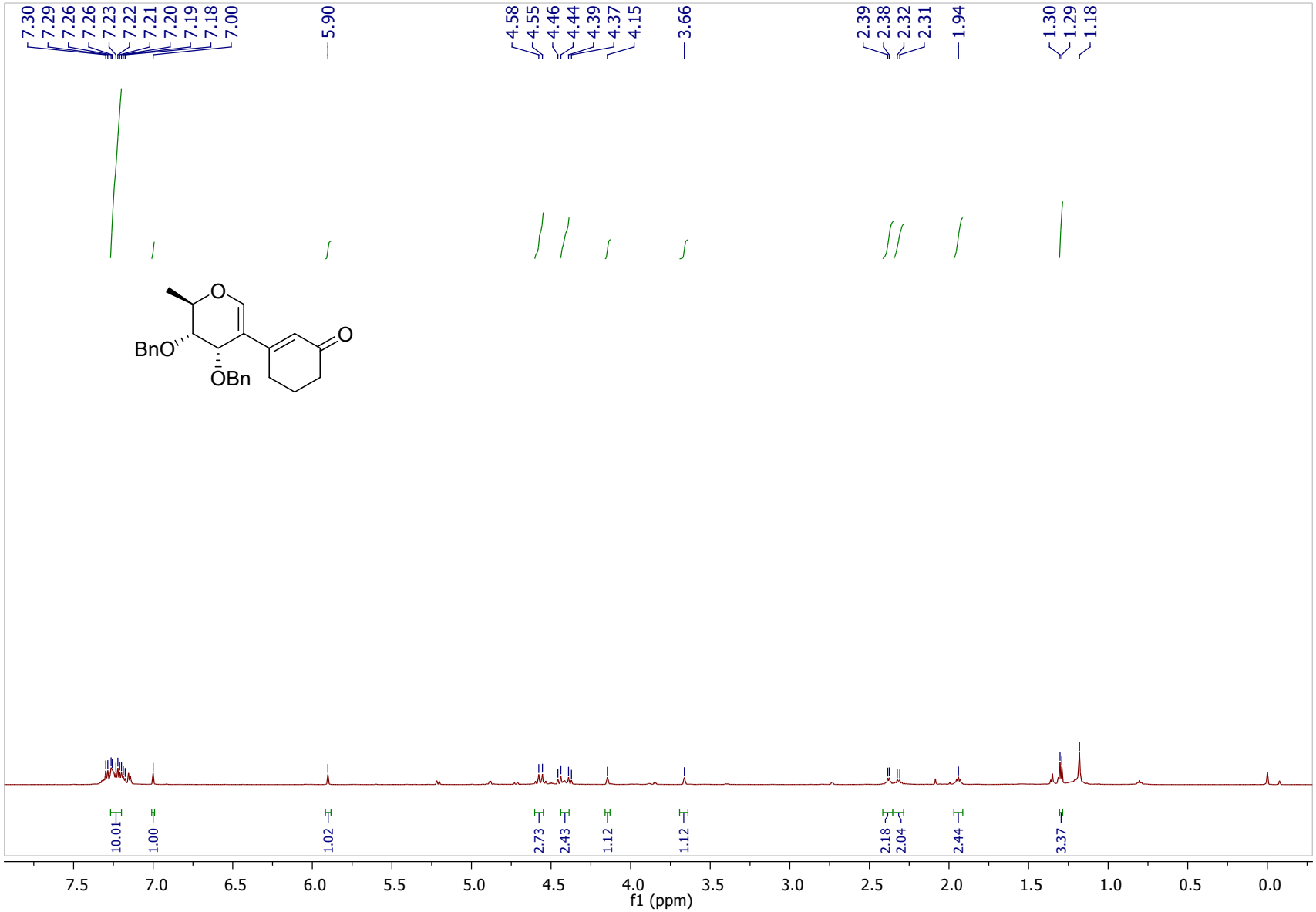
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3g**



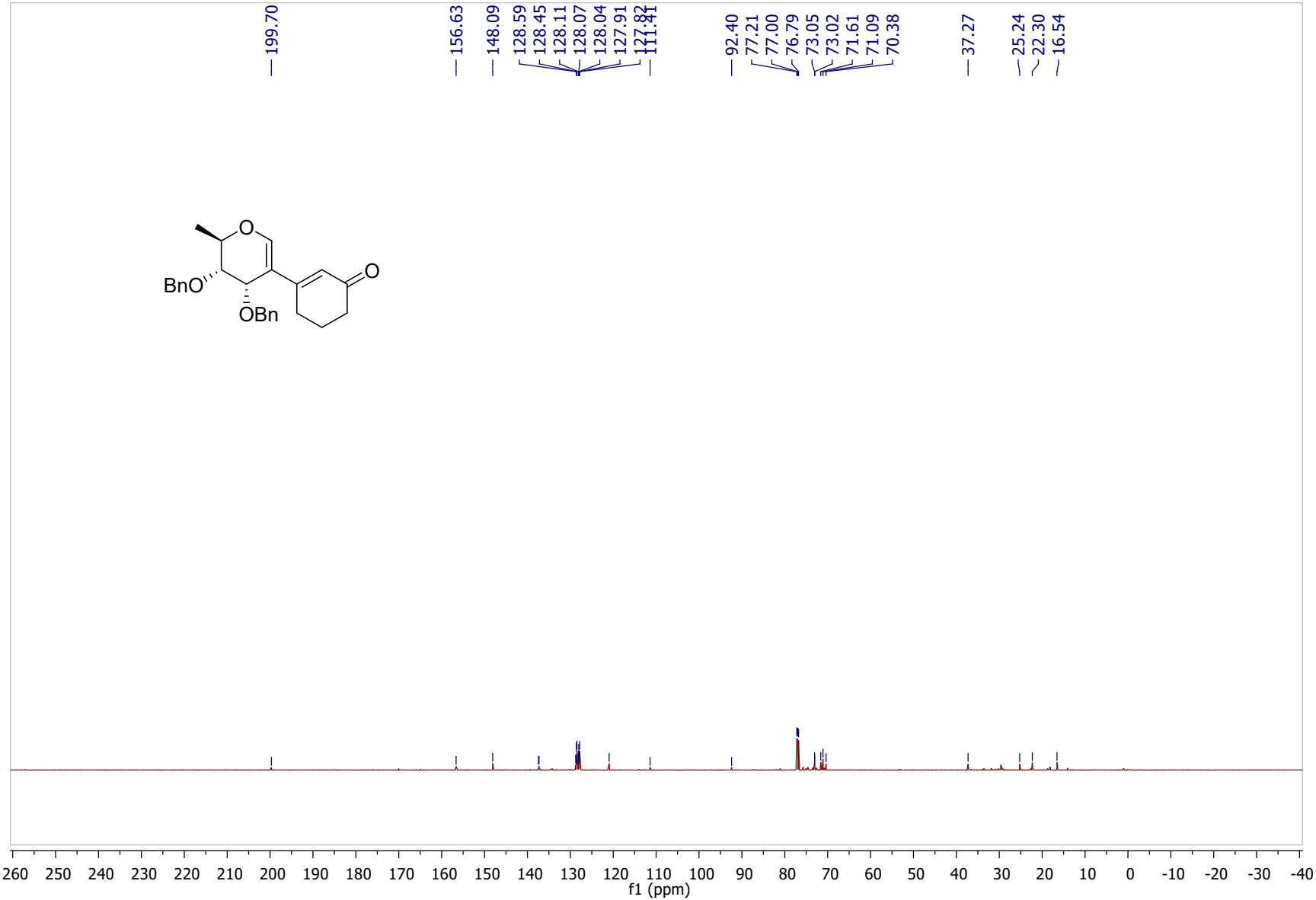
^{1}HNMR (600 MHz, $CDCl_3$) of compound **3h**



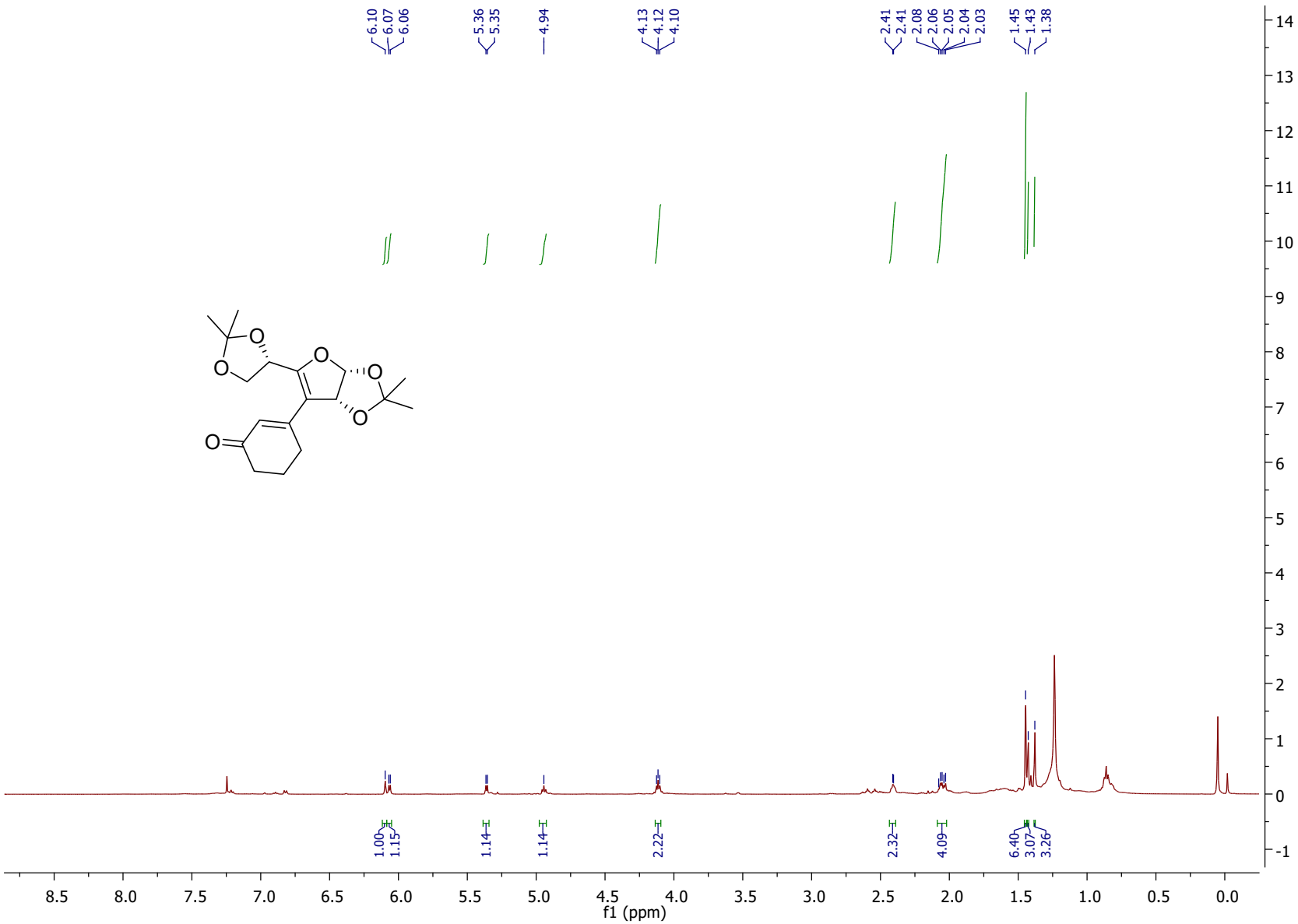
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3h**



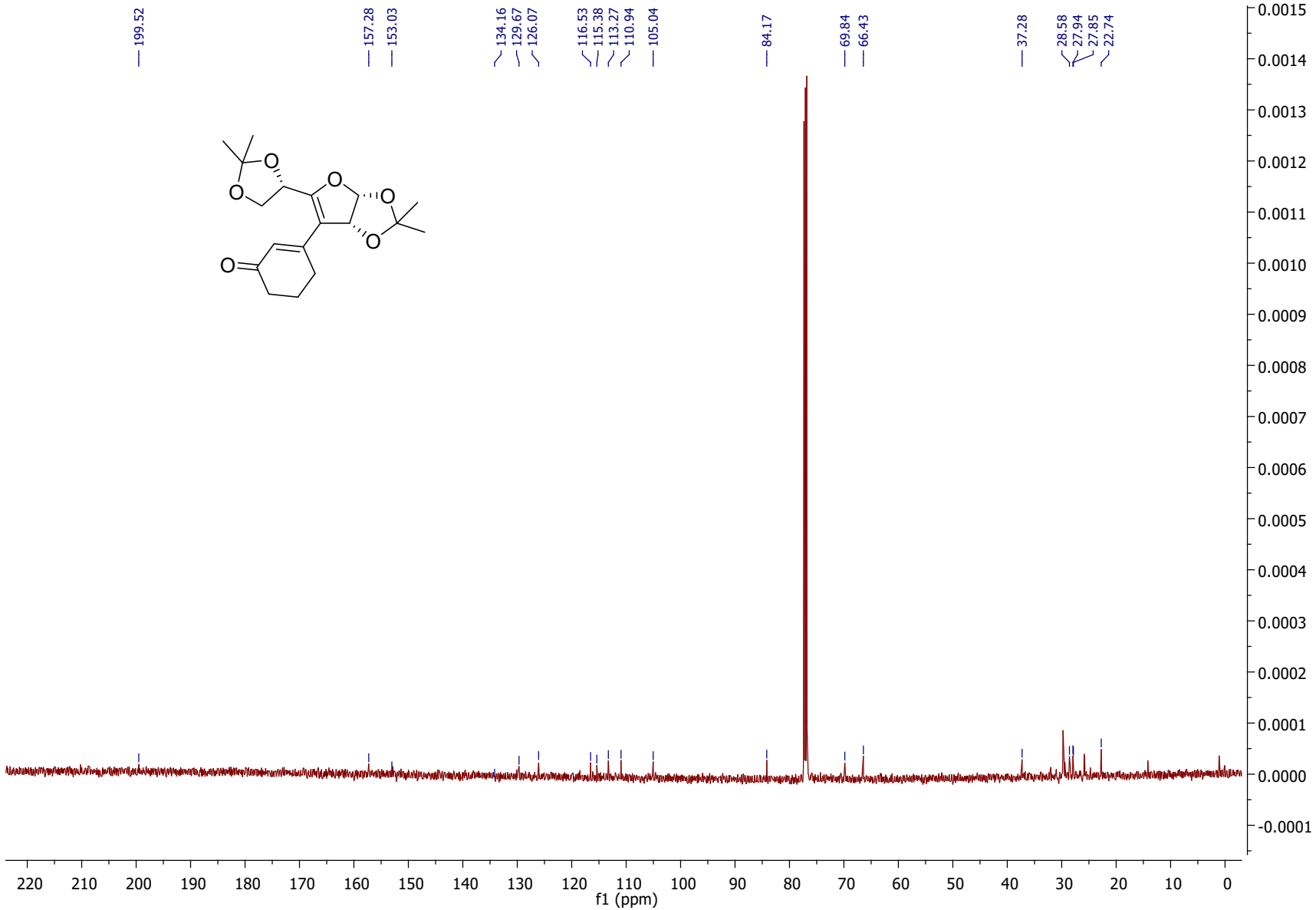
^{1}HNMR (600 MHz, $CDCl_3$) of compound **3i**



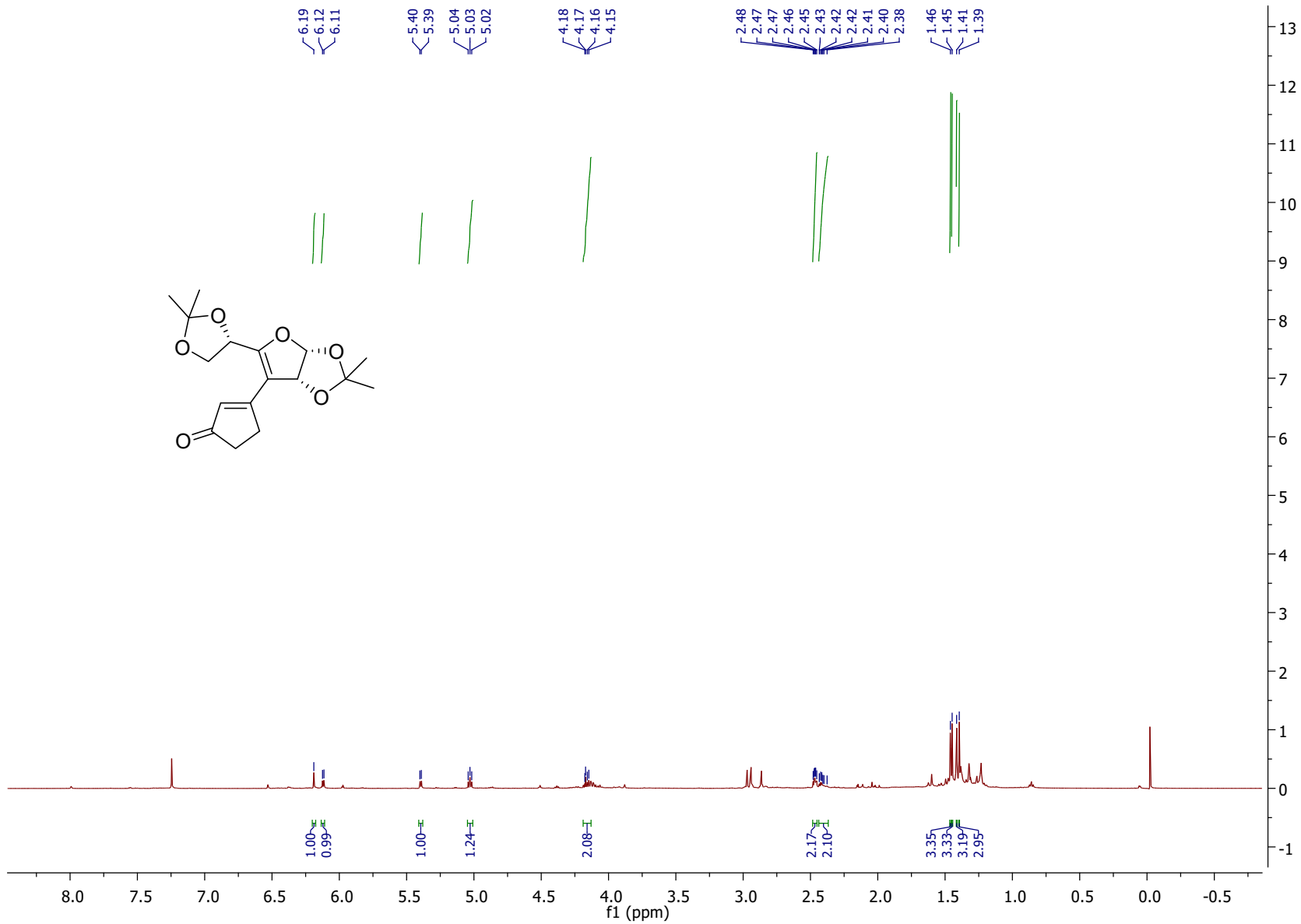
^{13}C NMR (151 MHz, $CDCl_3$) of compound **3i**



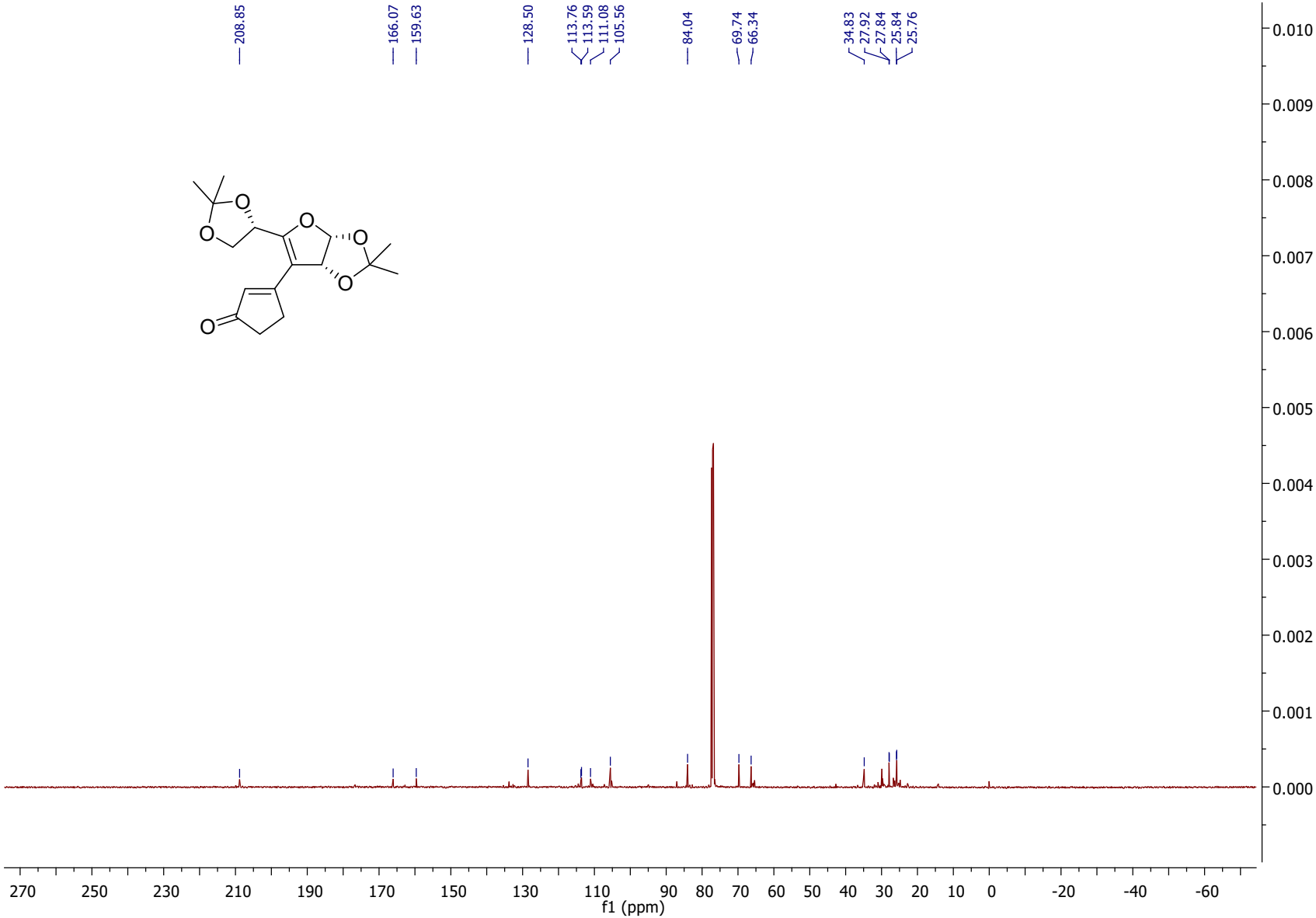
^{1}HNMR (500 MHz, $CDCl_3$) of compound **3j**



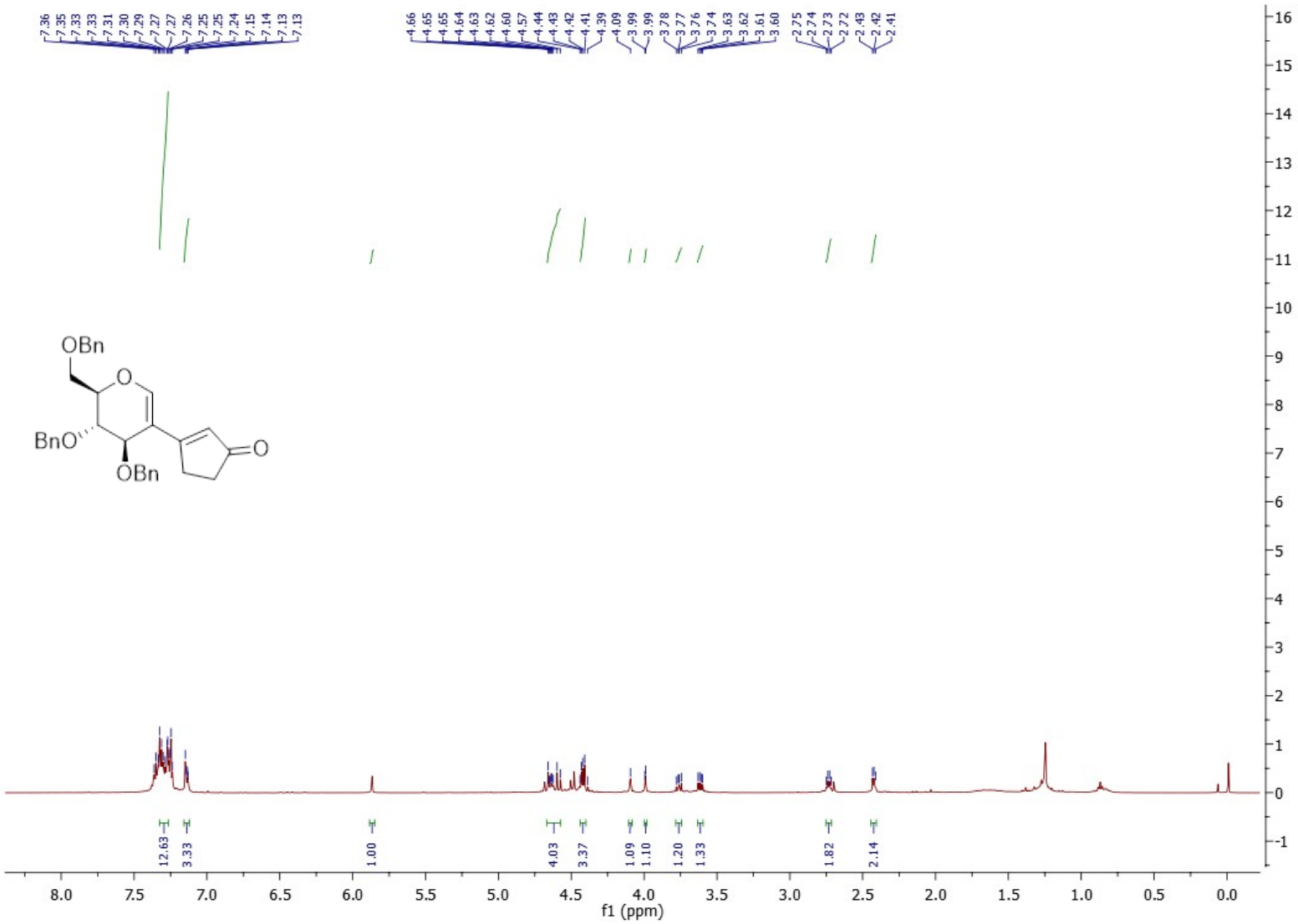
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3j**



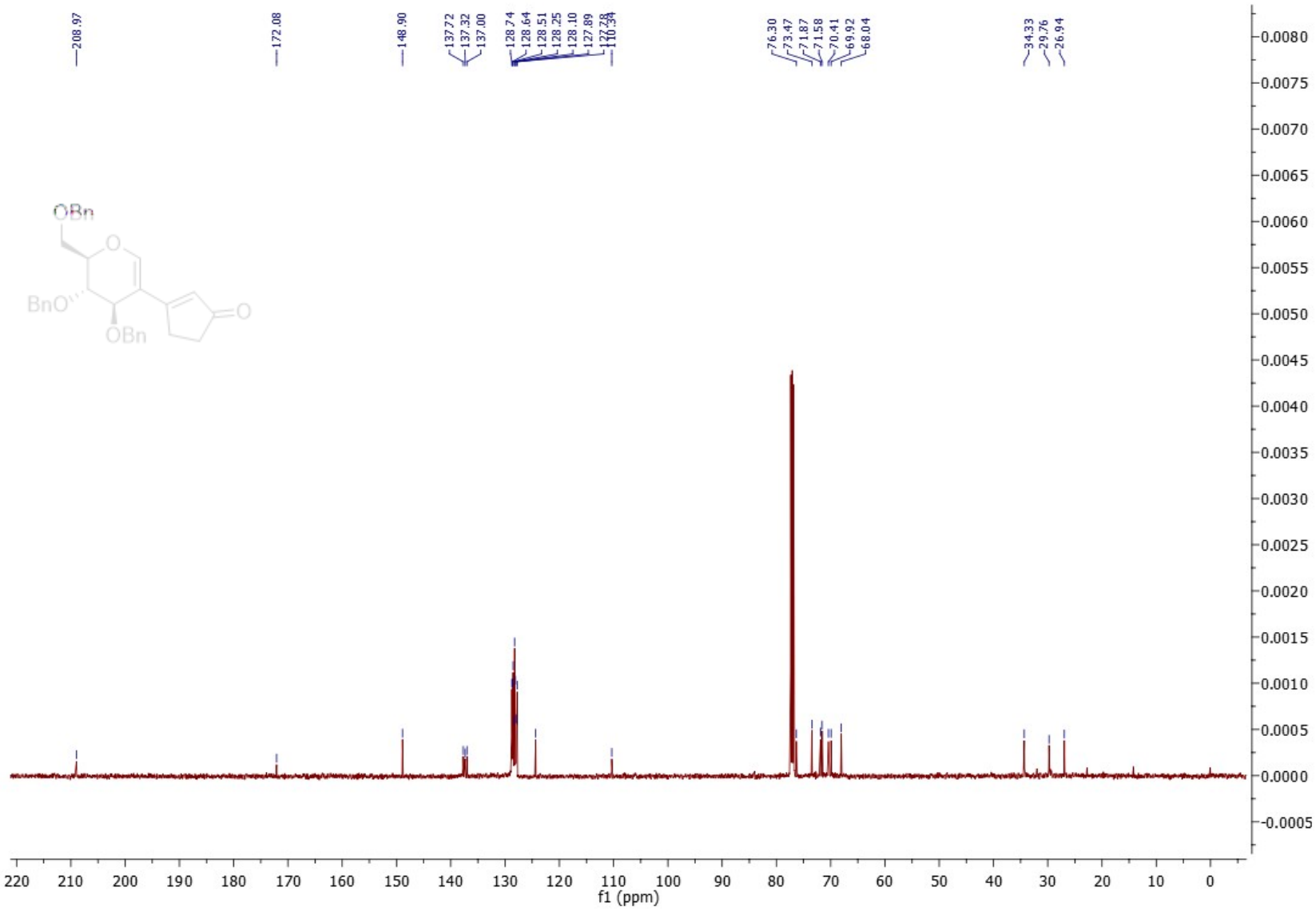
^{1}H NMR (500MHz, $CDCl_3$) of compound **3k**



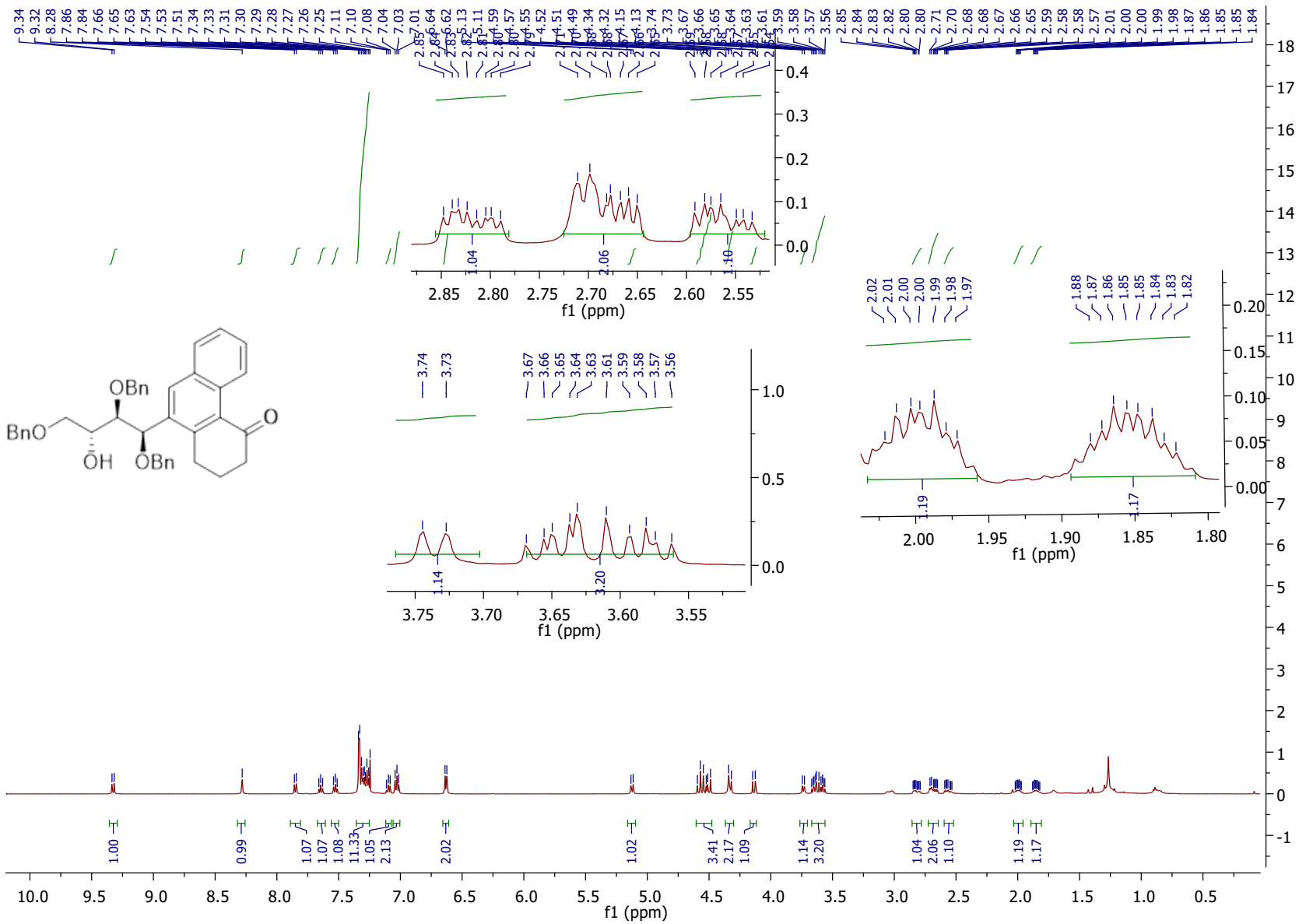
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3k**



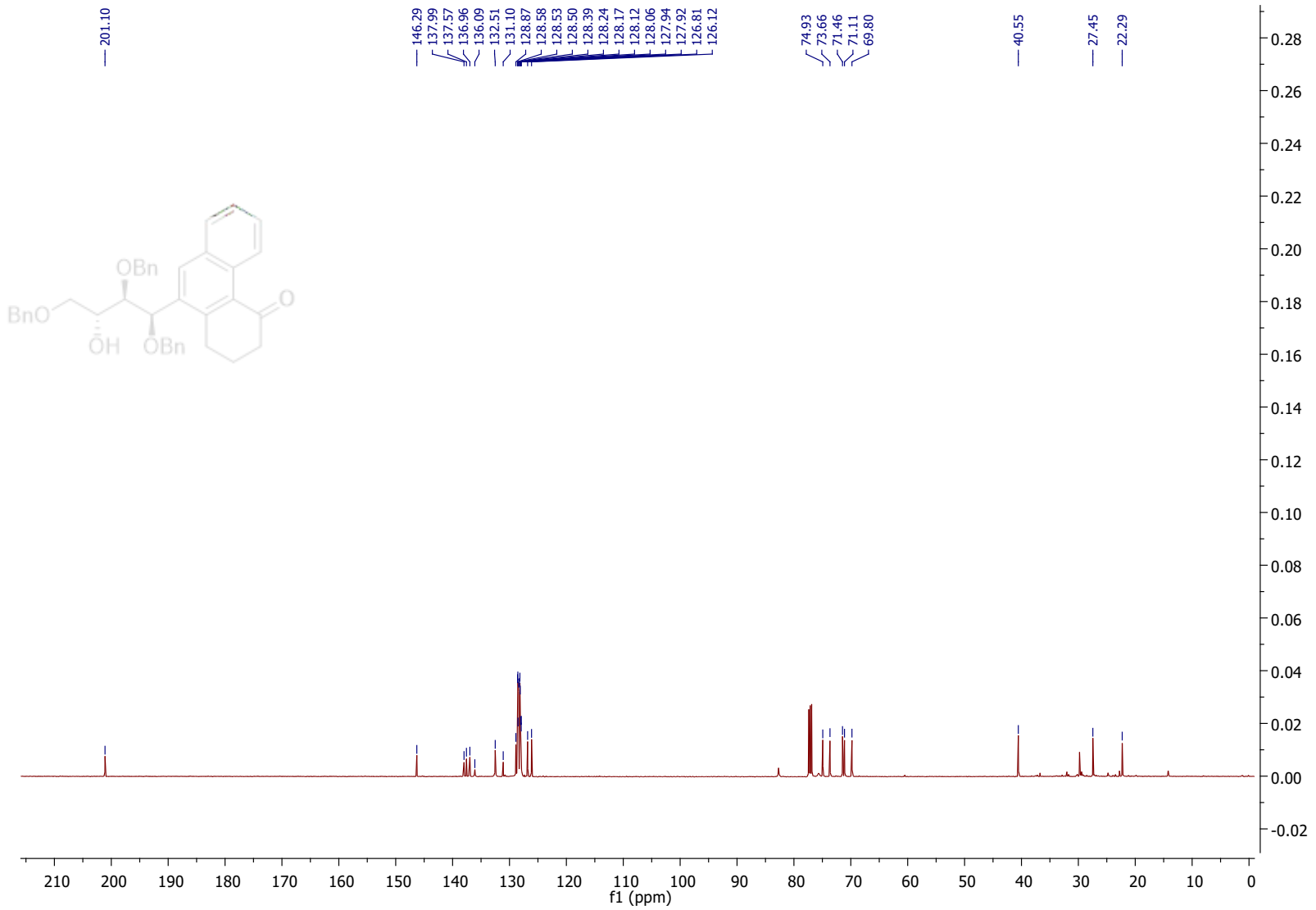
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**



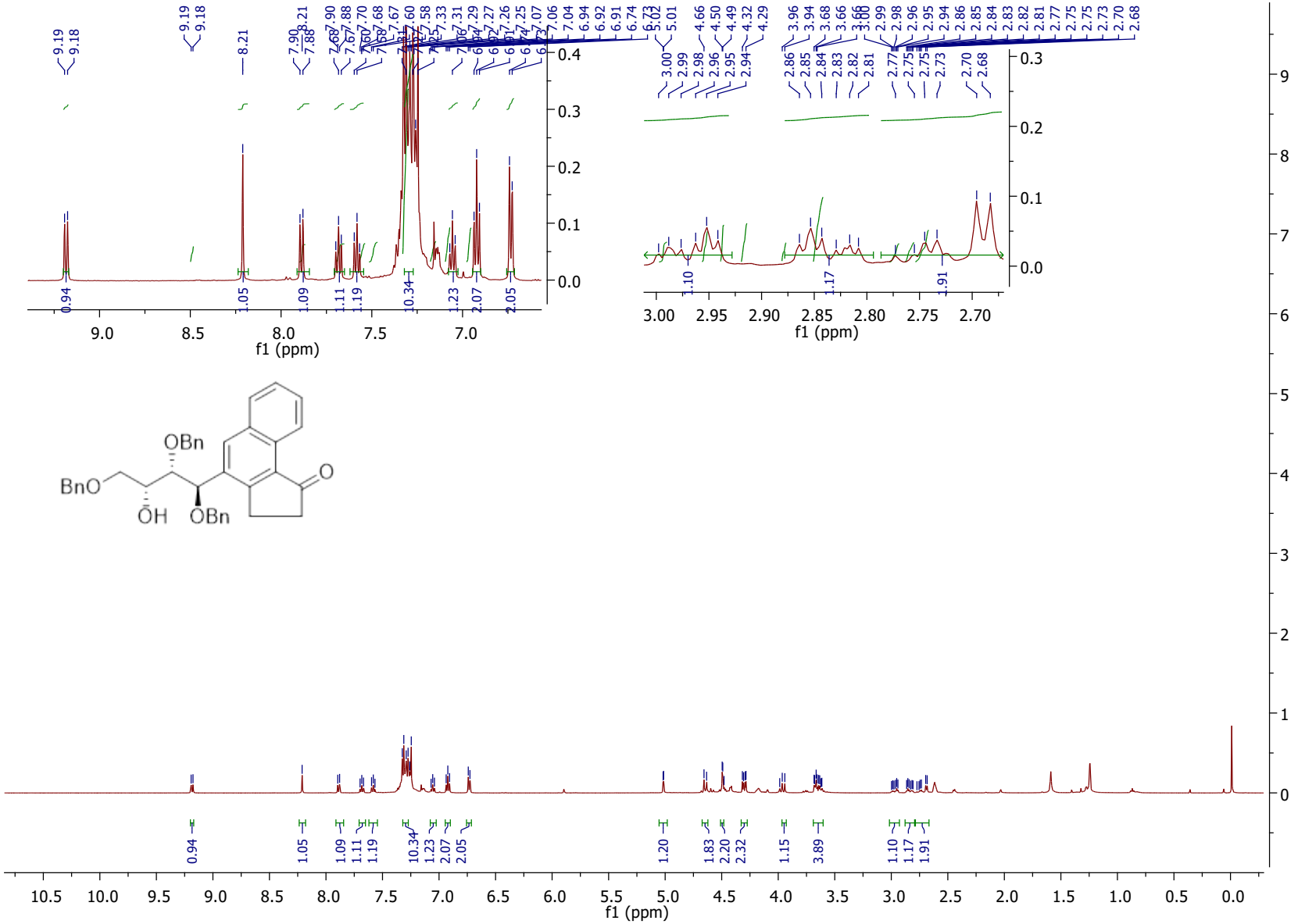
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3l**



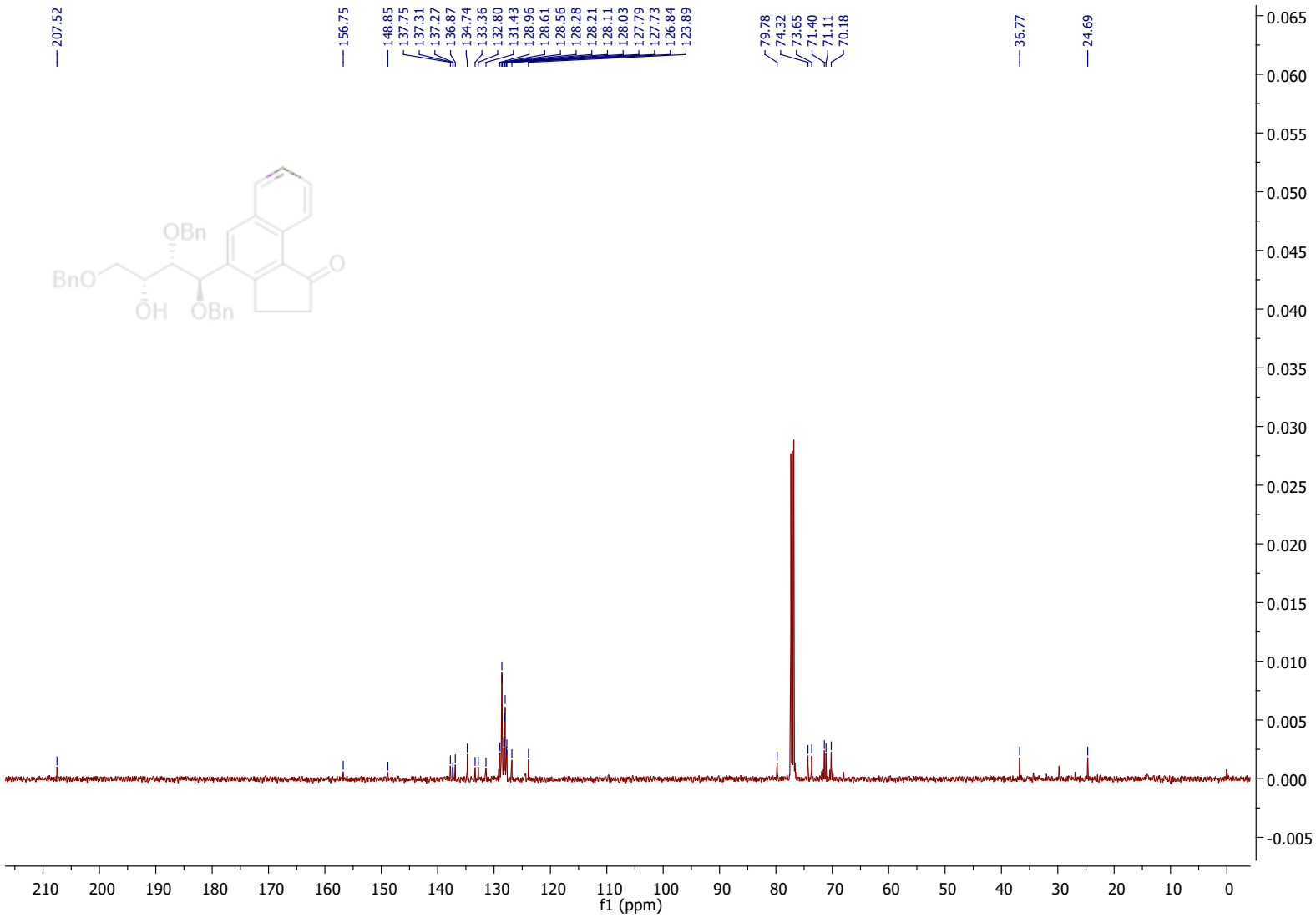
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5a**



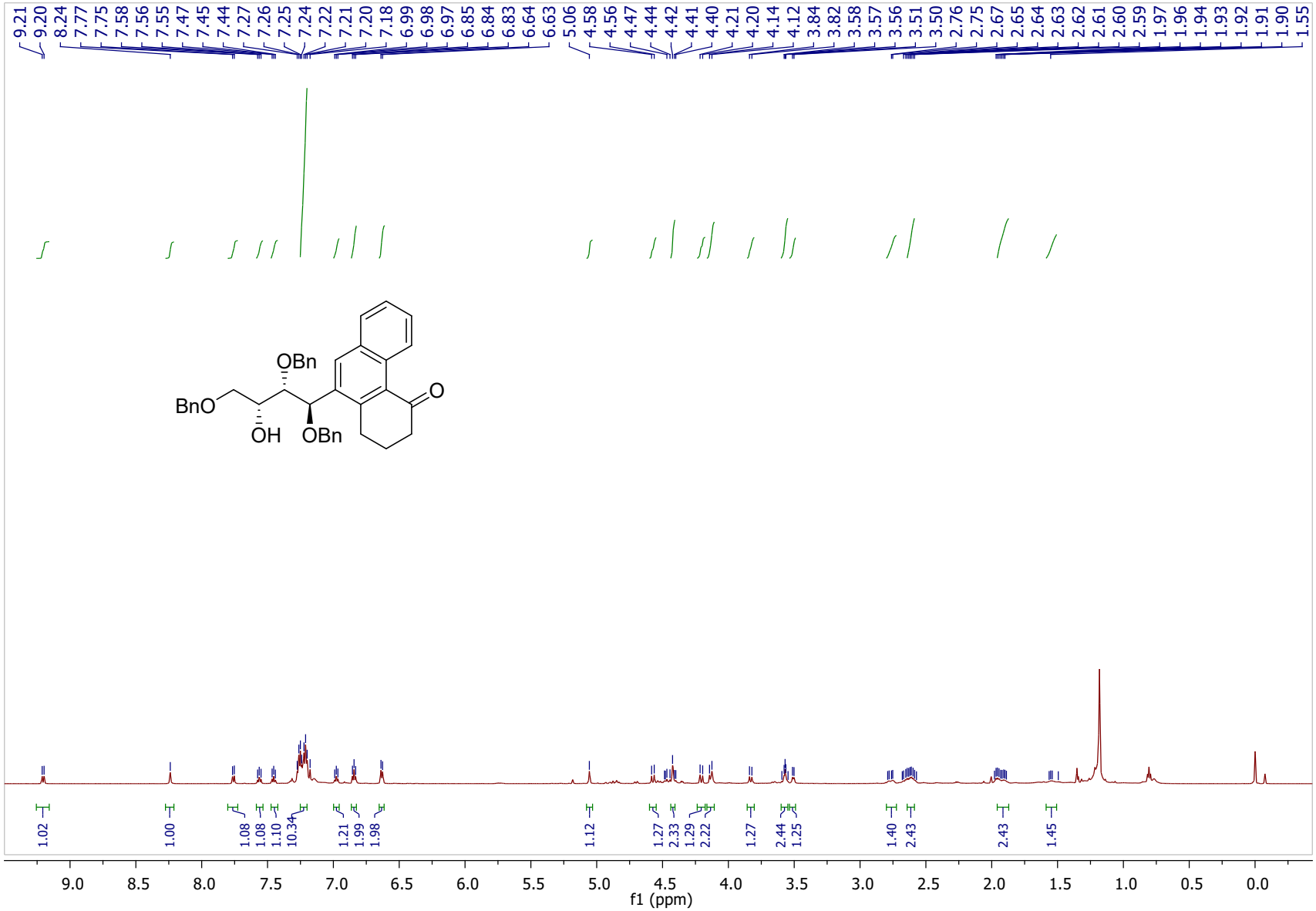
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5a**



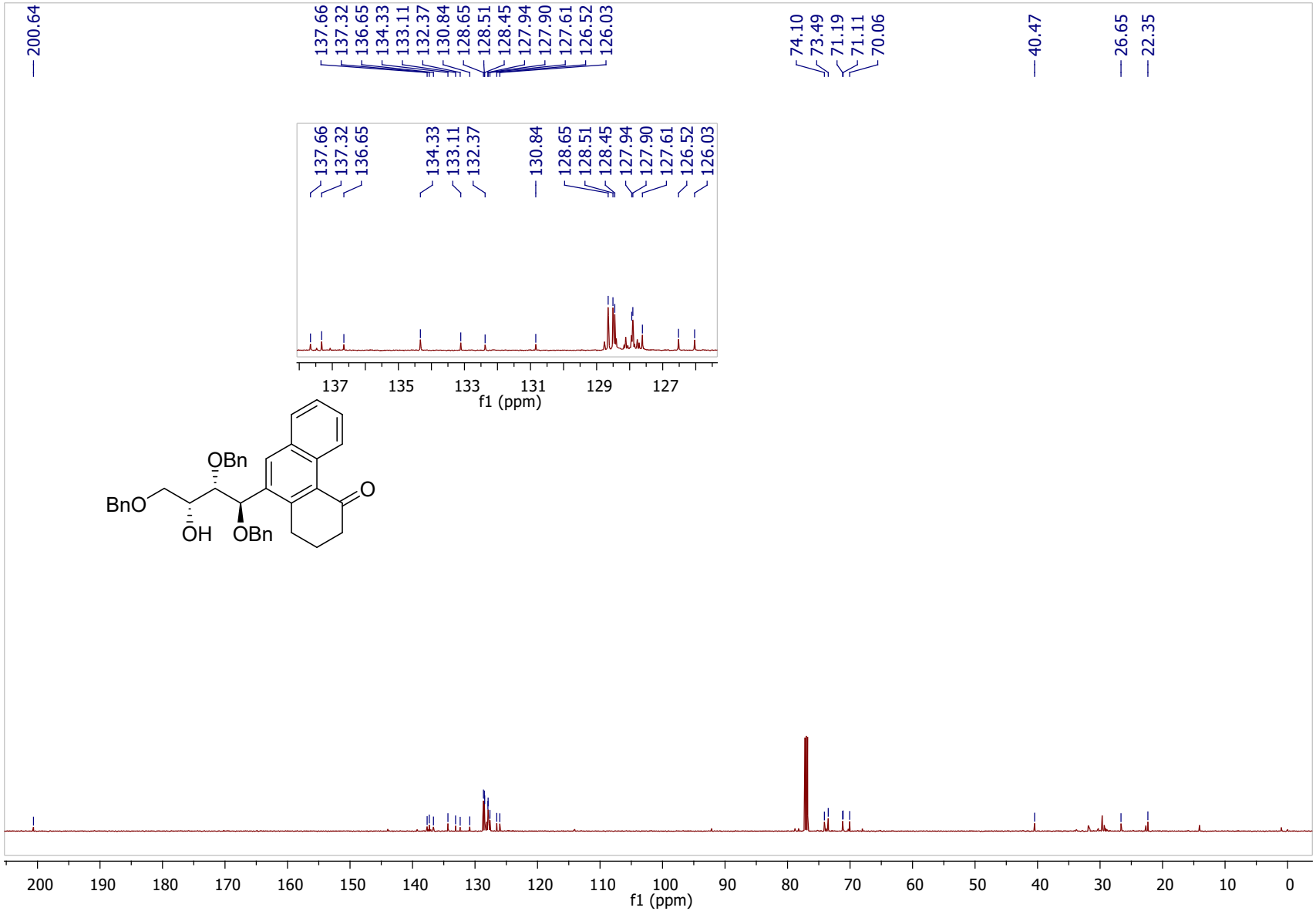
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5b**



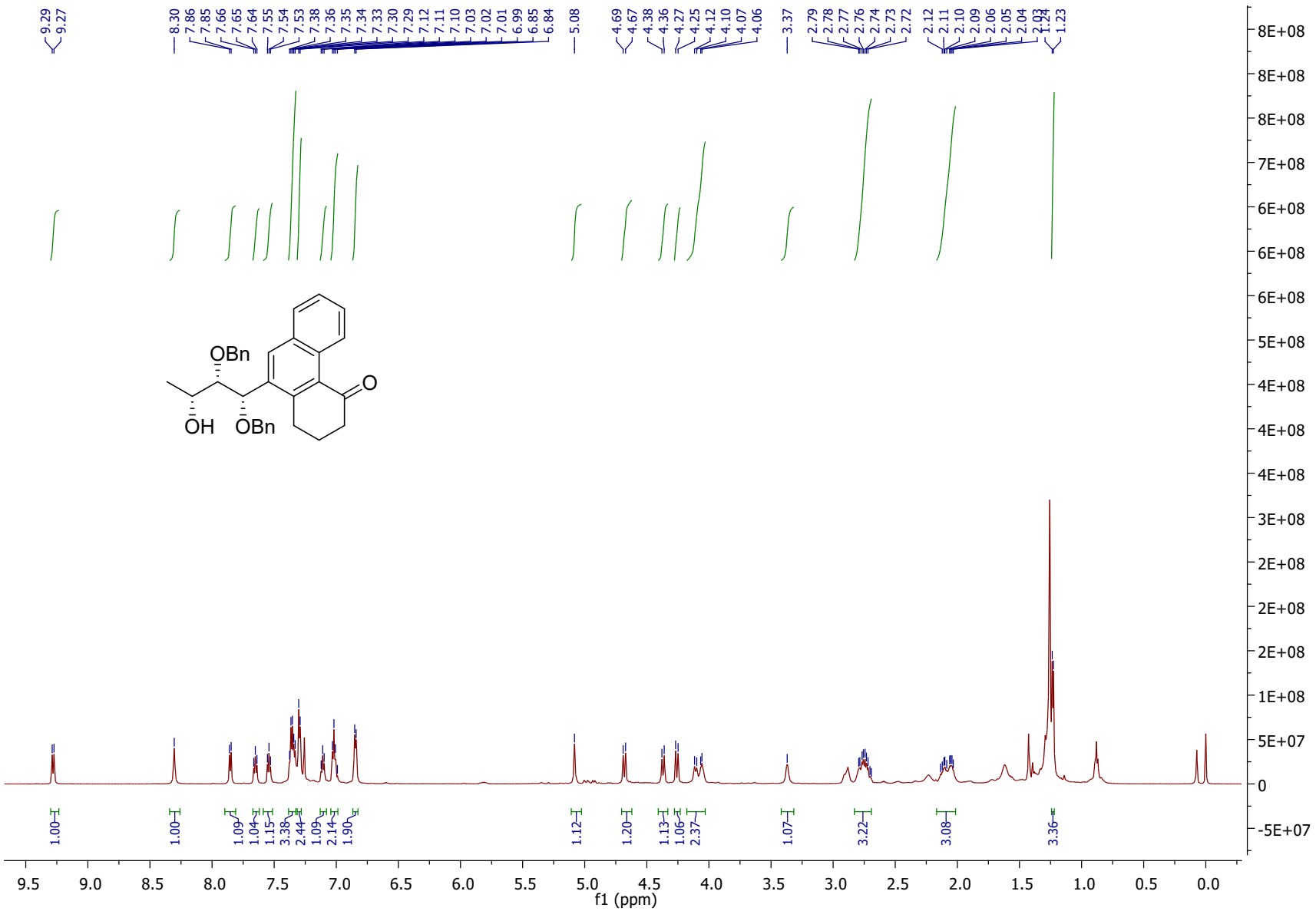
^{13}C NMR (126 MHz, $CDCl_3$) of compound **5b**



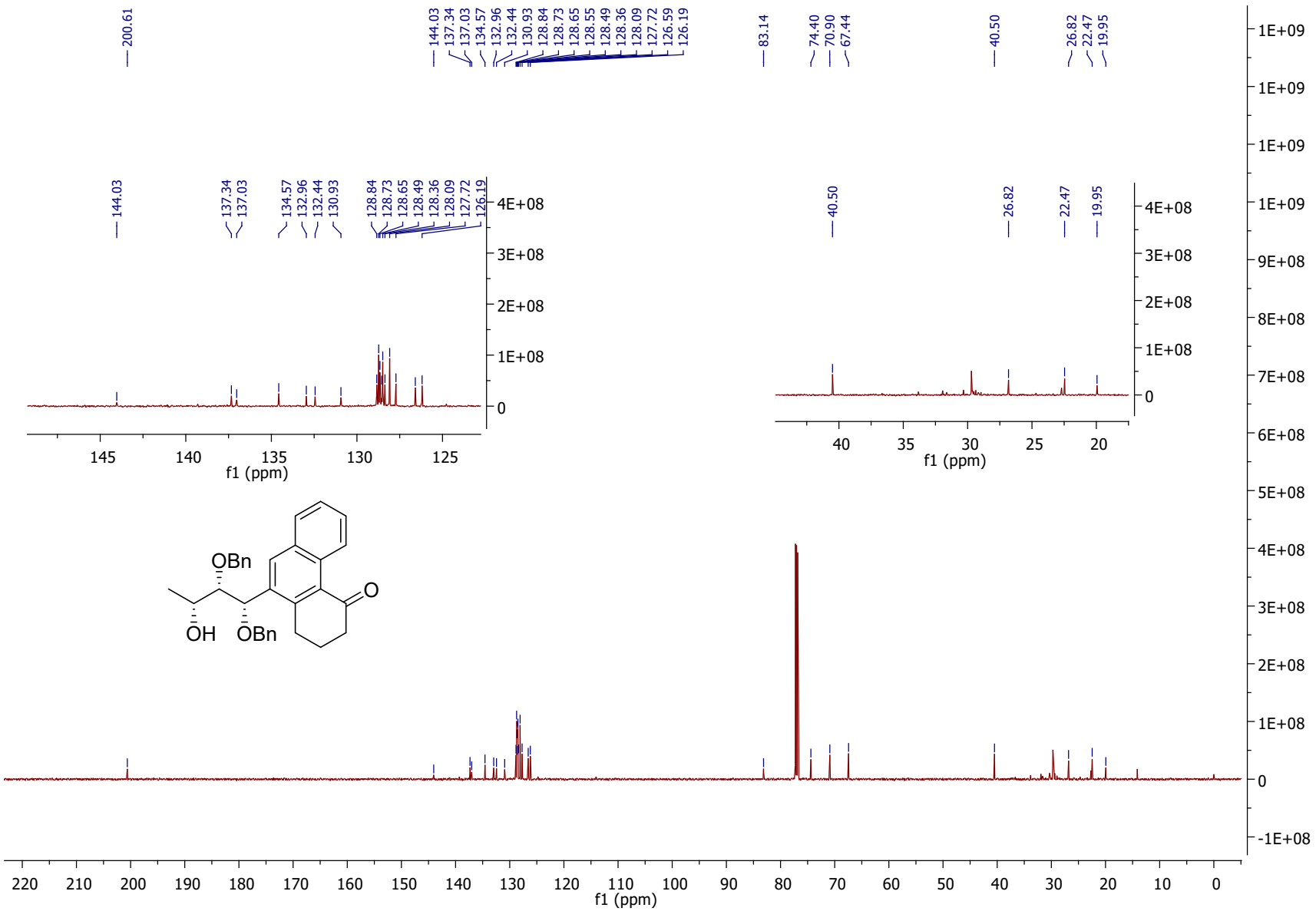
^{1}HNMR (600 MHz, $CDCl_3$) of compound **5c**



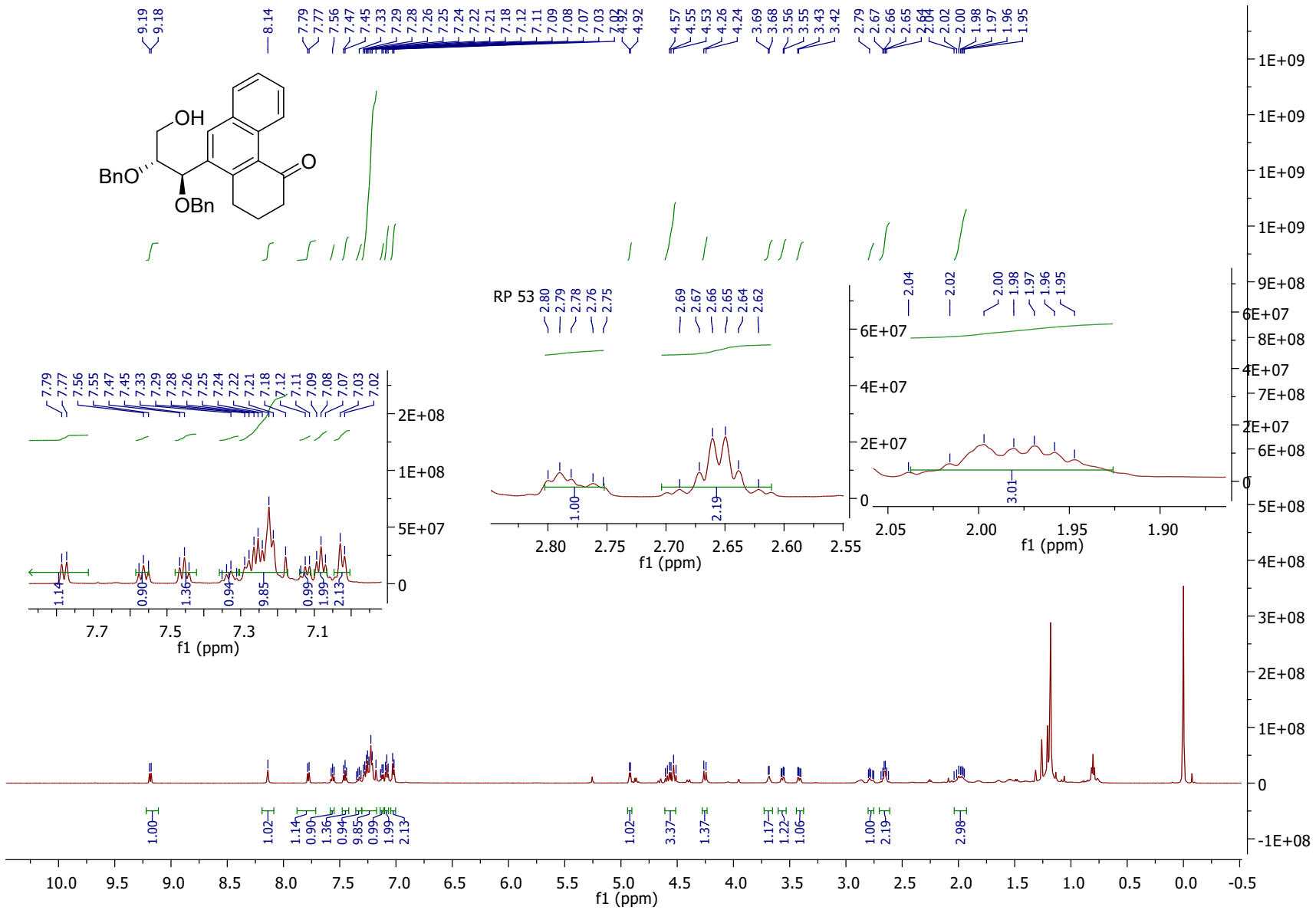
^{13}C NMR (151 MHz, $CDCl_3$) of compound **5c**



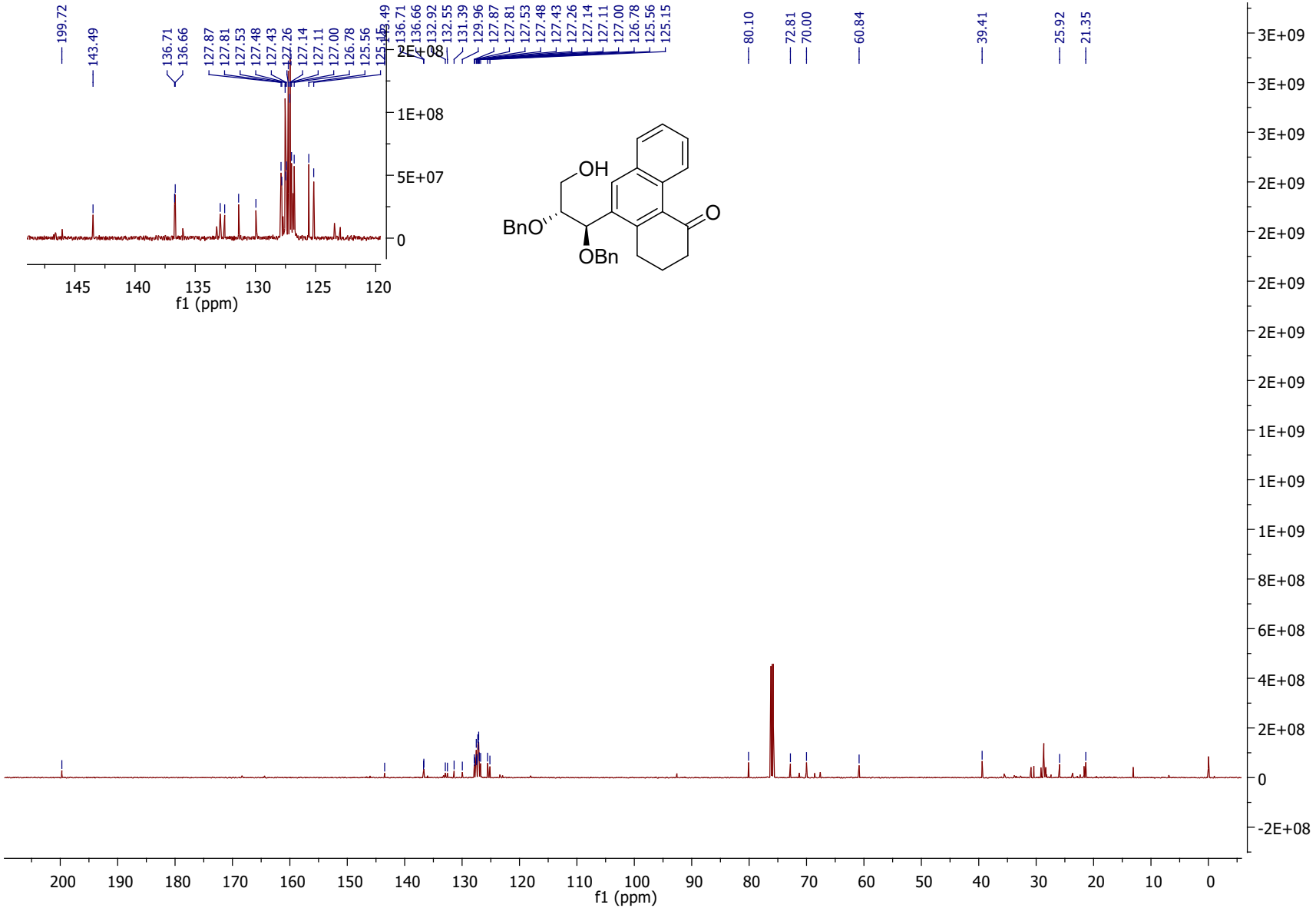
^{1}HNMR (600 MHz, $CDCl_3$) of compound **5d**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **5d**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **5e**



^{13}C NMR (151 MHz, $CDCl_3$) of compound **5e**