Supporting Information

Synthesis of Taurospongin A

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Procedures for Scheme 2

(*R*)-2-Hydroxy-8-methylnon-8-en-4-one

A suspension of dry Mg turnings (2.38 mg, 97.9 mmol) in anhydrous ether (3.7 mL) was stirred vigorously and 1-bromo-4-methylpent-4-ene[1] (10 drops of 7.98 g, 49.0 mmol) was added. The reaction initiated easily and began to reflux. The mixture was diluted with ether (40 mL) and the rest of the bromide was added dropwise over 3 min. The reaction mixture was heated gently to maintain gently for 15 min and was then left at RT before use. Meanwhile, isopropyl magnesium bromide (2.0 M in THF, 9.77 mL, 19.5 mmol) was added dropwise to a pre-cooled (0 °C) solution of Weinreb amide **7**[2] (2.88 g, 19.5 mmol) in anhydrous ether (60 mL); a white precipitate was generated during the addition. The mixture was stirred at 0 °C for 10 min then left at RT for 30 min; the freshly-prepared solution of (4-methylpent-4-enyl)magnesium bromide was then added dropwise *via* cannula at 0 °C. The mixture was stirred at 0 °C for 30 min then allowed to warm to RT over 4 h. The mixture was poured into NH_4Cl solution (sat. aq., 300 mL) at 0 °C and extracted with ethyl acetate (4 × 200 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. Flash chromatography (silica gel, petrol/ether, 7:3) afforded the *title compound* as a pale yellow oil (2.32 g, 70%). R_f 0.24 (petrol/ether, 1:1); $[\alpha]_D^{20}$ –42.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3 H, d, $J_{1,2}$ = 6.5 Hz, C(1)H_3), 1.65–1.74 (5 H, m, C(8)CH_3 and C(6)H_2), 2.01 (2 H, t, $J_{6,7}$ = 7.5 Hz, C(7)H_2), 2.40 (2 H, t, $J_{5,6}$ = 7.5 Hz, C(5)H_2), 2.45–2.60 (2 H, m, C(3)H_2), 3.17 (1 H, br s, OH), 4.16–4.23 (1 H, m, H-2), 4.64 and 4.70 (2 × 1 H, 2 × s, C(9)H_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1 (C-6), 22.1 (C(8)*C*H_3), 22.3 (C-1), 36.9 (C-7), 42.7 (C-5), 50.5 (C-3), 63.8 (C-2), 110.7 (C-9), 144.8 (C-8), 212.1 (C-4); IR (film) ν_{max}/cm^{-1} 3509 (br, w), 2973 (m), 1703 (s), 1378 (m), 1098 (w), 909 (s), 734 (s), 650 (m), 446 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{10}H_{18}NaO_2$ [MNa^+] 193.1199, found 193.1193.

(2*R*,4*S*)-8-Methylnon-8-ene-2,4-diol (8)[3]

To a stirred solution of (*R*)-2-hydroxy-8-methylnon-8-ene-4-one (2.32 g, 13.6 mmol) in anhydrous THF (107 mL) and anhydrous methanol (27.6 mL) was added dropwise diethylmethoxyborane (2.1 mL, 16.0 mmol) at –78 °C. The resulting mixture was stirred for 15 min and $NaBH_4$ (600 mg, 15.9 mmol) added carefully in portions; stirring was continued for a further 3 h and the reaction was quenched by the careful addition of acetic acid (14.3 mL). The mixture was diluted with ethyl acetate (150 mL) and washed with $NaHCO_3$ solution (sat. aq., 20 mL). The organic solution was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The residue was co-evaporated with methanol (5 × 25 mL) affording the title compound (**8**) as a colourless oil (2.35 g, 100%). R_f 0.16 (petrol/ether, 1:1); $[\alpha]_D^{20}$ –1.4 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (3 H, d, $J_{1,2}$ = 6.2 Hz, C(1)H_3), 1.42–1.63 (6 H, m, C(3)H_2, C(5)H_2 and C(6)H_2), 1.71 (3 H, s, C(8)CH_3), 2.09 (2 H, t, $J_{6,7}$ = 6.1 Hz, C(7)H_2), 2.76–2.82 (2 H, m, 2 × OH), 3.86–3.91 (1 H, m, H-4), 4.03–4.10 (1 H, m, H-2), 4.67–

4.68 and 4.71–4.72 (2 × 1 H, 2 × m, C(9)H_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3 (C(8)*C*H_3), 23.2 (C-6), 24.1 (C-1), 37.6 (C-5), 38.9 (C-7), 44.4 (C-3), 69.1 (C-4), 72.8 (C-2), 110.0 (C-9), 145.7 (C-8); IR (film) ν_{max}/cm^{-1} 3384 (br, m), 2968 (m), 2935 (m), 1715 (m), 1650 (s), 1454 (s), 1377 (m), 1262 (s), 1131 (m), 1092 (m), 911 (s), 735 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{10}H_{20}NaO_2$ [MNa$^+$] 195.1356, found 195.1359.

(2*R*)-1-[(2′*S*,6′*RS*)-6′-(Iodomethyl)-6′-methyltetrahydro-2′*H*-pyran-2′-yl]propan-2-ol

To a stirred solution of diol **8** (2.50 g, 14.5 mmol) and $NaHCO_3$ (3.65 g, 43.5 mmol) in acetonitrile (30 mL) at 0 °C was added dropwise a suspension of I_2 (11.1 g, 43.7 mmol) in acetonitrile (110 mL). The mixture was then stirred at 0 °C for 3 h, diluted with ether (600 mL) and the mixture washed successively with $Na_2S_2O_3$ solution (10% aq., 3 × 200 mL), $NaHCO_3$ solution (sat. aq., 3 × 200 mL), and brine (2 × 200 mL). The organic solution was dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The residue, the *title compound*, a mixture of two diastereomers **A** and **B** (4.34 g, 100%, **A**/**B** = 1:1), was obtained as a yellow oil and was used without purification. R_f 0.21 (petrol/ether, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (6 H, d, $J_{2,3}$ = 6.3 Hz, C(3)H_3-**AB**), 1.28 (3 H, s, C(6′)CH_3-**A**), 1.35 (3 H, s, C(6′)CH_3-**B**), 1.40–1.79 (16 H, m, C(1)H_2-**AB**, C(3′)H_2-**AB**, C(4′)H_2-**AB**, and C(5′)H_2-**AB**), 3.17–3.28 (3 H, m, three of CH_2I-**AB**), 3.60–3.69 (1 H, m, H-2′-**A** or **B**), 3.77–3.83 (2 H, m, H-2′-**B** or **A**, and one of CH_2I-**AB**), 3.92 (1 H, br s, OH-**A** or **B**), 3.98–4.06 (2 H, m, OH-**B** or **A**, and H-2-**A** or **B**), 4.12–4.20 (1 H, m, H-2-**B** or **A**); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (CH_2-**A** or **B**), 19.4, 20.4, 21.1, 21.5, 23.2, 23.4, 30.1, 31.2, 31.7, 32.3 and 33.3 (C-3-**AB**, C(3′-5′)**AB**, C(6′)*C*H_3-**AB**, CH_2-**A** or **B**), 44.5 and 45.0 (C-1-**AB**), 68.0 and 68.5 (C-2-**AB**), 71.7 and 72.0 (C6′-**AB**), 72.5 and 73.4 (C2′-**AB**); IR (film) ν_{max}/cm^{-1} 3492 (br, s), 2937 (s), 1459 (m), 1378 (m), 1098 (m), 906 (s), 736 (s), 651 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{10}H_{19}INaO_2$ [MNa$^+$] 321.0322, found 321.0317.

***O*-Triethylsilyl (2*R*)-1-[(2′*S*,6′*RS*)-6′-(Iodomethyl)-6′-methyltetrahydro-2′*H*-pyran-2′-yl]propan-2-ol (9)**

To a solution of (2*R*)-1-[(2′*S*,6′*RS*)-6′-(iodomethyl)-6′-methyltetrahydro-2′*H*-pyran-2′-yl]propan-2-ol (360 mg, 1.21 mmol) in anhydrous pyridine (6 mL) was added chlorotriethylsilane (0.6 mL, 3.58 mmol). The mixture was stirred at 60 °C for 14 h and was then poured into $CuSO_4$ solution (sat. aq., 20 mL) at 0 °C. The aqueous layer was extracted with ether (3 × 30 mL) and the combined organic portions were washed successively with $CuSO_4$ solution (sat. aq., 3 × 15 mL) and water (15 mL), then dried ($MgSO_4$), filtered, and the solvent removed under reduced pressure. Flash chromatography (silica gel, petrol) afforded the *title compound* (**9**), a mixture of two diastereomers (**A**/**B** = 2:1), as a pale yellow oil (413 mg, 84%). R_f 0.80 (petrol/ether, 9:1); IR (film) ν_{max}/cm^{-1} 2936 (s), 2912 (s), 2843 (s), 1458 (m), 1374 (m), 1237 (m), 1213 (m), 1089 (s), 1036 (m), 1019 (s), 905 (w), 883 (w), 746 (s), 724 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{16}H_{33}INaO_2Si$ [MNa$^+$] 435.1187, found 435.1184. **NMR data for diastereomer A**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (6 H, q, *J* = 7.8 Hz, (CH_3CH_2)$_3$Si), 0.97 (9 H, t, *J*

= 7.8 Hz, ($CH_3CH_2)_3Si$), 1.20 (3 H, d, $J_{2,3}$ = 6.0 Hz, C(3)H_3), 1.25 (3 H, s, C(6′)CH_3), 1.35–1.82 (8 H, m, C(1)H_2, C(3′)H_2, C(4′)H_2, and C(5′)H_2), 3.21–3.27 (1 H, m, C*H*H′I), 3.38–3.45 (1 H, m, H-2′), 3.64 (1 H, d, J_{gem} = 10.6 Hz, CH*H′*I), 4.04–4.15 (1 H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9 (($CH_3CH_2)_3Si$), 7.0 (($CH_3CH_2)_3Si$), 14.4 (CH_2I), 19.8 (C-3′ or C-4′ or C-5′), 24.0 (C-3), 30.3 (C(6′)CH_3), 31.1 (C-3′ or C-4′ or C-5′), 32.6 (C-3′ or C-4′ or C-5′), 47.2 (C-1), 65.0 (C-2), 67.8 (C-2′) 71.1 (C-6′); **NMR data for diastereomer B**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (6 H, q, *J* = 7.8 Hz, ($CH_3CH_2)_3Si$), 0.97 (9 H, t, *J* = 7.8 Hz, ($CH_3CH_2)_3Si$), 1.15 (3 H, d, $J_{2,3}$ = 6.0 Hz, C(3)H_3), 1.27 (3 H, s, C(6′)CH_3), 1.35–1.82 (8 H, m, C(1)H_2, C(3′)H_2, C(4′)H_2, and C(5′)H_2), 3.21–3.27 (2 H, m, CH_2I), 3.52–3.58 (1 H, m, H-2′), 4.04–4.15 (1 H, m, H-2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9 (($CH_3CH_2)_3Si$), 7.0 (($CH_3CH_2)_3Si$), 20.4 (C(6)CH_3), 20.6 (C-3′ or C-4′ or C-5′), 22.1 (CH_2I), 23.3 (C-3), 31.6 (C-3′ or C-4′ or C-5′), 33.6 (C-3′ or C-4′ or C-5′), 46.6 (C-1), 65.1 (C-2), 68.4 (C-2′) 71.0 (C-6′).

(2*R*,4*S*)-8-Methyl-2-[(triethylsilyl)oxy]non-8-en-4-ol

A suspension of commercial Zn powder (2.0 g, 30.8 mmol) and hydrochloric acid (10%, 5 mL) was stirred in a conical flask for 1 min and then filtered under reduced pressure. The powder was washed successively with hydrochloric acid (10%, 3 × 20 mL), distilled water (3 × 20 mL), acetone (3 × 20 mL), and ether (3 × 20 mL). The powder was then dried under reduced pressure and retained for the following reaction. Iodide **9** (300 mg, 0.728 mmol) was dissolved in ethanol (12 mL), freshly activated Zn powder (708 mg, 10.8 mmol) was added, and the mixture was heated to reflux for 3 h and then cooled to RT. Solid NH_4Cl (1.16 g, 21.7 mmol) and ether (60 mL) were added, the suspension was stirred for 5 min, filtered through a short pad of Celite® and the filtrate was concentrated under reduced pressure. Flash chromatography (silica gel, petrol/ether, 9:1) afforded the *title compound* as a colourless oil (200 mg, 97%). R_f 0.33 (petrol/ether, 9:1); $[\alpha]_D^{25}$ –21.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (6 H, q, *J* = 8.0 Hz, ($CH_3CH_2)_3Si$), 0.98 (9 H, t, *J* = 8.0 Hz, ($CH_3CH_2)_3Si$), 1.20 (3 H, d, $J_{1,2}$ = 6.1 Hz, C(1)H_3), 1.35–1.62 (6 H, m, C(3)H_2, C(5)H_2, and C(6)H_2), 1.72 (3 H, s, C(8)CH_3), 2.03 (2 H, t, $J_{6,7}$ = 7.1 Hz, C(7)H_2), 3.70 (1 H, br s, OH), 3.76–3.82 (1 H, m, H-2), 4.07–4.15 (1 H, m, H-4), 4.68 and 4.70 (2 × 1 H, 2 × s, C(9)H_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1 (($CH_3CH_2)_3Si$), 6.8 (($CH_3CH_2)_3Si$), 22.4 (C(8)CH_3), 23.4 (C-6), 24.7 (C-1), 37.4 (C-7), 37.9 (C-5), 45.7 (C-3), 70.4 (C-2), 71.7 (C-4), 109.8 (C-9), 146.0 (C-8); IR (film) ν_{max}/cm^{-1} 3534 (br, m) 3529 (br, m), 3073 (w), 2968 (s), 2937 (s), 1650 (w), 1458 (m), 1375 (m), 1261 (m), 1239 (m), 1103 (s), 1019 (s), 886 (m), 805 (w), 750 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{16}H_{34}NaO_2Si$ [MNa^+] 309.2220, found 309.2213.

(2*R*,4*S*)-4-Acetoxy-8-methyl-2-[(triethylsilyl)oxy]non-8-ene

Acetic anhydride (0.16 mL, 1.69 mmol) was added to a solution of (2*R*,4*S*)-8-methyl-2-[(triethylsilyl)oxy]-non-8-en-4-ol (263 mg, 0.918 mmol), triethylamine (0.18 mL, 1.29 mmol) and DMAP (18.0 mg, 0.147 mmol) in

anhydrous dichloromethane (7 mL) at 0 °C. The reaction mixture was then allowed to warm up to RT and stirred for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, petrol) to afford the *title compound* as a colourless oil (308 mg, 100%). R_f 0.60 (petrol/ether, 9:1); $[\alpha]_D^{25}$ +2.4 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59 (6 H, q, *J* = 7.8 Hz, $(CH_3CH_2)_3Si$), 0.97 (9 H, t, *J* = 7.8 Hz, $(CH_3CH_2)_3Si$), 1.18 (3 H, d, $J_{1,2}$ = 6.1 Hz, $C(1)H_3$), 1.41–1.62 (5 H, m, C(3)*H*H′, $C(5)H_2$, and $C(6)H_2$), 1.70 (3 H, s, $C(8)CH_3$), 1.82 (1 H, ddd, J_{gem} = 13.8 Hz, $J_{2,3 \text{ or } 3,4}$ = 8.6 Hz, $J_{2,3 \text{ or } 3,4}$ = 5.0 Hz, C(3)H*H*′), 2.01 (2 H, t, $J_{6,7}$ = 7.4 Hz, $C(7)H_2$), 2.04 (3 H, s, Ac), 3.79–3.86 (1 H, m, H-2), 4.67 and 4.71 (2 × 1 H, 2 × s, $C(9)H_2$), 4.92–4.99 (1 H, m, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.9 ($(CH_3CH_2)_3Si$) 6.8 ($(CH_3CH_2)_3Si$), 21.2 (CH_3CO), 22.2 ($C(8)CH_3$), 23.1 (C-6), 23.5 (C-1), 34.2 (C-7) , 37.5 (C-5), 44.4 (C-3), 65.4 (C-2), 71.8 (C-4), 110.2 (C-9), 145.4 (C-8), 170.7 (CH_3CO); IR (film) ν_{max}/cm^{-1} 3073 (w), 2969 (s), 2876 (s), 1743 (s), 1650 (w), 1469 (s), 1375 (s), 1112 (s), 1065 (s), 1019 (s), 887 (m), 822 (m), 748 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{18}H_{36}NaO_3Si$ [MNa$^+$] 351.2326, found 351.2323.

(2*R*,4*S*)-4-Acetoxy-2-[(triethylsilyl)oxy]nonan-8-one (6)

Ozone was bubbled through a solution of (2*R*,4*S*)-4-acetoxy-8-methyl-2-[(triethylsilyl)oxy]non-8-ene (118 mg, 0.359 mmol) in anhydrous dichloromethane (10 mL) at –78 °C until a faint blue colour persisted. Oxygen was then bubbled through the reaction mixture until the blue colour dissipated, and a solution of triphenylphosphine (145 mg, 0.552 mmol) in anhydrous dichloromethane (5 mL) was then added. The mixture was allowed to warm up to RT over 14 h and most of the solvent was removed under reduced pressure. The residue was diluted with ether (20 mL) and washed successively with water (5 mL) and brine (5 mL). The organic solution was dried ($MgSO_4$), filtered and the solvent was removed under reduced pressure to leave a residue that was purified by flash chromatography (silica gel, petrol/ether, 9:1 then 4:1), affording the *title compound* (**6**) as a colourless oil (90.0 mg, 76%). R_f 0.32 (petrol/ether, 7:3); $[\alpha]_D^{25}$ –0.59 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.59 (6 H, q, *J* = 7.9 Hz, $(CH_3CH_2)_3Si$), 0.96 (9 H, t, *J* = 7.9 Hz, $(CH_3CH_2)_3Si$), 1.17 (3 H, d, $J_{1,2}$ = 6.1 Hz, $C(1)H_3$), 1.53–1.60 (5 H, m, C(3)*H*H′, $C(5)H_2$, and $C(6)H_2$), 1.82 (1 H, ddd, J_{gem} = 13.7 Hz, $J_{2,3 \text{ or } 3,4}$ = 8.4 Hz, $J_{2,3 \text{ or } 3,4}$ = 5.1 Hz, C(3)H*H*′), 2.04 (3 H, s, Ac), 2.13 (3 H, s, $C(9)H_3$), 2.38–2.50 (2 H, m, $C(7)H_2$), 3.79–3.85 (1 H, m, H-2), 4.92–4.97 (1 H, m, H-4); ^{13}C NMR (125 MHz, $CDCl_3$) δ 4.9 ($(CH_3CH_2)_3Si$), 6.8 ($(CH_3CH_2)_3Si$), 19.2 (C-6), 21.2 (CH_3CO), 23.5 (C-1), 29.9 (C-9), 33.9 (C-5), 43.2 (C-7), 44.2 (C-3), 65.4 (C-2), 71.3 (C-4), 170.7 (CH_3CO), 208.5 (C-8); IR (film) ν_{max}/cm^{-1} 3453 (w), 2957 (s), 2878 (s), 2734 (w), 1737 (s), 1720 (s), 1459 (m), 1416 (m), 1372 (s), 1243 (s), 1069 (s), 879 (m), 774 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{17}H_{34}NaO_4Si$ [MNa$^+$] 353.2119, found 353.2114.

Procedures for Scheme 3

2-(Trimethylsilyl)ethyl (7*S*,9*R*,2*E*)-7-acetoxy-3-methyl-9-[(triethylsilyl)oxy]dec-2-enoate (5)

To a solution of phosphonate **10**[4] (250 mg, 0.844 mmol) in THF (3 mL) at 0 °C was added butyllithium (1.6 M in hexane, 0.525 mL, 0.840 mmol). The reaction mixture was stirred for 30 min at 0 °C and a solution of ketone **6** (111 mg, 0.336 mmol) in THF (3 mL) was added. The ice bath was removed and the mixture was stirred for 24 h at RT. NH_4Cl solution (sat. aq., 15 mL) and ether (20 mL) were added and the separated aqueous layer was extracted with ether (3 × 20 mL). The combined organic portions were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Flash chromatography (silica gel, petrol/ether, 9:1 then 1:1) afforded the *title compound* (**5**), a pale yellow oil, as a 4:1 *E/Z* mixture (117 mg, 75%, 100% based on recovered starting material (**6**)). A sample of the pure *E*-isomer was obtained by preparative TLC (petrol/ether, 9:1) for analysis. R_f 0.28 (petrol/ether, 9:1); $[\alpha]_D^{25}$ +87.0 (*c* 0.83, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.04 (9 H, s, $(CH_3)_3Si$), 0.58 (6 H, q, *J* = 7.9 Hz, $(CH_3CH_2)_3Si$), 0.95 (9 H, t, *J* = 7.9 Hz, $(CH_3CH_2)_3Si$), 0.99–1.02 (2 H, m, CH_2SiMe_3), 1.16 (3 H, d, $J_{9,10}$ = 6.1 Hz, $C(10)H_3$), 1.44–1.60 (5 H, m, $C(5)H_2$, $C(6)H_2$, and C(8)*H*H′), 1.81 (1 H, ddd, J_{gem} = 13.7 Hz, $J_{7,8 \text{ or } 8,9}$ = 8.4 Hz, $J_{7,8 \text{ or } 8,9}$ = 5.1 Hz, C(8)H*H*′), 2.03 (3 H, s, Ac), 2.10–2.14 (5 H, m, $C(3)CH_3$ and $C(4)H_2$), 3.78–3.84 (1 H, m, H-9), 4.16–4.19 (2 H, m, CH_2O), 4.92–4.97 (1 H, m, H-7), 5.62 (1 H, s, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) δ –1.5 ($(CH_3)_3Si$), 4.9 ($(CH_3CH_2)_3Si$), 6.8 ($(CH_3CH_2)_3Si$), 17.4 (CH_2SiMe_3), 18.5 ($C(3)CH_3$), 21.2 (CH_3CO), 22.9 (C-5), 23.5 (C-10), 34.1 (C-6), 40.5 (C-4), 44.3 (C-8), 61.6 (CH_2O), 65.4 (C-9), 71.4 (C-7), 116.0 (C-2), 159.1 (C-3), 166.9 (C-1), 170.6 (CH_3CO); IR (film) ν_{max}/cm^{-1} 2954 (s), 2876 (s), 1743 (s), 1716 (s), 1651 (m), 1458 (m), 1374 (m), 1251 (s), 1177 (m), 1151 (s), 1019 (s), 862 (s), 837 (s), 748 (m); HRMS (ESI^+) *m/z* calcd. for $C_{24}H_{48}NaO_5Si_2$ [MNa^+] 495.2932, found 495.2944.

2-(Trimethylsilyl)ethyl (2*S*,3*R*,7*S*,9*R*)-7-acetoxy-2,3-dihydroxy-3-methyl-9-[(triethylsilyl)oxy]decanoate (11)

To a stirred mixture of water (1.5 mL) and *t*-BuOH (1.5 mL) at RT was added AD-mix-*β* (355 mg, 1 mol% osmium) and $(DHQD)_2PHAL$ (2.25 mg, 2.89 μmol). Once the two phases became clear (*ca.* 15 min) the mixture was cooled to 0 °C and methanesulfonamide (10.0 mg, 0.105 mmol) was added in one portion. After 20 min at 0 °C a solution of ester **5** (purified *E*-isomer; 50.0 mg, 0.106 mmol) in toluene (0.5 mL) was added and the slurry was stirred vigorously for 24 h at RT. The mixture was then cooled to 0 °C, diluted with ethyl acetate (25 mL) and water (10 mL), and Na_2SO_3 (160 mg, 1.27 mmol) added in portions before stirring for 1 h at RT. The separated aqueous layer was extracted with ethyl acetate (3 × 25 mL) and the combined organic layers were washed with brine (15 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure and flash chromatography (silica gel, petrol/ether, 7:3) afforded the *title compound* (**11**) as a colourless oil (50.0 mg, 93%). R_f 0.23 (petrol:ether, 1:1); $[\alpha]_D^{25}$ +9.00 (*c* 0.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.07 (9 H, s,

$(CH_3)_3Si$), 0.59 (6 H, q, J = 7.9 Hz, $(CH_3CH_2)_3Si$), 0.97 (9 H, t, J = 7.9 Hz, $(CH_3CH_2)_3Si$), 1.05–1.09 (2 H, m, CH_2SiMe_3), 1.16 (3 H, s, $C(3)CH_3$), 1.18 (3 H, d, $J_{9,10}$ = 6.1 Hz, $C(10)H_3$), 1.43–1.70 (7 H, m, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$ and C(8)*H*H′), 1.83 (1 H, ddd, J_{gem} = 13.8 Hz, $J_{7,7 \text{ or } 8,9}$ = 8.6 Hz, $J_{7,7 \text{ or } 8,9}$ = 5.0 Hz, C(8)H*H′*), 2.04 (3 H, s, Ac), 2.48 (1 H, br s, C(3)OH), 3.12 (1 H, d, $J_{OH,2}$ = 6.6 Hz, C(2)OH), 3.80–3.86 (1 H, m, H-9), 3.96 (1 H, d, $J_{2,OH}$ = 6.6 Hz, H-2), 4.30–4.34 (2 H, m, CH_2O), 4.94–4.99 (1 H, m, H-7); ^{13}C NMR (125MHz, $CDCl_3$) δ –1.6 ($(CH_3)_3Si$), 4.9 ($(CH_3CH_2)_3Si$), 6.8 ($(CH_3CH_2)_3Si$), 17.6 (CH_2SiMe_3), 19.1 (C-5), 21.2 (CH_3CO), 22.4 ($C(3)CH_3$), 23.5 (C-10), 35.1 (C-6), 38.0 (C-4), 44.4 (C-8), 64.6 (CH_2O), 65.4 (C-9), 71.6 (C-7), 73.8 (C-3), 75.9 (C-2), 170.7 (CH_3CO), 173.3 (C-1); IR (film) ν_{max}/cm^{-1} 3463 (br, m), 2956 (s), 2924 (s), 1736 (s), 1459 (m), 1376 (m), 1250 (s), 1088 (m), 937 (w), 861 (m), 838 (m); HRMS (ESI^+) *m/z* calcd. for $C_{24}H_{50}NaO_7Si_2$ [MNa^+] 529.2987, found 529.2994.

2-(Trimethylsilyl)ethyl (2*S*,3*R*,7*S*,9*R*)-7-acetoxy-3-methyl-2,3-thiocarbonyldioxy-9-[(triethylsilyl)oxy]decanoate (12)

A stirred solution of diol **11** (30 mg, 59.3 μmol), 1,1′-thiocarbonyldiimidazole (16 mg, 89.8 μmol), and DMAP (9.4 mg, 76.9 μmol) in anhydrous dichloromethane (3 mL) was heated at reflux under argon atomosphere for 5 h. The reaction mixture was then cooled to RT, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (silica gel, petrol/ether, 9:1 then 4:1) to afford the *title compound* (**12**) (33 mg, 100%) as a colourless oil. R_f 0.82 (petrol/ether, 1:1); $[\alpha]_D^{20}$ +9.6 (*c* 0.83, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 0.07 (9 H, s, $(CH_3)_3Si$), 0.59 (6 H, q, J = 7.8 Hz, $(CH_3CH_2)_3Si$), 0.97 (9 H, t, J = 7.8 Hz, $(CH_3CH_2)_3Si$), 1.04–1.11 (2 H, m, CH_2SiMe_3), 1.18 (3 H, d, $J_{9,10}$ = 6.0 Hz, $C(10)H_3$), 1.44 (3 H, s, $C(3)CH_3$), 1.46–1.53 (2 H, m, $C(5)H_2$), 1.56–1.66 (3 H, m, $C(6)H_2$ and C(8)*H*H′), 1.80–1.88 (2 H, m, C(4)*H*H′, C(8)H*H′*), 1.92–1.98 (1 H, m, C(4)H*H′*), 2.06 (3 H, s, Ac), 3.81–3.87 (1 H, m, H-9), 4.31–4.39 (2 H, m, CH_2O), 4.85 (1 H, s, H-2), 4.95–5.00 (1 H, m, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ –1.6 ($(CH_3)_3Si$), 4.9 ($(CH_3CH_2)_3Si$), 6.8 ($(CH_3CH_2)_3Si$), 17.6 (CH_2SiMe_3), 18.8 (C-5), 19.9 ($C(3)CH_3$), 21.2 (CH_3CO), 23.5 (C-10), 34.3 (C-6), 39.5 (C-4), 44.2 (C-8), 65.3 (C-9 and CH_2O), 70.8 (C-7), 83.7 (C-2), 91.3 (C-3), 165.4 (C-1), 170.7 (CH_3CO), 189.5 (CS); IR (film) ν_{max}/cm^{-1} 2956 (s), 2914 (s), 2877 (s), 1815 (w), 1760 (s), 1737 (s), 1458 (m), 1309 (s), 1249 (s), 1177 (s), 1047 (s), 937 (m), 860 (s), 839 (s), 745 (s); HRMS (ESI^+) *m/z* calcd. for $C_{25}H_{48}NaO_7SSi_2$ [MNa^+] 571.2551, found 571.2549.

2-(Trimethylsilyl)ethyl (3*R*,7*S*,9*R*)-7-acetoxy-3-hydroxy-3-methyl-9-[(triethylsilyl)oxy]decanoate (4)

To a solution of thionocarbonate **12** (72 mg, 0.131 mmol) in degassed toluene (4.2 mL) under an argon atmosphere was added tributyltin hydride (46 μL, 0.171 mmol) followed by a solution of AIBN (0.12 M in toluene, 0.17 mL, 0.02 mmol). The resulting mixture was heated at reflux for 3 h and then cooled and quenched

with NH_4Cl solution (sat. aq., 5 mL). The separated aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Careful flash chromatography (silica gel, petrol/ether, 9:1 then 4:1) furnished the *title compound* (**4**) as a colourless oil (60 mg, 93%). R_f 0.58 (petrol/ether, 1:1); $[\alpha]_D^{21}$ +1.9 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (9 H, s, $(CH_3)_3Si$), 0.59 (6 H, q, J = 7.9 Hz, $(CH_3CH_2)_3Si$), 0.96 (9 H, t, J = 7.9 Hz, $(CH_3CH_2)_3Si$), 0.99–1.03 (2 H, m, CH_2SiMe_3), 1.17 (3 H, d, $J_{9,10}$ = 6.0 Hz, $C(10)H_3$), 1.22 (3 H, s, $C(3)CH_3$), 1.29–1.67 (7 H, m, $C(4)H_2$, $C(5)H_2$, $C(6)H_2$, and $C(8)HH'$), 1.82 (1 H, ddd, J_{gem} = 13.8 Hz, $J_{7,8 \text{ or } 8,9}$ = 8.6 Hz, $J_{7,8 \text{ or } 8,9}$ = 5.0 Hz, $C(8)HH'$), 2.04 (3 H, s, Ac), 2.41 and 2.47 (2 × 1 H, 2 × d, J_{gem} = 15.7 Hz, $C(2)H_2$), 3.60 (1 H, br s, OH), 3.79–3.86 (1 H, m, H-9), 4.20–4.23 (2 H, m, CH_2O), 4.93–4.98 (1 H, m, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ –1.6 ($(CH_3)_3Si$), 4.9 ($(CH_3CH_2)_3Si$), 6.8 ($(CH_3CH_2)_3Si$), 17.3 (CH_2SiMe_3), 19.5 (C-5), 21.2 (CH_3CO), 23.5 (C-10), 26.5 ($C(3)CH_3$), 35.0 (C-6), 41.7 (C-4), 44.4 (C-8), 45.0 (C-2), 63.0 (CH_2O), 65.4 (C-9), 70.8 (C-3), 71.6 (C-7), 170.7 (CH_3CO), 173.2 (C-1); IR (film) ν_{max}/cm^{-1} 3509 (br, w), 2956 (s), 2915 (m), 2878 (m), 1736 (s), 1458 (m), 1376 (m), 1249 (s), 1174 (m), 1137 (m), 1065 (m), 1045 (m), 1018 (m), 860 (m), 838 (m); HRMS (ESI$^+$) *m/z* calcd. for $C_{24}H_{50}NaO_6Si_2$ [MNa^+] 513.3038, found 513.3036.

Procedures for Scheme 4

(*R*)-2-Hydroxynon-8-en-4-one[5]

To a suspension of magnesium (3.10 g, 129 mmol) in ether (15 mL) was added neat 5-bromo-1-pentene (1.5 mL, 12.7 mmol) to initiate the reaction. Then, the remaining 5-bromo-1-pentene (6.9 mL, 58.2 mmol) was added as a solution in ether (40 mL). At the end of the addition, the mixture was heated at reflux for 50 min. In parallel, to a solution of amide **7**[2] (4.74 g, 32.2 mmol) in ether (125 mL) at 0 °C was added dropwise isopropylmagnesium chloride (2.0 M in THF, 16.1 mL, 32.2 mmol). The resulting suspension was stirred at 0 °C for 30 min and then at RT for 50 min. The freshly-prepared pentenyl Grignard reagent was added at 0 °C by cannula and the mixture was stirred for 1.5 h at 0 °C and for 20 h at RT. The reaction was quenched with NH_4Cl solution (sat. aq., 200 mL), the aqueous layer was extracted with ethyl acetate (3 × 200 mL), and the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford the title compound (5.00 g, nominally 100% although this contained *ca.* 3% amide **7**), a colourless oil, which was used in the next step without purification. R_f 0.60 (petrol/ethyl acetate, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (3 H, d, $J_{1,2}$ = 6.4 Hz, CH_3), 1.61 (2 H, quint, $J_{5,6} = J_{6,7}$ = 7.4 Hz, C(6)H_2), 1.96–2.01 (2 H, m, C(7)H_2), 2.37 (2 H, t, $J_{5,6}$ = 7.4 Hz, C(5)H_2), 2.45 (1 H, dd, J_{gem} = 17.3 Hz, $J_{2,3}$ = 8.2 Hz) and 2.52 (1 H, dd, J_{gem} = 17.3 Hz, $J_{2,3}$ = 3.8 Hz, C(3)H_2), 3.31 (1 H, bs, OH), 4.11–4.19 (1 H, m, H-2), 4.89–4.92 and 4.92–4.96 (2 × 1 H, 2 × m, C(9)H_2), 5.68 (1 H, ddt, $J_{8,9\text{-}trans}$ = 17.0 Hz, $J_{8,9\text{-}cis}$ = 10.2 Hz, $J_{7,8}$ = 6.7 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3 (C-6), 22.4 (C-1), 32.9 (C-7), 42.6 (C-5), 50.6 (C-3), 63.8 (C-2), 115.3 (C-9), 137.8 (C-8), 211.9 (C-4).

(2*R*,4*S*)-Non-8-ene-2,4-diol (13)[6]

To a stirred solution of (*R*)-2-hydroxynon-8-en-4-one (8.62 g, 55.2 mmol) in THF (400 mL) and methanol (100 mL) was added dropwise diethylmethoxyborane (8.4 mL, 64.0 mmol). The resulting mixture was stirred for 55 min at –78 °C and then $NaBH_4$ (2.42 g, 64.0 mmol) was added. After 3 h at –78 °C, the reaction was quenched by the addition of acetic acid (90 mL), diluted with ethyl acetate (300 mL) and washed with $NaHCO_3$ solution (sat. aq., 3 × 150 mL). The organic layer was dried ($MgSO_4$), filtered, concentrated *in vacuo* and co-evaporated several times with methanol to afford the title compound (**13**) (7.63 g, 87%) as a colourless oil. R_f 0.20 (petrol/ethyl acetate, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3 H, d, $J_{1,2}$ = 6.2 Hz, CH_3), 1.35–1.57 (6 H, m, C(3)H_2, C(5)H_2 and C(6)H_2), 2.02–2.07 (2 H, m, C(7)H_2), 3.72–3.92 (3 H, m, H-4 and 2 × OH), 3.97–4.05 (1 H, m, H-2), 4.91–4.94 and 4.96–5.01 (2 × 1 H, 2 × m, C(9)H_2), 5.78 (1 H, ddt, $J_{8,9\text{-}trans}$ = 17.0 Hz, $J_{8,9\text{-}cis}$ = 10.2 Hz, $J_{7,8}$ = 6.7 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2 (C-1), 24.7 (C-6), 33.7 (C-7), 37.6 and 44.5 (C-3 and C-5), 69.1 (C-2), 72.8 (C-4), 114.7 (C-9), 138.7 (C-8).

(2*R*)-1-[(2′*S*,6′*RS*)-6′-(Iodomethyl)tetrahydro-2′*H*-pyran-2′-yl]propan-2-ol

To a solution of diol **13** (2.70 g, 17.1 mmol) in acetonitrile (40 mL) at RT was added $NaHCO_3$ (4.30 g, 51.2 mmol); the mixture was cooled to 0 °C and a solution/suspension of iodine (13.0 g, 51.2 mmol) in acetonitrile (135 mL) added. The mixture was stirred for 6.5 h at 0 °C, then diluted with ether (300 mL) and washed with $Na_2S_2O_3$ solution (sat. aq., 2 × 200 mL). The aqueous layer was extracted with ether (3 × 200 mL). The combined organic layers were washed successively with $NaHCO_3$ solution (sat. aq., 150 mL) and brine (150 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product (4.26 g, 88%), a colourless oil, was obtained as a pair of diasteromers (1.8:1 ratio, less polar/more polar) used in the next step without purification. A sample was purified by flash chromatography (silica gel, petrol/ethyl acetate, 85:15) for characterization. **Less polar diastereomer**: R_f 0.50 (petrol/ethyl acetate, 7:3); $[\alpha]_D^{20}$ –65.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (3 H, d, $J_{2,3}$ = 6.2 Hz, CH_3), 1.20–1.32 (2 H, m, C(3′)*H*H′ and C(5′)*H*H′), 1.48–1.59 (3 H, m, C(1)*H*H′, C(3′)H*H′* and C(4′)*H*H′), 1.65 (1 H, dt, J_{gem} = 14.6 Hz, $J_{1,2} = J_{1,2'}$ = 9.9 Hz, C(1)H*H′*), 1.76–1.86 (2 H, m, 2 H, C(4′)H*H′* and C(5′)H*H′*), 3.08–3.12 (1 H, m) and 3.20 (1 H, dd, J_{gem} = 10.4 Hz, $J_{H,6'}$ = 3.6 Hz, CH_2I), 3.46–3.52 (1 H, m, H-6′), 3.60–3.67 (1 H, m, H-2′), 3.88 (1 H, bs, OH), 4.05–4.12 (1 H, m, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.4 (CH_2I), 23.2 (C-4′), 23.5 (C-3), 31.4 and 31.7 (C-3′ and C-5′), 44.5 (C-1), 68.5 (C-2), 77.7 (C-6′), 80.3 (C-2′); IR (film) ν_{max}/cm^{-1} 3517 (b), 2693 (m), 2935 (s), 2858 (m), 1414 (m), 1204 (m), 1085 (s), 1055 (m), 943; (m); HRMS (ESI$^+$) *m/z* calcd. for $C_9H_{17}INaO_2$ [MNa$^+$] 307.0165, found 307.0163. **More polar diastereomer**: R_f 0.45 (petrol/ethyl acetate, 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (3 H, d, $J_{2,3}$ = 6.3 Hz, CH_3), 1.29–1.38 (1 H, m, C(3′)*H*H′), 1.44 (1 H, dt, J_{gem} = 14.5 Hz, $J_{1,2} = J_{1,2'}$ = 2.4 Hz, C(1)*H*H′), 1.58–1.68 (4 H, m, C(3′)H*H′*, C(4′)H_2 and C(5′)*H*H′), 1.73–1.85 (2 H, m, C(1)H*H′* and C(5′)H*H′*), 3.25 (1 H, dd, J_{gem} = 10.5 Hz, $J_{H,6'}$ = 5.2 Hz, C*H*HI), 3.45–3.58 (2 H, m, CH*H*I and OH), 3.85–3.91 (1 H, m, 1 H, H-2′), 3.98–4.04 (1 H, m, H-6′), 4.05–4.12 (1 H, m, H-2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.9 (CH_2I), 18.1 (C-4′), 23.4 (C-3), 28.6 (C-5′), 31.2 (C-3′), 43.1 (C-1), 68.2 (C-2), 71.8 (C-6′), 72.3 (C-2′); HRMS (ESI$^+$) *m/z* calcd. for $C_9H_{17}INaO_2$ [MNa$^+$] 307.0165, found 307.0169.

***O*-tert-Butyldiphenylsilyl (2*R*)-1-[(2′*S*,6′*RS*)-6′-(Iodomethyl)tetrahydro-2′*H*-pyran-2′-yl]propan-2-ol (14)**

To a solution of (2*R*)-1-[(2′*S*,6′*RS*)-6′-(iodomethyl)tetrahydro-2′*H*-pyran-2′-yl]propan-2-ol (4.26 g, 15.0 mmol) in DMF (21 mL) was added imidazole (2.56 g, 37.5 mmol) followed by TBDPSCl (4.86 mL, 18.7 mmol). The mixture was stirred for 14 h at RT. After addition of water (20 mL), the aqueous layer was extracted with ether (3 × 30 mL), and the combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 97:3) afforded the *title compound* (**14**) as a colourless oil (7.84 g, 100%). **Less polar diastereomer**: R_f 0.30 (petrol/ether, 98:2); $[\alpha]_D^{20}$ –19.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (9 H, s, $(CH_3)_3C$-), 1.05–1.08 (1 H, m, C(3′)*H*H′), 1.08–1.13 (1 H,

m, C(5′)*H*H′), 1.11 (3 H, d, $J_{2,3}$ = 6.2 Hz, C(3)H_3), 1.32–1.50 (3 H, m, C(1)*H*H′, C(3′)H*H′* and C(4′)*H*H′), 1.73–1.79 (2 H, m, C(4′)H*H′* and C(5′)H*H′*), 1.83–1.90 (1 H, m, C(1)H*H′*), 3.07 (1 H, dd, J_{gem} = 10.1 Hz, $J_{H,6'}$ = 6.9 Hz) and 3.10 (1 H, dd, J_{gem} =10.1 Hz, $J_{H,6'}$ = 5.2 Hz, CH_2I), 3.23–3.29 (1 H, m, H-6′), 3.40–3.46 (1 H, m, H-2′), 4.10 (1 H, sext, $J_{2,3}$ = $J_{1,2}$ = 6.2 Hz, H-2), 7.34–7.43 (6 H, m) and 7.66–7.70 (4 H, m, 2 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.0 (CH_2I), 19.4 ($(CH_3)_3$*C*-), 23.5 and 23.6 (C-3 and C-4′), 27.2 ($(CH_3)_3$C-), 31.3 and 31.4 (C-3′ and C-5′), 46.0 (C-1), 66.9 (C-2), 75.6 (C-2′), 77.3 (C-6′), 127.55, 127.64, 129.5 and 129.6 (Ph), 134.7 and 135.0 (*i*-Ph), 136.03 and 136.05 (Ph); IR (film) ν_{max}/cm^{-1} 3048 (m), 2997 (s), 2856 (s), 1472 (m), 1427 (m), 1361 (m), 1110 (s), 1084 (s), 702 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{25}H_{35}INaO_2Si$ [MNa$^+$] 545.1343, found 545.1355. **More polar diastereomer**: R_f 0.20 (petrol/ether, 98:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (9 H, s, $(CH_3)_3$C-), 1.14–1.22 (1 H, m, C(3′)*H*H′), 1.20 (3 H, d, $J_{2,3}$ = 6.1 Hz, C(3)H_3), 1.25–1.32 (2 H, m, C(1)*H*H′ and C(5′)*H*H′), 1.38–1.48 (2 H, m, C(4′)H_2), 1.50–1.56 (2 H, m, C(3′)H*H′* and C(5′)H*H′*), 2.00 (1 H, ddd, J_{gem} = 14.3 Hz, $J_{1,2 \text{ or } 1,2'}$ = 9.5 Hz, $J_{1,2 \text{ or } 1,2'}$ = 5.3 Hz, C(1)H*H′*), 2.97–3.01 (2 H, m, CH_2I), 3.03–3.08 (1 H, m, H-6′), 3.84–3.89 (1 H, m, H-2′), 3.97–4.04 (1 H, m, H-2), 7.36–7.43 (6 H, m) and 7.68–7.72 (4 H, m, 2 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.8 (CH_2I), 18.3 (C-4′), 19.4 ($(CH_3)_3$*C*-), 23.1 (C-3), 27.2 ($(CH_3)_3$C-), 29.2 (C-3′), 30.0 (C-5′), 41.6 (C-1), 66.8 (C-2), 69.4 (C-2′), 69.6 (C-6′), 127.6, 127.7, 129.59 and 129.63 (Ph), 134.7 and 134.8 (*i*-Ph), 136.1 and 136.2 (Ph); IR (film) ν_{max}/cm^{-1} 3070 (w), 2932 (s), 2857 (s), 1472 (m), 1427 (s), 1380 (m), 1112 (s), 1082 (m), 998 (m), 702 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{25}H_{35}INaO_2Si$ [MNa$^+$] 545.1343, found 545.1337.

(2*R*,4*S*)-2-[(*tert*-Butyldiphenylsilyl)oxy]non-8-en-4-ol

A suspension of zinc dust (5.0 g) in hydrochloric acid (1 M, 50 mL) was stirred at RT for 15 min. The zinc was then removed by filtration, washed with water (2 × 50 mL) then ether (2 × 50 mL) and dried under vacuum. A sample of the activated zinc (1.25 g, 19.1 mmol) was added to a solution of iodide **14** (1.00 g, 1.91 mmol) in THF (15 mL) and water (4 mL). The reaction mixture was heated at 40 °C for 3 h in an ultrasonic cleaning bath and then filtered through Celite® washing through with dichloromethane (40 mL). The filtrate was washed with $NaHCO_3$ solution (sat. aq., 20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product, the *title compound* (749 mg, 99%), a colourless oil, was used in the next step without purification. R_f 0.10 (petrol/ether, 95:5); $[\alpha]_D^{20}$ –10.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (3 H, d, $J_{1,2}$ = 6.1 Hz, C(1)H_3), 1.05 (9 H, s, $(CH_3)_3$C-), 1.37–1.47 (3 H, m, C(5)H_2 and C(6)*H*H′), 1.49–1.58 (2 H, m, C(3)*H*H′ and C(6)H*H′*), 1.68 (1 H, dt, J_{gem} = 14.3 Hz, $J_{2,3}$ = $J_{3,4}$ = 8.8 Hz, C(3)H*H′*), 2.03–2.08 (2 H, m, C(7)H_2), 2.89 (1 H, bs, OH), 3.78–3.84 (1 H, m, H-4), 4.10–4.16 (1 H, m, H-2), 4.94–4.97 and 4.99–5.03 (2 × 1 H, 2 × m, C(9)H_2), 5.81 (1 H, ddt, $J_{8,9\text{-}trans}$ = 16.9 Hz, $J_{8,9\text{-}cis}$ = 10.2 Hz, $J_{7,8}$ = 6.7 Hz, H-8), 7.38–7.47 (6 H, m) and 7.72–7.75 (4 H, m, 2 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3 ($(CH_3)_3$*C*), 24.3 (C-1), 24.8 (C-6), 27.1 ($(CH_3)_3$C), 33.9 (C-7), 37.3 (C-5), 46.5

(C-3), 70.8 and 70.9 (C-2 and C-4), 114.6 (C-9), 127.6, 127.9, 129.8 and 130.0 (Ph), 133.7 and 134.5 (*i*-Ph), 135.98 and 136.03 (Ph), 139.0 (C-8); IR (film) ν_{max}/cm^{-1} 3445 (m), 3072 (m), 2932 (s), 2858 (s), 1640 (m), 1589 (w), 1472 (m), 1428 (s), 1378 (m), 1111 (s), 910 (m), 706 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{25}H_{36}NaO_2Si$ [MNa$^+$] 419.2388, found 419.2381.

(2*R*,4*S*)-4-Benzyloxy-2-[(*tert*-butyldiphenylsilyl)oxy]non-8-ene (15)

Trifluoromethanesulfonic acid (18 μL, 0.20 mmol) was added dropwise to a solution of (2*R*,4*S*)-2-[(*tert*-butyldiphenylsilyl)oxy]non-8-en-4-ol (1.80 g, 4.54 mmol) and benzyltrichloroacetimidate (940 μL, 5.00 mmol) in cyclohexane (7.2 mL) and dichloromethane (3.6 mL) at 0 °C. The mixture was warmed to RT and stirred for 14 h. The reaction was then quenched with $NaHCO_3$ solution (sat. aq., 10 mL) and the aqueous layer was extracted with ether (3 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 99:1) afforded the *title compound* (**15**) (1.78 g, 81%) containing traces of (?) dibenzylether, as a colourless oil. Some starting material (15%) was recovered during the purification. R_f 0.40 (petrol/ether, 98:2); $[\alpha]_D^{20}$ +7.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02–1.07 (12 H, m, C(1)H_3 and $(CH_3)_3$C-), 1.39–1.35 (1 H, m, C(6)*H*H′), 1.38–1.54 (4 H, m, C(3)*H*H′, C(5)H_2 and C(6)H*H*′), 1.92–2.00 (3 H, m, C(3)H*H*′ and C(7)H_2), 3.46–3.51 (1 H, m, H-4), 3.95–4.01 (1 H, m, H-2), 4.39 (2 H, s, C*H*$_2$Ph), 4.93–4.95 and 4.96–4.99 (2 × 1 H, 2 × m, C(9)H_2), 5.76 (1 H, ddt, $J_{8,9\text{-}trans}$ = 16.9 Hz, $J_{8,9\text{-}cis}$ = 10.2 Hz, $J_{7,8}$ = 6.7 Hz, H-8), 7.21–7.43 (11 H, m) and 7.68 (4 H, d, *J* = 7.6 Hz, 3 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4 ((CH$_3$)$_3$*C*), 23.9 (C-1), 24.7 (C-6), 27.2 ((*C*H$_3$)$_3$C), 33.6 (C-5), 34.0 (C-7), 44.1 (C-3), 67.4 (C-2), 70.4 (*C*H$_2$Ph), 76.2 (C-4), 114.6 (C-9), 127.5, 127.6, 127.7, 127.8, 128.4, 129.6 and 129.7 (Ph), 134.4 and 134.9 (*i*-Ph), 136.0 and 136.1 (Ph), 139.0 (C-8), 139.1 (*i*-Ph); IR (film) ν_{max}/cm^{-1} 3071 (m), 2932 (s), 2858 (s), 1640 (w), 1589 (w), 1455 (m), 1111 (s), 1067 (m), 739 (m), 702 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{32}H_{42}NaO_2Si$ [MNa$^+$] 509.2846, found 509.2849.

(6*S*,8*R*)-6-Benzyloxy-8-[(*tert*-butyldiphenylsilyl)oxy]nonan-2-one (16)

To a solution of alkene **15** (980 mg, 2.01 mmol) in *N,N*-dimethylacetamide (3.4 mL) and water (0.5 mL) at RT was added $Cu(OAc)_2$ (732 mg, 4.02 mmol) followed by $PdCl_2$ (36 mg, 0.20 mmol). The ambient atmosphere was replaced with oxygen and the mixture was stirred for 66 h. The reaction mixture was filtered through a pad of Celite® and the filtrate was diluted with water (5 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 9:1) afforded the *title compound* (**16**) (792 mg, 78%) as a colourless oil. R_f 0.15 (petrol/ether, 9:1); $[\alpha]_D^{20}$ +7.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (9 H, s, (CH$_3$)$_3$C-), 1.06 (3 H, d, $J_{8,9}$ = 6.1 Hz, C(9)H_3), 1.34–1.39 (2 H, m, C(5)H_2), 1.47–1.55 (2 H, m, C(4)*H*H′ and

C(7)*H*H′), 1.58–1.67 (1 H, m, C(4)H*H*′), 1.93–1.98 (1 H, m, C(7)H*H*′), 2.09 (3 H, s, C(1)H_3), 2.32 (2 H, t, $J_{3,4}$ = 7.5 Hz, C(3)H_2), 3.49 (1 H, app. quint, $J_{6,7} = J_{5,6}$ = 6.0 Hz, H-6), 3.97 (1 H, sext, $J_{7,8} = J_{8,9}$ = 6.1 Hz, H-8), 4.37 and 4.41 (2 × 1 H, 2 × d, J_{gem} = 11.6 Hz, C*H*$_2$Ph), 7.22–7.30 (5 H, m), 7.35–7.43 (6 H, m) and 7.66–7.69 (4 H, m, 3 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4 (*C*(CH_3)$_3$), 19.7 (C-4), 23.9 (C-9), 27.2 (C(*C*H$_3$)$_3$), 29.9 (C-1), 33.5 (C-5), 43.8 (C-3), 44.0 (C-7), 67.3 (C-8), 70.4 (*C*H$_2$Ph), 75.9 (C-6), 127.5, 127.6, 127.7, 127.9, 128.4, 129.6 and 129.7 (Ph), 134.3 and 134.8 (*i*-Ph), 136.0 and 136.1 (Ph), 138.9 (*i*-Ph), 209.0 (C-2); IR (film) ν_{max}/cm^{-1} 3070 (m), 2998 (s), 2858 (s), 1716 (s), 1589 (w), 1454 (s), 1428 (s), 1162 (s), 1140 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{32}H_{42}NaO_3Si$ [MNa$^+$] 525.2795, found 525.2800.

(2*R*,4*S*,8*R*)-4-Benzyloxy-2-(*tert*-butyldiphenylsilyl)oxy-8-[(*R*)-1′,2′-diphenylethyl]oxy-8-methylundec-10-ene (17)

Trifluoromethanesulfonic acid (8 μL, 0.092 mmol; *the reaction is more successful when reagent is dispenses from a freshly-opened glass ampoule*; this particular run was performed with reagent that had been opened 3 months previously) was added dropwise to a solution of ketone **16** (229 mg, 0.455 mmol), (*R*)-(1,2-diphenylethoxy)trimethylsilane (123 mg, 0.455 mmol) and allyltrimethylsilane (72 μL, 0.455 mmol) in dichloromethane (2.0 mL) at –78 °C. The mixture was stirred at –78 °C for 11 h and the reaction was then quenched with triethylamine (0.1 mL) and the solvent removed *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 97:3) afforded the *title compound* (**17**) (225 mg, 68%) as a colourless oil, and 60 mg (26%) of ketone **16** was recovered. R_f 0.40 (petrol/ether, 95:5); $[\alpha]_D^{20}$ +17.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77 (3 H, s, C(8)CH_3), 1.02 (3 H, d, $J_{1,2}$ = 6.0 Hz, C(1)H_3), 1.05 (9 H, s, (CH_3)$_3$C-), 1.06–1.15 (2 H, m, C(5)*H*H′ and C(6)*H*H′), 1.20–1.30 (4 H, m, C(5)H*H*′, C(6)H*H*′ and C(7)*H*H′), 1.41–1.46 and 1.84–1.89 (2 × 1 H, 2 × m, C(3)H_2), 1.99–2.07 (2 H, m, C(9)H_2), 2.81 (1 H, dd, J_{gem} = 13.2 Hz, $J_{1',2'}$ = 5.8 Hz) and 2.94 (1 H, dd, J_{gem} = 13.2 Hz, $J_{1',2'}$ = 7.5 Hz, C(2′)H_2), 3.31–3.37 (1 H, m, H-4), 3.92–4.00 (1 H, m, H-2), 4.30 and 4.33 (2 × 1 H, 2 × d, J_{gem} = 11.7 Hz, OC*H*$_2$Ph), 4.59 (1 H, dd, $J_{1',2'}$ = 7.5 Hz, $J_{1',2'}$ = 5.8 Hz, H-1′), 4.85–4.95 (2 H, m, C(11)H_2), 5.76 (1 H, ddt, $J_{10,11\text{-}trans}$ = 17.3 Hz, $J_{10,11\text{-}cis}$ = 10.1 Hz, $J_{9,10}$ = 7.2 Hz, H-10), 7.06 (2 H, m), 7.15–7.28 (13 H, m), 7.33–7.43 (6 H, m) and 7.67–7.70 (4 H, m, 5 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.4 (C-6), 19.6 ((CH_3)$_3$*C*), 23.7 (C-1 and C(8)*C*H$_3$), 27.2 ((*C*H$_3$)$_3$C), 34.6 (C-5), 39.7 (C-7), 43.6 (C-9), 44.3 (C-3), 47.2 (C-2′), 67.4 (C-2), 70.4 (O*C*H$_2$Ph), 75.7 (C-1′), 76.3 (C-4), 78.2 (C-8), 117.0 (C-11), 126.2, 126.5, 126.9, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.3, 129.6, 129.7 and 130.2 (Ph), 134.4 and 134.9 (*i*-Ph), 135.2, 136.01 and 136.04 (Ph), 139.0, 139.1 and 145.9 (*i*-Ph); IR (film) ν_{max}/cm^{-1} 3134 (m), 3069 (m), 2931 (s), 2857 (s), 1639 (w), 1603 (w), 1454 (m), 1428 (m), 1377 (m), 1110 (s), 1058 (s), 938 (m), 703 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{49}H_{60}NaO_3Si$ [MNa$^+$] 747.4204, found 747.4212.

(3*R*,7*S*,9*R*)-7-Benzyloxy-2-(*tert*-butyldiphenylsilyl)oxy-3-[(*R*)-1′,2′-diphenylethyl]oxy-8-methyldecan-oic acid

To a solution of alkene **17** (430 mg, 0.593 mmol) in THF (3.2 mL) and water (3.2 mL) was added OsO_4 (2.5% in water, 164 μL, 0.016 mmol) followed by $NaIO_4$ (693 mg, 3.24 mmol). The reaction mixture was stirred at RT for 14 h and was then quenched with Na_2SO_3 solution (sat. aq., 5 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give the crude aldehyde (440 mg; the oxidation was noted to have proceeded partially to the acid at this stage), an oil, which was taken directly into the next reaction without purification. To a solution of this aldehyde (200 mg, 0.275 mmol) in *tert*-butanol/water (3:1, 12 mL) at RT was added 2-methyl-2-butene (2.9 mL, 27.5 mmol) followed by $NaH_2PO_4.H_2O$ (379 mg, 2.75 mmol). The mixture was cooled to –5 °C and a solution of $NaClO_2$ (22 mg, 0.248 mmol) in *tert*-butanol/water (3:1, 4 mL) was added dropwise. After 25 min, the reaction mixture was quenched with $NaHSO_3$ solution (sat. aq.; 20 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/acetone, 95:5→9:1) afforded the *title compound* (143 mg, 70%) as a colourless oil. R_f 0.20 (petrol/acetone, 85:15); $[\alpha]_D^{20}$ +8.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88–1.16 (4 H, m, C(5)H_2 and C(6)H_2), 0.97 (3 H, s, C(3)CH_3), 0.99 (3 H, d, $J_{9,10}$ = 6.2 Hz, C(10)H_3), 1.03 (9 H, s, $(CH_3)_3$C-), 1.24–1.38 (3 H, m, C(4)H_2 and C(8)*H*H′), 1.75–1.80 (1 H, m, C(8)H*H*′), 2.27 and 2.41 (2 × 1 H, 2 × d, J_{gem} = 15.0 Hz, C(2)H_2), 2.91 (1 H, dd, J_{gem} = 13.4 Hz, $J_{1',2'}$ = 5.8 Hz) and 2.99 (1 H, dd, J_{gem} = 13.4 Hz, $J_{1',2'}$ = 7.9 Hz, C(2′)H_2), 3.18–3.24 (1 H, m, H-7), 3.89 (1 H, sext, $J_{9,10}$ = 6.2 H, H-9), 4.22 and 4.25 (2 × 1 H, 2 × d, J_{gem} = 11.6 Hz, OC*H*$_2$Ph), 4.69 (1 H, dd, $J_{1',2'}$ = 7.9 Hz, $J_{1',2'}$ = 5.8 Hz, H-1′), 7.03–7.07 (2 H, m), 7.12–7.15 (2 H, m), 7.17–7.29 (11 H, m), 7.31–7.42 (6 H, m) and 7.63–7.66 (4 H, m, 5 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3 ($(CH_3)_3$*C*), 20.2 (C-5), 23.1 (C(3)*C*H$_3$), 23.7 (C-10), 27.2 ((*C*H$_3$)$_3$C), 34.4 (C-6), 39.7 (C-4), 44.2 (C-8), 44.6 (C-2), 46.6 (C-2′), 67.2 (C-9), 70.5 (O*C*H$_2$Ph), 76.1 (C-7), 76.9 (C-1′), 78.8 (C-3), 126.4, 126.8, 127.5, 127.6, 127.7, 127.8, 127.9, 128.38, 128.41, 128.6, 129.6, 129.65, 129.70 and 129.8 (Ph), 134.3 and 134.8 (*i*-Ph), 136.0 and 136.03 (Ph), 137.7, 138.9 and 143.6 (*i*-Ph), 172.5 (C-1); IR (film) ν_{max}/cm^{-1} 3067 (m), 3029 (m), 2931 (s), 2858 (m), 1707 (s), 1454 (m), 1428 (m), 1111 (s), 1056 (s), 701 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{48}H_{58}NaO_5Si$ [MNa$^+$] 765.3946, found 765.3941.

(3*R*,7*S*,9*R*)-9-(*tert*-Butyldiphenylsilyl)oxy-3,7-dihydroxy-3-methyldecanoic acid (18)

To a solution of (3*R*,7*S*,9*R*)-7-benzyloxy-2-(*tert*-butyldiphenylsilyl)oxy-3-[(*R*)-1′,2′-diphenylethyl]oxy-8-methyldecan-oic acid (170 mg, 0.229 mmol) in ethyl acetate (4.2 mL) and ethanol (4.2 mL) was added Pd black

(43 mg). The mixture was stirred at RT for 24 h under a hydrogen atmosphere (balloon) and another portion of Pd black (43 mg) was added. After a further 42 h at RT, the mixture was filtered through a pad of Celite® and the filtrate was concentrated *in vacuo*. Purification by flash chromatography (silica gel, dichloromethane/methanol, 95:5→9:1) afforded *acid* **18** (92 mg, 85%) as a colourless oil. R_f 0.10 (dichloromethane/methanol, 95:5); $[\alpha]_D^{20}$ –4.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (3 H, d, $J_{9,10}$ = 6.1 Hz, C(10)H_3), 1.04 (9 H, s, $(CH_3)_3C$-), 1.30 (3 H, s, C(3)CH_3), 1.34–1.44 (3 H, m, C(5)*H*H′ and C(6)H_2), 1.47–1.67 (4 H, m, C(4)H_2, C(5)H*H*′ and C(8)*H*H′), 1.70–1.79 (1 H, m, C(8)H*H*′), 2.46 and 2.54 (d, J_{gem} = 15.7 Hz, C(2)H_2), 3.81–3.90 (1 H, m, H-7), 4.06–4.14 (1 H, m, H-9), 7.33–7.46 (6 H, m) and 7.69–7.74 (4 H, m, 2 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2 and 19.7 ($(CH_3)_3C$ and C-5), 24.0 (C-10), 26.9 (C(3)CH_3), 27.1 ($(CH_3)_3C$), 37.5 (C-6), 41.3 (C-4), 44.9 (C-2), 46.4 (C-8), 70.0 (C-9), 70.6 (C-7), 72.0 (C-3), 127.6, 127.8, 129.7 and 129.9 (Ph), 133.7 and 134.5 (*i*-Ph), 135.9 and 136.0 (Ph), 176.4 (C-1); IR (film) ν_{max}/cm^{-1} 3357 (m), 2963 (s), 2857 (m), 1705 (s), 1427 (m), 1309 (m), 1110 (s), 703 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{27}H_{40}NaO_5Si$ [MNa$^+$] 495.2537, found 495.2528.

(2*R*,4*S*)-2,4-[Bis(triethylsilyl)oxy]non-8-ene (19)

To a solution of diol **13** (256 mg, 1.62 mmol) in pyridine (2.7 mL) was added TESCl (1.09 mL, 6.47 mmol). The mixture was stirred at 60 °C for 14 h. Ether (10 mL) was added, the organic layer was washed with $CuSO_4$ solution (sat. aq., 4 × 10 mL) and the aqueous layer was extracted with ether (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 99:1) afforded the *title compound* (**19**) (545 mg, 87%) as a colourless oil. R_f 0.10 (petrol); $[\alpha]_D^{20}$ –4.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 and 0.59 (2 × 6 H, 2 × q, *J* = 8.0 Hz, 2 × $(CH_3CH_2)_3Si$), 0.97 (18 H, t, *J* = 8.0 Hz, 2 × $(CH_3CH_2)_3Si$), 1.15 (3 H, d, $J_{1,2}$ = 6.0 Hz, C(1)H_3), 1.37–1.55 (5 H, m, C(3)*H*H′, C(5)H_2 and C(6)H_2), 1.66–1.72 (1 H, m, C(3)H*H*′), 2.00–2.07 (2 H, m, C(7)H_2), 3.75–3.79 (1 H, m, H-4), 3.91 (1 H, sext, $J_{1,2}$= $J_{2,3}$ = 6.0 Hz, H-2), 4.94–4.96 and 4.98–5.03 (2 × 1 H, 2 × m, C(9)H_2), 5.81 (1 H, ddt, $J_{8,9\text{-}trans}$ = 16.9 Hz, $J_{8,9\text{-}cis}$ = 10.2 Hz, $J_{7,8}$ = 6.6 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1 and 5.3 ($(CH_3CH_2)_3Si$), 7.0 and 7.1 ($(CH_3CH_2)_3Si$), 24.2 (C-1), 24.7 (C-6), 34.1 (C-7), 37.0 (C-5), 47.8 (C-3), 65.9 (C-2), 69.8 (C-4), 114.5 (C-9), 139.0 (C-8); IR (film) ν_{max}/cm^{-1} 2955 (s), 2878 (s), 1642 (w), 1459 (m), 1415 (m), 1378 (m), 1239 (m), 1071 (s), 1006 (s), 910 (m), 741 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{21}H_{46}NaO_2Si$ [MNa$^+$] 409.2929, found 409.2930.

(2*R*,4*S*)-2,4-[Di(*tert*-butyldiphenylsilyl)oxy]non-8-ene (20)

To a solution of diol **13** (50 mg, 0.136 mmol) in DMF (0.4 mL) at RT was added imidazole (108 mg, 1.58 mmol) followed by TBDPSCl (205 μL, 0.790 mmol) and the mixture was stirred for 14 h. Water (2 mL) was

added and the mixture extracted with ether (3 × 5 mL); the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 9:1) afforded the *title compound* (**20**) (207 mg, 100%) as a colourless oil. R_f 0.20 (petrol); $[\alpha]_D^{20}$ +13.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3 H, d, $J_{1,2}$ = 5.8 Hz, C(1)H_3), 1.04 (18 H, s, 2 × $(CH_3)_3C$-), 1.25–1.45 (4 H, m, C(5)H_2 and C(6)H_2), 1.56–1.63 (1 H, m, C(3)*H*H′), 1.83–1.88 (2 H, m, C(7)H_2), 1.94 (1 H, dt, J_{gem} = 13.3 Hz, $J_{2,3}$ = $J_{3,4}$ = 6.7 Hz, C(3)H*H′*), 3.89–4.02 (2 H, m, H-2 and H-4), 4.91–4.96 (2 H, m, C(9)H_2), 5.65–5.75 (1 H, m, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3 and 19.5 ($(CH_3)_3C$), 23.6 and 23.9 (C-1 and C-6), 27.1 and 27.2 ($(CH_3)_3C$), 33.9 (C-7), 36.3 (C-5), 46.5 (C-3), 67.4 (C-2), 70.8 (C-4), 114.4 (C-9), 127.47, 127.52, 127.57, 127.63, 129.46, 129.51, 129.52 and 129.6 (Ph), 134.4, 134.6, 134.7 and 135.0 (*i*-Ph), 136.0, 136.05 and 136.08 (Ph), 139.0 (C-8); IR (film) ν_{max}/cm$^-$ 3071 (m), 2932 (s), 2858 (s), 1640 (w), 1590 (w), 1472 (m), 1427 (s), 1378 (m), 1111 (s), 822 (m), 702 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{41}H_{54}NaO_2Si_2$ [MNa$^+$] 567.3555, found 567.3558.

(2*R*,4*S*)-2,4-Di(benzyloxy)non-8-ene (21)

To a solution of diol **13** (50 mg, 0.316 mmol) in THF (1 mL) was added NaH (60% dispersion in mineral oil, 38 mg, 0.948 mmol). After 30 min, tetrabutylammonium iodide (117 mg, 0.316 mmol) and benzyl bromide (113 μl, 0.948 mmol) were added, the reaction mixture was stirred for 14 h at RT, and the reaction was then quenched with water (1 mL). The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ether, 96:4) afforded the *title compound* (**21**) (83 mg, 78%) as a colourless oil. R_f 0.45 (petrol/ethyl acetate, 96:4); $[\alpha]_D^{20}$ –15.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (3 H, d, $J_{1,2}$ = 6.1 Hz, CH_3), 1.36–1.59 (5 H, m, C(3)*H*H′, C(5)H_2 and C(6)H_2), 1.97–2.10 (3 H, m, C(3)H*H′* and C(7)H_2), 3.47–3.73 (2 H, m, H-2 and H-4), 4.42 (1 H, d, J_{gem} = 11.7 Hz, C*H*H′Ph), 4.48 (2 H, s, CH_2Ph), 4.58 (1 H, d, J_{gem} = 11.7 Hz, CH*H′*Ph), 4.91–5.04 (2 H, m, C(9)H_2), 5.79 (1 H, ddt, $J_{8,9\text{-}trans}$ = 16.9 Hz, $J_{8,9\text{-}cis}$ = 10.2 Hz, $J_{7,8}$ = 6.6 Hz , H-8), 7.27–7.35 (10 H, m, 2 × Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.9 (C-1), 24.6 (C-6), 33.5 (C-5), 33.9 (C-7), 41.4 (C-3), 70.4 and 70.7 (CH_2Ph), 72.1 (C-2), 76.0 (C-4), 114.6 (C-9), 127.6, 127.8, 127.9, 128.42 and 128.43 (Ph), 138.9 and 139.0 (C-8 and *i*-Ph); IR (film) ν_{max}/cm^{-1} 3064 (m), 3031 (m), 2934 (s), 2864 (m), 1640(w), 1454 (s), 1374 (m), 1092 (s), 1066 (s) 912 (m), 698 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{23}H_{30}NaO_2$ [MNa$^+$] 361.2138, found 361.2132.

(6*S*,8*R*)-6,8-Bis[(triethylsilyl)oxy]nonan-2-one (22)

Pyridine (4 μl, 0.049 mmol) was added to a suspension of $Pd(OAc)_2$ (2.9 mg, 0.013 mmol) in toluene (1.3 mL). The ambient atmosphere was replaced with oxygen, the mixture was heated to 60 °C, and propan-2-ol (260 μL) was added. After 5 min, a solution of alkene **19** (100 mg, 0.259 mmol) in propan-2-ol (1 mL) was added and the

mixture was stirred for 14 h at 60 °C. The mixture was cooled, the solvent was evaporated *in vacuo* and the residue was then purified by column chromatography (petrol/ether, 99:1→95:5) to afford the *title compound* (**22**) (80 mg, 76%) as a colourless oil. R_f 0.40 (petrol/ether, 9:1); $[\alpha]_D^{20}$ –4.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 and 0.59 (2 × 6 H, 2 × q, J = 7.9 Hz, 2 × $(CH_3CH_2)_3Si$), 0.95 (18 H, t, J = 7.9 Hz, 2 × $(CH_3CH_2)_3Si$), 1.14 (3 H, d, $J_{8,9}$ = 6.0 Hz, $C(9)H_3$), 1.33–1.71 (6 H, m, $C(4)H_2$, $C(5)H_2$ and $C(7)H_2$), 2.11 (3 H, s, $C(1)H_3$), 2.40 (2 H, t, $J_{3,4}$ = 7.5 Hz, $C(3)H_2$), 3.72–3.76 (1 H, m, H-6), 3.87 (1 H, sext, $J_{7,8}$ = $J_{8,9}$ = 6.0 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.1 and 5.2 ($(CH_3CH_2)_3Si$), 6.99 and 7.03 ($(CH_3CH_2)_3Si$), 19.7 (C-4), 24.2 (C-9), 29.8 (C-1), 36.8 and 47.6 (C-5 and C-7), 44.1 (C-3), 65.8 (C-8), 69.4 (C-6), 209.0 (C-2); IR (film) ν_{max}/cm^{-1} 2956 (s), 2878 (s), 1720 (s), 1459 (m), 1415 (m), 1375 (m), 1239 (m), 1006 (s), 742 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{21}H_{46}NaO_3Si_2$ [MNa$^+$] 425.2878, found 425.2879.

(6*S*,8*R*)-6,8-Di[(*tert*-butyldiphenylsilyl)oxy]nonan-2-one (23)

Pyridine (2.5 μl, 0.031 mmol) was added to a mixture of $Pd(OAc)_2$ (1.8 mg, 0.008 mmol) and toluene (0.8 mL). The ambient atmosphere was replaced with oxygen, the mixture was heated to 60 °C, and propan-2-ol (160 μL) was added. After 5 min, a solution of alkene **20** (100 mg, 0.157 mmol) in propan-2-ol (0.6 mL) was added and the mixture was stirred for 14 h at 60 °C. The mixture was cooled, the solvent was evaporated *in vacuo* and the residue was then purified by column chromatography (petrol/ether, 99:1) to afford the *title compound* (**23**) (97 mg, 95%) as a colourless oil. R_f 0.20 (petrol/ether, 9:1); $[\alpha]_D^{20}$ +69.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (3 H, d, $J_{8,9}$ = 6.0 Hz, $C(9)H_3$), 1.00 and 1.01 (2 × s, 2 × 9 H, 2 × $(CH_3)_3C$-), 1.21–1.50 (4 H, m, $C(4)H_2$ and $C(5)H_2$), 1.55–1.61 and 1.88–1.94 (2 × 1 H, 2 × m, $C(7)H_2$), 2.03 (3 H, s, $C(1)H_3$), 2.12 (2 H, t, $J_{3,4}$ = 7.4 Hz, $C(3)H_2$), 3.85–3.91 (1 H, m, H-6), 3.92–3.97 (1 H, m, H-8), 7.31–7.37 (8 H, m), 7.40–7.45 (4 H, m) and 7.61–7.64 (8 H, m, 4 × Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0 (C-4), 19.3 and 19.5 ($(CH_3)_3C$), 23.6 (C-9), 27.1 and 27.2 ($(CH_3)_3C$), 29.8 (C-1), 36.1 (C-5), 43.8 (C-3), 46.3 (C-7), 67.3 (C-8), 70.5 (C-6), 127.5, 127.58, 127.61, 127.64, 129.5 and 129.6 (Ph), 134.4, 134.6 and 134.9 (*i*-Ph), 135.96 and 136.03 (Ph), 209.0 (C-2); IR (film) ν_{max}/cm^{-1} 3071 (s), 2998 (s), 2857(s), 1716 (s), 1589 (m), 1472 (s), 1427 (s), 1361 (s), 1110 (s), 822 (s), 701 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{41}H_{54}NaO_3Si_2$ [MNa$^+$] 673.3504, found 673.3484.

(6*S*,8*R*)-6,8-Di(benzyloxy)nonan-2-one (24)

A mixture of $PdCl_2$ (20.2 mg, 0.114 mmol) and CuCl (113 mg, 1.14 mmol) in aqueous dimethylformamide (DMF/water, 7:1, 0.91 mL) was stirred at RT for 1 h under an oxygen atmosphere. The initially black solution gradually became green as oxygen was absorbed. Then, a solution of alkene **21** (385 mg, 1.14 mmol) in aqueous dimethylformamide (DMF/water, 7:1, 171 μL) was added and the mixture was stirred at RT for 24 h. Water (2 mL) was added, the aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layers

were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography (silica gel, petrol/ethyl acetate, 95:5→9:1) afforded the *title compound* (**24**) (243 mg, 60%) as a colourless oil. R_f 0.10 (petrol/ethyl acetate, 96:4); $[\alpha]_D^{20}$ –4.5 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (3 H, d, $J_{8,9}$ = 6.1 Hz, C(9)H_3), 1.45–1.71 (5 H, m, C(4)H_2, C(5)H_2 and C(7)*H*H′), 2.00–2.07 (1 H, m, C(7)H*H′*), 2.09 (3 H, s, C(1)H_3), 2.35 (2 H, t, $J_{3,4}$ = 7.3 Hz, C(3)H_2), 3.53 (1 H, quint, $J_{5,6}$ = $J_{6,7}$ = 5.9 Hz, H-6), 3.60–3.67 (1 H, m, H-8), 4.41 (1 H, d, J_{gem} = 11.7 Hz, C*H*HPh), 4.48 (2 H, s, CH_2Ph), 4.58 (1 H, d, J_{gem} = 11.7 Hz, CH*H*Ph), 7.28–7.36 (10 H, m, 2 × Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6 (C-4), 19.9 (C-9), 29.9 (C-1), 33.3 (C-5), 41.2 (C-7), 43.7 (C-3), 70.3 and 70.6 (*C*H_2Ph), 72.0 (C-8), 75.8 (C-6), 127.5, 127.6, 127.8, 128.0 and 128.4 (Ph), 138.8 and 138.9 (*i*-Ph), 209.1 (C-2); IR (film) ν_{max}/cm^{-1} 3365 (m), 2932 (s), 1714 (s), 1453 (m), 1374 (m), 1276 (m), 1093 (m), 714 (m); HRMS (ESI$^+$) *m/z* calcd. for $C_{23}H_{30}NaO_3$ [MNa$^+$] 377.2087, found 377.2081.

Procedures for Scheme 5

Ethyl 8-hydroxyoct-4-ynoate

To a cold (–85 °C) solution of ethyl pent-4-ynoate **25**[7] (500 mg, 3.96 mmol) in THF (3.5 mL) was added butyllithium (1.6 M in hexane, 2.50 mL, 4.0 mmol) and stirring was continued for 15 min. $BF_3{\cdot}OEt_2$ (0.49 mL, 3.97 mmol) was added, the mixture stirred for another 15 min, then oxetane (130 µL, 2.00 mmol) was added. The mixture was stirred for 3 h and the temperature was then slowly raised to RT over 30 min. The mixture was then poured into $NaHCO_3$ solution (sat. aq., 15 mL) and the aqueous layer was extracted with ether (3 × 25 mL). The combined organic extracts were washed with brine (15 mL), dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. Flash chromatography (silica gel, petrol/ether, 4:1) afforded the *title compound* as a colourless oil (230 mg, 63%). R_f 0.30 (petrol/ether, 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (3 H, t, J = 7.1 Hz, CH_3), 1.56 (1 H, br s, OH), 1.73 (2 H, quint, $J_{6,7} = J_{7,8}$ = 6.5 Hz, C(7)H_2), 2.27 (2 H, t, $J_{6,7}$ = 6.5 Hz, C(6)H_2), 2.46–2.52 (4 H, m, C(2)H_2 and C(3)H_2), 3.75 (2 H, t, $J_{7,8}$ = 6.5 Hz, C(8)H_2), 4.16 (2 H, q, J = 7.1 Hz, CH_2CH$_3$); ^{13}C NMR (125MHz, $CDCl_3$) δ 14.2 (CH_3), 14.7 (C-3), 15.3 (C-6), 31.4 (C-7), 34.0 (C-2), 60.6 (CH$_2$CH$_3$), 61.9 (C-8), 78.9 (C-4), 80.2 (C-5), 172.2 (C-1); IR (film) ν_{max}/cm^{-1} 3409 (br, m), 2937 (m), 1735 (s), 1436 (m), 1375 (m), 1256 (m), 1166 (m), 1052 (m), 939 (w), 854 (w); HRMS (ESI$^+$) *m/z* calcd. for $C_{10}H_{16}NaO_3$ [MNa$^+$] 207.0992, found 207.0992.

Ethyl 8-oxooct-4-ynoate (26)

To a cooled (0 °C) solution of ethyl 8-hydroxy-4-octynoate (50 mg, 0.271 mmol) in anhydrous dichloromethane (6 mL) was added Dess–Martin periodinane (345 mg, 0.813 mmol). The mixture was stirred for 15 min at 0 °C and then allowed to warm to RT. After stirring at RT for 5 h the mixture was diluted with ether (10 mL) and aqueous buffer [10 mL of a solution made from $Na_2S_2O_3$ (*ca*. 100–158 g/L) and Na_2CO_3 (*ca*. 100 g/L)], the resulting mixture was stirred for 15 min and the layers were separated. The aqueous layer was extracted with ether (3 × 10 mL) and the combined organic portions were washed with brine (10 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure and flash chromatography (silica gel, petrol/ether, 7:3) afforded the *title compound* (**26**) as a colourless oil (46 mg, 94%). R_f 0.47 (petrol/ether, 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (3 H, t, J = 7.1 Hz, CH_3), 2.46–2.48 (6 H, m, C(2)H_2, C(3)H_2, and C(6)H_2), 2.62 (2 H, t, $J_{6,7}$ = 6.8 Hz, C(7)H_2), 4.16 (2 H, q, J = 7.1 Hz, CH_2O), 9.79 (1 H, s, H-8); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.0 (C-6), 14.2 (CH_3), 14.7 (C-3), 33.8 (C-2), 42.8 (C-7), 60.6 (CH_2O), 78.7 (C-5), 79.4 (C-4), 172.0 (C-1), 200.8 (C-8); IR (film) ν_{max}/cm^{-1} 2982 (m), 2918 (m), 2849 (w), 2731 (w), 1732 (s), 1375 (m), 1166 (m), 1043 (m), 853 (w); HRMS (ESI$^+$) *m/z* calcd. for $C_{10}H_{14}NaO_3$ [MNa$^+$] 205.0835, found 205.0832.

Ethyl (*Z*)-pentacos-8-en-4-ynoate (27)

NaHMDS solution (1.0 M in THF, 2.0 mL, 2.0 mmol) was added to a suspension of heptadecyltriphenyl-phosphonium iodide[8] (1.38 g, 2.20 mmol) in THF (9 mL) at 0 °C. The resulting orange solution was allowed to warm to RT, stirred for 1 h, then cooled to –20 °C. A solution of aldehyde **26** (200 mg, 1.10 mmol) in THF (4.5 mL) was added and the resulting mixture was warmed to RT and stirred for 3 h. The mixture was then poured into a mixture of ether (60 mL) and NH_4Cl solution (sat. aq., 32 mL), the layers were separated, and the organic layer was washed with brine (20 mL), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (silica gel, petrol then petrol/ether, 99:1) to afford the *title compound* (**27**) as a colourless oil (300 mg, 68%). R_f 0.52 (hexane/ethyl acetate, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3 H, t, $J_{24,25}$ = 6.9 Hz, C(25)H_3), 1.25 (31 H, app. br s, CH_3CH$_2$O and C(11–24)H_2), 2.02 (2 H, q, $J_{9,10}$ = $J_{10,11}$ = 6.8 Hz, C(10)H_2), 2.11–2.24 (4 H, m, C(6)H_2 and C(7)H_2), 2.43–2.52 (4 H, m, C(2)H_2 and C(3)H_2), 4.15 (2 H, q, J = 7.1 Hz, CH$_2$O), 5.35–5.45 (2 H, m, H-8 and H-9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (C-25), 14.2 (*C*H$_3$CH$_2$O), 14.8 (C-3), 19.1 (C-6), 22.7 (? C-24), 26.9 (C-7), 27.3 (C-10), 29.3–31.9 (C-(11–23)), 34.1 (C-2), 60.5 (CH$_2$O), 78.3 (C-4), 80.6 (C-5), 127.8 (C-8), 131.3 (C-9), 172.2 (C-1) [minor resonances at δ 128.3 and 131.8 were attributed to the *E* alkene stereoisomer]; IR (film) ν_{max}/cm^{-1} 2924 (s), 2854 (s), 1741 (s), 1466 (m), 1373 (m), 1163 (m), 1046 (w); HRMS (ESI$^+$) *m/z* calcd. for $C_{27}H_{48}NaO_2$ [MNa$^+$] 427.3547, found 427.3551.

(*Z*)-Pentacos-8-en-4-ynoic acid[8,9] (3)

To a solution of ester **27** (13 mg, 32.1 μmol) in THF (0.378 mL) and methanol (0.122 mL) was added LiOH solution (aq., 1 M, 0.1 mL, 0.1 mmol). The resulting mixture was stirred for 3 h at RT during which time a white precipitate formed. The reaction mixture was then poured into a mixture of $CHCl_3$ (5 mL) and hydrochloric acid (1.2 M, 2 mL). The layers were separated and the aqueous layer was extracted with $CHCl_3$ (3 × 5 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the title compound (**3**) as a white solid (12 mg, 100%). R_f 0.20 (hexane/ethyl acetate, 95:5); M.p. = 70–74 °C (lit.[8] m.p. = 73–75 °C, lit.[9] m.p. = 75–77 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3 H, t, $J_{24,25}$ = 6.9 Hz, C(25)H_3), 1.25 (28 H, app. br s, C(11–24)H_2), 2.02 (2 H, q, $J_{9,10}$ = $J_{10,11}$ = 6.8 Hz, C(10)H_2), 2.14–2.24 (4 H, m, C(6)H_2 and C(7)H_2), 2.47 (2 H, t, $J_{2,3}$ = 6.8 Hz, C(3)H_2), 2.56 (2 H, t, $J_{2,3}$ = 6.8 Hz, C(2)H_2), 5.35–5.45 (2 H, m, H-8 and H-9); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (C-25), 14.5 (C-3), 19.1 (C-6), 22.7 (? C-24), 26.8 (C-7), 27.3 (C-10), 29.3-31.9 (C-(11–23)), 33.9 (br, C-2), 78.0 (C-4), 80.9 (C-5), 127.8 (C-8), 131.3 (C-9), 177.5 (br, C-1) [minor resonances at δ 128.3 and 131.8 were attributed to the *E* alkene stereoisomer]; IR (film) ν_{max}/cm^{-1} 3445 (br, w), 2916 (s), 2849 (s), 1695 (s), 1470 (m), 1302 (w), 1260 (m), 1212 (w), 1104 (m), 1018 (m), 912 (w), 798 (m); HRMS (ESI$^+$) *m/z* calcd. for $C_{25}H_{44}NaO_2$ [MNa$^+$] 399.3234, found 399.3241.

Procedures for Scheme 6

2-(Trimethylsilyl)ethyl (3*R*,7*S*,9*R*)-7-acetoxy-3,9-dihydroxy-3-methyldecanoate

To a stirred solution of ester **4** (35 mg, 71.4 μmol) in acetonitrile (1.6 mL) at RT was added hydrofluoric acid (aq., 1%, 0.15 mL, 71.4 μmol) and the mixture was stirred for 1 h then quenched with $NaHCO_3$ aolution (sat. aq., 4.5 mL). The mixture was extracted with ethyl acetate (3 × 10 mL) and the combined organic extracts were washed with NH_4Cl solution (sat., 6 ml), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue, the *title compound* (27 mg, 100%), a colourless oil, was taken into the next step without further purification. R_f 0.48 (ether); $[\alpha]_D^{25}$ –1.2 (*c* 1.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (9 H, s, $(CH_3)_3Si$), 1.00–1.03 (2 H, m, C*H*$_2$SiMe$_3$), 1.21 (3 H, d, $J_{9,10}$ = 6.2 Hz, C(10)H$_3$), 1.22 (3 H, s, C(3)CH$_3$), 1.35–1.67 (7 H, m, C(4)H$_2$, C(5)H$_2$, C(6)H$_2$, and C(8)*H*H′), 1.76–1.83 (1 H, m, C(8)H*H*′), 2.06 (3 H, s, Ac), 2.41 and 2.48 (2 × 1 H, 2 × d, J_{gem} = 15.7 Hz, C(2)H$_2$), 3.62 (1 H, br s, OH), 3.84–3.92 (1 H, m, H-9), 4.20–4.24 (2 H, m, CH$_2$O), 4.98–5.03 (1 H, m, H-7); ^{13}C NMR (125 MHz, $CDCl_3$) δ –1.5 ((CH$_3$)$_3$Si), 17.3 (*C*H$_2$SiMe$_3$), 19.5 (C-5), 21.3 (*C*H$_3$CO), 23.8 (C-10), 26.5 (C(10)*C*H$_3$), 35.0 (C-6), 41.6 (C-4), 43.7 (C-8), 45.0 (C-2), 63.0 (CH$_2$O), 65.8 (C-7), 70.8 (C-3), 72.5 (C-9), 171.0 (CH$_3$*C*O), 173.2 (C-1); IR (film) ν_{max}/cm^{-1} 3418 (br, s), 2955 (s), 2924 (s), 1732 (s), 1461 (m), 1375 (m), 1249 (s), 1174 (m), 946 (w), 859 (m), 837 (m); HRMS (ESI$^+$) *m/z* calcd. for $C_{18}H_{36}NaO_6Si$ [MNa$^+$] 399.2173, found 399.2175.

2-(Trimethylsilyl)ethyl (3*R*,7*S*,9*R*)-7-acetoxy-3-hydroxy-3-methyl-9-[(*Z*)-pentacos-8′-en-4′-ynoyloxy]-decanoate (28)

To a solution of 2-(trimethylsilyl)ethyl (3*R*,7*S*,9*R*)-7-acetoxy-3,9-dihydroxy-3-methyldecanoate (27 mg, 71.4 μmol) and acid **3** (54 mg, 0.143 mmol) in dichloromethane (1.5 mL) at RT was added successively diisopropylethylamine (62.5 μL, 0.359 mmol), DMAP (9 mg, 73.7 μmol) and *N*,*N*′-diisopropylcarbodiimide (56 μL, 0.362 mmol). The resulting mixture was stirred for 15 h at RT then poured into a mixture of NH_4Cl solution (sat. aq., 5 mL) and ether (20 mL). The layers were separated and the organic layer was washed successively with hydrochloric acid (1.2 M, 5 mL), $NaHCO_3$ solution (sat. aq., 5 mL), and brine (5 mL). The organic soluion was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica gel, petrol/ether, 85:15) to afford the *title compound* (**28**) as a colourless oil (42 mg, 80%). R_f 0.60 (petrol/ether, 1:1); $[\alpha]_D^{25}$ –1.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (9 H, s, $(CH_3)_3Si$), 0.89 (3 H, t, $J_{24',25'}$ = 6.9 Hz, C(25′)H$_3$), 1.00–1.03 (2 H, m, C*H*$_2$SiMe$_3$), 1.22 (3 H, s, C(3)CH$_3$), 1.25 (3 H, d, $J_{9,10}$ = 6.4 Hz, C(10)H$_3$), 1.26 (28 H, app. br s, C(11′–24′)H$_2$), 1.38–1.58 (6 H, m, C(4)H$_2$, C(5)H$_2$, and C(6)H$_2$), 1.68 (1 H, ddd, J_{gem} = 14.1 Hz, $J_{7,8\text{ or }8,9}$ = 6.6 Hz, $J_{7,8\text{ or }8,9}$ = 4.9 Hz) and 1.95 (1 H, ddd, J_{gem} = 14.1 Hz, $J_{7,8\text{ or }8,9}$ = 7.8 Hz, $J_{7,8\text{ or }8,9}$ = 6.6 Hz, C(8)H$_2$), 2.01–2.04 (2 H, m, C(10′)H$_2$), 2.05 (3 H, s, Ac), 2.15–2.23 (4 H,

m, C(6′)H_2 and C(7′)H_2), 2.41 (1 H, d, J_{gem} = 15.6 Hz, C(2)*H*H′), 2.47 (4 H, app. s, C(2′)H_2 and C(3′)H_2), 2.48 (1 H, d, J_{gem} = 15.6 Hz, C(2)H*H*′), 3.61 (1 H, s, OH), 4.20–4.24 (2 H, m, CH_2O), 4.92–4.99 (2 H, m, H-7 and H-9), 5.36–5.45 (2 H, m, H-8′ and H-9′); ^{13}C NMR (125 MHz, $CDCl_3$) δ –1.5 ($(CH_3)_3Si$), 14.1 (C-25′), 14.8 (C-3′), 17.3 (*C*H_2SiMe_3), 19.1 (C-6′), 19.4 (C-5), 20.0 (C-10), 21.2 (*C*H_3CO), 22.7 (? C-24′), 26.5 (C(3)*C*H_3), 26.8 (C-7′), 27.3 (C-10′), 29.3–31.9 (C-(11′–23′)), 34.3 (C-2′), 34.6 (C-6), 40.1 (C-8), 41.6 (C-4), 45.0 (C-2), 63.0 (CH_2O), 68.3 (C-9), 70.7 (C-7), 70.9 (C-3), 78.2 (C-4′), 80.7 (C-5′), 127.8 (C-8′), 131.2 (C-9′), 170.6 (CH_3*C*O), 171.5 (C-1′), 173.2 (C-1) [minor resonances at δ 128.3 and 131.7 were attributed to the *E* alkene stereoisomer]; IR (film) ν_{max}/cm^{-1} 3520 (br, w), 2925 (s), 2854 (s), 1737 (s), 1459 (m), 1374 (m), 1249 (s), 1175 (m), 860 (m), 838 (m); HRMS (ESI$^+$) *m/z* calcd. for $C_{43}H_{78}NaO_7Si$ [MNa$^+$] 757.5409, found 757.5415.

(3*R*,7*S*,9*R*)-7-Acetoxy-3-hydroxy-3-methyl-9-[(*Z*)-pentacos-8′-en-4′-ynoyloxy]decanoic acid[8,9]

To a solution of ester **28** (20 mg, 27.2 μmol) in DMF (0.3 mL) was added a solution of tris(dimethylamino)sulfonium difluorotrimethylsilicate (0.145 M in DMF, 0.38 mL, 55.1 μmol) at RT and the resulting mixture was stirred for 1 h. Ethyl acetate (20 mL) was added and the organic solution was washed with hydrochloric acid (1.2 M, 5 mL), dried ($MgSO_4$), and filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica gel, petrol/ethyl acetate, 4:1 then ethyl acetate) to afford the title compound (15 mg, 87%), a colourless oil. R_f 0.33 (dichloromethane/methanol, 20:1); $[\alpha]_D^{25}$ –2.2 (*c* 0.37, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (3 H, t, $J_{24',25'}$ = 6.9 Hz, C(25′)H_3), 1.23–1.60 (40 H, m, C(4–6)H_2, C(10)H_3, C(3)CH_3, and C(11′–24′)H_2), 1.65–1.70 and 1.92–1.98 (2 × 1 H, 2 × m, C(8)H_2), 1.99–2.05 (5 H, m, Ac and C(10′)H_2), 2.12–2.23 (4 H, m, C(6′)H_2 and C(7′)H_2), 2.41–2.62 (6 H, m, C(2)H_2, C(2′)H_2, and C(3′)H_2), 4.91–5.00 (2 H, m, H-7 and H-9), 5.35–5.44 (2 H, m, H-8′ and H-9′); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (C-25′), 14.8 (C-3′), 19.1 (C-6′), 19.4 (br, C-5), 20.0 (C-10), 21.2 (*C*H_3CO), 22.7 (? C-24′), 26.7 (br, C(3)*C*H_3), 26.8 (C-7′), 27.3 (C-10′), 29.3–31.9 (C-(11′–23′)), 34.3 (C-2′), 34.5 (C-6), 40.2 (C-8), 41.5 (br, C-4), 44.7 (br, C-2), 68.3 (C-9), 70.7 (C-7), 71.0 (br, C-3), 78.2 (C-4′), 80.7 (C-5′), 127.8 (C-8′), 131.3 (C-9′), 170.9 (CH_3*C*O), 171.5 (C-1′), 176.0 (br, C-1) [minor resonances at δ 128.3 and 131.8 were attributed to the *E* alkene stereoisomer]; IR (film) ν_{max}/cm^{-1} 3445 (br, m), 2924 (s), 2853 (s), 1737 (s), 1463 (m), 1375 (m), 1260 (s), 1092 (m), 1022 (s), 800 (s); HRMS (ESI$^+$) *m/z* calcd. for $C_{38}H_{66}NaO_7$ [MNa$^+$] 657.4701, found 657.4695.

Taurospongin A (1)[8,9,10]

N-Hydroxysuccinimide (8.0 mg, 69.5 μmol) then dicyclohexylcarbodiimide (14.6 mg, 70.8 μmol) were added to a solution of (3*R*,7*S*,9*R*)-7-acetoxy-3-hydroxy-3-methyl-9-[(*Z*)-pentacos-8′-en-4′-ynoyloxy]-decanoic acid (15 mg, 23.6 μmol) in 1,4-dioxane (0.80 mL) at RT. The reaction mixture was stirred for 2 h and then diluted with ether (2 mL). The resulting white suspension was filtered and concentrated under reduced pressure to afford the

N-hydroxysuccinate derivative which was immediately taken into the coupling reaction without further purification. A solution of taurine (13.3 mg, 0.106 mmol) and triethylamine (30 μL, 0.215 mmol) in 1,4-dioxane (0.48 mL) and water (0.40 mL) was added to the freshly-prepared *N*-hydroxysuccinate derivative and the reaction mixture was stirred at RT for 1 h. Toluene (2 mL) was added and the reaction mixture was concentrated under reduced pressure to remove water azeotropically (× 2). The residue was freed of the excess taurine by ion-exchange column chromatography (Amberlite® IR-120 Na^+ form, dichloromethane/methanol, 4:1)[†] and then further purified by flash chromatography on silica gel (dichloromethane/methanol, 4:1) to afford taurospongin A (**1**) as a waxy solid (15 mg, 86% for two steps). R_f 0.30 (chloroform/methanol, 4:1); $[\alpha]_D^{25}$ –3.4 (*c* 1.0, $CHCl_3$) [lit.[10] $[\alpha]_D^{27}$ +2.4 (*c* 0.20, solvent not specified), lit.[9] $[\alpha]_D^{25}$ –3.5 (*c* 0.37, $CHCl_3$)]; ^{1}H NMR (500 MHz, CD_3OD) δ 0.90 (3 H, t, $J_{24',25'}$ = 6.9 Hz, C(25′)H_3), 1.21 (3 H, s, C(3)CH_3), 1.25 (3 H, d, $J_{9,10}$ = 6.3 Hz, C(10)H_3), 1.29 (28 H, app. br s, C(11′–24′)H_2), 1.33–1.60 (6 H, m, C(4)H_2, C(5)H_2, and C(6)H_2), 1.75 (1 H, ddd, J_{gem} = 14.3 Hz, $J_{7,8 \text{ or } 8,9}$ = 6.0 Hz, $J_{7,8 \text{ or } 8,9}$ = 5.0 Hz) and 1.91–1.97 (1 H, m, C(8)H_2), 2.01–2.07 (5 H, m, C(10′)H_2 and Ac), 2.13–2.15 (2 H, m, C(6′)H_2), 2.17–2.21 (2 H, m, C(7′)H_2), 2.30 and 2.36 (2 × 1 H, 2 × d, J_{gem} = 14.1 Hz, C(2)H_2), 2.40–2.48 (4 H, m, C(2′)H_2 and C(3′)H_2), 2.99 (2 H, t, *J* = 6.6 Hz, C*H*$_2$NH), 3.63 (2 H, t, *J* = 6.6 Hz, C*H*$_2$$SO_3H$), 4.93–4.99 (2 H, m, H-7 and H-9), 5.37–5.47 (2 H, m, H-8′ and H-9′); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3 H, t, $J_{24',25'}$ = 6.9 Hz, C(25′)H_3), 1.19 (3 H, br s, C(3)CH_3), 1.23–1.61 (37 H, m, C(4–6)H_2, C(10)H_3, and C(11′–24′)H_2), 1.63–1.73 and 1.88–1.98 (2 × 1 H, 2 × m, C(8)H_2), 1.98–2.08 (5 H, m, C(10′)H_2 and Ac), 2.10–2.23 (4 H, m, C(6′)H_2 and C(7′)H_2), 2.24–2.51 (6 H, m, C(2)H_2, C(2′)H_2, and C(3′)H_2), 2.52–2.90 (3 H, br s, NH, OH and SO_3H), 3.13 (2 H, br s, C*H*$_2$NH), 3.66 (2 H, br s, C*H*$_2$$SO_3H$), 4.85–4.99 (2 H, m, H-7 and H-9), 5.34–5.45 (2 H, m, H-8′ and H-9′); ^{13}C NMR (125 MHz, CD_3OD) δ 14.5 (C-25′), 15.6 (C-3′), 19.9 (C-6′), 20.4 (C-10), 20.7 (C-5), 21.2 (*C*H_3CO), 23.8 (? C-24′), 26.8 (C(3)*C*H_3), 28.0 (C-7′), 28.3 (C-10′), 30.4–33.1 (C-(11′–23′)), 35.4 (C-2′), 35.9 (C-6), 36.5 (CH_2SO_3H), 41.4 (C-8), 43.0 (C-4), 47.8 (C-2), 51.5 (CH_2NH), 69.9 (C-9), 72.6 (C-3 and C-7), 79.3 (C-4′), 81.5 (C-5′), 129.2 (C-8′), 132.0 (C-9′), 172.6 (CH_3*C*O), 173.3 (C-1′), 174.2 (C-1) [minor resonances at δ 128.3 and 131.7 were attributed to the *E* alkene stereoisomer]; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1 (C-25′), 14.8 (C-3′), 19.1 (C-6′), 19.6 (br, C-5), 20.0 (C-10), 21.2 (*C*H_3CO), 22.7 (? C-24′), 26.1 (br, C(3)*C*H_3), 26.8 (C-7′), 27.3 (C-10′), 29.3-31.9 (C-(11′–23′)), 34.3 (C-2′), 34.9 (br, C-6), 35.2 (br, CH_2SO_3H), 40.4 (br, C-8), 42.2 (br, C-4), 46.5 (br, C-2), 50.0 (br, CH_2NH), 68.5 (C-9), 71.1 (C-7), 71.8 (br, C-3), 78.2 (C-4′), 80.7 (C-5′), 127.8 (C-8′), 131.2 (C-9′), 171.0 (CH_3*C*O), 171.6 (C-1′), 173.1 (br, C-1) [minor resonances at δ 128.9 and 132.7 were attributed to the *E* alkene stereoisomer]; IR (film) ν_{max}/cm^{-1} 3376 (br, m),

[†] The resin was activated by stirring it gently in a beaker in sufficient hydrochloric acid (1 M) to cover it. After 45 min the resin was separated and washed repeatedly with distilled water until the washings were neutral. The wet resin was then transferred to the column (1.0 cm dia., 8.5 cm bed depth) and washed through with distilled water (× 2) then dichloromethane/methanol (4:1, × 4) prior to loading the sample.

2918 (s), 2850 (s), 1734 (s), 1643 (m), 1375 (m), 1242 (s), 1172 (s), 1050 (m); HRMS (ESI$^-$) *m/z* calcd. for $C_{40}H_{70}NO_9S$ $[M–H]^-$ 740.4777, found 740.4780.

References to known compounds and starting materials

(1) For example: Kraft, P.; Bruneau, A. *Eur. J. Org. Chem*. **2007**, 2257–2267.
(2) Cohen, F.; Overman, L. E. *J. Am. Chem. Soc.* **2001**, *123*, 10782–10783.
(3) The enantiomer has been reported: Redlich, H.; Schnieder, B.; Hofmann, R. W.; Geueke, K.-J. *Liebigs Ann. Chem.* **1983**, 393–411.
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(10) Ishiyama, H.; Ishibashi, M.; Ogawa, A.; Yoshida, S.; Kobayashi, J. *J. Org. Chem.* **1997**, *62*, 3831–3836.

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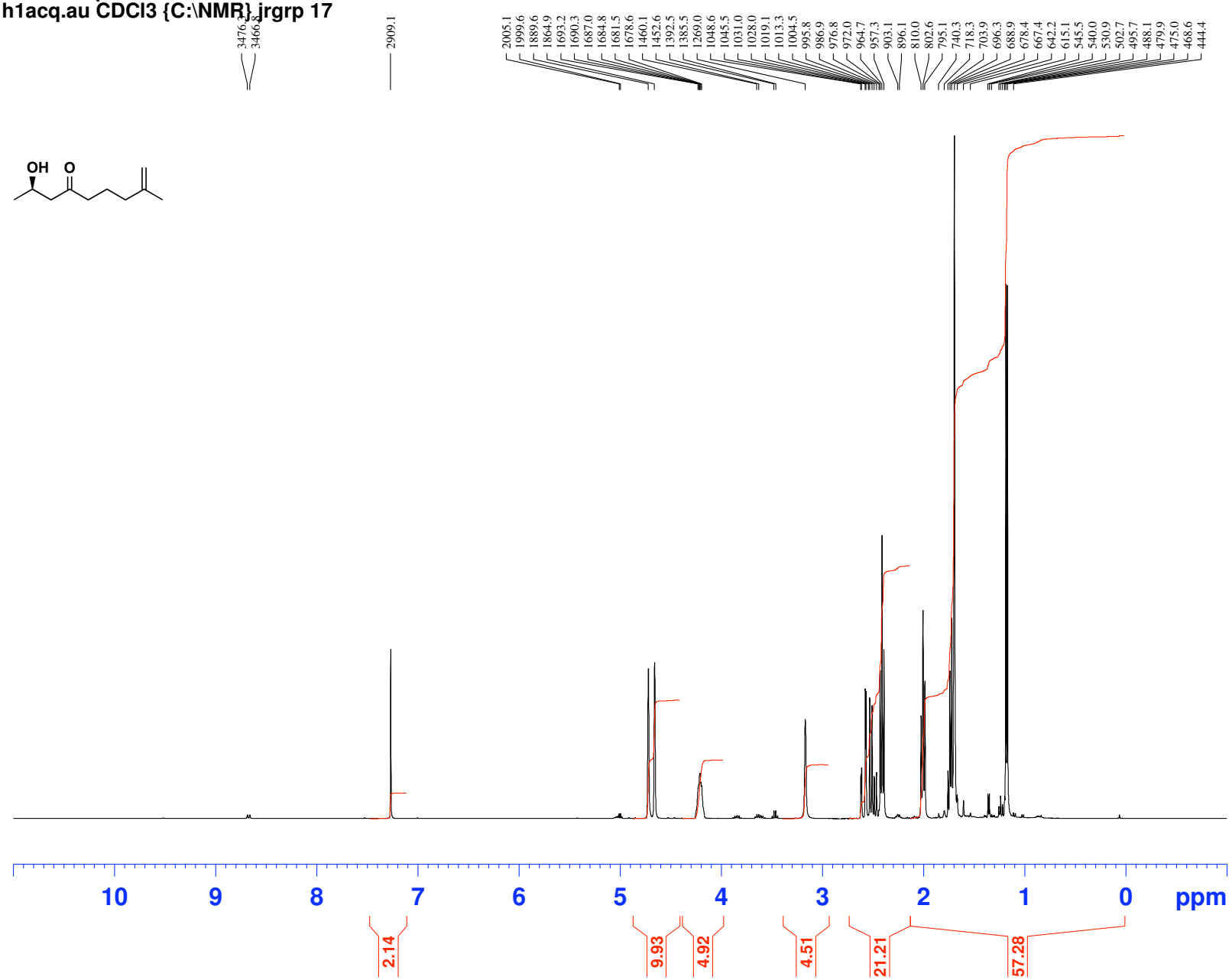

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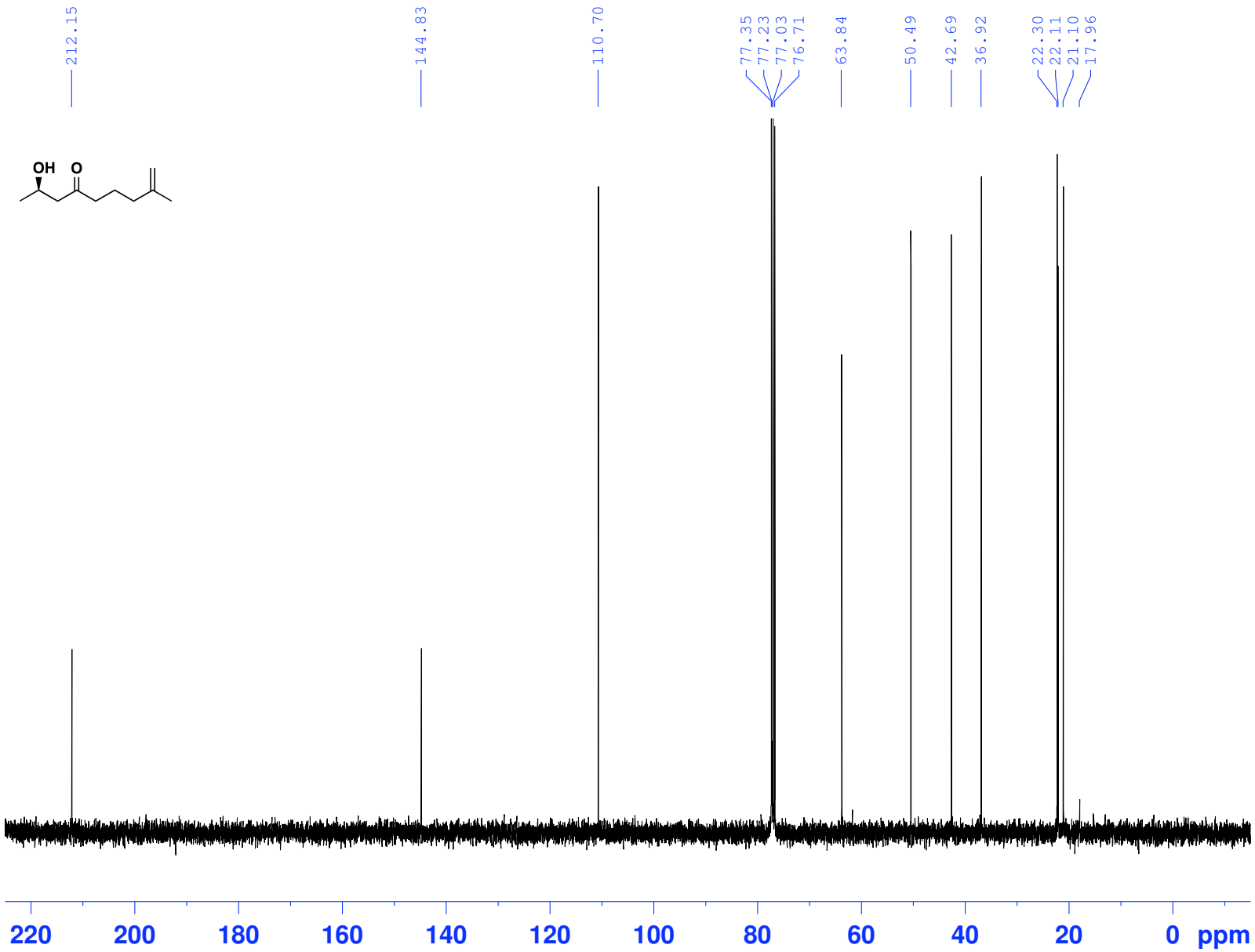


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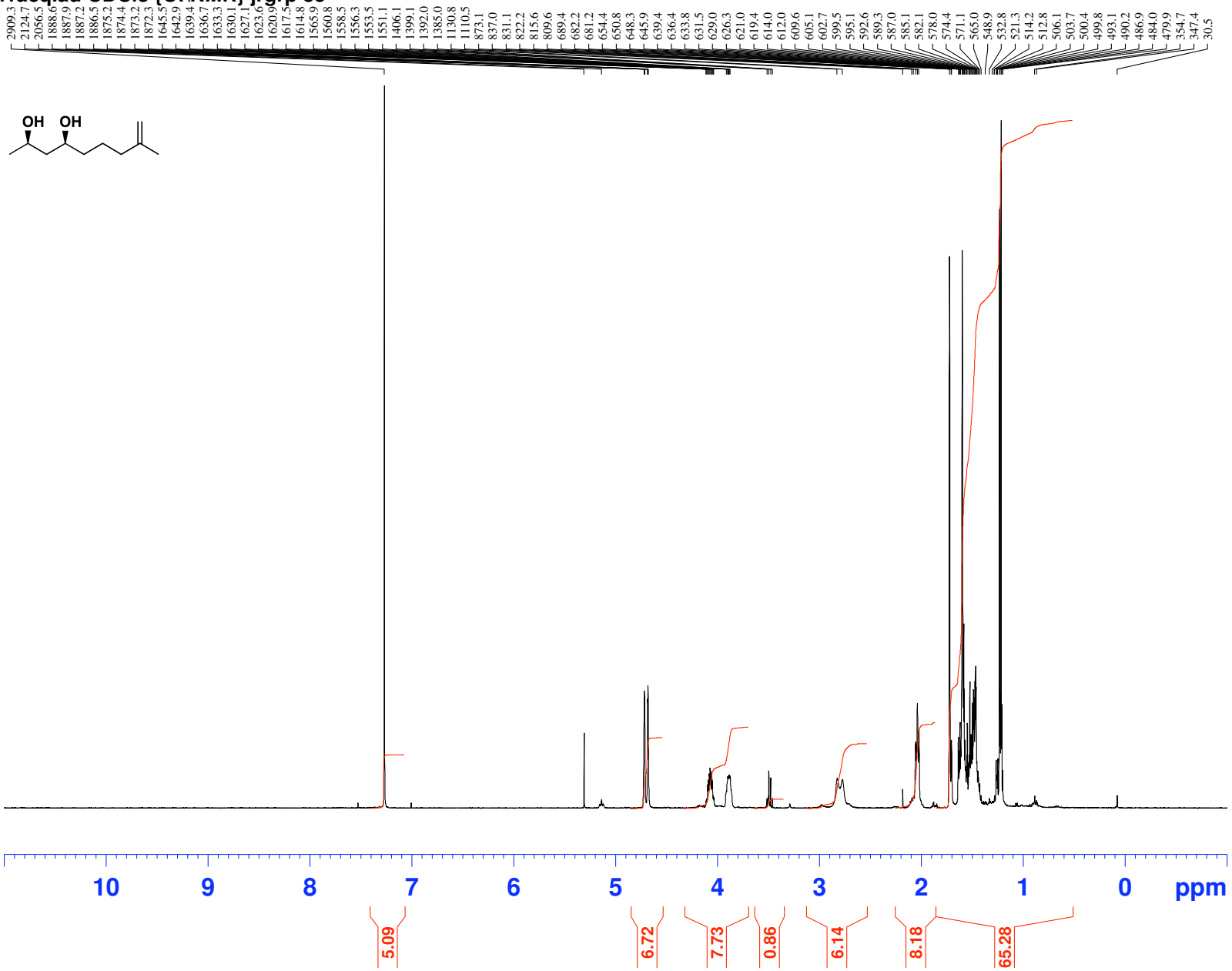


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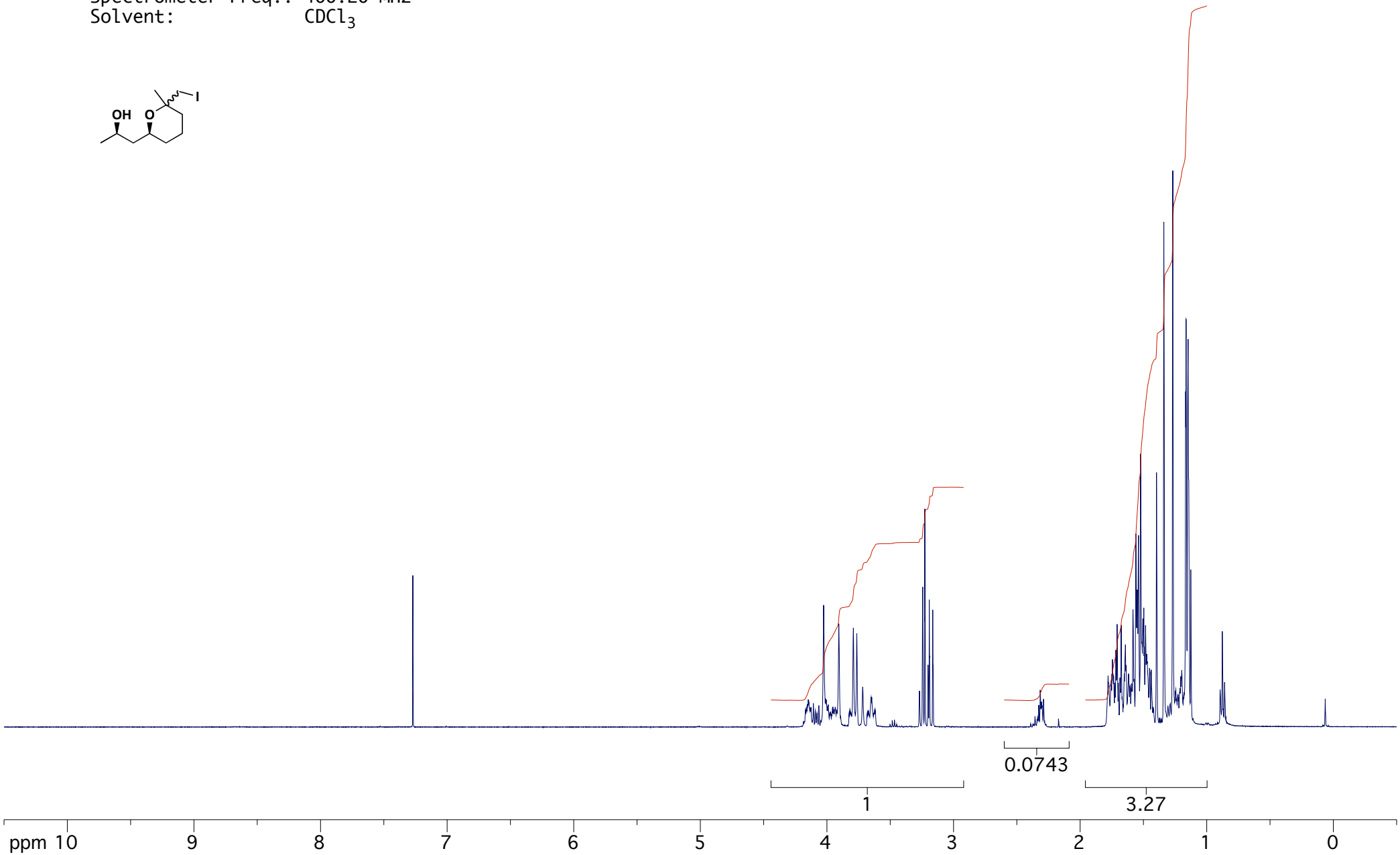

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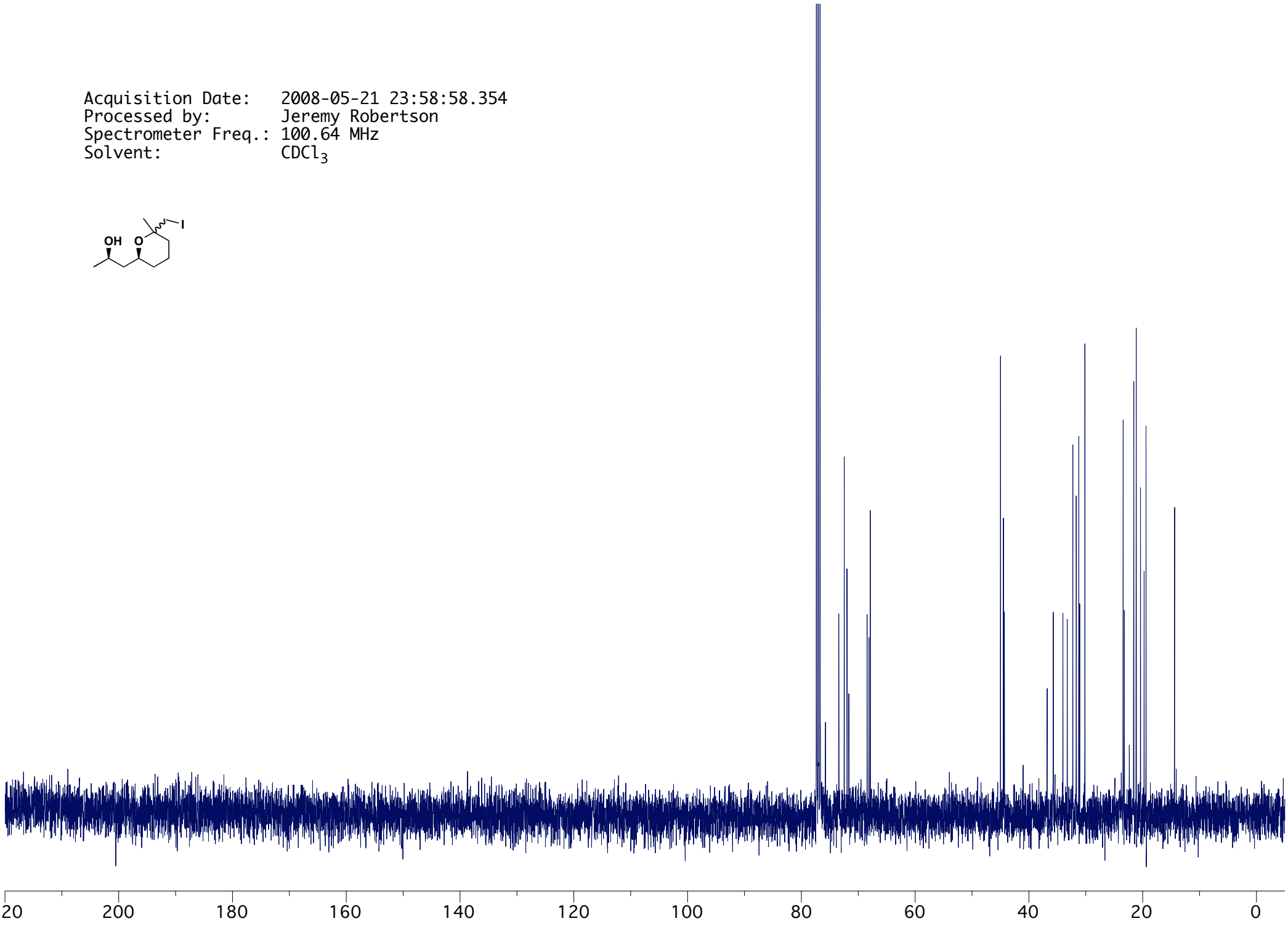

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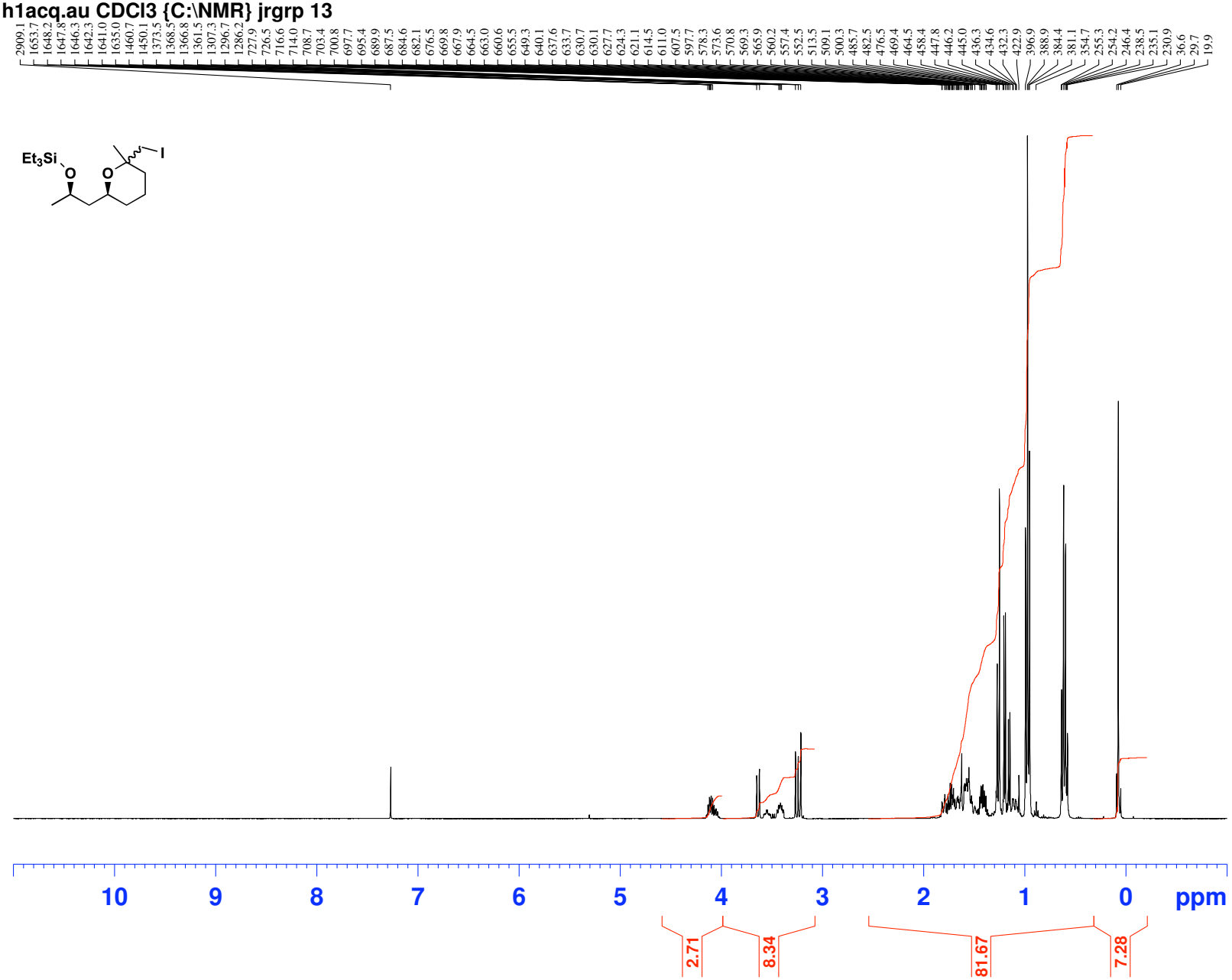

NMR@CHEM.OX

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Instrument DQX400
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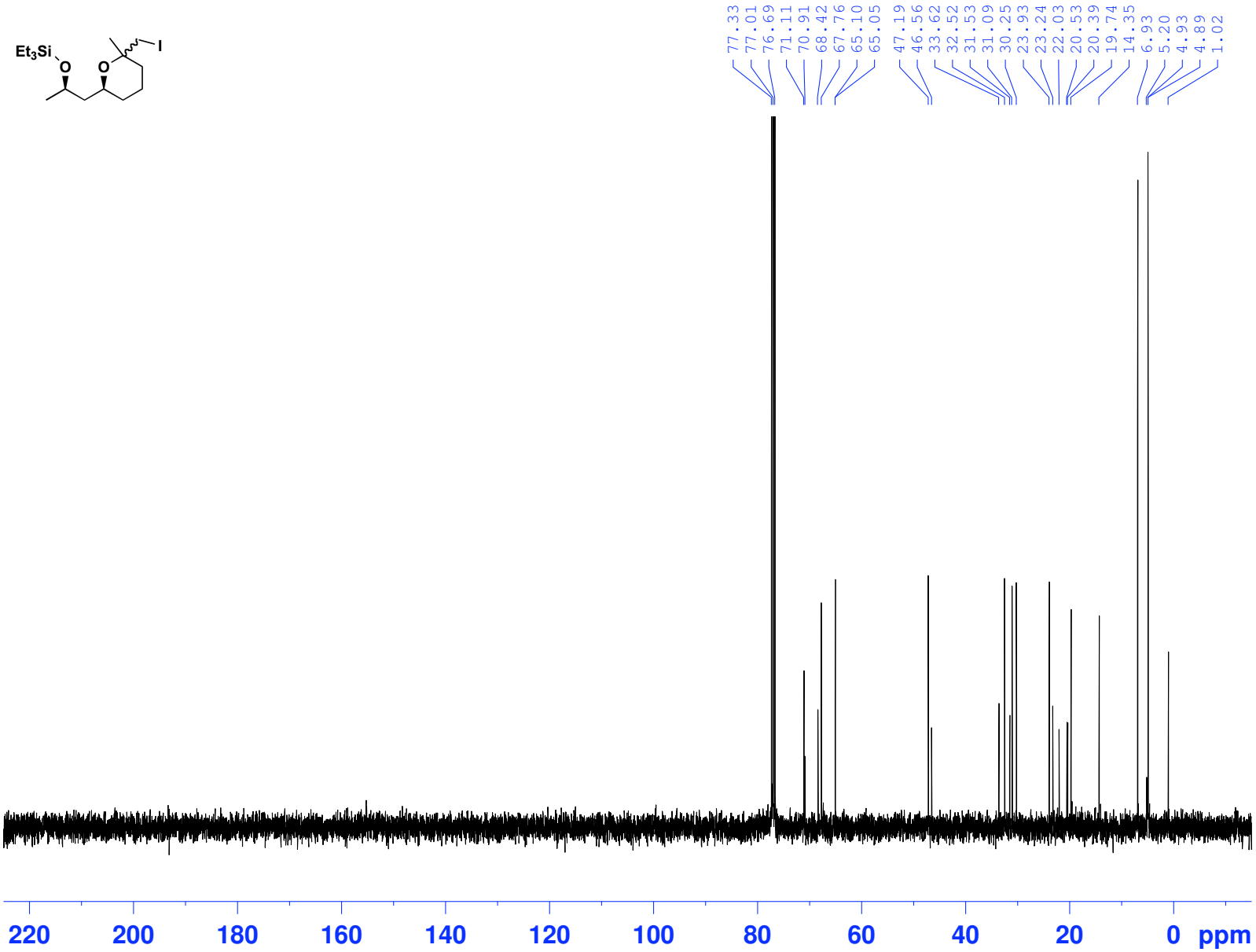
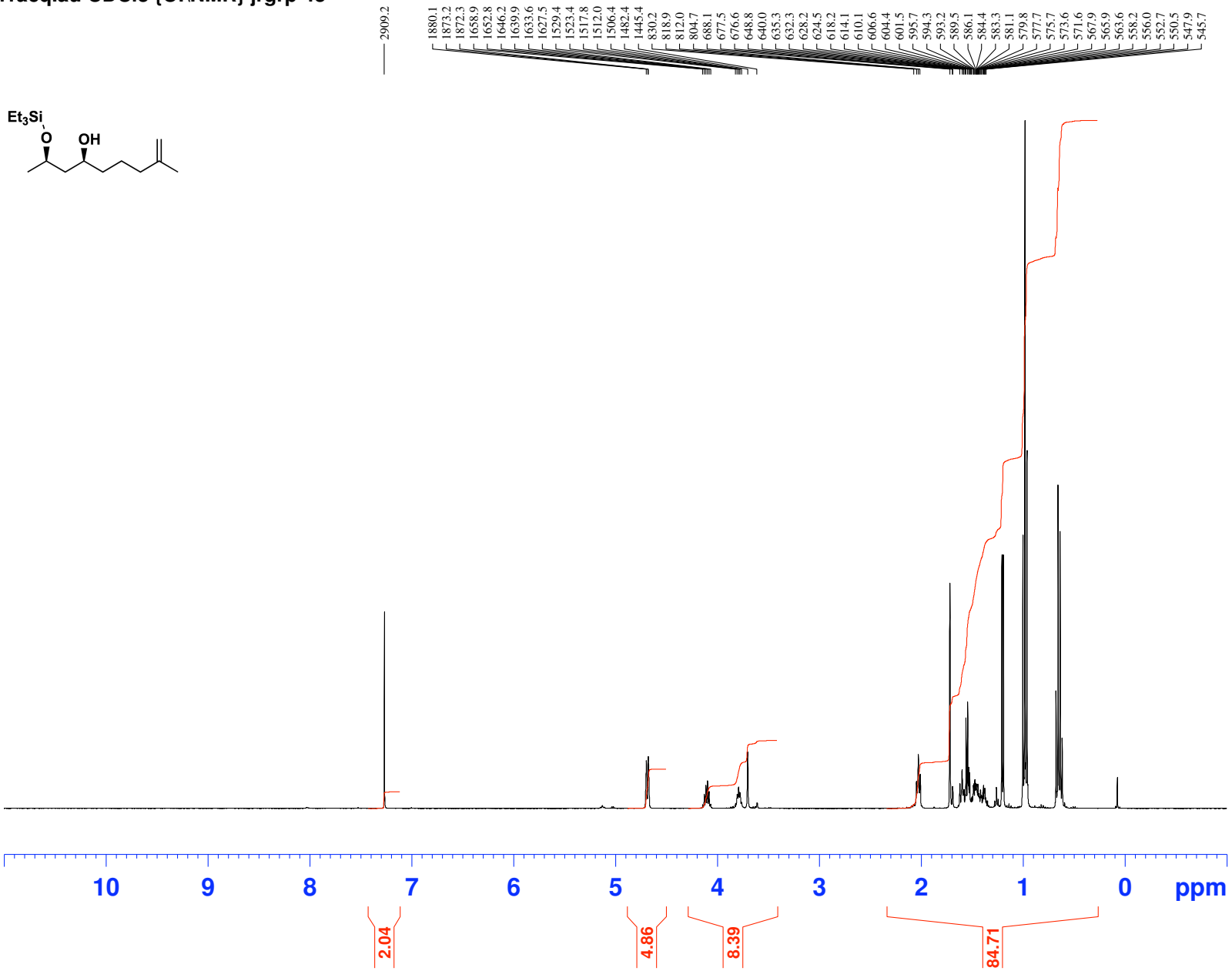
WBS022–column–9–16
c13acq.au CDCl3 {C:\NMR} jrgrp 13



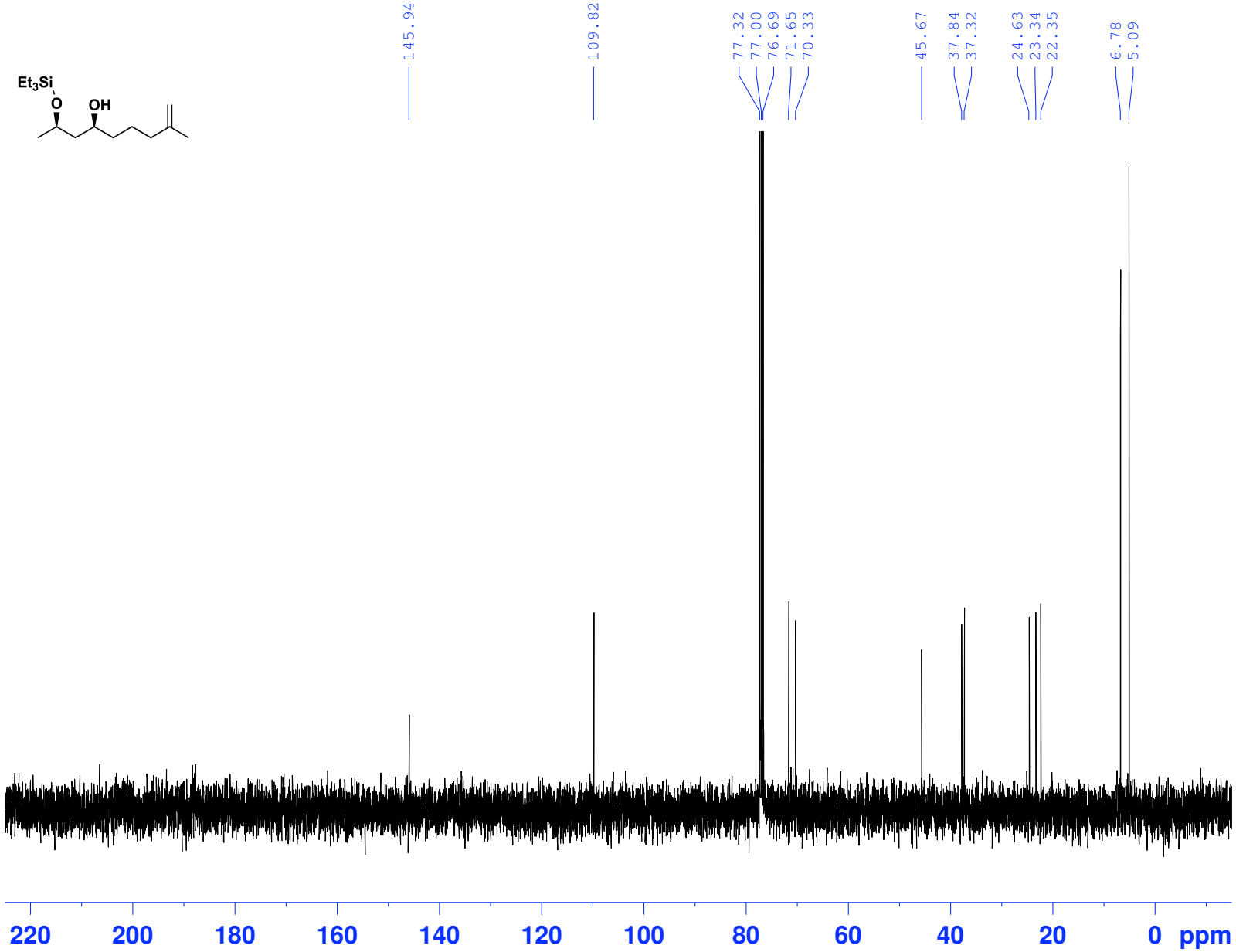

```
Current Data Parameters
NAME       Nov26-2008-13
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20081126
Time               11.00
INSTRUM            av400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           26178.010 Hz
FIDRES         0.798889 Hz
AQ            0.6259188 sec
RG                32768
DW               19.100 usec
DE                7.50 usec
TE               300.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 0.00 dB
SFO1        100.6403931 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL12              19.00 dB
PL13              25.00 dB
PL2                0.00 dB
SFO2        400.2016008 MHz

F2 - Processing parameters
SI                32768
SF        100.6303718 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Instrument DQX400
Chemist BW
Group JR
WBS–Zinc deprotection
h1acq.au CDCl3 {C:\NMR} jrgrp 43



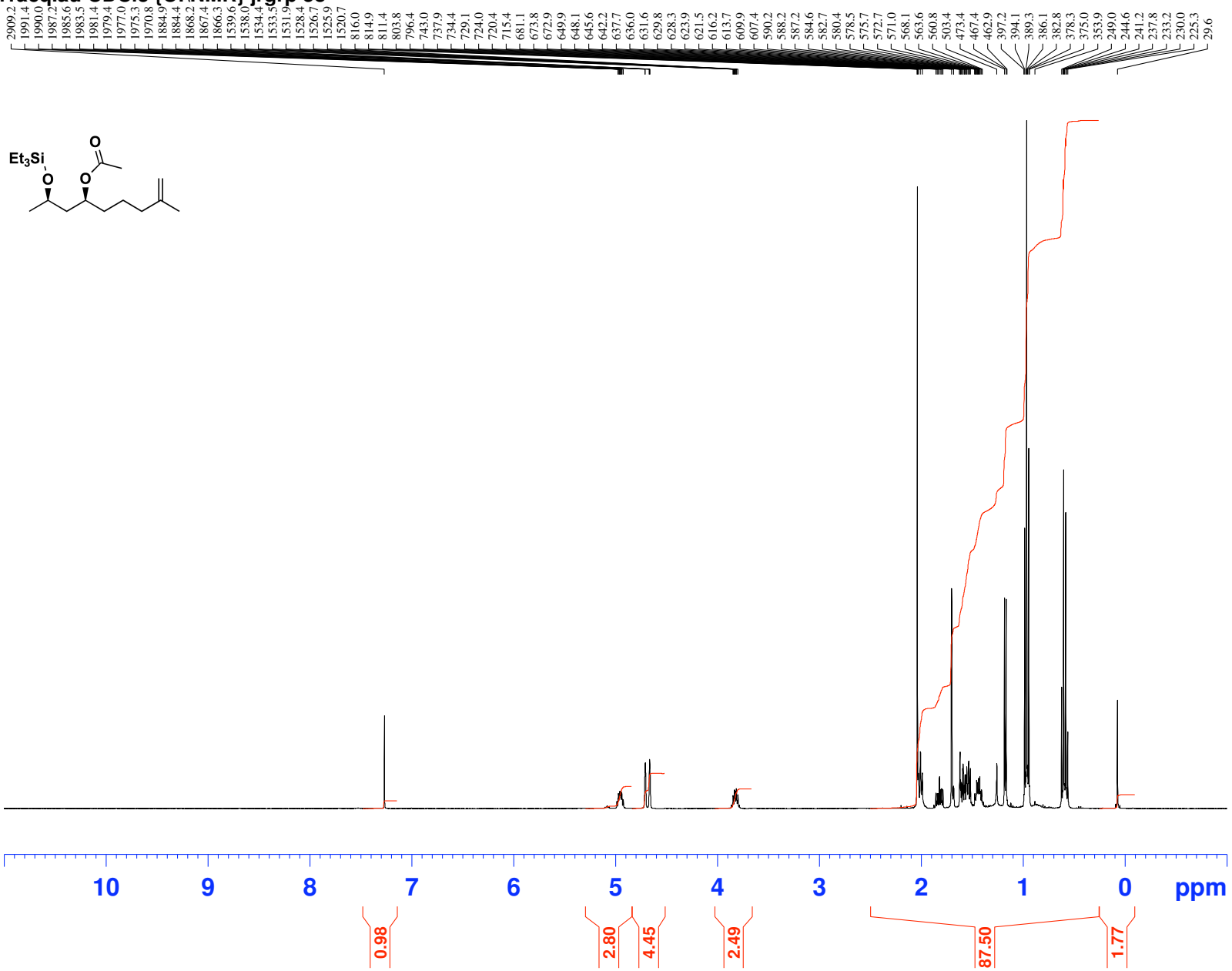

```
Current Data Parameters
NAME        Nov27-2008-43
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081128
Time                 2.23
INSTRUM            av400
PROBHD   5 mm QNP 1H/13
PULPROG             zg60
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   181
DW                60.400 usec
DE                 7.50 usec
TE                300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.00 usec
PL1                0.00 dB
SFO1         400.2024714 MHz

F2 - Processing parameters
SI                 32768
SF          400.2000028 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Instrument DQX400
Chemist BW
Group JR
WBS–Zinc deprotection
c13acq.au CDCl3 {C:\NMR} jrgrp 43



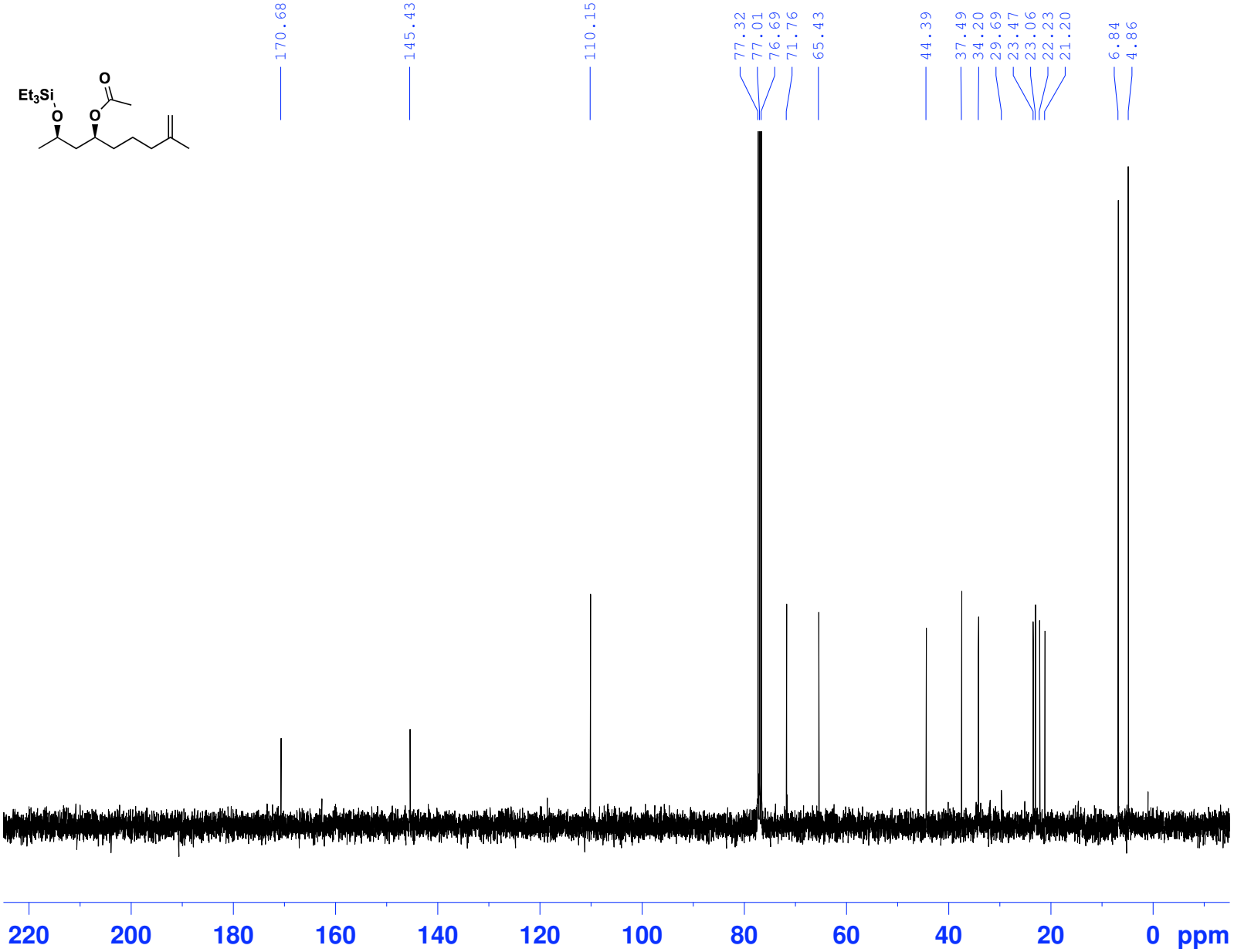

```
Current Data Parameters
NAME       Nov27-2008-43
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20081128
Time                2.31
INSTRUM            av400
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            26178.010 Hz
FIDRES          0.798889 Hz
AQ             0.6259188 sec
RG                 32768
DW                19.100 usec
DE                 7.50 usec
TE                 300.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 0.00 dB
SFO1         100.6403931 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL12               19.00 dB
PL13               25.00 dB
PL2                 0.00 dB
SFO2         400.2016008 MHz

F2 - Processing parameters
SI                 32768
SF          100.6303718 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Instrument DQX400
Chemist BW
Group JR
WBS028–characterization
h1acq.au CDCl3 {C:\NMR} jrgrp 58



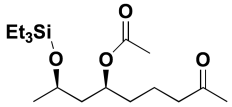

```
Current Data Parameters
NAME        Dec05-2008-58
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20081205
Time                13.06
INSTRUM             av400
PROBHD   5 mm QNP 1H/13
PULPROG              zg60
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   90.5
DW                 60.400 usec
DE                  7.50 usec
TE                 300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  9.00 usec
PL1                 0.00 dB
SFO1         400.2024714 MHz

F2 - Processing parameters
SI                  32768
SF          400.2000028 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

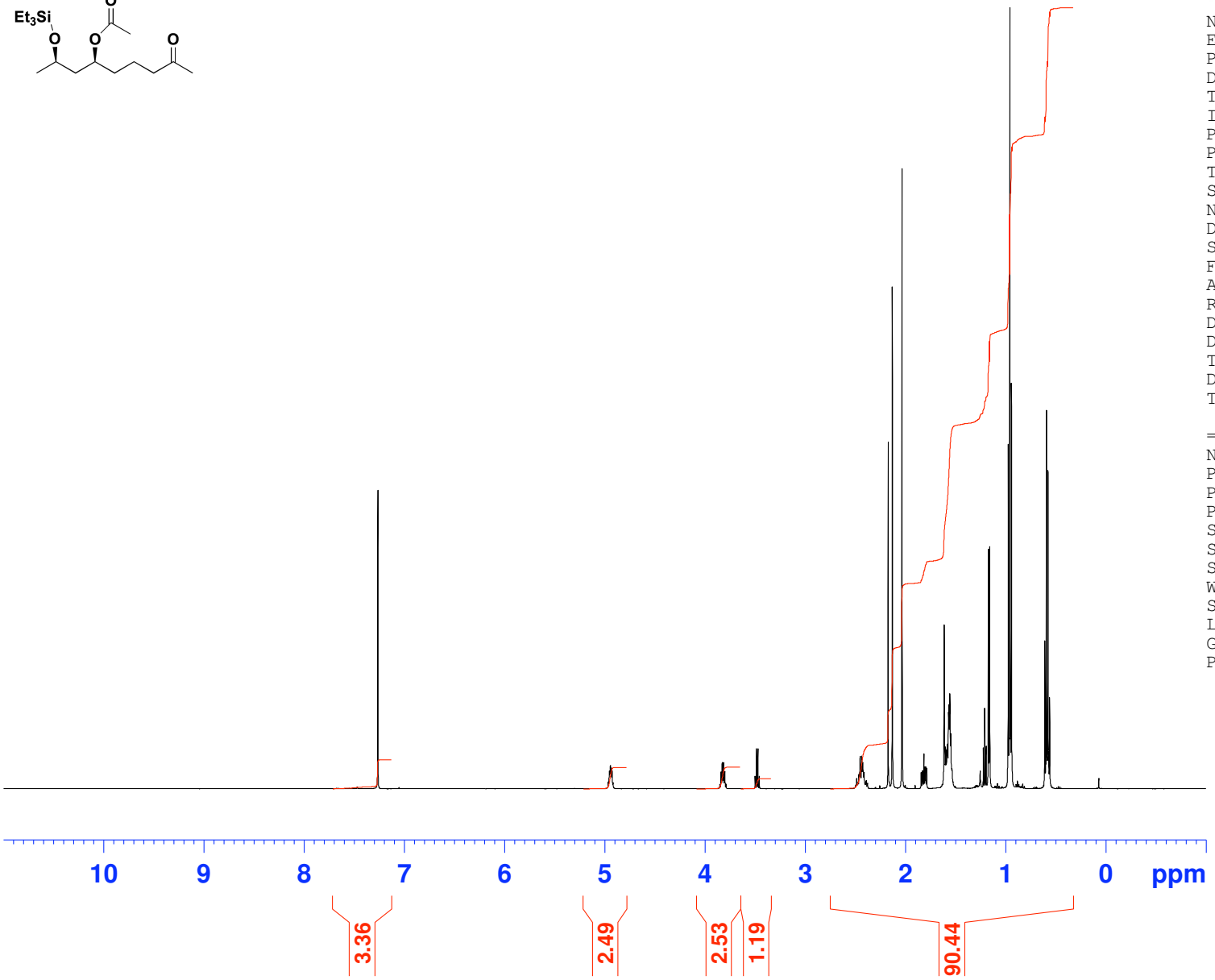
Instrument DQX400
Chemist BW
Group JR
WBS028–characterization
c13acq.au CDCl3 {C:\NMR} jrgrp 58




```
Current Data Parameters
NAME       Dec05-2008-58
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20081205
Time               13.14
INSTRUM            av400
PROBHD   5 mm QNP 1H/13
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           26178.010 Hz
FIDRES         0.798889 Hz
AQ            0.6259188 sec
RG                32768
DW               19.100 usec
DE                7.50 usec
TE               300.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 0.00 dB
SFO1        100.6403931 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL12              19.00 dB
PL13              25.00 dB
PL2                0.00 dB
SFO2        400.2016008 MHz

F2 - Processing parameters
SI                32768
SF        100.6303718 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

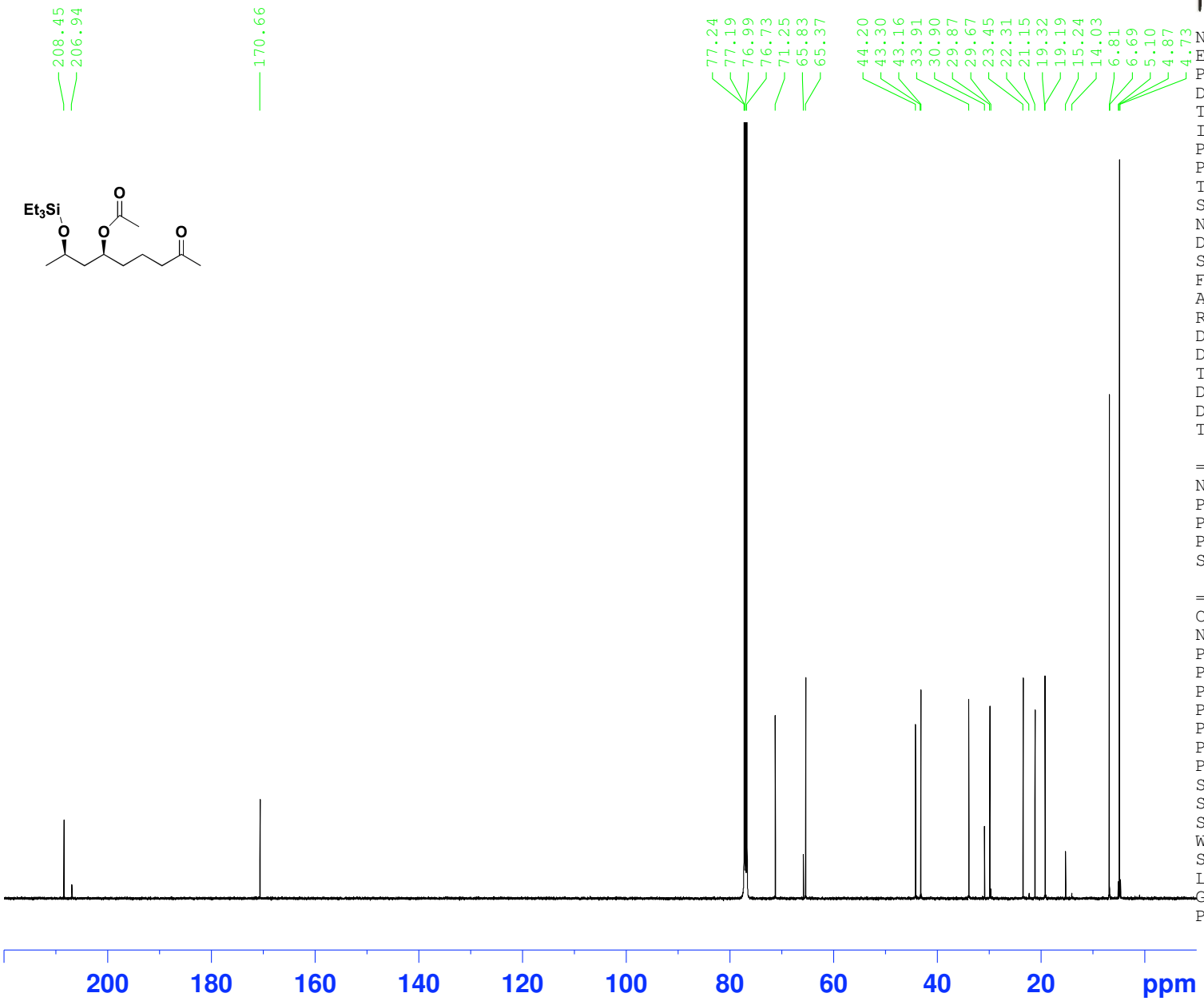
Instrument AVC500
3774 Boshen Wu 9/4/09





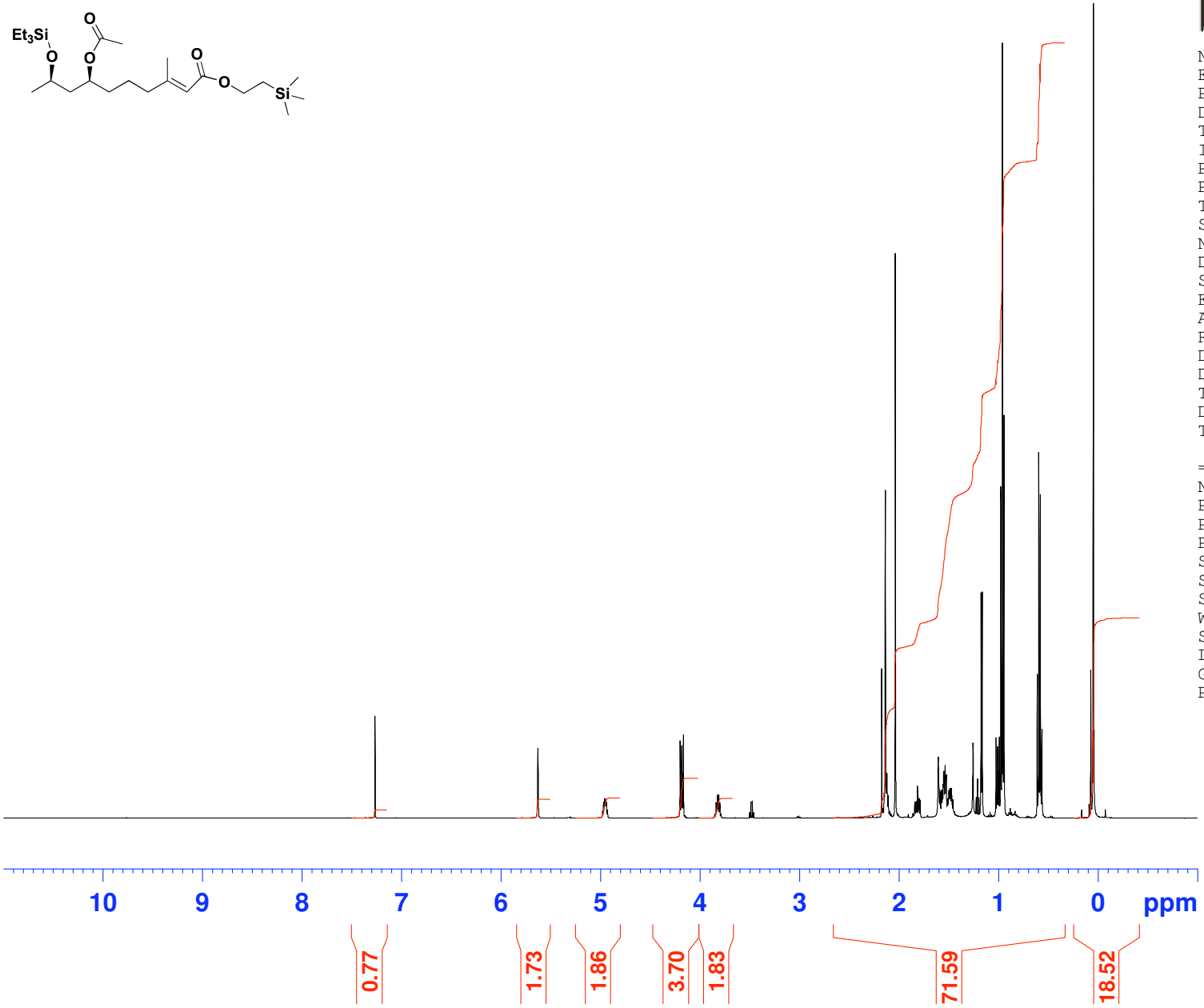

```
NAME          bw37740904
EXPNO                  1
PROCNO                 1
Date_           20090415
Time               23.37
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Instrument AVC500
3774 Boshen Wu 9/4/09




```
NAME          bw37740904
EXPNO                  4
PROCNO                 1
Date_           20090416
Time                0.47
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE                20.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
PL13               17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

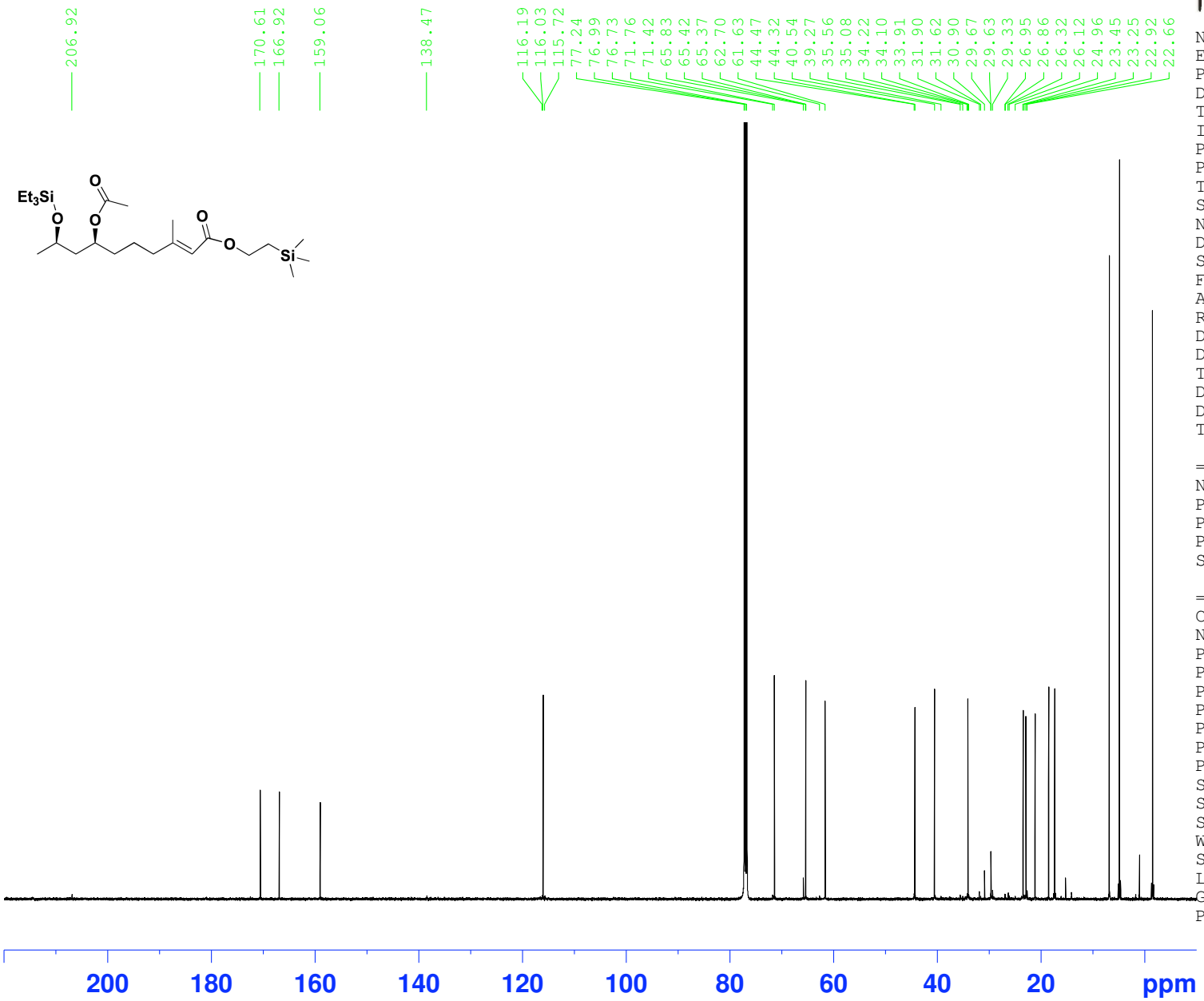
Instrument AVC500
BOSHEN WU 3507 23/3/09



NMR@CHEM.OX

```
NAME          bw35072303
EXPNO                  1
PROCNO                 1
Date_           20090325
Time               12.36
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

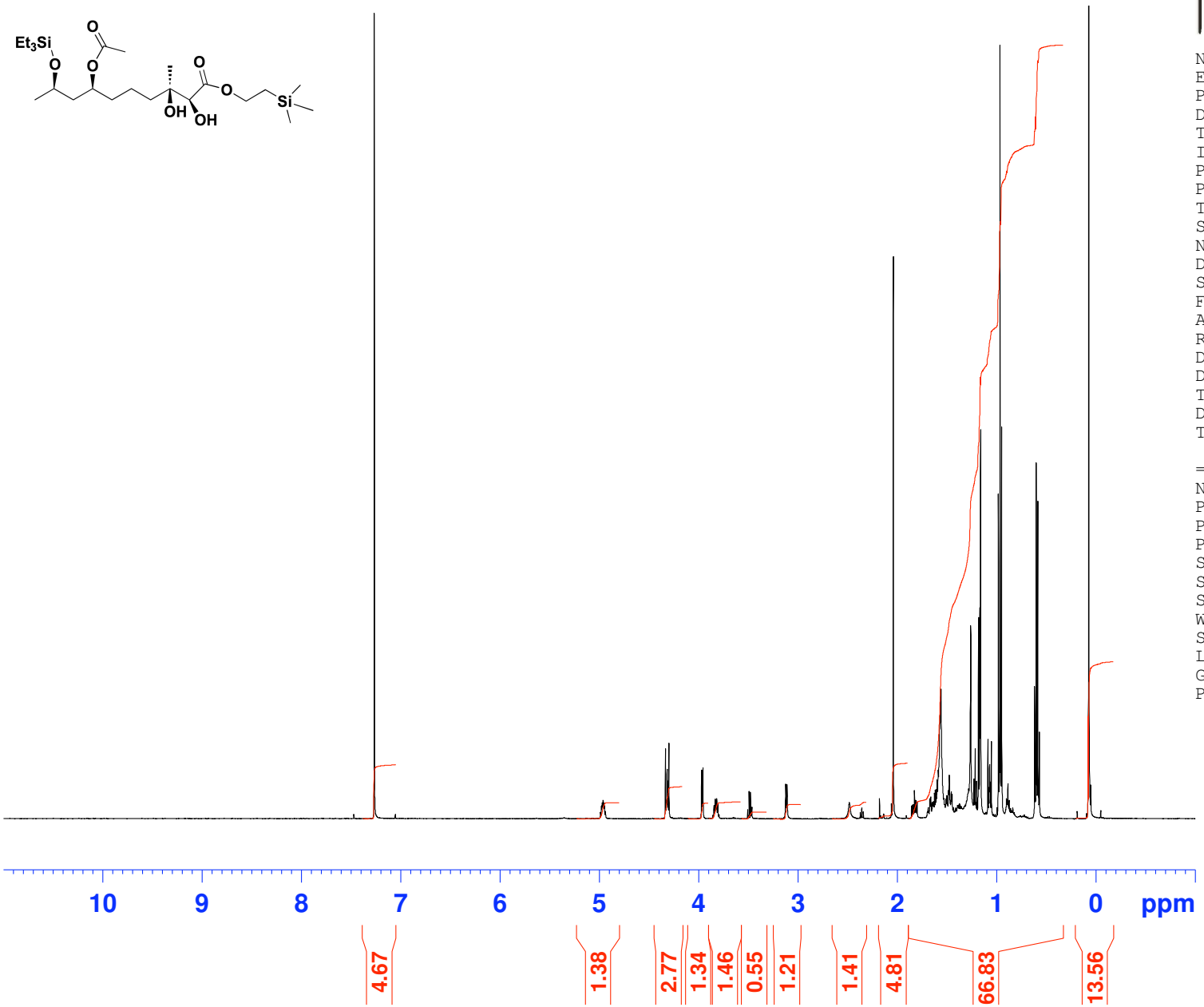
Instrument AVC500
BOSHEN WU 3507 23/3/09



NMR@CHEM.OX

```
NAME          bw35072303
EXPNO                  4
PROCNO                 1
Date_           20090325
Time               13.46
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0486259 sec
RG                 1820
DW                16.000 usec
DE                20.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
PL13               17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

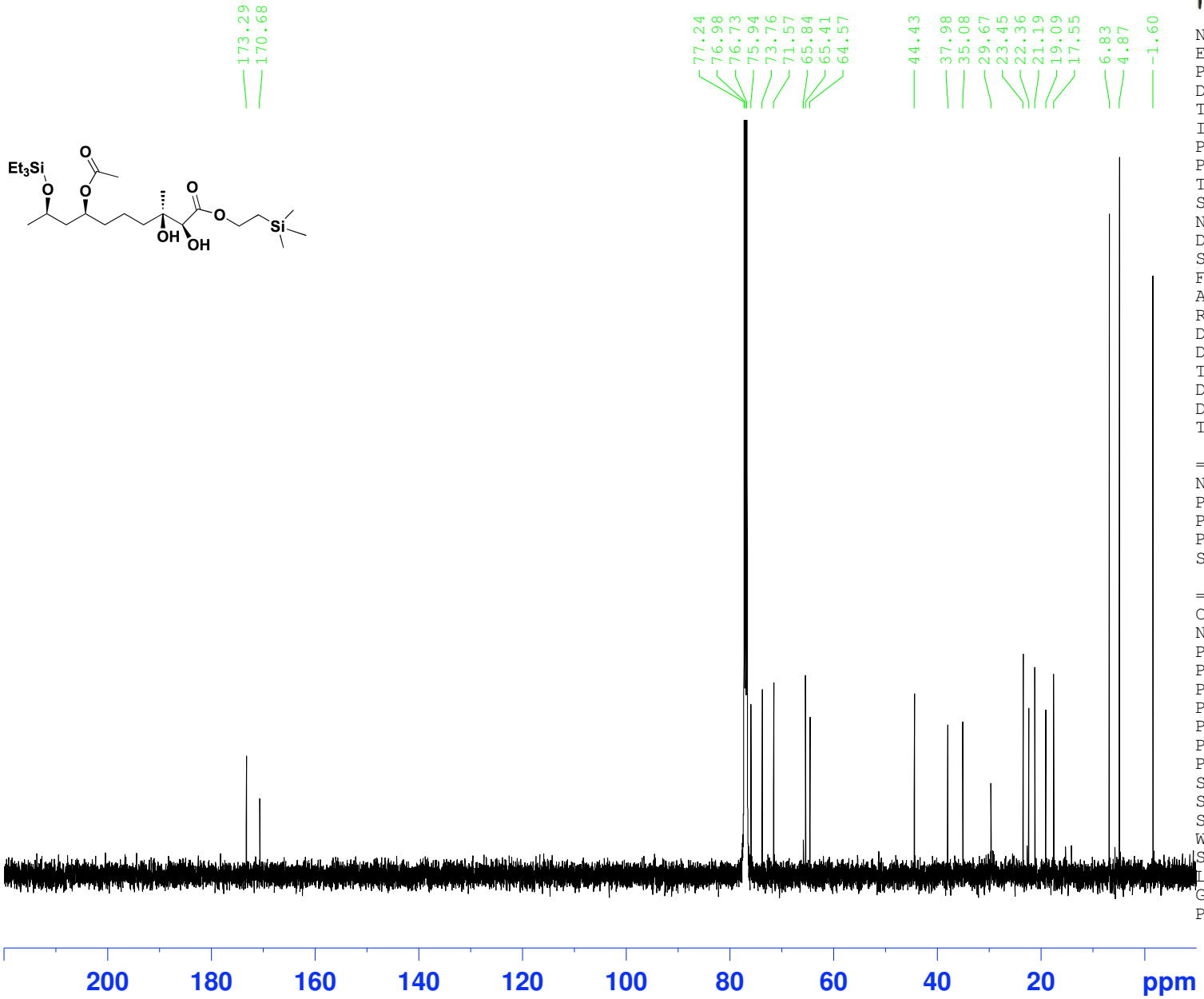
Instrument AVC500
4225 Boshen Wu 11/5/09



NMR@CHEM.OX

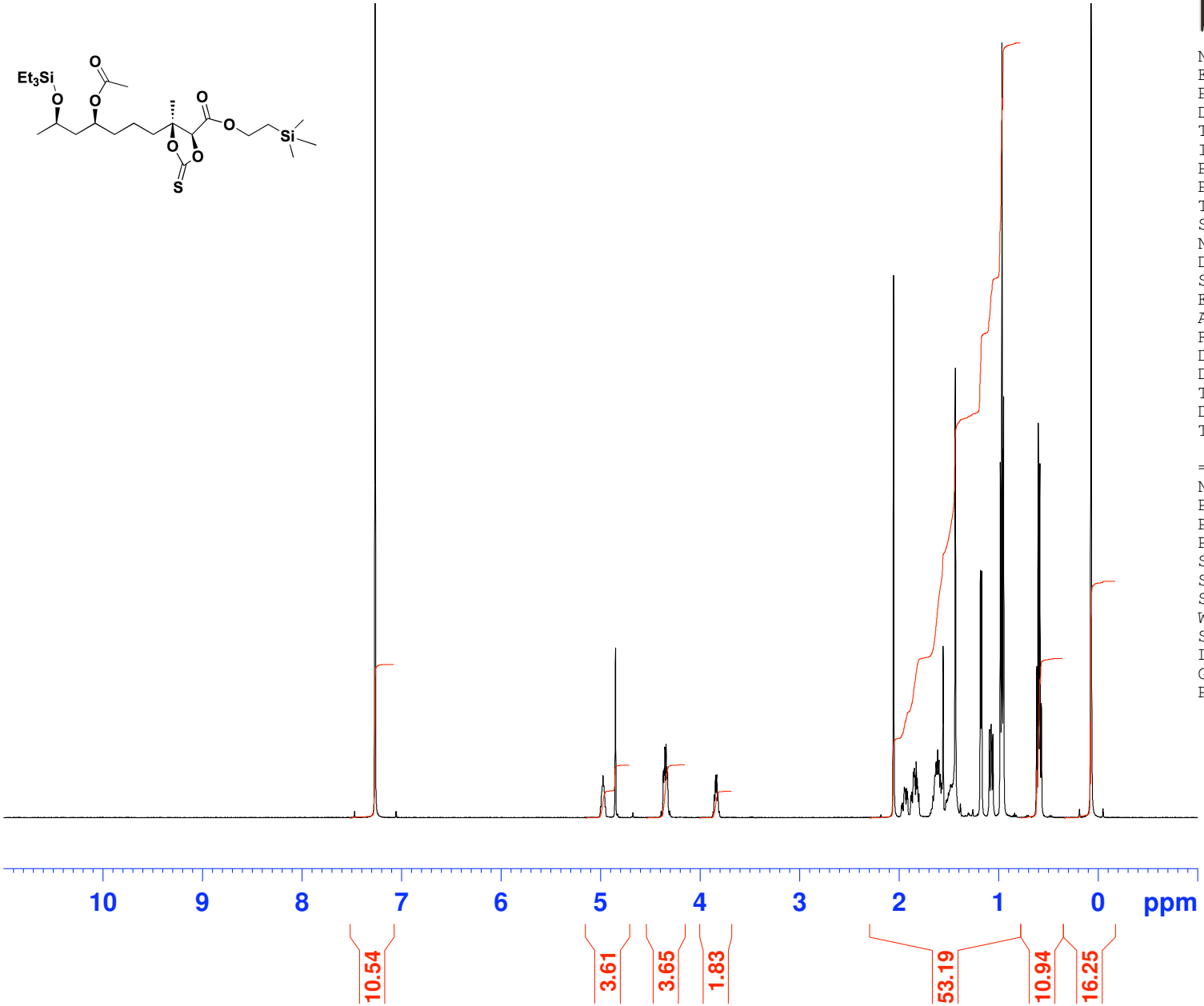
```
NAME          bw42251105
EXPNO                  1
PROCNO                 1
Date_           20090511
Time               14.54
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

Instrument AVC500
4225 Boshen Wu 11/5/09



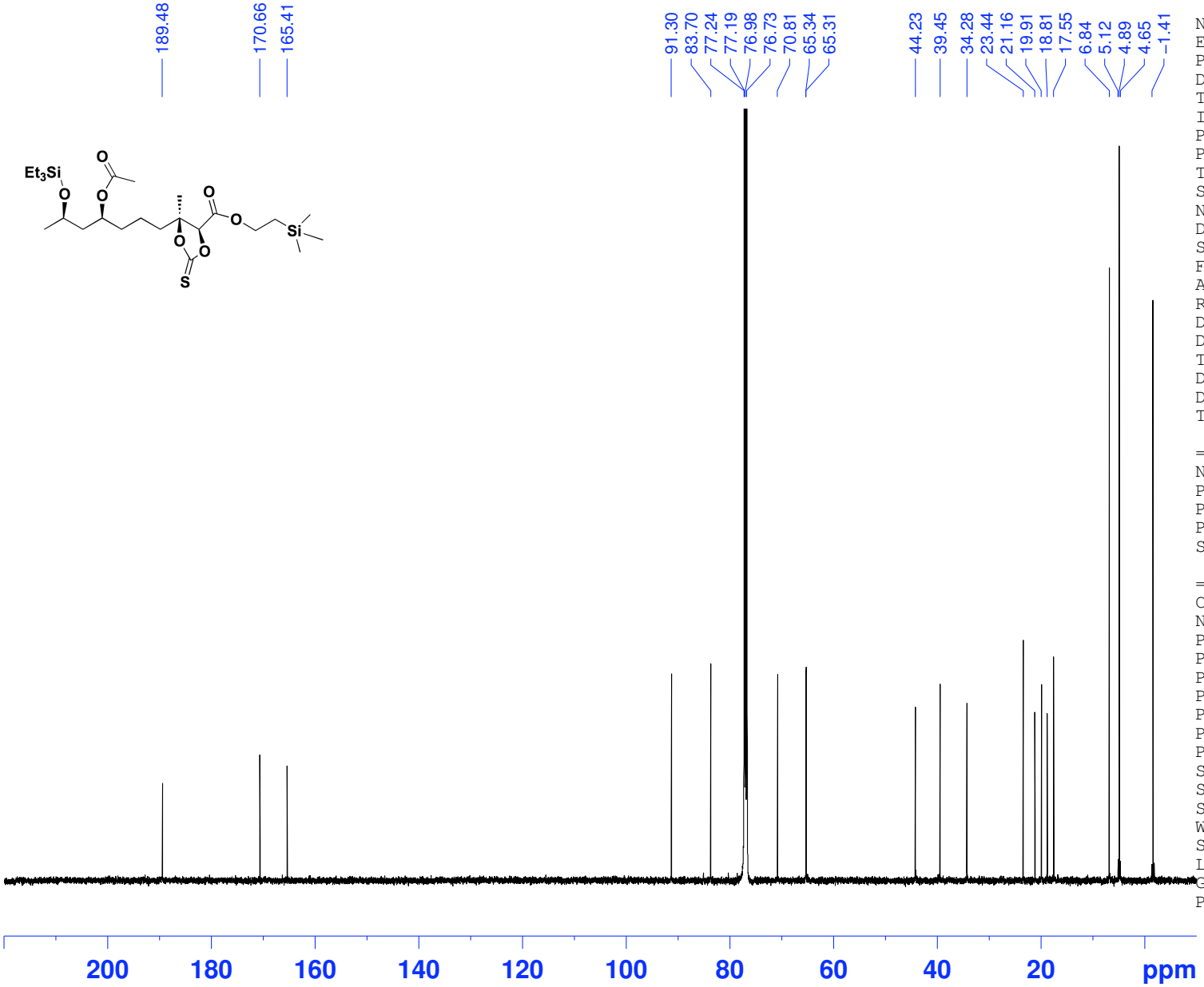

```
NAME          bw42251105
EXPNO                  4
PROCNO                 1
Date_           20090511
Time               15.29
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   378
DS                     2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0486259 sec
RG                  1820
DW                16.000 usec
DE                 20.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
PL13               17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Instrument AVC500
Group JR
7578 Boshen Wu 9/2/10



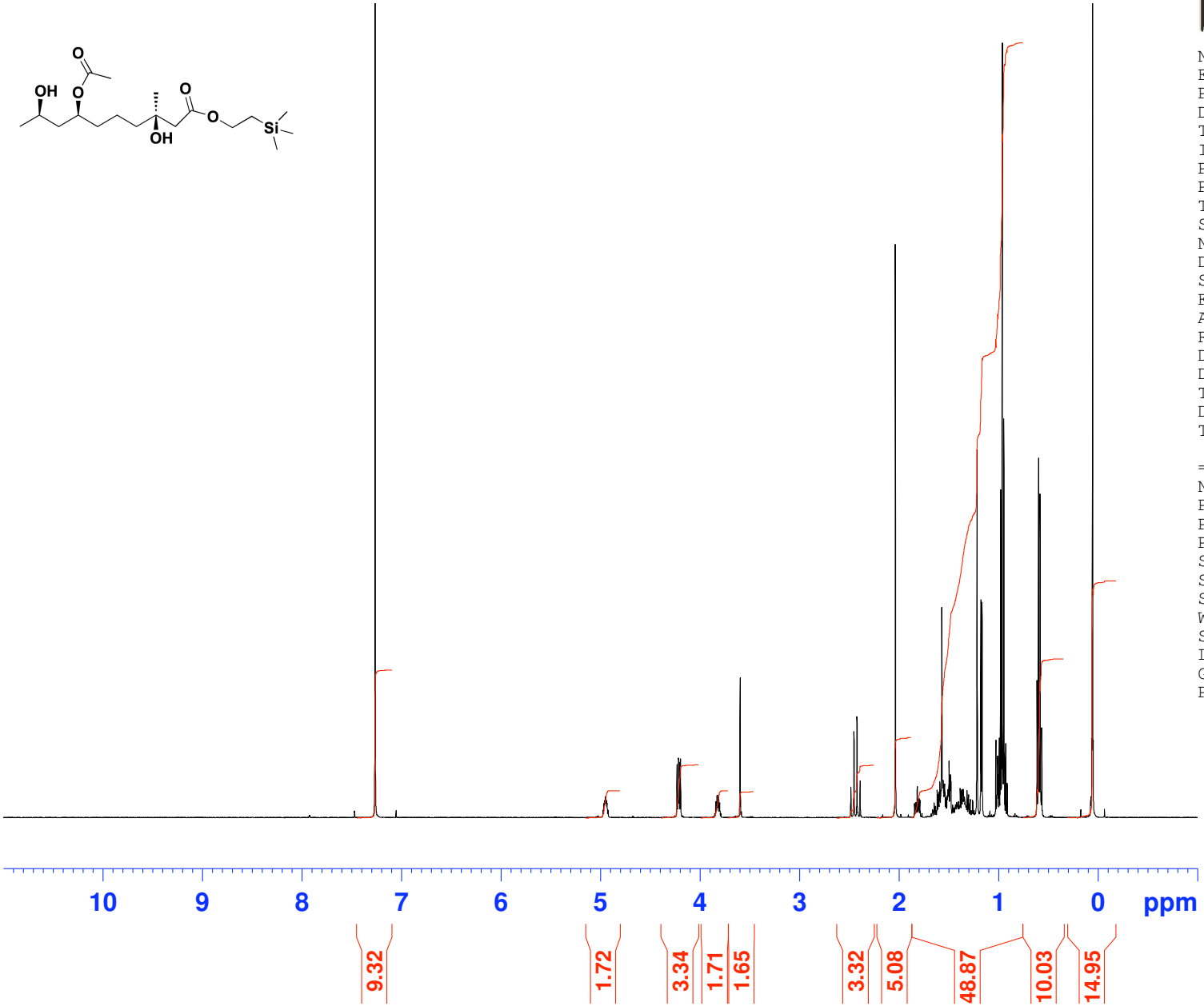

```
NAME          bw75780902
EXPNO                  1
PROCNO                 1
Date_           20100209
Time                8.33
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Instrument AVC500
Group JR
7578 Boshen Wu 9/2/10




```
NAME          bw75780902
EXPNO                  4
PROCNO                 1
Date_           20100209
Time                9.20
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1691
DS                     2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0486259 sec
RG                  1820
DW                16.000 usec
DE                 20.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
PL13               17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

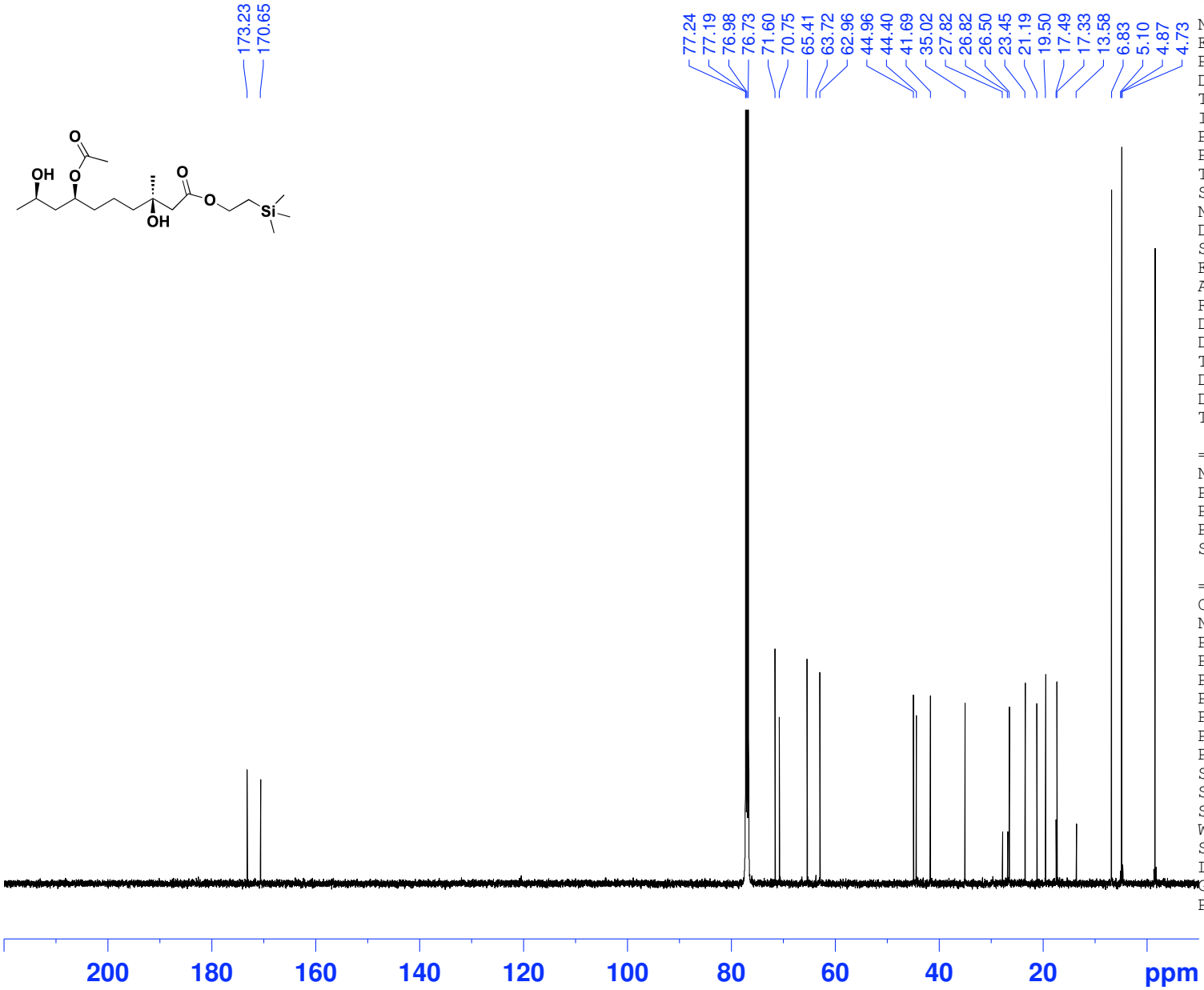
Instrument AVC500
Group JR
7603 Boshen Wu 10/2/10



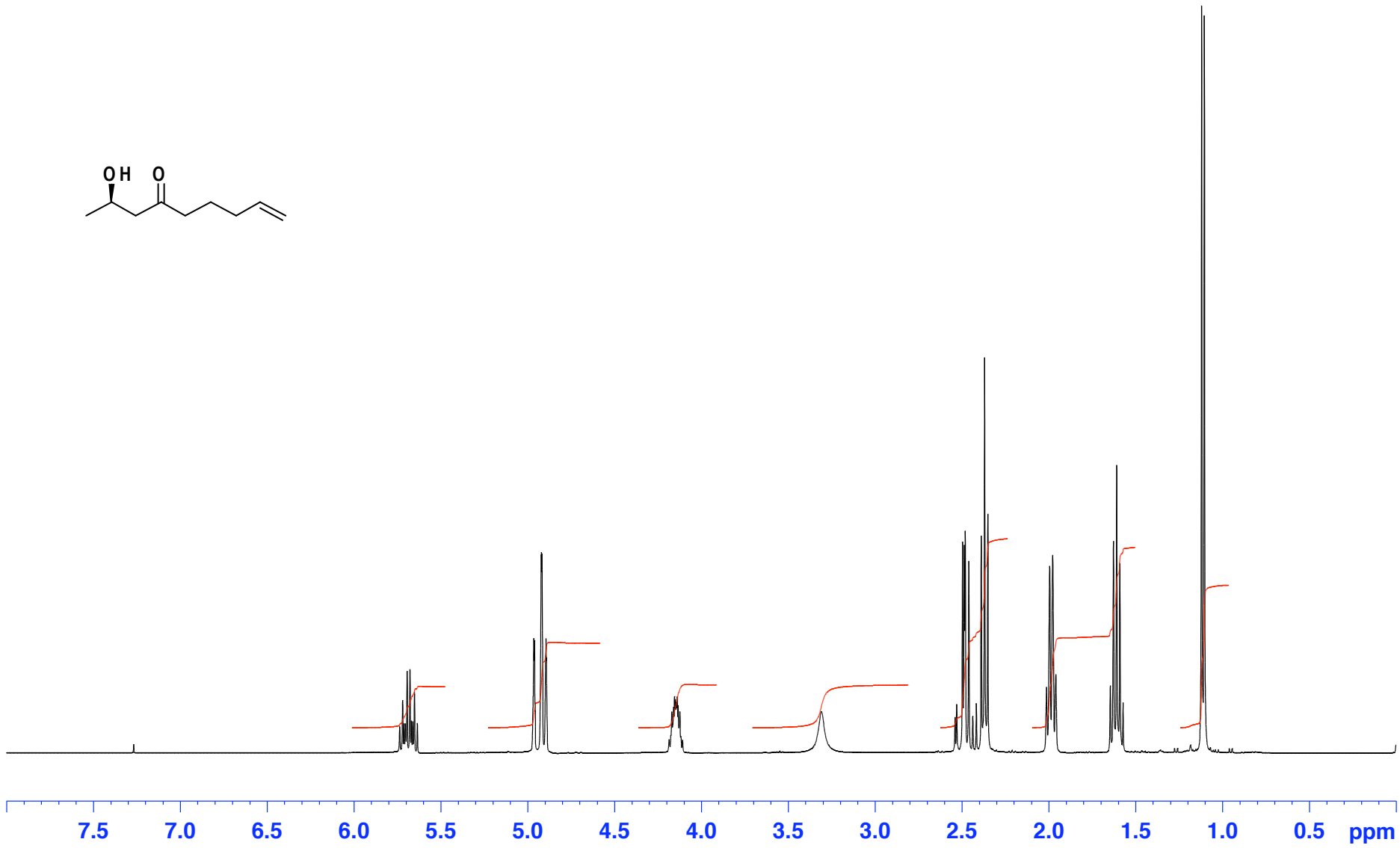
NMR@CHEM.OX

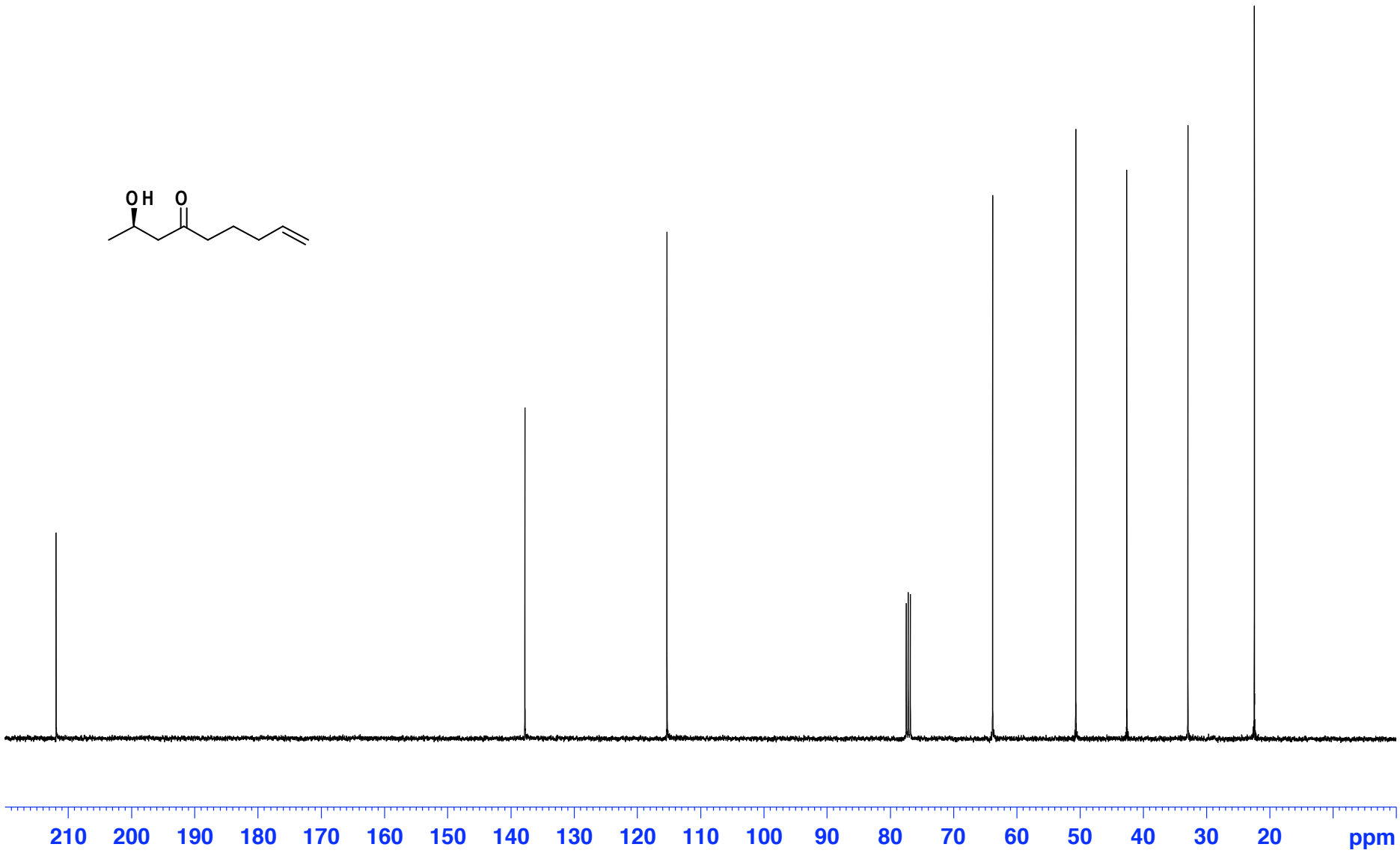
```
NAME          bw76031002
EXPNO                  1
PROCNO                 1
Date_           20100210
Time               19.44
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Instrument AVC500
Group JR
7603 Boshen Wu 10/2/10

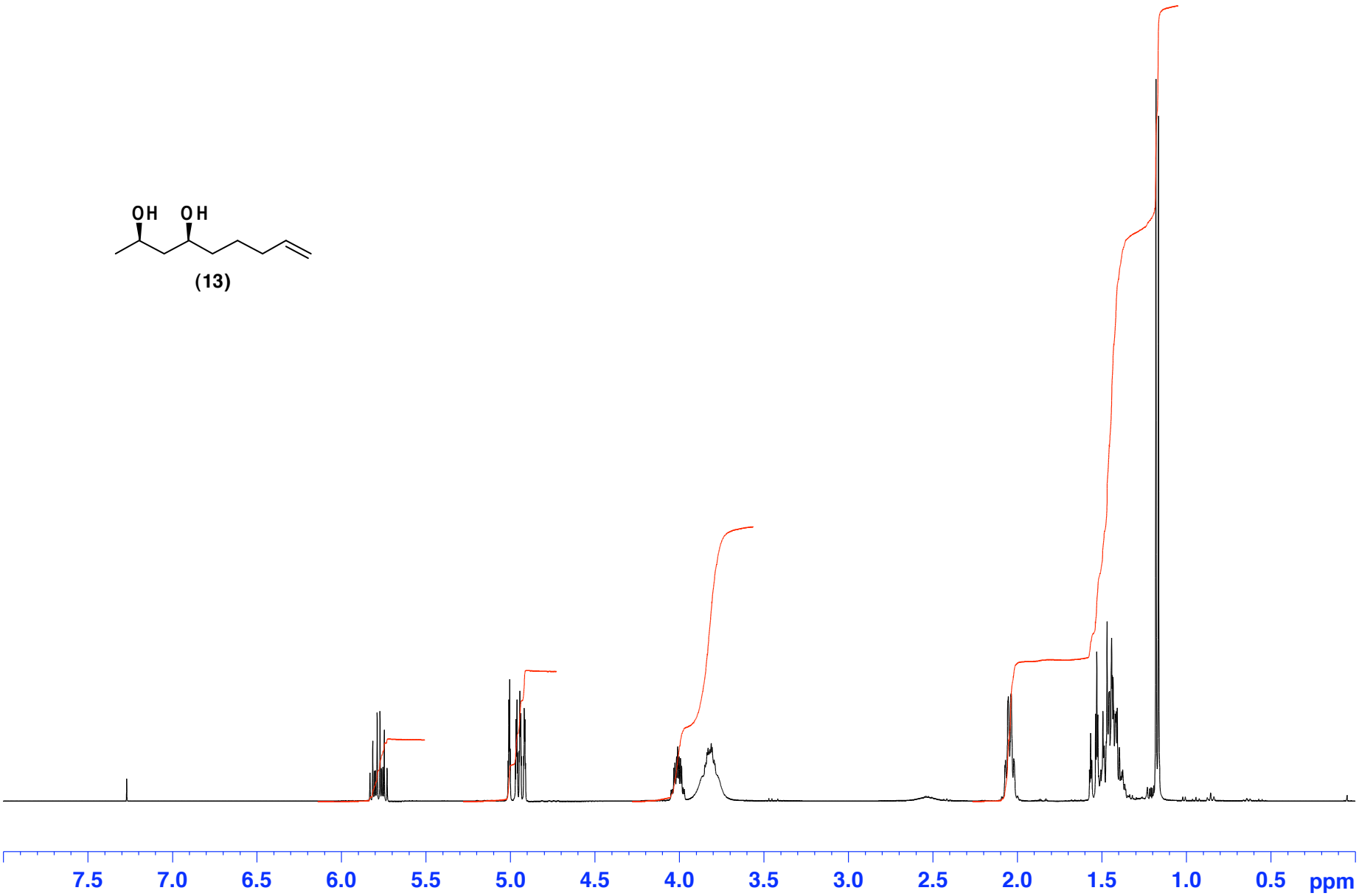


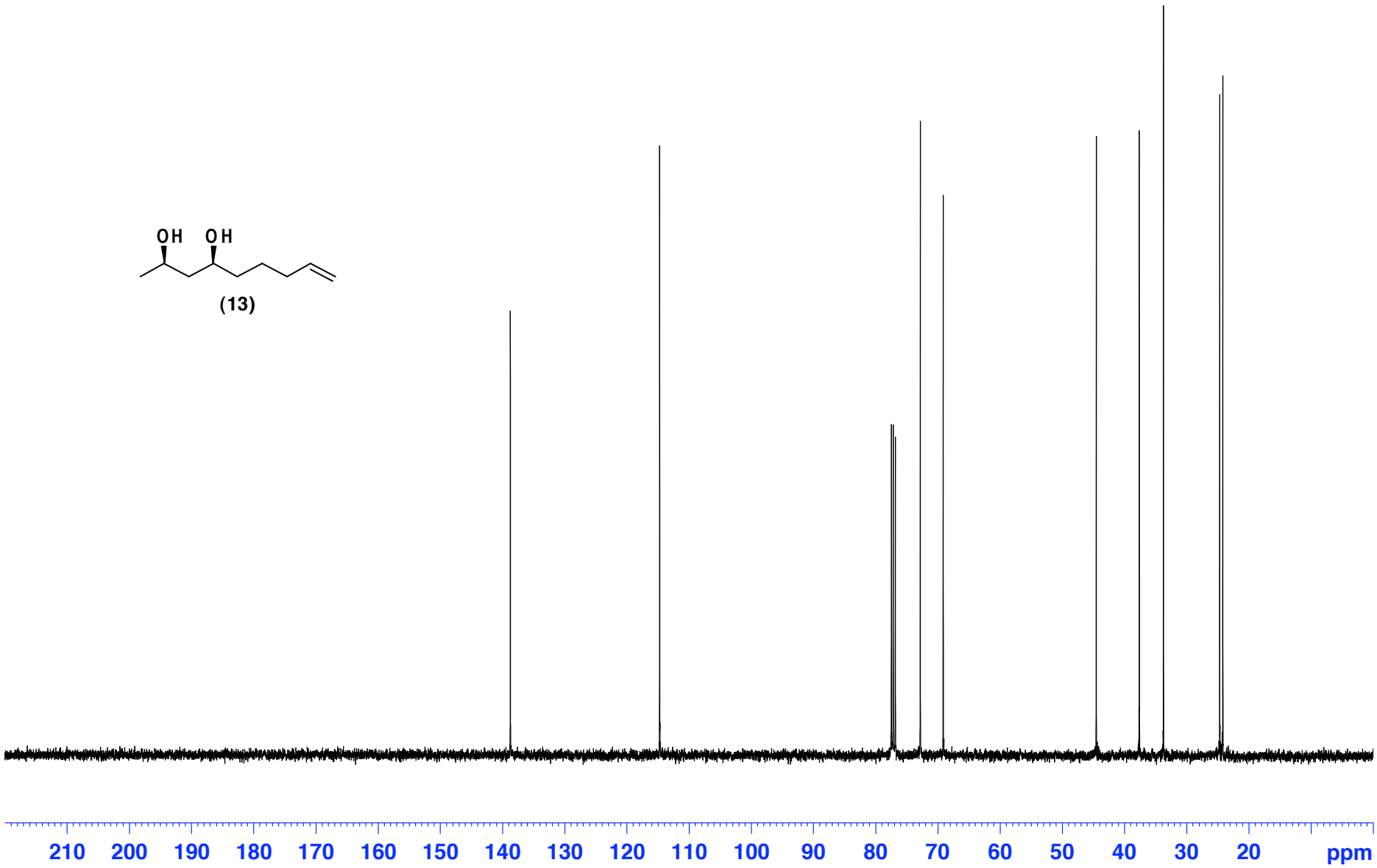

```
NAME          bw76031002
EXPNO                  4
PROCNO                 1
Date_           20100210
Time               20.54
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE                20.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
PL13               17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

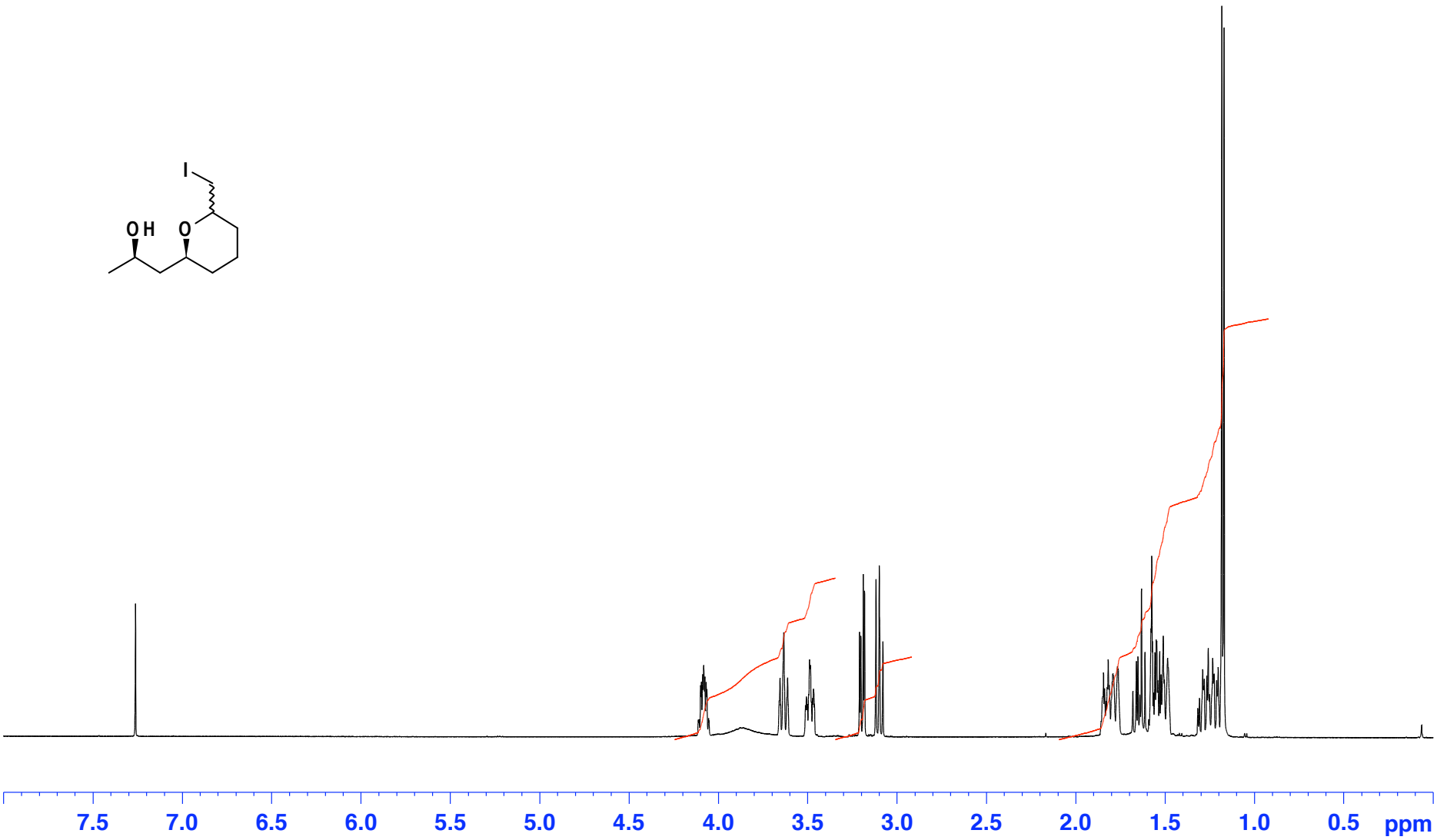

OH
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

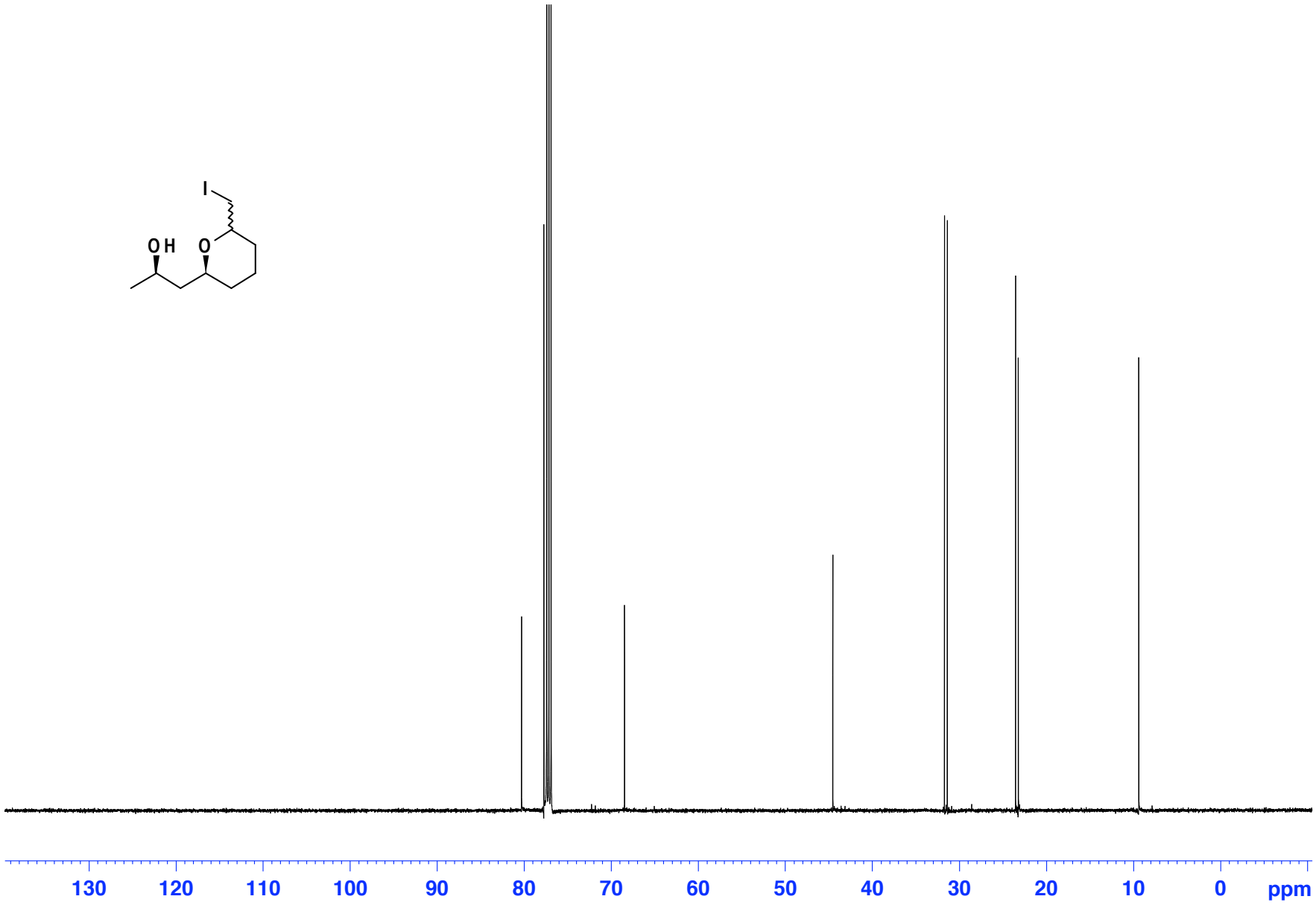

OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

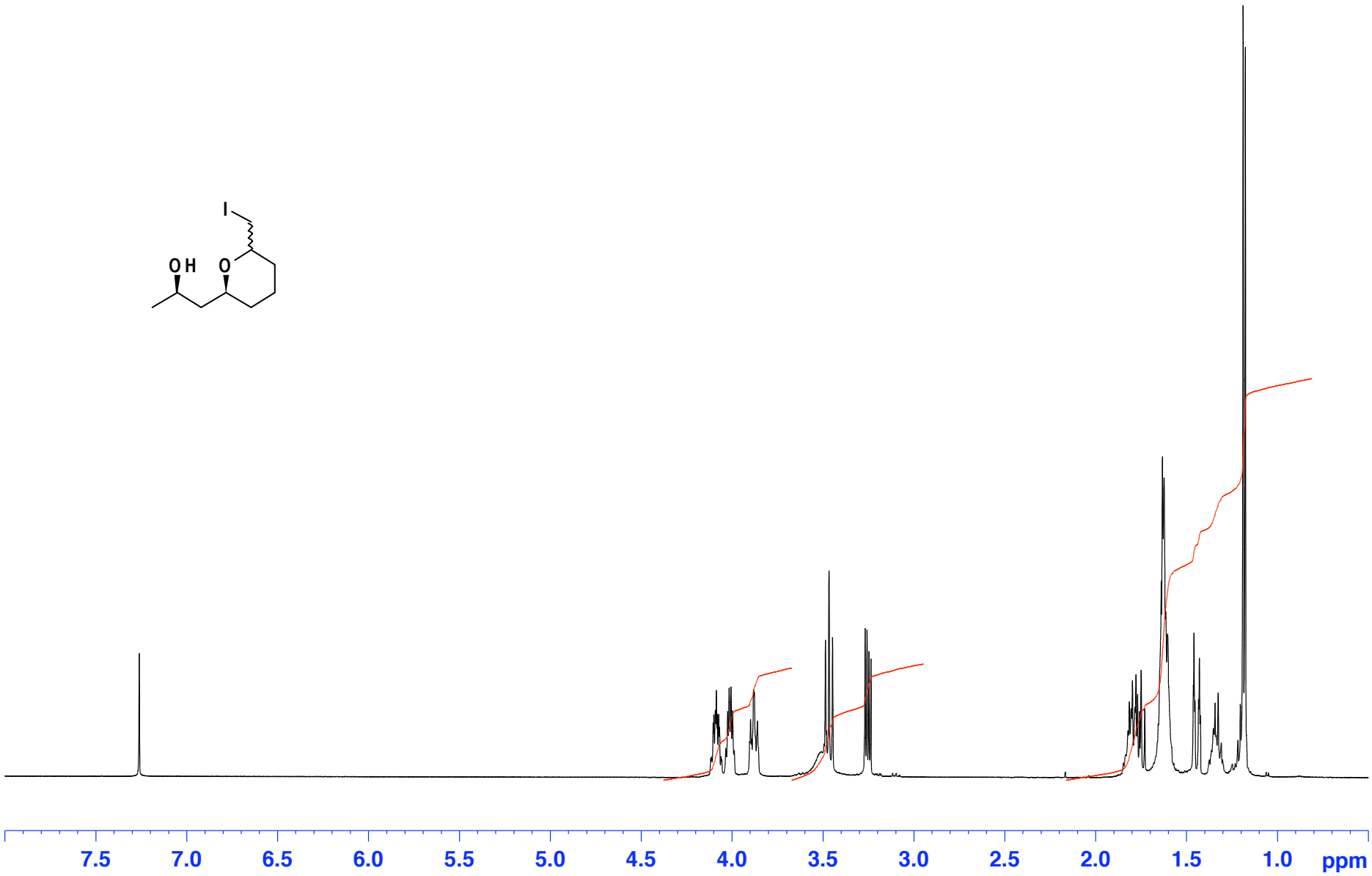
(13)

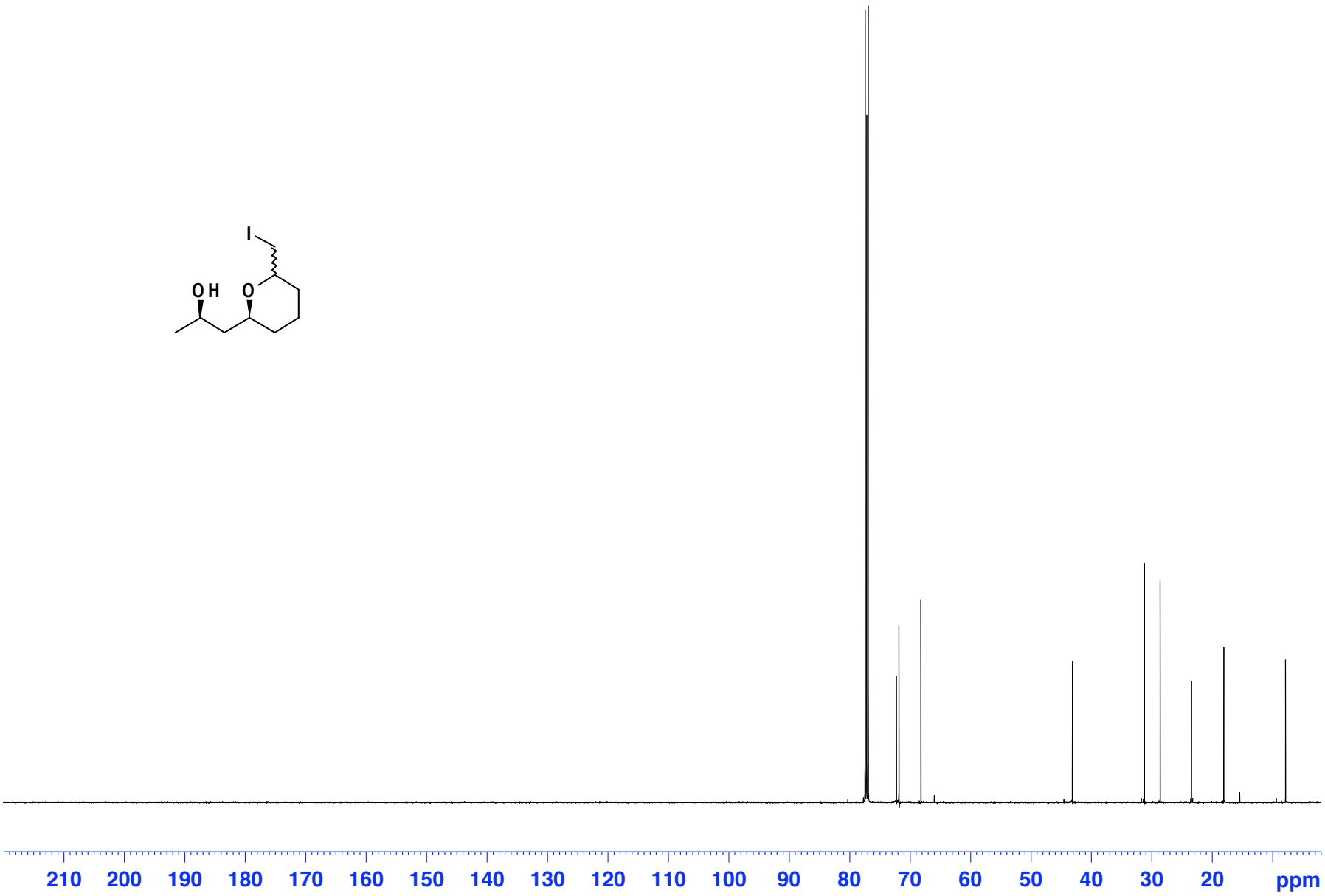


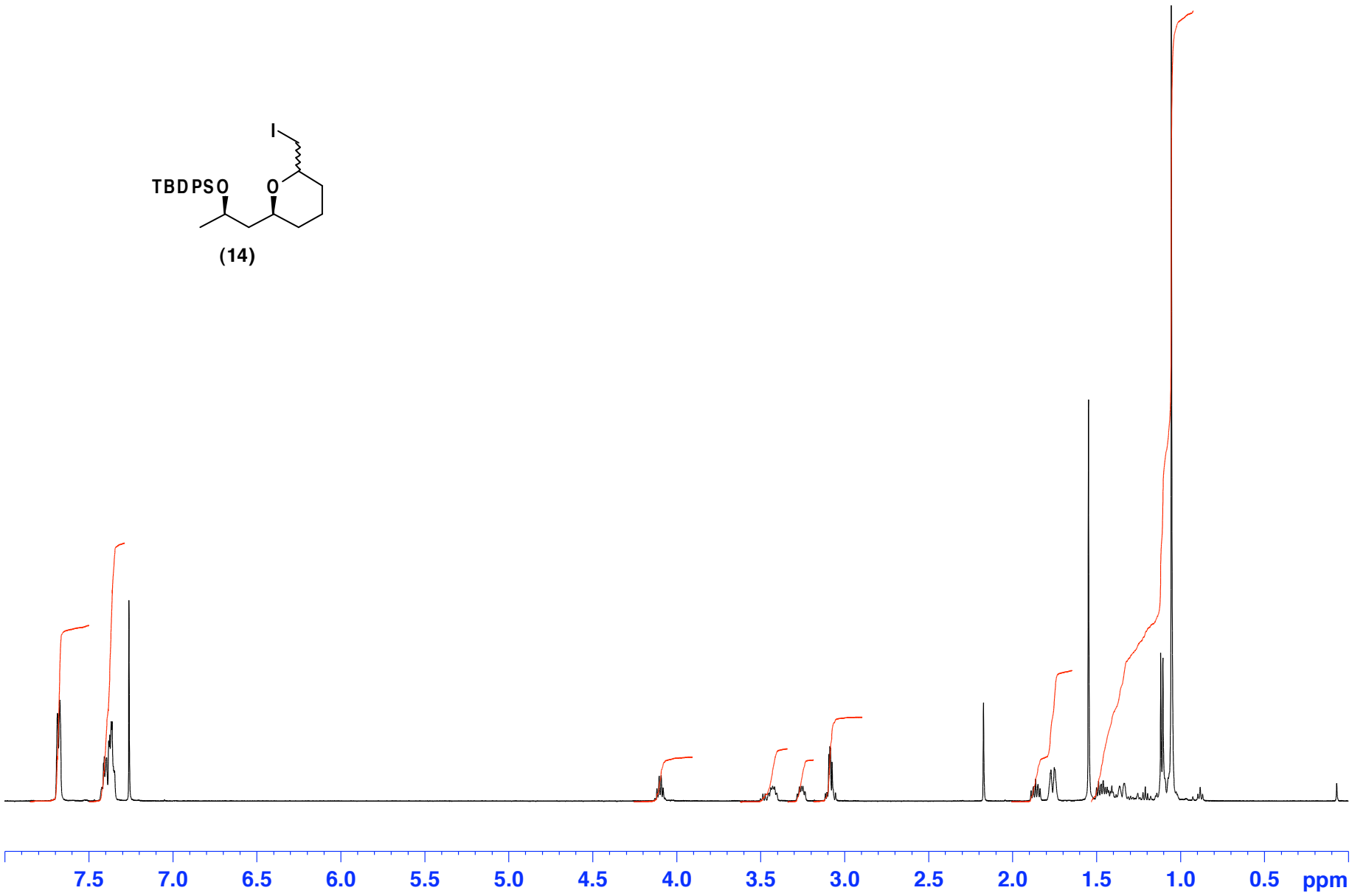

OH
OH
(13)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

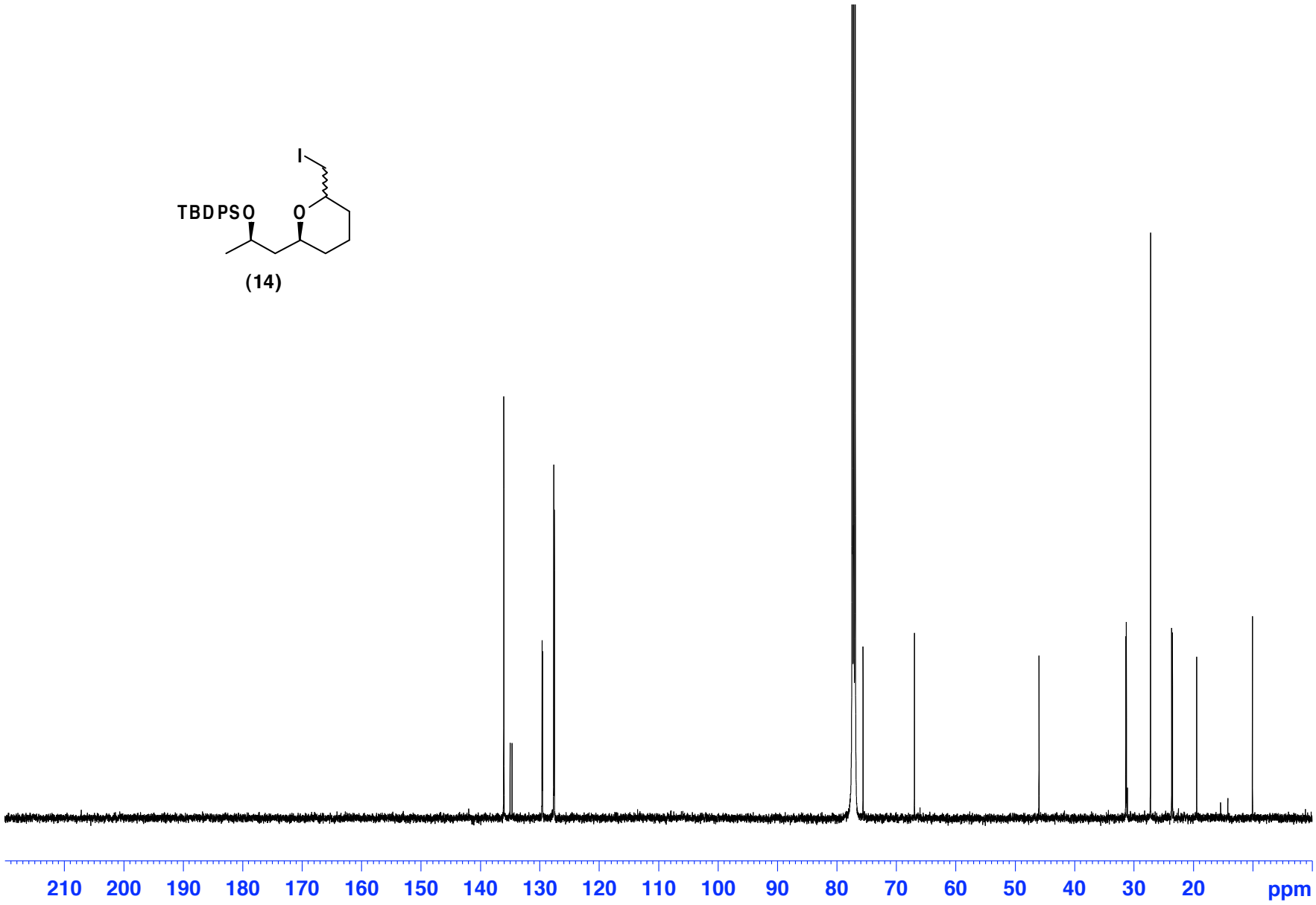

I
OH
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


I
OH
O
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

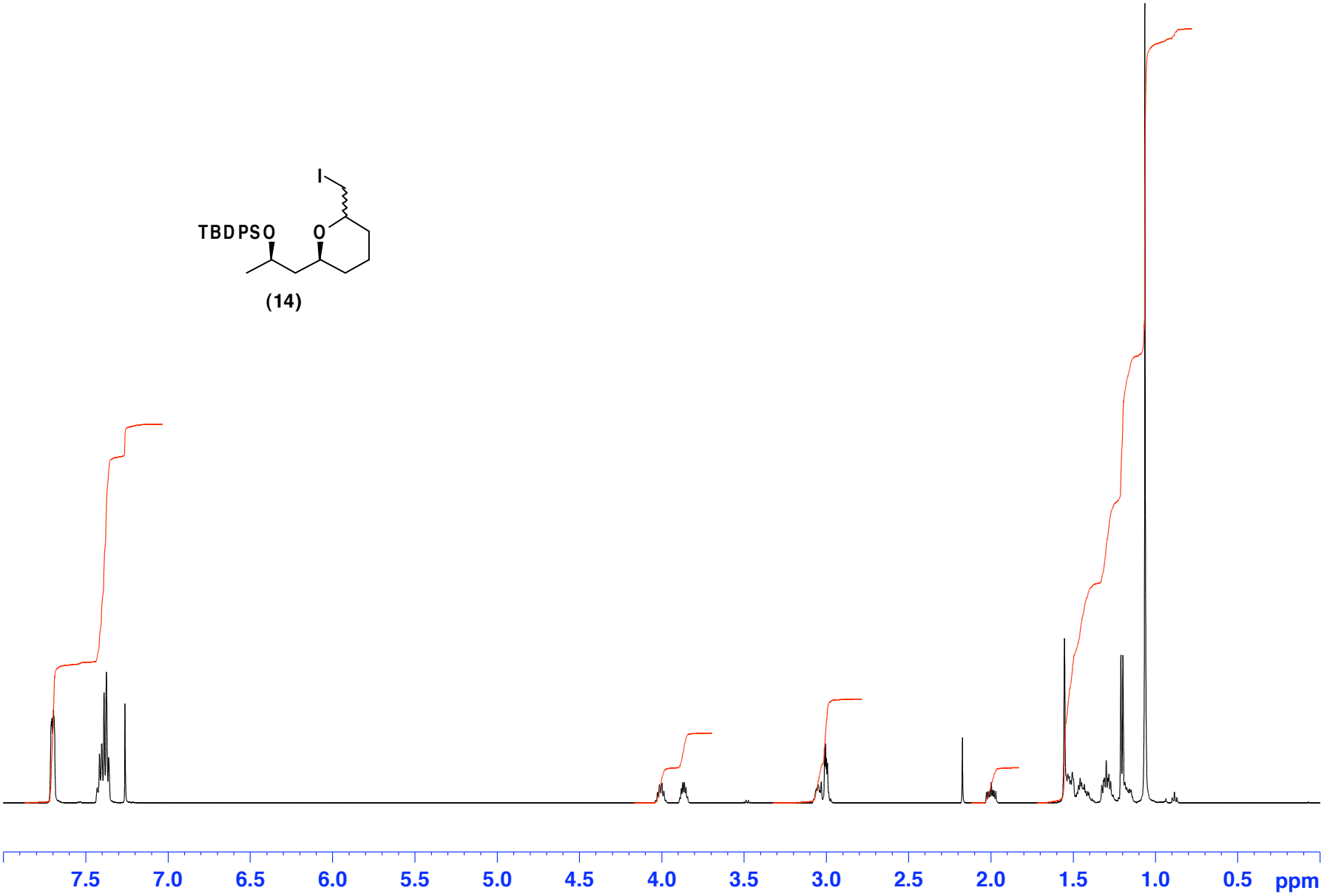

I
OH
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


I
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


I
TBDPSO
O
(14)
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

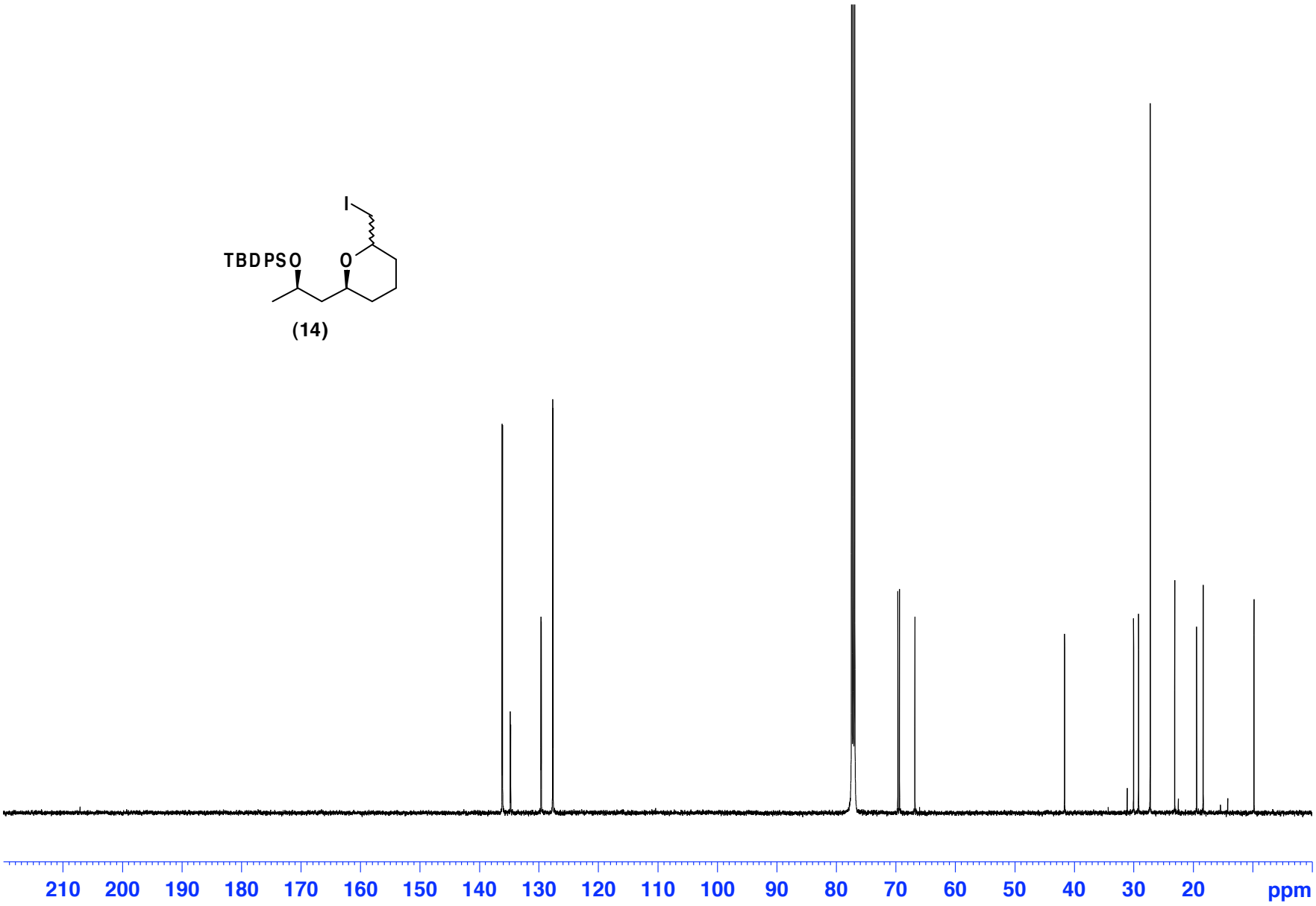

I
TBDPSO
O
(14)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

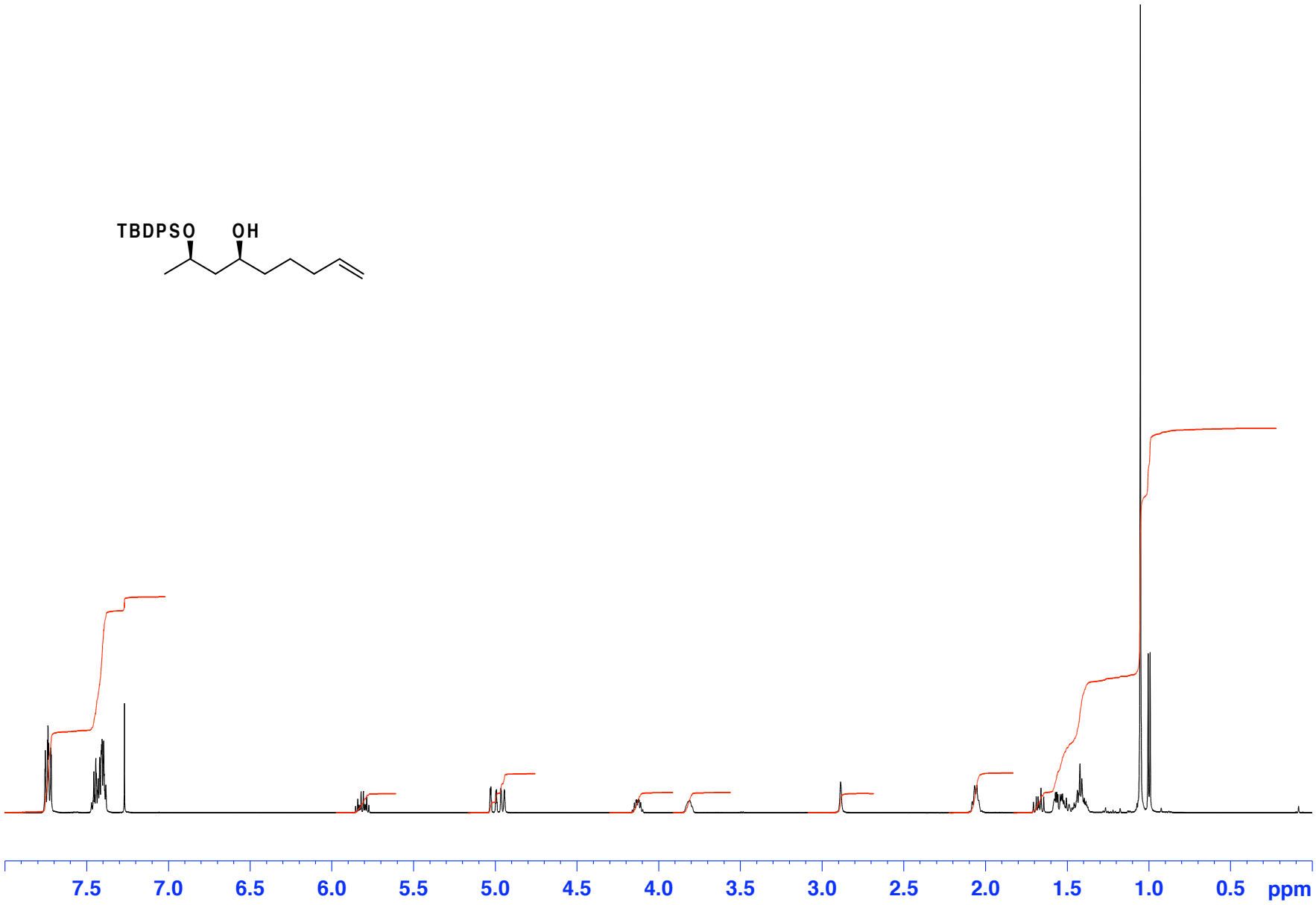
(14)

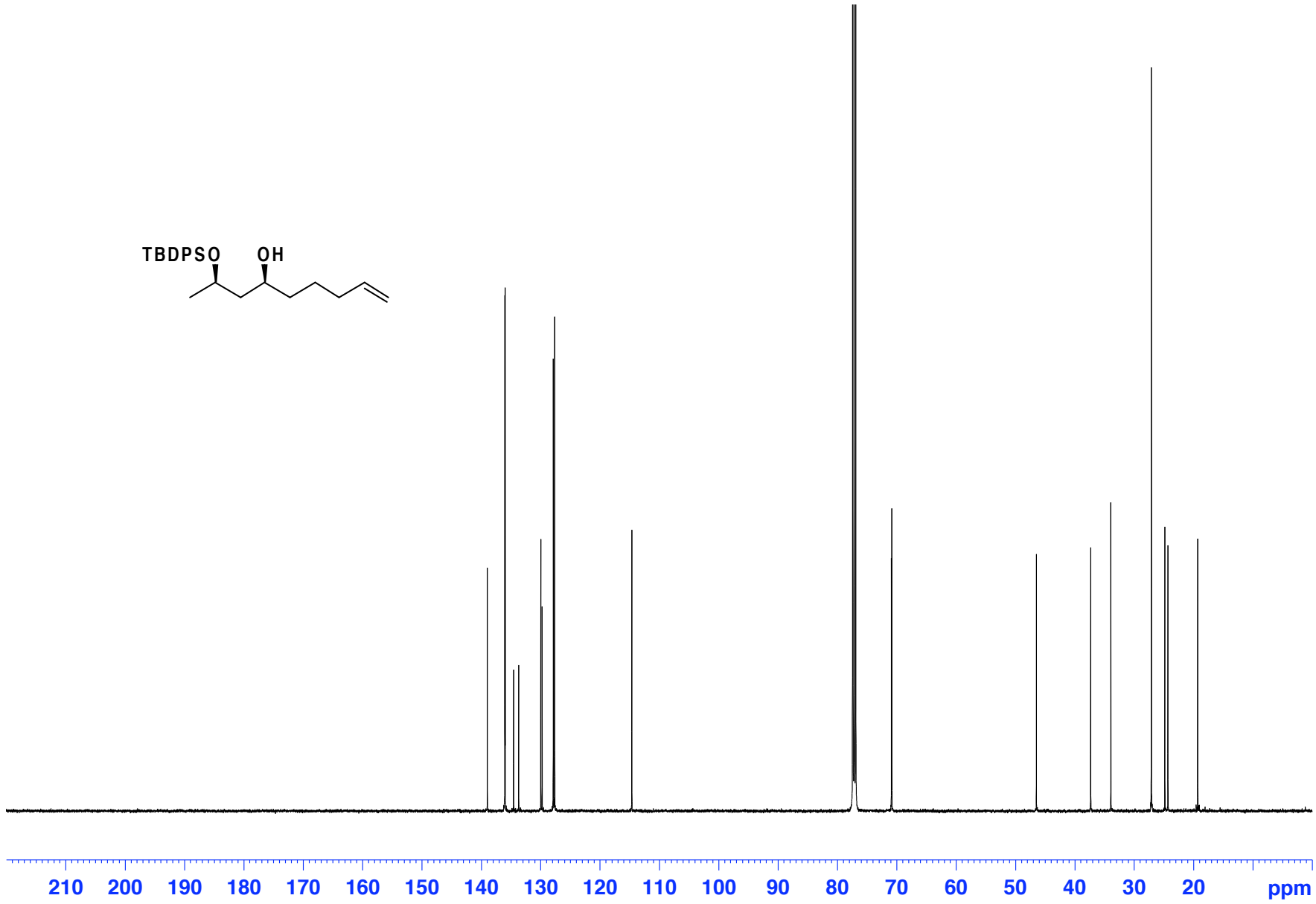


I
TBDPSO
O

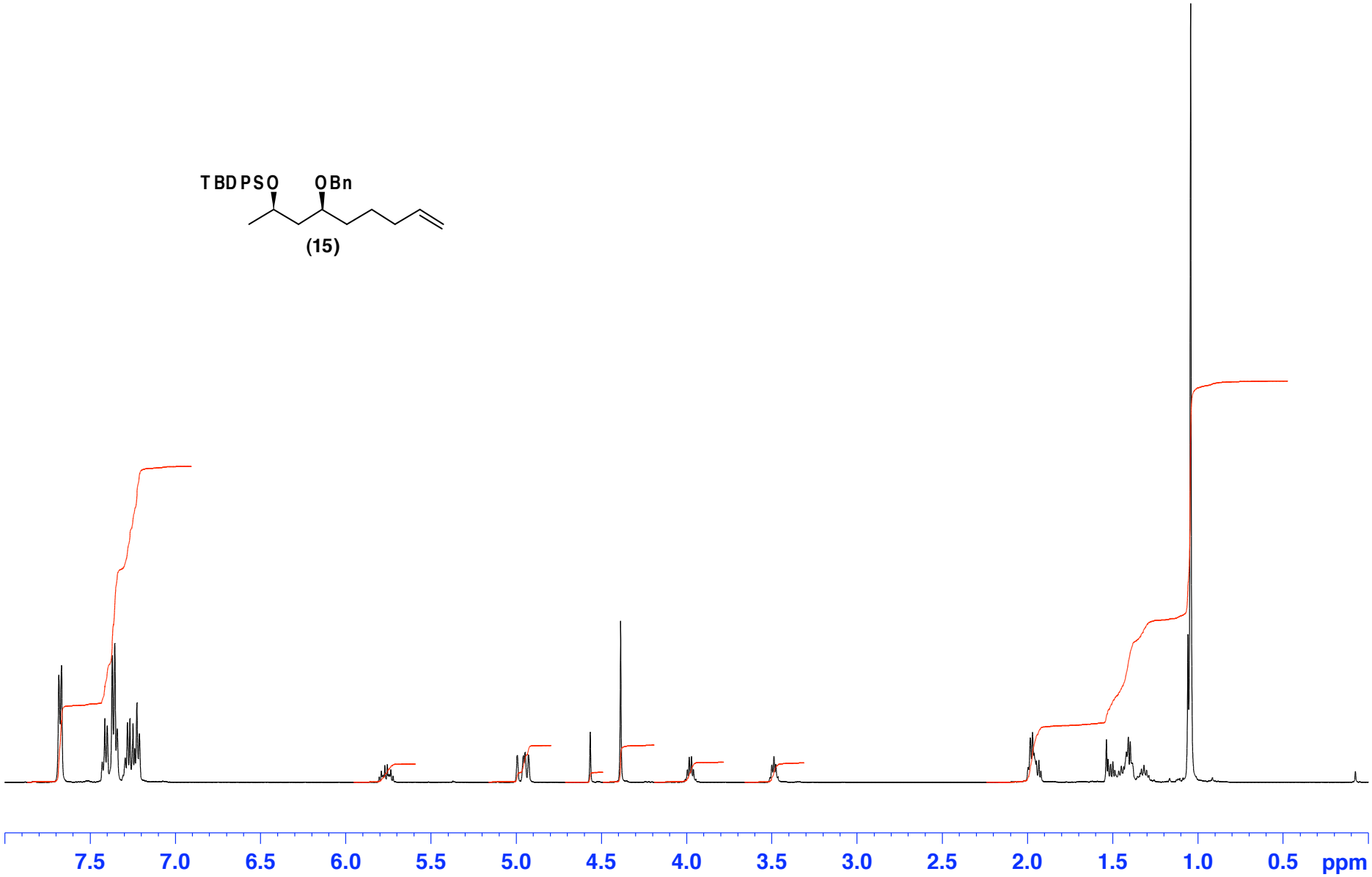
(14)

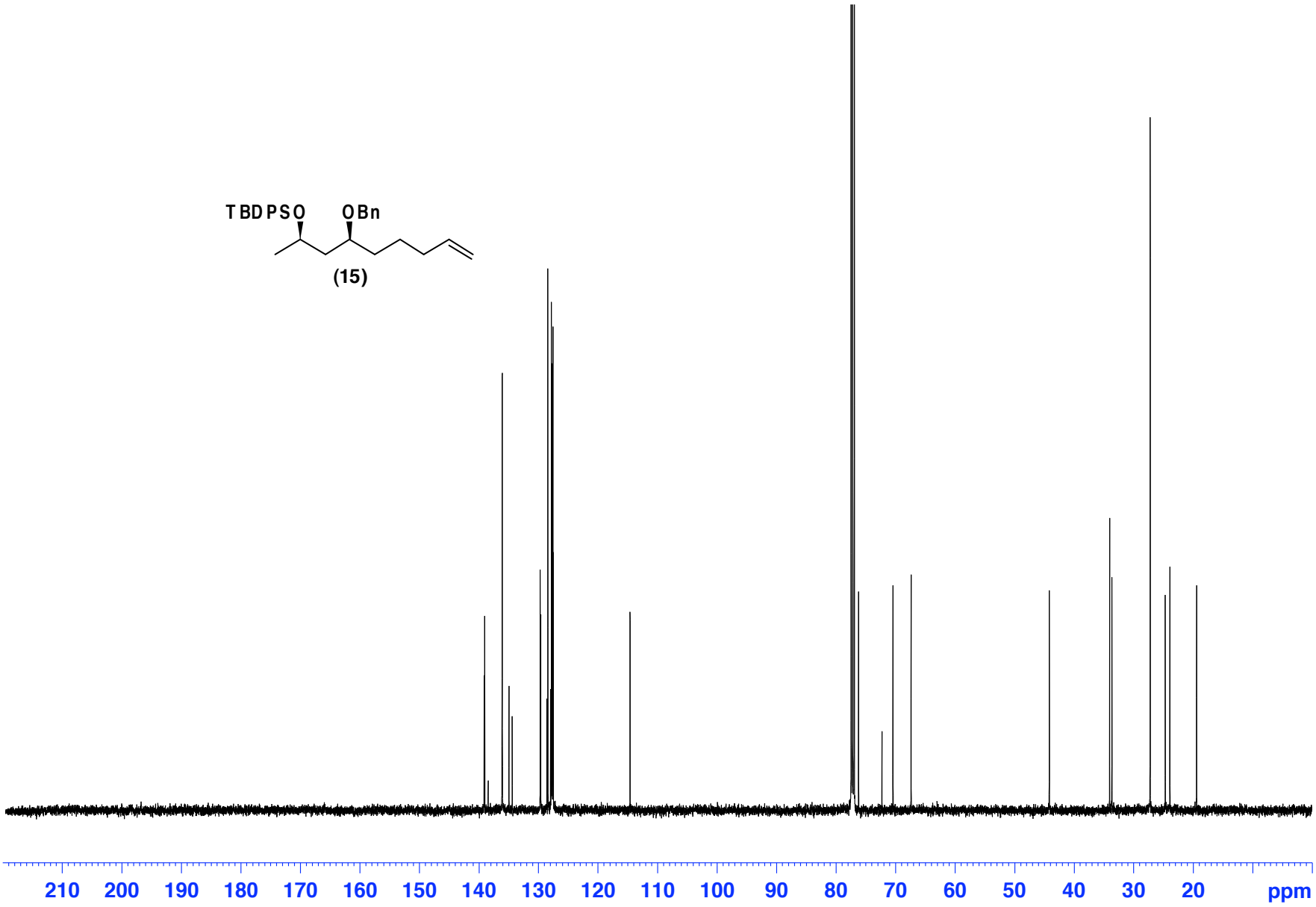

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


TBDPSO
OH
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

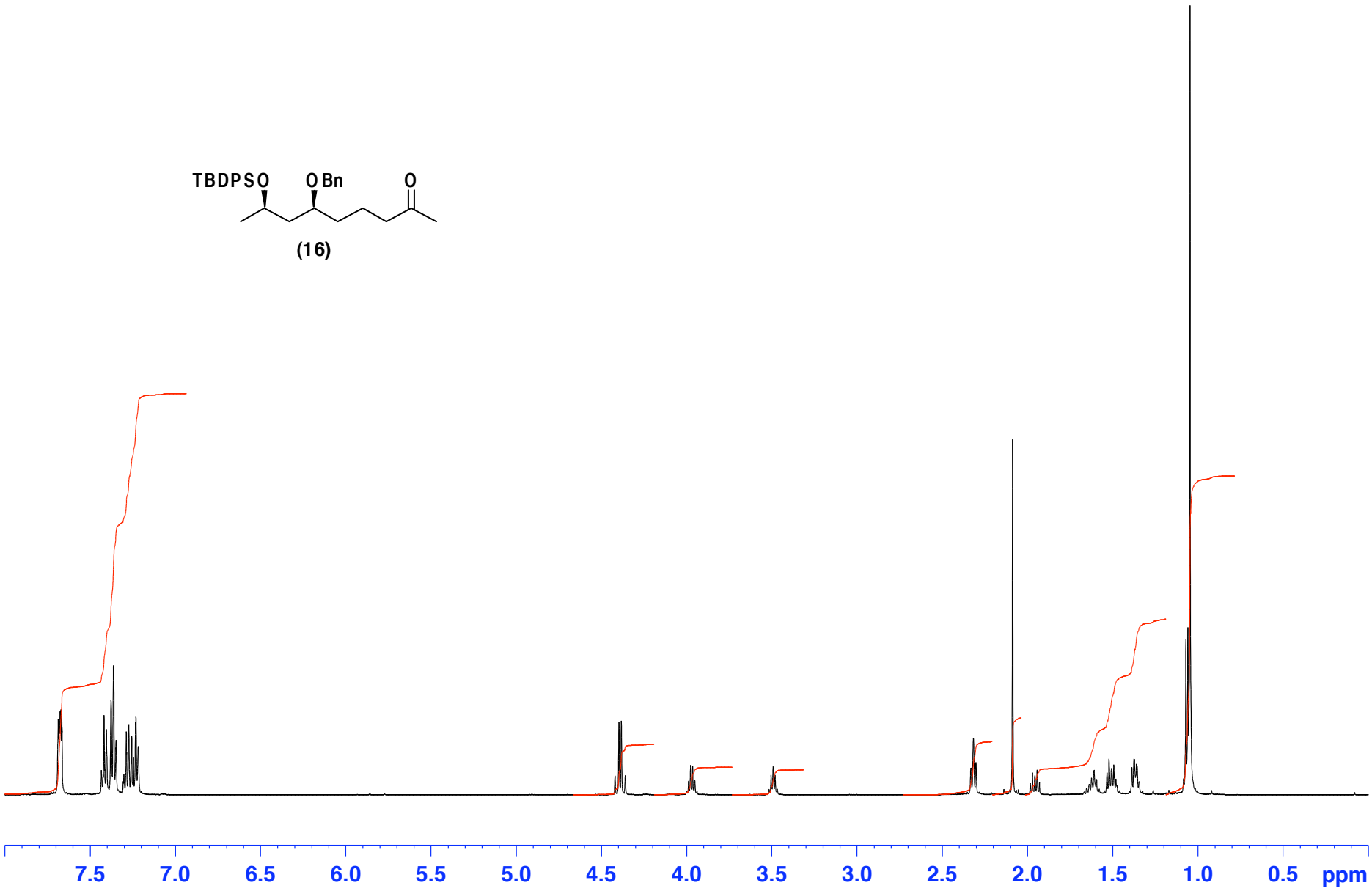

TBDPSO
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

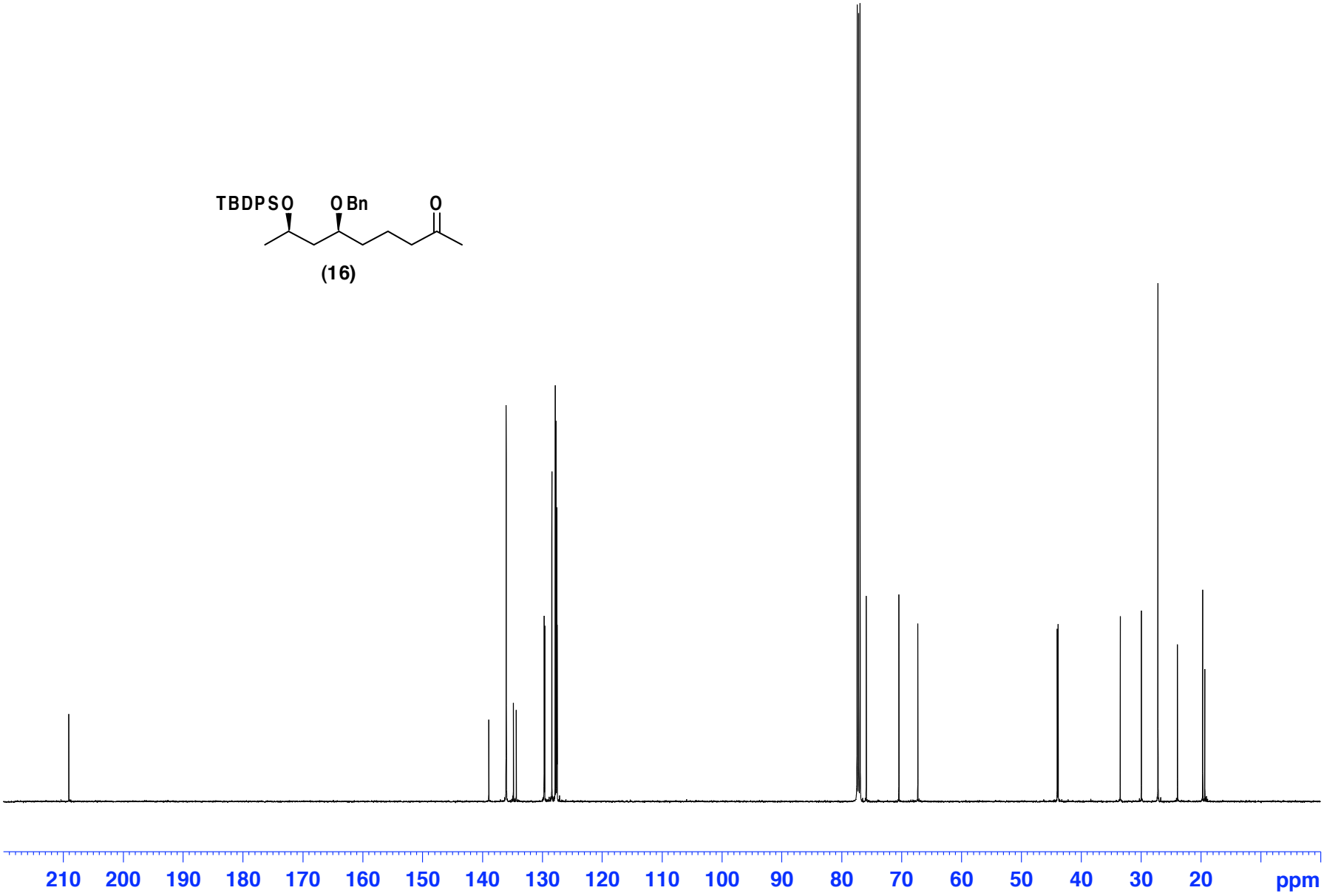
(15)



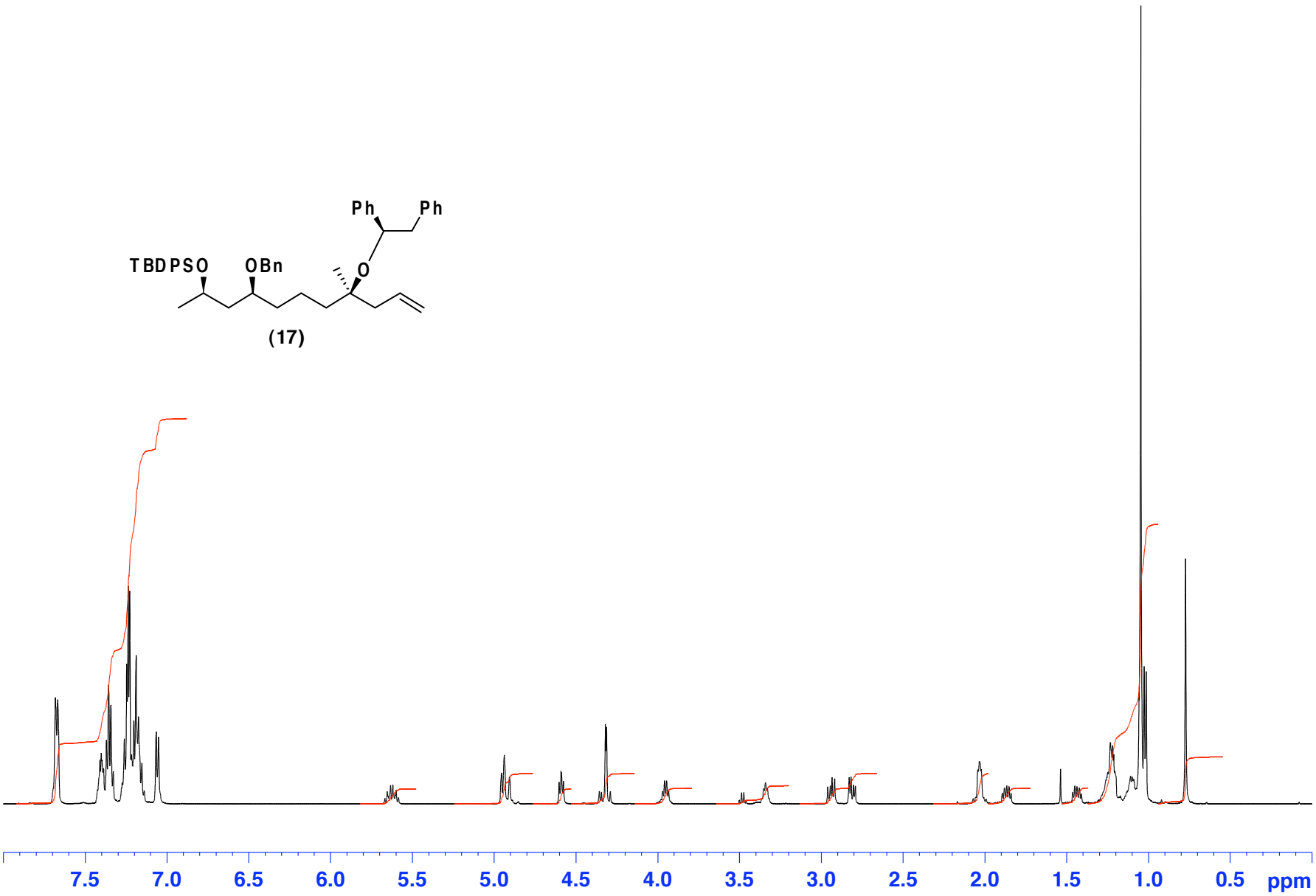

TBDPSO
OBn
(15)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

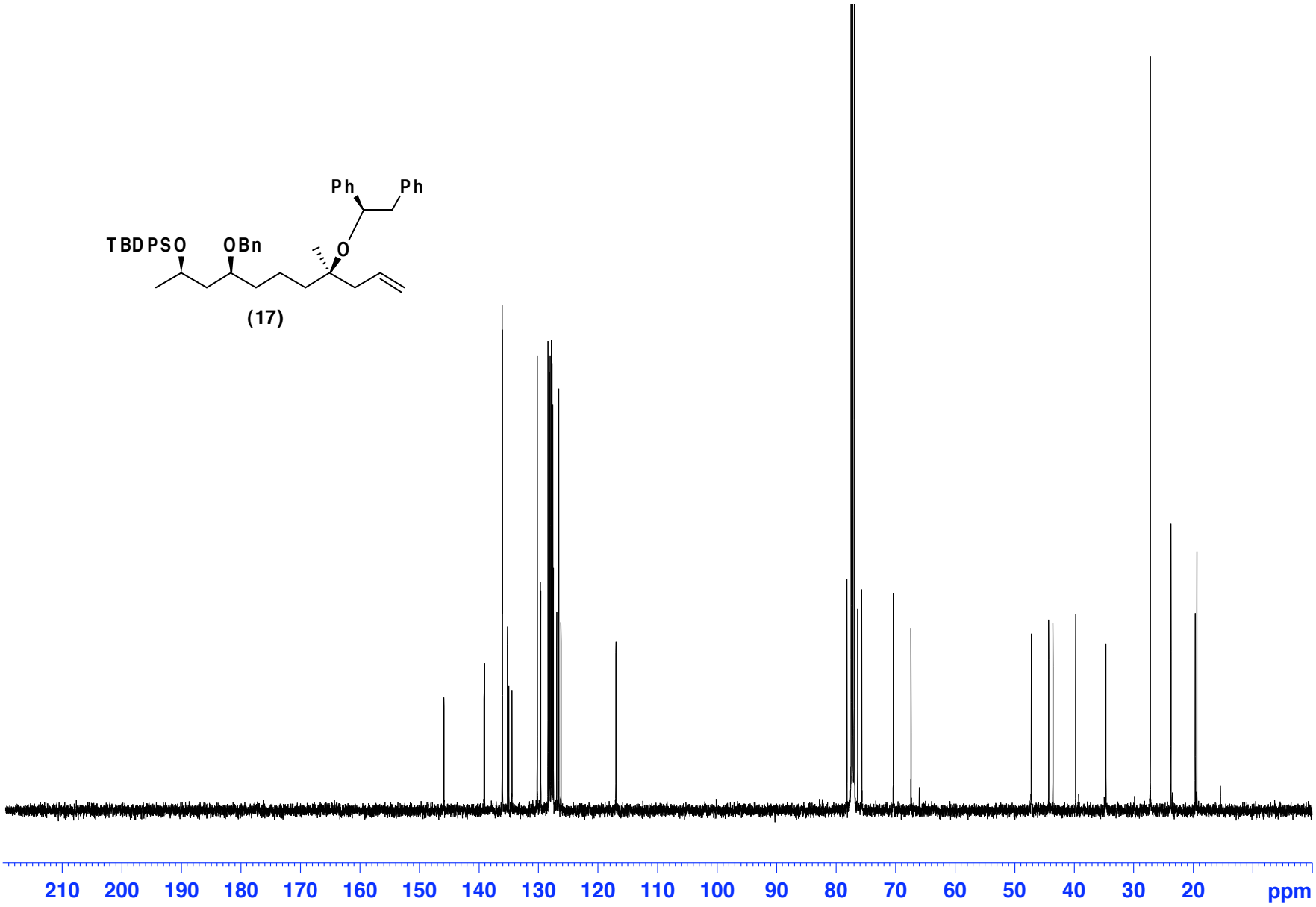
(16)

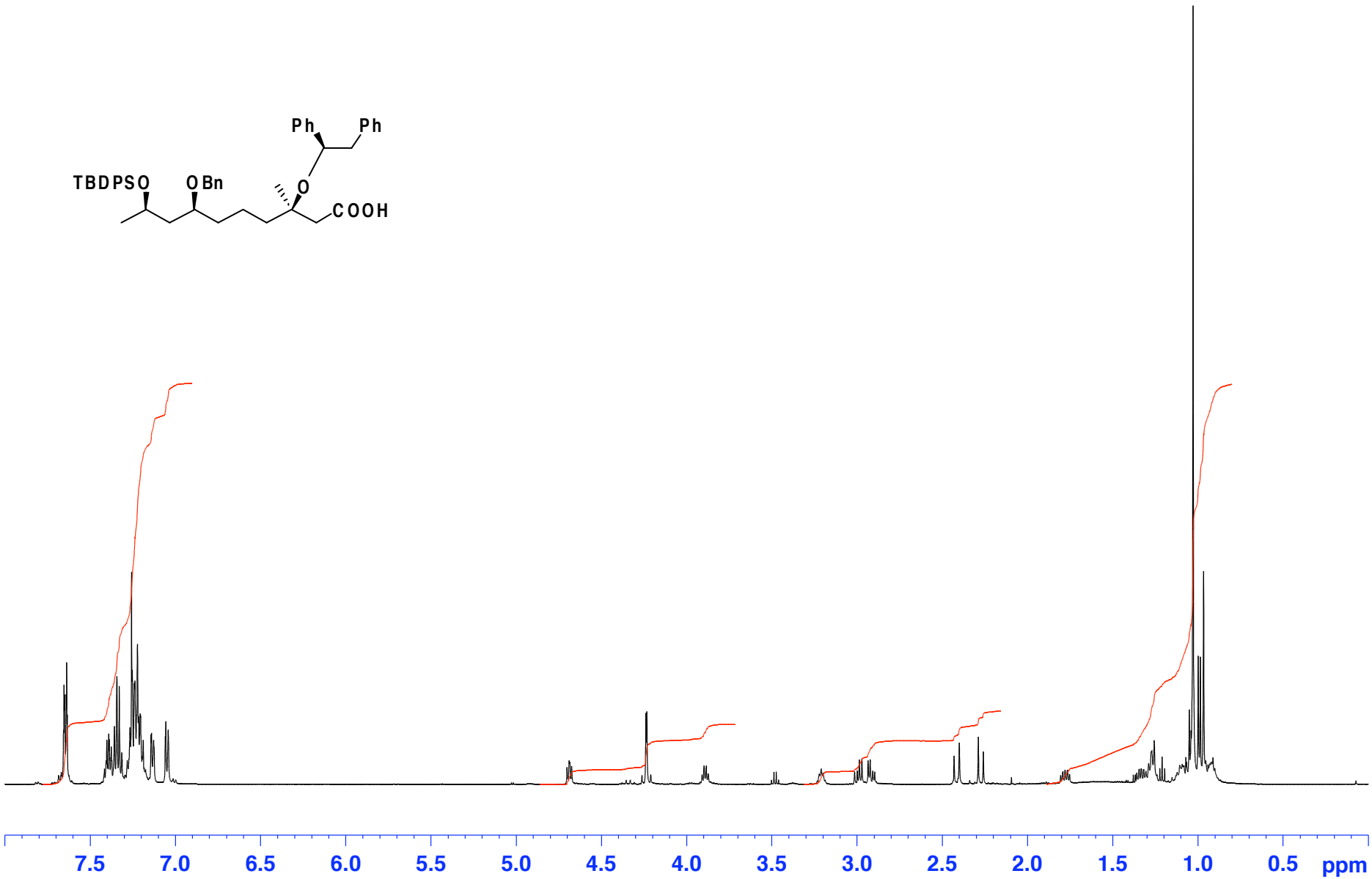


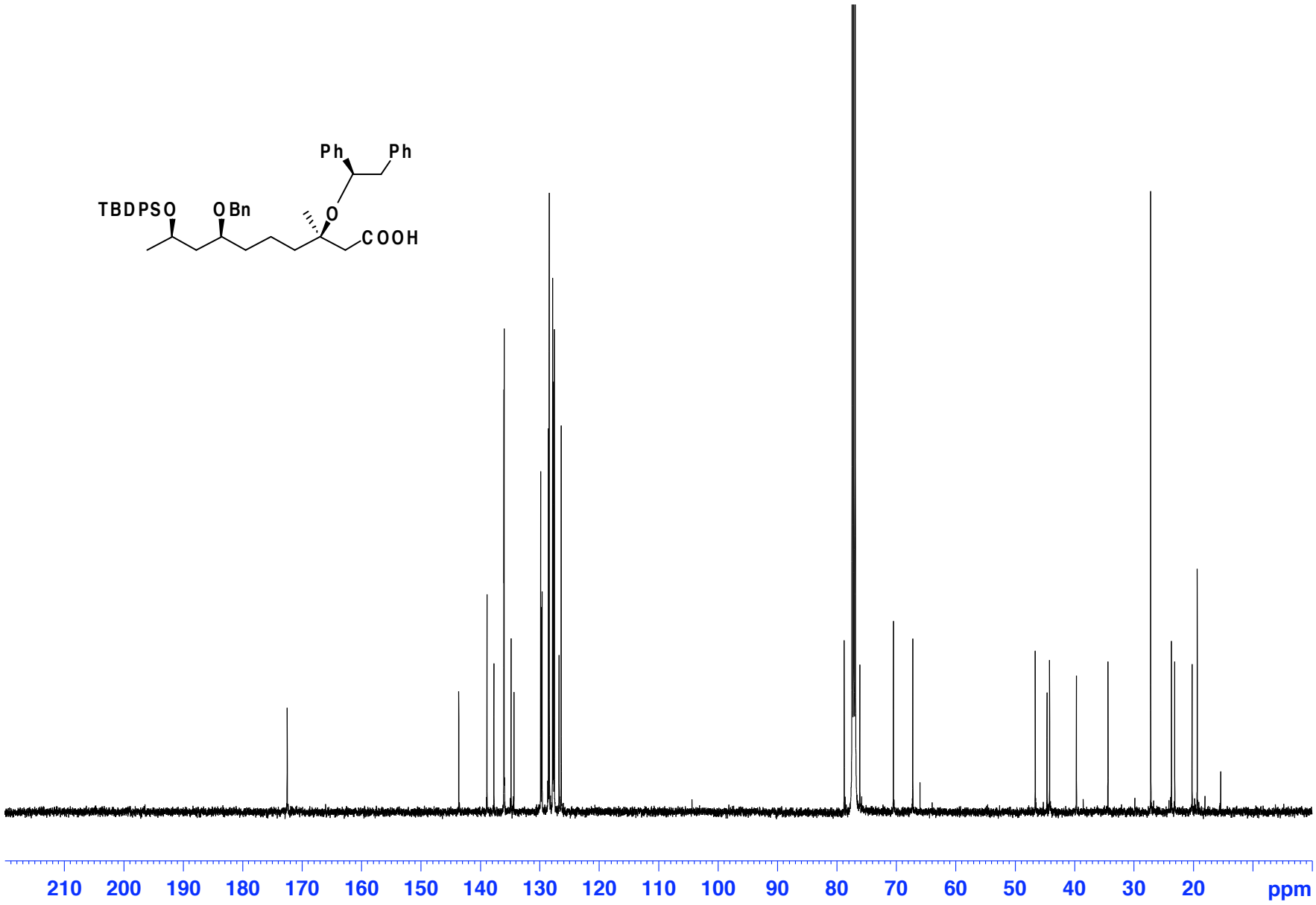

TBDPSO
OBn
O
(16)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

(17)

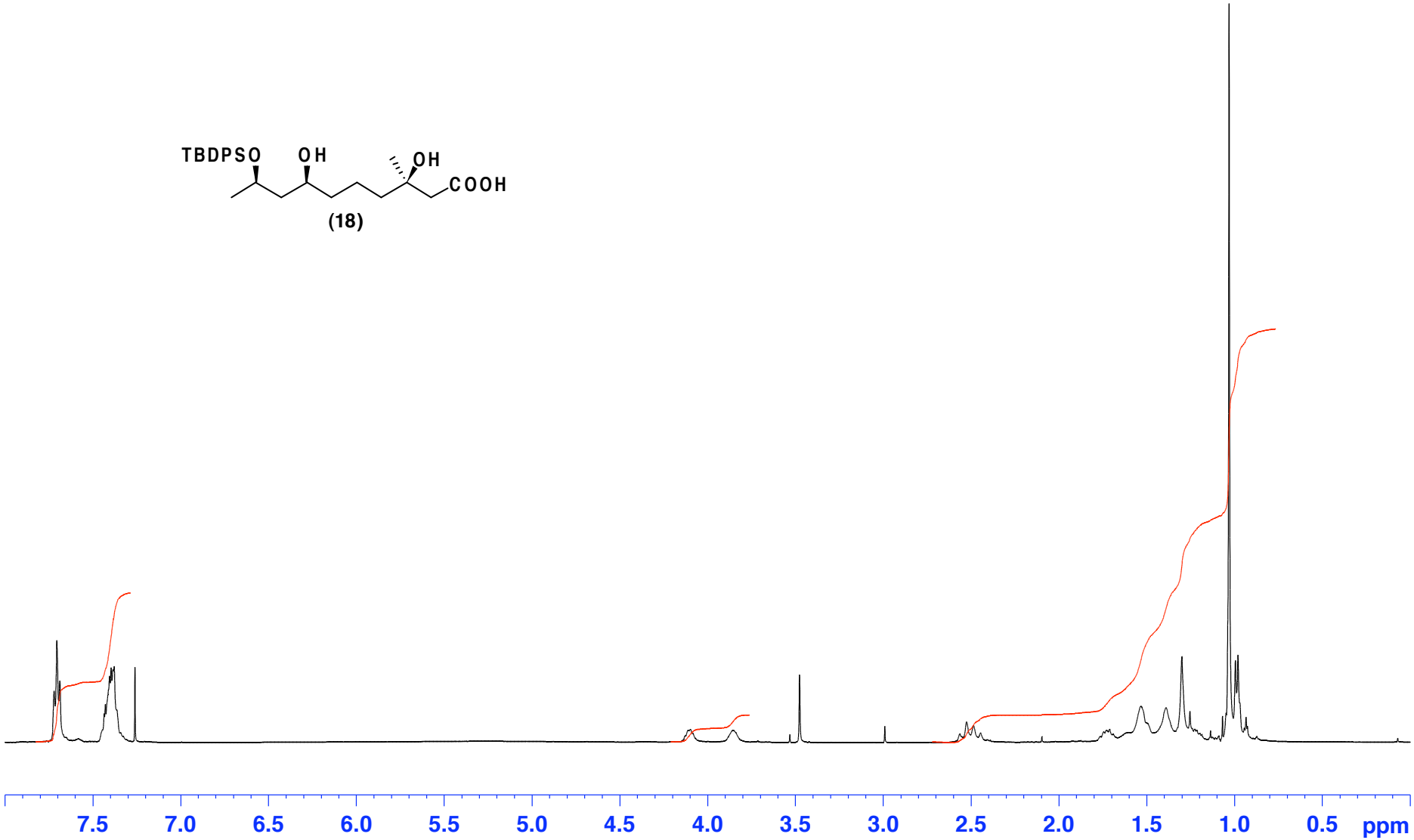


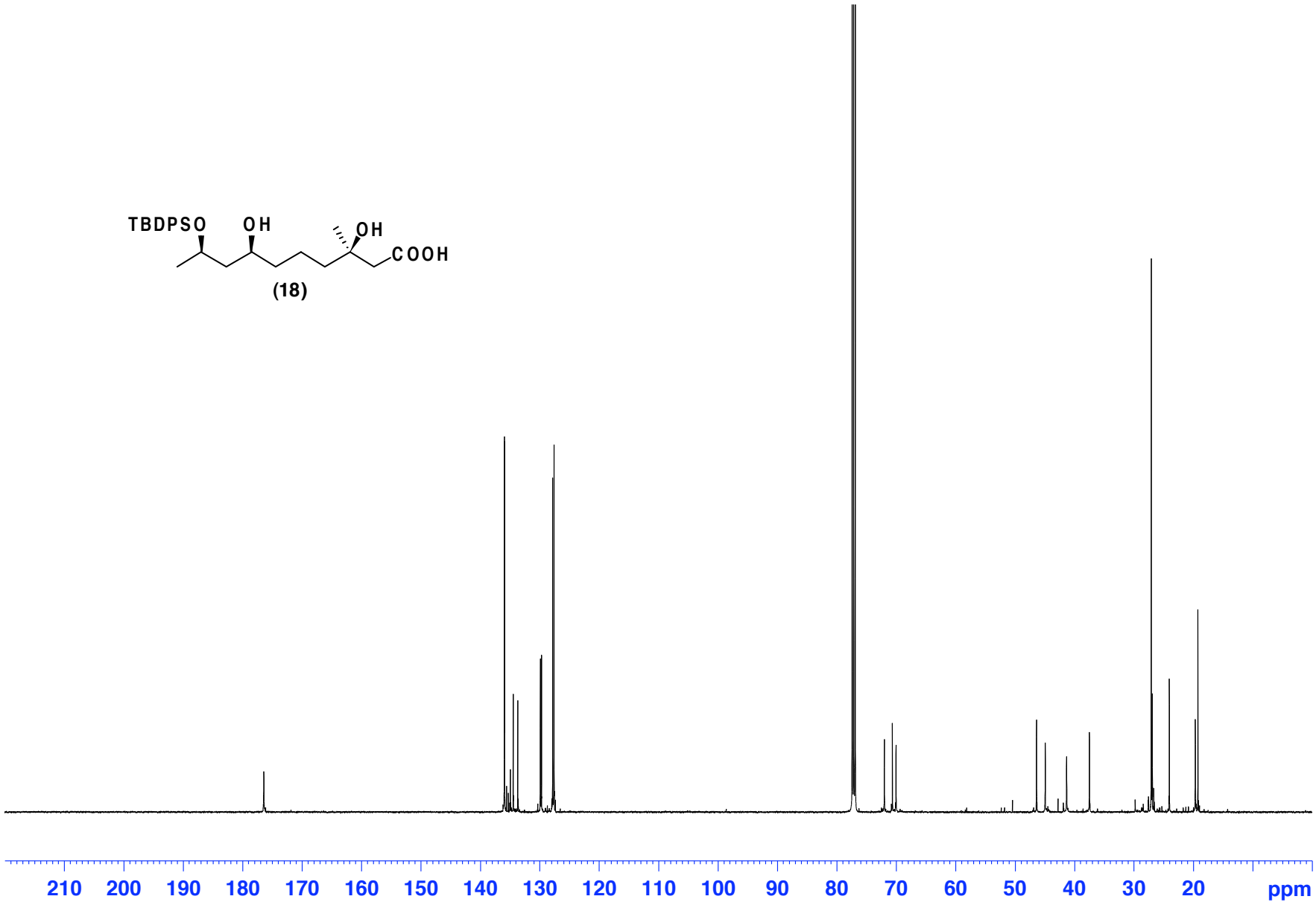

Ph
Ph
TBDPSO
OBn
O
(17)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

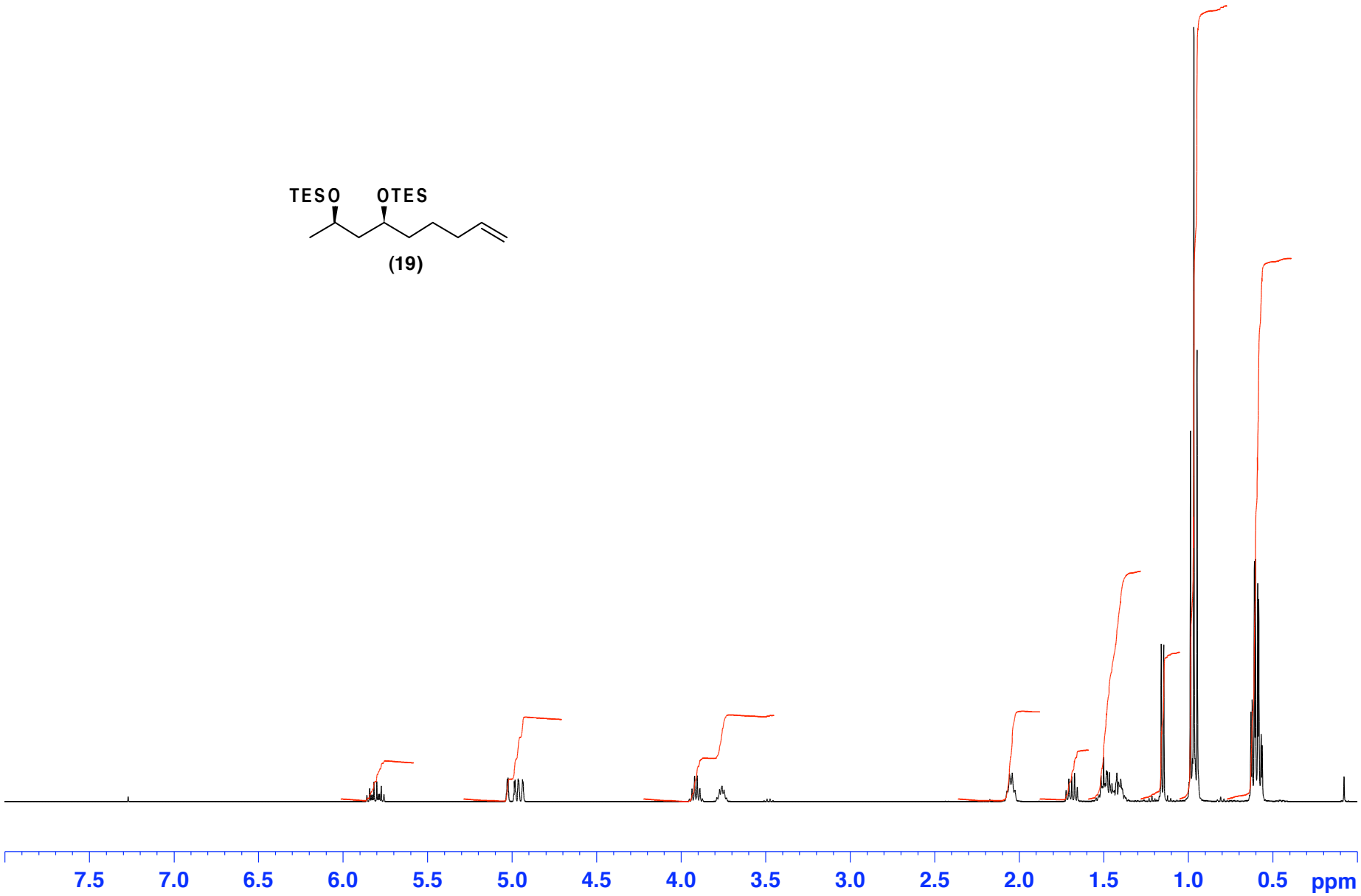

Ph
Ph
TBDPSO
OBn
O
COOH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


Ph
Ph
TBDPSO
OBn
O
COOH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

(18)

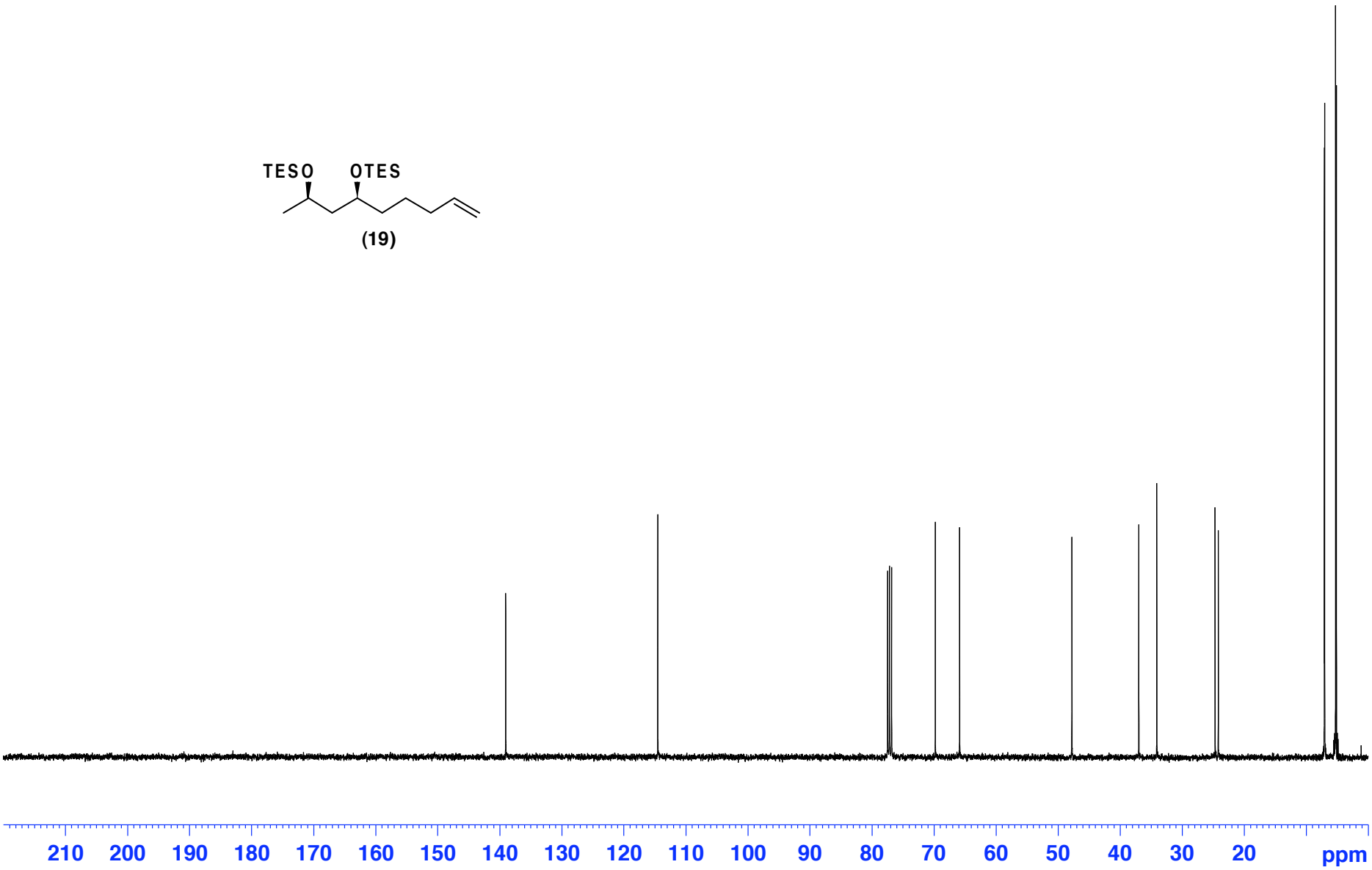


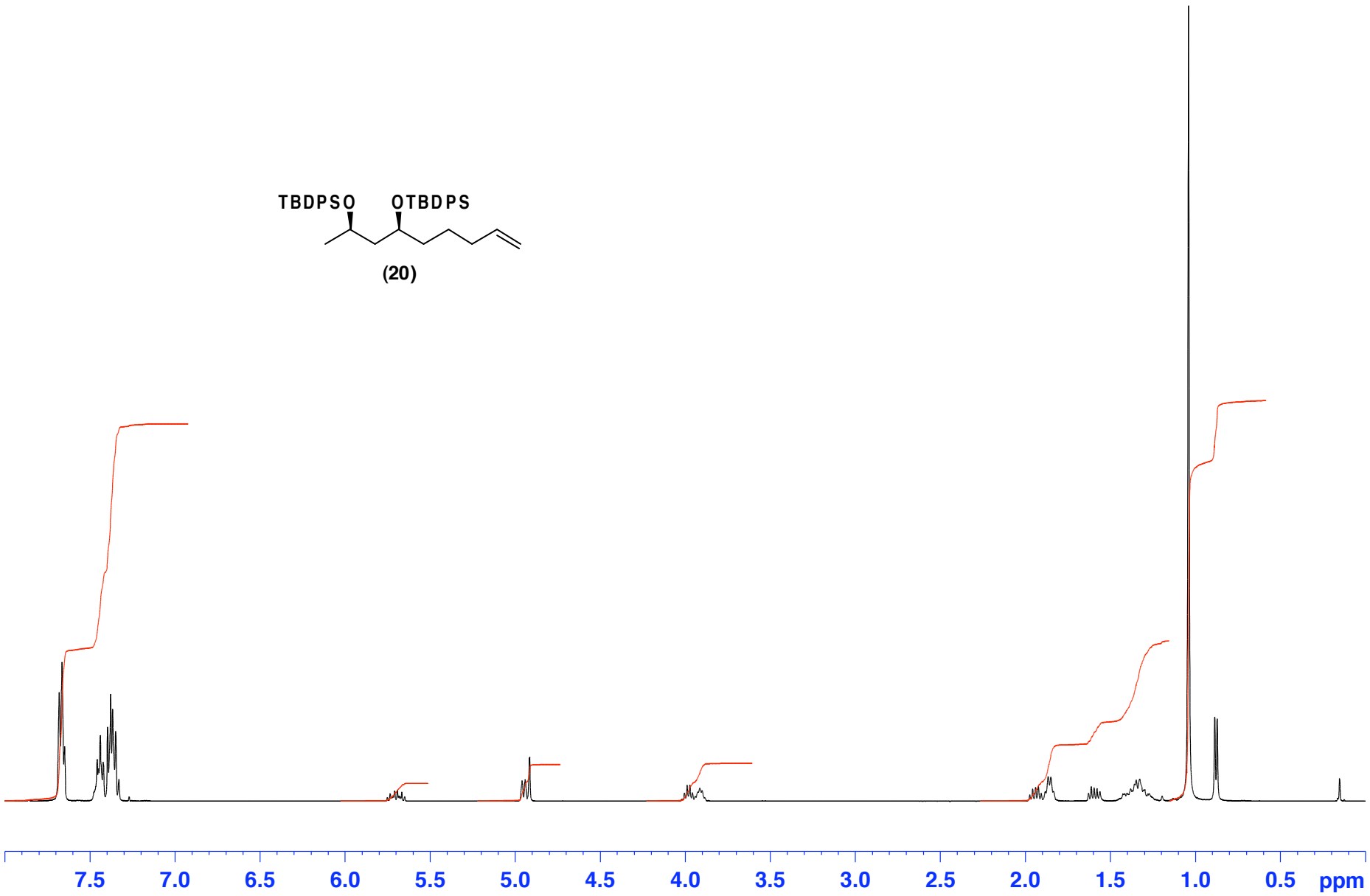

TBDPSO
OH
OH
COOH
(18)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

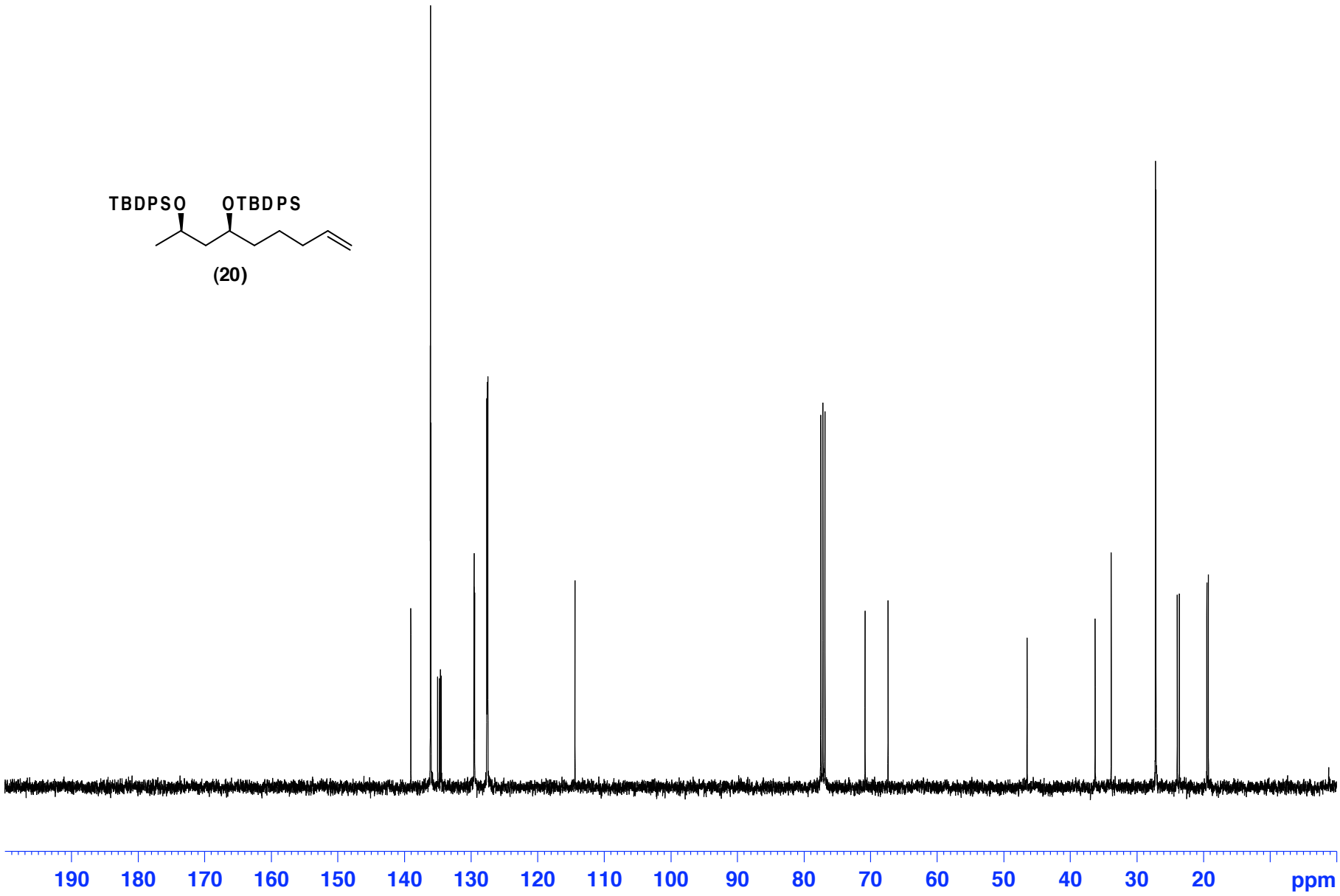

TESO
OTES
(19)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

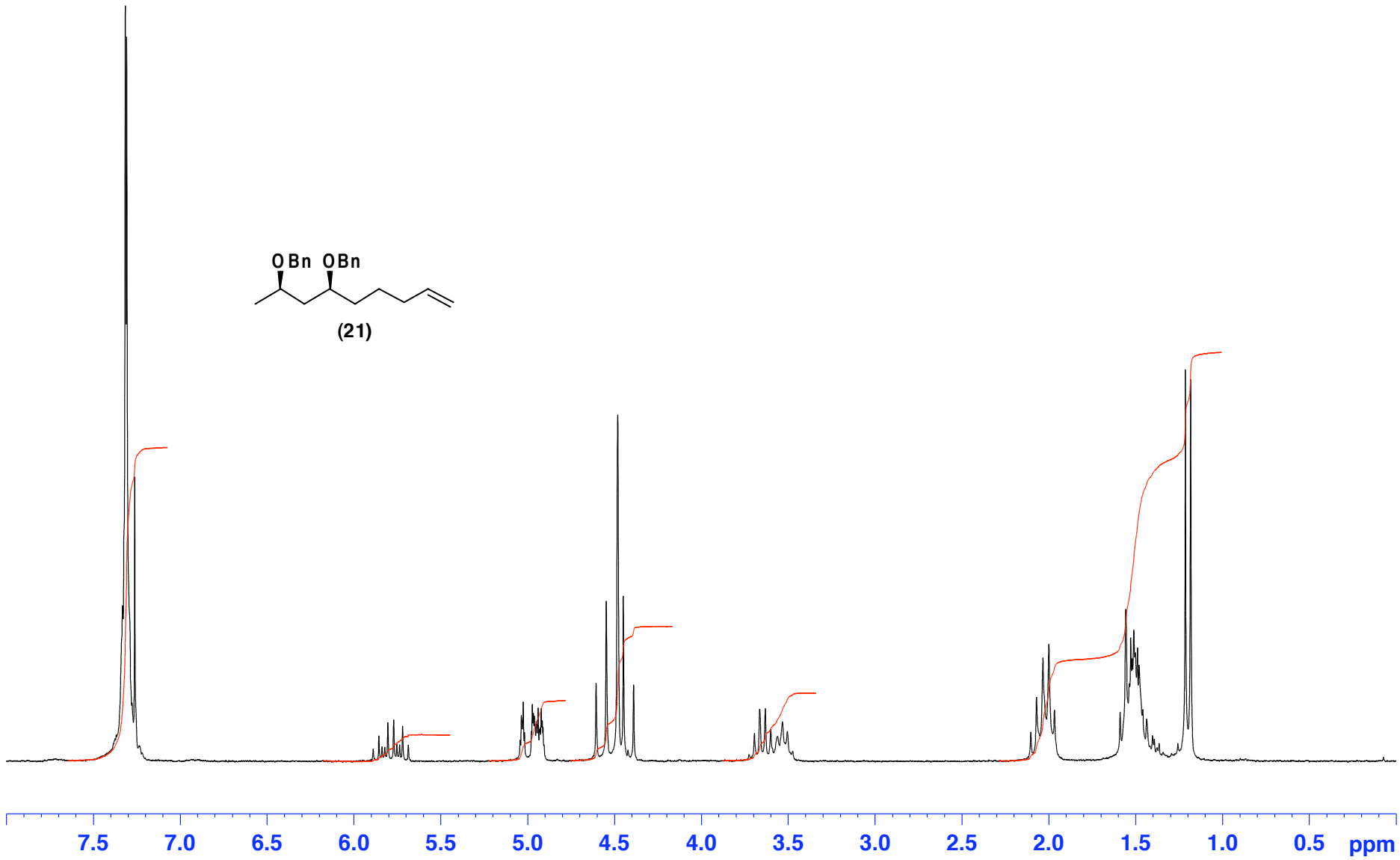
TESO
OTES

(19)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


TBDPSO
OTBDPS
(20)
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


TBDPSO
OTBDPS
(20)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OBn OBn
(21)
7.5
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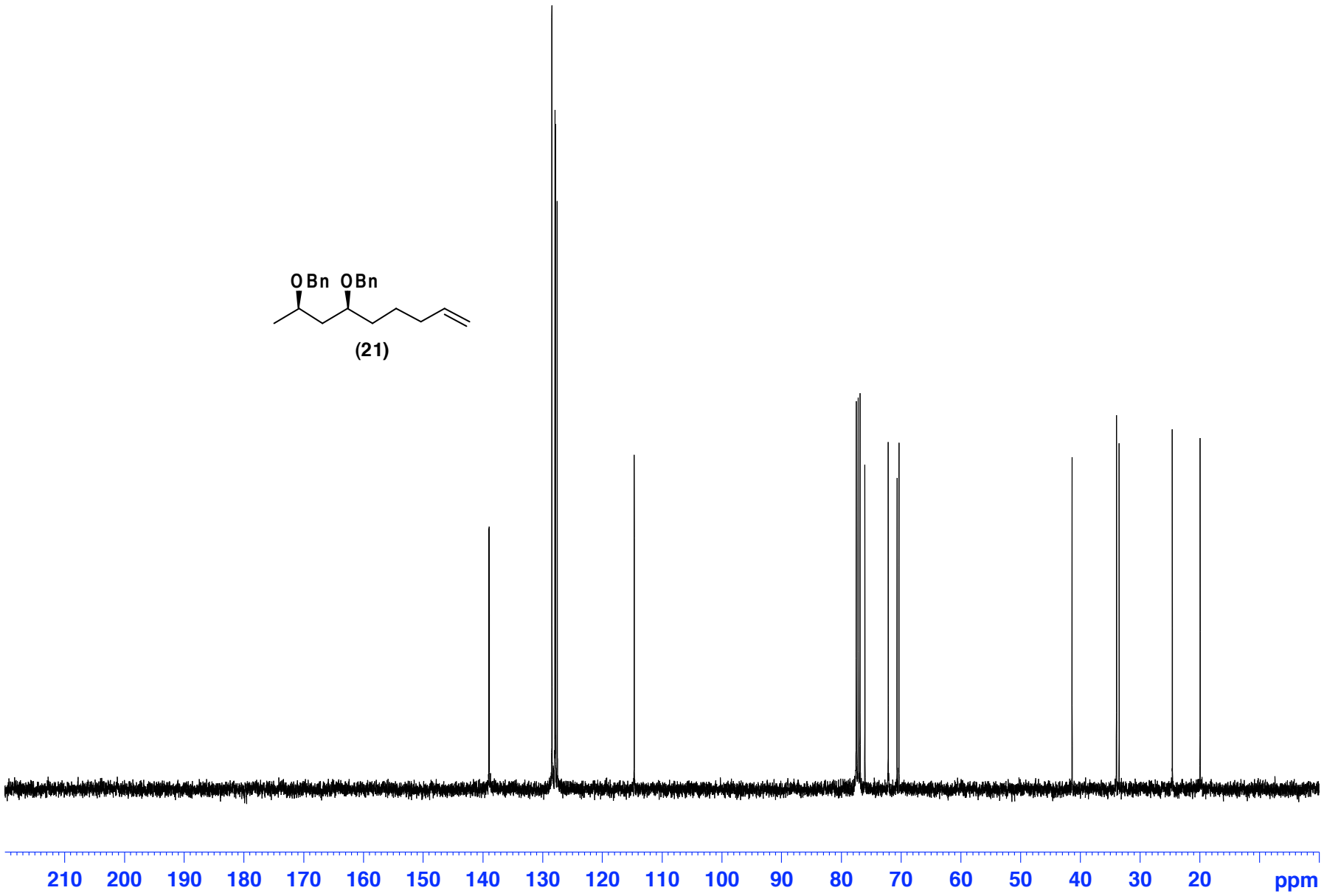
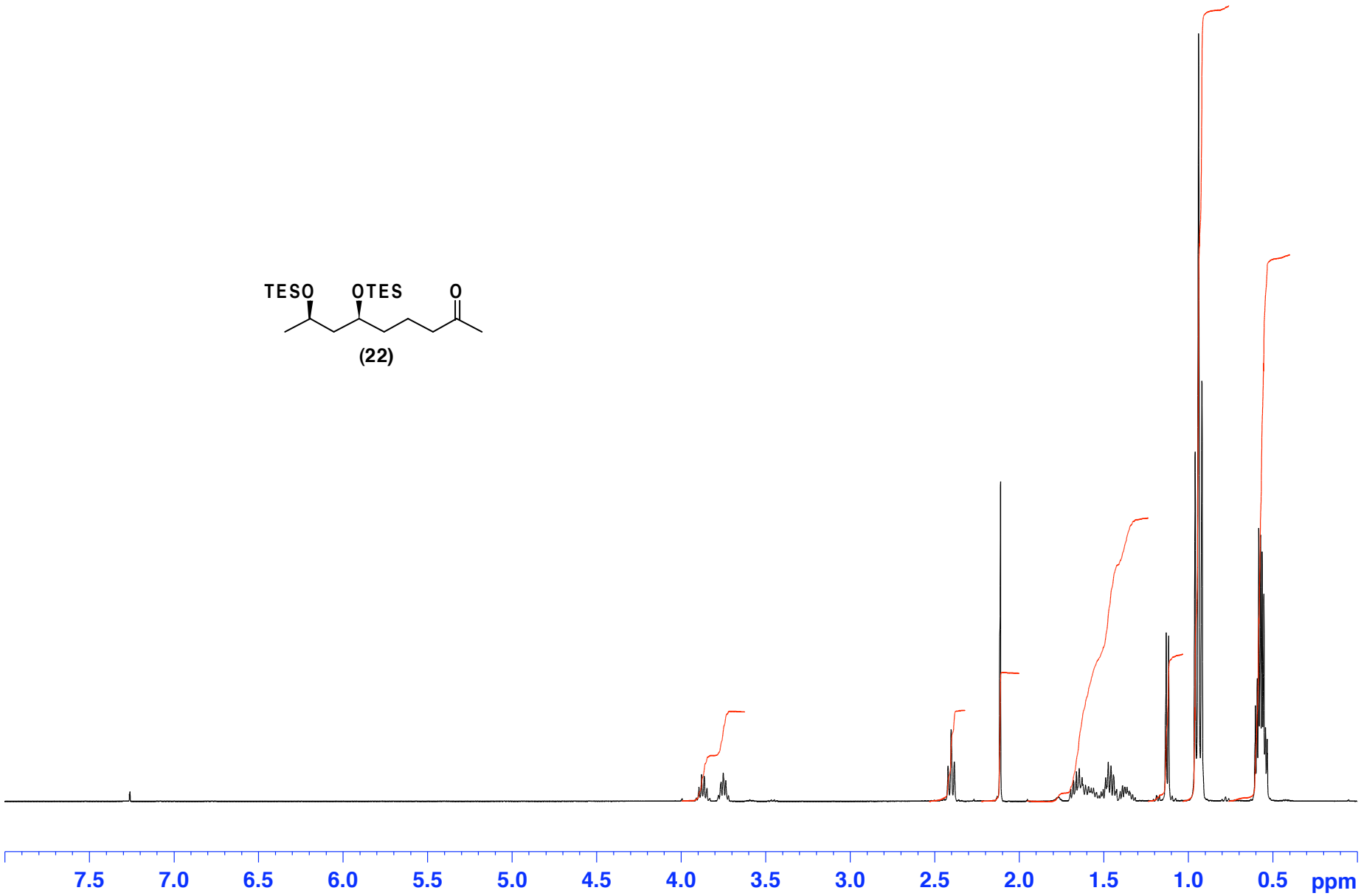
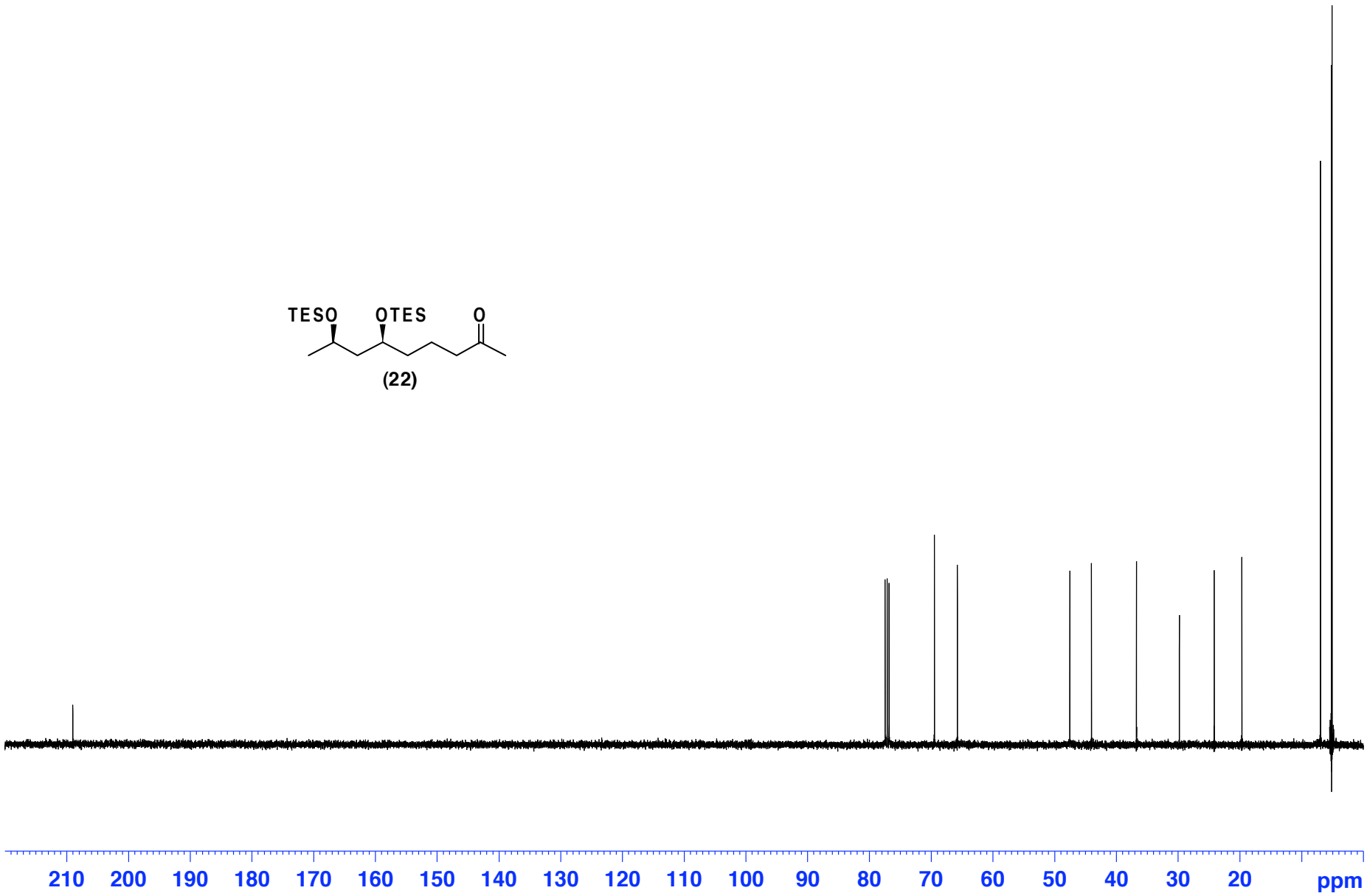
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


OBn OBn
(21)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

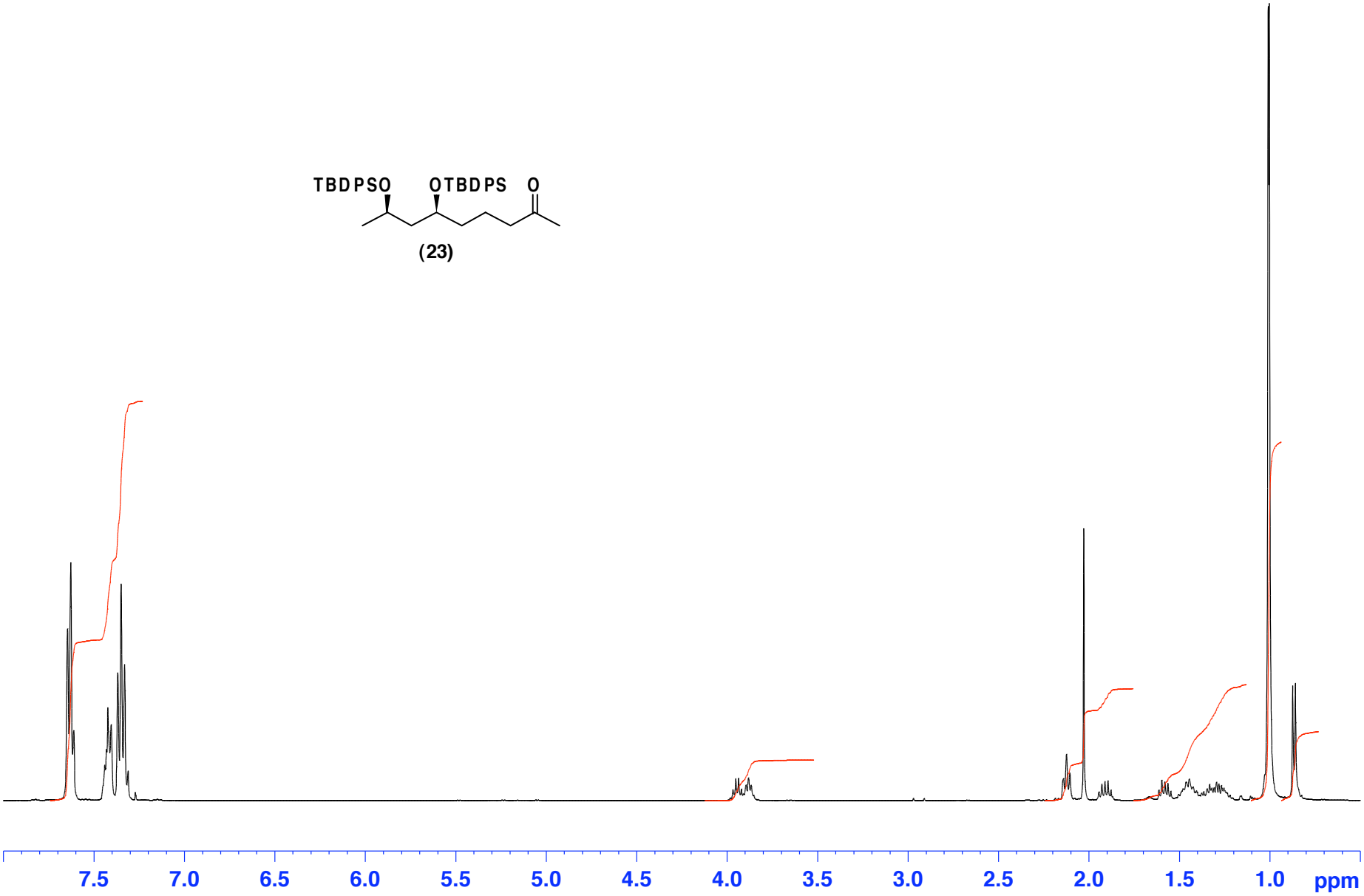

TESO
OTES
O
(22)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

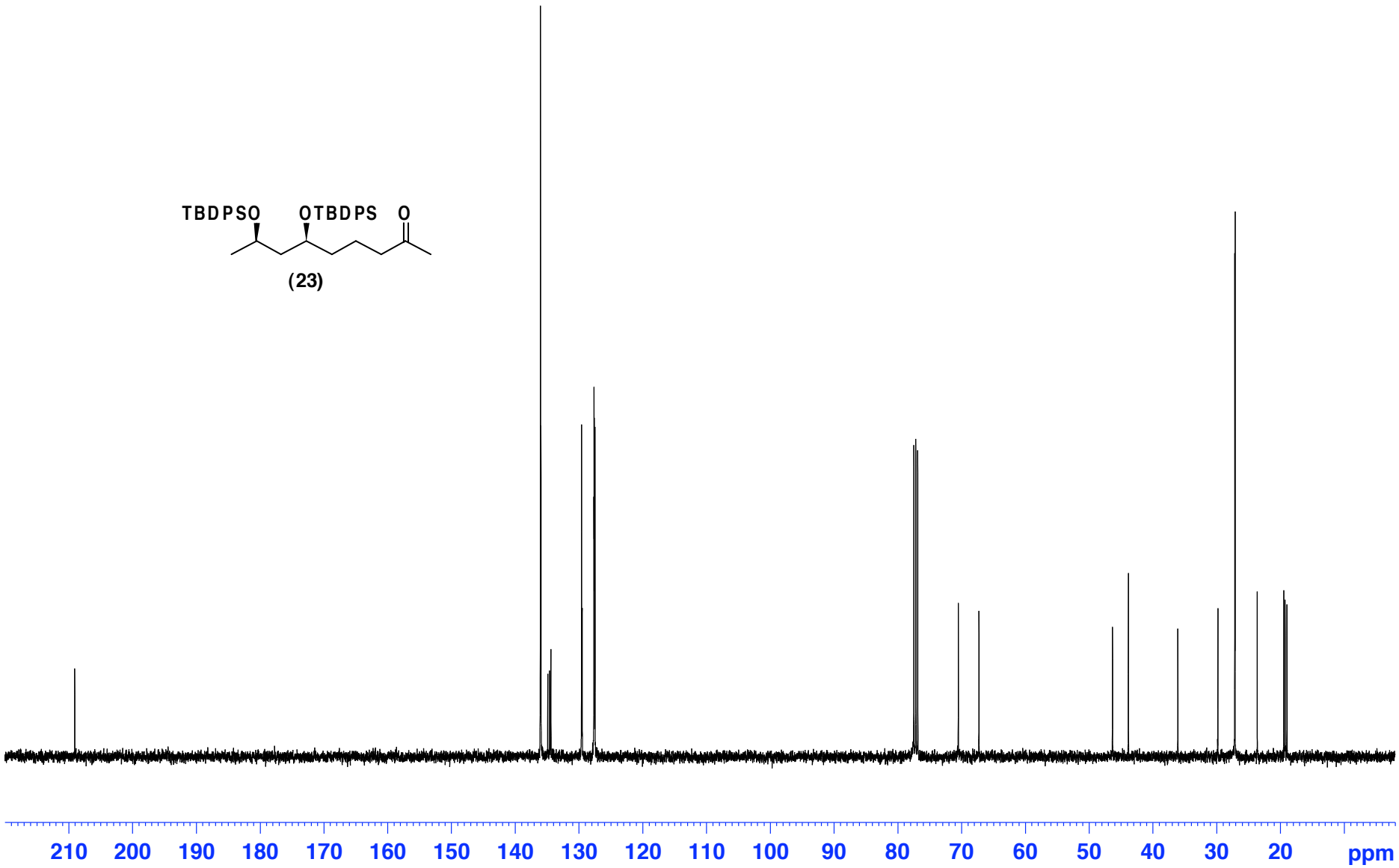
TESO
OTES
O

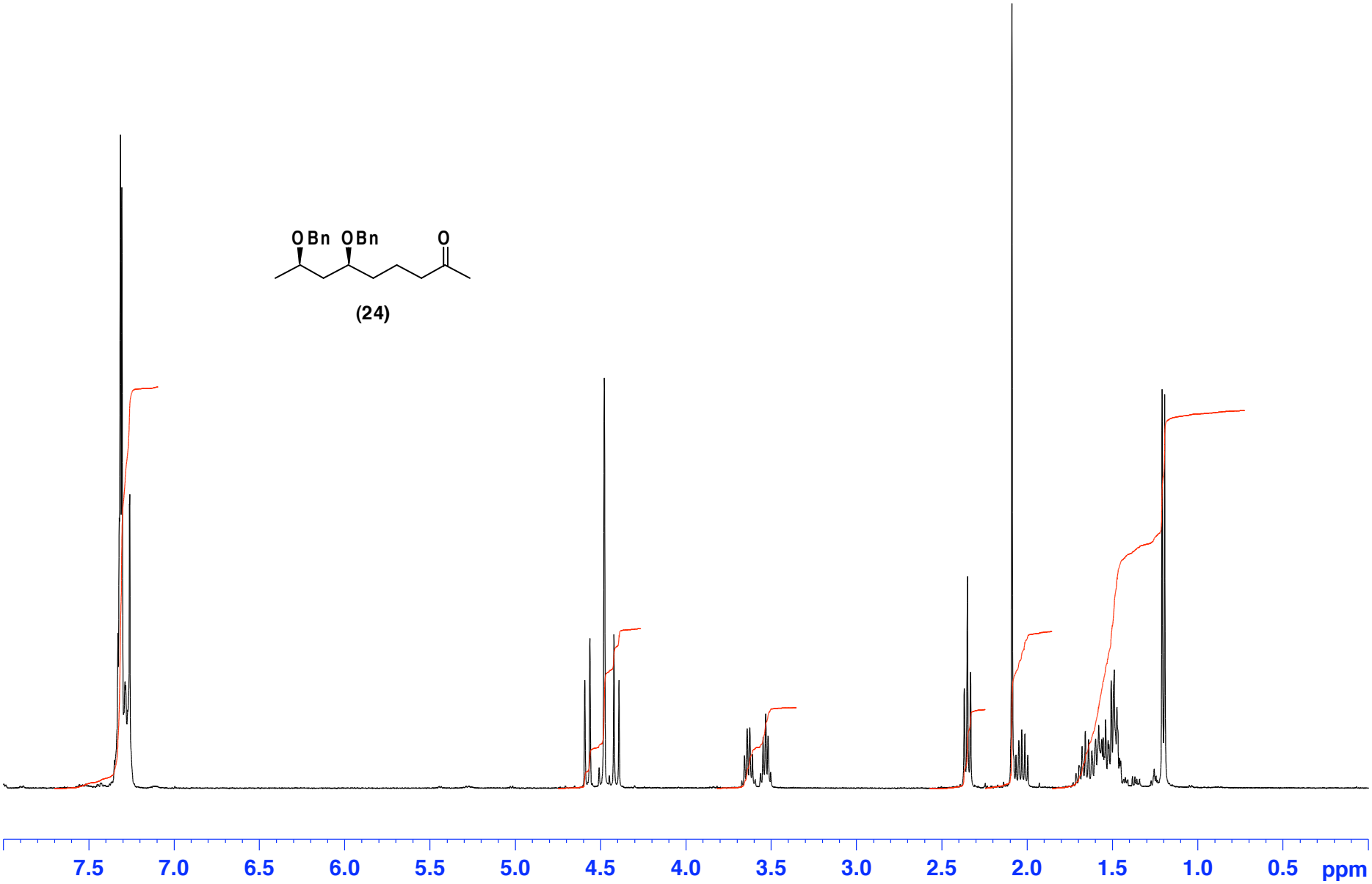
(22)

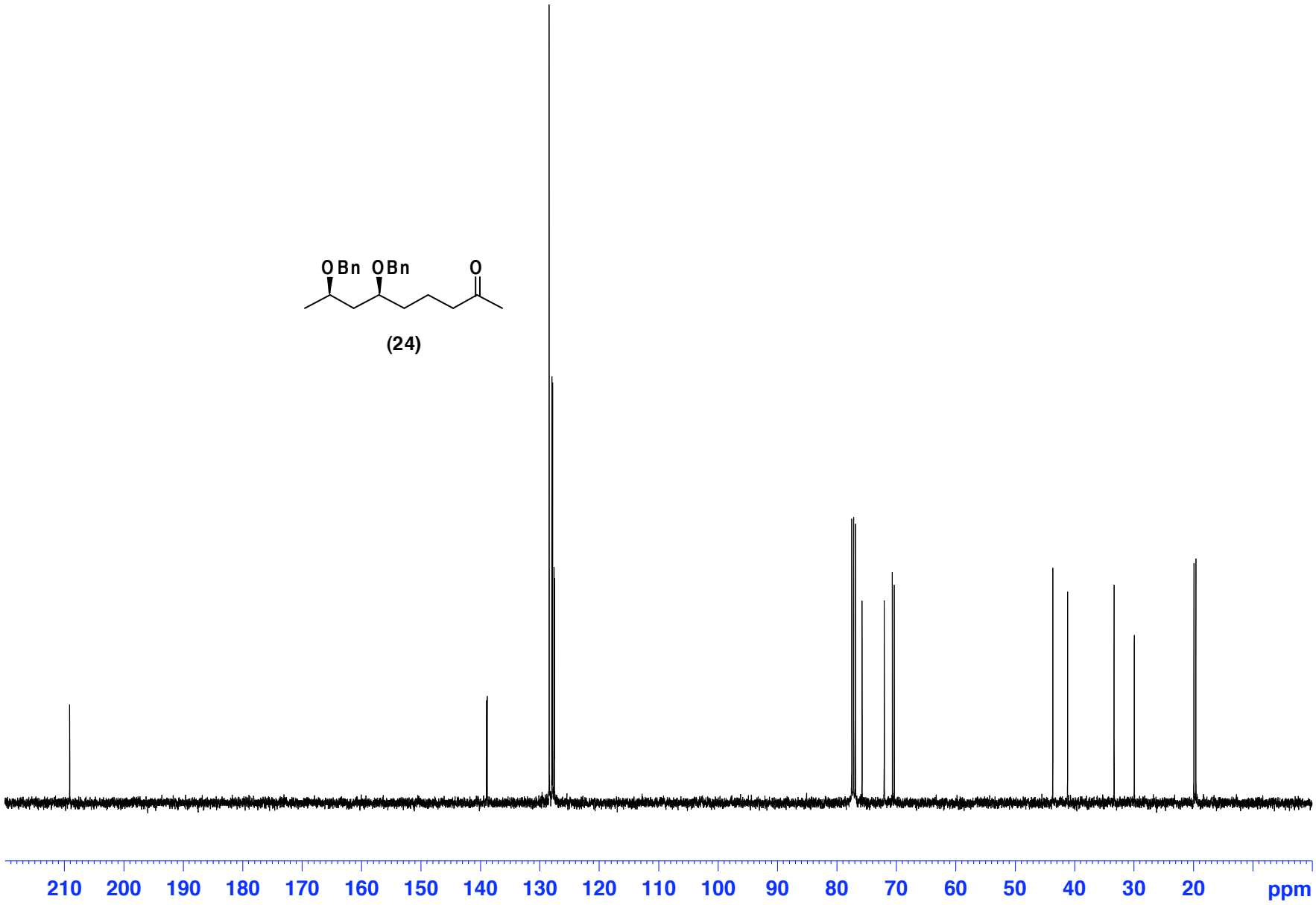

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

(23)

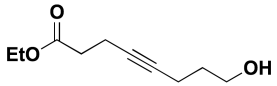


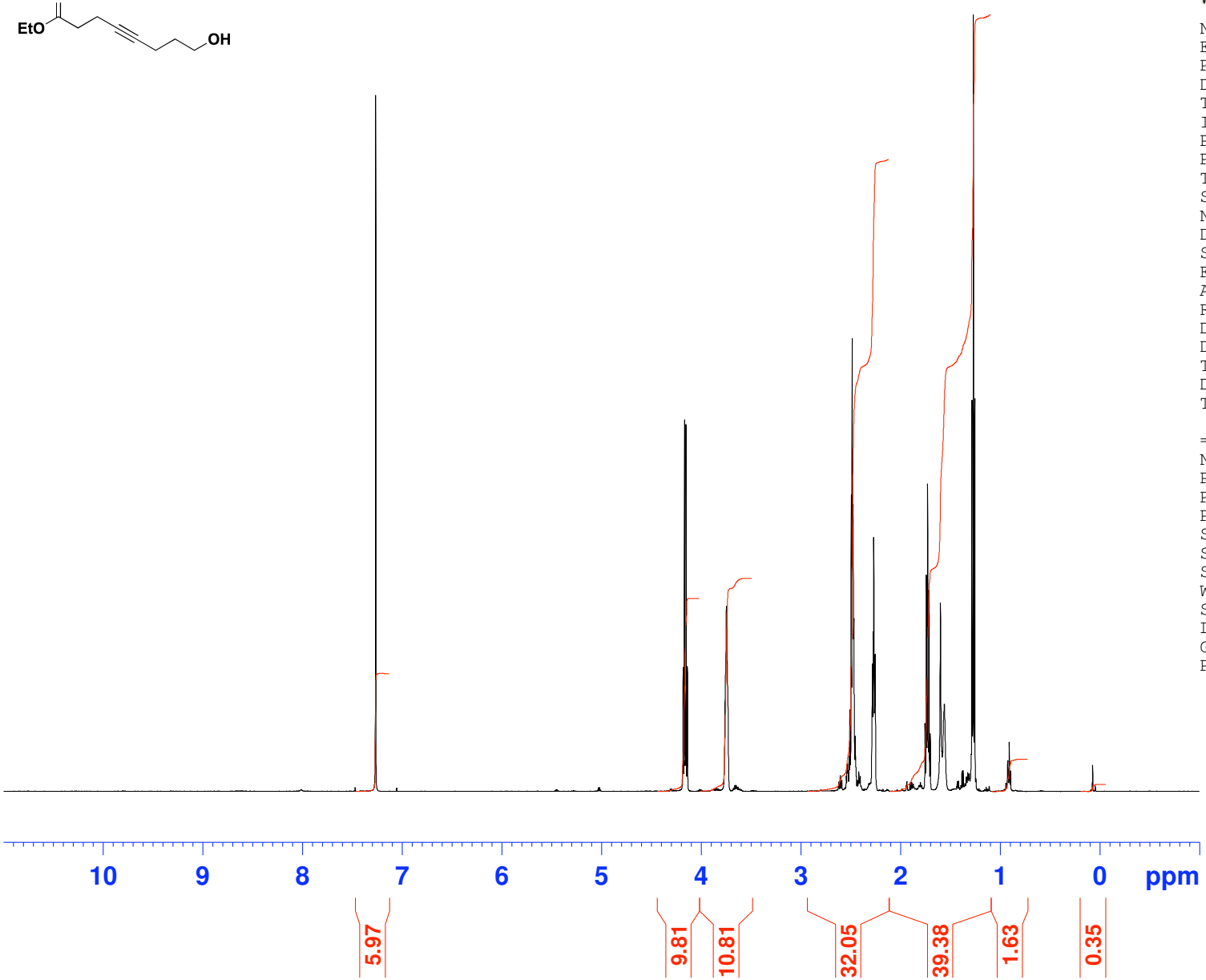

TBDPSO
OTBDPS
O
(23)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


OBn OBn O
(24)
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


OBn OBn O
(24)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

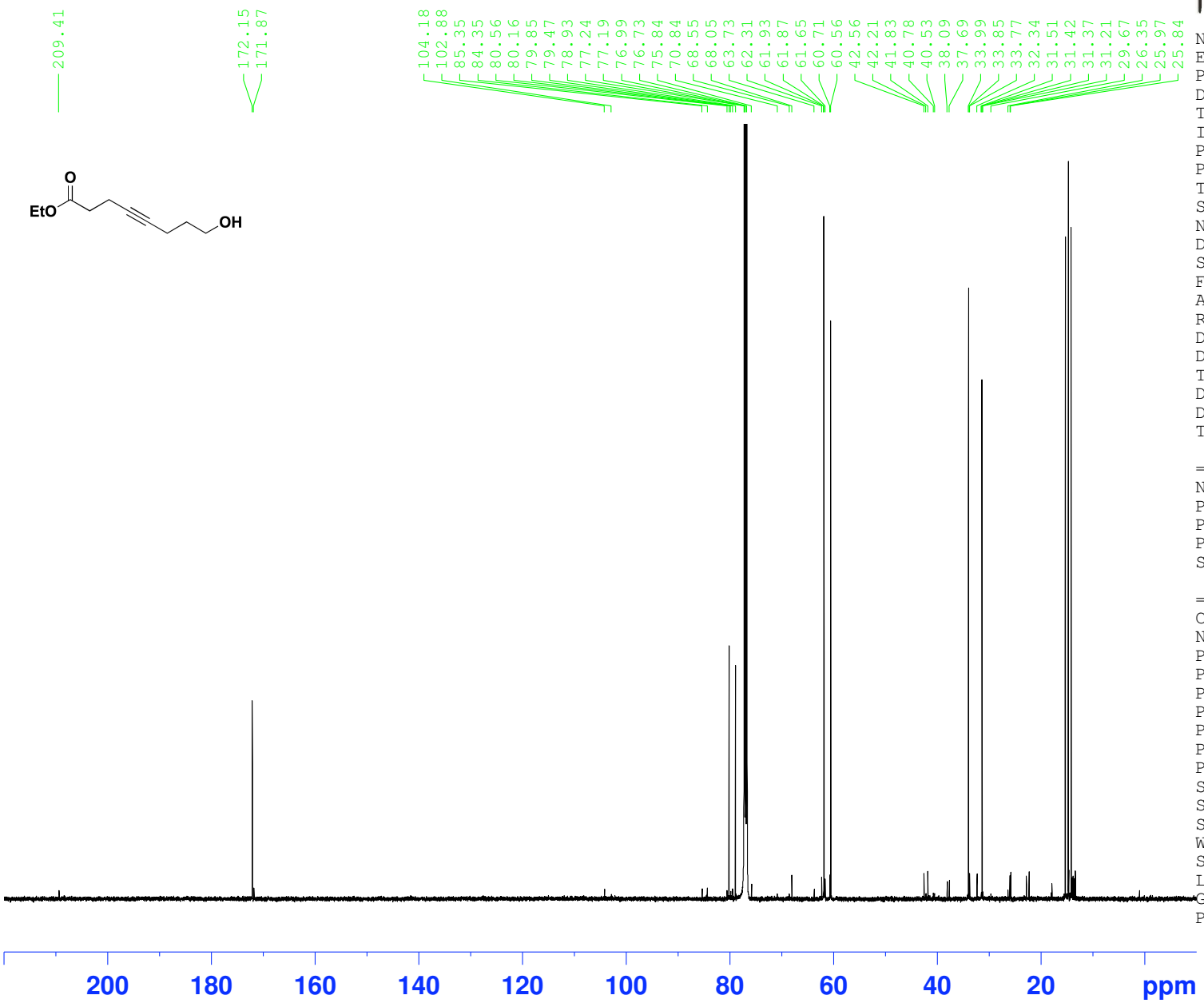
Instrument AVC500
BOSHEN WU 5496 7/8/09





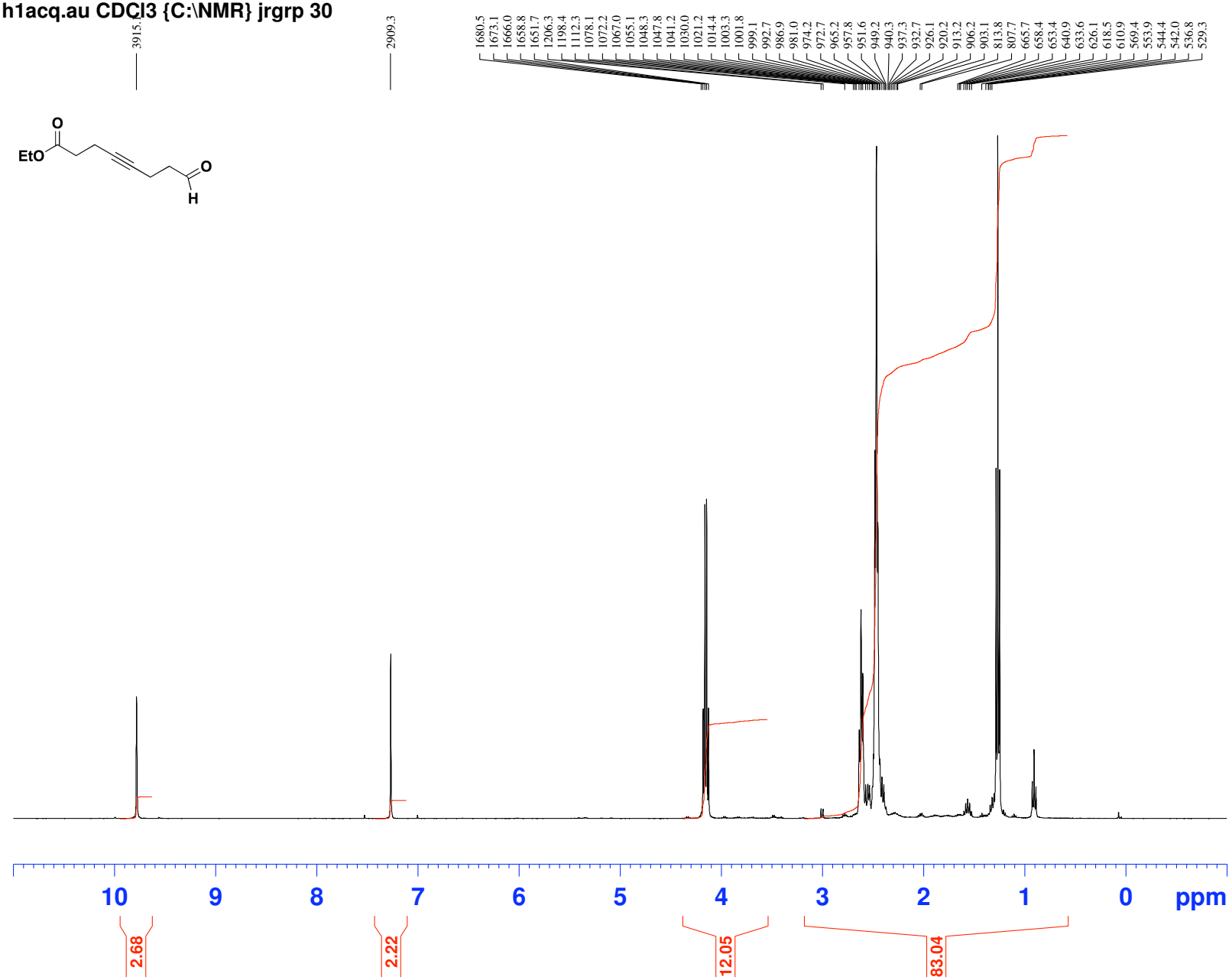

```
NAME          bw54960708
EXPNO                  1
PROCNO                 1
Date_           20090807
Time               14.42
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Instrument AVC500
BOSHEN WU 5496 7/8/09




```
NAME          bw54960708
EXPNO                  4
PROCNO                 1
Date_           20090807
Time               17.38
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 3072
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                  812
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                8.00 usec
PL1              -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -6.00 dB
PL12             12.40 dB
PL13             17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB               1.00 Hz
GB                    0
PC               1.40
```

Instrument DQX400
Chemist BW
Group JR
WBS214–FR.40
h1acq.au CDCl3 {C:\NMR} jrgrp 30



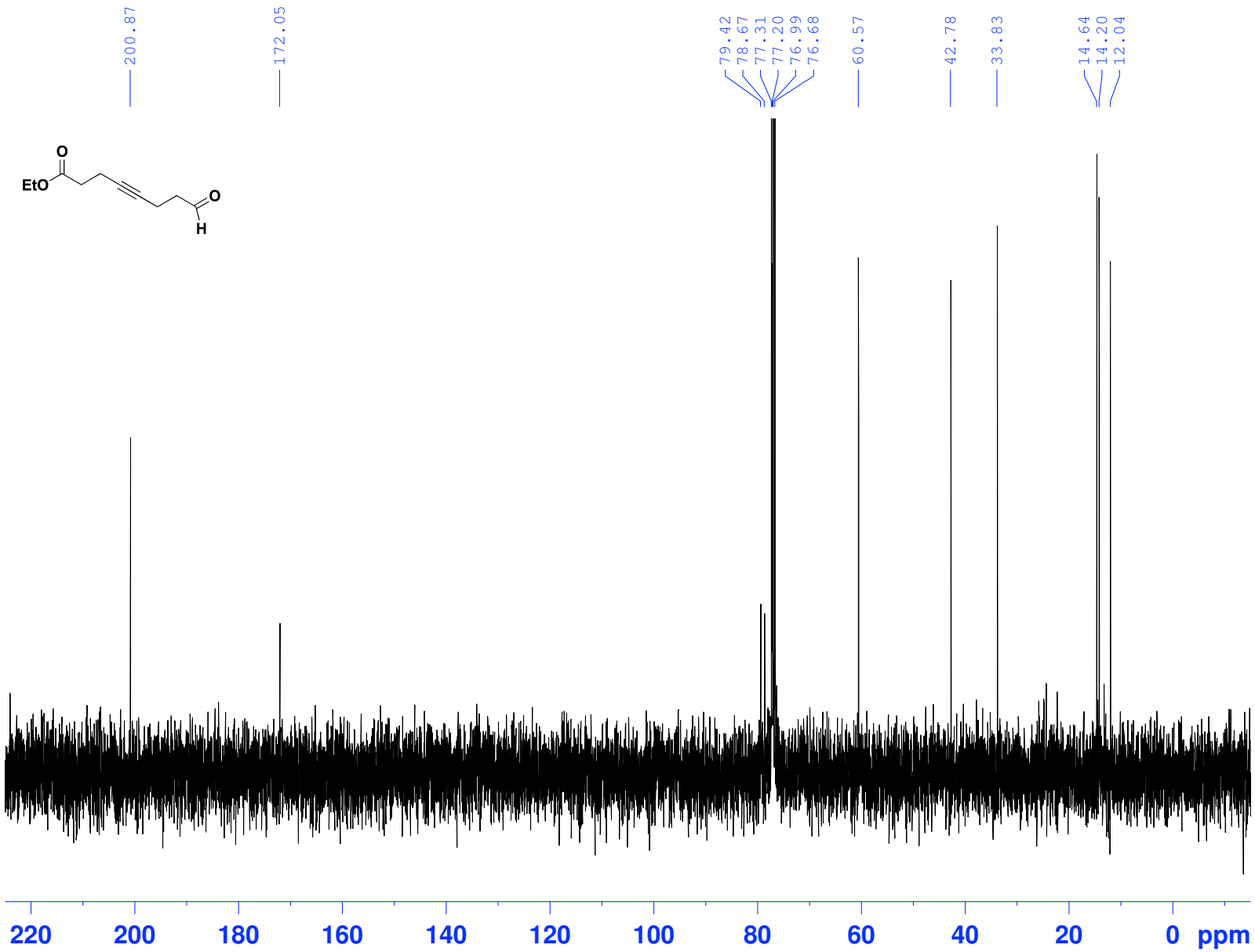
NMR@CHEM.OX

NAME	Dec09-2009-30
EXPNO	1
PROCNO	1
Date_	20091210
Time	8.36
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zg60
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	181
DW	60.400 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec

======== CHANNEL f1 ========

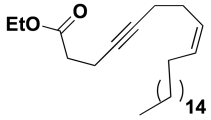
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	400.2024714 MHz
SI	32768
SF	400.2000028 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

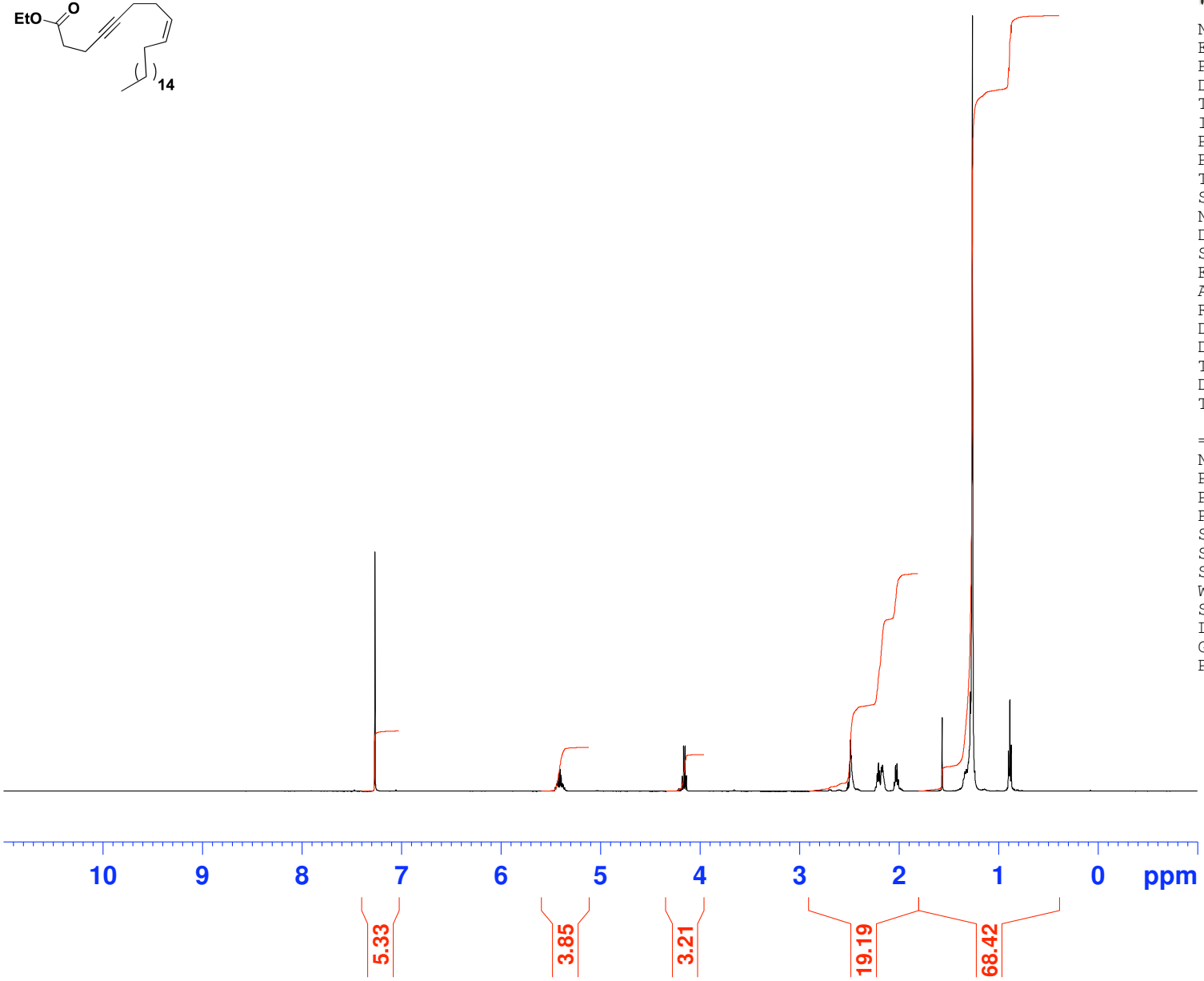
Instrument DQX400
Chemist BW
Group JR
WBS214–FR.40
c13acq.au CDCl3 {C:\NMR} jrgrp 30




```
NAME        Dec09-2009-30
EXPNO                   2
PROCNO                  1
Date_            20091210
Time                 8.44
INSTRUM            av400
PROBHD    5 mm QNP 1H/13
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            26178.010 Hz
FIDRES          0.798889 Hz
AQ             0.6259188 sec
RG                 32768
DW                19.100 usec
DE                 7.50 usec
TE                300.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 0.00 dB
SFO1         100.6403931 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              19.00 dB
PL13              25.00 dB
SFO2         400.2016008 MHz
SI                 32768
SF           100.6303718 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

Instrument AVC500
Group JR
BOSHEN WU 9/11/09

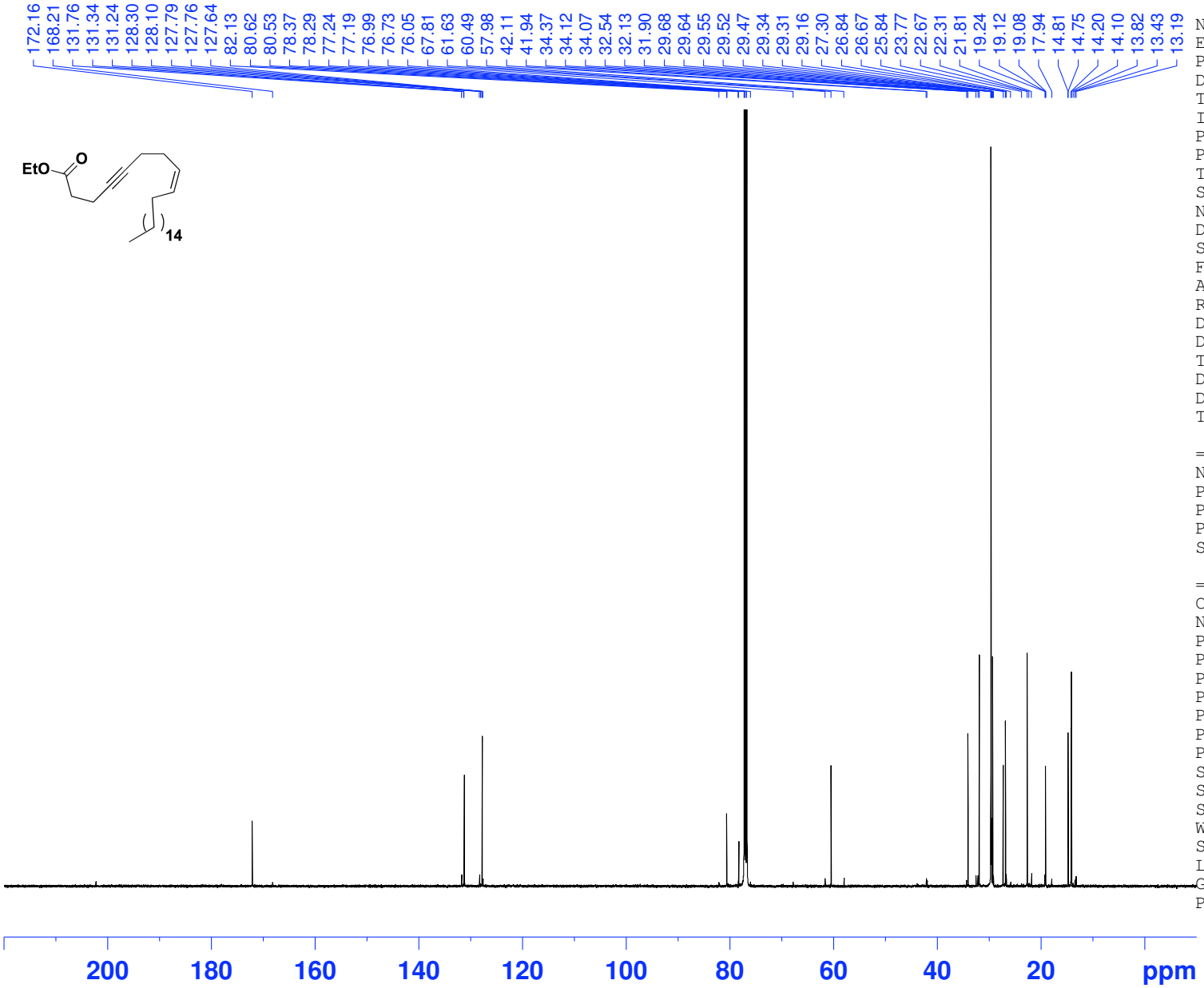




NMR@CHEM.OX

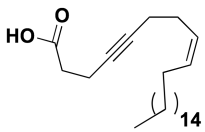
```
NAME          bw65980911
EXPNO                  1
PROCNO                 1
Date_           20091110
Time                0.07
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

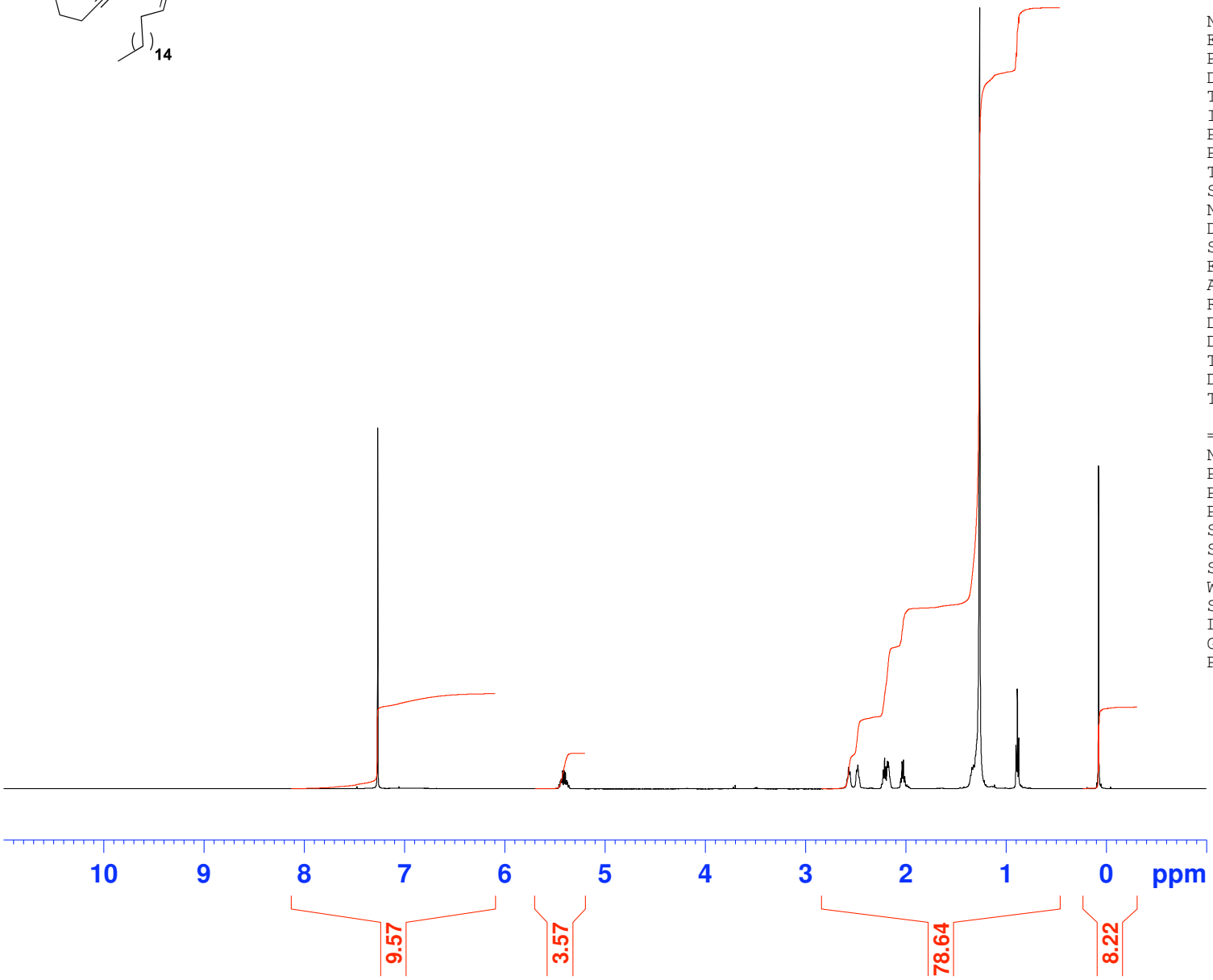
Instrument AVC500
Group JR
BOSHEN WU 9/11/09




```
NAME          bw65980911
EXPNO                  2
PROCNO                 1
Date_           20091110
Time                1.01
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE                20.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Instrument AVC500
5888 Boshen Wu 14/9/09

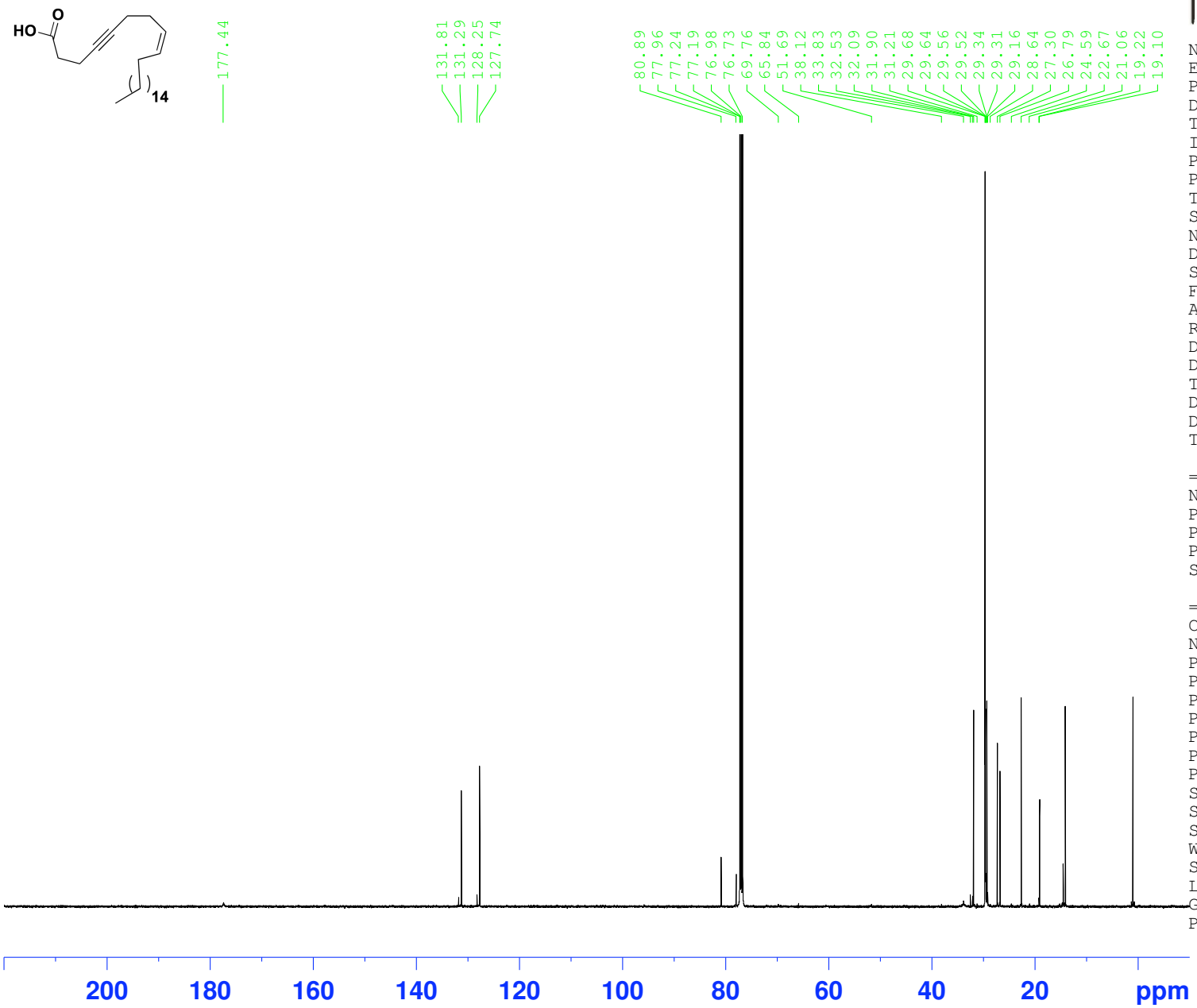




NMR@CHEM.OX

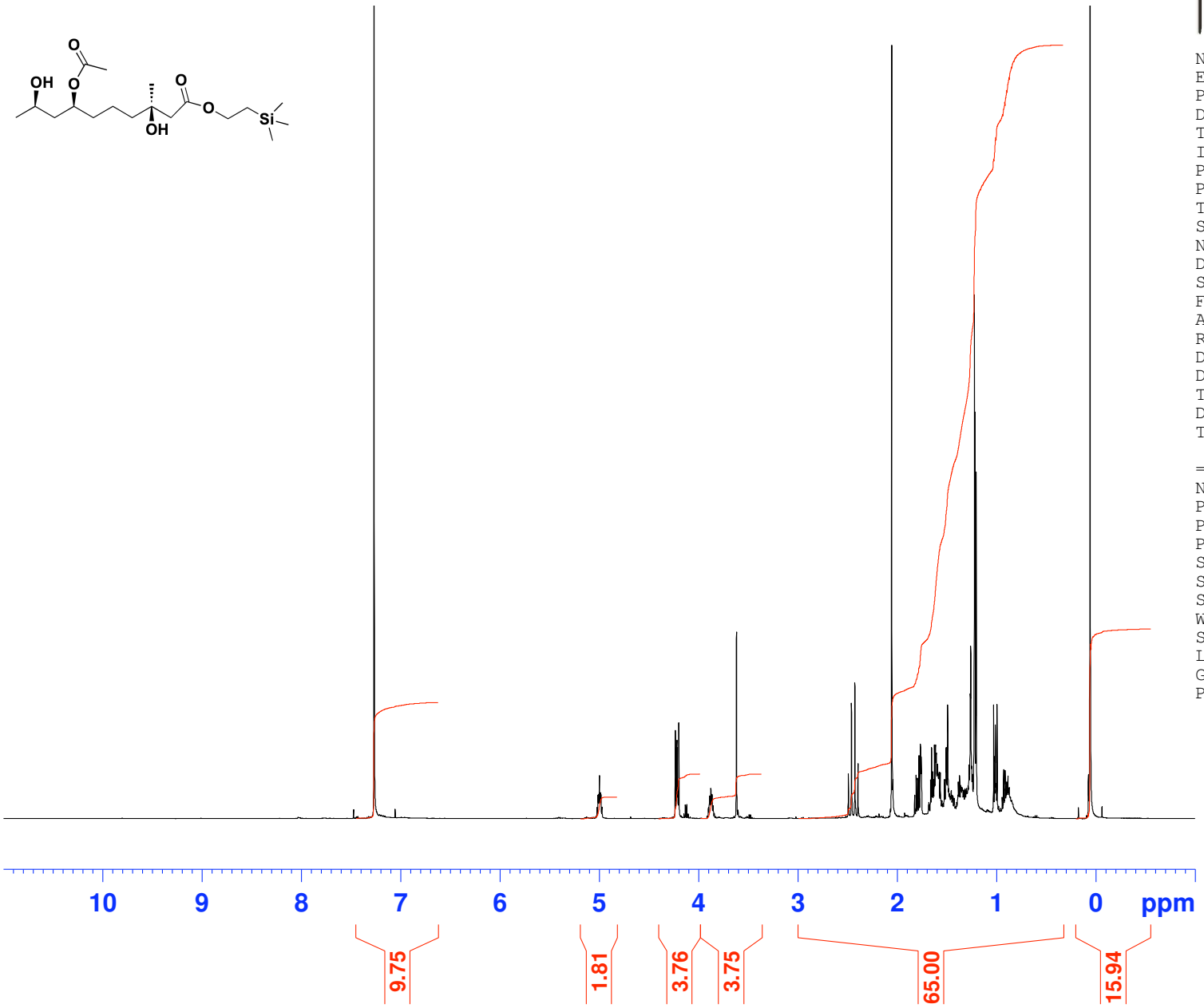
```
NAME          bw58881409
EXPNO                  1
PROCNO                 1
Date_           20090914
Time               12.20
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Instrument AVC500
5888 Boshen Wu 14/9/09




```
NAME          bw58881409
EXPNO                  4
PROCNO                 1
Date_           20090914
Time               13.03
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0486259 sec
RG                  1030
DW                16.000 usec
DE                 20.00 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.00 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
PL13               17.00 dB
PL2W        15.19999981 W
PL12W        0.21970686 W
PL13W        0.07618046 W
SFO2        500.3020012 MHz
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

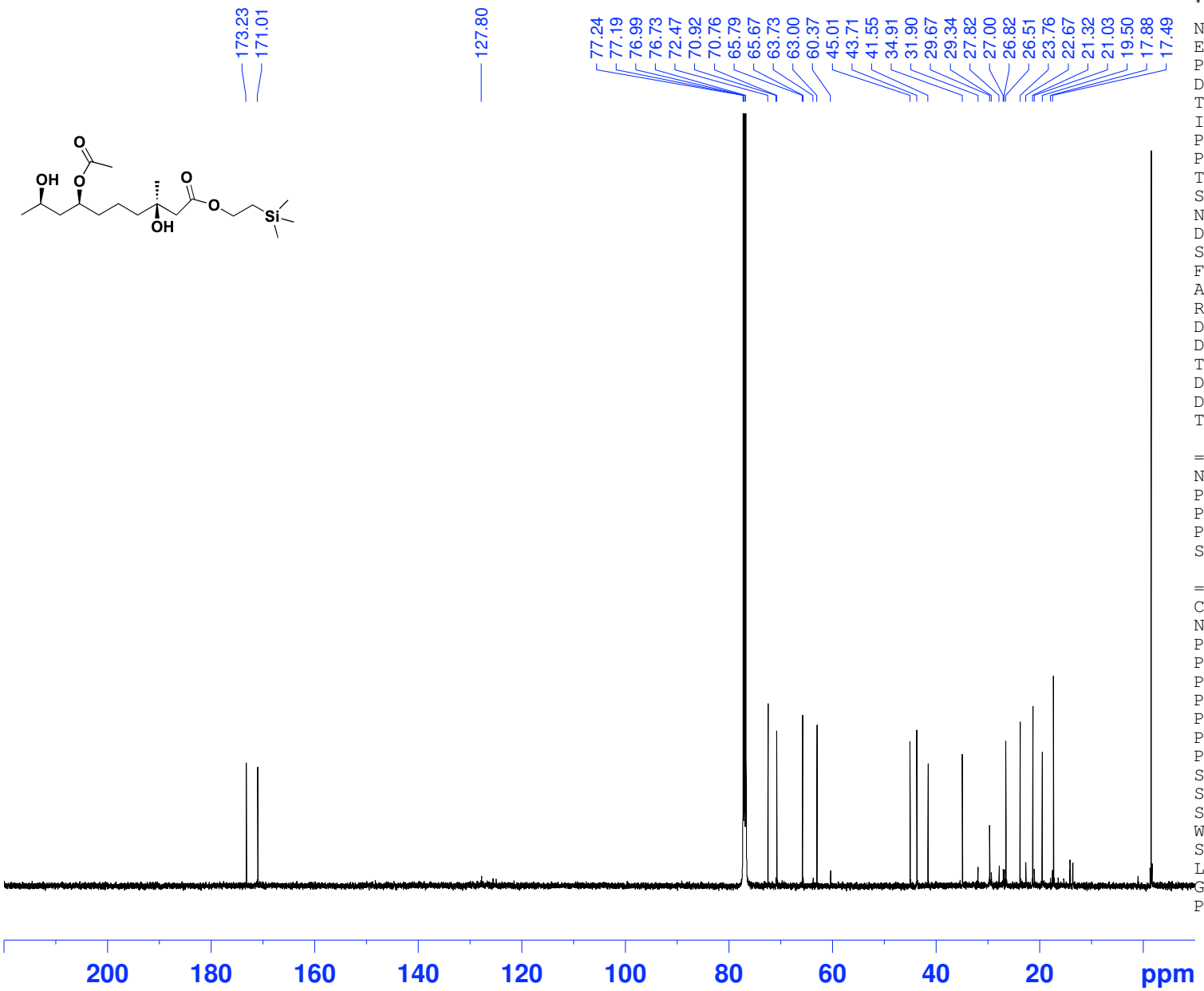
Instrument AVC500
Group JR
7804 Boshen Wu 1/3/10



NMR@CHEM.OX

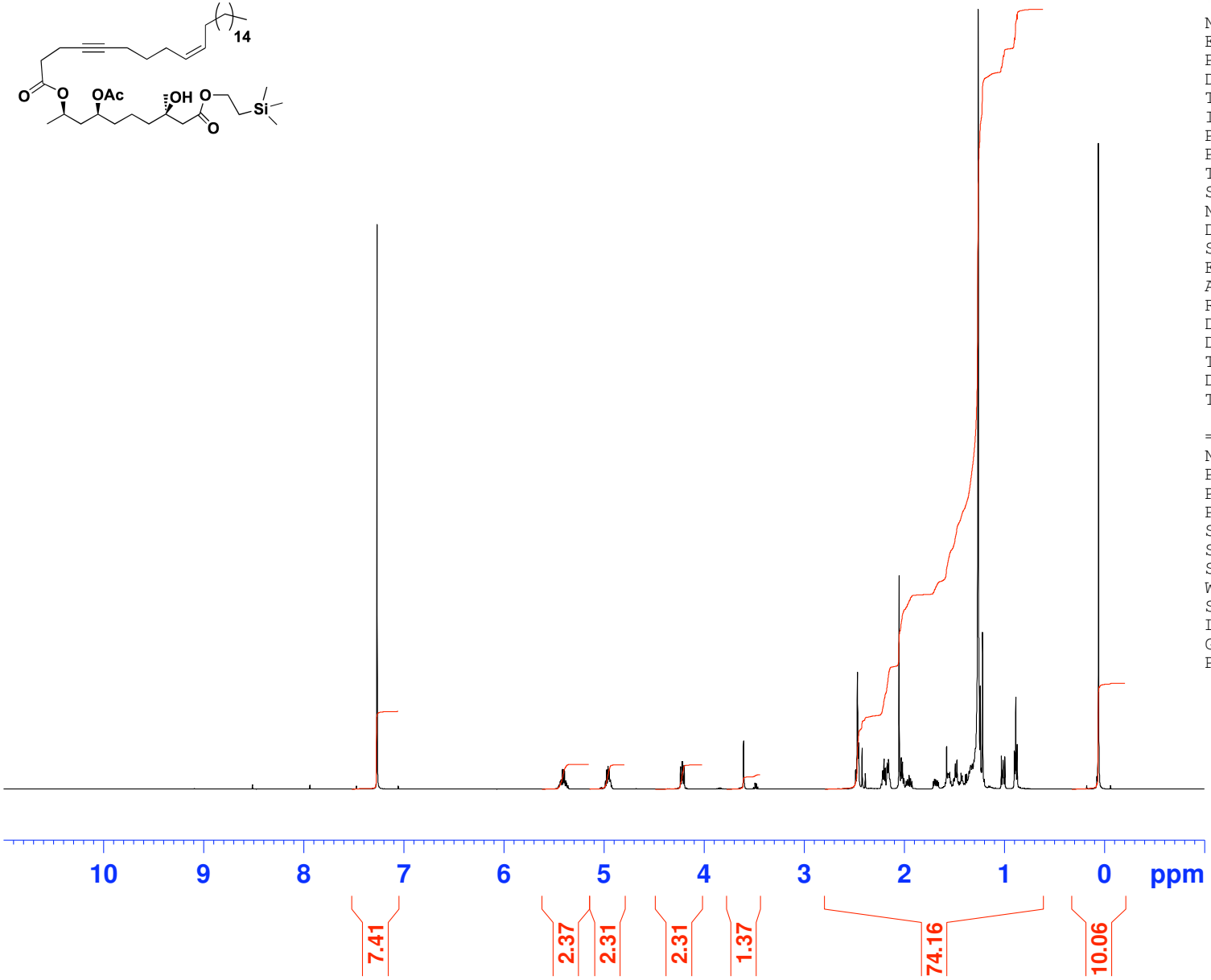
```
NAME          bw78840103
EXPNO                  1
PROCNO                 1
Date_           20100301
Time               16.40
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Instrument AVC500
Group JR
7804 Boshen Wu 1/3/10



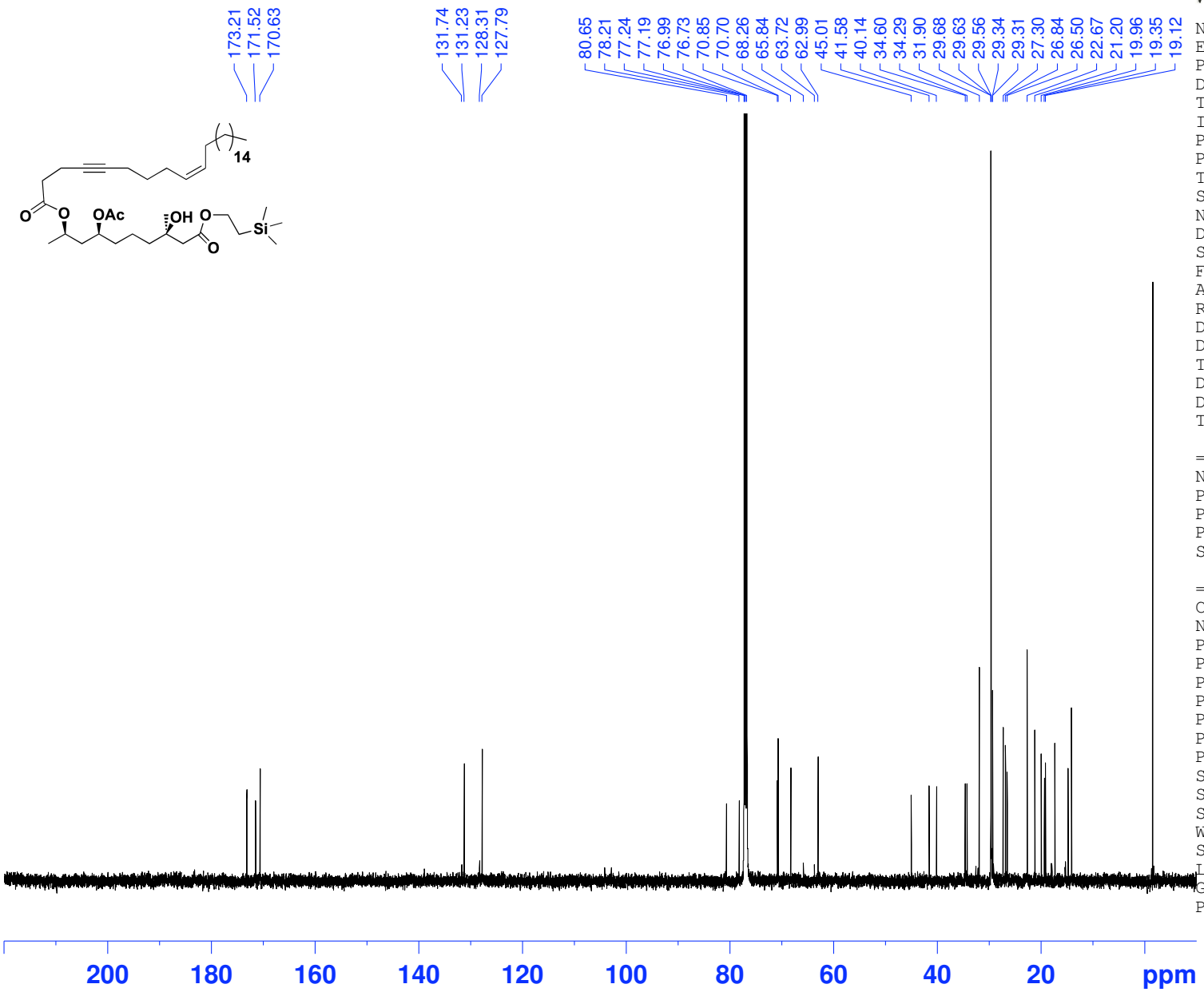

```
NAME          bw78840103
EXPNO                  4
PROCNO                 1
Date_           20100301
Time               17.50
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE                20.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.42 dB
PL13             120.00 dB
PL2W        15.19999981 W
PL12W        0.21869738 W
PL13W        0.00000000 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Instrument AVC500
Group JR
BOSHEN 7906 2/3/10



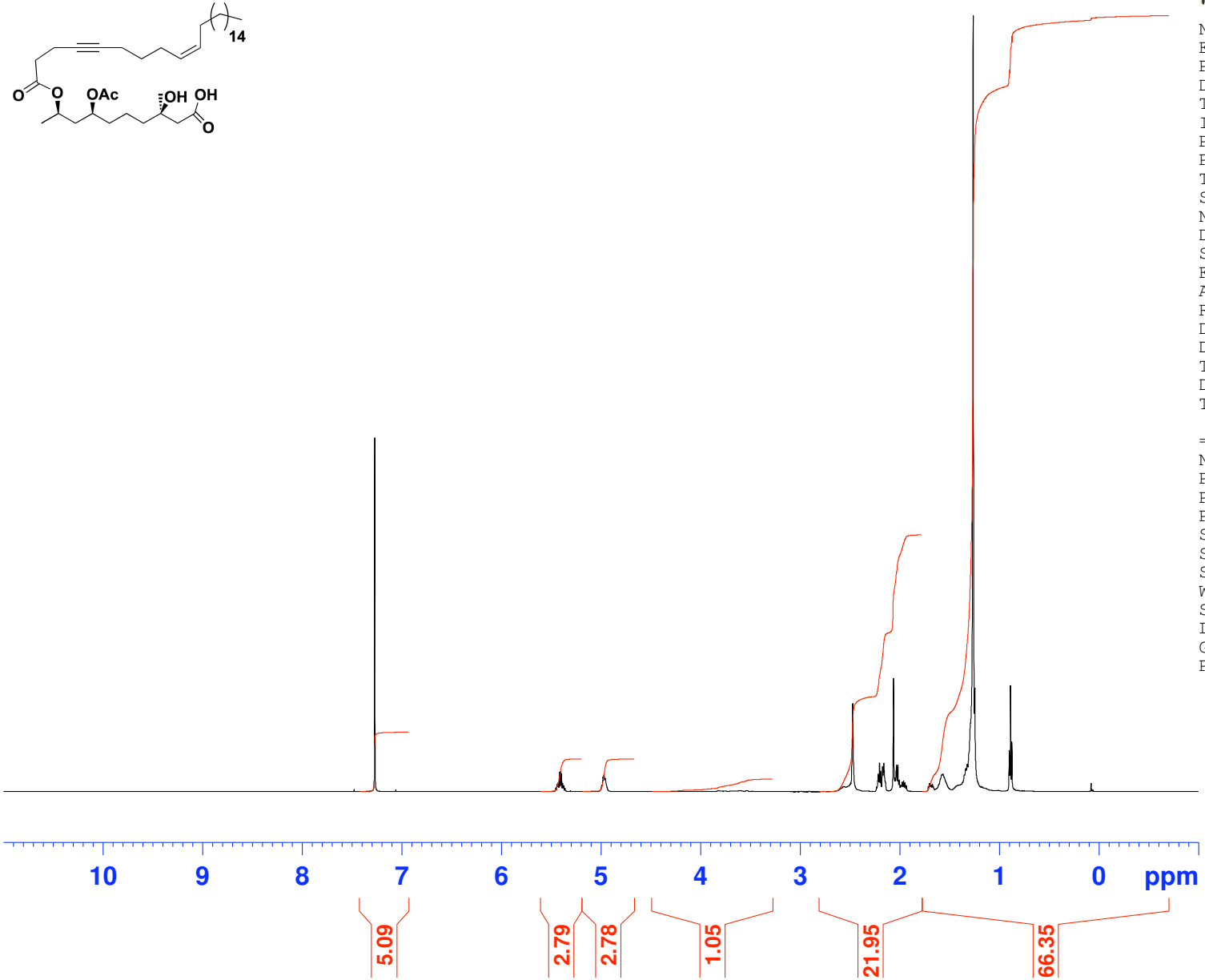

```
NAME          bw79060203
EXPNO                  1
PROCNO                 1
Date_           20100303
Time                4.23
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Instrument AVC500
Group JR
BOSHEN 7906 2/3/10



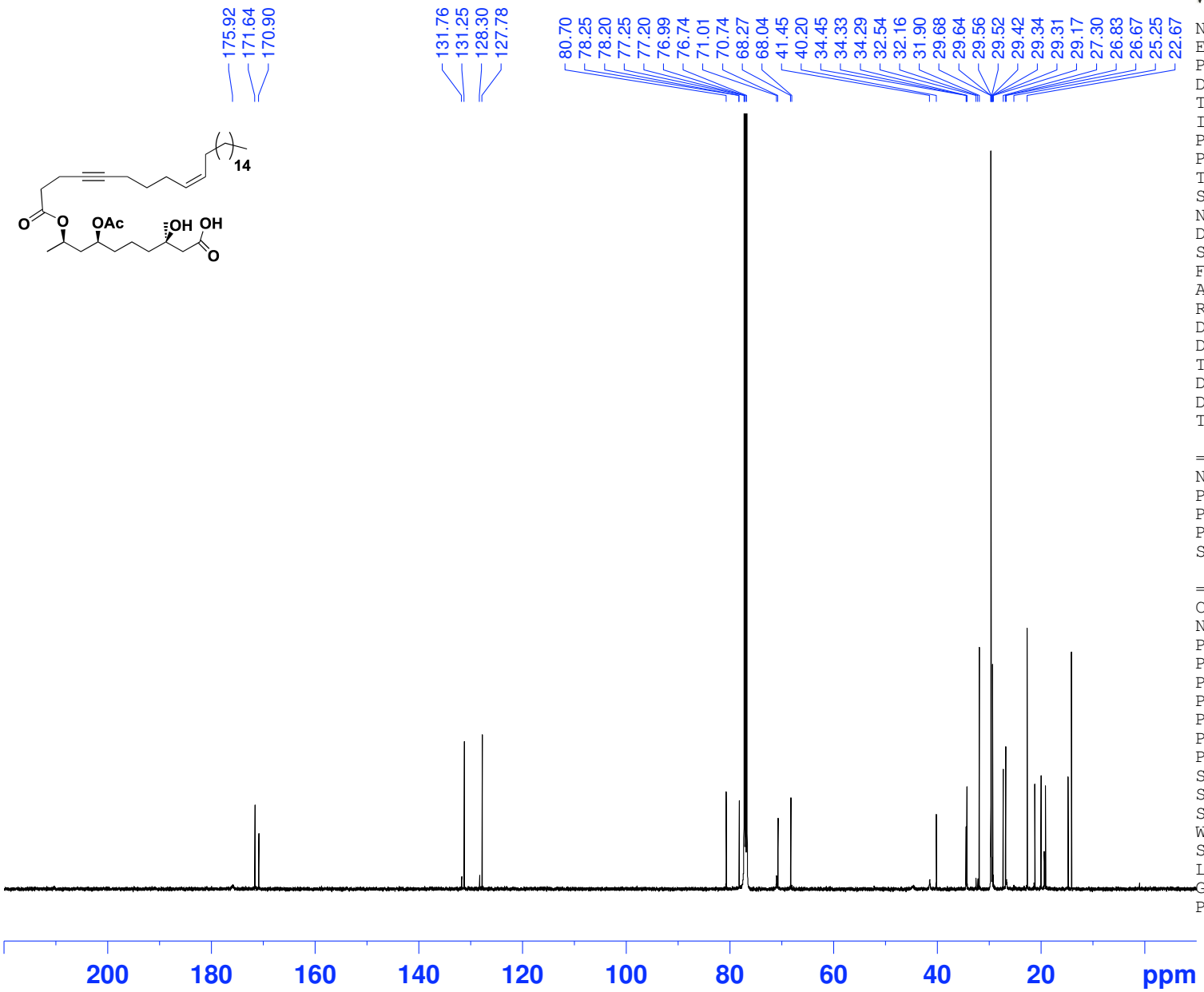

```
NAME          bw79060203
EXPNO                  4
PROCNO                 1
Date_           20100303
Time                4.53
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE                20.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.42 dB
PL13              120.00 dB
PL2W        15.19999981 W
PL12W        0.21869738 W
PL13W        0.00000000 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Instrument AVC500
Group JR
8133 Boshen Wu 17/3/10



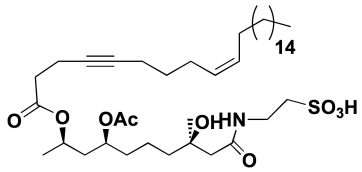

```
NAME          bw81331703
EXPNO                  1
PROCNO                 1
Date_           20100318
Time                2.12
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

Instrument AVC500
Group JR
8133 Boshen Wu 17/3/10

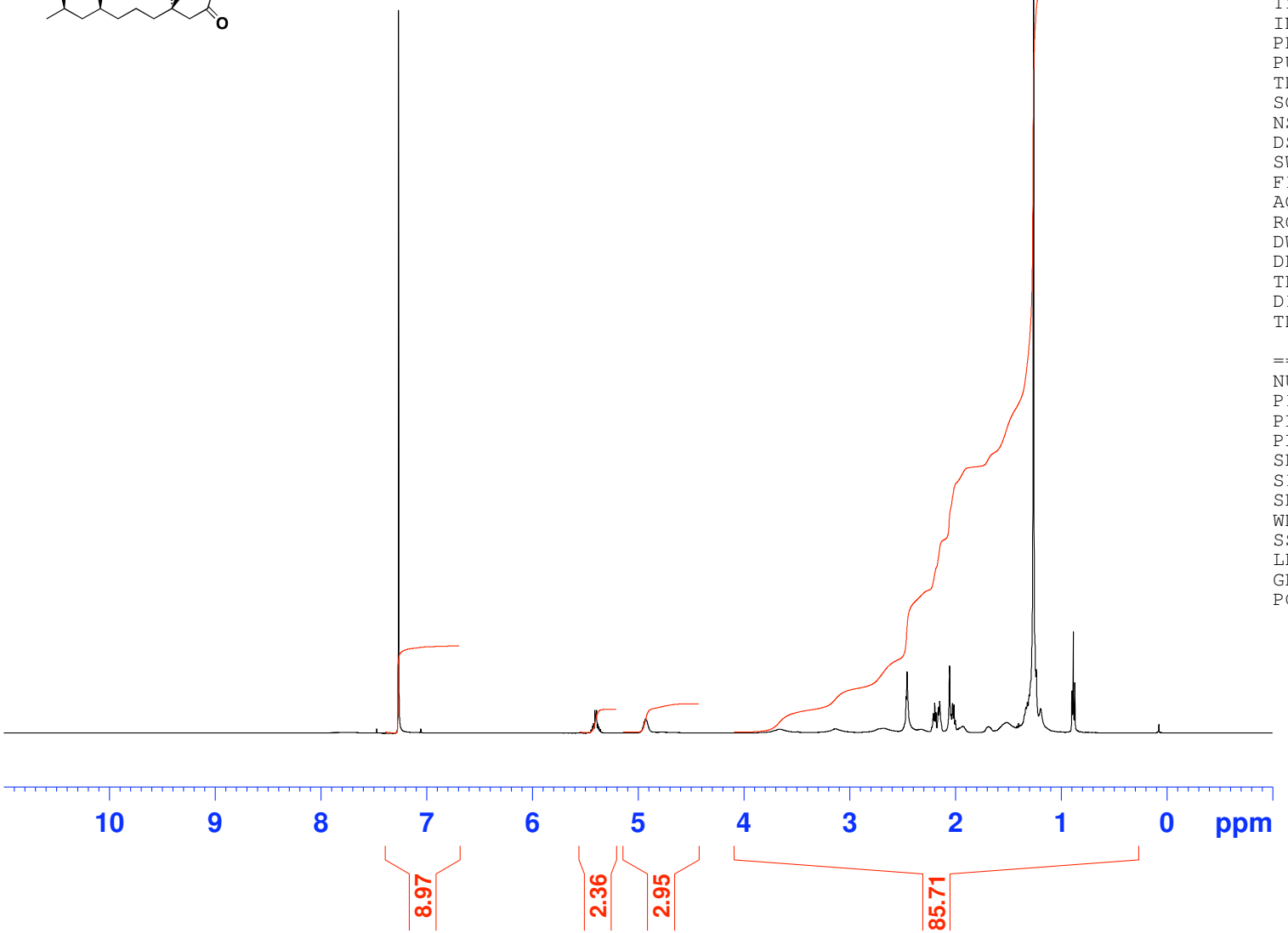



```
NAME          bw81331703
EXPNO                  4
PROCNO                 1
Date_           20100318
Time                3.22
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE                20.00 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.42 dB
PL13              120.00 dB
PL2W        15.19999981 W
PL12W        0.21869738 W
PL13W        0.00000000 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Instrument AVC500
Group JR
8177 Boshen Wu 19/3/10



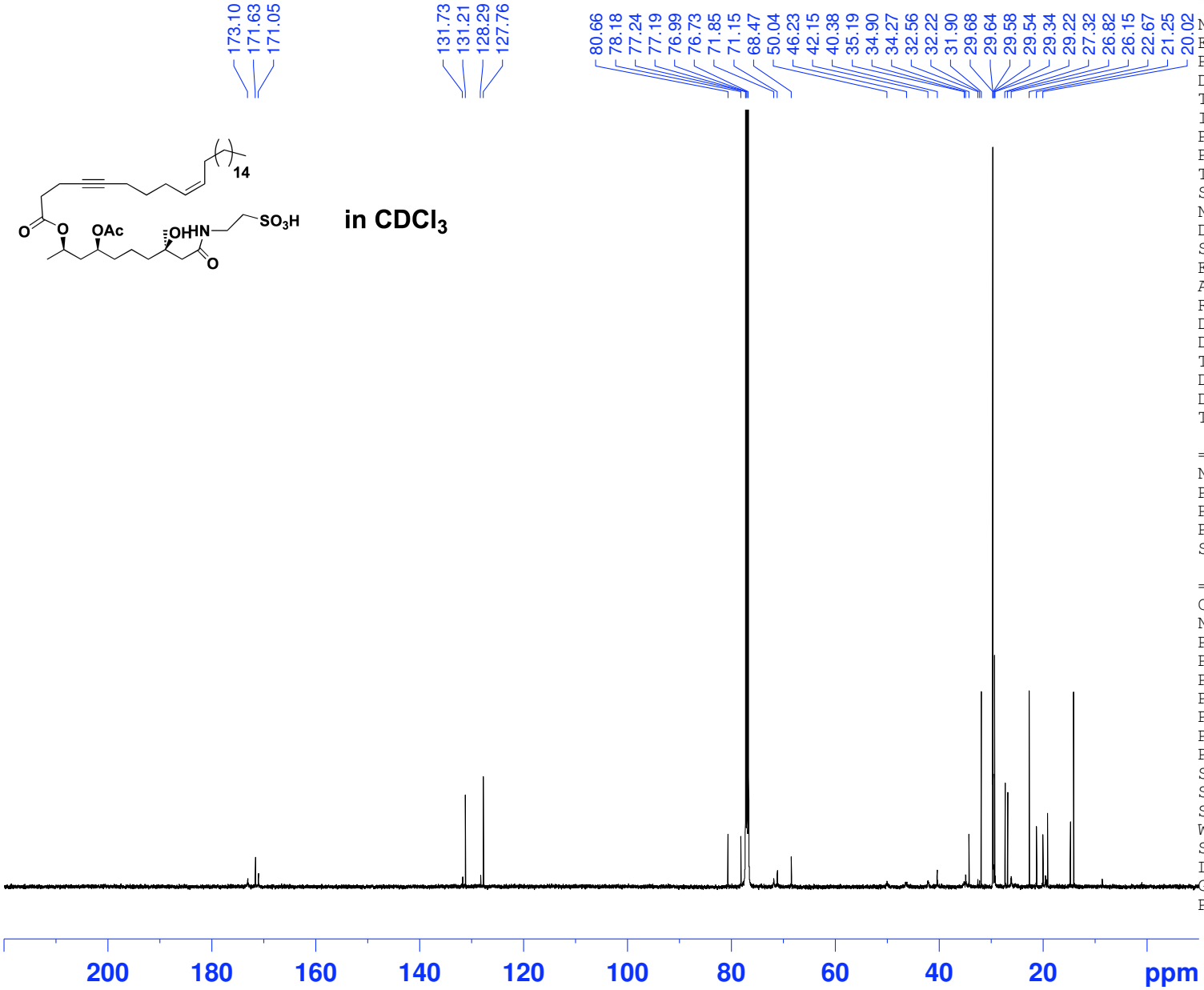
in $CDCl_3$




```
NAME          bw81771903
EXPNO                  1
PROCNO                 1
Date_           20100319
Time               16.48
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

Instrument AVC500
Group JR
8177 Boshen Wu 19/3/10

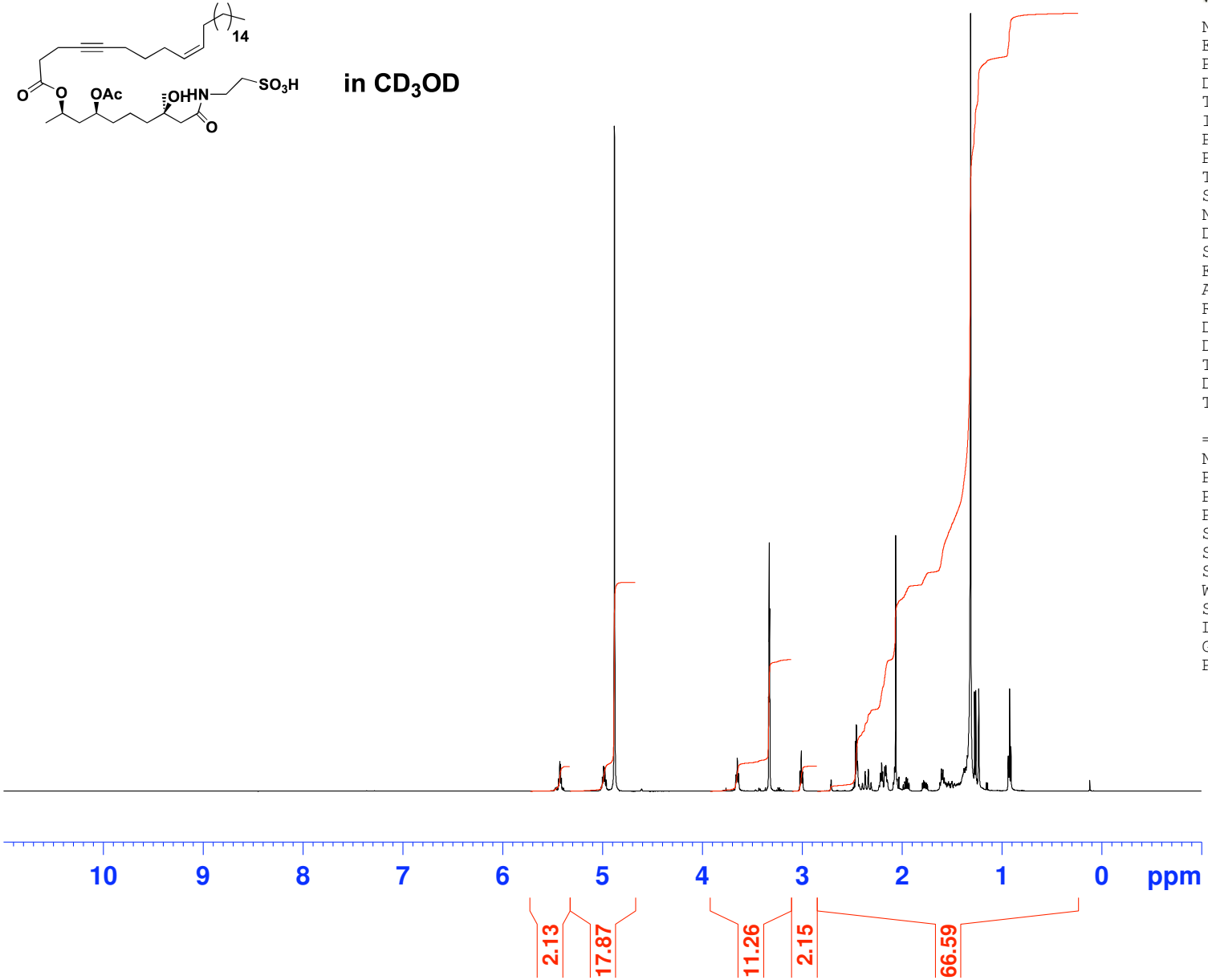
in $CDCl_3$




```
NAME          bw81771903
EXPNO                  5
PROCNO                 1
Date_           20100322
Time               11.53
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0486259 sec
RG                  1820
DW                16.000 usec
DE                 20.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.42 dB
PL13              120.00 dB
PL2W        15.19999981 W
PL12W        0.21869738 W
PL13W        0.00000000 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8005438 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

Instrument AVC500
Group JR
8167 Boshen Wu 19/3/10

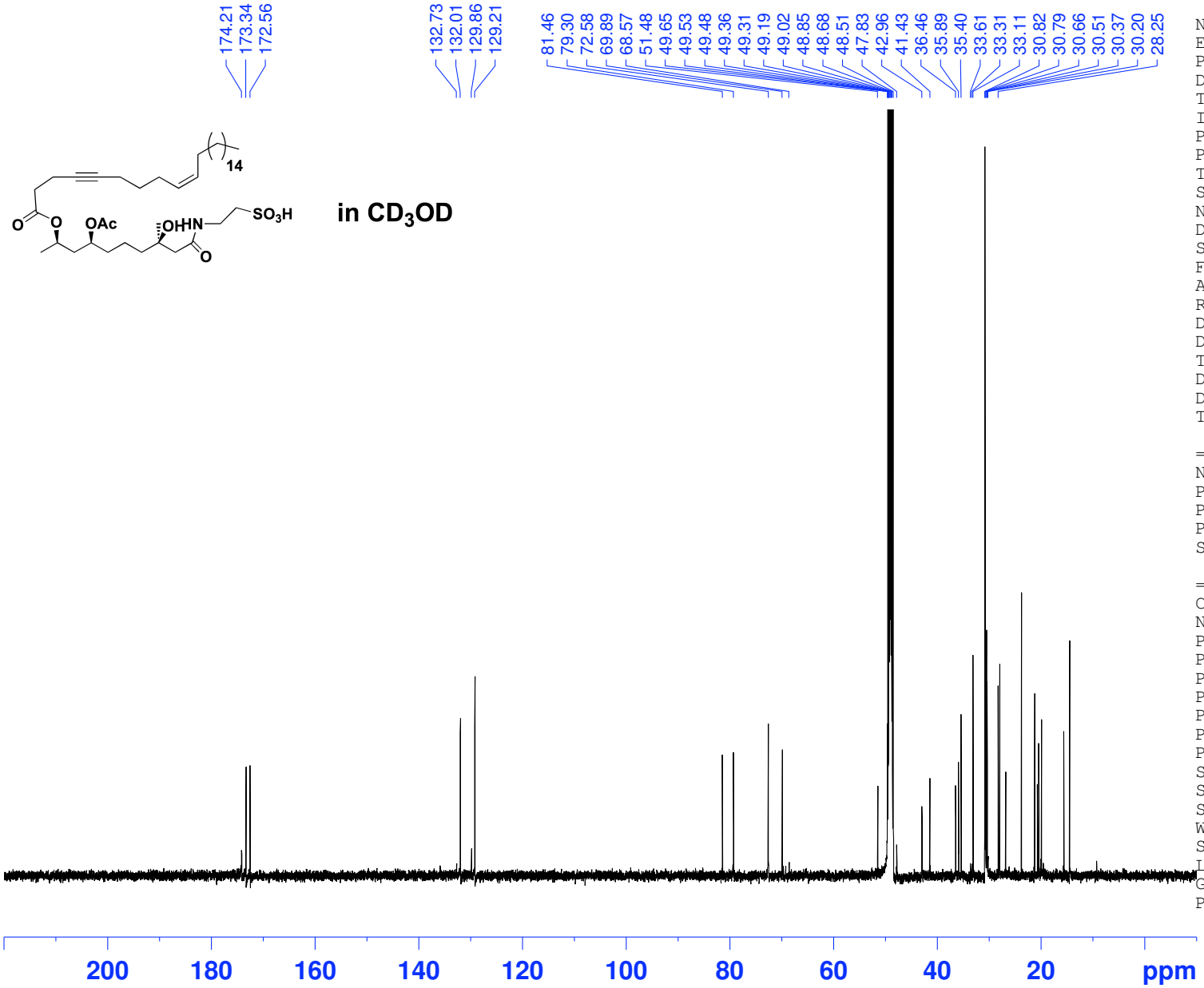
in CD_3OD




```
NAME          bw81671903
EXPNO                  1
PROCNO                 1
Date_           20100319
Time               12.14
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
PL1W        15.19999981 W
SFO1        500.3030896 MHz
SI                32768
SF          500.3000000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

Instrument AVC500
Group JR
8167 Boshen Wu 19/3/10

in CD_3OD




```
NAME          bw81671903
EXPNO                  4
PROCNO                 1
Date_           20100319
Time               13.23
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT             MeOD
NS                  1024
DS                     2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0486259 sec
RG                  1820
DW                16.000 usec
DE                 20.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                -4.40 dB
PL1W        28.15752029 W
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.42 dB
PL13              120.00 dB
PL2W        15.19999981 W
PL12W        0.21869738 W
PL13W        0.00000000 W
SFO2        500.3020012 MHz
SI                32768
SF          125.8003564 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```