Supplementary Information for "Total Synthesis and Structural Elucidation of *ent*-Micropyrone and (+)-Ascosalipyrone

by Claire Gregg and Michael V. Perkins*

Contents:

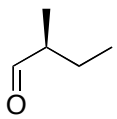
1. General experimental conditions and experimental procedures.
2. Experimental details and data for compounds **13-15, 33, 11, 17, 34, 35, 36, 16, 37, 38, 39, 40, 23, 41, 42, 43, 44, 45, 46** and **29.**
3. X-ray crystallographic data for compounds **22** and **23**.
4. **Table 1.** Comparison of the ^{1}H and ^{13}C NMR data for micropyrone (**1**) and synthetic isomers **22** and **23**.
5. **Table 2.** Comparison of the ^{1}H and ^{13}C NMR data for ascosalipyrone (**2**) and synthetic isomers **28** and **29**.
6. **^{1}H and ^{13}C NMR** spectra for compounds **14, 11, 18, 20, 22, 25-29, 16, 37, 39, 23, 41, 43** and **44.**
7. 300 MHz ^{1}H NMR spectrum of authentic ascosalipyrone in $CDCl_3$.
8. 75.5 MHz ^{13}C NMR spectrum of authentic ascosalipyrone in $CDCl_3$.

General experimental

All reactions were carried out under an atmosphere of nitrogen (N_2) or argon (Ar) in oven-dried glassware. Most starting materials and reagents were purchased from the the Sigma-Aldrich Chemical Co. and were used as supplied, or dried and distilled using standard procedures.[1] Triethylamine (Et_3N) and pyridine were distilled from calcium hydride (CaH_2). Tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried using sodium metal and then distilled, as required, from sodium-benzophenone under N_2. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride under N_2 as required. Other solvents used for reactions, extractions and purification were distilled prior to use. *n*-Butyllithium was freshly standardised by titration against *N*-pivaloyl-o-toluidine prior to use.[2] Sodium hydride (NaH) (60% dispersion in mineral oil) was washed with mixed hexanes and dried under N_2 before use.

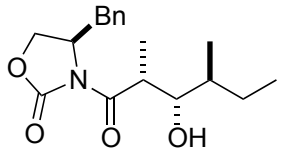
Room temperature (rt) varied between 20-25 °C. Analytical thin layer chromatography (TLC) was conducted on aluminium-backed 0.2 mm thick silica gel 60 F_{254} plates (Merck) and the plates were visualised under a 254 nm UV lamp and/or by treatment with either anisaldehyde dip (*p*-anisaldehyde, 9.2 mL; H_2SO_4, 12.5 mL; CH_3CO_2H, 3.75 mL; EtOH, 338 mL) or potassium permanganate dip ($KMnO_4$, 3 g; K_2CO_3, 20 g; 5% NaOH, 5 mL; H_2O, 300 mL), followed by heating with a heat gun. Column chromatography was conducted using silica gel 60 (mesh size 0.040-0.063 mm) as the stationary phase and the analytical reagent solvents indicated. When purifying compounds with acid sensitivity, column chromatography was performed on buffered silica as indicated. Buffered silica was prepared by spinning 100 g of silica gel 60 (mesh size 0.040-0.063 mm) with 10 mL of pH 7 phosphate buffer on a rotary evaporator overnight at atmospheric pressure.

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker Avance II spectrometer at 400 or 600 MHz for proton and 100 or 151 MHz for carbon nuclei, respectively. Chemical shifts were recorded as δ values in parts per million (ppm). Spectra were acquired either in deuterochloroform ($CDCl_3$) or deuteromethanol (CD_3OD) at ambient temperature. For ^{1}H NMR spectra recorded in $CDCl_3$, the peak due to residual $CHCl_3$ (δ 7.26) was used as the internal reference and for CD_3OD the peak due to residual CH_3OH (δ 3.31) was used as the internal reference. ^{1}H NMR spectral data are recorded as follows: chemical shift (δ), relative integral, multiplicity (defined as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, apt = apparent), coupling constant(s) *J* (Hz), assignment. For proton-decoupled ^{13}C NMR spectra recorded in $CDCl_3$, the central peak (δ 77.16) of the $CDCl_3$ triplet was used as the internal reference and for CD_3OD the central peak (δ 49.00) of the CD_3OD septet was used as the internal reference and all data are given as chemical shift (δ). ^{1}H and ^{13}C assignments were confirmed by conducting homonuclear (^{1}H-^{1}H) correlation spectroscopy (COSY), nuclear Overhauser effect (nOe) spectroscopy (NOESY) and heteronuclear (^{1}H-^{13}C) correlation spectroscopy (HMQC) experiments. Optical rotations were recorded on a PolAAR 21 polarimeter, referenced to the sodium D line (589 nm) at 20 °C, using the spectroscopic grade solvent specified ($CHCl_3$ or CH_2Cl_2) and at the concentration (*c*, g/100 mL) indicated. Measurements were carried out in a cell with a 1 dm path length. Infrared (IR) spectra were recorded on either a Perkin-Elmer 1600 series FTIR, BIO-RAD FTS-40-A or Nicolet Avatar 370 DTGS Fourier Transform spectrophotometer, with the absorptions recorded in wavenumbers (n_{max}/cm^{-1}). Liquid samples were analysed as thin films on NaCl discs, with solids made into a KBr disc. High resolution mass spectra were recorded on either a Bruker BioApex II 47e FTMS fitted with an Analytica ESI source or or an Agilent G1969A LC-TOF utilizing an Agilent 1100 Series LC.



(S)-2-methylbutanal (13). To a stirred solution of DMSO (3.92 mL; 55.2 mmol) in CH_2Cl_2 (150 mL) at -78 °C was added oxalyl chloride (13.8 mL; 27.6 mmol) dropwise and the resulting solution stirred at -78 °C for 30 min. A solution of (S)-2-methylbutanol (2.00 mL; 18.4 mmol) in CH_2Cl_2 (30 mL) was added dropwise

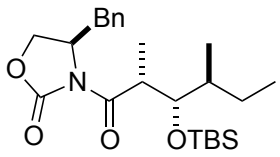
via cannula to the reaction mixture and the resulting solution was stirred at -78 °C for 45 min. Et_3N (15.4 mL; 110 mmol) was added dropwise and stirring was continued at -78 °C for 30 min before warming slowly to 0 °C for a further 30 min. The reaction was quenched by addition of sat. aq. NH_4Cl (300 mL) and the mixture was extracted with CH_2Cl_2 (3 x 150 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (100% CH_2Cl_2) gave aldehyde (**13**) (1.19 g; 75%) as a colourless oil. **R*f*** = 0.56 (100% CH_2Cl_2); **$[\alpha]^{20}_D$** = +21.5 (c 1.54, CH_2Cl_2); **^{1}H NMR** (400MHz, $CDCl_3$) δ 9.62 (1H, d, J = 2.0 Hz, C*H*O), 2.28 (1H, dddq, J = 14.0, 7.2, 6.8, 2.0 Hz, C*H*(CH_3)CHO), 1.75 (1H, ddq, J = 14.0, 7.6, 6.8 Hz, CH(CH_3)CH_AH$_B$$CH_3$), 1.44 (1H, ddq, J = 14.0, 7.6, 7.2 Hz, CH(CH_3)CH_AH$_B$$CH_3$), 1.09 (3H, d, 6.8 Hz, CH(CH_3)CH_2CH_3), 0.95 (3H, dd, J = 7.6, 7.2 Hz, CH_2CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.5, 47.9, 23.6, 12.9, 11.4.



14

(4*R*)-Benzyl-3-((2*R*,3*S*,4*S*)-3-hydroxy-2,4-dimethylhex-anoyl)oxazolidin-2-one (14). To a stirred solution of oxazolidine (*R*)-(**12**) (1.63 g; 7.00 mmol) in CH_2Cl_2 (14 mL) at 0 °C was added Bu_2BOTf (8.39 mL; 1M in CH_2Cl_2; 8.39 mmol) dropwise, giving a red solution. After 30 min Et_3N (1.27 mL; 9.09 mmol) was added and the resulting yellow solution was stirred for a further 30 min before cooling to -78 °C. Aldehyde (**13**) (1.19 g; 13.8 mmol) in CH_2Cl_2 (7 mL) was added dropwise *via* cannula and the reaction mixture stirred at -78 °C for 30 min and then at 0 °C for 4 h, at which time the reaction was quenched by addition of pH 7 buffer (16 mL) and MeOH (24 mL). A solution of 2:1 MeOH/H_2O_2 (24 mL) was then added and the mixture stirred at rt for 1 hour. The volatiles were removed in *vacuo* and the resulting slurry was extracted with CH_2Cl_2 (3 x 50 mL), the combined organic extracts washed with sat. aq. $NaHCO_3$ (50 mL) and brine (50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (5% Et_2O/CH_2Cl_2) gave aldol adduct (**14**) (960 mg; 66%, >98% ds) as a white solid (known compound[3]). **R*f*** = 0.33

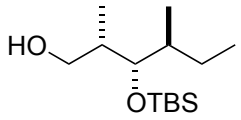
(5% Et_2O/CH_2Cl_2); **mp.** 69-70 °C; **[α]$^{20}_D$** = -40.0° (c 1.10, $CHCl_3$); **^{1}H NMR** (400 MHZ, $CDCl_3$) δ 7.35-7.31 (2H, m, Ar*H*), 7.29-7.25 (1H, m, Ar*H*), 7.21-7.18 (2H, m, Ar*H*), 4.70 (1H, dddd, J = 9.6, 7.6, 3.6, 3.2, C*H*CH_2Ph), 4.23 (1H, dd, J = 9.2, 7.6 Hz, OC*H*$_A$H$_B$CHCH$_2$N), 4.18 (1H, dd, J = 9.2, 3.2 Hz, OCH$_A$*H*$_B$CHN), 3.95 (1H, dq, J = 7.2, 3.2 Hz, C(=O)C*H*(CH_3)), 3.62 (1H, ddd, J = 9.2, 3.2, 2.4 Hz, C*H*OH), 3.25 (1H, dd, J = 13.6, 3.6 Hz, C*H*$_A$H$_B$Ph), 2.96 (1H, d, J = 3.6 Hz, O*H*), 2.79 (1H, dd, J = 13.2, 9.2 Hz, CH$_A$*H*$_B$Ph), 1.79 (1H, ddq, J = 13.6, 7.6, 4.4 Hz, CH(OH)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.52 (1H, m, CH(OH)C*H*(CH_3)CH_2CH_3), 1.22 (3H, d, J = 6.8 Hz, CH(OH)CH(C*H*$_3$)CH_2CH_3), 1.18 (1H, ddq, 13.6, 8.4, 7.2, CH(OH)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 0.91 (3H, dd, J = 7.6, 7.2 Hz, CH_2C*H*$_3$), 0.86 (3H, d, J = 6.8 Hz, C(=O)CH(C*H*$_3$)CHOH); **^{13}C NMR** (100 MHZ, $CDCl_3$) δ 178.2, 153.0, 135.2, 129.5, 129.1, 127.5, 74.9, 66.3, 55.2, 39.6, 37.9, 37.1, 25.3, 14.8, 11.0, 9.7; **IR** (KBr, cm^{-1}) 3499, 3090, 3064, 3032, 2969, 2940, 2903, 2882, 2854, 1947, 1797, 1686, 1606, 1583, 1488, 1500, 1457, 1384, 1356, 1303, 1244, 1212, 1136, 1121, 1097, 1077, 928, 831, 764, 735, 700, 640, 601, 573, 504, 471.



15

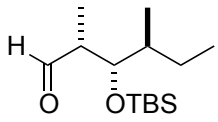
(4*R*)-4-Benzyl-3-{(2*R*,3*S*,4*S*)-3-[(*tert*-butyl)dimethylsilyloxy]-2,4-dimethylhexanoyl}oxazolidin-2-one (15). To a stirred solution of alcohol (**14**) (1.93 g; 6.06 mmol) in CH_2Cl_2 (60 mL) at -78 °C was added 2,6-lutidine (1.41 mL; 12.1 mmol) followed by TBSOTf (2.09 mL; 9.09 mmol). The resulting solution was stirred at -78 °C for 7 h before warming to 0 °C for 10 min. The reaction was quenched by addition of 5% $NaHCO_3$ (60 mL) and the mixture was extracted with CH_2Cl_2 (3 x 50 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (50% X4/CH_2Cl_2) gave TBS-ether (**15**) (2.54 g; 97%) as a white solid (enantiomer known[4]). **R*f*** = 0.34 (50%, X4/CH_2Cl_2); **mp.** 85-86 °C; **[α]$^{20}_D$** = -47.1 (c 1.11, $CHCl_3$); **^{1}H NMR** (400 MHZ, $CDCl_3$) δ 7.35-7.31 (2H, m, Ar*H*), 7.29-7.25 (1H, m, Ar*H*), 7.23-7.20 (2H, m, Ar*H*), 4.63 (1H, m, C*H*CH_2Ph), 4.17 (2H, d, J = 4.8Hz, OC*H*$_2$CHN), 3.98 (1H, m, C*H*OTBS), 3.96 (1H, dq, J = 6.6, 6.4 Hz, C(=O)C*H*(CH_3)CHOTBS), 3.27 (1H, dd, J = 13.2, 4.8 Hz, C*H*$_A$H$_B$Ph), 2.75 (1H, dd, J = 13.2, 9.6 Hz, CH$_A$*H*$_B$Ph), 1.52-1.43 (2H, m, CH(OTBS)CH(CH_3)C*H*$_A$H$_B$$CH_3$

and CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.23 (3H, d, J = 6.4 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 1.04-0.95 (1H, m, CH(OTBS)CH(CH_3)$CH_AH_BCH_3$), 0.93 (3H, d, J = 7.2 Hz, C(=O)CH(C*H*$_3$)CHOTBS), 0.92 (9H, s, OSiC(C*H*$_3$)$_3$), 0.87 (3H, dd, J = 7.2, 6.8 Hz, CH_2C*H*$_3$), 0.07 (3H, s, OSi(C*H*$_3$)CH_3), 0.04 (3H, s, OSi(CH_3)C*H*$_3$); **^{13}C NMR** (100 MHZ, $CDCl_3$) δ 176.3, 153.0, 135.5, 129.6, 129.1, 127.5, 76.3, 66.1, 55.8, 41.2, 40.9, 37.8, 26.2, 25.0, 18.5, 15.4, 14.1, 12.5, -3.8, -4.1; **IR** (KBr, cm^{-1}) 3520, 2963, 2930, 2883, 2858, 1957, 1767, 1700, 1491, 1458, 1393, 1364, 1312, 1294, 1274, 1228, 1253, 1210, 1179, 1154, 1104, 1072, 1055, 1023, 994, 968, 933, 910, 884, 838, 805, 776, 766, 702, 671, 588, 507.



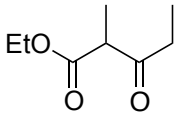
32

(2*S*,3*S*,4*S*)-3-[(*tert*-butyl)dimethylsilyloxy]-2,4-dimethylhexan-1-ol (33). To a stirred solution of oxazolidinone (**15**) (2.52 g; 5.81 mmol) in Et_2O (116 mL) at -10 °C was added EtOH (814 μL; 13.9 mmol) and LiBH4 (13.9 mL; 1 M in THF; 13.9 mmol). The resulting solution was stirred at -10 °C for 4 h, then quenched with 1 M NaOH (100 mL) and stirring continued at 0 °C for 15 min. The mixture was then poured into brine (60 mL), extracted with Et_2O (4 x 100 mL), dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (5% Et_2O/CH_2Cl_2) gave alcohol (**33**) (1.09 g; 72%) as a colourless oil (enantiomer known[4]). **R*f*** = 0.58 (5%, Et_2O/CH_2Cl_2); **[α]$^{20}_D$** = +3.33 (c 1.20, $CHCl_3$); **^{1}H NMR** (600 MHZ, $CDCl_3$) δ 3.62 (1H, dd, J = 5.4, 2.4 Hz, C*H*OTBS), 3.56 (1H, dd, J = 9.6, 9.0 Hz, CH_AH_BOH), 3.45 (1H, dd, J = 9.6, 6.0 Hz, CH_AH_BOH), 1.92 (1H, s, O*H*), 1.87 (1H, m, C*H*(CH_3)CH_2OH), 1.57-1.50 (2H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3) and CH(OTBS)CH(CH_3)C$H_AH_BCH_3$), 1.11-1.03 (1H, ddq, J = 14.4, 7.2, 3.0 Hz, CH(OTBS)CH(CH_3)$CH_AH_BCH_3$), 0.89 (9H, s, OSiC(C*H*$_3$)$_3$), 0.89 (3H, dd, J = 7.6, 7.2, Hz, CH_2C*H*$_3$), 0.88 (3H, d, J = 6.6 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 0.85 (3H, d, J = 7.2 Hz, CH(C*H*$_3$)CH_2OH), 0.06 ((3H, s, OSi(C*H*$_3$)CH_3), 0.05 (3H, s, OSi(CH_3)C*H*$_3$); **^{13}C NMR** (151 MHZ, $CDCl_3$) δ 76.8, 66.8, 39.4, 38.7, 26.2, 25.9, 18.5, 16.2, 12.2, 12.0, -3.9, -4.2; **IR** (film, cm^{-1}) 3341, 2959, 2931, 2858, 1467, 1383, 1254, 1100, 1036, 939, 898, 862, 835, 773, 672.



11

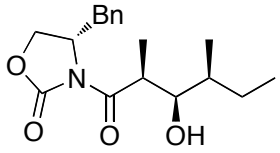
(2*R*,3*S*,4*S*)-3-[(*tert*-butyl)dimethylsilyloxy]-2,4-dimethylhexanal (11). To a stirred solution of DMSO (872 μL; 12.3 mmol) in CH_2Cl_2 (41 mL) at -78 °C was added oxalyl chloride (3.08 mL; 2M in CH_2Cl_2; 6.15 mmol) dropwise and the resulting solution stirred at -78 °C for 30 min. A solution of alcohol (**30**) (1.07 g; 4.10 mmol) in CH_2Cl_2 (10 mL) was added dropwise *via* cannula to the reaction mixture and the resulting solution was stirred at -78 °C for 45 min. Et_3N (3.43 mL; 24.6 mmol) was added dropwise and stirring was continued at -78 °C for 30 min before warming slowly to 0 °C for a further 30 min. The reaction was quenched by addition of sat. aq. NH_4Cl (80 mL) and the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracted were dried (Na_2SO_4) and concentrated in *vacuo*. Purification by column chromatography (100% CH_2Cl_2) gave aldehyde (**11**) (1.05 g; 99%) as a colourless oil (enantiomer known[4]). **R*f*** = 0.66 (100%, CH_2Cl_2); **$[\alpha]^{20}_D$** = -37.4 (c 2.03, CH_2Cl_2); **^{1}H NMR** (400 MHZ, $CDCl_3$) δ 9.72 (1H, d, J = 0.8 Hz, C*H*O), 4.00 (1H, dd, J = 5.6, 3.2 Hz, C*H*OTBS), 2.46 (1H, ddq, J = 7.2, 3.6, 1.2, CH(OTBS)C*H*(CH_3)CHO), 1.55 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.45 (1H, ddq, J = 13.2, 7.2, 3.6 Hz, CH(OTBS)CH(CH_3)C$H_A$$H_B$$CH_3$), 1.12-1.02 (1H, m, CH(OTBS)CH(CH_3)C$H_A$$H_B$$CH_3$), 1.09 (3H, d, J = 6.8 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 0.88 (3H, d, J = 6.8 Hz, CH(OTBS)CH(C*H*$_3$)CHO), 0.88 (3H, dd, J = 7.6, 7.2 Hz, CH_2CH_3), 0.86 (9H, s, OSiC(C*H*$_3$)$_3$), 0.05 (3H, s, OSi(C*H*$_3$)CH_3), -0.01 (3H, s, OSi(CH_3)CH_3); **^{13}C NMR** (100 MHZ, $CDCl_3$) δ 205.5, 75.0, 50.1, 31.0, 26.0, 25.3, 18.4, 15.6, 11.9, 8.8, -4.1, -4.1.



17

Ethyl 2-methyl-3-oxo-pentanoate (17). Sodium hydride (772 mg; 32.2 mmol) was added to ethyl propionate (10.0 mL; 86.9 mmol) with stirring and the mixture was slowly heated to 70 °C. When all the hydride had dissolved the mixture was heated at 70 °C for a further 18 h, before cooling to 0 °C. A few drops

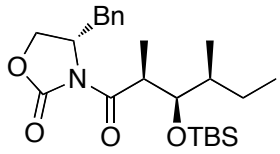
of EtOH were added to kill any remaining hydride and the reaction mixture was then poured into 1 M HCl (30 mL), extracted with Et_2O (3 x 50 mL) and washed with brine (50 mL). The organic phase was dried (Na_2SO_4) and concentrated in *vacuo* to give the crude β-ketoester as a yellow oil. Distillation under reduced pressure gave β-ketoester **17** (4.08 g; 30%) as a colourless oil. **bp.** 85-86 °C at 0.3 mmHg; **^{1}H NMR** (600 MHZ, $CDCl_3$) δ 4.17 (1H, q, J = 7.2 Hz, $CH_3CH_AH_BO$), 4.16 (1H, q, J = 7.2 Hz, $CH_3CH_AH_BO$), 3.51 (1H, q, J = 7.2 Hz, $C(=O)CH(CH_3)C=O$), 2.60 (1H, dq, J = 18.0, 7.2, $C(=O)CH_AH_BCH_3$), 2.51 (1H, dq, J = 18.0, 7.2, $C(=O)CH_AH_BCH_3$), 1.32 (3H, d, J = 7.2 Hz, $C(=O)CH(CH_3)C=O$), 1.25 (3H, t, J = 7.2 Hz, CH_3CH_2O), 1.06 (3H, t, J = 7.2 Hz, $C(=O)CH_2CH_3$); **^{13}C NMR** (151 MHZ, $CDCl_3$) δ 206.7, 170.8, 61.4, 34.8, 14.2, 13.0, 7.8.



(4*S*)-Benzyl-3-((2*S*,3*R*,4*S*)-3-hydroxy-2,4-dimethylhex-anoyl)oxazolidin-2-one (34).

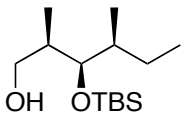
The previous procedure used for the preparation of **14** was followed with oxazolidinone *S*-(**12**) (1.73 mg; 7.42 mmol), Bu_2BOTf (8.90 mL; 1 M in CH_2Cl_2; 8.90 mmol), Et_3N (1.35 mL; 9.65 mmol), aldehyde (**13**) (1.26 g; 14.6 mmol) and CH_2Cl_2 (15 mL). Purification by column chromatography (5% Et_2O/CH_2Cl_2) gave aldol adduct (**34**) (2.01 g; 85%, > 98% ds) as a white solid (known compound[4,5]). **R*f*** = 0.29 (5% Et_2O/CH_2Cl_2); **mp.** 91-92 °C; **$[\alpha]^{20}_D$** = +38.4 (c 1.25, $CHCl_3$); **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.35-7.31 (2H, m, Ar*H*), 7.29-7.25 (1H, m, Ar*H*), 7.21-7.18 (2H, m, Ar*H*), 4.69 (1H, dddd, 9.6, 7.6, 3.6, 3.6, $CHCH_2Ph$), 4.22 (1H, dd, J = 9.2, 7.6 Hz, $OCH_AH_BCH_2N$), 4.18 (1H, dd, J = 8.8, 2.8 Hz, OCH_AH_BCHN), 3.98 (1H, dq, J = 6.8, 4.0 Hz, $C(=O)CH(CH_3)CHOH$), 3.69 (1H, ddd, J = 7.2, 4.0, 3.6 Hz, *CH*OH), 3.25 (1H, dd, J = 13.6, 3.6 Hz, CH_AH_BPh), 2.78 (1H, dd, J = 13.6, 9.6 Hz, CH_AH_BPh), 2.67 (1H, d, J = 4.4 Hz, O*H*), 1.56-1.41 (1H, m, $CH(OH)CH(CH_3)CH_AH_BCH_3$), 1.56-1.41 (1H, m, $CH(OH)CH(CH_3)CH_2CH_3$), 1.26 (3H, d, J = 7.2 Hz, $CH(OH)CH(CH_3)CH_2CH_3$), 1.20-1.08 (1H, ddq, J = 8.8, 7.2, 5.2, $CH(OH)CH(CH_3)CH_AH_BCH_3$), 0.97 (3H, d, J = 6.4 Hz, $C(=O)CH(CH_3)CHOH$), 0.90 (3H, dd, J = 7.6, 7.2 Hz, CH_2CH_3); **^{13}C NMR** (100MHz, $CDCl_3$) δ 177.7, 153.0, 135.2,

129.5, 129.1, 127.5, 75.1, 66.2, 55.2, 40.0, 37.8, 37.3, 25.7, 14.7, 11.3, 11.3; **IR** (KBr, cm^{-1}) 3525, 3066, 3028, 2964, 2934, 2878, 1779, 1692, 1603, 1490, 1457, 1383, 1353, 1288, 1241, 1201, 1140, 1111, 1076, 1049, 1015, 993, 971, 931, 918, 858, 837, 790, 764, 751, 724, 644, 624, 617, 574, 506.



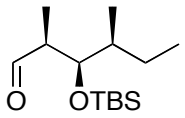
(4R)-4-Benzyl-3-{(2*S*,3*R*,4*S*)-3-[(*tert*-butyl)dimethylsilyloxy]-2,4-dimethylhexanoyl}oxazolidin-2-one (35).

The previous procedure used for the preparation of **15** was followed with alcohol (**34**) (1.99 g; 6.23 mmol), 2,6-lutidine (1.45 mL; 12.5 mmol), TBSOTf (2.15 mL; 9.35 mmol) and CH_2Cl_2 (62 mL). Purification by column chromatography (50% x4/CH_2Cl_2) gave TBS-ether (**35**) (2.46 g; 91%) as a white solid (known compound[4]). **R*f*** = 0.38 (50%, X4/CH_2Cl_2); **mp.** 72-73 °C; **$[\alpha]^{20}_D$** = +44.6 (c 1.17, $CHCl_3$); **^{1}H NMR** (400MHz, $CDCl_3$) δ 7.35-7.31 (2H, m, Ar*H*), 7.29-7.25 (1H, m, Ar*H*), 7.23-7.20 (2H, m, Ar*H*), 4.64 (1H, m, C*H*CH_2Ph), 4.18 (2H, m, OC*H*$_2$CHCH_2N), 4.00 (1H, dd, J = 7.6, 2.8 Hz, C*H*OTBS), 3.98 (1H, dq, J = 7.2, 6.8 Hz, C(=O)C*H*(CH_3)CHOTBS), 3.26 (1H, dd, J = 13.2, 4.8 Hz, CH_AH$_B$Ph), 2.76 (1H, dd, J = 13.2, 9.6 Hz, CH$_A$*H*$_B$Ph), 1.57-1.48 (1H, m, CH(OTBS)CH(CH_3)CH_AH$_B$$CH_3$), 1.41-1.34 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.24 (3H, d, J = 6.8 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 1.22-1.10 (1H, m, CH(OTBS)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 0.92 (9H, s, OSiC(C*H*$_3$)$_3$), 0.89 (3H, dd, J = 7.6, 7.2 Hz, CH_2C*H*$_3$), 0.84 (3H, d, J = 6.8 Hz, C(=O)CH(C*H*$_3$)CHOTBS), 0.08 (3H, s, OSi(C*H*$_3$)CH_3), 0.07 (3H, s, OSi(CH_3)C*H*$_3$); **^{13}C NMR** (100MHz, $CDCl_3$) δ 176.4, 153.0, 135.4, 129.6, 129.1, 127.5, 76.1, 66.0, 55.6, 41.8, 40.8, 37.8, 26.6, 26.3, 18.6, 15.1, 14.2, 12.5, -3.6, -3.8; **IR** (KBr, cm^{-1}) 3519, 2963, 2858, 1767, 1700, 1493, 1458, 1394, 1363, 1332, 1290, 1252, 1211, 1179, 1129, 1072, 1024, 993, 970, 934, 881, 836, 812, 772, 702, 690, 673, 588, 545, 495.



(2*R*,3*R*,4*S*)-3-[(*tert*-butyl)dimethylsilyloxy]-2,4-dimethylhexan-1-ol (36).

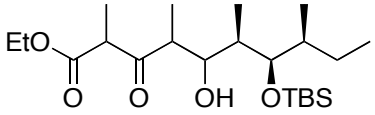
The previous procedure used for the preparation of **27** was followed with oxazolidinone (**35**) (2.43 g; 5.61 mmol), EtOH (786 μL; 13.5 mmol), $LiBH_4$ (13.5 mL; 1 M in THF; 13.5 mmol) and Et_2O (112 mL). Purification by column chromatography (5% Et_2O/CH_2Cl_2) gave alcohol (**36**) (956 mg; 66%) as a colourless oil (known compound[4]). **R*f*** = 0.56 (5%, Et_2O/CH_2Cl_2); **[α]$^{20}_D$** = -3.64 (c 1.10, $CHCl_3$); **^{1}H NMR** (600MHz, $CDCl_3$) δ 3.63 (1H, dd, J = 3.6, 3.6 Hz, C*H*OTBS), 3.63 (1H, m, CH_AH_BOH), 3.46 (1H, m, CH_AH_BOH), 2.25 (1H, s, O*H*), 1.93 (1H, dddq, J = 9.0, 8.4, 6.0, 3.0 Hz, CH(OTBS)C*H*(CH_3)CH_2OH), 1.54-1.48 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.44 (1H, ddq, J = 13.2, 6.6, 4.2 Hz, CH(OTBS)CH(CH_3)C$H_AH_B$$CH_3$), 1.15 (1H, ddq, J = 13.2, 8.4, 7.2 Hz, CH(OTBS)CH(CH_3)C$H_AH_B$$CH_3$), 0.90 (3H, d, J = 6.6 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 0.89 (9H, s, OSiC(C*H*$_3$)$_3$), 0.87 (3H, dd, J = 7.8, 7.2 Hz, CH_2CH_3), 0.84 (3H, d, J = 7.2 Hz, CH(OTBS)CH(C*H*$_3$)CH_2OH), 0.07 (3H, s, OSi(C*H*$_3$)CH_3), 0.05 (3H, s, OSi(CH_3)CH_3); **^{13}C NMR** (151MHz, $CDCl_3$) δ 77.4, 66.6, 39.7, 38.1, 27.5, 26.2, 18.4, 15.5, 12.7, 12.4, -4.0, -4.1; **IR** (film, cm^{-1}) 3346, 2959, 2858, 1466, 1384, 1360, 1253, 1100, 1035, 939, 898, 836, 809, 773, 673.



(2*S*,3*R*,4*S*)-3-[(*tert*-butyl)dimethylsilyloxy]-2,4-dimethylhexanal (16).

The previous procedure used for the preparation of **11** was followed with alcohol (**36**) (519 mg; 1.99 mmol), DMSO (424 μL; 5.98 mmol), oxalyl chloride (1.49 mL; 2M in CH_2Cl_2; 2.99 mmol), Et_3N (1.67 mL; 9.60 mmol) and CH_2Cl_2 (20 mL). Purification by column chromatography (100% CH_2Cl_2) gave aldehyde (**16**) (514 mg; 99%) as a colourless oil (known compound[4]). **R*f*** = 0.80 (100%, CH_2Cl_2); **[α]$^{20}_D$** = +49.1 (c 1.63, CH_2Cl_2); **^{1}H NMR** (600MHz, $CDCl_3$) δ 9.79 (1H, d, J = 0.6 Hz, C*H*O), 3.97 (1H, dd, J = 4.8, 4.2 Hz, C*H*OTBS), 2.49 (1H, ddq, J = 7.2, 4.8, 1.2 Hz, CH(OTBS)C*H*(CH_3)CHO), 1.51-1.44 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.45 (1H, ddq, J = 13.2, 7.2, 4.2 Hz, CH(OTBS)CH(CH_3)C$H_AH_B$$CH_3$), 1.13 (1H, ddq, J = 13.2,

9.0, 7.8 Hz, CH(OTBS)CH(CH_3)$CH_AH_BCH_3$), 1.05 (3H, d, J = 7.2 Hz, CH(OTBS)CH(CH_3)CH_2CH_3), 0.87 (3H, dd, J = 7.8, 7.2 Hz, CH_2CH_3), 0.87 (9H, s, OSiC(CH_3)$_3$), 0.82 (3H, d, J = 6.6 Hz, CH(OTBS)CH(CH_3)CHO), 0.05 (3H, s, OSi(C*H*$_3$)CH_3), 0.01 (3H, s, OSi(CH_3)CH_3); **^{13}C NMR** (151MHz, $CDCl_3$) δ 205.5, 75.3, 50.9, 39.1, 26.6, 26.0, 18.3, 14.5, 12.2, 9.4, -4.0, -4.2.

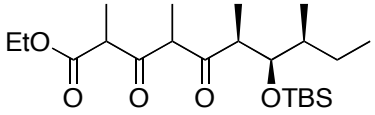


Ethyl (6*R*,7*R*,8*S*)-7-[(*tert*-butyl)dimethylsilyloxy]-5-hydroxy-2,4,6,8-tetramethyl-3-oxodecanoate (37).

The previous procedure for the preparation of **18** was used with β-ketoester (**17**) (358 mg; 2.26 mmol), NaH (94.9 mg; 3.96 mmol), *n*-BuLi (1.41 mL; 1.6 M in hexanes; 2.26 mmol), aldehyde (**16**) (293 mg; 1.13 mmol) and THF (11 mL). The crude product was filtered through a plug of buffered silica (100% CH_2Cl_2) to give a complex mixture of isomers of alcohol (**37**) (463 mg; 98%) as a clear oil.

^{1}H NMR (600MHz, $CDCl_3$) δ 4.16-4.10 (2H, m, CH_3C*H*$_2$O), 4.04 (0.25H, m, C*H*OTBS), 3.91-3.85 (0.75H, m, C*H*OTBS), 3.80-3.77 (0.25H, C*H*OH), 3.78, 3.73, 3.67, 3.63, (4 x 0.25H, q, J = 7.2 Hz, CH_3CH_2OC(=O)C*H*(CH_3)C=O), 3.59 (0.25H, dd, J = 4.2, 3.6 Hz, C*H*OH), 3.56 (0.25H, dd, J = 4.2, 3.6 Hz, C*H*OH), 3.54 (0.25H, dd, J = 4.2, 3.6 Hz, C*H*OH), 2.97, 2.95, 2.81, 2.79 (4 x 0.25H, dq, J = 7.2, 6.6 Hz, C(=O)C*H*(CH_3)CHOH), 1.71-1.65 (0.25H, m, C(OH)C*H*(CH_3)CHOTBS), 1.60-1.37 (2.75H, m, C(OH)C*H*(CH_3)CHOTBS, C*H*(CH_3)CH_2CH_3 and CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.30-1.27 (3H, m, CH_3CH_2OC(=O)CH(C*H*$_3$)C(=O)), 1.24-1.20 (3H, m, C*H*$_3$$CH_2$O), 1.16 (1H, d, J = 6.6 Hz, C(=O)CH(*CH*$_3$)CHOH), 1.08-0.99 (3.25H, m, C(=O)CH(*CH*$_3$)CHOH and CH(CH_3)CH_A*H*$_B$$CH_3$), 0.94 (0.75H, d, J = 6.6 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 0.91-0.78 (15.5H, CH(OTBS)CH(C*H*$_3$)CH_2CH_3, OSiC(C*H*$_3$)$_3$, CH(OH)CH(C*H*$_3$)CHOTBS) and CH(CH_3)CH_2C*H*$_3$), 0.76 (0.75H, d, J = 7.2 Hz, CH(OH)CH(C*H*$_3$)CHOTBS), 0.73 (0.75H, d, J = 7.2 Hz, CH(OH)CH(C*H*$_3$)CHOTBS), 0.07-0.02 (6H, m, OSi(C*H*$_3$)$_2$), (OH not assigned); **^{13}C NMR** (151MHz, $CDCl_3$) δ 211.5, 211.3, 211.2, 210.0, 209.5, 206.6, 205.5, 170.9, 170.8, 170.5, 170.4, 170.20, 170.17, 104.7, 85.4, 83.3, 79.20, 79.18, 78.9, 78.4, 78.0, 77.0, 75.54, 75.47, 75.3, 74.9, 74.6, 72.4, 71.6, 61.5, 61.50, 61.46, 61.40,

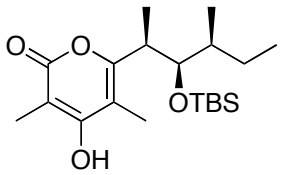
61.36, 61.35, 54.1, 53.6, 53.5, 52.7, 51.8, 51.7, 50.9, 50.7, 50.4, 50.0, 49.8, 49.7, 49.2, 49.1, 48.98, 48.96, 48.0, 47.9, 47.5, 47.4, 44.1, 44.0, 40.3, 40.2, 40.1, 39.9, 39.8, 39.6, 39.3, 38.9, 38.60, 38.58, 38.52, 38.2, 37.9, 37.8, 37.5, 37.4, 37.1, 36.5, 34.7, 34.4, 33.7, 32.0, 30.4, 29.8, 27.3, 26.23, 26.19, 26.16, 26.14, 26.10, 26.0, 25.93, 25.90, 25.83, 25.80, 25.76, 25.72, 25.50, 25.45, 25.3, 23.3, 22.31, 22.30, 18.51, 18.49, 18.43, 18.40, 18.37, 18.31, 18.29, 15.9, 15.82, 15.81, 15.76, 15.0, 14.9, 14.71, 14.65, 14.14, 14.13, 13.9, 13.6, 13.23, 13.20, 13.19, 13.04, 13.01, 12.94, 12.89, 12.69, 12.68, 12.66, 12.61, 12.58, 12.3, 12.23, 12.15, 12.09, 12.07, 12.00, 11.7, 11.6, 11.2, 9.6, 9.5, 9.3, 8.00, 7.96, 7.75, 7.71, 7.5, 7.4, -3.4, -3.7, -3.9, -4.0, -4.13, -4.15, -4.17, -4.19, -4.20, -4.29, -4.33; **IR** (film, cm^{-1}) 3479, 2959, 2858, 1727, 1462, 1381, 1254, 1058, 1025, 836, 811, 774, 675.



Ethyl (6*S*,7*R*,8*S*)-7-[(*tert*-butyl)dimethylsilyloxy]-2,4,6,8-tetramethyl-3,5-dioxodecanoate (38).

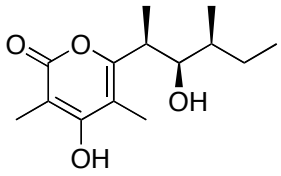
The previous procedure for the preparation of **19** was used with alcohol (**37**) (762 mg; 1.83 mmol), DMP (1.16 g; 2.74 mmol), CH_2Cl_2 (18 mL) and CH_2Cl_2 (sat., 12 x 1.72 mL). The crude residue was filtered through buffered silica (100% CH_2Cl_2) to afford tricarbonyl (**38**) (758 mg; 100%) as a clear oil. **^{1}H NMR** (600MHz, $CDCl_3$) δ 4.20-4.10 (2.25H, m, CH_3CH_2O and C(=O)C*H*(CH_3)C(=O)CH(CH_3)CHOTBS), 4.09, 4.04, 4.03 (3 x 0.25H, q, J = 7.2 Hz, C(=O)C*H*(CH_3)C(=O)CH(CH_3)CHOTBS), 3.93 (0.25 H, dd, J = 6.0, 2.4 Hz, C*H*OTBS), 3.92 (0.25 H, dd, J = 6.6, 2.4 Hz, C*H*OTBS), 3.86 (0.25 H, dd, J = 7.2, 2.4 Hz, C*H*OTBS), 3.83 (0.25 H, dd, J = 7.2 2.4 Hz, C*H*OTBS), 3.27 (0.25H, q, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C(=O)$), 3.72 (0.25H, q, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C(=O)$), 3.64 (0.25H, q, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C(=O)$), 3.62 (0.25H, q, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C(=O)$), 2.91 (0.5H, dq, J = 7.2, 6.6 Hz, C(=O)C*H*(CH_3)CHOTBS), 2.86 (0.25H, dq, J = 7.2, 6.6 Hz, C(=O)C*H*(CH_3)CHOTBS), 2.82 (0.25H, dq, J = 7.2, 7.2 Hz, C(=O)C*H*(CH_3)CHOTBS), 1.55-1.36 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.34-1.27 (4.5H, $CH_3CH_2OC(=O)CH(CH_3)C(=O)$ and

C(=O)CH(*CH*$_3$)C(=O)CH(CH$_3$)CHOTBS), 1.26-1.16 (5.5H, C(=O)CH(*CH*$_3$)C(=O)CH(CH$_3$)CHOTBS, C*H*$_3$CH$_2$O and CH(CH$_3$)C*H*$_A$H$_B$CH$_3$), 1.13 (0.75H, d, J = 6.6Hz, CH(OTBS)CH(C*H*$_3$)CH$_2$CH$_3$), 1.12-1.00 (1H, m, CH(CH$_3$)CH$_A$*H*$_B$CH$_3$), 1.06 (0.75H, d, J = 6.6Hz, CH(OTBS)CH(C*H*$_3$)CH$_2$CH$_3$), 1.05 (0.75H, d, J = 7.2 Hz, CH(OTBS)CH(C*H*$_3$)CH$_2$CH$_3$) 1.04 (0.75H, d, J = 7.2Hz, CH(OTBS)CH(C*H*$_3$)CH$_2$CH$_3$), 0.89-0.80 (12.75H, m, CH(CH$_3$)CH$_2$C*H*$_3$, OSiC(C*H*$_3$)$_3$ and C(=O)CH(C*H*$_3$)CHOTBS), 0.79 (0.75H, d, J = 7.2 Hz, C(=O)CH(C*H*$_3$)CHOTBS), 0.78 (0.75H, d, J = 6.6 Hz, C(=O)CH(C*H*$_3$)CHOTBS), 0.75 (0.75H, d, J = 6.6 Hz, C(=O)CH(C*H*$_3$)CHOTBS), 0.06- -0.01 (6H, s, OSi(C*H*$_3$)$_2$); **^{13}C NMR** (151MHz, CDCl$_3$) δ 210.9, 210.6, 209.32, 209.26, 203.40, 203.36, 202.3, 202.2, 194.7, 194.5, 193.3, 192.6, 171.0, 170.7, 170.08, 170.05, 76.6, 76.50, 76.47, 75.8, 75.5, 74.9, 61.68, 61.64, 61.58, 61.33, 61.31, 61.28, 59.8, 59.33, 59.27, 57.9, 52.7, 52.4, 51.6, 51.2, 50.9, 50.4, 49.9, 49.8, 49.5, 49.1, 46.3, 46.1, 44.1, 43.6, 42.1, 41.9, 40.9, 40.4, 40.22, 40.19, 40.11, 40.06, 40.00, 37.9, 37.5, 37.2, 35.9, 34.7, 34.5, 33.8, 32.0, 29.79, 29.75, 29.5, 27.22, 27.19, 27.11, 27.03, 27.01, 26.24, 26.22, 26.19, 26.17, 25.52, 25.46, 25.35, 23.3, 22.8, 22.3, 19.4, 18.59, 18.54, 18.53, 18.51, 18.50, 17.8, 16.0, 16.0, 14.92, 14.88, 14.84, 14.6, 14.21, 14.17, 14.15, 14.12, 14.11, 13.98, 13.95, 13.86, 13.83, 13.80, 13.7, 13.62, 13.57, 13.37, 13.31, 13.13, 13.11, 13.05, 12.9, 12.8, 12.6, 12.34, 12.31, 12.29, 12.28, 7.77, 7.72, 7.5, -3.66, -3.68, -3.70, -3.73, -3.87 -3.89, -3.91; **IR** (film, cm^{-1}) 3467, 2931, 2857, 1734, 1611, 1460, 1378, 1303, 1254, 1192, 1113, 1063, 1030, 1005, 938, 861, 836, 809, 775, 674.



6-[(1*S*,2*R*,3*S*)-2-[(*tert*-butyl)dimethylsilyloxy]-1,3-dimethylpentyl]-4-hydroxy-3,5-dimethyl-2H-pyran-2-one (39).

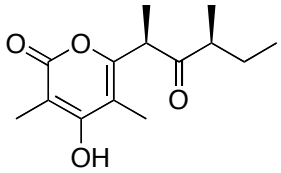
The previous procedure for the preparation of **20** was used with tricarbonyl (**38**) (361 mg; 872 μmol), DBU (65 μL; 436 μmol) and benzene (9 mL). The residue was triturated with hexanes to give α-pyrone (**39**) (173 mg; 54%) as white needles. **R*f*** = 0.29 (10% Et_2O/CH_2Cl_2); **mp.** 196-198 °C; **$[\alpha]^{20}_D$** = +140.9 (c 0.66, MeOH); **^{1}H NMR** (600MHz, $CDCl_3$) δ 7.65 (1H, br s, O*H*), 3.91 (1H, dd, J = 9.0, 1.2 Hz, C*H*OTBS), 2.96 (1H, dq, J = 9.0, 6.6Hz, C(-O-)C*H*(CH_3)CHOTBS), 1.99 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.99 (3H, s, C(OH)C(C*H*$_3$)=C(-O-)), 1.44-1.37 (1H, m, CH(OTBS)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.23-1.17 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.21 (3H, d, J = 6.6 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 1.13-1.05 (1H, m, CH(OTBS)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 0.90 (9H, s, OSiC(C*H*$_3$)$_3$), 0.81 (3H, dd, J = 7.8, 7.2 Hz, CH_2C*H*$_3$), 0.73 (3H, d, J = 6.6 Hz, CH(OTBS)C*H*(CH_3)CH_2CH_3), 0.07 (3H, s, OSi(C*H*$_3$)CH_3), 0.05 (3H, s, OSi(CH_3)C*H*$_3$); **^{13}C NMR** (151Mz, $CDCl_3$) δ 166.1, 165.0, 161.3, 106.6, 98.2, 77.3, 39.8, 39.1, 26.9, 26.3, 18.6, 17.2, 13.5, 12.6, 10.0, 8.8, -3.5, -3.5; **IR** (KBr, cm^{-1}) 2960, 2933, 2883, 2859, 1680, 1657, 1574, 1537, 1462, 1405, 1381, 1360, 1344, 1256, 1215, 1177, 1153, 1125, 1064, 1082, 1039, 959, 936, 853, 837, 807, 777, 758, 695, 671, 621, 515, 473.



6-[(1*S*,2*R*,3*S*)-2-hydroxy-1,3-dimethylpentyl]-4-hydroxy-3,5-dimethyl-2H-pyran-2-one (40).

The previous procedure for the preparation of **21** was used with TBS-ether (**39**) (255 mg; 692 μmol), 40% aq. HF (1.10 mL) and 1:1 CH_3CN/CH_2Cl_2 (36 mL). The product with triturated with acetone to give alcohol (**40**) (175 mg; 99%) as a white foam. **R*f*** = 0.43 (100%, EtOAc); **$[\alpha]^{20}_D$** = +98.0 (c 1.25, MeOH); **^{1}H NMR**

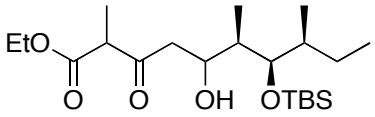
(600MHz, CD_3OD) δ 5.05 (1H, br s, C(CH_3)=C(OH)C*H*=C(-O-)), 3.78 (1H, dd, J = 9.6, 2.4 Hz, C*H*OH), 3.02 (1H, dq, J = 9.6, 7.2 Hz, C(-O-)C*H*(CH_3)CHOH), 2.00 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.91 (3H, s, C(OH)C(C*H*$_3$)=C(-O-)), 1.41 (1H, ddq, J = 13.8, 7.2, 6.0 Hz, CH(OH)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.29 (3H, d, J = 7.2 Hz, CH(OH)CH(C*H*$_3$)CH_2CH_3), 1.29-1.20 (1H, m, CH(OH)C*H*(CH_3)CH_2CH_3), 1.11 (1H, ddq, J = 13.8, 7.2, 1.8 Hz, CH(OH)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 0.85 (3H, dd, J = 7.8, 7.2 Hz, CH_2C*H*$_3$), 0.80 (3H, d, J = 7.2 Hz, C(-O-)CH(C*H*$_3$)CHOH), **^{13}C NMR** (151Mz, CD_3OD) δ 168.3, 168.0, 161.7, 109.3, 98.8, 76.1, 39.7, 39.0, 28.3, 16.4, 13.1, 12.3, 10.1, 8.8; **IR** (KBr, cm^{-1}) 3333, 2966, 2932, 2878, 1671, 1568, 1458, 1410, 1380, 1230, 1145, 1086, 1032, 994, 956, 872, 760, 737, 704.



6-[(1*R*,3*S*)-1,3-dimethyl-2-oxopentyl]-4-hydroxy-3,5-dimethyl-2H-pyran-2-one (23).

The previous procedure for the preparation of **22** was used with alcohol (**40**) (168 mg; 659 μmol), Jones reagent (1.15 mL) and acetone (17 mL). The crude product was triturated with hexanes to remove impurities, giving 6-[(1*R*,3*S*)-1,3-dimethyl-2-oxopentyl]-4-hydroxy-3,5-dimethyl-2H-pyran-2-one **(23)** (104 mg; 63%) as colourless plates. **R*f*** = 0.52 (100% EtOAc); **mp.** 168-170 °C; **[α]$^{20}_D$** = -4.67 (c 1.07, MeOH); **^{1}H NMR** (600MHz, $CDCl_3$) δ 8.74 (1H, br s, O*H*), 3.90 (1H, q, J = 7.2 Hz, C(-O-)C*H*(CH_3)C=O), 2.54 (1H, ddq, J = 13.8, 7.2, 6.6 Hz, C(=O)C*H*(CH_3)CH_2CH_3), 2.02 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.99 (3H, s, C(OH)C(C*H*$_3$)=C(-O-)), 1.65 (1H, ddq, J = 13.8, 7.8, 7.2 Hz, C(=O)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.39 (3H, d, J = 7.2 Hz, C(=O)CH(C*H*$_3$)CH_2CH_3), 1.20 (1H, ddq, J = 13.8, 7.2, 6.0 Hz, C(=O)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 1.02 (3H, d, J = 7.2 Hz, C(-O-)CH(C*H*$_3$)C=O), 0.76 (3H, dd, J = 7.8, 7.2 Hz, CH_2CH_3); **^{13}C NMR** (151Mz, $CDCl_3$) δ 210.6, 166.0, 165.2, 155.7, 109.4, 99.4, 47.5, 45.6, 25.9, 17.6, 13.6, 11.9, 10.1, 8.8; **IR** (KBr, cm^{-1}) 3188, 2934, 2964, 2876, 1727, 1680, 1636, 1575, 1455, 1428, 1379, 1340, 1250, 1207, 1174, 1128, 1078, 1041, 1001, 969, 870, 850, 751,

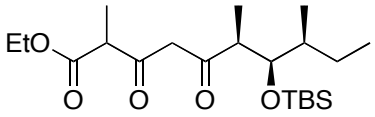
713, 670, 642, 581, 479; **HRESIMS** calculated for $C_{14}H_{20}O_4Na^+$: 275.1254; found: 274.1266.



Ethyl (6*R*,7*R*,8*S*)-7-[(*tert*-butyl)dimethylsilyloxy]-5-hydroxy-2,6,8-trimethyl-3-oxodecanoate (41).

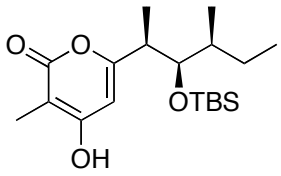
The previous procedure for the preparation of **18** was used with β-ketoester (**24**) (242 μL; 1.71 mmol), NaH (72.0 mg; 3.00 mmol), *n*-BuLi (1.07 mL; 1.6 M in hexanes; 1.71 mmol), aldehyde (**16**) (222 mg; 857 μmol) and THF (8.6 mL). The crude product was filtered through a plug of buffered silica (100% CH_2Cl_2) to give a complex mixture of isomers of alcohol (**41**) (341 mg; 99%) as a yellow oil. **^{1}H NMR** (600MHz, $CDCl_3$) δ 4.17-4.12 (2H, m, CH_3CH_2O), 4.10-4.06 (0.5H, m, CHOTBS), 3.97-3.94 (0.5H, m, CHOTBS), 3.79 (0.5H, ddd, J = 4.2, 4.2, 3.0 Hz, CHOH), 3.62 (0.5H, dd, J = 4.8, 3.6 Hz, CHOH), 3.57, 3.55, 3.51, 3.50 (4 x 0.25H, q, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C=O$), 2.75-2.70 (1H, m, $C(=O)CH_AH_BCHOH$), 2.65-2.58 (0.5H, m, $C(=O)CH_AH_BCHOH$), 2.57 (0.25H, dd, J = 16.8, 8.4 Hz, $C(=O)CH_AH_BCHOH$), 2.53 (0.25H, dd, J = 16.8, 9.0 Hz, $C(=O)CH_AH_BCHOH$), 1.73-1.66 (0.5H, m, $CH(OH)CH(CH_3)CHOTBS$), 1.62-1.57 (0.5H, m, $CH(OH)CH(CH_3)CHOTBS$), 1.55-1.37 (2H, m, $CH(CH_3)CH_2CH_3$ and $CH(CH_3)CH_AH_BCH_3$), 1.31 (1.5H, d, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C=O$), 1.29 (1.5H, d, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C=O$), 1.23 (1H, t, J = 7.2 Hz, CH_3CH_2O), 1.23 (2H, t, J = 7.2 Hz, CH_3CH_2O), 1.11-1.04 (1H, m, $CH(CH_3)CH_AH_BCH_3$), 0.89 (0.75H, d, J = 6.6 Hz, $C(=O)CH(CH_3)CHOTBS$), 0.88 (1.5H, d, J = 7.2 Hz, $C(=O)CH(CH_3)CHOTBS$), 0.87-0.82 (12.75H, m, $C(=O)CH(CH_3)CHOTBS$, $OSiC(CH_3)_3$ and $CH(CH_3)CH_2CH_3$), 0.80 (1.5H, d, J = 6.6 Hz, $CH(OH)CH(CH_3)CHOTBS$), 0.75 (0.75H, d, J = 6.6 Hz, $CH(OH)CH(CH_3)CHOTBS$), 0.75 (0.75H, d, J = 6.6 Hz, $CH(OH)CH(CH_3)CHOTBS$), 0.06 (1H, s, $OSi(CH_3)_2$), 0.05 (1H, s, $OSi(CH_3)_2$), 0.03 (2H, s, $OSi(CH_3)_2$), -0.02 (2H, s, $OSi(CH_3)_2$), (OH not assigned); **^{13}C NMR** (151MHz, $CDCl_3$) δ 206.93, 206.85, 206.81, 206.7, 170.5, 170.44, 170.37, 170.28, 77.5, 77.4, 76.6, 70.2, 70.0, 69.6, 69.3, 61.53, 61.51, 61.47, 61.43, 53.8, 53.47, 53.44, 51.7, 46.9, 46.8, 46.50, 46.47, 42.0, 41.8, 40.8, 40.7,

39.62, 39.57, 38.40, 38.36, 37.7, 34.6, 31.6, 31.0, 29.8, 27.2, 27.1, 26.3, 26.22, 26.18, 26.14, 26.12, 26.10, 23.33, 23.30, 22.3, 18.5, 18.4, 15.65, 15.64, 14.56, 14.51, 14.1, 12.7, 12.60, 12.59, 12.5, 12.12, 12.07, 12.04, 10.3, 10.2, -3.5, -3.99, -4.02, -4.09, -4.13; **IR** (film, cm^{-1}) 3494, 2929, 1726, 1463, 1379, 1253, 1189, 1058, 939, 835, 810, 774, 734, 673.



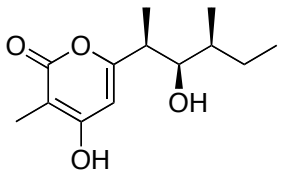
Ethyl (6*S*,7*R*,8*S*)-7-[(*tert*-butyl)dimethylsilyloxy]-2,6,8-trimethyl-3,5-dioxodecanoate (42).

The previous procedure for the preparation of **19** was used with alcohol (**41**) (524 mg; 1.30 mmol), DMP (827 mg; 1.95 mmol), CH_2Cl_2 (13 mL) and CH_2Cl_2 (sat., 12 x 2.17 mL). The crude residue was filtered through buffered silica (100% CH_2Cl_2) to afford tricarbonyl (**42**) (473 mg; 91%) as a yellow oil. **(enol tautomer) ^{1}H NMR** (600MHz, $CDCl_3$) δ 5.58 (0.5H, s, C(OH)=C*H*C=O), 5.57 (0.5H, s, C(=O)=C*H*COH), 4.18-4.12 (2H, m, CH_3CH_2O), 3.79 (1H, dd, J = 6.0, 3.0 Hz, C*H*OTBS), 3.36 (2 x 0.5H, q, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C=O$), 2.49-2.43 (1H, m, C(=O)C*H*(CH_3)CHOTBS), 1.46-1.37 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.36 (2 x 1.5H, d, J = 7.2 Hz, $CH_3CH_2OC(=O)CH(CH_3)C=O$), 1.27-1.20 (1H, m, $CH(CH_3)CH_AH_BCH_3$), 1.23 (3H, t, J = 7.2 Hz, CH_3CH_2O), 1.16-1.06 (1H, m, $CH(CH_3)CH_AH_BCH_3$), 1.12 (3H, d, J = 7.2 Hz, $CH(CH_3)CH_2CH_3$), 0.90-0.81 (15H, m, $OSiC(CH_3)_3$, C(=O)CH(CH_3)CHOTBS and $CH(CH_3)CH_2CH_3$), 0.02 (3H, s, $OSi(CH_3)CH_3$), -0.02 (3H, s, $OSi(CH_3)CH_3$), (enol OH not assigned); **^{13}C NMR** (151MHz, $CDCl_3$) δ 194.74, 194.65, 193.4, 193.3, 170.9, 98.5, 98.2, 76.83, 76.80, 61.4, 53.5, 49.8, 49.7, 45.8, 39.7, 26.2, 18.5, 14.3, 14.23, 14.18, 14.16, 14.08, 14.03, 13.97, 13.86, 12.2, -3.74, -3.75, -3.94, -4.95; **IR** (film, cm^{-1}) 2927, 1738, 1608, 1463, 1378, 1254, 1061, 939, 837, 774, 735, 672.



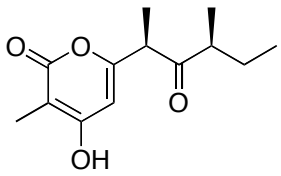
6-[(1*S*,2*R*,3*S*)-2-[(*tert*-butyl)dimethylsilyloxy]-1,3-dimethylpentyl]-4-hydroxy-3-methyl-2H-pyran-2-one (43) and 6-[(1*R*,2*R*,3*S*)-2-[(*tert*-butyl)dimethylsilyloxy]-1,3-dimethylpentyl]-4-hydroxy-3-methyl-2H-pyran-2-one (44).

The previous procedure for the preparation of **20** was used with tricarbonyl (**42**) (381 mg; 952 μmol), DBU (71 μL; 476 μmol) and benzene (9.5 mL). The residue was triturated with hexanes to give a 73:27 mixture of α-pyrones (**43**) and (**44**) (93.1 mg; 28%) as yellow needles. **R*f*** = 0.29 (10% Et_2O/CH_2Cl_2); **mp.** 166-168 °C; **$[\alpha]^{20}_D$** = -47.1 (c 0.79, MeOH); **^{1}H NMR** (600MHz, $CDCl_3$) **major isomer:** δ 7.93 (1H, br s, O*H*), 5.99 (1H, s, CH(OH)C*H*=C(-O-)), 3.84 (1H, dd, J = 6.0, 3.6 Hz, C*H*OTBS), 2.68 (1H, dq, J = 7.2, 6.6 Hz, C(-O-)C*H*(CH_3)CHOTBS), 1.96 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.50-1.42 (1H, m, CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.40-1.34 (1H, m, CH(OTBS)C*H*(CH_3)CH_2CH_3), 1.20 (3H, d, J = 6.6 Hz, CH(OTBS)CH(C*H*$_3$)CH_2CH_3), 1.19-1.10 (1H, m, CH(CH_3)CH$_A$*H*$_B$$CH_3$), 0.87 (9H, s, OSiC(C*H*$_3$)$_3$), 0.85 (3H, t, J = 7.2 Hz, CH_2C*H*$_3$), 0.81 (3H, d, J = 6.6 Hz, C(-O-)CH(C*H*$_3$)CHOTBS), 0.02 (3H, s, OSi(C*H*$_3$)CH_3), -0.08 (3H, s, OSi(CH_3)C*H*$_3$); **minor isomer:** δ 7.93 (1H, br s, OH), 6.01 (1H, s, CH(OH)CH=C(-O-), 3.87 (1H, dd, J = 7.8, 2.4 Hz, CHOTBS), 2.71-2.66 (1H, m, C(-O-)CH(CH_3)CHOTBS), 1.96 (3H, s, C(=O)C(CH_3)=COH), 1.50-1.42 (1H, m, CH(CH_3)CH$_A$H$_B$$CH_3$), 1.40-1.34 (1H, m, CH(OTBS)CH(CH_3)CH_2CH_3), 1.25 (3H, d, J = 7.2 Hz, CH(OTBS)CH(CH_3)CH_2CH_3), 1.19-1.10 (1H, m, CH(CH_3)CH$_A$H$_B$$CH_3$), 1.14 (3H, d, J = 7.2 Hz, C(-O-)CH(CH_3)CHOTBS), 0.86 (3H, t, J = 7.2 Hz, CH_2CH_3) 0.82 (9H, s, OSiC(CH_3)$_3$), 0.01 (3H, s, OSi(CH_3)CH_3), -0.25 (3H, s, OSi(CH_3)CH_3); **^{13}C NMR** (151Mz, $CDCl_3$) **major isomer:** δ 166.1, 165.1, 100.1, 98.8, 76.8, 42.3, 39.7, 31.1, 26.5, 26.2, 18.5, 14.7, 14.3, 12.3, 8.3, -3.6, -4.1; **minor isomer:** δ 167.1, 166.0, 101.8, 99.0, 76.4, 43.9, 38.0, 29.9, 27.2, 26.2, 18.4, 15.6, 13.0, 12.5, 8.3, -3.8, -4.7; **IR** (KBr, cm^{-1}) 3155, 2963, 2931, 2889, 2858, 2702, 1655, 1590, 1457, 1408, 1369, 1294, 1255, 1155, 1124, 1065, 1043, 1021, 969, 937, 884, 861, 835, 774, 753, 675, 642, 536.



6-[(1*S*,2*R*,3*S*)-2-hydroxy-1,3-dimethylpentyl]-4-hydroxy-3-methyl-2H-pyran-2-one (45) and 6-[(1*R*,2*R*,3*S*)-2-hydroxy-1,3-dimethylpentyl]-4-hydroxy-3-methyl-2H-pyran-2-one (46).

The previous procedure for the preparation of **21** was used with TBS-ether (**43**) (91.8 mg; 259 μmol), 40% aq. HF (1.10 mL) and 1:1 CH_3CN/CH_2Cl_2 (13 mL). The product with triturated with acetone to give alcohol (**45**) (as a mixture with its C7 epimer **46**) (54.8 mg; 88%) as a white powder. **R*f*** = 0.51 (100%, EtOAc); **mp.** 159-161 °C; **$[\alpha]^{20}_D$** = +7.41 (c 2.30, MeOH); **^{1}H NMR** (600MHz, CD_3OD) **major isomer:** δ 6.08 (1H, s, C(OH)C*H*=C(-O-)), 5.22 (1H, br s, $C(CH_3)$=C(OH)C*H*=C(-O-)), 3.65 (1H, dd, J = 7.8, 3.6 Hz, C*H*OH), 2.71 (1H, dq, J = 7.8, 7.2 Hz, C(-O-)C*H*(CH_3)CHOH), 1.85 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.50-1.40 (1H, m, CH(OH)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.34-1.28 (1H, m, CH(OH)C*H*(CH_3)CH_2CH_3), 1.28 (1H, s, CHO*H*), 1.27 (3H, d, J = 6.6 Hz, CH(OH)CH(C*H*$_3$)CH_2CH_3), 1.26-1.20 (1H, m, CH(OH)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 0.89 (3H, d, J = 6.6 Hz, C(-O-)CH(C*H*$_3$)CHOH), 0.88 (3H, dd, J = 7.8, 7.2 Hz, CH_2CH_3); **minor isomer:** δ 6.06 (1H, s, C(OH)C*H*=C(-O-)), 5.22 (1H, br s, $C(CH_3)$=C(OH)C*H*=C(-O-)), 3.70 (1H, dd, J = 9.0, 5.4 Hz, C*H*OH), 2.68 (1H, dq, J = 9.6, 7.2 Hz, C(-O-)C*H*(CH_3)CHOH), 1.85 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.55 (1H, ddq, J = 13.8, 6.6, 3.0 Hz, CH(OH)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.34-1.28 (1H, m, CH(OH)C*H*(CH_3)CH_2CH_3), 1.26-1.20 (1H, m, CH(OH)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 1.15 (3H, d, J = 7.2 Hz, CH(OH)CH(C*H*$_3$)CH_2CH_3), 0.94 (3H, dd, J = 7.8, 7.2 Hz, CH_2CH_3) 0.87 (3H, d, J = 6.6 Hz, C(-O-)CH(C*H*$_3$)CHOH); **^{13}C NMR** (151Mz, $CDCl_3$) **major isomer:** δ 168.9, 167.8, 166.9, 101.3, 99.1, 76.2, 43.0, 38.9, 27.7, 14.9, 13.5, 11.9, 8.3; **minor isomer:** δ 169.3, 168.0, 167.1, 102.0, 99.1, 75.6, 43.8, 37.6, 28.0, 15.9, 12.3, 12.2, 8.3; **IR** (KBr, cm^{-1}) 3143, 2969, 2926, 2878, 2710, 1679, 1656, 1591, 1463, 1416, 1380, 1234, 1179, 1144, 1122, 1101, 1077, 1047, 980, 958, 935, 833, 818, 748, 717, 696, 636, 578, 534, 501.



6-[(1*R*,3*S*)-1,3-dimethyl-2-oxopentyl]-4-hydroxy-3-methyl-2H-pyran-2-one (29).

The previous procedure for the preparation of **25** was used with alcohol (**45**) (45.9 mg; 191 μmol), Jones reagent (330 μL) and acetone (5 mL). The crude product was triturated with hexanes to remove impurities, giving 6-[(1*R*,3*S*)-1,3-dimethyl-2-oxopentyl]-4-hydroxy-3-methyl-2H-pyran-2-one (**29**) (23.3 mg; 51%) as a yellow powder. **R*f*** = 0.57 (100% EtOAc); **mp.** 113-115 °C; **$[\alpha]^{20}_{D}$** = -48.9 (c 1.17, MeOH); **^{1}H NMR** (600MHz, $CDCl_3$) **major isomer:** δ 9.70 (1H, br s, C(=O)C(CH_3)=CO*H*), 6.22 (1H, s, C(OH)C*H*=C(-O-)), 3.82 (1H, q, J = 7.2 Hz, C(-O-)C*H*(CH_3)C=O), 2.69 (1H, ddq, J = 13.8, 7.2, 6.6 Hz, C(=O)C*H*(CH_3)CH_2CH_3), 1.95 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.68 (1H, ddq, J = 13.8, 7.2, 7.2 Hz, C(=O)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.37 (3H, d, J = 7.2 Hz, C(=O)CH(C*H*$_3$)CH_2CH_3), 1.35 (1H, ddq, J = 13.8, 7.2, 6.6 Hz, C(=O)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 1.08 (3H, d, J = 6.6 Hz, C(-O-)CH(C*H*$_3$)C=O), 0.81 (3H, dd, J = 7.8, 7.2 Hz, CH_2C*H*$_3$); **minor isomer:** δ 9.70 (1H, br s, C(=O)C(CH_3)=CO*H*), 6.20 (1H, s, C(OH)C*H*=C(-O-)), 3.78 (1H, q, J = 7.2 Hz, C(-O-)C*H*(CH_3)C=O), 2.73-2.67 (1H, m, C(=O)C*H*(CH_3)CH_2CH_3), 1.95 (3H, s, C(=O)C(C*H*$_3$)=COH), 1.70-1.59 (1H, m, C(=O)CH(CH_3)C*H*$_A$H$_B$$CH_3$), 1.43-1.35 (1H, m, C(=O)CH(CH_3)CH$_A$*H*$_B$$CH_3$), 1.35 (3H, d, J = 7.2 Hz, C(=O)CH(C*H*$_3$)CH_2CH_3), 1.06 (3H, d, J = 6.6 Hz, C(-O-)CH(CH_3)C=O), 0.86 (3H, dd, J = 7.8, 7.2 Hz, CH_2C*H*$_3$); **^{13}C NMR** (151Mz, $CDCl_3$) **major isomer:** δ 211.5, 167.8, 166.4, 160.6, 101.8, 99.9, 49.1, 47.0, 25.8, 16.5, 14.6, 11.7, 8.3; **minor isomer:** δ 211.6, 167.8, 166.4, 160.8, 101.7, 99.9, 49.5, 47.1, 26.2, 16.0, 14.4, 11.7, 8.3; **IR** (KBr, cm^{-1}) 3410, 3106, 2971, 2934, 2879, 2664, 1713, 1665, 1634, 1578, 1561, 1457, 1272, 1242, 1179, 1141, 1097, 1056, 1035, 995, 950, 936, 869, 757, 616, 565, 531; **HRESIMS** calculated for $C_{13}H_{18}O_4Na^+$: 261.1097; found: 261.1114.

References:

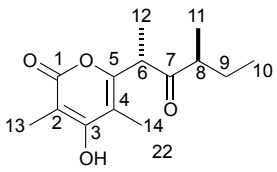
(1) Perrin, D. D., Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3 ed.; Pergamon Press: Oxford, 1988.
(2) Suffert, J. *J. Org. Chem.* **1989**, *54*, 509.
(3) Rychnovsky, S. D.; Richardson, T. I.; Rogers, B. N. *J. Org. Chem.* **1997,** *62,* 2925.
(4) Kinoshita, K.; Khosla, C.; Cane, D. E. *Helv. Chim. Acta* **2003**, *86*, 3889.
(5) Dias, L. C.; Meira, P. R. R. *J. Org. Chem.* **2005**, *70*, 4762.

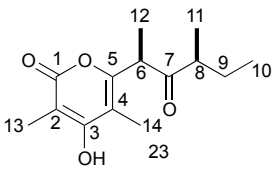
Table 1 X-ray crystallographic data for compounds **22** and **23**

Compound reference	Compound **22**	Compound **23**
Chemical formula	$C_{14}H_{20}O_4$	$C_{14}H_{20}O_4$
Formula Mass	252.30	252.30
Crystal system	Orthorhombic	Orthorhombic
a/Å	8.8972(2)	8.1642(3)
b/Å	12.2375(3)	12.0184(5)
c/Å	12.7413(3)	14.2772(5)
α/°	90.00	90.00
β/°	90.00	90.00
γ/°	90.00	90.00
Unit cell volume/Å^3	1387.27(6)	1400.89(9)
Temperature/K	150(2)	150(2)
Space group	*P*212121	*P*212121
No. of formula units per unit cell, *Z*	4	4
No. of reflections measured	13678	10454
No. of independent reflections	3664	3600
R_{int}	0.0272	0.0219
Final R_1 values ($I > 2\sigma(I)$)	0.0451	0.0374
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1149	0.0907
Final R_1 values (all data)	0.0640	0.0487
Final $wR(F^2)$ values (all data)	0.1196	0.0935

Supplementary Information for "Total Synthesis and Structural Elucidation of *ent*-Micropyrone and (+)-Ascosalipyrone by Claire Gregg and Michael V. Perkins*

Table 1. Comparison of the ^{1}H and ^{13}C NMR data for micropyrone (**1**) and synthetic isomers **22** and **23**.





C no.	micropyrone[a]		isomer **22**[b]			isomer **23**[b]		
	δH (m, *J*[Hz])[c]	δC[c]	δH (m, *J*[Hz])[c]	δC[c]	Δδ[d]	δH (m, *J*[Hz])[c]	δC[c]	Δδ[d]
1		166.2		166.3	-0.1		166.2	0.0
2		99.5		99.4	0.1		99.3	0.2
3		155.7		155.7	0.0		155.5	0.2
4		109.5		109.5	0.0		109.5	0.0
5		165.6		165.6	0.0		165.5	0.1
6	3.84 (q, 6.9)	48.2	3.83 (q, 7.2)	48.2	0.0	3.9 (q, 7.2)	47.2	1.0
7		210.5		210.7	-0.2		210.5	0.0
8	2.58 (m)	45.3	2.58 (qdd, 7.2, 6.6, 6.6)	45.3	0.0	2.54 (qdd, 7.2, 7.2, 6.6)	45.5	-0.2
9a	1.60 (m)	26.9	1.59 (dqd, 13.8, 7.2, 6.6)	26.9	0.0	1.65 (dqd, 13.8, 7.2, 7.2)	25.7	1.2
9b	1.34 (m)		1.34 (m)			1.28 (dqd, 13.8, 7.2, 6.6)		
10	0.81 (t, 6.7)	11.5	0.81 (t, 7.2)	11.6	-0.1	0.75 (t, 7.2)	11.7	-0.2
11	1.36 (d, 6.7)	16.1	1.36 (d, 7.2)	16.1	0.0	1.39 (d, 7.2)	17.4	-1.3
12	0.99 (d, 6.7)	13.3	0.98 (d, 7.2)	13.4	-0.1	1.02 (d, 7.2)	13.4	-0.1
13	2.02 (s)	8.7	2.02 (s)	8.7	0.0	2.02 (s)	8.7	0.0
14	2.00 (s)	9.9	1.99 (s)	9.9	0.0	1.99 (s)	10.0	-0.1
OH	-		8.84 (br s)			8.74 (br s)		

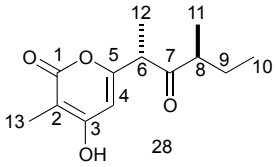
a Chemical shifts and coupling constants (400 MHz) as reported in Appendino, G., Ottino, M., Marquez, N., Bianchi, F., Giana, A., Ballero. M., Sterner, O., Fiebich, B. L., Munoz, E. *J. Nat. Prod.* **2007,** *70*, 608-612.

b Bruker 600 MHz NMR Spectrometer ($CDCl_3$). Assignments assisted by ^{1}H-^{13}C HMBC, ^{1}H-^{13}C HMQC, ^{1}H-^{1}H COSY, ^{1}H-^{1}H TOCSY.

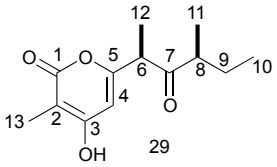
c Chemical shifts in ppm referenced to $CHCl_3$ at 7.26 ppm and to $CDCl_3$ at 77.00 ppm (for comparison the natural product).

d. This is the difference in the ^{13}C chemical shift of the isomer and that reported for the natural product.

Table 2. Comparison of the ^{1}H and ^{13}C NMR data for ascosalipyrone (**2**) and synthetic isomers **28** and **29**.



28



29

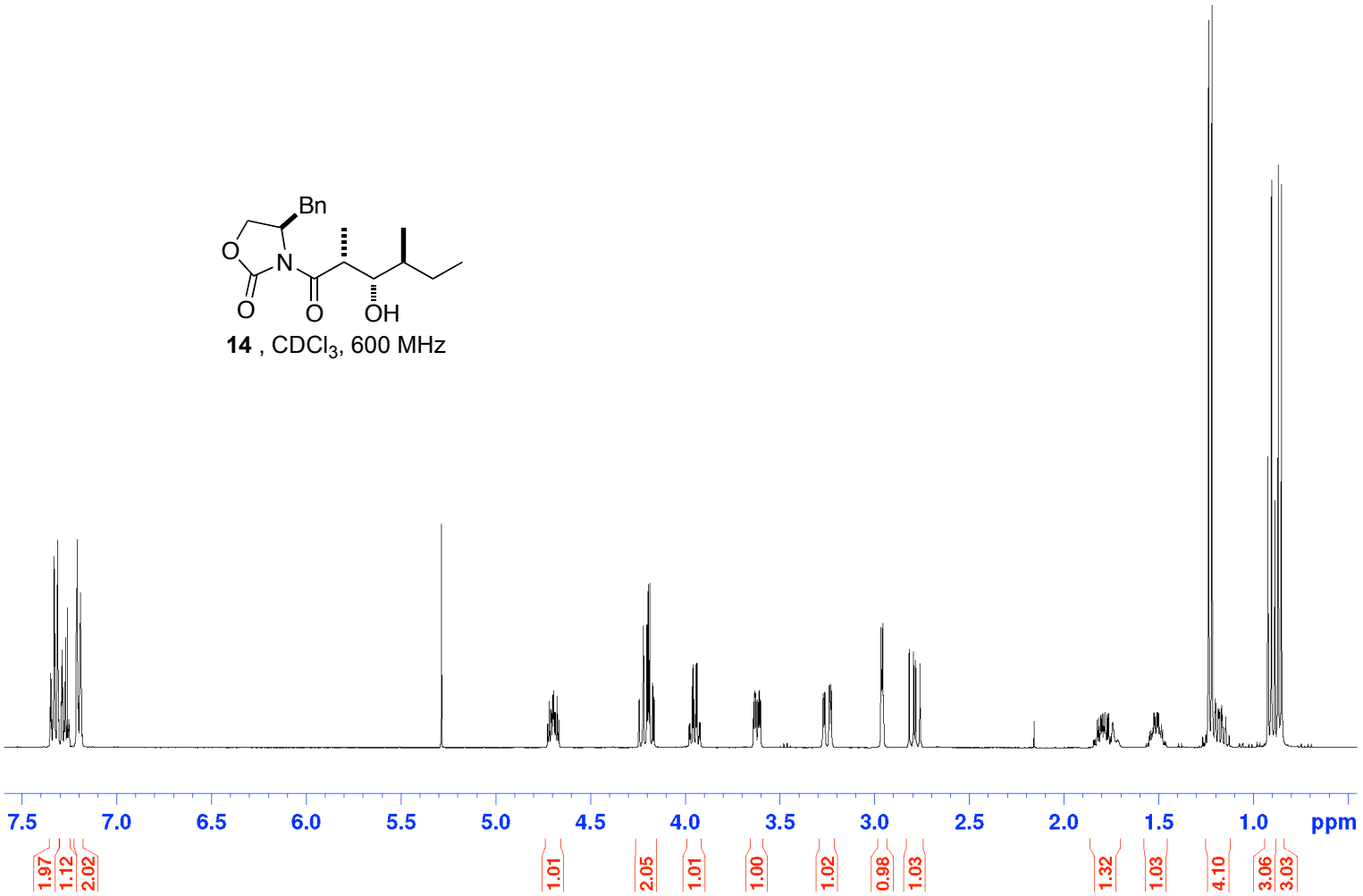
C no.	ascosalipyrone[a]		isomer **28**[b]			isomer **29**[b]		
	δH (m, *J*[Hz])[c]	δC[c]	δH (m, *J*[Hz])[c]	δC[c]	Δδ[d]	δH (m, *J*[Hz])[c]	δC[c]	Δδ[d]
1		167.6		167.6	0.0		167.6	0.0
2		99.8		99.7	0.1		99.7	0.1
3		166.2		166.3	-0.1		166.3	-0.1
4	6.21 (s)	101.6	6.25 (s)	101.6	0.0	6.22 (s)	101.7	-0.1
5		160.7		160.7	0.0		160.5	0.2
6	3.77 (q, 7.0)	49.3	3.80 (q, 7.2)	49.2	0.1	3.82 (q, 7.2)	49.0	0.3
7		211.5		211.5	0.0		211.4	0.2
8	2.68 (m)	47.1	2.70 (dqd, 7.5, 7.2, 6.6)	47.0	0.1	2.69 (dqd, 7.2, 7.2, 6.6)	46.9	0.2
9a	1.69 (m)	26.1	1.67 (dqd, 13.8, 7.5, 6.6)	26.0	0.1	1.68 (dqd, 13.8, 7.5, 7.2)	25.6	0.5
9b	1.38 (m)		1.38 (m)			1.35 (dqd, 13.8, 7.5, 6.6)		
10	0.82 (t, 7.3)	11.6	0.85 (t, 7.5)	11.6	0.0	0.81 (t, 7.5)	11.5	0.1
11	1.38 (d, 7.2)	15.9	1.36 (d, 7.2)	15.9	0.1	1.37 (d, 7.2)	16.3	-0.4
12	1.05 (d, 7.0)	14.4	1.05 (d, 6.6)	14.3	0.1	1.07 (d, 6.6)	14.4	0.0
13	1.94 (s)	8.2	1.94 (s)	8.2	0.0	1.94 (s)	8.2	0.0
OH	9.7 (br s)		9.91 (br s)			9.69 (br s)		

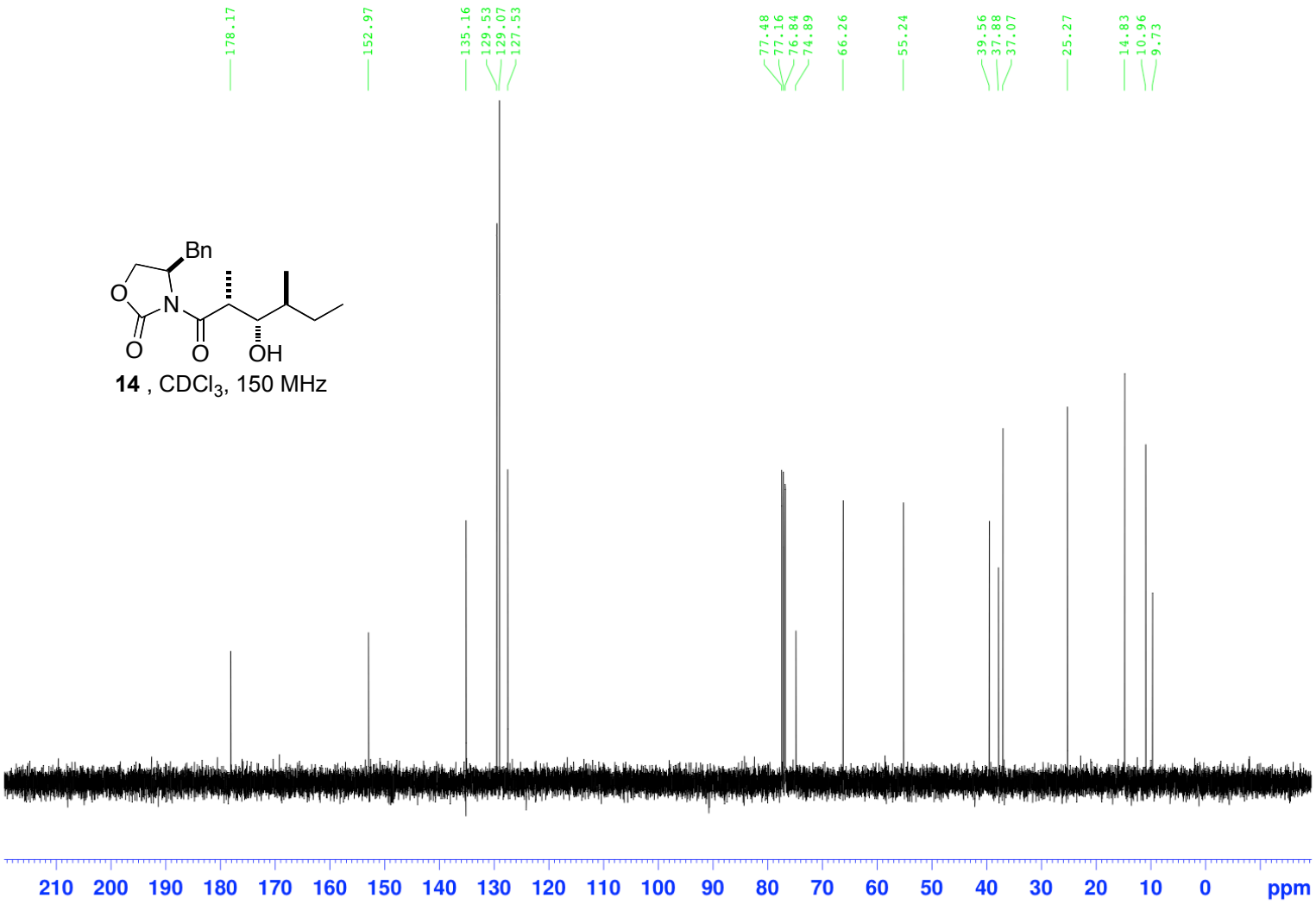
a Chemical shifts and coupling constants (300 MHz) as reported in Osterhage, C., Kaminsky, R., König, G. M., Wright, A. D. *J. Org. Chem.* **2000,** *65*, 6412-6417.

b Bruker 600 MHz NMR Spectrometer ($CDCl_3$). Assignments assisted by ^{1}H-^{13}C HMBC, ^{1}H-^{13}C HMQC, ^{1}H-^{1}H COSY, ^{1}H-^{1}H TOCSY.

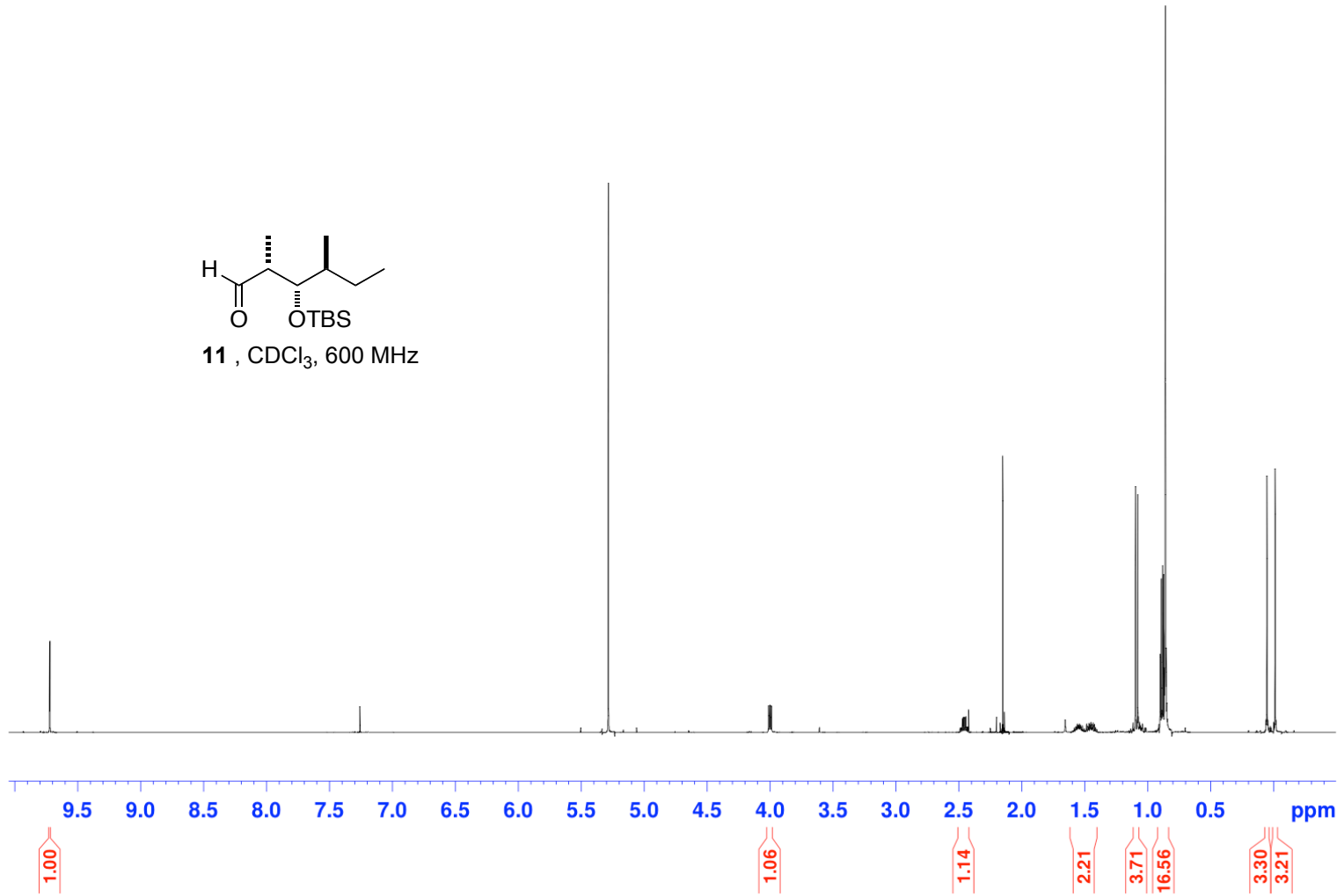
c Chemical shifts in ppm referenced to $CHCl_3$ at 7.26 ppm and to $CDCl_3$ at 77.00 ppm (for comparison the natural product).

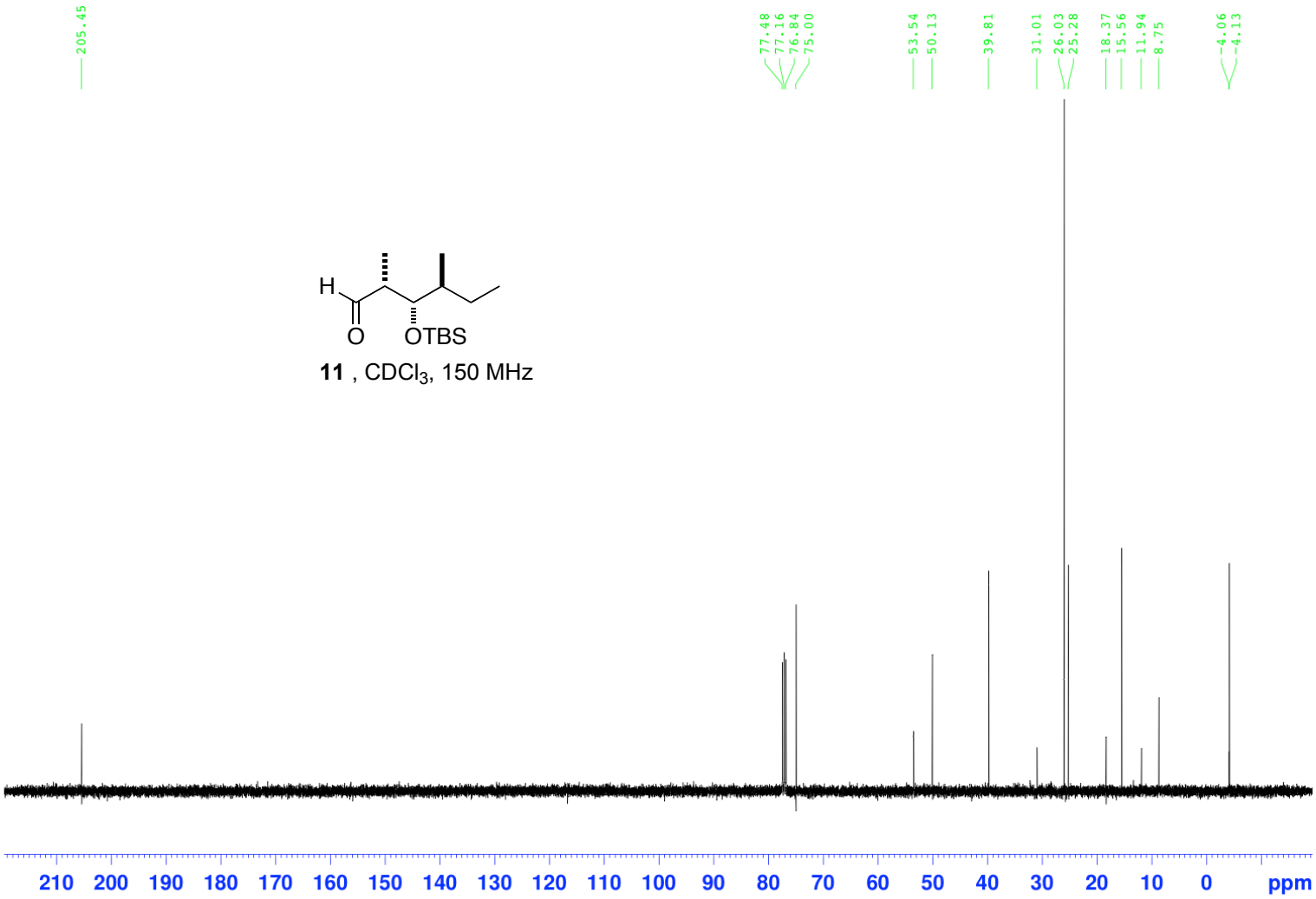
d. The difference in the ^{13}C chemical shift of the isomer and that reported for the natural product.



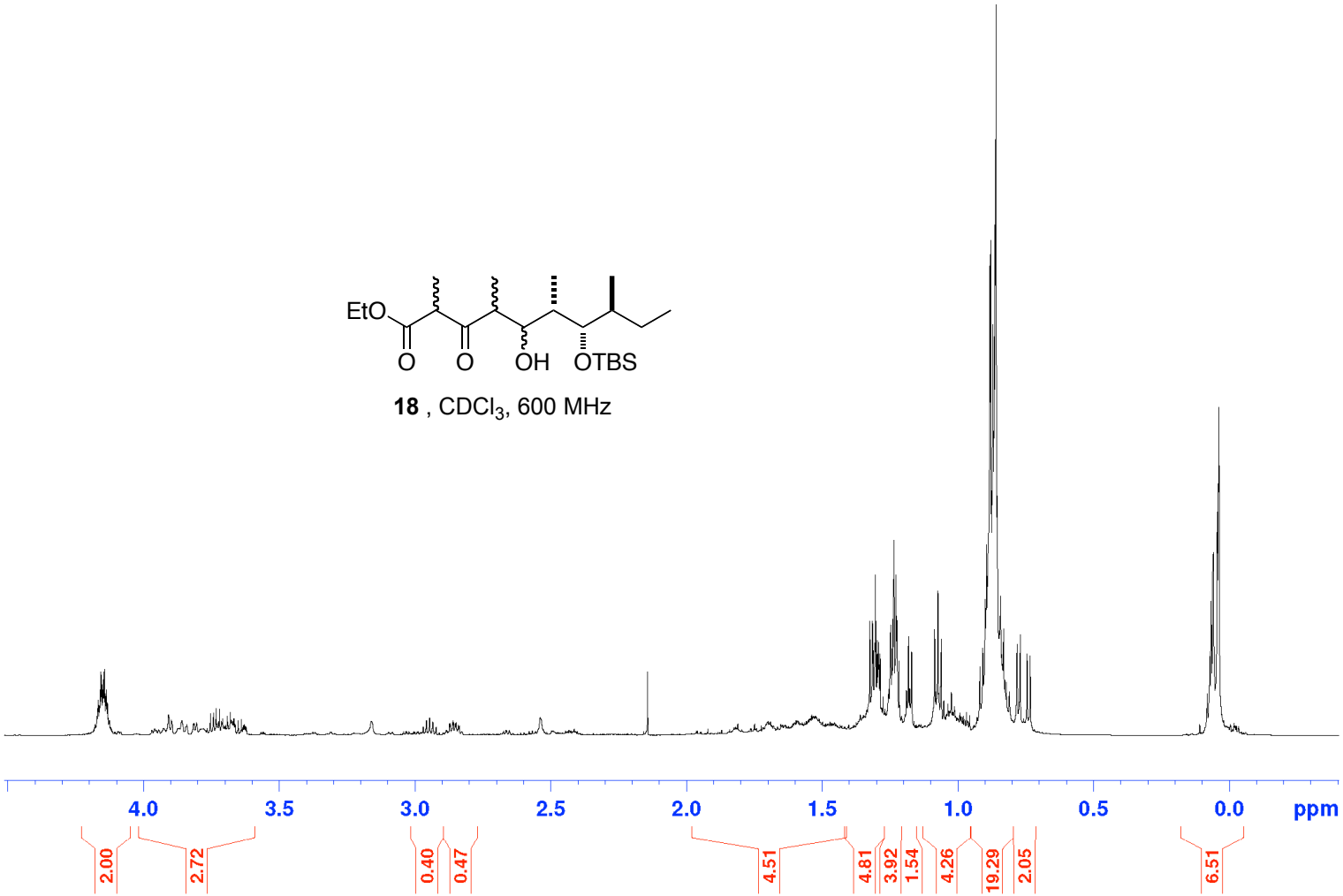


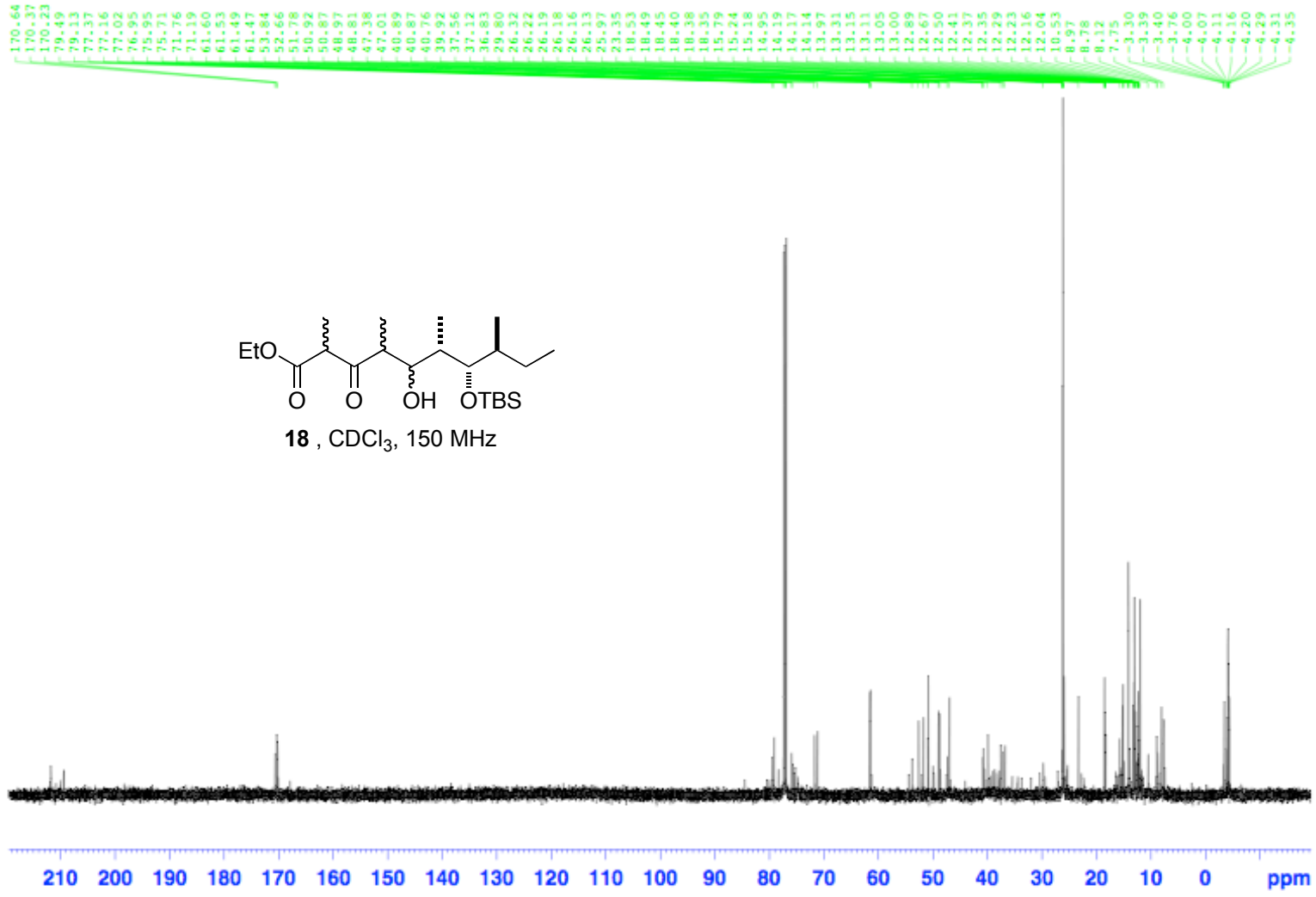
14 , $CDCl_3$, 150 MHz

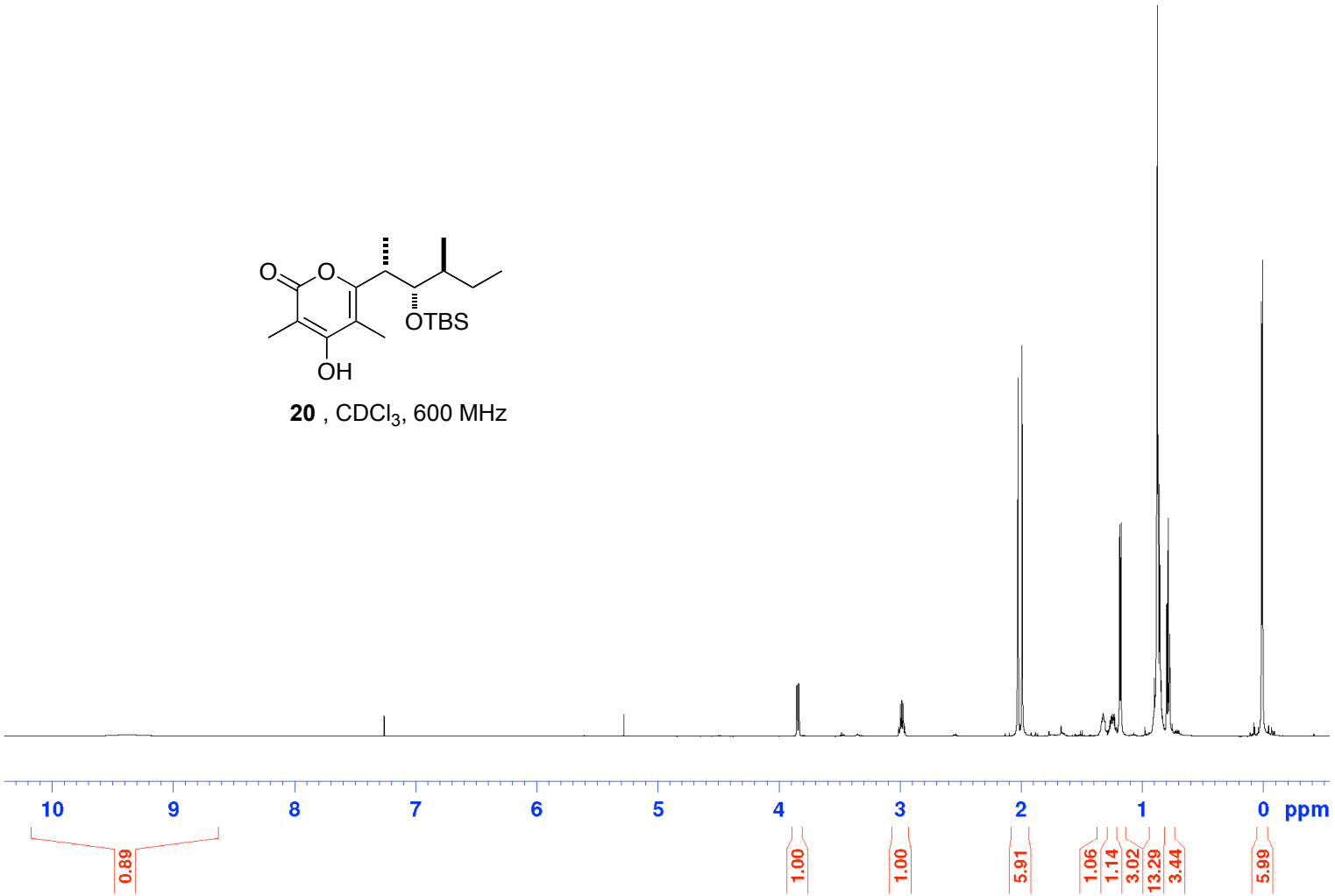




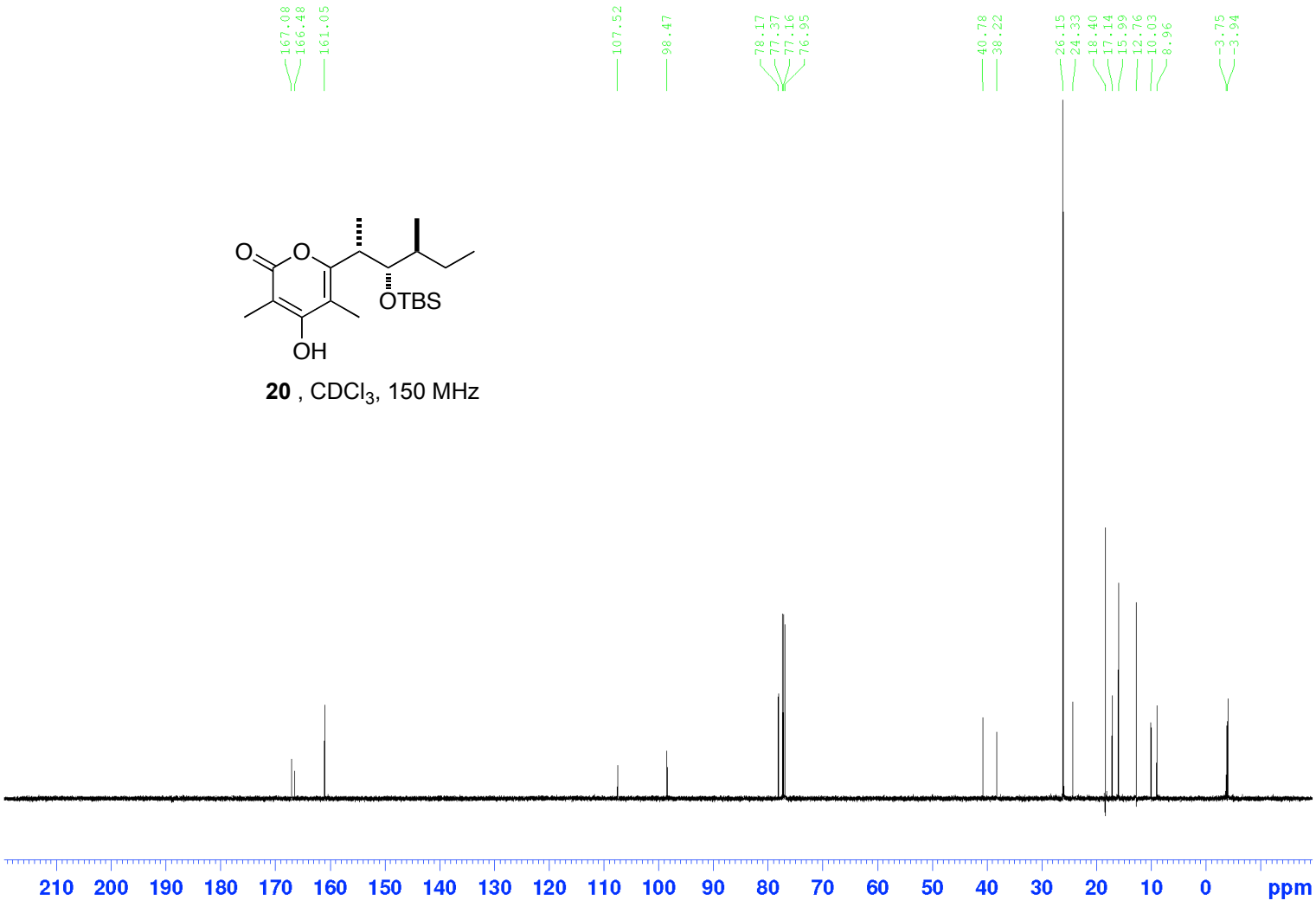
11 , $CDCl_3$, 150 MHz



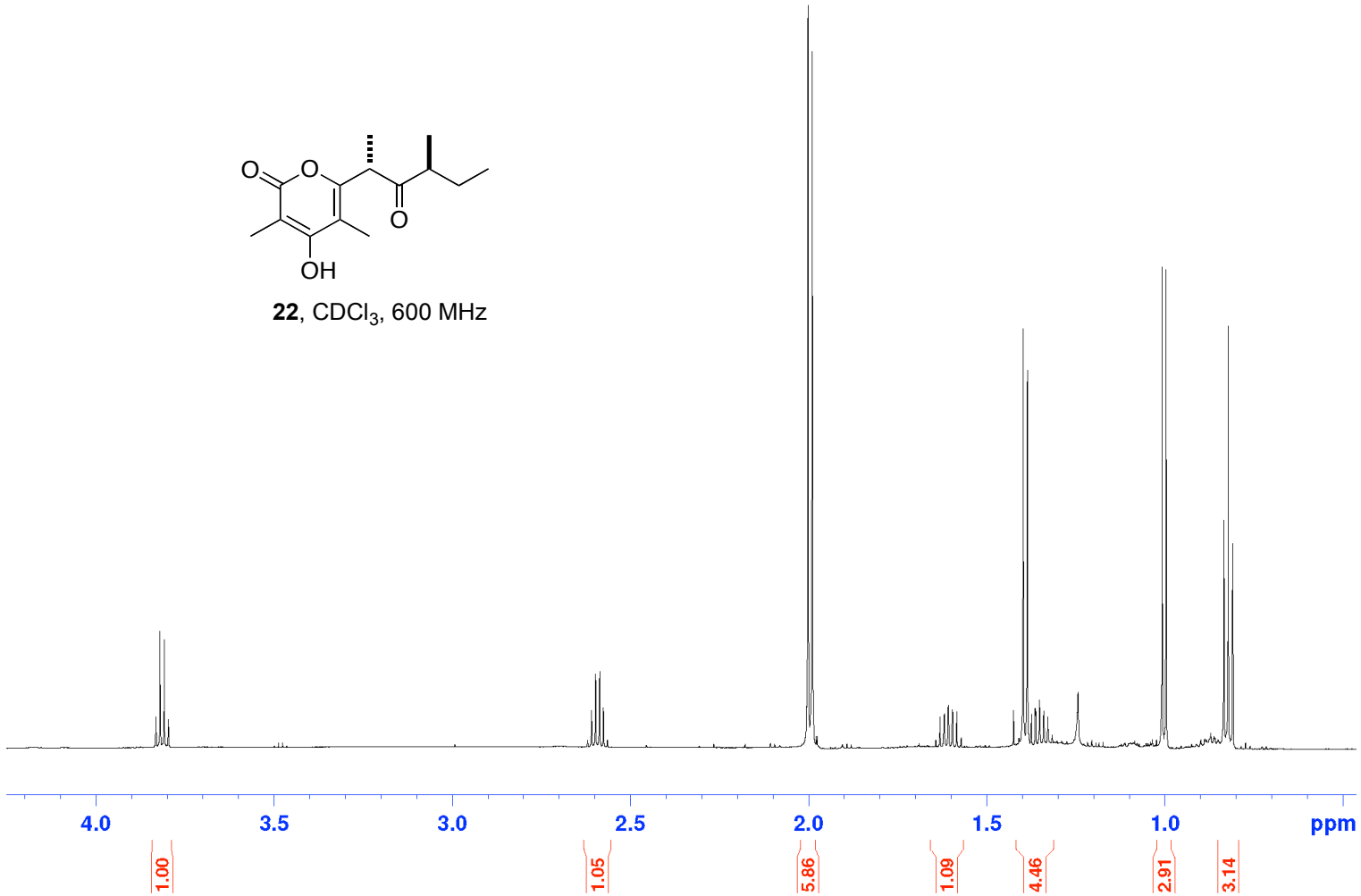

EtO
O
O
OH
OTBS
18 , CDCl3, 150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



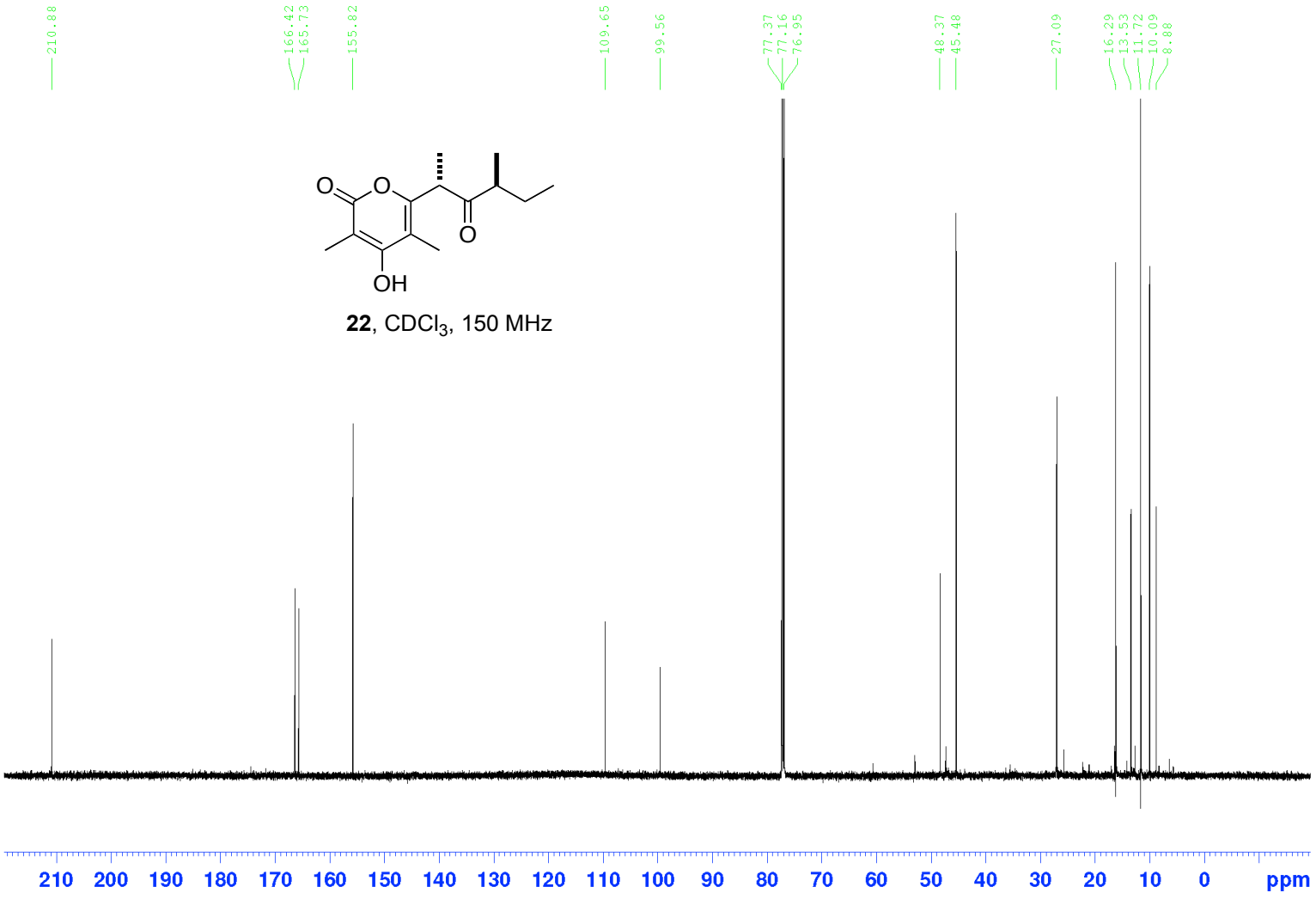
20 , $CDCl_3$, 600 MHz



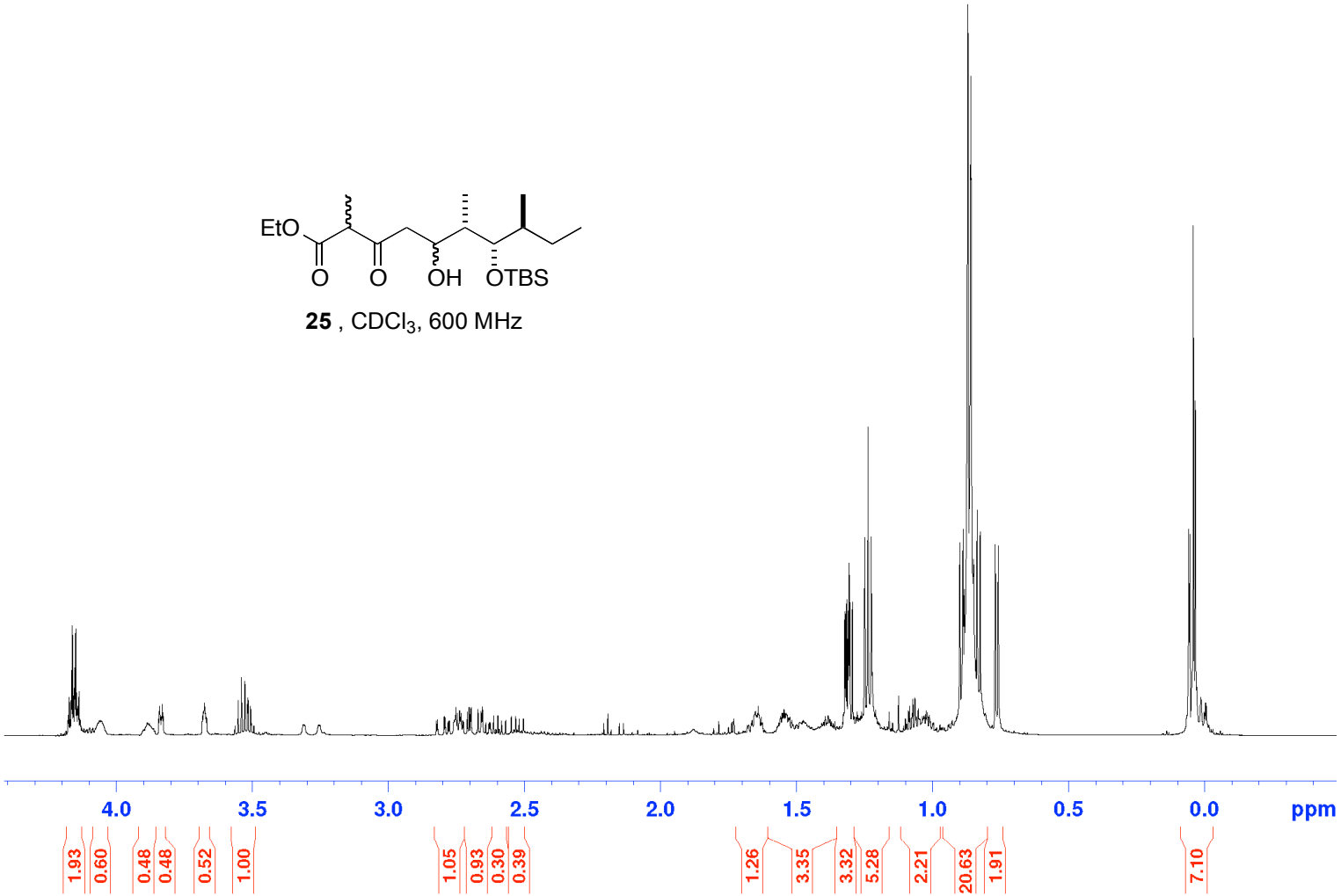
20 , $CDCl_3$, 150 MHz

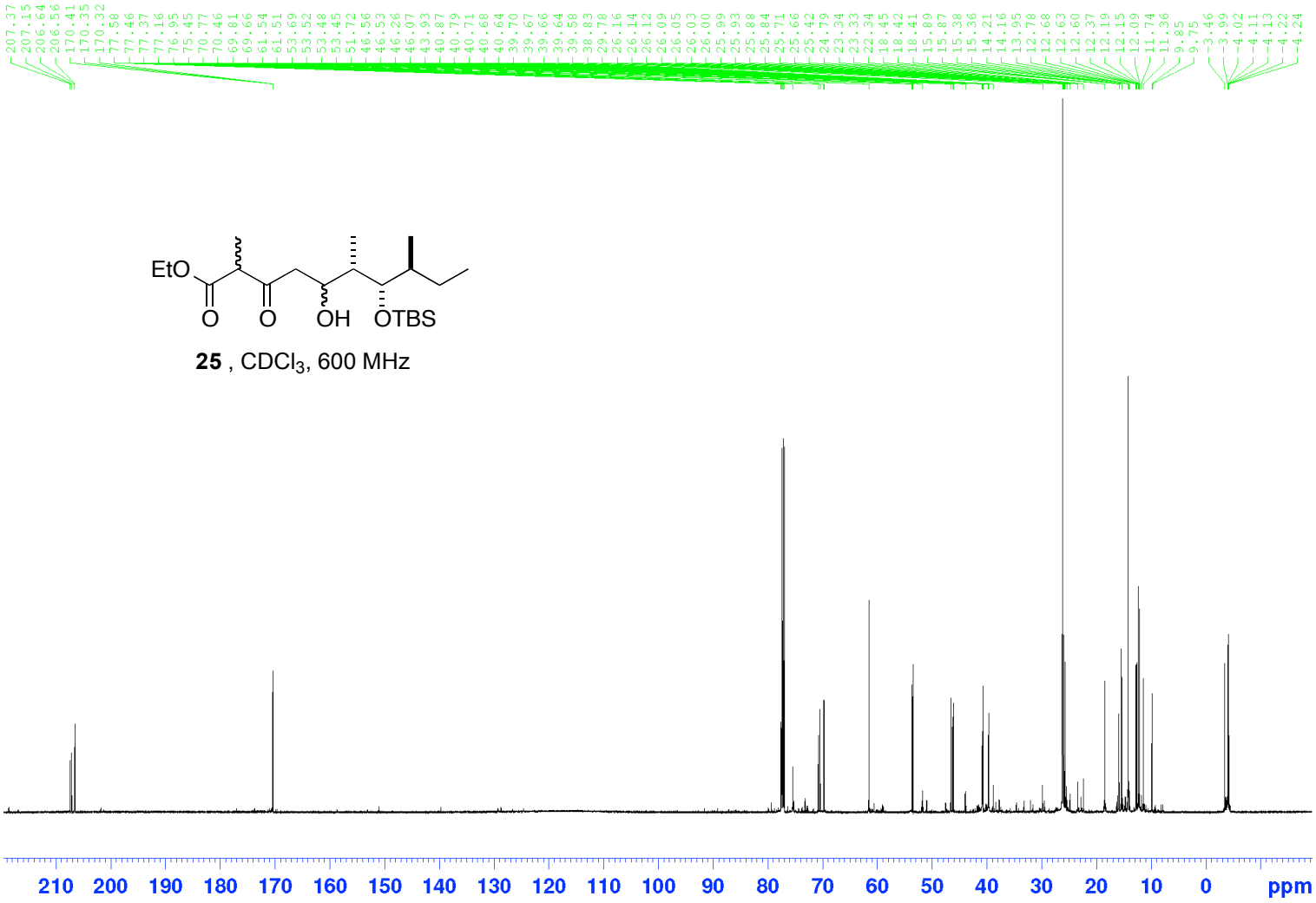


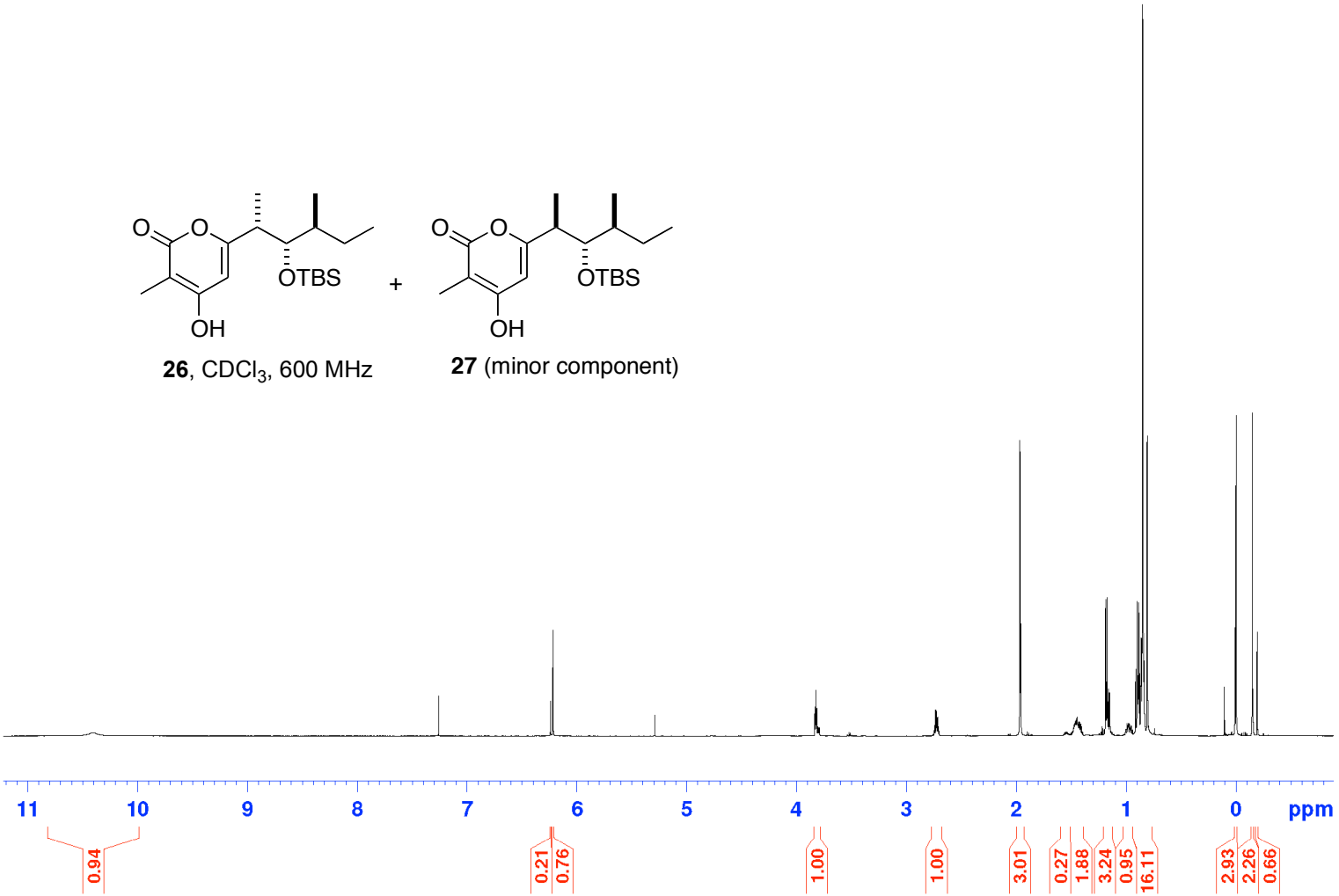
22, $CDCl_3$, 600 MHz

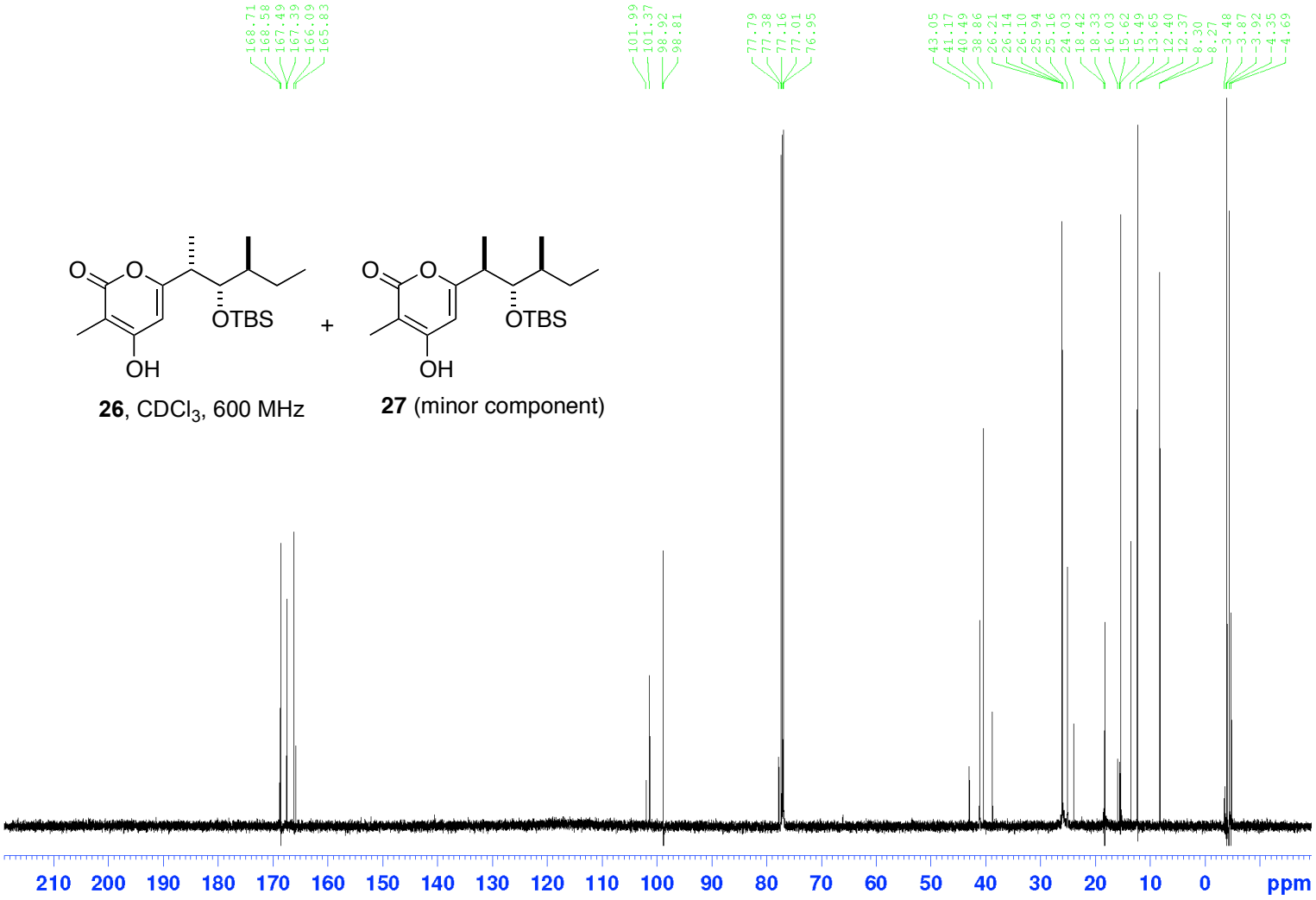


22, $CDCl_3$, 150 MHz



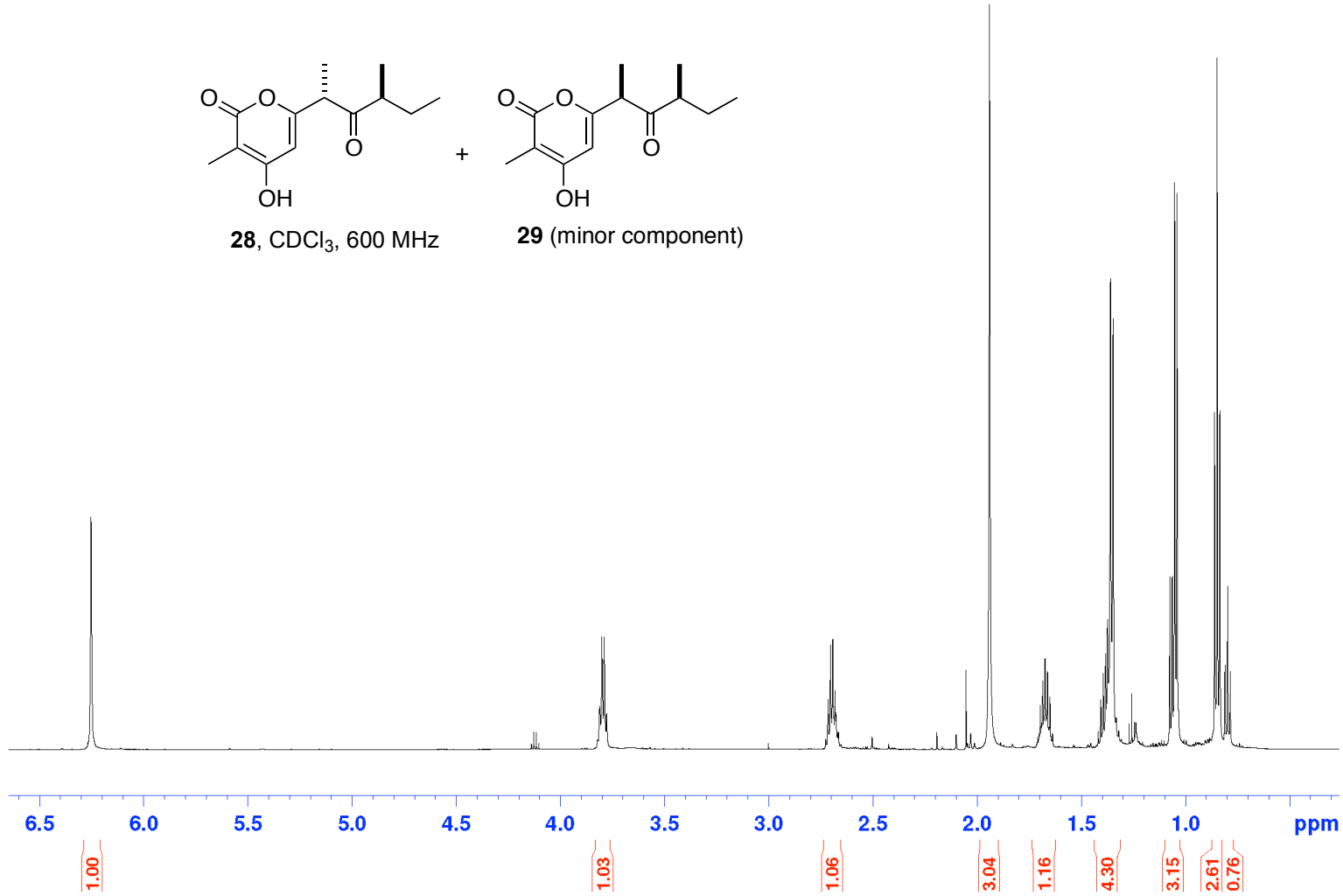

EtO
O
O
OH
OTBS
25 , CDCl3, 600 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





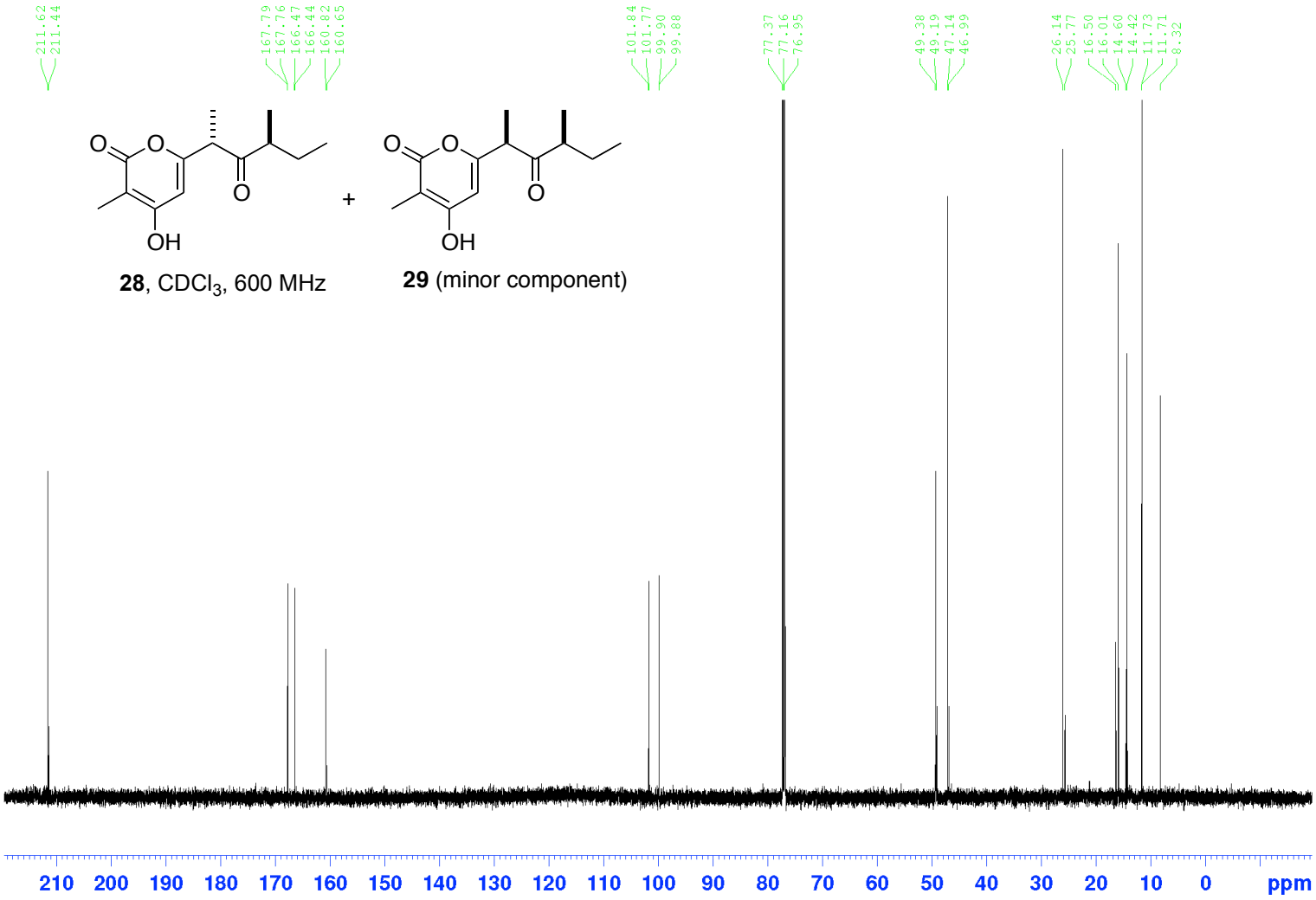
26, $CDCl_3$, 600 MHz

27 (minor component)



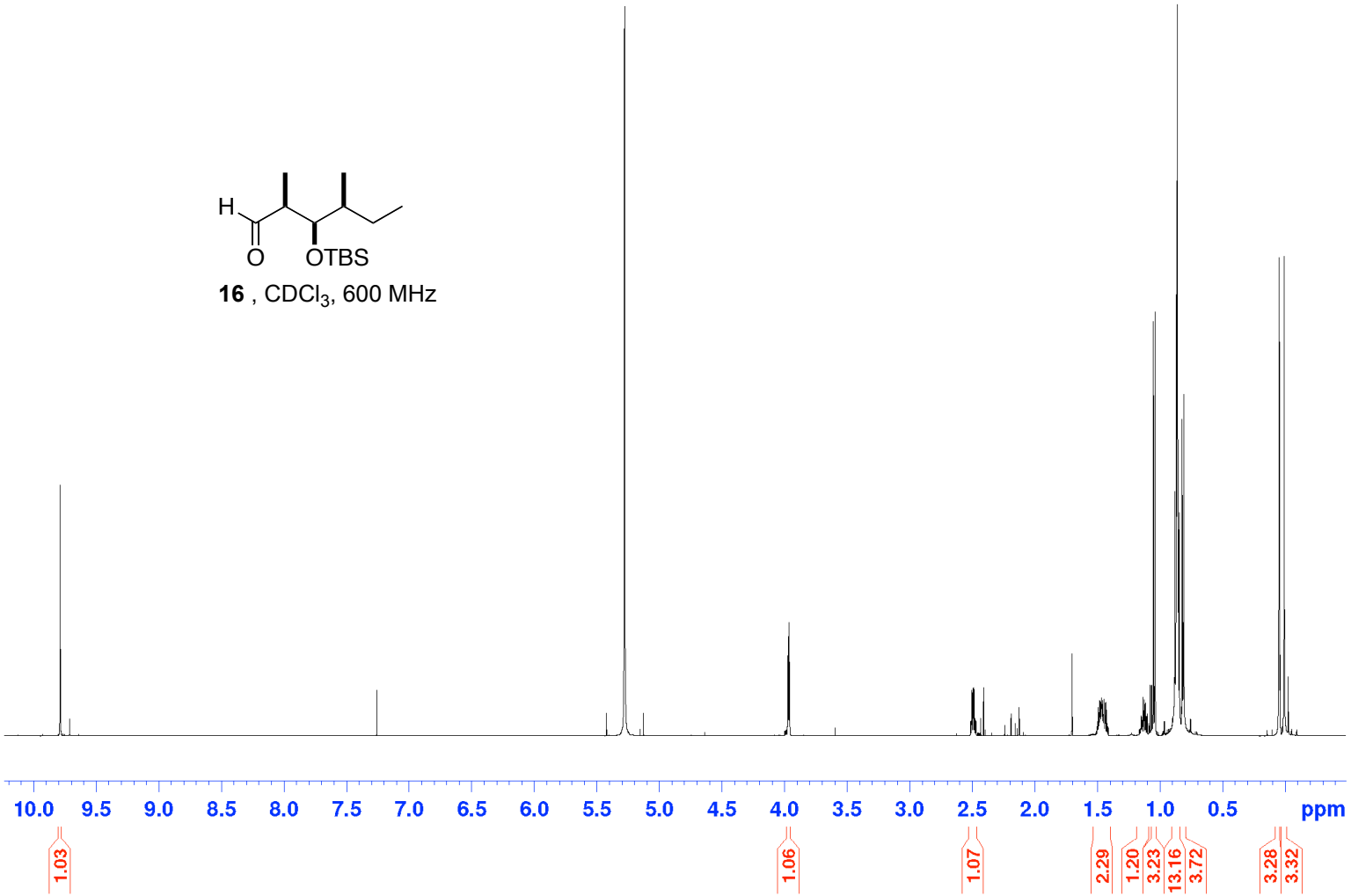
28, $CDCl_3$, 600 MHz

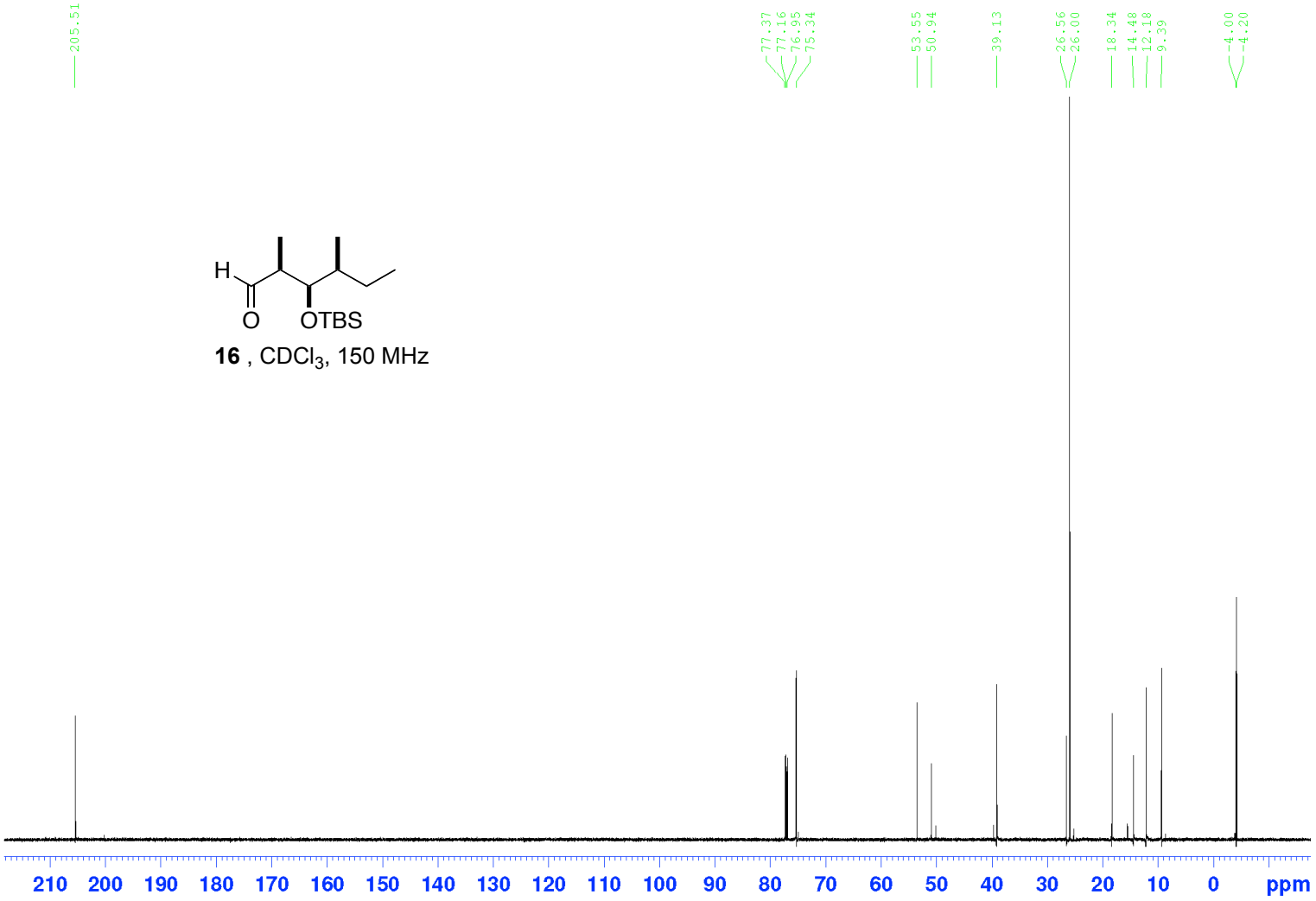
29 (minor component)

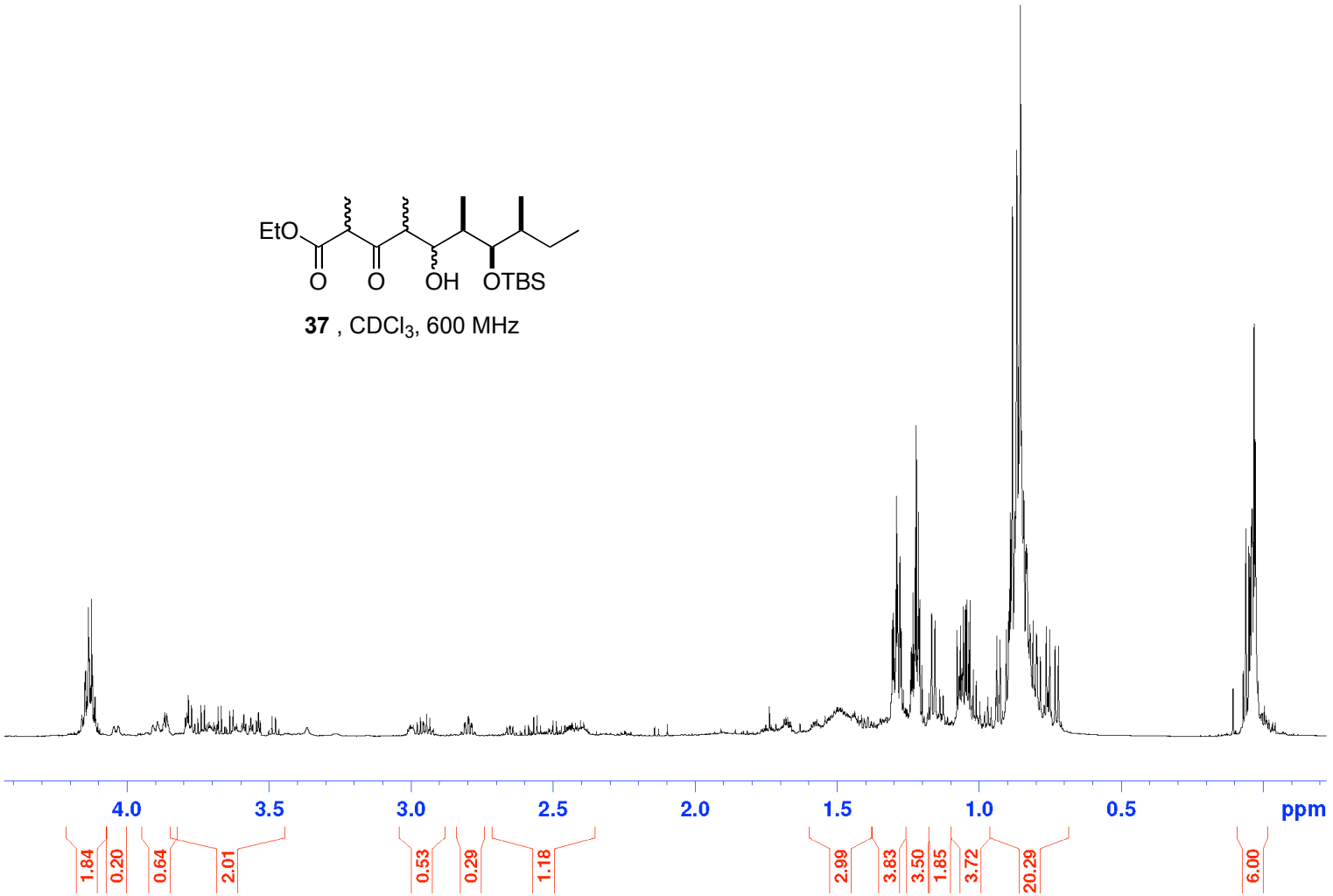


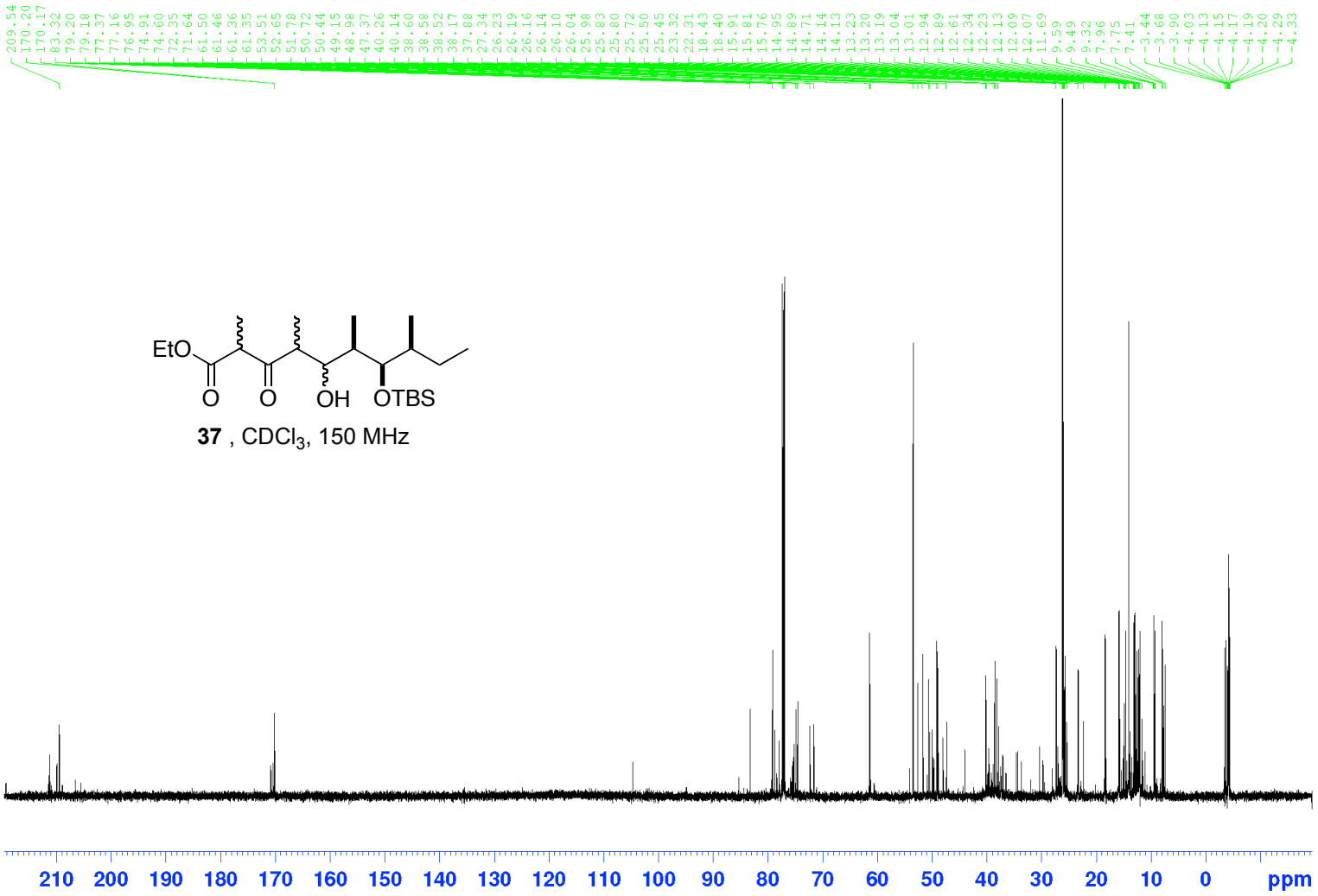
28, $CDCl_3$, 600 MHz

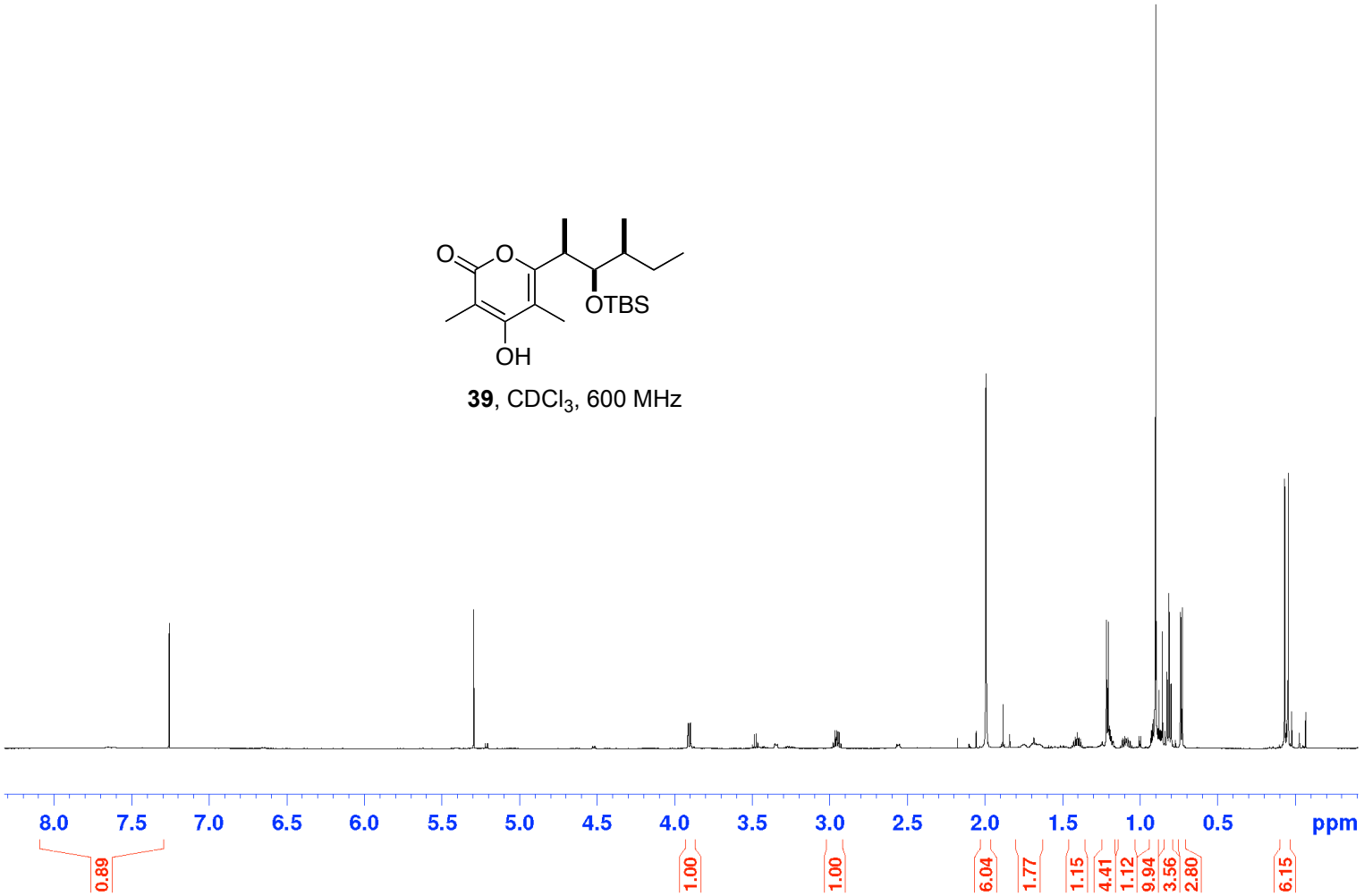
29 (minor component)

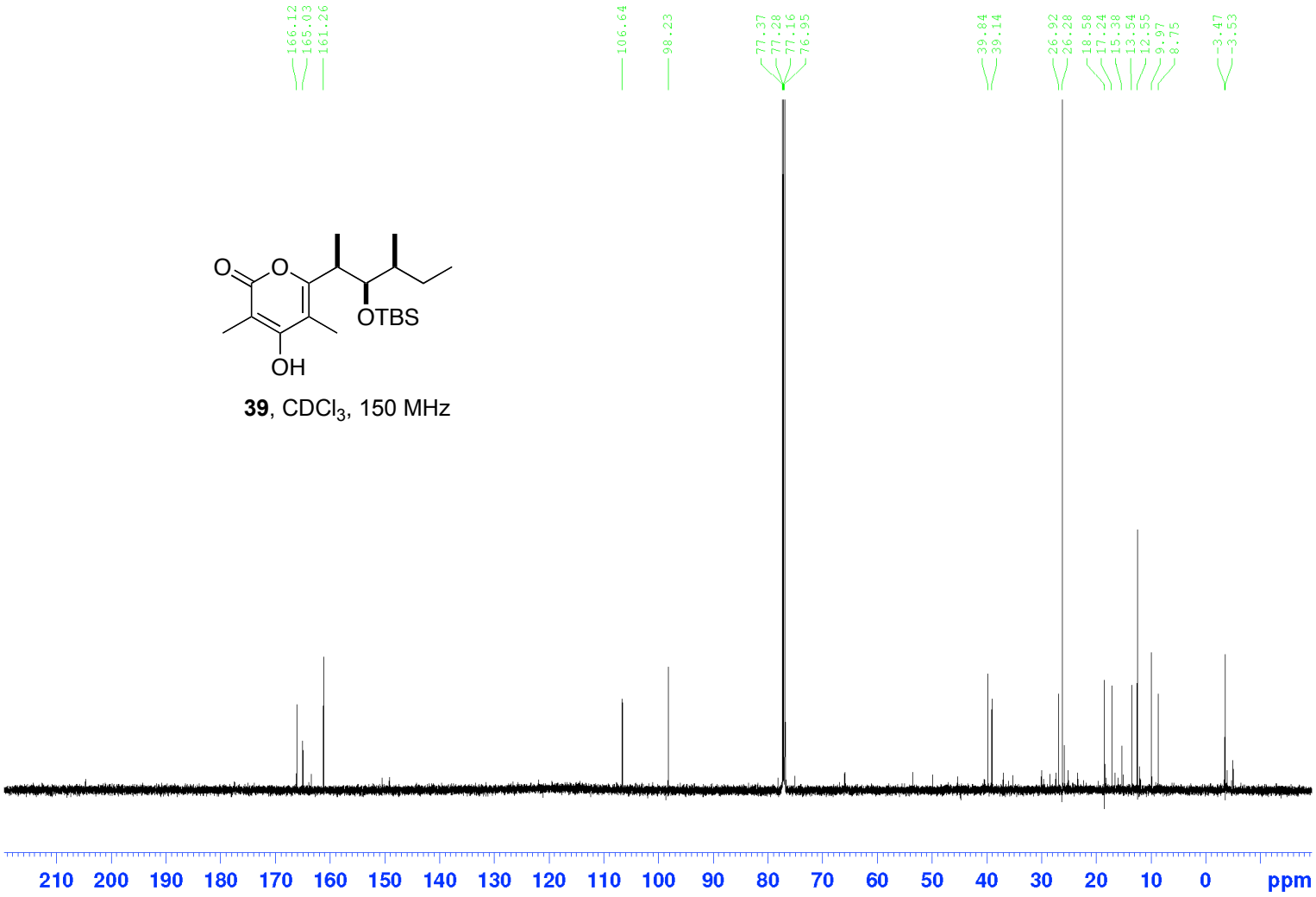



205.51
77.37
77.16
76.95
75.34
53.55
50.94
39.13
26.56
26.00
18.34
14.48
12.18
9.39
4.00
4.20
H
O
OTBS
16 , CDCl3, 150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

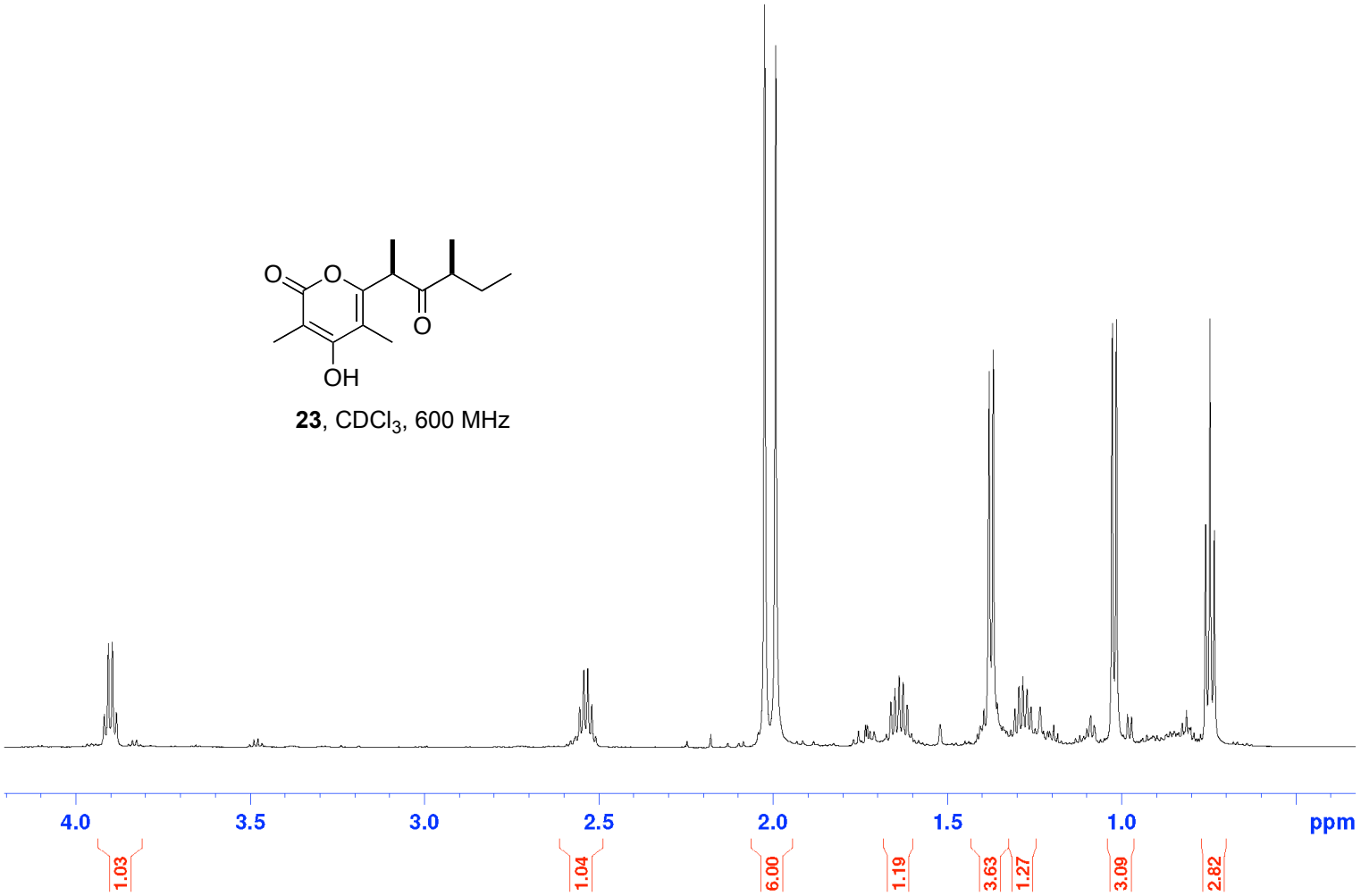



EtO
O
O
OH
OTBS
37 , CDCl3, 150 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

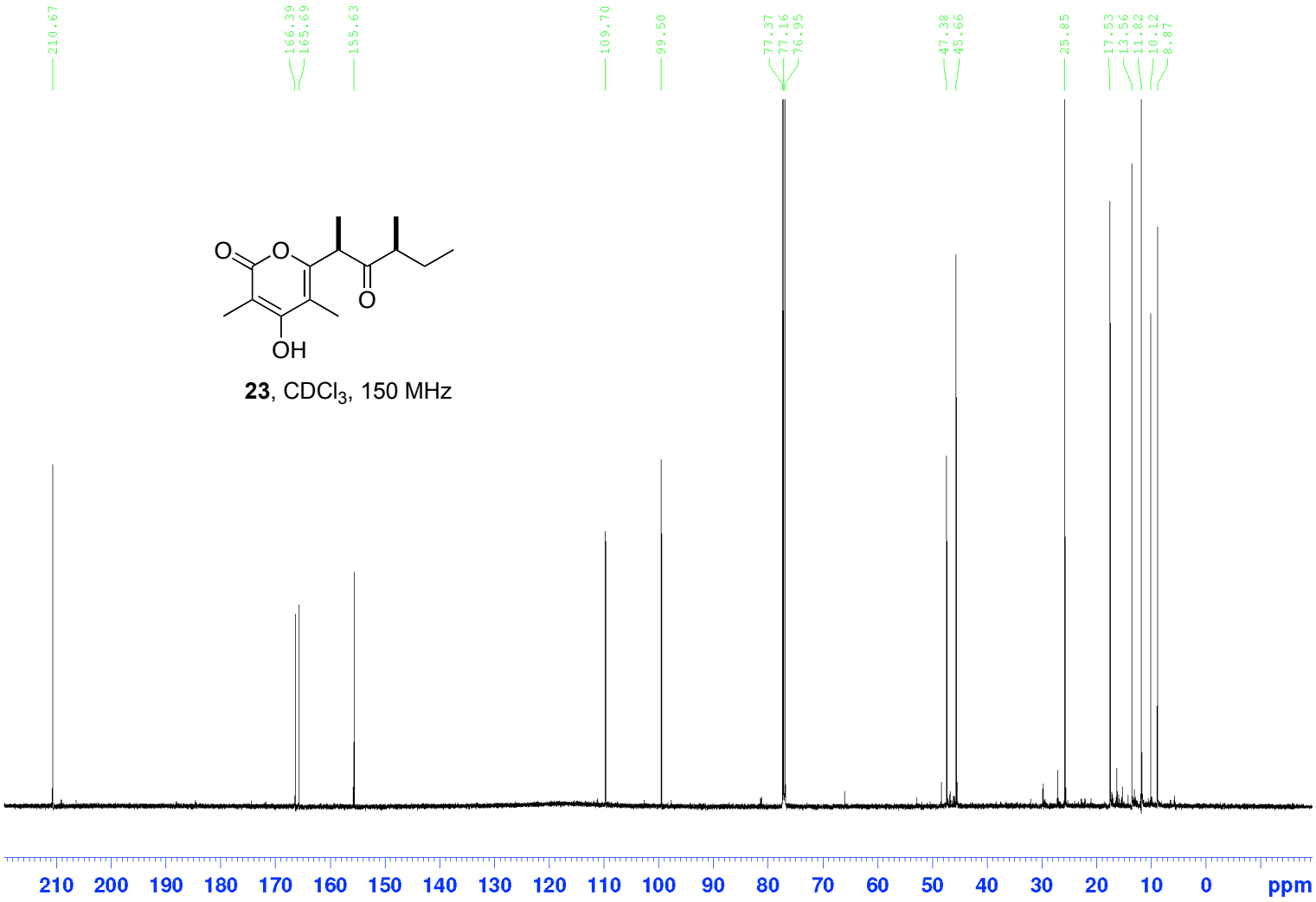

O
O
OTBS
OH
39, CDCl3, 600 MHz
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.89
1.00
1.00
6.04
1.77
1.15
4.41
1.12
9.94
3.56
2.80
6.15



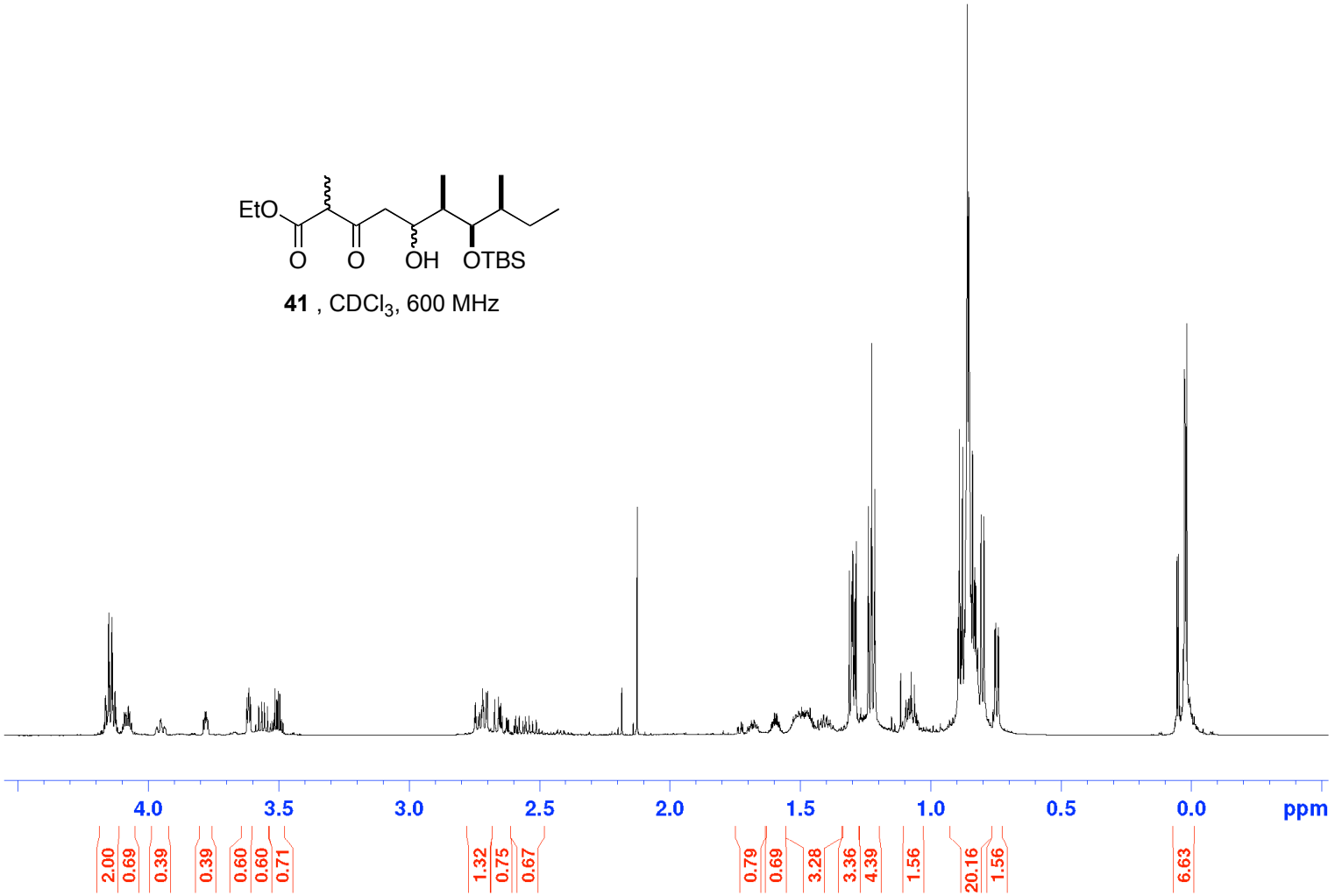
39, $CDCl_3$, 150 MHz

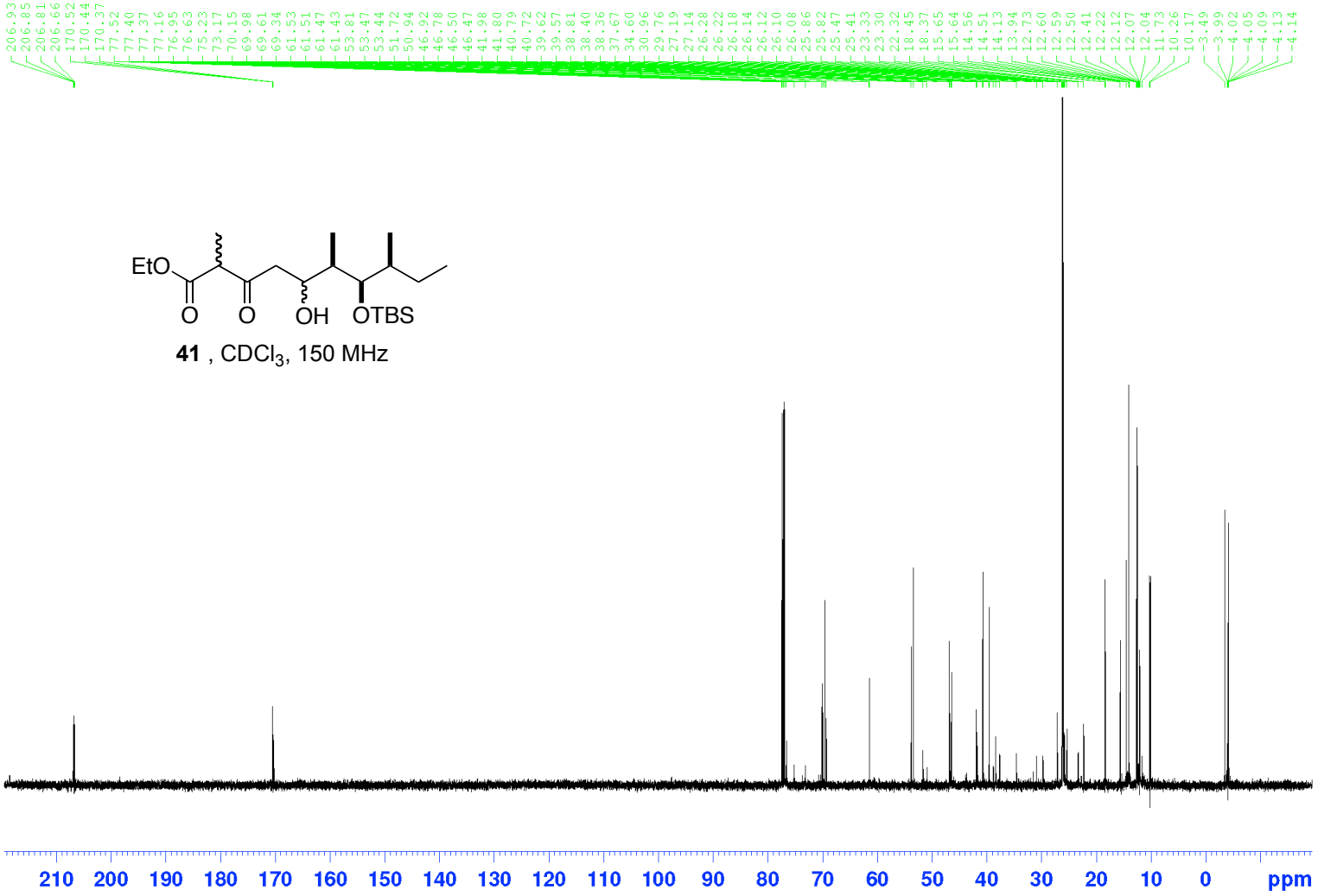


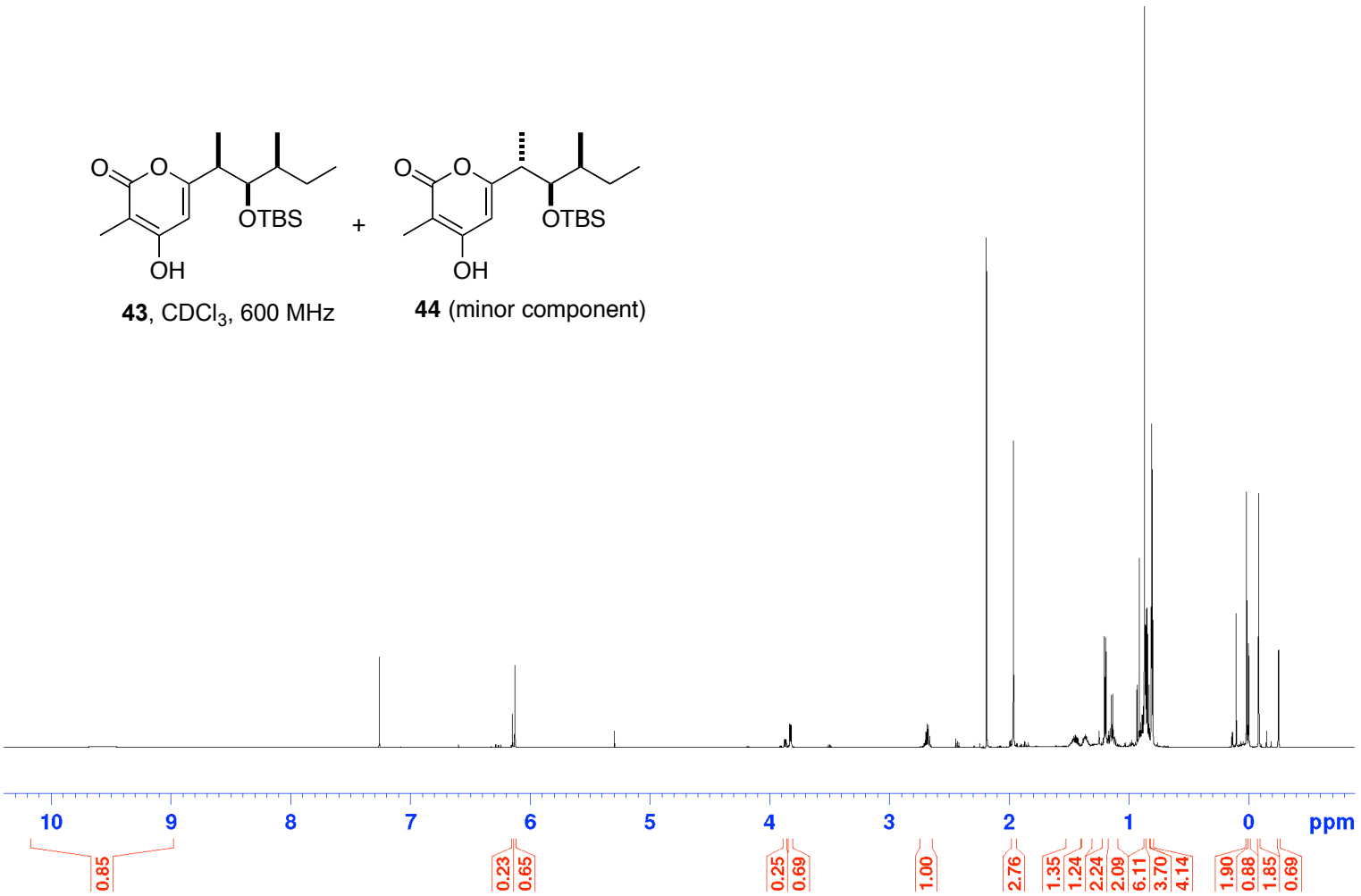
23, $CDCl_3$, 600 MHz



23, $CDCl_3$, 150 MHz

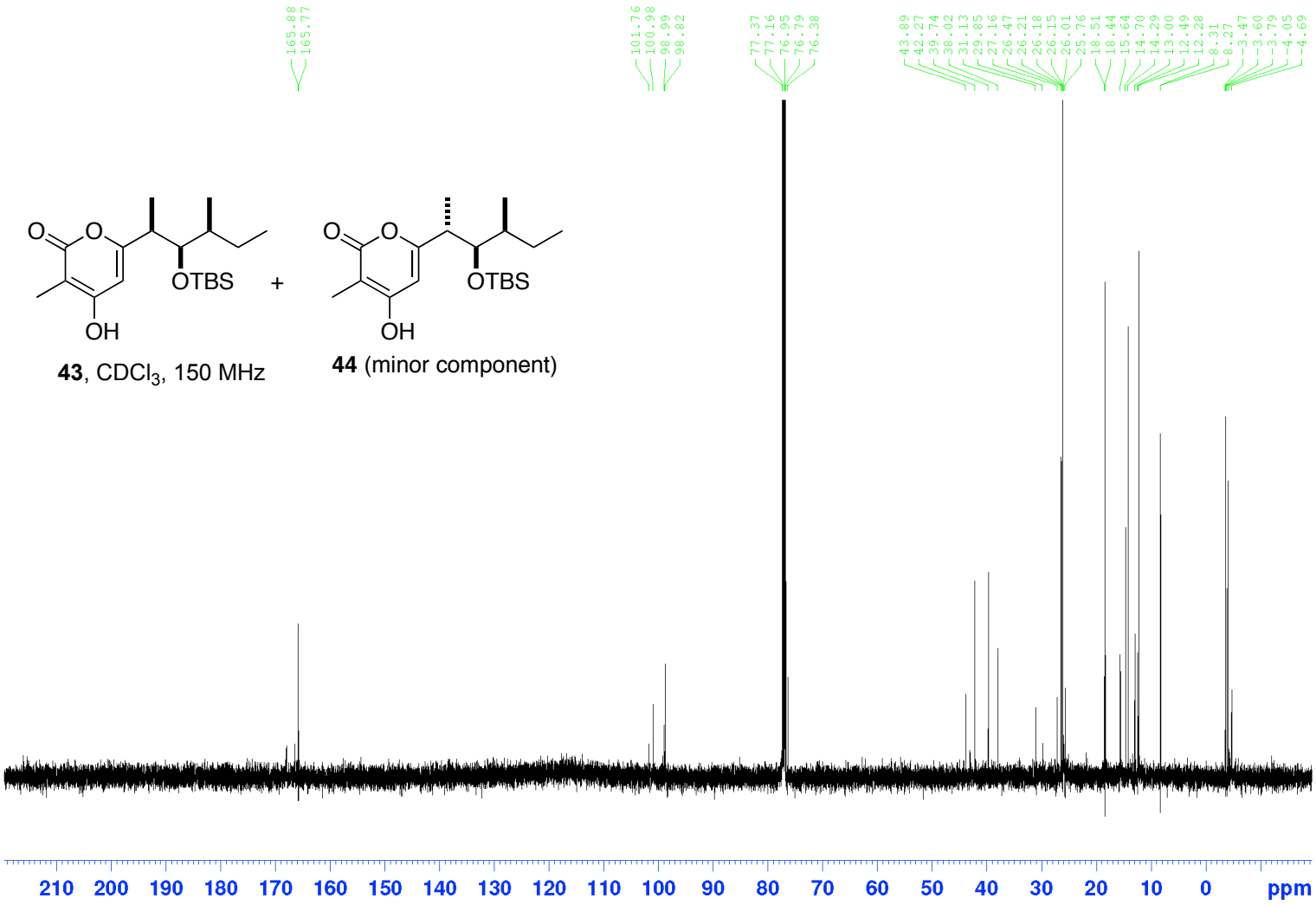

EtO
O
O
OH
OTBS
41 , CDCl3, 600 MHz
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
0.69
0.39
0.39
0.60
0.60
0.71
1.32
0.75
0.67
0.79
0.69
3.28
3.36
4.39
1.56
20.16
1.56
6.63


206.93
206.85
206.81
206.66
170.52
170.44
170.37
77.52
77.40
77.37
77.16
76.95
76.63
75.23
73.17
70.15
69.98
69.61
69.34
61.53
61.51
61.47
61.43
53.81
53.47
53.44
51.72
50.94
46.92
46.78
46.50
46.47
41.98
41.80
40.79
40.72
39.62
39.57
38.81
38.40
38.36
37.67
34.60
30.96
29.76
27.19
27.14
26.28
26.22
26.18
26.14
26.12
26.10
26.08
25.86
25.82
25.47
25.41
23.33
23.30
22.32
18.45
18.37
15.65
15.64
14.56
14.51
14.13
13.94
12.73
12.60
12.59
12.50
12.41
12.22
12.12
12.07
12.04
11.73
10.26
10.17
3.49
3.99
4.02
4.05
4.09
4.13
4.14
EtO
O
O
OH
OTBS
41 , CDCl3, 150 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



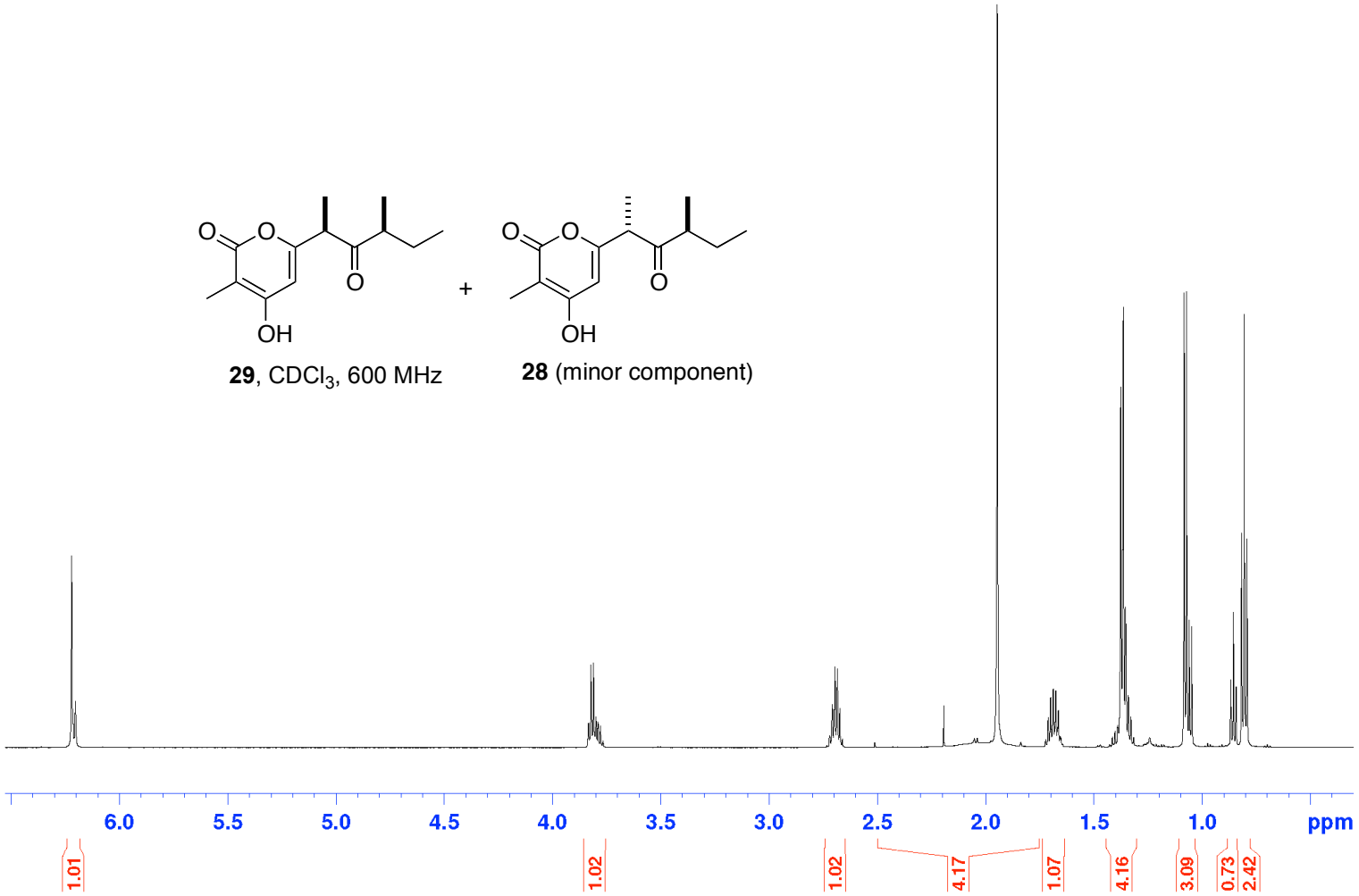
43, $CDCl_3$, 600 MHz

44 (minor component)



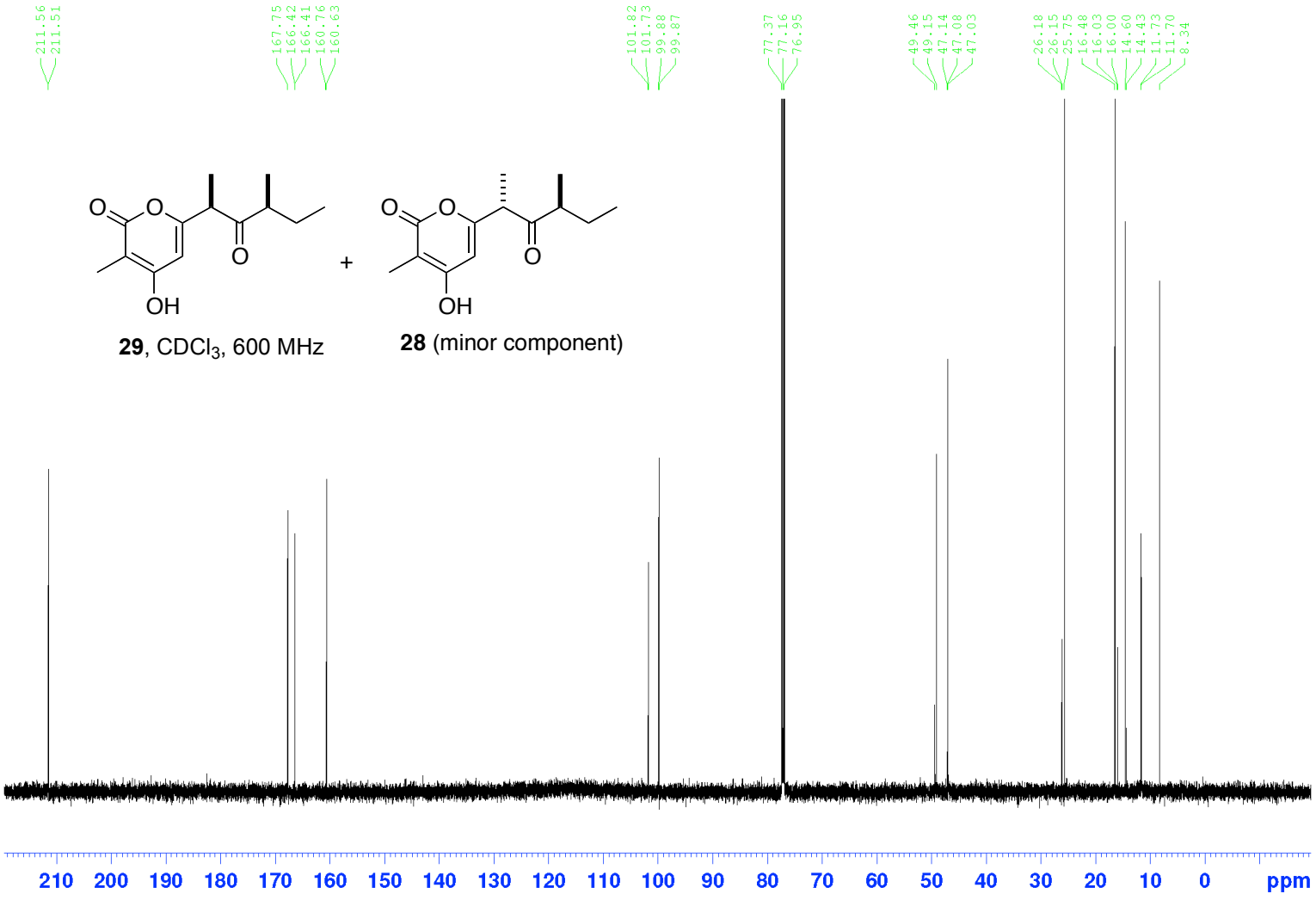
43, $CDCl_3$, 150 MHz

44 (minor component)



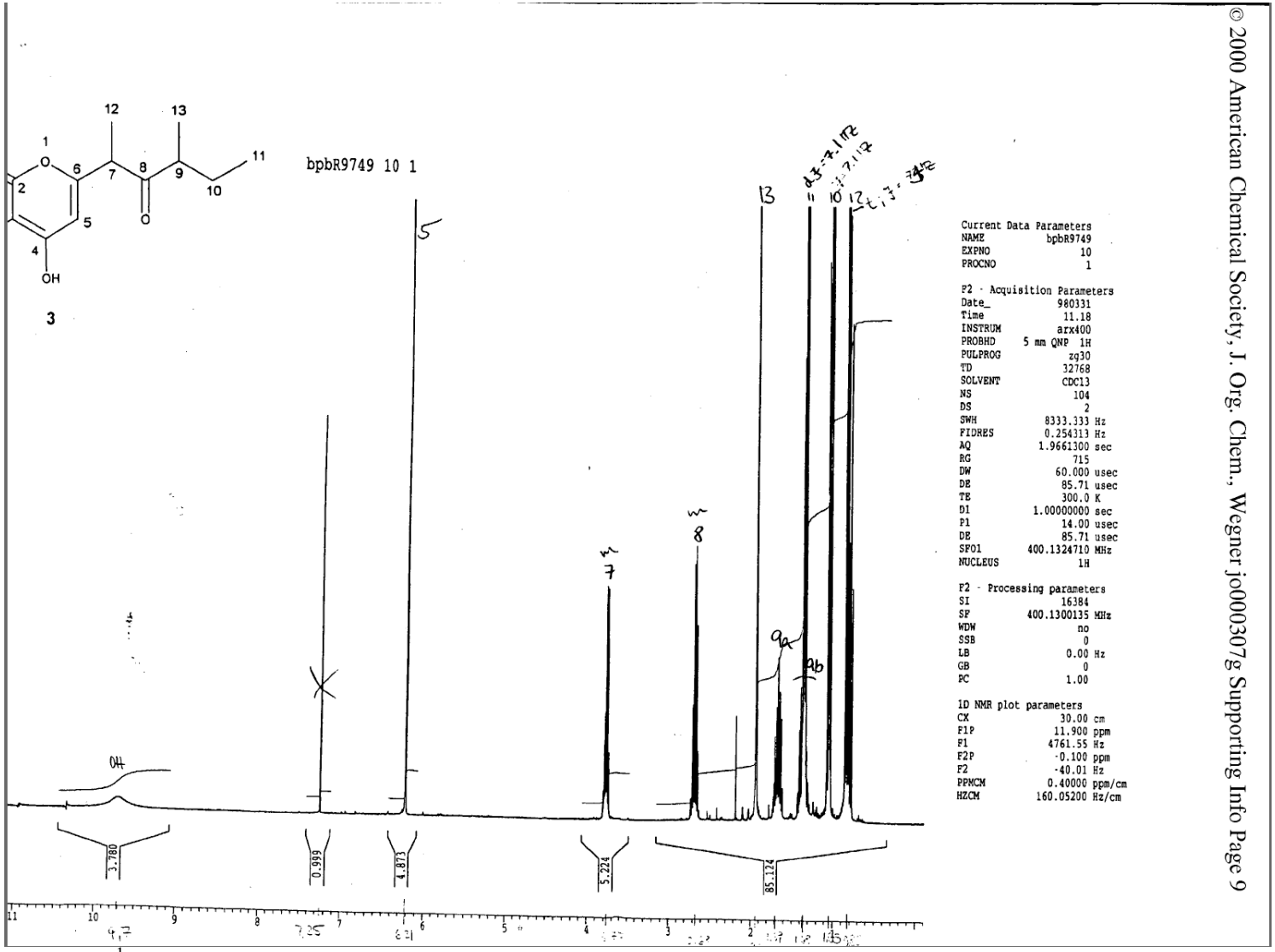
29, $CDCl_3$, 600 MHz

28 (minor component)

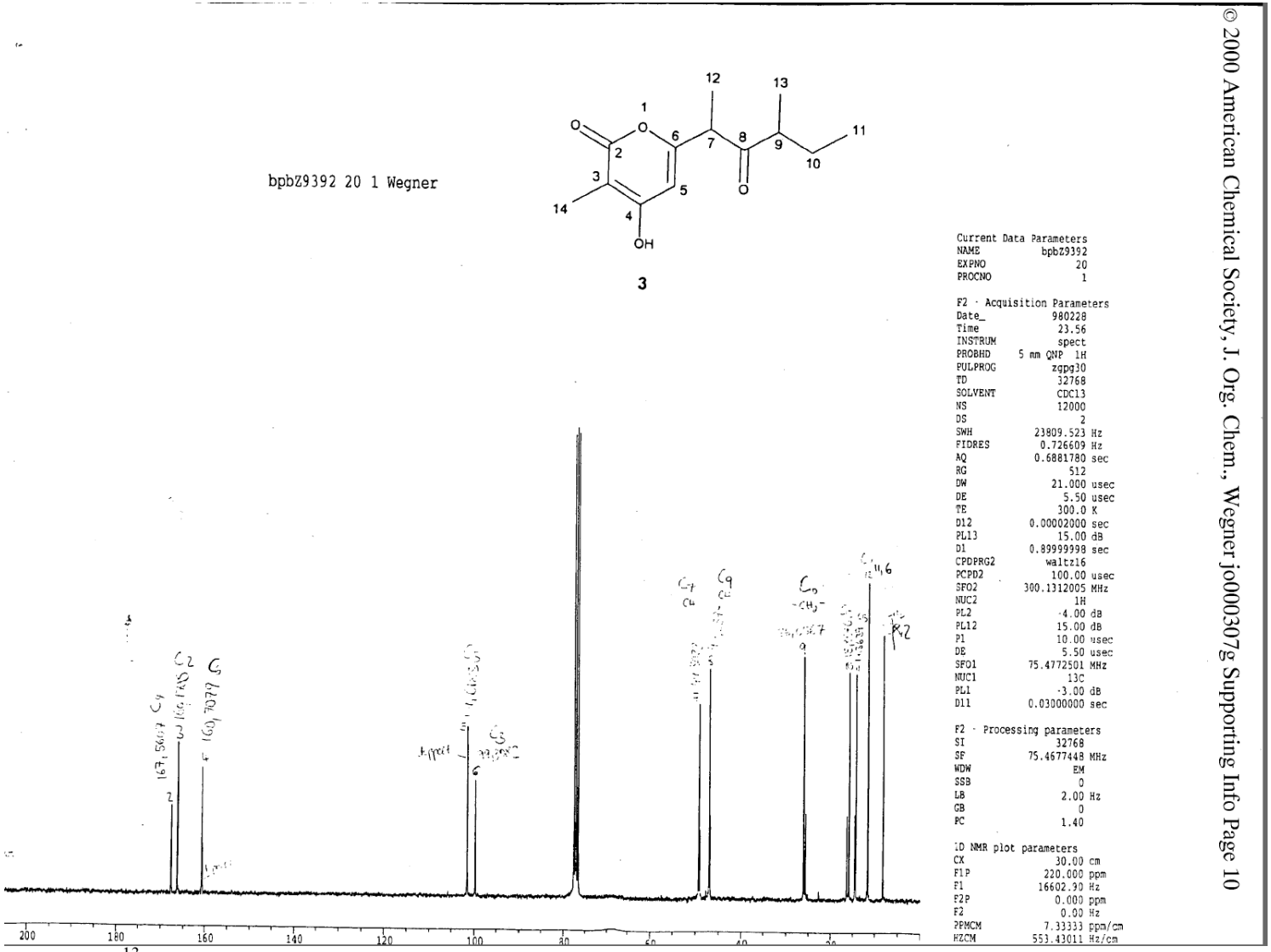


29, $CDCl_3$, 600 MHz

28 (minor component)



300 MHz ^{1}H NMR spectrum of authentic ascosalipyrone in $CDCl_3$ (Osterhage, C., Kaminsky, R., Konig, G. M., Wright, A. D. *J. Org. Chem.* **2000,** *65*, 6412-6417).



75.5 MHz ^{13}C NMR spectrum of authentic ascosalipyrone in $CDCl_3$ (Osterhage, C., Kaminsky, R., Konig, G. M., Wright, A. D. *J. Org. Chem.* **2000,** *65*, 6412-6417.)