Supplementry Information
for

Synthesis of Polyprenylated Acylphloroglucinols (PPAPs) using Bridgehead Lithiation: The Total Synthesis of Clusianone and a Formal Synthesis of Garsubellin A.

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Contents

General Methods. All reactions were carried out in dry solvents under an atmosphere of dry N_2. THF was freshly distilled from sodium-benzophenone) and dichloromethane (DCM) from CaH_2. Anhydrous Et_2O (water < 0.03%) was further dried and purified by pressure filtration under N_2 through activated alumina. All other reagents were used as received from commercial suppliers unless otherwise stated. All yields are isolated yields after purification by column chromatography, except where stated. Melting points were obtained using a standard hotplate apparatus and are uncorrected. Infrared spectra were recorded using an FTIR spectrophotometer as sample solutions in chloroform and are reported in cm^{-1}. High resolution mass spectra were acquired using a TOF mass spectrometer, using electrospray ionisation (ESI). ^{1}H and ^{13}C NMR spectra were recorded at 400 or 500 MHz, using $CDCl_3$ or C_6D_6 as solvents, and calibrated on residual solvents signals. *J* values are recorded in Hz and quoted to the nearest 0.1. Reaction progress was monitored by thin layer chromatography (TLC) and plates were visualized under UV light or by development using *p*-anisaldehyde. Flash column chromatography was performed using the indicated solvent systems and commercial silica gel 60A (35-70µ).

(+/-)-(2*S*,4*R*)-2-Benzoyl-3,3-dimethyl-4-prenyl-cyclohexanone (31) and (+/-)-(2*R*,4*R*)-2-benzoyl-3,3-dimethyl-4-prenyl-cyclohexanone (32)

To a solution of CuI (22 mg, 112 mmol, 0.1 eq) and enone **30** (200 mg, 1.12 mmol) in THF (7 mL) and Me_2S (1 mL) at -15 °C was slowly added MeMgBr (560 µL, 3.0 M in Et_2O, 1.68 mmol, 1.5 eq) over 20 min. The reaction mixture was stirred for 15 min, then benzaldehyde (342 µL,

3.36 mmol, 3 eq) was added drop-wise. The mixture was then stirred 1 h from -15 °C to 0 °C, then the reaction was stopped by adding an NH_4OH/NH_4Cl aqueous solution (10%, 1/1 v/v), and extracted with Et_2O. The organic phase was dried ($MgSO_4$) and evaporated *in vacuo*. The residue was dissolved in DCM (10 mL) and Dess-Martin periodinane (5 mL, 15% solution in DCM, 2.24 mmol, 2 eq) was added. The resulting solution was stirred 2 h at rt, then quenched by adding $Na_2S_2O_3$(aq) (10%, 5 mL) and saturated $NaHCO_3$(aq) (5 mL). The resulting two phase mixture was vigorously stirred for one hour. The mixture was extracted with DCM, washed with saturated $NaHCO_3$ and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography (eluent petroleum ether/AcOEt 95/5 to 9/1) to provide **31** (107 mg) and then **32** (87 mg). Overall yield 58%. (**32)** Colorless oil; R_f = 0.27 (petroleum ether/AcOEt 9/1); FTIR ($CHCl_3$) 2914, 2874, 1708, 1667, 1370 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) 7.98 (d, *J* = 7.5, 2H), 7.56 (t, *J* = 7.5, 1H), 7.45 (t, *J* = 7.5, 2H), 5.20 (br t, *J* = 6.0, 1H), 4.32 (d, *J* = 1.5, 1H), 2.84 (td, *J* = 13.5, 7.0, 1H), 2.56 (app t, *J* = 11.0, 1H), 2.35 (br t, *J* = 13.5, 1H), 2.15 (m, 2H), 1.73 (s, 3H), 1.72 (m, 1H), 1.61 (s, 3H), 1.48 (m, 1H), 0.99 (s, 3H), 0.94 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 208.2, 196.6, 138.4, 133.3, 132.6, 128.7, 128.6, 123.5, 71.2, 42.6, 39.9, 39.3, 27.9, 27.8, 26.3, 25.8, 22.2, 17.8; HRMS (ESI) *m/z* calcd for $C_{20}H_{27}O_2$: 299.2011, found 299.1991 $[M+H]^+$. (**31)** White solid, mp = 122-123 °C; R_f = 0.15 (Petroleum ether/AcOEt 9:1); FTIR ($CHCl_3$) 2968, 2931, 1715, 1687, 1370 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) 7.81 (d, *J* = 7.5, 2H), 7.53 (t, *J* = 7.5, 1H), 7.43 (t, *J* = 7.5, 2H), 5.15 (t, *J* = 6.0, 1H), 4.41 (s, 1H), 2.50 (m, 2H), 2.27 (m, 1H), 2.14 (m, 1H), 1.78 (m, 1H), 1.73 (s, 3H), 1.68 (m, 1H), 1.62 (s, 3H), 1.59 (m, 1H), 1.16 (s, 3H), 1.13 (s, 3H). Irradiation at 4.41 ppm (H1) results in a 3% enhancement at 1.68 ppm (H7); ^{13}C-NMR ($CDCl_3$, 100 MHz) 207.7, 197.1, 138.8, 133.1, 133.0, 128.6, 127.8, 123.1, 67.1, 48.5, 43.7, 41.8, 28.0, 27.5, 27.1, 25.9, 17.9, 17.8; HRMS (ESI) *m/z* calcd for $C_{20}H_{27}O_2$: 299.2011, found 299.2006 $[M+H]^+$.

(+/-)-(4*S*,6*S*)-1-(*tert*-Butyldimethylsilyloxy)-4-prenyl-5,5-dimethyl-6-benzoyl-cyclohex-1-ene (33)

A mixture of diketone **31** (694 mg, 2.33 mmol), TBSCl (523 mg, 3.50 mmol, 1.5 eq), Et_3N (650 µL, 4.66 mmol, 2.0 eq) and NaI (523 mg, 3.50 mmol, 1.5 eq) in CH_3CN (15 mL) was heated at reflux for 1 h, when it was cooled to rt, and the solvent evaporated *in vacuo*. The resulting black solid was triturated with petroleum ether, filtrated and washed with petroleum ether. After evaporation of the solvents *in vacuo*, the residue was purified by column chromatography (petroleum ether/AcOEt/Et_3N 98/1/1). Enol ether **33** was isolated as a white solid (500 mg, 52%). mp = 67-69 °C; R_f = 0.64 (petroleum ether/AcOEt 9/1); FTIR ($CHCl_3$) 2927, 2857, 1681, 1362, 1344, 872 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 7.98 (d, *J* = 7.5, 2H), 7.51 (t, *J* = 7.5, 1H), 7.43 (t, *J* = 7.5, 2H), 5.15 (m, 1H), 4.97 (dd, *J* = 5.0, 2.5, 1H), 3.89 (s, 1H), 2.30 (dt, *J* = 17.5, 5.5, 1H), 2.09 (m, 2H), 1.75-1.64 (overlap, 2H), 1.69 (s, 3H), 1.59 (s, 3H), 1.00 (s, 3H), 0.84 (s, 3H), 0.69 (s, 9H), 0.11 (s, 3H), 0.00 (s, 3H). ^{13}C-NMR ($CDCl_3$, 125 MHz) 202.9, 148.4, 140.1, 132.5, 131.6, 128.5, 128.4, 124.0, 104.2, 58.0, 37.5, 37.2, 27.5, 27.3, 25.8, 25.7, 25.5, 22.8, 17.9, 17.8, -4.3, -4.8; HRMS (ESI) *m/z* calcd for $C_{26}H_{40}O_2SiNa$: 435.2695, found 435.2671 $[M+Na]^+$.

(+/-)-(4*S*,6*R*)-1-(*tert*-Butyldimethylsilanoxy)-4-prenyl-5,5-dimethyl-6-benzoyl-cyclohex-1-ene (34)

Obtained using the same procedure as for compound **33**; yield = 86%. White solid, mp = 94-96 °C; R_f = 0.62 (petroleum ether/AcOEt 9/1). FTIR ($CHCl_3$) 2929, 2857, 1680, 1370, 1344, 881 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 7.96 (d, *J* = 7.0, 2H), 7.50 (t, *J* = 7.0, 1H), 7.41 (t, *J* = 7.0, 2H), 5.10 (br t, *J* = 7.0, 1H), 4.92 (dt, *J* = 6.0, 2.0, 1H), 4.22 (br s, 1H), 2.15 (m, 2H), 1.77 (m, 2H), 1.70 (s, 3H), 1.60 (s, 3H), 1.42 (m, 1H), 0.94 (s,

3H), 0.90 (s, 3H), 0.64 (s, 9H), 0.08 (s, 6H). ^{13}C-NMR ($CDCl_3$, 125 MHz) 200.6, 148.6, 140.2, 132.3, 132.1, 128.5, 128.2, 123.7, 103.5, 58.2 (br), 45.0, 37.1, 28.0, 27.4, 27.1, 25.8, 25.4, 17.8, 17.7, 16.9, -4.6, -4.7; HRMS (ESI) *m/z* calcd for $C_{26}H_{40}O_2SiNa$: 435.2695, found 435.2698 $[M+Na]^+$.

(+/-)-(4*S*,6*S*)-3-Methyl-4,6-bis-(prenyl)-cyclohex-2-enone (35)

A solution of *n*BuLi (2.0 mL, 3.2 mmol, 1.15 eq) was added to a 0 °C solution of $^{i}Pr_2NH$ (473 µL, 3.37 mmol, 1.2 eq) in THF (8 mL). After 15 min, the solution was cooled to -78 °C, and a solution of ketone **30** (500 mg, 2.8 mmol) in THF (3mL) was transfered *via* cannula. The resulting yellow solution was stirred at -78 °C for 15 min, then at 0 °C for 30 min, and then cooled to -78 °C. Prenyl bromide (364 µL, 3.15 mmol, 1.1 eq) was added, and the resulting solution was allowed to reach rt over 4 h, before quenching by adding NH_4Cl(aq). The phases were separated and the aqueous phase extracted using Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (eluent petroleum ether/Et_2O 95/5) to provide the title compound as a 9:1 mixture of diastereoisomers (530 mg, 77%). Slightly yellow oil. The major isomer could be isolated in pure form on an analytical scale by preparative TLC. R_f = 0.54 (petroleum ether/AcOEt 4/1). Data for the major diastereoisomer : FTIR ($CHCl_3$) 2914, 1660, 1454, 1380, 893 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 5.78 (s, 1H), 5.09 (m, 1H), 5.03 (m, 1H), 2.52 (m, 1H), 2.32 (m, 2H), 2.27 – 2.10 (m, 3H), 2.01 (m, 1H), 1.95 - 1.90 (m, 1H), 1.93 (s, 3H), 1.70 (s, 3H), 1.67 (s, 3H), 1.59 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 201.0, 164.5, 133.6, 133.1, 126.3, 122.2, 121.9, 41.7, 39.7, 31.2, 29.6, 27.8, 25.7 (2 C), 22.8, 17.7 (2 C); HRMS (ESI) *m/z* calcd for $C_{17}H_{26}ONa$ 269.1876, found 269.1874, $[M+Na]^+$.

(+/-)-(2*S*,4*S*)-5,5-Dimethyl-2,4-bis-(prenyl)-cyclohexanone (36)

MeMgBr (980 µL, 2.93 mmol, 1.5 eq) was added drop-wise to a solution of enone **35** (480 mg, 1.95 mmol) and CuI (37 mg, 10 mol%, 195 µmol) in a mixture of THF (10 mL) and Me_2S (1 mL) at 0 °C. After completion of the addition, the mixture was stirred for a further 15 min at 0 °C, then the reaction was stopped by adding NH_4Cl(aq). The phases were separated and the aqueous phase extracted using Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by flash column chromatography (eluent petroleum ether/Et_2O 95/5) to provide the title compound as a 9/1 mixture of diastereoisomers. Slightly yellow oil (450 mg, 88%). R_f (major) = 0.16 (petroleum ether/Et_2O 95/5), R_f (minor) = 0.20 (petroleum ether/Et_2O 95/5). Data for the major isomer : FTIR ($CHCl_3$) 2966, 2930, 2870, 1703, 1453, 1376 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 5.08 (m, 1H), 4.98 (m, 1H), 2.25 (m, 3H), 2.18 & 2.13 (2d, AB, *J* = 13.5, 2H), 2.05 (m, 1H), 1.87 (m, 1H), 1.70 (s, 3H), 1.70-1.66 (overlap, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H), 1.55 (m, 1H), 0.99 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 214.2, 133.3, 132.4, 123.6, 121.6, 52.2, 47.9, 42.4, 39.1, 31.4, 29.4, 28.9, 27.3, 25.8, 25.7, 23.8, 17.8 (2 *C*); HRMS (ESI) *m/z* calcd for $C_{18}H_{30}ONa$ 285.2189, found 285.2183, $[M+Na]^+$.

1-*tert*-Butyldimethylsilyloxy-5,5-dimethyl-2,4-bis-(prenyl)-cyclohex-1-ene (37)

To a solution of ketone **36** (450 mg, 1.72 mmol) in MeCN (10 mL) was added Et_3N (720 µL, 5.15 mmol, 3 eq), NaI (336 mg, 2.24 mmol, 1.3 eq) and TBSCl (336 mg, 2.24 mmol, 1.3 eq). The resulting mixture was heated under reflux for 1.5 h. The mixture was cooled to rt, more TBSCl (50

mg, 0.2 eq) and NaI (50 mg, 0.2 eq) were added, and the mixture was heated under reflux for 1 h. The solvent was then evaporated *in vacuo*, and the residue was triturated with petroleum ether. The organic extract was concentrated to provide an oil which was purified by flash column chromatography (eluent petroleum ether/Et_2O 99/1 + 0.5% Et_3N) to provide the title compound as a colorless oil (560 mg, 87%). R_f = 0.75 (petroleum ether/Et_2O 95/5). FTIR ($CHCl_3$) 2929, 1602, 1361 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 5.09 (br t, *J* = 6.6, 1H), 5.03 (br t, *J* = 7.0, 1H), 2.78 (dd, *J* = 14.5, 7.0, 1H), 2.68 (dd, *J* = 14.5, 7.0, 1H), 2.10 (br d, *J* = 13.5, 1H), 1.99 (dd, *J* = 17.0, 5.4, 1H), 1.89 & 1.77 (2 d, AB, *J* = 16.5, 2H), 1.70 (s, 6H), 1.70 – 1.58 (m, 2H), 1.62 (s, 3H), 1.59 (s, 3H), 1.22 (m, 1H), 0.95 (s, 9H), 0.93 (s, 3H), 0.85 (s, 3H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) 141.3, 131.6, 131.5, 124.4, 122.9, 113.0, 44.8, 43.3, 33.4, 30.5, 28.8, 28.5, 27.9, 25.9, 25.8, 25.7 (2 C), 22.4, 18.2, 17.8, -3.7; HRMS (ESI) *m/z* calcd for $C_{24}H_{45}OSi$ 377.3234, found 377.3241, $[M+H]^+$.

(+/-)-(1*S*,5*R*,7*S*)-2-Methoxy-8,8-dimethyl-5,7-bis-(prenyl)-bicyclo[3.3.1]non-2-ene-4,9-dione (39) and (+/-)-(1*S*,5*R*,7*S*)-4-methoxy-8,8-dimethyl-5,7-bis-(prenyl)-bicyclo[3.3.1]non-3-ene-2,9-dione (40)

To a solution of enol ether **37** (1.00 g, 2.66 mmol) in Et_2O (2 mL) at -20 °C (dry ice / CCl_4 bath) was added drop-wise malonyl dichloride (517 µL, 5.32 mmol, 2 eq). The reaction mixture was stirred at -20 °C for 24 h, then benzyltriethylammonium chloride (10 mg, 44 µmol, 0.015 eq) was added, followed by a solution of KOH (1.34 g, 23.9 mmol, 9 eq) in H_2O (3 mL). The reaction mixture was allowed to reach rt and stirred for 6 h. After dilution with water (25 mL) and petroleum ether (25 mL), the pH was adjusted at ~10 using 2M NaOH. The phases were separated and the aqueous phase was further extracted using petroleum ether (2 × 25 mL). The combined organic phases were dried over $MgSO_4$ and the

solvent evaporated. The residue obtained was purified by column chromatography (eluent petroleum ether/AcOEt 95/5) to provide ketone **36** (400 mg, 57%). The aqueous layer was cooled to 0 °C, carefully acidified to pH ~1 using 2M HCl, and then extracted using DCM (4 × 30 mL). The combined organic layers were dried over $MgSO_4$, and the solvent removed *in vacuo* to provide crude **38** as an orange foam (370 mg). ^{1}H-NMR ($CDCl_3$, 400 MHz) 9.20 (br s, 1H, O*H*), 5.89 (s, 1H), 4.97 (t, *J* = 7.2, 1H), 4.95 (t, *J* = 7.5, 1H), 2.87 (s, 1H), 2.40 (d, *J* = 6.8, 2H), 2.06 (m, 1H), 1.91 (dd, *J* = 13.5, 4.0, 1H), 1.79-1.55 (m, 2H), 1.66 (s, 3H), 1.64 (s, 3H), 1.61 (s, 3H), 1.54 (s, 3H), 1.35 (t, *J* = 13.5, 1H), 1.12 (s, 3H), 0.90 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 207.7, 195.5, 181.3, 133.9, 133.2, 122.3, 119.4, 108.2, 67.9, 61.7, 42.0, 40.0, 39.9, 29.3, 27.9, 26.9, 25.9, 25.8, 20.6, 18.0, 17.9. Crude **38** obtained above was dissolved in acetone (20 mL), K_2CO_3 (770 mg, 5 eq) and Me_2SO_4 (106 µL, 1.0 eq) were added and the resulting suspension was heated under reflux for 1 h under N_2. The mixture was cooled to rt, the solid was removed by filtration, and the solvent removed *in vacuo*. The residue was purified by column chromatography (eluent petroleum ether/CH_2Cl_2/AcOEt 70/28/2, then 50/40/10) to give pure **39** (170 mg) and then pure **40** (100 mg), 29% overall. (**39**) R_f = 0.27 (petroleum ether/AcOEt 9/1), white solid; mp = 95-97 °C; FTIR ($CHCl_3$) 2969, 2934, 1731, 1650, 1605, 1361 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 5.69 (s, 1H), 4.96 (m, 2H), 3.74 (s, 3H), 2.81 (s, 1H), 2.39 (m, 2H), 2.05 (m, 1H), 1.91 (dd, *J* = 13.0, 4.0, 1H), 1.65 (s, 6H), 1.61 (s, 3H), 1.69 – 1.56 (overlap, 2H), 1.53 (s, 3H), 1.33 (t, *J* = 13.0, 1H), 1.02 (s, 3H), 0.89 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) 207.5, 197.7, 174.4, 133.7, 133.1, 122.4, 119.8, 105.9, 65.9, 63.9, 56.4, 41.8, 40.8, 39.7, 29.4, 28.1, 27.1, 25.9, 25.8, 20.5, 18.0, 17.9. HRMS (ESI) *m/z* calcd for $C_{22}H_{33}O_3$ 345.2424, found 345.2416, $[M+H]^+$. (**40**) R_f = 0.19 (petroleum ether/AcOEt 9/1); white solid; mp = 72-74 °C; FTIR ($CHCl_3$) 2970, 2938, 1731, 1644, 1595, 1372 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 5.71 (s, 1H), 4.96 (m, 2H), 3.74 (s, 3H), 2.82 (s, 1H), 2.45 (dd, *J* = 14.5, 6.5, 1H), 2.36 (dd, *J* = 14.5, 8.0, 1H), 2.09 (m, 1H), 1.90 (dd, *J* = 14.0, 4.0, 1H),

1.68 (s, 3H), 1.67 – 1.65 (overlap, 2H), 1.64 (s, 3H), 1.63 (s, 3H), 1.55 (s, 3H), 1.33 (t, *J* = 13.5, 1H), 1.08 (s, 3H), 0.85 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) 206.6, 193.8, 177.8, 133.7, 133.1, 122.5, 119.3, 106.1, 74.6, 57.1, 56.8, 42.9, 40.7, 39.3, 29.6, 27.6, 26.6, 25.9, 25.8, 20.7, 17.9, 17.8. HRMS (ESI) *m/z* calcd for $C_{22}H_{33}O_3$ 345.2424, found 345.2417, $[M+H]^+$

(+/-)-(1*S*,5*R*,7*S*)-2-Methoxy-8,8-dimethyl-3,5,7-tris-(prenyl)-bicyclo[3.3.1]non-2-ene-4,9-dione (42)

To a cold (-78 °C) solution of **39** (25 mg, 72.6 µmol) in THF (1 mL) was added LTMP (0.5 M solution in THF, 290 µL, 145 µmol, 2 eq) drop-wise *via* syringe. The resulting yellow solution was stirred for 20 min. at that temperature, then a Li(2-Th)CuCN solution (0.25 M in THF, 580 µL, 145 µmol, 2 eq) was added drop-wise, and the resulting solution was stirred at -40 °C for 30 min. The mixture was cooled to -78 °C and prenyl bromide (42 µL, 363 µmol, 5 eq) was added. The solution was stirred while gradually warming up from -78 °C to -40 °C over 1.5 h. The reaction was stopped by adding NH_4Cl (aq), allowed to reach rt and extracted with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated to a yellow oil. Purification by column chromatography (eluent petroleum ether/AcOEt 9/1) to afford the title compound as a white solid (22 mg, 74%). R_f = 0.49 (petroleum ether/AcOEt 9/1); mp = 60-62 °C; FTIR ($CHCl_3$) 2968, 2914, 1727, 1651, 1610, 1375, 1346 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 5.00 (br t, *J* = 7.0, 1H), 4.93 (m, 2H), 3.78 (s, 3H), 3.21 (s, 1H), 3.05 (m, 2H), 2.39 (m, 2H), 2.04 (m, 1H), 1.88 (dd, *J* = 13.5, 4.0, 1H), 1.68 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H), 1.59-1.55 (m, 2H), 1.52 (s, 3H), 1.30 (t, *J* = 13.0, 1H), 1.08 (s, 3H), 0.92 (s, 3H). ^{13}C-NMR ($CDCl_3$, 125 MHz) 207.7, 197.3, 167.7, 133.5, 133.2, 131.8, 125.9, 122.4, 122.0, 119.9, 63.7, 60.5, 56.5, 42.0, 40.4, 39.0, 29.7, 27.9, 25.9, 25.8 (2 C), 25.7, 22.3, 20.8, 18.0, 17.8, 17.7. HRMS (ESI) *m/z* calcd for $C_{27}H_{41}O_3$ 413.3050, found 413.3035, $[M+H]^+$.

(+/-)-(1*S*,5*R*,7*S*)-4-Methoxy-8,8-dimethyl-3,5,7-tris-(prenyl)-bicyclo[3.3.1]non-3-ene-2,9-dione (41)

Prepared using the same procedure as for **42**; yield = 78%. R_f = 0.52 (petroleum ether/AcOEt 4/1); FTIR ($CHCl_3$) 2930, 1729, 1650, 1596, 1375, 1344, 1061 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) 5.01 (m, 2H), 4.97 (br t, *J* = 6.5, 1H), 3.89 (s, 3H), 3.12 (d, *J* 6.5, 2H), 2.89 (s, 1H), 2.48 (dd, *J* 14.5, 6.0, 1H), 2.34 (dd, *J* 14.5, 7.2, 1H), 2.10 (m, 1H), 1.97 (dd, *J* = 14.0, 3.6, 1H), 1.69 – 1.64 (overlap, 2H), 1.69 (s, 6H), 1.68 (s, 3H), 1.66 (s, 3H), 1.64 (s, 3H), 1.57 (s, 3H), 1.35 (dd, *J* = 13.5, 12.5, 1H), 1.04 (s, 3H), 0.84 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 206.9, 194.7, 174.5, 133.4, 133.3, 132.5, 126.7, 122.6, 122.1, 119.9, 75.1, 62.1, 58.9, 43.2, 41.3, 39.1, 30.1, 27.4, 26.6, 25.8, 25.7, 25.6, 23.3, 20.6, 18.0, 17.9, 17.8. HRMS (ESI) *m/z* calcd for $C_{27}H_{41}O_3$ 413.3050, found 413.3047, $[M+H]^+$.

(+/-)-(1*S*,5*R*,7*S*)-2-Methoxy-8,8-dimethyl-3-(prenyl)-1,7-bis-(prenyl)-bicyclo[3.3.1]non-2-ene-4,9-dione (43)

To a cold (-78 °C) solution of **42** (35 mg, 85 µmol) in THF (7 mL) was added TMSCl (43 µL, 340 µmol, 4 eq) followed by a LDA solution (0.5 M solution in THF, 680 µL, 340 µmol, 4 eq) drop-wise *via* syringe. The resulting yellow solution was stirred 2 min. at that temperature, then 12 min. at 0 °C. I_2 (193 mg, 765 µmol, 9 eq) in THF (1 mL) was added to the previous solution, and the resulting mixture was stirred at 0 °C for 20 min. The reaction mixture was diluted with a mixture of AcOEt and petroleum ether (1/2 v/v, 25 mL), and washed succsesively with $Na_2S_2O_3$(aq) and brine. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude oil obtained was purified by column chromatography (eluent petroleum ether/AcOEt 9/1) to provide **43** as a colorless oil (21 mg, 60%); FTIR ($CHCl_3$) 2968, 2914, 1729, 1651, 1589, 1454, 1372,

1355 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 7.16 (d, *J* = 16.5, 1H), 6.45 (d, *J* = 16.5, 1H), 5.07 (s, 1H), 5.04 (s, 1H), 4.93 (m, 2H), 3.88 (s, 3H), 3.31 (s, 1H), 2.43 (m, 2H), 2.05 (m, 1H), 1.95 (dd, *J* = 13.5, 4.0, 1H), 1.93 (s, 3H), 1.66 – 1.57 (overlap, 2H), 1.65 (s, 6H), 1.62 (s, 3H), 1.53 (s, 3H), 1.34 (dd, *J* = 13.5, 1H), 1.12 (s, 3H), 0.95 (s, 3H). ^{13}C-NMR ($CDCl_3$, 125 MHz) 206.7, 197.3, 168.8, 143.0, 136.1, 133.7, 133.2, 122.2, 121.4, 119.7, 118.1, 117.5, 64.0, 61.7, 57.2, 43.0, 40.9, 39.0, 29.8, 28.0, 25.9, 25.8 (2C), 20.9, 18.2, 18.0, 17.9. HRMS (ESI) *m/z* calcd for $C_{27}H_{39}O_3$ 411.2899, found 411.2894, $[M+H]^+$.

(+/-)-(1*S*,5*R*,7*S*)-3-Benzoyl-4-methoxy-8,8-dimethyl-5,7-bis-(prenyl)-bicyclo[3.3.1]non-3-ene-2,9-dione (44)

Prepared using the same procedure as for **29**, yield 80%. R_f = 0.32 (petroleum ether/AcOEt 4/1). FTIR ($CHCl_3$) 2914, 1794, 1676, 1644, 1587, 1462, 1381, 1096, 890 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) 7.86 (d, *J* = 7.5, 2H), 7.57 (t, *J* = 7.5, 1H), 7.45 (t, *J* = 7.5, 2H), 5.14 (br t, *J* = 6.8, 1H), 5.10 (br t, *J* = 7.5, 1H), 3.67 (s, 3H), 2.92 (s, 1H), 2.55 (dd, *J* 14.2, 5.2, 1H), 2.43 (dd, *J* 14.2, 8.8, 1H), 2.18 (m, 1H), 2.11 (dd, *J* 13.2, 4.5, 1H), 2.01 (m, 1H), 1.75 (m, 1H), 1.73 (s, 3H), 1.71 (s, 3H), 1.65 (s, 3H), 1.62 (s, 3H), 1.45 (t, *J* = 13.2, 1H), 1.11 (s, 3H), 0.88 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 205.8, 195.4, 192.8, 174.3, 137.9, 134.3, 133.8, 133.5, 129.2, 128.9, 122.4, 121.4, 119.5, 75.0, 60.8, 58.8, 43.9, 41.3, 40.0, 30.3, 27.7, 26.6, 26.0, 25.9, 20.7, 20.6, 17.9. HRMS (ESI) *m/z* calcd for $C_{29}H_{37}O_4$ 449.2686, found 449.2679, $[M+H]^+$.

(+/-)-(1*R*,5*R*/*S*,8*S*,10*S*)-5-Hydroxy-9,9-dimethyl-1,10-bis-(prenyl)-5-phenyl-3-oxa-tricyclo[6.3.1.0^{2,6}]dodec-2(6)-ene-7,12-dione (45)

To a cold (-78 °C) solution of **44** (28 mg, 62.5 µmol) in THF (1 mL) was added LTMP (0.5 M solution in THF, 624 µL, 312 µmol, 5 eq) drop-wise *via* syringe. The resulting brown solution was stirred 45 min. at that temperature, then prenyl bromide (72 µL, 624 µmol, 10 eq) was added. The solution was allowed to stir at -78 °C for 1 h. The reaction was stopped by adding NH_4Cl (aq), allowed to reach rt and extracted with AcOEt. The combined organic phases were dried ($MgSO_4$) and concentrated to a yellow oil. Purification by column chromatography (eluent petroleum ether/AcOEt 95/5 gradually to 8/2) afforded **45** as a colorless oil (12 mg, 43%); R_f = 0.17 (petroleum ether/AcOEt 9/1); FTIR ($CHCl_3$) 3560 (br), 2970, 2932, 1732, 1650, 1626, 1453, 1396, 1376, 1071 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) 7.32 – 7.24 (m, 5H), 5.15 (br t, *J* = 7.2, 1H), 5.06 (br t, *J* = 7.2, 1H), 4.82 & 4.44 (2 d, AB, *J* 10.5, 2H), 3.33 (s, 1H, exchange with D_2O, OH), 2.75 (s, 1H), 2.55 (dd, *J* 14.0, 6.0, 1H), 2.45 (dd, *J* 14.0, 8.4, 1H), 2.15 (m, 1H), 2.10 (dd, *J* 13.6, 4.5, 1H), 1.85 (m, 1H), 1.76 (m, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.66 (s, 3H), 1.59 (s, 3H), 1.46 (t, *J* = 13.0, 1H), 1.11 (s, 3H), 0.89 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) 205.9, 188.3, 180.3, 143.3, 135.0, 133.5, 128.6, 127.7, 124.7, 123.3, 122.4, 118.7, 88.5, 82.1, 73.6, 55.3, 42.8, 40.9, 38.2, 29.1, 27.7, 26.6, 25.9, 25.8, 20.9, 18.0, 17.9. HRMS (ESI) *m/z* calcd for $C_{29}H_{37}O_4$ 449.2686, found 449.2673, $[M+H]^+$.

(+/-)-(1*S*,5*R*,7*S*)-4-Methoxy-8,8-dimethyl-5,7-bis-(prenyl)-3-trimethylsilanyl-bicyclo[3.3.1]non-3-ene-2,9-dione (46)

To a cold (-78 °C) solution of **40** (90 mg, 261 µmol) in THF (3 mL) was added LTMP (0.5 M solution in THF, 1.05 mL, 523 µmol, 2 eq) drop-wise *via* syringe, followed by freshly distilled TMSCl (99 µL, 783 µmol, 4 eq). The resulting yellow solution was stirred 30 min at that temperature, then the reaction was stopped by adding NH_4Cl (aq), allowed to reach rt and extracted with AcOEt. The combined organic phases

were dried ($MgSO_4$) and concentrated to a yellow oil. Purification by column chromatography (eluent petroleum ether/AcOEt 95/5 gradually to 9/1) afforded **46** as a colorless oil (85 mg, 78%). R_f = 0.5 (petroleum ether/EtOAc 9/1); FTIR ($CHCl_3$) 2969, 1728, 1643, 1561, 1379, 895 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz) 5.03 (m, 1H), 4.99 (br t, *J* = 7.0, 1H), 3.85 (s, 3H), 2.81 (s, 1H), 2.52 (dd, *J* = 14.5, 6.5, 1H), 2.37 (dd, *J* = 14.5, 7.5, 1H), 2.11 (m, 1H), 1.97 (dd, *J* = 13.5, 3.5, 1H), 1.69 (s, 3H), 1.69 – 1.63 (overlap, 2H), 1.65 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H), 1.39 (dd, *J* = 14.0, 12.5, 1H), 1.06 (s, 3H), 0.84 (s, 3H), 0.23 (s, 9H). ^{13}C-NMR ($CDCl_3$, 125 MHz) 207.3, 198.4, 186.6, 133.6, 133.5, 127.4, 122.5, 119.6, 75.9, 63.9, 59.8, 43.2, 41.9, 39.0, 29.8, 27.3, 26.6, 25.8, 25.7, 20.5, 18.0, 17.9, 0.6; HRMS (ESI) *m/z* calcd for $C_{25}H_{41}O_3Si$ 417.2819, found 417.2856, $[M+H]^+$.

(+/-)-(1*S*,5*R*,7*S*)-1-Iodo-4-methoxy-8,8-dimethyl-5,7-bis-(prenyl)-3-trimethylsilanyl-bicyclo[3.3.1]non-3-ene-2,9-dione (47)

To a cold (-78 °C) solution of **46** (32 mg, 77 µmol) in THF (7 mL) was added TMSCl (45 µL, 307 µmol, 4 eq) followed by a LDA solution (0.5 M solution in THF, 614 µL, 307 µmol, 4 eq) drop-wise *via* syringe. The resulting yellow solution was stirred 2 min. at that temperature, then 12 min. at 0 °C. I_2 (176 mg, 693 µmol, 9 eq) in THF (1 mL) was added to the previous solution, and the resulting mixture was stirred at 0 °C for 20 min. The reaction mixture was diluted with AcOEt:petroleum ether (1:2, 40 mL), and washed succsesively with $Na_2S_2O_3$(aq) and brine. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude oil obtained was purified by column chromatography (eluent petroleum ether/AcOEt 9/1) to provide **47** as a colorless oil (18 mg, 40%); R_f = 0.35 (petroleum ether/EtOAc 9/1); FTIR ($CHCl_3$) 2914, 1734, 1646, 1562, 1375, 1055 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) 5.02 (m, 2H), 3.87 (s, 3H), 2.60 (dd, *J* = 14.0, 6.5, 1H), 2.48 (dd, *J* = 14.0, 7.2, 1H),

2.22 (m, 1H), 1.92 (dd, *J* = 13.5, 4.0, 1H), 2.11 (m, 1H), 1.80-1.64 (overlap, 2H), 1.68 (s, 3H), 1.66 (s, 6H), 1.57 (s, 3H), 1.45 (dd, *J* = 14.0, 12.5, 1H), 1.26 (s, 3H), 0.90 (s, 3H), 0.23 (s, 9H); ^{13}C-NMR ($CDCl_3$, 125 MHz) 206.6, 194.5, 184.7, 134.2, 133.9, 126.0, 122.4, 119.2, 88.2, 64.2, 60.1, 48.2, 41.1, 37.9, 31.4, 29.5, 27.8, 25.9, 25.8, 20.8, 18.1, 17.9, 0.5. HRMS (ESI) *m/z* calcd for $C_{25}H_{39}IO_3SiNa$ 565.1611, found 565.1593, $[M+Na]^+$.

(+/-)-(2*S*,4*S*)-4-Allyl-5,5-dimethyl-2-prenyl-cyclohexanone (63)

Methylmagnesium bromide (14.4 mL, 3 M in Et_2O, 1.5 eq.) was slowly cannulated into a solution of enone **62** (6.35 g, 0.029 mol) and copper iodide (0.275 g, 1.45 mmol, 0.05 eq.) in THF:DMS (120:12 mL) at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 15 min, then poured into a mixture of saturated aqueous NH_4Cl:NH_4OH (1:1, 60 mL) and Et_2O (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (3 x 80 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo* to a dark yellow oil. Purification by column chromatography (petroleum ether/EtOAc 97/3 to 95/5) gave **63** (inseparable 10:1 mixture of diastereoisomers) as a pale yellow oil (4.75 g, 70%); R_f = 0.81 (petroleum ether/EtOAc 4/1); FTIR ($CHCl_3$) 2931, 1708, 1639, 1456, 1370, 1109, 994, 913 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ - for major isomer) 5.81-5.70 (m, 1H), 5.07-5.00 (m, 3H), 2.46-2.39 (m, 1H), 2.32-2.11 (m, 4H), 2.10-2.04 (m, 1H), 1.94-1.85 (m, 1H), 1.73 (td, *J* = 6.0, 1.5, 2H), 1.66 (s, 3H), 1.66-1.60 (m, 1H), 1.58 (s, 3H), 1.00 (s, 3H),0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 213.7, 137.7, 133.3, 121.5, 116.0, 52.0, 47.6, 41.5, 39.0, 33.5, 31.4, 29.4, 29.0, 25.7, 23.9, 19.7; HRMS (ESI) *m/z* calcd for $C_{16}H_{27}O$ 235.2061, found 235.2067 $[M+H]^+$.

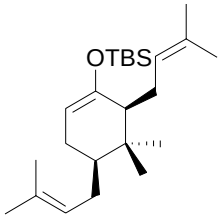
1-*tert*-Butyldimethylsilyloxy-4-allyl-5,5-dimethyl-2-prenyl-cyclohex-1-ene (64)

Sodium iodide (6.0 g, 0.04 mol, 2 eq.), *tert*-butyldimethylsilyl chloride (6.02 g, 0.04 mol, 2eq.), and freshly distilled triethylamine (12.8 mL, 0.09 mol, 4.5 eq.) were added to a solution of cyclohexanone **63** (4.75 g, 0.02 mol) in CH_3CN (35 mL). The reaction mixture was heated under reflux for 3 h, then cooled to rt and concentrated to a brown solid. After trituration of the solid with petroleum ether and concentration *in vacuo*, a pale yellow oil was obtained which was purified by column chromatography (petroleum ether/Et_3N 99/1) to give the title compound **64** as a clear, colourless oil (6.53 g, 95%); FTIR ($CHCl_3$) 3670, 3598, 2865, 1705, 1682, 1638, 1606, 1471, 1362, 1069, 1005, 940, 840 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 5.81-5.72 (m, 1H), 5.06-4.95 (m, 3H), 2.72 (dd, *J* = 14.5, 7.3, 1H), 2.32-2.26 (m, 1H), 2.20 (dd, *J* = 17.0, 5.3, 1H), 1.93 (d, *J* = 17.0, 1H), 1.77 (d, *J* = 17.0, 1H), 1.69 (s, 3H), 1.76-1.64 (m, 3H), 1.63 (s, 3H), 1.34-1.27 (m, 1H), 0.95 (s, 12H), 0.84 (s, 3H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 141.3, 138.7, 131.7, 122.8, 115.2, 113.0, 44.9, 42.3, 34.1, 33.4, 30.4, 28.8, 28.4, 25.9, 25.7, 22.1, 18.2, 17.8, -3.6; HRMS (ESI) *m/z* calcd for $C_{22}H_{41}OSi$ 349.2927, found 349.2932 $[M+H]^+$.

Preparation of derivatives (57) & (58) via (65)

Malonyl dichloride (0.56 mL, 5.73 mmol, 2 eq.) was added dropwise to a solution of the enol ether **64** (1g, 2.86 mmol) in Et_2O (4 mL) at -20 °C (dry ice/CCl_4 bath). The reaction mixture was stirred at –20 °C for 24 h, then a solution of $BnEt_3NCl$ (33 mg, 0.14 mmol, 0.05 eq.) and KOH (1.28 g, 22.9 mmol, 8 eq.) in H_2O (4 mL) was added dropwise. The reaction mixture was allowed to reach rt over 6 h. After dilution with H_2O (15 mL) and petroleum ether (15 mL), the pH was adjusted to ~12 using 1 M KOH. The phases were separated and the aqueous phase was extracted using petroleum ether (2 x 15 mL). The combined organic phases were dried over $MgSO_4$ and then concentrated *in vacuo*. Purification by column chromatography gave ketone **63** as a clear yellow oil (389 mg, 58%). The aqueous layer was then acidified to pH ~1 using 2M HCl, and extracted using CH_2Cl_2 (3 x 20 mL). The combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo* to give the title compound **65** as an orange foam (251 mg). The bicyclic compound **65** was used without purification in the next step.

The crude bicyclic product **65** was dissolved in CH_2Cl_2 (15 mL), and the solution cooled to 0 °C. *m*CPBA was added and the reaction mixture stirred at 0 °C for 2.5 h. After this period, the solution was washed successively with saturated aqueous $NaHCO_3$ (3 x 20 mL) and then with saturated aqueous NaCl (20 mL). The aqueous washings were extracted with CH_2Cl_2 (3 x 20 mL) and combined, dried over $MgSO_4$, and concentrated *in vacuo*. Purification by column chromatography (petroleum ether/EtOAc 85/15) gave firstly the title compound **58** and secondly the title compound **57** in a 1:2 ratio (200 mg, 22 % over two steps from enol ether **64**); data as described previously.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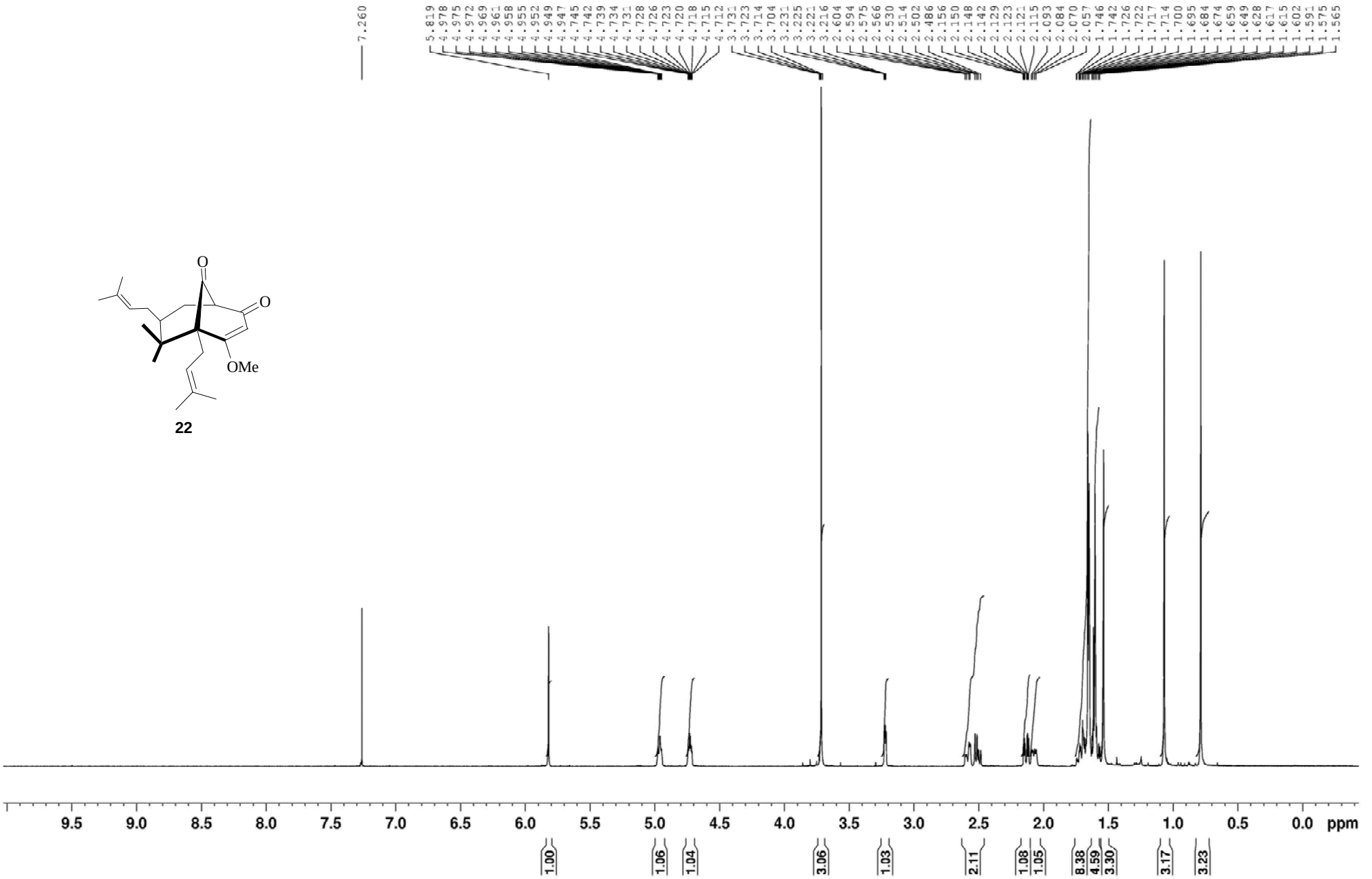
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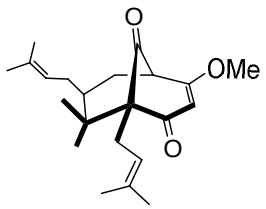
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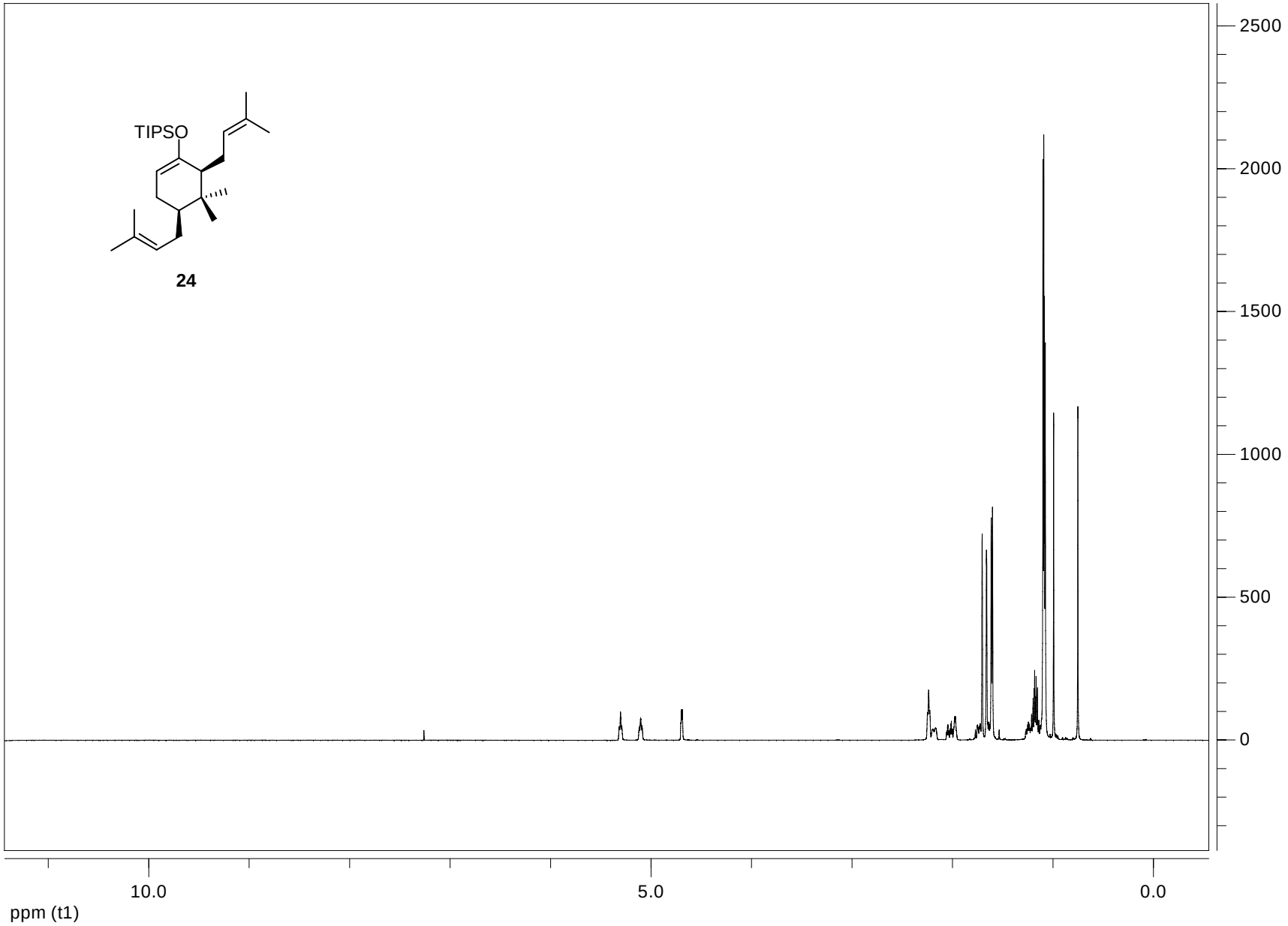
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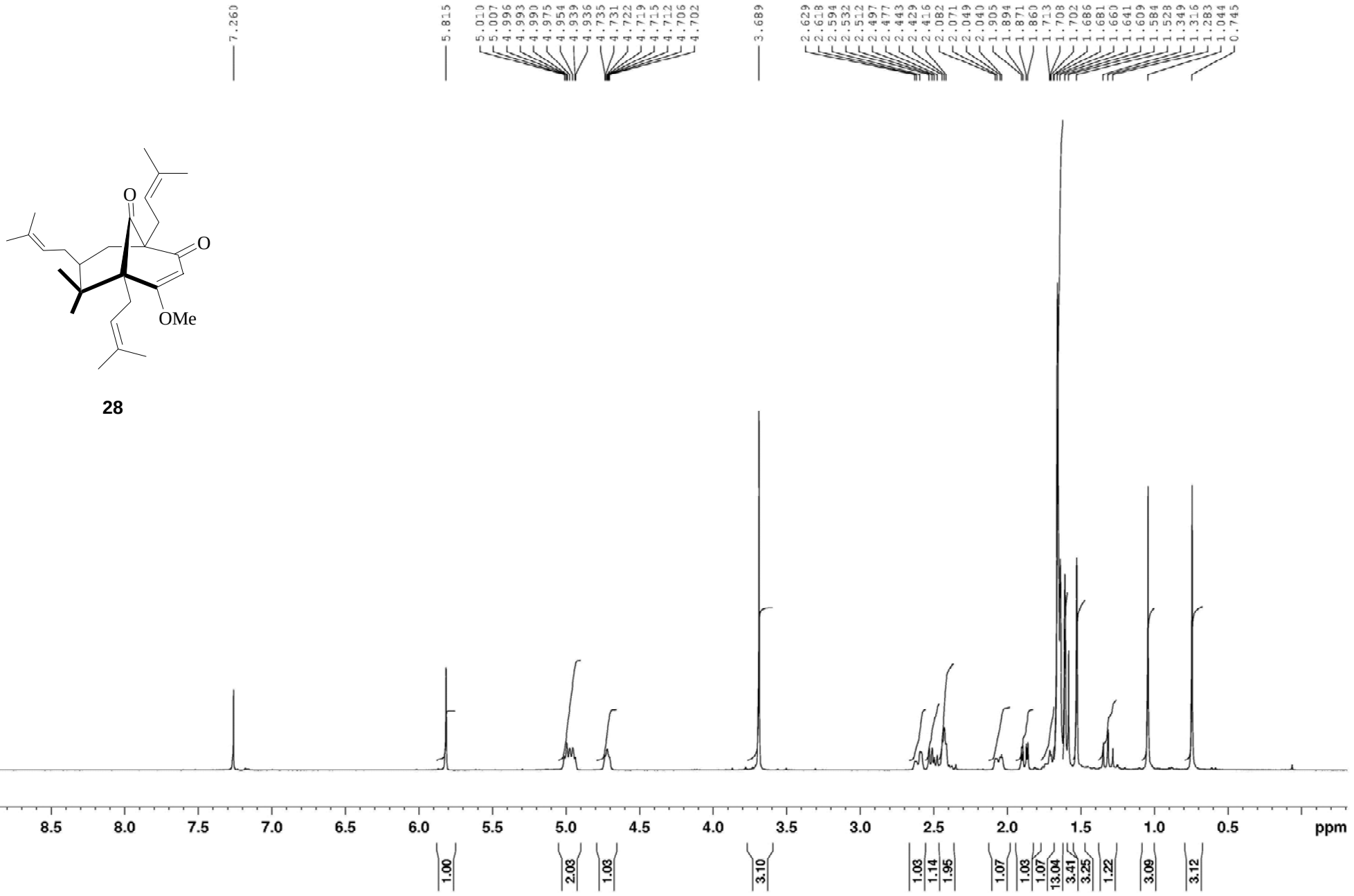
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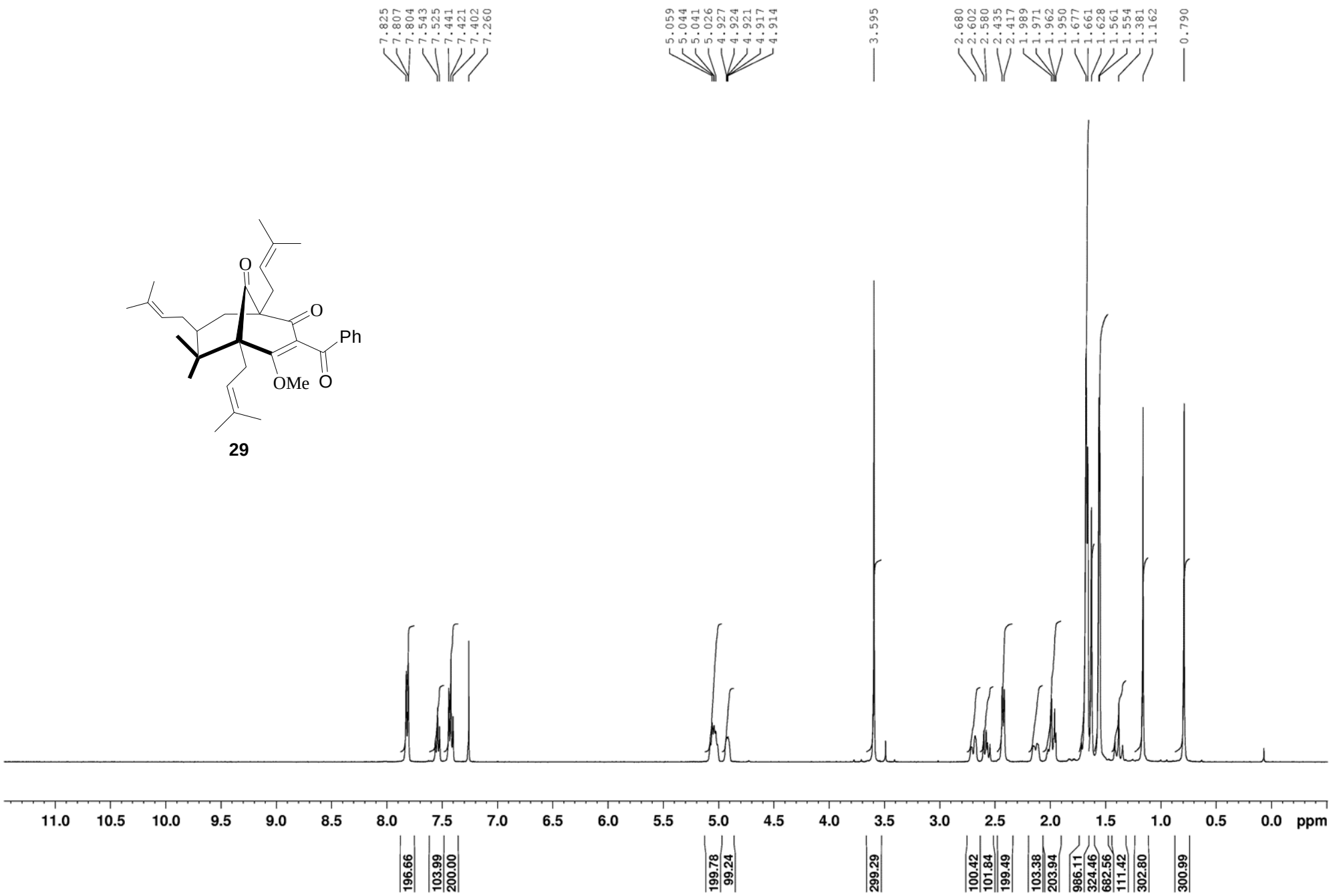
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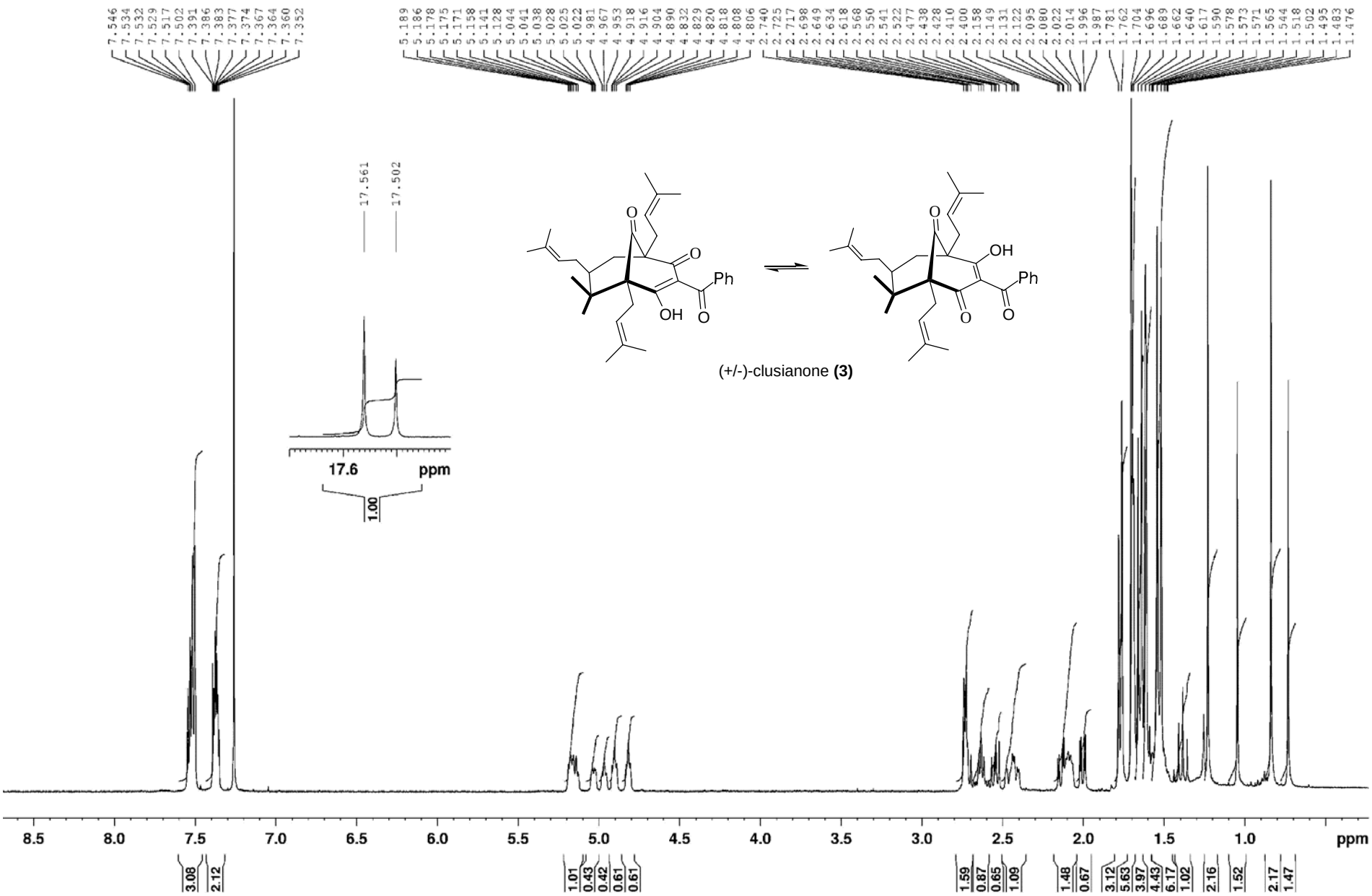
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
196.66
103.99
200.00
199.78
99.24
299.29
100.42
101.84
199.49
103.38
203.94
986.11
324.46
682.56
111.42
302.80
300.99

29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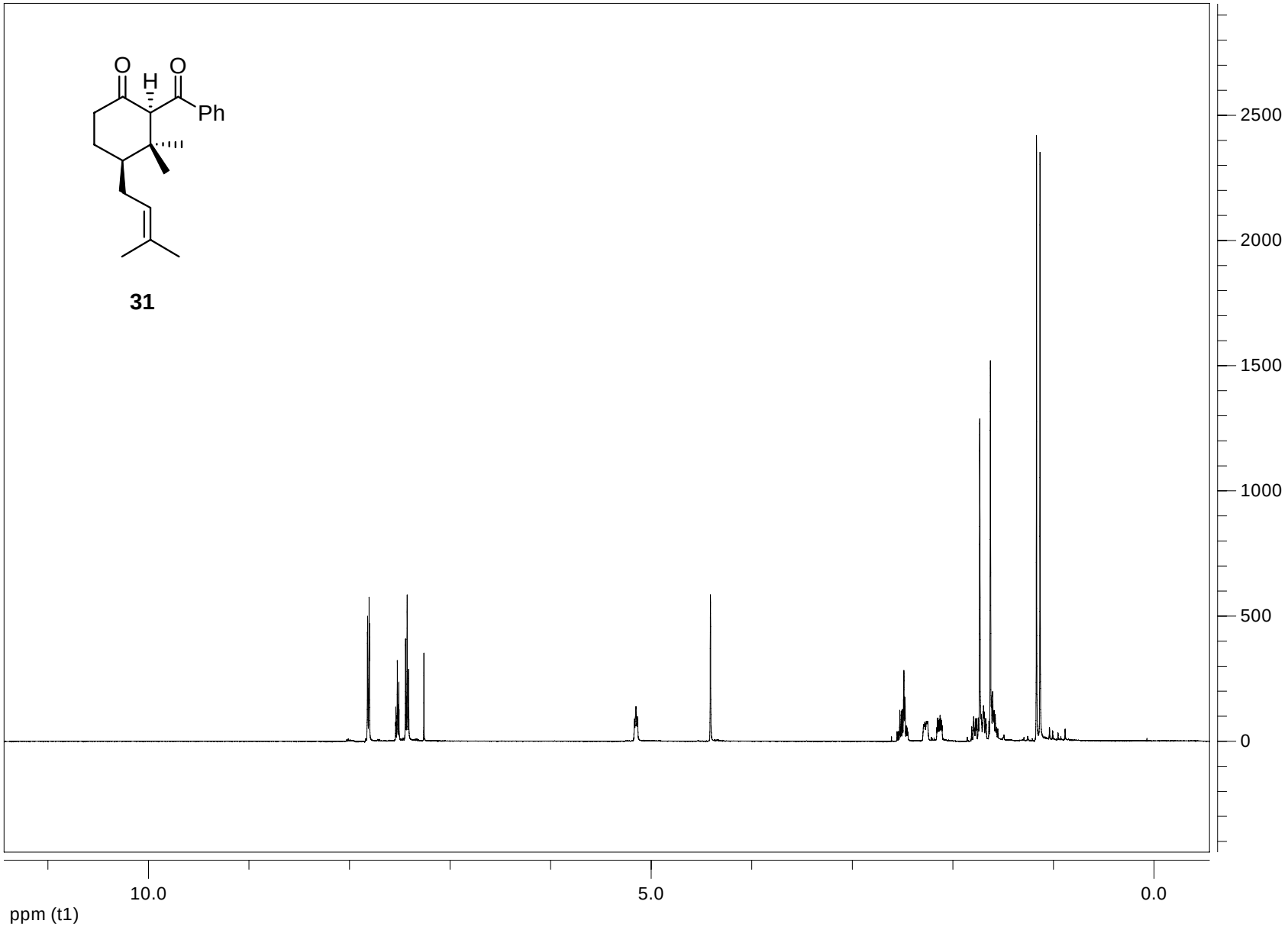
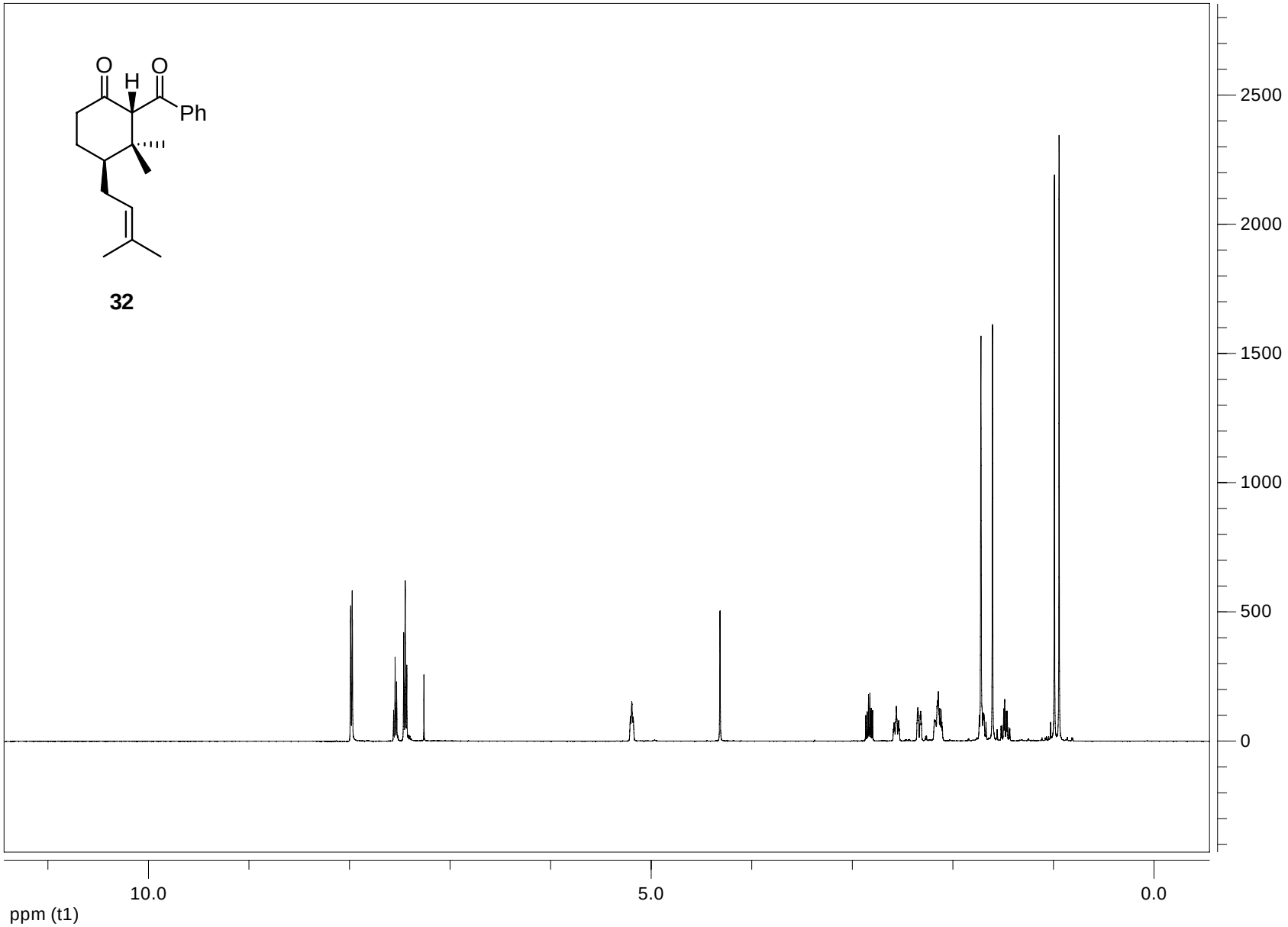
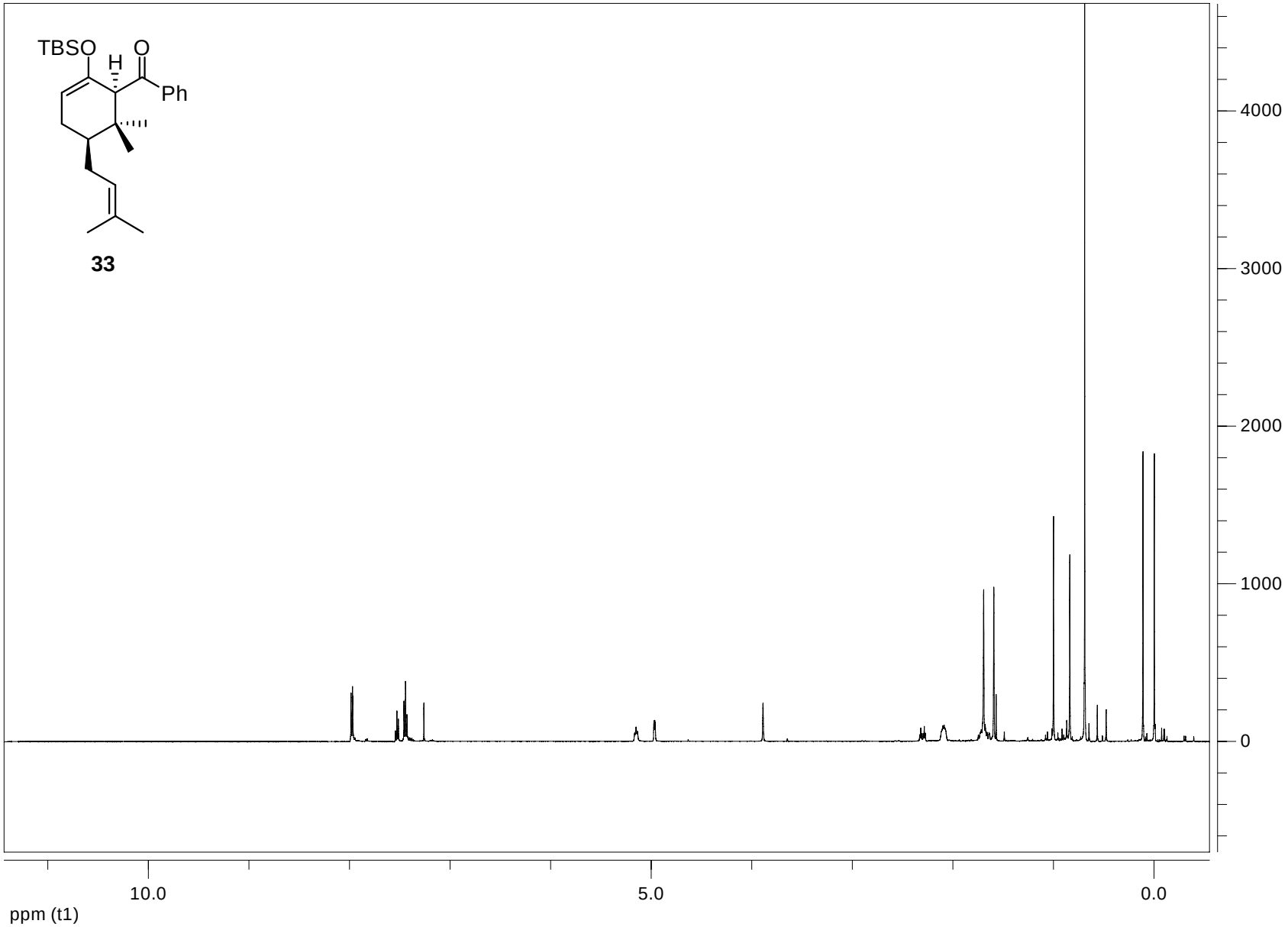
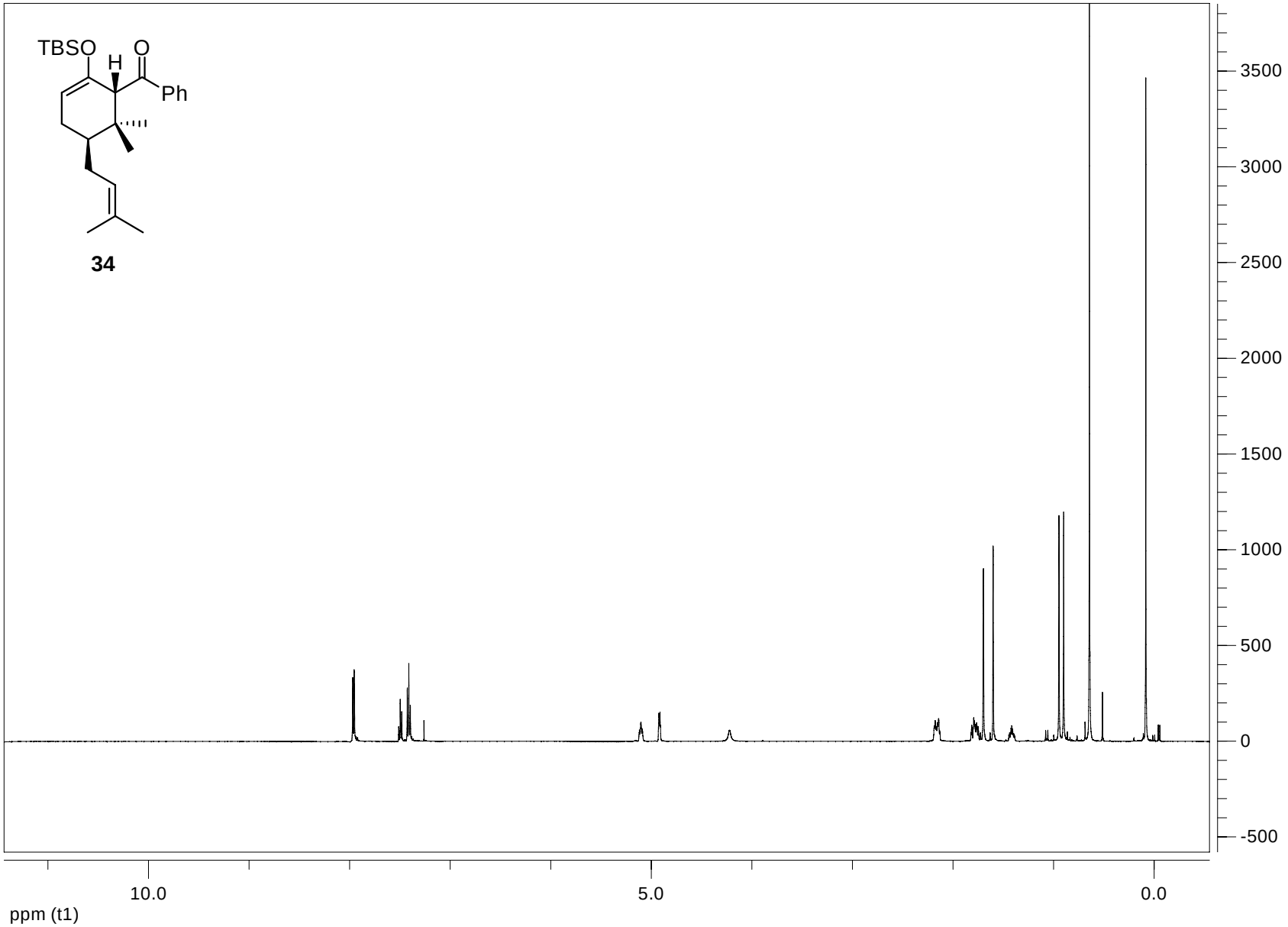
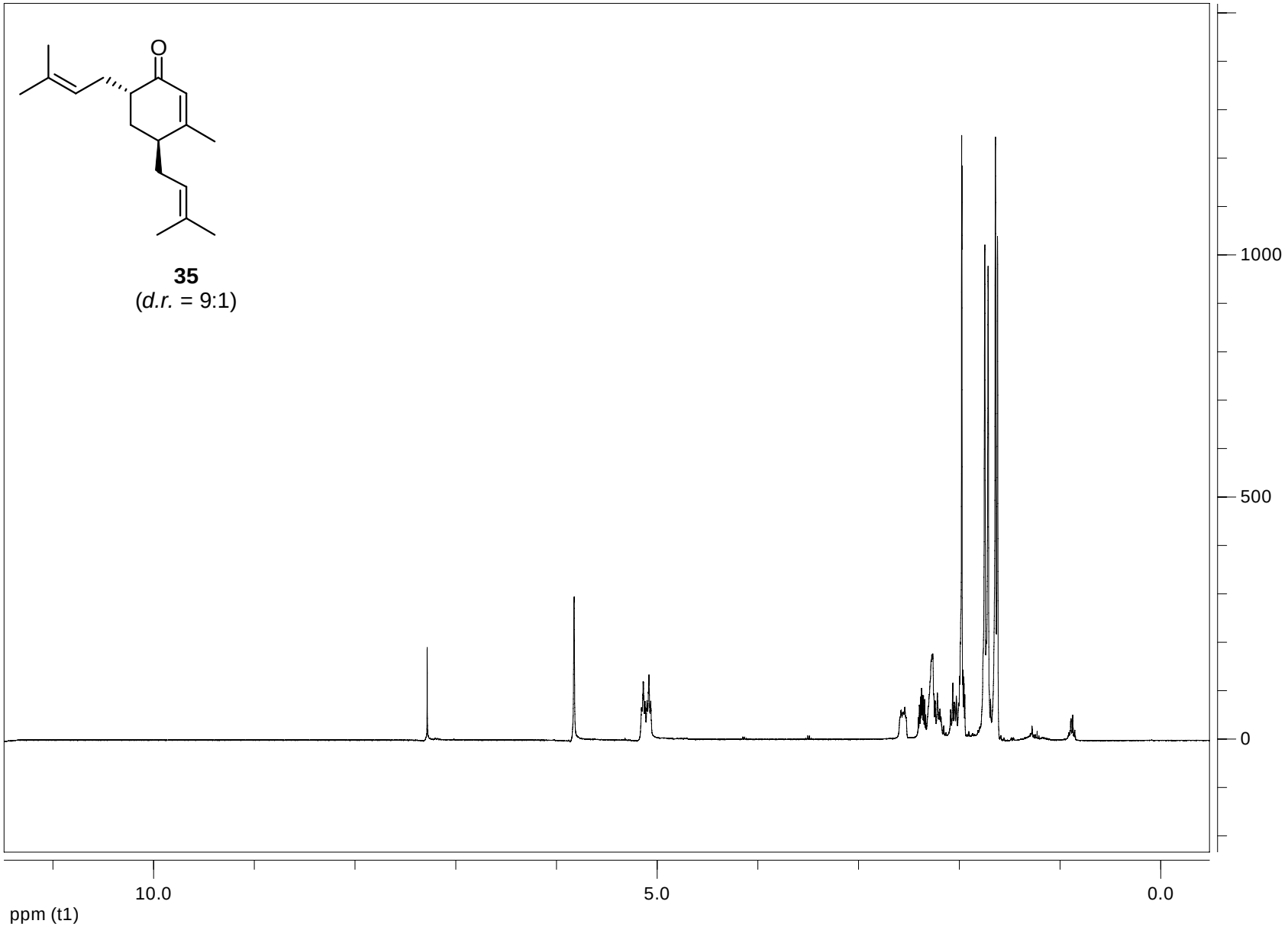
7.534
7.532
7.529
7.517
7.502
7.391
7.386
7.383
7.377
7.374
7.367
7.364
7.360
7.352
5.189
5.186
5.178
5.175
5.171
5.158
5.141
5.128
5.044
5.041
5.038
5.028
5.025
5.022
4.981
4.967
4.953
4.918
4.916
4.904
4.890
4.832
4.829
4.820
4.818
4.808
4.806
2.740
2.725
2.717
2.698
2.649
2.634
2.618
2.568
2.550
2.541
2.522
2.477
2.438
2.428
2.410
2.400
2.158
2.149
2.131
2.122
2.095
2.080
2.022
2.014
1.996
1.987
1.781
1.762
1.704
1.696
1.689
1.662
1.640
1.617
1.590
1.578
1.573
1.571
1.565
1.544
1.518
1.502
1.495
1.483
1.476
17.561
17.502
17.6
ppm
1.00
O
O
Ph
O
OH
O
OH
Ph
O
O
(+/-)-clusianone (3)
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
ppm
3.08
2.12
1.01
0.43
0.42
0.61
0.61
1.59
0.87
0.65
1.09
1.48
0.67
3.12
5.63
3.97
4.43
6.17
1.02
2.16
1.52
2.17
1.47

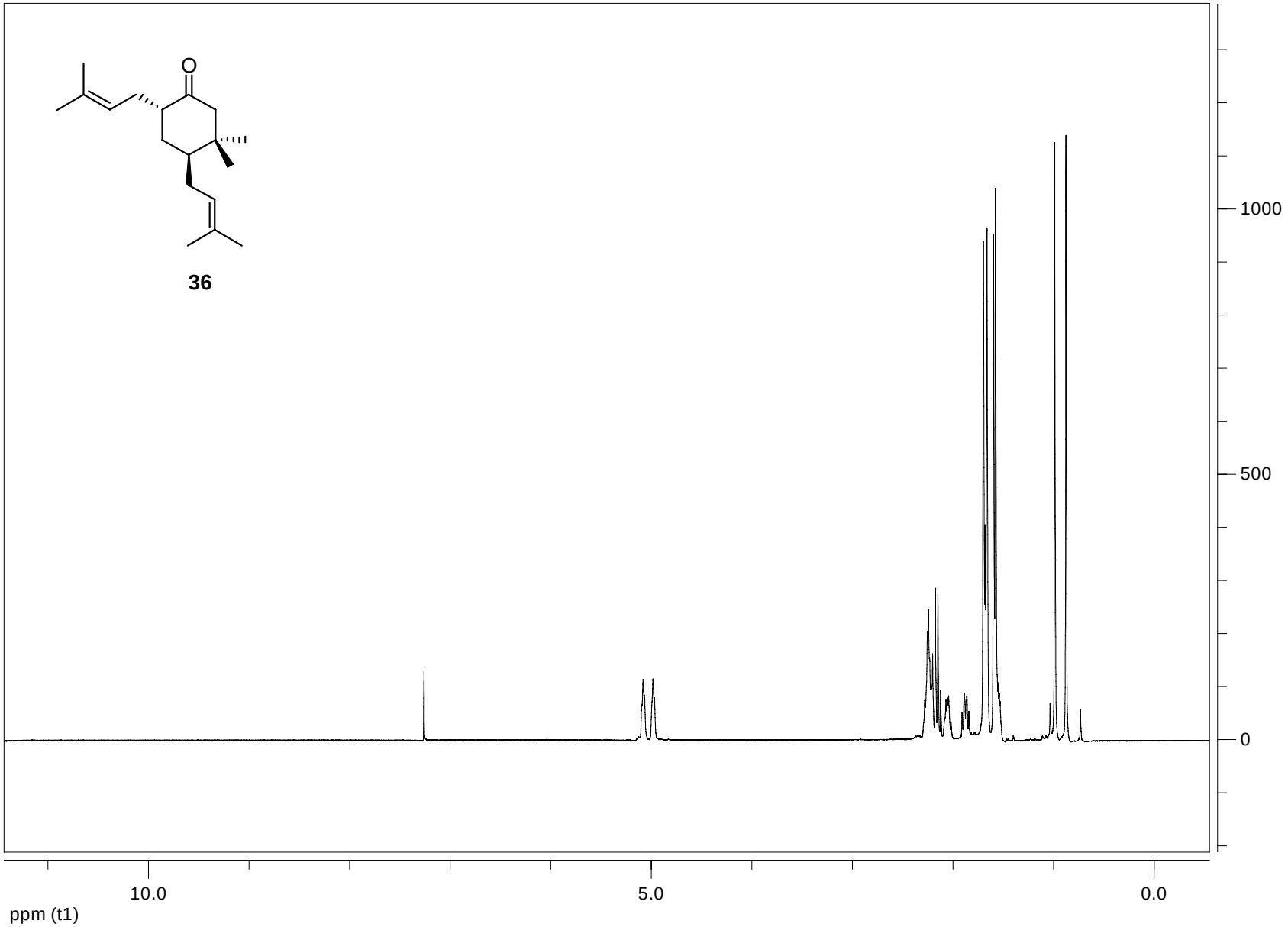

O
H
O
Ph
31
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

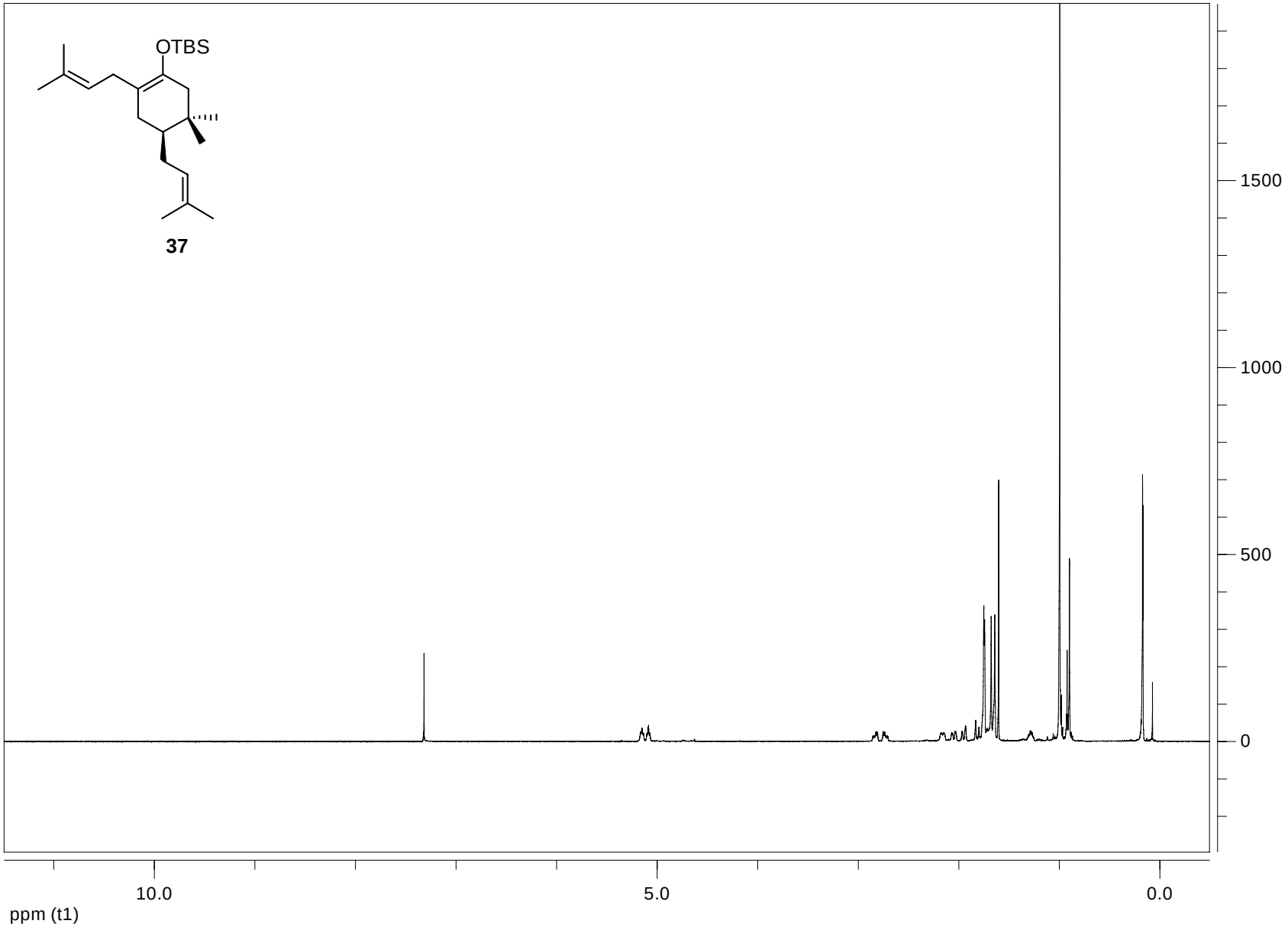

O
H
O
Ph
32
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

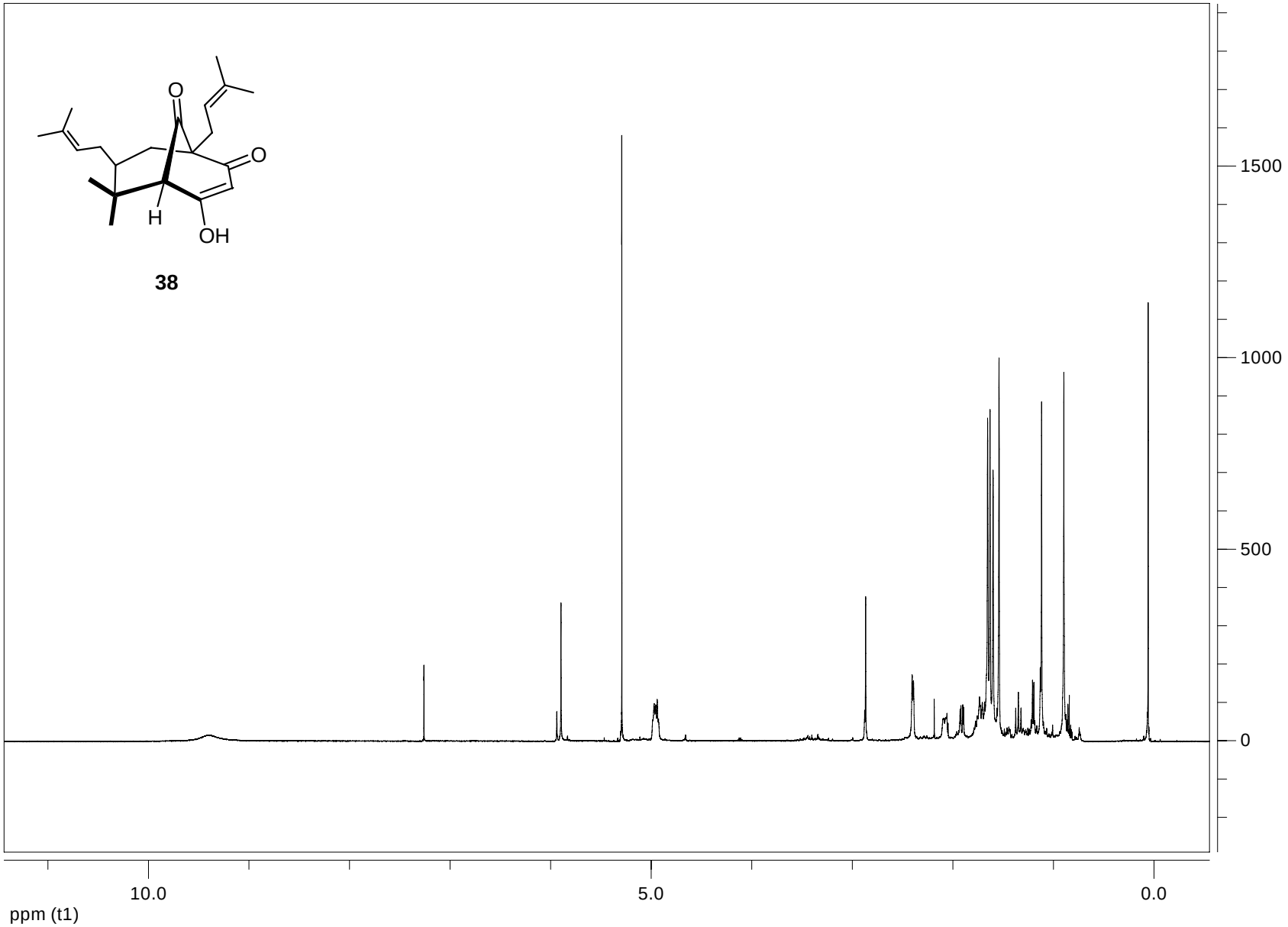

TBSO
H
O
Ph
33
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)

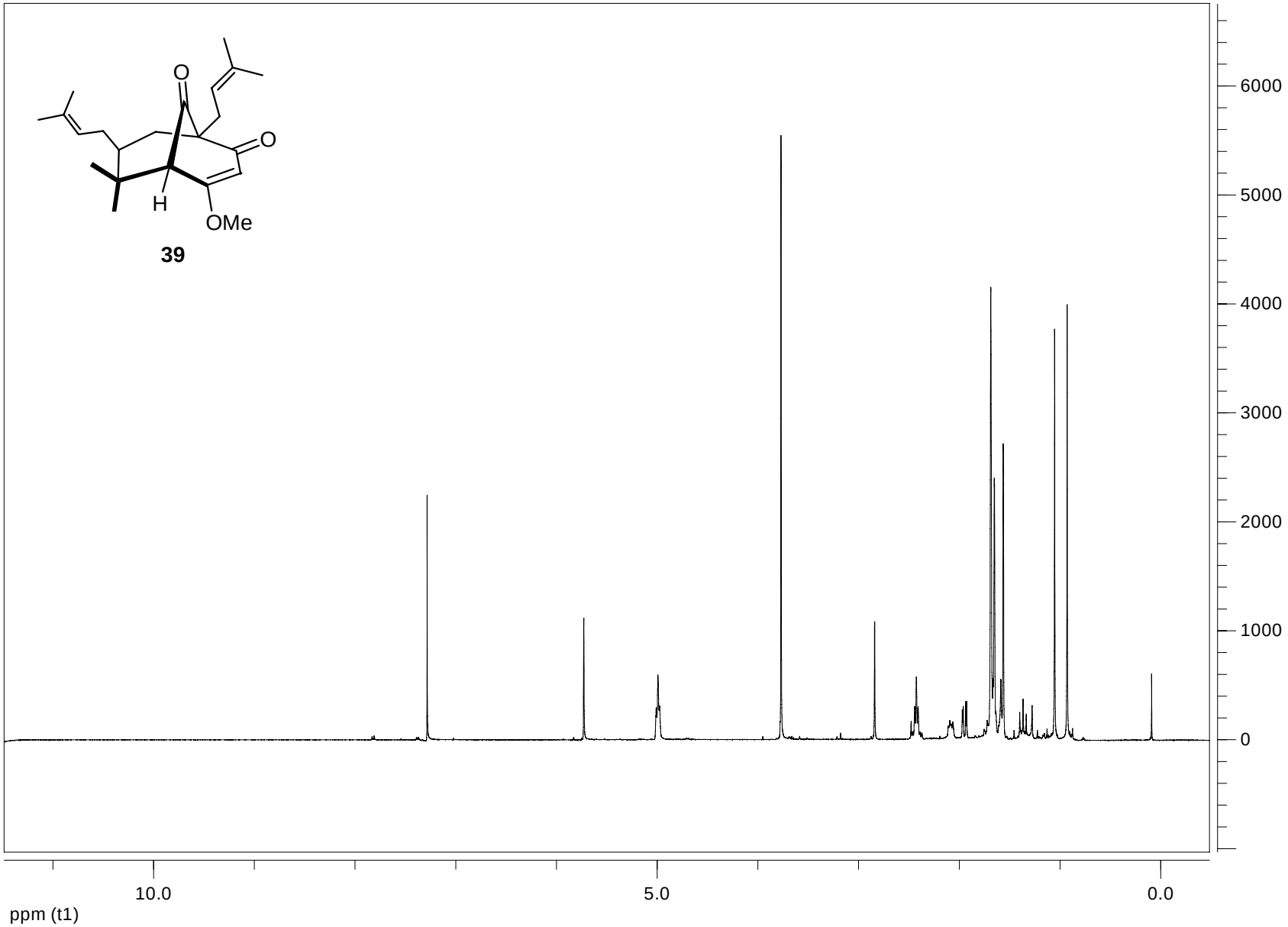

TBSO
H
O
Ph
34
3500
3000
2500
2000
1500
1000
500
0
-500
10.0
5.0
0.0
ppm (t1)

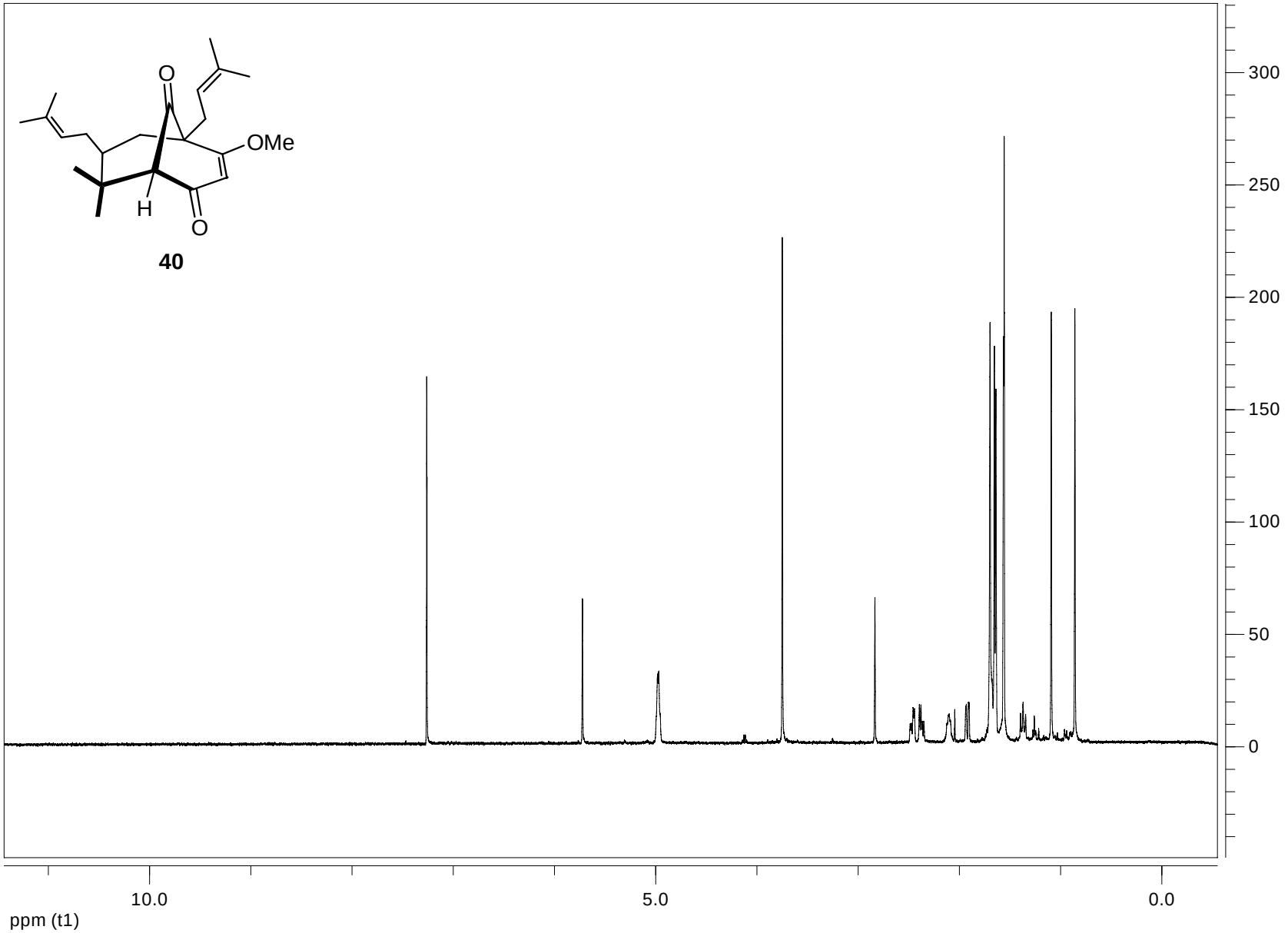

O
35
(d.r. = 9:1)
1000
500
0
10.0
5.0
0.0
ppm (t1)

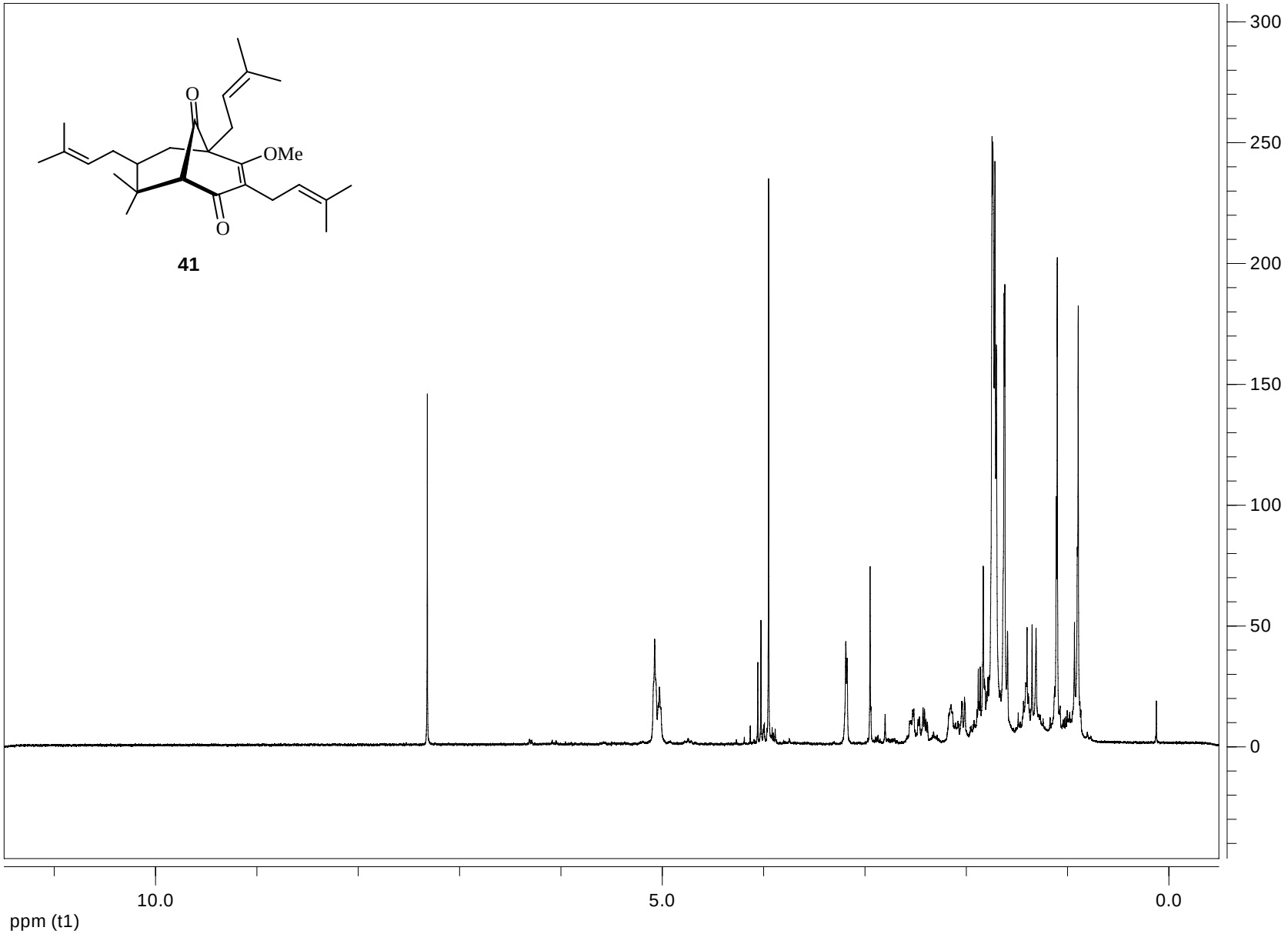

O
36
1000
500
0
10.0
5.0
0.0
ppm (t1)

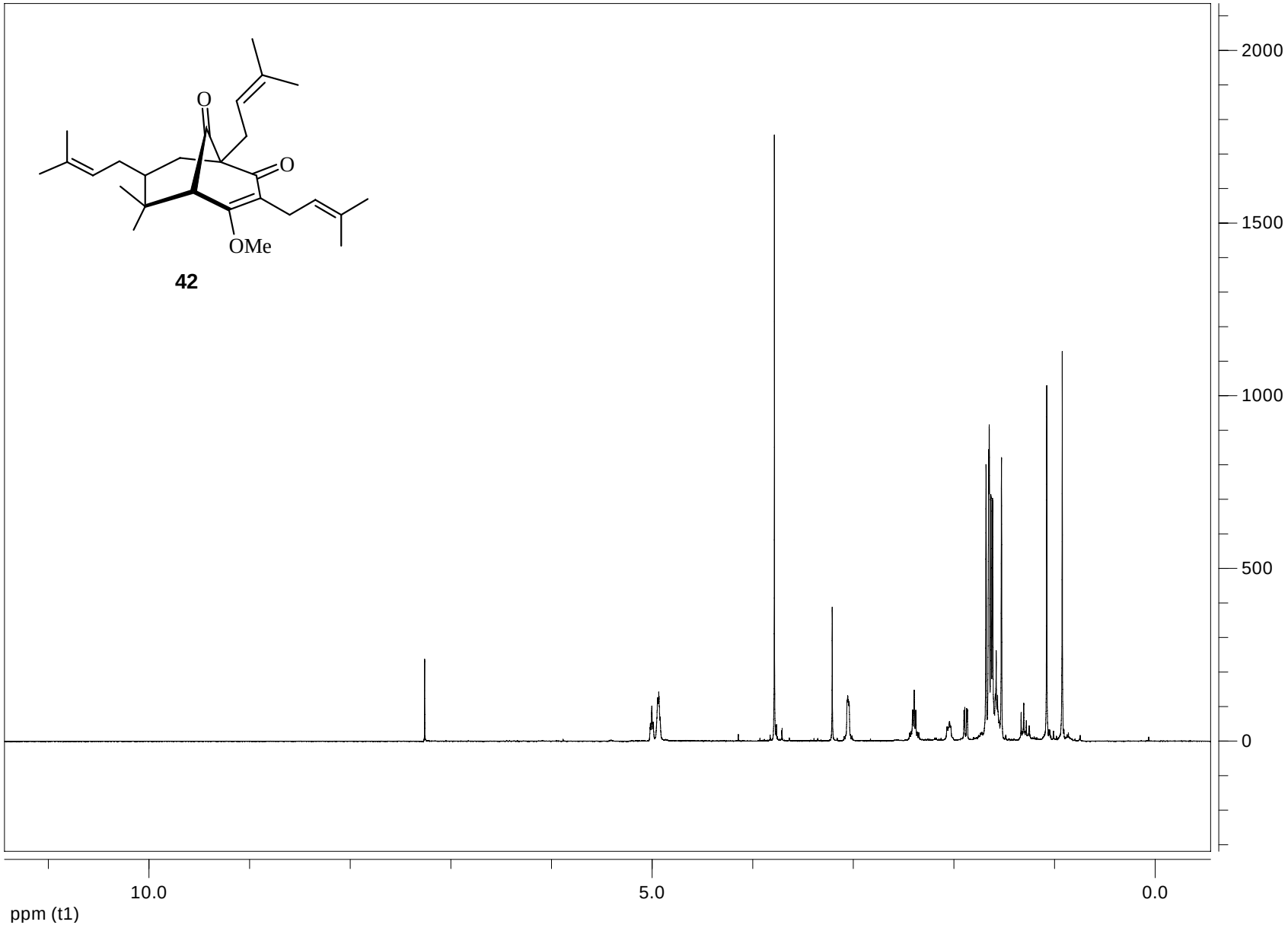

OTBS
37
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

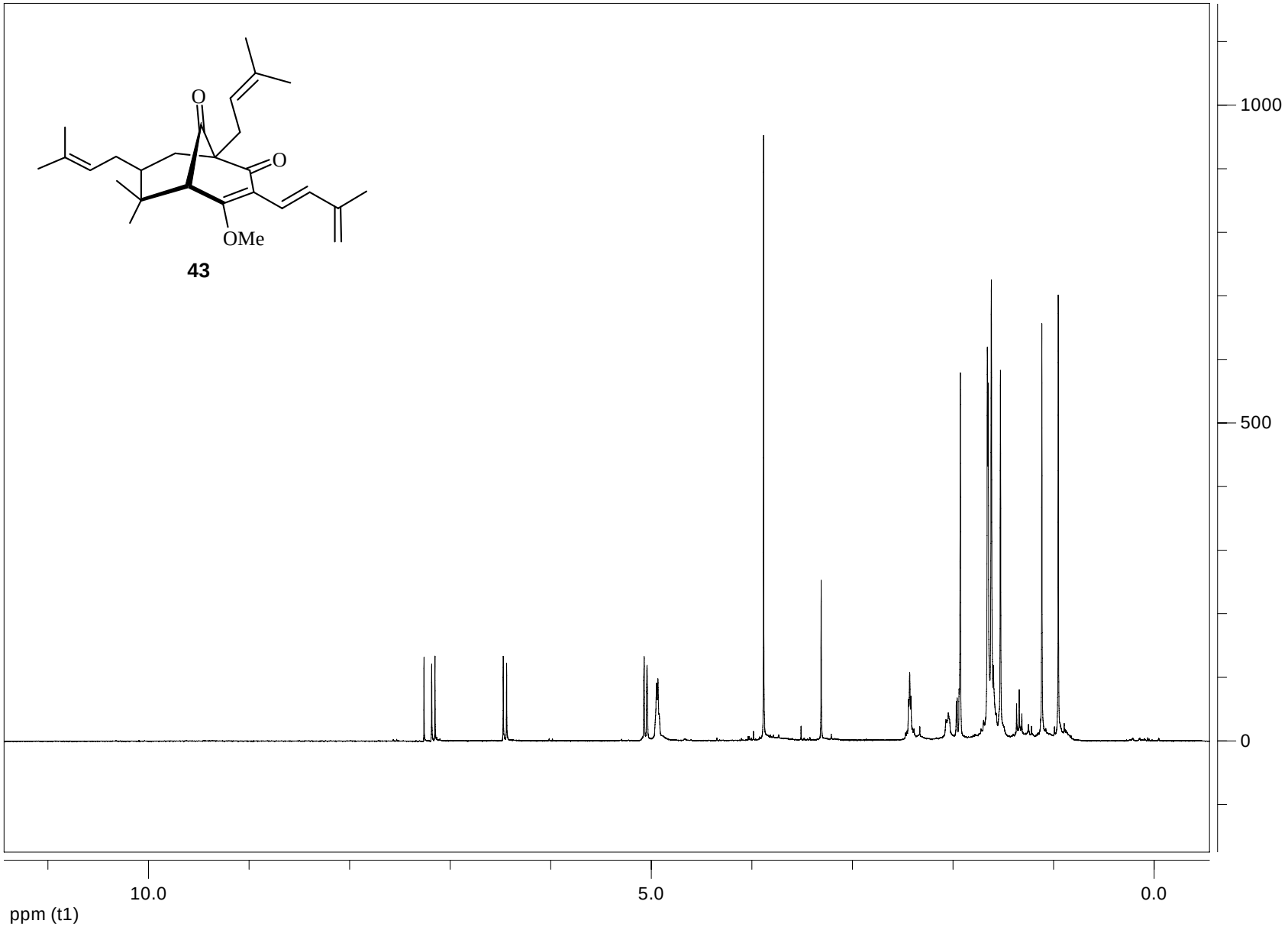

O
O
H
OH
38
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

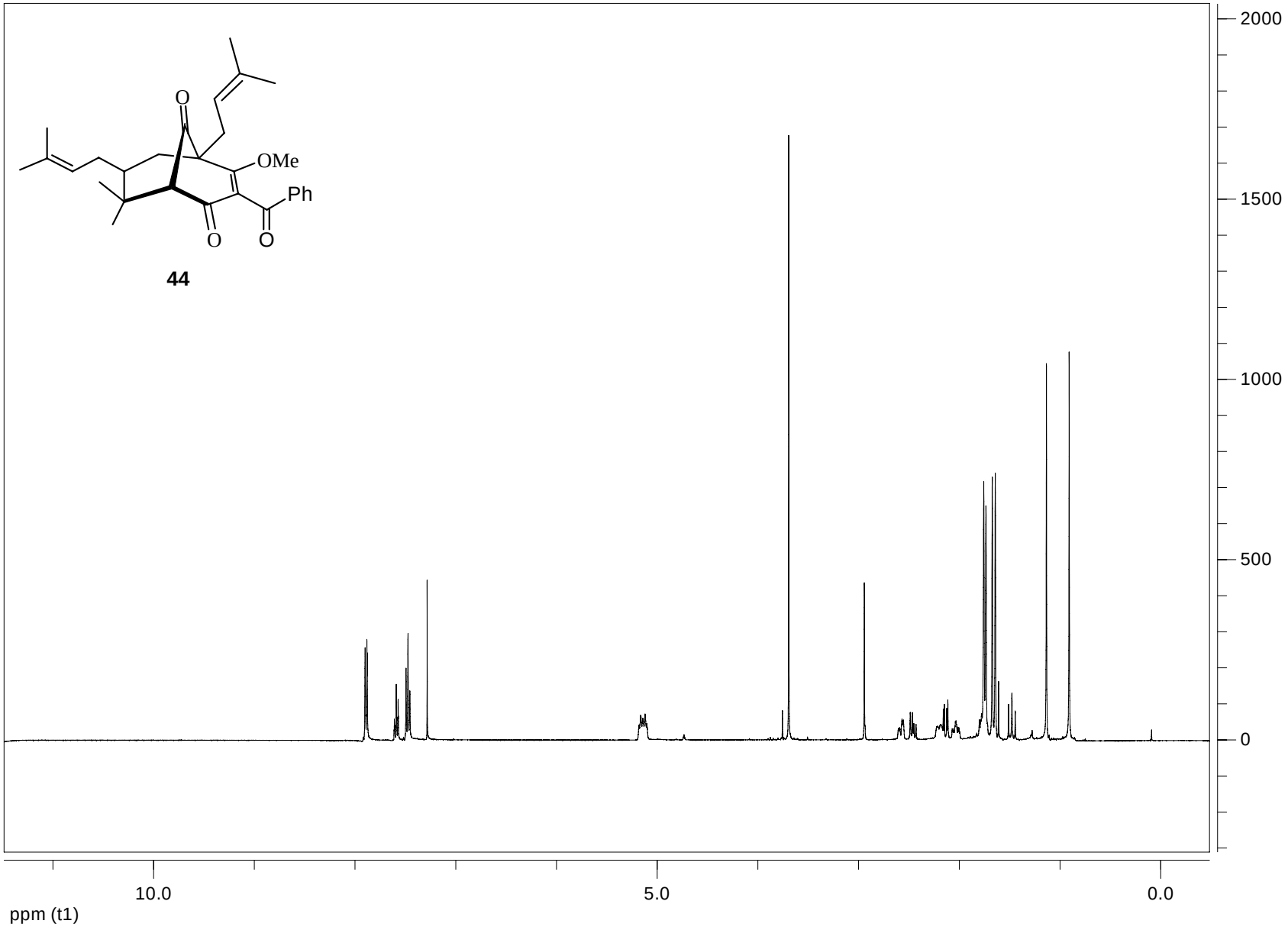

O
O
H
OMe
39
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)

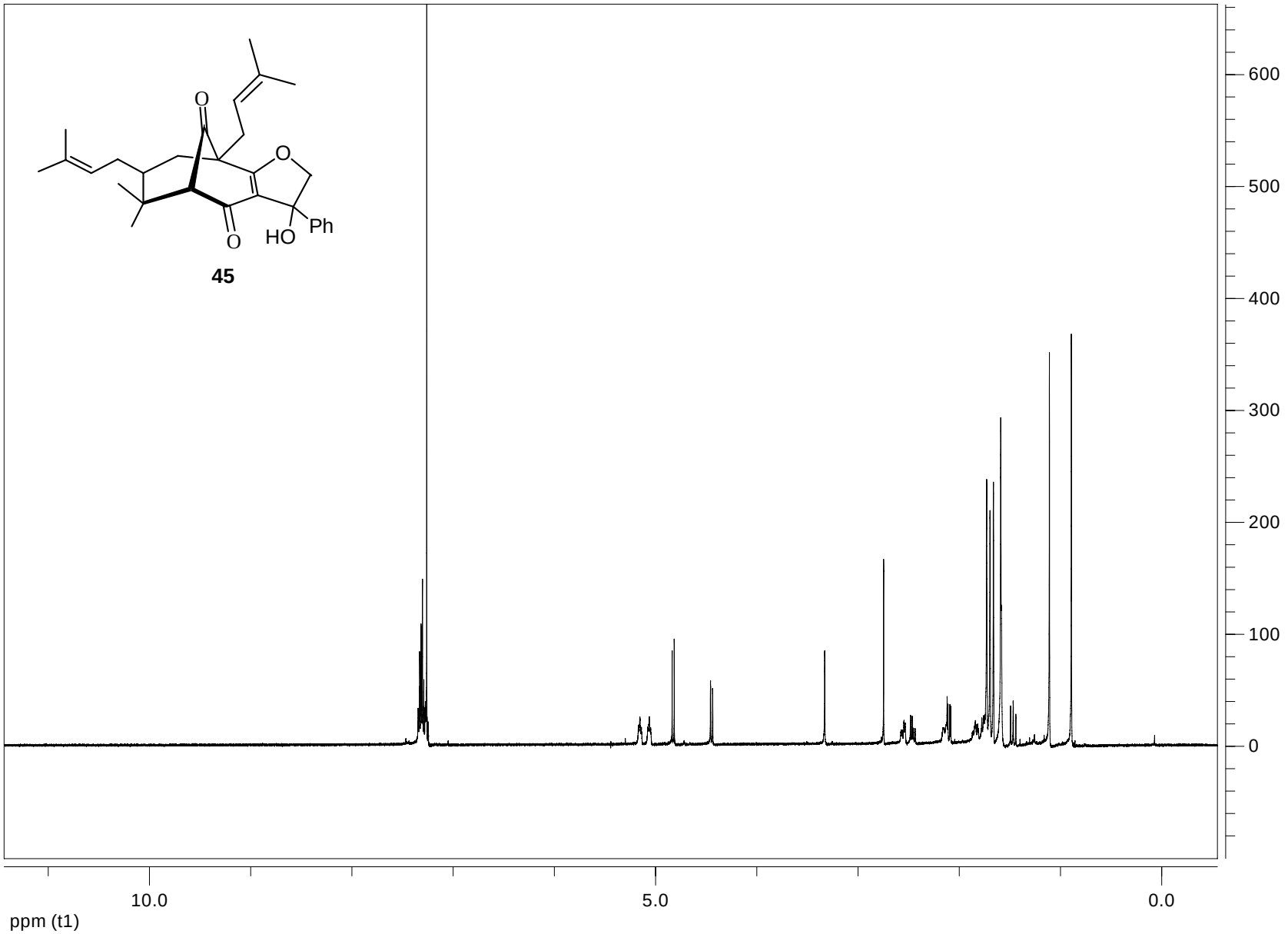

O
OMe
H
O
40
300
250
200
150
100
50
0
10.0
5.0
0.0
ppm (t1)

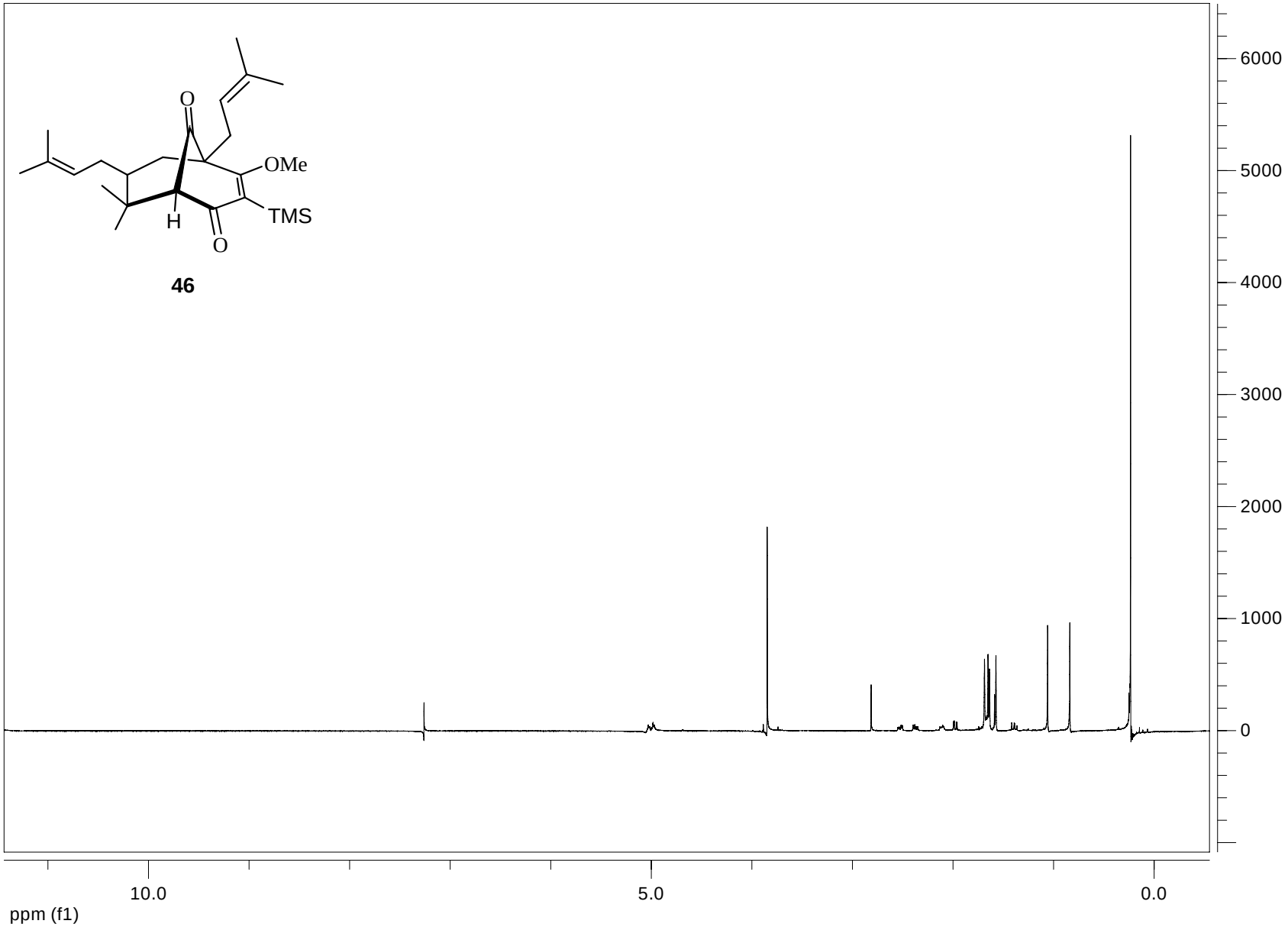

O
OMe
O
41
300
250
200
150
100
50
0
10.0
5.0
0.0
ppm (t1)

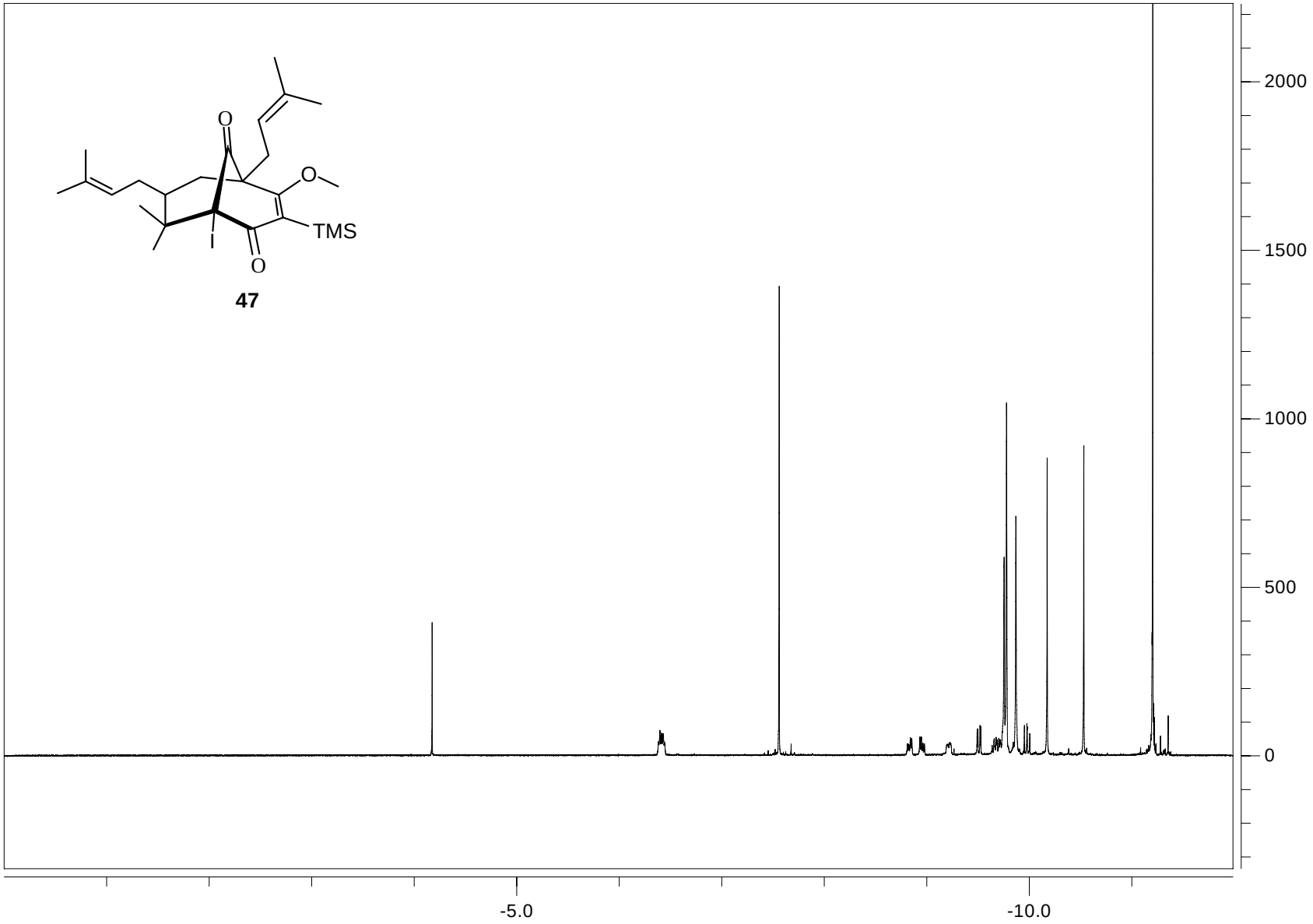

O
O
OMe
42
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

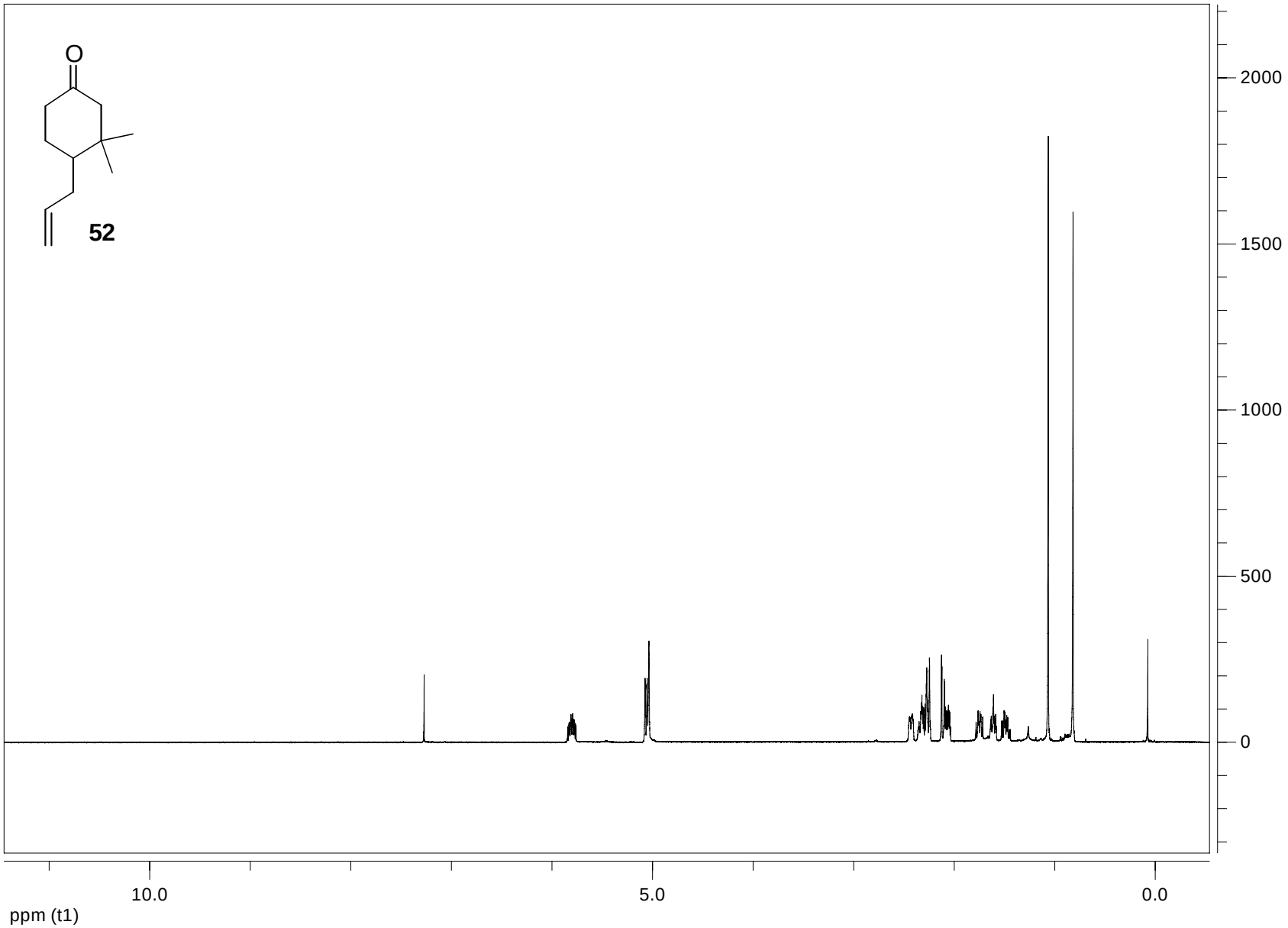

O
O
OMe
43
1000
500
0
10.0
5.0
0.0
ppm (t1)

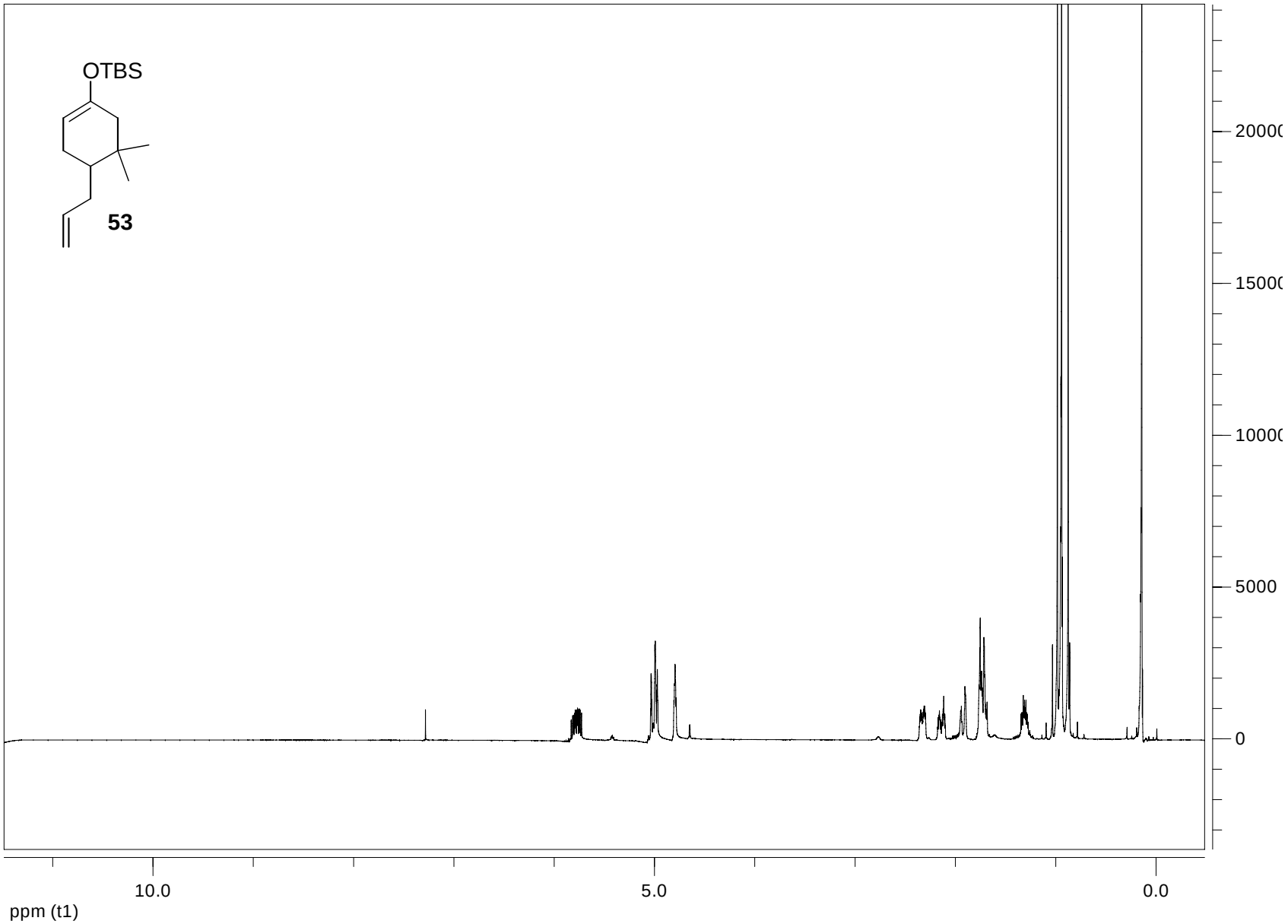

O
OMe
Ph
O
O
44
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

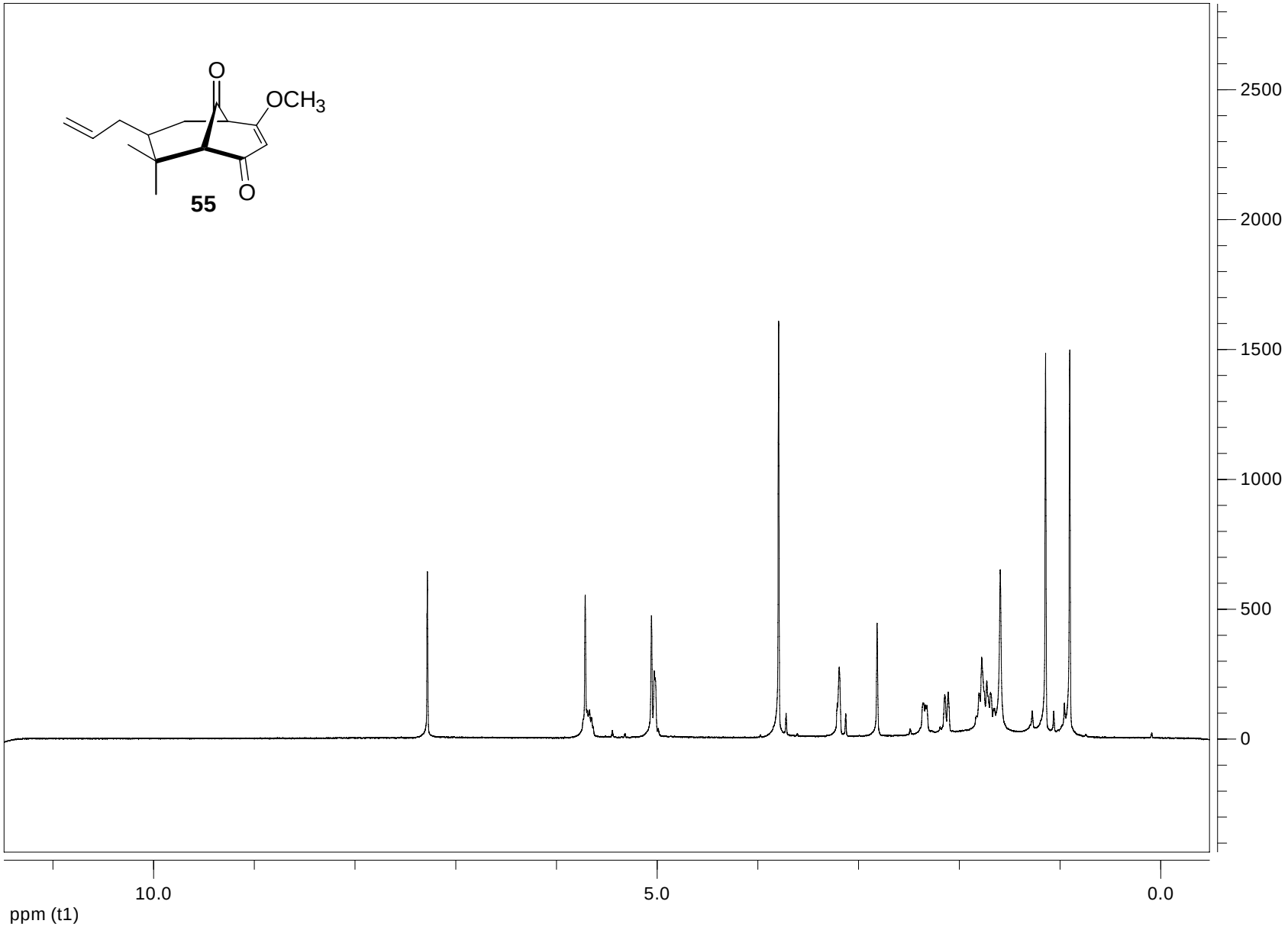

O
O
O
HO
Ph
45
600
500
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)

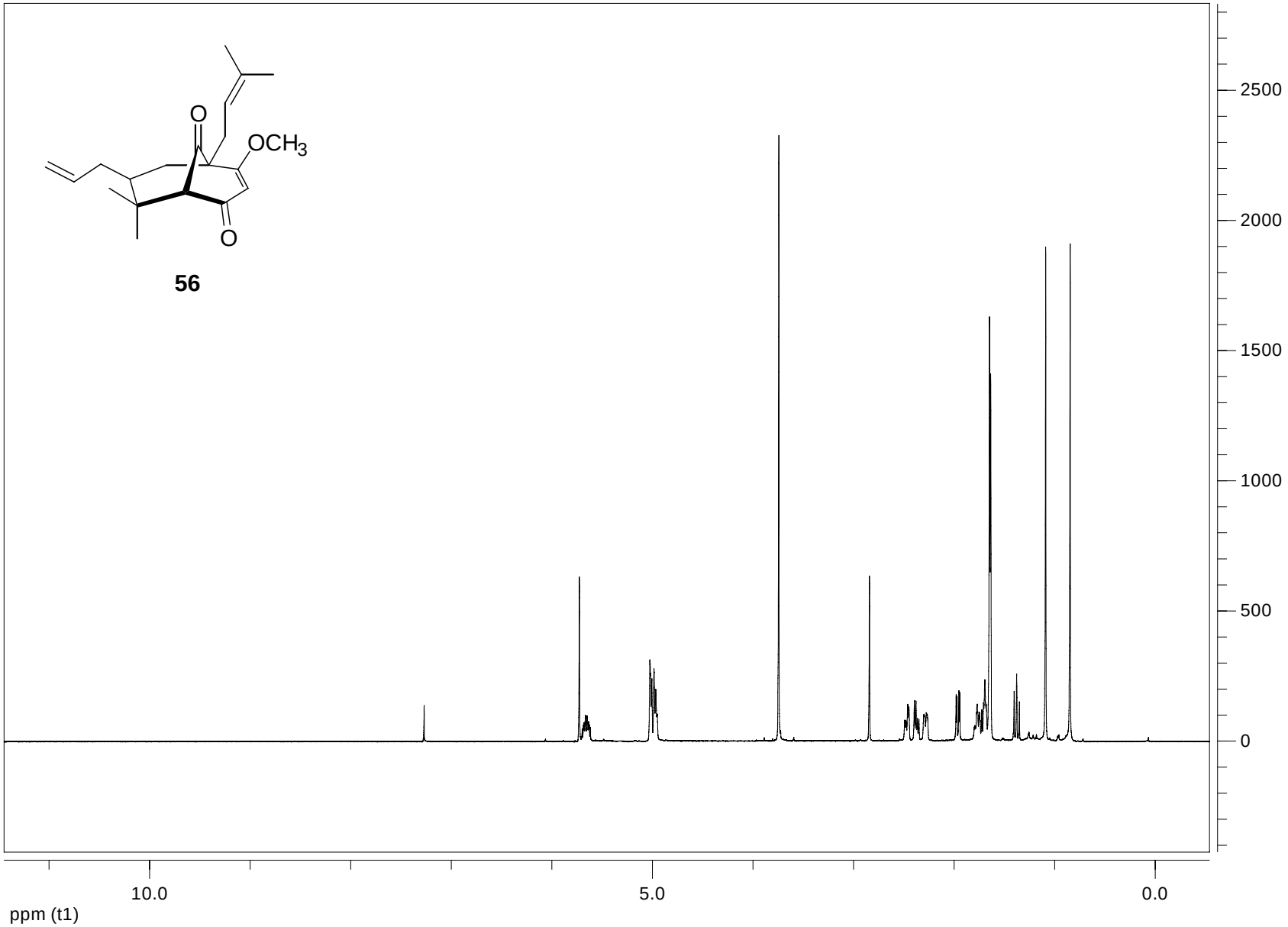

O
OMe
H
TMS
O
46
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)

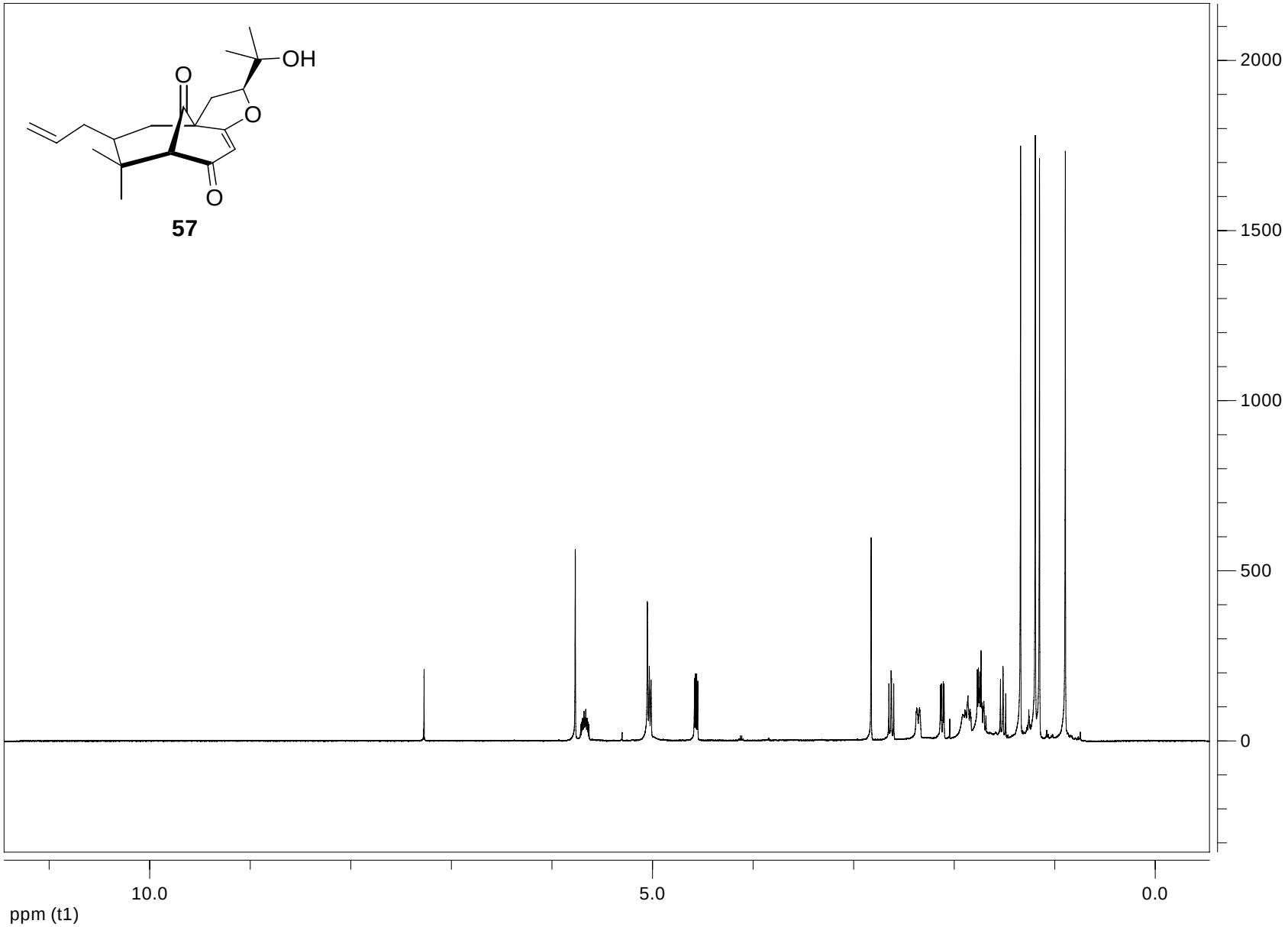

O
O
O
TMS
I
O
47
2000
1500
1000
500
0
-5.0
-10.0
ppm (t1)

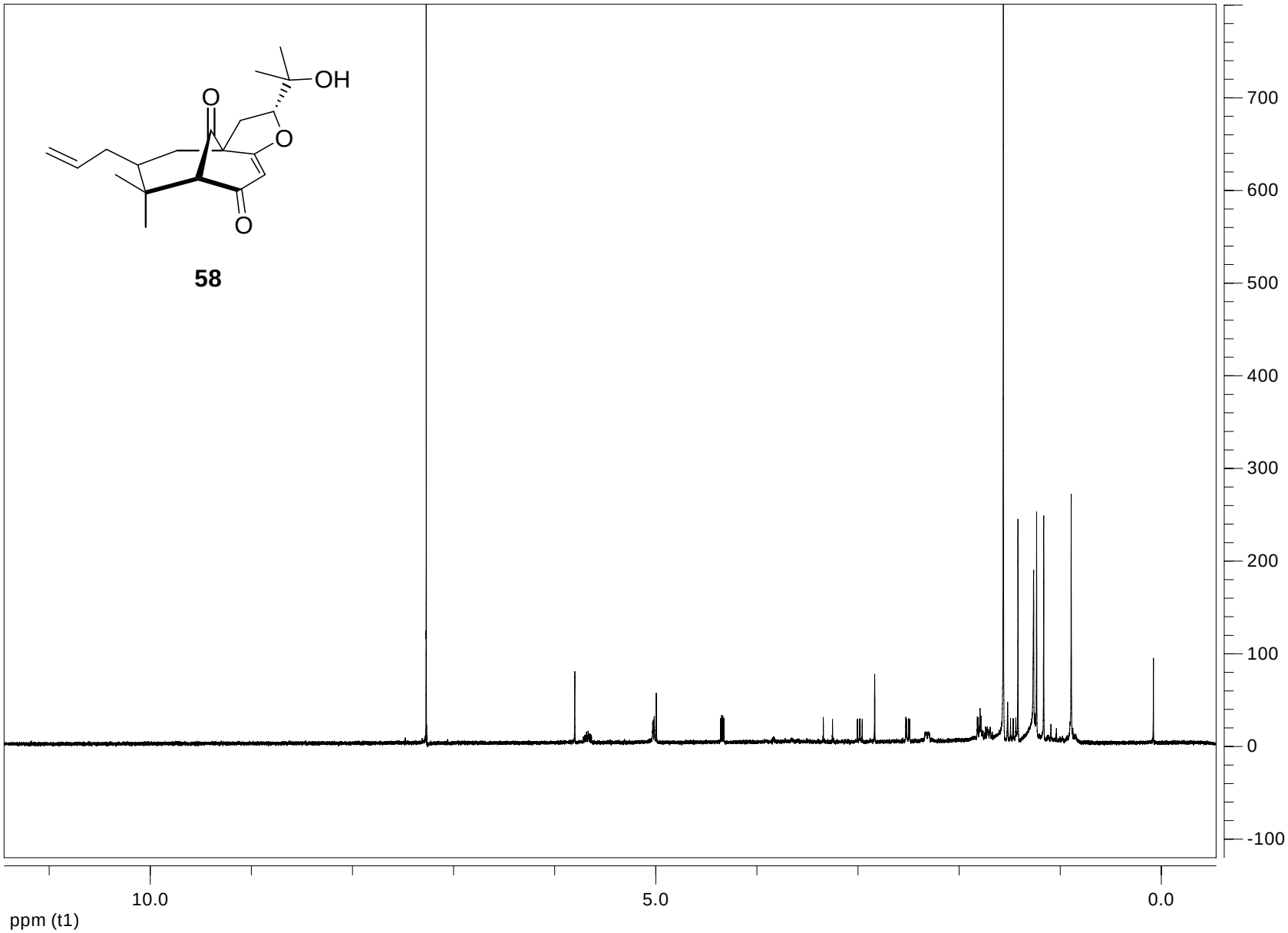

O
52
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

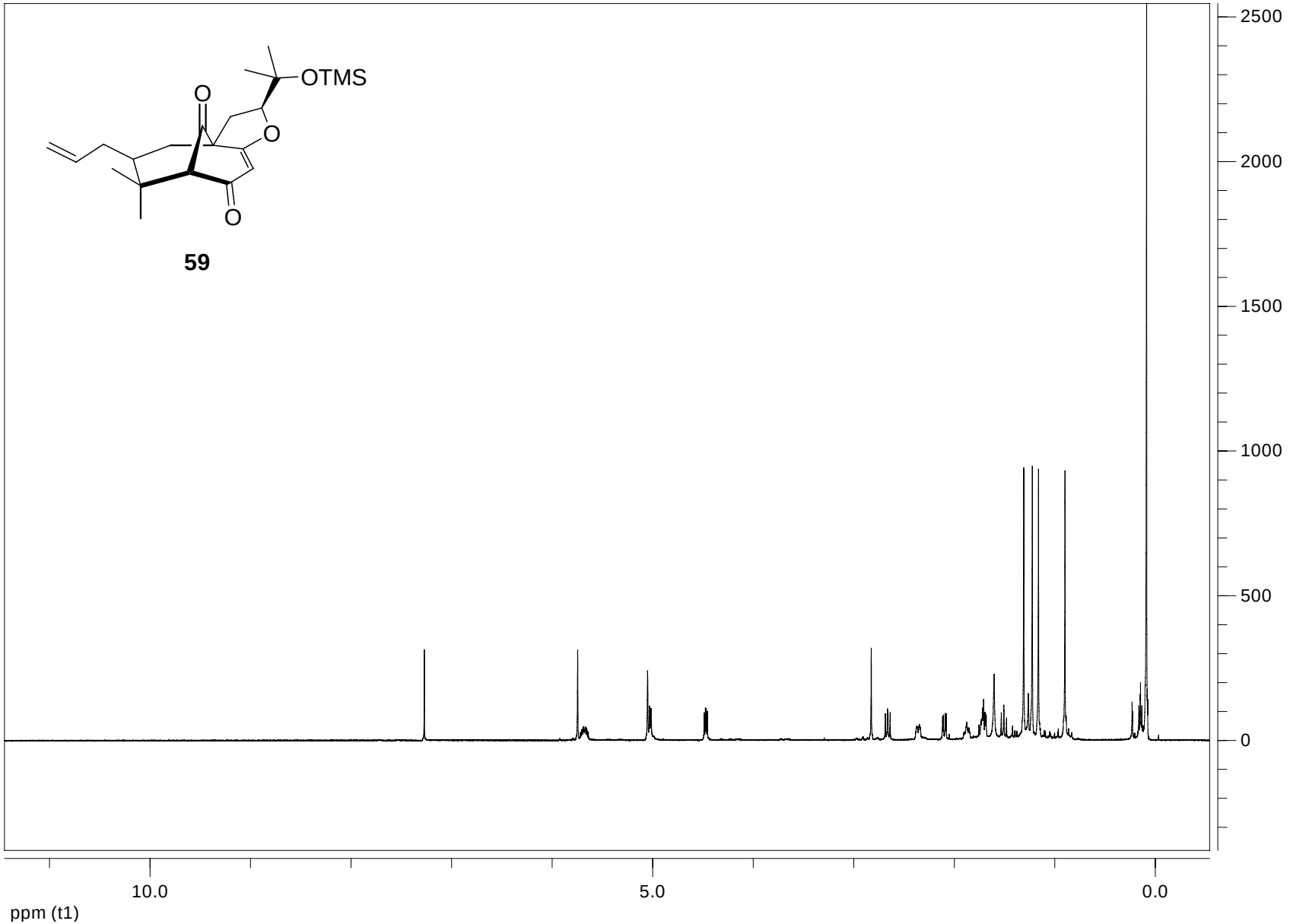

OTBS
53
20000
15000
10000
5000
0
10.0
5.0
0.0
ppm (t1)

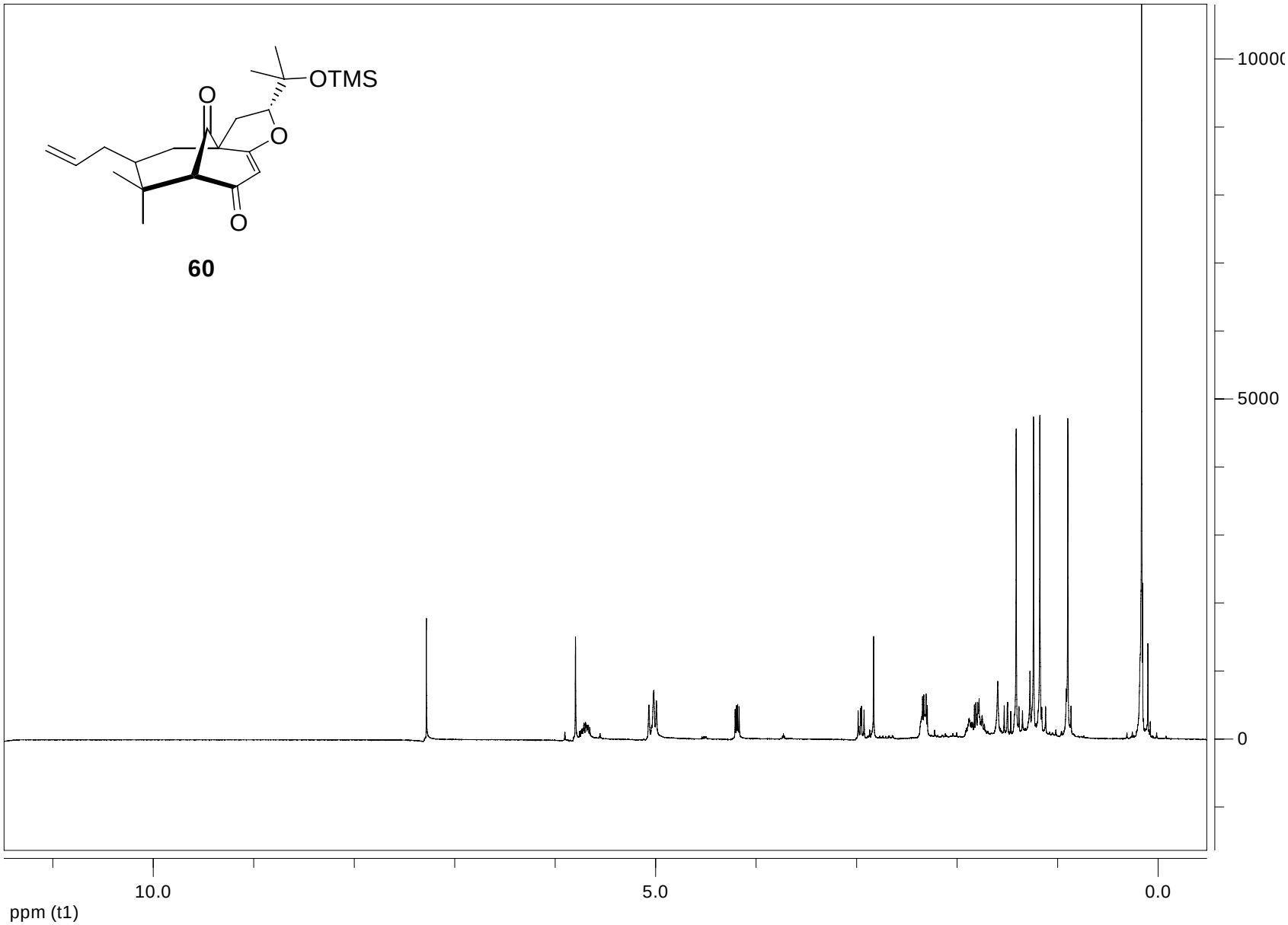

O
OCH3
O
55
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

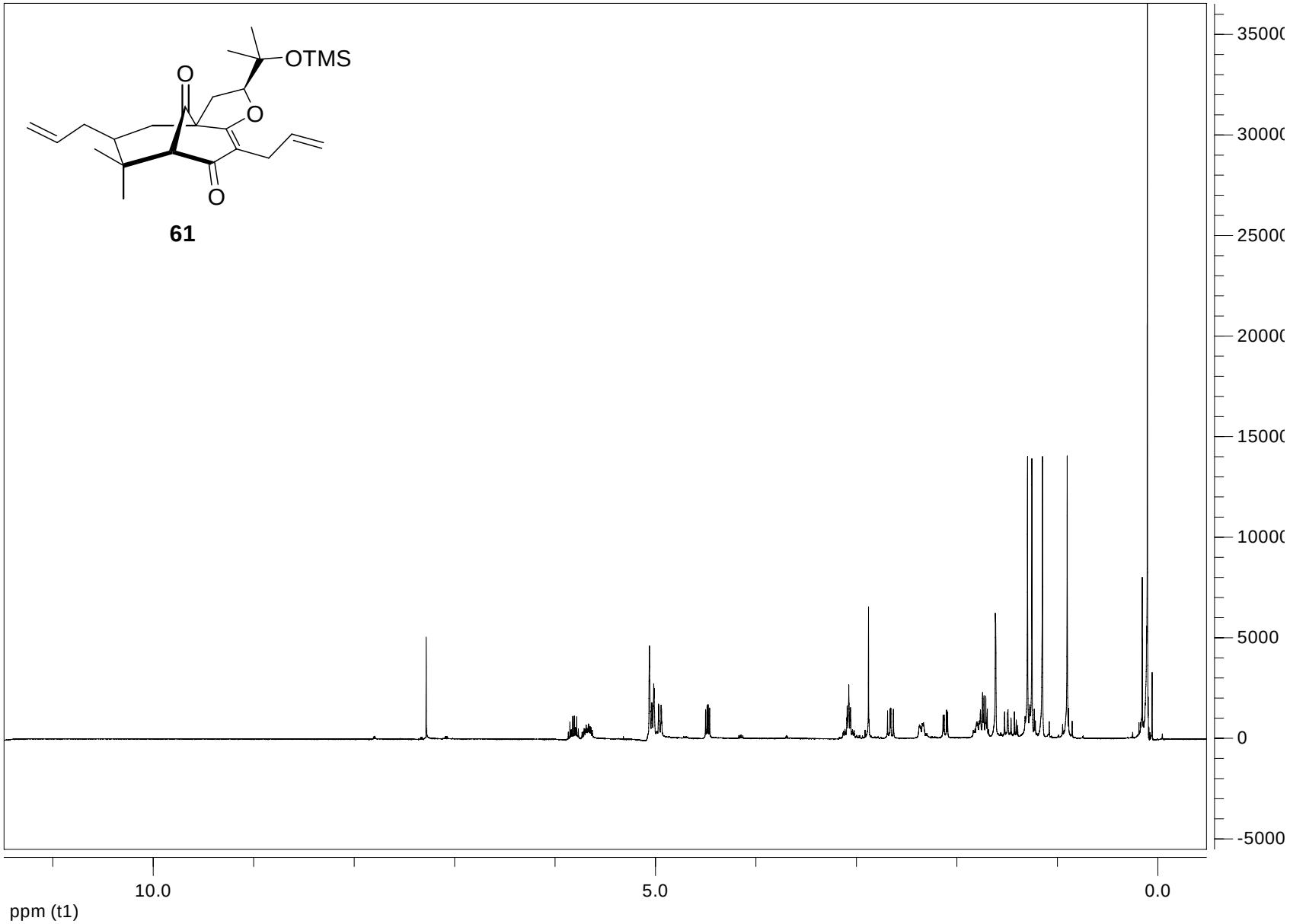

O
OCH3
O
56
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

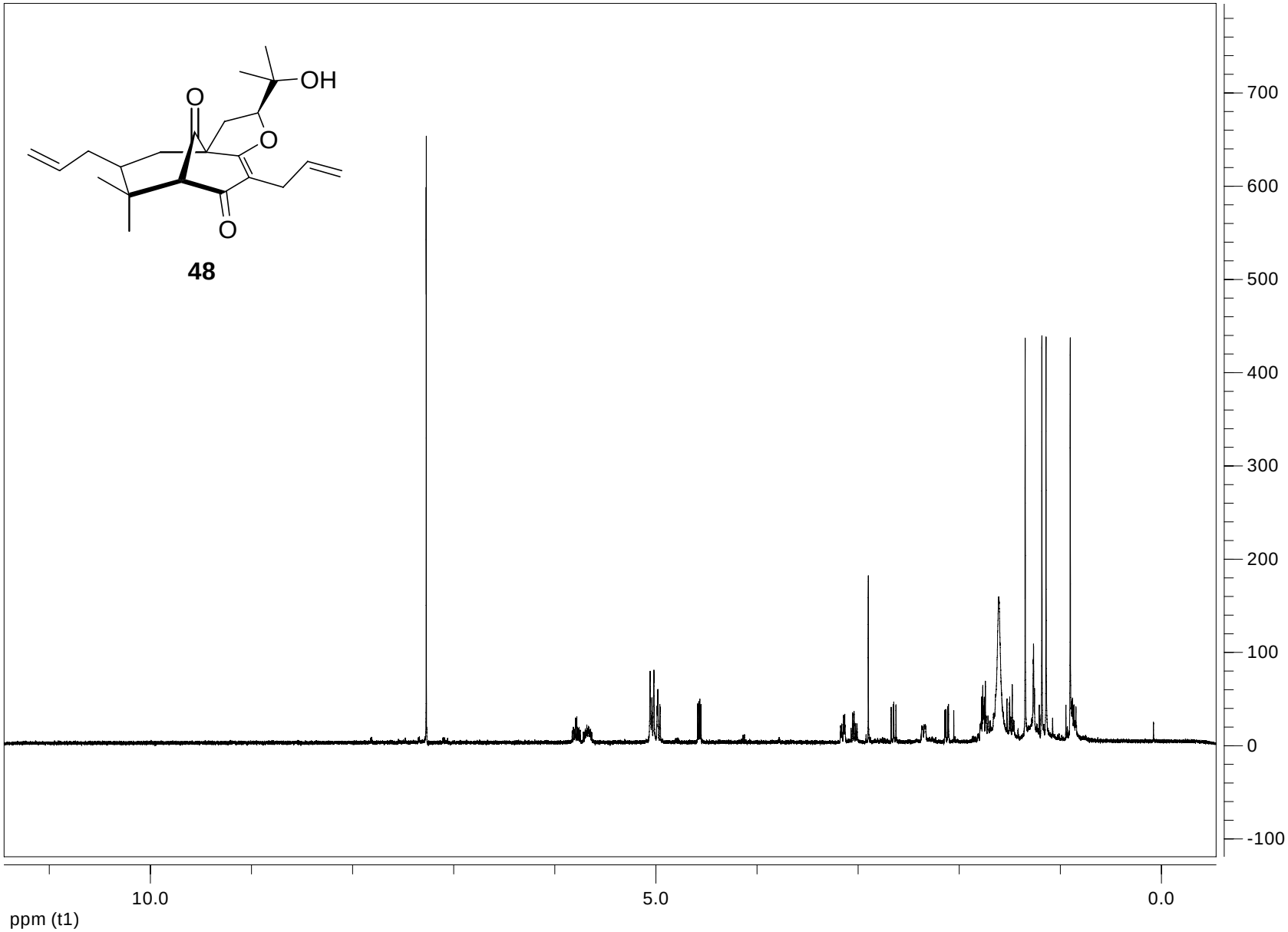

OH
O
O
O
57
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

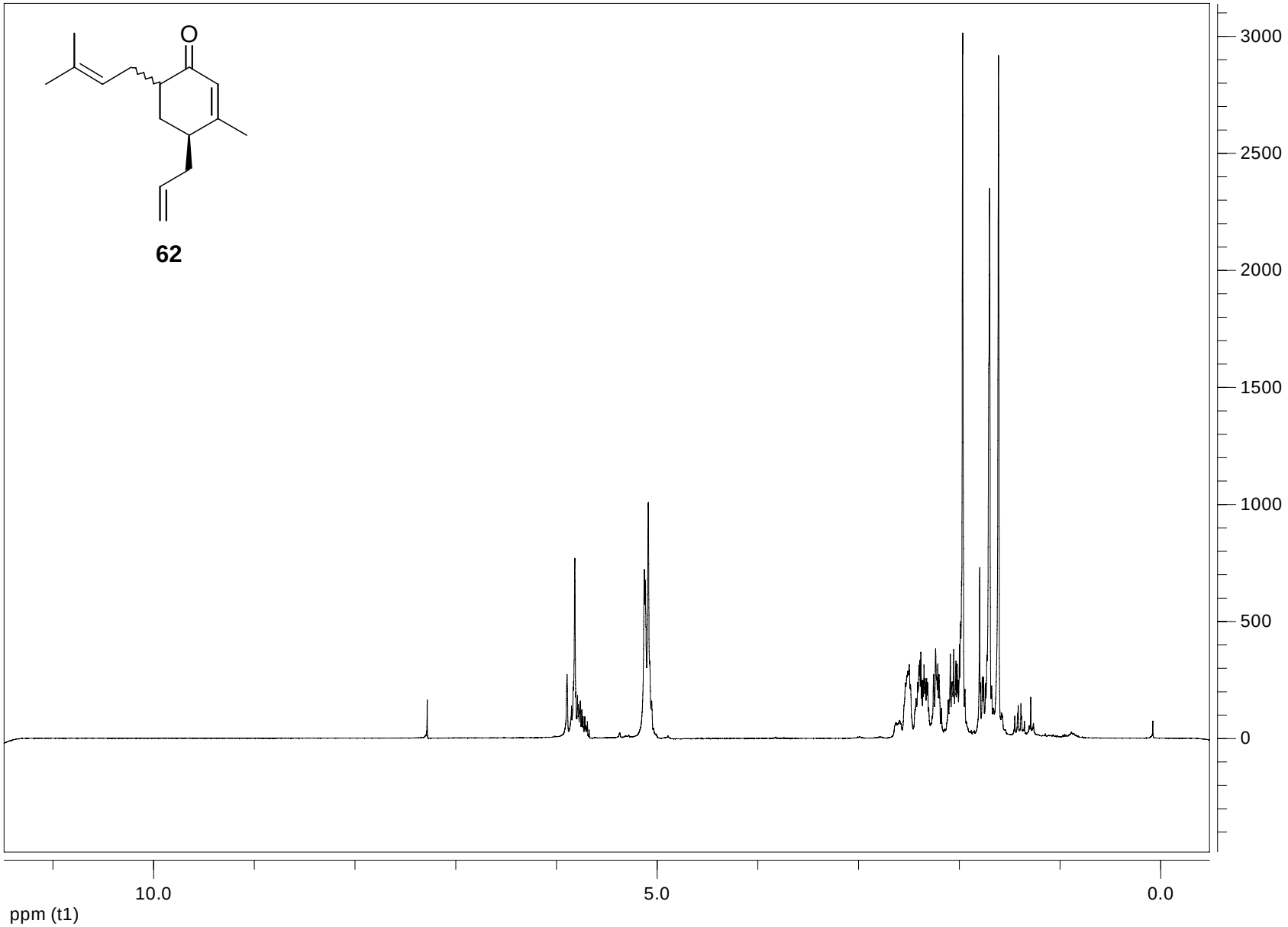

OH
O
O
O
58
700
600
500
400
300
200
100
0
-100
10.0
5.0
0.0
ppm (t1)

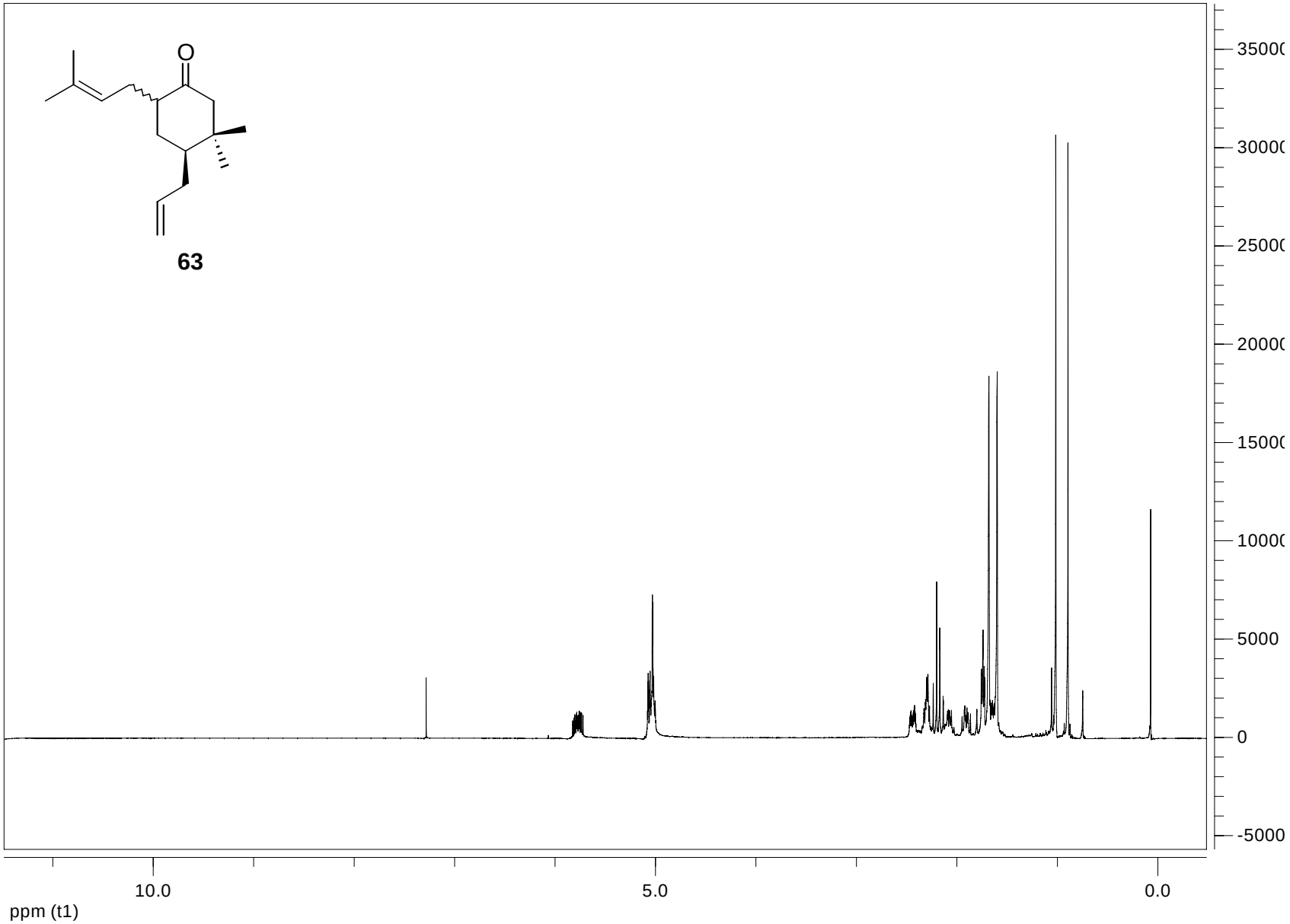

OTMS
O
O
O
59
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

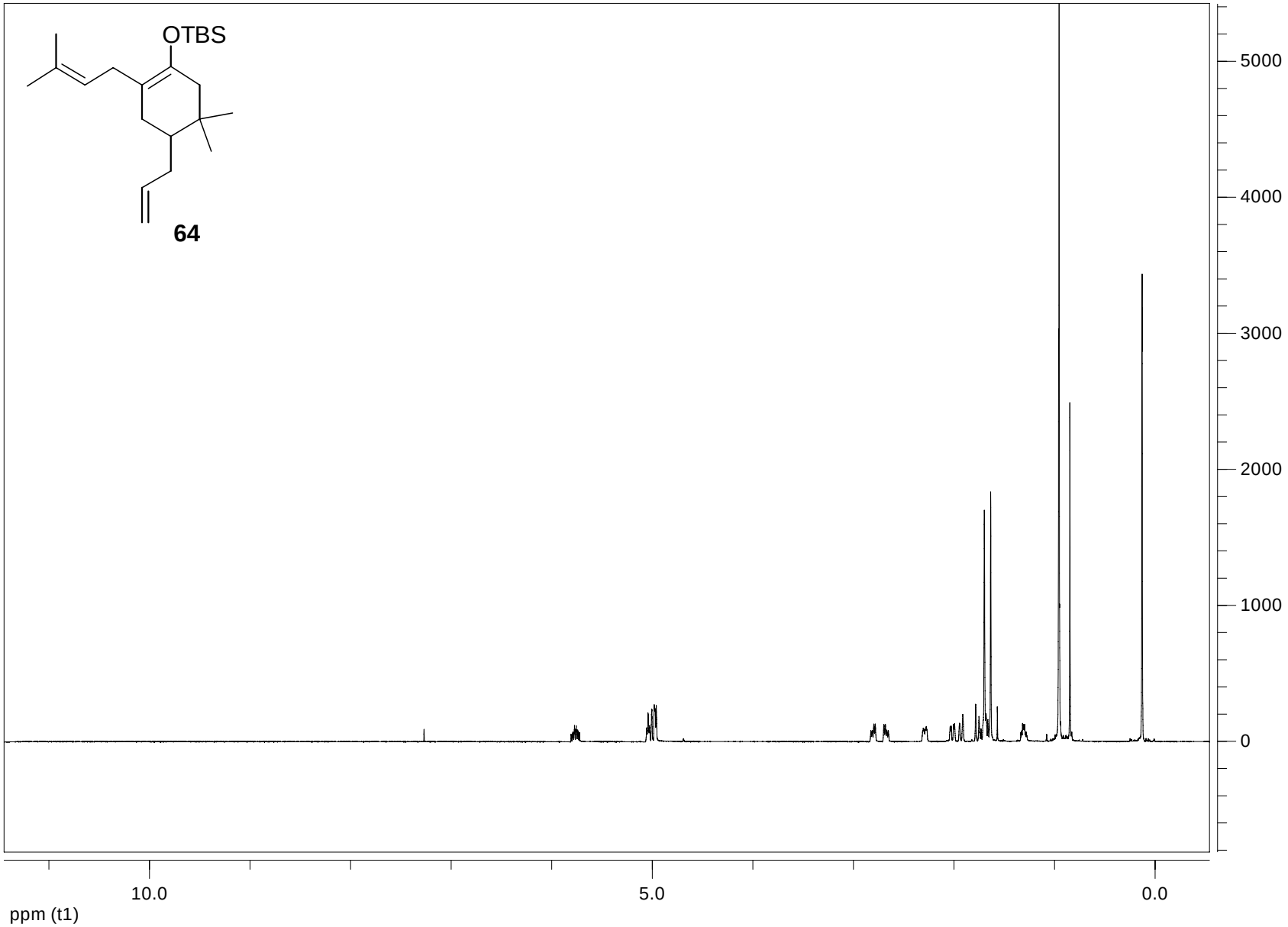

OTMS
O
O
O
60
10000
5000
0
10.0
5.0
0.0
ppm (t1)


OTMS
O
O
O
61
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.0
5.0
0.0
ppm (t1)

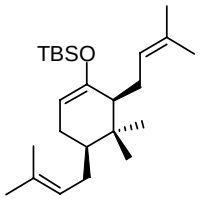

OH
O
O
O
48
700
600
500
400
300
200
100
0
-100
10.0
5.0
0.0
ppm (t1)


O
62
3000
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)


O
63
35000
30000
25000
20000
15000
10000
5000
0
-5000
10.0
5.0
0.0
ppm (t1)


OTBS
64
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)

v_rod 419 3 1
DRX 500 CDCl3



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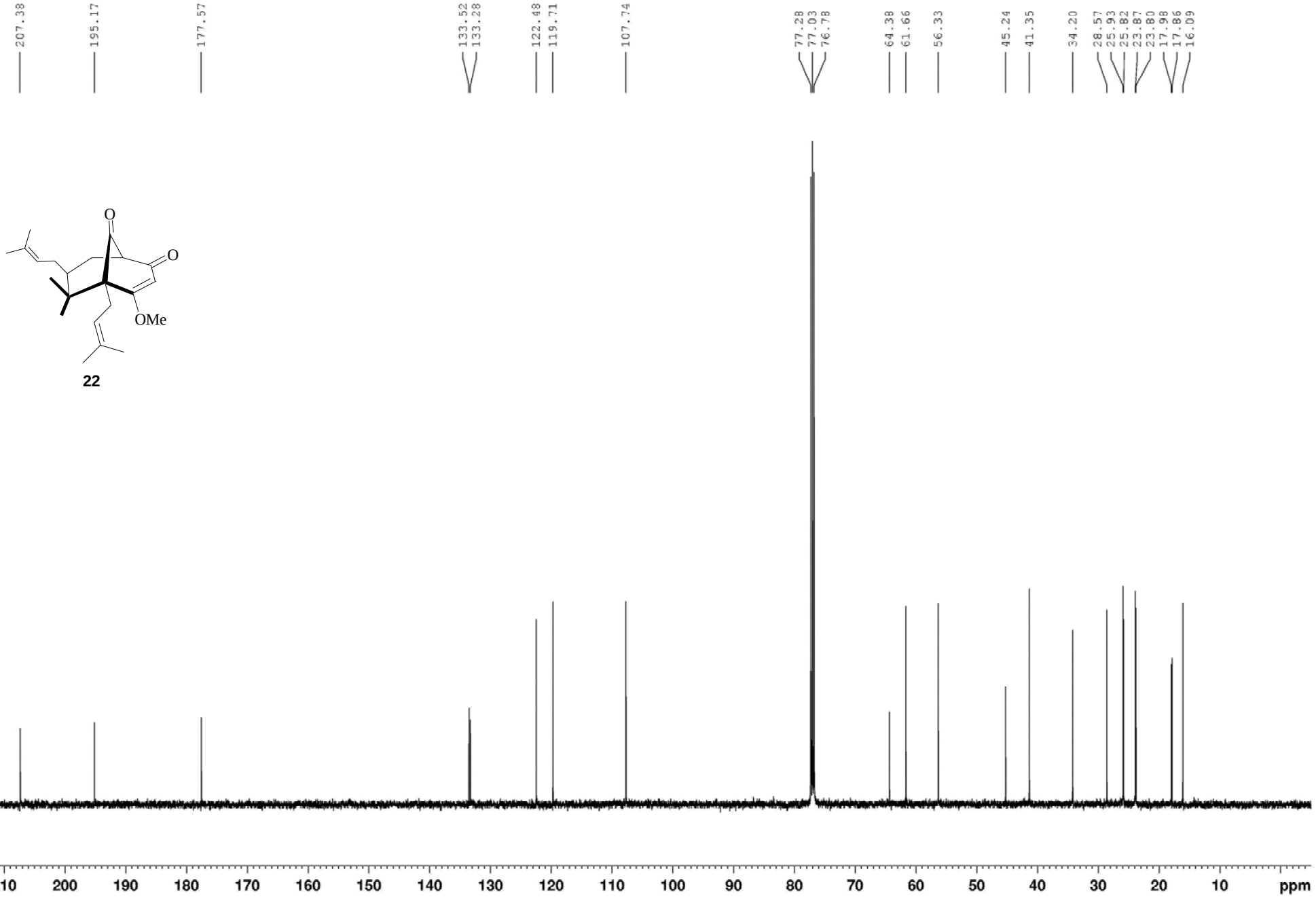
207.38
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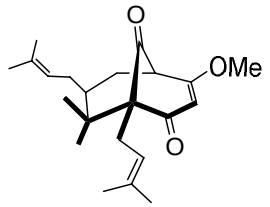
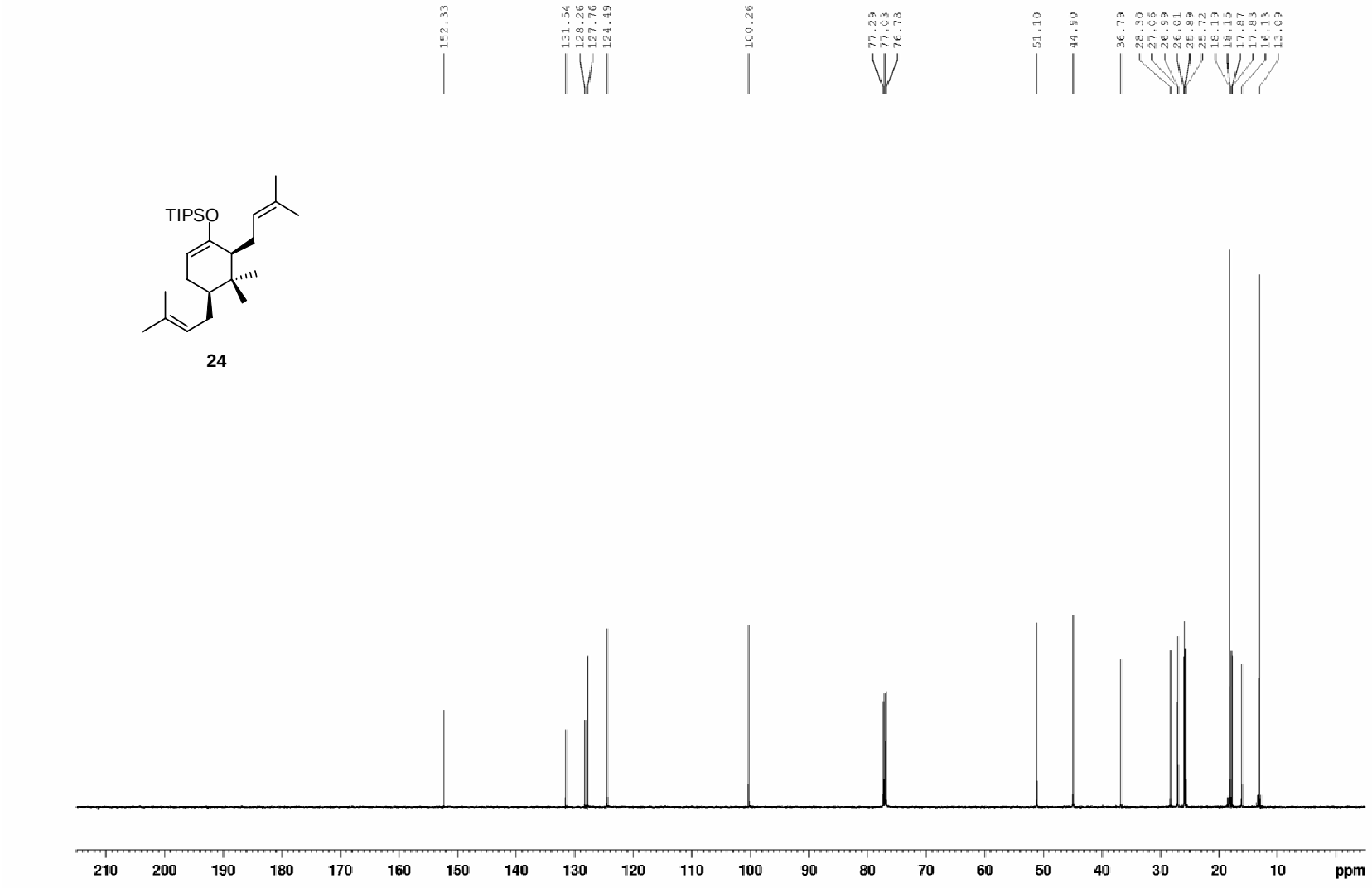
177.57
133.52
133.28
122.48
119.71
107.74
77.28
77.03
76.78
64.38
61.66
56.33
45.24
41.35
34.20
28.57
25.93
25.82
23.87
23.80
17.98
17.86
16.09
O
O
OMe
22
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

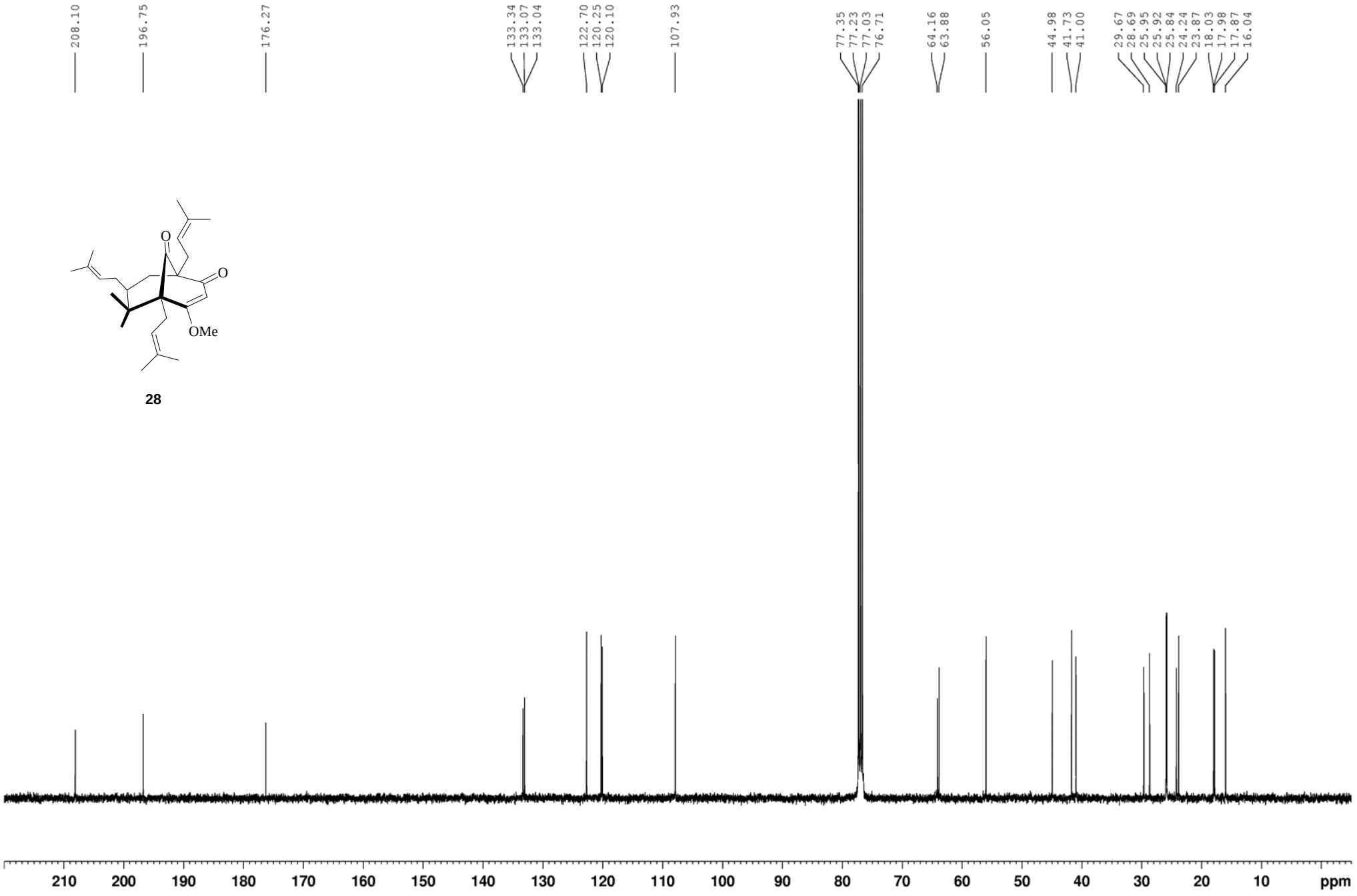


23

v_rod.456 bis 2 1 drx 500 cdcl3



24


208.10
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176.27
133.34
133.07
133.04
122.70
120.25
120.10
107.93
77.35
77.23
77.03
76.71
64.16
63.88
56.05
44.98
41.73
41.00
29.67
28.69
25.95
25.92
25.84
24.24
23.87
18.03
17.98
17.87
16.04
O
O
OMe
210
200
190
180
170
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140
130
120
110
100
90
80
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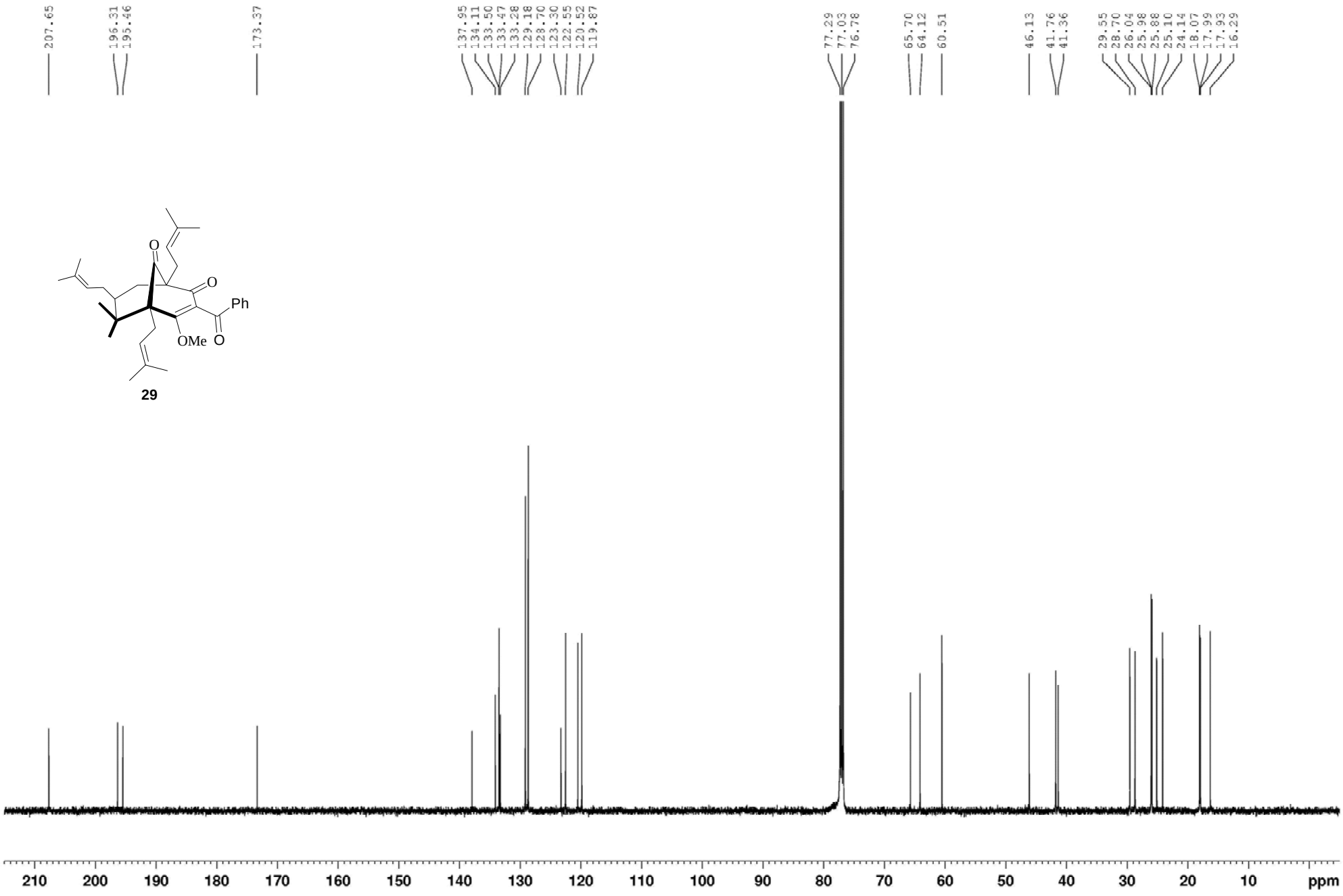
60
50
40
30
20
10
ppm

28


207.65
196.31
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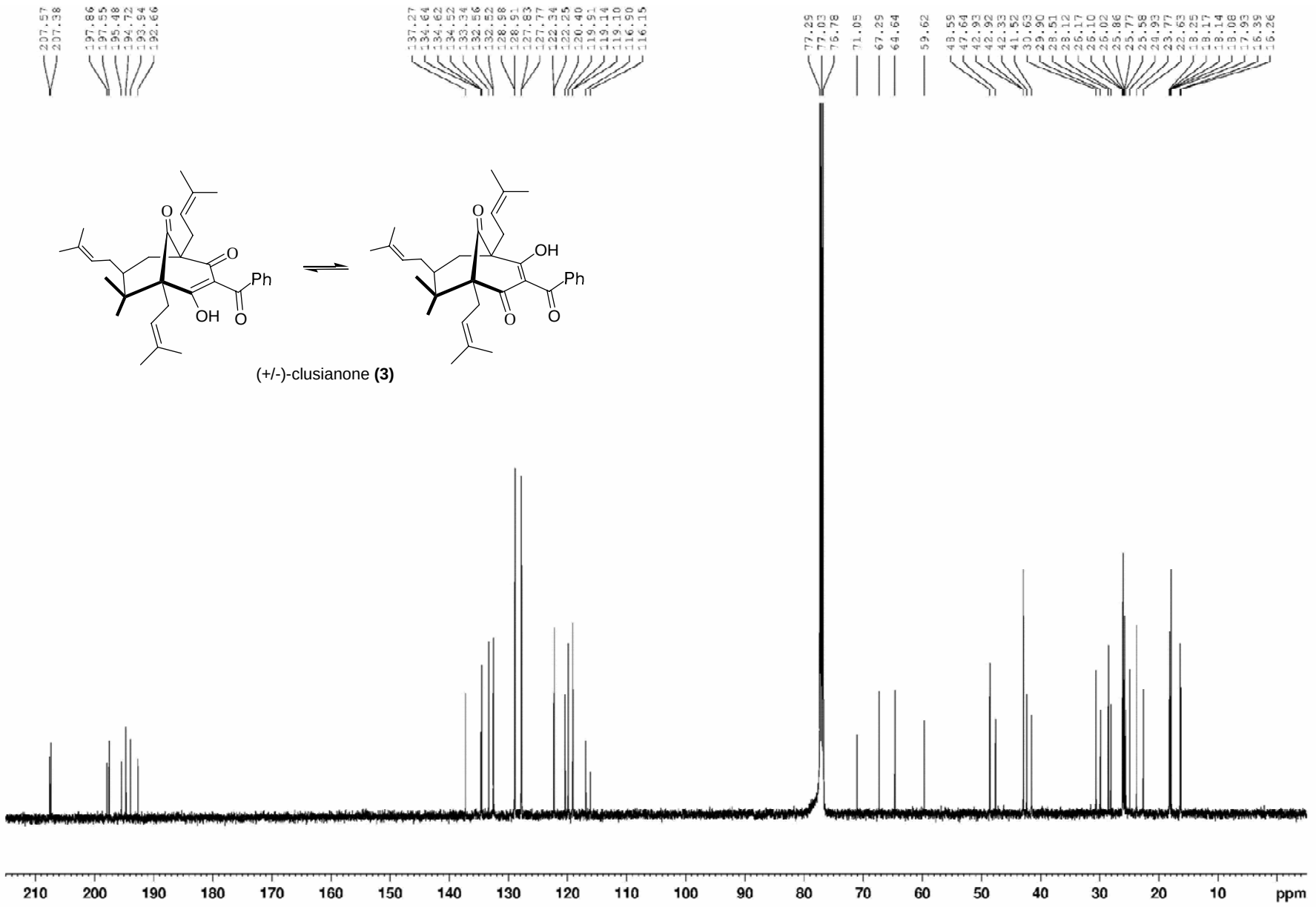
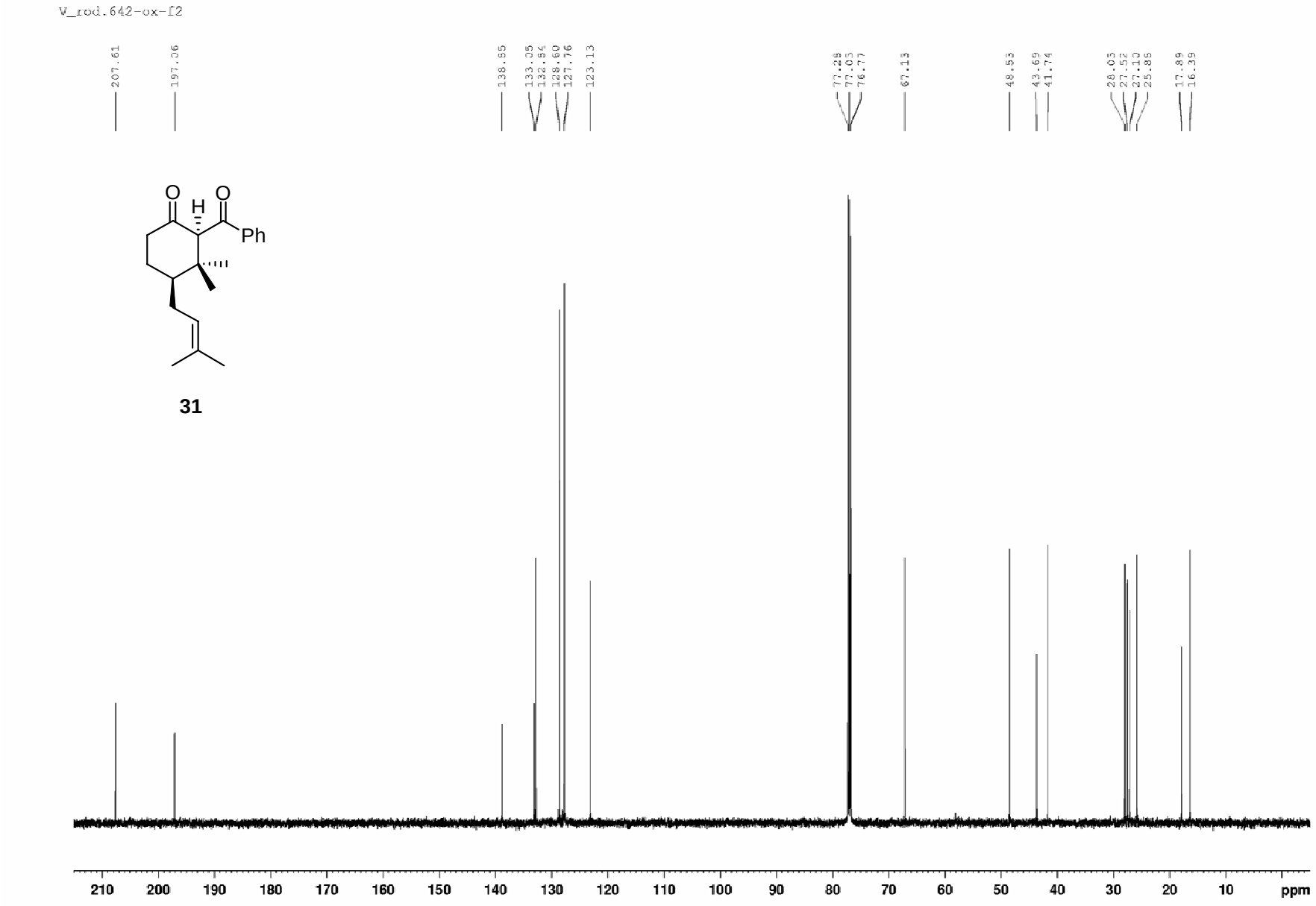
173.37
137.95
134.11
133.50
133.47
133.28
129.18
128.70
123.30
122.55
120.52
119.87
77.29
77.03
76.78
65.70
64.12
60.51
46.13
41.76
41.36
29.55
28.70
26.04
25.98
25.88
25.10
24.14
18.07
17.99
17.93
16.29
O
O
Ph
OMe
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

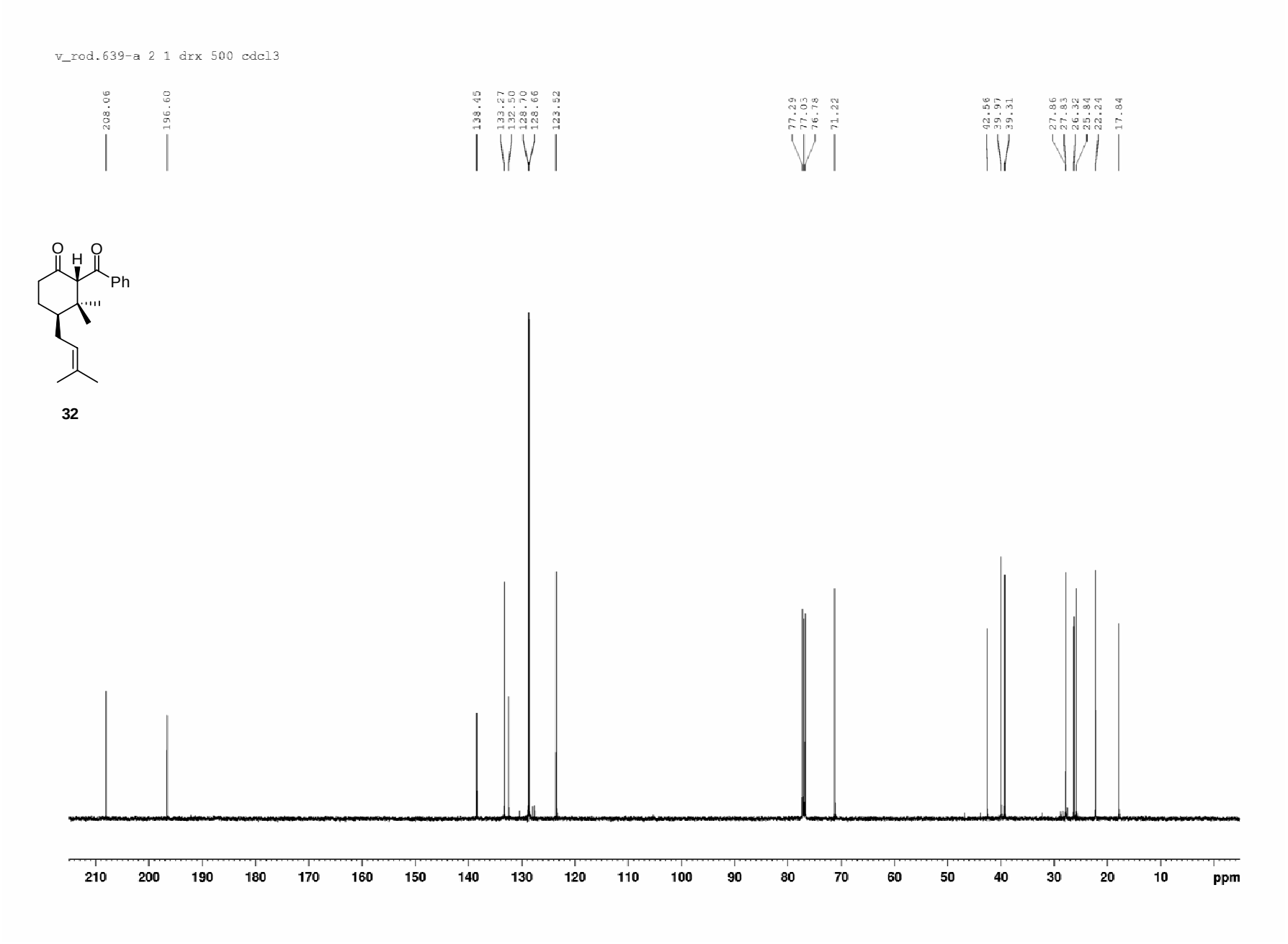
29



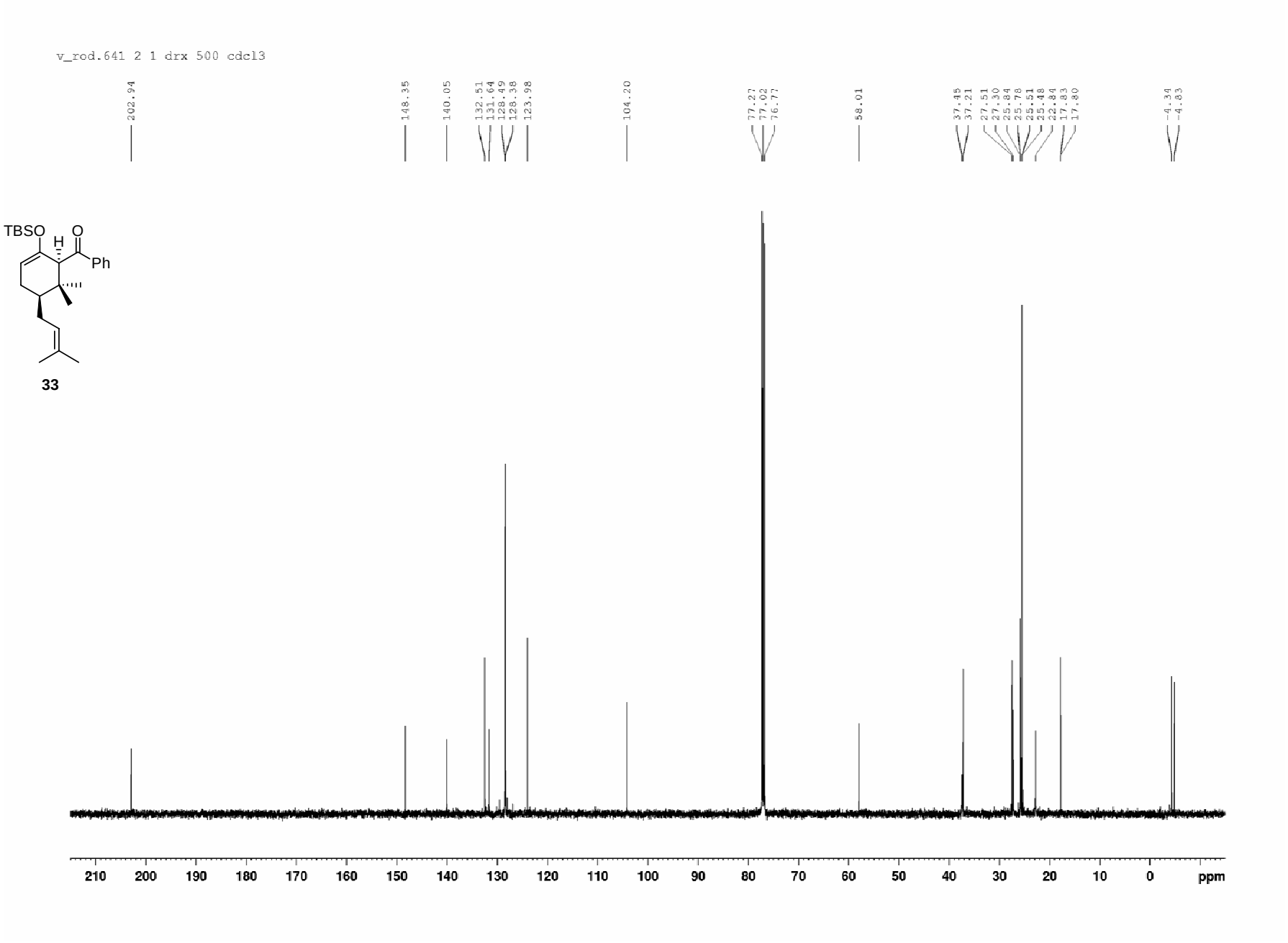
(+/-)-clusianone **(3)**

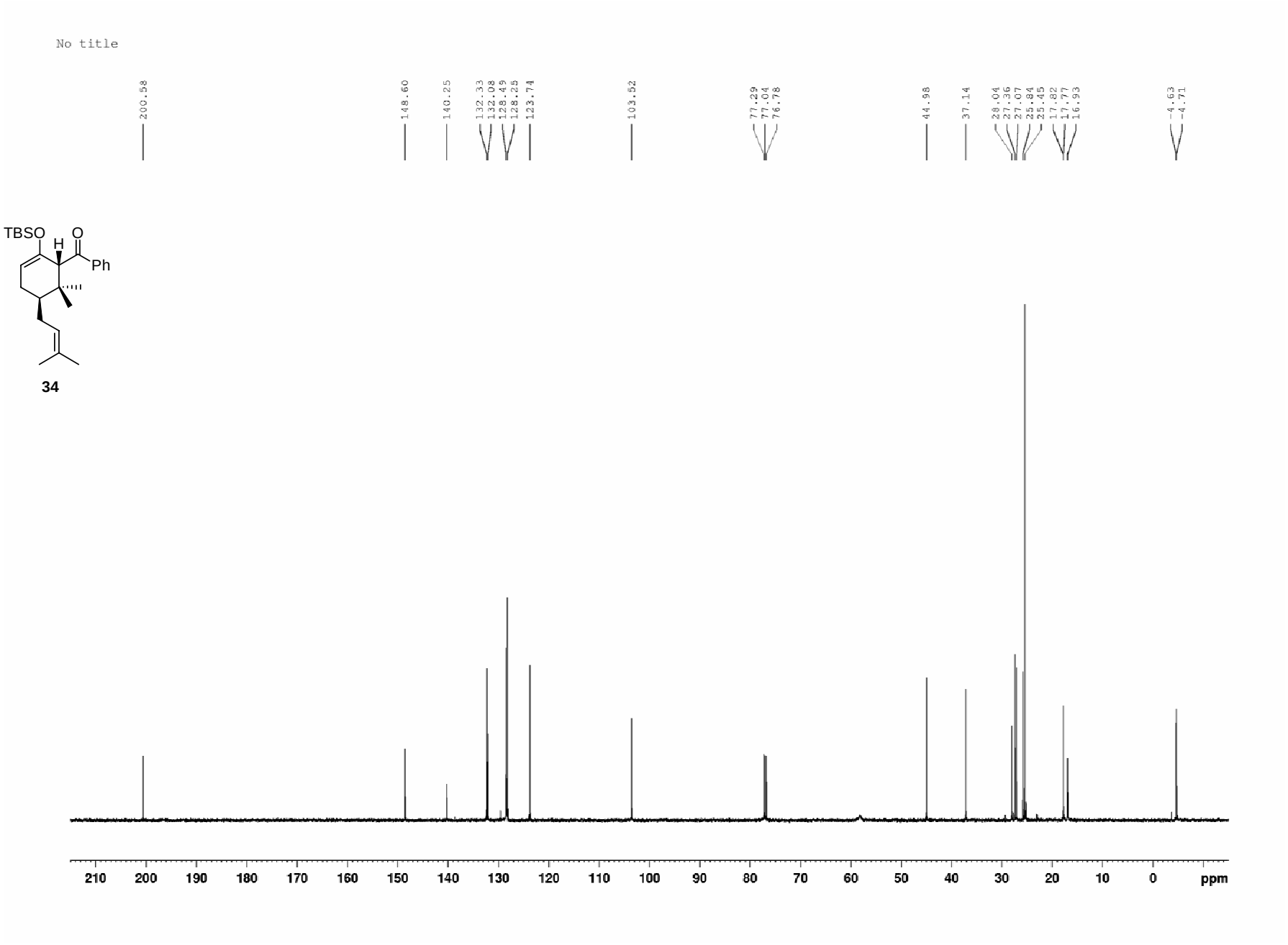

V_rod.642-ox-f2
207.61
197.06
138.85
133.05
132.84
128.60
127.76
123.13
77.28
77.03
76.77
67.13
48.53
43.69
41.74
28.03
27.52
27.13
25.88
17.89
16.39
O
H
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

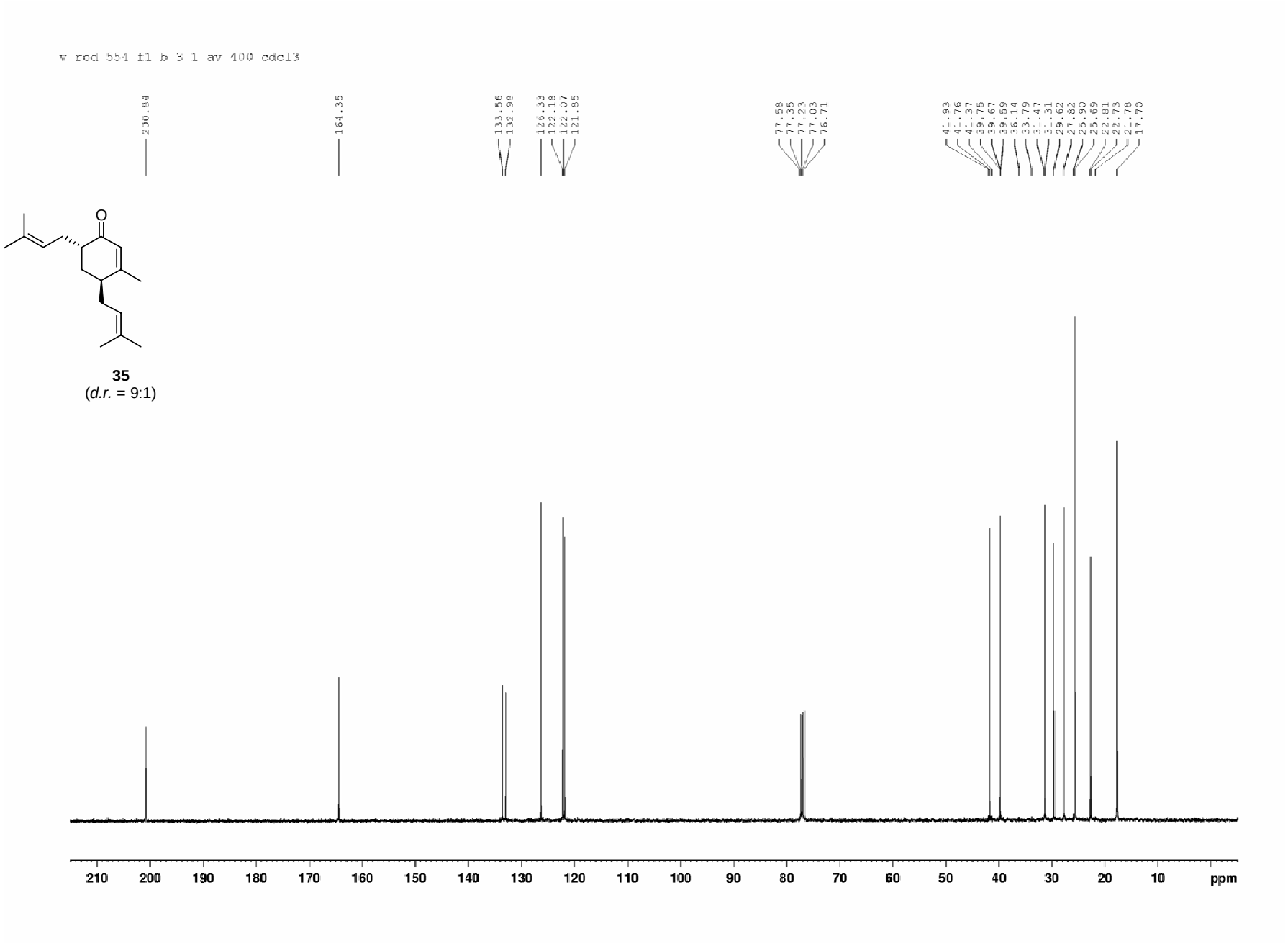
31


v_rod.639-a 2 1 drx 500 cdcl3
208.06
196.60
138.45
133.27
132.50
128.70
128.66
123.52
77.29
77.03
76.78
71.22
42.56
39.97
39.31
27.86
27.83
26.32
25.84
22.24
17.84
O
H
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

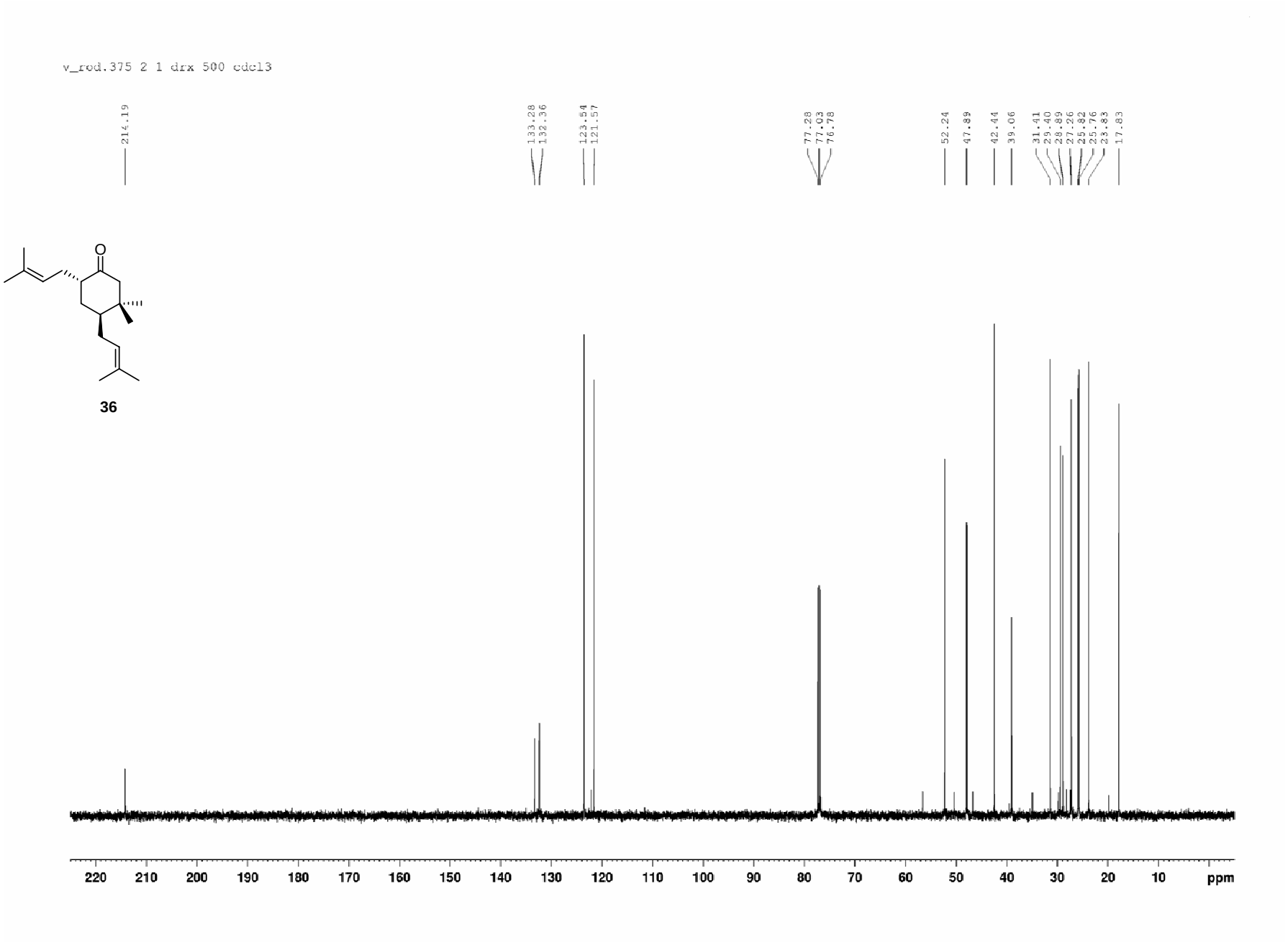
32


v_rod.641 2 1 drx 500 cdcl3
202.94
148.35
140.05
132.51
131.64
128.49
128.38
123.98
104.20
77.27
77.02
76.77
58.01
37.45
37.21
27.51
27.30
25.84
25.78
25.51
25.48
22.84
17.83
17.80
-4.34
-4.83
TBSO
H
O
Ph
33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

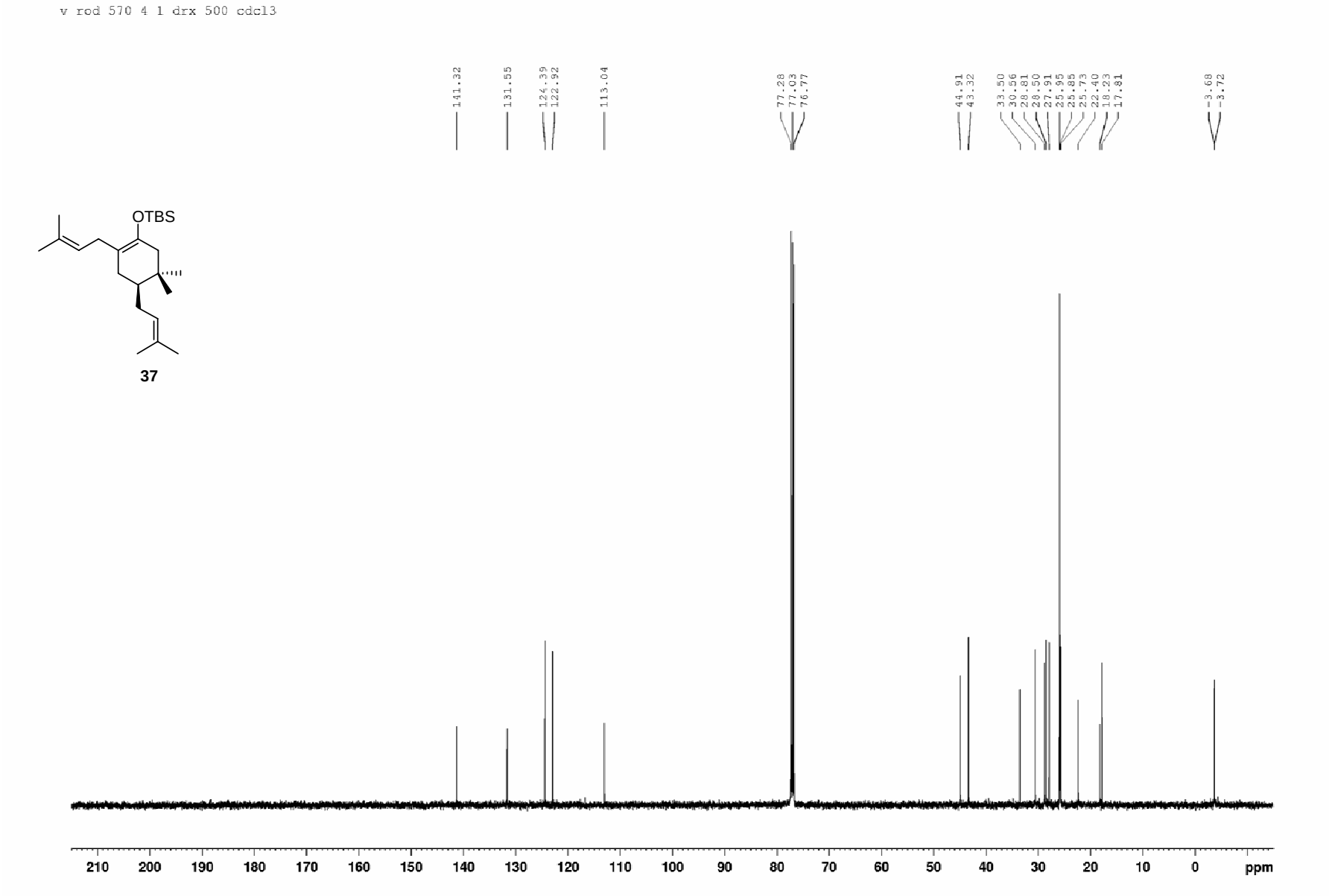

No title
200.58
148.60
140.25
132.33
132.08
128.49
128.25
123.74
103.52
77.29
77.04
76.78
44.98
37.14
28.04
27.36
27.07
25.84
25.45
17.82
17.77
16.93
-4.63
-4.71
TBSO
H
O
Ph
34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

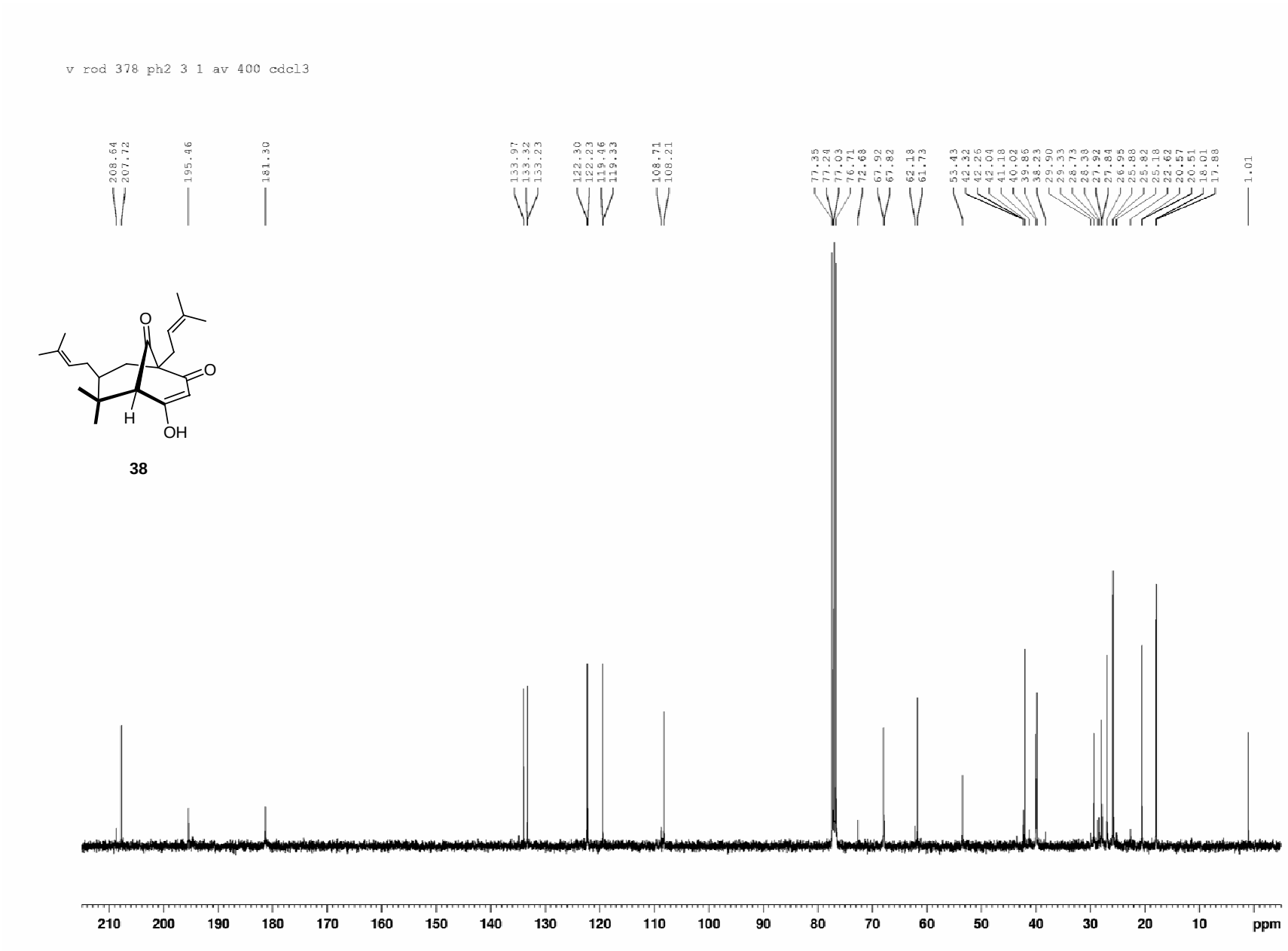

v rod 554 f1 b 3 1 av 400 cdcl3
200.84
164.35
133.56
132.98
126.33
122.18
122.07
121.85
77.58
77.35
77.23
77.03
76.71
41.93
41.76
41.37
39.75
39.67
39.59
36.14
33.79
31.47
31.31
29.62
27.82
25.90
25.69
22.81
22.73
21.78
17.70
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

35
(*d.r.* = 9:1)

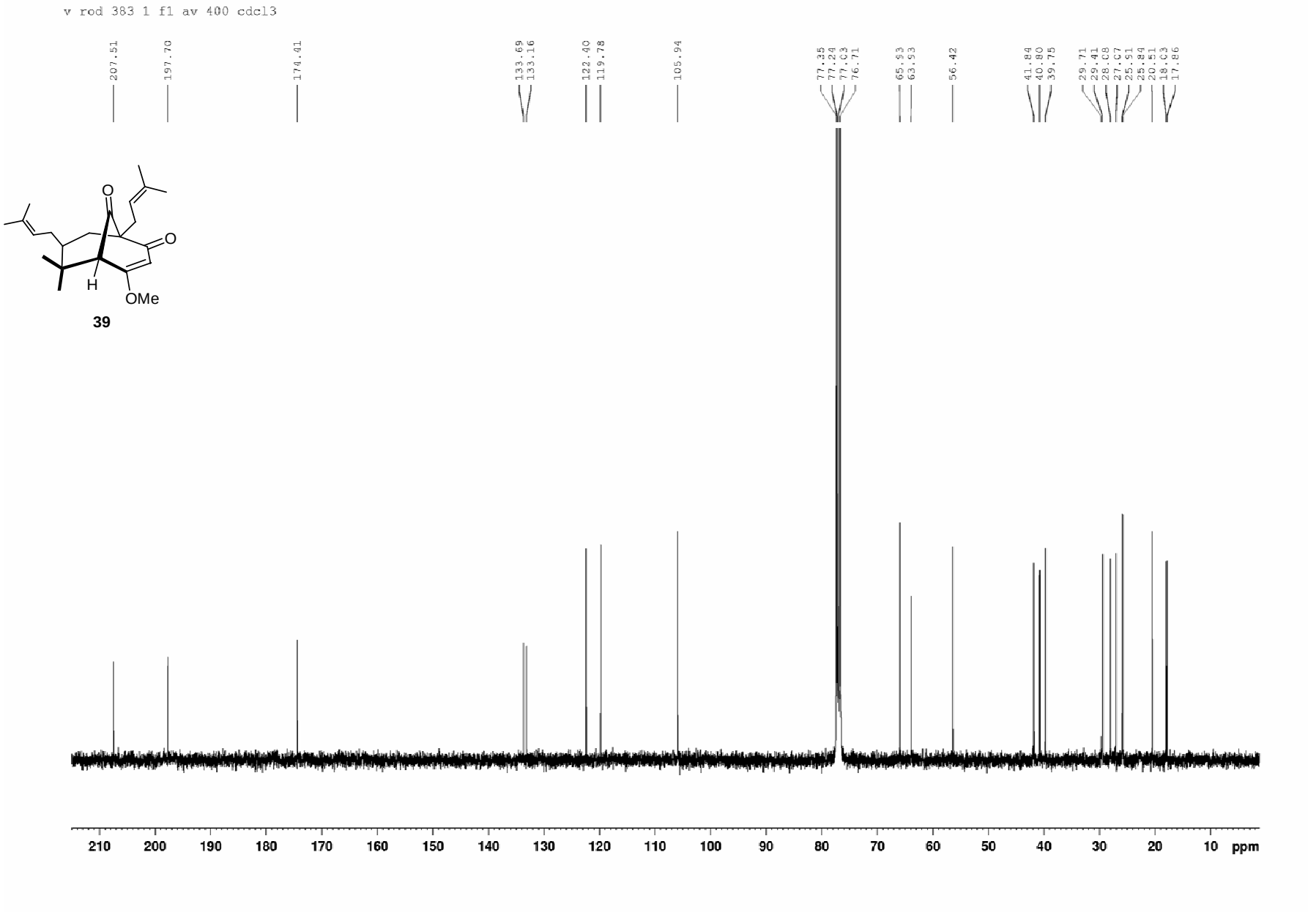

v_rod.375 2 1 drx 500 cdcl3
214.19
133.28
132.56
123.54
121.57
77.28
77.03
76.78
52.24
47.89
42.44
39.06
31.41
29.40
28.89
27.26
25.82
25.76
23.83
17.83
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

36

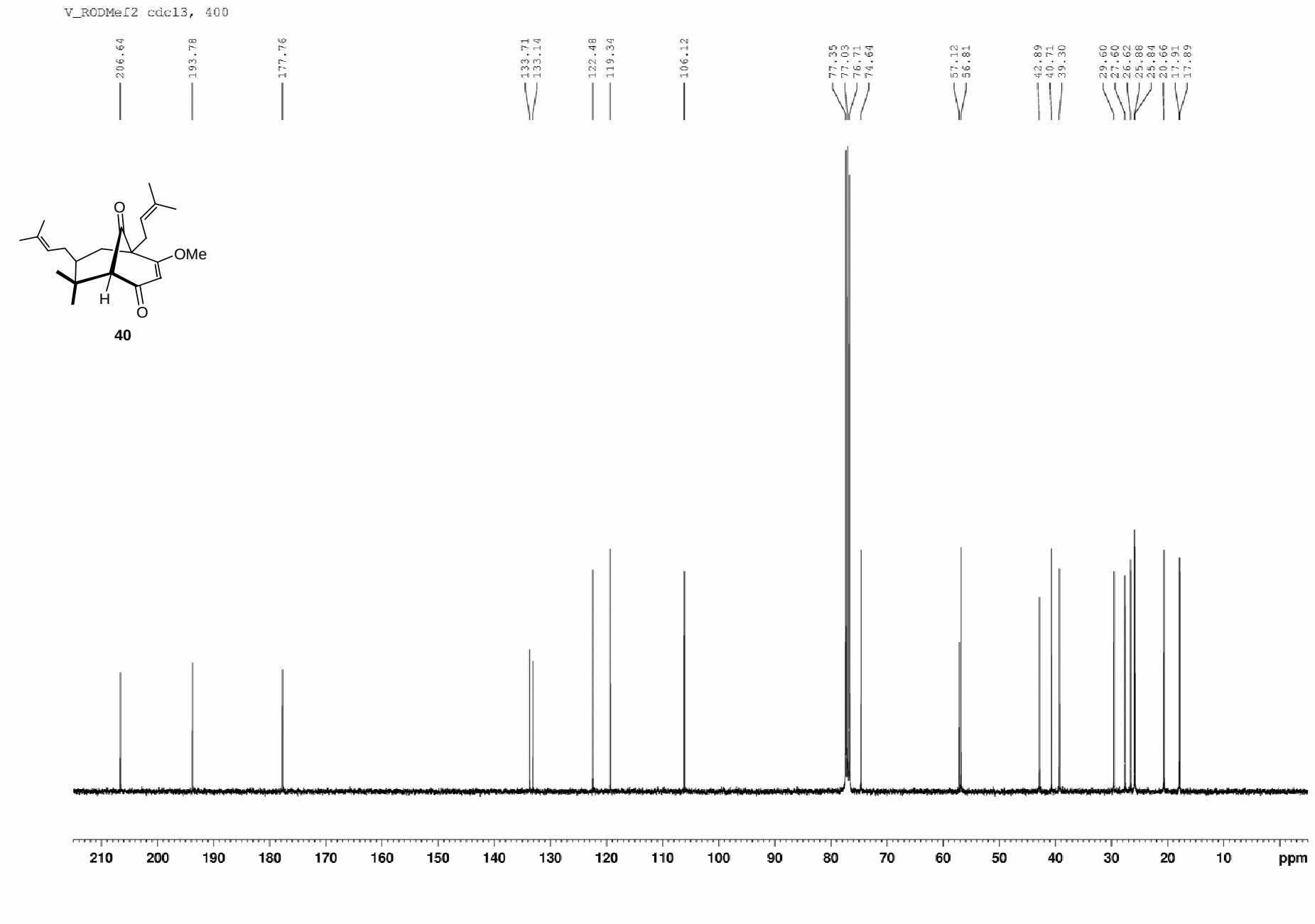

v rod 570 4 1 drx 500 cdcl3
141.32
131.55
124.39
122.92
113.04
77.28
77.03
76.77
44.91
43.32
33.50
30.56
28.81
29.50
27.91
25.95
25.85
25.73
22.40
18.23
17.81
-3.68
-3.72
OTBS
37
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


v rod 378 ph2 3 1 av 400 cdcl3
208.64
207.72
195.46
181.30
133.97
133.32
133.23
122.30
122.23
119.46
119.33
108.71
108.21
77.35
77.24
77.03
76.71
72.68
67.92
67.82
62.18
61.73
53.43
42.32
42.25
42.04
41.18
40.02
39.85
38.23
29.90
29.33
28.73
28.38
27.92
27.84
26.95
25.88
25.82
25.18
22.62
20.57
20.51
18.01
17.88
1.01
O
O
H
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

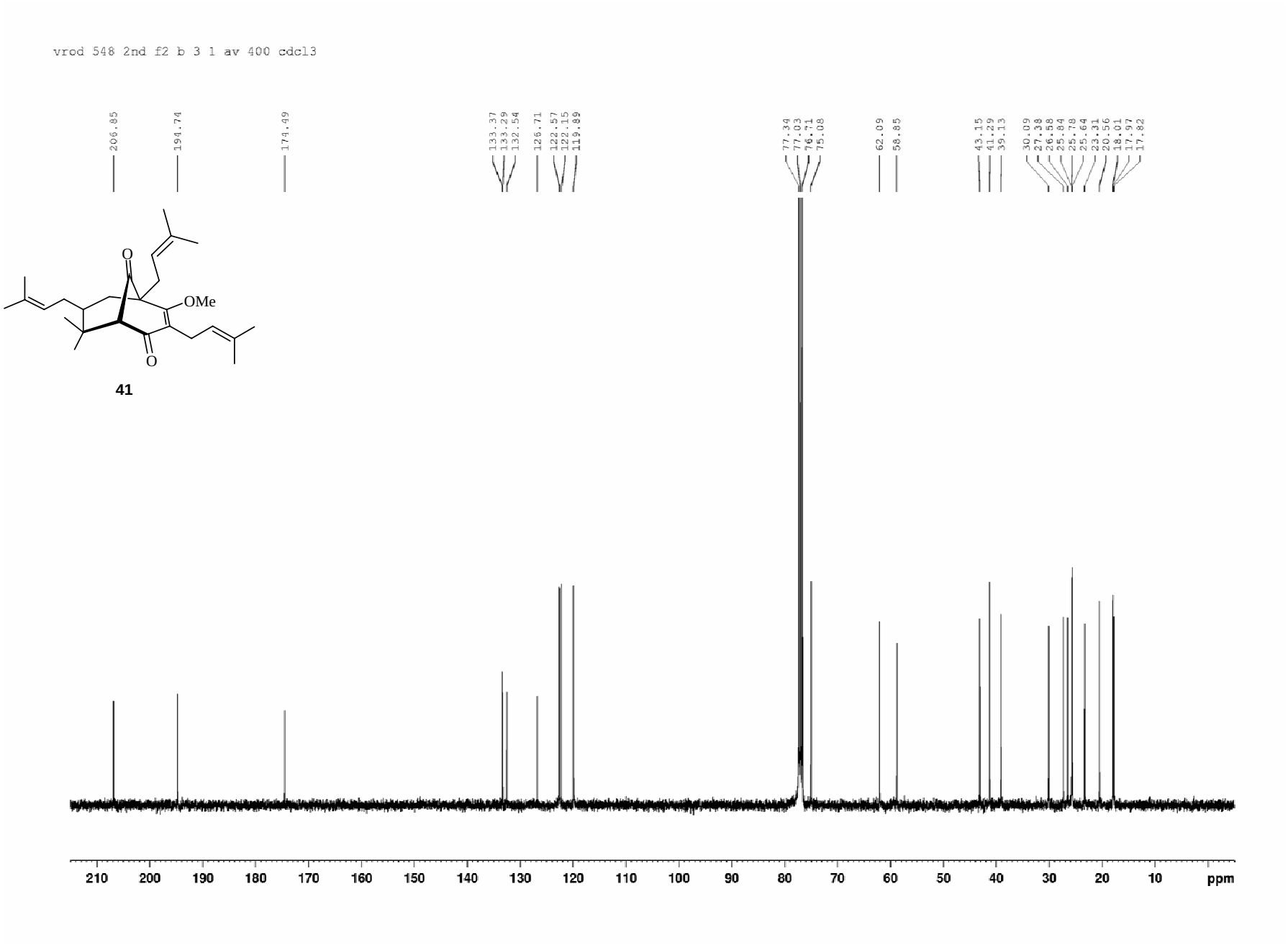
38

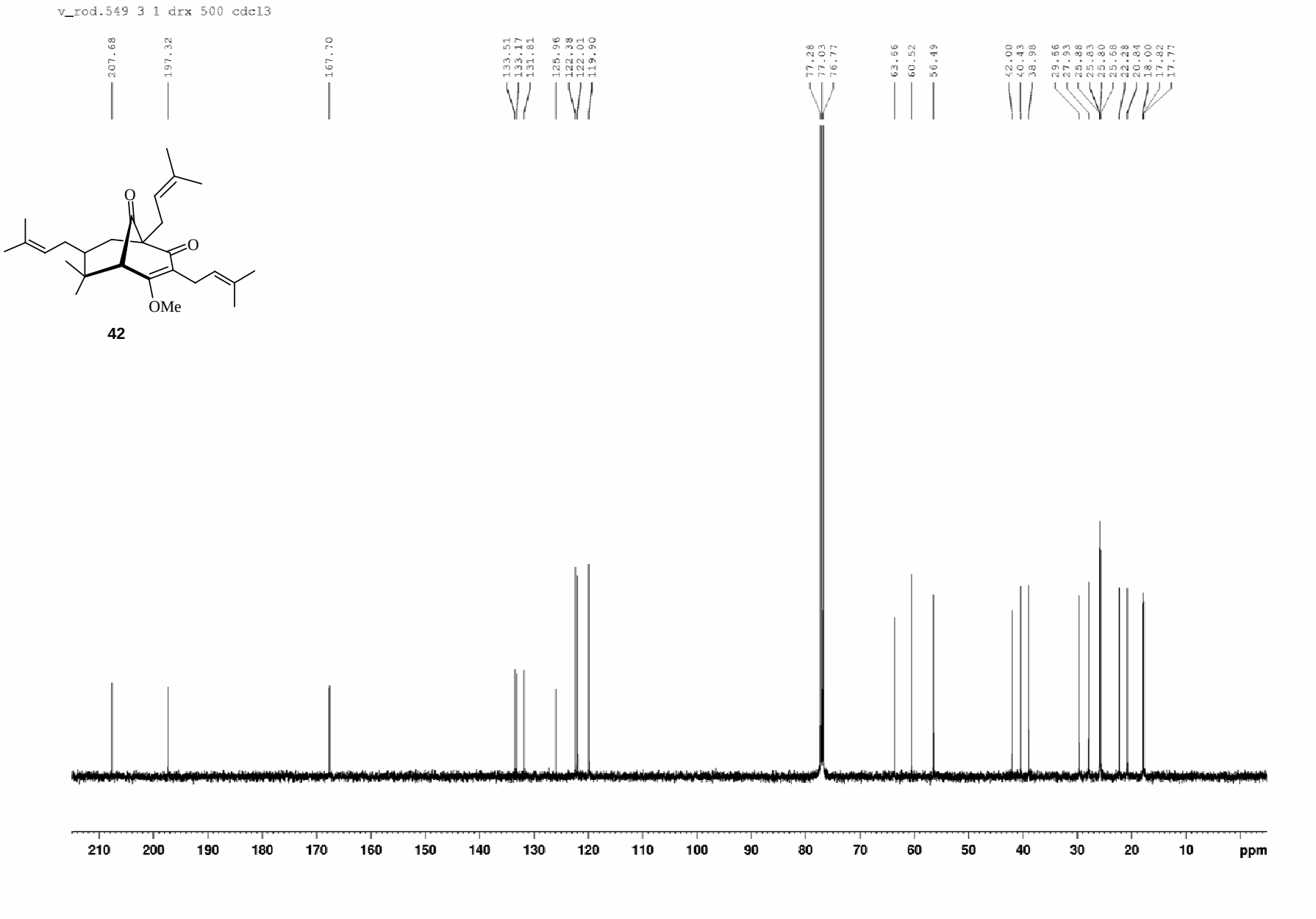

v rod 383 1 f1 av 400 cdcl3
207.51
197.70
174.41
133.69
133.16
122.40
119.78
105.94
77.35
77.24
77.03
76.71
65.93
63.93
56.42
41.84
40.80
39.75
29.71
29.41
28.08
27.67
25.91
25.84
20.51
18.63
17.86
O
O
H
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

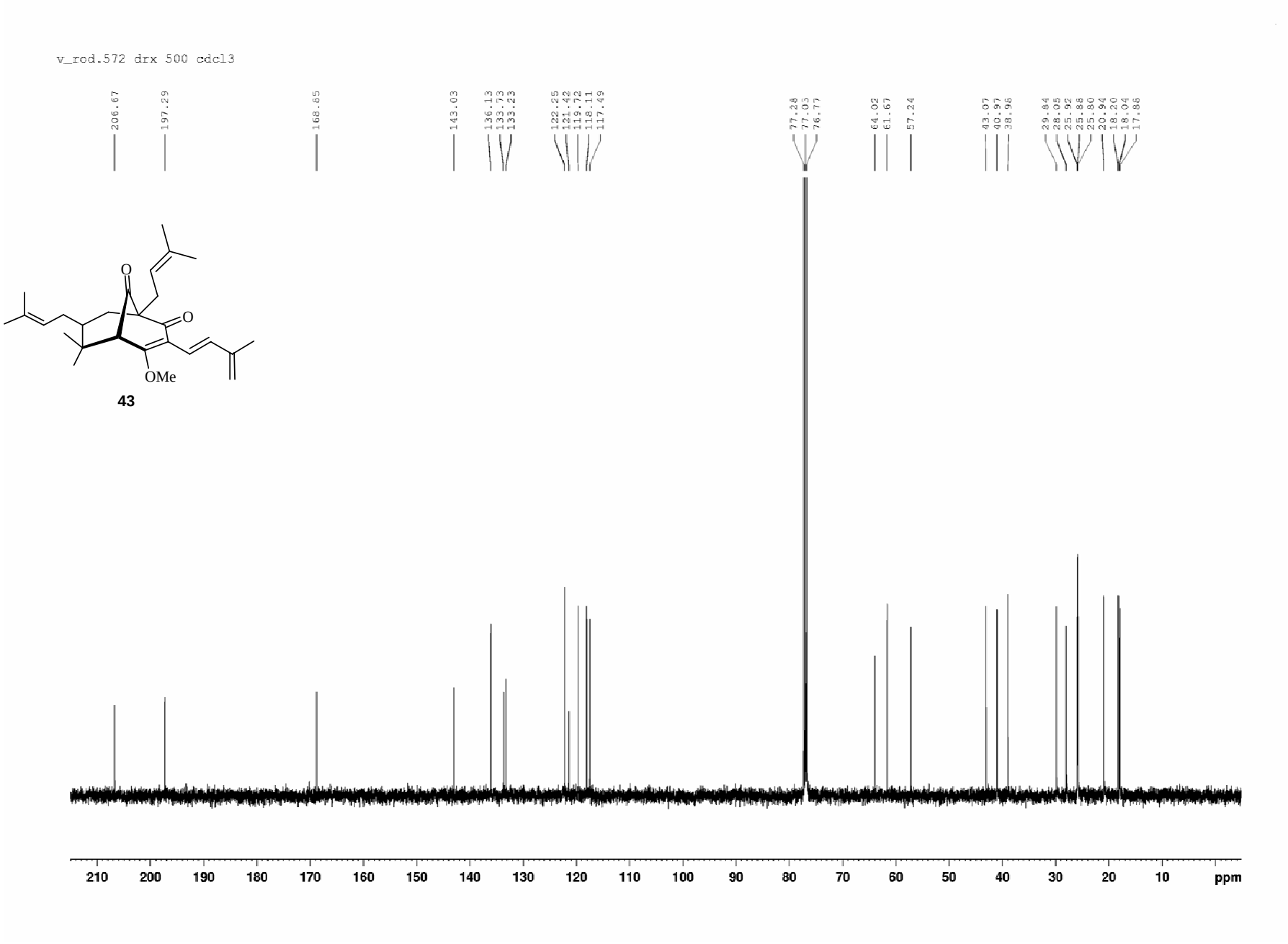
39

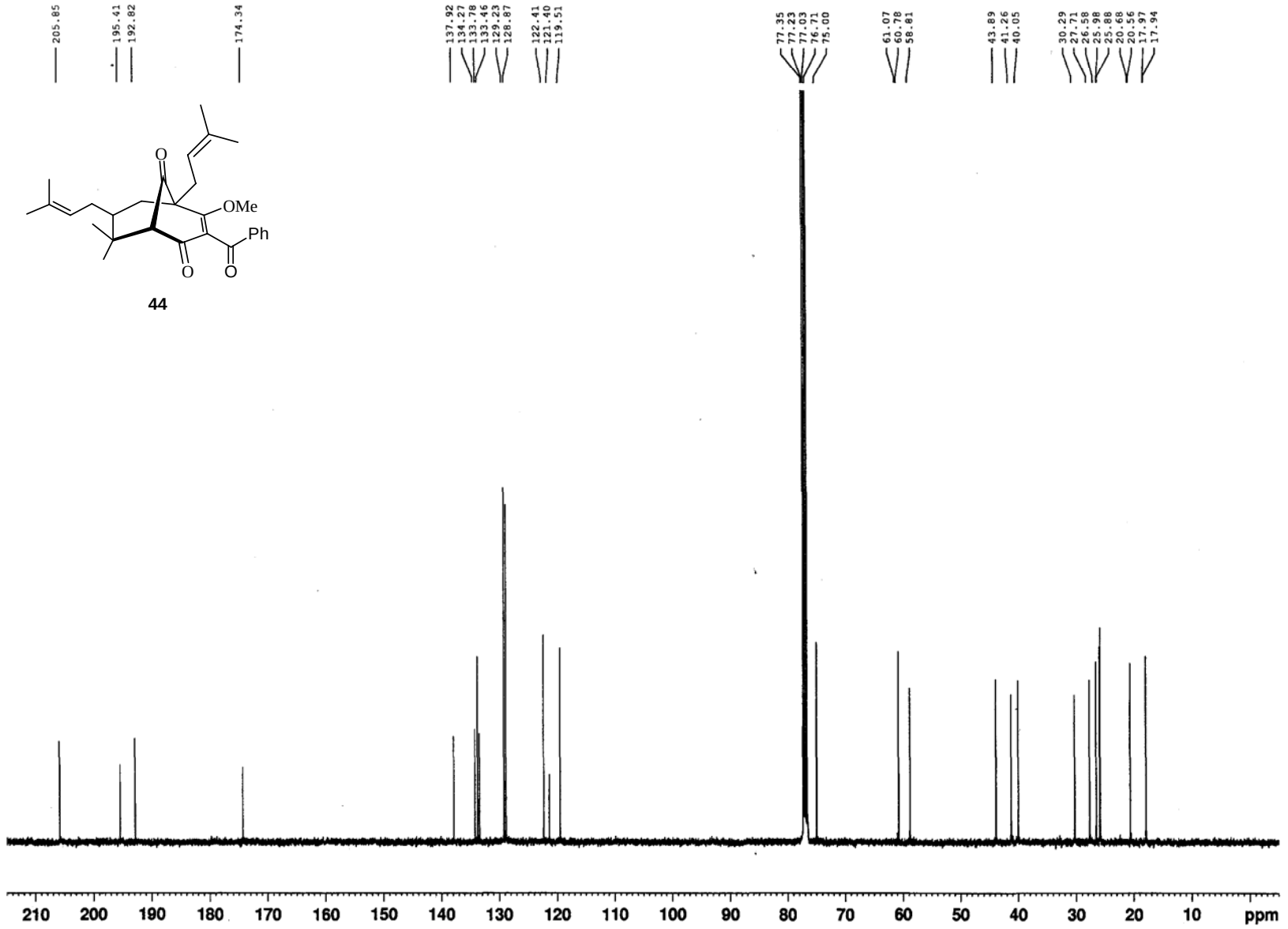

V_RODMef2 cdcl3, 400
206.64
193.78
177.76
133.71
133.14
122.48
119.34
106.12
77.35
77.03
76.71
74.64
57.12
56.81
42.89
40.71
39.30
29.60
27.60
26.62
25.88
25.84
20.66
17.91
17.89
O
OMe
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

40

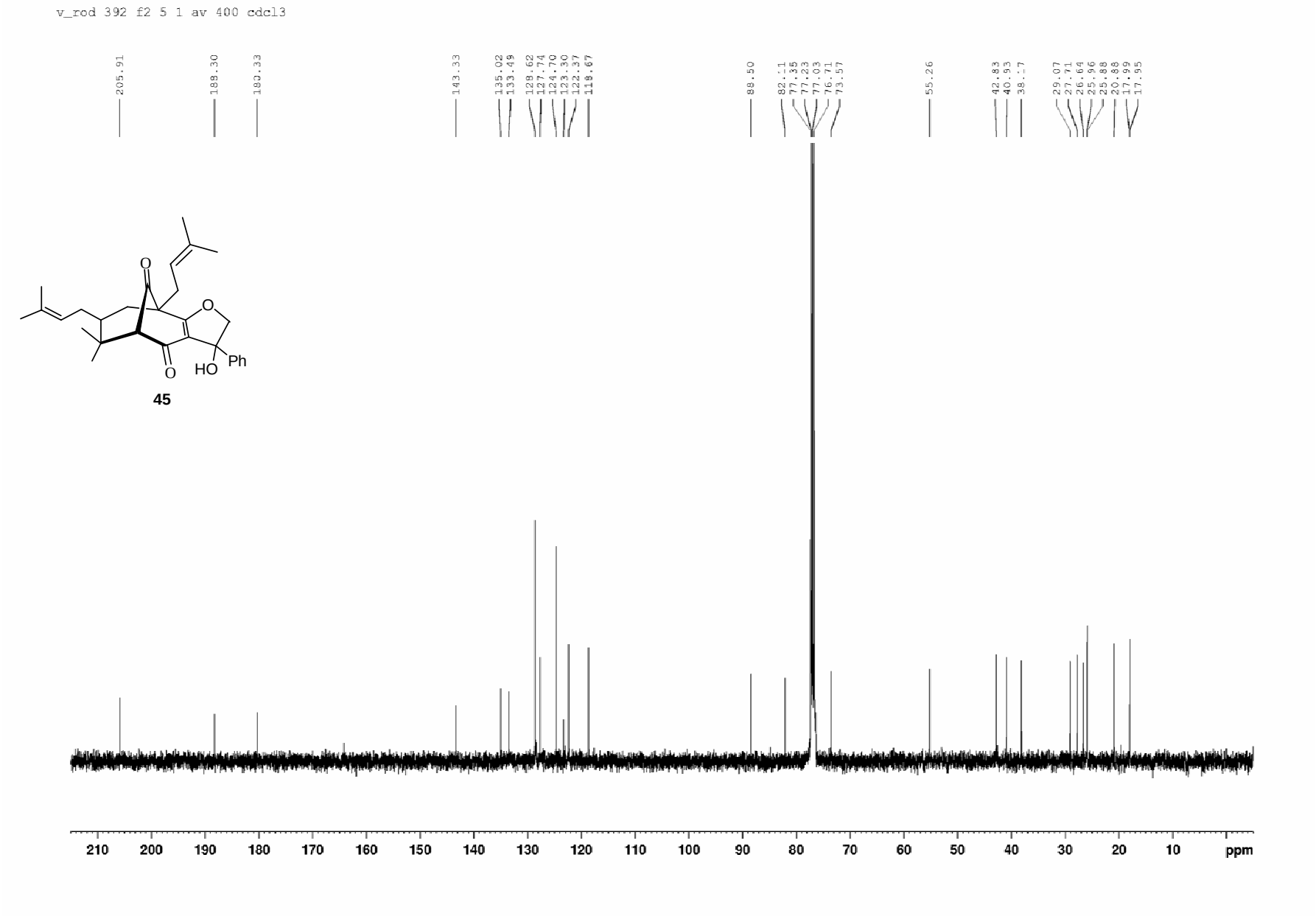

vrod 548 2nd f2 b 3 1 av 400 cdcl3
206.85
194.74
174.49
133.37
133.29
132.54
126.71
122.57
122.15
119.89
77.34
77.03
76.71
75.08
62.09
58.85
43.15
41.29
39.13
30.09
27.38
26.58
25.84
25.78
25.64
23.31
20.56
18.01
17.97
17.82
O
OMe
O
41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


v_rod.549 3 1 drx 500 cdcl3
207.68
197.32
167.70
133.51
133.17
131.81
125.96
122.38
122.01
119.90
77.28
77.03
76.77
63.66
60.52
56.49
42.00
40.43
38.98
29.66
27.93
25.88
25.83
25.80
25.68
22.28
20.84
18.00
17.82
17.77
O
O
OMe
42
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

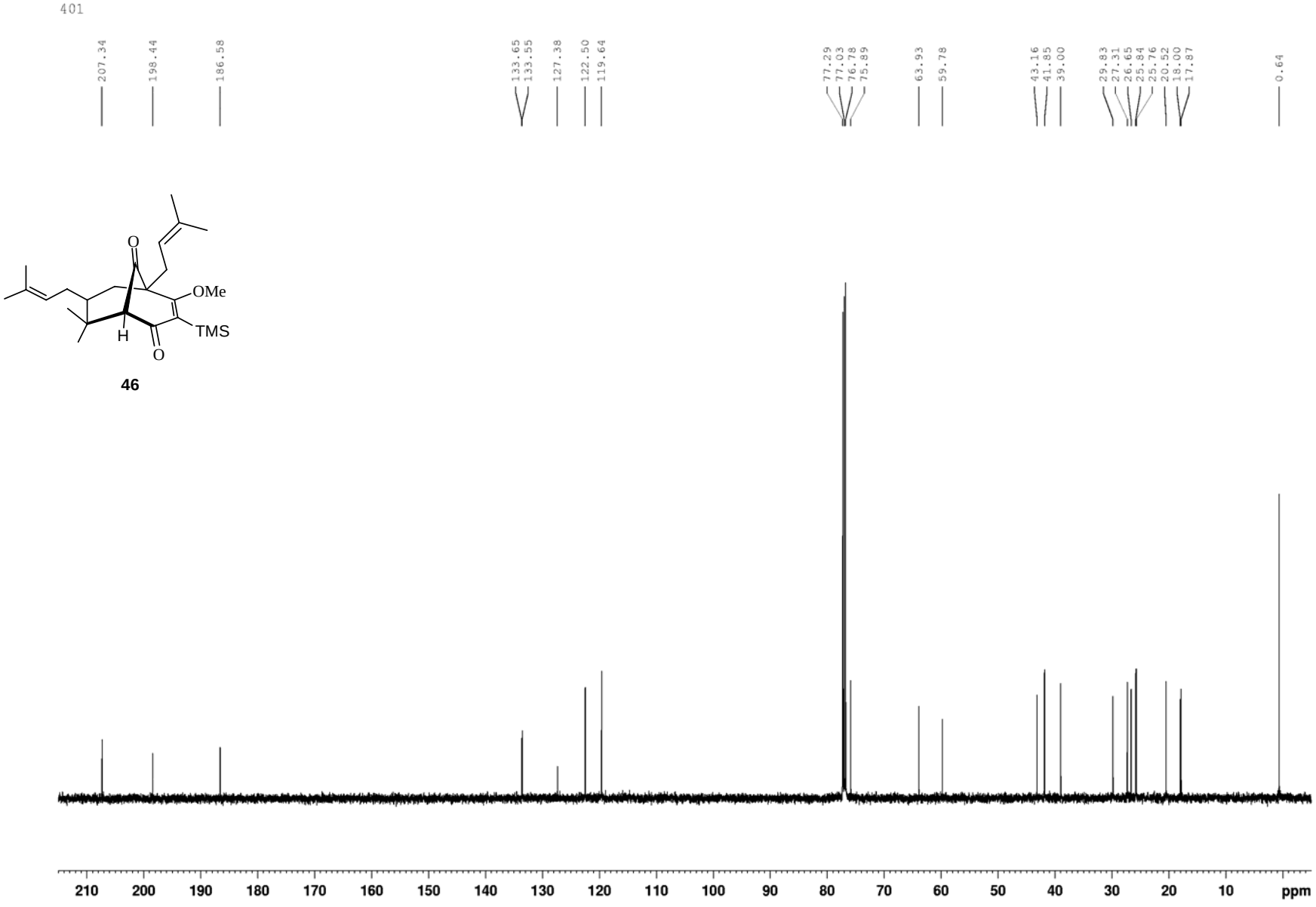

v_rod.572 drx 500 cdcl3
206.67
197.29
168.85
143.03
136.13
133.73
133.23
122.25
121.42
119.72
118.11
117.49
77.28
77.05
76.77
64.02
61.67
57.24
43.07
40.97
38.96
29.84
28.05
25.92
25.88
25.80
20.94
18.20
18.04
17.86
O
O
OMe
43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


205.85
195.41
192.82
174.34
137.92
134.27
133.78
133.46
129.23
128.87
122.41
121.40
119.51
77.35
77.23
77.03
76.71
75.00
61.07
60.78
58.81
43.89
41.26
40.05
30.29
27.71
26.58
25.98
25.88
25.68
20.56
17.97
17.94
OMe
Ph
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

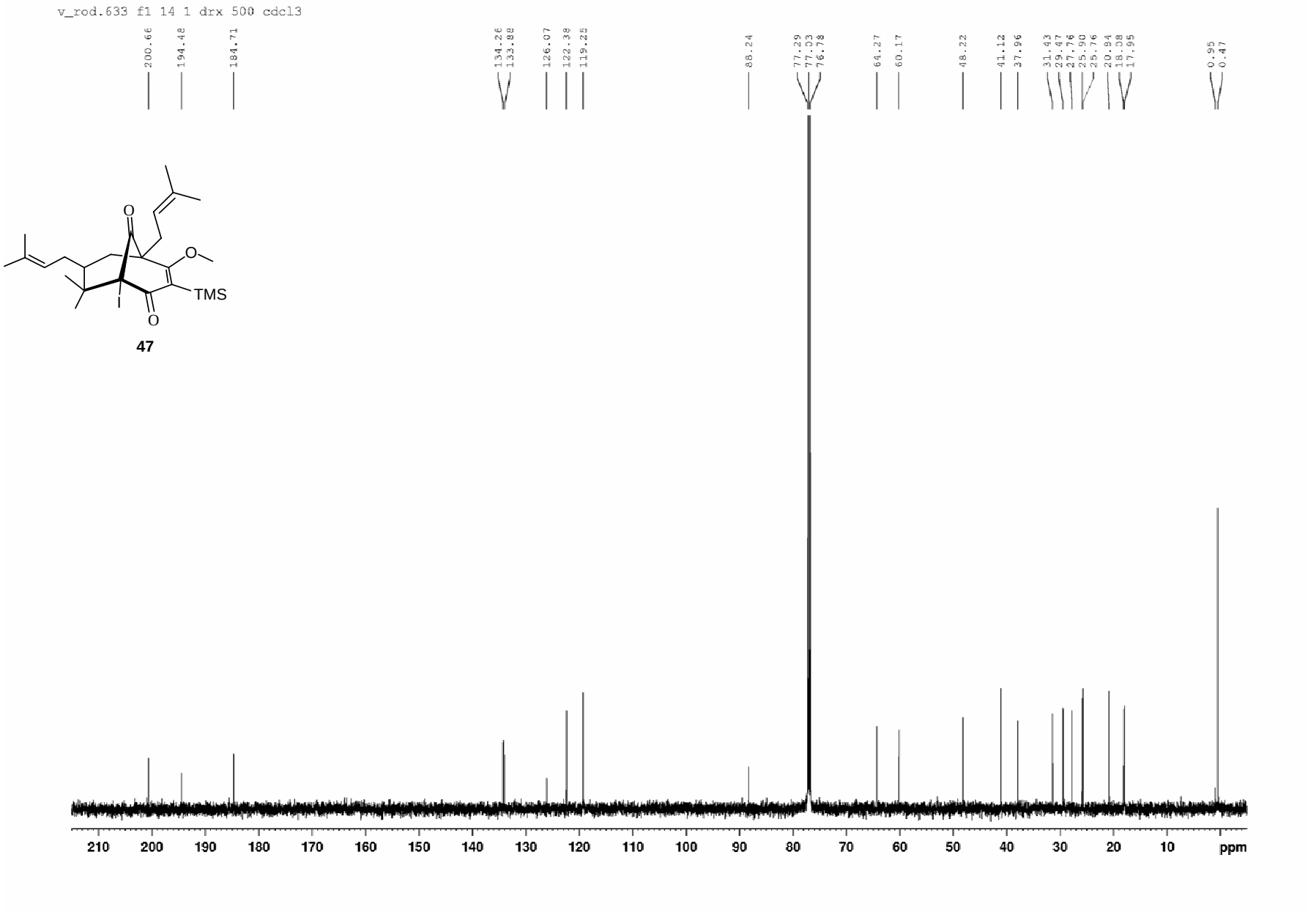
44


v_rod 392 f2 5 1 av 400 cdcl3
205.91
188.30
180.33
143.33
135.02
133.49
129.62
127.74
124.70
123.30
122.37
118.67
88.50
82.11
77.35
77.23
77.03
76.71
73.57
55.26
42.83
40.93
38.17
29.07
27.71
26.64
25.96
25.88
20.88
17.99
17.95
O
O
O
HO
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

45

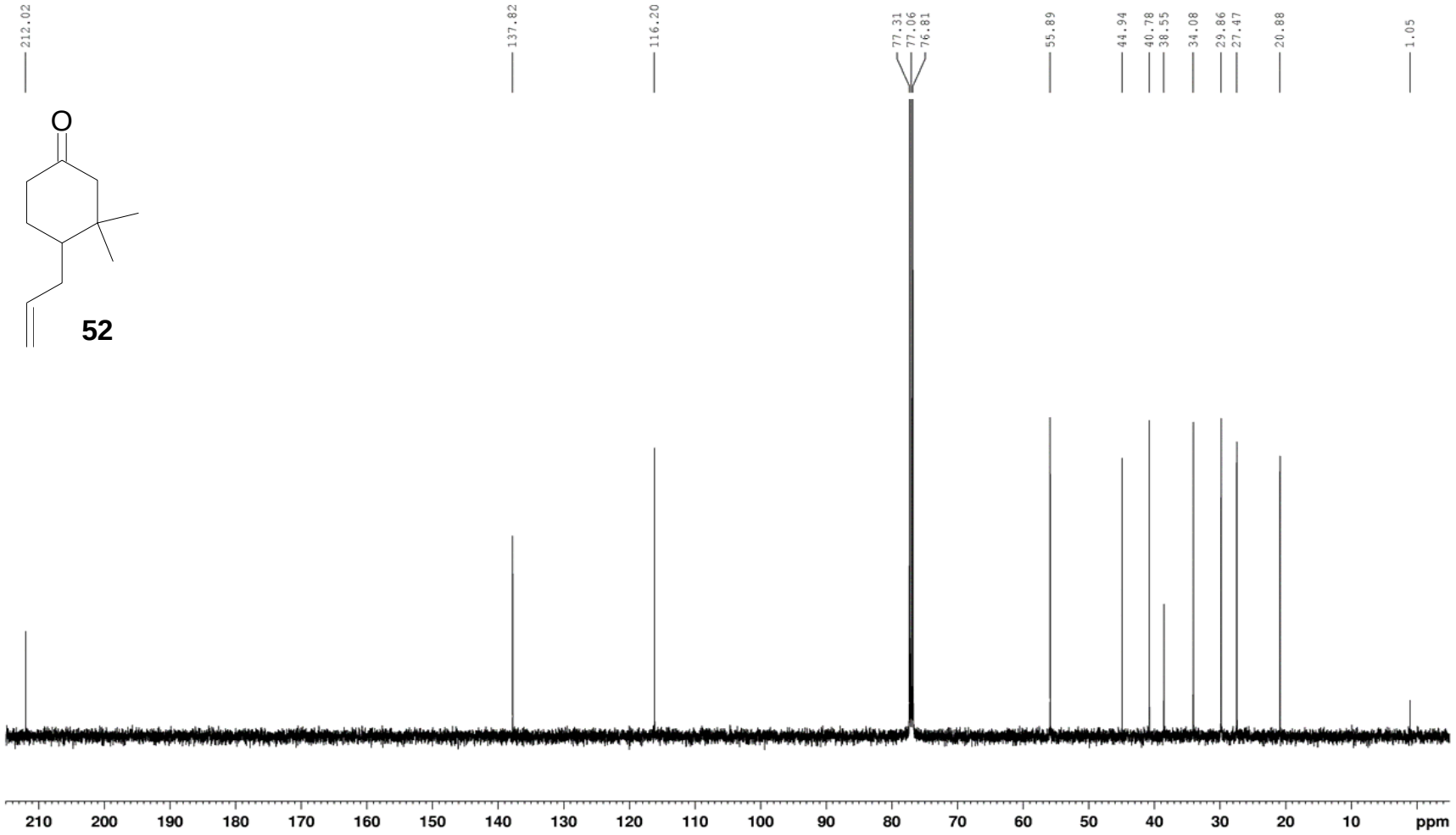

401
207.34
198.44
186.58
133.65
133.55
127.38
122.50
119.64
77.29
77.03
76.78
75.89
63.93
59.78
43.16
41.85
39.00
29.83
27.31
26.65
25.84
25.76
20.52
18.00
17.87
0.64
O
OMe
TMS
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

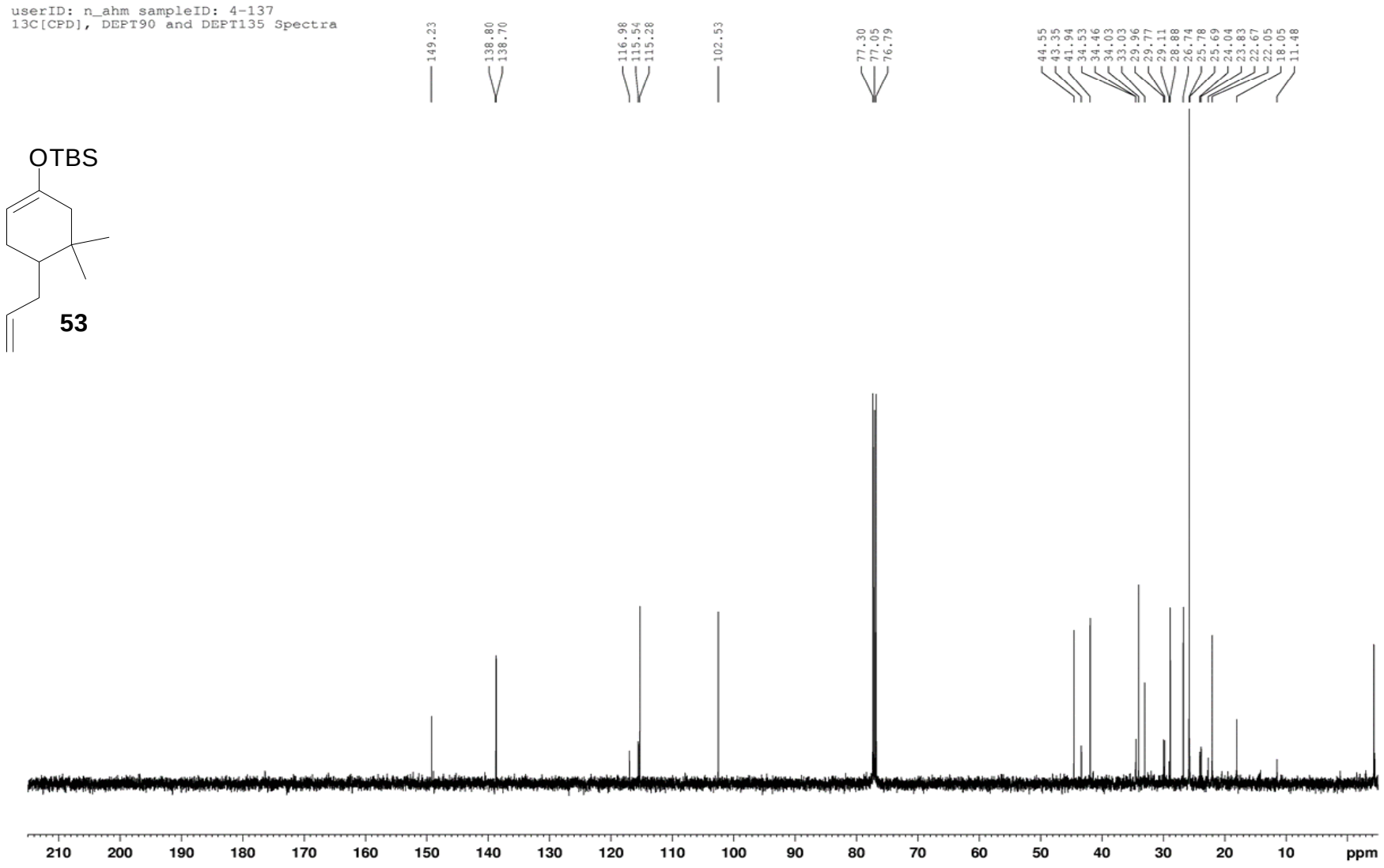
46

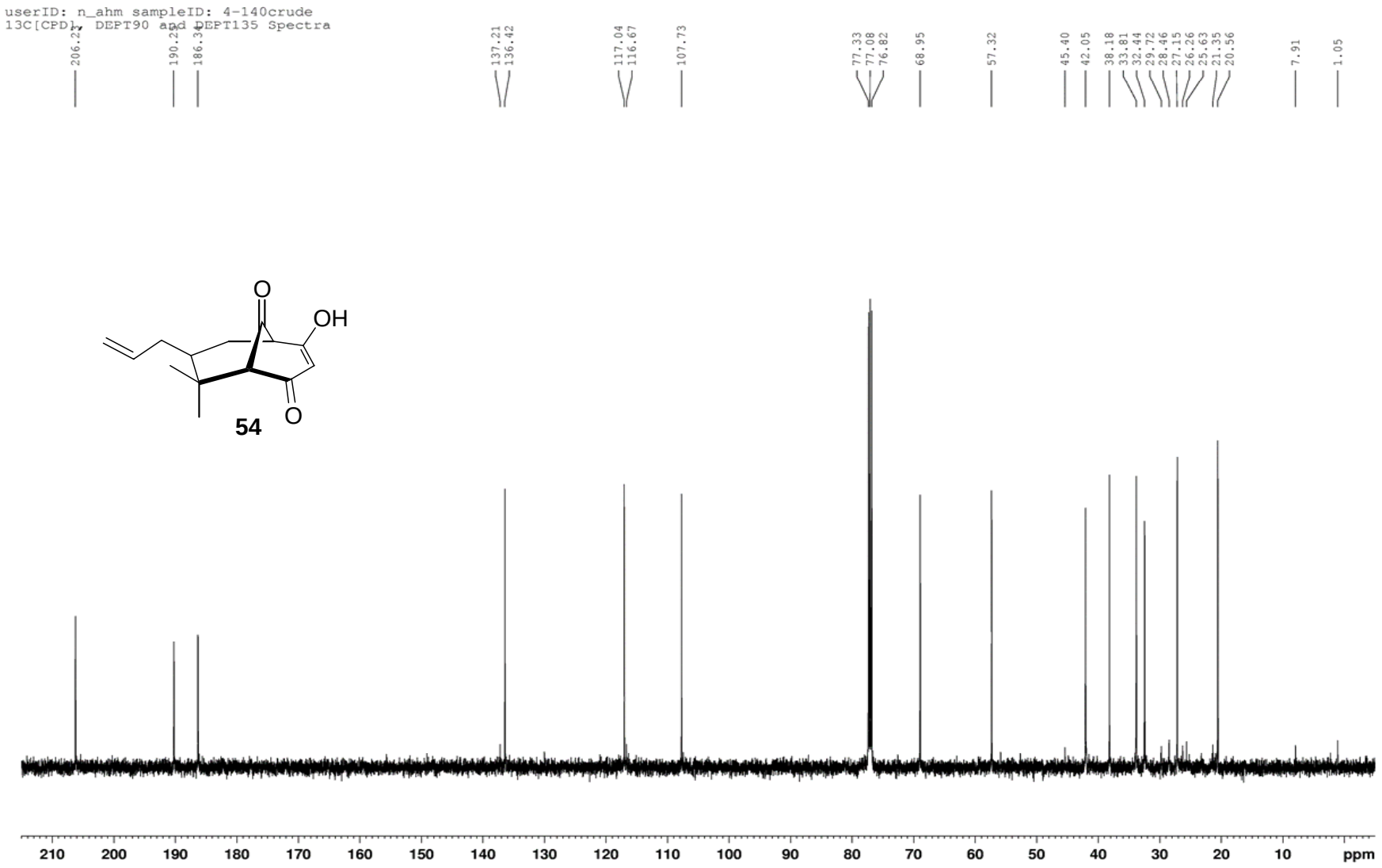

v_rod.633 f1 14 1 drx 500 cdcl3
200.66
194.48
184.71
134.26
133.89
126.07
122.38
119.25
88.24
77.29
77.03
76.78
64.27
60.17
48.22
41.12
37.96
31.43
29.47
27.76
25.90
25.76
20.84
18.08
17.95
0.95
0.47
O
O
O
TMS
I
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

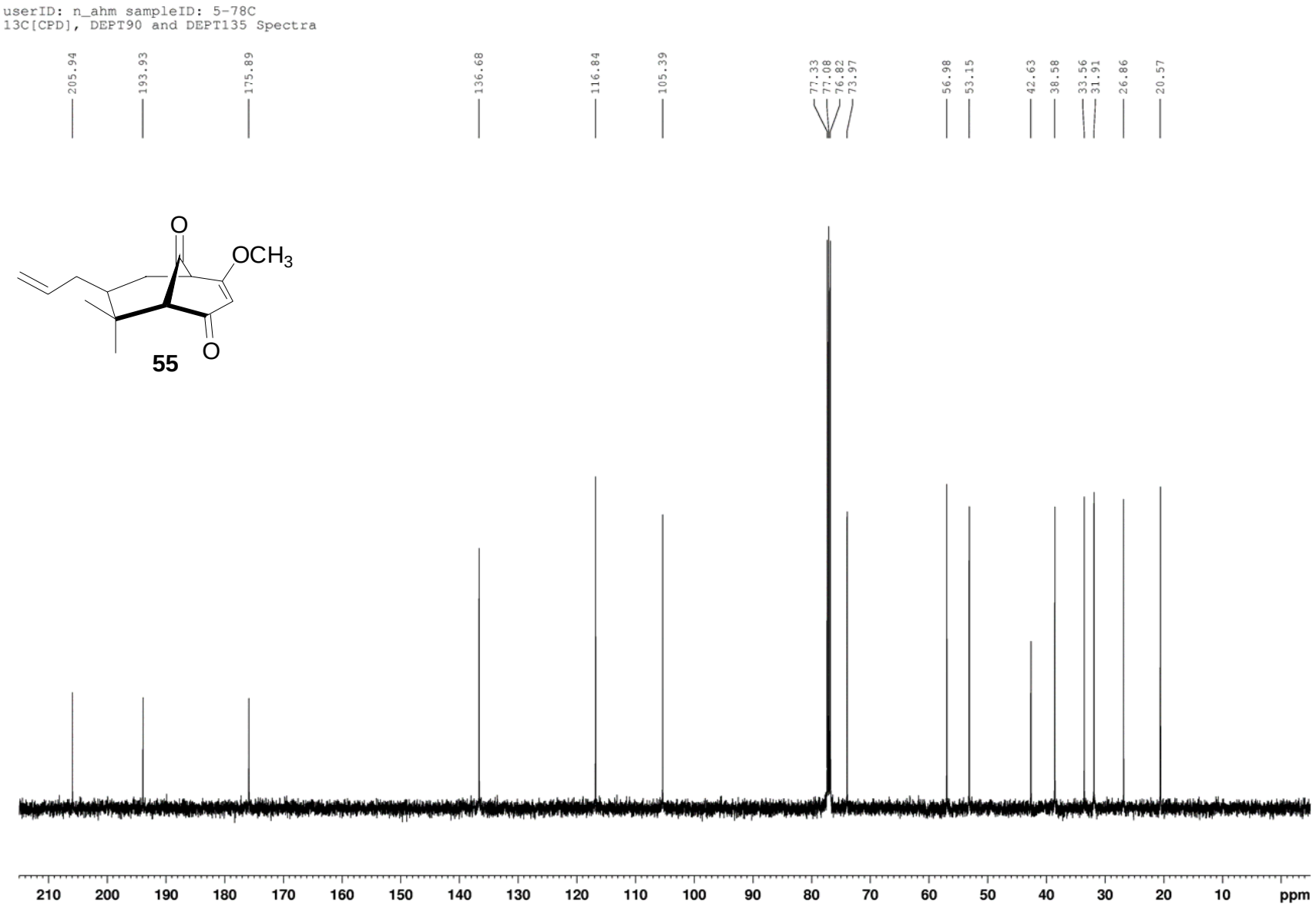
47

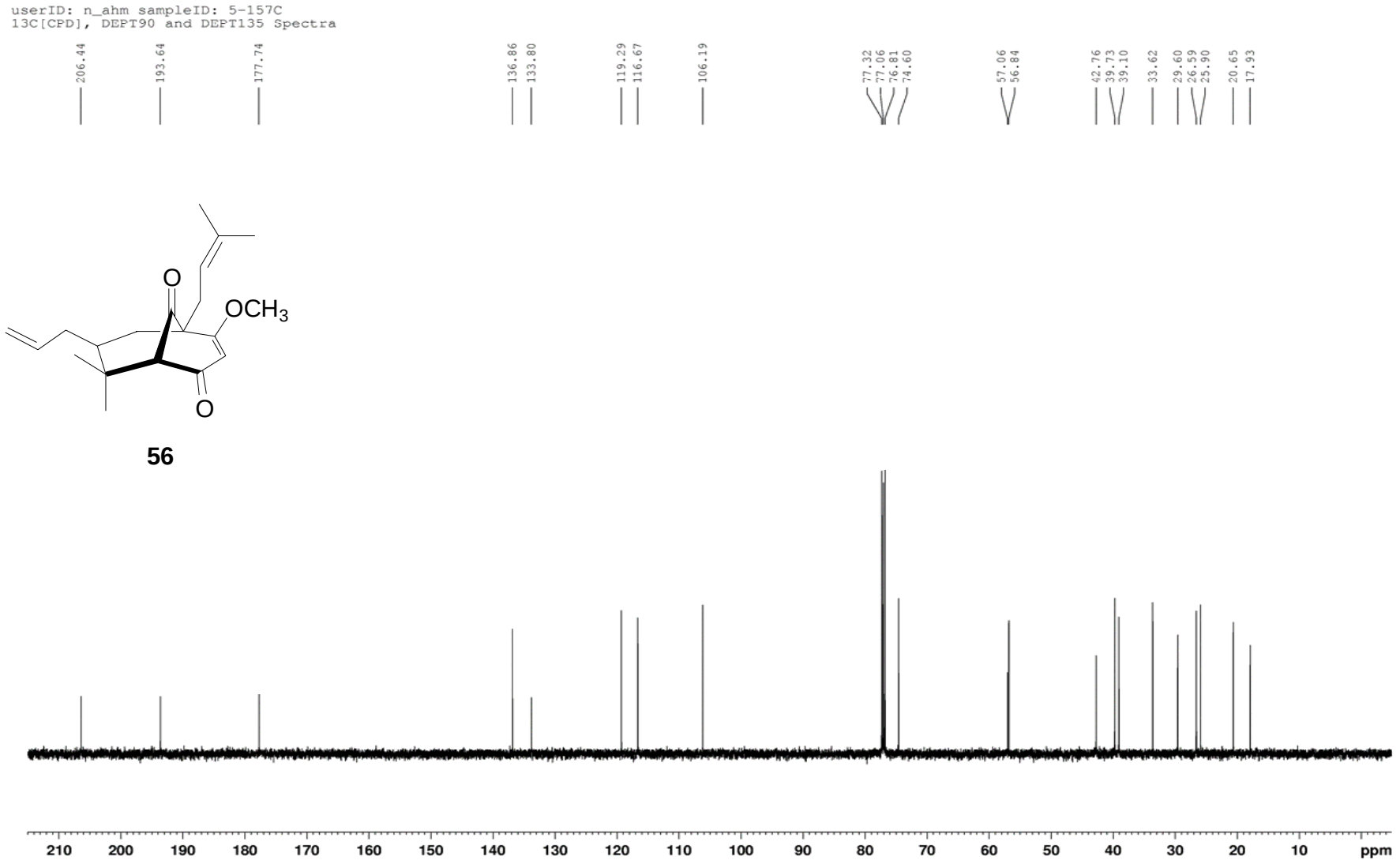
userID: n_ahm sampleID: 5-135rsmC
13C[CPD], DEPT90 and DEPT135 Spectra



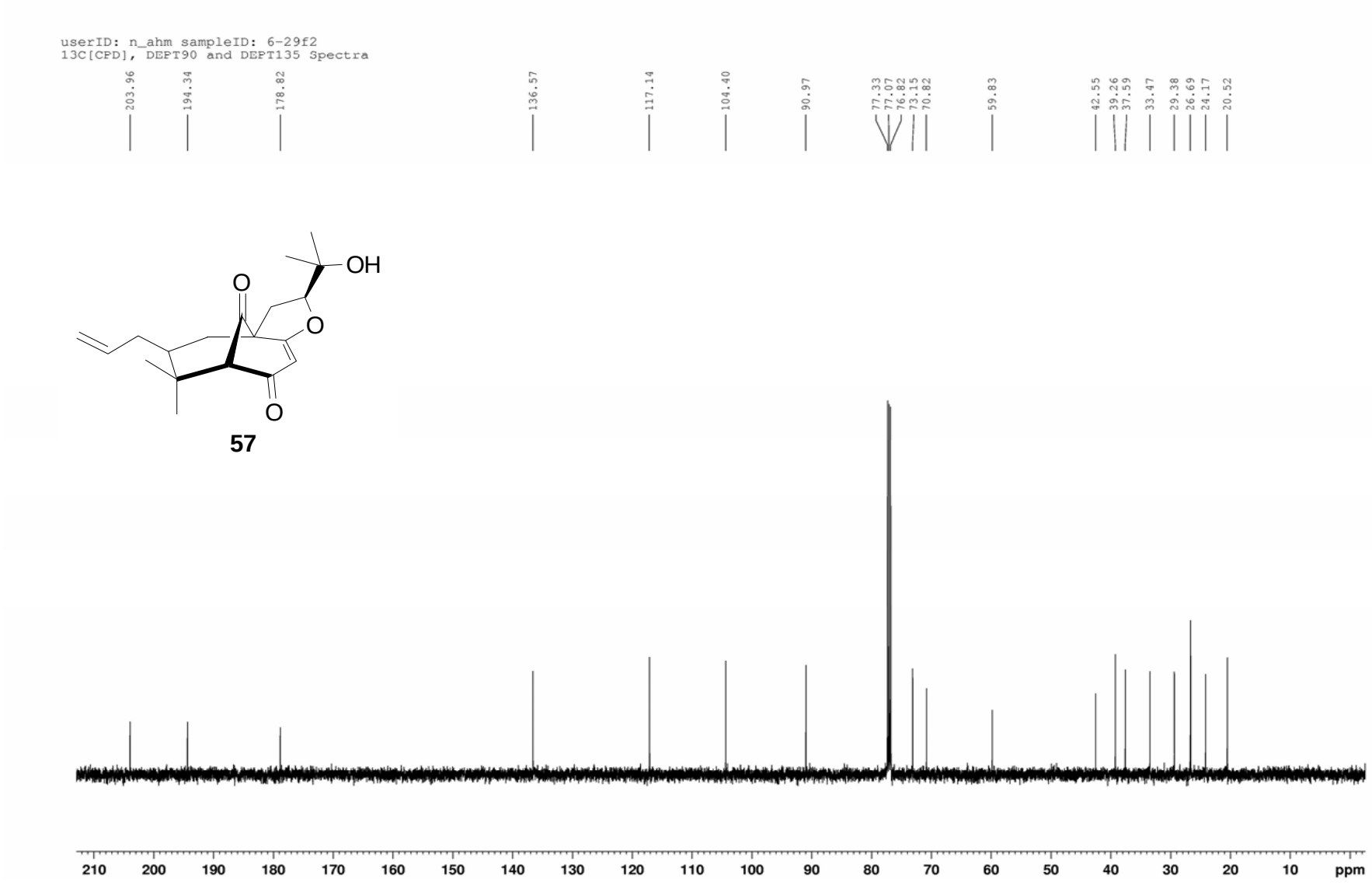

userID: n_ahm sampleID: 4-137
13C[CPD], DEPT90 and DEPT135 Spectra
149.23
138.80
138.70
116.98
115.54
115.28
102.53
77.30
77.05
76.79
44.55
43.35
41.94
34.53
34.46
34.03
33.03
29.96
29.77
29.11
28.88
26.74
25.78
25.69
24.04
23.83
22.67
22.05
18.05
11.48
OTBS
53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


userID: n_ahm sampleID: 4-140crude
13C[CPD], DEPT90 and DEPT135 Spectra
206.22
190.28
186.36
137.21
136.42
117.04
116.67
107.73
77.33
77.08
76.82
68.95
57.32
45.40
42.05
38.18
33.81
32.44
29.72
28.46
27.15
26.26
25.63
21.35
20.56
7.91
1.05
O
OH
O
54
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


userID: n_ahm sampleID: 5-78C
13C[CPD], DEPT90 and DEPT135 Spectra
205.94
193.93
175.89
136.68
116.84
105.39
77.33
77.08
76.82
73.97
56.98
53.15
42.63
38.58
33.56
31.91
26.86
20.57
O
OCH3
O
55
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

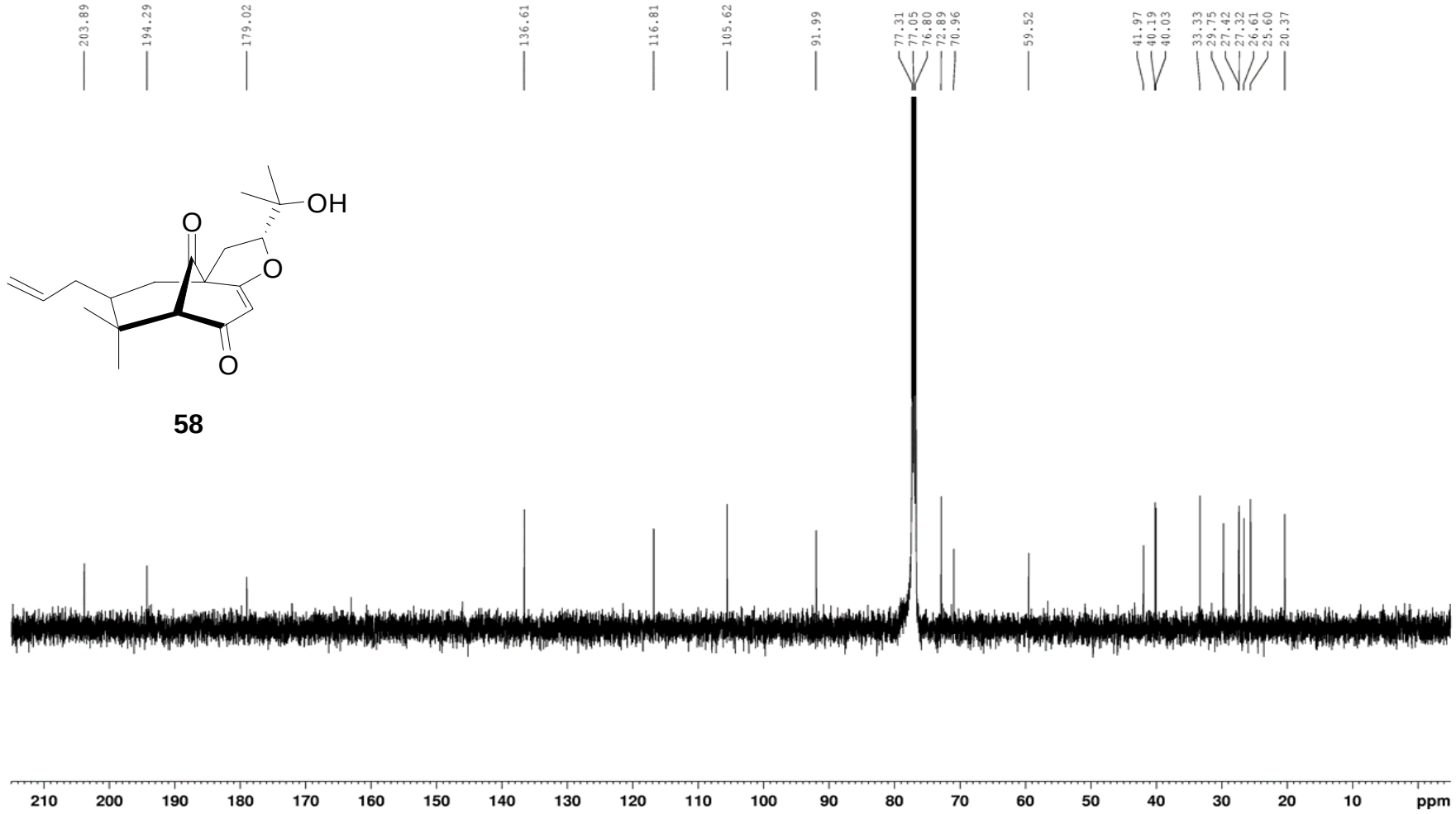

userID: n_ahm sampleID: 5-157C
13C[CPD], DEPT90 and DEPT135 Spectra
206.44
193.64
177.74
136.86
133.80
119.29
116.67
106.19
77.32
77.06
76.81
74.60
57.06
56.84
42.76
39.73
39.10
33.62
29.60
26.59
25.90
20.65
17.93
O
OCH3
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

56

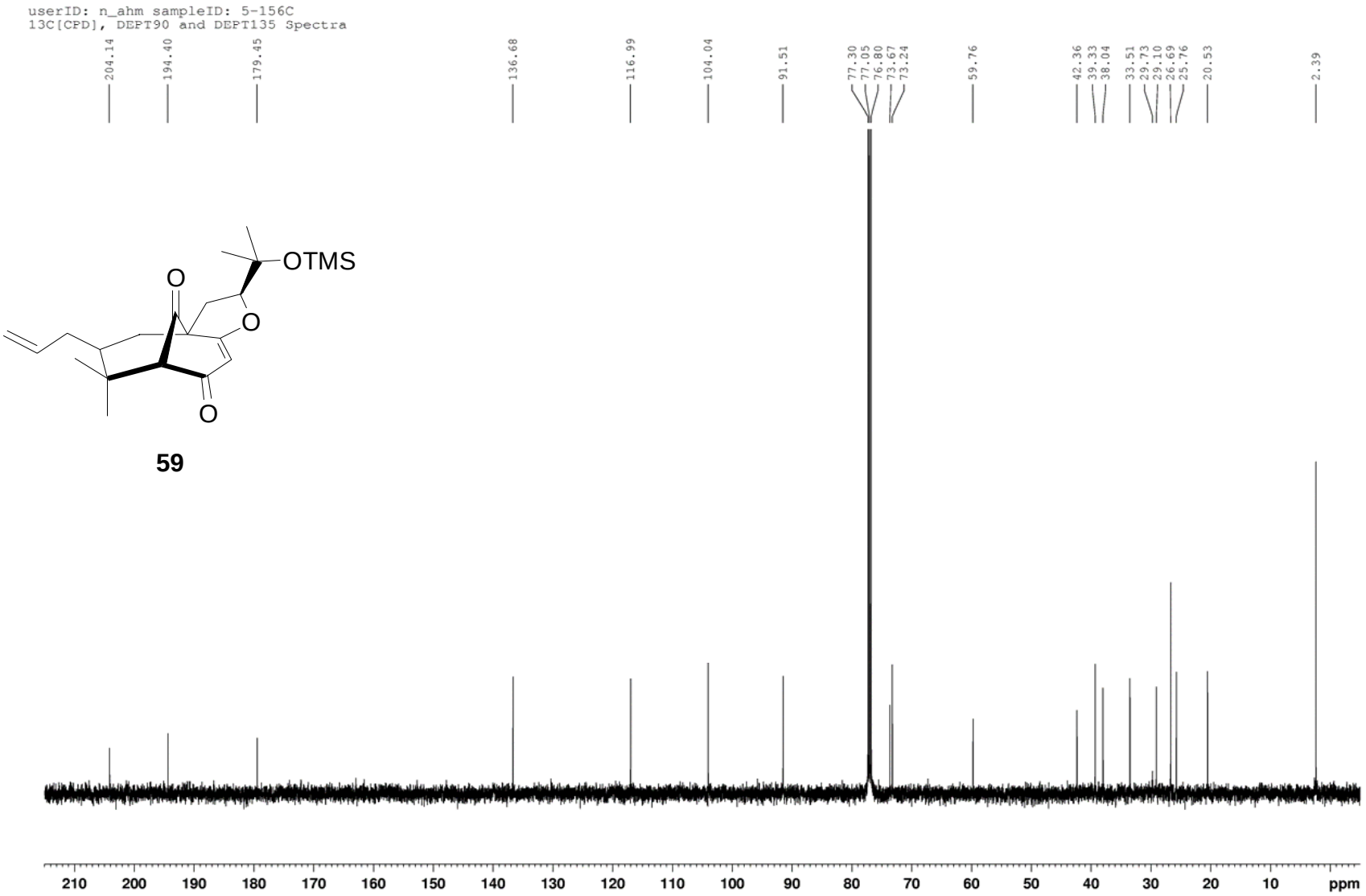

userID: n_ahm sampleID: 6-29f2
13C[CPD], DEPT90 and DEPT135 Spectra
203.96
194.34
178.82
136.57
117.14
104.40
90.97
77.33
77.07
76.82
73.15
70.82
59.83
42.55
39.26
37.59
33.47
29.38
26.69
24.17
20.52
OH
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

57

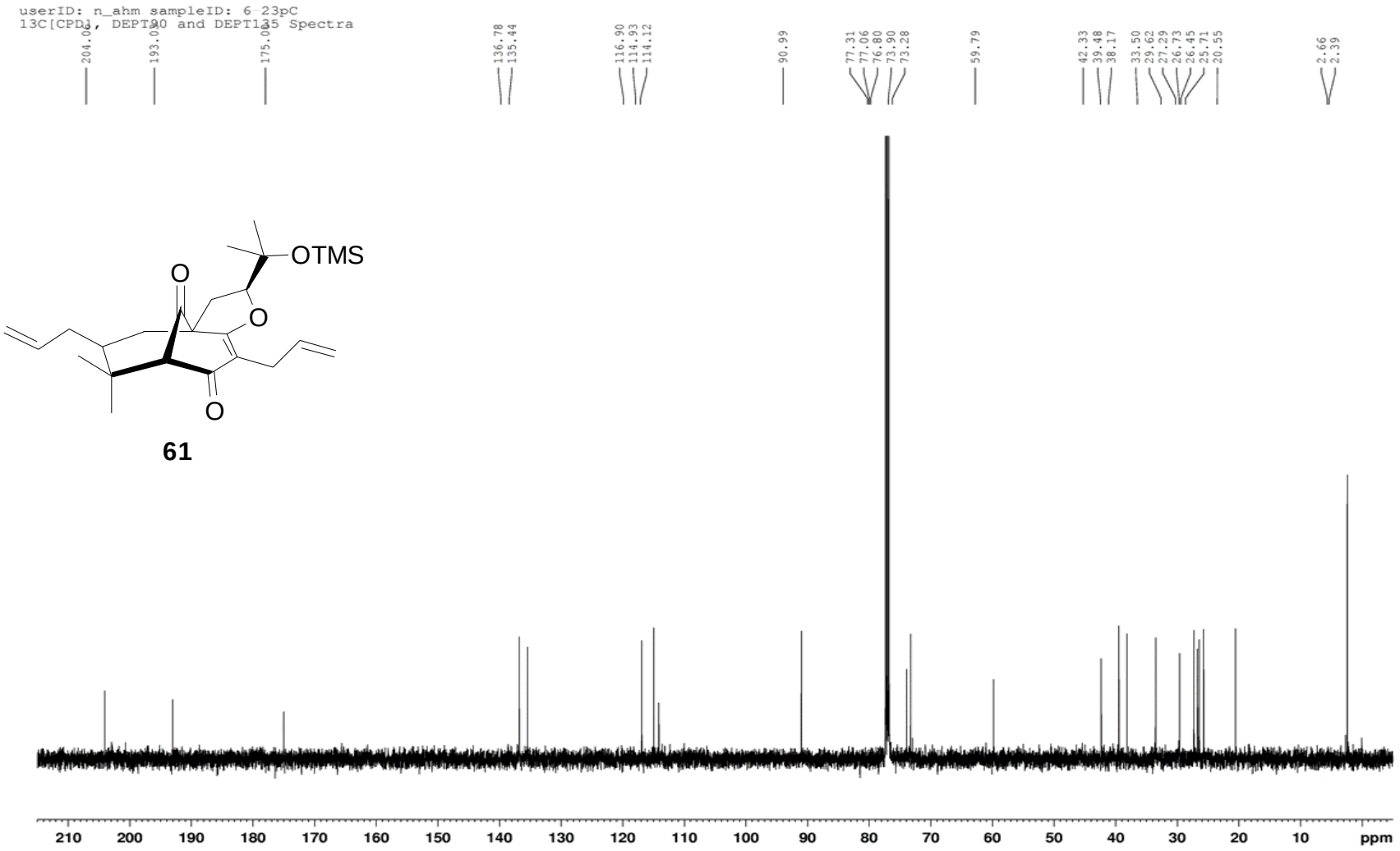
userID: n_ahm sampleID: 6-2f2C
13C{CPD}, DEPT90 and DEPT135 Spectra



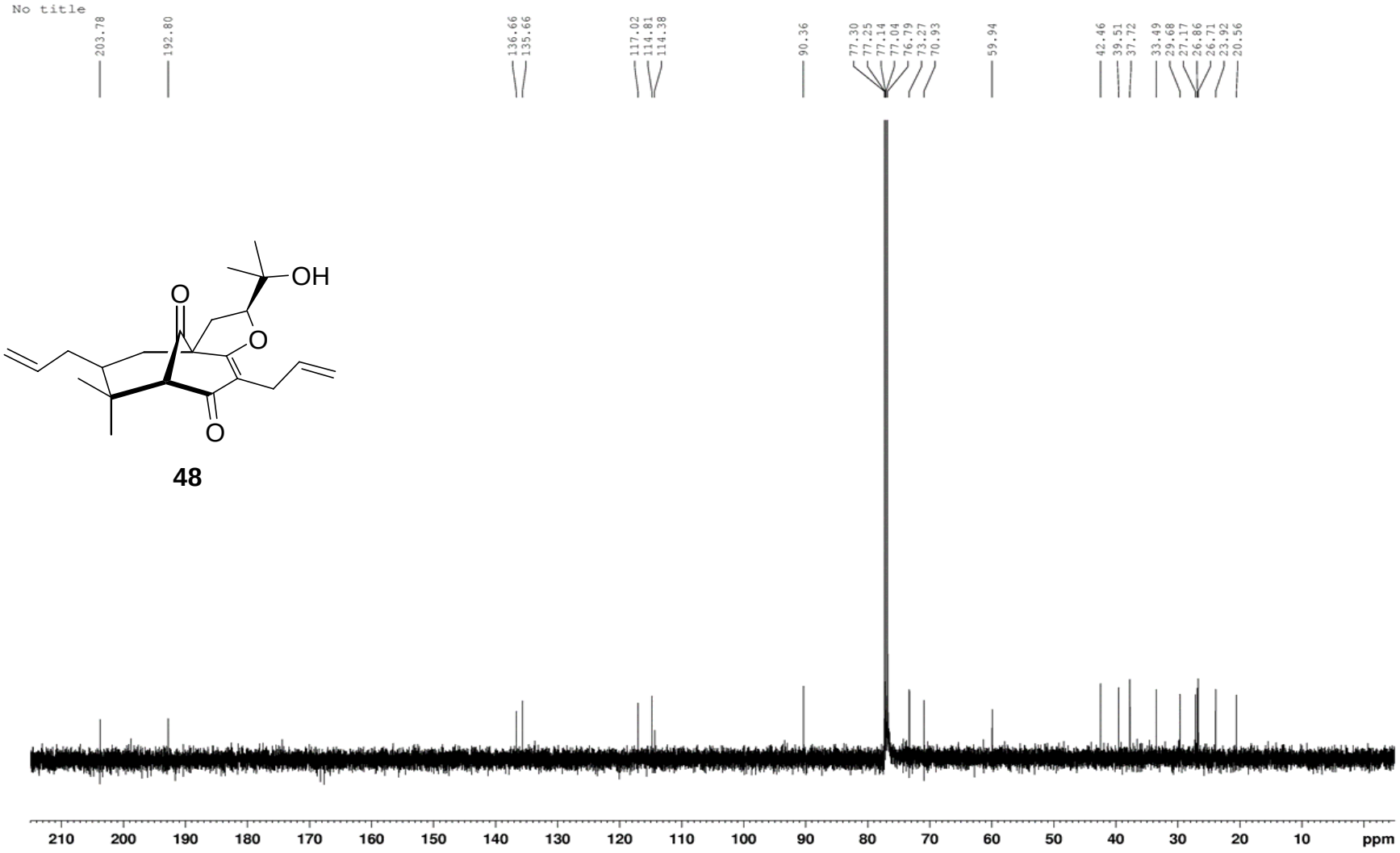
58


userID: n_ahm sampleID: 5-156C
13C[CPD], DEPT90 and DEPT135 Spectra
204.14
194.40
179.45
136.68
116.99
104.04
91.51
77.30
77.05
76.80
73.67
73.24
59.76
42.36
39.33
38.04
33.51
29.73
29.10
26.69
25.76
20.53
2.39
OTMS
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

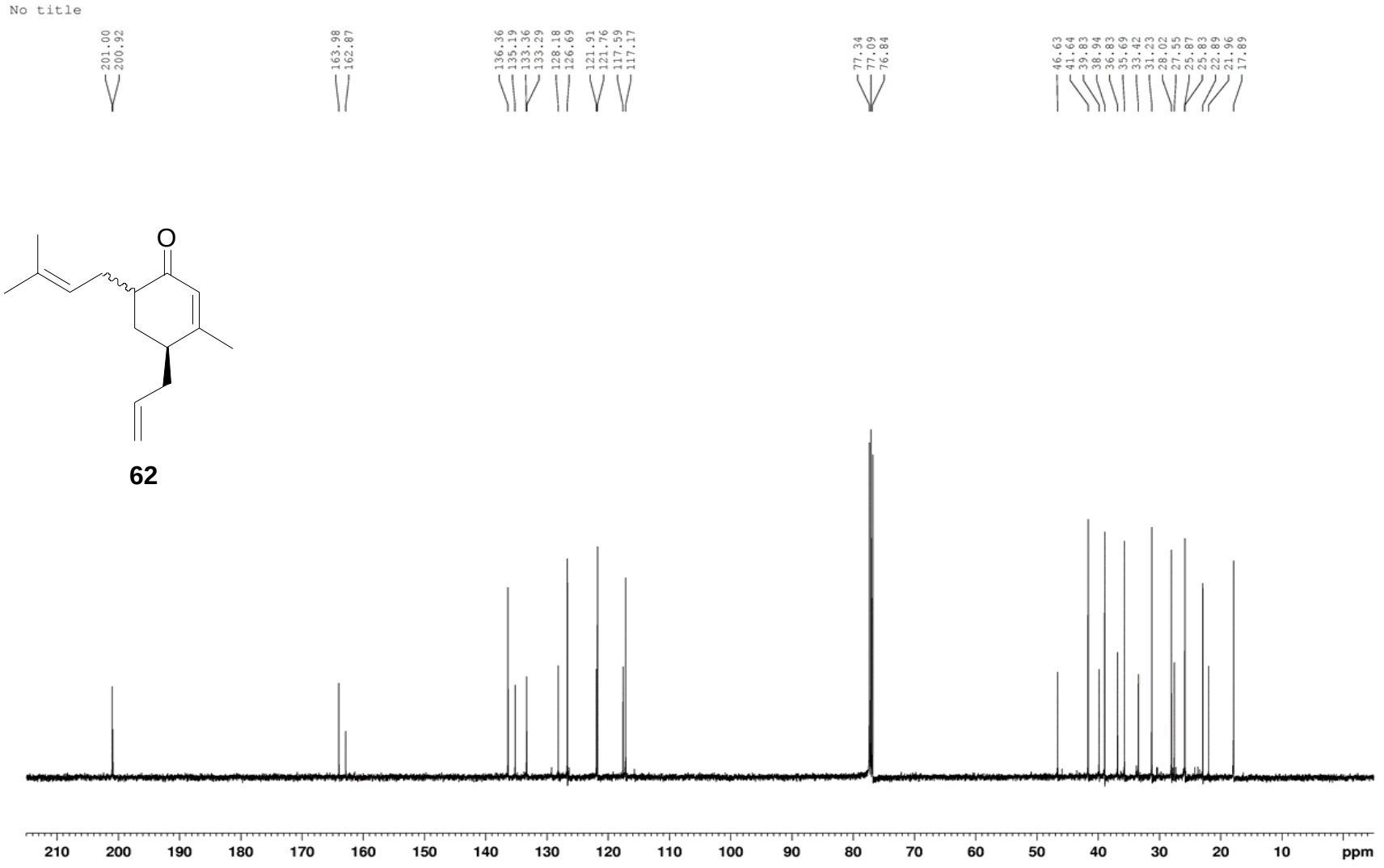
59


userID: n_ahm sampleID: 6-23pC
13C[CPD], DEPT90 and DEPT135 Spectra
204.04
193.03
175.05
136.78
135.44
116.90
114.93
114.12
90.99
77.31
77.06
76.80
73.90
73.28
59.79
42.33
39.48
38.17
33.50
29.62
27.29
26.73
26.45
25.71
20.55
2.66
2.39
OTMS
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

61


No title
203.78
192.80
136.66
135.66
117.02
114.81
114.38
90.36
77.30
77.25
77.14
77.04
76.79
73.27
70.93
59.94
42.46
39.51
37.72
33.49
29.68
27.17
26.86
26.71
23.92
20.56
OH
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

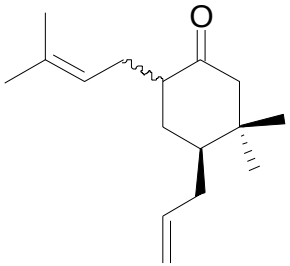
48


No title
201.00
200.92
163.98
162.87
136.36
135.19
133.36
133.29
128.18
126.69
121.91
121.76
117.59
117.17
77.34
77.09
76.84
46.63
41.64
39.83
38.94
36.83
35.69
33.42
31.23
28.02
27.55
25.87
25.83
22.89
21.96
17.89
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

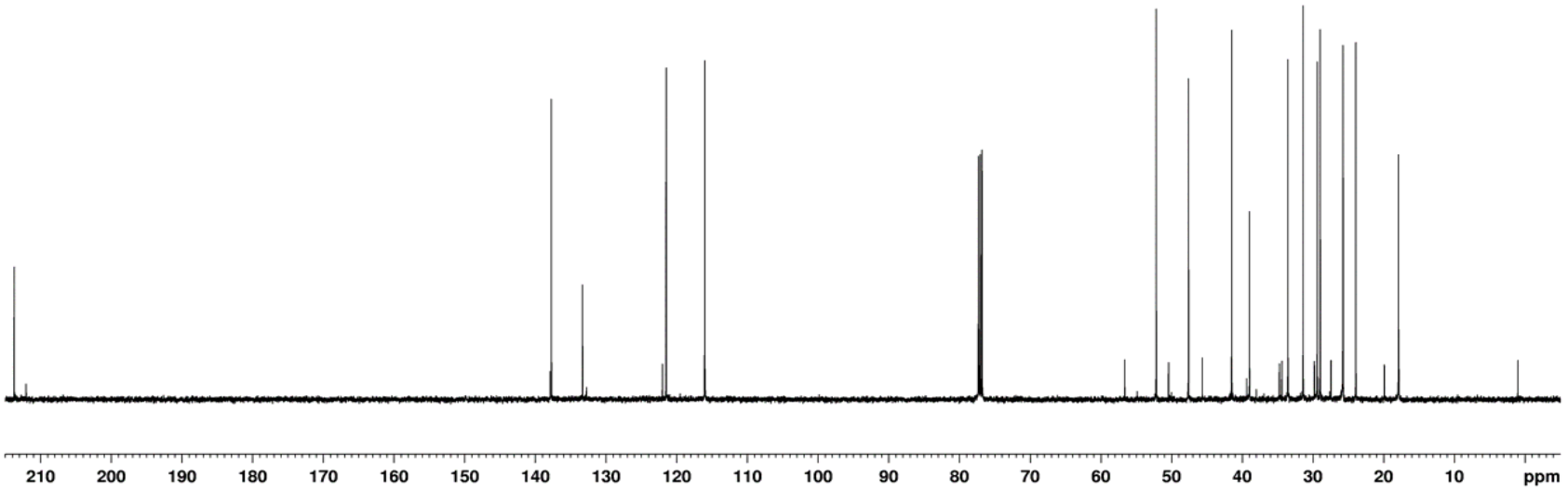
62

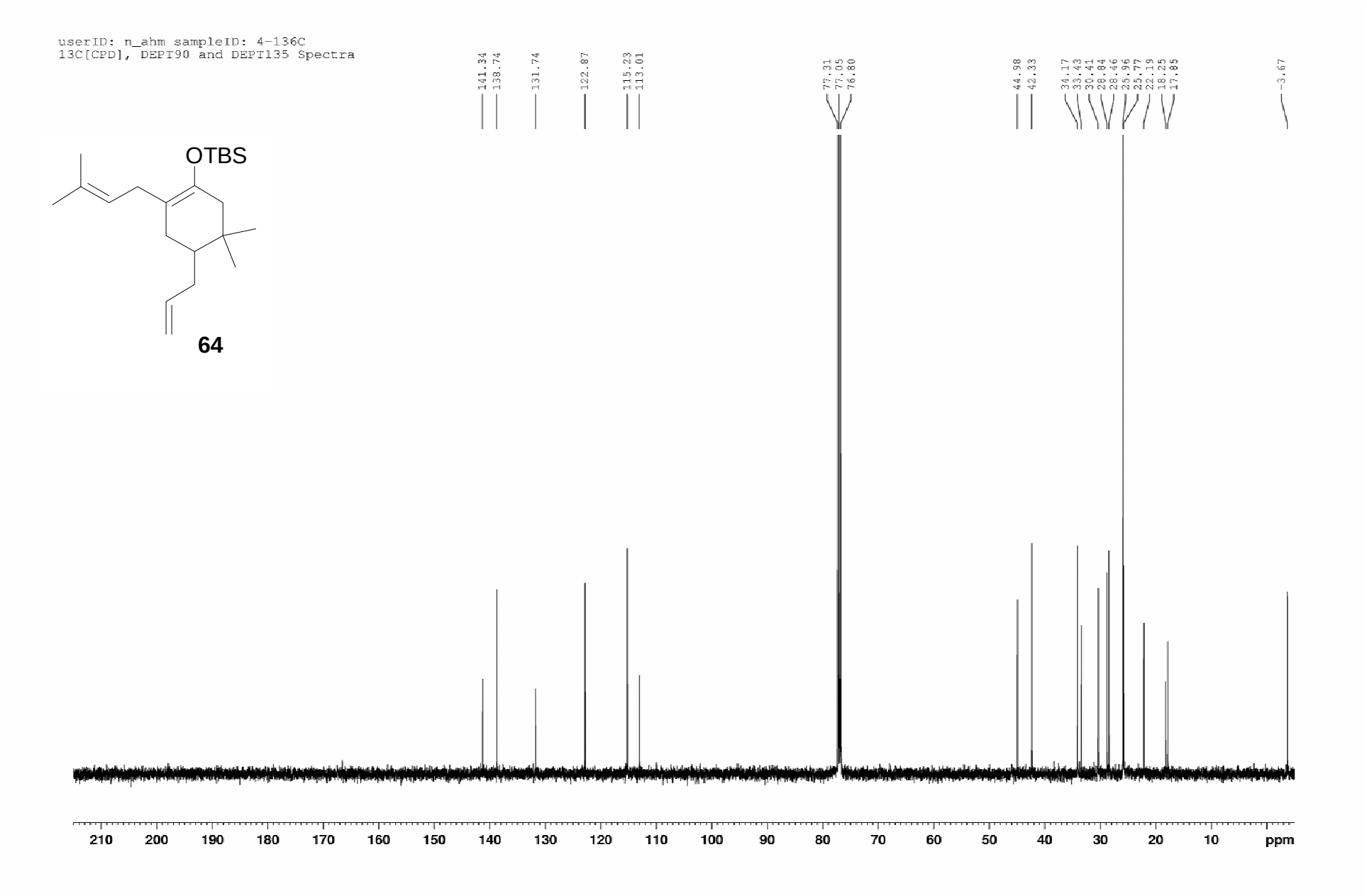
userID: n_ahm sampleID: 4-149
13C[CPD], DEPT90 and DEPT135 Spectra

212.08
137.89
137.78
133.36
132.81
122.06
121.53
116.06
77.33
77.08
76.82
56.65
54.90
52.20
50.46
50.04
47.75
47.62
45.67
41.64
41.51
39.41
39.01
38.04
34.78
34.41
33.58
31.53
31.42
29.81
29.41
29.00
27.72
27.47
26.04
25.76
23.95
19.92
17.93
17.82
1.03

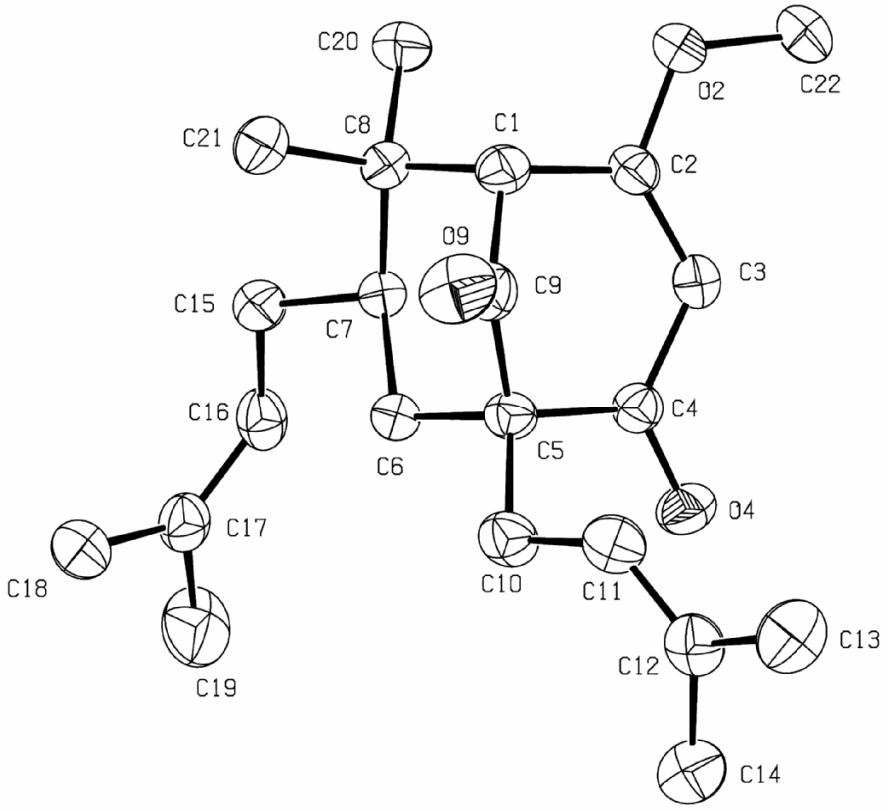


63




userID: n_ahm sampleID: 4-136C
13C[CPD], DEPT90 and DEPT135 Spectra
141.34
138.74
131.74
122.87
115.23
113.01
77.31
77.05
76.80
44.98
42.33
34.17
33.43
30.41
28.84
28.46
25.96
25.77
22.19
18.25
17.85
-3.67
OTBS
64
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

X-ray structure of **39**



X-ray structure of derivative **56**