10.1071/CH09267_AC
CSIRO 2009
Australian Journal of Chemistry, 2009, 62(9), 980-982

Total Synthesis of (±)-Vibsanin E.

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General Methods

^{1}H and ^{13}C n.m.r spectra were recorded on Bruker AV400 (400.13MHz; 100.62 MHz), AV300 (300.13 MHz; 75.47 MHz) and DRX500 (500.13 MHz; 125.76 MHz) instruments in the solvents specified. Coupling constants are given in Hz and chemical shifts are expressed as δ values in ppm. High resolution electrospray ionisation (HRESIMS) 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 reference calibrant. Low and high resolution electron impact ionisation mass measurements were recorded on a Finnigan MAT 900XL-TRAP (EI 70 eV) using perfluorokerosene-H as reference calibrant. Column chromatography was undertaken on silica gel (Flash Silica gel 230–400 mesh), with distilled solvents. Anhydrous solvents were prepared according to Perin and Armarego, 'Purification of laboratory solvents', 3rd Ed. Tetrahydrofuran was freshly distilled from a sodium/benzophenone still. Melting points were determined on a Fischer Johns Melting Point apparatus and are uncorrected. Fine chemicals were purchased from the Aldrich Chem. Co. Microwave irradiation was conducted with a CEM Discover microwave in 10 mL pressurized vials. The tricyclic intermediate **10** was prepared by the procedure described in Davies, H. M. L.; Loe, Ø.; Stafford, D. G. *Org. Lett.* **2005**, 5561.

*Conjugate addition of $LiCH_2OMOM$ to **10***

To a stirred solution of *n*-Bu_3SnCH_2OMOM[i] (1.56 g, 4.28 mmol) in anhydrous THF (10 mL) was added a solution of *n*-BuLi (2.90 mL, 4.28 mmol, 1.48 M in hexanes) at −78 °C under an argon atmosphere. After 5 minutes the reaction mixture was transferred via a cannula to a solution of TMEDA (0.97 mL, 6.42 mmol) and CuI (410 mg, 2.14 mmol) in THF (8 mL) at −78°C. The reaction was stirred for 30 mins after which time TMSCl (810 μL, 6.42 mmol) was added dropwise followed by a solution of **10** (500 mg, 2.14 mmol) in THF (5 mL). The reaction was stirred at −78 °C for 1 hour then warmed slowly to −20 °C and stirred for a further 45 minutes. The mixture was then poured into ice cold saturated sodium bicarbonate solution (25 mL) and extracted with ether (3 × 25 mL). The combined organic layer was then washed with a 10% aqueous ammonia solution (2 × 20 mL) followed by brine (15 mL) then dried (Na_2SO_4) and concentrated *in vacuo* to provide an oil which was purified by flash chromatography (1:20 ether:pet. spirit) which gave **12** as a colourless oil (745 mg, 91%). ^{1}H NMR (400 MHz, C_6D_6) δ 0.26 (s, 9H), 0.96–1.02 (m, 1H), 0.98 (s, 3H), 1.14 (s, 3H), 1.17 (s, 3H), 1.21–1.28 (m, 2H), 1.33–1.41 (m, 1H), 1.63–1.69 (m, 1H), 1.99–2.12 (m, 4H), 2.38 (qd, *J* = 13.4, 4.5 Hz, 1H), 3.23 (s, 3H), 3.40 (ddd, *J* 11.4, 2.8, 0.7 Hz, 1H), 3.53 (dd, *J* = 9.4, 6.2 Hz, 1H), 3.57 (dd, *J* = 9.4, 4.4 Hz, 1H), 4.46 (dd, *J* = 11.4, 1.5 Hz, 1H), 4.51 (AB,

J = 6.7 Hz, 2H), 5.24 (ddd, *J* = 7.64, 2.59, 0.75 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ 0.5 (3C), 23.8, 24.3, 28.1, 31.9, 32.6, 32.8, 40.7, 43.3, 43.8, 44.6, 48.1, 55.0, 63.5, 71.5, 73.2, 96.9, 111.7, 152.9. GC/MS EI m/z (%) 382 ($M^{+\cdot}$, 17) 367 (2), 320 (3), 307 (10), 279 (17), 249 (44), 167 (7), 73 (100), 45 (64). HRMS Calculated for $[C_{21}H_{38}O_4Si]^+$: 382.2539, Found: 382.2538.

*Allylation of **12***

A solution of methyl lithium in diethyl ether (0.73 mL, 0.94 mmol, 1.3 M) was added dropwise to a solution of **12** (200 mg, 0.524 mmol) in anhydrous THF (5 mL) at –20 °C under an argon atomsphere. The reaction was stirred for 45 minutes, cooled to –78 °C then HMPA (0.45 mL, 2.02 mmol) and allyl bromide (560 mg, 4.62 mmol) were added sequentially by dropwise addition. The reaction was stirred for 45 minutes and then warmed to –40 °C and stirred for a further 45 minutes. The reaction was quenched by pouring into ice cold saturated sodium bicarbonate solution (25 mL) and extracted with ether (3 × 25 mL). The combined organic layer was then washed with an aqueous 10% lithium chloride solution (20 mL) and brine (15 mL) then dried (Na_2SO_4). The solution was concentrated *in vacuo* which afforded an oil that was purified by flash chromatography (1:20 ether:pet. spirit) to give **13** (137 mg, 74%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (s, 3H), 1.09 (s, 3H), 1.17–1.33 (m, 2H), 1.27 (s, 3H), 1.37–1.44 (m, 2H), 1.64–1.73 (m, 1H), 2.04–2.22 (m, 3H), 2.28–2.40 (m, 2H), 3.30 (s, 3H), 3.44 (dd, *J* = 9.3, 7.0 Hz, 1H), 3.51 (ddd, *J* = 11.5, 2.9, 0.7 Hz, 1H), 3.59 (dd, *J* = 9.3, 4.3 Hz, 1H), 4.12–4.30 (m, 2H), 4.45 (dd, *J* = 11.6, 1.8 Hz, 1H), 4.55 (s, 2H), 4.84 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.13 (app. qd, *J* = 10.5, 1.5 Hz, 1H), 5.29 (app. qd, *J* = 17.3, 1.7 Hz, 1H), 5.98 (ddt, *J* = 17.3, 10.4, 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 24.4, 27.7, 31.8, 32.3, 32.4, 40.5, 42.1, 42.9, 44.3, 47.2, 55.1, 62.7, 68.4, 71.5, 73.5, 96.6, 103.2, 116.1, 134.3, 155.3. HRMS Calculated for $[C_{21}H_{34}O_4]^+$: 350.2452, Found: 350.2452.

*Microwave promoted Claisen rearrangement of **13***

A solution of *O*-allylated material **13** (40 mg, 0.11 mmol) in anhydrous toluene (6 mL) was heated under microwave irradiation for 5 hours (maximum temperature 185 °C, 300 W). The solvent was removed *in vacuo* which afforded an oil that was purfied by flash chromatography (1:10 ether:pet. spirit) to give *C*-allylated isomers **14** (13.5 mg, 34%) and **15** (11 mg, 26%) as colourless oils. *Syn Isomer* **14** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.09 (s, 3H), 1.28 (s, 3H), 1.23–1.33 (m, 1H), 1.39 (ddd, *J* = 14.1, 4.9, 1.4 Hz, 1H), 1.42–1.52 (m, 1H), 1.66–1.81 (m, 4H), 2.06 (dt, *J* = 15.2, 8.3 Hz, 1H), 2.20 (td, *J* = 14.4, 2.8 Hz, 1H), 2.36–2.40 (m, 1H), 2.43–2.48 (m, 1H), 2.79–2.87 (m, 1H), 3.28–3.32 (m, 1H), 3.29 (s, 3H), 3.45 (dd, *J* = 10.7, 4.8 Hz, 1H), 3.55 (dd, *J* = 10.7, 2.2 Hz, 1H), 3.78 (dd, *J* = 12.1, 4.7 Hz, 1H), 4.21 (dd, *J* = 12.1, 1.1 Hz, 1H), 4.42 (d, *J* = 6.6 Hz, 1H),

4.46 (d, *J* = 6.6 Hz, 1H), 4.98–5.07 (m, 2H), 5.74 (dddd, *J* = 16.7, 10.1, 8.6, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 24.3, 27.1, 30.1, 33.0, 33.7, 33.9, 39.4, 39.7, 41.1, 48.7, 51.8, 52.2, 55.7, 64.6, 65.4, 73.8, 96.6, 116.3, 137.5, 214.3. HRMS Calculated for $[C_{21}H_{34}O_4]^+$: 350.2452, Found: 350.2461 *Anti Isomer* **15** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03–1.21 (m, 2H), 1.09 (s, 3H), 1.14 (s, 3H), 1.23 (s, 3H), 1.32–1.41 (m, 3H), 1.44–1.52 (m, 2H), 2.10–2.20 (m, 2H), 2.38 (dt, *J* = 14.9, 2.1 Hz, 1H), 2.52–2.61 (m, 2H), 2.94 (td, *J* = 11.1, 3.2 Hz, 1H), 3.36 (s, 3H), 3.49–3.56 (m, 2H), 3.63 (dd, *J* = 10.5, 2.1 Hz, 1H), 4.16 (d, *J* = 11.9 Hz, 1H), 4.55 (AB, *J* = 6.6 Hz, 2H), 4.85–4.99 (m, 2H), 5.64 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 23.3, 27.9, 29.5, 30.3, 33.1, 34.1, 42.1, 42.7, 43.5, 45.3, 50.9, 50.9, 56.1, 59.0, 67.3, 72.9, 97.0, 116.2, 137.1, 214.9. GC/MS EI m/z (%) ($M^{+\cdot}$-15, 1), 320 (0.3), 288 (1), 275 (10), 247 (0.3), 189 (1), 135 (6), 79 (14), 45 (100). HRMS Calculated for $[C_{21}H_{34}O_4]^+$: 350.2452, Found: 350.2466.

*Epimerisation of the Syn isomer **14***

A mixture of **14** (86 mg, 0.25 mmol) in a methanolic solution of potassium carbonate (2 mL, 0.15 M) was heated under microwave irradiation for 90 min (maximum temperature 100 °C, 50 W). The solution was diluted with ether and then the mixture was filtered through a short plug of Celite™. The resulting solution was concentrated *in vacuo* then purifed by flash chromatography (1:10 ether:pet. spirit) to afford **15** (44 mg, 51%) and recovery of **14** (33 mg 38%).

*Deprotection of **15***

A mixture of **15** (25 mg, 71 μmol) in THF (1 mL), water (0.5 mL) and aqueous hydrochloric acid (100 μL, 10M) was heated under microwave irradiation for 45 min (maximum temperature 100 °C, 50 W). The solution was concentrated *in vacuo* then purifed by flash chromatography (1:1 ether:pet. spirit) to provide the alcohol **20** (17 mg, 78%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04–1.14 (m, 2H), 1.10 (s, 3H), 1.20 (s, 3H), 1.22–1.41 (m, 3H), 1.16–1.20 (m, 1H), 1.24 (s, 3H), 1.46–1.53 (m, 2H), 2.14 (dd, *J* = 7.6, 3.2 Hz, 1H), 2.26 (dddt, *J* = 13.3, 7.1, 3.6, 1.20, Hz, 1H), 2.38 (dt, *J* = 15.0, 2.5 Hz, 1H), 2.55–2.64 (m, 2H), 2.95 (td, *J* = 10.8, 3.7 Hz, 1H), 3.52 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.77 (dd, *J* = 11.6, 4.3 Hz, 1H), 3.85 (dd, *J* = 11.6, 2.5 Hz, 1H), 4.17 (d, *J* = 12.0 Hz, 1H), 4.90 (tdd, *J* = 10.2, 2.0, 1.0 Hz, 1H), 5.00 (ddt, *J* = 17.2, 1.9, 1.4 Hz, 1H), 5.61–5.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 23.3, 27.9, 29.5, 30.2, 33.4, 34.2, 42.3, 42.8, 43.4, 47.0, 50.6, 50.9, 59.0, 61.5, 73.0, 116.3, 137.2, 215.0. GC/MS EI m/z (%) 306 ($M^{+\cdot}$,1), 291 (7), 275 (36), 247 (2), 193 (11), 153 (52), 135 (22), 121 (20), 105 (33), 93 (71), 79 (65), 67 (40), 55 (68), 41 (100). HRMS Calculated for $[C_{19}H_{30}O_3]^+$: 306.2194, Found 306.2195

*Swern oxidation of **20***

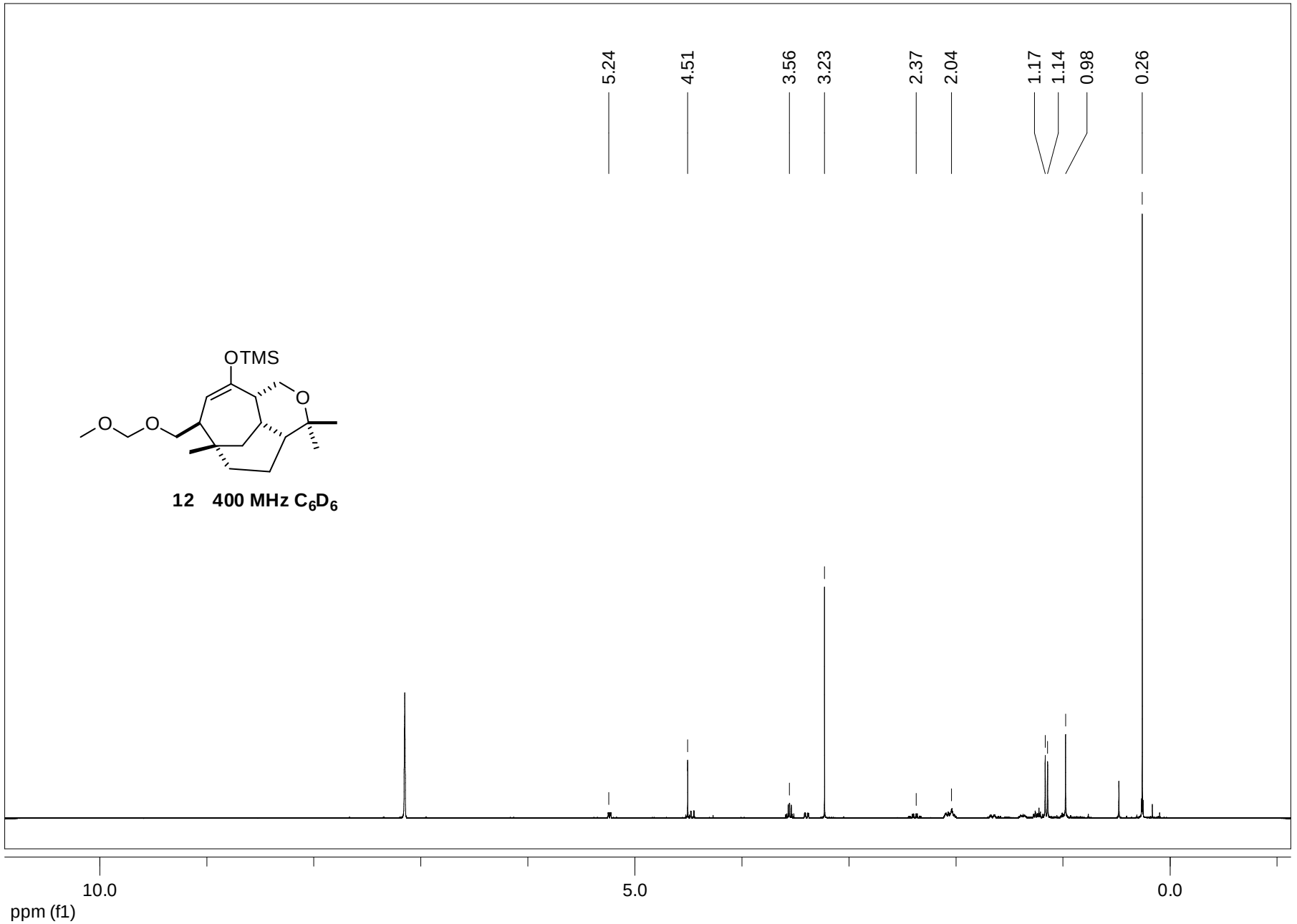
To a stirred solution of oxalyl chloride (77 μL, 0.88 mmol) in anhydrous dichloromethane (10 mL) under an argon atmosphere at –78°C was added dimethylsulfoxide (78 μL, 1.1 mmol) dropwise. After 10 mins a solution of alcohol **20** in dichloromethane (2 mL) was added dropwise. After 1 hour at –78°C excess anhydrous triethylamine (370 μL, 2.65 mmol) was added and stirring continued at that temperature for a further 15 mins. The solution was warmed to 0°C and stirred for 20 mins, then diluted with dichloromethane (30 mL), washed with brine (10 mL) and dried ($MgSO_4$). Evaporation *in vacuo* gave a residue which was subjected to column chromatography (1:1 ether:pet. spirit) which afforded ketoaldehyde **21** (69 mg, 51%) as a colourless paste. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 3H), 1.07–1.21 (m, 3H), 1.11 (s, 3H), 1.25 (s, 3H), 1.35–1.45 (m, 1H), 1.57 (dd, J = 15.0, 5.5 Hz, 1H), 1.63–1.69 (m, 1H), 1.76-1.83 (m, 1H), 2.01 (dd, J = 12.0, 5.7 Hz, 1H), 2.26 (dd, J = 7.2, 3.0 Hz, 1H), 2.41–2.48 (m, 1H), 2.48–2.56 (m, 1H), 2.62–2.68 (m, 1H), 3.05–3.11 (m, 1H), 3.57 (dd, J = 12.0, 3.2 Hz, 1H), 4.17 (d, J = 12.0 Hz, 1H), 4.90–4.97 (m, 2H), 5.61 (ddt, J = 16.9, 10.2, 6.7, Hz, 1H), 9.52 (d, J = 5.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 23.1, 27.9, 29.4, 30.3, 32.9, 34.2, 41.5, 43.3, 44.0, 49.2, 51.1, 59.2, 59.2, 73.0, 117.1, 135.5, 201.9, 211.2. GC/MS EI m/z (%) 304 ($M^{+\cdot}$,5), 289 (5), 275 (9), 246 (2), 217 (3), 152 (7), 94 (97), 79 (43), 67 (34), 55 (100). HRMS Calculated for $[C_{19}H_{28}O_3]^+$: 304.2033, Found: 304.2030.

*Wacker oxidation of ketoaldehyde **21***

Ketoaldehyde **21** (69 mg, 0.23 mmol) was dissolved in a mixture of *N*,*N*-dimethylformamide and water (7:1, 1 mL), and to this was added palladium dichloride (5 mg, 28 μmol) and copper (II) chloride dihydrate (38 mg, 0.23 mmol). The reaction mixture was then stirred under a balloon of oxygen for 1 hour. Filtration through celite followed by evaporation under high vacuum gave a residue which was subjected to column chromatography (1:1 ethyl acetate:petroleum spirit) affording diketoaldehyde **18** (35 mg, 48%) as a colourless foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (s, 3H), 1.06–1.20 (m, 3H), 1.09 (s, 3H), 1.25 (s, 3H), 1.34–1.44 (m, 1H), 1.57 (dd, J = 15.1, 5.5 Hz, 1H), 1.61–1.67 (m, 1H), 1.95 (dd, J = 12.4, 5.6 Hz, 1H), 2.06 (s, 3H), 2.17 (dd, J = 18.0, 2.9 Hz, 1H), 2.48 (dt, J = 15.0, 2.4 Hz, 1H), 2.57 (dd, J = 7.4, 3.1 Hz, 1H), 2.63–2.69 (m, 1H), 3.08 (dd, J = 18.0, 11.0 Hz, 1H), 3.41–3.48 (m, 1H), 3.57 (dd, J = 12.1, 3.2 Hz, 1H), 4.12 (d, J = 12.1 Hz, 1H), 9.44 (d, J = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 23.2, 27.9, 29.5, 29.9, 30.2, 34.3, 41.6, 43.3, 43.6, 43.9, 44.1, 50.2, 58.2, 59.3, 72.9, 201.4, 207.3, 211.7. GC/MS EI m/z (%) 320 ($M^{+\cdot}$, 0.3), 305 (2), 292 (0.4), 262 (2), 233 (2), 219 (1), 168 (5), 151 (4), 131 (12), 94 (40), 79 (13), 43 (100). HRMS Calculated for $[C_{18}H_{28}O_4]^+$: 320.1982, Found: 320.1986.

*Vibsanin E (**1**)*

A suspension of [(3-methylbut-2-enoyloxy)methyl]triphenylphosphonium chloride (90 mg, 0.220 mmol) in anhydrous tetrahydrofuran (3 mL) under an argon atmosphere was sonicated for 10 minutes until a uniform milky dispersion had formed. The mixture was then cooled to –78°C and a solution of sodium bis(trimethylsilyl)amide solution (220 µL, 0.220 mmol, 1M solution in THF) was added strictly dropwise. The brightly orange coloured reaction mixture was stirred for 10 minutes then a solution of diketoaldehyde **18** (35 mg, 0.110 mmol) in anhydrous tetrahydrofuran (2 mL) was added dropwise and after complete addition the solution turned colourless. The reaction was stirred for 2 minutes then the mixture was poured onto saturated ice-cold sodium bicarbonate (5 mL) and extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with brine, dried over sodium sulfate and concentrated *in vacuo*. The residue was purified by flash chromatography (ethyl acetate: Pet. Spirit / 1:5) on silica gel to give a colourless oil. Crystallisation from diethyl ether/benzene/pet. spirit gave **1** as colourless crystals (18 mg, 40%). ^{1}H NMR (600 MHz, C_6D_6) δ 0.67 (ddd, *J* = 12.6, 4.0, 4.0 Hz, 1H), 0.76 (ddd, *J* = 14.2, 14.2, 3.3 Hz, 1H), 0.79 (s, 3H), 1.04 (s, 3H), 1.10 (dd, *J* = 14.6, 5.5 Hz, 1H), 1.11 (s, 3H), 1.14–1.18 (m, 1H), 1.22-1.29 (m, 2H), 1.38 (d, *J* = 1.4 Hz, 3H), 1.62 (s, 3H), 1.71 (dd, *J* = 11.7, 11.7 Hz, 1H), 2.00-2.02 (m , 1H), 2.06 (d, *J* = 1.1 Hz, 3H), 2.10–2.14 (m, 1H), 2.13 (dd, *J* = 17.7, 2.9 Hz, 1H), 2.26 (dd, *J* = 7.6, 3.2 Hz, 1H), 2.97 (dd, *J* = 17.8, 10.8 Hz, 1H), 3.05 (ddd, *J* = 11.1, 11.1, 3.2 Hz, 1H), 3.32 (dd, *J* = 11.9, 3.4 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 5.09 (dd, *J* = 11.8, 11.8 Hz, 1H), 5.68-5.70 (m, 1H), 7.25 (d, *J* = 12.3 Hz, 1H). ^{13}C NMR (150 MHz, C_6D_6) δ 19.1, 20.2, 23.3, 27.0, 28.3, 29.5, 29.8, 31.9, 34.9, 41.2, 42.4, 43.4, 46.0, 46.1, 47.7, 50.0, 59.2, 72.5, 115.1, 116.3, 135.1, 159.8, 163.2, 207.0, 212.9. HRESIMS Calculated for $[C_{25}H_{36}NaO_5]^+$: 439.2455, Found: 439.2448.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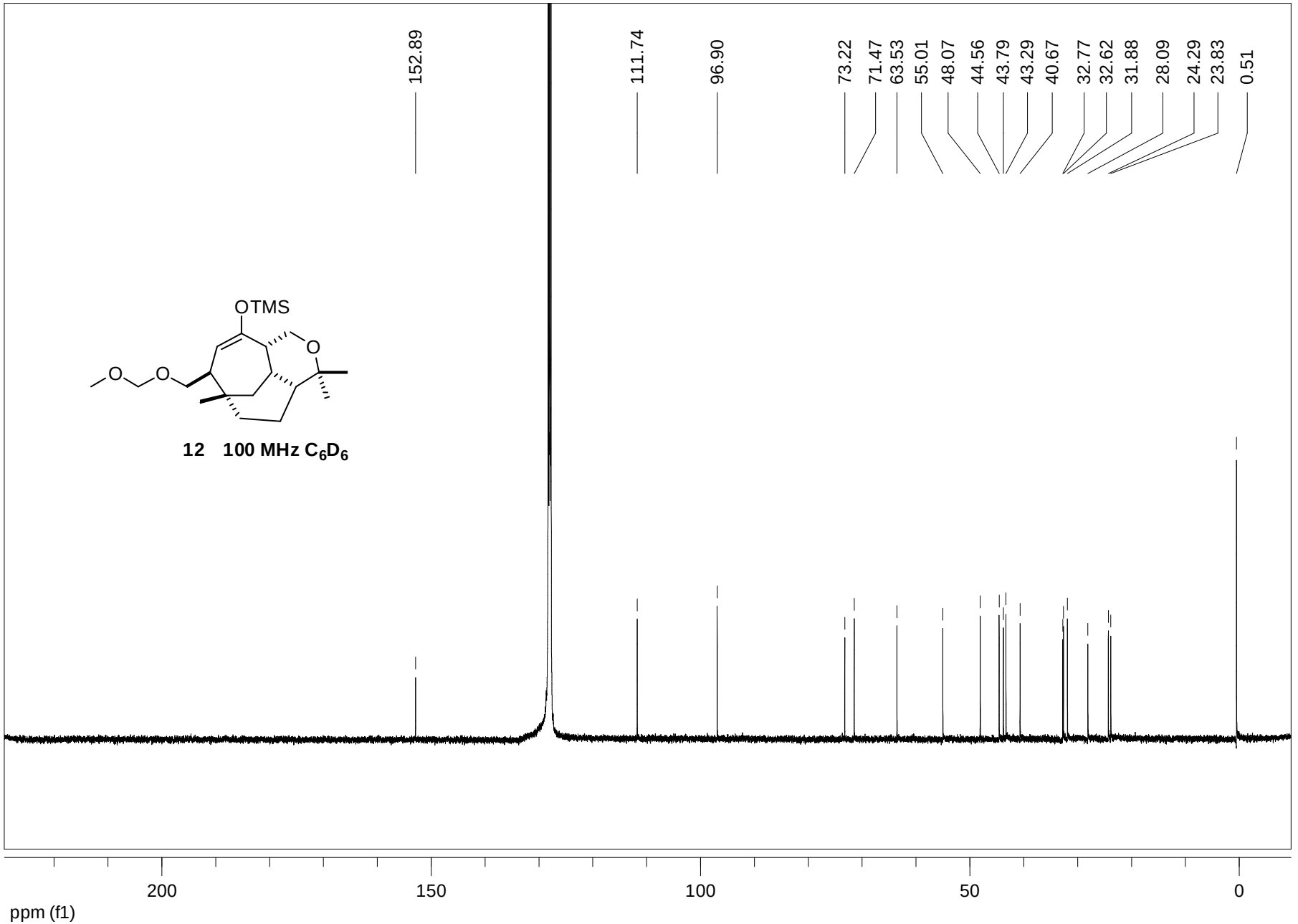
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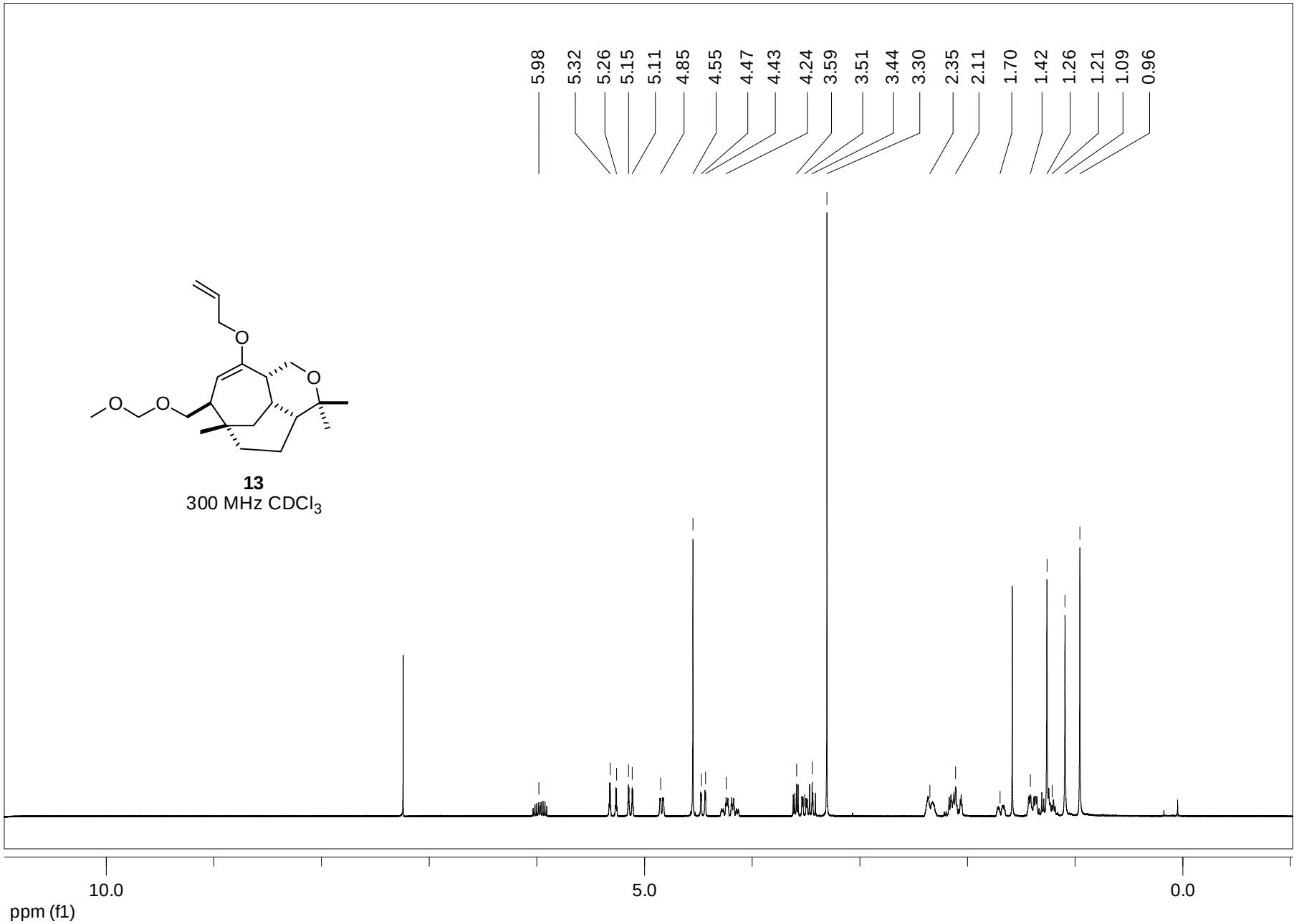
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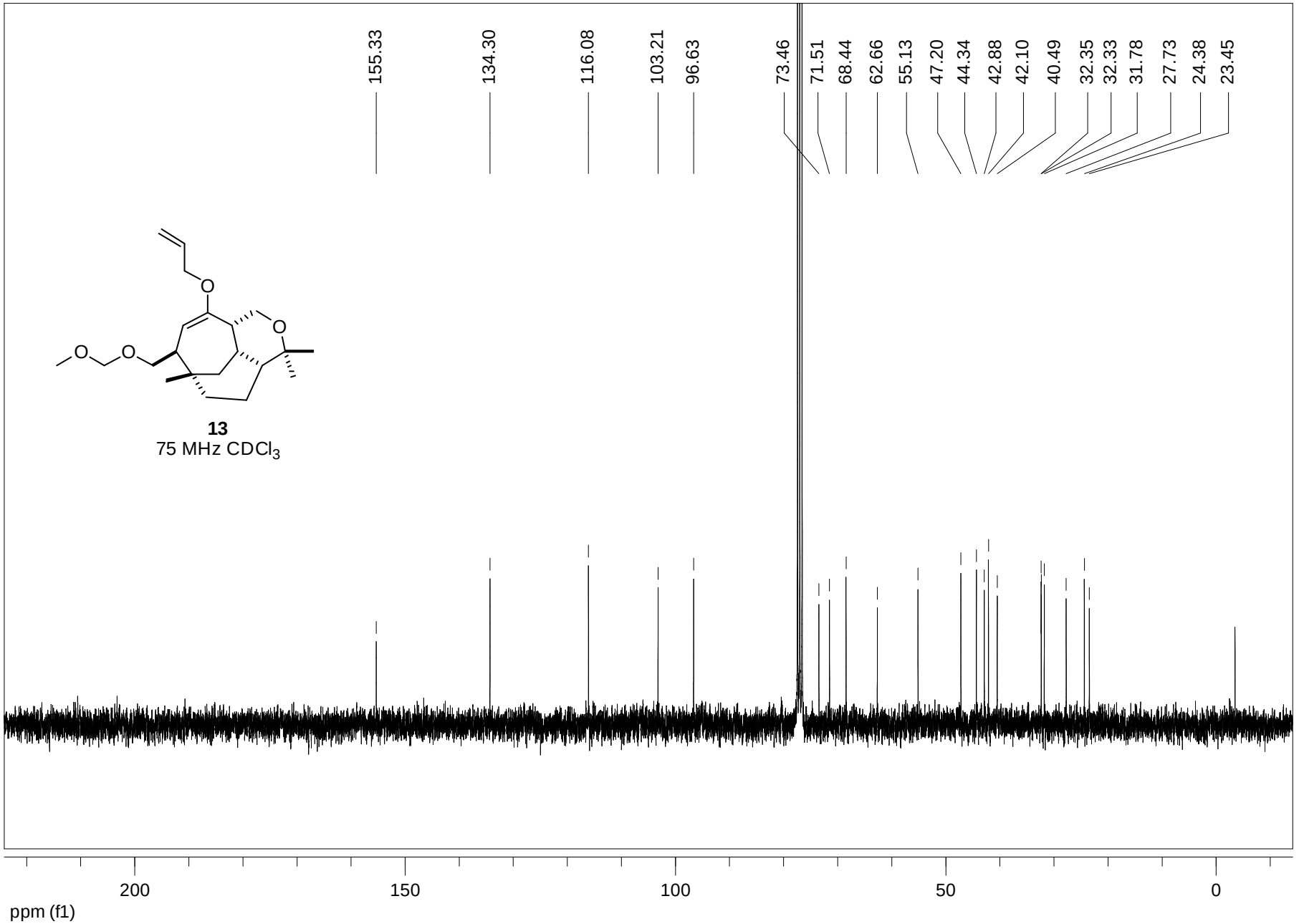
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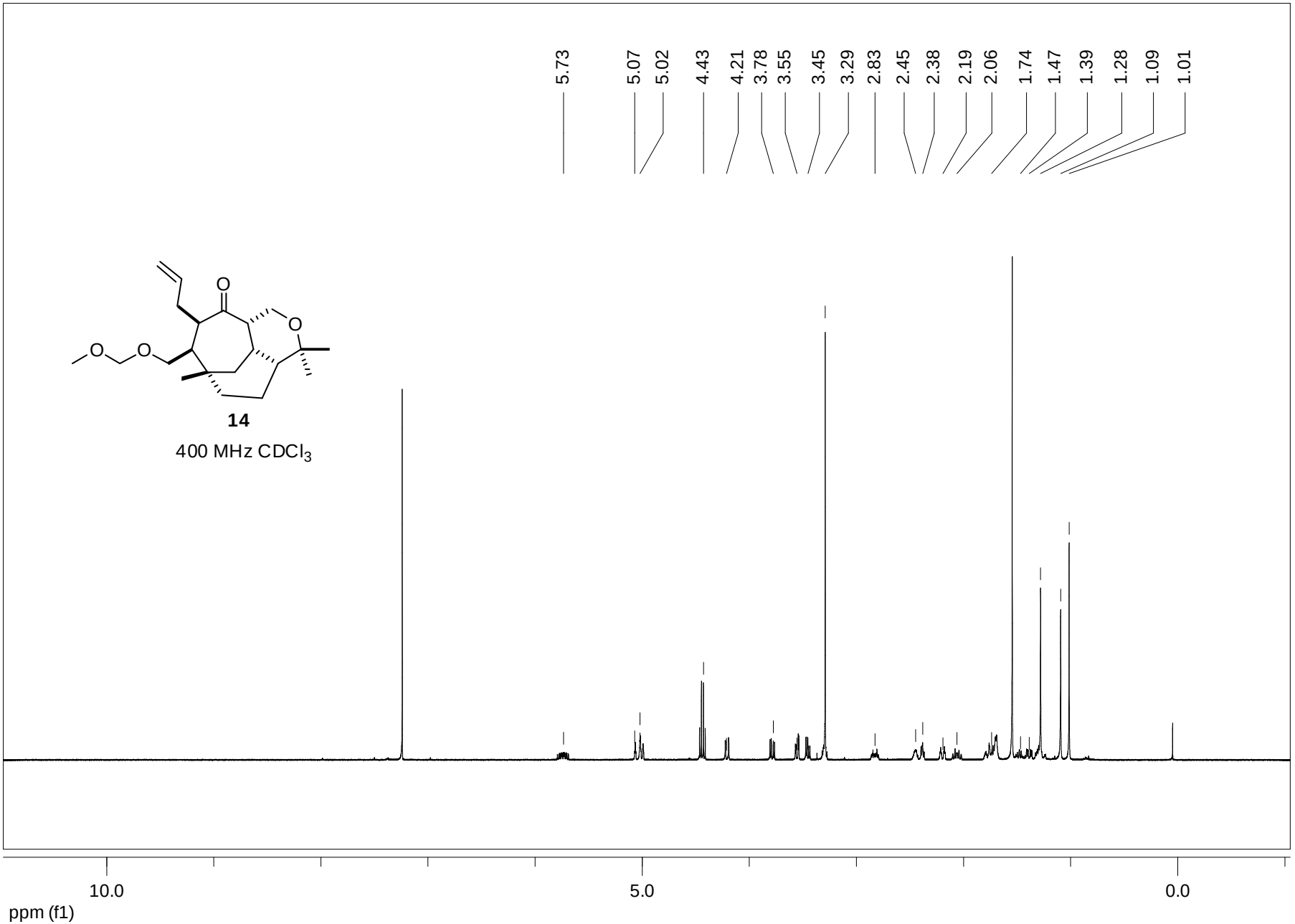
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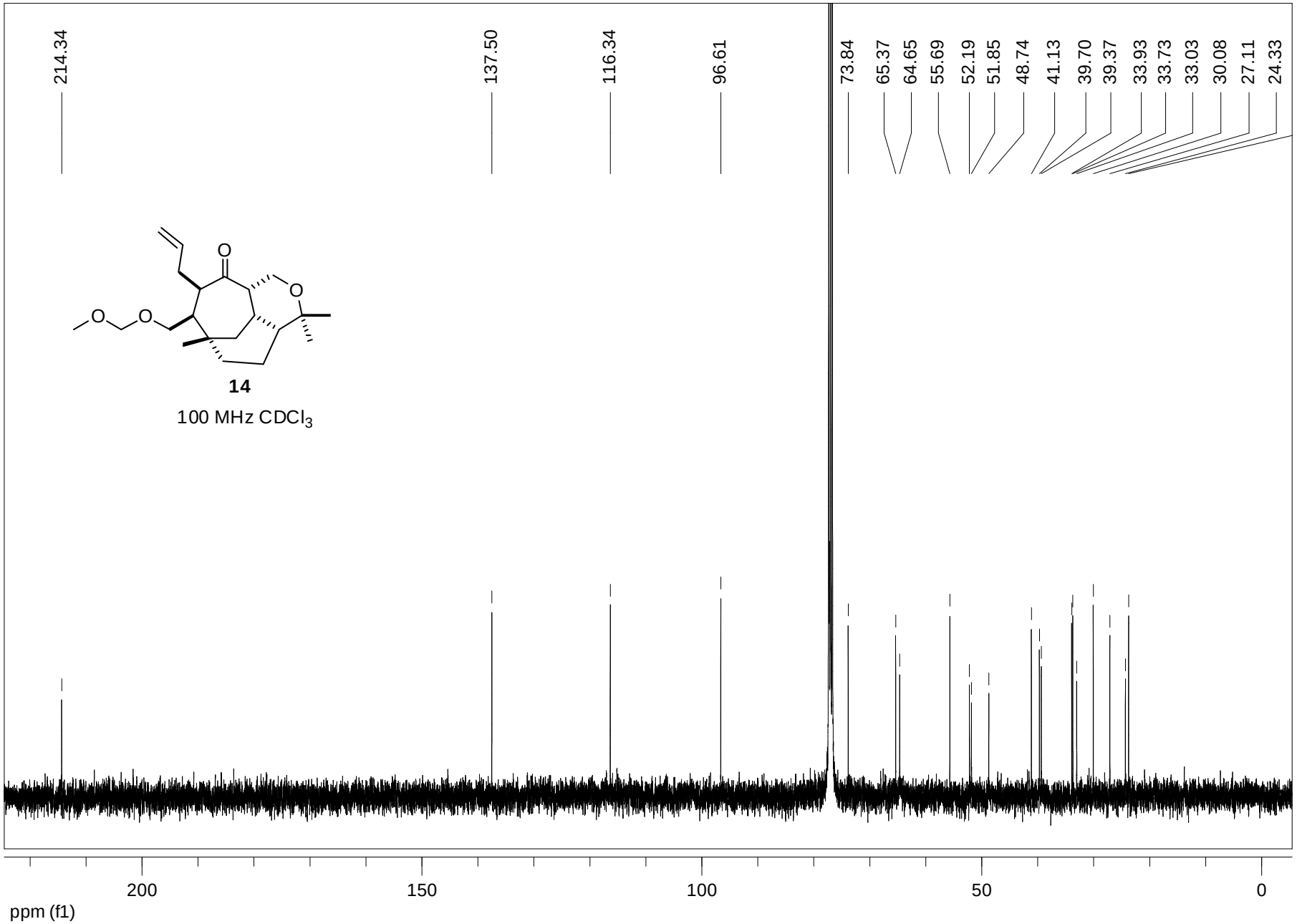
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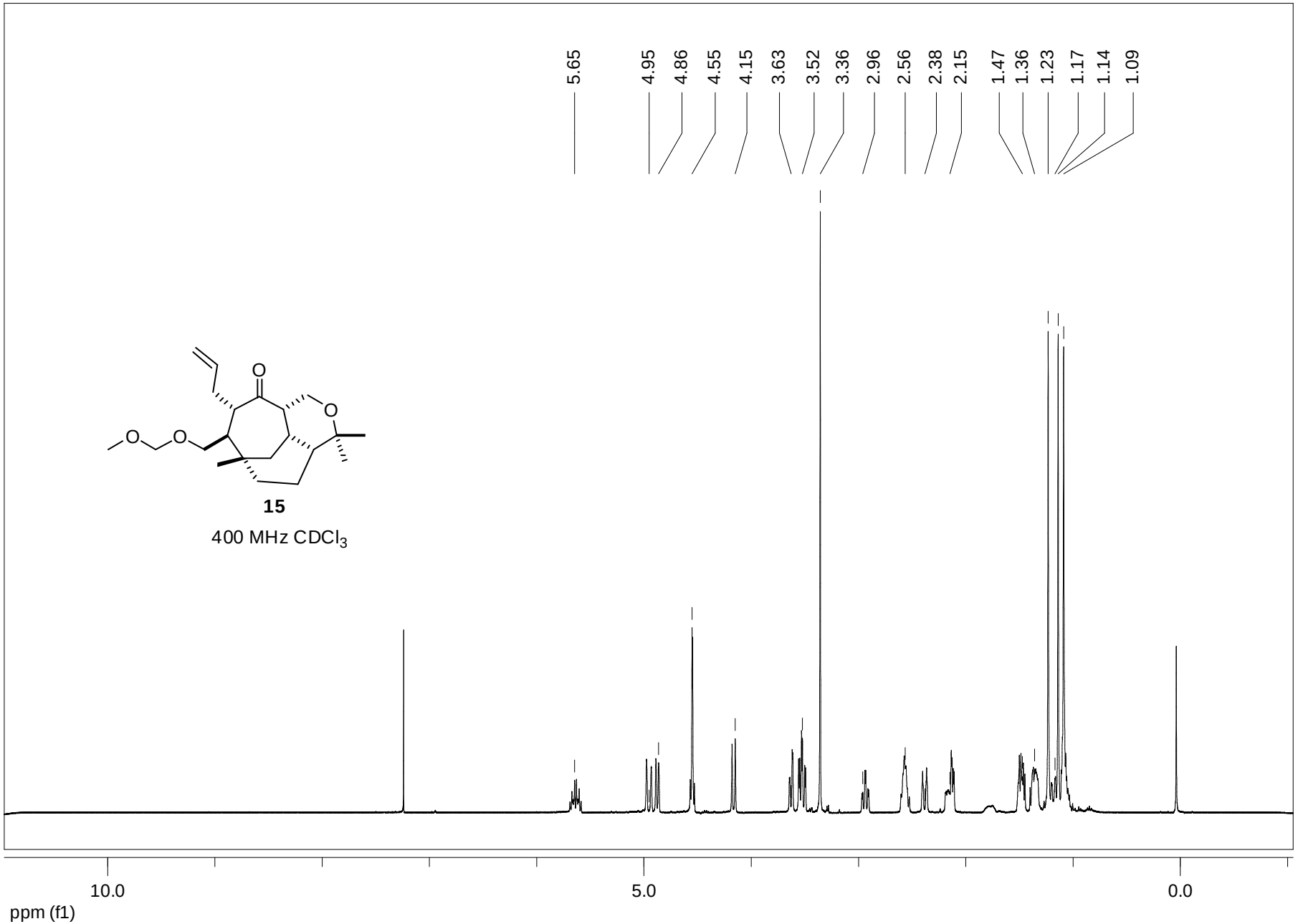
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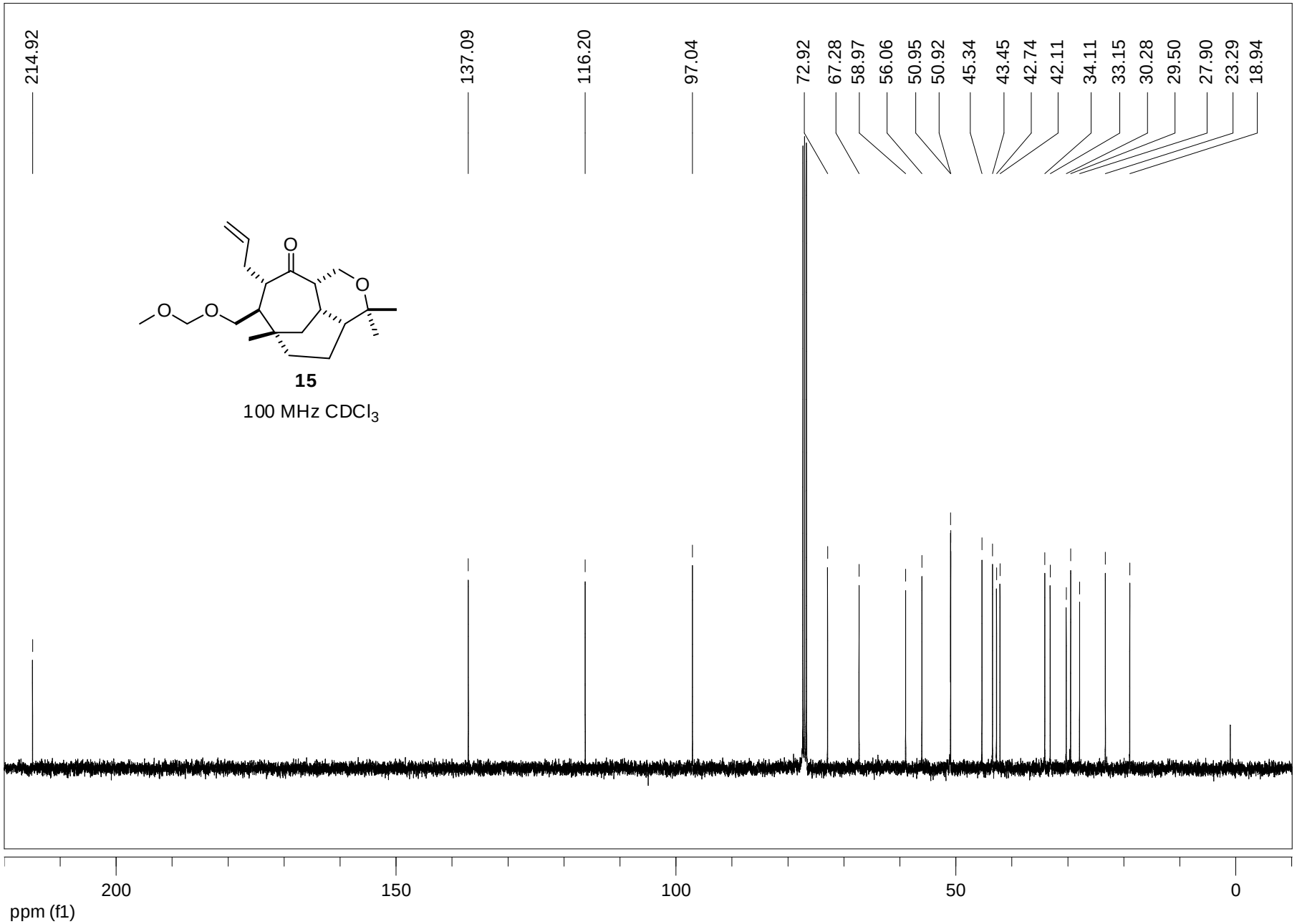
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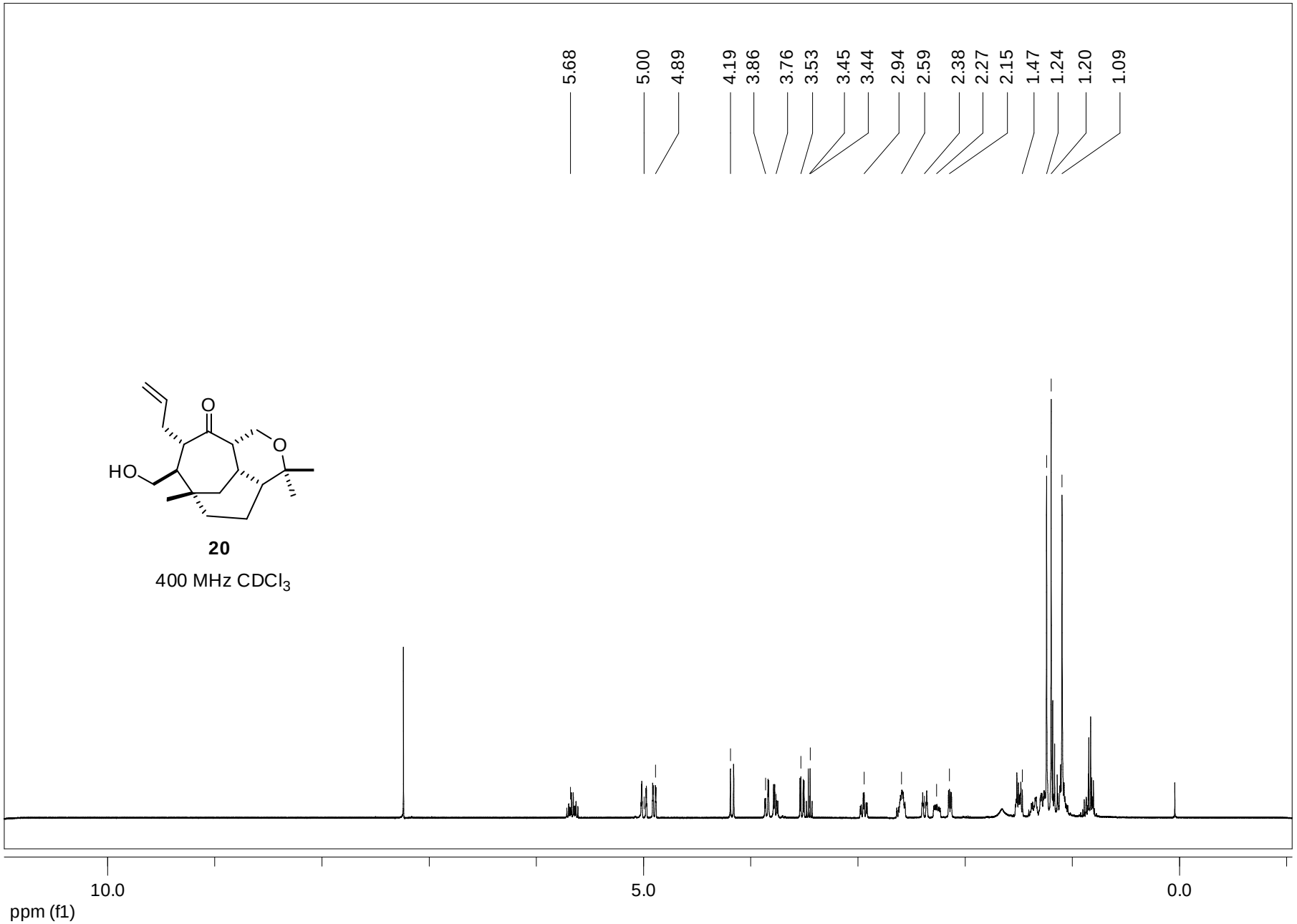
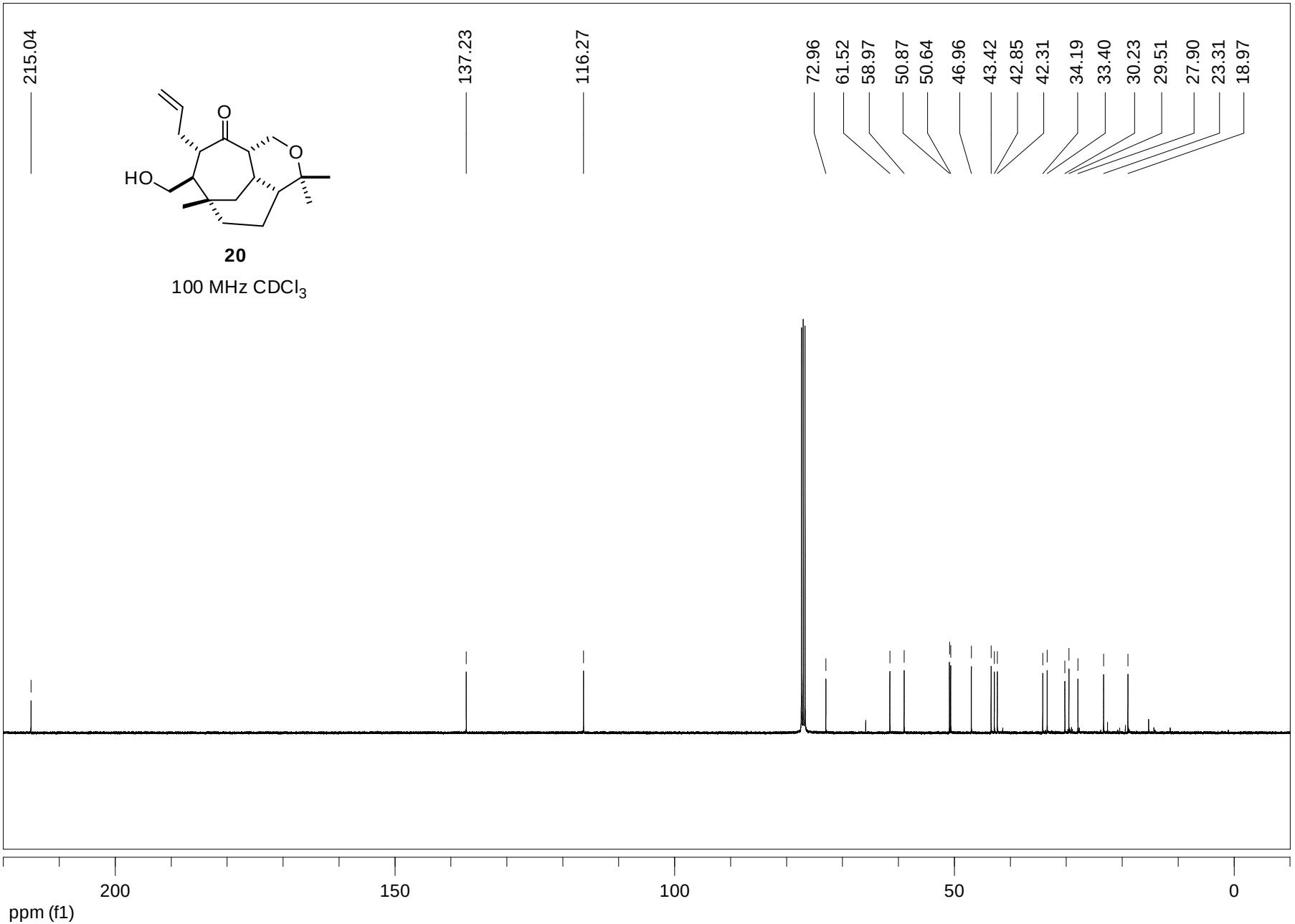
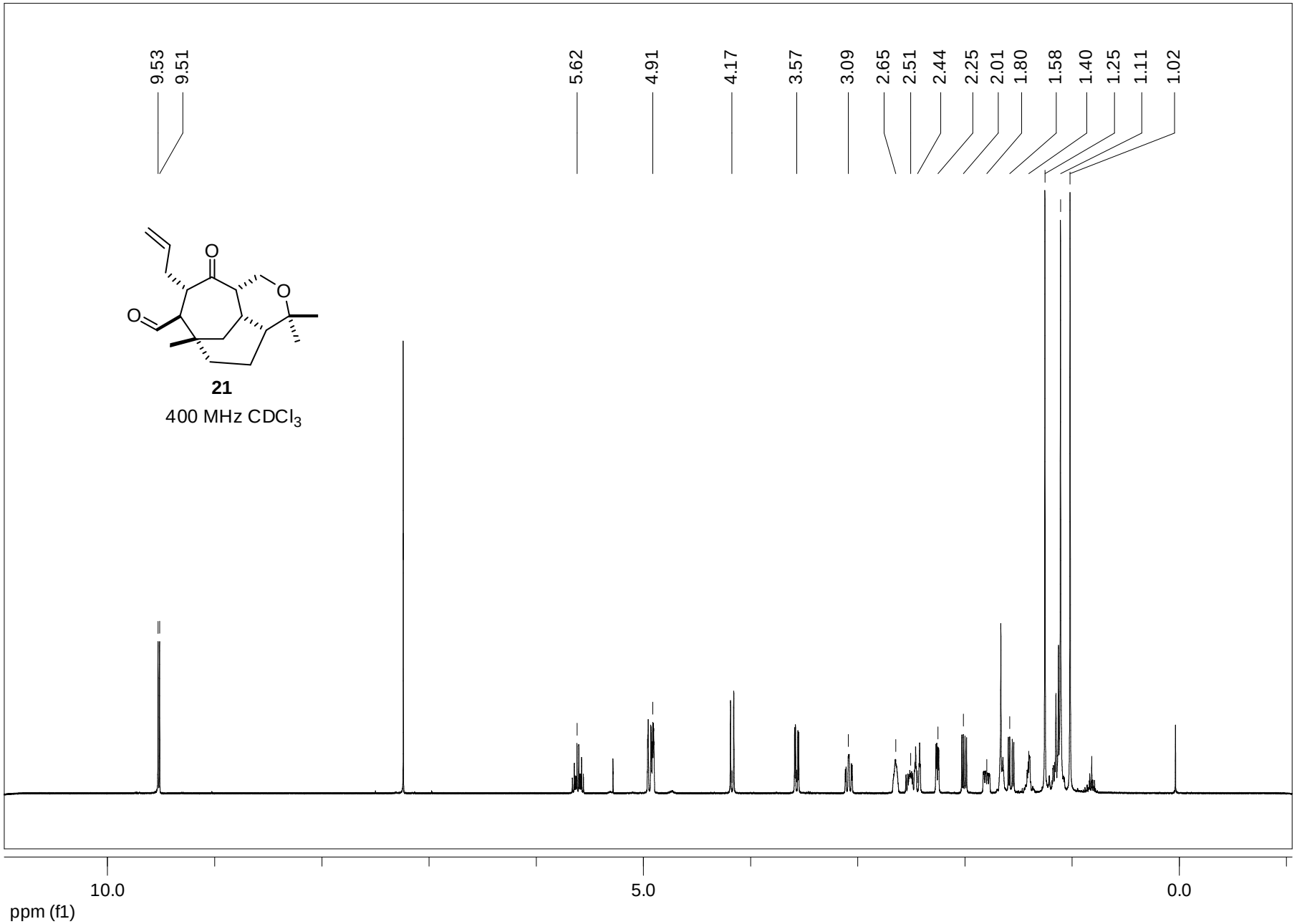
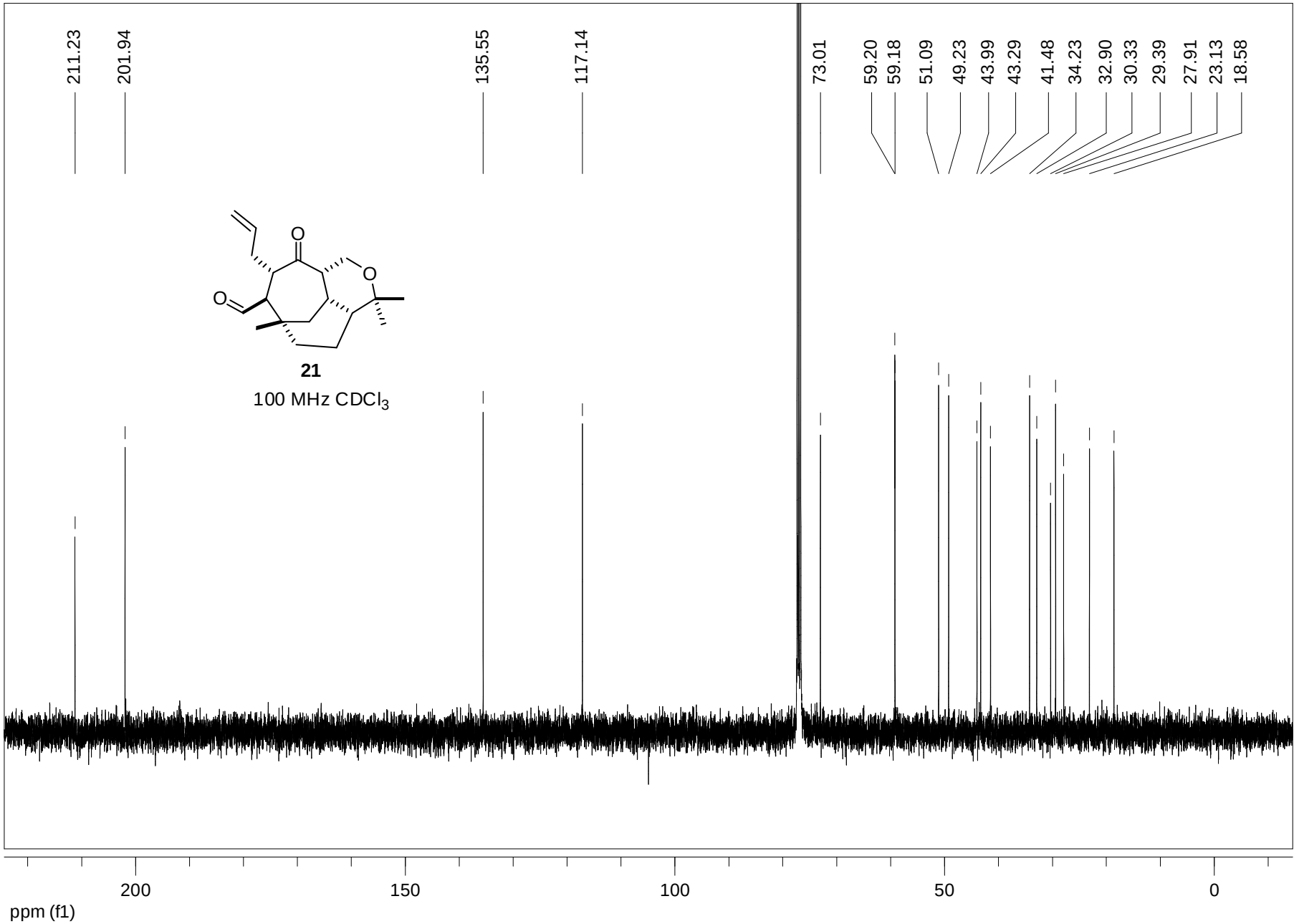
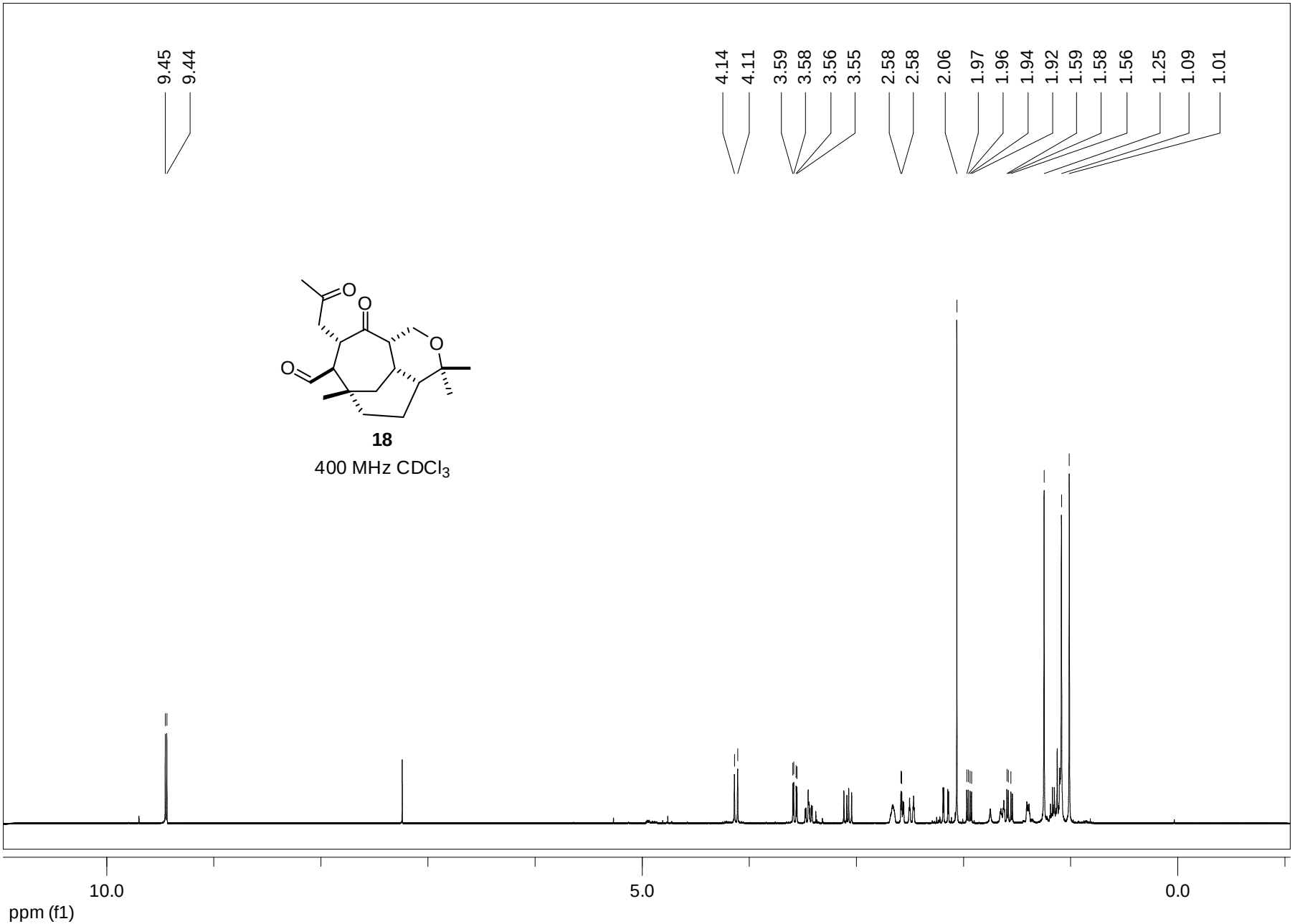
137.09
116.20
97.04
72.92
67.28
58.97
56.06
50.95
50.92
45.34
43.45
42.74
42.11
34.11
33.15
30.28
29.50
27.90
23.29
18.94
O
O
O
O
15
100 MHz CDCl3
200
150
100
50
0
ppm (f1)


5.68
5.00
4.89
4.19
3.86
3.76
3.53
3.45
3.44
2.94
2.59
2.38
2.27
2.15
1.47
1.24
1.20
1.09
O
O
HO
20
400 MHz CDCl3
10.0
5.0
0.0
ppm (f1)


215.04
137.23
116.27
72.96
61.52
58.97
50.87
50.64
46.96
43.42
42.85
42.31
34.19
33.40
30.23
29.51
27.90
23.31
18.97
HO
O
O
20
100 MHz CDCl3
200
150
100
50
0
ppm (f1)

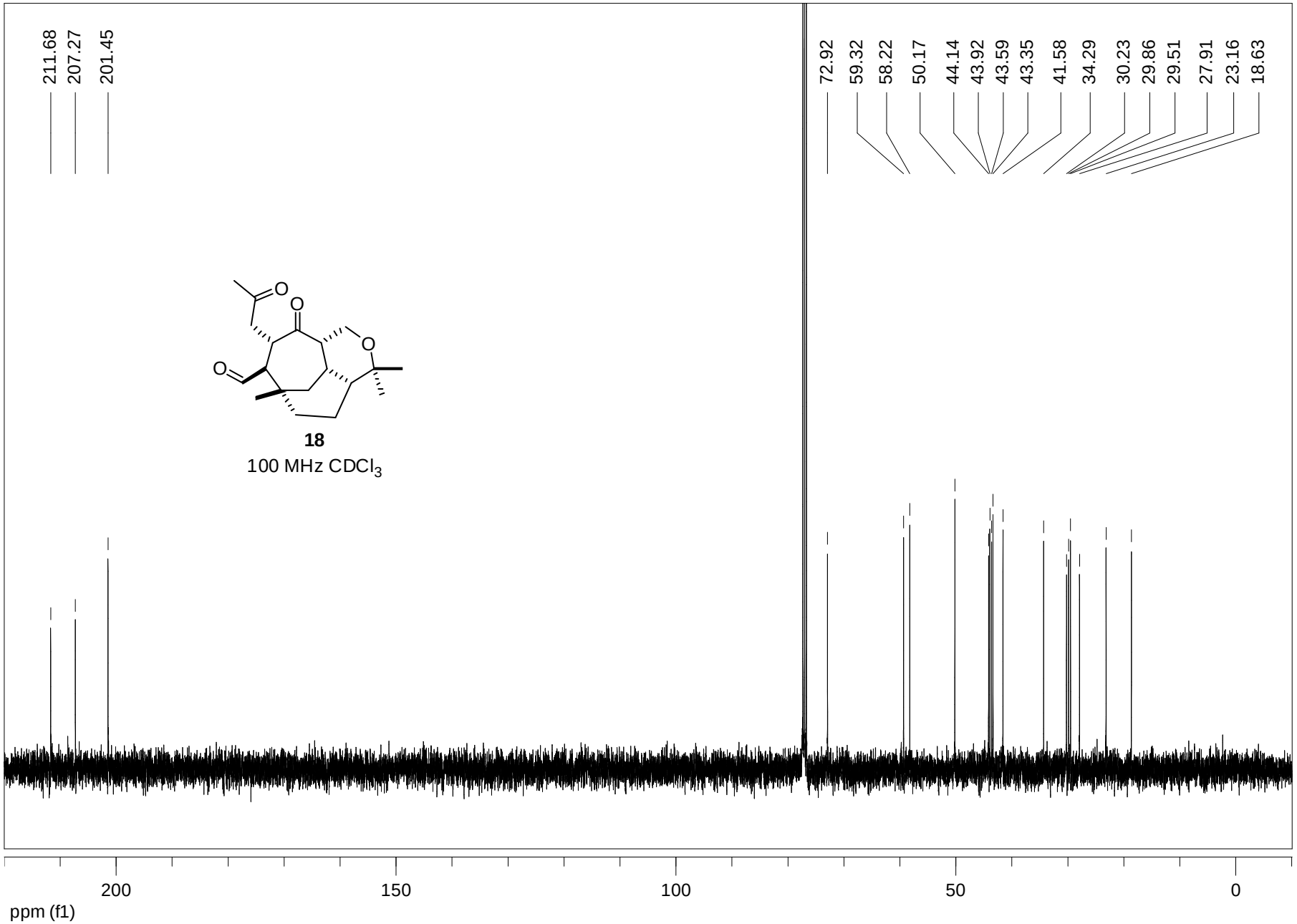

9.53
9.51
5.62
4.91
4.17
3.57
3.09
2.65
2.51
2.44
2.25
2.01
1.80
1.58
1.40
1.25
1.11
1.02
O
O
O
21
400 MHz CDCl3
10.0
5.0
0.0
ppm (f1)

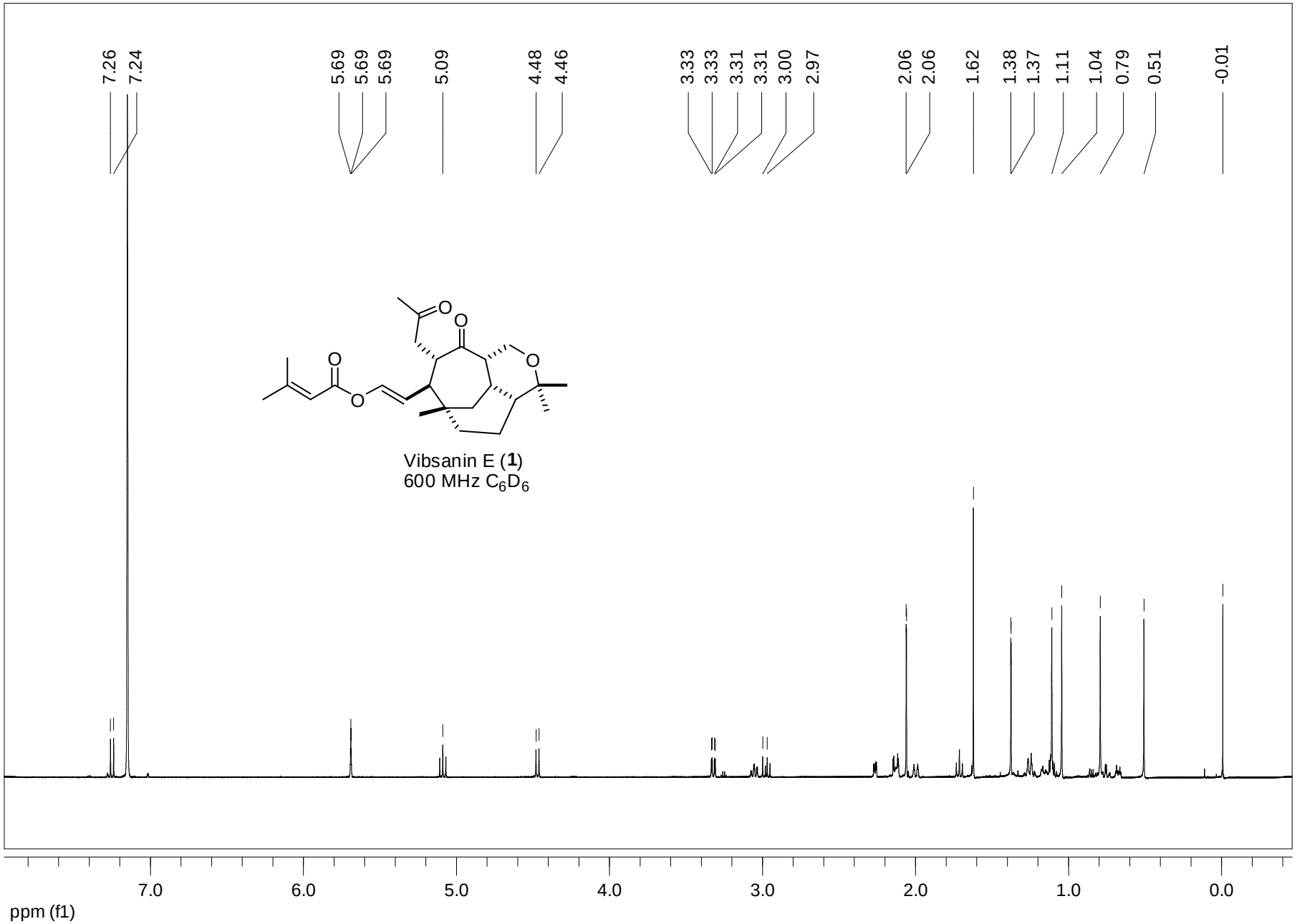

211.23
201.94
135.55
117.14
73.01
59.20
59.18
51.09
49.23
43.99
43.29
41.48
34.23
32.90
30.33
29.39
27.91
23.13
18.58
O
O
O
21
100 MHz CDCl3
200
150
100
50
0
ppm (f1)

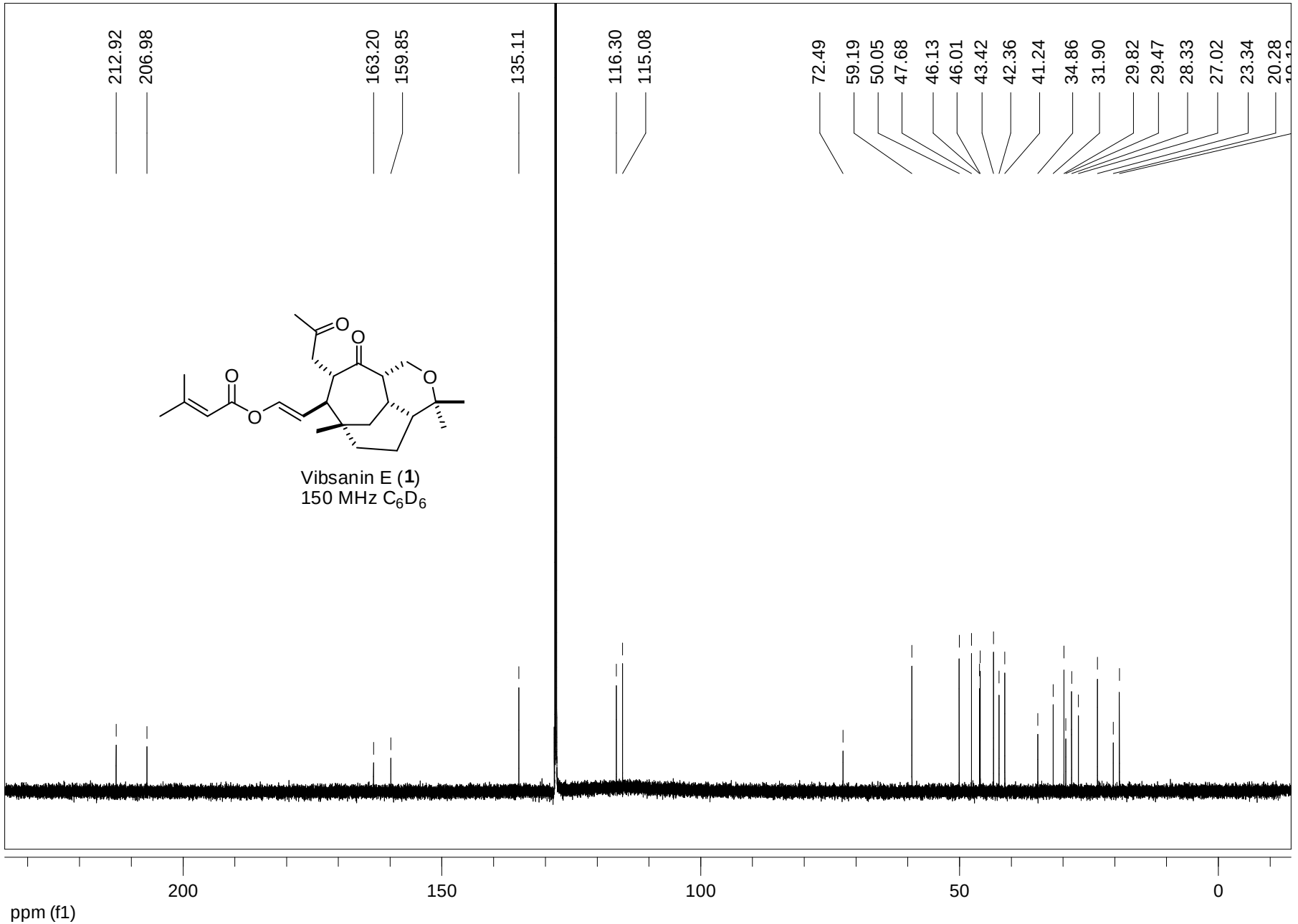


18

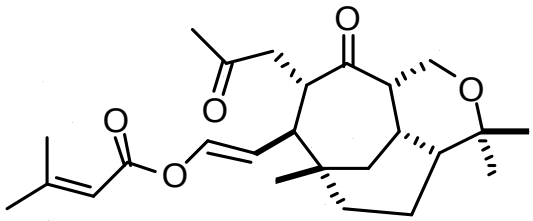
400 MHz $CDCl_3$


211.68
207.27
201.45
72.92
59.32
58.22
50.17
44.14
43.92
43.59
43.35
41.58
34.29
30.23
29.86
29.51
27.91
23.16
18.63
O
O
O
O
18
100 MHz CDCl3
200
150
100
50
0
ppm (f1)


7.26
7.24
5.69
5.69
5.69
5.09
4.48
4.46
3.33
3.33
3.31
3.31
3.00
2.97
2.06
2.06
1.62
1.38
1.37
1.11
1.04
0.79
0.51
-0.01
O
O
O
O
O
Vibsanin E (1)
600 MHz C6D6
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

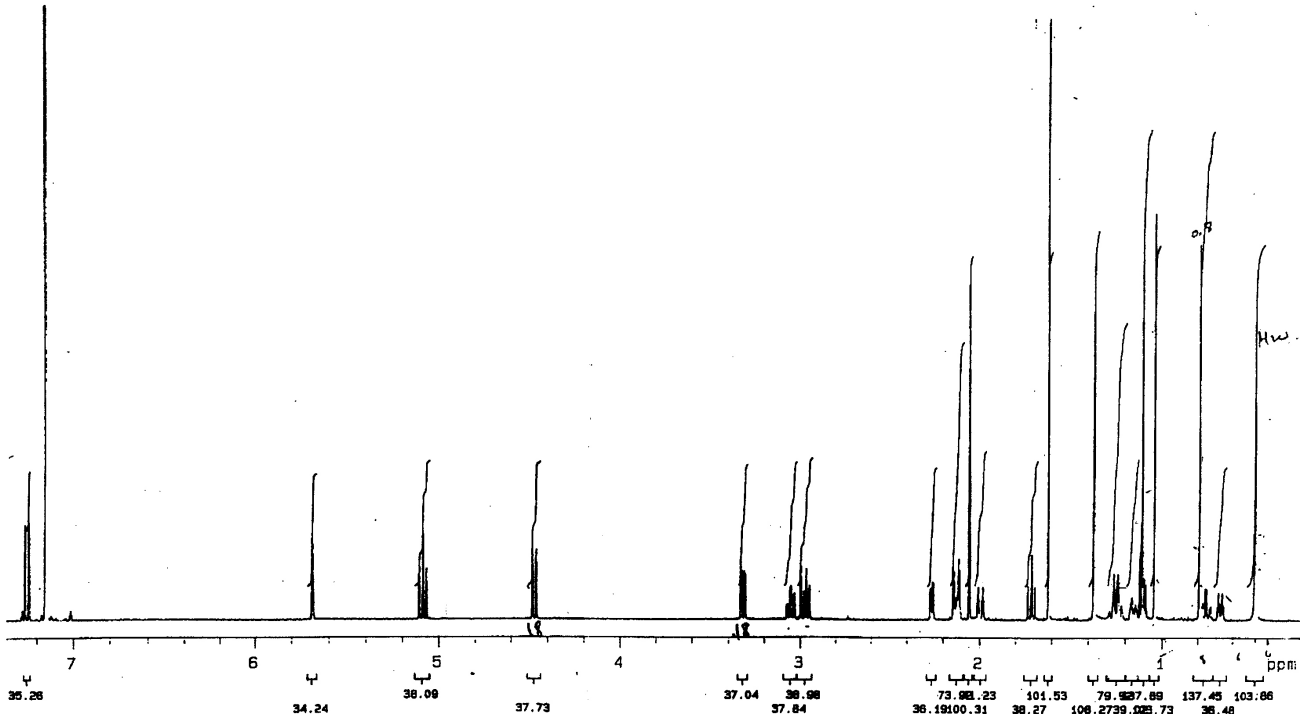

212.92
206.98
163.20
159.85
135.11
116.30
115.08
72.49
59.19
50.05
47.68
46.13
46.01
43.42
42.36
41.24
34.86
31.90
29.82
29.47
28.33
27.02
23.34
20.28
O
O
O
O
O
Vibsanin E (1)
150 MHz C6D6
200
150
100
50
0
ppm (f1)

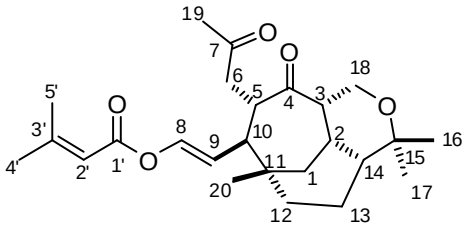
Synthetic



Vibsanin E (**1**)

Natural





Vibsanin E (**1**) 600 / 150 MHz C_6D_6

	Natural Vibsanin E[2]		Synthetic (±)-Vibsanin E	
Position	δ H	δ C	δ H	δ C
1	1.10 (dd, 14.8, 5.5)	41.3	1.10 (dd, 14.6, 5.5)	41.2
	2.00 (br d, 14.8)		2.00–2.02 (m)	
2	2.13 (m)	29.8	2.10–2.14 (m)	29.8
3	2.26 (dd, 7.7, 3.3)	50.1	2.26 (dd, 7.6, 3.2)	50.0
4		212.9		212.9
5	3.06 (ddd, 11.5, 10.7, 3.0)	47.7	3.05 (ddd, 11.1, 11.1, 3.2)	47.7
6	2.13 (dd, 17.6, 3.0)	46.1	2.13 (dd, 17.7, 2.9)	46.1
	2.98 (dd, 17.6, 10.7)		2.97 (dd, 17.8, 10.8)	
7		206.9		207.0
8	7.25 (d, 12.4)	135.1	7.25 (d, 12.3)	135.1
9	5.09 (dd, 12.4, 11.8)	116.3	5.09 (dd, 11.8 11.8)	116.3
10	1.72 (dd, 11.8, 11.5)	46.0	1.71 (dd, 11.7 11.7)	46.0
11		34.9		34.9
12	0.76 (ddd, 14.1, 14.1, 3.3)	42.4	0.76 (ddd,14.2, 14.2, 3.3)	42.4
	1.25 (m)		1.22–1.29 (m)	
13	1.16 (m), 1.25 (m)	19.1	1.14–1.18 (m), 1.22-1.29 (m)	19.1
14	0.67 (ddd, 12.6, 4.4, 4.1)	43.4	0.67 (ddd, 12.6, 4.0, 4.0)	43.4
15		72.5		72.5
16	1.11 (s)	23.3	1.11 (s)	23.3
17	1.04 (s)	28.3	1.04 (s)	28.3
18	3.32 (dd, 11.8, 3.3)	59.2	3.32 (dd, 11.9, 3.4)	59.2
	4.48 (d, 11.8)		4.47 (d, 11.9)	
19	1.62 (s)	29.5	1.62 (s)	29.5
20	0.79 (s)	31.9	0.79 (s)	31.9
1’		163.2		163.2
2’	5.69 (qq, 1.1, 1.1)	115.1	5.68–5.70 (m)	115.1
3’		159.8		159.8
4’	1.37 (d, 1.1)	20.3	1.38 (d, 1.4)	20.2
5’	2.06 (d, 1.1)	27.3	2.06 (d, 1.1)	27.0

[1] Danheiser R. L.; Romines, K. R; Koyama, H.; Gee, S. K.; Johnson, C. R.; Medich, J. R. *Org. Synth.* ***1993****, 71, 133.*
[2] Fukuyama, Y.; Minami, H.; Kagawa, M.; Kodama, M.; Kawazu, K. *J. Nat. Prod.* **1999,** *62,* 337-339.