Electronic Supplementary Material (ESI) for Chemical Communications
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Enantioselective total synthesis of (-)-neovibsanin G and (-)-14-*epi*-neovibsanin G

Supporting information

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General methods

Anhydrous diethyl ether and tetrahydrofuran were freshly distilled from sodium/benzophenone under argon.

Column chromatography was undertaken with distilled solvents. Petroleum spirit refers to the hydrocarbon fraction with boiling points between 40 – 60 °C. Melting points were determined on a DigiMelt Stanford Research Systems melting point apparatus and are uncorrected. Enantiomeric excess determinations were performed by the University of Queensland Enantioselective Chromatography Facility on a Daicel Chiralpak IC column (4.6 × 250 mm, DAICEL Chemical IND, LDT).

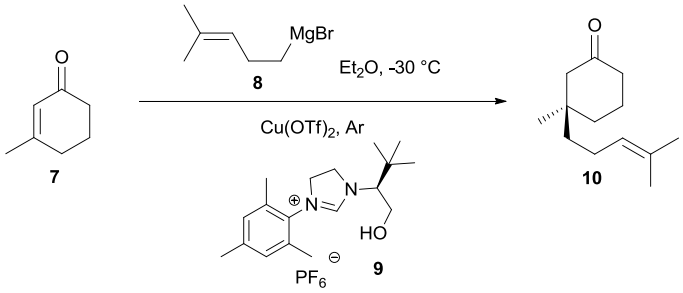
The ^{1}H and ^{13}C NMR spectra were acquired on Bruker AV300 (300 MHz; 75 MHz), AV400 (400 MHz; 100 MHz) or AV500 (500 MHz; 125 MHz) instruments. The ^{1}H and ^{13}C NMR spectra data of the natural products were acquired on a Bruker 900 MHz NMR spectrometer equipped with a cryoprobe. Chemical shifts were reported in parts per million (ppm) on a δ scale relative to the solvent peak (^{1}H, $CDCl_3$ δ 7.24 ppm, C_6D_6 δ 7.15 ppm; ^{13}C $CDCl_3$ δ 77.0 ppm, C_6D_6 δ 128.0 ppm).

High resolution electrospray ionization (HRMS) accurate mass measurements were recorded in positive mode on a Bruker MicrOTOF-Q (quadrupole-Time of Flight) instrument with a Bruker ESI source. Accurate mass measurements were carried out with external calibration using sodium formate as a reference calibrant.

Infrared spectra were recorded on a Perkin-Elmer Spectra 2000 FT-IR spectrometer.

Optical rotations were performed on a JASCO P-2000 polarimeter.

Experimental procedures

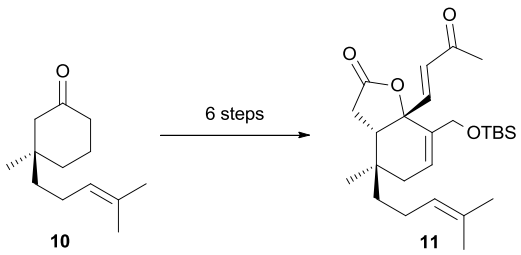


Following a similar procedure to Kehrli et al,[1] a flask was charged with magnesium shavings (4.07 g, 170 mmol), and was dried by heating with a heat gun under vacuum. After charging the flask with argon, anhydrous diethyl ether was added (10 mL) as well as a portion of 5-bromo-2-methylpent-2-ene (4 mL, 30 mmol). Once the reaction was initiated, a solution of remaining 5-bromo-2-methylpent-2-ene (15 mL, 112 mmol) in anhydrous diethyl ether (70 mL) was added via a pressure equalising dropping funnel to maintain a gentle reflux. On completion, the reaction was refluxed for a further 30 minutes, then allowed to cool to room temperature.

Into a separate heat gun dried flask was added **9** (1.89 g, 4.36 mmol) and copper(II) triflate (1.182 g, 3.27 mmol). The flask was then placed under vacuum for 1.5 hours. After charging the flask with argon, anhydrous diethyl ether was added (140 mL), then cooled to -30 °C. The solution of Grignard **8** was added dropwise to the vigorously stirred copper suspension by syringe. Upon addition of Grignard **8**, the reaction initially turns greyish-blue, then bright yellow, and then dark blue. A solution of **7** (12 g, 109 mmol) in anhydrous diethyl ether (480 mL) was added dropwise to the vigorously stirred reaction at -30 °C by cannula, over 1.5 hours, maintaining the reaction at the same temperature. [For smaller scale reactions, the addition of enone **7** solution should be performed via a syringe pump over 30 minutes.] The reaction mixture was stirred for another 15 minutes until starting material was consumed. The reaction mixture was then poured onto saturated ammonium chloride solution (350 mL) and stirred overnight. The reaction was partitioned, and the aqueous phase was extracted with diethyl ether (3 × 200 mL). The combined organic phases were successively washed with saturated sodium bicarbonate solution (350 mL) and brine (350 mL) before drying over magnesium sulfate and evaporating to dryness *in vacuo*. The crude oily product was distilled *in vacuo*. The fraction between 90 and 100 °C at 0.5 mmHg was collected to give **10** as a colorless oil (14.73 g, 70 %). Spectral data matched the data reported for the racemic compound.[2] After oxidation[3] of a small amount of the product to the corresponding enone, the enantiomeric excess of the reaction was determined by chiral HPLC (2 % isopropanol in hexane) as 91 %.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.05 (1H, m), 2.25 (2H, t, *J* = 6.8 Hz), 2.18 (1H, d, *J* = 13.6 Hz), 2.09 (1H, d, *J* = 13.2 Hz), 1.94 – 1.81 (4H, m), 1.65 (3H, s), 1.57 (3H, s), 1.63 – 1.50 (2H, m), 1.26 (2H, m), 0.91 (3H, s).

$[\alpha]^{24}_D$ -13.2 (*c* 13.3, Et_2O)



Compound **11** was synthesised from **10** according to the procedures reported in the racemic series.[3-5] Spectral data matched the data reported for the racemic compound.[5]

m.p. 90.5 – 91.5 °C (recrystallised from petroleum spirit).

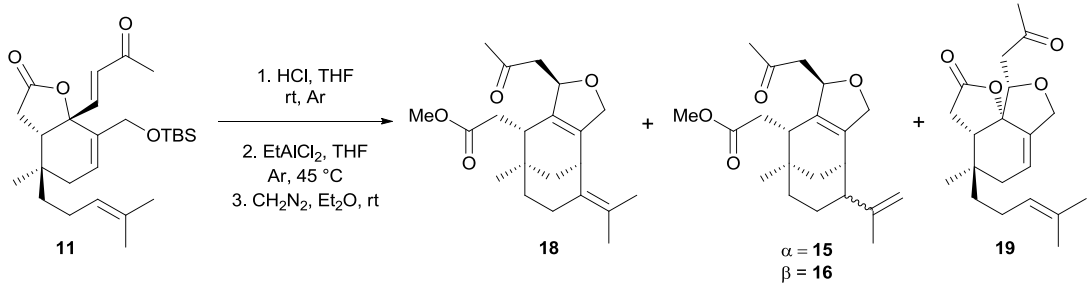
^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.61 (1H, d, *J* = 15.8 Hz), 6.31 (1H, d, *J* = 15.7 Hz), 6.03 (1H, m), 4.98 (1H, t, *J* = 7.0 Hz), 4.06 (2H, m), 2.55 – 2.32 (3H, m), 2.20 (3H, s), 2.11 – 2.02 (2H, m), 1.96 – 1.85 (2H, m), 1.62 (3H, s), 1.53 (3H, s), 1.43 – 1.37 (1H, m), 1.24 – 1.18 (1H, m), 0.86 (3H, s), 0.84 (9H, s), -0.01 (3H, s), -0.02 (3H, s).

^{13}C NMR ($CDCl_3$, 125 MHz): 197.0, 175.1, 146.2, 133.1, 132.0, 128.3, 124.8, 123.6, 84.6, 61.3, 48.3, 40.2, 34.4, 34.1, 30.4, 28.3, 25.8, 25.6, 21.9, 21.8, 18.2, 17.6, -5.50, -5.55.

HRMS (ESI) Calculated for $C_{26}H_{42}O_4SiNa^+$ [M + Na^+] 469.2745 Found 469.2755.

IR (ATR, cm^{-1}) *v* 2958, 2855, 1766, 1252, 1116, 982, 776.

$[\alpha]^{24}_D$ +33.9 (*c* 2.0, EtOAc)



Part A – To a stirred solution of **11** (60.6 mg, 0.136 mmol) in anhydrous tetrahydrofuran (7 mL) was added hydrochloric acid (32 %, 70 μL) dropwise at room temperature under argon. After 1 hour, the reaction was quenched by addition of saturated sodium bicarbonate solution (7.5 mL), then extracted with diethyl ether (3 × 12.5 mL). The combined organic layers were washed with brine (12.5 mL), dried over magnesium sulfate, and then concentrated *in vacuo* to give **19** as a colourless oil. No further purification was performed.

Part B – A mixture of **19** above in anhydrous tetrahydrofuran (4.9 mL) was cooled to -78 °C under argon, to which ethyl aluminium dichloride (1.8 M in toluene, 980 μL, 1.76 mmol) was added dropwise. The reaction mixture was then warmed rapidly to room temperature, then heated to 45 °C for 4 hours, during which time the reaction mixture became reddish-brown in colour. On cooling to room temperature, the reaction mixture was diluted with ethyl acetate (7.5 mL) before carefully adding water (7.5 mL) while vigorously stirring. The reaction

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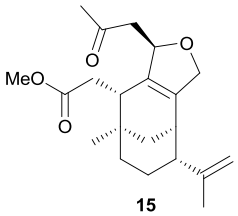
mixture was extracted with ethyl acetate (3 × 12.5 mL). The combined organic phases were washed with brine (12.5 mL), dried over magnesium sulfate, then concentrated *in vacuo* to give a reddish-brown semi-solid. No further purification was performed.

Part C- Using smooth glassware and a smooth stir bar, the crude material was dissolved in diethyl ether (7 mL) at room temperature and a solution of diazomethane in diethyl ether was added dropwise, until TLC analysis (silica, 10:1 diethyl ether/dichloromethane) showed complete consumption of the carboxylic acids, which appear as baseline spots. After degassing the reaction with a stream of nitrogen, the solvent was removed *in vacuo* to give a reddish-brown oil. No further purification was performed.

The crude material was subjected to the procedure outlined in Part A again. This was necessary to encourage any primary alcohols isomeric to the product to cyclise to form the dihydrofuran ring. The crude oil was purified by column chromatography (silica gel, 1:3 ethyl acetate/petroleum spirit) to give **19** (6 mg, 13 %) and a mixture of **15**, **16** and **18** (28 mg, 60 %, 73 % brsm, 1:2:1.5). The isomeric methyl esters can be separated completely through repeated and careful argentation chromatography in the dark (1:100 crude product to silica ratio, 10% silver nitrate on silica gel, 1:3 ethyl acetate/petroleum spirit with 1% triethylamine). The silver nitrate impregnated silica gel was prepared by forming a silica gel slurry with a solution of silver nitrate in acetonitrile (10% w/w silver nitrate to silica gel), and removing the acetonitrile *in vacuo* in the dark.



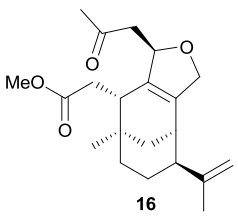
15

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.37 (1H, br m), 4.90 (1H, q, *J* = 1.5 Hz), 4.83 (1H, s), 4.44 (1H, ddd, *J* = 12.1, 5.5, 2.9 Hz), 4.32 (1H, complex d, *J* = 12.1), 3.37 (3H, s), 2.65 (1H, dd, *J* = 14.9, 3.4 Hz), 2.43 (1H, dd, *J* = 15.0, 8.9 Hz), 2.41 (1H, m), 2.19 (1H, m), 2.18 (1H, dd, *J* = 16.0, 7.0 Hz), 2.08 (1H, dd, *J* = 16.0, 6.0 Hz), 1.93 (3H, s), 1.80 (1H, br s), 1.60 – 1.52 (1H, m), 1.55 (3H, s), 1.49 – 1.39 (2H, m), 1.26 (1H, dtd, *J* = 12, 4.5, 2.0 Hz), 1.21 (1H, dd, *J* = 13, 2.5 Hz), 1.08 (1H, m), 0.78 (3H, s).

^{13}C NMR (C_6D_6, 125 MHz): δ = 205.2, 173.4, 146.2, 137.6, 137.4, 111.1, 83.3, 74.7, 51.4, 48.4, 40.2, 39.7, 37.7, 35.5, 32.8, 30.9, 30.6, 29.9, 28.2, 22.4, 22.3.

HRMS (ESI) Calculated for $C_{21}H_{30}ONa^+$ [M + Na^+] 369.2036 Found 369.2038.

$[\alpha]^{25}_D$ +0.31 (*c* 0.76, EtOAc)



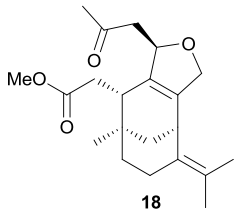
16

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.36 (1H, br m), 4.70 (1H, q, *J* = 1.5 Hz), 4.66 (1H, s), 4.66 – 4.62 (1H, m), 4.31 (1H, dt, *J* = 12.0, 2.6 Hz), 3.37 (3H, s), 2.67 (1H, dd, *J* = 14.9, 3.5 Hz), 2.49 (1H, br m), 2.46 (1H, dd, *J* = 15.0, 8.3 Hz), 2.32 (1H, br s), 2.13 (2H, m), 1.90 (3H, s), 1.68 – 1.35 (5H, m), 1.52 (3H, d, *J* = 0.5 Hz), 1.10 – 1.05 (1H, m), 0.94 (1H, dd, *J* = 12.6, 2.3 Hz), 0.81 (3H, s).

^{13}C NMR (C_6D_6, 125 MHz): δ = 205.4, 173.3, 148.0, 138.4, 134.7, 110.0, 83.1, 76.6, 51.4, 49.1, 45.1, 42.7, 39.1, 38.0, 35.6, 32.7, 32.3, 30.9, 28.0, 23.6, 22.5.

HRMS (ESI) Calculated for $C_{21}H_{30}ONa^+$ [M + Na^+] 369.2036 Found 369.2029.

$[\alpha]^{24}_D$ -29.3 (*c* 0.39, EtOAc)



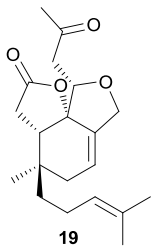
18

^{1}H NMR (C_6D_6, 500 MHz): δ = 5.39 (1H, br m), 4.45 – 4.36 (2H, m), 3.39 (3H, s), 3.04 (1H, br s), 2.62 (1H, dd, *J* = 14.9, 3.3 Hz), 2.48 (1H, t, *J* = 6.2 Hz), 2.40 (1H, dd, *J* = 14.9, 9.0 Hz), 2.24 (1H, dd, *J* = 15.9, 6.9 Hz), 2.22 – 2.16 (1H, m), 2.12 (1H, dd, *J* = 15.9, 6.2 Hz), 2.08 – 2.00 (1H, m), 1.89 (3H, s), 1.55 (3H, s), 1.51 (1H, m), 1.48 (3H, d, *J* = 1.2 Hz), 1.44 (1H, m), 1.22 (1H, m), 1.05 (1H, dd, *J* = 12.5, 2.3 Hz), 0.79 (3H, s).

^{13}C NMR (C_6D_6, 125 MHz): δ = 205.3, 173.4, 136.8, 136.7, 129.7, 122.7, 83.1, 74.9, 51.5, 48.3, 41.7, 39.6, 35.75, 35.66, 32.8, 32.5, 30.7, 27.7, 23.7, 20.6, 19.9.

HRMS (ESI) Calculated for $C_{21}H_{30}ONa^+$ [M + Na^+] 369.2036 Found 369.2042.

$[\alpha]^{24}_D$ -148.1 (*c* 1.3, EtOAc)



19

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.82 (1H, m), 5.00 (1H, m), 4.44 (1H, dp, *J* = 11.5, 1.5 Hz), 4.28 (1H, d, *J* = 11.0 Hz), 4.14 (1H, dd, *J* = 8.0, 4.5 Hz), 2.91, (1H, dd, *J* = 17.0, 7.5 Hz), 2.59 – 2.47 (4H, m), 2.18 (3H, s), 2.03 (1H, m), 1.94 (1H, dd, *J* = 17.5, 6.0 Hz), 1.90 – 1.79 (2H, m), 1.63 (3H, d, *J* = 1.0 Hz), 1.54 (3H, s), 1.29 – 1.21 (2H, m), 0.92 (3H, s).

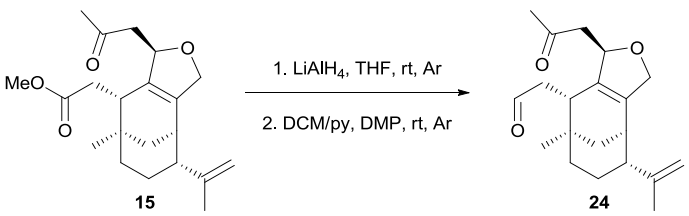
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 206.3, 175.1, 136.1, 131.9, 123.7, 123.4, 88.2, 80.3, 68.4, 43.0, 40.8, 38.8, 37.0, 32.0, 31.01, 30.99, 25.6, 23.0, 22.3, 17.5.

^{13}C NMR (C_6D_6, 100 MHz): δ = 205.3, 174.1, 136.8, 131.5, 124.6, 123.1, 87.4, 81.2, 68.4, 43.0, 40.6, 39.2, 36.5, 32.9, 31.0, 30.6, 25.8, 22.6, 22.4, 17.6.

HRMS (ESI) Calculated for $C_{20}H_{28}O_4Na^+$ [M + Na^+] 355.1880 Found 355.1875.

$[\alpha]^{23}_D$ -29.3 (*c* 0.49, EtOAc)

IR (ATR, cm^{-1}) *v* 2973, 2928, 2869, 1777, 1732, 1717, 1380, 1162, 1116, 833, 570.



15 24

Following a procedure similar to that of Chen,[6] methyl ester **15** (7.4 mg, 0.021 mmol) was dissolved in anhydrous tetrahydrofuran (1 mL) under argon. Lithium aluminium hydride (5.2 mg, 0.137 mmol) was then added in one portion at room temperature and stirred under argon for 10 minutes. The reaction was quenched with sodium sulfate decahydrate and stirred until

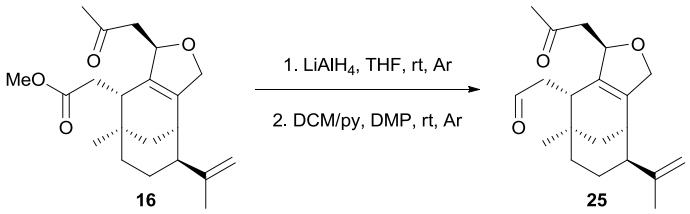
the reaction became completely white, before filtering through celite and eluting with ethyl acetate. After removing the solvent *in vacuo*, the residue was taken up in dichloromethane/pyridine (1:1, 0.5 mL) under argon, to which was added Dess-Martin periodinane (38 mg, 0.090 mmol) in one portion. After 10 minutes, TLC showed that the reaction was complete. The reaction was diluted with diethyl ether (1 mL), and the resulting white suspension was poured onto 10 % sodium thiosulfate solution (1 mL) and saturated sodium bicarbonate solution (1 mL), and stirred until the white precipitate was dissolved. The layers were partitioned, and the aqueous layer was extracted with diethyl ether (2 × 2 mL). The combined organic layers were successively washed with saturated sodium bicarbonate solution (2 mL) and brine (2 mL), before drying over magnesium sulfate and removing the solvent *in vacuo*. Column chromatography (silica gel, 1:3 ethyl acetate/petroleum spirit) gave the aldehyde product **24** (4.9 mg, 73 %) as an amorphous solid.

^{1}H NMR (C_6D_6, 500 MHz): δ = 9.34 (1H, t, *J* = 1.5 Hz), 5.25 (1H, br m), 4.91 (1H, sext, *J* = 1.5 Hz), 4.84 (1H, br m), 4.43 (1H, ddd, *J* = 12.2, 5.5, 3.0 Hz), 4.29 (1H, ddd, *J* = 12.2, 1.8, 0.9 Hz), 2.43 (1H, dd, *J* = 15.2, 4.5 Hz), 2.39 (1H, dd, *J* = 15.0, 7.8 Hz), 2.29 (1H, br m), 2.19 (1H, br m), 1.98 (1H, ddd, *J* = 17.8, 7.3, 1.7 Hz), 1.89 (1H, ddd, *J* = 17.8, 4.2, 1.4 Hz) 1.89 (3H, s), 1.80 (1H, br m), 1.57 – 1.52 (2H, m), 1.56 (3H, d, *J* = 0.5 Hz), 1.42 – 1.35 (1H, m), 1.22 – 1.17 (2H, m), 0.99 (1H, m), 0.62 (3H, s).

^{13}C NMR (C_6D_6, 125 MHz): δ = 205.2, 200.3, 146.0, 137.4, 137.3, 111.2, 83.0, 74.7, 48.4, 44.7, 40.2, 37.6, 37.1, 32.6, 30.8, 30.6, 30.3, 28.8, 22.5, 22.2.

HRMS (ESI) Calculated for $C_{20}H_{28}O_3Na^+$ [M + Na^+] 339.1931 Found 339.1937.

$[\alpha]^{24}_D$ +1.35 (*c* 0.49, EtOAc)



16 25

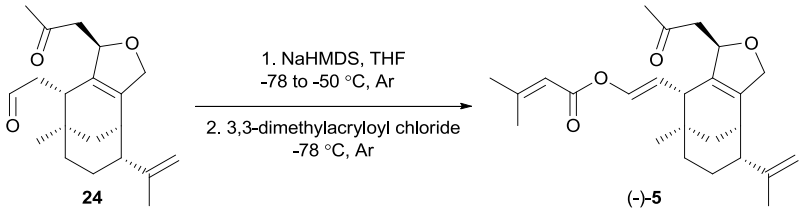
Treating **16** (3mg, 0.0087 mmol) with an analogous procedure to its epimer **15** gave **25** as an oil (1.6 mg, 59 %).

^{1}H NMR (C_6D_6, 500 MHz): δ = 9.35 (1H, t, *J* = 1.7 Hz), 5.21 (1H, br m), 4.70 (1H, q, *J* = 1.4 Hz), 4.65 (1H, s), 4.61 (1H, ddd, *J* = 12.1, 5.4, 3.3 Hz), 4.28 (1H, dddd, *J* = 12.1, 3.1, 2.2, 0.7 Hz), 2.50 (1H, dd, *J* = 15.0, 4.4 Hz), 2.39 (1H, dd, *J* = 14.7, 7.2 Hz), 2.35 (1H, br m), 2.29 (1H, br s), 1.96 (1H, dd, *J* = 7.3, 1.8 Hz), 1.94 (1H, dd, *J* = 4.0, 1.6 Hz), 1.87 (3H, s), 1.65 (1H, br d, *J* = 11.3 Hz), 1.61 – 1.53 (1H, m), 1.52 (3H, s), 1.49 – 1.45 (1H, m), 1.39 – 1.27 (2H, m), 1.03 (1H, td, *J* = 13.6, 5.2 Hz), 0.91 (1H, dd, *J* = 12.6, 2.4 Hz), 0.65 (3H, s).

^{13}C NMR (C_6D_6, 125 MHz): δ = 205.5, 200.4, 147.9, 138.1, 134.8, 110.0, 82.9, 76.7, 49.0, 45.1, 44.7, 42.5, 38.3, 36.9, 32.2, 30.9, 30.2, 28.7, 23.5, 22.5.

HRMS (ESI) Calculated for $C_{20}H_{28}O_3Na^+$ [M + Na^+] 339.1931 Found 339.1925.

$[\alpha]^{24}_D$ -35.9 (*c* 0.16, EtOAc)



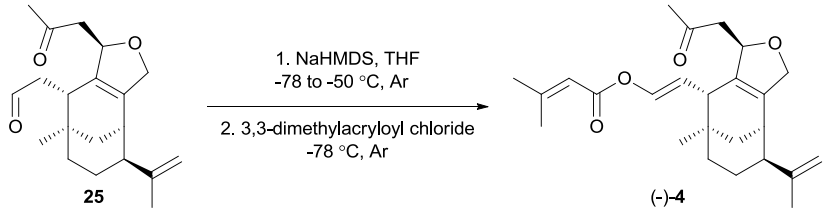
To a solution of **24** (2 mg, 0.0063 mmol) in anhydrous tetrahydrofuran (1 mL) was added dropwise sodium hexamethyldisilazide solution (0.25 M in tetrahydrofuran, 25 µL, 0.0063 mmol) at -78 °C under argon. The reaction was warmed to -50 °C and held at this temperature for 5 minutes, then immediately cooled to -78 °C, before a solution of 3,3-dimethylacryloyl chloride in anhydrous tetrahydrofuran (5 % v/v, 14 µL, 0.0087 mmol) was added to the reaction dropwise under argon. The reaction mixture was quenched by the addition of saturated sodium bicarbonate solution (1 mL). After warming to room temperature, and adding water to dissolve any solids, the reaction mixture was extracted with diethyl ether (3 × 2 mL). The combined organic layers were washed with brine (2 mL), dried over magnesium sulfate, before evaporating *in vacuo*. Purification of the crude mixture by column chromatography (silica gel, 1:12 ethyl acetate/petroleum spirit with 1 % triethylamine) gave (-)-**5** (0.24 mg, 9 %, 13 % brsm), which was further purified by chiral HPLC to give a colorless oil. Spectra data of (-)-**5** matched that of natural 14-*epi*-neovibsanin G.[7]

^{1}H NMR (C_6D_6, 900 MHz): δ 7.39 (1H, d, *J* = 12.5 Hz), 5.64 (1H, m), 5.30 (1H, m), 5.22 (1H, dd, *J* = 12.5, 10.5 Hz), 4.93 (1H, br s), 4.89 (1H, br s), 4.44 (1H, ddd, *J* = 12.0, 5.5, 3.0 Hz), 4.32 (1H, br d, *J* = 12.4 Hz), 2.45 (1H, dd, *J* = 14.3, 3.8 Hz), 2.37 (1H, dd, *J* = 14.0, 8.2 Hz), 2.24 – 2.22 (2H, m), 2.03 (3H, d, *J* = 0.9 Hz), 1.96 (3H, s), 1.81 (1H, br s), 1.68-1.64 (1H, m), 1.60 (1H, m), 1.57 (3H, s), 1.46 (1H, td, *J* = 13.5, 5.5 Hz), 1.36 (3H, s), 1.29 (1H, dd, *J* = 13.0, 2.1 Hz), 1.22 (1H, br d, *J* = 13.9 Hz), 1.18 (1H, br d, *J* = 12.6 Hz), 0.77 (3H, s).

^{13}C NMR (C_6D_6, 225 MHz): δ 205.3, 163.3, 159.7, 146.1, 137.5, 136.5, 136.4, 115.2, 114.0, 111.3, 83.6, 74.9, 48.4, 42.7, 40.1, 37.6, 33.0, 30.9, 30.41, 30.37, 29.7, 27.0, 22.6, 22.1, 20.2.

HRMS (ESI) Calculated for $C_{25}H_{34}O_4Na^+$ [M + Na^+] 421.2349 Found 421.2359.

$[\alpha]^{24}_D$ -153.1 (*c* 0.036, EtOH)



Treating a mixture of **24** and **25** (1:1 ratio, 9.7 mg, 0.031 mmol, 0.015 mmol of **25**) with an analogous procedure to **24** gave (-)-**4** as an oil (0.5 mg, 8 %, 12 % brsm), which was further purified by chiral HPLC to give a colorless oil. Spectra data† of (-)-**4** matched that of natural neovibsanin G.[7]

^{1}H NMR (C_6D_6, 900 MHz): δ 7.40 (1H, d, *J* = 12.4 Hz), 5.63 (1H, m), 5.24 (1H, m), 5.17 (1H, dd, *J* = 12.4, 10.6 Hz), 4.70 (2H, s), 4.62 (1H, ddd, *J* = 11.9, 5.5, 3.1 Hz), 4.30 (1H, m), 2.56 (1H, dd, *J* = 13.8, 3.9 Hz), 2.41 (1H, dd, *J* = 14.0, 7.0 Hz), 2.37 (1H, m), 2.34 (1H, br s), 2.03 (3H, d, *J* = 0.90 Hz), 1.97 (3H, s), 1.70 (2H, m), 1.53 (3H, s), 1.51 (1H, m), 1.46 (1H, dt, *J* = 12.5, 3.2 Hz), 1.40 (1H, m), 1.35 (3H, d, *J* = 1.0 Hz), 1.12 (1H, m), 1.02 (1H, dd, *J* = 12.5, 2.2 Hz), 0.79 (3H, s).

^{13}C NMR (C_6D_6, 225 MHz): δ 205.8, 163.3, 159.6, 147.9, 137.2, 136.3, 134.9, 115.2, 114.3, 110.1, 83.9, 77.0, 48.5, 45.0, 42.5, 42.3, 38.3, 32.9, 32.6, 30.9, 29.5, 27.0, 23.5, 22.5, 20.2.

HRMS (ESI) Calculated for $C_{25}H_{34}O_4Na^+$ [M + Na^+] 421.2349 Found 421.2356.

$[\alpha]^{22}_D$ -152.6 (*c* 0.02, EtOH)

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† The 1H and 13C spectra of (-)-4 and (-)-5 matched the spectra of natural neovibsanin G and 14-*epi*-neovibsanin G provided by Prof. Y. Fukuyama in every way. However, there are a number of typographical discrepancies between the spectra of natural neovibsanin G and the its tabulated NMR data in the original article[7]. The chemical shifts of neovibsanin G at the C-10 position should read 2.37 and 42.5 ppm (^{1}H and ^{13}C respectively), while at C-18, the ^{1}H chemical shifts should read 4.62 and 4.30 ppm.

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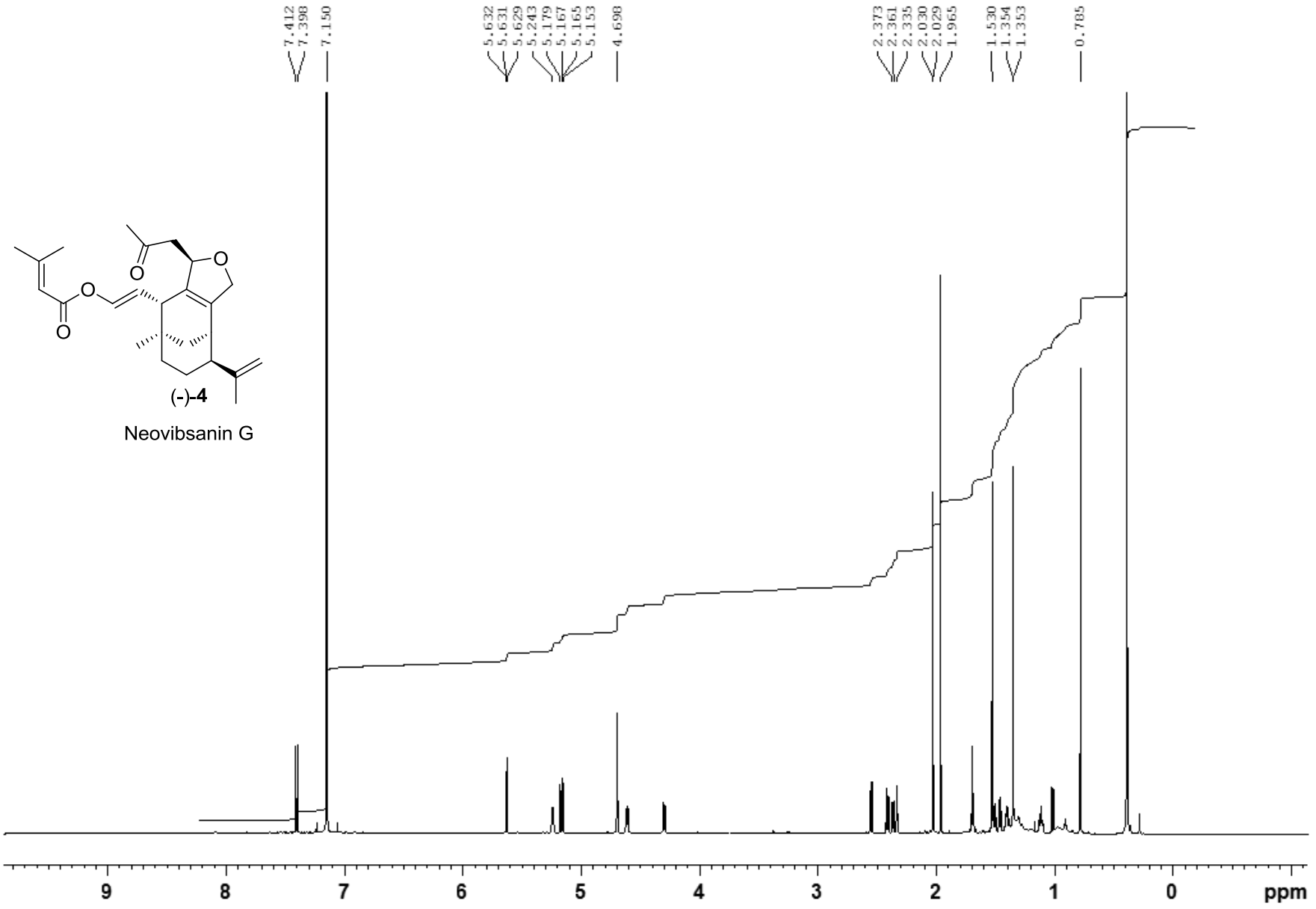

(-)-**4**

Neovibsanin G

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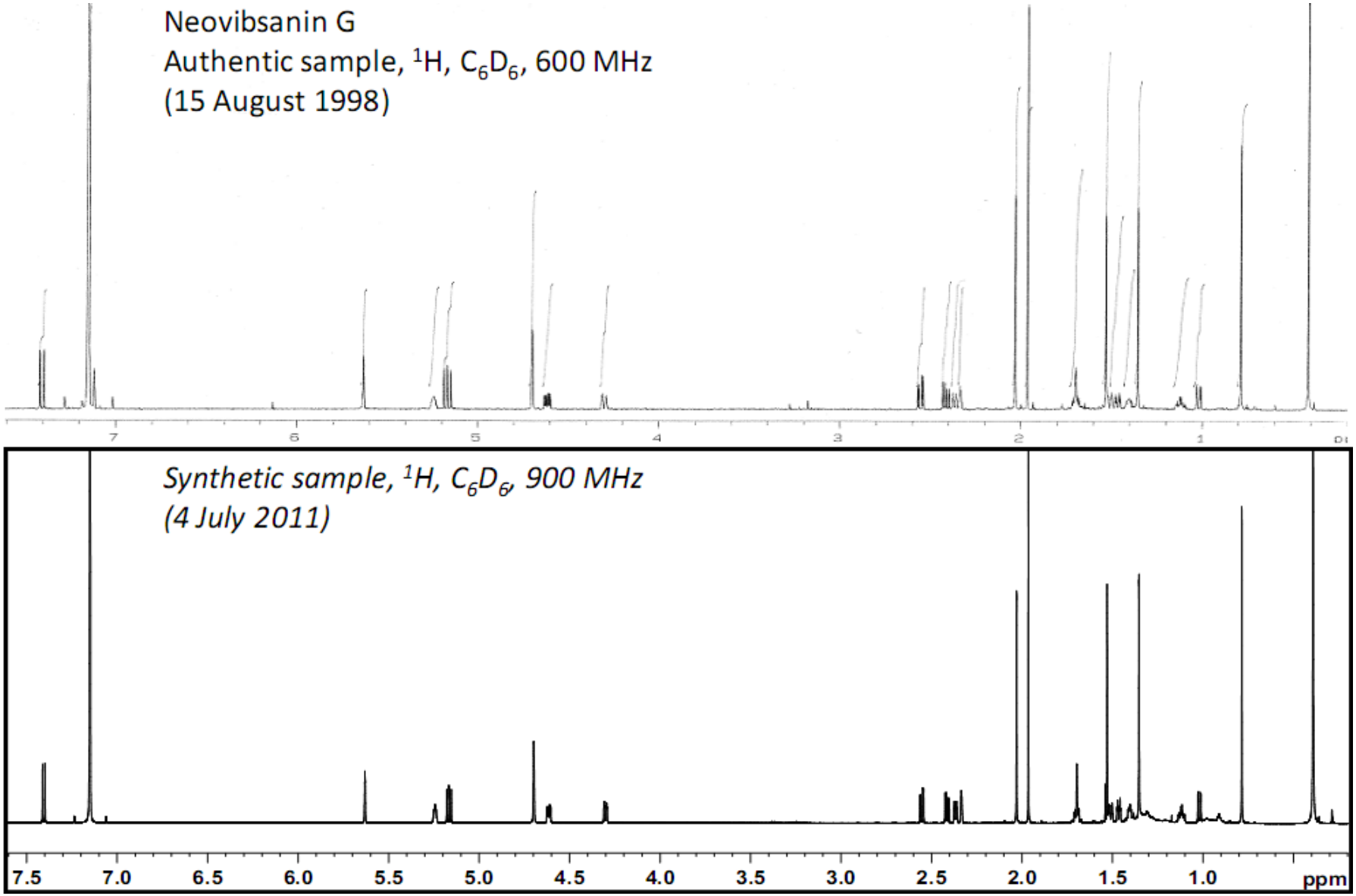

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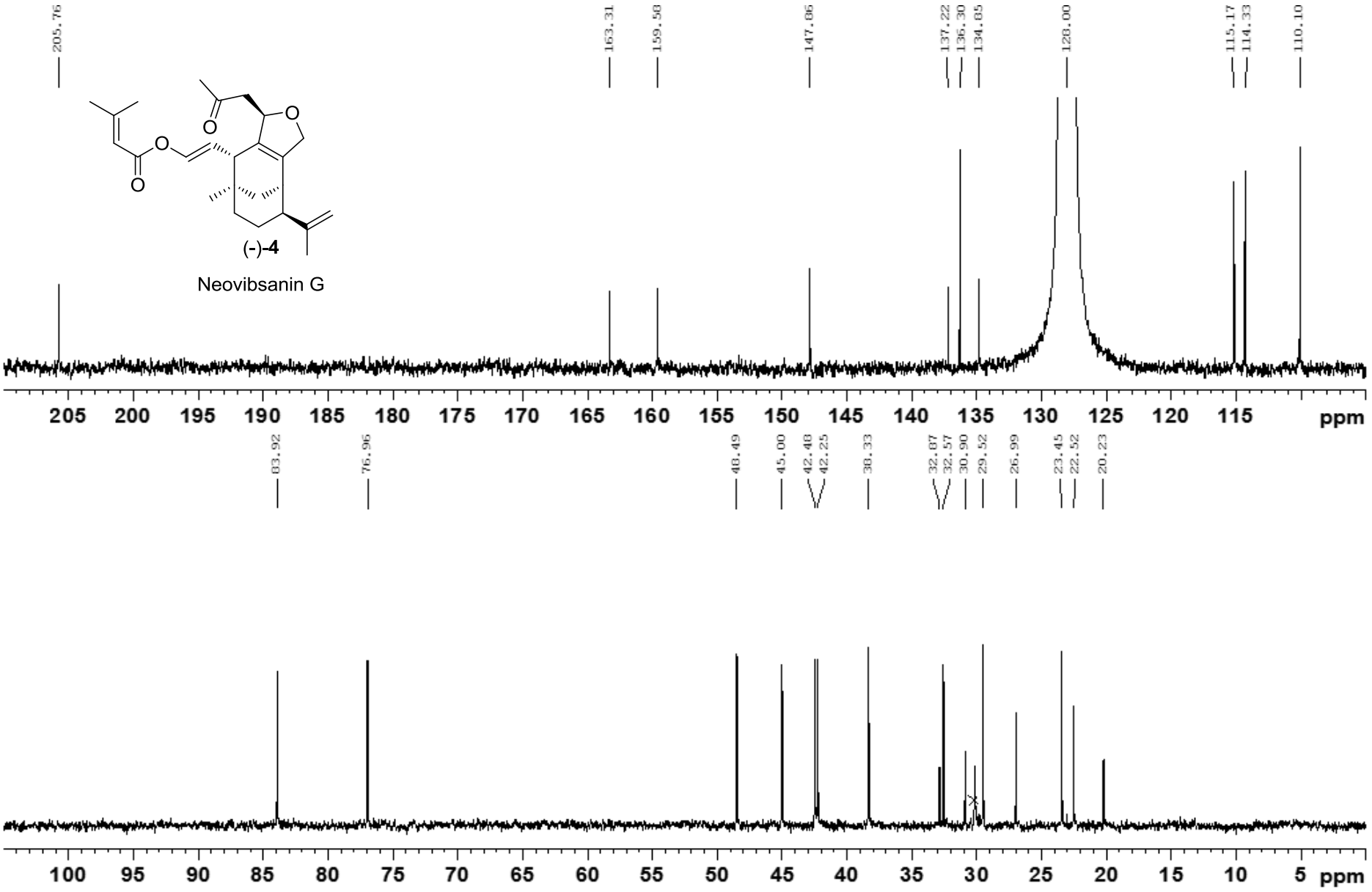

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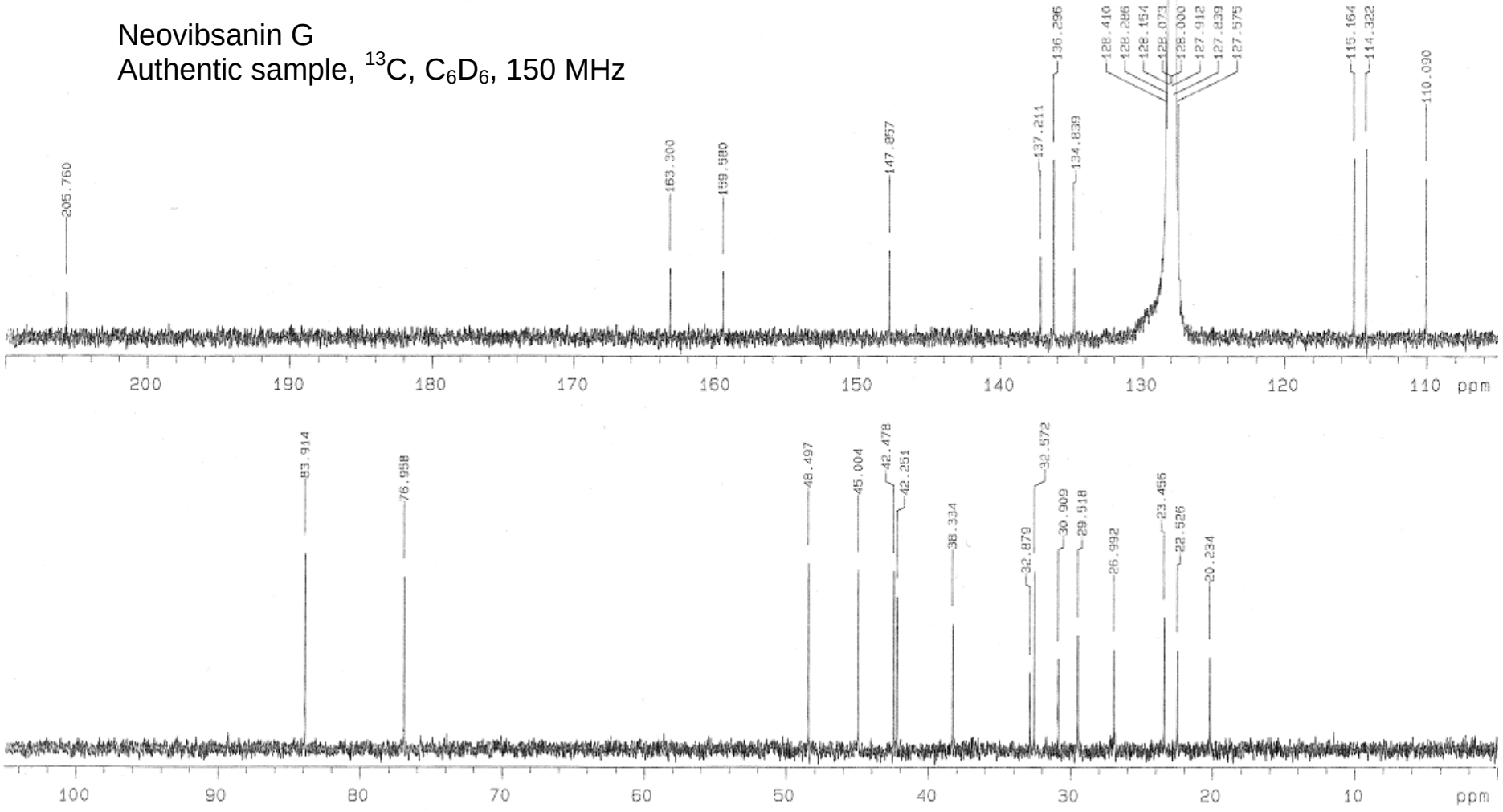
Neovibsanin G
Authentic sample, ^{13}C, C_6D_6, 150 MHz



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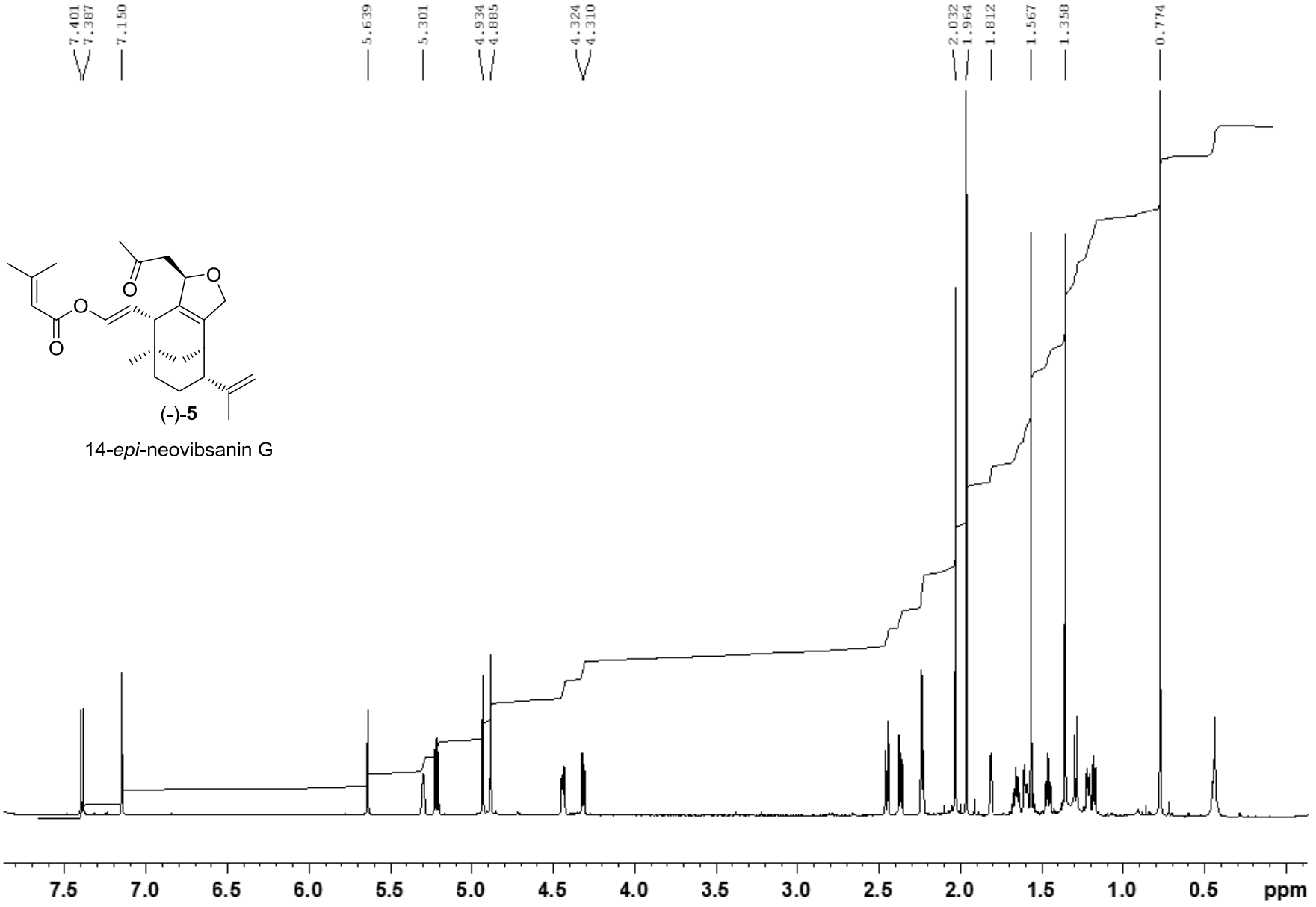

(-)-**5**

14-*epi*-neovibsanin G

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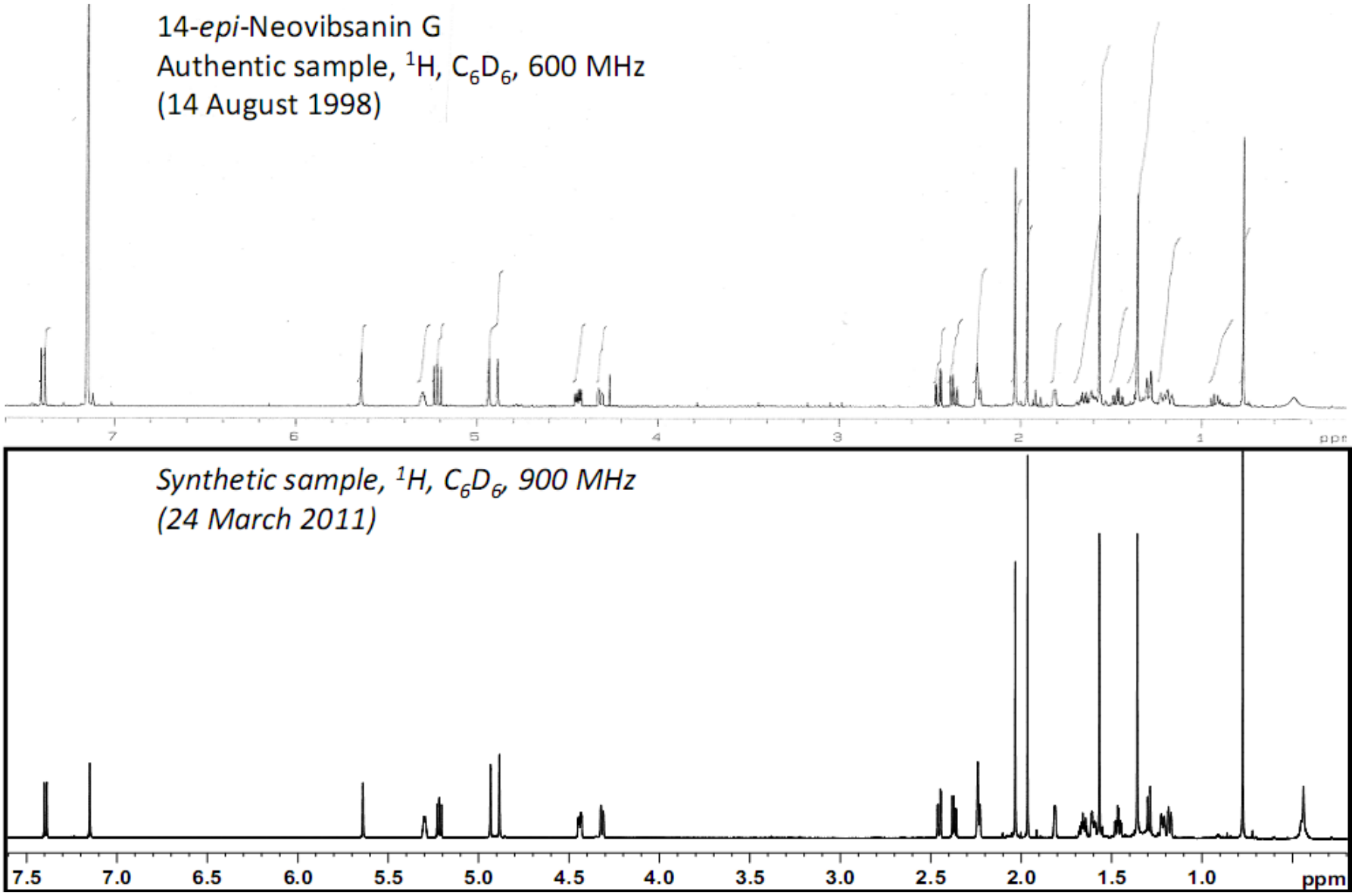

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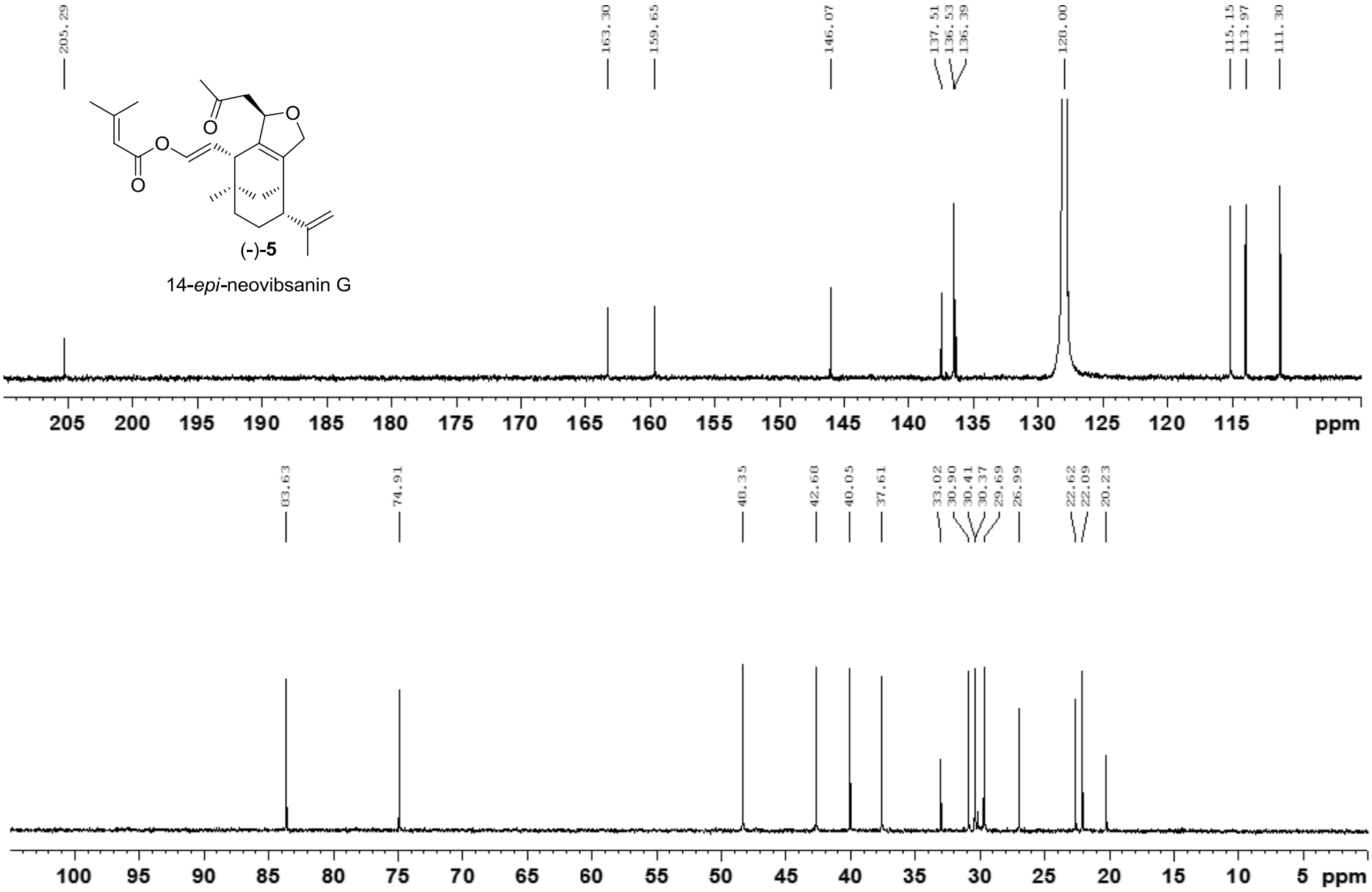

(-)-**5**

14-*epi*-neovibsanin G

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14-*epi*-neovibsanin G
Authentic sample, ^{13}C, C_6D_6, 150 MHz